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THESE

Présentée à

l'Université Louis Pasteur de Strasbourg

pour obtenir le grade de

DOCTEUR

de l'Université Louis Pasteur

SPECIALITE: CHIMIE

Par

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Développement et applications de nouveaux ligands π-conjugués aminoquinoniques.

Soutenue le 8 Mai 2004 devant la commission d'examen:

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A Sèverine pour m’avoir toujours soutenu et pour tout !

A mes parents qui m’ont toujours encouragé dans les études

à tous ceux que j'aime... et à Mylène !

’’Science sans conscience n’est que ruine de l’âme’’

François Rabelais

Ce travail a été réalisé au Laboratoire de Chimie de Coordination de l'Université Louis Pasteur à Strasbourg. Qu'il me soit permis d'exprimer ma profonde gratitude à Monsieur le Dr. Pierre Braunstein, directeur de recherche au CNRS et directeur de notre laboratoire, pour m'avoir accueilli dans son laboratoire. Je le remercie pour tous ses conseils et pour la formation de haut niveau en chimie organique et inorganique que j'ai pu acquérir pendant ses 3 années.

Je remercie profondément le Dr. Olivier Siri pour la formation scientifique qu'il m'a apporté. J'aimerais te dire comment j'ai pu apprécier ta disponibilité presque permanente, ton enthousiasme et la passion que tu as essayé de me transmettre pour les systèmes π!! Merci également pour la liberté que tu m'as laissé pour développer les projets qui me tenaient à coeur, je sais que peu de doctorants ont pu avoir cette chance. Je pense que je me souviendrai longtemps de tous les bons moments passés ensemble, au labo ou en dehors...je pense en particulier a notre séjour scientifique......en Pologne !

Je tiens à adresser mes plus vifs remerciements au Professeur M. Chetcuti ainsi qu'aux Docteurs P. Batail, R. Laï, M. Bénard et H. Metz pour avoir accepté de juger ce travail.

Je tiens à remercier le Pr. Richard Welter du laboratoire DECMET (cristallographie) pour avoir collaboré à ce travail et pour sa sympathie et son humour (soit un peu plus indulgent à l'avenir avec les petits thésards qui se donnent tant de mal à avoir des beaux cristaux dans des tubes et qui ramènent de la poudre dans des schlenks..), ainsi que le Dr. Jean-Paul Collin pour les études électrochimiques et les Dr. M. Bénard et M.-M. Rohmer pour la réalisation des études théoriques. Un grand merci également à Roland Graff et Jean-Daniel Sauer pour la réalisation de nombreux spectres RMN.

Je tiens à remercier également Anne, d'abord pour le travail de synthèse et en particulier les heures passées à faire du zwitterion, je pense que tu t'en souviendras longtemps, mais également pour tes précieux conseils en fin de thèse quand l'impatience etait plus que présente...; Marc pour le travail technique rapide et efficace, et pour son aide précieuse dans l'utilisation initiale des réacteurs (je crois que je serais encore en thèse si tu n'avais pas été là); ainsi que bien sur tous les chercheurs du laboratoire, Xavier dont j'aurais vraiment souhaité qu'il soit présent le jour de ma soutenance mais Oslo est un peu trop loin, Roby et Jacky et pour leur sympathie.

Je remercie également tous mes collègues du laboratoire avec qui j'ai passées trois et demi agréables années. Je commencerais par mon collègue de bureau cette dernière année, Magno le Portugais, qui m'a également donné un sacré coup de pousse pour la catalyse ; Assia pour sa gentillesse et avec qui j'ai eu beaucoup de discussions sur la chimie, l'avenir professionnel, ainsi que ses coutumes religieuses ; mon grand ami Nabil, qui trouvera peut être une rachala en ce jour, ainsi qu'Adel et ses mariages à répétition; Nicola, la championne de la RMN; Yang, Coco et la Aude, mes voisins de paillasse durant une année, pour toutes nos discussions animées...; Luc, mon grand adversaire politique de toujours, mais avec qui j'aurais passé une super 3eme année de thèse; Catherine, Mireia, Anthony et Pierre pour leur grande gentillesse et sympathie; je n'oublierais pas non plus tous mes anciens collègues Guislaine, Céline, Fanny, Walter, Jing, Fredy, Nicolas, Andreas et Jérome mais aussi tous les stagiaires et étudiants Erasmus qui m'ont croisé pendant mes trois années et demi de thèse; Je pense plus particulièrement à Bénédikt et Sabrina, les deux stagiaires que j'ai pu encadrer avec beaucoup de plaisir, mais aussi à Vito, Roberto, Sarah, et Marion. Difficile de résumer 3 ans de vie professionnelle commune, j'ai été court, mais je pense n'avoir oublié personne, c'est l'essentiel !!

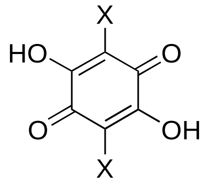
Enfin, je tiens à remercier ma famille et tous mes amis, en particulier Oud, Sandryne et Xavier, qui m'ont encouragé par leur réconfort dans mes moments les plus difficiles...

SOMMAIRE

Introduction Générale

Historiquement, la chimie des molécules comportant une structure quinonique a attiré l'attention d'une grande communauté scientifique depuis plus d'un siècle de par l'étendue de leurs applications aussi bien en tant que colorants et molécules d'intérêt biologique, que dans le domaine de la chimie organométallique, la catalyse et l'électrochimie. Ainsi les benzoquinones, connues depuis toujours pour leurs propriétés redox, sont devenues parmi les produits naturels ceux qui présentent une des chimies les plus diverses.

Plus spécificiquement, la 2,5-dihydroxy-1,4-benzoquinone **1** (X = H) et ses homologues chlorosubstitués et alkylsubstitués (X = Cl ou R) font partie d'une classe de ligands quinoniques fonctionnels tétradentates parmi les plus utilisés en chimie de coordination de par la grande variété des sites de chélation permettant de construire des édifices organométalliques mono-, di- et polynucléaires, avec ou sans délocalisation électronique du système à 12 électrons π.[1-4] Ainsi, plus de 200 complexes métalliques ont pu être préparé à partir de cette famille de ligands, suivant cinq grands modes de coordination où le ligand se trouve sous forme monoanionique ou dianionique.



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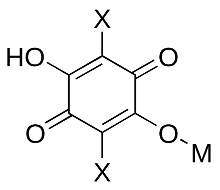
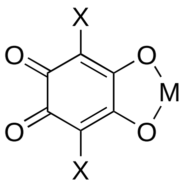
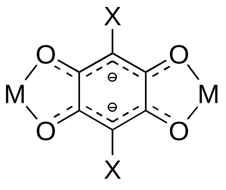


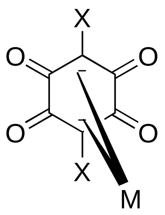
monodentate



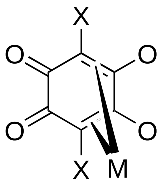
bidentate



bis-bidentate

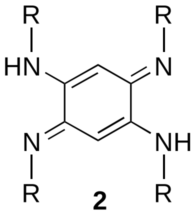


bidentate (bis-carbanion)



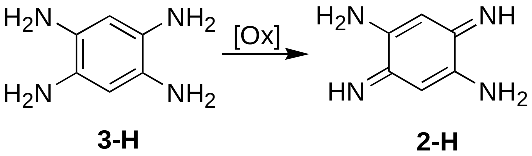
bidentate (π-lié)

Deux grands types de structures cristallines ont pu être mis en évidence à partir de ces complexes. La première est un auto-assemblage supramoléculaire de molécules discrètes, la seconde correspond plutôt à un polymère de coordination constitué d'unités élementaires organométalliques reliées entre elles par liaisons covalentes. De plus, les propriétés redox des ligands de type **1**, en particulier la possibilité d'une communication électronique entre les deux centres métalliques par délocalisation du système π dans les structures bis-bidentate, ont permis la préparation de complexes binucléaires à valence mixte.[4] A l'opposé, la chimie de coordination de l'analogue tétraazoté, la 2,5-diamino-1,4-benzoquinonediimine **2**, est restée très peu explorée, en raison de l'accès très limité à ce type de composés.



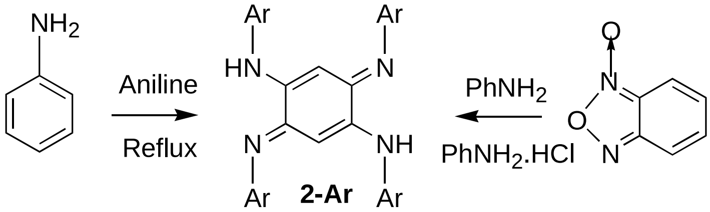
2

En effet, jusqu'en 2000, seule la préparation des ligands non-substitués ou substitués par des groupements aromatiques sur l'azote (composés de type azophénine) était connue et cela depuis plus d'un siècle.[5-9]. Dès 1887, Nietzki a décrit l'oxydation spontanée à l'air et à température ambiante du 1,2,4,5-tétraaminobenzene **3-H** conduisant à la 2,5-diamino-1,4-benzoquinonediimine **2-H** (schema 1).[6,10]



Schema 1. Synthèse de la 2,5-diamino-1,4-benzoquinonediimine **2-H**.

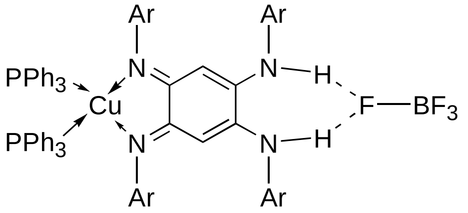
Quelques années auparavant, Kimish décrivait la première synthèse de composés 2,5-diarylamino-1,4-benzoquinonediimine **2-Ar**, plus connus sous le nom de dérivés du type azophénine.[5] Ces composés sont accessibles, avec de faibles rendements et accompagnés de la formation d'une multitude de sous-produits, par des réactions d'auto-condensation de l'aniline ou de la 1,3-diaminobenzene, ce qui limite considérablement la nature des substituants portés par les atomes d'azote (schema 2).



Schema 2. Synthèse de dérivés du type azophenine **2-Ar**.

La synthèse de ce type de composés a été récemment améliorée par Pätzold *et al.* qui ont mis au point une synthèse efficace de l'azophenine, avec un rendement de 60%, par co-condensation de l'aniline avec la 1,2-benzoquinonedioxime à reflux de l'aniline (schema 2).[11]

Néanmoins, la faible solubilité et la difficile accessibilité des produits finaux limitaient considérablement leur utilisation en chimie de coordination. En effet, jusqu'en 2000, seuls deux complexes avaient été synthétisés à partir de **2-H** et **2-Ar**. La première synthèse d'un complexe métallique utilisant le ligand **2-Ar** fut décrite par Kaim *et al.* en 1998 qui ont observé une isomérisation *para-ortho* de l'azophenine induite par coordination métallique d'un atome de Cu(I) conduisant à la formation d'un complexe cationique mononucléaire **4**, dans lequel l'atome de cuivre est coordiné de manière chélatante par deux atomes d'azote de type imine.[12] En 2000, Lever *et al.* ont à leur tour décrit la première synthèse d'un complexe binucléaire de ruthénium **5** à partir du ligand **2-H**, par réaction avec [Ru(bpy)$_2$Cl$_2$], mais ils ont uniquement obtenu une forme oxydée d'un complexe binucléaire, dans lequel le ligand **2-H** a subit un réarrangement vers une forme bis *o*-quinonediimine, sans possibilité de communication électronique entre les deux centres métalliques.[13] Ce type de chimie est d'une grande actualité puisque très récemment, le groupe de Kaim a décrit la synthèse d'un complexe neutre mononucléaire de rhénium **6**, similaire à **4**, obtenu par réaction de l'azophénine avec [ReCl(CO)$_5$].[14]



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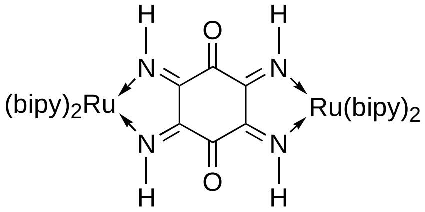

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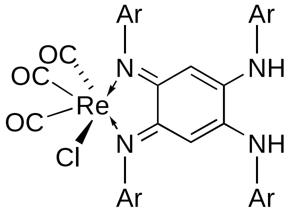

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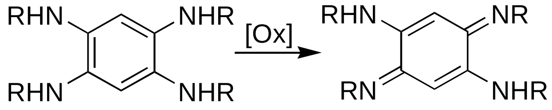
Il semblait ainsi extrêmement intéressant de mettre au point une méthode de synthèse efficace des ligands de type **2**, en particulier porteurs de N-substituants alkyls permettant d'augmenter leur solubilité, en vue d'accéder à une vaste gamme de composés utilisables en chimie de coordination. En utilisant en particulier le résultat obtenu par Nietzki en 1887 sur l'oxydation spontanée à l'air et à température ambiante du 1,2,4,5-tétraaminobenzene **3-H** conduisant à la 2,5-diamino-1,4-benzoquinonediimine **2-H** (schema 1),[6,10] nous avons envisagé un comportement similaire des composés tétraaminobenzene substitués du type **3** (schema 3).

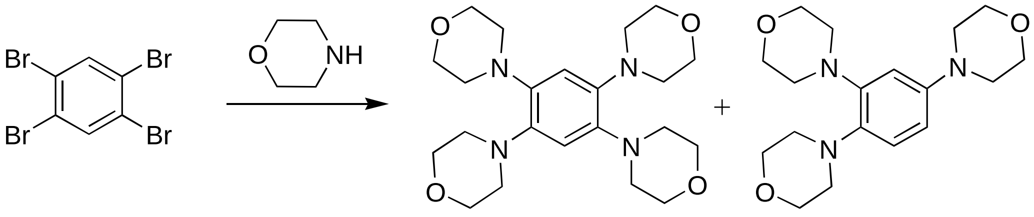


3-R **2-R**

Schema 3. Synthèse de la 2,5-diamino-1,4-benzoquinonediimine **2**.

Afin de préparer le 1,2,4,5-tétraaminobenzene **3-H**, plusieurs approches étaient envisageables, en particulier suivant deux voies principales:

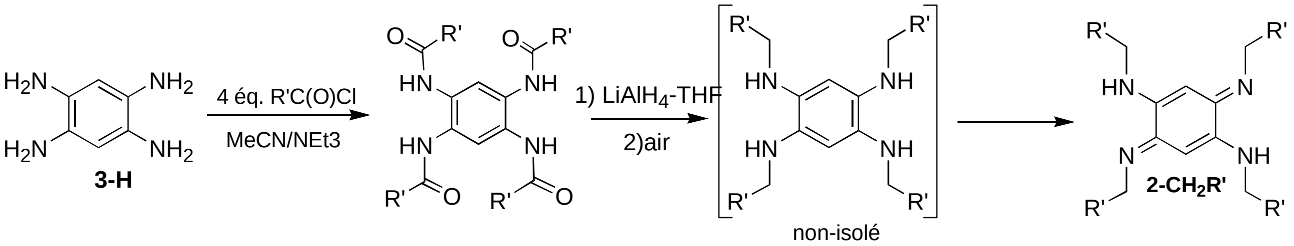
- A partir du 1,2,4,5-tétrabromobenzene **7**, par substitution nucléophile aromatique avec une amine déprotonée ou par réaction d'amination d'Hardwig-Buchwald catalysée par le palladium. Le succès de cette seconde voie avait été démontré par Witulski *et al.* qui ont synthétisé le 1,2,4,5-tetramorpholinobenzene **8** avec un bon rendement de 72% (schema 4).[15]



7 **8** (72 %) **9** (21 %)

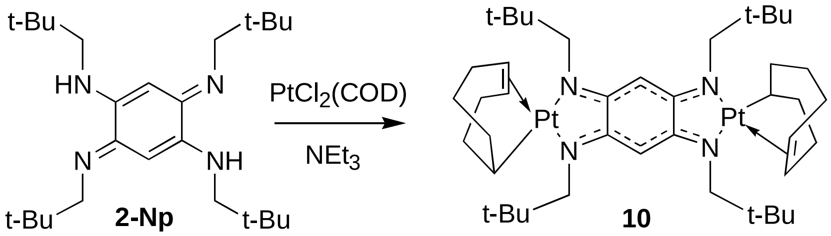
Schema 4. Conditions opératoires: [$Pd_2(dba)_3$] (3 mol %), BINAP (9 mol %), 4.8 equiv. morpholine, 5.5 equiv. NaOtBu, Toluène, 100 °C, 2 jours.[15]

- A partir du 1,2,4,5-tétraaminobenzene **3-H**, soit par substitution nucléophile sur un halogénoalcane, soit par addition nucléophile sur un aldéhyde, soit par addition nucléophile sur un chlorure d'acide ou un anhydride suivie de la réduction de la double liaison C=X (X = N, O). La méthode par addition nucléophile sur un aldéhyde a été particulièrement étudiée,[16-25] permettant de préparer des ligands macrocycliques ou hautement fonctionnalisés, mais est limitée aux aldéhydes aromatiques. Notre laboratoire s'est intéressé plus spécialement à la méthode par addition nucléophile sur un chlorure d'acide suivie de la réduction de la double liaison C=O. Ainsi, en 2000, Siri *et al.* ont mis au point une synthèse efficace en deux étapes à partir du 1,2,4,5-tétraaminobenzene qui est condensé avec un chlorure d'acide pour fournir l'amide correspondant avec des rendements de 70-80%, puis celui-ci est réduit par $LiAlH_4$ à reflux du THF. L'intermédiaire tétraaminobenzene s'oxyde très facilement à l'air ce qui permet d'accéder aux ligands **2-CH₂R'** avec des rendements de 70-80% (schema 5).[26]



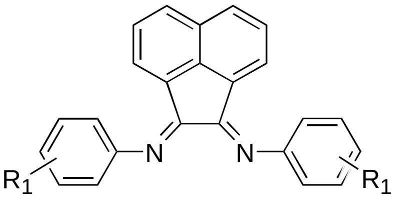
Schema 5. Synthèse des ligands **2-CH₂R'** décrite en 2000.[26]

La solubilité accrue des ligands de type **2-CH₂R'** porteurs de N-substituants alkyles permet d'envisager leur utilisation ultérieure en chimie de coordination, en particulier en vue de préparer des complexes binucléaires pontés par le ligand quinonique doublement déprotoné tels que ceux obtenus dans le cas du ligand tétraoxygéné **1**. Ainsi, en 2000, Siri *et al.* ont synthétisé le premier complexe binucléaire **10** par réaction entre **2-Np** et 2 equiv. de [$PtCl_2$(COD)] en milieu basique, avec néanmoins un faible rendement de 15% (schema 6).[26]



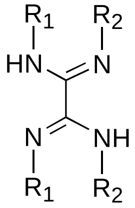
Schema 6. Synthèse du premier complexe binucléaire décrite en 2000.[26]

La structure moléculaire de ce complexe fut établie par diffraction des rayons X. Elle montre clairement la centrosymétrie de la molécule ainsi que la délocalisation du système à 12 électrons π de la quinonediimine entre les deux centres platine (longueurs des liaisons C-C et C-N intermédiaires entre liaisons simple et double). Ce premier résultat montrait clairement la possibilité de construire des édifices binucléaires à partir des ligands **2**, en particulier en vue d'applications électrochimiques et catalytiques. En effet, les cinq dernières années ont été marquées par une forte croissance des activités de recherche en catalyse de polymérisation et d'oligomérisation des oléfines par les métaux de transition de la droite du tableau périodique,[27-28] en particulier depuis la préparation par Brookhart *et al.* des premiers complexes cationiques de nickel et de palladium **11** hautement actifs en catalyse de polymérisation et d'oligomérisation d'éthylène, en présence d'un grand excès de MAO jouant le rôle de cocatalyseur, construits autour d'un ligand bidentate N-N diimine encombré.[29-32] A partir de ces catalyseurs, les principaux produits obtenus sont des α-oléfines à chaîne longue et moyenne, qui peuvent être séparées par distillation.[30] Plus récemment, Walther *et al.* ont développé une chimie de coordination riche et variée des ligands pontants de type oxalamidine **12-H** dont la structure peut être reliée à celle des ligands de type **2**.[33-41] En particulier, ils ont montré qu'il était possible de synthétiser des complexes binucléaires de nickel et palladium du type **12-M**, où T est un groupement terminal acac ou allyl, dans lequel le système à 8 électrons π du ligand est délocalisé, et qui sont actifs en catalyse de polymérisation ou d'oligomérisation de l'éthylène.[34,38,42]

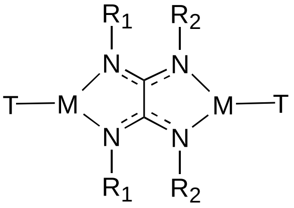


R1 = 2,6-isopropyl, 2,6-tBu

11



12-H

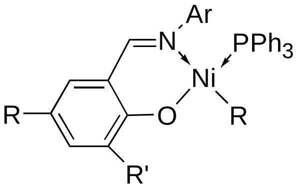


M = Ni, Pd
T = acac, allyl

12-M

Dans ce cadre, il apparaît clairement que la structure et les propriétés électroniques et stériques du ligand sont parmi les points clefs du contrôle de la réactivité et de la sélectivité du catalyseur. En effet, de légères modifications structurales sur les ligands permettent souvent de moduler les performances catalytiques. Ainsi les ligands quinonediimine **2**, facilement accessibles et dont les propriétés stériques sont parfaitement contrôlables, pourraient être d'excellents candidats pour la catalyse d'oligomérisation de l'éthylène, à laquelle notre laboratoire s'intéresse ces dernières années.[43,44]

Dans le domaine de la polymérisation et de l'oligomérisation de l'éthylène, une autre classe de catalyseurs en plein essor est constituée par les catalyseurs de nickel neutres construits autour d'un ligand (N,O), dont les atomes d'azote sont porteurs de groupements aryles stériquement encombrés. Ces catalyseurs ont d'abord été développés par Grubbs *et al.* qui utilisent des ligands du type salicylaldimine **13**,[45] alors que Brookhart *et al.* utilisent des ligands du type anilinotropone **14**.[46] Très récemment, le premier catalyseur binucléaire neutre de nickel du type bis (N,O) **15**, construit autour d'une structure 2,5-diamino-*p*-benzoquinone, a été décrit et utilisé avec succès en polymérisation de l'éthylène.[47]



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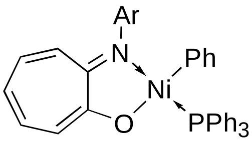

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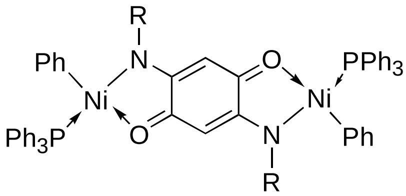

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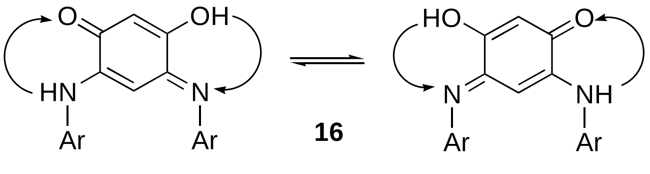
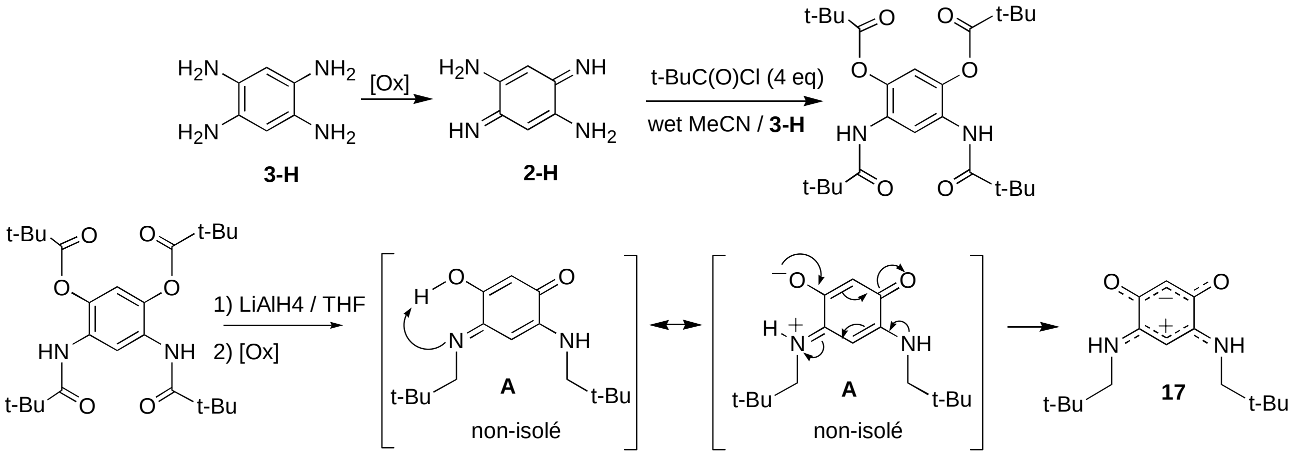
Dans le domaine de la chimie des quinones porteurs d'hétéroatomes mixtes N,O, les dérivés du type quinonemonoimines occupent un rôle central dans de nombreuses applications, en particulier dans le domaine de la photographie et des colorants capillaires, dans lesquels la couleur du colorant est souvent associée à une structure du type benzoquinonemonoimine, étant donné que les colorants d'oxydation sont les seuls qui puissent donner aux cheveux des colorations permanentes avec une grande variété de tons.[48-51] Cependant, les difficultés rencontrées dans la synthèse de ces composés, qui généralement est basée sur des attaques nucléophiles d'amines substituées sur des dérivés quinoniques et conduit à un mélange de produits, ont longtemps considérablement limité leur utilisation en vue d'applications synthétiques, en particulier en chimie de coordination. Des chercheurs de L'Oréal® ont été les premiers à décrire une structure de ces composés aminobenzoquinoneimine du type **16**.[52]



16

Ils établirent que la RMN ^{1}H de ces types de composés était simplifiée par la présence d'un équilibre rapide entre deux formes tautomères en supposant une migration de proton entre le NH et le C=O d'une part, et entre le OH et le C=N d'autre part.

La présence de deux sites de chélation différents (N,O) pour la première fois dans une même molécule ainsi que le succès des ligands (N,O) de Grubbs et Brookhart a montré l'intérêt de développer une voie de synthèse efficace des composés du type **16**. Celle ci fut amorcée par la découverte fortuite d'un autre composé lors de la synthèse du tétraamidobenzene, précurseur des ligands **2**. En effet, comme l'avait déjà montré Nietzki, le 1,2,4,5-tetraaminobenzene **3-H** est un composé facilement oxydable en sa forme quinonique **2-H**, et sa réaction avec un chlorure d'acide dans l'acétonitrile en milieu basique conduit à la formation attendue du 1,2,4,5-tetraamidobenzene, mais aussi à la formation d'un diamidodiester obtenu avec un rendement de 25%, dont la structure a été obtenue par diffraction des rayons X.[53] La réduction de ce composé par $LiAlH_4$ dans le THF à reflux suivi par un traitement aérobique fournit un composé pourpre **17** dont les données RMN pouvaient correspondre à la forme canonique **16**. Néanmoins, la structure exacte de ce composé fut obtenue par diffraction des rayons X. En réalité, le composé est un zwittérion à 12 électrons π délocalisés dans lequel la charge négative est délocalisée entre les atomes d'oxygène et la charge positive entre les atomes d'azote. La formation de ce composé résulte d'une migration de proton depuis l'atome d'oxygène vers l'atome d'azote iminique plus basique et qui s'accompagne d'une délocalisation de charge (Schema 7).[53]



Schema 7. Synthèse du ligand zwittérionique **17** décrite en 2002.[53]

La délocalisation électronique dans la molécule **17** représente un nouveau schéma électronique pour les composés du type mérocyanine. En particulier, la présence d'une charge positive délocalisée entre les atomes d'azote rend ce composé potentiellement très intéressant dans de nombreuses applications que nous étudierons en détails. On peut d'abord citer la chimie des colorants capillaires, du fait de la présence d'une charge négative sur la kératine pouvant induire une interaction électrostatique forte avec **17**. Ce composé présente également un intérêt certain en chimie de coordination puisque la présence de 2 sites de chélation (N,O) pourrait conduire à la synthèse de complexes mono ou polynucléaires potentiellement actifs en catalyse de polymérisation, comme prouvé par l'activité des complexes du type **15**, où à des complexes à valence mixte originaux.

Dans le présent travail, nous exposerons dans un premier chapitre la chimie de coordination des ligands du type 2,5-diamino-1,4-benzoquinonediimine **2** qui se révèlera très variée et souvent inattendue. Diverses applications des complexes synthétisés seront également présentées, en particulier la catalyse d'oligomérisation de l'éthylène, qui est encore un des grands enjeux de l'industrie pétrochimique, mais aussi leur potentiel en tant que complexes à valence mixte.

Dans un second chapitre, nous présenterons une étude complète et détaillée de la molécule zwittérionique **17**, qui a rapidement été l'objet d'une grande curiosité intellectuelle de la part de chimistes théoriciens du monde entier. Ainsi, dans un premier temps, nous présenterons une nouvelle voie de synthèse plus efficace de cette molécule permettant d'étudier plus facilement toutes ses applications synthétiques. Ainsi nous montrerons qu'il est possible de contrôler la délocalisation électronique du système à 12 électrons π et d'accéder à une vaste gamme de complexes organométalliques. La structure quinonemonoimine de **17** nous permettra également d'évaluer le potentiel de ces dérivés cationiques comme colorant capillaire en partenariat avec un industriel. L'ensemble de ces étude expérimentales sera couplé à une étude théorique par méthode DFT du zwittérion **17** et de trois de ses dérivés, réalisée au laboratoire de Chimie Théorique de l'Université Louis Pasteur.

Enfin, dans un dernier chapitre, nous présenterons l'étude complète et détaillée du mécanisme de formation du zwittérion **17**, conduisant à la découverte d'une autre classe d'aminobenzoquinones, dont nous étudierons en particulier la chimie supramoléculaire.

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PART 1: Studies on the Reactivity of New Conjugated 2,5-diamino-1,4-benzoquinonediimine Ligands

This first part contains four chapters in the form of publications and their corresponding annexes. The first chapter is a publication in press in *Comptes Rendus de Chimie de l'Académie des Sciences*, corresponding mainly to the work carried out by a DEA-student, Aude Demessence. Related to this article, a publication has been submitted on new very surprising properties of *cis*-[W(CO)$_4$(piperidine)$_2$], but does not appear in this manuscript. The second chapter is a publication, to be submitted, which describes electrochemical studies that have been performed in collaboration with Laboratoire de Chimie Organo-Minerale. The third and fourth chapters are publications to be submitted.

Chapter 1: Revised manuscript MGC8

for the Comptes Rendus Chimie de l'Académie des Sciences

special issue Le Floch/Crabtree

Relocalization of the π system in benzoquinonediimines induced by metal coordination

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Abstract

We report the synthesis and characterization of the tungsten carbonyl complexes *cis*-[$W(CO)_4C_6H_2(NHR)_2(=NR)_2$] (**8**, R = neopentyl ; **10**, R = benzyl), which contain a chelating ortho-diimine moiety. Their formation can be explained by a metal coordination-induced relocalization of the π system of the precursor *para*-benzoquinonediimine ligand $C_6H_2(NHR)_2(=NR)_2$ (**3**, R = neopentyl ; **9**, R = benzyl). The UV-visible spectra of the complexes revealed the presence of a strong band at 607 et 620 nm, respectively, which is characteristic of a MLCT transition.

Résumé

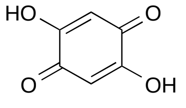
Nous décrivons la synthèse et la caractérisation des complexes carbonyles du tungstène *cis*-[$W(CO)_4C_6H_2(NHR)_2(=NR)_2$] (**8**, R = néopentyl ; **10**, R = benzyl) qui contiennent un fragment ortho-diimine chélatant. Leur formation peut s'expliquer par une relocalisation du système π de la *para*-benzoquinonediimine de départ $C_6H_2(NHR)_2(=NR)_2$ (**3**, R = néopentyl ; **9**, R = benzyl), qui est induite par la coordination du centre métallique. Les spectres UV-visibles de ces composés ont révélé la présence d'une bande intense à 607 et 620 nm, respectivement, caractéristique d'une transition MLCT.

Keywords: π-systems; benzoquinonediimines; metal coordination; UV-visible absorption; tungsten carbonyl complexes

Mots clés: systèmes π; benzoquinonediimines; coordination métallique; absorption UV-visible; complexes carbonyles du tungstène

1. Introduction

The rich chemistry of molecules exhibiting a quinonoid structure has attracted the interest of a large scientific community for decades owing to their implications in organic and physical chemistry but also as ligands in coordination chemistry [1]. More specifically, the 2,5-dihydroxy-1,4-benzoquinone ligand **1** has been much used because it can provide a variety of binding sites to metal cations and has allowed the preparation of a large number of metal complexes [2]. Although the 2,5-diamino-1,4-benzoquinonediimine family $C_6H_2(NHR)_2(=NR)_2$, which includes **2-4**, is closely related to **1**, it is surprising that its coordination chemistry has remained unexplored.



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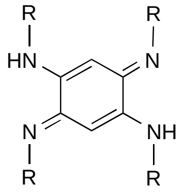
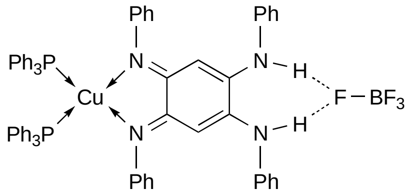


2 R = Ph
3 R = Np
4 R = H

Indeed, whereas the preparation of the derivative **2** (R = phenyl), was reported more than one century ago (1875) [3], its first use as a ligand for the synthesis of metal complexes was only described in 1998 by Kaim and co-workers who observed a *para→ortho* isomerization induced by metal coordination and the formation of the mononuclear Cu(I) complex **5** [4]. The stabilization of the higher energy *ortho* form in **5** was suggested to result from the secondary amine functionalities in the 4,5-positions which interact with a fluorine atom of the tetrafluoroborate anion via N-H···F···H-N hydrogen bonding [4].



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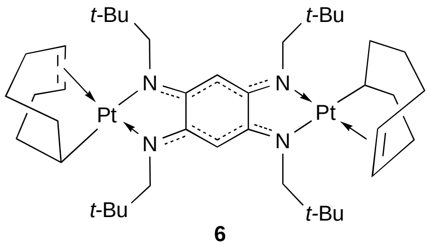

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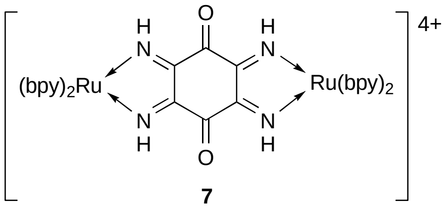

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More recently, we reported the synthesis of ligand **3** in which the N-substituent is for the first time an alkyl group [5]. In its diplatinum complex **6**, the π system is fully delocalized [5]. Note that Lever and coworkers recently reported the preparation of a dinuclear complex by metalation of **4** (R = H). They did not obtain the expected compound but an oxidized form of the bridging ligand, as shown in **7** [6]. Therefore, to the best of our knowledge, only two complexes have been reported in the literature that were obtained from a metalation reaction of molecules of the type **2** and **3**.

Herein, we wish to describe the synthesis of two new complexes, *cis*-[$\mathrm{W(CO)_4C_6H_2(NHR)_2({=}NR)_2}$] (**8**, R = neopentyl ; **10**, R = benzyl), which illustrate a further aspect to be considered in the coordination chemistry of quinonoid ligands.

2. Results and discussion

Reaction of *cis*-[$\mathrm{W(CO)_4(NHC_5H_{10})_2}$] [7], which has two labile piperidine ligands, with ligand **3** [5] in THF led to the formation of a deep blue product (Fig. 1).

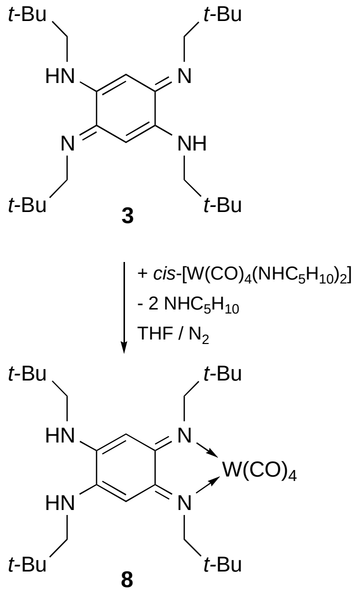


Fig. 1. Synthesis of the mononuclear complex **8**.

The spectroscopic data revealed the formation of the mononuclear tetracarbonyl complex **8** which resulted from a coordination-induced rearrangement of the electronic situation within the ligand, leading to a chelating *cis*-diimine moiety. Its IR spectrum in the ν(CO) region is consistent with a *cis* coordination of the ligand and a C_{2v} local symmetry about the metal centre [8]. The room temperature ^{1}H NMR spectra of **8** and of **3** for comparison are reported in Fig. 2 [5].

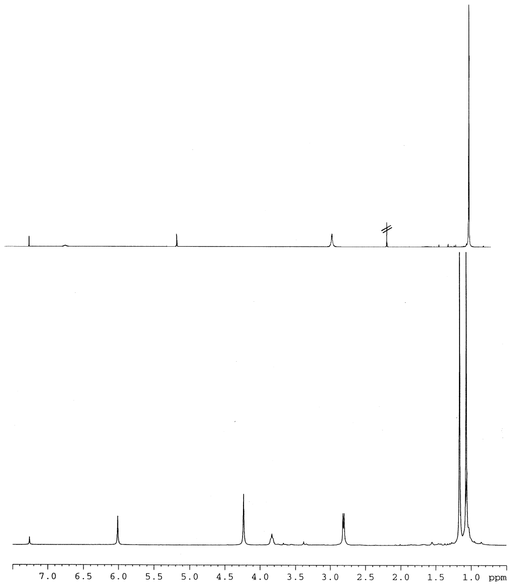


Fig 2. Room temperature ^{1}H NMR spectra of **3** (top) and **8** (bottom) in $CDCl_3$.

Whereas the ^1H NMR spectrum of **3** (Fig. 2, top) shows a structure of higher symmetry consistent with a fast intramolecular double proton transfer at room temperature involving two identical tautomers in solution [9], which generates a centrosymmetric average structure **3a** (Fig. 3), the spectrum of **8** indicates the presence of two chemically different neopentyl groups which confirms the C_{2v} symmetry of the molecule (Fig. 2, bottom).

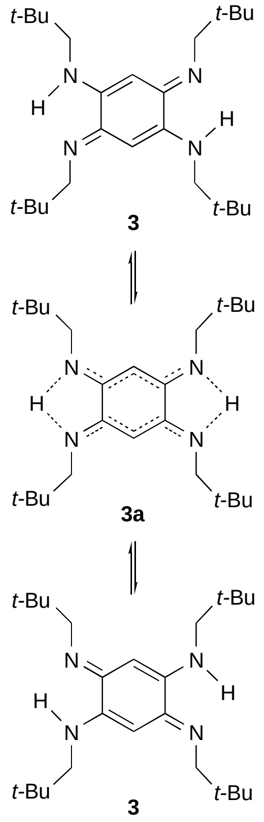


Fig 3. Intramolecular double proton transfer of **3** at room temperature

The CH_2 groups linked to the amine functions appear as a doublet at 2.81 ppm since each of them experiences a ^3J(HH) coupling with a N-H proton. The CH_2 groups linked to the imine functions are strongly downfield shifted (4.24 vs 2.95 ppm) upon coordination owing to the resulting decrease of electron density.

Previous studies have shown that complexes of the type [$M(CO)_4$(α-diimine)] (M = Cr, Mo or W) play an important role in the understanding of the photophysical behaviour of chromophoric complexes with low-lying metal to ligand charge transfer (MLCT) excited states [10,11] and this prompted us to study the electronic properties of the new *cis*-[W(CO)$_4$(α-diimine)] complex **8**. In contrast to the UV-vis absorption spectrum of **3** which shows an intense absorption band at 340 nm that is assigned to the intraquinone transition [12], that of **8** revealed a very strong absorption at 607 nm (ε = 30800 mol^{-1}·dm^3·cm^{-1}), consistent with a MLCT transition (W(CO)$_4$→N,N) [10] (Fig. 4).

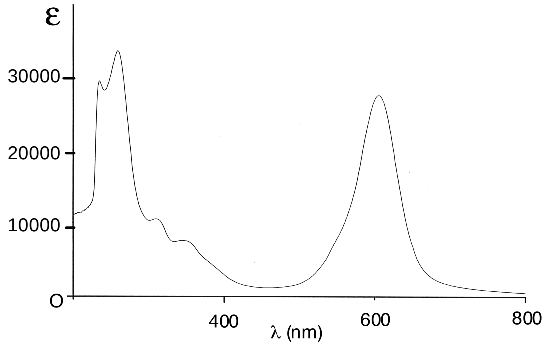
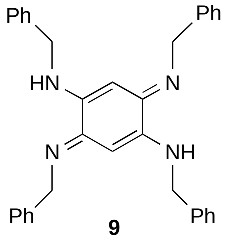


Fig. 4. UV-visible absorption spectrum of **8** in dichloromethane (ε in mol^{-1}·dm^3·cm^{-1}).

A fluorescence study of **8** at 345 and 606 nm in degassed CH_2Cl_2 revealed no significant signal at room temperature. By analogy with aryl-containing polyamine receptors, the use of benzyl groups as N-substituents is expected to lead to fluorescent probes [13-15]. Therefore, we prepared compound **9** [15] and the corresponding tungsten complex **10** according to the procedure used for the synthesis of **8**.



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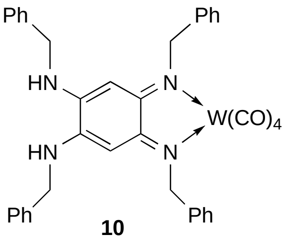

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Similarly to **8**, compound **10** is deep blue and shows a similar UV-visible absorption spectrum with a intense band at 620 nm (ε = 26500 mol^{-1}·dm^3·cm^{-1}). No emission was observed at room temperature although we have previously found that molecule **9** is an efficient fluorescent probe [15]. This could be explained by a transfer of energy in the excited state from the fluorescent benzyl moiety to the metal centre [16].

Although the formation of complexes **8** and **10** is related to that of compound **5**, our results demonstrate that hydrogen bonding interactions involving secondary amine functionalities in the 4,5-positions are not necessary for the stabilization of the higher energy *ortho* form of the quinonoid structure [4]. Furthermore, Kaim *et al.* explained the formation of **5** by a *para*→*ortho* isomerization induced by coordination. We suggest to describe the formation of complexes **8** and **10** as resulting from a metal-induced relocalization of the π system of the benzoquinonediimine average structure **3a**.

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk tube and cannula techniques. Solvents were dried and distilled under nitrogen before use. Compound **3**, **9** and *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ were prepared according to published procedures [7, 12, 15] and NEt_3 was purchased from commercial suppliers and used without further purification. Chromatographic separations were performed on silica gel 60, 40-63 μm granulometry, Merck. The ^1H and ^{13}C NMR spectra were recorded on a AC300 Bruker spectrometer. Infrared spectra were recorded on a Perkin Elmer FT-IR 1600 spectrometer. Elemental C, H and N analyses were performed by the ″Services de Microanalyses″ (Institut Charles Sadron, Strasbourg, France).

3.2. Synthesis of the complexes

*3.2.1 Compound **8***

To a yellow solution of *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (1.00 g, 2.15 mmol) in 150 ml of THF was added yellow solid **3** (0.90 g, 2.15 mmol) under vigorous stirring. The reaction mixture was heated to reflux. After 15 h, the green solution was filtered and the filtrate was chromatographed on a silica gel column neutralised with NEt_3. First, a mixture of pentane/NEt_3 (90:10, v/v) was used as eluent to eliminate all of the yellow ligand. Then CH_2Cl_2 was introduced to allow the migration of the blue product. Compound **8** was purified by extraction with CH_2Cl_2/H_2O, then *n*-hexane was added to the organic phase and the air-sensitive product was dried in vacuo. Yield: 0.70 g (46%). Although no satisfactory elemental analyses were obtained owing to the instability of **8**, the C,H,N data were consistent with a 1:1 metal/ligand ratio.

IR (CH_2Cl_2): ν (cm^{-1}) = 1994 (s, $\nu_{C\equiv O}$), 1891 (s, $\nu_{C\equiv O}$), 1831 (m, $\nu_{C\equiv O}$). ^1H NMR ($CDCl_3$): δ = 6.01 (s, 2 H, $C_{sp2}H$), 4.24 (s, 4 H, CH_2), 3.83 (t, $^3J(HH)$ = 6.0 Hz, 2 H, NH), 2.81 (d, $^3J(HH)$ = 6.0 Hz, 4 H, CH_2), 1.16 (s, 18 H, CH_3), 1.07 (s, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 163.17 (C=N), 141.99 (C_{sp2}–NH), 94.52 ($C_{sp2}H$), 69.50, 55.17 (CH_2), 35.83, 31.33 (*C*Me_3), 30.42, 27.86 (CH_3). UV-vis (CH_2Cl_2, 298 K): λ (nm), (ε) ($mol^{-1}\cdot dm^3\cdot cm^{-1}$) 259 (37400); 310 (11700); 344 (8400); 607 (30800).

*3.2.2. Compound **10***

Following a procedure similar to that described for **8**, **10** was isolated as a blue solid. Yield: 17%. IR (CH_2Cl_2): ν (cm^{-1}) = 1997 (vs, $\nu_{C\equiv O}$), 1902 (s, $\nu_{C\equiv O}$), 1837 (m, $\nu_{C\equiv O}$). ^1H NMR ($CDCl_3$): δ = 7.26 (m, 20 H, $H_{aromatic}$), 6.16 (s, 2 H, $C_{sp2}H$), 5.44 (s, 4 H, CH_2), 4.30 (t, $^3J(HH)$ = 6.0 Hz, 2 H, NH), 4.13 (d, $^3J(HH)$ = 6.0 Hz, 4 H, CH_2). UV-vis (CH_2Cl_2, 298 K): λ (nm), (ε) ($mol^{-1}\cdot dm^3\cdot cm^{-1}$) 258 (25400); 315 (10900) 620 (26500).

Acknowledgements

We thank Dr. Mourad Elhabiri (Laboratoire de Physico-Chimie Bioinorganique, UMR 7509 CNRS, ECPM, ULP Strasbourg) for the absorption and emission spectra. This work was

supported by the CNRS and the Ministère de la Recherche et des Nouvelles Technologies (Paris).

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ANNEX

We have previously reported the synthesis and characterization of the tungsten carbonyl complexes *cis*-$[\overline{W(CO)_4C_6H_2(NHR)_2(=N}R)_2]$ (**8**, R = neopentyl ; **10**, R = benzyl), which contain a chelating ortho-diimine moiety. The choice of tungsten as a metal precursor was motivated by our preliminar results in molybdenum chemistry. Indeed, we had first attempted the reaction of **3** with $Mo(CO)_6$ in refluxing toluene. As in the reaction with tungsten, we observed a color change from yellow to intense blue, confirming the formation of the mononuclear molybdenum complex **11** (Fig. 5)

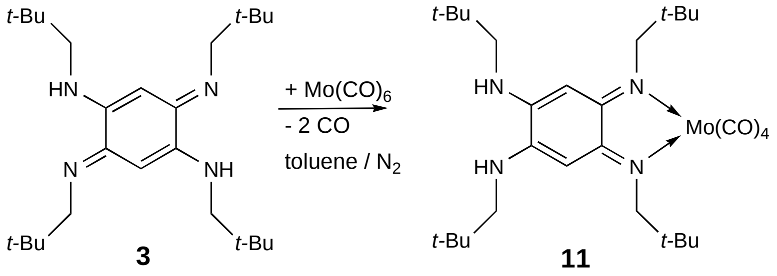

Fig. 5. Synthesis of the mononuclear complex **11**.

The ^{1}H NMR spectrum of the crude product revealed the formation of a mononuclear complex with the same symmetry than **8**. However, owing to a very low conversion of the starting material and the high unstability of the final product, we prefered to leave this reaction and explore its tungsten version (higher stability and high lability of the piperidine group in the metal precursor). Note that, owing to the presence of impurities in *cis*-$[W(CO)_4(NHC_5H_{10})_2]$, we have attempted to prepare **8** by reaction of **3** with $W(CO)_6$ in refluxing xylene, but only decomposition of the starting metal precursor was observed.

In order to compare our results with those of Kaim,[4] in particular to see the influence of the N-substituent on the reactivity, we have also attempted the reaction of **3** with $[Cu(CH_3CN)_4]BF_4$ in THF at room temperature (Kaim's procedures) (Fig. 6)

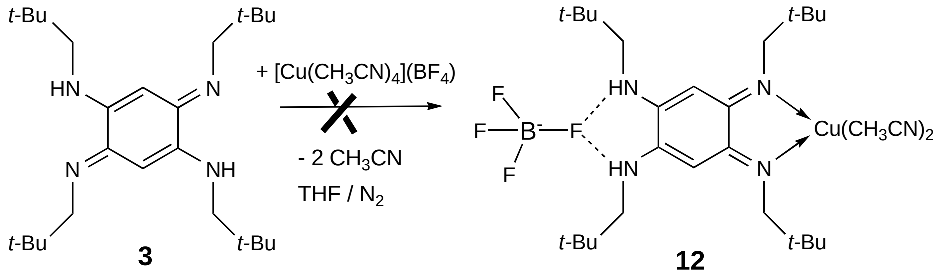

Fig. 6. Reaction of **3** with $[Cu(CH_3CN)_4]BF_4$.

However, despite a rapid color change from yellow to green, we did not succeed to isolate a new product after purification by column chromatography.

Experimental Section

Reaction of 3 with $Mo(CO)_6$ at 110 °C in toluene: To a suspension of $Mo(CO)_6$ (0.13 g, 0.48 mmol) in 100 ml of toluene was added yellow solid **3** (0.20 g, 0.48 mmol) under nitrogen. The reaction mixture was heated to reflux with CO release. After 3 h, the green solution was evaporated. The ^1H NMR spectrum of the residue show the presence of signals corresponding to **11**, together with unreacted **3** major.

Reaction of 3 with $W(CO)_6$ at 140 °C in xylene: To a suspension of $W(CO)_6$ (0.30 g, 0.85 mmol) in 100 ml of xylene was added yellow solid **3** (0.35 g, 0.85 mmol) under nitrogen. The reaction mixture was heated to reflux. After 3 days, no CO release was observed and the color of the solution became brown.

Reaction of 3 with $[Cu(CH_3CN)_4]BF_4$ in THF: To a suspension of $[Cu(CH_3CN)_4]BF_4$ (0.08 g, 0.24 mmol) in 100 ml of THF was added yellow solid **3** (0.10 g, 0.24 mmol) under nitrogen at room temperature. After 1 h, the green solution was evaporated. The residue was chromatographed on silicagel but only unreacted **3** (0.06 g) was obtained by elution with acetone/hexane.

Chapter 2: Novel Tunable Mixed-Valence Complexes Displaying Ligand-Mediated Metal-Metal Interaction

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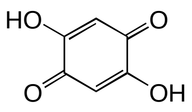
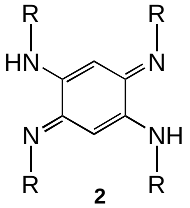
[**] This work was supported by the Centre National de la Recherche Scientifique and the Ministère de la Recherche et des Nouvelles Technologies. We also thank Prof. R. Welter for the X-ray structure determination and Dr D. Mandon for measurement of the NIR spectra.

Electronic communication within a multicomponent molecule is central to the emergence of new properties in biological, physical and chemical systems.[1,2] 35 years after the pioneering studies on the Creutz-Taube diruthenium complex linked by a pyrazine bridging ligand,[3,4] which provided the first example of an interaction between two metal centers mediated by an organic linker, a considerable research effort is still dedicated to the field of electronic communication between transition metal centers.[5-11] Studying the molecular magnetism, the electrochemical behavior and the intervalence band in mixed-valence systems provides typical probes of this electronic communication, and a great diversity of linkers is being used to mediate the electron transfer between the redox centers by providing effective overlap between their π system and the orbitals of the metals (non-innocent behaviour).[1,2,12-15] Chelating 1,2-dioxolenes (type **1**) have recently attracted much attention as spacers since they combine ligand-based and metal-based redox activity.[16] Extending such studies to their nitrogen analogues **2**[17-19] would allow further fine-tuning of the electronic communication between the metal centres since replacement of the oxygen atom by the NR group should not only directly affect the metal coordination but also allow variations at the R substituent.



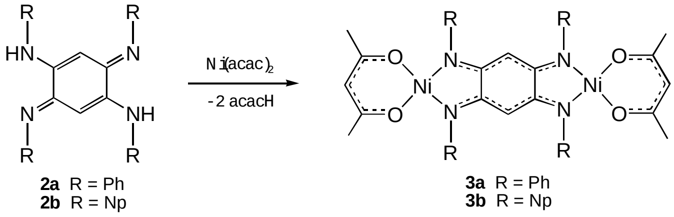
1



2

The first and only binuclear complex prepared from a 2,5-diamino-1,4-benzoquinonediimine derivative **2** (in which R = Np, see molecule **2b**),[17,18] a diplatinium(II) compound, was recently isolated in only *ca.* 15% yield, which limited considerably its study.[17] Herein, we describe the high yield synthesis and properties of new class III (Robin-Day classification[20]), fully delocalized mixed-valence dinickel complexes. The influence of the N-substituents on the extent of metal-metal interaction is clearly demonstrated and has allowed to reach a comproportionation constant K_c as high as 3.7 x 10^{14} for **3b**, which is eight orders of magnitude larger than that of the Creutz-Taube ion[4] and six orders of magnitude larger than that the strongest known coupled Ni^{II}-Ni^{III} complex reported so far.[21]

The metallation reaction of the long known azophenine **2a**[19] with [Ni(acac)$_2$] (2 equiv.) in THF (Scheme 1) afforded **3a** as a violet crystalline solid (*ca.* 82% yield).[22]



Scheme 1. Synthesis of the dinuclear complexes **3a** and **3b**.

Its ^{1}H NMR spectrum revealed no NH resonance and the presence of four magnetically equivalent methyl groups, which is consistent with a fully delocalized π system. This electronic delocalization prompted us to study the ability of **3a** to display ligand-mediated metal-metal interaction. Its electrochemical properties have been studied by cyclic and linear sweep voltammetry in anhydrous THF containing N(*n*-Bu)$_4$PF$_6$ as supporting electrolyte. The cyclovoltammogram of **3a** shows two reversible redox waves resulting from two successive one-electron oxidation processes. The separation between these two waves $\Delta E_{1/2}$ = 300 mV corresponds to a comproportionation constant K_c of 1.2 x 10^5.[20,23]

Systems **2** offering the advantage over **1** to allow additional fine-tuning of the electronic properties by varying the nature of the R substituents, we decided to replace the π-acceptor N-substituent in **3a** by a σ-donor group, which should stabilize the $[Ni^{II}-Ni^{III}]^+$ species. Thus, the dinuclear complex **3b**[22] was prepared in toluene by metallation reaction of **2b**, similarly to **3a**. Its molecular structure has been elucidated by X-ray diffraction which confirmed the centrosymmetry of the molecule (Figure 1).[24] The dianion derived from **2b** acts as a tetradentate bridging ligand in a bis(chelating) fashion.

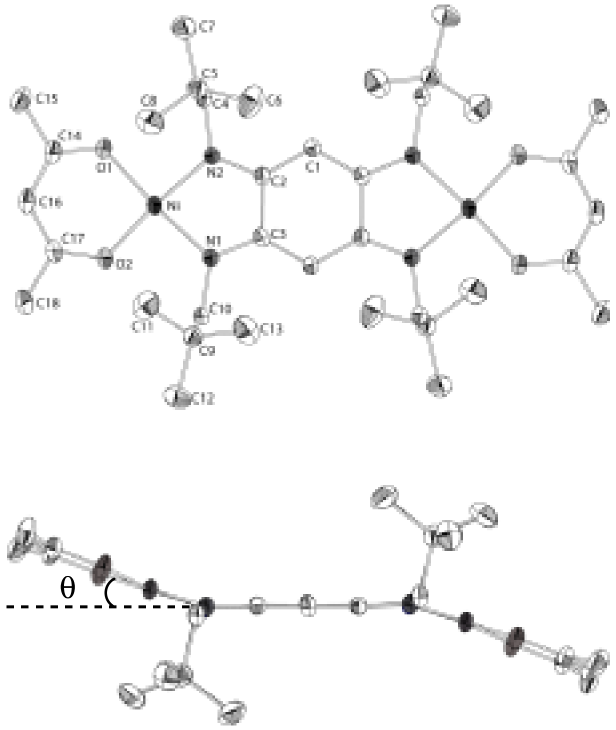


Figure 1. Top and side views of the crystal structure of **3b**. Selected bond distances (Å) and bond angles (°): Ni-N(1) 1.876(2), Ni-O(2) 1.848(2), Ni-O(1) 1.852(2), Ni-N(2) 1.877(2), N(1)-C(3) 1.332(3), C(3)-C(2) 1.500(3), C(2)-C(1) 1.404(3), C(2)-N(2) 1.333(3); N(1)-Ni-N(2) 83.27(8), N(1)-Ni-O(1) 175.10(7), N(1)-Ni-O(2) 91.01(7), O(1)-Ni-O(2) 93.84(7), Ni-N(1)-C(3) 114.2(2), N(2)-C(2)-C(3) 112.0(2), N(1)-C(3)-C(2) 111.7(2), N(2)-C(2)-C(1) 128.7(2).

The coordination geometry around the nickel centers is square planar with the metal being only slightly out the plane containing the C_6 ring (deviation of the Ni centre with respect to plane is θ = 23°). The Ni···Ni separation of 7.62(2) Å is similar to that found in a binuclear nickel complex containing **1**.[25] Examination of the bond distances within the N(1)-C(3)-C(1′)-C(2′)-N(2′) and N(2)-C(2)-C(1)-C(3′)-N(1′) moieties shows an equalisation of the C-C and C-N distances which is consistent with a complete electronic delocalisation of the π system. There is no conjugation between these two moieties since the C(2)-C(3) distance of 1.500(3) Å corresponds to a typical single bond.[17]

The voltammogram of **3b** shows two reversible redox processes located at 0.05 V and 0.91 V vs Fc^+/Fc. The ratio of the peak currents (Ip_a/Ip_c) is unity and the peak separation (Ep_a-Ep_c) is around 80 mV at different scan rates for each signal. The two redox couples described by the equations (1) and (2) (Figure 2) correspond to monoelectronic electron transfers as demonstrated by coulometry and linear sweep voltammetry experiments.

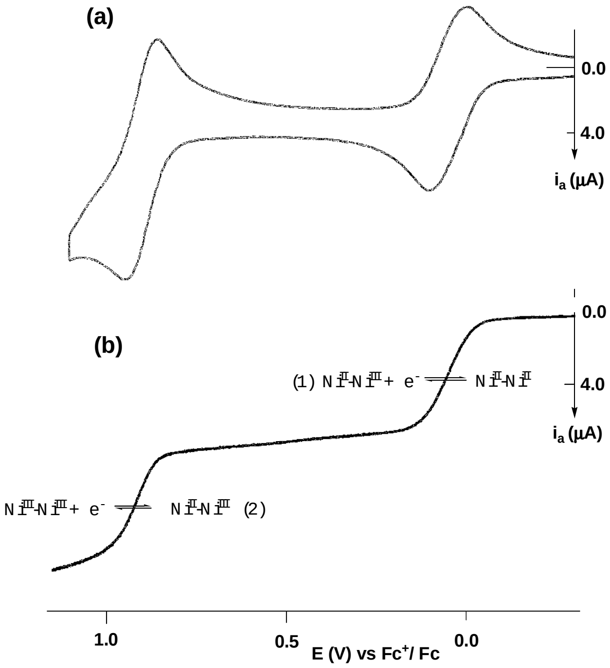


Figure 2. (a) Cyclic voltammogram of **3b** in anhydrous CH_2Cl_2 (0.1 M $N(n\text{-}Bu)_4PF_6$) at a scan rate of 100 $mV.s^{-1}$; (b) Linear-sweep voltammogram of the same solution at Pt rotating disk electrode (scan rate = 5 $mV.s^{-1}$, rotation rate = 1000 rpm).

The separation between the two redox processes $\Delta E_{1/2}$ = 850 mV for **3b** is much larger than for **3a** and the comproportionation constant K_c corresponding to equilibrium (3) is equal to 3.7 x 10^{14}.

$$Ni^{II}\text{-}Ni^{II} + Ni^{III}\text{-}Ni^{III} \xrightleftharpoons{K_C} 2\ Ni^{II}\text{-}Ni^{III} \quad (3)$$

This value indicates the much higher stability of the $[Ni^{II}\text{-}Ni^{III}]^+$ state of **3b** in relation to **3a** owing to the influence of the N-substituents (σ-donor alkyl vs π-acceptor aryl groups), and is consistent with a class III mixed-valence complex (fully delocalized) which should then be described as $[Ni^{2.5+}\text{-}Ni^{2.5+}]$.[13,20]

The electronic spectrum of **3b** shows two transitions at 479 and 510 nm in CH_2Cl_2 (Figure 3). The first band is typical of a $\pi \rightarrow \pi^*$ transition of the benzoquinonediimine bridging ligand,[18] whereas the second band corresponds to a MLCT transition.[13] The electronic spectrum of the mixed-valence complex [**3b**]$^+$ exhibits the corresponding red shifted bands at 512 and 542 nm. The NIR spectrum recorded during coulometry experiment ($E_{applied}$ = 0.5 V vs Fc^+/Fc) displays a broad shoulder band at 1030 nm consistent with the expected inter-valence charge transfer.

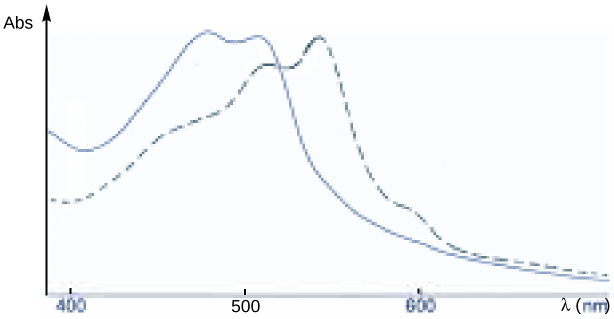


Figure 3. Electronic spectra in CH_2Cl_2 of **3b** (——) and the mixed-valence complex [**3b**]$^+$ (---).

In conclusion, we have discovered a new family of mixed-valence complexes which display for **3b**, to the best of our knowledge, the largest comproportionation constant described in dinickel chemistry with the exception of a very recently reported metal-metal bonded $Ni^{0.5+}$-$Ni^{0.5+}$ complex.[26] In contrast to most previously studied systems,[6,13-16] ligands such as **2** will also allow modifications of the N-substituents, thus making possible fine-tuning of the properties of the corresponding binuclear compounds as demonstrated here with **3a** and **3b**. Further variations will now become possible. Furthermore, these complexes are currently studied as homogeneous catalysts for olefin oligomerization since binuclear complexes displaying metal-metal interaction are of growing interest in catalysis.[27,28]

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[22] *Selected data:* for **3a**: ligand **2a**[19] (0.68 mmol, 0.30 g) was dissolved in 100 mL of THF and Ni(acac)$_2$ (1.36 mmol, 0.35 g) was added to the red solution which turned immediately into intense purple. The reactionnal mixture was stirred

at room temperature overnight. The solution was then filtered on Celite and the filtrate was evaporated, redissolved in 100 mL of dichloromethane and slowly evaporated to afford **3a** as a violet cristalline product. Yield: 0.42 g (82 %). $C_{40}H_{36}N_4O_4Ni_2$; anal. Calcd.: C, 63.71; H, 4.81; N, 7.43; found: C, 63.84; H, 5.02; N, 7.33. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ••1.35 (s, 12 H, CH_3–acac), 4.34 (s, 2 H, N⎓C⎓C–H), 5.20 (s, 2 H, CH–acac), 7.2 (m, 20 H, CH–aryl); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K) δ: 24.60 (CH_3–acac), 89.28 (H–*C*⎓C), 100.90 (CH–acac), 124.52, 126.94, 127.57, (CH–aryl), 145.11 (C–aryl), 165.51 (C⎓N), 186.21 (C⎓O). MS (Maldi-TOF): m/z: 753.231 [*M+1*]$^+$. UV-visible (CH_2Cl_2) λ(nm), ε($M^{-1}.cm^{-1}$): 523 (16600), 555 (19500).

For **3b**: **2b**[17,18] (0.48 mmol, 0.20 g) and $Ni(acac)_2$ (0.96 mmol, 0.25 g) were dissolved in 100 mL of toluene and heated to reflux for one night. The solution was then concentrated and green crystals suitable for an X–ray analysis were isolated by filtration. Yield: 0.19 g (55%). Elemental analysis (%) calcd for $C_{36}H_{60}N_4O_4Ni_2$:C 59.21, H 8.28, N 7.67; found: C 59.22, H 8.18, N 7.69. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ••1.05 (s, 36 H, CH_3), 1.79 (s, 12 H, CH_3–acac), 2.11 (s, 8 H, N–CH_2), 4.93 (s, 2 H, N⎓C⎓C–H), 5.34 (s, 2 H, CH–acac). ^{13}C NMR (50 MHz, $CDCl_3$, 298 K) δ: 25.45 (CH_3–acac), 29.00 (C*Me*$_3$), 34.82 (C*Me*$_3$), 51.72 (N–CH_2), 88.13 (H–*C*⎓C), 101.13 (CH–acac), 167.02 (C⎓N), 185.86 (C⎓O). UV-visible (CH_2Cl_2) λ(nm), ε($M^{-1}.cm^{-1}$): 479 (13500), 510 (14700).

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[24] Crystal data for **3b**: $C_{36}H_{60}N_4O_4Ni_2$, M_r = 730.30 $g.mol^{-1}$, green prism, size 0.08 x 0.10 x 0.13 mm, triclinic, space group *P*-1, *a* = 9.7060(10), *b* = 10.2970(10), *c* = 10.9920(10) Å, α = 63.863(5), β = 88.607(5), γ = 77.502(5)°, *V*= 959.70(16) Å^3, *T* = 293 K, Z = 1, ρ_{calc} = 1.264 $g.cm^{-3}$, μ(Mo-Kα) = 1.021 mm^{-1}, *F*(000) = 392, 10595 reflections in *h*(-13/10), *k*(-

14/14), *l*(-15/15), measured in the range 2.1°≤ θ ≤ 30.0°, 5582 independant reflections, R_{int} = 0.039, 4207 reflections with $I > 2\sigma(I)$, 208 parameters , $R1_{obs}$ = 0.0459, $wR2_{obs}$ = 0.1375, GOF = 1.071, largest difference peak and hole 0.66/-0.85 e/$Å^{-3}$. CCDC 230827 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Chapter 3: Nickel and Palladium dinuclear complexes with bridging 2,5-diamino-1,4-benzoquinonediimines: Synthesis, Structures and Catalytic Oligomerization of Ethylene

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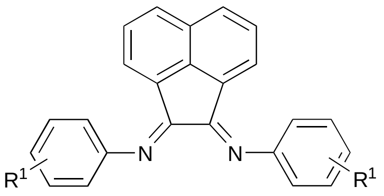
Abstract: Dinuclear acetylacetonato complexes of Ni(II) and Pd(II) have been prepared by the reaction of the corresponding bis(acetylacetonato)metal precursor with different 2,5-diamino-1,4-benzoquinonediimines as bridging ligand. All complexes were fully characterized, including by X-ray diffraction for **9b** and **10a**. In all complexes, the coordination geometry of the metal ions is square-planar and a complete electronic delocalization of the quinonoid π system occurs over the two N⎓C⎓C⎓C⎓N halves of the ligand, between the metal centers. The nature of the N-substituent explains the differences between the supramolecular stacking arrangements of **9a** and **9b**. All complexes were tested in catalytic ethylene oligomerization with $AlEtCl_2$ or MAO as cocatalyst, in particular in order to study possible cooperative effects resulting from electronic communication between the metal centers, and to examine the influence of the N-substituent on the activity and selectivity.

Introduction

The field of ethylene polymerization and oligomerization catalysis with late transition metals has witnessed a phenomenal growth over the past ten years.[1,2] It was triggered by the preparation by Brookhart and coworkers of highly active Ni(II)- and Pd(II) diimine precatalysts for ethylene polymerization and oligomerization in the presence of a large excess of MAO (300 to 1000 equiv), build up around sterically hindered diimine ligands of type **1**.[3-6] Some catalysts produced oligomers in the range $C_6 - C_{24}$ with a high selectivity of 94% for α-olefins.[4] During the same period, other interesting N-N chelating ligands, in particular bis-amino ligands **2**[7] and amino-imine ligands **3**,[8] have been successfully applied to olefin polymerization.[9]



R^1 = 2,6-*i*-Pr, 2,6-*t*-Bu

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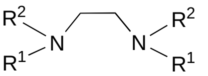

a: R^1 = Et, R^2 = Ph
b: R^1 = H, R^2 = Cy

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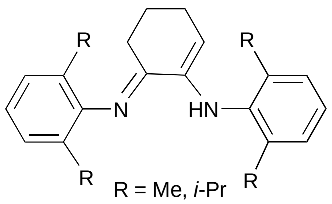

R = Me, *i*-Pr

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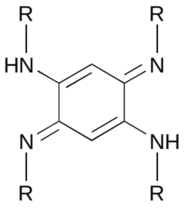
It is obvious that the design of organometallic precatalysts, in particular the nature and the architecture of the chelating ligands, is a key point for the control of the reactivity and selectivity. In the course of our studies on the use of functionnal ligand to design new active catalysts for the oligomerization of ethylene,[10-19] we noticed that the coordination chemistry of 2,5-diamino-1,4-benzoquinonediimine ligands of type **4** has been very little explored, despite the presence of two amino-imine chelating sites in the same molecule. Such ligands could be viewed as hybrids between the diamine and diimine type ligands mentioned above.



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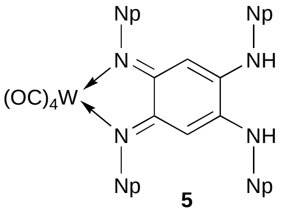
The first use of **4** (R = Ph) as ligand for the synthesis of metal complexes was only described in 1998 by Kaim and coworkers who observed a *para-ortho* isomerization of azophenine induced by metal coordination and the formation of a cationic mononuclear copper complex.[20] Very recently, this group has also reported a related neutral mononuclear rhenium complex[21] whereas we obtained, at the same time, a mononuclear tetracarbonyl tungsten complex, **5**, from **4** (R = Np).[22] In 2000, Lever and coworkers described the synthesis of a dinuclear ruthenium complex using **4** (R = H) but the product contained an oxidized form of the bridging ligand, which prevented electronic communication between the two metal centers.[23] To the best of our knowledge, only one dinuclear complex, **6**, has been prepared in 15% yield by metallation reaction of a ligand of type **4** (R = Np) with $PtCl_2(COD)$ in basic medium. The X-ray structure of this diplatinum compound revealed a benzoquinonediimine structure in which the π system is fully delocalized between the metal centers and over the nitrogen atoms of the bridging ligand.[24]



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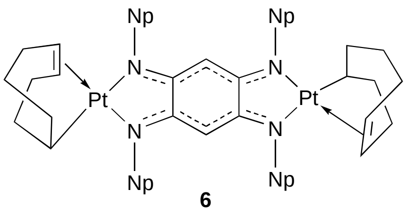

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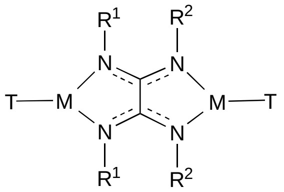
This type of dinuclear complex can be related to homodinuclear oxalamidinato complexes of type **7** reported by Walther and coworkers during the course of the present study.[25,26] These authors have shown that only the Ni(II) complexes bearing acac groups, with their π system fully delocalized between the metal centers, are selective precatalysts in the oligomerization or polymerization of ethylene upon activation with MAO or $AlEt_3$.



M = Ni, Pd; T = acac, allyl

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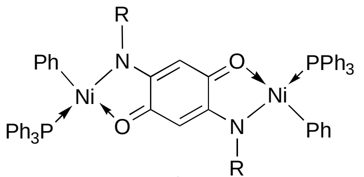
We decided to explore in more detail the coordination properties of 2,5-diamino-1,4-benzoquinonediimine ligands of type **4**, which are now readily accessible and whose steric and electronic properties can be fine-tuned.[27,28] We first needed to find general methods for metal complexation and anticipated that dinuclear late transition metal complexes, connected *via* the extended conjugated π system of the ligand, could be attractive candidates for studies on cooperative effects in catalytic reactions, in particular the oligomerization of ethylene, which is a reaction of considerable interest in both academic and industrial sectors.[29-32] These cooperative effects were recently emphasized by the preparation of highly active dinuclear 2,5-disubstituted amino-*p*-benzoquinone-Ni(II) complexes of type **8** used as single-component catalysts in ethylene polymerisation.[33]



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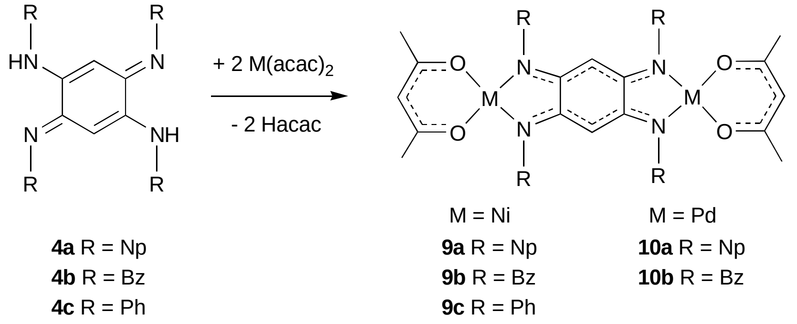
Here we describe the preparation, structural and dynamic properties of well-defined dinuclear Ni(II) and Pd(II) complexes containing 2,5-diamino-1,4-benzoquinonediimine ligands. The capacity of Ni(II) complexes to act as precatalysts in the oligomerization of ethylene upon activation with Et_2AlCl or MAO has also been investigated.

Results and Discussion

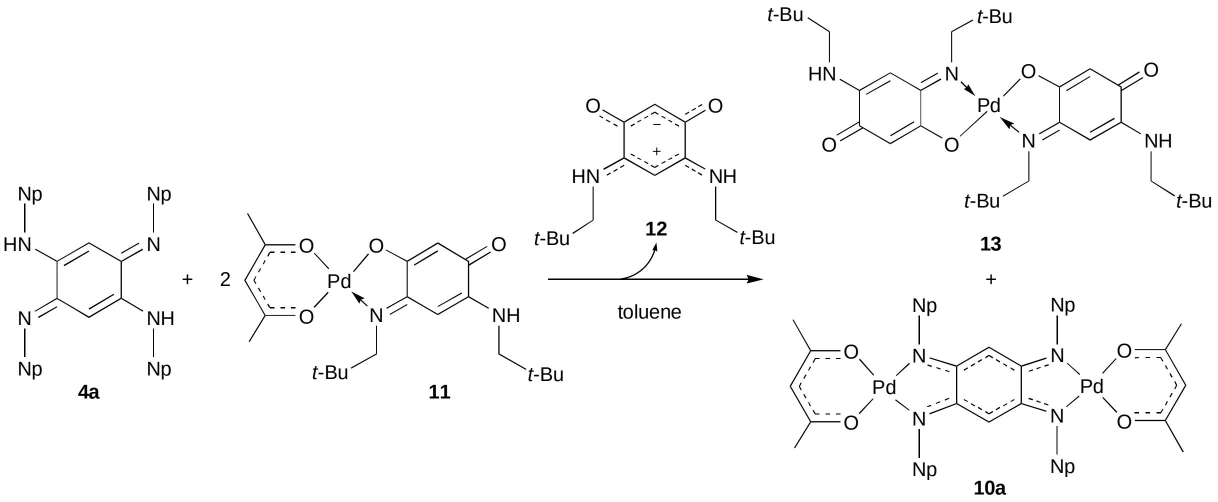
Synthesis of Ni(II) and Pd(II) Dinuclear Complexes. Dinuclear acetylacetonato complexes were prepared, in good yields, by the reaction of the corresponding bis(acac) metal precursor with the previously described[24,27,28] 2,5-diamino-1,4-benzoquinonediimines **4a-4c** (2 equiv of $[Ni(acac)_2]$ and 1 equiv of ligand for the Ni complexes, 1.6 equiv of $[Pd(acac)_2]$ and 1 equiv of ligand for the Pd complexes (Scheme 1). In these reactions, acetylacetone is eliminated and neutral complexes of the type [(acac)M(dabqdi)M(acac)] are obtained (abbreviation dabqdi for 2,5-diamino-1,4-benzoquinonediimine). We have used a slight excess of benzoquinonediimine ligand in the synthesis of the Pd complexes in order to convert all the Pd precursor which is more difficult to separate from the reaction mixture than the free ligand.

Scheme 1. Synthesis of the dinuclear complexes **9 – 10**



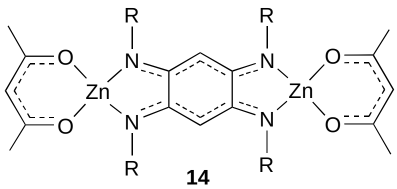
The reactions were carried out in THF at room temperature or in refluxing toluene for 12 h for the Ni complexes, in refluxing toluene for 3 days for the Pd complexes. After workup, the complexes [(acac)M(dabqdi)M(acac)] (**9**–**10**) were isolated as crystalline products in good yields. Note that **10a** could also be prepared, in good yield, by the reaction between **4a** and 2 equiv of the mononuclear palladium complex **11**,[34] leading after ligand redistribution to the formation of **10a** and the bis(benzoquinonemonoimine) Pd(II) complex **13** (Scheme 2).

Scheme 2. Alternative synthesis of **10a**.



The formation of the products may be explained by a higher basicity of the quinonic chelate than that of the acetylacetonate chelate and of **4a**. Complex **11** would react first with **4a** leading to the formation of **10a** and the eliminated zwitterion **12** could then react with **11** still present in solution, to afford **13** which precipitates in toluene.[34]

The synthesis of [(acac)Zn(dabqdi)Zn(acac)] **14** was also attempted starting from [Zn(acac)$_2$] but the product appeared to be unstable in solution, unlike its Ni and Pd analogs.



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In contrast, the reaction of **4a** with [Pt(acac)$_2$] (1.6 equiv of [Pt(acac)$_2$] and 1 equiv of ligand for the Pt complexes) was unsuccessful owing to the reduced reactivity of the platinum precursor.

The formation of coordination oligomers was never observed, indicating the stability and reduced reactivity of the terminal acac in complexes **9**–**10** which was also confirmed by the absence of reaction between **10a** and zwitterion **12** in THF (1 equiv of **10a** and 2 equiv of **12**), and between **10a** and 2 equiv of chlorotrimethylsilyle in refluxing toluene. Nevertheless, these acac groups react with organoaluminium compounds to form active catalysts.

Spectroscopic Properties and Crystal Structures. The dinuclear complexes **9**–**10** were characterized by elemental analysis, mass spectrometry and ^{1}H and ^{13}C{^{1}H} NMR spectroscopic methods. For each compound, the ^{1}H NMR spectrum revealed a structure with the same symmetry than for the free ligand,[24] with no N−H resonance. Furthermore, the presence of only one signal for each type of protons assigned to the bridging and terminal ligands and the relative integration of all signals clearly proved the centrosymmetry of the molecule.

A fluxional behaviour of the N–CH$_2$–*t*-Bu groups of **9a** and **10a** was observed by variable temperature ^{1}H NMR. The signal of the CH$_2$ groups appears as a very broad singlet at room temperature and becomes an AB system below coalescence temperature ($^{2}J_{\mathrm{AB}} \neq 8.5$ Hz). Note that for one of the two CH$_2$ protons, the shape of the signal is a multiplet instead of the expected doublet and this is so far unexplained. The $\Delta G^{\neq}$ values calculated for this dynamic behaviour are 55.3 and 61 kJ/mol, respectively. This phenomenon, which was not observed with complexes **9b** and **10b** where the N-CH$_2$–Bz substituents are less sterically hindered, could be explained by steric interactions between these CH$_2$ protons and the acac group, as already noticed in related systems,[35] which hinders the free rotation of the neopentyl group around the C–N bond at low temperature.

The N⎓C⎓C–H proton of **10a** appears at room temperature as a broad singlet and the signal for the corresponding H–C⎓C in the ^{13}C{^{1}H} NMR spectrum is broad and weak. This can be improved by increasing the pulse delay to 2 s. Furthermore, an interaction between one CH$_2$ proton and the N⎓C⎓C–H proton was detected by NOE, and further shown by a H-H ROESY experiment at –40 °C.[35]

Green single crystals of complex **9b**, grown from a dichloromethane solution, were used to determine its structure by X-ray analysis (Figure 1). Crystallographic data, selected bond lengths and bond angles are reported in Tables 1-3. The structure of **9b** consists of a dinuclear centrosymmetric unit in which the 2,5-diamino-1,4-benzoquinonediimine bridging ligand behaves as a bis-chelate and bridges two (acac)nickel(II) fragments. Examination of the bond distances within the N(1)–C(2)–C(1)–C(3')–N(2') and N(2)–C(3)–C(1')–C(2')–N(1') moieties reveals an equalization of the C–C and C–N bonds, which is consistent with a complete electronic delocalization of the π system over these moieties. The C(2)–C(3) and C(2')–C(3') bonds, whose length of 1.497(5) Å corresponds to a single bond, connect the two 6π subunits but do not provide conjugation between them.[28] The coordination geometry around the nickel center is square-planar and, in contrast to **9a**[36] in which the metal centers are slightly out of the plane containing the atoms C(1)-C(3), the 2,5-dibenzylamino-1,4-benzoquinonediimine ligand and the two Ni(acac) fragments are nearly coplanar in **9b** (Figure 2). These geometries lead to differences in the stacking arrangements of **9a** and **9b**, imposed by the intermolecular steric crowding generated by the four N-substituents. Thus the distance between the normals to two successive C_6 rings is of 9.09 Å and 7.68 Å in **9a** and **9b**, respectively. The shorter distance in **9b** results in an intermolecular separation of 3.34 Å between the nickel centers.

The solid-state structure of complex **10a**, which is very similar to that of the corresponding dinickel complex **9a**,[35] is shown in Figure 3 and crystallographic data, selected bond lengths and angles are reported in Tables 1-3.

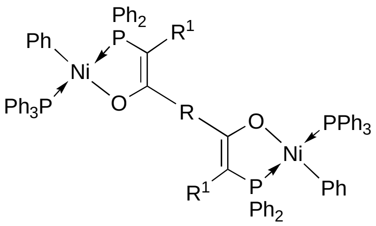
As expected, the coordination geometry around the palladium centers is square-planar. Further comments are not needed for this structure, except the confirmation of the interaction between one CH_2 proton and the N⎓C⎓C–H proton, evidenced by H-H ROESY experiment at –40 °C, with a distance of 2.08 Å.

Electronic Spectra. The electronic spectral data are reported in Table 4. In contrast to the UV-vis. absorption spectrum of the free ligand **4a** which shows an intense absorption band at 339 nm corresponding to the $\pi\rightarrow\pi^*$ intraquinone charge transfer,[28] that of the diplatinum complex **6** revealed two strong absorptions at 479 nm and 504 nm,[24] the latter corresponding to a metal-to-ligand charge transfer (MLCT) transition.[37]

Similarly to the UV-vis. absorption spectra of **6**, the dinuclear Ni(II) complexes are characterized by two strong absorptions in the range 400-600 nm corresponding to a $\pi\rightarrow\pi^*$ intraquinone charge transfer and a metal-to-ligand charge transfer (MLCT), respectively.[36] A significant red shift can be observed from **9a** or **9b** to **9c** which is attributed to an extension of the delocalization of the π system over the phenyl groups of the nitrogen atoms.

The UV-vis absorption spectra of the dinuclear Pd(II) complexes **10a** and **10b** are characterized by three strong absorptions at nearly the same wavelengths, but with a significant blue-shift in comparison to the Ni complexes. The most intense corresponds to a metal-to-ligand charge transfer (MLCT) and the other two probably to intraquinone charge transfers. There is a difference in the absorption intensities between **10a** and **10b**, which was not the case for **9a** and **9b**.

Catalytic Oligomerization of Ethylene. To our knowledge, only few dinuclear Ni(II) and Pd(II) complexes with bridging ligands have been used in ethylene oligomerization and polymerization.[1,38-41] In the neutral bridged dinuclear Ni(II) complexes of type **15** with two (P,O) chelates, Kurtev and coworkers have shown a beneficial effect of the conjugation between the active centers separed by a short distance through the spacer ligand R, which makes these complexes much more active ethylene polymerization catalysts than the mononuclear ones.[40,41]



R = aryl, 1,1'-(η^5-C_5H_4)$_2$Fe
R^1 = H, Ph, Me, SO_3Na
15

Furthermore, complexes of type **7**[25,26] and **8,**[33] with a delocalized π system on the bridging ligand, led to higher activities in ethylene oligomerization and/or polymerization.

One of our objectives was to determine whether cooperative effects by electronic communication between the metal centers would lead to improved catalytic activity and/or selectivity,[25,26,33] in particular for the production of short chain oligomers in the presence of only small quantities of cocatalyst. The activity and selectivity of the catalysts were compared to those of [$NiCl_2(PCy_3)_2$], a typical catalyst for the dimerization of α-olefins.[42] All selectivities reported in the following refer to the total amount of products formed in each catalytic test. In all cases, ethylene pressurisation resulted in a rapid exothermic event, indicative of no or very short induction period. The results of the ethylene oligomerization tests for Ni(II) complexes are reported in Tables 5 and 6. All Pd(II) complexes were completely inactive in the presence of Et_2AlCl or MAO, consistent with observations made on related systems.[25]

In general, and despite the presence of two potentially active sites, all catalysts were moderately active compared to [$NiCl_2(PCy_3)_2$] (Table 5) and they were completely inactive when less than 6 equiv of $AlEtCl_2$ were added. In general, it also appears that complex **9b** with N-benzyl substituents is the most active catalyst precursor, with either $AlEtCl_2$ and MAO as cocatalyst. Thus activation with only 6 equiv of $AlEtCl_2$ leads to a TOF of 22000 C_2H_4/mol Ni·h for complex **9b**. Increasing of amount of $AlEtCl_2$ to 10 equiv leads to an increased activity of all catalysts. The most spectacular increase was observed for **9a**, from 10500 C_2H_4/mol Ni·h to 30500 mol C_2H_4/mol Ni·h. Interestingly, only a slight increase of activity of **9a** was observed when 14 equiv of cocatalyst were used, instead of 10.

The main products were C_4 and C_6 oligomers in comparable quantities. Increasing the amount of cocatalyst tends to favor the formation of C_6 oligomers in the case of **9b** and **9c**. Only small quantities of octenes and no long-chain oligomers were observed, which indicates that chain transfer is much faster than chain propagation. Favored by the relatively low-pressure of ethylene, the branched fraction of the C_6 oligomers (linear C_6 include 1,5-butadiene, hex-1-ene, hex-2-ene, hex-3-ene), produced by insertion of butenes in the Ni–C bond of the active species formed after the first ethylene insertion in the catalytic ethylene oligomerization process (C_4 + C_2, consecutive reaction), was significant (around 50-65% of the C_6 oligomers). Poor selectivities for 1-butene within the C_4 fraction were observed (maximum of 12%), comparable to $[NiCl_2(PCy_3)_2]$, and an increase in the amount of cocatalyst resulted in a severe decrease of its formation together with a decrease of the linear C_6 fraction. There are no notable differences beween the three complexes in terms of selectivity.

When MAO was used as cocatalyst in the oligomerization of ethylene, $[NiCl_2(PCy_3)_2]$ decomposed whereas **9a** and **9b** showed TOF between 8000 and 11000 mol C_2H_4/mol Ni·h (Table 5). As for the reactions with $AlEtCl_2$, the main products formed were C_4 and C_6 oligomers in comparable quantities, except for **9a** with 200 equiv of MAO where the product distribution was shifted towards the formation of C_6 oligomers and the formation of C_8 oligomers increased to 13%. Small amounts of polymer were only observed with **9b** and 200 equiv of MAO. It thus appears that although MAO is a less suitable cocatalyst than $AlEtCl_2$ in terms of activity, it leads to a higher selectivity for 1-butene. The k_α values given in Tables 5 and 6 correspond to the molar ratios hexenes/butenes and not to a Schultz-Flory constant. They are larger than observed recently for Ni(II) catalyst precursors containing (P,N)-chelates.[10-13]

Conclusion

The dinuclear acetylacetonato Ni(II) and Pd(II) complexes with diamino benzoquinonediimine bridges **9–10** have been prepared in order to see how metal coordination affects the electronic situation in the $6\pi + 6\pi$ ligand and to evaluate their potential in the catalytic oligomerization of ethylene. The crystal structures of **9b** and **10a** confirmed that in all complexes the geometry of the metal ions is square-planar and a complete electronic delocalization of the quinonoid π-system occurs between the metal centers, over the two halves of the ligand. A strong influence of the N-substituent in the supramolecular stacking arrangements of **9a** and **9b** was revealed. Whereas the dinuclear Pd(II) complexes **10a** and **10b** were inactive in the oligomerization of ethylene, the dinuclear Ni(II) complexes **9a–9c** were moderately active in the presence of $AlEtCl_2$, with a maximum TOF of 34500 mol C_2H_4/mol Ni·h for **9a** activated with 14 equiv of cocatalyst. Nevertheless, they were highly selective for the formation of C_4 and C_6 short chain oligomers but with poor selectivities for 1-butene. In the presence of MAO, they were less active but slightly more selective for 1-butene.

This new class of molecules represents one of the rare examples of hybrid amino-imine ligands in which, not only their catalytic properties but also their potential as precursor of mixed-valence complexes, may be further tuned by the nature of the N-substituent.[36] Further studies are needed in order to rationalise the effect of the electronic communication between the metal centers on the catalytic activity and/or selectivity, and to understand better the influence of the N-substituent on the molecular properties, in particular for the preparation of dinuclear complexes with more sterically hindered N-substituents, which could probably lead to more selective catalysts, and/or for the preparation of dinuclear complexes with different coordination geometries of the metal centers.

Experimental Section.

General. All solvents were dried and distilled using common techniques unless otherwise stated. All manipulations were performed using standard Schlenk techniques under dry nitrogen atmosphere. ^{1}H NMR (300 or 400 MHz), ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC–300 or AMX–400 instrument. FAB mass spectra were recorded on an autospec HF mass spectrometer. Elemental analyses were performed by the « Service de Microanalyse, Université Louis Pasteur (Strasbourg, France) ». The 2,5-dialkylamino-1,4-benzoquinonediimines **4a** and **4b**, azophenine **4c**, complexes **9a** and **9c** were prepared according to the literature.[24,27,36,43] Gas chromatographic analyses were performed on a thermoquest GC8000 Top Series gas chromatograph using a HP PONA column (50 m, 0.2 mm diameter, 0.5 mm film thickness).

Synthesis of 9b. Complex **4b** (0.30 g, 0.60 mmol) was dissolved in 100 mL of THF and solid [Ni(acac)$_2$] (0.31 g, 1.20 mmol) was added to the yellow solution which turned rapidly brick red. The reaction mixture was stirred overnight at room temperature and the resulting red powder of **4b** was filtered, washed with hexane and dried under vacuum. The filtrate was evaporated and redissolved in dichloromethane. Red crystals suitable for X–ray analysis were obtained by slow evaporation of this solution. Yield: 0.37 g (76%).^{1}H NMR (300 MHz, CDCl$_3$, 298 K) δ:1.68 (s, 12 H, CH$_3$ acac), 3.43 (s, 8 H, N–CH$_2$), 4.60 (s, 2 H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C–H), 5.32 (s, 2 H, CH acac), 7.23 (m, 20 H, aryl); $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl$_3$, 298 K) δ: 25.58 (CH$_3$–acac), 47.18 (N–CH$_2$), 86.77 (H–*C*$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N), 101.76 (CH acac), 126.02, 127.34, 128.12 (aryl CH), 140.49 (aryl C), 166.68 (C⎓N), 186.73 (C⎓O). Anal. calcd. for $C_{44}H_{44}N_4O_4Ni_2$: C, 65.22; H, 5.47; N, 6.91; found: C, 65.16; H, 5.37; N, 6.79.

Synthesis of 10a. Complex **4a** (0.51 g, 1.23 mmol) and [Pd(acac)$_2$] (0.60 g, 2.00 mmol) were dissolved in 100 mL of toluene and heated to reflux for 3 days. The green solution was evaporated at room temperature and the residue was washed with cold hexane (4∗100 mL). This powder was then redissolved in 100 mL of dry dichloromethane, the solution was filtered through Celite and evaporated under vacuum to afford **10a** as a green powder. Green crystals suitable for X-ray analysis were obtained at –30 °C in toluene. Yield: 0.56 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$, 328 K) δ:1.02 (s, 36 H, CH_3), 1.93 (s, 12 H, CH_3 acac), 2.85 (br s, 8 H, N–CH_2), 5.22 (br s, 2 H, N⎓C⎓C–H), 5.30 (s, 2 H, CH acac); ^{1}H NMR (400 MHz, $CDCl_3$, 213 K) δ:1.02 (br s, 36 H, CH_3), 1.93 (br s, 12 H, CH_3 acac), 2.67 (m, $^2J_{HH}$ = 8.4 Hz, 4 H, N–CH*H*), 2.92 (d, $^2J_{HH}$ = 8.4 Hz, 4 H, N–CH*H*), 5.08 (s, 1 H, N⎓C⎓C-H), 5.22 (s, 1 H, N⎓C⎓C–H), 5.32 (s, 1 H, CH acac), 5.33 (s, 1 H, CH acac); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K) δ: 26.60 (CH_3 acac), 29.26 (C*Me*$_3$), 35.50 (br, *C*Me$_3$), 56.17 (N–CH_2), 86.50 (br, H–*C*⎓C⎓N), 100.80 (CH acac), 169.40 (C⎓N), 185.99 (C⎓O); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 233 K) δ: 27.045 (CH_3 acac), 27.05 (CH_3 acac), 29.18 (C*Me*$_3$), 29.34 (C*Me*$_3$), 34.99 (*C*Me$_3$), 36.23 (*C*Me$_3$), 55.76 (N–CH_2), 55.95 (N–CH_2), 85.78 (H–*C*⎓C⎓N), 86.88 (H–*C*⎓C⎓N), 100.17 (CH acac), 169.09 (C⎓N), 169.32 (C⎓N), 186.12 (C⎓O). The doubling of ^{1}H and $^{13}C\{^1H\}$ NMR resonances at very low temperature (–60 °C) is so far unexplained. Anal. calcd. for $C_{36}H_{60}N_4O_4Pd_2$: C, 52.36; H, 7.32; N, 6.79; found: C, 52.80; H, 7.48; N, 6.86.

Synthesis of 10b. Complexes **4b** (0.42 g, 0.96 mmol) and [Pd(acac)$_2$] (0.47 g, 1.54 mmol) were dissolved in 200 mL of toluene and heated to reflux for 3 days. The green solution was evaporated at room temperature and the residue was washed with cold hexane (5x100 mL). This powder was redissolved in 100 mL of dry dichloromethane, and the solution was filtered through Celite and evaporated under vacuum to afford **10b** as a brown powder. Yield: 0.43 g (49%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ:1.88 (s, 12 H, CH_3 acac), 4.12 (s, 8 H, N–CH_2), 4.87 (s, 2 H, N⎓C⎓C–H), 5.31 (s, 2 H, CH acac), 7.20 (m, 20 H, aryl). The ^{13}C NMR spectrum could not be recorded owing to the poor solubility of **10b**. MS (Maldi-TOF): *m/z*: 905.955 $[M+1]^+$. Anal. calcd. for $C_{44}H_{44}N_4O_4Pd_2$: C, 58.35; H, 4.90; N, 6.19; found: C, 59.43; H, 4.46; N, 6.10. No better analyses could be obtained.

Catalytic Oligomerization of ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 100 mL stainless-steel autoclave. The interior of the autoclave was protected from corrosion by a protective coating. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurised to the desired pressure. The temperature increase that was observed resulted solely from the exothermicity of the reaction. The reactor was continuously fed with ethylene by a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. ethylene uptake. In all of the catalytic experiments, 4.10^{-2} mmol of Ni complex were used. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test, the reactor was cooled to 10 °C before transferring the gaseous phase into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated for GC analysis. The products in the reactor were hydrolyzed *in situ* by the addition of ethanol (10 mL), transferred in a Schlenk flask, and separated from the metal complexes by trap-to-trap distillation (120 °C, 20 Torr). All volatiles were evaporated (120 °C, 20 Torr, static pressure) and recovered in a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. For GC analyses, 1-heptene was used as an internal reference. The required amount of complex was dissolved in 10 mL of chlorobenzene and injected into the reactor. Depending on the amount of cocatalyst added, between 0 and 5 mL of cocatalyst solution were added so that the total volume of all solutions was 15 mL. When MAO was used as the cocatalyst, the total volume was increased to 20 mL.

Crystal Structure Determination. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The relevant data are summarized in Table 1. Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[44,45] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C–H}$ = 0.95 Å, U_{11} = 0.04). Full data collection parameters, and structural data are available as Supporting Information. Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC xxx. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union

Road, Cambridge CB2 1EZ, UK (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Acknowledgments. We thank the CNRS and the Ministère de la Recherche (Paris) for a PhD grant (J.p.T.) and the Institut Français du Pétrole for support. We are also grateful to M. Agostinho and M. Mermillon-Fournier for technical assistance.

Supporting Information Available: tables of atomic coordinates, bond distances, angles and anisotropic thermal parameters and ORTEP views for **9a** and **10b**; X-ray data in CIF format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Crystal data and details of the structure determination for compounds **9b** and **10a**.

Crystal Data	9b	10a
Formula	$C_{44}H_{44}N_4O_4Ni_2$	$C_{36}H_{60}N_4O_4Pd_2$
Formula weight (g.mol^{-1})	810.25	825.68
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a [Å]	8.3480(10)	9.6470(10)
b [Å]	11.403(2)	10.5210(10)
c [Å]	11.905(2)	11.1550(10)
α [°]	95.18(5)	62.43(5)
β [°]	110.25(5)	88̃13̣□̣
γ [°]	111.35(5)	76.50(5)
V [Å^3]	959.4(7)	972.2(6)
Z	1	1
Density (calc) [g.cm^{-3}]	1.402	1.410
μ(MoKα) [mm^{-1}]	1.030	0.965
F(000)	424	428
Temperature (K)	173	173
θ Min-Max [°]	1.9, 27.5	2.8, 30.1
Data set [h ;k ;l]	-10/10 ; -12/14 ; -15/15	-13/13 ; -12/14 ; 0/15
Tot., Uniq. Data, R(int)	7808, 4307, 0.053	5676, 5675, 0.000
Observed data [$I > 2\sigma(I)$]	2993	4186
N*reflections*, N*parameters*	4307, 244	5675, 208
R, wR$_2$, GOF	0.0660, 0.1304, 1.08	0.0446, 0.1054, 0.84

Table 2. Selected Interatomic Distances (Å) in **9b** and **10a**.

	9b	**10a**
C(1)-C(2)	1.394(6)	1.416(5)
C(1)-C(3')	1.397(6)	1.401(6)
C(2)-C(3)	1.497(5)	1.490(4)
C(2)-N(1)	1.326(6)	1.330(5)
C(3)-N(2)	1.327(6)	1.335(5)
M-N(1)	1.874(4)	1.984(3)
M-N(2)	1.873(4)	1.986(3)
M-O(1)	1.848(2)	2.008(3)
M-O(2)	1.847(2)	2.008(2)

Table 3. Selected bond Angles (°) in **9b** and **10a**.

	9b	**10a**
N(1)-M-N(2)	83.56(16)	80.19(14)
N(1)-M-O(2)	174.22(15)	172.63(14)
N(1)-M-O(1)	90.72(14)	94.28(13)
N(2)-M-O(2)	90.93(14)	93.37(13)
N(2)-M-O(1)	173.71(15)	174.44(12)
O(2)-M-O(1)	94.70(12)	92.11(12)

Table 4. Electronic spectra λ (nm) in CH_2Cl_2

Compd.	λ (log ε)
9a	479 (4.13), 510 (4.17)
9b	486 (4.46), 519 (4.54)
9c	523 (4.22), 555 (4.29)
10a	430 (4.45), 456 (4.64), 491 (4.82)
10b	437 (3.82), 456 (4.00), 488 (4.00)

Table 5. Influence of the nitrogen substituent and of the amount of $EtAlCl_2$ used as cocatalyst on the oligomerization of ethylene.[a]

	9a	**9a**	**9a**	**9b**	**9b**	**9c**	**9c**	**REF**[e]
$AlEtCl_2$ (equiv)	6	10	14	6	10	6	10	6
selectivity C_4 (mass %)	56	58	57	56	49	58	47	86
selectivity C_6 (mass %)	40	38	40	40	44	36	48	14
selectivity C_8 (mass %)	4	4	3	4	6	6	5	traces
Productivity[b]	5000	14500	16500	10500	15000	7000	11000	13000
TOF[c]	10500	30500	34500	22000	31500	14500	23500	27000
linear C_6 (mass %)	52	42	40	49	40	52	35	
$\tilde{\alpha}$olefin (C_4) (mol %)	10	5	4	12	2	12	1	9
k_α[d]	0.48	0.4	0.46	0.48	0.6	0.41	0.68	0.13

[a] Conditions: 10 bar C_2H_4, 35 min, T = 30 °C, $4 \cdot 10^{-2}$ mmol Ni complex, solvent: 15 mL toluene; [b] Productivity : g C_2H_4 consumed/g Ni • h; [c] TOF : mol C_2H_4 consumed/mol Ni • h.; [d] k_α = mol C_6/ mol C_4; [e] REF = $[NiCl_2(PCy_3)_2]$.

Table 6. Influence of the nitrogen substituent and of the amount of MAO used as co-catalyst on the oligomerization of ethylene.[a]

	9a	**9a**	**9b**	**9b**
MAO (equiv)	100	200	100	200
selectivity C_4 (mass %)	41	46	40	36
selectivity C_6 (mass %)	44	43	47	49
selectivity C_8 (mass %)	15	11	13	14
selectivity C_{10} (mass %)	---	---	---	1
Polymer (g)	---	---	---	0.25
Productivity[b]	4000	3500	5500	3500
TOF[c]	8500	8000	11000	8000
linear C_6 (mass %)	52	52	50	54
$\tilde{\alpha}$olefin (C_4) (mol %)	15	15	12	16
k_α[d]	0.71	0.62	0.77	0.9

[a] Conditions: 10 bar C_2H_4, 35 min, T = 30 °C, $4 \cdot 10^{-2}$ mmol Ni complex, solvent: 20 mL toluene; [b] Productivity : g C_2H_4 consumed/g Ni • h; [c] TOF : mol C_2H_4 consumed/mol Ni • h.; [d] k_α = mol C_6/ mol C_4.

Figure 1. ORTEP view of **9b**. The aryl protons of the benzyl groups have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

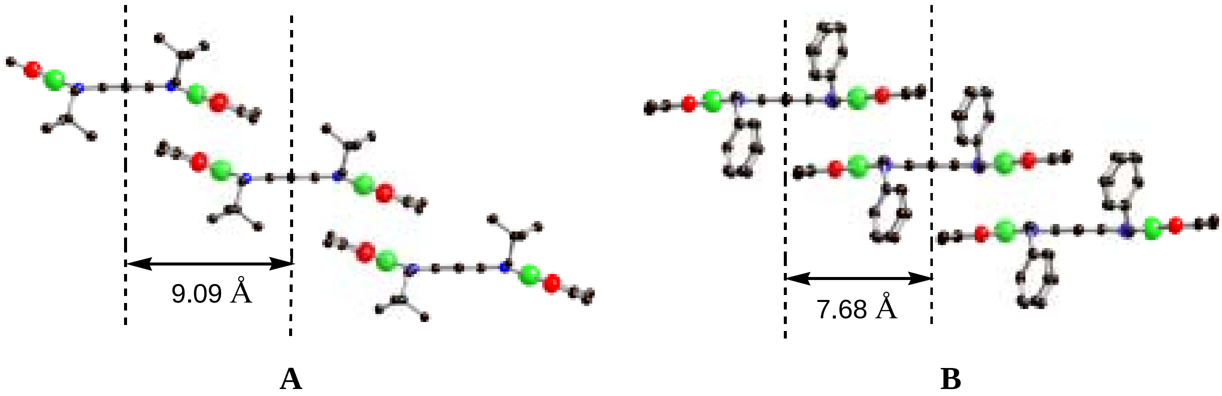


Figure 2. (A) CrystalMaker Views of the stacking arrangements generated in the solid state by **9a**; and (B) for comparison by **9b**. Color coding: nitrogen, blue; oxygen, red; nickel, green. Hydrogen atoms have been omitted for clarity.

Figure 3. ORTEP view of **10a**. The CH_3 protons of the neopentyl groups have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

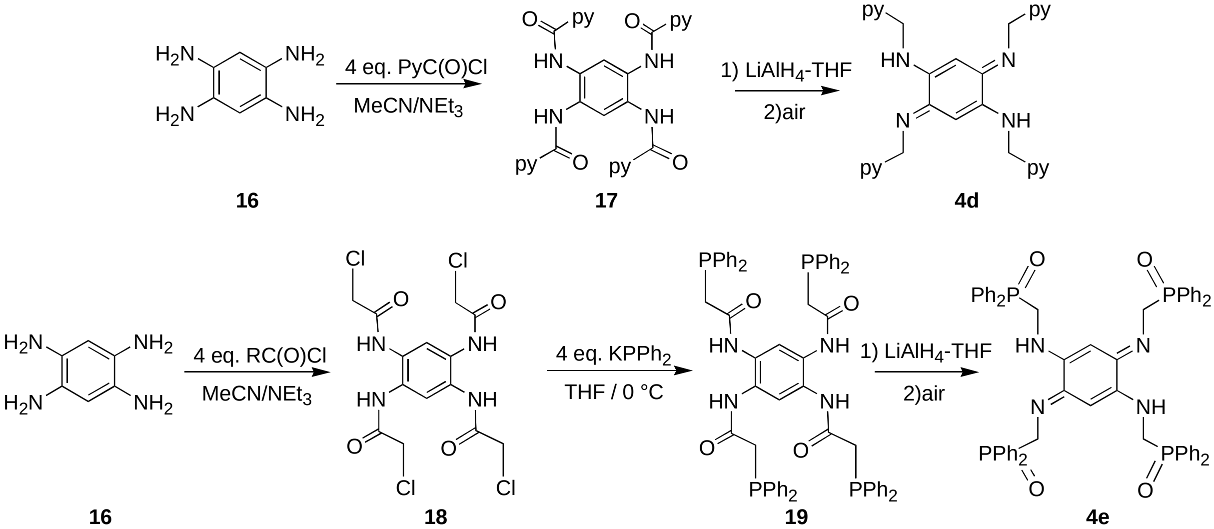
ANNEX

We have also attempted the preparation of new ligands of type **4** with pendant functionnalities of type pyridine or phosphine oxide for their use in coordination chemistry. We have tried to phosphorylate the two N-H functions by reaction with $PPh_2N(iPr)_2$ as phosphorus precursor.

We have studied the reactivity of **4a** with $FeCl_2$ and $CoCl_2$, in order to prepare new binuclear pre-catalysts for the oligomerization of ethylene. We have also tried to isolate the bisanion of **4a** by double deprotonation in hexane, and study its reaction with [PdMeCl(COD)].

Synthesis of new ligands with pendant functionnalities. By adapting the strategy used for the synthesis of non-functionalized quinonoid ligands **4**,[23-27,28] we have attempted to prepare **4d** with pyridine functionnalities and **4e** with phosphine oxide functionnalities (Scheme 3).

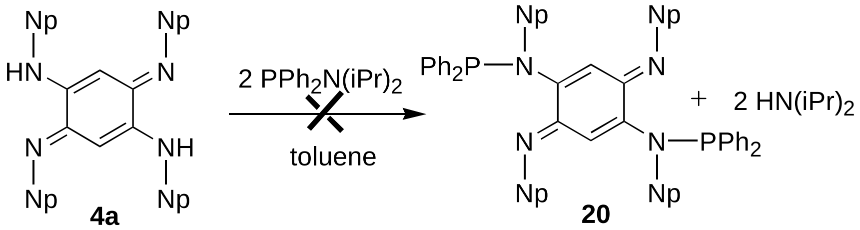
Scheme 3. Strategy for the synthesis of **4d** and **4e**



At this stage, we have succeeded to prepare the tetraamide precursors **17** and **19**. We have started to work on the reduction step, but for the moment we are still having difficulties. Nevertheless, owing to the ease and good yield of the first step, we think that the synthesis could be carried out.

Phosphorylation of 4a. We have tried to phosphorylate the two N-H functions by reaction of 0.5 equiv of **4a** with $PPh_2N(iPr)_2$ in refluxing toluene (Scheme 4).

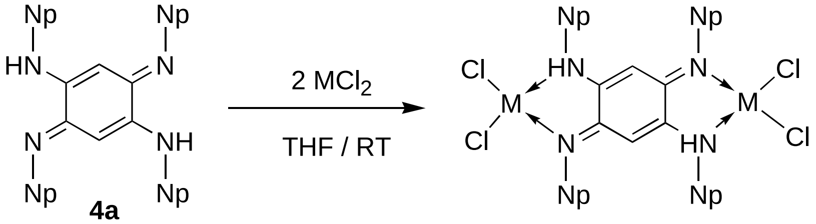
Scheme 4. Reaction of **4a** with $PPh_2N(iPr)_2$



Unfortunately, after one night, the $^{31}P\{^1H\}$ NMR spectrum does not show any appearance of new pics which could correspond to **20**, and after evaporation of the solvent, unreacted **4a** was recovered. Probably, the release of a volatile amine in the reaction is not sufficient to allow the formation of a new P-N bond, which is not furthermore more thermodynamically favored than in the phosphorus precursor.

Reaction of 4a with $FeCl_2$ and $CoCl_2$. We have tried to react **4a** with $FeCl_2$ and $CoCl_2$ in order to prepare new binuclear pre-catalysts for the oligomerization of ethylene.[1] We have performed this reaction by mixing **4a** with 2 equiv of MCl_2 (M = Fe or Co) in THF at room temperature (Scheme 5).

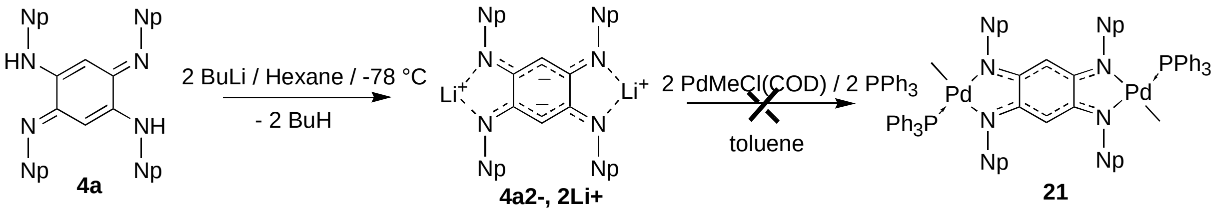
Scheme 5. Reaction of **4a** with MCl_2 (M = Fe, Co)



We observed a rapid color change from yellow to red in the case of Fe, from yellow to deep brown in the case of Co. Unfortunately, owing to the paramagnetism of the final compounds and the fact that no suitable crystals for an X-ray analysis were obtained, we are unable at this stage to know if we obtain discret binuclear complexes of coordination polymers.

Deprotonation of 4a and reaction with [PdMeCl(COD)]. Before the successful use of $[M(acac)_2]$, we have tried to isolate the bisanion of **4a** by deprotonation in hexane. This one was *in situ* reacted with [PdMeCl(COD)], in order to prepare a binuclear Pd complex with a Pd-C bond (Scheme 6).[42]

Scheme 6. Deprotonation of **4a** with BuLi and reaction with [PdMeCl(COD)]



4a

4a2-, 2Li+

21

The bisanion of **4a** was found extremely unstable and spontaneously inflammable in air. Therefore, attempts to isolate it for the preparation of binuclear complexes of type **21** were given up in favor of the *in situ* method which, although it revealed a rapid color change from red to green, was unsuccessful (no characterizable product was isolated after workup).

Experimental Section

Formation of 17: Similarly to the procedure described for the synthesis of analogs,[23-27,28] compound **17** was obtained as a white solid (49% yield).

Reduction of 17: Similarly to the procedure described for the synthesis of analogs,[23-27,28] compound **17** was reduced with excess $LiAlH_4$ in refluxing THF. After aerobic work up, a brown powder was obtained by precipitation in a dichloromethane/hexane mixture, but no signals corresponding to quinonoid protons were observed in the ^1H NMR spectrum.

Formation of 18: Similarly to the procedure described for the synthesis of analogs,[23-27,28] compound **18** was obtained as a white solid (50% yield). ^1H NMR (300 MHz, DMSO-[d$_6$]) δ: 4.28 (s, 8 H, CH_2), 7.74 (s, 2 H, aryl), 9.74 (s, 4 H, N-H).

Reduction of 18: To a solution of $KPPh_2$ (6.96 mL, 3.48 mmol, 0.5 M in THF) in 200 mL of dry THF at 0 °C was added in small fractions white solid **18** (0.4 g, 0.87 mmol) under stirring. The red solution turns progressively yellow. After 2 h of stirring at 0 °C, the solvent was evaporated and 100 mL of distilled water was added leading to the precipitation of a yellow solid which was filtered carefully under nitrogen. The yellow powder was then washed with a large volume of water and with 100 mL of Et_2O. After drying under vacuum, **19** was obtained as a yellow powder which was no further purified. ^1H NMR (300 MHz, DMSO-[d$_6$]) δ: 3.15 (s, 8 H, CH_2), 7.29-7.80 (m, 40 H, aryl), 8.86 (s, 2 H, aryl), 9.46 (s, 4 H, N-H); $^{31}P\{^1H\}$ NMR (121 MHz, DMSO-[d$_6$]) δ: -16.31.

Reduction of 18: Similarly to the procedure described for the synthesis of analogs,[23-27,28] compound **18** was reduced whith excess $LiAlH_4$ in refluxing THF. After aerobic work up, only decomposition was obtained.

Reaction of 4a with $PPh_2N(iPr)_2$ at 110 °C in Toluene: To a solution of **4a** (0.15 g, 0.36 mmol) in anhydrous toluene (100 mL) was added a solution of $PPh_2N(iPr)_2$ (0.20 g, 0.72 mmol) in anhydrous toluene (20 mL). The mixture was refluxed overnight, with a color change from purple to red. The reaction progress was monitored by $^{31}P\{^1H\}$ NMR. After one night, the solvent was evaporated and unreacted **4a** was recovered by precipitation in methanol.

Reaction of 4a with $FeCl_2$ at 25 °C in THF: To a solution of **4a** (0.10 g, 0.24 mmol) in anhydrous THF (100 mL) was added a solution of $FeCl_2$ (0.06 g, 0.48 mmol) in anhydrous THF (30 mL). The mixture was then stirred at room temperature for 1 h, with a rapid color change from yellow to red. After concentration, the unreacted $FeCl_2$ was precipitated by addition of pentane. Then the filtrate was evaporated leading to a violet powder which was dried under vacuum (0.09 g).

Reaction of 4a with $CoCl_2$ in THF: To a solution of **4a** (0.20 g, 0.50 mmol) in anhydrous THF (100 mL) was added a solution of $CoCl_2$ (0.06 g, 0.50 mmol) in anhydrous THF (30 mL). The mixture was stirred at room temperature for 1 h, with a rapid color change from yellow to brown. After concentration, the unreacted $CoCl_2$ was precipitated by addition of pentane. Then the filtrate was evaporated leading to a brown powder which was dried under vacuum (0.08 g).

Deprotonation of 4a and reaction with [PdMeCl(COD)]: To a solution of **4a** (0.20 g, 0.50 mmol) in anydrous hexane (50 mL) was added dropwise a solution of BuLi (0.60 mL, 0.97 mmol, 1.6 M in hexane). The solution becomes red with release of butane, and **$4a^{2-}\bullet 2Li^+$** precipitates as a red powder. After stirring for 30 min at room temperature, the colorless solution was carefully filtered. Then 50 mL of toluene was added to the residue and solid [PdMeCl(COD)] (0.26 g, 0.97 mmol) was added in small fractions to the solution, followed by solid PPh_3 (0.25 g, 0.97 mmol). The red solution turns progressively to green. After stirring overnight at room temperature, the white precipitate of LiCl was filtered and the filtrate was evaporated under vacuum.

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Chapter 4: One-electron Oxidation of a 2,5-diamino-1,4-benzoquinonediimine: A Chemical and Electrochemical Investigation

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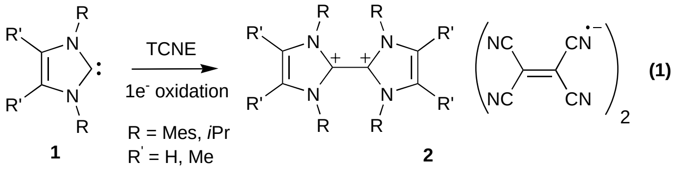
Abstract

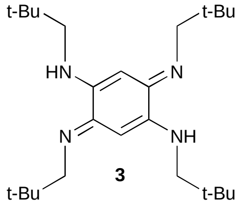
The one-electron oxidation of N, N', N'', N'''-tetraneopentyl-2,5-diamino-1,4-benzoquinonediimine **3** has been carried out using Ag(I) as oxidising agent, which leads to the formation of the postulated nitrogen-based radical cation **B**. This unstable species can evolve by following two competitive pathways, either a hydrogen abstraction from a THF solvent molecule which leads to the N, N', N'', N'''-tetraneopentyl-2,5-diamino-1,4-benzoquinonemonoiminemonoiminium **5**, or a dimerization of two carbon-based radical cations **C** which affords the new dimer **4**. An X-ray diffraction study established the presence of a centre of symmetry in the middle of the newly formed C_{sp3}-C_{sp3} bond. Breaking of this bond upon reduction reversibly regenerates **3** under mild conditions. Electrochemical studies performed in THF confirm the proposed mechanism for the one-electron oxidation.

Introduction

The transfer of one electron from a strong electron donor molecule to a strong electron acceptor compound has emerged over the last 15 years as a valuable concept for accomplishing novel reactions in organic[1] and transition-metal chemistry.[2] Among them, oxidative dimerization of radical cations is generating increasing interest since it plays a key role in the industrial electropolymerisation of pyrroles and thiophenes.[3] The oxidative dimerization induced by metal ions such as Ag(I), Tl(III) or Sc(III) is also an efficient method to couple aromatic compounds such as benzenoid derivatives,[4, 5] and porphyrins,[6-13] allowing the preparation of larger nanoscale arrays. A large number of organic one-electron oxidizing agents, including triarylaminium salts and tetracyanoolefinic compounds such as tetracyanoethylene or 7,7,8,8-tetracyanodiquinodimethane, are also used efficiently in radical organic synthesis. In particular, Clyburne and coworkers have recently applied the one-electron oxidation induced by tetracyanoethylene (TCNE) to couple *N*-heterocyclic carbenes **1** under mild conditions, which afforded the new air-sensitive 1,2-dicationic dimers of type **2** (eq. 1).[14]



Quinonoid compounds form a well-known class of electroactive molecules, with a well-documented behaviour in reduction which leads to the formation of radical anions semiquinones and/or aromatic hydroquinones.[15] In contrast, very few examples of oxidation reactions of quinonoid compounds have been reported in the literature such as the direct oxidative dimerization resulting in symmetrical bisquinones linked by C_{sp2} atoms.[16-21] As part of our interest for new multifunctionnal quinonoid ligands,[22,23] we decided to explore the behaviour of N, N', N'', N'''-tetraneopentyl-2,5-diamino-1,4-benzoquinonediimine **3**[24] in oxidation reactions.



We describe its chemical and electrochemical one-electron oxidation and the first regioselective oxidative dimerization reaction without dehydrogenation of the coupling site in quinonoid chemistry. The chemical reversibility of this reaction will be discussed.

Results and Discussion

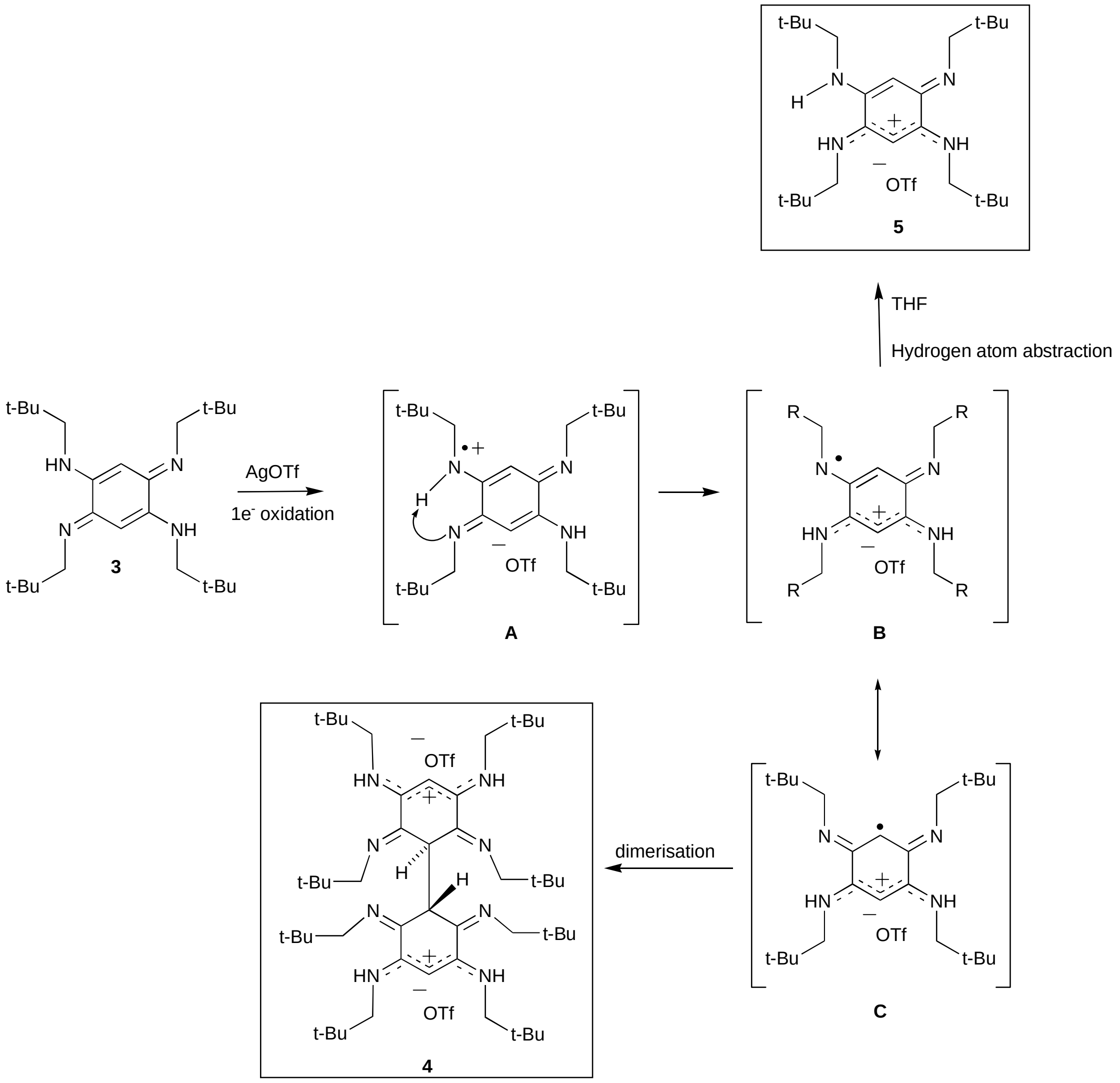
Treatment of **3** in THF with 0.8 equiv. of AgOTf for one week resulted in a colour change from yellow to red and precipitation of a pale-yellow material **4** in 34% yield (Scheme 1). Its ^{1}H NMR spectrum revealed the presence of an olefinic proton (δ= 6.70) and of a tertiary methine sp^3 proton (δ = 4.80). Furthermore, the presence of two different signals for the neopentyl groups clearly indicated a lower molecular symmetry of **4** compared to **3**. We observed only one signal at δ= 8.34 for the N-H protons which is consistent with the presence of C⎓NH groups.[25] The ^{13}C spectrum (DEPT 135 experiment) confirmed the presence of a sp^3 carbon bearing only one proton ($\delta_{C\text{-}H}$ =40.88). Formation of a dicationic dimer was supported by electrospray mass spectrometry on the solid dissolved in CH_3CN, which showed in the positive mode peaks at 416.3999 and 831.7947 amu corresponding to [**4**]$^{2+}$ and [**4**-H]$^+$ respectively. Evaporation of the red THF filtrate, followed by the addition of hexane to remove soluble **3** in excess, led in addition to a red precipitate. Comparison of its ^{1}H and ^{13}C NMR spectra with that of analogs,[22] clearly showed the formation of **5,** the monoprotonated form of **3**, in 44% yield (Scheme 1). The identity of this compound was then confirmed by the preparation of an authentic sample of **6** *via* direct protonation of **3** with triflic acid.

Colourless crystals of compound **4**•2H_2O suitable for an X-ray analysis were obtained by slow evaporation of an acetone/chlorobenzene solution. However, owing to the insufficient quality of the crystals, and despite numerous attempts and changes in the crystallization solvents, only the structure motif could be determined which, however, clearly established a dicationic dimeric structure resulting from coupling of two C_6 ring moieties without dehydrogenation of the coupling site (Fig. 1). Selected bond lengths and bond angles are reported in Table 1.

There is a centre of symmetry in the middle of the newly formed C(1)–C(1') bond whose length of 1.576(6) Å corresponds to a single bond between the two cycles. Examination of the bond distances within the N(1)–C(3)–C(4)–C(5)–N(2) moiety shows a equalization of the C–C and C–N bond distances which is consistent with the delocalization of the 6π electrons system and the planar geometry of this moiety.[22] In contrast, the C–C and C–N distances within the N(3)–C(6)–C(1)–C(2)–N(4) moiety reveal two consecutive C–C single bonds and two C=N double bonds consistent with the presence of the sp^3 carbon atom C(1). The C(1)–C(6) and C(2)–C(3) distances of 1.516(4) Å and 1.504(4) Å, respectively, correspond to single bonds and indicate the lack of conjugation between the two halves of the C_6 ring moiety.

We observed that $AgBF_4$ was similarly effective for this reaction but with a significant acceleration (reaction in three days instead of one week), and that the reaction with either AgOTf or $AgBF_4$ was further accelerated by the addition of one equivalent of I_2 (reaction in one day). Note that direct treatment of **3** with only I_2 resulted in no reaction after one week.

By analogy with related studies,[19, 26, 27] a possible mechanism (Scheme 1) for this reaction could involve first the one-electron oxidation of an amino nitrogen atom of **3**, leading to the nitrogen-centered radical cation **A**. Proton migration to the more basic proximal sp^2 nitrogen atom would result in the protonation of the other vinamidine moiety and the formation of a cyanine-type structure stabilised by intramolecular electronic delocalization between the two nitrogen atoms (intermediate **B**).[22] This postulated radical cation **B** can evolve by following two competitive pathways. The first one involves the abstraction of a hydrogen atom from THF used as solvent,[28-30] which leads to the monoprotonated benzoquinonediimine **5**. The second possibility consists in the delocalization of the radical onto the central electrophilic carbon atom (intermediate **C)** and the dimerization of two such radical cations (**R**adical **R**adical **C**ation (**RRC**) mechanism)[1] leading to the dicationic C–C dimer **4**. Interestingly, related σ-dimeric structures have been isolated as intermediates in the oxidative dimerization of aromatic compounds (aminobenzenes).[4] Similar pathways involving hydrogen atom abstraction or radical cations dimerization have also been observed in the study of the reactions of *N*-heterocyclic carbenes **1**, but in this case only hydrogen atom abstraction or only dimerization of two radical cations occurred, selectively depending on the one-electron oxidant used.[14]



Scheme 1 Proposed mechanism for the formation of **4** and **5**.

We were unable to spectroscopically confirm the formation of a radical cation [**3**]$^{\cdot+}$, so that we turned to computational studies to obtain some informations on its structure. Qualitative computations were performed on [**3**]$^{\cdot+}$ using the Extended Hückel Theory (EHT) with the CACAO program (**C**omputer **A**ided **C**omposition of **A**tomic **O**rbitals).[31]

The most interesting result on the calculated radical cation obtained from **3** is the high spin density concentrated on the central olefinic carbon atoms, which is also consistent with the calculated net charge on these carbon atoms which increases from -0.296 e in the neutral molecule **3** to -0.049 e in the radical cation [**3**]$^{\cdot+}$ (Fig. 2). Thus the shape of the SOMO suggests that dimerization of the radical cation will occur through C–C bond formation.

The yields obtained for **4** and **5**, slightly in favor of **5**, could be explained by the relatively slow kinetics of the dimerization reaction. Indeed, the rate determining step of the overall reaction is presumably the formation of the radical cation from **3** and, under our reaction conditions, at any given time only a small amount of radical cations is generated which limits the dimerization process. Thus alternative reaction pathways become possible, and in particular the abstraction of a hydrogen atom from the solvent, which is a well-known reaction in radical chemistry,[28-30] and leads to **5**. Nevertheless, the yield of **4** is comparable to those observed in the oxidative coupling reactions of Zn(II) porphyrins.[12, 13, 32]

The proposed mechanism for the formation of **4** and **5** suggests that electrochemical oxidation could also lead to the formation of the dicationic dimer **4**, as also observed for the formation of the *meso,meso*-coupled porphyrin arrays.[12] Thus exploration of the electrochemical oxidation of **3** was performed using cyclic voltammetry and controlled potential electrolysis in anhydrous THF containing $N(n\text{-}Bu)_4PF_6$ as supporting electrolyte, with a platinum net as working electrode. The cyclovoltammogram of **3** (Fig. 3) shows an irreversible oxidation wave at 1.08 V *vs* SCE resulting from one-electron oxidation process, and consequently leading to the formation of a radical cation. The irreversibility of the electrochemical process is consistent with the irreversible formation of the radical cation **B** by proton migration in the radical cation precursor **A**. A controlled potential electrolysis during two hours in anhydrous THF was realized at 1.3 V *vs* SCE in order to see whether the electrochemical oxidation leads to the same ratio of products **4** and **5** as the chemical oxidation. Unfortunately, no precipitation of **4** was observed and the colour of the solution, which turned from yellow before electrolysis to red, indicates obviously the formation of **6** by a hydrogen atom abstraction from THF, consistent with the formation at the electrode of a small amount of radical cation, which disfavors its dimerization in solution.

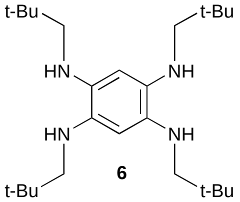
Deprotonation of **4** was also attempted, in particular in order to prepare a new neutral bis(amino-imine) ligand for coordination chemistry. Thus dimer **4** was reacted in CH_2Cl_2 with NEt_3 and after 5 min, the reaction mixture was quenched with water, the organic phase was separated and the solvent evaporated to dryness. The solid residue was taken up in hexane and the yellow filtrate was slowly evaporated, leading to the formation of pure yellow prisms which could be separated and analyzed by ^1H NMR spectroscopy. Unexpectedly, the benzoquinonediimine **3** was recovered in 50% yield, together with the not-always reproducible formation of a white, still unidentified, compound in variable yields (the ^1H and

^{13}C NMR data suggest an hydrolysis product of **4**). The clean chemical reduction by redox titration of the dimer **4** was achieved with two equivalents of benzophenonecetyl radical (-1.88 V *vs* SCE)[33], previously generated by reaction of excess sodium with benzophenone in THF, and **3** was obtained in quantitative yield. This reaction, which consumes two electrons, clearly shows the reversibility of the C–C σ-bond formation. This is consistent with the data of the cyclic voltammetry of **4** in anhydrous CH_2Cl_2 which showed only an irreversible reduction wave at -0.72 V *vs* SCE. Although new in quinonoid chemistry, this type of chemically-induced reversible process is not unprecedented since Berke and coworkers have recently described a similar chemical formation/breaking of a C–C single bond in dimeric manganese carbyne complexes.[34]

There is also an interesting analogy between the behaviour of **4** in basic medium and the slow decomposition in $CHCl_3$ of σ-dimeric 5,15-dioxoporphodimethenes, obtained by oxidation of Zn(II) octaethylporphyrin with Tl(III), into the monomeric dioxoporphodimethene and an unknown compound.[32]

Conclusion

The Ag^{I}-promoted oxidative coupling reaction of N, N', N'', N'''-tetraneopentyl-2,5-diamino-1,4-benzoquinonediimine **3**, which is itself the two electrons oxidation product of the aromatic compound **6**, resulted in the formation of radical cations which evolve either by a hydrogen atom abstraction or by dimerisation reaction, the latter being the first non-dehydrogenative and reversible C-C coupling in quinonoid chemistry.



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The extension of this reaction to other benzoquinonediimines is in progress and should provide an easy entry into a new class of amino-imine type ligands. Further studies on the deprotonation of the dimer **4** are also in progress in order to fully understand the mechanism of the C-C bond breaking induced by deprotonation, as well as studies of the influence of the nature of the one-electron oxidizing agent used on the reactivity of **3**.

Experimental

General.

All solvents were dried and distilled using common techniques unless otherwise stated. All manipulations were performed using standard Schlenk techniques under dry nitrogen atmosphere. ^{1}H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC–300 or AMX–400 instrument. ESI mass spectra were recorded on an autospec HF mass spectrometer. Elemental analyses were performed by the « Service de Microanalyse, Université Louis Pasteur (Strasbourg, France) ». The N,N’,N’’,N’’’-tetraneopentylamino-1,4-benzoquinonediimine **3** was prepared according to the literature.[22, 24]

Reaction of 3 with AgOTf

A mixture of **3** (1.00 g, 2.40 mmol) and AgOTf (0.49 g, 1.92 mmol) in dry THF (150 mL) was stirred at room temperature, in the absence of light, for one week under nitrogen. Formation of a silver mirror and a precipitate was observed. Extraction of the solid with CH_2Cl_2, flash evaporation of the solvent and drying under vacuum gave **4** as a cream powder. The red filtrate of the reaction mixture was taken to dryness. Addition of hexane removed excess **3** and afforded **5** as a red powder.

4 (0.37 g, 34% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ□ 1.00 (s, 36 H, CH3), 1.03 (s, 36 H, CH_3), 3.30 (s, 8 H, CH_2–N), 3.58-3.64 (m, 8 H, CH_2–NH), 4.80 (s, 2 H, N=C–C–H), 6.70 (s, 2 H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C-H), 8.35 (br s, 4 H, N–H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ: 27.48 (C*Me3*), 27.69 (C*Me3*), 32.60 (*C*Me3), 33.01 (*C*Me3), 40.88 (N=C–*C*–H), 54.82 (*C*H_2–NH), 63.76 (*C*H_2–N), 93.08 (N$\overset{\cdots}{-}$C–*C*–H), 151.85 (C$\overset{\cdots}{-}$N), 156.25 (C=N); HRMS (ESI) calcd for $C_{52}H_{96}N_8$ (m/z), ([M]$^{2+}$): 416.3879, found: 416.3999; ([M-H]$^{+}$): 831.7679, found: 831.7947; ([M+OTf]$^{+}$): 981.7278, found: 981.7595; Anal. Calcd. for $C_{54}H_{96}F_6N_8O_6S_2$: C, 57.32; H, 8.55; N, 9.90. Found: C, 57.00; H, 8.47; N, 10.02; UV–vis (CH_2Cl_2): broad band at λ_{max} = 368 nm (log ε = 4.64).

5 (0.48 g, 44% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.03 (s, 18 H, CH_3), 1.04 (s, 18 H, CH_3), 3.13 (s, 4 H, CH_2–N), 3.21 (d, $^{3}J_{HH}$ = 6.06 Hz, 4 H, CH_2–NH), 5.46 (s, 2 H, HC_{sp2}), 7.69 (br t, 2 H, NH), 8.29 (br s, 1 H, NH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ: 27.70 (CH_3), 27.90 (CH_3), 32.32 (*C*Me_3), 33.89 (*C*Me_3), 55.50 (CH_2N), 58.59 (CH_2N), 87.24 (HC_{sp2}), 150.74 ($C_{sp2}N$), 152.47 ($C_{sp2}N$). The NMR data of **5** are consistent with a rapid equilibrium between two tautomers generating an average structure of higher symmetry in solution.[22]

Reaction of 5 with the benzophenonecetyl radical

A blue solution of 5 mL of benzophenonecetyl radical in THF, previously generated by reaction of benzophenone (0.07 mg, 0.4 mmol) with excess solid Na in 5 mL of dry THF, was added dropwise to a suspension of **4** (0.23 g, 0.20 mmol) in dry THF (150 mL) at room temperature. The yellow solution was taken to dryness to recover quantitatively **3** as a yellow powder. **3** was characterized by comparison of its ^{1}H NMR data with those of an authentic sample.[22]

Electrochemical Measurements

Electrochemical experiments were performed with a three-electrode system consisting of a platinum working electrode, a platinum-wire counter electrode, and a standard reference saturated calomel electrode (SCE), versus which all potentials are reported. All measurements were carried out under Ar, in degassed THF (previously distilled from Na/benzophenone under N_2) or CH_2Cl_2 (distilled from CaH_2 under N_2), using 0.1 M $N(n\text{-}Bu_4)PF_6$ solutions as the supporting electrolyte. An EG&G Princeton Applied Research Model 273A potentiostat connected to a computer (Programme Research Electrochemistry Software) and a Brucker EI 30M potentiostat connected to a printing table were used for the cyclic voltammetry measurements.

X-ray data

Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated MoKa radiation (1 = 0.71073 Å). The relevant data are summarized in Table 2. Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[35,36] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C–H}$ = 0.95 Å, U_{11} = 0.04). The insufficient quality of the crystals precluded a completely satisfactory refinement of the structure which was therefore not deposited at the CCDC.

Supporting Information Available

Computational details and crystallographic data of **4** including full collection parameters. This material is available free of charge via the Internet at http://pubs.acs.ORG.

Acknowledgments

This work was supported by the Centre National de la Recherche Scientifique and the Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche (Ph.D grant for J.-p. T.). We are also grateful to Prof. R. Welter (ULP Strasbourg) for the crystal structure analysis.

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Table 1. Selected Interatomic Distances (Å) and bond angles (°) in **4**.

C(1)-C(1’)	1.576(6)	C(1')-C(1)-C(2)	109.9(3)
C(1)-C(2)	1.518(4)	C(1')-C(1)-C(6)	110.0(3)
C(1)-C(6)	1.516(4)	C(2)-C(1)-C(6)	107.9(2)
C(2)-C(3)	1.504(4)	C(1)-C(2)-C(3)	115.2(3)
C(5)-C(6)	1.503(4)	C(2)-C(3)-C(4)	120.2(3)
C(4)-C(5)	1.392(4)	N(1)-C(3)-C(4)	125.7(3)
C(2)-N(4)	1.265(4)	N(4)-C(2)-C(1)	129.0(3)
C(6)-N(3)	1.263(4)		
C(3)-N(1)	1.315(4)		
C(5)-N(2)	1.324(4)		

Table 2. Crystallographic data for compound **4**•$2H_2O$.

Formula	$C_{54}H_{96}N_8F_6O_6S_2 \cdot 2H_2O$
Formula weight (g.mol^{-1})	1167.54
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	12.3030(3)
b [Å]	17.0200(4)
c [Å]	16.8770(6)
β[°]	96.6510(11)
V [Å^3]	3510.21(17)
Z	2
ρ_{calc} [g.cm^{-3}]	1.105
μ(MoKα) [mm^{-1}]	0.141
F(000)	1260
Temperature (K)	173
θ Min-Max [°]	2.3, 32.1
Data set [h ;k ;l]	-18/18 ; 0/25 ; 0/25
Tot., Uniq. Data, R(int)	12183, 12182, 0.1451

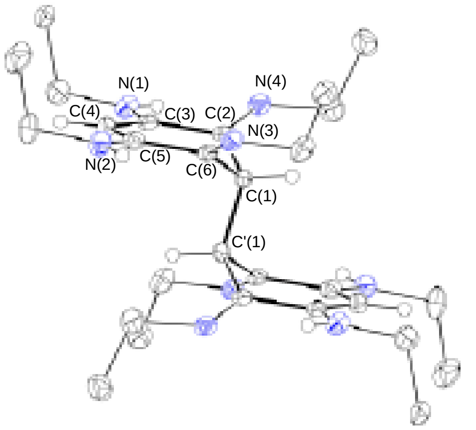

Fig. 1 Structure motif of **4** in **4**•2H_2O (methyls of *t*-Bu groups and triflate counter-ions have been omitted for clarity). Thermal ellipsoids enclose 50% of the electron density.

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Fig. 2 Representation of the frontier orbital SOMO for the radical cation $[\mathbf{3}]^{\cdot+}$.

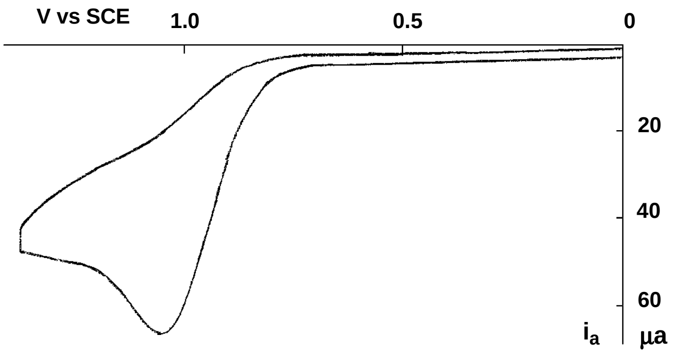


Fig. 3 Cyclic voltammogram of **3** in anhydrous THF (0.1 M N(n-Bu)$_4$PF$_6$) at a scan rate of 100 mV.s^{-1}.

PART 2: Synthesis, Reactivity and Theoretical Studies on the first 6π + 6π Potentially Antiaromatic Zwitterion in Quinonoid Chemistry

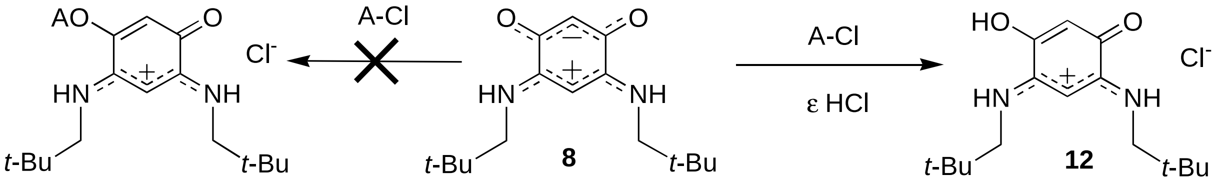
This second part contains two chapters in the form of publications and their corresponding annexes. The first chapter is a publication in the *Journal of American Chemical Society* **2003**, *125*, 12246-12256 (PDF format). The theoretical studies have been performed by the Laboratoire de Chimie Quantique. The second chapter is a publication to be submitted. A patent concerning the synthesis and use of cationic derivatives of the zwitterion as hair colorings has also been filed (O. Siri, J.p. Taquet et P. Braunstein, FR 0209144 to Université Louis Pasteur), but does not appear in this manuscript.

Article uniquement disponible dans la version papier

ANNEX

We have first realized a broad study of the reactivity of **8** with different organic and inorganic electrophiles without preliminary deprotonation of the NH function. All these reactions were unsuccessful, but they have confirmed the experimental and theoretical data of the very high stability of the zwitterionic form, and its poor reactivity toward electrophiles. Owing to the widespread application of phosphonite ligands in homogeneous catalysis,[52] we have attempted the reaction with PPh_2Cl with the aim to phosphorylate the zwitterion at one oxygen atom for obtaining, to the best of our knowledge, the first dissymetric bis-bidentate (P,N)/(O,N) ligand. In a similar manner, we have attempted the reactions of **8** with PCl_3, TsCl (tosyl chloride) and TmsCl (trimethylsilyl chloride) (Scheme 7).

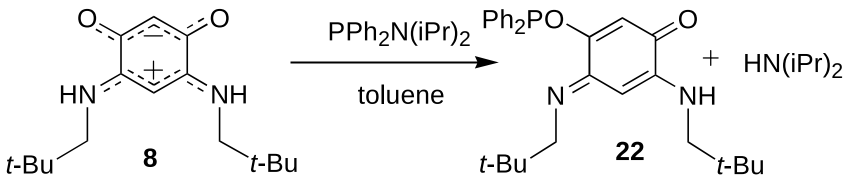
Scheme 7. Reaction of **8** with organic electrophiles



A-Cl = PPh_2Cl, PCl_3, TsCl, TmsCl

Despite numerous attempts under different conditions, in particular many solvent changes, at room temperature or in refluxing solvent, only instantaneous protonation was observed, owing to the presence of HCl traces in all reagents and of the very high sensitivity of the zwitterion to acids. In the presence of distilled NEt_3, nothing occurred owing to a rapid protonation-deprotonation sequence. Nevertheless, this lack of reaction between **8** and typical organic electrophiles is consistent with the absence of reaction between **8** and methyl iodide, one of the most powerful alkylating reagents.[53] In the case of the reaction with PPh_2Cl, we have attempted to circumvent the problem of the presence of HCl in the reaction medium by replacing PPh_2Cl with $PPh_2N(iPr)_2$ as phosphorus precursor, as already tested in previous studies about the synthesis of phosphinito-pyridine ligands.[54] We have realized this reaction by refluxing $PPh_2N(iPr)_2$ with 0.7 equiv of **8** overnight in toluene (Scheme 8).

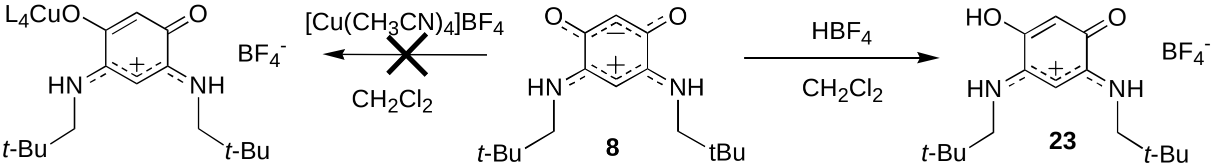
Scheme 8. Reaction of **8** with $PPh_2N(iPr)_2$



The kinetics of the reaction was found very slow, with a very poor conversion of **8**, but a new signal at 113 ppm in $^{31}P\{^{1}H\}$ NMR is consistent with the formation of a phosphonite group, together with the formation of many by-products. This promising reaction has to be improved.

In coordination chemistry, similar results were obtained during reactivity studies of the zwitterion with cationic inorganic electrophiles. For example, the reaction of **8** with $[Cu(CH_3CN)_4]BF_4$ led only to its protonation by residual HBF_4 (Scheme 9).

Scheme 9. Reaction of **8** with $[Cu(CH_3CN)_4]BF_4$



Despite many changes in the procedure (solvent, temperature), without the presence of base, only instantaneous protonation was observed. The same result was observed with $[Pd(CH_3CN)_4](BF_4)_2$ or with AgOTf.

Nevertheless, all these results can be explained by the unavailability of the delocalized negative charge, which maintains the charge equilibrium and then the zwitterionic structure. Furthermore they also confirm all our previous experimental studies and the theoretical calculations on the properties of **8**.[53]

Experimental Section

Reaction of 8 with PPh_2Cl at 60 °C in THF: To a solution of **8** (0.10 g, 0.36 mmol) in anhydrous THF (100 mL) was added one equiv. of PPh_2Cl (0.08 g, 0.36 mmoL), which resulted in an instantaneous color change to intense violet. The mixture was then refluxed overnight. The reaction progress was monitored by ^{31}P-NMR. After one night, the solvent was evaporated and impure **12** was obtained as a purple powder by precipitation in a dichloromethane/hexane mixture. **12** was characterized by comparison of its ^{1}H NMR data with those of an authentic sample.[53]

Reaction of 8 with TsCl at 0 °C in CH_2Cl_2: To a solution of **8** (0.08 g, 0.29 mmol) in anhydrous dichloromethane (100 mL). The solution was cooled at 0 °C and one equiv. of

TsCl (0.06 g, 0.29 mmol) was added followed by one equiv. of NEt_3 (0.04 g, 0.29 mmol). Ater stirring overnight at room temperature, 100 mL of water was added. The organic phase was then extracted with dichloromethane (100 mL), dried on magnesium sulfate, filtered and evaporated. **8** was recovered quantitatively by recrystallization from a dichloromethane/hexane mixture.

Reaction of 8 with PCl_3 at 25 °C in THF: To a solution of **8** (0.10 g, 0.36 mmol) in anhydrous THF (100 mL) was added dropwise one equiv. of PCl_3 (0.05 g, 0.36 mmol), which resulted in an instantaneous color change from intense pink. The mixture was then stirred at room temperature, during which time the reaction progress was monitored by ^{31}P-NMR. After 2 h, the solvent was evaporated and impure **12** was obtained as a purple powder by precipitation in a dichloromethane/hexane mixture. **12** was characterized by comparison of its ^{1}H NMR data with those of an authentic sample.[53]

Reaction of 8 with $PPh_2N(iPr)_2$ at 110 °C in toluene: To a solution of **8** (0.10 g, 0.36 mmol) in anhydrous toluene (100 mL) was added a solution of $PPh_2N(iPr)_2$ (0.16 g, 0.54 mmol) in anhydrous toluene (20 mL). The mixture was then refluxed overnight, with a color change from purple to red. The reaction progress was monitored by $^{31}P\{^{1}H\}$ NMR.

Reaction of 8 with $[Cu(CH_3CN)_4]BF_4$ at 25 °C in dichloromethane: To a solution of **8** (0.05 g, 0.18 mmol) in anhydrous dichloromethane (100 mL) was added dropwise a solution of $[Cu(CH_3CN)_4]BF_4$ (0.06 g, 0.18 mmol) in anhydrous dichloromethane (20 mL), which resulted in an instantaneous color change to intense violet. The mixture was then stirred at room temperature. After 3 h, the solvent was evaporated and impure **23** was obtained as a purple powder by precipitation in a dichloromethane/hexane mixture. **23** was characterized by comparison of its ^{1}H and $^{13}C\{^{1}H\}$ NMR data with those of an authentic sample. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.07 (s, 18 H, CH_3), 3.27 (d, $^{3}J_{HH}$ = 6.6 Hz, 4 H, CH_2), 5.51 (s, 1 H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C-H), 5.78 (s br, 1 H, O-C=C-H), 8.10 (s br, 2 H, N-H); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$) δ: 27.38 (CMe_3), 32.72 (*C*Me_3), 54.93 (CH_2-N), 82.68 (H-*C*$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N), 100.88 (H-*C*$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N), 155.67 (C$\overset{\cdots}{-}$N), 171.44 (C$\overset{\cdots}{-}$O).

Reaction of 8 with $[Pd(CH_3CN)_4](BF_4)_2$ at 25 °C in THF: To a solution of **8** (0.03 g, 0.1 mmol) in anhydrous THF (100 mL) was added dropwise a solution of $[Pd(CH_3CN)_4]$ $(BF_4)_2$ (0.05 g, 0.10 mmol) in anhydrous THF (20 mL), which resulted in an instantaneous color change to intense red. The mixture was then stirred at room temperature. After 3 h, the solvent was evaporated and impure **23** was obtained as a purple powder by precipitation in a dichloromethane/hexane mixture. **23** was characterized by comparison of its ^{1}H and ^{13}C NMR data with those of an authentic sample.

Reaction of 8 with AgOTf: To a solution of **8** (0.30 g, 1.08 mmol) in anydrous THF (50 mL) was added one equiv. of AgOTf (0.28 g, 1.08 mmol). The mixture was then stirred at room temperature for two weeks. A silver mirror was slowly deposited and filtered. The filtrate was then evaporated yielding **12.HOTf**, which was characterized by comparison of its ^{1}H NMR data with those of an authentic sample. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.04 (s, 18 H, CH_3), 3.19 (d, ^3J(H,H) = 6.6 Hz, 4 H, CH_2), 5.49 (s, 1 H, N-C=C-H), 5.76 (s br, 1 H, O-C=C-H), 8.74 (s br, 2 H, N-H).

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(54) Speiser, F. Ph.D Thesis, Université Louis Pasteur, Strasbourg, France, 2002.

Chapter 2: Stepwise Synthesis, Structures and Reactivity of Mono- and Polynuclear Metal Complexes with the first 6π + 6π Zwitterionic Ligand in Quinonoid Chemistry

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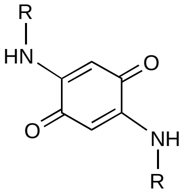
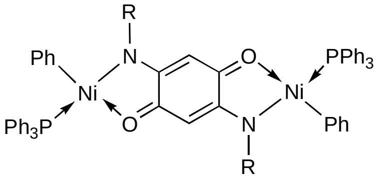
Abstract: The benzoquinonemonoimine **6** is a rare example of organic zwitterion being more stable than its canonical form and it is best described as constituted of two chemically connected but electronically not conjugated 6π electron subunits. The two successive acidities of **6** allow the preparation of mono-, bi- and trinuclear complexes in which the control of the π system delocalization becomes possible. Reaction of **6** with NaO*t*-Bu results in monodeprotonation of one N–H function, and the isolated sodium salt **9**, which is stable under nitrogen, reacts with chloride-bridged Pd(II) dinuclear complexes, [AuCl(PPh_3)] or *trans*–[NiCl(Ph)(PPh_3)$_2$] precursors to afford the mononuclear complexes **10-15** in which the π system is localized. A second *in situ* deprotonation of the remaining N–H amino function of **10** with NaH followed by reaction with [Pd(8–mq)(μ–Cl)]$_2$ affords the homobinuclear complex **17** in which the π system of the quinonoid ligand is delocalized between the two metal centers. Double deprotonation of the two N–H amino functions of the square-planar complex *trans*–[Ni(N,O)$_2$] **15** with NaH and reaction with [Pd(8–mq)(μ–Cl)]$_2$ affords the heterotrinuclear (Pd, Ni, Pd) complex **18** in which the π–system of the two quinonoid ligands is delocalized between the three metal centers. The crystal structures of the mononuclear complexes **10** and **13** and of the dipalladium complex **17** are reported and consequences of metal coordination discussed. Complex **15** was tested in catalytic ethylene oligomerization with $AlEtCl_2$ as cocatalyst.

Introduction

The last few years have witnessed a phenomenal growth in research activity on chelating N,O ligands, in particular for the preparation of highly active nickel and palladium catalysts for olefin polymerization, co-polymerization and oligomerization,[1-23] but also for the synthesis of porphyrin dimers and oligomers connected by metal ions.[24-27] In contrast, very few examples of mono or polynuclear metal complexes based on N,O ligands supported by a quinonoid core have been reported in the literature.[28-30] Furthermore, to the best of our knowlegde, only one example of N,O,N,O benzoquinone compound has been reported, very recently, as ligand in the preparation of metal complexes for catalytic applications.[31] These authors prepared and characterized a series of 2,5-disubstituted amino-*p*-benzoquinone ligands **1**, their binuclear Ni(II) complexes of type **2** and have applied them as highly active single-component catalysts in ethylene polymerization. Despite the lack of crystals of these binuclear complexes suitable for X-ray diffraction, the very wide molecular weight distribution of the polyethylene formed during the reaction was explained by electronic cooperative interactions between their Ni(II) centers.[31]

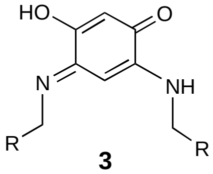


1



2

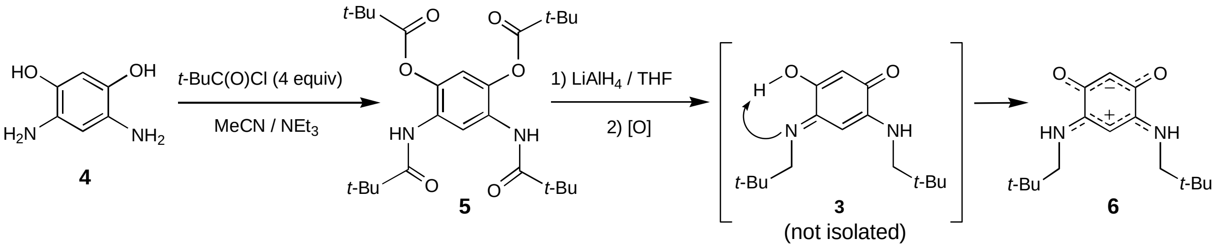
Sequential monodeprotonation/metallation of **1** was not possible and its first metal complexes, **2**, which is a centrosymmetric molecule, was obtained by double deprotonation in a one-pot reaction. Therefore, a molecule such as 2-amino-5-hydroxy-*p*-benzoquinonemonoimine **3**, which is closely related to **1** but has the advantage of possessing two different N,O chelation sites, would be of particular interest in view of its potential in coordination and organometallic chemistry. It could allow the stepwise synthesis of mono- and binuclear complexes, and also the elaboration of linear metallic chains.



3

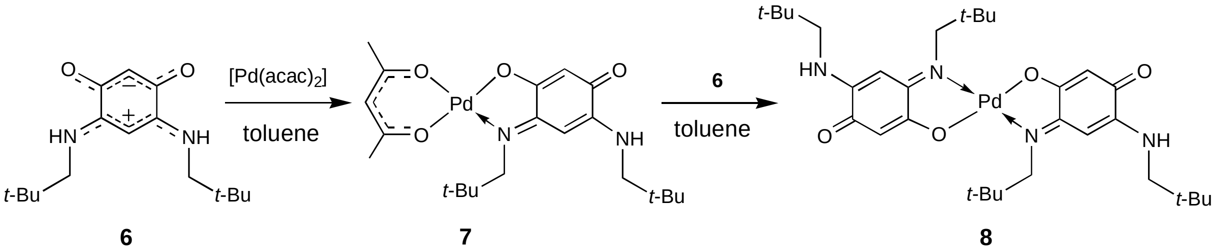
We recently developed a versatile access to a structural isomer of this molecule from the commercially available diaminoresorcinol **4**•2HCl which was reacted with *t*-BuC(O)Cl in wet CH_3CN and excess NEt_3 to afford **5** (Scheme 1). Reduction of **5** and aerobic workup led to intermediate **3** which rearranges, by proton migration from the oxygen atom to the more basic nitrogen site, to the zwitterionic quinonemonoiminium **6** (Scheme 1).[32,33]

Scheme 1. Synthesis of zwitterion **6** as reported in 2003.[32]



The zwitterion **6** is a planar and potentially antiaromatic 12π electron system,[32] constituted by two conjugated and fully delocalized 6π electron subunits which are connected by two C–C single bonds. We have previously shown that it is possible to deprotonate selectively one N–H function, by reaction with [M(acac)$_2$] (M = Ni, Pd, Cu or Zn) and to obtain mononuclear complexes, such as **8**, in which the π-system is localized. This was confirmed by the X-ray structure analysis of the intermediate Pd(II) complex **7** which was isolated by reaction of **6** with [Pd(acac)$_2$] (Scheme 2).[32]

Scheme 2. Reaction of **6** with [Pd(acac)$_2$].

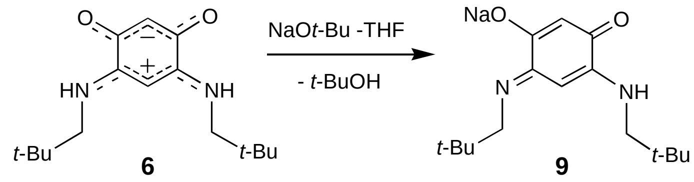


As part of our current interest in the coordination chemistry of multifunctionnal quinonoid ligands, we describe here how metallation by successive deprotonation of the two N–H functions leads in the metal complexes to different electronic distributions of the 6π + 6π system of **6**. In this paper, we describe mono-, bi- and trinuclear complexes in which the π–system of the quinone is completely localized or fully delocalized between two or three metal centers.

Results and Discussion

Mononuclear Complexes. Monodeprotonation of **6** with one equiv of NaO*t*-Bu, in THF at room temperature, yielded the corresponding benzoquinonemonoimine sodium enolate **9** as an orange powder which was fully characterized, except by X-ray crystallography (Scheme 3). Its poor solubility in THF or DMSO suggests a polymeric structure.

Scheme 3. Reaction of **6** with NaO*t*-Bu.

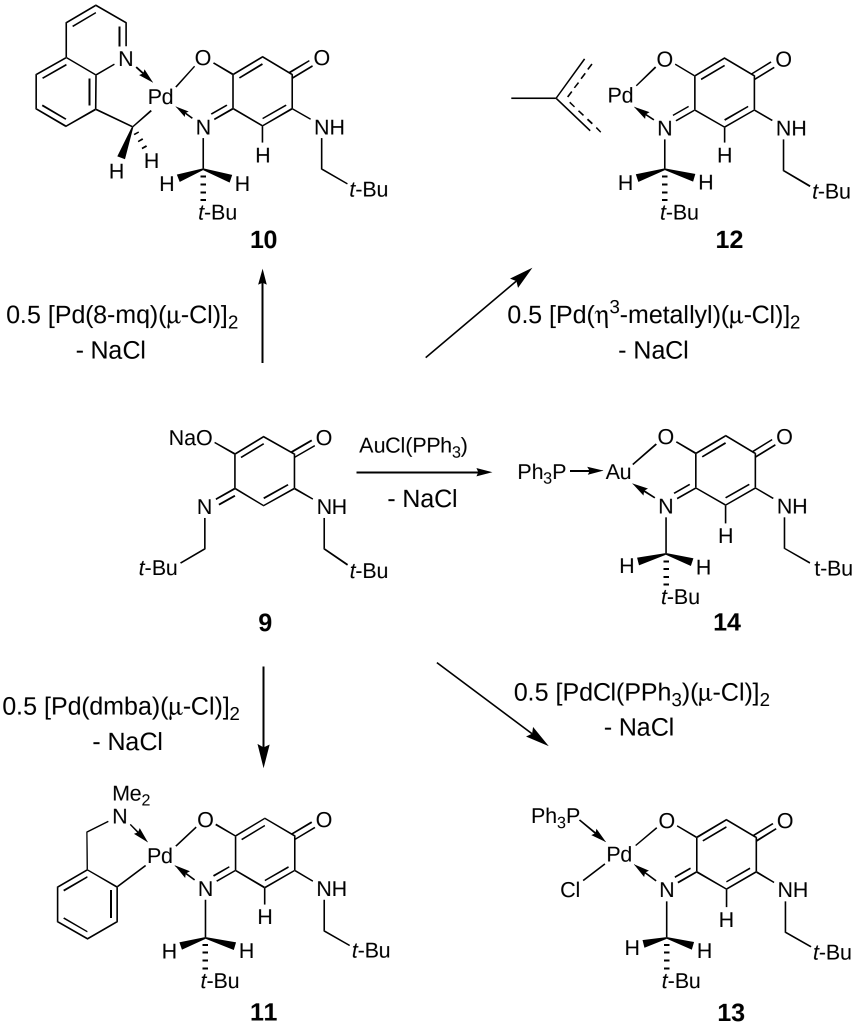


The ^{1}H NMR data of **9** revealed the presence of two *t*-Bu groups and two CH$_2$ signals (δ□2.81 and 3.11 ppm), consistent with a lower molecular symmetry than in **6**.[33] Only one N–H signal is observed at δ□6.08 ppm for the aminic proton. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum contains two signals at δ = 161.54 and 180.23 ppm which are consistent with a localized π-system (δ(C–O) and δC=O), respectively), in contrast to **6** for which the negative charge is delocalized between the two oxygen atoms (δC$\overset{\cdots}{-}$O) = 172.13 ppm).[33]

The isolated sodium salt **9**, which is stable in the solid state under nitrogen for weeks, was reacted with chloride–bridged dinuclear Pd(II) complexes and with [AuCl(PPh$_3$)] to afford complexes **10-14** in good yields, as a result of chloride substitution (Scheme 4). Note that **10** was also prepared directly from the zwitterion **6** by reaction with 0.5 equiv of [Pd(8–mq)(μ–OAc)]$_2$ in refluxing THF (see Experimental Section, Procedure B), in a similar manner to the synthesis of **7**.[32] For these five complexes, formation of a σ–bond between the oxygen and the metal center and of a dative bond between the nitrogen and the metal center have occurred, in accordance with the structures of related compounds.[32]

In the case of **10**, **11** and **13**, only one isomer was observed by ^{1}H and ^{13}C NMR spectroscopy. In all Pd(II) complexes, the ^{1}H NMR data revealed the presence of two singlets for the chemically different neopentyl CH$_3$ protons. Only one N–H signal is observed in the range δ = 6.40-6.56 ppm which is consistent with an aminic proton. A fluxional behaviour of the Pd–N–CH$_2$ protons of **10**, **11** and **13** was observed in the ^{1}H NMR spectrum, since their signal appears as a very broad singlet at room temperature and becomes an AB system below coalescence temperature ($^2J_{AB} \neq 12$ Hz). The $\Delta G^{\neq}$ values calculated for this dynamic behaviour are 54.7, 58.8 and 50.6 kJ/mol, respectively. This phenomenon could be explained by steric interactions between these protons and the CH$_2$ protons of the 8-methylquinoline group in **10**, the ortho C–H proton of the aromatic cycle of *N*,*N*-dimethylbenzylamine group in **11** or the chloride atom in **13**, which hinder the free rotation of this neopentyl group around the N–C bond at low temperature. Furthermore**,** in these complexes, a through-space interaction between a $Pd\overset{\frown}{N}CH_2$ proton and the olefinic N=C–C–H proton was detected by NOE, and further shown by a H-H ROESY experiment at –20 °C in the case of **10**. In the case of **13**, a $^{1}H\{^{31}P\}$ NMR spectrum at 213 K allowed to analyse the Pd̃ÑCH$_2$ signal as an ABX system (X=P) with $^{4}J_{PH}$ coupling constants of 8.8 and 3.2 Hz.

Scheme 4. Reaction of **9** with chloride-bridged Pd(II) dinuclear complexes and with [AuCl(PPh$_3$)]

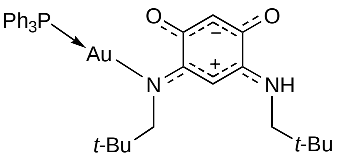


Compounds **10** and **13** were isolated as red crystalline solids from solutions of dichloromethane / *n*-hexane and analyzed by X-ray diffraction. Their structures are shown in Figures 1 and 2, respectively. Crystallographic data, selected bond lengths and angles are reported in Tables 1-3. The coordination geometry around the palladium center in **10** is square-planar, with a *trans* arrangement of the two N atoms. Chelation of the Pd center by the 8-methylquinoline ligand is reflected in the Pd–N(3) and Pd–C(17) distances of 2.009(3) and 2.014(4) Å, respectively, and in the N(3)–Pd–C(17) angle of 83.03(14) °. These values are similar to those reported for other complexes containing this ligand.[34-36] Furthermore, the proximity between the Pd–N–CH$_2$ protons and the 8-mq CH$_2$ protons is evidenced by a distance of 2.288 Å, and the interaction between a proton at C(12) and the olefinic N=C–C(4)–H proton by a distance of 2.020 Å.

Complex **13** has a P *trans* to N arrangement, which is consistent with the vast majority of structurally characterized square-planar Pd(II) complexes with PR_3, halide and a N,O chelating ligand.[30,37,38] Like in **10**, the C(12)–C(13) bond is almost perpendicular to the metal coordination plane. There are short intramolecular distances between Cl or C(4)H proton and the $C(12)H_2$ protons of 2.724 Å and 2.140 Å, respectively.

In both complexes **10** and **13**, examination of the respective bond distances within the O(1)–C(2)–C(1)–C(6)–O(2) and N(1)–C(3)–C(4)–C(5)–N(2) moieties reveals an alternation of single and double bonds, which is consistent with two conjugated but localized π-systems (Table 2). This result is in agreement with the localization of the π system found in **7**, whereas **6** presents a perfect bonds equalization.[32,33] As in all previously described related crystallographic structures,[32,33] the C(2)–C(3) and C(6)–C(5) distances around 1.52 Å correspond to single bonds and indicate the lack of conjugation between the two 6π □□□units. From these observations, we can draw a more general conclusion: when reactions with **6** result in monodeprotonation, leading to mononuclear complexes, the π-system becomes completely localized.

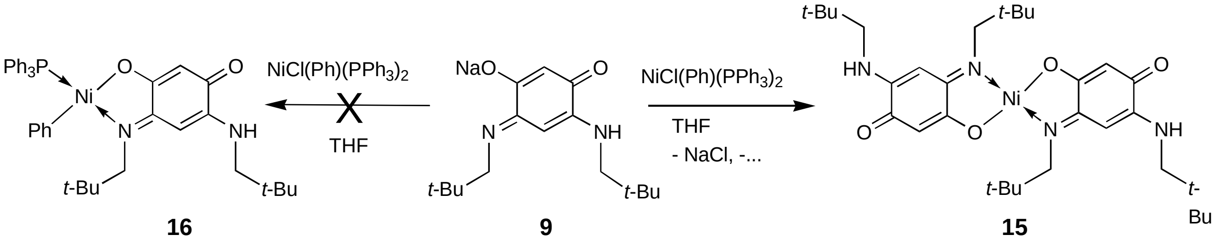
Compound **14** is the first example of a mononuclear gold complex obtained from **6**. In comparison with Pd(II) complexes, the aminic N–H signal is downfield shifted to δ□7.06 ppm. We can suspect a tricoordination of the Au(I) center, as drawn in Scheme 4, owing to the presence of the C=N vibration at 1580 cm^{-1} in the IR spectrum in CH_2Cl_2 which is very similar to that of **13** at 1588 cm^{-1}. Nevertheless, without X-ray analysis, a linear two-coordination around Au cannot be completely ruled out. In particular, the zwitterionic structure drawn below, based on the isolobal analogy $H^+ \longleftrightarrow (Ph_3P)Au^+$, is conceivable on the basis of the $^{13}C\{^1H\}$ NMR data for the C$\cdots$O resonance. We have noticed a higher instability of **14** in solution compared to the Pd(II) complexes.



Catalytic Ethylene Oligomerization with a Mononuclear Ni(II) Complex. By analogy with recent single component olefin polymerization and oligomerization catalysts containing a monoanionic N,O ligand,[1-3,6,7,9-12,14,15,18-23] we have attempted the reaction of **9**

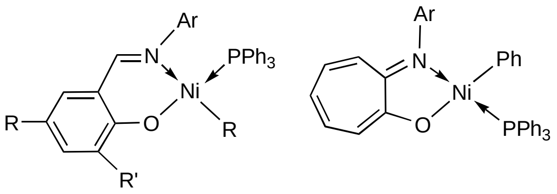
with *trans*–[NiCl(Ph)(PPh_3)$_2$]. The reaction did not lead to the desired product **16** but instead to the quantitative formation, even at low temperature (-10 °C), of the bis(benzoquinonemonoimine) Ni(II) complex **15** (Scheme 5). This complex has previously been prepared by reaction of the zwitterion **6** with 0.5 equiv of [Ni(acac)$_2$].[32]

Scheme 5. Reaction of **9** with *trans*–[NiCl(Ph)(PPh_3)$_2$]



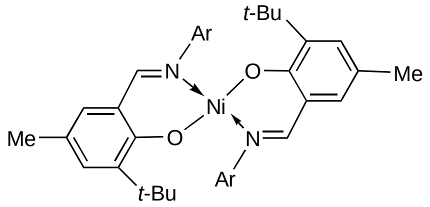
Complex **15** appears to be thermodynamically favored, as also indicated by the lack of transmetallation reaction when **15** was reacted with [$PdCl_2$(SEt)$_2$]. Formation of the bis-N,O chelate results in the loss of a phenyl ligand, which is surprising in view of the strong covalent Ni–C bond, but this sort of reactivity has already been noted in related systems.[1,7,39,40]

The remarkable catalytic properties of Ni(II) complexes with a single N,O chelate are now well documented.[1-3,6,7,9-12,14,15,18-23,31]



Typical mono-N,O type catalysts

In contrast and despite numerous reports on the synthesis and structural properties of type **15** complexes, relatively few studies have been performed on their catalytic behavior, which include the bis–N,O type catalyst shown below.[8,13,17]



A bis-N,O type catalyst

It has already been demonstrated that these Ni(II) complexes with two N,O chelates can be easily activated with a Lewis acid cocatalyst, which displaces one of the N,O chelates and generates the active species.[8,13,17]

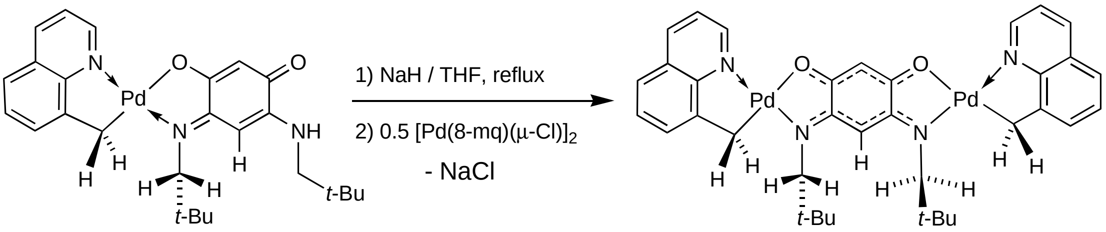
As part of our interest for new ethylene oligomerization Ni(II) catalysts,[41-50] we have evaluated complex **15** for this reaction with the aim of producing short chain oligomers in the presence of only small quantities of alkylaluminium cocatalyst. $AlRCl_2$ compounds are used in the IFP Dimersol® process where in situ formation of a Ni-alkyl complex leads to the active Ni-hydride species after β-elimination. The activity and selectivity of **15** were compared to those of $[NiCl_2(PCy_3)_2]$, a typical catalyst for the Ni-catalyzed dimerization of α-olefins.[51] All selectivities reported in the following refer to the total amount of products formed in each catalytic test. In all cases, ethylene pressurisation resulted in a rapid exothermic event, indicative of very short induction periods.

Compound **15** was completely inactive when less than 6 equiv of $AlEtCl_2$ were added. However, turnover frequencies of 28500 and 45000 mol C_2H_4/mol Ni·h were obtained in the presence of 6 or 10 equiv of cocatalyst, respectively, to be compared to 27000 mol C_2H_4/mol Ni·h for $[NiCl_2(PCy_3)_2]$ (Table 4). The main products were C_4 and C_6 oligomers in comparable quantities, independently of the Al/Ni ratio. Only small quantities of octenes and no long-chain oligomers were observed, which indicates that chain transfer is much faster than chain propagation. Favored by the relatively low-pressure of ethylene, the branched fraction of the C_6 oligomers (linear C_6 include 1,5-butadiene, hex-1-ene, hex-2-ene, hex-3-ene), produced by insertion of butenes in the Ni–C bond of the active species formed after the first ethylene insertion in the catalytic ethylene oligomerization process (C_4 + C_2, consecutive reaction), was significant (around 50%). A selectivity for 1-butene within the C_4 fraction of only 14% was observed with 6 equiv of $AlEtCl_2$ and an increase in the amount of cocatalyst resulted in its decrease together with a slight decrease of the C_6 linear fraction.

Bi- and Trinuclear Complexes. The use of metalloligands for the stepwise synthesis of polymetallic compounds is gaining increasing importance in organometallic chemistry. Much effort has been made to find binucleating ligands, with different reactivities of the chelating sites, suitable for successive coordination of metal ions.[52,53] The presence of a free amino N–H function in all the mononuclear complexes suggests that it should be possible, by convergent or divergent strategy, to obtain homo and heteropolynuclear complexes likely to display electronic interaction between the two metal centers through the benzoquinonemonoimine bridge.

In preliminary experiments, we attempted to isolate the sodium salt resulting from deprotonation of **10** with NaH, but only **10** was recovered owing to the high moisture sensitivity of the metalloligand salt which undergoes reprotonation. This observation is consistent with related studies on the synthesis of complexes with anilinoperinaphthenone[12] or anilinoanthraquinone ligands.[30] Therefore, we favored an *in situ* method for the preparation of polynuclear complexes. Deprotonation of **10** with excess NaH in refluxing THF was directly followed by addition of solid [Pd(8–mq)(μ–Cl)]$_2$ (Scheme 6).

Scheme 6. *In situ* deprotonation of **10** and reaction with [Pd(8–mq)(μ–Cl)]$_2$



10 **17**

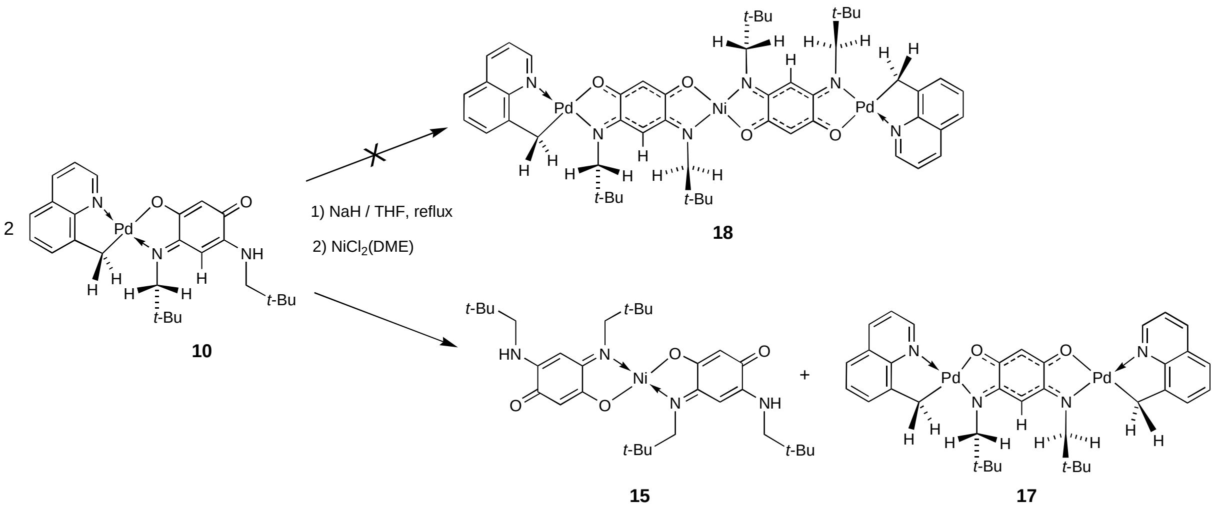
The excess NaH in the reaction mixture does not react with either the Pd precursor or the final product and can be filtered through Celite before product isolation. The binuclear complex **17** was obtained as a green powder in good yield after recrystallization. Examination of its ^{1}H and ^{13}C{^{1}H} NMR spectra revealed the presence of only one signal for the two Np groups and one signal for the CH$_2$ protons of the two 8-methylquinoline groups, which is consistent with a higher molecular symmetry than in **10**, a symmetry axis passing now through the two H–C$\overset{\cdots}{-}$C carbon atoms. The signals at 165.62 and 188.52 ppm in the ^{13}C{^{1}H} NMR spectrum, (δ(C$\overset{\cdots}{-}$N) and δC$\overset{\cdots}{-}$O), respectively), are consistent with a delocalized π-system, as in **6**. Surprisingly, the olefinic N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C–H proton appears in the ^{1}H NMR spectrum as a broad singlet, and the corresponding H–*C*$\overset{\cdots}{-}$C resonance in the ^{13}C{^{1}H} NMR spectrum can only be observed when increasing the pulse delay to 2 s at room temperature. By analogy with the situation described above for **10**, the Pd–N–CH$_2$ protons undergo fluxional behaviour owing to hindered rotation of the neopentyl group around the N–C bond. The $\Delta G^{\neq}$ value calculated for this dynamic behaviour is 54.3 kJ/mol, which is nearly the same value that in **10** which presents the same steric crowding. A through-space interaction between a Pd–N–CH$_2$ proton and the olefinic N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C–H proton was detected by NOE, and further shown by a H-H ROESY experiment at –20 °C.

Compound **17**·2THF could be isolated as a green crystalline solid by slow evaporation of a THF solution and analyzed by X-ray crystallography. Its structure is shown in Figure 3 and crystallographic data, selected bond lengths and angles are reported in Tables 1-3. This complex appears to be the first crystallographically characterized binuclear complex with a N_2O_2 benzoquinone type ligand set.

There is a crystallographically imposed C_2 symmetry axis passing through C(1) and C(4). The N donor atoms N(1) and N(2) are in a mutual *trans* arrangement. The C(2)–C(3) distance of 1.517(4) Å corresponds to a single bond and indicates the lack of conjugation between the two π-systems. In contrast, the other C–C distances within the O–C(2)–C(1)–C(2')–O' and N(1)–C(3)–C(4)–C(3')–N(1') moieties reveal a remarkable bond equalization. Therefore, deprotonation of the N–H amino function of **10**, a molecule with a localized π-electron system, and metallation has led to a homobinuclear complex, **17**, in which the π–system of the quinonoid ligand becomes delocalized between the two Pd centers.

Owing to the successful synthesis of **17**, based on a convergent strategy from a mononuclear complex, we have attempted to synthesize a trinuclear complex by *in situ* deprotonation of **10** with excess NaH in refluxing THF followed by reaction with 0.5 equiv of [NiCl$_2$(DME)] (Scheme 7).

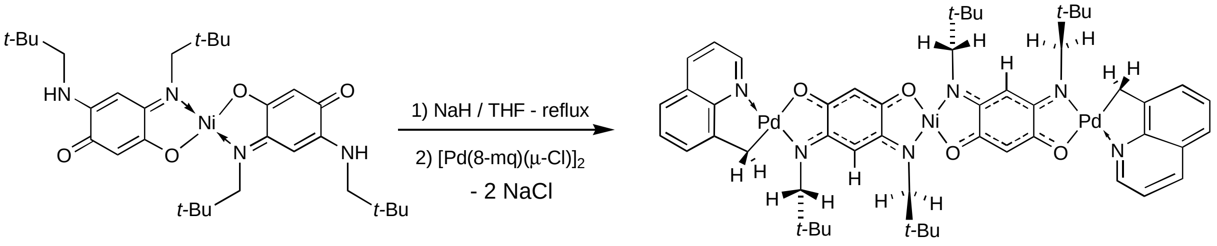
Scheme 7. *In situ* deprotonation of **10** and reaction with [NiCl$_2$(DME)]



Surprisingly, this reaction did not lead to the heterotrinuclear compound **18**, but to the binuclear complex **17** in 50% yield and the bis-chelate **15** in 25% yield. Their formation results from a transmetallation reaction. A related result was obtained by *in situ* deprotonation of **10** and reaction with [PdCl$_2$(SEt)$_2$], which afforded **8** and **17**.

This undesired reaction was circumvented in the case of **15** by using a divergent strategy. *In situ* double deprotonation of the N–H amino functions of **15** with NaH, in a large volume of THF because of the poor solubility of the bis-chelate complex, followed by reaction with [Pd(8–mq)(μ–Cl)]$_2$ led to the formation of the heterotrinuclear NiPd$_2$ complex **18** (Scheme 8). In order to prepare the related homotrinuclear Pd$_3$ complex, we have used **8** instead of **15** under similar conditions, but only the zwitterion **6** and Pd(0) were obtained after work-up, consistent with decomposition of the bis sodium salt of **8** in refluxing THF. We have then attempted to deprotonate **8** at room temperature, which was successful with a rapid color change from black-red to green and gazeous release, but after subsequent reaction with [Pd(8–mq)(μ–Cl)]$_2$, only decomposition was observed, confirming the instability of the bis sodium salt of **8**.

Scheme 8. *In situ* deprotonation and reaction of **15** with [Pd(8–mq)(μ–Cl)]$_2$



15 **18**

Complex **18** was isolated as black-violet powder in good yield after recrystallization. It is stable in the solid state but decomposes in solution in air to reform the mononuclear Pd complex **10** after loss of the nickel and reprotonation. We could not obtain crystals suitable for X-ray diffraction, but examination of the ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data revealed a high molecular symmetry with only one signal for the two Pd–N–Np groups and one signal for the two Ni–N–Np groups. As in **17**, the CH$_2$ protons of the two 8-methylquinoline groups, the two N⎓C⎓C–H and the two O⎓C⎓C–H protons give rise to only one signal. The four signals at 162.64 and 165.14 (δ(C⎓N)) and 187.28 and 187.85 ppm (δC⎓O)) in the ^{13}C NMR spectrum are consistent with a delocalized π-system. Furthermore, as in **17**, the N=C–C–H proton appears also as a broad singlet in the ^{1}H NMR spectrum and the corresponding H–*C*=C resonance in the ^{13}C{^{1}H} NMR spectrum can only be observed after increasing the pulse delay to 2 s at room temperature. All these data, together with the MALDI-TOF mass spectrum and elemental analyses, are consistent with a trinuclear complex in which a Ni atom occupies a center of symmetry and in which the π–system of the two quinonoid ligands is delocalized between the three metal centers. As in the case of **15**, no transmetallation reaction was observed between **18** and [PdCl$_2$(SEt)$_2$].

Conclusion

The two successive acidities of the N–H protons of the unusual zwitterionic benzoquinonemonoimine **6** allow the preparation of mononuclear, homo or heterobinuclear and trinuclear complexes in which the control of the π–system delocalization becomes possible. Ligand **6** was easily monodeprotonated with NaO*t*-Bu and the isolated sodium salt **9** reacted with chloride-bridged dinuclear Pd(II) complexes, [AuCl(PPh_3)] or *trans*–[NiCl(Ph)(PPh_3)$_2$] to afford the mononuclear complexes **10-15** in which the π–system is localized. A second *in situ* deprotonation of the free N–H amino function of the metallo ligand **10** followed by metallation affords, following a convergent strategy, the homobinuclear complex **17** in which the π–system of the quinonoid ligand is delocalized between the metal centers. Using a divergent strategy, the double *in situ* deprotonation of the two N–H amino functions of **15** followed by metallation affords the heterotrinuclear complex **18** in which the π–system of the two quinonoid ligands is delocalized between the three metal centers. These new strategies could now be extended to a range of heterobinuclear complexes, in particular for studies of cooperative effects in homogeneous catalysis and electronic communication in mixed-valence complexes, and to the preparation of quinonoid oligomers linked by metal ions.

Experimental Section

General: ^{1}H NMR (300, 400 or 500 MHz), ^{13}C NMR (75, 100 or 125 MHz) and ^{31}P NMR (121.5 MHz) spectra were recorded on a Bruker AC-300 or AMX-400 or AMX 500 instrument. FAB mass spectra were recorded on an autospec HF mass spectrometer and Maldi-TOF mass spectral analyses were recorded on a Finnigan TSQ 700. Elemental analyses were performed by the Service de Microanalyse, Institut Charles Sadron (Strasbourg, France). Solvents were freshly distilled under nitrogen prior to use. Compounds **6**,[32] [Pd(8–mq)(μ–Cl)]$_2$,[54] [Pd(8–mq)(μ–OAc)]$_2$,[55] [Pd(dmba)(μ–Cl)]$_2$,[56] [Pd(η^3-metallyl)(μ–Cl)]$_2$,[57] [PdCl(PPh_3)(μ–Cl)]$_2$,[58] [AuCl(PPh_3)][59] and *trans*–[NiCl(Ph)(PPh_3)$_2$][60] were prepared according to the literature. Characterization of **15** and the synthesis of **8** have been reported in a previous paper.[32] All reactions of air- or water-sensitive compounds were performed using standard Schlenk techniques under dry argon atmosphere. Gas chromatographic analyses were performed on a thermoquest GC8000 Top Series gas chromatograph using a HP PONA column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of 9. The zwitterion **6** (0.80 g, 2.88 mmol) was dissolved in 50 mL of anhydrous THF and solid NaO*t*-Bu (0.28 g, 2.88 mmol) was added to the solution and the mixture was stirred overnight at room temperature with progressive precipitation of an orange solid. After evaporation of the solvent, **9** was obtained as an orange powder and used without further purification (0.86 g, 93% yield). ^{1}H NMR (300 MHz, DMSO–[d$_6$], 298 K) δ:0.92 (s, 9 H, CH_3), 0.94 (s, 9 H, CH_3), 2.81 (br s, 2 H, CH_2), 3.11 (s, 2 H, CH_2), 4.90 (s, 1 H, N=C–C–H), 5.15 (s, 1 H, O=C–C–H), 6.08 (br t, 1 H, N–H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO–[d_6], 298 K) δ: 28.36 (CMe_3), 28.77 (CMe_3), 32.64 (CMe$_3$), 33.24 (CMe$_3$), 53.36 (CH_2N), 62.60 (CH_2N), 84.11 (H–*C*=C–N), 100.78 (H–*C*=C–O), 147.27 (C–N), 161.54 (C–O), 176.01 (C=N), 180.23 (C=O). HRMS (EI$^-$, 70 eV): *m/z*: 277 [*M-Na*]$^-$.

Synthesis of 10: Procedure A. To a solution of [Pd(8–mq)(μ–Cl)]$_2$ (0.10 g, 0.17 mmol) in anhydrous THF (100 mL) was added solid **9** (0.10 g, 0.33 mmol) and the mixture was stirred overnight at room temperature. After filtration through Celite, the solvent was evaporated and **10** was obtained as a brown powder by recrystallization from a dichloromethane-hexane mixture (0.13 g, 75% yield). Red crystals suitable for an X-ray analysis were isolated from a solution of dichloromethane / *n*-hexane.

Procedure B. To a solution of [Pd(8–mq)(μ–OAc)]$_2$ (0.34 g, 0.54 mmol) in anhydrous THF (100 mL) was added solid zwitterion **6** (0.30 g, 1.08 mmol) and the mixture was refluxed for 1.5 h. After evaporation of the solvent, **10** was obtained as a brown powder by recrystallization from a dichloromethane-hexane mixture (0.50 g, 82% yield).

^1H NMR (300 MHz, $CDCl_3$, 298 K) δ: 1.02 (s, 9 H, CH_3), 1.14 (s, 9 H, CH_3), 2.90 (d, $^3J_{HH}$ = 6.3 Hz, 2 H, NH–CH_2), 3.38 (s, 2 H, Pd–CH_2), 3.50 (br s, 2 H, N–CH_2), 5.36 (s, 1 H, N=C–C–H), 5.61 (s, 1 H, O=C–C–H), 6.56 (br t, 1 H, N–H), 7.41-7.61 (m, 4 H, aryl), 8.27 (dd, 1 H, aryl), 8.96 (d, 1 H, aryl); ^1H NMR (400 MHz, $CDCl_3$, 213 K) δ: 1.02 (s, 9 H, CH_3), 1.14 (s, 9 H, CH_3), 2.84 and 2.89 (ABX system (X = N*H*), $^2J_{AB}$ = 13 Hz, $^3J_{AX}$ = 6.4 Hz, $^3J_{BX}$ = 6 Hz, 2 H, NH–CH_2), 3.22 (d, B part of an AB system, $^2J_{AB}$ = 12 Hz, 1 H, N–CH*H*), 3.37 (s, 2 H, Pd–CH_2), 3.62 (d, A part of an AB system, $^2J_{AB}$ = 12 Hz, 1 H, N–CH*H*), 5.36 (s, 1 H, N=C–C–H), 5.61 (s, 1 H, O=C–C–H), 6.56 (br t, 1 H, N–H), 7.42-7.61 (m, 4 H, aryl), 8.28 (dd, 1 H, aryl), 8.93 (dd, 1 H, aryl); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 253 K) δ: 27.19 (Pd–CH_2), 27.66 (CMe_3), 29.47 (CMe_3), 32.27 (CMe$_3$), 36.20 (CMe$_3$), 54.09 (CH_2N), 61.43 (CH_2N), 85.89 (H–*C*=C–N), 102.17 (H–*C*=C–O), 121.47, 123.35, 128.27, 128.87, 128.88, 137.56, 147.39, 149.49, 153.10 (aryl C), 148.64 (C–NH), 171.28 (C–O), 179.26 (C=N–Np), 181.32 (C=O). Anal. Calcd. for $C_{26}H_{33}N_3O_2Pd$: C, 59.37; H, 6.32; N, 7.99. Found: C, 59.49; H, 6.37; N, 7.44. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 313 nm (3.93), 388 (br) nm (4.40), 513 (br) nm (2.98).

Synthesis of 11, 12 and 13: General procedure. To a solution of the dinuclear Pd(II) precursor (0.17 mmol) in anhydrous THF (100 mL) was added solid **9** (0.10 g, 0.33 mmol) and the mixture was stirred overnight at room temperature. After filtration through Celite, the solvent was evaporated. **12** was directly obtained as a violet powder by recrystallization from a dichloromethane-hexane mixture. For **11**, the red–brown residue was dissolved in hexane and placed at –30 °C and red crystals of pure **11** were obtained after 2 days. For **13**, the red residue was dissolved in dichloromethane and purified by preparative chromatography on silica gel (average particle size of 40 μm, eluant : CH_2Cl_2/MeOH 95/5) to afford **13**·CH_2Cl_2 as a red crystalline solid. Red crystals of **13** suitable for an X-ray analysis were obtained from a solution of dichloromethane / *n*–hexane.

11: (0.11 g, 65% yield). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ: 0.95 (s, 9 H, CH_3), 1.00 (s, 9 H, CH_3), 2.56 (s br, 3 H, N–CH_3), 2.89 (d, $^3J_{HH}$ = 6.2 Hz, 2 H, NH–CH_2), 2.96 (br s, 3 H, N–CH_3), 3.41 (br s, 1 H, *H*–CH–NMe_2), 3.66 (br s, 2 H, N–CH_2), 4.44 (br s, 1 H, *H*–CH–NMe_2), 5.37 (s, 1 H, N=C–C–H), 5.50 (s, 1 H, O=C–C–H), 6.56 (br t, 1 H, N–H), 6.99–7.04 (m, 4 H, aryl); ^1H NMR (500 MHz, $CDCl_3$, 273 K) δ: 0.95 (s, 9 H, CH_3), 1.00 (s, 9 H, CH_3), 2.56 (s, 3 H, N-CH_3), 2.89 (center of an ABX system (X = N*H*), $^2J_{AB}$ = 13.3 Hz, $^3J_{AX}$ = $^3J_{BX}$ = 6.5 Hz, 2 H, NH–CH_2), 2.96 (s, 3 H, N–CH_3), 3.40 (d, B part of an AB system, $^2J_{AB}$ = 13 Hz, 1 H, *H*–CH–NMe_2), 3,57 (d, B part of an AB system, $^2J_{AB}$ = 12 Hz, 1 H, N–CH*H*), 3.75 (d, A part of an AB system, $^2J_{AB}$ = 12 Hz, 1 H, N–CH*H*), 4.45 (d, A part of an AB system, $^2J_{AB}$ = 13 Hz, 1 H, *H*–CH–NMe_2), 5.37 (s, 1 H, N=C–C–H), 5.50 (s, 1 H, O=C–C–H), 6.56 (br t, 1 H, N–H), 6.99–7.04 (m, 4 H, aryl); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 268 K) δ: 27.23 (C*Me*$_3$), 28.67 (C*Me*$_3$), 31.97 (*C*Me$_3$), 36.07 (*C*Me$_3$), 49.96 (N–CH_3), 51.67 (N–CH_3), 53.50 (CH_2N), 59.17 (CH_2N), 72.47 (CH_2–NMe_2), 85.27 (H–*C*=C–N), 101.60 (H–*C*=C–O), 121.52, 123.49, 124.73, 132.59 (aryl CH), 146.82, 147.18 (aryl C), 149.24 (C–NH), 170.43 (C–O), 179.07 (C=N), 180.63 (C=O). Anal. Calcd. for $C_{25}H_{37}N_3O_2Pd$: C, 57.97; H, 7.20; N, 8.11, Found: C, 58.48; H, 7.41; N, 7.70. MS (Maldi-TOF): *m/z*: 518.564 $[M+1]^+$. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 395 (br) nm (4.31), 503 (br) nm (3.10).

12: (0.11 g, 75% yield). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ: 1.00 (s, 9 H, CH_3), 1.05 (s, 9 H, CH_3), 2.10 (s, 3 H, CH_3), 2.76 (s, 1 H, CH allyl), 2.82 (s, 1 H, CH allyl), 2.87 (d, $^3J_{HH}$ = 6.3 Hz, 2 H, NH–CH_2), 3.35 (d, $^2J_{HH}$ = 2.7 Hz, 1 H, CH allyl), 3.68 and 3.71 (d, AB system, $^{2}J_{AB}$ = 8.6 Hz, 2 H, N–CH$_2$), 3.82 (d, $^{2}J_{HH}$ = 2.7 Hz, 1 H, CH allyl), 5.25 (s, 1 H, N=C–C–H), 5.59 (s, 1 H, O=C–C–H), 6.48 (br t, 1 H, N–H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 298 K) δ: 23.06 (allyl CH$_3$), 27.63 (C*Me*$_3$), 29.19 (C*Me*$_3$), 32.30 (*C*Me$_3$), 36.13 (*C*Me$_3$), 54.05 (CH$_2$N), 57.12, 57.31 (CH$_2$ allyl), 66.36 (CH$_2$N), 84.39 (H–*C*=C–N), 102.56 (H–*C*=C–O), 128.97 (allyl C$\overset{\cdots}{-}$*C*$\overset{\cdots}{-}$C), 147.27 (C–NH), 168.26 (C–O), 179.91 (C=N), 182.18 (C=O). Anal. Calcd. for $C_{20}H_{32}N_2O_2Pd$: C, 54.73; H, 7.35; N, 6.38, Found: C, 53.64; H, 7.26; N, 5.81. Despite numerous attempts of purification, no better analyses were obtained. MS (Maldi-TOF): *m/z*: 461.617 [*M*+Na]$^+$. UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 365 nm (4.36), 506 (br) nm (2.88).

13·CH$_2$Cl$_2$**:** (0.20 g, 79% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K) δ:0.99 (s, 9 H, CH$_3$), 1.13 (s, 9 H, CH$_3$), 2.87 (d, $^{3}J_{HH}$ = 6.3 Hz, 2 H, NH–C*H$_2$*), 3.80 (br, 2 H, N–CH$_2$), 5.24 (s, 1 H, N=C–C–H), 5.32 (s, 1 H, O=C–C–H), 6.40 (br t, 1 H, N–H), 7.45-7.65 (m, 15 H, aryl); ^{1}H NMR (500 MHz, CDCl$_3$, 213 K) δ: 0.96 (s, 9 H, CH$_3$), 1.08 (s, 9 H, CH$_3$), 2.82 and 2.87 (ABX system (X = N*H*), $^{2}J_{AB}$ = 13.5 Hz, $^{3}J_{AX}$ = 6.2 Hz, $^{3}J_{BX}$ = 6 Hz, 2 H, NH–C*H$_2$*), 3.21 (dd, $^{2}J_{HH}$ = 11.5 Hz, $^{4}J_{PH}$ = 8.8 Hz, 1 H, N–CH*H*), 3.96 (dd, $^{2}J_{HH}$ = 11.5 Hz, $^{4}J_{PH}$ = 3.2 Hz, 1 H, N–CH*H*), 5.25 (s, 1 H, N=C–C–H), 5.33 (s, 1 H, O=C–C–H), 6.34 (br t, 1 H, N–H), 7.43-7.63 (m, 15 H, aryl); ^{31}P {^{1}H} NMR (125 MHz, CDCl$_3$, 268 K) δ: 25.5; ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 268 K) δ: 27.71 (C*Me*$_3$), 29.24 (C*Me*$_3$), 32.43 (*C*Me$_3$), 36.47 (*C*Me$_3$), 54.07 (CH$_2$N), 58.15 (CH$_2$N), 85.13 (H–*C*=C–N), 103.17 (H–*C*=C–O), 128.44, 128.56, 131.46, 134.78, 134.89, 135.13 (aryl C), 146.69 (C–N), 170.27 (C–O), 180.33 (C=N), 183.98 (C=O). Anal. Calcd. for $C_{34}H_{40}N_2O_2PPdCl\cdot CH_2Cl_2$: C, 54.85; H, 5.52; N, 3.65. Found: C, 54.76; H, 5.57; N, 3.41. UV–vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 280 nm (4.13), 379 (br) nm (4.43), 479 (br) nm (3.11).

Synthesis of 14·CH$_2$Cl$_2$**.** To a solution of [AuCl(PPh$_3$)] (0.17 g, 0.33 mmol) in anhydrous THF (100 mL) was added solid **9** (0.10 g, 0.33 mmol) and the mixture was stirred overnight at room temperature. After filtration through Celite to retain metallic gold, the solvent was evaporated and **14**·CH$_2$Cl$_2$ was obtained as a red–orange powder by recrystallization from a dichloromethane-hexane mixture (0.20 g, 73% yield). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K) δ:1.02 (s, 9 H, CH$_3$), 1.08 (s, 9 H, CH$_3$), 2.95 (d, $^{3}J_{HH}$ = 6.3 Hz, 2 H, NH–C*H$_2$*), 3.65 (s, 2 H, N–CH$_2$), 5.25 (s, 1 H, N=C–C–H), 5.54 (s, 1 H, O=C–C–H), 7.06 (br t, 1 H, N–H), 7.50 (m, 15 H, aryl); ^{31}P{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K) δ: 31.5; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K) δ: 27.71 (C*Me*$_3$), 29.36 (C*Me*$_3$), 32.50 (*C*Me$_3$), 35.01 (*C*Me$_3$), 54.03 (CH_2N), 65.08 (CH_2N), 84.99 (H–*C*=C–N), 101.43 (H–*C*=C–O), 129.02, 129.17, 131.46, 134.03, 134.22, 134.64 (aryl), 151.04 (C–N), 166.29 (C–O), 175.78 (C=N), 176.74 (C=O). Anal. Calcd. for $C_{34}H_{40}N_2O_2PAu\cdot CH_2Cl_2$: C, 51.17; H, 5.15; N, 3.41. Found: C, 51.47; H, 4.96; N, 2.84. MS (Maldi-TOF): *m/z*: 737.514 [*M*+1]$^+$. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 338 nm (4.41), 351 nm (4.45).

Formation of 15. To a solution of *trans*–[NiCl(Ph)(PPh$_3$)$_2$] (0.23 g, 0.33 mmol) in anhydrous THF (100 mL) was added solid **9** (0.10 g, 0.33 mmol) and the mixture was stirred overnight at room temperature. After filtration through Celite , the solvent was evaporated and **15** was obtained quantitatively as a green powder by recrystallization from a dichloromethane-hexane mixture. **15** was characterized by comparison of its ^{1}H NMR data with those of an authentic sample.[32]

Synthesis of 17. To a solution of **10** (0.20 g, 0.38 mmol) in anhydrous THF (100 mL) was added excess NaH (0.29 g, 1.14 mmol). The mixture was then refluxed overnight and solid [Pd(8–mq)(μ–Cl)]$_2$ (0.11 g, 0.19 mmoL) was added under nitrogen at room temperature. The solution was stirred at room temperature for 3 h. After filtration through Celite, 3/4 of the solvent was evaporated under reduced pressure and **17** was obtained as a green powder by addition of hexane and drying (0.25 g, 85% yield). Green crystals of **17**·2THF suitable for an X-ray analysis were isolated by slow evaporation of a THF solution. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 1.13 (s, 18 H, CH_3), 3.33 (br, 4 H, N–CH_2), 3.36 (s br, 4 H, Pd–CH_2), 5.50 (s br, 1 H, N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$H), 5.64 (s, 1 H, O$\overset{\cdots}{-}$C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$H), 7.39–7.60 (m, 8 H, aryl), 8.24 (dd, 2 H, aryl), 8.98 (dd, 2 H, aryl); ^{1}H NMR (500 MHz, $CDCl_3$, 213 K) δ: 1.13 (s, 18 H, CH_3), 2.91 (d, B part of an AB system, $^{2}J_{AB}$ = 12.3 Hz, 2 H, N–CH*H*), 3.27 (d, B part of an AB system, $^{2}J_{AB}$ = 14.5 Hz, 2 H, Pd–CH*H*), 3.36 (d, A part of an AB system, $^{2}J_{AB}$ = 14.5 Hz, 2 H, Pd–CH*H*), 3.42 (d, A part of an AB system, $^{2}J_{AB}$ = 12.3 Hz, 2 H, N–CH*H*), 5.60 (s, 1 H, N=C–C–H), 5.64 (s, 1 H, O=C–C–H), 7.42-7.64 (m, 8 H, aryl), 8.32 (dd, 2 H, aryl), 8.98 (dd, 2 H, aryl); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K) δ: 26.63 (Pd–CH_2), 29.78 (C*Me*$_3$), 36.22 (*C*Me$_3$), 60.59 (CH_2N), 88.79 (H-*C*$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N), 102.69 (H–*C*$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O), 121.41, 123.13, 128.16, 128.78, 128.90, 137.08, 149.16, 149.32, 153.00 (aryl), 165.62 (C$\overset{\cdots}{-}$N), 188.52 (C$\overset{\cdots}{-}$O). Anal. Calcd. for

$C_{36}H_{40}N_4O_2Pd_2$: C, 55.90; H, 5.21; N, 7.24. Found: C, 55.63; H, 5.32; N, 7.02. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 289 nm (4.23), 427 nm (4.41), 444 nm (4.37), 646 (br) nm (3.67).

Synthesis of 18. To a solution of **15** (0.09 g, 0.15 mmol) in anhydrous THF (100 mL) was added excess NaH. The mixture was then refluxed for overnight and solid $[Pd(8\text{–}mq)(\mu\text{–}Cl)]_2$ (0.09 g, 0.15 mmol) was added under nitrogen at room temperature. The solution was stirred at room temperature for one day. After filtration through Celite and washing of the Celite with 100 mL of THF, the solvent was evaporated under reduced pressure and **18** was obtained as black-violet powder by recrystallization from a dichloromethane-heptane mixture, washing with cold heptane and drying (0.11 g, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 1.08 (s, 18 H, CH_3), 1.12 (s, 18 H, CH_3), 2.47 (s, 4 H, Ni–N–CH_2), 3.32 (br, 4 H, Pd–N–CH_2), 3.38 (s, 4 H, Pd–CH_2), 5.20 (s, 2 H, N⎓C⎓C⎓H), 5.34 (s, 2 H, O⎓C⎓C⎓H), 7.40–7.58 (m, 8 H, aryl), 8.24 (d, 2 H, aryl), 8.90 (d, 2 H, aryl); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ: 26.94 (Pd–CH_2), 29.23 (C*Me*$_3$), 29.64 (C*Me*$_3$), 35.65 (*C*Me$_3$), 36.23 (*C*Me$_3$), 56.32 (CH_2N), 61.47 (CH_2N), 89.79 (H-*C*⎓C⎓N), 101.66 (H–*C*⎓C⎓O), 121.44, 123.25, 128.32, 128.82, 128.94, 137.26, 137.59, 149.04, 149.57 (aryl), 162.64 (C⎓N), 165.14 (C⎓N), 187.28 (C⎓O), 187.85 (C⎓O). Anal. Calcd. for $C_{52}H_{64}N_6O_4Pd_2Ni$: C, 56.34; H, 5.82; N, 7.58. Found: C, 56.63; H, 5.74; N, 7.31. MS (Maldi-TOF): *m/z*: 1107.241 [*M*+1]$^+$. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 309 nm (4.30), 388 nm (4.71), 495 (br) nm (3.89), 710 (br) nm (3.54), 786 (br) nm (3.68), 873 (br) nm (3.20).

Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 100 mL stainless-steel autoclave. The interior of the autoclave was protected from corrosion by a protective coating. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the co-catalyst under a constant low flow of ethylene, the reactor was pressurised to the desired pressure. The temperature increase that was observed resulted solely from the exothermicity of the reaction. The reactor was continuously fed with ethylene by a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. ethylene uptake. In all of the catalytic experiments, 4.10^{-2} mmol of Ni complex were used. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test, the reactor was cooled to 10 °C before transferring the gaseous phase into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated for GC analysis. The products in the reactor were hydrolyzed *in situ* by the addition of ethanol (10 mL), transferred in a Schlenk flask, and separated from the metal complexes by trap-to-trap distillation (120 °C, 20 Torr). All volatiles were evaporated (120 °C, 20 Torr, static pressure) and recovered in a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. For GC analyses, 1-heptene was used as an internal reference. The required amount of complex was dissolved in 10 mL of chlorobenzene and injected into the reactor. Depending on the amount of cocatalyst added, between 0 and 5 mL of cocatalyst solution were added so that the total volume of all solutions was 15 mL.

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The relevant data are summarized in Table 1. Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[61,62] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{\mathrm{C–H}}$ = 0.95 Å, U_{11} = 0.04). Full data collection parameters, and structural data are available as Supporting Information. Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC xxx. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Acknowledgments. We are grateful to the CNRS for support and to the Ministère de la Recherche for a Ph-D grant to J.p.T. and to Dr. J.-D. Sauer for NMR experiments.

Supporting Information Available. Tables of atomic coordinates, bond distances and angles and anisotropic thermal parameters and ORTEP views for **10, 13** and **17**·2THF; X-ray data in CIF format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Crystal data and details of the structure determination for compounds **10**, **13** and **17**·$2C_4H_8O$.

Crystal Data	10	13	17·**$2C_4H_8O$**
Formula	$C_{26}H_{33}N_3O_2Pd$	$C_{34}H_{40}ClN_2O_2PPd$	$C_{36}H_{40}N_4O_2Pd_2\cdot 2(C_4H_8O)$
Formula weight (g.mol^{-1})	525.95	681.50	917.73
Crystal system	Monoclinic	Orthorombic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1\ 2_1\ 2_1$	$C\ 2/c$
a [Å]	18.708(5)	12.8590(10)	15.612(2)
b [Å]	13.535(5)	10.5290(10)	12.394(2)
c [Å]	19.687(5)	24.102(2)	22.147(2)
β [°]	95.710(5)	90	˜ı7̃84̣□̣
V [Å^3]	4960(3)	3263.2(5)	4079.0(9)
Z	8	4	4
Density (calc) [g.cm^{-3}]	1.409	1.387	1.494
μ(MoKα) [mm^{-1}]	0.775	0.732	0.929
F(000)	2176	1408	1888
Temperature (K)	173	173	173
θ Min-Max [°]	1.1, 30.0	1.7, 27.0	1.9, 30.0
Data set [h ;k ;l]	-11/26 ; -16/18 ; -27/23	-15/16 ; -13/12 ; -22/30	0/21 ; 0/17 ; -31/29
Tot., Uniq. Data, R(int)	27159, 14221, 0.050	23770, 7078, 0.075	5936, 5936, 0.000
Observed data [$I > 2\sigma(I)$]	9508	5419	4274
N*reflections*, N*parameters*	14221, 577	7078, 370	5936, 245
R, wR$_2$, GOF	0.0640, 0.1434, 1.11	0.0476, 0.1136, 1.05	0.0456, 0.1384, 1.08

Table 2. Comparison of selected interatomic distances (Å) in **6**,[32,33] one of the two molecules of **10**, **13** and **17**·$2C_4H_8O$.

	6	**10**	**13**	**17**·$2C_4H_8O$
C(1)-C(2)	1.379(5)	1.369(5)	1.363(7)	1.387(4)
C(1)-C(6)	1.399(5)	1.402(5)	1.413(7)	
C(2)-C(3)	1.516(5)	1.521(5)	1.507(7)	1.517(4)
C(3)-C(4)	1.393(5)	1.415(5)	1.431(7)	1.396(4)
C(4)-C(5)	1.389(5)	1.362(5)	1.357(7)	
C(5)-C(6)	1.523(5)	1.519(5)	1.517(7)	
C(2)-O(1)	1.265(4)	1.279(4)	1.316(6)	1.267(4)
C(3)-N(1)	1.323(5)	1.307(4)	1.313(6)	1.337(4)
C(5)-N(2)	1.320(5)	1.337(5)	1.331(6)	
C(6)-O(2)	1.254(4)	1.242(4)	1.247(6)	
Pd-O(1)		2.107(3)	2.012(3)	2.110(2)
Pd-N(1)		2.028(3)	2.080(4)	2.023(3)
Pd-C(17)		2.014(4)		
Pd-N(3)		2.009(3)		
Pd-Cl			2.2843(13)	
Pd-P			2.2465(14)	
Pd-C(10)				2.018(4)
Pd-N(2)				2.006(3)

Table 3. Selected bond angles (°) in one of the two molecules of **10**, **13** and **17**·$2C_4H_8O$.

	10	**13**	**17**·$2C_4H_8O$
O(1)-Pd-N(1)	79.75(11)	80.34(15)	79.79(11)
O(1)-Pd-C(17)	174.61(13)		
O(1)-Pd-N(3)	97.61(11)		
N(1)-Pd-C(17)	99.48(14)		
N(1)-Pd-N(3)	177.04(11)		
C(17)-Pd-N(3)	83.03(14)		
O(1)-Pd-Cl		177.58(10)	
O(1)-Pd-P		95.12(10)	
N(1)-Pd-Cl		97.61(12)	
N(1)-Pd-P		174.59(12)	
Cl-Pd-P		86.99(5)	
O(1)-Pd-C(10)			178.37(13)
O(1)-Pd-N(2)			97.70(13)
N(1)-Pd-C(10)			99.42(14)
N(1)-Pd-N(2)			177.03(13)

C(10)-Pd-N(2)	83.05(15)

Table 4. Oligomerization of Ethylene by **15** and **[$NiCl_2(PCy_3)_2$]** with $AlEtCl_2$ as Cocatalyst.[a]

	15	**15**	**$NiCl_2(PCy_3)_2$**
$AlEtCl_2$ (equiv)	6	10	6
selectivity C_4 (mass %)	49	51	86
selectivity C_6 (mass %)	45	43	14
selectivity C_8 (mass %)	6	6	traces
Productivity (g C_2H_4/g Ni • h)	13500	21500	13000
TOF (mol C_2H_4/mol Ni • h)	28500	45000	27000
$\tilde{\alpha}$olefin (C_4) (mol %)	14	7	9
linear C_6 (mass %)	51	45	---
k_α[b]	0.6	0.57	0.13

[a] Conditions: 10 bar C_2H_4, 35 min, T = 30 °C, $4 \cdot 10^{-2}$ mmol Ni complex, solvent: 15 mL toluene; [b] k_α = mol C_6/ mol C_4

Figure 1. ORTEP view of **10**. The unit cell is constituted by two independent but very similar molecules. The aromatic and CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

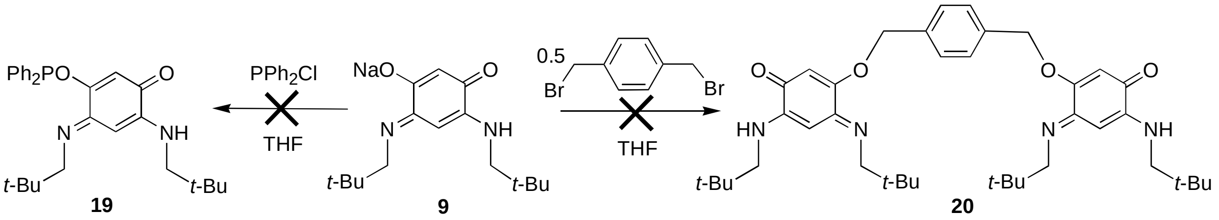
Figure 2. ORTEP view of **13**. The phenyl groups on the phosphorus atom, except the ipso carbons, and the CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

Figure 3. ORTEP view of **17** in **17**·2THF. The aromatic and CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

ANNEX

We have first studied the reactivity of **9** with organic electrophiles. Owing to the widespread application of phosphonite ligands in homogeneous catalysis, we have attempted the reaction with PPh_2Cl in the aim to phosphorylate the quinonoid ligand at one oxygen atom, which was not possible starting directly from the zwitterion **6** as already shown. We have also attempted the reaction of **9** with 1,4-dibromodimethylbenzene in order to link two quinonoid units by a diether bridge (Scheme 9).

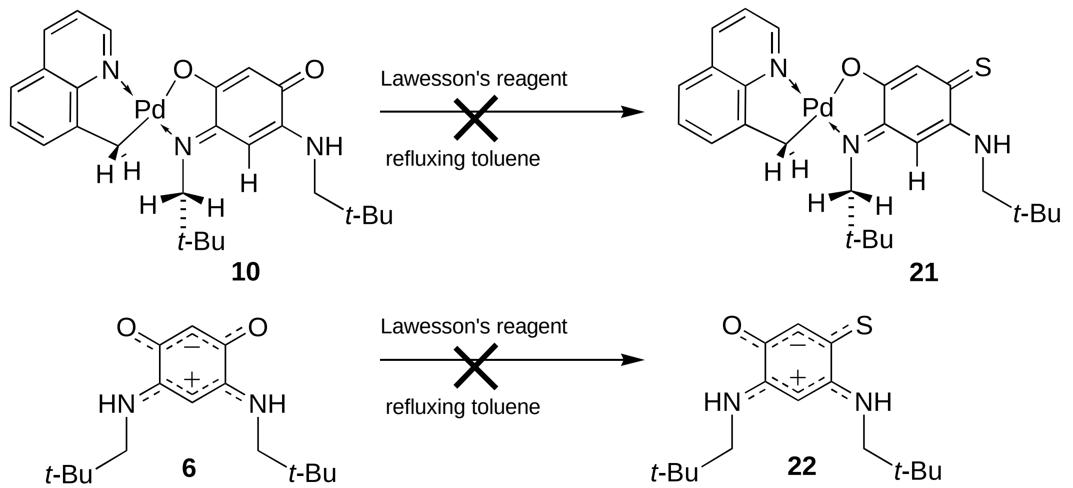
Scheme 9. Reactions of **9** with PPh_2Cl and 1-4-dibromodimethylbenzene



Unfortunately, these two reactions do not work, probably owing to the presence of HCl traces in the diphenylchlorophosphine in the first reaction, which led very quickly to the reprotonation of **9** and the formation of the starting zwitterion **6**, and owing to the poor reactivity of **9** towards organic electrophiles in the case of the reaction with 1,4-dibromodimethylbenzene.

In a second part, by analogy with Callot and coworkers' studies about thionation of porphyrins bearing enaminoketone and enaminoaldehyde groups,[62] we have attempted to convert the ketone group in **10** in thioketone by using the Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide), which is a reagent of choice in this reaction (Scheme 10).[63] Furthermore, we expected that the replacement of the oxygen atom by sulfur could lead to novel interesting properties of the newly formed binuclear complex with two very different chelating sites.

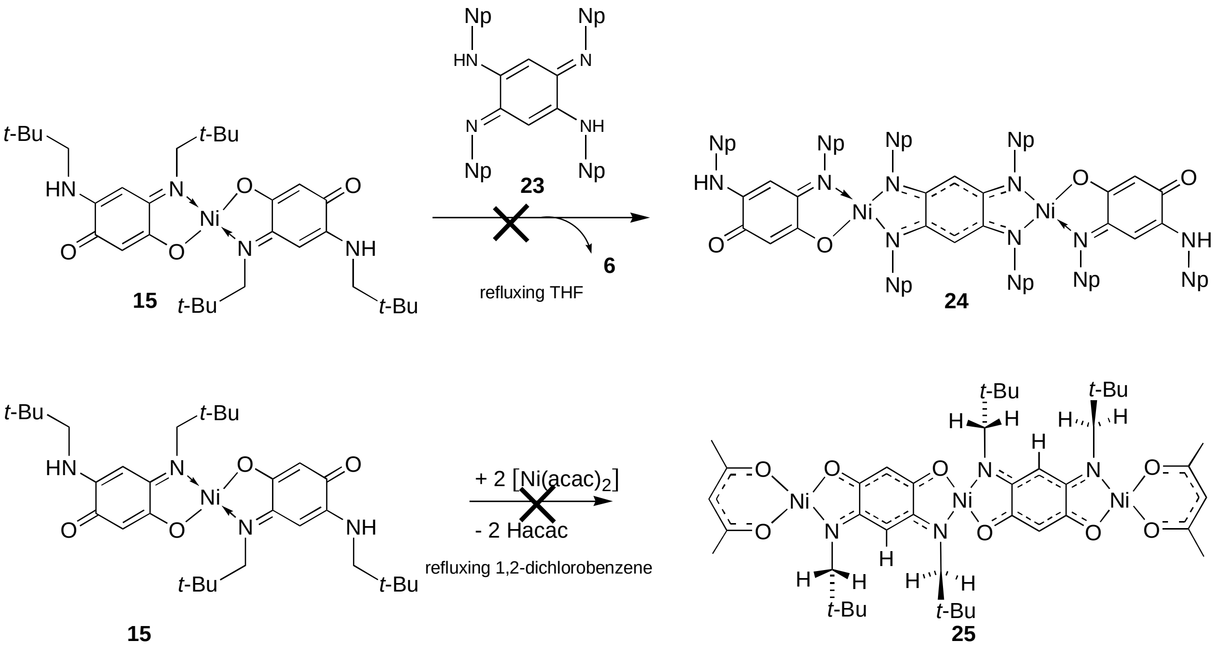
Scheme 10. Reactions of **6** and **10** with Lawesson's reagent



Unfortunately, under standard conditions (refluxing toluene), only decomposition of the palladium complex and formation of Pd(0) was observed. The same reaction was attempted starting directly from the zwitterion **6**, with the aim to prepare a dissymmetric zwitterion with a negative charge delocalized between an oxygen atom and a sulfur atom (Scheme 10). But, despite a nice color change from purple to yellow in refluxing toluene, only a complex mixture of products was obtained, most of them still containing phosphorus. Nevertheless, these results are consistent with the studies on the porphyrin derivatives[61] and with related studies about the unusual reaction of the Lawesson's reagent on substituted 2-amino-1,4-naphtoquinones.[64]

In a third part, we have confirmed the impossibility of using **15** as a metallo-ligand without using very harsh conditions. Indeed, we have attempted the reaction of **15** with 2,5-dineopentylamino-1,4-benzoquinonediimine **23**[65] in refluxing THF, in order to prepare a binuclear complex by double deprotonation of **23**, and the reaction of **15** with [Ni(acac)$_2$] in refluxing 1,2-dichlorobenzene in order to prepare a trinuclear complex (Scheme 11).

Scheme 11. Reactions of **15** with **23** and with [Ni(acac)$_2$]



Unfortunately, these reactions do not work. The first one confirms the fact that **15** is a thermodynamic sink, and the second one the impossibility to deprotonate the N-H function in **15** without using very harsh conditions (excess NaH in refluxing THF).

Experimental Section

Reaction of 9 with chlorodiphenylphosphine: To a solution of PPh_2Cl (0.23 g, 1.04 mmol) in anhydrous THF (100 mL) was added solid **9** (0.29 g, 1.04 mmol) and the mixture was stirred overnight at room temperature. After filtration through Celite, the solvent was evaporated and reprotonated **6** was obtained as a purple powder by recrystallization from a dichloromethane/hexane mixture.

Reaction of 9 with 1-4-dibromodimethylbenzene: To a solution of 1-4-dibromodimethylbenzene (0.05 g, 0.17 mmol) in anhydrous THF (100 mL) was added solid **9** (0.10 g, 0.33 mmol) and the mixture was stirred overnight at room temperature. Unreacted **9** was recovered by filtration.

Reaction of 10 with Lawesson's reagent: To a solution of **10** (0.15 g, 0.29 mmol) in anhydrous toluene (100 mL) was added one equiv. of solid Lawesson's reagent (0.12 g, 0.29 mmol) and the mixture was refluxed overnight. The black solution was filtered and the filtrate evaporated yielding only decomposition of the starting materials.

Reaction of 6 with Lawesson's reagent: To a solution of **6** (0.20 g, 0.72 mmol) in anhydrous toluene (100 mL) was added one equiv. of solid Lawesson's reagent (0.29 g, 0.72 mmol) and the mixture was then refluxed overnight during which time the red solution turns intense yellow. The solution was evaporated and the residue chromatographed on silicagel, yielding after elution only unidentified products containing phosphorus.

Reaction of 15 with 2,5-dineopentylamino-1,4-benzoquinonediimine 23: solid **15** (0.08 mmol, 0.05 g) and solid **24** (0.04 mmol, 0.02 g) were suspended in 100 mL of THF and heated to reflux overnight. At room temperature, the solution was evaporated. Unreacted **15** was precipitated by addition of toluene and filtered. The filtrate was evaporated to recover unreacted **23**.

Reaction of 15 with [Ni(acac)$_2$]: 15 (0.08 mmol, 0.05 g) and [Ni(acac)$_2$] (0.04 mmol, 0.04 g) were suspended in 100 mL of 1,2-dichlorobenzene and heated to reflux for 3 days. At room temperature, unreacted **15** was filtered.

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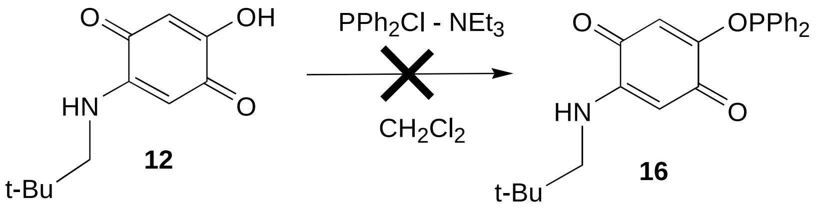
PART 3: Toward a $6\pi + 6\pi$ Zwitterion or a Bioinhibitors-Related OH-Substituted Aminoquinone: Identification of a Key Intermediate in their pH Controled Synthesis

This third part is presented in the format of a publication published as advanced article in *Chemistry: A European Journal* **2004** (PDF format) and its corresponding annex.

Article uniquement disponible dans la version papier

ANNEX

We have made various studies on the reactivity of **12** with organic and inorganic electrophiles. As already attempted with the zwitterion **8**, we have first tried the reaction with PPh_2Cl in basic medium in order to phosphorylate the quinonoid ligand at the oxygen atom (Scheme 2).

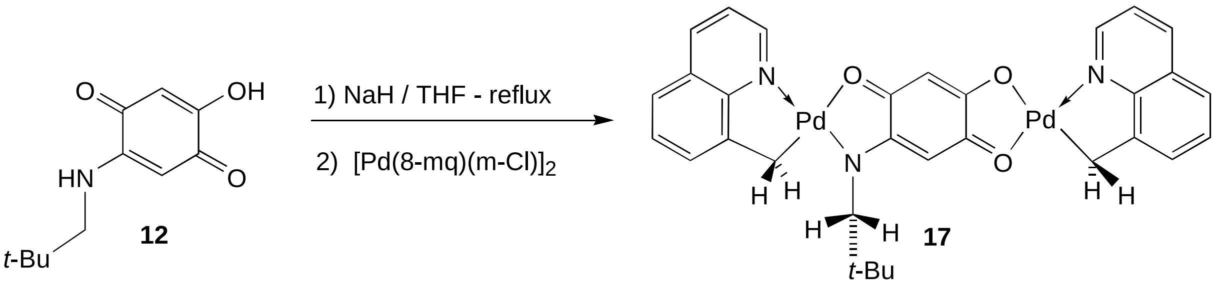


Scheme 2. Reaction of **12** with PPh_2Cl

Unfortunately, this reaction does not occur, which confirms the impossibility to convert the conjugated enol or enolate group in our chemistry by using conventionnal methods.

In order to dimerize two aminoquinone units by oxidative coupling,[22] we have attempted the reaction of **12** with AgOTf but, as in the case of **8**, no coupling reaction occurred.

We have also studied of the coordination chemistry of **12**. By using similar procedures to that with the zwitterion **8**, a promising result was obtained by first in situ deprotonation of **12** with excess NaH in refluxing THF, followed by addition of one equiv. of solid $[Pd(8\text{–}mq)(\mu\text{–}Cl)]_2$ (Scheme 3).



Scheme 3. In situ deprotonation of **12** and reaction with $[Pd(8\text{–}mq)(\mu\text{–}Cl)]_2$

The excess NaH in the reaction mixture does not react with either the Pd precursor or the final product and can be filtered through Celite before product isolation. We only obtained the ^1H NMR spectrum of the crude product which revealed the presence of only one signal for the neopentyl group, consistent with the presence of only one isomer in solution. Furthermore, the presence of two Pd-CH_2 signals and the relative integration of all signals clearly shows a binuclear complex of type **17**. Owing to the limited quantity of starting material available at this time, we did not succeed to purify the final complex. Now, this problem has been circumvented and this reaction, and in a more general manner the metallation strategy, could be reexamined.

Experimental Section

Reaction of 12 with chlorodiphenylphosphine: To a solution of **12** (0.24 g, 1.14 mmol) in anhydrous dichloromethane (100 mL) was added one equiv. of distilled NEt_3 (0.12 g, 1.14 mmol) and one equiv. of PPh_2Cl (0.25 g, 1.14 mmol). The mixture was then stirred overnight at room temperature. The solvent was evaporated yielding unreacted starting reagents.

Reaction of 12 with AgOTf: To a solution of **12** (0.20 g, 0.95 mmol) in anydrous THF (50 mL) was added one equiv. of AgOTf (0.25 g, 0.95 mmol). The mixture was then stirred at room temperature for two weeks. A silver mirror was slowly deposited and filtered. The filtrate was then evaporated yielding unreacted **12**.

Formation of 17: To a solution of **12** (0.08 g, 0.38 mmol) in anydrous THF (100 mL) was added excess NaH (25 mg, 1.00 mmol). The mixture was then refluxed overnight and solid $[Pd(8\text{–}mq)(\mu\text{–}Cl)]_2$ (0.02 g, 0.38 mmol) was added under nitrogen at room temperature. The solution was stirred at room temperature for 3 h. After filtration through Celite, 3/4 of the solvent was evaporated under reduced pressure and crude **17** was obtained as a green powder by addition of hexane, filtration and drying. ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ: 1.09 (s, 9 H, CH_3), 3.45 (s, 2 H, Pd–CH_2), 3.50 (s br, 2 H, N–CH_2), 3.84 (s, 2 H, Pd–CH_2), 5.66 (s, 1 H, $\mathrm{N\overset{\cdots}{-}C\overset{\cdots}{-}C{-}H}$), 5.83 (s, 1 H, $\mathrm{O\overset{\cdots}{-}C\overset{\cdots}{-}C{-}H}$), 7.50 (m, 8 H, aryl), 8.24 (dd, 2 H, aryl), 8.98 (dd, 2 H, aryl).

References

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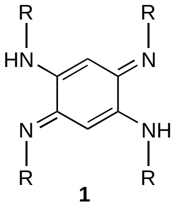
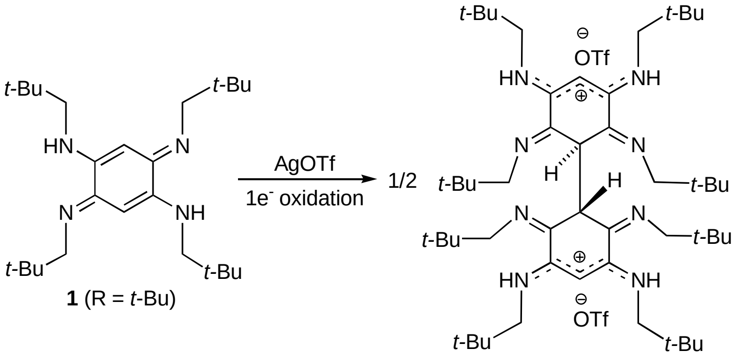
Conclusion Générale et Perspectives

Dans la première partie de ce mémoire, nous avons étudié de manière globale la chimie de coordination, ainsi que les applications en chimie organique, électrochimie et catalyse, de nouveaux ligands bis-bidentates conjugués du type 2,5-diamino-1,4-benzoquinonediimines du type **1**. Ces ligands ont pu être synthétisés de diverses manières à partir de méthodes décrites dans la littérature, depuis déjà plus d'un siècle dans le cas de substituants N-aryles, et très récemment décrites par notre laboratoire dans le cas de substituants N-alkyles.



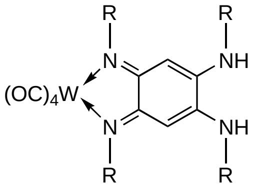
1

En synthèse organique, un résultat très original et complètement inattendu a été obtenu lors de l'étude de la réaction de **1** (R = *t*-Bu) avec Ag^+. En effet, nous avons mis en évidence la formation d'un dimère dicationique **2** résultant du couplage oxydant de deux radicaux cations (schema), engendrés par l'oxydation à un électron de **1**. Cette réaction, qui est le premier exemple de couplage C-C renversable en chimie des quinones, nous a permis de faire une analogie intéressante entre des dérivés porphyriniques et des dérivés aminoaromatiques.



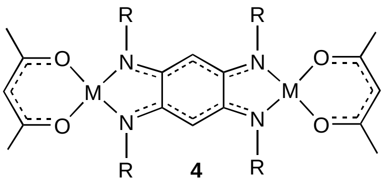
Schema. Réaction de couplage oxydant.

En chimie de coordination, notre étude s'est d'abord orientée sur les métaux de la gauche du tableau périodique, à savoir les métaux carbonyles du groupe VI à bas degré d'oxydation. Par réaction de **1** avec *cis*-$[W(CO)_4(pip)_2]$, nous avons observé une relocalisation et une isomérisation *para→ortho* du système π de la para-benzoquinonediimine de départ, induite par coordination du centre métallique, et conduisant à la formation de complexes mononucléaires neutres du type **3**. Le comportement spectro-photochimique de ces complexes a également été étudié.



3

En s'inspirant des résultats obtenus par Walther *et al.* lors de l'étude de la chimie de coordination des ligands pontants oxalamidines, nous avons développé la chimie des métaux de transition de la droite du tableau périodique (nickel et palladium) sur nos ligands. Ainsi, à partir de précurseurs organométalliques porteurs de groupements basiques oxygénés du type acac, nous avons observé une double déprotonation des deux fonctions N–H suivie par la coordination du centre métallique, ce qui conduit à des complexes homobinucléaires du type **4** avec complète délocalisation du système π de la quinone entre les centres métalliques.



4

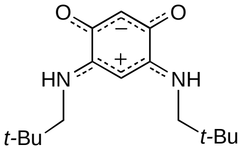
M = Ni, Pd

L'étude électrochimique des complexes binucléaires de nickel(II) a démontré une très forte interaction métal-métal, avec une constante de comproportionation parmi les plus élevées à ce jour en chimie du nickel, et qui pour la première fois est modulée par la nature des substituants portés par les atomes d'azote. L'étude RPE de ces complexes est en cours afin de confirmer le centre d'oxydation (métal ou ligand). Ces nouveaux complexes de nickel se sont également révélés être de bons pré-catalyseurs dans la réaction d'oligomérisation de l'éthylène. Après activation des complexes en présence d'alkylaluminium, nos catalyseurs présentent de bonnes activités et sont très sélectifs dans la formation de courtes chaînes C_4 et C_6, mais hélas sont très isomérisants avec des pourcentages très faibles d'α-oléfines.

Il serait maintenant utile de mettre au point une synthèse des ligands du type **1** porteurs de N-substituants très encombrés, mais également de synthétiser des quinones dissymétriques, avec différents N-substituants sur une même molécule, afin de voir les conséquences sur les sélectivités dans les réactions catalytiques, mais également en vue d'étendre le système π. Il serait aussi particulièrement intéressant de poursuivre le travail amorcé concernant la synthèse de ligands porteurs de fonctions pendantes, telles que des groupements pyridines ou phosphines, afin d'obtenir des ligands bis-tridentes permettant de complexer facilement le fer ou le cobalt, en vue d'applications en catalyse d'oligomérisation, ainsi qu'envisager le greffage de fonctions alkoxysilyles pour la catalyse hétérogène. Toujours dans le domaine de la catalyse, on peut espérer que les complexes de palladium que nous avons préparés, et qui sont inactifs en catalyse d'oligomérisation de l'éthylène, pourraient être de bons candidats pour des réaction catalytiques de cross-coupling, telles que les réactions de Heck ou Suzuki, de par leur très haute stabilité thermique.

La réaction de couplage oxydant décrite précédemment est également extrêmement intéressante et mérite une étude plus approfondie. Des études électrochimiques, ainsi que l'étude de la dimérisation avec d'autres agents d'oxydation à un électron tels que le 7,7,8,8-tetracyanodiquinodimethane, sont en cours afin de confirmer la validité du mécanisme proposé, mais également pour comprendre les limitations de cette réaction de dimérisation par Ag^+ en terme de rendement. Elle a néanmoins permis de montrer que les ligands du type **1** peuvent avoir une réactivité du type radicalaire, ce qui parait prometteur dans le but de substituer les protons oléfiniques par des halogènes en présence d'activateurs radicalaires ou de manière photochimique.

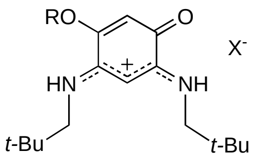
Dans une deuxième partie, nous nous sommes intéressés à la synthèse et l'étude des premiers ligands zwittérioniques de type benzoquinonemonoimine **5**.



5

Le zwittérion **5** est une molécule plane potentiellement antiaromatique avec un système à 6π + 6π électrons délocalisés, dans lequel les deux sous-unités 6π sont chimiquement connectées mais électroniquement indépendantes. Ce composé représente l'un des rares exemples où une forme zwittérionique est plus stable que sa forme canonique, ce qui a été par la suite confirmé par des études théoriques et par sa faible réactivité en chimie organique vis-à-vis des électrophiles usuels tels que l'iodure de méthyle ou les chlorophosphines. Nous avons montré qu'il était possible de contrôler la délocalisation du système πdu coeur quinonique selon la nature de l'électrophile additionné. Ainsi l'ajout d'un électrophile organique cationique conduit à des composés du type **6** dans lequel l'un des deux sous-systèmes est localisé et l'autre délocalisé.

Nous avons développé une chimie de coordination très riche de cette molécule, principalement en chimie du palladium, en utilisant une stratégie basée sur des métallations succéssives. Ainsi la monodéprotonation suivie de la métallation conduit à des complexes mononucléaires du type **7** dans lequel les deux sous-systèmes π sont localisés. Une deuxième déprotonation des métalloligands suivie de la métallation conduit à la formation de complexes polynucléaires, tels que le complexe binucléaire **8**, dans lequel le système π est délocalisé entre les deux centres métalliques. Ainsi, suivant l'électrophile ajouté et le degré de déprotonation du zwittérion **5**, il est possible de contrôler parfaitement la distribution du sytème π du coeur quinonique.



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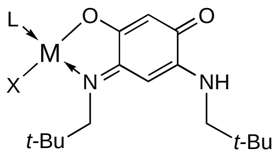

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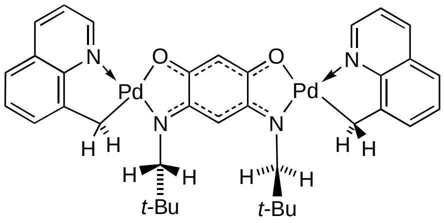
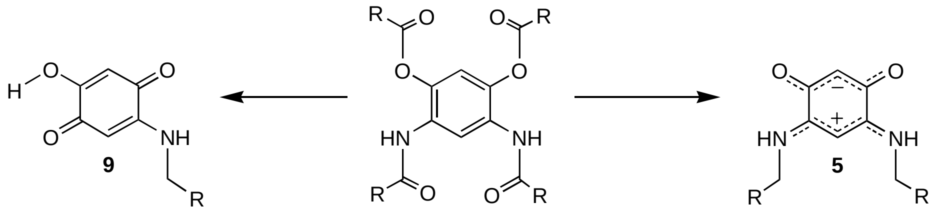


8

Nous avons également trouvé diverses applications à la majorité des nouveaux composés préparés, en particulier l'application des composés du type **6** en coloration capillaire a conduit à un dépôt de brevet, ainsi qu'en catalyse. Il reste maintenant encore beaucoup d'études à réaliser sur cette passionnante molécule, en particulier l'accès à des molécules dissymétriques et/ou porteuses de fonctions pendantes au niveau des N-substituants, des études théoriques et électrochimiques des complexes polynucléaires, mais également l'étude de la réactivité du zwittérion vis-à-vis de nucléophiles et d'agents réducteurs, qui est maintenant en cours et donne des résultats très prometteurs. Il serait aussi intéréssant de trouver une stratégie efficace pour la phosphorylation du zwittérion au niveau d'un atome d'oxygène, puisque les méthodes usuelles sont inefficaces, afin de rajouter un nouveau site potentiel de chélation.

La dernière partie de ce mémoire a été consacrée à l'étude complète du mécanisme de formation du zwittérion **5**, ce qui a abouti à la préparation d'une nouvelle classe de composés du type aminobenzoquinones **9**.



En effet l'étude complète de la réaction de réduction du diamidodiester conduisant à **5** a montré que, en fonction du pH, on pouvait obtenir les deux classes de quinones **4** et **8**. Par la suite, nous avons réalisé une étude de chimie supramoléculaire afin de montrer le rôle du nombre des substituants N-alkyles sur les différents arrangements supramoléculaires observés pour **1**, **5** et **9**. L'aminoquinone **9** se révèle également un candidat particulièrement attrayant pour la biochimie et la chimie de coordination, dont nous avons abordé les premières études.