Inorg. Chem. **2004**, *43*, 6944–6953

Inorganic Chemistry
Article

Stepwise Synthesis, Structures, and Reactivity of Mono-, Di-, and Trimetallic Metal Complexes with a $6\pi + 6\pi$ Quinonoid Zwitterion[†]

Jean-philippe Taquet,[‡] Olivier Siri,[‡] Pierre Braunstein,[*,‡] and Richard Welter[§]

Laboratoire de Chimie de Coordination and Laboratoire DECMET, UMR 7513 CNRS,
Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France

Received June 7, 2004

The benzoquinonemonoimine *N,N′*-dineopentyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium $[C_6H_2(\overset{\cdot\cdot}{-}NHCH_2t\text{-}Bu)_2(\overset{\cdot\cdot}{-}O)_2]$ **6**, which is a rare example of an organic zwitterion being more stable than its canonical form, 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-, di-, and trimetallic 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 N_2, reacts with chloride-bridged Pd(II) homodimetallic complexes, $[AuCl(PPh_3)]$ or *trans*-$[NiCl(Ph)(PPh_3)_2]$, to afford the monometallic 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 $[Pd(8\text{-mq})(\mu\text{-Cl})]_2$ (8-mq = orthometalated 8-methylquinoline) affords the homodimetallic complex **17** in which the π-system of the quinonoid ligand is delocalized between the two metal centers. Deprotonation of both N–H amino functions of the square-planar complex *trans*-$[Ni(N,O)_2]$ **15** with NaH and reaction with $[Pd(8\text{-mq})(\mu\text{-Cl})]_2$ affords the heterotrimetallic (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 monometallic 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 past 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, copolymerization, and oligomerization,[1−14] but also for the synthesis of porphyrin dimers and oligomers connected by metal ions.[15] In contrast, very few examples of mono- or polynuclear metal complexes based on N,O ligands supported by a quinonoid core have

---

[*] Author to whom correspondence should be addressed. E-mail: braunst@chimie.u-strasbg.fr.

[†] Dedicated to Prof. J. J. Ziolkowski on the occasion of his 70th birthday, with our warmest congratulations.

[‡] Laboratoire de Chimie de Coordination.

[§] Laboratoire DECMET (X-ray diffraction studies).

(1) Qian, Y.; Zhao, W.; Huang, J. *Inorg. Chem. Commun.* **2004**, *7*, 459−461.

(2) (a) Sun, W.-H.; Zhang, W.; Gao, T.; Tang, X.; Chen, L.; Li, Y.; Jin, X. *J. Organomet. Chem.* **2004**, *689*, 917−929. (b) Sun, W.-H.; Yang, H.; Li, Z.; Li, Y. *Organometallics* **2003**, *22*, 3678−3683.

(3) (a) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869−873. (b) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623−4629.

(4) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315.

(5) He, X.; Yao, Y.; Luo, X.; Zhang, J.; Liu, Y.; Zhang, L.; Wu, Q. *Organometallics* **2003**, *22*, 4952−4957.

(6) Darensbourg, D. J.; Ortiz, C. G.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 6915−6922.

(7) (a) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272−2273. (b) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2842−2854. (c) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *288*, 1750−1751. (d) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462. (e) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149−3151.

(8) (a) Carlini, C.; Raspolli Galletti, A. M.; Sbrana, G. *Polymer* **2003**, *44*, 1995−2003. (b) Carlini, C.; Isola, M.; Liuzzo, V.; Raspolli Galletti, A. M.; Sbrana, G. *Appl. Catal., A* **2002**, *231*, 307−320.

(9) (a) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533−3545. (b) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250−256.

(10) (a) Zhang, D.; Jin, G.-X.; Hu, N.-H. *Eur. J. Inorg. Chem.* **2003**, 1570−1576. (b) Zhang, D.; Jin, G.-X.; Hu, N. *Chem. Commun.* **2002**, 574−575.

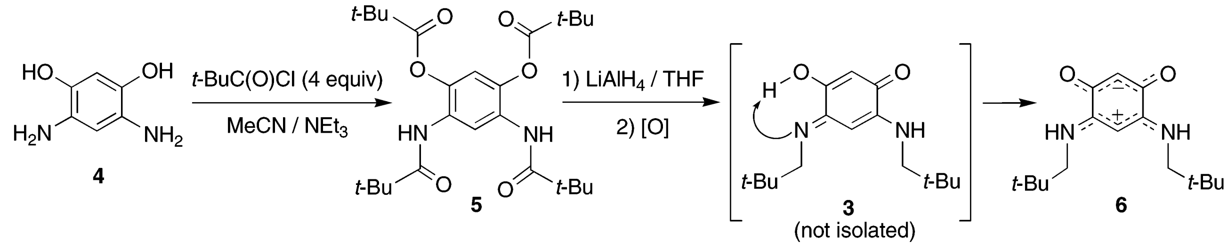
(11) Pickel, M.; Casper, T.; Rahm, A.; Dambouwy, C.; Chen, P. *Helv. Chim. Acta* **2002**, *85*, 4337−4352.

(12) Li, X.-F.; Li, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2680−2685.

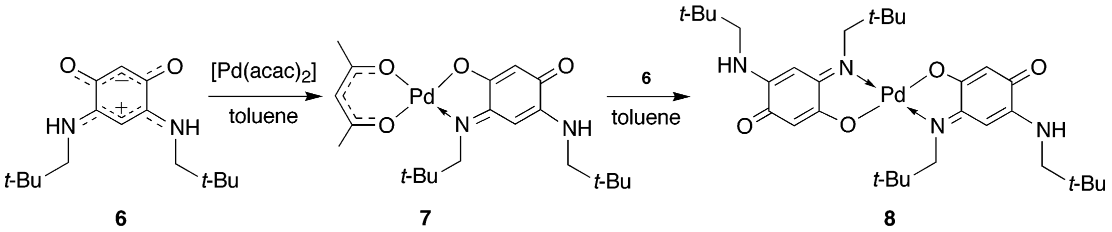
(13) Novak, B.-M.; Tian, G.; Nodono, M.; Boyle, P. *Polym. Mat. Sci. Eng.* **2002**, *86*, 326−327.

10.1021/ic049263a CCC: $27.50

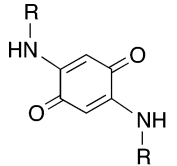
Scheme 1. Synthesis of Zwitterion **6** as Reported in 2003[20a]

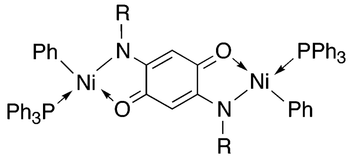


Scheme 2. Reaction of **6** with [Pd(acac)$_2$]

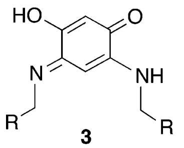


been reported in the literature.[16−18] Furthermore, to the best of our knowledge, only one example of N,O,N,O benzoquinone ligand has been reported, very recently, for the preparation of catalytically active metal complexes.[19] The authors prepared and characterized a series of 2,5-disubstituted amino-*p*-benzoquinone ligands **1** and used their dimetallic Ni(II) complexes of type **2** as single-component catalysts in ethylene polymerization. Despite the lack of X-ray quality crystals, the very wide molecular weight distribution of the polyethylene formed during the reaction was explained by electronic cooperative interactions between their Ni(II) centers.[19]


1


2

Sequential monodeprotonation/metallation of **1** was not possible and its first metal complex, **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 with 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, for example, allow the stepwise synthesis of mono- and dimetallic complexes, and 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 quinonemonoimine **6** (Scheme 1).[20]

The zwitterion **6** is a planar and potentially antiaromatic 12π electron system,[20a] 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 obtain monometallic 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 obtained by reaction of **6** with [Pd(acac)$_2$] (Scheme 2).[20a]

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-, di-, and trimetallic complexes in which the π-system of the quinone is localized or fully delocalized between two or three metal centers.

---

(14) Speiser, F.; Braunstein, P.; Saussine, L. *Inorg. Chem.* **2004**, *43*, 4234−4240.

(15) (a) Richeter, S.; Jeandon, C.; Sauber, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Porphyrins Phthalocyanines* **2002**, *6*, 423−430. (b) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2002**, 266−267. (c) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168−6179. (d) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2001**, 91−92.

(16) Moriuchi, T.; Watanabe, T.; Ikeda, I.; Ogawa, A.; Hirao, T. *Eur. J. Inorg. Chem.* **2001**, 277−287.

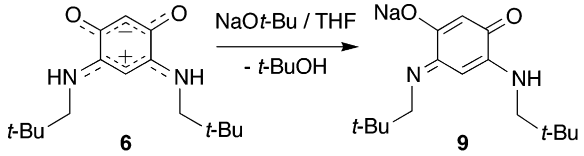
(17) Elduque, A.; Aguilera, F.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Pinillos, M. T. *Inorg. Chim. Acta* **1998**, *274*, 15−23.

(18) Kühlwein, F.; Polborn, K.; Beck, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1931−1944.

(19) Zhang, D.; Jin, G.-X. *Organometallics* **2003**, *22*, 2851−2854.

(20) (a) Braunstein, P.; Siri, O.; Taquet, J.-p.; Rohmer, M.-M.; Bénard, M.; Welter, R. *J. Am. Chem. Soc.* **2003**, *125*, 12246−12256. (b) Siri, O.; Braunstein, P. *Chem. Commun.* **2002**, 208−209.

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



Results and Discussion

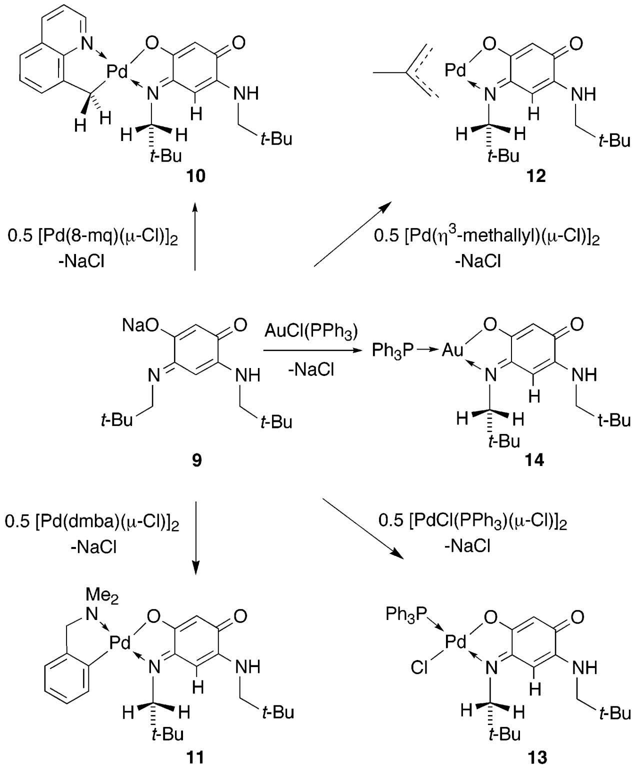
Monometallic Complexes. Monodeprotonation of **6** with one equiv of NaO*t*-Bu, in THF at room temperature, yielded the corresponding benzoquinonemonoimine sodium enolate **9** as an orange powder which was characterized, except by X-ray crystallography (Scheme 3). Its poor solubility in THF or DMSO suggests a polymeric structure.[21]

The ^{1}H NMR data of **9** revealed the presence of two *t*-Bu groups and two CH_2 signals ($\delta = 2.81$ and 3.11), consistent with a lower molecular symmetry than that in **6**.[20b] Only one N−H signal is observed at $\delta = 6.08$ for the aminic proton. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum contains two signals at $\delta = 161.54$ and 180.23 which are consistent with a localized π-system (δ(C−O) and δ(C=O), respectively), in contrast to **6** for which the negative charge is delocalized between the two oxygen atoms ($\delta(C\overset{...}{-}O) = 172.13$).[20b]

The isolated sodium salt **9**, which is stable in the solid state under N_2 for weeks, was reacted with chloride-bridged dimetallic Pd(II) complexes and with $[AuCl(PPh_3)]$ to afford complexes **10**−**14** in good yields, as a result of chloride substitution (Scheme 4). Complex **10** could also be obtained directly from the zwitterion **6** by reaction with 0.5 equiv of $[Pd(8\text{-mq})(\mu\text{-OAc})]_2$ (8-mq = orthometalated 8-methylquinoline) in refluxing THF (see Experimental Section, Procedure B), in a manner similar to the synthesis of **7**.[20a] 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 has occurred, in accordance with the structures of related compounds.[20a]

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 $\delta = 6.34$−6.56 which is consistent with an aminic proton. A fluxional behavior 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 ($^2J_{AB} \simeq 12$ Hz). The $\Delta G^{\neq}$ values calculated for this dynamic behavior are 54.7 ± 0.5, 58.8 ± 0.5, and 50.6 ± 0.5 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 the orthometalated *N*,*N*-dimethylbenzylamine (dmba) group in **11**, or the chloride atom in **13**, which hinder the free rotation of the neopentyl group around the N−C bond at low temperature. Furthermore, a through-space interaction between a Pd−N−CH_2 proton and the olefinic N=C−C−H proton was detected by NOE in these complexes and further shown by a H−H ROESY experiment at −20 °C in the case of **10**. In the case of **13**, a $^1H\{^{31}P\}$ NMR spectrum at 213 K allowed analysis of the Pd−N−CH_2 signal as an ABX system (X = P) with $^4J_{PH}$ coupling constants of 8.8 and 3.2 Hz.

Scheme 4. Reaction of **9** with Chloride-Bridged Pd(II) Homodimetallic Complexes and with $[AuCl(PPh_3)]$



Compounds **10** and **13** were isolated as red crystalline solids from solutions of CH_2Cl_2/*n*-hexane and analyzed by X-ray diffraction. Their structures are shown in Figures 1 and 2, respectively. Crystallographic data, and selected bond lengths and angles are reported in Tables 1−3. The coordination geometry around the palladium center in **10** is square-

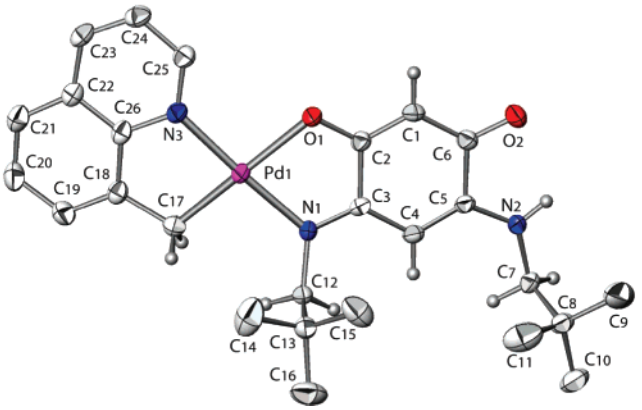


Figure 1. ORTEP view of **10**. The unit cell is constituted by two independent but very similar molecules. The aromatic and CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

---

(21) Preliminary X-ray diffraction data on **9** indicated a polymeric structure, however the poor quality of the crystals precluded refinement of the structure.

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	$C_{26}H_{33}N_3O_2Pd$	$C_{34}H_{40}ClN_2O_2PPd$	$C_{36}H_{40}N_4O_2Pd_2$·$2(C_4H_8O)$
formula weight (g·mol^{-1})	525.95	681.50	917.73
crystal system	monoclinic	orthorombic	monoclinic
space group	$P2_1/c$	$P2_1\,2_12_1$	$C2/c$
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 [deg]	95.710(5)	90	107.84(5)
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(Mo Kα) [mm^{-1}]	0.775	0.732	0.929
F(000)	2176	1408	1888
temperature (K)	173	173	173
θ min−max [deg]	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., unique data, R(int)	27159, 14221, 0.050	23770, 7078, 0.075	5936, 5936, 0.000
observed data [$I > 2\sigma(I)$]	9508	5419	4274
No. reflns, No. params	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**,[20] 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 (deg) 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)

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.[22] 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 is evidenced by a distance of 2.020 Å.

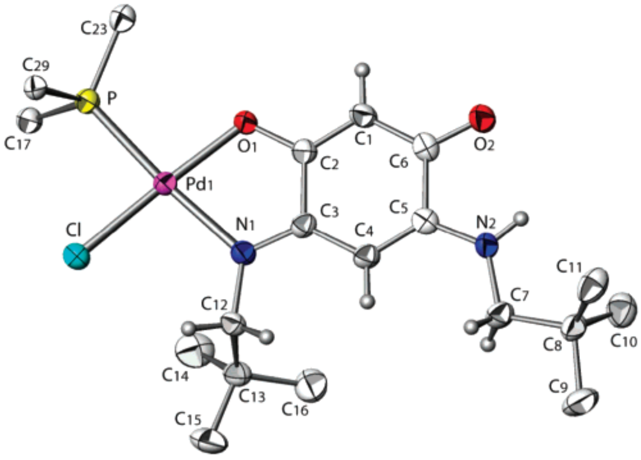


Figure 2. ORTEP view of **13**. The phenyl groups on the phosphorus atom, except the ipso carbons, and the CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

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.[18,23] Like that 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 and 2.140 Å, respectively.

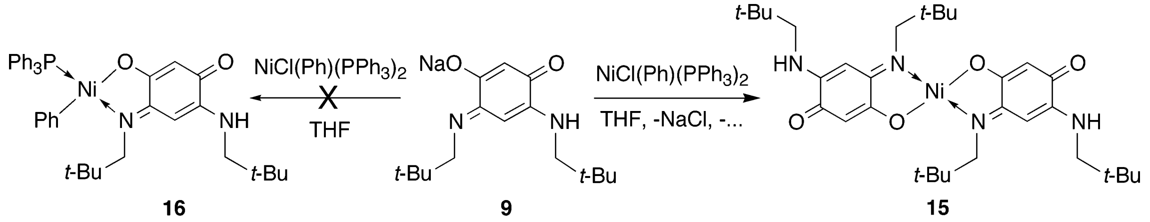
In both complexes **10** and **13**, examination of the respective bond distances within the O(1)−C(2)−C(1)−C(6)−O(2)

---

(22) (a) Andrieu, J.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1996**, *35*, 5975−5985. (b) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410−421. (c) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115−5125.

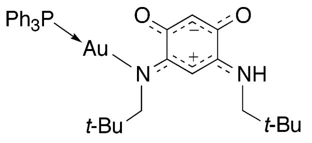
(23) (a) Koch, D.; Polborn, K.; Sünkel, K.; Beck, W. *Inorg. Chim. Acta* **2002**, *334*, 365−370. (b) Gomez-Simon, M.; Jansat, S.; Muller, G.; Panyella, D.; Font-Bardia, M.; Solans, X. *Dalton Trans.* **1997**, 3755−3764.

Scheme 5. Reaction of **9** with *trans*-[NiCl(Ph)(PPh$_3$)$_2$]

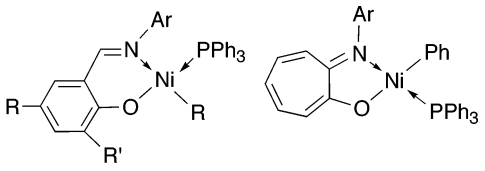


and N(1)−C(3)−C(4)−C(5)−N(2) moieties reveals an alternation of single and double bonds,[24] which is consistent with two conjugated but localized π-systems (Table 2). This result is in agreement with the localization of the π-system found in **7**, whereas **6** presents a perfect bonds equalization.[20] As in all previously described related crystallographic structures,[20] 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 subunits. From these observations, we can draw a more general conclusion: when reactions with **6** result in monodeprotonation, leading to monometallic complexes, the π-system becomes more localized.

Compound **14** is the first example of a monometallic gold complex obtained from **6**. In comparison with Pd(II) complexes, the aminic N−H signal is downfield shifted to $\delta = 7.06$. We can suspect a tricoordination of the Au(I) center, as drawn in Scheme 4, rather than binding solely through the oxygen atom, owing to the presence of the C═N vibration at 1580 cm^{-1} in the IR spectrum in CH$_2$Cl$_2$ 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 $H^+ \leftarrow\!\circ\!\rightarrow (Ph_3P)Au^+$, 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 Monometallic Ni(II) Complex. By analogy with recent single-component olefin polymerization and oligomerization catalysts containing a monoanionic N,O ligand,[1,2,3b,6,7,9,10,12,14,19] we have attempted the reaction of **9** with *trans*-[NiCl(Ph)(PPh$_3$)$_2$].

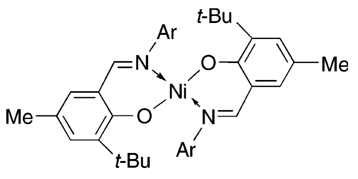


Typical mono-N,O type catalysts

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)$_2$].[20a]

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.[1,7a,25,26]

Despite numerous reports on the synthesis and structural properties of *bis*-N,O type complexes, relatively few studies have been performed on their catalytic behavior; an example is shown below.[8,11] Such Ni(II) complexes can be activated with a Lewis acid cocatalyst, which displaces one of the N,O chelates and generates the active species.[8,11]



A bis-N,O type catalyst

As part of our interest for new ethylene oligomerization Ni(II) catalysts,[14,27] we have evaluated complex **15** for this reaction with the aim of producing short chain oligomers in the presence of only small quantities of alkylaluminum 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

---

[24] van Bolhuis, F.; Kiers, C. Th. *Acta Crystallogr., Sect. B: Struct. Sci.* **1978**, *34*, 1015−1016.

[25] Klein, H.-F.; Bickelhaupt, A. *Inorg. Chim. Acta* **1996**, *248*, 111−114.

[26] Klabunde, U.; Ittel, S. D. *J. Mol. Catal. A: Chem.* **1987**, *41*, 123−134.

[27] (a) Speiser, F.; Braunstein, P.; Saussine, L. *Dalton Trans.* **2004**, *10*, 1539−1545. (b) Speiser, F.; Braunstein, P.; Saussine, L. *Organometallics* **2004**, *23*, 2633−2640. (c) Speiser, F.; Braunstein, P.; Saussine, L. *Organometallics* **2004**, *23*, 2625−2632. (d) Speiser, F.; Braunstein, P.; Saussine, L.; Welter, R. *Organometallics* **2004**, *23*, 2613−2624. (e) Speiser, F.; Braunstein, P.; Saussine, L.; Welter, R. *Inorg. Chem.* **2004**, *43*, 1649−1658. (f) Pietsch, J.; Braunstein, P.; Chauvin, Y. *New J. Chem.* **1998**, 467−472. (g) Braunstein, P.; Pietsch, J.; Chauvin, Y.; Mercier, S.; Saussine, L.; DeCian, A.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1996**, 3571−3574. (h) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L.; DeCian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2203−2204.

Table 4. Oligomerization of Ethylene with **15** and $AlEtCl_2$ as Cocatalyst and Comparison with $[NiCl_2(PCy_3)_2]$[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)	13 500	21 500	13 000
TOF (mol C_2H_4/mol Ni·h)	28 500	45 000	27 000
α-olefin (C_4) (mol %)	14	7	9
linear C_6 (mass %)	51	45	
k_α[b]	0.6	0.57	0.13

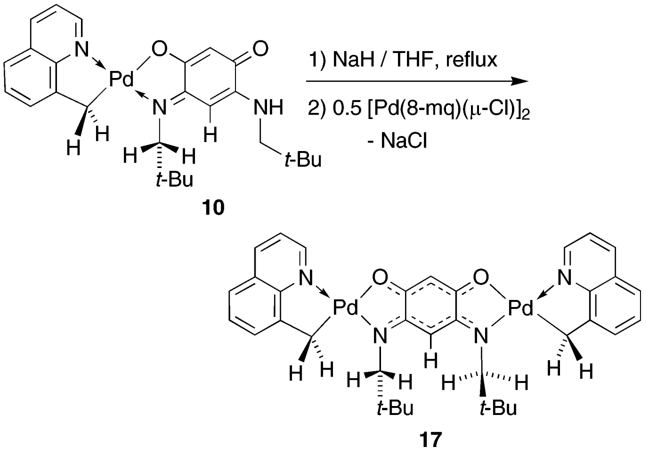
[a] Conditions: 10 bar C_2H_4, 35 min, $T = 30$ °C, 4×10^{-2} mmol Ni complex, solvent 15 mL of toluene. [b] k_α = mol C_6/ mol C_4.

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.[28] All selectivities reported in the following refer to the total amount of products formed in each catalytic test. In all cases, ethylene pressurization resulted in a rapid exothermic event, indicative of very short induction periods.

Compound **15** was completely inactive when less than 6 equiv of $AlEtCl_2$ was added. However, turnover frequencies of 28 500 and 45 000 mol C_2H_4/mol Ni·h were obtained in the presence of 6 or 10 equiv of cocatalyst, respectively, compared to 27 000 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 includes 1,5-butadiene, hex-1-ene, hex-2-ene, and 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.

Di- and Trimetallic 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.[29,30] The presence of a free amino N−H function in all the monometallic complexes suggests that it should be possible, by convergent or divergent strategy, to obtain homo- and heteropolymetallic complexes likely to display electronic interaction between the two metal centers through the benzoquinonemonoimine bridge.

Scheme 6. In Situ Deprotonation of **10** and Reaction with $[Pd(8\text{-mq})(\mu\text{-Cl})]_2$



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[9b] or anilinoanthraquinone ligands.[18] Therefore, we favored an in situ method for the preparation of polymetallic complexes. Deprotonation of **10** with excess NaH in refluxing THF was directly followed by addition of solid $[Pd(8\text{-mq})(\mu\text{-Cl})]_2$ (Scheme 6).

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 dimetallic complex **17** was obtained as a green powder in good yield after recrystallization. Examination of its ^1H and $^{13}C\{^1H\}$ 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*⋯C carbon atoms. The signals at 165.62 and 188.52 in the $^{13}C\{^1H\}$ NMR spectrum, (*δ*(C⋯N) and *δ*(C⋯O), respectively), are consistent with a delocalized *π*-system, as in **6**. Surprisingly, the olefinic N⋯C⋯C−H proton appears in the ^1H NMR spectrum as a broad singlet, and the corresponding H−*C*⋯C resonance in the $^{13}C\{^1H\}$ 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 behavior owing to hindered rotation of the neopentyl group around the N−C bond. The $\Delta G^{\neq}$ value calculated for this dynamic behavior is 54.3 ± 0.5 kJ/mol, which is nearly the same as that in **10** which presents a similar steric crowding. A through-space interaction between a Pd−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.

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, and selected bond lengths

---

(28) Commereuc, D.; Chauvin, Y.; Léger, G.; Gaillard, J. *Rev. Inst. Fr. Pét.* **1982**, *37*, 639−649.

(29) Gavrilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, *104*, 349−383.

(30) Kahn, O. *Adv. Inorg. Chem.* **1995**, *43*, 179−259.

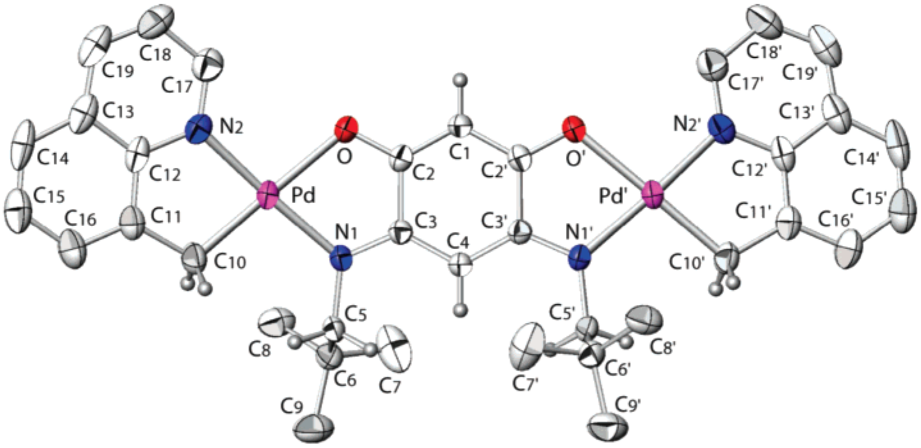
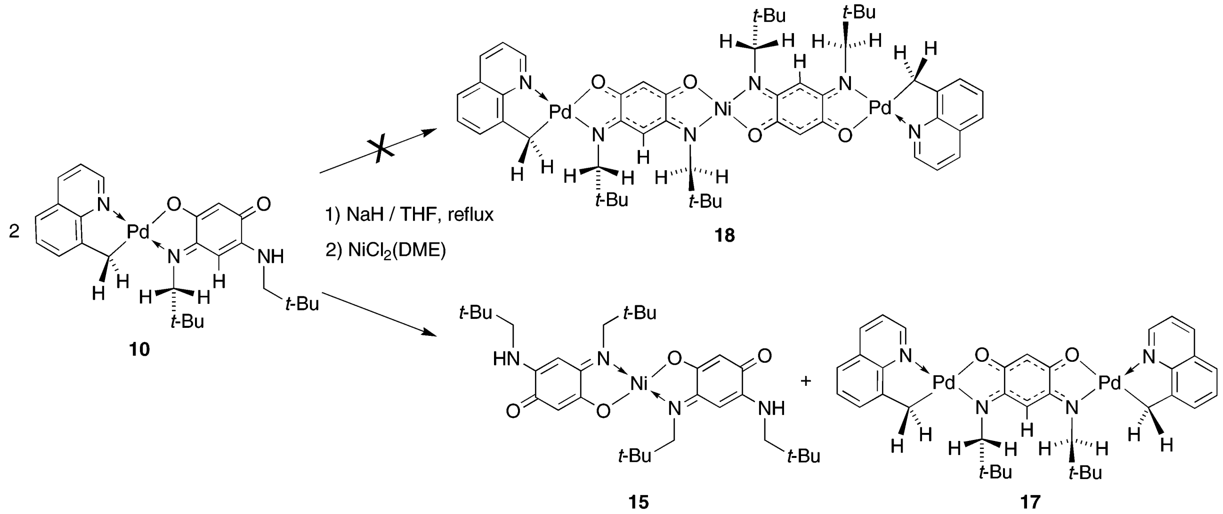


Figure 3. ORTEP view of **17** in **17**·2THF. The aromatic and CH_3 protons have been omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.

Scheme 7. In Situ Deprotonation of **10** and Reaction with $[NiCl_2(DME)]$



and angles are reported in Tables 1−3. This complex appears to be the first crystallographically characterized dimetallic 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 led to a homodimetallic complex, **17**, in which the π-system of the quinonoid ligand becomes delocalized between the two Pd centers.

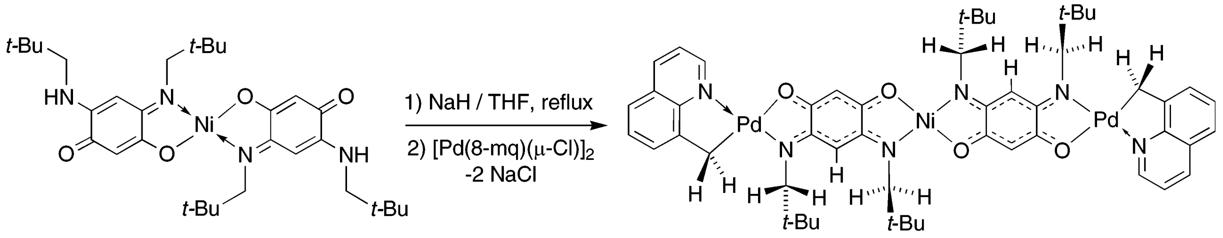
Following the successful synthesis of **17**, based on a convergent strategy from a monometallic complex, we have attempted to synthesize a trimetallic complex by in situ deprotonation of **10** with excess NaH in refluxing THF followed by reaction with 0.5 equiv of $[NiCl_2(DME)]$ (Scheme 7).

Surprisingly, this reaction did not lead to the heterotrimetallic compound **18**, but rather to the homodimetallic 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 heterotrimetallic $NiPd_2$ complex **18** (Scheme 8). To prepare the related homotrimetallic Pd_3 complex, we have used **8** instead of **15** under similar conditions, but only the zwitterion **6** and Pd(0) were obtained after workup, 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 gaseous 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**.

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 monometallic Pd complex **10** after loss of the nickel and reprotonation.

Scheme 8. In Situ Deprotonation and Reaction of **15** with [Pd(8-mq)(μ-Cl)]$_2$



15

18

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$\cdots$C$\cdots$C−H and the two O$\cdots$C$\cdots$C−H protons give rise to only one signal. The four signals at δ 162.64 and 165.14 (δ(C$\cdots$N)) and 187.28 and 187.85 (δ(C$\cdots$O)) in the ^{13}C NMR spectrum are consistent with a delocalized π-system. Furthermore, as in **17**, the N$\cdots$C−C−H proton appears also as a broad singlet in the ^{1}H NMR spectrum, and the corresponding H−*C*$\cdots$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 heterotrimetallic 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 monometallic, homodimetallic, and heterotrimetallic 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 homodimetallic Pd(II) complexes, [AuCl(PPh$_3$)] or *trans*-[NiCl(Ph)(PPh$_3$)$_2$] to afford the monometallic complexes **10**−**15** in which the π-system is more localized. A second in situ deprotonation of the free N−H amino function of the metalloligand **10** followed by metallation affords, following a convergent strategy, the homodimetallic 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 heterotrimetallic 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 heterodimetallic 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, 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 N$_2$ prior to use. *N,N′*-dineopentyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium [C$_6$H$_2$-($\cdots$NHCH$_2$*t*-Bu)$_2$($\cdots$O)$_2$] **6**,[20] and the metal complexes [Pd(8-mq)-(μ-Cl)]$_2$,[31] [Pd(8-mq)(μ-OAc)]$_2$,[32] [Pd(dmba)(μ-Cl)]$_2$,[33] [Pd(η^3-methallyl)(μ-Cl)]$_2$,[34] [PdCl(PPh$_3$)(μ-Cl)]$_2$,[35] [AuCl(PPh$_3$)],[36] and *trans*-[NiCl(Ph)(PPh$_3$)$_2$][37] were prepared according to the literature. Characterization of **15** and the synthesis of **8** have been reported in a previous paper.[20a] All reactions of air- or water-sensitive compounds were performed using standard Schlenk techniques under a dry Ar 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 *N,N′*-dineopentyl-2-amino-5-sodium alcoholate-1,4-benzoquinonemonoimine [C$_6$H$_2$(NHCH$_2$*t*-Bu)(=NCH$_2$*t*-Bu)-(=O)(ONa)] 9. The zwitterion **6** (0.80 g, 2.88 mmol) was dissolved in 50 mL of anhydrous THF, 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{^{1}H} NMR (100 MHz, DMSO-[d_6], 298 K) δ: 28.36 (C*Me$_3$*), 28.77 (C*Me$_3$*), 32.64 (*C*Me$_3$), 33.24 (*C*Me$_3$), 53.36 (CH$_2$N), 62.60 (CH$_2$N), 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

---

(31) Hartwell, G. E.; Laurence, R. V.; Smas, M. J. *J. Chem. Soc. D: Chem. Commun.* **1970**, 912.
(32) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117−131.
(33) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909−913.
(34) Tatsuno, Y.; Yoshida, T.; Osuka, S. *Inorg. Synth.* **1979**, *29*, 220−223.
(35) Kläui, W.; Glaum, M.; Hahn, E.; Lügger, T. *Eur. J. Inorg. Chem.* **2000**, 21−28.
(36) Braunstein, P.; Lehner, H.; Matt, D. *Inorg. Synth.* **1990**, *27*, 218−221.
(37) Zeller, A.; Herdtweck, E.; Strassner, T. *Eur. J. Inorg. Chem.* **2003**, 1802−1806.

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 CH_2Cl_2-hexane mixture (0.13 g, 75% yield). Red crystals suitable for an X-ray analysis were isolated from a CH_2Cl_2/*n*-hexane solution.

Procedure B. To a solution of $[Pd(8\text{-mq})(\mu\text{-OAc})]_2$ (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 CH_2Cl_2/hexane mixture (0.50 g, 82% yield). ^{1}H 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−C*H$_2$*), 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). ^{1}H 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−C*H$_2$*), 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 (C*Me$_3$*), 29.47 (C*Me$_3$*), 32.27 (*C*Me$_3$), 36.20 (*C*Me$_3$), 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 $C_{26}H_{33}N_3O_2$-Pd: 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 homodimetallic 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 CH_2Cl_2/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 CH_2Cl_2 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 CH_2Cl_2/*n*-hexane solution.

11. (0.11 g, 65% yield). ^{1}H 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−C*H$_2$*), 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). ^{1}H 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−C*H$_2$*), 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-NMe2}), 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. Despite numerous attempts of purification, no better analyses were obtained. 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). ^{1}H 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−C*H$_2$*), 3.35 (d, $^2J_{HH}$ = 2.7 Hz, 1 H, CH allyl), 3.68 and 3.71 (d, AB system, $^2J_{AB}$ = 8.6 Hz, 2 H, N−CH_2), 3.82 (d, $^2J_{HH}$ = 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). $^{13}C\{^1H\}$ 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_2N), 57.12, 57.31 (CH_2 allyl), 66.36 (CH_2N), 84.39 (H−*C*═C−N), 102.56 (H−*C*═C−O), 128.97 (allyl C$\cdots$*C*$\cdots$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_2Cl_2): λ_{max} (log ϵ) = 365 nm (4.36), 506 (br) nm (2.88).

13·CH_2Cl_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, $^3J_{HH}$ = 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*), $^2J_{AB}$ = 13.5 Hz, $^3J_{AX}$ = 6.2 Hz, $^3J_{BX}$ = 6 Hz, 2 H, NH−C*H$_2$*), 3.21 (dd, $^2J_{HH}$ = 11.5 Hz, $^4J_{PH}$ = 8.8 Hz, 1 H, N−CH*H*), 3.96 (dd, $^2J_{HH}$ = 11.5 Hz, $^4J_{PH}$ = 3.2 Hz, 1 H, N−CH*H*), 5.25 (s, 1 H, N═C−C−H), 5.26 (s, CH_2Cl_2**)**, 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). $^{31}P\{^1H\}$ NMR (125 MHz, $CDCl_3$, 268 K) δ: 25.5. $^{13}C\{^1H\}$ 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_2N), 58.15 (CH_2N), 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_2Cl_2): λ_{max} (log ϵ) = 280 nm (4.13), 379 (br) nm (4.43), 479 (br) nm (3.11).

Synthesis of 14·CH_2Cl_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 the mixture was filtered through Celite to retain metallic gold, the solvent was evaporated and **14·**CH_2Cl_2 was obtained as a red-orange powder by recrystallization from a CH_2Cl_2−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, $^3J_{HH}$ = 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). $^{31}P\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K) δ: 31.5. $^{13}C\{^1H\}$ 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 the mixture was filtered through Celite, the solvent was evaporated and **15** was obtained quantitatively as a green powder after recrystallization from a CH$_2$Cl$_2$−hexane mixture. **15** was characterized by comparison of its ^{1}H NMR data with those of an authentic sample.[20a]

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 N$_2$ at room temperature. The solution was stirred at room temperature for 3 h. After the mixture was filtered 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$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$H), 5.64 (s, 1 H, O$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$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, $^2J_{AB}$ = 12.3 Hz, 2 H, N−CH*H*), 3.27 (d, B part of an AB system, $^2J_{AB}$ = 14.5 Hz, 2 H, Pd−CH*H*), 3.36 (d, A part of an AB system, $^2J_{AB}$ = 14.5 Hz, 2 H, Pd−CH*H*), 3.42 (d, A part of an AB system, $^2J_{AB}$ = 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$_2$N), 88.79 (H-*C*$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$N), 102.69 (H−*C*$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$O), 121.41, 123.13, 128.16, 128.78, 128.90, 137.08, 149.16, 149.32, 153.00 (aryl), 165.62 (C$\overset{\cdot\cdot}{-}$N), 188.52 (C$\overset{\cdot\cdot}{-}$O). Anal. Calcd for C$_{36}$H$_{40}$N$_4$O$_2$Pd$_2$: C, 55.90; H, 5.21; N, 7.24. Found: C, 55.63; H, 5.32; N, 7.02. UV−vis (CH$_2$Cl$_2$): 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 overnight and solid [Pd(8-mq)(μ-Cl)]$_2$ (0.09 g, 0.15 mmol) was added under N$_2$ at room temperature. The solution was stirred at room temperature for 1 day. After the solution was filtered through Celite and the Celite was washed with 100 mL of THF, the solvent was evaporated under reduced pressure, and **18** was obtained as black-violet powder after recrystallization from a CH$_2$Cl$_2$/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$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$H), 5.34 (s, 2 H, O$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$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$_2$N), 61.47 (CH$_2$N), 89.79 (H−*C*$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$N), 101.66 (H−*C*$\overset{\cdot\cdot}{-}$C$\overset{\cdot\cdot}{-}$O), 121.44, 123.25, 128.32, 128.82, 128.94, 137.26, 137.59, 149.04, 149.57 (aryl), 162.64 (C$\overset{\cdot\cdot}{-}$N), 165.14 (C$\overset{\cdot\cdot}{-}$N), 187.28 (C$\overset{\cdot\cdot}{-}$O), 187.85 (C$\overset{\cdot\cdot}{-}$O). Anal. Calcd for C$_{52}$H$_{64}$N$_6$O$_4$Pd$_2$Ni: 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$_2$Cl$_2$): 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.[27] The interior of the autoclave was protected from corrosion by a protective ceramic 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 pressurized 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. In all of the catalytic experiments, 4×10^{-2} mmol of Ni complex was 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.[27] 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 was 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 Mo Kα 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,[38] 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.

Acknowledgment. We are grateful to the CNRS and the European Commission (Network Palladium HPRN-CT-2002-00196 and COST D17) 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: ORTEP views for **10**, **13**, and **17** in **17**·2THF (PDF); X-ray data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for all structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC 237963-237965. 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; http://www.ccdc.cam.ac.uk).

IC049263A

---

(38) (a) Kappa CCD Operation Manual; Nonius B. V., Delft, The Netherlands, 1997. (b) Sheldrick, G. M. SHELXL97, Program for the refinement of crystal structures; University of Göttingen, Germany, 1997.