Inorg. Chem. **2009**, *48*, 1624−1637

Inorganic Chemistry
Article

Bis(diphenylphosphino)methane-Phosphonate Ligands and Their Pd(II), Ni(II) and Cu(I) Complexes. Catalytic Oligomerization of Ethylene

Adel Hamada and Pierre Braunstein*

Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

Received October 24, 2008

The bis(diphenylphosphino)methane-phosphonate-based (dppm-phosphonate) ligands $(Ph_2P)_2CHP(O)(OR)_2$ (R = Me, **L**^{1}; R = Ph, **L**^{2}) form metal complexes by selective coordination of the diphosphine moiety to Pd(II) and Ni(II) centers. The formation of complexes containing the chelating, deprotonated form of ligand **L**^{1} or **L**^{2} occurred when basic ligands were present in the precursor complex, such as Me or dmba (on Pd(II)) or acac (on Ni(II)). The Cu(I) complex [Cu**L**^{1}]$_2$(BF$_4$)$_2$ (**9**) was obtained that is suggested to be dinuclear, each Cu(I) being chelated by a phosphine and a P═O donor and further bound to the phosphine group of another ligand. The crystal structures of the mononuclear complexes $[PdCl_2\{(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}] (**2a**), $[PdCl_2\{(Ph_2P)_2CHP(O)(OPh)_2$-*P,P*}] (**2b**), $[Pd\{(Ph_2P)_2CP(O)(OMe)_2$-*P,P*$\}_2]$ (**6a**) in **6a**·2CH$_2$Cl$_2$, $[Pd\{(Ph_2P)_2CP(O)(OPh)_2$-*P,P*$\}_2]$ (**6b**), $[Ni\{(Ph_2P)_2CP(O)(OMe)_2$-*P,P*$\}_2]$ (**10a**) in **10a**·4CHCl$_3$, $[Ni\{(Ph_2P)_2CP(O)(OPh)_2$-*P,P*$\}_2]$ (**10b**) in **10b**·4CHCl$_3$, $[NiCl_2\{(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}] (**11a**) in **11a**·CHCl$_3$ and of the dinuclear complexes $[Pd(\mu$-Cl)$\{(Ph_2P)_2CP(O)(OMe)_2$-*P,P*$\}]_2$ (**7a**) and $[Pd(\mu$-Cl)$\{(Ph_2P)_2CP(O)(OPh)_2$-*P,P*$\}]_2$ (**7b**) have been determined by X-ray diffraction. The complexes $[Ni\{(Ph_2P)_2CC(O)NPh_2$-*P,P*$\}_2]$ (**13**) and $[Ni\{Ph_2PC(Ph)P(O)(OEt)_2$-*P,O*$\}_2]$ (**15**) were prepared by reaction of [Ni(acac)$_2$] with the known, neutral ligands $(Ph_2P)_2CHC(O)NPh_2$ and $Ph_2PCH(Ph)P(O)(OEt)_2$, respectively. The Ni(II) complexes were evaluated for the catalytic oligomerization of ethylene and afforded similar results when AlEtCl$_2$ was used as cocatalyst. Complexes **11a**,**b** were the most active, with a turnover frequency (TOF) of 78 300 mol of C_2H_4/(mol of Ni)h) for complex **11b** in the presence of 10 equiv of AlEtCl$_2$ and showed a high selectivity for C_4 and C_6 olefins with up to 93% C_4 for **10a** in the presence of 6 equiv AlEtCl$_2$, whereas when only 3 equiv cocatalyst was used with **10a**, 64% trimers were observed. In the presence of methylalumoxane (MAO) as cocatalyst, precatalysts **10a**,**b**, **11a**,**b**, and **15** gave moderate TOFs, up to 11 660 mol of C_2H_4/(mol of Ni)h) for complex **11a** with 400 equiv of MAO. Mostly ethylene dimers were formed but up to 39% trimers were observed with **10a** in the presence of 400 equiv MAO.

Introduction

Despite the continuing interest in the design of new functional ligands, phosphine ligands containing a phosphoryl function, that is, phosphonate, phosphinate, or phosphate, have received relatively little attention, although it is established that their P═O group can coordinate to a metal center via its oxygen atom.[1−11] As part of our interest in the synthesis, coordination properties and reactivity of multifunctional phosphine ligands containing hard and soft donor functions, in particular of the P,O and P,N type,[12−14] we describe here complexes with new dppm-phosphonate ligands, which can behave as P,P and/or P,O chelates and may find widespread applications in coordination chemis-

---

* To whom correspondence should be addressed. E-mail: braunstein@chimie.u-strasbg.fr. Fax: (+33) (0)3 90 24 13 22.

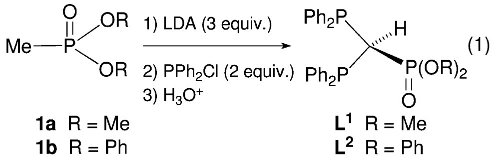
(1) Gahagan, M.; Mackie, R. K.; Cole-Hamilton, D. J.; Cupertino, D. C.; Harman, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2195.
(2) Weis, K.; Rombach, M.; Vahrenkamp, H. *Inorg. Chem.* **1998**, *37*, 2470.
(3) Morise, X.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2003**, *42*, 7752.
(4) Morise, X.; Braunstein, P.; Welter, R. C. R. *Chimie* **2003**, *6*, 91.
(5) Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629.
(6) Oberbeckmann-Winter, N.; Morise, X.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2005**, *44*, 1391.
(7) Sgarbossa, P.; Pizzo, E.; Scarso, A.; Mazzega Sbovata, S.; Michelin, R. A.; Mozzon, M.; Strukul, G.; Benetollo, F. *J. Organomet. Chem.* **2006**, *691*, 3659.
(8) (a) Heinicke, J.; Musina, E.; Peulecke, N.; Karasik, A. A.; Kindermann, M. K.; Dobrynin, A. B.; Litvinov, I. A. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1995. (b) Reisinger, C. M.; Nowack, R. J.; Volkmer, D.; Rieger, B. *Dalton. Trans.* **2007**, 272.
(9) Cadierno, V.; Díez, J.; García-Alvarez, J.; Gimeno, J.; Rubio-García, J. *Dalton Trans.* **2008**, 5737.

10.1021/ic8020436 CCC: $40.75

try.[4,6,15] We focus here mostly on Pd(II) and Ni(II) complexes and the catalytic properties of the latter in ethylene oligomerization.

Results and Discussion

Synthesis and Characterization of the Ligands. The new dppm-phosphonate ligands $(Ph_2P)_2CHP(O)(OR)_2$ (R = Me, **L**^{1}; R = Ph, **L**^{2}) were prepared by deprotonation of the corresponding phosphonates $MeP(O)(OR)_2$ (R = Me, **1a**; R = Ph, **1b**), followed by reaction with PPh_2Cl (eq 1). Ligands **L**^{1,2} are white solids and were characterized by IR, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopic methods.



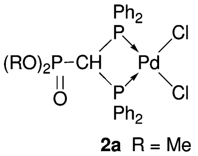
(1)

1a R = Me
1b R = Ph

L^1 R = Me
L^2 R = Ph

The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **L**^{1} consists of a doublet for the PPh_2 groups at δ −11.1 ppm and a triplet for the phosphonate group at δ 28.1 ppm. A similar pattern is observed for **L**^{2} at δ −9.3 and δ 19.1 ppm, respectively.

Synthesis and Reactivity of Pd(II) Complexes. Mononuclear Complexes. The reaction of **L**^{1} and **L**^{2} with $[PdCl_2(COD)]$ or $[PdCl_2(NCPh)_2]$ afforded the mononuclear, square-planar complexes **2a** and **2b**. Their $^{31}P\{^1H\}$ NMR spectrum contains a doublet at δ −43.9 (^2J(P,P) = 18 Hz) and δ −42.0 (^2J(P,P) = 19 Hz) ppm, respectively, which is assigned to the equivalent phosphine donors of a *P*,*P* chelating ligand. Such a shielding is typical for a four-membered ring structure.[16] The P=O resonance of **2a**,**b** appears as a triplet at δ 17.1 (^2J(P,P) = 18 Hz) and δ 7.1 (^2J(P,P) = 19 Hz) ppm, respectively, and their IR spectrum (KBr) contains a strong ν(P=O) absorption at 1262 and 1275 s cm^{-1}, respectively.



2a R = Me
2b R = Ph

Slow diffusion of hexane into a chloroform solution of **2a** and of petroleum ether into a dichlomethane solution of **2b** led to the formation of yellow crystals suitable for X-ray diffraction. Selected bond distances and angles are given in Table 1 and a view of their molecular structure is shown in Figures 1 and 2, respectively. The coordination geometry around the Pd center in **2a** and **2b** is square planar, with the ligands **L**^{1} and **L**^{2} acting as *P*,*P* chelates. The P(1)−C(25) and P(2)−C(25) distances in **2a** and **2b** are longer than those in $[PdCl_2(dppm\text{-}P,P)]$ (dppm = $Ph_2PCH_2PPh_2$).[17]

Table 1. Selected Structural Data in $[PdCl_2\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}]$ (**2a**) and $[PdCl_2\{(Ph_2P)_2CHP(O)(OPh)_2\text{-}P,P\}]$ (**2b**)

bond lengths (Å)	**2a**	**2b**
Pd−Cl(1)	2.353(7)	2.346(9)
Pd−Cl(2)	2.367(5)	2.360(1)
Pd−P(1)	2.233(1)	2.229(8)
Pd−P(2)	2.230(8)	2.236(2)
P(1)−C(25)	1.870(3)	1.869(5)
P(2)−C(25)	1.862(2)	1.859(5)
P(3)−C(25)	1.806(3)	1.793(5)
bond angles (deg)	**2a**	**2b**
Cl(1)−Pd−Cl(2)	92.89(3)	93.47(6)
P(1)−Pd−Cl(2)	170.28(3)	171.69(6)
P(2)−Pd−Cl(2)	96.19(3)	96.81(6)
P(1)−Pd−Cl(1)	96.38(3)	94.52(5)
P(2)−Pd−Cl(1)	170.19(3)	169.29(5)
P(1)−Pd−P(2)	74.76(3)	75.09(5)
Pd−P(2)−C(25)	96.16(9)	95.4(2)
Pd−P(1)−C(25)	95.9(1)	95.5(2)
P(1)−C(25)−P(2)	93.2(2)	93.8(2)

Although dppm is a well-known chelating ligand for Pd(II), which can be easily opened upon reaction for example, with nucleophilic metal reagents to form dimetallic

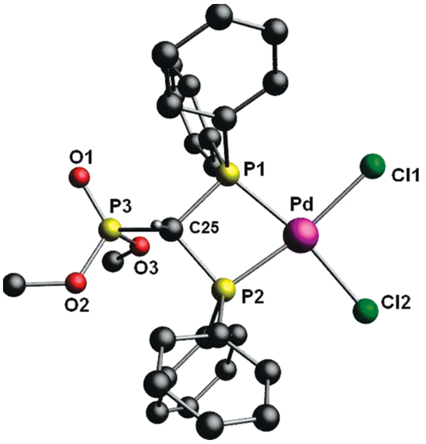


Figure 1. Diamond 3.1 view of the structure of $[PdCl_2\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}]$ (**2a**).

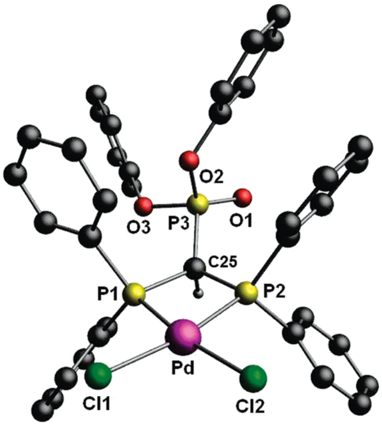


Figure 2. Diamond 3.1 view of the structure of $[PdCl_2\{(Ph_2P)_2CHP(O)(OPh)_2\text{-}P,P\}]$ (**2b**).

---

(10) Chandrasekhar, V.; Azhakar, R.; Senapati, T.; Thilagar, P.; Ghosh, S.; Verma, S.; Boomishankar, R.; Steiner, A.; Kögerler, P. *Dalton Trans.* **2008**, 1150.
(11) Konar, S.; Clearfield, A. *Inorg. Chem.* **2008**, *47*, 5573.
(12) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.
(13) Braunstein, P. *Chem. Rev.* **2006**, *106*, 134.
(14) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784.
(15) Hamada, A.; Braunstein, P. *Inorg. Chem.* **2008**, *47*, 3934.
(16) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

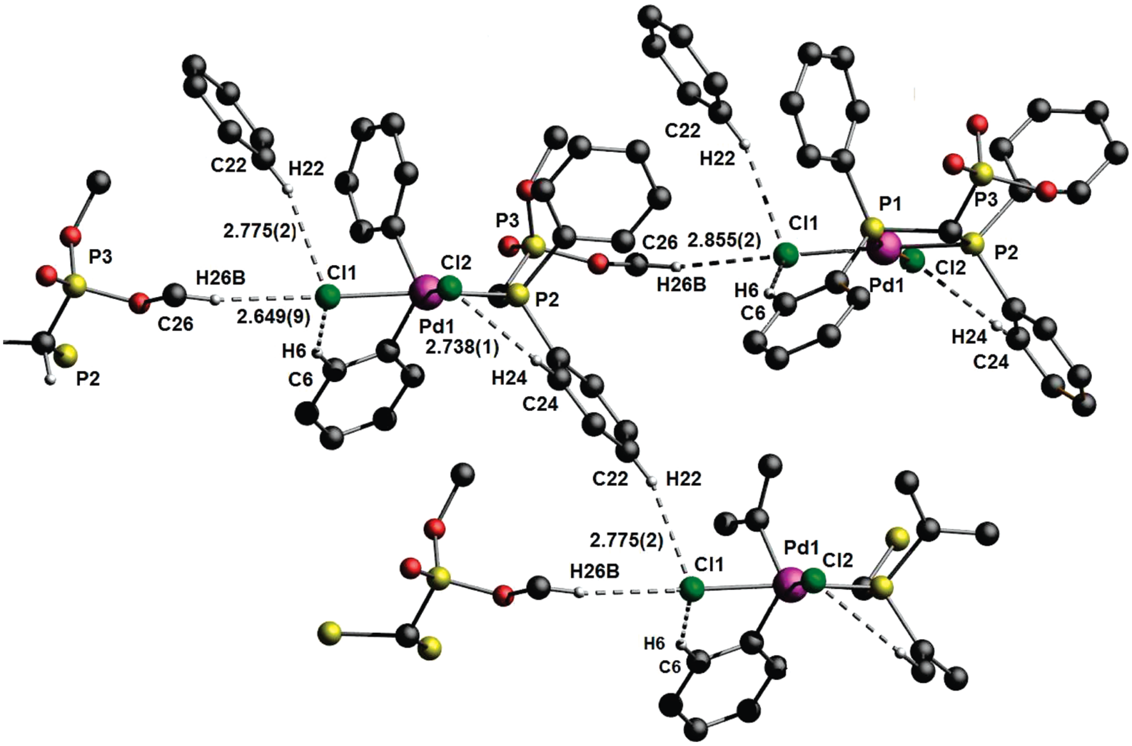
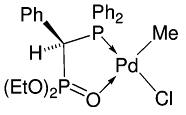


Figure 3. Diamond 3.1 view of the Cl−H inter- and intramolecular interactions in **2a**.

five-membered rings,[18,19] it was also conceivable to envisage for $\mathbf{L}^2$ a *P,O*-chelating behavior in view of the structures of the related complexes [PdCl(Me){$Ph_2PCHPhP(O)(OEt)_2$-*P,O*}] (**3**)[6] or *cis*-[Pd{$Ph_2PCHPhP(O)(OEt)_2$-*P,O*}$_2$]$^{2+}$.[4]



3

No classical intermolecular hydrogen bonding was detected in **2a**, but nonconventional C−H···Cl hydrogen bonds are present (Figure 3). They involve the Cl(1) ligand and a C-*H* atom of a phenyl group [C(22)−H(22)···Cl(1) = 2.776(2) Å)] and a methoxy C-*H* hydrogen atom from a phophonate group [C(26b)-H(26b)···Cl(1) = 2.855(2) Å. Furthermore, an intramolecular interaction exists between the C(24)−H(24) hydrogen of a phenyl group and Cl(2) [C(24)−H(24)···Cl(2) = 2.738(1) Å], and between the C(6)−H(6) phenyl hydrogen and Cl(1) [C(6)−H(6)···Cl(1) = 2.649(2) Å].

Similarly for **2b**, an intermolecular interaction involves the Cl(2) ligand and a phenyl hydrogen [C(35)−H(35)···Cl(2) = 2.843(2) Å] (Figure 4) and intramolecular interactions exist between C(7)−H(7) and Cl(1) [C(7)−H(7)···C(1) 2.748(1) Å] and C(37)−H(37) and Cl(2) [C(37)−H(37)···Cl(2) = 2.828(1) Å)].

In addition, intra- and intermolecular $\pi-\pi$ interactions of 3.820(4) and 3.760(1) Å exist between a phenyl ring of the phosphonate ligand and one of the phosphine phenyl groups, respectively (Figure 5). The dihedral angles between the phenyl ring of the phosphonate group and these phosphine phenyl groups are 8.9(3) and 7.2(3)°, respectively.

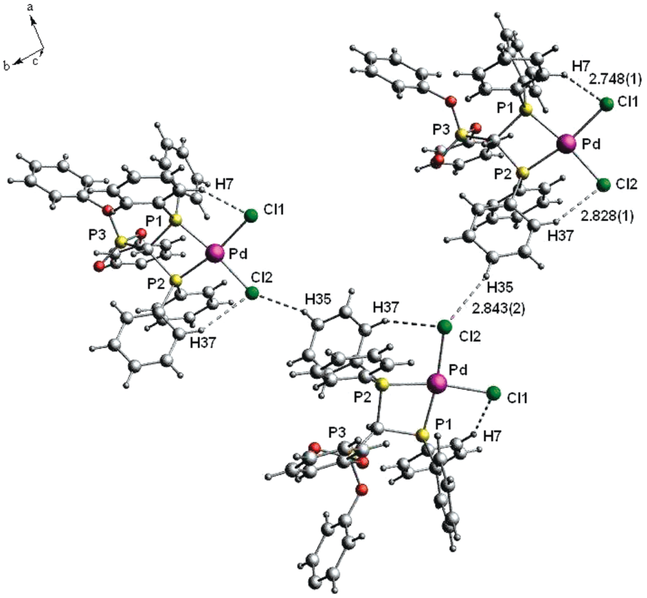


Figure 4. Diamond 3.1 view of the Cl−H inter- and intramolecular interactions in **2b**.

The dicationic complex [Pd(NCMe)$_2${$(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}](BF_4)$_2$ (**4**) was prepared by chloride abstraction from **2a** with $AgBF_4$ or, alternatively, by coordination of $\mathbf{L}^1$ to [Pd(NCMe)$_4$](BF_4)$_2$ (Scheme 1). Its spectroscopic properties (see Experimental Section) confirm that the ligand remains *P*,*P*-chelated to palladium.

When the reaction between $\mathbf{L}^1$ and [Pd(NCMe)$_4$](BF_4)$_2$ was performed in a 2:1 ratio, the symmetrical bischelate complex [Pd{$(Ph_2P)_2CHP(O)(OMe)_2$-*P*,*P*}$_2$](BF_4)$_2$ (**5**) was

---

(17) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

(18) Braunstein, P.; Guarino, N.; de Méric de Bellefon, C.; Richert, J.-L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 88.

(19) Braunstein, P.; Oswald, B.; DeCian, A.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1991**, 2685.

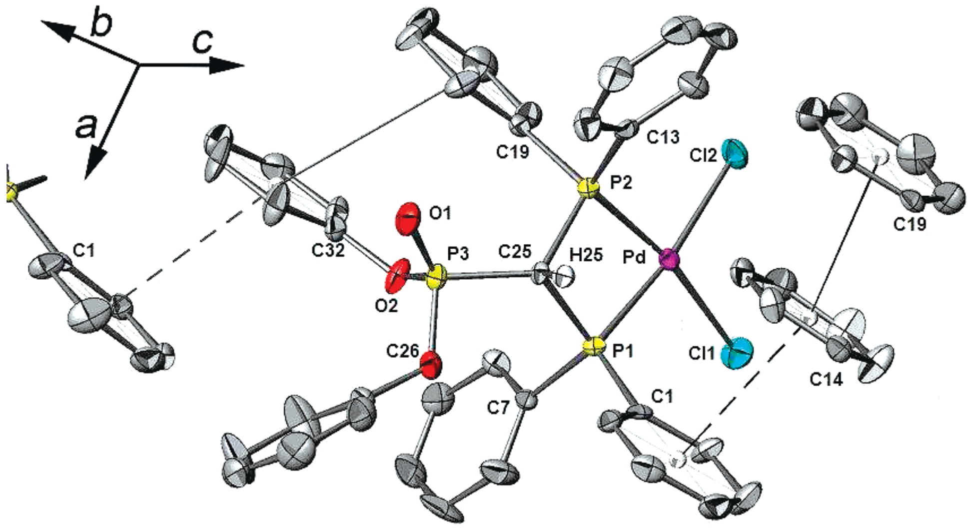
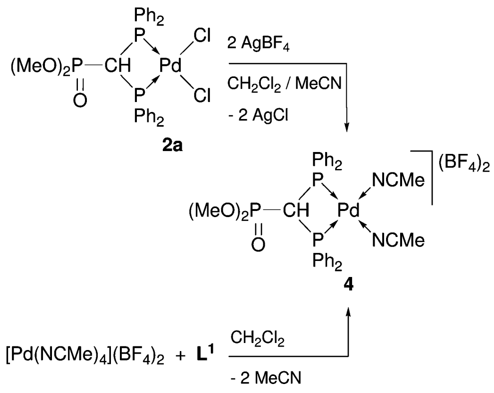
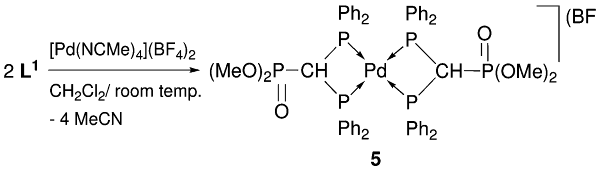


Figure 5. PLATON view of **2b** showing the inter- and intramolecular $\pi-\pi$ interactions. Thermal parameters enclose 50% of the electron density.

Scheme 1

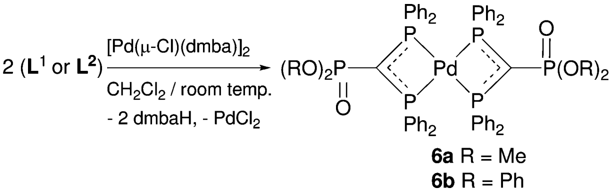


obtained (eq 2). Its $^{31}P\{^1H\}$ NMR spectrum shows a doublet at δ −13.6 (^2J(P,P) = 5.8 Hz) for the PPh_2 groups and a triplet at δ 15.6 (^2J(P,P) = 5.8 Hz) for the P═O resonance. The ν(P═O) vibration occurs at 1224 s cm^{-1} in the IR spectrum (KBr). Although we do not have a firm proof for it, we believe that the orientation of the P═O groups bonded to the tetrahedral PCP carbons is such that the molecule possesses a center of symmetry, as do **6a**,**b** (see below).



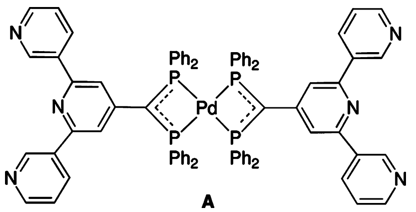
(2)

In contrast, the reaction of $\mathbf{L}^1$ or $\mathbf{L}^2$ with the dinuclear, cyclometalated complex $[Pd(\mu\text{-}Cl)(dmba)]_2$ (dmbaH = $C_6H_5CH_2NMe_2$) yielded the neutral, bischelate complex $[Pd\{(Ph_2P)_2CP(O)(OMe)_2\text{-}P,P\}_2]$ (**6a**) or $[Pd\{(Ph_2P)_2CP(O)(OPh)_2\text{-}P,P\}_2]$ (**6b**), respectively, in low yield in the latter case (eq 3).



(3)

Their formation resulted from phosphine coordination and deprotonation by the chelated dmba ligand, which is eliminated as dmbaH. The $^{31}P\{^1H\}$ NMR spectrum of **6a** and **6b** contains a singlet for the phosphine donors at −31.4 and −31.0 ppm and a singlet for the P═O moiety at 25.6 and 15.1 ppm, respectively, indicating the absence of coupling between these nuclei. A single-crystal X-ray diffraction analysis showed that **6a** and **6b** form discrete, almost centrosymmetrical molecules in which the Pd atom is chelated by two diphosphine moieties whereas the phosphonate groups remain uncoordinated (Table 2, Figures 6 and 7). The planar geometry around the sp^2-hybridized PCP carbon atom confirms the deprotonation reaction mentioned above. Owing to the anionic nature of the coordinated diphosphosphonate ligand, the P−C(25) and P−C(52) bond distances (ca. 1.74 Å) are shorter than when the ligand is neutral, as in $[PdCl_2(dppm\text{-}P,P)]$ (ca. 1.83 Å),[17,20] but similar to those in the related Pd(II) dppm-terpyridine complex **A**).[21] Not unexpectedly, reaction of **5** with NEt_3 in CH_2Cl_2 afforded **6a** in quantitative spectroscopic yields after a few hours.



A

Dinuclear Complexes. With the original objective to study the reactivity of the Pd−C bond of methyl complexes containing the ligands $\mathbf{L}^1$ or $\mathbf{L}^2$, the latter were reacted with [PdCl(Me)(COD)]. However, this reaction afforded the dinuclear, chloride-bridged complexes $[Pd(\mu\text{-}Cl)\{(Ph_2P)_2CP(O)(OR)_2\text{-}P,P\}]_2$ (**7a** R = Me; **7b** R = Ph) as yellow

---

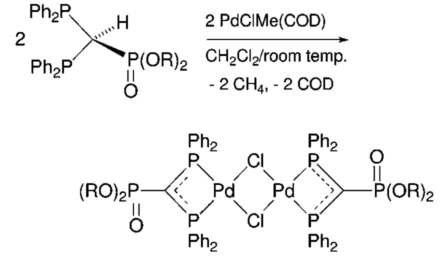
(20) Barkley, J.; Ellis, M.; Higgins, S. J.; McCart, M. K. *Organometallics* **1998**, *17*, 1725.

(21) Pickaert, G.; Cesario, M.; Douce, L.; Ziessel, R. *Chem. Commun.* **2000**, 1125.

Table 2. Selected Structural Data in Complexes **6a**·$2CH_2Cl_2$ and **6b**

bond lengths (Å)	**6a**·$2CH_2Cl_2$	**6b**
Pd(1)−P(1)	2.3441(8)	2.3239(6)
Pd(1)−P(2)	2.3229(8)	2.3316(6)
Pd(1)−P(4)	2.337(6)	2.3255(6)
Pd(1)−P(5)	2.332(2)	2.3396(6)
P(1)−C(25)	1.746(3)	1.755(2)
P(2)−C(25)	1.759(3)	1.749(2)
P(3)−C(25)	1.723(3)	1.722(2)
bond angles (deg)	**6a**·$2CH_2Cl_2$	**6b**
P(1)−Pd-P(2)	70.34(3)	70.68(2)
P(1)−C(25)−P(2)	100.2(2)	100.5(2)
P(4)−Pd(1)−P(5)	70.56(3)	70.71(2)

solids (eq 4). Their ^1H NMR spectra indicated the absence of the Pd-Me group and of the $Ph_2PC\mathit{H}PPh_2$ proton, which have been eliminated in the form of methane. The $^{31}P\{^1H\}$ NMR spectrum of **7a** contains singlets for the equivalent phosphine donors at δ −45.9 ppm and at δ 24.1 ppm for the uncoordinated P=O group. These resonances are found in **7b** at δ −45.0 and 13.2 ppm, respectively. Like in **4** or **6a,b**, no ^2J(P,P) coupling was observed. The centrosymmetrical structure of these new complexes was confirmed by an X-ray diffraction study (Table 3, Figures 8 and 9).



(4)

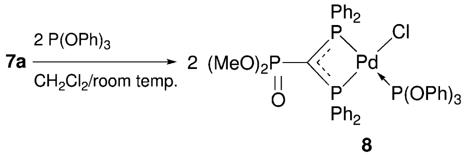
7a R = Me
7b R = Ph

The palladium atom in **7a** or **7b** is in a square-planar environment containing the two bridging chlorides and two phosphine P atoms. The geometry around C(25) is planar (sum of the angles = 359.71° in **7a** and 359.86° in **7b**), consistent with its sp^2 hybridization. Because of the loss of the PCH proton of $\mathbf{L}^1$ or $\mathbf{L}^2$, the P,P-chelating ligand is anionic and the charge is delocalized over P(1), C(25), and P(2), as shown by shorter P(1)−C(25) and P(2)−C(25) bond distances of 1.742(4) and 1.743(4) Å in **7a** or 1.746(2) and 1.742(2) Å in **7b**, respectively, when compared to the P−C sp^3 single bond in **2a** or **2b** (Table 1) or in $[PdCl_2(dppm\text{-}\mathit{P,P})]$ (1.834(3), 1.830(3) Å).[17]

Although no classical intramolecular hydrogen bonding was detected in **7a**, an interaction between an ortho phenyl C−H atom and a bridging Cl atom was observed [C(41)-H(41)···Cl(2) = 2.872(2) Å) (Figure 10).

In the crystal structure of **7b**, an interaction between a C−H moiety of a phenyl ring and the Pd centers [C(36)H(36)···Pd = 2.872(2) Å] creates infinite cross-linked chains (Figure 11).

The chloride bridges of **7a** are readily cleaved by nucleophiles such as $P(OPh)_3$ which affords the mononuclear complex $[PdCl\{(Ph_2P)_2CP(O)(OMe)_2\text{-}\mathit{P,P}\}\{P(OPh)_3\}]$ (**8**) (eq 5). Its spectroscopic data are given in the Experimental Section.



(5)

8

Synthesis of a Dinuclear Cu(I) Complex. The reaction of $[Cu(NCMe)_4]BF_4$ with one equivalent of $\mathbf{L}^1$ afforded a new complex which was characterized in $^{31}P\{^1H\}$ NMR spectroscopy by the presence of two broad signals at δ 1.4 and 28.0 ppm, assigned to the PPh_2 and P(O)(OMe) groups, respectively (eq 6). By analogy with results obtained earlier with the diphosphine ligand $(Ph_2P)_2CHC(O)NPh_2$,[22] we suggest for this complex a similar,

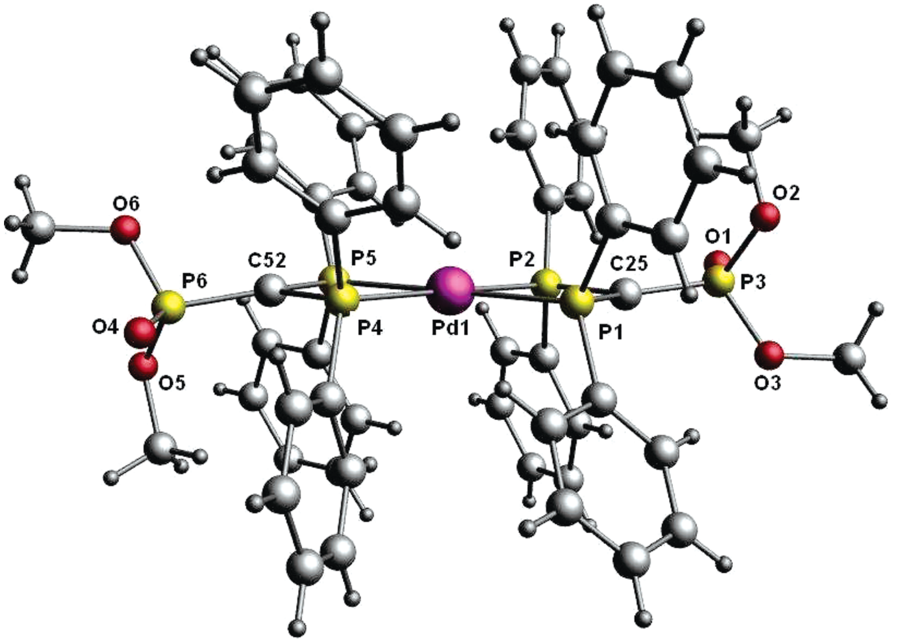


Figure 6. Diamond 3.1 view of the structure of $[Pd\{(Ph_2P)_2CP(O)(OMe)_2\text{-}\mathit{P,P}\}]$ (**6a**) in **6a**·$2CH_2Cl_2$.

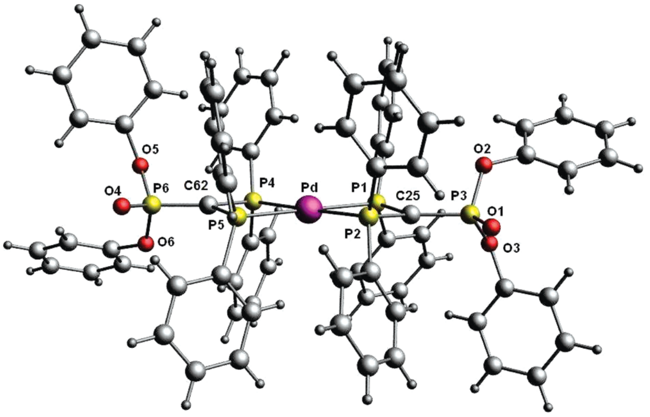
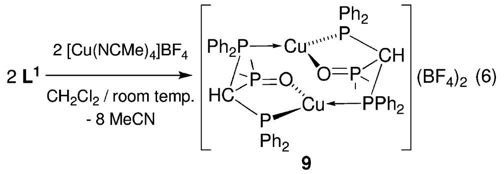


Figure 7. Diamond 3.1 view of the structure of [Pd{$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}$_2$] (**6b**).

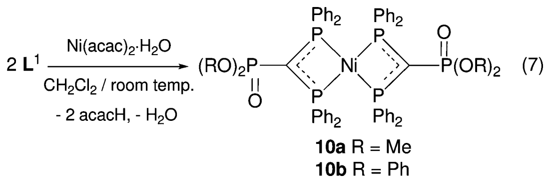
Table 3. Selected Bond Lengths and Angles in Complexes **7a** and **7b**

bond lengths (Å)	**7a**	**7b**
Pd(1)−P(1)	2.234(7)	2.225(6)
Pd(1)−P(2)	2.245(6)	2.236(6)
Pd(1)−Cl(1)	2.427(5)	2.430(6)
P(1)−C(25)	1.742(4)	1.746(2)
P(2)−C(25)	1.743(4)	1.742(2)
P(3)−C(25)	1.722(4)	1.718(2)
bond angles (deg)	**7a**	**7b**
P(1)−Pd−P(2)	70.85(4)	71.11(3)
P(1)−Pd−Cl(1)	99.72(4)	99.61(3)
P(2)−Pd−Cl(1)′	170.34(4)	170.66(3)
P(1)−C(25)−P(2)	96.3(2)	96.1(1)
Cl(1)−Pd−Cl(1)′	87.94(4)	88.87(3)

dinuclear structure **9**, in which a dynamic behavior of the phosphine donors accounts for the broad resonances observed.



Synthesis and Reactivity of Ni(II) Complexes. When the ligand $\mathbf{L}^1$ or $\mathbf{L}^2$ was reacted with $[Ni(acac)_2]\cdot H_2O$ in a 2:1 molar ratio at room temperature in dichloromethane, the mononuclear, diamagnetic bischelated complex [Ni{$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}$_2$] (**10a**) or [Ni{$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}$_2$] (**10b**) was obtained in 70 and 90% yield, respectively (eq 7).



The $^{31}P\{^1H\}$ NMR spectra of **10a,b** contain a singlet for the phosphine donors at −22.4 and −22.1 ppm and a singlet for the P═O moiety at 23.1 and 12.3 ppm, respectively, indicating again the absence of coupling between these nuclei. In the IR spectrum (KBr), ν(PO) vibration occurs at 1232 (**10a**) and 1244 cm^{-1} (**10b**), ca. 15 and 21 cm^{-1} higher than in the free ligand. A single-crystal X-ray diffraction analysis of $\mathbf{10a}\cdot 4CHCl_3$ and $\mathbf{10b}\cdot 4CHCl_3$ showed that the crystals consist of discrete neutral centrosymmetric molecules, the Ni atom being located on an inversion center, and confirmed the chelating behavior of the phosphine donors and the presence of two uncoordinated phosphonate groups. A view of a molecule of **10a** and **10b** is shown in Figures 12 and 13, respectively. The coordination geometry around the Ni(II) center is square planar. There are no significant intermolecular interaction between complex **10a** and the chloroform solvate molecules, but an intramolecular CH(19)···Ni interaction of 2.869(1) Å is found above and below the metal coordination plane (Figure 12).

The planar geometry around the C(25) atom adjacent to the phosphine donors (sum of the angles = 359.80°) is consistent with its sp^2 hybridization (Table 4). The ligand anionic charge is delocalized over the atoms P(1), C(25), and P(2), as indicated by the P(1)−C(25) and P(2)−C(25) bond lengths of 1.748(3) and 1.746(3) Å in **10a** and 1.755(4) and 1.750(4) Å in **10b**, respectively, which are shorter than the P-Csp^3 single bond in

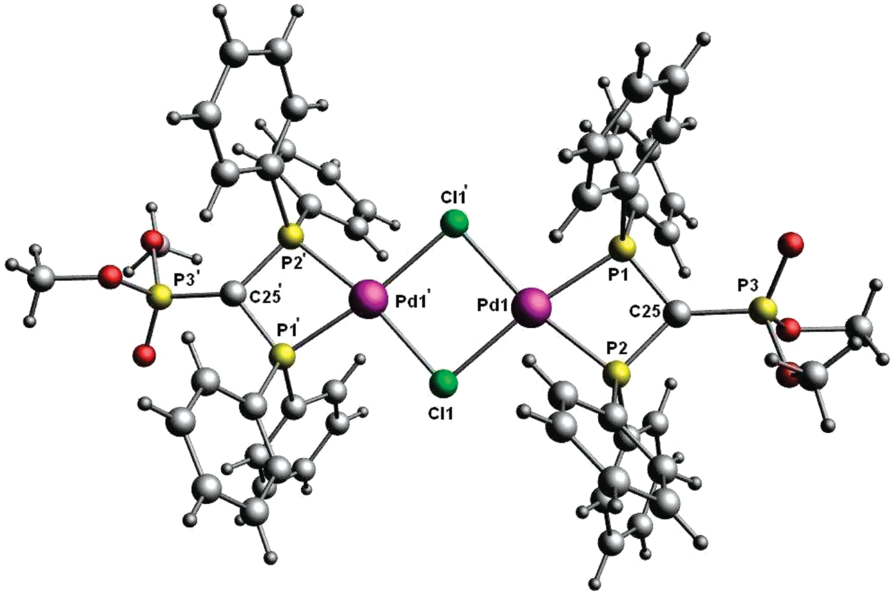


Figure 8. View of the structure of [Pd(μ-Cl)$_2${$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}]$_2$ (**7a**).

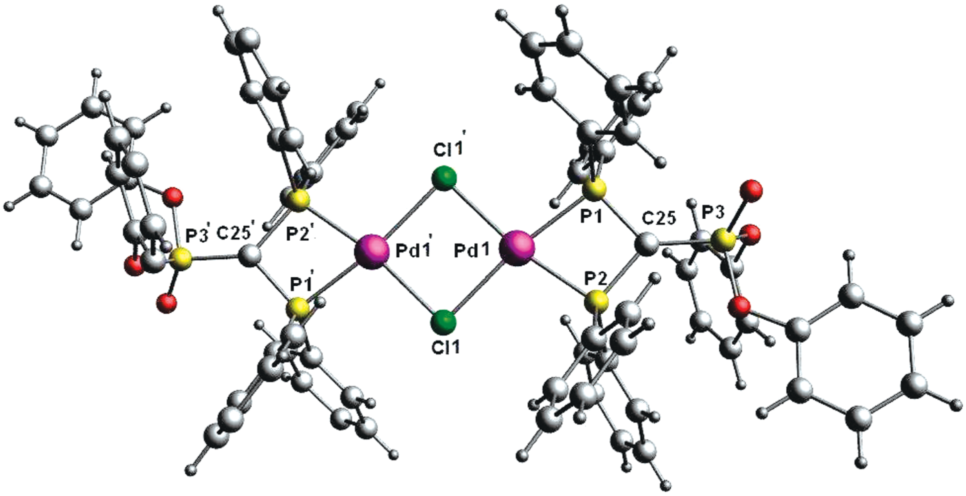


Figure 9. Diamond 3.1 view of the structure of [Pd(μ-Cl){$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}]$_2$ (**7b**).

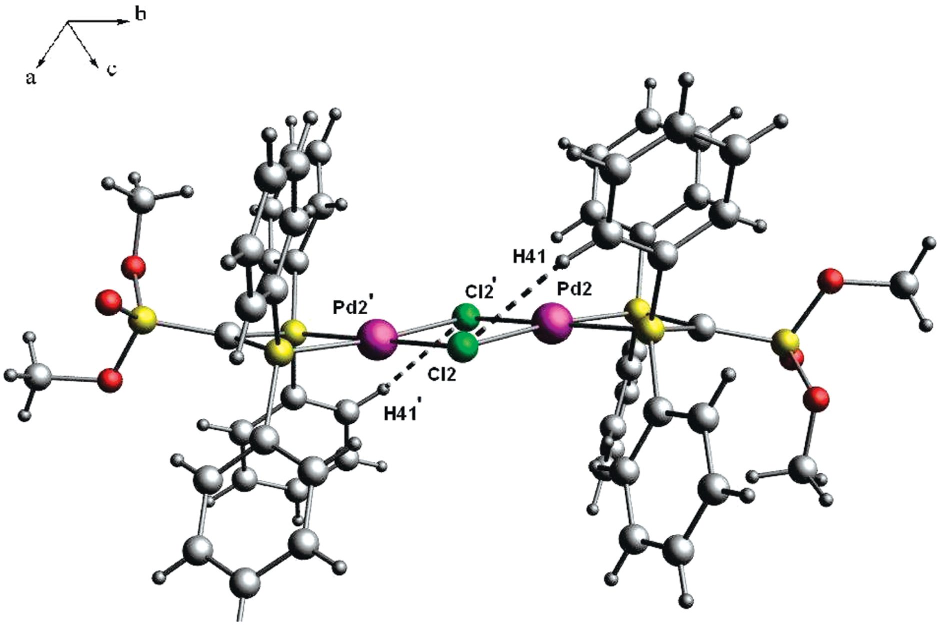
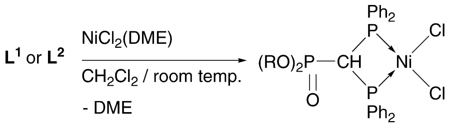


Figure 10. Intramolecular hydrogen bonding between ortho aromatic hydrogen atoms and the bridging chloride ligands in complex **7a**.

2a (1.870(3), 1.862(2) Å) or **2b** (1.869(5), 1.859(5) Å) or in the Ni(II) complex [Ni(dppm)$_2$](BF$_4$)$_2$ (1.81(4) and 1.82(4) Å).[23]

In complex **10b**·4CHCl$_3$ (Figure 13), the bonding parameters are very similar to those in **10a** and will not be discussed in detail.

Reaction of the ligands **L**^{1} and **L**^{2} with [NiCl$_2$(DME)] in a 1:1 molar ratio at room temperature in dichloromethane, afforded quantitatively the mononuclear, diamagnetic complexes [NiCl$_2${$(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}] (**11a**) and [NiCl$_2${$(Ph_2P)_2CHP(O)(OPh)_2$-*P,P*}] (**11b**), respectively (eq 8).



(8)

11a R = Me
11b R = Ph

Their $^{31}P\{^1H\}$ NMR spectrum consists of a doublet for the phosphine donors and a triplet for the P═O moiety (see Experimental Section). Slow diffusion of hexane into a chloroform solution of **11a** led to the formation of yellow crystals of **11a**·CHCl$_3$ suitable for X-ray diffraction analysis. Selected bond distances and angles are given in Table 5.

The square planar coordination geometry around the Ni(II) center is consistent with the diamagnetism of the complex. The geometry around the sp^3-hybridized C(25) atom is tetrahedral and as expected, the P(1)−C(25) and P(2)−C(25) bonds are longer than in the anionic chelates of **10a**.

For comparison, we extended our studies with the dppm-phosphonate ligands **L**^{1}and **L**^{2} to the dppm-C(O)NPh$_2$ ligand **12**.[22] Its reaction with [Ni(acac)$_2$] in a 2:1 molar ratio at room temperature in dichloromethane afforded the bischelate mononuclear complex **13** (eq 9). This complex is diamagnetic and its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −28.6 ppm. In the IR spectrum (KBr), the ν(CO) vibration occurs at 1652 cm^{-1}. Here too, spontaneous

---

(22) Andrieu, J.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1996**, *35*, 5975.

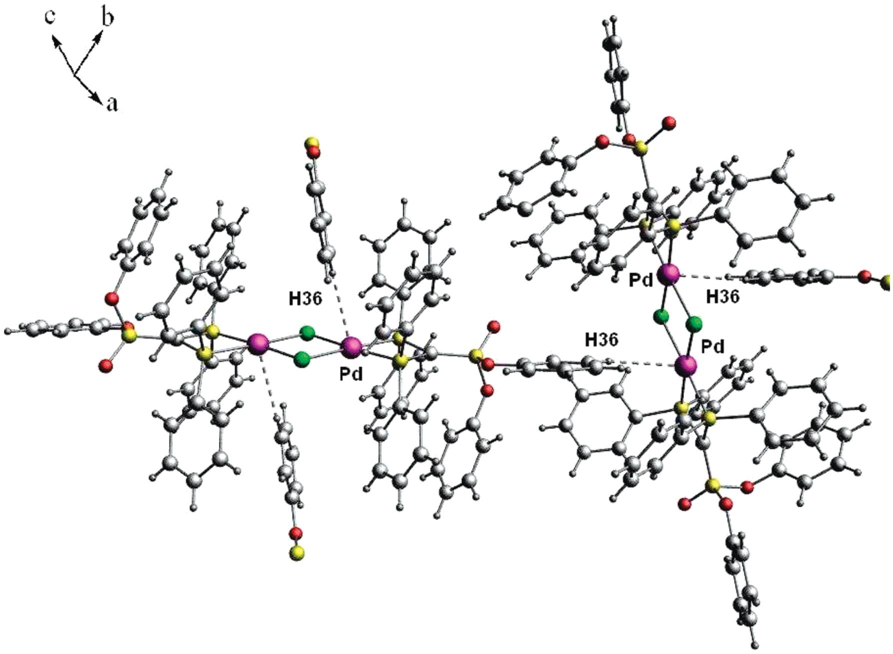


Figure 11. Intermolecular hydrogen bonding between a hydrogen atom of the phenyl group of the phosphonate function and the palladium center in **7b**.

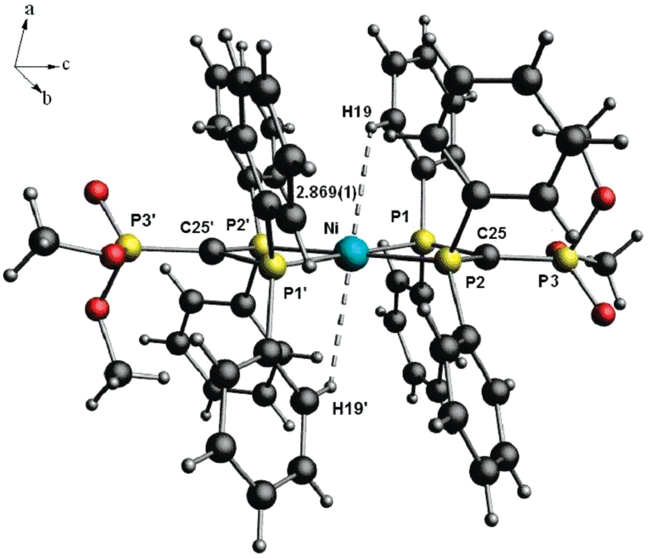
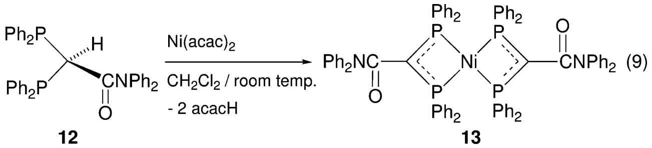


Figure 12. Diamond 3.1 view of the structure of [Ni{($Ph_2P)_2CP(O)(OMe)_2$-*P,P*}$_2$] (**10a**) in **10a**·4$CHCl_3$ with the labeling scheme.

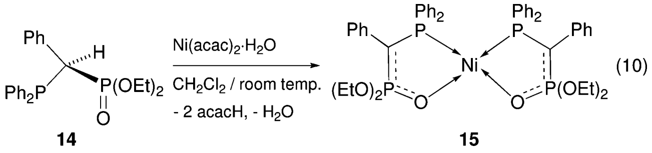
Table 4. Comparison of the Structural Data for [Ni{($Ph_2P)_2CP(O)(OMe)_2$-*P,P*}$_2$] (**10a**) in **10a**·4$CHCl_3$ and in [Ni(dppm)$_2$](BF_4)$_2$[23]

bond lengths (Å)	**10a**	**10b**	[Ni(dppm)$_2$](BF_4)$_2$
Ni−P(1)	2.2177(8)	2.2214(1)	2.219(8)
Ni−P(2)	2.2178(8)	2.2229(1)	2.228(9)
P(1)−C(25)	1.748(3)	1.755(4)	1.81(4)
P(2)−C(25)	1.746(3)	1.750(4)	1.82(4)
P(3)−C(25)	1.728(3)	1.715(4)	
bond angles (deg)	**10a**	**10b**	[Ni(dppm)$_2$](BF_4)$_2$
P(1)−Ni−P(2)	73.21(3)	73.52(4)	73.2(3)
P(1)−C(25)−P(2)	98.4(2)	98.7(2)	94.0(2)

deprotonation of the diphosphine ligand has occurred because of the presence of the basic acac ligand in the Ni(II) precursor.



Similarly, reaction of the related *β*-phosphonato-phosphine *P,O* ligand **14**[4] with [Ni(acac)$_2$]·H_2O in a 2:1 molar ratio at room temperature in dichloromethane was accompanied by ligand deprotonation (eq 10). This afforded the mononuclear, paramagnetic complex **15** in 65% yield. Its IR *ν*(PO) vibration occurs at 1251 cm^{-1} (KBr).



A Pd(II) complex containing the deprotonated form of ligand **14** featured in **15** has been previously structurally characterized.[4]

Catalytic Oligomerization of Ethylene. Chelating ligands play a major role in the academic and industrial development of late transition metal catalysts for the oligomerization and polymerization of olefins.[14,24−31] The discovery of the "Nickel effect" by Ziegler in 1953 indicated that this metal favors the oligomerization of ethylene[32] and many nickel complexes have been studied as catalysts for the oligomerization and polymerization of ethylene,[27,33−37] in the presence or not of a cocatalyst. The product chain length distribution strongly depends on the ligands properties. Anionic bidentate P,O$^-$ and neutral N,N chelating ligands occupy central positions and the SHOP process remains a

---

(23) Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.* **1991**, *30*, 417.

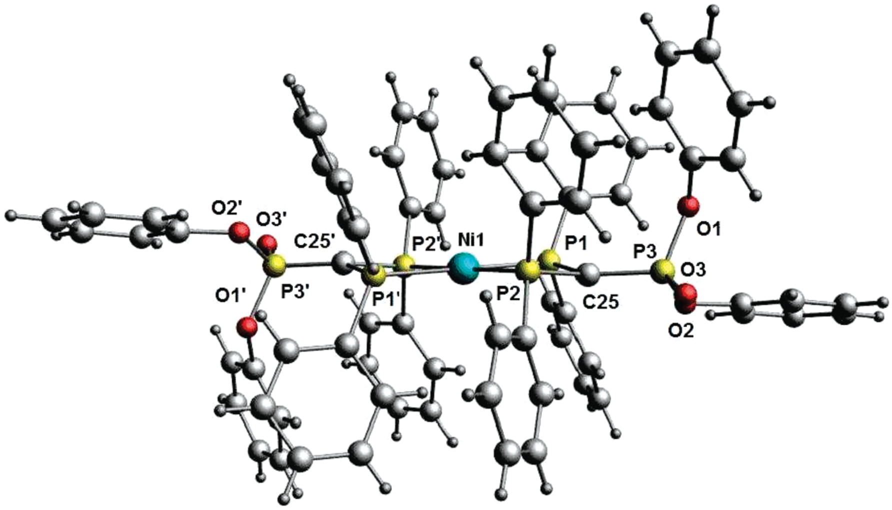


Figure 13. Diamond 3.1 view of complex of [Ni{$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}$_2$] (**10b**) in **10b**·4$CHCl_3$.

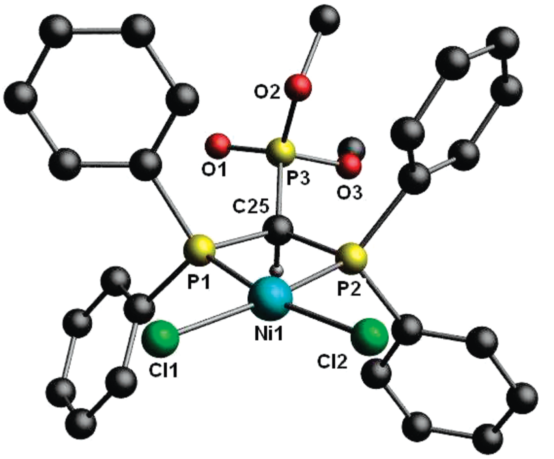
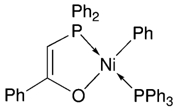


Figure 14. Diamond 3.1 view of the structure [$NiCl_2${$(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}] (**11a**) in **11a**·$CHCl_3$.

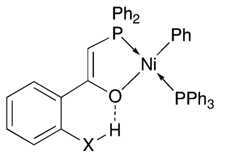
Table 5. Selected Structural Data for [$NiCl_2${$(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*}] (**11a**) in **11a**·$CHCl_3$

bond lengths (Å)	**11a**
Ni−Cl(1)	2.213(6)
Ni−Cl(2)	2.195(6)
Ni−P(1)	2.133(6)
Ni−P(2)	2.150(6)
P(1)−C(25)	1.861(2)
P(2)−C(25)	1.865(2)
P(3)−C(25)	1.799(2)
bond angles (deg)	
Cl(1)−Ni−Cl(2)	97.69(2)
P(1)−Ni−Cl(2)	169.04(3)
P(2)−Ni−Cl(2)	93.07(2)
P(1)−Ni−Cl(1)	92.42(2)
P(2)−Ni−Cl(1)	169.17(3)
P(1)−Ni−P(2)	76.95(2)
Ni−P(2)−C(25)	95.34(6)
Ni−P(1)−C(25)	96.04(7)
P(1)−C(25)	91.35(9)

reference in the oligomerization of ethylene with its remarkable selectivity for LAO.[38] Seemingly minor changes of the substituents on SHOP-related P,O ligands allowing different types of intramolecular hydrogen bonding interactions within the ligand moiety have been shown to significantly affect the activity and selectivity of their Ni complexes (**B** versus **C** and **D**),[39−41]

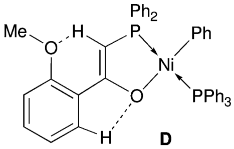


B



X = O, NMe, NPh

C



D

We have evaluated the *P*,*P*-nickel complexes **10a**,**b** and **11a**,**b** and the *P*,*O*-complex **15** as precatalysts in the presence of as little as possible $AlEtCl_2$ or MAO as cocatalyst. Such a comparison should provide information about the influence of (i) a chelating vs a monodentate ligand, (ii) the nature of the phosphonate substituents (methyl versus phenyl groups), (iii) the metal coordination geometry, and (iv) the nature of the cocatalyst ($AlEtCl_2$, or MAO). The results were also compared with those of [$NiCl_2(PCy_3)_2$], a typical α-olefin dimerization catalyst.[42,43] These precatalysts showed moderate to high activities for the dimerization and trimerization of ethylene (Tables 6 and 7).

All these precatalysts afforded similar results with $AlEtCl_2$ as cocatalyst. Complexes **11a**,**b** were the most active with a turnover frequency (TOF) of 78 300 mol of

---

(24) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534.
(25) *Late Transition Metal Polymerization Catalysis*; Rieger, B., Saunders Baugh, L., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003.
(26) Heinicke, J.; Köhler, M.; Peulecke, N.; He, M.; Kindermann, M. K.; Keim, W.; Fink, G. *Chem.—Eur. J.* **2003**, *9*, 6093.
(27) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.
(28) McGuinness, D. S.; Gibson, V. C.; Wass, D. F.; Steed, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 12716.
(29) Ionkin, A. S.; Marshall, W. J. *J. Organomet. Chem.* **2004**, *689*, 1057.
(30) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600.
(31) Small, B. L.; Schmidt, R. *Chem.—Eur. J.* **2004**, *10*, 1014.
(32) Ziegler, K.; Gellert, H. G.; Holzkamp, E.; Wilke, G. *Brennst. Chem.* **1954**, *35*, 321.
(33) Klabunde, U.; Ittel, S. D. *J. Mol. Catal. A: Chem.* **1987**, *41*, 123.
(34) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.
(35) Keim, W. *Angew. Chem., Int. Ed.* **1990**, *29*, 235.

Table 6. Catalytic Results for Complexes **10a**,**b**, **11a**,**b**, **15** and [$NiCl_2(PCy_3)_2$] in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

		selectivity (mass %)				productivity (g C_2H_4/ (g Ni)h)	TOF (mol C_2H_4/ (mol Ni)h)	α-olefin (mol%)			
	$AlEtCl_2$(equiv)	C_4	C_6	C_8	C_{10}			C_4	C_6	C_8	Kα
10a	3	34	64	<3		450	1000	36			1.25
10a	6	93	7	<1		13450	29185	10	2		0.05
10a	10	83	28	<1		11850	24860	17	4		0.22
10a	14	81	19	<1		12070	25310	20	4		0.15
10b	3	90	10			340	720	14			0.07
10b	10	88	12	<1		12730	25000	30			0.09
11a	6	60	36	4	<1	31710	66510	4	1	4	0.39
11a	10	61	36	4	<1	32310	67750	4	<1	3	0.39
11b	6	59	36	4	<1	36030	75550	4	<1	3	0.41
11b	10	56	39	5	<1	37330	78300	4	<1	3	0.47
15	3	90	10			200	420	27			0.07
15	6	87	13			14170	24520	20	5		0.16
15	10	85	15	<1		26710	45830	16	3		0.12
15	14	71	27	<3		14590	30600	12	2	3	0.11
ref	6	59	34	34		27600	57800	11			0.38
	10	65	31			24400	51500	9			0.32

[a] Conditions: $T = 23$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-5} mol Ni complex, total solvent volume 15 mL ($V_{Ni} + V_{EADC}$), solvent: chlorobenzene for **10a** and toluene for **10b**, **11a**,**b**, and **15**, $\alpha =$ (mol of hexenes/mol of butenes). Reference: $NiCl_2(PCy_3)_2$.

Table 7. Catalytic Results for Complexes **10a**,**b**, **11a**,**b**, **15** and [$NiCl_2(PCy_3)_2$] in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

		selectivity (mass %)				productivity (g C_2H_4/(g Ni)h)	TOF (mol C_2H_4/(mol Ni)h)	α-olefin (mol%)			
	MAO (equiv)	C_4	C_6	C_8	C_{10}			C_4	C_6	C_8	Kα
10a	100	71	29			120	260	72			0.27
10a	200	79	21			650	1360	66	47		0.17
10a	400	61	39			800	1680	71	31		0.86
10b	200	78	22			1490	3130	70	25		0.18
10b	400	65	35		<1	1540	3230	59	19	39	0.35
11a	100	91	9	1		1420	2980	34	20	15	0.06
11a	200	88	11		<1	4230	8880	13	5	2	0.08
11a	400	86	13	2	<1	5560	11660	12	2	1	0.10
11b	100	91	9	<1		1120	2360	48	41		0.06
11b	200	91	9	<1		400	830	24	7		0.07
11b	400	87	12	1		4440	9320	15	3		0.09
15	100	83	16	<1		3300	6940	57	12	4	0.13
15	200	83	15	2		3210	5550	53	12	2	0.12
15	400	83	15	2		3710	7790	45	9	2	0.11
ref	200	74	18	8		600	1200	76			0.16
ref	400	70	26	4		3000	6400	72			0.24

[a] Conditions: $T = 23$ °C, 10 bar of C_2H_4, 35 min, 4×10^{-5} mol Ni complex, total solvent volume 20 mL ($V_{Ni} + V_{MAO}$), solvent: chlorobenzene for **10a**, toluene for **10b**, **11a**,**b**, and **15**, $K\alpha =$ (mol of hexenes/mol of butenes). Reference: $NiCl_2(PCy_3)_2$.

C_2H_4/(mol of Ni)h) for complex **11b** (Table 6) in the presence of 10 equiv of $AlEtCl_2$. All precatalyst showed a high selectivity for C_4 and C_6 olefins and only traces of C_8 olefins were observed. Up to 93% C_4 was obtained with **10a** in the presence of 6 equiv $AlEtCl_2$, whereas when only 3 equiv cocatalyst was used with **10a**, 64% trimers were formed. The mononuclear, bischelate complexes **10a**,**b** and **15** led to higher selectivities for α-C_4 than the mononuclear complexes **11a** and **11b**. The use of different amounts of $AlEtCl_2$ as cocatalyst generally affected the selectivity less than the productivity.

In the presence MAO as cocatalyst, precatalysts **10a**,**b**, **11a**,**b**, and **15** gave moderate TOFs up to 11 660 mol of C_2H_4/(mol of Ni)h) (Table 7) for complex **11a** with 400 equiv of MAO. Mostly ethylene dimers were formed but up to 39% trimers were observed with **10a** in the presence of 400 equiv MAO. This is reminiscent of the behavior of this precatalysts in the presence of 3 equiv $AlEtCl_2$ (see above). The α-olefins contained mostly 1-butene, but up to 47% 1-hexene was obtained with **10a** in the presence of 200 equiv MAO.

In conclusion, we have found that bis(diphenylphosphino)methane-phosphonate-based ligands $(Ph_2P)_2CHP(O)(OR)_2$ (R = Me, $\mathbf{L}^1$; R = Ph, $\mathbf{L}^2$) form metal complexes by selective coordination of the diphosphine moiety to Pd(II) and Ni(II) centers, resulting in four-membered ring chelates. Spontaneous deprotonation of these ligands at the PCHP site occurred when basic ligands were present in the precursor metal complex, such as dmba or methyl in the case of Pd(II) or acac in the case of Ni(II). A range of mono- and dinuclear complexes was structurally characterized and some Ni(II) complexes revealed interesting catalytic properties for the selective oligomerization of ethylene.

---

(36) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(37) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(38) Ostoja Starzewski, K. A. *In Late Transition Metal Polymerization Catalysis*; Rieger, B., Saunders Baugh, L., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003; p 1.

(39) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2203.

(40) Pietsch, J.; Braunstein, P.; Chauvin, Y. *New J. Chem.* **1998**, 467.

(41) Kermagoret, A.; Braunstein, P. *Dalton Trans.* **2008**, 822.

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

(43) Knudsen, R. D. *Prepr. -Am. Chem. Soc., Div. Pet. Chem.* **1989**, 572.

Experimental Section

General Consideration. All the reactions and manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk tube techniques. The following solvents were dried and distilled under nitrogen before use: hexane, pentane, and toluene over sodium, tetrahydrofuran and diethyl ether over sodium-benzophenone, and dichloromethane over calcium hydride. Nitrogen (Air liquide, R-grade) was passed through BASF R3−11 catalyst and molecular sieve columns to remove residual oxygen and water. Elemental C, H, and N analyses were performed by the Service de Microanalyses (Université Louis Pasteur, Strasbourg). Infrared spectra were recorded on an IFS 66 Bruker FT-IR spectrometer. The ^{1}H and ^{31}P{1H} NMR spectra were recorded at 300.1 and 121.5 MHz, respectively, on a Bruker AC300 instrument.The ^{1}H NMR chemical shifts of the aromatic protons have been omitted for clarity, since they are unexceptional. $AgBF_4$ (Avocado) was dried overnight in vacuo before use. The chlorodiphenylphosphine and the phosphonates $MeP(O)(OR)_2$ (R = Me, Ph) (Aldrich) were distilled and degassed before use. The compounds $Ph_2PCH(Ph)P(O)(OEt)_2$,[4] $(Ph_2P)_2CHC(O)NPh_2$,[22] $[PdCl_2(COD)]$,[44] $[PdCl(Me)(COD)]$,[45] $[Cu(NCMe)_4]BF_4$,[46] $[Pd(NCMe)_4](BF_4)_2$,[47,48] $[Pd(\mu\text{-Cl})(dmba)]_2$,[49] and $[NiCl_2(DME)]$ (DME = 1,2-dimethoxyethane)[50] were prepared according to literature procedures.

$(Ph_2P)_2CHP(O)(OMe)_2$ (L^1). In a 250 mL Schlenk tube containing a solution of *n*-BuLi in hexane (30.22 mL, 48.35 mmol, 1.6 M Aldrich) cooled at −20 °C was added a solution of diisopropylamine (5.290 g, 48.3 mmol) in THF (30 mL). After 10 min, a solution of $MeP(O)(OMe)_2$ (2.000 g, 16.1 mmol) in THF (40 mL) was added, and the mixture was stirred for 10 min during which the temperature was kept below −65 °C. It was then cooled again to −78 °C, and a solution of Ph_2PCl (7.100 g, 5.79 mL, 32.2 mmol) in THF (20 mL) was added dropwise. The temperature was then allowed to warm to 0 °C while stirring was maintained. The reaction mixture was quenched at −20 °C by addition of a degassed 5N HCl solution untill pH 4 was reached. The organic layer was then collected and the aqueous phase was extracted with diethylether (2 × 20 mL). The combined organic phases were then dried over degassed $MgSO_4$. After filtration and removal of the volatiles under vacuum, the ligand was obtained as a white solid (6.100 g, 77%). Anal. Calcd for $C_{27}H_{27}O_3P_3$: C, 65.86; H, 5.53. Found: C, 66.09; H, 5.70. ^{1}H NMR ($CDCl_3$): δ 3.19 (6H, d, ^3J(P,H) = 11.1 Hz, OCH_3), 3.71 (1H, d, ^2J(PO,H) = 21.6 Hz, CH), 7.23−8.04 (20H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −11.1 (d, ^2J(P,P) = 21 Hz, PPh_2), 28.1 (t, ^2J(P,P) = 21 Hz, PO). IR (KBr): $\nu_{P=O}$ = 1247 (s) cm^{-1}.

$(Ph_2P)_2CHP(O)(OPh)_2$ (L^2). This ligand was prepared according to the same procedure as that described above for $(Ph_2P)_2CHP(O)(OMe)_2$, using $MeP(O)(OPh)_2$ (1.890 g, 7.61 mmol), *n*-BuLi (14.25 mL, 22.8 mmol, 1.6 M Aldrich), diisoprylamine (2.490 g, 22.8 mmol), and PPh_2Cl (3.350 g, 2.73 mL, 15.2 mmol). It was obtained as a beige solid (3.370 g, 72%). Anal. Calcd for $C_{37}H_{31}O_3P_3$: C, 72.08; H, 5.07. Found: C, 71.31; H, 5.11. ^{1}H NMR ($CDCl_3$): δ 3.9 (1H, d, ^2J(PO,H) = 22.9 Hz, CH), 6.60−7.65 (30H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −9.3 (d, ^2J(P,P) = 21.5 Hz, PPh_2), 19.1 (t, ^2J(P,P) = 21.5 Hz, PO); IR (KBr): $\nu_{P=O}$ = 1265 (s) cm^{-1}.

$[PdCl_2\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}]$ (2a). Solid $[PdCl_2(COD)]$ (0.579 g, 2.03 mmol) was added to a solution of $(Ph_2P)_2CHP(O)(OMe)_2$ (1.000 g, 2.03 mmol) in CH_2Cl_2 (45 mL). The mixture was stirred for 30 min, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a yellow solid (1.087 g, 80%). Anal. Calcd for $C_{27}H_{27}Cl_2O_3P_3Pd$: C, 48.42; H, 4.06. Found: C, 48.50; H, 4.12. ^{1}H NMR ($CDCl_3$): δ 3.07 (6H, d, ^3J(P,H) = 11.5, OCH_3), 5.30 (1H, dt, ^2J(PO,H) = 23 Hz, ^2J(P,H) = 11 Hz, CH), 7.50−8.39 (40H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −43.9 (d, ^2J(P,P) = 18 Hz, PPh_2), 17.1 (t, ^2J(P,P) = 18 Hz). IR (KBr): $\nu_{P=O}$ = 1262 (s) cm^{-1}.

$[PdCl_2\{(Ph_2P)_2CHP(O)(OPh)_2\text{-}P,P\}]$ (2b). Solid $[PdCl_2(NCPh)_2]$ (0.556 g, 1.45 mmol) was added to a solution of $(Ph_2P)_2CHP(O)(OPh)_2$ (0.875 g, 1.45 mmol) in CH_2Cl_2 (20 mL) at ambient temperature. The mixture was stirred for 30 min, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a yellow solid (1.139 g, 99%). Anal. Calcd for $C_{37}H_{31}Cl_2O_3P_3Pd$: C, 55.98; H, 3.94. Found: C, 56.89; H, 4.68 (despite recrystallizations, no better analyses could be obtained). ^{1}H NMR ($CDCl_3$): δ 5.35 (H, dt, ^2J(PO,H) = 23 Hz, ^2J(P,H) = 13 Hz, CH), 6.32−6.35 (10H, m, OPh), 7.04−8.42 (20H, m, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −42.0 (d, ^2J(P,P) = 19 Hz, PPh_2), 7.1 (t, ^2J(P,P) = 19 Hz, PO). IR (KBr): $\nu_{P=O}$ = 1275 (s) cm^{-1}.

$[Pd\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}(NCMe)_2][BF_4]_2$ (4). The complex $[PdCl_2\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}]$ (0.450 g, 0.67 mmol) was treated with $AgBF_4$ (0.261 g, 1.34 mmol) in a 1:1 mixture of CH_2Cl_2/MeCN at ambient temperature. The reaction mixture was stirred for 1 h, then the solution was filtered and the volatiles were removed under reduced pressure to leave a gray solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 15 mL) and dried under vacuum (0.458 g, 80%). ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 6H, CH_3CN), 3.32 (d, 6H, ^3J(P,H) 11.2 Hz, MeO), 3.87 (d, ^2J(P,H) = 12 Hz, CH), 6.55−7.89 (20H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −49.0 (s, PPh_2), 14.3 (s, PO). IR (KBr): $\nu_{P=O}$ = 1261 (s) cm^{-1}.

The following is an alternative procedure: solid $[Pd(NCMe)_4](BF_4)_2$ (0.400 g, 0.90 mmol) was added to a solution of $(Ph_2P)_2CHP(O)(OMe)_2$ (0.450 g, 0.91 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred for 1 h, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a yellow solid (0.700 g, 90%). Anal. Calcd for $C_{31}H_{33}B_2F_8N_2O_3P_3Pd$: C, 43.57; H, 3.89. Found: C, 44.35; H, 4.41.

$[Pd\{(Ph_2P)_2CHP(O)(OMe)_2\text{-}P,P\}_2](BF_4)_2$ (5). Solid $(Ph_2P)_2CHP(O)(OMe)_2$ (0.400 g, 0.81 mmol) and $[Pd(NCMe)_4](BF_4)_2$ (0.177 g, 0.81 mmol) were placed in a Schlenk flask and THF (20 mL) was added. The mixture was stirred at room temperature for 45 min, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a gray solid (0.379 g, 75%). Anal. Calcd for $C_{54}H_{54}B_2F_8O_6P_6Pd$: C, 51.28; H, 4.30. Found: C, 50.82; H, 5.00. ^{1}H NMR ($CDCl_3$): δ 3.32 (d, 6H, ^2J(P,H) = 11.5 Hz, $POCH_3$), 3.87 (d, 1H, ^2J(P,H) = 11.6 Hz), 7.15−7.82 (40H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −13.6 (d, ^2J(P,P) = 5.8 Hz, PPh_2), 15.6 (t, ^2J(P,P) = 5.8 Hz, PO). IR (KBr): $\nu_{P=O}$ = 1224 (s) cm^{-1}.

$[Pd\{(Ph_2P)_2CP(O)(OMe)_2\text{-}P,P\}_2]$ (6a). Solid $(Ph_2P)_2CHP(O)(OMe)_2$ (0.256 g, 0.52 mmol) and $[Pd(\mu\text{-Cl})(dmba)]_2$ (0.291 g, 0.52 mmol) were placed in a Schlenk flask and THF (45 mL) was added. The mixture was stirred at room temperature for 45 min, and then the yellow solid precipitate was filtered (0.032 g, 6%). Anal. Calcd for $C_{54}H_{52}O_6P_6Pd$: C, 59.54; H, 4.81. Found: C, 57.82;

---

(44) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.

(45) (a) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769. (b) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.

(46) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

(47) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1984**, *23*, 3257.

(48) Wayland, B. B.; Schrammz, R. F. *Inorg. Chem.* **1969**, *8*, 971.

H, 5.38. ^{1}H NMR ($CDCl_3$): δ 2.74 (d, 6H, ^2J(P,H) = 11.3 Hz, Me), 7.05−7.50 (40H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −31.4 (s, PPh_2), 25.6 (s, PO). IR (KBr): $\nu_{P=O}$ = 1222 (s) cm^{-1}.

[Pd{$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}$_2$] (6b). Solid $(Ph_2P)_2CHP(O)(OPh)_2$ (0.300 g, 0.48 mmol) and [Pd(μ-Cl)(dmba)]$_2$ (0.132 g, 0.24 mmol) were placed in a Schlenk flask and CH_2Cl_2 (30 mL) was added. The mixture was stirred for 30 min, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 15 mL) and pentane (2 × 20 mL), which afforded a yellow solid (0.141 g, 33%). Anal. Calcd for $C_{74}H_{60}O_6P_6Pd$: C, 66.45; H, 4.52. Found: C, 66.55; H, 5.35. ^{1}H NMR ($CDCl_3$): δ 6.5−8.1 (60H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −31.0 (s, PPh_2), 15.1 (s, PO). IR (KBr): $\nu_{P=O}$ = 1246 (s) cm^{-1}.

[Pd(μ-Cl){$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}]$_2$ (7a). Solid [PdCl(Me)(COD)] (0.215 g, 0.81 mmol) and $(Ph_2P)_2CHP(O)(OMe)_2$ (0.400 g, 0.81 mmol) were placed in a Schlenk flask and CH_2Cl_2 (30 mL) was added at ambient temperature. The yellow reaction mixture was stirred for 1 h and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 15 mL) and pentane (2 × 20 mL), which afforded a yellow solid (0.615 g, 60%). Anal. Calcd for $C_{54}H_{52}Cl_2O_6P_6Pd_2$: C, 51.21; H, 4.14. Found: C, 51.05; H, 4.34. ^{1}H NMR ($CDCl_3$): δ 2.98 (12H, d, ^3J(PO,H) = 11.5 Hz, OCH_3), 7.24−7.97 (40H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −45.9 (s, PPh_2), 24.1 (s, PO). IR (KBr): $\nu_{P=O}$ = 1229 (s) cm^{-1}.

[Pd(μ-Cl){$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}]$_2$ (7b). This complex was prepared as described above for [Pd{$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}(μ-Cl)]$_2$ from $(Ph_2P)_2CHP(O)(OPh)_2$ (0.300 g, 0.48 mmol) and [PdCl(Me)(COD)] (0.128 g, 0.48 mmol). It was obtained as a yellow solid (0.429 g, 59%). Anal. Calcd for $C_{74}H_{60}Cl_2O_6P_6Pd_2$: C, 58.67, H, 3.99. Found: C, 58.10; H, 4.49. ^{1}H NMR ($CDCl_3$): δ 6.53−7.91 (m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −45.0 (s, PPh_2), 13.2 (s, PO). IR (KBr): $\nu_{P=O}$ = 1194 (s) cm^{-1}.

[PdCl{$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}{$P(OPh)_3$}] (8). Pure $P(OPh)_3$ (0.120 g, 0.38 mmol) was added to a solution of **7a** (0.244 g, 0.19 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 3 h, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a yellow solid (0.168 g, 94%). Anal. Calcd for $C_{45}H_{41}ClO_6P_4Pd$: C, 57.28; H, 4.38. Found: C, 56.91; H, 4.63. ^{1}H NMR ($CDCl_3$): δ 2.95 (d, 6H, ^3J(PO,H) = 12 Hz, OCH_3), 6.85−7.99 (35H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −49.4 (dd, ^2J(P,P) = 75 Hz, ^2J(P,P)$_{trans}$ = 644 Hz, PPh_2 trans to $P(OPh)_3$), −39.8 (dd, ^2J(P,P) = 75 Hz, ^2J(P,P)$_{cis}$ = 28 Hz, PPh_2 cis to $P(OPh)_3$), 24.6 (d, ^4J(P,P) = 19 Hz, *P* = O), 110.0 (ddd, ^2J(P,P)$_{trans}$ = 644 Hz, ^2J(P,P)$_{cis}$ = 28 Hz, ^4J(P,P) = 19 Hz, $P(OPh)_3$). IR (KBr): $\nu_{P=O}$ = 1221 (s) cm^{-1}.

[Cu_2{$(Ph_2P)_2CHP(O)(OMe)_2$}$_2$](BF_4)$_2$ (9). Solid [Cu(NCMe)$_4$](BF_4) (0.250 g, 0.79 mmol) and $(Ph_2P)_2CHP(O)(OMe)_2$ (0.389 g, 0.79 mmol) were placed in a Schlenk flask and CH_2Cl_2 (20 mL) was added. The mixture was stirred for 2 h, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 20 mL) and pentane (2 × 20 mL), which afforded a white solid. Anal. Calcd for $C_{54}H_{54}B_2Cu_2F_8O_6P_6$: C, 50.45; H, 4.23. Found: C, 49.5; H, 4.43. ^{1}H NMR ($CDCl_3$): δ 2.35 (br, 12H, OCH_3), 3.75 (br, 2H, CH), 7.23−7.82 (40H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 1.4 (br, PPh_2), 28.0 (vbr, PO). IR (KBr): $\nu_{P=O}$ = 1247 (s) cm^{-1}, $\nu_{P=OCu}$ = 1182 (s) cm^{-1}.

[Ni{$(Ph_2P)_2CP(O)(OMe)_2$-*P,P*}$_2$] (10a). Solid [Ni(acac)$_2$]·H_2O (0.410 g, 1.52 mmol) was added to a solution of $(Ph_2P)_2CHP(O)(OMe)_2$ (1.500 g, 3.05 mmol) in CH_2Cl_2 at ambient temperature. The reaction mixture was stirred for 1 h, then the solution was filtered and the volatiles were removed under reduced pressure to give a yellow solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 20 mL) and dried under vacuum to give a yellow solid (1.10 g, 70%). Anal. Calcd for $C_{54}H_{52}NiO_6P_6$·0.5 CH_2Cl_2: C, 60.39; H, 4.93. Found: C, 60.09; H, 5.14. ^{1}H NMR ($CDCl_3$): δ 2.62 (d, 6H, ^3J(P,H) = 7.2 Hz, OCH_3), 6.91−8.01 (40H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.4 (s, PPh_2), 23.1 (PO). IR (KBr): $\nu_{P=O}$ = 1232 (s) cm^{-1}. Mass spectrum (ESI): 1041.13 (M^+ + 1). Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a chloroform solution of the complex.

[Ni{$(Ph_2P)_2CP(O)(OPh)_2$-*P,P*}$_2$] (10b). Using a similar procedure to that for **10a**, solid [Ni(acac)$_2$] (0.075 g, 0.29 mmol) was added to a solution of $(Ph_2P)_2CHP(O)(OPh)_2$ (0.360 g, 0.58 mmol) in CH_2Cl_2 at ambient temperature. The reaction mixture was stirred for 1 h, then the yellow solution was filtered and the volatiles were removed under reduced pressure to give a yellow solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 20 mL) and dried under vacuum to yield a yellow solid (0.330 g, 90%). Anal. Calcd for $C_{74}H_{60}NiO_6P_6$: C, 68.91; H, 4.69%. Found: C, 68.97; H, 4.77%. ^{1}H NMR ($CDCl_3$): δ 6.19−7.60 (60H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.1 (s, PPh_2), 12.3 (s, PO). IR (KBr): $\nu_{P=O}$ = 1244 (s) cm^{-1}. Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a chloroform or a dichloromethane solution of the complex.

[$NiCl_2$($(Ph_2P)_2CHP(O)(OMe)_2$-*P,P*] (11a). CH_2Cl_2 (30 mL) was added to a mixture of solid $(Ph_2P)_2CHP(O)(OMe)_2$ (0.170 g, 2.37 mmol) and [$NiCl_2$(DME)] (0.520 g, 2.37 mmol) in a 100 mL Schlenk tube, and the mixture was stirred at room temeperature for 1 h. The solution was filtered, and the volatiles were removed under reduced pressure to give an ocre solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 20 mL) and dried under vacuum to give an ocre solid (0.710 g, 79%). Anal. Calcd for $C_{27}H_{27}Cl_2NiO_3P_3$·0.5CH_2Cl_2: C, 49.71; H, 4.25. Found: C, 49.70; H, 4.26. ^{1}H NMR ($CDCl_3$): δ 3.02 (d, 6H, ^2J(P,H) = 11.3 Hz), 4.42 (m, 1H, PCHP), 7.26−8.50 (20H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −34.5 (d, ^2J(P,P) = 16 Hz, PPh_2), 25.6 (t, ^3J(P,P) = 16 Hz, PO). IR (KBr): $\nu_{P=O}$ = 1241 (s) cm$^{-1.}$

[$NiCl_2$($(Ph_2P)_2CHP(O)(OPh)_2$-*P,P*] (11b). CH_2Cl_2 (40 mL) was added to a mixture of solid $(Ph_2P)_2CHP(O)(OPh)_2$ (0.750 g, 1.21 mmol) and [$NiCl_2$(DME)] (0.267 g, 1.21 mmol) in a 100 mL Schlenk tube and the mixuture was sitrred at room temperature overnight. The solution was filtered and the volatiles were removed under reduced pressure to give an ocre solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 20 mL) and dried under vacuum to afford an ocre solid (1.220 g, 82%). Anal. Calcd for $C_{37}H_{31}Cl_2NiO_3P_3$: C, 59.56; H, 4.19. Found: C, 60.67; H, 4.82. ^{1}H NMR ($CDCl_3$): δ 3.48 (m, 1H, PCHP), 6.24−8.59 (30H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −34.2 (d, ^2J(P,P) = 16.7, PPh_2), 7.24 (t, ^3J(P,P) = 16.7, PO). IR (KBr): $\nu_{P=O}$ = 1270 (s) cm^{-1}.

[Ni{$(Ph_2P)_2CC(O)NPh_2$-*P,P*}$_2$] (13). THF (20 mL) was added at ambient temperature to a mixture of $(Ph_2P)_2CHC(O)NPh_2$ (92.75 g, 0.16 mmol) and [Ni(acac)$_2$] (0.045 g, 0.08 mmol) in a 100 mL Schlenk tube. The reaction mixture was stirred for 1 h, the green solution was filtered, the solvent was removed under reduced pressure, and the solid was extracted in CH_2Cl_2. Solvent evaporation under reduced pressure afforded a green solid (0.022 g, 44%). Anal. Calcd for $C_{76}H_{60}N_2NiO_2P_4$: C, 75.07; H, 4.97; N, 2.22. Found: C, 74; H, 4.57 N, 1.47. ^{1}H NMR ($CDCl_3$): δ 6.12−7.92 (60H, m, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −28.6 (s, PPh_2). IR (KBr): $\nu_{P=O}$ = 1652 (s) cm^{-1}.

[Ni{$Ph_2PC(Ph)P(O)(OEt)_2$-*P,O*}$_2$] (15). Solid [Ni(acac)$_2$]·H_2O (0.410 g, 1.85 mmol) was added to a solution of $(Ph_2P)CH(Ph)P(O)(OEt)_2$ (1.52 g, 3.7 mmol) in CH_2Cl_2 (30 mL) at ambient temperature. The reaction mixture was stirred for 1 h, then the solution

Table 8. Crystal Data and Details of the Structure Determinations for the Palladium Complexes **2a**, **2b**, **6a**$\cdot$2CH$_2$Cl$_2$, **6b**, **7a** and **7b**

	2a	**2b**	**6a**$\cdot$2CH$_2$Cl$_2$	**6b**	**7a**	**7b**
formula	$C_{27}H_{27}Cl_2O_3P_3Pd$	$C_{37}H_{31}Cl_2O_3P_3Pd$	$C_{54}H_{52}O_6P_6Pd$, 2(CH$_2$Cl$_2$)	$C_{74}H_{60}O_6P_6Pd$	$C_{54}H_{52}Cl_2O_6P_6Pd_2$	$C_{74}H_{60}Cl_2O_6P_6Pd_2$
M_r	669.70	793.83	1259.03	1337.44	1266.48	1514.74
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	10.9438(6)	10.4790(10)	9.8929(2)	12.3080(2)	9.8880(10)	10.5160(10)
b, (Å)	16.4162(11)	15.764(2)	11.7832(3)	21.6970(3)	14.344(3)	19.337(2)
c(Å)	16.8743(7)	20.732(3)	24.8050(6)	24.3410(4)	19.349(4)	16.642(2)
α (°)	90	90	83.8140(10)	90	102.815(5)	90
β (°)	114.693(3)	97.21(5)	88.885(2)	100.00(6)	94.658(5)	90.64 (5)
γ (°)	90	90	80.004(2)	90	90.533(5)	90
V (Å^3)	2754.4(3)	3397.7(7)	2831.04(11)	6401.43(17)	2666.1(8)	3383.9(6)
Z	4	4	2	4	2	2
D_x (Mg m^{-3})	1.615	1.552	1.477	1.388	1.578	1.487
μ (mm^{-1})	1.07	0.88	0.74	0.49	1.00	0.81
crystal size (mm)	0.30 × 0.20 × 0.10	0.10 × 0.10 × 0.10	0.30 × 0.25 × 0.15	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
R_{int}	0.053	0.122	0.053	0.048	0.0000	0.0000
θ_{max} (°)	27.5	27.6	30.1	30.1	35.0	35.0
R[$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.042, 0.079, 1.04	0.083, 0.149, 1.14	0.050, 0.134, 0.97	0.046, 0.119, 1.05	0.071, 0.147, 0.85	0.045, 0.108, 0.90
ρ_{max}, ρ_{min} (e Å^{-3})	0.44, −0.66	0.80, −0.76	1.22, −1.49	0.66, −1.42	1.90, −0.73	0.66, −1.40

Table 9. Crystal Data and Details of the Structure Determinations of the Nickel Complexes **10a**,**b** and **11a**$\cdot$CHCl$_3$

	10a$\cdot$4CHCl$_3$	**10b**$\cdot$4CHCl$_3$	**11a**$\cdot$CHCl$_3$
formula	$C_{54}H_{52}NiO_6P_6$, 4(CHCl$_3$)	$C_{74}H_{60}NiO_6P_6$, 4(CHCl$_3$)	$C_{27}H_{27}Cl_2NiO_3P_3$, CHCl$_3$
M_r	1518.96	1767.22	741.37
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.2810(5)	11.3934(2)	10.7000(3)
b (Å)	11.8690(5)	15.7103(4)	16.4637(3)
c (Å)	14.9440(10)	24.1342(6)	19.4248(5)
α (°)	81.1620(14)	107.948(1)	97.557(1)
β (°)	77.9320(16)	95.481(1)	97.688(1)
γ (°)	76.1380(14)	94.839(2)	105.517(10)
V (Å^3)	1720.98(16)	4061.22(16)	3217.00(14)
Z	1	2	4
D_x (Mg m^{-3})	1.466	1.445	1.531
μ (mm^{-1})	0.93	0.80	1.20
crystal size (mm)	0.14 × 0.12 × 0.10	0.30 × 0.20 × 0.15	0.50 × 0.40 × 0.30
R_{int}	0.035	0.066	0.044
θ_{max} (°)	30.2	27.5	30.0
R[$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.072, 0.200, 1.03	0.072, 0.190, 1.03	0.044, 0.115, 1.07
ρ_{max}, ρ_{min} (e Å^{-3})	1.69,−1.21	1.12,−1.11	0.85,−0.81

was filtered and the volatiles were removed under reduced pressure to give a green solid, which was washed with diethylether (2 × 15 mL) and pentane (2 × 20 mL) and dried under vacuum to give a pale green solid (1.10 g, 70%). Anal. Calcd for $C_{46}H_{50}NiO_6P_4$: C, 62.68; H, 5.72. Found: C, 59.25; H, 6.05. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −5.8 (br s, PPh$_2$), 27.4 (br s, PO). IR (KBr): $\nu_{P=O} = 1251$ (s) cm^{-1}. Mass spectrum (ESI): *m/z* 883.21 [M$^+$ + H].

Crystal Structure Determinations. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane or pentane into a dichloromethane solution of the complex at 5 °C. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) (Tables 8 and 9). Data were collected using φ-scans and the structures were solved by direct methods using the SHELX 97 software and the refinement was by full-matrix least-squares on F^2.[51,52] 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, $U_{11} = 0.04$). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC 705823−705831. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

Oligomerization of Ethylene. All catalytic tests were started between 25 and 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 10 bar. A temperature increase was observed that resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 min), a dry ice bath was used to rapidly cool down the reactor, thus stopping the reaction. An ice bath was then used and when the inner temperature reached 0 °C, the ice bath was removed allowing the temperature to slowly rise to 10 °C. The gaseous phase was then transferred 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 into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

With AlEtCl$_2$ (Table 6), 4 × 10^{-5} mol of Ni complex were dissolved in cholorobenzene and injected into the reactor under an ethylene flux. Then a cocatalyst solution corresponding to 3, 6, 10,

---

(49) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(50) Cotton, F. A. *Inorg. Synth.* **1971**, *13*, 160.
(51) *Kappa CCD Operation Manual*; Nonius BV, D.: The Nederland.
(52) Sheldrick, G. M. *SHELXL97, Program for the refinement of crystal structures*; University of Göttingen: Germany, 1997.

or 14 equiv was added to form a total volume of 15 mL with the precatalyst solution.

With MAO (Table 7), 4 × 10^{-5} mmol of Ni complex was dissolved in chlorobenzene and injected into the reactor under an ethylene flux. Then a cocatalyst solution corresponding to 100, 200, or 400 equiv of MAO respectively, was added to form a total volume of 20 mL with the precatalyst solution.

Acknowledgment. Dedicated to Professor Richard J. Puddephatt for his numerous and outstanding contributions to inorganic and organometallic chemistry. This work was supported by the Centre National de la Recherche Scientifique and the Ministère de l'Enseignement Supérieur et de la Recherche. We are grateful to Drs. L. Brelot and A. DeCian and Professor R. Welter (ULP Strasbourg) for the resolution of the crystal structures, to Dr. X. Morise for his contribution, and to M. Mermillon-Fournier for technical assistance.

Supporting Information Available: Crystallographic details for all structures in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8020436