Chemoselective Reactions of the Phosphino Enolate Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] with Ph_2P-Cl and M−Cl Bonds (M = Pd, Pt). Coordination Properties of the New Functional Diphosphine Ligand $(Ph_2P)_2CHC(O)NPh_2$. Hemilabile Behavior of $[Cu_2\{(Ph_2P)_2CHC(O)NPh_2\text{-}P,P,O\}_2](BF_4)_2$. Reactivity and Molecular Structure of [(8-mq)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}]†

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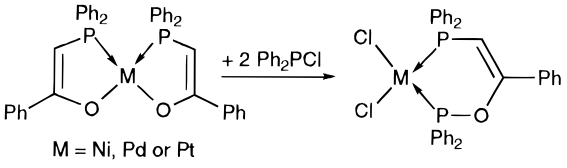
The functional phosphine $Ph_2PCH_2C(O)NPh_2$ (**L**[1]) was obtained by P−C selective coupling of Ph_2PCl with Li[$CH_2\cdots C(\cdots O)NPh_2$] and we have studied the influence of the $-NPh_2$ substituent on the reactivity of the corresponding enolate Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] toward P−Cl and M−Cl bonds (M = Pd, Pt). A selective P−C coupling reaction with Ph_2PCl allowed the synthesis of the new diphosphine ligand $(Ph_2P)_2CHC(O)NPh_2$ [bis(diphenylphosphino)-*N*,*N*-diphenylacetamide] (**L**[2]). The dicationic dinuclear complex $[Cu_2\{(Ph_2P)_2CHC(O)NPh_2\text{-}P,P,O\}_2](BF_4)_2$ (**3**) has been obtained from the reaction of $[Cu(NCMe)_4](BF_4)$ with **L**[2]. A preliminary X-ray diffraction study revealed a μ_2-η^3 tripod-like bonding for **L**[2] in this centrosymmetric dimeric complex: each copper atom is P,O-chelated by one ligand and P-bonded to the other ligand. An eight-membered $Cu_2P_4C_2$ ring is thus formed with the functional diphosphine ligand. The dynamic behavior has been studied in $CHCl_3$ solution of mono- and binuclear copper(I) complexes of **L**[1] and **L**[2]. Reversible oxygen-metal dissociation occurs in the presence of donor solvents such as NCMe or SMe_2. The reaction of Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] with [(C N)Pd($\mu$-Cl)$_2$] afforded the complexes [(C N)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] [(**9**) (C N) = dimethylbenzylamine (dmba); (**10**) (C N) = 8-methylquinoline (8-mq)]. The molecular structure of [(8-mq)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] has been determined by single-crystal X-ray diffraction: it crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 8.801(2)$ Å, $b = 31.483(6)$ Å, $c = 10.939(2)$ Å, $\beta = 101.37(2)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares methods on the basis of 2863 observed reflections to R and R_w values of 0.0268 and 0.0338, respectively. A temperature dependence of the reaction of Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] with [$PtCl_2(NCPh)_2$] has been observed which leads to *cis*-Pt[$Ph_2PCH\cdots C(\cdots O)NPh_2$]$_2$ (**11**) at −60 °C and to *trans*-Pt[$Ph_2PC\{=C(NH)Ph\}\{C(O)NPh_2\}$]$_2$ (**12**) at 0 °C. The high reactivity of *cis*-Pt[$Ph_2PCH\cdots C(\cdots O)NPh_2$]$_2$ toward *p*-MeC_6H_4NCO leads to two diastereoisomeric products *cis*-Pt[$Ph_2PCH\{C(O)N(p\text{-}MeC_6H_4)\}\{C(O)NPh_2\}$]$_2$ (**16a,b** in a 1:1 ratio), which contain new chiral heterodifunctional phosphines.

Introduction

As part of our interest in the synthesis, coordination properties and reactivity of multifunctional phosphine ligands containing hard and soft donor functions, we have previously described the reactions of transition metal complexes containing phosphino enolate ligands of the type $[Ph_2PCH\cdots(C\cdots O)Ph]^-$ with chlorophosphines such as Ph_2PCl and $PhPCl_2$.[2,3] Some of these reactions are given in eqs 1 and 2. Both reactions occurred with P−O bond formation. Likewise, reaction of the lithium phosphino enolate Li[$Ph_2PCH\cdots C(\cdots O)Ph$] with Ph_2PCl resulted in the formation of a P−O bond to yield a phosphine, phosphinite-type ligand (eq 3).[4]



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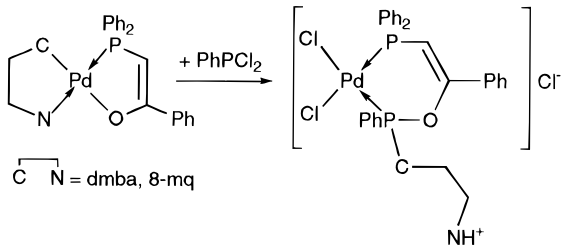

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† Dedicated to Professor Max Herberhold on the occasion of his 60th birthday (August 2, 1996), with our sincere congratulations and warmest wishes.

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(1) (a) Université Louis Pasteur. (b) Università di Parma.
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Table 1. Selected IR and ^{1}H and ^{31}P{^{1}H} NMR Data

compounds		IR/cm^{-1}		
no.	formula	ν(C=O)[a]	^{1}H NMR[b]	^{31}P{^{1}H} NMR[c]
L^1	$Ph_2PCH_2C(O)NPh_2$	1658 (vs)	(PCH_2) 3.20 (s, br)	−14.6 (s)
L^2	$(Ph_2P)_2CHC(O)NPh_2$	1651 (vs)	(P_2CH) 4.60 (s, br)	−1.4 (s)
1	*cis*-[$PtCl_2${$(Ph_2P)_2CHC(O)NPh_2$-*P*,*P*}]	1658 (vs)	(P_2CH) 4.32 (d, ^2J(PH) = 4.1, 2.1)	−48.6 (s, ^1J(PtP) = 3412)
2	[(dmba)Pd{$(Ph_2P)_2CHC(O)NPh_2$-*P*,*N*}](BF_4)	1650 (vs)	(P_2CH) 5.44 (d, ^2J(PH) = 8.9, 6.0)	10.9 (d, ^2J(PP) = 63.9) −17.7 (d, ^2J(PP) = 63.9)
3	[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P*,*P*,*O*}$_2$](BF_4)$_2$	1566 (s) 1658 (m),	(P_2CH) 5.27 (quint, ^2J(PH) = 3.3)	19.1 (s, br)
4	[Cu{$Ph_2PCH_2C(O)NPh_2$}{L^1}](BF_4)	1618 (m)	(PCH_2) 3.46 (s, br)	−7.0 (s, br)
5a	[Cu{$Ph_2PCH_2C(O)NPh_2$}$_2$(NCMe)](BF_4)	1662 (vs)	(PCH_2) 3.22 (d, ^2J(PH) = 6.8)	−11.8 (s, br)
5b	[Cu{$Ph_2PCH_2C(O)NPh_2$}$_2$(SMe_2)](BF_4)	1659 (vs)	(PCH_2) 3.17 (s, br)	−8.7 (s, br)
6a	[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P*,*P*}$_2$($NCMe)_2$](BF_4)$_2$	1653 (vs)	(P_2CH) 4.99 (t, ^2J(PH) = 6.8)	5.2 (s, br)
6b	[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P*,*P*}$_2$($SMe_2)_2$](BF_4)$_2$	1650 (vs)	(P_2CH) 4.93 (t, ^2J(PH) = 6.6)	8.1 (s, br)
7	[(dmba)PdCl{$Ph_2PCH_2C(O)NPh_2$}]	1657 (vs)	(PCH_2) 3.72 (d, ^2J(PH) = 10.6)	30.8 (s)
8	[(dmba)Pd{$Ph_2PCH_2C(O)NPh_2$}](BF_4)	1559 (vs)	(PCH_2) 4.00 (d, ^2J(PH) = 11.4)	31.4 (s)
9	[(dmba)Pd{$Ph_2PCH{\cdots}C({\cdots}O)NPh_2$}]		(PCH) 3.28 (d, ^2J(PH) = 1.5)	25.0 (s)
10	[(8-mq)Pd{$Ph_2PCH{\cdots}C({\cdots}O)NPh_2$}]		(PCH) 3.28 (d, ^2J(PH) = 1.0)	20.8 (s)
11	*cis*-Pt[$Ph_2PCH{\cdots}C({\cdots}O)NPh_2$]$_2$		(PCH) 3.02 (d, ^2J(PH) = 4.3)	2.0 (s, ^1J(PtP) = 3500)
12	*trans*-Pt[Ph_2PC{=C(NH)Ph}{C(=O)NPh_2}]$_2$	1607 (s)	(NH) 4.97 (s, ^2J(PtH) = 44.4)	42.6 (s, ^1J(PtP) = 2534)
13	[*trans*-Pt{Ph_2PC[C(=O)NPh_2][=C(NH_2)Ph]}$_2$](BF_4)$_2$	1663 (vs)	(NH) 5.81 (t, ^4J(PH) = 1.2) (NH···O) 10.95	46.3 (s, ^1J(PtP) = 2677)
14a	[(dmba)Pd{$Ph_2PC[{\cdots}C({\cdots}O)NH$(*p*-$MeC_6H_4$)][C(O)$NPh_2$]}]	see text	(NH···O) 10.4	38.1 (s)
14b	[(dmba)Pd{Ph_2PCH[C(O)N(*p*-MeC_6H_4)][C(O)NPh_2]}]	see text	(PCH) 4.84 (d, ^2J(PH) = 12.8)	37.2 (s)
15a	[(8-mq)Pd{$Ph_2PC[{\cdots}C({\cdots}O)NH$(*p*-$MeC_6H_4$)][C(O)$NPh_2$]}]	see text	(NH···O) 10.4	36.4 (s) or 33.4 (s)
15b	[(8-mq)Pd{Ph_2PCH[C(O)N(*p*-MeC_6H_4)][C(O)NPh_2]}]	see text	(PCH) 5.02 (d, ^2J(PH) = 12.2)	33.4 (s) or 36.4 (s)
16a,b	*cis*-Pt[Ph_2PCH{C(O)N(*p*-MeC_6H_4)}{C(O)NPh_2}]$_2$	1662 (vs), 1617 (vs)	(PCH) 4.79 (d, ^2J(PH) = 11.7) (PCH) 5.14 (d, ^2J(PH) = 10.8)	11.6 (s, br, ^1J(PtP) = 3100) 8.6 (s, ^1J(PtP) = 3175)

[a] Recorded as KBr pellet, except for **3**, **4**, **8**, and **9** in CH_2Cl_2; **5a**, **6a** in MeCN; and **5b**, **6b** in SMe_2. For complexes containing BF_4^-, a typical absorption is found around 1055 cm^{-1} (KBr pellet). [b] All spectra were recorded in $CDCl_3$, except for **5a**, **6a** in CD_3CN; **5b** in $CDCl_3/SMe_2$; **6b** in CD_2Cl_2/SMe_2; and **1**, **2**, **3**, **13**, and **16** in CD_2Cl_2; *J* values in Hz. [c] All spectra were recorded in $CDCl_3$, except for **5a**, **6a** in CD_3CN; **5b** in $CDCl_3/SMe_2$; **6b** in CD_2Cl_2/SMe_2; **7**, **8**, **10** in C_6D_6/CH_2Cl_2; **1**, **2**, **13**, and **16** in CD_2Cl_2/THF; and **15a,b** in C_6D_6/THF; *J* values in Hz.

$$Li[Ph_2PCH{\cdots}C({\cdots}O)Ph] \xrightarrow[-\ LiCl]{+\ Ph_2PCl\ /\ Et_2O} Ph_2PCH{=}C(Ph)OPPh_2 \quad (3)$$

That selective P−O coupling would take place might have been anticipated on the basis of the known oxophilicity of chlorophosphines, although reaction of the lithium enolate of acetophenone, Li[$CH_2{\cdots}C({\cdots}O)Ph$], with Ph_2PCl exclusively occurred by P−C bond formation, yielding the corresponding ketophosphine ligand $Ph_2PCH_2C(O)Ph$ in high yield.[5] The generality of this method has since been demonstrated.[6]

We were interested in investigating the role of the substituent R in Li[$Ph_2PCH{\cdots}C({\cdots}O)R$] on the chemoselectivity of such reactions and set out to study the system in which R = NPh_2.

Results

Synthesis and Reactivity of the New Functional Diphosphine Ligand $(Ph_2P)_2CHC(O)NPh_2$ (L^2). We have recently prepared the ligand 2-diphenylphosphino-*N*,*N*-diphenylacetamide $Ph_2PCH_2C(O)NPh_2$ (**L^1**) by the completely chemoselective reaction of Ph_2PCl with Li[$CH_2{\cdots}C({\cdots}O)NPh_2$] in THF at −70 °C.[7] This ligand can coordinate to metals via the phosphorus atom only, as with [Pd(dba)$_2$] (dba = dibenzylideneacetone), or can form unsymmetrical *P*,*O* chelates with palladium(II) complexes.[7] Its corresponding enolate has been readily obtained by deprotonation with Li[N(^{i}Pr)$_2$)] (LDA) and reacted with Ph_2PCl in THF at −70 °C. The new diphosphine $(Ph_2P)_2CHC(O)NPh_2$ (**L^2**) was formed as a result of P−C bond formation and isolated in high yield. Its spectroscopic characteristics include a singlet resonance in the ^{1}H NMR spectrum for the P_2CH proton at δ 4.60 and a singlet in the ^{31}P{^{1}H} NMR spectrum at δ −1.4. The strong absorption in the IR spectrum at 1651 cm^{-1} is similar to that observed at 1658 cm^{-1} for **L^1** (Table 1).[7] Obviously, the *C*-nucleophilicity of the enolate derived from **L^1** has been restored on going from R = Ph to R = NPh_2 (Scheme 1).

Reaction of ligand **L^2** with *n*-BuLi or LDA in THF at −60 °C, followed by addition of Ph_2PCl, did not lead to further P−O or P−C coupling reactions.

The ligand **L^2** could in principle bind to metal centers by forming a four-membered *P*,*P* chelate, like dppm or $(Ph_2P)_2$-CHC(O)Ph,[8] five-membered *P*,*O* or *P*,*N* chelates, or a *P*,*P*,*O* or *P*,*P*,*N* bridge. To explore these possibilities, we reacted **L^2** with different metal complexes. Formation of a four-membered *P*,*P* chelate was observed in the reaction of **L^2** with $PtCl_2$-$(NCPh)_2$ which yielded *cis*-[$PtCl_2${$(Ph_2P)_2CHC(O)NPh_2$-*P*,*P*}]

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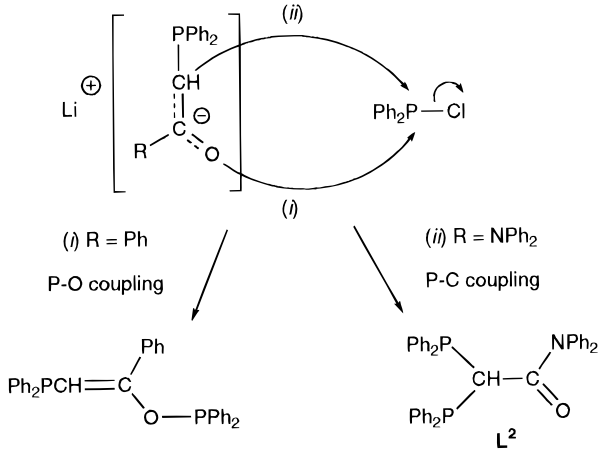
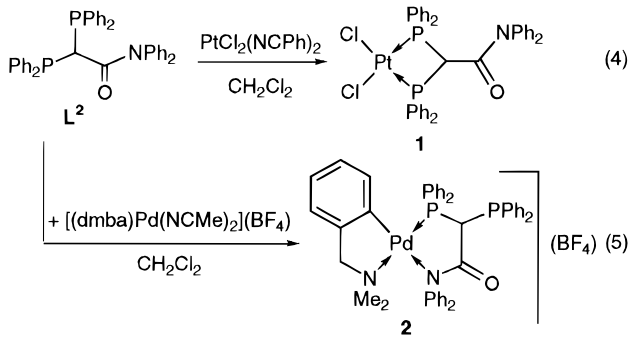
Scheme 1

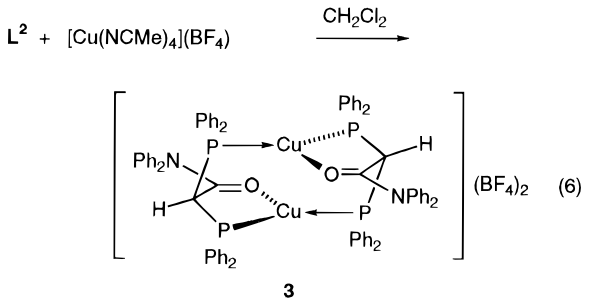


(**1**) (eq 4); as indicated by the $^{31}P\{^1H\}$ NMR resonance at δ −48.6 with $^1J(PtP) = 3214$ Hz and an IR absorption at 1658



cm^{-1} for the amide function, similar to that in free $\mathbf{L^2}$. Reaction of $\mathbf{L^2}$ with the palladium complex [(dmba)Pd(NCMe)$_2$](BF$_4$)[9] (dmba = *o*-C$_6$H$_4$CH$_2$NMe$_2$) yielded [(dmba)Pd{(Ph$_2$P)$_2$CHC(O)NPh$_2$-*P,N*}](BF$_4$) (**2**) in which $\mathbf{L^2}$ forms a five-membered *P,N* chelate (eq 5). This was established by $^{31}P\{^1H\}$ NMR spectroscopy where two doublets were observed at δ −17.7 for the uncoordinated P atom and at δ 10.9 for the coordinated P atom with $^2J(PP) = 63.9$ Hz. The ν(C═O) value of 1650 cm^{-1} indicates *P,N*- rather than *P,O*-chelation. If the latter bonding mode were to occur, a ν(C═O) absorption around 1560 cm^{-1} would be expected, as observed for **8** (see below).

When $\mathbf{L^2}$ was reacted with 1 equiv of [Cu(NCMe)$_4$](BF$_4$)[10] in CH$_2$Cl$_2$, a complex was isolated which corresponds to the formulation [Cu$\mathbf{L^2}$](BF$_4$) (eq 6). A preliminary X-ray structure



determination of [Cu$_2${(Ph$_2$P)$_2$CHC(O)NPh$_2$-*P,P,O*}$_2$](BF$_4$)$_2$ (**3**) established its centrosymmetric, dimeric nature.[11] Each ligand acts as a μ_2-η^3 tripod, being a *P,O*-chelate to a Cu ion and

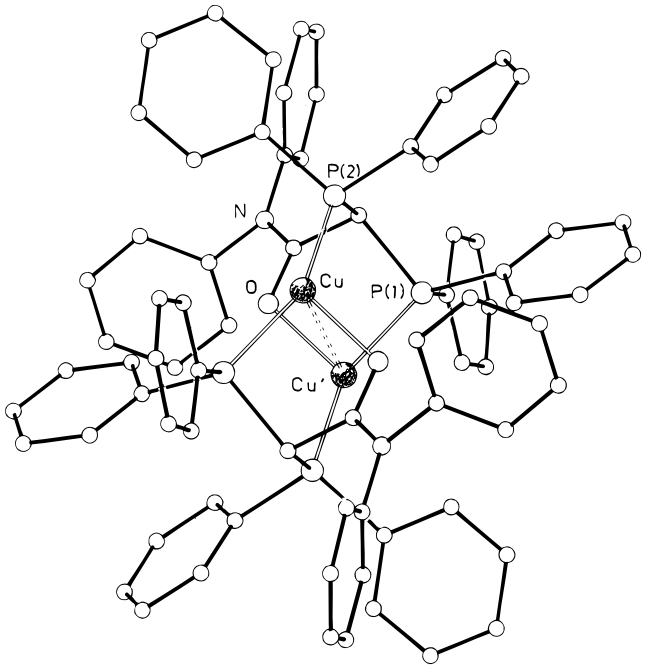
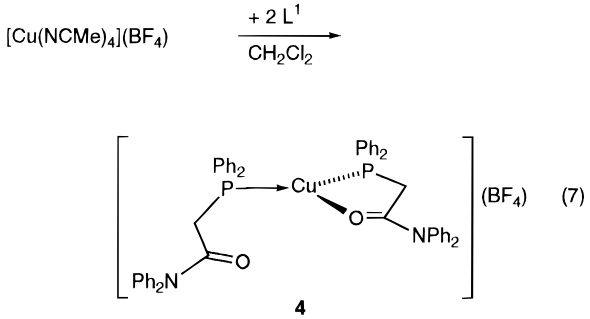


Figure 1. View of the molecular structure of the complex [Cu$_2${(Ph$_2$P)$_2$-CHC(O)NPh$_2$-*P,P,O*}$_2$] (BF$_4$)$_2$ (**3**) (see text).

P-bound to the other (Figure 1). The two Cu(I) centers are maintained at a relatively short distance[12] of 2.857(2) Å by this new assembling ligand. The bond distances involving the copper coordination are as follows: Cu−P = 2.263(3) and 2.205(3) Å and Cu−O = 2.148(7) Å. An eight-membered Cu$_2$P$_4$C$_2$ ring and a 10-membered Cu$_2$P$_2$O$_2$C$_4$ ring may be identified in this unusual structure. The IR spectrum of **3** shows a strong band at 1566 cm^{-1} for the coordinated carbonyl function. At room temperature, the $^{31}P\{^1H\}$ spectrum NMR in CDCl$_3$ (see Table 1) indicates that the four phosphorus atoms are equivalent at δ 19.1 ppm, as a consequence of dynamic exchange between the ligands (see below). A pseudoquintet resonance in the ^{1}H NMR spectrum at δ 5.27 with $^2J(PH) = 3.3$ Hz spectrum is assigned to the P$_2$CH proton.

Hemilabile Behavior of the Ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ in Copper(I) Complexes. The complex [Cu(NCMe)$_4$](BF$_4$) was reacted with two equivalents of $\mathbf{L^1}$ in CH$_2$Cl$_2$ at room temperature and gave the monocationic complex [Cu{Ph$_2$PCH$_2$C(O)NPh$_2$}{Ph$_2$-CH$_2$C(O)NPh$_2$}](BF$_4$) (**4**) (eq 7). The IR spectrum of **4** displays



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(10) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90−91.
(11) The crystals of the copper complex **3** were of very small size and of poor quality, so it was possible to determine its structure, but a satisfactory refinement was prevented. Crystal data: [C$_{76}$H$_{62}$Cu$_2$N$_2$O$_2$P$_4$]-[BF$_4$]$_2$·2CHCl$_3$, monoclinic, space group $P2_1/n$, a = 14.829(3) Å, b = 17.731(4) Å, c = 14.796(3) Å, β = 96.71(2)°, V = 3864(3) Å^3, Z = 2, and R = 0.0115.
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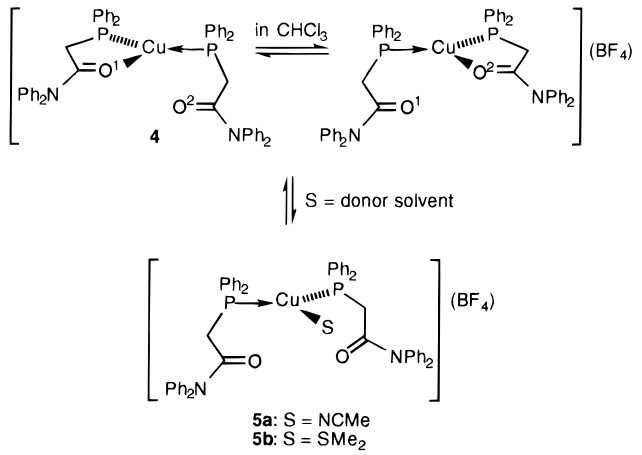
absorption bands at 1658 and 1618 cm^{-1}, indicating the coexistence in the molecule of two bonding modes for $\mathbf{L^1}$, namely *P*-monodentate and *P,O*-chelate. However, the $^{31}P\{^1H\}$ spectrum NMR (see Table 1) in $CDCl_3$ shows that the two phosphorus atoms are equivalent at room temperature, which is confirmed in the ^1H NMR spectrum by broad signals for the methylene groups of $\mathbf{L^1}$. This observation suggests a dynamic exchange between the ligands around a tricoordinated metal center, similar to that previously observed in mononuclear copper(I) complexes containing β-ketophosphine ligands[13] (Scheme 2). When the mononuclear complex **4** was dissolved

Scheme 2



in a donor solvent such as acetonitrile, formation of **5a** was observed. The IR spectrum of **5a** contains only one band in the carbonyl region at 1662 cm^{-1}, which is assigned to the dangling oxygen atoms of the ligands $\mathbf{L^1}$ (Scheme 2). Accordingly, the $^{31}P\{^1H\}$ and ^1H NMR spectra (see Table 1) in CD_3CN indicate the equivalence of the two phosphorus atoms with a singlet at δ −11.8, and a well-resolved doublet for the CH_2 protons of the chemically equivalent ligand $\mathbf{L^1}$. When the NMR solvent CD_3CN was removed *in vacuo* from a solution of **5a** in a NMR tube, complex **4** was regenerated (identified by ^1H and $^{31}P\{^1H\}$ NMR). Moreover, when **4** was dissolved in a mixture of CD_2Cl_2/CH_3CN, the $^{31}P\{^1H\}$ NMR spectrum exhibited a resonance at −9.4 ppm, a chemical shift which is intermediate between those of **4** at −7.0 ppm and of **5a** at −11.8 ppm. The lability of the oxygen−copper bond in complex **4** has also been observed in SMe_2 to give **5b** (see Experimental Section). These experiments show the reversible coordination of small molecules (RCN, SR_2) to complex **4**, accompanied by opening and closing of the *P,O*-chelate. Related reversible displacement reactions have been observed with Re(I) and Ru(II) complexes containing a β- or a γ-ketophosphine ligand, respectively.[14]

From these results, it was anticipated that complex **3** would also undergo a dynamic behavior. This has been studied by variable temperature $^{31}P\{^1H\}$ NMR in CD_2Cl_2. At −50 °C, two different signals are observed at 20.0 and 17.5 ppm which correspond to the bonding modes *P*-monodentate and *P,O*-chelate of $\mathbf{L^2}$ respectively, and coalescence was observed around 5 °C (Scheme 3) (Figure 2).

As with complex **4**, reversible coordination of small molecules CH_3CN (or SMe_2) has been observed for the binuclear complex

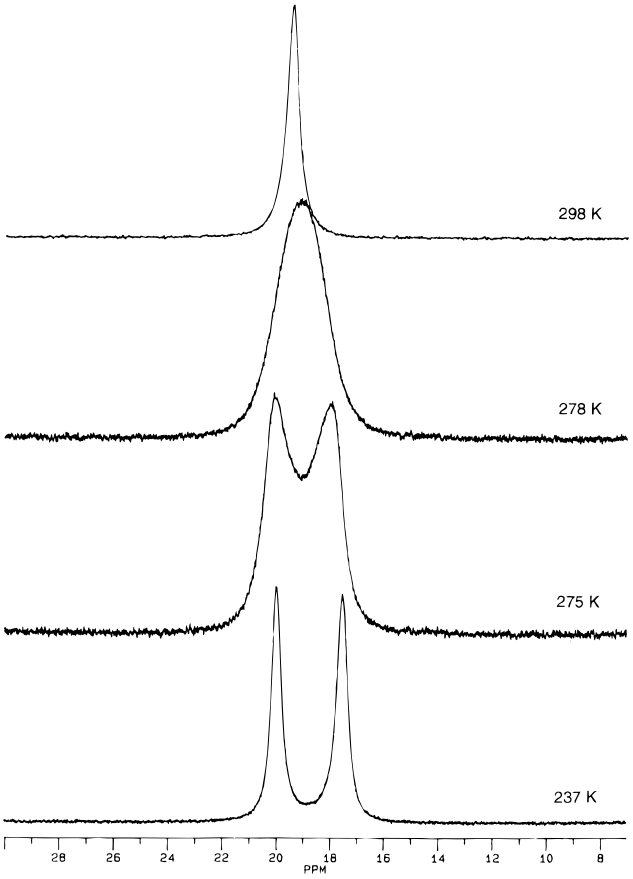


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectrum of complex **3**.

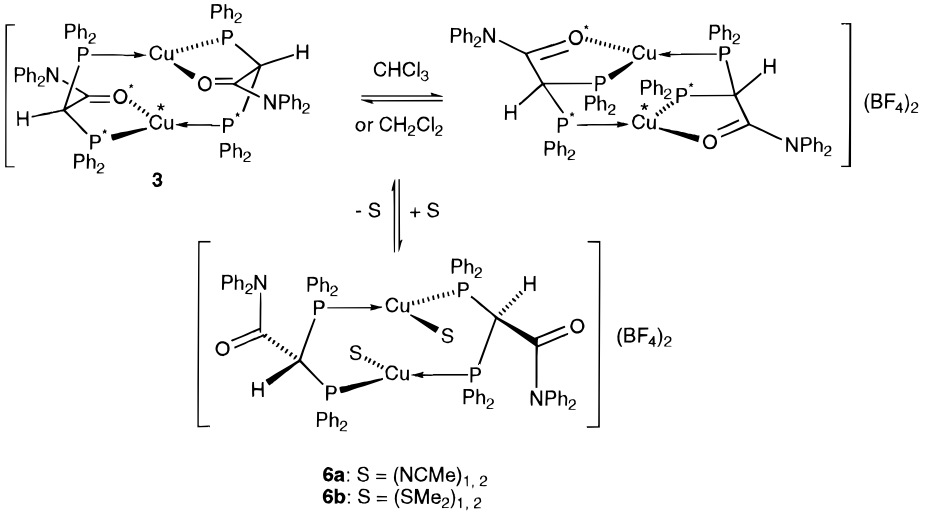
3 (see below). In CH_3CN, a new IR band grows in at 1653 cm^{-1} at the expense of that at 1566 cm^{-1}, indicating displacement of the oxygen donor by acetonitrile. Addition of CH_2Cl_2 progressively restores the IR band at 1566 cm^{-1} and the *P,P,O* bonding for the bridging ligand $\mathbf{L^2}$ in **3** (Scheme 3).

Synthesis of Phosphino Enolate Complexes. We have seen above that the chemo selectivity of the reaction between the lithium phosphino enolates Li[$Ph_2PCH\cdots C(\cdots O)R$] (R = Ph, NPh_2) and Ph_2PCl is governed by the nature of R. We wished to extend to M−Cl bonds a comparison of their reactivity. The reaction of Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] with [(dmba)Pd($\mu$-Cl)]$_2$ led to the phosphino enolate-*P,O* chelate complex [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] (**9**). Its spectroscopic data (Table 1) are similar to those of the corresponding complex with [$Ph_2PCH\cdots C(\cdots O)Ph$]$^-$.[5] Complex **9** has also been obtained in lower yield by deprotonation of the complexes [(dmba)PdCl{$Ph_2PCH_2C(O)NPh_2$}] (**7**) or [(dmba)Pd{$Ph_2PCH_2C(O)NPh_2$}](BF_4) (**8**) with NaH or LDA respectively (Scheme 4). The crystal structure determination of [(8-mq)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] (**10**), the 8-mq analog of **9**,[7] established the molecular structure drawn.

Crystal Structure of [(8-mq)Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] (10). A view of the structure of complex **10** is shown in Figure 3; selected bond distances and angles are given in Table 2. The palladium has a square planar coordination involving the N(1) and C(10) atoms from the 8-mq ligand [Pd−N(1) = 2.076(3) Å and Pd−C(10) = 2.026(7) Å] and the O(1) and P atoms from the phosphino enolate ligand [Pd−P = 2.232(2) Å and Pd−O(1) = 2.108(4) Å], both acting as chelating ligands. The coordinated atoms are perfectly coplanar with the metal

(13) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *J. Organomet. Chem.* **1989**, *367*, 117−132.
(14) (a) Braunstein, P.; Douce, L.; Balegroune, F.; Grandjean, D.; Bayeul, D.; Dusausoy, Y.; Zanello, P. *New J. Chem.* **1992**, *16*, 925−929. (b) Demerseman, B.; Le Lagadec, R.; Guilbert, B.; Renouard, C.; Crochet, P.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 2269 −2283.

Scheme 3



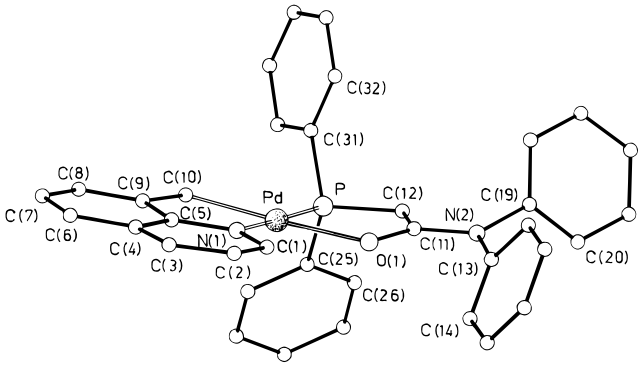
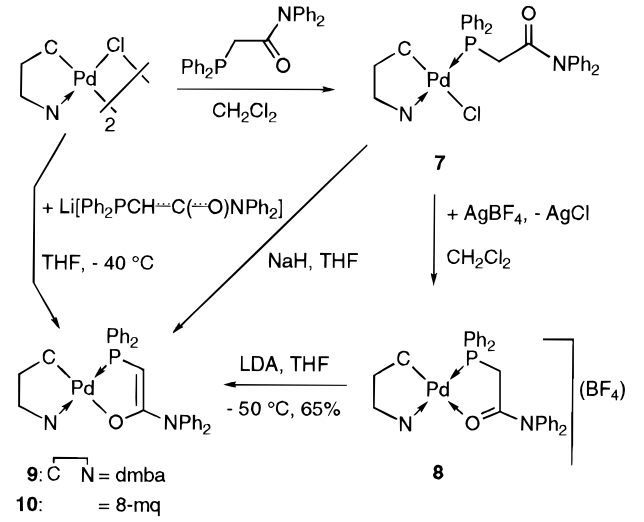


Figure 3. View of the molecular structure of the complex [(8-mq)-Pd{$Ph_2PCH\cdots C(\cdots O)NPh_2$}] (**10**).

Scheme 4



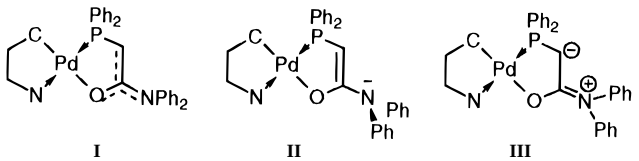
atom which deviates by 0.048(1) Å from this plane. In both pentaatomic chelating rings the four atoms of the ligands are perfectly coplanar, and the palladium atom deviates only slightly from the 8-mq plane (0.082(1) Å) but more significantly from the phosphino enolate plane (0.297(1) Å). These two planes form an angle of 11.4(2)°. The structural parameters within the Pd(8-mq) moiety are similar to those found in related complexes.[15a,16] For example in the structure of [(8-mq)PdBr{$Ph_2PCH_2C(O)OEt$}], in which the N atom is also trans with respect to the P atom, the Pd−P, Pd−N and Pd−C bond distances are

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **10**

Pd−P	2.232(2)	Pd−O(1)	2.108(4)
Pd−N(1)	2.076(3)	Pd−C(10)	2.026(7)
P−C(12)	1.737(5)	P−C(25)	1.827(4)
P−C(31)	1.827(4)	O(1)−C(11)	1.302(5)
N(1)−C(1)	1.322(6)	N(1)−C(5)	1.375(7)
N(2)−C(11)	1.390(5)	N(2)−C(13)	1.436(5)
N(2)−C(19)	1.439(5)	C(5)−C(9)	1.407(6)
C(9)−C(10)	1.519(6)	C(11)−C(12)	1.378(5)

N(1)−Pd−C(10)	83.5(2)	O(1)−Pd−N(1)	93.6(1)
P−Pd−C(10)	98.7(2)	P−Pd−O(1)	84.0(1)
Pd−P−C(31)	117.7(1)	Pd−P−C(25)	118.0(1)
Pd−P−C(12)	100.0(2)	C(25)−P−C(31)	102.8(2)
C(12)−P−C(31)	108.4(2)	C(12)−P−C(25)	109.6(2)
Pd−O(1)−C(11)	114.8(2)	Pd−N(1)−C(5)	113.1(3)
Pd−N(1)−C(1)	127.6(3)	C(1)−N(1)−C(5)	119.3(4)
C(13)−N(2)−C(19)	116.6(3)	C(11)−N(2)−C(19)	120.8(3)
C(11)−N(2)−C(13)	122.2(3)	N(1)−C(5)−C(9)	116.7(5)
C(5)−C(9)−C(10)	117.6(4)	O(1)−C(11)−N(2)	115.7(3)
N(2)−C(11)−C(12)	120.7(3)	O(1)−C(11)−C(12)	123.6(4)
P−C(12)−C(11)	116.3(3)		

2.232(1), 2.094(5), and 2.042(6) Å, respectively. In the phosphino enolate ligand of **10**, the double bond delocalization is shown by the value of the P−C(12) bond distance, 1.737(5) Å, which is much shorter than those of the P−C(25) and P−C(31) bonds, 1.827(4) Å, and by the values of the C(11)−C(12) and C(11)−O(1) bonds, 1.378(5) and 1.302(5) Å, which are in agreement with a partial double bond character (see form **I**). The structural parameters in this ligand are similar to those



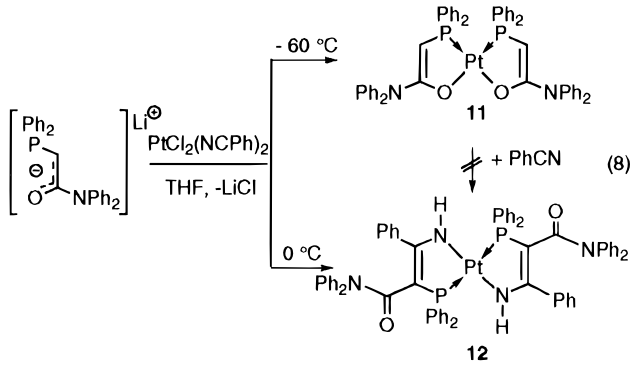
found in other complexes with the related ligand [$Ph_2PCH\cdots C(\cdots O)Ph]^-$, such as [{$Ru(\mu\text{-}Cl)[Ph_2PCH\cdots C(\cdots O)Ph](CO)_2\}_2$].[17] The planar geometry around the nitrogen atom N(2) (sum of its valency angles 360.6°) together with the short

(15) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115−5125. (b) Braunstein, P.; Matt, D; Nobel, D.; Bouaoud, S.-E.; Grandjean, D. *J. Organomet. Chem.* **1986**, 301, 401−410.

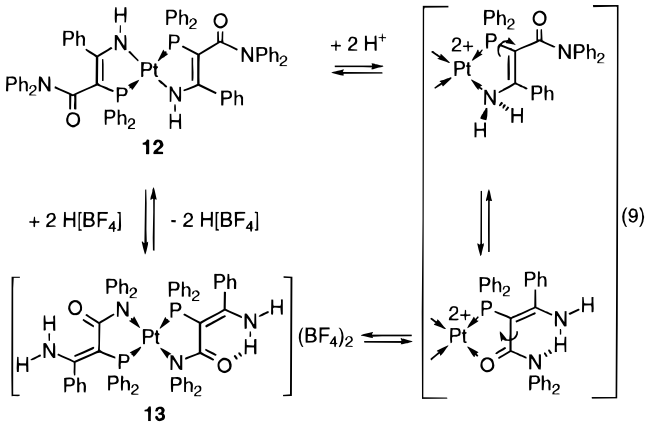
(16) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410−421.

N(2)−C(11) distance of 1.390(5) Å are consistent with a significant double bond character for the latter bond and a greater contribution of resonance form **III** over form **II** to the overall structure.[18] The Pd−P and Pd−O bond distances are comparable with those found in [(dmba)Pd{$Ph_2PCH\cdots C(\cdots O)OEt$}], 2.242(2) and 2.117(5) Å, respectively, in which the enolate of the ethyl diphenylphosphinoacetate ligand forms a three-electron donor (*P,O*)-chelate ring strictly related to that of **10**,[15a] and in [(dmba)Pd{$Ph_2PCH_2C(O)O$}], 2.218(1) and 2.105(3) Å, in which a phosphinoacetato ligand chelates the Pd(II) center.[15b]

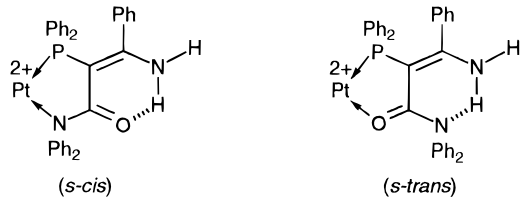
Reactivity of the Lithium Enolate toward Coordinated Benzonitrile. When Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] was reacted with [$PtCl_2(NCPh)_2$] in THF at −60 °C, the complex *cis*-Pt[$Ph_2PCH\cdots C(\cdots O)NPh_2$]$_2$ (**11**) was formed and isolated in high yield. Its spectroscopic properties (Table 1) are very similar to those of *cis*-Pt[$Ph_2PCH\cdots C(\cdots O)Ph$]$_2$.[5] However, when this reaction was performed at 0 °C, another product was isolated instead, the analytical and spectroscopic data of which are consistent with the structure *trans*-Pt[$Ph_2PC\{=C(NH)Ph\}\{C(O)NPh_2\}$]$_2$ (**12**) (eq 8). In the $^{31}P\{^1H\}$ NMR spectrum a



singlet resonance is found at δ 42.6 with ^1J(PtP) = 2534 Hz, and in the ^{1}H NMR spectrum the NH proton gives rise to a singlet at δ 4.97 with ^{195}Pt satellites (^2J(PtH) = 44.4 Hz). In the IR spectrum, the ν(NH) and ν(CO) vibrations are found at 3374 and 1607 cm^{-1}, respectively. In this complex, the benzonitrile ligand has formally inserted into the PC−H bond of the enolate anion. Obviously, the nucleophilic carbon atom of [$Ph_2PCH\cdots C(\cdots O)NPh_2$]$^-$ has attacked the CN carbon atom of the coordinated benzonitrile ligand, this being followed by proton transfer from the enolate carbon to the nitrogen atom. When the platinum complexes [$PtCl_2(NC{-}CH{=}CH_2)_2$] or [$PtCl_2$(1,5-COD)] were reacted with Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$], either at −60 °C or at 0 °C, only *cis*-Pt[$Ph_2PCH\cdots C(\cdots O)NPh_2$]$_2$ (**11**) was isolated. This is most likely due to the greater lability of the $CH_2{=}CH{-}CN$ and 1,5-COD ligands. Furthermore, the reaction of a mixture of Li[$Ph_2PCH\cdots C(\cdots O)NPh_2$] and PhCN at −60 °C with [$PtCl_2$(COD)] did not lead to complex **12** but to **11**, confirming that metal coordination of the benzonitrile ligand results in its activation toward nucleophiles.[19] Reaction of **12** with acids resulted in protonation of the coordinated ligand and formation of *trans*-[Pt{$Ph_2PC[C(O)NPh_2][{=}C(NH_2)Ph]$}$_2$](BF$_4$)$_2$ (**13**) which contains unusual phosphine amide, enamine ligands (eq 9).



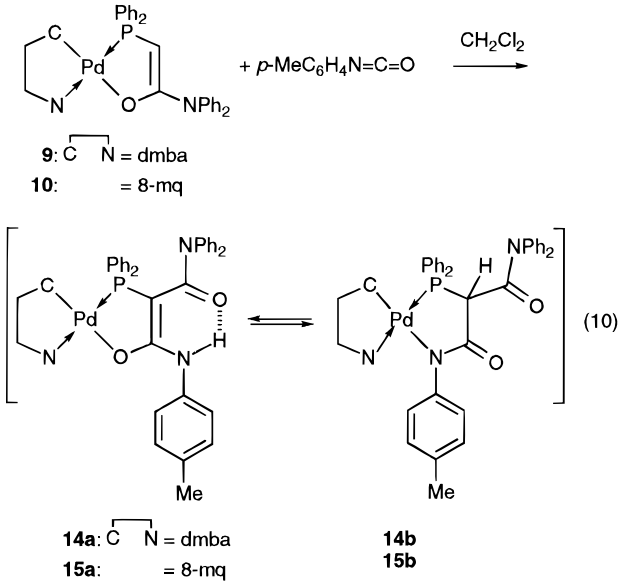
Protonation is likely to occur at the coordinated nitrogen atom (although alternatives are conceivable) and would be followed by rotation of the ligand about the P−C bond and coordination of the NPh_2 donor group. The isomeric structure *s-trans* with



respect to the C_P-C_N bond was ruled out on the basis of the ^{1}H NMR resonance for the NH proton at δ 10.95, a chemical shift more consistent with a NH···O than a NH···N hydrogen bond.[20] Deprotonation of **13** by NaH or NEt_3 occurs readily and regenerates **12** (eq 9).

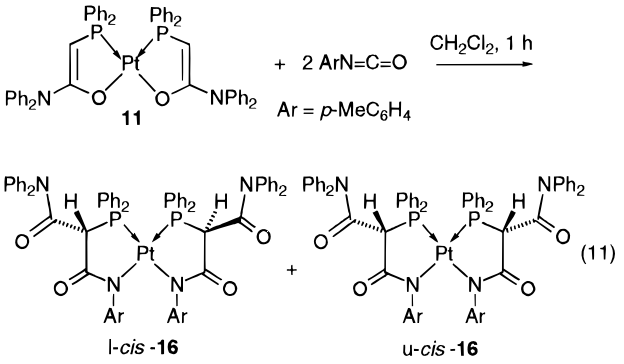
Reactivity of Phosphino Enolate Complexes toward Organic Isocyanates. We found that the nucleophilic character of the enolate carbon of **10** was not sufficient for any reaction to occur with CO_2 (12 atm) at room temperature in THF, contrasting to the case where the NPh_2 group is replaced by OEt.[15a] We therefore examined the behavior of organic isocyanates, which are known to be more reactive than CO_2.[21] Complexes **9** and **10** react with *p*-MeC_6H_4NCO in CH_2Cl_2 by formation of C−C bonds to produce complexes **14** and **15**, respectively. This reactivity is a consequence of the *C*-nucleophilic character of the *P,O* chelate (eq 10). Isomers **14a** and **15a** were identified by ^{1}H NMR spectroscopy: NH···O resonances are visible at δ 10.0 (**14a**) and 10.4 (**15a**) whereas for isomers **14b** and **15b** a doublet is observed for the PC*−H group at δ 4.84 with ^2J(PH) = 12.8 Hz and at 5.02 with ^2J(PH) = 12.2 Hz, respectively. Moreover, the presence of a chiral carbon atom in **14b** leads to an ABX spin system for the dmba protons $CH^AH^BPdPC^*$ which appear as a "doublet" (part A)

(17) (a) Braunstein, P.; Coco Cea, S.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, 423, C38−C42. (b) Braunstein, P.; Coco Cea, S.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1992**, 2539−2542. (c) Braunstein, P.; Kelly, D. G.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1993**, *32*, 4845−4852.
(18) Barton, D. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, U.K., 1979; Vol. 2, pp 986−999.
(19) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763−764. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 1410−1417. (c) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 1765−1774. (d) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299−338.
(20) (a) Altman, L. J.; Laugani, D.; Gunnarson, G; Wennerström, H.; Forsén, S. *J. Am. Chem. Soc.* **1978**, *100*, 8264−8266. (b) Andrieu, J.; Braunstein, P. Unpublished results.
(21) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927−1945.



and "doublet of doublets" (part B) at δ 4.61 and 3.23 respectively, with $J(H^AH^B) = 13.2$ Hz and $^4J(PH^B) = 2.9$ Hz. The equilibrium between isomers (**14a,b**) and (**15a,b**) was confirmed by rapid exchange of the NH···O proton when D_2O was added to a $CDCl_3$ solution, which led to disappearence of both the signals at δ 10.0 and 5.02. The IR spectrum of the mixture **14a,b** or **15a,b** contains strong absorptions in the ν(C═O) and ν(C···C) + ν(C···O) region. A precise assignment was not possible although the absorptions at 1658 (**14b**) and 1662 (**15b**) most likely correspond to the ν(C═O) vibration of the $Ph_2NC(O)$ moiety. The absorption at 1616 cm^{-1} in the spectrum of **14** could correspond to the PdN(C═O) vibration of isomer **b**, by analogy with the data for **16** (see below).

Noteworthy is that only one geometrical isomer **16** was obtained from the reaction of *p*-MeC_6H_4NCO with the platinum complex **11** in CH_2Cl_2 (eq 11). The diastereoisomers l-*cis*-**16**

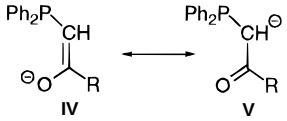


and u-*cis*-**16**, formed in a 1:1 ratio, as determined by integration of the PCH resonances in the ^1H NMR spectrum, contain chiral bifunctional phosphine ligands. They were characterized by their different chemical shifts in ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopies (Table 1).

Discussion

Enolates are known to be ambident reagents but the reaction of $Li[CH_2{\cdot\cdot}C({\cdot\cdot}O)Ph]$ with Ph_2PCl in THF affords the ketophosphine $Ph_2PCH_2C(O)Ph$ in a completely chemoselective manner. The same holds true with $Li[CH_2{\cdot\cdot}C({\cdot\cdot}O)NPh_2]$ which leads to $Ph_2PCH_2C(O)NPh_2$ (**L¹**).[7,22] Related 2-(diphenylphosphino)acetamide ligands have been prepared by reaction of $KPPh_2$ with $ClCH_2C(O)NHR$ (R = H, Me, Ph).[23] The reactivity of stable metal complexes containing P-coordinated α-phosphino enolates $[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)R]^-$ (R = OEt, Ph) toward electrophiles has accordingly given rise to reactions which led to $C_{enolate}$−electrophile or $O_{enolate}$−electrophile bond formation. The former situation has been encountered with electrophilic reagents such as CO_2[15] (only when R = OEt), ArNCO,[24] $MeO_2CC{\equiv}CCO_2Me$,[25] $[(dmba)Pd(\mu\text{-}Cl)]_2$, $[(8\text{-}mq)Pd(\mu\text{-}Cl)]_2$,[15a] or $[Au(PPh_3)]^+$ [26a] and the latter with Ph_2PCl and $PhPCl_2$.[5] The possibility of coordinating the phosphorus donor to a metal center allows a tuning of the enolate reactivity, although the $C_{enolate}$ atom is not directly bonded to the metal. Whereas reactions of the lithium salts $Li[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)R]$ (R = OEt, Ph) with CO_2 or $MeO_2CC{\equiv}CCO_2Me$ did not take place or did not lead to any isolated product,[26a] the reaction of $Li[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)Ph]$ with Ph_2PCl in Et_2O yielded the $P{-}O_{enolate}$ coupling product $Ph_2PCH{=}C(Ph)OPPh_2$.[4] Note that a coordinated isomer of the latter ligand, $(Ph_2P)_2CHC(O)Ph$, has been obtained by deprotonation with *n*-BuLi of $[(CO)_4M(dppm\text{-}P,P)]$ (M = Cr, Mo, W), followed by addition of benzoyl chloride. However, these complexes in solution were unstable to light, and migration of a PPh_2 substituent from carbon to oxygen occurred to yield the thermodynamic product $[(CO)_4W(Ph_2PCH{=}C(Ph)OPPh_2]$.[8]

We have now found that the presence of the more electron donating group NPh_2 in $Li[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)NPh_2]$ reverses the chemoselectivity of the reaction with Ph_2PCl since only $P{-}C_{enolate}$ coupling is observed in Et_2O or THF, leading to **L²**. As far as the reactivity of $[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)R]^-$ is concerned, one may therefore say that it behaves toward P−Cl bonds according to the limiting form **IV** when R = Ph and to the limiting form **V** when $R = NPh_2$. These contrasting chemo-



selectivities could be related to different structures of the alkali metal phosphino enolate reagents in solution as a function of the R group. In this context, it is interesting to note the structural effect of the cation since the solid-state structures of K(18-crown-6)$[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)Ph]$ and K(Kryptofix-2,2,2) $[Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)Ph]$ contain monomeric entities[26a] whereas that of $[Na\{Ph_2PCH{\cdot\cdot}C({\cdot\cdot}O)Ph\}]_4$ is of the cubane type.[26b]

The ligand **L²** was found to bind to Pt(II) as a *P,P* chelate in *cis*-$[PtCl_2\{(Ph_2P)_2CHC(O)NPh_2\text{-}P,P\}]$ (**1**), in the manner of a functionalized dppm ligand (eq 4). In the Pd(II) complex **2**, it behaves as a *P,N* chelate, formally leaving the second phosphorus group and the amide oxygen available for further coordination to Lewis acid metal centers (eq 5). In the dicopper complex $[Cu_2\{(Ph_2P)_2CHC(O)NPh_2\text{-}P,P,O\}_2](BF_4)_2$ (**3**), **L²** adopts a μ_2-η^3 bonding mode. These bonding modes of **L²** are reminiscent of those found in Rh(I) complexes containing the ligand PNP [PNP = 2-(bis(diphenylphosphino)methyl)pyridine]

(22) Matt, D.; Sutter-Beydoun, N.; El Amiri A.; Brunette, J. P.; Briard, P.; Grandjean, D. *Inorg. Chim. Acta* **1993**, *208*, 5−8.

(23) Satyanarayana, T.; Veera Reddy, K. *Transition Met. Chem.* **1994**, *19*, 283−289.

(24) Bouaoud, S. E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279−2286.

(25) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *Organometallics* **1989**, *8*, 1737−1743.

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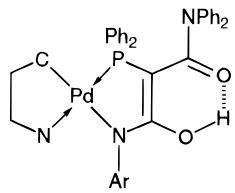
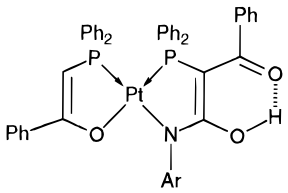
(eq 6).[27] The centrosymmetric structure of complex **3** was established by X-ray diffraction although the quality of the crystals did not allow a refinement of the structure.[11] The dynamic behavior of this complex involves opening of the Cu,P,O chelates and closing of the Cu*,P*,O chelates. This hemilabile behavior extends to a dinuclear complex observations made with **4** (Scheme 2) and previously with mononuclear Cu(I), Ru(II), or Rh(III) complexes with *P,O* ligands such as $Ph_2PCH_2C(O)Ph$, $Ph_2PCH_2C(O)[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$, $Ph_2PCH_2C(O)OEt$, or $Ph_2PCH_2CH_2OMe$.[13,28−31] To the best of our knowledge, **3** represents the first example of a binuclear species containing a hemilabile oxygen-phosphorus ligand (Scheme 3). These results show that the ligand $\mathbf{L^2}$ combines the coordination properties of a bridging diphosphine similar to dppm with the reversible dissociation of the oxygen function in the presence of NCMe or SMe_2 found with ligand $\mathbf{L^1}$.

Nitrile coordination to an electron-withdrawing metal center enhances the electrophilicity of the nitrile carbon and makes it susceptible to nucleophilic attack by reagents such as hydroxide ions, alcoholates, amides, or carbanions.[19] The nature of the products obtained by reaction of $Li[Ph_2PCH\cdots C(\cdots O)NPh_2]$ with $[PtCl_2(NCPh)_2]$ was found to be strongly temperature dependent, complex **11** being obtained at −60 °C whereas **12** was formed at 0 °C. Formation of **11** simply involves ligand displacement reactions, whereas that of **12** involves nucleophilic attack of the $C_{enolate}$ on the coordinated nitrile ligand. A similar reaction has been observed with $[Ph_2PCH\cdots C(\cdots O)R]^-$ when R = OEt[19a,b] but not when R = Ph (less electron donating), illustrating the role of R in controlling the reactivity of the $C_{enolate}$ carbon atom center. The reasons for this temperature-dependent reactivity are not clear at the moment but could reside in the occurence of different structures (and therefore reactivities) of the phosphino enolate reagent as a function of temperature. Notwithstanding the counterintuitive finding that the benzonitrile ligand is displaced from Pt at −60 °C and remains in the coordination sphere of the metal at 0 °C, we believe that nucleophilic attack of the $C_{enolate}$ occurs on the coordinated PhCN ligand, as observed in the case of the reaction with $[Ph_2PCH\cdots C(\cdots O)OEt]^-$. This would also be consistent with the observation that $[PtCl_2(NC{-}CH{=}CH_2)_2]$ or $[PtCl_2(1,5\text{-}COD)]$ only led to **11**, whatever the reaction temperature, owing to the high lability of these ligands. This lability should not have prevented an hypothetical intermolecular reaction to occur between the enolate and the free organonitrile, but this was not observed. In fact, the reaction at −60 °C of a mixture of $Li[Ph_2PCH\cdots C(\cdots O)NPh_2]$ and PhCN, stirred for 1 h, with $[PtCl_2(COD)]$ did not lead to complex **12** but to *cis*-$Pt[Ph_2PCH\cdots C(\cdots O)NPh_2]_2$ (**11**). Pure **11** was independently shown not to react with PhCN. Protonation of **12** induces a rearrangement of the coordination sphere of the metal and the product **13** can be reversibly deprotonated to **12**.

Reactions of **9** and **10** with organic isocyanates resulted in carbon−carbon bond formation with the enolate carbon (eq 10). The presence of isomers **14a** and **14b** (**15a** and **15b**) was established by spectroscopic methods, and their interconversion illustrates the hemilabile character of the multifonctional phosphine ligand. It is noteworthy that it results from breaking of a covalent rather than dative bond. In a related study with $[(C\ N)Pd\{Ph_2PCH\cdots C(\cdots O)Ph\}]$, it was shown that such isomerizations are intramolecular and do not proceed by deinsertion of the organic isocyanate.[24] An isomeric structure of the functional ligand of the type shown in **B** was ruled out on the basis of the spectroscopic data and the need for a stereogenic center that renders the CH_2N protons of the dmba ligand diastereotopic.



B



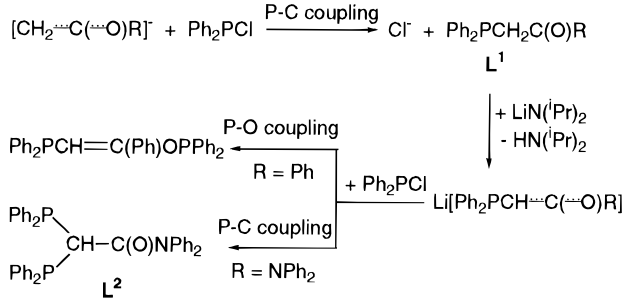
C

Note however that a ligand arrangement similar to that found in **B** has been observed for complex **C**.[24] In the complexes *cis*-$Pt[Ph_2PCH\cdots C(\cdots O)R]_2$, the *C*-nucleophilicity of the chelating phosphino enolate toward ArNCO was strongly influenced by the nature of the substituent R. When R = Ph, insertion of ArNCO into the enolate C−H bond was observed in only one of the *P,O* chelates after a week.[24] However, when R = NPh_2, insertion occurred in both *P,O* chelates after only 1 h, emphasizing that in complex **11**, the $-NPh_2$ substituent is a better donor than the phenyl group. However, these donor properties are not sufficient to produce reaction of the enolate moiety of $[(8\text{-mq})Pd\{Ph_2PCH\cdots C(\cdots O)NPh_2\}]$ with CO_2, in contrast to its analog where R = OEt.[15a] This observation suggests that the $-NPh_2$ group is a weaker donor than the OEt substituent.

Conclusions

Reactions of various (functional) enolates with Ph_2PCl have led to coupling products with a chemoselectivity strongly dependent upon the nature of the substituents (Scheme 5). The

Scheme 5



complete chemoselectivity of these reactions makes them synthetically useful. The P−C coupling pathways lead to functional phosphines such as $\mathbf{L^1}$ or to the functional diphosphine $\mathbf{L^2}$. The synthesis of new chiral, functional diphosphine ligands by the selective P−C coupling reaction of $Li[Ph_2PCH\cdots C(\cdots O)NPh_2]$ with different chlorophosphines is currently in progress (eq 12). We have begun to explore the coordination properties of the latter species and found a diversity of bonding modes (*P,P*; *P,N*, and *P,P,O*) which further illustrates the

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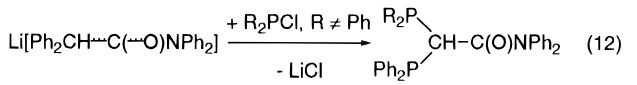

(12)

versatility and potential of polyfunctional phosphine ligands in synthetic chemistry. This includes extensions in polynuclear chemistry. The ligands **L[1]** and **L[2]** co-ordinated to mono- and binuclear copper(I) complexes present a dynamic behavior in $CDCl_3$ solution and a facile reversible oxygen-donor dissociation in the presence of small molecules such as NCMe or SMe_2. This feature could lead to interesting catalytic properties.

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed using Schlenk-techniques under dry nitrogen. The solvents were distilled and dried prior to use under nitrogen. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded at 300.13, 121.5, and 75.5 MHz, respectively, on a FT Bruker AC 300 instrument. IR spectra were recorded in the 4000−400 cm^{-1} range on a Bruker IFS66 FT spectrometer.

B. Syntheses. The syntheses of $Ph_2PCH_2C(O)NPh_2$ (**L[1]**) and [(8-mq)Pd{Ph_2PCH···C(···O)NPh_2}] (**10**) have been described elsewhere.[7] The complexes $[Cu(NCMe)_4](BF_4)$,[10] [(C N)Pd$(NCMe)_2$](BF_4),[9] [(C N)Pd$(\mu$-Cl$)_2$] [(C N) = dmba-H, dimethylbenzylamine; 8-mq-H, 8-methylquinoline],[32] $[PtCl_2(COD)]$ (COD: 1,5-cyclooctadiene),[33] and $[PtCl_2(NCPh)_2]$[34] were prepared according to the literature. $[PtCl_2(NCPh)_2]$ is predominantly obtained as the *cis* isomer, but isomerization to the *trans* form is a facile process.[35]

Ph_2PCH═C(Ph)OPPh_2. A hexane solution (1.60 mol L^{-1}) of *n*-BuLi (8.8 mL, 14.0 mmol) was added dropwise at −70 °C to a solution of diisopropylamine (2.0 mL, 14.0 mmol) in diethyl ether (30 mL). After 15 min, a suspension of $Ph_2PCH_2C(O)Ph$ (4.25 g, 14.0 mmol) in diethyl ether (20 mL) was slowly added at −70 °C. After being stirred for 15 min, a solution of Ph_2PCl (2.50 mL, 14.0 mmol) in diethyl ether (10 mL) was added dropwise at −70 °C over 1 h. The mixture was stirred for 2.5 h with a progressive increase in temperature from −70 °C to room temperature. The solvent was removed *in vacuo*. The residue was dissolved in toluene (50 mL). The pale yellow solution was filtered and concentrated, and addition of hexane afforded a white powder which was isolated by filtration and dried *in vacuo* (3.90 g, 57%). IR (KBr): 1595 m, 1564 mw, 1045 s (ν(P−O)). ^{1}H NMR (CD_2Cl_2): δ 7.6−7.2 (m, 25 H, aromatic), 6.02 (dd, 1 H, PCH, ^2J(PH) = 2.7, ^4J(PH) = 0.8 Hz). ^{1}H NMR (C_6D_6): δ 7.75−7.0 (m, 25 H, aromatic), 6.27 (dd, 1 H, PCH, ^2J(PH) = 1.5, ^4J(PH) = 0.4 Hz).^{31}P{^{1}H} NMR (C_6D_6): δ 118.25 (d, Ph_2PO, ^4J(PP) = 65 Hz), −30.5 (d, Ph_2PC, ^4J(PP) = 65 Hz). Anal. Calcd for $C_{32}H_{26}OP_2$ (M = 488.14) C, 78.66; H, 5.37. Found: C, 78.21; H, 5.19.

Li[Ph_2PCH···C(···O)NPh_2] (A). To a 1.6 M hexane solution of *n*-BuLi (2.0 mL) in THF (30 mL) was added dropwise at −60 °C dry diisopropylamine (0.4 mL). After ca. 0.5 h, a solution of **L[1]** (1.20 g, 3.03 mmol) in THF (10 mL) was added dropwise at −60 °C. The mixture was stirred for 1 h, and was considered to contain only the lithium enolate. This solution was used for further reactions.

$(Ph_2P)_2CHC(O)NPh_2$ (L[2]). A hexane solution (1.60 mol L^{-1}) of *n*-BuLi (4 mL, 6.40 mmol) was added dropwise at −70 °C to a solution of diisopropylamine (0.9 mL, 6.40 mmol) in THF or in Et_2O (20 mL). After 0.5 h, a solution of $Ph_2PCH_2C(O)NPh_2$ (2.50 g, 6.32 mmol) in THF (10 mL) was added dropwise at −70 °C. After stirring for 1.5 h, a solution of Ph_2PCl (1.15 mL, 6.40 mmol) in THF (5 mL) was added dropwise at −70 °C. The mixture was stirred for 2.5 h with a progressive increase in temperature from - 70 °C to room temperature. The solvent was removed *in vacuo*. The residue was dissolved in toluene (50 mL). The pale yellow solution was filtered and concentrated, and addition of pentane afforded a white powder, which was washed with cold ethanol (20 mL) and dried *in vacuo* (3.75 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.6−6.2 (m, 30 H, aromatic), 4.60 (s, 1 H, P_2-CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 169.25 (s, CO), 143.0−126.4 (m, aromatic), 43.84 (t, P_2CH, J(PC) = 30 Hz). Anal. Calcd for $C_{38}H_{31}NOP_2$ (M = 579.62) C, 78.74; H, 5.39; N, 2.42. Found: C, 78.51; H, 5.39; N, 2.44.

***cis*-[$PtCl_2${$(Ph_2P)_2CHC(O)NPh_2$-*P,P*}] (1).** A mixture of $[PtCl_2(NCPh)_2]$ (0.080 g, 0.085 mmol) and **L[2]** (0.100 g, 0.085 mmol) was stirred in THF (10 mL). After 0.5 h, the solvent was removed *in vacuo* and the white residue washed with pentane. Recrystallization from CH_2Cl_2/pentane afforded a white powder (0.113 g, 79%). ^{1}H NMR (CD_2Cl_2): δ 8.2−6.1 (m, 30 H, aromatic), 4.32 (dd, 1 H, ^2J(PH) = 4.1, 2.1 Hz, J(PtH) = 57 Hz). Anal. Calcd for $C_{38}H_{31}Cl_2NOP_2Pt$ (M = 845.61) C, 53.98; H, 3.69; N, 1.66. Found: C, 54.03; H, 3.67; N, 1.67.

[(dmba)Pd{$(Ph_2P)_2CHC(O)NPh_2$-*P,N*}](BF_4) (2). A mixture of [(dmba)Pd$(NCMe)_2$](BF_4) (0.250 g, 0.61 mmol) and **L[2]** (0.354 g, 0.61 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 h. The solution was concentrated to half its original volume. Addition of pentane afforded white needles of **2** (0.568 g, 98%). ^{1}H NMR (CD_2Cl_2): δ 7.9−6.3 (m, 34 H, aromatic), 5.44 (dd, 1 H, PCHP, ^2J(PCH) = 8.9, 6.0 Hz), 4.31 (part A of ABX spin system, 1 H, CH^AH^BNPdPC*, $J(H^AH^B)$ = 14.1 Hz, $^4J(PH^A)$ < 5 Hz), 4.24 (part B of ABX spin system, 1 H, CH^AH^BNPdPC*, $J(H^AH^B)$ = 14.1 Hz, $^4J(PH^B)$ < 5 Hz), 3.16 (3 H, m, Me^ANPdPC*), 3.00 (3 H, m, Me^BNPdPC*). Anal. Calcd for $C_{47}H_{43}BF_4N_2OP_2Pd\cdot0.5CH_2Cl_2$ (M = 949.51) C, 60.09; H, 4.67; N, 2.95. Found: C, 60.17; H, 4.48; N, 2.86.

[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P,P,O*}$_2$]$(BF_4)_2$ (3). A mixture of $[Cu(NCMe)_4](BF_4)$ (0.108 g, 0.343 mmol) and **L[2]** (0.200 g, 0.344 mmol) was stirred in CH_2Cl_2 for 6 h. Concentration of the resulting colorless solution and addition of Et_2O resulted in the precipitation of a white solid, which was washed with Et_2O and dried *in vacuo*. Recrystallization from $CHCl_3$ afforded white crystals, which were suitable for X-ray analysis (0.246 g, 92%). ^{1}H NMR (CD_2Cl_2): δ 7.7−5.9 (m, 60 H, aromatic), 5.27 (quintuplet, 2 H, P_2CH, ^2J(PH) = 3.3 Hz). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 168.69 (s, CO, br), 143.53−121.56 (m, aromatic), 47.68 (s, br, P_2CH). Anal. Calcd for $C_{76}H_{62}B_2F_8N_2O_2P_4Cu_2\cdot1.25CHCl_3$ (M = 1609.17) C, 57.66; H, 3.96; N, 1.74. Found: C, 57.77; H, 4.08; N, 1.79.

[Cu{$Ph_2PCH_2C(O)NPh_2$}{$Ph_2PCH_2C(O)NPh_2$}](BF_4) (4). Following the procedure for **3**, complex **4** was obtained from $[Cu(NCMe)_4](BF_4)$ (0.100 g, 0.318 mmol) and **L[1]** (0.251 g, 0.635 mmol). Recrystallization from CH_2Cl_2/pentane afforded white pellets (0.285 g, 95%). ^{1}H NMR ($CDCl_3$): δ 7.4−7.0 (m, 40 H, aromatic), 3.46 (s, br, 4 H, PCH_2). Anal. Calcd for $C_{52}H_{44}BF_4N_2O_2P_2Cu$ (M = 941.23) C, 66.36; H, 4.71; N, 2.98. Found: C, 66.54; H, 4.90; N, 3.04.

[Cu{$Ph_2PCH_2C(O)NPh_2$}$_2$($NCCH_3$)](BF_4) (5a). Complex **4** was dissolved in CD_3CN. ^{1}H NMR (CD_3CN): δ 7.4−7.0 (m, 40 H, aromatic), 3.22 (d, 4 H, PCH_2, ^2J(PH) = 6.8 Hz).

[Cu{$Ph_2PCH_2C(O)NPh_2$}$_2$(SMe_2)](BF_4) (5b). Complex **4** was dissolved in a 3:1 mixture of $CDCl_3$/Me_2S. ^{1}H NMR ($CDCl_3$/Me_2S): δ 7.3−6.8 (m, 40 H, aromatic), 3.17 (s, br, 4 H, PCH_2).

[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P,P*}$_2$($NCMe)_2$]$(BF_4)_2$ (6a). Complex **3** was dissolved in CH_3CN and **6a** was characterized in solution. ^{1}H NMR (CD_3CN): δ 7.6−6.4 (m, 60 H, aromatic), 4.99 (t, 2 H, P_2CH, ^2J(PH) = 6.8 Hz). ^{13}C{^{1}H} NMR (CD_3CN): δ 168.07 (s, CO), 142.76−118.40 (m, aromatic), 46.29 (s, P_2CH).

[Cu_2{$(Ph_2P)_2CHC(O)NPh_2$-*P,P*}$_2$($SMe_2)_2$]$(BF_4)_2$ (6b). Complex **3** was dissolved in a 3:1 mixture of CD_2Cl_2/Me_2S and **6b** was characterized in solution. ^{1}H NMR (CD_2Cl_2/Me_2S): δ 7.6−6.3 (m, 60 H, aromatic), 4.93 (t, 2 H, P_2CH, ^2J(PH) = 6.6 Hz).

[(dmba)PdCl{$Ph_2PCH_2C(O)NPh_2$}] (7). A solution of **L[1]** (0.285 g, 0.72 mmol) in CH_2Cl_2 (15 mL) was added to a stirred solution of [(dmba)Pd$(\mu$-Cl$)]_2$ (0.200 g, 0.36 mmol) in CH_2Cl_2 (20 mL). After being stirred for 1 h, the solution was concentrated to two-thirds of its original volume *in vacuo*. Addition of pentane afforded yellow crystals (0.360 g, 76%). ^{1}H NMR ($CDCl_3$): δ 8.0−6.3 (m, 24 H, aromatic), 4.05 (d, 2 H, NCH_2, ^4J(PH) = 1.8 Hz), 3.72 (d, 2 H, PCH_2, ^2J(PH) = 10.6 Hz), 2.85 (d, 6 H, NMe_2, ^4J(PH) = 2.6 Hz). Anal. Calcd for

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$C_{35}H_{34}ClN_2OPPd$ (M = 671.52) C, 62.60; H, 5.10; N, 4.17. Found: C, 62.85; H, 5.18; N, 4.06.

[(dmba)Pd{$Ph_2PCH_2C(O)NPh_2$}](BF_4) (8). Solid $AgBF_4$ (0.062 g, 0.318 mmol) was added to a solution of **7** (0.230 g, 0.316 mmol) in CH_2Cl_2 (20 mL). After being stirred for 1 h, the suspension was filtered and the solution was concentrated to two-thirds of its original volume. Addition of pentane afforded white crystals (0.190 g, 83%). ^{1}H NMR ($CDCl_3$): δ 7.8−6.2 (m, 24 H, aromatic), 4.00 (d, 2 H, NCH_2, ^4J(PH) = 1.8 Hz), 4.00 (d, 2 H, PCH_2, ^2J(PH) = 11.4 Hz), 2.77 (d, 6 H, NMe_2, ^4J(PH) = 2.5 Hz). Anal. Calcd for $C_{35}H_{34}BF_4N_2OPPd$ (M = 722.87) C, 58.15; H, 4.74; N, 3.87. Found: C, 58.10; H, 4.70; N, 3.87.

[(dmba)Pd{$Ph_2PCH{\cdots}C({\cdots}O)NPh_2$}] (9). A yellow suspension of [(dmba)Pd(μ-Cl)]$_2$ (0.838 g, 1.50 mmol) in THF (10 mL) was added dropwise at −40 °C to an enolate solution **A** prepared as above. After a few minutes, a white suspension was obtained and stirred for 2 h with a slow increase in temperature from −40 °C to room temperature. The solvent was removed *in vacuo*. The white residue was dissolved in CH_2Cl_2 (30 mL) and filtered. Addition of pentane afforded white crystals (1.95 g, 94%). IR (CD_2Cl_2): 1505 w, 1496 vs, 1487 vs. The ν(C⋯C) + ν(C⋯O) absorption of the enolate moiety is obscured by these strong bands. ^{1}H NMR ($CDCl_3$): δ 7.8−6.7 (m, 24 H, aromatic), 3.90 (d, 2 H, NCH_2, ^4J(PH) = 1.6 Hz), 3.28 (d, 1 H, PCH, ^2J(PH) = 1.5 Hz), 2.68 (d, 6 H, NMe_2, ^4J(PH) = 13.5 Hz); solvent of crystallization identified by recording a spectrum in $CDCl_3$. Anal. Calcd for $C_{35}H_{33}N_2OPPd{\cdot}0.75CH_2Cl_2$ (M = 635.06) C, 61.45; H, 4.97; N, 4.00. Found: C, 61.21; H, 5.00; N, 3.75.

***cis*-Pt[$Ph_2PCH{\cdots}C({\cdots}O)NPh_2$]$_2$ (11).** A suspension of [$PtCl_2$-(1,5-COD)] (0.565 g, 1.51 mmol) in THF (20 mL) was added dropwise at −50 °C to a solution of **A** prepared as above. The suspension was stirred for 2 h with a slow increase in temperature from −50 °C to room temperature. A colourless solution was obtained. After the mixture was stirred for 1 h, the solvent was removed *in vacuo*. The residue was extracted with toluene (ca. 100 mL) and the solution filtered. The solvent was removed *in vacuo* and recrystallization from CH_2Cl_2/pentane afforded white needles of **11** (1.20 g, 81%). IR (KBr): 1496 vs, 1483 vs. The ν(C⋯C) + ν(C⋯O) absorption of the enolate moiety is obscured by these strong bands. ^{1}H NMR ($CDCl_3$): δ 7.3−6.7 (m, 40 H, aromatic), 3.02 (d, 2 H, PCH, ^2J(PH) = 4.3 Hz). Anal. Calcd for $C_{52}H_{42}N_2O_2P_2Pt$ (M = 983.95) C, 63.47; H, 4.30; N, 2.85. Found: C, 63.58; H, 4.33; N, 2.79.

***trans*-Pt[Ph_2PC{=C(NH)Ph}{C(O)NPh_2}]$_2$ (12).** A suspension of [$PtCl_2(NCPh)_2$] (0.715 g, 1.51 mmol) in THF (20 mL) was added dropwise at −5 °C to a solution of **A**. After a few minutes, a yellow solution was obtained. It was stirred with a slow increase in temperature from −5 °C to room temperature and after 1 h, the solvent was removed *in vacuo*. The residue was extracted with toluene (ca. 100 mL) and the solution filtered. The solvent was removed *in vacuo* and the residue was washed with Et_2O (2 × 20 mL) and then dried *in vacuo* (1.40 g, 78%). IR (KBr): 3374 w (NH). ^{1}H NMR ($CDCl_3$): δ 8.1−6.4 (m, 50 H, aromatic), 4.97 (s, 2 H, HNPt, ^2J(PtH) = 44.4 Hz). Anal. Calcd for $C_{66}H_{52}N_4O_2P_2Pt$ (M = 1190.20) C, 66.60; H, 4.40; N, 4.71. Found: C, 66.68; H, 4.51; N, 4.76.

***trans*-[Pt{Ph_2PC[C(O)NPh_2][=C(NH_2)Ph]}$_2$](BF_4)$_2$ (13).** To a solution of **12** (0.080 g, 0.067 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C a solution of $HBF_4{\cdot}Et_2O$ (0.020 g, 0.17 mmol) in CH_2Cl_2 (5 mL). After the mixture was stirred for 10 min, the solvent was removed *in vacuo*. The white residue was washed with Et_2O (2 × 10 mL) and then dried *in vacuo*. Recrystallization from CH_2Cl_2/pentane afforded white crystals (0.088 g, 95%). ^{1}H NMR (CD_2Cl_2): δ 10.95 (s, br, 2 H, NH⋯O, exchanges with D_2O), 8.2−6.5 (m, 50 H, aromatic), 5.81 (t, 2 H, NH, ^4J(PH) = 1.2 Hz, exchanges with D_2O). Anal. Calcd for $C_{66}H_{54}B_2F_8N_4O_2P_2Pt{\cdot}0.25CH_2Cl_2$ (M = 1387.02) C, 57.37; H, 3.96; N, 4.04. Found: C, 57.20; H, 3.97; N, 3.93.

Deprotonation of 13. NaH (0.010 g, 0.42 mmol) was added to a solution of **13** (0.070 g, 0.050 mmol) in THF (10 mL). After a few minutes, a yellow solution was obtained and stirred for 15 min. The solution was filtered and the solvent removed *in vacuo*. The yellow residue was characterized as complex **12** by ^{31}P{^{1}H} and ^{1}H NMR spectroscopic methods, (spectroscopic yield 100%, isolated 0.055 g, 92%).

[(dmba) Pd{$Ph_2PC[{\cdots}C({\cdots}O)NH(p$ - $MeC_6H_4)$] [C(O)NPh_2]}] (14a) and [(dmba)Pd{Ph_2PCH[C(O)N(*p*-MeC_6H_4)][C(O)NPh_2]}] (14b). To a stirred solution of **9** (0.130 g, 0.186 mmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of *p*-MeC_6H_4NCO (23 μL, 0.192 mmol) in CH_2Cl_2 (5 mL). After being stirred for 2 h, the solution was concentrated to half its original volume and filtered. Addition of pentane afforded white crystals (0.130 g, 91%). Both isomers **14a** and **14b** were found to be present in a ca. 7:3 ratio in CD_2Cl_2 and 3:7 ratio in $CDCl_3$. IR (KBr): 1658 vs, 1616 s, 1592 vs, 1580 sh, 1504 s. ^{1}H NMR ($CDCl_3$): δ 10.0 (s, 1 H, NH of **14a**, exchanges with D_2O), 8.2−6.4 (m, 28 H, aromatic), 3.87 (s, 2 H, NCH_2 of **14a**), 2.79 (d, 3 H, CH_3, isocyanate of **14a**), 4.84 (d, 1 H, PCH of **14b**, ^2J(PH) = 12.8 Hz, exchanges with D_2O), 4.61 (part A of ABX spin system of **14b**, 1 H, CH^AH^BNPdPC*, $J(H^AH^B)$ = 13.2 Hz, $^4J(PH^A)$ < 1 Hz), 3.23 (part B of ABX spin system of **14b**, 1 H, CH^AH^BNPdPC*, $J(H^AH^B)$ = 13.2 Hz, $^4J(PH^B)$ = 2.9 Hz), 2.28−2.13 (m, 12 H, NMe_2 of **14a,b** and 3 H, CH_3, isocyanate of **14b**). Anal. Calcd for $C_{43}H_{40}N_3O_2PPd$ (M = 768.21) C, 67.23; H, 5.25; N, 5.47. Found: C, 67.43; H, 5.36; N, 5.38.

[(8-mq) Pd{$Ph_2PC[{\cdots}C({\cdots}O)$ NH(*p* - MeC_6H_4)] [C(O)NPh_2]}] (15a) and [(8-mq)Pd{Ph_2PCH[C(O)N(*p*-MeC_6H_4)][C(O)NPh_2]}] (15b). To a stirred solution of **10** (0.095 g, 0.147 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of *p*-MeC_6H_4NCO (18 μL, 0.150 mmol) in CH_2Cl_2 (5 mL). After being stirred for 2 h, the solution was concentrated to half its original volume and filtered. Addition of pentane afforded white crystals (0.109 g, 95%). Both isomers **15a** and **15b** were found to be present in a ca. 1:1 ratio in CD_2Cl_2 or in $CDCl_3$. IR (KBr): 1662 m, 1580 s, 1540 s, 1513 s, 1504 vs. ^{1}H NMR ($CDCl_3$): δ 10.4 (s, 1 H, NH of **15a**, exchanges with D_2O), 8.8−6.7 (m, 60 H, aromatic of **15a,b**), 5.02 (d, 1 H, PCH of **15b**, ^2J(PH) = 12.2 Hz, exchanges with D_2O), 3.04 (br, 2 H) and 2.97 (s, 2 H) $PdCH_2$ of **15a,b**, 2.35 (s, 3 H, CH_3, isocyanate), 2.33 (s, 3 H, CH_3, isocyanate). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.07 (d, CO, ^2J(PC) = 29.1 Hz), 173.81 (s, CO), 172.14 (d, CO, ^2J(PC) = 12.1 Hz), 166.57 (s, CO), 55.17 (d, PCH of **15b**, J(PC) = 28.7 Hz), 23.68 (s, PdC), 23.01 (s, PdC), 21.08 (s, CH_3, isocyanate), 20.98 (s, CH_3, isocyanate). Anal. Calcd for $C_{44}H_{36}N_3O_2PPd$ (M = 776.19) C, 68.09; H, 4.68; N, 5.41. Found: C, 68.07; H, 4.73; N, 5.63.

***cis*-Pt[Ph_2PCH{C(O)N(*p*-MeC_6H_4)}{C(O)NPh_2}]$_2$ (16).** To a solution of complex **11** (0.400 g, 0.406 mmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of *p*-MeC_6H_4NCO (0.100 mL, 0.835 mmol) in CH_2Cl_2 (5 mL). After being stirred for 2 h, the solution was concentrated to half its original volume and filtered. Addition of pentane afforded white crystals (0.508 g, 76%). Both diastereoisomers l-*cis*-**16** and u-*cis*-**16** were found to be present in a ca. 1:1 ratio in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2): δ 7.4−6.7 (m, 96 H, aromatic protons), 5.14 (d, 2 H, PCH of l-*cis*-**16** or u-*cis*-**16**, ^2J(PH) = 10.8 Hz), 4.79 (d, 2 H, PCH of u-*cis*-**16** or l-*cis*-**16**, ^2J(PH) = 11.7 Hz), 2.27 (s, 6 H, CH_3, isocyanate), 2.21 (s, 6 H, CH_3, isocyanate). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.4 (s, CO), 165.7 (s, CO), 57.36 (d, PCH, J(PC) = 35.7 Hz), 54.63 (d, PCH, J(PC) = 34.0 Hz), 21.10 (s, CH_3, isocyanate), 21.03 (s, CH_3, isocyanate). Anal. Calcd for $C_{68}H_{56}N_4O_4P_2Pt$ (M = 1250.25) C, 65.32; H, 4.51; N, 4.48. Found: C, 65.08; H, 4.54; N, 4.38.

X-ray Crystal Structure Determination of Complex 10. The crystal data are summarized in Table 3. Data were collected at room temperature on a Philips PW 1100 diffractometer using the $\theta/2\theta$ scan type. The reflections were collected with variable scan speed of 3−12° min^{-1} and a scan width of (1.20 + 0.346 tan θ)°. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the data collection period. Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods, first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-

Table 3. Summary of Crystallographic Data for Complex **10**

mol formula	$C_{36}H_{29}N_2OPPd$
mol wt	643.01
cryst system	monoclinic
space group	$P2_1/c$
radiatn (Mo Kα)	graphite-monochromated ($\lambda = 0.710\ 73$ Å)
a, Å	8.801(2)
b, Å	31.483(6)
c, Å	10.939(2)
β, deg	101.37(2)
V, Å^3	2972(1)
Z	4
D_{calcd}, g cm^{-3}	1.437
F(000)	1312
cryst dimens, mm	0.22 × 0.25 × 0.33
μ(Mo Kα), cm^{-1}	7.10
2θ range, deg	6−52
no. of reflcns measd	$\pm h,k,l$
tot. no. of unique data	5544
no. of unique obsd data	2863 [$I > 2\sigma(I)$]
R^a	0.0268
$R_w{}^b$	0.0338

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.4285 and 0.0011, respectively. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 36. The final cycles of refinement were carried out on the basis of 371 variables. The largest remaining peak in the final difference map was equivalent to about 0.31 e/Å^3. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[37]

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Supporting Information Available: Tables of atomic coordinates for the non-hydrogen atoms (Table S-I), atomic coordinates for the hydrogen atom (Table S-II), thermal parameters for the non-hydrogen atoms (Table S-III), and complete lists of bond distances and angles (Table S-IV) (6 pages). Ordering information is given on any current masthead page.

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