Synthesis of New Phosphino Amino Alcohol Ligands via Ortho-Alkyllithiation Reactions. Versatile Coordination Behavior toward Copper(I) and Palladium(II)

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Received June 27, 1997

2-[Methyl(2-methylphenyl)amino]ethanol undergoes an ortho-alkyllithiation reaction with *n*-butyllithium to lead to a new mixed benzyllithium−lithium alkoxide. This organolithium species reacts with PPh_2Cl, with selective P−C bond formation, to afford the ligand 2-[methyl-(2-((diphenylphosphino)methyl)phenyl)amino]ethanol **L[1]**. The coordination of the ligand **L[1]** to copper(I) leads to the complex $[Cu(L^1)_2](BF_4)$, whose structure has been determined by an X-ray diffraction study. In the solid state, one of the ligands acts as a monodentate phosphine while the other adopts a tridentate P,N,O coordination mode. A variable-temperature ^{31}P NMR study demonstrated the existence of an equilibrium between the two modes in solution, with a coalescence temperature of *ca.* 0 °C, indicating a double-hemilabile behavior for the nitrogen and the oxygen functions. **L[1]** reacts with [Pd(Me)(Cl)(COD)] to give a dinuclear complex in which the ligand appears to behave as a bridging anionic P,O ligand. Such a complex could serve as a model for a key intermediate in the proposed mechanism for the homogeneous catalysis of the methoxycarbonylation of propyne by certain palladium(II) complexes containing P,N ligands. **L[1]** can undergo a second ortho-alkylmetalation reaction with *n*-butyllithium which, after addition of PPh_2Cl, provides the new ligand 2-{methyl[2-(bis(diphenylphosphino)methyl)phenyl]amino}ethanol **(L[2])** in high yield.

Introduction

In the last 10 years, there has been a considerable increase in the interest shown toward mono- or diphosphine ligands containing nitrogen and/or oxygen functions and toward their applications. Such chelating ligands, which combine two or more donor atoms with different "hard" or "soft" basic character, have been shown to produce palladium complexes which are very useful for homogeneous catalysis, e.g., for the copolymerization of olefins and CO to form polyketones[1] or for the methoxycarbonylation of propyne to produce methyl methacrylate.[2] A P,P,N,O ligand, i.e., a ligand possessing two phosphorus, one nitrogen, and one oxygen atom as potential donors, such as the chiral ferrocenyldiphosphinoethanolamine ligand has been used successfully in the catalytic asymmetric allylation of β-diketones. The higher selectivity observed for this functional ligand has been ascribed to hydrogen bonding between the hydroxyl group of the ligand and the attacking enolate anion.[3] Diphosphine ligands containing both amino and alcohol functions constitute only a very small fraction of functional diphosphines due to the limited number of synthetic procedures available. Generally, the reported methods for the synthesis of functional diphosphine ligands involve either (i) the preparation of diphosphines following the introduction of a nitrogen[4] or oxygen function[5] or (ii) the functionalization of nitrogenated or oxygenated organic compounds by two phosphorus-containing groups.[6] To open up routes to new phosphino amino alcohol ligands (P,N,O), we have developed a synthetic strategy which involves the preparation of a new mixed benzyllithium−lithium alkoxide by an ortho-alkylmetalation reaction with *n*-BuLi, followed by a P−C coupling of the organolithium species with chlorodiphenylphosphine. In fact, as the nucleophilic character of the benzyl anion should be stronger than that of the alkoxide, we expected to observe selective P−C bond formation in this second reaction. Moreover, we also wished to explore the coordination chemistry of these new functional phosphines and, in particular, the competition between the coordination modes of the amino and alcohol functions.

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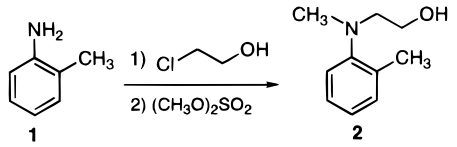
(1) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663−681.
(2) Drent, E.; Arnoldy, P.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1993**, 455, 247−253.
(3) (a) Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586−2592. (b) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257−276.
(4) (a) Anderson, M. P.; Mattson, B. M. *Inorg. Chem.* **1983**, *22*, 2644−2647. (b) Anderson, M. P.; Tso, C. C.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1983**, *22*, 3267−3275.
(5) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863−867.
(6) Luo, H.; Orvig, C. *Can. J. Chem.* **1996**, *74*, 722−729.

S0276-7333(97)00550-5 CCC: $15.00
Publication on Web 02/13/1998

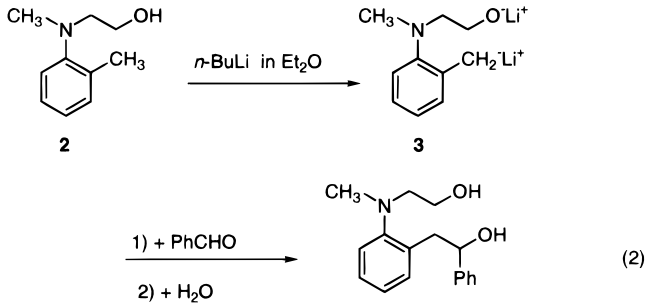
Results and Discussion

Ortho-Alkyllithiation Reaction. Our starting material, **2**, was prepared from 2-methylaniline (**1**) by following the synthetic method outlined in eq 1.



1 2 (1)

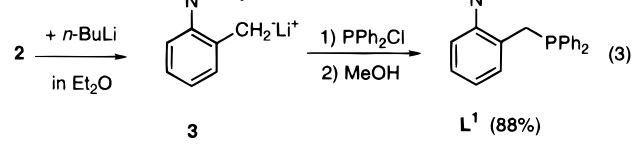
The ortho-metalated compound **3** was obtained from **2** under conditions similar to those described for the ortho lithiation of *N*,*N*-dimethylbenzylamine (eq 2).[7] In



2 3 4 (2)

contrast to [2-((dimethylamino)methyl)phenyl]lithium, the organodilithium salt **3** is somewhat soluble in Et_2O and cannot be isolated in the solid state by filtration. The yield of **3** was determined by reaction with benzaldehyde (eq 2) to be at least 91%.

Synthesis of the Mono(diphenylphosphino) Amino Alcohol Ligand L[1]. As the ortho-metalated compound **3** contains two nucleophilic centers, we have explored its reactivity toward chlorodiphenylphosphine. The reaction of **2** with 2.1 equiv of *n*-BuLi followed by the addition of 1.1 equiv of PPh_2Cl afforded the new ligand **L[1]** in high yield (see eq 3). The coupling is



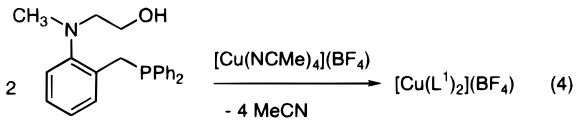
3 L[1] (88%) (3)

predominantly with the carbanionic center, but a very small amount (5−10%) of coupling to the alkoxide group can also occur. The alcohol function can be restored by subsequent addition of methanol.

The virtually quantitative P−C bond formation is confirmed by ^1H NMR spectroscopy. However, a P−O coupling reaction between the dianionic species and PPh_2Cl can be observed under two other conditions, namely (i) by addition of 1 equiv of *n*-BuLi to **2**, followed by the addition of 1 equiv of PPh_2Cl (in this case, only the alkoxide is formed and there is no ortho metalation; see Experimental Section), and (ii) by addition of 2.1 equiv of *n*-BuLi, followed by the addition of more than 1 equiv of PPh_2Cl. These observations show that a mixed benzyllithium−lithium alkoxide species such as **3** reacts with the P−Cl bond in chlorodiphenylphosphine with a much higher selectivity for P−C bond formation. This chemoselectivity could be due to the stronger nucleophilic character of benzylic compared to alkoxide anionic fragments and clearly provides the basis for the success of our method. Other reported synthetic procedures involve either multistep reactions which require protection of the alcohol function or a coupling reaction between ortho-metalated triarylphosphines with bis(trifluoromethyl) ketone. The yields of these preparations, however, were limited to between 45 and 50%.[6,8]

Coordination Modes of the Phosphino Amino Alcohol Ligand L[1]. As the ligand **L[1]** is formally a potential six-electron donor with the three ligating heteroatoms P, N, and O, several coordination modes can be envisaged. To explore the selective coordination properties of this ligand, we examined its behavior with the two late transition metals copper(I) and palladium(II).

Two equivalents of **L[1]** in the presence of 1 equiv of a cationic copper(I) complex led to complex **5** in good yield (eq 4).



L[1] 5 (4)

The FAB mass spectrum of this complex did not exhibit the molecular peak expected for **5** (without the tetrafluoroborate anion) at *m*/*z* 762.4 but gave another at *m*/*z* 411.9 corresponding to one ligand per metal. However, the ratio of two ligands to one copper atom in **5** was confirmed by elemental analysis. In contrast to the free ligand, we observed that the chemical shifts of CH_2N, CH_3N, and OH in **5** were shifted from 3.25 to 2.77, from 2.75 to 2.40, and from 3.80 to 6.50 ppm, respectively. Moreover, the ^1H NMR spectrum of **5** at room temperature shows only broad signals for the CH_3- and CH_2- groups. These observations indicate that those substituents are in the coordination sphere of, or very close to, the copper metal center with the formation of a P,N and/or P,O chelate. It is known that cationic copper(I) complexes usually adopt a tetragonal geometry with eight-electron-donor ligands. Of course, in complex **5**, each ligand is potentially a six-electron donor, and thus the two nitrogen and two oxygen atoms from the two ligands cannot all be coordinated to the metal. This suggests then that a dynamic exchange is taking place between the ligands around a tetracoordinated metal center. In view of the molecular structure of **5** (see Figure 2), it seems reasonable to propose an equilibrium between the two isomeric structures **5a** and **5b** in $CDCl_3$ solution (see eq 5).

To obtain more evidence for this proposal, we studied the solution behavior of the complex by variable-temperature $^{31}P\{^1H\}$ NMR in $CDCl_3$. At 263 K (−10 °C), two different signals are observed at −3.0 and −17.6 ppm which correspond to the tridentate chelate P,N,O bonding mode and P monodentate bonding mode of **L[1]**, respectively. Coalescence was observed around 273 K (0 °C) (see Figure 1).

(7) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068−8073.

(8) Boeré, R. T.; Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1985**, *24*, 3680−3687.

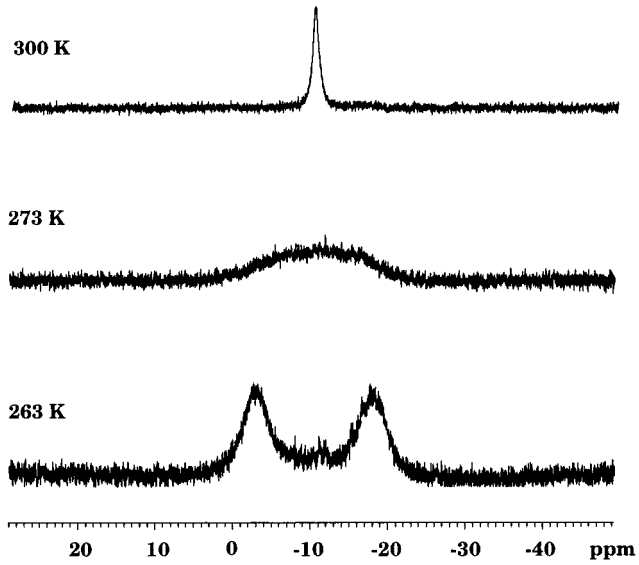
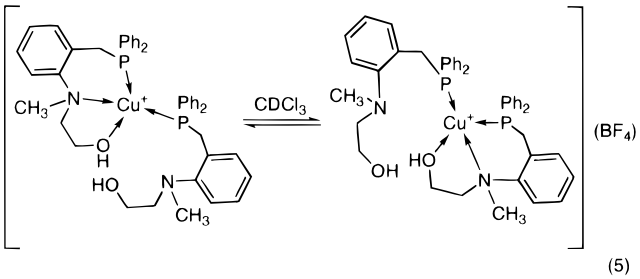


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **5** in $CDCl_3$.



(5)

The equilibrium described in eq 5 gives the first example of the opening and closing of a double chelate P,N and P,O ligand.

X-ray Structure Determination of 5. The crystal data for **5** indicate a centrosymmetric structure due to the presence of both enantiomeric forms (containing respectively the Cu(1) and Cu(2) metal atoms) in the unit cell; see Table 1). Views of one enantiomer are given in Figures 2 and 3, in which the hydrogen atoms and BF_4^- anion are omitted for clarification (see below). Figure 2 shows that the copper metal center Cu(1) has a pseudotetrahedral coordination geometry with angles N(2)−Cu(1)−O(2) and P(2)−Cu(1)−P(1) of 80.3 and 131.3°, respectively. It is quite interesting to observe that the two ligands adopt different coordination modes in **5**. One, labeled P(1)−N(1)−O(1), is only P-coordinated, as is more clearly shown in the alternative projection given in Figure 3. The second one, P(2)−N(2)−O(2), adopts a tridentate η^3(P,N,O) coordination mode, forming the two nonplanar chelates P(2)Cu(1)N(2) (with a six-membered ring) and N(2)Cu(1)O(2) (with a five-membered ring). The Cu(1)−N(2) and Cu(1)−O(2) distances of 2.366(7) and 2.117(6) Å are consistent with dative coordination bonds.[9−11] The formation of the P(2)−N(2) chelate leads to a shortening of the Cu−P bond to 2.212(2) Å, as compared to 2.235(2) Å for the P-coordination mode (see Table 2).

Table 1. Crystal Data and Structure Refinement for 5

empirical formula	$C_{88}H_{96}B_2Cu_2F_8N_4O_4P_4$
fw	1898.63
temp	293(2) K
wavelength	0.710 69 Å
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimens	a = 15.573(6) Å
	b = 18.485(6) Å
	c = 19.085(7) Å
	α = 72.00(8)°
	β = 76.90(8)°
	γ = 74.91(8)°
V	4980.5 Å^3
Z, calcd density	2, 1.281 Mg/m^3
F(000)	2020
cryst size	0.2 × 0.2 × 0.1 mm
θ range for data collection	2.68−20.81°
index ranges	$0 \le h \le 15$, $-16 \le k \le +18$, $-18 \le l \le +19$
no. of reflcns, collected/unique	9247/9238 (R(int) = 0.0000)
refinement method	full-matrix-block least-squares on F^2
no. of data/restraints/params	9238/0/1096
goodness of fit on F^2	1.091
final R indices ($I > 2\sigma(I)$)	R1 = 0.0740, wR2 = 0.1893
R indices (all data)	R1 = 0.1305, wR2 = 0.2200
extinction coeff	0.0003(5)
largest diff peak and hole	+0.441 and −0.363 e A^{-3}

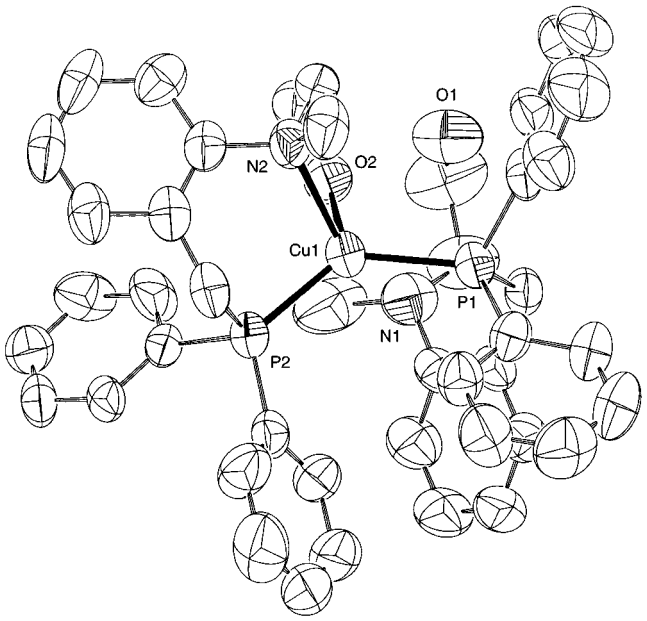


Figure 2. ORTEP plot of **5**. H atoms are omitted for clarity.

Thus, the observation of both the η^1(P) and η^3(P,N,O) coordination modes of $\mathbf{L^1}$ in **6** in the solid state corroborates the dynamic behavior of this complex in $CDCl_3$ solution (see eq 5), in which the ligand $\mathbf{L^1}$ acts reversibly as a mono- and tridentate ligand, exhibiting an unusual double hemilabile character for both nitrogen and oxygen functions.

Since functional phosphines such as P,N ligands are of great interest in homogeneous catalysis, for example in the catalytic copolymerization of olefins/CO and/or for stabilization of the catalytic species,[12] we have

(9) Dekker, G.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P.; Smeets, W.; Spek, A.; Wang, Y.; Stam, C. *Organometallics* **1992**, *11*, 1937−1948.

(10) (a) Kapteijn, G. M.; Spee, M. P. R.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 1405−1413. (b) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206−4207. (c) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890−1901.

(11) Andrieu, J.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1996**, *35*, 5975−5985.

(12) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303−306.

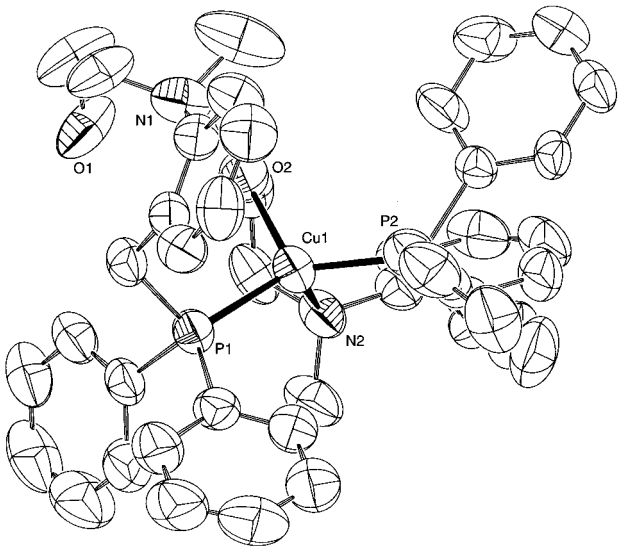
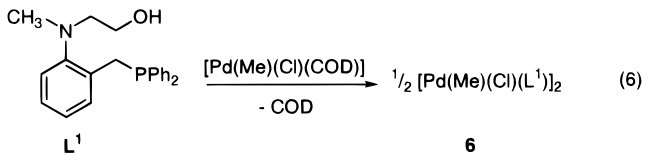


Figure 3. ORTEP plot of **5** (alternative projection). H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

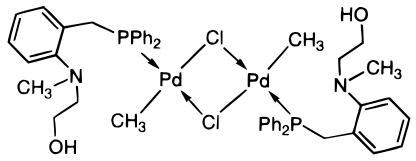
Cu(1)−O(2)	2.117(6)	Cu(2)−O(4)	2.124(5)
Cu(1)−P(2)	2.212(2)	Cu(2)−P(4)	2.210(2)
Cu(1)−P(1)	2.235(2)	Cu(2)−P(3)	2.231(2)
Cu(1)−N(2)	2.366(7)	Cu(2)−N(4)	2.352(6)
O(2)−Cu(1)−P(2)	117.0(2)	O(4)−Cu(2)−P(4)	116.4(2)
O(2)−Cu(1)−P(1)	106.0(2)	O(4)−Cu(2)−P(3)	108.5(2)
P(2)−Cu(1)−P(1)	131.30(10)	P(4)−Cu(2)−P(3)	129.66(9)
O(2)−Cu(1)−N(2)	80.3(3)	O(4)−Cu(2)−N(4)	79.5(2)
P(2)−Cu(1)−N(2)	94.7(2)	P(4)−Cu(2)−N(4)	94.6(2)
P(1)−Cu(1)−N(2)	114.8(2)	P(3)−Cu(2)−N(4)	115.4(2)

investigated the coordination properties of $\mathbf{L^1}$ with an alkylpalladium(II) complex. The reaction of $\mathbf{L^1}$ with 1 equiv of [Pd(Me)(Cl)(COD)] (COD = cycloocta-1,5-diene) afforded a complex, **6**, with an elemental analysis compatible with $[Pd(Cl)Me(L^1)]_n$. Crystals suitable for

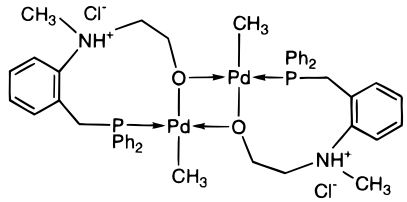


(6)

X-ray diffraction could not be obtained, and our conclusions regarding the probable structure of this complex are thus based on spectroscopic data. The ESI mass spectrum of **6** exhibited a signal at *m*/*z* 941 (relative intensity 100%), which is greater than that expected for the monomer and is consistent with that expected for a dimeric complex with the loss of two chlorides and one proton. A dinuclear structure was also indicated by ^{1}H NMR spectroscopy with two doublets at δ 3.75 ($^2J_{P,H}$ = 12 Hz) and 0.69 ($^3J_{P,H}$ = 1.7 Hz) for the PCH_2 and $PdCH_3$ protons, respectively. A likely structure for the dimer would be **6a** and, while the presence of the singlet which is observed at δ 45.6 in the $^{31}P\{^1H\}$ NMR spectrum would be consistent with either a *cis* or *trans* arrangement of the phosphorus nuclei, literature precedents indicate the *trans* configuration to be more



6a



6b

reasonable.[12,13] The ESI MS data, however, are not easily accommodated by such a structure. In the case of the Cu(I) complex above, the failure to observe the expected molecular ion is quite readily explained by the loss of a neutral ligand, whereas in the case of **6a** a major rearrangement process in the mass spectrometer would have to be invoked to explain the loss of H + 2Cl. The complex generated under mass spectroscopy conditions could, however, be derived quite readily from a dimer of structure **6b**, which contains alkoxide bridges. In contrast to the copper(I) complex **5**, the ^{1}H NMR spectrum of **6** shows a significant shift for the protons of the CH_2O group from δ 3.77 for the free ligand to δ 4.25 in the complex, which is the consequence of the covalent Pd−O bond. To confirm the presence of the ammonium group, we compared the chemical shifts in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the *N*-methyl group of MeN (or $MeNH^+$) in **6**, $\mathbf{L^1}$, with those for *N*,*N*-dimethylbenzylamine and its related ammonium chloride salt (see Table 3). These values indicate that the chemical shifts observed at δ 3.11 and at δ 46.5 in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra are consistent with the ammonium fragment in **6b** and certainly make **6a** a much less likely structure.

It is surprising to note, however, that the NH^+ proton of the ammonium group in **6** was not observed in the ^{1}H NMR spectrum. To understand this, we recorded the ^{1}H NMR spectrum of *o*-$CH_3C_6H_4NMe_2H^+Cl^-$ at different concentrations in $CDCl_3$. We observed that, as the concentration decreased, the signal for NH^+ at δ 12.9 ppm became much broader and was eventually not observable. As the dinuclear palladium complex **6** has a low solubility in $CDCl_3$, a similar phenomenon could explain the absence of the proton NH^+ in its ^{1}H NMR spectrum.

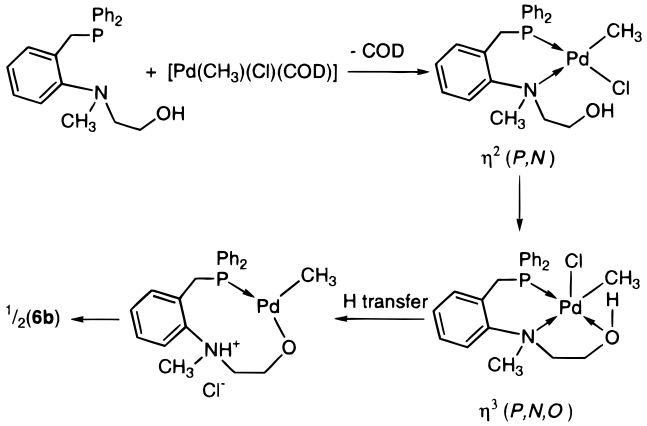
Such a binuclear complex could possibly arise via a complex where $\mathbf{L^1}$ is initially coordinated to the palladium atom in a η^2(P,N) mode with the chloride atom in a trans position with respect to the phosphorus (see Scheme 1). Similar coordination behavior has been observed for other chloromethylpalladium complexes containing P,N ligands, e.g. P,N = 1-(dimethylamino)-8-(diphenylphosphino)naphthalene (PAN) and 1-(dimethylamino)-3-(diphenylphosphino)propane (PC_3N).[9] The close proximity of the alcohol function to the metal would then permit the possibility of amine-assisted

(13) Andrieu, J.; Braunstein, P.; Naud, F. *J. Chem. Soc., Dalton Trans.* **1996**, 2903−2909.

Table 3. Chemical Shifts (ppm) of the *N*-Methyl Group

compd	^{1}H NMR (in $CDCl_3$)	$^{13}C\{^1H\}$ NMR (in $CDCl_3$)	N-alkyl group
L^1	2.70	44.2	CH_3N
o-$CH_3C_6H_4NMe_2$	2.83	44.1	CH_3N
o-$CH_3C_6H_4NMe_2H^+Cl^-$	3.18	46.3	CH_3NH^+
6	3.11	46.5	CH_3NH^+

Scheme 1

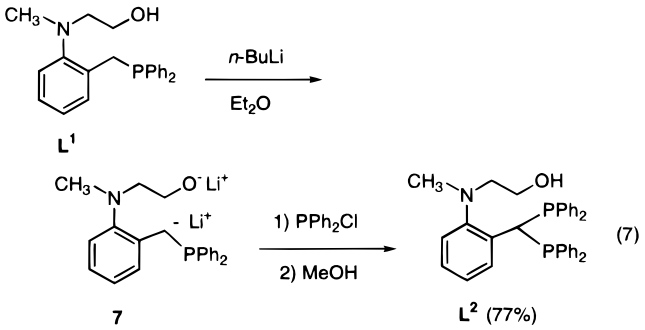


deprotonation and formation of a palladium−alkoxide species, leading subsequently to the dinuclear structure **6b** stabilized by the formation of an alkoxide bridge. A structure such as **6b** is quite attractive and interesting because similar species have been proposed as catalytic intermediates in the preparation of methyl methacrylate. For example, Drent has suggested that methanol solvent could be deprotonated by the strongly basic nitrogen function of a P,N ligand mediated by a palladium(II) complex.[2] We note also that a few examples of mixed methylpalladium alkoxide or arylpalladium complexes containing alkoxide bridges have been recently characterized by X-ray structure determination.[10]

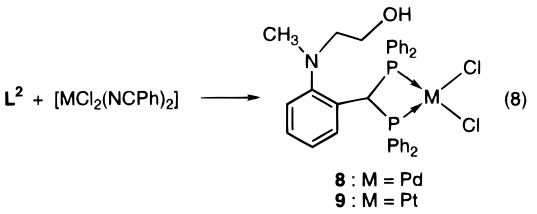
With the objective of preparing a related neutral complex from **6**, we investigated the reaction with **6** in the presence of a base such as MeONa in toluene.[13] The occurrence of a deprotonation reaction was indicated by the formation of a new peak at δ 41.2 in the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$, but unfortunately, the complex could not be fully characterized due to its instability in solution and rapid decomposition with the formation of palladium metal.

Synthesis of the Bis(diphenylphosphino) Amino Alcohol Ligand L^2. As diphosphine ligands containing amino and alcohol functions are poorly represented in the literature, we wished to extend the preparation of **L^1** to the bis(diphenylphosphino) amino alcohol ligand **L^2** via a second ortho-alkylmetalation reaction. By a procedure similar to that for **L^1**, the functional diphosphine ligand **L^2** was obtained in high yield (eq 7).

The $^{13}C\{^1H\}$ NMR spectrum showed a triplet at δ 36.6 ($^2J_{P,H}$ = 24 Hz), which confirms the presence of the second phosphorus atom in the PCHP fragment. It is interesting to note the marked chemical shift of the proton PCHP from δ 3.60 in the ligand **L^1** to the region for aromatic protons in **L^2**. This has been substantiated by a proton−carbon correlation NMR experiment. As for **L^1**, the reaction (see above) between the mixed organodilithium species **7**, derived from the metalation of **L^1**, and chlorodiphenylphosphine occurred with a high selectivity for P−C bond formation.



The ligand **L^2** reacts with palladium(II) and platinum(II) dihalides to give complexes **8** and **9**, respectively (eq 8).



The $^{31}P\{^1H\}$ NMR spectra exhibit a singlet at δ −25.6 for **8** and at δ −40.8 ($^1J_{Pt,P}$ = 2906 Hz) for **9**. Such negative values are typical of a P,P coordination mode.[11]

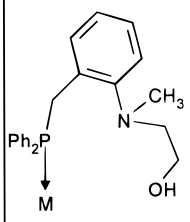
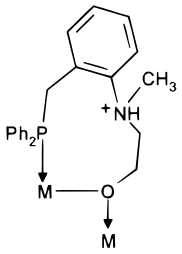
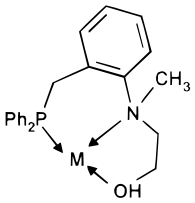
Concluding Remarks

We have developed a generally applicable synthetic methodology for the preparation of new mixed benzyllithium−lithium alkoxides such as **3** by an ortho-alkylmetalation reaction with *n*-butyllithium. The reactivity of **3** toward the P−Cl bond of diphenylchlorophosphine showed a remarkable selectivity for P−C bond formation and led to the new phosphino amino alcohol ligand **L^1**. The coordination chemistry of **L^1** has been explored with two late-transition-metal complexes, and the results obtained indicate that it behaves as a rather versatile ligand. Its coordination properties are summarized in Table 4. We have demonstrated that the association of two different functions (amine and alcohol) in the same phosphorus ligand does not merely constitute a sum of the coordination properties of each function but generates new properties such as the double hemilabile character of the different functions and intramolecular proton transfer.

An unusual proton transfer from the alcohol to the amino group of **L^1** appears to take place to give a dinuclear palladium complex (**6b**). Such a transfer would represent a catalytic model for OH activation by palladium dihalides in the presence of nitrogen base. Such a process has been proposed as a key step in, for example, the homogeneous catalysis of the methoxycarbonylation of propyne by palladium complexes containg bifunctional phosphino amine ligands.[2]

The mono(diphenylphosphino)amino alcohol ligand **L^1** underwent a second ortho-alkylmetalation reaction, and again a selective P−C coupling reaction with chlorodiphenylphosphine allowed access to the new functional diphosphine ligand **L^2**. We have just started to explore the coordination properties of **L^2**, and its behavior seems to be similar to that of the dppm ligand (dppm = bis(diphenylphosphino)methane). Further

Table 4. Coordination Properties of the P,N,O Ligand L[1]

Ligand	monodentate 	bidentate 	tridentate 
Coordination modes	*P*-coordinated η^1 (*P*)	*P,O* chelated μ-η^1 (*O*):η^2 (*P,O*)	*P,N* and *P,O* chelated η^3 (*P,N,O*)
Ligand donor	2 electrons	5 electrons	6 electrons

investigations are currently in progress in order to evaluate the effect of the 2-amino alcohol function of **L[1]** and **L[2]**, whether free or coordinated (and the related ammonium salts), on the solubility properties of the complexes in biphasic solutions.

Experimental Section

General Comments. All reactions were performed in Schlenk-type flasks under argon. Solvents were purified and dried under argon by conventional methods. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 300.13, 75.04, and 121.47 MHz, respectively, on a Bruker AC 300 instrument. Assignments of ^{1}H and/or ^{13}C{^{1}H} NMR spectra were confirmed by DEPT experiments and/or proton−carbon correlations. FAB (glycerol matrix) and ESI mass spectra and elemental analyses were performed at the National Hellenic Research Foundation in Athens. The complexes [Pd(Me)(Cl)(COD)] (COD = cycloocta-1,5-diene), [Cu(NCMe)$_4$](BF$_4$), [PdCl$_2$(NCPh)$_2$], and [PtCl$_2$(NCPh)$_2$] were prepared according to literature procedures.[12,14,15] The solution of *n*-butyllithium in methylcyclohexane (1.87 M) was prepared by following the conventional procedure. The organic compounds *o*-toluidine (2-methylaniline) (**1**), ethylene chlorohydrin (2-chloroethanol), and chlorodiphenylphosphine were commercial products (Aldrich).

Synthesis of 2-[Methyl(2-methylphenyl)amino]ethanol (2).[16] A mixture of *o*-toluidine (**1**; 50.0 g, 0.467 mol) and 2-chloroethanol (37.6 g, 0.467 mol) was heated at 160 °C for 15 min. After cooling to room temperature, a solution of NaOH (0.47 mol in 300 mL of water) and CH_2Cl_2 (50 mL) were added. The organic phase was separated. All solvents were removed *in vacuo*, and a yellow viscous oil was obtained. Distillation under high vacuum (0.8 mmHg) at 115 °C afforded the functionalized *o*-toluidine as a colorless oil. The oil obtained (47.6 g, 0.315 mol) and $NaHCO_3$ (45.0 g, 0.630 mol) were dissolved in methanol (200 mL). Dimethyl sulfate (30 mL, 0.315 mol) was added dropwise at room temperature. The reaction started after a few minutes with the formation of carbon dioxide. After the mixture was stirred for 3 days, the methanol was removed *in vacuo*. The yellow residue obtained was dissolved in a mixture of water (200 mL) and CH_2Cl_2 (200 mL). The organic phase was separated and concentrated *in vacuo*. Compound **2** was purified by distillation under high vacuum (1 mmHg) at 93−95 °C: yield 36.9 g (48% based on *o*-toluidine). The product was identical with that produced by a previously reported procedure.[16] ^{1}H NMR ($CDCl_3$): δ 7.25−7.02 (m, 4H, aromatic), 3.68 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2O), 3.10 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2N), 2.66 (s, 3H, CH_3N), 2.45 (s, br, 1H, OH, exchange with D_2O), 2.34 (s, 3H, CH_3−C_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.5, 133.2, 131.0, 126.5, 123.7, 120.5 (s, 6C, aromatic), 58.9 (s, 1C, CH_2OH), 57.5 (s, 1C, CH_2N), 41.9 (s, 1C, CH_3N), 17.9 (s, 1C, CH_3−C_{Ar}). $C_{10}H_{15}NO$ (M_r = 165.11).

Synthesis of 4. A solution of **2** (1.65 g, 10.0 mmol) in Et_2O (10 mL) was cooled to 0 °C. After the mixture was stirred for 10 min, *n*-butyllithium (14 mL, 25.0 mmol) was added dropwise. The mixture was stirred and warmed slowly from 0 °C to room temperature. After 1 h, the pale yellow solution was heated under reflux for 3 h. The formation of the orthometalated compound **3** was then complete and took the form of a mustard yellow suspension. After cooling to 0 °C, benzaldehyde (1.1 mL, 11.0 mmol) was added and the mixture stirred for 20 min. Water (5 mL) and CH_2Cl_2 (20 mL) were then introduced. The organic phase was separated and afforded a pale yellow oil after evaporation of solvents *in vacuo*. The oil was analyzed by ^{1}H NMR and, by integration of the peaks at δ 4.89 corresponding to the proton C*H*(Ph)(OH) of **4** and at δ 2.34 for the protons CH_3−C_{Ph} of **2**, the yield of product, and thus also that of the intermediate metalated species, was estimated to be greater than 91%. White crystals of **4** were obtained from the oil by crystallization in cold methanol: yield 1.41 g (52%). ^{1}H NMR ($CDCl_3$): δ 7.38−7.08 (m, 4H, aromatic), 5.60 (s, br, 2H, OH, exchange with D_2O), 4.89 (dd, 1H, $^2J_{H_A,H_X}$ = 9.0 Hz, $^2J_{H_B,H_X}$ = 2.8 Hz, $CH^X(Ph)(OH)$), 3.68 (t, 2H, $^2J_{H,H}$ = 5.1 Hz, CH_2O), 3.34 (dd, 1H, $^1J_{H_A,H_B}$ = 14.1 Hz, $^2J_{H_A,H_X}$ = 9.0 Hz, part A from ABX spin system of CH^AH^B−$CH^X(Ph)(OH)$), 3.05 (t, 2H, $^2J_{H,H}$ = 5.1 Hz, CH_2N), 2.96 (dd, 1H, $^1J_{H_A,H_B}$ = 14.1 Hz, $^2J_{H_B,H_X}$ = 2.8 Hz, part B from ABX spin system of CH^AH^B−$CH^X(Ph)(OH)$), 2.68 (s, 3H, CH_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.5−121.2 (m, 12C, aromatic), 75.6 (s, 1C, *C*H(Ph)(OH)), 59.0 (s, 2 C, CH_2OH + CH_2N), 42.8 (s, 1C, CH_3N), 42.2 (s, 1C, CH_2−CH(Ph)(OH)), 17.9 (s, 1C, CH_3−C(Ph)). Anal. Calcd for $C_{17}H_{21}NO_2$ (M_r = 271.16): C, 75.25; H, 7.79; N, 5.16. Found: C, 75.11; H, 7.72; N, 5.22.

Synthesis of 2-[Methyl(2-((diphenylphosphino)methyl)phenyl)amino]ethanol (L[1]). To a solution of **2** (4.96 g, 30 mmol) in Et_2O (30 mL) was added dropwise *n*-butyllithium (35 mL, 63 mmol). After it was stirred at room temperature overnight, this mixture was heated under reflux for 3 h and then cooled to 0 °C. Chlorodiphenylphosphine (5.9 mL, 33 mmol) was added dropwise and the mixture stirred overnight.

(14) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90−91.
(15) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60−63.
(16) Lattes, A.; Verdier, A. *Bull. Soc. Chim. Fr.* **1965**, 2037−2043.

Methanol (50 mL) was introduced. After this mixture was stirred for 3 h, all organic solvents were removed in vacuo. The viscous oil obtained was dissolved in toluene (100 mL), and the solution was filtered through Celite. Evaporation of toluene *in vacuo* afforded the functional phosphine ligand **L¹** as a pale yellow oil, which was dried at 80 °C under high vacuum for 2 h. Satisfactory elemental analyses could not be obtained, apparently due to tenacious retention of solvent. The oil was used for further reactions without other purification: yield 9.20 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.55−7.17 (m, 14H, aromatic), 3.80 (s, br, 1H, OH, exchange with D_2O), 3.73 (t, 2H, $^2J_{H,H}$ = 5.1 Hz, CH_2O), 3.52 (d, 2H, $^2J_{P,H}$ = 2.4 Hz, CH_2P), 3.20 (t, 2H, $^2J_{H,H}$ = 5.1 Hz, CH_2N), 2.70 (s, 3H, CH_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.3−121.5 (m, 18C, aromatic), 59.4 (s, 1C, CH_2OH), 58.1 (s, 1C, CH_2N), 44.2 (s, 1C, CH_3N), 32.3 (d, 1C, $^1J_{P,C}$ = 12.8 Hz, CH_2P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −14.8 (s). $C_{22}H_{24}NOP$ (M_r = 349.16).

Synthesis of *N*-(2-Diphenylphosphinyl)ethyl)-*N*,2-dimethylbenzenamine. By a procedure similar to that for ligand **L¹**, the isomer was obtained from **3** (0.66 g, 4.0 mmol), *n*-butyllithium (2.3 mL, 4.2 mmol), chlorodiphenylphosphine (0.75 mL, 4.2 mmol), after addition of only few milliliters of methanol, as a viscous white oil: yield of crude product 1.05 g (75%). Further purification proved unsuccessful. ^{1}H NMR (C_6D_6): δ 7.84−6.88 (m, 14H, aromatic), 3.86 (dt, 2H, $^3J_{P,H}$ = 12.0 Hz, $^2J_{H,H}$ = 6.0 Hz, CH_2OP), 3.04 (t, 2H, $^2J_{H,H}$ = 6.0 Hz, CH_2N), 2.42 (s, 3H, CH_3N), 2.24 (s, 3H, $CH_3{-}C_{Ph}$). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.3−120.5 (m, 18C, aromatic), 68.0 (d, 1C, $^2J_{P,C}$ = 18.7 Hz, CH_2OP), 57.0 (s, 1C, CH_2N), 42.4 (s, 1C, CH_3N), 18.5 (s, 1C, $CH_3{-}C_{Ph}$). ^{31}P{^{1}H} NMR (C_6D_6): δ 112.0 (s). $C_{22}H_{24}NOP$ (M_r = 349.16).

Synthesis of 5. To a solution of **L¹** (0.900 g, 2.57 mmol) in CH_2Cl_2 (15 mL) was added the complex $[Cu(NCMe)_4](BF_4)$ (0.400 g, 0.127 mmol). The colorless solution was stirred for 2 days. Slow addition of diethyl ether afforded white crystals of **5**, which were filtered, washed with ether, and dried in vacuo: yield 0.982 g (91%). ^{1}H NMR ($CDCl_3$): δ 7.38−6.30 (m, 28H, aromatic), 6.50 (s, br, 2H, OH, exchange with D_2O), 3.90 (s, br, 4H, CH_2P), 3.74 (s, br, 4H, CH_2O), 2.77 (s, br, 4H, CH_2N), 2.40 (s, br, 6H, CH_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.9−120.0 (m, 36C, aromatic), 65.7 (s, 2C, CH_2OH), 58.6 (s, 2C, CH_2N), 43.9 (s, 2C, CH_3N), 31.4 (s, br, 2C, CH_2P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −10.2 (s, br). IR (KBr): 1080 cm^{-1} (vs, $\nu_{BF_4^-}$). Mass spectrum (FAB; glycerol matrix): *m/z* (relative intensity) 411.9 (100%, $M^+ - L^1 - BF_4$). Anal. Calcd for $C_{44}H_{48}BF_4N_2O_2P_2Cu$ (M_r = 849.18): C, 62.23; H, 5.70; N, 3.30. Found: C, 61.84; H, 5.74; N, 3.14.

Synthesis of 6. By a procedure similar to that for complex **5**, but with **L¹** (0.262 g, 0.75 mmol) and [Pd(Me)(Cl)(COD)] (0.200 g, 0.75 mmol), as starting materials, **6** was obtained as a pale yellow powder: yield 0.450 g (59%). ^{1}H NMR ($CDCl_3$): δ 7.65−6.94 (m, 28H, aromatic), 4.25 (s, br, 4H, CH_2O), 3.75 (d, 4H, $^2J_{P,H}$ = 12 Hz, CH_2P), 3.36 (s, br, 4H, CH_2N), 3.11 (s, 6H, CH_3N), 0.69 (d, 6H, $^3J_{P,H}$ = 1.7 Hz, CH_3Pd). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 133.2−119.5 (m, 36C, aromatic), 62.2 (s, 2C, CH_2O), 60.8 (s, 2C, CH_2N), 46.5 (s, 2C, CH_3N), 34.3 (d, 2C, $^1J_{P,C}$ = 25 Hz, CH_2P), 0.9 (s, br, 2C, CH_3Pd). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.6 (s). Mass spectrum (electrospray ionization): *m/z* (relative intensity) 941.1 (100%, $M^+ - 2\,Cl - 1\,H$). Anal. Calcd for $C_{46}H_{54}Cl_2N_2O_2P_2Pd_2$ (M_r = 1010.11): C, 54.65; H, 5.39; N, 2.77. Found: C, 54.44; H, 5.24; N, 2.74.

Synthesis of L². By a procedure similar to that for the ligand **L¹**, the functional diphosphine ligand **L²** was obtained by reaction between the mixed organolithium species **7** (prepared from **L¹** (3.38 g, 9.7 mmol) and *n*-butyllithium (11.3 mL, 21 mmol)) and chlorodiphenylphosphine (1.8 mL, 10.8 mmol), as a waxy solid: yield 4.0 g (77%). Retention of small amounts of solvent precluded the acquisition of satisfactory elementary analyses. ^{1}H NMR ($CDCl_3$): δ 7.65−5.45 (m, 24H, aromatic with 1H from PCHP group), 3.55 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2O), 2.30 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2N), 2.23 (s, 3H, CH_3N), 2.00 (s, 1H, OH, exchange with D_2O). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.4−122.0 (m, 26C, aromatic), 59.4 (s, 1C, CH_2OH), 58.6 (s, 1C, CH_2N), 41.2 (s, 1C, CH_3N), 36.6 (t, 1C, $^1J_{P,C}$ = 24 Hz, PCHP). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 0.6 (s). $C_{34}H_{33}NOP_2$ (M_r = 533.20).

Synthesis of 8. To a solution of **L²** (0.152 g, 0.28 mmol) in CH_2Cl_2 (10 mL) was added $[PdCl_2(NCPh)_2]$ (0.104 g, 0.28 mmol). After it was stirred for 1 h, the solution was concentrated *in vacuo*. Addition of hexane afforded an orange powder, which was filtered off and dried *in vacuo*: yield 0.152 g (75%). ^{1}H NMR ($CDCl_3$): δ 8.06−5.48 (m, 24H, aromatic with 1H from PCHP group), 3.67 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2O), 2.86 (t, 2H, $^2J_{H,H}$ = 5.4 Hz, CH_2N), 2.43 (s, 3H, CH_3N), 2.13 (s, br, 1H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.7−121.5 (m, 30C, aromatic), 59.2 (s, 1C, CH_2N), 58.8 (s, 1C, CH_2OH), 50.0 (s, br, 1C, PCHP), 42.3 (s, 1C, CH_3N). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −25.6 (s). Anal. Calcd for $C_{34}H_{33}Cl_2NOP_2Pd{\cdot}{}^1/_2CH_2Cl_2$ (M_r = 751.02): C, 55.02; H, 4.56; N, 1.87. Found: C, 54.73; H, 4.88; N, 1.86.

Synthesis of 9. To a solution of **L²** (0.240 g, 0.45 mmol) in CH_2Cl_2 (10 mL) was added $[PtCl_2(NCPh)_2]$ (0.213 g, 0.45 mmol). After it was stirred for 1 h, the solution was concentrated *in vacuo*. Addition of hexane afforded a white powder, which was filtered off and dried *in vacuo*: yield 0.295 g (82%). ^{1}H NMR ($CDCl_3$): δ 8.01−5.56 (m, 24H, aromatic with 1H from PCHP group), 3.66 (t, 2H, $^2J_{H,H}$ = 5.7 Hz, CH_2O), 2.88 (t, 2H, $^2J_{H,H}$ = 5.7 Hz, CH_2N), 2.43 (s, 3H, CH_3N), 2.20 (s, br, 1H, OH exchange with D_2O). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.5−112.2 (m, 30C, aromatic), 59.9 (s, 1C, CH_2N), 59.5 (s, 1C, CH_2OH), 55.2 (t, 1C, $^1J_{P,C}$ = 33 Hz, PCHP), 43.5 (s, 1C, CH_3N). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −40.8 (s, with ^{195}Pt satellites, $^1J_{Pt,P}$ = 2906 Hz). Anal. Calcd for $C_{34}H_{33}Cl_2NOP_2Pt$ (M_r = 798.10): C, 51.12; H, 4.17; N, 1.75. Found: C, 51.32; H, 4.29; N, 1.51.

X-ray Structure Determination of 5. The crystal of **5** used for data collection was mounted in a capillary at room temperature, and data were collected using a small (180 mm diameter) Mar (X-ray Research) scanner mounted on a 3 kW molybdenum sealed-tube source. A total of 95 frames of data were collected using a 2° rotation angle and a crystal-to-plate distance of 75 mm, giving an overall completeness of 88.54%, a multiplicity of 1.88, and a merging *R* of 4.99% on intensities. The structure was solved using the direct-methods routine within the program Shelxs (courtesy of George Sheldrick, University of Göttingen) and refined using full-matrix least-squares methods to a final conventional *R* factor of 7.51%. Hydrogen atoms were included in calculated positions. The asymmetric unit of the crystal contains two distinct molecules, each of which shows one ligand to be tridentate and the other to be monodentate, giving an overall distorted-tetrahedral geometry at each copper center. Disordered solvent, equivalent to three molecules of ether, can be seen in the final difference electron density map, and although an attempt to model this was made, no satisfactory model could be found, giving a relatively high observed *R* factor. Hydrogen atoms were inserted in calculated positions. Crystal data are given in Table 1, selected bond lengths and angles are shown in Table 2, and a single molecule of the complex with a partial numbering scheme is displayed in Figures 2 and 3. The full data have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgment. This work was supported by the European Union Human Capital and Mobility Network Contract No. ERBCHRXCT 930281.

Supporting Information Available: Further details of the structure determination, including a fully numbered ORTEP drawing and tables of atomic coordinates, bond lengths and angles, and thermal parameters for **5** (16 pages). Ordering information is given on any current masthead page.

OM970550E