Reversible P–C bond formation for saturated α-aminophosphine ligands in solution: stabilization by coordination to Cu(I)

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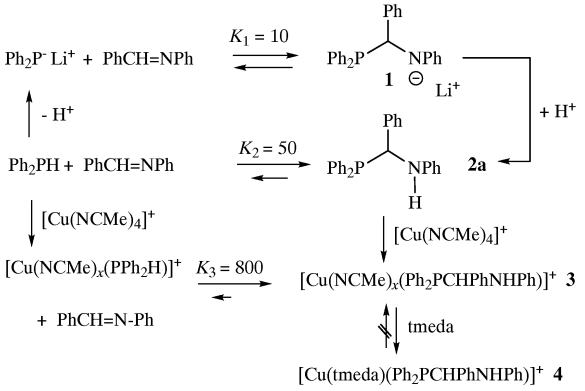
The saturated α-aminophosphine ligands containing a secondary amine function $Ph_2PCH(R')NHR''$ establish a solution equilibrium with Ph_2PH and $R'CH{=}NR''$ and are stabilized by electron-withdrawing substituents R′ and R″ and by coordination of the phosphorous donor to Cu(I).

Since the discovery that bifunctional P,N ligands increase considerably the activity and/or the selectivity of palladium, ruthenium or rhodium catalysts[1–4] the preparation of this type of ligand has been the subject of extensive investigations. Amongst these ligands, α-aminophosphines crucially control the activity and selectivity of alkyne methoxycarbonylation catalysts.[1] Unsaturated ligands of this type (having an sp^2-hybridized N donor) are exemplified by 2-$PyPPh_2$ (Py = C_5H_4N). Saturated versions of this class, *i.e.* $Ph_2PCH(R)NR'R''$ have received little attention. While the Mannich reaction between Ph_2PH, CH_2O and the Me_2NH compounds leads to the stable (both in the solid state and in solution) $Ph_2PCH_2NMe_2$ ligand having a tertiary amine function,[5] aminophosphines prepared by addition of Et_2PH to $CH_2{=}N^tBu$[5] or Ph_2PH to PhCH=NPh[6] *without solvent* have only been described in the solid state. The subsequent reaction with iodomethane leads to an unexpected P–C bond cleavage.[6] Anionic α-P,N ligands prepared by nucleophilic addition of $Ph_2P^-Li^+$ to PhCH=NPh or RLi to 2-$PyPPh_2$ have also showed instability in solution.[7,8] We now wish to present NMR and synthetic studies that enable us to rationalise the solution instability of α-P,N ligands with secondary amine functions and to understand the electronic factors that favor their stabilization.

The reaction of $Ph_2P^-Li^+$ with one equivalent of *N*-benzylideneaniline, followed by quenching with water and extraction in toluene affords the desired product **2a**, see Scheme 1.

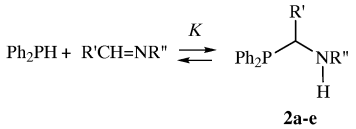
The ^{31}P and ^1H NMR spectroscopic properties confirm the nature of the product. However, the NMR spectra of the redissolved crystallised product show the presence of the diphenylphosphine and imine starting materials in amounts that increase with time, indicating a reversible P–C bond cleavage. NMR monitoring of this process in $CDCl_3$ (integration of the ^1H NMR imine CH=N and product P–CH–N signals) reveals the establishment of a stable equilibrium position ($t_{1/2}$ = 10 min; K_2 = 50 after >2 d), which was independently confirmed by NMR monitoring of the reaction between Ph_2PH and PhCH=NPh. A closer examination shows that an analogous equilibrium is also established for the anionic species, although this is shifted to a weaker extent toward the PCN product **1** relative to the neutral system (K_1 = 10 by ^{31}P NMR integration in THF–C_6D_6). Thus, our NMR experiments show that the instability of the α-P,N ligand and of its related anionic form in solution is due to a reversible P–C bond formation, with proton migration for the neutral species.



Scheme 1

The generalization to a wider group of imines establishes the substituent effect on the equilibrium position (see Scheme 2). In particular, the presence of an electron-withdrawing group has a beneficial effect on the ligand formation when this is located either on the nitrogen atom (**d** > **a** > **b** > **c**) or on the carbon atom (**e** > **b**). This study shows that the careful choice of substituents may allow the synthesis of stable (in solution) α-P,N saturated ligands.

As we are interested in the exploration of the coordinating properties of these P,N ligands, we wished to examine whether coordination to a suitable metal could also affect the stability of the P–C bond. The above mentioned 2-$PyPPh_2$ ligand is known to act as an assembling ligand (adopting a μ-η^2 coordination mode) in dinuclear copper(I) and in numerous other polynuclear complexes.[4,9] Addition of one equivalent of $[Cu(NCMe)_4][BF_4]$[10] to the equilibrium mixture containing **2**, Ph_2PH and PhCH=NPh in $CDCl_3$ produces a solution with a major ^{31}P NMR resonance at δ − 3.90 and a minor one at δ − 35.2 corresponding to the copper complexes $[Cu(NCMe)_x(Ph_2PCHPhNHPh)][BF_4]$ **3**, and



2a-e

	R′	R″	*K*
a	Ph	Ph	50
b	Ph	CHMePh	10
c	Ph	CH_3	0.2
d	Ph	*p*-$NO_2C_6H_4$	>1000
e	*p*-$NO_2C_6H_4$	CHMePh	390

Scheme 2

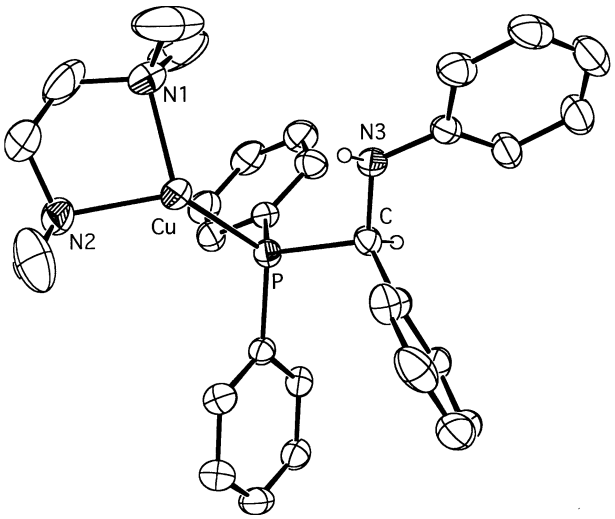


Fig. 1 An ORTEP[14] view of the cation of compound **4**. Selected bond distances (Å) and angles (°): Cu–N1 2.073(6), Cu–N2 2.104(6), Cu–P 2.153(2), P–C 1.878(6), C–N3 1.466(8); N1–Cu–N2 87.7(2), N1–Cu–P 133.9(2), N2–Cu–P 126.8(2), N3–C–P 104.8(4).

$[Cu(NCMe)_x(PPh_2H)][BF_4]$, respectively (Scheme 1). Only traces of coordinated Ph_2PH and free PhCH=NPh have been detected in the ^1H NMR spectrum ($K_3 = 800$), indicating an almost quantitative shift of the equilibrium. This result shows that removal of electron density from the phosphine end of the molecule also stabilizes the P–C bond.

Compound **3** is highly unstable, even in neat MeCN, leading to the slow precipitation of metallic copper. Addition of $Me_2NCH_2CH_2NMe_2$ (tmeda), on the other hand, yields stable $[Cu(tmeda)(Ph_2PCHPhNHPh)][BF_4]$ **4**, with NMR properties quite similar to those of **3**. Colourless single crystals of **4** were obtained from $CHCl_3$. The geometry of the cation, shown in Fig. 1, reveals a rare example of three-coordination for a Cu(I) complex.[11,12] The α-P,N ligand is only P-coordinated and the amino function remains dangling, whereas the analogous 2-$PyPPh_2$ ligand always adopts a μ-P, N coordination mode in dinuclear copper complexes.[9,11] Note that a fluxional behaviour interconverting P- and N-coordinated ligands in solution is inconsistent with the observed variation of the ^{31}P chemical shift from the free to the coordinated ligand, which is similar to that observed for the 2-$PyPPh_2$ system.

In conclusion, we have shown that the instability of α-P,N ligands with a secondary amine function and their corresponding anions in solution is due to reversible P–C bond formation, which can be reduced or suppressed by a decrease of electron density. This can be accomplished by either electron withdrawing substituents on the nitrogen or carbon atoms, or by coordination of the phosphorus donor. These results allow an easy and rapid access to new complexes with saturated α-aminophosphine ligands. Further studies are in progress in order to control the chirality of the central carbon atom (P–C*–N) and to explore the coordination properties of α-P,N ligands toward early and late transition metals.

Experimental

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. All chemical shifts are given in ppm.

Reversible formation of compounds 2a–e

To a solution of PhCH=NPh (0.312 g, 1.72 mmol) in $CDCl_3$ (10 ml) was added Ph_2PH (0.300 ml, 1.72 mmol). The mixture was stirred for 2 h, yielding an equilibrium of **2a** with the starting materials. ^1H NMR ($CDCl_3$): δ 7.97–6.68 (m, 20 H, aromatics), 5.16 [dd, 1H, PCH, $^2J(P,H) = 3.2$, $^3J(H,H) = 6.5$], 4.41 [dd, 1H, NCH, $^3J(P,H) = 3.8$, $^3J(H,H) = 6.5$ Hz, exchange readily with D_2O]. ^{31}P NMR ($CDCl_3$): δ 3.70 (s). ^{13}C NMR ($CDCl_3$): δ 140.00–113.72 (m, 24C, aromatics), 56.92 [d, 1C, PCH, $^1J(PC) = 14.0$ Hz].

By analogous reactions, equilibrium mixtures of compounds **2b–e** with the corresponding starting materials were obtained (equilibrium constants as indicated in Scheme 2). ^1H NMR ($CDCl_3$). *PCHN proton:* δ 4.12 and 4.10 (**2b**, d, $^2J_{PH}$ = 9.8, and $^2J_{PH} = 5.6$ respectively), 4.22 (**2c**, d, $^2J_{PH} = 9$), 5.20 (**2d**, dd, $^2J_{PH} = 7.0$, $^3J_{HH} = 2.9$), 4.63 and 4.27 (**2e**, d, $^2J_{PH} = 9.8$ and $^2J_{PH} = 5.6$ Hz respectively); *NH proton:* δ 2.35 (**2b,** s, br), 4.28 (**2c**, d, $^3J_{PH} = 5.8$), 5.05 (**2d**, dd, $^3J_{PH} = 6.7$, $^3J_{HH} = 2.9$ Hz), 2.03 (**2e**, s, br). ^{31}P NMR ($CDCl_3$): δ 1.49 and 0.89 (**2b**), 1.20 (**2c**), 5.78 (**2d**), 4.85 and 4.61 (**2e**). Compounds **2b** and **2e** are present as both possible diastereoisomers.

Preparation of compound 4

The equilibrium solution of ligand **2a** obtained as described above was transferred to a Schlenk tube containing $[Cu(NCMe)_4][BF_4]$ (0.540 g, 1.72 mmol) and the mixture was stirred for 1 h. ^1H NMR ($CDCl_3$): δ 7.46–6.46 (m, 20 H, aromatics), 5.23 (s, br, 1H, PCH), 4.61 (s, br, 1H, NCH), 2.00 (s, br, 12H, CH_3CN, free and coordinated were not separated). ^{31}P NMR ($CDCl_3$): δ −3.90 (s). ^{13}C NMR ($CDCl_3$): δ 145.57–113.57 (m, 48C, aromatics), 56.95 (s, br, 2C, PCH). In a control experiment, coordination of $PHPh_2$ to $[Cu(MeCN)_4]^+$ yields a ^{31}P NMR resonance at δ −3.47. To this solution was added tmeda (0.26 ml, 1.72 mmol). The resulting solution was stirred for 2 h, filtered and concentrated to half volume. Complex **4** was isolated by precipitation with Et_2O and washed twice with this solvent. Colorless crystals were obtained from $CHCl_3$ (0.742 g, 68%). ^1H NMR ($CDCl_3$): δ 7.58–6.60 (m, 20H, aromatics), 5.36 (m, 2H, PCH + NCH), 2.61 (s, br, 4H, NCH_2 coordinated), 2.43 (s, br, 12H, NCH_3 coordinated). ^{31}P NMR ($CDCl_3$): δ 13.77 (s). ^{13}C NMR ($CDCl_3$): δ 134.32–114.27 (m, 24C, aromatics), 58.00 (s, br, 1C, PCH), 48.36 (s, br, 6C, $NCH_3 + NCH_2$ from tmeda coordinated) (Calc. for $C_{32}H_{38}N_3PF_4Cu$: C, 60.55; H, 6.04; N 6.62; Found: C, 60.33; H, 5.92; N 6.43%).

Crystal structure analysis of compound 4

Crystal dimensions: 0.3 × 0.3 × 0.2 (mounted in capillary). The data collection was carried out on a CAD4 Enraf-Nonius goniometer. The structure was solved by interpretation of the Patterson map and subsequent difference Fourier techniques. All non-hydrogen atoms were refined anisotropically.[13] Crystal and refinement data: $C_{32}H_{38}N_3PF_4Cu$, M_r = 634.20, orthorhombic, space group $Pna2_1$, $a = 19.528(1)$, $b = 16.812(1)$, $c = 9.719(1)$ Å, $Z = 4$, $V = 3190.8(4)$ Å^3, ρ_{calc} = 1.320 g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å), μ(Mo-Kα) = 0.782 mm^{-1}, $T = 298$ K, $F(000) = 1320$, 2369 independent reflections measured up to $\sin(\theta)/\lambda = 0.616$. Final residual indices: $R_w(F^2) = 0.096$ for all data and $R(F) = 0.035$ for 1867 reflections with $I > 2\sigma(I)$, $S = 1.072$. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-105288.

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