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Unusual properties of the first copper complex containing a $\pi(\eta^2)$-coordinated phosphorus–carbon double bond moiety†

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Received (in Cambridge, UK) 1st May 2002, Accepted 3rd July 2002
First published as an Advance Article on the web 19th July 2002

The first stable phosphaarene π-complex of copper displays unusual ^{31}P NMR data that suggest a novel interpretation of ^{31}P coordination shifts in π-complexes of phosphorus containing multiple bonds.

Copper(I)–olefin complexes play an important role in modern organic and biochemistry; in particular, valuable transformations such as Cu-catalysed addition of carbanions to α,β-unsaturated carbonyls and alkene cyclopropanation/aziridination involve these compounds as catalytically active species or resting states.[1] Recently, interaction between copper and aromatic π-systems has gained attention, and some Cu(I)–arene complexes have been characterised.[2] Despite the analogy between C=C and P=C double bonds and the ability of the latter to form π-complexes with transition metals,[3] stable copper π-complexes of phosphaarenes or phosphaalkenes are still unknown, although Cu-mediated coupling of phosphaalkenes has been successfully applied in synthesis.[4] During our studies on zwitterionic benzo[*c*]phospholides such as **1a**,[5] we prepared complex **2a** (Scheme 1) comprising the first example of a π-bound P=C unit at a copper atom. Apart from the rare trapping of different coordination modes for identical ligands at one metal, a solid state NMR study revealed an unusually low ^{31}P coordination shift for the π-bound ligand. Computational analysis of this effect lead to a new interpretation of coordination shifts that allows novel insight into the nature of metal–ligand bonding in π-complexes of phosphorus containing multiple bond systems.

Reaction of CuI (1 equiv.) with **1a**[5] (2 equiv.) in CH$_2$Cl$_2$ gave a yellow solution whose work-up yielded orange crystals of **2a**.‡ A single crystal X-ray diffraction study§ revealed the presence of complexes [(**1a**)$_2$CuI] whose metal atom is coordinated in a Ψ-trigonal geometry defined by the iodide, the phosphorus atom of a η^1(P)-bound benzophospholide, and a η^2-coordinated P=C double bond of another molecule of **1a** (Fig. 1). The Cu1–I1 (2.5218(6) Å) and Cu1–P1′ (2.2262(12) Å) distances match those in Cu-complexes of bis-phosphonio-benzophospholides (Cu–I 2.501(2), Cu–P 2.20–2.25 Å[6]). The distance between the metal and the η^2(P=C)-moiety (Cu–Centroid 2.206(2) Å) exceeds analogous distances in olefin complexes (Cu–Centroid 2.00 ± 0.11[7]). The π-coordinated P1–C9 bond (1.749(4) Å) is longer than the corresponding bonds in the η^1(P)-bound ligand in **2a** (P1′–C9′ 1.704(4) Å) and free **1a** (1.7171(14) Å[8]), but still shorter than those in η^2-complexes of phosphoniobenzophospholides with Co(I) or Mo(0) (1.81–1.83 Å[9]). In contrast to these, the geometry at the C9 atom is planar (sum of intra-ligand angles 360(2)°), and other intra-ligand distances and angles match those in free **1a**.[8] The modest structural distortion of the π-bound phosphaarene in **2a** is similar to Cu(I)–arene complexes[2] and suggests a lower degree of π-bond localization and M→L(π*) charge-transfer than in other benzophospholide π-complexes.[5,9]

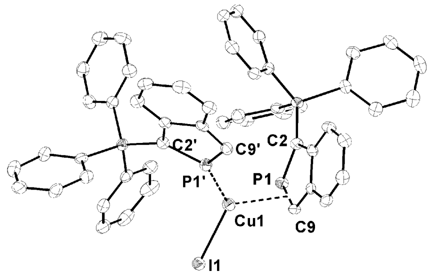
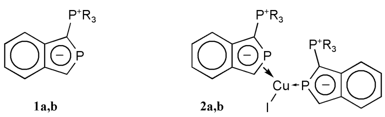


Fig. 1 ORTEP style drawing of **2a** (thermal ellipsoids at the 50% probability level; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): I1–Cu1 2.5218(6), Cu1–P1′ 2.2262(12), Cu1–C9 2.312(4), Cu1–P1 2.4332(12), P1–C9 1.749(4), P1′–C9′ 1.704(4); I1–Cu1–P1′ 125.47(4), P1′–Cu1-Cent(P1,C9) 116.5(1), I1–Cu1–Cent(P1,C9) 116.9(1).

The inequivalence of the benzophospholide ligands in **2a** is as well reflected in solid state ^{31}P MAS NMR spectra. The metal bound phosphorus nuclei give rise to two distinct signals with nearly identical isotropic chemical shift, but different spin–spin couplings to the ^{63}Cu (69.1%, I = 3/2) and ^{65}Cu (30.9%, I = 3/2) nuclei (Fig. 2): one resonance is split into an asymmetric 1 : 1 : 1 : 1 quartet by the combined effects of scalar and residual dipolar coupling,[10] while the second one is an unresolved singlet that is superimposed to one quartet line. All J(P,P) couplings are unresolved. The quartet shows a similar habit as was found in Cu(I)–phosphine complexes[11] and is assigned to the η^1(P)-coordinated phosphorus atom, and the singlet to that in the η^2(P=C) unit. This interpretation was supported by spectral simulation[12] (Fig. 2) which yielded δ^{31}P = 149.5/153.8 and $^1J(^{63}$Cu, ^{31}P) = 1460/125 Hz for the η^1(P)/η^2 (P=C) sites, respectively. The relative magnitudes of ^1J(M,P) agree with earlier assignments in η^1(P)- and π-complexes of phosphaalkenes,[3,13] but—quite surprisingly—the π-bound ligand in **2b** fails to show a large negative coordination shift which was up to now considered an unmistakable characteristic for π (P=C)-coordination.[3,9,13] The signals of the phosphonio groups appear as a single broad line at δ^{31}P = 10.7.

Solution ^{31}P{^{1}H} NMR spectra of **2a** in CH$_2$Cl$_2$ display at −90 °C an [AX]$_2$ pattern with resolved couplings J(A,X) = 78



Scheme 1 R = Ph (**1a**, **2a**), H (**1b**, **2b**).

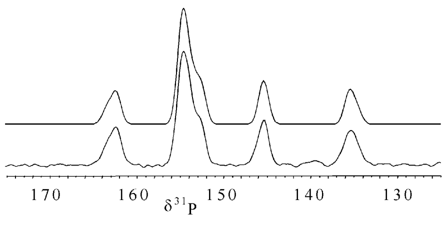


Fig. 2 Expansion of the ^{31}P{^{1}H} MAS NMR spectrum of **2a** (161.9 MHz, rotor frequency 9 kHz) showing the isotropic line (bottom trace), and results of a spectral simulation (top trace).

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† Electronic supplementary information (ESI) available: experimental procedure for **2a**, details on computational studies and simulation of the solid state NMR data of **2a**. See http://www.rsc.org/suppdata/cc/b2/b24144h/

DOI: 10.1039/b204144h

Hz (intra-ligand) and $J(\mathrm{A,A'})$ = 105 Hz (P–M–P). At higher temperatures, the multiplets broaden and finally collapse due to intermolecular ligand exchange. Even if one cannot rule out that the equivalence of both benzophospholides at low temperature owes to dynamic interchange of σ- and π-bound ligands, the large value of $J(\mathrm{A,A'})$ agrees better with a static structure with two η^1(P)-bound ligands. A low preference of **2a** for π-coordination in solution resembles the behavior of Cu(I)–arene complexes,[2] and π/σ-coordination shifts are known for phosphaalkene complexes.[3]

In order to rationalise the unusual spectroscopic and structural features associated with phosphaarene π-coordination in **2a**, we initiated a DFT computational study of the model complexes [(**1b**)$_2$CuI].[14] A survey of coordination isomers revealed almost equal energies for [{η^2(π)-**1b**}{ η^1(P)-**1b**}CuI] (**2b**) and the C_2-symmetric complexes [{η^1(P)-**1b**}$_2$CuI] (ΔE = −0.1 kcal mol^{-1}) and [{η^2(π)-**1b**}$_2$CuI] (ΔE = −0.4 kcal mol^{-1}), thus providing a rationale for conformational fluxionality of **2a** and suggesting that its solid state structure may be determined by crystal packing effects. Comparison of geometric features of **2b** revealed that the η^2-coordinated P=C bond (1.753 Å, *cf.* 1.719 Å in η^1(P)-bound and 1.721 Å in free **1b**) displays only moderate lengthening and weak deviations from planarity (sum of bond angles at C = 358.5°). A charge decomposition analysis[15] of M–L donor–acceptor interactions in **2b** yielded values of 0.28/0.20 and 0.27/0.23 electrons for charge donation/back-donation involving η^2(π)- and η^1(P)-**1b**, respectively, suggesting that the ligand is a weaker π-acceptor towards Cu(I) when present in π- rather than in σ(P)-coordination mode. Computed ^{31}P chemical shifts for **2b** obtained with energy optimised or experimental geometries yield even smaller negative coordination shifts $\Delta\delta^{31}$P for η^2(π)- than for η^1(P)-bound **1b** (Table 1), reproducing the unusually low observed coordination shift for the π-bound ligand in **2a**.

To explain this effect, one has to consider that trends of chemical shifts among non-hydrogen nuclei arise generally from changes in the paramagnetic shielding term whose magnitudes depend on the availability of excited states that are connected with the ground state by magnetic-dipole allowed transitions. For a phosphorus atom in a multiple bond system, the dominant contribution is associated with a n→π* excitation, and low transition energies correlate with large deshieldings.[16] A decrease of δ^{31}P upon η^1(P)-coordination is in this context attributable to a higher n–π* transition energy which results from combined lowering of the n- and raising of the π*-orbital by the effects of L(n)→M and M→L(π*) charge-transfer. While π-coordination renders little stabilisation of the n-orbital, the π*-orbital may here face severe destabilisation due to π-bond pyramidalisation and concurrent σ/π-rehybridisation effects associated with M→L charge-transfer. Trends in ^{31}P coordination shifts in π-complexes reflect thus mainly changes in M→L charge-transfer and should allow to gauge the degree of M→L back-donation. In this respect, the lower $\Delta\delta^{31}$P and structural distortion of the (η^2)π-bound phosphoniobenzophospholide in **2a** as compared to similar Co(I) or Mo(0) complexes[9] indicate a reduced degree of M→L charge-transfer and thus a lesser metallacycle character in the frame of the Dewar-Chatt-Duncanson formalism, in accord with a lower back-donating ability of Cu(I) than of Co(I) or Mo(0).

Table 1 Experimental (**2a**) and computed (**2b**) values of δ^{31}P and $\Delta\delta^{31}$P for the η^1(P) and η^2(π)-coordinated phosphorus nuclei in **2a**,**b**

	2a		**2b**: Exptl. geometry[a]		**2b**: Optimized geometry[b]	
	δ^{31}P	$\Delta\delta^{31}$P[cd]	δ^{31}P	$\Delta\delta^{31}$P[ce]	δ^{31}P	$\Delta\delta^{31}$P[cf]
η^1(P)	149.5	−38.3	173.9	−62.9	185.1	−70.2
η^2(P=C)	153.8	−34.0	197.7	−39.1	215.4	−39.3

[a] Based on atomic coordinates from the X-ray structure of **2a**. [b] Energy optimised molecular geometry of **2b**. [c] $\Delta\delta^{31}$P = δ^{31}P(complex) − δ^{31}P(ligand). [d] δ^{31}P(**1a**) 187.8. [e] δ^{31}P(**1b**) 236.8. [f] δ^{31}P(**1b**) 255.3.

In principle, the described approach to the analysis of ^{31}P coordination shifts should be more general, and we believe it likewise to be applicable to analysis of the bonding in π-complexes of other types of unsaturated phosphorus ligands.

We thank Dr W. Hoffbauer (Universität Bonn) for the recording of solid state NMR spectra.

Notes and references

‡ *Characterization data* for **2a**: yield 75%, mp 149 °C (decomp.); (+)-FAB–MS: *m/z* = 851 [M − I]$^+$, 457 [**1a** + Cu]$^+$, 395 [**1a** + H]$^+$.

§ *Crystal data* for **2a** at 123 K: $C_{52}H_{40}CuP_4I$, M = 979.2, triclinic, space group *P*1, a = 10.5944(2), b = 11.4496(2), c = 20.0383(15) Å, α = 88.5390(10), β = 78.5760(10), γ = 64.676(2)°, V = 2148.8(2) Å^3, Z = 2; 7328 reflections collected, R_1 = 0.042 ($I > 2\sigma(I)$), wR_2 = 0.109, the H atoms attached to C9 and C9′ were located and refined freely; CCDC reference number 184981. See http://www.rsc.org/suppdata/cc/b2/b204144h/ for crystallographic data in CIF or other electronic format.

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