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Synthesis and Structure of the First Phosphine Oxide Complex of Copper(I): Evidence for a Marked 'Borderline' Character of the Metal Centre

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The remarkable stability of [Cu(dppf)(odppf)]BF_4 [dppf = 1,1′-bis(diphenylphosphino)ferrocene, odppf = 1,1′-bis(oxodiphenylphosphoranyl)ferrocene], characterized in the solid state by X-ray analysis and in solution by ^{31}P NMR spectroscopy, reveals a marked borderline character of copper(I).

It is well known that copper(I) forms stable and well characterized homo- and hetero-leptic complexes with tertiary phosphines.[1] Moreover, phosphine oxides are known as good ligands towards oxophilic metal centres (*i.e.* hard Lewis acidic metal centres[2]) such as Al^{III}, Ti^{IV}, Zr^{IV}, M^{III} (M = lanthanoid or actinoid) and also with the borderline centre Cu^{II}.[1] Copper(I) is considered a typical soft metal centre,[1] and thus is expected to be unable to form reasonably stable complexes with phosphine oxides. In the frame of our ongoing interest in the basic co-ordination chemistry of the ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf)[3] we came across a copper(I) complex analysing as $[Cu\{Fe(C_5H_4PPh_2)_2\}\{Fe(C_5H_4PPh_2)[C_5H_4P(O)Ph_2]\}]PF_6$, for which spectroscopic evidence strongly suggested the involvement of the oxygen atom of the ferrocenylphosphine monoxide in ligand to metal bonding.[4] Here, we report on the X-ray crystal structure of the ligand 1,1′-bis(oxodiphenylphosphoranyl)ferrocene[5] (odppf) and on the synthesis and characterization of the first bis(phosphine oxide) complex of copper(I), [Cu(dppf)(odppf)]BF_4 **1**. We also present unambiguous evidence for the simultaneous involvement of two phosphorus and two oxygen ligating sites in the co-ordination sphere of copper(I) both in the solid state (X-ray analysis) and in solution (^{31}P NMR spectroscopy). The crystal structure of odppf† reveals that the molecule is centrosymmetric, with the inversion centre at the iron atom. The two cyclopentadienyl rings are consequently parallel and staggered, with a transoid overall arrangement of the P(O)Ph_2 units (Fig. 1). It is noteworthy that the angles at the phosphorus atoms approach the theoretical value for sp^3 hybridization, at variance with the dppf parent molecule.[3b] As a general comment on the structure of odppf, it can be observed that P–C(phenyl) and P–C(cyclopentadienyl) bonds appear to be significantly shorter than in the case of dppf, whilst the P–O distance is in the normal range.[8]

Complex **1** can be readily obtained‡ upon progressive and controlled replacement of the MeCN ligands in $[Cu(MeCN)_4]^+$ with dppf and odppf in 1,2-dichloroethane under mild conditions. The crystal structure of **1** reveals that the cationic complex contains monomeric units in which the co-ordination around Cu is distorted tetrahedral (Fig. 2).§ The cyclopentadienyl rings are all planar, the maximum deviation from the mean plane being 1.5 pm. Rings denoted as A and C and B and D are practically parallel: mean planes through A and C make an angle of 3.0(5)° and planes B and D 0.5(6)°. Rings A and C are staggered, being rotated with respect to each other by *ca.* 36°, while rings B and D are 'half-staggered', with an angle of *ca.* 15°. Both dppf and odppf act as chelating ligands, with P–Cu–P and O–Cu–O angles of 110.1(4) and 102.1(6)°, respectively. The Cu–P distances (227.16 pm average) compare well with those of related complexes containing the CuO_2P_2 chromophore, *e.g.* 225 pm in $[Cu(O_2NO)(PPh_3)_2]$[9] and 223.5 pm in $[Cu(O_2CMe)(PPh_3)_2]$.[10] On the contrary the average Cu–O distance in **1**, 211.2 pm, is remarkably shorter than the corresponding average distances of the above mentioned complexes, *i.e.* 223.9 and 220.9 pm, respectively. Moreover, on considering that Cu^{II}–O distances in phosphine oxide complexes of Cu^{II} range typically from 196 to 210 pm,[8a] it appears that the copper(I)–oxygen bonds in **1** are to be considered as strongly covalent in character.

The four-co-ordinate structure of Cu in **1** appears to be

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† The compound odppf was prepared as previously reported.[3i] Crystallization from CH_2Cl_2–MeCN yielded single crystals suitable for X-ray analysis. Crystal data: $C_{34}H_{28}FeO_2P_2$, M = 586.39, triclinic, space group $P\bar{1}$, a = 1400.8(2), b = 849.6(2), c = 630.0(2) pm, α = 70.44(2), β = 81.42(2), γ = 84.15(2)°; Z = 1, $F(000)$ = 304. Philips PW 1100 four-circle diffractometer, Mo-Kα radiation, graphite monochromator, θ–2θ scan mode, 3383 observed independent reflections up to θ = 28° of which 2546 had $I > 2.5\sigma(I)$, σ being calculated from counting statistics. Heavy-atom method with refinement by standard full-matrix least squares. In the last cycles of refinement the Fe, P, O and C atoms were allowed to vibrate anisotropically, and H atoms included in ideal positions. Quantity minimized $\Sigma w(|F_o| - |F_c|)^2$ [$w = 1/(\sigma^2 + 0.0001F^2)$]. The phenyl rings were refined as rigid bodies, with C–C and C–H distances fixed at 139.5 and 108 pm. The final R = 0.048, R' = 0.045. All calculations were performed by using the SHELX 76 program[6] for structure determination. The scattering factor for all the atoms was taken from ref. 7.

‡ Complex **1** was obtained, operating in an inert atmosphere, on stirring a mixture of $[Cu(MeCN)_4]BF_4$ (768 mg, 2.44 mmol) and dppf (1.335 g, 2.44 mmol) in 1,2-dichloroethane (25 cm^3) under ambient conditions until a clear solution was formed. After the addition of odppf (1.43 g, 2.44 mmol), the resulting mixture was refluxed for about 15 min. The clear red solution was cooled to room temperature and evaporated to dryness under vacuum. The residue was dissolved in ethanol (15 cm^3) and heated to reflux with stirring until a yellow solid was precipitated. After cooling in the refrigerator, the solid was collected by filtration, washed with cold EtOH, Et_2O and then dried under vacuum, yield 2.60 g (83%) (Found: C, 63.20; H, 4.35. Calc. for $C_{68}H_{56}BCuF_4Fe_2O_2P_4$: C, 63.25; H, 4.35%). Crystallization from CH_2Cl_2–EtOH in a refrigerator yielded single crystals suitable for X-ray analysis. ^1H NMR (89.55 MHz, CD_2Cl_2, 300 K) δ 7.62–7.03 (40 H, Ph), 4.60 (4 H), 4.40 (4 H), 4.33 (4 H), 4.21 (4 H) (C_5H_4). Resonances due to small amounts of crystallization solvents were also detectable.

§ Crystal data for **1**: $C_{68}H_{56}BCuF_4Fe_2O_2P_4$, M = 1291.14, monoclinic, space group $P2_1/n$, a = 2259.0(2), b = 1591.6(2), c = 1927.4(2) pm, β = 105.15(2)°, Z = 4, $F(000)$ = 2648. 15 105 Observed independent reflections up to θ = 28° of which 5249 had $I > 2.5\sigma(I)$, σ being calculated from counting statistics. The structure was solved as for odppf. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ [$w = 1/(\sigma^2 + 0.0001F^2)$], R = 0.074, R' = 0.068. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

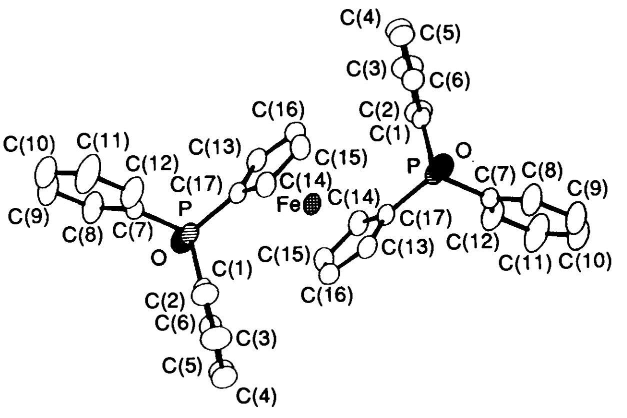

Fig. 1 A side view of odppf showing the atom numbering scheme. Selected distances (pm) and angles (°): P–O 149.3(2), P–C(1) 180.7(3); P–C(7) 180.8(3), P–C(17) 178.3(4), individual iron–carbon distances 204.2(3)–205.1(5); C(1)–P–C(17) 108.2(2), C(1)–P–C(7) 108.1(2), C(7)–P–C(17) 106.5(2), C(1)–P–O 111.3(2), C(7)–P–O 110.7(2), C(17)–P–O 111.9(2), C(14)–C(17)–P 131.5(2), C(13)–C(17)–P 121.9(3)

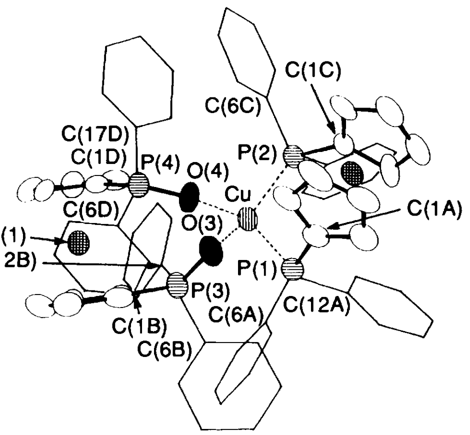

Fig. 2 The crystal structure of the $[Cu(dppf)(odppf)]^+$ ion of **1**. Selected bond lengths (pm) and angles (°): Cu–P(1) 226.7(4), Cu–P(2) 227.5(4), Cu–O(3) 211.4(7), Cu–O(4) 211.1(7), P(3)–O(3) 149.7(7), P(4)–O(4) 150.1(7), P(1)–C(1A) 180(1), P(2)–C(1C) 184.0(9), P(3)–C(1B) 179(1), P(4)–C(1D) 180.0(9); P(1)–Cu–P(2) 110.1(4), O(3)–Cu–O(4) 102.1(6), P(3)–O(3)–Cu 156.0(5), P(4)–O(4)–Cu 160.4(6)

maintained in chlorinated solvents at 173 K, as shown by ^{31}P NMR spectroscopy. Thus, a perfectly resolved triplet is apparent at δ 32.90 ($^3J_{PP}$ 8.8 ± 0.3 Hz) and an unresolved triplet occurs at δ -20.2. The lower field signal is clearly attributable to co-ordinated odppf (for the free ligand δ 28.24 in CD_2Cl_2 at 178 K) and the higher field one has to be attributed to the co-ordinated dppf. In fact, the multiplicity of these signals can be explained *only* by the simultaneous co-ordination of *both* ligands. The resonance value of dppf is actually surprising in that it falls at slightly higher field than that for free dppf (δ -19.84 in CD_2Cl_2 at 173 K, δ -17.30 at 300 K), in contrast with the general trend associated with the co-ordination of dppf to a metal centre and in general for phosphine ligands. In particular, in the closely related complexes $[\{Cu(dppf)\}_2(\mu\text{-}dppf)]^{2+}$ and $[Cu(dppf)(MeCN)_2]^+$ the phosphorus resonances are in the range δ -8.5 to -6.[3h] Although we are aware that ^{31}P chemical shifts are notoriously difficult to rationalize, we argue that the abnormal resonance value of the co-ordinated dppf in **1** (δ $-$ 20.2) reflects a significant degree of π-back donation from the copper(I) to the d orbitals of phosphorus. Gradual raising of the temperature of the CD_2Cl_2–$CDCl_3$ solution of **1** causes a marked change of the ^{31}P NMR pattern. Thus, the resonance at δ 32.90 gradually broadens and becomes a sharp singlet at ambient temperature, without any change in the chemical shift value (δ 32.88 at 300 K). On the contrary, the resonance at δ $-$ 20.2 gradually changes to a very broad signal and moves slightly to lower field (δ $-$ 19.2 at 300 K). In spite of the possible complication due to quadrupolar $^{63/65}Cu$ coupling, we believe that these observations point to the occurrence of a dissociative equilibrium involving the dppf ligand and leading to a probable three-co-ordinated complex $[Cu(odppf\text{-}O,O')(dppf\text{-}P)]^+$.

The X-ray and NMR data show that the mixed soft-hard co-ordination sphere represented by dppf and odppf does stabilize Cu^I, both in the solid state and in solution. In fact, at ambient conditions $[Cu(dppf)(odppf)]^+$ undergoes partial ligand dissociation but, most remarkably,[11] the soft ligand and not the hard one tends to leave the metal co-ordination sphere.

A quite independent support for this conclusion stems from the redox behaviour of **1** in 1,2-dichloroethane containing 0.2 mol dm^{-3} NBu_4PF_6. Thus, cyclic voltammetry reveals that both complexed ligands undergo an uncomplicated reversible ferrocene-based oxidation with potential values ($E^\circ = 0.320$ and 0.703 V *vs.* ferrocene–ferrocenium) more anodic than for the free ligands [E°(dppf) = 0.183 V, E°(odppf) = 0.430[3i]]. On the basis of the reasonable assumption[3c,4] that the two redox centres do not electronically interact when dppf and odppf are metal-bonded, these anodic shifts in the ferrocenyl oxidation potentials, ΔE°, embody important bonding implications. Thus, the measured ΔE° values (0.137 and 0.273 V for dppf and odppf, respectively) reveal that not only are both dppf and odppf Cu^I-co-ordinated (see above) but, more remarkably, stronger ligand-to-metal bonding is apparent for odppf. It is worth underlining that the anodic shifts observed for dppf in the related complexes $[\{Cu(dppf)\}_2(\mu\text{-}dppf)]^{2+}$ and $[Cu(dppf)(MeCN)_2]^+$ are 0.254 and 0.257 V, respectively.[4]

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