DALTON COMMUNICATION

A new route to $(N)_n$-donor functionalised phosphines; novel homo- and hetero-nuclear complexes of a phosphino-substituted triazacyclononane ligand

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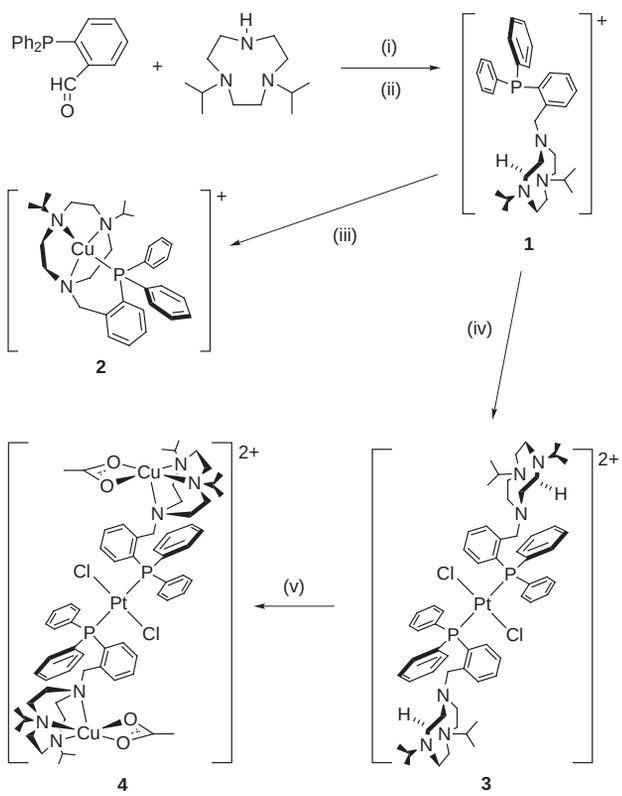
A phosphino-substituted triazacyclononane ligand, oPtacn, has been prepared by a new, potentially versatile route, the complexes $[Cu^{I}(oPtacn)][PF_6]$, $[Pt^{II}Cl_2\{H\text{-}(oPtacn)\}_2][PF_6]_2$ and $[Pt^{II}Cl_2\{(oPtacn)[Cu^{II}(OAc)]\}_2][PF_6]_2$ made, and the crystal structure of $[Cu^{I}(oPtacn)][PF_6]$ determined.

Heterobimetallic systems offer prospects for advantageous synergistic effects; for example, catalysis of olefin hydroformylation is markedly enhanced when a separate cobalt complex is added to a bis(phosphine)palladium catalyst.[1] Discrete systems comprised of two different metal ions stabilised by binucleating ligands have the potential to further enhance these cooperative effects. Binucleating ligands possessing both $(N)_n$ and P-donor domains are among the more interesting because they can exhibit site selectivity for "hard" and "soft" metal ions.[2,3] However, whereas the synthesis and coordination chemistry of functionalised derivatives of $(N)_n$-donor macrocyclic ligands such as 1,4,7-triazacyclononane has attracted much recent attention,[4] only a handful of nitrogen macrocycles with phosphine pendants have been reported.[2,3,5,6] Moreover, most have flexible *N*-alkyl "arms" linking the $(N)_n$ and P-donor domains[3,5,6] and, as a result, only mononuclear complexes with the metal ion bound by both the phosphine and the macrocycle have been isolated. Indeed the only crystallographically characterised metal complex of this type of ligand shows 1-(diphenylphosphinopropyl)-1,4,7-triazacyclononane coordinated to a zinc ion through the phosphine and all three amine groups.[5] The formation of dimeric, heteronuclear complexes of a triphenylphosphine-pendant C-tethered cyclam has been reported.[2] However, the synthesis of the ligand is lengthy, low in yield and not readily adaptable to other macrocycles.

We present here an example of a new, potentially general route to $(N)_n$-donor functionalised phosphine ligands *via* the reductive amination of secondary amine groups with (diphenylphosphino)benzaldehydes. This method should allow functionalisation of all or some of the secondary nitrogen atoms in a wide range of macrocycles and indeed ought to be applicable to any secondary amine. The new phosphino-macrocycle, oPtacn, was synthesised by the reductive amination of 1,4-diisopropyl-1,4,7-triazacyclononane[7a] with 2-(diphenylphosphino)benzaldehyde[7b] using sodium triacetoxyborohydride in 1,2-dichloroethane, Scheme 1. The product, oPtacn, was contaminated by some unreacted aldehyde but was easily purified by treatment with ammonium hexafluorophosphate in methanol. Recrystallisation from acetonitrile–diethyl ether gave the pure hemihydrate of the monoprotonated ligand hexafluorophosphate, $[H(oPtacn)][PF_6]\cdot 0.5H_2O$ **1**, in 72% yield.†

Coordination complexes can be prepared directly from **1**, Scheme 1. For example, reaction of **1** with one equivalent of $[Cu(MeCN)_4][PF_6]$ gave $[Cu(oPtacn)][PF_6]$ **2** as a white powder which was recrystallised from acetonitrile–diethyl ether. Elemental analysis and the ES-mass spectrum confirm the formulation of **2**.‡ The crystal structure, Fig. 1, reveals that oPtacn acts as a mononucleating N_3P-donor ligand to the copper(I) ion.§



Scheme 1 (i) $Na[BH(OAc)_3]$, 1,2-dichloroethane; (ii) $[NH_4][PF_6]$, MeOH; (iii) $[Cu(MeCN)_4][PF_6]$, CH_2Cl_2; (iv) $[PtCl_2(PhCN)_2]$, CH_2Cl_2; (v) NEt_3 + $[Cu_2(OAc)_4(H_2O)_2]$, MeCN.

The coordination geometry for the copper centre is distorted tetrahedral (*e.g.* the sum of the six bond angles about the copper ion is 631° compared to 657° for a perfect tetrahedron) with three similar Cu–N bond lengths [2.150(4), 2.132(4), 2.106(3) Å] and a Cu–P bond length of 2.141(1) Å close to that observed in $[CuL(PPh_3)][BF_4]$, (L = 1,3,5-triisopropyl-1,3,5-triazacyclohexane).[8]

Protonation of oPtacn protects the macrocyclic domain and enables selective binding of the phosphine group to second or third row transition metals. For example, reaction of $[PtCl_2(PhCN)_2]$ with **1** (2 equivalents) gave mononuclear $[PtCl_2\{H(oPtacn)\}_2][PF_6]_2$, **3**, in 87% yield.¶ Noteworthy data for the complex include: a molecular ion (M^{2+}) peak at 621 *m/z* in the ES mass spectrum; a significant downfield shift for the benzylic protons in the ^1H NMR spectrum compared to the ligand salt as well as changes in the aromatic region, all consistent with coordination of the phosphine to the platinum ion; also in the ^1H NMR spectrum, methylene resonances virtually unshifted from those for **1** reveal no change for the protonated macrocyclic domain; and a sharp singlet at δ 15.44 flanked by ^{31}P–^{195}Pt satellites with a *trans* coupling constant ($^1J_{PPt}$ 2597 Hz)

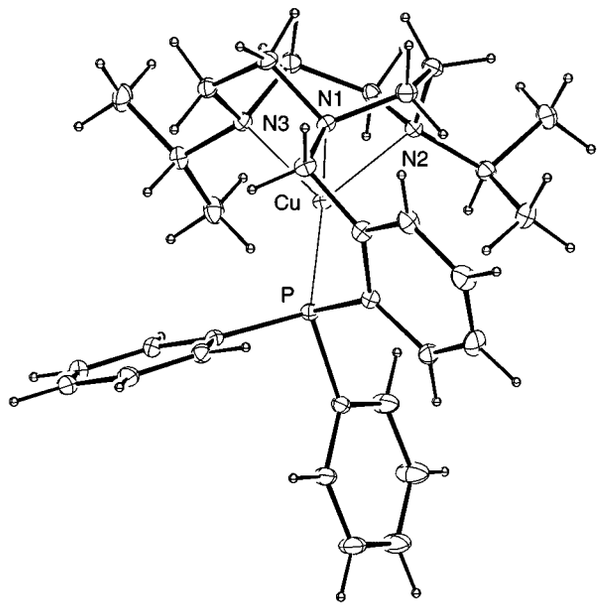


Fig. 1 Drawing of the complex cation **2** showing the 20% thermal ellipsoids.

in the ^{31}P NMR spectrum. In sum this evidence leads to the structure for **3** in Scheme 1.

Addition of base frees the macrocyclic centres in **3** and allows selective formation of trimers. For example, reaction of **3** with triethylamine and $[Cu_2(OAc)_4(H_2O)_2]$ gave $[PtCl_2\{oPtacn[Cu(OAc)]\}_2][PF_6]_2$, **4**, in 56% yield. The base is essential in the preparation of this heterometallic trimer; whilst the coordination of "soft" Pt(II) and Cu(I) ions by the phosphine group in oPtacn is relatively facile, coordination of the "hard" Cu(II) ion requires deprotonation of the macrocyclic domain and, therefore, is pH dependent. Partial analytical data for C, H and N and data for the Cu : P : Pt ratio agree with the formulation of **4**, as does the ES mass spectrum which shows a prominent peak at 743 *m*/*z* for the molecular ion (M^{2+}).‖ The UV/VIS spectrum reveals a band at 661 nm with a distinct low energy tail and an axial EPR spectrum is observed. These spectroscopic data closely match those of a similar crystallographically-characterised N_3O_2-coordinated copper(II) complex[9] and are indicative for isolated mononuclear copper(II) centres with distorted square-pyramidal coordination. The structure proposed for **4** in Scheme 1 is consistent with these results.

We have shown that reductive amination of nitrogen macrocycles with (diphenylphosphino)benzaldehydes provides a convenient synthesis of novel phosphino-substituted macrocycles. The ligating properties of multinucleating ligands of this type can be tuned by varying the relative orientation of the phosphine and macrocycle groups by changing from *ortho* to *meta* or *para* aryl substitution. Studies of other heterometallic oligomers, including those bridged by the obligatory binucleating *meta*-analogue of oPtacn [prepared from 3-(diphenylphosphino)benzaldehyde[7c]] and, as well, with new ligands derived from other secondary amines, are underway. The challenge to demonstrate novel reactivities for these heterometallic oligomers remains.

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Notes and references

† **1**, $[H(oPtacn)][PF_6]\cdot 0.5H_2O$ (Found: C, 57.91; H, 6.47; N, 6.60. $C_{31}H_{43}N_3P_2F_6\cdot 0.5H_2O$ requires C, 57.94; H, 6.90; N, 6.54%); $\delta_P(CDCl_3)$ −14.22 (s), −143.78 [sept, *J*(PF) 707 Hz]; $\delta_H(CDCl_3)$ 7.37–7.32 (8 H, m), 7.24–7.17 (5 H, m), 6.90–6.85 (1 H, m), 3.97 (2 H, d), 3.11 (2 H, sept), 3.00–2.93 (4 H, m), 2.79 (8 H, br s), 1.21 (6 H, d), 1.14 (6 H, d); *m*/*z* (ES-MS) 488 $\{[H(oPtacn)]^+\}$.

‡ **2**, $[Cu(oPtacn)][PF_6]$ (Found: C, 52.62; H, 6.41; N, 6.10. $C_{31}H_{42}N_3P_2F_6Cu\cdot 0.5H_2O$ requires C, 52.80; H, 6.15; N, 5.96%); $\delta_P[(CD_3)_2CO]$ −0.3 (br s), −142.00 [sept *J*(PF) 707 Hz]; $\delta_H[(CD_3)_2CO]$ 7.65–7.50 (8 H, m), 7.50–7.45 (5 H, m), 6.94 (1 H, t), 3.88 (2 H, s), 3.39 (2 H, sept), 3.15–2.55 (12 H, m), 1.47 (6 H, d), 1.13 (6 H, d); *m*/*z* (ES-MS) 550 $\{[Cu(oPtacn)]^+\}$.

§ Crystal data for **2**: $C_{31}H_{42}CuF_6N_3P_2$, $M = 696.2$, monoclinic, space group $P2_1/c$, $a = 15.091(6)$, $b = 14.532(3)$, $c = 17.990(9)$ Å, $\beta = 123.87(2)°$, $U = 3276(2)$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-1}, Enraf-Nonius CAD-4 diffractometer, μ(Mo-Kα: $\lambda = 0.71073$ Å) = 8.21 cm^{-1}, $F(000) = 1448.0$, $T = 294$ K, final $R = 0.037$, $R_w = 0.051$ for 2821 observed data [$I > 3\sigma(I)$, $2\theta < 46°$]. CCDC reference number 186/1414. See http:/www.rsc.org/suppdata/dt/1999/1539/ for crystallographic files in .cif format.

¶ **3**, $[PtCl_2\{H(oPtacn)\}_2][PF_6]_2$ (Found: C, 48.07, H, 5.33, N, 5.13. $C_{62}H_{86}N_6P_4Cl_2F_{12}Pt\cdot H_2O$ requires C, 48.06, H, 5.72, N, 5.42%); $\delta_P[(CD_3)_2CO]$ 15.44 [s, *J*(PPt) 2597], −142.05 [sept, *J*(PF) 707 Hz]; $\delta_H[(CD_3)_2CO]$ 7.95–7.75 (10 H, m), 7.65–7.45 (14 H, m), 7.29 (2 H, t), 7.09 (2 H, q), 4.50 (4 H, s), 3.35 (4 H, sept), 3.27 (4 H, m), 3.10–2.60 (20 H, m), 1.30 (12 H, d), 1.18 (12 H, d); *m*/*z* (ES-MS) 1387 ($[PtCl_2\{H(oPtacn)\}_2 + PF_6]^+$), 621 ($[PtCl_2\{H(oPtacn)\}_2]^{2+}$).

‖ **4**, $[PtCl_2\{(oPtacn)[Cu(OAc)]\}_2][PF_6]_2$ (Found: C, 44.08, H, 4.99, N, 4.43. $C_{66}H_{90}N_6O_4P_4Cl_2F_{12}Cu_2Pt\cdot H_2O$ requires C, 44.17, H, 5.17, N, 4.68%); inductively-coupled-plasma analysis (±10%): ratio Cu : P : Pt = 2.0 : 3.6 : 0.9; λ_{max}/nm (MeCN) 661 (ε/dm^3 mol^{-1} cm^{-1} 797); EPR (MeCN, 77 K): $g_\parallel$ 2.25 ($A_\parallel$ 164 G), $g_\perp$ 2.07; $\delta_P[(CD_3)_2CO]$ −141.97 [sept, *J*(PF) 707 Hz]; *m*/*z* (ES-MS) 743 ($[PtCl_2\{(oPtacn)[Cu(OAc)]\}_2]^{2+}$).

1 Y. Ishii, K. Miyashita, K. Kamita and M. Hidai, *J. Am. Chem. Soc.*, 1997, **119**, 6448.
2 E. Kimura, Y. Kodama, M. Shionoya and T. Koike, *Inorg. Chim. Acta*, 1996, **246**, 151.
3 A. Carroy, C. R. Langick, J.-M. Lehn, K. E. Matthes and D. Parker, *Helv. Chim. Acta*, 1986, **69**, 580.
4 K. P. Wainwright, *Coord. Chem. Rev.*, 1997, **166**, 35; L. Spiccia, B. Graham, M. T. W. Hearn, G. Lazarev, B. Moubaraki, K. S. Murray and E. R. T. Tiekink, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4089; S. Mahapatra, S. Kaderli, A. Llobet, Y.-M. Neuhold, T. Palanché, J. A. Halfern, V. G. Young, Jr., T. A. Kaden, L. Que, Jr., A. D. Zuberbühler and W. B. Tolman, *Inorg. Chem.*, 1997, **36**, 6343; L. J. Farrugia, P. A. Lovatt and R. D. Peacock, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 911; A. Sokolowski, J. Müller, T. Weyhermüller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe and K. Wieghardt, *J. Am. Chem. Soc.*, 1997, **119**, 8889; M. Di Vaira, F. Mani and P. Stoppioni, *Inorg Chim. Acta*, 1998, **273**, 151.
5 D. Ellis, L. J. Farrugia, D. T. Hickman, P. A. Lovatt and R. D. Peacock, *Chem. Commun.*, 1996, 1817.
6 H. Hope, M. Viggiano, B. Moezzi and P. P. Power, *Inorg. Chem.*, 1984, **23**, 2550.
7 (*a*) J. A. Halfern and W. B. Tolman, *Inorg. Synth*, 1998, **32**, 75; (*b*) T. B. Rauchfuss and D. A. Wrobleski, *Inorg Synth.*, 1982, **21**, 175; (*c*) G. P. Schiemenz and H. Kaack, *Liebigs Ann. Chem.*, 1973, 1480.
8 R. D. Köhn, G. Seifert and G. Kociok-Köhn, *Chem. Ber.*, 1996, **129**, 1327.
9 P. Bradford, R. C. Hynes, N. C. Payne and C. J. Willis, *J. Am. Chem. Soc.*, 1990, **112**, 2647.

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