A New Type of Phosphabenzene Coordination

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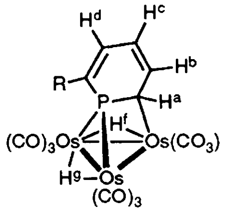
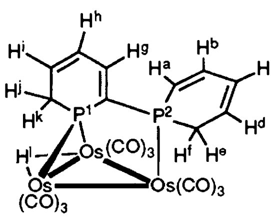
Phosphabenzene reacts with $[Os_3H_2(CO)_{10}]$ to give the compound $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_5H_5P)(CO)_9]$ (X-ray structure of the 2-*tert*-butyl substituted derivative is reported) containing a four-electron donating μ_3-phosphabenzene ligand, and the phosphabenzene-coupled product, $[Os_3(\mu\text{-}H)(\mu_3\text{-}C_{10}H_{11}P_2)(CO)_9]$ (X-ray structure is reported).

Phosphabenzene is known to coordinate like pyridine or tertiary phosphines through its lone-pair, through the π-system or through both simultaneously (see refs. 1 and 2 for examples). We now report the discovery of phosphabenzene as a σ-bonded, four-electron donating μ_3-ligand and the coupling of two phosphabenzene ligands to give a new diphosphine ligand. Its cluster chemistry is totally unlike that of pyridine or its chemistry with single metal atoms.

Pyridine (py) reacts with $[Os_3H_2(CO)_{10}]$ in refluxing cyclohexane to give the same products as from $[Os_3(CO)_{12}]$: $[Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$, $[Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_9(py)]$ and $[Os_3(\mu\text{-}H)_2(\mu\text{-}C_5H_4N)_2(CO)_8]$.[3] Reaction probably occurs *via* the adduct $[Os_3H(\mu\text{-}H)(CO)_{10}(py)]$ which loses H_2 rather than CO as do the corresponding adducts with tertiary phosphines.[4] No evidence for the substitution product $[Os_3H_2(CO)_9(py)]$, analogous to $[Os_3H_2(CO)_9(PR_3)]$,[4,5] was obtained. We have now studied the corresponding reaction of the phosphorus analogue (phosphabenzene) with $[Os_3H_2(CO)_{10}]$ and have discovered a new mode of phosphabenzene coordination. Reaction of $[Os_3H_2(CO)_{10}]$ with phosphabenzene in refluxing cyclohexane gave a rapid colour change from purple to yellow. The mixture was separated to give traces of unconverted starting cluster, two very minor products which we have yet to characterise, the cluster $[Os_3(\mu\text{-}H)_2(C_5H_5P)(CO)_9]$ **1** (20%) containing coordinated phosphabenzene and $[Os_3(\mu\text{-}H)(C_{10}H_{11}P_2)(CO)_9]$ **2** (30%) derived by coupling two phosphabenzene ligands.† An analogue of cluster **1**, $[Os_3(\mu\text{-}H)_2(2\text{-}Bu^tC_5H_4P)(CO)_9]$ **3** was obtained similarly from 2-*tert*-butylphosphabenzene.‡ No analogue of **2** was obtained in this case.



1; R = H^e
3; R = Bu^t



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Clusters **1** and **3** have almost identical IR spectra around 2000 cm⁻¹ and hence have directly related structures. The

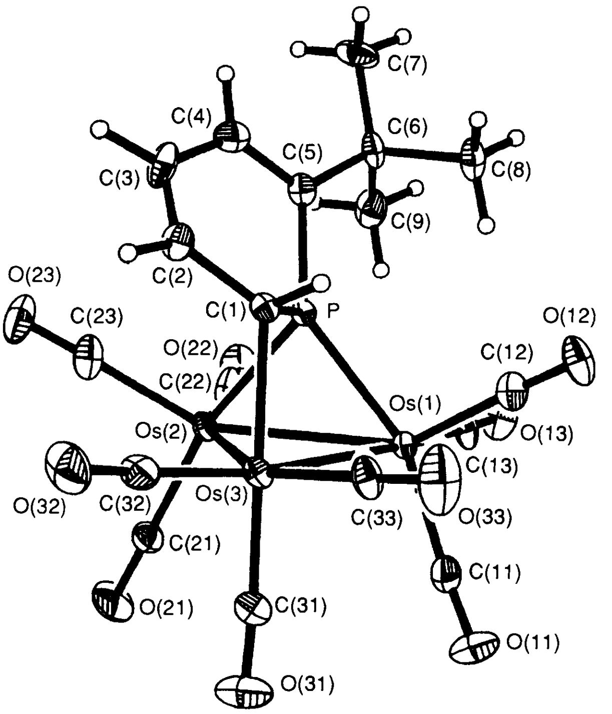

Fig. 1 Molecular structure of the cluster $[Os_3H_2(\mu_3\text{-}Bu^tC_5H_4P)(CO)_9]$ **3**: selected bond lengths (Å) and angles (°): Os(1)–Os(2), 2.947(1); Os(1)–Os(3), 2.866(1); Os(2)–Os(3), 3.008(1); Os(1)–P, 2.357(3); Os(2)–P, 2.392(3); Os(3)–C(1), 2.23(1); P–C(1), 1.80(2); P–C(5), 1.85(1); C(1)–C(2), 1.45(2); C(2)–C(3), 1.33(3); C(3)–C(4), 1.46(3); C(4)–C(5), 1.36(2); C(5)–C(6) 1.51(2); Os(1)–P–Os(2), 76.7(1); Os(1)–P–C(5), 138.3(4); Os(2)–P–C(5), 121.4(5); Os(3)–Os(1)–P, 67.0(1); Os(3)–Os(2)–P, 64.2(1); Os(1)–Os(3)–C(1), 80.3(3); Os(2)–Os(3)–C(1), 77.5(4); Os(3)–C(1)–C(2), 124.0(9); P–C(1)–C(2), 113(1); Os(3)–C(1)–P, 92.0(5)

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† Phosphabenzene. On addition of phosphabenzene (0.011 cm³) to a solution of $[Os_3H_2(CO)_{10}]$ (0.100 g) in cyclohexane (30 cm³), the colour changed from purple to yellow. The solvent was removed after 3 h reflux and TLC on SiO_2 eluting with pentane gave a trace of $[Os_3H_2(CO)_{10}]$, yellow compound **1** (20%), yellow compound **2** (30%) and traces of two uncharacterised compounds. Crystals of **2** for structure determination were from hexane. IR data ν/cm⁻¹ for cyclohexane solutions; ^1H NMR data (300 MHz, *J* in Hz). **1**: ν(CO), 2105m, 2078vs, 2051vs, 2034s, 2022s, 2009vs, 1998s, 1982s, 1953w; ^1H NMR (CD_2Cl_2, 236 K), δ 6.74 (dd, H^d), 6.56 (ddd, H^b), 6.01 (m, H^c), 5.76 (ddd, H^e), 2.90 (dd, H^a), −17.75 (dd, H^f), −19.49 (ddd, H^g) [$J(H^aH^g)$ 3.1, $J(H^bH^c)$ 6.2, $J(H^bH^e)$ 11.5, $J(H^cH^d)$ 9.7, $J(H^cH^e)$ 1.5, $J(H^dH^e)$ 1.1, $J(H^fH^g)$ 1.0, $J(H^aP)$ 11.8, $J(H^bP)$ 31.3, $J(H^cP)$ 0, $J(H^dP)$ 24.5, $J(H^eP)$ 25.4, $J(H^fP)$ 8.7, $J(H^gP)$ 5.8]; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 K) δ −23.2(s). At 225 K two extra weak hydride signals were resolved at δ −17.56 and −19.20 for a minor isomer (mol ratio, major : minor = 40 : 1). The minor isomer is in rapid equilibrium with the major one at 300 K. **2**: ν(CO), 2080m, 2050vs, 2026s, 2002s, 1978vs, 1953w; ^1H NMR (C_6D_6, 300 K), δ 6.21 (ddd, H^g), 5.91 (m, H^a), 5.86 (m, H^b), 5.46 (m, H^c, H^h), 5.29 (ddd, H^i), 5.13 (m, H^d), 2.89 (m, H^k), 2.82 (m, H^j), 2.58 (m, H^f), 2.18 (m, H^e), −19.36 (dd, H^1) [$J(H^cH^e)$ 1.6, $J(H^cH^f)$ 7.3, $J(H^dH^e)$ 6.0, $J(H^dH^f)$ 3.5, $J(H^eH^f)$ 18.5, $J(H^gH^h)$ 6.2, $J(H^hH^i)$ 10.0, $J(H^iH^j)$ 5.0 $J(H^iH^k)$ 5.0, $J(H^jH^k)$ 18.0, $J(H^aP^2)$ 25.6, $J(H^bP^2)$ 25.3, $J(H^dP^2)$ 17.0, $J(H^eP^2)$ 8.2, $J(H^fP^2)$ 16.0, $J(H^gP^1)$ 28.2, $J(H^gP^2)$ 17.3, $J(H^iP^1)$ 16.0, $J(H^jP^1)$ 17.0, $J(H^kP^1)$ 5.1, $J(H^1P^1)$ 26.1, $J(H^1P^2)$ 9.2] (probable assignments); $^{31}P\{^1H\}$ ($CDCl_3$, 300 K) δ −17.6 (d, P^1), −59.9 (d, P^2), $J(P^1P^2)$ 166.

‡ 2-*tert*-Butylphosphabenzene. The phosphabenzene (0.0089 cm³) was added to a purple solution of $[Os_3H_2(CO)_{10}]$ (0.050 g) in cyclohexane (30 cm³) and the yellow solution refluxed for 1 h. Separation by TLC gave unreacted $[Os_3H_2(CO)_{10}]$, yellow compound **3** (30%), and a trace of another compound. **3**: ν(CO), 2105m, 2077vs, 2050vs, 2034s, 2022ms, 2008vs, 1995ms, 1980s; ^1H NMR ($CDCl_3$, 245 K), δ 6.61 (ddd, H^b), 6.35 (dd, H^d), 5.91 (m, H^c), 2.85 (d, H^a), 1.15 (s, Bu^t), −17.54 (d, H^f), −19.14 (dd, H^g), [$J(H^aH^b)$ 2.0, $J(H^aH^c)$ 2.0, $J(H^aH^g)$ 4.9, $J(H^bH^c)$ 9.2, $J(H^cH^d)$ 6.6, $J(H^aP)$ 10.7, $J(H^bP)$ 24.4, $J(H^cP)$ 2.0, $J(H^dP)$ 29.4, $J(H^fP)$ 8.8, $J(H^gP)$ 4.9]; very weak hydride signals for a minor isomer were observed at δ −17.29 and −18.38. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, 298 K) δ −26.7 (s).

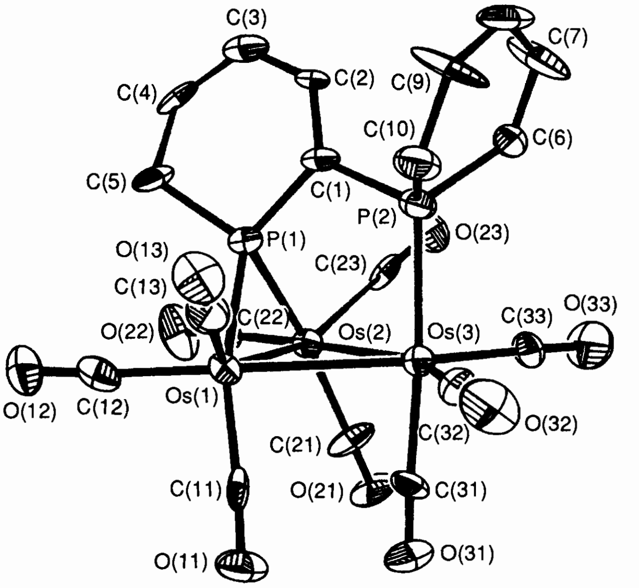

Fig. 2 Molecular structure of the cluster $[Os_3H(\mu_3\text{-}C_5H_6PC_5H_5P)(CO)_9]$ **2**: selected bond lengths (Å) and angles (°): Os(1)–Os(2), 2.934(2); Os(1)–Os(3), 2.889(2); Os(2)–Os(3), 2.901(2); Os(1)–P(1), 2.346(6); Os(2)–P(1), 2.362(6); Os(3)–P(2), 2.401(7); P(1)–C(1), 1.78(3); P(1)–C(5), 1.84(3); C(1)–C(2), 1.35(3); C(2)–C(3), 1.47(4); C(3)–C(4), 1.35(5); C(4)–C(5), 1.45(4); P(2)–C(1), 1.81(3); P(2)–C(6), 1.81(2); P(2)–C(10), 1.81(3); C(6)–C(7), 1.45(5); C(7)–C(8), 1.37(5); C(8)–C(9), 1.36(4); C(9)–C(10), 1.43(5); Os(1)–P(1)–Os(2), 77.1(2); Os(3)–Os(1)–P(1), 79.0(1); Os(3)–Os(2)–P(1), 78.5(2); Os(1)–Os(3)–P(2), 90.1(1); Os(2)–Os(3)–P(2), 93.4(2); Os(3)–P(2)–C(1), 109.4(9); P(2)–C(1)–P(1), 118(1); Os(1)–P(1)–C(1), 119.2(8); Os(2)–P(1)–C(1), 114.1(8)

single crystal X-ray structure of cluster **3** (Fig. 1)§ is quite unlike those of related tertiary phosphine compounds of type $[Os_3H_2(CO)_9L]$ (L = tertiary phosphine) which are structurally related to $[Os_3H_2(CO)_{10}]$ as CO-substituted derivatives, are purple, have L as a normal terminal two-electron donor ligand, and are formally coordinatively unsaturated. Yellow cluster **3** contains phosphabenzene as a new type of μ_3 four-electron donor and is coordinatively saturated. The phosphabenzene forms a phosphido bridge between Os(1) and Os(2) and the *ortho* carbon C(1) is σ bonded to Os(3). This leaves the atoms C(2)–C(5) as a diene unit and the ring is distinctly non-planar as a result of the tetrahedral geometries at the P and C(1) atoms. The hydride ligands (^{1}H NMR, $CDCl_3$, d at δ −17.54 and −19.14) were not located in the X-ray study but bridge the Os(1)–Os(2) and Os(2)–Os(3) edges on the basis of the metal–metal bond lengths and the positions of the other ligands. At 225 K the hydride ligands for **1** and **3** have resolved into two sets corresponding to a mol ratio 40 : 1. The minor isomer probably has hydrides along the Os(1)–Os(2) and Os(1)–Os(3) edges.

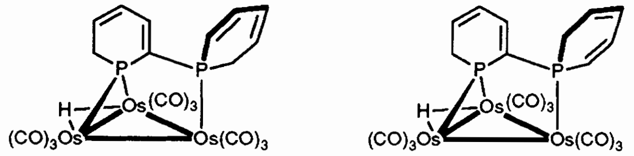

Fig. 3 The X-ray structure of cluster **2** is interpreted in terms of disordering of these two enantiomeric forms

The cluster **2** is derived by coupling of two phosphabenzene ligands (X-ray structure, Fig. 2).§ The phosphorus atoms are in very different environments [^{31}P NMR, $CDCl_3$, δ −17.6 and −59.9, *J*(PP) 166 Hz]. The diphosphine ligand is coordinated through a phosphido bridging atom, P(1), and through a tertiary phosphine atom, P(2), and hence behaves as a five-electron donor consistent with the cluster being a monohydride (^{1}H NMR, $CDCl_3$, δ −19.36). The ring containing P(1) is well refined and C(1)–C(2) and C(3)–C(4) can be identified as C=C bonds and C(5) as a methylene carbon atom. The ring containing P(2) is less well refined and appears to be the result of disorder between the asymmetric forms shown in Fig. 3. The C(6) and C(10) pair of atoms and likewise the C(7) and C(9) pair are geometrically indistinguishable. Consistent with this, the thermal elipsoids for the atoms C(7) and C(9) are particularly elongated perpendicular to the ring as expected for the disorder to two slightly puckered rings.

Although the mechanism of formation of the diphosphine ligand is unclear, it involves various H-atom shifts as well as the formation of the P(2)–C(1) bond. Hydrogen atoms have been lost from C(1) and added to C(5) and to C(6) or C(10) on reaction of $[Os_3H_2(CO)_{10}]$ with two phosphabenzene ligands.

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§ *Crystal structure determinations*: **3**: pale-yellow, $C_{18}H_{15}O_9Os_3P$, 0.18 × 0.35 × 0.38 mm^3, M = 976.90, triclinic, space group $P\bar{1}$, a = 8.963(2), b = 9.851(2), c = 15.600(4) Å, α = 82.26(2), β = 77.41(2), γ = 61.78(2)°, U = 1183.5(5) Å^3, Z = 2, λ = 0.71073 Å, μ(Mo-Kα) = 162.0 cm^{-1}, $F(000)$ = 876. Direct methods (SHELXTL-PLUS), 5425 unique absorption-corrected data between $5 \leqslant 2\theta \leqslant 55°$ and with $I_o \geqslant 3\sigma(I_o)$ used, 280 parameters (all non-H atoms anisotropic), final R = 0.0517 and R_w = 0.0552, with $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.0060F_o{}^2]$. H-atoms in calculated positions (C–H 0.96 Å, U_{iso} = 0.08 Å^2). **2**: yellow, $C_{19}H_{12}O_9Os_3P_2$, 0.14 × 0.25 × 0.08 mm^3, M = 1016.85, monoclinic, space group $P2_1/n$, a = 14.587(3), b = 11.269(5), c = 15.442 Å, β = 105.74(2)°, U = 2443(1) Å^3, Z = 4, λ = 0.71073 Å, μ(Mo-Kα) = 157.5 cm^{-1}, $F(000)$ = 1824. Direct methods (SHELXTL-PLUS), 4216 unique absorption-corrected data between $5 \leqslant 2\theta \leqslant 50°$ and with $I_o \geqslant 2\sigma(I_o)$ used, 298 parameters (all non-H atoms anisotropic), final R = 0.0546 and R_w = 0.0520, with $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o) + 0.00041F_o{}^2]$. H-atoms in calculated positions (C–H 0.96 Å, U_{iso} = 0.08 Å^2). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 J. Deberitz and H. Nöth, *Chem. Ber.*, 1970, **103**, 2541 and 1973, **106**, 2222; *J. Organomet. Chem.*, 1973, **49**, 453; H. Vahrenkamp and H. Nöth, *Chem. Ber.*, 1973, **106**, 2227; K. C. Nainan and C. T. Sears, *J. Organomet. Chem.*, 1978, **148**, C31; F. Nief, C. Charrier, F. Mathey and M. Simalty, *J. Organomet. Chem.*, 1980, **187**, 277; K. Dimroth and H. Kaletsch, *J. Organomet. Chem.*, 1983, **247**, 271; C. Elschenbroich, M. Nowotny, B. Metz, W. Massa, J. Graulich, K. Biehler and W. Sauer, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 547.

2 G. Markl, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990, pp. 220–257.

3 C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1975, 2091.

4 J. R. Shapley, J. B. Keister, M. R. Churchill and B. G. De Boer, *J. Am. Chem. Soc.*, 1975, **97**, 4145; A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **114**, 313; S. Aime, R. Gobetto, D. Osella, L. Milone and E. Rosenberg, *Organometallics*, 1982, **1**, 640; J. G. Bentsen and M. S. Wrighton, *Inorg. Chem.*, 1984, **23**, 512.

5 R. E. Benfield, B. F. G. Johnson, J. Lewis, P. R. Raithby and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1979, **35**, 2210.