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Formation of novel delocalised diphosphazene upon complexation—the preparation and X-ray structure of $Os_3(CO)_{10}[(CF_3)_2P{=}N{=}PPh_3]_2$

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Abstract

The compound $Os_3(CO)_{10}[(CF_3)_2P{=}N{=}PPh_3]_2$ obtained from the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with $(CF_3)_2P{-}N{=}PPh_3$, has been characterized by X-ray crystallography. The osmium atoms form an approximate isoceles triangle. Both diphosphazene ligands which assume equatorial sites, contain unusually short P–N bonds, from P–N=P to P=N=P upon coordination to osmium metals.

The study of cyclo- and polyphosphazenes has received considerable interests in recent years [1–5]. However little attention has been given to that of diphosphazenes and no report has been made on their coordinating properties. We now report on the complex formation of a new diphosphazene $(CF_3)_2P-N{=}PPh_3$ (L) [6] with $Os_3(CO)_{10}(CH_3CN)_2$, yielding $Os_3(CO)_{10}[(CF_3)_2P{=}N{=}PPh_3]_2$ (1) in which L has undergone some electronic rearrangements resulting in the two P–N bonds being nearly equidistant.

Reaction of $(CF_3)_2P{-}N{=}PPh_3$ with $Os_3(CO)_{10}(CH_3CN)_2$ in dichloromethane affords $Os_3(CO)_{10}[(CF_3)_2P{-}N{=}PPh_3]_2$ **1** which can be isolated as yellow crystals by TLC followed by recrystallisation from acetonitrile. Spectroscopic data * are consistent with those expected for 1,2-disubstituted diequatorial triosmium carbonyl cluster. Furthermore it is of interest to note that the difference in chemical shifts of

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* Spectroscopic data for 1: ν(CO) IR (cyclohexane): ν(CO) 2094s, 2038vs, 2009vs, 1978s; $\nu(C_6H_5)$ 3014w, 2925w, 1590w, 1482w, 1438m, 851m, 561s, 531s. ν(P=N) 1322s, 1306s; ν(C–F) 1181s, 1151s, 1145s, 1115s; ν(P–N) 999w; ^{19}F NMR ($CDCl_3$): 6.90d ($J_{FP(1)}$ = 78.12 Hz); 6.47dd ($J_{FP(1)}$ = 78.13 Hz, $J_{FP(2)}$ = 14.65 Hz); ^{31}P NMR (H_3PO_4): P(1), 24.23m (J_{PP} = 29.29 Hz, $J_{P(1)F}$ = 78.13 Hz); P(2), 11.98d (J_{PP} = 29.29 Hz).

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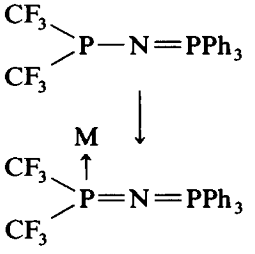
the two phosphorus atoms in L has been reduced from 30 to 12 ppm (in going fr the free L to **1**.

The structure of $Os_3(CO)_{10}[(CF_3)_2P{=}N{=}PPh_3]_2$ is shown in Fig. 1 * whi includes some important bond parameters. The osmium atoms define an appro mate isosceles triangle with the two bulky diphosphazene ligands taking up eq torial sites that are *trans* to each other. The corresponding Os–Os edge, Os(2)–Os(3) is somewhat longer (0.018 Å) than the average Os–Os distance $Os_3(CO)_{12}$ [7]. The remaining two osmium–osmium bonds lie within 0.010 Å of t average.

The osmium–phosphorus bond lengths (2.285(10), 2.282(11) Å) are shorter th those reported for $Os_3(CO)_{10}(PPh_3)_2$ (2.358(4), 2.354(4) Å) and for $Os_3(CO)_{10}$[P $(OMe)_2]_2$ (2.298(3), 2.290(3) Å) [8]. The bond lengths are, in fact, similar to those $Os_3(CO)_7(PPh_2)_2(C_6H_4)$ [9] (2.27 Å), $HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$ (2.26 and $HOs_3(CO)_7(PPh_2C_6H_4C_6H_3)$ (2.26 Å) [10], each of which contains a PF moiety bridging two osmium atoms.

Significantly, the two phosphorus–nitrogen bond lengths within the diph phazene ligand are similar. Furthermore these are comparable to the P=N bo distances in free ligands such as $Ph_3P{=}NC_6H_4Br$ [11] (1.567 Å) and $Ph_2FP{=}N$ (1.641 Å) [12,13]. The values from covalent radii of P–N single and double bor are 1.78 Å and 1.64 Å respectively. Thus it appears that there is a delocalis electronic structure in the unsymmetrical P–N–P system of the coordinat $(CF_3)P{-}N{=}PPh_3$ ligand. This suggests that L has undergone electronic rearran ment upon complexation as follows:



In the highly delocalised moiety $(CF_3)_2P{=}N{=}PPh_3$, the strongly electronegative C group and the P→Pd donation make the P sufficiently electron poor for N(*pπ*)–P(*pπ*) bonding to be significant.

A comparison of the relevant bond parameters in **1** and those of the bis(triph ylphosphine) iminum cation in several complexes lends further support to formulation of L as $(CF_3)_2P{=}N{=}PPh_3$. The average P–N bond distances are typi of P=N for **1** as well as for those found in $[(Ph_3PN)_2N][HFe_2(CO)_8]$ (1.566(

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* *Crystal data* $C_{50}H_{30}N_2O_{10}F_{12}P_4Os_3$: $M = 1741.3$, *a* 9.531(2), *b* 20.378(6), *c* 14.525(4) Å, 92.93(2) 2817.5 Å^3, $Z = 2$, d_{calc} 2.05 g/cm^3, $F(000)$ 1640, (Mo-K_α) 69.6 cm^{-1}, monoclinic space group *Structure determination*: A crystal of dimensions 0.2×0.2×0.6 mm was used to collect 5113 uni data in the range $5 < 2 < 50$ on a Nicolet *R3mV* diffractometer equipped with a graphite monocl mated Mo X-ray tube. The positions of the osmium atoms were found by direct methods and remaining non-hydrogen atoms by iterative application of least-squares refinement and differe Fourier synthesis. Phenyl rings were idealised as were hydrogen atom coordinates. The struc refined to $R = 0.0871$, $R_w = 0.0829$ ($w^{-1} = \sigma^2F + 0.00109F^2$). All computations were carried out Microvax II computer using the SHELXTL PLUS program package.

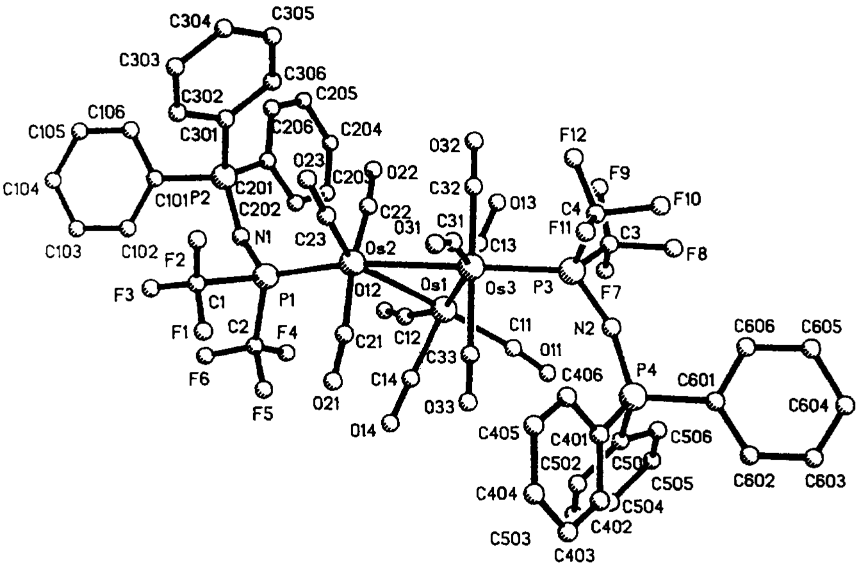

Fig. 1. Molecular structure of $\{Os_3(CO)_{10}[(CF_3)_2P{=}N{=}PPh_3]_2\}$ (1) showing the atom labelling scheme. Important parameters Os(1)–Os(2) 2.884(2), Os(1)–Os(3) 2.886(2), Os(2)–Os(3) 2.896(2), Os(2)–P(1) 2.285(10), Os(3)–P(3) 2.282(11), P(1)–N(1) 1.60(4), P(2)–N(1) 1.54(4), P(3)–N(2) 1.58(4), P(4)–N(2) 1.57(4) Å, P(1)–N(1)–P(2) 150(2)°, P(3)–N(2)–P(4) 159(3)°.

1.583(7) Å [14]) and $[(Ph_3P)_2N][Cr_2(CO)_{10}(\mu\text{-}H)]$ (1.571(5), 1.553(2) Å [15]). Moreover the P–N–P bond angles in **1** are also quite similar to the reported values for $\{[PPN][Cr_2(CO)_{10}(\mu\text{-}H)\}$ (154.8(4)°) and $\{(PPN)[HFe_2(CO)_8]\}$ (140.9(5)°).

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