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Synthesis, and spectral and X-ray structural studies of a novel delocalised triphosphazene $(CF_3)_2P=N=P(CF_3)_2=N=PPh_3$ and the triosmium cluster complex $Os_3(CO)_{11}[(CF_3)_2P=N=P(CF_3)_2=N=PPh_3]$

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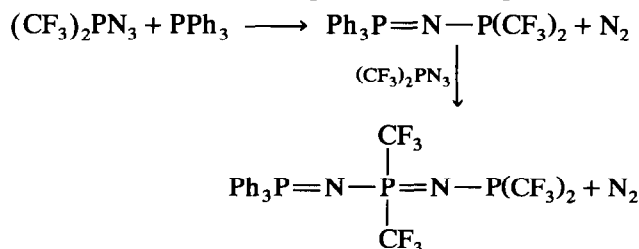(Received August 15, 1992; in revised form September 25, 1992)

Abstract

The triphosphazene $(CF_3)_2P=N=P(CF_3)_2=N=PPh_3$ (L), prepared by the reaction of $(CF_3)_2PN_3$ with $(CF_3)_2P=N=PPh_3$, has been found to afford the cluster $[Os_3(CO)_{11}\{(CF_3)_2P=N=P(CF_3)_2=N=PPh_3\}]$ (1) with $[Os_3(CO)_{11}(MeCN)]$. Both L and 1 have been shown by X-ray crystallography to have an unusual and highly delocalised P=N=P=N=P moiety containing P^{IV}, P^{V} and P^{VI} atoms.

1. Introduction

The diphosphazene $(CF_3)_2P=N=PPh_3$ has been shown to possess an unusual and novel delocalised P=N=P moiety containing P^{IV} and P^{V} atoms; furthermore, this delocalised electronic structure is retained upon coordination to a metal centre as in $[Fe(CO)_4-\{(CF_3)_2P=N=PPh_3\}]$ and $[Fe(CO)_3\{(CF_3)_2P=N=PPh_3\}_2]$ [1], $[Pd_2Cl_4\{(CF_3)_2P=N=PPh_3\}_2]$ [2], $[Os_3(CO)_{10}\{(CF_3)_2P=N=PPh_3\}_2]$ [3] and $[Os_3(CO)_{11}\{(CF_3)_2P=N=PPh_3\}]$ [4]. We now report the complex formation of the novel triphosphazene $(CF_3)_2P=N=P(CF_3)_2=N=PPh_3$ (L) with $[Os_3(CO)_{11}(MeCN)]$, to yield $[Os_3(CO)_{11}\{(CF_3)_2P=N=P(CF_3)_2=N=PPh_3\}]$ (1) in which L is shown from X-ray structural analysis to contain a highly delocalised electronic structure.

The triphosphazene L was obtained in 78% yield by the reaction of $(CF_3)_2PN_3$ with the diphosphazene $(CF_3)_2P=N=PPh_3$ in dichloromethane at room temperature for 4 days, according to the following reaction:

$$(CF_3)_2PN_3 + PPh_3 \longrightarrow Ph_3P=N-P(CF_3)_2 + N_2$$

$$\downarrow (CF_3)_2PN_3$$

$$Ph_3P=N-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{P}}=N-P(CF_3)_2 + N_2$$

These reactions demonstrate the feasibility of propagating the active terminal phosphorus. Moreover L has been found to react with $[Os_3(CO)_{11}MeCN]$ in dichloromethane at room temperature for 18 h to afford 1 in 71% yield. The compositions of L and 1 were established by elemental analyses (C, H, N) and ^{19}F and ^{31}P NMR spectroscopy (see Experimental section). In addition, the mass spectrum of L showed the presence of the parent ion. Crystals of L and 1 for X-ray structural studies were obtained from solutions in CH_2Cl–hexane at low temperatures.

The molecular structure of 1, as shown in Fig. 1, comprises an approximate isosceles triangle of osmium atoms, each of which exhibits distorted octahedral coordination geometry. The bulky triphosphazene ligand $(CF_3)_2P=N=P(CF_3)_2=N=PPh_3$ bonds to Os(2), taking up an equatorial site. All three osmium–osmium bonds lie within 0.010 Å of the average Os–Os distance (2.877(1) Å) in $Os_3(CO)_{11}[(CF_3)_2P=N=PPh_3]$ [4]. The osmium–phosphorus bond length Os(2)–P (2.280(2) Å) is somewhat shorter than that in $Os_3(CO)_{11}[(CF_3)_2P=N=PPh_3]$ (2.296(6) Å) [4]. The molecular structure [5*] of free L is essentially similar to that of the complexed form. The most significant feature is that the four phosphorus–nitrogen bond lengths within L (1.523–1.584 Å) as well as in 1 (1.518–1.572 Å) are not only

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* Reference number with an asterisk indicates a note in the list of references.
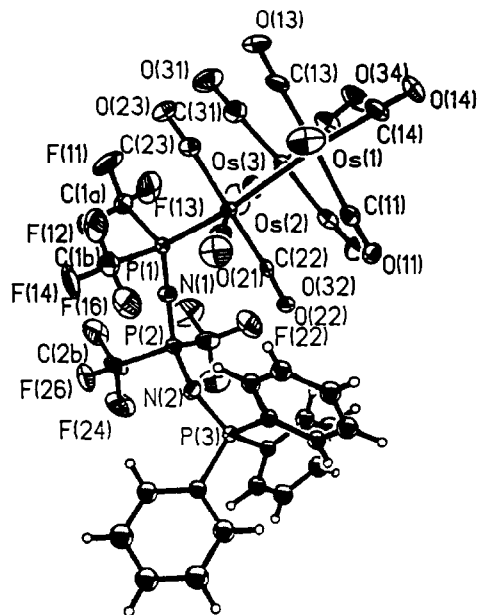
Fig. 1. Molecular structure of Os₃(CO)₁₁[(CF₃)₂P=N=P(CF₃)₂=N=PPh₃] showing the atom labelling scheme. Important parameters Os(1)–Os(2) 2.878(1), Os(1)–Os(3) 2.876(1), Os(2)–Os(3) 2.903(1), Os(2)–P(1) 2.280(2), P(1)–N(1) 1.572(8), N(1)–P(2) 1.518(7), P(2)–N(2) 1.551(9), N(2)–P(3) 1.565(8) Å, P(1)–N(1)–P(2) 162.4(8); N(1)–P(2)–N(2) 122.7(5), P(2)–N(2)–P(3) 154.1(6)°.

close to being equidistant but also typical of the P=N double bond (1.55–1.62 Å). In addition, the two P=N=P segments within the triphosphazene moieties in L and 1 are nearly linear, the P–N–P angles being 153.15° and 148.1° in L, and 162.4° and 154.1° in 1. However, the $P^{IV}=N=P^{VI}=N=P^{V}$ segments are bent at the central P^{VI} atoms, with the N–P–N angles being 125.1° in L and 122.7° in 1.

It is also of interest to note that ^{31}P–^{31}P couplings within the P=N=P=N=P moiety in 1 are $J(P^1P^2) = 53.71$ Hz and $J(P^2P^3) = 14.64$ Hz, but become non-detectable in free L. In the diphosphazene analogues, the ^{31}P–^{31}P couplings were observed in both the free ligand (CF₃)₂P=N=PPh₃ ($J(PP) = 117.79$ Hz) [1] and complexed form Os₃(CO)₁₁[{(CF₃)₂P=N=PPh₃}] ($J(PP) = 31.74$ Hz) [4].

Thus the present study has established that the highly delocalised electronic structures reported for the diphosphazene (CF₃)₂P=N=PPh₃ [1] as well as its complexes are also displayed by the triphosphazene and its cluster derivative, viz. L and 1. These compounds represent the first example of an extended P=N=P=N=P non-linear structure containing a four-valent as well as a five-valent terminal phosphorus atom. The central phosphorus atom assumes a valency of six.

2. Experimental section

The solvents for the reactions were distilled under nitrogen from appropriate drying agents. All reactions were carried out under the high vacuum condition or the dry nitrogen atmosphere using high vacuum line or glove box and Schlenk-type techniques. The diphosphazene (CF₃)₂P=N=PPh₃ and the phosphinous azide (CF₃)₂PN₃ were prepared by reported methods [1]. Triosmium clusters Os₃(CO)₁₂ and Os₃(CO)₁₁(CH₃CN) were synthesised according to literature methods [6,7]. Thin layer chromatography was performed in air on plates coated with silica (Merck Kieselgel 60GF). IR spectra were recorded on a Perkin–Elmer 983G spectrometer calibrated with the polystyrene absorption at 1601.4 and 906.7 cm⁻¹. NMR data were collected in CDCl₃ on a Joel FX 90Q FT NMR spectrometer. ¹H NMR was measured with respect to TMS and ¹⁹F NMR with respect to CF₃COOH. ³¹P NMR spectra were proton decoupled. Mass spectra were recorded on a V.G. Micromass Spectrometer (electron ionisation, 70 ev). Elemental analyses were performed on a Perkin–Elmer 2400.

2.1. Crystal data for 1.

$C_{33}H_{15}N_2O_{11}F_{12}P_3Os_3$: triclinic, $P\overline{1}$; $a = 9.154(2)$ Å, $b = 12.208(2)$ Å, $c = 21.478(4)$ Å, $\alpha = 73.100(2)°$, $\beta = 78.900(4)°$, $\gamma = 68.920(1)°$; $V = 2132.3(7)$ Å³; $Z = 2$; $D_{calcd} = 2.347$ g/cm³; $F(000) = 1392$; $\mu(Mo\ K\alpha) = 91.48$ cm⁻¹; temp = 25°C, Siemens R3m/V, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Of 7951 data (3° ≤ 2θ ≤ 50°), 7444 were independent ($R_{int} = 1.61\%$), and 5729 were observed ($5\sigma(F_o)$). The structure was solved by direct methods and Fourier difference technique. Refinement: full-matrix least-squares analysis, all non-hydrogen atoms anisotropic, all hydrogen atoms idealised. $R_F j = 3.53\%$, $R_{wF} = 4.45\%$, GOF = 1.02. $N_o/N_v = 1.75$, $\Delta/\sigma = 0.111$, $\Delta/\sigma_{max} = 0.529$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0011F^2$. SHELXTL software used for all computations. (G. Sheldrick, Siemens, Madison, WI, USA). An empirical (psi-scan) correction was performed. The ratio of transmission coefficients was 1.75.

2.2. p,p,p'p'-Tetrakis(trifluoromethyl)-p",p",p"-triphenyl triphosphazene (CF₃)₂P=N=P(CF₃)₂=N=PPh₃ (L)

The preparation of L was carried out in a conventional vacuum line fitted with greaseless PTFE O-ring taps. Bis(trifluoromethyl)phosphinous azide (41.0 mg, 0.194 mmol) was condensed into a Pyrex glass ampoule containing 51.0 mg (0.115 mmol) of p,p-bis(trifluoromethyl)-p',p',p'-triphenyl diphosphazene in 5 ml of dichloromethane. The ampoule was allowed to warm from the −96°C slush to room temperature and was then kept in the fume cupboard for 4 days. On frac-

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $Os_3(CO)_{11}[(CF_3)_2P=N=P-(CF_3)_2=N = PPh_3]$

	x	y	z	U_{eq} [a]
Os(1)	3677(1)	8121(1)	9649(1)	43(1)
Os(2)	4338(1)	9081(1)	8273(1)	38(1)
Os(3)	2185(1)	7690(1)	8723(1)	45(1)
P(1)	4643(3)	9493(2)	7159(1)	46(1)
N(1)	3324(10)	10426(7)	6719(4)	61(4)
P(2)	2219(3)	11598(2)	6350(1)	44(1)
N(2)	1952(8)	12844(6)	6481(4)	49(3)
P(3)	942(3)	14021(2)	6712(1)	37(1)
C(11)	2116(11)	9738(9)	9588(4)	46(4)
C(12)	5178(14)	8539(8)	9942(6)	67(5)
C(13)	5235(14)	6549(9)	9642(5)	62(5)
C(14)	2670(16)	7442(10)	10451(5)	72(6)
C(21)	5472(11)	10007(8)	8392(5)	54(4)
C(22)	2369(10)	10396(8)	8191(4)	43(3)
C(23)	6228(13)	7691(9)	8342(5)	64(5)
C(31)	4018(16)	6351(10)	8566(6)	72(6)
C(32)	374(13)	9108(9)	8847(5)	53(4)
C(33)	1385(13)	7744(10)	7940(5)	65(5)
C(34)	1209(15)	6667(10)	9365(5)	69(6)
O(11)	1266(8)	10668(6)	9580(3)	58(3)
O(12)	6151(11)	8724(8)	10113(5)	108(6)
O(13)	6186(10)	5648(6)	9677(5)	91(4)
O(14)	2056(12)	7089(9)	10957(4)	111(6)
O(21)	6125(10)	10591(9)	8460(5)	103(5)
O(22)	1272(8)	11220(6)	8104(3)	58(3)
O(23)	7379(11)	6914(8)	8368(5)	114(5)
O(31)	5020(14)	5519(8)	8475(5)	116(6)
O(32)	−749(9)	9868(7)	8923(4)	72(4)
O(33)	913(12)	7756(10)	7500(4)	104(6)
O(34)	570(14)	6075(9)	9743(5)	111(6)
C(1A)	5300(16)	8143(10)	6788(6)	73(5)
C(1B)	6417(14)	10006(12)	6786(7)	82(6)
C(2A)	334(16)	11292(10)	6390(7)	74(6)
C(2B)	2838(21)	11772(10)	5456(5)	87(7)
F(11)	6575(12)	7326(7)	7020(5)	136(5)
F(12)	5512(12)	8395(7)	6153(3)	129(5)
F(13)	4249(12)	7600(8)	6940(5)	128(6)
F(14)	6729(10)	10136(9)	6151(4)	127(5)
F(15)	7677(9)	9278(10)	7061(5)	138(6)
F(16)	6145(11)	11078(9)	6918(5)	132(6)
F(21)	535(11)	10371(7)	6161(5)	130(6)
F(22)	−275(9)	11051(8)	7016(4)	105(5)
F(23)	−770(9)	12213(7)	6080(4)	105(4)
F(24)	1798(12)	12620(8)	5093(4)	125(5)
F(25)	3218(14)	10748(7)	5267(3)	140(6)
F(26)	4110(11)	12109(8)	5303(4)	116(5)
C(111)	1329(9)	13956(7)	7511(4)	39(2)
C(112)	2778(11)	13257(8)	7721(5)	48(2)
C(113)	3135(12)	13237(8)	8328(5)	53(2)
C(114)	2013(12)	13890(9)	8731(5)	57(2)
C(115)	574(12)	14587(9)	8520(5)	57(2)
C(116)	205(11)	14631(8)	7917(5)	49(2)
C(221)	1454(10)	15280(7)	6169(4)	41(2)
C(222)	2411(12)	15185(9)	5600(5)	60(3)
C(223)	2815(14)	16167(10)	5195(6)	75(3)
C(224)	2229(14)	17264(11)	5351(6)	75(3)
C(225)	1282(14)	17375(11)	5896(6)	75(3)
C(226)	874(13)	16383(9)	6334(6)	65(3)
C(331)	−1131(9)	14334(7)	6727(4)	39(2)
C(332)	−1931(11)	15118(8)	6205(5)	52(2)

TABLE 1. (continued)

	x	y	z	U_{eq} [a]
C(333)	−3487(13)	15315(9)	6198(5)	62(3)
C(334)	−4266(14)	14714(10)	6716(6)	71(3)
C(335)	−3482(15)	13893(11)	7241(6)	82(3)
C(336)	−1909(12)	13709(9)	7244(5)	60(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

tionation *in vacuo*, a non-condensable gas (presumably dinitrogen) was detected. A white solid was obtained when all of the solvent was removed. This was recrystallised from dichloromethane to remove any insoluble solid. Further recrystallisation of the white solid thus obtained using dichloromethane/hexane at −15°C afforded colourless crystals of L (m.p. 91–93°C, 56.2 mg, 78% yield based on $(CF_3)_2P=N=PPh_3$ used]. ^{31}P NMR (referenced to H_3PO_4): $\delta 1$ 46.98, m, P^1, $J(F^1P^1) = 78.04$ Hz; $\delta 2$ 21.40, m, P^3, $J(F^2P^3) = 7.32$ Hz; $\delta 3$ −12.65, m, P^2, $J(F^2P^2) = 112.29$ Hz. ^{19}F NMR (referenced to CF_3CO_2H): $\delta 1$ 9.29, d, F^1, $J(P^1F^1) = 78.13$

TABLE 2. Bond lengths (Å) for $Os_3(CO)_{11}[(CF_3)_2P=N=P(CF_3)_2=N = PPh_3]$

Os(1)–Os(2)	2.878(1)	Os(1)–Os(3)	2.876(1)
Os(1)–C(11)	1.962(9)	Os(1)–C(12)	1.890(15)
Os(1)–C(13)	1.938(9)	Os(1)–C(14)	1.901(11)
Os(2)–Os(3)	2.903(1)	Os(2)–P(1)	2.280(2)
Os(2)–C(21)	1.880(13)	Os(2)–C(22)	1.932(7)
Os(2)–C(23)	1.933(9)	Os(3)–C(31)	1.931(11)
Os(3)–C(32)	1.962(10)	Os(3)–C(33)	1.934(13)
Os(3)–C(34)	1.894(12)	P(1)–N(1)	1.572(8)
P(1)–C(1A)	1.891(13)	P(1)–C(1B)	1.899(14)
N(1)–P(2)	1.518(7)	P(2)–N(2)	1.551(9)
P(2)–C(2A)	1.874(16)	P(2)–C(2B)	1.867(11)
N(2)–P(3)	1.565(8)	P(3)–C(111)	1.790(10)
P(3)–C(221)	1.792(9)	P(3)–C(331)	1.791(9)
C(11)–O(11)	1.132(11)	C(12)–O(12)	1.140(19)
C(13)–O(13)	1.123(11)	C(14)–O(14)	1.162(14)
C(21)–O(21)	1.136(18)	C(22)–O(22)	1.136(9)
C(23)–O(23)	1.134(12)	C(31)–O(31)	1.135(14)
C(32)–O(32)	1.132(12)	C(33)–O(33)	1.107(18)
C(34)–O(34)	1.142(16)	C(1A)–F(11)	1.305(14)
C(1A)–F(12)	1.300(13)	C(1A)–F(13)	1.299(19)
C(1B)–F(14)	1.315(16)	C(1B)–F(15)	1.300(14)
C(1B)–F(16)	1.345(20)	C(2A)–F(21)	1.294(18)
C(2A)–F(22)	1.343(15)	C(2A)–F(23)	1.317(13)
C(2B)–F(24)	1.302(15)	C(2B)–F(25)	1.333(16)
C(2B)–F(26)	1.324(22)	C(111)–C(112)	1.372(12)
C(111)–C(116)	1.401(12)	C(112)–C(113)	1.395(16)
C(113)–C(114)	1.381(14)	C(114)–C(115)	1.365(14)
C(115)–C(116)	1.383(16)	C(221)–C(222)	1.368(13)
C(221)–C(226)	1.383(15)	C(222)–C(223)	1.385(16)
C(223)–C(224)	1.367(19)	C(224)–C(225)	1.327(17)
C(225)–C(226)	1.421(17)	C(331)–C(332)	1.378(12)
C(331)–C(336)	1.384(13)	C(332)–C(333)	1.359(15)
C(333)–C(334)	1.371(16)	C(334)–C(335)	1.389(16)
C(335)–C(336)	1.377(18)		

TABLE 3. Bond angles (°) for $Os_3(CO)_{11}$-[$(CF_3)_2$P=N=P-$(CF_3)_2$=N=PPh$_3$]

Os(2)–Os(1)–Os(3)	60.6(1)	Os(2)–Os(1)–C(11)	82.7(2)
Os(3)–Os(1)–C(11)	90.7(3)	Os(2)–Os(1)–C(12)	97.1(3)
Os(3)–Os(1)–C(12)	156.8(3)	C(11)–Os(1)–C(12)	92.9(5)
Os(2)–Os(1)–C(13)	93.4(3)	Os(3)–Os(1)–C(13)	86.6(4)
C(11)–Os(1)–C(13)	176.0(4)	C(12)–Os(1)–C(13)	88.4(5)
Os(2)–Os(1)–C(14)	160.8(5)	Os(3)–Os(1)–C(14)	100.9(5)
C(11)–Os(1)–C(14)	93.1(4)	C(12)–Os(1)–C(14)	101.8(6)
C(13)–Os(1)–C(14)	90.3(4)	Os(1)–Os(2)–Os(3)	59.7(1)
Os(1)–Os(2)–P(1)	166.2(1)	Os(3)–Os(2)–P(1)	107.2(1)
Os(1)–Os(2)–C(21)	94.6(3)	Os(3)–Os(2)–C(21)	153.1(3)
P(1)–Os(2)–C(21)	98.9(3)	Os(1)–Os(2)–C(22)	94.8(2)
Os(3)–Os(2)–C(22)	80.9(3)	P(1)–Os(2)–C(22)	86.9(2)
C(21)–Os(2)–C(22)	94.7(4)	Os(1)–Os(2)–C(23)	85.1(3)
Os(3)–Os(2)–C(23)	95.4(4)	P(1)–Os(2)–C(23)	92.2(3)
C(21)–Os(2)–C(23)	89.6(5)	C(22)–Os(2)–C(23)	175.7(5)
Os(1)–Os(3)–Os(2)	59.7(1)	Os(1)–Os(3)–C(31)	91.7(5)
Os(2)–Os(3)–C(31)	84.1(4)	Os(1)–Os(3)–C(32)	88.0(4)
Os(2)–Os(3)–C(32)	93.2(4)	C(31)–Os(3)–C(32)	177.0(5)
Os(1)–Os(3)–C(33)	164.4(4)	Os(2)–Os(3)–C(33)	105.0(4)
C(31)–Os(3)–C(33)	90.1(5)	C(32)–Os(3)–C(33)	89.4(5)
Os(1)–Os(3)–C(34)	94.3(4)	Os(2)–Os(3)–C(34)	153.6(4)
C(31)–Os(3)–C(34)	92.9(5)	C(32)–Os(3)–C(34)	90.2(4)
C(33)–Os(3)–C(34)	101.2(6)	Os(2)–P(1)–N(1)	123.2(3)
Os(2)–P(1)–C(1A)	116.1(3)	N(1)–P(1)–C(1A)	102.1(5)
Os(2)–P(1)–C(1B)	113.0(5)	N(1)–P(1)–C(1B)	102.5(5)
C(1A)–P(1)–C(1B)	95.6(6)	P(1)–N(1)–P(2)	162.4(8)
N(1)–P(2)–N(2)	122.7(5)	N(1)–P(2)–C(2A)	105.5(5)
N(2)–P(2)–C(2A)	112.7(5)	N(1)–P(2)–C(2B)	108.7(5)
N(2)–P(2)–C(2B)	105.5(5)	C(2A)–P(2)–C(2B)	99.3(8)
P(2)–N(2)–P(3)	154.1(6)	N(2)–P(3)–C(111)	112.1(4)
N(2)–P(3)–C(221)	109.0(4)	C(111)–P(3)–C(221)	106.4(5)
N(2)–P(3)–C(331)	112.9(5)	C(111)–P(3)–C(331)	107.8(4)
C(221)–P(3)–C(331)	108.4(4)	Os(1)–C(11)–O(11)	177.0(9)
Os(1)–C(12)–O(12)	175.6(9)	Os(1)–C(13)–O(13)	174.6(12)
Os(1)–C(14)–O(14)	175.6(13)	Os(2)–C(21)–O(21)	178.3(8)
Os(2)–C(22)–O(22)	174.5(7)	Os(2)–C(23)–O(23)	176.6(11)
Os(3)–C(31)–O(31)	174.9(14)	Os(3)–C(32)–O(32)	174.2(12)
Os(3)–C(33)–O(33)	178.4(10)	Os(3)–C(34)–O(34)	177.5(11)
P(1)–C(1A)–F(11)	111.7(11)	P(1)–C(1A)–F(12)	115.1(8)
F(11)–C(1A)–F(12)	108.9(10)	P(1)–C(1A)–F(13)	110.6(8)
F(11)–C(1A)–F(13)	105.1(9)	F(12)–C(1A)–F(13)	104.8(13)
P(1)–C(1B)–F(14)	115.0(12)	P(1)–C(1B)–F(15)	111.6(9)
F(14)–C(1B)–F(15)	108.2(10)	P(1)–C(1B)–F(16)	107.6(8)
F(14)–C(1B)–F(16)	108.3(11)	F(15)–C(1B)–F(16)	105.7(14)
P(2)–C(2A)–F(21)	112.4(9)	P(2)–C(2A)–F(22)	109.4(11)
F(21)–C(2A)–F(22)	107.5(11)	P(2)–C(2A)–F(23)	114.1(9)
F(21)–C(2A)–F(23)	107.5(13)	F(22)–C(2A)–F(23)	105.5(9)
P(2)–C(2B)–F(24)	113.2(9)	P(2)–C(2B)–F(25)	113.3(8)
F(24)–C(2B)–F(25)	109.1(13)	P(2)–C(2B)–F(26)	109.7(11)
F(24)–C(2B)–F(26)	104.8(10)	F(25)–C(2B)–F(26)	106.2(12)
P(3)–C(111)–C(112)	119.2(7)	P(3)–C(111)–C(116)	121.5(6)
C(112)–C(111)–C(116)	119.2(9)	C(111)–C(112)–C(113)	120.4(8)
C(112)–C(113)–C(114)	120.1(9)	C(113)–C(114)–C(115)	119.5(11)
C(114)–C(115)–C(116)	121.2(9)	C(111)–C(116)–C(115)	119.6(8)
P(3)–C(221)–C(222)	122.3(8)	P(3)–C(221)–C(226)	118.8(7)
C(222)–C(221)–C(226)	118.9(9)	C(221)–C(222)–C(223)	121.1(10)
C(222)–C(223)–C(224)	120.3(11)	C(223)–C(224)–C(225)	119.3(12)
C(224)–C(225)–C(226)	122.2(12)	C(221)–C(226)–C(225)	118.2(10)
P(3)–C(331)–C(332)	120.6(7)	P(3)–C(331)–C(336)	119.6(6)
C(332)–C(331)–C(336)	119.7(9)	C(331)–C(332)–C(333)	121.0(9)
C(332)–C(333)–C(334)	119.4(10)	C(333)–C(334)–C(335)	121.0(12)
C(334)–C(335)–C(336)	119.0(11)	C(331)–C(336)–C(335)	119.9(9)

Hz; $\delta 2$ 3.14, dd, F^2, J(P^{2}F^2) = 112.31 Hz, J(P^{3}F^2) = 7.32 Hz. IR (KBr pellet): ν(C$_6$H$_5$) 3064w, 1587w, 1485w, 1438s, 815w, 757m, 745w, 723vs, 691s, 668w, 616w, 564s, 532vs; ν(P=N) 1359s, 1299s, 1278s; ν(C–F) 1190vs, 1169vs, 1131vs, 1115vs; ν(P–N) 998m. EIMS (m$^+$/z): 628 (M^+, 33%), 609 [(M–F)$^+$, 3%], 509 [(M–C$_2$F$_5$)$^+$, 100%], 409 [(M–C$_4$F$_9$)$^+$, 32%], 326 [(M–C$_4$F$_{11}$P)$^+$, 85%]. Anal. Found: C, 41.94; H, 2.20; N, 4.34; C$_{22}$H$_{15}$N$_2$F$_{12}$P$_3$ calc.: C, 42.03; H, 2.38; N, 4.45%.

TABLE 4. Anisotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for $Os_3(CO)_{11}$[$(CF_3)_2$P=N=P(CF$_3$)$_2$=N=PPh$_3$]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	56(1)	38(1)	34(1)	−16(1)	−14(1)	−3(1)
Os(2)	35(1)	31(1)	38(1)	−4(1)	−3(1)	−3(1)
Os(3)	60(1)	43(1)	38(1)	−24(1)	−9(1)	−8(1)
P(1)	47(1)	36(1)	40(1)	−3(1)	7(1)	−5(1)
N(1)	67(5)	44(4)	47(5)	3(4)	−7(4)	0(4)
P(2)	60(1)	35(1)	30(1)	−9(1)	−4(1)	−7(1)
N(2)	40(4)	43(4)	65(5)	−12(3)	5(4)	−22(4)
P(3)	38(1)	35(1)	37(1)	−10(1)	−2(1)	−10(1)
C(11)	57(6)	52(6)	35(5)	−22(5)	−9(4)	−12(4)
C(12)	85(8)	41(5)	76(8)	−12(5)	−47(6)	−2(5)
C(13)	86(8)	38(5)	52(6)	−19(5)	−15(6)	7(4)
C(14)	110(10)	60(6)	47(6)	−40(7)	−11(6)	6(5)
C(21)	43(5)	48(5)	70(7)	−12(4)	−13(5)	−10(5)
C(22)	39(5)	44(5)	30(4)	−8(4)	9(4)	0(4)
C(23)	57(6)	57(6)	60(7)	−1(5)	−10(5)	−4(5)
C(31)	97(9)	52(6)	77(8)	−22(6)	−13(7)	−29(6)
C(32)	64(7)	57(6)	44(5)	−32(5)	−14(5)	1(4)
C(33)	75(7)	75(7)	55(7)	−25(6)	−16(6)	−23(5)
C(34)	110(9)	58(6)	55(6)	−45(7)	−26(6)	−3(5)
O(11)	61(4)	51(4)	52(4)	−5(3)	−5(3)	−16(3)
O(12)	108(7)	86(6)	152(9)	−29(5)	−81(7)	−22(6)
O(13)	97(7)	43(4)	103(7)	7(4)	−26(5)	0(4)
O(14)	144(9)	108(7)	59(6)	−48(7)	11(6)	9(5)
O(21)	78(6)	109(7)	141(9)	−46(6)	−33(6)	−26(6)
O(22)	47(4)	43(4)	57(4)	−1(3)	2(3)	3(3)
O(23)	76(6)	80(6)	110(8)	37(5)	5(5)	4(5)
O(31)	145(9)	69(6)	127(9)	6(6)	−34(7)	−50(6)
O(32)	48(4)	82(5)	90(6)	−16(4)	−5(4)	−33(5)
O(33)	126(8)	147(9)	67(6)	−50(7)	−32(5)	−42(6)
O(34)	177(10)	89(6)	85(6)	−91(7)	8(6)	1(5)
C(1A)	88(9)	50(6)	62(7)	−7(6)	18(6)	−19(5)
C(1B)	55(7)	79(8)	87(10)	−17(6)	15(7)	−2(7)
C(2A)	96(9)	45(6)	85(9)	−20(6)	−25(8)	−14(6)
C(2B)	169(15)	53(7)	31(6)	−40(8)	−1(7)	−1(5)
F(11)	139(8)	79(5)	145(8)	48(5)	−28(6)	−57(5)
F(12)	215(10)	83(5)	49(4)	−16(6)	35(5)	−29(4)
F(13)	167(9)	111(6)	132(7)	−53(7)	30(7)	−86(6)
F(14)	114(7)	178(9)	70(5)	−69(6)	46(5)	−7(5)
F(15)	56(5)	172(9)	153(8)	−35(6)	21(5)	−11(7)
F(16)	123(7)	118(7)	167(9)	−86(6)	36(6)	−27(6)
F(21)	148(8)	101(6)	187(10)	−56(6)	−32(7)	−77(6)
F(22)	92(5)	125(6)	110(6)	−71(5)	−8(5)	0(5)
F(23)	101(6)	94(5)	129(7)	−22(4)	−64(5)	−20(5)
F(24)	184(9)	113(6)	52(4)	−33(6)	−42(5)	19(4)
F(25)	278(12)	92(5)	53(4)	−65(7)	20(6)	−40(4)
F(26)	142(8)	122(7)	66(5)	−49(6)	46(5)	−21(4)

The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

TABLE 5. H-atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $Os_3(CO)_4[(CF_3)_2P=N=P(CF_3)_2=N=PPh_3]$

	x	y	z	U
H(11A)	3540	12779	7448	80
H(11B)	4165	12779	8467	80
H(11C)	2240	13847	9157	80
H(11D)	−191	15049	8800	80
H(11E)	−809	15125	7772	80
H(22A)	2804	14417	5488	80
H(22B)	3506	16079	4802	80
H(22C)	2507	17948	5073	80
H(22D)	851	18151	6000	80
H(22E)	199	16461	6732	80
H(33A)	−1382	15536	5842	80
H(33B)	−4042	15870	5835	80
H(33C)	−5366	14854	6712	80
H(33D)	−4032	13464	7598	80
H(33E)	−1352	13162	7608	80

2.3. p,p,p′,p′-Tetrakis(trifluoromethyl)-p″,p″,p″-triphenyl triphosphazene undecacarbonyl triosmium $Os_3(CO)_{11}$ $[(CF_3)_2P=N=P(CF_3)_2=N=PPh_3]$ (1)

$Os_3(CO)_{11}(CH_3CN)$ (24.3 mg, 0.0262 mmol) and $(CF_3)_2P=N=P(CF_3)_2=N=PPh_3$ (20.4 mg, 0.0325 mmol) were added to a glass reaction vessel containing 5 ml of dichloromethane. The vessel was evacuated and sealed on the vacuum line. The reaction mixture was then kept stirring at room temperature for 18 h whereupon the colour of the solution changed from greenish yellow to a bright yellow. TLC using 10% dichloromethane in hexane as eluent afforded a major band [$R_F = 0.31$, 35.7 mg, 71% yield based on 2 used] from which yellow crystals of 1 was obtained by recrystallisation using hexane at −20°C. For $Os_3(CO)_{11}[(CF_3^1)_2P^1=N=P^2(CF_3^2)_2=N=P^3Ph_3]$ (1): ^{31}P NMR (referenced to H_3PO_4): $\delta 1$ 24.09, double septet, P^1, $J(F^1P^1) = 85.45$ Hz, $J(P^2P^1) = 53.71$ Hz, $\delta 2$ 17.97, d, P^3, $J(P^2P^3) = 14.64$ Hz; $\delta 3$ −38.36, dds, P^2, $J(P^1P^2) = 53.71$ Hz, $J(P^3P^2) = 14.64$ Hz, $J(F^2P^2) = 122.07$ Hz. ^{19}F NMR (referenced to CF_3CO_2H): $\delta 1$ 5.60, d, F^1, $J(P^1F^1) =$ 85.44 Hz; $\delta 2$ 3.85, d, F^2, $J(P^2F^2) = 122.04$ Hz. IR (dichloromethane): $\nu(CO)$ 2113s, 2059vs, 2045vs, 2026vs, 2005vs, 1995vs; $\nu(C_6H_5)$ 3065w, 1590m, 1436s, 859w, 810w, 743m, 725m, 690s, 663s, 601s; $\nu(P=N)$ 1360s, 1311w, 1251s, 1201s; $\nu(C-F)$ 1194s, 1182s, 1157s, 1118s, $\nu(P-N)$ 999w. Anal. Found: C, 26.52; H, 0.99; N, 1.77; $C_{33}H_{15}N_2O_{11}F_{12}P_3Os_3$ calc.: C, 26.28; H, 1.00; N, 1.86%.

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References and notes

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5 Crystal data for L: $C_{22}H_{15}N_2F_{12}$, monoclinic, $P2_1/n$, $a = 11.947(2)$, $b = 14.368(3)$, $c = 15.576(3)$ Å, $\beta = 92.17(3)°$, $U = 2671.8(9)$ Å^3, $Z = 4$. $D_c = 1.523$ g cm^{-3}, $\mu = 3.17$ cm^{-1}; T = 25°C, Siemens R3m/v, Mo $K\alpha$ radiation ($\lambda = 0.71069^+$). Due to the poor quality of the crystal of L and the extensive disorder of the terminal $(CF_3)_2P$ moiety, the structure of L could only be refined to $R_F = 14.77\%$, $R_{wF} = 20.24\%$ for 5172 reflections ($3° \le 2\theta \le 50.0°$) of which 4711 were independent ($R_{int} = 1.85\%$) and 2731 were observed $|6\sigma(F_0)|$. The structure was solved by direct methods and Fourier difference technique. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized. GOF = 1.23 $\Delta/\sigma = 0.045$, $\Delta/\sigma_{max} = 0.430$, weighting scheme $w^{-1} = \sigma^2(F) + 0.0300F^2$. SHELXTL software used for all computations (G. Sheldrick, Siemens, Madison, WI, USA).

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