Synthesis and Crystal Structures of $(CF_3)_2As{-}N{=}PPh_3$, $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ and $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$†

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Bis(trifluoromethyl)arsinous azide $(CF_3)_2AsN_3$ undergoes a Staudinger reaction with PPh_3 to give the arsinophosphazene $(CF_3)_2As{-}N{=}PPh_3$ which reacts with $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ **1** and $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2** respectively. Single-crystal X-ray structural studies show that upon complexation $(CF_3)_2As{-}N{=}PPh_3$ assumes a highly delocalized electronic structure over the unsymmetrical As–N=P segment with the As–N bond distance assuming that of an As=N double bond. These two complexes represent the first examples of neutral compounds containing a highly delocalized As=N=P non-linear structure.

The syntheses and reactivities of non-fluorinated organophosphazene and -arsinophosphazenes such as $Me_2P{-}N{=}PMe_3$ and $Me_2As{-}N{=}PMe_3$ were reported by Schmidbaur and Jones.[1] However, very little is known about their ligand properties. Only two perfluoroorganophosphazenes $(C_6F_5)_2P{-}N{=}PPh_3$[2] and $(CF_3)_2P{=}N{=}PPh_3$[3] have been reported. Fluorophosphazenes of the type $RF_2P{=}N{-}PF_2$ (R = F or Ph) have been shown to displace the co-ordinated cyclic alkene from $[Mo(C_7H_8)(CO)_4]$ to yield *cis*-$[Mo(RF_2P{=}N{=}PF_2)(CO)_4]$.[4,5]

In this paper we present the synthesis and structural characterisation of the ligand $(CF_3)_2As{-}N{=}PPh_3$ as well as those of two clusters $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ **1** and $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2** obtained from reaction of $(CF_3)_2As{-}N{=}PPh_3$ with $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, respectively.

Results and Discussion

Structure of $(CF_3)_2As{-}N{=}PPh_3$.—Bis(trifluoromethyl)arsinous azide undergoes a Staudinger reaction with triphenylphosphine to give bis(trifluoromethyl)arsinophosphazene. The ν(P=N) absorption of $(CF_3)_2As{-}N{=}PPh_3$ is observed at 1188 cm^{-1}, which is somewhat lower than the value of 1257 cm^{-1} observed in $(CF_3)_2P{=}N{=}PPh_3$.[3] The structure of $(CF_3)_2As{-}N{=}PPh_3$ has been determined by single-crystal X-ray diffraction, and, as shown in Fig. 1, is isostructural with that of $(CF_3)_2P{=}N{=}PPh_3$.[3] The atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. Whereas the P–N bond of 1.564(10) Å is typical of P=N, the As–N bond of 1.783(10) Å is considerably shorter than the As–N single-bond distance of 1.87 Å calculated from Pauling's covalent single-bond radii. It has been reported[3] that in $(CF_3)_2P{=}N{=}PPh_3$, the unsymmetrical PNP segment is characterised by the P=N and N=P bonds which are close to P=N double bonds. This highly delocalised electronic structure has been attributed to the strongly electron-withdrawing CF_3 groups which lower the energies of the 3d orbitals of the phosphorus atom, and here facilitates N→P dative π bonding. However, such dative π bonding is not expected to be as effective in $(CF_3)_2As{-}N{=}PPh_3$ because the 4d orbitals of arsenic are more diffuse than the 3d orbitals of phosphorus, and may account for the smaller reduction in As–N bond distance.

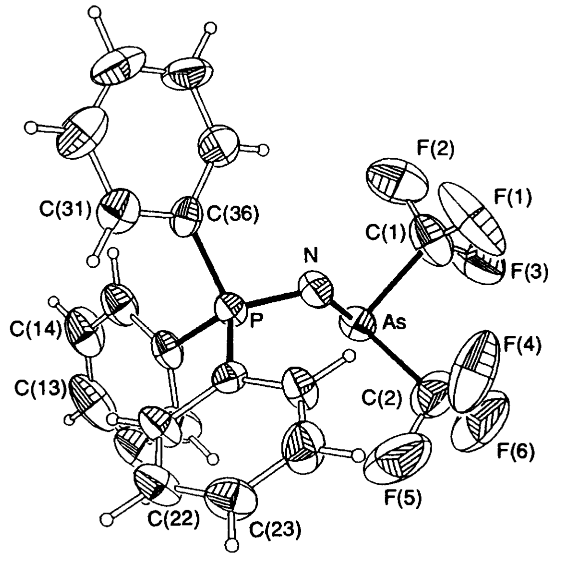

Fig. 1 The molecular structure of $(CF_3)_2As{-}N{=}PPh_3$ showing the atom labelling

Structures of $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ **1** *and* $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2**.—The molecular structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction and are shown in Figs. 2 and 3 respectively. For **1**, the atomic coordinates are given in Table 3 and selected bond lengths and angles in Table 4 while those for **2** are given in Tables 5 and 6. The structure in each case comprises an approximate isosceles triangle of osmium atoms. Complex **1** is isostructural to $[Os_3(CO)_{11}\{(CF_3)_2P{=}N{=}PPh_3\}]$.[6] The distribution of ligands in **2** is similar to those in $[Os_3(\mu\text{-}H)_2(CO)_9(PPh_3)]$[7] and $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2P{=}N{=}PPh_3\}]$[8] where both hydrides bridge the short Os–Os edge. In both structures each osmium atom exhibits distorted octahedral co-ordination geometry and the bulky ligand $(CF_3)_2As{=}N{=}PPh_3$ is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Atomic coordinates (× 10^4) for $(CF_3)_2As-N=PPh_3$

Atom	*x*	*y*	*z*
As	236(1)	2 307(1)	8 781
P	−226(2)	1 702(1)	9 941(3)
N	349(5)	1 952(2)	9 646(10)
F(1)	1 645(6)	2 373(3)	9 602(19)
F(2)	949(9)	2 592(4)	10 723(15)
F(3)	1 202(6)	2 785(2)	8 955(15)
F(4)	1 335(9)	2 025(3)	7 353(17)
F(5)	342(10)	1 989(3)	6 539(12)
F(6)	856(8)	2 412(3)	6 381(13)
C(1)	1 080(11)	2 515(4)	9 543(24)
C(2)	750(14)	2 183(5)	7 195(17)
C(11)	−1 397(7)	1 863(3)	8 527(14)
C(12)	−2 060(9)	1 992(4)	8 392(19)
C(13)	−2 433(8)	2 087(4)	9 429(27)
C(14)	−2 152(8)	2 059(3)	10 632(21)
C(15)	−1 510(7)	1 925(3)	10 801(15)
C(16)	−1 130(6)	1 828(2)	9 756(13)
C(21)	−672(6)	1 146(2)	8 780(14)
C(22)	−588(7)	886(3)	8 071(13)
C(23)	52(7)	823(3)	7 497(14)
C(24)	596(8)	1 027(3)	7 688(14)
C(25)	507(6)	1 288(3)	8 425(12)
C(26)	−126(6)	1 359(2)	8 996(11)
C(31)	−366(7)	1 310(3)	12 090(14)
C(32)	−273(10)	1 232(4)	13 390(16)
C(33)	93(9)	1 420(5)	14 150(14)
C(34)	354(8)	1 705(4)	13 677(16)
C(35)	255(7)	1 782(3)	12 425(14)
C(36)	−112(6)	1 587(3)	11 597(11)

Table 2 Selected bond distances (Å) and angles (°) for $(CF_3)_2As-N=PPh_3$

As–N	1.783(10)	Mean P–C	1.801
P–N	1.564(10)	Mean F–C	1.304
As–C(1)	2.007(2)		
As–C(2)	1.984(20)		
As–N–P	126.7(6)	C(1)–As–C(2)	112.5(5)
N–As–C(1)	94.8(6)	Mean N–P–C	111.9
N–As–C(2)	97.4(7)		

co-ordinated through the arsenic atom in the equatorial plane of the Os_3 triangle. An Os–As distance of 2.424(2) Å is found for both **1** and **2** and is comparable to that in the terminal tertiary arsine in $[Os_3(CO)_8(\mu_3\text{-}C_6H_3Me\text{-}4)(\mu_3\text{-}AsC_6H_4Me\text{-}4)\{As(C_6H_4Me\text{-}4)_3\}]$[9] [2.427(5) Å].

In **1**, two of the Os–Os distances are similar to the average Os–Os distance in the more symmetrical complex $[Os_3(CO)_{12}]$.[10] The third distance, Os(1)–Os(3), is 0.025 Å longer than this average. This is most likely a consequence of the proximity of the Os(1)–Os(3) bond to the bulky, equatorially bound ligand. In **2**, Os(2)–Os(3) is similar in length to the two unbridged bonds [mean 2.815(1) Å][11] in the parent dihydride but Os(1)–Os(2) which is *trans* to the As atom is significantly shorter than the corresponding one in $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. In the complex $[Os_3(\mu\text{-}H)_2(CO)_9(PPh_3)]$, the Os(1)–Os(3) bond *trans* to the P atom is similar in length to the two unbridged bonds in the parent dihydride, but the dihydrido-bridged Os(2)–Os(3) is slightly longer.

In the structure of **1** the steric effects due to the ligand are clearly manifested in the large deviations from ideal values for

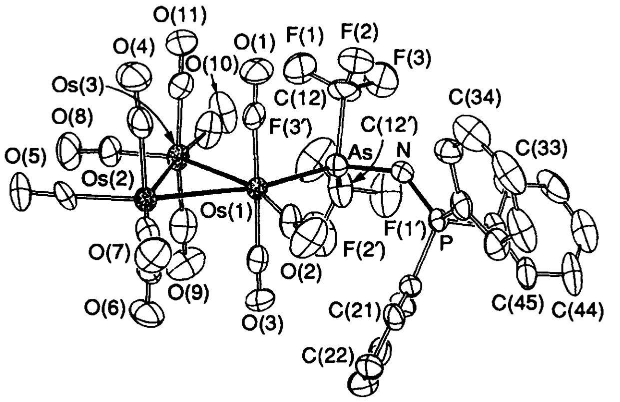

Fig. 2 The molecular structure of $[Os_3(CO)_{11}\{(CF_3)_2As=N=PPh_3\}]$ **1** showing the atom labelling

Table 3 Atomic coordinates (× 10^4) for $[Os_3(CO)_{11}\{(CF_3)_2As=N=PPh_3\}]$ **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	6 283.6(6)	1 603.5(2)	2 214.6(4)	C(5)	9 839(16)	2 652(8)	1 811(15)
Os(2)	8 354.3(7)	2 160.9(3)	1 669.1(5)	C(6)	9 444(17)	1 555(7)	2 228(14)
Os(3)	7 870.2(7)	2 365.0(3)	3 497.0(5)	C(7)	8 220(16)	1 870(7)	441(12)
As	4 703(2)	1 331(1)	3 068(1)	C(8)	9 249(18)	2 845(8)	3 822(14)
P	3 288(4)	285(2)	2 222(3)	C(9)	8 884(22)	1 739(10)	3 985(15)
N	3 457(12)	888(5)	2 687(11)	C(10)	7 262(24)	2 442(10)	4 636(13)
F(1)	4 245(15)	2 392(5)	3 685(13)	C(11)	6 670(18)	2 940(7)	2 972(12)
F(2)	2 851(13)	2 102(5)	2 565(12)	C(12)	3 629(21)	1 934(9)	3 406(16)
F(3)	2 854(15)	1 807(7)	3 893(12)	C(12′)	5 269(24)	1 093(11)	4 394(14)
F(1′)	4 515(16)	743(7)	4 678(10)	C(21)	5 207(11)	−217(5)	1 487(7)
F(2′)	6 407(17)	809(8)	4 524(10)	C(22)	6 345	−505	1 595
F(3′)	5 536(20)	1 496(6)	4 988(9)	C(23)	6 982	−680	2 483
O(1)	4 540(14)	2 543(5)	1 298(11)	C(24)	6 479	−568	3 264
O(2)	5 414(17)	941(5)	439(9)	C(25)	5 341	−280	3 156
O(3)	7 970(14)	622(5)	3 004(12)	C(26)	4 704	−105	2 267
O(4)	6 708(15)	3 166(6)	840(12)	C(31)	2 164(12)	−143(4)	456(9)
O(5)	10 639(13)	2 933(6)	1 872(11)	C(32)	1 406	−102	−446
O(6)	10 148(15)	1 207(6)	2 462(12)	C(33)	916	410	−790
O(7)	8 091(16)	1 659(6)	−283(10)	C(34)	1 185	883	−231
O(8)	10 130(15)	3 108(7)	3 987(12)	C(35)	1 944	843	671
O(9)	9 506(18)	1 381(7)	4 342(11)	C(36)	2 434	330	1 014
O(10)	6 898(16)	2 529(8)	5 278(11)	C(41)	1 603(12)	107(5)	3 333(9)
O(11)	6 010(15)	3 278(5)	2 725(12)	C(42)	800	−210	3 748
C(1)	5 244(17)	2 210(6)	1 647(13)	C(43)	773	−785	3 647
C(2)	5 741(16)	1 155(7)	1 122(11)	C(44)	1 548	−1 043	3 130
C(3)	7 376(18)	999(7)	2 727(12)	C(45)	2 350	−726	2 714
C(4)	7 275(18)	2 792(8)	1 144(14)	C(46)	2 378	−151	2 816

the *cis* Os–Os–C(equatorial) and *cis* C–Os–C(equatorial) angles particularly those associated with Os(1) and Os(3). The six equivalent *cis* Os–Os–C(equatorial) angles in $[Os_3(CO)_{12}]$ range from 96.1(3) to 99.3(3)° (average 98.2°); the *cis*-diequatorial C–Os–C(equatorial) angles in $[Os_3(CO)_{12}]$ range from 102.8(5) to 104.2(4)° (average 103.5°). In contrast, the angles Os(3)–Os(1)–As and Os(1)–Os(3)–C(10) increase to 103.0(1) and 110.6(7)°, respectively; and the angles C(10)–Os(3)–C(8) and As–Os(1)–C(2) are reduced to 97.4(10) and 98.9(6)°, respectively. However, the electronic effects attributable to the $(CF_3)_2As$ moiety are not distinct.

On the other hand, the Os(1)–Os(2) bond in **2** appears to be unaffected by the presence of the arsine ligand and its length is not significantly different from those found in the complexes $[Os_3(\mu\text{-}H)_2(CO)_9L]$ [L = CO,[11] PPh_3,[7] $(CF_3)_2P{=}N{=}PPh_3$,[8] PPr^i_3[12] or PMe_2Ph[13]]. To facilitate comparisons, selected bond lengths and angles of these clusters are given in Table 7. The hydride bridged Os–Os separations in these complexes show very little variation and imply that substitution at this site has little effect on the cluster bonding. The fact that the hydride ligands exert a steric influence has been illustrated.[14] The Os–Os–C(carbonyl) [mean 131.4° at Os(1) and 128.5° at Os(2)] angles involving Os(1), Os(2), C(1), C(2), C(4), C(5) show that the carbonyls bend away from the short Os(1)–Os(2) edge.

The diminished steric effect due to the arsine ligand in going from **1** to **2** would be expected on the basis of the increase in Os(2)–Os(1)–As and Os(3)–Os(1)–As angles from 103.0(1) and 162.5(1) to 106.7(1) and 168.1(1)° respectively.

The Unusual As=N=P *Moiety in Complexes* **1** *and* **2**.—The P–N bond distances of **1** [1.598(14) Å] and **2** [1.577(16) Å], as in the free ligand are close to that of a P=N double bond. The

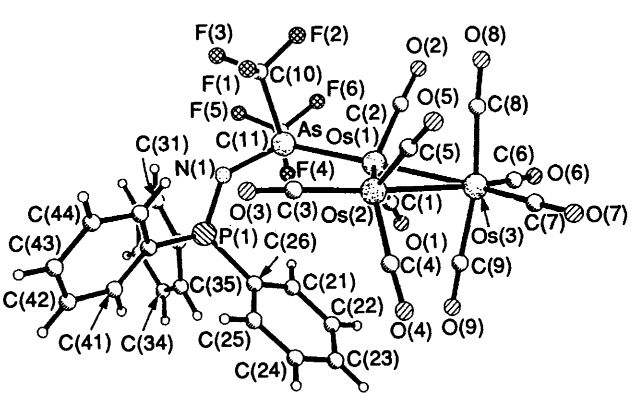

Fig. 3 The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2** showing the atom labelling

Table 4 Selected bond distances (Å) and angles (°) for $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ **1**

Os(1)–Os(2)	2.878(1)	Mean As–C	1.9885
Os(1)–Os(3)	2.902(1)	Mean P–C	1.7967
Os(2)–Os(3)	2.877(1)	Mean Os–CO	1.9266
Os(1)–As	2.424(2)	Mean C–O	1.1256
As–N	1.716(13)		
P–N	1.598(14)		
Os(1)–Os(2)–Os(3)	60.6(1)	As–N–P	135.4(9)
Os(1)–Os(3)–Os(2)	59.7(1)	C(12)–As–C(12′)	92.3(10)
Os(2)–Os(1)–Os(3)	59.7(1)	Mean Os(1)–As–C	117.7
Os(2)–Os(1)–As	162.5(1)	Mean N–As–C	97.6
Os(3)–Os(1)–As	103.0(1)	Mean Os–C–O	175.0
Os(1)–As–N	126.7(6)		

Table 6 Selected bond distances (Å) and angles (°) for $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2**

Os(1)–Os(2)	2.685(1)	Mean As–C	2.017
Os(1)–Os(3)	2.787(1)	Mean P–C	1.796
Os(2)–Os(3)	2.807(1)	Mean Os–CO	1.903
Os(1)–As	2.424(2)	Mean C–O	1.139
As–N(1)	1.739(16)		
P(1)–N(1)	1.577(16)		
Os(1)–Os(2)–Os(3)	61.0(1)	As–N(1)–P(1)	133.0(8)
Os(1)–Os(3)–Os(2)	57.4(1)	C(12)–As–C(12′)	97.4(8)
Os(2)–Os(1)–Os(3)	61.7(1)	Mean Os(1)–As–C	111.4
Os(2)–Os(1)–As	106.7(1)	Mean N–As–C	99.3
Os(3)–Os(1)–As	168.1(1)	Mean Os–C–O	176.2
Os(1)–As–N(1)	132.1(4)		

Table 5 Atomic coordinates (× 10^4) for $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2**

Atom	*x*	*y*	*z*
Os(1)	955(1)	5627(1)	2130(1)
Os(2)	1930(1)	6150(1)	3595(1)
Os(3)	2948(1)	4994(1)	2895(1)
As	−694(1)	6392(1)	1686(1)
P(1)	−2173(3)	5987(3)	2552(3)
N(1)	−1607(10)	6600(8)	2126(8)
F(1)	−106(11)	8121(7)	2062(7)
F(2)	78(11)	7731(8)	992(8)
F(3)	−1380(10)	8061(7)	1047(8)
F(4)	−1935(10)	5190(8)	650(6)
F(5)	−2397(10)	6494(9)	282(6)
F(6)	−1034(9)	5970(9)	142(6)
O(1)	192(12)	3836(9)	1446(9)
O(2)	1483(13)	6046(11)	695(9)
O(3)	592(10)	7402(9)	4146(8)
O(4)	2555(13)	5065(10)	5073(9)
O(5)	3900(11)	7221(9)	4200(9)
O(6)	3007(11)	3768(10)	1590(9)
O(7)	5073(14)	4783(10)	4130(11)
O(8)	3709(13)	6656(10)	2283(10)
O(9)	1981(13)	3535(9)	3574(10)
C(1)	448(14)	4508(12)	1702(10)
C(2)	1231(16)	5867(12)	1211(12)
C(3)	1026(14)	6929(13)	3883(11)
C(4)	2293(14)	5499(13)	4517(11)
C(5)	3145(15)	6839(11)	3969(11)
C(6)	3008(13)	4220(12)	2089(11)
C(7)	4271(16)	4866(13)	3668(15)
C(8)	3394(14)	6053(15)	2504(14)
C(9)	2322(15)	4074(12)	3322(14)
C(10)	−514(16)	7654(11)	1429(13)
C(11)	−1585(17)	5998(14)	603(11)
C(21)	−1335(13)	4329(10)	2579(12)
C(22)	−778(16)	3582(12)	2914(13)
C(23)	−345(18)	3536(13)	3708(14)
C(24)	−533(19)	4218(16)	4113(15)
C(25)	−1074(17)	4962(13)	3811(11)
C(26)	−1457(14)	5023(10)	3029(11)
C(31)	−3892(13)	6190(12)	1307(11)
C(32)	−4858(21)	5909(19)	841(14)
C(33)	−5298(18)	5131(19)	953(18)
C(34)	−4771(20)	4553(17)	1519(18)
C(35)	−3852(16)	4819(12)	1996(13)
C(36)	−3404(13)	5626(12)	1898(10)
C(41)	−3172(17)	6397(13)	3589(13)
C(42)	−3415(18)	6890(15)	4124(12)
C(43)	−2913(21)	7682(16)	4342(13)
C(44)	−2151(17)	7962(15)	4049(12)
C(45)	−1927(15)	7420(14)	3504(12)
C(46)	−2465(13)	6637(11)	3264(10)

most significant feature of these structures is that the As–N bond distances in $(CF_3)_2As{=}N{=}PPh_3$ [1.783(10) Å], **1** [1.716(13) Å] and **2** [1.739(16) Å] are significantly shorter than that expected for a As–N single bond (1.87 Å). This value of 1.87 Å has been found in the adamantane-type compound $As_4(NMe)_6$.[15] The As–N bond distances of **1** and **2** are also somewhat shorter than the value of 1.749(3) Å reported for the symmetrical ionic compound $[Ph_3As{-}N{-}AsPh_3]Cl$[16] and also the average As–N bond distances of 1.758(4) Å in 2,2,4,4,6,6-hexaphenyl-2λ^5,4λ^5,6λ^5-cyclotriarsaza-1,3,5-triene.[17]

Conclusion

Thus, it is clear that the neutral molecule $(CF_3)_2As{-}N{=}PPh_3$ upon co-ordination assumes a highly delocalised electronic structure over the unsymmetrical As=N=P segment. The enhanced delocalisation upon complexation over the As=N=P segment represents the first example of a delocalised non-linear structure involving an As^{III} atom. Enhanced delocalisation upon complexation of $(CF_3)_2As{-}N{=}PPh_3$ is reflected not only in the shortening of the As–N bond length but also in the increase in As–N–P angles from 126.7(6)° in $(CF_3)_2As{-}N{=}PPh_3$ to 135.4(9) and 133.0(8)° in the complexes **1** and **2**, respectively.

Experimental

X-Ray Structural Determination.—Crystal data and details of measurements for $(CF_3)_2As{-}N{=}PPh_3$, **1** and **2** are reported in Table 8. Diffraction intensities were collected at 298 K on a Siemens P_4 X-ray diffractometer for $(CF_3)_2As{-}N{=}PPh_3$ and **2** and on a Nicolet-R3M X-ray diffractometer for **1** with graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å), scan range 1.00°, and $4 < 2\theta < 45°$ for $(CF_3)_2As{-}N{=}PPh_3$, $4 < 2\theta < 50°$ for **1** and $4 < 2\theta < 48°$ for **2**. Indices $+h, +k, \pm l$ for $(CF_3)_2As{-}N{=}PPh_3$ and $\pm h, +k, +l$ for **1** and **2** were measured and all computations were carried out using the SHELXTL PLUS program package.[18] The structures were solved by direct methods and Fourier difference techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions. An empirical (ψ scan) correction was performed for **1** and **2**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Methodology.—All manipulations were carried out using a conventional Pyrex vacuum system. The reactions were performed under nitrogen using standard Schlenk tubes fitted with Teflon taps or all-glass break seal ampoules. The solvents used were distilled and de-gassed by freeze-pump-thaw prior to use. Infrared spectra were recorded on a Perkin Elmer 983G grating infrared spectrophotometer; ^1H, ^{19}F and $^{31}P-\{^1H\}$ NMR spectra in $CDCl_3$ were recorded on a JEOL 90 MHz spectrophotometer with tetramethylsilane, trifluoroacetic acid and 85% phosphoric acid respectively, as standards; mass spectra were recorded on a Hewlett Packard HP 5988A mass spectrometer. Complexes $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ were prepared by literature methods,[19] bis(trifluoromethyl)arsinous azide was synthesized by a method developed in our laboratory.[20] **CAUTION**: covalent azides are known to be explosive. Although we experienced no difficulties in handling this azide, they should be treated as potentially hazardous materials.

Synthesis of $(CF_3)_2As{-}N{=}PPh_3$.—Bis(trifluoromethyl)-arsinous azide (0.1142 g, 0.4478 mmol) was condensed into an ampoule containing a methylene chloride solution of triphenylphosphine (0.1146 g, 0.4369 mmol) chilled to liquid-nitrogen temperature. When the reaction mixture attained room temperature, rapid evolution of gas (presumably dinitrogen) occurred for about 20 min. It was then left at room temperature

Table 7 Selected bond lengths (Å) and angles (°) for complexes $[Os_3(\mu\text{-}H)_2(CO)_9L]$

L	Os(1)–Os(2)	Os(1)–Os(3)	Os(2)–Os(3)	L–Os(1)–Os(2)	Os(1)–Os(2)–C(3)	Ref.
$(CF_3)_2As{=}N{=}PPh_3$	2.685(1)	2.787(1)	2.807(1)	106.7(1)	108.0(5)	—
CO	2.683(1)	2.814 (mean)	2.813 (mean)	106.81(4)	107.35(5)	13
PPh_3	2.683(2)	2.813(2)	2.822(2)	105.8(1)	105.8(3)	11
PPr^i_3	2.689(1)	2.822(1)	2.816(1)	108.1(2)	—	14
PMe_2Ph	2.703	2.828	2.833	106.3	112.5	15

Table 8 Crystal data and details of measurements for $(CF_3)_2As{-}N{=}PPh_3$, **1** and **2**

	$(CF_3)_2As{-}N{=}PPh_3$	**1**	**2**
Formula	$C_{20}H_{15}AsF_6NP$	$C_{31}H_{15}AsF_6NO_{11}Os_3P$	$C_{29}H_{17}AsF_6NO_9Os_3P$
M	489.2	1367.95	1311.9
Crystal symmetry	Orthorhombic	Monoclinic	Monoclinic
Space group	Fdd_2	$P2_1/n$	$P2_1/n$
a/Å	19.114(5)	10.849(6)	13.7457(16)
b/Å	42.918(8)	24.117(9)	15.0939(17)
c/Å	10.378(3)	14.618(8)	18.3746(23)
β/°		102.76(4)	109.94(9)
U/Å^3	8513(3)	3730.2(34)	3583.8(7)
Z	16	4	4
F(000)	3904	2371	2392
D_c/g cm^{-3}	1.527	2.435	2.431
μ(Mo-Kα)/cm^{-1}	17.29	111.98	116.52
Measured reflections	3141	6890	6033
Independent reflections	2788	6345	5585
Observed reflections $[F > n\sigma(F)]$ (n)	2191 (n = 4)	3944 (n = 5)	3734 (n = 4)
Absorption correction $[I(\max)/I(\min)]$		3.730	3.425
R	0.0634	0.0577	0.0478
R'[a]	0.0752	0.0618	0.0512
g	0.0008	0.0008	0.0008
S[b] (p)	1.72 (p = 270)	1.022 (p = 451)	1.142 (p = 461)

[a] Weighting scheme $w^{-1} = \sigma^2(F) + |g|F^2$ where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$.

with continuous stirring for another hour to ensure complete reaction. Solvents and excess azide were removed under *vacuo*. The white solid was then recrystallised from CH_2Cl_2–hexane to yield a colourless crystalline solid of $(CF_3)_2As{-}N{=}PPh_3$ (0.2094 g, 98% yield), m.p. 123–125 °C (Found: C, 49.35; H, 2.50; N, 2.65. Calc. for $C_{20}H_{15}AsF_6NP$: C, 49.10; H, 3.05; N, 2.85%). IR (KBr) $\nu_{asym}(P{=}N)$ 1188s; $\nu(CF_3)$ 1115 (sh), 1127vs, 1150 (sh); $\delta(CF_3)$ 765m, 722s; $\nu_{sym}(P{=}N)$ 635m; $\nu(As{-}C_2)$ 537s; $\nu(As{-}N)$ 443w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.5 (m); ^{31}P, δ 24.9 (s); ^{19}F, δ 15.9 (s). Mass spectrum *m*/*z* 489 (M^+, 0.7), 420 ($M^+ - CF_3$, 43.9), 370 ($M^+ - C_2F_5$, 100.0), 350 (9.2), 292 (7.1), 262 (4.5), 227 (7.0), 183 (36.0), 78 (6.2), 77 (14.8), 69 (6.8) and 50 (5.9%).

Synthesis of $[Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}]$ **1**.—The ligand $(CF_3)_2As{-}N{=}PPh_3$ (11.2 mg, 0.0229 mmol) and $[Os_3(CO)_{11}(MeCN)]$ (21.5 mg, 0.0234 mmol) were allowed to react at room temperature in CH_2Cl_2 for *ca.* 24 h. The resultant bright yellow solution was then concentrated and purified by TLC using CH_2Cl_2–hexane (1 : 9) as eluent. An intense yellow band ($R_f = 0.37$) was extracted and recrystallised from CH_2Cl_2–hexane to obtain yellow crystals of **1** (21.8 mg, 70% yield) (Found: C, 27.15; H, 1.20; N, 1.10. Calc. for $C_{31}H_{15}AsF_6NO_{11}Os_3P$: C, 27.20; H, 1.10; N, 1.00%); IR (cyclohexane) $\nu(CO)$ 2112m, 2059s, 2043m, 2025vs, 2006m, 1994m, 1985m; $\nu_{asym}(As{=}N{=}P)$ 1216s (br); $\nu(CF_3)$ 1163s, 1140s, 1114s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.6 (m); ^{31}P, δ 16.8 (s); ^{19}F, δ 12.9 (s).

Synthesis of $[Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}]$ **2**.—The ligand $(CF_3)_2As{-}N{=}PPh_3$ (20.2 mg, 0.0413 mmol) and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (34.4 mg, 0.0413 mmol) were allowed to react at 80 °C in CH_2Cl_2 in an evacuated reaction tube for 6 h. At the end of the reaction, the colour of the solution changed from purplish to wine-red. The resultant wine-red solution was then concentrated and purified by TLC using CH_2Cl_2–hexane (1 : 9) as eluent. An intense purplish band ($R_f = 0.41$) was extracted and recrystallised from CH_2Cl_2–hexane to obtain purplish red crystals of **2** (16.2 mg, 31% yield) (Found: C, 26.50; H, 1.20; N, 1.10. Calc. for $C_{29}H_{17}AsF_6NO_9Os_3P$: C, 26.50; H, 1.30; N, 1.05%). IR (cyclohexane) $\nu(CO)$ 2096m, 2057vs, 2025vs, 2014vs, 2009vs, 1991m, 1979m, 1970w; $\nu_{asym}(As{=}N{=}P)$ 1200s (br); $\nu(CF_3)$ 1165s, 1149s, 1121s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.5 (m), −11.7 (s, Os–H–Os); ^{31}P, δ 20.3 (s); ^{19}F, δ 11.7 (s).

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