Synthesis, and Spectral and X-Ray Structural Studies of a Novel Delocalised Diphosphazene $(CF_3)_2P=N=PPh_3$ and the Iron Carbonyl Complexes $[Fe(CO)_4\{(CF_3)_2P=N=PPh_3\}]$ and $[Fe(CO)_3\{(CF_3)_2P=N=PPh_3\}_2]$

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The diphosphazene $(CF_3)_2P=N=PPh_3$ L prepared from the reaction of $(CF_3)_2PN_3$ with PPh_3 has been shown from a single-crystal X-ray structural study to possess an unusual and novel delocalised P=N=P moiety containing P^{IV} and P^{V} atoms; the P=N=P structure is retained upon coordination to Fe in the complexes $[Fe(CO)_4\{(CF_3)_2P=N=PPh_3\}]$ **1** and $[Fe(CO)_3\{(CF_3)_2P=N=PPh_3\}_2]$ **2**.

The study of cyclo- and poly-phosphazenes as ligands with transition metals has attracted considerable interest.[1-3] However, the coordinating properties of diphosphazenes have only begun to receive attention recently. Reactions of diphosphazenes of the type $RF_2P=N-PF_2$ (R = F or Ph) with $[Mo(C_7H_8)(CO)_4]$ (C_7H_8 = bicyclo[3.2.0]hepta-2,6-diene) have been shown to yield *cis*-$[Mo(RF_2P=N-PF_2)(CO)_4]$ by the displacement of the cyclic alkene.[4,5] The title diphosphazene $(CF_3)_2P=N=PPh_3$ (L) has been shown to react with $PdCl_2$ giving $[Pd_2Cl_4L_2]$[6] and to displace the acetonitrile molecules from $[Os_3(CO)_{10}(MeCN)_2]$[7] and $[Os_3(CO)_{11}(MeCN)]$.[8] We report now the syntheses and spectral and structural studies of $(CF_3)_2P{=}N{=}PPh_3$, and complexes **1** and **2**.

$(CF_3)_2P{=}N{=}PPh_3$
L
$[Fe(CO)_4\{(CF_3)_2P{=}N{=}PPh_3\}]$
1
$[Fe(CO)_3\{(CF_3)_2P{=}N{=}PPh_3\}_2]$
2

The diphosphazene $(CF_3)_2P{=}N{=}PPh_3$ was obtained in 91% yield by the reaction of $(CF_3)_2PN_3$ with triphenylphosphine in dichloromethane at room temperature for 4 days. The reaction of L with $[Fe_2(CO)_9]$ in hexane at room temperature for 24 h afforded **1** (60%) and **2** (28%). The composition of each of these compounds was established by elemental analyses (C, H, N) and ^1H, ^{19}F and ^{31}P NMR spectroscopy.† Crystals of L, **1** and **2** were obtained from solutions in CH_2Cl_2–hexane at low temperatures.

The molecular structures‡ of L, **1** and **2** are shown in Figs. 1–3 while Table 1 gives the important bond parameters. In **1** and **2** the Fe atom assumes a nearly trigonal bipyramidal structure with the ligand moiety taking up axial positions. The molecular structure of L is nearly the same in both the free and complexed forms. The most striking and unusual feature is the equidistant P=N and N=P bonds found in L, **1** and **2**. Furthermore all these lie within the range of values of 1.55–1.62 Å expected for P=N double bond.[9,10] This suggests that the unsymmetrical PNP segment is highly delocalised presumably owing to the effect of the strongly electron-withdrawing CF_3 moiety. Enhanced delocalisation upon complexation of L is reflected in (*a*) the increase in P–N–P angle from 131° in L to 151° in both complexes **1** and **2**, (*b*) the significantly longer Fe–C(4) bond (1.771 Å) in **1** in comparison to the three equatorial Fe–C bonds (1.746 Å), (*c*) most importantly, the axial and diaxial configurations of L found in **1** and **2** respectively, and (*d*) the resultant units P(1)–Fe–C(4) in **1** and P(1)–Fe–P(1A) in **2** being very nearly linear owing to the high degree of conjugation. The Fe–P(1) distances of 2.184 Å for **1** and 2.167 Å for **2** are somewhat shorter than that of 2.244 Å for $[Fe(CO)_4PPh_3]$.[11] Furthermore the shorter Fe–P(1) bond in **2** is consistent with more extensive delocalisation resulting from the diaxial configuration of the two L moieties. Apparently this effect is in turn transmitted to the

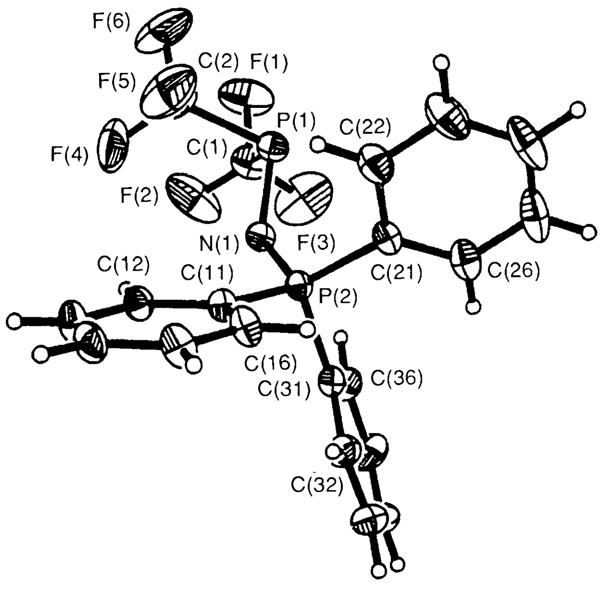

Fig. 1 Molecular structure of $(CF_3)_2P{=}N{=}PPh_3$ L showing the atom labelling scheme

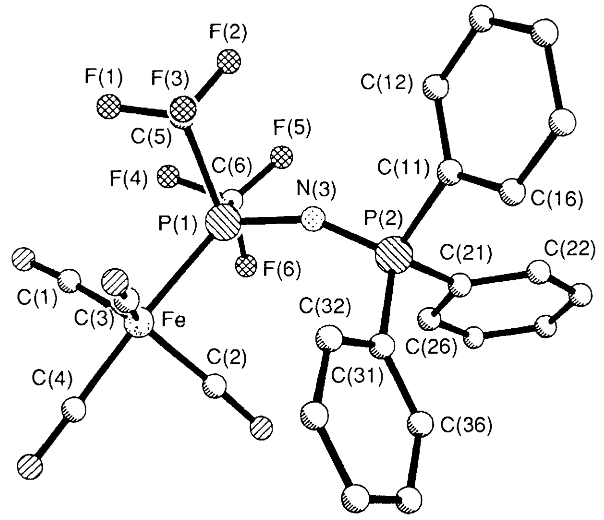

Fig. 2 Molecular structure of $[Fe(CO)_4\{(CF_3)_2P{=}N{=}PPh_3\}]$ **1** showing the atom labelling scheme

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† *Selected spectroscopic data*, for $(CF_3)_2P{=}N{=}PPh_3$ L: ^{31}P NMR (referenced to H_3PO_4): δ1 54.99, J_{PP} 117.79 Hz, J_{PF} 78.12 Hz; δ2 25.71, J_{PP} 117.19 Hz. ^{19}F NMR (referenced to CF_3CO_2H): δ 9.90, J_{PF} 78.13 Hz.

For $[Fe(CO)_4\{(CF_3)_2P{=}N{=}PPh_3\}]$ **1**: ^{31}P NMR: δ1 111.59, J_{PP} 14.73 Hz, J_{PF} 78.12 Hz; δ2 16.827, J_{PP} 14.65 Hz. ^{19}F NMR: δ 6.125, J_{PF} 78.12 Hz.

For $[Fe(CO)_3\{(CF_3)_2P{=}N{=}PPh_3\}_2]$ **2**: ^{31}P NMR: δ1 117.789, J_{PP} 17.09 Hz, J_{FP} 75.69 Hz; δ2 14.84, J_{PP} 17.09 Hz. ^{19}F NMR: δ 6.356, J_{PF} 75.69 Hz.

‡ *Crystal data* for $C_{20}H_{15}NF_6P_2$ L: orthorhombic, *Fdd*2; a = 18.989(4), b = 42.820(9), c = 10.355(2) Å, V = 8420(3) Å^3; Z = 16; D_c = 1.405 g cm^{-3}; $F(000)$ = 3616; μ(Mo-Kα) = 2.57 cm^{-1}; T = 25 °C, Nicolet R3m/V, Mo-Kα radiation (λ = 0.71069 Å). Of 8695 data ($3.0 \leqslant 2\vartheta \leqslant 45°$), 1476 were independent (R_{int} = 1.29%), and 1126 were observed $[F_o > 6\sigma(F_o)]$. 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 idealized. R_F = 3.48%, R_{wF} = 4.11%, GOF = 2.08. SHELXTL software used for all computations.

Crystal data for $C_{24}H_{15}NO_4F_6P_2Fe$ **1**: triclinic, $P\bar{1}$; a = 9.215(2), b = 10.758(4), c = 14.555(6) Å, α = 111.290(0), β = 91.920(0), γ = 97.750(10)°; V = 1326.9(8) Å^3; Z = 2; D_c = 1.535 g cm^{-3}; $F(000)$ = 616; μ(Mo-Kα) = 7.56 cm^{-1}; T = 25 °C, Nicolet R3m/V, Mo-Kα radiation (λ = 0.71069 Å). Of 3689 data ($3° \leqslant 2\vartheta \leqslant 55°$), 3434 were independent (R_{int} = 1.05%), and 2241 were observed $[F_o > 6\sigma(F_o)]$. 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 idealized. R_F = 5.36%, R_{wF} = 6.15%, GOF = 2.76. SHELXTL software used for all computations. An empirical (psi-scan) correction was performed. The ratio of transmission coefficients was 1.13.

Crystal data for $C_{43}H_{30}N_2O_3F_{12}P_4Fe$ **2**: monoclinic, *C*2/*c*; a = 15.5840(10), b = 17.418(2), c = 16.7730(10) Å, β = 95.470(0)°, V = 4532.3(7) Å^3; Z = 4; D_c = 1.510 g cm^{-3}; $F(000)$ = 2080 μ(Mo-Kα) = 5.58 cm^{-1}; T = 25 °C, Nicolet R3m/V, Mo-Kα radiation (λ = 0.71069 Å). Of 7836 data ($3.5 \leqslant 2\vartheta \leqslant 50°$), 3782 were independent (R_{int} = 0.00), and 2649 were 'observed' $[F_o > 4\sigma(F_o)]$. 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 idealized. R_F = 3.85%, R_{wF} = 4.87%, GOF = 1.09. SHELXTL software used for all computations. An empirical (psi-scan) correction was performed. The ratio of transmission coefficients was 1.22.

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.

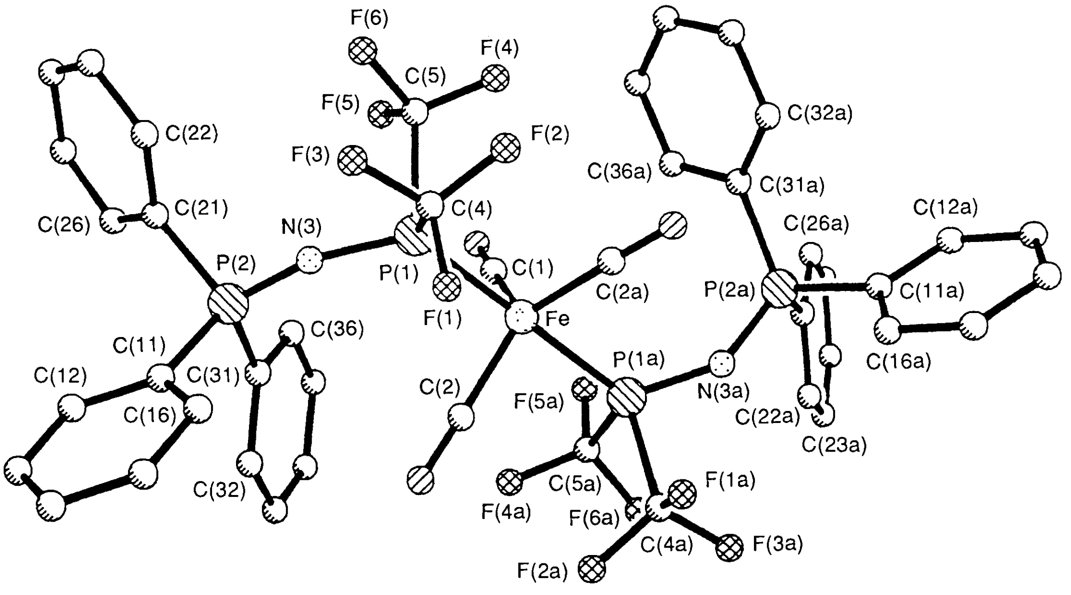

Fig. 3 Molecular structure of $[Fe(CO)_3\{(CF_3)_2P{=}N{=}PPh_3\}_2]$ **2** showing the atom labelling scheme

Table 1 Selected bond lengths (Å) and angles (°) in L, **1** and **2**

Bond lengths L		**1**		**2**	
P(1)-N(1)	1.612(5)	Fe-P(1)	2.184(2)	Fe-P(1)	2.167(1)
P(1)-C(1)	1.880(10)	Fe-C(2)	1.749(12)	Fe-C(2)	1.782(3)
P(1)-C(2)	1.871(11)	Fe-C(4)	1.771(10)		
P(2)-N(1)	1.576(5)	P(1)-N(3)	1.568(5)	P(1)-N(3)	1.576(3)
P(2)-C(11)	1.812(6)	P(2)-N(3)	1.560(6)	P(2)-N(3)	1.565(3)
P(2)-C(21)	1.799(6)	P(1)-C(5)	1.892(7)	P(1)-C(5)	1.903(4)
		P(2)-C(11)	1.786(5)	P(2)-C(11)	1.801(4)
Bond angles L		**1**		**2**	
P(1)-N(1)-P(2)	130.7(3)	P(1)-Fe-C(1)	93.8(3)	P(1)-Fe-C(1)	91.1(1)
N(1)-P(1)-C(1)	98.9(3)	P(1)-Fe-C(4)	176.4(5)	P(1)-Fe-P(1A)	177.8(1)
N(1)-P(1)-C(2)	100.5(3)	C(1)-Fe-C(2)	122.8(5)	P(1)-Fe-C(2)	87.0(1)
C(1)-P(1)-C(2)	95.5(5)	P(1)-Fe-C(3)	91.6(4)	P(1)-Fe-C(2A)	92.0(1)
N(1)-P(2)-C(11)	110.6(3)	P(1)-N(3)-P(2)	151.8(4)	P(1)-N(3)-P(2)	149.7(2)
		N(3)-P(1)-C(5)	102.4(3)	N(3)-P(1)-C(5)	103.4(2)

Fe–C (equatorial) bonds which are 0.03 Å longer than those in **1**.

Finally, it is of interest to note that **1** and **2** retain the same symmetry in going from solid state to solution. This is demonstrated by the solution IR spectra which consist of two and one carbonyl stretching respectively, consistent with a C_{3v} symmetry for **1** and a D_{3h} symmetry for **2**.

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