Studies of Phosphazenes. Part 34.[1] Group 6 Metal Carbonyl Complexes of Bis(pyrazolyl)cyclotriphosphazenes†

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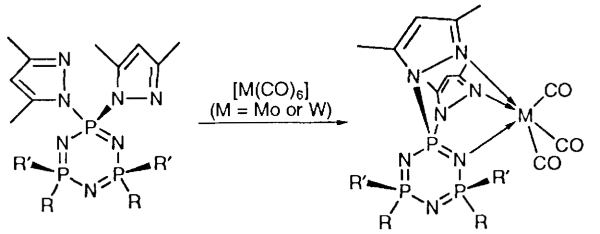
Reactions of the bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazenes *gem*-$N_3P_3Ph_4(C_3HN_2Me_2)_2$ (L^1) and $N_3P_3(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2$ (L^2) with $[M(CO)_6]$ (M = Mo or W) afford complexes of the type $[M(CO)_3L]$ (L = L^1 or L^2), which have been characterised by IR and NMR spectroscopic data. The structures of $[Mo(CO)_3L^1]$, $[W(CO)_3L^2]$ and the ligand L^2 have been determined by single-crystal X-ray diffraction. The phosphazenes act as novel tridentate NNN-donor ligands with two pyrazolyl nitrogen atoms and one phosphazene ring nitrogen atom bonded to the metal atom.

Continuing our interest in the transition-metal chemistry of cyclophosphazenes,[2,3] we report in this paper details of the synthesis and spectroscopic and structural studies of zerovalent Group 6 metal carbonyl complexes of geminally substituted bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazenes. These complexes provide rare examples in which a cyclotriphosphazene is co-ordinated to a metal *via* one of its ring nitrogen atoms.[4]

Results and Discussion

Synthesis of Complexes.—Reaction of the bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene $N_3P_3Ph_4(C_3HN_2Me_2)_2$ (L^1) with $[M(CO)_6]$ (M = Mo or W) in boiling acetonitrile gives the metal tricarbonyl complexes $[M(CO)_3L^1]$ (M = Mo **1** or W **2**) (see Scheme 1). The molybdenum complex **1** is sparingly soluble in most organic solvents. Therefore in an effort to improve the solubility of complexes of this type, a new bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene, *viz*, $N_3P_3(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2$ (L^2), has been synthesized from the reaction of $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ (whose structure has been established by X-ray crystallography)[5] with 3,5-dimethylpyrazole in chloroform in the presence of triethylamine. The reaction of L^2 with $[M(CO)_6]$ affords complexes $[M(CO)_3L^2]$ (M = Mo **3** or W **4**). The molybdenum complex **3** is much more soluble in organic solvents than **1**. The tungsten complexes **2** and **4** are more soluble in organic solvents and also more stable to atmospheric air compared to their molybdenum analogues **1** and **3**.

IR and NMR Spectroscopy.—The IR and NMR spectroscopic data for the ligands and the complexes are listed in Tables 1 and 2. The IR spectra of complexes **1**–**4** (Table 1) show strong absorptions in the carbonyl stretching region, 1910–1755 cm^{-1}, suggesting the presence of a $M(CO)_3$ moiety co-ordinated to three nitrogen atoms. The ν_{CO} bands for complexes **1**–**4** are at higher wavenumbers compared to those for the tris(3,5-dimethylpyrazol-1-yl)borate complexes, $[NEt_4][M(CO)_3\{HB(C_3HN_2Me_2)_3\}]$[7] ($\nu_{CO}$ at 1891, 1751 for M = Mo and 1881, 1744 cm^{-1} for M = W) and for tricarbonyl(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)molybdenum (ν_{CO} at 1886, 1743 cm^{-1})[8] indicating the less electron-donating character of the bis(pyrazolyl)phosphazenes. The ring P=N stretching frequencies of the ligands appear as two split bands in the region 1225–1180 cm^{-1}. These are further split into three absorptions in the spectra of the complexes and appear in the regions 1285–1235, 1210–1185 and 1175–1155 cm^{-1}. The degeneracy of the P=N vibrational modes is lifted and this observation provides support for the co-ordination of a ring nitrogen atom to the metal (see below).



L^1; R = R′ = Ph
L^2; R,R′ = N(Me)CH_2CH_2O

1; R = R′ = Ph, M = Mo
2; R = R′ = Ph, M = W
3; R,R′ = N(Me)CH_2CH_2O, M = Mo
4; R,R′ = N(Me)CH_2CH_2O, M = W

Scheme 1

The ^{31}P NMR spectra of the cyclotriphosphazenes L^1 and L^2 are of the A_2X type. The spectrum of L^2 shows a doublet and a triplet at δ 31.2 and 6.0 which are assigned to P(spiro) and P-$(C_3HN_2Me_2)_2$ respectively. The spiro phosphorus nuclei of L^2 are deshielded by 2.7 ppm and the coupling constant is increased by 5 Hz compared to the values for $N_3P_3(MeNCH_2CH_2O)_2Cl_2$.[5]

The ^{31}P NMR spectra of complexes **1**–**4** show an ABX pattern (see Table 1). The two PPh_2 phosphorus nuclei which are equivalent in L^1 become non-equivalent in complexes **1** and **2** and are also deshielded. Similarly, the two P(spiro) phosphorus nuclei of **3** or **4** are non-equivalent but are shielded or unaffected. These data are consistent with the co-ordination of a phosphazene ring nitrogen atom to the metal (for X-ray crystallographic confirmation of the structures, see below). The upfield PPh_2 resonances of **1** and **2** and the downfield P(spiro) resonances of **3** and **4** are assigned to the phosphorus atoms closer to the co-ordinating ring nitrogen atom on the basis of the lower $^2J_{PP}$ coupling to the $P(C_3HN_2Me_2)_2$ phosphorus nucleus. The chemical shift of the $P(C_3HN_2Me_2)_2$ phosphorus is influenced by several factors, *viz*. co-ordination of N(1), formation of a six-membered chelate ring involving both pyrazolyl groups and formation of two five-membered chelate rings involving each pyrazolyl ring and phosphazene ring nitrogen [N(1)]. The combined effect of all these factors is to cause either a slight shielding (for the molybdenum complexes **1** and **3**) or almost no change (for the tungsten complexes **2** and **4**).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Infrared and ^{31}P NMR spectral data for L^1 and L^2 and complexes **1**–**4**

			δ(P)			J/Hz		
Compound	ν_{CO}/cm^{-1}	$\nu_{PN}{}^a/cm^{-1}$	P(A)	P(B)	$P(X)^b$	J(AB)	J(AX)	J(BX)
L^{1c}	—	1224–1214	18.2		−5.2	—	20	—
1	1900, 1775, 1770	1235, 1185, 1175	23.9	19.8^d	−7.7	0	20	15.5
2	1896, 1767	1240, 1195, (1160)	24.3	20.4^d	−5.2	0	21	15
L^2	—	1225, 1180	31.2		6.0	—	68	—
3	1910, 1790, 1770	1265, 1210, (1160)	27.3	30.6^d	3.3^e	52.5	66	61
4	1900, 1780, 1755	1285, 1200, (1155)	26.1	30.1^d	6.5	55	64	60

[a] Values in parentheses refer to weak absorptions. [b] P(X) for $P(C_3HN_2Me_2)_2$ phosphorus. [c] Ref. 6. [d] Phosphorus near the co-ordination site. [e] The value (δ −3.3) given in ref. 2(*a*) is incorrect.

Table 2 Proton and ^{13}C NMR spectral data for L^2 and its complexes

	NMe	NCH_2	OCH_2	CH_3 $(C_3HN_2Me_2)$	CH $(C_3HN_2Me_2)$	C(quaternary)
(*i*) ^1H NMR $(\delta)^a$						
L^2	2.62 (12)	3.3	4.3	2.36, 2.21, 2.17, 2.08	5.88, 5.87	
3	2.67 (11), 2.62 (11)	4.0, 3.4	4.8, 4.3	2.49, 2.43	$5.92, 5.90^b$	
4	2.68 (12), 2.63 (12)	4.1, 3.4	4.9, 4.4	2.53, 2.50, 2.49, 2.42	$5.95, 5.91^c$	
(*ii*) ^{13}C NMR $(\delta)^d$						
L^2	31.1	49.5 (6.8) 49.4 (6.6)	64.1	$13.8, 13.2, 12.3^e$	109.9, 109.5	152.8, 152.1, 146.4, 146.1
3^f	30.9, 30.2	49.5 (6.8) 49.2 (7.6)	65.8 64.9	$14.7, 12.5, 12.4^e$	110.3 (8) 110.1 (8)	157.6, 157.5, 145.7, 145.2

[a] $^3J_{PH}$ Values in parentheses; NCH_2 and OCH_2 protons appear as multiplets. [b] Both doublets (J = 3 Hz). [c] Both doublets (J = 4.5 Hz). [d] P–C coupling constants are given in parentheses for doublets. [e] Intensity ratio 2:1:1. [f] δ_{CO} at 230.4, 230.0 and 229.3.

The ^1H NMR spectrum of L^2 shows that the two pyrazolyl groups are non-equivalent due to the spatial differences that arise as a result of the *cis* orientation of the spiro $N(Me)CH_2CH_2O$ groups with OCH_2 groups on one side and $N(Me)CH_2$ groups on the other side of the plane of the phosphazene ring. After co-ordination to the metal (complexes **3** and **4**), the OCH_2, NCH_2 and NMe proton resonances are further split as a consequence of the non-equivalence of the spiro rings (see Table 2). The chemical shifts of the NMe protons of the spiro rings are very close but the OCH_2 and NCH_2 protons of the spiro ring near the co-ordination site are deshielded by 0.5 and 0.7–0.8 ppm respectively. Presumably as a result of complexation, there is a drift of electron density from the spiro ring closer to the co-ordination site. The spiro ring far from the co-ordination site is almost unaffected. The pyrazolyl methyl protons are also deshielded upon complexation.

The ^{13}C NMR spectrum of L^2 (see Table 2) shows that the two pyrazolyl groups are non-equivalent as shown by the ^1H NMR spectrum. The spectrum of complex **3** displays two resonances for the OCH_2, NCH_2 and NMe carbon atoms. The ^{13}C chemical shifts for the complex show a difference of −0.9 to +5.4 ppm when compared to those of the ligand L^2. The maximum positive shifts (+4.8 and +5.4 ppm) are seen for two of the quaternary pyrazolyl carbon atoms which are closer to the metal. The pyrazolyl tertiary carbon atoms are deshielded by 0.35 and 0.60 ppm and appear as doublets. The pyrazolyl methyl carbon atoms show only three resonances with an intensity ratio 2:1:1 similar to the ligand. Three resonances are observed for the carbonyl groups attached to the metal; the two carbonyls *trans* to the pyrazolyl nitrogen atoms are in distinctly different environments.

X-Ray Crystallography.—The crystal structures of L^2 and complexes **1** and **4** have been determined by X-ray crystallography. A perspective view of each of the structures together with their atom numbering scheme are shown in Figs. 1–3. Table 3 gives selected structural parameters for the three compounds. In the lattice the molecules are stabilized by C–H • • • O/N hydrogen bonds whose presence is being realized as an important factor in determining the packing of molecules in the crystal lattice.[9]

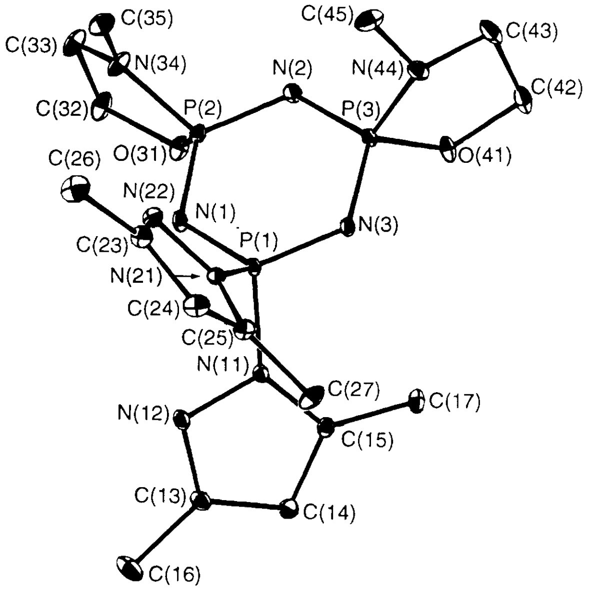

Fig. 1 A perspective view of $N_3P_3(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2$ (L^2)

Crystal Structure of L^2.—The structural parameters for L^2 (Table 3) show that there is no apparent change in the phosphazene ring upon the introduction of pyrazolyl groups. The phosphazene ring P–N bonds are almost similar and lie in the range 1.569(3)–1.592(3) Å. In the precursor compound $N_3P_3(MeNCH_2CH_2O)_2Cl_2$,[5] the P–N bonds are not similar; three bonds are close to 1.565 Å and the other three are around 1.600 Å. Such clear differences are not observed for L^2. The pyrazolyl rings lie in two different planes with a dihedral angle of 76.2° thereby reducing the steric effect. The P_3N_3 ring in L^2

is more planar than that in $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ as reflected by the sum of modulus of deviation of the ring atoms from the mean plane (0.26 Å for $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ and 0.15 Å for L^2). The oxazaphospholidine (spiro) rings are almost planar in $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ with a maximum deviation of 0.1 Å. However, in L^2, one of these spiro rings [that on P(2)] is distinctly non-planar; C(33) deviates from the mean plane formed by the other four atoms [P(2), O(31), C(32) and N(34)] by 0.46 Å. Furthermore, the C–N bond length within this spiro ring is increased to 1.447 Å from 1.405 Å observed for $N_3P_3(MeNCH_2CH_2O)_2Cl_2$. For the other spiro ring, the maximum deviation from planarity (0.15 Å) is observed for C(42).

Crystal and Molecular Structures of $[Mo(CO)_3L^1]$ **1** *and* $[W(CO)_3L^2]$ **4**.—The crystal structures of complexes **1** and **4** show that the phosphazene ring has been severely affected due to the co-ordination of a ring nitrogen atom to the metal. The P–N distances within the phosphazene ring in both the complexes are dissimilar; the P(2)–N(1) bond is the longest and P(1)–N(3) the shortest among them. The phosphazene ring is non-planar; in complex **1**, N(2) and P(3) deviate (by 0.19 and 0.15 Å respectively) from the mean plane formed by the other four skeletal atoms whereas in **4**, N(1) deviates by 0.20 Å from the mean plane formed by the other five atoms. The metal is 0.04 and 0.07 Å from the respective mean planes mentioned above and in **4**, it lies on the same side of the NMe groups. The geometry around N(1) in complex **1** is almost planar (sum of the angles 360°) although two of the angles deviate considerably from 120°. For complex **4**, the geometry around N(1) is slightly non-planar (sum of the angles 357°); the PN_2C_2 rings are non-planar with deviations of 0.39 Å for C(33) and 0.10 Å for C(42) from the mean plane formed by the other four atoms.

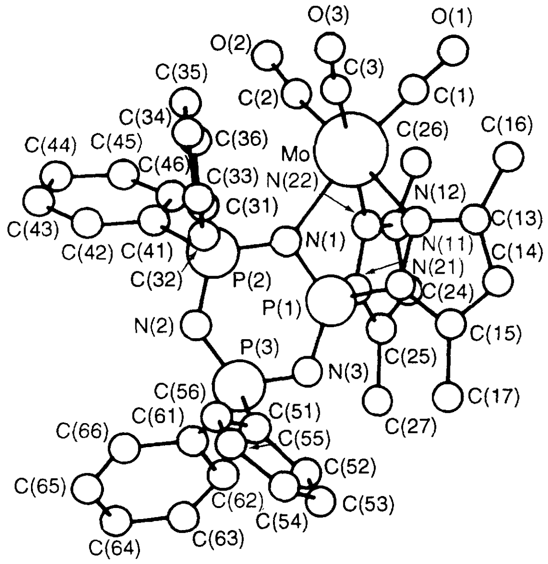

Fig. 2 A perspective view of $[Mo(CO)_3\{N_3P_3Ph_4(C_3HN_2Me_2)_2\}]$ **1**

The geometry around the metal is a distorted-trigonal antiprism with longer M–N bonds on one face and shorter M–C bonds on the opposite face. The six-membered metallacycle [P(1)–N(11)–N(12)–Mo(or W)–N(22)–N(21)] adopts a boat form and the heads of the boat [P(1) and metal] are bridged by the phosphazene ring nitrogen atom [N(1)]. The phosphazene ring nitrogen–metal bond is appreciably longer in **1** (by 0.08 Å) than the pyrazolyl nitrogen–metal bonds whereas for complex **4** this difference is only *ca.* 0.05 Å. The incorporation of amino substituents on the phosphorus atoms adjacent to the $P(C_3HN_2Me_2)_2$ phosphorus in ligand L^2 enhances the donor characteristics of the phosphazene ring nitrogen atoms, so that in complex **4** the ring nitrogen–metal bond length [W–N(1)] is nearly equal to that of the pyrazolyl nitrogen–metal bonds.

A comparison of the structure of complex **1** with the molybdenum tricarbonyl complex of tris(3,5-dimethylpyrazol-1-yl)borate shows that the bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene L^1 is a weaker σ donor as indicated by the IR spectroscopic data. The mean Mo–N(pyrazolyl) distance in $[NEt_4][Mo(CO)_3\{HB(C_3HN_2Me_2)_3\}]$[7] is 2.265 Å and the mean Mo–C distance is 1.942 Å, whereas in **1**, the Mo–N distances [2.299(2), 2.312(3) Å] are longer and the M–C bonds *trans* to the pyrazolyl nitrogen [1.933(3), 1.939(4) Å] do not differ significantly. However, the M–N bonds are shorter and the M–C bonds longer in **1** compared to those for tricarbonyl(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)molybdenum (M–N 2.335, 2.373 and 2.395 Å; M–C 1.897–1.913 Å) in which all the nitrogen atoms are in the sp^3 state.[8]

The P–N bonds in the phosphazene ring are quite dissimilar in complex **4** compared to L^2. In the former, the P(2)–N(1) bond is lengthened by 0.044 Å and N(3)–P(1) bond is shortened by 0.024 Å. The P–N (*exo*) bond in the spiro ring closer to the co-ordination site is shortened by 0.045 Å. The nearly planar phosphazene ring of L^2 becomes non-planar in **4** as a result of complexation and the co-ordinating nitrogen atom [N(1)] deviates from the plane of the other skeletal atoms. For the spiro rings of complex **4** the deviations from planarity are slightly reduced compared to L^2. The dihedral angle between the

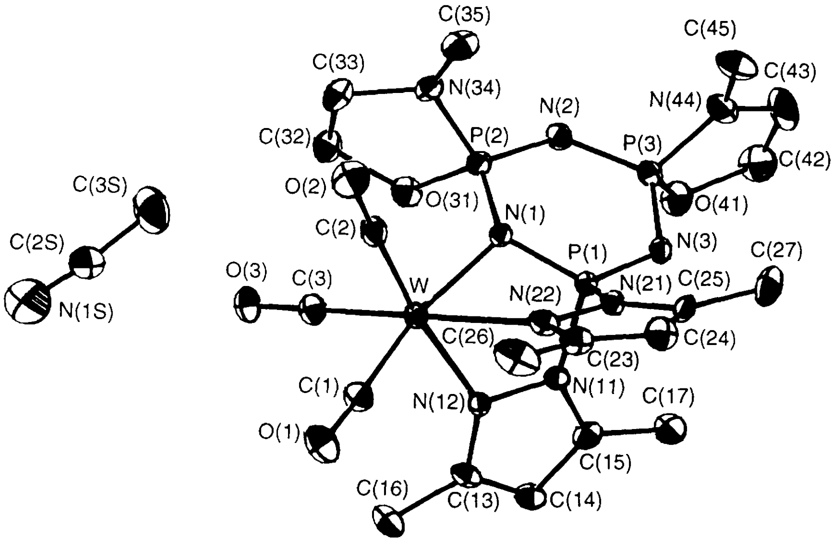

Fig. 3 A perspective view of $[W(CO)_3\{N_3P_3(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2\}]\cdot MeCN$ **4**

Table 3 Selected structural data for L^2 and complexes **1** and **4**; distances in Å, angles in °

	1	**4**	L^2
(*i*) Phosphazene ring bond lengths			
P(1)–N(1)	1.594(2)	1.579(7)	1.575(3)
N(1)–P(2)	1.636(2)	1.628(7)	1.584(3)
P(2)–N(2)	1.598(3)	1.569(7)	1.589(3)
N(2)–P(3)	1.587(3)	1.586(7)	1.592(3)
P(3)–N(3)	1.627(2)	1.593(8)	1.589(3)
N(3)–P(1)	1.557(2)	1.545(7)	1.569(3)
(*ii*) Bond lengths exocyclic to the P_3N_3 ring			
P(1)–N(11)	1.701(2)	1.696(7)	1.688(3)
P(1)–N(21)	1.709(3)	1.702(7)	1.699(3)
P(2)–O(31)	—	1.589(7)	1.583(3)
P(2)–N(34)	—	1.604(8)	1.649(4)
P(3)–O(41)	—	1.602(7)	1.598(3)
P(3)–N(44)	—	1.613(9)	1.630(4)
P(2)–C(31)	1.797(4)	—	—
P(2)–C(41)	1.799(3)	—	—
P(3)–C(51)	1.805(2)	—	—
P(3)–C(61)	1.799(3)	—	—
(*iii*) Bond angles within the P_3N_3 ring			
N(1)–P(1)–N(3)	122.3(1)	121.6(4)	119.4(2)
N(1)–P(2)–N(2)	114.4(2)	111.5(4)	116.0(2)
N(2)–P(3)–N(3)	115.9(2)	113.6(4)	115.4(2)
P(1)–N(1)–P(2)	120.2(2)	120.4(4)	121.8(2)
P(2)–N(2)–P(3)	126.4(2)	130.0(5)	124.6(2)
P(1)–N(3)–P(3)	120.1(2)	121.0(4)	122.3(2)
(*iv*) Bond angles exocyclic to the P_3N_3 ring			
N(11)–P(1)–N(21)	99.9(1)	102.0(3)	100.6(1)
O(31)–P(2)–N(34)	—	96.5(4)	95.8(2)
O(41)–P(3)–N(44)	—	96.7(4)	94.9(2)
C(31)–P(2)–C(41)	106.0(2)	—	—
C(51)–P(3)–C(61)	107.4(2)	—	—
(*v*) Bond lengths involving the metal			
M–N(1)	2.394(2)	2.310(7)	—
M–N(12)	2.299(2)	2.250(7)	—
M–N(22)	2.312(3)	2.274(7)	—
M–C(1)	1.911(3)	1.935(10)	—
M–C(2)	1.933(3)	1.951(10)	—
M–C(3)	1.939(4)	1.934(11)	—

pyrazole ring planes (76.2°) in L^2 is reduced slightly (74.0°) in complex **4**.

The structures of compounds **1** and **4** can be compared with that of $[CuCl_2\{N_3P_3(C_3HN_2Me_2)_6\}]$[4c] in which co-ordination to copper occurs *via* the nitrogen atoms of the two pyrazolyl groups on different phosphorus atoms. In all these complexes a ring nitrogen is also involved in co-ordination and the P_3N_3 ring is non-planar. A pronounced difference in the P–N ring bond lengths is observed in **1** and **4** in contrast to the copper complex where no such clear-cut differences in skeletal P–N bond lengths are observed owing to the weaker co-ordination of the ring nitrogen. A similar trend has been noted by us in the palladium chloride complex $[PdCl_2\{cis\text{-}N_3P_3(OPh)_4(C_3HN_2Me_2)_2\}]$ where there is only a weak interaction of the phosphazene ring nitrogen atom with the metal.[2b]

The structural data for L^2 and complexes **1** and **4** are consistent with the bonding model proposed by Craig and Paddock.[10] When the ring nitrogen lone-pair is involved in coordination to the metal, its interaction with phosphorus orbitals (termed as π' bonding) becomes less dominant. As a result, the P–N bonds around the donor nitrogen become longer than the other ring P–N bonds. When an amino group is attached to phosphorus (as in L^2 and complex **4**), enhanced π' bonding causes a decrease in the exocyclic P–N bond lengths.

Conclusion

Geminally substituted bis(pyrazolyl)phosphazenes act as novel tridentate NNN donors toward Group 6 metal carbonyls to form metal tricarbonyl complexes. The study brings out an attractive feature of cyclophosphazenes as ligands; the donor characteristics of the ring nitrogen and hence the strength of the ring nitrogen–metal bond can be altered by varying the substituents on adjacent or even remote phosphorus atoms. Even the rigid six-membered cyclotriphosphazenes, if suitably functionalized, can bind to transition metals through their ring nitrogen atoms by undergoing substantial distortion from planarity of the P_3N_3 ring.

Experimental

3,5-Dimethylpyrazole was prepared by the literature method.[11] The cyclotriphosphazene $N_3P_3Ph_4(C_3HN_2Me_2)_2$ (L^1) was prepared according to the procedure of Gallicano and Paddock[6] with a slight modification; boiling toluene was used as the reaction medium instead of boiling xylene. The compound $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ was prepared as reported earlier.[5] Solvents were distilled over sodium metal or P_2O_5 (for halogenated solvents and acetonitrile). Reactions with metal carbonyls were carried out under a dry nitrogen atmosphere and the products were preserved in sealed ampoules under vacuum.

The IR spectra were recorded on a Perkin Elmer model 781 spectrometer. Proton NMR spectra were recorded on a Bruker WH270 or Bruker ACF200 spectrometer in $CDCl_3$ solution with tetramethylsilane ($SiMe_4$) as internal standard; $^{31}P\text{-}\{H\}$ NMR spectra were recorded on a Varian FT-80A (32.2 MHz) or Bruker ACF200 (81.1 MHz) spectrometer in CH_2Cl_2 solution (with D_2O capillary for lock) with 85% H_3PO_4 as external standard. The ^{13}C NMR spectra were recorded on a Bruker WH270 (67.9 MHz) spectrometer in $CDCl_3$ solution with $SiMe_4$ as the internal standard.

Synthesis of $N_3P_3(MeNCH_2CH_2O)_2(C_3HN_2Me_2)_2$ (L^2).—A solution of $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ (10.7 g, 30 mmol), 3,5-dimethylpyrazole (5.8 g, 61 mmol) and triethylamine (10 cm^3) in chloroform (100 cm^3) was heated under reflux for 3 d. The solution was washed with water (5 × 100 cm^3) and dried with anhydrous sodium sulfate. Solvent was removed from the solution and the residue recrystallised from light petroleum (b.p. 60–80 °C)–dichloromethane (1 : 1) to give L^2. Yield 4.2 g (30%), m.p. 240° C (Found: C, 40.9; H, 6.0; N, 26.8. Calc. for $C_{16}H_{28}N_9O_2P_3$: C, 40.8; H, 6.0; N, 26.7%). Single crystals suitable for X-ray studies were obtained by slow evaporation of a solution of L^2 in light petroleum–dichloromethane (1 : 1).

Synthesis of $[Mo(CO)_3L^1]$ **1**.—A mixture of L^1 (0.5 g, 0.79 mmol) and $[Mo(CO)_6]$ (0.2 g, 0.76 mmol) in acetonitrile (40 cm^3) was heated under reflux for 7 h. The product, precipitated as yellow crystals, was separated by filtration, washed with hot acetonitrile and dried under vacuum. Yield 500 mg (76%); decomposes above 200 °C. The complex was sparingly soluble in dichloromethane or acetonitrile (Found: C, 55.0; H, 4.2; N, 12.1. Calc. for $C_{37}H_{34}MoN_7O_3P_3$: C, 54.6; H, 4.2; N, 12.0%). Single crystals suitable for X-ray studies were obtained by repeating the reaction with half of the quantity of the reactants in the same volume of the solvent and cooling the resultant yellow solution to 0° C.

Synthesis of $[W(CO)_3L^1]$ **2**.—A mixture of L^1 (0.2 g, 0.32 mmol) and $[W(CO)_6]$ (0.1 g, 0.28 mmol) in acetonitrile (30 cm^3) was heated under reflux for 20 h. Solvent from the yellow solution was removed under vacuum and the residue extracted with light petroleum–dichloromethane (1 : 1) (40 cm^3). Addition of light petroleum (100 cm^3) resulted in the precipitation of a yellow solid which was filtered off and dried under vacuum. Yield 100 mg (39%); decomposes above 180 °C [Found: C, 44.7;

Table 4 Crystal data and final refinement parameters

Compound	1[a]	4	L^2
Molecular formula	$C_{37}H_{34}MoN_7O_3P_3$	$C_{21}H_{31}N_{10}O_5P_3W$	$C_{16}H_{28}N_9O_2P_3$
M	813.6	782.3	471.4
Crystal size/mm	0.20 × 0.26 × 0.36	0.10 × 0.22 × 0.36	—
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	$P2_1/a$
a/Å	10.764(4)	15.717(4)	8.801(2)
b/Å	11.591(2)	17.596(1)	16.158(5)
c/Å	15.113(2)	21.491(3)	16.078(3)
β/°	89.52(4)	—	95.38(2)
U/Å^3	1810	5944	2276
Z	2	8	4
D_c/g cm^{-3}	1.493	1.748	1.376
F(000)	832	3088	992
μ/cm^{-1}	4.92	42.75	2.45
θ range/°	1–30	1–25	1–25
Unique reflections	10 521	6466	4948
Observed reflections	8060	3750	3588
Sigma cut-off (on *F*)	6.0	6.0	4.0
Residual density/e Å^{-3}	0.51	2.07	0.48
Final *R*[b]	0.039	0.047	0.052
Final *R'*[c]	0.047	0.053	0.067
k, *g*[c]	1, 0.002 070	1, 0.001 803	1, 0.003 241

[a] α = 100.98(2), γ = 78.26(4)°. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $w = k/[\sigma^2(F_o) + gF_o^2]$.

Table 5 Fractional atomic coordinates (× 10^4) for complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	1809.8(3)	1847.8(3)	3429.5(3)	C(27)	−3165(4)	0777(3)	3409(3)
C(1)	2910(3)	1186(3)	4274(2)	C(31)	0966(2)	4353(3)	1720(2)
O(1)	3623(3)	0783(3)	4781(2)	C(32)	0384(3)	5562(3)	1895(2)
C(2)	3010(3)	0714(3)	2562(2)	C(33)	1114(4)	6433(3)	1963(3)
O(2)	3805(3)	0032(3)	2095(2)	C(34)	2402(4)	6105(4)	1844(3)
C(3)	3034(3)	2868(3)	3442(2)	C(35)	2973(4)	4921(5)	1679(4)
O(3)	3864(3)	3374(3)	3465(2)	C(36)	2278(3)	4043(3)	1631(3)
P(1)	−1138(1)	2633(1)	3112.5(4)	C(41)	0715(3)	2054(3)	0714(2)
N(1)	0120(2)	2672(2)	2566(1)	C(42)	1168(4)	0890(3)	0802(2)
P(2)	0021(1)	3229(1)	1646.2(5)	C(43)	1682(5)	0015(4)	0057(3)
N(2)	−1387(2)	3844(2)	1442(2)	C(44)	1719(4)	0283(5)	−0761(3)
P(3)	−2662(1)	3787(1)	1951.5(5)	C(45)	1263(5)	1463(5)	−0864(3)
N(3)	−2491(2)	3104(2)	2802(1)	C(46)	0761(4)	2340(4)	−0142(2)
N(11)	−0947(2)	3312(2)	4190(1)	C(51)	−3519(2)	5311(2)	2350(2)
N(12)	0302(2)	3098(2)	4455(1)	C(52)	−4463(3)	5580(3)	3030(2)
C(13)	0243(3)	3603(2)	5325(2)	C(53)	−5045(4)	6773(3)	3372(3)
C(14)	−1023(3)	4114(3)	5632(2)	C(54)	−4699(4)	7691(3)	3041(3)
C(15)	−1770(3)	3896(2)	4912(2)	C(55)	−3811(4)	7426(3)	2332(3)
C(16)	1407(4)	3593(3)	5844(2)	C(56)	−3210(3)	6247(3)	1989(2)
C(17)	−3181(3)	4233(4)	4860(2)	C(61)	−3641(3)	3049(3)	1171(2)
N(21)	−0948(2)	1177(2)	3246(2)	C(62)	−4372(3)	2298(3)	1417(2)
N(22)	0302(2)	0680(2)	3404(2)	C(63)	−5091(3)	1726(3)	0776(3)
C(23)	0249(4)	−0338(3)	3667(2)	C(64)	−5085(4)	1905(5)	−0077(3)
C(24)	−1005(4)	−0487(3)	3705(3)	C(65)	−4405(5)	2682(5)	−0324(3)
C(25)	−1765(3)	0488(3)	3456(2)	C(66)	−3671(4)	3269(4)	0287(2)
C(26)	1444(4)	−1134(3)	3883(3)				

H, 3.6; N, 9.9. Calc. for $C_{38}H_{36}Cl_2N_7O_3P_3W$ (**2**·CH_2Cl_2): C, 46.2; H, 3.6; N, 9.9%].

Synthesis of $[Mo(CO)_3L^2]$ **3**.—A mixture of L^2 (0.3 g, 0.64 mmol) and $[Mo(CO)_6]$ (0.2 g, 0.76 mmol) in acetonitrile (50 cm^3) was heated under reflux for 6 h. The reaction mixture was worked-up as described above for **2** to obtain the product. Yield 220 mg (53%); decomposes above 210 °C (Found: C, 35.3; H, 4.4; N, 19.3. Calc. for $C_{19}H_{28}MoN_9O_2P_3$: C, 35.4; H, 4.3; N, 19.4%).

Synthesis of $[W(CO)_3L^2]$·MeCN **4**.—A mixture of L^2 (0.3 g, 0.64 mmol) and $[W(CO)_6]$ (0.3 g, 0.85 mmol) in acetonitrile (40 cm^3) was heated under reflux for 17 h. The reaction mixture was worked-up as described above for **2** to obtain the product. Yield 200 mg (41%); decomposes above 170 °C (Found: C, 32.3; H, 4.0; N, 17.9. Calc. for $C_{21}H_{31}N_{10}O_5P_3W$: C, 32.3; H, 4.3; N, 18.0%). Single crystals suitable for X-ray studies were obtained from acetonitrile solution.

X-Ray Crystallography.—Data collection. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The cell parameters were refined using 25 well centred reflections in the θ ranges 7.9–13.6, 7.6–16.9 and 12.1–19.6° for **1**, L^2 and **4** respectively. The data were collected using the ω–2θ scan mode (θ range 1–30° for **1** and 1–25° for L^2 and **4**). The crystals of **1** and **4** were coated with paraffin oil to protect them from atmospheric

Table 6 Fractional atomic coordinates (× 10^4) for L^2

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
P(1)	0329(1)	0592.4(4)	2931.5(5)
N(1)	−1468(3)	0628(2)	2847(2)
P(2)	−2476(1)	−0122.2(4)	2477(1)
N(2)	−1568(3)	−0923(2)	2233(2)
P(3)	0234(1)	−1032.7(4)	2391(1)
N(3)	1150(3)	−0233(2)	2723(2)
N(11)	0957(3)	0908(2)	3905(2)
N(12)	2537(3)	1008(2)	4035(2)
C(13)	2794(4)	1246(2)	4819(2)
C(14)	1441(4)	1302(2)	5207(2)
C(15)	0274(4)	1083(2)	4625(2)
C(16)	4396(5)	1418(4)	5174(3)
C(17)	−1388(4)	1044(3)	4722(3)
N(21)	1022(3)	1362(1)	2354(2)
N(22)	1623(3)	1155(2)	1616(2)
C(23)	1972(4)	1871(2)	1292(2)
C(24)	1588(5)	2538(2)	1790(2)
C(25)	0981(4)	2204(2)	2461(2)
C(26)	2720(7)	1903(3)	0496(3)
C(27)	0365(6)	2639(2)	3169(3)
O(31)	−3696(3)	−0372(2)	3095(2)
C(32)	−5256(4)	−0226(3)	2749(3)
C(33)	−5209(5)	−0154(3)	1826(4)
N(34)	−3727(4)	0194(2)	1715(2)
C(35)	−3269(7)	0304(3)	0890(3)
O(41)	0593(3)	−1799(1)	3007(2)
C(42)	1535(5)	−2417(2)	2676(3)
C(43)	1546(6)	−2258(3)	1754(3)
N(44)	0999(4)	−1452(2)	1608(2)
C(45)	1024(6)	−1047(3)	0813(3)

Table 7 Fractional atomic coordinates (× 10^4) for complex **4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	2359.1(3)	0610.1(3)	0247.1(3)
C(1)	1781(6)	−0033(6)	−0349(4)
O(1)	1440(5)	−0406(5)	−0713(3)
C(2)	1391(6)	1303(6)	0216(4)
O(2)	0823(5)	1728(5)	0213(4)
C(3)	2841(6)	1103(6)	−0476(5)
O(3)	3100(4)	1410(4)	−0924(3)
P(1)	3387(1)	0547(1)	1487(1)
N(1)	3118(4)	1205(4)	1028(3)
P(2)	3599(1)	2024(1)	1051(1)
N(2)	4134(5)	2117(4)	1663(3)
P(3)	4331(2)	1520(1)	2197(1)
N(3)	3913(5)	0708(4)	2080(3)
N(11)	3872(4)	−0090(4)	1013(3)
N(12)	3488(4)	−0149(4)	0417(3)
C(13)	3981(6)	−0631(5)	0118(4)
C(14)	4638(6)	−0903(5)	0489(4)
C(15)	4563(5)	−0562(5)	1050(4)
C(16)	3812(7)	−0821(6)	−0537(4)
C(17)	5083(6)	−0673(6)	1630(5)
N(21)	2458(4)	0096(4)	1659(3)
N(22)	1928(4)	0038(4)	1142(3)
C(23)	1272(6)	−0364(5)	1346(5)
C(24)	1356(7)	−0561(6)	1959(5)
C(25)	2123(7)	−0263(5)	2159(4)
C(26)	0506(7)	−0475(7)	0913(6)
C(27)	2535(8)	−0257(8)	2801(6)
O(31)	4169(4)	2118(4)	0445(3)
C(32)	3871(7)	2726(6)	0028(5)
C(33)	3005(6)	2979(6)	0267(5)
N(34)	2991(5)	2739(4)	0923(3)
C(35)	2219(6)	2878(6)	1287(5)
O(41)	5337(4)	1414(4)	2281(3)
C(42)	5569(8)	1513(8)	2942(6)
C(43)	4872(9)	1778(8)	3295(5)
N(44)	4143(6)	1830(5)	2890(4)
C(45)	3328(10)	2019(8)	3137(6)
N(1S)	1114(12)	1764(9)	−2367(7)
C(2S)	1123(9)	1917(7)	−1857(7)
C(3S)	1125(9)	2167(10)	−1267(6)

air. Three standard reflections were measured after every 1 h of irradiation to check the stability of the crystal. No significant decay was observed for all the compounds. Three standard reflections were measured for every 400 reflections to check the deviations in the orientation of the crystal. The data were corrected for Lorentz and polarization effects. An absorption correction was applied to complex **4** using ψ-scan data.

Structure solution and refinement. The structures of complexes **1** and **4** were solved by the Patterson heavy-atom method and by subsequent Fourier difference syntheses using SHELX 76.[12] The structure of L^2 was solved by direct methods using SHELXS 86.[13] Many hydrogen atoms were located from Fourier difference syntheses and refined once isotropically and the remaining hydrogen atoms were fixed in calculated positions. The non-hydrogen atoms were refined anisotropically. For compound **4**, there was a residual electron density of 2.07 e Å^{-3} at 0.87 Å from the metal.

The crystal data and some details pertinent to structure solution and refinement are given in Table 4. The fractional atomic coordinates are listed in Tables 5–7.

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

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