Organometallic Derivatives of Diphosphazanes. 2.[1] Seven-Coordinated Group 6 Metal Tricarbonyl Complexes of Diphosphazane Ligands. X-ray Crystal Structure of $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$

Maravanji S. Balakrishna, Setharampattu S. Krishnamurthy,* and Hattikudur Manohar

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received July 10, 1990

Summary: The reactions of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) with the diphosphazane ligands $RN\{P(OPh)_2\}_2$ (R = Me, Ph) in CH_2Cl_2 at room temperature afford new seven-coordinated complexes of the type $[MI_2(CO)_3\{P(OPh)_2\}_2NR]$. The molybdenum complexes are sensitive to air oxidation even in the solid state, whereas the tungsten complexes are more stable in the solid state and in solution. The structure of the tungsten complex $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ has been determined by single-crystal X-ray diffraction. It crystallizes in the orthorhombic system with the space group $Pna2_1$, a = 19.372 (2) Å, b = 11.511 (1) Å, c = 15.581 (1) Å, and Z = 4. Full-matrix least-squares refinement with 3548 reflections ($I > 2.5\sigma(I)$) led to final R and R_w values of 0.036 and 0.034, respectively. The complex adopts a slightly distorted pentagonal-bypyramidal geometry rarely observed for such a type of complexes; two phosphorus atoms of the diphosphazane ligand, two iodine atoms, and a carbonyl group occupy the equatorial plane, and the other two carbonyl groups, the apical positions.

There is a growing interest in the synthesis, structure, and reactivity of seven-coordinate derivatives of group 6 metal carbonyls containing monodentate or bidentate ligands. Seven-coordinate complexes of the type $[MI_2(CO)_3L_2]$ (M = Mo, W; L_2 = two tertiary phosphines, diphosphine; X = Br, I) can function as useful catalysts for the ring-opening polymerization of norbornene or norbornadiene.[2] As part of our study[1] of the organometallic chemistry of diphosphazane ligands,[3] we report in this paper the first examples of seven-coordinated diphosphazane complexes of the type $[MI_2(CO)_3\{P(OPh)_2\}_2NR]$ (M = Mo, W; R = Me, Ph). We also report the determination of the structure of the tungsten complex $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ by single-crystal X-ray diffraction, which shows the rare pentagonal-bipyramidal geometry around the metal center. A preliminary account of this work has been reported.[4j]

Experimental Section

General Procedure. All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk-line techniques.[5] Solvents were distilled under nitrogen and degassed prior to use. Metal hexacarbonyls $M(CO)_6$ (M = Mo, W) were purchased from Strem Chemicals. The ligands $RN\{P(OPh)_2\}_2$ (R = Me, Ph) were prepared as described previously.[1] The complexes $[MI_2(CO)_3(NCMe)_2]$ were prepared according to literature methods.[6]

NMR spectra were recorded on a Varian T-60 spectrometer (^1H NMR; standard Me_4Si) and a Varian FT-80A spectrometer (^{31}P NMR; 85% H_3PO_4 external reference). All NMR chemical shifts were expressed on the δ scale with upfield shifts being negative. Infrared spectra were obtained from a Perkin-Elmer Model 457 spectrometer. Elemental analyses were obtained from City University, London, U.K., through the kind offices of Dr. S. A. Matlin.

Synthesis of $[MI_2(CO)_3\{P(OPh)_2\}_2NR]$ (1, M = Mo, R = Me; 2, M = Mo, R = Ph; 3, M = W, R = Me; 4, M = W, R = Ph). To a stirred solution of $[MI_2(CO)_3(NCMe)_2]$ (prepared in situ at 0 °C; 1.5 mmol) in 25 mL of CH_2Cl_2 was added a solution of $RN\{P(OPh)_2\}_2$ (1.55 mmol) in 15 mL of CH_2Cl_2 dropwise with vigorous stirring. Stirring was continued for 30 min, and the solution was filtered through Celite. Concentration of the resulting solution under reduced pressure followed by the addition of *n*-hexane gave crystalline products 1–4 in 65–80% yield.

X-ray Crystallography. Single crystals were grown from CH_2Cl_2/petroleum ether (bp 60–80 °C) (1:2) solutions stored under dinitrogen. The data were collected with a Enraf-Nonius CAD4 automatic four-circle diffractometer. The intensities were corrected for decay, Lorentz, polarization, and absorption effects.[7] The structure was solved by a combination of Patterson function and Fourier difference maps and refined by a full-matrix least-squares treatment.[8] All the non-hydrogen atoms except the phenyl carbon atoms were refined anisotropically. All the hydrogen atoms were geometrically fixed. A σ-weighting scheme was applied, and the quantity minimised during the refinement was $w[|F_o| - |F_c|]^2$, where w is the weighting factor.

The crystal data, experimental conditions for data collection, and details of structure and refinement are given in Table III. Atomic coordinates are listed in Table IV; selected bond lengths and angles are given in Table V.

Results and Discussion

Synthesis and Spectroscopic Data. The reaction of an equimolar quantity of $RN\{P(OPh)_2\}_2$ with $[MI_2(CO)_3(NCMe)_2]$[6] (generated in situ) in CH_2Cl_2 solution gives the new seven-coordinated complexes $[MI_2(CO_3\{P(OPh)_2\}_2NR]$ (M = Mo, W; R = Me, Ph). Under mild conditions, two acetonitrile ligands are readily replaced by the diphosphazane ligands (see Scheme I). The complexes 1–4 are the first examples of seven-coordinated derivatives of diphosphazane ligands. The molybdenum complexes are sensitive to air oxidation even in the solid state and decompose to give insoluble deep violet residues that may contain molybdenum in higher oxidation states. The

---

[1] Part 1: Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U.; Hosamane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203.

[2] (a) Drew, M. G. B.; Rix, C. J. *J. Organomet. Chem.* **1975**, *102*, 467. (b) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67 and references cited therein. (c) Baker, P. K.; Fraser, S. G. *Inorg. Chim. Acta* **1986**, *116*, L1. (d) *Ibid.* **1986**, *116*, L3. (e) *Ibid.* **1987**, *130*, 61. (f) Baker, P. K.; Fraser, F. G.; Harding, P. *Inorg. Chim. Acta* **1986**, *116*, L5. (g) Baker, P. K.; Bury, A. *J. Organomet. Chem.* **1989**, *359*, 189 and references cited therein.

[3] The coordination chemistry of diphosphazanes is notable for the number of unusual structures that can be realized.[4]

[4] (a) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243. (b) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 1918. (c) King, R. B.; Shimura, M.; Brown, G. M. *Inorg. Chem.* **1984**, *23*, 1398. (d) Field, J. S.; Haines, R. J.; Sampson, C. N.; Sundermeyer, J.; Moodley, K. G. *J. Organomet. Chem.* **1987**, *322*, C7. (e) Engel, D. W.; Moodley, K. G.; Subramony, L.; Haines, R. J. *J. Organomet. Chem.* **1988**, *349*, 393. (f) Leeuw, G. D.; Field, J. S.; Haines, R. J. *J. Organomet. Chem.* **1989**, *359*, 245. (g) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, *7*, 983. (h) Mague, J. T.; Johnson, M. P.; Lloyd, C. L. *J. Am. Chem. Soc.* **1989**, *111*, 5012. (i) Uson, R.; Fornies, J.; Navarro, R.; Tomas, M.; Fortuno, C.; Cebollada, J. I. *Polyhedron* **1989**, *8*, 1045. (j) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49/50*, 409. (k) Mague, J. T.; Johnson, M. P. *Organometallics* **1990**, *9*, 1254.

[5] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

[6] Baker, P. K.; Fraser, S. G.; Keys, E. M. *J. Organomet. Chem.* **1986**, *309*, 319.

[7] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[8] Sheldrick, G. M. SHELX-76, Programme for Crystal Structure Determination; University of Cambridge: Cambridge, U.K., 1976.

0276-7333/91/2310-2522$02.50/0

Table I. Physical and Analytical[a] Data for the Complexes $[MI_2(CO)_3\{P(OPh)_2\}_2NR]$

complex	color/mp, °C[b]	yield, %	C, %	H, %	N, %
$[MoI_2(CO)_3\{P(OPh)_2\}_2NMe]$ (1)	brown/110	64	36.7 (37.5)	2.5 (2.6)	1.7 (1.6)
$[MoI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (2)	brown/119	68	41.1 (41.3)	2.5 (2.6)	1.3 (1.4)
$[WI_2(CO)_3\{P(OPh)_2\}_2NMe]$ (3)	maroon/135	79	34.0 (34.1)	2.2 (2.3)	1.2 (1.4)
$[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (4)	dark red/140	72	37.7 (37.8)	2.3 (2.4)	1.4 (1.3)

[a] Calculated values in parentheses. [b] Melts with decomposition.

Table II. IR[a] and NMR Data for the Complexes $[MI_2(CO)_3\{P(OPh)_2\}_2NR]$

complex	IR	NMR		
	ν(CO), cm^{-1}	^1H,[b] δ	^{31}P,[c] δ	$\Delta\delta$[d]
$[MoI_2(CO)_3\{P(OPh)_2\}_2NMe]$ (1)	2050 (m), 1990 (s), 1970 (s)	3.20 (t, NMe, $^3J(PH) = 11$ Hz)	104.8	−30.3
$[MoI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (2)	2070 (m), 1990 (s), 1945 (w)		98.2	−29.5
$[WI_2(CO)_3\{P(OPh)_2\}_2NMe]$ (3)	2050 (m), 1975 (s), 1960 (m)	3.22 (t, NMe, $^3J(PH) = 11$ Hz)	72.1	−63.0
$[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (4)	2070 (s), 1975 (br)		69.0	−58.7

[a] Recorded in Nujol mulls. Abbreviations: s, strong; m, medium; w, weak; br, broad. [b] In $CDCl_3$ solution; δ of phenyl protons omitted. [c] In CH_2Cl_2 solution, relative to 85% H_3PO_4. [d] δ_P(complex) − δ_P(free ligand).

Table III. Crystallographic Data and Details of the Structure Solution for $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (4)

mol formula	$C_{33}H_{25}I_2NO_7P_2W$
mol wt	1047
color	dark red
cryst syst	orthorhombic
space group	$Pna2_1$
a, Å	19.372 (2)
b, Å	11.511 (1)
c, Å	15.581 (1)
V, Å^3	3476.2
Z	4
D_{calc}, $g{\cdot}cm^{-3}$	2.00
F_{000}	1983
radiation, Å	λ(Mo Kα) = 0.71069
cryst size, mm	0.18 × 0.25 × 0.20
temp, K	293 (±1)
max 2θ, deg	59
scan	$\omega/2\theta$
octants collected	h (0–23), k (0–13), l (0–18)
no. of rflns measd	5356
no. of unique rflns	4977
no. of data used [$I > 2.5\sigma(I)$]	3548
linear abs coeff, cm^{-1}	55.4
R	0.0362
R_w	0.0335
w	$2.0959/(\sigma^2(F) + 0.0F^2)$
max shift/esd	0.002
decay, %	~2

tungsten complexes are more resistant to oxidation by air both in the solid state and in solution. Unlike the diphosphine complexes $[MX_2(CO)_3L_2]$ (M = Mo, W; L_2 = dppe, dppm; X = Cl, Br, I),[9,10] the diphosphazane complexes 1–4 do not undergo carbonyl substitution when heated in solution even in the presence of the diphosphazane ligand to form complexes of the type $[MX_2(CO)_2(L_2)_2]$. In contrast to the monophosphine complexes $[MX_2(CO)_3(L)_2]$ (M = Mo, W; L = PPh_3,[11] PEt_3[12]), complexes 1–4 do not undergo decarbonylation to give the octahedral complexes $[MI_2(CO)_2L_2]$ (L_2 = diphosphazane). Attempts to prepare seven-coordinated complexes by the oxidative-addition reactions of M(0) complexes *cis*-$[M(CO)_4\{P(OPh)_2\}_2NR]$[1] with halogens have been unsuccessful.

Scheme I

$$[M(CO)_3(NCMe)_3] \xrightarrow[0\ ^\circ C]{I_2,\ CH_2Cl_2} [MI_2(CO)_3(NCMe)_2] \xrightarrow{RN\{P(OPh)_2\}_2} \underset{1-4}{[MI_2(CO)_3\{P(OPh)_2\}_2NR]}$$

M = Mo, W; R = Me, Ph

The elucidation of the structures of the seven-coordinated complexes 1–4 is based on elemental analyses (C, H, and N; Table I), IR and ^1H and ^{31}P NMR spectroscopic data (Table II), and also single-crystal X-ray analysis of the tungsten complex $[WI_2(CO)_3\{P(OPh)_2\}_2NPh]$ (4).

The infrared spectra of complexes 1–4 show three carbonyl vibrations in the region 2070–1945 cm^{-1}, as expected. The ^{31}P NMR spectra show broad singlets upfield to that for the free ligand with coordination shifts in the range 29–31 and 57–63 ppm, respectively, for Mo(II) and W(II) complexes. This is in contrast to the ^{31}P NMR data for *cis*-$[M(CO)_4(PX_2)_2NR]$ complexes,[1] for which the ^{31}P chemical shifts in the four-membered chelate ring are shifted downfield from those of the corresponding free ligands. Cotton and Matusz have reported[13] similar observations for the molybdenum complex $[MoI_2(CO)_2(dppm)_2]$. The ^1H NMR spectra of the complexes $[MI_3(CO)_3\{P(OPh)_2\}_2NMe]$ (1, 3) show the *N*-methyl proton signals at 3.20 and 3.22 ppm, respectively; these chemical shifts are shifted downfield to those observed (2.95 and 3.10 ppm) for the M(0) complexes $[M(CO)_4\{P(OPh)_2\}_2NMe]$.[1] The increase in acidity of the metal when it is oxidized from zero to a +2 oxidation state is reflected in the increase of $^3J(PH)$ (11.0 Hz) for the M(II) complexes (1, 3) compared to the 8.5–10.0 Hz observed for the M(0) complexes.

Structure of $[WI_2(CO)_2\{P(OPh)_2\}_2NPh]$ (4). A perspective view of the molecule with numbering scheme is shown in Figure 1. Selected bond lengths and bond angles are listed in Table V.

The tungsten atom in 4 is seven-coordinate with a slightly distorted pentagonal-bipyramidal environment. Two phosphorus atoms of the diphosphazane ligand, two iodine atoms, and a carbonyl group are in the equatorial plane; the other two carbonyl groups are in apical positions (Figure 1). The displacement of the tungsten atom from the pentagonal plane is <0.05 Å. This type of geometry is rare for seven-coordinated complexes of the type $[MI_2(CO)_3L_2]$ (M = Mo, W; L_2 = diphosphine, diarsine). With the exception of the dppm complex $[WI_2$-

---

[9] Anker, M. W.; Colton, R.; Rix, C. J.; Tomkins, I. B. *Aust. J. Chem.* **1969**, *22*, 1341. Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1143.

[10] Abbreviations used: dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphophino)ethane, dmpe = bis(dimethylphosphino)ethane.

[11] Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 305.

[12] Moss, J. R.; Shaw, B. L. *J. Chem. Soc A* **1970**, 595.

[13] Cotton, F. A.; Matusz, M. *Polyhedron* **1987**, *6*, 261.

Table IV. Atomic Coordinates for 4 with Isotropic Displacement Parameters (Å^2 × 10^4) (Esd's in Parentheses)

atom	x/a	y/b	z/c	U_{eq}[a]
W	0.98279 (2)	0.86924 (3)	0.5000	336 (1)
I1	0.83952 (3)	0.81216 (6)	0.50276 (8)	563 (2)
I2	0.93060 (4)	1.10097 (6)	0.52237 (5)	533 (2)
C1	0.9735 (6)	0.9076 (1)	0.3721 (7)	488 (37)
O1	0.9672 (5)	0.9363 (8)	0.3023 (6)	719 (36)
C2	1.0615 (6)	0.9830 (8)	0.5240 (9)	536 (36)
O2	1.1049 (4)	1.0407 (6)	0.5390 (7)	770 (38)
C3	0.9764 (5)	0.8456 (10)	0.6296 (9)	452 (36)
O3	0.9705 (4)	0.8339 (8)	0.7012 (5)	611 (33)
P1	0.9741 (1)	0.6589 (2)	0.4835 (1)	325 (8)
P2	1.0884 (1)	0.7633 (2)	0.4748 (2)	313 (6)
O4	0.9333 (3)	0.5957 (6)	0.4081 (4)	379 (21)
O5	0.9581 (3)	0.5735 (6)	0.5603 (4)	408 (22)
O6	1.1508 (3)	0.7682 (5)	0.5442 (4)	383 (20)
O7	1.1337 (4)	0.7721 (5)	0.3891 (4)	427 (22)
N1	1.0586 (4)	0.6279 (6)	0.4695 (5)	353 (22)
C11	1.0943 (5)	0.5186 (8)	0.4553 (6)	348 (19)
C12	1.1642 (6)	0.5122 (10)	0.4724 (7)	484 (24)
C13	1.1988 (8)	0.4077 (13)	0.4571 (9)	667 (33)
C14	1.1631 (7)	0.3125 (12)	0.4286 (9)	650 (33)
C15	1.0948 (7)	0.3182 (12)	0.4124 (9)	567 (29)
C16	1.0600 (6)	0.4231 (10)	0.4262 (7)	472 (25)
C21	0.8978 (5)	0.5253 (7)	0.5952 (6)	349 (19)
C22	0.8625 (7)	0.4420 (10)	0.5514 (8)	576 (28)
C23	0.8082 (8)	0.3856 (12)	0.5921 (9)	656 (33)
C24	0.7914 (9)	0.4138 (15)	0.6762 (10)	803 (39)
C25	0.8277 (7)	0.4975 (12)	0.7198 (9)	653 (32)
C26	0.8828 (6)	0.5531 (10)	0.6788 (8)	531 (26)
C31	1.1395 (5)	0.7586 (8)	0.6316 (6)	385 (20)
C32	1.1091 (5)	0.6623 (9)	0.6679 (7)	451 (23)
C33	1.0992 (7)	0.6575 (11)	0.7557 (9)	582 (30)
C34	1.1225 (8)	0.7499 (13)	0.8049 (10)	675 (35)
C35	1.1506 (9)	0.8470 (15)	0.7695 (11)	718 (39)
C36	1.1610 (7)	0.8498 (12)	0.6824 (9)	606 (33)
C41	1.1629 (6)	0.8720 (9)	0.3533 (7)	405 (22)
C42	1.1447 (7)	0.8957 (11)	0.2691 (8)	564 (29)
C43	1.1744 (7)	0.9919 (12)	0.2313 (9)	647 (32)
C44	1.2215 (7)	1.0600 (11)	0.2745 (8)	570 (29)
C45	1.2392 (6)	1.0324 (10)	0.3577 (7)	473 (24)
C46	1.2099 (6)	0.9380 (9)	0.3985 (7)	417 (22)
C51	0.9330 (6)	0.6379 (9)	0.3225 (7)	386 (20)
C52	0.9924 (6)	0.6430 (9)	0.2751 (8)	438 (23)
C53	0.9878 (7)	0.6758 (11)	0.1902 (8)	548 (27)
C54	0.9242 (7)	0.6999 (13)	0.1537 (9)	636 (32)
C55	0.8660 (8)	0.6952 (12)	0.2024 (9)	667 (33)
C56	0.8691 (7)	0.6637 (10)	0.2885 (8)	514 (27)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \vec{a}_i\vec{a}_j$.

(CO)$_3$dppm][14] most of the seven-coordinate complexes that have been structurally characterized exhibit a capped-octahedral geometry around the metal center.[15]

Kepert[15] has shown that the seven-coordinate complexes of the type [$MX_2(CO)_3L_2$] (M = Mo(II), W(II); L_2 = diphosphine, diarsine; X = Br, I), containing a bidentate ligand with a "normalized bite"[16] $b < 1.11$, would exhibit pentagonal-bipyramidal geometry and those with $b > 1.11$ would exhibit either capped-octahedral or capped-trigonal-prismatic geometry. The observed geometry of the tungsten complex 4 with a normalized bite of 1.03 for the diphosphazane ligand is in accord with the conclusions of Kepert.

It is interesting to compare the structure of the octahedral molybdenum(0) complex *cis*-[Mo(CO)$_4${P(OPh)$_2$}$_2$NPh][1] with that of the seven-coordinate tungsten complex 4, since both contain the same chelating diphosphazane ligand. The mean P–N distance and the P–N–P bond angle in the molybdenum complex are 1.690 (6) Å and 101.3°, respectively, with a P···P bite of 2.613 (3) Å, whereas in the tungsten complex 4 the mean P–N bond distance and P–N–P bond angle are 1.676 (5) Å and 97.6 (4)°, respectively, with a relatively smaller P···P bite of 2.523 (3) Å. The smaller P···P bite in complex 4 is also reflected in the smaller P–M–P bond angle (62.6 (1)°) compared to that in the Mo(0) complex, in which it is 64.9°. These changes are probably a consequence of the presence of two bulky iodine atoms in the equatorial plane in complex 4 instead of a carbonyl group in the Mo complex and reflect the flexibility of the P–N–P skeleton. However, the four-membered MPNP chelate ring and the geometry around the nitrogen atom are planar in both structures.[17] The W–I distances in 4 (2.8529 (3) and 2.875

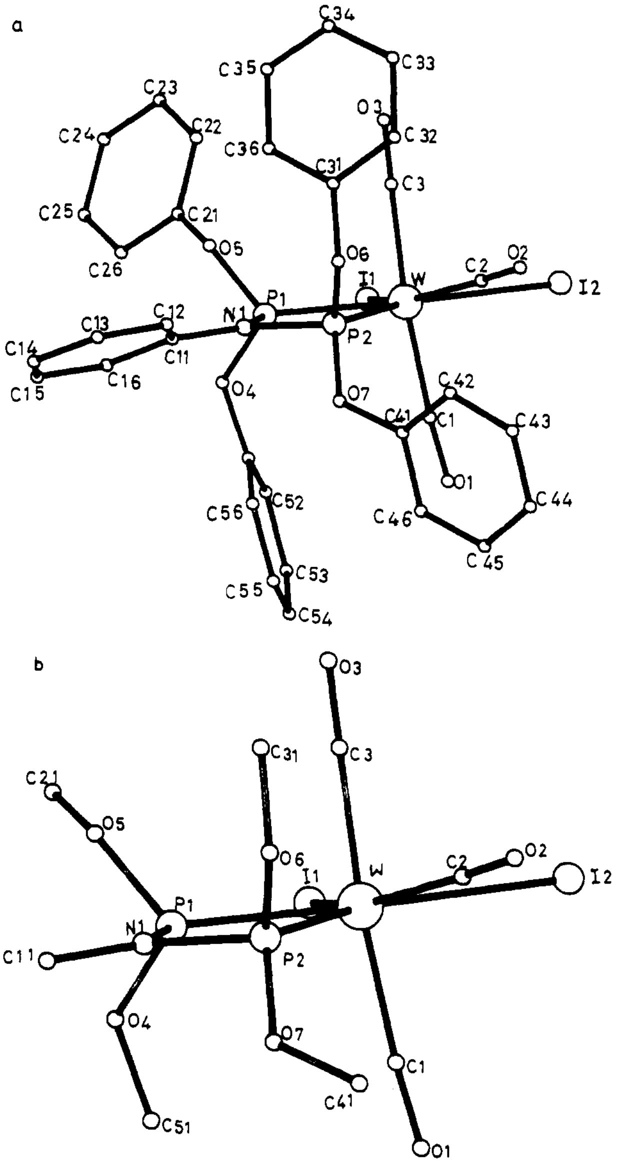

Figure 1. (a) Molecular structure of [WI$_2$(CO)$_3${P(OPh)$_2$}$_2$NPh] (4) showing the atomic numbering scheme. (b) Coordination geometry around tungsten.

---

[14] Foy, R. M.; Kepert, D. L.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 440.

[15] Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41 and references cited therein.

[16] The "normalized bite" of the bidentate ligand is defined as the distance between the donor atoms of the chelate ring divided by the metal–ligand distance.[15]

[17] The known tetracarbonyl chelate complexes of diphosphazanes adopt a planar MP$_2$N ring except in one instance, viz. [Mo(CO)$_4$(*meso*-{P(Ph)(NHPr^i)}$_2$NPr^i)],[18] where there is a slight deviation of the four-membered ring from planarity as a consequence of the presence of the bulky isopropylamine substituents on both phosphorus atoms.

[18] Hill, T. G.; Haltiwanger, R. C.; Prout, T. R.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 3461.

Table V. Selected Structural Parameters for 4

Bond Lengths (Å)			
W-I1	2.8529 (3)	C1-O1	1.144 (14)
W-I2	2.875 (1)	C2-O2	1.097 (13)
W-C1	2.050 (10)	C3-O3	1.130 (16)
W-C2	2.045 (11)	P1-O4	1.592 (7)
W-C3	2.042 (14)	P1-O5	1.580 (7)
W-P1	2.440 (2)	P2-O6	1.623 (7)
W-P2	2.414 (2)	P2-O7	1.602 (7)
P1-N1	1.664 (7)	P1...P2	2.523 (3)
P2-N1	1.689 (8)		
Bond Angles (deg)			
P1-W-P2	62.6 (1)	I1-W-P2	135.3 (1)
C3-W-P2	98.4 (3)	I1-W-P1	72.9 (1)
C3-W-P1	88.2 (3)	I1-W-C3	84.0 (3)
C2-W-P2	73.8 (3)	I1-W-C2	150.5 (3)
C2-W-P1	134.9 (3)	I1-W-C1	88.8 (3)
C2-W-C3	87.1 (5)	I1-W-I2	82.5 (1)
C1-W-P2	91.4 (3)	W-C1-O1	175.5 (10)
C1-W-P1	96.1 (4)	W-C2-O2	177.1 (10)
C1-W-C3	170.2 (4)	W-C3-O3	177.6 (9)
C1-W-C2	96.1 (5)	W-P1-N1	99.0 (3)
I2-W-P2	141.9 (1)	W-P2-N1	100.8 (3)
I2-W-P1	155.4 (1)	P1-N1-P2	97.6 (4)
I2-W-C3	89.0 (3)	P2-N1-C11	130.7 (5)
I2-W-C2	69.2 (3)	P1-N1-C11	131.7 (5)
I2-W-C1	83.5 (3)		

(1) Å) are comparable to those found in dppm[14] and dmpe[2a] complexes. Surprisingly there is no difference between the axial and equatorial W-C or C-O bond distances (see Table V).

Conclusion

Diphosphazanes are versatile, and a range of organometallic complexes can be prepared with these ligands, comparable to the rich chemistry of dppm and analogous ligands.[19] However, unlike the dppm system,[13] the η^1 mode of coordination is rare with the diphosphazane ligands[4k] presumably because of the tendency of the nitrogen atoms to adopt a planar geometry, which seems to be the overriding factor that determines the mode of coordination of diphosphazanes.

Acknowledgment. We thank the Department of Science and Technology, New Delhi, India, for support and Dr. M. Nethaji and Mr. R. Murugavel for checking the crystallographic computations. We thank one of the reviewers for his useful suggestions. The elemental analyses were carried out at the City University, London, U.K., by Dr. S. A. Matlin, thanks to the support of the International Organization of Chemical Sciences in Development (IOC-D), which is acknowledged.

Supplementary Material Available: A table of anisotropic thermal parameters for 4 (1 page); a table of structure factors (21 pages). Ordering information is given on any current masthead page.

---

(19) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99 and references cited therein. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.