Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 106, No. 1, February 1994, pp. 37–43.

Organometallic chemistry of diphosphazanes. Part IX: Syntheses and spectroscopic studies of molybdenum and tungsten tetracarbonyl complexes of unsymmetrical diphosphazanes

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MS received 11 October 1993

Abstract. The unsymmetrical diphosphazanes $X_2PN(Pr^i)PYY'$(1a–1h) {X = Ph, YY' = $O_2C_6H_4$ (1a) or YY' = $O_2C_{12}H_8$ (1b); X = Ph, Y = Ph, Y' = OC_6H_4Me–4 (1c), OC_6H_4Br–4 (1d), $OC_6H_3Me_2$–3,5 (1e), OC_5H_4N–2 (1f), $N_2C_3HMe_2$–3,5 (1g) or Cl (1h)} react with $[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) to yield the *cis*-chelate complexes $[M(CO)_4\{X_2PN(Pr^i)PYY'\}]$ {M = Mo (2a–2h); M = W (3f, 3g)}. These complexes have been characterized by ^1H, ^{31}P and ^{13}C NMR and IR spectroscopic studies.

Keywords. Unsymmetrical diphosphazane ligands; group 6 carbonyl complexes.

1. Introduction

Diphosphazanes have attracted considerable attention in recent years as "short-bite" ligands in transition metal organometallic chemistry (King 1980; Mague and Lin 1992; Balakrishna *et al* 1993, 1994; Field *et al* 1993; Rossi *et al* 1993). However, studies with unsymmetrically substituted diphosphazanes are sparse (Colquhoun and McFarlane 1977; Babu *et al* 1991, 1993). We had earlier established a correlation between the ^{31}P NMR chemical shifts of metal carbonyl complexes of the type *cis*-$[Mo(CO)_4\{X_2PN(R)PX_2\}]$ and the π-acceptor ability of the phosphorus centres (Balakrishna *et al* 1990). In order to extend the validity of the correlation, we have synthesized group 6 metal–tetracarbonyl complexes of a series of unsymmetrically substituted diphosphazanes of the type *cis*-$[M(CO)_4\{X_2PN(Pr^i)PYY'\}]$ and characterised them by IR and NMR spectroscopy. The results of these studies are presented here. These unsymmetrically substituted diphosphazanes offer an advantage in that the two-bond P–P coupling constants in the ligands as well as in the complexes can be directly measured from their ^{31}P NMR spectra.

2. Experimental details

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk-tube technique (Shriver and Drezdzon 1986). Solvents were purified

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For Part VIII see, Babu *et al* (1993)

Table 1. IR, ^{1}H NMR, elemental analyses and melting point data for the diphosphazane complexes.

Compound	m.p.[a] (°C)	Elemental analyses %* C	H	N	IR[b] ν(CO) (cm^{-1})	^{1}H NMR[c] Me(Pr^i)
$[Mo(CO)_4\{Ph_2PN(Pr^i)P(O_2C_6H_4)\}]$ (2a)	193 (d)	52·2 (50·9)	3·6 (3·6)	3·3 (2·4)	2026, 1932, 1896	1·2
$[Mo(CO)_4\{Ph_2PN(Pr^i)P(O_2C_{12}H_8)\}]$ (2b)	188 (md)	56·6 (56·0)	4·2 (3·8)	2·4 (2·1)	2020, 1930, 1880	0·87
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{–}4)\}]$ (2c)	150 (d)	58·8 (57·8)	4·7 (4·4)	2·8 (2·1)	2020, 1911, 1890	1·29, 0·35 2·33[d]
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{–}4)\}]$ (2d)	195 (md)	52·4 (51·0)	3·7 (3·6)	2·8 (1·9)	2014, 1929, 1896	1·27, 0·34
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{–}3,5)\}]$ (2e)	150 (d)	59·5 (58·3)	4·7 (4·6)	2·8 (2·1)	2014, 1932, 1890	1·29, 0·34 2·30[d]
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_5H_4N\text{–}2)\}]$ (2f)	150 (d)	56·1 (55·2)	4·4 (4·0)	4·8 (4·3)	2010, 1925, 1880	1·32, 0·29
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPhCl\}]$[e] (2h)	—	—	—	—	2024, 1916, 1892	0·72, 0·01
$[W(CO)_4\{Ph_2PN(Pr^i)PPh(OC_5H_4N\text{–}2)\}]$ (3f)	180 (d)	49·5 (48·7)	3·9 (3·6)	4·3 (3·8)	2010, 1915, 1870	1·31, 0·28
$[W(CO)_4\{Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{–}3,5)\}]$ (3g)	185 (d)	49·3 (48·6)	4·4 (4·0)	5·9 (5·7)	2006, 1894, 1867	1·22, 0·07 2·42, 2·25[f]

*Found (calculated); [a] d = decomposed, md = melted with decomposition. [b] nujol mull; [c] methyl(Pr^i) resonances are doublets with $^3J_{HH} \approx 7$ Hz, CH(Pr^i) resonances are multiplets centred at $\approx$ 3·6 ppm; [d] CH_3 on the aryl ring; [e] obtained as an air-sensitive waxy solid, satisfactory C, H, N analyses could not be obtained; [f] pyrazolyl methyls.

by standard methods. IR, and NMR spectra were recorded as reported previously (Babu *et al* 1993). C, H, N, analyses were carried out with a Heraeus CHN–O Rapid instrument. The diphosphazane ligands (1c, –1f) were prepared by the reaction $Ph_2PN(Pr^i)PPhCl$ (Cross *et al* 1976) with the corresponding phenol or secondary amine in boiling benzene in the presence of triethylamine (Babu, unpublished results). The diphosphazane (1a) was prepared as reported earlier (Babu *et al* 1991); diphosphazane (1b) was prepared in a similar manner (Babu, unpublished results). The precursor complex $[Mo(CO)_4(NHC_5H_{10})_2]$ was prepared by a published procedure (Darensbourg and Kump 1978).

2.1 *Preparation of cis-*$[Mo(CO)_4\{X_2PN(Pr^i)PYY'\}]$ (2a–2h)

A mixture of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ (5×10^{-4} mol) and the diphosphazane ligand (5×10^{-4} mol) was dissolved in 25 ml of dichloromethane and the solution was stirred for 30 min. The resultant solution was filtered through silica gel and the solvent evaporated under reduced pressure. Crystallisation of the residue from a dichloromethane-petrol mixture (1:1), yielded the tetracarbonyl complex as a pale yellow solid. Yield 80–90%.

2.2 *Preparation of cis-*$[W(CO)_4\{X_2PN(Pr^i)PYY'\}]$ (3f, 3g)

The procedure is similar to that of the molybdenum complex. In this case, the reaction mixture was heated under reflux for 3 h. Yield 75–80%.

The analytical and spectroscopic data are summarised in tables 1–3.

Table 2. $^{13}C\{^1H\}$ NMR data (carbonyl resonances only) for some diphosphazane complexes[a].

Diphosphazane complex	^{13}C NMR values δ(ppm)	$^2J_{PC}$(Hz)
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{–}4)\}]$	218·6 (dd)	25·0, 10·5
(2c)	218·3 (dd)	30·5, 10·0
	213·0 (t)	8·1
	208·1 (t)	9·0
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{–}4)\}]$	218·4 (dd)	25·5, 10·0
(2d)	217·8 (dd)	30·0, 9·5
	212·7 (t)	8·5
	208·2 (t)	10·0
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{–}3,5)\}]$	220·4 (t)	15·0
(2e)	219·9 (dd)	15·0, 11·6
	215·0 (t)	8·0
	209·6 (t)	9·7
$[Mo(CO)_4\{Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{–}3,5)\}]$	219·1 (dd)	25·5, 10·0
(2g)[b]	218·1 (dd)	29·0, 9·9
	214·4 (t)	9·0
	207·2 (t)	8·0

[a]Recorded at 50·32 MHz, internal standard TMS; [b]Babu *et al* 1993
dd – doublet of doublets; t – triplet

Table 3. $^{31}P\{^{1}H\}$ NMR data for diphosphazane ligands and their complexes[a].

Compound	Diphosphazane			Mo complex[b]			$\Delta\delta$	
	PYY′	PPh_2	$^2J_{PP}$	PYY′	PPh_2	$^2J_{PP}$	PYY′	PPh_2
$Ph_2PN(Pr^i)P(O_2C_6H_4)$ (1a)	155·8	28·9	14·0	163·5	75·1	32·0	7·7	46·2
$Ph_2PN(Pr^i)P(O_2C_{12}H_8)$ (1b)	148·6	27·9	25·4	154·0	74·8	33·0	5·4	46·9
$Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{–}4)$ (1c)	127·4	39·5	21·2	147·0	82·3	15·8	19·6	42·8
$Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{–}4)$ (1d)	129·1	39·4	22·1	148·6	82·7	16·0	19·5	43·3
$Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{–}3,5)$ (1e)	126·3	38·6	22·7	146·7	82·3	17·0	20·4	43·7
$Ph_2PN(Pr^i)PPh(OC_5H_4N\text{–}2)$ (1f)	126·4	40·2	21·8	142·5	85·0	19·0	16·1	44·8
$Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{–}3,5)$ (1g)	71·6	43·8	29·8	110·6	85·3	10·8	39·0	41·5
$Ph_2PN(Pr^i)PPhCl$ (1h)	134·2	44·0	29·0	133·1	88·8	17·5	−1·1	44·8
$Ph_2PN(Pr^i)PPh_2$		48·8			89·4[c]			40·6

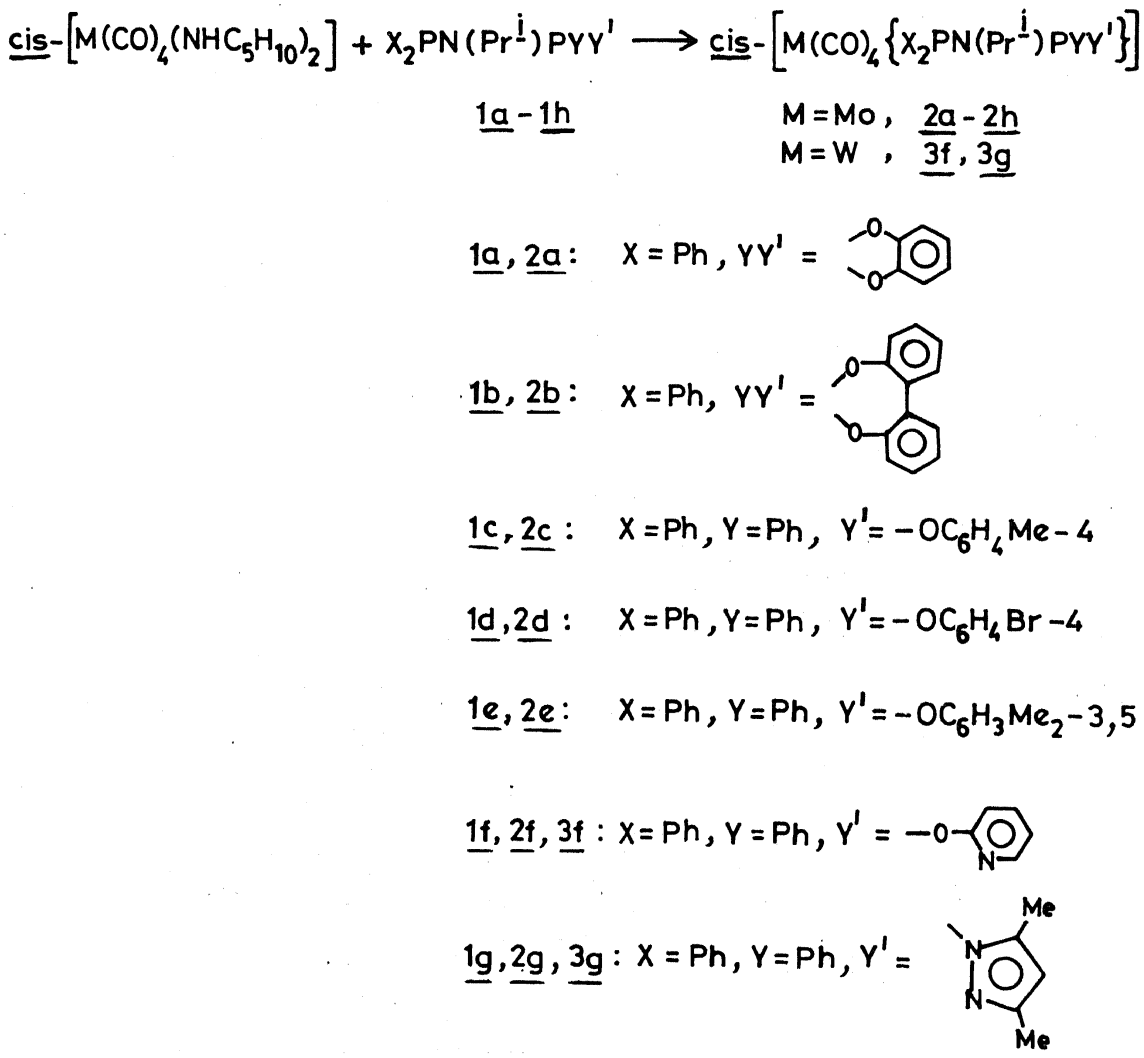
[a]Recorded at 81·02 MHz; external standard 85% H_3PO_4; [b]the ^{31}P NMR values for the tungsten complexes are as follows: 3f 114·8(*d*)($^1J_{PW}$ = 256 Hz), 62·0(*d*)($^1J_{PW}$ = 216 Hz), $^2J_{PP}$ = 30·0 Hz; 3g 83·1(*d*)($^1J_{PW}$ = 242 Hz), 61·5(*d*)($^1J_{PW}$ = 208 Hz), $^2J_{PP}$ = 19·0 Hz; [c]Keat *et al* (1981); Balakrishna *et al* (1990).

3. Results and discussion

Treatment of *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) with an equimolar quantity of the unsymmetrical diphosphazane in dichloromethane yields the chelate complexes *cis*-$[M(CO)_4\{X_2PN(Pr^i)PYY'\}]$ (scheme 1). The molybdenum complexes are readily formed within 10 min at room temperature, whereas the formation of the tungsten complexes requires the heating of the reaction mixture under reflux for three hours. The presence of an excess of the diphosphazane ligand also favours the formation of *cis*-chelate complexes.

The infra-red spectra of these complexes exhibit three strong ν_{CO} absorptions in the range 2030 to 1865 cm^{-1} (table 1), characteristic of an $M(CO)_4$ moiety bonded to strong π-acceptor ligands such as $MeN(PF_2)_2$ (King and Lee 1982; Cotton and Kraihanzel 1962). These values are in the range observed for similar type of diphosphazane complexes (Balakrishna *et al* 1990).

The ^1H NMR spectra for the complexes 2a and 2b display a doublet for the methyl protons of the isopropyl group (table 1). These protons are shielded by ~0·5 ppm



Scheme 1.

in comparison with the observed chemical shifts for the free ligand. The spectra of 2c–2h show two different resonance for the two methyl groups owing to the presence of an adjacent chiral phosphorus centre; one of these resonances is strongly shielded (~ 1 ppm) and appears in the region 0·3–0·0 ppm suggesting that these protons lie in the shielding zone of one of the phenyl groups on the phosphorus as observed in $[Mo(CO)_3(MeCN)\{Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{–}3,5)\}]$ (Babu *et al* 1993).

The $^{13}C\{^1H\}$ NMR spectra displays four different chemical shifts for the carbonyl carbons (table 2). The carbonyls which are *trans*- to phosphorus atoms resonate as a doublet of doublets, whereas the *cis*-carbonyls display triplet resonances. The $^2J_{PC}$ values are in the range 10–30 Hz and are higher for the *trans* carbonyls (25–30 Hz), with the exception of 2e.

The $^{31}P\{^1H\}$ NMR spectra of the complexes exhibit a doublet of doublets owing to the non-equivalence of the phosphorus nuclei (table 3). The resonances are considerably deshielded. The extent of deshielding of the PPh_2 phosphorus remains more or less the same whereas the coordination shift (Balakrishna *et al* 1990) ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) (table 3) for the PYY′ resonance depends upon the electronegativity of the substituents on the phosphorus which in turn determines its π-acceptor capabilities. There is no regular trend in $^2J_{PP}$ values. Diphosphazane ligands can exist as different conformers in solution (Keat *et al* 1981), whereas in the tetracarbonyl complexes the conformational mobility is severely restricted. Furthermore, in the complexes the P–P coupling will be an algebraic sum of the coupling through the nitrogen as well

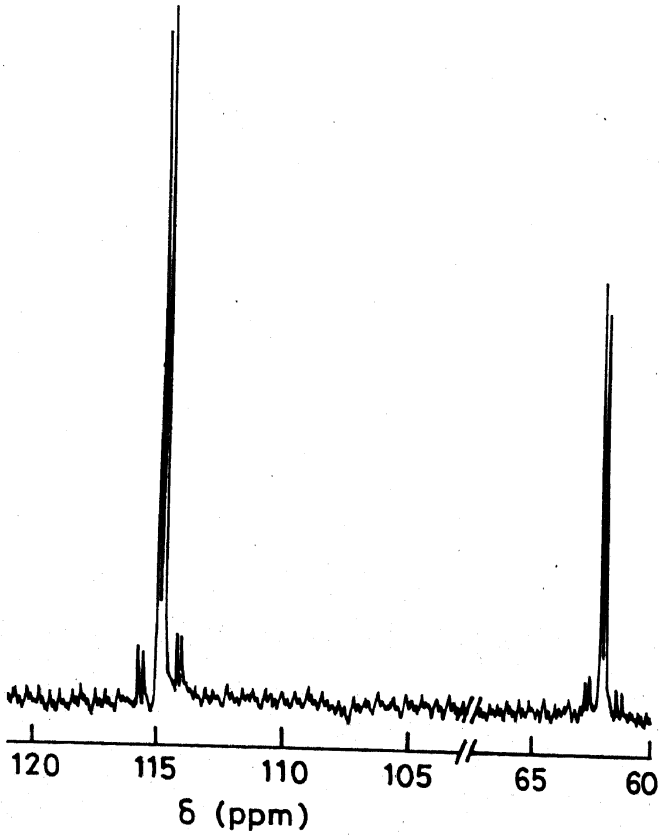


Figure 1. The ^{31}P NMR spectrum (81·02 MHz) of $[W(CO)_4\{Ph_2PN(Pr^i)PPh(OC_5H_4N\text{–}2)\}]$, (3f).

as through the metal and it is difficult to assess each of these two contributions separately.

The ^{31}P NMR spectra of the tungsten complexes 3f and 3g display ^{183}W satellites. The spectrum of 3f is shown in figure 1. The tungsten-phosphorus coupling constants lie in the range 208–256 Hz, the more electronegative phosphorus being associated with a higher coupling constant. In spite of the presence of an additional donor atom in these diphosphazanes, the PP chelate formation is clearly favoured. This result further substantiates the earlier report that diphosphazanes with bulky substituents at the phosphorus atom show a pronounced tendency to form four-membered monometallic chelate complexes (Balakrishna *et al* 1991; Browning *et al* 1992).

Acknowledgement

The authors thank the Department of Science and Technology, New Delhi, for support.

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