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## Organometallic chemistry of diphosphazanes

VIII \*. Synthesis, spectroscopic studies and crystal structure of *fac*-[Mo(CO)<sub>3</sub>(MeCN){Ph<sub>2</sub>PN(<sup>i</sup>Pr)P(Ph)(DMP)}] \*\*, and its reactions with tertiary phosphines

R.P. Kamalesh Babu, S.S. Krishnamurthy and M. Nethaji

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

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## Abstract

The reaction of *fac*-[Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>] with the unsymmetrical diphosphazane Ph<sub>2</sub>PN(<sup>i</sup>Pr)P(Ph)(DMP) (L) gives the complex *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (2) in almost quantitative yield. The structure of the complex has been determined by an X-ray diffraction study. The compound reacts with PR<sub>3</sub> (where R = Ph, OPh) to give *fac*-[Mo(CO)<sub>3</sub>(PR<sub>3</sub>)(L)] (3a, 4a), which undergoes an intramolecular isomerization to afford *mer*-[Mo(CO)<sub>3</sub>(PR<sub>3</sub>)(L)] (3b, 4b). Synthesis of *cis*-[Mo(CO)<sub>4</sub>(L)] (1) and *fac*-[Mo(CO)<sub>3</sub>(L)] (2a) and their spectroscopic data are also reported.

## 1. Introduction

Diphosphazanes have attracted considerable attention in recent years as “short-bite” ligands in transition metal organometallic chemistry comparable in their versatility to the analogous bis-(phosphino)methane-type ligands such as dppm [1–3]. The method of synthesis used for diphosphazanes [4] lends itself to facile incorporation of other donor atoms in the ligand. We report below the synthesis of a new unsymmetrical diphosphazane *viz.* Ph<sub>2</sub>PN(<sup>i</sup>Pr)P(Ph)(DMP) (L), potentially a tridentate PPN donor ligand, and its molybdenum carbonyl complexes *cis*-[Mo(CO)<sub>4</sub>(L)] (1) and *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (2) and *fac*-[Mo(CO)<sub>3</sub>(L)] (2a). The structure of 2, as determined by X-ray crystallography, reveals bidentate coordination of the diphosphazane ligand through its phosphorus centres,

and the presence of a labile MeCN ligand bonded to the metal, which can be readily replaced by a tertiary phosphine ligand PPh<sub>3</sub> or P(OPh)<sub>3</sub>.

## 2. Experimental details

All manipulations were carried out under dry dinitrogen by standard Schlenk-tube techniques. Solvents were purified by standard methods. The unsymmetrical diphosphazane Ph<sub>2</sub>PN(<sup>i</sup>Pr)P(Ph)(DMP) (L) was prepared by the reaction of Ph<sub>2</sub>PN(<sup>i</sup>Pr)PPhCl [4] with 3,5-dimethylpyrazole in boiling benzene in the presence of triethylamine [5\*]. The complexes *cis*-[Mo(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>] and *fac*-[Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>] were prepared by published procedures [6, 7]. The NMR spectra were recorded as reported previously [8]. IR spectra were obtained with a Hitachi 750-50 spectrometer. C, H and N analyses were carried out with a Heraeus CHN-O Rapid instrument. The FAB-mass spectrum was recorded at 25°C on a JEOL SX 102/DA-6000 Mass Spectrometer/Data system using argon (6 KV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol as the matrix. Only the most intense ions are reported.

Correspondence to: Prof. S.S. Krishnamurthy.

\* Part VII, M.S. Balakrishna, R. Murugavel, S.S. Krishnamurthy, I.I. Mathews and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, (1993) 477.

\*\* Abbreviations used: DMP = 3,5-dimethyl, 1-pyrazolyl; dppm = bis(diphenylphosphino)methane.

### 3. Syntheses

#### 3.1. *cis*-[Mo(CO)<sub>4</sub>(L)] (1)

A mixture of *cis*-[Mo(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>] (0.20 g, 5.3 × 10<sup>-4</sup> mol) and the ligand **L** (0.24 g, 5.4 × 10<sup>-4</sup> mol) was dissolved in 30 mL of dichloromethane and the solution was stirred for 30 min. Evaporation of the solvent, followed by crystallization of the residue from dichloromethane–petrol mixture (1:1), yielded **1** as a pale yellow solid. (Yield 0.27 g, 80%). M.p. 160°C (with dec.) Anal. Found: C, 55.5; H, 4.6; N, 6.8. C<sub>30</sub>H<sub>29</sub>MoN<sub>3</sub>O<sub>4</sub>P<sub>2</sub> calc.: C, 55.2; H, 4.5; N, 6.4%. IR (Nujol):  $\nu(\text{CO})$  2030s, 1920s, 1910b cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.26–8.18 (m, Ph); 6.06 (s, CH-DMP); 3.92 (m, CH-<sup>1</sup>Pr); 2.43 (s, Me-DMP); 2.26 (s, Me-DMP); 1.22 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, Me-<sup>1</sup>Pr); 0.05 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, Me-<sup>1</sup>Pr). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 219.1 (dd, 10, J(PC) = 25.5 Hz, CO), 218.1 (dd, 9.9, J(PC) = 29 Hz, CO), 214.4 (t, J(PC) = 9 Hz, CO), 207.2 (t, J(PC) = 8 Hz, CO).

#### 3.2. *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (2)

A solution of **L** (0.88 g, 2.0 × 10<sup>-3</sup> mol) in 25 mL of acetonitrile was added dropwise to a solution of *fac*-[Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>] (prepared *in situ* by heating Mo(CO)<sub>6</sub> (0.5 g, 1.9 × 10<sup>-3</sup> mol) in 20 mL of MeCN for 24 h) at 45°C. The mixture was stirred for 30 min, concentrated *in vacuo* to 20 mL, and kept at -10°C overnight to give the title compound (**2**) as pale yellow crystal (Yield 0.97 g, 77%). M.p. 180°C (with dec.). Anal. Found C, 55.5; H, 4.9; N, 8.5. C<sub>31</sub>H<sub>32</sub>MoN<sub>4</sub>O<sub>3</sub>P<sub>2</sub> calc.: C, 55.9; H, 4.8; N, 8.4%. IR (Nujol):  $\nu(\text{CO})$  1938s, 1857s, 1791s cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.19–8.3 (m, Ph); 5.9 (s, CH-DMP); 3.8 (m, CH-<sup>1</sup>Pr); 2.37 (s, Me-DMP); 2.21 (s, Me-DMP); 2.19 (s, Me-MeCN); 1.15 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Me-<sup>1</sup>Pr); 0.01 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Me-<sup>1</sup>Pr). Even traces of moisture in acetonitrile solvent lowered the yield of **2**, and led to the formation of substantial quantities of **1**.

#### 3.3. *fac*-[Mo(CO)<sub>3</sub>(L)] (2a)

##### 3.3.1. Method A

A solution of **2** (0.10 g, 1.5 × 10<sup>-4</sup> mol) in 20 mL of heptane was heated under reflux for 1 h. The title compound separated as a pale yellow solid, which was filtered off and washed with heptane (Yield 0.019 g, 20%). M.p. 170°C (with dec.). Mass spectral data: *m/z* = 627, [Mo(CO)<sub>3</sub>(L)]<sup>+</sup> (37); *m/z* = 571, [Mo(CO)(L)]<sup>+</sup> (100); *m/z* = 543, [Mo(L)]<sup>+</sup> (94). IR (Nujol):  $\nu(\text{CO})$  1925s, 1832s, 1814s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 6.8–7.9 (m, Ph); 5.45 (s, CH-DMP); 3.4 (m, CH-<sup>1</sup>Pr); 2.25 (s, Me-DMP); 1.94 (s, Me-DMP); 0.87 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, Me-<sup>1</sup>Pr); 0.84 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, Me-<sup>1</sup>Pr).

##### 3.3.2. Method B

A suspension of **1** [0.20 g, 3.06 × 10<sup>-4</sup> mol] in 25 mL of heptane was heated under reflux for 24 h. A pale-yellow solid separated, and was filtered off and identified as **2a** from its IR spectrum [Yield 0.068 g, 36%].

Compound **2a** is highly sensitive to air, and decomposed upon storage even under nitrogen for several days, yielding the tetracarbonyl complex **1** and other unidentified products. In view of this instability of **2a** satisfactory C, H, and N analyses could not be obtained.

#### 3.4. *mer*-[Mo(CO)<sub>3</sub>(PR<sub>3</sub>)(L)] (R = Ph (3b) and R = OPh (4b))

A solution of PPh<sub>3</sub> (0.094 g, 3.6 × 10<sup>-4</sup> mol) in 20 mL of benzene was added dropwise to **2** (0.20 g, 3 × 10<sup>-4</sup> mol) and the resulting yellow solution was stirred overnight. Solvent was removed *in vacuo* to obtain a yellow oil. Dissolution of the oil in toluene:petrol (1:1) and cooling of the solution afforded crystals of **3b** (Yield 0.22 g, 81%). M.p. 187°C (with dec.). Anal. Found: C, 65.7; H, 5.4; N, 5.5. C<sub>48</sub>H<sub>44</sub>MoN<sub>3</sub>P<sub>3</sub>O<sub>6</sub> calc.: C, 64.1; H, 4.9; N, 4.7%. IR (Nujol):  $\nu(\text{CO})$  1974m, 1872s, 1851s cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.1–8.05 (m, Ph); 5.94 (s, CH-DMP); 3.90 (m, CH-<sup>1</sup>Pr); 2.39 (s, Me-DMP); 2.11 (s, Me-DMP); 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Me-<sup>1</sup>Pr); -0.31 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Me-<sup>1</sup>Pr).

TABLE 1. Crystal data and intensity collection parameters for *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (2)

|   |  |
|---|--|
| Formula                                       | C <sub>31</sub> H <sub>32</sub> MoN <sub>4</sub> O <sub>3</sub> P <sub>2</sub> |
| Molecular weight                              | 666.5  |
| Crystal system                                | Monoclinic   |
| Space group                                   | P2 <sub>1</sub> /c   |
| Z   | 4  |
| <i>a</i> (Å)                                  | 10.182(5)  |
| <i>b</i> (Å)                                  | 16.947(2)  |
| <i>c</i> (Å)                                  | 19.086(2)  |
| $\beta$ (°)                                   | 91.95(2)   |
| <i>V</i> (Å <sup>3</sup> )                    | 3291(3)  |
| <i>F</i> (000)                                | 1279.8   |
| Radiation (graphite monochromator)            | Mo-K $\alpha$ ( $\lambda$ = 0.71069 Å)   |
| Linear abs. coeff. (cm <sup>-1</sup> )        | 4.82   |
| Scan technique                                | $\omega/2\theta$   |
| $\theta$ range                                | 1–25°  |
| Total no. of reflections                      | 8336   |
| Unique reflections                            | 5785   |
| Observed reflections ( $F_o > 5\sigma(F_o)$ ) | 4037   |
| <i>R</i>                                      | 0.0388   |
| <i>R<sub>w</sub></i>                          | 0.0408   |
| Largest peak in final diff.                   | 0.129  |
| map (e Å <sup>-3</sup> )                      |  |

$$R = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|}; R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}}{w = 1.0000 / (\sigma^2(F) + 0.000001(F)^2)}$$

The analogous complex **4b** was prepared from  $P(\text{OPh})_3$  (0.111 g,  $3.6 \times 10^{-3}$  mol) and **2** (0.2 g,  $3 \times 10^{-4}$  mol). In this case, the reaction mixture was heated under reflux for 4 h (Yield 0.22 g, 76%). M.p. 190°C (with dec.). Anal. Found: C, 61.5; H, 5.2; N, 5.5.  $C_{48}H_{44}MoN_3P_3O_6$  calc.: C, 60.8; H, 4.7; N, 4.4%. IR (Nujol):  $\nu(\text{CO})$  1995m, 1890s, 1863s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 6.88–8.3 (m, Ph); 5.95 (s, CH-DMP); 3.9 (m, CH- $^i\text{Pr}$ ); 2.37 (s, Me-DMP); 2.11 (s, Me-DMP); 1.17 (d,  $^3J_{\text{HH}} = 7$  Hz, Me- $^i\text{Pr}$ ); -0.08 (d,  $^3J_{\text{HH}} = 7$  Hz, Me- $^i\text{Pr}$ ).

TABLE 2. Non-hydrogen atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (**2**)

| Atom | x          | y         | z         | $U_{\text{eq}}$ |
|------|------------|-----------|-----------|-----------------|
| Mo   | 0.1653(1)  | 0.3067(1) | 0.7910(1) | 392(1)          |
| P1   | 0.1519(1)  | 0.2420(1) | 0.9072(1) | 388(4)          |
| N1   | 0.3144(4)  | 0.2422(2) | 0.9282(2) | 432(12)         |
| P2   | 0.3815(1)  | 0.2767(1) | 0.8529(1) | 443(4)          |
| C1   | 0.2270(6)  | 0.3527(4) | 0.7021(3) | 680(23)         |
| O1   | 0.2654(6)  | 0.3813(3) | 0.6526(3) | 1200(26)        |
| C2   | -0.0210(6) | 0.3211(3) | 0.7620(3) | 546(19)         |
| O2   | -0.1301(4) | 0.3342(3) | 0.7477(2) | 890(20)         |
| C3   | 0.1509(5)  | 0.4135(3) | 0.8256(3) | 504(19)         |
| O3   | 0.1369(4)  | 0.4790(2) | 0.8439(2) | 725(17)         |
| C10  | 0.3667(6)  | 0.2242(3) | 1.0014(3) | 608(19)         |
| C20  | 0.4905(8)  | 0.1685(4) | 1.0011(4) | 1033(34)        |
| C30  | 0.4020(7)  | 0.2982(4) | 1.0413(3) | 710(24)         |
| N11  | 0.1089(5)  | 0.1415(2) | 0.9104(2) | 563(16)         |
| N12  | 0.2017(6)  | 0.0863(3) | 0.9331(3) | 802(21)         |
| C13  | 0.1416(7)  | 0.0166(4) | 0.9235(5) | 913(30)         |
| C14  | 0.0153(9)  | 0.0265(4) | 0.8981(5) | 1076(38)        |
| C15  | -0.0052(7) | 0.1069(4) | 0.8888(4) | 794(26)         |
| C16  | 0.2180(9)  | 0.0550(5) | 0.9427(8) | 1866(69)        |
| C17  | -0.1112(8) | 0.1502(6) | 0.8630(6) | 1367(46)        |
| C21  | 0.0713(5)  | 0.2795(3) | 0.9839(2) | 423(13)         |
| C22  | 0.0171(7)  | 0.2315(3) | 1.0343(3) | 717(25)         |
| C23  | -0.0478(8) | 0.2650(4) | 1.0914(3) | 855(29)         |
| C24  | -0.0535(6) | 0.3442(4) | 1.0975(3) | 700(23)         |
| C25  | 0.0033(6)  | 0.3928(3) | 1.0497(3) | 550(18)         |
| C26  | 0.0637(5)  | 0.3612(3) | 0.9937(3) | 503(18)         |
| C31  | 0.5068(5)  | 0.3483(3) | 0.8809(3) | 535(19)         |
| C32  | 0.4691(5)  | 0.4249(3) | 0.8918(3) | 628(21)         |
| C33  | 0.5581(8)  | 0.4793(4) | 0.9194(4) | 901(30)         |
| C34  | 0.6846(8)  | 0.4566(5) | 0.9349(4) | 1029(35)        |
| C35  | 0.7243(7)  | 0.3833(5) | 0.9220(4) | 1032(36)        |
| C36  | 0.6371(6)  | 0.3282(4) | 0.8944(4) | 856(30)         |
| C41  | 0.4775(5)  | 0.1995(3) | 0.8131(3) | 625(23)         |
| C42  | 0.5568(7)  | 0.2223(5) | 0.7569(4) | 995(30)         |
| C43  | 0.6232(10) | 0.1637(9) | 0.7213(6) | 1488(56)        |
| C44  | 0.6073(11) | 0.0864(8) | 0.7386(7) | 1690(65)        |
| C45  | 0.5260(8)  | 0.0657(5) | 0.7928(5) | 1255(43)        |
| C46  | 0.4639(6)  | 0.1220(4) | 0.8300(4) | 849(28)         |
| N51  | 0.1732(4)  | 0.1839(3) | 0.7507(2) | 553(15)         |
| C52  | 0.1768(6)  | 0.1193(3) | 0.7377(3) | 605(21)         |
| C53  | 0.1855(9)  | 0.0343(4) | 0.7242(4) | 1086(37)        |

### 3.5. Crystal structure determination of **2**

A summary of the crystal data for complex **2** and some details of the structure determination are given in Table 1. The crystal was sealed in a Lindemann capillary to protect it from atmosphere during data collection. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo- $K\alpha$  radiation. Cell constants were obtained by least-squares refinement of the setting angles of 24 reflections in the range  $19 < 2\theta < 25^\circ$ . During the data collection, no decrease in intensity was revealed by periodic monitoring. Lorentz polarization corrections were applied to the intensity data, but no absorption correction was made.

The structure was solved by the Patterson Heavy atom method using the SHELXS-86 [9] program, and least-square refinements were performed by the full-matrix method using SHELX-76 [10]. All hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Non-hydrogen atom coordinates are given in Table 2.

## 4. Results and discussion

### 4.1. Synthesis and spectroscopic data

The mononuclear molybdenum tetracarbonyl derivative, *cis*-[Mo(CO)<sub>4</sub>(L)] (**1**) can be prepared by the displacement of piperidine from *cis*-[Mo(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>] by the diphosphazane ligand **L** (Scheme 1). The chelated complex **1** has been characterized by elemental analyses, IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopic data. The infrared spectrum of **1** exhibits  $\nu(\text{CO})$  absorptions at 2030s, 1920s and 1910b  $\text{cm}^{-1}$ , that are characteristic of a Mo(CO)<sub>4</sub> moiety bonded to a strong  $\pi$ -acceptor ligand, and are in the range observed for a similar type of diphosphazane complex [2b].

The  $^{31}\text{P}$  NMR coordination shifts ( $\Delta\delta = \delta_{(\text{complex})} - \delta_{(\text{ligand})}$ ) observed for this complex are 41.5 ppm and 39.0 ppm for the diphenyl-substituted phosphorus and the pyrazolyl-substituted phosphorus respectively (Table 3). These values are close to that observed for the complex *cis*-[Mo(CO)<sub>4</sub>(Ph<sub>2</sub>PN( $^i$ Pr)PPh<sub>2</sub>)] [2b].

The  $^{13}\text{C}$  NMR spectrum displays four different chemical shifts for carbonyl carbons (Fig. 1). The signals centered at 219.1 ppm and 218.1 ppm show coupling constants ( $^2J_{\text{CP}}$ ) in the range 10 Hz and 25–29 Hz; these are assigned to the carbonyls in equatorial positions and *trans*- to the phosphorus atoms. The signals at 214.4 ppm and 207.2 ppm show coupling constants in the range 7–10 Hz, and are assigned to the carbonyls in axial positions.

Reaction of *fac*-[Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>] with an equimolar quantity of the new unsymmetrical diphosphaz-

ane **L** results in the quantitative formation of *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (**2**) [Scheme 1]. The IR spectrum of **2** shows three carbonyl stretching vibrations at 1938, 1857 and 1791, close to the values observed for the molybdenum [11] and tungsten [12] complexes of dppm. The <sup>1</sup>H NMR spectrum shows two different resonances for the two methyl groups (0.01 ppm and 1.15 ppm) of the isopropyl substituent owing to the presence of an adjacent chiral phosphorus centre. The high shielding of one of the methyl groups (δ 0.01) suggests that these protons lie in the shielding zone of one of the phenyl groups on phosphorus. A single crystal X-ray crystallographic study supports this conclusion (see below).

The <sup>31</sup>P NMR spectrum of **2** shows an AX pattern and the chemical shifts are shown in Table 3. The coordination shifts observed for this complex are 45.7 ppm and 39.4 ppm for the diphenyl-substituted phosphorus and the pyrazolyl-substituted phosphorus respectively. Thus the PPh<sub>2</sub> phosphorus atom in the tricarbonyl complex **2** is deshielded relative to that of the tetracarbonyl complex **1**, apparently because of the presence of the weakly coordinated acetonitrile ligand in place of a strong π-acceptor carbonyl ligand.

The tricarbonyl complex **2** was heated under reflux in acetonitrile for 1 h to find out whether the pyrazolyl nitrogen would replace the coordinated acetonitrile ligand. After 1 h, signals resulting from the starting material **2** had disappeared from the <sup>31</sup>P NMR spectrum, and only the signals from the tetracarbonyl complex **1** were observed. The tricarbonyl complex **2** is not stable in hot acetonitrile solution and undergoes a redistribution to give the stable tetracarbonyl complex **1**. In contrast, heating a solution of **2** in heptane (a non-coordinating solvent) gives an insoluble pale-yellow compound **2a** in low yield (20%) along with the tetracarbonyl complex (**1**) as the major product. Com-

pound **2a** shows three new carbonyl stretching vibrations in the IR spectrum at 1925, 1832 and 1814 cm<sup>-1</sup>. This compound also exhibits NMR spectroscopic features different from those of **2** (see section 2). In its mass spectrum the highest peak at *m/z* = 627 can be assigned to the molecular ion *fac*-[Mo(CO)<sub>3</sub>(L)]<sup>+</sup>. These results indicate that the diphosphazane in **2a** acts as a tridentate ligand, bonded through the two phosphorus atoms and the pyrazolyl pyridinic nitrogen atom. The shift in the carbonyl stretching vibration from 1791 cm<sup>-1</sup> for compound **2**, to 1814 cm<sup>-1</sup> for compound **2a**, supports the above conclusion that the σ-donor acetonitrile ligand is replaced by the weakly π-accepting pyrazolyl nitrogen. Pyrolysis of the tetracarbonyl complex **1** for 24 h in boiling heptane also gives **2a**.

The <sup>31</sup>P NMR spectrum of **2a** shows an AX pattern. As a result of the tridentate coordination of the diphosphazane ligand *via* the two phosphorus and pyridinic nitrogen atoms, the δ<sub>p</sub> values for PPh<sub>2</sub> and PPh(DMP) phosphorus nuclei are very different from those observed for **2**. More significantly, the pyrazolyl substituted phosphorus in **2a** is deshielded to about 8 ppm, whereas the PPh<sub>2</sub> phosphorus is appreciably shielded (about 20 ppm). Nevertheless the PPh<sub>2</sub> phosphorus in **2a** is deshielded relative to that in the free ligand.

#### 4.2. X-ray structure of **2**

The solid-state structure of **2** is established by X-ray crystallography. A perspective view of the molecule is shown in Fig. 2. Selected bond lengths and bond angles are shown in Table 4. The diphosphazane ligand is coordinated to molybdenum in a chelating mode utilizing its two phosphorus donor sites. The pyrazolyl nitrogen is not involved in coordination to the metal. The

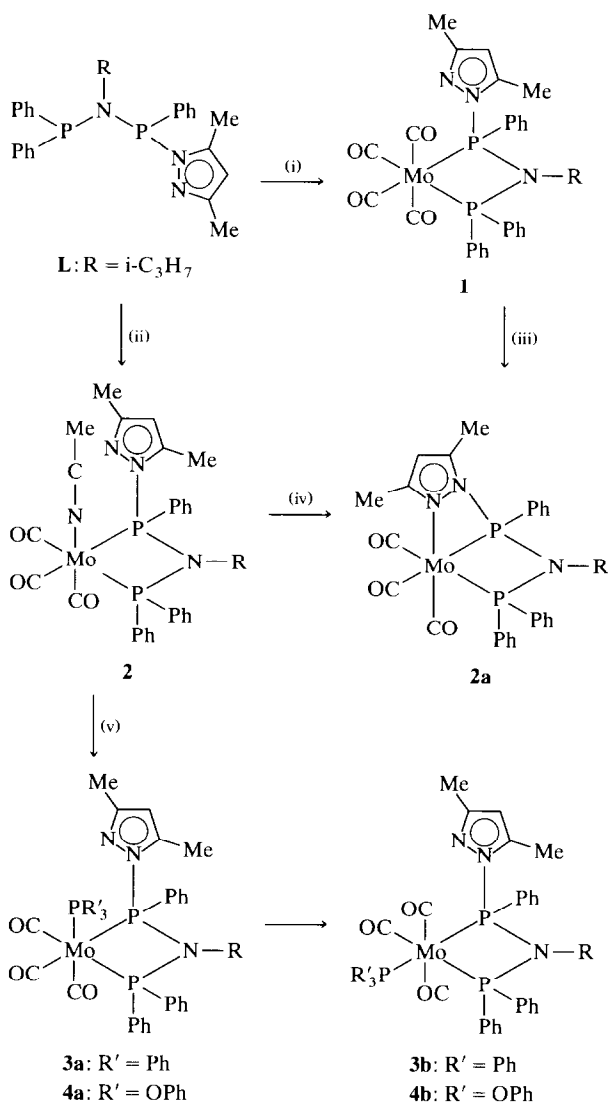
TABLE 3. <sup>31</sup>P NMR data for complexes **1–4b** <sup>a</sup>

| Compound   | PPh <sub>2</sub> |      | PPh(DMP) |      | <sup>2</sup> J <sub>PP</sub> (Hz) |
|--|------------------|------|----------|------|-----------------------------------|
|  | δ                | Δδ   | δ        | Δδ   |                                   |
| Ph <sub>2</sub> PN(Pr)P(Ph)(DMP)(L)                    | 43.8             | –    | 71.6     | –    | 29.8                              |
| <i>cis</i> -[Mo(CO) <sub>4</sub> (L)] ( <b>1</b> )     | 85.3             | 41.5 | 110.6    | 39.0 | 10.8                              |
| <i>fac</i> -Mo(CO) <sub>3</sub> (MeCN)(L) ( <b>2</b> ) | 89.5             | 45.7 | 111.0    | 39.4 | 25.0                              |
| <i>fac</i> -Mo(CO) <sub>3</sub> (L) ( <b>2a</b> )      | 69.3             | 25.5 | 118.6    | 47.0 | 25.6                              |

| Compound               | δ                   |                     |                      |             | <sup>2</sup> J <sub>PP</sub> (Hz) |      |       |
|------------------------|---------------------|---------------------|----------------------|-------------|-----------------------------------|------|-------|
|                        | PR <sub>3</sub>     | PR <sub>3</sub> (A) | PPh <sub>2</sub> (M) | PPh(DMP)(X) | AM                                | MX   | AX    |
| <b>3a</b> <i>fac</i> - | PPh <sub>3</sub>    | 34.5                | 88.5                 | 111.0       | 22.6                              | 31.9 | 29.0  |
| <b>3b</b> <i>mer</i> - | PPh <sub>3</sub>    | 53.5                | 77.8                 | 128.1       | 26.4                              | 10.0 | 88.0  |
| <b>4a</b> <i>fac</i> - | P(OPh) <sub>3</sub> | 169.5               | 90.2                 | 96.1        | 34.7                              | 7.0  | 143.0 |
| <b>4b</b> <i>mer</i> - | P(OPh) <sub>3</sub> | 169.7               | 86.1                 | 120.1       | 37.0                              | 8.8  | 164.8 |

<sup>a</sup> Measured at 81 MHz in toluene for compounds **2–4b**, and in dichloromethane for **L** and **1**; Δδ = δ(complex) - δ(ligand)



Scheme 1. (i) Mo(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>; (ii) Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>; (iii) heptane 96°C, 24 h; (iv) heptane 96°C, 1 h; (v) PR<sub>3</sub> (R' = Ph or OPh).

acetonitrile ligand is present in the axial position *trans*- to a CO atom, and the other two carbonyls are present *trans*- to phosphorus atoms.

The coordination geometry of the complex is that of an octahedron with a slight distortion because of the small bite angle of the diphosphazane ligand (P1MoP2

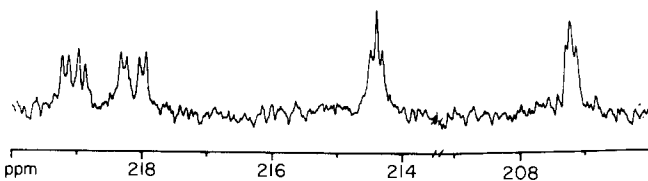


Fig. 1. The <sup>13</sup>C NMR (100.6 MHz) spectrum (<sup>13</sup>CO region only) of *cis*-[Mo(CO)<sub>4</sub>(L)] (**1**).

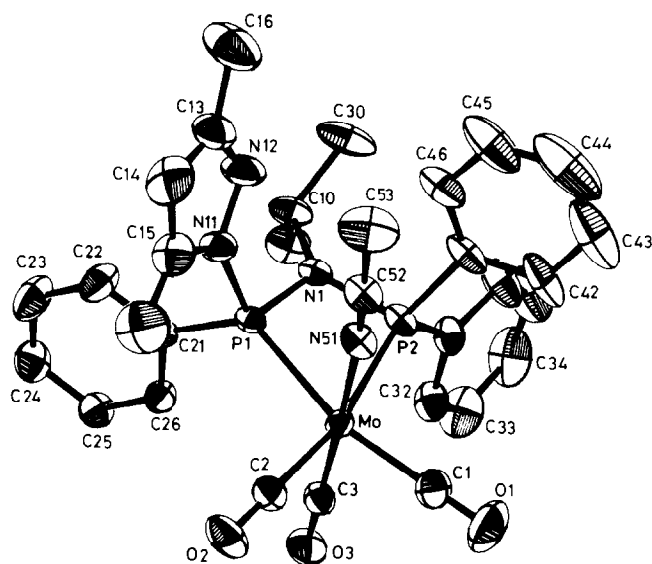


Fig. 2. ORTEP diagram of *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (**2**).

angle is 64.2(1)°. The P–N–P angle is 102.5(2)°, close to that observed for the tetracarbonyl molybdenum diphosphazane complexes *cis*-[Mo(CO)<sub>4</sub>RN(PX<sub>2</sub>)<sub>2</sub>] [**2b**]. The geometry of the complex is similar to that observed for the analogous dppm tungsten complex *fac*-[W(CO)<sub>3</sub>(MeCN)(dppm)] [**12**].

The P1–N1 bond distance (1.689(4) Å) is slightly shorter than the P2–N1 distance (1.715(4) Å). This difference is presumably because of the increased π-bonding in the P(1)–N(1) segment arising from the increased electron withdrawing effect of the dimethyl pyrazole group, as observed for the unsymmetrical diphosphazane ligand Ph<sub>2</sub>PN(<sup>i</sup>Pr)P(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) [**2a**]. The Mo–P1 bond length (2.482(3) Å) at the pyrazole-substituted phosphorus is shorter than the Mo–P2 bond length (2.515(2) Å) at the diphenyl-substituted phosphorus; the distances are comparable to the M–P distances in *cis*-[Mo(CO)<sub>4</sub>{PhN(P(NHPh)<sub>2</sub>)<sub>2</sub>}] [**13**] and *cis*-[W(CO)<sub>4</sub>{<sup>i</sup>PrN(PPh<sub>2</sub>)<sub>2</sub>}] [**2b**] respectively. In the tungsten dppm complex the mean W–P bond length is (2.51 Å). Evidently the pyrazolyl–phosphorus acts as a slightly stronger π-acceptor ligand than the diphenyl-substituted phosphorus. The three Mo–CO bond lengths are 1.988(6), 1.973(6) and 1.934(6) Å, where the shortest distance pertains to the carbonyl ligand located *trans*- to the acetonitrile group. The axial acetonitrile ligand is slightly tilted towards the diphosphazane ligand (mean N–Mo–P 85°); this tilt is larger than that observed for *fac*-[W(CO)<sub>3</sub>(MeCN)(dppm)]. The Mo–N bond distance, 2.221(5) Å, is also longer than the corresponding distance in the tungsten dppm complex, 2.190(5) Å, suggesting that the acetonitrile ligand in **2** would be more labile.

### 4.3. Reactions of 2 with $PR_3$

The acetonitrile complex **2** reacts with triphenylphosphine or triphenylphosphite to yield initially *fac*-[Mo(CO)<sub>3</sub>(PR<sub>3</sub>)(L)] (**3a** or **4a**), which undergoes intramolecular rearrangement to give the *mer*-[Mo(CO)<sub>3</sub>(PR<sub>3</sub>)(L)] (**3b** or **4b**) complex (Scheme 1). The reactions were monitored by <sup>31</sup>P NMR spectroscopy; the *fac*- and *mer*- complexes give clear AMX type spectra (Fig. 3). The intramolecular *fac* → *mer*- rearrangement is fast in the case of the PPh<sub>3</sub> complex, and is essentially complete in 6 h at room temperature. In addition to the two AMX patterns, another AX pattern is observed that arises from *cis*-[Mo(CO)<sub>4</sub>(L)] (**1**) formed by the decomposition of the complex **2**.

In the reaction of P(OPh)<sub>3</sub> with **2**, even after one day in solution at room temperature, the peaks result-

TABLE 4. Selected bond distances (Å) and bond angles (°) in *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (**2**)

| Bond distances (Å) |          | Bond angles (°) |          |
|--------------------|----------|-----------------|----------|
| Mo-P1              | 2.482(2) | C3-Mo-N51       | 177.7(2) |
| Mo-P2              | 2.515(2) | C2-Mo-N51       | 93.7(2)  |
| Mo-C1              | 1.988(6) | C2-Mo-C3        | 84.1(2)  |
| Mo-C2              | 1.973(6) | C1-Mo-N51       | 93.2(2)  |
| Mo-C3              | 1.934(6) | C1-Mo-C3        | 87.4(3)  |
| Mo-N51             | 2.221(5) | C1-Mo-C2        | 92.3(3)  |
| P1-N1              | 1.689(4) | P2-Mo-N51       | 86.1(1)  |
| P1-N11             | 1.760(4) | P2-Mo-C3        | 95.9(2)  |
| P1-C21             | 1.817(5) | P2-Mo-C2        | 167.1(2) |
| N1-P2              | 1.715(4) | P2-Mo-C1        | 100.6(2) |
| N1-C10             | 1.509(7) | P1-Mo-N51       | 84.2(1)  |
| P2-C31             | 1.827(5) | P1-Mo-C3        | 95.8(2)  |
| P2-C41             | 1.815(6) | P1-Mo-C2        | 102.9(2) |
| C1-O1              | 1.143(8) | P1-Mo-C1        | 164.6(2) |
| C2-O2              | 1.156(7) | P1-Mo-P2        | 64.2(1)  |
| C3-O3              | 1.174(6) | Mo-P1-C21       | 127.3(2) |
| N11-N12            | 1.388(7) | Mo-P1-N11       | 118.7(2) |
| N11-C15            | 1.353(9) | Mo-P1-N1        | 97.4(2)  |
| N12-C13            | 1.340(9) | N11-P1-C21      | 101.0(2) |
| C21-C22            | 1.388(7) | N1-P1-C21       | 105.9(2) |
| N51-C52            | 1.123(7) | N1-P1-N11       | 103.7(2) |
|                    |          | P1-N1-C10       | 122.1(4) |
|                    |          | P1-N1-P2        | 102.5(2) |
|                    |          | P2-N1-C10       | 134.9(4) |
|                    |          | Mo-P2-N1        | 95.5(2)  |
|                    |          | N1-P2-C41       | 109.9(2) |
|                    |          | N1-P2-C31       | 105.9(2) |
|                    |          | Mo-P2-C41       | 115.1(2) |
|                    |          | Mo-P2-C31       | 126.5(2) |
|                    |          | C31-P2-C41      | 102.7(3) |
|                    |          | Mo-C1-O1        | 177.2(6) |
|                    |          | Mo-C2-O2        | 175.3(5) |
|                    |          | Mo-C3-O3        | 176.4(5) |
|                    |          | P1-N11-C15      | 128.4(4) |
|                    |          | P1-N11-N12      | 119.7(4) |
|                    |          | P1-C21-C26      | 118.8(3) |
|                    |          | P1-C21-C22      | 123.7(4) |
|                    |          | Mo-N51-C52      | 172.5(4) |

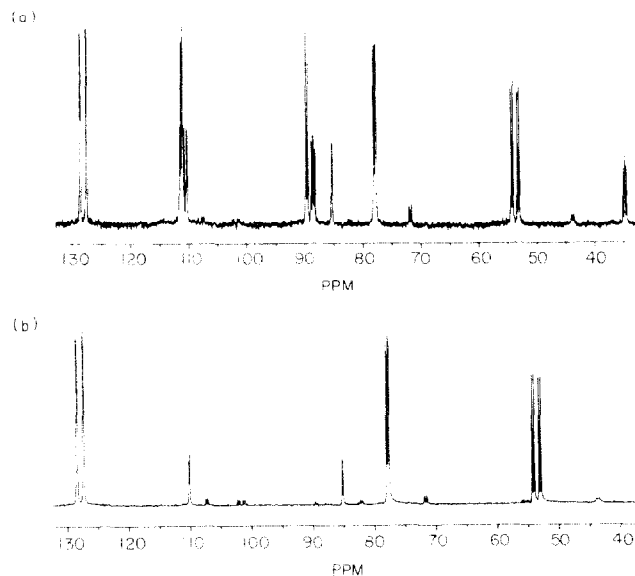


Fig. 3. The <sup>31</sup>P NMR spectrum (81 MHz) of the products of the reaction of *fac*-[Mo(CO)<sub>3</sub>(MeCN)(L)] (**2**) with PPh<sub>3</sub> in benzene: (a) after 30 min; (b) after 6 h. (For assignment of the observed resonances see Table 3).

ing from the initially formed *fac*- isomer are still seen. Complete conversion can be achieved by heating the solution under reflux in benzene for 4 h. The difference in the rate of *fac* → *mer*- rearrangement for the PPh<sub>3</sub> and P(OPh)<sub>3</sub> ligands parallels the relative rate of intramolecular isomerization of [M(CO)<sub>4</sub>L<sub>2</sub>] {L = PR<sub>3</sub>, P(OR)<sub>3</sub>} complexes [14]. There are insufficient data to allow clear separation of the electronic and steric factors responsible for this difference between PR<sub>3</sub> and P(OR)<sub>3</sub> type ligands in isomerization reactions [14] but it is conceivable that steric factors dominate in the present case. (The Tolman cone angle for PPh<sub>3</sub> is 145°, compared with 121° for P(OPh)<sub>3</sub> [15]).

In the *mer*- isomers, the DMP-substituted phosphorus is *trans*- to the PR<sub>3</sub>; this is obvious from the P-P coupling constants observed (Table 3).

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