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#### Key indicators

Single-crystal synchrotron study  
 $T = 120$  K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.059  
 $wR$  factor = 0.164  
 Data-to-parameter ratio = 25.3

For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

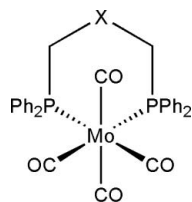
## {*N,N*-Bis[(diphenylphosphino)methyl]aniline}- tetracarbonylmolybdenum(0)

The title compound,  $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PCH}_2\text{N}(\text{Ph})\text{CH}_2\text{PPh}_2\}]$  or  $[\text{Mo}(\text{C}_{32}\text{H}_{29}\text{NP}_2)(\text{CO})_4]$ , is a tetracarbonylmolybdenum(0) complex of a chelating ditertiary phosphine with a P—C—N—C—P backbone. The geometry at the Mo centre is octahedral, while both diphenylphosphino centres coordinate in a *cis* fashion.

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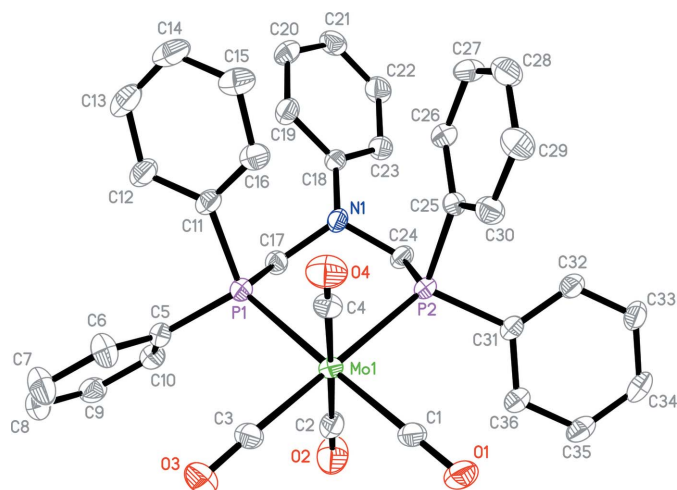
### Comment

Organometallic compounds containing the group 6 metals Mo, Cr and W have been extensively studied over the past few decades for a variety of substitution reactions, one example being with phosphine ligands. Ligand substitution reactions have been accomplished in several ways, including under thermal or photolysis conditions, or displacement of labile precursors [*e.g.* piperidine, norbornadiene (nbd), THF,  $\text{CH}_3\text{CN}$ ] from appropriate Mo starting materials. Thus, neutral, octahedral compounds of the general type  $\text{Mo}(\text{CO})_n(\text{PR}_3)_{6-n}$  ( $n = 3-5$ ) can be obtained using monodentate tertiary phosphines. Of these, one particular class of compound of interest are the tetracarbonylmolybdenum(0) diphosphine complexes  $\text{Mo}(\text{CO})_4(\text{P}-\text{P})$  [P—P is a symmetric (Bookham *et al.*, 1993; Fernández *et al.*, 1996; Gaw *et al.*, 2000, 2002; Powell *et al.*, 1992) or non-symmetric ligand (Affandi *et al.*, 1989)]. Recent interest has also focused on tetracarbonylmolybdenum(0) complexes with bidentate ligands bearing group 15 (Heinze & Jacob, 2002) or group 16 donor centres (Heuer *et al.*, 2002). We describe here the synthesis of  $\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PCH}_2\text{N}(\text{Ph})\text{CH}_2\text{PPh}_2\}$ , (1), and its single-crystal X-ray structure.



- (1) X =  $\text{NC}_6\text{H}_5$
- (2) X =  $\text{CH}_2$
- (3) X =  $\text{CCH}_2$

The molecular structure of compound (1) is shown in Fig. 1, with selected geometric data in Table 1, together with those for the related compounds  $\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}$ , (2) (Ueng & Hwang, 1991), and  $\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PCH}_2\text{C}(\text{CH}_2)\text{CH}_2\text{PPh}_2\}$ , (3) (Bookham *et al.*, 1993). The structure of (1) comprises a *cis*-chelating  $\text{Ph}_2\text{PCH}_2\text{N}(\text{Ph})\text{CH}_2\text{PPh}_2$  ligand and four terminal CO ligands. The Mo—P bond lengths in (1) are slightly shorter than those of (2) and (3). The variations in


**Figure 1**

The molecular structure of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity.

Mo–C distances are as expected for the different  $\pi$ -acceptor properties of CO and –PPh<sub>2</sub> groups. The Mo–C–O bond angles are all close to linear. The P–Mo–P bite angle is similar to those of (2) and (3). As anticipated, this bite angle is enlarged with respect to those found in complexes of the type Mo(CO)<sub>4</sub>[Ph<sub>2</sub>PN(R)PPh<sub>2</sub>] [*R* = H, P–Mo–P 65.29 (6)°; *R* = 2-MeOC<sub>6</sub>H<sub>4</sub>, P–Mo–P = 65.78 (2)°] in which the chelating Ph<sub>2</sub>PN(R)PPh<sub>2</sub> ligands adopt near planar four-membered ring conformations (Gaw *et al.*, 2000; Knorr & Strohmann, 1999). The six-membered chelate ring in (1) adopts a chair conformation with N1 above the P<sub>2</sub>C<sub>2</sub> mean plane by 0.736 (3) Å and Mo below the plane by 0.986 (2) Å. The Mo–P–C–N–C–P metallacyclic ring is similar to those previously seen for other M–P–C–N–C–P compounds (Zhang *et al.*, 2002). The *N*-arene is twisted about the N1–C18 axis by 47.2 (2)° with respect to the central heterocycle.

## Experimental

A solution of Mo(CO)<sub>4</sub>(nbd) (0.0613 g, 0.206 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>N(Ph)CH<sub>2</sub>PPh<sub>2</sub> (0.101 g, 0.206 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was stirred for 12 h at room temperature under N<sub>2</sub>. The volume was reduced to ca 2–3 ml under reduced pressure. Addition of diethyl ether (20 ml) and petroleum ether (b.p. 333–353 K, 10 ml) gave a pale-yellow solid which was collected by suction filtration. Yield 0.071 g, 50%. X-ray quality crystals of (1) were obtained by slow evaporation of the CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether/petroleum ether filtrate. Calculated for C<sub>36</sub>H<sub>29</sub>MoNO<sub>4</sub>P<sub>2</sub>·0.5C<sub>6</sub>H<sub>14</sub>: C 63.25, H 4.90, N 1.89; found: C 63.09, H 4.75, N 1.87%.

### Crystal data

[Mo(C <sub>32</sub> H <sub>29</sub> NP <sub>2</sub> )(CO) <sub>4</sub> ]	<i>V</i> = 1610.84 (17) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 697.48	<i>Z</i> = 2
Triclinic, <i>P</i> 1̄	<i>D<sub>x</sub></i> = 1.438 Mg m <sup>−3</sup>
<i>a</i> = 10.2072 (6) Å	Synchrotron radiation
<i>b</i> = 11.2800 (7) Å	$\lambda$ = 0.6910 Å
<i>c</i> = 14.5527 (9) Å	$\mu$ = 0.55 mm <sup>−1</sup>
$\alpha$ = 100.047 (1)°	<i>T</i> = 120 (2) K
$\beta$ = 93.162 (1)°	Plate, colourless
$\gamma$ = 101.316 (1)°	0.15 × 0.06 × 0.03 mm

### Data collection

Bruker APEX II CCD diffractometer	19074 measured reflections
$\omega$ scans	10047 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	8204 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>T</i> <sub>min</sub> = 0.923, <i>T</i> <sub>max</sub> = 0.984	<i>R</i> <sub>int</sub> = 0.065
	$\theta$ <sub>max</sub> = 31.0°

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )] = 0.059	<i>w</i> = 1/[ $\sigma^2(F_o^2) + (0.0783P)^2$ ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.164	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 1.00	( $\Delta\sigma$ ) <sub>max</sub> = 0.001
10047 reflections	$\Delta\rho$ <sub>max</sub> = 0.70 e Å <sup>−3</sup>
397 parameters	$\Delta\rho$ <sub>min</sub> = −0.97 e Å <sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (1) and a comparison with reported compounds (2) and (3).

	(1)	(2)	(3)
Mo–C ( <i>trans</i> to C)	2.016 (3)/2.043 (3)	2.035 (7)/2.023 (7)	2.016 (4)/2.030 (4)
Mo–C ( <i>trans</i> to P)	2.007 (3)/1.994 (3)	1.968 (5)/1.968 (5)	1.999 (4)/1.986 (4)
Mo–P	2.5005 (8)/2.4986 (8)	2.538 (1)/2.538 (1)	2.5199 (11)/2.5094 (13)
C–Mo–C ( <i>trans</i> to C)	178.21 (12)	174.8 (3)	171.0 (2)
C–Mo–C ( <i>cis</i> , av.)	89.72 (13)	88.7 (2)	88.3 (2)
P–Mo–P	86.75 (2)	89.74 (4)	85.14 (4)

(1) This work. (2) Ueng & Hwang (1991). (3) Bookham *et al.* (1993).

H atoms were positioned geometrically (C–H = 0.95 Å for aryl H and 0.99 Å for methylene H), and refined using a riding model. *U*<sub>iso</sub>(H) values were set to 1.2*U*<sub>eq</sub>(C).

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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## References

- Affandi, S., Nelson, J. H. & Fischer, J. (1989). *Inorg. Chem.* **28**, 4536–4544.
- Bookham, J. L., Clegg, W., McFarlane, W. & Raper, E. S. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3567–3573.
- Bruker (2000). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2005). APEX2 and SAINT (Version 7.23A). Bruker AXS Inc., Madison, Wisconsin, USA.
- Fernández, E. J., Gimeno, M. C., Jones, P. G., Laguna, A., Laguna, M. & Olmos, E. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3603–3608.
- Gaw, K. G., Smith, M. B. & Slawin, A. M. Z. (2000). *New J. Chem.* **24**, 429–435.
- Gaw, K. G., Smith, M. B. & Steed, J. W. (2002). *J. Organomet. Chem.* **664**, 294–297.
- Heinze, K. & Jacob, V. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2379–2385.
- Heuer, B., Matthews, M. L., Reid, G. & Ripley, M. (2002). *J. Organomet. Chem.* **655**, 55–62.
- Knorr, M. & Strohmann, C. (1999). *Organometallics*, **18**, 248–257.

Powell, J., Lough, A. & Wang, F. (1992). *Organometallics*, **11**, 2289–2295.  
Sheldrick, G. M. (2004). *SADABS*. Version 2004/1. University of Göttingen, Germany.

Ueng, C.-H. & Hwang, G.-Y. (1991). *Acta Cryst.* **C47**, 522–525.  
Zhang, J., Vittal, J. J., Henderson, W., Wheaton, J. R., Hall, I. H., Hor, T. S. A. & Yan, Y. K. (2002). *J. Organomet. Chem.* **650**, 123–132.