Smith, G. D., Fanwick, P. E. & Rothwell, I. P. (1990). *Inorg. Chem.* **29**, 3221–3226.
Sutton, L. E. (1958). *Tables of Interatomic Distances and Configurations in Molecules and Ions.* Special Publication No. 11. London: The Chemical Society.
Thomas, I. M. (1961). *Can. J. Chem.* **39**, 1386–1388.

*Acta Cryst.* (1994). C**50**, 898–899

# $[Mo\{P(Ph)_2OC_6H_3(Ph)(\eta^6\text{-}Ph)\}(CO)_2]$

DAN JAQUES, JANET R. CLARK, DIEGO E. CHEBI, PHILLIP E. FANWICK AND IAN P. ROTHWELL*

*Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393, USA*

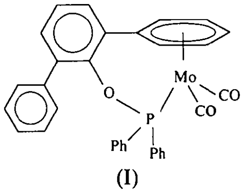
(*Received* 25 *February* 1993; *accepted* 22 *October* 1993)

## Abstract

Dicarbonyl[(2-$\eta^6$-phenyl-6-phenylphenoxy)diphenylphosphine-*P*]molybdenum contains a new phosphine ligand bound to Mo through the O atom and *via* an $\eta^6$-arene interaction. A 'three-legged-piano-stool' geometry is present with Mo—P = 2.354 (1) Å, Mo—C(carbonyl) = 1.942 (4) and 1.944 (5) Å and Mo—C(aryl) = 2.295 (4)–2.339 (4) Å.

## Comment

Previous work by our group has shown that the molecule 2,6-diphenylphenol can react with $Mo(CO)_6$ to produce the complex $[Mo(HOC_6H_3Ph\text{-}\eta^6\text{-}Ph)(CO)_3]$ (Kerschner, Torres, Fanwick & Rothwell, 1989) in which the metal is $\pi$ bonded to one of the substituent arene rings of the aryl alcohol. The phenolic group remains unreacted. As an extension of this work we have synthesized the new phosphine ligand (2,6-diphenylphenoxy)diphenylphosphine, $[P(Ph)_2OC_6H_3(Ph)_2]$. In this case the initial coordination of the P atom to the metal should allow chelation *via* an $\eta^6$ interaction with either the central phenoxy ring or with one of the substituent aryl rings. We report here the structure of the product (I) obtained on reacting this ligand with $[Mo(CO)_6]$ in which chelation occurs to one of the substituent rings.



(I)

A view of the molecule is given in Fig. 1. The molecule can be seen to adopt a 'three-legged-piano-stool' geometry about the metal center. The presence of the chelate ring between the donor P atom and the $\eta^6$-bonded arene ring does not appear to distort the geometry from that typical for the ubiquitous $[(\eta^6\text{-arene})M(L)_3]$ ($M$ = Cr, Mo, W) class of compounds. The Mo—C(arene) distances fall in the narrow range of 2.295 (4) Å to the *ipso* C atom to 2.339 (4) Å to C(123). These distances are typical of molybdenum $\eta^6$-arene complexes of this type (Kerschner, Torres, Fanwick & Rothwell, 1989).

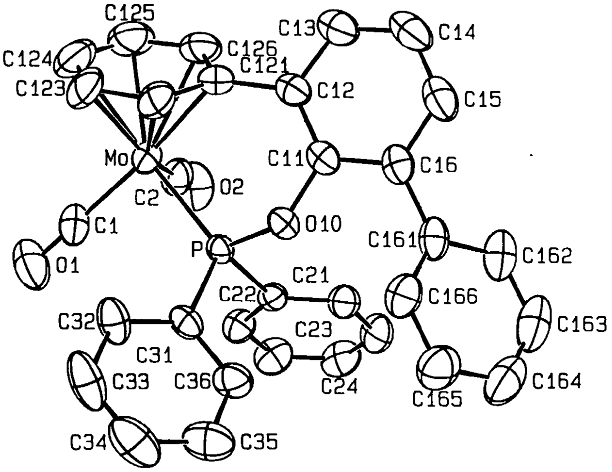


Fig. 1. A view of the molecule emphasizing the central coordination sphere. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

## Experimental

$[Mo(CO)_2\{P(Ph)_2OC_6H_3(Ph)_2\}]$ was obtained in low yield by refluxing a mixture of $[Mo(CO)_6]$ (0.61 g, 2.3 mmol) and $[P(Ph)_2OC_6H_3(Ph)_2]$ (1.00 g, 2.33 mmol) in octane for 9 h. The resulting crude product was recrystallized from a chloroform solution layered with hexane.

*Crystal data*

$[Mo(C_{30}H_{23}OP)(CO)_2]$
$M_r$ = 581.45
Orthorhombic
*Pbca*
$a$ = 8.942 (2) Å
$b$ = 20.445 (2) Å
$c$ = 28.448 (4) Å
$V$ = 5200 (2) Å$^3$
$Z$ = 8
$D_x$ = 1.488 Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 19–23°
$\mu$ = 0.583 mm$^{-1}$
$T$ = 293 K
Needle
0.46 × 0.38 × 0.22 mm
Yellow

*Data collection*

Enraf-Nonius CAD-4 diffractometer

2629 observed reflections [$F > 3\sigma(F)$]

$\omega$-$2\theta$ scans
Absorption correction:
empirical (*DIFABS*: Walker & Stuart, 1983)
$T_{\min}$ = 0.81, $T_{\max}$ = 1.00
3854 measured reflections
3854 independent reflections

$\theta_{\max}$ = 22.5°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 30$
3 standard reflections
frequency: 83 min
intensity variation: <5%

*Refinement*

Refinement on $F$
$R$ = 0.028
$wR$ = 0.036
$S$ = 0.992
2629 reflections
334 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + (0.02F)^2 + 1 - F]$
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.18 e Å$^{-3}$
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Mo | 0.17105 (4) | 0.06072 (2) | 0.10051 (1) | 3.009 (6) |
| P | −0.0037 (1) | 0.14584 (4) | 0.10987 (3) | 2.33 (2) |
| O(1) | −0.0685 (4) | −0.0296 (2) | 0.0553 (1) | 6.09 (8) |
| O(2) | 0.0770 (4) | −0.0049 (1) | 0.1943 (1) | 5.59 (7) |
| O(10) | 0.0682 (2) | 0.2211 (1) | 0.11141 (7) | 2.65 (5) |
| C(1) | 0.0215 (5) | 0.0046 (2) | 0.0718 (1) | 3.82 (9) |
| C(2) | 0.1103 (5) | 0.0200 (5) | 0.1592 (1) | 3.85 (9) |
| C(11) | 0.2011 (4) | 0.2432 (2) | 0.1305 (1) | 2.66 (7) |
| C(12) | 0.3323 (4) | 0.2074 (2) | 0.1287 (1) | 3.05 (8) |
| C(13) | 0.4605 (4) | 0.2334 (2) | 0.1499 (1) | 4.05 (9) |
| C(14) | 0.4582 (5) | 0.2953 (2) | 0.1698 (2) | 4.8 (1) |
| C(15) | 0.3283 (5) | 0.3307 (2) | 0.1695 (1) | 4.29 (9) |
| C(16) | 0.1962 (4) | 0.3058 (2) | 0.1510 (1) | 2.98 (7) |
| C(21) | −0.1228 (4) | 0.1468 (2) | 0.1621 (1) | 2.46 (7) |
| C(22) | −0.2083 (4) | 0.0918 (2) | 0.1713 (1) | 3.29 (8) |
| C(23) | −0.2939 (5) | 0.0877 (2) | 0.2115 (1) | 4.25 (9) |
| C(24) | −0.2948 (5) | 0.1390 (2) | 0.2428 (1) | 4.29 (9) |
| C(25) | −0.2144 (5) | 0.1947 (2) | 0.2334 (1) | 4.22 (9) |
| C(26) | −0.1278 (4) | 0.1988 (2) | 0.1934 (1) | 3.24 (8) |
| C(31) | −0.1358 (4) | 0.1673 (2) | 0.0633 (1) | 2.74 (7) |
| C(32) | −0.1265 (5) | 0.1379 (2) | 0.0196 (1) | 4.02 (9) |
| C(33) | −0.2261 (6) | 0.1576 (2) | −0.0157 (1) | 5.6 (1) |
| C(34) | −0.3316 (5) | 0.2047 (2) | −0.0070 (1) | 5.6 (1) |
| C(35) | −0.3398 (5) | 0.2337 (2) | 0.0363 (2) | 5.0 (1) |
| C(36) | −0.2423 (4) | 0.2152 (2) | 0.0714 (1) | 3.67 (8) |
| C(121) | 0.3458 (4) | 0.1426 (2) | 0.1052 (1) | 3.38 (8) |
| C(122) | 0.3076 (4) | 0.1350 (2) | 0.0564 (1) | 3.91 (9) |
| C(123) | 0.3259 (5) | 0.0741 (2) | 0.0349 (2) | 5.0 (1) |
| C(124) | 0.3780 (5) | 0.0200 (2) | 0.0611 (2) | 5.8 (1) |
| C(125) | 0.4179 (5) | 0.0267 (2) | 0.1078 (2) | 5.7 (1) |
| C(126) | 0.4040 (4) | 0.0888 (2) | 0.1296 (2) | 4.5 (1) |
| C(161) | 0.0558 (4) | 0.3436 (2) | 0.1553 (1) | 3.19 (8) |
| C(162) | 0.0185 (5) | 0.3717 (2) | 0.1987 (1) | 4.5 (1) |
| C(163) | −0.1135 (6) | 0.4054 (2) | 0.2043 (2) | 5.6 (1) |
| C(164) | −0.2113 (5) | 0.4128 (2) | 0.1679 (2) | 5.4 (1) |
| C(165) | −0.1768 (5) | 0.3859 (2) | 0.1245 (2) | 4.8 (1) |
| C(166) | −0.0440 (5) | 0.3524 (2) | 0.1184 (1) | 3.86 (9) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Mo—P | 2.354 (1) | Mo—C(124) | 2.318 (5) |
| Mo—C(1) | 1.942 (4) | Mo—C(125) | 2.324 (5) |
| Mo—C(2) | 1.944 (5) | Mo—C(126) | 2.313 (4) |
| Mo—C(121) | 2.295 (4) | C(1)—O(1) | 1.165 (5) |
| Mo—C(122) | 2.318 (4) | C(2)—O(2) | 1.158 (5) |
| Mo—C(123) | 2.339 (4) | | |
| P—Mo—C(1) | 91.6 (1) | Mo—C(1)—O(1) | 178.8 (4) |
| P—Mo—C(2) | 91.9 (1) | Mo—C(2)—O(2) | 178.5 (4) |
| C(1)—Mo—C(2) | 85.2 (2) | Mo—P—O(10) | 115.39 (9) |
| P—O(10)—C(11) | 130.1 (2) | | |

The structure was solved using the Patterson heavy-atom method, which revealed the position of the Mo atom. The remaining atoms were located using *DIRDIF* (Beurskens *et al.*, 1984) and in succeeding difference Fourier syntheses. H atoms were located and included in the structure-factor calculations, but their positions were not refined. The structure was refined by full-matrix least squares where the function minimized was $\Sigma w(|F_o|-F_c|)^2$ and the weight, $w$, was defined according to the method of Killean & Lawrence (1969) with terms of 0.20 and 1.0. Scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in $F_c$ (Ibers & Hamilton, 1964); the values for $f'$ and $f''$ were those of Cromer (1974). There were three correlation coefficients greater than 0.50. The highest peak in the final difference Fourier map had a height of 0.22 e Å$^{-3}$ with an estimated error based on $\Delta F$ (Cruickshank, 1949) of 0.05. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using *SDP* (Frenz, 1978).

We thank the National Science Foundation (grant No. CHE-8915573) for support of this research.

---

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71781 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1064]

---

## References

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A., Noordik, J. H., Beurskens, G., Parthasarthi, V., Bruins Slot, H. J., Haltiwanger, R. C., Strumpel, M. & Smits, J. M. M. (1984). *DIRDIF. Technical Report* 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academics Publishers, Dordrecht.)

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 154–157.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.

Kerschner, J. L., Torres, E. M., Fanwick, P. E. & Rothwell, I. P. (1989). *Organometallics*, **8**, 1424–1431.

Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.