Cotter, W. D. & Bercaw, J. E. (1993). Unpublished results.
Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Duchamp, D. J. (1964). *Am. Crystallogr. Assoc. Meet., Bozeman, Montana*, Paper B14, p. 29.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Marsh, R. E., Schaefer, W. P., Coughlin, E. B. & Bercaw, J. E. (1992). *Acta Cryst.* C**48**, 1773–1776.
Schaefer, W. P., Köhn, R. D. & Bercaw, J. E. (1992). *Acta Cryst.* C**48**, 251–253.
Shapiro, P. J., Bunel, E., Schaefer, W. P. & Bercaw, J. E. (1990). *Organometallics*, **9**, 867–869.

Acta Cryst. (1993). C**49**, 1492–1493

A Second Crystal Form of Bis-μ-[bis(dimethylphosphino)methane]-bis(tricarbonylrhenium)(*Re*—*Re*), $Re_2(dmpm)_2(CO)_6$

David R. Tyler and Timothy J. R. Weakley

Department of Chemistry, University of Oregon, Eugene, OR 97403, USA

(*Received* 3 *August* 1992; *accepted* 15 *February* 1993)

Abstract

The second crystalline form, (II), of the title compound has the same space group ($P2_1/n$) as form (I) of known structure [Milder, Castellani, Weakley, Tyler, Miskowski, & Stiegman (1990). *J. Phys. Chem.* **94**, 6599–6603] but has a different packing. There is no disorder in (II) [in contrast to (I)] and the Re—Re bond length is significantly longer [3.126 (1) *versus* 3.105 (1) Å] despite the smaller (*ca* 1.3%) molecular volume.

Comment

The data crystal of form (II) came from the air-stable batch which earlier (Milder *et al.*, 1990) had afforded the crystal of form (I). Both forms have space group $P2_1/n$ with two molecules per cell, but they clearly differ in molecular packing. The unit cell of (II), and hence the molecular volume, is 1.3% smaller. Accurately centrosymmetric $Re_2(dmpm)_2(CO)_6$ moelcules with Re—Re bonds, bridging dmpm ligands, *trans* P—Re—P geometry, and generally similar dimensions, are present in both forms. The principal points of difference are as follows. The Re—Re bond in (II) [3.126 (1) Å] is significantly longer than in (I) [3.105 (1) Å]. Alternative positions for three of the five dmpm C atoms are discernible in (I), but (II) is free from disorder, a feature that accounts for the more efficient molecular packing in (II) and the fact that the C—P—C angles lie within the range 100.9–104.0 (6)° compared with 86–116 (1)° for the major conformer in (I).

A series of events led us to determine the unit cells of 20 crystals from a stable batch. Eight proved to be of form (II). The two forms, both amber prisms, cannot be readily distinguished under the polarizing microscope. We think it is unlikely that most workers routinely find the cell dimensions for several crystals from an apparently homogeneous sample if the first crystal proves suitable for data collection. We feel, therefore, that the presence of two crystalline forms in one batch may be more common than is generally supposed.

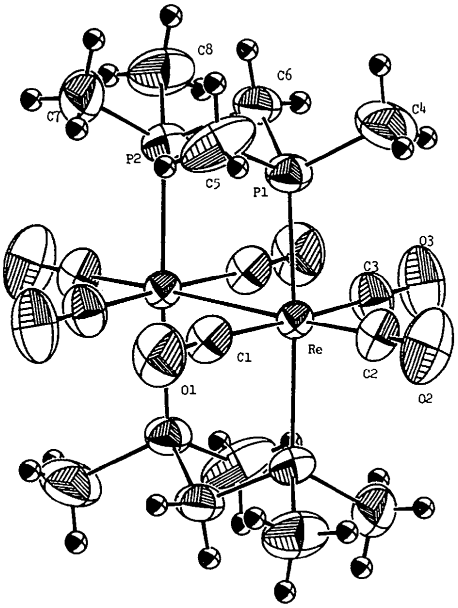

Fig. 1. View of the $Re_2(dmpm)_2(CO)_6$ molecule showing thermal ellipsoids.

Experimental

Crystal data

$[Re_2(C_5H_{14}P_2)_2(CO)_6]$
$M_r = 812.70$
Monoclinic
$P2_1/n$
$a = 9.938\ (2)$ Å
$b = 8.579\ (3)$ Å
$c = 14.783\ (3)$ Å
$\beta = 93.53\ (2)°$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.5\text{-}16.1°$
$\mu = 10.0\ \text{mm}^{-1}$
$T = 297$ K
Prism
0.30 × 0.25 × 0.15 mm

$V = 1258.0\ (9)$ Å^3
$Z = 2$
$D_x = 2.145$ Mg m^{-3}

Amber
Crystal source: recrystallized from chloroform/hexane

Data collection

Rigaku AFC-6R diffractometer
ω-2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.768$, $T_{\max} = 1.286$
2532 measured reflections
2220 independent reflections

1463 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.050$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 300 reflections intensity variation: ±1%

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.038$
$S = 1.55$
1463 reflections
127 parameters
H atoms riding, B(H) = 1.2 $B_{\rm eq}$(C)
$w = 1/[\sigma^2(F)+0.02F^2]$

$(\Delta/\sigma)_{\max} = 0.15$
$\Delta\rho_{\max} = 0.64$ e Å^{-3} (near Re)
$\Delta\rho_{\min} = -0.90$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Re	0.35525 (3)	0.50154 (5)	0.53574 (2)	0.0370 (3)
P(1)	0.2926 (3)	0.6832 (3)	0.4195 (2)	0.053 (1)
P(2)	0.5760 (3)	0.6894 (3)	0.3539 (2)	0.051 (1)
O(1)	0.2733 (8)	0.2280 (10)	0.4078 (5)	0.090 (6)
O(2)	0.0773 (8)	0.5147 (11)	0.6080 (6)	0.088 (6)
O(3)	0.4578 (8)	0.7735 (11)	0.6604 (6)	0.092 (6)
C(1)	0.3062 (10)	0.3342 (13)	0.4532 (6)	0.054 (6)
C(2)	0.1808 (10)	0.5124 (12)	0.5801 (6)	0.051 (5)
C(3)	0.4262 (10)	0.6699 (13)	0.6143 (7)	0.060 (7)
C(4)	0.1694 (12)	0.8299 (16)	0.4506 (8)	0.103 (10)
C(5)	0.2157 (12)	0.5958 (18)	0.3134 (7)	0.096 (9)
C(6)	0.4277 (10)	0.8028 (12)	0.3805 (6)	0.057 (7)
C(7)	0.5365 (12)	0.6273 (15)	0.2364 (7)	0.081 (8)
C(8)	0.6977 (11)	0.8444 (15)	0.3375 (8)	0.089 (9)

Table 2. *Geometric parameters* (Å, °)

Re—Re$^{\rm i}$	3.126 (1)	P(1)—C(6)	1.812 (10)
Re—P(1)	2.374 (3)	P(2)—C(6)	1.829 (10)
Re—P(2$^{\rm i}$)	2.382 (3)	P(2)—C(7)	1.836 (11)
Re—C(1)	1.928 (10)	P(2)—C(8)	1.824 (12)
Re—C(2)	1.893 (9)	O(1)—C(1)	1.166 (11)
Re—C(3)	1.957 (11)	O(2)—C(2)	1.132 (12)
P(1)—C(4)	1.834 (12)	O(3)—C(3)	1.152 (12)
P(1)—C(5)	1.860 (12)		
Re$^{\rm i}$—Re—P(1)	88.10 (8)	Re—P(1)—C(5)	114.9 (5)
Re$^{\rm i}$—Re—P(2$^{\rm i}$)	89.69 (8)	Re—P(1)—C(6)	115.8 (3)
Re$^{\rm i}$—Re—C(1)	89.0 (2)	C(4)—P(1)—C(5)	104.0 (6)
Re$^{\rm i}$—Re—C(2)	177.6 (3)	C(4)—P(1)—C(6)	102.2 (5)
Re$^{\rm i}$—Re—C(3)	84.4 (2)	C(5)—P(1)—C(6)	103.5 (5)
P(1)—Re—P(2$^{\rm i}$)	176.76 (8)	Re—P(2$^{\rm i}$)—C(6$^{\rm i}$)	114.8 (3)
P(1)—Re—C(1)	89.2 (3)	Re—P(2$^{\rm i}$)—C(7$^{\rm i}$)	119.0 (4)
P(1)—Re—C(2)	90.8 (3)	Re—P(2$^{\rm i}$)—C(8$^{\rm i}$)	115.3 (4)
P(1)—Re—C(3)	90.8 (3)	C(6)—P(2)—C(7)	103.3 (5)
P(2$^{\rm i}$)—Re—C(1)	88.4 (3)	C(6)—P(2)—C(8)	100.9 (5)
P(2$^{\rm i}$)—Re—C(2)	91.5 (3)	C(7)—P(2)—C(8)	101.0 (6)
P(2$^{\rm i}$)—Re—C(3)	91.3 (3)	Re—C(1)—O(1)	175.7 (8)
C(1)—Re—C(2)	93.1 (4)	Re—C(2)—O(2)	177.9 (9)
C(2)—Re—C(3)	93.6 (4)	Re—C(3)—O(3)	174.6 (9)
C(1)—Re—C(3)	173.3 (4)	P(1)—C(6)—P(2)	112.9 (5)
Re—P(1)—C(4)	114.8 (4)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Sample preparation: Milder *et al.* (1990). Scan speed: 16° min^{-1} in ω. Scan width: $(1.00 + 0.30\tan\theta)°$. Structure analysis package: *TEXSAN* (Molecular Structure Corporation, 1989). Re position: *PHASE* (subprogram of *DIRDIF*; Beurskens *et al.*, 1984).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71097 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1037]

References

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., Van den Hark, T. E. M., Prick, P. A. J., Noordik, K. H., Beurskens, G., Parthasarathi, 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.

Milder, S. J., Castellani, M. P., Weakley, T. J. R., Tyler, D. R., Miskowski, V. M. & Stiegman, A. E. (1990). *J. Phys. Chem.* **94**, 6599–6603.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package.* Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1993). C**49**, 1493–1496

Structure of Tri-μ-chloro-bis[(η^6-benzene)ruthenium(II)] Hexafluoroarsenate

Fred B. McCormick* and William B. Gleason†

3M Corporate Research Laboratories, St. Paul, Minnesota 55144, USA

(*Received* 16 *October* 1992; *accepted* 9 *February* 1993)

Abstract

The cationic portion of the tri-μ-chloro-bis[(η^6-benzene)ruthenium(II)] hexafluoroarsenate molecule consists of two (η^6-C_6H_6)Ru moieties [Ru to ring plane distances are 1.6392 (4) and 1.6486 (4) Å] symmetrically bridged by three Cl atoms [Ru—Cl$_{\rm av}$ = 2.423 (7) Å]. The benzene rings are planar and lie

---

† Current address: Biomedical Engineering Center, University of Minnesota, Minneapolis, MN 55455, USA.