N30—Cu1—N1	92.1 (2)	N40—Cu2—S40^i	88.42 (12)
N3—Cu1—N1	103.92 (14)	N6—Cu2—S40^i	87.49 (12)
N2—Cu1—N1	76.34 (14)	N5—Cu2—S40^i	93.12 (12)

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

The structure was solved by Patterson methods (Sheldrick, 1990) and refined against all F^2 using the gamma-test version of *SHELXL*93 (Sheldrick, 1993).

We are grateful to Professor W. T. Robinson for the X-ray data collection and to B. M. Clark for the FAB mass spectrum (University of Canterbury, New Zealand).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[M_2(CO)_{10}(\mu\text{-dppp}_e)]$ [M = Cr, W; $dppp_e$ = $Ph_2P(CH_2)_5PPh_2$]

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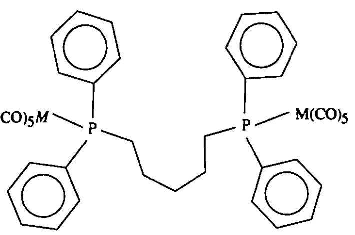
Abstract

The $dppp_e$ monobridged bimetallic complexes μ-1,5-bis(diphenylphosphino)pentane-P:P'-bis(pentacarbonylchromium), $[Cr_2(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]$, (I), and μ-1,5-bis(diphenylphosphino)pentane-P:P'-bis(pentacarbonyltungsten), $[W_2(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]$, (II), are isomorphous and isostructural. In each molecule, a crystallographic twofold axis passes through the central methylene C atom of the $dppp_e$ pentane chain. The torsion angles P—C_α—C_β—C_γ and C_α—C_β—C_γ—C_δ are 169.1 (2) and 59.0 (2)°, respectively, for (I), and 169.5 (7) and 60.6 (5)°, respectively, for (II).

Comment

There are several reports of syntheses of Group 6 metal–carbonyl derivatives containing the long-backbone diphosphine ligand $dppp_e$. The monobridged dinuclear complexes $[M_2(CO)_{10}(\mu\text{-dppp}_e)]$ have been prepared from $[M(CO)_6]$ and $dppp_e$ under reflux in $EtOCH_2CH_2OCH_2CH_2OH$ solution (M = Mo) (Dietsche, 1966) and from the same starting materials with Me_3NO as initiator in CH_3CN (M = Cr, Mo and W) (Hor, 1989). $[Mo(CO)_4(dppp_e)]$, which contains an eight-membered chelate ring, was synthesized from $[Mo(CO)_4(NBD)]$ (NBD = norborna-2,5-diene) and $dppp_e$ (Ueng & Hwang, 1994*a*). The structure of the doubly bridged 16-membered bimetallacycle *trans*-$[Mo_2(CO)_8(\mu\text{-dppp}_e)_2]$, synthesized from $[Mo(CO)_6]$ and $dppp_e$ (mole ratio 1:1), has been described (Ueng & Hwang, 1994*b*). For comparison, the crystal structures of the title compounds, (I) and (II), which contain only a single $dppp_e$ bridge, have been determined.



(I) M = Cr
(II) M = W

The molecules consist of two metal atoms each bonded to five carbonyls and one P atom from the diphosphine ligand. The coordination around each metal is distorted octahedral with the deviation of the metal from the equatorial least-squares plane formed by C(1), C(2), C(4) and C(5) being −0.029 (2) Å for the Cr complex and −0.023 (6) Å for the W complex. In each

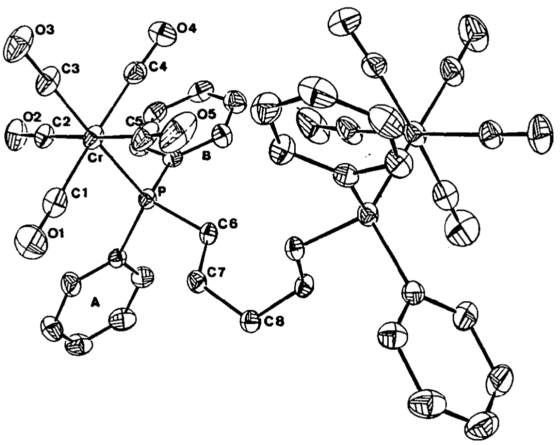


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure of $[Cr_2(CO)_{10}(\mu\text{-dppp}_e)]$ with H atoms omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

complex, the *M*—CO bond *trans* to the P atom is shorter than the other *M*—CO bonds.

Instead of the typical zigzag arrangement of methylene groups found in *trans*-[$Mo_2(CO)_8(\mu$-dppp$_e)_2$] (Ueng & Hwang, 1994*b*) and *trans*-[$Mo_2(CO)_8(\mu$-dpph$)_2$] [dpph = $Ph_2P(CH_2)_6PPh_2$] (Ueng & Hwang, 1991), the title compounds display a twist conformation of the polymethylene chain with torsion angles P—C(6)—C(7)—C(8) and C(6)—C(7)—C(8)—C(7) of 169.1 (2) and 59.0 (2)°, respectively, for (I), and 169.5 (7) and 60.6 (5)°, respectively, for (II). The orientations of the two unique phenyl groups *A* and *B* relative to the metal coordination polyhedron are different: the dihedral angles between the equatorial least-squares plane and groups *A* and *B* are 68.4 (1) and 15.3 (1)°, respectively, for (I), and 66.6 (3) and 14.2 (3)°, respectively, for (II). The P—C bond lengths and the C—C bond lengths of the phosphines are normal and there are no intermolecular contacts of structural significance.

Experimental

Compound (I)

Crystal data

[$Cr_2(C_{29}H_{30}P_2)(CO)_{10}$]
$M_r = 824.59$
Monoclinic
$C2/c$
$a = 25.640$ (5) Å
$b = 8.4901$ (8) Å
$c = 17.662$ (2) Å
$\beta = 94.22$ (1)°
$V = 3834.3$ (9) Å^3
$Z = 4$
$D_x = 1.428$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.90$–$18.26°$
$\mu = 0.69$ mm^{-1}
$T = 298$ K
Block
0.55 × 0.50 × 0.50 mm
Light yellow
Crystal source: evaporation from CH_2Cl_2/n-hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.944$, $T_{max} = 0.999$
3447 measured reflections
3368 independent reflections

2764 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 25.0°$
$h = -30 \rightarrow 30$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.034$
$wR = 0.029$
$S = 3.13$
2764 reflections
241 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.007$

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 3.2 (1) μm
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

[$W_2(C_{29}H_{30}P_2)(CO)_{10}$]
$M_r = 1088.30$
Monoclinic
$C2/c$
$a = 25.956$ (4) Å
$b = 8.553$ (1) Å
$c = 17.784$ (3) Å
$\beta = 94.04$ (1)°
$V = 3938$ (1) Å^3
$Z = 4$
$D_x = 1.836$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.75$–$12.50°$
$\mu = 6.10$ mm^{-1}
$T = 298$ K
Needle
0.50 × 0.30 × 0.25 mm
Light yellow
Crystal source: evaporation from CH_2Cl_2/n-hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.507$, $T_{max} = 0.998$
2573 measured reflections
2573 independent reflections

2074 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 22.5°$
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.026$
$S = 2.92$
2047 reflections
241 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.81$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 1.32 (4) μm
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cr	0.35360 (2)	0.23753 (5)	0.20762 (2)	3.28 (2)
P	0.39417 (3)	0.05918 (8)	0.12442 (4)	2.73 (3)
O(1)	0.3102 (1)	−0.0142 (3)	0.3068 (1)	7.2 (1)
O(2)	0.25879 (7)	0.2404 (3)	0.0938 (1)	5.4 (1)
O(3)	0.29949 (9)	0.4785 (3)	0.2979 (1)	7.0 (1)
O(4)	0.41226 (9)	0.5044 (3)	0.1377 (1)	6.2 (1)
O(5)	0.4444 (1)	0.2544 (3)	0.3244 (1)	8.8 (2)
C(1)	0.3260 (1)	0.0767 (4)	0.2668 (2)	4.5 (2)
C(2)	0.2943 (1)	0.2380 (3)	0.1352 (1)	3.6 (1)
C(3)	0.3200 (1)	0.3864 (4)	0.2635 (2)	4.5 (1)
C(4)	0.3882 (1)	0.4039 (3)	0.1601 (2)	4.1 (1)
C(5)	0.4106 (1)	0.2431 (4)	0.2791 (2)	4.9 (2)
C(6)	0.45610 (9)	−0.0283 (3)	0.1617 (1)	3.0 (1)
C(7)	0.45061 (9)	−0.1379 (3)	0.2294 (1)	3.0 (1)
C(8)	1/2	−0.2331 (4)	1/4	3.1 (2)
C(1*A*)	0.35863 (9)	−0.1125 (3)	0.0844 (1)	2.9 (1)
C(2*A*)	0.3162 (1)	−0.1755 (3)	0.1170 (2)	4.1 (1)
C(3*A*)	0.2913 (1)	−0.3085 (4)	0.0862 (2)	5.3 (2)
C(4*A*)	0.3087 (1)	−0.3774 (4)	0.0229 (2)	5.6 (2)
C(5*A*)	0.3507 (1)	−0.3165 (4)	−0.0102 (2)	5.2 (2)
C(6*A*)	0.3759 (1)	−0.1848 (3)	0.0199 (2)	4.0 (1)
C(1*B*)	0.4108 (1)	0.1616 (3)	0.0384 (1)	3.0 (1)
C(2*B*)	0.3708 (1)	0.1939 (3)	−0.0169 (2)	3.7 (1)

C(3*B*)	0.3804 (1)	0.2859 (4)	−0.0789 (2)	4.8 (2)
C(4*B*)	0.4292 (1)	0.3478 (4)	−0.0859 (2)	5.0 (2)
C(5*B*)	0.4691 (1)	0.3153 (4)	−0.0326 (2)	4.8 (2)
C(6*B*)	0.4600 (1)	0.2223 (3)	0.0294 (2)	3.9 (2)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for* (II)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
W	0.35340 (1)	0.24254 (5)	0.20882 (2)	3.16 (2)
P	0.39599 (9)	0.0548 (3)	0.1220 (1)	2.8 (1)
O(1)	0.3087 (3)	−0.020 (1)	0.3121 (5)	8.1 (5)
O(2)	0.2560 (2)	0.244 (1)	0.0893 (4)	5.9 (4)
O(3)	0.2973 (3)	0.4959 (9)	0.3007 (4)	7.8 (5)
O(4)	0.4158 (3)	0.5134 (8)	0.1331 (5)	6.9 (5)
O(5)	0.4470 (3)	0.259 (1)	0.3305 (5)	11.0 (6)
C(1)	0.3241 (5)	0.073 (1)	0.2723 (6)	5.3 (7)
C(2)	0.2905 (3)	0.242 (1)	0.1311 (5)	4.0 (5)
C(3)	0.3177 (4)	0.402 (1)	0.2679 (6)	4.8 (5)
C(4)	0.3912 (4)	0.416 (1)	0.1565 (5)	4.2 (5)
C(5)	0.4143 (4)	0.249 (1)	0.2868 (6)	5.9 (6)
C(6)	0.4571 (3)	−0.0318 (9)	0.1600 (4)	3.0 (4)
C(7)	0.4512 (3)	−0.1364 (8)	0.2285 (4)	2.7 (4)
C(8)	1/2	−0.231 (1)	1/4	3.0 (5)
C(1*A*)	0.3603 (3)	−0.1135 (9)	0.0831 (5)	3.0 (4)
C(2*A*)	0.3182 (4)	−0.175 (1)	0.1178 (5)	4.1 (5)
C(3*A*)	0.2928 (4)	−0.306 (1)	0.0872 (7)	5.6 (6)
C(4*A*)	0.3090 (5)	−0.375 (1)	0.0224 (7)	6.0 (6)
C(5*A*)	0.3509 (5)	−0.316 (1)	−0.0124 (6)	5.4 (6)
C(6*A*)	0.3767 (4)	−0.186 (1)	0.0179 (5)	4.1 (5)
C(1*B*)	0.4119 (3)	0.1579 (9)	0.0376 (5)	2.9 (4)
C(2*B*)	0.3725 (3)	0.1891 (9)	−0.0167 (5)	3.8 (4)
C(3*B*)	0.3824 (4)	0.287 (1)	−0.0783 (5)	5.0 (5)
C(4*B*)	0.4306 (5)	0.350 (1)	−0.0855 (6)	5.1 (6)
C(5*B*)	0.4696 (4)	0.316 (1)	−0.0332 (6)	5.0 (6)
C(6*B*)	0.4609 (3)	0.217 (1)	0.0284 (5)	4.2 (5)

Table 3. *Selected geometric parameters* (Å, °) *for* (I)

Cr—P	2.3998 (8)	Cr—C(3)	1.854 (3)
Cr—C(1)	1.888 (3)	Cr—C(4)	1.896 (3)
Cr—C(2)	1.913 (3)	Cr—C(5)	1.859 (3)
P—Cr—C(1)	94.56 (9)	C(1)—Cr—C(5)	87.2 (1)
P—Cr—C(2)	87.16 (8)	C(2)—Cr—C(3)	88.7 (1)
P—Cr—C(3)	174.41 (9)	C(2)—Cr—C(4)	94.4 (1)
P—Cr—C(4)	87.77 (9)	C(2)—Cr—C(5)	178.2 (1)
P—Cr—C(5)	94.44 (9)	C(3)—Cr—C(4)	88.8 (1)
C(1)—Cr—C(2)	93.4 (1)	C(3)—Cr—C(5)	89.6 (1)
C(1)—Cr—C(3)	89.5 (1)	C(4)—Cr—C(5)	84.9 (1)
C(1)—Cr—C(4)	171.9 (1)		
C(3)—Cr—P—C(1*A*)	−90.1 (10)	Cr—P—C(6)—C(7)	65.6 (1)
C(3)—Cr—P—C(1*B*)	27.6 (10)	P—C(6)—C(7)—C(8)	169.1 (2)
C(3)—Cr—P—C(6)	145.6 (10)	C(6)—C(7)—C(8)—C(7′)	59.0 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

W—P	2.534 (2)	W—C(3)	1.99 (1)
W—C(1)	2.02 (1)	W—C(4)	2.04 (1)
W—C(2)	2.064 (9)	W—C(5)	2.03 (1)
P—W—C(1)	94.8 (3)	C(1)—W—C(5)	86.8 (5)
P—W—C(2)	87.1 (3)	C(2)—W—C(3)	88.8 (4)
P—W—C(3)	174.3 (3)	C(2)—W—C(4)	94.6 (4)
P—W—C(4)	86.4 (3)	C(2)—W—C(5)	178.1 (4)
P—W—C(5)	94.7 (3)	C(3)—W—C(4)	89.9 (4)
C(1)—W—C(2)	93.5 (4)	C(3)—W—C(5)	89.3 (4)
C(1)—W—C(3)	89.4 (4)	C(4)—W—C(5)	85.1 (4)
C(1)—W—C(4)	171.8 (4)		
C(3)—W—P—C(1*A*)	−91 (4)	W—P—C(6)—C(7)	64.2 (4)
C(3)—W—P—C(1*B*)	26 (4)	P—C(6)—C(7)—C(8)	169.5 (7)
C(3)—W—P—C(6)	144 (4)	C(6)—C(7)—C(8)—C(7′)	60.6 (5)

Data collection and cell refinement were performed using Enraf–Nonius CAD-4 diffractometer software. All other calulcations were performed using the *NRCVAX* package (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N*,*N*-dimethylformamide)(μ-sulfato)-dioxouranium(VI)

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Abstract

In the title compound, $[UO_2(SO_4)(C_3H_7NO)_2]$, the uranyl ion is in a pentagonal pseudo-planar equatorial environment, comprising two dimethylformamide and three sulfate O atoms. The uranyl ions are bridged by sulfate groups, giving rise to an infinite chain structure, *i.e.* *catena*-poly[(*NN*-dimethylformamide)dioxouranium-μ-sulfato-$O,O':O''$]. Two of the sulfate O atoms are bonded to the same uranyl ion in a coordination mode previously not observed in uranyl sulfates.

Comment

Several structures of uranyl sulfates have been determined, in either their dehydrated forms (Ross & Evans,