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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cu1	1/4	1/4	0	0.0260 (2)
O1	0.4138 (2)	0.30353 (13)	0.0486 (2)	0.0335 (5)
O2	0.3401 (2)	0.4285 (2)	0.1066 (2)	0.0625 (8)
O3	0.1264 (2)	0.36690 (14)	0.0818 (2)	0.0537 (7)
O4	0.0326 (2)	0.48717 (15)	0.1279 (2)	0.0514 (6)
N1	0.2466 (2)	0.18386 (14)	0.1297 (2)	0.0291 (6)
N2	0.3028 (3)	0.0978 (2)	0.2575 (2)	0.0423 (7)
C1	0.4277 (3)	0.3779 (2)	0.0862 (2)	0.0386 (8)
C2	0.5604 (3)	0.4130 (3)	0.1057 (5)	0.0649 (12)
C3	0.6685 (3)	0.3591 (3)	0.0830 (4)	0.0506 (9)
C4	−0.2082 (3)	0.4088 (3)	0.1030 (4)	0.0603 (11)
C5	−0.0937 (3)	0.3636 (3)	0.0765 (4)	0.0629 (12)
C6	0.0273 (3)	0.4126 (2)	0.0979 (2)	0.0371 (8)
C7	0.1444 (3)	0.1652 (2)	0.1856 (3)	0.0441 (9)
C8	0.1790 (3)	0.1118 (2)	0.2641 (3)	0.0460 (9)
C9	0.3401 (3)	0.1411 (2)	0.1760 (3)	0.0398 (8)

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

Cu1—N1	1.964 (2)	Cu1—O3^{i}	2.499 (2)
Cu1—N1^{i}	1.964 (2)	O3—C6	1.292 (4)
Cu1—O1^{i}	1.992 (2)	O4—C6	1.212 (4)
Cu1—O1	1.992 (2)	O1—C1	1.249 (4)
Cu1—O3	2.499 (2)	O2—C1	1.253 (4)
N1—Cu1—N1^{i}	180.0	N1—Cu1—O3	88.62 (9)
N1—Cu1—O1^{i}	89.75 (9)	N1^{i}—Cu1—O3	91.38 (9)
N1^{i}—Cu1—O1^{i}	90.25 (9)	O1^{i}—Cu1—O3	87.81 (8)
N1—Cu1—O1	90.25 (9)	O1—Cu1—O3	92.19 (8)
N1^{i}—Cu1—O1	89.75 (9)	O4—C6—O3	123.0 (3)
O1^{i}—Cu1—O1	180.0	O1—C1—O2	125.4 (3)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

All H atoms were located in the difference Fourier map and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe, Le Page, White & Lee, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DE1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ-1,4-Bis(diphenylphosphino)phenylene-*P*:*P*′-bis[*μ*$_3$-benzylidyne-octacarbonyl-*triangulo*-tricobalt(3 *Co*—*Co*)]

NATALYA C. ALEXANDER, BRIAN H. ROBINSON AND JIM SIMPSON

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: jsimpson@alkali.otago.ac.nz

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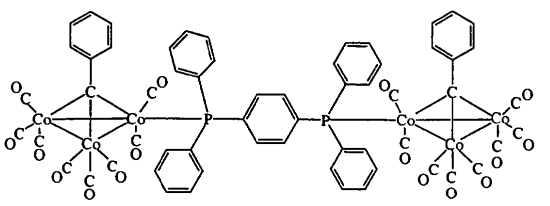
Abstract

The title compound, *μ*-[1,4-phenylenebis(diphenylphosphino)]-*P*:*P*′-bis[*μ*$_3$-phenylmethylidyne-octacarbonyl-1κ^2*C*,2κ^3*C*,3κ^3*C*-*triangulo*-tricobalt(3 *Co*—*Co*)], $[\{Co_3(CO)_8(C_7H_5)\}_2(C_{30}H_{24}P_2)]$, lies about an inversion centre and consists of two approximately tetrahedral Co_3C units capped with phenyl groups and linked by a 1,4-bis(diphenylphosphino)phenylene ligand which replaces an equatorial carbonyl group on each cluster unit. The apical phenyl substituents and a phenyl ring from each P atom are arranged such that steric repulsion within the molecule is minimized.

Comment

As part of our investigation into the formation of conductive links between redox-active metal centres, we have targeted the substitution reactions of the readily reducible tricobalt–carbon cluster complexes

$YCCo_3(CO)_9$ (Y = Me, Ph) with the diphosphine ligand 1,4-bis(diphenylphosphino)phenylene. The conformation of this diphosphine ligand precludes chelation to metal centres within the cluster moiety and offers the possibility of linking two or more cluster centres *via* a rigid rod. The principal products of the thermal substitution reactions are the linked-cluster complexes $YCCo_3(CO)_8Ph_2PC_6H_4PPh_2(CO)_8Co_3CY$ (Y = Me, Ph). Reductive electrochemistry of the resulting linked clusters reveals an irreversible two-electron process, suggesting that the diphosphine ligand does not provide a conducting link between the two cluster centres and that the linked complexes are easily fragmented upon reduction. We report here the structure of the title compound, (I), and compare it with those of $[PhCCo_3(CO)_8]_2$(dppe) [dppe is 1,2-bis(diphenylphosphino)ethane; Downard, Robinson & Simpson, 1986] and $[MeCCo_3(CO)_8]_2$(dppf) [dppf is 1,1′-bis(diphenylphosphino)ferrocene; Onaka *et al.*, 1994], which, to our knowledge, are the only examples of diphosphine-linked tricobalt–carbon clusters to have been structurally characterized.



(I)

The title structure consists of discrete molecules with a closest intermolecular contact not involving H atoms of 3.127 (8) Å (Nardelli, 1983). The molecule lies about an inversion centre (at the centroid of the phenylene ring) and the phenyl substituents on the apical C atoms of each cluster unit are thus mutually *trans* with respect to the phenylene ring plane. Phosphorus substitution on each of the cluster units has replaced a terminal carbonyl ligand from an equatorial site, the normal mode of coordination for monodentate phosphine substitution (Bruce, Penfold, Robinson & Taylor, 1970; Matheson & Penfold, 1977).

The phenyl substituents on the diphosphine ligand are arranged such that the C211–C216 ring is approximately parallel to the apical C2–C7 ring [interplanar angle 6.1 (2)°; Nardelli, 1983]. A similar orientation is found in the corresponding dppe-linked molecule and has been ascribed to the minimization of non-bonded contacts between the H atoms on the two rings (Downard, Robinson & Simpson, 1986). The angles Co1—P1—C111 of 117.7 (2)° and Co1—P1—C211 of 115.8 (2)° are widened considerably to accommodate this configuration and to minimize steric interactions between the phenyl rings and the adjacent carbonyl ligands. High anisotropic displacement parameters for the carbonyl O21 and O23 atoms are indicative of possible disorder but this was not investigated further.

The CCo_3 units are distorted tetrahedra with the Co1—Co3 distance [2.501 (1) Å] lengthened significantly in comparison with Co1—Co2 [2.469 (1) Å] and Co2—Co3 [2.476 (1) Å]. Similar variations are observed

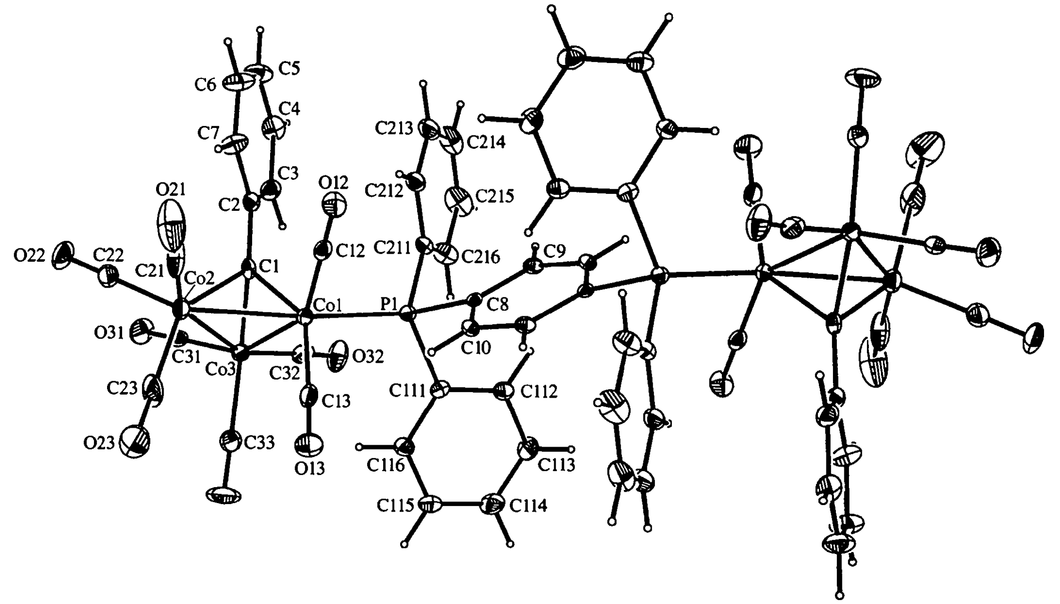


Fig. 1. Perspective drawing of the title molecule showing the atom-numbering scheme with displacement ellipsoids drawn at the 30% probability level.

in the analogous dppe system (Downard, Robinson & Simpson, 1986) and to a lesser extent in the dppf-linked system (Onaka *et al.*, 1994). Corresponding differences occur in the Co—C$_{\text{apical}}$ bond lengths, with C1—Co2 [1.946 (5) Å] significantly longer than C1—Co1 [1.905 (5) Å] and C1—Co3 [1.897 (6) Å]. The Co1—P1 bond is unremarkable at 2.233 (2) Å, while the Co1—C12 bond to the equatorial carbonyl group on the phosphine-substituted Co1 atom is predictably shorter [1.760 (7) Å] than those to Co2 and Co3 atoms, which carry three strongly π-accepting carbonyl substituents each [Co2—C21 1.780 (8), Co2—C22 1.793 (7), Co3—C31 1.796 (6) and Co3—C32 1.808 (7) Å].

Experimental

$PhCCo_3(CO)_9$ (0.50g, 1.0 mmol) and $C_6H_4(PPh_2)_2$ (0.30 g, 0.67 mmol) were refluxed in hexane (40 ml). The reaction was monitored by IR spectroscopy and TLC, and halted before all of the starting cluster was consumed in order to minimize decomposition. The hexane-soluble products were separated on silica plates with CH_2Cl_2/hexane (1:2) as eluant. The major red-brown band gave the title compound in $\sim$20% yield as black blocks on recrystallization from hexane. Analysis calculated for $C_{60}H_{34}Co_6O_{16}P_2$: C 50.52, H 2.40%; found: C 50.03, H 2.60%. IR (CH_2Cl_2): ν(CO) 2078 (*s*), 2036 (*vs*), 2027 (*vs*), 2014 (*m*); ^{31}P NMR ($CDCl_3$): δ 48.2 (*s*). An equivalent reaction starting with $MeCCo_3(CO)_9$ (0.634 g, 1.38 mmol) and $C_6H_4(PPh_2)_2$ (0.30 g, 0.67 mmol) gave $MeCCo_3(CO)_8(Ph_2PC_6H_4PPh_2)(CO)_8Co_3CMe$ in 32% yield. Analysis calculated for $C_{50}H_{30}Co_6O_{16}P_2$: C 46.11, H 2.32%; found: C 46.16, H 2.60%. IR (CH_2Cl_2): ν(CO) 2077 (*s*), 2032 (*vs*), 2016 (*vs*); ^{31}P NMR ($CDCl_3$): δ 48.2 (*s*).

Crystal data

$[Co_6(C_7H_5)_2(C_{30}H_{24}P_2)(CO)_{16}]$
$M_r = 1426.39$
Monoclinic
$P2_1/n$
$a = 9.324\ (3)$ Å
$b = 17.688\ (4)$ Å
$c = 17.810\ (6)$ Å
$\beta = 95.77\ (3)°$
$V = 2922.4\ (15)$ Å^3
$Z = 2$
$D_x = 1.621$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–$30°$
$\mu = 1.787$ mm^{-1}
$T = 193\ (2)$ K
Block
0.38 × 0.12 × 0.10 mm
Black

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
$T_{\min} = 0.704$, $T_{\max} = 0.836$
5127 measured reflections
5127 independent reflections

3369 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: 1.04%

Refinement

Refinement on *F*
$R = 0.0487$
$wR = 0.0434$
S not available (*SHELX*76 refinement; Sheldrick, 1976)
5127 reflections
385 parameters
H atoms riding (C—H 0.92–0.98 Å; *AFIX* in *SHELX*76)

$w = 1.0979/[\sigma^2(F) + 0.000241F^2]$
$(\Delta/\sigma)_{\max} = 0.055$
$\Delta\rho_{\max} = 0.454$ e Å^{-3}
$\Delta\rho_{\min} = -0.576$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co1—Co2	2.469 (1)	Co1—C13	1.814 (7)
Co1—Co3	2.501 (1)	C13—O13	1.140 (7)
Co2—Co3	2.476 (1)	Co2—C21	1.780 (8)
Co1—C1	1.905 (5)	C21—O21	1.157 (8)
Co2—C1	1.946 (5)	Co2—C22	1.793 (7)
Co3—C1	1.897 (6)	C22—O22	1.148 (7)
C1—C2	1.467 (7)	Co2—C23	1.818 (8)
Co1—P1	2.233 (2)	C23—O23	1.119 (8)
P1—C8	1.845 (5)	Co3—C31	1.796 (6)
C8—C9	1.398 (7)	C31—O31	1.139 (6)
P1—C111	1.830 (6)	Co3—C32	1.808 (7)
P1—C211	1.834 (5)	C32—O32	1.133 (7)
Co1—C12	1.760 (7)	Co3—C33	1.831 (7)
C12—O12	1.150 (7)	C33—O33	1.135 (7)
C12—Co1—P1	91.6 (2)	C211—P1—C8	100.6 (2)
C13—Co1—P1	100.3 (2)	C111—P1—C211	108.5 (3)
C111—P1—C8	98.1 (2)	C111—P1—Co1	117.7 (2)
C8—P1—Co1	113.6 (2)	C211—P1—Co1	115.8 (2)

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990).

The authors thank Professor W. T. Robinson (University of Canterbury) for data collection. This work is supported by a grant from the Division of Sciences, University of Otago, New Zealand.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Reinvestigation of *mer,trans*-(Acetonitrile)trichlorobis(triphenylphosphine)-rhenium(III)

MARTIN DAVIS, FRANCINE BÉLANGER-GARIÉPY, DAVIT ZARGARIAN AND ANDRÉ L. BEAUCHAMP

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: beauchmp@ere.umontreal.ca

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Abstract

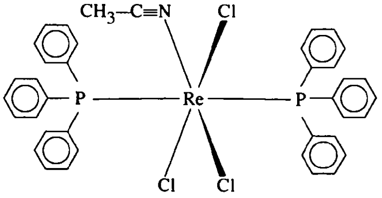
The crystals of (*OC*-6-13)-(acetonitrile-*N*)trichlorobis(triphenylphosphine-*P*)rhenium(III), $[ReCl_3(C_2H_3N)(C_{18}H_{15}P)_2]$, contain distorted octahedral molecules in which the phosphine ligands are *trans* with respect to one another and the Cl ligands adopt a meridional arrangement. In contrast to the isostructural $[OsCl_3(PPh_3)_2(CH_3CN)]$ complex, where the Os—Cl distances do not differ greatly, the Re—Cl bond *trans* to the nitrile ligand [2.393 (2) Å] is appreciably longer than the mutually *trans* Re—Cl bonds [2.344 (2) and 2.350 (2) Å].

Comment

For our studies of Re–ligand multiply bonded compounds, we required a convenient route to complexes of the type $Cp'ReL_2X_2$ (where Cp′ is cyclopentadienyl and its alkyl-substituted derivatives). A recent report has shown that $[ReCl_3(PPh_3)_2]$, generated *in situ* from $[ReOCl_3(PPh_3)_2]$ and PPh_3, undergoes a direct metathetic reaction with the triazenido anion Li(*R*N—N═N*R*) to give *trans*-$[ReCl_2(PPh_3)_2(RN—N—NR)]$, in which the triazenido ligand acts as a bidentate ligand (Rossi *et al.*, 1982). This finding prompted us to explore the reaction of the Cp′ anions with *mer*-$[ReCl_3(PPh_3)_2(CH_3CN)]$ as a more direct route to the desired $Cp'ReL_2X_2$ compounds.

Addition of Cp′Li to a THF solution of $[ReCl_3(PPh_3)_2(CH_3CN)]$ yielded a dark green solid. Surprisingly, the ^{1}H NMR and IR spectra of the solid were virtually identical to the corresponding spectra of the orange rhenium precursor (Pearson & Beauchamp, 1995) and contained no signals attributable to the Cp′ ligand. The same dark green solid was obtained when the reaction was repeated in refluxing toluene or when *trans*-$[ReOCl_3(PPh_3)_2]$ and PPh_3 were used instead of $[ReCl_3(PPh_3)_2(CH_3CN)]$.

We undertook an X-ray diffraction study of the dark green crystals and discovered that the compound was in fact $[ReCl_3(PPh_3)_2(CH_3CN)]$, (I), whose structure had been reported previously by Drew, Tisley & Walton (1970), but it had been refined only to 7.7% and no atomic coordinates were provided. In order to compare the structural parameters obtained for the dark green crystals with those of the orange precursor, we recrystallized the orange solid prepared according to Rouschias & Wilkinson (1967) from CH_2Cl_2/Et_2O and subjected it to an X-ray diffraction study under similar conditions. The structures refined to $R = 0.0367$ (green) and 0.0371 (orange). At this point, the possibility was considered that the green material could show substitutional disorder resulting from the replacement of some $[ReCl_3(PPh_3)_2(CH_3CN)]$ by, for instance, $[ReOCl_2(PPh_3)_2(CH_3CN)]$. Parkin (1993) has recently described a number of systems of this type, *e.g.* $[MoOCl_2(PR_3)_3]/[MoCl_3(PR_3)_3]$. Analysis of distances and angles, displacement ellipsoids and electron-density contours, however, revealed no anomalies. Careful microscopic examination eventually showed that the green material actually consisted of an orange core covered with an amorphous dark green crust; the specimen appeared uniformly opaque under normal illumination, but some orange light was transmitted through the middle of the crystal when a more powerful light source was used. The results obtained with a green specimen are described here.



(I)

Our unit-cell parameters and space group correspond to those reported by Drew *et al.* (1970). The related $[OsCl_3(PPh_3)_2(CH_3CN)]$ compound studied by Parkes, Payne & Sherman (1980) is isostructural, since the cell parameters are the same as ours after their $P2_1/c$ unit cell is converted to $P2_1/n$.

The overall structure reported earlier is confirmed by the present study. The low steric requirement of CH_3CN is reflected by a general displacement of the *cis* ligands to its side. The effect is particularly significant for the Re—Cl bonds; Cl1—Re—Cl2 171.37 (6), N1—Re—Cl1 85.98 (15), N1—Re—Cl2 85.41 (15), Cl1—Re—Cl3 94.41 (6) and Cl2—Re—Cl3 94.20 (6)°. Very similar distortions are found in the Os^{III} complex, but the