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A *cyclo*-Triarsenic Complex of Chromium

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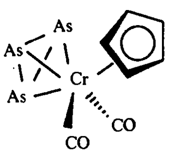
Abstract

The structure of dicarbonyl(η^5-cyclopentadienyl)(η^3-*cyclo*-triarsenido)chromium, [Cr(η^5-C_5H_5)(CO)$_2$(η^3-As_3)], has been determined. The *cyclo*-As_3 ligand possesses an average As—As distance of 2.338 Å and As—As—As angles of 59.71 (6), 60.32 (5) and 59.97 (6)°.

Comment

To date there have been only a few reports of tetrahedral metal–As_3 complexes (Dimaio & Rheingold, 1990). The first cyclotriarsenic complex reported was [Co(CO)$_3$(η^3-As_3)] (Foust, Campana, Sinclair & Dahl, 1969, 1979), which was obtained from the reaction of $Co_2(CO)_8$ with *cyclo*-(PhAs)$_6$ at 473 K in hexane under 100 atm (1 atm = 101.325 kPa) of CO. More than a decade later, [(C_5Me_5)Mo(CO)$_2$(η^3-As_3)] was isolated from the reaction of the triply bonded complex [(C_5Me_5)Mo(CO)$_2$]$_2$ with As_4S_4 (Bernal, Brunner, Meier, Pfisterer, Wachter & Ziegler, 1984) and yellow As_4 (Scherer, Sitzmann & Wolmershäuser, 1986), respectively. The latter reaction with yellow As_4 was later extended to the analogous Cr≡Cr complex (Scherer, Wiedemann & Wolmershäuser, 1990) and to an Ru—Ru bonded complex (Scherer, Blath, Heckmann & Wolmershäuser, 1991). Recently, we have isolated [CpCr(CO)$_2$(η^3-As_3)] (Cp = η^5-C_5H_5), (I), from the reaction of the highly reactive [CpCr(CO)$_3$]$_2$ with elemental grey As (Goh, Wong, Yip & Mak, 1991). Its structure is described herein.



(I)

The molecular structure of the title compound is illustrated in Fig. 1. The molecule has similar geometry to those of the Mo (Bernal *et al.*, 1984) and the (C_5Me_5) analogues (Scherer *et al.*, 1990). The Cr atom is situated at the apex of a tetrahedron with an essentially equilateral basal As_3 triangle. The As—As bond lengths [2.331 (2)–2.346 (2) Å] fall between those of the single As—As bond (2.44 Å), as in As_4 (Maxwell, Hendricks & Mosley, 1935), and the As=As double bond (2.24 Å) (Cowley, Lasch, Norman & Pakulski, 1983; Cowley & Norman, 1986). There is good agreement with the values of As—As bond lengths in the (η^3-As_3) complexes known to date, as illustrated in Table 3. Foust *et al.* (1969) had attributed the shortening of the As—As bond length from that of the single-bond value in As_4 to a reduction in interarsenic repulsions by the introduction of the more electronegative organometallic fragment. The molecular structure is also similar to that of its (η^3-P_3) analogue (Goh, Chu, Wong & Hambley, 1989), with differences in *E*—*E* and *M*—*E* bond lengths (*E* = P, As) commensurate with the covalent radii of P and As.

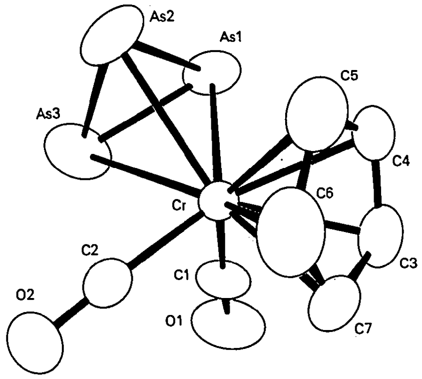


Fig. 1. Molecular structure of [Cr(η^5-Cp)(CO)$_2$(η^2-As_3)] with displacement ellipsoids drawn at the 50% probability level.

Experimental

The compound crystallized as golden brown plates from a saturated solution in toluene layered with hexane after 5-6 d at 245 K. The crystal used for data collection was coated in epoxy glue.

Crystal data

[Cr(As_3)(C_5H_5)(CO)$_2$]
M_r = 397.88
Monoclinic
$P2_1/a$
a = 7.537 (2) Å
b = 10.992 (1) Å
c = 12.670 (2) Å
β = 100.59 (1)°
V = 1031.7 (3) Å^3
Z = 4
D_x = 2.561 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–16°
μ = 10.58 mm^{-1}
T = 300 K
Plate
0.28 × 0.28 × 0.14 mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.580$, $T_{\max} = 0.999$
2063 measured reflections
1804 independent reflections

1189 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 400 reflections intensity variation: 0.026%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.043$
$S = 0.658$
1189 reflections
118 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0004F^2 + 1]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.90$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}
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)

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

	x	y	z	B_{eq}
As1	0.3365 (2)	0.1149 (1)	0.91273 (7)	4.72 (2)
As2	0.1542 (2)	−0.0587 (1)	0.90711 (8)	5.31 (2)
As3	0.0340 (2)	0.1217 (1)	0.82753 (9)	7.29 (3)
Cr	0.2623 (2)	0.0017 (1)	0.73393 (9)	2.58 (2)
O1	0.242 (1)	0.2379 (7)	0.6150 (6)	7.1 (2)
O2	−0.0982 (8)	−0.0558 (7)	0.6001 (5)	5.3 (2)
C1	0.248 (1)	0.1501 (9)	0.6640 (7)	4.2 (2)
C2	0.037 (1)	−0.0336 (8)	0.6543 (6)	3.4 (2)
C3	0.519 (1)	−0.013 (1)	0.6806 (8)	5.1 (2)
C4	0.541 (1)	−0.066 (1)	0.7798 (7)	5.6 (3)
C5	0.424 (1)	−0.164 (1)	0.7756 (9)	6.2 (2)
C6	0.329 (1)	−0.1728 (9)	0.6712 (9)	5.6 (2)
C7	0.387 (1)	−0.080 (1)	0.6109 (7)	5.1 (2)

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

As1—As2	2.346 (2)	O2—C2	1.15 (1)
As1—As3	2.338 (2)	As1—Cr	2.555 (2)
As2—As3	2.331 (2)	As2—Cr	2.565 (1)
C3—C4	1.37 (1)	As3—Cr	2.619 (2)
Cr—C1	1.85 (1)	Cr—C2	1.85 (1)
C3—C7	1.41 (1)	Cr—C3	2.169 (9)
C4—C5	1.39 (2)	Cr—C4	2.207 (9)
Cr—C5	2.20 (1)	Cr—C6	2.17 (1)
C5—C6	1.39 (2)	Cr—C7	2.158 (9)
O1—C1	1.14 (1)	C6—C7	1.39 (2)
As2—As1—As3	59.71 (6)	As2—As1—Cr	62.95 (4)
As3—As1—Cr	64.54 (5)	As1—As2—As3	59.97 (6)
As1—As2—Cr	62.52 (4)	As3—Cr—C1	77.7 (3)
As3—As2—Cr	64.46 (5)	As3—Cr—C2	74.9 (3)
As1—As3—As2	60.32 (5)	As1—As3—Cr	61.76 (5)
As2—As3—Cr	62.10 (5)	As1—Cr—As2	54.53 (4)
As1—Cr—As3	53.70 (5)	As1—Cr—C1	88.8 (3)
C1—Cr—C2	87.5 (4)	As1—Cr—C2	128.0 (3)
As2—Cr—As3	53.44 (5)	As2—Cr—C1	129.7 (3)
As2—Cr—C2	90.5 (2)	Cr—C1—O1	175.5 (9)
C4—C3—C7	108 (1)	Cr—C2—O2	176.2 (7)
C3—C4—C5	109 (1)	C5—C6—C7	108 (1)
C4—C5—C6	108 (1)	C3—C7—C6	107 (1)

Table 3. *A comparison of* As—As *and* M—As *bond lengths* (Å) *in* (η^3-As$_3$) *complexes*

	As—As	M—As
[Co(CO)$_3$(η^3-As$_3$)]^a	2.372 (5)	2.439 (5)
[(C$_5$Me$_5$)Mo(CO)$_2$(η^3-As$_3$)]^b	2.372 (1)–2.377 (2)	2.639 (1)–2.706 (2)
[(C$_5$Me$_5$)Cr(CO)$_2$(η^3-As$_3$)]^c	2.347 (2)–2.361 (2)	2.542 (1)–2.635 (2)
[(C$_5$H$_5$)Cr(CO)$_3$(η^3-As$_3$)]^d	2.331 (2)–2.356 (2)	2.555 (2)–2.619 (2)
[{(C$_5$Me$_4$Et)Ru}$_3$Ru(η^3-As$_3$)-μ_3-(η^3-As$_3$)(μ_3-As$_3$)]^e	2.310 (7)–2.329 (1)*	2.521 (5)–2.536 (5)†

References: (*a*) Foust *et al.* (1969); (*b*) Bernal *et al.* (1984); (*c*) Scherer *et al.* (1990); (*d*) this work; (*e*) Scherer *et al.* (1991).

* In (η^3-As$_3$) ligand.

† For Ru to (η^3-As$_3$) ligand.

The structure was solved by direct methods with *MULTAN*80 (Main *et al.*, 1980); the H atoms were generated with C—H = 0.95 Å and were allowed to ride on their respective C atoms. Computer programs used for structure solution and refinement were from the *MolEN* (Fair, 1990) package and were run on a MicroVAX II minicomputer.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71704 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1050]

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μ-[1,2-Bis(diethylphosphino)ethane]-*P*:*P'*-bis[bis(diethyldithiocarbamato-*S*,*S'*)zinc(II)] Ditoluene Solvate

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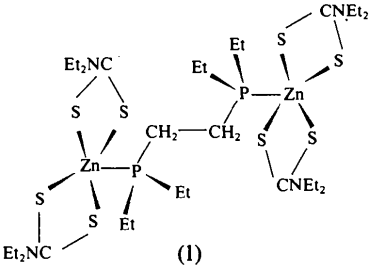
Abstract

The title complex, $[Zn_2(C_5H_{10}NS_2)_4(C_{10}H_{24}P_2)]$, is positioned symmetrically about an inversion center at the cell origin, which is situated at the center of the bridging diphosphine ligand. Toluene is disordered in this structure such that the rotation between the two positions of the methyl C atom is 36°. The geometry about Zn can be described as a distorted trigonal bipyramid. The Zn—P distance is 2.388 (2) Å and the Zn—S distances range from 2.320 (2) to 2.653 (2) Å.

Comment

The structure of the title complex (1), shown in Fig. 1, shows some similarity to that of the parent dimer bis(diethyldithiocarbamato)zinc(II), (2) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). In the latter, one dithiocarbamate ligand bridges both Zn atoms of this dimeric complex, while the other type chelates to each Zn. A five-coordinate distorted trigonal-bipyramidal environment for Zn results from the long (2.81 Å) sulfur bridge. The inversion center of the monoclinic cell lies at the center of the zinc dimer (2) between the bridging dithiocarbamate ligands. Upon introducing the diphosphine ligand, an expansion of the monoclinic cell is observed with a contraction of β. However, the symmetry of the cell, $P2_1/c$, remains the same. Both dithiocarbamate ligands become chelating, whereupon the diphosphine bridges the Zn atoms and the inversion center lies between the P atoms. In the title complex (1), the Zn coordination geometry remains similar to that of the parent compound and can also be represented by a distorted trigonal bipyramid.



(1)

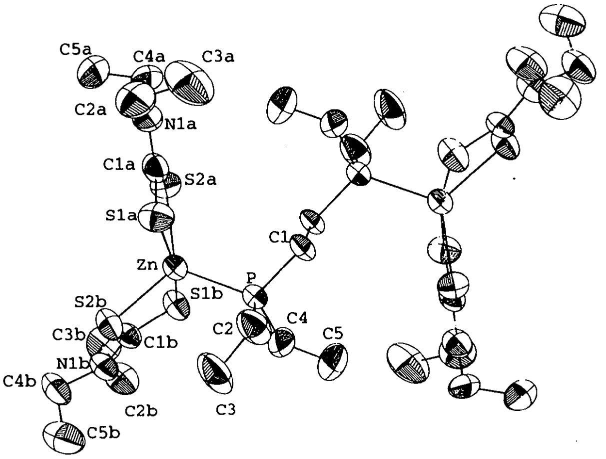


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the zinc dimer. Each half of the molecule is related to the other by the inversion center. The disordered toluene rings are not shown for the purpose of clarity.

Experimental

The synthesis of this compound is described elsewhere (Zeng & Hampden-Smith, 1994). The crystal used for data collection was recrystallized from toluene and mounted in a 0.2 mm diameter sealed capillary tube containing the mother liquor in order to prevent decomposition, as the loss of solvated toluene is rapid in the open atmosphere. (However, the large decrease in intensity of the standard reflections revealed that degradation of the crystal still occurred.)

Crystal data

$[Zn_2(C_5H_{10}NS_2)_4(C_{10}H_{24}P_2)]$.-$2C_7H_8$
M_r = 1114.4
Monoclinic
$P2_1/c$
a = 12.960 (1) Å
b = 11.311 (2) Å
c = 20.129 (5) Å
β = 96.46 (1)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 45 reflections
θ = 5.5–13.5°
μ = 1.189 mm^{-1}
T = 298 K
Needle
0.4 × 0.2 × 0.2 mm

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