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(η^6-Biphenyl)tricarbonylchromium and μ-(η^6:η^6)-biphenyl-bis(tricarbonylchromium)

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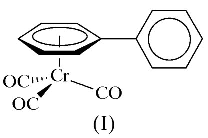
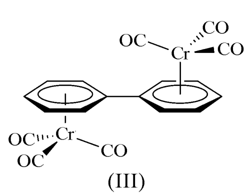
The title compounds, $[Cr(C_{12}H_{10})(CO)_3]$ and $[Cr_2(C_{12}H_{10})(CO)_6]$, serve as a fundamental standard of comparison for other mono- and polysubstituted (η^6-biphenyl)tricarbonylchromium compounds. (η^6-Biphenyl)tricarbonylchromium has a typical piano-stool coordination about the Cr center, and the dihedral angle between the planes of the phenyl rings is 23.55 (5)°. The corresponding angle in μ-(η^6:η^6)-biphenyl-bis(tricarbonylchromium) is 0° because the molecule occupies a crystallographic inversion center; the Cr atoms reside on opposite sides of the biphenyl ligand. Density functional theory and natural bonding orbital theory analyses were used to scrutinize the geometry of these and closely related compounds to explain important structural features.

Comment

As part of an ongoing study of *ortho*-substituted (biphenyl)-tricarbonylchromium compounds, we became interested in (η^6-biphenyl)tricarbonylchromium, (I), since it is the simplest unsubstituted version of all other mono- or polysubstituted compounds in the series. Recently, polysubstituted analogs of (I) have been used in stereoselective syntheses of biologically important molecules (Kamikawa *et al.*, 2003; Fogel *et al.*, 2001) and metal carbene benzannulation reactions (Kretschik *et al.*, 1996), and the (η^6-biphenyl)dicarbonylchromium fragment has been incorporated into Fischer carbene complexes (Merlic *et al.*, 1992). Surprisingly, the solid-state structure of the unsubstituted analog (I) has not been reported to date, though several methods for its synthesis have been described previously (Fischer *et al.*, 1959; Ercoli *et al.*, 1959; Rieke *et al.*, 1982). The importance of this compound as a fundamental standard of comparison for other mono- and polysubstituted (η^6-biphenyl)tricarbonylchromium compounds prompted us to explore the solid-state structure of (I), which is reported here.

We first became interested in (I) (Fig. 1) because it relates to the structure of the brominated analog (η^6-2-bromo-1,1′-biphenyl)tricarbonylchromium, (II), which we reported previously (Czerwinski *et al.*, 2003). We found that (II) reacts with *tert*-butyllithium at 195 K in ether in a metal–halogen exchange reaction that forms (I) in ~10% yield after protonation with methanol. In an effort to prepare an authentic sample of (I) for comparison, a 1:1 mixture of biphenyl and hexacarbonylchromium was refluxed in dibutyl ether/tetrahydrofuran (Nicholls & Whiting, 1959). Unexpectedly, the ^{1}H NMR spectrum of the resulting crude yellow solid showed that the product was a mixture containing 70% of the desired compound, (I), and 30% of μ-(η^6:η^6)-biphenyl-bis(tricarbonylhexchromium), (III). Recrystallization from hexane/ether led to the formation of some single crystals of (III) but was not an efficient method for effecting complete separation of the two compounds. However, they have markedly different polarities and were readily separated using thin-layer chromatography (Top & Jaouen, 1979). Slow evaporation of a hexane/ether solution of (I) led to single crystals suitable for crystallographic analysis.


(I)


(III)

We also report the structure of (III) (Fig. 2), which crystallizes in space group $P2_1/c$. We include atomic coordinates for the monoclinic cell that were not reported in a previous study, which showed that (III) crystallizes in two different space groups, $P\overline{1}$ and $P2_1/c$ (Corradini & Allegra, 1960). Compound (III) has attracted attention recently in electrochemical reactions leading to substituted biphenyl compounds (Rieke *et al.*, 1992), and substituted variations of (III) have been the subject of crystallographic studies related to the electrochemistry (Pierce & Geiger, 1994) and novel coupling reactions (Rosemunch *et al.*, 1991; Uemura *et al.*, 1994) of (arene)tricarbonylchromium compounds.

Because of the importance of (I) and (III), we scrutinized their solid-state geometries and performed density functional theory (DFT) studies of (I) and (III), referred to as (I)-DFT and (III)-DFT, respectively, and of $[Cr(\eta^6-C_6H_6)(CO)_3]$, (IV),

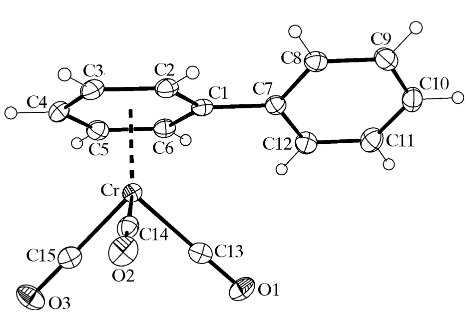


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

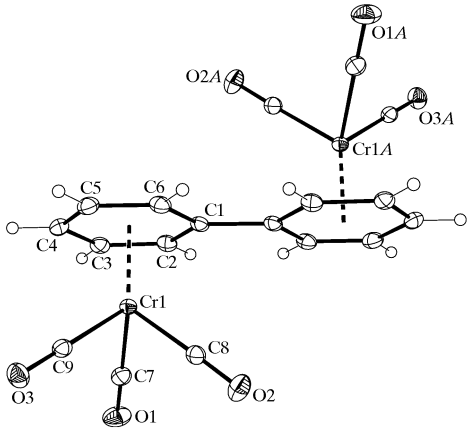


Figure 2
The molecular structure of (III). Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (*A*) $1 - x, -y, -z$.]

with *GAUSSIAN*98 (Frisch *et al.*, 1998). Selected geometric parameters are presented in Table 1, while selected bond lengths are tabulated in Tables 2 and 3. Literature data for the relevant bond distances in related complexes reported to the Cambridge Structural Database (Allen, 2002) were previously compiled and analyzed by us (Czerwinski *et al.*, 2003).

The Cr—C(O), Cr—C(Ph) and Cr—centroid(Ph) distances in (I) and (III) are in excellent agreement with one another, the corresponding parameters in (II) and the literature data for related complexes. Interestingly, in the structures of (I)-DFT, (III)-DFT and (IV) optimized at the B3LYP/LANL2DZ level of theory, the Cr—C(O) distances are shorter (by 0.01–0.02 Å) than those in (I) and (III), while the Cr—C(Ph) distances are longer (by almost 0.1 Å) than the respective bond lengths in (I) and (III), a very substantial difference. It is noteworthy that the natural atomic charges of the Cr centers in (I)-DFT, (III)-DFT and (IV) are −0.87 in all three cases, a result not intuitively obvious since the formal metal oxidation state in these compounds is zero. The natural bond theory analysis revealed that the hybridization of the Cr atoms is sd^2 in (I)-DFT and (III)-DFT, and $sp^{0.5}d^{4.5}$ in (IV), indicating contribution of the *p* orbitals in the latter case. However, it is not clear why the hybridization states would differ in these compounds.

The C—C distances in the ligated ring of the solid-state structures of (I) and (III) [1.412 (12) and 1.414 (11) Å, respectively] are, as expected, longer than those of an ideal benzene molecule. The corresponding value in (IV) is 1.415 (11) Å, confirming that the Cr—C interactions in all three cases are similar. Calculating the average C—C distances in the coordinated rings in (I)-DFT and (IV) may be misleading since the theoretical geometries indicate alternating bond lengths (1.43 and 1.42 Å) in all three cases.

The *ipso*-C—*ipso*-C distances in (I), (II), (III), (I)-DFT, (III)-DFT and the free biphenyl molecule optimized at the B3LYP/6-311++G** level of theory are 1.488 (2), 1.497 (3), 1.493 (3), 1.488, 1.486 and 1.486 Å, respectively, and are not statistically different, despite the fact that the dihedral angles between the phenyl rings in these compounds are different. The Ph—Ph dihedral angles in (I) and (I)-DFT differ dramatically (Table 1), but the value in (I)-DFT is closer to the theoretical value of the dihedral angle in free biphenyl (40.84°). In the solid-state structure of (III), the molecule occupies a crystallographic inversion center, which results in a torsion angle of 0° between the phenyl rings.

Experimental

A mixture of hexacarbonylchromium (0.900 g, 4.09 mmol) and biphenyl (0.680 g, 4.02 mmol) in di-*n*-butyl ether (30 ml) and tetrahydrofuran (3 ml) was degassed and heated at reflux for 24 h under a nitrogen atmosphere. Tetrahydrofuran, di-*n*-butyl ether and the remaining unreacted hexacarbonylchromium were removed by vacuum distillation. Purification of the remaining yellow residue by preparative thin-layer chromatography (silica gel, 2:1 hexane/diethyl ether) gave a yellow band ($R_F = 0.35$) from which (I) was isolated as a yellow air-stable solid (0.722 g, 62% yield based on biphenyl) and an orange band ($R_F = 0.15$) from which (III) was isolated as a yellow air-stable solid (0.192 g, 11% yield based on biphenyl). Crystals of (I) were obtained by slow evaporation of a 3:1 hexane/ether solution and crystals of (III) were obtained by slow evaporation of a 1:1 hexane/ether solution.

Compound (I)

Crystal data

$[Cr(C_{12}H_{10})(CO)_3]$
$M_r = 290.23$
Monoclinic, $P2_1/n$
$a = 12.3982\ (5)$ Å
$b = 7.1029\ (3)$ Å
$c = 14.8428\ (6)$ Å
$\beta = 108.969\ (1)^\circ$
$V = 1236.12\ (9)$ Å^3
$Z = 4$
$D_x = 1.560$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8453 reflections
$\theta = 2.6$–26.4°
$\mu = 0.92$ mm^{-1}
$T = 100\ (2)$ K
Block, yellow
$0.38 \times 0.32 \times 0.28$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000–2003)
$T_{min} = 0.720$, $T_{max} = 0.782$
13 192 measured reflections
2526 independent reflections
2384 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 26.4^\circ$
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 8$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.072$
$S = 1.07$
2526 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.6246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Geometric parameters (Å, °) for (I), (I)-DFT, (III), (III)-DFT and (IV).

Compound	(I)	(III)	(I)-DFT	(III)-DFT	(IV)
Cr—C(O)	1.843 (8)	1.851 (3)	1.831 (1)	1.832 (3)	1.832
Cr—C(Ph)	2.229 (15)	2.219 (11)	2.320 (17)	2.318 (15)	2.317 (7)
Cr—centroid(Ph)	1.725 (2)	1.710 (2)	1.830	1.827	1.82
(Ph)C—C(Ph)	1.488 (2)	1.493 (3)	1.488	1.486	
Ph–Ph angle	23.55 (5)	0.0	37.4	30.9	

Table 2
Selected interatomic distances (Å) for (I).

Cr—C15	1.8374 (15)	Cr—C3	2.2250 (14)
Cr—C14	1.8393 (15)	Cr—C2	2.2252 (14)
Cr—C13	1.8518 (15)	Cr—C4	2.2259 (14)
Cr—C5	2.2148 (14)	Cr—C1	2.2592 (14)
Cr—C6	2.2240 (14)		

Compound (III)

Crystal data

$[Cr_2(C_{12}H_{10})(CO)_6]$
$M_r = 426.26$
Monoclinic, $P2_1/c$
$a = 10.7256\ (12)$ Å
$b = 10.6894\ (12)$ Å
$c = 7.1789\ (8)$ Å
$\beta = 104.875\ (2)^\circ$
$V = 795.48\ (15)$ Å^3
$Z = 2$

$D_x = 1.780$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4396 reflections
$\theta = 2$–25°
$\mu = 1.40$ mm^{-1}
$T = 100\ (2)$ K
Block, orange
0.37 × 0.32 × 0.31 mm

Data collection

Bruker SMART CCD 1000 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000–2003)
$T_{\min} = 0.625$, $T_{\max} = 0.671$
7141 measured reflections

1943 independent reflections
1838 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.3^\circ$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 13$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.091$
$S = 1.09$
1943 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.5575P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (III).

Cr1—C9	1.8484 (18)	Cr1—C6	2.2150 (17)
Cr1—C8	1.8507 (18)	Cr1—C2	2.2201 (17)
Cr1—C7	1.8549 (19)	Cr1—C4	2.2207 (18)
Cr1—C3	2.2070 (18)	Cr1—C1	2.2384 (17)
Cr1—C5	2.2137 (18)		

All H atoms were included in the structure-factor calculations at idealized positions and were allowed to ride on their neighboring atoms with relative isotropic displacement coefficients.

For both compounds, data collection: *SMART* (Bruker, 2000–2003); cell refinement: *SAINT* (Bruker, 2000–2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000–2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1212). Services for accessing these data are described at the back of the journal.

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