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(η^6-2-Bromo-1,1′-biphenyl)-tricarbonylchromium

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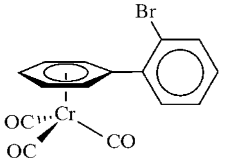
The title compound, $[Cr(C_{12}H_9Br)(CO)_3]$, crystallizes in the triclinic space group $P\overline{1}$ with close Br···Br separations. These contacts, along with several other factors, influence the (Ph)C—C(o-BrC_6H_4) dihedral angle of 58.82 (6)°. The typical piano-stool coordination about the Cr atom is in excellent agreement with the results of density functional theory calculations.

Comment

In the course of synthesizing functionalized biphenyl–chromium–tricarbonyl complexes, we became interested in (η^6-2-bromo-1,1′-biphenyl)tricarbonylchromium, (I), since the possibility of metal–halogen exchange at the 2-position of the molecule suggests its potential use as an intermediate in synthetic and mechanistic studies. Compound (I) has been previously described as being unexpectedly unreactive toward metal–halogen exchange when treated with *n*-butyllithium, apparently due to steric interactions (Oprunenko *et al.*, 1991; Oprunenko, 2000). In an effort to explore some of the steric interactions in the molecule, we studied the low-temperature ^{1}H NMR spectra of (I) but saw no decoalescence of peaks at temperatures as low as 183 K, placing an upper boundary of 9 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) on the rotational barrier about the (Ph)C—C(o-BrC_6H_4) bond of the biphenyl ligand. This relatively low barrier, similar to MP3 results of 9.06 kcal mol^{-1} for the free ligand, suggests only a small amount of rotational steric hindrance in (I). Also, we have recently established that, while the compound is unreactive toward *n*-butyllithium, the more reactive reagent *tert*-butyllithium successfully brings about metal–halogen exchange in (I). This unexpected selectivity toward alkyllithium reagents, uncertainties regarding steric interactions in the molecule, and the lack of any published monosubstituted biphenyl–chromium–tricarbonyl structures, prompted us to explore the solid-state structure of (I), which is reported here.

In the solid-state structure of (I), the Cr atom is in a typical piano-stool geometry, displaced by 1.7178 (11) Å from the plane of the phenyl ring. A Cambridge Structural Database (CSD, Version 5.24 and three updates; Allen, 2002) search on all the tricarbonylchromium compounds with the Cr atom coordinating in a η^6 fashion to a substituted phenyl ring returned 579 hits, from which the average Cr—C(Ph), Cr–centroid(Ph) and Cr—CO distances were 2.23 (4), 1.73 (2) and 1.83 (2) Å, respectively. Similar parameters for tricarbonylchromium with a monosubstituted η^6-coordinated phenyl ring are 2.22 (2), 1.716 (10) and 1.836 (12) Å, respectively, based on 77 hits in the CSD. These parameters are in excellent agreement with the data observed in the solid-state structure of (I), which are 2.225 (7), 1.7178 (11) and 1.849 (5) Å, respectively.



(I)

An interesting aspect of the structure of (I), also detected by the *PLATON* checking software (Spek, 2003), is the length of the C—C bonds within the coordinated phenyl ring. These average 1.415 (11) Å, a value noticeably exceeding the length of the idealized C—C bond with bond order 1.5. The corresponding C—C bond length in relevant compounds averaged 1.401 (16) Å, based on 242 entries in the CSD. During this CSD search it became obvious that, in a number of complexes, authors used the idealized C—C distance of 1.39 Å for their Cr-ligated phenyl rings; thus, we excluded those entries from the statistics cited above.

The dihedral angle between the planes of the phenyl rings in (I) is 58.82 (6)°, a value in excellent agreement with the angle of 59.1° in the structure of (I) optimized at the B3LYP/LANL2DZ level of theory (*GAUSSIAN*98; Frisch *et al.*, 1998) and close to the dihedral angle of 62.5° in free 2-bromobiphenyl optimized at the B3LYP/6-31+G* level. These angles are close to the corresponding torsion angles between the phenyl rings in 2-hydroxybiphenyl [57.0 (7)°; Perrin *et al.*, 1987] and 2-fluorobiphenyl [54 (3)°; Rajnikant *et al.*, 1995]. In the solid-state structure of (I), the torsion angle in question depends on the close Br···Br($2 - x$, $1 - y$, $-z$) contacts [3.5882 (6) Å] that fall within the sum of two bromine van der Waals radii (3.70 Å). Additionally, each Br atom is in the vicinity of a third Br atom. However, this Br···Br($3 - x$, $-y$, $-z$) separation [4.2645 (6) Å] is outside the van der Waals contact sphere. These two contacts, the interaction between the *ortho*-H atom of the non-coordinated ring with the $Cr(CO)_3$ core, and the interaction between the Br atom and the *ortho*-H atom of the coordinated ring (Br···H6 = 3.09 Å)

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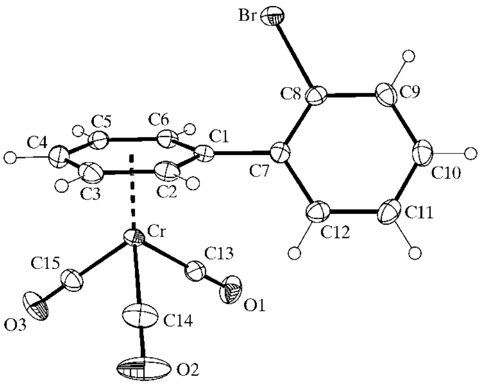

Figure 1
The molecular structure of (I), with displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

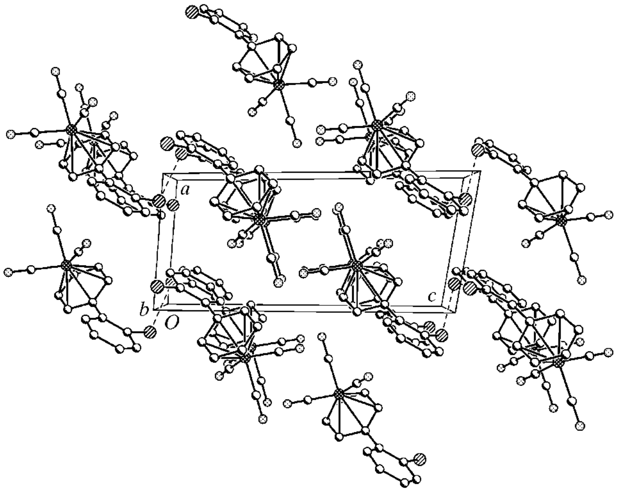

Figure 2
A packing diagram for (I), viewed along the *b* axis. The dashed lines show close Br···Br contacts.

all play a role in determining the Ph—Ph torsion angle. However, it is impossible to quantify these contributions. If the observed conformation is predominant in solution, it appears that the Br atom of (I) would be easily accessible for Li–Br exchange, since it is known that metal–halogen exchange reactions require a 180° $R—X—R$ geometry between an aryl halide $R—X$ and an attacking alkyllithium reagent *R*–Li (Beak & Allen, 1992).

Experimental

The title compound was prepared according to the published procedure of Oprunenko (2000). Crystals were grown by slow evaporation of a diethyl ether solution of (I).

Crystal data

$[Cr(C_{12}H_9Br)(CO)_3]$
$M_r = 369.13$
Triclinic, $P\overline{1}$
$a = 7.3186\ (8)$ Å
$b = 7.3934\ (8)$ Å
$c = 14.5131\ (16)$ Å
$\alpha = 79.330\ (2)°$
$\beta = 78.867\ (2)°$
$\gamma = 62.067\ (2)°$
$V = 676.67\ (13)$ Å^3
$Z = 2$
$D_x = 1.812$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 949 reflections
$\theta = 2–25°$
$\mu = 3.80$ mm^{-1}
$T = 100\ (2)$ K
Block, colorless
0.44 × 0.22 × 0.16 mm

Data collection

Burker SMART1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000–2003)
$T_{min} = 0.268$, $T_{max} = 0.546$
7381 measured reflections
3220 independent reflections
2885 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 28.4°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.099$
$S = 1.10$
3220 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.1534P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

H atoms were included in structure-factor calculations at idealized positions and allowed for as riding (C—H = 0.95 Å).

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: SQ1136). Services for accessing these data are described at the back of the journal.

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