

Pentacarbonyl[ethoxy(2-ethoxy-4,5-diphenyl-1,3-cyclopentadienyl)carbene]-chromium(0)

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

R factor = 0.038

wR factor = 0.113

Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Cr}(\text{C}_{22}\text{H}_{23}\text{O}_2)(\text{CO})_5]$, is shown to have a slightly distorted octahedral geometry around the Cr atom and a $\text{Cr}=\text{C}$ carbene bond length of 2.111 (5) Å, clearly showing double-bond character. The axial $\text{Cr}-\text{C}_{\text{CO}}$ bond *trans* to the $\text{Cr}=\text{C}$ carbene bond is significantly shorter than the equatorial $\text{Cr}-\text{C}_{\text{CO}}$ bonds.

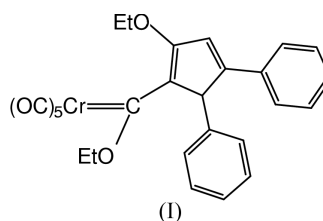
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Comment

Few examples of highly reduced Fischer carbene complexes are found in the literature. However, Krusic *et al.* (1976) have reported the reduction of group 6 alkoxyaryl-carbene complexes by Na/K alloy, and Lee & Cooper (1990) have published results dealing with the reduction of $[\text{Bu}_3\text{P}(\text{CO})_4\text{CrC}(\text{OMe})\text{Ph}]$ by potassium 1-methylnaphthalenide. In the case of reduction of α,β -unsaturated group 6 carbenes, there are few reports, and these deal mainly with the use of simple reducing agents (Gómez-Gallego *et al.*, 2000; Mancheño *et al.*, 1999). Studies have also been extended to include potassium graphite as a reducing agent for a variety of chromium and tungsten carbenes (Sierra *et al.*, 2002). Normally, bis-carbene complexes are produced from this reaction when quenched with 10% H_2SO_4 , but, in the case of reduction of pentacarbonyl(1-ethoxy-3-phenyl-2-propynylidene)chromium(0), a product containing only one carbene moiety was isolated in good yield. From NMR spectroscopic analysis, it was not possible to solve the structure and hence X-ray analysis was necessary.



The title compound, (I), crystallizes in the orthorhombic non-centrosymmetric space group $Pc2_1n$ (non-standard setting of $Pna2_1$). The molecular structure, with the atomic numbering scheme, is shown in Fig. 1. The dihedral angle between phenyl group C16–C21 and the cyclopentadienyl ring is 82.1 (2)°, while that between phenyl group C22–C27 and the cyclopentadienyl ring is 27.2 (2)°. The two phenyl groups are almost perpendicular to each other, with an angle of 88.6 (1)° between the two planes. Atoms C6, O7 and C22 are displaced by 0.026 (8), 0.065 (8) and 0.045 (9) Å, respectively, from the plane of the cyclopentadienyl group; atom C6 is on the opposite side of the plane from atoms O7 and C22.

A slightly distorted octahedral geometry is present about the Cr atom. The Cr1=C6 carbene bond length is 2.111 (5) Å, clearly showing double-bond character when compared to other Cr–C bonds (Orpen *et al.*, 1994). The axial Cr–C_{CO} bond *trans* to the Cr=C carbene bond is significantly shorter [1.832 (6) Å] than the equatorial Cr–C_{CO} bonds [1.877 (7)–1.907 (7) Å]. This is in agreement with the results found in other investigations (Pohl *et al.*, 1995; Fischer, 1974). The average value for the equatorial C≡O bonds is 1.138 (12) Å, compared to a value of 1.166 (7) Å for the axial C≡O bond, all in good agreement with the values found for other terminal carbon monoxide metal complexes (Orpen *et al.*, 1994). All other bond lengths in the title molecule are within normal ranges (Allen *et al.*, 1987).

Experimental

Crystals were placed in a vial and dissolved by addition of a small amount of dichloromethane, followed by a few drops of *n*-hexane. Owing to the dark colour of the solution, it was impossible to determine the saturation point. Crystals were grown by evaporation of the solvent in a refrigerator.

Crystal data

[Cr(C ₂₂ H ₂₃ O ₂)(CO) ₅]	Mo K α radiation
$M_r = 510.45$	Cell parameters from 3 reflections
Orthorhombic, $Pc2_1n$	$\theta = 12\text{--}16^\circ$
$a = 10.174$ (4) Å	$\mu = 0.50$ mm ⁻¹
$b = 12.653$ (3) Å	$T = 298$ (2) K
$c = 19.559$ (9) Å	Block, dark red
$V = 2517.9$ (16) Å ³	0.70 × 0.50 × 0.40 mm
$Z = 4$	
$D_x = 1.347$ Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	1658 reflections with $I > 2\sigma(I)$
ω - 2θ scans	$\theta_{\max} = 25.0^\circ$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$h = 0 \rightarrow 12$
$T_{\min} = 0.722$, $T_{\max} = 0.826$	$k = 0 \rightarrow 14$
2315 measured reflections	$l = 0 \rightarrow 23$
2315 independent reflections	3 standard reflections
	frequency: 120 min
	intensity decay: 5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\max} = 0.005$
$S = 1.00$	$\Delta\rho_{\max} = 0.24$ e Å ⁻³
2315 reflections	$\Delta\rho_{\min} = -0.23$ e Å ⁻³
318 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.02 (3)

H atoms were refined using a riding model, with Csp²–H = 0.93 Å, C(methyl)–H = 0.96 Å, C(methylene)–H = 0.97 Å and other Csp³–H = 0.98 Å. $U_{\text{iso}}(\text{H})$ values were set equal to 1.3 U_{eq} (1.4 U_{eq} for methyl H atoms) of the carrier atom.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *CELDIM* in *CAD-4-PC Software*; data reduction: *XCAD4* (McArdle & Higgins, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (McArdle, 1995); software used to prepare material for publication: *OSCAIL* (Version 8; McArdle, 1993).

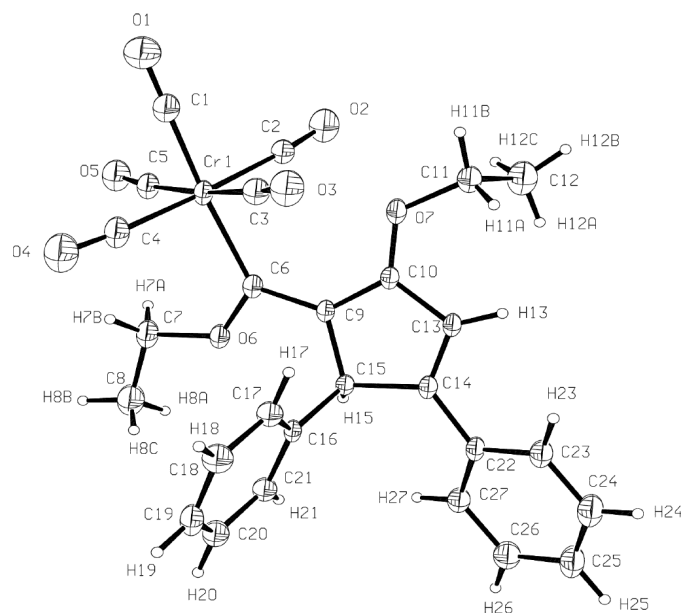


Figure 1

A view of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

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