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The synthesis and crystal structure of μ-{di-η^6-phenyl(trimethylsilyl)methane}-{bis(tricarbonyl)chromium}

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Abstract

The compound [μ-(η^6-$Ph_2CHSiMe_3$){$Cr(CO)_3$}$_2$] was obtained in 80% yield from hexacarbonylchromium and $SiMe_3CHPh_2$. It crystallised in the unsymmetrical so-called "in-out" configuration with one $Cr(CO)_3$ group between the two phenyl rings and the other between a phenyl and the trimethylsilyl group. The methine proton was removed by methyllithium, but attempts to use the resulting anion in syntheses were not successful.

Introduction

In considering ligands suitable for the study of steric effects in organometallic compounds [1,2], our attention was drawn to the compound [μ-(η^6-$Ph_2CHSiMe_3$)-{$Cr(CO)_3$}$_2$] (**1**) [3], which can readily be deprotonated at the methine carbon [3,4]. We hoped to convert the resulting carbanion into a variety of derivatives [η^6-Ph_2C-($SiMe_3$)($SiMe_2X$){$Cr(CO)_3$}$_2$] (**2**) (e.g. X = Me, Cl, or H) and then to study reactions at the Si–X bond. This line of research was not successful, but during our work we devised an improved synthesis and determined the crystal structure of the bis-chromium derivative (**1**).

Experimental

Air and moisture were excluded by the use of Schlenk tube techniques. Solvents were purified by standard procedures.

Preparation of [μ-(η^6-$Ph_2CHSiMe_3$){$Cr(CO)_3$}$_2$] (1)

A mixture of $SiMe_3CHPh_2$ (1.7 g, 7.1 mmol), $Cr(CO)_6$ (4.4 g, 20 mmol), dibutyl ether (100 cm^3), and tetrahydrofuran (10 cm^3) was heated under reflux for 48 h with protection from light. The resulting solution was filtered hot to remove traces of a

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green deposit. The filtrate was concentrated and then kept at −10 °C overnight to give yellow crystals, which were recrystallised from heptane and shown to be $[\mu\text{-}(\eta^6\text{-}Ph_2CHSiMe_3)\{Cr(CO)_3\}_2]$, m.p. 168 °C (3 g, 82%) (lit. 3 168 °C). Found: C, 50.4; H, 3.6; $C_{22}H_{20}Cr_2O_6Si$ calc: C, 51.6; H, 3.9%; δ(H) ($CDCl_3$) 0.2 (9H, s, $SiMe_3$), 2.75 (1H, s, CH), 5.25 ppm (10H, m, Ph); ν(CO): 1965, 1900 cm^{-1}; m/z 428 (2%, $[M-3CO]^+$), 400 (4, $[M-4CO]^+$), 376 (8, $[M-Cr(CO)_3]^+$, 372 (3, $[M-5CO]^+=[M']^+$), 344 (5, $[M-6CO]^+=[M'']^+$), 292 (90, $[M''-Cr]^+$), 243 (50, $[M'-Cr-Ph]^+$), 240 (16, $[Ph_2CHSiMe_3]^+$), 214 (50, $[M''-Cr-PhH]^+$ or $[C_6H_6Cr(CO)_3]^+$), 201 (30), 167 (25, $[Ph_2CH]^+$), 165 (20, $[Ph_2CH-H_2]^+$), 130 (80, $[C_6H_6Cr]^+$), 73 (100, $[SiMe_3]^+$), 59 (25, $[SiMe_2H]^+$), and 52 (60, $[Cr]^+$).

The reaction of $[\mu\text{-}(\eta^6\text{-}Ph_2CHSiMe_3)\{Cr(CO)_3\}_2]$ (1) with methyllithium

A solution of MeLi (1.95 mmol) in ether (2.05 cm^3) was added with stirring to **1** (1.00 g, 1.95 mmol) in thf (10 cm^3) at room temperature. Gas was evolved briskly and the colour changed from yellow to red and then brown. After 1 h, $SiMe_3Cl$ (1.95 mmol) was added, but there was no further colour change. After another 2 h more $SiMe_3Cl$ (9.75 mmol) was added and the mixture was heated under reflux for a further 2 h. The mixture was allowed to cool then poured into water. Ether extraction, followed by drying ($MgSO_4$) and evaporation of the extract gave a yellow solid, shown by its m.p. and NMR spectrum to be only **1** in low yield. Reactions with $SiMe_2HCl$ and $SiMe_2Cl_2$ gave similar results.

In another experiment the brown solution obtained as above from MeLi (1.95 mmol) and **1** (1.95 mmol) was treated with D_2O (5 mmol). The solvent was removed and the residue extracted with heptane. The extract was filtered and the filtrate concentrated to give yellow crystals. The ^1H NMR spectrum of these in $C_6D_5CD_3$ showed that the methine signal at δ 2.75 had disappeared, but there had also been changes in the aromatic signals, indicating that the lithiation had not been effected cleanly at the methine proton only.

Crystal structure determination

Crystal data. $C_{22}H_{20}Cr_2O_6Si$, M 512.5 monoclinic, space group $P2_1/n$, a 8.329(1), b 22.840(5), c 12.276(1) Å, β 95.94(1)°, U 2322.9 $Å^3$, $Z=4$, D_c 1.52 g cm^{-3}, $F(000)$ 1048. Monochromated Mo-K_α radiation, λ 0.71069 Å, μ 9.95 cm^{-1}.

Data were obtained on an Enraf–Nonius CAD4 diffractometer with a crystal of ca. 0.2 × 0.2 × 0.1 mm obtained from heptane solution. Final values of cell dimensions were calculated from setting angles of 25 reflections with $\theta \sim 14°$. Intensities for h, k, $\pm l$ reflections with $2 < \theta < 23°$ were measured by a $\theta/2\theta$ scan with a scan width $\Delta\theta = (1.0 + 0.35 \tan\theta)°$. Two standard reflections monitored every hour showed no significant variation. After correction for Lorentz and polarisation (Lp) effects but not for absorption, and averaging of equivalent reflections, 1336 with $|F^2| > \sigma(F^2)$ were used in the structure refinement. Values of $\sigma(F^2)$ were $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The structure was solved by direct methods (MULTAN) [6] and refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least-squares. Hydrogen atoms, found on a difference map, were included with $B = 6.0$ $Å^2$. Refinement converged at $R = 0.043$, $R' = 0.040$ when the maximum shift/error was 0.59 (using the weighting scheme $w = 1/\sigma^2(F)$). A final difference map was everywhere featureless.

The structure determination and refinement was carried out on a PDP 11/34 computer using the Enraf–Nonius structure determination package. Scattering factors for neutral atoms were from ref. 7. Final coordinates are listed in Table 1. Lists of hydrogen atom coordinates, temperature factors, and final structure factors are available from the authors.

Results and discussion

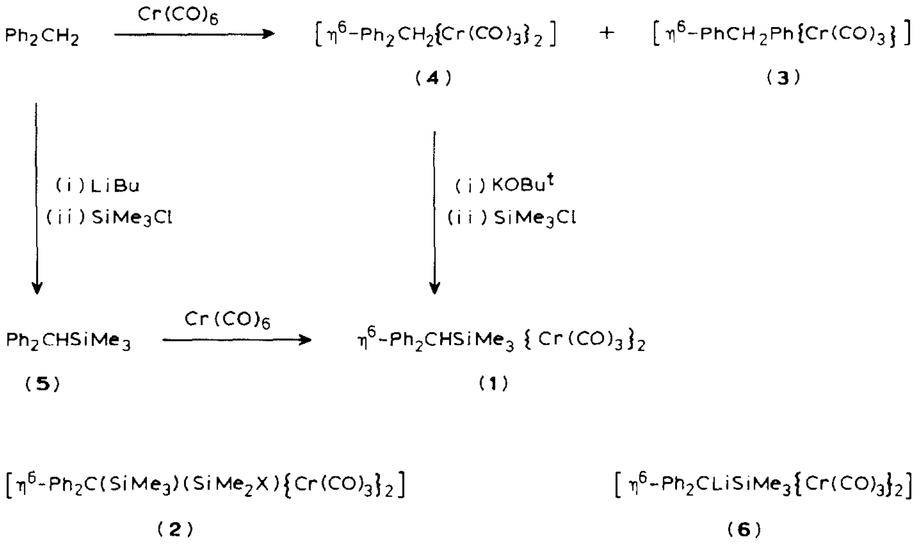
The mono- and bis-chromium derivatives **3** and **4** were made as described previously [5], and **4** was converted into the complex **1** (Scheme 1). A much better route to **1** involved first making the silane **5** and then heating it with hexacarbonylchromium. In this way, the bis-complex **1** was readily obtained without the need for purification by chromatography.

In crystals of the compound **1** the well separated molecules (Fig. 1) have dimensions (Table 2) which are similar to those in analogous species. The central

Table 1

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for **1**

Atom	*x*	*y*	*z*
Cr(1)	4727(2)	2244(1)	8894(1)
Cr(2)	1546(1)	−48(1)	8110(1)
Si	4667(3)	1275(1)	5823(2)
O(1)	−525(8)	−1005(3)	8849(6)
O(2)	3165(6)	106(3)	10369(4)
O(3)	−843(7)	857(3)	8612(5)
O(4)	7619(8)	2695(3)	7910(5)
O(5)	4864(8)	3287(3)	10353(5)
O(6)	2634(9)	2923(3)	7243(6)
C(1)	3382(8)	1161(3)	7025(6)
C(2)	3502(10)	973(4)	4598(7)
C(3)	5003(13)	2050(4)	5589(8)
C(4)	6608(11)	874(5)	6046(7)
C(5)	3931(8)	1374(3)	8155(5)
C(6)	5519(9)	1339(4)	8619(6)
C(7)	5977(10)	1480(4)	9732(7)
C(8)	4847(11)	1682(4)	10354(6)
C(9)	3237(10)	1736(4)	9922(6)
C(10)	2789(9)	1578(3)	8834(6)
C(11)	2899(8)	532(3)	7021(5)
C(12)	1443(9)	333(3)	6477(6)
C(13)	1067(11)	−270(4)	6352(6)
C(14)	2113(12)	−670(4)	6868(7)
C(15)	3531(10)	−500(4)	7433(6)
C(16)	3924(8)	101(3)	7516(5)
C(17)	71(9)	496(4)	8446(6)
C(18)	264(11)	−624(4)	8570(7)
C(19)	2538(9)	36(4)	9497(6)
C(20)	6483(11)	2522(4)	8306(7)
C(21)	4815(10)	2877(4)	9790(7)
C(22)	3469(11)	2663(4)	7873(8)



Scheme 1

Si-C(1) bond (1.928(8) Å) is significantly longer than the Si–Me bonds (mean 1.837(10) Å), as in other crowded compounds such as $(Me_3Si)_2CH_2$ [8] and a number of $(Me_3Si)_3C$ derivatives [9]. The mean Cr–CO (1.819(9) Å) and C–O (1.160(10) Å) bond lengths and the Cr–ring centroid distances (1.714 Å) are similar

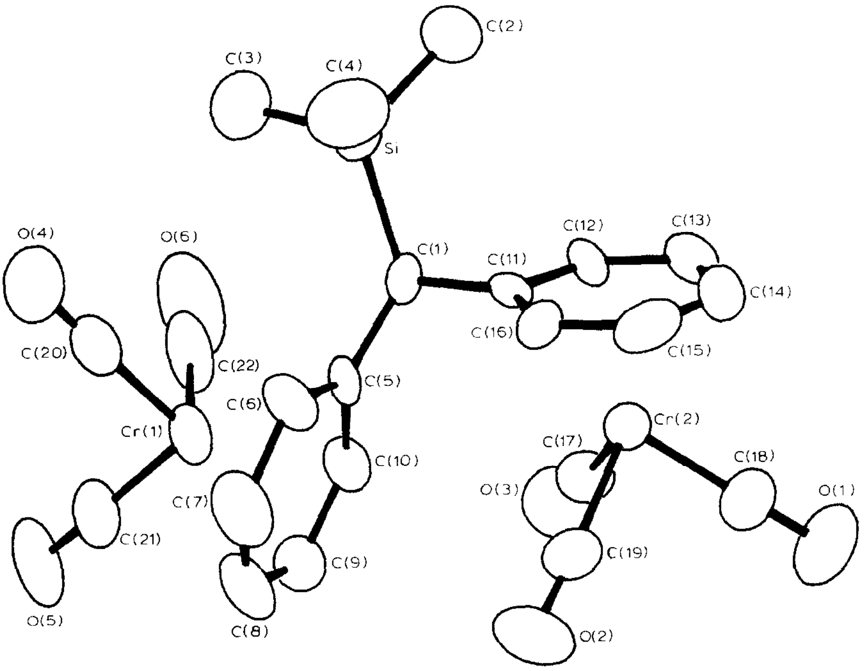


Fig. 1. The molecular structure of **1**.

Table 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for **1** [a]

Si–C(1)	1.928(8)	Si–C(2)	1.838(9)
Si–C(3)	1.819(10)	Si–C(4)	1.853(10)
O(1)–C(18)	1.162(12)	O(2)–C(19)	1.153(8)
O(3)–C(17)	1.156(10)	O(4)–C(20)	1.175(12)
O(5)–C(21)	1.162(10)	O(6)–C(22)	1.151(11)
C(1)–C(5)	1.497(9)	C(1)–C(11)	1.492(10)
C(5)–C(6)	1.387(10)	C(5)–C(10)	1.407(11)
C(6)–C(7)	1.418(11)	C(7)–C(8)	1.353(12)
C(8)–C(9)	1.396(12)	C(9)–C(10)	1.396(11)
C(11)–C(12)	1.398(10)	C(11)–C(16)	1.401(10)
C(12)–C(13)	1.418(12)	C(13)–C(14)	1.372(12)
C(14)–C(15)	1.362(12)	C(15)–C(16)	1.412(11)
Cr(1)–C(20)	1.812(9)	Cr(1)–C(21)	1.814(8)
Cr(1)–C(22)	1.820(9)	Cr(1)–*C(1)*	1.721
Cr(2)–C(17)	1.823(8)	Cr(2)–C(18)	1.822(9)
Cr(2)–C(19)	1.824(7)	Cr(2)–*C(2)*	1.706
Cr(1)–C(5)	2.254(7)	Cr(1)–C(6)	2.205(8)
Cr(1)–C(7)	2.227(9)	Cr(1)–C(8)	2.198(8)
Cr(1)–C(9)	2.190(9)	Cr(1)–C(10)	2.213(8)
Cr(2)–C(11)	2.263(7)	Cr(2)–C(12)	2.178(7)
Cr(2)–C(13)	2.213(8)	Cr(2)–C(14)	2.172(9)
Cr(2)–C(15)	2.185(9)	Cr(2)–C(16)	2.206(7)
C(1)–Si–C(2)	106.7(4)	C(1)–Si–C(3)	111.0(4)
C(1)–Si–C(4)	111.4(4)	C(2)–Si–C(3)	108.2(4)
C(2)–Si–C(4)	108.3(4)	C(3)–Si–C(4)	111.0(5)
Si–C(1)–C(5)	121.7(5)	Si–C(1)–C(11)	107.4(5)
C(5)–C(1)–C(11)	111.9(6)	C(1)–C(5)–C(6)	123.3(6)
C(1)–C(5)–C(10)	119.8(6)	C(6)–C(5)–C(10)	116.8(6)
C(5)–C(6)–C(7)	122.1(7)	C(6)–C(7)–C(8)	119.2(7)
C(7)–C(8)–C(9)	120.9(7)	C(8)–C(9)–C(10)	119.5(8)
C(5)–C(10)–C(9)	121.5(7)	C(1)–C(11)–C(12)	122.3(6)
C(1)–C(11)–C(16)	121.6(6)	C(12)–C(11)–C(16)	116.0(7)
C(11)–C(12)–C(13)	122.6(7)	C(12)–C(13)–C(14)	118.3(7)
C(13)–C(14)–C(15)	121.4(8)	C(14)–C(15)–C(16)	119.8(7)
C(11)–C(16)–C(15)	121.7(6)	C(20)–Cr(1)–C(21)	88.7(4)
C(20)–Cr(1)–C(22)	88.4(4)	C(20)–Cr(1)–*C(1)*	127.0
C(21)–Cr(1)–C(22)	89.0(4)	C(21)–Cr(1)–*C(1)*	126.0
C(22)–Cr(1)–*C(1)*	125.5	C(17)–Cr(2)–C(18)	89.5(4)
C(17)–Cr(2)–C(19)	88.2(3)	C(17)–Cr(2)–*C(2)*	126.9
C(18)–Cr(2)–C(19)	90.5(4)	C(18)–Cr(2)–*C(2)*	124.6
C(19)–Cr(2)–*C(2)*	125.6		

[a] *C(1)* and *C(2)* denote the centroids of C(5)–C(10) and C(11)–C(16), respectively.

to those in $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (1.841(2), 1.158(2) and 1.724 Å, respectively) [10] and $[Cr(\eta^6\text{-}C_6Me_6)(CO)_3]$ (1.814(13), 1.163(12) and 1.726 Å) [11]. There are no significant differences between the two benzene rings. Both are planar; there is no distortion such as that in $[\mu\text{-}(\eta^6\text{-}ArP{=}PAr\text{-}\eta^6)\{Cr(CO)_3\}_2]$ (7) (Ar = 2,4,6-$Bu^t_3C_6H_2$) [12], but the C–C–C angles adjacent to the methine C (116.8(6) and 116.0(7)°) are slightly smaller than those for a regular hexagon. Torsion angles describing the orientations of $Cr(CO)_3$ groups with respect to the phenyl rings are given in Table 3. Carbonyl groups are rotated from the symmetrical staggered conformations

Table 3

Torsion angles

Atom	1	2	3 [a]	4	Angle (°)
	C(20)	Cr(1)	*C(1)*	C(6)	−19.1
	C(21)	Cr(1)	*C(1)*	C(8)	−20.2
	C(22)	Cr(1)	*C(1)*	C(10)	−19.0
	C(17)	Cr(2)	*C(2)*	C(12)	−11.8
	C(18)	Cr(2)	*C(2)*	C(14)	−12.0
	C(19)	Cr(2)	*C(2)*	C(16)	−11.7

[a] *C(1)* and *C(2)* denote the centroids of C(5)–C(10) and C(11)–C(16), respectively.

found in the benzene or hexamethylbenzene derivatives towards conformations in which they partly eclipse the 2, 4, and 6 positions. Though the orientations of $Cr(CO)_3$ groups are sometimes determined by electronic effects [13], steric effects probably dominate in **1**: the 1, 3, and 5 positions are completely eclipsed in $[\mu\text{-}(\eta^6\text{-ArP=PAr-}\eta^6)\{Cr(CO)_3\}_2])$ (7).

The configuration of the molecule as a whole is similar to that of $[\mu\text{-}(\eta^6\text{-}Ph_2SnMe_2)\{Cr(CO)_3\}_2]$ and described as "in-out" [14]. The $Cr(CO)_3$ fragments fold into the space between the bonds at the central carbon, causing the Si–C(1)–C(5) and C(5)–C(1)–C(11) angles to be expanded from the tetrahedral value and the Si–C(1)–C(11) angle to be slightly compressed.

Methyllithium reacted rapidly with **1** to give a dark red solution reminiscent of the solution obtained from the reaction between MeLi and $(Me_3Si)_3CH$. On evaporation of solvent a brown solid was obtained: this was extracted with heptane and solvent evaporated from the filtered extract to give yellow crystals shown by NMR to contain lithium. However, on further recrystallisation from heptane, the product isolated proved to be only **1**, which had either not reacted at all or had been formed by accidental hydrolysis of the hoped-for lithium compound $[\eta^6\text{-}Ph_2CLiSiMe_3\{Cr(CO)_3\}_2]$ (**6**). Attempts to form derivatives of **6** by treatment of the red-brown solution with Me_3SiCl, Me_2SiCl_2, or Me_2SiHCl proved fruitless.

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References

1 C. Eaborn, J. Organomet. Chem., 239 (1982) 93; H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Ellis Horwood, Chichester, (1985), pp. 123–130.
2 J.D. Smith, Pure Appl. Chem., 58 (1986) 623.
3 S. Top, G. Jaouen, B.G. Sayer and M.J. McGlinchey, J. Am. Chem. Soc., 105 (1983) 6426.
4 F. Terrier, P.G. Farrell, J. Lelievre, S. Top, and G. Jaouen, Organometallics, 4 (1985) 1291.
5 S. Top and G. Jaouen, J. Organomet. Chem., 182 (1979) 381.
6 G. Germain, P. Main, and M.M. Woolfson, Acta Crystallogr., A27 (1971) 368.
7 International Tables for X-Ray Crystallography, Vol. 4 (1974), Kynoch Press, Birmingham.
8 T. Fjeldberg, R. Seip, M.F. Lappert, and A.J. Thorne, J. Mol. Struct., 99 (1983) 295, and references therein.

9 G.A. Ayoko, N.H. Buttrus, C. Eaborn, P.B. Hitchcock, and J.D. Smith, J. Organomet. Chem., 320 (1987) 137, and references therein.

10 B. Rees and P. Coppens, Acta Crystallogr., B29 (1973) 2516.

11 M.F. Bailey and L.F. Dahl, Inorg. Chem., 4 (1965) 1298.

12 M. Yoshifuji, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., (1985) 1109.

13 O.L. Carter, A.T. McPhail, and G.A. Sim, J. Chem. Soc. A, (1967) 228, 1619.

14 U. Schubert, B.R. Willeford, and J.J. Zuckerman, J. Organomet. Chem., 215 (1981) 367.