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TRICARBONYL(1-TRIMETHYLSILYL-2,3-DIMETHOXYBENZENE)- CHROMIUM: A NEW CONFORMATION OF THE TRICARBONYLCHROMIUM ENTITY WITH RESPECT TO A BULKY SUBSTITUENT

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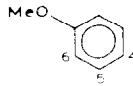
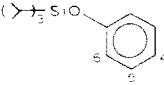
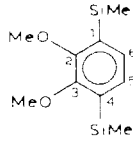
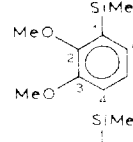
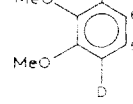
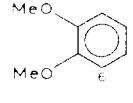
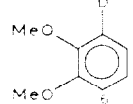
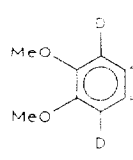

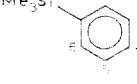
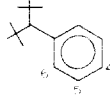
Summary

Because of steric effects the $\text{Cr}(\text{CO})_3$ group in tricarbonyl(1-trimethylsilyl-2,3-dimethoxybenzene)chromium does not take up an anti-eclipsed conformation with respect to the trimethylsilyl group, but instead adopts the opposed conformation nearly eclipsing that group.

Lithiation of arenetricarbonylchromium complexes is well documented [1,2]. For example, Card and Trahanovsky [3] and Semmelhack [4] observed the concurrent formation of 2-methyl- and 2,6-dimethyl-anisole after treatment of (anisole)tricarbonylchromium with $n\text{-BuLi}$, MeI , and $h\nu$ or I_2 : lithiation occurred *ortho* to the methoxy group on a carbon not eclipsed by a $\text{Cr}-\text{CO}$ bond (^1H NMR data: Table 1, entry 1). When the oxygen of the phenoxy group carried a bulky group, Widdowson et al. [5] observed a regiocontrolled lithiation predominantly *meta* to the heteroatom in the case of (η^6 -triisopropylsiloxybenzene)tricarbonylchromium (^1H NMR data: Table 1, entry 2): lithiation occurred mainly at a carbon eclipsed by a $\text{Cr}-\text{CO}$ bond*.

* In the case of the toluene [3], ethylbenzene [3], *meta*-xylene [3], *meta*-diisopropylbenzene [10], *N,N*-disubstituted aniline [3,11,12] and 2-methyl-7-methoxy-1-*endo*-tetralol [13] tricarbonylchromium complexes, lithiation occurs mainly on a carbon eclipsed by a $\text{Cr}-\text{CO}$ bond of the most stable conformer. These carbons are also attacked during a nucleophilic reaction by α -cyano- or α -alkoxy-carbanions [1,2,6]. In the case of the bulkier *t*-butylbenzenetricarbonylchromium attack by α -cyano-carbanions [14] and deprotonation [3] mainly occurred at the *meta* position.

TABLE 1. ^1H NMR DATA FOR ARENETRICARBONYLCHROMIUM COMPLEXES (C) AND THEIR CORRESPONDING FREE ARENES (F)

Entry		H(4)	H(5)	H(6)	Shielding on complexation ^a			Solvent	Ref.	
					<i>i</i> = 4	<i>i</i> = 5	<i>i</i> = 6			
1		(F) 6.93 (C) 5.14	7.25 5.85	6.90 5.44	1.79	1.40	1.46 ^b	(b)	8	
2		(F) 6.93 (C) 5.11	7.25 5.84	6.91 5.40	1.82	1.41	1.51 ^b	(b)	This work	
3		(F) 7.09 (C) 5.23					1.86	(b)	This work	
4		(F) 6.90 (C) 5.73	6.99 5.37	6.99 5.08	1.26	1.62	1.91	(b)	This work	
5		(F) 6.97 (C) 5.40	6.97 5.12			1.57	1.85	(b)	This work ^c	
6		(F) 6.85 (C) 5.33	6.85 5.33	6.85 5.75	1.52	1.52	1.10	(b)	6	
7		(F) ^k 6.89 (C) 5.33	6.89 5.33	6.89 5.72	1.56	1.56	1.17	(b)	This work ^d	
8		(F) ^h 6.87 (C) 5.33	6.87 5.33		1.54	1.54		(b)	6	
9		(F) 7.03 (C) 5.31	7.16 5.14	7.29 5.42	1.72	2.02	1.87	(a)	7	
10		(F) 7.11 (C) 5.67	7.25 5.52	7.37 5.84	1.44	1.73	1.53	(b)	8	
		(F) 7.05 (C) 5.82	7.04 5.43	7.25 5.71	1.23	1.61	1.54	(b)	8	
11		(F) 7.20 (C) 5.89	7.29 7.23 5.38	7.50 7.07 6.08	1.31	1.92	1.32	(b)	8	
			5.89	5.31	5.75	1.31	1.92	1.32		

^a CDCl_3 , ^b Acetone- d_6 , ^c **4** treated by $n\text{-BuLi}$ and D_2O , ^d **4** treated by $\text{CF}_3\text{CO}_2\text{D}$; ^e $\delta(\text{H}_i(\text{F})) - \delta(\text{H}_i(\text{C}))$, ^f **4** + $n\text{-BuLi}$, D_2O , ^g **4** treated by $\text{CF}_3\text{CO}_2\text{D}$, ^h **3** treated by $\text{CF}_3\text{CO}_2\text{D}$, ⁱ ± 0.07 ppm, ^j H(6) does not show shielding on complexation similar to that of H(4) because substituent effects on the chemical shifts of the arenic protons are different for the free arene and for the complex due to the lowering of the ring current in the latter [16].

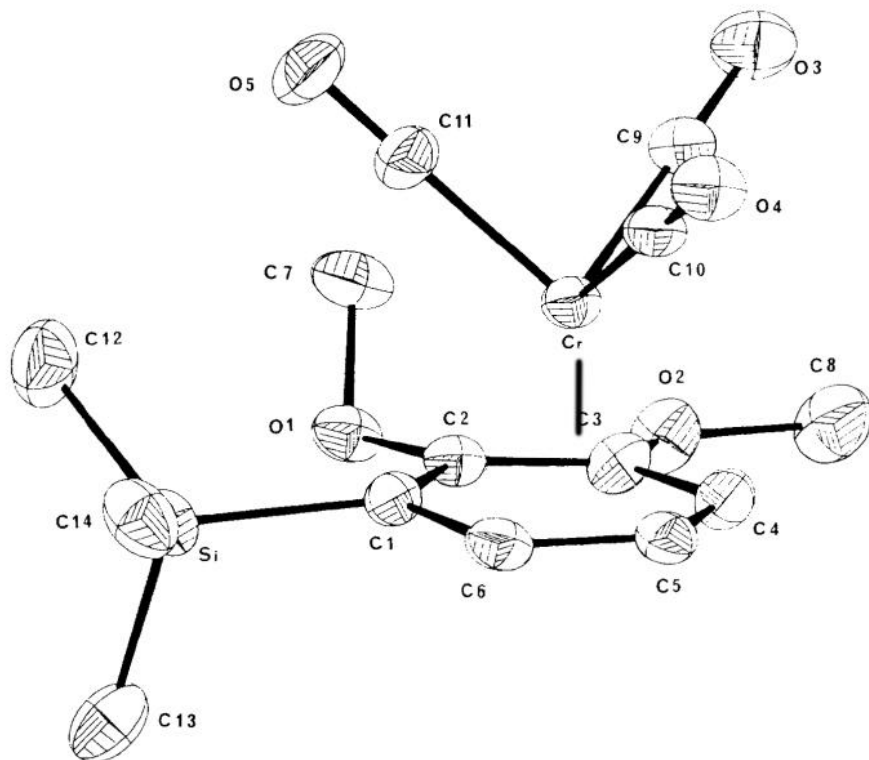


Fig. 1. ORTEP view of the structure of $[\text{Cr}(\text{CO})_3(\eta^6\text{-1-trimethylsilyl-2,3-dimethoxybenzene})]$ (**4**).

We reported [6] that lithiation of (veratrole)tricarbonylchromium (staggered conformation in the solid state) by *n*-BuLi in THF at -78°C followed by silylation with Me_3SiCl gave 1,4-bis(trimethylsilyl)-2,3-dimethoxybenzenetricarbonylchromium (**3**) and (1-trimethylsilylveratrole)tricarbonylchromium (**4**).

We report here the results of a study of the conformation of complex **4** in solution and in the solid state. We present ^1H NMR data determined for some arenetricarbonylchromium complexes and their corresponding free arenes in order to see whether the resonances of the arenic protons could provide information about the regioselectivity of the lithiation of arenetricarbonylchromium complexes.

The ^1H NMR spectrum of (1-trimethylsilylveratrole)tricarbonylchromium* contained a doublet (5.08 ppm) assigned to the *ortho* proton H(6) to the SiMe_3 group, the H(5) and H(4) protons giving rise, respectively, to a triplet (5.37) and a doublet (5.73) (Table 1, entry 4). The H(6) proton was therefore the most shielded arenic proton. The shielding on complexation for H(6), given by $[\delta(\text{H}(6)(1\text{-trimethylsilylveratrole}) - \delta(\text{H}(6)(1\text{-trimethylsilylveratroletricarbonylchromium}))]$ was 1.91 ppm, the largest observed (Table 1, entry 4). ^1H NMR data for other veratroletricarbonylchromium derivatives are also reported in Table 1 in order to establish the

* Complexes **3** and **4** are obtained in similar yields (32% in each case) when the reactions are performed without TMEDA (tetramethylethylenediamine); complex **3** is the major product when (veratrole)tricarbonylchromium is treated with *n*-BuLi and Me_3SiCl with TMEDA at -78°C in THF.

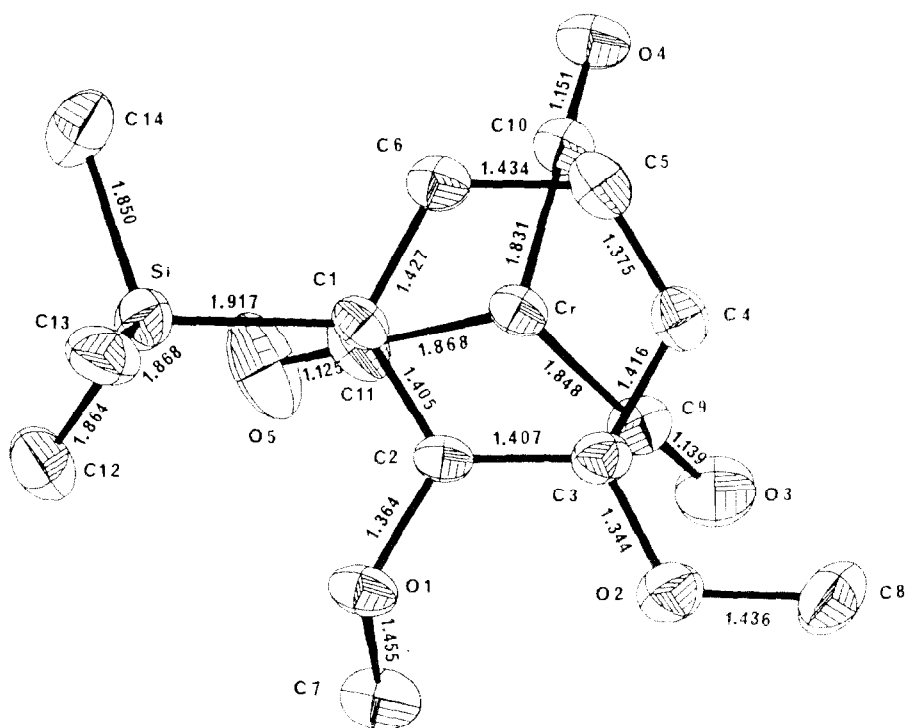


Fig. 2. Projection of the tripod $\text{Cr}(\text{CO})_3$ on the plane of the arene ring. Distances are in Å (e.s.d. are less than 0.009 Å).

chemical shifts of the arenic protons of complex **4**. These data indicated clearly that in solution complex **4** did not possess the expected *anti*-eclipsed conformation (**4a**) with respect to the SiMe_3 group*.

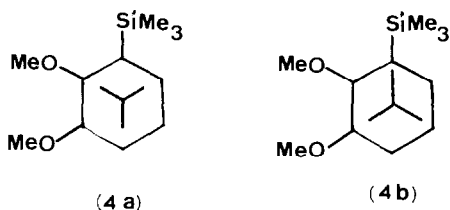
Some ^1H NMR data were previously reported [7,8] for arenetricarbonylchromium complexes containing bulky substituents. For this type of *anti*-eclipsed monosubstituted arenetricarbonylchromium complex, such as *t*-butyl [7] (Table 1, entry 9) α,α -di-*t*-butyltoluenetricarbonylchromium [8] (Table 1, entry 11; the X-ray structure confirmed an *anti*-eclipsed conformation [15]) or *ortho*-disubstituted complexes having a defined conformation [9], it is well known that the chemical shifts of *ortho*- and *para*-eclipsed arenic proton signals appear further downfield than *meta*-*anti*-eclipsed arenic protons; the shielding on complexation of eclipsed arenic protons, $\delta(\text{H}(\text{F})) - \delta(\text{H}(\text{C}))$ are the smallest [6,8,9] (Table 1, entries 9, 10, 11). We observed exactly the opposite result for the H(6) proton of complex **4** showing that this complex adopts another conformation.

In the light of the above NMR data, the X-ray structure of (1-trimethylsilyl-veratrole)tricarbonylchromium (**4**) was determined. This clearly demonstrated that

* MS (CI) M^+ = 346; ^1H NMR (δ (ppm), $\text{Me}_2\text{CO}-d_6$): SiMe_3 0.49 (9H), OMe 3.82 (3H), OMe 3.90 (3H); ArH 5.08 (d, J 6.1 Hz, 1H), ArH 5.37 (dd, J 6.1–6.6 Hz, 1H), ArH 5.73 (d, J 6.6 Hz, 1H); IR (cm^{-1} , CHCl_3): 1965, 1880.

complex **4** adopted an unprecedented almost eclipsed conformation (**4b**) relative to the SiMe_3 group in the solid state. An ORTEP view of structure **4** is represented in Fig. 1, and shows the 2-methoxy group perpendicular to the arene ring and directed toward the $\text{Cr}(\text{CO})_3$ entity. A projection of the tripod $\text{Cr}(\text{CO})_3$ onto the plane of the arene ring is shown in Fig. 2: the torsion angles $\text{C}(3)\text{-G-Cr-C}(9)$, $\text{C}(5)\text{-G-Cr-C}(10)$ and $\text{C}(1)\text{-G-Cr-C}(11)$ are, respectively, $14.5(6)^\circ$, $14.0(6)^\circ$ and $13.8(5)^\circ$ (G is the centre of the arene ring).

Compound **4** represents the first example of an arenetricarbonylchromium complex with a conformation in which a chromium-carbonyl bond almost eclipses a bulky group such as SiMe_3 :



Experimental

The crystal selected for X-ray analysis was a truncated parallelepiped ($0.060 \times 0.034 \times 0.020 \text{ mm}^3$). Preliminary precession and Laue photographs showed the crystal to be monoclinic space group $P2_1/c$ with a 16.787(6), b 7.668(4), c 12.980(7) Å, β $95.18(4)^\circ$ and V 1664 \AA^3 . The measured density (1.39 g cm^{-3}) agreed with

TABLE 2

ATOMIC COORDINATES FOR $[(\eta^6\text{-1-TRIMETHYLSILYL-2,3-DIMETHOXYBENZENE})\text{TRICARBONYLCHROMIUM}]$ IN Å AND e.s.d.s IN PARENTHESES

Atom	x/a	y/b	z/c	B_{iso}
Cr	0.19307(6)	0.0337(1)	-0.00246(7)	3.79(2)
Si	0.3770(1)	0.2597(3)	-0.0974(1)	4.84(5)
O(1)	0.2452(3)	0.0840(5)	-0.2443(3)	4.8(1)
O(2)	0.0839(3)	0.0770(6)	-0.2337(3)	5.6(1)
O(3)	0.0885(4)	-0.2810(7)	-0.0327(4)	7.5(2)
O(4)	0.1817(3)	-0.0003(6)	0.2246(3)	5.4(1)
O(5)	0.3337(4)	-0.2073(8)	0.0259(5)	9.2(2)
C(1)	0.2651(3)	0.2291(8)	-0.0837(4)	3.9(2)
C(2)	0.2126(4)	0.1482(7)	-0.1596(4)	3.6(2)
C(3)	0.1293(4)	0.1464(8)	-0.1534(4)	4.2(2)
C(4)	0.0983(4)	0.2212(9)	-0.0656(5)	4.7(2)
C(5)	0.1485(4)	0.3025(9)	0.0093(5)	5.0(2)
C(6)	0.2330(4)	0.3135(8)	0.0015(5)	4.5(2)
C(7)	0.2352(5)	-0.1013(8)	-0.2668(6)	6.1(2)
C(8)	-0.0007(4)	0.059(1)	-0.2268(7)	6.9(3)
C(9)	0.1285(4)	-0.161(1)	-0.0231(5)	4.6(2)
C(10)	0.1859(4)	0.0123(8)	0.1369(5)	4.3(2)
C(11)	0.2814(5)	-0.115(1)	0.0144(5)	5.7(2)
C(12)	0.4252(5)	0.062(1)	-0.1481(7)	8.1(3)
C(13)	0.3837(5)	0.447(1)	-0.1886(6)	6.7(2)
C(14)	0.4262(5)	0.315(1)	0.0319(5)	6.9(3)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) IN [(*η*⁵-1-TRIMETHYLSIYL-2,3-DIMETHOXY-BENZENE)TRICARBONYLCHROMIUM]

Cr-C(9)	1.848(8)	C(4)-C(5)	1.375(9)
Cr-C(10)	1.831(6)	C(5)-C(6)	1.434(8)
Cr-C(11)	1.868(8)	C(6)-C(1)	1.427(8)
Si-C(1)	1.917(8)	C(2)-O(1)	1.364(6)
Si-C(12)	1.864(8)	C(3)-O(2)	1.344(7)
Si-C(13)	1.868(7)	C(7)-O(1)	1.455(7)
Si-C(14)	1.850(7)	C(8)-O(2)	1.436(8)
C(1)-C(2)	1.405(8)	C(9)-O(3)	1.139(8)
C(2)-C(3)	1.407(8)	C(10)-O(4)	1.151(6)
C(3)-C(4)	1.416(8)	C(11)-O(5)	1.125(8)
C(9)-Cr-C(10)	88.9(3)	C(2)-C(1)-C(6)	119.1(5)
C(9)-Cr-C(11)	88.4(3)	C(6)-C(1)-Si	117.2(4)
C(10)-Cr-C(11)	87.2(3)	C(1)-C(2)-C(3)	121.8(5)
Cr-C(9)-O(3)	177.9(6)	C(1)-C(2)-O(1)	116.9(5)
Cr-C(10)-O(4)	179.7(3)	C(3)-C(2)-O(1)	121.0(5)
Cr-C(11)-O(5)	178.6(6)	C(2)-O(1)-C(7)	117.8(5)
C(1)-Si-C(12)	113.1(4)	C(2)-C(3)-C(4)	118.3(6)
C(1)-Si-C(13)	105.6(4)	C(2)-C(3)-O(2)	117.2(5)
C(1)-Si-C(14)	107.7(4)	O(2)-C(3)-C(4)	124.1(6)
C(12)-Si-C(13)	110.2(4)	C(3)-O(2)-C(8)	118.9(5)
C(12)-Si-C(14)	109.4(4)	C(3)-C(4)-C(5)	120.4(6)
C(13)-Si-C(14)	110.7(4)	C(4)-C(5)-C(6)	121.5(6)
C(2)-C(1)-Si	123.1(4)	C(5)-C(6)-C(1)	118.2(6)

$Z = 4$. 2111 independent reflexions were collected at room temperature on a home-made automatic diffractometer with Mo- K_{α} radiation in the $\theta - 2\theta$ scan mode up to $2\theta_{\max} = 46^{\circ}$. The scan width was $\Delta\theta = 1.20 + 0.345\tan\theta$ taking into account the $K_{\alpha 1} - K_{\alpha 2}$ dispersion. Two standard reflexions (0 8 0, $\bar{7}$ 2 4) monitored every 100 reflexions remained constant. Intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 4.84 \text{ cm}^{-1}$). 1779 reflexions with $I > 3\sigma(I)$ were considered as observed and used in further calculations.

The structure was solved by the heavy-atom method. Successive Fourier syntheses led to the atomic coordinates of all non hydrogen atoms. Hydrogens were introduced in theoretical calculated positions. Full matrix least-squares refinements of atomic parameters led to the final discrepancy factors $R = (\sum ||F_o| - |F_c|| / \sum |F_o|) = 0.055$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.046$ with $w = 1.66/\sigma(F)^2$. In the last least-squares cycle Δ/σ was less than 0.02. All calculations were performed on the IRIS 80 computer of the Université Pierre et Marie Curie using the program SHELX 76.

The atomic coordinates for non-hydrogen atoms are shown in Table 2, and significant bond lengths and angles in Table 3. Lists of thermal parameters and calculated and observed structure factors are available from the authors on request.

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