Journal of Organometallic Chemistry, 335 (1987) 91–95
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The crystal structure of tetracarbonyl[η^4-(1,1,3,4-tetramethylsilole)]chromium

G.E. Herberich*, B. Hessner,

Institut für Anorganische Chemie der Technischen Hochschule Aachen, Professor-Pirlet-Str. 1, D-5100 Aachen (Bundesrepublik Deutschland)

E. Colomer and M. Lheureux

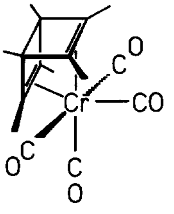
Laboratoire "Hétérochimie et Aminoacides", U.A. CNRS 1097, Institut de Chimie Fine, USTL, Place Eugène Bataillon, F-34060 Montpellier Cédex (France)

(Received April 21st, 1987)

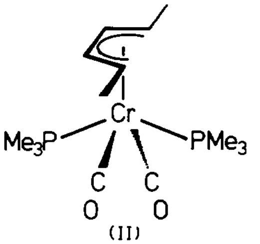
Abstract

An X-ray diffraction study has shown that tetracarbonyl[η^4-(1,1,3,4-tetramethylsilole)]chromium has a conjugated 1,3-diene bonded to a distorted piano stool $Cr(CO)_4$ fragment. The intra-ring C–C bond lengths (139.2, 145.8 and 139.0 pm) indicate predominant diene-to-metal donor bonding. The bending angle of the silole ligand is 37.7°, and the $Cr(CO)_2$ *trans* angles are 105.87 and 149.12°.

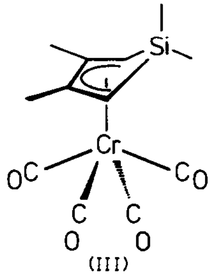
Chromium group tetracarbonylmetal fragments $M(CO)_4$ (M = Cr, Mo, W) seem to prefer to complex with non-conjugated dienes such as 1,5-cyclooctadiene. As illustrated by the structure of the hexamethylbicyclo[2.2.0]hexadiene complex I [1], the $M(CO)_4$ group in these complexes is a slightly distorted C_{2v} octahedral fragment with *trans* angles (α and β) of 92.1(9) and 168.6(8)° [1]. Complex formation with conjugated dienes is less well known [2], probably because such complexes tend to decompose, frequently with formation of the related dicarbonylbis(ligand) complexes and $Cr(CO)_6$. The structure of the bis(phosphane) derivative II shows a stronger pyramidal distortion of the octahedral fragment with α 100.8(10) and 101.1(8)° (i.e. for the angle C–Cr–C), and β 151.6(2) and 152.4(2)° (i.e. for the angle P–Cr–P) [3]. We now describe the crystal and molecular structure of tetracarbonyl[η^4-(1,1,3,4-tetramethylsilole)]chromium (III) [4], the first structure of a 1,3-diene complex with an unsubstituted $Cr(CO)_4$ group.



(I)



(II)



(III)

0022-328X/87/$03.50

X-Ray diffraction results and discussion

The molecular structure of complex III is shown in Fig. 1 which also shows the atom-numbering scheme. Details of the structure determination and of the structure are given in Tables 1–4. The structure was solved by means of the SDP program system [5] (including the programs DIFABS [6] and MULTAN [7]).

The complex crystallizes with one molecule in the asymmetric unit. The molecule consists of a monofacially bound η^4-1,1,3,4-tetramethylsilole ligand and a tetracarbonylchromium fragment. The crystal structures of the related complexes $[\{\eta^4\text{-}(3,4\text{-}Me_2C_4H_2SiMe_2)\}Co(PMe_3)_3]BPh_4$ (IV) [8], $Ni[\eta^4\text{-}(2,5\text{-}Ph_2C_4H_2SiMe_2)]_2$ [9], $[\eta^4\text{-}(2,5\text{-}Ph_2C_4H_2SiMe_2)]Ru(CO)_3$ [10], $[\eta^4\text{-}\{1\text{-}exo\text{-}Me(\eta^2\text{-}1\text{-}endo\text{-}R)\text{-}2,5\text{-}Ph_2C_4H_2\text{-}Si\}]Mo(CO)_3$ with $R = CH_2{=}CH$ (V) and $CH_2{=}CHCH_2$ [11], and $[\eta^4\text{-}(3,4\text{-}Me_2C_4H_2SiMe_2)]_2Mo(CO)_2$ [12], have been described previously.

The overall geometry of the silole ring conforms to the general pattern that was established in the earlier structural work [8–12]. The intra-ring C–C bond lengths for III (139.2, 145.8 and 139.0 pm) indicate that the silole is essentially bonded as a donor ligand; this is consistent with the predominant acceptor character of the $Cr(CO)_4$ fragment [13]. The silole ring is folded along the line C(11)–C(14), the bending angle being 37.7°. In spite of this folding, the non-bonding distance Cr–Si of 302.01(4) pm is still a remarkably short contact. Known bending angles vary from 8.9° for V [11] to 41.3° for IV [8]. The usual explanation for the bending in, e.g., cyclopentadiene complexes is based on the participation in the bonding of the diene LUMO. Having noted that the metal-to-ligand back bonding in III is of minor importance, we conclude that the comparatively large bending angle of III must, at least partially, be the result of intramolecular repulsive interactions. Steric effects have previously been suggested as the cause for the rather large bending in IV [12]. The variability of the bending angle in silole complexes is a consequence of the higher flexibility of a silole as compared to a cyclopentadiene ring.

The $Cr(CO)_4$ fragment shows near C_{2v} symmetry, and is rotated by 9.6° with respect to an idealized conformation with mirror symmetry. The *trans* angles α 105.87 and β 149.12° do not differ much from the values observed for II. As

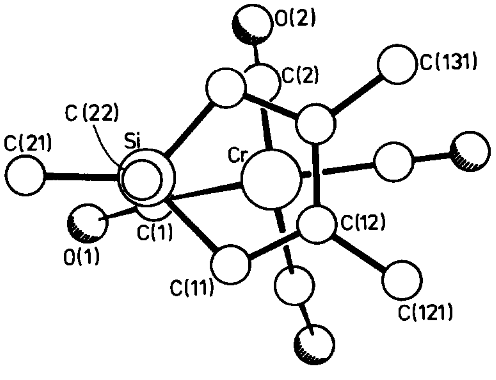


Fig. 1. The molecular structure of III.

Table 1

Positional parameters for III

Atom	x	y	z
Cr	0.69812(4)	0.10852(2)	0.83041(4)
C(1)	0.6002(3)	0.0073(2)	0.7806(3)
O(1)	0.5305(2)	−0.0514(1)	0.7684(2)
C(2)	0.7850(3)	0.0411(2)	0.9702(3)
O(2)	0.8383(3)	−0.0008(2)	1.0542(2)
C(3)	0.7426(3)	0.1902(2)	0.9619(3)
O(3)	0.7648(2)	0.2381(1)	1.0483(2)
C(4)	0.5079(3)	0.1326(2)	0.8818(3)
O(4)	0.3902(2)	0.1499(2)	0.9117(3)
C(11)	0.6432(2)	0.1472(1)	0.6072(2)
C(12)	0.7300(2)	0.2062(1)	0.6803(2)
C(121)	0.6816(3)	0.2948(1)	0.6952(3)
C(13)	0.8768(2)	0.1744(1)	0.7292(2)
C(131)	0.9990(3)	0.2276(2)	0.7973(3)
C(14)	0.8967(2)	0.0918(1)	0.6959(2)
Si	0.77433(7)	0.07126(4)	0.53748(6)
C(21)	0.7192(3)	−0.0371(2)	0.4952(3)
C(22)	0.8531(3)	0.1141(2)	0.3793(3)

Table 2

Bond lengths (pm) and bond angles (°) in III

Cr–C(1)	190.3(2)	C(1)–O(1)	113.9(2)
Cr–C(2)	186.5(2)	C(2)–O(2)	113.7(2)
Cr–C(3)	185.9(2)	C(3)–O(3)	114.7(2)
Cr–C(4)	184.5(2)	C(4)–O(4)	114.6(2)
Cr–C(11)	226.9(1)	Si–C(11)	185.7(1)
Cr–C(12)	217.9(1)	C(11)–C(12)	139.2(2)
Cr–C(13)	220.5(1)	C(12)–C(13)	145.8(2)
Cr–C(14)	228.8(1)	C(13)–C(14)	139.0(2)
		C(14)–Si	185.1(1)
C(12)–C(121)	150.7(2)	Si–C(21)	186.0(1)
C(13)–C(131)	150.7(2)	Si–C(22)	186.1(2)
Cr–C(1)–O(1)	169.7(2)	Si–C(11)–C(12)	107.12(9)
Cr–C(2)–O(2)	179.1(2)	C(11)–C(12)–C(13)	112.4(1)
Cr–C(3)–O(3)	175.9(1)	C(12)–C(13)–C(14)	113.0(1)
Cr–C(4)–O(4)	177.8(2)	C(13)–C(14)–Si	106.6(1)
C(1)–Cr–C(2)	80.87(7)	C(11)–Si–C(14)	86.14(6)
C(2)–Cr–C(3)	82.01(7)	C(21)–Si–C(22)	106.26(7)
C(3)–Cr–C(4)	79.82(7)	C(11)–Si–C(21)	122.67(7)
C(4)–Cr–C(1)	80.42(7)	C(14)–Si–C(21)	118.93(7)
C(1)–Cr–C(3)	149.12(7)	C(11)–Si–C(22)	109.62(7)
C(2)–Cr–C(4)	105.87(7)	C(14)–Si–C(22)	112.23(7)
C(11)–C(12)–C(121)	123.2(1)	C(12)–C(13)–C(131)	123.4(1)
C(121)–C(12)–C(13)	124.2(1)	C(131)–C(13)–C(14)	123.4(1)

Table 3

Definition of best planes, and angles (°) between planes for III

Plane A ≡ [C(11)...C(14)]	∢(A,B)	37.7
Plane B ≡ [C(11), Si, C(14)]	∢(C,D)	89.4
Plane C ≡ [C(1), Cr, C(3)]	∢(C,E)	9.6
Plane D ≡ [C(2), Cr, C(4)]	∢(D,E)	80.7
Plane E ≡ [C(12,13) [a], Cr, Si]		

[a] Midpoint between C(12) and C(13).

Table 4

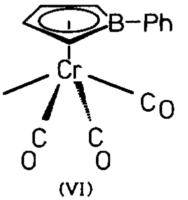
Crystallographic data, data collection parameters, and refinement parameters for III

Formula	$C_{12}H_{14}CrO_4Si$	Radiation, λ (pm)	Mo-K_α, 71.073
Formula weight	302.32 g/mol	Monochromator	graphite
Space group	$P2_1/n$ (no. 14)	Temperature	$-80\,^\circ$C
a (pm)	893.9(2)	Scan mode (θ range (°))	$\omega-2\theta$ $(0.1 < \theta < 35)$
b (pm)	1618.6(5)	No. of unique reflcns [a]	3810 $(I > \sigma(I))$
c (pm)	967.3(2)	N_o, No. of reflcns used	3295 $(I > 3\sigma(I))$
β (°)	93.93(2)	N_p, No. of params refined	163
V (nm^3)	1.396(1)	R [b]	0.038
Z	4	R_w [c]	0.048
d_c (g/cm^3)	1.43	w^{-1}	$(\sigma^2(I)+(pF_o^2)^2)/4F_o^2$ $(p = 0.03)$
Crystal size (mm^3)	$0.55 \times 0.27 \times 0.37$		
μ(Mo-K_α)	8.85 cm^{-1}	GOF [d]	2.8
Diffractometer	CAD4 (Enraf–Nonius)	Residual (e pm^{-3})	0.44×10^{-6}

[a] An empirical absorption correction was applied; the method of differential absorption was used [6]. [b] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. [d] $[\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_p]^{1/2}$.

expected [14], the larger *trans* angle β is spanned by the CO groups which are close to the idealized mirror plane.

Finally we can compare the structure of the silole complex III with that of the borole complex $(\eta^5\text{-}C_4H_4BPh)Cr(CO)_4$ (VI) [15]. The intra-ring C–C bond lengths for VI (140.9, 142.1, and 140.6 ppm) as well as the bending angle of 6.8° reveal the dissimilarity of silole and borole ligands. It is the boron in VI that causes stronger metal-to-ligand back bonding. In agreement with this view, the Cr–C(ring) bond lengths are shorter (at a 3σ significance level) for VI by 3.4 pm (av.), and the pyramidal distortion of the $Cr(CO)_4$ group (with *trans* angles α 115.6 and β 142.6 °) approaches more closely to the limiting tetragonal pyramid (with α, $\beta \approx 120\,^\circ$) found in $CpV(CO)_4$ [16,17].



(VI)

Experimental

III was prepared as described previously [4]. Details of the data collection are given in Table 4. The data collected were corrected for absorption by means of the program DIFABS [6]. The structure was solved by direct methods by means of the program MULTAN [7]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed at calculated positions (d(C–H) 95.0 pm, B_{eq} 5.0×10^4 pm^2) and were not refined.

Lists of thermal parameters and structure factors are available from the authors.

Acknowledgement

This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie.

References

1 G. Huttner and O.S. Mills, J. Organomet. Chem., 29 (1971) 275.
2 C.G. Kreiter, Adv. Organomet. Chem., 26 (1986) 297.
3 C.G. Kreiter, M. Kotzian, U. Schubert, R. Bau and M.A. Bruck, Z. Naturforsch. B, 39 (1984) 1553.
4 G.T. Burns, E. Colomer, R.J.P. Corriu, M. Lheureux, J. Dubac, A. Laporterie and H. Iloughmane, Organometallics, in press.
5 B.A. Frenz, Enraf–Nonius, Delft, The Netherlands.
6 N. Walker and D. Stuart, Acta Cryst. A, 39 (1983) 159.
7 G. Germain, P. Main and M.M. Woolfson, Acta Cryst. A, 27 (1971) 368.
8 L.C. Ananias de Carvalho, M. Dartiguenave, F. Dahan, Y. Dartiguenave, J. Dubac, A. Laporterie, G. Manuel and H. Iloughmane, Organometallics, 5 (1986) 2205.
9 F. Carré, E. Colomer, J.Y. Corey, R.J.P. Corriu, C. Guérin, B.J.L. Henner, B. Kolani and W.W.C. Wong Chi Man, Organometallics, 5 (1986) 910.
10 K.W. Muir, R. Walker, E.W. Abel, T. Blackmore and R.J. Whitley, J. Chem. Soc., Chem. Commun., (1975) 698.
11 F. Carré, R.J.P. Corriu, C. Guérin, B.J.L. Henner, B. Kolani and W.W.C. Wong Chi Man, J. Organomet. Chem., 328 (1987) 15.
12 F. Carré, E. Colomer, R.J.P. Corriu, M. Lheureux and A. Cave, J. Organomet. Chem., submitted.
13 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
14 T.A. Albright, R. Hoffmann, Y. Tse and T. D'Ottavio, J. Am. Chem. Soc., 101 (1979) 3812.
15 G.E. Herberich, B. Hessner, M. Negele and J.A.K. Howard, J. Organomet. Chem., submitted.
16 J.B. Wilford, A. Whitla and H.M. Powell, J. Organomet. Chem., 8 (1967) 495.
17 P. Kubáček, R. Hoffmann and Z. Havlas, Organometallics, 1 (1982) 180.