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Metal Hydride vs Side-on σ-Bonded Trichlorosilane Complexes of Arene−Chromium Derivatives: $(\eta^6\text{-arene})Cr(CO)(H)_2(SiCl_3)_2$[†]

Balaji R. Jagirdar,[1a] Roger Palmer,[1b] Kenneth J. Klabunde,[*,1a] and Lewis J. Radonovich[*,1b]

Departments of Chemistry, Kansas State University, Manhattan, Kansas 66506, and
University of North Dakota, Grand Forks, North Dakota 58202

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Photolytic decarbonylation of $(\eta^6\text{-arene})Cr(CO)_3$ in the presence of $HSiCl_3$ initially yields $(\eta^6\text{-arene})Cr(CO)_2H(SiCl_3)$ followed by $(\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2$. An additional species, a novel chromium dihydride, $(\eta^6\text{-arene})Cr(CO)(H)_2(SiCl_3)_2$, which is generated en route to the formation of $(\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2$ has been isolated and characterized. The two hydride ligands of this complex show fluxional behavior. X-ray structural elucidations of $(\eta^6\text{-arene})Cr(CO)(H)_2(SiCl_3)_2$, where η^6-arene = fluorobenzene or mesitylene, are presented. The data more strongly support a formulation as Cr(IV) dihydride derivatives as opposed to σ-bonded side-on $H-SiCl_3$ groups. In addition, the data do not support formulation as η^2-dihydrogen complexes.

Introduction

Recently we reported[2a] the synthesis, characterization, and chemistry of $(\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2$ complexes. Two step photolytic processes are involved starting from $(\eta^6\text{-arene})Cr(CO)_3$ and $HSiCl_3$ leading to the formation of $(\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2$, in which a hydride, $(\eta^6\text{-arene})Cr(CO)_2H(SiCl_3)$ is an intermediate, isolable compound (eqs 1 and 2).[2b] Our

$$(\eta^6\text{-arene})Cr(CO)_3 + HSiCl_3 \xrightarrow{h\nu} (\eta^6\text{-arene})Cr(CO)_2H(SiCl_3) + CO \quad (1)$$

$$(\eta^6\text{-arene})Cr(CO)_2H(SiCl_3) + HSiCl_3 \xrightarrow{h\nu} (\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2 + H_2 \quad (2)$$

earlier ^1H NMR studies of this process showed the presence of a second hydride intermediate which we proposed to be $(\eta^6\text{-arene})Cr(CO)_2(H)_2(SiCl_3)_2$. We isolated this intermediate recently in reasonable yields. X-ray crystallographic studies of this species however revealed the presence of only one carbon monoxide ligand on the chromium center as opposed to two as proposed earlier, but confirmed the presence of *two* hydride ligands. The unusual nature of these compounds prompted us to carry out further studies.

Herein we present the syntheses, structures, and studies of two such compounds: $(\eta^6\text{-arene})Cr(CO)(H)_2(SiCl_3)_2$, where η^6-arene = fluorobenzene, mesitylene. The formulation of these species as Cr(IV) dihydrides or as possibly possessing one or two side-on σ-bonded $H-SiCl_3$ groups is discussed.

Experimental Section

General Procedures. All reactions were carried out under Ar at room temperature using standard Schlenk[3] and inert atmosphere techniques unless otherwise specified. Tetrahydrofuran (THF) was distilled under Ar from Na/benzophenone. Methylene chloride (CH_2Cl_2) and pentane were distilled from CaH_2 under Ar. Fluorobenzene was stored over molecular sieves for several days before distillation under Ar. Mesitylene was distilled from Na under Ar and stored over sodium wire.

Infrared spectra were obtained using a Perkin Elmer 1330 spectrophotometer and referenced to the 1601 cm^{-1} band in polystyrene film. The ^1H NMR data were obtained using a WM-400 Bruker 400 MHz instrument, usually in C_6D_6 solvent. For variable temperature ^1H NMR experiments, the dihydride complex was dissolved in toluene-d_8 and the NMR spectra were recorded in the temperature range +30 to −75 °C. The arene proton resonance of toluene-d_8 (7.04 ppm, m) was used as an internal standard. Elemental analyses were obtained from Galbraith Laboratories, Inc. The starting (arene)tricarbonylchromium complexes, $(\eta^6\text{-}C_6H_5F)Cr(CO)_3$ and $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)_3$, were prepared according to published procedures.[4]

Synthesis (Isolation) of $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$. A mixture of $(\eta^6\text{-}C_6H_5F)Cr(CO)_3$ (0.65 g, 2.8 mmol), $HSiCl_3$ (6 mL, 59 mmol), and fluorobenzene (50 mL) was placed in a quartz tube equipped with a water cooled probe and irradiated with a 450-W UV lamp for 9.15 h. The resulting orange-yellow solution was filtered through a Celite pad on a filter frit, and then the solvent from the filtrate was removed in vacuo. The orange-yellow powder was recrystallized from CH_2Cl_2−pentane (10:120 v/v) at −3 °C for several days. A mixture of yellow and brown/orange crystals was obtained in approximately 54% (0.72 g) and 9% (0.12 g) yields respectively. Brown/orange crystals were mechanically separated from the recrystallized product, and this material was identified by NMR as $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ mixed with disilyl complex, whereas the yellow crystals proved to be made up of the pure disilyl complex, $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2$.[5] ^1H NMR of dihydride complex δ (C_6D_6): 4.50 - 5.18 ppm (m), −10.97 ppm (s), −11.22 ppm (s). IR (CH_2Cl_2): 1912 cm^{-1} (vs), 1955 cm^{-1} (m), 1970 cm^{-1} (m). Anal. Calcd for $C_{15}H_{12}Cl_{12}Cr_2F_2Si_4O_3$: C, 19.58; H, 1.31. Found: C, 19.25; H, 1.57. Note: $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ is stable only for a few days. Even in an inert atmosphere box and in the dark the brown/orange crystals change to yellow in color over a period of time. However, the decomposition is much faster in solution than in the solid state.

Synthesis (Isolation) of $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$. During 6.15 h, $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)_3$ (0.65 g, 2.5 mmol), $HSiCl_3$ (6 mL, 59 mmol), and mesitylene (40 mL) were irradiated in the setup described above. Once again the workup procedure followed was similar to the

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(1) (a) Kansas State University. (b) University of North Dakota.

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(5) Synthesis, characterization, and chemistry of $(\eta^6\text{-arene})Cr(CO)_2(SiCl_3)_2$ (η^6-arene = fluorinated arenes) complexes will be reported elsewhere.

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Table 1. Crystal Data

	$(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$	$(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$
formula	$Cr_2Si_4Cl_{12}F_2C_{15}H_{12}$	$Cr_1Cl_6Si_2O_1C_{10}H_{14}$
fw	872.03	471.10
space group	$P2_1/c$	$P2_1/c$
cryst dimens, mm	0.33 × 0.37 × 0.27	0.26 × 0.33 × 0.36
a, Å	25.490(3)	15.568(5)
b, Å	14.093(2)	8.701(3)
c, Å	14.200(2)	13.708(4)
β, deg	140.676(2)	97.72(1)
Z	4	4
V, Å^3	3232.71	1840.06
ϱ(calcd), g cm^{-3}	1.72	1.70
radiation; λ, Å	Mo Kα; 0.7107	Mo Kα; 0.7107
abs coeff (μ), cm^{-1}	18.37	16.07
transm factor range (I)	0.65−0.50	0.69−0.61
temp, °C	22	22
diffractometer	Picker (Crystal Logic)	Picker (Crystal Logic)
R^a	0.061	0.052
$R_w{}^b$	0.059	0.053

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2)^{1/2}$.

previous case. The crude product was obtained in 63% (0.75 g) yield. NMR identified the product as a mixture of the $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)_2H(SiCl_3)$ (small amount), $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$ (major portion), and $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)_2(SiCl_3)_2$ complexes. A small portion (0.45 g) of this crude mixture was redissolved in ca. 20 mL of CH_2Cl_2, a large excess (ca. 110 mL) of pentane was layered on top, and the mixture was stored in the freezer for several days. Two kinds of crystals were isolated: manual separation yielded bright orange-colored crystals (50 mg) and yellow crystals (230 mg). NMR identified the orange crystals to be made up of the dihydride complex, $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$, while the yellow ones were the disilyl complex, $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)_2(SiCl_3)_2$. ^1H NMR of dihydride (C_6D_6): δ 4.89 ppm (s, 3H), 1.82 ppm (s, 9H), −10.84 ppm (s, 2H). IR (CH_2Cl_2): 1928 cm^{-1} (vs), 1898 cm^{-1} (m). Anal. Calcd for $C_{10}H_{14}Cl_6CrOSi_2$: C, 25.49; H, 2.99. Found: C, 25.08; H, 1.90.[6a] Note: The $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$ complex is stable for several days in the solid state. However, it starts to decompose in solution after 2 days.

X-ray Structure Determination of 1:1 Cocrystallite $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$. An orange-brown crystal of the 1:1 co-crystallite $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ was cut and wedged in a glass capillary under an argon atmosphere. The unit cell was determined and intensity data were collected using Mo Kα radiation (instead of a monochromator, a 1 mil Zr β filter was used) with a Picker diffractometer that was automated with the Crystal Logic package.[6b] Lattice constants were determined from the least squares fit of 21 reflections and confirmed with Laue photographs. A summary of the crystal data is given in Table 1. The three standard reflections displayed a decrease in intensity of 18.1% over the 142.0 h of exposure time a decay correction was applied to the data. All non-hydrogen atoms were located using direct methods[6b] and all refinement cycles utilized $1/\sigma^2(F_o)$ weighting, where σ was calculated from counting statistics and included an instability factor of 0.04. Isotropic refinement of all of the non-hydrogen atoms located produced $R = 0.163$ and $R_w = 0.181$. Because a difference synthesis at this stage suggested the possibility of disorder for the ring fluorine atoms, further refinement was carried out treating all atoms anisotropically except the fluorine and hydride atoms which were treated isotropically with fixed thermal parameters of 10 and 5 Å^2, respectively. This refinement produced $R = 0.074$ and $R_w = 0.080$. In order to check the disorder the fluorine atoms were excluded from a structure factor calculation and the subsequent difference synthesis was examined. For the $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2$ molecule a single intense peak was observed at the F(10) position. For the $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ molecule, however, three peaks were observed above noise level corresponding to F(02), F(03), and F(05). The peak at the F(02) position was approximately three times the magnitude of the other two. Additional cycles of refinement in which the occupancies of these atoms were allowed to vary independently led to an approximate model that was incorporated in the final refinement cycles. Accordingly, three positions were included for the disordered fluorine atom with occupancies fixed at F(02) = 0.55, F(05) = 0.25, and F(03) = 0.20. Hydride and fluorine atoms were treated isotropically with the disordered positions at F(05) and F(03) fixed at 6 Å^2 while all other atoms were treated anisotropically. In addition, theoretical positions for the ring hydrogen atoms, calculated at a distance of 0.95 Å, were included with fixed thermal parameters of 5 Å^2. Partial occupancy factors were used for hydrogens at the disordered fluorine positions so that the total occupancy at any position was unity. Isotropic thermal parameters for the observed hydride positions were allowed to vary. After inclusion of absorption corrections, from average path length calculations, the final refinement produced $R = 0.060$ and $R_w = 0.058$. Correlations above 0.8 were observed between thermal parameters for Si(01), Si(02), Cl(01), Cl(04), Cl(05), C(05), O(08), and O(09) as well as between thermal parameters and positional parameters for Cl(01) and Cl(04). The largest negative electron densities were located near the fluorine atoms reflecting the crude nature of the disordered model. No consistent pattern for an alternate model was established, however. Final positional parameters are listed in Table 2 and bond lengths are listed in Table 3.

X-ray Structure Determination of $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$. An orange crystal of $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$ was cut under a stream of argon and wedged inside a 0.3 mm capillary. The structure determination paralleled that of the previous compound with the following exceptions. Cell constants were determined from the least squares treatment of 17 reflections and a decay of 13.4% was observed over 139.9 h of exposure time. Isotropic refinement of the non-hydrogen atoms produced $R = 0.129$ and $R_w = 0.167$. Full matrix anisotropic refinement of the non-hydrogen atoms was allowed to converge before the two hydrides were located from a difference synthesis. Sensible positions for the ring hydrogen peaks were also evident, however, theoretical positions for the ring and methyl hydrogen atoms were used in the final refinement that produced $R = 0.052$ and $R_w = 0.053$. A final difference synthesis was quite clean indicating the adequacy of the model structure and no large correlations were observed. The final positional parameters are listed in Table 4 and bond lengths are listed in Table 5.

Results

Structures of 1:1 Cocrystallite $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ and $(\eta 6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$. The compound $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ exists in the solid state as a 1:1 co-crystallite. An ORTEP diagram displaying one molecule of $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2$ and one molecule of $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ as they exist in the asymmetric unit of structure is shown in Figure 1 (the mesitylene dihydride analog is shown in Figure 2). Figure 3A shows a projection of the σ-bonded ligands onto the arene plane. The structure of the $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2$ molecule is very similar to that of the pure substance, which has been isolated and the X-ray structure determined, except for the rotation of the $\eta^6\text{-}C_6H_5F$ plane relative to the $CrL_2L'_2$ plane.[5] Consequently, those details will be discussed in a separate paper.[5]

The $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ molecule in the co-crystallite can be described as a distorted three-legged piano

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(6) (a) Satisfactory elemental analyses could not be obtained for hydrogen. (b) The Crystal Logic package includes modified versions of the following programs: REDUCE (Broach, Coppens, Becker, and Blessing), peak profile analysis and Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least squares refinement; ORFEE (Busing, Martin, and Levy), distance, angle, and error calculations; ABSORB (Coppens, Becker, and Hamilton), absorption correction calculations; ORTEP (Johnson), figure plotting; HYDROGEN (Trueblood), calculation of hydrogen atomic positions; SHELX-86 (Sheldrick), direct methods. All calculations were performed on a DEC Microvax 3100 computer. Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV.

Table 2. Positions and Equivalent Isotropic Temperature Factors (Å^2)[a] in $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$

atom	x	y	z	$U_{ex} \times 10^4$ or B_{iso}
Cr(01)	0.34446(6)	0.71345(7)	0.09458(11)	425(17)
Cr(02)	−0.1397(1)	0.7466(1)	−0.9982(1)	457(18)
Si(01)	0.2519(1)	0.6792(1)	−0.1580(2)	498(36)
Si(02)	0.3972(1)	0.8669(1)	0.1356(2)	515(37)
Si(03)	−0.0646(1)	0.6024(1)	−0.8783(2)	540(35)
Si(04)	−0.2855(1)	0.7552(1)	−1.2209(2)	564(33)
Cl(01)	0.3055(2)	0.6268(2)	−0.2047(3)	842(56)
Cl(02)	0.1678(1)	0.5724(1)	−0.2413(2)	740(40)
Cl(03)	0.1760(1)	0.7853(1)	−0.3094(2)	783(40)
Cl(04)	0.4846(1)	0.8699(2)	0.1504(3)	866(55)
Cl(05)	0.4646(1)	0.9305(1)	0.3361(2)	725(42)
Cl(06)	0.3125(2)	0.9674(1)	−0.0189(3)	967(54)
Cl(07)	−0.0015(1)	0.5878(2)	−0.6652(2)	874(42)
Cl(08)	0.0274(1)	0.5814(2)	−0.8490(3)	849(48)
Cl(09)	−0.1327(1)	0.4796(1)	−0.9807(2)	739(41)
Cl(10)	−0.3471(2)	0.8308(2)	−1.2054(3)	1066(57)
Cl(11)	−0.3222(1)	0.8202(2)	−1.3956(2)	926(41)
Cl(12)	−0.3477(1)	0.6273(1)	−1.3115(2)	715(35)
C(01)	0.2416(4)	0.7406(5)	−0.0026(7)	483(124)
O(01)	0.1790(3)	0.7577(4)	−0.0555(6)	795(111)
C(02)	0.3715(5)	0.6215(6)	0.2568(9)	703(169)
C(03)	0.4379(6)	0.6821(6)	0.3362(8)	750(158)
C(04)	0.4779(4)	0.6852(6)	0.3067(9)	685(148)
C(05)	0.4525(5)	0.6240(6)	0.2012(11)	731(194)
C(06)	0.3835(5)	0.5639(5)	0.1184(9)	689(168)
C(07)	0.3422(5)	0.5641(5)	0.1451(9)	665(161)
C(08)	−0.1838(4)	0.6830(5)	−0.9596(8)	557(139)
C(09)	−0.1609(4)	0.6776(5)	−1.1345(9)	601(148)
O(08)	−0.2110(4)	0.6470(4)	−0.9311(7)	788(144)
O(09)	−0.1748(4)	0.6375(5)	−1.2222(7)	882(141)
C(10)	−0.0605(6)	0.8375(5)	−0.7959(8)	671(167)
C(11)	−0.0108(5)	0.8041(5)	−0.7975(10)	721(163)
C(12)	−0.0341(6)	0.8212(6)	−0.9240(12)	818(206)
C(13)	−0.1068(6)	0.8714(6)	−1.0422(10)	845(210)
C(14)	−0.1553(5)	0.9042(5)	−1.0348(9)	727(154)
C(15)	−0.1342(5)	0.8857(5)	−0.9136(10)	718(164)
F(02)	0.3309(6)	0.6178(7)	0.2812(11)	7.7(2)
F(03)	0.4683(11)	0.7395(12)	0.4414(21)	6.0
F(05)	0.4917(15)	0.6316(15)	0.1808(26)	6.0
F(10)	−0.0399(4)	0.8210(4)	−0.6778(8)	9.9(2)
H(01A)	0.3326(41)	0.7547(46)	−0.1232(74)	2(1)
H(01B)	0.3366(39)	−0.8132(44)	0.1232(71)	3(2)

[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

Table 3. Interatomic Distances (Å) in $(\eta^6\text{-}C_6H_5F)Cr(CO)_2(SiCl_3)_2\cdot(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$

Cr(01)−H(01A)	1.42(7)	Si(02)−Cl(04)	2.070(3)
Cr(01)−H(01B)	1.52(6)	Si(02)−Cl(05)	2.072(3)
Cr(01)−C(01)	1.825(7)	Si(03)−Cl(09)	2.054(3)
Cr(01)−C(04)	2.224(7)	Si(03)−Cl(08)	2.062(3)
Cr(01)−C(03)	2.235(7)	Si(03)−Cl(07)	2.063(3)
Cr(01)−C(02)	2.238(8)	Si(04)−Cl(10)	2.045(3)
Cr(01)−C(05)	2.239(8)	Si(04)−Cl(12)	2.065(3)
Cr(01)−C(07)	2.240(7)	Si(04)−Cl(11)	2.068(3)
Cr(01)−C(06)	2.242(7)	C(01)−O(01)	1.146(8)
Cr(01)−Si(01)	2.361(2)	C(01)−H(01B)	1.85(6)
Cr(01)−Si(02)	2.368(2)	C(02)−F(02)	1.32(1)
Cr(02)−C(08)	1.822(9)	C(02)−C(07)	1.38(1)
Cr(02)−C(09)	1.835(9)	C(02)−C(03)	1.38(1)
Cr(02)−C(10)	2.235(7)	C(03)−F(03)	1.30(2)
Cr(02)−C(13)	2.236(8)	C(03)−C(04)	1.37(1)
Cr(02)−C(14)	2.245(7)	C(04)−C(05)	1.38(1)
Cr(02)−C(15)	2.246(7)	C(05)−F(05)	1.24(2)
Cr(02)−C(12)	2.252(8)	C(05)−C(06)	1.41(1)
Cr(02)−C(11)	2.255(7)	C(06)−C(07)	1.37(1)
Cr(02)−Si(04)	2.376(2)	C(08)−O(08)	1.156(8)
Cr(02)−Si(03)	2.377(2)	C(09)−O(09)	1.146(9)
Si(01)−H(01A)	1.75(7)	C(10)−F(10)	1.334(9)
Si(01)−Cl(03)	2.041(3)	C(10)−C(11)	1.37(1)
Si(01)−Cl(01)	2.062(3)	C(10)−C(15)	1.39(1)
Si(01)−Cl(02)	2.083(3)	C(11)−C(12)	1.41(1)
Si(02)−H(01B)	1.60(6)	C(12)−C(13)	1.39(1)
Si(02)−Cl(06)	2.038(3)	C(13)−C(14)	1.40(1)
Si(02)−H(01A)	2.06(7)	C(14)−C(15)	1.37(1)

Table 4. Positions and Equivalent Isotropic Temperature Factors (Å^2)[a] in $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$

atom	x	y	z	$U_{eq} \times 10^4$ or B_{iso}
Cr(01)	0.73916(4)	0.13233(7)	0.86965(4)	338(3)
Si(01)	0.8628(1)	0.0261(1)	0.8118(1)	459(7)
Si(02)	0.6476(1)	−0.0863(1)	0.8650(1)	395(6)
Cl(01)	0.9652(1)	0.1674(2)	0.7920(1)	900(12)
Cl(02)	0.9292(1)	−0.1346(2)	0.9065(1)	720(9)
Cl(03)	0.8399(1)	−0.0860(2)	0.6789(1)	872(11)
Cl(04)	0.5162(1)	−0.0386(2)	0.8572(1)	693(9)
Cl(05)	0.6667(1)	−0.2330(1)	0.9850(1)	660(8)
Cl(06)	0.6494(1)	−0.2373(1)	0.7494(1)	637(8)
C(01)	0.6649(3)	0.1436(5)	0.7543(3)	443(24)
C(02)	0.7161(3)	0.3817(4)	0.9066(3)	547(29)
C(03)	0.8049(3)	0.3576(5)	0.9315(3)	541(28)
C(04)	0.8325(3)	0.2326(5)	0.9928(3)	522(28)
C(05)	0.7733(3)	0.1417(5)	1.0364(3)	469(25)
C(06)	0.6850(3)	0.1728(5)	1.0121(3)	465(26)
C(07)	0.6549(3)	0.2928(5)	0.9480(3)	513(28)
C(08)	0.8688(4)	0.4682(6)	0.8985(5)	888(47)
C(09)	0.8066(4)	0.0227(6)	1.1114(3)	677(35)
C(10)	0.5605(4)	0.3350(6)	0.9281(4)	759(39)
O(01)	0.6197(2)	0.1555(4)	0.6806(2)	678(24)
H(01A)	0.7932(29)	0.1699(50)	0.7871(33)	2(1)
H(01B)	0.7711(26)	−0.0418(49)	0.8764(30)	2.0(9)

[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

stool where two legs are trichlorosilyl ligands and the third leg is a carbonyl ligand. The two hydrides bridge the two Si−Cr bonds and the monofluorobenzene forms the seat of the stool. The two Cr−H bonds are 1.42(7) Å for the bond to H(01A) and 1.52(6) Å for H(01B). Both hydrides also appear to bridge adjacent Si atoms with H−Si distances of 1.75(7) Å for H(01A) and 1.60(6) Å for H(01B). These bridging hydride distances are within 3 esds of the 1.61(4) Å distance observed in $(\eta^6\text{-}C_6Me_6)Cr(CO)_2(H)(SiHPh_2)$[7] for both the Cr−H and Si−H bridging distances. Unfortunately, the apparent disorder of the $(\eta^6\text{-}C_6H_5F)$ ligand combined with the inherent inaccuracy in determining hydrogen positions from X-ray data leads to a good deal of uncertainty in these parameters.

In order to eliminate the disorder problem, we sought to isolate a similar complex with a di- or trisubstituted η^6-arene that was not as prone toward disorder. Indeed we were successful in preparing, isolating, and determining the structure of $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$ which is free of the disorder problem. An ORTEP diagram depicting one molecule of the complex and the atomic numbering scheme is given in Figure 2. Figure 3B shows a projection of the σ-bonded ligands onto the arene plane. A three-legged piano stool structure is again observed similar to $(\eta^6\text{-}C_6H_5F)Cr(CO)(H)_2(SiCl_3)_2$ in the co-crystallite. The Cr−H distances of 1.53(5) Å for H(01A) and 1.59(4) Å for H(01B) are considerably closer to the 1.61(4) Å distance observed in $(\eta^6\text{-}C_6Me_6)Cr(CO)_2(H)(SiHPh_2)$.[7] Hydride H(01A) also bridges Si(01) at a Si−H distance of 1.66(4) Å; however, H(01B) is considerably further and almost equidistant from Si(01) and Si(02). Thus, the observed lengths for Si−H for H(01B) are 1.87(4) Å for Si(01) and 1.95(4) Å for Si(02).

Variable Temperature ^{1}H NMR Study of $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(CO)(H)_2(SiCl_3)_2$. The room temperature ^{1}H NMR spectrum of the pure mesitylene dihydride complex in toluene-d_8 exhibits only one signal in the hydride region, −11.00 ppm. As the temperature is lowered, this signal broadens and at −23 °C two separate broad signals appear. The ^{1}H NMR spectra of

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[7] Schubert, U.; Muller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469.

Table 5. Interatomic Distances (Å) in (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)(H)$_2$(SiCl$_3$)$_2$

Cr(01)–H(01A)	1.53(5)	Si(02)–H(01B)	1.95(4)
Cr(01)–H(01B)	1.59(4)	Si(02)–Cl(06)	2.062(2)
Cr(01)–C(01)	1.832(4)	Si(02)–Cl(05)	2.072(2)
Cr(01)–C(04)	2.251(4)	Si(02)–Cl(04)	2.076(2)
Cr(01)–C(06)	2.257(4)	C(01)–O(01)	1.156(5)
Cr(01)–C(02)	2.268(4)	C(01)–H(01A)	2.00(4)
Cr(01)–C(05)	2.278(4)	C(02)–C(03)	1.395(7)
Cr(01)–C(07)	2.282(4)	C(02)–C(07)	1.405(7)
Cr(01)–C(03)	2.319(4)	C(03)–C(04)	1.406(6)
Cr(01)–Si(01)	2.365(1)	C(03)–C(08)	1.497(7)
Cr(01)–Si(02)	2.373(1)	C(04)–C(05)	1.407(6)
Si(01)–H(01A)	1.66(4)	C(05)–C(06)	1.397(6)
Si(01)–H(01B)	1.87(4)	C(05)–C(09)	1.502(6)
Si(01)–Cl(03)	2.055(2)	C(06)–C(07)	1.404(6)
Si(01)–Cl(01)	2.060(2)	C(07)–C(10)	1.504(7)
Si(01)–Cl(02)	2.085(2)		

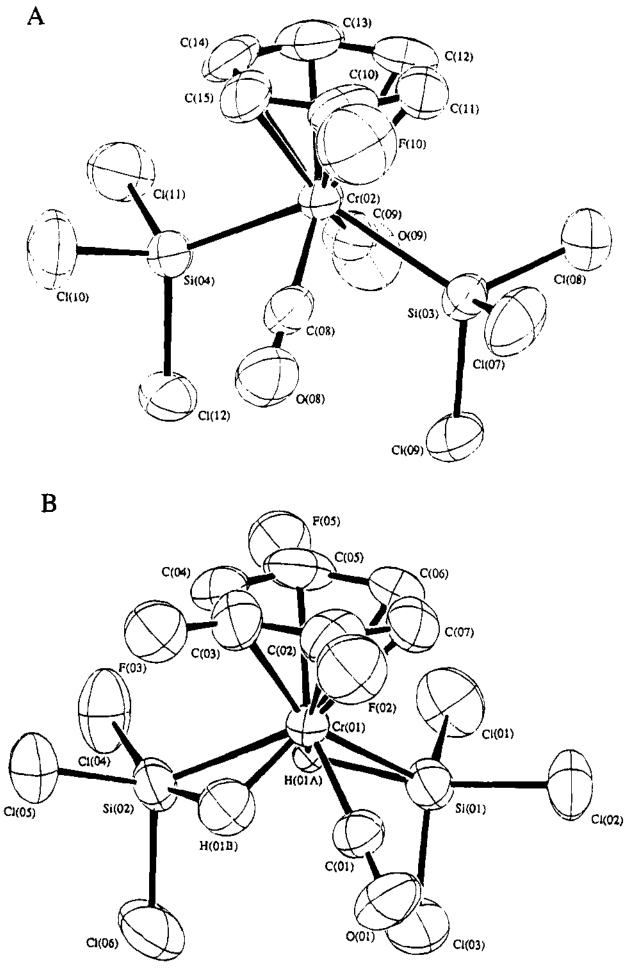


Figure 1. (A) ORTEP diagram of one molecule of (η^6-C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$ in the 1:1 co-crystallite (η^6-C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$·(η^6-C$_6$H$_5$F)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ depicting the atomic numbering scheme and thermal ellipsoids at 50% probability. (B) ORTEP diagram of one molecule of (η^6-C$_6$H$_5$F)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ in the 1:1 co-crystallite (η^6-C$_6$H$_5$F)Cr(CO)$_2$(SiCl$_3$)$_2$·(η^6-C$_6$H$_5$F)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ depicting the atomic numbering scheme and thermal ellipsoids at 50% probability. The fluorine atom is displayed at the three disordered positions.

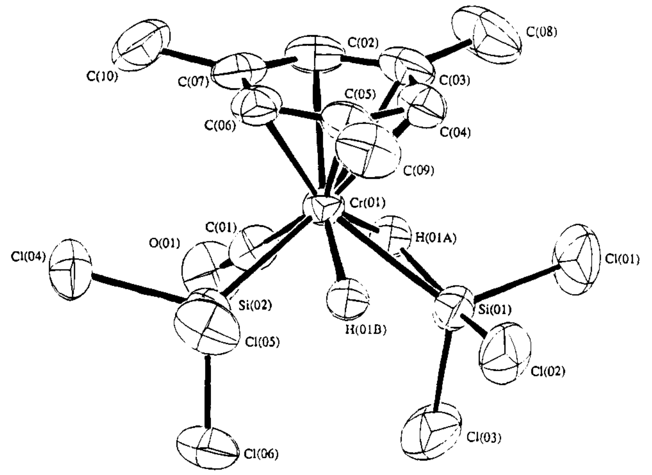


Figure 2. ORTEP diagram of one molecule of (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ depicting the atomic numbering scheme and thermal ellipsoids at 50% probability.

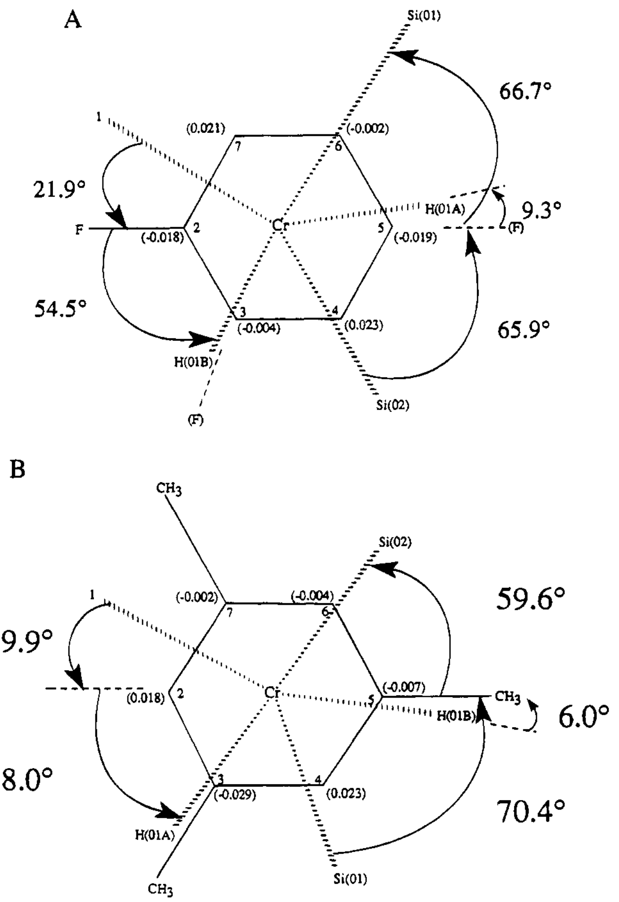


Figure 3. (A) Projection of the σ-bonded ligands in (η^6-C$_6$H$_5$F)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ onto the arene plane. (B) Projection of the σ-bonded ligands in (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)(H)$_2$(SiCl$_3$)$_2$ onto the arene plane.

the hydride region at various temperatures are shown in Figure 4. These data suggest that this molecule is fluxional wherein the two hydride ligands are rapidly exchanging positions. At the low temperature limit of −58 °C, static structures were observed. The separate chemical shifts for the two hydride ligands are δ −10.33 ppm and −11.87 ppm respectively.

Numerous attempts were made to determine the ^{29}Si–H coupling constant in this complex by expanding the hydride resonance region. We were never able to detect this coupling, indicating that either it must be smaller than the line width of the hydride resonance, which is about 160 Hz at room temperature, or the dynamics of the molecule precludes observation of the coupling.

From the variable temperature spectra using free energy relationships,[8] we can estimate the coalescence temperature for the two hydride signals to be −21 °C and the free energy of activation, $\Delta G^\ddagger$ can be calculated, which is 46.0 kJ/mol.

Reactions with CO and D$_2$. It has been observed that some dihydrogen complexes undergo facile exchange of H$_2$ with

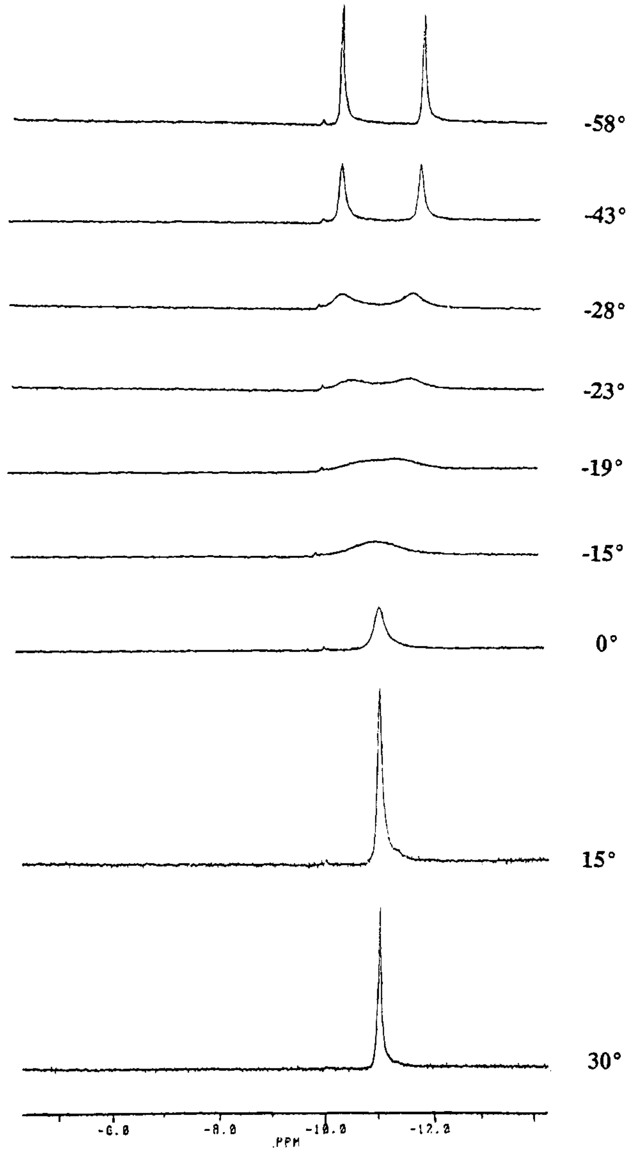


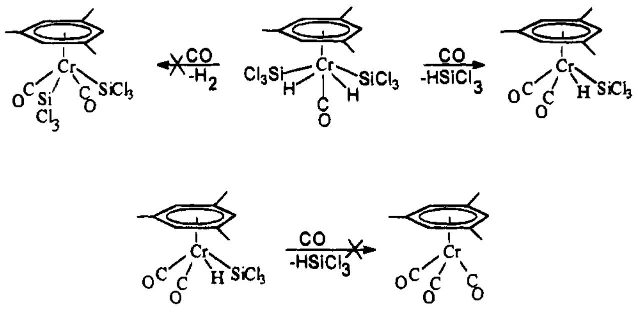
Figure 4. NMR study of fluxional behavior of $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr(CO)(H)}_2(\text{SiCl}_3)_2$ (Bruker WM-400 MHz, deuterotoluene solvent, proton resonance at 7.04 ppm used as internal standard).

D_2.[9,10] When D_2 gas was bubbled through a solution of the mesitylene dihydride in toluene-d_8, no exchange product was obtained which further rules out the molecular form of H_2 coordination to the Cr (eq 3). Also of interest is the fact that

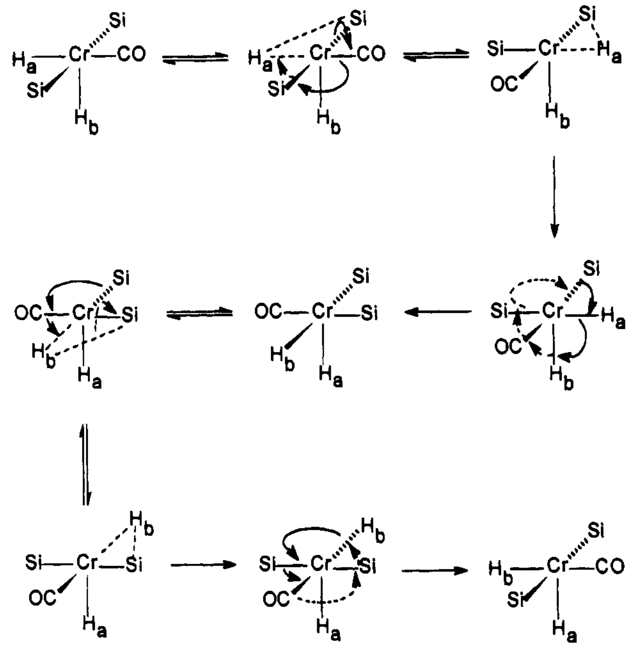
$$(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr(CO)(H)}_2(\text{SiCl}_3)_2 + \text{D}_2 \not\rightarrow (\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr(CO)(D)}_2(\text{SiCl}_3)_2 + \text{H}_2 \quad (3)$$

the mesitylene dihydride complex reacted with CO via reductive elimination of $HSiCl_3$ to yield the monohydride complex. However, the resultant monohydride complex did not undergo further reaction with CO gas. These results are illustrated in Scheme 1.

Scheme 1. Reaction of $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr(CO)(H)}_2(\text{SiCl}_3)_2$ with CO



Scheme 2. Mechanism for the Fluxional Process in Dihydride Complexes—Partial Cr−H Bond Cleavage Mechanism



Discussion

A dihydrogen (η^2-H_2) formulation for (η^6-mesitylene)Cr(CO)-$(H)_2(SiCl_3)_2$ can be excluded on the basis of the observation of two non-equivalent hydrogens in the low temperature NMR (rotation about the metal−(H_2) bond vector in η^2-dihydrogen complexes is generally so fast, that no non-equivalence can be observed by NMR[11,12]). Also, the finding that D_2 gas does not exchange with H_2 suggests that the η^2-H_2 formulation is not present. Indeed, if a reversible equilibrium existed between the dihydrogen and dihydride forms (as is the case in several literature examples[13−17]), exchange with D_2 might be expected (although such lack of reactivity cannot be taken as conclusive evidence for the absence of a dihydrogen form).

Next, we need to deal with the question as to whether the $H-SiCl_3$ moieties are fully oxidatively added or are side-on bound. The X-ray structural data are suggestive of side-on

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(8) $k_c = \pi\Delta\nu/2^{1/2}$ and $\Delta G^{\ddagger} = 2.301RT_c(10.32 + \log(T_c/k_c))$: Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; MacMillan: New York 1976; Chapter 6.

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bonding, at least for one H−SiCl$_3$ moiety. For the mesitylene complex, the Cr−H distances of 1.53(5) Å for H(01A) and 1.59(4) Å for H(01B) are within the error limits of each other. However, the H(01A) distance to Si(01) is 1.66(4) Å, but H(01B) is considerably further and almost equidistant from Si(01) and Si(02). Unfortunately, the uncertainty in all of the hydrogen distances just do not allow any firm conclusions.

The NMR data suggests that side-on bonding is not very likely. First of all, the hydride resonances in both the fluorobenzene and mesitylene complexes are very far upfield in the vicinity of −11 ppm. For a side-on bonded species it would be expected that this resonance would be closer to that observed for free H−SiCl$_3$, which is +5 ppm. Furthermore, the H−^{29}Si coupling in pure H−SiCl$_3$ is about 400 Hz. We were not able to detect any H−^{29}Si coupling. Either it cannot be observed in the molecule, or it is smaller than about 160 Hz. Although this is negative evidence, it does at least show that the coupling is much smaller than in pure H−SiCl$_3$.

We conclude that the formulation as a dihydride is most appropriate for these compounds, and thus they are formally Cr(IV) complexes, and the hydride ligands are fluxional. Two mechanistic possibilities for this fluxionality arise: (1) an intramolecular distortion involving arene ring slippage from η^6 to η^4 (opening up a vacant site) followed by rapid rotations of the carbonyl and the two silyl groups, and subsequent movement of the hydride ligands. At room temperature the two hydrides would thus appear equivalent on the NMR time scale. (2) another possible mechanism may involve reversible Cr−H bond cleavage with Si−H bond formation, followed by rotations and ligand rearrangement around the Cr center. Scheme 2 illustrates this process in a simplified way approximating octahedral symmetry, and also illustrates that the two hydrides H$_a$ and H$_b$ would be chemically nonequivalent when low temperature stops the rearrangement processes.

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Supplementary Material Available: A complete set of tables, giving crystallographic data, bond angles, anisotropic temperature factors, and least squares plane calculations (25 pages). Ordering information is given on any current masthead page.

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