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Supplementary Material Available: A figure of the molecular structure of **2d** with the complete labeling scheme and tables of final positional, isotropic, and anisotropic parameters and interatomic distances and angles for **2d** (14 pages); a listing of observed and calculated structure factors for **2d** (10 pages). Ordering information is given on any current masthead page.

Synthesis, Chemistry, and Structures of Mono-η^6-arene Complexes of Chromium(II) Bearing Trichlorosilyl and Carbon Monoxide Ligands

George N. Glavee, Balaji R. Jagirdar, Joerg J. Schneider,[1a] Kenneth J. Klabunde,*[,1b]
Lewis J. Radonovich,*[,1c] and Kelly Dodd[1c]

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

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(η^6-Arene)chromium tricarbonyl complexes have been photolyzed in the presence of trichlorosilane. The first reaction to take place is the expected loss of CO followed by oxidative addition to yield (η^6-arene)$Cr(CO)_2(H)(SiCl_3)$. However, further photolysis causes the elimination of H_2 and formation of (η^6-arene)$Cr(CO)_2(SiCl_3)_2$. During this process the arene ligand becomes labilized and undergoes exchange with other arene ligands present. In some instances, the hydride intermediate is too short-lived to be isolated and the $-Cr(CO)_2(SiCl_3)_2$ derivative is preferentially formed. Evidence is presented that the presence of the $SiCl_3$ groups helps labilize the η^6-arene group both thermally and photochemically. Attempts to incorporate heteroatom-containing arenes are discussed, and X-ray structural elucidations of (η^6-mesitylene)$Cr(CO)_2(SiCl_3)_2$ and square-planar (2,4,6-collidine)$_2CrCl_2$ are presented.

Introduction

In 1971 Jetz and Graham reported on the oxidative addition of $H-SiCl_3$ to photochemically generated (benzene)$Cr(CO)_2$, yielding (benzene)$Cr(CO)_2(H)(SiCl_3)$.[2] Since that time extensive work on $H-SiR_3$ oxidative additions has been carried out by Schubert, Jaouen, Corriu, and their co-workers.[3] A variety of hydride–arene and Cp complexes of Mn, Cr, and Fe have been prepared, usually by photochemical decarbonylation followed by $H-SiR_3$ addition.

Initially our interest was in preparing similar derivatives and studying η^6-arene lability, as an extension of earlier work with somewhat analogous Co(II) and Ni(II) systems.[4,5] However, new results and new compounds were quickly discovered. It was found that two-step photolytic processes were possible, leading to (η^6-arene)$Cr(CO)_2(SiCl_3)_2$ systems with enhanced η^6-arene labilities and other interesting properties.

Experimental Section

General Procedures. All reactions were carried out under Ar at room temperature using standard Schlenk[6] and inert atmosphere techniques unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under Ar from

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(1) (a) On leave from the Max-Planck-Institute für Kohlenforschung, 4330 Mulheim/Ruhr, Germany. (b) Kansas State University. (c) University of North Dakota.

(2) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

(3) (a) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469. (b) Matarasso-Tchoroulechine, E.; Jaouen, G. *Can. J. Chem.* **1988**, *66*, 2157. (c) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151 and references therein. (d) Schubert, U.; Ackerman, K.; Kraft, G.; Wörle, B. *Z. Naturforsch.* **1983**, *38b*, 1488. (e) Colomer, E.; Corriu, R. J. P.; Vioux, A. *Inorg. Chem.* **1979**, *18*, 695. (f) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368. (g) Carré, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 971. (h) Matarasso-Tchiroukhine, E.; Jaouen, G. *Can. J. Chem.* **1988**, *66*, 2157. (i) Knorr, M.; Schubert, U. *Transition Met. Chem.* **1986**, *11*, 269. (j) Schubert, U. *Transition Met. Chem.* **1991**, *16*, 136.

(4) (a) Anderson, B. B.; Behrens, C. L.; Radonovich, L. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 5390. (b) Gastinger, R. G.; Anderson, B. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 4959. (c) Groshens, T. J.; Klabunde, K. J. *Organometallics* **1982**, *1*, 564. (d) Lin, S. T.; Narske, R. N.; Klabunde, K. J. *Organometallics* **1985**, *3*, 571. (e) Brezinski, M. M.; Klabunde, K. J. *Organometallics* **1983**, *2*, 1116. (f) Groshens, T. J.; Klabunde, K. J. *J. Organomet. Chem.* **1983**, *259*, 337. (g) Klabunde, K. J.; Anderson, B. B.; Neuenschwander, K. *Inorg. Chem.* **1980**, *19*, 3719.

(5) (a) Choe, S. B.; Kanai, H.; Klabunde, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 2875. (b) Choe, S. B.; Schneider, J. J.; Klabunde, K. J.; Radonovich, L. J.; Ballantine, T. A. *J. Organomet. Chem.* **1989**, *376*, 419. (c) Brezinski, M. M.; Schneider, J. J.; Radonovich, L. J.; Klabunde, K. J. *Inorg. Chem.* **1989**, *28*, 2414.

(6) (a) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley, New York, 1986. (b) Herzog, S.; Dehnert, J.; Luhder, K. In *Technique of Inorganic Chemistry*; Johnassen, H. B., Ed.; Interscience: New York, 1969; Vol. VII.

Table I. Infrared Spectral Data of the Complexes in CH_2Cl_2

complex	no.	ν_{CO}, cm^{-1}	ν_{CN}, cm^{-1}
$[\eta^6\text{-}C_6H_3(CH_3)_3]Cr(CO)_2(SiCl_3)_2$	I	1962 (m), 1910 (vs)	
$[\eta^6\text{-}C_6H_3(CH_3)_3]Cr(CO)_2H(SiCl_3)$	II	1966 (vs), 1907 (s)	
$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$	III	1971 (m), 1917 (vs)	
$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2H(SiCl_3)$	IV	1969 (vs), 1911 (s)	
$[\eta^6\text{-}(C_6(CH_3)_6]Cr(CO)_2(SiCl_3)_2$	V	1951 (m), 1898 (vs)	
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(SiCl_3)_2$	VI	1974 (m), 1916 (vs)	
$(\eta^6\text{-}C_6H_6)Cr(CO)_2H(SiCl_3)$	VII	1979 (vs), 1920 (s)	
(cyclobuta-η^6-benzene)$Cr(CO)_2(SiCl_3)_2$	VIII	1965 (m), 1911 (vs)	
(cyclobuta-η^6-benzene)$Cr(CO)_2(H)(SiCl_3)$	IX	1955 (s, br), 1896 (s)	
(p-xylene)$Cr(CO)_2(SiCl_3)_2$	X		
(2,4,6-collidine)$_2CrCl_2$	XI		
$(CH_3CN)_4Cr(SiCl_3)_2$[a]	XII		2310
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CH_3CN)$[a]	XIII	1981 (s), 1781	2271

[a] In Nujol mull.

Table II. ^1H NMR Spectral Data (δ) of the Complexes in C_6D_6

complex	arene	other resonances
I[a]	4.86 (s, 3 H)	2.02 (s, 9 H, Me)
II	4.47 (s, 3 H)	1.61 (s, 9 H, Me), −9.98 (s, 1 H)
III	5.06, 4.97 (m, 5 H)	1.42 (s, 3 H, Me)
IV	4.64, 4.46 (m, 5 H)	1.36 (s, 3 H, Me), −10.45 (s, 1 H)
V		1.64 (s, 18 H, Me)
VI	4.84 (s, 6 H)	
VII	4.45 (s, 6 H)	−10.58 (s, 1 H)
VIII	5.37, 4.48 (m, 4 H)	2.69, 2.09 (m, 4 H, CH_2)
IX	4.84, 4.40 (m, 4 H)	2.51, 2.09 (m, 4 H, CH_2); −10.41 (s, 1 H)
X[b]	5.15 (m, 4 H)	1.78 (s, 6 H)
XII[b]		3.60 (s, br, 12 H)
XIII[b]	4.70 (s, 6 H)	2.20 (s, 3 H)

[a] In CD_2Cl_2. [b] In acetone-d_6.

Na/benzophenone. Methylene chloride (CH_2Cl_2), hexanes, pentane, toluene, xylene, pyridine, and methyl-substituted pyridines were distilled from CaH_2 under Ar. Benzene and mesitylene were distilled from $CaSO_4$ and stored over sodium wire. Acetonitrile, p-difluorobenzene, and m-bis(trifluoromethyl)benzene were stored over molecular sieves for several days before distillation under Ar. Benzocyclobutene was prepared by vacuum pyrolysis of 2-methylbenzyl chloride according to literature methods.[7]

Infrared spectra were obtained using a Perkin-Elmer 1330 spectrophotometer and referenced to the 1601-cm^{-1} band in polyethylene film. The ^1H and ^{13}C NMR data were obtained using a WM-400 Bruker 400-MHz instrument. All shifts are reported on the δ scale. The shift of the deuterated solvent was used as an internal reference. Electronic spectra were obtained on a Spectronic 2000 spectrophotometer. Mass spectra were recorded on a Finnigan MAT CH5 instrument with the fractional sublimation technique. Elemental analyses were obtained from Galbraith Laboratories Inc. The starting arene tricarbonyl complexes $(C_6H_3Me_3)Cr(CO)_3$ (XIV), $(C_6H_6)Cr(CO)_3$ (XV), $(C_6H_5Me)Cr(CO)_3$ (XVI), [cyclobuta-η^6-benzene]$Cr(CO)_3$ (XVII), $(C_6Me_6)Cr(CO)_3$ (XVIII), (2,4,6-collidine)$Cr(CO)_3$ (XIX), (p-$C_6H_4F_2$)$Cr(CO)_3$ (XX), and [m-$C_6H_4(CF_3)_2$]$Cr(CO)_3$ (XXI) were prepared using known literature methods[8] or by refluxing the metal hexacarbonyl complex and the appropriate aromatic solvent. In some cases small amounts of THF were added to solubilize the hexacarbonyl complex.

Synthesis of (Benzene)$Cr(CO)_2(SiCl_3)_2$ (VI). A benzene (50 mL) solution of $(C_6H_6)Cr(CO)_3$ (0.25 g, 1.2 mmol) and $HSiCl_3$ (1.0 mL, 9.9 mmol) in a quartz tube equipped with a water-cooled probe was irradiated with a 450-W UV lamp for 4 h. The resulting gold-colored solution was filtered using a fine filter frit. The filtrate was concentrated in vacuo, layered with excess pentane, and stored in the freezer for several days. The resulting gold needlelike crystals were isolated and dried under vacuum. A yield of 43% was obtained. Anal. Calcd for $C_8H_6Cl_6CrO_2Si_2$: C, 21.1; H, 1.33. Found: C, 21.3; H, 1.50. The electronic spectrum of this compound showed absorption maxima at 327.7 and 246.6 nm.

Irradiation of $(C_6H_6)Cr(CO)_3$ (0.20 g, 0.93 mmol) and $HSiCl_3$ (1.0 mL, 9.9 mmol) in toluene for 5 h yielded 0.25 g of a mixture of the benzene and toluene disilyl complexes. Analysis of the ^1H NMR of this mixture indicated that $(C_6H_6)Cr(CO)_2(SiCl_3)_2$ and $(C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$ were present in 10% (40 mg) and 48% (210 mg) yields, respectively..

Synthesis of $[C_6H_3(CH_3)_3]Cr(CO)_2H(SiCl_3)$ (II). Irradiation of $[C_6H_3(CH_3)_3]Cr(CO)_3$ (0.19 g, 0.74 mmol) and $HSiCl_3$ (0.40 mL, 4.0 mmol) in hexanes (50 mL) in the setup described above for 45 min yielded the mesitylene analogue of $(C_6H_6)Cr(CO)_2H(SiCl_3)$ described by Jetz and Graham.[2] $[C_6H_3(CH_3)_3]Cr(CO)_2H(SiCl_3)$ (II) (0.20 g) was isolated in 70% yield upon crystallization from a CH_2Cl_2/pentane mixture. The electronic spectrum of this compound in CH_2Cl_2 showed a peak at 314.8 nm. See Tables I and II for spectral data.

Synthesis of $[C_6H_3(CH_3)_3]Cr(CO)_2(SiCl_3)_2$ (I). Irradiation of $[C_6H_3(CH_3)_3]Cr(CO)_3$ (0.46 g, 1.8 mmol) and $HSiCl_3$ (1.0 mL, 9.9 mmol) in hexanes (300 mL), using a photolytic reactor equipped with an immersion well, for 3 h yielded a yellow-brown residue. Upon removal of the hexanes the residue was extracted with CH_2Cl_2 (50 mL), layered with pentane (200 mL), and stored in the freezer for several days. The $[C_6H_3(CH_3)_3]Cr(CO)_2(SiCl_3)_2$ complex was isolated as yellow cubelike crystals in 45% yield. The electronic spectrum of the compound in CH_2Cl_2 showed bands at 318.1 and 243.7 nm. Anal. Calcd for $C_{11}H_{12}Cl_6CrO_2Si_2$: C, 26.6; H, 2.43. Found: C, 26.9; H, 2.55. See Tables I and II.

The same reaction carried out in benzene (50 mL), starting with (0.15 g) $[C_6H_3(CH_3)_3]Cr(CO)_3$ and 0.5 mL of $HSiCl_3$ yielded a mixture of $(C_6H_6)Cr(CO)_2(SiCl_3)_2$ (VI) (60 mg, 24%) and $[C_6H_3(CH_3)_3]Cr(CO)_2(SiCl_3)_2$ (I) (91 mg, 33%). Compound I was only sparingly soluble in benzene and precipitated out of solution and was recrystallized from CH_2Cl_2/pentane.

Synthesis of $(C_6H_5CH_3)Cr(CO)_2H(SiCl_3)$ (IV). A hexanes (50 mL) solution of $(C_6H_5CH_3)Cr(CO)_3$ (0.17 g, 0.75 mmol) and $HSiCl_3$ (0.20 mL, 2.0 mmol) in a quartz tube equipped with a water-cooled probe was irradiated for 1 h using a 450-W Hg lamp. The solvent was removed in vacuo from the resulting gold fluffy solid. The residue was extracted with CH_2Cl_2 (20 mL), layered with hexanes (100 mL), and stored in the freezer for several days. The $(C_6H_5CH_3)Cr(CO)_2H(SiCl_3)$ was obtained as a yellow powder. See Tables I and II for spectral data.

Synthesis of $(C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$ (III). Irradiation of a toluene (50 mL) solution of $(C_6H_5CH_3)Cr(CO)_3$ (0.25 g, 1.1 mmol) and $HSiCl_3$ (0.50 mL, 4.9 mmol) for 90 min with a 450-W Hg lamp yielded a yellow-brown solution. The solvent was removed in vacuo and the residue extracted with toluene (20 mL), layered with pentane (150 mL), and stored in the freezer for several days. The $(C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$ complex was obtained as a yellow powder in 52% yield. The electronic spectrum showed bands at 326.7 and 238.5 nm. Anal. Calcd for $C_9H_8Cl_6CrO_2Si_2$: C, 23.0; H, 1.72. Found: C, 22.7; H, 1.83. See Tables I and II for spectral data.

The complex $(C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$ was also prepared from the irradiation of (mesitylene)$Cr(CO)_3$ (0.20 g, 0.78 mmol) and $HSiCl_3$ (0.40 mL, 4.0 mmol) in toluene (40 mL) for 135 min. Crystallization in toluene/pentane yielded a yellow powder which was made up of $(C_6H_5CH_3)Cr(CO)_2(SiCl_3)_2$ (33% yield) and (mesitylene)$Cr(CO)_2(SiCl_3)_2$ (28% yield).

Synthesis of $[C_6(CH_3)_6]Cr(CO)_2(SiCl_3)_2$ (V). A hexane (50 mL) solution of $[C_6(CH_3)_6]Cr(CO)_3$ (0.15 g, 0.50 mmol) and $HSiCl_3$ (0.80 mL, 7.9 mmol) was irradiated for $2^1/_2$ h in a quartz tube equipped with a cooling probe. An immediate precipitation of a yellow fluffy solid was observed. The solvent was removed by filtration, the residue dissolved in CH_2Cl_2, and the product crystallized out of a CH_2Cl_2/hexane mixture at 0 °C. The $[C_6(Me)_6]Cr(CO)_2(SiCl_3)_2$ complex was isolated in 44% yield. The same reaction carried out in benzene and toluene starting with 0.23 and 0.25 g of $[C_6(CH_3)_6]Cr(CO)_3$, respectively, yielded only $[C_6(CH_3)_6]Cr(CO)_2(SiCl_3)_2$ in 58% and 80% yields, respectively. Anal. Calcd for $C_{14}H_{18}Cl_6CrO_2Si_2$: C, 31.2; H, 3.36; Si, 10.4.

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[7] Schiess, P. *Thermochem. Acta* **1987**, *112* (1), 31.

[8] (a) Magomedov, G. K.-I.; Grenkel, A. S.; Blokhina, E. I. *Zh. Obshch. Khim.* **1985**, *55*, 1323. (b) Nicholls, B.; Whitting, M. C. *J. Chem. Soc.* **1959**, 551.

Found: C, 31.2; H, 3.46; Si, 10.5. See Tables I and II for spectral data.

Synthesis of (Cyclobuta-η^6-benzene)Cr(CO)$_2$(H)(SiCl$_3$)$_2$ (IX). Irradiation of (cyclobuta-η^6-benzene)Cr(CO)$_3$ (0.33 g, 1.4 mmol) and $HSiCl_3$ (1.0 mL, 9.9 mmol) in hexanes (50 mL) for 3 h in a quartz tube as described above yielded (cyclobuta-η^6-benzene)Cr(CO)$_3$H(SiCl$_3$) (0.40 g, 84%). The electronic spectrum showed absorption maxima at 324.9 and 243.9 nm. See Tables I and II for spectral data.

Synthesis of (Cyclobuta-η^6-benzene)Cr(CO)$_2$(SiCl$_3$)$_2$ (VIII). A solution of (cyclobuta-η^6-benzene)Cr(CO)$_2$H(SiCl$_3$) (0.15 g, 0.43 mmol) and $HSiCl_3$ (0.5 mL, 4.9 mmol) in 1,3-bis(trifluoromethyl)benzene (45 mL) was irradiated for 3 h. The solvent was then removed in vacuo and the residue extracted with CH_2Cl_2 (50 mL). The CH_2Cl_2 extract was reduced in volume to ~20 mL after filtration, layered with hexanes (100 mL), and stored in the freezer for 1 week. The (cyclobuta-η^6-benzene)Cr(CO)$_2$(SiCl$_3$)$_2$ (70 mg) was isolated as light yellow crystals in 34% yield. Anal. Calcd for $C_{10}H_8Cl_6CrO_2Si_2$: C, 25.0; H, 1.66. Found: C, 24.8; H, 1.73. See Tables I and II for spectral data.

Photochemical Reaction of (Mesitylene)Cr(CO)$_3$ with *p*-Xylene. The mesitylene complex was placed in the reactor (150 mg, 0.58 mmol) and was dissolved in 50 mL of *p*-xylene, and $HSiCl_3$ (3 mL, 33.6 mmol) was added. Irradiation was started and continued for 8 h using a 450-W Hg lamp in a quartz tube equipped with a water-cooled probe. At the end of the reaction the solvent as well as excess $HSiCl_3$ was removed under vacuum, leaving a yellow crystalline residue which was redissolved in CH_2Cl_2, filtered, and layered with hexanes. Cooling to -20 °C for 1 week afforded a mixture of crystals identified by NMR as (*p*-xylene)Cr(CO)$_2$(SiCl$_3$)$_2$ (X) in a yield of 13% and (mesitylene)Cr(CO)$_2$(SiCl$_3$)$_2$ in a yield of 47%. See Tables I and II for spectral data.

Thermal Reaction of (Benzene)Cr(CO)$_2$(SiCl$_3$)$_2$ with *p*-Xylene. The (benzene)Cr(CO)$_2$(SiCl$_3$)$_2$ (0.70 g, 0.46 mmol) complex was dissolved in 50 mL of *p*-xylene and the resultant solution heated to 110 °C for 4 h. The resulting greenish yellow solution was filtered through a pad of Celite to remove decomposition products and pumped dry. Recrystallization of the yellow residue from CH_2Cl_2/hexane and NMR analysis identified the material as starting compound together with a small amount (<5%) of thermal exchange product (*p*-xylene) Cr(CO)$_2$(SiCl$_3$)$_2$ (X).

Photolytic Exchange Reactions: Example of Photolysis of (C_6H_6)Cr(CO)$_2$(SiCl$_3$)$_2$ in Toluene. The (C_6H_6)Cr(CO)$_2$(SiCl$_3$)$_2$ complex was prepared by photolyzing (C_6H_6)Cr(CO)$_3$ (0.20 g, 0.90 mmol) and $HSiCl_3$ (1.0 mL, 9.9 mmol) in C_6H_6. The formation of (C_6H_6)Cr(CO)$_2$(SiCl$_3$)$_2$ was confirmed by infrared spectrometry. The solvent was removed in vacuo, the residue redissolved in toluene (45 mL), and the mixture irradiated for 3 h. The ^{1}H NMR of the product mixture indicated the presence of (C_6H_6)Cr(CO)$_2$(SiCl$_3$)$_2$ and ($C_6H_5CH_3$)Cr(CO)$_2$(SiCl$_3$)$_2$ in 41% and 5.7% yields, respectively. The ^{1}H NMR of the product mixture after further irradiation (6 h) showed the (C_6H_6)Cr(CO)$_2$(SiCl$_3$)$_2$ and ($C_6H_5CH_3$)Cr(CO)$_2$(SiCl$_3$)$_2$ to be present in 15% and 8.4% yields, respectively.

In these photolytic exchange experiments, extended photolysis was carried out until little or no further exchange was occurring (although decomposition as a side reaction precluded much longer photolysis times). We assume, based on these results, that the systems studied were at or near equilibrium after photolysis.

Synthesis of Dichlorobis(2,4,6-collidine)chromium (XI). During 5 h, a solution of (mesitylene)Cr(CO)$_3$ (0.30 g, 7.17 mmol), 2,4,6-collidine (10 g, 82.6 mmol), and $HSiCl_3$ (5 mL, 49.6 mmol) was irradiated using a 450-W Hg lamp in 60 mL of methylene chloride. The color of the solution changed from deep yellow to deep red. Solvent and excess reactants were pumped off, leaving a gray-red solid residue which was redissolved in a minimum amount of CH_2Cl_2 and filtered. The resulting bright purple-red solution was cooled to -20 °C overnight, giving a white and purple precipitate. The white material could be identified as a compound containing a protonated 2,4,6-collidine ring (ν_{N-H} = 3260 cm^{-1}). Manual separation of most of the purple and white material in a glovebox could be achieved. The purple-red material was redissolved in 200 mL of CH_2Cl_2 and the mixture filtered again: The CH_2Cl_2 solution was placed in a beaker inside a desiccator in which 200 mL of pentane was added. Slow diffusion at room temperature during 2 weeks produced purple crystals of XI (112 mg, 0.31 mmol, 26.5%) still containing small amounts of a white byproduct. Therefore, no satisfactory elemental analysis could be obtained. Mp: 258–260 °C (sealed tube, uncorrected).

Reaction of (2,4,6-Collidine)Cr(CO)$_3$ with $HSiCl_3$ in CH_2Cl_2. The (2,4,6-collidine)Cr(CO)$_3$ complex (0.30 g, 7.16 mmol) was dissolved in 60 mL of CH_2Cl_2, and $HSiCl_3$ (3.0 mL, 33.6 mmol) was added. The resulting deep yellow solution was irradiated using a 450-W lamp for 3 h during which time a deep red solution was obtained. Filtration and removal of solvent produced a semisolid red material which showed identical ν_{CO} absorptions as the starting material. This material was redissolved in CH_2Cl_2, giving a red solution, and placed in a beaker together with an excess amount of pentane. Over a 2-week period, two compounds precipitated (purple and white). Both compounds appeared to be identical to the products obtained from the aforementioned reaction. Yield of the compound mixture: 130 mg.

Synthesis of Tetrakis(acetonitrile)bis(trichlorosilyl)chromium (XII). The [$C_6H_3(CH_3)_3$]Cr(CO)$_2$(SiCl$_3$)$_2$ (0.20 g, 0.78 mmol) was dissolved in 50 mL of acetonitrile, resulting in a bright yellow solution. Irradiation of the unstirred mixture was continued for 4 h using a 450-W Hg lamp. After 0.5 h the formation of light green needles could be observed within the reaction mixture together with a gradual change of the color from yellow to greenish white. At the end of the reaction most of the product crystallized out of the reaction solution. The light green acetonitrile solution was carefully decanted, and the crystals of XII were dried under vacuum. Yield: 120 mg, 0.24 mol, 30.8%. Mp: >360 °C (sealed tube). Anal. Calcd for $C_8H_{12}N_4Si_2Cl_6Cr$: C, 19.4; H, 2.44; N, 11.3. Found: C, 20.4; H, 2.81; N, 11.4.

Synthesis of (η^6-Benzene)(acetonitrile)dicarbonylchromium (XIII). The (benzene)Cr(CO)$_3$ complex (0.20 g, 0.94 mmol) was dissolved in 50 mL of acetonitrile and the resultant mixture irradiated using a 450-W Hg lamp for 3 h. The resulting bright red solution was filtered and reduced to a volume of 10 mL. Cooling to -10 °C overnight afforded 117 mg (0.515 mmol, 55%) of XIII as red crystals. IR (Nujol mull): $\nu_{C\equiv N}$ 2260, ν_{CO} 1880, 1770 cm^{-1}. Anal. Calcd for $C_{10}H_9NO_2Cr$: C, 52.9; H, 3.99; N, 6.18. Found: C, 52.6; H, 3.96; N, 6.21.

X-ray Structure Determination of [$C_6H_3(CH_3)_3$]Cr(CO)$_2$(SiCl$_3$)$_2$ (I). A crystal of I was wedged in a glass capillary under an argon atmosphere. Lattice constants[9] were determined from 19 centered reflections using the auto index routine supplied by Crystal Logic[10] and were verified with Laue photographs. A list of crystal data is given in Table III. Intensity data were collected without a monochromator, and a set of three standard reflections displayed a decrease in intensity of only 1.0% over the 107.1 h of exposure time. Thus, no decay correction was applied to the data. A total of three observed reflections (022, 040, 220) had intensities that exceeded the maximum allowable intensity and were recollected at reduced tube power. These three reflections were given a separate scale factor during refinement. The positions of all non-hydrogen atoms were located using direct methods.[10] Full-matrix isotropic refinement of these positions produced R = 13.2% and R_w = 16.7%. Full-matrix anisotropic refinement produced R = 5.4% and R_w = 7.8%. Coordinates for hydrogen atoms were then calculated and included in final refinement, as fixed contributors, which converged with R = 4.7% and R_w = 6.6%. Atomic coordinates from this final refinement are given in Table IV.

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(9) These lattice constants correspond to the following in the convectional space group *Pbca*: a = 17.706 (4), b = 27.738 (6), and c = 15.683 (3) Å.

(10) The programs used in these structure determinations were supplied by Crystal Logic. The Crystal Logic package includes modified versions of the following programs: REDUCE (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ORFFE (Busing, Martin, and Levy), distance, angle, and error calculation; ABSORB (Coppens, Edwards, and Hamilton), absorption correction calculation; ORTEP (Johnson), figure plotting; HYDROGEN (Trueblood), calculation of hydrogen atomic positions; SHELXS-86 (Sheldrick), direct methods. All calculations were performed on a DEC Micro VAX computer. $R = (\sum|F_o - F_c|/\sum|F_o|)$ and $R_w = (\sum w|F_o - F_c|^2\sum w|F_o|^2)^{1/2}$, where F_o and F_c are observed and calculated structure factors, respectively, and $w = 1/\sigma^2(F_o)$.

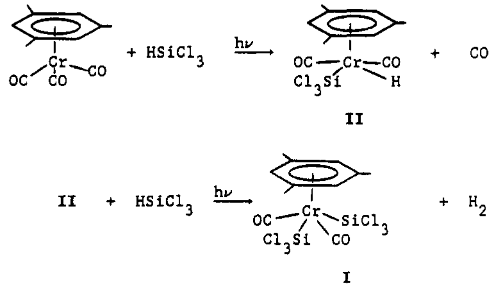
Table III. Crystal Data for (η^6-$C_6H_3(CH_3)_3$)Cr($SiCl_3$)$_2$(CO)$_2$ (I) and ($NC_5H_2(CH_3)_3$)$_2$Cr(Cl)$_2$ (XI)

	I	XI
fw	996.21	365.27
cryst syst	orthorhombic	monoclinic
space group	*Pcab*	$P2_1/c$
cryst dimens, mm	0.33 × 0.32 × 0.48	0.50 × 0.25 × 0.43
cryst color	yellow	purple
cryst habit	rectangular parallelepiped	rhombic parallelepiped
a, Å	15.683 (3)	7.594 (1)
b, Å	27.738 (6)	14.878 (2)
c, Å	17.706 (4)	7.880 (1)
α, deg	90.00	90.00
β, deg	90.00	92.860 (5)
γ, deg	90.00	90.00
Z	8	2
V, Å	7702.36	889.28
ρ(calcd), g cm^{-3}	1.72	1.36
radiation; λ, Å	Mo Kα; 0.7107	Mo Kα; 0.7107
abs coeff (μ), cm^{-1}	15.44	9.26
transmission factor range	0.69–0.56	0.82–0.66
F(000)	3984	380
temp, °C	24	24
diffractometer	Picker/Crystal Logic	Picker/Crystal Logic
scan mode; speed, deg/min	θ–2θ; 3.0	θ–2θ; 3.0
2θ range, deg	1–45.77	1–50.67
total data collcd, unique, obsd	5856, 5273, 3121 ($I > 3\sigma(I)$)	1750, 1558, 1109 ($I > 3\sigma(I)$)
no. params refined	398	98
shift/error; max av	0.040, 0.006	0.018, 0.004
final diff map, max, e/Å^3	1.25	1.20
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.047	0.042
$R_w = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|)^2)^{1/2}$	0.066	0.058

X-ray Structure Determination of Dichlorobis(2,4,6-collidine)chromium (XI). A crystal of XI was wedged in a glass capillary with minimum air exposure by blowing a stream of nitrogen gas across the microscope stage during mounting. The structure determination was carried out in a manner paralleling that of I except for the noted differences. Lattice constants were determined from 18 reflections. The intensities of the set of standards decreased by 2.07% over the total exposure time of 32.4 h. Three reflections (011, 110, 112) had intensities that exceeded the maximum allowable count rate and were recollected at reduced tube power. Full-matrix isotropic refinement of all non-hydrogen atoms produced R = 11.1% and R_w = 14.3% while anisotropic refinement reduced R to 5.3% and R_w to 7.7%. Inclusion of absorption corrections had no effect on the R values. The inclusion of hydrogen atoms in the final refinement at theoretical positions, as fixed contributors, produced R = 4.2% and R_w = 5.8%. The final atomic coordinates are given in Table V.

Results and Discussion

Photolytic decarbonylation of [η^6-1,3,5-$C_6H_3(CH_3)_3$]Cr(CO)$_3$ for 3 h in hexanes in the presence of excess $HSiCl_3$ led to the formation of the –Cr(CO)$_2$($SiCl_3$)$_2$ derivative (I) (eq 1). It was apparent that two $HSiCl_3$ groups had reacted. Therefore, we tried short photolysis times and found that the hydride derivative II could also be prepared in good yield. Further photolysis of II in the presence of $HSiCl_3$ led to the formation of I showing that the hydride must be an intermediate, isolable compound.



(1)

Table IV. Atomic Coordinates in (η^6-$C_6H_3(CH_3)_3$)Cr($SiCl_3$)$_2$(CO)$_2$ (I)

	x	y	z	U_{eq} ×10^4 [a]
Cr(01)	0.03999 (8)	0.23846 (4)	0.50238 (7)	268 (7)
Si(01)	−0.0391 (2)	0.1751 (1)	0.5601 (1)	389 (15)
Si(02)	0.0559 (2)	0.2386 (1)	0.3686 (1)	428 (16)
Cl(01)	0.0251 (2)	0.1291 (1)	0.6322 (2)	652 (18)
Cl(02)	−0.1409 (2)	0.1957 (1)	0.6271 (2)	620 (18)
Cl(03)	−0.0960 (2)	0.1272 (1)	0.4863 (2)	734 (20)
Cl(04)	−0.0049 (2)	0.1832 (1)	0.3133 (2)	829 (23)
Cl(05)	0.1792 (2)	0.2328 (1)	0.3281 (2)	669 (18)
Cl(06)	0.0098 (2)	0.2994 (1)	0.3139 (1)	631 (19)
C(01)	0.0908 (6)	0.1818 (3)	0.4755 (5)	437 (60)
C(02)	−0.0695 (7)	0.2414 (3)	0.4624 (5)	390 (57)
C(03)	0.0496 (6)	0.2647 (3)	0.6229 (5)	391 (56)
C(04)	0.1308 (6)	0.2488 (3)	0.6018 (5)	360 (53)
C(05)	0.1676 (6)	0.2701 (3)	0.5361 (5)	391 (56)
C(06)	0.1269 (6)	0.3066 (3)	0.4961 (5)	353 (54)
C(07)	0.0435 (6)	0.3194 (3)	0.5175 (5)	402 (58)
C(08)	0.0052 (6)	0.2996 (3)	0.5820 (5)	429 (60)
C(17)	−0.0803 (6)	0.3189 (4)	0.6088 (6)	620 (71)
C(18)	0.1729 (7)	0.3356 (3)	0.4364 (6)	569 (68)
C(19)	0.1806 (7)	0.2139 (4)	0.6480 (6)	626 (72)
O(01)	0.1264 (5)	0.1460 (2)	0.4626 (4)	725 (53)
O(02)	−0.1367 (4)	0.2464 (3)	0.4403 (4)	635 (49)
Cr(02)	−0.21989 (9)	0.49384 (5)	0.33551 (8)	330 (8)
Si(03)	−0.1633 (2)	0.4379 (1)	0.4245 (2)	578 (20)
Si(04)	−0.1305 (2)	0.5567 (1)	0.2913 (2)	576 (20)
Cl(07)	−0.0367 (3)	0.4468 (1)	0.4514 (3)	1211 (32)
Cl(08)	−0.1678 (2)	0.3658 (1)	0.3955 (2)	753 (20)
Cl(09)	−0.2208 (3)	0.4360 (1)	0.5295 (2)	1221 (33)
Cl(10)	−0.1710 (2)	0.6266 (1)	0.3137 (2)	905 (25)
Cl(11)	−0.1096 (3)	0.5574 (1)	0.1759 (2)	1182 (31)
Cl(12)	−0.0081 (2)	0.5575 (1)	0.3345 (3)	1055 (28)
C(09)	−0.3022 (6)	0.4418 (3)	0.2683 (6)	482 (66)
C(10)	−0.3352 (6)	0.4444 (3)	0.3422 (6)	492 (65)
C(11)	−0.3578 (6)	0.4889 (4)	0.3755 (6)	567 (71)
C(12)	−0.3487 (6)	0.5310 (4)	0.3325 (7)	608 (75)
C(13)	−0.3231 (7)	0.5297 (4)	0.2571 (8)	702 (85)
C(14)	−0.2946 (7)	0.4853 (4)	0.2277 (6)	608 (74)
C(15)	−0.1259 (7)	0.4659 (4)	0.2931 (6)	566 (71)
C(16)	−0.1900 (7)	0.5284 (3)	0.4180 (6)	554 (71)
O(03)	−0.0716 (5)	0.4462 (3)	0.2617 (5)	957 (68)
O(04)	−0.1752 (6)	0.5522 (3)	0.4706 (5)	919 (65)
C(20)	−0.3987 (9)	0.4920 (5)	0.4479 (9)	1197 (124)
C(21)	−0.2785 (8)	0.3944 (4)	0.2315 (7)	773 (87)
C(22)	−0.3297 (9)	0.5726 (4)	0.2071 (9)	1127 (116)

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

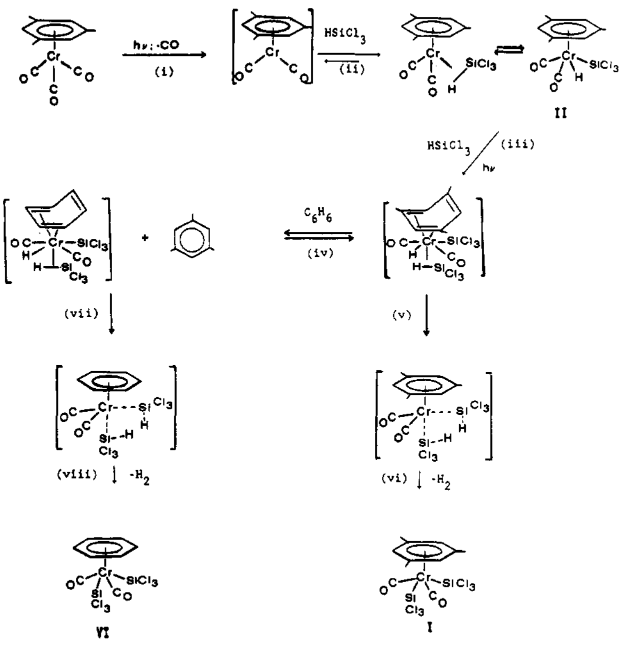
Table V. Atomic Coordinates in ($NC_5H_2(CH_3)_3$)$_2$Cr(Cl)$_2$ (XI)

	x	y	z	U_{eq} × 10^4 [a]
Cr(01)	0.0000	0.0000	0.0000	396 (5)
N(01)	−0.1557 (4)	0.1157 (2)	0.0221 (4)	390 (18)
Cl(01)	−0.1496 (1)	−0.0385 (1)	−0.2547 (2)	612 (8)
C(01)	−0.3109 (5)	0.1089 (3)	0.0983 (5)	426 (23)
C(02)	−0.4191 (5)	0.1818 (3)	0.1150 (5)	467 (25)
C(03)	−0.3687 (5)	0.2660 (3)	0.0610 (5)	491 (25)
C(04)	−0.2078 (5)	0.2728 (3)	−0.0146 (5)	475 (25)
C(05)	−0.1065 (5)	0.1973 (3)	−0.0338 (5)	431 (24)
C(06)	−0.3525 (6)	0.0193 (3)	0.1721 (7)	568 (29)
C(07)	−0.4801 (7)	0.3474 (3)	0.0868 (7)	730 (34)
C(08)	0.0680 (5)	0.2013 (3)	−0.1192 (7)	646 (31)

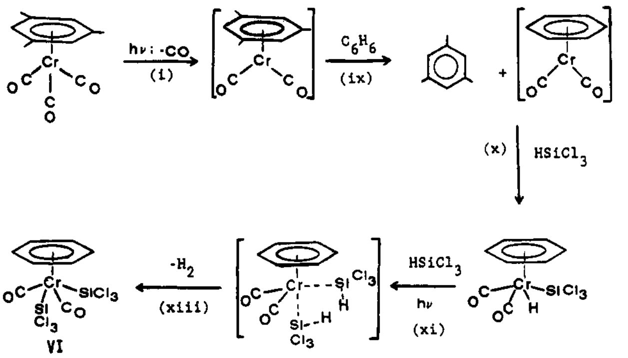
[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

Compound II will not react thermally with $HSiCl_3$ to give I. Photolytic conditions are necessary. In an effort to learn more about this process, a series of reactions were monitored by ^{1}H NMR and these were carried out in C_6D_6 at room temperature. It was determined that the formation of II from starting material was inhibited by the presence of 1 atm of CO. However, the second step forming I was not so inhibited. These are the expected results

Scheme I



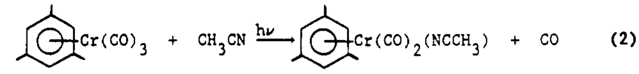
Scheme II



according to stoichiometry presented in eq 1. Indeed, the formation of II is apparent after just 10 min of irradiation, and its concentration reached a maximum after 45 min.

The formation of the bis(trichlorosilyl) derivative I was encouraged by the presence of excess $HSiCl_3$. Furthermore, uncoordinated mesitylene was observed early on during the photolysis (within 15 min, reaching a maximum after 2 h). Although the amount of free mesitylene generated was significant, and cannot be due to small amounts of decomposition, the quantity did not reflect the amount expected if complete arene exchange had occurred (η^6-mesitylene → η^6-C_6D_6; at equilibrium with C_6D_6 in very large excess). This finding was further supported by larger scale preparative reactions where the (mesitylene)$Cr(CO)_3$ was irradiated in benzene, toluene, and p-xylene, which gave the following results: Irradiation in benzene yielded 33% mesitylene complex I and 24% benzene complex VI, in toluene 28% I plus 33% toluene complex III, and in p-xylene 47% I plus 13% xylene complex X.

Schemes I and II attempt to summarize these results. The first step, the loss of CO upon photolysis of (arene)-$Cr(CO)_3$ is well documented (step i).[11] We were also able to trap the dicarbonyl intermediate in acetonitrile solution, where we found after 3 h of irradiation only the monoacetonitrile complex XIII[11b] was produced (eq 2). The



(2)

second step, H–$SiCl_3$ oxidative addition, is also well-known.[2,3] The hydride complex II can be isolated and was observed in the NMR experiments. The NMR studies also showed the presence of uncoordinated mesitylene within the first 10 min of reaction, suggesting that some arene exchange took place early in the reaction. However, most of the exchange took place during conversion of the hydride (step iv), probably via the postulated unstable intermediate which results from ring slippage necessary for the oxidative addition of a second $HSiCl_3$ moiety (step iii).

Since methyl-substituted arenes possess more π-electron density, chromium complexation to mesitylene should be more favorable than to toluene or benzene. However, the exchange in step iii obviously has some steric constraints as well, and these should give the opposite trend. We carried out extended photolysis of (benzene)$Cr(CO)_3$ in toluene and observed (toluene)$Cr(CO)_2(SiCl_3)_2$ and (benzene)$Cr(CO)_2(SiCl_3)_2$ in yields of 48% and 10%, respectively. Photolysis of (mesitylene)$Cr(CO)_3$ in toluene yielded (toluene)$Cr(CO)_2(SiCl_3)_2$ and (mesitylene)Cr-$(CO)_2(SiCl_3)_2$ in 33% and 28% yields, respectively. Presuming that these reactions were approaching equilibrium, these results simply show that steric effects are also important in determining the extent of exchange. However, the electronic effects can be dominant. We found that extended photolysis of (hexamethylbenzene)$Cr(CO)_3$ in toluene only yielded (hexamethylbenzene)$Cr(CO)_2(SiCl_3)_2$; no exchange took place. Finally, (mesitylene)$Cr(CO)_3$ was photolyzed in benzene, and both (mesitylene)$Cr(CO)_2$-$(SiCl_3)_2$ and (benzene)$Cr(CO)_2(SiCl_3)_2$ were found in yields of 33% and 24%, respectively. Photolysis of (mesitylene)$Cr(CO)_3$ in p-xylene yielded (mesitylene)$Cr(CO)_2$-$(SiCl_3)_2$ and (p-xylene)$Cr(CO)_2(SiCl_3)_2$ in 47% and 13% yields, respectively. These results illustrate that the exchange is fairly facile even when the incoming arene is comparatively electron-deficient (benzene vs mesitylene) and suggests that an interplay of electronic and steric factors determines the extent of the exchange.

The final product, (arene)$Cr(CO)_2(SiCl_3)_2$, undergoes arene exchange both *thermally* and *photochemically*. For example, the benzene analogue will exchange with xylene at 110 °C over a period of 4 h. Benzene is also displaced photochemically by toluene over 6 h at ambient temperature.

Structure of [η^6-$C_6H_3(CH_3)_3$]$Cr(SiCl_3)_2(CO)_2$ (I). An ORTEP[10] drawing depicting the two independent molecules of I in the asymmetric unit of structures is given in Figure 1 (A and B). Both chromium atoms have a trans square-pyramidal coordination sphere if the η^6-arene is taken as one ligand bonded at the ring center (Ct). Ignoring the methyl groups, the coordination sphere has approximate C_{2v} symmetry. A projection of the σ-bonded ligands onto the arene plane in Figure 2 reveals deviations from idealized geometry and shows that the Cr–Si bonds are close to eclipsing the ring carbon atoms. Specifically, the angles of rotation for planes defined by Si(01)–Cr(01)–Si(02)/Si(03)–Cr(02)–Si(04) and C(03)–Ct(01)–C(06)/C(10)–Ct(02)–C(13) are 3.9°/4.1° for molecules A/B, respectively. Moreover the $CrSi_2$ plane and CrC_2 plane are within $2^1/_2$° of being perpendicular to their respective arene planes and are within 0.2° of being perpendicular to one another. The basal plane consisting of four σ-bonded donor atoms is slightly ruffled by 0.08 Å/0.09 Å and is 1.5°/1.7° from being parallel to their respective

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(11) (a) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 3, p 1036. (b) Knoll, L.; Reiss, K.; Schafer, J.; Klüfers, P. *J. Organomet. Chem.* 1980, *193*, C40.

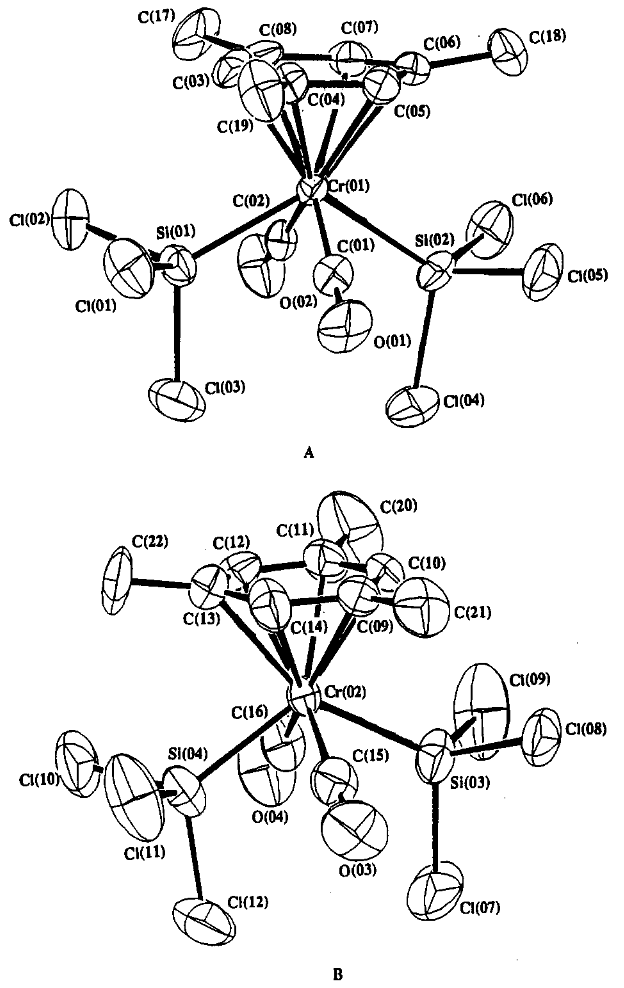

Figure 1. ORTEP diagram depicting the two independent molecules of I in the asymmetric unit of structure at 50% probability.

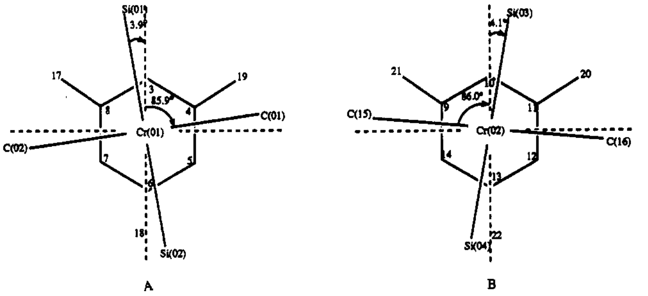

Figure 2. Projection of the σ-bonded ligands in I onto their respective arene planes.

Table VI. Bond Distances (Å) in $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(SiCl_3)_2(CO)_2$ (I)

	Molecule A		
Cr(01)–C(01)	1.83 (1)	Si(01)–Cl(03)	2.067 (4)
Cr(01)–C(02)	1.86 (1)	Si(02)–Cl(04)	2.057 (4)
Cr(01)–Si(01)	2.383 (3)	Si(02)–Cl(05)	2.069 (4)
Cr(01)–Si(02)	2.382 (3)	Si(02)–Cl(06)	2.075 (4)
C(01)–O(01)	1.16 (1)	C(03)–C(04)	1.40 (1)
C(02)–O(02)	1.13 (1)	C(04)–C(05)	1.43 (1)
Cr(01)–C(03)	2.259 (8)	C(05)–C(06)	1.39 (1)
Cr(01)–C(04)	2.281 (8)	C(06)–C(07)	1.41 (1)
Cr(01)–C(05)	2.265 (8)	C(07)–C(08)	1.40 (1)
Cr(01)–C(06)	2.332 (8)	C(08)–C(03)	1.39 (1)
Cr(01)–C(07)	2.261 (8)	C(04)–C(19)	1.49 (1)
Cr(01)–C(08)	2.271 (8)	C(06)–C(18)	1.51 (1)
Si(01)–Cl(01)	2.066 (4)	C(08)–C(17)	1.52 (1)
Si(01)–Cl(02)	2.069 (4)		
	Molecule B		
Cr(02)–C(15)	1.83 (1)	Si(03)–Cl(09)	2.067 (5)
Cr(02)–C(16)	1.81 (1)	Si(04)–Cl(10)	2.079 (4)
Cr(02)–Si(03)	2.382 (3)	Si(04)–Cl(11)	2.069 (5)
Cr(02)–Si(04)	2.371 (3)	Si(04)–Cl(12)	2.066 (5)
C(15)–O(03)	1.15 (1)	C(09)–C(10)	1.41 (1)
C(16)–O(04)	1.17 (1)	C(10)–C(11)	1.41 (1)
Cr(02)–C(09)	2.272 (9)	C(11)–C(12)	1.40 (1)
Cr(02)–C(10)	2.272 (9)	C(12)–C(13)	1.39 (2)
Cr(02)–C(11)	2.28 (1)	C(13)–C(14)	1.41 (2)
Cr(02)–C(12)	2.27 (1)	C(14)–C(09)	1.41 (1)
Cr(02)–C(13)	2.35 (1)	C(09)–C(21)	1.51 (1)
Cr(02)–C(14)	2.25 (1)	C(11)–C(20)	1.44 (2)
Si(03)–Cl(07)	2.057 (5)	C(13)–C(22)	1.49 (2)
Si(03)–Cl(08)	2.066 (4)		

Table VII. Bond Angles (deg) in $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(SiCl_3)_2(CO)_2$ (I)

	Molecule A		
C(01)–Cr(01)–C(02)	110.0 (4)	Cl(02)–Si(01)–Cl(03)	102.0 (2)
C(01)–Cr(01)–Si(01)	72.7 (3)	Cl(04)–Si(02)–Cl(05)	102.1 (2)
C(01)–Cr(01)–Si(02)	72.3 (3)	Cl(04)–Si(02)–Cl(06)	102.9 (2)
C(02)–Cr(01)–Si(01)	73.4 (3)	Cl(05)–Si(02)–Cl(06)	103.1 (2)
C(02)–Cr(01)–Si(02)	73.6 (3)	C(03)–C(04)–C(05)	117.1 (8)
Si(01)–Cr(01)–Si(02)	118.8 (1)	C(04)–C(05)–C(06)	122.1 (8)
O(01)–C(01)–Cr(01)	175.6 (9)	C(05)–C(06)–C(07)	118.2 (8)
O(02)–C(02)–Cr(01)	175.0 (9)	C(06)–C(07)–C(08)	121.2 (9)
Cl(01)–Si(01)–Cr(01)	117.8 (1)	C(07)–C(08)–C(03)	118.7 (9)
Cl(02)–Si(01)–Cr(01)	116.4 (1)	C(08)–C(03)–C(04)	122.4 (8)
Cl(03)–Si(01)–Cr(01)	115.3 (1)	C(03)–C(04)–C(19)	122.4 (8)
Cl(04)–Si(02)–Cr(01)	115.1 (1)	C(05)–C(04)–C(19)	120.3 (8)
Cl(05)–Si(02)–Cr(01)	116.3 (2)	C(03)–C(08)–C(17)	121.6 (9)
Cl(06)–Si(02)–Cr(01)	115.4 (1)	C(07)–C(08)–C(17)	119.6 (9)
Cl(01)–Si(01)–Cl(02)	101.1 (2)	C(05)–C(06)–C(18)	121.6 (9)
Cl(01)–Si(01)–Cl(03)	101.8 (2)	C(07)–C(06)–C(18)	121.2 (9)
	Molecule B		
C(15)–Cr(02)–C(16)	110.4 (5)	Cl(08)–Si(03)–Cl(09)	100.6 (2)
C(15)–Cr(02)–Si(03)	72.3 (4)	Cl(10)–Si(04)–Cl(11)	103.2 (2)
C(15)–Cr(02)–Si(04)	72.5 (3)	Cl(10)–Si(04)–Cl(12)	101.7 (2)
C(16)–Cr(02)–Si(03)	73.4 (3)	Cl(11)–Si(04)–Cl(12)	102.6 (2)
C(16)–Cr(02)–Si(04)	73.9 (3)	C(09)–C(10)–C(11)	121.6 (9)
Si(03)–Cr(02)–Si(04)	118.5 (1)	C(10)–C(11)–C(12)	118 (1)
O(03)–C(15)–Cr(02)	174 (1)	C(11)–C(12)–C(13)	122 (1)
O(04)–C(16)–Cr(02)	176 (1)	C(12)–C(13)–C(14)	118 (1)
Cl(07)–Si(03)–Cr(02)	115.8 (2)	C(13)–C(14)–C(09)	122 (1)
Cl(08)–Si(03)–Cr(02)	116.9 (2)	C(10)–C(09)–C(14)	117.5 (9)
Cl(09)–Si(03)–Cr(02)	116.7 (2)	C(10)–C(09)–C(21)	122.4 (9)
Cl(10)–Si(04)–Cr(02)	116.3 (2)	C(14)–C(09)–C(21)	120 (1)
Cl(11)–Si(04)–Cr(02)	115.3 (2)	C(10)–C(11)–C(20)	122 (1)
Cl(12)–Si(04)–Cr(02)	115.8 (2)	C(12)–C(11)–C(20)	119 (1)
Cl(07)–Si(03)–Cl(08)	101.9 (2)	C(12)–C(13)–C(22)	122 (1)
Cl(07)–Si(03)–Cl(09)	102.5 (2)	C(14)–C(13)–C(22)	120 (1)

arene plane. The chromium atom lies 1.134 Å/1.126 Å above this basal plane.

Bond distances and angles are listed in Tables VI and VII. The Cr–C_{ring} distances range from 2.252 (10) to 2.353 (11) Å, with the methyl-substituted carbons having an average distance that is 0.04 Å longer than the average for the other ring carbons. The overall average Cr–C_{ring} distance of 2.27 (8) Å/2.283 (10) Å is ~0.05 Å longer than those observed in benzene tricarbonylchromium complexes which are compared in Table VIII, while the carbonyl parameters are similar. This indicates that the presence of the $SiCl_3$ groups, and concomitant increase in coordination number and formal oxidation state of chromium, does not affect the Cr–CO bonding but decreases the importance of the π-arene bonding as evidenced by an increase in the perpendicular Cr-ring distance by ~0.07 Å. This is similar to the observation made by Bailey and Dahl[12,13] that the Cr–ring distance increases by ~0.1 Å when three strong-bonding CO groups replace one arene in $(C_6H_6)_2Cr$. Thus, the order of increasing importance

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(12) (a) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1298. (b) Rees, B.; Coppens, R. *Acta Crystallogr.* **1973**, *B29*, 2516.

(13) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314.

Table VIII. Comparison of Selected Average Bond Parameters[a]

type	$(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(SiCl_3)_2(CO)_2$[b]		$(\eta^6\text{-}C_6(CH_3)_6)Cr(CO)_3$[c]	$(\eta^6\text{-}C_6H_6)Cr(CO)_3$[d]	$(\eta^6\text{-}C_6H_3(CH_3)_3)Ni(SiCl_3)_2$[e]
	molecule A	molecule B			
$Cr\text{-}C_{ring}$	2.278 (8)	2.283 (10)	2.233 (10)	2.221 (8)	
⊥ Cr–ring	1.797	1.800	1.726	1.724	
Cr–CO	1.843 (10)	1.819 (11)	1.814 (12)	1.841 (9)	
C–O	1.148 (10)	1.160 (11)	1.163 (12)	1.143 (7)	
Si–Cl	2.067 (4)	2.067 (5)			2.064 (2)
Cl–Si–Cl	102.17 (17)	102.09 (21)			102.52 (7)
Cr–Si–Cl	116.05 (14)	116.12 (17)			115.66 (6)

[a] Distances are in angstroms; angles are in degrees. [b] This work. [c] Reference 16a. [d] Reference 17. [e] Reference 18.

of π-arene bonding would be $(\eta^6\text{-}C_6H_3(CH_3)_3)Cr(SiCl_3)_2(CO)_2 < (\eta^6\text{-}C_6H_6)Cr(CO)_3 < (C_6H_6)_2Cr$.

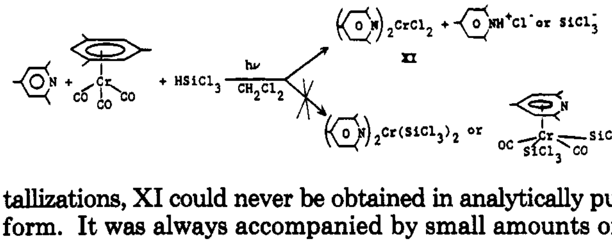
The average Cr–Si bond length of 2.383 (3) Å/2.377 (3) Å is significantly shorter than the 2.456 (1) Å distance observed in $(C_6(CH_3)_6)Cr(CO)_2(H)SiHPh_2$.[3a] However, the scarcity of literature data on Cr–Si bonds makes it difficult to use this parameter as a probe to access the extent of π back-bonding. Although less sensitive as a probe, the Si–Cl bonds should lengthen as π back-bonding from M to $SiCl_3$ increases. The observed Si–Cl average length of 2.067 (5) Å is ~0.03 Å longer than that in $Ni(CO)_3(SiCl_3)_2$,[14] where little or no π back-bonding is expected, and is within experimental error to that observed in $(\eta^6\text{-}C_6H_3(CH_3)_3)Ni(SiCl_3)_2$.[15] Thus, it is likely that some π back-bonding is occurring in I and the observed Cr–Si lengths are shorter than a typical single-bond value. Further work is under way in our laboratories to characterize $M\text{-}SiX_3$ bonding.

Synthesis and Reactions of Other Chromium Arene Complexes. In an effort to generate compounds with increased η^6-arene thermal lability, the synthesis of a variety of $(arene)Cr(CO)_2R_2$ complexes was undertaken.

As described earlier, the benzene and toluene analogues of $(arene)Cr(CO)_2(SiCl_3)_2$ could be prepared by long-term irradiation of their respective $(arene)Cr(CO)_3$ derivatives or by irradiation of $(mesitylene)Cr(CO)_3$ in benzene or toluene solvents. The intermediate hydride complexes also were isolable. We were also able to form a complex with benzocyclobutene as the arene and isolate both the hydride and $-Cr(CO)_2(SiCl_3)_2$ derivative.

In the case of hexamethylbenzene, only the $-Cr(CO)_2(SiCl_3)_2$ derivative was formed upon photolysis of $(hexamethylbenzene)Cr(CO)_3$. The intermediate hydride was not detected or isolable. For this compound, arene exchange could not be induced by photolytic or thermal means. Since the hydride species is definitely an intermediate in all of these reactions, we would expect that it would form in this case too. However, it must immediately react thermally with excess $HSiCl_3$, so no ring slippage (Scheme I) takes place. Therefore, arene exchange does not occur. These results are in contrast to the work of Schubert and co-workers[3a,b] who were able to isolate and structurally characterize $(hexamethylbenzene)Cr(CO)_2(H)(SiPh_2H)$.[3a] Possibly the steric constraints in the Schubert compound are so great that the reaction of a second mole of H_2SiPh_2 is not favorable.

The reaction sequences proposed in Schemes I and II suggest a unique opportunity to prepare heteroatom-containing aromatic complexes. Reaction of an excess of 2,4,6-trimethylpyridine (2,4,6-collidine) and $HSiCl_3$ with $(\eta^6\text{-}mesitylene)Cr(CO)_3$ in CH_2Cl_2 resulted in a color change from yellow to bright red. Workup yielded a mixture of compounds (eq 3). Despite several recrys-



(3)

tallizations, XI could never be obtained in analytically pure form. It was always accompanied by small amounts of a pyridinium salt which made satisfactory elemental analysis impossible. Furthermore, its paramagnetic nature (→-Cr(II), square-planar high-spin) precluded NMR spectroscopic characterization. However, we were able to obtain crystals which finally allowed unambiguous identification of XI through X-ray structure determination.

An ORTEP[10] drawing of XI is depicted in Figure 3. The molecule adapts a trans square-planar coordination sphere, with the Cr atom residing on a crystallographic center of inversion. The collidine ring plane is rotated 86.0° from the coordination plane which is within 4° of approximating D_{2h} molecular symmetry. Bond distances and angles are listed in Tables IX and X. The Cr–N distance of 2.101 (3) Å is slightly shorter than the 2.145 (2) Å $Cr\text{-}N_{pyridine}$

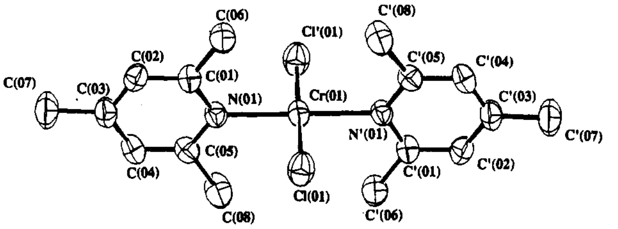


Figure 3. ORTEP diagram of XI depicting the atomic numbering scheme and thermal ellipsoids at 50% probability. Prime notation is used for those atoms related by a center of inversion.

Table IX. Bond Distances (Å) in $(NC_5H_2(CH_3)_3)_2Cr(Cl)_2$ (IX)

Cr(01)–N(01)	2.101 (3)	C(03)–C(04)	1.390 (6)
Cr(01)–Cl(01)	2.328 (1)	C(04)–C(05)	1.374 (5)
N(01)–C(01)	1.351 (5)	C(01)–C(06)	1.494 (5)
N(01)–C(05)	1.353 (5)	C(03)–C(07)	1.497 (6)
C(01)–C(02)	1.371 (5)	C(05)–C(08)	1.517 (5)
C(02)–C(03)	1.383 (6)		

Table X. Bond Angles (deg) in $(NC_5H_2(CH_3)_3)_2Cr(Cl)_2$ (XI)

N(01)–Cr(01)–N'(01)	180.0 (0)	C(03)–C(04)–C(05)	119.8 (4)
N(01)–Cr(01)–Cl(01)	91.2 (1)	C(04)–C(05)–N(01)	122.2 (4)
N(01)–Cr(01)–Cl'(01)	88.8 (1)	C(05)–N(01)–C(01)	118.3 (3)
Cl(01)–Cr(01)–Cl'(01)	180.0 (0)	N(01)–C(01)–C(06)	116.4 (3)
C(02)–C(01)–C(06)	121.9 (4)	C(02)–C(03)–C(07)	121.6 (4)
N(01)–C(01)–C(02)	121.5 (4)	C(04)–C(03)–C(07)	121.0 (4)
C(01)–C(02)–C(03)	120.7 (4)	N(01)–C(05)–C(08)	116.2 (4)
C(02)–C(03)–C(04)	117.4 (4)	C(04)–C(05)–C(08)	121.5 (4)

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(14) Janikowski, S. K.; Radonovich, L. J.; Groshens, T. J.; Klabunde, K. J. *Organometallics* 1985, 3, 396.

(15) Janikowski, S. K. Ph.D. Dissertation, The University of North Dakota, Grand Forks, ND, 1985.

Table XI. Mass Spectral Data (EI, 70 eV) of the Complexes

III[a]	466 (M^+), 431 ($M^+ - Cl$), 410 ($M^+ - 2CO$), 375 [$M^+ - (2CO + Cl)$], 318 [$Cr(SiCl_3)_2]^+$, 277 [$M^+ - (2CO + SiCl_3)$], 144 [$Cr(C_6H_5CH_3)^+$, base peak]
V[a]	536 (M^+), 501 ($M^+ - Cl$), 480 ($M^+ - 2CO$), 347 [$M^+ - (2CO + SiCl_3)$], 214 [$Cr(C_6(CH_3)_6^+$, base peak]
VI[a]	452 (M^+), 417 ($M^+ - Cl$), 396 ($M^+ - 2CO$), 361 [$M^+ - (2CO + Cl)$], 318 [$Cr(SiCl_3)_2]^+$, 263 [$M^+ - (2CO + SiCl_3)$], 130 [$Cr(C_6H_6)^+$, base peak]
VIII[a]	478 (M^+), 443 ($M^+ - Cl$), 422 ($M^+ - 2CO$), 387 [$M^+ - (2CO + Cl)$], 318 [$Cr(SiCl_3)_2]^+$, 287 [$M^+ - (2CO + SiCl_3)$], 156 [$M^+ - (2CO + 2SiCl_3)$, base peak]
IX[a]	311 ($M^+ - Cl$), 255 [$M^+ - (2CO + Cl)$], 156 [$M^+ - (2CO + 2\ SiCl_3)$]
XIII	227 (M^+), 171 ($M^+ - 2CO$), 130 [$M^+ - (2CO + CH_3CN)$], 93 [$Cr(CH_3CN)^+$, base peak]

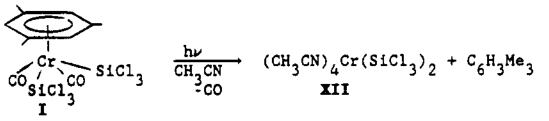
[a] Isotopic pattern expected for six Cl atoms observed.

distance[16] in $(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_2Cr(py)_2$. The Cr–Cl distance is similar to that reported for another Cr(II) complex,[17] and other bond parameters are not unusual.

Even though the number of structurally characterized chromium(II) complexes is large, square-planar Cr(II) compounds are still rare.[18] It is especially interesting to note that in the late-transition-metal complex Ni(2,4,6-collidine)$_2$(SiCl$_3$)$_2$[5b] the heterocyclic ligands are cis-coordinated even though the sterically demanding $SiCl_3$ groups are present. In contrast, the heterocyclic ligands are trans in XI as well as the earlier reported Cr(II) complex $Cr(O_2CCF_3)_2(2,6\text{-lutidine})_2$.[19] It therefore appears that electronic factors are responsible for the observed stereochemistry in the two Cr(II) compounds.

The formation of XI in eq 3 surprised us, since the isolated chromium reaction product contains no $SiCl_3$ groups. We were especially careful in using thoroughly dried reagents, being aware of the hydrolytic lability of trichlorosilyl complexes.[5c] Excess $HSiCl_3$ or an intermediate species containing coordinated $SiCl_3$ cannot be ruled out as a source for the Cl^- observed in the final product XI. Reaction carried out in cyclohexane instead of CH_2Cl_2 also yielded XI as the product. Therefore, the CH_2Cl_2 could be ruled out as a possible source of Cl^- ions. At present, we do not have a full understanding concerning the formation of XI in the above reaction. It appears that the steric hindrance around the nitrogen lone pair in 2,4,6-collidine is not sufficient to favor the desired η^6- over η^1-coordination mode. This parallels our results for the late transition metal Ni(II).[5b] In an attempt to achieve the η^6-coordination mode, the photolytic reaction of (η^6-2,4,6-collidine)Cr(CO)$_3$ and $HSiCl_3$ in CH_2Cl_2 was carried out. As already observed in the free 2,4,6-collidine reaction, a mixture of XI and a pyridinium salt was isolated. Here, surprisingly, a decomplexation occurred, which was accompanied by an $\eta^6 \rightarrow \eta^1$ slippage of the 2,4,6-collidine ring system. Obviously, the reactions of the heteroaromatic counterparts of benzene and its methyl-substituted derivatives are more complex than initially thought, and more work is needed to understand them completely. However, the η^6–η^1 shift observed in this heteroatom system suggests this process can occur in other arene complexes as well.

It is interesting to compare the reactivities of the tricarbonyl complex $[\eta^6\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$ (XIV) and our bis(trichlorosilyl) compound I with acetonitrile. As expected, the irradiation of XIV led to the displacement of one coordinated CO[20] (eq 2). In contrast, irradiation of I resulted in the substitution of two carbonyl groups and the η^6-bonded arene (eq 4). This photolytically induced



(4)

arene/CO removal in I represents a rare case of arene labilization in early-transition-metal chemistry, which to our knowledge has not been previously observed. Indeed, only when strong donor ligands are present, e.g., $P(OMe)_3$, can the photolytic displacement of a second CO be achieved in the tricarbonyl complex.[21] Clearly, the different electronic environment around the Cr(II) in I must be responsible for its enhanced reactivity. The strong electron-withdrawing effects of the trichlorosilyl groups, coupled with the Cr oxidation state (II), lower the backbonding into the π^* orbitals of the CO ligands and the complexed mesitylene ring. As a result, the CO ligands and mesitylene ring are strongly labilized and can be removed photolytically under mild conditions. Our inability to isolate the electronically and sterically demanding $p\text{-}C_6H_4F_2$ and $m\text{-}C_6H_4(CF_3)_2$ analogues of these compounds, either by exchange reactions or from compounds XX and XXI, also suggests that such is the case. This further implies that it may be possible to prepare stable, isolable, reactive arene chromium complexes with a potentially rich chemistry, by proper modification of the aromatic ligands and the substituent R groups. Efforts in this direction are continuing.

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Registry No. I, 138605-68-2; II, 138605-69-3; III, 138605-70-6; IV, 138605-71-7; V, 138605-72-8; VI, 138605-73-9; VII, 32915-10-9; VIII, 138605-74-0; IX, 138605-75-1; X, 138605-76-2; XI, 138605-77-3; XII, 138605-78-4; XIII, 75503-66-1; XIV, 12129-67-8; XV, 12082-08-5; XVI, 12083-24-8; XVII, 99537-78-7; XVIII, 12088-11-8; XIX, 55853-04-8; XX, 56213-60-6; XXI, 138605-79-5; $HSiCl_3$, 10025-78-2.

Supplementary Material Available: Tables of thermal parameters and least-squares planes for I and XI (13 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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[16] Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 214.

[17] Ferrira, V.; Krause, R. A. *Inorg. Chim. Acta* **1988**, *145*, 29.

[18] For a survey of compounds structurally characterized until 1986: Larkworthy, L. F.; Nolan, K. B.; O'Brien, P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 3, p 772.

[19] Eremenko, I. L.; Pasynskii, A. A.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *Inorg. Chim. Acta* **1981**, *54*, L85.

[20] Kluefers, P.; Knoll, L.; Reiners, C.; Reiss, K. *Chem. Ber.* **1985**, *118*, 1825 and references therein.

[21] Jaouen, G.; Dabard, R. *J. Organomet. Chem.* **1973**, *61*, C36.