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Photochemical Synthesis of (η^6-Arene)chromium Hydrido Stannyl and (η^6-Arene)chromium Bis(stannyl) Complexes

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Photolysis of (η^6-arene)Cr(CO)$_3$ complexes and HSnPh$_3$ in aromatic solvents at room temperature has led to two classes of complexes: hydrido stannyl compounds containing the η^2-H−SnPh$_3$ ligand and bis(stannyl) compounds containing two SnPh$_3$ ligands. The ratio between the two complexes simultaneously produced depends on the choice of the arene. Complexes with different arenes (mesitylene, toluene, benzene, fluorobenzene, and difluorobenzene) have been obtained and characterized including X-ray structures for (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_2$(H)(SnPh$_3$) (**1a**), (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_2$(SnPh$_3$)$_2$ (**1b**), (η^6-C$_6$H$_5$F)Cr(CO)$_2$(SnPh$_3$)$_2$ (**4b**), and (η^6-C$_6$H$_4$F$_2$)Cr(CO)$_2$(SnPh$_3$)$_2$ (**5b**). X-ray crystallography of the last three compounds has given the following results: **1b**, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.905(4)$ Å, $b = 18.499(2)$ Å, $c = 17.708(2)$ Å, $Z = 4$, $V = 4285(1)$ Å^3; **4b**, orthorhombic, space group $Pca2_1$ (No. 29), $a = 16.717(2)$ Å, $b = 18.453(2)$ Å, $c = 25.766(2)$ Å, $Z = 8$, $V = 7948(2)$ Å^3; **5b**, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.756(2)$ Å, $b = 18.560(2)$ Å, $c = 17.159(2)$ Å, $Z = 4$, $V = 4372(2)$ Å^3. The relatively high $J(^{119}$Sn−Cr−H) and $J(^{117}$Sn−Cr−H) values as well as the X-ray structural data provide evidence for the existence of three-center two-electron bonds in the hydrido stannyl complexes. The ^{1}H NMR data of the complexes are compared with chromium−arene bond distances, and a sensible trend is observed and discussed.

Introduction

The addition of H−M′R$_3$, where M′ is a main group IV metal, to transition metal fragments (L$_n$M) has been of great interest in the last 30 years. An extensive work has been carried out on the addition of HSiR$_3$ (R = Cl or alkyl group).[1−3] Most of the work has been done on complexes stabilized by Cp or alkyl-substituted Cp rings, and less work on arene-containing complexes has been reported. The photochemical decarbonylation of metal tricarbonyl complexes followed by addition of HSiR$_3$ has led to a variety of Cp and arene−hydride−SiR$_3$ complexes of Mn, Cr, and Fe.[1−3] To a lesser extent, the addition of HSnR$_3$ and HGeR$_3$ has been also studied.[4−6] The complete oxidative addition of HSiR$_3$ to a transition metal complex moiety (L$_n$M) would totally cleave the H−Si bond giving a hydrido silyl complex with both M−H and M−Si bonds. After A. G. Graham et al. isolated and chraracterized a number of complexes of the general formula Cp(CO)$_2$Mn(H)SiR$_3$, in the early 1970s, chemical and spectroscopic evidence for the presence of Mn, H, Si three-center two-electron bonds has been gathered and discussed.[7,8]

The possibility of a three-center bond involving a SnR$_3$ ligand has been considered. In 1989, Schubert et al. reported the first example of a transition metal, hydrogen, tin three-center two-electron bond in the Mn complex (MeCp)(CO)$_2$Mn(H)SnPh$_3$.[4a] Later in 1991 Schubert and co-workers reported the structure of the complex (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_2$(H)SnPh$_3$ obtained from the photochemical reaction of HSnPh$_3$ with (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_3$.[4c] Under different reaction conditions we have obtained the same complex and, for the first time under photochemical conditions, the bis(stannyl) complex (η^6-C$_6$H$_3$(CH$_3$)$_3$)Cr(CO)$_2$(SnPh$_3$)$_2$.

In this paper we report the synthesis, characterization, and structure of two types of arene−chromium complexes: Hydrido stannyl complexes which have Cr, hydrogen, tin three-center two-electron bonds, i.e., an η^2-coordination of H−Sn to the Cr center, and the bis(stannyl) complexes containing two stannyl ligands (SnPh$_3$). These complexes have been characterized by ^{1}H NMR, IR, elemental analysis, and X-ray crystallography. This is an extension of previous work to prepare new arene−metal complexes in unusual oxidation states and study their arene lability as well as their catalytic potential in different processes.[9] Since the overall goal of our work in this area is to gain access to compounds with labile η^6-arene ligands, we were particularly interested in the bis(stannyl) complexes and their structures. This is because the bulky nature of two SnPh$_3$ groups causes, we have noted, enhanced lability of the η^6-arene.

Results and Discussion

The photochemical reaction of (arene)Cr(CO)$_3$ complexes with an excess of HSnPh$_3$ in the appropriate arene as a solvent

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for 4 h led to the formation of two types of complexes, (η^6-arene)Cr(CO)$_2$H(SnPh$_3$) and (η^6-arene)Cr(CO)$_2$(SnPh$_3$)$_2$:

$$(\text{arene})\text{Cr(CO)}_3 + \text{HSnPh}_3 \xrightarrow{h\nu} \underset{\textbf{a}}{(\text{arene})\text{Cr(CO)}_2\text{H(SnPh}_3)} + \underset{\textbf{b}}{(\text{arene})\text{Cr(CO)}_2(\text{SnPh}_3)_2}$$

Previous work on similar reactions has shown that the first step in such reactions is the loss of CO upon photolysis of the (arene)Cr(CO)$_3$ followed by the addition of HSnPh$_3$.[10] The second step, to form the bis(stannyl) complex, is less well understood but most likely involves a second photolytic loss of CO, a second oxidative addition, H$_2$ loss, and CO scavenging.[3,11]

$$(\text{arene})\text{Cr(CO)}_2\text{H(SnPh}_3) \xrightarrow[-\text{CO}]{h\nu} \xrightarrow[\text{Ox addition}]{\text{HSnPh}_3} \xrightarrow{-\text{H}_2} \xrightarrow{+\text{CO}} (\text{arene})\text{Cr(CO)}_2(\text{SnPh}_3)_2$$

The following complexes have been prepared:

arene	hydrido stannyl complex	bis(stannyl) complex
mesitylene	**1a**	**1b**
toluene	**2a**	**2b**
benzene	**3a**	**3b**
fluorobenzene	**4a**	**4b**
difluorobenzene	**5a**	**5b**

Schubert and co-workers have reported the complex (η^6-mesitylene)Cr(CO)$_2$H(SnPh$_3$) from a similar reaction but in petroleum ether and at −10 °C. Under these conditions they obtained only the hydrido stannyl complex. They treated the hydrido stannyl complex with excess HSnPh$_3$ under thermal conditions in an attempt to obtain the bis(stannyl) complex but were unsuccessful.[4c] In mesitylene at room temperature we were able to synthesize both of these compounds simultaneously, and separate and purify them by column chromatography.

The major product is the hydrido stannyl complex in the case of mesitylene, while it is the bis(stannyl) complex in the cases of other arenes. It may be that steric effects control this ratio of hydrido stannyl/bis(stannyl); i.e., in the case of mesitylene, the hydrido stannyl complex is easier to form as compared to the more bulky bis(stannyl) complex due to steric hindrance by the two stannyl ligands and the methyl groups on the arene ring. In the case of fluorobenzene and difluorobenzene, electronic factors become more important and the more stable bis(stannyl) complexes are preferred.

Structure of (Arene)Cr(CO)$_2$H(SnPh$_3$) Complexes. The X-ray structure of (mesitylene)Cr(CO)$_2$H(SnPh$_3$) was obtained and compared with the one reported earlier by Schubert et al.[4c] From X-ray structural data, the Sn−H distance is 1.95 Å, which is only 0.24 Å longer than that in methyl-substituted stannanes[12] indicating a bonding interaction between both atoms. Additional evidence for Sn−H interaction can be obtained from the geometry of the complex which suggests a delocalized Cr, Sn, H bond. The Sn−Cr−H angle (45°) is too small to suggest that Sn and H atoms occupy two coordination sites around the Cr center. This means that H−SnPh$_3$ must be considered as one ligand such that the Sn−H bond occupies one coordination site. The angle between the two cis-CO ligands is 84.4°, which is smaller than that in the bis(stannyl) complex **1b** (104°) which contains two trans-CO ligands in a four-legged piano stool geometry. These considerations indicate that an η^2-bond type between the Cr and H−Sn is preferred.

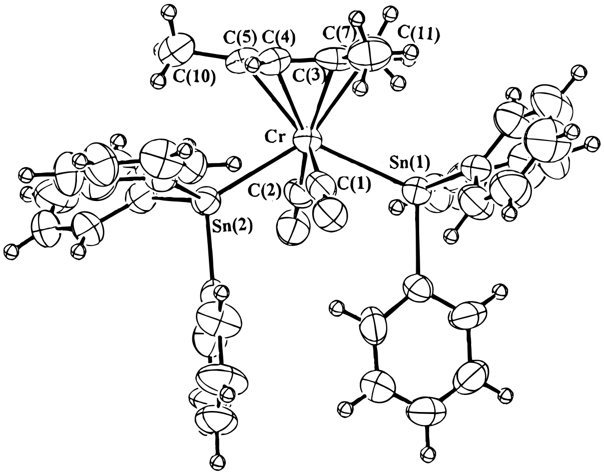

Figure 1. Diagram of the structure of (η^6-C$_6$H$_3$(CH$_3$)$_3$Cr(CO)$_2$(SnPh$_3$)$_2$.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for **1b**

Bond Distances			
Cr−Sn(1)	2.72(2)	Cr−Sn(2)	2.70(2)
Cr−C(1)	1.81(1)	Cr−C(2)	1.83(1)
Cr−C(3)	2.27(1)	Cr−C(4)	2.27(1)
Cr−C(5)	2.29(2)	Cr−C(6)	2.26(1)
Cr−C(7)	2.25(1)	Cr−C(8)	2.23(1)
Bond Angles			
C(1)−Cr−C(2)	103.5(5)	C(1)−Cr−Sn(1)	72.9(4)
C(1)−Cr−Sn(2)	73.7(4)	C(2)−Cr−Sn(1)	73.5(4)
C(2)−Cr−Sn(2)	73.1(4)	Sn(1)−Cr−Sn(2)	124.8(7)

Other evidence for a Sn−Cr−H three-center bond can be obtained from the ^{1}H NMR spectra of complexes **1a**−**5a**. For free HSnPh$_3$ $^1J(^{119}\text{Sn}-^1\text{H})$ and $^1J(^{117}\text{Sn}-^1\text{H})$ are 1936 and 1848 Hz, respectively, while they are in the range 321−338 and 306−322 Hz in our hydrido stannyl complexes. For *cis*-(CO)$_4$Os(H)SnCl$_3$, where there should be no interaction between the hydride and SnCl$_3$, $J(^{119}\text{Sn}-\text{Os}-\text{H})$ and $J(^{117}\text{Sn}-\text{Os}-\text{H})$ were found to be 136 and 129.5 Hz, respectively.[4a] The significantly higher values of J(Sn−Cr−H) in complexes **1a**−**5a** provide spectroscopic evidence for Sn−H interaction in these compounds.

Crystal Structure of (η^6-Mesitylene)Cr(CO)$_2$(SnPh$_3$)$_2$ (1b). An ORTEP drawing of the structure is shown in Figure 1. Selected bond distances and angles are given in Table 1. The ligands adopt a piano stool arrangement around the Cr center where the arene ring represents the seat and the two CO ligands and two stannyl ligands represent the legs. The two CO ligands are trans to each other with a C(1)−Cr−C(2) angle of of 103.5-

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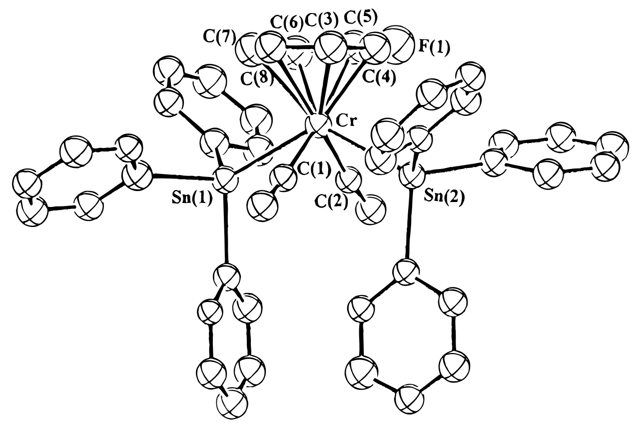

Figure 2. Diagram of the structure of (η^6-C_6H_5F)$Cr(CO)_2(SnPh_3)_2$ (molecule A).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **4b**

Bond Distances (A)			
Cr−Sn(1)	2.70(3)	Cr−Sn(2)	2.68(3)
Cr−C(1)	1.90(2)	Cr−C(2)	1.88(2)
Cr−C(3)	2.16(2)	Cr−C(4)	2.13(2)
Cr−C(5)	2.18(2)	Cr−C(6)	2.23(2)
Cr−C(7)	2.26(2)	Cr−C(8)	2.23(2)
C(5)−F	1.38(2)		
Bond Distances (B)			
Cr−Sn(1)	2.70(3)	Cr−Sn(2)	2.70(3)
Cr−C(1)	1.77(2)	Cr−C(2)	1.83(2)
Cr−C(3)	2.31(2)	Cr−C(4)	2.33(2)
Cr−C(5)	2.31(2)	Cr−C(6)	2.22(2)
Cr−C(7)	2.22(2)	Cr−C(8)	2.26(2)
C(5)−F	1.32(2)		
Bond Angles (A)			
C(1)−Cr−C(2)	100.1(6)	Sn(1)−Cr−Sn(2)	127.8(1)
Sn(1)−Cr−C(1)	72.5(5)	Sn(1)−Cr−C(2)	71.4(4)
Sn(2)−Cr−C(1)	75.8(5)	Sn(2)−Cr−C(2)	74.8(4)
C(3)−Cr−C(4)	38.5(7)	C(4)−Cr−C(5)	37.9(7)
C(5)−Cr−C(6)	35.8(7)	C(6)−Cr−C(7)	36.7(7)
C(7)−Cr−C(8)	37.6(7)	C(8)−Cr−C(3)	36.5(7)
Bond Angles (B)			
C(1)−Cr−C(2)	107.2(7)	Sn(1)−Cr−Sn(2)	129.2(1)
Sn(1)−Cr−C(1)	79.4(5)	Sn(1)−Cr−C(2)	76.2(5)
Sn(2)−Cr−C(1)	74.9(5)	Sn(2)−Cr−C(2)	70.8(5)
C(3)−Cr−C(4)	35.9(6)	C(4)−Cr−C(5)	35.8(6)
C(5)−Cr−C(6)	36.5(6)	C(6)−Cr−C(7)	36.9(7)
C(7)−Cr−C(8)	36.4(7)	C(8)−Cr−C(3)	35.8(7)

(5)°. The two stannyl ligands are also trans to each other with a Sn(1)−Cr−Sn(2) angle of 124.8(7)°. The Cr−Sn distances are 2.72 and 2.70 Å. The distance between the arene ring center and the Cr is 1.79 Å, which is 0.07 Å longer than that in the analogous hydrido stannyl complex **1a**. This longer distance is probably a result of larger steric hindrance from the two stannyl ligands and the methyl groups on the arene ring. C(10) almost eclipses Sn(2), and C(9) and C(11) are staggered with Sn(1) to avoid steric effects. The effect of the steric hindrance can be seen in the distances of the methyl groups from the arene plane, which are 0.13 and 0.11 Å for C(9) and C(11) and 0.26 Å for C(10) as a result of the eclipsed position.

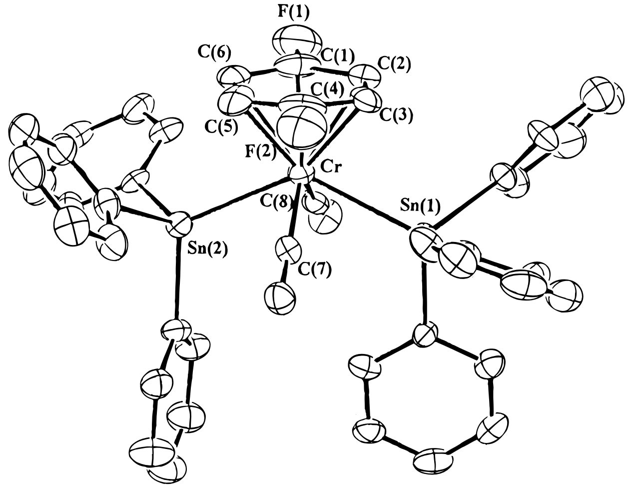

Figure 3. Diagram of the structure of (η^6-$C_6H_4F_2$)$Cr(CO)_2(SnPh_3)_2$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **5b**

Bond Distances			
Cr−Sn(1)	2.70(2)	Cr−Sn(2)	2.71(2)
Cr−C(1)	2.17(1)	Cr−C(2)	2.24(1)
Cr−C(3)	2.24(1)	Cr−C(4)	2.18(1)
Cr−C(5)	2.25(1)	Cr−C(6)	2.27(1)
Cr−C(7)	1.82(1)	Cr−C(8)	1.86(1)
C(1)−F(1)	1.38(2)	C(4)−F(2)	1.41(2)
Bond Angles			
Sn(1)−Cr−Sn(2)	128.09(8)	Sn(1)−Cr−C(7)	73.3(4)
Sn(1)−Cr−C(8)	75.8(4)	Sn(2)−Cr−C(7)	73.3(4)
Sn(2)−Cr−C(8)	75.5(4)	C(7)−Cr−C(8)	104.5(5)
Cr−Sn(1)−C(9)	116.2(4)	Cr−Sn(1)−C(15)	111.9(3)
Cr−Sn(1)−C(21)	113.9(3)	Cr−Sn(2)−C(33)	115.7(4)
Cr−Sn(2)−C(39)	106.8(4)	Cr−Sn(2)−C(27)	117.3(3)
C(1)−Cr−C(2)	37.5(6)	C(2)−Cr−C(3)	36.5(5)
C(3)−Cr−C(4)	36.2(6)	C(4)−Cr−C(5)	37.6(6)
C(5)−Cr−C(6)	35.9(5)	C(6)−Cr−C(1)	36.1(6)
C(6)−Cr−C(3)	80.9(6)		

Crystal Structure of (η^6-Fluorobenzene)$Cr(CO)_2)(SnPh_3)_2$ (4b). An ORTEP drawing of the structure is shown in Figure 2. Two independent molecules (A and B) have been found in an asymmetric unit. Table 2 shows selected bond angles and distances of the molecule. The two CO ligands as well as the two stannyl ligands are trans to each other with C(1)−Cr−C(2) and Sn(1)−Cr−Sn(2) angles of 100.1° (A), 107.2° (B) and 127.8° (A), 129.2° (B), respectively. Similar to the structure of **1b**, the ligands around the Cr center display a piano stool arrangement.

Crystal Structure of (η^6-Difluorobenzene)$Cr(CO)_2(SnPh_3)_2$ (5b). Figure 3 displays an ORTEP diagram of the molecule. Again the two CO ligands and the two stannyl ligands are in trans positions with C(7)−Cr−C(8) and Sn(1)−Cr−Sn(2) angles of 104.5° and 128.09°, respectively (Table 3). The Cr−Sn distances are similar to those in **1b** and **4b**, 2.7 Å. The two fluorine atoms eclipse the two CO ligands avoiding the steric effect from the two bulky $SnPh_3$ ligands. The arene ring undergoes boat distortion where C(1) and C(4) that carry the two fluorines are each bent up 0.05 Å.

^{1}H NMR Studies and Correlation with Arene−Chromium Interaction. In (arene)$Cr(CO)_3$ complexes, the more alkyl (electron-donating) substituents the arene ring has, the stronger is the arene−chromium interaction and the more stable is the complex. In the same sense, electronegative substituents on the arene ring decrease the arene−chromium interaction giving less stable complexes. In our hydrido stannyl and bis(stannyl) complexes there are two competing factors: steric and electronic effects. One of the best parameters to study and compare the degree of interaction between the arene and the chromium center is the ^{1}H NMR chemical shift of the arene protons. For free arenes, the ^{1}H chemical shifts are downfield to around 7 ppm. When an arene ring binds to a metal in an η^6-fashion it loses its aromaticity as it donates electrons to the metal center and its protons become less deshielded and their resonances shift upfield strongly to the region between 3 and 5 ppm. The

Table 4. ^1H NMR Data (δ) for Complexes **1**−**5** in C_6D_6 at Room Temperature (ppm) and Coupling Constants (Hz)

	arene, methyl	hydride	phenyl	$J(Sn-H)^a$
1a	4.37 (s, 3H), 1.54 (s, 9H)	−8.14 (s, 1H)	7.2−7.9 (m, 15H)	329.2
1b	4.82 (s, 3H), 1.48 (s, 9H)		7.2−7.9 (m, 30H)	
2a	4.3-4.5 (d, 2H; t, 2H; t, 1H), 1.48 (s, 3H)	−8.72 (s, 1H)	7.3−7.8 (m, 15H)	328.8
2b	4.1-5.1 (d, 2H; t, 2H; t, 1H), 1.036 (s, 3H)		7.2−7.9 (m, 30H)	
3a	4.41 (s, 6H)	−8.78 (s, 1H)	7.3−7.8 (m, 15H)	
3b	4.65 (s, 6H)		7.2−7.8 (m, 30H)	
4a	3.9-4.6 (m, 5H)	−8.52 (s, 1H)	7.2−7.8 (m, 15H)	338.0
4b	3.8-5.05 (m, 5H)		7.2−7.8 (m, 30H)	
5b	4.98 (m, 4H)		7.18−7.8 (m, 30H)	

[a] $^1J(^{119}Sn-^1H)$.

stronger the arene binds to the metal, the more deshielded its protons are and the more upfield their resonance is.

The amount of this shift can be used as a parameter to study and compare arene−chromium bond interaction in complexes **1**−**5**. We will compare the differences of chemical shifts between the free and the bonded arene protons. The smaller the difference supposedly the less the arene−chromium interaction. The chemical shifts for the arene protons of the complexes are given in Table 4, and the differences from the free arenes are given in Table 5. It is clear that for the same arene complexes, the arene proton chemical shifts go downfield (closer to the free arene region) as we go from the tricarbonyl to the hydrido stannyl to the bis(stannyl) complex. This indeed suggests that for the same arene the arene metal strength of interaction increases as follows: bis(stannyl) complexes < hydrido stannyl complexes < tricarbonyl complexes The chromium−arene distances obtained from the X-ray structural analysis support this trend. The chromium−arene distance is 1.79 Å for **1b** and 1.72 Å for **1a**.

In the same way, complexes with different arenes can be compared. As shown in Table 5, two different trends are observed for the methyl-substituted and the fluorine-substituted arene complexes. The difference in the chemical shifts of arene protons between the free arene and the bonded arene increases by going from mesitylene to the less methyl-substituted arene (toluene and benzene) complexes. In these complexes, steric effects seem to control the extent of interaction with the chromium center. The difference between the free and bonded arene proton chemical shifts increase as follows: mesitylene complexes < toluene complexes < benzene complexes (Table 5). In the fluorine-substituted arene complexes, electronic factors seem to become more important. More fluorine substituents lead to a more electron-demanding arene and a weaker chromium−arene interaction.

In conclusion, we have found that the (η^6-arene)$Cr(CO)_2H(SnPh_3)$ complexes, **1a**−**4a**, possess a three-center Cr−H−Sn bond, which is in contrast to similar (η^6-arene)$Cr(CO)(H)_2(SiCl_3)_2$ derivatives.[11] The (η^6-arene)$Cr(CO)_2(SnPh_3)_2$ compounds have stronger chromium−arene interaction when the arene is less sterically encumbered. Finally, we have noted that ^1H NMR chemical shift data correlate roughly with X-ray determined chromium−(arene center) distances.

Experimental Section

All reactions were carried out under Ar using standard Schlenk techniques.[13] Photochemical reactions were carried out in a quartz tube equipped with a water-cooled probe. A 450-W UV lamp was used for irradiation. Solid transfers were accomplished in a glovebox. Toluene, hexanes, pentane, benzene, and mesitylene were distilled from sodium and potassium/benzophenone. Fluorobenzene, CH_2Cl_2, and difluorobenzene were distilled from CaH_2 under argon. $HSnPh_3$ was purchased from Aldrich and used without further purification. (Arene)$Cr(CO)_3$ complexes were prepared by refluxing $Cr(CO)_6$ in the appropriate aromatic solvent for 3−4 days and then purified after solvent removal by washing with pentane or sublimation under vacuum at temperatures between 60 and 70 °C. Infrared spectra were obtained using a Perkin-Elmer 1330 instrument. The ^1H NMR spectra were recorded on a Varian XL-400 operating at 400 MHz. ^1H chemical shifts are reported relative to tetramethylsilane. ^1H NMR data for complexes **1**−**4** are given in Table 4. Elemental analyses were obtained from Galbraith Laboratories.

Synthesis of the Mesitylene Complexes 1a and 1b. A yellow solution of 0.20 g (0.78 mmol) of (mesitylene)$Cr(CO)_3$ and 1.00 mL (3.92 mmol) of $HSnPh_3$ in 35 mL of mesitylene was magnetically stirred under UV irradiation at room temperature for 4 h. Removing the solvent from the resulting red solution gave about 1/2 mL of an oily red-brown mixture which was dissolved in 5 mL of toluene and treated on a silica gel chromatography column using hexanes/toluene as an eluting solvent. Solutions of hydrido stannyl and bis(stannyl) complexes were collected separately, the hydrido stannyl complex eluting first. After removing the solvents in vacuo, each product was dissolved in about 10 mL of CH_2Cl_2, layered with about 120 mL of pentane, and stored in the freezer for recrystallization. Needle yellow crystals of both complexes were obtained within 5 days (about 30% yield of **1a** and about 10% yield of **1b**). IR of **1a** (cm^{-1}, nujol mull): ν_{Cr-H} 1945, ν_{CO} 1900, 1840. Anal. Calcd for $CrSnO_2C_{29}H_{28}$ (**1a**): C, 60.13; H, 4.87. Found: C, 59.78; H, 4.88. IR of **1b** (cm^{-1}, nujol mull): ν_{CO} 1880, 1832. Anal. Calcd for $CrSn_2O_2C_{47}H_{42}$ (**1b**): C, 60.8; H, 4.56; Cr, 5.60. Found: C, 58.7; H, 4.52; Cr, 5.59.

Synthesis of Toluene Complexes 2a and 2b. A solution of 0.20 g (0.88 mmol) of (toluene)$Cr(CO)_3$ and 1.00 mL (3.92 mmol) of $HSnPh_3$ in 45 mL of toluene was stirred under UV light at room temperature for 4 h. After work-up, purification on the column and recrystallization from CH_2Cl_2/pentane, yellow needle crystals of **2a** and **2b** were obtained respectively in about 20% and 15% yield. IR of **2a** (cm^{-1}, nujol mull): ν_{Cr-H} 1918, ν_{CO} 1870, 1830. IR of **2b** (cm^{-1}, nujol mull): ν_{CO} 1883, 1825.

Synthesis of Benzene Complexes 3a and 3b. Both 0.20 g (0.93 mmol) of (benzene)$Cr(CO)_3$ and 1.00 mL (3.92 mmol) of $HSnPh_3$ were dissolved in 40 mL of benzene. The solution was irradiated with UV light and stirred at room temperature for 4 h. After filtration, solvent removal and purification by column chromatography and recrystallization from CH_2Cl_2/pentane as previously described, yellow crystals of **3a** and **3b** were obtained in about 10% and 20% yield, respectively. IR of **3a** (cm^{-1}, nujol mull): ν_{Cr-H} 1942, ν_{CO} 1895, 1858. IR of **3b** (cm^{-1}, nujol mull): ν_{CO} 1895, 1842. Anal. Calcd for $CrSn_2O_2C_{44}H_{36}$ (**3b**): C, 59.64; H, 4.09. Found: C, 58.26; H, 3.94.

Synthesis of Fluorobenzene Complexes 4a and 4b. A solution of 0.20 g (0.86 mmol) of (fluorobenzene)$Cr(CO)_3$ and 1.00 mL of $HSnPh_3$ in 45 mL of fluorobenzene was stirred under UV irradiation at room temperature for 4.5 h. The same previous work-up and purification methods led to mainly the bis(stannyl) complex **4b** (about 15% yield) and a small amount of the hydrido stannyl complex **4a** (about 3% yield). IR of **4a** (cm^{-1}, nujol mull): ν_{Cr-H} 1950 and ν_{CO} 1889, 1839. IR of **4b** (cm^{-1}, nujol mull): ν_{CO} 1890 and 1838. Anal. Calcd for $CrSn_2FO_2C_{44}H_{35}$ (**4b**): C, 58.45; H, 3.90. Found: C, 59.15; H, 3.85.

Synthesis of Difluorobenzene Complexes 5a and 5b. Both 0.20 g (0.80 mmol) of (difluorobenzene)$Cr(CO)_3$ and 1.00 mL of $HSnPh_3$ were dissolved in 50 mL of difluorobenzene. The solution was stirred and irradiated with UV light at room temperature for 4.5 h. Following the same previous work-up and purification techniques, the bis(stannyl) complex **5b** was mainly obtained (10−15% yield) and only small traces of the hydrido stannyl complex were obtained for which purification and recrystallization attempts failed. Anal. Calcd for $CrSn_2F_2O_2C_{44}H_{34}$ (**5b**): C, 57.3; H, 3.72. Found: C, 58.7; H, 4.32.

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(13) (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 5. Arene Proton Chemical Shifts (ppm) (Differences between Free Arene and Complexed Arene Proton Chemical Shifts in Parentheses)

	mesitylene	toluene	benzene	fluorobenzene	difluorobenzene
free arene	6.72	7.0−7.1	7.16	6.8−6.9	6.5
Cr−TC[a]	4.08 (2.65)	4.2−4.5 (2.68)	4.27 (2.89)	3.6−4.3 (2.89)	4.27 (2.23)
Cr−hyd[b]	4.37 (2.36)	4.3−4.6 (2.58)	4.41 (2.75)	3.9−4.6 (2.58)	
Cr−bis(stn)[c]	4.82 (1.90)	4.1−5.1 (2.48)	4.65 (2.50)	3.8−5.1 (2.33)	4.98 (1.52)

[a] (arene)$Cr(CO)_3$. [b] (arene)$Cr(CO)_2H(SnPh_3)$. [c] (arene)$Cr(CO_2)(SnPh_3)_2$.

Table 6. Crystallographic Data for Complexes **1b**, **4b**, and **5b**

	1b	**4b**	**5b**
formula	$CrSn_2O_2C_{47}H_{42}$	$CrSn_2FO_2C_{44}H_{35}$	$CrSn_2F_2O_2C_{44}H_{34}$
formula weight	928.22	904.14	922.13
crystal system	monoclinic	orthorhombic	monoclinic
a (Å)	13.905(4)	16.717(2)	13.756(2)
b (Å)	18.499(2)	18.453(2)	18.560(2)
c (Å)	17.708(2)	25.766(2)	17.159(2)
b (deg)	109.84(1)	93.69(1)	
V (Å^3)	4285(1)	7948(2)	4372(2)
space group	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)
Z	4	8	4
D_{calc} (g/cm^3)	1.467	1.663	1.510
μ(Cu Kα) (cm^{-1})	117.92	140.28	116.60
λ (Å)	1.54178	1.54178	1.54178
take-off-angle (deg)	6.0	6.0	6.0
scan rate (deg/min)	16.0	8.0	16.0
trans. factor *s*	0.83−1.29	0.89−1.02	0.79−1.06
no. of observations	4845	4626	3801
no. of variables	481	474	514
R; R_w[a]	0.082; 0.091	0.049; 0.073	0.064; 0.060

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

X-ray Structural Analysis. Yellow crystals of complexes **1a**−**4a** and **1b**−**5b** were obtained by slow recrystallization from CH_2Cl_2/pentane at low temperature. All measurements were carried out on a Rigaku AFC5R diffractometer with graphite-monochromated Cu Kα radiation and a 12-kW rotating anode generator. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. An empirical absorption correction using the program DIFABS was applied. The data were corrected for Lorentz and polarization effects. Crystal data for **1b**, **4b**, and **5b** are given in Table 6.

X-ray Structural Analysis of (η^6-$C_6H_3(CH_3)_3$)$Cr(CO)_2(SnPh_3)_2$ (1b). A yellow needle crystal having approximate dimensions of 0.20 × 0.10 × 0.30 mm was mounted in a glass capillary. Cell constants and an orientation matrix for data collection were obtained from 25 carefully centered reflections in the range $50.50 < 2\theta < 61.49°$. On the basis of the systematic absences and the successful solution and refinement of the structure the space group was determined to be $P2_1/c$ (No. 14). The data were collected at a temperature of 23 °C using the $\omega-2\theta$ scan technique: 6122 reflections were collected, 5844 of them were unique ($R_{int} = 0.045$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection. The structure was solved by combination of the Patterson method and direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement produced $R = 0.082$ and $R_w = 0.091$.

X-ray Structural Analysis of (η^6-C_6H_5F)$Cr(CO)_2(SnPh_3)_2$ (4b). A yellow plate crystal of approximate dimensions of 0.50 × 0.30 × 0.10 mm was mounted on a glass fiber. A total of 25 carefully centered reflections in the range $64.59° < 2\theta < 69.10°$ was used to obtain cell constants and an orientation matrix for data collection. The space group was determined to be $Pca2_1$ (No. 29). The data were collected at −160 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 112.3°. A total of 5895 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection. The structure was solved by direct methods. The final cycle of full-matrix least-squares refinement gave residuals of $R = 0.049$ and $R_w = 0.073$.

X-ray Structural Analysis of (η^6-$C_6H_4F_2$)$Cr(CO)_2(SnPh_3)_2$ (5b). A yellow plate crystal having approximate dimensions of 0.50 × 0.30 × 0.03 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $63.86° < 2\theta < 68.68°$. The space group was determined to be $P2_1/c$ (No. 14). The data were collected at 23 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 112.7°. Of the 6253 reflections which were collected, 5962 were unique ($R_{int} = 0.03$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection. The structure was solved by direct methods. Anisotropic refinement on non-hydrogen atoms gave $R = 0.064$ and $R_w = 0.060$.

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Supporting Information Available: Tables of thermal parameters, least-squares-planes, and complete tables of bond distances and angles for complexes **1b, 4b,** and **5b** (38 pages). Ordering information is given on any current masthead page.

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