



Photochemical synthesis of new (η^6 -arene)Cr–hydrido stannyl and (η^6 -arene)Cr–bis-stannyl complexes. Ligand effects on the Sn–H interaction in the hydrido stannyl compounds

Abbas Khaleel^{a,b}, Kenneth J. Klabunde^{b,*}, Alison Johnson^{a,b}

^a Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA

^b Department of Chemistry, St. Cloud State University, St. Cloud, MN 56304, USA

Received 8 December 1997; received in revised form 6 August 1998

Abstract

Hydrido stannyl compounds containing the η^2 -H–SnPh₃ ligand and bis-stannyl compounds containing two SnPh₃ ligands have been obtained from the photolysis of (η^6 -arene)Cr(CO)₃ and HSnPh₃. New complexes with different arenes (mesitylene, trifluorotoluene and 1,4-dimethoxybenzene) have been obtained and characterized by X-ray diffraction: (η^6 -C₆H₄(OCH₃)₂)Cr(CO)₂(HSnPh₃) (**3a**), (η^6 -C₆H₄(OCH₃)₂)Cr(CO)₂(SnPh₃)₂ (**3b**). Structural data for **3a**: monoclinic; space group *P*2₁/*c* (No. 14); *a* = 17.445(3), *b* = 9.820(3) and *c* = 16.302(5) Å; *Z* = 4; *V* = 2539.2(12) Å³; **3b**: monoclinic; space group *P*2₁/*n* (No. 14); *a* = 13.904(3), *b* = 20.567(5) and *c* = 13.911(3) Å; *Z* = 4; *V* = 3994(2) Å³. ¹H-NMR as well as X-ray provided evidence for the existence of three-center two-electron bonds in the hydrido stannyl complexes. The effects of different ligands on bonding and spectroscopic parameters were studied. Arene exchange reactions of the bis-stannyl complexes, as well as reactions of some of these compounds with P(C₂H₅)₃ and CO, were also investigated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Arene complexes; Hydrido stannyl compounds; Ligand displacement

1. Introduction

In an earlier study, the authors reported the synthesis of a series of (η^6 -arene)Cr–hydrido stannyl and (η^6 -arene)Cr–bis-stannyl complexes [1]. The addition of H–M'R₃ (M' = main group metal) to a transition metal center (M) led to M–hydride compounds, with M–H and M–M' bonds as a result of the total oxidative addition of the H–M' bond, or to compounds containing an η^2 M'⋯H⋯M' bonding mode. The formation of three-center two-electron bonds between a transition metal, H and Si has been well-established by chemical and spectroscopic evidence after Graham et al. isolated and characterized a number of complexes of the general formula Cp(CO)₂Mn(H)SiR₃, in the early 1970s [2]. 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)₂Mn(H)SnPh₃ [3].

Herein, this paper reports on the synthesis of additional stannyl complexes, namely (η^6 -arene)Cr(CO)₂(HSnR₃) and (η^6 -arene)Cr(CO)₂(SnR₃)₂, and X-ray structural data for two of these. The authors also discuss the effect of ligands at the Cr and Sn centers on the degree of interaction between the H and Sn atoms in the hydrido stannyl compounds; in other words, the effect of these ligands on the nature of the addition of the H–Sn bonds to the Cr center.

One of the driving forces for this research has been the preparation of materials with high chemical reactivities, especially η^6 -arene lability. The lability of the arene ring facilitates its displacement by other ligands, which could be an initiative step in some catalytic

* Corresponding author. Tel.: +1-785-532-6665; Fax: +1-785-532-6666.

reactions. This phenomenon was the key factor in the high catalytic potential of $(\pi\text{-arene})\text{Ni}$ complexes, of the general formula $(\eta^6\text{-arene})\text{NiR}_2$ ($\text{R} = \text{SiCl}_3$, SiF_3 , C_6F_5), in 1-butene isomerization and ethylene and propylene dimerization as reported by Klabunde et al. [4].

The displacement of $\pi\text{-arene}$ ligands has attracted special attention. The displacement of chromium bound $\pi\text{-arene}$ ligands by other arenes has been investigated at 170°C for $(\pi\text{-arene})\text{Cr}(\text{CO})_3$ complexes by Mahaffy and Pauson [5]. They found that the resistance to arene exchange of (arene)tricarbonyl complexes of chromium decreases in the order: hexamethylbenzene > mesitylene > *N,N*-dimethylaniline $\geq$ xylene > toluene = benzene > chlorobenzene $\gg$ naphthalene. It is clear that electronic factors govern the reactivity of these complexes such that the more electron-rich arenes give more unreactive compounds, and thermal stability shows similar trends.

Arene exchange processes have also been investigated at temperatures between 110 and 170°C for $(\pi\text{-arene})\text{Cr}(\text{CO})_2(\text{SiCl}_3)_2$ complexes [6], analogous to the present bis-stannyl compounds. Mesitylene displaced fluorobenzene and difluorobenzene and again, electronic effects of the arene seemed to play a dominant role in the reactivity of these compounds (the more electron-rich the arenes were, the more difficult to exchange).

The authors have attempted to study arene exchange reactions of bis-stannyl complexes with different arenes at temperatures between 110 and 170°C . They found that these complexes behave differently as compared with the analogous tricarbonyl or bis-silyl complexes discussed above. Besides the electronic effects from the arene ligand, steric effects from the large stannyl ligands have been found to play an important role in the stability and reactivity of these compounds. The authors have also studied the reactions of some of the compounds with triethylphosphine and CO.

2. Experimental section

2.1. General procedures

All reactions were carried out under Ar using standard Schlenk techniques [7]. Photochemical reactions were carried out in a quartz tube equipped with a water-cooled probe. A UV mercury lamp (450 W) was used for irradiation. Solid transfers were accomplished in a glove box. Toluene, hexanes, mesitylene, fluorobenzene, pyridine and pentane were distilled from Na- and K-benzophenone. Butyl ether was distilled from CaH_2 under argon. HSnPh_3 , decalin, $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{HSn}(\text{n-Bu})_3$, 1,4-dimethoxybenzene and deuterated solvents were purchased from Aldrich and used without further purification. Hexaphenyldistanane, Sn_2Ph_6 , was purchased from Gelest. Silica gel (230–400 mesh) was purchased from Fisher. Arene- $\text{Cr}(\text{CO})_3$ complexes were prepared according to literature [1] and in the case of (1,4-dimethoxybenzene) $\text{Cr}(\text{CO})_3$, butyl ether was used as the solvent. IR spectra were obtained using a Perkin–Elmer 1330 instrument. $\nu_{\text{Cr-H}}$ was distinguished from ν_{CO} based on literature [1]. The ^1H -NMR spectra were recorded on a Varian XL-400 operating at 400 MHz. ^1H chemical shifts are reported relative to tetramethylsilane. Elemental analyses were obtained from Galbraith Laboratories.

2.2. Synthesis of $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{HSn}(\text{n-Bu})_3)$, **1a**, and $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{Sn}(\text{n-Bu})_3)_2$, **1b**

$(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_3$ (0.2 g) was dissolved in 45 ml of hexanes and 2.0 ml of $\text{HSn}(\text{n-Bu})_3$ were added. The yellow solution was stirred and irradiated with UV light at r.t. for 4 h, giving a dark red solution. The solvent was removed under vacuum giving a yellow–orange oily residue, which was dissolved in 5 ml of toluene and treated on a silica gel chromatography column using hexanes/toluene as an eluting solvent.

Table 1
 ^1H -NMR data (δ , ppm) in C_6D_6 for **1a**, **1b**, **2**, **3a** and **3b**

Compound ^a	Arene/methyls	R: butyls or phenyls	Hydride
1a	4.3 (s, 3H)/1.80 (s, 9H)	1.00–1.54 (m, 27H)	–9.86 (s, 1H)
1b	4.55 (s, 3H)/1.82 (s, 9H)	1.07–1.92 (m, 54 H)	–
2	3.84 (t, 1H), 5.34 (d, 2H), 5.05 (t, 2H)	7.19–7.81 (m, 30H)	–
3a	4.64 (s, 4H)/2.81 (s, 6H)	7.20–7.90 (m, 15H)	–8.22 (s, 1H)
3b	5.11 (s, 4H)/2.64 (s, 6H)	7.20–7.94 (m, 30H)	–

^a **1a** is $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{HSn}(\text{n-But})_3)$; **1b** is $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{Sn}(\text{n-Bu})_3)_2$; **2** is $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_2(\text{Sn}(\text{n-Bu})_3)_2$; **3a** is $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSn}(\text{Ph})_3)$; **3b** is $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{Sn}(\text{Ph})_3)_2$.

Solutions of unreacted starting material, hydrido stannyl compound (**1a**) and bis-stannyl compound (**1b**) were collected separately, the bis-stannyl compound eluting first followed by the hydrido stannyl compound. Removing the solvents under vacuum gave yellow–orange crystalline solids of the products, with about 25 and 10% yield of **1a** and **1b**, respectively. $^1\text{H-NMR}$ data are given in Table 1. IR data of **1a** (cm^{-1} , nujol mull): ν_{CO} 1860, 1900; $\nu_{\text{Cr-H}}$ 1919. IR data of **1b** (cm^{-1} , nujol mull): ν_{CO} 1832, 1880. Anal. Calc. for $\text{CrSn}_2\text{O}_2\text{C}_{35}\text{H}_{66}$ (**1b**): Cr, 6.43; C, 51.80; H, 8.23. Found: Cr, 6.59; C, 49.70; H, 7.72.

2.3. Synthesis of $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **2**

$(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_3$ (0.3 g) was dissolved in 40 ml of hexanes and 1.0 ml of HSnPh_3 was added. The resulting yellow solution was stirred under UV light at r.t. for 3 h giving a red solution. The solvent was removed under vacuum giving a dark red oily residue. Separation on the silica gel column led to the isolation of two compounds: hexaphenyldistannane (Sn_2Ph_6), which formed white crystals upon recrystallization from toluene/pentane, and the chromium bis-stannyl complex, $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **2**, in ca. 10% yield. No hydrido stannyl compound was formed. $^1\text{H-NMR}$ data of **2** are listed in Table 1. IR data of **2** (cm^{-1} , nujol mull): ν_{CO} 1848, 1903. Anal. Calc. for $\text{CrSn}_2\text{F}_3\text{O}_2\text{C}_{45}\text{H}_{35}$ (**2**): C, 56.69; H, 3.70. Found: C, 57.81; H, 4.30.

2.4. Synthesis of $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**, and $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**

$(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_3$ (0.45 g) was dissolved in 45 ml of hexanes and 5 ml of toluene. HSnPh_3 (1.4 ml) was added and the yellow solution was stirred and irradiated for 6 h at r.t. giving an orange solution. Removing the solvents under vacuum gave an orange oily residue. The product was dissolved in 15 ml toluene and treated on the silica gel column using hexanes/toluene as the eluting solvent. Solutions of hydridostannyl, **3a**, and bis-stannyl, **3b**, compounds were collected separately, the bis-stannyl eluting first. Removing the solvent under vacuum and recrystallization from toluene/pentane gave yellow needle crystals of **3a** (30% yield) and yellow–orange crystals of **3b** (10% yield). $^1\text{H-NMR}$ data of both compounds are presented in Table 1. IR data of **3a** (cm^{-1} , nujol mull): ν_{CO} 1830, 1912; $\nu_{\text{Cr-H}}$ 1940. Anal. Calc. for $\text{CrSnO}_4\text{C}_{25}\text{H}_{28}$ (**3a**): C, 56.31; H, 4.39. Found: C, 55.89; H, 4.25. IR data of **3b** (cm^{-1} , nujol mull): ν_{CO} 1840, 1890. Anal. Calc. for $\text{CrSn}_2\text{O}_4\text{C}_{46}$ (**3b**): C, 58.52; H, 4.27. Found: C, 58.48; H, 4.24.

Table 2

Crystal data for $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**, and $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**

Compound	3a	3b
Empirical formula	$\text{SnCrC}_{28}\text{O}_4\text{H}_{26}$	$\text{Sn}_2\text{CrC}_{46}\text{O}_4\text{H}_{40}$
Formula weight	597.19	946.19
Temperature (K)	293	293
Wavelength ($\text{\AA}$)	0.70930	0.70930
Symmetry	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
<i>a</i> ($\text{\AA}$)	17.445(3)	13.904(3)
<i>b</i> ($\text{\AA}$)	9.820(3)	20.567(5)
<i>c</i> ($\text{\AA}$)	16.302(5)	13.911(3)
α ($^\circ$)	90.0	90.0
β ($^\circ$)	114.60(2)	91.65(2)
γ ($^\circ$)	90.0	90.0
<i>V</i> ($\text{\AA}^3$)	2539.2(12)	3994(2)
<i>Z</i>	4	4
<i>D</i> _{calc.} (g cm^{-3})	1.562	1.574
Standards number	2	3
Reflections	4215	5447
Reflections θ min/max	0.00/22.43	0.00/22.43
Refinement	<i>F</i>	<i>F</i>
Refinement method	Full-matrix	Full-matrix
Weighting scheme	$1/2\sigma(F)$	$1/2\sigma(F)$
Number reflections	1856	3810
Number parameters	182	226
<i>R</i> factor ^a	0.057	0.036
<i>R</i> _w factor ^b	0.050	0.030
Goodness-of-fit	2.52	2.09
Difference density min/max	−1.18/1.93	−1.19/1.11

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

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

2.5. X-ray structural analysis

Crystals of **3a** and **3b** were obtained by slow recrystallization from toluene/pentane at low temperature. Analysis was carried out on an Enraf–Nonius diffractometer with graphite monochromated Mo–K $_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz and polarization effects and for decay (see Table 2). An empirical absorption correction based on ψ scan data was performed on both data sets; however, application of the absorption correction to **3a** obscured the location of the bridging hydrogen atom between the tin and chromium atoms. Thus, the absorption correction was not used in the solution and refinement of **3a**.

2.6. X-ray structural analysis of $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**

A yellow plate-like crystal having approximate dimensions of $0.50 \times 0.40 \times 0.10 \text{ mm}^3$ was glued with epoxy inside an argon-filled capillary tube and was optically aligned on the diffractometer. A monoclinic cell was obtained from a least-squares fit of 20 centered reflections. The Laue symmetry was confirmed

by comparison of the intensities of symmetry equivalent reflections. The measured intensities of two independent octants of the reciprocal lattice were collected via 2θ scans over $4.0^\circ \leq 2\theta \leq 45^\circ$. Of the 3317 data collected, 1856 with $I > 2.5\sigma$ were utilized in the structural refinement. The probable space group $P2_1/c$ (No. 14) was later corroborated by successful structural refinement.

Direct methods were employed to locate the tin and chromium atoms. Successive Fourier syntheses coupled with least-squares refinement yielded the positions of all remaining non-hydrogen atoms. Since a $^1\text{H-NMR}$ spectrum of this compound suggested the presence of a metal-bonded hydrogen atom, the difference map was carefully scrutinized. It yielded the position of a probable hydrogen atom bridging the tin and chromium atoms in a chemically reasonable environment. Idealized coordinates for the hydrogen atoms on the phenyl groups and the methoxy groups were calculated with site occupations tied to the associated carbon atoms. Isotropic refinement of all non-hydrogen atoms was followed by anisotropic refinement of all non-hydrogen atoms. Due to its proximity to the large tin atom, the coordinates of the bridging hydrogen were not refined; however, the isotropic thermal parameter was refined ($U = 0.05(4)$). After several cycles of anisotropic refinement, each phenyl ring in the triphenyl tin ligand was constrained as a rigid group (idealized to the well-known D_{6h} geometry of the benzene ring). The phenyl group orientation angles anisotropic thermal parameters were refined when least-squares refinement was resumed. Refinement converged with $R = 0.057$, $R_w = 0.050$. A final difference map revealed no unusual features.

2.7. X-ray structural analysis of $(\eta^6\text{-}1,4\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**

An orange plate crystal having approximate dimensions of $0.20 \times 0.30 \times 0.40 \text{ mm}^3$ was glued with epoxy inside an argon-filled capillary tube and was optically aligned on the diffractometer. A monoclinic cell was obtained from a least-squares fit of 24 centered reflections. The Laue symmetry was confirmed by comparison of the intensities of symmetry equivalent reflections. The measured intensities of two independent octants of the reciprocal lattice were collected via 2θ scans over $4.0^\circ \leq 2\theta \leq 45^\circ$. Of the 5192 data collected, 3810 with $I > 2.5\sigma$ were utilized in the structural refinement. The probable space group $P2_1/n$ (No. 14) was later corroborated by the successful structural refinement.

Direct methods were employed to locate the tin and chromium atoms. Successive Fourier syntheses coupled with least-squares refinement yielded the positions of all remaining non-hydrogen atoms. Idealized coordinates for the hydrogen atoms on the phenyl and methoxy groups were calculated with site occupations tied to the

associated carbon atoms. Isotropic refinement of all non-hydrogen atoms was followed by anisotropic refinement of all non-hydrogen atoms. After several cycles of anisotropic refinement, each phenyl ring in the triphenyl tin ligand was constrained as a rigid group (idealized to the well-known D_{6h} geometry of the benzene ring). The phenyl group orientation angles anisotropic thermal parameters were refined when least-squares refinement was resumed. Refinement converged with $R = 0.036$, $R_w = 0.030$. A final difference map revealed no unusual features.

2.8. Reactions with CO

Reactions of $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **4a** [1], and $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **4b** [1], with carbon monoxide (CO) were investigated at r.t., 60°C and 150°C . At r.t. and 60°C , the reactions were carried out by dissolving 0.05 g of **4a** or **4b** (8.6×10^{-5} mol **4a** or 5.3×10^{-5} mol **4b**) in 20 ml toluene in a Schlenk tube under argon. CO gas was allowed to bubble through the solution at the desired temperature for 12 h. The solvent was then removed under vacuum and the yellow precipitate obtained was studied by $^1\text{H-NMR}$ and IR. The reaction at 150°C was carried out in an NMR tube by dissolving 0.015 g (1.6×10^{-5} mol) of **4b** in 1.0 ml of deuterated bromobenzene. CO gas was allowed to bubble through the solution at 150°C (in a mineral oil bath) for 6 h, during which the yellow solution turned colorless due to the complete conversion of the starting material to $\text{Cr}(\text{CO})_6$ and free mesitylene.

2.9. Reaction of Sn_2Ph_6 with $\text{Cr}(\text{CO})_6$

Sn_2Ph_6 (1.35g; 1.9×10^{-3} mol) and 0.45 g (2.0×10^{-3} mol) of $\text{Cr}(\text{CO})_6$ were dissolved in 60 ml benzene under argon. The colorless solution was irradiated with UV light and stirred at r.t. for 3 h giving a dark red solution. A brown–yellow solid was obtained upon removing the solvent under vacuum. A $^1\text{H-NMR}$ spectrum of the products showed a mixture of π -arene- and stannyl-containing products that were not investigated further. The desired bis-stannyl compound $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$ was not observed.

2.10. Reaction of Sn_2Ph_6 with $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$

A solution of 0.15 g (7.0×10^{-4} mol) of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and 0.45 g (6.4×10^{-4} mol) of Sn_2Ph_6 in 25 ml benzene and 40 ml hexanes was stirred and irradiated with UV light for 3 h at r.t. The starting yellow solution turned dark red and removing the solvents under vacuum resulted in a brown–yellow solid containing the bis-stannyl compound $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$ in ca. 25% yield.

2.11. Reaction of $(\eta^6\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**, with triethylphosphine

Compound **3a** (0.04 g; 6.7×10^{-5} mol) was dissolved in 5 ml $\text{P}(\text{C}_2\text{H}_5)_3$ in a Schlenk tube under argon. The yellow solution obtained was stirred at r.t. for 12 h. Removing the excess phosphine under vacuum led to an oily brown–yellow residue, which was then dissolved in 10 ml hexanes. Upon slow evaporation of the hexanes, a green–yellow precipitate and yellow–orange crystals of $(\eta^6\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2\text{P}(\text{C}_2\text{H}_5)_3$ (**5**) were obtained. IR data (cm^{-1} , nujol mull): ν_{CO} 1824(s) and 1884(vs). $^1\text{H-NMR}$ (δ , ppm, in C_6D_6): 0.96 (d of t, 9H), 1.43 (d of q, 6H), 3.23 (s, 6H, OCH_3), 4.41 (d, 4H, arene).

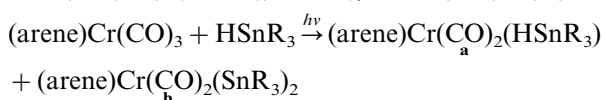
2.12. Arene exchange reactions

The following general procedure was used in all reactions of bis-stannyl compounds with free arenes. The bis-stannyl compound (0.05 g of each) was dissolved under argon in 10 ml decalin in a 50-ml 3-neck round-bottom flask equipped with a condenser and an argon inlet. A twentyfold excess of free arene was added and the solution was stirred in an oil bath at the desired temperature. At different reaction times, the flask was cooled to r.t. and 0.1 ml of the solution was withdrawn by a syringe for IR analysis. In some reactions, the solvent was finally removed under vacuum and a $^1\text{H-NMR}$ spectrum was recorded for the solid residue in C_6D_6 .

3. Results and discussion

3.1. Synthesis of complexes

The photochemical reaction of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes with an excess of HSnR_3 ($\text{R} = n\text{-butyl}$ or phenyl) in the appropriate solvent usually led to the formation of both types of complexes, $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{HSnR}_3)$ and $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{SnR}_3)_2$:



However, in the reaction of $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_3$ with HSnPh_3 , no hydrido stannyl compound was isolated. Besides the bis-stannyl compound, $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$ (**2**), hexaphenyldistannane (Sn_2Ph_6) formed and was isolated. One might expect that Sn_2Ph_6 could be generated from two SnPh_3 fragments (they may be radicals) as a result of photochemical cleavage of the H–Sn bond of free HSnPh_3 . However, the fact that the photolytic cleavage of the H–Sn bond in free HSnPh_3 has not been observed in other cases where HSnPh_3 existed in excess, and it has not been observed before except by hydrogen abstraction with

radical initiators [8], suggests that the $\text{Ph}_3\text{Sn-SnPh}_3$ forms via reductive elimination of the two SnPh_3 ligands from the final bis-stannyl compound, $(\eta^6\text{-C}_6\text{H}_5\text{CF}_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$ (**2**).

3.2. Crystal structure of $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**

An ORTEP drawing of the structure is shown in Fig. 1. Selected bond distances and angles are given in Table 3. The ligands adopt a piano stool arrangement around the Cr center, where the arene ring represents the seat and the two CO ligands and the hydrido stannyl ligand represent the legs. X-ray structural analysis as well as $^1\text{H-NMR}$ data indicate that the triphenyltinhydride ligand binds in an η^2 fashion to the chromium center. The Sn–Cr–H angle (56°) is too small to suggest that the Sn and H atoms occupy two coordination sites around the Cr center; rather, the H–SnPh₃ must be considered as one ligand such that the Sn–H bond occupies one coordination site, with the H forming a delocalized, three-center two-electron bond with the Sn and Cr. Although the position of the H atom could not be refined owing to its close proximity to the large Sn electron cloud, its calculated distance of 2.23 Å from the Sn atom suggests some bonding interaction between both atoms. Compared with the analogous mesitylene complex, $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$ (**4a**), the Sn–H interaction in this complex is weaker; in other words, the oxidative addition is more complete. This difference is indicated by the calculated larger Sn–Cr–H angle, 56° , and the longer Sn–H distance, 2.23 Å, as compared with 45° and 1.95 Å in the analogous

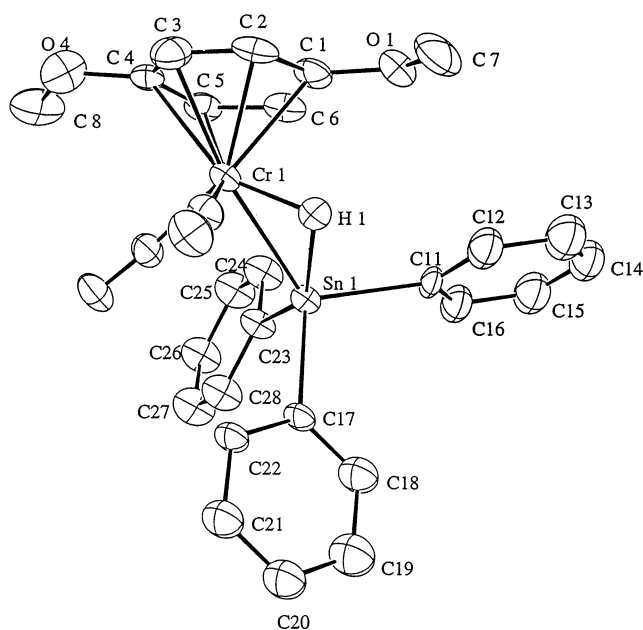


Fig. 1. ORTEP drawing of $(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **3a**.

Table 3

Bond lengths (Å) and angles (°) in $(\eta^6\text{-}1,4\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)_2$, **3a**

Bond lengths (Å)			
Sn1–Cr1	2.688(3)	O1–C1	1.37(2)
Sn1–C1	12.173(9)	O1–C7	1.46(2)
Sn1–C1	72.18(1)	O4–C4	1.39(2)
Sn1–C2	32.17(1)	O4–C8	1.35(2)
Cr1–C1	2.24(2)	O9–C9	1.14(2)
Cr1–C2	2.19(1)	O10–C10	1.15(2)
Cr1–C3	2.19(2)	C1–C2	1.44(3)
Cr1–C4	2.26(2)	C1–C6	1.40(3)
Cr1–C5	2.22(1)	C2–C3	1.35(3)
Cr1–C6	2.20(1)	C3–C4	1.40(3)
Cr1–C9	1.82(2)	C4–C5	1.40(3)
Cr1–C10	1.83(2)	C5–C6	1.41(3)
Bond angles (°)			
Cr1–Sn1–C11	117.3(3)	C5–Cr1–C6	37.1(7)
Cr1–Sn1–C17	114.0(2)	C5–Cr1–C9	155.5(7)
Cr1–Sn1–C23	112.5(3)	C5–Cr1–C10	91.5(7)
C11–Sn1–C17	104.8(4)	C9–Cr1–C10	85.8(8)
C17–Sn1–C23	103.7(4)	C3–Cr1–C10	112.4(8)
Sn1–Cr1–C1	101.9(5)	C1–O1–C7	119(1)
Sn1–Cr1–C2	136.9(6)	C4–O4–C8	116(1)
Sn1–Cr1–C3	164.6(5)	Cr1–C1–O1	130(1)
Sn1–Cr1–C6	84.3(4)	O1–C1–C2	122(2)
Sn1–Cr1–C9	103.1(5)	O1–C1–C6	117(2)
Sn1–Cr1–C10	74.3(6)	C2–C1–C6	121(2)
C1–Cr1–C9	118.2(7)	Cr1–C2–C1	73.1(9)
C2–Cr1–C3	36.0(8)	Cr1–C4–O4	130(1)
C2–Cr1–C4	64.8(7)	Cr1–C4–C5	70.3(9)
C3–Cr1–C9	91.5(7)	O4–C4–C3	112(2)
Cr1–C10–O10	175(2)	O4–C4–C5	127(2)

mesitylene complex. This is well-supported by the ^1H -NMR data that shows that the $J(^{119}\text{Sn}\text{--Cr--H}) = 212$ Hz in **3a**, which is much smaller than that in the mesitylene complex (329.2 Hz). Although the Sn–H coupling constants of **3a** are much lower than those in the analogous compounds, **1a** and **4a**, they are still too high to conclude

that a complete oxidative addition has taken place. This is based on a comparison with the known osmium compound, *cis* $(\text{CO})_4\text{Os}(\text{H})\text{SnCl}_3$, where there should be no interaction between the hydride and SnCl_3 , and the $J(^{119}\text{Sn}\text{--Os--H})$ and $J(^{117}\text{Sn}\text{--Os--H})$ were found to be 136 and 129.5 Hz, respectively [3].

The angle between the two CO ligands in **3a** is 85.8° . The arene ring is oriented such that the methoxy groups on the arene are staggered with respect to the Sn atom, presumably to avoid steric hindrance between the methoxy groups and the triphenyltin ligand. The distance between the Cr and the center of the arene ring is 1.69 Å, 0.04 Å shorter than the corresponding distance in the analogous bis-stannyl compound (**3b**). The arene ring adopts a boat conformation, with the C(1) and C(4) atoms bent out of the plane of the ring by 0.10 and 0.08 Å, respectively. This deviation could be a result of electronic effects, as was reported for similar $(\text{arene})\text{M}(\text{C}_6\text{F}_5)_2$ complexes by Radonovich et al. ([9]a). Analogously, Hunter and co-workers ([9]b) attributed such distortion to the strong electron donating ability of methoxy groups.

3.3. X-ray structure of $(\eta^6\text{-}1,4\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**

An ORTEP drawing of the structure is shown in Fig. 2. Selected bond distances and angles are given in Table 4. 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(9)–Cr(1)–C(10) angle of 105.4° . The two stannyl ligands are also *trans* to each other with a Sn(1)–Cr(1)–Sn(2) angle of 123.47° . The Cr–Sn distances are 2.707 and 2.706 Å. The distance between the arene

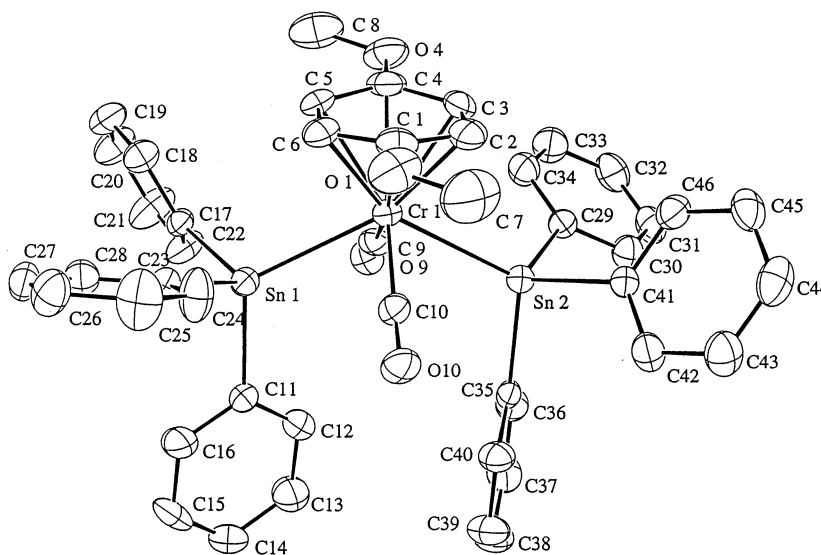
Fig. 2. ORTEP drawing of $(\eta^6\text{-}1,4\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**.

Table 4

Bond lengths (Å) and angles (°) in $(\eta^6\text{-}1,4\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**

Bond lengths (Å)			
Sn1–Cr1	2.707(1)	Cr1–C5	2.228(7)
Sn1–C9	2.749(7)	Cr1–C6	2.217(7)
Sn1–C10	2.850(7)	Cr1–C9	1.825(8)
Sn1–C11	2.168(4)	Cr1–C10	1.859(7)
Sn1–C17	2.161(4)	O1–C1	1.37(1)
Sn1–C23	2.176(4)	O1–C7	1.33(1)
Sn2–Cr1	2.706(1)	O4–C4	1.35(1)
Sn2–C9	2.740(7)	O4–C8	1.42(1)
Sn2–C10	2.879(7)	O9–C9	1.17(1)
Sn2–C29	2.164(4)	O10–C10	1.141(9)
Sn2–C35	2.168(4)	C1–C2	1.39(1)
Sn2–C41	2.167(4)	C1–C6	1.38(1)
Cr1–C1	2.284(8)	C2–C3	1.41(1)
Cr1–C2	2.225(7)	C3–C4	1.40(1)
Cr1–C3	2.217(7)	C4–C5	1.41(1)
Cr1–C4	2.314(8)	C5–C6	1.39(1)
Bond angles (°)			
Cr1–Sn1–C11	117.9(1)	C6–Cr1–C9	135.7(3)
Cr1–Sn1–C17	111.9(1)	C6–Cr1–C10	102.1(3)
Cr1–Sn1–C23	114.2(1)	C9–Cr1–C10	105.4(3)
C11–Sn1–C17	102.7(2)	C1–O1–C7	117.9(8)
C11–Sn1–C23	104.3(2)	C4–O4–C8	117.6(7)
C17–Sn1–C23	104.2(2)	O1–C1–C2	125.1(8)
Cr1–Sn2–C29	114.2(1)	O1–C1–C6	114.9(8)
Sn1–Cr1–C3	148.7(2)	O4–C4–C3	117.9(7)
Sn1–Cr1–C5	84.3(2)	O4–C4–C5	124.1(8)
Sn1–Cr1–C9	71.7(2)	Cr1–C5–C6	71.3(4)
Sn1–Cr1–C10	74.7(2)	Cr1–C5–C4	75.3(4)
Sn2–Cr1–C9	71.4(2)	Cr1–C9–O9	178.0(6)
Sn2–Cr1–C10	75.7(2)	Cr1–C10–O10	173.8(6)

ring center and the Cr atom is 1.732 Å, which is 0.04 Å longer than that in the analogous hydrido stannyl complex. This longer distance is probably a result of larger steric hindrance from the two stannyl ligands and the methoxy groups on the arene ring. The methoxy groups are staggered with respect to the tin atoms, presumably to avoid steric hindrance. In this complex as well, there is a deviation of the arene ring from planarity. The arene ring adopts a boat conformation, with C(1) and C(4) bent out of the plane by 0.08 and 0.09 Å, respectively.

3.4. Ligand effect on the Sn–H interaction in the hydrido stannyl compounds

The nature of the product of the addition of a Sn–H bond to a transition metal (M) moiety can be investigated by studying the Sn···H interaction in the resulting compound. The Sn–H NMR coupling constants, $J(^{119}\text{Sn}-\text{M}-^1\text{H})$ and $J(^{117}\text{Sn}-\text{M}-^1\text{H})$, serve as a good tool to measure this interaction, where higher coupling constants indicate stronger residual Sn–H bonding. As might be expected, electronic effects of the ligands on the transition metal and the ligands on the Sn atom greatly affect the degree of such interaction. Indeed, the authors have found that electron-withdrawing groups on the Sn and electron-donating groups on the transition metal lead

to weaker Sn–H interaction, in other words, such ligands favor oxidative addition of the Sn–H bond to the Cr center. Comparison of the coupling constants in these compounds clearly shows these effects (Table 5). The coupling $J(^{119}\text{Sn}-\text{Cr}-^1\text{H}) = 373.6$ Hz in complex **1a**, which decreases to 329.2 Hz in the mesitylene complex (**4a**) upon replacing the three butyl ligands with weaker σ -electron-donating phenyl ligands. It decreases further to 213.6 Hz in complex **3a** as the methyl groups are replaced with much stronger electron-donating groups, namely OCH_3 , on the arene ligand. The weaker Sn–H interaction in **3a** is also supported by X-ray structural analysis, where the Sn–H distance is 1.95 Å in **4a**, while it is 2.23 Å in **3a**. These observations show that the choice of the ligands is a key factor in determining the nature of the Sn–Cr–H bonding. Thus, stronger electron-donating substituents on the arene ring, and more electron-demanding ligands on the Sn encourage more ‘complete’ oxidative addition of the Sn–H bond to Cr.

3.5. Reactions with CO

The hydrido stannyl complex $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{HSnPh}_3)$, **4a**, did not react with CO at r.t., while the reaction did take place at 60°C, giving both the tricarbonyl analog and the bis-stannyl compound $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **4b**, in ca. a 1:2 ratio. The bis-stannyl complex **4b** showed no tendency to react with CO at r.t. or at 60°C. At an elevated temperature (150°C), the reaction took place as a result of reductive elimination of the two stannyl ligands, giving hexaphenyldistannane, Sn_2Ph_6 , and the tricarbonyl analog, $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_3$. The ^1H -NMR spectrum of the reaction solution was recorded at different periods of reaction, indicating that the reaction took place within the first 10 min forming the tricarbonyl compound and Sn_2Ph_6 . After 30 min, most of the starting material reacted and most of the tricarbonyl compound produced reacted further with CO to give free arene and $\text{Cr}(\text{CO})_6$. The reaction was complete after 4 h, after which only free mesitylene and Sn_2Ph_6 were observed in the ^1H -NMR spectrum and the color of the solution turned, as expected, from yellow to colorless (Scheme 1).

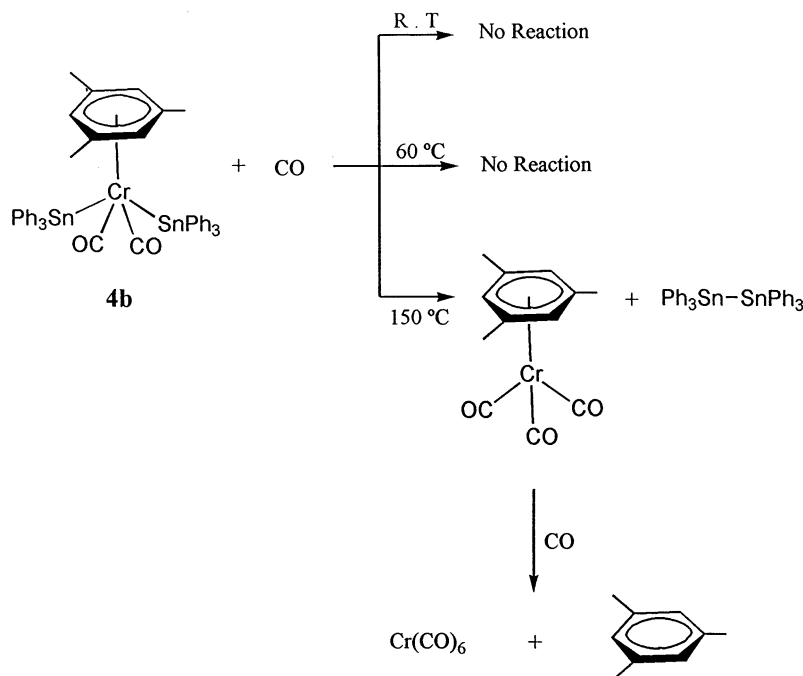
3.6. Reaction of Sn_2Ph_6 with $\text{Cr}(\text{CO})_6$ and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$

In an attempt to photochemically reverse the thermal reaction of bis-stannyl compounds with CO, the reac-

Table 5

Coupling constants (Hz) in **1a**, **4a** and **3a**

	1a	4a	3a
$J(^{119}\text{Sn}-\text{Cr}-^1\text{H})$	373.60	329.20	213.60
$J(^{117}\text{Sn}-\text{Cr}-^1\text{H})$	359.6	314.4	208.0

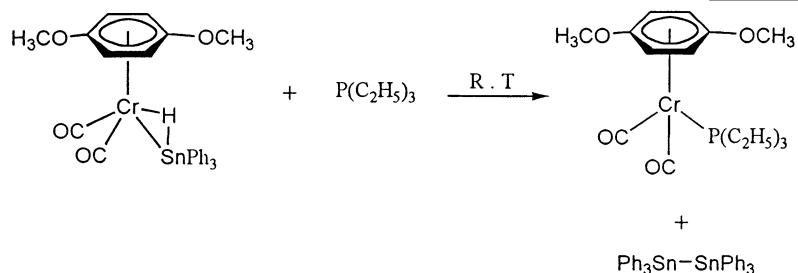


Scheme 1.

tion of Sn_2Ph_6 with Cr(CO)_6 in benzene was carried out under UV light. Due to gradual photolytic decarbonylation of the hexacarbonyl chromium compound, several unknown products formed as determined from the $^1\text{H-NMR}$ spectrum of the products of the reaction. A similar photochemical reaction between $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$ and Sn_2Ph_6 in a mixture of benzene and hexanes led to the formation of the bis-stannyl complex, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_2(\text{SnPh}_3)_2$, **6**. About 10% of the starting tricarbonyl compound was converted to the bis-stannyl complex, **6**, during a 3-h reaction as a result of photochemical decarbonylation of the tricarbonyl compound and reaction with Sn_2Ph_6 (Scheme 2). (It is possible that ‘ SnPh_3 ’ radicals were involved, since the photochemical cleavage of Sn_2Ph_6 has been reported to give two SnPh_3 radicals [10].)

3.7. Reaction of $(\eta^6\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr(CO)}_2(\text{H-SnPh}_3)$, **3a**, with $\text{P(C}_2\text{H}_5)_3$

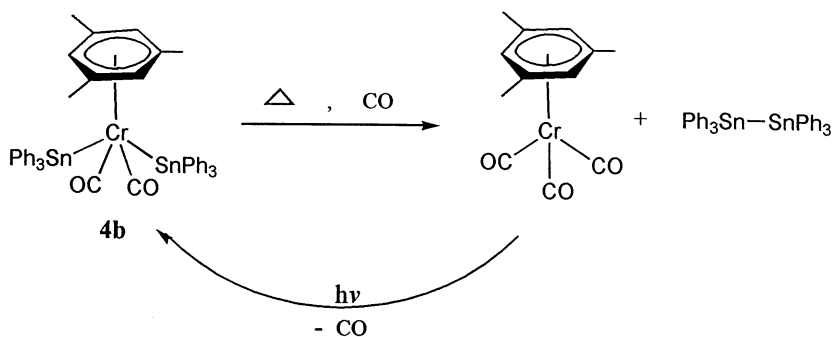
The reaction of **3a** with triethylphosphine at r.t. resulted in a yellow oily residue containing Sn_2Ph_6 and $(\eta^6\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr(CO)}_2\text{P(C}_2\text{H}_5)_3$ (**5**) as indicated by $^1\text{H-NMR}$.



The reaction went to completion as no starting material was observed. After several recrystallization attempts, small orange crystals and a yellow–green precipitate were obtained upon slow evaporation of hexanes from a 10 ml solution of the residue. The $^1\text{H-NMR}$ spectrum of the crystals showed signals for $(\eta^6\text{-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr(CO)}_2\text{P(C}_2\text{H}_5)_3$, and that the CH_2 and CH_3 protons are coupled to the phosphorus with $J(^1\text{H-}^{31}\text{P}) = 7.6$ Hz giving a doublet of quartets for CH_2 , which appears as five lines due to overlapping peaks, and a doublet of triplets for CH_3 , which shows five lines due to overlapping as well. The protons of the arene are also coupled to the phosphorous with a coupling constant of 3.2 Hz.

The IR spectrum of the phosphine adduct showed two sharp peaks for ν_{CO} that are shifted to lower energy by 28 and 6 wavenumbers, as compared with the starting hydrido stannyl compound **3a**. This shift could be due to an increase in the electron density at the metal from the donor ligand, $\text{P(C}_2\text{H}_5)_3$, which increases the back-bonding to the CO ligands.

Similar reactions between PPh_3 and $\text{CpMn(CO)}_2(\text{H})(\text{EPh}_3)$ ($\text{E} = \text{Si, Ge}$) have led to the displacement of the silane or germane by the phosphine ligand [11].



In the reaction of triethylphosphine with **3a**, the HSnPh_3 ligand probably was eliminated, followed by $\text{P}(\text{C}_2\text{H}_5)_3$ coordination to the metal center. The HSnPh_3 obtained reacted with the excess $\text{P}(\text{C}_2\text{H}_5)_3$ to form Sn_2Ph_6 , which is supported by the results of a separate reaction between free HSnPh_3 and excess $\text{P}(\text{C}_2\text{H}_5)_3$ in which 0.2 ml HSnPh_3 and 2.0 ml $\text{P}(\text{C}_2\text{H}_5)_3$ were stirred under argon for 2 days, and Sn_2Ph_6 was obtained, isolated and identified by $^1\text{H-NMR}$ spectroscopy.

3.8. Arene exchange reactions

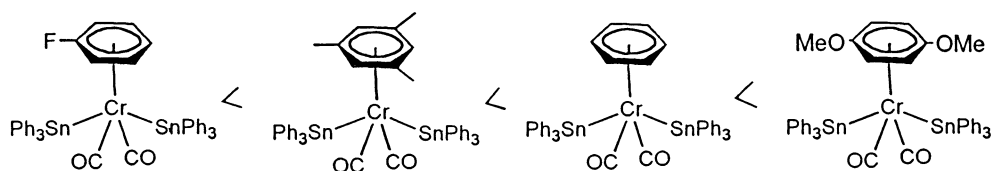
The IR study of the reaction of $(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$ with free mesitylene at 170°C in decalin showed no arene exchange but instead complete decomposition to $(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Cr}(\text{CO})_3$ and (mesitylene) $\text{Cr}(\text{CO})_3$. $^1\text{H-NMR}$ spectra of the solid products after the solvents were removed indicated the formation of Sn_2Ph_6 also. The ratio between the products changed with the time of the reaction. The fluorobenzene tricarbonyl compound formed first, and then it exchanged the fluorobenzene ligand with free mesitylene giving the mesitylene tricarbonyl derivative, $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_3$. As the reaction progressed, more arene exchange took place until the major product was the mesitylene-tricarbonyl compound after 30 h of reaction.

The reaction of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **6**, with free mesitylene was studied at 170°C by IR and $^1\text{H-NMR}$. Complex **6** showed high stability at this temperature and after 6 h of reaction, less than 10% of the starting material decomposed giving the tricarbonyl derivative, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and Sn_2Ph_6 . As the reaction progressed, the $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ exchanged the benzene ligand with free mesitylene to give $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{Cr}(\text{CO})_3$. The starting compound, **6**, showed no tendency to exchange its arene with free mesitylene, which is in contrast to what has been reported for the analogous silyl complexes, where benzene complexes showed a higher tendency to

exchange [6]. The reason that the mesitylene-bis-stannyl compound did not favorably form in this process could be the steric hindrance from the bulky stannyl ligands and the methyl groups on the arene ring.

The reaction of the mesitylene-bis-stannyl complex with free benzene was studied by IR and $^1\text{H-NMR}$ at 110 and 150°C . At 110°C , neither decomposition nor arene exchange took place. At 150°C , the starting compound completely decomposed within 6 h of reaction via reductive elimination of the two stannyl ligands forming Sn_2Ph_6 and (mesitylene) $\text{Cr}(\text{CO})_3$ (in ca. a 1: 1 ratio) before any arene exchange could take place. This indicates that the dissociation of the two SnPh_3 ligands from the bis-stannyl complex is faster when the arene ring is mesitylene than when it is benzene. This behavior could be due, again, to the steric hindrance from the methyl groups and the stannyl ligands, especially since one methyl group eclipses one of the stannyl ligands.

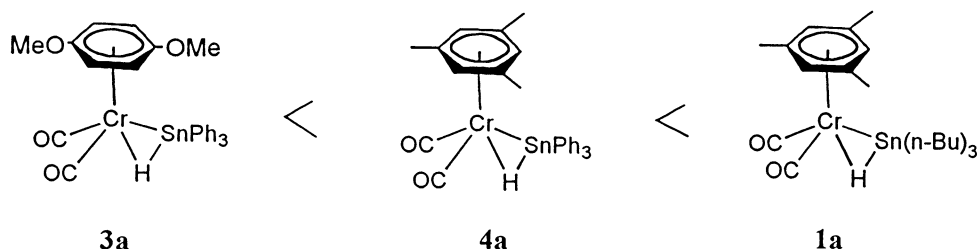
$(\eta^6\text{-1,4-C}_6\text{H}_4(\text{OCH}_3)_2)\text{Cr}(\text{CO})_2(\text{SnPh}_3)_2$, **3b**, showed the highest thermal stability among the compounds that have been discussed in this study. A reaction between **3b** and free benzene in decalin at 170°C for 30 h showed no decomposition or arene exchange. There are two competing factors that affect the stability of **3b**: first, electronic effects from the arene that carries two strong electron donating methoxy groups, which in turn enhances the arene-Cr interaction, inhibiting any arene exchange with other less electron-rich arenes and increases the electron density at the Cr center, strengthening the Cr-Sn bonds. Second, steric hindrance from the two stannyl ligands and the two methoxy groups on the arene should facilitate reductive elimination of the stannyl ligands as well as decrease the metal-arene interaction. Apparently, the electronic effects in this compound dominate and enhance its stability. The geometry of the complex in which the two methoxy groups are in staggered positions with the two stannyl ligands minimizes the steric effect. Based on this study, the following trend in stability can be concluded:



X-ray determined Cr–arene distances for some of these compounds also correlate with this trend. The center of arene ring–Cr distance in the mesitylene complex, **4b**, was determined to be 1.79 Å, as compared with 1.73 Å in the dimethoxybenzene complex, **3b**.

4. Conclusions

A series of (η^6 -arene)Cr(CO)₂(HSnR₃) and (η^6 -arene)Cr(CO)₂(SnR₃)₂ compounds have been synthesized by the photochemical addition of HSnR₃ to (η^6 -arene)Cr(CO)₃. The authors found that the substituents on the arene ring and at the Sn atom have dramatic effects on the nature of the Sn–H bond addition to the Cr center. More ‘complete’ oxidative addition was obtained when stronger electron donating substituents on the arene and electron demanding ligands at the Sn were used. As a result, the following trend was observed for the degree of remaining Sn–H interaction in the hydrido stannyl compounds.



¹H-NMR coupling constants, as well as X-ray determined Sn–H distances (1.95 Å in **4a** and 2.23 Å calculated for **3a**), provided additional evidence for this trend.

Substituents on the arene ring were also found to have a great effect on the stability of the bis-stannyl compounds. Electron demanding arenes, such as fluorobenzene, led to weaker arene–Cr interaction, and in turn to less stable compounds. On the other hand, electron-rich arenes led to very stable compounds with stronger arene–Cr interaction, as was found in compound **3b**, (η^6 -1,4-C₆H₄(OCH₃)₂)Cr(CO)₂(SnPh₃)₂. However, steric hindrance has a significant effect if the geometry of the compound creates considerable steric problems, as in compound **4b**, (η^6 -C₆H₃(CH₃)₃)Cr(CO)₂(SnPh₃)₂ [1]. In compound **3b**, the two methoxy groups are in staggered positions compared with the

two stannyl ligands, which minimizes the steric hindrance effect.

Acknowledgements

The support of National Science Foundation is acknowledged with gratitude.

References

- [1] A. Khaleel, K. Klabunde, *J. Inorg. Chem.* 35 (1996) 3223.
- [2] (a) W. Jetz, W.A.G. Graham, *Inorg. Chem.* 10 (1971) 4. (b) W.A.G. Graham, *J. Organomet. Chem.* 300 (1986) 81.
- [3] U. Schubert, E. Kunz, B. Harkers, J. Willnecker, J. Meyer, *J. Am. Chem. Soc.* 111 (1989) 2572.
- [4] (a) H. Kanai, S.B. Choe, K.J. Klabunde, *J. Am. Chem. Soc.* 108 (1986) 2019. (b) S.B. Choe, H. Kanai, K.J. Klabunde, *J. Am. Chem. Soc.* 111 (1989) 2875.
- [5] C.A.L. Mahaffy, P.L. Pauson, *J. Chem. Res. Synop.* 126 (M) (1979) 1752.
- [6] B.R. Jagirdar, K.J. Klabunde, *J. Coord. Chem.* 34 (1995) 31.
- [7] (a) D.F. Shriver, M.A. Drezdon, *The Manipulation of Air Sensitive Compounds*, 2nd ed., Wiley, New York, 1986. (b) S. Herzog, J. Dehnert, K. Luhder, in: H.B. Johnassen (Ed.), *Technique of Inorganic Chemistry*, vol. VII, Interscience, New York, 1969.
- [8] (a) R. Davis, L.A.P. Kane-Maguire, in: G. Wilkinson (Ed.), *Comprehensive Organometallic Chemistry*, vol. 3, Pergamon Press, New York, 1987, p. 1036. (b) L. Knoll, K. Reiss, J. Schafer, P. Klüfers, *J. Organomet. Chem.* 193 (1980) C40.
- [9] (a) L.J. Radonovich, F.J. Koch, T.A. Albright, *Inorg. Chem.* 19 (1980) 3373. (b) A.D. Hunter, L. Shilliday, W.S. Furey, M. Zaworotko, *J. Organomet.* 11 (1992) 1550.
- [10] (a) B.J. Aylett, *Organometallic Compounds*, vol. 1, part 2, 4th edn., Chapman and Hall, London, 1979. (b) D.S. Ferth, R.B. King, *Journal of Organometallic Chemistry Library*, vol. 4, New York, 1977.
- [11] F. Carre, E. Colomor, R.J.P. Corriu, A. Vioux, *Organometallics* (1984).