

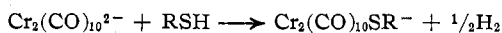
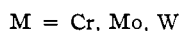
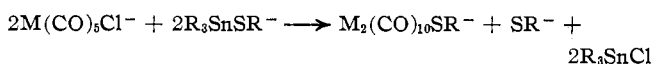
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## The Chemistry of Dinuclear Carbonyl Anions. VII. Anionic Metal Carbonyl Mercaptides<sup>1</sup>

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Mercaptans and organic disulfides have long been utilized as reagents for the preparation of mercapto-metal carbonyl derivatives particularly within the iron group transition metals.<sup>3</sup> Less is known about the mercapto chemistry of the group VI metal carbonyls. Anionic derivatives of the type  $M(\text{CO})_5\text{SR}^-$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) are of particular interest for two reasons: they are isoelectronic with the corresponding neutral manganese compounds,  $\text{Mn}(\text{CO})_5\text{SR}$ ; and since the bound sulfur still has nonbonded electron pairs, condensation with the formation of mercapto bridges may occur. This is observed for numerous iron and manganese derivatives. Initial attempts to prepare the group VI mercapto derivatives,  $M(\text{CO})_5\text{SR}^-$ , via the reactions shown below led to singly bridged species.<sup>4,5</sup> No



mononuclear species could be isolated regardless of the relative amounts of reagents employed or their mode of addition in these reactions.<sup>4</sup>

The application of a new redox reaction which occurs between the dinuclear dianions of the group VI metal carbonyls and either mercuric or silver salts<sup>6</sup> led to the preparation of the desired mercaptide derivatives. During the course of this work an alternate synthesis of this type of mercaptide derivative was reported by Beck and Tadros<sup>7</sup> via the reaction of sodium mercaptides with the photochemically procured  $\text{Cr}(\text{CO})_5 \cdot \text{THF}$  moiety.<sup>8</sup>

### Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Mr. M. L. Kshatriya of this department.

**Materials.**—Bis(phenylthio)mercury was prepared by refluxing mercuric oxide and excess thiophenol in dichloromethane for 2 hr. The insoluble bis(phenylthio)mercury was filtered and washed with dichloromethane. Bis(methylthio)mercury was prepared by addition of mercuric oxide to dichloromethane in a glass pressure vessel fitted with a Fisher-Porter valve. Methanethiol was condensed into the vessel and the mixture was stirred overnight. The excess methanethiol and solvent were removed under vacuum to yield insoluble bis(methylthio)mercury. Bis(trifluoromethylthio)mercury was prepared according to Man, Coffman, and Muettterties.<sup>9</sup> Trimethyl(methylthio)tin was

prepared by reaction of trimethyltin chloride with an equimolar amount of methanethiol in diethyl ether in the presence of 1 equiv of triethylamine at ambient temperature. After removal of the precipitated triethylammonium chloride by filtration, the solvent was removed from the filtrate under vacuum and the residue was distilled yielding trimethyl(methylthio)tin, bp 164° (lit.<sup>10</sup> bp 163°). The preparation of  $\text{W}(\text{CO})_5\text{SCH}_3\text{Sn}(\text{CH}_3)_3$  was carried out in a manner analogous to that recently reported for the chromium derivative.<sup>11</sup> A typical preparation is given below. A solution of 3.5 g of  $\text{W}(\text{CO})_6$  in 100 ml of THF was irradiated for 2 hr with a H44 4GS mercury vapor ultraviolet lamp. To the  $\text{W}(\text{CO})_5 \cdot \text{THF}$  solution formed was added 2.25 g of  $(\text{CH}_3)_3\text{SnSCH}_3$ . The solution was evaporated to dryness under reduced pressure and the residue was dissolved in 100 ml of pentane and filtered. Upon cooling the solution to  $-78^\circ$ , 2.6 g (50% yield) of  $\text{W}(\text{CO})_5\text{S}(\text{CH}_3)_3\text{Sn}(\text{CH}_3)_3$  was obtained.

**Preparation of [PPN][M(CO)<sub>5</sub>SR] Compounds.**—All the compounds were prepared in a similar manner. In a typical reaction, 1.8 g (1.1 mmol) of  $[\text{PPN}]_2[\text{W}_2(\text{CO})_{10}]$  and 0.29 g (1 mmol) of  $\text{Hg}(\text{SCH}_3)_2$  were stirred together in 25 ml of dichloromethane for 15 min. After addition of 100 ml of diethyl ether the mixture was allowed to stand at  $-10^\circ$  for 30 min. The solution was then filtered through a sintered-glass funnel covered with Celite filteraid. To the filtrate was added, in small portions, 100 ml of pentane and the mixture was allowed to stand at  $-10^\circ$  until addition was complete. A 1.15-g (63%-yield) sample of  $[\text{PPN}][\text{W}(\text{CO})_5\text{SCH}_3]$  was obtained.

**Preparation of [PPN][W(CO)<sub>5</sub>(Ph<sub>3</sub>P)SR] Compounds (R = CH<sub>3</sub>, CF<sub>3</sub>).**—Both compounds were made in the same manner. For example a 2-g sample of  $[\text{PPN}][\text{W}(\text{CO})_5\text{SCH}_3]$  and 10 g of triphenylphosphine were irradiated together in 200 ml of freshly distilled tetrahydrofuran with a H44-4GS mercury vapor spotlight for 2 hr. The solution was evaporated to dryness at reduced pressure. To the residue was added 25 ml of dichloromethane followed by 150 ml of diethyl ether. A 2.1-g (95%-yield) sample of yellow crystalline  $[\text{PPN}][\text{W}(\text{CO})_5(\text{Ph}_3\text{P})\text{SCH}_3]$  was obtained upon filtration.

**Preparation of [PPN][M(CO)<sub>5</sub>S(CH<sub>3</sub>)M'(CO)<sub>5</sub>] Compounds.**—In a typical preparation, 1 g of  $[\text{PPN}][\text{W}(\text{CO})_5\text{SCH}_3]$  was dissolved in 50 ml of dichloromethane. After addition of 1.5 g of  $\text{Cr}(\text{CO})_5\text{S}(\text{CH}_3)\text{Sn}(\text{CH}_3)_3$ , the solution was stirred for 1 hr. The solvent was removed at reduced pressure and the residue was dissolved in 100 ml of diethyl ether. After filtration, pentane was added to the solution in small portions and the solution was allowed to stand at  $-10^\circ$ . Filtration yielded 0.9 g (91% yield) of orange crystalline  $[\text{PPN}][\text{W}(\text{CO})_5\text{S}(\text{CH}_3)\text{Cr}(\text{CO})_5]$ . The same yield was obtained when  $[\text{PPN}][\text{W}(\text{CO})_5\text{Cl}]$  was substituted for  $[\text{PPN}][\text{W}(\text{CO})_5\text{SCH}_3]$  or when  $[\text{PPN}][\text{Cr}(\text{CO})_5\text{Cl}]$  and  $\text{W}(\text{CO})_5\text{S}(\text{CH}_3)\text{Sn}(\text{CH}_3)_3$  were employed as starting materials.

The melting points, yields, colors, and analyses of the new sulfur derivatives are summarized in Table I.

**Infrared Spectra.**—The infrared spectra in the  $\nu(\text{CO})$  region of the compounds prepared in this work (Table II) were obtained on a Perkin-Elmer Model 621 spectrometer with grating optics. Tetrahydrofuran solutions were used with a concentration of 5–15 mg/ml and a 0.2-mm path length. The spectrometer was calibrated with indene.

**Nmr Spectra.**—All the nmr spectra (Table III) were determined on a Perkin-Elmer Hitachi Model R-20 spectrometer at ambient temperature. Tetramethylsilane was used as an internal standard for the proton spectra. Trichlorofluoromethane was used as the internal standard for the <sup>19</sup>F nmr spectra.

**Conductivity.**—Conductance measurements were made in nitromethane solution using a standard type conductivity cell with a cell constant of 0.1792 cm<sup>-1</sup>. The conductivity bridge was a Model 31 instrument by Yellow Springs Mfg. Co. The specific conductance of the nitromethane was  $5.7 \times 10^{-7}$  ohm<sup>-1</sup>. The equivalent conductances of approximately  $1.5 \times 10^{-3}$  M solutions are presented in Table III. The conductivity of two of the salts as a function of concentration was also determined.

The molar concentration ( $c \times 10^{-3}$ ) and conductance (cm<sup>2</sup>/ohm equiv) of  $[\text{PPN}][\text{W}(\text{CO})_5\text{SCH}_3]$  are as follows: 3.0, 69.9; 1.5, 74.9; 0.75, 77.9; 0.38, 81.0. The extrapolated conductance at infinite dilution is 85.5 cm<sup>2</sup>/ohm equiv and a plot of

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TABLE I  
SULFUR COMPOUNDS

Anion	Mp, °C	Anal., %												Yield, %	Color		
		Calcd						Found									
		C	H	N	O	F	S	M	C	H	N	O	F	S	M		
Cr(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	98-101	60.6	3.6	1.7		6.9	3.9	6.3	60.3	3.7	1.9		6.8	4.0	6.3	24	Pale yellow
Mo(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	96-98	57.6	3.5	1.6		6.5	3.7	10.9	58.0	3.6	1.7		6.5	3.7	10.0	37	Pale yellow
W(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	117-120	52.4	3.1	1.5		5.9	3.3	19.1	52.6	3.2	1.6		6.1	3.4	19.6	78	Yellow
W(CO) <sub>5</sub> SCH <sub>3</sub> <sup>-</sup>	165-168	55.5	3.6	1.5	8.8		3.5	20.2	55.7	3.3	1.7	8.6		3.5	20.9	65	Bright yellow
W(CO) <sub>5</sub> SC <sub>6</sub> H <sub>5</sub> <sup>-</sup>	123-125	58.1	3.6	1.4	8.2		3.3	19.0	58.6	3.5	1.6	8.1		3.3	19.5	51	Yellow
W(CO) <sub>4</sub> Ph <sub>2</sub> PSCCH <sub>3</sub> <sup>-</sup>	201-208	61.9	4.2	1.2					62.2	4.1	1.2					68	Yellow
W(CO) <sub>4</sub> Ph <sub>3</sub> PSCF <sub>3</sub> <sup>-</sup>		59.1	3.8	1.2					58.6	4.0	1.5						Yellow
CrW(CO) <sub>10</sub> SCH <sub>3</sub> <sup>-</sup>	109-111	51.2	3.0			2.9	<i>a</i>		51.8	3.0			3.0	<i>a</i>		91	Orange
W(CO) <sub>5</sub> S(CH <sub>3</sub> )Sn(CH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	49-51	20.2	2.3			6.0	<i>c</i>		20.5	2.0			5.7	<i>c</i>		50	Light yellow

<sup>a</sup> Calcd: Cr, 4.7; W, 16.7. Found: Cr, 4.7; W, 17.9. <sup>b</sup> Neutral compound. <sup>c</sup> Calcd: W, 34.4; Sn, 22.2. Found: W, 33.1; Sn, 21.1.

TABLE II  
INFRARED DATA OF SULFUR COMPOUNDS

Species	—Metal carbonyl freq, cm <sup>-1</sup> —
Cr(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	2053 w, 1926 s, 1864 m
Mo(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	2067 w, 1931 s, 1863 m
W(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	2063 w, 1918 s, 1855 m
W(CO) <sub>5</sub> SCH <sub>3</sub> <sup>-</sup>	1067 w, 1917 s, 1839 m
W(CO) <sub>5</sub> SC <sub>6</sub> H <sub>5</sub> <sup>-</sup>	2058 w, 1913, 1842 m
W(CO) <sub>4</sub> Ph <sub>3</sub> PSCCH <sub>3</sub> <sup>-</sup>	2003 m, 1881-1876 s, 1801 m
W(CO) <sub>4</sub> Ph <sub>3</sub> PSCF <sub>3</sub> <sup>-</sup>	2004 m, 1887 s, sh, 1874 s, 1813 m
CrW(CO) <sub>10</sub> SCH <sub>3</sub> <sup>-</sup>	2061 w, 2043 m, 1960 w, sh, 1932 vs, 1906 m, 1872 s
W(CO) <sub>5</sub> S(CH <sub>3</sub> )Sn(CH <sub>3</sub> ) <sub>3</sub>	2069 w, 1974 s, 1927 s, 1897 m

TABLE III  
NMR AND CONDUCTANCE OF SULFUR COMPOUNDS

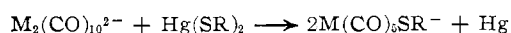
Species	Nmr, ppm	Conductance, A <sub>∞</sub> , cm <sup>2</sup> /ohm equiv (c = 1.5 × 10 <sup>-3</sup> M)
W(CO) <sub>5</sub> SCH <sub>3</sub> <sup>-</sup>	-2.06	74.9
W(CO) <sub>5</sub> SC <sub>6</sub> H <sub>5</sub> <sup>-</sup>	<i>a</i>	72.2
W(CO) <sub>4</sub> Ph <sub>2</sub> PSCCH <sub>3</sub> <sup>-</sup>	-2.00	93.3
W(CO) <sub>5</sub> S(CH <sub>3</sub> )Sn(CH <sub>3</sub> ) <sub>3</sub>	S-CH, -1.68; Sn-CH, 0.05 <sup>b</sup>	
Cr(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	21.2 <sup>c</sup>	73.2
Mo(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	21.1 <sup>c</sup>	75.1
W(CO) <sub>5</sub> SCF <sub>3</sub> <sup>-</sup>	23.5 <sup>c</sup>	73.2
W(CO) <sub>4</sub> Ph <sub>3</sub> PSCF <sub>3</sub> <sup>-</sup>	22.9 <sup>c</sup>	54.3

<sup>a</sup> Spectrum not determined due to cation phenyl spectrum. <sup>b</sup>  $J(^{117}\text{SnCH}) = 53.5$  Hz;  $J(^{119}\text{SnCH}) = 56.0$  Hz. <sup>c</sup> Fluorine-19 nmr vs. internal CFCI<sub>3</sub>.

$\Lambda_{\infty} - \Lambda$  vs.  $\sqrt{c}$  gives a slope of 260. For [PPN][W(CO)<sub>5</sub>SC<sub>6</sub>H<sub>5</sub>], the concentrations ( $c \times 10^{-3}$  M) and conductances (cm<sup>2</sup>/ohm equiv) are as follows: 3.0, 67.4; 1.5, 72.2; 0.75, 75.6; 0.38, 79.1. The extrapolated conductance at infinite dilution is 84.8 cm<sup>2</sup>/ohm equiv and the slope of a plot of  $\Lambda_{\infty} - \Lambda$  vs.  $\sqrt{c}$  is 294.<sup>12</sup>

### Results and Discussion

The reaction of mercuric mercaptides with the dinuclear dianions of the group VI metal carbonyls proved to be the best method for the preparation of anionic mercaptide derivatives of the type M(CO)<sub>5</sub>SR<sup>-</sup>. (See Table I for the compounds prepared.) Although this redox reaction is formally similar to that reported by Behrens, Lindner, and Birkle<sup>5</sup> for the



preparation of the singly bridged dinuclear mercaptide derivatives, Cr<sub>2</sub>(CO)<sub>10</sub>SR, only small amounts of the bridged compound (<10%) were formed when the mercuric mercaptides were employed. The alternate

preparation of the mononuclear anions M(CO)<sub>5</sub>SR<sup>-</sup> involving the reaction of the M(CO)<sub>5</sub>·THF moiety with a mercaptide ion also results in the formation of small amounts of the singly bridged species.<sup>4</sup> All the mononuclear mercaptide derivatives were isolated using the bis(triphenylphosphiniminium) cation as the counterion (hereafter abbreviated as PPN) and were relatively stable since they could be stored for several months under nitrogen at -10° and handled briefly in air.

The infrared spectra of the mononuclear anions M(CO)<sub>5</sub>SR<sup>-</sup> contained three bands in the  $\nu_{\text{CO}}$  stretching region and are consistent with C<sub>4v</sub> symmetry around the metal (2 A<sub>1</sub> + E). The frequencies of the absorption bands are similar to those found for other group VI metal pentacarbonyl anionic derivatives M(CO)<sub>5</sub>X<sup>-</sup> (X = I, Br, Cl, CN, NCS)<sup>6,13,14</sup> and consequently it is likely that much of the negative charge density resides on the metal. Weak ir absorptions due to the mercaptide ligands could not be unambiguously assigned due to interference from cation absorptions. However, the presence of the ligand in the complexes was easily demonstrated by <sup>1</sup>H or <sup>19</sup>F nmr spectroscopy. All nmr spectral data are reported in Table III except for the compounds containing SC<sub>6</sub>H<sub>5</sub><sup>-</sup> as a ligand. The integrated ratio of the methyl protons vs. the phenyl protons in the cation was in agreement with the proposed formulations for (PPN)W(CO)<sub>5</sub>SCH<sub>3</sub> and (PPN)W(CO)<sub>4</sub>(Ph<sub>3</sub>P)SCH<sub>3</sub>. The <sup>19</sup>F nmr spectrum of the W(CO)<sub>5</sub>(SCF<sub>3</sub>)<sup>-</sup> anion consists of a singlet at  $\delta$  23.5 which is close to that observed for the isoelectronic species, Re(CO)<sub>5</sub>SCF<sub>3</sub> ( $\delta$  26.7).<sup>15</sup>

Further support for the present formulation of the anions came from conductivity measurements. The equivalent conductance of (PPN)W(CO)<sub>5</sub>SCH<sub>3</sub> and (PPN)W(CO)<sub>5</sub>SC<sub>6</sub>H<sub>5</sub> determined as a function of concentration demonstrated that these materials behaved as 1:1 electrolytes in nitromethane. The equivalent conductance at a concentration of 1.5 × 10<sup>-3</sup> M was determined for the other salts (see Table III) and they also appear to be 1:1 electrolytes.

The formulation of the (PPN)M(CO)<sub>5</sub>SR salts as 1:1 electrolytes and the observed C<sub>4v</sub> site symmetry around the metal eliminates the possibility of having a double-bridged species such as [M(CO)<sub>4</sub>SR]<sub>2</sub><sup>2-</sup> or more highly condensed systems such as [M(CO)<sub>3</sub>SR]<sub>*n*</sub><sup>*n-*</sup>.

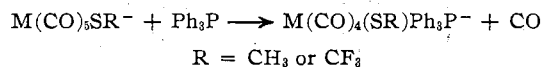
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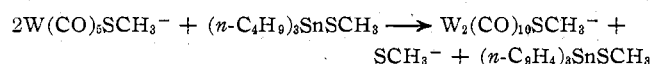
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Both such systems are normally obtained when the metal is manganese or rhenium, especially the dimeric system. In fact the only mononuclear manganese compound identified,  $Mn(CO)_5SC_6F_5$ , is unstable at ambient temperature.<sup>16</sup> The rhenium analogs are more stable and the monomers  $Re(CO)_5SCF_3$ <sup>15</sup> and  $Re(CO)_5SC_6F_5$ <sup>16</sup> are known. They undergo condensation to dimers under mild activation. The stability of the group VI metal anions  $M(CO)_5SR^-$  is in contrast to this behavior since no evidence for a similar condensation reaction was observed when the  $M(CO)_5SR^-$  salts were subjected to irradiation or refluxing in THF. If irradiation was carried out in the presence of  $Ph_3P$ , substitution of a carbonyl group by the phosphine occurred and displacement of the sulfur ligand was not observed. The bis-substituted products appear to

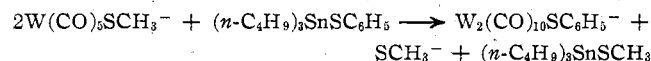


have a cis configuration since four  $\nu_{C=O}$  stretching frequencies are observed in the infrared spectrum (see Table II).

Since only singly bridged species were obtained upon reaction of  $(n-C_4H_9)_3SnSR$  with chlorocarbonyl anions,<sup>4</sup>  $M(CO)_5Cl^-$ , it was felt that the sulfur in the presumed mononuclear mercaptide intermediate was highly nucleophilic. However, attempts to demonstrate this nucleophilicity failed and no reaction was observed between the anion  $W(CO)_5SCH_3^-$  and  $W(CO)_6$  or the photochemically produced  $W(CO)_5 \cdot THF$ . Conversion of the  $M(CO)_5SR^-$  anions to the bridged mercaptide derivatives  $M_2(CO)_{10}SR^-$  occurred readily in the presence of organotin mercaptides. For example treatment of the anion  $W(CO)_5SCH_3^-$  with  $(n-C_4H_9)_3SnSCH_3$  resulted in the formation of  $W_2(CO)_{10}SCH_3^-$  in good yield. The source of the bridging



mercapto group was shown to be the mercapto group bonded to tin and not to the pentacarbonyl moiety since the following reaction was observed. No evidence for an equilibrium mixture was observed using



<sup>1</sup>H nmr. This reaction is completely analogous to the reaction of the  $M(CO)_5Cl^-$  anions with the organotin mercaptides.<sup>4</sup>

Since the organotin compound was intimately involved in the conversion of  $M(CO)_5SR^-$  to  $M_2(CO)_{10}SR^-$  anions, the recently reported compound  $Cr(CO)_5S(CH_3)Sn(CH_3)_3$  was felt to be a likely intermediate. Therefore the known compound  $Cr(CO)_5S(CH_3)_3Sn(CH_3)_3$  and its tungsten analog were prepared. When  $W(CO)_5S(CH_3)Sn(CH_3)_3$  was allowed to react with either  $W(CO)_5SCH_3^-$  or  $W(CO)_5Cl^-$ , the known dinuclear carbonyl mercaptide derivative was formed according to the following equation. The new bridged  $W(CO)_5S(CH_3)Sn(CH_3)_3 + W(CO)_5L^- \longrightarrow W_2(CO)_{10}SCH_3^- + (CH_3)_3SnL$  ( $L = Cl, SCH_3$ )

mixed-metal mercaptide  $[(CO)_5CrS(CH_3)W(CO)_5]^-$  was formed when  $Cr(CO)_5S(CH_3)Sn(CH_3)_3$  was allowed

to react with either  $W(CO)_5Cl^-$  or  $W(CO)_5SCH_3^-$ . This compound was found to be similar to other dinuclear carbonyl tungsten mercaptides reported earlier,<sup>4</sup> as determined by its analytical data and infrared spectrum. These results suggest the following reaction scheme. The trialkyltin mercaptide  $R_3SnSR'$  reacts with the tungsten pentacarbonyl halide or mercaptide anion to form the neutral compound  $W(CO)_5S(R')SnR_3$ . Thus displacement of halide or mercaptide ion occurs rather than sulfur-tin bond cleavage. The sulfur in the trialkyltin mercaptide would be expected to be more nucleophilic than the sulfur in a related alkyl sulfide due to the electropositive character of the tin atom compared to that of a carbon atom. This was demonstrated by addition of diethyl sulfide to the mononuclear carbonyl mercaptide. No reaction occurred and the starting mercaptide derivative was recovered. Attack on the neutral intermediate by another tungsten pentacarbonyl halide or mercaptide ion results in sulfur-tin bond cleavage as shown above. The lability of the sulfur-tin bond has been demonstrated by Ehrl and Vahrenkamp<sup>17</sup> by allowing compounds of the type  $R_nEY$  ( $Y = \text{alkyl or halogen; } E = \text{Li, Mg, B, C, P, As, or S}$ ) to react with the neutral carbonylthiotin derivative  $Cr(CO)_5S(CH_3)SnR_3$ . Cleavage of the sulfur-tin bond resulted (*e.g.*,  $Cr(CO)_5S(CH_3)SnR_3 + CH_3MgBr \rightarrow SnCH_3 + Cr(CO)_5S(CH_3)MgBr$ ). This reaction scheme explains the formation of the singly bridged species from both  $M(CO)_5Cl^-$  and  $M(CO)_5SR^-$  ions and the formation of the mixed-metal-bridged compound.

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## Enthalpies of Decomposition of Mercuric Halide-Dioxane Complexes

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There has been renewed interest in the complexes of 1,4-dioxane (DX) with the mercuric halides. The far-infrared spectra<sup>1</sup> and nuclear quadrupole resonance spectra<sup>2</sup> of  $HgX_2 \cdot DX$  and the dipole moments of  $HgX_2$  in dioxane solution<sup>3</sup> have been reported. Each of these studies suggests that the interaction of DX with  $HgX_2$  decreases in the order  $HgCl_2 > HgBr_2 > HgI_2$ . The enthalpies of decomposition reported by Crenshaw, Cope, Finklestein, and Rogan (CCFR)<sup>4</sup> appear to indicate the order of stability to be  $HgBr_2 \cdot DX > HgI_2 \cdot DX > HgCl_2 \cdot DX$ . CCFR reported  $\Delta H$  for reac-

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