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# Syntheses of Chromium Pentacarbonyl Derivatives of Arsenic(V) and Antimony(V). Contrasting Chemical Reactivity with Organic Halogen Derivatives

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We have synthesized a new series of chromium–group 15 dihydride and hydride complexes  $[\text{H}_2\text{As}\{\text{Cr}(\text{CO})_5\}_2]^-$  (**1**) and  $[\text{HE}\{\text{Cr}(\text{CO})_5\}_2]^-$  ( $\text{E} = \text{As}$ , **2a**;  $\text{E} = \text{Sb}$ , **2b**), which represent the first examples of group 6 complexes containing E–H fragments. The contrasting chemical reactivity of **2a** and **2b** with organic halogen derivatives is demonstrated. The reaction of **2a** with  $\text{RBr}$  ( $\text{R} = \text{PhCH}_2$ , **3**;  $\text{R} = \text{C}_3\text{H}_5$ , **4**), while the treatment of **2b** with  $\text{RX}$  ( $\text{RX} = \text{PhCH}_2\text{Br}$  or  $\text{HC}\equiv\text{CCH}_2\text{Br}$ ,  $\text{CH}_3(\text{CH}_2)_5\text{C}(\text{O})\text{Cl}$ ) forms the halo-substituted complexes  $[\text{XSb}\{\text{Cr}(\text{CO})_5\}_2]^-$  ( $\text{X} = \text{Br}$ , **5**;  $\text{X} = \text{Cl}$ , **6**). Moreover, the dihaloantimony complexes  $[\text{XX}'\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]^-$  can be obtained from the reaction of **2b** with the appropriate organic halides. In this study, a series of organoarsenic and antimony chromium carbonyl complexes have been synthesized and structurally characterized and the role of the main group on the formation of the resultant complexes is also discussed.

## Introduction

Transition metal carbonyl complexes incorporating main group fragments have attracted great attention because of their unusual bonding and versatile reactivity patterns.<sup>1</sup> In contrast to the well-developed iron–group 15 complexes,<sup>2</sup> most of the previously described As–Cr–CO and Sb–Cr–CO complexes exhibit trigonal-planar structures such as  $\text{XAs}\{\text{Cr}(\text{CO})_5\}_2$  ( $\text{X} = \text{Br}$ , **1**, **2a**, **2b**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **29**, **30**, **31**, **32**, **33**, **34**, **35**, **36**, **37**, **38**, **39**, **40**, **41**, **42**, **43**, **44**, **45**, **46**, **47**, **48**, **49**, **50**, **51**, **52**, **53**, **54**, **55**, **56**, **57**, **58**, **59**, **60**, **61**, **62**, **63**, **64**, **65**, **66**, **67**, **68**, **69**, **70**, **71**, 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## Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.<sup>10</sup> Solvents were purified, dried, and distilled under nitrogen prior to use.  $\text{Cr}(\text{CO})_6$  (Strem),  $\text{As}_2\text{O}_3$  (WAKO), and  $\text{Sb}_2\text{O}_3$  (Aldrich) were used as received. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in  $\text{CaF}_2$  cells. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken on a JEOL 400 instrument at 399.78 and 100.53 MHz, respectively. FAB mass spectra were taken on a JEOL SX-102A mass spectrometer. Quantitative analysis of the organic products was performed on a Shimadzu GC-9A instrument and GC Hewlett-Packard 6890 instrument equipped with a Hewlett-Packard 5973 MS selective detector. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

**Syntheses of  $[\text{Et}_4\text{N}][\text{H}_2\text{As}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ ) and  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ).** To a mixture of 5.40 g (96.2 mmol) of KOH, 0.20 g (1.00 mmol) of  $\text{As}_2\text{O}_3$ , and 1.32 g (6.01 mmol) of  $\text{Cr}(\text{CO})_6$  was added 20 mL of MeOH. After being stirred for 3 days at room temperature, the solution was filtered and an aqueous solution of 1.35 g (6.40 mmol) of  $\text{Et}_4\text{NBr}$  was added, precipitating the orange product. The product was collected by filtration, washed with  $\text{H}_2\text{O}$ , and dried under vacuum. The residue was washed with hexane and extracted with ether to give 0.55 g (0.93 mmol) of  $[\text{Et}_4\text{N}][\text{H}_2\text{As}\{\text{Cr}(\text{CO})_5\}_2]$  (47% based on As). Crystals suitable for X-ray diffraction were grown from hexanes/ $\text{CH}_2\text{Cl}_2$ . IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2032 s, 1929 vs, 1881  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  0.0 (s, 2H) (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ). Negative ion FABMS:  $m/z$  460.8. Anal. Calcd for  $[\text{Et}_4\text{N}][\mathbf{1}]$ : C, 36.56; H, 3.75; N, 2.37. Found: C, 36.43; H, 3.66; N, 2.16. The residue was then extracted with THF, and the THF extract was recrystallized from ether/THF to give 0.32 g (0.35 mmol) of  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ) (18% based on As). IR ( $\nu_{\text{CO}}$ , THF): 2007 vs, 1914 vs, 1847  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  -2.0 (s, 1H) (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ). Anal. Calcd for  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ : C, 40.80; H, 4.53; N, 3.07. Found: C, 40.50; H, 4.45; N, 3.11. Crystals suitable for X-ray diffraction were grown from ether/ $\text{CH}_2\text{Cl}_2$ .

**Synthesis of  $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ).** To a mixture of 5.39 g (96.0 mmol) of KOH, 0.27 g (0.93 mmol) of  $\text{Sb}_2\text{O}_3$ , and 1.25 g (5.67 mmol) of  $\text{Cr}(\text{CO})_6$  was added 25 mL of MeOH. After being stirred for 3 days at room temperature, the solution was filtered and an aqueous solution of 1.53 g (5.95 mmol) of  $\text{Et}_4\text{NBr}$  was added, precipitating the orange product. This product was collected by filtration, washed with  $\text{H}_2\text{O}$ , and dried under vacuum. Recrystallization from  $\text{Et}_2\text{O}$ /THF gave 1.41 g (1.47 mmol) of  $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ) (79% based on Sb). IR ( $\nu_{\text{CO}}$ , THF): 2003 vs, 1919 vs, 1860  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  -5.5 (s, 1H) (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ). Anal. Calcd for  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ : C, 38.81; H, 4.31; N, 2.92. Found: C, 38.51; H, 4.34; N, 2.76. Crystals suitable for X-ray diffraction were grown from ether/THF.

**Reaction of  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ) with  $\text{PhCH}_2\text{Br}$ .** To a solution of 0.35 g (0.38 mmol) of  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$  in 5 mL of THF was added 0.05 mL (0.42 mmol) of  $\text{PhCH}_2\text{Br}$ . The resulting solution was stirred in an ice/water bath for 10 min, then warmed to room temperature, and stirred for another 20 h. The solvent was removed under vacuum, and the organic product—toluene (0.239 mmol, 63% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ) was quantified and identified by GC and GC/MS. The ether extract was recrystallized with hexane/ $\text{CH}_2\text{Cl}_2$  to give 0.08 g (0.11 mmol) of the pure compound  $[\text{Et}_4\text{N}][(\text{Br})(\text{PhCH}_2)\text{As}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[\text{Et}_4\text{N}][\mathbf{3}]$ ) (29% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ). Crystals suitable for X-ray diffraction were grown from ether/ $\text{CH}_2\text{Cl}_2$ . IR ( $\nu_{\text{CO}}$ , THF): 2056 w, 2037 m, 1942 vs, 1933 vs, sh, 1897  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , 298 K, ppm):  $\delta$  7.42, 7.41, 7.29, 7.27, 7.22, 7.20 (m, 5H), 4.11 (s, 2H) (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 298 K, ppm):  $\delta$  227.69, 220.42, 141.46, 130.84, 128.99, 127.48, 49.18

(chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ). Negative ion FABMS:  $m/z$  628.8. Anal. Calcd for  $[\text{Et}_4\text{N}][\mathbf{3}]$ : C, 39.49; H, 3.58; N, 1.84. Found: C, 39.26; H, 3.33; N, 1.85. The residue was then extracted with THF, and the THF extract was recrystallized with hexanes/ $\text{CH}_2\text{Cl}_2$  to give 0.11 g (0.273 mmol) of the known compound  $[\text{Et}_4\text{N}][\text{BrCr}(\text{CO})_5]^{11}$  (24% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ). IR ( $\nu_{\text{CO}}$ , THF): 2054 w, 1921 vs, 1862 vs  $\text{cm}^{-1}$ . Anal. Calcd for  $[\text{Et}_4\text{N}][\text{BrCr}(\text{CO})_5]$ : C, 38.82; H, 5.01; N, 3.48. Found: C, 38.76; H, 4.97; N, 3.27.

**Reaction of  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ) with  $\text{HC}\equiv\text{CCH}_2\text{Br}$ .** To a solution of 0.33 g (0.36 mmol) of  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$  in 20 mL of THF was added 0.04 mL (0.53 mmol) of  $\text{HC}\equiv\text{CCH}_2\text{Br}$ . The resulting solution was stirred in an ice/water bath for 20 min, then warmed to room temperature, and stirred for another 2 days. The ether extract was recrystallized with hexane/ $\text{CH}_2\text{Cl}_2$  to give 0.15 g (0.21 mmol) of the pure compound  $[\text{Et}_4\text{N}][(\text{Br})(\text{C}_3\text{H}_3)\text{As}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[\text{Et}_4\text{N}][\mathbf{4}]$ ) (58% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$ ). IR ( $\nu_{\text{CO}}$ , THF): 2058 m, 2046 m, 2038 s, 1972 m, 1943 vs, 1900  $\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , 298 K, ppm):  $\delta$  6.80 (t, 1H,  $J = 6.23$  Hz), 5.06 (d, 2H,  $J = 6.23$  Hz) (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 298 K, ppm):  $\delta$  227.58, 220.21, 204.35, 98.46, 77.92 (chemical shifts not given for  $[\text{Et}_4\text{N}]^+$ ). Negative ion FABMS:  $m/z$  578.7. Anal. Calcd for  $[\text{Et}_4\text{N}][\mathbf{4}]$ : C, 35.61; H, 3.27; N, 1.98. Found: C, 35.29; H, 3.40; N, 1.77. The residue was then extracted with THF, and the THF extract was recrystallized with hexanes/ $\text{CH}_2\text{Cl}_2$  to give the known compound  $[\text{Et}_4\text{N}][\text{BrCr}(\text{CO})_5]^{11}$ .

**Reaction of  $[\text{Bu}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Bu}_4\text{N}]_2[\mathbf{2b}]$ ) with  $\text{PhCH}_2\text{Br}$ .** To a solution of 0.72 g (0.61 mmol) of  $[\text{Bu}_4\text{N}]_2[\mathbf{2b}]$  in 7.5 mL of THF was added 0.08 mL (0.67 mmol) of  $\text{PhCH}_2\text{Br}$ . The resulting solution was stirred in an ice/water bath for 20 min, then warmed to room temperature, and stirred for another 2.5 h. The solvent was removed under vacuum, and the organic product—toluene (0.373 mmol, 61% based on  $[\text{Bu}_4\text{N}]_2[\mathbf{2b}]$ ) was quantified and identified by GC and GC/MS. Then the THF extract was recrystallized with ether/THF to give 0.50 g (0.396 mmol) of the pure compound  $[\text{Bu}_4\text{N}][\text{BrSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Bu}_4\text{N}][\mathbf{5}]$ ) (65% based on  $[\text{Bu}_4\text{N}]_2[\mathbf{2b}]$ ). IR ( $\nu_{\text{CO}}$ , THF): 2012 vs, 1929 vs, 1865  $\text{s cm}^{-1}$ . Anal. Calcd for  $[\text{Bu}_4\text{N}][\mathbf{5}]$ : C, 44.71; H, 5.75; N, 2.22. Found: C, 44.61; H, 5.82; N, 2.05.

**Reaction of  $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ) with  $\text{HC}\equiv\text{CCH}_2\text{Br}$ .** To a solution of 0.52 g (0.54 mmol) of  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$  in 20 mL of THF was added 0.055 mL (0.73 mmol) of  $\text{HC}\equiv\text{CCH}_2\text{Br}$ . The resulting solution was stirred in an ice/water bath for 20 min, then warmed to room temperature, and stirred for another 4 h. The solvent was removed under vacuum, and the  $\text{CH}_2\text{Cl}_2$  extract was recrystallized with  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  to give 0.43 g (0.41 mmol) of the pure compound  $[\text{Et}_4\text{N}][\text{BrSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}][\mathbf{5}]$ ) (76% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ).

**Reaction of  $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ) with  $\text{CH}_3(\text{CH}_2)_5\text{C}(\text{O})\text{Cl}$ .** To a solution of 0.63 g (0.66 mmol) of  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$  in 7.5 mL of THF was added 0.12 mL (0.78 mmol) of  $\text{CH}_3(\text{CH}_2)_5\text{C}(\text{O})\text{Cl}$ . The resulting solution was stirred in an ice/water bath for 20 min, then the solvent was removed under vacuum. The organic product— $\text{CH}_3(\text{CH}_2)_5\text{CHO}$  (>0.40 mmol, 61% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ) was quantified and identified by GC and GC/MS. The THF extract was recrystallized with ether/THF to give 0.55 g (0.55 mmol) of the pure compound  $[\text{Et}_4\text{N}][\text{ClSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}][\mathbf{6}]$ ) (83% based on  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$ ). IR ( $\nu_{\text{CO}}$ , THF): 2012 vs, 1930 vs, 1869  $\text{s cm}^{-1}$ . Anal. Calcd for  $[\text{Et}_4\text{N}][\mathbf{6}]$ : C, 37.46; H, 4.06; N, 2.82. Found: C, 37.44; H, 4.01; N, 2.69.

**Reaction of  $[\text{Et}_4\text{N}]_2[\text{BrSb}\{\text{Cr}(\text{CO})_5\}_3]$  ( $[\text{Et}_4\text{N}][\mathbf{5}]$ ) with  $\text{CH}_3\text{C}(\text{O})\text{Cl}$ .** To a solution of 0.24 g (0.23 mmol) of  $[\text{Et}_4\text{N}][\mathbf{5}]$  in 20 mL of THF in an ice/water bath was added 0.04 mL (0.56 mmol) of  $\text{CH}_3\text{C}(\text{O})\text{Cl}$ . The mixture was stirred in an ice/water bath for 30 min and then warmed to room temperature and stirred for 1 day. The resultant solution was filtered to collect the filtrate, and the solvent was removed under vacuum. The residue was extracted with mixed solvents of THF/hexanes = 2:3; the extract was then recrystallized with hexanes/ $\text{CH}_2\text{Cl}_2$  to give 0.09 g (0.13 mmol) of the pure compound  $[\text{Et}_4\text{N}][\text{Cl}_2\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[\text{Et}_4\text{N}][\mathbf{7}]$ ) (57% based on  $[\text{Et}_4\text{N}][\mathbf{5}]$ ). Crystals suitable

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**Table 1.** Crystallographic Data for [Et<sub>4</sub>N][H<sub>2</sub>As{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][1]), [Et<sub>4</sub>N]<sub>2</sub>[HSb{Cr(CO)<sub>5</sub>}<sub>3</sub>] ([Et<sub>4</sub>N][2b]), and [Bu<sub>4</sub>N][BrISb{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> ([Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>)

	[Et <sub>4</sub> N][1]	[Et <sub>4</sub> N][2b]	[Bu <sub>4</sub> N][8]·0.5CH <sub>2</sub> Cl <sub>2</sub>
empirical formula	C <sub>18</sub> H <sub>22</sub> AsCr <sub>2</sub> NO <sub>10</sub>	C <sub>31</sub> H <sub>41</sub> Cr <sub>3</sub> N <sub>2</sub> O <sub>15</sub> Sb	C <sub>26.5</sub> H <sub>37</sub> NO <sub>10</sub> Cr <sub>2</sub> SbIBrCl
fw	591.28	959.40	997.58
cryst syst	triclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Pcnb</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	8.988(5)	13.224(5)	17.073(3)
<i>b</i> , Å	12.123(4)	23.477(3)	14.288(3)
<i>c</i> , Å	12.4341(21)	26.754(4)	17.074(3)
$\alpha$ , deg	79.769(2)		
$\beta$ , deg	78.60(3)		110.42(3)
$\gamma$ , deg	74.15(4)		
<i>V</i> , Å <sup>3</sup>	1266.6(8)	8306(3)	3903.3(13)
<i>Z</i>	2	8	4
<i>D</i> (calcd), g cm <sup>-3</sup>	1.550	1.534	1.698
$\mu$ , cm <sup>-1</sup>	22.0	14.7	31.362
diffractometer	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)
radiation $\lambda$ , Å	0.709 30	0.709 30	0.710 73
temp, °C	25	25	25
$2\theta$ range, deg	18.46–24.18	20.50–27.88	18.40–21.54
<i>t</i> <sub>min</sub> / <i>t</i> <sub>max</sub>	0.53/0.62	0.58/0.72	0.375/0.503
independent reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3271	3691	4104
<i>R</i> , <sup>a</sup> <i>R</i> <sub>w</sub> <sup>a</sup>	0.048, 0.041	0.057, 0.048	0.036, 0.038

<sup>a</sup> The functions minimized during least-squares cycles were  $R = \sum |F_o - F_c| / \sum F_o$  and  $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ .

**Table 2.** Crystallographic Data for [Et<sub>4</sub>N]<sub>2</sub>[HAS{Cr(CO)<sub>5</sub>}<sub>3</sub>] ([Et<sub>4</sub>N][2a]), [Et<sub>4</sub>N][(Br)(PhCH<sub>2</sub>)As{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][3]), and [Et<sub>4</sub>N][Cl<sub>2</sub>Sb{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][7])

	[Et <sub>4</sub> N][2a]	[Et <sub>4</sub> N][3]	[Et <sub>4</sub> N][7]
empirical formula	C <sub>31</sub> H <sub>41</sub> AsCr <sub>3</sub> N <sub>2</sub> O <sub>15</sub>	C <sub>25</sub> H <sub>27</sub> AsBrCr <sub>2</sub> NO <sub>10</sub>	C <sub>18</sub> H <sub>20</sub> Cl <sub>2</sub> Cr <sub>2</sub> NO <sub>10</sub> Sb
fw	912.58	760.31	707.00
cryst syst	monoclinic	monoclinic	orthorhombic
space group	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>	<i>Pna2<sub>1</sub></i>
<i>a</i> , Å	13.4332(3)	21.5470(30)	11.9041(3)
<i>b</i> , Å	13.8294(4)	12.39990(10)	13.1714(4)
<i>c</i> , Å	22.4643(6)	23.5648(3)	35.6497(7)
$\beta$ , deg	92.410(1)	100.1770(10)	
<i>V</i> , Å <sup>3</sup>	4169.6(2)	6197.00(13)	5589.6(2)
<i>Z</i>	4	8	8
<i>D</i> (calcd), g cm <sup>-3</sup>	1.454	1.630	1.680
$\mu$ , cm <sup>-1</sup>	16.18	31.02	19.61
diffractometer	SMART CCD	SMART CCD	SMART CCD
radiation $\lambda$ , Å	0.710 73	0.710 73	0.710 73
temp, °C	22	-123	23
$\theta$ range, deg	1.73–23.26	1.76–25.00	1.14–25.00
independent reflns	5991 ( <i>R</i> <sub>int</sub> = 0.0476)	5465 ( <i>R</i> <sub>int</sub> = 0.0289)	4912 ( <i>R</i> <sub>int</sub> = 0.0334)
goodness-of-fit on <i>F</i> <sup>2</sup>	1.050	1.041	1.146
<i>R</i> <sup>1</sup> / <i>wR</i> <sup>2</sup> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0496/0.1097	0.0289/0.0681	0.0396/0.0998
<i>R</i> <sup>1</sup> / <i>wR</i> <sup>2</sup> <sup>b</sup> (all data)	0.0878/0.1306	0.0437/0.0762	0.0451/0.1098

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

for X-ray diffraction were grown from hexanes/CH<sub>2</sub>Cl<sub>2</sub>. IR ( $\nu_{CO}$ , THF): 2065 m, 2043 s, 1950 vs cm<sup>-1</sup>. Negative ion FABMS: *m/z* 576.6. Anal. Calcd for [Et<sub>4</sub>N][7]: C, 30.58; H, 2.85; N, 1.98. Found: C, 30.68; H, 2.87; N, 1.96. The residue was then extracted with CH<sub>2</sub>-Cl<sub>2</sub>, and the CH<sub>2</sub>Cl<sub>2</sub> extract was recrystallized with hexanes/CH<sub>2</sub>Cl<sub>2</sub> to give 0.05 g (0.11 mmol) of the known compound [Et<sub>4</sub>N][ClCr(CO)<sub>5</sub>].<sup>11</sup> IR ( $\nu_{CO}$ , THF): 2060 w, 1923 vs, 1856 m cm<sup>-1</sup>. Anal. Calcd for [Et<sub>4</sub>N]-[ClCr(CO)<sub>5</sub>]: C, 43.65; H, 5.63; N, 3.92. Found: C, 43.65; H, 5.62; N, 3.80.

**Reaction of [Bu<sub>4</sub>N]<sub>2</sub>[BrSb{Cr(CO)<sub>5</sub>}<sub>3</sub>] ([Bu<sub>4</sub>N]<sub>2</sub>[5]) with CH<sub>2</sub>I<sub>2</sub>.** To a solution of 0.51 g (0.40 mmol) of [Bu<sub>4</sub>N]<sub>2</sub>[5] in 20 mL of THF in an ice/water bath was added 0.1 mL (1.24 mmol) of CH<sub>2</sub>I<sub>2</sub>. The mixture was stirred in an ice/water bath for 10 min and then warmed to room temperature and stirred for 4 days. The resultant solution was filtered to collect the filtrate, and the solvent was removed under vacuum. The residue was extracted with mixed solvents of ether/hexanes = 2:1; the extract was then recrystallized with hexanes/CH<sub>2</sub>-Cl<sub>2</sub> to give 0.23 g (0.24 mmol) of the pure compound [Bu<sub>4</sub>N][BrISb{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Bu<sub>4</sub>N][8]) (60% based on [Bu<sub>4</sub>N]<sub>2</sub>[5]). Crystals suitable for X-ray diffraction were grown from hexanes/CH<sub>2</sub>Cl<sub>2</sub>. IR ( $\nu_{CO}$ , THF): 2061 m, 2042 s, 1950 vs, 1920 s cm<sup>-1</sup>. Negative ion FABMS:

*m/z* 712.7. Anal. Calcd for [Bu<sub>4</sub>N][8]: C, 31.91; H, 3.74; N, 1.40. Found: C, 31.92; H, 3.68; N, 1.35. The residue was then extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the extract was then recrystallized with hexanes/CH<sub>2</sub>Cl<sub>2</sub> to give the known compound [Bu<sub>4</sub>N][ICr(CO)<sub>5</sub>].<sup>11</sup> IR ( $\nu_{CO}$ , THF): 2052 w, 1922 vs, 1865 s cm<sup>-1</sup>. Anal. Calcd for [Bu<sub>4</sub>N][ICr(CO)<sub>5</sub>]: C, 44.93; H, 6.46; N, 2.49. Found: C, 44.89; H, 6.26; N, 2.53.

**X-ray Structural Characterization of Complexes [Et<sub>4</sub>N][1], [Et<sub>4</sub>N]<sub>2</sub>[2a], [Et<sub>4</sub>N]<sub>2</sub>[2b], [Et<sub>4</sub>N][3], [Et<sub>4</sub>N][7], and [Bu<sub>4</sub>N][8].** A summary of selected crystallographic data for [Et<sub>4</sub>N][1], [Et<sub>4</sub>N]<sub>2</sub>[2a], [Et<sub>4</sub>N]<sub>2</sub>[2b], [Et<sub>4</sub>N][3], [Et<sub>4</sub>N][7], and [Bu<sub>4</sub>N][8] is given in Tables 1 and 2. Data collection for [Et<sub>4</sub>N][1], [Et<sub>4</sub>N]<sub>2</sub>[2b], and [Bu<sub>4</sub>N][8] was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation at 25 °C employing the  $\theta/2\theta$  scan mode. A  $\psi$ -scan absorption correction was made.<sup>12</sup> Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,<sup>13</sup> and atomic scattering factors were taken from ref 14. Data

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**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for [Et<sub>4</sub>N][H<sub>2</sub>AsCr<sub>2</sub>{(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][1])

(A) Distances			
As—Cr(1)	2.518(2)	As—Cr(2)	2.515 (1)
(B) Angles			
Cr(1)—As—Cr(2)	133.86(5)	H(1)—As—H(2)	89.56(4)
Cr(1)—As—H(1)	101.87(5)	Cr(1)—As—H(2)	99.91(5)
Cr(2)—As—H(1)	114.59(5)	Cr(2)—As—H(2)	107.36(5)

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg) for [Et<sub>4</sub>N]<sub>2</sub>[HAsCr<sub>3</sub>{(CO)<sub>5</sub>}<sub>3</sub>] ([Et<sub>4</sub>N][2a])

(A) Distances			
As—H	1.58(4)	As—Cr(1)	2.6120(10)
As—Cr(2)	2.6151(11)	As—Cr(3)	2.6127(11)
(B) Angles			
H—As—Cr(1)	100.9(13)	H—As—Cr(2)	101.2(13)
H—As—Cr(3)	98.0(12)	Cr(1)—As—Cr(2)	116.60(4)
Cr(1)—As—Cr(3)	117.90(4)	Cr(2)—As—Cr(3)	116.61(4)

collection for [Et<sub>4</sub>N]<sub>2</sub>[2a], [Et<sub>4</sub>N][3], and [Et<sub>4</sub>N][7] was carried out on a SMART CCD diffractometer. A SADABS scan absorption correction was made,<sup>15</sup> and all calculations were performed using SHELXTL packages.<sup>16</sup>

**Structures of [Et<sub>4</sub>N][1], [Et<sub>4</sub>N]<sub>2</sub>[2a], [Et<sub>4</sub>N]<sub>2</sub>[2b], [Et<sub>4</sub>N][3], [Et<sub>4</sub>N][7], and [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>.** The crystal of [Et<sub>4</sub>N][1] chosen for diffraction measurement was ca. 0.50 mm × 0.15 mm × 0.12 mm. The crystal of [Et<sub>4</sub>N]<sub>2</sub>[2a] had dimensions 0.38 mm × 0.25 mm × 0.05 mm. The crystal of [Et<sub>4</sub>N]<sub>2</sub>[2b] had dimensions 0.35 mm × 0.30 mm × 0.30 mm. The crystal of [Et<sub>4</sub>N][3] had dimensions 0.25 mm × 0.20 mm × 0.20 mm. The crystal of [Et<sub>4</sub>N][7] had dimensions 0.40 mm × 0.35 mm × 0.30 mm, and the crystal of [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub> had dimensions 0.40 mm × 0.30 mm × 0.20 mm. Cell parameters were obtained from 25 reflections with 2θ angle in the range 18.46–24.18° for [Et<sub>4</sub>N][1], 20.5° < 2θ < 27.88° for [Et<sub>4</sub>N]<sub>2</sub>[2b], 18.4° < 2θ < 21.54° for [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>, 1.73° < θ < 23.26° for [Et<sub>4</sub>N]<sub>2</sub>[2a], 1.76° < θ < 25.00° for [Et<sub>4</sub>N][3], and 1.14° < θ < 25.00° for [Et<sub>4</sub>N][7]. A total of 3271 reflections with *I* > 2.5σ(*I*) for [Et<sub>4</sub>N][1] (5991 reflections with *I* > 2.0σ(*I*) for [Et<sub>4</sub>N]<sub>2</sub>[2a], 3691 reflections with *I* > 2.0σ(*I*) for [Et<sub>4</sub>N]<sub>2</sub>[2b], 5163 reflections with *I* > 2.0σ(*I*) for [Et<sub>4</sub>N][3], 4827 reflections with *I* > 2.0σ(*I*) for [Et<sub>4</sub>N][7], and 4104 reflections with *I* > 2.0σ(*I*) for [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>) were refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. For [Et<sub>4</sub>N][1], the dihydrides were found from Fourier difference maps, approximately 1.600 Å from the As atom, but not refined in the least-squares cycle. For [Et<sub>4</sub>N]<sub>2</sub>[2a], the hydride was located crystallographically and refined isotropically, while for [Et<sub>4</sub>N]<sub>2</sub>[2b], the hydride was found from Fourier difference maps, approximately 1.799 Å from the Sb atom, but not refined in the least-squares cycle. Full-matrix least-squares refinement led to convergence with *R* = 4.9% and *R*<sub>w</sub> = 4.2% for [Et<sub>4</sub>N][1], with *R*1 = 4.96% and *wR*2 = 10.97% for [Et<sub>4</sub>N]<sub>2</sub>[2a], with *R* = 5.6% and *R*<sub>w</sub> = 4.7% for [Et<sub>4</sub>N]<sub>2</sub>[2b], with *R*1 = 2.89% and *wR*2 = 6.81% for [Et<sub>4</sub>N][3], with *R*1 = 3.69% and *wR*2 = 9.98% for [Et<sub>4</sub>N][7], and with *R* = 3.6% and *R*<sub>w</sub> = 3.8% for [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>.

The selected bond distances and angles for [Et<sub>4</sub>N][1], [Et<sub>4</sub>N]<sub>2</sub>[2a], [Et<sub>4</sub>N]<sub>2</sub>[2b], [Et<sub>4</sub>N][3], [Et<sub>4</sub>N][7], and [Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub> are represented in Tables 3–8, respectively. Additional crystallographic data are available as Supporting Information.

## Results and Discussion

**Syntheses of the Hydrido Complexes 1, 2a, and 2b.** Chromium hexacarbonyl can react with As<sub>2</sub>O<sub>3</sub> in concentrated methanolic KOH solution to give the chromium–arsenic

**Table 5.** Selected Bond Distances (Å) and Bond Angles (deg) for [Et<sub>4</sub>N]<sub>2</sub>[HSbCr<sub>3</sub>{(CO)<sub>5</sub>}<sub>3</sub>] ([Et<sub>4</sub>N][2b])

(A) Distances			
Sb—Cr(1)	2.727(2)	Sb—Cr(2)	2.741(2)
Sb—Cr(3)	2.738(2)		
(B) Angles			
H(1)—Sb—Cr(1)	95.42(5)	H(1)—Sb—Cr(2)	103.83(5)
H(1)—Sb—Cr(3)	101.57(5)	Cr(1)—Sb—Cr(2)	116.79(6)
Cr(1)—Sb—Cr(3)	116.86(7)	Cr(2)—Sb—Cr(3)	116.98(7)

**Table 6.** Selected Bond Distances (Å) and Bond Angles (deg) for [Et<sub>4</sub>N][(Br)(PhCH<sub>2</sub>))As{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][3])

(A) Distances			
As(1)—Cr(1)	2.5071(6)	As(1)—Cr(2)	2.5115(5)
As(1)—Br(1)	2.4081(4)	As(1)—C(11)	2.001(3)
C(11)—C(12)	1.495(4)		
(B) Angles			
Cr(1)—As(1)—Cr(2)	124.00(2)	C(11)—As(1)—Br(1)	95.11(9)
Br(1)—As(1)—Cr(1)	106.12(5)	Br(1)—As(1)—Cr(2)	108.16(2)
C(11)—As(1)—Cr(1)	114.51(9)	C(11)—As(1)—Cr(2)	105.18(8)

**Table 7.** Selected Bond Distances (Å) and Bond Angles (deg) for [Et<sub>4</sub>N][Cl<sub>2</sub>Sb{Cr(CO)<sub>5</sub>}<sub>2</sub>] ([Et<sub>4</sub>N][7])

(A) Distances			
Sb(1)—Cl(1)	2.441(4)	Sb(1)—Cl(2)	2.419(4)
Sb(1)—Cr(1)	2.582(2)	Sb(1)—Cr(2)	2.587(2)
(B) Angles			
Cr(1)—Sb(1)—Cr(2)	129.01(6)	Cl(1)—Sb(1)—Cl(2)	93.7(2)
Cl(1)—Sb(1)—Cr(1)	107.2(1)	Cl(1)—Sb(1)—Cr(2)	107.7 (1)
Cl(2)—Sb(1)—Cl(1)	107.1(1)	Cl(2)—Sb(1)—Cr(2)	106.5(1)

**Table 8.** Selected Bond Distances (Å) and Bond Angles (deg) for [Bu<sub>4</sub>N][BrSb{Cr(CO)<sub>5</sub>}<sub>2</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub> ([Bu<sub>4</sub>N][8]·0.5CH<sub>2</sub>Cl<sub>2</sub>)

(A) Distances			
Sb—Br	2.697(1)	Sb—I	2.7974(8)
Sb—Cr(1)	2.621 (1)	Sb—Cr(2)	2.627(1)
(B) Angles			
Cr(1)—Sb—Cr(2)	132.96(4)	I—Sb—Br	93.02(3)
Br—Sb—Cr(1)	104.11(4)	Br—Sb—Cr(2)	105.90(4)
I—Sb—Cr(1)	106.23(3)	I—Sb—Cr(2)	107.44(3)

dihydrido complex [H<sub>2</sub>As{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> (**1**) as the major product and the monohydrido complex [HAs{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> (**2a**) as the minor product. Under similar conditions, the reaction with Sb<sub>2</sub>O<sub>3</sub> only yields the monohydrido complex [HSb{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> (**2b**); however, the dihydrido complex [H<sub>2</sub>Sb{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> is not observed. This can be rationalized that the larger size of Sb could favor the three chromium substituents to bind more than for As where two chromium substituents may be accommodated easily but three are sterically less favorable. The anionic complexes **1**, **2a**, and **2b** can be isolated as the [Et<sub>4</sub>N]<sup>+</sup> salts by metathesis, and they are fully characterized by single-crystal X-ray analyses and/or spectroscopic methods. Complex **1** can be viewed as a central As(V) ion coordinated to two Cr(CO)<sub>5</sub><sup>2−</sup> groups and two hydrides. Similarly, complexes **2** and **3** are described as a central As(V) or Sb(V) ion each bonded to three Cr(CO)<sub>5</sub><sup>2−</sup> groups and one hydride.

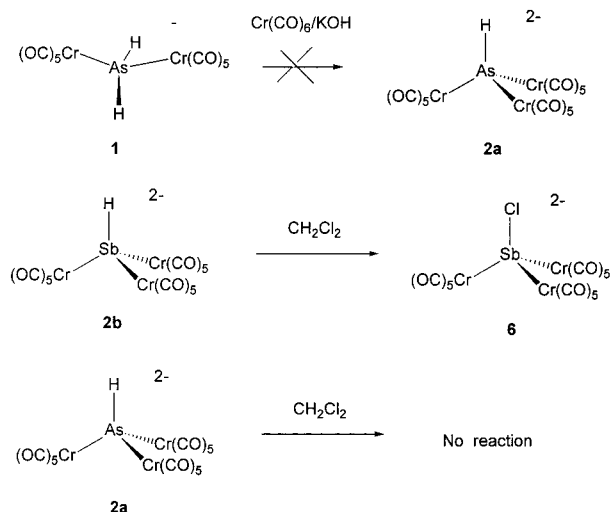
The most interesting feature of **1**, **2a**, and **2b** is the presence of the hydrides bound to the main group atom. They can be located from the difference maps of the X-ray analyses and are also inferred on the basis of electron-counting considerations, and, most importantly, from <sup>1</sup>H NMR data analysis. The <sup>1</sup>H NMR spectra exhibit singlets at δ 0.0 for [H<sub>2</sub>As{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> (**1**), δ −2.0 for [HAs{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> (**2a**), and δ −5.5 for [HSb{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> (**2b**). These results indicate that the hydridic character of the hydrogens increases in the order of **1** < **2a** < **2b** attributable to the increased negative charge of the complexes

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

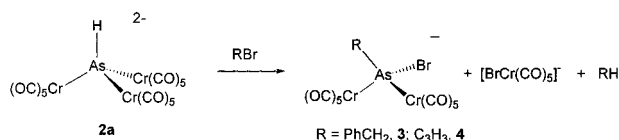
(15) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1996.

(16) Sheldrick, G. M. *SHELXTL, Program for Crystal Structure Detection*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

## Scheme 1



## Scheme 2



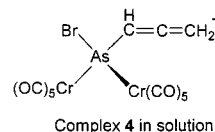
and the increased acidity from As to Sb. Moreover, the values for the monohydrido complexes (**2a** and **2b**) are different from those in the isoelectronic iron complexes  $[\text{HAs}\{\text{Fe(CO)}_4\}_3]^{2-}$  ( $\delta$  1.34) and  $[\text{HSb}\{\text{Fe(CO)}_4\}_3]^{2-}$  ( $\delta$  -1.39).<sup>7</sup> This implies that these hydrogens in chromium-containing complexes **2a** and **2b** are more hydridic than those in the corresponding iron complexes because of the more electropositive character of Cr.

**General Reactivity of 1, 2a, and 2b.** Is the dihydrido complex **1** an intermediate for the formation of the monohydrido complex **2a**? To answer this, we treated **1** with  $\text{Cr(CO)}_6/\text{KOH}$  under controlled conditions. However, **1** was not transformed into **2a**. Therefore, complexes **1** and **2a** result from different reaction pathways. Interestingly, while the hydridoantimony complex **2b** was found to form the chloroantimony complex  $[\text{ClSb}\{\text{Cr(CO)}_5\}_3]^{2-}$  (**6**) in  $\text{CH}_2\text{Cl}_2$  solutions, the hydridoarsenic complex **2a** was not transformed to the corresponding chloroarsenic complex in  $\text{CH}_2\text{Cl}_2$  solutions (Scheme 1).

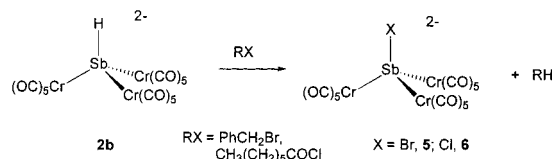
**Reactions of 2a and 2b with RX.** Knowing that the hydride atom of **2b**, but not **2a**, can be easily replaced by chloride in  $\text{CH}_2\text{Cl}_2$  solutions, we systematically compared the chemical reactivity of **2a** and **2b** with organic halogen derivatives.

In the As–Cr system, surprisingly, complex **2a** was found to react with  $\text{RBr}$  ( $\text{R} = \text{PhCH}_2$ ,  $\text{HC}\equiv\text{CCH}_2$ ), via the formation of the As–R and As–Br bonds, to give the  $\text{RX}$  addition products  $[(\text{R})(\text{Br})\text{As}\{\text{Cr(CO)}_5\}_2]^-$  ( $\text{R} = \text{PhCH}_2$ , **3**;  $\text{R} = \text{C}_3\text{H}_5$ , **4**) along with  $[\text{BrCr(CO)}_5]^-$  (Scheme 2). In the former case, the hydrogen-transferred organic product  $\text{RH}$ —toluene was also detected and identified by GC and GC/MS. The yield of  $\text{RH}$  is around 60% based on **2a**. However, the detailed mechanism for the formation of  $\text{R-H}$  is not clear and may occur via hydride transfer<sup>17</sup> or single electron-transfer processes.<sup>18</sup> Further study is required to understand the mechanistic details.

## Scheme 3



## Scheme 4



Complexes **3** and **4** were shown to have the tetrahedral  $(\text{R})(\text{X})\text{AsCr}_2$  core geometry based on spectroscopic data, and the structure of **3** was further characterized by the single-crystal X-ray diffraction method. Note that the  $\text{C}_3\text{H}_5$  ligand of **4** in solution is of the  $\eta^1$ -allenyl type of ligation according to the  $^1\text{H}$  NMR data (two resonances at 6.80 (t, 1H,  $J = 6.23$  Hz) and 5.06 (d, 2H,  $J = 6.23$  Hz)) (Scheme 3).<sup>19</sup>

In the Sb–Cr system, the reactions of **2b** with  $\text{RX}$  ( $\text{RX} = \text{PhCH}_2\text{Br}$  or  $\text{HC}\equiv\text{CCH}_2\text{Br}$ ,  $\text{CH}_3(\text{CH}_2)_5\text{C(O)Cl}$ ), however, gave the haloantimony complexes  $[\text{XSb}\{\text{Cr(CO)}_5\}_3]^{2-}$  ( $\text{X} = \text{Br}$ , **5**;  $\text{X} = \text{Cl}$ , **6**). The corresponding hydrogen-transferred organic products  $\text{RH}$  ( $\text{R} = \text{PhCH}_2$ ,  $\text{CH}_3(\text{CH}_2)_5\text{C(O)}$ ) have been characterized and quantified by GC and GC/MS spectroscopy (Scheme 4). Note that the yields of the hydrogen-transferred product  $\text{RH}$  in both cases are around 60% based on **2b**, close to that found in the As–Cr system and indicative of the comparable hydrogen-transferring efficiency of **2a** and **2b**.

From the above-mentioned results, the contrasting chemical reactivity of complexes **2a** and **2b** toward organic halides is evident. While complex **2a** produces the  $\text{RX}$  addition products, complex **2b** gives the  $\text{X}$ -substituted products. The size effect of As and Sb could be taken into account in terms of toleration of the negative charge of the resultant complexes. The  $\text{RX}$  addition products **3** and **4** each bear only one negative charge, which can be stabilized by the smaller As atom, whereas the haloantimony complexes **5** and **6** each possess two negative charges that are better stabilized by the larger Sb atom. However, on the basis of the yields of formation of  $\text{R-H}$ , the hydrogen transferring efficiency of **2a** and **2b** is about the same and cannot be distinguishable under our conditions, although the  $^1\text{H}$  NMR chemical shifts indicate that the hydrogen atom of **2b** is more hydridic than that of **2a**.

**Mixed Dihaloantimony Complexes.** Different halides can be introduced into **2b**. The bromoantimony complex **5** can be produced from **2b** with  $\text{PhCH}_2\text{Br}$ . The mixed dihaloantimony complex  $[\text{BrISb}\{\text{Cr(CO)}_5\}_2]^-$  (**8**) can be obtained from the further reaction of complex **5** with  $\text{CH}_2\text{I}_2$ . These dihaloantimony complexes may form via the formation of the intermediate halostibinidene complex  $[\text{XSb}\{\text{Cr(CO)}_5\}_2]$  followed by the attack of the incoming halide. This assumption is consistent with the fact that the chloroarsinidene complex  $[\text{ClAs}\{\text{Cr(CO)}_5\}_2]$  can be attacked by Lewis bases to form the adduct.<sup>20</sup> However, if complex **5** were treated with  $\text{CH}_3\text{C(O)Cl}$ , a dichloroantimony complex  $[\text{Cl}_2\text{Sb}\{\text{Cr(CO)}_5\}_2]^-$  (**7**) would be obtained instead of the expected mixed bromochloroantimony complex. The results

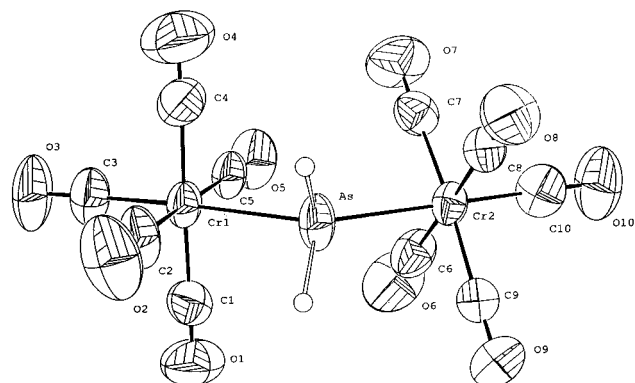
(17) (a) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646.

(b) Kao, S. C.; Gaus, P. L.; Youngdahl, K.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 1601.

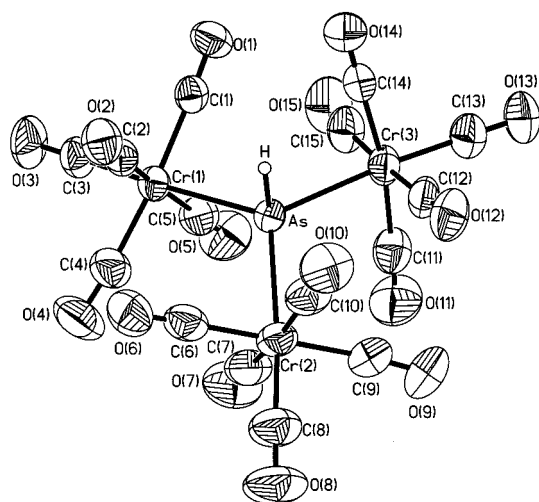
(18) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(19) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289 and references therein.

(20) von Seyerl, J.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 233.

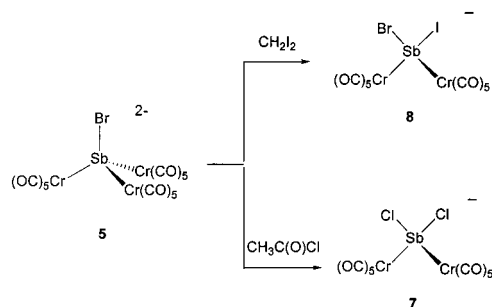


**Figure 1.** ORTEP diagram showing the structure and atom labeling for the anion **1**.



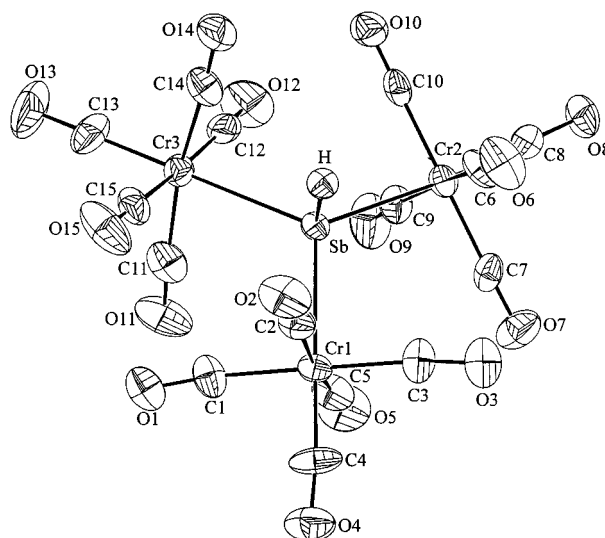
**Figure 2.** ORTEP diagram showing the structure and atom labeling for the dianion **2a**.

#### Scheme 5

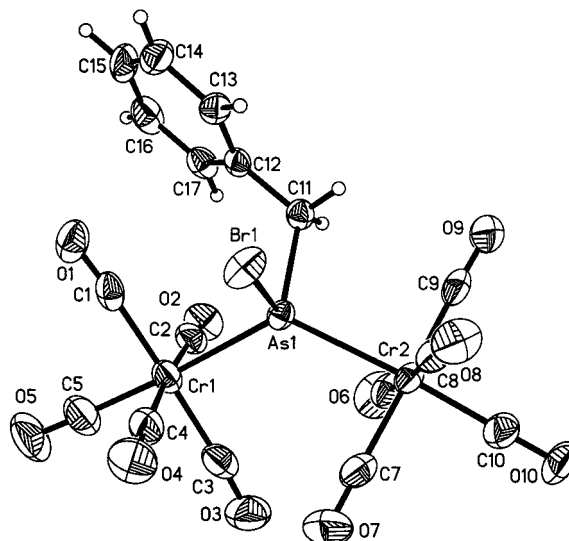


indicate that the formation of mixed dihaloantimony complexes could result from other complicated pathways and that the outcome strongly depends on the reactivity of the incoming organic halides (Scheme 5).

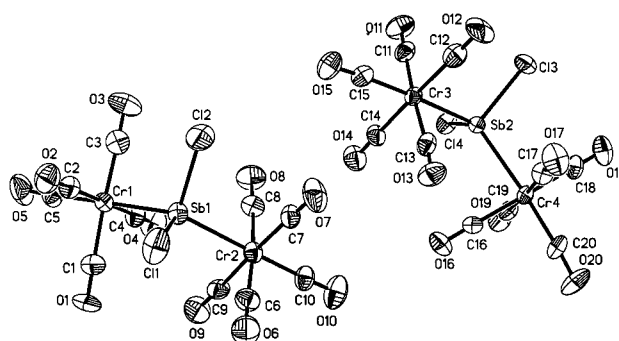
**Complexes 1–8.** All the new complexes **1–8** are fully characterized by spectroscopic methods and/or by X-ray analysis. The structures of  $[\text{Et}_4\text{N}][\mathbf{1}]$  (Figure 1),  $[\text{Et}_4\text{N}]_2[\mathbf{2a}]$  (Figure 2),  $[\text{Et}_4\text{N}]_2[\mathbf{2b}]$  (Figure 3),  $[\text{Et}_4\text{N}][\mathbf{3}]$  (Figure 4),  $[\text{Et}_4\text{N}][\mathbf{7}]$  (Figure 5), and  $[\text{Bu}_4\text{N}][\mathbf{8}]$  (Figure 6) are further determined by single-crystal X-ray diffraction in which the central atoms (As or Sb) are all in distorted tetrahedral environments. The analyses show that the dianionic complexes **2a**, **2b**, **5**, and **6** each consist of a central antimony(V) or arsenic(V) ion tetrahedrally coordinated to one hydride (or halide) and three  $\text{Cr}(\text{CO})_5^{2-}$  groups. The monoanions **1** and **7** (or **8**) are structurally similar to the dianionic **2a** or **6** (or **5**) except that one  $\text{Cr}(\text{CO})_5^{2-}$  group



**Figure 3.** ORTEP diagram showing the structure and atom labeling for the dianion **2b**.



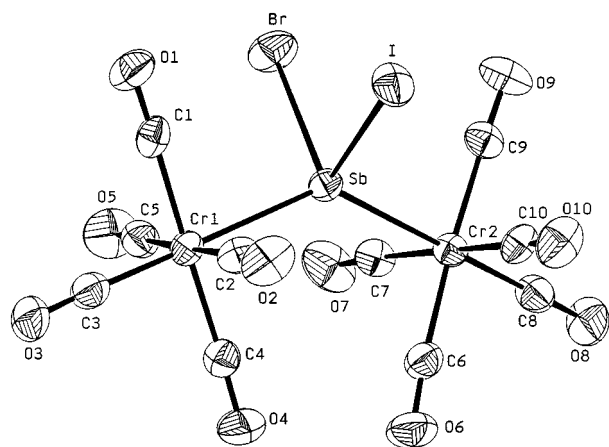
**Figure 4.** ORTEP diagram showing the structure and atom labeling for the anion **3**.



**Figure 5.** ORTEP diagram showing the structure and atom labeling for the anion **7**.

is replaced by another hydride or halide, respectively. Similarly, the monoanions **3** and **4** each display a central arsenic(V) ion bonded to two  $\text{Cr}(\text{CO})_5^{2-}$  groups, one organic  $\text{R}^-$  group, and one bromide moiety.

For comparison, the average  $\text{Cr}-\text{E}-\text{Cr}$  angle and the  $\text{E}-\text{Cr}$  distance in these tetrahedral complexes are listed in Table 9. Of the As–Cr complexes **1**, **2a**, and **3**, the average As–Cr



**Figure 6.** ORTEP diagram showing the structure and atom labeling for the anion **8**.

**Table 9.** Comparison of the Average Cr–E–Cr Angles and the Average E–Cr Distances in **1**, **2a**, **2b**, **3**, **7**, and **8**

complex	Cr–E–Cr, deg	E–Cr, Å
[H <sub>2</sub> As{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <sup>2−</sup> ( <b>1</b> )	133.86	2.516
[HAs{Cr(CO) <sub>5</sub> } <sub>3</sub> ] <sup>2−</sup> ( <b>2a</b> )	117.04	2.613
[(Br)(PhCH <sub>2</sub> )As{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <sup>−</sup> ( <b>3</b> )	124.00	2.509
[HSb{Cr(CO) <sub>5</sub> } <sub>3</sub> ] <sup>2−</sup> ( <b>2b</b> )	116.88	2.735
[Cl <sub>2</sub> Sb{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <sup>−</sup> ( <b>7</b> )	129.01	2.585
[BrISb{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <sup>−</sup> ( <b>8</b> )	132.96	2.624

distance in **2a** is the greatest because of the steric effect of the Cr(CO)<sub>5</sub> group. The average As–Cr bond length in **2a** is 2.613(1) Å, which is not only significantly longer than those of the As–Cr multiple bonds in ClAs{Cr(CO)<sub>5</sub>}<sub>2</sub> (av 2.324(2) Å),<sup>3</sup> PhAs{Cr(CO)<sub>5</sub>}<sub>2</sub> (av 2.385(3) Å),<sup>3</sup> Mn(CO)<sub>5</sub>As{Cr(CO)<sub>5</sub>}<sub>2</sub> (av 2.429(4) Å),<sup>4</sup> Mn(CO)<sub>5</sub>As(μ-CO){Cr(CO)<sub>4</sub>}<sub>2</sub> (av 2.349(5) Å),<sup>4</sup> and (tBu)As{Cr(CO)<sub>5</sub>}<sub>2</sub> (av 2.345(1) Å)<sup>21</sup> but also greater than those of the As–Cr single bonds in [Et<sub>4</sub>N]<sub>2</sub>[**1**] (av 2.516(2) Å) and As<sub>2</sub>Cr<sub>3</sub>Co<sub>2</sub>(CO)<sub>20</sub> (av 2.422(2) Å).<sup>22</sup> For **1** and **3**, the average As–Cr bond lengths are 2.516 and 2.509 Å, respectively, and are close to those of the reported As–Cr single bonds. The lengthening of the As–Cr bonds in **2a** is evident and caused

by the steric crowding of the three chromium carbonyl fragments. On the other hand, the Cr–As–Cr bond angle increases as the number of the Cr(CO)<sub>5</sub> fragments decreases.

Similarly, of the Sb–Cr complexes **2b**, **7**, and **8**, the Sb–Cr distance is the greatest in **2b** and similar to those in **7** and **8**. The average Sb–Cr bond length in [Et<sub>4</sub>N]<sub>2</sub>[**2b**] is 2.735(2) Å, which is larger than those of the Sb–Cr multiple bonds in [Sb{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>−</sup> (av 2.630(3) Å)<sup>4</sup> and that in [SbFe<sub>3</sub>Cr(CO)<sub>17</sub>]<sup>−</sup> (2.6382(9) Å).<sup>23</sup> However, the Sb–Cr distances in **7** and **8** (2.585(2), 2.624(1) Å) are normal. The lengthening of these Sb–Cr bonds in **2b** is again influenced by the steric crowding of the three chromium carbonyl fragments. As shown, the steric effect of the substituents on the Sb atoms is also reflected in the trends of the Cr–Sb–Cr angles.

## Conclusion

We have developed a facile route to a new series of group 15–chromium carbonyl hydrido complexes [H<sub>2</sub>As{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> and [HE{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> (E = As, Sb). The contrasting reactivity patterns of the dianionic hydrido complexes [HE(Cr(CO)<sub>5</sub>)<sub>3</sub>]<sup>2−</sup> (E = As, Sb) toward organic halogen derivatives are demonstrated. While the reaction of [HAs{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> with RX yields the RX addition products [(R)(X)As{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup>, the treatment of [HSb{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> with RX forms the halo-substituted complexes [XSb{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>2−</sup> probably because of the greater ease of toleration of the higher negative charge of the resultant complexes by the larger Sb atom. The hydrogen-transferring efficiency of [HE(Cr(CO)<sub>5</sub>)<sub>3</sub>]<sup>2−</sup> (E = As, Sb) with RX to form R–H is comparable under our conditions. Additionally, the interesting dihaloantimony complexes [XX'Sb{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> can be obtained from the reaction of [HSb(Cr(CO)<sub>5</sub>)<sub>3</sub>]<sup>2−</sup> with the appropriate organic halides.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for complexes [Et<sub>4</sub>N][**1**], [Et<sub>4</sub>N]<sub>2</sub>[**2a**], [Et<sub>4</sub>N]<sub>2</sub>[**2b**], [Et<sub>4</sub>N]-[**3**], [Et<sub>4</sub>N][**7**], and [Bu<sub>4</sub>N][**8**]·0.5CH<sub>2</sub>Cl<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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