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Synthesis and Characterization of the New Series of Chromium–Group 15 Hydride Complexes $[\text{Et}_4\text{N}]_2[\text{HE}\{\text{Cr}(\text{CO})_5\}_3]$ (E = As, Sb)

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Summary: The new series of trigonal-pyramidal chromium complexes $[\text{HE}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$ (E = As (**1a**), Sb (**1b**)) were obtained from the reactions of E_2O_3 (E = As, Sb) with $\text{Cr}(\text{CO})_6$ in concentrated KOH methanolic solution. These are the first examples of group 6 complexes containing E–H fragments (E = As, Sb), and the hydrogens are shown to be more hydridic than those in the related iron complexes due to the more electropositive character of Cr.

Transition-metal complexes containing main-group fragments have attracted extensive attention due to

their unusual bonding and reactivity patterns.¹ The rich chemistry of iron carbonyl species in combination with group 15 elements² prompted us to explore the chromium–group 15 carbonyl system. In contrast to the well-developed iron–group 15 carbonyl complexes, studies of the class of Cr–E–CO complexes (E = As, Sb) have been rare.^{3,4} This is largely because of the absence of generally applicable synthetic methods. In this study, we developed a facile route to the class of Cr–E–CO

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compounds and successfully synthesized the new series of trigonal-pyramidal chromium anionic complexes $[\text{HE}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$ ($\text{E} = \text{As}$ (**1a**), Sb (**1b**)). In comparison to the *closo*-tetrahedral clusters obtained in the $\text{Mo}-\text{E}-\text{CO}$ system ($\text{E} = \text{Bi}$,⁵ Sb ,⁵ As ,⁶), these chromium anionic complexes, in contrast, exhibit an open geometry. To the best of our knowledge, there are relatively few well-characterized metal carbonyl complexes containing $\text{E}-\text{H}$ ($\text{E} = \text{As}$, Sb) fragments, and the structurally authenticated examples are limited to $(\mu\text{-HAs})\text{-}\{\text{CpMn}(\text{CO})_2\}_2$,⁷ $[\text{HAS}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$,^{8,9} and $[\text{HSb}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$.⁹ Complexes **1a** and **1b** represent the first examples of group 6 complexes incorporating $\text{E}-\text{H}$ moieties ($\text{E} = \text{As}$, Sb).

Complexes **1a** and **1b** can be respectively obtained from the convenient reagents E_2O_3 ($\text{E} = \text{As}$, Sb) and $\text{Cr}(\text{CO})_6$ in highly concentrated KOH methanolic solution at room temperature. The reaction solutions were stirred for 3 days; then they were filtered, and the alkali-metal salts of **1a**¹⁰ and **1b**¹¹ were converted to the $[\text{Et}_4\text{N}]^+$ salts by cation metathesis. Different from the conditions for the $\text{Mo}-\text{E}-\text{CO}$ system ($\text{E} = \text{Bi}$, Sb , As),^{5,6} these reactions with $\text{Cr}(\text{CO})_6$ proceed in concentrated KOH methanolic solution. Single crystals of $[\text{Et}_4\text{N}]_2[\text{1a}]$

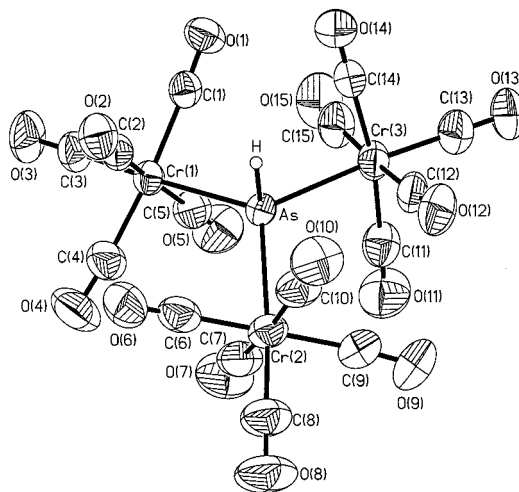


Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion of **1a**. Selected bond distances (\AA) and angles (deg): $\text{As}-\text{H} = 1.58(4)$, $\text{As}-\text{Cr}(1) = 2.612(1)$, $\text{As}-\text{Cr}(2) = 2.615(1)$, $\text{As}-\text{Cr}(3) = 2.613(1)$; $\text{Cr}(1)-\text{As}-\text{Cr}(2) = 116.60(4)$, $\text{Cr}(1)-\text{As}-\text{Cr}(3) = 117.90(4)$, $\text{Cr}(3)-\text{As}-\text{Cr}(2) = 116.61(4)$.

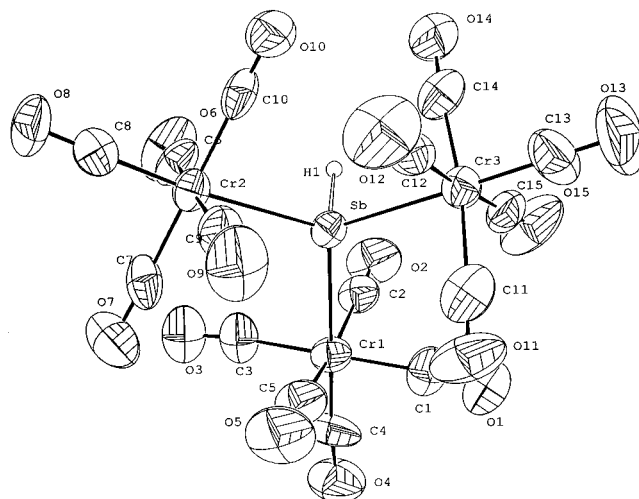


Figure 2. ORTEP diagram showing the structure and atom labeling for the dianion of **1b**. Selected bond distances (\AA) and angles (deg): $\text{Sb}-\text{Cr}(1) = 2.727(2)$, $\text{Sb}-\text{Cr}(2) = 2.741(2)$, $\text{Sb}-\text{Cr}(3) = 2.738(2)$; $\text{Cr}(1)-\text{Sb}-\text{Cr}(2) = 116.79(6)$, $\text{Cr}(1)-\text{Sb}-\text{Cr}(3) = 116.86(7)$, $\text{Cr}(2)-\text{Sb}-\text{Cr}(3) = 116.98(7)$.

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(10) The experiment was performed under a nitrogen atmosphere. To a mixture of 5.395 g (96.15 mmol) of KOH , 0.197 g (0.996 mmol) of As_2O_3 , and 1.322 g (6.007 mmol) of $\text{Cr}(\text{CO})_6$ was added 20 mL of MeOH . After it was stirred for 3 days at room temperature, the solution was filtered and an aqueous solution of 1.346 g (6.40 mmol) of Et_4NBr added, precipitating the orange product. This was collected by filtration, washed with H_2O , and dried under vacuum. Recrystallization from $\text{Et}_2\text{O}/\text{THF}$ gave 0.32 g (17.6% based on As) of $[\text{Et}_4\text{N}]_2[\text{HAS}\{\text{Cr}(\text{CO})_5\}_3]$ (**1a**). IR (ν_{CO} (cm^{-1}), THF): 2007 vs, 1914 vs, 1847 s. Anal. Calcd (found) for **1a**: C, 40.80 (40.50); H, 4.53 (4.45); N, 3.07 (3.11). ^1H NMR ($\text{DMSO}-d_6$, ppm): -2.0 s.

(11) The experiment was performed under a nitrogen atmosphere. To a mixture of 5.388 g (96.03 mmol) of KOH , 0.271 g (0.93 mmol) of Sb_2O_3 , and 1.251 g (5.685 mmol) of $\text{Cr}(\text{CO})_6$ was added 25 mL of MeOH . After it was stirred for 3 days at room temperature, the solution was filtered and an aqueous solution of 1.532 g (5.95 mmol) of Et_4NBr added, precipitating the orange product. This was collected by filtration, washed with H_2O , and dried under vacuum. Recrystallization from $\text{Et}_2\text{O}/\text{THF}$ gave 1.41 g (79% based on Sb) of $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$ (**1b**). IR (ν_{CO} (cm^{-1}), THF): 2003 vs, 1919 vs, 1860 s. Anal. Calcd (found) for **1b**: C, 38.81 (38.51); H, 4.31 (4.34); N, 2.92 (2.76). ^1H NMR ($\text{DMSO}-d_6$, ppm): -5.5 s.

(12) Crystal data for $[\text{Et}_4\text{N}]_2[\text{HAS}\{\text{Cr}(\text{CO})_5\}_3]$: monoclinic, space group $P2_1/n$, $a = 13.4332(3)$ \AA , $b = 13.8294(4)$ \AA , $c = 22.4643(6)$ \AA , $\beta = 92.410(1)^\circ$, $V = 4169.6(2)$ \AA^3 , $Z = 4$; CCD SMART diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation and Sadabs absorption correction ($T_{\text{min}} = 0.55$, $T_{\text{max}} = 0.76$). A total of 18 424 reflections were measured, and 5991 unique reflections ($2\theta < 46.52^\circ$, $R_{\text{int}} = 0.048$) were used in the refinement. All the non-hydrogen atoms were refined with anisotropic temperature factors, while the hydride was located crystallographically and refined isotropically. Full-matrix least-squares refinement on F^2 converged to $R = 0.088$ (all data), 0.050 ($I > 2\sigma(I)$); $R_w = 0.110$ (all data), 0.131 ($I > 2\sigma(I)$). All calculations were performed using SHELXTL packages.

(13) Crystal data for $[\text{Et}_4\text{N}]_2[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]$: orthorhombic, space group $Pcnb$, $a = 13.224(5)$ \AA , $b = 23.477(3)$ \AA , $c = 26.754(4)$ \AA , $V = 8306(4)$ \AA^3 , $Z = 8$, $2\theta_{\text{max}} = 51.8^\circ$, $T = 25^\circ\text{C}$, $R = 0.056$, $R_w = 0.047$ for $I > 2\sigma(I)$, Nonius CAD-4 diffractometer, $\text{Mo K}\alpha$ radiation. All the non-hydrogen atoms were refined with anisotropic temperature factors, while the hydride was found from Fourier difference maps, approximately 1.799 \AA from the Sb atom, but not refined in the least-squares cycle. All data reduction and structural refinement were performed using the NRCC-SDP-VAX packages.

suitable for X-ray analysis were grown from an ether/ CH_2Cl_2 solution,¹² and $[\text{Et}_4\text{N}]_2[\text{1b}]$ crystals were grown from a THF solution layered with ether.¹³ The ORTEP diagrams of **1a** and **1b** are shown in Figures 1 and 2, respectively, and **1a** and **1b** are isostructural. Each anion (**1a** or **1b**) displays a trigonal-pyramidal geometry of the central As (or Sb) atom and three $\text{Cr}(\text{CO})_5$ groups, in which the chromium atoms adopt an octahedral arrangement.

The average $\text{As}-\text{Cr}$ bond length in $[\text{Et}_4\text{N}]_2[\text{1a}]$ is 2.613(1) \AA , which is not only significantly longer than those of the $\text{As}-\text{Cr}$ multiple bonds in $\text{ClAs}\{\text{Cr}(\text{CO})_5\}_2$ (average 2.324(2) \AA),^{3c} $\text{PhAs}\{\text{Cr}(\text{CO})_5\}_2$ (average 2.385(3) \AA),^{3c} $\text{N}(\text{SiMe})_2\text{As}\{\text{Cr}(\text{CO})_5\}_2$ (2.381(1) \AA),^{3g} $\text{Mn}(\text{CO})_5\text{As}\{\text{Cr}(\text{CO})_5\}_2$ (average 2.429(4) \AA),^{4a} and $\text{Mn}(\text{CO})_5\text{As}(\mu\text{-CO})\{\text{Cr}(\text{CO})_4\}_2$ (average 2.349(5) \AA)^{4a} but also longer than the $\text{As}-\text{Cr}$ single bonds in $\text{As}_2\text{Cr}_3\text{Co}_2(\text{CO})_{20}$ (average 2.425(2) \AA).¹⁴ Similarly, the average $\text{Sb}-\text{Cr}$

bond length in $[\text{Et}_4\text{N}]_2[\mathbf{Ib}]$ is 2.735(2) Å, which is longer than the Sb–Cr multiple bonds in $[\text{Sb}\{\text{Cr}(\text{CO})_5\}_3]^-$ (average 2.630(3) Å)^{4a} and longer than the Sb–Cr bond in $[\text{SbFe}_3\text{Cr}(\text{CO})_{17}]^-$ (2.6382(9) Å) as well.¹⁵ The lengthening of these E–Cr bonds is significant and is probably caused by steric crowding of the carbonyls on the chromium fragments.

The interesting feature of these molecules is the presence of a hydrogen atom bound to the main-group atom. The hydrogens can be found from the Fourier difference maps of the X-ray analyses,^{12,13} inferred on the basis of electron-counting considerations, and, most importantly, from ¹H NMR investigation. The ¹H NMR spectra exhibit singlets at $\delta -2.00$ for $[\text{HAs}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$ and $\delta -5.54$ for $[\text{HSb}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$. The values are different from those observed for the isoelectronic complexes $[\text{HAs}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$ ($\delta 1.34$) and $[\text{HSb}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$ ($\delta -1.39$).⁹ This implies that the hydrogens in the chromium-containing complexes **Ia** and **Ib** are more hydridic than those in the related iron-containing complexes due to the more electropositive character of Cr.

Similar in part to the case for $[\text{HSb}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$,¹⁶ the hydride in **Ib** is easily replaced by halides, as evidenced by the reactions of **Ib** with $\text{Me}(\text{CH}_2)_5\text{C}(\text{O})\text{Cl}$ or PhCH_2Br to form the isostructural halo complexes $[\text{XSbCr}_3(\text{CO})_{15}]^{2-}$ ($\text{X} = \text{Cl}$,¹⁷ Br ¹⁸) and the corresponding hydride-transferred organic products, respectively. How-

ever, unlike $[\text{HSb}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$,⁹ **Ib** cannot be deprotonated with KOBU^t . This may be explained by the fact that the hydrogen in **Ib** is more hydridic than that in $[\text{HSb}\{\text{Fe}(\text{CO})_4\}_3]^{2-}$. On the other hand, the heating of **Ia** or **Ib** in THF failed to induce metal–metal bond formation but instead induced decomposition to give the monochromium product, attributable to the long Cr–Cr distances and the weaker bonding nature of the E–Cr bonds.

In summary, the new series $[\text{HE}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$ (E = As, Sb) has been developed from common starting materials, making them convenient reagents for the synthesis of other chromium complexes containing arsenic and antimony. The hydrogens in **Ia** and **Ib** are shown to be more hydridic than those in the related iron complexes. Further reactivity studies of **Ia** and **Ib** are underway.

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Supporting Information Available: Complete listings of crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for **Ia** and **Ib**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Yield: 94% based on Sb for the $[\text{Et}_4\text{N}]^+$ salt. IR (ν_{CO} (cm^{-1}), CH_2Cl_2): 2012 vs. 1930 vs. 1869 s. Anal. Calcd: C, 37.46; H, 4.06; N, 2.82. Found: C, 37.65; H, 4.05; N, 2.73.

(18) Yield: 85% based on Sb for the $[\text{Bu}_4\text{N}]^+$ salt. IR (ν_{CO} (cm^{-1}), CH_2Cl_2): 2012 vs. 1930 vs. 1865 s. Anal. Calcd: C, 44.71; H, 5.75; N, 2.22. Found: C, 44.61; H, 5.82; N, 2.05.