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Synthesis and Characterization of the New Series of Chromium−Group 15 Hydride Complexes $[Et_4N]_2[HE\{Cr(CO)_5\}_3]$ (E = As, Sb)

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*Summary: The new series of trigonal-pyramidal chromium complexes $[HE\{Cr(CO)_5\}_3]^{2-}$ (E = As (**Ia**), Sb (**Ib**)) were obtained from the reactions of E_2O_3 (E = As, Sb) with $Cr(CO)_6$ 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 elements[2] 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 $[HE\{Cr(CO)_5\}_3]^{2-}$ (E = As (**Ia**), Sb (**Ib**)). In comparison to the *closo*-tetrahedral clusters obtained in the Mo−E−CO system (E = 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 E−H (E = As, Sb) fragments, and the structurally authenticated examples are limited to $(\mu$-HAs)-$\{CpMn(CO)_2\}_2$,[7] $[HAs\{Fe(CO)_4\}_3]^{2-}$,[8,9] and $[HSb\{Fe(CO)_4\}_3]^{2-}$.[9] Complexes **Ia** and **Ib** represent the first examples of group 6 complexes incorporating E−H moieties (E = As, Sb).

Complexes **Ia** and **Ib** can be respectively obtained from the convenient reagents E_2O_3 (E = As, Sb) and $Cr(CO)_6$ in highly concentrated KOH methanolic solution at room temperature. The reaction solutions were stirred for 3 days; then they were filtered, and the alkaimetal salts of **Ia**[10] and **Ib**[11] were converted to the $[Et_4N]^+$ salts by cation metathesis. Different from the conditions for the Mo−E−CO system (E = Bi, Sb, As),[5,6] these reactions with $Cr(CO)_6$ proceed in concentrated KOH methanolic solution. Single crystals of $[Et_4N]_2$[**Ia**] suitable for X-ray analysis were grown from an ether/CH_2Cl_2 solution,[12] and $[Et_4N]_2$[**Ib**] crystals were grown from a THF solution layered with ether.[13] The ORTEP diagrams of **Ia** and **Ib** are shown in Figures 1 and 2, respectively, and **Ia** and **Ib** are isostuctural. Each anion (**Ia** or **Ib**) displays a trigonal-pyramidal geometry of the central As (or Sb) atom and three $Cr(CO)_5$ groups, in which the chromium atoms adopt an octahedral arrangement.

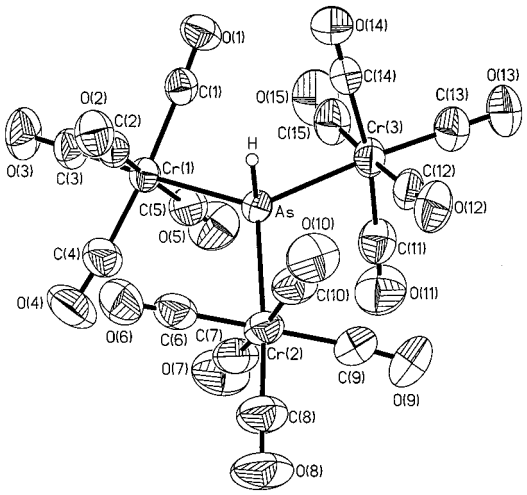

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion of **Ia**. Selected bond distances (Å) and angles (deg): As−H = 1.58(4), As−Cr(1) = 2.612(1), As−Cr(2) = 2.615(1), As−Cr(3) = 2.613(1); Cr(1)−As−Cr(2) = 116.60(4), Cr(1)−As−Cr(3) = 117.90(4), Cr(3)−As−Cr(2) = 116.61(4).

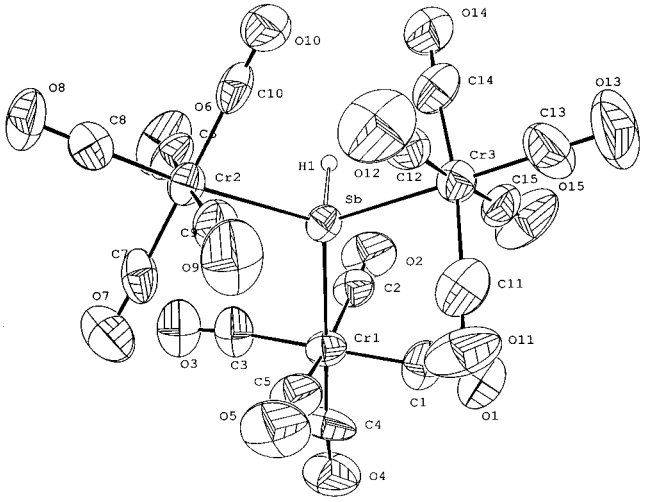

Figure 2. ORTEP diagram showing the structure and atom labeling for the dianion of **Ib**. Selected bond distances (Å) and angles (deg): Sb−Cr(1) = 2.727(2), Sb−Cr(2) = 2.741(2), Sb−Cr(3) = 2.738(2); Cr(1)−Sb−Cr(2) = 116.79(6), Cr(1)−Sb−Cr(3) = 116.86(7), Cr(2)−Sb−Cr(3) = 116.98(7).

The average As−Cr bond length in $[Et_4N]_2$[**Ia**] is 2.613(1) Å, which is not only significantly longer than those of the As−Cr multiple bonds in $ClAs\{Cr(CO)_5\}_2$ (average 2.324(2) Å),[3c] $PhAs\{Cr(CO)_5\}_2$ (average 2.385(3) Å),[3c] $N(SiMe)_2As\{Cr(CO)_5\}_2$ (2.381(1) Å),[3g] $Mn(CO)_5As\{Cr(CO)_5\}_2$ (average 2.429(4) Å),[4a] and $Mn(CO)_5As(\mu$-CO$)\{Cr(CO)_4\}_2$ (average 2.349(5) Å)[4a] but also longer than the As−Cr single bonds in $As_2Cr_3Co_2(CO)_{20}$ (average 2.425(2) Å).[14] Similarly, the average Sb−Cr

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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 $Cr(CO)_6$ 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 Et_2O/THF gave 0.32 g (17.6% based on As) of $[Et_4N]_2[HAs\{Cr(CO)_5\}_3]$ (**Ia**). IR (ν_{CO} (cm^{-1}), THF): 2007 vs, 1914 vs, 1847 s. Anal. Calcd (found) for **Ia**: C, 40.80 (40.50); H, 4.53 (4.45); N, 3.07 (3.11). ^1H NMR (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 $Cr(CO)_6$ 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 Et_2O/THF gave 1.41 g (79% based on Sb) of $[Et_4N]_2[HSb\{Cr(CO)_5\}_3]$ (**Ib**). IR (ν_{CO} (cm^{-1}), THF): 2003 vs, 1919 vs, 1860 s. Anal. Calcd (found) for **Ib**: C, 38.81 (38.51); H, 4.31 (4.34); N, 2.92 (2.76). ^1H NMR (DMSO-d_6, ppm): −5.5 s.

(12) Crystal data for $[Et_4N]_2[HAs\{Cr(CO)_5\}_3]$: monoclinic, space group $P2_1/n$, a = 13.4332(3) Å, b = 13.8294(4) Å, c = 22.4643(6) Å, β = 92.410(1)°, V = 4169.6(2) Å^3, Z = 4; CCD SMART diffractometer with graphite-monochromated Mo Kα radiation and Sadabs absorption correction (T_{mim} = 0.55, T_{max} = 0.76). A total of 18 424 reflections were measured, and 5991 unique reflections (2θ < 46.52°, R_{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 $[Et_4N]_2[HSb\{Cr(CO)_5\}_3]$: orthorhomic, space group *Pcnb*, a = 13.224(5) Å, b = 23.477(3), c = 26.754(4) Å, V = 8306(4) Å^3, Z = 8, $2\theta_{max}$ = 51.8°, T = 25 °C, R = 0.056, R_w = 0.047 for $I > 2\sigma(I)$, Nonius CAD-4 diffractometer, Mo Kα radiation. All the non-hydrogen atoms were refined with anisotropic temperature factors, while the hydride was found from Fourier difference maps, approximately 1.799 Å 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.

bond length in $[Et_4N]_2$[**Ib**] is 2.735(2) Å, which is longer than the Sb−Cr multiple bonds in $[Sb\{Cr(CO)_5\}_3]^-$ (average 2.630(3) Å)[4a] and longer than the Sb−Cr bond in $[SbFe_3Cr(CO)_{17}]^-$ (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 ^{1}H NMR investigation. The ^{1}H NMR spectra exhibit singlets at δ −2.00 for $[HAs\{Cr(CO)_5\}_3]^{2-}$ and δ −5.54 for $[HSb\{Cr\ (CO)_5\}_3]^{2-}$. The values are different from those observed for the isoelectronic complexes $[HAs\{Fe(CO)_4\}_3]^{2-}$ (δ 1.34) and $[HSb\{Fe(CO)_4\}_3]^{2-}$ (δ −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 $[HSb\{Fe(CO)_4\}_3]^{2-}$,[16] the hydride in **Ib** is easily replaced by halides, as evidenced by the reactions of **Ib** with $Me(CH_2)_5C(O)Cl$ or $PhCH_2Br$ to form the isostructural halo complexes $[XSbCr_3(CO)_{15}]^{2-}$ (X = Cl,[17] Br[18]) and the corresponding hydride-transferred organic products, respectively. However, unlike $[HSb\{Fe(CO)_4\}_3]^{2-}$,[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 $[HSb\{Fe(CO)_4\}_3]^{2-}$. 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 $[HE\{Cr(CO)_5\}_3]^{2-}$ (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 $[Et_4N]^+$ 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 $[Bu_4N]^+$ 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.