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Reaction of Diantimony Anion with Mononuclear Metal Carbonyls. First Observed Instance of an Antimony−Transition-Metal (M≡Sb) Triple Bond

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In recent years there has been an increasing interest in species displaying multiple bonds between transition-metal and main-group elements.[1] This interest has been driven by many factors, including their postulated role as intermediates in catalytic processes,[2] their potential application as novel synthons for the formation of mixed main-group to metal clusters for the materials industry,[3] and their fundamental interest as novel examples of bonding. Most of the work to date has involved second-row, main-group elements (C, N, O), with very few examples of heavier elements. Only recently has a significant number of examples involving third-row or later elements been reported, including Te[4] and Se,[5] as naked terminal atoms, and Si,[6] as R_2Si, among others.

Despite successes with the heavier congeners of group 14 and group 16, there have been reported fewer examples of metal complexes of phosphinidines[7] and arsinidines[8] (RP, RAs) and no unequivocal antimony species, either stibinidines (RSb) or stibido (Sb) species.[9] Therefore, we focused our attention on the heavier pnictogens and herein report the first transition metal to antimony triply bonded species, synthesized in the gas phase through the use of a Fourier transform ion cyclotron resonance spectrometer (FT-ICR).[10]

The dinuclear Sb_2^- ion, formed by the laser ablation of elemental antimony, was chosen for study due to its high abundance, the lack of additional reaction modes for tri- and tetranuclear cluster anions, and the low reactivity of mononuclear Sb^-, which is limited to charge-transfer reactions.[11] Cationic species also displayed reactivity limited to charge-transfer reactions.

The diantimony anion is shown to react with metal carbonyls by the general reaction shown in eq 1.[12] Conversion was complete in 60 s or less at nominal pressures of 1.0×10^{-7}, 8.0×10^{-8}, 4.0×10^{-8}, and 5.6×10^{-7} Torr for the Cr, Mo, W, and Fe reactions.[13] No subsequent reactions were observed

$$\mathrm{Sb_2^-} + \underset{\substack{n = 6;\ \mathrm{M} = \mathrm{Cr, Mo, W}\\ n = 5;\ \mathrm{M} = \mathrm{Fe}}}{\mathrm{M(CO)}_n} \rightarrow \mathrm{(CO)}_{n-2}\mathrm{M{\equiv}Sb^-} + 2\mathrm{CO} + \mathrm{Sb} \quad (1)$$

for trapping times as long as 420 s. Analysis of the kinetic data suggests that the products of eq 1 react with $M(CO)_n$ at least 100 times more slowly than Sb_2^-, if at all. This indicates a formal electron count of 18 for the product of eq 1 and precludes the possibility of forming of a metal−antimony−isocyanate analogue, $(CO)_{n-3}MSb{=}CO$, which contains a 16 e metal center.[14] Metal carbonyl ions that are electronically unsaturated have been found to cluster efficiently with neutral metal carbonyls in the gas phase.[15]

The observed rate constants of reaction 1 for Cr, Mo, and W are 7.6×10^{-12}, 9.7×10^{-12}, and 5.36×10^{-11} cm^3 $(molecule{\cdot}s)^{-1}$, respectively, based on nominal ionization gauge pressures. Since molecules as similar as the group-6 metal hexacarbonyls are anticipated to have similar ionization cross sections, the ionization gauge pressures are reasonably accurate.

The extreme stability of the products, as well as their formal 18-electron count ($4CO = 8e^-$, $M^0 = 6e^-$, $Sb^- = 4\ e^-$), leads to the conclusion that the observed species contains a triple bond between antimony and the transition metal. By isolobal analogies Sb^- is therefore related to a Te^0, and the observed species is related to the terminal tellurido and selenido species $(PMe)_4W({=}E)_2$, E = Se or Te, of Parkin et al.

In an attempt to probe the nature of the bonding in the complexes, *ab-initio* MP2 calculations were performed using the program GAMESS[16] and employing effective core potentials and valence-only basis sets[17] augmented with d-functions on the main-group elements on $SbMo(CO)_4^-$. It is expected that the essential features of the bonding and geometry will be reproduced well by this level of theory.[18] The calculation predicts a square-based pyramidal (C_{4v}) geometry, with an antimony−molybdenum bond length of 2.55 Å and an Sb−Mo−CO bond angle of 112°. The atomic charges on Mo and Sb are predicted by the Mulliken method to be −1.49 and −0.25 au, respectively, indicating a transfer of electron density from Sb to the central metal. The Sb−Mo bond length of 2.55 Å is approximately 9.6% shorter than an antimony−molybdenum

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(11) Unpublished results. Sb_3^- reacts with $Fe(CO)_5$ to initially form $Sb_2Fe(CO)_3^-$, which rapidly decays to $SbFe(CO)_3^-$, the same product as results from the reaction with Sb_2^-.

(12) Observed masses with relative intensities in parentheses: $(CO)_4CrSb^-$, 283 (3.23), 285 (100), 286 (14.52), 287 (77.72), 288 (20.97), 289 (8.06); $(CO)_4MoSb^-$: 325 (27.08), 326 (9.72), 327 (52.78), 328 (31.94), 329 (56.25), 330 (88.89), 331 (100), 332 (22.22), 333 (56.25), 334 (2.78), 335 (8.33); $(CO)_4WSb^-$, 415 (48.73), 416 (26.48), 417 (82.73), 418 (22.85), 419 (100), 420 (unresolved by peak selection routine), 421 (40.95).

(13) Sb_2^- formed by laser ablation of bulk Sb sample. During 1-s induction period all other charged species were ejected. Neutral metal carbonyls were continuously present at background pressure of 5.0×10^{-8} to 5.6×10^{-7} Torr. Reaction allowed to proceed for 1−420 s before detection event.

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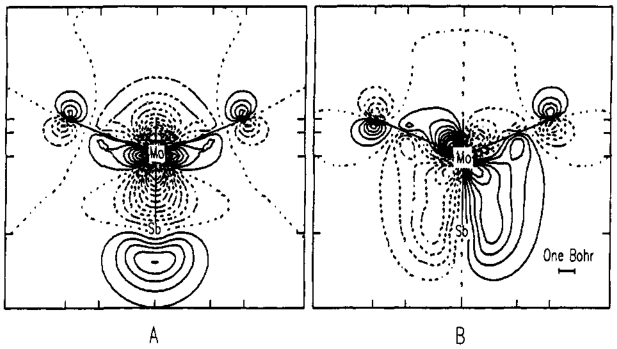
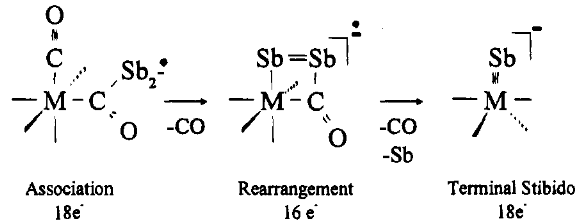


Figure 1. Contour plots of the σ (A) and π (B) orbitals of $SbMo(CO)_4^-$ with C_{4v} symmetry in the xz plane and Mo and Sb aligned along the z axis. The plot of orbitals in the yz plane is identical. Contours are plotted at intervals of 0.02 $bohr^{-3/2}$.

single bond and is in the expected range for a double to triple bond.[19] Contour plots of the RHF orbitals in the xz plane of the molecule show clearly a low-lying σ bond formed primarily from the interaction between a metal-centered d_{z^2} orbital and an antimony-centered sp hybrid and one of two equivalent π bonds, formed from metal ($d_{xz}p$ and $d_{yz}p$) hybrids and antimony p_x and p_y orbitals, which are polarized slightly toward the central metal (Figure 1). The observed bonding, while weaker than that displayed between the lighter pnictides and transition metals, has the characteristics of a true transition metal to antimony triple bond and should be considered as such. The pyramidalization is the result of a π-type interaction between a CO π* orbital and the metal d_{z^2}, allowing the removal of two electrons from the π-antibonding level and stabilizing the M−Sb bond. This is reflected in the calculated M−Sb bond order of 2.54, indicating the retention of some antibonding character. This has the additional effect of decreasing the interaction between the CO ligands and the metal p_x and p_y orbitals as they are bent away from the axial ligand. This allows the metal p_x and p_y orbitals to hybridize with the d_{xz} and d_{yz} orbitals, thereby improving the overlap with the p_x and p_y orbitals of the antimony fragment and strengthening the bond.[20]

Scheme 1



The mechanism through which the reaction proceeds is not unequivocally known, but a likely candidate is shown in Scheme 1. It is presumed to proceed through a nucleophilic attack by Sb_2^- on a carbonyl ligand, followed by CO ejection, formation of a four-centered intermediate, and subsequent ejection of CO and Sb^0, to dissipate internal energy. This mechanism is similar to that proposed by Squires in flowing afterglow experiments involving small nucleophiles and transition-metal carbonyl complexes.[21] Due to the thermalizing effects of the background neutral metal carbonyl, it is anticipated that, by the time significant reactivity is observed, the overall energy of the system is that of a Boltzman's distribution at 298 K. Therefore, higher energy pathways are not anticipated to make any significant contribution to the overall reactivity. The low density of reactants at the experimental pressure also rules out reactions involving dissociation of a carbonyl group to form a vacant coordination site prior to antimony coordination.

Similar reactivity is observed for iron pentacarbonyl. Further experiments to obtain accurate rate information, as well as possible further reactivity, are in progress. Calculations at a higher level of theory are being performed in an effort to elucidate the reaction path. Results of experiments detailing similar reactivity involving $(C_5H_4Me)Mn(CO)_3$, $CpCo(CO)_2$, and $Co(CO)_3NO$ will be reported in upcoming communications.

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[19] Mean Sb−Mo distance is 2.820 Å from 17 examples found in the Cambridge Crystallographic Database, Cambridge, U.K., April 1994.

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