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Preliminary communication

Indium(III) and thallium(III) complexes of the tetracarbonylcobaltate anion

W.R. ROBINSON and D.P. SCHUSSLER
Department of Chemistry, Purdue University, Lafayette, Indiana 47907 (U.S.A.)

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The Lewis basicity of the transition metal in numerous transition metal carbonyls and their derivatives has been recognized for several years[1,2]. More recent investigations have demonstrated the ability of transition metal carbonylate anions to react with compounds containing an acidic post-transition metal to produce complex ions containing one or more metal–metal bonds. Examples of these systems include $Hg[Co(CO)_4]_3^-$ [3], $Cd[Co(CO)_4]_3^-$ [4], $InBr_3Co(CO)_4^-$ [5], and $InBr_2[Co(CO)_4]_2^-$ [6]. Studies in our laboratory indicate that both $In[Co(CO)_4]_3$ and $Tl[Co(CO)_4]_3$ have sufficient acidity to produce the complex anions $M[Co(CO)_4]_4^-$. These are the first reported examples of complexes of Group III metals in which the metal is coordinated solely by transition metals.

Addition of $(C_6H_5)_4AsCo(CO)_4$ to a dichloromethane–heptane solution of a 10% excess of $In[Co(CO)_4]_3$ [7] or a 100% excess of $Tl[Co(CO)_4]_3$ [7] followed by removal of the dichloromethane under reduced pressure yields red crystals★ of $[(C_6H_5)_4As]\{In[Co(CO)_4]_4\}$ or black crystals★ of $[(C_6H_5)_4As]\{Tl[Co(CO)_4]_4\}$, respectively. (The excess of $M[Co(CO)_4]_3$ prevents coprecipitation of $(C_6H_5)_4AsCo(CO)_4$ formed by reaction 1.) These salts are somewhat more air stable than the parent compounds with the solid indium salt decomposing in air in about one hour and the thallium salt in about 12 hours.

The basic site of the $Co(CO)_4^-$ group which bonds to the Group III metal in $M[Co(CO)_4]_3$ could be either the oxygen atom of a CO group as observed in $\{(\pi\text{-}C_5H_5)FeCO[COAl(C_2H_5)_3]\}_2$ [8] and $Al[(\pi\text{-}C_5H_5)W(CO)_3]_3$ [9] or the Co atom as postulated for $Hg[Co(CO)_4]_3^-$ [3] and observed in $InBr_2[Co(CO)_4]_2^-$ [5] and $[(\pi\text{-}C_5H_5)Co(CO)_2]HgCl_2$ [10]. Infrared spectra of both the thallium and indium anions in the carbonyl stretching region and in the far IR are consistent only with a system containing 4 M–Co bonds in a tetrahedral array. For neither anion have CO frequencies lower than that of $Co(CO)_4^-$ been observed, while bonding of a transition metal carbonyl via an oxygen has been reported to produce unusually low CO stretching frequencies[8,9]. Moreover, for a CO bridged system of overall C_{3v} symmetry with local C_{3v} symmetry about the Co atoms, nine terminal CO stretching modes active in the IR would be expected. For four M–Co bonds in a system of overall T_d symmetry and local C_{3v} symmetry about the Co atoms, three infrared active

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★Analyses: Found: C, 40.6; H, 1.88; Co, 19.1; In, 9.6 $(C_6H_5)_4AsInCo_4(CO)_{16}$. Calcd.: C, 40.6; H, 1.71; Co, 20.0; In, 9.7%.
Found: C, 37.6; H, 1.79; Co, 17.3; Tl, 16.4 $(C_6H_5)_4AsTlCo_4(CO)_{16}$. Calcd.: C, 37.8; H, 1.59; Co, 18.6; Tl, 16.1%.

vibrations are expected. In all solvents in which $M[Co(CO)_4]_4^-$ is not completely dissociated (*vide infra*), only three CO modes attributable to this anion are observed. In dichloromethane, for example, $In[Co(CO)_4]_4^-$ exhibits peaks at 2047 m, 1980 vs, and 1950 w cm^{-1}.

The trigonal pyramidal arrangement of M–Co bonds which would arise if a bridging CO group were bonded to M would be expected to produce two IR active M–Co stretching modes, while a tetrahedral $M{-}Co_4$ unit should have only one IR active M–Co stretching mode. Only one strong vibration is observed in the far IR occurring at 128 cm^{-1} with $In[Co(CO)_4]_4^-$ and at 107 cm^{-1} with $Tl[Co(CO)_4]_4^-$.

The positions of the CO absorptions in $M[Co(CO)_4]_4^-$ reflect the fractional negative charge on each $Co(CO)_4$ group of the anion. The approximately 20 cm^{-1} shift to lower energies of the CO vibrations of the anion relative to those of $M[Co(CO)_4]_3$ [7] is similar to that observed on going from $Hg[Co(CO)_4]_2$ to $Hg[Co(CO)_4]_3^-$ [3] or from $Co_4(CO)_{12}$ to $FeCo_3(CO)_{12}^-$ [11]. The reduction of the frequency of the M–Co stretching mode from 166 cm^{-1} in $In[Co(CO)_4]_3$ and 146 cm^{-1} in $Tl[Co(CO)_4]_3$ upon formation of the tetrahedral anion is expected for the increase in coordination number[12]. Similar shifts are observed in the $Hg[Co(CO)_4]_3^-$ system.

Tetraphenylarsonium salts of both the indium and thallium anions dissolve in polar organic solvents with some dissociation according to reactions 1 and 2. The position of these

$$M[Co(CO)_4]_4^- \rightleftarrows M[Co(CO)_4]_3 + Co(CO)_4^- \qquad (1)$$

$$M[Co(CO)_4]_3 \rightleftarrows M^{3+} + 3Co(CO)_4^- \qquad (2)$$

equilibria is very solvent dependent with the extent of dissociation increasing as the basicity of the solvent increases. In dichloromethane only traces of $M[Co(CO)_4]_3$ and $Co(CO)_4^-$ are observed in the IR spectrum of the solutions. The spectra of THF solutions show appreciable amounts of $M[Co(CO)_4]_3$ and $Co(CO)_4^-$, and in DMSO only the spectrum of $Co(CO)_4^-$ is observed. In all solvents in which $M[Co(CO)_4]_4^-$ is not completely dissociated, the indium anion is less dissociated than the thallium anion. A similar decrease in stability with increasing atomic weight has been observed[4] in the series $M[Co(CO)_4]_3^-$ where M = Cd, Hg.

Interpretation of the spectra of the thallium system is somewhat complicated by the equilibrium[13] shown in reaction 3. However, this equilibrium lies well to the

$$Tl[Co(CO)_4]_3 \rightleftarrows TlCo(CO)_4 + Co_2(CO)_8 \qquad (3)$$

left and does not cause serious problems. No indication of the formation of $InCo(CO)_4$ was observed.

Lewis base adducts of $In[Co(CO)_4]_3$ are not limited to metal carbonyls. Reaction with triphenylphosphine oxide produces a weak adduct, $(C_6H_5)_3POIn[Co(CO)_4]_3$, and reaction with $(C_6H_5)_4AsCl$ produces a halide bridged anion $Cl\{In[Co(CO)_4]_3\}_2^-$. No evidence for a 1/1 halide–indium species was observed even with an excess of chloride ion.

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