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Highly reduced organometallics

XXVII *. Synthesis, isolation and characterization of trisodium tricarbonylcobaltate(3 –), and initial studies on its derivative chemistry

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Abstract

Reduction of A[Co(CO)$_4$] by three equivalents of A (A = sodium or potassium) in liquid ammonia provides salts containing tricarbonylcobaltate(3 –). A satisfactorily pure sodium compound, Na$_3$[Co(CO)$_3$] is described for the first time. Reactions of A$_3$[Co(CO)$_3$] with two equivalents of Ph$_3$ECl (E = Ge, Sn, Pb) provides 50–70% yields of *trans*-(Ph$_3$E)$_2$Co(CO)$_3^-$ which have been isolated as analytically pure Et$_4$N$^+$ salts. Treatment of liquid ammonia slurries of K$_3$[Co(CO)$_3$] with three equivalents of NH$_4$Cl in the presence of PR$_3$ or CNR, results in evolution of hydrogen gas and the formation of Co(CO)$_3$L$^-$. In the case of L = t-BuNC, the first such isocyanide substituted carbonylcobaltate(1 –) species was prepared and isolated in a 67% yield by this procedure. A possible pathway for the formation of Co(CO)$_3$L$^-$ from K$_3$[Co(CO)$_3$] is discussed in light of similar protonation reactions reported for other carbonylmetallate trianions.

Introduction

Approximately 25 years after Mond and co-workers had prepared the first carbonyl of cobalt, Co$_2$(CO)$_8$ [2], Hieber obtained HCo(CO)$_4$ by the acidification of salts containing Co(CO)$_4^-$ [3], one of the first established carbonylmetallates [4]. In 1941 Behrens, a student of Hieber, initiated his important and extensive investigations on the reductions of metal carbonyls and their derivatives by alkali and alkaline earth metals in liquid ammonia [5]. At this time he established that various salts of Co(CO)$_4^-$, including Na[Co(CO)$_4$] and K[Co(CO)$_4$], could be obtained from

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* For previous parts in this series see ref. 1.

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the neutralization of $HCo(CO)_4$ or the reduction of $Cd(Co(CO)_4)_2$ by sodium or potassium in liquid ammonia [6]. On the basis of Behrens' pioneering studies, we were initially quite pessimistic concerning the possibility that $Co(CO)_4^-$ could be reduced further in liquid ammonia, since it seemed likely that Behrens would have reported such a reaction long ago. However, after we observed that $[Mn(CO)_5]^-$ and $[V(CO)_6]^-$ readily reacted with Na or K in liquid ammonia to provide the "superreduced" carbonyl anions, $[Mn(CO)_4]^{3-}$ [7] and $[V(CO)_5]^{3-}$ [8], respectively, it was felt that an investigation of the interaction of $[Co(CO)_4]^-$ with alkali metals in liquid ammonia was in order. Several years ago preliminary results in this study were reported and provided good evidence for the reduction of $Co(CO)_4^-$ by sodium in liquid ammonia [9]. Although the nature of the reduction product remained obscure, it was formulated to contain $[Co(CO)_3]^{3-}$ on the basis of infrared spectra and derivative studies. In this paper, we will provide more substantial evidence for the existence of tricarbonylcobaltate(3 −) by describing the first isolation of the satisfactorily pure trisodium salt, $Na_3[Co(CO)_3]$, from this reaction as well as the first full account of some of its reactions with electrophiles. Formally, the trisodium salt contains $Co(CO)_3{}^{3-}$, an exceedingly rare example of a 3-coordinate, 18-electron metal ion which is isoelectronic with zinc! Although the preparation of the isoelectronic $Co(NO)_3$ has been reported, its existence remains unconfirmed [10]. To our knowledge the only previously well characterized example of such a compound is $Ni(C_2H_4)_3{}^{2-}$, which is formally present in $[Li(TMEDA)]_2[Ni(C_2H_4)_3]$ [11].

Experimental

General procedures and starting materials. See a previous paper in this series for a discussion of general procedures in the handling of highly reduced organometallics and the purification of solvents [1]. All reagents were obtained from commercial sources except $Na[Co(CO)_4]$ and $K[Co(CO)_4]$, which were made by the method of Edgell and Lyford [12]. Since a detailed procedure for the preparation of pure $K[Co(CO)_4]$ has apparently not been previously reported in the scientific literature, one will be presented here.

Synthesis of $K[Co(CO)_4]$ (1)

Potassium hydroxide pellets (48 g, ca. 0.65 mol) were ground to a powder in a nitrogen filled dry box or glove bag and placed in a flask along with $Co_2(CO)_8$ (6.0 g, 18 mmol). After the flask was opened to a bubbler to permit escape of carbon monoxide, freshly distilled THF (40 ml) was added by cannula. Much gas evolution occurred at this stage. The mixture was vigorously stirred until gas evolution ceased. Depending on how finely divided the KOH was and the stir rate, the reaction generally required 6–12 h. Ultimately a clear pale yellow solution and a pink to purple solid formed. After filtration and removal of solvent in vacuo a creamy-white solid was isolated. It was dried in vacuo for 24 h (4.8 g, 64%). The very air sensitive compound was found to melt with decomposition at about 203 °C. Anal. Found: C, 22.63; H, 0.06; K, 18.77. C_4CoKO_4 calcd.: C, 22.77; H, 0.00; K, 18.53%. IR (THF), $\nu(CO)$: 1890 vs, 1856 m sh cm^{-1} (Nujol mull): See Fig. 1.

$Na_3[Co(CO)_3]$ (2)

Approximately 100 ml of ammonia, free of oxygen and water, was vacuum distilled into a flask containing sodium metal (0.41 g, 18 mmol) and anhydrous $Na[Co(CO)_4]$ (1.16 g, 6.0 mmol) at −78 °C. A red precipitate was observed in the deep blue solution after 5 h stirring at −78 °C. Following removal in vacuo of the ammonia, the yellow-brown solid was brought to room temperature. Much unreacted sodium metal was present and was removed by two 25 ml washings with liquid ammonia. The isolated solid was dried in vacuo at room temperature yielding 0.31 g of impure $Na_3[Co(CO)_3]$. The Nujol mull IR spectrum confirmed the presence of $[Co(CO)_3]^{3-}$ and the absence of $[Co(CO)_4]^-$: ν(CO) 1744 m sh, 1614 vs br cm^{-1}. The solid was then treated with 0.40 g of cryptand-2.2.2 in 30 ml of anaerobic ethylenediamine, stirred for 2 h, and filtered on a coarse porosity frit. The deep red brown filtrate showed a very weak band in the infrared spectrum due to $Co(CO)_4^-$ as well as a stronger band at 1794 cm^{-1} due to an uncharacterized, quite air sensitive species. Attempts to obtain tractable materials from the ethylenediamine cryptand-2.2.2 filtrate were unsuccessful. The product on the glass frit was washed with ethylenediamine and then dried in vacuo. Satisfactory analyses for unsolvated $Na_3[Co(CO)_3]$ were obtained for the resulting olive brown highly air sensitive solid (0.25 g, 20% yield), which appeared to be stable indefinitely at room temperature under a nitrogen atmosphere. Anal. Found: C, 16.70; Co, 27.71; Na, 32.69; O (by difference), 22.90. $C_3CoNa_3O_3$ calcd.: C, 17.00; Co, 27.81; Na, 32.54; O, 22.65%. IR (Nujol), ν(CO): 1740 m sh, 1610 vs, br cm^{-1}.

More recently, satisfactory analyses of the related $Na_3[Ir(CO)_3]$ have also been obtained [13]. Although, $Na-NH_3$ reductions of $Na[Co(CO)_4]$ often remained incomplete at −33 °C, even after 2 days, corresponding $K-NH_3$ reductions of $K[Co(CO)_4]$ proceeded to completion much more rapidly.

Impure $K_3[Co(CO)_3]$ (3)

Creamy-white $K[Co(CO)_4]$ (1.00 g, 4.8 mmol) and freshly cut potassium metal (0.56 g, 14 mmol) were loaded into a flask equipped with a glass-covered magnetic stir bar in the dry box. Liquid ammonia (50 ml) was condensed onto the mixture. The reaction mixture was stirred at −33 °C until the deep blue color had faded (ca. 4 h). The ammonia evaporated as the reaction mixture slowly warmed to 25 °C. Infrared spectra (Nujol) of the yellow green product always revealed the presence of $K_2C_2O_2$ (ν(CO) 2140 cm^{-1}) [14] as a contaminant of the $K_3[Co(CO)_3]$. However, unreacted $K[Co(CO)_4]$ was generally not present in the product. Attempts to remove the $K_2C_2O_2$ [15] or to obtain satisfactorily pure $K_3[Co(CO)_3]$ by other means have been unsuccessful to date. Typically, about 1.5 g of **2** was isolated from this reaction; however, the product was generally used immediately in a subsequent reaction without isolation and/or weighing (vide infra). IR (Nujol), ν(CO): 2140 w, 1757w, 1640 vs, br cm^{-1}.

Both **1** and **2** appear to survive indefinitely at room temperature under a nitrogen atmosphere and are insoluble in all unreactive solvents.

$[Et_4N][(Ph_3Ge)_2Co(CO)_3]$ (4)

$K_3[Co(CO)_3]$ was prepared in the usual manner from $K[Co(CO)_4]$ (1.02 g, 4.85 mmol) by reduction with potassium metal (0.58 g, 15 mmol, 3.1 eq.) in 50 ml of liquid ammonia. The isolated yellow-green solid was dried in vacuo at 20 °C for 0.5

h. A slurry of the trianion in 20 ml of THF was treated with a solution of Ph_3GeBr (5.6 g, 15 mmol) in 20 ml of THF at −78 °C. Stirring was continued as the temperature slowly rose to 0 °C over 4 h. A large excess of $[Et_4N]Br$ (5 g) was added to the muddy brown suspension and stirred while the solvent was being removed in vacuo at −10 °C (1.2 h). Metathesis was completed by addition of 80 ml of ethanol. The tan precipitate was collected on a medium porosity frit and dried in vacuo. Recrystallization from acetone/excess diethyl ether and THF/excess heptane gave 2.1 g (50% based on $K[Co(CO)_4]$) of compound **3**. This white microcrystalline product provided satisfactory elemental analyses and decomposed without melting above 240 °C. Anal. Found: C, 64.10; H, 5.64; N, 1.47. $C_{47}H_{50}NCoGe_2O_3$ calcd.: C, 64.03; H, 5.72; N, 1.59%. IR (Nujol), $\nu(CO)$: 1903 vs, 1892 vs cm^{-1}; (THF): 1914 vs, 1900 s, sh. cm^{-1}. Much lower yields of **3**, ca. 10–15% were generally obtained from $Na_3[Co(CO)_3]$, due to incomplete reduction of the $Na[Co(CO)_4]$.

$[Et_4N][(Ph_3Sn)_2Co(CO)_3]$ (5)

The reduction of $K[Co(CO)_4]$ (0.57 g, 2.7 mmol) by potassium metal (0.32 g, 8.2 mmol) in ca 100 ml of liquid ammonia was carried out as described above. The trianion was vacuum dried at room temperature. The yellow-green powder, slurried in 10 ml of THF, was treated with a solution of Ph_3SnCl (3.2 g, 8.3 mmol) in 25 ml of THF. The color of the suspension changed from yellow to a dark yellow-brown. The solution was stirred for an additional hour, filtered through a medium porosity frit, concentrated in vacuo, and treated with a solution of $[Et_4N]Br$ (1.0 g, 5 mmol) in 10 ml of ethanol. Subsequent addition of 100 ml of water gave a flocculent precipitate which was washed with water and vacuum dried overnight. The solid was washed with toluene and diethyl ether, taken up in THF and filtered. Addition of excess heptane yielded 1.46 g (55%) of pale yellow crystals. A second recrystallization from acetone/heptane provided a nearly colorless crystalline sample of **4** of satisfactory purity. This material survived for many weeks in air and appeared to be indefinitely stable under an inert atmosphere at room temperature. It was quite thermally robust and decomposed without melting above 250 °C. Anal. Found: C, 58.07; H, 5.20; N, 1.35; Sn, 23.93. $C_{47}H_{50}NCoO_3Sn_2$ calcd.: C, 58.00; H, 5.19; N, 1.44; Sn, 24.39%. IR (Nujol), $\nu(CO)$: 1892 vs, 1880 vs, 1858 sh cm^{-1}; (THF): 1907 vs cm^{-1}.

In subsequent preparations up to 72% isolated yields of compound **4** were obtained by addition of Ph_3SnCl directly to liquid ammonia slurries of $K_3[Co(CO)_3]$, followed by the usual workup. See the synthesis of compound **5** below.

$[Et_4N][(Ph_3Pb)_2Co(CO)_3]$ (6)

$K_3[Co(CO)_3]$ was formed in the reaction of $K[Co(CO)_4]$ (0.45 g, 2.1 mmol) and potassium metal (0.25 g, 6.3 mmol) in liquid ammonia for 7 h at −78 °C. A THF (35 ml) solution of Ph_3PbCl (3.1 g, 6.5 mmol) was cooled to −78 °C and added via cannula to the trianion. Stirring was continued for 4.5 h as the temperature rose to reflux (under nitrogen) and a yellow suspension formed. After removing the solvent in vacuo, the tan solid was washed with diethyl ether (4 × 40 ml) and vacuum dried. Metathesis with excess $[Et_4N]Br$ in ethanol and recrystallization from THF/excess heptane gave 1.3 g (53%) of yellow crystalline $[Et_4N][(Ph_3Pb)_2Co(CO)_3]$, which provided satisfactory analyses. This substance was less themally stable than compounds **3** and **4** and began to decompose without melting under nitrogen above 150 °C. Anal. Found: C, 48.91; H, 4.08; N, 0.91. $C_{47}H_{50}NCoO_3Pb_2$ calcd.: C, 49.01; H, 4.38; N, 1.22%. IR (Nujol), ν(CO): 1902 vs, 1888 vs, 1875 sh; (THF): 1915 vs cm^{-1}.

[Et_4N][$Co(CO)_3(CNtBu)$] (7)

A slurry of $K_3[Co(CO)_3]$ (ca. 4.74 mmol) in liquid ammonia (100 ml) was generated by the reaction of $K[Co(CO)_4]$ (1.00 g, 4.76 mmol) with potassium metal (0.558 g, 14.3 mmol) as described previously. Three equivalents of solid NH_4Cl (0.764 g, 14.3 mmol) were added via a bent Schlenk tube. The flask contents were stirred while the temperature was maintained at reflux (ca. −33 °C) until no solid $K_3[Co(CO)_3]$ could be seen. The flask was then cooled to −78 °C and t-butyl isocyanide (1.8 ml, ca. 3 equiv. per Co) was added via syringe. It was stirred for 10 min and the solidified t-butyl isocyanide was seen to dissolve with concurrent loss of color of the solution. After stirring was stopped, a white solid was observed to settle out. Cold THF (60 ml) at −78 °C was transferred by cannula into the flask and it was stirred at reflux for 30 min prior to cooling again to −78 °C. Solid $[Et_4N]Br$ (3.00 g, 14.3 mmol) was then added via a bent Schlenk tube and the mixture was stirred for 3 h at reflux. The ammonia slowly evaporated. The orange THF solution was filtered and then solvents were removed in vacuo. The solid was washed with pentane (3 × 50 ml) and dried in vacuo. The residue was then dissolved in THF (50 ml) and filtered. Concentration to ca. 8 ml followed by treatment with 200 ml of pentane produced a pale yellow solid. Pentane was removed by cannula and the solid was dried. The solid was recrystallized from THF/ether to yield 1.13 g (67% yield). Above 110 °C the white crystals darkened and melting occurred with decomposition at 114 °C. Anal. Found: C, 53.85; H, 8.21; N, 7.77. $C_{16}H_{29}CoN_2O_3$ calcd.: C, 53.99; H, 8.20; N, 7.86%. IR (THF), ν(CN): 2042; ν(CO): 1912 s, 1850 vs. cm^{-1}. ^{1}H NMR (CD_3CN) δ: 3.12 (q, 8H, CH_2 of Et_4N^+), 1.28 (s, 9H, tBu), 1.18 (t of t, 12H, CH_3 of Et_4N^+).

Results and discussion

General comments on the ease of reduction of $M(CO)_x^-$

Of the homoleptic carbonylmetallates(1 −) we have attempted to reduce, $Co(CO)_4^-$ appears to be the most difficult. While the sodium salts of $M(CO)_6^-$ (M = V, Nb and Ta) [14,16] undergo facile reduction in liquid ammonia by sodium metal to provide the corresponding "superreduced" trianions, $M(CO)_5^{3-}$, it seems unlikely that we have ever effected complete reduction of $Na[Co(CO)_4]$ to $Na_3[Co(CO)_3]$. Even after 2 days of refluxing at −33 °C anhydrous ammonia solutions of $Na[Co(CO)_4]$ with excess Na, considerable amounts of the tetracarbonylcobaltate(1 −) remain. Low yields of a heterogeneous appearing brown to olive brown insoluble solid can be isolated which has been shown to contain $Na_3[Co(CO)_3]$ (vide infra). As in the case of $Re(CO)_5^-$ [1b], we have found that solutions of potassium in liquid ammonia are far more effective at reducing $Co(CO)_4^-$. However, unlike $Re(CO)_5^-$ [1b], $Rh(CO)_4^-$ or $Ir(CO)_4^-$ [13], there is no evidence that $Co(CO)_4^-$ is reduced by sodium or potassium metal in hexamethylphosphoric triamide (HMPA). We have observed that excess sodium naphthalenide slowly (over a period of 40–50 h at room temperature) converts

$Na[Co(CO)_4]$ in THF to an impure and insoluble brown powder which contains $Na_3[Co(CO)_3]$, but this synthesis is of little or no utility. Since $Fe(CO)_4PPh_3$ can be readily converted to $Fe(CO)_4^{2-}$ by $K[HB(secBu)_3]$ or Na-Ph_2CO in THF [1a], it was felt that perhaps $Co(CO)_3^{3-}$ could be obtained by the Na-HMPA reduction of $Na[Co(CO)_3PPh_3]$. The latter was prepared by the method of Hieber [17]. In fact, four equivalents of Na in HMPA converts $Na[Co(CO)_3PPh_3]$ to another substance, believed to be $Co(CO)_3PPh_2^{2-}$ on the basis of IR data: ν(CO)(HMPA), 1870 m, 1778 vs. cm^{-1} and its protonation to give $Co(CO)_3(PPh_2H)^-$ [18]. Thus, it appears that coordinated PPh_3 was reduced in this reaction, perhaps according to eq. 1.

$$Na[Co(CO)_3PPh_3] + 2\ Na \rightarrow Na_2[Co(CO)_3PPh_2] + NaPh \qquad (1)$$

Reduction of $Co(CO)_4^-$; unusual purification of $Na_3[Co(CO)_3]$

Reduction of $Co(CO)_4^-$ by sodium or potassium in liquid ammonia appears to proceed according to eq. 2 (shown for the potassium reaction).

$$KCo(CO)_4 + 3\ K \rightarrow K_3[Co(CO)_3] + \tfrac{1}{2}[K_2C_2O_2] \qquad (2)$$

The presence of $K_2C_2O_2$ in the reaction product has been established by comparison of the mineral mull IR spectrum of bonafide $K_2C_2O_2$, prepared from the reaction of free CO and potassium metal in liquid ammonia [15], and that of the impure $K_3[Co(CO)_3]$. Both contain a weak but sharp absorption at about 2140 cm^{-1}, which is characteristic of $K_2C_2O_2$. Although efforts to separate the $K_2C_2O_2$ from $K_3[Co(CO)_3]$ have been unsuccessful to date, we did succeed in purifying a small sample of $Na_3[Co(CO)_3]$ by a rather surprising procedure. This method was inspired by Corbett's studies on Zintl ions [19]. He found that $[Na(cryptand\text{-}2.2.2)]_3Sb_7$ could be prepared by the solubilization of NaSb alloy with cryptand-2.2.2 (i.e. $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$) in neat ethylenediamine. In our attempt to prepare $[Na(cryptand\text{-}2.2.2)]_3[Co(CO)_3]$, an impure sample of $Na_3[Co(CO)_3]$, containing both $Na_2C_2O_2$ and some $NaNH_2$, was treated with cryptand-2.2.2 in ethylenediamine at room temperature. Rather quickly, a deep red brown color formed in the ethylenediamine and we thought that we had solubilized the $Na_3[Co(CO)_3]$! Surprisingly however, instead the cryptand apparently dissolved all of the impurities! Filtration of the aforementioned solution provided an insoluble homogeneous yellow to olive solid which proved to be analytically pure $Na_3[Co(CO)_3]$!! Unfortunately, this method seems unlikely to be of any importance in the routine purification of $Na_3[Co(CO)_3]$ in view of the high price of cryptand-2.2.2 (ca. US $40 per gram). But we were quite amused at this rather unusual use of a cryptand in cleaning up a material that had defied previous, more conventional, attempts at its purification. The nature of the materials dissolved in the ethylenediamine solution remain largely unknown. No $Na_3[Co(CO)_3]$ and very little $Na[Co(CO)_4]$ were present. One attempt to prepare $[K(cryptand\text{-}2.2.2)]_3[Co(CO)_3]$ by reduction of preformed $[K(cryptand\text{-}2.2.2)][Co(CO)_4]$ with three equivalents of $[K(cryptand(2.2.2)]^+\ e^-$ [20] in liquid ammonia was also carried out. Very interestingly, no reduction of $Co(CO)_4^-$ was observed to occur under these conditions. If this experiment and our other observations are of any consequence, it may well indicate that the formation and/or existence of $Co(CO)_3^{3-}$ depends on strong cation–anion interactions in the solid state. If this is true then attempts to solubilize salts containing $Co(CO)_3^{3-}$ may be doomed to failure. Indeed, it has been observed

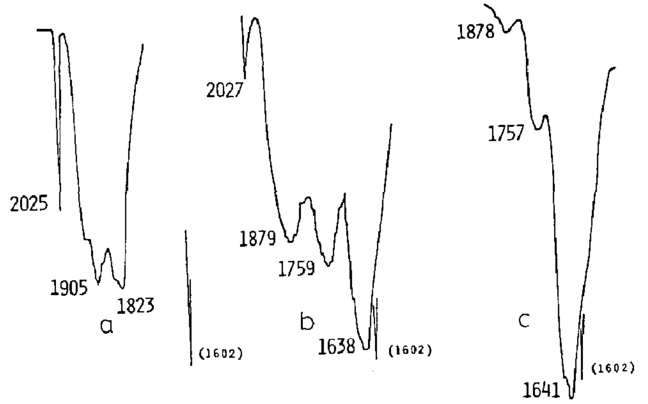

Fig. 1. Nujol mull infrared spectra in the carbonyl stretching frequency region of unsolvated K[Co(CO)$_4$] (a), product after reduction of K[Co(CO)$_4$] with two equiv. of K (b), and K$_3$[Co(CO)$_3$] (c), the product resulting from reduction of K[Co(CO)$_4$] with three equiv. of K. Approximate band positions are shown in cm^{-1}.

that treatment of Na$_3$[Co(CO)$_3$] with the very polar solvent HMPA resulted in decomposition and the formation of Na[Co(CO)$_4$] as the only observable carbonylmetallate in solution. Surprisingly, however, solutions of Na$_3$[Rh(CO)$_3$] and Na$_3$[Ir(CO)$_3$] in HMPA have been obtained [13].

Progress of the reduction of K[Co(CO)$_4$] by potassium metal in liquid metal to form K$_3$[Co(CO)$_3$] has been monitored by taking Nujol mull infrared spectra of the isolated product after addition of 2 and 3 equivalents of potassium metal. The resulting spectra in the ν(CO) region are shown in Fig. 1 and demonstrate that the reduction was still substantially incomplete after consumption of two equivalents of K. However, the third equivalent of potassium metal caused all but traces of the Co(CO)$_4^-$ to disappear and left mainly K$_3$[Co(CO)$_3$]. It is not yet clear whether the band at about 1760 cm^{-1} is due to an intermediate reduction product or K$_3$[Co(CO)$_3$]. Nujol mull spectra of the pure Na$_3$[Co(CO)$_3$] (Fig. 2) show a much weaker shoulder in this region. It is important to note however, that the most intense bands centered at about 1610 cm^{-1} for Na$_3$[Co(CO)$_3$] or 1640 cm^{-1} for K$_3$[Co(CO)$_3$] are in the same region as those of corresponding bands observed for

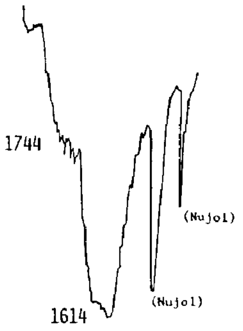

Fig. 2. Nujol mull infrared spectrum in the ν(CO) region of unsolvated Na$_3$[Co(CO)$_3$]. Band positions are shown in cm^{-1} units.

mull IR spectra of other carbonylmetallate(3 −) salts including $K_3[V(CO)_5]$, 1812 m, 1600 vs br cm^{-1} [14] and $Na_3[Mn(CO)_4]$, 1790 w, 1600 vs br cm^{-1} [1b]. Also shown in Fig. 1 is the previously unreported mull spectrum of unsolvated $K[Co(CO)_4]$ which shows the effect of substantial ion pairing of potassium ion and $Co(CO)_4^-$ in the solid state, a phenomenon previously discussed in some detail for $Na[Co(CO)_4]$ by Edgell and co-workers [21] and recently reviewed by M. Darensbourg [22].

Reaction of $A_3[Co(CO)_3]$, (A = Na or K) with electrophiles

Ph_3ECl, E = Ge, Sn, Pb. Treatment of a suspension of $A_3[Co(CO)_3]$ (A = Na or K) in THF or liquid ammonia with two to three equivalents of Ph_3ECl (E = Ge, Sn, Pb), followed by cation exchange, provides 50–70% isolated yields of colorless (E = Ge, Sn) or yellow (E = Pb) fairly air and moisture stable tetraethylammonium salts containing anions of the composition $(Ph_3E)_2Co(CO)_3^-$.

$$2\,Ph_3ECl + Co(CO)_3^{3-} \rightarrow trans\text{-}(Ph_3E)_2Co(CO)_3^- + 2\,Cl^- \qquad (3)$$

Formation of these derivatives in good yields provides important additional evidence for the existence of $Na_3[Co(CO)_3]$ and $K_3[Co(CO)_3]$. Although it seems likely that the reaction proceeds by the intermediate formation of tetrahedral dianions of the type $(Ph_3E)Co(CO)_3^{2-}$ and we have IR spectral evidence to suggest that such materials do exist, attempts to isolate satisfactorily pure samples of these dianions have not been successful to date. These monoanions are analogous to the previously known cations *trans*-$[(Ph_3Y)_2Co(CO)_3]^+$ (Y = P, As or Sb) [22]. Since IR solution spectra of $[Et_4N][(Ph_3E)_2Co(CO)_3]$ show only one band in the ν(CO) region, it is very likely that these anions also contain *trans*-disubstituted trigonal bipyramidal units.

Protonation of $A_3[Co(CO)_3]$ (A = Na or K); synthesis of $Co(CO)_3L^-$ (L = PR_3, CNR)

While the protonation reactions of the carbonyl trianions of the group 5 [24] and group 7 [1b] elements have been examined in some detail, little is presently known about corresponding reactions of the group 9 carbonyl trianions. Treatment of a slurry of $K_3[Co(CO)_3]$ in liquid ammonia at −78 °C with two equivalents of ethanol provided an orange yellow solution. A ^1H NMR spectrum of this solution at −50 °C in the hydride region showed a very broad band (FWHH 720 Hz) centered at δ −7.8 ppm. Provisionally this band is assigned to $H_2Co(CO)_3^-$, but the possibility that it is some other cobalt hydride cannot be ruled out presently. Clearly more work needs to be done to properly characterize this material. It is of interest that low temperature matrix isolation studies have provided evidence for the existence of $H_3Co(CO)_3$, which may be considered to be the conjugate acid of $H_2Co(CO)_3^-$ [25].

Addition of three equivalents of NH_4Cl to a liquid ammonia slurry of $K_3[Co(CO)_3]$ followed by treatment with PPh_3 or $P(C_6H_{11})_3$, and cation exchange resulted in the isolation of 40 and 45% isolated yields of satisfactorily pure $[Et_4N][Co(CO)_3PPh_3]$ and $[Ph_4As][Co(CO)_3P(C_6H_{11})_3]$, respectively. No attempts to improve these yields were made since the identical materials are more readily obtained by the method of Hieber, which involves reduction of the respective dimers, $[Co(CO)_3(PR_3)]_2$ by Na-Hg, followed by cation exchange [17,26]. However, isocyanide substituted carbonylcobaltate ions are not available by Hieber's route since the precursors, $Co_2(CO)_6(CNR)_2$ are unknown. Attempts to prepare these materials by the substitution of $Co_2(CO)_8$ by isocyanides, results in the disproportionation of the carbonyl in accordance with the following equation [27].

$$Co_2(CO)_8 + 5\ RNC \xrightarrow{-4CO} [Co(CNR)_5][Co(CO)_4] \qquad (4)$$

For this reason, it was felt that the synthesis of anions of the type $Co(CO)_3(CNR)^-$ would be a significant extension of our general procedure. In fact, treatment of $Na_3[Co(CO)_3]$ with three equivalents of NH_4Cl, followed by the addition of RNC (R = t-Bu, C_6H_{11} and 2,6-dimethylphenyl) provides complexes of the type $Co(CO)_3CNR^-$. All were characterized by IR solution spectra. In addition, $Co(CO)_3(CN\text{-}t\text{-}Bu)^-$ was isolated as a satisfactorily pure tetraethylammonium salt and further characterized by its ^1H NMR spectrum. The other anions were not isolated as pure substances, but have IR spectra very similar to that of $Co(CO)_3(CN\text{-}t\text{-}Bu)^-$; i.e., $[Et_4N][Co(CO)_3(CN\text{-}2,6\text{-}Me_2C_6H_3)]$, IR(THF), ν(CN, CO): 2040 w, 1900 s, 1860 s, 1586 w cm^{-1}; $[Et_4N][Co(CO)_3(CNC_6H_{11})]$, IR(THF), ν(CN, CO): 2040 w, 1915 s, 1850 s cm^{-1}. These $Co(CO)_3L^-$ species are believed to be formed by the following reaction sequence. But it must be regarded as a very speculative pathway, since none of the intermediates, $HCo(CO)_3^{2-}$, $H_2Co(CO)_3^-$ or $Co(CO)_3NH_3^-$ have been unambiguously identified. Such a scheme is attractive, however, in terms of what is known about the great instability of $H_3Co(CO)_3$ [25],

$$Na_3[Co(CO)_3] + \xrightarrow[-NaCl]{+NH_4Cl} Na_2[HCo(CO)_3] \xrightarrow[-NaCl]{+NH_4Cl} Na[H_2Co(CO)_3]$$

$$Na[H_2Co(CO)_3] \xrightarrow[-NaCl]{+NH_4Cl} [H_3Co(CO)_3] \xrightarrow[-H_2,\ -NH_4^+]{+2\ NH_3} Co(CO)_3NH_3^-$$

$$Co(CO)_3NH_3^- \xrightarrow[-NH_3]{+L} Co(CO)_3L^-$$

the high lability of the known amminecarbonylmetallates(1 −) [14,16] and related studies on the protonation reactions of other carbonyl trianions, $Na_3[M(CO)_5]$ (M = V, Nb and Ta) [16] and $Na_3[M(CO)_4]$ (M = Mn and Re) [1b].

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