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PREPARATION OF METAL CARBONYLATE ANIONS BY HYDRIDE REDUCTION

K. INKROTT, R. GOETZE, and S. G. SHORE*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210
(U.S.A.)

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Summary

Reductive cleavage of $[Mn(CO)_5]_2$, $[Co(CO)_4]_2$, $[(Ph_3P)Co(CO)_3]_2$, $[(C_5H_5)Mo(CO)_3]_2$, and $[(C_5H_5)Fe(CO)_2]_2$ by KH in THF or HMPA/THF affords $KMn(CO)_5$, $KCo(CO)_4$, $K(Ph_3P)Co(CO)_3$, $K(C_5H_5)Mo(CO)_3$, and $K(C_5H_5)Fe(CO)_2$, respectively, in near quantitative yields.

Introduction

Until relatively recently, the conventional method for the preparation of monometal carbonyl anions[1,2] employed sodium-mercury amalgam to cleave reductively the corresponding metal-metal dimers. This method is handicapped by the necessity to remove relatively large quantities of mercury from the system. Furthermore, contamination of the metal carbonylate product through the formation of mercury derivatives is possible.[3]

Alternative synthetic procedures which minimize or preclude these problems have been described recently. These include the use of sodium-potassium alloy (NaK)[4] or trialkylborohydrides[5] to achieve reductive cleavage. While the use of NaK provides for an inherently fast and clean reductive cleavage, more highly reduced species can be inadvertantly formed due to inadequate control of reaction time or temperature.[4] Furthermore, for those systems in which the carbonylate product is unstable at room temperature, low temperature reactions are limited by the freezing point[6] of the NaK system. Finally, the use of NaK always poses a potentially serious fire hazard. While trialkylborohydrides are also effective for reductive cleavage, it is necessary to remove the trialkylborane formed in the reaction. In view of the basic character of the carbonylate anion, there is a real possibility for coordination of the trialkylborane to the anion,[7] thereby inhibiting its removal, especially if the carbonylate ion is to be isolated at low temperatures.

We present here a simple procedure for the reductive cleavage of dinuclear carbonyls which, using potassium hydride as the reducing agent, eliminates the aforementioned problems. Highly reduced species are not formed as by-products, hydrogen gas is the only other product of the reduction reaction, and reaction temperatures are not restricted by the nature of the reducing agent. Furthermore, although reductive cleavage with KH can be carried out in a conventional Schlenk system using infrared spectroscopy to monitor the extent of reaction, a simple vacuum line equipped with a Toepler pump[8] for measuring H_2 evolution can also be used. The vacuum line method is especially useful since the extent of reaction can be readily monitored without opening the system.

Results and discussion

Using the following general reaction, (1),

$$[M(L)(CO)_x]_2 + 2KH \longrightarrow 2K[M(L)(CO)_x] + H_2 \qquad (1)$$

$$L = CO,\ PPh_3,\ \eta^5\text{-}C_5H_5$$

a number of representative dimers were cleaved: $[Co(CO)_4]_2$, $[(Ph_3P)Co(CO)_3]_2$, $[Mn(CO)_5]_2$, $[(C_5H_5)Mo(CO)_3]_2$, and $[(C_5H_5)Fe(CO)_2]_2$ in THF or 50/50 HMPA/THF. The reactions occurred cleanly, giving near quantitative yields of carbonylate ions. Reaction times could be varied over a wide range of temperatures (-78° to 30°) and still give quantitative yields in 12 hr or less. Dicobaltoctacarbonyl, for example, is completely reduced in THF solution after 12 hr at -78°. While $Mn(CO)_5^-$ was quantitatively generated in THF solution at 30° within 4 hr, no adverse secondary reactions were noted when the system was maintained at room temperature for 24 hr. Interestingly, the formyl complex $CO)_5Mn\text{-}Mn(CO)_4(CHO)^-$ has been reported[5] as an intermediate in the cleavage of $Mn_2(CO)_{10}$ by $Li(C_2H_5)_3BH$. Analogous formyl intermediates have been postulated to exist in the trialkylborohydride reduction of other dimeric systems.[5] We observed no formyl intermediates in the systems which were reductively cleaved by KH. Rather, H_2 evolution is a gradual and continuous process throughout the time of reaction. The failure to observe any formyl species, if one is formed during the KH reduction, may be attributed to the low solubility of KH and the instability of the formyl intermediate.

Quantitative preparation of $[(C_5H_5)Fe(CO)_2]^-$ could not be accomplished in THF; addition of the strongly coordinating HMPA was required. Reduction was complete in 4 hr at 30° in 50/50 HMPA/THF. In this mixed solvent $K[(C_5H_5)Fe(CO)_2]$ produces only two bands assigned to CO stretching modes in the infrared spectrum (1867, 1792 cm^{-1}). The sodium salt of the anion, prepared[9] from sodium metal and $[(C_5H_5)Fe(CO)_2]_2$ in HMPA, also shows two absorptions at 1869, 1797 cm^{-1} (HMPA). On the other hand, $K[(C_5H_5)Fe(CO)_2]$ in THF produces three such bands (1868, 1792, 1772 cm^{-1}).[4] The third band is believed[4,9] to be a consequence of significant ion-pair formation in THF which is precluded in the presence of HMPA. Detailed infrared and conductance studies[10,11] of manganese carbonylates in coordinating and non-coordinating solvents are consistent with this interpretation for $K[(C_5H_5)Fe(CO)_2]$.

Of all the metal dimer systems investigated, only $Re_2(CO)_{10}$ withstood facile attack by KH in THF or HMPA/THF. Trialkylborohydrides are also not effective reducing agents for this metal carbonyl.[5] Reduction of $Re_2(CO)_{10}$ with $NaBH_4$ has been reported[12] to give a solution which initially exhibits metal hydride shifts at τ 15.0 and 16.8. Species such as $HRe(CO)_4^{2-}$ and $H_2Re_2(CO)_8^{2-}$ were postulated[12] as intermediates likely to be present. We observe a proton resonance at 16.9 τ after extended exposure of $Re_2(CO)_{10}$ to KH in HMPA/THF at 70°.

Experimental

General

All manipulations were carried out either under vacuum or under an atmosphere of prepurified nitrogen. The dimers $[(Ph_3P)Co(CO)_3]_2$, $[(C_5H_5)Fe(CO)_2]_2$, $[Mn(CO)_5]_2$ (Strem Chemicals, Newburyport, Massachusetts) and $[(C_5H_5)Mo(CO)_3]_2$ (Pressure Chemical Company, Pittsburgh, Pennsylvania) were used as received, while $[Co(CO)_4]_2$ (Strem Chemicals) was sublimed and stored in the dark at -78° before use. Bis(triphenylphosphine)iminium chloride, [PPN]Cl, was prepared according to the literature method.[13] Triphenyltin chloride (Eastman Organic Chemicals, Rochester, New York) was used as received. Tetrahydrofuran (THF), pentane, and diethyl ether were distilled from $LiAlH_4$, hexamethylphosphorous triamide (HMPA) from CaH_2 under reduced pressure ($\sim$110°/10 torr), and CH_2Cl_2 from P_2O_5.

Infrared spectra of the intermediate potassium salts of the metal carbonyl anions in THF were obtained on a Perkin-Elmer 457 spectrometer using matched KBr 0.1 mm cells. Observed ν(CO) absorptions corresponded well to those reported by Ellis and Flom[4] except for $K[(C_5H_5)Fe(CO)_2]$ which was recorded in the mixed solvent THF/HMPA (50/50) as noted below. Proton nmr spectra were recorded using a Varian EM-360L spectrometer. Samples were checked for formyl and metal hydride shifts in the range from +20 to -20 δ (TMS).

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Manipulation of standardized potassium hydride

Potassium hydride (obtained as a mineral oil slurry from Research Organic/Inorganic Chemicals, Hillside, New Jersey) was repeatedly extracted with pentane and dried under high vacuum. The resulting free-flowing white powder was shown to be >92% hydride active by methanolysis and measurement of the evolved hydrogen. A short length of 5 mm glass tubing fused to a glass rod and tightly packed with KH was used in a glove bag or dry box to tap a calibrated aliquot of KH into the bottom of a reaction flask. For example, one such addition tube was calibrated by methanolysis to deliver 0.24 mmol hydride active KH, reproducible to ± 0.03 mmol. In this manner small scale reactions could be easily run without requiring the use of a sensitive balance to weigh out the KH. The purified KH is stable indefinitely under dry nitrogen. Filtered residues from the metal dimer-KH reduction reactions are safely destroyed with a 90/10 mixture of acetone/t-butyl alcohol.

Reduction of $[(Ph_3P)Co(CO)_3]_2$; preparation and characterization of metal anion derivatives

One basic procedure is applicable to the preparation of all of the carbonylate salts described in this study. This procedure is illustrated by the preparation of $K[(Ph_3P)Co(CO)_3]$ and its conversion to $Ph_3Sn(Ph_3P)Co(CO)_3$ and $[PPN][(Ph_3P)Co(CO)_3]$.

In a dry box, 1.9 mmol KH was added to 0.689 g $[(Ph_3P)Co(CO)_3]_2$, 0.85 mmol, in a round-bottomed vessel containing a magnetic stir bar. The reaction vessel was fitted with a vacuum stopcock adapter, placed on the vacuum line and evacuated. Twelve ml of dry THF was distilled onto the solids at -196°. The rust-red slurry of the slightly soluble $[(Ph_3P)Co(CO)_3]_2$ and insoluble KH was consumed after stirring 4 hr at 30°, affording a yellow-green solution of $K[(Ph_3P)Co(CO)_3]$. The gas evolved (0.895 mmol) was measured with a Toepler system and shown to be greater than 97% H_2 by mass spectral analysis. Infrared spectra of the solution filtered through a medium-porosity glass frit revealed complete reduction of the dimer to $(Ph_3P)Co(CO)_3^-$. ν(CO): 1930s, 1851s, 1822m,br cm^{-1} (THF). Addition of an equivalent amount of Ph_3SnCl, removal of KCl by filtration, and precipitation with pentane yielded 1.17 g of tannish-white $Ph_3Sn(Ph_3P)Co(CO)_3$, 91% yield based on dimer. Similar treatment of $K[(Ph_3P)Co(CO)_3]$ with [PPN]Cl and recrystallization from CH_2Cl_2/Et_2O yielded yellow $[PPN][(Ph_3P)Co(CO)_3]$ in 80% yield. ν(CO): 1928m, 1841vs cm^{-1} (THF).

Reaction conditions and product yields are summarized below for other systems starting with 0.80 to 0.90 mmol of metal dimer, 1.9 mmol KH, and 10 ml THF. All derivative yields are based on starting dimer and are comparable with those previously reported.[4,5]

$K[Co(CO)_4]$: Reduction of $[Co(CO)_4]_2$ was complete after stirring 1 hr at 0°, and an additional 0.5 hr at 25°. The resulting clear filtered solution of $K[Co(CO)_4]$ was treated with an equivalent of Ph_3SnCl, filtered, and concentrated. Recrystallization from cold hexane gave a 72% yield of orange $Ph_3SnCo(CO)_4$. In a separate experiment, the reduction of $[Co(CO)_4]_2$ was allowed to proceed under vacuum at -78° for 12 hr. Ninety percent of the theoretically expected H_2 was evolved, with negligible carbon monoxide impurity. Addition of [PPN]Cl and similar work-up gave the white salt [PPN][$Co(CO)_4$], which was recrystallized from cold CH_2Cl_2/Et_2O and isolated in 79% yield. Anal. found: C, 68.21; H, 4.56; P, 8.86. $C_{40}H_{30}CoNO_4P_2$ calcd.: C, 67.71; H, 4.23; P, 8.73%.

K[$(C_5H_5)Mo(CO)_3$]: Reduction of [$(C_5H_5)Mo(CO)_3$]$_2$ was complete after stirring 2 hr at 30°. Addition of an equivalent amount of [PPN]Cl to the resulting yellow-orange filtered solution of K[$(C_5H_5)Mo(CO)_3$] gave, after work-up and recrystallization from cold THF/Et_2O, an 87% yield of yellow [PPN][$(C_5H_5)Mo(CO)_3$]. The corresponding tannish-white triphenyltin derivative prepared in an analogous fashion was recrystallized from cold THF/pentane and isolated in 77% yield.

K[$Mn(CO)_5$]: Consumption of the yellow THF slurry of [$Mn(CO)_5$]$_2$/KH is complete in 4 hr at 30°. Addition of an equivalent amount of [PPN]Cl in CH_2Cl_2 to the filtered red* THF solution of K[$Mn(CO)_5$] gave after removal of KCl by filtration, concentration, and recrystallization from cold CH_2Cl_2/Et_2O, a 73% yield of yellow [PPN][$Mn(CO)_5$]. Anal. found: C, 65.85; H, 4.22; Mn, 7.11; N, 1.76. $C_{41}H_{30}MnNO_5P_2$ calcd.: C, 67.13; H, 4.12; Mn, 7.49; N, 1.91%. An x-ray powder pattern of the isolated KCl was identical to that of an authentic sample. Metathesis of K[$Mn(CO)_5$] with Ph_3SnCl gave after work-up and recrystallization from cold THF/pentane a 78% yield of cream-white $Ph_3SnMn(CO)_5$.

K[$(C_5H_5)Fe(CO)_2$]: Cleavage of [$(C_5H_5)Fe(CO)_2$]$_2$ with KH in THF was only 50% complete after stirring two days at room temperature. However, reduction was complete after 4 hr at 30° in 50/50 HMPA/THF. Filtration gave a red solution of K[$(C_5H_5)Fe(CO)_2$]. $\nu(CO)$: 1867s, 1792s cm^{-1} (50/50 HMPA/THF). Methathesis with Ph_3SnCl gave after work-up and recrystallization from HMPA/EtOH/H_2O an 81% yield of yellow $Ph_3Sn(C_5H_5)Fe(CO)_2$.

K[$Re(CO)_5$]: THF solutions of $Re_2(CO)_{10}$ are virtually unchanged after stirring over KH at 25° for 48 hr as monitored by infrared and the absence of significant gas evolution. Attempted reduction of the dimer in 50/50 HMPA/THF gradually gave a red solution under vigorous reaction conditions (12 hr at 70°) which gave a complex infrared absorption spectrum. At least ten $\nu(CO)$ stretches were observed. Those assignable[4] to $Re(CO)_5^-$ at 1910s, 1862s, 1834sh cm^{-1} (50/50 HMPA/THF) were of moderate intensity. A proton nmr spectrum showed, besides those shifts due to HMPA and THF, a weak resonance at 16.9 τ.

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*A referee has suggested that the reddish coloration noted for our solutions of $Mn(CO)_5^-$ may be due to $Mn_3(CO)_{14}^-$. We have not found any infrared evidence for this species, however.

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