benzene complex, **1** resists condensation to a binuclear species. In acetone solution, **1** converts to $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)](TFMS)_2$ and free TMB with an approximate half-life of 0.5 h.[12]

In certain applications it is possible to reduce $Os(NH_3)_5(TFMS)_3$ with the ligand in situ, thereby avoiding the use of tetramethylbenzene to stabilize the osmium(II). We have used this method of reduction with only limited success; a complication arises in that $[Os(NH_3)_5DME]^{2+}$ rapidly reacts with the unreduced Os(III) starting material, producing $[Os(NH_3)_6]^{2+}$ and other unidentified products. We have found this method to be reliable only for cases in which the ligand concentration can be kept in 10-100-fold excess of that for the osmium.

For applications in which the desired product is short-lived, thus requiring both a rapid reduction and substitution, we have had success with homogeneous reducing agents such as $CoCp_2$ or $[Os(NH_3)_6](TFMS)_2$, but the target ligand must be present or the solution of pentaammineosmium(II) will decompose. In particular, we find that $[Os(NH_3)_5]^{2+}$ will react with $CoCp_2^+$, resulting in several unidentified products.

For the vast majority of reactions that we have investigated, we find **1** to be a convenient precursor for pentaammineosmium(II) chemistry.

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Registry No. 1, 109242-80-0; TMB, 488-23-3; $[Os(NH_3)_5TFMS](TFMS)_2$, 83781-30-0; $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)](TFMS)_2$, 105164-48-5; $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)](TFMS)_2$, 109281-96-1; $[Os(NH_3)_5(CH_3CN)](TFMS)_2$, 109242-81-1; $[Os(NH_3)_5DME](TFMS)_2$, 109281-98-3; $[Os(NH_3)_6](TFMS)_2$, 109242-82-2; $CoCp_2$, 1277-43-6.

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(11) The products were analyzed in situ by electrochemical and NMR data. A more complete characterization of the ketone and arene complexes has been reported in separate publications.[4,5] The reaction of **1** with esters and amides will be reported separately. The complex $[Os(NH_3)_5CH_3CN]^{2+}$ has been fully characterized and is described by Sekine et al. in a separate note currently submitted for publication.

(12) The reaction was followed by ^1H NMR in acetone-d_6.

Contribution from the Department of Chemistry,
University at Buffalo, State University of New York,
Buffalo, New York 14214

Reaction of Bis(triphenylphosphine)tricarbonylcobalt(I) with Metal Carbonyl Anions $[Co(CO)_4]^-$, $[Co(CO)_3PBu_3]^-$, $[Mn(CO)_5]^-$, and $[CpFe(CO)_2]^-$: Kinetics and Mechanism of the Reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$

Jim D. Atwood

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We have begun an examination of the conceptually simple reactions between metal carbonyl cations and anions, which may be similar to reactions between stabilized carbocations and carbanions leading to carbon-carbon bond formation.[1-4] In this manuscript, we report the reaction of the cation, $[Co(CO)_3(PPh_3)_2]^+$ with the metal carbonyl anions $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, and $[CpFe(CO)_2]^-$ and a kinetic study of the reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$.

Experimental Section

Materials. $Co_2(CO)_8$ was purchased from Alfa Products and extracted into hexanes before use. THF was twice dried and distilled; CH_3CN was dried over CaH_2 and distilled. Other solvents were dried by standard procedures. All solvents were stored in an inert-atmosphere glovebox.

$[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ was prepared by modification of the literature procedure.[5] A hexane solution of $Co_2(CO)_8$ was cooled in an inert-atmosphere glovebox by vacuum removal of some hexanes, and an excess of PPh_3 was added. After 1 h the precipitate was collected containing $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ and $Co_2(CO)_6(PPh_3)_2$. The red-brown $Co_2(CO)_6(PPh_3)_2$ was removed by dissolution into acetone and slow addition of H_2O. The first precipitate, which was red-brown, was discarded. Further H_2O was added to the light yellow solution, causing precipitation of a yellow powder. The infrared spectrum showing $[Co(CO)_3(PPh_3)_2]^+$ at 2005 (m) cm^{-1} and $[Co(CO)_4]^-$ at 1885 (vs) cm^{-1} is consistent with that previously reported.[5]

The very stable $Co_2(CO)_6(PPh_3)_2$ was prepared by literature procedures,[6] with an infrared spectrum ($CHCl_3$) having peaks at 1974 (sh, w) and 1955 (s, br) cm^{-1}.

$[Co(CO)_3(PPh_3)_2][BPh_4]$ was prepared from $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ by anion exchange, as previously reported.[5] Recrystallization led to a pale yellow product. IR (THF): 2070 (vvw), 2005 (vs) cm^{-1}.

$[PPN][Co(CO)_4]$ (PPN = bis(triphenylphosphine)nitrogen(1+) cation) was prepared as previously described.[7] Further purification was necessary to remove traces of [PPN][Cl]—the product was extracted with THF, the THF removed, and the solid recrystallized from CH_2Cl_2/Et_2O as described (IR (THF): 1880 cm^{-1}).[7]

$[PPN][Mn(CO)_5]$ was prepared similarly to $[PPN][Co(CO)_4]$ as described above. Careful washing of the product produced a light yellow compound with infrared absorptions at 1890 (s) and 1858 (vs) cm^{-1} in THF.

$[PPN][CpFe(CO)_2]$ was prepared similarly, giving a product with infrared bands at 1860 (s) and 1788 (s) cm^{-1} in THF, which compare favorably with those previously reported for the NBu_4^+ salt.[8]

$[PPN][Co(CO)_3PBu_3]$ was prepared by Na/Hg reduction of $Co_2(CO)_6(PBu_3)_2$ and treatment with [PPN][Cl].[7] Recrystallization was effected from THF/Et_2O, giving yellow crystals with infrared absorption at 1878 cm^{-1} in THF.

Kinetic Measurements. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer in the absorbance mode, using 1.0-mm NaCl solution cells. Quantitative data on the reaction between $[Co(CO)_3(PPh_3)_2]^+$ and $[Co(CO)_4]^-$ were obtained on either the 2005-cm^{-1} absorption for $[Co(CO)_3(PPh_3)_2]^+$ or the 1885-cm^{-1} absorption for $[Co(CO)_4]^-$. Beer's law plots were linear for each within the concentration range utilized. For a typical reaction a jacketed reaction vessel was taken into an inert-atmosphere glovebox where $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ dissolved in THF was added. An infrared sample was taken (for $t = 0$ and an accurate determination of the concentration) and the vessel sealed and removed from the glovebox. The reaction vessel was connected to a Haake constant temperature circulator, wrapped in foil, and shrouded in black plastic. Samples for infrared analysis were taken periodically by syringe under a positive pressure of nitrogen.

Exchange Reaction. The ^{13}CO exchange reaction with $[Co(CO)_3(PPh_3)_2]^+$ was investigated in 1,2-dichloroethane. THF could not be used because of solvent interference with the ^{13}CO absorption at 1960 cm^{-1}. The exchange utilized 90% ^{13}CO, circulated by a Masterflex tubing pump in an apparatus previously described.[9] The disappearance of the band at 2005 cm^{-1} was followed. A plot of ln $(A_\infty - A_t)$ vs. time gave the specific rate constant (at 60 °C $k = 2.8 \times 10^{-5}$ s^{-1}) from the slope. This rate constant is quoted to only two significant figures because (1) the rate constant relies on an accurate measurement of A_∞, which is difficult, and (2) no attempt was made to correct for changing enrichment during the reaction. The enrichment changes from 90% to ~60% as the ^{12}CO from the complex becomes free.

Results

Product Analysis. The reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ leads exclusively to $Co_2(CO)_6(PPh_3)_2$ under an inert atmosphere.

$$[Co(CO)_3(PPh_3)_2]^+ + [Co(CO)_4]^- \rightarrow Co_2(CO)_6(PPh_3)_2 + CO \quad (1)$$

The kinetics of appearance of $Co_2(CO)_6(PPh_3)_2$ were not evaluated because of interference from THF absorptions eliminating the region from 1990 to 1940 cm^{-1} for quantitative work. $Co_2(CO)_6(PPh_3)_2$ was identified by removing the THF at completion

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Table I. Effect of Added Ligands on the Rate Constant for the Reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ at 50.3 °C in THF

added ligand	10^4 k, s^{-1}	added ligand	10^4 k, s^{-1}
none	2.10 ± 0.10	PPh_3 (2.0×10^{-3} M)	2.1 ± 0.2
CO^a	1.10 ± 0.06	none^b	2.4 ± 0.2

^{a} At 1 atm of pressure. ^{b} $[Co(CO)_3PBu_3]^-$ as the anion.

Table II. Effect of Innocent Salt on the Reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ at 50.0 °C

10^4[[PPN][BPh_4]], M	10^4k, s^{-1}	10^4[[PPN][BPh_4]], M	10^4k, s^{-1}
0	2.0 ± 0.2	5.5	1.0 ± 0.2
1.1	1.8 ± 0.2	6.0^a	0.52 ± 0.05
2.8	1.6 ± 0.2	5.6^b	0.96 ± 0.2

^{a} At 1 atm of CO. ^{b} 3.1×10^{-3} M PPh_3.

Table III. Averaged Rate Constants at Various Temperatures

T, °C	k, s^{-1}	T, °C	k, s^{-1}
40	3.16×10^{-5}	50	2.24×10^{-4}
45	7.38×10^{-5}	55	6.79×10^{-4}

$\Delta H^\ddagger = 42 \pm 3$ kcal/mol $\Delta S^\ddagger = 52 \pm 10$ eu

Table IV. Effect of Solvent on the Rate Constant for the Reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ at 50.2 °C

solvent	k, s^{-1}	ϵ
THF	$(2.13 \pm 0.09) \times 10^{-4}$	7.58
$C_2H_4Cl_2$	$(2.78 \pm 0.10) \times 10^{-5}$	10.36
CH_3CN	$(1.31 \pm 0.05) \times 10^{-5}$	35.95

of the reaction and dissolution in CH_2Cl_2 (IR = 1950 (br) cm^{-1}, identical with that of an independently prepared sample). Reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ under an atmosphere of CO leads initially to $Co_2(CO)_7PPh_3$ (identified by the absorptions at 2075 (m), 2022 (m), and 2000 (s) cm^{-1},[10] which eventually converted to $Co_2(CO)_6(PPh_3)_2$. The rate of appearance of $Co_2(CO)_7PPh_3$ was, within experimental error, the same as for disappearance of the cation and anion.

Reaction of $[PPN^+][Mn(CO)_5^-]$ with $[Co(CO)_3(PPh_3)_2^+][BPh_4^-]$ occurs rapidly at room temperature. Removal of the THF and extraction with hexanes shows $Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_{10}$, with $Mn_2(CO)_9PPh_3$ predominant.[11] Further extraction of the solid with toluene shows $Co_2(CO)_6(PPh_3)_2$.

$$2[Co(CO)_3(PPh_3)_2]^+ + 2[Mn(CO)_5]^- \rightarrow Co_2(CO)_6(PPh_3)_2 + Mn_2(CO)_9PPh_3 + PPh_3 \quad (2)$$

Similar reaction of $[PPN^+][CpFe(CO)_2^-]$ with $[Co(CO)_3(PPh_3)_2^+][BPh_4^-]$ very rapidly yields only $Cp_2Fe_2(CO)_4$ and $Co_2(CO)_6(PPh_3)_2$ as shown by infrared analysis.

$$2[Co(CO)_3(PPh_3)_2]^+ + 2[CpFe(CO)_2]^- \rightarrow Co_2(CO)_6(PPh_3)_2 + Cp_2Fe_2(CO)_4 + 2PPh_3 \quad (3)$$

The latter two reactions were rapid, while reaction 1 occurred at an appropriate rate for kinetic investigation. In each of the reactions (eq 1–3), a net electron transfer has taken place in proceeding from reactants to products.

Kinetic Analysis. Following the disappearance of $[Co(CO)_3(PPh_3)_2]^+$ in reaction with $[Co(CO)_4]^-$ shows a first-order decay for 3 half-lives. This first-order behavior is retained in the presence of additional $[Co(CO)_3(PPh_3)_2]^+$ added as the $[BPh_4]^-$ salt. Added $[Co(CO)_4]^-$ as the $[PPN]^+$ salt has no effect on the kinetic behavior. Thus the reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$ is first order in $[Co(CO)_3(PPh_3)_2]^+$ and zero order in $[Co(CO)_4]^-$. The independence on the cobalt anion was further shown by using $[Co(CO)_3PBu_3]^-$, which reacted at the same rate as $[Co(CO)_4]^-$. The rate law is thus

$$\text{rate} = k[Co(CO)_3(PPh_3)_2^+] \quad (4)$$

The presence of 1 atm of CO causes a significant inhibition of the rate; an excess of PPh_3 has no effect on the rate constant as shown by the data in Table I. The presence of the "innocent salt", [PPN][BPh_4], inhibits the reaction, with the rate decreasing linearly with the concentration of added [PPN][BPh_4]. In the presence of [PPN][BPh_4], CO continues to show an inhibiting effect on the reaction (shown in Table II). Activation parameters were determined from rate data at four temperatures (40, 45, 50, and 55 °C) as $\Delta H^\ddagger = 42 \pm 3$ kcal/mol and $\Delta S^\ddagger = 52 \pm 10$ eu. Averaged rate constants at these temperatures are shown in Table III. There is a solvent effect (shown in Table IV), with the more polar solvent inhibiting the reaction.

Discussion

We propose the reaction of a metal carbonyl cation with a metal carbonyl anion leading to dinuclear compounds to be among the most direct examples of reactions involving *net* electron transfer.[12-16] The mechanism of such reactions has not been previously investigated and is not meant to be implied by use of the term "electron transfer", merely the result. If the dimer is considered to be composed of two metal centers in zero oxidation states, we consider that a net electron transfer has taken place. Although this type of electron transfer is commonly observed between organometallic complexes, relatively few mechanistic studies have been accomplished.[17]

The reaction of $[Co(CO)_3(PPh_3)_2]^+$ with $[Co(CO)_4]^-$, occurs at convenient rates for examination with the rate law in eq 4. This rate law is atypical for electron-transfer mechanisms. The first-order dependence on $[Co(CO)_3(PPh_3)_2^+]$ could arise from PPh_3 dissociation or from CO dissociation before reaction with $[Co(CO)_4]^-$. The inverse dependence on [CO] and lack of dependence on [PPh_3], as shown in Table I, indicate that CO dissociation is occurring. This is confirmed by ^{13}CO exchange experiments on $[Co(CO)_3(PPh_3)_2]^+$, which showed that CO exchange occurs at 8.4×10^{-5} s^{-1} (3 × specific rate constant) at 60 °C in 1,2-dichloroethane which may be compared to the rate of 1.0×10^{-4} for reaction under comparable conditions. There was no evidence in the infrared spectrum for products of PPh_3 dissociation in the ^{13}CO exchange reaction. The activation parameters for electron transfer confirm the first-order reaction and are consistent with CO dissociation (Table III). The magnitude (a factor of 10) and direction of the solvent effect are also consistent with CO dissociation, with the higher dielectric constant giving a slower reaction. This is just as observed for CO dissociation from neutral carbonyl complexes.[18] Thus all of the evidence supports CO dissociation from $[Co(CO)_3(PPh_3)_2^+]$ as the rate-determining step in reaction 1.

Two pieces of evidence suggest that $[Co(CO)_3(PPh_3)_2]^+$ and $[Co(CO)_4]^-$ are associated in THF.[19] The addition of the innocent salt, [PPN][BPh_4], causes an inhibition of the reaction that is linearly dependent on the concentration of [PPN][BPh_4] up to a saturated solution (a 2-fold excess of [PPN][BPh_4]). At a 1:1 ratio of [PPN][BPh_4] and $[Co(CO)_3(PPh_3)_2]^+$ $[Co(CO)_4]^-$, the decrease in rate is 20% compared to no added innocent salt. The inhibition of the rate of the electron-transfer reaction by added CO is much smaller than commonly observed for CO dissociation.[18] Calculation of the competition ratio of $[Co(CO)_4]^-$ and CO for the intermediate generated by CO dissociation from $[Co(CO)_3(PPh_3)_2]^+$ gives a value of 8.0 ± 1.0. Normal values

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of the competition ratio for CO dissociation in substitution reactions with neutral ligands are about 1.0.[20-23] Thus $[Co(CO)_4]^-$ is very efficient at trapping the intermediate $[Co(CO)_2(PPh_3)_2]^+$, probably from being in close proximity.

The necessity for CO dissociation from $[Co(CO)_3(PPh_3)_2]^+$ before reaction with $[Co(CO)_4]^-$ makes it difficult to distinguish a single electron-transfer mechanism from two-electron donation by the $[Co(CO)_4]^-$ to the 16-electron cation, $[Co(CO)_2(PPh_3)_2]^+$. That the final product has PPh_3 substituted on each cobalt indicates that such an acid-base mechanism would be followed by metal-metal bond cleavage, probably homolytic to allow PPh_3 transfer between the cobalt centers. For reactions of $[CpFe(CO)_2]^-$ and $[Mn(CO)_5]^-$ with $[Co(CO)_3(PPh_3)_2]^+$, which occur at rates more rapid than CO dissociation and lead to products that are typical of 17-electron species,[18] a second path must be available for the electron transfer, most likely a single-electron transfer. While at this point, there is no direct evidence regarding the second pathway, that the weak nucleophile, $[Co(CO)_4]^-$, cannot proceed by the second pathway suggests the importance of nucleophilic attack of the carbonyl anion on the carbon of a carbonyl of the cation. The reaction of $[Re(CO)_5(C_2H_4)]^+$ with $[Re(CO)_5]^-$ serves as a model for such nucleophilic attack.[24]

$$[Re(CO)_5(C_2H_4)]^+ + [Re(CO)_5]^- \rightarrow (CO)_5ReC_2H_4Re(CO)_5 \quad (5)$$

Nucleophilic attack at the carbon of carbon monoxide attached to cations has been observed for carbanions and alkoxides and is a plausible step for precursor complex formation. Further work will be necessary to substantiate the possibility of nucleophilic attack for electron transfer in organometallic systems.

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Registry No. $[Co(CO)_3(PPh_3)_2]^+$, 47854-84-2; $[Co(CO)_4]^-$, 14971-27-8; $[Co(CO)_3(PBu_3)]^-$, 22955-42-6; $[Mn(CO)_5]^-$, 14971-26-7; $[CpFe(CO)_2]^-$, 12107-09-4; CO, 630-08-0.

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Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Aspects of the Chemistry of Water in Ambient-Temperature Chloroaluminate Ionic Liquids: ^{17}O NMR Studies

Thomas A. Zawodzinski, Jr., and R. A. Osteryoung*

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Room-temperature ionic liquids composed of mixtures of $AlCl_3$ and organic chloride salts, RCl (R = *N*-(1-butyl)pyridinium cation ($Bupy^+$) or 1-ethyl-3-methylimidazolium cation (Im^+)), have been used as solvents for a wide variety of chemical studies.[1] These molten salts have several desirable properties, including a high chloride ion activity for basic (excess RCl) melt compositions, high Lewis acidity, and nearly aprotic conditions. However, the residual protons present in the melt have been found to have significant effects on the chemistry of certain solutes.[2-4]

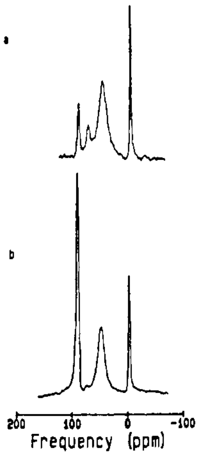

Figure 1. ^{17}O NMR spectra of 50 mM solutions of H_2O in (a) a 1.2:1.0 melt and (b) a 1.73:1.0 melt ($AlCl_3/ImCl$).

The primary source of protonic impurities in the room-temperature chloroaluminate melts is water associated with the organic chloride component of the melts. The latter salts are extremely hygroscopic, and it has proven extremely difficult to remove water completely. Associated with the protonic impurities in the melts is oxide from water and additionally from impurities in $AlCl_3$. Since these impurities are nearly always present in the melts, it is important to understand their chemistry in chloroaluminate media.

Initial studies of oxide in room-temperature melts were concerned with the development of a titration procedure for the determination of oxide impurities in melts.[5,6] It was found that Ti(IV) exhibited two voltammetric reduction waves. These were shown to be due to the reduction of the hexachlorotitanate anion and to the oxotetrachlorotitanate anion. A voltammetric procedure for oxide determination was developed. Surprisingly, the addition of water to a solution of Ti(IV) with a known oxide content shifted the equilibrium between $TiCl_6^{2-}$ and $TiOCl_4^{2-}$ away from the oxochloro complex.[5] This was believed to be due to the formation of an Al-OH-containing species that is unreactive with the hexachloro complex. Subsequent infrared work indicated that an -OH moiety is indeed formed upon addition of water to both basic and acidic melts.[7]

A study of the reduction of protons on a Pt electrode in melts has been reported.[8] The limiting currents for proton reduction increased in a roughly linear fashion with the concentration of water added to basic melts. Less current was observed for an equivalent amount of water added to an acidic melt. Finally, the addition of water to nearly neutral melts apparently results in a release of 2 protons per water molecule.[9]

As part of an ongoing effort to study the chemistry of water in the room-temperature chloroaluminate melts, we have used ^{17}O NMR spectra of water added to the melt to obtain information on the speciation of oxide and protons. This is a preliminary report of our findings, which enable a qualitative description of the nature of the species formed.

Experimental Section

The preparation, purification, and handling of melt components and solutions are fully described elsewhere.[10] Water enriched to 20 or 30%

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