The relative stability of the rhodium(I) fluoride described above in aprotic media suggests that in nonionizing systems, organometallic fluorides[18–21] may prove viable homogeneous catalysts.[22,23] We are currently extending our studies to related systems to examine the significance of steric effects[24] in the chemistry of low-valent organo transition-metal fluorides.

Acknowledgment. This work was supported by the University of South Alabama Research and Public Service Council, the University of South Alabama Research Committee, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corp. We are grateful for technical assistance from our colleagues Drs. Richard Legendre and N. Dale Ledford and for helpful discussions with Profs. Ronald J. Clark of Florida State University, Marcetta Darensbourg of Texas A&M University, and Mitsuru Kubota of Harvey Mudd/Claremont College. We also appreciate the use of materials at the Florida State University Strozier Library.

Registry No. $Rh(PPh_3)_2(CO)F$, 58167-05-8; $Rh(PPh_3)_2(CO)Cl$, 15318-33-9; $Rh(PPh_3)_2(CO)Br$, 17070-17-6; $Rh(PPh_3)_2(CO)I$, 15094-66-3; PPNCl, 21050-13-5; PPNBr, 20545-30-6; PPNI, 38011-33-5; F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2.

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(20) van Gaal, H. L. M.; van den Bekerom, F. L. A.; Verlaan, J. P. J. *J. Organomet. Chem.* **1976**, *114*, C35. Stability for $[Rh(c\text{-}C_8H_{14})_2Hal]_n$ follows Hal = F > Cl > Br > I.

(21) McAuliffe, C. A.; Pollock, R. *J. Organomet. Chem.* **1974**, *74*, 463. Ir(dap)(CO)F exists solely in pentacoordinate nonionized form in nitromethane, whereas solutions of its halide analogues contain both tetracoordinate halide-dissociated cations and the neutral pentacoordinate halide-bound complexes.

(22) Few studies using low-valent organometallic fluorides have been reported, particularly in aprotic systems. Interesting results have been reported for olefin hydrogenation catalyzed by $Rh(PPh_3)_3F$ in benzene[20] and for reaction of R_3SiH with R′OH to form R_3SiOR' promoted by $Ir(PPh_3)_2(CO)F$.[22a] Protic fluoro systems, where solvolysis of F^- is likely, have been unremarkable catalysts.[22b,c] (a) Blackburn, S. N.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* **1980**, *192*, 329. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508. (c) Spencer, A. *J. Organomet. Chem.* **1980**, *194*, 113.

(23) The potential enhanced reactivity[18b] of such fluoro complexes due to their containing both a soft metal center and the hard, small fluoride ligand is intriguing.

(24) Preliminary results indicate preference of $RhL_2(CO)^+$ for F^- vs. Cl^- is remarkably independent of the steric and electronic[25] properties of L.

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Synthesis of $[Os(NH_3)_5(\eta^2\text{-}TMB)]^{2+}$: A Valuable Precursor for Pentaammineosmium(II) Chemistry

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A major interest in the chemistry of ruthenium(II) and osmium(II) ammines has been in their affinity for π-acid ligands.[1] Although the effects of this affinity are more dramatic in osmium,[2] the development of this chemistry has been hampered by the lack of a general synthetic method. Pentaammineosmium(II) is rapidly oxidized by protic solvents,[3] forms inert π-bound complexes with olefins, aldehydes, ketones,[4] and arenes,[5] and degrades amides and esters.[6] Recently, we reported the synthesis of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$. Although the benzene could be readily displaced by other ligands, attempted substitution reactions with this complex often resulted in the formation of the substitution-inert binuclear condensation product $[(Os(NH_3)_5)_2(C_6H_6)]^{4+}$. By utilizing the sterically hindered arene 1,2,3,4-tetramethylbenzene (TMB), we hoped to eliminate this undesirable side reaction. Below we present the synthesis of $[Os(NH_3)_5TMB](TFMS)_2$, which we find to be a versatile precursor to pentaammineosmium(II) chemistry (TFMS = $CF_3SO_3^-$).

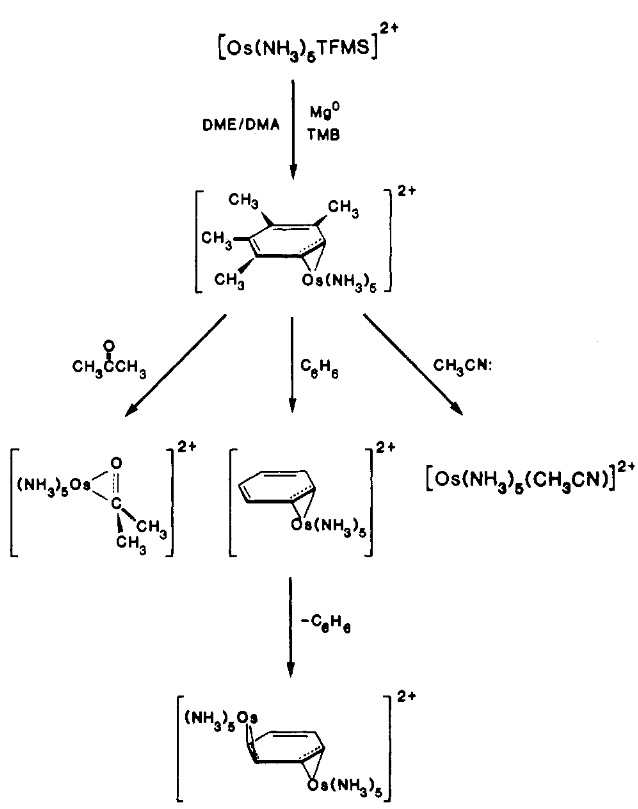

Figure 1. Schematic representation of the chemistry associated with the complex $[Os(NH_3)_5TMB]^{2+}$.

Synthesis of $[Os(NH_3)_5TMB](TFMS)_2$ (1)

A 100-mg amount of $[Os(NH_3)_5TFMS](TFMS)_2$[7] and 2.0 mL of TMB are dissolved in a cosolvent mixt. of 0.5 mL of dimethylacetamide (DMA) and 15 mL of dimethoxyethane (DME). To this is added 2.0 g of activated magnesium,[8] and the solution is stirred for 50 min. The resulting orange solution is shown by cyclic voltammetry to contain $[Os(NH_3)_5(\eta^2\text{-}TMB)]^{2+}$ (**1**) in high yield and may be used without isolating the product. When the filtered solution is added slowly to 100 mL of chilled CH_2Cl_2, an orange precipitate forms, which, after washing with CH_2Cl_2, contains >90% of **1**.[9] At 0 °C, **1** can be stored for several weeks as a solid under argon.

Electrochemical and NMR data of **1** confirm that the arene ligand is bound to the metal center in an η^2 fashion at the 5,6-position.[10] We find that **1** reacts efficiently with other aromatic hydrocarbons, ketones, amides, and esters, as well as more conventional π-acidic ligands[11] (Figure 1). Unlike the analogous

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(8) The surface of the magnesium was cleaned with an iodine solution of DME and was then copiously washed with DMA.

(9) This estimate of purity is based on electrochemical and NMR data.[10]

(10) Characterization of **1**. ^1H NMR (400 MHz, acetone-d_6): 3.55 (cis NH_3; 12 H, br), 4.75 (trans NH_3; 3 H, br), 2.12 (CH_3; 6 H, s), 5.42 (CH; 2 H, s), 2.36 (CH_3; 6 H, s). Electrochemistry: irreversible oxidation wave at +0.15 V (NHE) (v = 200 mV/s; 0.5 M NaTFMS in DME; E_λ = +1.0 to −1.5 V). These values compare favorably with the respective data reported for $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$.[5]

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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.

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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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