For the PTol$_3$ case, we cannot completely exclude phosphine dissociation and note only that if this does occur, it is much slower than the exchange induced due to SnCl$_2$ moving in and out of a Pt–Cl bond and lies outside the range of our magnetization "mixing" time (see Experimental Section). In contrast to the case for the PEt$_3$ complexes, mixing solutions of analytically pure **6a** and *cis*-PtCl(SnCl$_3$)(AsTol$_3$)$_2$ *does* produce the mixed arsine–phosphine complex slowly at room temperature.[11b]

Part of our interest in the dynamics of these *cis*-PtCl$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$ complexes stems from our previous study on their reactivity. With dihydrogen the tolyl complexes react in CDCl$_3$ at room temperature with 1 atm of H$_2$ within a period of minutes to give almost quantitative yields[15] of *trans*-PtHX(PTol$_3$)$_2$ (X = Cl, SnCl$_3$), whereas the Et analogue are *unreactive*[16] under the same conditions. Clearly, the relative kinetics and dynamics of these trichlorostannate complexes remain of interest and we consider that 2-D exchange spectroscopy will prove valuable in evaluating the latter.

Experimental Section

Complexes and Solutions. The complexes studied were synthesized as described previously,[9,11] and the solutions for NMR study were prepared as follows:

Mixtures of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$, [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(4-FC$_6$H$_4$CN)], and 4-FC$_6$H$_4$CN. (a) To a solution of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (18.0 mg, 15.0 μmol) in CDCl$_3$ (0.5 mL) was added *p*-fluorobenzonitrile (4.0 mg, 33.0 μmol), resulting in the following concentrations of compounds: **1**, 7.5 mM; **2**, 45.0 mM; **3**, 22.5 mM. This gives an equilibrium constant for reaction 1 of $K = 66\ \mathrm{M}^{-1}$.

NMR data for [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (**1**): $\delta(^{31}\mathrm{P}) = -8.7$, $^1J(\mathrm{Pt,P}) = 3626$ Hz, $^2J(\mathrm{Sn,P}) = 233$ Hz, $^1\mathrm{J}(\mathrm{Pt,Pt}) = 457$ Hz. NMR data for [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(4-FC$_6$H$_4$CN)] (**3**): $\delta(^{31}\mathrm{P}) = -14.9$, $^1J(\mathrm{Pt,P}) = 3540$ Hz, $^2J(\mathrm{Sn,P}) = 261$ Hz; $\delta(^{19}\mathrm{F}) = -107.2$; $\delta(^{119}\mathrm{Sn}) = -251$, $^1J(\mathrm{Pt,Sn}) = 28\,750$ Hz. NMR data for 4-FC$_6$H$_4$CN (**2**): $\delta(^{19}\mathrm{F}) = -112.0$.

(b) More *p*-fluorobenzonitrile (30.0 mg, 250 μmol) was added to the solution in (a), resulting in the disappearance of signals due to complex **1** in the ^{31}P NMR spectrum.

Solution Containing [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)]. To a solution of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (24 mg, 20 μmol) in CDCl$_3$ (0.5 mL) was added benzonitrile (ca. 50 mg).

NMR data for [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)]: $\delta(^{31}\mathrm{P}) = -15.0$, $^1J(\mathrm{Pt,P}) = 3524$ Hz, $^2J(\mathrm{Sn,P}) = 256$ Hz; $\delta(^{119}\mathrm{Sn}) = -255$, $^1J(\mathrm{Pt,Sn}) = 28\,883$ Hz.

Solutions Containing [Pt(Cl)$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$]. These solutions were prepared in analogy to previously reported methods.[9,11]

NMR Measurements. The NMR spectra were obtained as CDCl$_3$ solutions with Bruker WM-250 and AC-250 instruments operating at 235 MHz for ^{19}F, 101 MHz for ^{31}P, and 93 MHz for ^{119}Sn, respectively. The chemical shifts are recorded relative to CFCl$_3$ (^{19}F), H$_3$PO$_4$ (^{31}P), and SnMe$_4$ (^{119}Sn), with positive shifts to lower field.

One-Dimensional NMR Spectra. ^{19}F NMR spectra were measured with a sweep width of 9400 Hz and acquisition of 64K complex data points in a time of 3.5 s, resulting in a digital resolution of 0.29 Hz/point.

^{31}P NMR spectra were recorded with a sweep width of 8000 Hz and acquisition 32K complex data points in a time of 2 s. The digital resolution in the final spectrum was 0.5 Hz/point.

^{119}Sn NMR spectra were measured with a spectral width of 50 000 Hz and acquisition of 8K complex data points with an acquisition time of 82 ms. Transformation was done by zero filling to 16K data points, and an exponential multiplication with a line-broadening factor of 30 Hz was applied. The digital resolution in the final spectrum was 6 Hz/point.

Two-Dimensional NMR Spectra. The two-dimensional chemical exchange correlated NMR spectra were carried out by using the NOESY sequence 90°x–t_1–90°x–T–90°x–acquisition.[17] The time T, which allows for chemical exchange, was chosen to be 0.8 s for the [Pt(Cl)$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$] chemistry. The mixing time T was 0.6 s in the case of the reaction of the dimer with *p*-fluorobenzonitrile and 0.5 s in the case of benzonitrile itself. The mixing times are important to note in that very slow exchange will not be detected.

For phosphorus exchange experiments the following parameters and procedures were commonly employed: 512 FID's of 2048 data points covering a sweep width of 4800 Hz were measured with an acquisition time of 0.2 s and 32 transients each. Transformation was carried out with no zero filling in F2 by using shifted sine-bell apodization. In F1 zero filling to 1028 data points was applied and the same apodization function as for F2 was used. The resulting matrix was displayed in the magnitude mode and symmetrized with respect to the diagonal. The final digital resolution was typically 4.6 Hz/point.

For the fluorine exchange experiments the parameters were as follows: 128 FID's of 512 data points covering a range of 1600 Hz were measured with an acquisition time of 0.16 s. sixteen transients were recorded to give a sufficient signal/noise ratio. Zero filling was applied in the F1 domain but not in F2, and the data were transformed by using pseudo echo apodization in both frequency domains. The resulting matrix was displayed in the magnitude mode and symmetrized with respect to the diagonal. The final digital resolution was 6.4 Hz/point.

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Registry No. **1**, 109124-64-3; **2**, 1194-02-1; **3**, 109124-65-4; **4a**, 31173-67-8; **4b**, 15692-07-6; **5a**, 83199-43-3; **5b**, 67619-49-2; **6a**, 67656-58-0; **6b**, 109124-66-5; **7**, 109124-67-6; [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)], 109124-68-7; benzonitrile, 100-47-0.

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[15] Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1981**, *54*, 159.

[16] Rüegger, H. Ph.D. Thesis, ETH Zürich, 1983.

[17] Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

Contribution from the Department of Chemistry,
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Anion Affinity of Carbonylbis(triphenylphosphine)rhodium(I) in CH$_2$Cl$_2$: Fluoride vs. Its Halide Analogues

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Forster[1] earlier reported that halide preference in aprotic media for the d^8 complexes *trans*-M(PPh$_3$)$_2$(CO)X and *cis*-M(CO)$_2$X$_2^-$ (M = Rh, Ir) followed the order X = Cl > Br > I and suggested that "in rigorously aprotic solvents, fluoro derivatives may frequently be found to be the most stable halocarbonyl species". We report herein the first quantitative results to substantiate that speculation.

Experimental Section

trans-Rh(PPh$_3$)$_2$(CO)X (called RhX hereafter; X = Cl, Br, I) were prepared as in the literature.[2-4] The fluoro analogue (RhF) was synthesized according to Vaska's method.[5] All were dried at reduced pressure and checked for purity by using thin-layer chromatography (silica gel) and IR and visible spectroscopy. Dichloromethane (Fisher ACS reagent) was dried over freshly activated Mol Sieve 4A or via distillation under nitrogen from CaH$_2$ (indistinguishable results). The bis(triphenylphosphine)nitrogen(1+) salts, PPNX (X = Cl, Br, I),[6,7] were used as purchased from Strem after drying at reduced pressure. PPNF·CH$_2$Cl$_2$ was prepared as described by Ruff.[8] Solution preparations (in standard volumetric glassware) and manipulations were performed by using standard techniques in a Vacuum Atmospheres recirculating glovebox.

IR spectra were recorded in 5.0-mm CaF$_2$ cells on a Perkin-Elmer 1430 spectrophotometer equipped with a 3600 Data Station. The cells

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[1] Forster, D. *Inorg. Chem.* **1972**, *11*, 1686.

[2] Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

[3] Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437.

[4] Vaska, L.; Peone, J., Jr. *J. Chem. Soc., Chem. Commun.* **1971**, 418.

[5] Vaska, L.; Peone, J., Jr. *Inorg. Synth.* **1974**, *15*, 65.

[6] The PPNX salts were selected as halide sources due to ready availability, nonhygroscopic nature, reasonable solubility, and low molar absorptivity: Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

[7] Bekkevoll, S.; Svorstoel, I.; Hoeiland, H.; Songstad, J. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 935. Songstad's group has reported that some PPN salts displace Cl in dichloromethane at moderately rapid rates; however, the halides were not included in that group. We did not observe complications attributable to such reactions.

[8] Douglas, W.; Ruff, J. K. *J. Organomet. Chem.* **1974**, *65*, 65. We have found that the substance so synthesized functions as an adequate source of F$^-$ in preparative reactions but contains sufficient methanol to preclude its use in equilibrium studies.

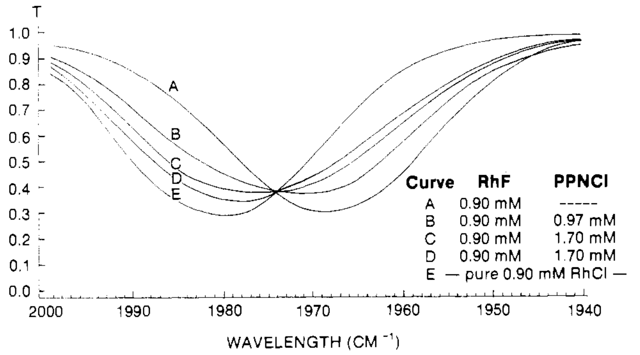

Figure 1. RhF/PPNCl mixtures.

were not thermostated (ca. 25 °C) but still gave absorbances reproducible within 1% for ten spectra of the same RhF/PPNBr sample. The spectroscopic range monitored, 1999–1940 cm^{-1}, covered most of the carbonyl stretching region of RhF and all RhX species. Because the bands of the species studied overlap extensively, absorbances were measured every 1 cm^{-1} over the range; the individual RhF and RhX concentrations were calculated by using a specially designed statistical package.[9] The validity of the instrumental/computer-analysis combination was confirmed by (i) obtaining satisfactory Beer's law plots over the pertinent concentration ranges for pure RhF and RhX solutions and (ii) obtaining RhF and RhX concentrations within experimental error for mixtures of known concentrations of RhF and RhX. Spectra for the sets of such mixtures at constant total Rh concentration but different [RhF]/[RhX] ratios displayed clear isosbestic points[10] as expected. Sets of solutions of identical initial RhF concentrations having different $[\mathrm{PPNX}]_0/[\mathrm{RhF}]_0$ ratios[11] also displayed the expected clear isosbestic points (after subtraction of the small PPN$^+$ absorptions) consistent with the presence of only the two rhodium species RhF and RhX (Figure 1).[10] Spectra of CH_2Cl_2 solutions of RhF/PPNF and RhX/PPNX mixtures revealed no interactions that would cause deviation from Beer's law behavior.

A typical set of experiments is described. A 353.1-mg sample of RhF was dissolved in CH_2Cl_2 to give 250.0 mL of 2.094 mM solution. Solutions of PPNX were prepared similarly: X = Cl, 371.2 mg/100.0 mL, 6.466 mM; X = Br, 199.4 mg/50.0 mL, 6.45 mM; X = I, 220.6 mg/50.0 mL, 6.63 mM. The solutions were dispensed from burets. Mixtures having identical total Rh concentrations (1.26 mM) were prepared by combining 15.0 mL of RhF solution, either 5.00, 7.50, or 10.00 mL of PPNX solution, and CH_2Cl_2 as needed in a 25-mL volumetric flask. The IR cell was filled with RhF/PPNX sample in the glovebox and taken out tightly stoppered. The spectrum was recorded, stored, and later processed on a Zenith ZW-158 PC using custom BASIC statistical analysis[9] to compute for eq 1 equilibrium constants and fraction of rhodium halides present as RhF for $[\mathrm{PPNX}]_0/[\mathrm{RhF}]_0 = 1$.

A total of 12, 9, and 9 mixtures were sampled to generate the numbers listed in Table I for the respective RhF/PPN$^+$X$^-$ (X = Cl, Br, I) equilibria.

Results and Discussion

The technique chosen to study the halide affinity in aprotic solvent of $\mathrm{Rh(PPh_3)_2(CO)^+}$ (called Rh$^+$; hereafter the fluoro complex is termed RhF and its analogues are termed RhX, where X = Cl, Br, and I) entailed analysis by infrared spectroscopy of solutions made by dissolving RhF and bis(triphenylphosphine)nitrogen(1+) halide, PPNX,[6,7] in appropriate ratios in CH_2Cl_2 to afford equilibrium 1. Data for the three $\mathrm{Rh(PPh_3)_2(CO)}$-

$$\mathrm{Rh(PPh_3)_2(CO)F + PPN^+X^- \rightleftharpoons Rh(PPh_3)_2(CO)X + PPN^+F^-} \quad (1)$$

F/PPNX sets (Table I) show that Forster's speculation[1] was indeed correct, with fluoride preferred over chloride in CH_2Cl_2 roughly 5 to 3 and over bromide and iodide much more so. The relatively large experimental error appears due to the lack of precision inherent in handling dichloromethane solutions in volumetric apparatus inside a glovebox to preclude contamination by water.

Table I. Data for

$$\mathrm{Rh(PPh_3)_2(CO)F + PPN^+X^-} \overset{K_{X/F}}{\rightleftharpoons} \mathrm{Rh(PPh_3)_2(CO)X + PPN^+F^-}$$

	X = Cl	X = Br	X = I
$K_{X/F}$	0.34 ± 0.17	0.013 ± 0.004	0.000 35 ± 0.00027
$X_{X/F}$[a]	0.63 ± 0.06	0.90 ± 0.01	0.98 ± 0.01

[a] $X_{X/F}$ represents the fraction of rhodium halides present as $\mathrm{Rh(PPh_3)_2(CO)F}$ for $[\mathrm{PPNX}]_0/[\mathrm{RhF}]_0 = 1$.[11]

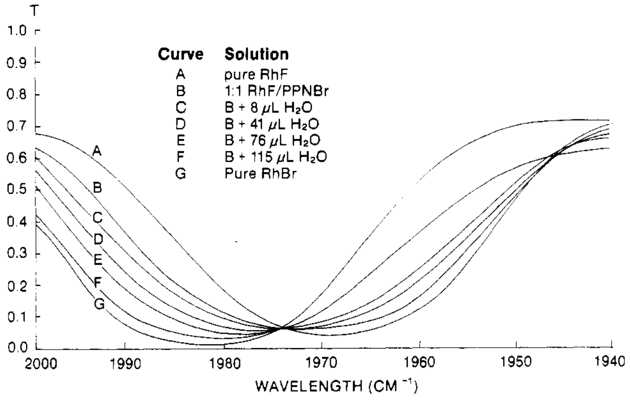

Figure 2. Effect of added H_2O on the RhF/PPNBr system.

The experiments are quite sensitive to the presence of polar molecules. Addition of small amounts of methanol or water to RhF/PPNX solutions shifts the equilibrium of eq 1 markedly to the right, presumably via strong hydrogen bonding of hydroxyl groups to uncomplexed fluoride. IR spectra show the effect of adding successive small volumes of H_2O to a RhF + PPNBr mixture in Figure 2.

Our data are consistent with those reported by Forster.[1] Using Hess' law and our $K_{Cl/F}$ and $K_{X/F}$ values to calculate the equilibrium constant $K_{Cl/I}$ for eq 2 affords a value of 972. That number

$$\mathrm{Rh(PPh_3)_2(CO)I + PPN^+Cl^- \rightleftharpoons Rh(PPh_3)_2(CO)Cl + PPN^+I^-} \quad (2)$$

is compatible with values[12] of $>10^3$ in 1,2-dichloroethane for the analogous iridium system and 250 for the rhodium system in the more polar solvent *N,N*-dimethylformamide.

Studies by Songstad and co-workers[13] have shown that all PPN$^+$ salts are strongly associated in CH_2Cl_2 as ion pairs, with association constants of 1.5 (±0.3) × 10^3 independent of anion nature. Their results suggest little thermodynamic preference in formation of PPN$^+$F$^-$ relative to PPN$^+$X$^-$; if so, then our $K_{X/F}$ values may be taken as estimates of relative stabilities of RhX and RhF in solution. Our observed halide preference is consistent with a strong π-back-bonding effect related to ability of anion to compete with trans CO ligand in removing electron density from Rh(I) d orbitals (F < Cl < Br < I).[14] The trend is opposite that predicted by the Pearson hard and soft acid and base interpretation[15,16] of relative stabilities in solution of low-valent transition-metal halide complexes of M–F < M–Cl < M–Br < M–I.

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(9) Hoffman, N. W.; McElroy, E. A.; Ramage, D. L.; Young, S. H., manuscript in preparation.

(10) Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, PA, 1977; pp 92–94.

(11) $[\mathrm{RhF}]_0$ and $[\mathrm{PPNX}]_0$ denote initial respective concentrations.

(12) Forster[1] used tetrabutylammonium (TBA) salts as halide sources.

(13) Svorstoel, I.; Hoeiland, H.; Songstad, J. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 885. TBA salts have ion-pair association constants (also relatively insensitive to anion nature) somewhat greater than those of PPN.

(14) (a) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J. Jr.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485. (b) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

(15) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 481, 683. (c) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265.

(16) Burmeister, J. L.; DeStefano, N. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1698. Existence of the N-bound rather than the (softer) Se-bound linkage isomer may also be influenced by the steric requirements of the two forms.[17]

(17) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; pp 516–518.

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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(18) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition-Metal Chemistry*; University Science Books: Mill Valley, CA, 1980: (a) p 52; (b) p 187.

(19) Kubota, M.; Kiefer, G. W.; Ishikawa, R. M.; Bencala, K. E. *Inorg. Chim. Acta* **1972**, *7*, 195. $Ir(PPh_3)_2(CO)F$ oxidatively adds CH_3I more rapidly than does its Ir–Cl analogue.

(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.

(25) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Contribution from the Department of Chemistry,
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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 = $CF_3SO_3^-$).

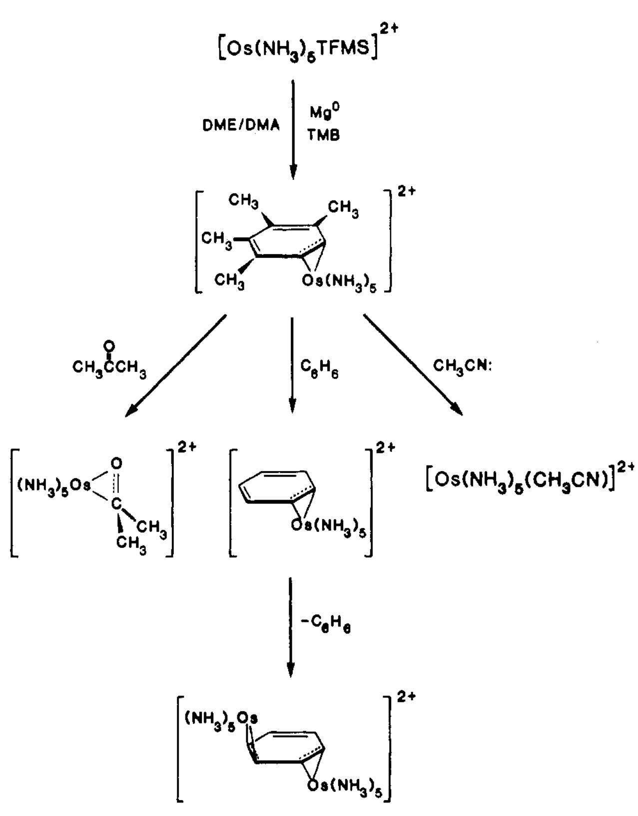

Figure 1. Schematic representation of the chemistry associated with the complex $[Os(NH_3)_5TMB]^{2+}$.

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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(1) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901–912.

(2) Reference 1; 901.

(3) Reference 1; 903.

(4) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(5) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

(6) Unpublished results.

(7) Lay, P. Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(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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