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Synthesis and Reactivity of *trans*-ReF(CO)₃(PPh₃)₂ and *trans*-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂

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The d⁶ fluoro complex *trans*-ReF(CO)₃(PPh₃)₂ (1) has been prepared in good yield by reaction of *trans*-ReCl(CO)₃(PPh₃)₂ (2) with Ag(SO₃CF₃) followed by [N(PPh₃)₂]F. Addition of 2 equiv of [N(PPh₃)₂]Cl to 1 affords not the expected simple anion-metathesis equilibrium, but a mixture containing 2 as well as other species. The lability of 1 toward carbonyl exchange with ¹³CO and toward reaction with NCS⁻ has been examined and is far greater than that for 2. Compound 1 reacts with V(NSiMe₃)-(OSiMe₃)₃ (4) to form Me₃SiF and *trans*-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂ (5), whereas no reaction is observed upon addition of the chloro complex 2 to 4. Reaction of 5 with Me₃SiCl cleanly substitutes chlorides for the trimethylsiloxy groups on vanadium to generate *trans*-Cl₃V≡NRe(CO)₃(PPh₃)₂ (6), with no evidence for the expected cleavage of the nitride bridge to yield 2 and 4. Spectroscopic and solution properties of this series of compounds and comparisons of the fluoro complex (1) with its heavier halo analogues are presented.

Introduction

Numerous data for square-planar d⁸ complexes indicate that halide affinity within such transition-metal systems is greatest for F⁻ when the halide ligand is trans to a strong π-acid.[4] Such is the case for the rhodium(I) Vaska system; our halide-metathesis equilibrium studies using bis(triphenylphosphine)nitrogen(1+) halides, hereafter abbreviated (PPN)X, have demonstrated a preference for fluoride over the heavier halides in aprotic media (eq 1).[5] We were interested in extending these studies to an
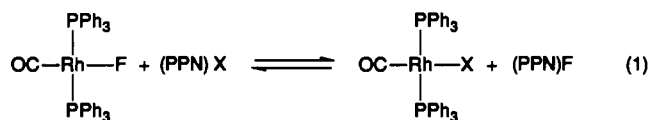
octahedral d⁶ system. Our target fluoro complex was *trans*-ReF(CO)₃(PPh₃)₂ (1), chosen on the basis of the stability of its heavier halo analogues,[6,7] the precedent of other ReF(CO)₃L₂ derivatives (L = SbPh₃; L₂ = dppe, tmeda, bipy),[8] and the existence of MnF(CO)₃(PPh₃)₂.[9] Here we report the preparation and characterization of 1 and a comparison of its reactivity to that of its chloro analogue (2).

The fluoro ligand confers significant lability upon 1, a characteristic which has been exploited to effect the first reaction of a coordinatively saturated fluoro complex with V(NSiMe₃)-(OSiMe₃)₃[10] (4) to form a nitride-bridged compound,[10a,11]

Table I

Table I. Carbonyl Stretching Frequencies (cm⁻¹) and Intensities (Molar Absorptivities in mM⁻¹ mm⁻¹ Where Indicated) for ReX(CO)₃(PPh₃)₂ (X = F, Cl, Br, I, NCS) in 1,2-C₂H₄Cl₂

F	Cl	Br	I	NCS
2039 (w)	2050 (w)	2052 (w)	2053 (w)	2054 (w)
1939 (0.27)	1950 (0.35)	1951 (vs)	1953 (vs)	1958 (0.38)
1890 (0.11)	1907 (0.13)	1908 (s)	1910 (s)	1919 (0.17)

trans-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂ (5). Synthesis and characterization of this species and of a related complex (6) in which the three trimethylsiloxides on vanadium have been replaced by chlorides are described herein.

Experimental Section

General Procedures. Syntheses of 1–3 and *trans*-ReX(CO)₃(PPh₃)₂ (X = Br, I, NCS) were performed in solvents dried over 4-Å molecular sieves, but the systems were not further protected from environmental moisture or air unless specifically indicated. All other reactions and manipulations were performed under standard anhydrous/anaerobic conditions using appropriately dried reagent grade solvents.[12] Elemental analyses were carried out by Atlantic Microlabs, Galbraith Laboratories, and Canadian Microanalytical Services. Infrared studies employed solutions in CaF₂ cells or mulls on NaCl plates; spectra were recorded on Perkin-Elmer 283, 1430, and 1600 spectrometers and are reported in cm⁻¹. Solution conductivity measurements were performed with an Industrial Instruments RC-18 conductivity bridge on samples of varying concentrations in a glass conductivity cell with platinum electrodes. NMR spectra were recorded on a Varian VXR300 (299.95 MHz, ¹H; 121.42 MHz, ³¹P; 78.57 MHz, ⁵¹V; 75.43 MHz, ¹³C) spectrometer at ambient temperatures. Chemical shifts are reported with positive values downfield in ppm relative to δ = 0 for SiMe₄ (¹H, ¹³C), V(O)Cl₃ (⁵¹V), and 85% H₃PO₄ (³¹P); coupling constants and peak half-widths are reported in Hz.

Bis(triphenylphosphine)nitrogen(1+) chloride, (PPN)Cl (Aldrich), was used as received, except in its reaction with 1, for which it was dried at 60 °C (10 mTorr). (PPN)F, a substance of variable composition,[13] was prepared according to the procedure described by Douglas and Ruff for (PPN)F·CH₂Cl₂.[14] (PPN)NCS was synthesized according to the method of Martinsen and Songstad.[15] Me₃SiCl (Aldrich) was dried over activated 4-Å molecular sieves; PPh₃ (Pressure Chemical) was purified by sublimation at 100 °C (2 Torr). Ag(SO₃CF₃) (Alfa) and Re(CO)₅Cl (Pressure Chemical) were used as received. V(NSiMe₃)(OSiMe₃)₃[10] (4) and V(NSiMe₃)Cl₃[16] were prepared according to literature methods.

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(7) Although fac isomers of ReX(CO)₃(PPh₃)₂ (X = Cl, Br, I) are the initial products of reactions between ReX(CO)₅ and PPh₃,[6a,b,e] the former are reported to isomerize to yield the more stable trans species under forcing conditions.[6b,c]
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(13) For example, samples of (PPN)F prepared by literature procedures[14,15] are frequently found to contain substantial amounts of (PPN)HF₂: Schomber, B. M.; Doherty, N. M. Unpublished results.
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Syntheses. *trans*-ReCl(CO)₃(PPh₃)₂^(6c-e) (2). Re(CO)₅Cl (500 mg, 1.38 mmol) and a moderate excess of PPh₃ (904 mg, 3.45 mmol) were dissolved in toluene, and the mixture was heated at reflux under nitrogen for 18 h. The resulting suspension was concentrated under reduced pressure to a volume of ca. 10 mL; complete crystallization of the product was effected by slow addition of 10 mL of diethyl ether and then 60 mL of heptane. The resulting white crystals were collected by filtration, washed with two 10-mL portions of 1:4 (v/v) diethyl ether/heptane, and dried under reduced pressure; yield 985 mg (89%). IR (CH₂Cl₂): ν_{CO} 2049 (w), 1950 (vs), 1907 (s). IR (1,2-C₂H₄Cl₂): see Table I.

trans-ReF(CO)₃(PPh₃)₂ (1). Complex 2 (750 mg, 0.903 mmol) and a moderate excess of Ag(SO₃CF₃) (302 mg, 1.18 mmol) were dissolved in 50 mL of nondegassed CH₂Cl₂, and the mixture was stirred under nitrogen overnight, protected from light. The resulting dark gray suspension was filtered through Celite to remove silver salts; concentration of the filtrate to ca. 5 mL and slow addition of 30 mL of heptane afforded off-white crystals. These were recrystallized by dissolution in 40 mL of 1:1 (v/v) CH₂Cl₂/benzene, filtration of the solution, concentration of the filtrate to ca. 5 mL, and then slow addition of 5 mL of diethyl ether followed by 60 mL of heptane. The white crystals of 3 thus obtained were collected by filtration, washed with hexanes, and dried at reduced pressure. Analytical data for 3 are consistent with formulation as either [Re(CO)₃(PPh₃)₂(H₂O)][SO₃CF₃]·H₂O or Re(CO)₃(PPh₃)₂-(SO₃CF₃)·2H₂O; yield 841 mg (95%). Anal. Calcd for C₄₀H₃₄F₃O₈P₂ReS: C, 49.03; H, 3.50. Found: C, 49.11; H, 3.27. IR (1,2-C₂H₄Cl₂): ν_{CO} 2068 (w), 1967 (vs), 1917 (s).

A solution containing 3 (100 mg, 0.102 mmol) and excess (PPN)F (118 mg, ca. 0.2 mmol) in 30 mL of CH₂Cl₂ was stirred for 15 min, shielded from light. The solvent was removed under reduced pressure and the resulting solid taken up in benzene to afford a slurry of white crystals of PPN salts. These were removed by filtration, and the resulting pale yellow solution was concentrated to ca. 5 mL. Slow addition of 5 mL of diethyl ether followed by 50 mL of heptane afforded off-white crystals of 1, which were collected by filtration, washed with hexanes, and dried under reduced pressure; yield 75 mg (90%). Anal. Calcd for C₃₉H₃₀FO₃P₂Re: C, 57.56; H, 3.72. Found: C, 57.39; H, 3.78. IR (CH₂Cl₂): ν_{CO} 2040 (w), 1941 (vs), 1890 (s). IR (1,2-C₂H₄Cl₂): see Table I. ¹H NMR (C₆D₆): 7.95 (q, J = 6, 12 H), 7.05 (t, J = 7, 12 H), 6.97 (q, J = 7, 6 H). ¹³C{¹H} NMR (C₆D₆): 194.9 (d, J_{CF} = 7, J_{PC} < 4), 193.1 (d, J_{CF} = 62, J_{PC} < 4), 135.4 (t, J_{PC} = 23), 133.9 (d, J_{PC} = 4), 130.2, 128.6. ¹³C{¹H} NMR (THF-d_8): 194.9 (d, J_{CF} = 7), 192.9 (d, J_{CF} = 61), 136.1, 134.4, 130.8, 128.9. ³¹P NMR (C₆D₆): 10.3 (d, J_{PF} = 35).

trans-Re(NCS)(CO)₃(PPh₃)₂. A colorless solution prepared by dissolving a mixture of 3 (251 mg, 0.256 mmol) and (PPN)NCS (168 mg, 0.282 mmol) in 30 mL of CH₂Cl₂ was stirred for 0.5 h. The solvent was removed under reduced pressure and the resulting solid extracted with two 50-mL portions of benzene. The extracts were combined and concentrated on a rotary evaporator to a volume of ca. 10 mL. Slow addition of 5 mL of diethyl ether followed by 60 mL of heptane afforded white microcrystals, which were collected by filtration, washed with hexanes, and dried under reduced pressure; yield 212 mg (97%). Anal. Calcd for C₃₇H₃₀NO₃P₂ReS: C, 56.33; H, 3.55. Found: C, 56.19; H, 3.44. IR (1,2-C₂H₄Cl₂): ν_{CO}, Table I; ν_{CN} 2093 (m).

trans-ReBr(CO)₃(PPh₃)₂^(6d,e) and trans-ReI(CO)₃(PPh₃)₂.^(6b,d) The bromo and iodo complexes were prepared by the above procedure from 3 and a slight excess of (PPN)Br or (PPN)I; they were isolated in 96% and 95% yields, respectively. IR (1,2-C₂H₄Cl₂): see Table I.

trans-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂ (5). A benzene solution of 1 (314 mg, 0.386 mmol) and V(NSiMe₃)(OSiMe₃)₃ (4) (144 mg, 0.355 mmol) was heated overnight at 70 °C in a closed vessel to afford an orange solution. The solvent was removed under reduced pressure and the resulting orange solid was stirred in 7 mL of pentane to afford orange crystals of 5; yield 256 mg (64%). Anal. Calcd for C₄₈H₅₇NO₆P₂ReSi₃V: C, 51.14; H, 5.10; N, 1.24. Found: C, 51.12; H, 5.21; N, 1.62. IR (THF): ν_{CO} 2044 (w), 1954 (vs), 1921 (s). IR (Nujol): 2039, 1932, 1920, 1480, 1437, 1250, 1243, 1091, 1024, 1018, 998, 975, 932, 903, 838, 744, 696, 616. ¹H NMR (C₆D₆): 7.99 (q, J = 6, 12 H), 7.20 (t, J = 8, 12 H), 7.04, (t, J = 8, 6 H), 0.17 (s, 27 H). ³¹P{¹H} NMR (C₆D₆): 11.1. ⁵¹V NMR (C₆D₆): −260 ($\nu_{1/2}$ = 1460).

trans-Cl₃V≡NRe(CO)₃(PPh₃)₂ (6). Me₃SiCl (10 Torr in 600 mL, 0.32 mmol) was condensed into a benzene solution of 5 (65 mg, 0.058 mmol); the resulting violet solution turned dark blue upon stirring for 0.5 h at 22 °C. The mixture was stirred an additional 12 h and the solvent removed under reduced pressure to produce a dark blue solid. Slow evaporation of toluene from a concentrated solution yielded thin blue crystalline plates of 6. ¹H NMR (C₆D₆): 7.96 (q, J = 6, 12 H), 7.21

(t, J = 8, 12 H), 6.96 (t, J = 7, 6 H). ³¹P{¹H} NMR (C₆D₆): 15.9. ⁵¹V NMR (C₆D₆): 430 ($\nu_{1/2}$ = 1320). IR (neat): 3377, 2923, 2851, 2056, 1959, 1939, 1480, 1434, 1092, 1027, 743, 695, 678, 611.

Reactions of 1 and 2 with (PPN)NCS and of 1 with (PPN)Cl. 1,2-C₂H₄Cl₂ solutions initially 1.0 mM in 1 or 2 and 2.0 mM in (PPN)NCS were transferred under N₂ to IR cells which were tightly capped with Teflon stoppers and kept in the dark at 25 °C. A similar procedure was followed for a 1,2-C₂H₄Cl₂ solution initially 1.0 mM in 1 and 2.0 mM in (PPN)Cl (Figure 1). IR spectra in the carbonyl region were recorded at appropriate time intervals. IR spectra of samples of pure 1, 2, and *trans*-Re(NCS)(CO)₃(PPh₃)₂ and of their respective binary mixtures were recorded under analogous conditions.

¹³CO-Exchange Reactions of 1 and 2. Two NMR tubes, equipped with ground-glass joints and needle valve adapters, were charged with 0.015 M solutions of 1 and 2 in THF-d_8 and linked via a small vacuum manifold to a bulb containing ¹³CO (Monsanto). The NMR tubes were degassed and cooled to −196 °C; the gas bulb was simultaneously opened to both to afford a CO pressure of roughly 300 Torr. Each NMR tube was sealed with a torch under these temperature and pressure conditions and warmed to 22 °C in the dark. Reaction was monitored by ¹³C{¹H} NMR spectroscopy.

Solution Conductivity Measurements of 1 and 2. For each sample, a solution of the concentration indicated was prepared and a portion transferred to a conductivity cell (cell constant = 0.363 cm⁻¹) which was placed in a constant-temperature bath and allowed to stabilize at the temperature indicated for 4–6 h prior to measurement of the conductivity or resistivity of the solution. Data are reported in the form of specific conductance (L) in units of μmho cm⁻¹: 1 (THF), 4.38 (1.00 mM, 23.0 °C), 0.71 (0.100 mM, 23.2 °C); 1 (benzene), 0.00 (1.03 mM, 23.0 °C); 2 (THF), 0.05 (1.01 mM, 23.0 °C).

Results

Abel and Tyfield found that heating a mixture of solid PPh₃ and *fac*-ReCl(CO)₃(PPh₃)₂ (prepared from ReCl(CO)₅ and PPh₃^(6a)) produces *trans*-ReCl(CO)₃(PPh₃)₂.^(6c) In contrast, Bond and co-workers reported that refluxing a suspension of *fac*-ReCl(CO)₃(PPh₃)₂ in heptane for 2 days does not produce the trans isomer.^(6c) We have found that *trans*-ReCl(CO)₃(PPh₃)₂ (2) is readily prepared in excellent isolated yield in high purity by heating a solution of ReCl(CO)₅ and 2.5 equiv of PPh₃ in toluene for 18 h.

The chloride ligand of 2 is smoothly removed upon reaction with a slight excess of Ag(SO₃CF₃) in CH₂Cl₂ to form a white crystalline compound 3 in nearly quantitative yield. Compound 3 can be formulated as either [Re(CO)₃(PPh₃)₂(H₂O)]-[SO₃CF₃]·H₂O or Re(CO)₃(PPh₃)₂(SO₃CF₃)·2H₂O based on elemental analysis and IR spectroscopy (the carbonyl bands for 3 show a pattern identical with that for 2, but shifted to higher frequency). The 2 equiv of water is derived from the environment (i.e., from solvent, glassware, and/or atmospheric moisture). The identity of the sixth ligand in the rhenium coordination sphere, aqua versus trifluoromethanesulfonate, has not been unequivocally demonstrated, although our evidence to date better supports the aqua cation formulation.^(17) Aqua complexes of several metal centers have been prepared by displacement of weakly coordinating anions,^(18) including replacement of trifluoromethanesulfonate by water at d^8 metal centers in Vaska-type complexes.^(19)

Treatment of intermediate 3 with a large excess of (PPN)F affords the desired fluoro complex (1) in good yield (eq 2). NMR

(2)

2   1
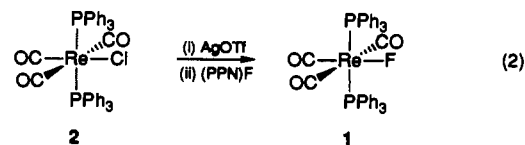
data indicate that 1 possesses two equivalent phosphine ligands

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(17) Further details on compound 3 will be reported as part of a larger study on d⁶ metal aqua versus trifluoromethanesulfonate complexes: Hoffman, N. W. Work in progress.
(18) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* 1985, *290*, 231.
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and two sets of carbonyl ligands in addition to the coordinated fluoride. The one ^{31}P and two ^{13}C NMR signals each display coupling to a single ^{19}F nucleus (J_{PF} = 35 Hz; J_{CF} = 7, 61–62 Hz), with the small and large carbon–fluorine values suggesting respective cis and trans disposition of the CO's and F. Surprisingly, no phosphorus–carbon coupling was observed. The NMR data are consistent with either the trans-phosphine mer-carbonyl structure proposed or an alternative cis-phosphine fac-carbonyl geometry. However, the absence of an observably large phosphorus–carbon coupling constant between the phosphine and carbonyl ligands argues against the fac isomer, which would have trans PPh$_3$ and CO ligands.[20] Complex 1 is a nonconductor in benzene but exhibits a small conductivity in THF which corresponds to less than 1% ionization due to dissociation of F$^-$; 2 displays a conductivity in THF roughly 100th that of 1 at a comparable concentration.

Analogous reactions of 3 with (PPN)X, where X$^-$ = Br$^-$, I$^-$, or NCS$^-$, produce *trans*-ReX(CO)$_3$(PPh$_3$)$_2$ compounds in excellent yield. IR spectra for the halo and isothiocyanato compounds (Table I) display a characteristic pattern of three carbonyl stretching bands, with weak, very strong, and strong intensities in decreasing frequency.[6a–c,e,f] This pattern matches that reported for structurally characterized *trans*-ReCl(CO)$_3$(PEt$_3$)$_2$[21] and contrasts with the three strong bands observed in the IR spectra of fac isomers in this system.[6] The bands for the fluoro complex (1) are at the lowest frequencies, with ν_{CO} for each mode increasing in the order F < Cl < Br < I < NCS (Table I).

The reaction of 1 with (PPN)Cl was examined in an attempt to determine relative preferences for fluoro versus chloro ligands in this system.[22] The IR spectrum of a sample of 1 and 2 equiv of (PPN)Cl in 1,2-C$_2$H$_4$Cl$_2$ changes systematically over about 24 h. Absorbances of bands for 1 decrease, while those of bands for 2 increase (Figure 1); final spectra indicate that 2 is the predominant ReX(CO)$_3$(PPh$_3$)$_2$ species in solution. However, these samples do not show the simple Beer's law behavior observed for mixtures of pure 1 and 2, and new broad weak bands at 1865 and 1842 cm^{-1} appear and increase in intensity during the 24 h period. Clearly, a simple anion-metathesis equilibrium is not operating; the lack thereof precludes determination of the halo ligand preference in this system.

The reactivity of the rhenium fluoro and chloro complexes upon treatment with 2 equiv of (PPN)NCS in 1,2-C$_2$H$_4$Cl$_2$ was examined by IR spectroscopy. After 1 h, the reaction involving 1 reaches a steady-state position characterized by maxima at 2096 (w), 2054 (s), 1903 (s), and 1817 (m) cm^{-1} in the IR spectrum; the reaction involving 2 requires 40 h to achieve an analogous steady state, which shows an additional IR band at 1836 (m) cm^{-1}. The products of these reactions have not yet been identified (and likely include isothiocyanato-bridged species[23]) but are clearly not simple mixtures of 1 or 2 and *trans*-Re(NCS)(CO)$_3$(PPh$_3$)$_2$. Nonetheless, the much shorter time required for disappearance of 1 versus 2 under these conditions indicates that the fluoro complex is significantly more labile than the chloro complex.

Qualitative comparison of the rates of ^{13}CO exchange at the rhenium centers in 1 and 2 in THF-d_8 solution has been performed. The fluoro complex shows rapid incorporation of label into the carbonyl sites cis to the fluoro ligand (δ 194.9, d, J_{CF} = 7 Hz), with significant intensity observed for this signal within 15 min under 300 Torr of ^{13}CO at ambient temperature. Much slower incorporation of ^{13}CO occurs at the trans site of 1 (δ 192.9, d, J_{CF} = 61 Hz). Under identical conditions, 2 undergoes slow reaction with ^{13}CO, introducing significant label into only a single

site at the rhenium center (δ 193.7, t, J_{PC} = 8 Hz), presumed to be cis to the chloro ligand, after 2 days.

Greater reactivity for the fluoro versus chloro complex is also observed in a condensation reaction with a vanadium silylimido compound; 1 reacts quantitatively with V(NSiMe$_3$)(OSiMe$_3$)$_3$ (4) in benzene at 70 °C to yield orange *trans*-(Me$_3$SiO)$_3$V≡NRe-(CO)$_3$(PPh$_3$)$_2$ (5) and Me$_3$SiF (eq 3). In contrast, the chloro
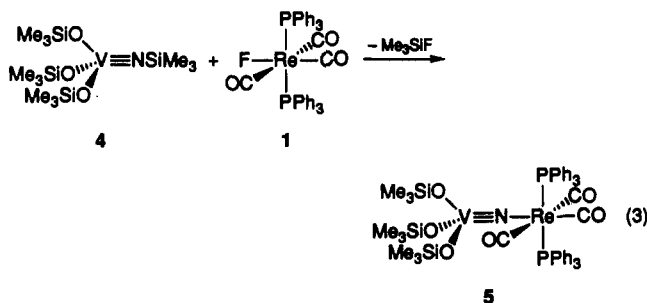
complex 2 does not produce 5 on reaction with 4; no reaction is observed in either benzene-d_6 or THF-d_8 up to temperatures at which 4 begins to decompose.[24]

Spectroscopic data for 5 support the structure shown in eq 3.[25] A singlet is observed at δ 11.1 in the ^{31}P{^{1}H} NMR spectrum for the two equivalent phosphine ligands, and the IR spectrum displays the expected weak, very strong, strong pattern for the carbonyl stretching bands. The ^{51}V NMR spectrum exhibits a broad signal at δ −260 ($\nu_{1/2}$ = 1460 Hz), consistent with attachment of the C_{2v} rhenium(I) center to the vanadium nitride fragment.[10a] Compound 5 undergoes only very slow reaction with ^{13}CO in THF-d_8 solution, competitive with its decomposition in that solvent, introducing the label into only a single site at the rhenium center (δ 195.0, t, J_{PC} = 9 Hz). Attempts to measure solution conductivities of 5 in THF are inconclusive because some decomposition occurs on the time scale of temperature equilibration of the sample.

Compound 5 undergoes a fast reaction with Me$_3$SiCl in benzene at room temperature, resulting in complete substitution of the trimethylsiloxy groups by chloro ligands, producing bright blue *trans*-Cl$_3$V≡NRe(CO)$_3$(PPh$_3$)$_2$ (6) and 3 equiv of hexamethyldisiloxane (detected by ^{1}H NMR spectroscopy) (eq 4).
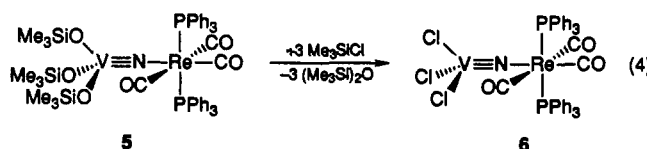
Surprisingly, compound 6 cannot be prepared from the trichlorovanadium silylimido complex. Instead, V(NSiMe$_3$)Cl$_3$ reacts with the rhenium fluoro complex 1 in benzene-d_6 to immediately form an uncharacterized black solid, with Me$_3$SiCl and Me$_3$SiF but no 6 detected in the brown supernatant by ^{1}H NMR spectroscopy.

Spectroscopic data for 6 support the existence of the nitride-bridged trans structure shown.[26] In comparison with those for 5, the carbonyl stretching frequencies for 6 are at significantly

(20) For example, in the ^{13}C NMR spectrum of ^{13}CO-enriched [Re(CO)$_4$-(dppe)]ClO$_4$, a triplet with $J_{PC(cis)}$ = 8 Hz and a doublet of doublets with $J_{PC(cis)}$ = 8 Hz and $J_{PC(trans)}$ = 41 Hz are observed: Anglin, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 4678.

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(22) The reverse reaction, 2 plus (PPN)F, was not examined due to the variable composition of (PPN)F.[13]

(23) This phenomenon is thought to occur in hindered rhodium Vaska systems.[5a]

(24) Decomposition of 4 produces V(O)(OSiMe$_3$)$_3$ as the predominant vanadium-containing species.[10a]

(25) Crystals of 5 were obtained by slow cooling of a hot pentane solution. Crystal data: monoclinic, $P2_1/c$; a = 20.606 (4) Å, b = 12.593 (2) Å, c = 22.550 (6) Å, β = 114.38 (3)°, V = 5330 (4) Å^3, Z = 4, D_{calcd} = 1.405 g cm^{-3}, 25 °C. Decay of the crystal during data collection provided a marginal-quality data set. Solution of the structure and least-squares refinement support the connectivity proposed from spectroscopic data for 5.

(26) Crystals of 6 were obtained by slow evaporation of a toluene solution. Crystal data: monoclinic, $P2_1/n$; a = 10.194 (2) Å, b = 19.016 (5) Å, c = 19.845 (4) Å, β = 94.05 (3)°, V = 3838 (2) Å^3, Z = 4, D_{calcd} = 1.672 g cm^{-3}, 24 °C. Decay of the crystal during data collection provided a marginal-quality data set. Solution of the structure and least-squares refinement support the connectivity proposed from spectroscopic data for 6.

Scheme I

(a) [chemical scheme structures]

(b) [chemical scheme structures]

(c) [chemical scheme structures]
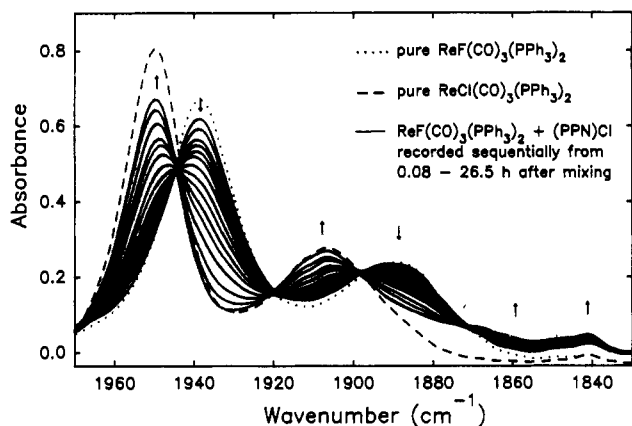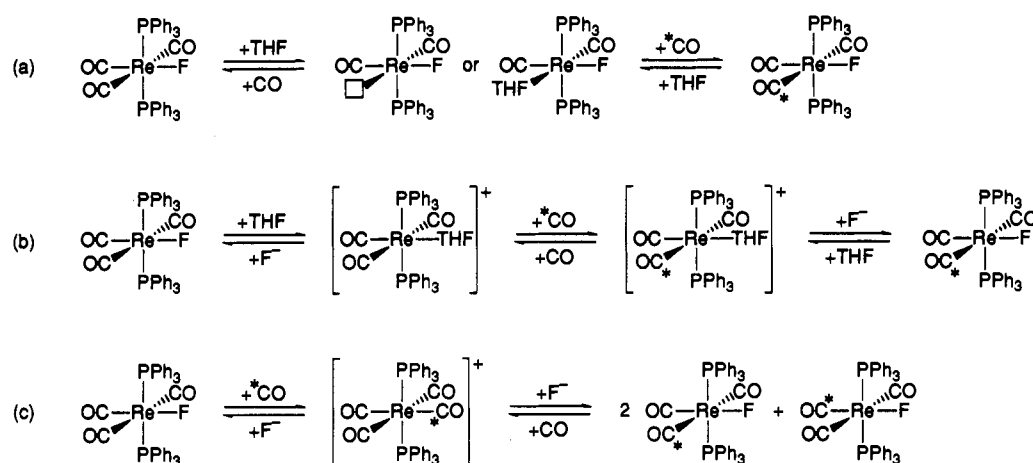
Figure 1. Sequential IR spectra for the reaction of *trans*-ReF(CO)$_3$-(PPh$_3$)$_2$ (1) and (PPN)Cl (1:2) in 1,2-C$_2$H$_4$Cl$_2$.

higher frequencies, consistent with our expectation that the [Cl$_3$V≡N] fragment should be more electron-withdrawing than [(Me$_3$SiO)$_3$V≡N] due to the poorer π-donor ability of the chloro versus siloxy substituents. The substantial downfield shift of the ^{51}V NMR signal for **6** (δ +430) relative to that of **5** (δ −260) parallels that observed for the vanadium silylimido compounds (V(NSiMe$_3$)Cl$_3$ at δ +10^{16} vs V(NSiMe$_3$)(OSiMe$_3$)$_3$ at δ −650^{10a}) and fits the detailed model put forward by Maatta and co-workers[27] for the ^{51}V NMR spectra of vanadium(V) oxo and imido derivatives.

Discussion

Our synthesis of *trans*-ReF(CO)$_3$(PPh$_3$)$_2$ (1) provides a new example of the facile replacement of weakly coordinating ligands by F$^-$ in weakly polar solvents. Reactions in which groups such as H$_2$O, SO$_3$CF$_3^-$, or BF$_4^-$ are replaced by fluoride from organic-solvent-soluble sources such as (PPN)F, (NR$_4$)F, or TASF ([S(NMe$_2$)$_3$]SiF$_2$Me$_3$) offer one of the most promising rational routes for the synthesis of organometallic fluoro complexes.[4] In the rhenium system described here, net metathesis of fluoride for chloride is accomplished in high yield by abstraction of Cl$^-$ from *trans*-ReCl(CO)$_3$(PPh$_3$)$_2$ (2) using Ag(SO$_3$CF$_3$), followed by addition of (PPN)F. The bromo, iodo, and isothiocyanato derivatives can be prepared analogously in high yield.

An interesting property of the fluoro ligand in the *trans*-ReX-(CO)$_3$(PPh$_3$)$_2$ system is its ability relative to the chloro ligand to accelerate substitution reactions at the rhenium center. The rate of exchange of ^{13}CO at the positions cis to the fluoride in **1** is roughly 2 orders of magnitude greater than that at positions cis to the chloride in **2**. This substitution could occur by a simple

dissociative mechanism via a coordinatively unsaturated intermediate or its THF adduct (Scheme Ia). For the heavier halo ligands, cis labilization follows the order Cl > Br > I.[28] Our observation that fluoride enhances cis exchange more than chloride in *trans*-ReX(CO)$_3$(PPh$_3$)$_2$ fits this cis-labilization series. Alternatively, cis incorporation of ^{13}CO could occur via THF/halide exchange followed by labilization of the CO's cis to THF in the intermediate [Re(THF)(CO)$_3$(PPh$_3$)$_2$]$^+$ (Scheme Ib). Because it is a relatively weak σ-donor and a weak π-acceptor, THF meets the criteria suggested by Atwood and Brown for a good cis-labilizing ligand.[28] In this case, the enhanced rate of cis exchange in **1** would be a function of a greater concentration of the intermediate species based on the higher degree of dissociation of the fluoride as indicated by solution conductivity measurements. Our data do not distinguish between the mechanistic possibilities in paths Ia and Ib.

The incorporation of label trans to the halo ligand is more than 10-fold slower than cis exchange in **1** and even slower in **2**, for which it cannot be detected on the time scale of the experiment. (Another example of stereoselective incorporation of ^{13}CO at an octahedral rhenium center occurs for [Re(CO)$_4$(dppe)]$^+$, which reacts with ^{13}CO to form only [*fac*-Re(^{13}CO)(CO)$_3$(dppe)]$^+$.[20]) The differing rates of cis versus trans exchange for **1** rule out the possibility that CO exchange occurs by substitution of ^{13}CO for the halide (Scheme Ic) because the intermediate, [*trans*-Re-(^{13}CO)(CO)$_3$(PPh$_3$)$_2$]$^+$, has four equivalent carbonyls and would therefore add halide to produce a statistical mixture of the possible labeled products.

The enhanced lability of the carbonyl ligands in the fluoro version of *trans*-ReX(CO)$_3$(PPh$_3$)$_2$ parallels the chemistry of the ReX(CO)$_5$ system. Whereas ReCl(CO)$_5$ is a stable and readily isolable compound,[29] reaction of AgF with ReBr(CO)$_5$ yields a structurally characterized tetramer, [ReF(CO)$_3$]$_4$, proposed to form via facile decarbonylation of the intermediate ReF(CO)$_5$ at ambient temperature.[30] The lability of the ligands in *trans*-ReX(CO)$_3$(PPh$_3$)$_2$ is likely responsible for the absence of simple anion-metathesis chemistry in this system. This in turn precludes determination of the halide preference by equilibrium studies, an original goal of this work.

IR spectra can be used to examine the influence of the identity of the halide on ground-state *trans*-ReX(CO)$_3$(PPh$_3$)$_2$. The carbonyl stretching frequencies for these rhenium compounds increase in the order F < Cl < Br < I (Table I). An identical trend in ν_{CO} has been noted for the rhodium Vaska halo series, *trans*-RhX(CO)(PPh$_3$)$_2$, which demonstrates a clear preference for fluoride over the heavier halides in aprotic media.[5] The trends in the rhodium system have been attributed to π-bonding effects,

(27) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408.

(28) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160 and references therein.

(29) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1985**, *23*, 41.

(30) (a) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 737. (b) Horn, E.; Wimmer, F. L.; Snow, M. R. *Inorg. Synth.* **1989**, *26*, 81.

consistent with the nature of fluoride as the weakest π-acceptor and strongest π-donor of the halo ligands, leading to enhanced carbonyl back-bonding and the most stable complex when X = F.[4,5] By this reasoning, *trans*-ReF(CO)₃(PPh₃)₂ (**1**), with the lowest ν_{CO} values in the rhenium halo series, would be expected to be the most stable complex. On the other hand, the greater degree of halide dissociation in coordinating solvents for **1** versus **2** could be argued to suggest a thermodynamic preference for chloride over fluoride; however, this does not take into account differences in solvation of the two halides. Our data do not provide a clear-cut conclusion about halide preference in this system.

The trend in ν_{CO} for these compounds appears to oppose the observation that *trans*-ReF(CO)₃(PPh₃)₂ (**1**) has the most labile carbonyls; by ground-state arguments the lowest carbonyl stretching frequencies indicate that **1** has the strongest rhenium-carbonyl bonding in the *trans*-ReX(CO)₃(PPh₃)₂ system. However, Lichtenberger and Brown have noted "the absence of a relationship between the bonding in six-coordinate ground state molecules and the kinetics of CO dissociation"[31] and have suggested that stabilization of the five-coordinate transition state by π-donor ligands is a dominant factor in enhancing cis labilization.[28,31]

The lability of the carbonyls in **1** is of importance in its reaction with V(NSiMe₃)(OSiMe₃)₃ (**4**). We have previously observed that a vacant coordination site is needed for formation of a nitride-bridged product by the condensation reaction.[10a] Formation of *trans*-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂ (**5**) constitutes our first example of the condensation of a coordinatively saturated metal fluoro complex with a metal silylimido complex.

Note that although nitride-bridged **5** and Me₃SiF are formed from **1** plus **4**, no reaction is observed between **2** and **4**. This difference in reactivity is likely a function of the thermodynamics of this system; the substantial difference in the energy of the Si–X bond in the Me₃SiX byproduct determines whether the condensation reaction occurs (Si–F in Me₃SiF is estimated at 159 ± 5 kcal mol⁻¹; Si–Cl in Me₃SiCl is reported as 113 ± 2 kcal mol⁻¹ [32]). We have seen this thermodynamic trend in the reaction of **4** with square-planar group VIII metal halides to form nitride-bridged compounds *trans*-(Me₃SiO)₃V≡NM(CO)(PPh₃)₂ (M = Rh, Ir) (eq 5).[10a] The nitride-bridged product is formed quantiatively when X = F but is readily cleaved to yield **3** and the chloro Vaska complex when X = Cl. These observations demonstrate that the pathway for the condensation reaction exists for both fluoro and chloro group VIII metal complexes; however, the energy of the

$$(5)$$
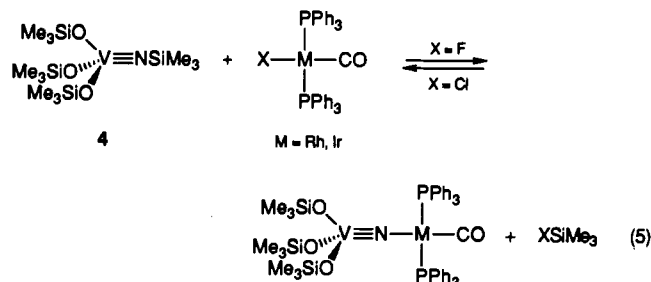
Si–X bond dominates in determining the direction of reaction which is favored.

In order to test whether the pathway for reaction of **4** and **2** exists, addition of Me₃SiCl to **5** was examined. Remarkably, clean formation of *trans*-Cl₃V≡NRe(CO)₃(PPh₃)₂ (**6**) is observed. The three siloxy ligands are replaced with chloro ligands from Me₃SiCl with release of hexamethyldisiloxane, (Me₃Si)₂O, instead of the expected cleavage of the nitride bridge. This chemistry, which may occur due to steric protection of the nitride bridge in **5** (and also in **6**) by the six-coordinate rhenium center, represents the first example in which we have been able to perform reactions on the vanadium center of our nitride-bridged compounds while keeping the bridge intact.

Conclusions

The d⁶ complex *trans*-ReF(CO)₃(PPh₃)₂ is readily prepared from its chloro analogue and is considerably more labile than *trans*-ReCl(CO)₃(PPh₃)₂, as demonstrated by fast cis and slower trans incorporation of ¹³CO into the rhenium coordination sphere. The enhanced lability of the fluoro complex has been exploited to synthesize the nitride-bridged compound *trans*-(Me₃SiO)₃V≡NRe(CO)₃(PPh₃)₂ and provides the first example of condensation of a coordinatively saturated metal fluoro complex with a metal silylimido derivative.

(31) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366–373.
(32) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 5.