Synthesis of Rhenium Complexes That Contain the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ Ligand

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The reaction between $[Et_4N]_2[ReOCl_5]$ and $(C_6F_5NHCH_2CH_2)_3N$ ($H_3[N_3N_F]$) in CH_3CN at room temperature in the presence of NEt_3 yielded air stable, emerald green, diamagnetic $[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]Re(O)Cl$ (**1**). The reaction between **1** and Ta(CH-t-Bu)$(THF)_2Br_3$ gave paramagnetic $[N_3N_F]ReBr$ (**2**). An X-ray structure of a sample of **2** showed it to be analogous to that of $[N_3N_F]MoCl$. Reduction of **2** by methyllithium (or more conveniently by Mg) in the presence of a variety of two-electron ligands gave complexes of the type $[N_3N_F]Re(L)$ (L = H_2, ethylene, propylene, CO, N_2, phosphines, pyridine, tetrahydrothiophene, acetonitrile, or silanes). An X-ray structure of $[N_3N_F]Re$(ethylene) showed η^2-ethylene to be bound in the apical "pocket" with its C−C axis lying in one of the N_{ax}−Re−N_{eq} planes. Protonation of the PMe_3 complex gave an authentic hydrido phosphine complex, $\{[N_3N_F]Re(H)(PMe_3)\}^+$, but protonation of other phosphine complexes gave species in which coupling between H and P is relatively large (∼60 Hz) and therefore that are believed to have some $\{[N_3N_F]Re(\eta^2\text{-}HPR_xH_{3-x})\}^+$ character. An X-ray study of $\{[N_3N_F]Re(H)(PHPh_2)\}^+$ confirmed that one proton is terminally bound to phosphorus and that the phosphorus is "off-axis" in order to accommodate the "hydride" in the same plane.

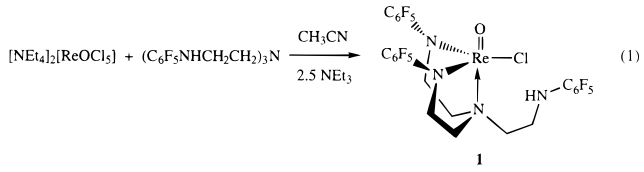
Introduction

A variety of complexes that contain a triamidoamine ligand ($[(RNCH_2CH_2)_3N]^{3-}$) and a metal in the 3+ or higher oxidation state have been prepared.[1−12] Triamidoamine ligands usually bind to a transition metal in a tetradentate manner, thereby creating a sterically protected, 3-fold-symmetric "pocket" in which only three orbitals are available to bond to additional ligands in that pocket, two degenerate p orbitals (approximately d_{xz} and d_{yz}) and a σ orbital (approximately d_{z^2}). The fact that the two frontier p orbitals in a C_3 symmetric triamidoamine complex are strictly degenerate and probably essentially pure d orbitals creates an environment that is especially favorable for formation of a metal−ligand triple bond.

The two most readily accessible $[(RNCH_2CH_2)_3N]^{3-}$ ligands are those in which R is $SiMe_3$ (or another trisubstituted silyl group such as $SiEt_3$) or C_6F_5 ($[(C_6F_5NCH_2CH_2)_3N]^{3-} = [N_3N_F]^{3-}$).[1] One attractive feature of the $[N_3N_F]^{3-}$ ligand[11] (compared to silyl-substituted ligands) is the stability of the N−C_6F_5 bond toward hydrolysis. $[N_3N_F]ML_x$ complexes have now been prepared that contain Mo or W,[11,12] Ti,[13] V,[14,15] and Re.[16] The Re complexes are relatively important, since $[(Me_3SiNCH_2CH_2)_3N]Re$ analogues so far have not been prepared and since the only other examples of Re complexes that contain a tripodal trianionic ligand appear to be $[N(CH_2CH_2S)_3]^{3-}$ complexes.[17−19] We report here the syntheses of a variety of rhenium complexes that contain the $[N_3N_F]^{3-}$ ligand. A small part of this chemistry has been communicated in a preliminary fashion.[16]

Results and Discussion

An entry into rhenium triamidoamine chemistry was discovered through the reaction shown in eq 1. We



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propose that emerald green diamagnetic **1** is an 18-electron species that contains one protonated "arm" of

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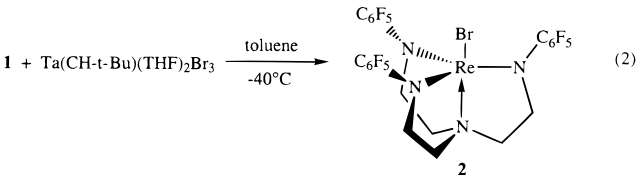
the $[N_3N_F]^{3-}$ ligand that is not coordinated to Re. A medium-strength, sharp NH stretch is observed in the IR spectrum at 3419 cm^{-1}, while fluorine and proton NMR data are more consistent with a structure that has C_s symmetry. Crystals suitable for a high-quality X-ray structure could not be obtained. Two "arm-off" structures have been structurally characterized so far. In $\{[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]V(O)\}_2$[14] the two amido ligands occupy equatorial positions in a pseudo-trigonal bipyramidal arrangement about the metal, while $[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo(NNSiMe_3)Me$[20] is a monomeric diazenido complex whose structure is analogous to that proposed for **1**. Several examples of TBP complexes that contain a diamido/donor ligand and in which the amido nitrogen atoms occupy "equatorial" coordination positions also have appeared in the literature in the last several years.[21−28] In **1** the oxo ligand would be pseudo-triply bound to the metal through the d_{xz} and d_{yz} orbitals (if the N−Re−O axis is the *z* axis), which is consistent with the observed Re═O stretch at 910 cm^{-1}, leaving the equatorial amido nitrogen atoms to form one p bond to the metal using the $d_{x^2-y^2}$ orbital (assuming Re−Cl is coincident with the *x* axis). An 18-electron count thereby could be achieved with the two electrons on the metal in the d_{xy} orbital. In this circumstance no ligands compete with each other for metal orbitals. An 18-electron pseudo-octahedral species is considered to be a less likely possibility, since the oxo ligand cannot be pseudo-triply bound to the metal in that circumstance. If the amine donor were bound to the Re on the NMR time scale, NMR spectra also should be considerably more complex.

An attempt to exchange the oxo ligand in **1** with the neopentylidene ligand in $Ta(CH\text{-}t\text{-}Bu)(THF)_2Br_3$[29] gave an olive-green paramagnetic species that we propose is $[N_3N_F]ReBr$ (**2**) in 60−85% yield (eq 2). On paper this



(2)

2

reaction consists of a formal exchange of the oxo ligand in **1** with Br_2 on Ta, loss of HCl from Re to give "$[N_3N_F]ReBr_2$", and then reduction of "$[N_3N_F]ReBr_2$" to $[N_3N_F]ReBr$. The final form of the tantalum and the mode of reduction of Re(V) to Re(IV) could not be determined. We have not been able to obtain any single completely satisfactory set of analyses for C, H, and N in six attempts, perhaps in part because of the presence of a somewhat variable amount (∼0.5 equiv) of dichloromethane (as confirmed by NMR) and the possibility that some $[N_3N_F]ReCl$ is present in some samples. (See the discussion of the X-ray study below and in the Experimental Section.) The average of six C, H, and N analyses and two Br and Cl analyses is satisfactory, however (see the Experimental Section), for a compound with the composition $C_{24}H_{12}N_4BrF_{15}Re(CH_2Cl_2)_{0.5}$. Several pieces of data are consistent with the proposed formulation. First, complex **2** should have a low-spin d^3 configuration, since the three electrons reside in degenerate d_{xz}/d_{yz} orbitals (taking the N−Re−Br axis as the *z* axis). A plot of the molar magnetic susceptibility as a function of temperature shows that **2** does behave as a Curie paramagnet with $\mu = 1.65(1)\ \mu_B$ between 5 and 300 K and that the effective magnetic moment remains constant in this temperature range (Figure 1), all consistent with a single unpaired spin in a d^3 complex with degenerate d_{xz} and d_{yz} orbitals. We originally proposed (on the basis of a single C, H, and N analysis and observation of a strong peak for $\{[N_3N_F]ReBr\}^+$ in the FAB mass spectrum, and in the absence of bromide and chloride analyses and SQUID data) that **2** was $\{[N_3N_F]ReBr\}Br$.[16] Compound **2** can be observed in mixtures from the reaction between $ReBr_4$(tetrahydrothiophene)$_2$, $H_3[N_3N_F]$, and NEt_3, although we

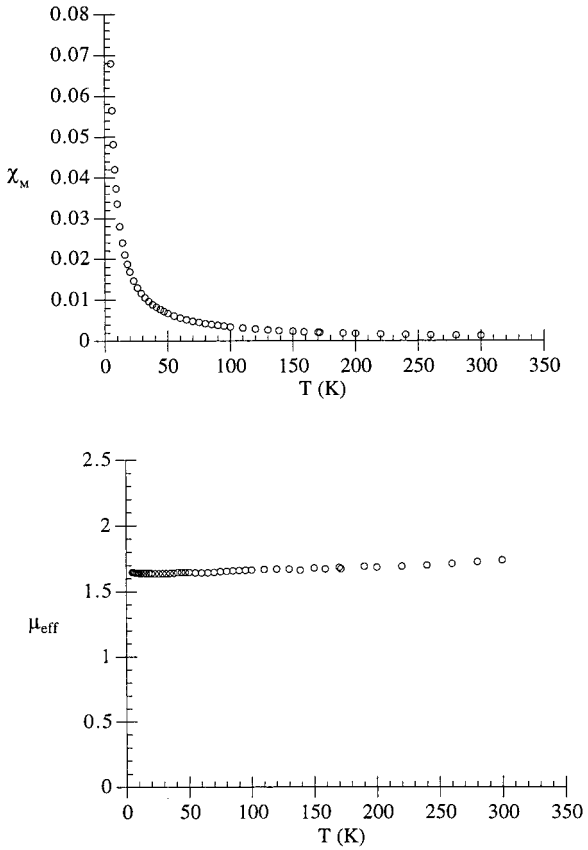


Figure 1. Plots of χ_M (top) and μ_{eff} (bottom) vs *T* for $[N_3N_F]ReBr$.

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $[N_3N_F]ReBr$ (2), $[N_3N_F]Re(C_2H_4)$ (3a), and $\{[N_3N_F]Re(H)(PHPh_2)\}BAr_4$ ($4gH^+$)[a]

	2	3a	$4gH^+$
empirical formula	$C_{24}H_{12}Br_{0.6}Cl_{0.4}F_{15}N_6Re$	$C_{26}H_{16}N_4F_{15}Re$	$C_{68}H_{36}N_4BF_{39}PRe$
formula weight	917.72	855.63	1877.99
crystal dimensions (mm)	0.19 × 0.14 × 0.08	0.21 × 0.18 × 0.13	0.20 × 0.15 × 0.30
crystal system	orthorhombic	triclinic	monoclinic
a (Å)	15.3411(1)	11.151(2)	21.0214(1)
b (Å)	18.9146(13)	11.421(2)	17.0496(2)
c (Å)	11.5416(8)	11.937(2)	22.7095(3)
α (deg)	90	105.622(2)	90
β (deg)	90	107.363(2)	116.759(1)
γ (deg)	90	93.121(2)	90
V (Å^3)	3349.0(4)	1382.2(5)	7267.5(1)
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
Z	4	2	4
D_{calc} (Mg/m^3)	1.820	2.056	1.716
F_{000}	1743	820	3672
temperature (K)	183	293(2)	188(2)
θ range for data collection (deg)	1.71−23.41	1.87−23.27	1.56−22.96
no. of independent reflections	4703	3860	9940
no. of data/restraints/parameters	4695/0/404	3853/0/415	9933/171/1042
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0408, wR2 = 0.1117	R1 = 0.0471, wR2 = 0.1180	R1 = 0.0632, wR2 = 0.1395
R indices (all data)	R1 = 0.0439, wR2 = 0.1341	R1 = 0.0489, wR2 = 0.1281	R1 = 0.0779, wR2 = 0.1493
GOF	1.083	1.079	1.180
extinction coefficient	0.0014(2)	(not applied)	0.00029(6)
largest diff peak and hole (e Å^{-3})	0.640 and −0.928	2.459 and −2.675	1.527 and −1.475

[a] All structures were solved on a Siemens SMART/CCD diffractometer using 0.710 73 Å Mo Kα radiation and *ω* scans. Solutions were refined using a full-matrix least-squares on F^2.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms in $[N_3N_F]MoCl$, $[N_3N_F]ReX$ (2), $[N_3N_F]Re(C_2H_4)$ (3b), and $\{[N_3N_F]Re(H)(PHPh_2)\}^+$ ($4gH^+$)

	$[N_3N_F]$-MoCl[a]	2	3b	$4gH^+$
M−N(1)	1.962(3)	1.940(8)	1.930(7)	1.949(7)
M−N(2)	1.957(3)	1.913(8)	1.965(7)	1.991(7)
M−N(3)	1.964(3)	1.917(8)	1.940(7)	1.998(7)
M−N(4)	2.182(3)	2.173(8)	2.178(8)	2.198(6)
N(1)−M(1)−N(2)	119.0(1)	117.1(3)	116.9(3)	114.5(3)
N(2)−M(1)−N(3)	117.4(1)	116.0(3)	118.3(3)	121.0(3)
N(1)−M(1)−N(3)	115.9(1)	120.2(4)	117.1(3)	115.4(3)
M−N(1)−C(11)	127.8(3)	125.3(6)	129.7(6)	129.5(5)
M−N(2)−C(21)	125.9(3)	118.8(6)	130.8(6)	133.2(5)
M−N(3)−C(31)	124.6(2)	124.9(7)	130.4(6)	129.0(5)
N(4)−M−N(1)−C[b]	177	173	173	175
N(4)−M−N(2)−C[b]	168	174	172	179
N(4)−M−N(3)−C[b]	172	179	170	161
M to ligand	2.367(1) (Cl)	2.442(2) (X)	2.182(8) (C(7))	2.410(2) (P)
Re−C(8)			2.147(11)	
C(7)−C(8)			1.406(14)	
N(4)−Re−P				160.2(2)
P−H(1)				1.39(7)
Re−P−H(1)				93.38(6)
C(11)−P−C(21)				103.3(4)

[a] See ref 11. Only one of two essentially identical molecules in the unit cell. [b] Taken from a Chem 3D model.

have not yet been able to synthesize it in pure form and high yield in this manner.

The most convincing evidence for the identity of **2** is an X-ray structural determination (Tables 1 and 2; Figure 2), although this structure was not completed without complications. In the bulk sample on the average approximately one Br and one Cl are present, with the majority of the Cl coming from ∼0.5 equiv of dichloromethane; however, it should be noted that analyses tend to be slightly high in Cl and low in Br (see Experimental Section). The dichloromethane (disordered) was found in the crystal chosen for the X-ray study, and in the process was removed using SQUEEZE

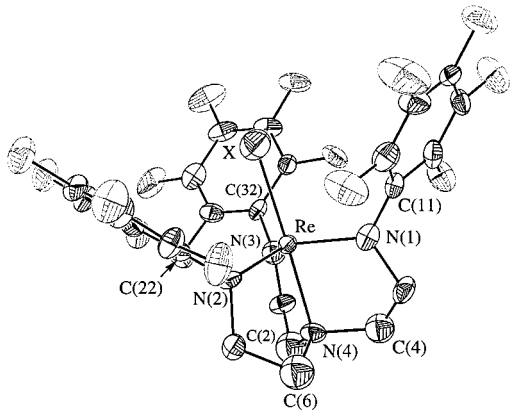


Figure 2. Side view (ORTEP) of the structure of $[N_3N_F]$-ReX, where X = 0.60Br/0.40Cl.

(see the Experimental Section). However, the axial ligand could not be refined satisfactorily as either Br or Cl, and some disorder was observed in the ligand backbone. The backbone disorder could be modeled readily. However, only refinement of the axial "halide" as 0.60 Br and 0.40 Cl led to a structure of relatively high quality. We surmise that the particular crystal chosen for the X-ray study happened to be a mixture of ∼60% $[N_3N_F]ReBr$ and ∼40% $[N_3N_F]ReCl$, but that this crystal is not representative of the bulk material.

The structure of $[N_3N_F]ReX$ (where X = 0.60 Br and 0.40 Cl; Figure 2) is analogous to that of $[N_3N_F]MoCl$,[11] as shown by the bond distances and angles listed in Table 2. The Re−N_{eq} distances in $[N_3N_F]ReX$ appear to be slightly shorter by up to 0.02 Å than the Mo−N_{eq} distances in $[N_3N_F]MoCl$, but the M−N(4) distance and the N_{eq}−Mo−N_{eq} and M−N−C angles in the two compounds are essentially identical. In each compound the C_6F_5 rings are turned so as to form a bowl around the apical halide atom, and the N_{ax}−Re−N_{eq}−C dihedral angles are all between 168° and 179°. The Re−X distance is of course longer than an expected Re−Cl

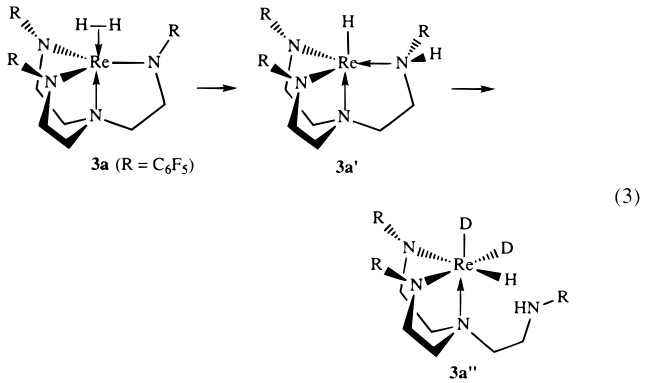
distance and shorter than an expected Re−Br distance, given the method of modeling the apical halide ligand.

Dihydrogen, Dinitrogen, CO, and Olefin Complexes. Attempts to alkylate **2** with methyllithium revealed that it is readily reduced to Re(III) and that in the presence of several two-electron donor ligands complexes with the formula $[N_3N_F]$Re(L) are produced.[16] We have since found that **2** is reduced smoothly by Mg powder and that $MgBr_2$ is easily removed as insoluble $[MgBr_2(dioxane)]_x$. Reduction of **2** by Mg is also more straightforward and is less likely to be susceptible to side reactions. Therefore reduction of **2** by Mg was the method of choice for preparing lower oxidation state Re species, although yields were not in any case necessarily greater than when methyllithium was employed as a reducing agent.

Reduction of **2** under dihydrogen gave $[N_3N_F]ReH_2$ (**3a**). A sharp resonance for the "hydrides" in **3a** was found at −0.89 ppm in the proton NMR spectrum in CD_2Cl_2, but no peak could be located in the IR spectrum. A T_1 measurement at 21 °C yielded a value of 138 ms, a possibly nonminimal value that would be more consistent with **3a** being a classical dihydride complex.[30−32] However, $[N_3N_F]$ReHD was prepared similarly and shown to have an HD coupling constant of 17 Hz, which indicates that **3a** has some characteristics of a dihydrogen complex. (Typically $J_{HD} = 30 \pm 4$ Hz in dihydrogen complexes.[30−32]) There are examples in the literature where neither description (a dihydrogen complex or a dihydride) is totally satisfactory,[33] and we suggest that is the case here, at least on the basis of the data available so far. For *purposes of discussion* we choose to view **3a** as an 18e dihydrogen complex of Re(III) in which two amido−Re π bonds can form[1] and in which the two orthogonal filled d_{xz} and d_{yz} orbitals contain the four d electrons. Since the d_{xz} and d_{yz} orbitals are equivalent in C_{3v} symmetry, back-bonding to the dihydrogen ligand does not "lock" the dihydrogen ligand in any given orientation.[30,31,34,35]

Approximately 2 equiv of D_2 was added to an NMR tube containing $[N_3N_F]ReH_2$ in toluene-d_8. At room temperature, the ^{1}H NMR spectrum showed only $[N_3N_F]ReH_2$, but after heating the sealed sample to 120 °C overnight the H_2 resonance at −0.58 ppm was replaced by a triplet at −0.63 ppm ($J_{HD} = 17$ Hz) arising from $[N_3N_F]$ReHD. The same experiment was repeated in toluene and monitored by ^{2}H NMR, whereupon a doublet at −0.51 ppm ($J_{HD} = 17$ Hz) and a singlet at −0.60 ppm in approximately a 1:1 ratio were observed for $[N_3N_F]$ReHD and $[N_3N_F]ReD_2$, respectively. We ruled out the possibility that solvent was playing a role in H/D exchange, since no H/D exchange occurred when $[N_3N_F]ReH_2$ was heated to 100 °C for 16 h in degassed toluene-d_8. Similar behavior was observed in ^{1}H and ^{2}H NMR experiments in which $[N_3N_F]ReD_2$ was treated with H_2 in toluene-d_8 and toluene, respectively. We have seen no evidence that deuterium scrambles into the backbone of the $[N_3N_F]^{3-}$ ligand.

Loss of H_2 to give "Re$[N_3N_F]$" alone would not explain the H/D exchange results above. We propose that one H in **3a** migrates to one of the amido nitrogen atoms to give a monohydride complex (**3a′**, eq 3). Both **3a** and



(3)

3a′ would be 16e Re(III) complexes since the two equatorial amido nitrogen atoms can form only one π bond to the metal. Further reaction of **3a′** with D_2 would yield an 18-electron complex, or if the amine donor dissociates, the 16-electron Re(V) complex **3a″**. Loss of HD from the 18-electron or 16-electron Re(V) complex and reformation of **3a′**-d_1 and then **3a** would complete one H/D exchange cycle. Complexes that contain Re(III), Re(IV), or Re(V) are a central theme in this paper, and therefore oxidation of Re(III) to Re(V) is a reasonable step to propose in the exchange process. An intermediate that contains "one arm off" is also feasible in view of the proposed structure of **1** and the known structure of $\{[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]V(O)\}_2$.[14] Finally, we have recently structurally characterized a d^2 molybdenum species related to **3a′**, $\{[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo(N{=}NSiMe_3)\}^+$, as well as the product of addition of MeMgCl to it, trigonal bipyramidal $[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo(N{=}NSiMe_3)(Me)$, in which the dimethylamine donor is not bound to the metal.[20] Therefore, both **3a′** and **3a″** are plausible intermediates in the proposed mechanism of the H/D exchange reaction shown in eq 3. The possibility that D_2 attacks **3a** to give a $[N_3N_F]Re(H_2)(D_2)$ intermediate in which H and D scramble seems less likely to us at this stage than the mechanism proposed in eq 3.

$[N_3N_F]Re(C_2H_4)$ (**3b**) was prepared by reduction of **2** in THF with magnesium under an atmosphere of ethylene. A proton NMR spectrum of **3b** in THF-d_8 revealed a resonance for coordinated ethylene at 2.61 ppm. The proton NMR spectrum of an analogous compound prepared from doubly ^{13}C labeled ethylene showed the expected pattern for an AA′A″A‴XX′ system[36] with a $J_{H^{13}C}$ coupling of ∼152 Hz. A non-first-order multiplet was observed at 54.7 ppm in the ^{13}C NMR spectrum of $[N_3N_F]Re(^{13}C_2H_4)$ in CD_2Cl_2, and upon decoupling ^{1}H, a singlet was observed with no discernible coupling to fluorine. The only significant change in the ^{1}H NMR spectrum upon cooling an NMR sample of $[N_3N_F]Re(C_2H_4)$ to −90° was resolution of four

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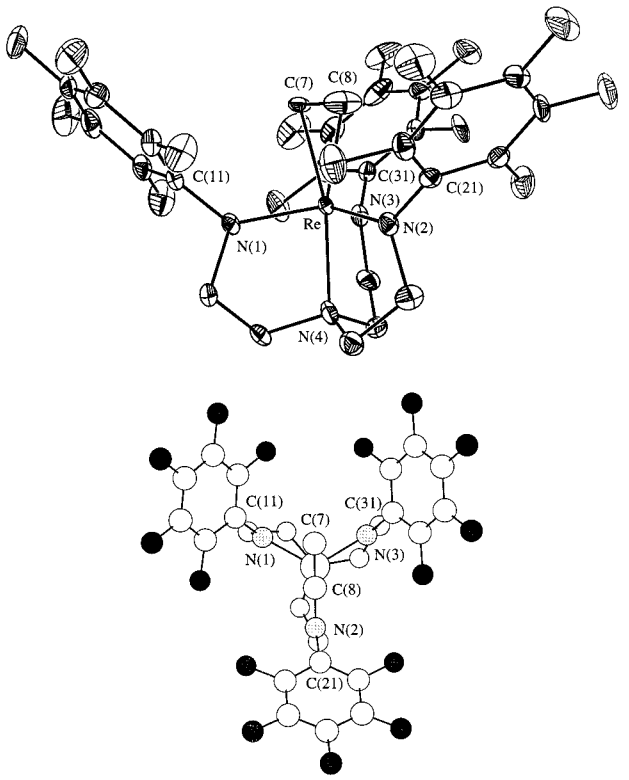

Figure 3. (a) Side view (ORTEP) of the structure of $[N_3N_F]$-Re(C_2H_4). (b) Top view of the structure of $[N_3N_F]$Re(C_2H_4).

types of backbone methylene resonances ascribed to the methylene $[N_3N_F]^{3-}$ protons as a consequence of the $[N_3N_F]^{3-}$ ligand becoming locked in a conformation with true C_3 symmetry. The d_{xz} and d_{yz} orbitals are still degenerate in the C_3 point group, so there is no "electronic" barrier that would prevent free rotation of the ethylene ligand. There is no evidence that ethylene rotation slows on the NMR time scale for steric reasons, i.e., that a complex with no symmetry is produced at −90 °C.

The structure of $[N_3N_F]$Re(C_2H_4) was elucidated in an X-ray study (Tables 1 and 2; Figure 3). The ethylene ligand lies approximately in the N(4)−Re−N(2) plane. The C(7)−C(8) bond length (1.406(14) Å) is typical of a bound ethylene, as are the Re−C(ethylene) bond lengths (2.182(8) Å and 2.147(1) Å). The Re atom is displaced above the equatorial nitrogen plane by 0.314 Å. Re−N_{eq} distances vary from 1.930 to 1.965 Å, Re−N_{eq}−C angles are all approximately 130°, and the Re−N(4) distance is 2.18 Å; all are typical for $[N_3N_F]^{3-}$ complexes of a second- or third-row metal[1] and similar to the analogous distances and angles in **2**. The Re−N_{eq}−C_{ipso} bond angles are consistently a few degrees larger than they are in $[N_3N_F]$ReX, presumably as a consequence of greater steric interaction between the C_6F_5 groups and ethylene versus a halide. For comparison, it should be noted that the acetylene ligand in $[(Me_3SiNCH_2CH_2)_3N]$Ta(HC≡CH) lies in one of the N_{ax}−Ta−N_{eq} planes with Ta−C = 2.09(1) and 2.10(1) Å with one end pointing directly toward one of the trimethylsilyl substituents on the triamidoamine ligand,[37] while the cyclopentylidene and the hydride ligands in $[(Me_3SiNCH_2CH_2)_3N]$W(H)(C_5H_8) lie in a N_{ax}−W−N_{eq} plane.[7]

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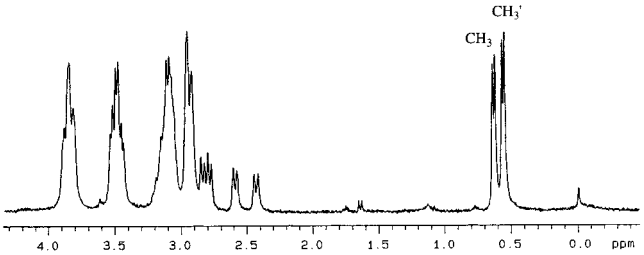
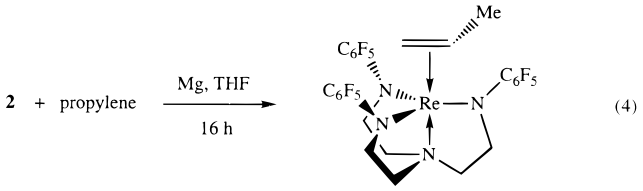


Figure 4. ^{1}H NMR spectrum (CD_2Cl_2, −90 °C) of $[N_3N_F]$Re(CH_3-CH=CH_2).

The C_6F_5 groups are oriented in a manner that creates a bowl-like trigonal cavity in **2** and **3b**. In this "bowl-like" configuration the $F_{ortho}\cdots F_{ortho}$ distances are on the order of 3.1 Å (3.12, 3.08, and 3.11 Å in **3b**). Therefore the trigonal arrangement is maintained to a significant degree by steric interaction between C_6F_5 rings. In contrast, the C_6F_5 rings in $[N_3N_F]$V lie approximately in the V−N_{eq}−C_{ipso} plane,[14] and the short V$\cdots F_{ortho}$ bond distances (2.652 Å) suggest a weak interaction of the ortho fluorines with the metal. Therefore one might expect some stabilization of "$[N_3N_F]$Re" in a similar manner, should it form, and conversely a considerable degree of steric interaction between a C_6F_5 ring that approaches an orientation in which it would lie approximately in the Re−N_{eq}−C_{ipso} plane and any ligand in the trigonal coordination pocket.

A propylene complex, $[N_3N_F]$Re(CH_3CH=CH_2) (**3c**), could be prepared in 65% yield as sparingly soluble dark green prisms (eq 4). A ^{1}H NMR spectrum at room



(4)

temperature reveals that **3c** is 3-fold symmetric and that the four resonances for a rapidly rotating propylene ligand are sharp and well-resolved. However, upon lowering the temperature of the sample, two sets of propylene resonances are obtained along with two sets of overlapping resonances characteristic of a C_3-symmetric ligand backbone (Figure 4). We assign the two sets of propylene resonances to two diastereomers of approximately equal energy formed when propylene binds to the face of the chiral (C_3) complex that is formed at low temperature. In each diastereomer the propylene is freely rotating on the NMR time scale, since only four ligand backbone resonances and one type of pentafluorophenyl ring are observed in each diastereomer.

Reduction of **2** under $^{14}N_2$ or $^{15}N_2$ yielded $[N_3N_F]$Re(N_2) (**3d**) or $[N_3N_F]$Re($^{15}N_2$) (**3d-$^{15}N_2$**), respectively. IR spectra of **3d** (ν_{NN} = 2004 cm^{-1}) and **3d-$^{15}N_2$** ($\nu_{^{15}N^{15}N}$ = 1935 cm^{-1}) are consistent with an end-on mode of dinitrogen binding, as is the ^{15}N NMR spectrum of **3d-$^{15}N_2$**, which reveals two doublet resonances at 281.3 and 332.0 ppm with $^1J_{NN}$ = 5.5 Hz. Exposure of **3d-$^{15}N_2$** to $^{14}N_2$ (22 °C, 1 atm) does not lead to exchange of $^{15}N_2$ for $^{14}N_2$ over a period of 24 h. $[N_3N_F]$Re(N_2) (d^4) is related to $[N_3N_F]$Mo(N_2) (d^3), which is believed to be an intermediate in reactions involving dinitrogen in the $[N_3N_F]$Mo system,[11] but which has not yet been observed. How-

Table 3. Properties of Phosphine Complexes

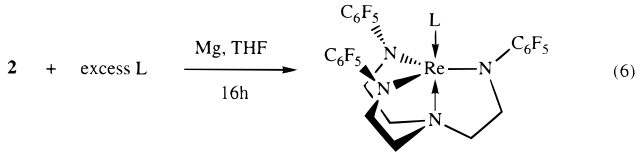
complex	color	δ P (ppm)	θ (deg)[a]	δ H (ppm)	J_{HP} (Hz)
$[N_3N_F]Re(PH_3)$ (**4a**)	red	−138.18	87		305
$[N_3N_F]Re(PMe_3)$ (**4b**)	red	−45.16	118		
$[N_3N_F]Re(PEt_3)$ (**4c**)	red	−24.92	132		
$[N_3N_F]Re[P(i\text{-}Pr)_3]$ (**4d**)	green	−11.56	160		
$[N_3N_F]Re(PMe_2Ph)$ (**4e**)	red-orange	−30.91	122		
$[N_3N_F]Re(PMePh_2)$ (**4f**)	red	−15.19	136		
$[N_3N_F]Re(PHPh_2)$ (**4g**)	orange	1.24	128		319
$\{[N_3N_F]Re(PMe_3)(H)\}^+$ (**4bH**$^+$)	green	−14.88		0.26	7
$\{[N_3N_F]Re(PEt_3)(H)\}^+$ (**4cH**$^+$)	amber	23.02		3.76	64
$\{[N_3N_F]Re(PMePh_2)(H)\}^+$ (**4fH**$^+$)	red-brown	23.74		4.72	62
$\{[N_3N_F]Re(PHPh_2)(H)\}^+$ (**4gH**$^+$)	coral	38.11		3.36	54, 375[b]

[a] See ref 40. [b] J_{HH} = 15 Hz.

ever, $[(Me_3SiNCH_2CH_2)_3N]No(N_2)$ (ν_{NN} = 1934 cm^{-1}) has been isolated and structurally characterized.[20,38]

Reduction of **2** under CO yields $[N_3N_F]Re(CO)$ (**3e**). The IR spectrum of **3e** has a CO band at 1875 cm^{-1} that shifts to 1830 cm^{-1} in $[N_3N_F]Re(^{13}CO)$. The value for ν_{CO} suggests that the amount of back-bonding is qualitatively significantly less that in $[N_3N]W(H)(CO)$, for example, where ν_{CO} = 1766 cm^{-1}.[10] The more "normal" value for ν_{CO} in **3e** is perhaps in part a reflection of the electron-withdrawing ability of the C_6F_5 groups relative to the $SiMe_3$ groups and the consequent reduced back-bonding or reducing ability of the metal. A d^3 tungsten analogue, $[N_3N_F]W(CO)$, has been prepared in which ν_{CO} = 1846 cm^{-1}.[39]

***σ* Donor Complexes.** Several phosphine complexes of the general formula $[N_3N_F]Re(PR_1R_2R_3)$ could be prepared by treating **2** with excess Mg in the presence of 2−4 equiv of $PR_1R_2R_3$ in degassed THF (eq 5). $^{31}P\{^1H\}$ NMR chemical shifts for the complexes and cone angles[40] for the free phosphines are summarized in Table 3. Mixtures containing a significant quantity of $[N_3N_F]Re(N_2)$ were generated if these reactions were performed under an atmosphere of dinitrogen. Addition of 1,4-dioxane and removal of $[MgBr_2(dioxane)]_x$ allowed the diamagnetic phosphine complexes to be isolated as moderately air-stable orange to red cubes. These species are soluble in dichloromethane, THF, and toluene and exhibit 3-fold symmetry on the NMR time scale in solution. An isolable PPh_3 complex could not be prepared under these conditions, we assume as a consequence of the relatively poor basicity of PPh_3 in combination with its large steric demands. The largest phosphine that can be accommodated is P(i-Pr)$_3$ (θ = 160°); its steric bulk presumably contributes to its lability (see below). These are the only phosphine complexes known to date in the general category of triamidoamine complexes.[1] The stability of the PH_3 complex might be attributed to protection against bimolecular decomposition reactions. In **4a** and **4g** the value for J_{HP} is relatively large (305 and 319 Hz, respectively), as expected by comparison to J_{HP} values in uncomplexed phosphines (180−230 Hz) and phosphonium salts (250−730 Hz).[41]



(5)

$PR_1R_2R_3$ = PH_3 (**4a**), PMe_3 (**4b**), PEt_3 (**4c**), P(i-Pr)$_3$ (**4d**), PMe_2Ph (**4e**), PPh_2Me (**4f**), PPh_2H (**4g**)

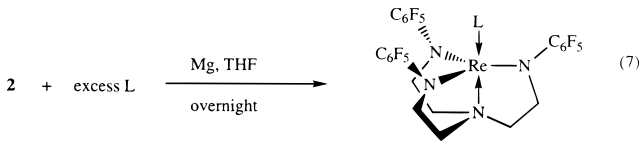
Several other complexes that contain σ donor ligands could be prepared readily, as shown in eq 6. All are

(6)

L = pyridine (**5**), THT (**6**), MeCN (**7**)

diamagnetic and 3-fold symmetric on the ^1H NMR time scale. The pyridine complex was isolated in 48% yield as dark burgundy needles, the tetrahydrothiophene complex in 68% yield as brown needles, and the acetonitrile complex in 61% yield as olive-green prisms. The ^1H NMR spectrum of **6** in CD_2Cl_2 showed only one broad singlet for the THT ligand centered at 1.23 ppm, which we ascribe to an accidental overlap of the THT α and β and exo and endo methylene protons; the $^{13}C\{^1H\}$ NMR spectrum shows clearly two sharp resonances for the two types of methylene carbons in the THT ligand. The IR spectrum of **7** in Nujol shows the CN stretch at 2152 cm^{-1}. Reduction of **2** in THF in the absence of any other potential ligand resulted only in decomposition; that is, no $[N_3N_F]Re(THF)$ complex could be observed. It should be noted that $[N_3N_F]V(THF)$ and $[N_3N_F]V(CH_3CN)$ are known and have been structurally characterized.[15]

Silane Complexes. The synthesis of what we propose is $[N_3N_F]Re(\eta^2\text{-}H_2)$ led us to speculate that alkylsilane complexes of the general form $[N_3N_F]Re(\eta^2$-alkylsilane) might be stable. Two examples could be prepared by reduction of **2** in the presence of excess alkylsilane, as shown in eq 7, and isolated readily as orange-red crystals. Proton NMR spectra in THF-d_8 showed that both have 3-fold symmetry on the NMR time scale. The resonance for what is assigned to the η^2-Si−H proton in **8a** is a singlet at −5.85 ppm with a value for J_{SiH} (44 Hz) that is in the upper range for η^2-silane complexes.[42,43] In contrast, the resonance for the terminal Si−H proton in **8a** is found at 5.83 ppm with J_{SiH} = 186 Hz. The methylene resonances in the Et_2SiH_2 ligand are found as two multiplets centered at −0.01 and −0.74 ppm, consistent with their diastereotopic nature, while the equivalent methyl groups give



(7)

L = H_2SiEt_2 (**8a**), H_3SiPh (**8b**)

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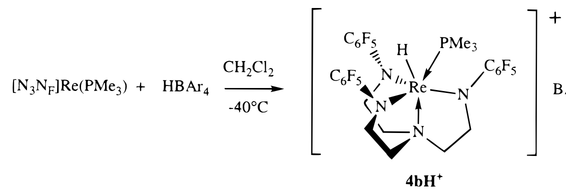
rise to one triplet at 0.32 ppm. The ^1H NMR spectrum of **8b** in CD_3CN showed that it is similar to **8a** in that the η^2-Si−H resonance is found at −3.86 ppm with J_{SiH} = 38 Hz, while the resonance for the two terminal Si−H protons is found at 5.00 ppm with J_{SiH} = 183 Hz.

Transition metal complexes that contain a silane ligand bound in an η^2 fashion are becoming more numerous.[31,42−46] The most reliable indicator for distinguishing an η^2-silane ligand from a silyl hydride is J_{SiH}, which for an η^2-silane ligand is usually in the range 15−60 Hz and for a silyl hydride complex is less than 15 Hz (if observed at all). In **8a** and **8b** J_{SiH} = 44 and 38 Hz, respectively, thus clearly establishing these complexes as η^2-silane complexes. Rhenium silane complexes of the type $(R_2SiH_2)Re_2(CO)_8$ (R = Ph or Me)[47] appear to have been the first reported examples of Re-(η^2-silane) complexes, and others are now known in the literature.[48−55]

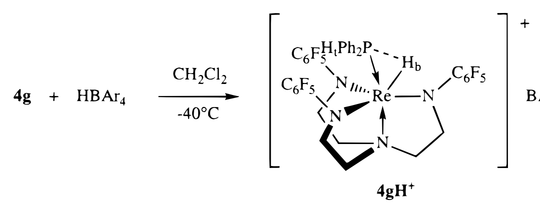
Ligand Substitution Reactions. When dichloromethane solutions of various phosphine complexes (except **4d**) were treated with 3−5 equiv of other phosphines, THT, or MeCN, and monitored by ^{19}F NMR, no bound phosphine was displaced by another ligand at 22 °C over a period of 3 days. Under identical conditions, the silane ligands in **8a** and **8b** were not replaced with H_3SiPh and H_2SiEt_2, respectively. $[N_3N_F]Re(N_2)$ also did not react with MeCN, PMe_3, or C_2H_4 under similar conditions. However, experiments in which solutions of **4d** in degassed toluene (28.9 mM, 85−120 °C, 16 h) were treated with other ligands (3 equiv) showed that $P(i\text{-}Pr)_3$ is readily replaced by MeCN, N_2, PMe_3, and C_2H_4. Likewise, $[N_3N_F]ReH_2$ (34.4 mM in CH_2Cl_2) reacted with PMe_3 (3 equiv) to give **4b** after 3 days at room temperature, while $[N_3N_F]$Re(propylene) was converted to **4b** in about 10% yield under the same conditions. More detailed studies will be required in order to determine whether the exchange reactions are associative or dissociative. However, the reactivity of **4d** seems likely to be ascribable to the lability of the $P(i\text{-}Pr)_3$ ligand (for steric reasons) and formation of intermediate "$[N_3N_F]$Re".

Protonation Reactions. When red $[N_3N_F]Re(PMe_3)$ is treated with 1 equiv of $HBAr_4$ in CH_2Cl_2 at −40 °C ($HBAr_4$ = $[H(OEt_2)_2]^+[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$),[56] green $\{[N_3N_F]Re(H)(PMe_3)\}BAr_4$ (eq 8) forms rapidly and could be isolated as large green cubes in 76% yield. **4bH**$^+$ is diamagnetic and has 3-fold symmetry on the NMR time scale at 25 °C in CD_2Cl_2; the hydride resonance is observed as a doublet at 0.26 ppm (J_{PH} = 7 Hz; Table 3). The $^{31}P\{^1H\}$ NMR spectrum indicates that the phosphorus resonance is shifted downfield from that in **4b** to −14.88 ppm, consistent with the cationic formulation for **4bH**$^+$. The protonation reaction is reversible; **4bH**$^+$ reacts with excess Et_3N over a period of several days at 25 °C to afford **4b** quantitatively (according to ^{19}F NMR).



(8)

Addition of $HBAr_4$ to **4c**, **4f**, or **4g** gave complexes that were slightly different from **4bH**$^+$. The "hydride" resonance was observed between ∼3 and ∼5 ppm and was found to be coupled to phosphorus to the extent of 54−64 Hz. These data suggest that the "hydride" ligand is coupled more strongly to phosphorus than in **4bH**$^+$, but not as strongly as a proton bound to phosphorus directly (e.g., 305 Hz in **4a** and 319 Hz in **4g**). The NMR spectra of the product formed upon protonation of **4g** with $HBAr_4$ were especially revealing. The ^1H NMR spectrum of **4gH**$^+$ in CD_2Cl_2 revealed a double doublet at 6.97 ppm with J_{PH} = 375 Hz and J_{HH} = 15 Hz, consistent with a phosphorus-bound proton. Another double doublet at 3.36 ppm with J_{PH} = 54 Hz was assigned to the Re "hydride". Therefore we propose that phosphine complexes are protonated to give a classical hydride with a small coupling to P when the phosphine is PMe_3, but a species in which the proton is more strongly interacting with the phosphorus in the other examples described here (e.g., eq 9). The "hydride" (H_b)



(9)

does not exchange rapidly on the NMR time scale with the terminal PH (H_t) in the phosphine ligand in **4gH**$^+$. In the extreme one should consider a description in which $[PPh_2H_2]^+$ is bound to the d^4 metal through one P−H bond, i.e., as $(\eta^2\text{-}HPR_xH_{3-x})^+$, the isoelectronic cationic analogue of an η^2-silane. Whatever the description, rotation of the $PR_1R_2R_3$/H unit about the Re−ligand bond axis must be facile, since the complexes show no evidence in solution of the approximate C_s symmetry that is found in the solid state (see below). An example of a proton bridging between a metal and phosphorus in a phosphine complex is known,[57] but we could find no example of what could be called an η^2-phosphonium complex in the literature. The "η^2-phosphonium" description is viable on the basis of the fact that **4bH**$^+$ and **4fH**$^+$ both react with ∼1 equiv of CO on an NMR scale to give **3e** and the corresponding phos-

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phonium salt, according to ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR. For convenience in later discussions the proton that is terminally bound to P will be labeled H_t, while that which is bound to Re and interacting with P will be labeled H_b.

Addition of 1 equiv of $DBAr_4$ to **4g** gave **4gD**$^+$, the ^{1}H NMR spectrum of which is identical to that of **4gH**$^+$ except that the resonances for H_t and H_b each integrate to ~0.5. The ^{2}H NMR spectrum (in CH_2Cl_2) reveals a doublet at 6.86 ppm (J_{DP} = 56 Hz) and another doublet at 3.24 ppm (J_{DP} = 7 Hz), showing that deuterium has been incorporated into both the H_t (6.97 ppm in **4gH**$^+$) and the H_b sites (3.36 ppm in **4gH**$^+$). The ^{31}P{^{1}H} NMR spectrum consists of a triplet at 37.36 ppm (J_{DP} = 56 Hz) that can be ascribed to a Re−H−P−D complex (^{1}H is decoupled) and a singlet at 38.11 ppm that arises from a Re−H−P−H complex. The singlet at 38.11 mostly obscures another triplet with a small J_{DP} that we ascribe to a small amount of a Re−D−P−H complex. There is no evidence in phosphorus NMR spectra for any Re−D−P−D complex under the conditions used so far, although the resonance may be weak and/or hidden. Therefore we observe directly by ^{31}P{^{1}H} NMR {[N_3N_F]-Re(D)($PHPh_2$)}$^+$, {[N_3N_F]Re(H)($PDPh_2$)}$^+$, and {[N_3N_F]-Re(H)($PHPh_2$)}$^+$. It is not known how H and D scramble in these species. One possibility is that H and D exchange intramolecularly between bridging and terminal positions on the chemical time scale and that H^+ or D^+ is lost to reform **4g** on a roughly equivalent time scale. Therefore $HBAr_4$ and [N_3N_F]Re($PDPh_2$) are available, and at least three of the four possible isotopomers can form competitively. In view of the possible η^2-phosphonium character to complexes such as **4gH**$^+$ it is worth entertaining the possibility that P−H_b exchanges on the chemical time scale with P−H_t in an intermediate in which *two* P−H bonds interact with Re in an equivalent manner, i.e., via an "η^3-phosphonium" intermediate.

An X-ray study of **4gH**$^+$ was carried out. Two views are shown in Figure 5, while selected bond distances and angles are presented in Table 2. The terminal proton (H(1)) was located and refined successfully during the intermediate stages of refinement; the P−H(1) bond distance (1.39(7) Å) falls within the expected range. A second proton (H(2)) was located between Re and P in the P−Re−N(3) plane, but became lost repeatedly in the electron density of Re during subsequent refinement. Therefore the Re−H(2) bond distance was arbitrarily constrained to 1.698(5) Å and the P−H(2) bond distance to 1.481(5) Å, both of which are consistent with values found in other phosphine complexes of Re hydrides.[58] The $PHPh_2$ ligand is tipped to one side (N(4)−Re−P = 160.2(2)°), presumably in order to allow H(2) to lie in the same plane as the Re−N(3) bond between P and N(3). The Re−N_{eq} bond distances and the Re−N(4) bond distance are slightly longer than those in [N_3N_F]Re(C_2H_4), consistent with more "steric pressure" in the coordination pocket where the phosphine resides. There is no feature of the triamido ligand in this complex that would be consistent with one of the amido nitrogen atoms being protonated. Interestingly, both phenyl rings of the $PHPh_2$ ligand are

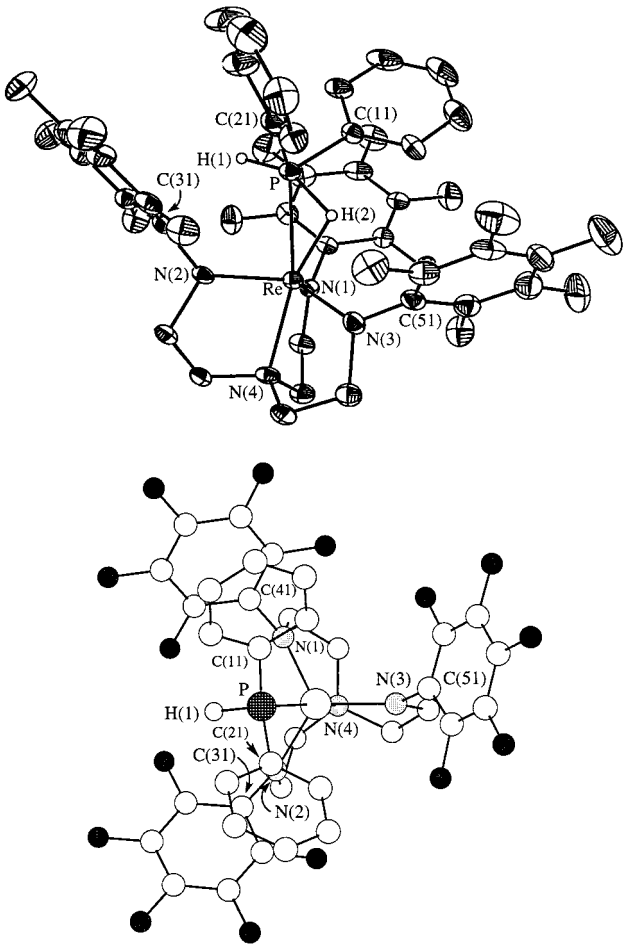
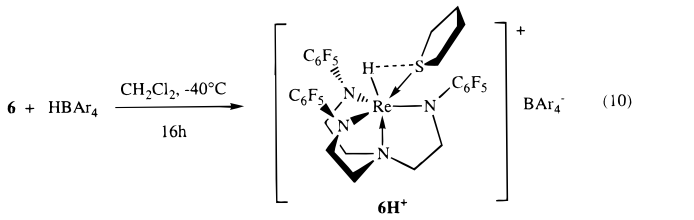


Figure 5. (a) Side view (ORTEP) of the structure of {[N_3N_F]Re(PPh_2H)(H)}$^+$. (b) Top view of the structure of {[N_3N_F]Re(PPh_2H)(H)}$^+$ (H(2) left out for clarity).

roughly parallel to two C_6F_5 rings ~4 Å away and slipped to one side. This configuration appears to be a manifestation of interaction between C_6H_5 and C_6F_5 rings.[59−61] The BAr_4^- anion suffered from some disorder in the CF_3 groups, several of which therefore were refined isotropically, as explained in detail in the Experimental Section.

Protonation of [N_3N_F]Re(THT) (**6**) with 1 equiv of $HBAr_4$ in cold CH_2Cl_2 gave **6H**$^+$ in 51% yield as green prisms upon crystallization from mixtures of dichloromethane and pentane (eq 10). The ^{1}H NMR spectrum



(10)

of **6H**$^+$ in CD_2Cl_2 shows it to be C_3 symmetric on the NMR time scale with a "hydride" resonance at 3.50 ppm, similar to the chemical shifts observed in **4cH**$^+$, **4fH**$^+$, and **4gH**$^+$. Four multiplets between 3.26 and 1.38 ppm are assigned to the eight THT protons, consistent with a tetrahydrothiophene bound to Re through one lone pair. In that circumstance exo and endo protons cannot equilibrate on the NMR time scale, even though rotation

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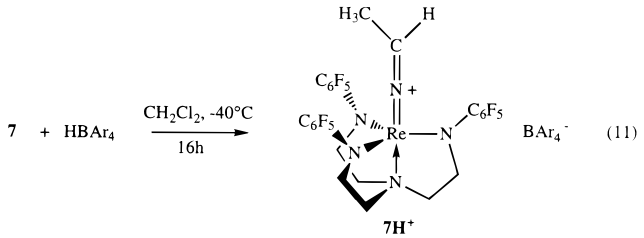
about the Re−S bond may be facile on the NMR time scale, as is rotation of the entire (H)(thiophene) unit relative to the $[N_3N_F]^{3-}$ ligand. The $^{13}C\{^1H\}$ NMR (CD_2Cl_2) spectrum shows only two THT resonances at 45.69 and 29.97 ppm, consistent with a plane of symmetry passing through the THT ligand. The only data that would support a proposal that the "hydride" is also interacting to some extent with the sulfur (eq 10) is the reaction of **6H**$^+$ with CO in CD_2Cl_2 to give **3e** and the (HTHT)BAr_4 salt. However, this reaction also could be viewed as a CO-induced reductive elimination reaction from a "classical" cationic Re(V) phosphine hydride complex.

Protonation of $[N_3N_F]$Re(CH_3CN) (**7**) led to formation of the azavinylidene complex (**7H**$^+$) in 75% yield as green-black crystals (eq 11). The ^1H NMR spectrum in



(11)

CD_2Cl_2 indicates that the molecule has C_3 symmetry on the NMR time scale. The methyl proton resonance at 3.57 ppm is split into a doublet (J_{HH} = 7 Hz) by the azavinylidene proton, for which a quartet is observed at 1.54 ppm. The ^{13}C NMR spectrum reveals a doublet at 118.25 ppm with $^1J_{CH}$ = 163 Hz that is ascribable to the β-carbon atom. Treatment of **7H**$^+$ with DBN (DBN = 1,5-diazabicyclo[4.3.0]non-5-ene) produced **7** rapidly. Azavinylidene complexes in general are rare, and we could find only one other example of an azavinylidene complex of Re.[62] We formulate the methyl azavinylidene ligand in **7H**$^+$ as a linear species with the positive charge formally located on the nitrogen atom. In this manner the d_{xz} or d_{yz} orbitals are both utilized, one to contain two electrons and one to form the Re=N covalent double bond. The 3-fold symmetry in solution is again a consequence of equivalent d_{xz} and d_{yz} orbitals.

Conclusions

We conclude that $[N_3N_F]$Re complexes that contain rhenium in the "mid" oxidation states (Re(III), Re(IV), and Re(V)) are viable. This finding is somewhat surprising in view of the rarity of monomeric rhenium complexes that contain more than one amido ligand.[63−79] There appears to be some preference for Re(III) complexes that contain η^2-bound ligands over Re(V) tautomers, perhaps in part as a consequence of the ability of the d^4 metal for back-bonding, balanced with a steric pressure to maintain the trigonal coordination pocket. The current entry into $[N_3N_F]$Re chemistry relies on an indirect synthesis of a low-spin d^3 starting material (**2**) that appears to be easily reduced. Rhenium triamidoamine chemistry would become more amenable to exploration if a more direct synthesis of a rhenium starting material could be found, especially if it is adaptable to the synthesis of triamidoamine complexes that contain ligands other than $[N_3N_F]^{3-}$.

Experimental Section

General Procedures. All air-sensitive compounds were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres drybox or under argon when using Schlenk techniques. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under N_2. Reagent grade diethyl ether, 1,2-dimethoxyethane, 1,4-dioxane, and tetrahydrofuran were distilled from sodium; CH_2Cl_2 was distilled from CaH_2; acetonitrile was distilled from P_2O_5. Deuterated solvents were passed through activated alumina and vacuum-transferred to solvent storage flasks until use. 2,2′,2″-Tris(pentafluorophenylamino)triethylamine ($H_3[N_3N_F]$),[11] Ta(CH-t-Bu)$Br_3(THF)_2$,[29] and $[H(OEt_2)_2]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$[56] ($HBAr_4$) were prepared by published methods. $[NEt_4]_2[ReOCl_5]$ was prepared by a method analogous to that reported for $[NMe_4]_2[ReOCl_5]$.[80] Phosphines and silanes were purchased from commercial sources and used as received. THT and pyridine were distilled from CaH_2 under N_2 (THT = tetrahydrothiophene).

NMR operating frequencies and reference standards for heteronuclei on the scale of ^1H (300 MHz, $SiMe_4$ = 0 ppm) are as follows: ^{13}C (75.4 Hz, $SiMe_4$ = 0 ppm), ^{31}P (121.4 MHz, 85% H_3PO_4 = 0 ppm), ^{19}F (282.2 Hz, $CFCl_3$ = 0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Fluorine and phosphorus spectra were referenced externally. Multiplicities in fluorine spectra are quantified as "*J*", a pseudo coupling constant. Chemical shifts are reported in ppm, and coupling constants are in hertz. All spectra were acquired at ∼22 °C unless otherwise noted.

IR spectra were recorded on a Perkin-Elmer FT-IR 16 spectrometer as Nujol mulls between KBr plates in an airtight cell. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory, or by Microlytics (South Deerfield, MA) or Schwarzkopf Microanalytical Laboratory (Woodside, NY).

$[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]$Re(O)Cl (1). A CH_3CN solution (3 mL) of $H_3[N_3N_F]$ (4.00 g, 6.207 mmol) and NEt_3

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(2.073 g, 20.480 mmol) was added to a stirred suspension of $[NEt_4]_2[ReOCl_5]$ (3.973 g, 6.207 mmol) in 20 mL of CH_3CN. A rapid color change to emerald green was observed. The solution was stirred for 30 min, and the volatile components were removed in vacuo. The resulting green residue was stirred into 30 mL of THF, the mixture was filtered to remove $[Et_3NH]Cl$, and the filtrate was concentrated in vacuo. The product was recrystallized twice from minimal methylene chloride by adding pentane and cooling the mixture to −40 °C; yield 643 mg (78%): ^{1}H NMR (CD_3CN) δ 2.15−4.70 (br, NH), 3.39 and 3.53 (m, 6), 3.82 (m, 4), 4.19 (m, 2); ^{13}C NMR (CD_3CN) δ 42.1 (br, CH_2), 61.5 (br, 2 CH_2), 66.4 (br, CH_2), 69.7 (br, 2 CH_2), 133−147 (C_{aryl}); ^{19}F NMR (CD_3CN) δ −173.9 (tt, J_{FF} = 21, 6.2), −166.8 (m), 166.4 (t, J_{FF} = 19), −162.4 (t, J_{FF} = 21), −160.3 (d, J_{FF} = 23), −150.4 (dd, J_{FF} = 23, 6.2), −149.9 (m); IR (Nujol) cm^{-1} 3419 (NH), 910 (Re═O). Anal. Calcd for $C_{24}H_{13}N_4ClF_{15}ORe$: C, 32.76; H, 1.49; N, 6.37; Cl, 4.03. Found: C, 32.44; H, 1.52; N, 6.21; Cl 4.06, 4.16.

[N_3N_F]ReBr (2). A solution of Ta(CH-t-Bu)$Br_3(THF)_2$ (699 mg, 1.16 mmol, 1.05 equiv) in 5 mL of toluene was slowly added to a suspension of **1** (970 mg, 1.10 mmol) in 15 mL of toluene at room temperature. After stirring the solution overnight, the volume was reduced to 3 mL and the green-brown precipitate was filtered off and washed twice with toluene. The precipitate was recrystallized from a mixture of methylene chloride and pentane at −40 °C to yield 814 mg of olive-green crystals (74%): ^{1}H NMR (CD_3CN) δ −34 (v br), −138 (v br); ^{19}F NMR (CD_3CN) δ −132.1 (br s), −151.2 (br s), −156.9 (br s); MS 907 (M^+). Anal. Calcd for $C_{24}H_{12}N_4BrF_{15}Re(CH_2Cl_2)_{0.5}$ or $C_{49}H_{26}N_8Br_2F_{30}Cl_2Re_2$: C, 30.98; H, 1.38; N, 5.90; Br, 8.41; Cl, 3.73. Found: C, 31.20; H, 1.39; N, 6.01; Br, 8.00, 8.22; Cl, 3.81, 3.85. (The C, H, and N values are the average of six determinations ranging from 29.73 to 31.82 in C, 1.19 to 1.49 in H, and 5.43 to 6.19 in N.) On the basis of the variable analyses we propose that the bulk sample is not homogeneous, in part as a consequence of variable amounts of dichloromethane in the crystals. (See also the discussion of the X-ray study below.)

[N_3N_F]ReH$_2$ (3a). Methyllithium was added to **2** (100 mg, 0.101 mmol) under dihydrogen (1 atm), and the reaction was stirred for 12 h. Solvents were removed in vacuo, and the residue was extracted with CH_2Cl_2. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo and stood at −40 °C to give 43 mg of dark red crystals (52% yield): ^{1}H NMR (CD_3CN) δ −0.68 (s, H_2), 3.10 (t, 6, J = 5.7), 3.79 (t, 6, J = 5.7); ^{1}H NMR (CD_2Cl_2) δ −0.89 (s, H_2), 3.07 (t, 6, J = 6.3), 3.80 (t, 6, J = 5.4); ^{19}F NMR (CD_3CN) δ −152.2 (m), −166.4 (t, J = 21), −167.1 (m); ^{19}F NMR (CD_2Cl_2) δ −152.0 (m), −165.8 (t, J = 22), −166.6 (m); ^{13}C NMR (CD_3CN) δ 57.6 (CH_2), 64.3 (CH_2), 136.7, 137.5, 139.8, 142.6, 144.3, 145.8 (all C_{aryl}). Anal. Calcd for $C_{24}H_{14}N_4F_{15}Re$: C, 34.75; H, 1.70; N, 6.75. Found: C, 34.49; H, 1.86; N, 7.14.

[N_3N_F]Re(H)(D) (3a-d$_1$). The synthesis was essentially the same as for **3a** from **2** (157 mg, 0.159 mmol) in the presence of HD gas at 1 atm for 48 h. Workup yielded 50 mg of dark red crystals (38%): ^{1}H NMR (CD_3CN) δ −0.74 (t, $^2J_{HD}$ = 17); ^{2}H NMR (CH_2Cl_2) δ −0.98 (d, $^2J_{HD}$ = 17). The remaining portions of the spectra were the same as for **3a**.

[N_3N_F]ReD$_2$ (3a-d$_2$). The synthesis was essentially the same as for **3a** from **2** (100 mg, 0.101 mmol) in the presence of D_2 gas at 1 atm for 12 h. Workup yielded 40 mg of dark red crystals (48%): ^{2}H NMR (THF) δ −0.43 (s). The remaining portions of the spectra were the same as for **3a**. Anal. Calcd for $C_{24}H_{12}D_2N_4F_{15}Re$: C, 34.66; H(D), 1.45; N, 6.74. Found: C, 34.32; H(D), 1.65; N, 6.91.

[N_3N_F]Re(C_2H_4) (3b). One side of a two-chamber vessel was charged with a solution of **2** (400 mg, 0.608 mmol) in 40 mL of THF. The other side was charged with Mg powder (295 mg, 12.150 mmol) and a stir bar. The solution was degassed by three freeze−pump−thaw cycles, and ethylene (excess) was condensed into the vessel. The solution was combined with the Mg, and the reaction mixture was stirred vigorously at room temperature overnight. All solvents were then removed in vacuo. The olive-green residue was extracted three times with 15 mL of THF. The extract was filtered, and excess 1,4-dioxane was added to the combined extracts. After 24 h $[MgBr_2(1,4\text{-dioxane})]_x$ was filtered off, THF was removed from the filtrate in vacuo, and the residue was crystallized from CH_2Cl_2/pentane at −40 °C to give small olive-green crystals; yield 346 mg (65%): ^{1}H NMR (THF-d_8) δ 2.61 (s, 4), 3.27 (t, 6, J = 5.7), 3.87 (t, 6, J = 5.7); ^{1}H NMR (CD_2Cl_2) δ 2.57 (br s, 4), 3.12 (t, 6, J = 5.7), 3.79 (t, 6, J = 5.7); ^{1}H NMR (CD_2Cl_2, −90 °C) δ 3.87 (m, 3), 3.55 (m, 3), 3.15 (m, 3), 3.04 (m, 3), 2.30 (s, 4); ^{19}F NMR (THF-d_8) δ −150.9 (m), −164.3 (t, J = 21), −166.6 (m); ^{19}F NMR (CD_2Cl_2) δ −151.1 (m), −163.2 (t, J = 21), −165.7 (m). Anal. Calcd for $C_{26}H_{16}N_4F_{15}Re$: C, 36.50; H, 1.88; N, 6.55. Found: C, 36.70; H, 1.81; N, 6.88.

The analogous compound prepared from doubly ^{13}C labeled ethylene showed a non-first-order multiplet in CD_2Cl_2 at δ 54.7 in the ^{13}C NMR spectrum. In the ^{13}C{^{1}H} NMR spectrum the singlet showed no coupling to fluorine.

[N_3N_F]Re(C_3H_6) (3c). One side of a two-chamber vessel was charged with a solution of **2** (600 mg, 0.608 mmol) in 40 mL of THF. The other side was charged with Mg powder (295 mg, 12.15 mmol) and a stir bar. The solution was degassed by three freeze−pump−thaw cycles, and propylene (excess) was condensed into the vessel. The solution was combined with the Mg and stirred vigorously at room temperature overnight. All solvents were then removed in vacuo from the olive-green mixture. The residue was extracted three times with 15 mL of THF. The extract was filtered, and excess 1,4-dioxane was added to the combined extracts. After 24 h $[MgBr_2(1,4\text{-dioxane})]_x$ was filtered off, THF was removed in vacuo, and the product was crystallized from CH_2Cl_2/pentane at −40 °C. Very dark green prisms were collected and dried in vacuo; yield 346 mg (65%): ^{1}H NMR (CD_2Cl_2) δ 3.76 (m, 6, NCH_2CH_2), 3.34 (m, 1, CH_3CHCH_2), 3.12 (d, 1, CH_3CHCHH, J_{HH} = 8.1), 3.05 (t, 6, NCH_2CH_2), 2.73 (d, 1, CH_3CHCHH, J_{HH} = 9.3), 0.75 (d, 3, CH_3CHCH_2, J_{HH} = 5.4); ^{13}C{^{1}H} NMR (THF/C_6D_6) δ 148−132 (m, NC_6F_5), 67.63, 61.56 (CH_3CHCH_2), 60.11 (CH_3CHCH_2), 56.46, 20.60 (CH_3CHCH_2); ^{19}F NMR (CD_2Cl_2) δ −150.20(m), −162.88 (m), −165.69 (m). Anal. Calcd for $C_{27}H_{18}N_4F_{15}Re$: C, 37.29; H, 2.09; N, 6.44. Found: C, 37.40; H, 1.90; N, 6.79.

[N_3N_F]Re(N_2) (3d). A solution of **2** (400 mg, 0.405 mmol) in 50 mL of THF was treated with Mg powder (295 mg, 12.15 mmol), and the mixture was stirred under N_2 for 1 h, then filtered to remove excess Mg. Excess 1,4-dioxane was added, the solution was allowed to stand for 16 h, and $[MgBr_2(1,4\text{-dioxane})]_x$ was filtered off. THF was removed in vacuo, and the orange product was crystallized from CH_2Cl_2/pentane as orange cubes; yield 104 mg (0.12 mmol, 72%): ^{1}H NMR (THF-d_8) δ 3.13 (t, 6, J = 5.6), 3.95 (t, 6, J = 5.6); ^{1}H NMR (CD_3CN) δ 3.07 (t, 6, J = 5.6), 3.90 (t, 6, J = 5.6); ^{19}F NMR (THF-d_8) δ −152.90 (m), −164.90 (t, J = 21), −166.59 (t, J = 20); ^{19}F NMR (CD_3CN) δ −152.5 (m), −164.7 (t, J = 21), −166.5 (t, J = 19); ^{13}C NMR (THF-d_8) δ 57.7 (t, CH_2, J = 139), 63.2 (t, CH_2, J = 139), 135−145 (C_{aryl}); ^{15}N NMR (CD_3CN) δ 281.3 and 332.0 (each a d, J_{NN} = 5.5); IR cm^{-1} 2004 (ν_{NN}, vs); MS 856 (M^+), 828 ($-N_2$). Anal. Calcd for $C_{24}H_{12}N_6F_{15}Re$: C, 33.69; H, 1.41; N, 9.82. Found: C, 33.52; H, 1.66; N, 9.48.

The reaction was repeated with 168 mg of **2** in the presence of $^{15}N_2$ to yield 105 mg of the ^{15}N-labeled compound (72%): IR cm^{-1} 1935 ($\nu_{^{15}N^{15}N}$, vs).

[N_3N_F]Re(CO) (3e). One side of a two-chamber vessel was charged with an olive-brown solution of **2** (500 mg, 0.506 mmol) in 40 mL of THF. The other side was charged with Mg powder (443 mg, 18.24 mmol) and a stir bar. The solution was degassed by three freeze−pump−thaw cycles, and CO (excess) was condensed into the vessel. The solution was combined with the Mg and stirred vigorously at room temperature overnight. All solvents were then removed in vacuo from the

pale yellow mixture. The residue was extracted with 3 × 15 mL of THF. The extract was filtered, and excess 1,4-dioxane was added to the combined extracts. After 24 h $[MgBr_2(1,4\text{-dioxane})]_x$ was filtered off, THF was removed in vacuo, and the product was crystallized from CH_2Cl_2/pentane at −40 °C as pale yellow blocks; yield 352 mg (81%). The reaction was repeated with 50 mg of **2** under ^{13}CO to give the ^{13}C-labeled product in the same yield: ^1H NMR (CD_2Cl_2) δ 3.16 (t, 6, J = 5.7), 3.95 (t, 6, J = 5.4); ^{19}F NMR (CD_2Cl_2) δ −152.0 (m), −163.7 (t, J = 22), −165.6 (m); ^{13}C NMR (THF-d_8) δ 55.5 (CH_2), 62.6 (CH_2), 135−145 (C_{aryl}); ^{13}C NMR (CD_2Cl_2) δ 199.5 (^{13}CO); IR (DME) cm^{-1} 1875 cm^{-1} (C═O), 1830 (^{13}C═O). Anal. Calcd for $C_{25}H_{12}N_4F_{15}ORe$: C, 35.10; H, 1.41; N, 6.55. Found: C, 35.25; H, 1.29; N, 6.50.

$[N_3N_F]Re(PH_3)$ (4a). One side of a two-chamber vessel was charged with a solution of **2** (485 mg, 0.491 mmol) in 50 mL of THF. The other side was charged with Mg powder (358 mg, 14.74 mmol) and a stir bar. The solution was degassed by three freeze−pump−thaw cycles, and PH_3 (∼10 equiv) was condensed into the vessel. The mixture was warmed to room temperature, combined with the Mg, and stirred vigorously at room temperature for 6 h. Solvents were then removed from the red mixture in vacuo. Excess PH_3 was decomposed by venting the trap to a saturated aqueous solution of $CuSO_4$. The red residue was extracted three times with 15 mL of THF. The extract was filtered and excess 1,4-dioxane was added to the combined extracts. After 16 h $[MgBr_2(1,4\text{-dioxane})]_x$ was filtered off, THF was removed in vacuo, and the product was crystallized from CH_2Cl_2/pentane at −40 °C. Light red crystals were collected in two crops; yield 171 mg (40%): ^1H NMR (CD_2Cl_2) δ 5.38 (d, 3, J_{PH} = 305) 3.79 (t, 6, NCH_2CH_2), 3.00 (t, 6, NCH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−132 (m, NC_6F_5), 65.49, 57.09; ^{19}F NMR (CD_2Cl_2) δ −152.50 (m), −165.34 (t, J_{FF} = 21), −166.16 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −138.18 (s). Anal. Calcd for $C_{24}H_{15}N_4F_{15}PRe$: C, 33.46; H, 1.75; N, 6.50. Found: C, 33.11; H, 1.55; N, 6.38.

$[N_3N_F]Re(PMe_3)$ (4b). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PMe_3 (123 mg, 1.620 mmol) in 50 mL of THF, and Mg powder (295 mg, 12.15 mmol); yield 274 mg, 75%: ^1H NMR (CD_2Cl_2) δ 3.63 (t, 6, NCH_2CH_2), 2.82 (t, 6, NCH_2CH_2), 0.14 (d, 9, J_{PH} = 5.4, PCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−132 (m, NC_6F_5), 67.21, 56.60, 23.27 (d, J_{PC} = 27, PCH_3); ^{19}F NMR (CD_2Cl_2) δ −150.74 (m), −164.85 (t, J_{FF} = 21), −165.90 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −45.16 (s). Anal. Calcd for $C_{27}H_{21}N_4F_{15}PRe$: C, 35.89; H, 2.34; N, 6.20. Found: C, 35.83; H, 2.37; N, 6.20.

$[N_3N_F]Re(PEt_3)$ (4c). The procedure was analogous to that used to prepare **4a** employing **2** (500 mg, 0.506 mmol), PEt_3 (90 mg, 0.760 mmol) in 40 mL of THF, and Mg powder (369 mg, 15.18 mmol); yield 313 mg (65%) of dark red crystals: ^1H NMR (CD_2Cl_2) δ 3.60 (t, 6, NCH_2CH_2), 2.77 (t, 6, NCH_2CH_2), 0.43 (m, 15, PEt_3); $^{13}C\{^1H\}$ NMR (THF/C_6D_6) δ 148−132 (m, NC_6F_5), 68.58, 56.29, 24.70 (d, CH_2, J_{CP} = 24.8), 8.51; ^{19}F NMR (CD_2Cl_2) δ −149.00 (b), −164.53 (t, J_{FF} = 21), −166.18 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −24.92 (s). Anal. Calcd for $C_{30}H_{27}N_4F_{15}PRe$: C, 38.10; H, 2.88; N, 5.92. Found: C, 38.35; H, 2.56; N, 5.94.

$[N_3N_F]Re[P(i\text{-}Pr)_3]$ (4d). The procedure was analogous to that used to prepare **4a** employing **2** (600 mg, 0.608 mmol), $P(i\text{-}Pr)_3$ (146 mg, 0.912 mmol) in 50 mL of THF, and Mg powder (443 mg, 18.23 mmol); yield 408 mg (68%) of dark green crystals: ^1H NMR (CD_2Cl_2) δ 3.53 (t, 6, NCH_2CH_2), 2.67 (t, 6, NCH_2CH_2), 0.81 (dd, 18, J_{HH} = 7, J_{PH} = 12, $PCHCH_3$), 0.48 (m, 3, $PCHCH_3$); $^{13}C\{^1H\}$ NMR (THF/C_6D_6) δ 145−135 (m, NC_6F_5), 71.41, 55.55, 33.19 (d, CHP, J_{PC} = 18.4), 19.69; ^{19}F NMR (CD_2Cl_2) δ −146.52 (m), −163.69 (t, J_{FF} = 21), −165.97 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −11.56 (s). Anal. Calcd for $C_{33}H_{33}N_4F_{15}PRe$: C, 40.13; H, 3.37; N, 5.67. Found: C, 40.21; H, 3.33; N, 5.55.

$[N_3N_F]Re(PMe_2Ph)$ (4e). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PMe_2Ph (168 mg, 1.215 mmol) in 50 mL of THF, and Mg powder (295 mg, 12.15 mmol); yield 165 mg (42%) of a red-orange microcrystalline solid: ^1H NMR (CD_2Cl_2) δ 7.08−6.77 (m, 5, Ph), 3.67 (t, 6, NCH_2CH_2), 2.87 (t, 6, NCH_2CH_2), 0.54 (d, 9, J_{PH} = 6.4, PCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−135 (m, NC_6F_5), 129.71 (d, Ph, J_{PC} = 10.9), 128.49 (s, Ph), 127.53 (d, Ph, J_{PC} = 8.4), 67.40, 56.14, 23.28 (d, CH_3, J_{PC} = 27.8); ^{19}F NMR (CD_2Cl_2) δ −149.25 (m), −164.70 (t, J_{FF} = 21), −165.83 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −30.91 (s). Anal. Calcd for $C_{32}H_{23}N_4F_{15}PRe$: C, 39.80; H, 2.40; N, 5.80. Found: C, 39.36; H, 2.16; N, 5.64.

$[N_3N_F]Re(PMePh_2)$ (4f). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), $PMePh_2$ (263 mg, 1.215 mmol) in 50 mL of THF, and Mg powder (295 mg, 12.15 mmol); yield 349 mg (84%) of red crystals: ^1H NMR (CD_2Cl_2) δ 6.48−7.10 (m, 10, Ph), 3.66 (t, 6, NCH_2CH_2), 2.87 (t, 6, NCH_2CH_2), 1.02 (d, 3, J_{PH} = 6.0, PCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−132 (m, NC_6F_5), 130.87 (d, J_{PC} = 9.5), 128.46, 127.81 (d, J_{PC} = 7.8), 68.32, 56.18, 22.10 (d, J_{PC} = 28.3, PCH_3); ^{19}F NMR (CD_2Cl_2) δ −148.76 (bs), −164.62 (t, J_{FF} = 21), −165.48 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −15.19 (s). Anal. Calcd for $C_{37}H_{25}N_4F_{15}PRe$: C, 43.24; H, 2.45; N, 5.45. Found: C, 43.19, H, 2.45; N, 5.45.

$[N_3N_F]Re(PHPh_2)$ (4g). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), $PHPh_2$ (226 mg, 1.215 mmol) in 50 mL of THF, and Mg powder (295 mg, 12.15 mmol); yield 376 mg (91%) of orange cubes: ^1H NMR (CD_2Cl_2) δ 9.40 (d, 1, J_{PH} = 319, PH), 6.45−7.12 (m, 10, Ph), 3.73 (t, 6, NCH_2CH_2), 2.96 (t, 6, NCH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 142−135 (m, NC_6F_5), 136.67, 131.92, 128.81, 128.33, 67.39, 56.63; ^{19}F NMR (CD_2Cl_2) δ −150.38 (m), −165.00 (t, J_{FF} = 21), −165.53 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 1.24 (s). Anal. Calcd for $C_{36}H_{23}N_4F_{15}PRe$: C, 42.65; H, 2.29; N, 5.53. Found: C, 42.71; H, 2.48; N, 5.36.

$[N_3N_F]Re(pyridine)$ (5). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol) and pyridine (160 mg, 2.03 mmol) in 50 mL of THF, and a solution of MeLi (1.4 M in Et_2O, 0.61 mL, 0.851 mmol) in 20 mL of diethyl ether. The residue was extracted three times with 15 mL of CH_2Cl_2 instead of THF; yield 179 mg (48%): ^1H NMR (CD_2Cl_2) δ 6.54 (d, 2, Ph), 6.15 (m, 2, Ph), 5.92 (m, 1, Ph), 3.64 (t, 6, NCH_2CH_2), 2.73 (t, 6, NCH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 158.03, 142−135 (m, NC_6F_5), 130.59, 122.39, 70.09, 61.27; ^{19}F NMR (CD_2Cl_2) δ −150.57 (m), −165.47 (t, J_{FF} = 21), −166.59 (m). Anal. Calcd for $C_{29}H_{17}N_5F_{15}Re$: C, 38.42; H, 1.89; N, 7.72. Found: C, 38.28; H, 2.02; N, 7.84.

$[N_3N_F]Re(THT)$ (6). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol) and THT (179 mg, 2.03 mmol) in 50 mL of THF and Mg powder (295 mg, 12.15 mmol); yield 252 mg (68%): ^1H NMR (CD_2Cl_2) δ 3.62 (t, 6, NCH_2CH_2), 2.80 (t, 6, NCH_2CH_2), 1.23 (br s, 8, THT); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−132 (m, NC_6F_5), 68.14, 59.82, 45.69, 29.97; ^{19}F NMR (CD_2Cl_2) δ −150.68 (m), −165.10 (t, J_{FF} = 21), −165.91 (m). Anal. Calcd for $C_{28}H_{20}N_4F_{15}ReS$: C, 36.73; H, 2.20; N, 6.12. Found: C, 36.59; H, 2.29; N, 6.17.

$[N_3N_F]Re(NCMe)$ (7). The procedure was analogous to that used to prepare **4a** employing **2** (2.00 g, 2.03 mmol) and MeCN (249 mg, 6.08 mmol) in 40 mL of THF and Mg powder (1.48 g, 60.78 mmol); yield 1.08 g (61%) of olive-green prisms: ^1H NMR (CD_2Cl_2) δ 3.80 (t, 6, NCH_2CH_2), 3.51 (s, 3, $NCCH_3$), 2.84 (t, 6, NCH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148−132 (m, NC_6F_5), 130.18, 65.97, 60.20, 0.93; ^{19}F NMR (CD_2Cl_2) δ −152.62 (m), −167.75 (m); IR (Nujol) 2151.8 cm^{-1} (C≡N). Anal. Calcd for $C_{26}H_{15}N_5F_{15}Re$: C, 35.95; H, 1.74; N, 8.06. Found: C, 35.81; H, 1.67; N, 8.26.

$[N_3N_F]Re(H_2SiEt_2)$ (8a). The procedure was analogous to that used to prepare **4a** employing **2** (2.00 g, 2.03 mmol) and Et_2SiH_2 (536 mg, 6.08 mmol) in 50 mL of THF and Mg powder (1.48 g, 60.8 mmol). The product was crystallized from DME/pentane at −40 °C; yield 911 mg (49%) of orange-red microcrystals: ^1H NMR (THF-d_8) δ 5.83 (s, 1, SiH, J_{SiH} = 186), 3.80

(t, 6, NCH_2CH$_2$), 3.11 (t, 6, NCH$_2$CH_2), 0.32 (t, 9, SiMe$_3$), −0.01 (m, 2, SiCH$_2$), −5.85 (s, 1, Si−H, J_{SiH} = 44); ^{13}C{^{1}H} NMR (THF/C$_6$D$_6$) δ 148−132 (m, NC$_6$F$_5$), 66.53, 55.93, 10.16 (s, SiCH$_2$CH_3), 7.38 (s, SiCH_2CH$_3$); ^{19}F NMR (CD$_2$Cl$_2$) δ −149.58 (b), −164.97 (t, J_{FF} = 21), −166.85 (m). Anal. Calcd for $C_{28}H_{24}N_4F_{15}ReSi$: C, 36.72; H, 2.64; N, 6.12. Found: C, 36.53; H, 2.47; N, 6.11.

[N$_3$N$_F$]Re(H$_3$SiPh) (8b). The procedure was analogous to that used to prepare **4a** employing **2** (500 mg, 0.506 mmol) and PhSiH$_3$ (110 mg, 1.013 mmol) in 30 mL of THF and Mg powder (369 mg, 15.18 mmol). Orange-red needles were obtained from DME/pentane at −40 °C; yield 431 mg (89%): ^{1}H NMR (CD$_3$CN) δ 7.07 (m, 1, Ph), 6.94 (m, 2, Ph), 6.60 (m, 2, Ph), 5.00 (s, 2, SiH, J_{SiH} = 183), 3.81 (t, 6, NCH_2CH$_2$), 3.15 (t, 6, NCH$_2$CH_2), −3.86 (s, 1, Si−H−Re, J_{SiH} = 38); ^{13}C{^{1}H} NMR (THF/C$_6$D$_6$) 145−138 (m, NC$_6$F$_5$), 134.61, 128.47, 127.53, 65.94, 55.94; ^{19}F NMR (CD$_3$CN) δ −150.37 (m), −163.92 (t, J_{FF} = 21), −166.36 (m). Anal. Calcd for $C_{30}H_{20}N_4F_{15}ReSi$: C, 38.51; H, 2.15 N, 5.99. Found: C, 38.57 H, 2.14; N, 6.06.

[D(OEt$_2$)$_2$]$^+$BAr$_4^-$. A 250 mL round-bottom Schlenk flask was charged with a stir bar and a solution of NaBAr$_4$ (5.00 g, 5.64 mmol) in 125 mL of diethyl ether. The flask was transferred to a high-vacuum line and cooled to −196 °C, and a slight excess of DCl was condensed into the flask. The mixture was stirred and warmed to room temperature. The mixture was allowed to stir for 5 min, and then the flask was pumped into the drybox. The reaction mixture was chilled to −40 °C, and the reaction solution was filtered through a bed of Celite. The pale yellow filtrate was concentrated, and the product was isolated as white crystals upon addition of pentane and cooling to −40 °C overnight; yield 4.10 g (72%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (b, 8, *o*-H), 7.58 (br, 4, *p*-H), 3.85 (q, 8, OCH_2-CH$_3$), 1.31 (t, 12, OCH$_2$CH_3); ^{2}H NMR (CH$_2$Cl$_2$) δ 12.84 (br).

{**[N$_3$N$_F$]Re(H)(PMe$_3$)**}$^+$**BAr$_4^-$ (4bH$^+$).** A solution of **4b** (200 mg, 0.221 mmol) in 15 mL of CH$_2$Cl$_2$ at −40 °C was stirred, and a solution of [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$[H(OEt$_2$)$_2$]$^+$ (224 mg, 0.221 mmol) in 2 mL of CH$_2$Cl$_2$ at −40 °C was added dropwise over a period of 1 min. The reaction mixture turned dark red-green immediately and gradually faded to green after being stirred overnight. The solution was concentrated, and the product was crystallized from CH$_2$Cl$_2$/pentane at −40 °C as emerald green blocks; yield 281 mg (76%): ^{1}H NMR (CD$_2$-Cl$_2$) δ 7.78 (s, 8, *o*-H), 7.59 (s, 4, *p*-H), 4.00 (t, 6, NCH_2CH$_2$), 3.43 (t, 6, NCH$_2$CH_2), 1.01 (d, 9, J_{PH} = 9, PMe), 0.26 (d, 1, J_{PH} = 7, Re−H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 162.44 (q, C$_{ipso}$, J_{BC} = 50), 146−136 (m, NC$_6$F$_5$), 135.48 (s, C$_o$), 129.27 (q, C$_m$, J_{CF} = 32), 125.25 (q, CF$_3$, J_{CF} = 272), 118.11 (s, C$_p$), 66.98, 55.23, 21.57 (d, PCH$_3$, J_{PC} = 41); ^{19}F NMR (CD$_2$Cl$_2$) δ −63.32 (m), −148.83 (m), −154.94 (t, J_{FF} = 21), −160.55 (m); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ −14.88. Anal. Calcd for $C_{59}H_{34}N_4BF_{39}PRe$: C, 40.08; H, 1.94; N, 3.17. Found: C, 40.21; H, 1.85; N, 3.11.

{**[N$_3$N$_F$]Re(H)(PEt$_3$)**}$^+$**BAr$_4^-$ (4cH$^+$).** This complex was prepared in a manner analogous to that employed to prepare **4bH**$^+$ from **4c** (195 mg, 0.206 mmol) in 10 mL of CH$_2$Cl$_2$ at −40 °C and [H(OEt$_2$)$_2$]BAr$_4$ (209 mg, 0.206 mmol) in 2 mL of CH$_2$Cl$_2$ at −40 °C; yield 323 mg of amber crystals (97%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.72 (s, 8, *o*-H), 7.57 (s, 4, *p*-H), 3.98 (t, 6, NCH_2CH$_2$), 3.71 (d, 1, Re−H−P, J_{PH} = 64), 3.40 (t, 6, NCH$_2$CH_2), 1.19 (m, 6, J_{PH} = 9, PCH_2CH$_3$), 0.66 (m, 9, PCH$_2$CH_3); ^{13}C{^{1}H} NMR (THF/C$_6$D$_6$) δ 162.83 (q, C$_{ipso}$, J_{BC} = 50), 146−136 (m, NC$_6$F$_5$), 135.60 (s, C$_o$), 130.00 (q, C$_m$, J_{CF} = 32), 125.50 (q, CF$_3$, J_{CF} = 272), 118.15 (s, C$_p$), 67.45, 54.76, 21.61 (d, PCH$_2$CH$_3$, J_{PC} = 35), 8.35 (d, PCH$_2$CH$_3$, J_{PC} = 6); ^{19}F NMR (CD$_2$Cl$_2$) δ −63.30 (m), −147.55 (m), −154.84 (t, J_{FF} = 21), −160.77 (m); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 23.02. Anal. Calcd for $C_{62}H_{40}N_4BF_{39}PRe$: C, 41.14; H, 2.23; N, 3.10. Found: C, 40.81; H, 2.12; N, 3.05.

{**[N$_3$N$_F$]Re(H)(PMePh$_2$)**}$^+$**BAr$_4^-$ (4fH$^+$).** This complex was prepared in a manner analogous to that employed to prepare **4bH**$^+$ from **4f** (200 mg, 0.195 mmol) in 15 mL of CH$_2$-Cl$_2$ at −40 °C and [H(OEt$_2$)$_2$]BAr$_4$ (197 mg, 0.195 mmol) in 2 mL of CH$_2$Cl$_2$ at −40 °C; yield 243 mg (66%) of red-brown blocks: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (bs, 8, *o*-H), 7.56 (s, 4, *p*-H), 6.73−7.40 (m, 10, Ph), 4.72 (d, 1, J_{PH} = 62, Re−H), 4.04 (t, 6, NCH_2CH$_2$), 3.48 (t, 6, NCH$_2$CH_2), 2.01 (d, 3, J_{PH} = 9.6, PCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 148−132 (m, NC$_6$F$_5$), 162.50 (q, C$_{ipso}$, J_{BC} = 50), 145−136 (m, NC$_6$F$_5$), 136.01 (s, C$_o$), 133.40 (d, C$_{ipso}$, J_{PC} = 2), 131.27 (s, C$_o$), 130.40 (m, C$_m$), 129.62 (q, C$_m$, J_{CF} = 29), 125.22 (q, CF$_3$, J_{CF} = 272), 118.22 (s, C$_p$), 118.08 (s, C$_p$), 67.45, 53.51, 23.69 (d, PCH$_3$, J_{PC} = 48); ^{19}F NMR (CD$_2$Cl$_2$) δ −63.24 (m), −146.03 (bs), −155.71 (t, J_{FF} = 21), −161.26 (m); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 23.74. Anal. Calcd for $C_{69}H_{38}N_4BF_{39}$-PRe: C, 43.80; H, 2.02; N, 2.96. Found: C, 43.88; H, 1.70; N, 2.82.

{**[N$_3$N$_F$]Re(H)(PHPh$_2$)**}$^+$**BAr$_4^-$ (4gH$^+$).** This complex was prepared in a manner analogous to that employed to prepare **4bH**$^+$ from **4g** (200 mg, 0.195 mmol) in 15 mL of CH$_2$Cl$_2$ at −40 °C and [H(OEt$_2$)$_2$]BAr$_4$ (197 mg, 0.195 mmol) in 2 mL of CH$_2$Cl$_2$ at −40 °C; yield 257 mg of coral-colored needles (69%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.73 (bs, 8, *o*-H), 7.56 (s, 4, *p*-H), 6.85−7.40 (m, 10, Ph), 6.97 (dd, 1, J_{HH} = 15, J_{PH} = 375, Re−H), 4.05 (t, 6, NCH_2CH$_2$), 3.57 (t, 6, NCH$_2$CH_2), 3.36 (dd, 1, J_{HH} = 15, J_{PH} = 54, Re−H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 162.42 (q, C$_{ipso}$, J_{BC} = 50), 145−136 (m, NC$_6$F$_5$), 135.44 (s, C$_o$), 133.00 (d, C$_{ipso}$, J_{PC} = 2), 131.22 (s, C$_o$), 130.40 (m, C$_m$), 129.49 (q, C$_m$, J_{CF} = 29), 125.24 (q, CF$_3$, J_{CF} = 272), 118.04 (s, C$_p$), 118.00 (s, C$_p$), 66.90, 55.51; ^{19}F NMR (CD$_2$Cl$_2$) δ −63.28 (m), −149.04 (s), −155.41 (t, J_{FF} = 21), −161.18 (m); ^{31}P{^{1}H} NMR (CD$_2$-Cl$_2$) δ 38.11. Anal. Calcd for $C_{68}H_{36}N_4BF_{39}PRe$: C, 43.49; H, 1.93; N, 2.98. Found: C, 43.70; H, 1.84; N, 2.60.

{**[N$_3$N$_F$]Re(D)(PHPh$_2$)**}$^+$**BAr$_4^-$ (4gD$^+$).** This complex was prepared in a manner identical to that used to prepare **4gH**$^+$ from **4g** (503 mg, 0.496 mmol) and [D(OEt$_2$)$_2$]BAr$_4$ (503 mg, 0.496 mmol); yield 691 mg (74%): ^{2}H NMR (CH$_2$Cl$_2$) δ 6.86 (d, Re−D−P, J_{DP} = 56), 3.24 (d, P−D, J_{DP} = 7); ^{31}P{^{1}H} NMR δ 38.11 (s), 38.10 (t, obscured by singlet at 38.11), 37.36 (t, J_{DP} = 56).

{**[N$_3$N$_F$]Re(H)(THT)**}$^+$**BAr$_4^-$ (6H$^+$).** This complex was prepared in a manner analogous to that employed to prepare **4bH**$^+$ from **6** (200 mg, 0.218 mmol) in 15 mL of CH$_2$Cl$_2$ at −40 °C and [H(OEt$_2$)$_2$]BAr$_4$ (221 mg, 0.218 mmol) in 2 mL of CH$_2$-Cl$_2$ at −40 °C; yield 193 mg of green prisms (51%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.75 (s, 8, H$_o$), 7.57 (s, 4, H$_p$), 3.81 (t, 6, NCH_2CH$_2$), 3.50 (s, 1, Re−H), 3.26 (t, 6, NCH$_2$CH_2), 2.92 (m, 2, THT), 2.48 (m, 2, THT), 2.08 (m, 2, THT), 1.38 (m, 2, THT); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 162.49 (q, C$_{ipso}$, J_{BC} = 50), 146−136 (m, NC$_6$F$_5$), 135.52 (s, C$_o$), 129.57 (q, C$_m$, J_{CF} = 32), 125.32 (q, CF$_3$, J_{CF} = 272), 118.15 (s, C$_p$), 65.19 (THT), 61.80, 56.15, 29.28 (THT); ^{19}F NMR (CD$_2$Cl$_2$) δ −63.27 (m), −148.78 (m), −155.30 (t, J_{FF} = 21), −159.92 (m); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ −14.88. Anal. Calcd for $C_{60}H_{33}N_4BF_{39}ReS$: C, 40.49; H, 1.87; N, 3.15. Found: C, 40.49; H, 1.57; N, 3.21.

{**[N$_3$N$_F$]Re[NC(H)Me]**}$^+$**BAr$_4^-$ (7H$^+$).** This complex was prepared in a manner analogous to that employed to prepare **4bH**$^+$ from **7** (200 mg, 0.230 mmol) in 15 mL of CH$_2$Cl$_2$ at −40 °C and [H(OEt$_2$)$_2$]BAr$_4$ (233 mg, 0.230 mmol) in 2 mL of CH$_2$-Cl$_2$ at −40 °C. The solution was allowed to stir for 2 h; yield 299 mg of green-black crystals (75%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.77 (s, 8, *o*-H), 7.58 (s, 4, *p*-H), 4.18 (t, 6, NCH_2CH$_2$), 3.77 (t, 6, NCH$_2$CH_2), 3.57 (d, 3, J_{HH} = 6.6, NCCH_3(H)), 1.54 (q, 1, J_{HH} = 6, NCCH$_3$(*H*)); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 162.62 (q, C$_{ipso}$, J_{BC} = 50), 146−136 (m, NC$_6$F$_5$), 135.66 (s, C$_o$), 129.73 (q, C$_m$, J_{CF} = 32), 125.25 (q, CF$_3$, J_{CF} = 272), 118.25 (s, N*C*CH$_3$(H), $^1J_{CH}$ = 163), 66.34, 57.78, −0.61 (s, NC*C*H$_3$(H)); ^{19}F NMR (CD$_2$Cl$_2$) δ −63.22 (m), −149.14 (m), −154.67 (t, J_{FF} = 21), −160.98 (m). Anal. Calcd for $C_{58}H_{27}N_5BF_{39}Re$: C, 40.23; H, 1.57; N, 4.04. Found: C, 40.51; H, 1.54; N, 4.11.

Ligand Substitution Experiments. In a typical experiment, 20 mg of a given complex was dissolved in CH$_2$Cl$_2$ (0.7 mL) at 22 °C with ∼3 equiv of donor ligand in an NMR tube, and the mixture was allowed to stand at ca. 22 °C for 1−3 days. Reactions were followed by ^{19}F NMR. For reactions at

high temperature the NMR tube was flame-sealed and kept at 85−120 °C for hours to days. Reactions were monitored by ^{19}F NMR.

Reaction of 4bH$^+$ with CO. A 120 mL pressure vessel was charged with a green solution of **4bH**$^+$ (500 mg, 0.299 mmol) in 25 mL of CH_2Cl_2. The solution was frozen to 77 K, the headspace evacuated, and ∼1 equiv CO was introduced to the vessel, which was then sealed. Upon warming the vessel to room temperature, the green slurry rapidly turned to a golden-brown solution. After 2 days the golden-brown solution was concentrated in vacuo. Upon addition of pentane to the mixture and cooling it to −40 °C, a green solid precipitated, which contained $(HPMe_3)BAr_4$ as the only identifiable species: ^1H NMR (CD_2Cl_2) δ 7.91, 7.66, 6.22 (m, $HP(CH_3)_3$), 1.95 (dd, $HP(CH_3)_3$); ^{19}F NMR (CD_2Cl_2) δ −62.86 (s).

Reactions of 4bH$^+$, 4fH$^+$, and 6H$^+$ with CO on an NMR Scale. In a typical experiment, an NMR tube containing ∼20 mg of the complex dissolved in 0.7 mL of CD_2Cl_2 was charged with ∼1 equiv CO and then flame-sealed. Reactions were followed by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR. After 1 day, reaction mixtures contained only **3e** and the $(HL)BAr_4$ salt.

Solid-State Magnetic Susceptibility Measurements. SQUID experiments were performed at 5 KG on a Quantum Design 5.5 T instrument running MSRP2 software. Samples were prepared in an N_2-filled drybox. A gelatin capsule and a 2.2 by 1.9 cm piece of Parafilm were weighed. The capsule was then loaded with the sample, and the Parafilm was folded and packed on top using plastic tongs. The capsule was closed and weighed again to determine the sample mass. It was then suspended in a straw. The straw was placed in a plastic bottle with a screw cap, and the bottle was tightly sealed. At the instrument the straw was quickly attached to the sample rod and transferred to the helium atmosphere. Measurements were taken in 1 deg intervals from 5 to 10 K, 2 deg intervals from 12 to 20 K, 3 deg intervals from 23 to 50 K, 5 deg intervals from 55 to 100 K, 10 deg intervals from 110 to 200 K, and 20 deg intervals from 220 to 300 K. A background measurement of an empty gel capsule, Parafilm square, and straw was taken over the entire temperature range and subtracted from the experimental values at each temperature. The susceptibility at each temperature also was corrected for the diamagnetic contribution by the ligands using Pascal's constants.

X-ray Structural Determination of 2, 3b, and 4gH$^+$. A Siemens SMART/CCD area detection system based upon a three-circle platform goniometer was used for all data collection. Unit cell parameters were obtained from 45 0.3° omega scans. Final cell parameters were determined by least-squares refinement of the largest ($>10\sigma(I)$) reflections measured with the SAINT package. Crystal data are given in Table 1. No absorption corrections were applied.

The initial solution of **2** was carried out by direct methods, and the positions of the remaining non-hydrogen atoms were ascertained from difference Fourier calculations. During the course of solution and refinement a number of issues arose. First, a considerable amount of electron density was located away from the ReN_4 core. The electron density (largest electron density of 4.6 e/Å^3) was most easily attributed to lattice methylene chloride. However, the position was only partially occupied by solvent, and the solvent was found to take up two positions in the asymmetric unit. In addition the solvent was disordered. The structure based upon the best modeling of the solvent gave a residual (R1) of 0.085. Upon removing the solvent contribution using SQUEEZE,[81] the residual was reduced to the reported value (R1 = 0.041). Distances and angles and their associated esd's were essentially unchanged within the main halide derivative.

The second problem that arose was the identity of the moiety in the trigonal coordination pocket. Elemental analyses were most consistent with the presence of ∼1 Br and ∼1 Cl per Re in the bulk sample. Refinement of that atom as a 100% bromide resulted in an equivalent isotropic thermal parameter, U, of 0.20 Å^2. Refinement as a 100% chloride gave a U of 0.009 Å^2. Hence, the site cannot be occupied by either bromide or chloride alone. A mixture of the two (60% bromide, 40% chloride) proved satisfactory. In the final refinement identical coordinate and anisotropic thermal parameters were imposed on each of the atoms. If this crystal were representative of the bulk sample and contained 0.5 equiv of dichloromethane, the elemental analyses should be different from the average observed in six analyses of bulk material. Therefore we surmise that the bulk sample is not homogeneous and that the particular crystal chosen for this X-ray study was not representative of the average elemental composition.

The crystal of **2** in this X-ray study also suffers from disorder in the ligand backbone; the carbon atoms attached to N(4) are found in the two positions that give a "clockwise" or "counterclockwise" twist to the NC_3 unit. This disorder was effectively modeled, and the disordered atoms appear in pairs as C(2) and C(2)′, C(4) and C(4)′, and C(6) and C(6)′ in the Supporting Information. (Only C(2), C(4), and C(6) are shown in Figure 2.) Owing to the disorder these carbon atoms were refined isotropically and the hydrogen atoms attached to them were not included in the final refinement, while all other non-hydrogen atoms were refined as anisotropic scatterers.

The solution of **3b** was carried out in a manner analogous to that described for **2**. All atoms were refined as anisotropic scatterers, and hydrogen atoms were placed in calculated positions. Large residual electron density resides within 1.0 Å of the Re atom.

The solution of **4gH**$^+$ was carried out in a manner analogous to that described for **2**. Two problems arose during refinement: a high degree of disorder in certain CF_3 groups in the anion, and the treatement of hydrogen atoms in the PPh_2H_2 ligand. The former problem was solved fortuitously by the fact that one CF_3 group was well-behaved. All disordered CF_3 groups were refined isotropically on the basis of the CF_3 group that was well-behaved (C(65), F(651), F(652), and F(653)). The latter problem was more significant. In the difference Fourier maps two peaks of approximately 1.1 e/Å^3 were located within 1.5 Å of the phosphorus atom. Free refinement of these as hydrogen atoms resulted in the encroachment of one, H(2), upon the rhenium atom. The final model is one based upon both hydrogen atoms fixed at ∼1.4 Å from the phosphorus atom.

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Supporting Information Available: Labeled ORTEP drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[N_3N_F]ReX$, $[N_3N_F]Re(C_2H_4)$, and $\{[N_3N_F]Re(H)(PHPh_2)\}BAr_4$ (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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