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Preparation of Rhenium(I) and Rhenium(II) Amine Dinitrogen Complexes and the Characterization of an Elongated Dihydrogen Species

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A series of rhenium(I) dinitrogen complexes were prepared containing predominantly amine ligands. On the basis of infrared and electrochemical data, a system was selected that was anticipated to be a suitable precursor for an elongated dihydrogen complex. Upon oxidation by AgOTf, the dinitrogen ligand of *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(N$_2$)]$^+$ (**3**) is replaced with triflate to generate **13**, *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(OTf)]OTf, a convenient precursor to rhenium(II) and rhenium(I) amine complexes. Reduction of the rhenium(II) triflate **13** under 1 atm of hydrogen gas generates the complex *fac*-[Re(dien)(PPh$_3$)(PF$_3$)(dien)(H$_2$)]$^+$ (*fac*-**14**). T_1 measurements indicate a dihydrogen species with a H−H distance of 1.38 ± 0.03 Å. The HD analog displays a J_{HD} of 6.7 Hz, corresponding to a H−H distance of 1.31 ± 0.03 Å, a value in good agreement with that determined from T_1 data and among the largest ever measured for an elongated dihydrogen system.

Introduction

While the vast majority of reported rhenium(I) compounds fall in the realm of organometallic chemistry,[1] a notable exception is a class of rhenium(I) dinitrogen complexes initially discovered by Chatt, Dilworth, and Leigh.[2] The synthetic approach to these materials from a general Re$^{\mathrm{V}}$ precursor offers an unusually high flexibility in the preparation of an inorganic ligand set for rhenium (*vide infra*), yet this versatile methodology has not been widely utilized. Our intention was to prepare for rhenium a series of low-valent dinitrogen complexes with amine-based ligand sets, a class of materials well represented for group VIII transition metals, but practically unknown for group VII. Parallel to the synthetic approach used for osmium ammines,[3] we hoped to replace the dinitrogen ligand with triflate upon oxidation to Re$^{\mathrm{II}}$, thus providing suitable precursors to a novel class of Re$^{\mathrm{II}}$ and Re$^{\mathrm{I}}$ coordination complexes.

One interesting application of this methodology would be toward the study of dihydrogen complexes.[4] The few dihydrogen complexes with nitrogen donor sets that have been prepared are currently limited to neutral ruthenium and osmium complexes containing porphyrin ligands,[5] cationic osmium complexes containing ammine or ethylenediamine ligands,[6] and neutral pyrazolylborate complexes of rhodium[7a] and ruthenium.[7b] We report herein the characterization in solution of the new triamine complexes *fac*-[Re(H··X)(dien)(PF$_3$)(PPh$_3$)]$^+$, X = H, D, where the H··H notation refers to an elongated dihydrogen ligand.[8]

Results and Discussion

Preparation and Properties of the Dinitrogen Complexes. The preparation of a number of organodiazenido complexes of the form ReCl$_2$(PPh$_3$)$_2$(NNC(O)Ph)L has been described by Chatt et al.,[2] and these compounds, as well as their Re$^{\mathrm{V}}$ precursor (**1**; Figure 1), are versatile synthons to rhenium(I) dinitrogen complexes containing phosphine ligands. We have found that this general methodology may be readily applied to amine-based complexes as the following examples illustrate.

Treatment of the chelate **1** with PF$_3$ results in the formation of ReCl$_2$(PPh$_3$)$_2$(NNC(O)Ph)(PF$_3$) (**2**) as originally described by Chatt et al.[2] When **2** is combined with the tridentate ligand dien, along with NaOTf to facilitate removal of the halide, the cationic dinitrogen complex *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(N$_2$)](OTf) (**3**) is recovered in 46% yield as a single stereoisomer. Significant features of **3** include a dinitrogen stretching frequency of 2033 cm^{-1} and a reversible Re$^{\mathrm{II}}$/Re$^{\mathrm{I}}$ reduction potential of 0.86 V (NHE). Crystals of **3**·2(acetone) were grown from an acetone solution, and the structure of the triflate salt was determined by X-ray diffraction (Table 1). An ORTEP representation of the cation (Figure 2) indicates a facial dien geometry with the central nitrogen *trans* to the triphenylphosphine. The Re−N$_2$ distance (1.927(9) Å) is predictably shorter than the corresponding bonds of the dien ligand, and the N−N

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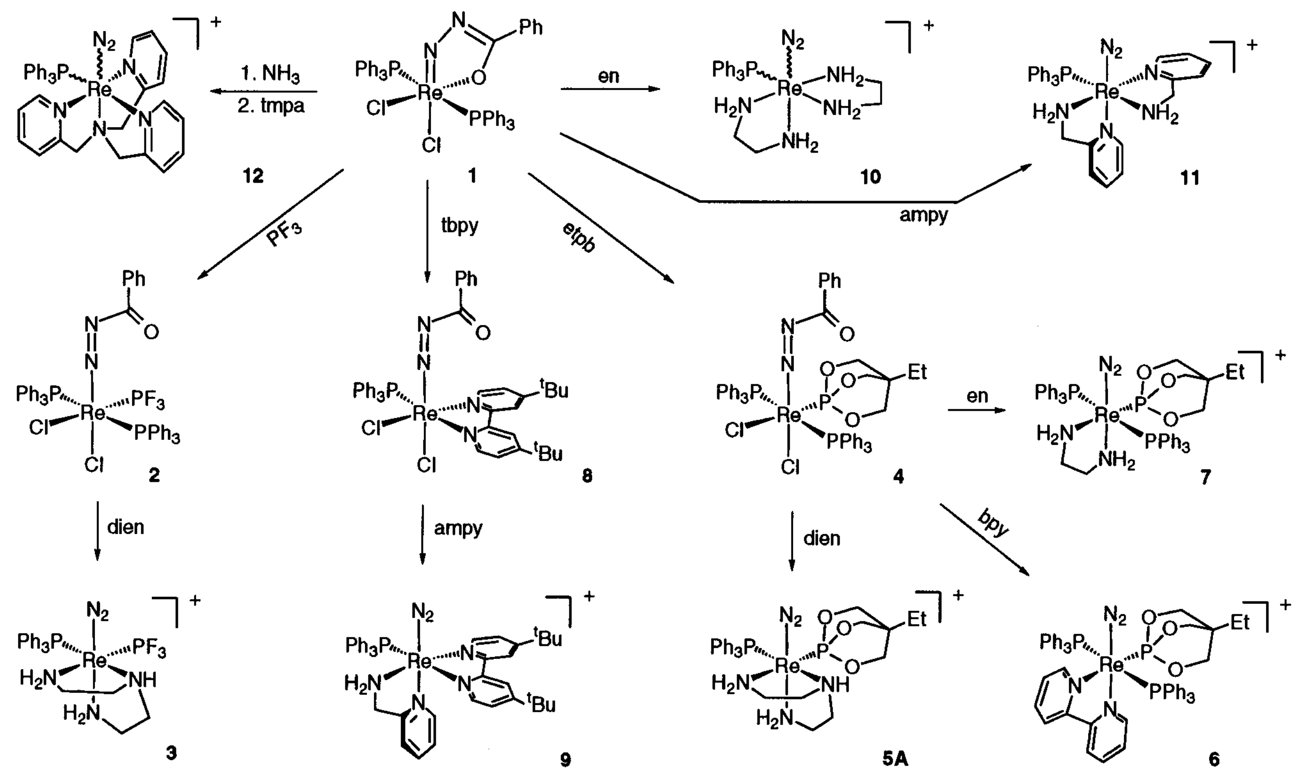

Figure 1. Preparation of assorted rhenium(I) dinitrogen amine complexes.

Table 1. Crystallographic Data for Compounds **3** and **15**

	3·2(acetone)	**15**
empirical formula	$C_{29}H_{40}N_5O_5F_6P_2SRe$	$C_{27}H_{34}N_3O_7F_9P_2S_2Re$
formula wt	932.87	995.83
a (Å)	11.363(4)	10.123(2)
b (Å)	9.760(3)	10.8123(11)
c (Å)	33.428(6)	17.577(3)
α (deg)		107.068(12)
β (deg)	90.16(2)	101.26(2)
γ (deg)		94.479(10)
vol (Å^3)	3707(3)	1784.9(5)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.67	1.85
λ (Å)	0.710 69	0.710 73
T (°C)	−120(2)	−100(2)
μ (cm^{-1})	35.31	37.05
$R(F)^a$	0.039 ($I > 3\sigma(I)$)	0.051 ($I > 2\sigma(I)$)
$R_w(F)^a$	0.052 ($I > 3\sigma(I)$)	0.106 ($I > 2\sigma(I)$)

$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

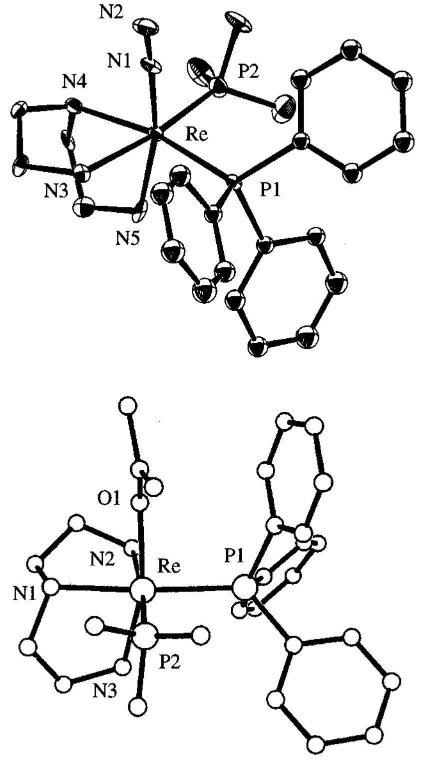

Figure 2. ORTEP drawings of the cations of [Re(N_2)(PPh_3)(PF_3)(dien)](OTf) (**3**; top) and [Re(η^1-acetone)(PPh_3)(PF_3)(dien)]($OTf)_2$ (**15**; bottom). Selected bond lengths (Å) for **3** Re−N1, 1.927(9); Re−P1, 2.346(3); Re−P2, 2.175(3); Re−N3, 2.241(7); Re−N4, 2.185(8); Re−N5, 2.195(8); N1−N2; 1.13(1). Selected bond lengths for **15**: Re−P1, 2.433(2); Re−P2, 2.178(2); Re−N1, 2.181(6); Re−N2, 2.211(6); Re−N3, 2.162(6); Re−O1, 2.098(5).

distance has increased to 1.13(1) Å. Both of these observations are a direct result of the rhenium−dinitrogen π-back-bonding interaction.

In a similar manner, a phosphite analog (**4**) of the organodiazenido complex **2** may be prepared from 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (etpb). This material reacts with dien to give the dinitrogen complex **5**, which is isolated in a ~5:4 ratio of two isomers. Chromatographic separation on alumina provides pure samples of both isomers, and the major component (**5A**) has been determined by X-ray diffraction to have a stereochemical arrangement identical to that of **3** where the dien ligand adopts a facial orientation with the central nitrogen *trans* to the triphenylphosphine (Figure 2). The stereochemistry of the second isomer (**5B**) has not been determined.

When the diazenido phosphite complex, **4**, is combined with 2,2′-bipyridine (bpy) or with ethylenediamine (en), dinitrogen complexes are isolated (**6** and **7**) with both arylphosphines intact. Compared to its dien analog (**5**), both the bpy (**6**) and en (**7**) complexes show a higher energy dinitrogen band and a more positive reduction potential, features that are consistent with a more electron-deficient metal center. A preliminary X-ray diffraction study for **6** confirms the stereochemistry shown in Figure 1. A product similar to **7** results when 1,2-diaminocyclohexane is used instead of ethylenediamine, and according to

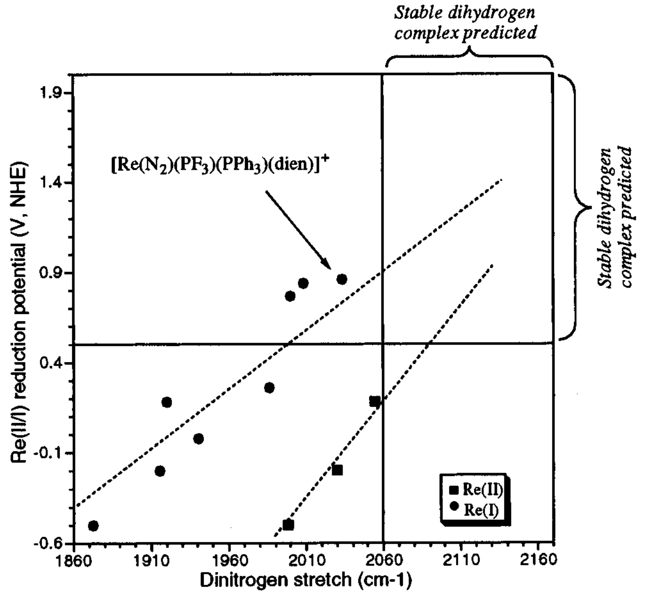

Figure 3. Correlation of dinitrogen stretching frequency (cm^{-1}) with Re^{II}/Re^I reduction potential for Re^I (circle) and Re^{II} (square) dinitrogen amine complexes.

preliminary X-ray diffraction data, this compound has stereochemistry identical to that of compound **6**. Thus, the stereochemistry of **7** is tentatively assigned to be that shown in Figure 1.

The ammonia diazenido complex $Re(NH_3)(NNC(O)Ph)(PPh_3)_2Cl_2$ originally reported by Dilworth[9] may be prepared directly from compound **1** and ammonia and may be used as a synthon to other amine complexes. As an example, when this product is treated with the tetradentate ligand tris(2-pyridylmethyl)amine (tmpa) along with NaOTf in methanol, the dinitrogen complex **12** is formed (Figure 1). Alternatively, a bipyridyl ligand can be coordinated to rhenium at the diazenido stage. As we have previously reported,[10] treatment of **1** with 4,4′-di-*tert*-butyl-2,2′-bipyridine results in the diazenido compound **8**, and this material may be combined with 2-(aminomethyl)pyridine (ampy) to give the tetraamine dinitrogen complex **9**. A similar reaction may be carried out with ethylenediamine to form the complex $[Re(N_2)(PPh_3)(tbpy)(en)]Cl$.

Finally, amine-rich dinitrogen complexes may be prepared directly from compound **1**. When a solution of **1**, ethylenediamine, sodium triflate, benzene, and methanol is refluxed for 3 h, spectral data for the isolated product are consistent with the formation of *cis*-$[Re(N_2)(PPh_3)(en)_2]OTf$ (**10**). Although attempts to obtain an analytically pure material were unsuccessful, ^1H and ^{13}C NMR data reveal a single diamagnetic compound with two asymmetric en groups and one PPh_3 ligand. In addition, infrared data indicate an extremely low-energy N−N stretch at 1872 cm^{-1} and cyclic voltammetric data show a reversible Re^{II}/Re^I reduction potential at −0.50 V. These observations are consistent with an extraordinarily electron-rich dinitrogen complex (Figure 3). Similarly, the reaction of **1** with ampy forms the bis(ampy) (**11**) analog, and X-ray diffraction data for this compound indicate a *cis*-stereochemistry for the cation as shown in Figure 1.

In Figure 3, infrared and electrochemical data are summarized for the series of Re^I amine dinitrogen complexes described above. Dinitrogen stretching frequencies for the complexes span a range of 1872−2033 cm^{-1} while the corresponding d^5/d^6 reduction potentials range from −0.50 to 0.86 V, indicating the electron-rich nature of the metal center. For several of the most reducing metal systems (**10**−**12**), oxidation by Ag^+ or $[FeCp_2]^+$ generates a stable Re^{II} dinitrogen complex (characterized by IR and cyclic voltammetry), and the infrared data for these complexes are reported in Table 2. For other cases, however, the one-electron oxidation of the Re^I dinitrogen complex causes the displacement of dinitrogen by solvent or counterion, thus creating a useful synthon. For example, in a recent communication,[10] the compound *cis*-$[Re(PPh_3)(ampy)(tbpy)(OTf)](OTf)$ was shown to be a useful precursor to a number of Re^I complexes including an η^2-benzaldehyde system.

Table 2. Infrared and Electrochemical Data for Rhenium Dinitrogen Amine Complexes

compound	ν(NN) (KBr, cm^{-1})	$E_{1/2}$ (Re^I/Re^{II}; V, NHE)
Rhenium(I)		
$[Re(N_2)(PPh_3)(en)_2]OTf$ (**10**)	1872	−0.50
$[Re(N_2)(PPh_3)(ampy)_2]OTf$ (**11**)	1915	−0.20
$[Re(N_2)(PPh_3)(tmpa)]OTf$ (**12**)	1920	0.18
$[Re(N_2)(PPh_3)(tbpy)(ampy)]Cl$ (**9**)	1940	−0.02
$[Re(N_2)(PPh_3)(etpb)(dien)]OTf$ (**5B**)	1969	0.27
$[Re(N_2)(PPh_3)(etpb)(dien)]OTf$ (**5A**)	1986	0.26
$[Re(N_2)(PPh_3)_2(en)(etpb)]OTf$ (**7**)	2004	0.78
$[Re(N_2)(PPh_3)_2(bpy)(etpb)]OTf$ (**6**)	2008	0.84
$[Re(N_2)(PPh_3)(PF_3)(dien)]OTf$ (**3**)	2033	0.86
Rhenium(II)		
$[Re(N_2)(PPh_3)(tmpa)](OTf)_2$	2054	0.18
$[Re(N_2)(PPh_3)(ampy)_2](OTf)_2$	2030	−0.20
$[Re(N_2)(PPh_3)(en)_2](OTf)_2$	1998	−0.50

Preparation and Properties of a Stretched Dihydrogen Complex. In the present study, our hope was to find a compound suitable for use in the preparation of a dihydrogen complex. As shown in Figure 3, the electrochemical potentials and dinitrogen stretching frequencies for complex **3**, $[Re(N_2)(PPh_3)(PF_3)(dien)]OTf$, are the closest to the prescribed "stability" range for a dihydrogen complex.[11] Thus, treatment of **3** with AgOTf in acetone followed by recrystallization from DME results in the formation of *fac*-$[Re(PPh_3)(PF_3)(dien)(OTf)](OTf)\cdot DME$ (**13**), a Re^{II} complex containing either a triflate or solvento ligand that is readily exchanged (Figure 4). Compound **13** is found to be a versatile synthon to a number of Re^I complexes with unsaturated organic ligands.[12] Moreover, when **13** is reduced (Mg^0) under an atmosphere of dihydrogen, the product (**14**) is found to be a 20:3 mixture of two rhenium(I)−hydride species fitting the stoichiometry $Re(PPh_3)PF_3(dien)(H_2)(OTf)$.

A sample of **14** in acetone-d_6 gives two signals in the hydride region (Figure 5a): a pseudotriplet at −5.97 ppm corresponding to the major isomer and a doublet of doublets of quartets at −4.04 ppm for the minor species. The equal H−P couplings in the pseudotriplet imply that both phosphorus ligands are *cis* to the hydrogen and, thus, that the dien ligand is required to have a *fac* configuration. Therefore, the pseudotriplet is assigned to *fac*-**14** with a stereochemistry similar to that of compounds **3** and **15** (Figure 4). The J_{PP} coupling of 25 Hz in the ^{31}P resonances of the major species is also indicative of mutually *cis* phosphorus ligands. The existence of a single hydride signal for the *fac* species implies that both hydrogen atoms occupy one site in the coordination polyhedron, that they are rapidly exchanging, or that they are coupled by quantum exchange.[13,14] With regard to the second isomer (*mer*-**14**), the multiplicity (ddq) of the −4.04 ppm peak indicates that this

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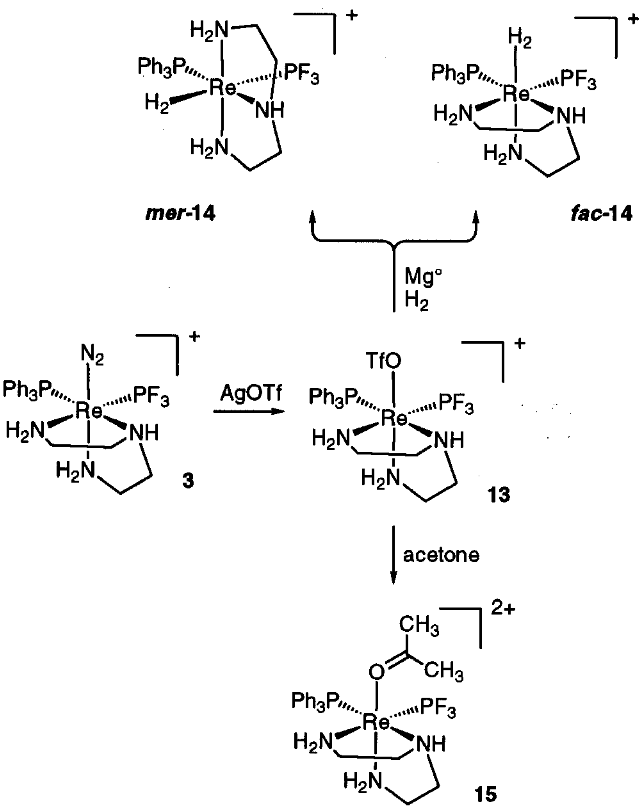

Figure 4. Reaction scheme for the preparation of dihydrogen complexes *mer*-**14** and *fac*-**14**.

signal arises from the hydride *trans* to PF$_3$. Thus, the second isomer *mer*-**14** is assigned the stereochemistry in Figure 4, where the dien ligand adopts a meridional geometry.

The minimum T_1 time for the ^{1}H resonance at −5.97 ppm of *fac*-**14** was found to be 43 ms at 300 MHz (226 K). After correcting the relaxation rate corresponding to this T_1 value for the dipolar contributions of the rhenium and the ortho phenyl hydrogens[15] and assuming a static HH ligand,[16] an H−H distance of 1.38 ± 0.03 Å was calculated.

The preparation of **14** with HD gas generates the sample **14**-d_1. Two sets of signals are observed for the **14**-d_1 sample in the hydride region. The signal arising from the *mer*-**14**-d_1 isomer (ddm, −4.05 ppm) is similar to that of the *mer*-**14** (ddq, −4.04 ppm). However, the *fac*-**14** signal has become a set of four multiplets, assigned as two broad, overlapping triplets. The broader upfield triplet (−6.03 ppm) arises from *fac*-**14**-d_1, where the deuterium is in a hydride position (*vide infra*). The downfield triplet (−5.97 ppm) arises from an impurity (in ∼1:1 ratio) that is thought to be an isomer of *fac*-**14**-d_1, where the deuterium has exchanged with a hydrogen in another part of the complex to produce an HH ligand and an N−D bond (e.g., as verified by ^{2}H NMR).

In order to obtain a clean hydride signal for the HD isomer of *fac*-**14**-d_1, it was necessary to "null out" the overlapping *fac*-**14** HH isomer impurities by use of an inversion−recovery NMR pulse sequence. The complex pattern appears to be a 1:2:1 (H−P) triplet of 1:1:1 (H−D) triplets of 1:3:3:1 H−F quartets (Figure 5c). The coupling constants obtained by simulation at 300 and 500 MHz were $^2J_{HP} = 22.5$ Hz, $^3J_{HF} = 3.5$ Hz, and $^1J_{HD} = 6.7$ Hz, with estimated errors of ±1 Hz. The H−H distance calculated from the H−D coupling constant[17] is 1.31 ± 0.03 Å, approximating the distance of 1.38 Å calculated from the minimum T_1 value. Such good agreement in the estimate of d_{HH} using these two methods suggests that a severely elongated dihydrogen ligand is present in *fac*-[Re(H··H)(dien)(PF$_3$)(PPh$_3$)]$^+$ (*fac*-**14**) and that it is not rotating fast enough to influence ^{1}H relaxation; therefore, its rotational frequency is much less than 300 MHz.

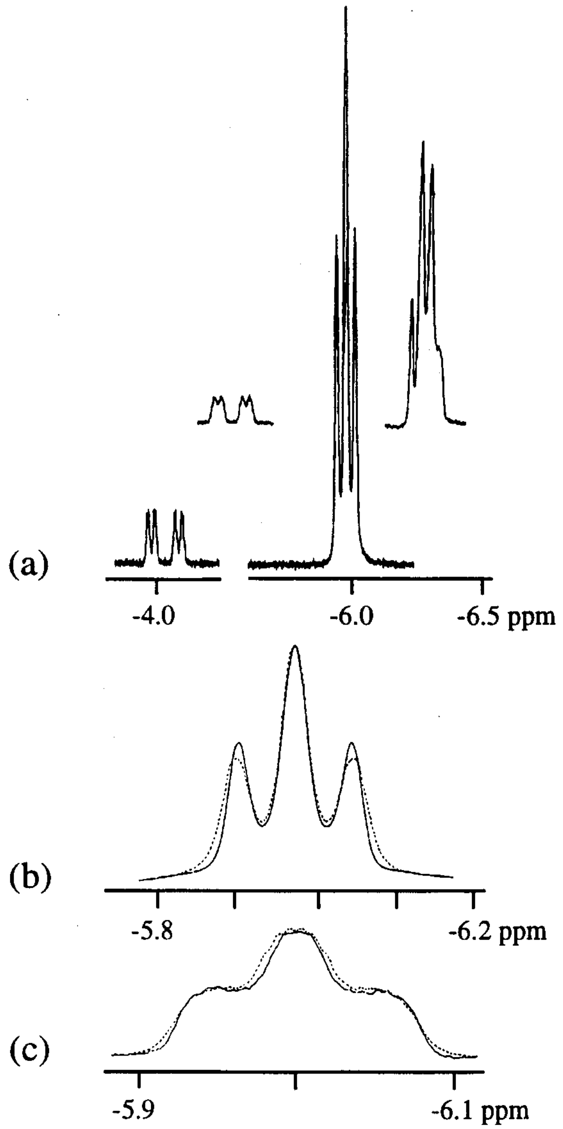

Figure 5. (a) Hydride region of a 500 MHz ^{1}H NMR spectrum (acetone-d_6) of *mer*-**14** and *fac*-**14**. (Offset shows **14**-d_1 spectrum.) (b) Simulation at 300 MHz of *fac*-**14** spectrum using $J_{HP} = 22.5$ Hz, $J_{HF} = 3.5$ Hz, with a line width of 5.5 Hz (exptl, —; calcd, ···). (c) Simulation of *fac*-**14**-d_1 (HD) spectrum at 500 MHz using $J_{HP} = 22.5$ Hz, $J_{HF} = 3.5$ Hz, $J_{HD} = 6.7$ Hz, with a line width of 5.5 Hz (exptl, —; calcd, ···). The *fac*-**14** (HH) resonance is nulled out as described in the Experimental Section.

The hydrides in *fac*-**14** could in principle occupy two inequivalent sites and yet still give rise to a single observable proton resonance through the extreme second-order effects of quantum mechanical exchange coupling.[13] However, such a coupling cannot occur for an HD complex. Thus, if quantum exchange coupling were responsible for the single hydride signal of *fac*-**14**, *fac*-**14**-d_1 would be expected to show two signals,

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[17] An empirical relationship between J_{HD} and d_{HH} has been derived: $d_{HH} = -0.0167J_{HD} + 1.42$ Å. Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407.

Table 3. NMR Coupling Constants and Calculated H−H Distances for Re Dihydrogen Complexes and Some Os Dihydrogen Complexes and Electrochemical Potentials of Corresponding Dinitrogen Complexes

complex (X = H or D)	ref	J_{HD} (Hz)	d_{HH} (Å) calcd from J_{HD}[a]	d_{HH} (Å) calcd from T_1(min)[b]	$E_{1/2}$ of ReN_2 (V vs NHE)
trans-$Re(H{\cdot\cdot}H)(Cl)(PMePh_2)_4$	22			1.58/1.25	0.5[c]
$Re(H{\cdot\cdot}H)(Cl)(dppe)_2$	23			1.55/1.23	0.53[22]
fac-$[Re(H{\cdot\cdot}X)(dien)(PF_3)(PPh_3)]^+$		6.7	1.31	1.38/1.09	0.8
cis-$[Re(H_2)(CO)(PMe_3)_4]^+$	25	27	0.96	1.03/0.81	1.3[c]
$[Re(H_2)(CO)_2\{CH_3C(CH_2PPh_2)_3\}]^+$	26	31	0.91	1.02/0.81	1.8[c]
$[Re(H_2)(CO)_2(PMe_3)_3]^+$	24	33.7	0.86	1.01/0.80	1.7[c]
$[Re(H_2)(CO)_3(PMe_3)_2]^+$	27	33	0.87	0.98/0.78	2.2[c]
$[Re(H_2)(CO)_3(P^iPr_3)_2]^+$	26	33	0.87	0.90/0.71	2.2[c]
$[Re(H_2)(CO)(NO)(C_5Me_5)]^+$	28	27	0.96	0.85/0.68	
trans-$[Os(H{\cdot\cdot}X)(en)_2(OAc)]^+$	6a	9.1	1.27	1.34/1.06	0.5[c,d]
$[Os(H{\cdot\cdot}X)(NH_3)_5]^{2+}$	6c	15	1.17		1.0
trans-$[Os(H{\cdot\cdot}X)(dppe)_2(Cl)]^+$	17	13.9	1.19	1.35/1.08	1.4[c]
trans-$[Os(H{\cdot\cdot}X)(dppe)_2(H)]^+$	17	25.5	0.99	1.3/1.02	1.3[c]

[a] $d_{HH} = -0.0167J_{HD} + 1.42$. [b] d_{HH} (slow spinning/fast spinning) calculated from the reported T_1(min) data. [c] $E_{1/2}(Re^{II}(N_2)L_5/Re^{I}(N_2)L_5)$ estimated by use of a ligand additivity method (see ref 11). [d] Based on $E = 0.83$ V for the related compound $[Os(NH_3)_4(N_2)(NH_2Pr)]^{2+}$, modified according to the ligand parameters put forth by Lever.[27]

arising from the two inequivalent hydrides.[14b] Since only one signal is observed (other than the *fac*-**14**-d_1 HH isomer), we can rule out this explanation.

Previously, no rhenium complexes with such small J_{HD} values have been reported (Table 3). The two neutral complexes of Re^{I} in Table 3 are thought to have elongated dihydrogen complexes on the basis of T_1 measurements and X-ray crystallography, but unfortunately, the J_{HD} coupling constants have not been obtained. Such elongated ligands are expected to have small couplings of less than 25 Hz.[4b] The other known cationic rhenium(I) dihydrogen complexes have large J_{HD} values and short d_{HH} values (Table 3). Yet, couplings of the same magnitude (4−10 Hz) as that of *fac*-**14** have been reported in some osmium complexes.[6a,b] The best characterized of these complexes is *trans*-$[Os(H{\cdot\cdot}H)(en)_2(OAc)]PF_6$ with $d_{HH} = 1.34$(2) Å and $J_{HD} = 9.1$ Hz, values comparable to those of *fac*-**14**.

The tendency of a d^6 metal complex to have a dihydride or dihydrogen structure has been discussed in terms of the electrochemical potential, $E_{1/2}(d^5/d^6)$, of the corresponding dinitrogen complex.[11] If $E_{1/2}$ lies much below 0.5 V vs NHE, then a dihydride structure may be expected (see also Figure 3). The two tetrakis(phosphine)rhenium compounds listed in Table 3 with $E_{1/2}$ values close to 0.5 V feature an elongated dihydrogen ligand, with H−H distances intermediate between those of dihydrogen and dihydride species. Similarly, *trans*-$[Os(H{\cdot\cdot}H)(en)_2(OAc)]PF_6$ has a H−H distance of 1.34 Å (neutron diffraction) and an estimated $E_{1/2}(Os^{III}/Os^{II})$ of ∼0.5 V (NHE) for the hypothetical dinitrogen complex $[Os(N_2)(en)_2(OAc)]PF_6$. The J_{HD} values for *fac*-**14**-d_1 and $[Os(HD)(NH_3)_5]^{2+}$ (see Table 3) indicate the presence of H··H distances of 1.31 Å for *fac*-**14** and 1.17 Å for $[Os(NH_3)_5(H_2)]^{2+}$, respectively. This is in reasonable agreement with the measured $E_{1/2}$ values of *fac*-**14** (0.86 V) and $[Os(NH_3)_5(N_2)]^{2+}$ (1 V), which are more positive than the dihydrides mentioned above. This trend breaks down for the complex *trans*-$[Os(H{\cdot\cdot}H)(dppe)_2(Cl)]^+$,[17] which has an observed H−H distance of 1.22(3) Å and a predicted $E_{1/2}$ value of 1.4 V (Table 3). A common factor in all of the dihydrogen complexes with elongated H−H distances is that the dihydrogen ligand is *trans* to an electronegative N, O, or Cl donor atom. A recent theoretical study concludes that weak-field ammine or chloride ligands when *trans* to dihydrogen cause an increase in d_{HH} and a decrease in J_{HD} values relative to the strong-field ligands hydride or cyanide (or CO, we assume), when trans to dihydrogen.[18] This is clearly observed in the osmium dppe complexes of Table 3 when the effects of the chloride and hydride *trans* ligands are compared.[17] The other complexes listed in Table 3 have short H−H distances with predicted $E_{1/2}$ values above 1 V as expected and with the dihydrogen ligand trans to less electronegative donor atoms P, C, or H.

In an attempt to prepare a Re^{II} dihydrogen complex that was isostructural to **14**, H_2 gas at atmospheric pressure was bubbled through an acetone solution of the Re^{II} precursor (**13**) for 30 min. Crystals of the product were grown from the degassed reaction mixture. The complex identified by single-crystal X-ray diffraction (Table 1; Figure 2) is *fac*-$[Re(\eta^1\text{-acetone})(PF_3)(PPh_3)(dien)](OTf)_2$. Evidence indicating that the desired Re^{II} dihydrogen complex analogous to **14** is thermodynamically unstable comes from the electrochemical data for **14**. A cyclic voltammogram recorded at 100 mV/s in CH_3CN shows a chemically irreversible wave at $E_{p,a} = 1.18$ V suggesting that an E_rC_i mechanism is operative.[19]

In Figure 2, drawings resulting from the structure determinations of the Re^{II} dinitrogen complex **3** and the Re^{II} acetone complex **14** are compared. Apparently, the process of oxidation, replacement of dinitrogen with triflate, and substitution of triflate by acetone does not alter the stereochemistry of the metal center. The one-electron oxidation of rhenium results in a lengthening of the Re−P bonds consistent with a decreased amount of π-back-bonding, but interestingly, the $Re^{II}-PF_3$ bond distance is still very short, compared to that for the triarylphosphine, evidence suggesting that PF_3 participates as a π-acid even on rhenium(II).

Conclusions

Synthetic routes to a variety of new rhenium complexes containing dinitrogen and nitrogen-donor ligands have been developed, and a linear correlation between $E_{1/2}(Re^{II}/Re^{I})$ and

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$\nu(N_2)$ is noted. As expected, the $Re^{II}(N_2)$ complexes have higher $\nu(N_2)$ than corresponding Re^{I} species. The complex *fac*-$[Re(H{\cdot\cdot}H)(dien)(PF_3)(PPh_3)]^+$ has been characterized as a severely elongated dihydrogen structure, and the corresponding HD complex has one of the lowest J_{HD} values measured for such a structure. This distortion of the hydrogen ligand is attributed in part to the electron-donating ability of the saturated nitrogen ligands, but also to the weak-field nature of the *trans* amine ligand.

Experimental Section

Abbreviations: dien = diethylenetriamine; DME = 1,2-dimethoxyethane; DMA = *N*,*N*-dimethylacetamide; OTf = trifluoromethanesulfonate (triflate); TBAH = tetrabutylammonium hexafluorophosphate; ampy = 2-(aminomethyl)pyridine; en = ethylenediamine; tmpa = tris(2-pyridylmethyl)amine; bpy = 2,2′-bipyridine; tbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; etpb = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

***fac*-[Re(PPh$_3$)(PF$_3$)(dien)(N$_2$)](OTf) (3).** Compound **2** (57.1 g, 56.9 mmol) was suspended in DME (1 L). Dien (15.73 g, 152.4 mmol) was added to the suspension, and the reaction mixture was refluxed for 3 h. NaOTf (35 g, 203 mmol) in 600 mL of MeOH was then added to the reaction mixture, and the mixture was refluxed for an additional 2 h. The mixture was held at 21 °C and then stirred for 18 h. The solvent was removed under reduced pressure and the resulting brown residue collected. The brown residue was washed with H_2O (3 × 200 mL) to yield an off-white solid. The solid was dried for 24 h under vacuum. The crude dinitrogen mixture was washed with Et_2O (2 × 200 mL) to remove any free PPh_3 and then chromatographed on a silica gel column, using CH_3CN as the eluent. The first yellow band was collected and the solvent removed to yield a yellow solid. The solid was washed with CH_2Cl_2 (200 mL) and then Et_2O (3 × 100 mL) to yield pure dinitrogen complex **3** (21.3 g, 26.1 mmol, 46%). ^1H NMR (CD_3CN): δ 7.49−7.37 (m, 15H, P*Ph*$_3$), 5.91 (br s, 1H), 3.43−2.53 (m, 12H, dien). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 138.14 (d, $J_{CP} = 45.5$ Hz), 133.60 (d, $J_{CP} = 11.4$ Hz), 130.60 (d, $J_{CP} = 2.1$ Hz), 129.58 (d, $J_{CP} = 9.3$ Hz), 54.36 (d, $J_{CP} = 4.1$ Hz), 53.81 (s), 46.11 (d, $J = 4.1$ Hz), 42.38 (br s). CV (DMA, TBAH, 100 mV/s): $E_{p,a} = 0.86$ V. IR (KBr): $\nu(N_2) = 2033\ cm^{-1}$. Anal. Calcd for $C_{23}H_{28}F_6N_5O_3P_2ReS$: C, 33.83; H, 3.45; N, 8.58. Found: C, 34.22; H, 3.58; N, 8.44.

***fac*-[Re(PPh$_3$)PF$_3$(dien)(OTf)](OTf)·DME (13).** Compound **3** (1.041 g, 1.27 mmol) was dissolved in acetone (10 mL). AgOTf (328 mg, 1.28 mmol) was dissolved in acetone (5 mL) and slowly added to the stirring rhenium solution over a 5 min period. The mixture was then filtered through Celite to remove the Ag^0, and the filtrate was collected. The solvent was removed under reduced pressure, yielding a yellow oil. The yellow oil was then redissolved in DME (5 mL) and the reaction mixture stirred for 3 h at room temperature. The resulting yellow precipitate was collected and washed with DME (3 × 2 mL) and Et_2O (3 × 2 mL) to yield complex **13** with 1 equiv of DME (508 mg, 49.4 mmol, 39%). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = -0.12$ V. Anal. Calcd for $C_{28}H_{38}F_9N_3O_8P_2ReS_2$: C, 32.72; H, 3.73; N, 4.09. Found: C, 32.66; H, 3.55; N, 4.35. The EPR spectrum of **13** was run on the powder at room temperature with a sweep width of 5000 G and a center field of 3480.01 G. A very strong, broad signal ($g = 1.7$−3.4) resulted, but no coupling was resolved. An acetone solution of **13** at −105 °C gives a weaker signal, but it was still impossible to resolve any fine structure.

***fac*-[Re(H··H)(PPh$_3$)(PF$_3$)(dien)](OTf) (14).** Compound **13** (380 mg, 0.369 mmol) was dissolved in DME (15 mL), and excess Mg^0 (1.23 g) was added to the Schlenk flask. A balloon was placed over the top of the flask and purged three times with H_2. The balloon was then inflated to ~1 L volume with H_2 gas. The reaction mixture was stirred at room temperature for 100 min. The remaining Mg^0 was filtered off through Celite, and the filtrate was collected. The solvent was removed under reduced pressure, and the resulting white residue was collected and washed with CH_2Cl_2 (2 mL) and Et_2O (5 mL) to yield compound **14** (150 mg, 0.190 mmol, 47%). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a} = 1.15$ V. Anal. Calcd for $C_{23}H_{30}F_6O_3N_3P_2ReS$: C, 34.94; H, 3.82; N, 5.31. Found: C, 35.49; H, 3.98; N, 5.39. ^1H NMR (acetone-d_6, 500 MHz): δ 7.70−7.66 (m, 1 H, Ph), 7.57−7.53 (m, 5.6 H, Ph), 7.52−7.41 (m, 9.25 H, Ph), 6.86 (br s, 1H, *fac* NH), 6.7 (br s, 0.13 H, *mer* NH), 4.45 (br s, 0.25 H, *mer* NH_2), 4.23 (br s, 2 H, *fac* NH_2), 4.1 (br s, 0.25 H, *mer* NH_2), 3.72 (br s, 1 H, *fac* NH_2), 3.4−2.9 (~11 H, overlapping CH_2 and NH_2 signals), 2.84−2.78 (m, 1 H, *mer* CH_2), −4.04 (d d qrt, $^2J_{HP(t)} = 67$ Hz, $^2J_{HP(c)} = 18$ Hz, $^3J_{HF} = 4$ Hz, 0.25 H, *mer* hydride), −5.97 ppm (t, $^2J_{HP} = 22$ Hz, 2 H, *fac* hydride). Temp/T_1 (HRe, 300 MHz) (°C/ms): 24/116 ± 6, 4/90 ± 5, −13/67 ± 6, −30/49 ± 2, −47/43 ± 1, −63/47 ± 1, −80/62 ± 2. ^{31}P NMR (acetone-d_6, referenced externally): The major species (*fac*-**14** with the hydride at −6 ppm in the ^1H spectrum) shows phosphorus resonances at 45.4 ppm (PPh_3; dq, $^2J_{PP} = 25$ Hz, $^1J_{PF} = 8$ Hz) and at 86.4 ppm (PF_3; qd, $^1J_{PF} = 1166$ Hz, $^2J_{PP} = 25$ Hz). The minor species (*mer*-**14**; hydride at −4 ppm) shows analogous resonances at 32.8 ppm (PPh_3; dq, $^2J_{PP} = 39$ Hz, $^3J_{PF} = 9$ Hz) and at 89.9 ppm (q, $^1J_{PF} = 1171$ Hz, $^2J_{PP}$ unresolved).

***fac*-[Re(H··D)(PPh$_3$)(PF$_3$)(dien)](OTf) (14-*d*$_1$).** HD gas was generated by adding D_2O (2 mL) dropwise to a NaH (1.5 g) suspension in DME (10 mL). The HD gas was passed through a $CaCl_2$ drying tube prior to use. Compound **13** (161 mg, 0.157 mmol) was dissolved in DME (12 mL), and excess Mg^0 (763 mg) was added to the Schlenk flask. A balloon containing ~450 mL of HD gas was placed on top of the Schlenk flask, and ~200 mL of HD was used to purge the Schlenk flask. The reaction mixture was stirred for 2 h at room temperature. The remaining Mg^0 was filtered off through Celite, and the filtrate was collected. The solvent was removed, and the resulting white residue was washed with Et_2O (3 × 10 mL) to yield compound **14**-*d*$_1$ (58 mg, 0.073 mmol, 47%). The D_2 complex (**14**-*d*$_2$) was prepared similarly to the H_2 complex, in a 49% yield.

^1H NMR (500 MHz, acetone-d_6): δ 7.70−7.66 (m, 1 H, Ph), 7.57−7.53 (m, 6 H, Ph), 7.52−7.41 (m, 8.5 H, Ph), 6.86 (br s, 1H, *fac* NH), 6.7 (br s, 0.25 H, *mer* NH), 4.45 (br s, 0.5 H, *mer* NH_2), 4.23 (br s, 2 H, *fac* NH_2), 4.1 (br s, 0.5 H, *mer* NH_2), 3.72 (br s, 1 H, *fac* NH_2), 3.4−2.9 (~11 H, overlapping CH_2 and NH_2 signals), 2.84−2.78 (m, 1 H, *mer* CH_2), −4.05 (ddm, $^2J_{HP(t)} = 68$ Hz, $^2J_{HP(c)} = 18$ Hz, 0.25 H, *mer* hydride), −6.0 ppm (m, 1.5 H, *fac* hydride). When the HH signal at −6 ppm is successfully nulled out in inversion−recovery experiments, a broad, inverted triplet at −6.01 ppm results. Reasonably "clean" HD signals were obtained both at 500 MHz and at 300 MHz by use of null times of 78 ms in both cases and of spectral windows that bracketed the resonance at −6 ppm.

The ^{31}P NMR (acetone-d_6, referenced externally) spectrum of **13**-*d*$_1$ was indistinguishable from that of **13**.

^2D NMR (sample of **14**-*d*$_2$ in acetone): 3.25, −4.01 (d, $^2J_{DP} = 11$ Hz), and −5.90 ppm.

[Re(PF$_3$)(PPh$_3$)(dien)(acetone)](OTf)$_2$ (15). [ReOTf(PF$_3$)(PPh$_3$)(dien)]OTf·DME (**13**, 70 mg, 0.068 mmol) was dissolved in acetone (10 mL) to give a deep yellow solution in a Schlenk tube in the N_2 glovebox. The tube was brought outside and exposed to Ar, and H_2 was bubbled through the solution. No color change was observed. After 30 min, the volume had been reduced to 3−5 mL, and hexanes were added under Ar to precipitate out a deep yellow powder. X-ray quality crystals were grown directly from the degassed reaction mixture by slow diffusion of degassed hexanes. The complex identified by single-crystal X-ray diffraction is *fac*-[Re(acetone)(PF$_3$)(PPh$_3$)(dien)](OTf)$_2$. MS (acetone, FAB/NBA matrix): 789, 638, 556, 551. Calcd: Re(OTf)(PF$_3$)(PPh$_3$)(dien), 789; Re(PF$_3$)(PPh$_3$)(dien) − 2H$^+$, 638; Re(PPh$_3$)(dien) − H$^+$, 551. An X-ray crystal structure determination reveals a *fac*-stereochemistry identical to that of the dinitrogen complex **3**.

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Supporting Information Available: Detailed synthesis and characterization for all compounds presented herein, complete crystallographic data for **3** and **15**, and ORTEP drawings for **5A**, **6**, and **11** (25 pages). Ordering information is given on any current masthead page.

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