The Asymmetric π-Bases *fac*-{Re(dien)(PPh_3)(PF_3)}$^+$ and *fac*-{Re(dien)(PPh_3)(CO)}$^+$: Evidence for Formation of an η^2-Furan Complex

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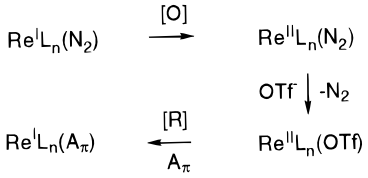
A series of complexes has been prepared of the form [Re(dien)(PPh_3)(PF_3)(L)]$^+$ (dien = diethylenetriamine), where L is an unsaturated organic molecule. The range of ligands which form η^2-coordinate complexes with this metal center includes aldehydes, olefins, and dienes. In addition, thiophene, benzo[*b*]thiophene, and acetonitrile bind through their heteroatoms. Although {Re(dien)(PPh_3)(PF_3)}$^+$ (dien = diethylenetriamine) displays chemical and spectroscopic characteristics of a potent π-base, it fails to form stable η^2-coordinated complexes with aromatic molecules. However, its carbonyl analogue {Re(dien)(PPh_3)(CO)}$^+$, when combined with furan, forms the complex [Re(η^2-furan)(dien)(PPh_3)(CO)][OTf], a rare example of a thermally stable η^2-heterocycle.

Introduction

The π-base pentaammineosmium(II) readily forms η^2-coordinated complexes with a variety of unsaturated organic molecules including arenes, aromatic heterocycles, olefins, aldehydes, and ketones.[1−7] The η^2 binding mode and the electron-rich metal of these complexes have the effect of promoting electrophilic addition reactions with the uncoordinated portion of the organic ligand. Our aim in this study was to develop a low-valent rhenium(I) complex isoelectronic with the {Os(NH_3)$_5$}$^{2+}$ system that would exhibit similar binding affinities for unsaturated organic molecules. The synthetic strategy for the preparation of this analogue takes advantage of a methodology developed by Chatt, Dilworth, and Leigh[8,9] for the preparation of rhenium(I) dinitrogen complexes from an *N*-benzoylhydrazido precursor. In a manner similar to that used for the osmium(II) system, oxidation of a rhenium dinitrogen complex in the presence of triflate forms a rhenium(II) triflato species. This Re(II) triflato complex serves as the immediate precursor to the desired Re(I) π base.



Since our synthesis of Re(I) dinitrogen complexes allows for flexibility in the choice of ancillary ligands, steric and electronic properties can be adjusted to optimize the performance of the complexing agent. Thus, to develop a rhenium analogue with electronic properties similar to those of the pentaammineosmium(II) system,[10] we attempted to match electrochemical and infrared data of the rhenium systems to the complex [Os(NH_3)$_5$(N_2)][OTf]$_2$ ($E_{1/2}$ = 0.98 V; ν_{N_2} 2037 cm^{-1}) by systematically altering the ligand set (Figure 1). An analogous strategy has been used to predict stable dihydrogen complexes.[11] The properties of the previously reported complex [Re(N_2)(dien)(PPh_3)(PF_3)][OTf] (dien = diethylenetriamine) were encouraging, with an $E_{1/2}$ value (0.86 V, NHE; DMAc) and dinitrogen stretching frequency (2033 cm^{-1}; KBr) very similar to those of the pentaammineosmium(II) analogue. The carbonyl analogue {Re(dien)(PPh_3)(CO)}$^+$ was also sought as a synthetic target, since it would present a less sterically hindered binding site while its reduction potential was expected to be similar to the PF_3 system.

Unlike the pentaammineosomium(II) system, the {Re(dien)(PPh_3)(PF_3)}$^+$ and {Re(dien)(PPh_3)(CO)}$^+$ systems incorporate a chiral metal center. Gladysz et al.[12−15] have shown for the system {Re(Cp)(NO)(PPh_3)}$^+$ that a chiral rhenium center with a combination of small (e.g. nitrosyl) and large (e.g. triphenylphosphine) ligands presented at the binding face coordinates prochiral ligands with high stereoselectivity.[16] In comparison, the {Re(dien)(PPh_3)(PF_3)}$^+$ and {Re(dien)(PPh_3)(CO)}$^+$ sys-

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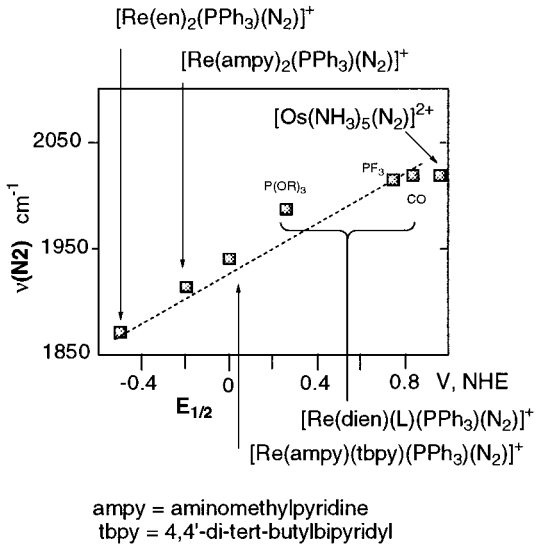


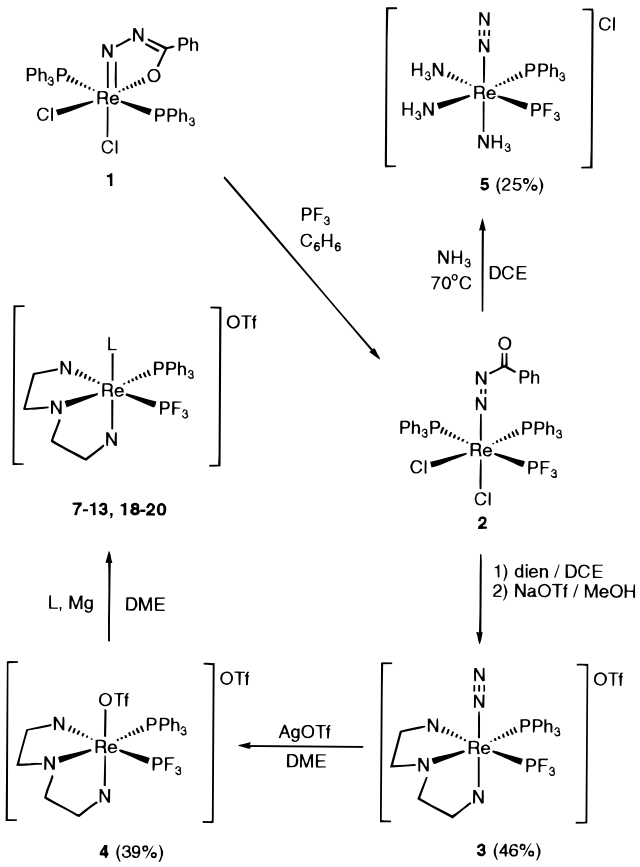
Figure 1. Correlation of electrochemical and infrared spectroscopic data for various rhenium(I) dinitrogen complexes.

tems contain the tridentate diethylenetriamine ligand, which is much less susceptible to electrophilic attack than is Cp. Furthermore, a more reducing metal center is provided by replacement of the NO^+ ligand with PF_3 or CO. With these changes, our hope was that an asymmetric π-base could be developed that ultimately could be used as a promotor for stereoselective *electrophilic* addition reactions with unsaturated molecules.

Results and Discussion

The preparation of the rhenium(II) precursor [Re(OTf)(dien)(PPh_3)(PF_3)][OTf] (**4**) from the chelate (*N*-benzoylhydrazido-*N′,O*)dichlorobis(triphenylphosphine)-rhenium(V) (**1**) has been previously reported (Scheme 1).[10] The electronic nature of the dinitrogen complex can be varied significantly by the ligand introduced at the diazenido stage. The trifluorophosphine ligand of **2** was initially selected as the primary π-acid over CO because the phosphine is not known to act as a bridging ligand. Addition of the σ-donor dien displaces one of the triphenylphosphine ligands and triggers the conversion of the Re(III)−diazenido species to the Re(I)−dinitrogen complex [Re(N_2)(dien)(PPh_3)(PF_3)](OTf) (**3**). Subsequent oxidation of **3** with AgOTf in DME affords the desired Re(II) triflato complex **4**. As shown in Scheme 1, compound **4** may be reduced to rhenium(I) using activated Mg^0 in the presence of an unsaturated ligand to form the η^2-bound complexes. The triammine analogue of **3** (*fac*-[Re(N_2)(NH_3)$_3$(PPh_3)(PF_3)](Cl) (**5**)) was prepared as the chloride salt by heating **2** in a pressure tube to 70 °C in DCE under an atmosphere of NH_3 (26 psi). While the ammine analogue maintained electronic characteristics similar to those of the dien complex, it exhibited a much less complicated ^{1}H NMR spectrum and a potentially less sterically demanding coordination site. Unfortunately, subsequent attempts to convert this compound to a rhenium(II) triflato species were unsuccessful.

Scheme 1. Reaction Scheme for Synthesis of Low-Valent Rhenium(I) Precursors Containing the PF_3 Ligand from (*N*-benzoylhydrazido-*N′,O*)dichlorobis(triphenylphosphine)rhenium(V)



The range of organic ligands that are bound by the {Re(dien)(PPh_3)(PF_3)}$^+$ fragment is summarized in Figure 2. Aldehydes coordinate to the metal in a diastereoselective fashion (**7**−**9**), and only η^2-bound isomers have been observed by NMR spectroscopy. Values for de reported in Figure 2 represent lower limits which were determined on the basis of integration of ^{1}H NMR siganals or the signal-to-noise ratio in the corresponding ^{13}C NMR spectrum. Interestingly, all of the aldehydes were bound exclusively through their carbonyl function, even in the case of crotonaldehyde (**9**), where the olefinic site is likely to be thermodynamically favored. Each of these compounds exhibits a cyclic voltammogram (DMAc at 100 mV/s) with a broad, chemically irreversible anodic peak between 0.6 and 0.9 V (NHE) as well as a methine resonance between 70 and 75 ppm in their ^{13}C NMR spectrum. These signals are shifted upfield by approximately 5−10 ppm relative to the analogous {Os(NH_3)$_5$}$^{2+}$ complexes.[17] The acetaldehyde complex **7** exhibits the most diagnostic ^{1}H NMR spectrum, since the bound aldehyde proton (which overlaps with dien resonances) is easily distinguished by its coupling to the methyl group. This signal (3.64 ppm) is shifted upfield by almost 2 ppm relative to the {Os(NH_3)$_5$}$^{2+}$ and {Re(terpy)(^{t}BuNC)$_2$}$^+$ systems.[18] The identification of the bound aldehyde proton for the benzaldehyde complex **8** (4.5 ppm) was accomplished by deuterating the

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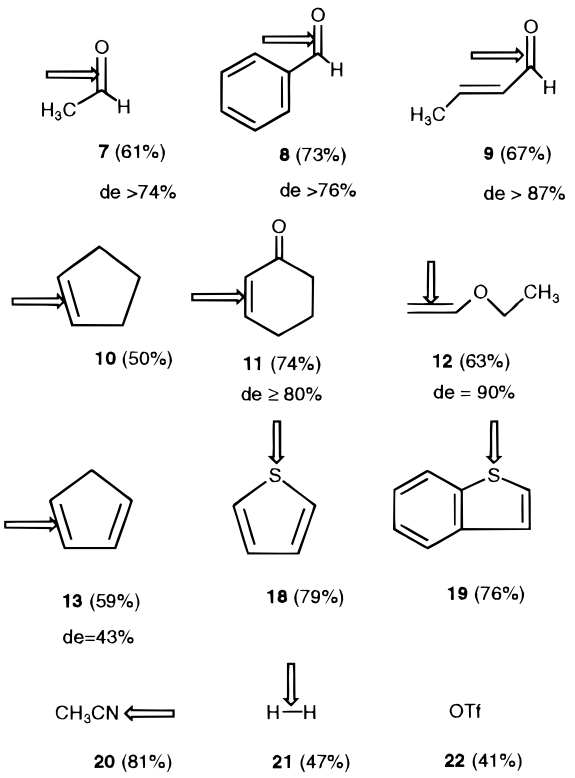


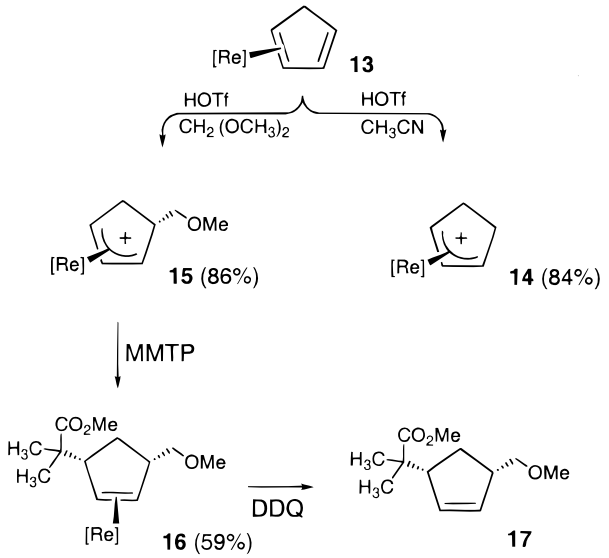
Figure 2. Scope of ligands which coordinate to the [Re(dien)(PPh_3)(PF_3)]$^+$ fragment with binding site, yield, and diastereomeric excess (where applicable).

amine protons with (^{i}Pr)$_2$(Et)N in MeOD. Attempts to generate the olefin-bound isomer of *fac*-[Re(η^2-crotonaldehyde)(dien)(PPh_3)(PF_3)][OTf] (**9**) by a protonation/deptotonation sequence similar to that used for osmium(II) failed for the rhenium system.[17] Coordination of 2-thiophenecarboxaldehyde also occurs through the carbonyl group, although this compound was not obtained in an analytically pure form. A cyclic voltammogram for this species produced $E_{p,a} = 0.59$ V, a value more positive (i.e. more difficult to oxidize) than would be expected for an *S*-bound isomer. Further evidence for the C,O-bound isomer is found in the ^{13}C NMR spectrum of this material, which shows a methine peak for the bound carbonyl at 69 ppm. Attempts to protonate or methylate these compounds with HOTf or MeOTf failed to produce the corresponding aldehydium complexes.[17]

The fragment {Re(dien)(PPh_3)(PF_3)}$^+$ readily forms η^2-bound complexes with dienes[19] and sterically congested olefins. A cyclic voltammogram of the cyclopentene complex **10** shows $E_{1/2} = 0.54$ V, and ^{13}C data indicate bound olefinic carbons at 56 and 51 ppm. In contrast to what is observed for crotonaldehyde, 2-cyclohexen-1-one does not form a kinetically stable carbonyl-bound complex but, rather, is found exclusively as its olefinic-bound isomer **11**. A resonance at 214 ppm in the ^{13}C NMR spectrum of **11** corresponds to the uncoordinated carbonyl, and the bound olefin resonances at 46 and 42 ppm confirm this assignment. A ^{1}H NMR spectrum taken of the crude reaction product indicated that a small amount (approximately 5−10%) of a second material was formed. This impurity was not generated in sufficient purity to allow for its characterization; therefore, formation of a diastereomer or linkage isomer could not be ruled out. Chromatography (silica/MeOH) allowed the separation of complex **11** from the minor product. *fac*-[Re(η^2-(2-cyclohexen-1-one))(dien)(PPh_3)(PF_3)][OTf] (**11**) undergoes clean protonation with HOTf to form what is thought to be a hydroxy allyl complex analogous to that observed for osmium.[17] Subsequent attempts to deprotonate this material with an amine base resulted in decomposition. Even the fragile olefin ethyl vinyl ether forms a stable complex with the rhenium system. Reduction of **4** in the presence of an excess of this ligand affords a 1:1 mixture of diastereomers initially. These diastereomers equilibrated to a 9:1 ratio (de 80%) upon standing at room temperature. One possible route to this equilibration is through an η^1-bound linkage isomer similar to that observed for [Os(NH_3)$_5$(aniline)][OTf]$_2$,[20] where the vinyl ether is temporarily bound though the oxygen. Subsequent bond rotation provides a route to the thermodynamically favored diastereomer upon rearrangement back to the η^2 form.

When a sample of *fac*-[Re(OTf)(dien)(PPh_3)(PF_3)][OTf] (**4**) was reduced with Mg^0 in the presence of cyclopentadiene the compound *fac*-[Re(η^2-CpH)(dien)(PPh_3)(PF_3)][OTf] (**13**) was isolated (59%) as a 5:2 equilibrium mixture of diastereomers. Treatment of this mixture with triflic acid in methanol or acetonitrile (Scheme 2) cleanly generates the π-allyl complex *fac*-[Re(η^3-C_5H_7)(dien)(PPh_3)(PF_3)][OTf]$_2$ (**14**) (84%). In a similar manner, when the diene complex **13** was combined with dimethoxymethane (22 °C) and TBSOTf with 2,6-di-*tert*-butylpyridine, a 5:2 diastereomeric mixture of the allyl species *fac*-[Re(η^3-methoxymethylcyclopentenyl)(dien)(PPh_3)(PF_3)][OTf]$_2$ (**15**) (86%) was formed, consistent with the original ratio of diene diastereomers. Treatment of **15** with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene (MMTP) in CH_3CN generated the cyclopentene complex **16** (62%) as a 5.5:1 mixture of isomers. When

Scheme 2. Reaction Scheme for Sequential Electrophilic/Nucleophilic Additions to *fac*-[Re(η^2-cyclopentadiene)(dien)(PPh_3)(PF_3)](OTf)



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16 was heated in an acetonitrile solution, the disubstituted cyclopentene **16** was recovered as a single stereoisomer (see Scheme 2). Recovery of the free cyclopentene (**17**) exclusively as the *cis* isomer confirms that electrophilic addition occurred from the *exo* face, similar to that observed for the osmium(II) and ruthenium(II) pentaammine systems.[21]

Thiophene and benzo[*b*]thiophene coordinate to the PF_3 system through sulfur to form complexes **18** and **19**, respectively (see Figure 2). Cyclic voltammetry for these S-bound complexes shows a characteristic reversible couple near 0.3 V (vs NHE). Furthermore, ^{1}H and ^{13}C NMR resonances for the coordinated ligand are similar to spectra of the free ligand. Attempts to trap a hypothetical η^2 isomer by methylation of sulfur with MeOTf failed. Coordination of acetonitrile generated an η^1-coordinated complex (**20**) (see Figure 2) which exhibited a nitrile stretching frequency (KBr) at 2217 cm^{-1}. This value corresponds to a shift of 41 cm^{-1} to lower energy compared with the free ligand. The analogous pentaammineosmium(II) complex displays a nitrile stretch (KBr) at 2191 cm^{-1}.[22] When *fac*-[Re(OTf)(dien)-(PPh_3)(PF_3)][OTf] (**4**) was reduced in the presence of dihydrogen gas (1 atm), the dihydrogen complex *fac*-[Re(H_2)(dien)(PPh_3)(PF_3)][OTf] (**21**) was generated.[10] This complex featured a calculated H−H bond length of 1.31 Å (calculated from HD coupling constants), which is one of the longest H−H bonds of any η^2-dihydrogen complex known. This value is 0.14 Å longer than that determined for the corresponding pentaammineosmium-(II) system.[23]

Unfortunately, all attempts to bind arenes or aromatic heterocycles (including furan, naphthalene, *N*-methylpyrrole, and benzene) in an η^2 fashion were unsuccessful with the {Re(dien)(PPh_3)(PF_3)}$^+$ system. Rather than the anticipated aromatic complex, a material was isolated from these reactions (**22**) whose combustion analysis is consistent with the formulation [Re(OTf)-(dien)(PPh_3)(PF_3)]. ^{1}H and ^{13}C NMR data for **22** indicate a *meridional* arrangement for the dien ligand. Our tentative assignment for **22** is the stereoisomer of the one-electron reduction product of **4** (i.e. *mer*-[Re(OTf)-(dien)(PPh_3)(PF_3)]), where the triflate ligand is *trans* to the PF_3 group. Supporting this interpretation, the reduction potential for **22** ($E_{1/2} = -0.23$ V in DMAc) is practically identical with that for **4** ($E_{1/2} = -0.26$V in DMAc) and ^{1}H and ^{13}C NMR data indicate only two chemically distinct methylene groups. The difference in reactivity of **22** and the reduced form of **4** is striking. Whereas reduction of **4** in acetonitrile rapidly forms the corresponding complex *fac*-[Re(CH_3CN)(dien)(PPh_3)-(PF_3)](OTf) (**20**), compound **22** is stable in neat acetonitrile at room temperature. However, heating **22** (60 °C) in acetonitrile for 2 h forms the *fac*-nitrile species **20** as the main product.

Where stable complexes are accessible, the {Re(dien)-(PPh_3)(PF_3)}$^+$ fragment shows a generally high degree of facial binding selectivity. For the aldehyde and vinyl ether complexes (**7**−**9**, **12**) the diastereomeric excess reported in Figure 2 is likely under thermodynamic control. For the aldehyde complexes, the facile $\eta^2-\eta^1$ linkage isomerization commonly observed for these systems is likely responsible for equilibration of the diastereomers. For the enone and diene species (**11**, **13**), it is likely that the observed diastereomer mixtures are generated under kinetic control for these complexes, since there is no heteroatom adjacent to the site of coordination. While the de values reported in Figure 2 are not as high as those observed with the {Re(Cp)(NO)-(PPh_3)}$^+$ system,[12−15] the chiral recognition of the binding site is clearly apparent. While we believe that the two observed species for the vinyl ether (**12**) and diene (**13**) systems are diastereomers, the existence of kinetically stable rotamers cannot be excluded without additional studies. Gladysz et al. have measured a $\Delta G^{\ddagger}$ value of 16 kcal/mol at 369 K for the complex [Re(Cp)(NO)(PPh_3)-(η^2-ethylene)][OTf],[12] and the barrier for rotation for the {Re(dien)(PPh_3)(PF_3)}$^+$ fragment could possibly be larger due to increased back-bonding resulting from the more π-basic nature of the metal in the PF_3 system.

Table 1. Comparison of Spectroscopic, Electrochemical, and Physical Properties of the {Os(NH_3)$_5$}$^{2+}$ and {Re(dien)(PPh_3)(PF_3)}$^+$ Systems

ligand	attribute	{Os(NH_3)$_5$}$^{2+}$ [c]	{Re(dien)-(PF_3)(PPh_3)}$^+$ [c]
CH_3CN	ν(CN) [b] (cm^{-1})	2191	2217
	$E_{1/2}$ [a] (V)	−0.10	0.11
N_2	ν(NN) [b] (cm^{-1})	2037	2033
	$E_{1/2}$ [d] (V)	0.98	0.86
H_2	H−H(calcd) (Å)	1.17	1.31
CpH	binding mode	η^2	η^2
	$E_{1/2}$ [a] (V)	0.65	0.51
	electrophilic addition	yes	yes
arenes	binding mode	η^2	none
thiophene	binding mode	η^2	S

[a] CH_3CN; TBAH. [b] KBr. [c] OTf^- counterion. [d] DMAc; TBAH (NHE).

In Table 1, various attributes of the {Re(dien)(PPh_3)-(PF_3)}$^+$ and {Os(NH_3)$_5$}$^{2+}$ systems are compared. Like the pentaammineosmium(II) fragment, the rhenium system coordinates an array of unsaturated ligands with η^2-coordination favored in most cases. In the case of cyclopentadiene, tolerance to strong acid and promotion of electrophilic addition reactions is common to both metal systems. For the ligands N_2, CH_3CN, H_2, and CpH, electrochemical and infrared data are remarkably similar for the complexes, indicating a close match in the electronic properties of these two metal centers. In contrast, binding stabilities differ widely for η^2-coordinated ligands between these two systems. While pentaammineosmium(II) has been shown to form stable complexes with arenes, the {Re(dien)(PPh_3)(PF_3)}$^+$ fragment cannot. The data summarized in Table 1 indicate that steric differences are responsible for this contrast in binding affinities. For small ligands, the rhenium system mirrors the spectroscopy and stability seen with osmium, but for larger ligands, the combination of the bulky triphenylphosphine and trifluorophosphine ligands most likely compromises the coordinating ability of the rhenium.

While the methodology of correlating dinitrogen stretching frequencies and electrochemical data for dinitrogen precursors to [Os(NH_3)$_5$(N_2)][OTf]$_2$ appears

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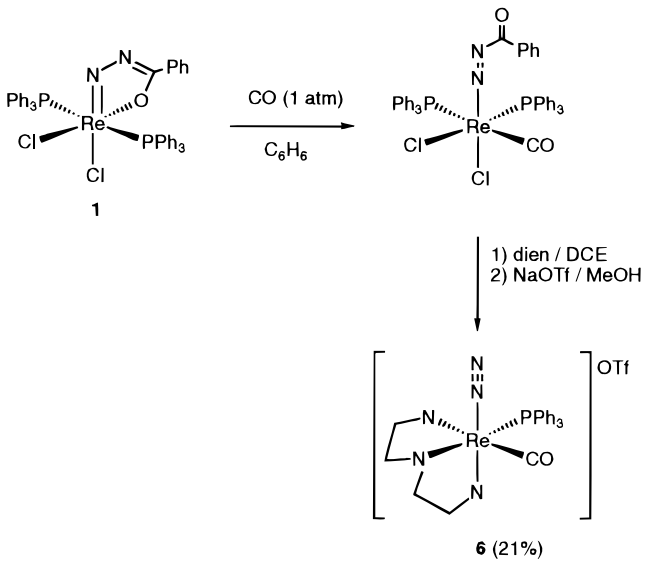
(23) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261.

Scheme 3. Synthesis of *fac*-[Re(N_2)(dien)(PPh_3)(CO)](OTf) from (*N*-Benzoylhydrazido-*N′,O*)-dichlorobis(triphenylphosphine)rhenium(V)



sound, it does not address steric issues at the coordination site. The replacement of PF_3 with CO, a smaller ligand of similar π-acidity, would further test our hypothesis that chemical properties of rhenium(I) could be adjusted to match those of osmium(II). Refluxing **1** in benzene under a purge of CO yields the seven-coordinate species [Re(N_2COPh)(CO)$_2$(PPh_3)$_2$Cl$_2$].[24] However, perfoming this reaction at 20 °C affords a light orange solid which exhibits a resonance in the IR spectrum at 2019 cm^{-1} and a cyclic voltammogram similar to that of **2**. Although the carbonyl analogue of **2** could not be isolated in pure form, when the crude product was combined with dien and NaOTf in DCE/MeOH (Scheme 3) the desired compound [Re(N_2)(dien)(PPh_3)(CO)][OTf] (**6**) was formed as the major product. The presence of two strong bands at 2036 and 1825 cm^{-1} in the IR spectrum and a Re(II/I) reduction potential similar to [Re(N_2)(dien)(PPh_3)(PF_3)][OTf] (**3**) confirmed the assignment of **6.**

In the presence of various aromatic ligands, compound **6** was first oxidized to Re(II), liberating the dinitrogen ligand, and then reduced back to rhenium(I). In the presence of furan, this procedure resulted in the formation of *fac*-[Re(*2,3*-η^2-furan)(dien)(PPh_3)(CO)][OTf] (**23**) (Scheme 4) as a single diastereomer (de > 90%). A ^{13}C DEPT (CD_3CN) experiment indicated four methine carbons resonating at 143, 110, 95, and 47 ppm. In comparison, the analogous complex [Os(NH_3)$_5$(η^2-furan)][OTf]$_2$ exhibits resonances at 143, 112, 99, and 49 ppm (acetone-d_6). The ^1H NMR spectrum (CD_3CN) of **6** also indicated an η^2-coordinated species with a signal for the unbound α-proton at 6.42 ppm (d) and three other furan resonances at 4.71 (t), 4.61 (dd) and 4.56 ppm (dd). For the pentaammineosmium(II) system both of the α-protons are well downfield of the β-protons but molecular modeling suggests that the bound α-proton for **23** is in the shielding region of one of the phenyl rings of the phosphine ligand. This may be the cause for the upfield shift of one of the unbound signals. Complexation of

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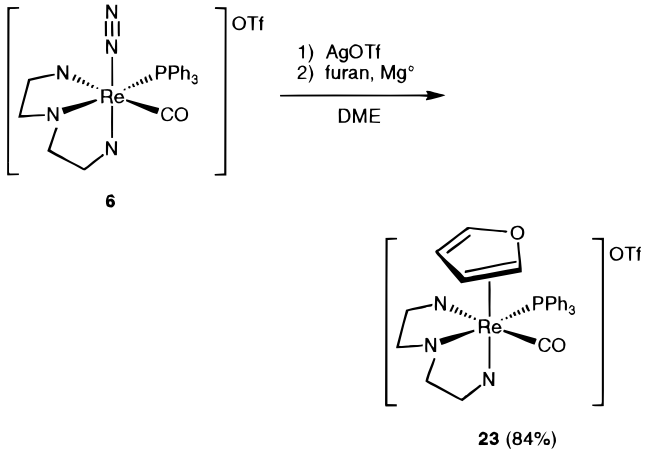
Scheme 4. Synthesis of an η^2-Furan Complex from *fac*-[Re(N_2)(dien)(PPh_3)(CO)](OTf)



furan-d_4 afforded a complex with a spectrum in which all of these resonances assigned to bound furan were absent. Electrochemical data for complex **23** exhibits a broad, irreversible anodic wave at +0.61 V (DMAc, NHE). This compares very favorably with [Os(NH_3)$_5$(η^2-furan)][OTf]$_2$, which shows a similar wave at +0.67 V (CH_3CN, NHE).

An NMR tube experiment with **23** indicated that the half-life for decomposition is on the order of 1 day in acetonitrile at 20 °C. A similar half-life was observed in acetone. In the solid state, however, the complex appears to be stable at room temperature. Although free furan was observed as one of the decomposition products (^1H NMR), the decomposition reaction resulted in a poorly defined mixture of products. When other aromatic molecules were attempted as ligands, spectroscopic and electrochemical data of the reaction mixtures suggested that the carbonyl analogue of **22** (*mer*-[Re(OTf)(dien)(PPh_3)(CO)]) superseded the formation of the desired aromatic complex.

The preparation of **23** is significant in that it represents the first example of a thermally stable complex of furan bound in a η^2-fashion other than the class of pentaammineosmium(II) complexes that we have attempted to mimic. Unlike the osmium systems, however, complex **23** contains a stereogenic metal center and is formed as one dominant diastereomer. The tendency of the {Re(dien)(PPh_3)(CO)}$^+$ and {Re(dien)(PPh_3)(PF_3)}$^+$ systems to isomerize to their meridional forms and their sterically encumbered coordination environments make the present systems impractical as dearomatization agents for organic synthesis. However, the basic premise that electrochemical and infrared data of dinitrogen complexes can be used to design metal systems capable of such unusual bonding patterns appears to be sound.

Experimental Section

Abbreviations: dien = diethylenetriamine; DCE = 1,2-dichloroethane; DME = 1,2-dimethoxyethane; DMF = *N*,*N*-dimethylformamide; DMAc = *N*,*N*-dimethylacetamide; OTf = trifluoromethanesulfonate (triflate); TBAH = tetrabutylammonium hexafluorophosphate; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; TBS = *tert*-butyldimethylsilyl; MMTP = 1-methoxy-2-methyl-1-(trimethylsiloxy)propene.

General Considerations. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and were recorded at room temperature unless otherwise noted. Chemical shifts are reported in ppm relative to TMS (tetramethylsilane) using residual protonated solvent (δ acetone-d_5) 2.04; δ(acetonitrile-d_2) 1.93; δ(DMSO-d_5) 2.49; δ(methanol-d_3) 3.30). 2D-NMR experiments (DEPT, COSY, NOESY, HETCOR) were recorded on a General Electric GN-300 spectrometer. ^{13}C multiplicities are supported by DEPT data. Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal progammer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.7 to −1.7 V utilizing a glassy-carbon electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in CH_3CN or DMAc (∼0.5 M TBAH) at 100 mV/s using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) or ferrocene ($E_{1/2} = 0.55$ V) in situ as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 80 and 100 mV for all reversible couples unless otherwise noted. All work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. Infrared spectra were recorded on a Mattson Cygnus 100 FT-IR spectrometer using either a KBr pellet or a glaze on a KBr salt plate. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer. Synthesis of the rhenium(II) precursor [Re(OTf)(dien)(PPh_3)(PF_3)](OTf) has been reported from the rhenium(V) complex [*N*-benzoylhydrazido-*N*′,*O*]dichlorobis(triphenylphosphine)rhenium(V).[10]

Solvents and Reagents. All solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated either by repeated freeze−pump−thaw cycles or vacuum distillation. All distillations were performed under nitrogen. Methanol was refluxed over Mg(OMe)$_2$ (prepared in situ from magnesium activated by I_2) and distilled. Acetonitrile was refluxed over CaH_2 and distilled. Aldrich anhydrous grade DMAc, DME, and DCE were used without further purification. Methylene chloride was passed through a column of activated alumina under an inert atmosphere.[25] Acetone was used as received. Acetonitrile-d_3 (Cambridge Isotope Labs) was distilled from CaH_2. Acetone-d_6, DMF-d_7, and DMSO-d_6 were used as received. Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under a nitrogen atmosphere, stirring for 1 h, and washing with DMAc, acetone, and diethyl ether. All ligands were used as received, except that they were deoxygenated prior to use.

***fac*-[Re(N$_2$)(NH$_3$)$_3$(PPh$_3$)(PF$_3$)]Cl (5).** [Re(N$_2$COPh)(PF$_3$)(PPh$_3$)$_2$Cl$_2$][10] (**2**) (1.941 g, 1.93 mmol) and 16 g of DCE were placed in a pressure tube fitted with a gas inlet valve and pressure release valve. The tube was sealed under nitrogen and was evacuated until the DCE boiled. The system was then charged with 26 psi of NH_3 and placed in an oil bath at 70 °C. After it was stirred at this temperature for 18 h, the tube was brought into the glovebox and the resulting solid filtered and rinsed with 15 mL of DCE, 15 mL of acetone, and 25 mL of ether. The crude chloride salt was dissolved in about 70 mL of MeOH and was chromatographed on a dry bed of silica gel. The initial yellow band was collected, and the solvent was concentrated under reduced pressure until the light yellow product began to precipitate. After the solid was filtered, it was rinsed with 2 × 2 mL of CH_2Cl_2 and 15 mL of ether to give 201 mg (25% yield) of the purified product. ^{1}H NMR (DMSO-d_6): δ 7.72−7.01 (m, 15H), 3.75 (br s, 3H), 3.20 (br s, 3H), 2.76 (br s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 137.04 (C), 132.68 (CH), 129.18 (CH), 128.33 (CH). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.64$ V (NHE). Anal. Calcd for $C_{18}ClH_{24}F_3N_5P_2Re$: C, 33.18; H, 3.72; N, 10.74. Found: C, 33.05; H, 3.59; N, 10.81.

(25) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

***fac*-[Re(N$_2$)(dien)(PPh$_3$)(CO)][OTf] (6).** The crude diazenido product [Re(N$_2$COPh)(PPh$_3$)$_2$(Cl)$_2$(CO)] (8.35 g, 8.86 mmol) was slurried in DCE (200 mL) along with dien (2.75 g, 26.7 mmol). This dark brown solution was refluxed for 3 h. A solution of NaOTf (4.88 g, 28.4 mmol) in MeOH (75 mL) was added, and the mixture was refluxed an additional 2 h. The slurry was then stirred at room temperature for 18 h. The solvent was removed under reduced pressure and washed with 200 mL of water. The residue was filtered and washed with approximately 250 mL of ether. The resulting crude solid was dissolved in CH_3CN and chromatographed on a dry silica gel column. The initial light yellow band was collected, concentrated to approximately half the volume, and precipitated by addition to ether. The light yellow solid was filtered and rinsed with 25 mL of ether to afford 1.41 g (21% yield) of the product. IR (glaze): ν_{NN} 2036 cm^{-1}, ν_{CO} 1825 cm^{-1}. CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.74$. Anal. Calcd for $C_{24}F_3H_{28}N_5O_4PSRe$: C, 38.09; H, 3.73; N, 9.25. Found: C, 37.84; H, 3.93; N, 9.46.

***fac*-[Re(η^2-acetaldehyde)(dien)(PPh$_3$)(PF$_3$)][OTf] (7).** *fac*-[Re(dien)(PPh$_3$)(PF$_3$)(OTf)][OTf] (**4**; 209 mg, 0.223 mmol) and acetaldehyde (383 mg, 8.69 mmol) were slurried together in 6.2 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 113 mg (61% yield) of the light beige product. ^{1}H NMR (acetonitrile-d_3): δ 7.25−7.88 (m, 15H), 6.19 (br s, 1H), 3.78 (br s, 1H), 3.64 (q, $J = 4.2$ Hz, 1H), 3.51 (br s, 1H), 2.34−3.31 (m, 8H), 2.28 (d, $J = 4.2$ Hz, 3H). ^{13}C{^{1}H} NMR (DMF-d_7): δ 134.01 (C), 133.23 (CH), 129.61 (CH), 127.87 (CH), 71.71 (CH), 57.79 (CH$_2$), 53.90 (CH$_2$), 43.01 (CH$_2$), 24.41 (CH$_3$). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.88$ V (NHE). Anal. Calcd for $C_{25}H_{32}F_6O_4N_3P_2ReS$: C, 36.06; H, 3.87; N, 5.05. Found: C, 35.61; H, 4.24; N, 4.52.

***fac*-[Re(*C*,*O*-η^2-benzaldehyde)(dien)(PPh$_3$)(PF$_3$)][OTf] (8).** *fac*-[Re(dien)(PPh$_3$)(PF$_3$)(OTf)][OTf] (**4**; 338 mg, 0.360 mmol) and benzaldehyde (1166 mg, 11.0 mmol) were slurried together in 6.5 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at room temperature for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 224 mg (73% yield) of the light yellow product. ^{1}H NMR (acetonitrile-d_3): δ 7.04−7.90 (m, 20H), 5.65 (br s, 1H), 4.49 (s, 1H), 3.77 (br s, 1H), 3.57 (br s, 1H), 3.30−2.27 (m, 8H). ^{13}C{^{1}H} NMR (acetonitrile-d_3): δ 134.59 (C), 134.47 (CH), 131.34 (CH), 129.52 (CH), 129.40 (CH), 129.26 (CH), 129.05 (CH), 124.70 (CH), 73.55 (CH), 59.42 (CH$_2$), 55.64 (CH$_2$), 44.72 (CH$_2$). 43.96 (CH$_2$). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.62$ V (NHE). Anal. Calcd for $C_{30}H_{34}F_6O_4N_3P_2ReS$: C, 40.26; H, 3.83; N, 4.70. Found: C, 40.34; H, 4.06; N, 4.42.

***fac*-[Re(*C*,*O*-η^2-crotonaldehyde)(dien)(PPh$_3$)(PF$_3$)][OTf] (9).** *fac*-[Re(dien)(PPh$_3$)(PF$_3$)(OTf)][OTf] (**4**; 202 mg, 0.215 mmol) and crotonaldehyde (317 mg, 4.52 mmol) were slurried together in 6.0 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 124 mg (67% yield) of the light yellow product. ^{1}H NMR (acetonitrile-d_3): δ 7.82−7.23 (m, 13H), 5.75 (br s, 1 H), 5.53 (br s, 1H), 4.04 (br s, 1H), 3.70−

2.27 (m, 10H). $^{13}C\{^1H\}$ NMR (DMF-d_7): δ 138.71 (CH), 133.44 (CH), 132.70 (C), 130.05 (CH), 128.34 (CH), 122.71 (CH), 75.15 (CH), 57.80 (CH_2), 54.13 (CH_2), 44.07 (CH_2), 42.80 (CH_2), 17.77 (CH_3). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.84$ V (NHE). Anal. Calcd for $C_{27}H_{34}F_6O_4N_3P_2ReS$: C, 37.76; H, 3.99; N, 4.89. Found: C, 37.54; H, 4.21; N, 4.79.

***fac*-[Re(η^2-cyclopentene)(dien)(PPh_3)(PF_3)][OTf] (10).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 210 mg, 0.224 mmol) and cyclopentene (234 mg, 3.44 mmol) were slurried together in 7.7 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 113 mg (50% yield) of the light yellow product. ^1H NMR (acetonitrile-d_3): δ 7.72−7.29 (m, 15H), 5.71 (br s, 1H), 3.62−1.93 (m, 17H), 1.46−1.28 (m, 3H). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3): δ 136.66 (C), 134.15 (CH), 130.59 (CH), 129.25 (CH), 59.58 (CH_2), 56.60 (CH), 55.03 (CH_2), 51.44 (CH), 51.29 (CH_2), 44.04 (CH_2), 43.98 (CH_2), 34.36 (CH_2), 21.67 (CH_2). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2} = +0.54$ V (NHE). Anal. Calcd for $C_{28}H_{36}F_6O_3N_3P_2ReS$: C, 39.25; H, 4.24; N, 4.90. Found: C, 39.28; H, 4.42; N, 5.02.

***fac*-[Re(*C,C*-η^2-2-cyclohexen-1-one)(dien)(PPh_3)(PF_3)][OTf] (11).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 120 mg, 0.128 mmol) and 2-cyclohexen-1-one (303 mg, 3.25 mmol) were slurried together in 3.9 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 84 mg (74% yield) of the light beige product. ^1H NMR (acetonitrile-d_3): δ 7.45−7.68 (m, 15H), 5.82 (br s, 1H), 4.23 (br s, 1H), 3.75 (br s, 1H), 3.73 (m, 1H), 3.13 (m, 1H), 2.40−2.86 (m, 8H), 2.16 (m, 2H), 1.80 (m, 2H), 1.62 (m, 2H). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3): δ 214 (C), 134.01 (C), 133.23 (CH), 129.61 (CH), 127.87 (CH), 58.21 (CH_2), 54.76 (CH_2), 46.39 (CH), 45.57 (CH_2), 44.19 (CH_2), 42.78 (CH), 34.56 (CH_2), 29.25 (CH_2), 27.82 (CH_2). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +1.07$ V, $E_{p,c} = -0.07$ V (NHE). Anal. Calcd for $C_{29}H_{36}F_6O_4N_3P_2ReS$: C, 39.36; H, 4.10; N, 4.75. Found: C, 39.75; H, 4.55; N, 4.41.

***fac*-[Re(η^2-ethyl vinyl ether)(dien)(PPh_3)(PF_3)][OTf] (12).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 5.460 g, 5.82 mmol) and ethyl vinyl ether (4.690 g, 65.0 mmol) were slurried together in 60 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 3 h. The mixture was treated with 30 mL of CH_3CN and was filtered through Celite to remove the magnesium. After the solvent was removed completely, the resulting solid was dissolved in CH_2Cl_2 and filtered. The filtrate was evaporated to dryness and triturated in 5:1 Et_2O/CH_2Cl_2. The solid was filtered and rinsed with the same solution until the washings were colorless to give 3.150 g (63% yield) of the product. ^1H NMR (acetonitrile-d_6): δ 7.52−7.33 (m, 16H), 6.33 (br s, 1H), 4.63 (m, 1H), 4.42 (br s, 1H), 4.09 (br s, 1H), 3.48 (m, 2H), 3.27 (m, 2H), 3.06 (m, 4H), 1.82 (br s, 1H), 1.69 (m, 1H), 0.86 (m, 3H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 136.36 (C), 134.20 (CH), 130.38 (CH), 129.07 (CH), 90.40 (CH), 72.40 (CH_2), 57.42 (CH_2), 55.73 (CH_2), 44.97 (CH_2), 43.52 (CH_2), 25.50 (CH_2), 18.51 (CH_3). CV (DMAc, TBAH, 100 mV/s): $E_{p,a} = +0.62$ V, $E_{p,c} = +0.38$ V (NHE). Anal. Calcd for $C_{27}H_{36}F_6O_4N_3P_2ReS$: C, 37.67; H, 4.22; N, 4.88. Found: C, 37.70; H, 4.57; N, 4.88.

***fac*-[Re(η^2-cyclopentadiene)(dien)(PPh_3)(PF_3)][OTf] (13).** *fac*-[Re(OTf)(PPh_3)(PF_3)(dien)][OTf] (**4**; 4.56 g, 4.86 mmol) and cyclopentadiene (5.2 g, 78.8 mmol) were placed into a 150 mL flask, and 35 mL of DME was added to the mixture. Mg^0 (4.5 g) was then added, and the reaction mixture was stirred for 2 h at 22 °C. The reaction mixture was filtered through a 30 mL fine frit, and the solvent was removed from the filtrate to afford an off-white solid. The residue was washed with 1 × 5 mL of CH_2Cl_2 and 3 × 10 mL of Et_2O to yield 2.46 g (59%) of the product as a 5:2 mixture of isomers. ^1H NMR (CD_3CN, both isomers): δ 7.64−7.31 (m, 15H), 6.23 (br s, 1H), 6.13 (br s, 1H), 5.93 (m, 1H), 5.27 (m, 1H), 5.09 (m, 1H), 4.00 (m, 1H), 3.84 (m, 1H), 3.69−2.29 (m, 12H), 2.18 (m, 1H), 2.02−1.64 (m, 3H). ^{13}C NMR (CD_3CN, both isomers): δ 141.43 (CH), 141.35 (CH), 136.63 (C), 136.49 (C), 134.53 (CH), 130.85 (CH), 129.62 (CH), 129.51 (CH), 129.41 (CH), 126.95 (CH), 59.46 (CH), 59.35 (CH), 57.25 (CH_2), 55.68 (CH_2), 54.49 (CH_2), 52.53 (CH_2), 47.72 (CH_2), 44.18 (CH_2), 43.92 (CH_2), 43.86 (CH_2), 41.52 (CH), 40.53 (CH). CV (CH_3CN/TBAH/100 mV/s): $E_{1/2} = 0.51$ V (NHE). Anal. Calcd for $C_{28}H_{34}F_6O_3N_3P_2ReS$: C, 39.34; H, 4.01; N, 4.92. Found: C, 39.82; H, 4.28; N, 4.90.

***fac*-[Re(η^3-C_5H_7)(dien)(PPh_3)(PF_3)][OTf]$_2$ (14).** A sample of **13** (134 mg, 0.16 mmol) was dissolved in 636 mg of CH_3CN. HOTf (178 mg, 1.19 mmol) in 200 mg of CH_3CN was added dropwise and the solution stirred for 10 min. The reaction mixture was then added dropwise to 65 mL of Et_2O. The resulting mixture was placed in a freezer (−30 °C) for 1.5 h, filtered, and washed with diethyl ether (2 × 10 mL) to afford 132 mg (84%) of a yellow powder. ^1H NMR (CD_3CN): δ 7.66−7.49 (m, 15H), 5.78 (br s, 1H), 4.60 (br s, 1H), 4.49 (br s, 1H), 4.43 (br s, 1H), 4.25 (br s, 1H), 4.02 (br s, 1H), 3.96−3.79 (m, 2H), 3.26−3.04 (m, 5H), 3.03−2.75 (m, 4H), 2.57 (m, 1H), 2.41 (m, 1H), 0.93 (dd, J = 6.1 Hz, 15.9 Hz, 1H). ^{13}C NMR (CD_3CN): δ 134.65 (CH), 132.50 (CH), 131.10 (C), 130.15 (CH), 78.42 (CH), 67.86 (CH), 65.57 (CH), 59.18 (CH_2), 55.54 (CH_2), 45.83 (CH_2), 44.66 (CH_2), 31.50 (CH_2), 31.40 (CH_2). Anal. Calcd for $C_{29}H_{35}F_9O_6N_3P_2ReS_2$: C, 34.66; H, 3.51; N, 4.18. Found: C, 34.63; H, 3.15; N, 4.10.

***fac*-[Re(η^3-1-(methoxymethyl)cyclopentenyl)(dien)(PPh_3)(PF_3)][OTf]$_2$ (15).** A sample of compound **13** (551 mg, 0.64 mmol) was dissolved in 4.1 g of CH_3CN. Dimethoxymethane (84 mg, 1.1 mmol) and di-*tert*-butylpyridine (109 mg, 0.57 mmol) were added, followed by TBSOTf (192 mg, 0.73 mmol), and the reaction mixture was allowed to stand for 1 h before being added to 50 mL of Et_2O to afford 577 mg (86%) of a yellow solid. ^1H NMR (CD_3CN, 5:2 ratio of isomers): δ 7.64−7.39 (m, 15H), 6.04 (br s, 1H), 5.92 (br s, 1H), 4.74 (br s, 1H), 4.68 (br s, 1H), 4.42 (br s, 1H), 4.35 (br s, 1H), 4.16 (br s, 1H), 3.98 (br s, 1H), 3.79 (br s, 1H), 3.66 (m, 1H), 3.24 (s, 3H), 3.02 (s, 3H), 3.31−2.71 (m, 20H), 2.40−2.03 (m, 9H), 1.25 (m, 3H). Partial ^{13}C NMR (CD_3CN, both isomers): δ 134.97 (CH), 134.82 (CH), 132.74 (C), 131.57 (CH), 131.19 (CH), 131.01 (C), 130.45 (CH), 130.38 (CH), 78.15 (CH), 78.07 (CH), 77.85 (CH), 77.01 (CH), 68.56 (CH), 67.61 (CH), 65.04 (CH), 64.08 (CH), 59.90 (CH_3), 59.75 (CH_3), 59.24 (CH_2), 55.93 (CH_2), 55.65 (CH_2), 45.96 (CH_2), 45.87 (CH_2), 45.26 (CH_2), 44.94 (CH_2), 35.56 (CH_2), 34.81 (CH_2). Three carbons were not assigned. Anal. Calcd for $C_{29}H_{39}N_3F_9O_7P_2S_2Re$: C, 33.99; H, 3.84; N, 4.10. Found: C, 33.71; H, 3.96; N, 4.11.

***fac*-[Re(η^2-3-(2-carbomethoxy-2-propyl)-5-(methoxymethyl)cyclopentene)(dien)(PPh_3)(PF_3)][OTf] (16).** To a solution of **15** (307 mg, 0.29 mmol) in 1.1 g of CH_3CN was added 96 mg (0.55 mmol) of MTMP. After 1 h, the reaction mixture was added to 50 mL of Et_2O, filtered, washed with Et_2O (2 × 10 mL), and dried in vacuo to afford 202 mg of **15** as a white powder, 59%. ^1H NMR (CD_3CN): δ 7.43−7.67 (m, 15 H), 6.12 (br s, 1 H), 3.95 (m, 1 H), 3.68 (s, 3H), 3.59 (m, 1 H), 3.25 (m, 4H), 3.01 (m, 2H) 2.89 (s, 3H), 2.80−2.53 (m, 6H), 2.44 (m, 2H), 2.21 (m, 2H), 1.80 (m, 1H), 1.63 (m, 1H), 1.13 (s, 3H), 1.05 (s, 3H). Used without further characterization.

3-(2-Carbomethoxy-2-propyl)-5-(methoxymethyl)cyclopentene (17). ^1H NMR ($CDCl_3$): δ 5.69 (m, 1H), 5.65 (m, 1H), 3.66 (s, 3H), 3.35 (s, 3H), 3.29 (m, 2H), 3.06 (m, 1H), 2.94 (m, 1H), 2.08 (m, 1H), 1.20 (m, 1H), 1.16 (s, 3H), 1.10 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 177.95 (CO), 133.02 (CH), 132.37 (CH), 77.19 (CH_2), 72.42 (CH), 58.92 (CH), 53.79 (CH_3), 51.66 (CH_3), 44.43 (C), 29.12 (CH_2), 22.79 (CH_3), 22.21 (CH_3). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.62; H, 9.88.

***fac*-[Re(*S*-thiophene)(dien)(PPh_3)(PF_3)][OTf] (18).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 203 mg, 0.216 mmol) and thiophene (555 mg, 6.60 mmol) were slurried together in 5.8 mL of DME. Mg^0 was added to the mixture, and the slurry was stirred at 23 °C for 2 h. The mixture was filtered with a coarse frit to remove the magnesium, and the turnings were washed with acetone (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether, and the resulting solid was filtered and rinsed with 10 mL of additional ether to give 150 mg (79% yield) of the light yellow product. ^{1}H NMR (acetonitrile-d_3): δ 7.56−7.07 (m, 16H), 5.52 (br s, 1H), 4.06 (br s, 1H), 3.24−2.27 (m, 10H), 1.76 (br s, 1H). ^{13}C{^{1}H} NMR (DMF-d_7): δ 138.06 (C), 133.74 (CH), 133.40 (CH), 133.26 (CH), 129.56 (CH), 129.32 (CH), 128.56 (CH), 128.45 (CH), 56.09 (CH_2), 53.87 (CH_2), 45.35 (CH_2), 42.56 (CH_2). CV (DMAc, TBAH, 100 mV/s): $E_{1/2}$ = +0.28 V (NHE). Anal. Calcd for $C_{27}H_{32}F_6O_3N_3P_2ReS_2$: C, 37.15; H, 3.70; N, 4.81. Found: C, 37.67; H, 3.75; N, 4.27.

***fac*-[Re(*S*-benzo[*b*]thiophene)(dien)(PPh_3)(PF_3)][OTf] (19).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 270.0 mg, 0.287 mmol) and benzothiophene (1.152 g, 8.58 mmol) were slurried in 15 mL of DME. Mg^0 was added to the reaction mixture, which was then stirred for 2 h at 23 °C. At the end of 1 h, the reaction slurry was filtered to remove excess magnesium, and the magnesium was washed with 8 × 3 mL of acetone until the washings were clear. The filtrate was collected, and the solvent was removed under reduced pressure. The resulting yellow solid was washed with 5 × 2 mL DME, followed by 2 × 1 mL of ether to give 185 mg of yellow product (76%). ^{1}H NMR (acetone-d_6): δ 7.91 (d, J = 7.4 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.62−7.36 (m, 17H), 7.31 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 5.7 Hz, 1H), 5.70 (br s, 1H), 4.50 (br s, 1H), 4.30 (br s, 1H), 3.83 (br s, 1H), 3.26 (m, 1H), 2.94−2.53 (m, 5H), 2.41 (br s, 1H), 1.68 (m, 2H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 140.79 (d, J = 42.4 Hz), 136.41 (s), 133.78 (d, J = 10.3 Hz), 133.52 (s), 133.16 (s), 130.83 (s), 130.35 (d, J = 2.3 Hz), 129.54 (d, J = 8.2 Hz), 127.91 (s), 127.74 (s), 126.79 (s), 123.68 (s), 56.45 (s), 56.00 (s), 45.39 (d, J = 3.4 Hz), 42.56 (d, J = 3.5 Hz). CV (DMAc, TBAH, 100 mV/s): $E_{1/2}$ = +0.29 V (NHE). Anal. Calcd for $C_{31}H_{34}F_6O_3N_3P_2ReS_2$: C, 40.35; H, 3.71; N, 4.55. Found: C, 39.93; H, 3.89; N, 4.77.

***fac*-[Re(η^1-acetonitrile)(dien)(PPh_3)(PF_3)][OTf] (20).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 224 mg, 0.239 mmol) was dissolved in 8.0 mL of acetonitrile. Mg^0 was added, and the mixture was stirred at room temperature for 2 h. The mixture was filtered through a coarse frit to remove the magnesium, and the turnings were washed with acetonitrile (3 × 2 mL) to ensure all of the product was in the filtrate. After the volume of the filtrate was reduced by half, it was added to ether and the resulting solid filtered and rinsed with 10 mL of additional ether to give 147 mg (81% yield) of the light yellow product. ^{1}H NMR (acetonitrile-d_3): δ 7.60−7.16 (m, 15H), 5.52 (br s, 1H), 3.29−2.38 (m, 15H), 2.56 (s, 3H). ^{13}C{^{1}H} NMR (acetonitrile-d_3): δ 141.69 (C), 133.70 (CH), 129.44 (CH), 128.92 (CH), 126.33 (CH), 53.75 (CH_2), 53.49 (CH_2), 48.06 (CH_2), 41.39 (CH_2), 5.08 (CH_3). IR (KBr): ν_{CN} = 2217 cm^{-1}. CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = +0.11 V (NHE). Anal. Calcd for $C_{25}H_{31}F_6O_3N_3P_2ReS$: C, 36.19; H, 3.77; N, 6.75. Found: C, 36.43; H, 3.54; N, 6.62.

***mer*-[Re(OTf)(dien)(PPh_3)(PF_3)] (22).** *fac*-[Re(dien)(PPh_3)(PF_3)(OTf)][OTf] (**4**; 496 mg, 0.529 mmol) was dissolved in 13.6 mL of acetone. Mg^0 was added, and the mixture was stirred at 23 °C ror 6.5 h. The acetone solution was decanted off and run down a dry plug of silica gel. The orange-yellow band was collected and concentrated to about 3 mL. This solution was added slowly to stirring ether to give 171 mg (41% yield) of the yellow product. ^{1}H NMR (acetonitrile-d_3): δ 7.39−7.15 (m, 15H), 5.00 (br s, 1H), 3.57 (br s, 2H), 3.42 (m, 2H), 3.32 (m, 2H), 2.97 (br s, 2H), 2.52 (m, 4H). ^{13}C{^{1}H} NMR (acetonitrile-d_3): δ 144.62 (C), 133.93 (CH), 128.80 (CH), 128.47 (CH), 53.54 (CH_2), 51.20 (CH_2). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = −0.23 V (NHE). Anal. Calcd for $C_{23}H_{27}F_6O_3N_3P_2ReS$: C, 35.03; H, 3.58; N, 5.33. Found: C, 34.46; H, 3.75; N, 5.89.

***fac*-[Re(η^2-furan)(dien)(PPh_3)(CO)][OTf] (23).** The dinitrogen complex **6** (765 mg, 1.01 mmol) was slurried in DME (10.7 mL) along with AgOTf (316 mg, 1.23 mmol). After about 10 min activated Mg^0 (approximately 1 g) was added along with furan (1387 mg, 20.3 mmol). After about 2 h, the Mg^0 was filtered off using a coarse frit, and the resulting filtrate was concentrated to approximately 3 mL and treated with 75 mL of ether. The beige solid was filtered and rinsed with 25 mL of ether to give 695 mg (or 86% yield) of the product. ^{1}H NMR (CD_3CN): δ 8.05−6.94 (m, 15H), 6.52 (br s, 1H), 6.42 (d, J = 2.0 Hz, 1H), 4.71 (t, J = 2.0 Hz, 1H), 4.61 (dd, J = 2.0 Hz, 1H), 4.56 (dd, J = 2.0 Hz, 1H), 4.00 (br s, 2H), 3.62−2.17 (m, 10H), 0.86 (m, 1H). ^{13}C{^{1}H} NMR (CD_3CN): δ 143.13 (CH), 136.14 (C), 134.12 (CH), 130.65 (CH), 129.71 (CH), 109.99 (CH), 94.83 (CH), 58.69 (CH_2), 52.90 (CH_2), 47.50 (CH), 44.00 (CH_2), 42.48 (CH_2). CV (DMAc, TBAH, 100 mV/s): $E_{p,a}$ = +0.61 V. IR (glaze): ν_{CO} 1814 cm^{-1}. Anal. Calcd for $C_{28}F_3H_{32}N_3O_5PSRe$: C, 42.21; H, 4.05; N, 5.27. Found: C, 41.73; H, 4.28; N, 5.25.

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