Rhenium(I) Terpyridine π -Bases: Reversible η^2 -Coordination of Ketones, Aldehydes, and Olefins in the Terpyridine Plane

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Received June 17, 1998

The complex *trans*-[Re(terpy)(Br)(PPh₃)₂][OTf] (**2**) (terpy = 2,2':6',2"-terpyridine) is a convenient precursor to the electron-rich π -basic fragment {(terpy)(L)₂Re}⁺ (L = 'BuNC or PMe₃). Reduction of **2** with activated magnesium in the presence of unsaturated organic molecules and an excess of either 'BuNC or PMe₃ yields complexes of the type *trans*-[(terpy)-(L)₂Re(η^2 - π)][OTf] (L = 'BuNC or PMe₃; π = olefin, aldehyde, or ketone). The dihapto-coordinated organic moieties show a preference for binding in the plane of the terpy ligand. Reaction of *trans*-[Re(terpy)('BuNC)₂(η^2 -acetone)][OTf] (**9**) with MeOTf yields an observable η^2 -ketonium complex. The electronic environment of these complexes has been probed by cyclic voltammetry, and the details of ligand exchange for the η^2 -ketone complexes are presented. Geometric features determined from X-ray crystal structure analyses of *trans*-[(terpy)('BuNC)₂Re(η^2 -acetophenone)][OTf] (**1**) are reported.

Introduction

Aldehydes and ketones have played an important role in the field of organic chemistry, and much is known about the reactivity of these carbonyl compounds.¹ One of the great utilities of transition metal chemistry is the ability to enhance the reactivity of organic compounds upon binding them to a metal fragment.² Although metal-bound carbonyl compounds were known prior to 1970,³ research in this field has gained intensity only recently. A large variety of aldehyde and ketone complexes have been isolated and characterized, and the reactivity of metal-bound carbonyl compounds has been described.^{4–10}

Two bonding modes exist for aldehyde and ketone complexes: η^1 (σ -complex) bound through oxygen and η^2 (π -complex) bound through both carbon and oxygen (Scheme 1).¹¹ Gladysz et al. have performed an elegant series of studies concerning the relative reactivity and equilibria of σ/π -bonding modes for aldehyde and ketone complexes of rhenium,^{6i,8i} and the η^1 to η^2 interconversion has been studied in detail for [(NH₃)₅Ru(acetone)]^{3+/2+}.^{9h} The effect of the metal

Scheme 1. η^1 and η^2 Bonding Modes for Aldehydes and Ketones



center on $\sigma\!/\!\pi\text{-bonding}$ modes for group VI aldehyde complexes has also been probed. 61

Whereas a number of aldehyde complexes have been reported, and both coordination modes are common,^{5,6} well-characterized examples of η^2 -ketone complexes are rare. Several π -coordinated ketone complexes have been observed;^{8–10} however, the majority of these ketones possess electron-withdrawing substituents.⁸ Systematic studies of η^2 -ketone complexes bearing simple alkyl substituents are uncommon.^{9a–e} The scarcity of η^2 -ketone complexes compared to their aldehyde analogues has been attributed to both electronic and steric factors. The π^* orbital that participates in metal-to-ligand backbonding lies higher in energy for ketones compared to the *x* orbital of aldehydes, and the disubstituted carbonyl of ketones is more sterically imposing than the singly substituted carbonyl of aldehydes.^{4a}

We recently reported a synthesis of unusually electronrich Re^I coordination complexes from the reduction of *trans*-[Re(terpy)(Cl)(PPh₃)₂]⁺ (terpy = 2,2':6',2"-terpyridine).¹² Although this material served as a useful precursor to activated olefin complexes of rhenium(I), reduction of *trans*-[Re(terpy)(Cl)(PPh₃)₂]⁺ in the presence of other unsaturated ligands (e.g., aldehydes, ketones, and arenes) produced only intractable mixtures of products. Hoping that replacement of the chloride

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ligand by a better leaving group would enhance the utility of this approach, we prepared the complex *trans*-[Re(terpy)(Br)(PPh₃)₂][OTf] (**2**). Unlike its chloride predecessor, this material has proven to be a versatile precursor to Re^I terpy complexes of the form *trans*-[(terpy)(L)₂Re(η^2 - π)]⁺ (where L = PMe₃, 'BuNC; π = cyclopentene, benzaldehyde, acetone, and acetophe-

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(8) For examples of η²-ketones with halogen-containing electronwithdrawing groups, see: (a) Clemens, J.; Green, M.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. **1973**, 375. (b) Countryman, R.; Penfold, B. R. J. Chem. Soc., Chem. Commun. **1971**, 1598. (c) Ittel, S. D. J. Organomet. Chem. **1977**, 137, 223. (d) Ittel, S. D. Inorg. Chem. **1977**, 16, 2589. (e) Green, M.; Howard, J. A. K.; Laguna, A.; Smart, L. E.; Spencer, J. L.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. **1977**, 278. (f) Burgess, J.; Chambers, J. G.; Clarke, D. A.; Kemmitt, R. D. W. J. Chem. Soc., Dalton Trans. **1977**, 1906. (g) Clarke, D. A.; Hunt, M. M.; Kemmitt, R. D. W. J. Organomet. Chem. **1979**, 175, 303. (h) Grassi, A.; Longo, P.; Musco, A.; Porzio, W.; Scrivanti, A. J. Organomet. Chem. **1985**, 289, 439. (i) Klein, D. P.; Dalton, D. M.; Méndez, N. Q.; Arif, A. M.; Gladysz, J. A. J. Organomet. Chem. **1991**, 412, C7. Scheme 2. Synthesis of *trans*-[Re(terpy)L₂(π)]⁺ (where π = Olefin, Ketone, or Aldehyde)



none). The coordination details, electrochemistry, solidstate geometrical features, and reactivity for this set of complexes are reported below.

Results

Reaction of the chelate complex $(Br)_2(PPh_3)_2Re(=N-N=C(Ph)-O-)$ (1) with excess terpy in a benzene/MeOH (1:1 v/v) mixture, followed by counterion metathesis upon treatment with AgOTf, produces *trans*-[Re(terpy)-(Br)(PPh_3)_2][OTf] (2). Complex 2 is characterized by combustion analysis and electrochemistry, as compared with the previously reported complex *trans*-[Re(terpy)-(Cl)(PPh_3)_2][OTf].¹²

Reaction with Cyclopentene. Reduction of **2** in the presence of cyclopentene yields a new compound assigned as $(terpy)Re(Br)(PPh_3)(\eta^2$ -cyclopentene) (**3**) (Scheme 2). Complex **3** is not isolable but can be observed by cyclic voltammetry. The positive shift in the

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⁽¹¹⁾ Within the context of η^2 bonding, some bound η^2 -ketones can be described as metalloxiranes. For a theoretical discussion of η^2 versus η^1 bonding, see: Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446.





Re^{II}/Re^I reduction potential for this complex ($E_{p,a} = 0.1$ V vs NHE) compared to that of **2** is consistent with replacement of a phosphine in the coordination set of **2** with the olefin. In situ reaction of **3** with excess 'BuNC or PMe₃ yields *trans*-[(terpy)(L)₂Re(η^2 -cyclopentene)]-[OTf] [L = 'BuNC (**4**); PMe₃ (**5**)] (Scheme 2).

Proton and carbon NMR and electrochemical data, as well as a solid-state X-ray structural study of 4 (vide infra), confirm the identities of 4 and 5. Upfield chemical shifts for the bound olefinic protons (3.8-4.7 ppm) in the ¹H NMR spectrum and ¹³C NMR resonances for the bound carbon atoms (64-66 ppm) are consistent with an η^2 -bound olefin. The inequivalence of the 'BuNC and PMe₃ ligands in 4 and 5, respectively, is consistent with either trans or cis geometries. ¹H NMR NOE experiments suggest that the cyclopentene ligand is bound in the plane of the terpy moiety with a trans configuration for the isonitrile or phosphine ligands. For complex 4, a large NOE interaction is observed between the ortho proton on the terpy ligand and the olefinic protons (13%) as well as an enhancement (5%) between the same terpy proton and one of the diastereotopic cyclopentene protons (Scheme 3). Both interactions are concordant with the geometry of **4** in the solid state (vide infra), and similar enhancements (12 and 9%) are observed for the PMe₃ complex 5.

Reaction with Benzaldehyde. Analogous to the reaction of trans-[Re(terpy)(Br)(PPh₃)₂][OTf] (2) with cyclopentene, the reduction of 2 with Zn/Hg in the presence of benzaldehyde produces a new product that exhibits a cyclic voltammogram consistent with the formation of (terpy)Re(Br)(PPh₃)(η^2 -benzaldehyde). Again, isolation of a new product was only possible after in situ addition of 'BuNC or PMe3. Isolation of trans-[(terpy)- $(L)_2 \operatorname{Re}(\eta^2 \operatorname{-benzaldehyde}) [OTf] \{L = {}^{t}\operatorname{BuNC} (\mathbf{6}); \operatorname{PMe}_3\}$ (7)} was achieved in 80 and 93% yield, respectively (Scheme 2). Upfield chemical shifts for the aldehydic proton and the carbonyl carbon in the ¹H and ¹³C NMR spectra are diagnostic for dihapto-coordinated aldehyde ligands.^{4a} Resonances at 6.65 and 6.75 ppm (¹H NMR spectrum) are assigned to the aldehyde protons of 6 and 7, respectively, and the ¹³C NMR spectra show upfield chemical shifts for the carbonyl carbons (6, 86.1 ppm; 7, 83.6 ppm).

Reactions with Ketones. The ability of the electronrich *trans*-{(terpy)(L)₂Re}⁺ fragment to bind olefins and benzaldehyde in an η^2 fashion prompted our exploration into the coordination of ketones. Specifically, we sought to probe the π -basicity of the rhenium metal center by comparing the proclivity for π versus σ binding of alkyl and aryl ketones.

Magnesium reduction of **2** in neat acetone yields $(terpy)(Br)(PPh_3)Re(\eta^2-acetone)$ (8; Scheme 2). Rotation of the ketone is hindered on the time scale of the NMR experiment as indicated by two resonances in the ¹H NMR spectrum for the methyl substituents of the acetone ligand. While sterics may contribute to this hindered rotation, it is likely that the $d\pi$ orbital discrepancy caused by back-bonding with the terpy and phosphine ligands contributes significantly to the rotational barrier. The ketone ligand of 8 is labile. An acetone- d_6 solution of **8** slowly exchanges the protioacetone ligand with the deuterated solvent. Thus, over time the resonances for the bound ligand disappear, and incipient resonances for free acetone are observed. Resonances for partially deuterated species due to proton exchange were not observed.

In situ reaction of 8 with 'BuNC or PMe₃ results in the displacement of PPh₃ and bromide (Scheme 2). In neither case is the displacement of acetone observed. Spectral features for *trans*-[(terpy)('BuNC)₂Re(η^2 -acetone) [OTf] (9) and trans-[(terpy)(PMe₃)₂Re(η^2 -acetone)]-[OTf] (10) are similar to those of 8. The ¹³C NMR spectra for 9 and 10 indicate resonances for the bound carbonyl carbons at 89.6 and 88.7 ppm, respectively. A notable difference from complex 8 is the equivalence of the methyl groups of the acetone ligand in the ¹H NMR spectra of 9 and 10. This equivalence is consistent with coordination of acetone in the plane of the terpy ligand. NOE enhancements are observed between the methyl resonances of the ketone and one of the terpy protons (21% for 9; 16% for 10). For complex 10, interactions are noted between the methyl groups of the PMe₃ ligand and the acetone ligand (5%) and between the phosphine ligands and terpy protons (4%).

The dihapto-coordinated acetophenone complexes trans-[(terpy)(L)₂Re(η^2 - π)](OTf) (L = 'BuNC or PMe₃; π = acetophenone (**11**, **12**)) can be prepared by reaction sequences similar to the preparation of **9** and **10** (Scheme 2). The (terpy)(Br)(PPh₃)Re(η^2 -acetophenone) intermediate can be observed with electrochemical experiments; however, unlike complex **8**, this putative complex eluded isolation. The trans-{(terpy)(L)₂Re}⁺ fragments have also been observed spectroscopically (¹H NMR) to form stable complexes with benzophenone and 2-butanone, although detailed characterization of these complexes was frustrated by the presence of impurities.

The observation of (terpy)Re(Br)(PPh₃)(η^2 -cyclopentene) (3) and $(terpy)Re(Br)(PPh_3)(\eta^2-acetone)$ (8) and their facile conversion to *trans*-[(terpy)(L)₂Re(π)][OTf] $(\pi = \text{cyclopentene or acetone}; L = {}^{t}\text{BuNC}, 4, 9; L =$ PMe₃, **5**, **10**) provides direct evidence for the mechanism of formation of the dihapto-coordinated complexes (Scheme 4). A single electron reduction of trans-[Re- $(terpy)(Br)(PPh_3)_2[OTf]$ (2) with Mg results in the loss of a single phosphine ligand and coordination of the unsaturated organic ligand (π) to yield (terpy)Re(Br)- $(PPh_3)(\eta^2 - \pi)$. It is difficult to discern between initial loss of bromide followed by coordination of π and displacement of a phosphine ligand by bromide (path A) and the other possible route, simple loss of phosphine, rearrangement, and coordination of π (path B). In situ reaction of $(terpy)Re(Br)(PPh_3)(\pi)$ with excess ^tBuNC or PMe₃ yields *trans*-[(terpy)(L)₂Re(η^2 - π)][OTf] (L = ^tBuNC, PMe₃). The nature of the halide ligand seemingly plays

Scheme 4. Possible Mechanisms for the Replacement of PPh₃ by π (where π = Olefin, Ketone, or Aldehyde; L = PMe₃, 'BuNC)



a vital role in these reactions. If bromide is replaced with chloride, access to *trans*-[(terpy)(L)₂Re(η^2 - π)][OTf] complexes is lost.¹²

Solid-State Structural Studies. Single-crystal Xray diffraction studies have provided geometric details of the solid-state structures of *trans*-[(terpy)('BuNC)₂Re-(η^2 -cyclopentene)][OTf] (**4**) and *trans*-[(terpy)('BuNC)₂Re-(η^2 -acetophenone)][OTf] (**11**). ORTEP diagrams for **4** and **11** are depicted in Figures 1 and 2, and relevant crystallographic data and collection parameters and selected bond lengths and angles are presented in Tables 1 and 2.

The structure of **4** is consistent with the assigned stereochemistry (vide supra), including coordination of cyclopentene in the plane of the terpy ligand with trans 'BuNC ligands (Figure 1). The olefinic C–C bond length of 1.46 Å is elongated from that of unbound cyclopentene (1.39 Å). The increase in bond length is indicative of metal back-bonding into the π^* orbital of the olefinic ligand. The cyclopentene ligand is complexed in an approximately symmetrical fashion. The rhenium– carbon bond distances of 2.21 and 2.22 Å are typical of rhenium–olefin complexes.¹³ The bond distances from rhenium to the terpy nitrogen atoms cis to cyclopentene are longer than the coordinated nitrogen juxtaposed trans to the olefin ligand (2.166(9) and 2.148(9) Å vs 2.04(1) Å).

The structure of **11** confirms the designated π bonding of the ketone ligand (Figure 2). The C–O bond length



Figure 1. ORTEP diagram for the complex *trans*-[Re-(terpy)('BuNC)₂(η^2 -cyclopentene)][OTf] (**4**).



Figure 2. ORTEP diagram for the complex *trans*-[Re-(terpy)(^{*t*}BuNC)₂(η^2 -acetophenone)][OTf] (**11**).

of 1.37 Å is increased from unbound acetophenone (1.26 Å).¹⁴ As with complex **4**, the coordination of the unsaturated organic molecule occurs in the plane of the terpy ligand, leaving the isonitrile ligands in a trans configuration. The Re–C(1) bond length is 2.17 Å, while the Re–O₁ distance is 2.02 Å. Direct comparison of the structural features of **11** with other rhenium–ketone complexes is difficult due to a lack of such examples. However, the rhenium–carbon and rhenium–oxygen bond lengths are similar to those reported for a series of rhenium η^2 -aldehyde complexes.⁶ As is observed with

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⁽¹⁴⁾ The C–O bond length is similar to other reported distances for η^2 -ketones. See, for example, refs 9b, 9c, 9e, 9j, and 9l.

Table 1	. Selected	Crystall	ographic	Data f	or
[Re(terpy)	('BuNC)2()	² -cyclope	entene)][() (4) and
[Re(terpy	('BuNC)2	$(\eta^2 - aceto)$	phenone)	[OTf]	(11)

	· · ·	
	[Re(terpy)('BuNC) ₂ (η ² -cyclopentene)] [OTf]•Et ₂ O (4)	$\begin{array}{l} [{\rm Re(terpy)}({}^{\prime}{\rm BuNC})_2 \\ (\eta^2 \text{-acetophenone})] \\ [{\rm OTf}] \ (11) \end{array}$
formula	C ₃₅ H ₄₇ N ₅ F ₃ O ₄ SRe	C ₃₄ H ₃₇ N ₅ F ₃ O ₄ SRe
mol wt	877.05	854.96
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	P1 (No. 2)
a, Å	14.266(3)	11.534(5)
<i>b</i> , Å	15.801(5)	16.597(7)
<i>c</i> , Å	17.482(5)	9.805(4)
α, deg	90	103.03(3)
β , deg	107.76(2)	94.90(3)
γ , deg	90	103.13(3)
$V, Å^3$	3758(3)	1762(3)
Ζ	4	2
$D_{\rm calcd}$, g cm ⁻³	1.55	1.61
cryst dimens,	$0.38\times0.32\times0.11$	$0.32\times0.23\times0.46~\text{mm}$
mm		
temp, °C	-120	-120
radiation	0.710 69	0.710 69
(λ, Å)		
2θ max, deg	46	46
μ(Μο Κα),	33.85	36.08
cm ⁻¹		
R	0.047	0.056
R	0.060	0.072

Table 2. Selected Bond Distances and Angles for $[Re(terpy)(BuNC)_2(\eta^2-cyclopentene)][OTf]$ (4) and $[Re(terpy)(BuNC)_2(\eta^2-acetophenone)][OTf]$ (11)

4		11	11				
Bond Distances (Å)							
Re-C1	2.22(1)	Re-C1	2.17(1)				
Re-C2	2.21(1)	Re-O1	2.024(7)				
Re-N1	2.166(9)	Re-N1	2.13(1)				
Re-N2	2.04(1)	Re-N2	2.03(1)				
Re-N3	2.148(9)	Re-N3	2.152(9)				
Re-C21	2.06(1)	Re-C24	2.09(1)				
Re-C26	2.05(1)	Re-C29	2.09(1)				
C1-C2	1.46(2)	C1-01	1.37(1)				
Bond Angles (deg)							
C1-Re-C21	83.4(5)	C1-Re-C24	90.3(4)				
C2-Re-C21	85.5(5)	O1-Re-C24	93.6(4)				
C1-Re-C26	95.6(5)	C1-Re-C29	89.9(4)				
C2-Re-C26	90.7(4)	O1-Re-C29	94.5(4)				
C1-Re-N1	86.3(4)	C1-Re-N1	92.0(4)				
C2-Re-N1	124.9(4)	C1-Re-N2	165.6(4)				
C1-Re-N2	160.0(4)	C1-Re-N3	117.9(4)				
C2-Re-N2	160.3(4)	O1-Re-N1	129.8(3)				
C1-Re-N3	123.9(4)	O1-Re-N2	154.0(4)				
C2-Re-N3	85.4(4)	O1-Re-N3	80.3(3)				
N1-Re-N3	149.7(4)	N1-Re-N3	149.6(3)				
N1-Re-N2	74.1(4)	N1-Re-N2	75.2(4)				
N2-Re-N3	75.7(4)	N2-Re-N3	75.7(4)				
N1-Re-C21	90.3(4)	N1-Re-C24	82.8(4)				
N1-Re-C26	94.6(4)	N1-Re-C29	84.3(4)				
N2-Re-C21	100.6(5)	N2-Re-C24	81.7(4)				
N2-Re-C26	82.0(4)	N2-Re-C29	95.2(4)				
N3-Re-C21	92.5(4)	N3-Re-C24	101.8(4)				
N3-Re-C26	84.0(4)	N3-Re-C29	89.5(5)				
Re-C1-C5	120.8(8)	Re-C1-C8	118.5(8)				
Re-C2-C3	119.2(8)	Re-C1-C2	121.4(8)				

the cyclopentene complex **4**, the rhenium-nitrogen bond distance trans to the unsaturated organic ligand is shorter than the distance to the cis nitrogen atoms (2.13-(1) and 2.152(9) Å vs 2.03(1) Å).

Although it is sterically the least favorable position, coordination in the plane of the terpy ligand is observed for all of the dihapto-coordinated complexes. The fact that the unsaturated organic compounds bind in this sterically hindered position reflects a strong electronic Scheme 5. Molecular Orbital Diagram for Complexes of the Form $[\text{Re}(\text{terpy})(L)_2(\pi)]^+$ (where π = Olefin, Ketone, or Aldehyde; L = PMe₃, 'BuNC)



 Table 3. Cyclic Voltammogram Data for Selected

 Complexes

complex	Re(II/I) ^a	$Re(I/0)^a$
[Re(terpy)(^{<i>t</i>} BuNC) ₂ (η^2 -cyclopentene)][OTf] (4) ^{<i>b</i>}	0.52	-1.38
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2 - \text{cyclopentene})][\text{OTf}] (5)^b$	0.22	-1.42
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2 - \text{benzaldehyde})][\text{OTf}] (7)^c$	0.28	-1.44
(terpy)Re(Br)(PPh ₃)(η^2 -acetone) (8) ^c	-0.04^{d}	-1.38
$[\text{Re(terpy)}(BuNC)_2(\eta^2 - \text{acetone})][OTf] (9)^b$	0.46^{d}	-1.42
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2 - \text{acetone})][\text{OTf}] (10)^c$	0.08^{d}	-1.46
$[Re(terpy)(BuNC)_2(\eta^2-acetophenone)][OTf]$ (11) ^c	0.34	-1.32
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2 - \text{acetophenone})][\text{OTf}]$ (12) ^c	0.22^{d}	-1.42

^a Volts vs NHE. ^b In DMA. ^c In acetone. ^d Reported for E_{p,a}.

preference for binding in the plane of the terpy ligand. All of the canonical $d\pi$ orbitals will be filled in these Re(I) d⁶ complexes. If the terpy ligand is assigned to reside in the *xy* plane, both d_{yz} and d_{xz} orbitals will participate in back-bonding with the polypyridyl ligand (Scheme 5). Back-bonding with the isonitrile and phosphine ligands will further stabilize the d_{xz} and d_{yz} orbitals. The HOMO of the {(terpy)Re(L₂)}⁺ fragment would then be the d_{xy} orbital. Thus, binding of π in the *xy* plane would allow maximum $d\pi$ metal-to-ligand bonding.

Electrochemistry. Electrochemical experiments provide a convenient analytical technique for characterization of these complexes. Table 3 provides a list of the (II/I) and (I/0) reduction potentials for complexes 4-5 and 7-12. The (I/0) reduction potentials are relatively invariant over the series of complexes. Thus, we attribute these couples to ligand-centered (terpy) reductions. Given the poor donating abilities of ketones, the metal-to-ligand π back-bonding interaction is vital to the stability of the η^2 -ketone complexes. Therefore, it is not surprising that a single-electron oxidation of the Re^I ketone complexes results in a destabilization of the dihapto-coordinated ketone. In accord with this, the (II/ I) oxidation couples for complexes 8-10 and 12 are irreversible on the time scale of the cyclic voltammogram experiment ($\nu = 50-200$ mV/s). In contrast to the ketone complexes, the cyclopentene complexes 4 and 5 exhibit reversible (II/I) oxidation waves. The better donating ability of the cyclopentene ligand compared to the ketone ligands and the absence of lone electron pairs capable of η^1 binding likely contribute to the increased stability of the Re(II) olefin complex compared to its ketone analogues. Interestingly, while the II/I couple for the PMe₃ complex *trans*-[(terpy)(PMe₃)₂Re(η^2 -acetophenone) [OTf] (12) is irreversible, trans-[(terpy)- $(^{t}BuNC)_{2}Re(\eta^{2}-acetophenone)][OTf]$ (11) has a reversible (II/I) oxidation couple. The electron-withdrawing aryl group lowers the energy of the π^* orbital and decreases the $d\pi - \pi^*$ energy gap. As a result, π back-bonding is expected to be more efficient with aryl ketones due to better orbital overlap. It is possible that π back-bonding is operative even for the oxidation product of 11 and that this factor is responsible for an apparent increase in stability compared to acetone. Inconsistent with this hypothesis is the observation that when the 'BuNC ligands are replaced with a weaker π -acid (PMe₃), the II/I oxidation couple becomes irreversible. Apparently, the increased steric bulk of the phosphine ligands relative to isonitrile destabilizes the Re(II) complex of 12.

The effect of the relative π -acceptor abilities of 'BuNC versus PMe₃ is seen by comparing the (II/I) oxidation potentials for pairs of complexes that differ only in their axial ligands. For example, *trans*-[Re(terpy)('BuNC)₂- $(\eta^2$ -cyclopentene)][OTf] (**4**) shows a (II/I) reduction potential 300 mV higher than *trans*-[Re(terpy)(PMe₃)₂- $(\eta^2$ -cyclopentene)][OTf] (**5**) (0.52 V versus 0.22 V). This difference in potential is consistent with the greater π -acidity of the isonitrile ligand versus PMe₃. Aldehydes are generally considered to be superior π -acids when compared to ketones (vide supra), and the positive shift for $E_{p,a}$ for the benzaldehyde complex for a compared to the complexes is consistent with this notion.

Ligand Exchange. As mentioned above, an acetone d_6 solution of (terpy)(Br)(PPh₃)Re(η^2 -acetone) (8) undergoes acetone ligand exchange. Partially deuterated acetone (free or bound) was not observed. Thus, ligand exchange is invoked to explain the disappearance of the bound acetone signals rather than proton exchange. In contrast to 8, even upon heating, the dihapto-acetone complexes 9 and 10 do not undergo analogous exchange reactions. The acetophenone ligand of complexes 11 and 12 is labile, as evidenced by the appearance of free acetophenone and the formation of trans-[Re(terpy)(L)2- $(\eta^2$ -acetone- d_6][OTf] (L = ^{*t*}BuNC or PMe₃) in an acetoned₆ solution. In a ¹H NMR experiment, treatment of **11** or **12** with cyclopentene yields the corresponding η^2 cyclopentene product. In contrast, the benzaldehyde complexes 6 and 7 show no signs of ligand exchange.

Ligand exchange reactions can in some cases be oxidatively catalyzed. For example, *trans*-[Re(terpy)-('BuNC)₂(η^2 -acetone)][OTf] (9) shows no signs of exchange in an acetone- d_6 solution after several days at 20 °C. But, addition of a catalytic amount of [Cp₂Fe]-[PF₆] (Cp = cyclopentadienyl) results in rapid incorporation of acetone- d_6 into the coordination sphere (less than 1 h to >95% completion). This exchange is likely the result of a mechanism similar to that elucidated for the {Os(NH₃)₅}²⁺ system.^{9h} Here, the catalyst oxidizes the d⁶ metal to its d⁵ configuration where an η^2 to η^1 linkage isomerization takes place. Once in its η^1 form, rapid ligand exchange may take place. Reversing this sequence of reactions reforms the catalyst.

Scheme 6. Methylation of an η^2 -Acetone Ligand by CH₃OTf



Scheme 7. Resonance Structures for the Methyl Acetonium Complex 13



Electrophilic Addition. The electron-rich trans- $[(terpy)(L)_2 Re]^+$ (L = ^tBuNC, PMe₃) functions as a potent π base, as evidenced by its ability to bind unsaturated organic molecules in an η^2 fashion. Electron donation from a metal $d\pi$ orbital to dihapto-coordinated moieties can serve to activate the η^2 ligands toward electrophilic attack. Reaction of *trans*-[(terpy)(${}^{t}BuNC$)₂Re(η^{2} -acetone)[[OTf] (9) with MeOTf yields the η^2 -ketonium complex trans-[(terpy)($^{t}BuNC$)₂Re{ η^{2} -(CH₃)₂C(OMe)}][OTf]₂ (13) (Scheme 6). A similar methylation has been observed for aldehyde complexes of pentaammineosmium-(II).¹⁵ Complex **13** could be structurally described by several different forms. The actual structure is likely somewhere along the continuum between the two bonding extremes shown in Scheme 7. The methylated acetone ligand in structure **I** remains bound in an η^2 fashion, while structure **II** represents a formal oxidation at the metal center {from Re(I) to Re(III)} and formation of an η^2 -methoxymethyl complex. The most compelling evidence that structure I dominates is a slight downfield shift for the carbonyl carbon of 13 (92.1 ppm) compared to that of the acetone complex 9 (89.6 ppm). A significant contribution from structure **II** would increase sp³ character for the carbonyl carbon, resulting in an upfield shift. The methyl group on the oxygen resonates at 4.30 ppm in the ¹H NMR spectrum and at 67.9 ppm in the ¹³C NMR spectrum. The equivalence of the ketone methyl groups and of the 'BuNC ligands in the NMR spectra of 13 suggests that a fluxional process is occurring that is rapid on the time scale of the NMR experiments. Apparently the methyl group on the oxygen undergoes a wiperlike inversion at oxygen that is rapid relative to the NMR time scale.

Conclusions

The complex *trans*-[Re(terpy)(PPh₃)₂Br]OTf has proven to be a versatile precursor to the fragments *trans*-

⁽¹⁵⁾ For similar reactions with $[(NH_3)_5Os(\eta^2-aldehyde)]^{2+}$ complexes, see: Spera, M. L.; Chen, H.; Moody, M. W.; Hill, M. M.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 12772.

{(terpy)(L)₂Re}⁺ (L = 'BuNC or PMe₃). These metal systems show exceptional π -donor ability, as is demonstrated by their propensity toward η^2 -coordination of unsaturated organic molecules and by the reactivity of one of these products, *trans*-[Re(terpy)('BuNC)₂(η^2 -acetone)]OTf, with methyl triflate.

Experimental Section

General Methods. Unless otherwise noted. all reactions were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. ¹H and ¹³C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer at room temperature. All chemical shifts are reported in ppm and are referenced to TMS using residual ¹H signals and to the ¹³C signals of the deuterated solvents. Coupling constants are given in hertz. Electrochemical experiments were performed under a nitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded (Kipp and Zonen BD90 XY recorder) in a standard three-electrode cell from +1.50 to -2.20 V with a glassy carbon working electrode. All potentials are reported vs NHE using ferrocene ($E_{1/2} = 0.55$ V) or cobaltinium hexafluorophosphate ($E_{1/2} = -0.78$ V) as internal standard. The peak-to-peak separation $(E_{p,a} - E_{p,c})$ was between 70 and 100 mV for all reversible couples. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer. All distillations were performed under a nitrogen atmosphere. Methylene chloride was distilled from P₂O₅; benzene, hexanes, and diethyl ether were distilled from Na/benzophenone ketyl; methanol was distilled from Mg-(OMe)₂ (freshly prepared from Mg activated by elemental iodine); acetonitrile and DMA were distilled from CaH₂; and DME was distilled from Na metal. All solvents were thoroughly purged with nitrogen prior to use. Deuterated solvents were deoxygenated by repeated freeze-pump-thaw cycles.

Re(O)(OEt)(Br)₂(PPh₃)₂ was prepared according to a literature procedure.¹⁶ Magnesium powder (Aldrich, 50 mesh) was activated by treatment with elemental iodine in DME, followed by washing with DMA, acetone, and diethyl ether. All other reagents were used as purchased from commercial sources. Note: Peak assignments for ¹³C NMR spectra of complexes **6**, **7**, **11**, and **13** were complicated by the large number of resonances in the range of approximately 120–150 ppm. Therefore, isochronous resonances resulted in only partial assignment of these spectra.

Abbreviations: DME = 1,2-dimethoxyethane; DMA = N,Ndimethylacetamide; NHE = normal hydrogen electrode; TBAH= tetrabutylammonium hexafluorophosphate; terpy = 2, 2': 6',2"-terpyridine; OTf = trifluoromethanesulfonate (triflate); 'BuNC = *tert*-butylisocyanide.

Re(=**N**−**NC**(**Ph**)**O**−)(**PPh**₃)₂**Br**₂ (1). This synthesis is a modification of a previously reported procedure.¹⁷ A suspension of Re(O)(OEt)(PPh₃)₂Br₃ (42.82 g, 45.96 mmol) and excess PPh₃ (43.64 g, 166.00 mmol) in EtOH (2100 mL) was prepared. In a separate flask, H₂NN(H)C(O)Ph (18.62 g, 136.77 mmol) was suspended in EtOH (100 mL). Concentrated HBr (48%, 23.05 g, 136.77 mmol) was slowly added to the EtOH suspension of H₂NN(H)C(O)Ph, causing total dissolution. Dropwise addition of the H₂NN(H)C(O)Ph/HBr/EtOH solution to the stirring rhenium suspension was made. The reaction solution was refluxed for 1.5 h and then cooled in an ice bath. The precipitate that formed upon cooling was collected by vacuum filtration and was washed with EtOH (2 × 10 mL) and Et₂O (2 × 25 mL). The dark green solid was extracted with hot benzene (~2 L) and filtered from the remaining

orange solid. Solvent removal under reduced pressure yielded a green solid (33.44 g, 73%).

trans-[Re(terpy)(Br)(PPh₃)₂][OTf] (2). Complex 1 (10.64 g, 10.60 mmol) was suspended in a benzene/MeOH (1:1 v/v, \sim 400 mL) mixture. Terpy (2.671 g, 11.45 mmol) was added to this suspension, and the reaction mixture was refluxed for 3 days. The solution color changed from green to black during the period of reflux. The solution was cooled, and the solvent volume was reduced to 35 mL under vacuum. Filtration yielded a dark black solid. The solid was washed with benzene $(3\times4~mL)$ and $Et_2O~(3\times5~mL)$ and dried in vacuo. The black solid has been assigned as trans-[Re(terpy)(Br)(PPh₃)₂][Br] (7.865 g collected, 67%; CV (DMA/TBAH/100 mV/s) $E_{1/2} = 0.52$ V, $E_{1/2} = -0.92$ V vs NHE). A portion of *trans*-[Re(terpy)(Br)-(PPh₃)₂][Br] (3.009 g, 2.72 mmol) was dissolved in MeOH (200 mL). To this solution was added AgOTf (0.701 g, 2.73 mmol) in MeOH (5 mL). A precipitate formed upon addition of the AgOTf. The reaction was stirred for 2 h, and then the solvent volume was brought to approximately 50 mL under reduced pressure. A dark brown precipitate was collected by vacuum filtration and washed with aliquots of MeOH until the washings were brown instead of green. Extraction of the remaining solid with acetone (4 \times 100 mL) was performed until an insoluble gray solid remained. The solvent from the extraction was removed under reduced pressure, and the dark brown residue was collected (2.567 g, 82%). CV (DMA/TBAH/100 mV/ $\,$ s): $E_{1/2} = 0.52$ V, $E_{1/2} = -0.94$ V vs NHE. Anal. Calcd for ReC₅₂H₄₁N₃BrF₃O₃P₂S: C, 53.25; H, 3.52; N, 3.58. Found: C, 53.21; H, 3.83; N, 3.78.

trans-[Re(terpy)('BuNC)₂(η²-cyclopentene)][OTf] (4). A flask was charged with a DMA suspension of trans-[Re(terpy)-(PPh₃)₂Br]OTf (2) (0.100 g) and excess cyclopentene (10 equiv). To the suspension was added excess Mg⁰ (1.3 g). The reaction was stirred vigorously for 15 min, and a color change from brown to green was observed. The Mg⁰ was filtered off and washed with DME (10 mL). The DME wash was combined with the DMA filtrate. The putative (terpy)Re(Br)(PPh₃)(η^2 cyclopentene) (3) can be observed electrochemically ($E_{p,a} = 0.1$ V) but not isolated. Excess 'BuNC (10 equiv) was added, and the reaction was stirred at room temperature for 30 min followed by heating at 60 °C for 15 min. After cooling to room temperature, the reaction mixture was filtered. The filtrate was slowly added to stirring Et₂O (100 mL), and a precipitate formed. The precipitate was collected by vacuum filtration and washed with Et₂O. The resulting solid was dried in vacuo (44% yield). ¹H NMR (acetone-*d*₆, δ): 9.62 (d, 2H), 8.68 (d, 4H), 7.92 (t, 2H), 7.76 (t, 1H), 7.57 (t, 2H), 4.31 (d, 2H), 3.80 (m, 2H), 2.56 (m, 2H), 1.92 (m, 2H), 0.98 (s, 9H), 0.79 (s, 9H). ¹³C NMR (acetone-d₆, δ): 157.0 (2C), 154.9 (2CH), 152.6 (2C), 136.3 (2CH), 132.5 (CH), 127.6 (2CH), 123.7 (2CH), 121.3 (2CH), 66.1 (bound cyclopentene, 2CH), 56.7 ({CH₃}₃CNC), 56.4 ({CH₃}₃-*C*NC), 36.5 (cyclopentene, 2CH₂), 31.6 ({*C*H₃}₃CNC), 31.2 ({*C*H₃}₃CNC), 25.2 (cyclopentene, CH₂), bound 'BuNC carbons not well resolved even at large delay times (9s). CV (DMA/ TBAH/100 mV/s): $E_{1/2} = 0.52$ V, $E_{1/2} = -1.38$ V vs NHE. IR (glaze): $\nu_{CN} = 2029 \text{ cm}^{-1}$. Anal. Calcd for ReC₃₁H₃₇N₅F₃O₃S: C, 46.36; H, 4.65; N, 8.72. Found: C, 45.69; H, 4.80; N, 8.91.

trans-[**Re(terpy)**(**PMe**₃)₂(η^2 -cyclopentene)][**OTf**] (5). The procedure for complex **4** was followed except PMe₃ was used instead of 'BuNC (66% yield). ¹H NMR (acetone- d_6 , δ): 9.83 (d, 2H), 8.55 (overlapping d, 4H), 7.70 (t, 2H), 7.39 (m, 3H), 4.63 (m, 2H), 3.89 (m, 2H), 2.77 (m, 2H), 2.03 (m, 1H), 1.98 (m, 1H), 0.24 (dd, 9H, $J_{PH} = 1$, 8 Hz), 0.12 (dd, 9H, $J_{PH} = 1$, 8 Hz). ¹³C NMR (acetone- d_6 , δ): 153.8 (2C), 152.9 (2CH), 149.9 (2C), 132.3 (2CH), 127.2 (CH), 126.0 (2CH), 122.1 (2CH), 117.6 (2CH), 65.3 (bound cyclopentene, 2CH), 34.6 (cyclopentene, 2CH₂), 26.1 (cyclopentene, CH₂), 9.7 ({ CH_3 }₃P, d, $J_{PC} = 26$ Hz), 5.7 ({ CH_3 }, P, d, $J_{PC} = 26$ Hz). CV (DMA/TBAH/100 mV/s): $E_{1/2} = 0.22$ V, $E_{1/2} = -1.42$ V vs NHE. Anal. Calcd for ReC₂₇H₃₇N₃F₃O₃P₂S: C, 41.11; H, 4.73; N, 5.33. Found: C, 40.43; H, 4.71; N, 4.99.

⁽¹⁶⁾ Chatt, J.; Rowe, G. A. J. Chem. Soc. 1962, 4019.
(17) Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Gupta, V. D. J. Chem. Soc. (A) 1971, 2631.

trans-[Re(terpy)(^tBuNC)₂(η^2 -benzaldehyde)][OTf] (6). Complex 2, trans-[Re(terpy)(Br)(PPh₃)₂][OTf] (0.100 g), was suspended in DMA (1 mL) and MeOH (3 mL). Excess benzaldehyde (10 equiv) was added to the suspension, followed by the addition of excess Zn⁰/Hg⁰ (1.5 g). The reaction was stirred with an observed color change from brown to olive green. After the cyclic voltammagram indicated the disappearance of all of the starting complex (approximately 3 h), the Zn⁰/Hg⁰ was removed by filtration and washed with MeOH (2 mL). The MeOH washing was combined with the DMA/MeOH filtrate. Excess 'BuNC (10 equiv) was added to the filtrate. The reaction was stirred at room temperature for 1 h and then heated overnight at 60 °C. After cooling to room temperature, a precipitate was removed by vacuum filtration and washed with MeOH (3 mL). The combined filtrate was then reduced to an oil. The oil was redissolved in a minimum amount of MeOH (2 mL) and precipitated by slow addition to stirring Et₂O (100 mL). The resulting solid was collected by filtration and dried under vacuum (80% yield). ¹H NMR (acetone- d_6 , δ): 9.98 (d, 1H), 9.78 (d, 1H), 8.76 (overlapping doublets, 4H), 8.08 (t, 1H), 7.88 (t, 1H), 7.80 (t, 1H), 7.64 (m, 4H), 7.31 (t, 2H), 7.04 (t, 1H), 6.65 (s, 1H), 1.03 (s, 9H), 0.57 (s, 9H). ¹³C NMR (acetone d_6, δ): 153.7, 153.4, 153.1, 148.4, 147.7, 147.3, 136.8, 134.1, $130.1,\ 126.9,\ 125.5,\ 125.3,\ 125.1,\ 125.0,\ 122.9,\ 121.8,\ 120.3,$ 119.3 (aromatic C's), 86.1 (bound benzaldehyde, CH), 56.0 ({CH₃}₃*C*NC), 55.3 ({CH₃}₃*C*NC), 29.9 (CH₃), 29.6 (CH₃), 29.2 (CH₃). The product is > 95% pure by ¹H and ¹³C NMR.

trans-[**Re(terpy)(PMe₃)**₂(η^2 -benzaldehyde)][**OTf**] (7). The procedure for complex **6** was followed (PMe₃ used in place of 'BuNC) (93% yield). ¹H NMR (acetone- d_6 , δ): 10.17 (d, 1H), 9.90 (d, 1H), 8.75 (m, 3H), 8.66 (d, 1H), 7.95 (d, 2H), 7.90 (t, 1H), 7.68 (m, 3H), 7.52 (m, 1H), 7.43 (t, 2H), 7.36 (t, 1H), 6.75 (d, 1H), 0.24 (dd, 9H, $J_{PH} = 1$, 8 Hz), -0.16 (dd, 9H, $J_{PH} = 1$, 8 Hz). ¹³C NMR (acetone- d_6 , δ): 152.3 (C), 151.7 (CH), 149.6 (C), 147.5 (C), 147.1 (CH), 146.2 (C), 144.4 (C), 134.9 (CH), 130.5 (CH), 129.0 (CH), 127.6 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 124.3 (CH), 122.8 (CH), 121.2 (CH), 118.8 (CH), 117.0 (CH), 83.6 (bound benzaldehyde, CH), 8.4 ({*C*H₃}, P, d, $J_{PC} = 25$ Hz), 6.1 ({*C*H₃}, P, d, $J_{PC} = 25$ Hz). CV (DMA/TBAH/ 100 mV/s): $E_{1/2} = 0.28$ V, $E_{1/2} = -1.46$ V vs NHE. CV (acetone/TBAH/100 mV/s): $E_{1/2} = 0.28$ V, $E_{1/2} = -1.44$ V vs NHE. The product is > 95% pure by ¹H and ¹³C NMR.

trans-[**Re(terpy)(Br)(PPh₃)**(η^2 -acetone)] (8). Excess Mg⁰ was added to an acetone (3 mL) suspension of *trans*-[Re(terpy)-(PPh₃)₂Br][OTf] (2) (0.100 g). The reaction mixture was stirred for 1 h, during which time the color changed from brown to green. The Mg⁰ was filtered off and washed with acetone (3 mL). The solid was collected upon solvent removal from the filtrate and dried in vacuo (66% yield). ¹H NMR (acetone-*d*₆, δ): 9.82 (d, 1H), 9.48 (d, 1H), 8.58 (d, 1H), 8.28 (d, 1H), 8.12 (d, 1H), 7.71 (d, 1H), 7.39 (m, 2H), 7.29 (t, 1H), 7.18 (m, 6H), 7.11 (m, 1H), 6.95 (m, 6H), 6.62 (t, 1H), 6.55 (m, 3H), 2.61 (s, 3H), 2.41 (s, 3H). CV (acetone/TBAH/100 mV/s): *E*_{p,a} = -0.04 V, *E*_{1/2} = -1.38 V vs NHE. The product is > 95% pure by ¹H NMR.

trans-[Re(terpy)('BuNC)₂(η²-acetone)][OTf] (9). The procedure for the preparation of complex 8 was followed. But, rather than isolating 8 after the acetone wash, excess 'BuNC was added to the filtrate. The reaction mixture was stirred at room temperature for 1 h, then heated to 60 °C for an additional hour. After cooling to room temperature, the reaction mixture was filtered to remove any precipitate. Addition of the filtrate to stirring Et₂O (10 mL) resulted in precipitate formation. The precipitate was discarded (the first precipitate was mostly the N₂ complex, trans-[Re(terpy)(PPh₃)₂(N₂)][OTf]. The remaining filtrate was reduced in volume to 2 mL and then precipitated by dropwise addition to Et₂O (75 mL) followed by the slow addition of hexanes (25 mL). The precipitate was collected by vacuum filtration, washed with Et₂O, and dried in vacuo (66% yield). ¹H NMR (acetone- d_6 , δ): 9.85 (d, 1H), 9.55 (d, 1H), 8.83 (d, 1H), 8.78 (d, 1H), 8.75 (d, 1H), 8.71 (d, 1H), 8.02 (t, 1H), 7.90 (t, 1H), 7.74 (t, 1H), 7.65 (t, 1H), 7.60 (t, 1H), 2.60 (s, 6H), 0.86 (s, 18H). ¹³C NMR (acetone- d_6 , δ): 153.6 (C), 153.3 (C), 152.2 (CH), 148.3 (C), 148.2 (C), 148.1 (CH), 139.4 (d, C, $J_{PC} = 13$ Hz), 136.4 (CH), 134.1 (CH), 129.2 (CH), 125.8 (CH), 124.7 (CH), 122.9 (CH), 121.4 (CH), 120.3 (CH), 119.2 (CH), 89.6 (bound acetone, C), 55.5 ({CH}_3)_3CNC), 30.2 (CH}_3), 29.4 (CH}_3). CV (DMA/TBAH/100 mV/s): $E_{p,a} = 0.46$ V, $E_{1/2} = -1.42$ V vs NHE. IR (glaze): $\nu_{CN} = 2083$ cm⁻¹. Anal. Calcd for ReC₂₉H₃₅N₅F₃O₄S: C, 43.93; H, 4.45; N, 8.83. Found: C, 44.22; H, 4.52; N, 8.68.

trans-[**Re(terpy)(PMe₃)**₂(η^2 -acetone)][**OTf**] (10). The procedure for complex **9** was followed except PMe₃ was used in place of 'BuNC (61% yield). ¹H NMR (acetone- d_6 , δ): 9.98 (d, 1H), 9.59 (d, 1H), 8.74 (overlapping d, 3H), 8.59 (d, 1H), 7.84 (t, 1H), 7.64 (m, 2H), 7.46 (t, 1H), 7.27 (t, 1H), 2.52 (s, 6H), 0.21 (t, 18H, $J_{PH} = 3$ Hz). ¹³C NMR (acetone- d_6 , δ): 154.3 (C), 152.2 (CH), 151.3 (C), 148.1 (CH and C overlapping), 145.7 (C), 136.3 (CH), 131.6 (CH), 126.3 (CH), 125.4 (CH), 125.1 (CH), 124.3 (CH), 122.0 (CH), 120.3 (CH), 118.4 (CH), 88.7 (bound acetone, C), 33.0 (acetone, CH₃), 9.4 ({ CH_3 }₃P, t, $J_{PC} = 2$ Hz). CV (DMA/TBAH/100 mV/s): $E_{p,a} = 0.12$ V, $E_{1/2} = -1.44$ V vs NHE. CV (acetone/TBAH/100 mV/s): $E_{1/2} = 0.08$ V, $E_{1/2} = -1.46$ V vs NHE. Anal. Calcd for ReC₂₅H₃₅N₃F₃O₄P₂S: C, 38.56; H, 4.53; N, 5.40. Found: C, 38.65; H, 4.90; N, 5.28.

trans-[**Re(terpy)**('**BuNC**)₂(η^2 -acetophenone)][**OTf**] (11). The procedure for complex **6** was followed, except acetophenone was used in place of benzaldehyde (68.0% yield). ¹H NMR (acetone- d_6 , δ): 10.09 (d, 1H), 9.87 (d, 1H), 8.70 (overlapping d, 4H), 8.06 (t, 2H), 7.84 (m, 2H), 7.70 (d, 2H), 7.68 (t, 1H), 7.30 (m, 2H), 7.03 (t, 1H), 2.80 (s, 3H), 0.94 (s, 9H), 0.50 (s, 9H). ¹³C NMR (CD₃CN, δ): 153.5 (C), 152.8 (C), 151.9 (CH), 151.5 (C), 148.3 (C), 148.0 (CH), 147.7 (C), 136.6, 134.2, 129.9, 126.8, 125.6, 125.2, 125.0, 124.7, 122.7, 121.4, 120.0, 119.0 (CH), 88.5 (bound acetophenone, C), 55.9 ({CH₃}₃*C*NC), 55.1 ({CH₃}₃*C*NC), 29.4 (CH₃), 29.0 (CH₃), 28.6 (CH₃). CV (DMA/TBAH/100 mV/s): $E_{p,a} = 0.42$ V, $E_{1/2} = -1.32$ V vs NHE. CV (acetone/TBAH/100 mV/s): $E_{1/2} = 0.34$ V, $E_{1/2} = -1.32$ V vs NHE. IR (glaze): $\nu_{CN} = 2083$ cm⁻¹. Anal. Calcd for ReC₃₄H₃₇N₅F₃O₄S: C, 47.77; H, 4.36; N, 8.19. Found: C, 47.21; H, 4.40; N, 7.61.

trans-[**Re(terpy)**(**PMe**₃)₂(η^2 -acetophenone)][**OTf**] (12). The procedure for complex **6** was followed (PMe₃ used in place of 'BuNC) (46% yield). ¹H NMR (acetone- d_6 , δ): 10.49 (d, 1H), 9.94 (d, 1H), 8.78 (d, 1H), 8.75 (d, 1H), 8.70 (d, 1H), 8.69 (d, 1H), 7.88 (t, 1H), 7.74 (t, 1H), 7.68 (m, 3H), 7.34 (m, 2H), 7.18 (m, 2H), 6.95 (m, 1H), 2.85 (s, 3H), 0.30 (d, 9H), -0.37 (d, 9H). ¹³C NMR (acetone- d_6 , δ): 153.9, 152.8, 151.9, 149.3, 147.1, 147.0, 144.8, 135.4, 131.7, 130.7, 129.0, 128.1, 127.6, 125.6, 125.3, 124.8, 124.1, 123.0, 120.9, 118.9, 117.0 (aromatic C), 86.8 (bound acetophenone, t, $J_{PC} = 4$ Hz), 31.6 (acetophenone CH₃), 8.5 ({ CH_3 }₃P, d, $J_{PC} = 25$ Hz), 8.0 ({ CH_3 }₃P, d, $J_{PC} = 25$ Hz). CV (acetone/TBAH/100 mV/s): $E_{p,a} = 0.22$ V, $E_{1/2} = -1.42$ V vs NHE. Anal. Calcd for ReC₃₀H₃₇N₃F₃O₄P₂S: C, 42.85; H, 4.44; N, 5.00. Found: C, 42.64; H, 4.37; N, 5.67.

trans-[Re(terpy)(^tBuNC)₂(η^2 -acetone(Me))][OTf]₂ (13). 2,6-Di-tert-butylpyridine (0.018 g) was added to an acetonitrile solution of trans-[(terpy)(tBuNC)₂Re(η^2 -acetone)][OTf] (9) (0.022 g). The solution was cooled to -35 °C, and MeOTf (0.021 g) was added. Upon warming to room temperature, a color change from purple to orange was noted. Slow addition of Et₂O (50 mL) yielded an orange precipitate. The orange solid was collected by vacuum filtration, washed with Et₂O, and dried in vacuo (75% yield). ¹H NMR (CD₃CN, δ): 9.18 (d, 1H), 8.76 (d, 1H), 8.65 (d, 1H), 8.61 (d, 1H), 8.54 (d, 1H), 8.51 (d, 1H), 8.08 (t, 1H), 8.00 (t, 1H), 7.97 (t, 1H), 7.76 (m, 2H), 4.30 (s, 3H), 2.60 (s, 6H), 0.90 (s, 18H). ¹³C NMR (acetone- d_6 , δ): 153.3, 150.6, 149.0, 148.8, 139.5 (CH), 138.5 (CH), 137.6 (CH), 127.6 (CH), 127.3 (CH), 124.7 (CH), 124.1 (CH), 121.8 (CH), 92.1 (bound ketonium C), 67.9 (*O*-bound CH₃), 56.8 ({CH₃}₃*C*NC), 29.0 (CH₃), 28.9 (CH₃).

Crystal Structure of *trans*-[**Re**(terpy)('**BuNC**)₂(η^2 **cyclopentene**)][**OTf**]·**Et**₂**O** (4). A dark purple plate of dimensions $0.38 \times 0.32 \times 0.11$ mm was grown by diffusion of diethyl ether into an acetone solution of **4**. The crystal was determined to be of monoclinic symmetry (P_{21}/n , No. 14) with the following cell dimensions (λ (Mo) = 0.710 69 Å): a = 14.266(3) Å; b =15.801(5) Å; c = 17.482(5) Å; $\beta = 107.76(2)^{\circ}$; Z = 4; V = 3758-(3) Å³; $F_w = 877.05$ ($C_{35}H_{47}N_5O_4F_3SRe$); $D_{calc} = 1.55$ g/cm³. Data were collected at -120 °C on a Rigaku AFC6C diffractometer as outlined in Table 1. A total of 5672 data were collected with 5455 unique reflections and 3323 reflections with $I > 3\sigma(I)$. The error fit was 1.79 and final R = 0.047 ($R_w = 0.060$). Empirical absorption corrections were applied using the ψ scan method with a range of transmission factors of 0.42-1.00.¹⁸

Crystal Structure of *trans*-[**Re(terpy)**('**BuNC**)₂(η^2 -ac**etophenone**)][**OTf**] (11). A black block (0.32 × 0.23 × 0.46 mm) was grown from diethyl ether diffusion into an acetone solution of 11. The crystal was determined to be triclinic (*P*1, No. 2) with the following cell dimensions (λ (Mo) = 0.71069 Å): a = 11.534(5) Å; b = 16.597(7) Å; c = 9.805(4) Å; $\alpha =$ 103.03(3)°; $\beta = 94.90(3)$ °; $\gamma = 103.13(3)$ °; Z = 2; V = 1762(3) Å³; $F_{\rm w} = 854.96$ ($C_{34}H_{37}N_5O_4F_3SRe$); $D_{\rm calc} = 1.61$ g/cm³. Data were collected on a Rigaku AFC6C diffractometer at -120 °C. A total of 5200 reflections were measured with 4898 unique reflections and 3938 reflections with $I > 3\sigma(I)$. The error fit was 2.27 and final R = 0.056 ($R_{\rm w} = 0.072$). Empirical absorption corrections were applied using the ψ scan method with a range of transmission factors of 0.31-1.00.

Acknowledgment is made to the National Science Foundation (NSF Young Investigator Program) and the Alfred P. Sloan Foundation for their generous support of this work.

Supporting Information Available: Tables containing complete positional and thermal parameters, bond lengths, and bond angles for **4** and **11** (19 pages). Ordering information is given on any current masthead page.

OM980500P