Inorg. Chem. **1995**, *34*, 2033−2041 **2033**

Rhenium(I) Coordination Chemistry: Synthesis, Reactivity, and Electrochemistry of Terpyridyl Complexes

Lisa E. Helberg, Joseph Barrera, Michal Sabat, and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received October 28, 1994[⊗]

The compound [Re^{II}(terpy)(PPh$_3$)$_2$Cl]$^+$ (with counterion Cl$^-$ (**I**) or OTf$^-$ (**II**)) has proven to be a useful synthon in the synthesis of a series of Re(I) and Re(III) compounds. Compound **I** can be oxidized in the presence of Cl$^-$ to form [Re^{III}(terpy)(PPh$_3$)Cl$_2$]$^+$ (**IV**) or Re^{III}(terpy)Cl$_3$ (**V**). Compound **II** can be reduced in the presence of cyclohexenone to form Re^{I}(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**). The chloride on compound **VI** undergoes facile substitution to form a series of Re(I)−terpyridyl derivatives (**VII**−**XIII**). The electrochemistry of these compounds has been studied and compared to that of other known rhenium compounds using an electrochemical parametrization model. A correlation is drawn between the number and strength of π-acidic ligands and the deviations of the observed II/I reduction potentials from the predicted values. An X-ray crystal structure determination for **II** is also reported. [Re^{II}(terpy)(PPh$_3$)$_2$Cl]OTf (**II**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $Z = 2$ and lattice parameters $a = 14.552(7)$ Å, $b = 15.726(7)$ Å, $c = 12.215(3)$ Å, $\alpha = 109.09(2)°$, $\beta = 96.98(3)°$, and $\gamma = 98.42(4)°$ at -80 °C.

Introduction:

The electron-rich pentaammineosmium(II) moiety shows a remarkable tendency to form stable η^2-complexes with aromatic molecules.[1] The ability of this coordination mode to activate an aromatic substrate toward novel synthetic chemistry has been demonstrated for a variety of complexes such as η^2-arenes, η^2-pyrroles, and η^2-furans.[2] An isoelectronic rhenium(I) system with a similar affinity for aromatic molecules could extend this *dearomatization* methodology to other transition metals.

One of our objectives in developing a coordination chemistry of low-valent rhenium that might be amenable to η^2-binding of aromatic molecules is to minimize the use of strong π-acids (e.g. CO, CNR, NO$^+$) since these ligands would compromise the strong back-bonding interaction necessary to stabilize the π-interaction between the metal and an aromatic molecule.[3] With the notable exception of the Re^{I}(N$_2$)L$_5$ complexes, where L = PR$_3$ or Cl,[4] the chemistry of Re(I) is presently dominated by electron-deficient compounds containing a number of strong π-acids.[5] Wishing to keep the octahedral geometry, low steric profile, and good σ-donor properties of the pentaammineosmium(II) ligand set, we desired a series of Re(I)−terpyridyl complexes.

For other low-valent transition metals (e.g. Os(II), Ru(II)), complexes containing polypyridyl ligands have demonstrated interesting photophysical[6] and electrochemical properties,[6a,7] yet surprisingly, compounds of Re(I) or Re(II) containing terpyridyl ligands are virtually unknown. To date, the only reported complexes containing an η^3-bound terpy ligand[8] on rhenium are [Re^{III}(terpy)$_2$X]$^{2+}$ (X = Cl, OH, NCS),[9] [Re^{V}O(terpy)(SC$_6$H$_4$-CH$_3$)$_2$]$^+$,[10] and Re^{I}(terpy)(CO)$_2$Br.[11] Herein, we report the first reactions of Re(I) and Re(II) complexes containing an η^3-bound terpy ligand as well as the first structural analysis of a Re^{II}-(terpy) complex. The terpyridyl ligand is found to stabilize rhenium(I) to such an extent that more conventional π-acids (i.e CO, CNR), usually needed to stabilize the electron-rich, low-valent rhenium center, are no longer required.

Abbreviations. ETPB = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane; tBuNC = *tert*-butyl isocyanide; tBupy = 4-*tert*-butylpyridine; terpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine; DMA = dimethylacetamide; TBAH = tetrabutylammonium hexafluorophosphate; OTf = trifluoromethanesulfonate (triflate); [PPN]Cl = bis(triphenylphosphoranylidene)ammonium chloride; DAB = 1,2-diaminobenzene; en = ethylenediamine; diphos = diphenylphosphinoethane; ampy =

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725. Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.

(2) For examples see: Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972. Kopach, M. E.; Kelsh, L. P.; Stork, K. C.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 5322. Hodges, L. M.; Koontz, J. I.; Gonzalez, J.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1993**, *58*, 4788. Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857. Chen, H.; Hodges, L. M.; Lui, R.; Stevens, W. C., Jr.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 5499.

(3) For an example of an amine-rich Re(I) system, see: Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026.

(4) Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Gupta, V. D. *J. Chem. Soc. A* **1971**, 2631. Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612.

(5) Casey, C. P. *Science* **1993**, *259*, 1552. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1994**, *131*, 127. Lewis, H. C., Jr.; Storhoff, B. N. *J. Organomet. Chem.* **1972**, *43*, 1.

(6) (a) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993. (b) Yip, H.; Che, C.; Zhou, Z.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, *18*, 1369. (c) Constable, E. C.; Thompson, A. M. C.; Armaroli, N.; Balzani, V.; Maestri, M. *Polyhedron* **1992**, *11*, 2707.

(7) Arana, C.; Yan, S.; Keshavarz, K. M.; Potts, K. T.; Abruna, H. D. *Inorg. Chem.* **1992**, *31*, 3680. Wilcox, B. E.; Deutsch, E. *Inorg. Chem.* **1991**, *30*, 688.

(8) An example of η^2-bound terpy is also known for the complex Re^{I}-(terpy)(CO)$_3$X where X = Cl or Br. Anderson, P. A.; Keene, F. R.; Horn, E.; Tiekink, E. R. T. *Appl. Organomet. Chem.* **1990**, *4*, 523. Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V. *J. Chem. Soc., Chem. Commun.* **1992**, 303. Civitello, E. R.; Dragovich, P. S.; Karpish, T. B.; Novick, S. G.; Bierach, G.; O'Connell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237.

(9) Re(III) is known to form 7-coordinate species: Rall, J.; Weingart, F.; Ho, D. M.; Heeg, M. J.; Tisato, F.; Deutsch, E. *Inorg. Chem.* **1994**, *33*, 3442.

(10) Chang, L.; Rall, J.; Tisato, F.; Deutsch, E.; Heeg, M. J. *Inorg. Chim. Acta* **1993**, *205*, 35.

(11) Abel, E. W.; Dimitrov, V. S.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 597.

0020-1669/95/1334-2033$09.00/0

2-(aminomethyl)pyridine; tBu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; tBu$_3$terpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine.

Results and Discussion

Chatt has shown that complexes of the form $\mathrm{Re^{I}(N_2)L_5}$ can be prepared from $\mathrm{Re^{V}({=}N{-}N{=}C(Ph)O{-})(PPh_3)_2Cl_2}$, proceeding through an intermediate Re(III) complex of the type $\mathrm{Re^{III}({-}N{=}N{-}C(O)Ph)L_5}$ (where L is a mixture of halides and phosphines).[4] Using a similar methodology, starting with $\mathrm{Re^{V}({=}N{-}N{=}C(Ph)O{-})(PPh_3)_2Cl_2}$, we have synthesized a variety of $\mathrm{Re^{I}}$(dinitrogen)(amine) compounds,[3] and our hope was that this route might also lead to a $\mathrm{Re^{I}}$(terpy)(dinitrogen) analog. The typical procedure for the synthesis of these dinitrogen compounds is to reflux the desired ligand with $\mathrm{Re^{V}({=}N{-}N{=}C(Ph)O{-})(PPh_3)_2Cl_2}$ in benzene/methanol. However, when this procedure was attempted with an excess of terpy, a compound characterized as $\mathrm{[Re^{II}(terpy)(PPh_3)_2Cl]Cl}$ (**I**) was recovered in nearly quantitative yield (Figure 1). Anion metathesis of **I** with AgOTf produces the triflate salt, $\mathrm{[Re^{II}(terpy)(PPh_3)_2Cl]OTf}$ (**II**), and a single crystal of this material, grown from $\mathrm{CH_2Cl_2}$, was structurally characterized (Tables 1−3). An ORTEP drawing of the complex $\mathrm{[Re^{II}(terpy)(PPh_3)_2Cl]^+}$ is shown in Figure 2, and selected bond distances and angles for the cation appear in Table 3. As expected from steric considerations, the phosphine ligands occupy axial positions with the terpy and chloride ligands lying in the equatorial plane. The nitrogen−, phosphorus−, and chloride−rhenium bond distances are typical of those reported for other low-valent rhenium complexes; however, the Re−Cl bond distance is somewhat longer than normal, indicating the electron rich nature of this complex.[12]

The formation of the rhenium(II) product (**I**) was unexpected. According to previous works,[4] rhenium(I)−dinitrogen or rhenium(III)−diazine compounds are typically generated from Re(V)−hydrazido species. For example, when the reaction of $\mathrm{Re^{V}({=}N{-}N{=}C(Ph)O{-})(PPh_3)_2Cl_2}$ and terpy is carried out in absence of methanol, the expected rhenium(III) product, $\mathrm{Re^{III}(terpy)(N{=}N{-}C(O)Ph)Cl_2}$ (**III**), is formed.[13] It is possible that, in the formation of **I**, a $\mathrm{Re^{I}}$(terpy)(dinitrogen) complex is formed initially but is subsequently oxidized to rhenium(II), either by the protic cosolvent or by a rhenium species of higher oxidation state. In fact, trace amounts (1−5%) of the terpy−dinitrogen species $\mathrm{Re^{I}(terpy)(N_2)(PPh_3)Cl}$ ($E_{1/2}$ (II/I) = −0.14 V) were isolated from a chromatographic separation of a reaction mixture containing **I**, but the yield could not be improved.

The crystal structure of **II**, shown in Figure 2, indicates that if one of the $\mathrm{PPh_3}$ groups could be removed, a completely unhindered binding site would become available, a result of the planarity of the tridentate terpy group. The $\mathrm{PPh_3}$ groups are readily removed from **I** by oxidation with $\mathrm{FeCp_2^+}$ followed by substitution by chloride. This substitution can be done stepwise to form $\mathrm{[Re^{III}(terpy)(PPh_3)Cl_2]PF_6}$ (**IV**) and $\mathrm{Re^{III}(terpy)Cl_3}$ (**V**); the latter is formed only in the presence of excess chloride, and both reactions are thought to proceed through an associative mechanism involving a 7-coordinate, 18-electron intermediate based on reactions of a similar system.[9] Unfortunately, in our hands, neither of these Re(III) species could be converted into other useful products.[14]

The reduction of $\mathrm{[Re^{II}(terpy)(PPh_3)_2Cl]OTf}$ (**II**) was also explored as a potential route to rhenium(I)−terpyridyl coordination complexes. In a series of experiments, compound **II** was reduced ($\mathrm{Mg^0}$ or $\mathrm{Na^0}$) in the presence of a variety of unsaturated organic ligands such as ketones, aldehydes, nitriles, aromatic compounds, and several olefins, including maleic anhydride, *N*-methylmaleimide, acrylonitrile, styrene, cyclohexene, and cyclohexenone. Surprisingly, only cyclohexenone formed a stable, isolable rhenium(I) complex in reasonable yield.[15]

$\mathrm{Re^{I}(terpy)(PPh_3)Cl}(\eta^2$-cyclohexenone), **VI**, is formed from the magnesium reduction of **II** (in DMA) with loss of one phosphine ligand. Large upfield shifts in the ^{1}H and ^{13}C NMR spectra of **VI** (cf. free cyclohexenone olefinic resonances (^{1}H = 7.1 and 6.1 ppm, ^{13}C = 150.7 and 129.3 ppm) with bound olefinic resonances (^{1}H = 4.8 and 4.6 ppm, ^{13}C = 66.9 and 60.8 ppm)) indicate that the cyclohexenone ligand is bound through the olefinic carbons. The terpy ligand is now spectroscopically asymmetric, showing 11 proton resonances. Assuming that rotation around the Re−olefin bond is rapid, the appearance of an asymmetric terpy ligand in the NMR spectrum indicates that the rhenium center remains bound to only one face of the cyclohexenone ligand on the NMR time scale. On the basis of spectroscopy alone, we cannot assign the stereochemistry of **VI** except to note that it is unlikely that the bulky triphenylphosphine would lie in the plane of the terpy ligand. Whereas both η^1-ketone and η^2-olefin isomers have been characterized for the more electron-deficient system $\mathrm{[Re^{I}Cp(NO)(PPh_3)(cyclohexenone)]^+}$,[16] the corresponding linkage isomers of **VI**, or any other of the reported cyclohexenone compounds (**VII**−**XIII**), have not been detected by NMR spectroscopy or cyclic voltammetry.

Although the range of rhenium(I) compounds produced directly from **II** was disappointingly narrow, the cyclohexenone complex (**VI**) has proven to be a useful synthon for a series of related rhenium(I)−terpy complexes through the removal of its chloride ligand. The halide of **VI** is easily removed with $\mathrm{Tl^+}$ at 20 °C.[17] In many cases, simple substitution occurs to give complexes of the form $\mathrm{[Re^{I}(terpy)(PPh_3)}(\eta^2$-cyclohexenone)$\mathrm{(L)]PF_6}$, and examples include L = tBupy (**VII**), tBuNC (**VIII**), $\mathrm{CH_3CN}$ (**IX**), and $\mathrm{NH_3}$. The $\mathrm{CH_3CN}$ (**IX**) and $\mathrm{NH_3}$ complexes readily decompose in solution ($\mathrm{CD_3CN}$ or acetone-d_6);[18] however, compound **IX** can be isolated. In contrast, complex **VIII**, with the more π-acidic tBuNC ligand, is stable in solution (acetone-d_6 or DMSO-d_6), even at elevated temperatures (80 °C), for many days. ^{1}H and ^{13}C NMR data for complexes **VII**−**IX** show cyclohexenone, terpy, and phosphine signals similar to that of **VI** and additional resonances consistent with the new ligand. As for **VI**, the stereochemistry of these complexes cannot be confirmed with the spectroscopic data available; however, we note that complexes have been generated directly

---

[12] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. The average Re−Cl bond distance is reported to be 2.380 Å. For the only closely related crystal structure, $\mathrm{[Re^{III}(terpy)_2Cl]^{2+}}$, reported in ref 8, the average Re−N bond distance is 2.10 Å and the reported Re−Cl distance is 2.28 Å.

[13] Compound **III** is unreactive with a variety of ligands in the benzene/methanol solvent system. The chloride ligands are inert toward removal by $\mathrm{Na^+}$ or $\mathrm{Tl^+}$, and the reduction of **III** has not led to any tractable Re(II) or Re(I) compounds.

[14] The analogous substitution of the phosphines does not proceed for other ligands tried such as $\mathrm{MeO^-}$, tBuNC, or $\mathrm{NH_3}$. Compound **IV** can be reduced to Re(II). Compound **V** does not reduce in the presence of either $\mathrm{Mg^0}$ or $\mathrm{Na^0}$.

[15] With ligands other than cyclohexenone, the rhenium(II) complex is either reduced to $\mathrm{Re^0}$, or the reaction follows the same pathway as the control reaction (DMA/DME/$\mathrm{Mg^0}$).

[16] Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699.

[17] Substitution has also been observed in the presence of a strong π-acid such as tBuNC or ETPB with no $\mathrm{Tl^+}$, but these reactions do not proceed cleanly. CO was also tried as a ligand, but several different sets of reaction conditions failed to yield clean products.

[18] In related reactions, $\mathrm{MeNH_2}$ and $\mathrm{C_6H_5NH_2}$ complexes were formed and characterized by electrochemistry, but the resulting compounds were found to be too unstable to isolate.

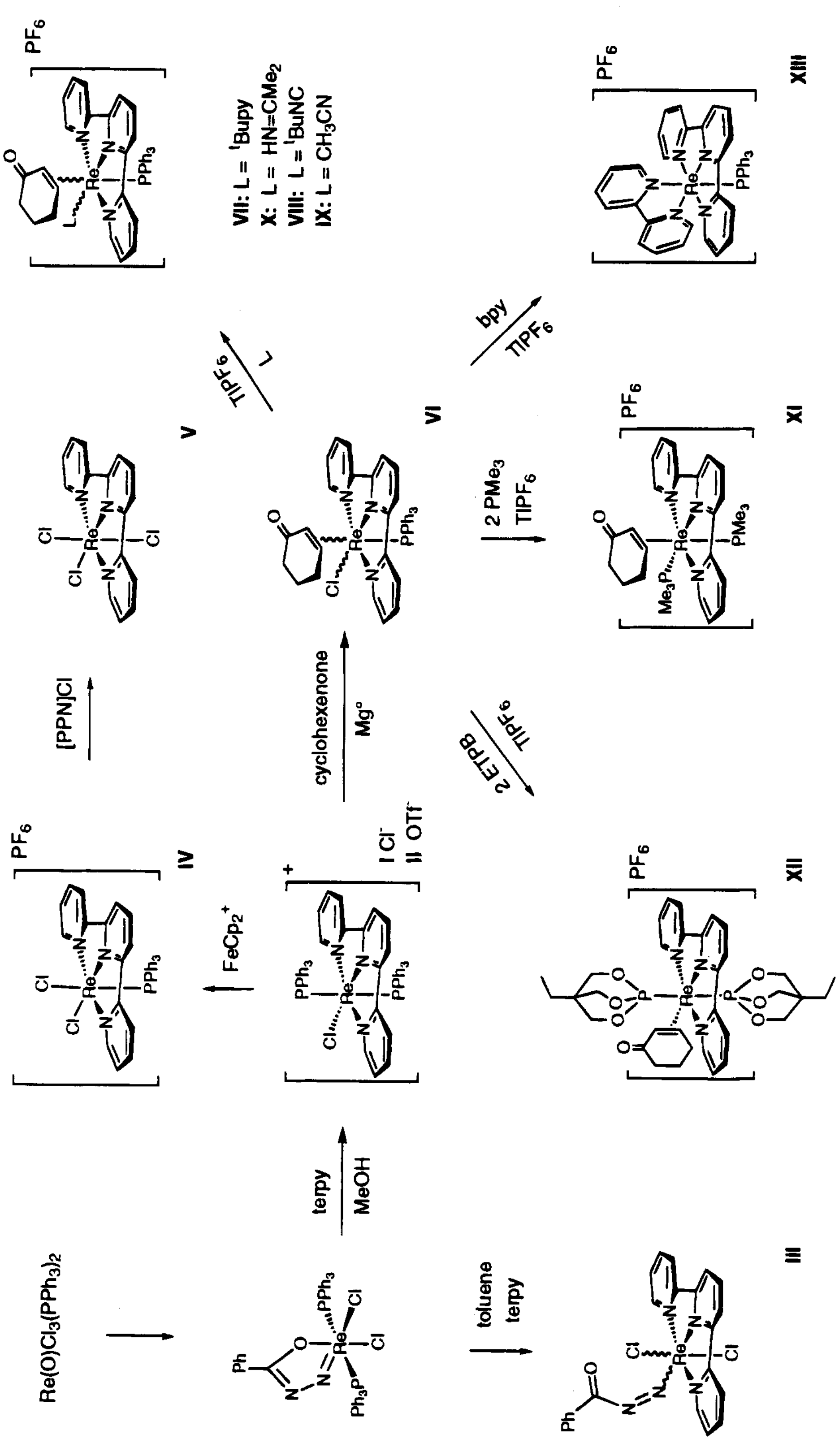

Figure 1. Reaction scheme summarizing the chemistry of rhenium(I)–terpyridyl complexes.

Table 1. Summary of Crystallographic Data for Compound **III**, $Re(terpy)(PPh_3)_2Cl]OTf\cdot 0.8\ CH_2Cl_2$

formula	$ReC_{52.8}H_{42.6}N_3Cl_{2.6}F_3SO_3P$	V, Å^3	2570(2)
fw	1196.52	Z	2
space group	$P\bar{1}$ (No. 2)	D_{calc}, g/cm^3	1.546
a, Å	14.552(7)	μ(Mo Kα), cm^{-1}	26.86
b, Å	15.726(7)	temp, °C	−80
c, Å	12.215(3)	$2\theta_{max}$, deg	46.0
α, deg	109.09(2)	λ, Å	0.710 69
β, deg	96.98(3)	R^a	0.044
γ, deg	98.42(4)	$R_w{}^b$	0.062

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

Table 2. Positional Parameters for the Crystal Structure of **II**

atom	x	y	z	occ
Re	0.16225(2)	0.23173(2)	0.17339(3)	
Cl(1)	0.0076(1)	0.1402(1)	0.0814(2)	
Cl(2)	0.6680(4)	0.2654(4)	0.5647(6)	0.50
Cl(3)	0.5138(5)	0.1231(7)	0.4139(8)	0.50
Cl(4)	0.5370(6)	0.1979(6)	0.7530(8)	0.30
Cl(5)	0.4543(8)	0.039(1)	0.793(2)	0.30
S	0.7226(2)	0.2863(2)	0.2140(3)	
P(1)	0.1532(2)	0.1812(2)	0.3408(2)	
P(2)	0.1703(2)	0.2807(1)	0.0043(2)	
F(1)	0.750(1)	0.4098(7)	0.121(1)	
F(2)	0.6139(9)	0.345(1)	0.093(1)	
F(3)	0.7133(7)	0.2771(7)	0.0003(7)	
O(1)	0.6990(6)	0.3508(6)	0.3145(7)	
O(2)	0.6554(8)	0.1993(6)	0.169(1)	
O(3)	0.8204(7)	0.280(1)	0.214(1)	
N(1)	0.1429(5)	0.3625(5)	0.2769(6)	
N(2)	0.2960(5)	0.3007(5)	0.2440(6)	
N(3)	0.2441(5)	0.1330(5)	0.1088(6)	
C(2)	0.0615(7)	0.3893(6)	0.2940(8)	
C(3)	0.0554(8)	0.4732(6)	0.3702(8)	
C(4)	0.136(1)	0.5338(7)	0.4340(9)	
C(5)	0.2221(8)	0.5097(7)	0.4172(8)	
C(6)	0.2257(7)	0.4242(6)	0.3388(7)	
C(7)	0.3128(6)	0.3908(6)	0.3166(7)	
C(8)	0.4042(8)	0.4396(7)	0.3627(8)	
C(9)	0.4795(7)	0.3956(7)	0.3364(8)	
C(10)	0.4614(7)	0.3029(7)	0.2648(8)	
C(11)	0.3690(6)	0.2566(6)	0.2174(7)	
C(12)	0.3401(6)	0.1624(6)	0.1415(7)	
C(13)	0.4014(7)	0.1028(7)	0.102(1)	
C(14)	0.3661(8)	0.0137(7)	0.030(1)	
C(15)	0.2679(8)	−0.0166(7)	−0.003(1)	
C(16)	0.2094(7)	0.0432(6)	0.0377(8)	
C(17)	0.696(1)	0.329(1)	0.100(1)	
C(18)	0.631(2)	0.179(2)	0.440(2)	0.50
C(19)	0.518(4)	0.143(4)	0.837(5)	0.30
C(111)	0.1848(6)	0.0695(6)	0.3197(7)	
C(112)	0.1228(7)	−0.0052(6)	0.2329(8)	
C(113)	0.1396(7)	−0.0936(7)	0.2019(8)	
C(114)	0.2215(7)	−0.1086(7)	0.2590(8)	
C(115)	0.2808(7)	−0.0366(8)	0.3449(9)	
C(116)	0.2637(6)	0.0524(7)	0.3767(8)	
C(121)	0.0447(6)	0.1694(6)	0.4005(7)	
C(122)	0.0455(7)	0.1322(6)	0.4907(8)	
C(123)	−0.0301(7)	0.1327(7)	0.5493(8)	
C(124)	−0.1076(7)	0.1684(7)	0.5192(8)	
C(125)	−0.1091(7)	0.2028(7)	0.4261(8)	
C(126)	−0.0344(6)	0.2020(6)	0.3669(8)	
C(131)	0.2322(6)	0.2639(6)	0.4730(7)	
C(132)	0.1929(8)	0.3277(7)	0.5539(8)	
C(133)	0.252(1)	0.3978(7)	0.6502(9)	
C(134)	0.349(1)	0.4037(9)	0.667(1)	
C(135)	0.3881(8)	0.345(1)	0.588(1)	
C(136)	0.3295(7)	0.2729(7)	0.4883(8)	
C(211)	0.1957(6)	0.1974(6)	−0.1267(7)	
C(212)	0.2613(7)	0.2179(6)	−0.1946(8)	
C(213)	0.2727(7)	0.1500(7)	−0.2949(8)	
C(214)	0.2190(7)	0.0630(7)	−0.3314(8)	
C(215)	0.1532(7)	0.0422(6)	−0.2660(8)	
C(216)	0.1412(6)	0.1087(6)	−0.1652(7)	
C(221)	0.0696(6)	0.3163(6)	−0.0642(7)	
C(222)	−0.0096(7)	0.3308(7)	−0.0164(8)	
C(223)	−0.0804(7)	0.3601(8)	−0.070(1)	
C(224)	−0.0738(7)	0.3772(7)	−0.1715(8)	
C(225)	0.0041(9)	0.363(1)	−0.222(1)	
C(226)	0.0738(8)	0.3324(9)	−0.169(1)	
C(231)	0.2646(6)	0.3819(6)	0.0439(7)	
C(232)	0.2426(6)	0.4699(6)	0.0838(8)	
C(233)	0.3107(8)	0.5465(7)	0.124(1)	
C(234)	0.4062(8)	0.5384(7)	0.1245(9)	
C(235)	0.4296(7)	0.4528(7)	0.0858(9)	
C(236)	0.3599(6)	0.3745(6)	0.0467(7)	

from **VI** both with the cyclohexenone in the plane and with it perpendicular to the plane of the terpy (*vide infra*). Infrared spectra of the nitrile and isocyanide complexes provide characteristic C−N stretches at 2244 and 2031 cm^{-1}, respectively. These values are lower in energy than those for the uncoordinated ligands (2254 and 2175 cm^{-1}) and indicate a moderate back-donation of electron density into these ligands even with the cyclohexenone ligand present.

When the chloride substitution reaction for **VI** was attempted with ammonia in acetone, a compound was formed that contained two methyl groups, observed by ^{1}H and ^{13}C NMR, not present in the rhenium starting material. Instead of the expected ammonia complex, the product of a condensation reaction with acetone and ammonia, $[Re^I(terpy)(PPh_3)(NH{=}CMe_2)(\eta^2\text{-cyclohexenone})]PF_6$ (**X**), was isolated. When the reaction was repeated in acetone-d_6, the methyl groups were not observed in the ^{1}H NMR of the product, **X**-d_6. On the basis of the similarity of reduction potential to that of the chloride complex **VI** and the low-field iminium carbon (187.9 ppm), the iminium ligand is assigned as being bound η^1 to the rhenium. An identical reaction has been reported for the condensation of $[Os^{II}(NH_3)_6]^{2+}$ and acetone.[19]

The extraction of the chloride from **VI** in the presence of the bulky ligands PMe_3 and ETPB has a different outcome from that observed with the nitrogen- and carbon-based ligands. Here, a double substitution was observed where both the chloride and a PPh_3 are replaced to give complexes of the type $[Re^I(terpy)(L)_2(\eta^2\text{-cyclohexenone})]PF_6$ where L = PMe_3 (**XI**) and ETPB (**XII**). In the case of the bis(phosphine) complex (**XI**), ^{1}H and ^{13}C NMR data indicate that these two ligands are inequivalent, requiring the geometric isomer illustrated in Figure 1 where the cyclohexenone−rhenium bond is perpendicular to the terpy ligand. In contrast, the bis(phosphite) complex (**XII**) has ^{1}H and ^{13}C NMR data that indicate that the ETPB ligands are equivalent and thus *trans* to each other. This geometry requires that the cyclohexenone take a position in the plane of the terpy ligand.

Several bidentate ligands have been combined with the cyclohexenone complex **VI** and Tl^+, including ampy, DAB, en, diphos, and bpy. Of these ligands, only bpy provided a clean, isolable product but with replacement of the cyclohexenone instead of the phosphine. Interestingly, the resulting rhenium(I) complex, $[Re^I(terpy)(bpy)(PPh_3)]PF_6$ (**XIII**), contains no strong π-acids, yet it is stable in solution over extended periods of time. In fact, compound **XIII** can be refluxed for 48 h in basic methanol or with the better π-acid ETPB with no observed substitution or decomposition.

In an attempt to form a stable Re(II) precursor to other rhenium(I) compounds, all of the solution-stable Re(I) cyclohexenone complexes were oxidized with a one-electron oxidant and observed for loss of the cyclohexenone ligand. AgOTf destroyed the $NH{=}CMe_2$ (**X**), PMe_3 (**XI**), and tBupy (**VII**) complexes with no observation of conversion to a clean Re(II) complex (electrochemical analysis). One equivalent of AgOTf

---

(19) Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261.

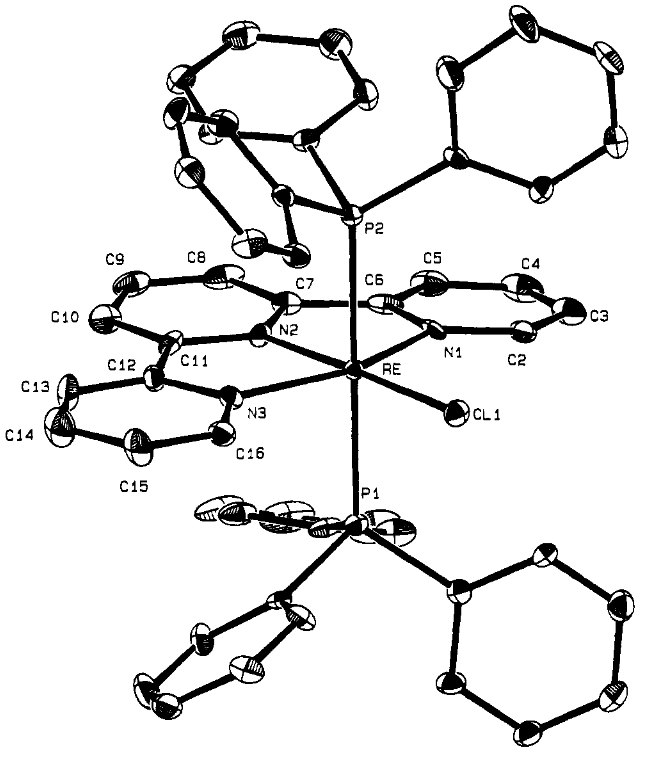

Figure 2. ORTEP drawing of $[Re^{II}(terpy)(PPh_3)_2Cl]^+$ (from **II**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Re^{II}(terpy)(PPh_{3)2}Cl]^+$

	Bond Lengths		
Re−Cl(1)	2.404(3)	Re−N(1)	2.113(7)
Re−P(1)	2.435(2)	Re−N(2)	2.017(7)
Re−P(2)	2.438(2)	Re−N(3)	2.104(7)
	Bond Angles		
Cl(1)−Re−P(1)	89.35(8)	P(1)−Re−N(3)	88.9(2)
Cl(1)−R−P(2)	90.13(8)	P(2)−Re−N(1)	90.9(2)
Cl(1)−Re−N(1)	106.8(2)	P(2)−Re−N(2)	89.6(2)
Cl(1)−Re−N(2)	175.8(2)	P(2)−Re−N(3)	90.8(2)
Cl(1)−Re−N(3)	99.3(2)	N(1)−Re−N(2)	77.4(3)
P(1)−Re−P(2)	179.36(7)	N(1)−Re−N(3)	153.8(3)
P(1)−Re−N(1)	89.6(2)	N(2)−Re−N(3)	76.5(3)
P(1)−Re−N(2)	90.9(2)		

was not powerful enough to efficiently oxidize the ETPB (**XII**) or tBuNC (**VIII**) complexes, although it did result in partial decomposition to unidentified products. When $NOPF_6$ was used to oxidize these complexes, the reaction yielded a complex mixture of intractable products, but free cyclohexenone was not detected in the ^1H NMR. In contrast, AgOTf cleanly converts $[Re^I(terpy)(PPh_3)(bpy)]^+$ (**XIII**) to its stable Re(II) counterpart, $[Re^{II}(terpy)(PPh_3)(bpy)]^{2+}$. This complex can be further oxidized in acetone to what appears to be, judging from ^1H NMR and cyclic voltammetric data, the diamagnetic Re(III) dimer $[(Re^{III}(terpy)(bpy))_2(\mu\text{-}O)]^{4+}$.[20]

The electrochemical data, given in Table 4 for most of the reported complexes, have proven useful in assigning the composition of complexes **II**−**XIII**. As the data indicate, significant differences are observed in the II/I couple of these complexes as the ligand set is altered. For example, the exchange of just one Cl^- ligand for a *tert*-butylisocyanide ligand results in a positive 700 mV shift in the Re(II/I) reduction potential. Similar shifts are seen in the III/II potentials. In contrast, the I/0 reduction wave, thought to be largely ligand-based, is relatively insensitive to changes in the ligand environment. For the cyclohexenone series **VI**−**XII**, there does not appear to be any correlation between the II/I reduction potential and the chemical shifts of the olefinic resonances of the cyclohexenone ligand in the ^1H and ^{13}C NMR.

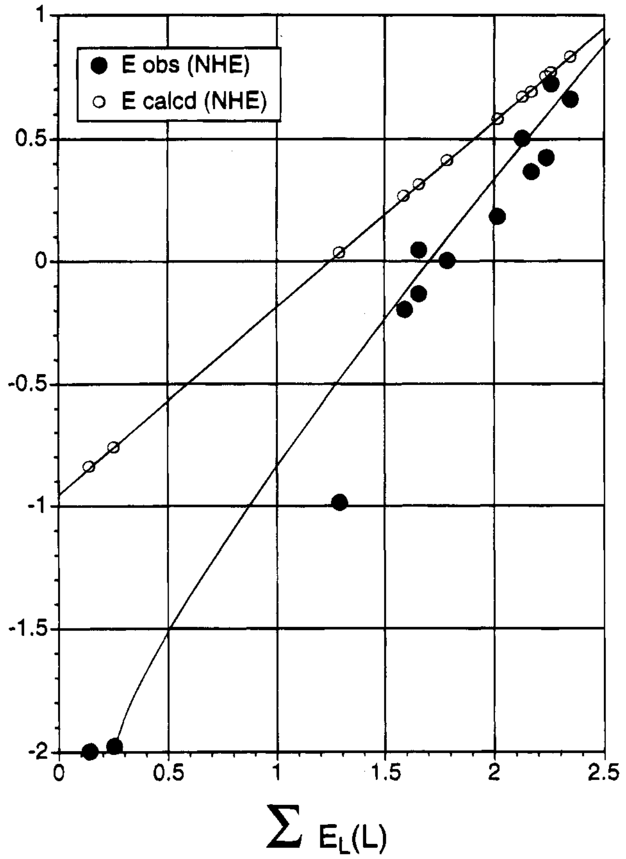

Figure 3. Graph of observed reduction potentials (black) and calculated reduction potentials (white) vs the sum of ligand parameters.

Recently, Lever demonstrated that the observed reduction potential of a transition metal complex can be estimated by a simple, empirical calculation taking into account individual ligand contributions.[21] In Table 5, each of the II/I reduction potentials for compounds **II**−**XIII** are listed along with the corresponding $\Sigma E_L(L)$, the sum of electrochemical ligand parameters, and the predicted value for the Re(II/I) reduction potential. The predicted potential is based on the formula $E_{calc} = S_M[\Sigma E_L(L)] + I_M$, where, for Re(II/I), $S_M = 0.76$ and $I_M = -0.95$ V (NHE).[22,23] We have included four other rhenium−amine complexes, $[Re^{III}(ampy)_2Cl_2]^+$, $[Re^{III}(en)_2(py)Cl]^{2+}$,[24] $[Re^I(ampy)_2(N_2)(PPh_3)]^+$, and $[Re^I(ampy)(tBu_2bpy)(N_2)(PPh_3)]^+$,[25] for comparison. Notably, the majority of the rhenium(I) complexes used to derive the reported values of S_M and I_M contain strong π-acids, typically with two or more carbonyl or

---

(20) Partial characterization: ^1H NMR (acetone-d_6): δ 8.92 (m, 5H), 8.87 (m, 3H), 8.50 (d, 1H), 8.45 (t, 2H), 7.93 (m, 4H), 7.78 (t, 1H), 7.23 (t, 1H), 6.98 (m, 1H), 6.78 (m, 1H). CV (DMA/TBAH/100 mV/s): $E_{p,a} = 0.89$ V, $E_{1/2} = -0.05$ V, $E_{1/2} = -0.27$ V, $E_{1/2} = -0.89$ V, $E_{1/2} = -1.11$ V vs NHE. The electrochemistry matches a related compound, $[(Tc^{III}(terpy)(bpy))_2(\mu\text{-}O)]^{4+}$, reported by: Barrera, J.; Bryan, J. C. Paper in progress.

(21) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(22) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980.

(23) In the determination of $\Sigma E_L(L)$ for a given complex, several values for $E_L(L)$ had to be approximated where an authentic value did not exist. The following changes were made: Cyclohexenone was replaced with ethene, tBupy was replaced with pyridine, and the acetone imine was replaced with imidazole.

(24) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 594.

(25) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026.

Table 4. Reduction Potentials (V) for Compounds **I**, **II**, **IV**−**XIII**[a]

compd (no.)	IV/III	III/II	II/I	I/0
[Re(terpy)(PPh$_3$)$_2$Cl]Cl (**I**)	1.16[b]	0.48[b]	−1.02	−1.89[c]
[Re(terpy)(PPh$_3$)$_2$Cl]OTf (**II**)	1.18[b]	0.51	−0.99	−1.89[c]
[Re(terpy)(PPh$_3$)Cl$_2$]PF$_6$ (**IV**)	1.18[b]	0.06	−1.32[c]	
Re(terpy)Cl$_3$ (**V**)	0.52	−0.49	−1.51[b]	
[Re(terpy)(PPh$_3$)Cl(η^2-cyclohexenone)] (**VI**)		0.94[b]	0.04	−1.46[c]
[Re(terpy)(PPh$_3$)(tBupy)(η^2-cyclohexenone)]PF$_6$ (**VII**)			0.50[b]	−1.24
[Re(terpy)(PPh$_3$)(tBuNC)(η^2-cyclohexenone)]PF$_6$ (**VIII**)		1.24[b]	0.72	−1.20[c]
[Re(terpy)(PPh$_3$)(CH$_3$CN)(η^2-cyclohexenone)]PF$_6$ (**IX**)		1.30[b]	0.42	−1.22[c]
[Re(terpy)(PPh$_3$)(NH=CMe$_2$)(η^2-cyclohexenone)]PF$_6$ (**X**)		1.10[b]	0.18	−1.34
[Re(terpy)(PMe$_3$)$_2$(η^2-cyclohexenone)]PF$_6$ (**XI**)		1.26[b]	0.36	−1.36
[Re(terpy)(ETPB)$_2$(η^2-cyclohexenone)]PF$_6$ (**XII**)			0.66	−1.38[c]
[Re(terpy)(PPh$_3$)(bpy)]PF$_6$ (**XIII**)		1.00[b]	−0.14	−1.46[c]

[a] DMA, 100 mV/s, TBAH electrolyte. [b] Reported value is for $E_{p,a}$. [c] Reported value is for $E_{p,c}$.

Table 5. Experimental ($E_{1/2}$) and Calculated Re(II/I) Reduction Potentials (V) for Rhenium−Amine Complexes[a]

compd (no.)	II/I	E_{calcd}	ΣE_L(L)
Re(terpy)Cl$_3$ (**V**)	−1.51[b]	−0.92	0.03
[Re(ampy)$_2$Cl$_2$]$^+$ [15]	−2.01[b]	−0.84	0.14
[Re(en)$_2$(py)Cl]$^{2+}$ [15]	−1.98[b]	−0.76	0.25
[Re(terpy)(PPh$_3$)Cl$_2$]$^+$ (**IV**)	−1.32[b]	−0.45	0.66
[Re(terpy)(PPh$_3$)$_2$Cl]OTf (**II**)	−0.99	0.03	1.29
[Re(ampy)$_2$(PPh$_3$)(N$_2$)]$^+$ [16]	−0.20	0.26	1.59
[Re(terpy)(PPh$_3$)(bpy)]PF$_6$ (**XIII**)	−0.14	0.31	1.66
[Re(ampy)(^{t}Bubpy)(PPh$_3$)(N$_2$)]$^+$ [16]	0.00	0.41	1.79
[Re(terpy)(PPh$_3$)(η^2-cyclohexenone)] (**VI**)	0.04	0.31	1.66
[Re(terpy)(PPh$_3$)(NH=CMe$_2$)(η^2-cyclohexenone)]PF$_6$ (**X**)	0.18	0.58	2.02
[Re(terpy)(PMe$_3$)$_2$(η^2-cyclohexenone)]PF$_6$ (**XI**)	0.36	0.69	2.17
[R(terpy)(PPh$_3$)(CH$_3$CN)(η^2-cyclohexenone)]PF$_6$ (**IX**)	0.42	0.75	2.24
[Re(terpy)(PPh$_3$)(tBupy)(η^2-cyclohexenone)]PF$_6$ (**VII**)	0.50[c]	0.67	2.13
[Re(terpy)(ETPB)$_2$(η^2-cyclohexenone)]PF$_6$ (**XII**)	0.66	0.83	2.35
[Re(terpy)(PPh$_3$)(tBuNC)(η^2-cyclohexenone)]PF$_6$ (**VIII**)	0.72	0.77	2.26

[a] DMA, 100 mV/s, TBAH electrolyte. [b] Reported value is for $E_{p,c}$. [c] Reported value is for $E_{p,a}$.

isocyanide ligands.[26] Correspondingly, for most of these compounds ΣE_L(L) is relatively large, falling in the range of 2−4 V (NHE). A second, much smaller set of reported Re(II/I) reduction potentials are available from rhenium(III) complexes (in cases where their III/II and II/I potentials are chemically reversible), but these compounds are generally unstable if left in their lower oxidation states. This latter set of compounds have ΣE_L(L) values that range from about 0.5−1.5 V (NHE).[27] Interestingly, this second group of compounds have observed reduction potentials that deviate sharply from calculated values when 0.76 and −0.95 V are used for S_M and I_M, and an alternative set of parameters (S_M = 0.27 and I_M = −1.43 V) has been proposed to account for these abnormalities.[22]

The data in Table 5 are significant in that the stable Re(II) and Re(I) compounds represented bear relatively few π-acids and have ΣE_L(L) values lying in a range not well represented in the current literature. In Figure 3, both the observed and calculated Re(II/I) reduction potentials are plotted vs the corresponding ΣE_L(L) values. Although there are not sufficient data to warrant any type of quantitative treatment, we note an interesting trend: For large values of ΣE_L(L), the observed potentials are in good agreement with values predicted from Lever's parametrization data (i.e. within 200 mV); however, as ΣE_L(L) decreases the observed reduction potentials deviate from those predicted, in an apparently systematic fashion, toward more negative values. We do not mean to imply that the reported value for S_M is incorrect; Lever has clearly demonstrated the accuracy and utility of this parameter for a large set of compounds whose ΣE_L(L) is greater than 1.5 V. However, as ΣE_L(L) decreases, the parameter S_M appears to *increase*. In other words, *as the metal becomes more reducing, the reduction potential becomes considerably more sensitive to small changes in the ligand set.* We have also made this observation for a large series of pentaammineosmium(II) complexes where the III/II potential (i.e. the d^5/d^6 reduction potential) deviates strongly in a negative direction from predicted values when ΣE_L(L) becomes too small.[28] Apparently, when the ability of a given ligand set to stabilize an electron-rich metal (e.g. Re(I) or Os(II)) is sufficiently diminished, the electrochemical potential of the metal becomes considerably more sensitive to small perturbations in the π-accepting ability of the ligands. Consider, for example, that replacing one triphenylphosphine in **II** with a cyclohexenone ligand (i.e. **VI**) results in a $\Delta E°$ of 1.03 V. The expected difference is only 280 mV.[29]

As suggested by Lever, it is possible that the plot of E_{obs} vs ΣE_L(L) may best be described as a curve rather than a straight line.[22] In fact, many of the rhenium(III) compounds used to calculate I_M and S_M for the "lower" Re(II/I) parameters reported in Lever's study also appear to fit the "curve" shown in Figure 3. In order to quantify this trend, more data points are required in the range of ΣE_L(L) = 0.5−1.5 V. Work is currently in progress in our laboratories to generate these data under a uniform set of experimental conditions (i.e. solvent, electrolyte) identical to that for the present data.

---

(26) With the exception of the complexes reported in ref 4.

(27) The one exception is for the compound Re^{II}Cl$_2$(CO)$_2$(PPr$_3$)$_2$ where ΣE_L = 2.22 V (NHE). Here, the reported value of −0.75 V for the Re(II/I) reduction potential appears abnormally low. For comparison, the compound Re^{I}Cl(CO)$_2$(PMe$_2$Ph)$_3$ has a corresponding observed value of 1.06 V. See ref 22 for specific details.

(28) The pentaammineosmium(II) data will be presented in detail along with the preparation and characterization of other electron-rich rhenium compounds: Orth, S. D.; Helberg, L. E.; Sabat, M.; Harman, W. D. Manuscript in preparation.

(29) A ligand parameter of 0.76 V is reported for ethene since one is not available for cyclohexenone. We expect this value to be only slightly lower than that for cyclohexenone.

Conclusions

Taking advantage of the benzoylhydrazide chemistry developed for rhenium by Chatt and co-workers,[4] an assortment of rhenium(III), rhenium(II), and rhenium(I) terpyridyl complexes have been prepared, most without any of the classical π-acids so common to this chemistry. In comparing the reduction potentials of these compounds with those predicted from the ligand parametrization approach set forth by Lever, we find that as the metal center becomes more reducing, the observed II/I reduction potential deviates in a negative manner from the predicted value.

Experimental Section

This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. Routine ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a General Electric QE-300 or GN-300 spectrometer at room temperature (23 °C). Chemical shifts are reported in ppm and are referenced to residual protonated solvent (δ acetone-d_5) = 2.04; δ(CHDCl$_2$) = 5.32; δ (DMSO-d_5) = 2.49) with coupling constants given in Hz. 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 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 and were determined in DMA (0.5 M TBAH) using ferrocene ($E_{1/2}$ = 0.55 V) or cobaltocenium hexafluorophosphate ($E_{1/2}$ = 0.78 V) *in situ* as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples. 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.

Solvents. All distillations were performed under nitrogen. All solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated by repeated freeze−pump−thaw cycles. Methylene chloride was refluxed for at least 8 h over P_2O_5 and distilled. Diethyl ether was refluxed for at least 8 h over Na^0/benzophenone and distilled. Methanol was refluxed over Mg(OMe)$_2$, prepared *in situ* from Mg^0 activated by I$_2$, and distilled. Acetonitrile was refluxed over CaH$_2$ and distilled. DMA was dried over CaH$_2$, refluxed for 24 h, and vacuum distilled. Acetone was deoxygenated prior to use. Benzene was refluxed for at least 24 h over Na^0/benzophenone and distilled. DME was refluxed over Na^0 and distilled. Hexanes were refluxed for at least 24 h over Na^0/benzophenone and distilled.

Reagents. Re^V(=N−N=C(Ph)O−)(PPh$_3$)$_2$Cl$_2$ was prepared according to literature methods.[4] Magnesium powder (Aldrich, 50 mesh) was activated by treatment with iodine in DME under nitrogen, stirring for several hours, and washing with DMA, acetone, and ether. ETPB (Strem) was sublimed (40 °C, 0.25 Torr) before use. tBupy was distilled prior to use. The NH$_3$ solution in DME was prepared by bubbling NH$_3$(g) through a flask of DME for 30 min. All of the other reagents were used as purchased.

Syntheses. (a) [Re^{II}(terpy)(PPh$_3$)$_2$Cl]Cl (I). Re^V(=N−N=C(Ph)O−)(PPh$_3$)$_2$Cl$_2$ (4.89 g, 5.35 mmol) and terpy (1.77 g, 7.59 mmol) were suspended in 55 mL each of methanol and benzene. The mixture was refluxed for 23 h with a color change from green to black. The solution was cooled to room temperature, and the solvent was removed *in vacuo*. The resulting black solid was washed with benzene (2 × 2 mL), methanol (1 × 2 mL), and Et$_2$O (4 × 2 mL) and dried *in vacuo*. Yield = 5.34 g (98%). This product was converted to compound **II** without further purification. CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 0.48 V, $E_{1/2}$ = −1.02 V, $E_{p,c}$ = −1.89 V vs NHE. Anal. Calcd for $ReC_{51}H_{41}N_3Cl_2P_2$: C, 60.35; H, 4.07; N, 4.14. Found: C, 57.54; H, 4.37; N, 3.44.

(b) [Re^{II}(terpy)(PPh$_3$)$_2$Cl]OTf (II). [Re^{II}(terpy)(PPh$_3$)$_2$Cl]Cl (**I**, 5.03 g, 4.95 mmol) was dissolved in 55 mL of methanol. AgOTf (1.41 g, 5.49 mmol) dissolved in 5 mL of methanol was added to the solution. A gray precipitate formed immediately. The brown solution was stirred for 4 h, then the precipitate was filtered off and washed with methanol (4 × 3 mL). The solid was extracted with acetone (2 × 200 mL), and the extract was filtered. The filtrate was evaporated to dryness, and the dark brown solid was collected. Yield = 3.94 g (71%). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.18 V, $E_{1/2}$ = 0.51 V, $E_{1/2}$ = −0.99 V, $E_{p,c}$ = −1.89 V vs NHE. Anal. Calcd for $ReC_{52}H_{41}N_3ClF_3O_3P_2S$: C, 55.34; H, 3.66; N, 3.72. Found: C, 55.24; H, 3.94; N, 3.52.

(c) Re^{III}(−N=N−C(O)Ph)Cl$_2$(terpy) (III). Re^V(=N−N=C(Ph)O−)(PPh$_3$)$_2$Cl$_2$ (0.986 g, 1.08 mmol) was suspended in 25 mL of toluene. Terpy (0.255 g, 1.09 mmol) dissolved in 5 mL of toluene was added to the green rhenium suspension. The reaction mixture was refluxed for 4 h, producing a brown precipitate. The solution was cooled to room temperature, and the precipitate was filtered off, washed with toluene (2 × 1 mL) and Et$_2$O (3 × 1 mL), and dried *in vacuo*. Yield = 0.617 g (92%). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 0.54 V, $E_{1/2}$ = −0.90 V vs NHE. IR: $\nu_{C=O}$ = 1595 cm^{-1}. Anal. Calcd for $ReC_{22}H_{16}N_5Cl_2O$: C, 42.38; H, 2.59; N, 11.23. Found: C, 43.67; H, 2.75; N, 9.68. This compound is highly insoluble and isolation has proven difficult. To provide better characterization, the analogous compound was synthesized with tBu$_3$terpy instead of terpy. This compound provided better NMR data, and the resonances are reported for the analogous Re(−N=N−C(O)Ph)Cl$_2$(tBu$_3$terpy) complex. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.83 (d, 2H), 8.24 (d, 2H), 7.79 (s, 2H), 7.56 (t, 1H), 7.43 (m, 4H), 7.32 (s, 1H), 1.42 (s, 9H), 1.39 (s, 18H). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 0.43 V, $E_{1/2}$ = −0.96 V, $E_{p,c}$ = −1.33 V vs NHE. Anal. Calcd for $ReC_{34}H_{40}N_5Cl_2O$: C, 51.57; H, 5.09; N, 8.85. Found: C, 51.10; H, 5.58; N, 8.33.

(d) [Re^{III}(terpy)Cl$_2$(PPh$_3$)]PF$_6$ (IV). [Re^{II}(terpy)(PPh$_3$)$_2$Cl]Cl (**I**, 0.128 g, 1.26 × 10^{-4} mol) was dissolved in 10 mL of CH$_2$Cl$_2$. [FeCp$_2$]PF$_6$ (0.042 g, 1.3 × 10^{-4} mol) dissolved in 10 mL of CH$_2$Cl$_2$ was added to the brown solution. The reaction mixture was stirred for 30 min. The solvent was reduced to 3 mL, and the product was precipitated with 100 mL of ether. The black precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. Yield = 0.084 g (77%). ^{1}H NMR (acetone-d_6): δ 22.47 (t, 2H), 16.20 (s, 6H), 11.29 (d, 3H), 9.77 (t, 6H), 9.07 (t, 2H), −2.87 (t, 2H), −6.30 (d, 2H), −6.99 (d, 2H), −36.8 (t, 1H). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.18 V, $E_{1/2}$ = 0.06 V, $E_{p,c}$ = −1.32 V vs NHE. Anal. Calcd for $ReC_{33}H_{26}N_3Cl_2F_6P_2$: C, 44.15; H, 2.92; N, 4.68. Found: C, 43.45; H, 3.09; N, 5.26.

(e) Re^{III}(terpy)Cl$_3$ (V). [Re^{III}(terpy)(PPh$_3$)Cl$_2$]PF$_6$ (**IV**, 0.056 g, 6.5 × 10^{-5} mol) was dissolved in 10 mL of CH$_2$Cl$_2$. An excess of [PPN]Cl (0.186 g, 3.24 × 10^{-4} mol) dissolved in 5 mL of CH$_2$Cl$_2$ was added. A black precipitate formed after 30 min and was filtered off, washed with Et$_2$O, and dried *in vacuo*. Yield = 0.027 g (79%).

This reaction also proceeds directly from **I** using an excess of [PPN]Cl and 1 equiv of [FeCp$_2$]PF$_6$. [Re^{II}(terpy)(PPh$_3$)$_2$Cl]Cl (**I**, 0.068 g, 6.7 × 10^{-5} mol) was dissolved in 7 mL of CH$_2$Cl$_2$. An excess of [PPN]Cl (0.117 g, 2.04 × 10^{-4} mol) dissolved in 3 mL of acetone was added to the brown rhenium solution followed by [FeCp$_2$]PF$_6$ (0.024 g, 7.3 × 10^{-5} mol) in 4 mL of acetone. The reaction mixture was stirred for 1 h. A black precipitate formed and was filtered off, washed with acetone (2 × 1 mL) and ether (2 × 1 mL), and dried *in vacuo*. Yield = 0.035 g (98%). ^{1}H NMR (DMF-d_7): δ 23.27 (t, 2H), 6.68 (d, 2H), −0.67 (d, 2H), −11.01 (t, 1H), −15.02 (t, 2H), −24.45 (d, 2H). CV (DMA/TBAH/100 mV/s): $E_{1/2}$ = 0.52 V, $E_{1/2}$ = −0.50 V, $E_{p,c}$ = −1.51 V vs NHE. Anal. Calcd for $ReC_{15}H_{11}N_3Cl_3$: C, 34.26; H, 2.11; N, 7.99. Found: C, 34.78; H, 2.16; N, 7.89.

(f) [Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone)] (VI). [Re^{II}(terpy)(PPh$_3$)$_2$Cl]OTf (**II**, 1.35 g, 1.19 mmol) was dissolved in 49 g of DMA. Cyclohexenone (0.229 g, 2.35 mmol) was added, followed by excess Mg^0 (1.69 g). While being stirred for 1 h, the solution changed from brown to forest green, and the Mg^0 was filtered off. The filtrate was added to 500 mL of a stirring 50/50 mixture of Et$_2$O/hexanes, and a green oil formed. After decanting off the supernate, the remaining oil was dissolved in 50 mL of CH$_2$Cl$_2$ and reprecipitated with 400 mL of a 3/1 mixture of Et$_2$O/hexanes. The resulting dark green powder was filtered off, washed with Et$_2$O (5 × 2 mL), and dried *in vacuo*. Yield = 0.792 g (82%). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.86 (d, 1H), 9.06 (d, 1H), 8.00 (m, 4H), 7.25 (m, 3H), 7.15 (t, 3H), 7.01 (t, 7H), 6.89 (t, 1H), 6.55 (t, 6H), 4.84 (m, 1H), 4.58 (m, 1H), 3.00 (m, 1H), 2.72 (m, 1H), 2.62 (m, 1H), 2.07 (m, 3H). ^{13}C NMR (DMSO-d_6): δ 217.90 (C), 156.16 (CH), 155.90 (C), 155.16 (CH), 154.05 (C), 151.31 (C), 150.85 (C), 134.05 (C, J_{C-P} = 41.0 Hz), 133.55 (CH), 133.30 (CH), 132.46 (CH, J_{C-P} = 8.6 Hz), 129.39 (CH), 128.55 (CH, J_{C-P} = 8.1 Hz), 125.37 (CH), 125.27 (CH), 122.65 (CH), 122.55 (CH), 117.86 (CH), 117.54 (CH), 66.92 (CH), 60.78 (CH), 42.43 (CH$_2$), 30.42 (CH$_2$), 27.15 (CH$_2$). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 0.94 V, $E_{1/2}$ = 0.04 V, $E_{p,c}$ = −1.46 V vs NHE. Anal. Calcd for ReC$_{39}$H$_{34}$ClN$_3$OP: C, 57.59; H, 4.21; N, 5.17. Found: C, 56.93; H, 4.37; N, 5.34.

(g) [Re^I(terpy)(PPh$_3$)(tBupy)(η^2-cyclohexenone)]PF$_6$ (VII). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.130 g, 0.16 mmol) was dissolved in 15 mL of acetone. Excess tBupy (1.74 g, 12.9 mmol) was added. TlPF$_6$ (0.058 g, 0.17 mmol) dissolved in 2 mL of acetone was added to the stirring green solution. The white precipitate that formed was filtered off. The volume of the filtrate was reduced to 3 mL before it was added to 100 mL of stirring Et$_2$O. The dark green precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. Yield = 0.128 g (76%). ^{1}H NMR (acetone-d_6): δ 9.98 (d, 1H), 9.45 (d, 1H), 8.50 (d, 1H), 8.45 (d, 1H), 8.32 (d, 1H), 8.28 (d, 1H), 7.60 (q, 2H), 7.37 (q, 2H), 7.23 (m, 4H), 7.13 (m, 6H), 6.89 (d, 2H), 6.69 (t, 6H), 6.55 (d, 2H), 5.13 (m, 1H), 4.51 (t, 1H), 3.08 (m, 1H), 2.06 (m, 2H), 1.76 (m, 1H), 1.64 (m, 1H), 0.96 (s, 9H), −0.10 (td, 1H). ^{13}C NMR (acetone-d_6): δ 216.00 (C), 162.17 (C), 156.38 (CH), 155.94 (CH), 155.10 (C), 153.75 (C), 150.81 (CH), 150.38 (C), 150.27 (C), 135.11 (CH), 134.66 (CH), 132.53 (CH, J_{C-P} = 8.8 Hz), 132.52 (C, J_{C-P} = 41.5 Hz), 130.60 (CH), 129.67 (CH), 128.53 (CH, J_{C-P} = 8.7 Hz), 127.15 (CH), 126.84 (CH), 123.78 (CH), 123.19 (CH), 123.13 (CH), 119.14 (CH), 118.64 (CH), 63.51 (CH), 61.20 (CH), 41.27 (CH$_2$), 35.01 (C), 29.47 (CH$_3$), 28.13 (CH$_2$), 26.54 (CH$_2$). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 0.50 V, $E_{1/2}$ = −1.24 V vs NHE. Anal. Calcd for ReC$_{48}$H$_{47}$N$_4$F$_6$OP$_2$: C, 54.49; H, 4.48; N, 5.30. Found: C, 54.51; H, 4.77; N, 5.03.

(h) [Re^I(terpy)(PPh$_3$)(tBuNC)(η^2-cyclohexenone)]PF$_6$ (VIII). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.11 g, 0.13 mmol) was suspended in 4 mL of acetone, and tBuNC (0.031 g, 0.37 mmol) was added. TlPF$_6$ (0.048 g, 0.14 mmol) dissolved in 2 mL of acetone was added to the solution. The dark green suspension immediately changed to a dark purple solution, and the white precipitate that formed was filtered off. After the volume of the filtrate was reduced to 3 mL, it was added to 100 mL of stirring Et$_2$O. The resulting dark purple precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. To remove the remaining TlCl in the sample, the solid was redissolved in 2 mL of CH$_2$Cl$_2$, the solution filtered through Celite, and the solid reprecipitated with 75 mL of Et$_2$O. Yield = 0.093 g (71%). ^{1}H NMR (acetone-d_6): δ 9.94, (d, 1H), 9.36 (d, 1H), 8.64 (d, 1H), 8.54 (t, 2H), 8.36 (d, 1H), 7.86 (t, 1H), 7.79 (m, 2H), 7.54 (t, 1H), 7.40 (t, 1H), 7.28 (t, 3H), 7.17 (td, 6H), 6.71 (td, 6H), 4.60 (m, 1H), 4.32 (t, 1H), 3.40 (m, 1H), 2.74 (m, 1H), 2.62 (td, 1H), 2.24 (d, 1H), 2.08 (m, 1H), 1.92 (m, 1H), 0.76 (s, 9H). ^{13}C NMR (acetone-d_6): δ 214.46 (C), 157.12 (CH), 156.55 (CH), 156.44 (C), 154.57 (C), 152.16 (C), 151.46 (C), 145.62 (C, J_{C-P} = 85.50 Hz), 136.93 (CH), 136.24 (CH), 133.31 (CH), 132.66 (CH, J_{C-P} = 9.36 Hz), 130.16 (CH), 129.73 (C, J_{C-P} = 35.0 Hz), 128.84 (CH, J_{C-P} = 8.23 Hz), 127.50 (CH), 127.02 (CH), 123.30 (CH), 123.06 (CH), 121.52 (CH), 121.39 (CH), 61.94 (CH), 58.36 (CH), 56.70 (C), 39.15 (CH$_2$), 32.28 (CH$_2$), 31.29 (CH$_3$), 29.12 (CH$_2$). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.24 V, $E_{1/2}$ = 0.72 V, $E_{p,c}$ = −1.20 V vs NHE. IR: υ_{CN} = 2031 cm^{-1}. Anal. Calcd for ReC$_{44}$H$_{43}$N$_4$F$_6$OP$_2$: C, 52.41; H, 4.31; N, 5.56. Found: C, 51.74; H, 4.22; N, 5.40.

(i) [Re^I(terpy)(PPh$_3$)(CH$_3$CN)(η^2-cyclohexenone)]PF$_6$ (IX). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.072 g, 8.8 × 10^{-5} mol) was dissolved in 10 mL of acetonitrile, forming a blue solution. TlPF$_6$ (0.034 g, 9.7 × 10^{-5} mol) dissolved in 2 mL of acetonitrile was added to the rhenium solution. A white precipitate formed. After 20 min, the solution was evaporated to dryness under vacuum. The resulting solid was suspended in 2 mL of acetone and the suspension filtered to remove the TlCl. The filtrate was added to 75 mL of stirring Et$_2$O, and the resulting blue precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. Yield = 0.065 g (77%). ^{1}H NMR (acetone-d_6): δ 9.81 (d, 1H), 9.28 (d, 1H), 8.54 (d, 1H), 8.41 (d, 2H), 8.38 (d, 1H), 7.66 (m, 2H), 7.49 (t, 1H), 7.36 (t, 1H), 7.25 (m, 4H), 7.12 (t, 6H), 6.66 (t, 6H), 4.75 (m, 1H), 4.36 (t, 1H), 3.06 (m, 1H), 2.40 (m, 1H), 2.19 (m, 3H), 2.13 (s, 3H), 1.92 (m, 1H). ^{13}C NMR (acetone-d_6): δ 215.41 (C), 157.60 (CH), 156.38 (C), 156.24 (CH), 154.48 (C), 151.92 (C), 151.36 (C), 135.68 (CH), 135.03 (CH), 132.92 (C, J_{C-P} = 42.08 Hz), 132.48 (CH, J_{C-P} = 8.93 Hz), 131.84 (CH), 129.60 (CH), 128.49 (CH, J_{C-P} = 8.70 Hz), 126.48 (CH), 126.36 (CH), 122.93 (CH), 122.76 (CH), 119.96 (CH), 119.70 (CH), 115.72 (C, J_{C-P} = 12.83 Hz), 64.55 (CH), 58.95 (CH), 41.26 (CH$_2$), 29.31 (CH$_2$), 28.29 (CH$_2$), 2.53 (CH$_3$). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.30 V, $E_{1/2}$ = 0.42 V, $E_{1/2}$ = −1.22 V vs NHE. IR: υ_{CN} = 2244 cm^{-1}. Anal. Calcd for ReC$_{41}$H$_{37}$N$_4$F$_6$OP$_2$: C, 51.08; H, 3.88; N, 5.81. Found: C, 50.33; H, 4.01; N, 6.29.

(j) [Re^I(terpy)(PPh$_3$)(NH=CMe$_2$)(η^2-cyclohexenone)]PF$_6$ (X). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.13 g, 0.16 mmol) was dissolved in 10 mL of acetone. A 1 M solution of NH$_3$ in DME (20 mL) was added. TlPF$_6$ (0.059 g, 0.17 mmol) dissolved in 2 mL of acetone was added to the stirring green solution. The white precipitate that formed was removed by filtration. The filtrate was evaporated to dryness and redissolved in 2 mL of acetone, and the resultant solution was added to 100 mL of stirring Et$_2$O. The dark green precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. To remove the remaining TlCl in the sample, the solid was redissolved in 2 mL of CH$_2$Cl$_2$, the solution filtered through Celite, and the solid reprecipitated with 75 mL of Et$_2$O. Yield = 0.13 g (82%). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.94 (d, 1H), 9.17 (d, 1H), 8.10 (m, 5H), 7.44 (m, 2H), 7.21 (m, 5H), 7.10 (t, 1H), 7.06 (td, 6H), 6.56 (td, 6H), 4.92 (m, 1H), 4.54 (t, 1H), 3.09 (t, 1H), 2.33 (d, 1H), 2.10 (m, 3H), 1.57 (s, 3H), 1.20 (td, 1H), 0.70 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 217.21 (C), 187.94 (C), 156.64 (CH), 156.34 (CH), 155.89 (C), 153.43 (C), 151.50 (C), 150.61 (C), 135.60 (CH), 133.91 (CH), 132.45 (CH, J_{C-P} = 8.5 Hz), 132.38 (C, J_{C-P} = 39.3 Hz), 131.14 (CH), 129.87 (CH), 128.86 (CH, J_{C-P} = 8.3 Hz), 126.98 (CH), 126.59 (CH), 123.53 (CH), 123.41 (CH), 119.09 (CH), 118.79 (CH), 64.92 (CH), 60.07 (CH), 41.58 (CH$_2$), 30.32 (CH$_2$), 29.86 (CH$_3$), 27.44 (CH$_2$), 22.54 (CH$_3$). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.10 V, $E_{1/2}$ = 0.18 V, $E_{1/2}$ = −1.34 V vs NHE. Anal. Calcd for ReC$_{42}$H$_{41}$N$_4$F$_6$OP$_2$: C, 51.47; H, 4.22; N, 5.72. Found: C, 50.60; H, 4.25; N, 5.80.

(k) [Re^I(terpy)(PMe$_3$)$_2$(η^2-cyclohexenone)]PF$_6$ (XI). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.043 g, 5.3 × 10^{-5} mol) was dissolved in 4 mL of CH$_2$Cl$_2$. A 1 M solution of PMe$_3$ in toluene (1 mL) was added via syringe. TlPF$_6$ (0.019 g, 5.3 × 10^{-5} mol) dissolved in 2 mL of DME was added to the green solution. The solution rapidly changed color from green to blue and back to green, and a white precipitate formed. The precipitate was filtered off, and the filtrate was reduced. The resulting green oil dissolved in 2 mL of acetone was added to 100 mL of stirring Et$_2$O. The green precipitate was filtered off, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. Yield = 0.031 g (73%) . ^{1}H NMR (acetone-d_6): δ 10.69 (d, 1H), 9.76 (d, 1H), 8.60 (m, 4H), 7.76 (m, 2H), 7.53 (t, 1H), 7.45 (t, 1H), 7.33 (t, 1H), 4.67 (m, 1H), 4.25 (q, 1H), 3.53 (m, 1H), 2.84 (m, 1H), 2.44 (m, 3H), 2.11 (m, 1H), 0.35 (d, J_{P-H} = 6.60 Hz, 9H), 0.22 (d, J_{P-H} = 6.90 Hz, 9H). ^{13}C NMR (acetone-d_6): δ 220.44 (C), 156.27 (CH), 155.24 (CH), 154.91 (C), 153.29 (C), 151.56 (C), 150.82 (C), 135.50 (CH), 135.02 (CH), 131.59 (CH), 127.25 (CH), 123.76 (CH), 123.58 (CH), 119.80 (CH), 119.48 (CH), 60.19 (CH), 56.51 (CH), 40.52 (CH$_2$), 32.09 (CH$_2$), 29.91 (CH$_2$), 12.43 (CH$_3$, J_{C-P} = 24.8 Hz), 7.20 (CH$_3$, J_{C-P} = 26.4 Hz). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.26 V, $E_{1/2}$ = 0.36 V, $E_{1/2}$ = −1.36 V, $E_{p,c}$ = −1.94 V vs NHE. Anal. Calcd for ReC$_{27}$H$_{37}$N$_3$F$_6$OP$_3$: C, 39.89; H, 4.60; N, 5.17. Found: C, 39.70; H, 4.29; N, 4.81.

(l) [Re^I(terpy)(ETPB)$_2$(η^2-cyclohexenone)]PF$_6$ (XII). Re^I(terpy)(PPh$_3$)Cl(η^2-cyclohexenone) (**VI**, 0.123 g, 0.151 mmol) was dissolved in 30 mL of acetone. ETPB (0.244 g, 1.50 mmol) dissolved in 3 mL of acetone was added to the rhenium solution. The TlPF$_6$ (0.055 g, 0.15 mmol) dissolved in 2 mL of acetone was immediately added to the solution. The solution changed from dark green to dark purple. The purple solution was gently heated for 20 min, changing to a brick red solution with a white precipitate that was removed by filtering through Celite. The filtrate was reduced in volume to 3 mL, and precipitation was effected by slow addition of ether. A dark red solid was collected, washed with Et$_2$O (2 × 2 mL), and dried *in vacuo*. Yield = 0.097 g (66%). ^{1}H NMR (acetone-d_6): δ 10.26 (d, 1H), 9.46 (d, 1H), 8.60 (m, 3H), 8.45 (d, 1H), 8.04 (t, 1H), 7.92 (t, 2H), 7.61 (t, 1H), 7.41 (t, 1H), 4.81 (m, 1H), 4.46 (q, 1H), 3.78 (d, J_{P-H} = 14.7 Hz, 12H), 3.23 (m, 1H), 2.96 (td, 1H), 2.28 (m, 3H), 2.01 (m, 1H), 0.97 (t, 4H), 0.56 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 219.51 (C), 157.75 (CH), 157.06 (C), 156.86 (CH), 155.45 (C), 153.86 (C), 153.33 (C), 137.71 (CH), 137.16 (CH), 135.64 (CH), 127.77 (CH), 127.35 (CH), 123.70 (CH), 123.30 (CH), 121.44 (CH), 121.21 (CH), 73.84 (CH_2, J_{C-P} = 11.55 Hz), 58.13 (CH), 52.98 (CH), 39.00 (CH_2), 34.94 (C, J_{C-P} = 15.00 Hz), 32.26 (CH_2), 30.69 (CH_2), 23.03 (CH_2, J_{C-P} = 6.08 Hz), 7.36 (CH_3). CV (DMA/TBAH/100 mV/s): $E_{1/2}$ = 0.66 V, $E_{p,c}$ = −1.38 V vs NHE. Repeated attempts to purify this material by chromatography or recrystallization were unsuccessful, but the product is estimated to be ~90% pure on the basis of cyclic voltammetry and ^{1}H NMR. Anal. Calcd for $ReC_{33}H_{41}N_3F_6O_7P_3$: C, 40.21; H, 4.20; N, 4.26. Found: C, 37.29; H, 3.98; N, 3.98. The impurity could be formulated to possibly be either [Re^I(terpy)(PPh_3)(ETPB)(η^2-cyclohexenone)]PF_6 or [Re^I(terpy)(PPh_3)$(ETPB)_2$]PF_6 on the basis of limited data available. This compound could not be isolated from the main product. The only observable wave in the electrochemistry is $E_{1/2}$ = 0.40 V vs NHE. The ^{1}H NMR shows peaks that could be attributed to PPh_3, terpy, and ETPB. Not all of the peaks are observed for these ligands.

(m) [Re^I(terpy)(PPh_3)(bpy)]PF_6 (XIII). Re^I(terpy)(PPh_3)Cl(η^2-cyclohexenone) (**VI**, 0.198 g, 0.242 mmol) was dissolved in 30 mL of acetone. Bpy (0.122 g, 0.781 mmol) dissolved in 2 mL of acetone was added to the rhenium solution. $TlPF_6$ (0.085 g, 0.24 mmol) dissolved in 2 mL of acetone was added to this solution. The reaction mixture was stirred for 1.5 h, changing from dark green to dark brown. A white precipitate formed and was filtered off. The filtrate was reduced to 5 mL and dropped into 100 mL of stirring ether. The dark brown precipitate was filtered off, washed with Et_2O (2 × 2 mL), and dried *in vacuo*. Yield = 0.087 g (38%). ^{1}H NMR (acetone-d_6): δ 9.11 (d, 1H), 8.57 (d, 1H), 8.27 (m, 3H), 8.18 (d, 2H), 7.70 (d, 2H), 7.34 (m, 5H), 7.13 (m, 7H), 6.90 (t, 2H), 6.80 (t, 1H), 6.73 (t, 7H), 6.26 (t, 1H), 6.20 (t, 1H), 6.15 (t, 1H). ^{13}C NMR (acetone-d_6): δ 158.44 (CH), 155.59 (C), 152.28 (C), 151.47 (C), 151.46 (C), 149.66 (CH), 145.37 (CH), 132.94 (CH, J_{C-P} = 10.05 Hz), 132.63 (CH), 131.72 (CH), 130.84 (C, J_{C-P} = 42.68 Hz), 129.89 (CH), 128.87 (CH, J_{C-P} = 9.15 Hz), 127.02 (CH), 126.83 (CH), 123.48 (CH), 123.11 (CH), 123.06 (CH), 122.30 (CH), 121.48 (CH), 120.96 (CH), 117.73 (CH). CV (DMA/TBAH/100 mV/s): $E_{p,a}$ = 1.00 V, $E_{1/2}$ = −0.14 V, $E_{p,c}$ = −1.46 V vs NHE. Anal. Calcd for $ReC_{43}H_{34}N_5F_6P_2$: C, 50.74; H, 3.62; N, 7.40. Found: C, 50.66; H, 3.69; N, 7.24.

Crystal Structure of [Re^{II}(terpy)$(PPh_3)_2$Cl]OTf (II). All X-ray data were collected on a Rigaku AFC6C diffractometer at −80 °C using graphite-monochromated Mo Kα radiation. Pertinent crystallographic parameters and refinement data are listed in Table 1. Intensities of three standard reflections were monitored showing neither significant decay nor instrument instability. Empirical absorption corrections were applied by using ψ scans of several reflections. All calculations were performed on a VAX station 3520 with the TEXSAN 5.0 software package.[30] The structure was solved by direct methods (SIR88).[31] Full-matrix least-squares refinement with anisotropic thermal displacement parameters for all non-hydrogen atoms except for the C atoms of the dichloromethane solvent molecules yielded a final R of 0.044 (R_w = 0.062). High thermal vibrations of the two dichloromethane solvent molecules indicated partial occupancy. Subsequently, the atoms belonging to the solvent molecules were refined with the population parameters of 0.5 and 0.3 for the molecules C(18), Cl(2), Cl(3) and C(19), Cl(4), Cl(5), respectively. The final difference Fourier map showed a peak of 1.6e/Å^3 in the vicinity of the rhenium atom. The atomic scattering factors for the non-hydrogen atoms were taken from ref 32.

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

Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles for [Re^{II}$(PPh_3)_2$(terpy)Cl]OTf (**II**) (11 pages). Ordering information is given on any current masthead page.

IC9412419

---

(30) *TEXSAN: Single Crystal Analysis Software*, Version 5.0; Molecular Structure Corp.: The Woodlands, TX 77381, 1989.

(31) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(32) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; pp 71−98, Table 2.2A.