{TpRe(bpy)}: A Novel Pentaaminerhenium System That Stabilizes Both High and Low Oxidation States (Tp = Hydridotris(pyrazolyl)borate; bpy = 2,2′-Bipyridyl)

T. Brent Gunnoe,[†] Scott H. Meiere, Michal Sabat, and W. Dean Harman*

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

Received June 27, 2000

Introduction

Since the pioneering studies of Werner and Jørgensen,[1−4] classic coordination chemistry has been dominated by high-valent metal complexes possessing saturated and strongly donating ligands.[5] Notable exceptions to this prevailing paradigm include the highly reducing complexes $\{Os(NH_3)_5(L)\}^{2+}$,[6,7] $\{Ru(NH_3)_5(L)\}^{2+}$,[8] and $\{Tc(NH_3)_4(H_2O)(L)\}^{2+}$.[9] While the electron-rich nature of these fragments can result in unusual chemical properties, accessing such systems can be difficult due to the inability of these σ-donating ligands to stabilize the electron-rich metal. Accordingly, the chemistry of low-valent rhenium complexes has been largely confined to metal systems containing strong π acids in the coordination sphere.[10−12] Our interest in the ability of low-valent metals to promote novel reactivity in aromatic systems[6,7] has prompted our investigation of low-valent rhenium complexes with coordination spheres composed mainly of nitrogen-based ligand sets.[13−17]

Nitrogen heterocycles have played an important role in the development of inorganic chemistry. In particular, the chemistry of polypyridyl ligands has been extensively investigated[18−21] due to their interesting spectroscopic, photophysical, photochemical, electrochemical, and redox properties.[22−35] Herein, we describe the preparation of the novel complex $[TpRe^{III}(bpy)(Cl)][OTf]$ (**1**) (Tp = hydridotris(pyrazolyl)borate; bpy = 2,2′-bipyridyl; OTf = trifluoromethanesulfonate), a species that possesses a pentaamine ligand set capable of supporting rhenium in four oxidation states while keeping the {TpRe(bpy)} frame intact.

Results and Discussion

The oxo compound $TpRe^{V}(Cl)_2(O)$[36,37] is susceptible to reduction by phosphines. Mayer and Brown have used the lability of the phosphine oxide ligand resulting from the combination of PPh_3 and $TpRe(Cl)_2(O)$ to access $TpRe(Cl)_2(L)$.[37,38] In similar fashion, treatment of $TpRe^{V}(Cl)_2(O)$ with trimethylphosphine yields the species $TpRe^{III}(Cl)_2(O{=}PMe_3)$.[39,40] In refluxing DME (1,2-dimethoxyethane) the phosphine oxide ligand of $TpRe^{III}(Cl)_2(O{=}PMe_3)$ is labile, and our group and others have utilized this and similar complexes as precursors to other TpRe(III) systems.[39−41] A similar reaction sequence performed in the presence of excess bpy and 1 equiv of thallium triflate yields the burgundy complex [TpRe(bpy)(Cl)][OTf] (**1**; 71% yield; Scheme 1). The resonances for complex **1** in its ^1H NMR spectrum are contact shifted (17.0 ppm to −21.9 ppm) due to the paramagnetic character of the metal center.[42,43] The equivalence of the two pyridyl rings and 2:1 pattern for the Tp ligand indicate that the complex possesses a mirror plane (C_s symmetry).

Solid State Structural Study of [TpRe(bpy)(Cl)][OTf] (1). Suitable crystals for an X-ray diffraction study of [TpRe(bpy)-

---

[†] Present address: North Carolina State University, Department of Chemistry, Raleigh, NC.

(1) Werner, A. *Classics of Coordination Chemistry Part I: The Selected Papers of Alfred Werner*; Dover: New York, 1968; Vol. IV.
(2) Werner, A. *Z. Anorg. Chem.* **1893**, *3*, 267.
(3) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins College Publishers: 1993.
(4) Kauffman, G. B. *J. Chem. Educ.* **1959**, *36*, 521.
(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988.
(6) Harman, W. D.; Lay, P. A. In *Recent Advances in Osmium Chemistry*; Sykes, A. G., Ed.; Academic Press: San Diego, 1991; Vol. 37, p 219.
(7) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.
(8) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901.
(9) Armstrong, R. A.; Taube, H. *Inorg. Chem.* **1976**, *15*, 1904.
(10) Casey, C. P. *Science* **1993**, *259*, 1552.
(11) Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1994**, *131*, 127.
(12) Lewis, H. C., Jr.; Storhoff, B. N. *J. Organomet. Chem.* **1972**, *43*, 1.
(13) Helberg, L. E.; Gunnoe, T. B.; Brooks, B. C.; Sabat, M.; Harman, W. D. *Organometallics* **1999**, *18*, 573.
(14) Helberg, L. E.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1995**, *34*, 2033.
(15) Helberg, L. E.; Orth, S. D.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1996**, *35*, 5584.
(16) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026.
(17) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 594.
(18) Ferguson, J.; Herren, F.; Krausz, E. R.; Maeder, M.; Vrbancich, J. *Coord. Chem. Rev.* **1985**, *64*, 21.
(19) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zeleesky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(20) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63.
(21) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C. *Chem. Rev.* **1994**, *94*, 993.
(22) Collins, J. E.; Lamba, J. J. S.; Love, J. C.; McAlvin, J. E.; Ng, C.; Peters, B. P.; Wu, X.; Fraser, C. L. *Inorg. Chem.* **1999**, *38*, 2020.
(23) Colin, J.-P.; Gavina, P.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1998**, 1.
(24) Meyer, G. J. *J. Chem. Educ.* **1997**, *74*, 656.
(25) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(26) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71.
(27) Shen, Y.; Sullivan, B. P. *J. Chem. Educ.* **1997**, *74*, 685.
(28) Demas, J. N.; DeGraff, B. A. *J. Chem. Educ.* **1997**, *74*, 690.
(29) Yu, L.; Chan, W. K.; Peng, Z.; Gharavi, A. *Acc. Chem. Res.* **1996**, *29*, 13.
(30) Langen, R.; Chang, I. J.; Germanas, J. P.; Richards, J. H.; Winkler, J. R.; Gray, H. B. *Science* **1995**, *268*, 1733.
(31) Arkin, M. R.; Stemp, E. D. A.; Holmlin, R. E.; Barton, J. K.; Hörmann, A.; Olson, E. J. C.; Barbara, P. F. *Science* **1996**, *273*, 475.
(32) Ishow, E.; Gourdon, A.; Launay, J.-P.; Chiorboli, C.; Scandola, F. *Inorg. Chem.* **1999**, *38*, 1504.
(33) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.
(34) Partigianoni, C. M.; Chodorowski-Kimmes, S.; Treadway, J. A.; Striplin, D.; Trammell, S. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 1193.
(35) Arounaguiri, S.; Maiya, B. G. *Inorg. Chem.* **1999**, *38*, 842.
(36) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.
(37) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091.
(38) Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325−332.
(39) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6499.
(40) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2000**, *19*, 728.
(41) Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951.
(42) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy: A Guide for Chemists*; Oxford University Press: Oxford, 1993.
(43) Jesson, J. P. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

10.1021/ic000707m CCC: $19.00

Scheme 1. Synthesis and Reduction of [TpRe(bpy)(Cl)][OTf] (**1**)

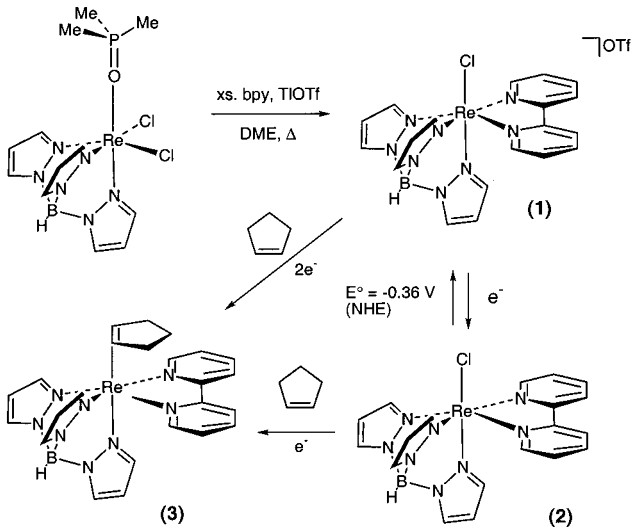


Table 1. Selected Crystallographic Data and Collection Parameters for [TpRe(bpy)(Cl)][OTf] (**1**)

empirical formula	$C_{20}H_{18}BN_8O_3F_3SClRe$
fw	738.94
cryst	dark red needle
cryst dimens, mm	0.23 × 0.21 × 0.44
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	9.067(2)
b Å	12.093(3)
c, Å	22.549(4)
β, deg	95.82(2)
V, $Å^3$	2459.7(8)
Z	4
D_{calcd}, g cm^{-3}	1.998
μ(Mo Kα), cm^{-1}	52.01
temp, °C	−80
2*θ* max, deg	46.1
total no. of reflns	3882
no. of reflns $I > 3\sigma(I)$	2716
R^a	0.025
$R_w{}^a$	0.035

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

Table 2. Selected Bond Distances (Å) for [TpRe(bpy)(Cl)][OTf] (**1**)

Re−Cl	2.357(2)	Re−N3	2.094(5)
Re−N1	2.085(5)	Re−N5	2.105(5)
Re−N2	2.085(5)	Re−N7	2.092(5)

(Cl)][OTf] (**1**) were grown by slow diffusion of hexanes into a methylene chloride solution (20 °C). Crystal data from the structural determination are presented in Table 1, selected bond distances and angles are depicted in Table 2, and an ORTEP diagram is shown in Figure 1. The coordination environment is a slightly distorted octahedral geometry, and the metal−ligand bond distances are typical of other Re^{III} complexes.[44] The Re−Cl bond distance {2.357(2) Å} is intermediate between those of other Re^{III}−Cl complexes synthesized in our lab.[15,17] The Re−N bond distances between the metal center and the bpy ligand are unremarkable and are similar to the bond lengths of the closely related complex *cis*-$[Re^{III}(bpy)_2Cl_2][PF_6]$.[15] The Re−Tp nitrogen bond distances are all three statistically equivalent. Thus, no significant trans effect is observed due to the presence of the chloride ligand. The three M−N (Tp) bond distances for complex **1** are shorter than those observed for the Re^I and Re^{II} complexes $TpRe^I(CO)(PMe_3)(\eta^2$-cyclohexene) and $TpRe^{II}(CO)(PMe_3)(OTf)$ (2.095 Å average distance versus 2.168 Å average).[39] This shortening is consistent with the notion that the Tp ligand is strongly donating for metals in high oxidation states.

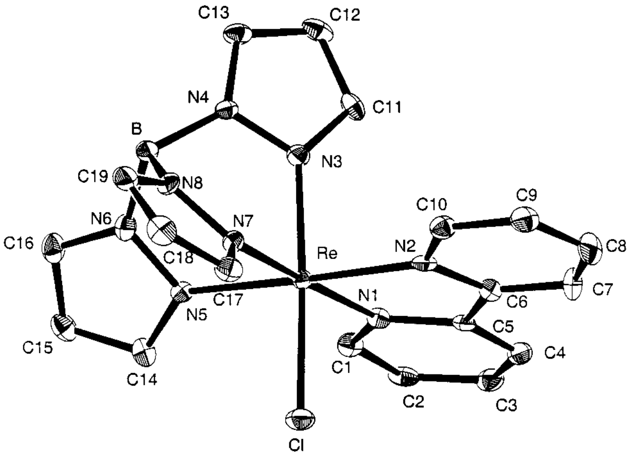


Figure 1. ORTEP diagram for [TpRe(bpy)(Cl)][OTf] (**1**) (30% ellipsoids; OTf counterion omitted).

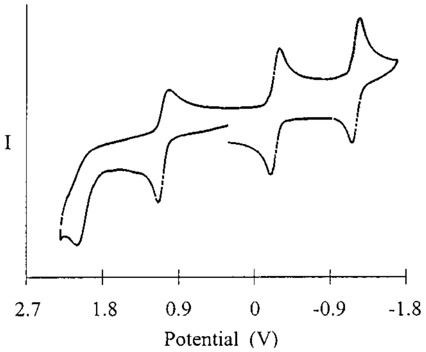


Figure 2. Cyclic voltammogram of [TpRe(bpy)(Cl)][OTf] (**1**) (CH_3CN; 100 mV/s).

Table 3. Summary of the Reduction Potentials for Rhenium−Amine Complexes[a]

complex	IV/III	III/II	II/I
$[Re(Tp)(bpy)Cl]^+$ (**1**)	1.06	−0.36	−1.42
[Re(Tp)(bpy)(cyclopentene)] (**3**)		0.50	−0.66
cis-$[Re(bpy)_2Cl_2]^+$ (ref 15)	0.99^a	−0.20	−1.01
trans$[Re(en)_2(py)Cl]^{2+}$ (ref 17)	0.64^a	−1.14	-2.14^c
trans-$[Re(ampy)_2Cl_2]^+$ (ref 17)	0.53^a	−1.15	-2.01^c

[a] $E_{1/2}$ values are reported vs NHE recorded at 100 mV/s in DMAc/TBAH. a = $E_{p,a}$ c = $E_{p,c}$.

Interestingly, a cyclic voltammogram of **1** recorded at 100 mV/s shows three fully reversible metal-centered redox couples with $E_{1/2}$ = 1.06 V (IV/III), −0.36 V (III/II), and −1.42 V(II/I) (NHE) (Figure 2). Thus, complex **1** is stable on the time scale of this cyclic voltammetry experiment through four oxidation states. Most striking is the reversibility of the redox couple at −1.42 V, which we assume to be a (II/I) metal-centered reduction,[15] given the strongly donating nature of the ligand set.[45−47] The significance of these data become apparent when they are compared to similar complexes containing a greater number of saturated amines (Table 3).

For example, the related chloropentamine complex $[Re(en)_2(py)Cl]^{2+}$ exhibits a III/II reduction potential of −1.14 V,

---

(44) Orpen, A. G.; Brammer, J.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

(45) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(46) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

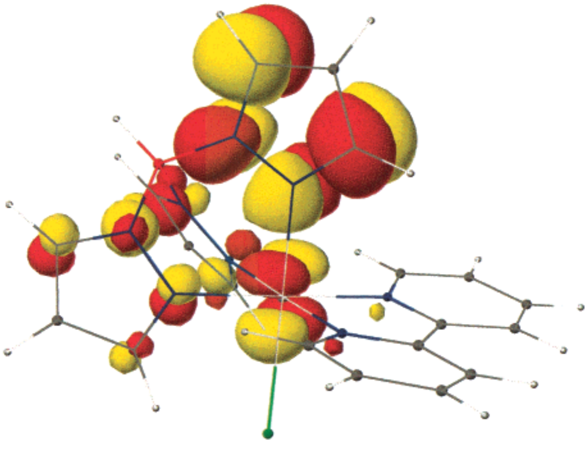
(47) Kitajima, N.; Tolman, W. D. *Prog. Inorg. Chem.* **1995**, *43*, 419.

whereas the corresponding potential for **1** is 780 mV more positive. This observation indicates that, despite its lower charge, [TpRe^{II}(bpy)(Cl)] is a much weaker reductant than [Re^{II}(en)$_2$(py)Cl]$^+$.[13−17] This trend continues when one compares II/I reduction potentials for these two species. Although part of this difference is certainly due to the π acidic nature of the bpy ligand,[15] it is possible that the pyrazole rings of the Tp ligand are also participating as weak π acids (vide infra). Furthermore, considering that the Re(III) complex *trans*-[Re(ampy)$_2$Cl$_2$]$^+$ [17] has an overall charge that is the same as that of **1**, and each of these complexes has two pyridyl rings as ligands, the difference in reduction potentials of these complexes is striking. Part of this difference in reduction potentials undoubtedly reflects the ability of the extra halide in [Re(ampy)$_2$Cl$_2$]$^+$ to stabilize the higher oxidation state through π donation. The closest match to the electrochemical properties of **1** reported for a rhenium(III) amine complex is *cis*-[Re(bpy)$_2$Cl$_2$]$^+$.[15] Here the IV/III reduction potentials are identical, and the III/II and II/I reduction potentials differ by 190 and 410 mV, respectfully. This comparison suggests that one bpy and one chloride ligand are roughly comparable to a Tp ligand, at least for higher oxidation states.

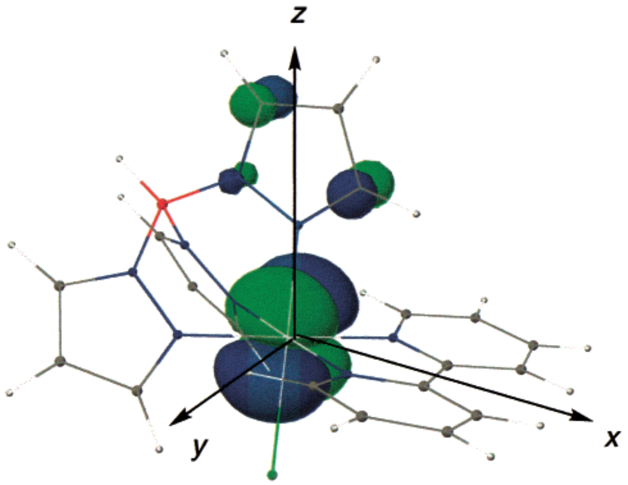
In an attempt to better understand the ability of Tp and bpy to stabilize Re(I), extended Hückel calculations were performed on the TpRe(bpy)(Cl) system (STO-3G). Most pertinent here is the (π back-bonding) interaction of the d_{yz} orbital of rhenium with one of the π* orbitals of the pyrazole ring trans to the chloride. In Figure 3, molecular orbitals that closely resemble the bonding and antibonding combinations of this π interaction are shown. In addition, a significant interaction between the d_{xy} orbital and the bpy π system is indicated. These calculations support the notion that extremely electron-rich metal centers may have significant π back-bonding interactions with both pyridine and pyrazole-based ligands.[15,16]

Treatment of [TpRe^{III}(bpy)(Cl)][OTf] (**1**) with Zn/Hg in MeOH yields the one-electron-reduction product TpRe^{II}(bpy)(Cl) (**2**) in 98% isolated yield (Scheme 1). The reduction of complex **1** results in a color change from burgundy to black. Complex **2** is paramagnetic and, as expected, is NMR silent. The Re(II) complex was characterized by cyclic voltammetry, UV−visible absorption spectra ($\lambda_{max} = 448$ nm ($\epsilon = 670$ M^{-1} cm^{-1})), and elemental analysis. The cyclic voltammogram of **2** is nearly identical to that of its Re(III) counterpart **1**. A slow-scan (5 mV/s) voltammogram with rapid stirring was performed to confirm that **2** was >90% reduced (*i.e.*, Re(II)). Attempts to remove the chloride ligand from **2** with thallium or sodium salts resulted in no observable reaction.

The reaction of TpRe^{II}(bpy)(Cl) (**2**) with Na/Hg in the presence of excess cyclopentene (20 equiv) yields TpRe^{I}(bpy)(η^2-cyclopentene) (**3**) in 70% isolated yield (Scheme 1). UV−visible spectra recorded in CH$_3$CN reveal two absorptions at $\lambda_{max} = 466$ nm ($\epsilon = 11000$ M^{-1} cm^{-1}) and $\lambda_{max} = 660$ nm ($\epsilon = 3600$ M^{-1} cm^{-1}).



LUMO +4



HOMO -1

Figure 3. Calculated HMOs (STO-3G; SHOMO −1 and LUMO +4) indicating bonding and antibonding combinations of d_{yz} and a π* orbital of a pyrazole ring.

The olefin complex **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy as well as cyclic voltammetry. Although the NMR spectra and a cyclic voltammogram of **3** showed no evidence of impurities, satisfactory analysis of this complex could not be obtained. The ^{1}H NMR spectrum of TpRe^{I}(bpy)(η^2-cyclopentene) (**3**) possesses multiplets at 3.38, 2.22, and 1.16 ppm which integrate for two protons each, and these resonances are assigned as cyclopentene protons. Two additional multiplets in the ^{1}H NMR spectrum which are assigned as cyclopentene resonances appear at 0.53 and −1.46 ppm (one proton each). The extreme upfield chemical shift is likely attributable to the shielding effect of the bpy ligand. To minimize steric strain, the olefin ligand is expected to lie over the bpy ligand, and aromatic shielding from the nitrogen heterocycles would result in the observed upfield chemical shifts. A resonance at 62.3 ppm in the ^{13}C NMR spectrum is attributed to the bound olefinic carbons. The $^1J_{CH}$ of this resonance (145 Hz) is indicative of a large increase in sp^3 hybrid character due to dπ back-bonding. Thus, the {TpRe^{I}(bpy)} fragment is a prolific π base, and this notion is supported by the cyclic voltammogram of **3** (vide infra).

As was observed for [TpRe^{III}(bpy)(Cl)][OTf] (**1**), the pyridyl rings are spectroscopically equivalent, and the ^{1}H and ^{13}C NMR spectra of complex **3** display 2:1 patterns for the Tp ligand. These data are consistent with the olefin C=C bond lying parallel to the C6−C6′ bond of the bipyridal ligand (C_s symmetry). Alternatively, complex **3** could be fluxional with the olefin favoring an asymmetric orientation; however, ^{1}H NMR spectra recorded at −60 °C (500 MHz) did not reveal a dynamic process.

The cyclic voltammogram of the olefin complex **3** displays two reversible oxidation waves at −0.66 (II/I) and 0.55 (III/II) V, and an irreversible reduction wave is observed at −2.02 V

(I/0). The reduction wave is attributed to a ligand-centered (bpy) reduction by comparison to similar values of related complexes.[14,15] The oxidation wave at −0.66 V corresponding to a II/I couple demonstrates the electron-rich nature of this complex. In comparison, the $TpRe^{I}(CO)(PMe_3)(\eta^2$-cyclohexene) complex, whose electron-rich nature is indicated by its low-energy CO stretching frequency of 1796 cm^{-1}, exhibits a II/I couple at 0.23 V vs NHE.[39]

Summary

We have reported the synthesis of a Re^{III} complex which possesses a strongly donating coordination environment composed primarily of nitrogen-based ligands. The Tp and bpy ligand set has been shown to stabilize rhenium in four oxidation states {Re(IV)−Re(I)}, and we attribute this stability to the ability of the nitrogen heterocyclic ligands to act as both weak π donors and π acceptors depending on the demand of the metal.

Experimental Section

General Methods. Unless otherwise noted, all reactions were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. ^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian INOVA-300 spectrometer at room temperature. All chemical shifts are reported in ppm and are referenced to residual ^1H signals or to the ^{13}C signals of the deuterated solvents. Coupling constants are reported in hertz (Hz). Peaks in the ^1H NMR due to the pyrazole ligands are listed by chemical shift and multiplicity only (all coupling constants are 2 Hz). Electronic spectra were recorded on an HP 8452A diode array spectrophotometer. Electrochemical experiments were performed under a dinitrogen 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 +1.80 to −2.10 V (unless otherwise noted) with a glassy carbon working electrode. All potentials are reported vs NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) as an internal standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was less than 100 mV for all reversible couples. Elemental analyses were obtained on a Perkin-Elmer PE−2400 series II CHN analyzer. Methanol was distilled under an atmosphere of dinitrogen from magnesium (freshly activated with iodine). Methylene chloride and hexanes were purified by passage through a column packed with activated alumina.[48] Ethanol, DME, and DMAc were purged with dinitrogen for 15 min and used without further purification. All solvents were thoroughly purged with dinitrogen prior to use (at least 10 min of purging). Deuterated solvents were deoxygenated by repeated freeze−pump−thaw cycles prior to storage in a glovebox under an inert atmosphere of dinitrogen.

Sodium mercury amalgam (5%), trimethylphosphine, hydrochloric acid, tetrabutylammonium hexafluorophosphate, 2,2′-bipyridal, thallium triflate, and cyclopentene were used as purchased from commercial sources. Perrhenic acid (Rhenium Alloys) was reacted with sodium bicarbonate to yield $NaReO_4$. Zn/Hg was prepared by washing Zn granules with 1 M HCl followed by distilled water, and then a saturated solution of mercuric chloride in distilled water was added. The reaction flask was swirled for approximately 10 min, filtered, and washed with distilled water followed by acetone. The Zn/Hg was stored under a dinitrogen atmosphere. $TpRe(Cl)_2(O)$ was prepared using the method reported by Mayer and Brown,[37] KTp was prepared according to a published procedure,[49] and $TpRe(Cl)_2(O{=}PMe_3)$ has previously been reported.[39] All other reagents were used as purchased from commercial sources.

Abbreviations. MeOH = methanol; DME = 1,2-dimethoxyethane; TBAH = tetrabutylammonium hexafluorophosphate; Tp = hydridotris(pyrazolyl)borate; OTf = trifluoromethanesulfonate (triflate); DMAc = *N*, *N*-dimethylacetamide; bpy = 2,2′-bipyridyl; ampy = 2-(aminomethyl)pyridine.

[$TpRe^{III}$(bpy)(Cl)][OTf] (1). A flask was charged with $TpRe(Cl)_2(O)$ (1.0967 g, 2.26 mmol), approximately 125 mL of DME, and trimethylphosphine (0.23 mL, 2.26 mmol). The royal blue solution was stirred overnight, during which time an orange slurry formed. To the resulting slurry was added bpy (2.0030 g, 12.8 mmol, 5.7 equiv) followed by TlOTf (0.8071 g, 2.28 mmol, 1.01 equiv). The solution was heated to reflux for 8.5 h, and during the course of the heating a color change from orange to burgundy was noted. The solution was filtered, and the filtrate was discarded. The burgundy product was extracted from the filter frit using approximately 200 mL of methylene chloride. The volume of the filtrate was reduced to approximately 25 mL, and hexanes (100 mL) were added. The resulting precipitate was collected via vacuum filtrate and dried under reduced pressure. A wine colored solid was isolated in 71% yield (1.1923 g). ^1H NMR (acetone-d_6, δ): 6.46, 3.20 (3H, 2:1, each a t, Tp C*H*), 0.31, −10.92, −17.61, −21.91 (6H, 2:1:2:1, each a d, Tp C*H*), 17.03, −8.41 (each 2H, each a t of d, J_{HH} = 7, 1 Hz, bpy 4, 4′, 5, and 5′ positions), 13.99, 9.64 (each 2 H, each a d, J_{HH} = 7 Hz, bpy 3, 3′, 6, and 6′ positions). UV−visible (CH_3CN/N_2): λ_{max} = 546 nm (ϵ = 2550 M^{-1} cm^{-1}). CV (DMAc, TBAH, 100 mV/s): $E_{1/2}$ = 1.06 V (IV/III); $E_{1/2}$ = −0.36 V (III/II); $E_{1/2}$ = −1.42 V (II/I); (CH_3CN, TBAH; 100 mV/s) $E_{p,a}$ = 2.13 V (V/IV); $E_{1/2}$ = 1.09 V (IV/III); $E_{1/2}$ = −0.35 V (III/II); $E_{1/2}$ = −1.37 V (II/I). Anal. Calcd for $C_{20}H_{18}BClF_3N_8O_3ReS$: C, 32.47; H, 2.45; N, 15.14. Found: C, 32.38; H, 2.63; N, 14.92.

$TpRe^{II}$(bpy)(Cl) (2). A flask was charged with approximately 100 mL of MeOH, [$TpRe^{III}$(bpy)(Cl)][OTf] (**1**) (1.1876 g, 1.60 mmol) and excess Zn/Hg (3.3300 g). The solution was stirred overnight, during which time a color change from burgundy to black was noted. The reaction solution was then vacuum filtered, the filter frit was washed with methylene chloride (approximately 125 mL), and the black filtrate was combined with the original methanol filtrate. The solvent was removed under reduced pressure, the resulting product dried in vacuo, and 0.9328 g of black solid collected (98% yield). UV−visible (CH_3CN/N_2) λ_{max} = 448 nm (ϵ = 670 M^{-1} cm^{-1}). CV (DMAc, TBAH, 100 mV/s): The CV of this complex was identical to that of [TpRe(bpy)(Cl)][OTf] (**1**). Anal. Calcd for $C_{19}H_{18}BClN_8Re$: C, 38.62; H, 3.07; N, 18.96. Found: C, 38.22; H, 3.44; N, 18.52.

$TpRe^{I}$(bpy)(η^2-cyclopentene) (3). Cyclopentene (0.90 mL, 10.3 mmol, 20 equiv) and $TpRe^{II}$(bpy)(Cl) (**2**) (0.3029 g, 0.513 mmol) were combined in a round-bottom flask with approximately 100 mL of DME. To the resulting black solution was added Na/Hg (5% Na, 1.4026 g, 3.05 mmol, 5.9 equiv), and the solution was stirred overnight. Vacuum filtration and in vacuo solvent removal from the dark filtrate yielded a black product. The black solid was dried under reduced pressure and isolated (0.2338 g, 70%). ^1H NMR (acetone-d_6, δ): 8.50, 7.73, 7.56, 5.25 (6H, 2:2:1:1, each a d, Tp C*H*), 6.46, 5.79 (3H, 2:1, each a t, Tp C*H*), 8.86, 8.30 (each 2H, each a d, J_{HH} = 6 Hz, bpy protons), 6.92, 6.58 (each 2H, m, bpy protons), 3.38, 2.22, −1.46 (5H, 2:2:1, each a m, cyclopentene protons), 1.16 (2H, dd, J_{HH} = 12, 9 Hz), 0.53 (1H, dd, J_{HH} = 9, 7 Hz). ^{13}C NMR (acetone-d_6): 169.1 (s, bpy ipso carbon), 152.2, 143.9, 136.2, 134.6 (d, Tp 3 and 5 position), 135.8 (d, J_{CH} = 185 Hz, bpy 6 and 6′), 125.1, 124.0 (each a dd, J_{CH} = 160−164 Hz, J_{CH} = 7 Hz, bpy 3 and 5 position), 124.7 (dt, J_{CH} = 162 Hz, J_{CH} = 7 Hz, bpy 4 and 4′), 106.7, 105.6 (each dt, J_{CH} = 176 Hz, J_{CH} = 6 Hz, Tp 4 position), 62.3 (d, $^1J_{CH}$ = 145 Hz, bound cyclopentene carbon), 33.9, 22.9 (cyclopentene methylene carbons). UV−visible (CH_3CN/N_2): λ_{max} = 466 nm (ϵ = 11000 M^{-1} cm^{-1}), λ_{max} = 660 nm (ϵ = 3600 M^{-1} cm^{-1}). CV (DMAc, TBAH, 100 mV/s): $E_{1/2}$ = 0.50 V (III/II); $E_{1/2}$ = −0.66 V (II/I); $E_{1/2}$ = −2.02 V (I/0).

Acknowledgment is made to the National Science Foundation (CHE9807375) and NIH (R01-GM49236) for their generous support of this work.

Supporting Information Available: Full details of the X-ray diffraction study of complex **1** including a labeled ORTEP diagram, crystal and refinement data, bond lengths and angles, atomic coordinates and anisotropic displacement parameters. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000707M

---

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

(49) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.