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An Enveloped Rhenium(V) Phenylimido Complex of 1,2-Bis(2,2′-bipyridyl-6-yl)ethane (*o*-bpy)

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Introduction

Information concerning the structural and reaction chemistry of multidentate cyclic ligands complexed to rhenium is limited, some notable examples being *trans*-$[Re(O)_2(cyclam)]^+$ [1] and $[Re(O)(L)(OMe)_2]ClO_4$,[2] where L is 2,2′:6′,2″:6″,2‴-quarterpyridine. Our recent efforts have focused on the chemistry of imidorhenium complexes with cyclic pyridyl and bipyridyl ligands,[3,4] which is important because of the usefulness of the phenylimido transition metal complexes as synthetic and catalytic intermediates.[5,6] Additionally, many nitrido and imido complexes of rhenium exhibit long-lived emissive electronic excited states, a feature which we hope to exploit in small molecule activation.[7] Consequently, we have examined the complexation of a phenylimidorhenium complex with the multidentate ligand 1,2-bis(2,2′-bipyridyl-6-yl)ethane (*o*-bpy),[8] and report here the synthesis and electrochemical and structural properties. From this and previous work, it is apparent that the *o*-bpy ligand is capable of stabilizing *trans* bpy geometries at metals as diverse as Re(V) and Ru(II).[9]

Experimental Section

Synthesis of $[Re(o\text{-}bpy)(NPh)(OC_2H_5)](PF_6)_2$. All starting materials were purchased from Aldrich Chemical Co. Solvents were distilled and dried according to standard laboratory procedures. The C, H, and N analyses were determined by Atlantic Microlab, Inc.

To 250 mL three-neck round-bottomed flask containing 150 mL of thoroughly degassed absolute ethanol and the ligand (338 mg, 1 mmol)[10] was added *trans,mer*-$[Re(NPh)Cl_3(PPh_3)_2]$[11] (272 mg, 0.3 mmol) under argon. The solution mixture was then heated to reflux, which caused the initial green suspension to dissolve. The reaction mixture was refluxed for 24 h and cooled. The solution was filtered, the filtrate collected, and the solvent removed by rotary evaporation. The solid residue was then loaded on a neutral alumina column and eluted first with 1:1 v/v dichloromethane−hexane; this first fraction contains the unreacted ligand. It was then eluted with acetonitrile and finally with ethanol to collect a deep green-black band. The ethanol was removed by rotary evaporation until the volume was reduced to 5 mL. To this was added 300 mg of NH_4PF_6 dissolved in 5 mL of ethanol to give a green precipitate, which was filtered and washed with 5 mL of ethanol and 25 mL of diethyl ether. Anal. Calcd for $ReC_{30}H_{28}N_5F_{12}OP_2$: C, 37.88; H, 2.95; N, 7.37. Found: C, 38.22; H, 3.05; N, 7.32. Yield: 80%. IR: 3091, 1597, 1573, 1496, 1412, 1378, 1294, 1251, 1167, 1091, 1018, 914, 838, 770, 644, 551 cm^{-1}.

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $C_{30}H_{28}F_{12}N_5OP_2Re$

	x	*y*	*z*	*U*(eq)[a]
Re(1)	2232(1)	200(1)	79(1)	49(1)
N(1)	1461(3)	1513(6)	509(3)	60(2)
N(2)	1338(3)	331(6)	−744(3)	57(2)
N(3)	3082(3)	−1130(6)	−292(3)	53(2)
N(4)	2994(3)	−113(6)	977(3)	58(2)
N(5)	2755(3)	1524(6)	−219(3)	52(2)
O(1)	1716(3)	−1345(5)	400(3)	59(2)
C(1)	1619(5)	2294(9)	1095(5)	79(3)
C(2)	1094(6)	3095(10)	1365(6)	91(4)
C(3)	388(6)	3098(12)	1027(7)	105(5)
C(4)	236(5)	2366(11)	424(6)	94(4)
C(5)	781(4)	1585(8)	164(5)	67(3)
C(6)	696(4)	875(8)	−525(4)	65(3)
C(7)	39(5)	835(11)	−949(6)	85(4)
C(8)	19(6)	302(11)	−1613(6)	96(4)
C(9)	681(5)	−173(10)	−1850(5)	83(3)
C(10)	1322(5)	−133(9)	−1421(5)	71(3)
C(11)	2036(5)	−595(9)	−1676(4)	68(3)
C(12)	2320(5)	−1942(8)	−1327(4)	72(3)
C(13)	3063(4)	−1807(7)	−921(4)	61(2)
C(14)	3702(5)	−2315(9)	−1164(5)	74(3)
C(15)	4369(5)	−2161(9)	−780(5)	75(3)
C(16)	4384(4)	−1552(8)	−130(5)	68(3)
C(17)	3738(4)	−1052(7)	105(4)	59(2)
C(18)	3688(4)	−521(7)	827(4)	61(2)
C(19)	4259(5)	−540(9)	1361(5)	75(3)
C(20)	4136(6)	−216(10)	2052(5)	87(4)
C(21)	3415(6)	70(9)	2205(5)	80(3)
C(22)	2869(5)	112(8)	1654(5)	70(3)
C(23)	3288(3)	2406(7)	−430(3)	50(2)
C(24)	3620(4)	2151(8)	−1046(4)	62(2)
C(25)	4159(4)	3009(8)	−1266(4)	65(3)
C(26)	4349(5)	4107(9)	−855(5)	72(3)
C(27)	4019(5)	4356(10)	−241(5)	83(3)
C(28)	3489(4)	3502(8)	−17(4)	68(3)
C(29)	1930(6)	−2612(11)	692(7)	105(4)
C(30)	1522(8)	−3257(18)	1076(13)	301(17)
P(1)	6289(1)	396(3)	3067(1)	74(1)
F(1)	5606(3)	1368(7)	2840(4)	115(3)
F(2)	6230(6)	−176(7)	2296(3)	138(4)
F(3)	6969(4)	−521(9)	3291(5)	145(4)
F(4)	6333(4)	1036(8)	3828(3)	127(3)
F(5)	5740(3)	−725(7)	3325(3)	105(3)
F(6)	6829(3)	1552(7)	2819(3)	106(2)
P(2)	1440(2)	743(3)	3398(1)	81(1)
F(7)	1768(7)	2077(11)	3152(8)	242(8)
F(8)	1435(6)	1462(12)	4098(5)	209(6)
F(9)	1161(5)	−556(9)	3637(10)	258(9)
F(10)	1516(6)	281(15)	2640(6)	238(8)
F(11)	629(4)	1219(10)	3187(5)	173(5)
F(12)	2263(4)	232(6)	3600(5)	119(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a JEOL 270 spectrometer. Electronic spectra were obtained by using 1×10^{-3} mol dm^{-3} solutions in acetonitrile on a Perkin-Elmer Lambda 9 spectrometer. Cyclic voltammograms were obtained with a BAS 100 A electrochemical analyzer. A three-electrode cell comprising a glassy-carbon or Pt-button working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Solutions of the complex (1×10^{-3} mol dm^{-3}) in acetonitrile were used. The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammo-

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(1) Blake, A. J.; Greig, J. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2645.

(2) Che, C.-M.; Wang, Y.-P.; Yeung, K.-S.; Wong, K.-Y.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1992**, 2675.

(3) Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127.

(4) Masood, M. Athar; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 2488.

(5) Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Pergamon, Oxford: **1982**; Vol. 2, Chapter 13.4.

(6) Nugent, W. A.; Haymore, B. C. *Coord. Chem. Rev.* **1980**, *31*, 123.

(7) Neyhart, G. A.; Bakir, M.; Boaz, J.; Vining, W. J.; Sullivan, B. P. *Coord. Chem. Rev.* **1991**, *111*, 27.

(8) Garber, T.; Van Wallendael, S.; Rillema, D. P.; Kirk, M.; Hatfield, W. E.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1990**, *29*, 2863.

(9) Masood, M. Athar; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.*, in press.

(10) The ligand was synthesized by a minor modification of a procedure given in ref 8, in which we use a heptane−ethylbenene−tetrahydrofuran solvent mixture for the dissolution of the lithium diisopropylamide.

(11) La Monica, G.; Cenini, S. *Inorg. Chim. Acta* **1978**, *29*, 183.

0020-1669/94/1333-5360$04.50/0

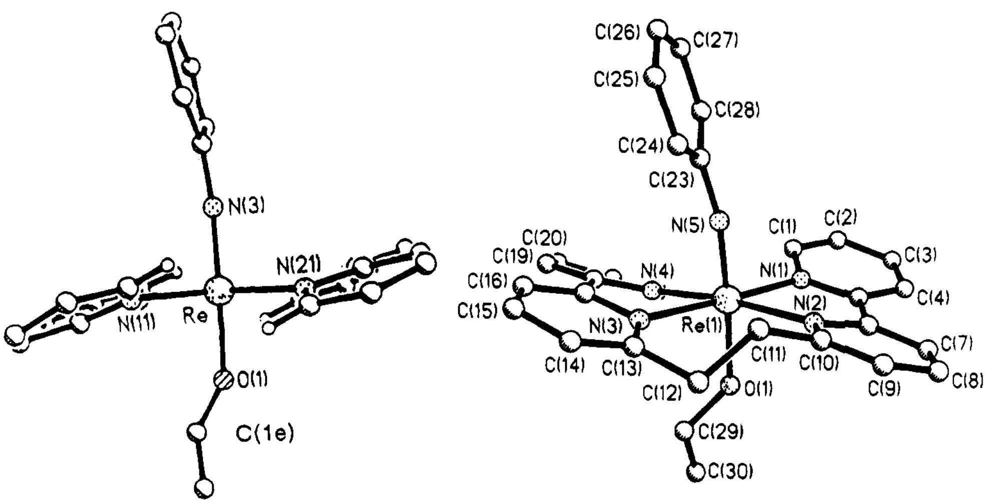

Figure 1. Comparison of the structure of the cation $[(NPh)Re(o\text{-}bpy)(OEt)]^{2+}$ in the crystals of the hexafluorophosphate salt (right side) with that of $[Re(NPh)(bpy)_2(OEt)]^{2+}$ (left side; reproduced from ref 3). Hydrogen atoms are omitted for clarity.

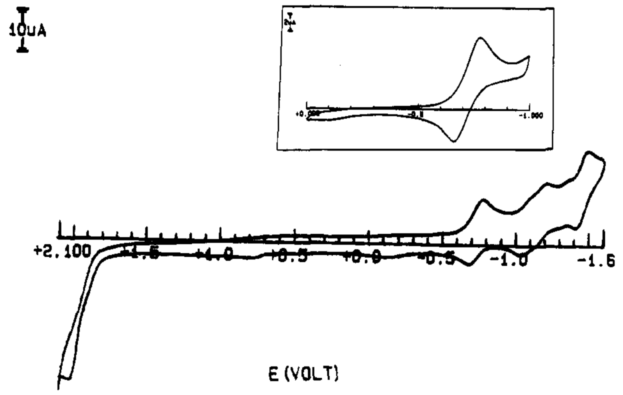

Figure 2. Cyclic voltammograms of the complex $[(NPh)Re(o\text{-}bpy)(OEt)](PF_6)_2$ in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte, with Pt-button working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. Scan rates: 100 mV s^{-1}. Voltage range: +2.1 to −1.6 V. Inset: voltage range 0 to −1.0 V.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $C_{30}H_{28}F_{12}N_5OP_2Re$

Re(1)−N(1)	2.112(6)	Re(1)−N(2)	2.150(6)
Re(1)−N(3)	2.180(6)	Re(1)−N(4)	2.114(6)
Re(1)−N(5)	1.735(5)	Re(1)−O(1)	1.914(5)
N(1)−Re(1)−N(2)	76.1(2)	N(1)−Re(1)−N(3)	175.7(2)
N(2)−Re(1)−N(3)	108.2(2)	N(1)−Re(1)−N(4)	101.0(2)
N(2)−Re(1)−N(4	171.0(2)	N(3)−Re(1)−N(4)	74.8(2)
N(1)−Re(1)−N(5)	92.9(2)	N(2)−Re(1)−N(5)	96.7(2)
N(3)−Re(1)−N(5)	86.5(2)	N(4)−Re(1)−N(5)	91.9(2)
N(1)−Re(1)−O(1)	91.1(2)	N(2)−Re(1)−O(1)	85.4(2)
N(3)−Re(1)−O(1)	89.5(2)	N(4)−Re(1)−O(1)	86.2(2)
N(5)−Re(1)−O(1)	175.8(2)		

nium perchlorate. All experiments were performed under a blanket of dry nitrogen at 22 ± 1 °C. All potentials are referred to Ag/AgCl.

X-ray Structure Determination. Black crystals of X-ray quality were grown from acetonitrile:ether solutions. A crystal of dimensions 0.72 × 0.60 × 0.40 mm^3 was mounted and the structure was determined at 22 °C (295 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\,26$ Å; $\lambda(K\alpha_2) = 0.713\,54$ Å] and graphite monochromator. The structure was solved by direct methods and refined by least-squares techniques, the programs being from the SHELXTL IRIS system.[12] Final values of the conventional R factors are $R = 0.0451$ and $R_w = 0.0566$, based on 5456 independent data with $F > 6\sigma(F)$. Atomic positional parameters are listed in Table 1, and selected bond lengths and bond angles are presented in Table 2.

Results and Discussion

Recently, we described the unexpected formation of a *trans*-bpy structure from the reaction of bpy with *trans-mer*-$[Re^V(NPh)(PPh_3)_2Cl_3]$ in ethanol. Reaction of the multidentate ligand *o*-bpy under similar conditions apparently follows the same reaction course, giving the complex $[Re^V(NPh)(o\text{-}bpy)(OEt)]^{2+}$, which was isolated as the hexafluorophosphate salt.

The sharp peak at 3090 cm^{-1} in the IR spectrum of $[Re^V(NPh)(o\text{-}bpy)(OEt)]^{2+}$ is attributable to coordinated ethanolate ion, and the peak at 840 cm^{-1}, to uncoordinated hexafluorophosphate ion. Other peaks in the IR are due to the coordinated ligand. The electronic absorption spectrum in acetonitrile exhibited bands at 609 nm (log ϵ 2.53), 530 nm (log ϵ 2.72), 425 nm (log ϵ 3.52), and 368 nm (log ϵ 3.94) and a band at 324 nm (log ϵ 4.41). Room temperature magnetic susceptibility measurement shows the complex to be diamagnetic. Additionally, the NMR spectrum exhibits a series of well-resolved peaks consistent with a d^2 Re(V) complex.

The geometry of the cation is compared to that of $[Re(NPh)(bpy)_2(OEt)]^{2+}$ [3] in Figure 1. In the present *o*-bpy complex, the cation adopts a distorted octahedral geometry, the equatorial coordination being provided by four nitrogen atoms [N(1), N(2), N(3), N(4)] from the two bipyridyl moieties of the *o*-bpy ligand while the axial ligands are the nitrogen atom [N(5)] from the phenylimido group and the oxygen atom [O(1)] of the coordinated ethanolate moiety. The extent of the distortion is evident from an examination of bond angles at the metal, the N(5)−Re(1)−O(1) bond angle being 175.8(2)° while the *cis* N−Re−N bond angles range from 74.8(2) to 108.2(2)°. The mean deviation from the four-atom least squares plane N(1), N(2), N(3), and N(4) lying 0.081 and 0.088 Å, respectively, above the plane while atoms N(1) and N(3) lie 0.087 and 0.081 Å, respectively, below the plane. The rhenium atom is displaced 0.074 Å below the plane, on the same side as N(1). The torsion angles C(10)−C(11)−C(12)−C(13), N(2)−C(10)−C(11)−C(12), and N(3)−C(13)−C(12)−(11) around the nominally single bonds C(11)−C(12), C(10)−C(11), C(12)−C(13) are −119.8, 70.9, and 72.6°, respectively. These torsion angles are

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[12] The complex is monoclinic, $P2_1/c$, $Z = 4$, with $a = 18.047(4)$ Å, $b = 9.906(2)$ Å, $c = 18.823(4)$ Å, and $\beta = 94.60(3)°$. Data were collected in the range $x < 2\theta < y$, the data gathered having $0 \le h \le 23$, $0 \le k \le 12$, $-24 \le l \le 24$, and were corrected for Lorentz−polarization and for absorption effects. Hydrogen atoms were placed in fixed calculated positions (C−H = 0.96 Å), while all other atoms were refined anisotropically.

similar to the those recently reported for a *trans*-ruthenium complex of this ligand.[9]

The Re–N(*o*-bpy) lengths vary between 2.112(6) and 2.180(6) Å. These bond lengths are notably shorter than found in *cis*-$[Re^VO_2(bpy)(py)_2]^+$,[13] but comparable to those of 2.134(6) and 2.163(6) Å found in *trans*-$[(NPh)Re(bpy)_2(OEt)]^{2+}$.[3] The Re–NPh and Re–OEt bond lengths of 1.735(5) and 1.914(5) Å in the present complex are normal. The dihedral angle between the two bipyridyl moieties in the ligand is 10.6°, slightly larger than the value of 7.7° found in the ruthenium complex.[9] The bond angles involving the five-membered chelation, [N(1)–Re–N(2) and N(3)–Re–N(4)] are 76.1(2) and 74.8(2)°, respectively, slightly smaller than the average value of 76.4(7)° in the ruthenium(II) complex[9] and significantly smaller than that of 81.6(2)° reported for a copper(II) complex of the present ligand.[8] As was also the case in the copper(II) and ruthenium(II) complexes, the Re–N bonds of 2.112(6) and 2.114(6) Å to the "open" side of the ligand [N(1) and N(4), respectively] are slightly shorter than those of 2.150(6) and 2.180(6) Å to the closed side [N(2) and N(3), respectively]. Of particular interest is the comparison of the distortion of the bpy ligands in $[Re(NPh)(bpy)_2(OEt)]^{2+}$ with that in the present *o*-bpy complex. As shown in Figure 1, the distortion is strikingly similar, thus suggesting that the $-CH_2-CH_2-$ bridge of *o*-bpy provides a distortion similar to that caused by the repulsive interactions of the *ortho* bpy protons.

The redox chemistry of the complex is similar to that of $[Re(NPh)(bpy)_2(OEt)]^{2+}$.[3] The cyclic voltammograms are shown in Figure 2. The complex exhibits three well defined reductive waves. The first wave in Figure 2 (see insert), at $E_{1/2}$ −0.715 V, is reversible (by comparison of anodic and cathodic peak currents) and comparison with the ferrocenium ↔ ferrocene couple as an internal standard demonstrates that it is an one-electron process, consistent with the Re(V)/Re(IV) couple. Electrochemical reversibility of the Re(V)/Re(IV) couple was also observed in the rhenium(V) complexes *trans*-$[Re(NPh)(dppe)_2Cl]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane], and *trans*-$[Re(NPh)(bpy)_2(OEt)]^{2+}$ [bpy = 2,2″-dipyridyl].[3] The redox processes in the present complex occur at more negative potentials than in these other complexes. However, this value is 0.45 V less negative than that observed for $[Re(NPh)(L)(OEt)](PF_6)_3$,[4] where L is 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, in which the rhenium is coordinated to both saturated and unsaturated amine donors. The relatively anodic value of the Re(V)/Re(IV) couple indicates that preparation of lower oxidation state *o*-bpy complexes should be straightforward, using synthetic procedures similar to those of Orth *et al.*[14]

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Supplementary Material Available: Tables S1 (anisotropic thermal parameters) and S2 (hydrogen atom parameters) for the complex (4 pages). For ordering information, see any current masthead page. Listings of observed and calculated structure amplitudes are available from D.J.H. on request.

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[13] Blackbourn, R. L.; Jones, L. M.; Ram, M. S.; Sabat, M.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 1791.

[14] Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 594.