Synthesis and Electrochemical and Structural Chemistry of Rhenium in High Oxidation States with Sterically Hindered Polypyridine Ligands

Md. Athar Masood,*,[†] B. P. Sullivan,* and Derek J. Hodgson*,[‡]

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

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The syntheses and electrochemical properties of several novel rhenium complexes containing the sterically-hindered ligands 6-methylbipyridine, 6-cyanobipyridine, and 2,9-dimethyl-1,10-phenanthroline are reported. The reaction of the ligands with *trans,mer*-[Re(NPh)(PPh$_3$)$_2$Cl$_3$] was different in every case, as is evident by formation of complexes in which rhenium ion exists in different oxidation states. The structures of the complexes have been determined by three-dimensional X-ray diffraction methods, and are found to produce novel coordination environments. Of particular note is the rare example of a five-coordinate Re(IV)−imido complex, [Re(NPh)(dmp)(PPh$_3$)(OEt)]$^+$, $C_{40}H_{37}F_6N_3OP_2Re$, which crystallizes in the space group $P2_1/c$ (no. 14) of the monoclinic system with four molecules in a cell of dimensions $a = 11.128(2)$ Å, $b = 30.474(6)$ Å, $c = 11.923(3)$ Å, and $\beta = 95.78(3)°$. The structure has been refined to a final value for the crystallographic R factor of 0.059 on the basis of 5248 independent reflections. The complex [Re(NPh)(6-mebpy)(PPh$_3$)(Cl)(OEt)]$^+$, $C_{37}H_{35}C_{l1}F_6N_3OP_2$-Re, crystallizes in the space group $P\bar{1}$ (no. 2) of the triclinic system with two molecules in a cell of dimensions $a = 10.700(2)$ Å, $b = 11.866(2)$ Å, $c = 15.280(3)$ Å, $\alpha = 93.24(3)°$, $\beta = 97.76(3)°$, and $\gamma = 106.89(3)°$. The structure has been refined to a final value for the crystallographic R factor of 0.040 on the basis of 8424 independent reflections.

Introduction

Sterically hindered ligands often convey unusual coordination geometries or oxidation states on transition metal centers.[1−3] Here we describe the unusual reaction chemistry of the hindered polypyridines 6-methylbipyridine (6-mebpy), 6-cyanobipyridine (6-cnbpy), and 2,9-dimethyl-1,10-phenanthroline (dmp) high-valent rhenium precursors. Most previous studies of amine-based ligands concern the chemistry of Re(I) with either with bipyridine or terpyridine and carbonyl ligands,[4,5] higher-valent rhenium with multidentate chelate ligands such as 2,2′:6′,2″:6″,2‴-quarterpyridine,[6] 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmt),[7] and 1,2-bis(2,2′-bipyridyl-6-yl)ethane (*o*-bpy),[8] or others containing “hard-soft” oxygen−phosphorus-based donor ligands.[9] Because of the demonstrations that the d^2 rhenium(V) center multiply bonded to a heteroatom such as oxygen or nitrogen has novel physicochemical and/or photophysical properties,[10−14] we have focused on the synthesis of imido−rhenium compounds.[7,8,12] Another important feature of the chemistry of rhenium which we hope to exploit is the large number of easily accessible oxidation states which interconvert under mild redox conditions.

Experimental Section

Syntheses. Starting materials were purchased from Aldrich Chemical Co. Solvents were distilled and dried according to standard laboratory procedures. 6-mebpy[15−17] and *trans,mer*-[Re(NPh)(PPh$_3$)$_2$Cl$_3$][18] were synthesized according to literature methods, while 6-cnbpy[19] was prepared in a 95% yield by improved methods (see below). The C, H, and N analyses were recorded by Atlantic Microlab, Inc.

(a) Improved Synthesis of the 6-cnbpy Ligand. 2,2′-Bipyridyl *N*-oxide,[20] 1.68 g (10 mmol), was dissolved in dry CH$_2$Cl$_2$ (20 mL). To this solution was added 1.4 mL (∼10 mmol) of trimethylsilylcyanide (TMSCN) under dinitrogen. After the solution was stirred for 30 min,

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[†] Present address: Igen International Inc., 16020 Industrial Dr., Gaithersburg, MD 20877.

[‡] Present address: EAB 203, University of Nebraska at Omaha, 6001 Dodge St., Omaha, NE 68182-0001.

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Table 1. Crystallographic Details for the Structures

	$[Re(6\text{-cnbpy-OEt})(PPh_3)_2(Cl)]^+$	$[Re(NPh)(6\text{-mebpy})(PPh_3)(Cl)(OEt)]^+$	$[Re(NPh)(dmp)(PPh_3)(OEt)]^+$
empirical formula	$C_{49}H_{42}Cl_1F_6N_3O_1P_3Re_1$	$C_{37}H_{35}Cl_1F_6N_3O_1P_2Re_1$	$C_{40}H_{37}F_6N_3O_1P_2Re_1$
fw	1117.47	935.3	937.9
T, K	295	295	295
λ, Å	0.71073	0.71073	0.71073
space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a, Å	15.143(3)	10.700(2)	11.128(2)
b, Å	19.590(4)	11.866(2)	30.474(6)
c, Å	17.538(4)	15.280(3)	11.923(3)
α, deg		93.24(3)	
β, deg	94.30(3)	97.76(3)	95.78(3)
γ, deg		106.89(3)	
V, Å^3	5188.01(2)	1830.02(6)	4022.6(13)
Z	4	2	4
ρ_{calcd} g cm^{-3}	1.657	1.698	1.549
μ, mm^{-1}	2.559	1.773	3.162
NO[a] (R_{int}, %)	9129 (13.84)	8424 (1.67)	5248 (3.08)
R^b ($R_w{}^c$)	0.12 (0.15)	0.04 (0.06)	0.06 (0.08)

[a] NO = number of observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$.

0.9 mL (∼10 mmol) of dimethylcarbamylchloride (DCC) was added, and the stirring was continued for 12 h at room temperature. After this period, an additional 0.8 mL of TMSCN and 0.8 mL of DCC were further added and stirred for 4 h more. Following this, 3.0 g of Na_2CO_3 dissolved in 25 mL of water was added and stirred for 15 min. The organic layer was collected, and the remaining aqueous layer was washed with three 25 mL portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and filtered, and the solution was removed by rotary evaporation to give a dark black solid. This solid was then loaded on a silica gel column and eluted with 1:5 v/v $CH_3COOC_2H_5$/hexane to give a yield of 1.68 g (95%) of a light yellow compound melting at 130 °C. ^{1}H NMR spectroscopy and C, H, and N analyses were consistent with the composition of the ligand.[19]

(b) $[Re(6\text{-cnbpy-OC}_2H_5)(PPh_3)_2(Cl)]PF_6$, Complex 1. To a 250 mL three-neck round-bottomed flask containing 150 mL of thoroughly degassed absolute C_2H_5OH and the ligand 6-cnbpy (398 mg, 2.2 mmol) was added *trans*,*mer*-$[Re(NPh)(PPh_3)_2Cl_3]$ (311 mg, 0.34 mmol) under argon. The solution mixture was then heated at reflux, causing the initial green suspension to dissolve to give a homogeneous solution. The heating was continued for another 24 h, after which time the reaction was cooled and filtered. The filtrate was collected, and the solvent was removed by rotary evaporation. The solid residue was then loaded on a neutral alumina column and eluted first with 1:1 v/v CH_2Cl_2/hexane, followed by CH_2Cl_2. During this procedure all the unreacted 6-cnbpy was recovered. The column was then eluted with 4:1 v/v CH_2Cl_2/CH_3CN, followed by elution with neat CH_3CN to collect the dark brown to black fraction. The solvent was then 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 C_2H_5OH, and the solution was stirred at room temperature to instantly give a black precipitate. The precipitate was collected by filtration and washed with 25 mL of ether followed by 25 mL of hexanes to give a 200 mg (50%) yield of the compound. Anal. Calcd for $ReC_{49}H_{42}ClF_6N_3OP_3$: C, 52.67; H, 3.79; N, 3.76. Found: C, 52.25; H, 3.85; N, 3.90. IR: 1560, 1525, 1431, 1384, 1366, 1337, 1313, 1278, 1237, 1184, 1143, 1114, 1090, 1025, 996, 838, 773, 755, 743, 696, 555, 508, 491 cm^{-1}.

(c) $[Re(NPh)(6\text{-mebpy})(PPh_3)(Cl)(OEt)]PF_6$, Complex 2. The reaction was carried out in a way similar to that described for complex **1** by reacting *trans*,*mer*-$[Re(NPh)(PPh_3)_2Cl_3]$ (170 mg, 0.186 mmol) with 6-mebpy (450 mg, 2.65 mmol) in C_2H_5OH. The reaction mixture was heated at reflux for 12 h. The black solid that deposited was removed from the solution by filtration. The residue which was obtained after rotoevaporation of the filtrate was loaded onto a neutral alumina column, and eluted consecutively with hexane, CH_2Cl_2, CH_3CN, and C_2H_5OH, respectively. Two bands were found, but only the first (fastest moving fraction) was collected. The volume of the solution was reduced to 5 mL, then 100 mg of NH_4PF_6 dissolved in 5 mL of C_2H_5OH was added, and the mixture was stirred at room temperature for 3 h. The precipitated solid was collected by filtration and washed sequentially with 25 mL portions of ether and hexanes to give 40 mg (20%) of a black compound. Anal. Calcd for $ReC_{37}H_{35}ClF_6N_3OP_2$: C, 47.52; H, 3.77; N, 4.49. Found: C, 47.32; H, 3.87; N, 4.29. IR: 2914, 2847, 1457, 1096, 1070, 1023, 926, 912, 903, 842, 764, 743, 694, 682, 667, 555, 527, 513 cm^{-1}.

(d) $[Re(NPh)(dmp)(PPh_3)(OEt)]PF_6$, Complex 3. The reaction and the isolation of this compound were accomplished in the same manner as the procedure described in section c. Yield: 30 mg (15%). Anal. Calcd for $ReC_{40}H_{37}F_6N_3OP_2$: C, 51.23; H, 3.98; N, 4.48. Found: C, 51.03; H, 4.11; N, 4.73. IR: 3058, 2961, 2920, 2847, 1618, 1584, 1501, 1475, 1430, 1375, 1350, 1180, 1159, 1099, 1070, 1020, 985, 918, 838, 762, 745, 694, 682, 555, 520 cm^{-1}.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Electronic spectra in the visible region were obtained by using 1×10^{-3} mol dm^{-3} solutions in MeCN on a Perkin-Elmer Lambda 9 spectrometer. In the UV region solutions of either 1×10^{-4} or 0.5×10^{-5} mol dm^{-3} were used. Cyclic voltammograms were obtained with a BAS 100 A electrochemical analyzer. A three-electrode cell comprising either a Pt button or a carbon black electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Solutions of the complexes (1×10^{-3} mol dm^{-3}) in MeCN were used. The supporting electrolyte was 0.1 mol dm^{-3} NEt_4ClO_4. All experiments were performed under a blanket of dry dinitrogen at 22 ± 1 °C. All potentials are referenced to Ag/AgCl.

X-ray Structure Determination. The crystals were grown from an acetonitrile solution for complex **1**, and for other complexes the X-ray-quality air-stable crystals were grown by slow diffusion of ether vapors in 3:1 v/v CH_3CN/C_2H_5OH solutions. Crystals of all the complexes were dark brown. The structures of the complexes were determined at 22 °C (295 K) by collecting intensities on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [λ(Mo Kα) = 0.710 73 Å] and a highly oriented graphite crystal monochromator. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 carefully centered reflections with $25° \leq 2\theta \leq 37°$. The structures were solved by direct methods[21] and refined by least squares techniques, the programs being from the SHELXTL IRIS system.[22] The data were corrected for Lorentz polarization and for absorption effects. Crystallographic details and cell constants for the complexes are found in Table 1.

Complex **1** crystallizes in the space group $P2_1/n$ (no. 14) of the monoclinic system. A crystal of dimensions $0.38 \times 0.38 \times 0.38$ mm^3 was mounted for data collection. Data were collected in the range $0 \leq h \leq 18$, $0 \leq k \leq 23$, $-20 \leq l \leq +20$. All hydrogen atoms were placed in fixed calculated positions (C−H = 0.96 Å). Atoms were refined isotropically, except for Re and chloride atoms which were refined

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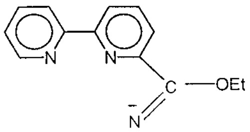

Figure 1. Attack of the ethanol solvent on the cyano group of the tridentate chelate ligand.

anisotropically. Final values of the conventional R factors were $R = 0.12$ and $R_w = 0.15$ based on 9807 independent data with $I > 3\sigma(I)$.

Complex **2** crystallizes in the space group $P\bar{1}$ (no. 2) of the triclinic system. A crystal of dimensions 0.60 × 0.30 × 0.25 mm^3 was used for data collection. Data were collected in the range $0 \leq h \leq 13$, $-15 \leq k \leq +14$, $-19 \leq l \leq +19$. Complex **3** crystallizes in the space group $P2_1/c$ (no. 14) of the monoclinic system, and a crystal of dimensions 0.90 × 0.10 × 0.20 mm^3 was used for data collection. Data were collected in the range $-12 \leq h \leq +12$, $-32 \leq k \leq 0$, $0 \leq l \leq 11$. For both complexes **2** and **3**, hydrogen atoms were placed in fixed calculated positions (C$-$H = 0.96 Å) with isotropic thermal parameters determined by the heavy atoms to which they are bonded, while all other atoms were refined anisotropically. Final values of the conventional R factors were $R = 0.04$ and $R_w = 0.06$ based on 8424 independent data with $I > 3\sigma(I)$ for complex **2**, and $R = 0.06$ and $R_w = 0.08$ based on 5248 independent data with $I > 3\sigma(I)$ for complex **3**.

Results and Discussion

During the course of a program concerned with the synthesis and structural characterization of new rhenium complexes containing chelate and multidentate amine ligands, we reported the unexpected formation of a *trans*-bpy structure from the reaction of bpy with *trans,mer*-[Re(NPh)(PPh$_3$)$_2$Cl$_3$] in C$_2$H$_5$OH.[14] Likewise, the reaction of the multidentate chelate ligand *o*-bpy under similar conditions was found to follow the same reaction course, giving the complex *trans*-[Re^V(NPh)(*o*-bpy)(OEt)]$^{2+}$ in which the ligand enveloped the rhenium ion.[8] In contrast, the reaction of *trans,mer*-[Re(NPh)(PPh$_3$)$_2$Cl$_3$] with the ligand tpmt in C$_2$H$_5$OH gave an unprecedented monomeric rhenium(V) complex in a tricationic state, [Re(NPh)(tpmt)(C$_2$H$_5$OH)]$^{3+}$, in which the central part of the molecule adopts a saddle-like conformation.[7] This latter observation suggested that rhenium with sterically hindered ligands, especially ortho to nitrogen atoms, might show novel physicochemical properties or exhibit unusual structures and/or oxidation states. Consequently, the sterically hindered chelates 6-cnbpy, 6-mebpy, and dmp were investigated.

Not surprisingly, the reaction of the ligands with *trans,mer*-[Re(NPh)(PPh$_3$)$_2$Cl$_3$] was different in every case. With 6-cnbpy, a Re(III) complex is obtained where the ethanol solvent has transformed the cyano group into an amidate ester chelate as shown in Figure 1. Here, the metal ion plays an active role by inducing long-range polarization through the ligand σ-bonding framework, which enhances the electrophilic character of the nitrile carbon. This leads to the attack of the alcohol on the nitrile carbon, generating an anionic species that is stabilized by coordination to rhenium.[23] Tridentate amine chelates at Re(III) are relatively rare, although many amine complexes are known.[24] Unfortunately as will be discussed later, the single-crystal diffraction structure was less than satisfying due to poor crystal quality.

For 6-mebpy, the $-$NPh group was retained, giving a pseudooctahedral Re(V) complex of composition [Re(NPh)(6-mebpy)(PPh$_3$)(Cl)(OEt)]$^+$. Of note is that the "sterically-sheltering" methyl group of 6-mebpy lies opposite the bulky PPh$_3$. This observation suggests that ligands such as 6-mebpy could be used in future studies to induce chirality into metal complexes in a highly specific fashion.

In the case of dmp a very unusual Re(IV)$-$imido complex is obtained. The only other reported complex containing the Re(IV)$-$NPh[25] grouping is unstable in air. An important feature of the dmp ligand, and perhaps a key to the stability of this complex, is its ability to block several coordination sites and to force sterically-bulky groups such as PPh$_3$ to the opposite pole of the coordination sphere.

Infrared and Electronic Absorption Spectroscopy. The IR spectrum of the complexes exhibited a broad band at ca. 838 cm^{-1} indicative of a PF$_6$ group, while the bands because of the NPh group are shadowed by the stretches from the ligands. In complex **1**, a significant peak is observed at 1560 cm^{-1}, probably due to an imine-like coordination of the cyano group of the 6-cnbpy ligand.

The visible region spectrum of complex **1** exhibited three prominent bands at 515, 447, and 388 nm (log ϵ = 3.46, 3.68, and 3.67 M^{-1} cm^{-1}, respectively). In the UV region, a band at 272 nm and two shoulders at 291 and 313 nm (log ϵ = 4.29, 4.23, and 4.09 M^{-1} cm^{-1}, respectively) were observed. The moderate intensity of the bands in the electronic spectrum indicates perturbed d$-$d transitions and suggests mixing with the metal-to-ligand charge-transfer states. The visible region spectrum of complex **2** showed a broad band centered at 530 nm and a shoulder at 421 nm (log ϵ = 2.39 and 3.05 M^{-1} cm^{-1}, respectively). In the ultraviolet region, a band at 272 nm and two shoulders at 291 and 313 nm (log ϵ = 4.29, 4.23, and 4.09 M^{-1} cm^{-1}, respectively) were observed. The visible spectrum observed for complex **3** is similar to that of complex **2** except the peaks were shifted to the blue. A broad band at 485 nm and a shoulder-like band at 402 nm (log ϵ = 2.98 and 3.34 M^{-1} cm^{-1} respectively) were exhibited. In the ultraviolet region, shoulders at 318 and 383 nm and a band at 275 nm with a shoulder at 283 nm (log ϵ = 4.28, 4.38, 4.60, and 4.57 M^{-1} cm^{-1}, respectively) were observed.

Electrochemistry. The redox chemistry for complex **1** containing the 6-cnbpy ligand is very rich and interesting. At $E_{1/2} = -1.25$ V ($E_{cat} = -1.28$ V and $E_{an} = -1.22$ V; cat = cathodic and an = anodic) a one-electron exchange takes place as the $\Delta E_p = 60$ mV value indicates. However, this redox wave is clearly a quasi-reversible exchange as can be seen from the difference in the size of the cathodic and anodic peak currents. At $E = -0.93$ V a new product is formed due to the preceding redox wave at $E_{1/2} = -1.25$ V. The inference is obtained because of the fact that this oxidation wave is not observed when cyclic voltammetry is run from 0.0 to -1.0 V. Hence, the wave at $E_{1/2} = -1.25$ V could thus be due to the Re(III) $\leftrightarrow$ Re(II) couple. Between 0.0 and 0.1 V still new product formation takes place, as these oxidation and reduction features are not observed when cyclic voltammetry is run from 1.0 to 0.0 V. At $E_{1/2} = 0.7$ V ($E_{cat} = 0.67$ V, $E_{an} = 0.73$ V, and $\Delta E_p = 60$ mV) a reversible exchange again takes place as demonstrated by the anodic and cathodic peak currents. The magnitude of ΔE_p for this peak potential is the same as that for the Fc/Fc$^+$ couple. The Fc/Fc$^+$ couple under our experimental conditions was displayed at 0.45 V *vs* Ag/AgCl. A representative peak profile in the entire scan range from +2.0 to -2.0 V is shown in Figure 2. The electrochemistry for complex **2** is also very complex. A series of oxidation and reduction waves were

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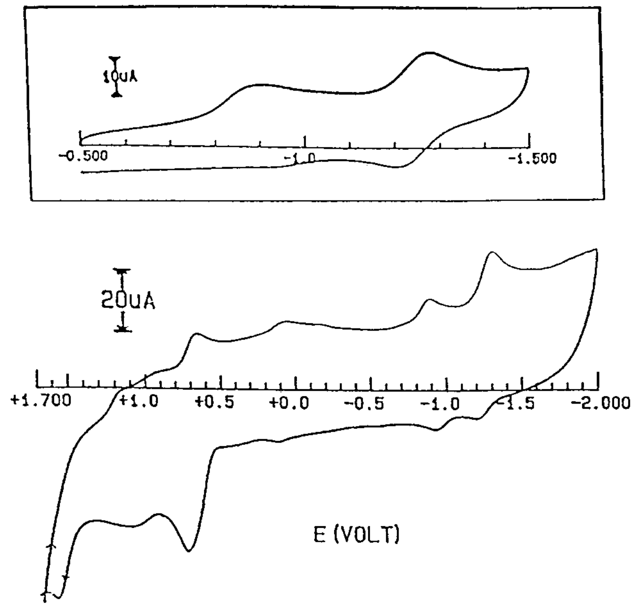

Figure 2. Cyclic voltammogram of the complex [Re(6-cnbpy-OEt)-(PPh$_3$)$_2$(Cl)]$^+$ at a scan rate of 100 mV/s. Inset: CV in the range of -0.5 V to $+1.5$ V.

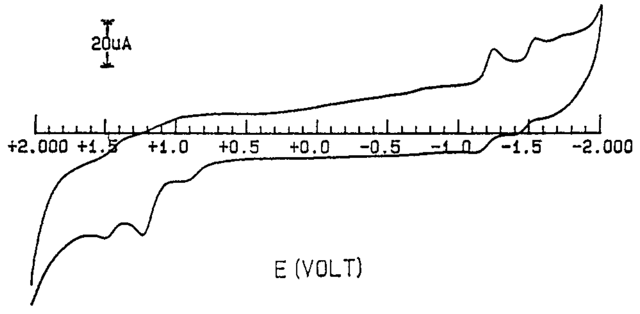

Figure 3. Cyclic voltammogram of the complex [Re(NPh)(dmp)(PPh$_3$)-(OEt)]$^+$ at a scan rate of 100 mV/s.

observed only between +1.0 to -1.0 V, the most prominent being an oxidative wave with a pronounced oxidative current at 0.7 V. The electrochemistry for complex **3** apparently looks similar to that of complex **1**. At -1.23 V a reduction wave is observed, and on reversing the scan an oxidative wave is observed at ca. -1.16 V ($E_{1/2} = -1.2$ V and $\Delta E_p = 70$ mV), again a one-electron quasi-reversible wave. As the reduction cycle continues, another reduction wave is displayed at -1.53 V, and on reversing the cycle, an oxidative wave is displayed at -1.4 V ($E_{1/2} = -1.47$ V and $\Delta E_p = 130$ mV). This could be either a ligand reduction or a new product formation. In the positive potential region, oxidative waves are observed at 0.9, 1.2, and 1.48 V which can be deduced as oxidative waves. A representative cyclic voltammogram is given in Figure 3.

X-ray Crystal Structures. The crystals for complex **1** could be grown only from CH$_3$CN, and no crystals could be obtained when other counterions or solvent combinations were used. The quality of the crystals was less than satisfactory. Of the several crystals tried (twinned, could not pass through the orientation matrix, or did not diffract), we could only collect the data from one crystal after deleting many reflections from the determination of the preliminary unit cell and orientation matrix, and filled it with Friedel pairs. Consequently, the data collected were unsatisfactory. Hence, we could not refine the atoms anisotropically but are only able to confirm the structure. Because of this, we are restricting our discussion on its crystal properties except for defining it as an octahedral complex. A view of the cation as the confirmation of the structure is depicted in Figure 4.

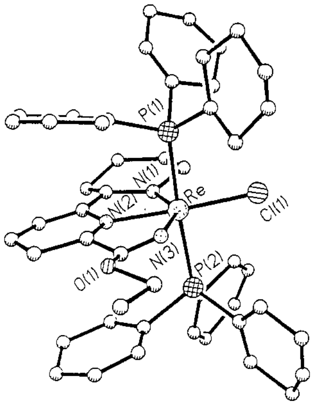

Figure 4. View of the structure of the cation as the confirmation of the structure [Re(6-cnbpy-OEt)(PPh$_3$)$_2$(Cl)]$^+$ in the crystals of the hexafluorophosphate salt. Hydrogen atoms are omitted for clarity.

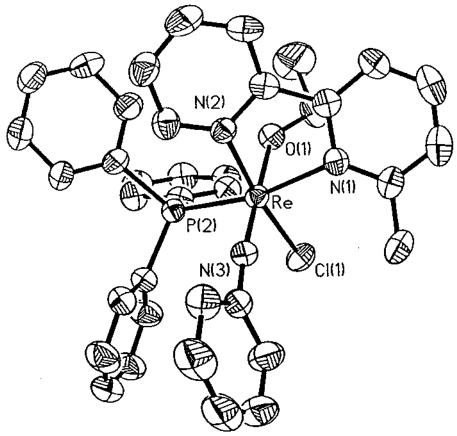

Figure 5. View of the structure of the cation [Re(NPh)(6-mebpy)-(PPh$_3$)(Cl)(OEt)]$^+$ in the crystals of the hexafluorophosphate salt. Hydrogen atoms are omitted for clarity.

(a) Structure of Complex 2, [Re(NPh)(6-mebpy)(PPh$_3$)-(Cl)(OEt)]$^+$. A view of the cation of the rhenium(V) complex is depicted in Figure 5, and selected bond lengths and angles in the structure are listed in Table 2. The geometry of the cation can be defined as a distorted octahedron. The equatorial plane can be either defined by those atoms which enclose the metal ion in its plane (the minimal deviation of the metal ion from the four-atom least-squares plane) or by the axial coordination bonds approximating 180°, with the other four atoms then constituting the plane. When the atoms N(1), N(2), Cl(1), and P(2) are considered to constitute the plane (with *trans*-phenylimido and -ethoxide groups), the average mean deviation from the four-atom least-squares plane is found to be 0.064 Å. Here the rhenium atom is 0.191 Å above the plane toward the N(3), and the *trans* bond angle N(3)−Re−O(1) is 177.7°. The bond angles of 142.8(4)° and 175.3(4)° for Re−O−C and Re−N−C in Re−OEt and Re−NPh groups, respectively, indicate the existence of multiple bonding for both the groups. However, none of the equatorial *cis* angles closely approximate to the idealized value of 90°. The minimum is found to be 75.7° for N(1)−Re−N(2) and the maximum 99.6° for N(1)−Re−Cl(1). In an alternate view N(2), N(3), O(1), and Cl(1) atoms are considered to constitute a plane; the *trans* bond angle N(1)−Re−P(2) is 166.4°, which deviates markedly from 180°. In this case, the mean deviation from the four-atom least-squares plane,

Table 2. Selected Intramolecular Distances (Å) and Bond Angles (deg) Involving [Re(NPh)(mebpy)(PPh$_3$)(Cl)(OEt)]$^+$ [a]

Re−N(1)	2.20(5)	Re−N(3)	1.75(5)	Re−O(1)	1.92(4)
Re−N(2)	2.12(5)	Re−Cl(1)	2.44(2)	Re−P(2)	2.45(2)
N(1)−Re−N(2)	75.7(2)	N(3)−Re−Cl(1)	92.6(2)	N(1)−Re−P(2)	166.4(1)
N(1)−Re−N(3)	96.1(2)	N(1)−Re−O(1)	81.8(2)	N(2)−Re−P(2)	98.7(1)
N(2)−Re−N(3)	93.7(2)	N(2)−Re−O(1)	85.1(2)	N(3)−Re−P(2)	96.6(2)
N(1)−Re−Cl(1)	99.6(1)	N(3)−Re−O(1)	177.7(2)	Cl(1)−Re−P(2)	98.7(1)
N(2)−Re−Cl(1)	172.5(1)	Cl(1)−Re−O(1)	88.5(1)	O(1)−Re−P(2)	85.5(1)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Intramolecular Distances (Å) and Bond Angles (deg) Involving [Re(NPh)(dmp)(PPh$_3$)(OEt)]$^+$ [a]

Re−N(1)	2.45(24)	Re−O(1)	1.87(15)		
Re−N(2)	2.18(22)	Re−P(2)	2.35(6)		
Re−N(3)	1.63(19)				
N(1)−Re−N(2)	77.4(9)	N(3)−Re−O(1)	174.8(9)	Re−N(3)−C(15)	169.4(20)
N(1)−Re−N(3)	100.8(8)	N(1)−Re−P(2)	109.0(5)	Re−O(1)−C(39)	136.0(19)
N(2)−Re−N(3)	101.9(9)	N(2)−Re−P(2)	164.8(6)	O(1)−C(39)−C(40)	121.2(37)
N(1)−Re−O(1)	84.1(7)	N(3)−Re−P(2)	91.4(7)		
N(2)−Re−O(1)	78.4(7)	O(1)−Re−P(2)	88.4(5)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

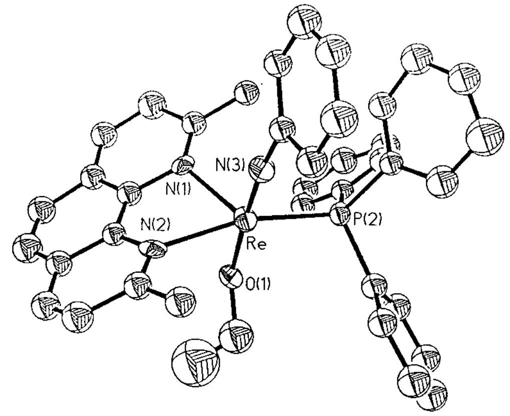

Figure 6. View of the structure of the cation [Re(NPh)(dmp)(PPh$_3$)(OEt)]$^+$ in the crystals of the hexafluorophosphate salt. Hydrogen atoms are omitted for clarity.

however, is only 0.024 Å. Furthermore, all the equatorial bond angles vary only between 85.1° and 93.7°. The equatorial bond length of 2.119(5) Å for Re−N(2) is shorter by about 0.082 Å compared to the axial bond length of 2.201(5) Å for Re−N(1), both the nitrogen donor atoms coming from the 6-mebpy ligand. Metal to other donor atom bond lengths in the complex are similar to those of reported cases.[8,26]

(b) Structure of complex 3, [Re(NPh)(dmp)(PPh$_3$)(OEt)]$^+$. A view of this cation is depicted in Figure 6, with selected bond lengths and angles in the structure listed in Table 3. The oxidation state of the metal ion in the complex is undoubtedly a rare Re(IV) with a five-coordinate geometry. In high-valent chemistry, one of the most accessible oxidation states of rhenium is VII, which is obtained by mild oxidation of the metal. Re(V) is also accessible for oxo, nitrido, and imido complexes.[27] Although Re(IV) is stable, it is rare and occurs with classical ligands (*i.e.*, predominantly σ donors),[26] and like other d^3 ions, the rhenium(IV) atom normally adopts an octahedral stereochemistry. Also, it is apparent from the literature that variable amounts of Re(IV) complexes are formed as byproducts in several reactions of Re(V) and Re(III), for example, *trans,mer*-[Re(PPh$_3$)$_2$Cl$_4$].[28−30] We have a strong reason to believe that this complex also is a byproduct, or might be the decomposed portion of the main product. Whatever may be the case, in the complex under discussion the Re(IV) atom adopts a highly unusual five-coordinate geometry. Five-coordinate trigonal bipyramidal/square pyramidal geometries are mostly preferred by Re(III) and Re(V) ions bonded to sterically congested thiolate ligands.[31−35]

As is invariably the case for five-coordinate metal complexes, the observed geometry could be described as either a distorted trigonal bipyramid or a distorted tetragonal pyramid. The τ test defined by Addison *et al.*[36] is applied by using the largest angle 174.8° as β and the next largest angle 164.8° as α, yielding $\tau = (\beta - \alpha)/60$ of 0.167, where a $\tau = 0$ would define a regular square planar geometry and $\tau = 1$ an undistorted trigonal bipyramid. Thus, the coordination geometry is a distorted tetragonal, with the N(1) atom occupying an apical position, and the rhenium atom is displaced from the four-atom least-squares plane by *ca.* 0.13 Å toward N(1); the plane itself has an average deviation of 0.05 Å. The N(1)−Re axial bond length of 2.44 Å is much longer than the N(2)−Re equatorial bond length of 2.17 Å. The N(3)−Re metal to phenylimido bond length of 1.62 Å is exceptionally short and is indicative of an extremely strong rhenium−nitrogen multiple bonding. The Re═NPh bond lengths usually lie in the range of 1.71−1.74 Å.[7,8,14,37] Likewise the Re-O(1) metal to ethoxide oxygen bond length of 1.87 Å is short and is suggestive of a multiple bonding,[26] which is aptly demonstrated by an exhibition of the Re−O−C angle of 136.1° for the grouping Re−OEt.[8,14,26,38] The bond angle of 174.8(9)° exhibited by (Ph)N−Re−O(Et) is similar to the values found in the literature.[8,14]

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As pertains to the above discussion, the rhenium ion in these reported complexes is in oxidation state V (higher oxidation state) and should be more Lewis acidic (strong acceptor). The Lewis acidity of the Re(IV) ion in the complex under discussion is evident by the very short bond lengths, and could be due to the low coordination of the rhenium atom. The extent of distortion in the square pyramidal geometric description is also evident from an examination of the *cis* bond angles at the metal, which vary from a minimum of 78.9° [N(2)−Re−O(1)], to a maximum of 100.7° [N(2)−Re−N(3)]. Furthermore, there is no indication of an interaction between the cation and the PF_6 anion in the structure, the distance from rhenium to the closest fluoride atom [F(6)] of the PF_6 counterion being 5.51 Å.

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Supporting Information Available: X-ray crystallographic determination of complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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