Synthesis and Characterization of Phenylimidorhenium(V) Compounds containing Polypyridyl Ligands. Crystal Structures of *mer*-[Re(NPh)Cl_3(bipy)], *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 (bipy = 2,2′-bipyridine, terpy = 2,2′:6′,2″-terpyridine)†

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The reaction between *mer*-[Re(O)Cl_3(L–L)] [L–L = 2,2′-bipyridine (bipy) or 4,4′-dimethyl-2,2′-bipyridine] and aniline in refluxing *o*-xylene gave phenylimido compounds formulated as *mer*-[Re(NPh)Cl_3(L–L)]. These compounds do not react with an alcohol (ROH) to form alkoxyimido compounds of the type *cis*-[Re(NPh)(OR)Cl_2(L–L)], but in the presence of an excess of the polypyridyl ligand, salts of the cation *trans*-[Re(NPh)(OEt)$(L\text{–}L)_2$]$^{2+}$ were obtained. When salts of *trans*-[Re(NPh)(OEt)$(L\text{–}L)_2$]$^{2+}$ were dissolved in MeCN solutions containing a few drops of concentrated hydrochloric acid rapid reactions occurred that resulted in the isolation of *mer*-[Re(NPh)Cl_3(L–L)]. The salt *trans*-[Re(NPh)Cl_2(terpy)]PF_6 was prepared from the reaction between *mer-trans*-[Re(NPh)$Cl_3(PPh_3)_2$] and 2,2′:6′,2″-terpyridine (terpy) in refluxing ethanol. The spectroscopic and electrochemical properties of these compounds were investigated and the structures of *mer*-[Re(NPh)Cl_3(bipy)], *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 determined by X-ray crystallography.

High-valent rhenium compounds containing organoimido group(s) have attracted much attention in recent years because of the rich physicochemical properties and reactivity patterns they exhibit.[1–6] Many synthetic routes for obtaining such compounds are available starting from oxorhenium(V) compounds such as *mer*-[Re(O)X_3L_2] (X = halide, L = tertiary phosphine).[7–11] Although, phenylimidorhenium(V) compounds containing phosphines,[12–14] dithiocarbamate[15] and 1,4,8,11-tetraazacyclotetradecane (cyclam)[2] ligands have been reported, such compounds containing polypyridyl ligands are scarce. In an earlier study, we briefly reported the synthesis, spectroscopic and electrochemical properties of *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ (bipy = 2,2′-bipyridine).[1a] In this report, a full account of the synthesis, spectroscopic and electrochemical properties of a series of phenylimidorhenium(V) compounds containing polypyridyl ligands together with the crystal structures of *mer*-[Re(NPh)Cl_3(bipy)] **1**, *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ **2** and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** (terpy = 2,2′: 6′,2″-terpyridine) is presented.

Experimental

Reagents and Reaction Procedures.—Solvents were reagent grade and thoroughly deoxygenated prior to use. All other reagents were obtained from commercial sources and used without further purification. The compounds *mer*-[Re(NPh)$Cl_3(PPh_3)_2$],[12] *mer*-[Re(O)Cl_3(bipy)][16] and *mer*-[Re(O)$Cl_3(PPh_3)_2$][17] were prepared by standard literature methods. All reactions were performed under a nitrogen atmosphere using standard vacuum-line techniques.

Preparations.—(*a*) *mer*-[Re(NPh)Cl_3(bipy)] **1**. A mixture of *mer*-[Re(O)Cl_3(bipy)] (200 mg, 0.43 mmol), NH_2Ph (1 cm^3) and *o*-xylene (50 cm^3) was refluxed for 2 d. The resulting reaction mixture was allowed to cool to room temperature and a purple solid was filtered off, washed with *o*-xylene, hexane, diethyl ether and dried. The product was chromatographed on an alumina column (MeCN as eluent) and recrystallized from MeCN–diethyl ether. The purple product was then washed with hexane, diethyl ether and dried; yield 150 mg, 0.28 mmol (65%) (Found: C, 36.25; H, 2.20; N, 7.65. $C_{16}H_{13}Cl_3N_3Re$ requires C, 35.60; H, 2.45; N, 7.80%).

(*b*) *mer*-[Re(NPh)Cl_3(dmbipy)]. In a procedure analogous to that described in (*a*) but using *mer*-[Re(O)Cl_3(dmbipy)] (dmbipy = 4,4′-dimethyl-2,2′-bipyridine) (200 mg, 0.40 mmol) the expected product was isolated in 30% yield (Found: C, 34.95; H, 2.80; N, 6.60. $C_{18}H_{17}Cl_3N_3Re$ requires C, 33.85; H, 2.30; N, 7.40%). The identity of the product was confirmed from its electrochemical and spectroscopic properties.

(*c*) *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ **2**. A mixture of *mer*-[Re(NPh)Cl_3(bipy)] (200 mg, 0.37 mmol), bipy (230 mg, 1.48 mmol) and EtOH (200 cm^3) was refluxed for 4 d. The resulting reaction mixture was filtered to remove any insoluble material and the brown filtrate evaporated to dryness. The resulting residue was dissolved in MeCN and chromatographed on an alumina column. The column was washed with CH_2Cl_2 and MeCN until all of the purple unreacted *mer*-[Re(NPh)Cl_3(bipy)] had been removed and the final brown fraction was eluted with ethanol. The ethanol fraction was reduced in volume to ≈10 cm^3, NH_4PF_6 (300 mg) added and the mixture stirred at room temperature for 1 h. A brown solid was filtered off, washed with ethanol, hexanes, diethyl ether and dried; yield 150 mg (43%) (Found: C, 36.40; H, 2.75; N, 7.55. $C_{28}H_{26}F_{12}N_5OP_2Re$ requires C, 36.35; H, 2.75; N, 7.55%).

(*d*) *trans*-[Re(NPh)(OEt)$(dmbipy)_2$][ClO_4]$_2$. Following a procedure analogous to (*c*) but using *mer*-[Re(NPh)Cl_3(dmbipy)] (200 mg, 0.35 mmol) and with $NaClO_4$ in place of NH_4PF_6 the expected product was isolated in 45% yield. The product was characterized from its electrochemical and spectroscopic properties.

(*e*) *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3**. A mixture of *mer*-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystal data for *mer*-[Re(NPh)Cl_3(bipy)] **1**, *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ **2** and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3**

	1	**2**	**3**
Formula	$C_{16}H_{13}Cl_3N_3Re$	$C_{28}H_{26}F_{12}N_5OP_2Re$	$C_{21}H_{16}Cl_2F_6N_4PRe$
M	539.8	924.7	726.4
Space group	$P2_12_12_1$	$P2_1/n$	$Pbca$
a/Å	6.9080(10)	11.032(3)	14.133(4)
b/Å	14.623(2)	8.485(2)	12.586(4)
c/Å	17.115(2)	34.642(6)	25.841(7)
β/°		98.32(2)	
U/Å^3	1728.9(4)	3208.6(13)	3099.1(10)
Z	4	4	8
D_c/Mg m^{-3}	2.074	1.914	3.114
μ/mm^{-1}	7.593	4.036	8.496
F(000)	1024	1800	2784
Crystal size/mm	0.50 × 0.26 × 0.17	0.14 × 0.16 × 0.36	1.00 × 0.86 × 0.50
λ(Mo-Kα)/Å	0.710 73	0.710 73	0.710 73
T/°C	23	−100	23
Scan type	ω	ω	2θ–θ
Data collection range, 2θ/°	4.0–60.0	4.0–50.0	4.0–50.0
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0010F^2$	$\sigma^2(F) + 0.0004F^2$	$\sigma^2(F) + 0.0030F^2$
Reflections collected	4531	8639	3026
Independent reflections	3977 (R_{int} = 0.080)	5631 (R_{int} = 0.0293)	3026 (R_{int} = 0.00)
Observed reflections [$F > 6.0\sigma(F)$]	2741	3704	2245
Number of parameters refined	208	442	316
Max., min. transmission	0.0360, 0.1017	0.1179, 0.1628	0.0004, 0.0081
Final R indices (observed data)	R = 0.0410, wR = 0.0490	R = 0.0332, wR = 0.0367	R = 0.0542, wR = 0.0718
R indices (all data)	R = 0.0667, wR = 0.0575	R = 0.0659, wR = 0.0450	R = 0.0677, wR = 0.0860
Goodness-of-fit	1.05	1.06	1.22
Largest and mean Δ/σ	0.004, 0.000	0.023, 0.003	0.098, 0.018
Largest difference peak/e Å^{-3}	1.31	0.64	1.98
Largest difference hole/e Å^{-3}	−1.75	−0.65	−0.63

[Re(NPh)Cl_3(PPh_3)$_2$] (200 mg, 0.22 mmol), terpy (100 mg, 0.43 mmol) and ethanol (100 cm^3) was refluxed for 3 d. The reaction mixture was then cooled to room temperature, filtered and the filtrate evaporated to dryness. The resulting residue was loaded on an alumina column which was washed with MeCN and CH_2Cl_2 and the product eluted with ethanol. The ethanol solution was reduced in volume to ≈10 cm^3, NH_4PF_6 (500 mg, 3.07 mmol) added and the mixture stirred at room temperature for 2 h. An orange solid was filtered off, washed with H_2O, ethanol, hexane and diethyl ether. The product was further recrystallized from MeCN–diethyl ether, filtered and dried; yield 120 mg (77%) (Found: C, 36.20; H, 2.25; Cl, 8.55; N, 7.65. $C_{21}H_{16}Cl_2F_6N_4PRe$ requires C, 34.75; H, 2.20; Cl, 9.75; N, 7.65%).

Reaction of trans-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ *with Aqueous* HCl.—A quantity of *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ (100 mg, 0.19 mmol) was dissolved in MeCN (100 cm^3) and 12 mol dm^{-3} HCl (3 cm^3) was added. The reaction mixture was refluxed for 12 h, and the resulting mixture was allowed to cool to room temperature. A red solid was filtered off, washed with diethyl ether and dried; yield 65 mg (63%). The resulting product was identified as *mer*-[Re(NPh)Cl_3(bipy)] from its electrochemical and spectroscopic properties.

Reaction of mer-[Re(NPh)Cl_3(bipy)] *with Alcohols.*—A mixture of *mer*-[Re(NPh)Cl_3(bipy)] (100 mg, 0.19 mmol), and ethanol (100 cm^3) was refluxed for 2 d. During this period there was no colour change. The resulting reaction mixture was allowed to cool to room temperature and a dark red solid was filtered off, washed with hexane, diethyl ether and dried; yield: 90 mg (89%). The resulting product was identified as *mer*-[Re(NPh)Cl_3(bipy)] from its electrochemical and spectroscopic properties.

Crystal Structure Determination of Complexes **1**–**3**.—Single crystals of *mer*-[Re(NPh)Cl_3(bipy)] **1**, *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ **2** and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** were grown by the slow diffusion of acetonitrile solutions of these compounds into diethyl ether. The resulting crystals were filtered off, washed with diethyl ether and dried in air.

Crystals of **1**–**3** were mounted on glass fibres with an epoxy cement and placed on a Nicolet R3m/V diffractometer. Crystallographic data for each crystal are listed in Table 1. The cell parameters were based on 50 reflections in the range 20 < 2θ < 30°. Six standard reflections for compounds **1** and **3** and three standard reflections for **2** were measured every 100 reflections during data collection and displayed no systematic variations in intensity. The solution programs used were from the SHELXTL system.[18] Absorption corrections were applied to each data set, based on azimuthal scans of several reflections with an Eulerian angle χ near 90°.

The structure of *mer*-[Re(NPh)Cl_3(bipy)] **1** was solved by direct methods and developed in a sequence of least-squares refinements and Fourier difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final least-squares cycle, 208 parameters were fitted to 2741 observations, for a data-to-parameter ratio of 13.2 : 1. The least-squares residuals and other relevant parameters are given in Table 1.

For *trans*-[Re(NPh)(OEt)$(bipy)_2$][PF_6]$_2$ **2** and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** the position of the rhenium atom was located from Patterson maps, and the remaining non-hydrogen atoms located in subsequent Fourier difference maps. In the final least-squares cycle for complex **2** 442 parameters were fitted to 3704 observations, for a data-to-parameter ratio of 8.38 : 1. In the case of complex **3** 316 parameters were fitted to 2245 observations, for a data-to-parameter ratio of 7.1 : 1. The least-squares residuals and other relevant parameters are given in Table 1.

In all structures, the positions of the hydrogen atoms were calculated by assuming an idealized geometry and a C–H bond distance of 0.96 Å.

Table 2 Electronic absorption spectral data and electrochemical properties

Compound	λ^a/nm (ε/dm^3 mol^{-1} cm^{-1})	E/V
mer-[Re(NPh)Cl_3(bipy)]	763 (468), 524 (4397), 298 (16 261), 228 (19 750)	−0.83 ($E_{p,c}$), +1.00 (ox)
mer-[Re(NPh)Cl_3(dmbipy)]	777 (336), 517 (5034), 298 (22 907), 230 (38 857)	−0.88 ($E_{p,c}$), +0.97 (ox)
mer-[Re(O)Cl_3(bipy)]	800 (80), 440 (2032), 413 (1732), 294 (13 470), 245 (11 839)	−0.52 ($E_{p,c}$), +1.73 (ox)
mer-[Re(O)Cl_3(dmbipy)]	800 (87), 432 (3315), 400 (1612), 290 (14 050), 248 (12 925)	−0.56 ($E_{p,c}$), +1.64 (ox)
trans-[Re(NPh)(OEt)$(bipy)_2$]$[PF_6]_2$	525 (424), 421 (sh) (3467), 364 (9535), 316 (23 114), 221 (43 339)	−0.55 (red), −0.90 (red), −0.96 (red), −1.28 (red)
trans-[Re(NPh)(OEt)$(dmbipy)_2$]$[PF_6]_2$	514 (775), 414 (sh) (3422), 364 (6715), 312 (14 798), 287 (sh) (18 270), 271 (sh) (19 208), 234 (39 400), 203 (59 191)	−0.066 (red), −1.02 (red), −1.1 (red), −1.43 (red)
trans-[Re(NPh)Cl_2(terpy)]PF_6	845 (421), 496 (2335), 455 (2464), 347 (18 613), 283 (sh) (26 118), 274 (27 619), 236 (sh) (30 020)	−0.31 (red), −0.55 (red), −0.65 (red), +1.43 (ox)

[a] Recorded on MeCN solutions. [b] Half-wave potentials (unless otherwise stated) *vs.* SCE. Recorded on solutions in 0.1 mol dm^{-3} $NBu^n_4PF_6$–MeCN using a platinum disc electrode (0.07 cm^2). Data obtained at ν = 100 mV s^{-1}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Physical Measurements.—Electronic absorption spectra were recorded on a Perkin-Elmer UV/VIS/NIR Lambda 9 spectrometer. Solution ^{1}H NMR spectra were recorded on JEOL GSX (270 MHz) and JEOL GX (400 MHz) Fourier-transform spectrometers. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Electrochemical measurements were made in solutions of MeCN with 0.1 mol dm^{-3} $NBu^n_4PF_6$ as the supporting electrolyte. A platinum disc (0.07 cm^2) was used as the working electrode. All potentials were referenced to the saturated sodium chloride calomel electrode (SSCE) at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with the use of a PAR 173 galvanostat/potentiostat in conjunction with a home-built supercycle, and a SOLTEC VP-6414S X-Y recorder. A PAR 179 digital coulometer was used in conjunction with a PAR 173 galvanostat/potentiostat for coulometry experiments. Infrared spectra were recorded as Nujol mulls on a MIDAC FTIR spectrometer.

Elemental microanalyses were performed by Desert Analytical, Tucson, Arizona.

Results and Discussion

Synthesis.—The reaction between *mer*-[Re(O)Cl_3(L–L)] (L–L = bipy **1** or dmbipy) and aniline in refluxing *o*-xylene gave phenylimidorhenium(v) compounds of the type *mer*-[Re(NPh)Cl_3(L–L)]. This reaction is similar to that reported for the synthesis of a variety of phenylimidorhenium(v) species containing phosphine ligands from the reaction between oxorhenium(v) species and aniline in refluxing xylene.[3] The resulting compounds *mer*-[Re(NPh)Cl_3(L–L)] do not react with an alcohol (ROH) under refluxing conditions to form *cis*-[Re(NPh)(OR)Cl_2(L–L)]. For example, when *mer*-[Re(NPh)Cl_3(bipy)] was allowed to react with absolute ethanol under refluxing conditions for 2 d only the starting material was recovered. This reaction is in contrast to that observed when *mer*-[Re(O)Cl_3(bipy)] is allowed to react with alcohols under refluxing conditions to give *cis*-[Re(O)(OR)Cl_2(bipy)] (R = Me, Et or Pr^n).[19] In the presence of an excess of a polypyridyl, *mer*-[Re(NPh)Cl_3(L–L)] (L–L = bipy or dmbipy) reacts with ethanol under refluxing conditions to give brown salts of the cation *trans*-[Re(NPh)(OEt)$(L–L)_2$]$^{2+}$. These salts represent the first examples of phenylimidorhenium(v) compounds containing two mutually *trans* polypyridyl ligands. The isolation of these salts was unexpected based upon the inertness of *mer*-[Re(NPh)Cl_3(L–L)] toward alcohols and the steric demand associated with placing two polypyridyl ligands in a *trans* position. When the brown salts of *trans*-[Re(NPh)(OEt)$(L–L)_2$]$^{2+}$ were allowed to dissolve at room temperature in MeCN solutions containing a few drops of concentrated hydrochloric acid rapid reactions occurred that resulted in the isolation of *mer*-[Re(NPh)Cl_3(L–L)]. These reactions proceed through the intermediacy of a dark green species whose identity and mechanism for its conversion to *mer*-[Re(NPh)Cl_3(L–L)] remain to be investigated. The salt, *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** was prepared from the reaction between *mer*-[Re(NPh)$Cl_3$$(PPh_3)_2$] and terpy in ethanol under refluxing conditions. The chloride salt of *trans*-[Re(NPh)Cl_2(terpy)]$^+$ is stable in MeCN solution containing hydrochloric acid.

Spectroscopic and Electrochemical Properties.—The electronic absorption spectral properties of the compounds measured in MeCN and the related oxorhenium(v) compounds containing polypyridyl ligands are summarized in Table 2. The spectra of these compounds show low-energy dπ–dπ transitions for the d^2 configuration of Re^V. These bands are LaPorte forbidden, and therefore, have relatively low molar absorption coefficients. The intense, high-energy bands (ε > 10^3 dm^3 mol^{-1} cm^{-1}) observed probably originate from ligand-to-metal charge-transfer (l.m.c.t.) transitions. Related features appeared in the spectra of *fac*-[Re(NR)X_3(dppbe)][4] [R = Pr^n, Bu^i or Et; X = halide; dppbe = 1,2-bis(diphenylphosphino)benzene] and *trans*-[Os^{VI}(N)Cl_2(terpy)]Cl.[20]

In the ^{1}H NMR spectra of these compounds, a series of resonances was observed that is consistent with the presence of co-ordinated ligands. For example, the ^{1}H NMR spectrum of *mer*-[Re(NPh)Cl_3(bipy)] **1** measured in CD_2Cl_2 shows the bipy resonance as a pseudo-doublet at δ 9.32, doublet at δ 8.45, pseudo-quartet at δ 8.09, pseudo-quartet at δ 7.93, pseudo-doublet at δ 7.75, pseudo-triplet at δ 7.5, pseudo-triplet at δ 7.38 and a pseudo-triplet at δ 7.17. These spectral properties are consistent with the *mer* geometry adopted by this compound. For *trans*-[Re(NPh)(OEt)$(bipy)_2$]$[PF_6]_2$ **2** the bipy resonances were observed as a pseudo-triplet at δ 7.89, pseudo-triplet at δ 8.52, pseudo-doublet at δ 8.72 and a doublet at δ 9.25. In the ethyl region a triplet and a doublet were observed at δ 0.32 and 3.25, respectively. The bipy/ethyl protons integrate in a ratio of 16:5. The phenyl resonances in both compounds **1** and **2** were observed well separated from the bipy resonances and integrated in the right ratio for co-ordinated bipy ligands. In the case of *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3**, a series of resonances characteristic of co-ordinated terpy was observed, together with resonances associated with the phenyl protons. There is no evidence of paramagnetic broadening or shifts of resonances confirming that these compounds are diamagnetic.

The IR spectra (Nujol mulls) of the compounds show ν(Ph) and ν(bipy or terpy) stretching and bending modes as expected. In the case of *trans*-[Re(NPh)(OEt)$(bipy)_2$]$[PF_6]_2$ **2** and *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** the ν(P–F) modes of PF_6^- were observed at 845 and 842 cm^{-1}, respectively. The ν(Re≛NPh) modes were not located as they may be mixed with other ν(Re–N) modes of the polypyridyl ligands.

The electrochemical properties of *mer*-[Re(NPh)Cl_3(L–L)], *trans*-[Re(NPh)(OEt)$(L–L)_2]^{2+}$ and *trans*-[Re(NPh)Cl_2(terpy)]$^+$ were investigated using cyclic voltammetry in 0.1 mol dm^{-3} $NBu^n{}_4PF_6$–MeCN solutions and the results are reported in Table 2. A comparison of the redox potentials of *mer*-[Re(NPh)Cl_3(L–L)] with *trans*-[Re(NPh)Cl_2(terpy)]$^+$ shows that replacing one chloride ion by a nitrogen atom from the terpy ligand causes the reversible Re^V–Re^{VI} couple and the couple *trans*-[Re(NPh)Cl_2(terpy)]$^{+/0}$ to shift to more positive potentials, consistent with the electron deficiency created on the metal centre by replacing a chloride ion with a nitrogen atom of terpy. A comparison of the electrochemistry of *mer*-[Re(NPh)Cl_3(L–L)] with the isoelectronic and isostructural oxorhenium(V) compounds,[18] shows that the introduction of a strong π-donor (oxo) ligand causes the redox potentials of both the Re^{VI}–Re^V couple and the irreversible reduction process to shift to more negative potentials. A comparison of the redox potentials of *trans*-[Re(NPh)Cl_2(terpy)]$^+$ with those of the isoelectronic and isostructural *trans*-[Os^{VI}(N)Cl_2(terpy)]$^+$ shows that the increase in metal basicity coupled with the decrease in π-donor ability of the imido ligand causes the redox potential of the couple *trans*-[Re(NPh)Cl_2(terpy)]$^{+/0}$ to approach that of *trans*-[Os(N)Cl_2(terpy)]$^{+/0}$.[20] The *trans*-[Re(NPh)Cl_2(terpy)]$^{+/0}$ couple was observed at −0.31 V and the *trans*-[Os(N)Cl_2(terpy)]$^{+/0}$ couple was reported at −0.28 V. On the oxidative side, the Re^V–Re^{VI} couple was observed at +1.43 V. The electrochemistry of *trans*-[Re(NPh)(OEt)$(bipy)_2]^{2+}$ is rich and has been previously communicated and compared with that of the isoelectronic and isostructural *trans*-[Re(NPh)Cl$(dppe)_2]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane].[1a] Due to changes in ligands and stereochemistry around the imidorhenium moiety, it is difficult to make constructive comparisons between the redox potentials of the imido alkoxy salt of *trans*-[Re(NPh)(OEt)$(bipy)_2]^{2+}$ and those of *mer*-[Re(NPh)Cl_3(bipy)] and *trans*-[Re(NPh)Cl_2(terpy)]$^+$.

Structure of mer-[Re(NPh)Cl_3(bipy)] **1**.—An ORTEP[21] drawing of the molecule is shown in Fig. 1. The atomic positional parameters are listed in Table 3 and selected bond distances and angles are given in Table 4. The molecule exhibits a distorted-octahedral co-ordination about the rhenium atom with an axial phenylimido ligand, three chloride ions and one nitrogen atom from the bipy ligand in the equatorial positions and the other axial position being occupied by the other nitrogen atom of the bipy ligand. The chelating bipy ligand essentially forms a planar five-membered metallacycle with a bipyridyl bite angle N(2)–Re–N(3) of 75.3 (3)°. The structure of this molecule is dominated by the strong *trans* effect and the large steric requirement exerted by the imido group. Thus, the Re–N(2) bond length of 2.243(9) Å is significantly greater than the Re–N(3) bond of 2.087(8) Å and all atoms *cis* to the nitrogen atom of the imido moiety are bent away from the imido group. The Re–N(1) and N(1)–C(11) bond distances are 1.710(8) and 1.381(12) Å, respectively and the Re–N(1)–C(11) bond angle 169.6(8)°. The Re–N(1) bond distance falls in the range observed in other phenylimidorhenium(V) compounds, for example, in *mer-trans*-[Re(NPh)$Cl_3(PPh_3)_2$] and [Re(NPr^n)Cl_3(dppbe)], the Re–N bond distances are 1.726(6) and 1.699(5) Å and the Re–N–C bond angles 172.6(6) and 178.7(8)°, respectively. The structural *trans* effect observed in this molecule is significant and is the first to be observed in phenylimidorhenium(V) compounds.

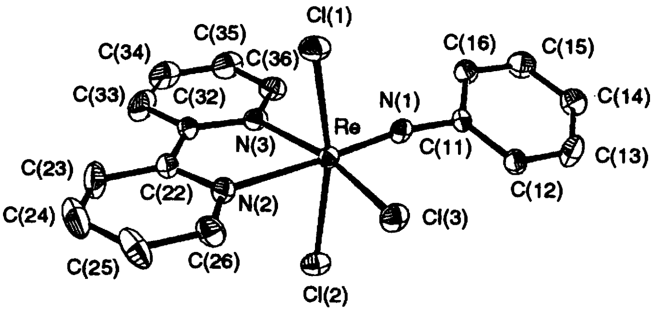

Fig. 1 ORTEP[21] drawing of the structure of *mer*-[Re(NPh)Cl_3(bipy)] **1**

Table 3 Atomic positional parameters (× 10^4) for *mer*-[Re(NPh)Cl_3(bipy)] **1**

Atom	*x*	*y*	*z*
Re	157(1)	522(1)	4277(1)
N(1)	1647(13)	1268(6)	3797(5)
N(2)	−1618(14)	−441(6)	5003(5)
N(3)	1677(13)	405(6)	5327(5)
Cl(1)	1662(5)	−868(2)	3855(2)
Cl(2)	−1831(5)	1645(2)	4883(2)
Cl(3)	−2167(4)	366(2)	3263(2)
C(11)	2552(15)	1915(6)	3336(5)
C(12)	4503(16)	2110(7)	3439(6)
C(13)	5356(18)	2764(9)	2971(8)
C(14)	4303(20)	3210(9)	2410(8)
C(15)	2347(24)	3006(9)	2316(8)
C(16)	1459(17)	2359(8)	2776(6)
C(22)	−838(17)	−638(7)	5708(6)
C(23)	−1750(25)	−1253(10)	6200(8)
C(24)	−3393(27)	−1691(10)	5958(9)
C(25)	−4214(23)	−1466(9)	5244(8)
C(26)	−3289(18)	−846(8)	4773(8)
C(32)	977(17)	−156(8)	5898(6)
C(33)	1919(25)	−258(11)	6605(8)
C(34)	3612(25)	206(11)	6736(7)
C(35)	4346(23)	733(10)	6157(8)
C(36)	3343(18)	860(9)	5467(7)

Table 4 Selected bond distances (Å) and angles (°) for *mer*-[Re(NPh)Cl_3(bipy)] **1** with estimated standard deviations (e.s.d.s) in parentheses

Re–N(1)	1.710(8)	N(2)–C(22)	1.352(14)
Re–N(2)	2.243(9)	N(2)–C(26)	1.356(15)
Re–N(3)	2.087(8)	N(3)–C(32)	1.365(14)
Re–Cl(1)	2.395(3)	N(3)–C(36)	1.351(16)
Re–Cl(2)	2.378(3)	C(22)–C(23)	1.384(18)
Re–Cl(3)	2.376(3)	C(22)–C(32)	1.475(16)
N(1)–C(11)	1.381(12)	C(32)–C(33)	1.381(17)
N(1)–Re–N(2)	174.7(4)	N(2)–Re–Cl(3)	88.6(2)
N(1)–Re–N(3)	99.4(4)	N(3)–Re–Cl(3)	163.9(3)
N(2)–Re–N(3)	75.3(3)	Cl(1)–Re–Cl(2)	165.5(1)
N(1)–Re–Cl(1)	97.7(3)	Cl(1)–Re–Cl(3)	89.5(1)
N(2)–Re–Cl(1)	82.6(2)	Cl(2)–Re–Cl(3)	89.7(1)
N(3)–Re–Cl(1)	88.4(3)	Re–N(1)–C(11)	169.6(8)
N(1)–Re–Cl(2)	96.7(3)	Re–N(2)–C(22)	114.2(7)
N(2)–Re–Cl(2)	82.9(2)	Re–N(2)–C(26)	125.4(8)
N(3)–Re–Cl(2)	88.4(3)	Re–N(3)–C(32)	119.2(7)
N(1)–Re–Cl(3)	96.7(3)	Re–N(3)–C(36)	122.8(7)

Structure of trans-[Re(NPh)(OEt)$(bipy)_2][PF_6]_2$ **2**.—The structure of compound **2** was briefly communicated.[1a] The atomic positional parameters are listed in Table 5 and selected bond distances and angles are given in Table 6. A complete drawing of the cation is shown in Fig. 2. The cation adopts a distorted-octahedral geometry with two mutually *trans* bipy ligands in the equatorial positions and the axial positions are occupied by a phenylimido group and an ethoxide ligand. The chelating bipy ligands adopt an envelope-type geometry with the N–C–C–N chain being essentially planar with one of the rings bent towards the phenylimido group and the other towards the ethoxide ligand. The Re–N(3) and N(3)–C(1) bond distances are 1.740(6) and 1.377(9) Å, respectively, with

Table 5 Atomic positional parameters (× 10^4) for *trans*-[Re(NPh)(OEt)(bipy)$_2$][PF$_6$]$_2$ **2**

Atom	*x*	*y*	*z*
Re	3380(1)	746(1)	1230(1)
N(11)	2580(5)	2963(7)	1338(2)
N(12)	4917(5)	2260(7)	1421(2)
N(21)	1839(5)	−720(8)	1000(2)
N(22)	4170(5)	−1423(8)	1074(2)
N(3)	3433(5)	49(8)	1705(2)
O(1)	3449(5)	1390(7)	710(1)
C(12)	3321(6)	3938(8)	1575(2)
C(13)	2876(7)	5312(10)	1719(2)
C(14)	1656(7)	5681(11)	1613(2)
C(15)	923(7)	4749(9)	1350(2)
C(16)	1431(7)	3418(10)	1220(2)
C(12P)	4635(7)	3520(10)	1633(2)
C(13P)	5529(7)	4399(11)	1854(2)
C(14P)	6749(7)	4032(10)	1849(2)
C(15P)	7032(7)	2838(11)	1605(2)
C(16P)	6082(7)	1988(10)	1398(2)
C(22)	2122(7)	−1966(10)	779(2)
C(23)	1189(7)	−2841(10)	569(2)
C(24)	−16(7)	−2482(11)	585(2)
C(25)	−284(7)	−1277(10)	830(3)
C(26)	670(7)	−411(10)	1028(2)
C(22P)	3417(7)	−2394(10)	829(2)
C(23P)	3860(7)	−3751(10)	677(2)
C(24P)	5093(8)	−4121(12)	775(2)
C(25P)	5820(7)	−3205(11)	1039(3)
C(26P)	5342(7)	−1865(10)	1177(2)
C(1)	3654(6)	−738(10)	2055(2)
C(2)	4869(7)	−1115(9)	2214(2)
C(3)	5079(8)	−2029(11)	2545(2)
C(4)	4113(9)	−2530(11)	2729(2)
C(5)	2938(9)	−2133(10)	2576(2)
C(6)	2696(7)	−1244(9)	2244(2)
C(1E)	3717(13)	935(14)	344(3)
C(2E)	3472(15)	2011(16)	47(3)
P(1)	8061(2)	3159(3)	527(1)
F(1)	8621(5)	2112(7)	892(2)
F(2)	7540(6)	4273(9)	175(2)
F(3)	8020(5)	4626(7)	818(2)
F(4)	6723(4)	2719(8)	594(2)
F(5)	8119(5)	1736(7)	240(2)
F(6)	9421(5)	3636(7)	470(2)
P(2)	8687(2)	8309(3)	1953(1)
F(7)	9847(5)	9087(8)	1810(2)
F(8)	9513(8)	7543(12)	2291(2)
F(9)	7881(6)	9097(9)	1587(2)
F(10)	7519(7)	7544(9)	2069(3)
F(11)	8861(6)	6823(8)	1682(2)
F(12)	8462(6)	9786(7)	2207(2)

Table 6 Selected bond distances (Å) and angles (°) for *trans*-[Re(NPh)(OEt)(bipy)$_2$][PF$_6$]$_2$ **2** with e.s.d.s in parentheses

Re–N(11)	2.134 (6)	N(12)–C(12P)	1.357 (10)
Re–N(12)	2.154 (6)	N(12)–C(16P)	1.320 (9)
Re–N(21)	2.163 (6)	N(21)–C(22)	1.369 (10)
Re–N(22)	2.139 (7)	N(21)–C(26)	1.334 (9)
Re–N(3)	1.740 (6)	N(22)–C(22P)	1.372 (10)
Re–O(1)	1.895 (5)	N(22)–C(26P)	1.344 (9)
N(11)–C(12)	1.355 (9)	N(3)–C(1)	1.377 (9)
N(11)–C(16)	1.332 (9)	O(1)–C(1E)	1.398 (12)
N(11)–Re–N(12)	75.3 (2)	Re–N(12)–C(12P)	113.9 (5)
N(11)–Re–N(21)	104.4 (2)	Re–N(12)–C(16P)	127.3 (5)
N(12)–Re–N(21)	176.3 (2)	Re–N(21)–C(22)	114.8 (4)
N(11)–Re–N(22)	175.4 (2)	Re–N(21)–C(26)	125.2 (5)
N(12)–Re–N(22)	105.1 (2)	Re–N(22)–C(22P)	116.1 (5)
N(21)–Re–N(22)	74.9 (2)	Re–N(22)–C(26P)	125.8 (5)
N(11)–Re–N(3)	95.3 (3)	Re–N(3)–C(1)	167.4 (6)
N(12)–Re–N(3)	89.7 (2)	Re–O(1)–C(1E)	145.7 (6)
N(21)–Re–N(3)	94.0 (2)	C(12)–N(11)–C(16)	118.3 (6)
N(22)–Re–N(3)	89.3 (3)	C(12P)–N(12)–C(16P)	118.2 (6)
N(11)–Re–O(1)	89.2 (2)	C(22)–N(21)–C(26)	119.6 (6)
N(12)–Re–O(1)	89.0 (2)	C(22P)–N(22)–C(26P)	118.0 (7)
N(21)–Re–O(1)	87.3 (2)	N(3)–C(1)–C(2)	119.4 (6)
N(22)–Re–O(1)	86.2 (2)	N(3)–C(1)–C(6)	121.0 (6)
N(3)–Re–O(1)	174.8 (3)	C(2)–C(1)–C(6)	119.5 (7)
Re–N(11)–C(12)	114.6 (4)	O(1)–C(1E)–C(2E)	116.9 (11)
Re–N(11)–C(16)	126.9 (5)		

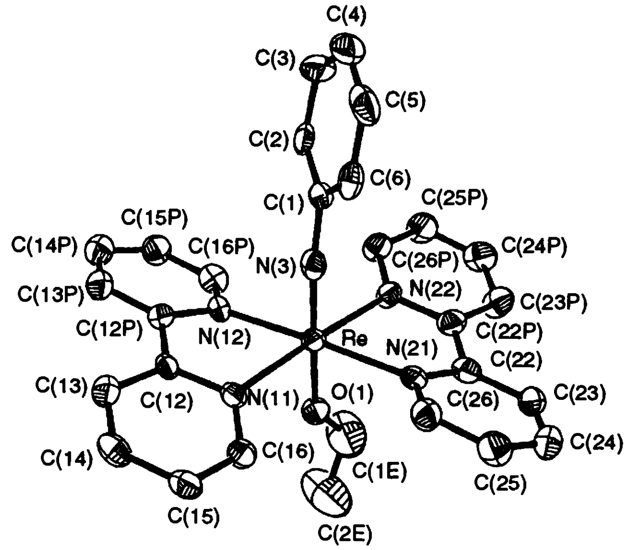

Fig. 2 ORTEP[21] drawing of the structure of the cation in crystals of *trans*-[Re(NPh)(OEt)(bipy)$_2$][PF$_6$]$_2$ **2**

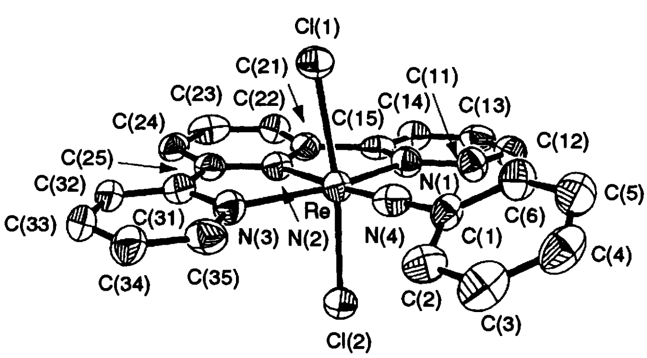

Fig. 3 ORTEP[21] drawing of the structure of the cation in crystals of *trans*-[Re(NPh)Cl$_2$(terpy)]PF$_6$ **3**

a Re–N(3)–C(1) bond angle of 167.4(6)°. The Re–N(3) bond distance is long compared to other compounds containing phenylimidorhenium(v) moieties as it reflects the high electron density around the rhenium atom as a result of the electron-donating properties of the ethoxide group. The Re–O(Et) bond distance of 1.895(5) Å reflects a multiple-bond character.

Structure of trans-[Re(NPh)Cl$_2$(terpy)]PF$_6$ **3**.—An ORTEP view of the cation of compound **3** is shown in Fig. 3. The atomic positional parameters are listed in Table 7 and Table 8 lists the key bond distances and angles. The co-ordination around the rhenium atom is pseudo-octahedral. The ligating atoms are a nitrogen from the phenylimido group, three nitrogens from terpy and two mutually *trans* chloride ions. The distortion from octahedral geometry is associated with the steric requirements of the imido ligand by which all atoms *cis* to this ligand are bent away from the imido linkage. The imido group has a short Re–N(4) bond distance of 1.702(10) Å and almost linear Re–N(4)–C(1) bond angle of 176.3(9)°. The imido group does not show any significant *trans* effect, which is consistent with its

Table 7 Atomic positional parameters (× 10^4) for *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3**

Atom	*x*	*y*	*z*
Re	11 272(1)	422(1)	1 394(1)
N(1)	11 072(7)	−1 013(7)	1 799(4)
N(2)	11 084(7)	−740(8)	806(4)
N(3)	11 303(7)	1 277(8)	686(4)
N(4)	11 476(6)	1 326(7)	1 871(4)
Cl(1)	12 894(2)	−21(3)	1 243(1)
Cl(2)	9 600(2)	593(3)	1 382(1)
C(11)	11 013(9)	−1 105(10)	2 301(5)
C(12)	10 842(9)	−2 039(10)	2 557(5)
C(13)	10 714(9)	−2 932(11)	2 253(6)
C(14)	10 772(9)	−2 876(9)	1 728(5)
C(15)	10 938(8)	−1 916(9)	1 501(5)
C(21)	10 997(8)	−1 759(10)	926(5)
C(22)	10 978(9)	−2 555(10)	580(5)
C(23)	11 066(10)	−2 259(13)	58(7)
C(24)	11 180(8)	−1 193(13)	−86(5)
C(25)	11 179(8)	−447(10)	310(5)
C(31)	11 313(8)	708(11)	238(5)
C(32)	11 399(9)	1 199(12)	−219(5)
C(33)	11 482(10)	2 299(14)	−235(6)
C(34)	11 443(10)	2 843(12)	193(6)
C(35)	11 354(9)	2 323(10)	659(6)
C(1)	11 635(8)	2 024(9)	2 292(4)
C(2)	11 435(8)	3 092(10)	2 208(6)
C(3)	11 515(11)	3 783(13)	2 613(7)
C(4)	11 823(11)	3 428(12)	3 080(6)
C(5)	12 054(9)	2 386(13)	3 138(5)
C(6)	11 940(10)	1 684(10)	2 750(5)
P(2)	6 057(3)	−289(2)	993(1)
F(1)	5 168(10)	−841(11)	875(6)
F(2)	5 628(8)	825(8)	936(4)
F(3)	6 559(10)	−1 431(8)	1 000(4)
F(4)	6 251(10)	−326(9)	381(5)
F(5)	5 885(15)	−248(11)	1 563(6)
F(6)	7 093(8)	286(10)	1 038(7)

Table 8 Selected bond distances (Å) and angles (°) for *trans*-[Re(NPh)Cl_2(terpy)]PF_6 **3** with e.s.d.s in parentheses

Re–N(1)	2.107(9)	N(4)–C(1)	1.416(15)
Re–N(2)	2.126(10)	C(11)–C(12)	1.370(18)
Re–N(3)	2.121(10)	C(14)–C(15)	1.364(17)
Re–N(4)	1.702(10)	C(15)–C(21)	1.501(17)
Re–Cl(1)	2.390(3)	C(21)–C(22)	1.343(18)
Re–Cl(2)	2.374(3)	C(24)–C(25)	1.390(19)
N(1)–C(11)	1.305(16)	C(25)–C(31)	1.478(18)
N(1)–C(15)	1.386(15)	C(31)–C(32)	1.340(19)
N(2)–C(21)	1.326(16)	C(34)–C(35)	1.377(22)
N(2)–C(25)	1.338(17)	C(1)–C(2)	1.390(17)
N(3)–C(31)	1.362(17)	C(1)–C(6)	1.331(17)
N(3)–C(35)	1.321(16)		
N(1)–Re–N(2)	75.5(4)	N(2)–Re–Cl(2)	85.9(3)
N(1)–Re–N(3)	150.0(4)	N(3)–Re–Cl(2)	87.9(3)
N(2)–Re–N(3)	74.6(4)	N(4)–Re–Cl(2)	96.7(3)
N(1)–Re–N(4)	103.6(4)	Cl(1)–Re–Cl(2)	166.9(1)
N(2)–Re–N(4)	177.2(4)	Re–N(1)–C(11)	125.3(8)
N(3)–Re–N(4)	106.4(4)	Re–N(1)–C(15)	116.4(8)
N(1)–Re–Cl(1)	90.6(3)	Re–N(2)–C(21)	120.6(8)
N(2)–Re–Cl(1)	81.0(3)	Re–N(2)–C(25)	118.8(8)
N(3)–Re–Cl(1)	87.6(3)	Re–N(3)–C(31)	117.8(8)
N(4)–Re–Cl(1)	96.4(3)	Re–N(3)–C(35)	123.6(10)
N(1)–Re–Cl(2)	87.1(3)	Re–N(4)–C(1)	176.3(9)

linear formulation as $\mathrm{Re}\overset{\leftarrow}{=}\mathrm{NPh}$. This formulation gives an 18-electron count for the metal centre and the absence of a structural *trans* effect is expected.[4b]

Conclusion

A series of phenylimidorhenium(v) compounds containing polypyridyl ligands have been isolated and structurally characterized. The strong *trans* effect observed in the structure of *mer*-[Re(NPh)Cl_3(bipy)] is unique as it has been manifested in the conversion between *mer*-[Re(NPh)Cl_3(L–L)] and *trans*-[Re(NPh)(OEt)$(L–L)_2]^{2+}$. The structure of *trans*-[Re(NPh)Cl_2(terpy)]$^+$ does not show any significant *trans* effect and is stable in alcoholic solutions containing hydrochloric acid.

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