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Oxidorhenium(V) Complexes of a Family of Bipyridine-Like Ligands Including Pyridyltriazines and Pyrazinyltriazine: Oxygen-Atom Transfer, Metal Redox and Correlations

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The title ligands (general abbreviation L) are bipyridine (bpy), its dimethyl (mbpy) and diphenyl (pbpy) derivatives, phenanthroline (phen), 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (ppyt) and its dimethyl (mpyt) and pyrazinyl (ppzt) analogues. The concerned oxido complexes are $[ReOCl_3(L)]$, $[ReOBr_3(ppyt)]$ and $[ReOBr_3(ppzt)]$. The chloro and bromo complexes of ppyt and ppzt were prepared by reacting these ligands with $[ReOX_3(AsPh_3)_2]$ (X = Cl, Br). The X-ray structures of $[ReOCl_3(ppyt)]$ and $[ReOCl_3(ppzt)]$ reveal that the $ReCl_3$ fragment is meridionally disposed and that the L ligand is *N*,*N*-coordinated such that the pyridine/pyrazine nitrogen lies *trans* to the oxido oxygen atom. The Re–O lengths [1.656(10)/1.625(9) Å] correspond to approximate triple bonding. The rate of oxygen-atom transfer from $[ReOX_3(L)]$ to triphenylphosphane in solution follows second-order kinetics and is associated with a large and negative entropy of activation (approx. $-30\ cal\,K^{-1}\,mol^{-1}$). The initial attack is believed to involve the phosphane lone pair and Re≡O π^*-orbitals. Electron withdrawal from the $Re^{V}O$ moiety by varying X or L facilitates oxygen-atom transfer. Thus, the rates follow the orders Br < Cl; mbpy < bpy < phen < pbpy << mpyt < ppyt < ppzt. The reduction potential of the quasireversible $Re^{VI}O/Re^{V}O$ couple displays similar trends and the logarithmic rate constant of oxygen-atom transfer is found to correlate linearly with the reduction potential.

Introduction

The oxygen-atom transfer ability of the oxidorhenium(V) moiety $Re^{V}O$ has been known for a long time,[1,2] and the nature and scope of the process have attracted significant recent attention.[3–9] In this laboratory we have been concerned[10] with the design and reactivity of $Re^{V}O$ complexes incorporating *N*,*N*-chelation by pyridyl ligands where the second nitrogen site belongs either to an acyclic function, such as an imine[11–13] or azo[13–16] group, or to a heterocyclic moiety. The scope of the latter alternative is potentially wide because of the many interesting variations possible in the form of aza-aromatic ligands.

Although a beginning in this direction was recently made with pyridylazole ligands,[17,18] the logical starting point would be the familiar didentate pyridyl aza-aromatic, viz. bipyridine (bpy). This has prompted us to examine the $Re^{V}O$ chemistry of bpy and certain bpy-like ligands including pyridyltriazine and pyrazinyltriazine. Very little is currently known about rhenium binding by the latter two ligands (vide infra).

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The oxygen-atom transfer potency of the family of $Re^{V}O$ complexes is estimated using triphenylphosphane as a model oxophile. The systematics in the rate of oxygen-atom transfer, which spans nearly two orders of magnitude, are scrutinized in terms of electron withdrawal and metal reduction potential.

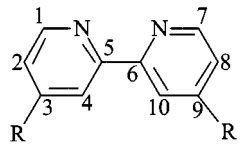
Results and Discussion

The $Re^{V}O$ Family

The ligand family used here consists of **1**–**4**, each member being abbreviated as shown below. The family spans three distinct types of bpy modifications: simple substitution (as in **1**), augmented conjugation (as in **2**) and incorporation of nitrogen hetero atoms (as in **3** and **4**).

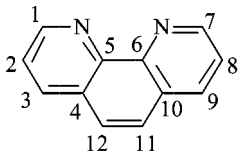
The nine oxido complexes (Table 1) of **1**–**4** are of coordination type **5**, abbreviated as $[ReOX_3(L)]$, where X = Cl or Br.

The complexes of **1** and **2** (X = Cl) were conveniently synthesised as yellow solids following a method previously used for bpy.[19] The pink chelates $[ReOCl_3(L)]$ (L = **3** and **4**) were prepared by the 1:1 reaction of $[ReOCl_3(AsPh_3)_2]$ with L in benzene at room temperature. The use of the arsane precursor is crucial for optimum yield. When $[ReOCl_3(PPh_3)_2]$ is employed the initially formed oxido com-



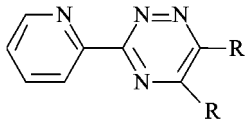
R	
H	bpy
Me	mbpy
Ph	pbpy

1



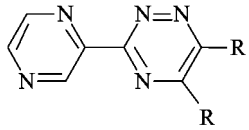
phen

2



R	
Me	mpyt
Ph	ppyt

3



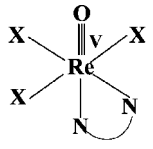
R	
Ph	ppzt

4

Table 1. The type **5** oxido complexes, their $Re^{VI}O/Re^{V}O$ reduction potential (in Volt vs. SCE) and oxygen-atom transfer rate to PPh_3.

Complex	$E_{½}$ [V] (ΔE_p [mV])[a]	10^3k [$M^{-1}s^{-1}$][b,c]
$[ReOCl_3(bpy)]$ (**5a**)	1.45 (100)	1.60(0.03)
$[ReOCl_3(mbpy)]$ (**5b**)	1.44 (80)	1.30(0.04)
$[ReOCl_3(pbpy)]$ (**5c**)	1.48 (100)	2.52(0.04)
$[ReOCl_3(phen)]$ (**5d**)	1.47 (100)	2.21(0.03)
$[ReOCl_3(ppyt)]$ (**5e**)	1.61 (90)	25.01(0.02)
$[ReOBr_3(ppyt)]$ (**5f**)	1.58 (90)	13.34(0.05)
$[ReOCl_3(mpyt)]$ (**5g**)	1.53 (130)	10.45(0.05)
$[ReOCl_3(ppzt)]$ (**5h**)	1.68 (90)	62.58(0.04)
$[ReOBr_3(ppzt)]$ (**5i**)	1.65 (100)	36.64(0.06)

[a] In acetonitrile; ΔE_p is peak-to-peak separation. [b] In dichloromethane, temperature: 303 K. [c] Least-squares deviations are given in parentheses.



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plex reacts with the liberated phosphane (vide infra), which affects the yield and purity of the product.

The use of $[ReOBr_3(AsPh_3)_2]$ in place of the chloro precursor gives the bromo system $[ReOBr_3(L)]$ for L = ppyt and ppzt. Attempted synthesis of the iodo analogue from $[ReOI_3(AsPh_3)_2]$ furnished only unstable products. However, in the presence of $ArNH_2$ in the reaction mixture the imido system $[Re(NAr)I_3(L)]$ could be isolated, which is a possible intermediate in the formation of the $Re^{V}O$ analogue.[20]

Selected spectroscopic data for $[ReOX_3(L)]$ are collected in the Experimental Section. The species uniformly display an Re≡O stretch near 1000 cm^{-1} and two absorption bands in the visible region around 500 and 750 nm, which are of diagnostic value in rate studies (vide infra). The complexes are diamagnetic ($5d^2$) and show well-resolved ^1H NMR spectra, which have been assigned.

Of the complexes listed in Table 1, $[ReOCl_3(bpy)]$[19,21] and $[ReOCl_3(phen)]$[22] have been reported before. The analytical[23] and coordination[24,25] chemistry of ppyt complexes has been well-documented, but the only reported rhenium complex is $[Re(CO)_3Cl(ppyt)]$,[26] which has recently been structurally characterised in this laboratory.[20] There is no report of rhenium complexes of mpyt and ppzt, which have otherwise been only sparsely studied as ligands.[25,27]

Structure

The X-ray structures of $[ReOCl_3(ppyt)]$ (**5e**) and $[ReOCl_3(ppzt)]$ (**5h**) were determined. Molecular views are shown in Figures 1 and 2, respectively, and selected bond parameters are listed in Table 2. In the distorted octahedral $ReOCl_3N_2$ coordination sphere the chloride ligands are meridionally disposed. In both molecules the coordinated nitrogen of the triazine ring is N2 and not N4, as also observed in copper[24b] and ruthenium[27] chelates of ppyt/ppzt. The coordinated pyridine nitrogen in **5e** and pyrazine nitrogen in **5h** lie *trans* to the oxido ligand. In both cases the chloride ligands and the triazine N2 atom define a good equatorial plane (mean deviation: 0.03 Å) from which the Re atom is displaced by 0.32 (**5e**) and 0.37 Å (**5h**) towards the oxygen atom. The chelate ring in both cases is satisfactorily planar (mean deviation of about 0.06 Å). The two heterocyclic rings deviate significantly from coplanarity, the dihedral angles being 6.9° (**5e**) and 13.3° (**5h**).

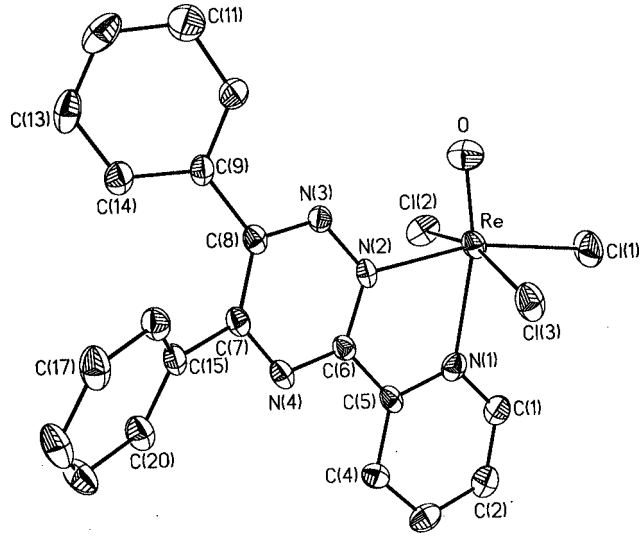


Figure 1. Molecular view and atom labelling scheme for $[ReOCl_3(ppyt)]$ (**5e**). All non-hydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms have been omitted for clarity.

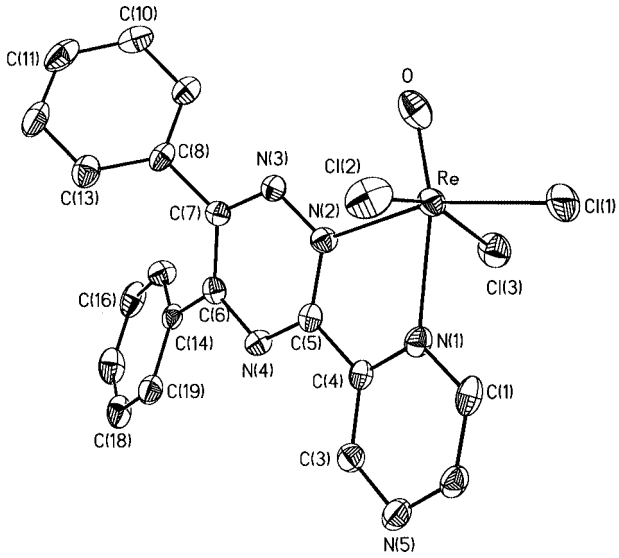


Figure 2.Molecular view and atom labelling scheme for [ReOCl$_3$(ppzt)] (**5h**). All non-hydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms have been omitted for clarity.

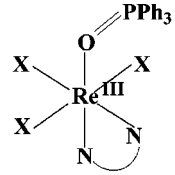
Table 2. Selected bond length [Å] and angles [°] for **5e** and **5h**.

	5e	**5h**
Re–O	1.656(10)	1.625(9)
Re–N(1)	2.262(11)	2.296(8)
Re–N(2)	2.104(9)	2.124(7)
Re–Cl(1)	2.313(4)	2.318(3)
Re–Cl(2)	2.332(3)	2.345(3)
Re–Cl(3)	2.363(3)	2.363(3)
N(2)–N(3)	1.327(13)	1.330(10)
O–Re–N(2)	90.5(4)	90.9(3)
N(2)–Re–N(1)	73.1(4)	71.9(3)
N(2)–Re–Cl(1)	164.4(3)	162.1(2)
O–Re–Cl(2)	99.3(4)	100.3(3)
O–Re–Cl(3)	97.8(4)	99.5(3)
N(2)–Re–Cl(3)	85.8(3)	87.4(2)
Cl(1)–Re–Cl(3)	88.77(14)	87.53(13)
O–Re–N(1)	163.5(4)	162.9(3)
O–Re–Cl(1)	104.8(4)	106.8(3)
N(1)–Re–Cl(1)	91.6(3)	90.3(2)
N(2)–Re–Cl(2)	91.4(3)	92.1(2)
N(1)–Re–Cl(3)	80.2(3)	79.9(2)
Cl(2)–Re–Cl(3)	162.76(14)	160.17(11)

The Re–O length, which corresponds to approximate triple bonding,[28] is somewhat longer in **5e** [1.656(10) Å] than in **5h** [1.625(9) Å]. The Re–N1 bond lying *trans* to Re≡O is longer than the Re–N2 bond by around 0.17 Å. Significantly, the shorter Re–O bond in **5h** is associated with a longer Re–N1 bond. The structure of the bpy complex of type **5**, viz. [ReOBr$_3$(bpy)], is known.[29] Here, the Re–O distance is significantly longer [1.689(8) Å] than those in **5e** and **5h**.

Oxygen-Atom Transfer

The [ReOX$_3$(L)] (X = Cl, Br) complexes are uniformly reactive towards triphenylphosphane in solution, furnishing a violet solution from which paramagnetic phosphane oxide complexes of type [Re^{III}(OPPh$_3$)X$_3$(L)] have been isolated. Characterisation data for two representative species are set out in the Experimental Section. The observed room-temperature magnetic moments (1.5–1.7 μ_B) are much lower than the idealised spin-only value for the t_{2g}^4 configuration due to strong orbital coupling, as is common for trivalent rhenium. As expected, the ^{1}H NMR spectra of the complexes are paramagnetically shifted.[14,17,19,30]



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Although no direct structural characterisation was possible due to lack of single crystals, our previous work[11–18,31] on related systems strongly supports the gross geometry of the phosphane oxide complexes to be **6**.

The rate of the reaction of Equation (1) was determined spectrophotometrically in dichloromethane solution.

$$Re^{V}OX_3(L) + PPh_3 \xrightarrow{k} Re^{III}(OPPh_3)X_3(L) \quad (1)$$

Selected rate data are listed in Tables 1 and 3. A representative time-evolution spectrum characterised by isosbestic points is shown in Figure 3. Under pseudo-first-order con-

Table 3. Variable-temperature rate constants for the reaction [ReOCl$_3$(L)] with PPh$_3$ in dichloromethane solution.[a,b]

	T [K]	[PPh$_3$] [M]	$10^4 k_{obs}$ [s^{-1}]	$10^3 k$ [M^{-1} s^{-1}]
ppyt	293	0.012	1.452	12.08(0.05)
		0.015	1.814	
		0.019	2.300	
	298	0.012	2.000	16.72(0.02)
		0.015	2.509	
		0.019	3.177	
	303	0.012	3.001	25.01(0.02)
		0.015	3.750	
		0.019	4.752	
	308	0.012	3.935	32.80(0.03)
		0.015	4.920	
		0.019	6.232	
ppzt	293	0.012	4.300	35.38(0.09)
		0.015	5.375	
		0.019	6.808	
	298	0.012	5.958	49.65(0.08)
		0.015	7.448	
		0.019	9.434	
	303	0.012	7.510	62.58(0.04)
		0.015	9.388	
		0.019	11.891	
	308	0.012	10.501	87.51(0.02)
		0.015	13.126	
		0.019	16.627	

[a] Initial concentrations of [ReOCl$_3$(ppyt)] and [ReOCl$_3$(ppzt)] are 5.43×10^{-5} M and 4.65×10^{-5} M, respectively. [b] Least-squares deviations are given in parentheses.

ditions (excess PPh_3), the rate is proportional to the concentration of the oxido complex, and the observed rate constant, k_{obs}, is proportional to the concentration of PPh_3. The reaction is thus second order in nature, see Equation (2).

$$\text{rate} = k_{obs}[ReOX_3(L)] = k[ReOX_3(L)][PPh_3] \quad (2)$$

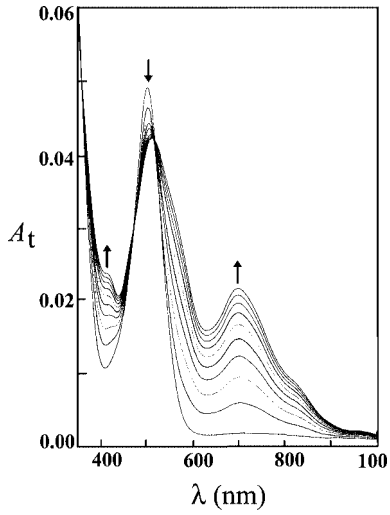
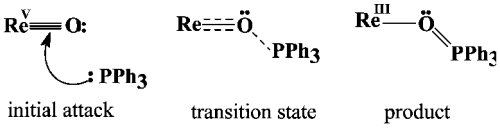


Figure 3. Time evolution spectra for the reaction of $[ReOCl_3(ppyt)]$ and PPh_3 in dichloromethane solution at 303 K (A_t is absorbance).

Rates for all the complexes were determined at 303 K (Table 1), although in the cases of $[ReOCl_3(ppyt)]$ (**5e**) and $[ReOCl_3(ppzt)]$ (**5h**) variable-temperature studies were also made (Table 3). In both cases the rate constant, k, was found to obey the Eyring equation. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are as follows: 11.66(0.26) kcal mol^{-1} and –27.48(0.88) cal K^{-1} mol^{-1} for **5e** and 9.94(0.28) kcal mol^{-1} and –31.95(0.95) cal K^{-1} mol^{-1} for **5h**. The large and negative entropy of activation implies close association of $[ReOX_3(L)]$ and PPh_3 in the transition state, as in the model **7**,[10,17] where initial attack involves the phosphane lone pair and Re≡O π*-orbitals.



7

Electron Withdrawal, Rate and Reduction Potential

The observed trend of reactivity is qualitatively consistent with the reaction model. Electron withdrawal from the $Re^{V}O$ moiety due to variation of X or due to modification of L is expected to favour the initial nucleophilic attack and thereby facilitate oxygen-atom transfer. This is systematically observed. We note that $[ReOCl_3(ppyt/ppzt)]$ is nearly twice as reactive as $[ReOBr_3(ppyt/ppzt)]$, in line with the higher electronegativity of Cl. Again, the rate trend $[ReOCl_3(mbpy)] < [ReOCl_3(bpy)] < [ReOCl_3(pbpy)]$ correctly reflects the electron-withdrawal power of the substituent (Me < H < Ph). The $[ReOCl_3(phen)]$ complex fits between the bpy and pbpy species. An increase in the number of nitrogen hetero atoms is a very effective instrument for achieving electron withdrawal.[32] Accordingly, the rate of oxygen-atom transfer in the case of $[ReOCl_3(ppzt)]$ is 2.5 and 25 times faster than that for $[ReOCl_3(ppyt)]$ and $[ReOCl_3(pbpy)]$, respectively (Table 1).

While electron withdrawal from the $Re^{V}O$ moiety by ligand variation facilities oxygen-atom transfer, it is also expected to make metal oxidation more difficult. Fortunately, the $[ReOX_3(L)]$ complexes are uniformly electroactive in acetonitrile solution, exhibiting a quasi-reversible one-electron oxidative response near 1.5 V vs. SCE assigned to the $Re^{VI}O/Re^{V}O$ couple. Representative voltammograms are shown in Figure 4 and reduction potential data are listed in Table 1.

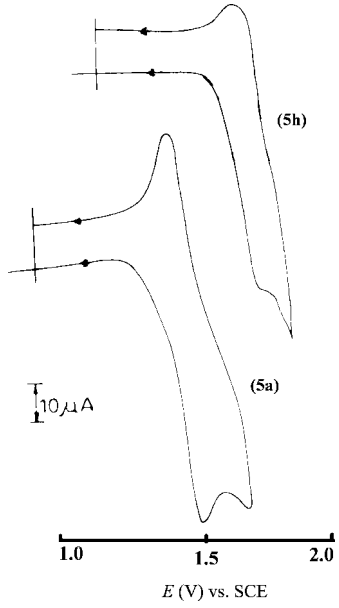


Figure 4. Cyclic voltammograms of $[ReOCl_3(bpy)]$ (**5a**) and $[ReOCl_3(ppzt)]$ (**5h**) in acetonitrile solution at platinum working electrode (scan rate: 100 mV s^{-1}).

The data of Table 1 reveal that the rate of oxygen-atom transfer rapidly increases with $E_{1/2}$ of the $Re^{VI}O/Re^{V}O$ couple. Indeed, there is a satisfactory linear correlation (correlation constant 0.99) between the logarithmic rate constant and the reduction potential (Figure 5). All the complexes except **5g** lie virtually on the least-squares line itself. The slope of the line is about 16. Evidently, a single linear equation of this type cannot encompass all $Re^{V}O$ complexes but it is gratifying to note that within a group where the L ligands belong to the same type (two six-membered N-heterocycles connected by a single bond) a simple correlation does exist.

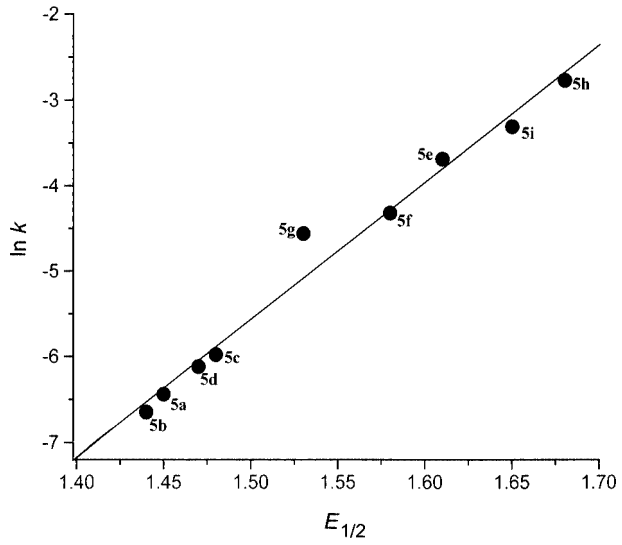


Figure 5. Plot of logarithmic rate constant vs. $Re^{VI}O/Re^{V}O$ reduction potential at 303 K.

Conclusion

In our search for reactive $Re^{V}O$ complexes of *N*,*N*-chelating heterocyclic ligands (L) the rhenium chemistry of the pyridyl- and pyrazinyltriazine heterocycles ppyt, mpyt and ppzt has been developed in the form of the complexes [$ReOX_3$(L)] (X = Cl, Br), two of which have been structurally characterised.

These undergo strongly associative oxygen-atom transfer to PPh_3 ($\Delta S^{\ddagger} \approx -30$ cal K^{-1} mol^{-1}). The rate of transfer has also been determined for other [$ReOCl_3$(L)] complexes (L = bpy, mbpy, pbpy and phen). The oxygen-atom transfer rates span nearly two orders of magnitude for the whole family examined here.

Consistent with the proposed reaction model based on nucleophilic attack of the PPh_3 lone pair on π*(Re≡O) orbitals, the transfer rate increases systematically with increasing electron withdrawal from $Re^{V}O$ due to variation of X (Cl > Br) or L (ppzt > ppyt > mpyt >> pbpy > phen > bpy > mbpy).

A second molecular parameter also responsive to electron withdrawal is the voltammetric $Re^{VI}O/Re^{V}O$ reduction potential, which shows the same trends as above. Indeed, the logarithmic rate of transfer correlates linearly with the $Re^{VI}O/Re^{V}O$ reduction potential within the present family of [$ReOX_3$(L)] complexes.

Experimental Section

Materials: The complexes [$ReOX_3(AsPh_3)_2$][33] and [$ReOCl_3(Me_2S)(OPPh_3)$][19] and the triazine ligands[25,27] were prepared by reported methods. The purification and drying of dichloromethane and acetonitrile for spectral and electrochemical work was done as before.[34] Tetrahydrofuran and benzene ware dried using standard methods. All other chemicals and solvent were of reagent grade and were used as received.

Physical Measurements: UV/Vis spectral measurements were carried out with a Shimadzu UVPC 1601 spectrometer fitted with thermostatted cell compartments. ^{1}H NMR spectra were recorded with a Bruker FT 300 MHz spectrometer. The atom numbering scheme used in ^{1}H NMR is the same as in crystallography. Electrochemical measurements were performed under nitrogen with a CH 620A electrochemical analyzer, using a platinum working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and potentials are referred to the standard calomel electrode (SCE). Room-temperature magnetic susceptibilities of powders were measured with a model 155 PAR vibrating sample magnetometer. Microanalyses (C,H,N) were performed using a Perkin–Elmer 2400 series II elemental analyzer. Mass spectra were measured with Q-TOF mass spectrometer.

Synthesis of Complexes: The complex [$ReOCl_3$(bpy)] (**5a**) was synthesised from [$ReOCl_3(Me_2S)(OPPh_3)$] and bpy by a reported procedure.[19] We found the procedure to be suitable for synthesis of **5b**–**5d** as well with some modifications. Details are given below for [$ReOCl_3$(phen)] (**5d**).

[$ReOCl_3$(phen)] (5d): A suspension of [$ReOCl_3(Me_2S)(OPPh_3)$] (84 mg, 0.13 mmol) and phen (30 mg, 0.15 mmol) in 10 mL of tetrahydrofuran was stirred for 5 h. Filtration and washing with diethyl ether (5 × 5 mL) gave 43 mg (0.09 mmol, 68%) of yellowish **5d** in pure form. $C_{12}H_8Cl_3N_2ORe$ (488.78): calcd. C 29.49, H 1.64, N 5.73; found C 29.40, H 1.69, N 5.78. UV/Vis (CH_2Cl_2 solution: λ_{max} (ε) = 270 nm (56500 $M^{-1}cm^{-1}$), 410 (4150), 456 (5690), 795 (160). IR (KBr): $\tilde{\nu}$ = 989 cm^{-1} ($\nu_{Re=O}$). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 10.03 (d, *J* = 5.20 Hz, H1), 9.31 (d, *J* = 8.10 Hz, H7), 8.98 (d, *J* = 5.01 Hz, H3), 8.62 (t, *J* = 7.62 Hz, H2), 8.60 (d, *J* = 7.98 Hz, H9), 8.55 (d, *J* = 5.32 Hz, H12), 8.52 (d, *J* = 5.30 Hz, H11), 8.30 (t, *J* = 8.02 Hz, H8) ppm.

[$ReOCl_3$(mbpy)] (5b): Yield: 44 mg (69%.) $C_{12}H_{12}Cl_3N_2ORe$ (492.81): calcd. C 29.25, H 2.45, N 5.68 found C 29.30, H 2.40, N 5.60. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 299 (47400), 458 (7670), 795 (225). IR (KBr): $\tilde{\nu}$ = 984 cm^{-1} ($\nu_{Re=O}$). ^{1}H NMR (300 MHz, [D_6]DMSO, 298 K): δ = 8.92 (s, H4), 8.55 (s, H10), 8.40 (d, *J* = 5.85 Hz, H1), 8.10 (d, *J* = 6.06 Hz, H7), 7.48 (d, *J* = 6.03 Hz, H2), 7.40 (d, *J* = 5.79 Hz, H8), 4.70 (s, 3 H, 3-Me), 3.65 (s, 3 H, 9-Me) ppm.

[$ReOCl_3$(pbpy)] (5c): Yield: 52 mg (65%). $C_{22}H_{16}Cl_3N_2ORe$ (616.96): calcd. C 42.79, H 2.59, N 4.53; found C 42.70, H 2.53, N 4.58. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 326 nm (50000 $M^{-1}cm^{-1}$), 465 (13100), 774 (253). IR (KBr): $\tilde{\nu}$ = 987 cm^{-1} ($\nu_{Re=O}$). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.08 (s, H4), 8.60 (d, *J* = 8.10 Hz, H1), 8.55 (d, *J* = 8.16 Hz, H2), 8.00–7.50 (m, 13 H, H3, H8, H10, 2Ph) ppm.

The Complexes 5e–5i: These complexes were prepared in 75–85% yield by the same general procedure based on the reaction of [$ReOX_3(AsPh_3)_2$] with L in benzene at room temperature. Details are given here for a representative case.

[$ReOCl_3$(ppyt)] (5e): The ligand ppyt (34 mg, 0.11 mmol) was added to a suspension of [$ReOCl_3(AsPh_3)_2$] (100 mg, 0.11 mmol) in 25 mL of benzene. The resulting mixture was stirred for 1 h at room temperature to produce a pink solution. The solvent was then removed under reduced pressure. The solid mass thus obtained was repeatedly washed with *n*-hexane to remove the liberated $AsPh_3$. The solid was then dissolved in 5 mL of dichloromethane and subjected to chromatography on a silica gel column (10 × 1 cm, 60–120 mesh) prepared in toluene. The pink complex was eluted with pure dichloromethane. Solvent removal from the eluate under reduced pressure afforded [$ReOCl_3$(ppyt)] in pure form, which was dried under vacuo over fused calcium chloride. Yield: 53 mg (78%). $C_{20}H_{14}Cl_3N_4ORe$ (618.93): calcd. C 38.81, H 2.28, N 9.05; found C 38.87, H 2.21, N

9.09. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 306 nm (35400 $M^{-1}cm^{-1}$), 508 (13800), 736 (550). IR (KBr): $\tilde{\nu}$ = 1000 cm^{-1} ($\nu_{Re\equiv O}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.91 (d, J = 9.09 Hz, H1), 8.52 (d, J = 7.41 Hz, H4), 8.14 (t, J = 7.20 Hz, H3), 7.94 (t, J = 7.74 Hz, H18), 7.72 (d, J = 7.98 Hz, 2 H, H10, H14), 7.64 (d, J = 7.05 Hz, 2 H, H16, H20), 7.59 (t, J = 7.95 Hz, 2 H, H11, H13), 7.53 (t, J = 6.93 Hz, 2 H, H17, H19), 7.44 (t, J = 7.79 Hz, H12), 7.37 (t, J = 6.60 Hz, H2) ppm.

[ReOBr$_3$(ppyt)] (5f): Yield: 60 mg (80%). $C_{20}H_{14}Br_3N_4ORe$ (752.28): calcd. C 31.93, H 1.88, N 7.45; found C 31.90, H 1.93, N 7.40. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 302 nm (34300 $M^{-1}cm^{-1}$), 514 (10900), 726 (1050). IR (KBr): $\tilde{\nu}$ = 996 cm^{-1} ($\nu_{Re\equiv O}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.92 (d, J = 5.82 Hz, H1), 8.51 (d, J = 7.89 Hz, H4), 8.14 (t, J = 7.77 Hz, H3), 7.72 (d, J = 7.41 Hz, 2 H, H10, H14), 7.63 (d, J = 7.08 Hz, 2 H, H16, H20), 7.58 (t, J = 8.88 Hz, 2 H, H11, H13), 7.53 (t, J = 8.22 Hz, 2 H, H17, H19), 7.42 (t, J = 7.68 Hz, H12), 7.42 (t, J = 7.74 Hz, H18), 7.34 (t, J = 5.24 Hz, H2) ppm.

[ReOCl$_3$(mpyt)] (5g): Yield: 41 mg (75%). $C_{10}H_{10}Cl_3N_4ORe$ (494.79): calcd. C 24.27, H 2.04, N 11.32; found C 24.30, H 2.08, N 11.40. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 300 nm (32900 $M^{-1}cm^{-1}$), 496 (6800), 701 (950). IR (KBr): $\tilde{\nu}$ = 994 cm^{-1} ($\nu_{Re\equiv O}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.74 (d, J = 5.02 Hz, H1), 7.92 (t, J = 7.77 Hz, H3), 7.76 (d, J = 7.74 Hz, H4), 7.60 (t, J = 5.90 Hz, H2), 2.68 (s, 3 H, 7-Me), 2.64 (s, 3 H, 8-Me) ppm.

[ReOCl$_3$(ppzt)] (5h): Yield: 57 mg (83%). $C_{19}H_{13}Cl_3N_5ORe$ (619.92): calcd. C 36.81, H 2.11, N 11.30; found C 36.86, H 2.17, N 11.35. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 310 nm (36400 $M^{-1}cm^{-1}$), 523 (13800), 737 (540). IR (KBr): $\tilde{\nu}$ = 1004 cm^{-1} ($\nu_{Re\equiv O}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.95 (s, H3), 8.85 (d, J = 6.00 Hz, H2), 7.95 (d, J = 4.20 Hz, 2 H, H9, H13), 7.88 (d, J = 7.20 Hz, H1), 7.74 (d, J = 7.80 Hz, 2 H, H15, H19), 7.65 (t, J = 6.90 Hz, 2 H, H10, H12), 7.54 (t, J = 10.80 Hz, 2 H, H16, H18), 7.45 (t, J = 7.80 Hz, H11), 7.45 (t, J = 7.80 Hz, H17) ppm.

[ReOBr$_3$(ppzt)] (5i): Yield: 64 mg (85%). $C_{19}H_{13}Br_3N_5ORe$ (753.27): calcd. C 30.30, H 1.74, N 9.30; found C 30.25, H 1.70, N 9.24. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 310 nm (35100 $M^{-1}cm^{-1}$), 531 (10600), 739 (850). IR (KBr): $\tilde{\nu}$ = 999 cm^{-1} ($\nu_{Re\equiv O}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.75 (s, H3), 8.81 (d, J = 4.76 Hz, H2), 8.60 (d, J = 4.88 Hz, H1), 7.74 (d, J = 7.59 Hz, 2 H, H9, H13), 7.66 (d, J = 6.42 Hz, 2 H, H15, H19), 7.56 (t, J = 7.80 Hz, 2 H, H10, H12), 7.52 (t, J = 6.42 Hz, 2 H, H16, H18), 7.48 (t, J = 5.90 Hz, H11), 7.46 (t, J = 7.44 Hz, H17) ppm.

Complexes [Re(OPPh$_3$)Cl$_3$(L)]: These were prepared in 75–80% yield by the same general procedure based on the reaction of [ReOX$_3$(L)] with triphenylphosphane in benzene at room temperature. Details are given below for a representative case and data for a second compound prepared analogously follow.

[Re(OPPh$_3$)Cl$_3$(ppyt)]: PPh_3 (68 mg, 0.28 mmol) was added to a solution of [ReOCl$_3$(ppyt)] (80 mg, 0.13 mmol) in 25 mL of dichloromethane. The resulting solution was magnetically stirred for 4 h at room temperature and during this time the colour of the solution changed from pink to violet. It was then subjected to chromatography on a silica gel column. Excess PPh_3 was eluted with benzene. A violet band was eluted with a benzene/acetonitrile (25:2) mixture. The solvent was removed under reduced pressure and the violet complex so obtained was dried under vacuo over fused calcium chloride. Yield: 90 mg (75%). $C_{38}H_{29}Cl_3N_4OPRe$ (881.22): calcd. C 51.80, H 3.32, N 6.35; found C 51.72, H 3.39, N 6.30. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 289 nm (31300 $M^{-1}cm^{-1}$), 532 (8700), 701 (5150). IR (KBr): $\tilde{\nu}$ = 1119 cm^{-1} ($\nu_{O=P}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 25.99 (t, J = 9.00 Hz, H2), 10.19 (t, J = 7.50 Hz, H12), 9.58 (d, J = 8.40 Hz, 2 H, H16, H20), 9.50 (t, J = 7.50 Hz, 2 H, H11, H13), 8.22 (d, J = 7.80 Hz, H1), 8.10 (d, J = 8.10 Hz, 2 H, H10, H14), 7.73 (t, J = 7.20 Hz, H18), 7.17 [d, J = 7.20 Hz, 6 H, o-H(PPh_3)], 6.77 [t, J = 7.50 Hz, 3 H, p-H(PPh_3)], 5.06 (t, J = 7.50 Hz, 2 H, H17, H19), 4.00 [t, J = 7.80 Hz, 6 H, m-H(PPh_3)], 2.79 (d, J = 4.80 Hz, H4), –17.01 (t, J = 9.00 Hz, H3) ppm. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.33 V (ΔE_p = 70 mV). μ (in powder): 1.51 μ_B (298 K). Q-TOF-MS: m/z 881.30.

[Re(OPPh$_3$)Br$_3$(ppzt)]: Yield: 104 mg (79%). $C_{37}H_{28}Br_3N_5OPRe$ (1015.56): calcd. C 43.76, H 2.78, N 6.96; found C 43.70, H 2.73, N 6.83. UV/Vis (CH_2Cl_2 solution): λ_{max} (ε) = 300 nm (32900 $M^{-1}cm^{-1}$), 525 (8400), 665 (5900). IR (KBr): $\tilde{\nu}$ = 1121 cm^{-1} ($\nu_{O=P}$). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 42.83 (d, J = 7.11 Hz, H1), 21.98 (s, H3), 8.78 (t, J = 7.62 Hz, 2 H, H10, H12), 8.62 (d, J = 7.08 Hz, 2 H, H9, H13), 7.93 (t, J = 6.87 Hz, H11), 7.68 (d, J = 7.89 Hz, H2), 7.41 [d, J = 6.72 Hz, 6 H, o-H(PPh_3)], 6.96 [t, J = 6.96 Hz, 3 H, p-H (PPh_3)], 6.27 (t, J = 6.36 Hz, H17), 6.13 [t, J = 8.03 Hz, 6 H, m-H(PPh_3)], 5.67 (t, J = 7.44 Hz, 2 H, H16, H18), 4.61 (d, J = 7.74 Hz, 2 H, H15, H19) ppm. $E_{1/2}$ (Re^{IV}/Re^{III} couple): 0.58 V (ΔE_p = 90 mV). μ (in powder): 1.67 μ_B (298 K). Q-TOF-MS: m/z 1015.34.

Rate Measurement: The representative case of the reaction of [ReOCl$_3$(ppyt)] with PPh_3 will be described. A known excess of PPh_3 was added to a solution of [ReOCl$_3$(ppyt)] (5.43×10^{-5} M) in dichloromethane at the desired temperature, and the thermostatted reaction was followed spectrophotometrically (quartz cell; path length: 1 cm) by measuring the absorbance (A_α) of the peak at 710 nm as a function of time (t). The absorbance (A_α) at the end of the reaction (24 h) was also measured. Values of k_{obs} and k were obtained from the slopes of the linear plots of $-[\ln(A_\alpha - A_t)]$ vs. t and k_{obs} vs. [PPh_3] respectively. The activation enthalpy and entropy parameters were determined from the linear plot of $-\ln(kh/k_BT)$ vs. T^{-1} using the Eyring equation, see Equation (3).

$$k = (k_BT/h)\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \quad (3)$$

Crystal Structure Determination: Single crystals of the complexes [ReOCl$_3$(ppyt)] (**5e**) and [ReOCl$_3$(ppzt)] (**5h**) were grown by slow diffusion of hexane into dichloromethane solutions of the respective compounds. Data were collected on a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by the ω-scan technique in the range $3° \leq 2\theta < 50°$. All data were corrected for Lorentz-polarisation and absorption.[35] The metal atoms were located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were then refined by a full-matrix least-squares procedure on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL™ V 5.03 program package.[36]

Data for 5e: $C_{20}H_{14}Cl_3N_4ORe$, monoclinic, $P2_1/n$, a = 8.920(2), b = 15.021(3), c = 15.558(3) Å, β = 92.05(3)°, V = 2083.2(3) Å^3, Z = 4, 3111 unique reflections (R_{int} = 0.0000). Final residuals R_1 = 0.0556 and wR_2 = 0.1405 [$I > 2\sigma(I)$].

Data for 5h: $C_{19}H_{13}Cl_3N_5ORe$, monoclinic, $P2_1/c$, a = 9.274(2), b = 16.418(3), c = 13.732(3) Å, β = 98.70(3)°, V = 2066.8(7) Å^3, Z = 4, 3617 unique reflections (R_{int} = 0.0648). Final residuals R_1 = 0.0472 and wR_2 = 0.1154 [$I > 2\sigma(I)$].

CCDC-292211 and -292212 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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