Syntheses and Characterization of Amino and Amido–Imido Technetium(v) and Rhenium(v) Complexes with (*o*-Aminophenyl)diphenylphosphine-*N,P*. Crystal Structures of $[TcNCl\{PPh_2(C_6H_4NH_2\text{-}2)\}_2]Cl\cdot MeCN$ and $[Re\{PPh_2(C_6H_4N\text{-}2)\}Cl_2\{PPh_2(C_6H_4NH\text{-}2)\}]$†

Fiorenzo Refosco,*[a] **Francesco Tisato,**[a] **Annarosa Moresco**[a] **and Giuliano Bandoli**[b]
[a] *Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati C. N. R., Area della Ricerca, Corso Stati Uniti 4, 35020 Padova, Italy*
[b] *Dipartimento di Scienze Farmaceutiche, Università di Padova, via F. Marzolo 5, 35131 Padova, Italy*

Reactions of $[NBu_4][MOCl_4]$ (M = Tc or Re) or $[ReOX_2(OEt)(PPh_3)_2]$ (X = Cl, Br or I) with the bidentate ligand (*o*-aminophenyl)diphenylphosphine (H_2L) under controlled reaction conditions gave neutral imido-metal(v) complexes of the type $[M(L)Cl_2(HL)]$; in particular, the neutral $[Re(L)Cl_2(HL)]$ complex **3**, the crystal structure of which has been determined contains HL^- and L^{2-} ligands 'twisted' relative to each other by 101.3°, with the imido group bonded *trans* to a Cl atom, while the other chloro is equatorial. Important molecular parameters are: Re–N(2) 1.780(7), Re–N(1) 1.973(7), Re–Cl(1) 2.404(2), Re–Cl(2) 2.384(2), Re–P(1) 2.438(2) and Re–P(2) 2.492(2) Å. The bent configuration of the imido core [Re–N(2)–C(12) 137.1(5)°] enforced by the intrinsic ligand geometry, along with the ν(Re=N–) stretch at 971 cm^{-1}, indicates the peculiarity of this nitrene core. The severe distortion from octahedral geometry is also represented by the Cl(2)–Re–N(2) angle of 157.0(2)° and by the 'bite' angles of 79.5(2) and 75.2(2)° for the HL^- and L^{2-} ligand, respectively. Substitution reactions on $[NBu_4][TcNCl_4]$ and $[MNCl_2(PPh_3)_2]$ (M = Re or Tc) with H_2L give cationic nitrido–metal(v) complexes of the type $[MNCl(H_2L)_2]Cl$, in which the co-ordination of two bidentate H_2L chelates occurs with a mutual *cis*-P configuration and with the amino-N on the equatorial plane of a distorted octahedron; the site *trans* to the M≡N unit is occupied by a Cl ligand. The crystal structure of $[TcNCl(H_2L)_2]Cl\cdot MeCN$ **2** has also been determined. Relevant molecular parameters are: Tc–N(3) 1.627(3), Tc–N(1) 2.178(3), Tc–N(2) 2.205(4), Tc–Cl(1) 2.593(2), Tc–P(1) 2.427(2), Tc–P(2) 2.439(1) Å, N(3)–Tc–Cl(1) 179.5(1)°.

In the recent past we have spent considerable time studying the reactivity of the bidentate ligand (*o*-aminophenyl)diphenylphosphine, $PPh_2(C_6H_4NH_2\text{-}2)$, abbreviated H_2L, toward technetium and rhenium. The H_2L ligand is a triphenylphosphine derivative where a primary amine group is introduced into one of the three phenyl rings, in an *ortho*-position with respect to the aromatic carbon holding the phosphorus(III) atom. The resulting phosphinoamine chelate possesses enhanced co-ordination ability owing to the mixed σ–π donor–acceptor properties of both the co-ordinating groups. By exploiting such characteristics we have obtained extensive results by varying the reaction conditions such as pH, ligand-to-metal stoichiometric ratio, solvent and starting materials. Hence, starting from $[TcO_4]^-$ and an excess of H_2L, the tris-substituted species $[Tc^{III}(HL)_2(H_2L)]^+$ has been prepared;[1] the complex contains two mono-deprotonated ligands with the nitrogen co-ordinated as amido and the third chelate as non-deprotonated amino. Performing the above reaction in basic polar solvents using a 1:2 metal:ligand stoichiometric ratio, two phosphinoamido ligands, *cis*-phosphorus-positioned, fully chelate the equatorial plane of an octahedron in metal(v)–oxo complexes of the type $[MO(HL)_2(OR)]$ (M = Tc or Re, OR = primary alkoxo). On the contrary, in the presence of hydrohalogenic acid, $[ReO(HL)_2X]$ (X = halide) type complexes are obtained. In their co-ordination spheres two ligands are mutually orthogonal, preserving the *cis*-P-configuration: one ligand bridging an equatorial and an apical position with its amido nitrogen *trans* to the Re=O core, and the second spanning two sites in the equatorial plane. Conversely, in similar acidic reaction conditions technetium leads to paramagnetic species of the type $[Tc^{III}(H_2L)_2Cl_2]^+$ and $[Tc^{IV}(HL)_2Cl_2]$.[2]

In this paper we report on a further series of technetium and rhenium compounds containing the H_2L phosphinoamino ligand. These nitrido and imido complexes have been prepared by treating H_2L, either in polar or non-polar solvents, with $[MOCl_4]^-$, $[MNCl_4]^-$, $[MNCl_2(PPh_3)_2]$ (M = Tc or Re) or $[ReOX_2(OEt)(PPh_3)_2]$ (X = Cl, Br or I). The crystal structures of cationic $[TcNCl(H_2L)_2]Cl$ **2** and neutral $[Re(L)Cl_2(HL)]$ **3** complexes are reported; H_2L acts as a pure amino donor in the nitrido technetium(v) complex and as both imido and amido donors in the rhenium(v) compounds. In the latter type of complex an X-ray analysis of the chloro derivative displays a peculiar stereochemistry of the rhenium–imido bond as a rare example of a bent monoimido rhenium(v) complex.[3]

Organoimido rhenium complexes have been prepared by the reaction of $[ReOX_3L_3]$ (X = Cl or Br, L = tertiary phosphines) with aniline in benzene since the early 1960s by Chatt and co-workers;[4] in these reactions the oxo core is replaced by an imido unit. Since then, many other examples have appeared in the literature including polyimido and polynuclear imido compounds.[3] Recently, high oxidation state organoimido rhenium complexes have received interest in the field of catalysis as possible alternatives to tungsten or molybdenum complexes. In particular, rhenium-(v) and -(VII)

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

imido complexes might be less reducible than the corresponding isoelectronic oxo compounds in alkylation reactions.[5]

The first technetium organoimido complex was prepared only in 1990[6] and, to date, few other arylimido complexes have been described.[7–9] Recently, the mononuclear tris(imido) $[Tc^{VII}(\eta^1\text{-}C_5H_5)(NR)_3]$ complex and the binuclear 'ethane like' hexaimido complex $[Tc^{VI}_2(NR)_6]$ (R = alkyl) have been reported.[10–12]

The organoimido core may be of great interest in Tc-radiopharmaceutical design since a large variety of organic substituents may be incorporated into a stable Tc core, allowing a fine chemical tuning of the biological properties of the complex by simply varying the organic portion of the imido unit. Besides, high-valent technetium–imido complexes are much more resistant to protic attack than technetium–oxo complexes which, conversely, undergo facile oxygen atom abstraction and consequent reduction to lower oxidation states *e.g.* in the presence of tertiary phosphines.[8,12]

Nitrido–technetium complexes are receiving much interest since a new and reliable labelling procedure at carrier-free level, has been proposed.[13]

Experimental

Physical Measurements.—Elemental analyses (C, H, N) were performed on a Carlo Erba model 1106 elemental analyser while for the rhenium samples, the Re:P:X (X = Cl, Br or I) ratios were determined by integral counting of the backscattered X-ray fluorescence radiation from a Philips XL 40 model scanning electron microscope equipped with an EDAX model data station with the procedure previously reported.[2] IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000–220 cm^{-1}) using KBr pellets or Nujol mulls between CsI discs. Proton and ^{31}P NMR spectra and magnetic susceptibility measurements (Evans method[14]) were run on a Bruker AC-200 instrument, using $SiMe_4$ (^1H spectra) as internal reference and 85% aqueous H_3PO_4 (^{31}P spectra) as external reference. UV/VIS spectra were recorded in CH_2Cl_2 using a Cary 17D spectrophotometer (700–220 nm). Conductivity measurements were made in MeCN–CH_2Cl_2 (90:10) at 25 °C using a Metrohm Herison E518 conductometer. Fast-atom bombardment mass spectra in the positive mode (FAB$^+$) were recorded by using a 3-nitrobenzyl alcohol matrix on a VG ZAB-2F spectrometer. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV. Data were collected over the mass range 100–1000 at 0.7 s per scan.

CAUTION: ^{99}Tc is a weak β-emitter (E_{max} = 0.292 MeV, *ca.* 4.67×10^{-17} J) with $t_{\frac{1}{2}} = 2.12 \times 10^5$ years. Handling of this material was carried out in laboratories approved for low-level radioactivity using glove-boxes under moderate vacuum for the synthesis and recovery operations.

Materials.—Unless otherwise stated, all chemicals and solvents were of reagent grade. $[NBu_4][MOCl_4]$,[15a,b] $[MNCl_2(PPh_3)_2]$[3,16] (M = Tc or Re), $[NBu_4][TcNCl_4]$[17] and $[ReOX_2(OEt)(PPh_3)_2]$[15c] (X = Cl, Br or I) were prepared as previously reported. The ligand H_2L was prepared according to the published method.[18]

Synthesis of Technetium Complexes.—$[Tc(L)Cl_2(HL)]$ **1**. The complex $[NBu_4][TcOCl_4]$ (59 mg, 0.12 mmol) was suspended in benzene (5 cm^3) and solid H_2L (66 mg, 0.24 mmol) was added to this mixture, the colour turning brown-green, upon dissolution of the ligand. After stirring for 1.5 h at room temperature under a nitrogen atmosphere, an oily brown solid was formed. The volume of the mixture was reduced to 1 cm^3 in a nitrogen stream. Upon addition of ethyl acetate (5 cm^3) and vigorous stirring, a brown solid precipitated which was washed twice with portions (2 cm^3) of ethyl acetate, followed by diethyl ether (3 cm^3) and dried under vacuum. Yield 63 mg, 73% (Found: C, 58.9; H, 3.9; N, 3.7. $C_{36}H_{29}Cl_2N_2P_2Tc$ requires C, 60.00; H, 4.05; N, 3.90%). The complex is soluble in dichloromethane, chloroform, acetone and acetonitrile and insoluble in diethyl ether, benzene, ethyl acetate and hydrocarbons. Both methanol and ethanol dissolve the complex with production of a red solution. The ^1H NMR spectrum in $CDCl_3$ shows clear signs of decomposition of the complex, since it changes with time. FAB mass spectrum: *m/z* 685, $[M - Cl]^+$. UV/VIS (λ_{max}/nm, CH_2Cl_2): 500 (ε = 2700 dm^3 mol^{-1} cm^{-1}), 385 (sh), 340 (11 000) and 305 (sh).

$[TcNCl(H_2L)_2]Cl\cdot MeCN$ **2**. *Method* 1, *from* $[TcNCl_2(PPh_3)_2]$. The complex $[TcNCl_2(PPh_3)_2]$ (42 mg, 0.06 mmol) was dispersed in ethanol (10 cm^3). To this mixture was added H_2L (34 mg, 0.12 mmol). Upon refluxing for 1 h, the colour turned from blue-violet to light brown. On cooling, concentrating to 5 cm^3 and addition of acetonitrile (1 cm^3), a pale yellow solid precipitated. The solid was filtered off and washed twice with portions (2 cm^3) of acetonitrile. The crude product was recrystallized from CH_2Cl_2–MeCN. Yield 36 mg, 78% (Found: C, 59.1; H, 4.4; N, 7.3. $C_{36}H_{32}Cl_2N_3P_2Tc$.MeCN requires C, 58.75; H, 4.55; N, 7.20%). The complex is soluble in dichloromethane, chloroform, methanol, ethanol and dimethylformamide (dmf), slightly soluble in acetonitrile and insoluble in acetone, diethyl ether and hydrocarbons. Molar conductivity in MeCN–CH_2Cl_2 (90:10): Λ_M = 125 ohm^{-1} cm^2 mol^{-1} (1:1 electrolyte). FAB mass spectrum: *m/z* 702, $[M]^+$. UV/VIS-(λ_{max}/nm): 470(sh), 395 (ε = 270 dm^3 mol^{-1} cm^{-1}) and 330 (370). Well formed crystals for X-ray determination were grown from a dichloromethane solution layered with acetonitrile.

Method 2, *from* $[NBu_4][TcNCl_4]$. The complex $[NBu_4][TcNCl_4]$ (46 mg, 0.09 mmol) was dissolved in ethanol (10 cm^3), and upon addition of H_2L (75 mg, 0.27 mmol), the colour immediately changed from orange to brown. The mixture was stirred at reflux for 1 h, during which the colour remained unaltered. After cooling the solution was taken to dryness in a nitrogen stream. Upon treatment with acetonitrile (2 cm^3) a pale yellow solid precipitated; after filtration it was washed three times with portions (1 cm^3) of acetonitrile followed by diethyl ether and dried under vacuum. Yield 50 mg, 69%.

Synthesis of Rhenium Complexes.—A similar general route to that used above was followed to prepare the $[Re(L)X_2(HL)]$ type complexes; except for the chloride for which two procedures are described.

$[Re(L)Cl_2(HL)]$ **3**. *Method* 1, *from* $[ReOCl_2(OEt)(PPh_3)_2]$. The complex $[ReOCl_2(OEt)(PPh_3)_2]$ (100 mg, 0.12 mmol) was dispersed in benzene or ethanol (10 cm^3) and to this mixture was added solid H_2L (66 mg, 0.24 mmol). After refluxing for 1 h in benzene (2.5 h in ethanol) a brown solid was formed. The benzene solution was taken to dryness in a nitrogen stream and the oily solid treated with ethanol (5 cm^3). When using ethanol as solvent a good quality solid precipitated directly from the reaction mixture. The green-brown solid was then collected by filtration, washed twice with portions (2 cm^3) of ethanol followed by diethyl ether (5 cm^3) and finally dried under vacuum. Yield 80 mg, 83% (Found: C, 53.6; H, 3.6; N, 3.3. $C_{36}H_{29}Cl_2N_2P_2Re$ requires C, 53.45; H, 3.60; N, 3.45%). SEM microanalyses 1:2:2 (Re:P:Cl). The compound is soluble in dichloromethane, chloroform, acetonitrile, acetone and dmf, slightly soluble in benzene and ethanol and insoluble in methanol, diethyl ether, water and hydrocarbons. FAB mass spectrum: *m/z* 810 $[M + H]^+$, 773 $[M - Cl]^+$, 738 and $[M + H - 2Cl]^+$. UV/VIS (λ_{max}/nm) 410 (ε = 8000 dm^3 mol^{-1} cm^{-1}), 330 (14 300) and 270 (sh).

Method 2, *from* $[NBu_4][ReOCl_4]$. The complex $[NBu_4][ReOCl_4]$ (110 mg, 0.19 mmol) was dispersed in benzene (5 cm^3) and to the mixture was added solid H_2L (105 mg, 0.38 mmol) leading to a green-brown colour. After refluxing for 2 h the mixture was cooled and the green-brown solid filtered off. The product was washed twice with portions of ethanol (2 cm^3) followed by diethyl ether (5 cm^3) and then dried under vacuum. Yield 123 mg, 81%. Crystals suitable for X-ray crystal structure

Table 1 Structure determination summary*

Crystal data	**2**	**3**
Empirical formula	$C_{38}H_{35}Cl_2N_4P_2Tc$	$C_{36}H_{29}Cl_2N_2P_2Re$
M	778.5	808.7
Colour, habit	Yellow cubes	Brown shining parallelepipeds
Crystal size/mm	0.3 × 0.3 × 0.3	0.10 × 0.20 × 0.20
Unit cell dimensions:		
a/Å	10.688(5)	10.094(2)
b/Å	11.910(5)	11.544(2)
c/Å	15.753(7)	14.968(2)
α/°	70.18(3)	96.29(2)
β/°	81.59(4)	97.06(2)
γ/°	74.96(3)	107.99(2)
U/Å^3	1818.1(1.4)	1625.8(7)
D_c/Mg m^{-3}	1.418	1.652
μ/mm^{-1}	0.66	4.03
F(000)	796	796
Data collection:		
2θ range/°	4.5–45.0	4.0–50.0
Index ranges, hkl	0–11, −12 to 12, −15 to 15	0–12, −13 to 13; −17 to 17
Reflections collected	4954	5994
Independent reflections	4740 (R_{int} = 0.025)	5771 (R_{int} × 0.023)
Observed reflections [$F_o > 3\sigma(F_o)$]	4174	4800
Solution and refinement:		
Weighting scheme (w^{-1})	$\sigma^2(F) + 0.0011F^2$	$\sigma^2(F) + 0.0696F^2$
Number of parameters refined	410	269
Final R,R' indices (observed data)	0.031, 0.045	0.049, 0.063
Goodness-of-fit	1.20	0.87

* Details in common: triclinic, space group $P\bar{1}$, $Z = 2$; Nicolet–Siemens R3m/V diffractometer, Mo-Kα radiation (λ = 0.710 73 Å), T = 294 K; highly oriented graphite crystal monochromator, ω–2θ scan mode, variable scan speed 4.51–14.65 min^{-1} in ω, scan range (ω) 0.60° + Kα separation; background measurement, stationary crystal and stationary counter at the beginning and end of scan, each for 25% of total scan time; 2 standard reflections every 200; function minimized $\Sigma w(|F_o| - |F_c|)^2$; H atoms introduced using a 'riding' model with common variable isotropic U values.

determination were grown from a dichloromethane solution layered with methanol.

[Re(L)Br$_2$(HL)] **4**. The complex [ReOBr$_2$(OEt)(PPh$_3$)$_2$] (160 mg, 0.175 mmol) was dispersed in toluene (10 cm^3) and then solid H$_2$L (97 mg, 0.35 mmol) was added and the mixture stirred under reflux for 2.5 h. Upon cooling and concentration in a nitrogen stream to half the volume a brown solid formed which was filtered off and washed twice with portions (2 cm^3) of toluene, followed by diethyl ether (5 cm^3), and dried under vacuum. Yield 124 mg, 79% (Found: C, 50.3; H, 3.4; N, 3.1. $C_{36}H_{29}Br_2N_2P_2Re$ requires C, 48.15; H, 3.25; N, 3.10%). SEM microanalyses 1:2:2 (Re:P:Br). The product is soluble in dichloromethane, chloroform and dmf, slightly soluble in acetone, toluene and benzene and insoluble in methanol, ethanol, acetonitrile, water, diethyl ether and hydrocarbons. FAB mass spectrum: m/z 898 $[M + H]^+$, 817 $[M - Br]^+$ and 738 $[M + H - 2Br]^+$. UV/VIS (λ_{max}/nm) 420 (ε = 8000 dm^3 mol^{-1} cm^{-1}), 380 (8400) and 310 (sh).

[Re(L)I$_2$(HL)] **5**. The complex was prepared from [ReOI$_2$(OEt)(PPh$_3$)$_2$] with a procedure identical to that of the bromo-derivative, but employing a reaction time of 4 h. Yield 69% (Found: C, 44.5, H, 3.1; N, 2.7. $C_{36}H_{29}I_2N_2P_2Re$ requires C, 43.60; H, 2.95; N, 2.85%). SEM microanalyses 1:2:2 (Re:P:I). The brown complex is soluble in dichloromethane, chloroform and dmf, slightly soluble in benzene and insoluble in acetone, acetonitrile, toluene, methanol, ethanol, water, diethyl ether and hydrocarbons. FAB mass spectrum: m/z 865 $[M - I]^+$ and 738 $[M + H - 2I]^+$. UV/VIS (λ_{max}/nm) 430 (ε = 8500 dm^3 mol^{-1} cm^{-1}), 375 (sh) and 335 (14 000).

[ReOCl$_2$(HL)(PPh$_3$)] **6**. The complex [ReOCl$_2$(OEt)(PPh$_3$)$_2$] (113 mg, 0.134 mmol) was dispersed in benzene (15 cm^3) with solid H$_2$L (37 mg, 0.134 mmol). The mixture was refluxed under nitrogen for 1 h during which the colour changed from green to brown. The solution was slowly evaporated in a nitrogen stream to 3 cm^3, the light brown crystalline solid which precipitated was filtered off, washed three times with aliquots (1 cm^3) of benzene and finally with diethyl ether (2 cm^3) and dried under vacuum. Yield 84 mg, 78% (Found: C, 53.5; H, 3.8; N, 1.7. $C_{36}H_{30}Cl_2P_2NORe$ requires C, 53.25; H, 3.75; N, 1.75%). SEM microanalyses 1:2:2 (Re:P:Cl). The compound is soluble in dichloromethane, chloroform and acetone, slightly soluble in acetonitrile and benzene and insoluble in ethanol, methanol, diethyl ether and hydrocarbons. FAB mass spectrum: m/z 813 $[M + H]^+$ and 776 $[M - Cl]^+$.

[ReNCl(H$_2$L)$_2$]Cl **7**. The complex [ReNCl$_2$(PPh$_3$)$_2$] (124 mg, 0.156 mmol) was dispersed in acetonitrile (25 cm^3) and to the suspension was added solid H$_2$L (87 mg, 0.31 mmol). The mixture was refluxed under nitrogen for 2 h, the initially orange solution turned yellow-brown and a light solid was formed. The mixture was concentrated in a nitrogen stream to 10 cm^3 and the pale-brown solid was filtered off, washed three times with aliquots (1 cm^3) of acetonitrile, then twice with aliquots (3 cm^3) of diethyl ether. Yield 116 mg (90%). The crude product was recrystallized by layering MeCN above a saturated dichloromethane solution, and yellow crystals formed (Found: C, 49.8; H, 4.1; N, 4.9. $C_{36}H_{32}Cl_2N_3P_2Re$ requires C, 52.35; H, 3.90; N, 5.10%). SEM microanalyses 1:2:2 (Re:P:Cl). The compound is soluble in dichloromethane, chloroform, ethanol and methanol, slightly soluble in acetonitrile and dmf and insoluble in acetone, benzene, water, diethyl ether and hydrocarbons. Molar conductivity in MeCN–CH$_2$Cl$_2$ (90:10): Λ_M = 110 ohm^{-1} cm^2 mol^{-1}. FAB mass spectrum: m/z 790, $[M]^+$. UV/ VIS (λ_{max}/nm) 435 (sh), 385 (ε = 1600 dm^3 mol^{-1} cm^{-1}) and 300 (sh).

Crystallography.—Details of the crystal data, intensity measurements and data processing for complexes **2** and **3** are summarized in Table 1. Cell parameters were determined from 40 high-angle data ($2\theta > 22°$). For the calculation of the

Table 2 Atomic coordinates (× 10^4) for complexes **2** and **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex 2							
Tc	1905.7(3)	2731.7(2)	2000.6(2)	C(14)	3895(4)	4515(3)	2755(3)
Cl(1)	−96.3(8)	1870.5(8)	2815.6(6)	C(15)	4813(4)	5071(4)	2892(3)
Cl(2)	1115.8(9)	6562.6(9)	9851.8(7)	C(16)	4621(5)	5541(4)	3602(3)
P(1)	1565.4(8)	3682.0(8)	3181.2(6)	C(17)	3526(5)	5476(4)	4162(3)
P(2)	3225.9(8)	662.1(7)	2582.2(6)	C(18)	2619(4)	4918(3)	4040(3)
N(1)	362(3)	4313(2)	1433(2)	C(19)	1188(3)	2828(3)	4348(2)
N(2)	1625(3)	1912(3)	1000(2)	C(20)	2221(4)	2068(3)	4862(3)
N(3)	3154(3)	3285(3)	1487(2)	C(21)	2000(5)	1371(4)	5755(3)
N(4)	6008(4)	7730(4)	372(3)	C(22)	769(6)	1442(4)	6138(3)
C(37)	5266(5)	7258(5)	295(3)	C(23)	−272(5)	2188(4)	5641(3)
C(38)	4276(6)	6705(6)	156(4)	C(24)	−65(4)	2874(4)	4738(3)
C(1)	110(3)	4889(3)	2826(2)	C(25)	4924(3)	573(3)	2183(2)
C(2)	−581(4)	5645(4)	3333(3)	C(26)	5532(4)	−58(4)	1594(3)
C(3)	−1719(4)	6455(4)	3049(3)	C(27)	6829(5)	−63(5)	1309(4)
C(4)	−2203(4)	6547(4)	2253(3)	C(28)	7502(5)	545(6)	1606(4)
C(5)	−1531(4)	5836(3)	1741(3)	C(29)	6911(5)	1165(5)	2183(3)
C(6)	−368(3)	5009(3)	2019(2)	C(30)	5618(4)	1196(4)	2482(3)
C(7)	2569(3)	−136(3)	2014(2)	C(31)	3301(3)	−368(3)	3750(2)
C(8)	2728(4)	−1396(3)	2283(3)	C(32)	4405(4)	−1279(4)	4032(3)
C(9)	2122(5)	−1941(4)	1859(3)	C(33)	4397(5)	−2111(4)	4898(3)
C(10)	1340(4)	−1213(4)	1155(3)	C(34)	3312(5)	−2017(4)	5483(3)
C(11)	1184(4)	43(3)	865(3)	C(35)	2222(5)	−1109(4)	5206(3)
C(12)	1790(3)	581(3)	1296(2)	C(36)	2204(4)	−289(3)	4335(2)
C(13)	2782(3)	4435(3)	3329(2)				
Complex 3							
Re	1861.0(3)	4851.6(3)	3279.2(2)	C(16)	7945(11)	6386(9)	3632(7)
Cl(1)	31(2)	3608(2)	3989(1)	C(17)	7156(11)	5789(9)	2823(7)
Cl(2)	59(2)	4917(2)	2115(2)	C(18)	5841(9)	5868(8)	2553(6)
P(1)	3513(2)	6601(2)	2789(1)	C(19)	3491(9)	7117(8)	1682(6)
P(2)	1813(2)	3015(2)	2216(1)	C(20)	4633(12)	7401(10)	1236(8)
N(1)	1720(6)	6226(6)	4128(4)	C(21)	4562(16)	7808(13)	433(10)
N(2)	3295(6)	4414(6)	3774(4)	C(22)	3326(16)	7929(14)	−2(12)
C(1)	3294(8)	7852(7)	3524(5)	C(23)	2163(18)	7666(15)	441(12)
C(2)	3947(9)	9102(8)	3514(6)	C(24)	2236(12)	7259(10)	1262(8)
C(3)	3730(9)	9981(8)	4122(7)	C(25)	1707(8)	2880(7)	989(5)
C(4)	2775(9)	9606(7)	4717(6)	C(26)	1371(9)	1739(9)	440(7)
C(5)	2125(9)	8392(7)	4733(6)	C(27)	1331(11)	1684(10)	−495(8)
C(6)	2354(8)	7480(7)	4132(5)	C(28)	1603(11)	2740(9)	−876(8)
C(7)	3509(7)	2896(7)	2672(5)	C(29)	1935(11)	3828(10)	−356(8)
C(8)	4275(10)	2198(9)	2305(7)	C(30)	2006(10)	3937(9)	584(7)
C(9)	5594(10)	2289(9)	2772(7)	C(31)	472(8)	1590(7)	2377(6)
C(10)	6099(9)	3046(9)	3625(7)	C(32)	−934(9)	1422(8)	2056(6)
C(11)	5346(8)	3732(8)	4000(6)	C(33)	−1965(11)	412(9)	2239(7)
C(12)	4059(8)	3667(7)	3502(5)	C(34)	−1621(11)	−411(10)	2745(8)
C(13)	5294(8)	6580(7)	3106(5)	C(35)	−233(13)	−248(11)	3063(9)
C(14)	6098(9)	7186(8)	3959(6)	C(36)	835(11)	760(9)	2886(7)
C(15)	7424(11)	7079(9)	4225(7)				

structure factors, corrections for Lorentz and polarization effects and absorption (using an empirical method based on ψ-scans of seven reflections at $\chi \approx 90°$ or 270°) were made. Transmission factors were in the range 0.54–0.86 for **2** and 0.43–0.74 for **3**. The structures were solved by standard heavy-atom methods with subsequent Fourier difference maps yielding the positions of the light atoms. The hydrogens were included in calculated positions, but were not refined. To ensure a good observation/variable ratio the MeCN atoms for **2** and the carbon phenyl atoms for **3** were treated isotropically. Difference maps, calculated after the refinement, were essentially featureless. Fractional atomic coordinates are given in Table 2, selected bond distances and angles in Table 3. The SHELXTL PLUS package[19a] of computer programs was employed for the solution and refinement of both structures and ORTEP[19b] used to plot the molecular structures.

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

Results and Discussion

Preparation and Reactivity of Imido Complexes.—The substitution reactions of $[ReOX_2(OEt)(PPh_3)_2]$ (X = Cl, Br or I) with H_2L either in polar (MeOH, EtOH or MeCN) or in non-polar solvents [benzene, or toluene (X = Cl and Br)] led to the formation of neutral and diamagnetic complexes of the type $[Re(L)X_2(HL)]$, which contain a dianionic P,N-ligand with the nitrogen bonded as an imido and a second monoanionic P,N-ligand with nitrogen acting as an amido ligand. Chloro- and bromo-derivatives can be prepared also from the $[NBu_4][ReOX_4]$ precursors, but only in benzene solutions, whereas, in polar solvents, the mono-oxo core is retained, as previously described.[2] However, the synthesis of these rhenium–imido compounds do not require anhydrous solvents or anaerobic conditions. A similar procedure was followed to prepare the analogous $[Tc(L)Cl_2(HL)]$ complex, which is exclusively obtained by a ligand-exchange reaction from $[NBu_4][TcOCl_4]$ in anhydrous benzene under nitrogen. Equations (1) and (2) outline the likely reaction stoichiometries.

$$[ReOX_2(OEt)(PPh_3)_2] + 2H_2L \xrightarrow{\text{benzene or EtOH}} [Re(L)X_2(HL)] + EtOH + 2PPh_3 + H_2O \quad (1)$$

$$[NBu_4][MOCl_4] + 2H_2L \xrightarrow{\text{benzene}} [M(L)Cl_2(HL)] + HCl + H_2O + [NBu_4]Cl \quad (2)$$

The presence of the PPh_3 in the starting material in the reaction (1) and the solvent polarity in reaction (2) seem to play a crucial role in determining the course of the reaction.

A number of experiments have been conducted to better understand the role played in the reaction mechanism by PPh_3, the metal : ligand ratio and solvent polarity.

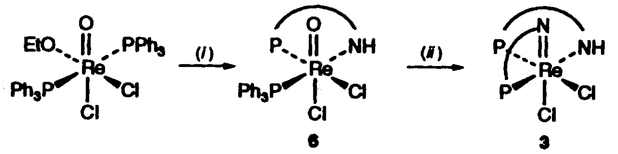
The presence of PPh_3 in the rhenium starting material allows the formation of the mono-substituted $[ReOCl_2(HL)(PPh_3)]$ derivative **6**, when using a 1 : 1 metal : ligand ratio in benzene solution. Its IR spectrum displays an intense absorption at 958 cm^{-1} and a sharp peak at 3332 cm^{-1} attributable to ν(Re=O) and ν(N–H), respectively. Phosphorus-31 NMR spectra show two signals indicating the presence of two magnetically inequivalent phosphorus atoms (Table 4) and the elemental analyses are consistent with the formulation $[ReOCl_2(HL)(PPh_3)]$. The value of the ν(Re=O) [which is indicative of a rhenium(v) complex with a chloride *trans* to the Re=O moiety], along with ^{31}P NMR data are in accordance with both HL^- and PPh_3 ligands being in equatorial position with mutually *cis*-P atoms.[2] A similar reaction to that described above but performed in ethanol leads to a mixture of unidentified species.

Further addition of H_2L to the mixed-phosphino rhenium(v)–oxo complex **6** in a 1 : 1 stoichiometric ratio, either in benzene or EtOH, leads to the formation of the imido–amido complex **3**.

Increasing the H_2L:Re ratio to ⩾3 : 1 causes reduction to Re^{III}, the loss of the oxo-core and the formation of the complex $[Re^{III}(HL)_2(H_2L)]^+$.[20]

Scheme 1 describes a tentative reaction mechanism for the formation of the chloro–imido–amido rhenium complex.

In the first step a simple exchange of one PPh_3 and of the ethoxo ligand for a phosphinoamido chelate occurs. The second step implies the substitution of the remaining PPh_3 and the replacement of the oxo core by the imido unit. A possible intimate mechanism for this latter process may involve the substitution of the second PPh_3 for the phosphorus atom of the H_2L ligand and the subsequent co-ordination, further promoted by the chelating effect, of the amino nitrogen to the metal centre. The consequent strong acidic character assumed by the protons of the amino group, bonded to a $(M{=}O)^{3+}$ centre, facilitates the proton transfer from the amine to the oxo ligand to yield the imido core and free water.[5] This pathway is further supported by the absence of O=PPh_3 (as confirmed by ^{31}P NMR spectroscopy) in the mother-liquor that excludes a mechanism involving the extraction of the oxo-core by PPh_3 from the metal centre.



Scheme 1 (*i*) H_2L, benzene; (*ii*) H_2L, benzene or EtOH

Table 3 Selected bond lengths (Å) and angles (°) for complexes **2** and **3** with e.s.d.s in parentheses

Complex **2**			
Tc–Cl(1)	2.593(2)	Tc–P(1)	2.427(2)
Tc–P(2)	2.439(1)	Tc–N(1)	2.178(3)
Tc–N(2)	2.205(4)	Tc–N(3)	1.627(3)
P(1)–C(1)	1.829(3)	P(1)–C(13)	1.840(4)
P(1)–C(19)	1.818(3)	P(2)–C(7)	1.819(5)
P(2)–C(25)	1.820(4)	P(2)–C(31)	1.833(3)
N(1)–C(6)	1.456(5)	N(2)–C(12)	1.461(4)
Cl(1)–Tc–P(1)	83.9(1)	N(1)–Tc–N(3)	99.1(1)
Cl(1)–Tc–N(1)	80.4(1)	Tc–P(1)–C(13)	120.5(1)
Cl(1)–Tc–N(2)	81.9(1)	Tc–P(2)–C(25)	111.9(1)
N(1)–Tc–N(2)	89.5(1)	Tc–N(2)–C(12)	117.1(2)
P(2)–Tc–N(3)	92.9(1)	P(1)–Tc–P(2)	107.9(1)
Tc–P(1)–C(1)	101.1(1)	P(2)–Tc–N(1)	164.4(1)
Tc–P(2)–C(7)	100.5(1)	P(2)–Tc–N(2)	79.0(1)
Tc–N(1)–C(6)	118.3(2)	P(1)–Tc–N(3)	95.8(1)
Cl(1)–Tc–P(2)	87.6(1)	N(2)–Tc–N(3)	98.3(2)
P(1)–Tc–N(1)	80.7(1)	Tc–P(1)–C(19)	120.6(1)
P(1)–Tc–N(2)	163.9(1)	Tc–P(2)–C(31)	128.7(1)
Cl(1)–Tc–N(3)	179.5(1)		
Complex **3**			
Re–Cl(1)	2.404(2)	Re–Cl(2)	2.384(2)
Re–P(1)	2.438(2)	Re–P(2)	2.492(2)
Re–N(1)	1.973(7)	Re–N(2)	1.780(7)
P(1)–C(1)	1.804(9)	P(2)–C(7)	1.815(8)
C(1)–C(6)	1.40(1)	C(7)–C(12)	1.39(1)
N(1)–C(6)	1.39(1)	N(2)–C(12)	1.38(1)
Cl(1)–Re–Cl(2)	88.0(1)	Cl(2)–Re–P(2)	82.7(1)
P(1)–Re–N(1)	79.5(2)	Re–P(1)–C(1)	100.0(3)
Cl(1)–Re–N(1)	84.0(2)	Cl(2)–Re–N(2)	157.0(2)
P(2)–Re–N(2)	75.2(2)	Cl(1)–Re–P(2)	91.4(1)
Cl(2)–Re–P(1)	89.2(1)	P(1)–Re–N(2)	90.3(2)
Re–N(1)–C(6)	127.3(5)	Cl(1)–Re–N(2)	98.8(2)
Re–N(2)–C(12)	137.1(5)	N(1)–Re–N(2)	107.7(3)
P(1)–Re–P(2)	105.0(1)	Cl(2)–Re–N(1)	94.8(2)
Cl(1)–Re–P(1)	162.9(1)	Re–P(2)–C(7)	99.1(2)
P(2)–Re–N(1)	174.8(2)		

Table 4 Infrared[a] (cm^{-1}) and NMR[b] spectral data

	IR			NMR(δ)		
Compound	ν(M=N)	N–H	M–Cl	^{31}P	N–^1H	$^1H_{arom}$
$[Re(L)Cl_2(HL)]$	971	3325	312, 292	9.31 (s), −9,13 (s)		6.10–7.90
$[Re(L)Br_2(HL)]$	967	3342		6.12 (s), −12.00 (s)	13.3 (br s)	6.20–7.80
$[Re(L)I_2(HL)]$	965	3303		−0.69 (s), −17.30 (s)	11.65 (s)	6.40–7.70
$[ReOCl_2(HL)(PPh_3)]$	958[c]	3332		7.40 (d), −21.70 (d)	11.96 (s)	6.75–7.65
$[Tc(L)Cl_2(HL)]$	951	3309	315, 282			
	ν(M≡N)					
$[TcNCl(H_2L)_2]Cl{\cdot}MeCN$[d]	1046	3182	302	n.d.	9.72 (d), 6.00 (d)	7.10–7.90 7.00–7.90
$[ReNCl(H_2L)_2]Cl$		3142	291	28.6 (s)	9.87 (br s)	

[a] As Nujol mulls for Tc and KBr pellets for Re. [b] Multiplicity in parentheses. [c] ν(Re=O). [d] ν(–C≡N), 2245 cm^{-1}; δ(MeCN), 2.00(s). s = Singlet, d = doublet, br = broad, n.d. = not detectable.

No stable oxo–amido intermediates are isolated starting from labile $[ReOX_4]^-$ precursors. In this case the solvent polarity plays the crucial role; indeed, when the reaction is performed in ethanol, the oxo complex $[ReOCl(HL)_2]$ is always obtained, even in the presence of an excess of PPh_3, while the use of benzene allows the recovery of the amido–imido species. Actually, phenylimido complexes of rhenium and neighbouring metals are commonly prepared in benzene or other non-polar solvents.[3]

Both imido–rhenium and –technetium compounds are air stable in the solid state; the chloro and bromo derivatives are also stable in solution and can be easily recrystallized from CH_2Cl_2–MeOH, whereas the iodo–rhenium analogue, is converted into the oxo-rhenium bis(amido) derivative $[ReO(HL)_2I]$[2] upon standing. The complex $[Tc(L)Cl_2(HL)]$ is unstable in alcohols, acetonitrile, acetone and chloroform and rearranges to the yellow $[Tc^{III}(H_2L)_2Cl_2]$ and $[Tc^{IV}(HL)_2Cl_2]$ species,[2] as evidenced by proton NMR spectroscopy (the spectrum shows several signals in the range δ 1–19 in $CDCl_3$).

Treatment of imido–rhenium complexes in basic ROH (R = Me or Et) or in basic acetonitrile solution leads to the formation of the 'equatorial' $[ReO(HL)_2(OR)]$ oxo species[2] and this process is irreversible.

The compounds were characterized by the usual chemico-physical techniques; their formulation is supported by elemental analyses plus diagnostic FAB^+ mass spectra, which show the molecular ions and the fragments due to the loss of one and two halides. The IR spectra of all the rhenium complexes show identical fingerprints and confirm the two co-ordination modes of H_2L, with a unique N–H amido stretch in the region 3303–3342 cm^{-1} (Table 4) at values different from those reported for the amido–amido derivatives.[2] In addition, a medium intense absorption is located in a narrow range around 970 cm^{-1}, which is the region typical of $\nu(Re{=}O)$ rather than $\nu(Re{=}N{-})$.[3] Moreover, the IR spectrum of the $[Tc(L)Cl_2(HL)]$ complex is superimposable on that of the rhenium analogue, except for the band at 951 cm^{-1}. A difference of about 20 cm^{-1} in $\nu(Re{=}O)$ is commonly observed between analogous rhenium and technetium oxo complexes. However, the eventual attribution of the bands at *ca.* 970 cm^{-1} to $\nu(Re{=}N{-})$ was possible only after an X-ray determination which established the absence of any oxo group and the co-ordination of one of the ligands in the imido mode. Furthermore, the Re=N–aryl angle of 137.1(5)°, suggests a nearly sp^2 hybridization of the nitrogen and a Re=N– bond order of *ca.* two. Indeed, the Re=N– distance [1.780(7) Å] is one of the longest among those reported in Table 5 and accounts for the low value of the Re=N– stretching frequency, which lies outside of the usual range exhibited by imido compounds (1000–1300 cm^{-1}).[3] Furthermore, in all IR spectra of the rhenium and imido-technetium compounds, an intense absorption is present in the region around 560 cm^{-1}. This band may be related to the bent imido ligand, since it is absent in the starting materials, in other linear phenylimido complexes such as $[Re(NPh)Cl_3(PPh_3)_2]$[4c] and in oxo bis(amido) H_2L rhenium derivatives.[2] In the region below 400 cm^{-1} only the chloro derivatives show assignable stretching vibrations at 292 and 282 cm^{-1}, for Re and Tc respectively for $\nu(M{-}Cl_{equatorial})$, and at 312 and 315 cm^{-1} for $\nu(M{-}Cl_{\mathit{trans}\text{-imido}})$. These values are consistent with the $Re{-}Cl(2)_{\mathit{trans}\text{-imido}}$ bond length of 2.384(2) Å which is shorter than the corresponding $Re{-}Cl(1)_{equatorial}$ bond of 2.404(2) Å.

Usually, in technetium and rhenium complexes the organoimido group assumes a linear configuration which is formally isoelectronic with the oxo moiety and the nitrogen atom behaves as a four-electron donor. Only few cases of bent imido (where the nitrogen is a two-electron donor) complexes have been reported.[3,21] For metals such as technetium and rhenium, which often obey the effective atomic number rule, a bent nitrene function would be expected if a linear configuration would formally cause the valence electron count to exceed 18, with a concomitant increase in the M–N distance and a decrease of the M–N–C angle from linearity. As evidenced by the structural features, in the $[Re(L)Cl_2(HL)]$ complex the bidentate ligand exists as a five-electron donor ($2e^-$ P + $3e^-$ N) in HL^- and a four-electron donor ($2e^-$ P + $2e^-$ N) in L^{2-}, giving a valence electron count of 18. Indeed, the bent configuration of the imido core, enforced by the intrinsic ligand geometry, actually diminishes the electron donor ability of the nitrene ligand (from formally $4e^-$ to $2e^-$) and such a decrease is compensated by the amido π-bonding to the metal, the measure of which is indicated by the shortening of the $Re{-}N_{amido}$ distance.

Proton NMR spectra of the rhenium compounds indicate the diamagnetism of all the compounds; they show signals due to the aromatic protons in the range δ 6.10–7.90 and a signal of the N–H amido proton at δ 13.3 and 11.65, for the bromo and the iodo derivatives, respectively. The ^{31}P NMR spectra exhibit two distinct signals for each rhenium compound indicating two magnetically inequivalent phosphorus atoms, with a nearly constant separation (average 17.8 ppm, see Table 4). The ^{31}P NMR signals for the technetium complex are not detectable at room temperature. UV/VIS spectroscopy shows for all rhenium compounds a typical three-band pattern following the expected bathochromic trend on going from the chloro to the iodo-derivative; conversely, the $[Tc(L)Cl_2(HL)]$ complex shows a four-band spectrum notably red-shifted with respect to those of the analogous rhenium complex.

Preparation and Reactivity of Nitrido Complexes.—The cationic nitrido complex $[TcNCl(H_2L)_2]Cl{\cdot}MeCN$ **2** has been prepared either by ligand exchange from $[Tc^VNCl_2(PPh_3)_2]$ or by reduction–substitution from $[NBu_4][Tc^{VI}NCl_4]$ and H_2L in 1:2 (Re:H_2L) stoichiometric ratio in ethanol or acetonitrile. An identical reaction between the $[ReNCl_2(PPh_3)_2]$ precursor and H_2L in ethanol or benzene produces a mixture of compounds from which a yellow species, $[ReNCl(H_2L)_2]Cl$ **7**, can be separated by column chromatography (C18 Sep-Pack). The yield of the yellow complex is maximised up to 90% when the reaction is performed in acetonitrile. The technetium and rhenium nitrido compounds are stable both in the solid state and in solution and are not reduced in the presence of an excess of ligand. Their formulation is assessed by elemental analyses and by positive-ion FAB^+ mass spectra, which show for both complexes the molecular cation peak. The ionic nature of the complexes is established by conductivity measurements in MeCN–CH_2Cl_2 (90:10) which give values in agreement for a monoelectrolyte; moreover, the chloride counter ion can be exchanged by metathesis reaction with $NaClO_4$.

The comparison of the IR spectra of the technetium and rhenium complexes allows assignment of the Tc≡N stretching band at 1046 cm^{-1}, while the attribution of $\nu(Re{\equiv}N)$, which is expected to be in the region 1000–1100 cm^{-1},[22] is not straightforward owing to interference by two ligand bands (at 1098 and 1068 cm^{-1} in both technetium and rhenium complexes).

Both rhenium and technetium nitrido complexes exhibit a three band UV/VIS spectrum, with two of these in the visible region. As expected, the rhenium complex exhibits corresponding visible bands at higher energy than the technetium analogue.

X-Ray Crystallography Studies.—The two complexes show the three modes of co-ordination for the nitrogen donor of the (*o*-aminophenyl)diphenylphosphine ligand: an amino (H_2L) mode in **2**, where the functionalized phosphine acts as a neutral bidentate ligand and both the imido (L^{2-}) and amido (HL^-) modes in **3**. The different co-ordinating modes can be ascertained from the M–N distances, which dramatically decrease from amino to amido to imido; moreover, the value of the M=N–aryl angle seems to be diagnostic; *ca.* 137° (imido), *ca.* 127° (amido) and *ca.* 117° (amino).

In both complexes the co-ordination geometry is highly distorted octahedral and the phosphorus atoms of two ligands

Table 5 Comparison of Re=N and Re=N–aryl data in octahedral arylimido rhenium(v) complexes

Compound	Re=N/Å	Re=N–aryl/°	Ref.
$[Re(NC_6H_4COMe\text{-}p)Cl_3(PEt_2Ph)_2]$	1.690(5)	175.8(1)	24
$[Re(NC_6H_4OMe\text{-}p)Cl_3(PEt_2Ph)_2]$	1.709(4)	171.8(4)	24
$[Re(NPh)(L^1)_2(PPh_3)]^{+a}$	1.709(8)	165.5(5)	25
$[Re(NPh)Cl_3(NH_2CMe_3)_2]$	1.71(1)	180.0	26
$[Re(NC_6H_4Me\text{-}p)Cl_2(MeN{=}CHC_6H_4O\text{-}o)(PPh_3)]$	1.71(1)	171(1)	27
$[Re(NPh)Cl_3(PPh_3)_2]$	1.726(6)	172.6(6)	28
$[Re(NPh)(bipy)_2(OEt)]^{2+b}$	1.740(6)	167.4(6)	29
$[Re(NC_6H_4Me\text{-}p)(S_2CNMe_2)_2(OEt)]$	1.745(5)	155.5(5)	21
$[Re(NC_6H_4Me\text{-}p)Cl_2(PhN{=}CHC_6H_4O\text{-}o)(PPh_3)]$	1.75(1)	168(1)	27
$[Re(NC_6H_4PPh_2)(HNC_6H_4PPh_2)Cl_2]$	1.780(7)	137.1(5)	This work

[a] L^1 = 3-Hydroxy-2-methyl-4-pyronate. [b] bipy = 2,2′-Bipyridine.

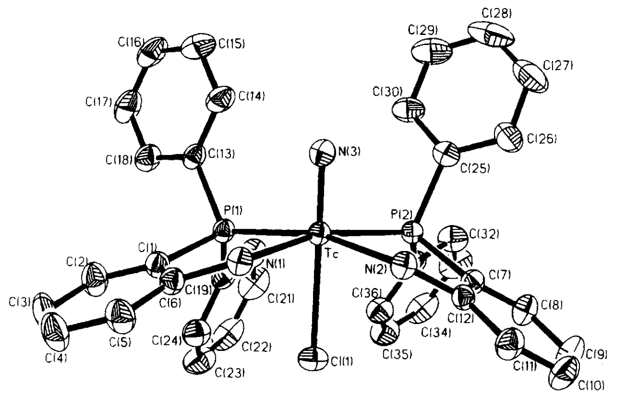


Fig. 1 An ORTEP view of complex **2**, showing the atom labelling scheme; the thermal ellipsoids are drawn at 40% probability level and hydrogen atoms are omitted for clarity

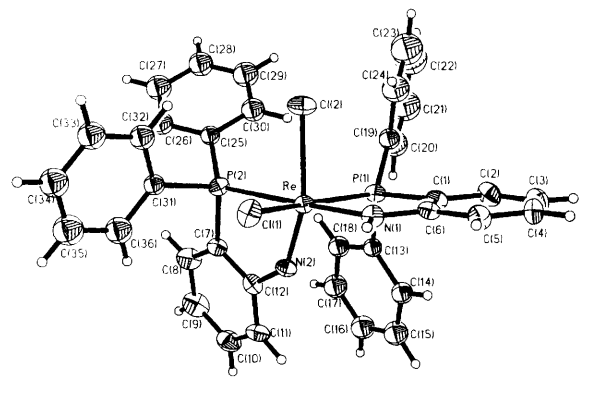


Fig. 2 An ORTEP view of complex **3**, showing the atom labelling scheme; the thermal ellipsoids are drawn at 40% probability level

are *cis*-co-ordinated. The most noticeable features of the monopositive complex $[TcNCl(H_2L)_2]^+$ (Fig. 1), compared with $[TcO(HL)_2(OMe)]$ and $[ReO(HL)_2(OEt)]$,[2] are: (*i*) the complex contains two neutral H_2L ligands symmetrically co-ordinated in the equatorial plane and the Tc–N lengths [2.178(3) and 2.205(4) Å] are consistent with the values found for $Tc–N_{amine}$ distances;[23] (*ii*) the technetium atom is displaced from the mean plane of the P_2N_2 donor atom set by 0.26 Å towards the 'nitrido' nitrogen atom (0.22 and 0.21 Å in the oxo complexes); (*iii*) the two PCCN rings are bent away from the nitrido N(3) atom (dihedral angles of 19.6 and 31.4° with the P_2N_2 mean plane), resulting in the complex assuming an 'umbrella' arrangement with the angles between the Tc≡N(3) and the equatorial atoms remarkably >90°, with an overall geometry resembling that of the oxo complexes; (*iv*) as expected, the Tc–Cl(1) distance of 2.593(2) Å is considerably longer than those found in the literature,[23] as the result of the strong *trans* influence of the multiply bonded nitrido group.

The neutral $[Re(L)Cl_2(HL)]$ complex **3** (Fig. 2) contains one 'equatorial' HL^- ligand and a L^{2-} ligand, 'twisted' relative to each other by 101.3°, with the imido group bonded *trans* to a chloride atom, and the other chloride co-ordinated equatorially. The severe distortions from octahedral geometry are reflected by a Cl(2)–Re–N(2) angle of 157.0(2)° and by the 'bite' angles of 79.5(2) and 75.2(2)° for HL^- and L^{2-} ligands, respectively. If one compares the structural data of **3** with those of $[ReO(HL)_2Cl]$ (both α- and β-forms),[2] the main differences concern the deviation of the Re atom from the mean P_2NCl equatorial plane and the Re–N(2) bond length. In **3** the deviation is only 0.07 Å towards the nitrogen imido donor, while in the oxo complexes the Re atom is pushed upwards by 0.26 Å towards the oxo atom.

As can be seen in Table 5, where the Re–N bond distances and Re–N–aryl angles for arylimido rhenium(v) octahedral complexes are given in the order of increasing Re–N bond length, complex **3** has the longest Re–N multiple bond distance [1.780(7) Å], associated with the smallest Re–N–aryl angle [137.1(5)°], and this suggests that the bond order is considerably less than three.

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