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THE SYNTHESIS AND CHARACTERIZATION OF ORGANOIMIDO- Re(V) COMPLEXES. THE X-RAY CRYSTAL STRUCTURES OF [ReCl(NC₆H₄Me-4) (OMe)('BuNC)₂(PPh₃)][BPh₄] AND [ReCl₂(NC₆H₄Me-4)(PPh₃) $\{4-ClC_6H_4(O)CNNCHPh-O,N\}$]

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Abstract—Reaction of $[ReCl_3(NAr)(PPh_3)_2]$ (NAr = NC₆H₄Me-4, NC₆H₃Me₂-2,6) with excess *tertiary*-butyl isocyanide, ('BuNC), in methanol yielded the red–brown Re(V) arylimido- complexes, $[ReCl(NAr)(OMe)('BuNC)_2(PPh_3)][BPh_4]$ where NAr = NC₆H₄Me-4, (1) or NAr = NC₆H₃Me-2,6, (2). The X-ray crystal structure of (1) revealed a distorted octahedral configuration about the central rhenium atom. The isocyanide ligands are disposed in a *cis* configuration and the chloride and phosphine ligands *trans*. The remaining sites are occupied by the tolylimido- and methoxide ligands. The Re—N(1) bond length of 1.739(3) Å and Re—N(1)—C(11) angle of 164.8(3) are consistent with the imido- ligand functioning as a linear four-electron donor (assuming the imido-ligand to be neutral).

The reaction between the tolylimido- Re(V) complex, $[\text{ReCl}_3(\text{NC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2]$, and aroylhydrazones, Ar(O)CNHNCRR'(Ar = Ph, R = R¹ = Me; Ar = 4-ClC₆H₄, R = H, R¹ = Ph), in a 1:1 toluene/ethanol mixture under reflux yielded the green Re(V) complexes $[\text{ReCl}_2(\text{NC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)\{\text{Ar}(\text{O})\text{CNNCRR'-O},\text{N}\}]$, where Ar = Ph, R = R' = Me (3) or Ar = 4-ClC₆H₄, R = H, R' = Ph (4). Complex (3) can also be synthesized from the reaction of $[\text{ReCl}_3(\text{NC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2]$ and the hydrazone generated *in situ* from benzoic hydrazide in a 1:1 toluene/acetone mixture. The X-ray crystal structure of (4) showed a distorted octahedral geometry with the oxygen and nitrogen atoms of the chelated hydrazone (1-) ligand being mutually *cis*. The nitrogen atom of the tolylimido- ligand is *trans* to the chelated oxygen and the phosphorus atom of the triphenylphosphine ligand is *trans* to the chelated nitrogen. The remaining sites are filled by the two chloride ligands. The Re—N(3) bond length of 1.706(5) Å and Re—N(3)—C(11) angle of 175.7(5)° are consistent with the imido- ligand functioning as a linear four-electron donor.

The organoimido core, M==N-R, could prove to be of great synthetic utility in radiopharmacology, since a variety of organic substituents can be incorporated into a stable rhenium or technetium–nitrogen core. This allows the chemical "fine-tuning" of the biological properties of the complex by vari-

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ation of the imido- core's organic substituent -R, which can be done independently of the other ligands on the metal. The R group can be varied widely and derivatives with R=alkyl,¹ aryl,² COPh² or SPh³ are known.

Several preparative routes to imido- complexes have been reported. These include the reactions of oxo- complexes with isocyanates $ArNCO^4$, phosphinimines $RN=PPh_3^2$ (R=alkyl or amyl), aryl-

azopyridines $YC_6H_4-N=NC_5H_4N$ (Y = H, 3-Me, RNH_{2} ,⁵ 4-Me. 4-Cl). amines silvlamines $RN(SiMe_3)_2$,⁶ hydrazines RNHNHR⁷ or RNHNHCOPh.⁸ Alternative routes include the alkylation (or arylation) of nitrido- complexes,9 thermolysis of alkyliminoalkyl metal complexes.¹⁰ addition to nitriles,¹¹ addition of organic azides,¹² or the homolytic cleavage and addition of azo compounds.¹³ The synthesis of imido- complexes directly from perrhenate is an essential step for any complexes to have viability as radiopharmaceuticals, as [ReO₄]⁻ (as 186 or 188 isotopes) is the sole precursor available from commercial generators. The use of 1-acyl-2-arylhydrazines for the preparation of imides from perrhenate in protic media will be discussed in a forthcoming paper.¹⁴

The first Re arylimido- complexes [ReCl₃(NAr) $(PPh_3)_2$ (Ar = aryl group) were reported by Chatt and Rowe in 1962, using aniline as the source of the imido- ligand.¹⁵ Syntheses of the analogous alkylimidocomplexes were subsequently reported.¹⁶ Since then there have been several papers dealing with the substitution chemistry of these complexes to give derivatives such as [PPh₄] $[Re(NPh)(SC_6H_2Pr_3^{i}-2,4,6)_4]^{17}$ or $[Re(NC_6H_4Me 4)(OEt)(S_2CNEt_2)_2].^{18}$ $[Re(NC_6H_4Me-4)(OEt)]$ $(S_2CNEt_2)_2$ is of interest as in contrast to the majority of structurally characterised mono-imidocomplexes the Re—N—C angle is $155.5(5)^{\circ}$. This suggests a reduction in the formal number of electrons donated to the metal and a metal-nitrogen lower bond order. When the Re—N—C bond angle is close to 180° the imido- ligand is regarded as donating four electrons.†

The coordinated imido- ligand can adopt a variety of geometries as shown in Fig. 1. The terminal linear geometry is most frequently observed in structurally characterized organoimido- complexes. There are a few known examples of complexes containing the bent imido- ligand, including [Mo(NPh)₂ (S₂CNEt₂)₂] where on M—N—C angle is 139°, a rare example of a complex where the M—N—C angle approaches the ideal terminal bent geometry of 120°.¹⁹

The aroylhydrazone ligand (Ar(O)CNHN-CRR') has two different modes of coordination. The neutral keto form, Fig. 2(a), is known to occur in complexes containing the first row transition metals, Mn, Co, Ni, Zn, Cu, and second row metal, Cd.²⁰ The uninegative enol form, Fig. 2(b), is observed especially in rhenium complexes of the type $[ReCl_2O(PPh_3){Ph(O)CNNCMe_2-O,N}]^{21}$ and $[ReCl(N)(PPh_3)_2{Ph(O)CNNCMe_2-O,N}]^{22}$

This paper follows on from previous work²³ on the coordination chemistry of the imido- core with a variety of coligands.

EXPERIMENTAL

All manipulations were carried out under an inert atmosphere of dry dinitrogen unless stated otherwise. Standard Schlenk-tube and vacuum line techniques were employed throughout where appropriate. Elemental analyses were performed by Medac Ltd., University of Brunel. IR spectra were measured in the range 200–4000 cm⁻¹ as nujol mulls (KBr plates) on a Perkin-Elmer 1600 Series FTIR spectrophotometer. ¹H and ³¹P $\{^{1}H\}$ NMR were recorded using a Jeol EX270 MHz instrument. Fast atom bombardment mass spectra were obtained from the University College of Swansea, using 3nitrobenzyl alcohol (3-NOBA) as the matrix material. The electrochemical measurements were recorded in dichloromethane solution at a platinum wire working electrode and silver wire pseudo reference electrode with 0.2M [Bu₄"N][BF₄] as the supporting electrolyte. Potentials are quoted relative to the ferrocene/ferricinium couple, which was taken as 0.0V. All other materials and reagents were obtained commercially (Aldrich, Fisons) and used without further purification. [ReCl₃(NC₆H₄Me- $4)(PPh_3)_2$] was prepared using the published procedure.30

Preparation of the complexes

Synthesis of [ReCl(NC₆H₄Me-4)(OMe)(^tBu $NC_{2}(PPh_{3})[BPh_{4}](1).$ $[ReCl_3(NC_6H_4Me-4)]$ (PPh₃)₂] (0.30 g, 0.33 mmol) and tertiary-butyl isocyanide (0.30 cm³, 2.65 mmol) were heated under reflux in methanol (20 cm³) for 90 min. A clear deep red-brown solution formed which was allowed to cool to room temperature. Addition of NaBPh₄(0.11 g, 0.33 mmol) resulted in the immediate precipitation of a red-brown solid which was recovered by filtration. washed with methanol and dried in vacuo. Yield 0.25 g, 69%. Recrystallization from CH₂Cl₂/MeOH afforded red-brown plates. Found : C, 65.4; H, 5.8; N, 3.8. C₆₀H₆₃N₃BClOPRe requires C, 65.2; H, 5.7; N, 3.8%, IR (KBr) $v(C \equiv N)$ 2210s, 2180s, v(Re = N) 1100s, v(Re = O)910s, v(CH), 824m, 750m and 700m cm⁻¹. ¹H NMR (CDCl₃) 2.3 (s, 3H, Me-4), 3.7 (s, 3H, OMe), 1.2 (s, 9H, 'BuNC), 1.5 (s, 9H, 'BuNC), 6.8 (d, 2H, H), 6.9 (d, 2H, H), 7.0-7.6 (m, 35H, aromatic) ppm; ${}^{31}P{}^{1}H$ NMR (CDCl₃) 6.0 ppm (s, PPh₃).

Synthesis of [ReCl(NC₆H₃Me₂-2,6)(OMe)(^tBu

⁺ Here the RN imido- ligand is taken to be neutral. If a dianionic charge is assumed then the formal number of electrons donated is 6.





Fig. 2. Coordination geometries of the arylhydrazonoligand.

 $NC(PPh_3)$ [BPh₄] (2). [ReCl₃(NC₆H₃Me₂-2,6) (PPh₃)₂] (0.20 g, 0.21 mmol) and tertiary-butyl isocyanide (0.19 cm³, 1.71 mmol) were heated under reflux in methanol (20 cm³) for 90 min. A clear deep red-brown solution formed which was allowed to cool to room temperature. Addition of NaBPh₄ (0.07 g, 0.21 mmol) resulted in the immediate precipitation of a red-brown solid which was recovered by filtration, washed with methanol and dried in vacuo. Yield 0.16 g, 76%. Recrystallization from CH₂Cl₂/MeOH afforded red-brown plates. Found : C, 61.9; H, 5.5; N, 3.5. C₆₂H₆₇N₃BCl₃ OPRe requires C, 61.8; H, 5.6; N, 3.5%, IR (KBr) $v(C \equiv N)$ 2160s, 2120s, v(Re = N)1093s, v(Re = O)910s, v(CH) 780m, 750m and 700m cm⁻¹. ¹H NMR (CDCl₃) 2.1 (s, 6H, Me-2,3), 3.7 (s, 3H, OMe), 1.3 (s, 9H, 'BuNC), 1.6 (s, 9H, 'BuNC), 6.8-7.6 (m, 38H, aromatic), 5.7 (s, 2H, CH_2Cl_2) ppm; ${}^{31}P{}^{1}H{}$ NMR (CDCl₃) 5.8 ppm (s, PPh₃).

Synthesis of $[ReCl_2(NC_6H_4Me-4)(PPh_3){Ph(O)}$ $CNNCMe_2-O,N$] (3). [ReCl₃(NC₆H₄Me-4)(PPh₃)₂] (0.20 g, 0.22 mmol) and PhCONHNH₂ (0.14 g, 1.00 mmol) were heated under reflux in a 1:1 mixture of toluene/acetone (20 cm^3) for 20 min. The clear green solution was cooled and the solvent

removed under vacuum to yield a dark green oil. Addition of ethanol (10 cm³) resulted in the precipitation of a turquoise solid which was recovered by filtration, washed with diethylether and dried *in* vacuo. Yield 0.12 g, 71%. Recrystallization from CH₂Cl₂/EtOH afforded turquoise prisms. Found : C, 52.3 ; H, 4.2 ; N, 5.2. C₃₅H₃₃N₃Cl₂OPRe requires C, 52.6 ; H, 4.1 ; N, 5.3%, IR (KBr) v(C=N) 1613s, 1545s, v(Re=N) 1094m, v(C-H) 823m 786s, and 700s cm⁻¹. ¹H NMR (CDCl₃) 2.1 (s, 3H, Me), 2.3 (s, 3H, Me), 2.8 (s, 3H, Me), 6.8 (d, 2H, H-2,6), 7.0 (d, 2H, H-3,5), 7.1–7.7 (m, 20H, aromatic) ppm ; ³¹P{¹H} NMR (CDcl₃) – 3.6 ppm (s, PPh₃).

Synthesis of $[ReCl_2(NC_6H_4Me-4)(PPh_3) \{C_6H_4-4-$ Cl(O)CNNCHPh-O,N] (4). [ReCl₃(NC₆H₄Me-4) $(PPh_3)_2$] (0.20 g, 0.22 mmol) and 4-ClC₆H₄ CONHNCHPh (0.27 g, 1.04 mmol) were heated under reflux for 20 min in a 1:1 mixture of toluene/ethanol (20 cm³). The solvent was removed under vacuum to yield a green oil, addition of ethanol (10 cm³) yielded a green solid which was recovered by filtration, washed with diethylether and dried in vacuo. Yield 0.13 g, 67%. Recrystallization from CH₂Cl₂/EtOH afforded green plates. Found : C, 52.6; H, 3.6; N, 4.6. C₃₉H₃₂N₃Cl₃OPRe requires C, 53.1; H, 3.6; N, 4.8%, IR (KBr) v(C=N) 1605s, 1532s, v(Re=N) 1094m, v(C-H) 845s, 822m, 757s, 739s, and 693s cm⁻¹. ¹H NMR (CDCl₃) 2.2 (s, 3H, Me), 6.5–8.1 (m, 28H, aromatic) ppm; ${}^{31}P{}^{1}H{}$ NMR (CDCl₃) 0.9 ppm (s, PPh₃).

X-ray crystallography

Data collection. Intensity data were collected on a Enraf-Nonius CAD4 diffractometer with graphite monochromated M_0 - K_{α} radiation ($\lambda = 0.17073$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the ranges $16 < \theta < 19^{\circ}$ (1) and 20 < $\theta < 25^{\circ}$ (4). The data were collected in the ω -2 θ scan mode and three standard reflections were measured every 2 h for (1), and every hour for (4) of exposure. Loss of intensity was observed, 11.9% for (1) and 5.9% for (4), which was linearly corrected during processing. Three standard reflections were measured for every 200 reflections to check crystal orientation. The data were corrected for Lorentz and polarization factors and absorbtion corrections were applied using ψ -scans of nine reflections. Because of initial uncertainty over the space group for (4) data were collected over a 3/4 sphere (k = -17 to 17, h = 0 to 13; l = -20 to 20 andh = -13 to -1, l = 0 to 20). After the structure had been determined and refined isotropically it became apparent that the space group was P-1 (#2); the Friedel pairs were then averaged.

Structure analysis and refinement. The structures were solved by the Patterson heavy atom method. Remaining non hydrogen atoms were located in succeeding cycles of Fourier difference syntheses and least squares refinement.³¹ Full-matrix leastsquares refinement on F converged with; (1) R = 0.020, R' = 0.036, max (shift/error) = 0.09and S = 1.20 and (4) R = 0.049, R' = 0.056, max(shift/error) = 0.01 and S = 1.74. Hydrogen atoms were added in calculated positions with B(eq) = 1.3 times B(eq) of the attached atom : they were included in structure factor calculations but were not refined. Neutral atom scattering factors were used.³² In (4) the 6 peaks in the final difference Fourier were approximately 1 Å from the rhenium atom, the first four forming a square around the rhenium atom. The remainder of the final difference map was featureless. The experimental details of the data collections and structure solutions are summarized in Table 1.

Complete listings of the hydrogen atom coordinates, thermal parameters, complete bond lengths and angles and calculated and observed factors have been deposited as supplementary material with the editor from whom copies are available upon request.

RESULTS AND DISCUSSION

Preparation and properties of the imido- complexes $[ReCl(NC_6H_4Me-4)(OMe)(^{1}BuNC)_2(PPh_3)][BPh_4]$ (1), $[ReCl(NC_6H_3Me_2-2,6)(OMe)(^{1}BuNC)_2$ (PPh_3)][BPh_4] (2), $[ReCl_2(NC_6H_4Me-4)(PPh_3)\{Ph$ (O)CNNCMe_2-O,N) (3) and $[ReCl_2NC_6H_4Me-4)$ (PPh_3) $\{4-ClC_6H_4(O)CNNCHPh-O,N\}$ (4)

The rhenium (V) precursor [ReCl₃(NAr)(PPh₃)] reacts readily with an excess of 'BuNC to yield the red-brown air stable complexes [ReCl(NAr) $(OMe)(^{BuNC})_{2}(PPh_{3})][BPh_{4}], where NAr = NC_{6}$ H_4Me-4 , (1) or $NC_6H_3Me-2,6$, (2). Complexes (1) and (2) represents rare examples of organoimido- transition metal complexes featuring the isocyanide ligand. Both complexes display two strong bands in the IR region 2110-2220 cm⁻¹, which are attributable to $v(C \equiv N)$ of the terminally bound isocyanide ligands. In complex (2) both bands are lower relative to complex (1) by approximately 50-60 cm⁻¹ consistent with slight reduction in the $C \equiv N$ bond orders for complex (2). The coordinated methoxide in (1) and (2) is observed in the IR with a band at 910 cm⁻¹, and the absorptions due to C-H deformations of the aryl groups for the corresponding arylimido-ligands are at 824 and 780 cm^{-1} . The ¹H NMR spectra of (1) and (2) each show 2 singlets, in the range 1.2–1.6 ppm, due to the

	(1)	(4)	
Crystal data			
Formula	C ₆₀ H ₆₃ N ₃ BClOPRe	$C_{39}H_{32}N_3Cl_3OPRe$	
Formula weight	1105.6	882.2	
Crystal size (mm)	$0.60 \times 0.10 \times 0.08$	$0.42 \times 0.33 \times 0.11$	
Crystal shape	Needle	Plate	
Crystal system	Triclinic	Trielinic	
Space group	P-1	P-1	
a (Å)	11.098 (9)	10.028 (2)	
b (Å)	14.881 (1)	11.622 (3)	
c (Å)	17.521 (2)	15.744 (4)	
α (°)	106.63 (1)	99.04 (2)	
β (°)	94.77 (1)	95.72 (2)	
γ (°)	84.86(1)	92.25 (2)	
$U(Å^3)$	2756.4 (8)	1800.3 (8)	
Ζ	2	2	
$D_0 ({\rm gcm}^{-3})$	1.33	1.63	
Temperature (K)	291	292	
Data collection			
Radiation type	Mo-K.	Mo- <i>K</i> ~	
Reflections collected	15151	8297	
Unique data	9637	6319	
Observed reflections	8485	5052	
h. k. l ranges	0-13	-7-11	
,,	-17-17	-13-13	
	-20-20	-18-18	
θ range for data collection (°)	1 5-25	1.5-25	
Scan mode	w-28	w-20	
E	1128	872	
R	0.036	0.032	
$\mu (M_0 - K) (mm^{-1})$	2 35	3 72	
Absorption correction factors $t = -t$	0.94-1.00	0.62-1.00	
Data refinement	0.94 1.00	0.02 1.00	
Data rejinentent D	0.036	0.049	
wP	0.030	0.056	
$W \mathbf{N}_2$ Lungast difference peak and halp (a $\mathbf{\hat{\lambda}}^{-3}$)	1.54 0.00	2.07 0.15	
Largest unterence peak and note (e A ⁻)	1.54, -0.09	5.07, -0.15	

Table 1. Crystallographic data for $[ReCl(NC_6H_4Me-4)(OMe)(BuNC)_2(PPh_3)][BPh_4]$ (1) and $[ReCl_2(NC_6H_4Me-4)(PPh_3)]\{4-ClC_6H_4(O)CNNCHPh-O,N\}]$ (4)

Data were collected on a Enraf-Nonius CAD4 diffractometer and the criterion for the reflections used was $F_o \ge 3.0\sigma$ (F_o).

Weighting scheme used for both structures was $w = 1/[\sigma^2 F_0) + (0.02F_0)^2]$.

inequivalent 'BuNC ligands. The arylimido- methyl proton resonances have chemical shift values of 2.3 and 2.1 ppm, for (1) and (2), respectively. The methyl protons from the coordinated methoxide ligand are present as a singlet at 3.7 ppm. A complicated aromatic region due to the aromatic protons is observed for complex (2). In contrast the aromatic region for complex (1) shows a non first-order AB splitting pattern for the tolylimido- protons at 6.8 and 6.9 ppm. The ³¹P{¹H} NMR spectra of both complexes show the expected singlets due to the lone coordinated phosphine ligands, at 6.0 ppm for complex (1) and 5.8 ppm for complex (2).

The turquoise Re(V) complex [ReCl₂(NC₆H₄Me-4)(PPh₃){Ph(O)CNNCMe₂-O,N}] (**3**) is prepared in high yield from the reaction of [ReCl₃ (NC₆H₄Me-4)(PPh₃)₂] with the hydrazone PhCONHNCMe₂ in toluene/ethanol. This complex can also be prepared by the reaction of [ReCl₃ (NC₆H₄Me-4)(PPh₃)₂] and the hydrazone generated *in situ* from the reaction of benzoic hydrazide in a 1:1 toulene/acetone mixture. Complex (**3**) is formally isoelectronic with the oxo species [ReCl₂O(PPh₃){Ph(O)CNNCMe₂-O,N}].²¹ Dilworth *et al.*²² have shown that if the pre-synthesised hydrazone reacts with the oxo- precursor $[ReOCl_3(PPh_3)_2]$, cleavage occurs to yield the nitrido species [ReCl(N)(PPh₃)₂{Ph(O)CNNMe₂-O,N]. This is in contrast to the reaction of the analogous arylimido- precursor [ReCl₃(NC₆H₄Me- $4)(PPh_3)_2$ and $4-ClC_6H_4CONHNCHPh$ which yields the hydrazone- complex [ReCl₂(NC₆H₄Me-4)(PPh₃){4-ClC₆H₄(O)CNNCHPh-O,N}] (4) where the ligand remains intact, which indicates the importance of Re=O for N-N bond cleavage. The presence of the enol form of the chelated hydrazone ligands in (3) and (4) is indicated by the absence of v(C=0) or v(N-H). Two sharp bands appear in the region $1530-1600 \text{ cm}^{-1}$ which are both assigned as v(C=N). Bands due to the arvl group of the phenylimido- ligand are located at 820 cm⁻¹. The ¹H NMR spectra of (3) and (4) reveal the singlets for the tolylimido-methyl protons at ~ 2.0 ppm. Both methyl groups of the hydrazone of (3) are magnetically inequivalent as shown by the two singlets at 2.3 and 2.8 ppm, consistent with restricted rotation about the C=N bond. The difference in chemical shift may be due to the shielding effect of the electrons around the rhenium; one methyl is directed towards the metal while the other is point-

Table 2. Selected bond lengths (Å) and angles (°) for $[ReCl(NC_6H_4Me-4)(OMe)(^BuNC)_2(PPh_3)][BPh_4]$ (1)

Bond length	
Re —N(1)	1.739(3)
Re-C(1)	2.115(4)
Re-C(2)	2.047(3)
Re—O	1.901(3)
Re-Cl	2.4165(9)
Re—P	2.4917(9)
N(1) - C(11)	1.393(5)
N(2)—C(3)	1.474(5)
N(3)—C(7)	1.455(6)
0C	1.374(6)
Bond angle	
Re-N(1)-C(11)	164.8(3)
Re-C(1)-N(3)	170.6(3)
Re-C(2)-N(2)	172.1(3)
O - Re - N(1)	171.2(1)
P - Re - C(1)	178.1(1)
Cl-Re-C(2)	171.0(1)
C(1)—Re— $C(2)$	84.6(1)
N(1)—Re— $C(1)$	88.8(1)
N(1)—Re— $C(2)$	87.2(1)
P-Re-N(1)	92.9(1)
Cl-Re-N(1)	101.0(1)
Re-O-C	143.9(3)
C(1) - N(3) - C(7)	177.4(4)
C(2) - N(2) - C(3)	171.3(4)
O-Re-C(2)	84.3(1)

ing away. The aromatic region shows the characteristic non first-order AB splitting pattern for the tolylimido- protons of (3) at 6.8 and 7.0 ppm. The respective ${}^{31}P{}^{1}H$ NMR chemical shift values are -3.6 and 0.9 ppm for the lone coordinated phosphine ligands of (3) and (4).

Our initial strategy was to synthesize low molecular weight derivatives for development as radiopharmaceutical imaging/therapeutic agents. Surprisingly the reaction of [Re(NC₆H₄Me-4) $Cl_3(PPh_3)_2$] with excess *t*-BuNC resulted in the substitution of only one phosphine ligand to yield $[ReCl(NC_6H_4Me-4)(OMe)(^{t}BuNC)_2 (PPh_3)]$ [BPh₄]. Use of the more sterically encumbered $[ReCl_3(NC_6H_3Me-2,6)(PPh_3)_2]$ yielded the analogous complex [ReCl(NO₆H₃Me-2,6)(OMe)(¹Bu $NC_{2}(PPh_{3})$ [BPh₄]. The sterically hindered analogue [ReCl₃(NC₆H₃Pr¹2,6)(PPh₃)₂] resulted in no reaction. The use of toluene in place of methanol as the reaction solvent resulted in the formation of a monoisonitrile complex [ReCl₃(NC₆H₄Me-4) ('BuNC)(PPh₃)] which is directly analogous to the cyclohexylisonitrile complex prepared by Cenini et al.²⁴ This suggests that in methanol the bis-isonitrile complex can be isolated due to the substitution of a relatively more labile methoxide ligand in an intermediate complex.

Description of the X-ray crystal structures of $[ReCl(NC_6H_4Me-4)(OMe)(BuNC)_2(PPh_3)][BPh_4]$ (1) and $[ReCl_2(NC_6H_4Me-4)(PPh_3)\{4-ClC_6H_4(O)CNNCHPh-O,N\}]$ (4)

A perspective view of the complex cation in (1) is shown in Fig. 3 and selected bond lengths and angles appear in Table 2. Details of the crystal data, data collections and structure solutions for both complexes are summarized in Table 1. The overall geometry about the Re is distorted octahedral, with the principal distortions coming from Cl—Re—C(2) and N(1)—Re—OMe bond angles, which are lowered from the ideal 180 to $171.0(1)^{\circ}$ and $171.2(1)^\circ$, respectively. Bond angles for the ligands cis to the Re-N multiple bond show that both isocyanides are bent slightly towards the multiple bond with N(1)-Re-Cisocyanide angles of less than 90°, and the phosphines are bent slightly away with a corresponding N(1)-Re-P angle of $92.9(1)^{\circ}$. The remaining chloride ligand is, however, significantly bent away with an N(1)-Re--Cl angle of 101.0(1). Other distortions are reflected in the deviations of angles involving O - Re - N(1)171.2(1) and O—Re—C(2) $84.3(1)^{\circ}$ from ideal values of 180 and 90°, respectively. The isocyanide ligands are disposed in a *cis* configuration with one trans to chloride and the other trans to phosphine.



Fig. 3. Perspective view of the $[\text{ReCl}(\text{NO}_6\text{H}_4\text{Me-4})(\text{OMe})(^{1}\text{BuNC})_2(\text{PPh}_3)]^+$ cation (1) showing the atom labelling scheme.

Completing the remaining *trans* sites are the tolylimido- and methoxide ligands, which are bent towards each other in a pseudo-mirror plane that relates the PPh₃, Cl and 'BuNC ligands.

An Re-N(1) bond length of 1.739(3) Å is consistent with multiple bonding between metal and imido nitrogen,²⁵ although the Re-N(1)-C(11) angle remains somewhat less than 180° at $164.8(3)^{\circ}$. The Re–O bond distance of 1.901(3) Å for the coordinated methoxide ligand and suggests that there is considerable multiple bonding between the metal and alkoxide which is similar to that reported for $[Re(OC_2H_5)(NC_6H_4Me-4)(S_2CNEt_2)_2]^{26}$ Both these values are in keeping with a bond order of 1.5 which infers that the methoxide is functioning as a 2 electron donor (neutral sense). In consequence the expected bond order of 3 for the Re-N moiety is reduced to 2.5 consistent with the imido ligand functioning as a 3-electron donor which results in a formal 18 electron count for the complex. The mutually cis isocyanides function as terminal linear 2-electron donors as evidenced by the Re-C(1)and Re—C(2) distances and near linear C(1)-N(3)-C(7) and C(2)-N(2)-C(3) angles.

The C(1)—N(3) and C(2)—N(2) bond lengths attest to the presence of C—N triple bonds.²⁷

A representation of the structure of complex (4) is shown in Fig. 4, together with an atom labelling scheme. Selected bond angles and lengths in Table 3. Again the geometry is best described as distorted octahedral with the principal distortions arising from the small bite angle of the chelate ligand 74.3(2) and the bending of the equatorial hydrazono- N(1) away from the high electron density in the imido- multiple bond, N(1)—Re—N(3)101.4(3). The trans chloride ligands also show a deviation from 180° at 165.54(9) which is also due to this bending away from the imido- ligand. The oxygen and nitrogen atoms of the chelated hydrazono (1-) ligand are mutually *cis*. The nitrogen atom of the tolylimido- ligand is trans to the chelated oxygen and the triphenylphosphine phosphorus atom is trans to the chelated nitrogen. The Re-N(3) distance of 1.706(5) Å and Re—N(3)—C(11) angle of $175.7(5)^\circ$ are in accordance with the tolylimido- ligand functioning as a terminal linear four-electron donor.^{25,28}

The geometry of the chelate ligand was found to



Fig. 4. Perspective view of $[ReCl_2(NC_6H_4Me-4)(PPh_3){4-ClC_6H_4(O)CNNCHPh-O,N}]$ (4) showing the atom labelling scheme.

be similar to that found in the isoelectronic oxo- complex [ReCl₂O(PPh₃){Ph(O)CNNCMe₂-O,N].²⁹ The bond lengths for the chelate ring indicate that the major contributor to the overall structure is the enol form, however, the C-O bond length shows a small amount of multiple bond character which indicates the keto form makes a minor contribution to the structure. The effect on the hydrazone- Re-O bond length of different trans ligands is negligible (2.031(5) Å in (4) and 2.013(7) Å in $[ReCl_2O(PPh_3){Ph(O)CNNCMe_2}$ -O,N]). The Re-N(1) and Re-O bond lengths are near to the values for single bonds which indicates little delocalization around the central rhenium atom. The only difference between the structure of (4) and [ReCl₂O(PPh₃) {Ph(O)CNN CMe_2-O,N] is that in the latter complex the chloride ligands are disposed in a cis configuration, but this difference in geometry has no effect on the bond distances within the chelate ligand. Complex (4) shows a slightly shorter Re— N_{imido} bond length than complex (1) [1.706(5) versus 1.739(3) Å] which is probably due to the greater trans effect of the methoxide compared to the hydrazone-oxygen. An interesting feature of the structure is that the imido-phenyl group C(11)-C(16) is nearly stacked with the benzylidene ring of the chelate ligand C(21)—C(22), the dihedral angle between the planes of the phenyl rings being 10.11.

Electrochemistry of complexes (1) *and* (2)

The cyclic voltammetry data for complexes (1) and (2) are summarized in Table 4 and the cyclic voltammograms are shown in Fig. 5. Both complexes (1) and (2) display an irreversible oxidation process at +0.56V due to oxidation of the [BPh₄]⁻ counterion. A peak at an identical potential is observed in the CV of sodium tetraphenylborate under the same conditions. On the negative potential sweep, reversible and irreversible one electron processes are exhibited for complexes (1) and (2), the former indicating the comparative stability of the neutral rhenium (IV) species, [ReCl(NAr) $(OMe)(BuNC)_2(PPh_3)$ [where $NAr = NC_6H_4$ Me-4 (1) or $NC_6H_3Me_2-2,6$ (2)] in solution and the latter the instability of the rhenium(III) [ReCl(NAr)(OMe)(¹BuNC)₂(PPh₃)] species in solution. The electrochemical reversibility of the first reduction was confirmed by the $\Delta E_{\rm p}$ value of 90mV, which is close to the value for ferrocene/ferrocenium sample in the same solvent. Convolution analysis using Condecon[®] software also The synthesis and characterization of organoimido- Re(V) complexes

for	$[ReCl_{2}(NC_{6}H_{4}Me-4))(PPh_{3})\{4-ClC_{6}H_{4}(O)CNNCH Ph-O,N\}] (4)$			
	Bond length			
	Re-N(1)	2.136(7)		
	Re-N(3)	1.706(5)		
	Re—O	2.031(5)		
	Re—P	2.433(2)		
	Re-Cl(1)	2.408(2)		
	Re-Cl(2)	2.410(2)		
	N(1) - N(2)	1.415(9)		
	C(30)—O	1.32(1)		
	N(1)C(20)	1.31(1)		
	N(2)-C(30)	1.29(1)		
	Bond angle			
	Re-N(3)-C(11)	175.7(5)		
	Re-N(1)-C(20)	133.7(6)		
	N(1)—Re— $N(3)$	101.4(3)		
	P-Re-N(1)	164.2(2)		
	P-Re-N(3)	93.5(2)		
	Cl(1)—Re— $Cl(2)$	165.54(9)		
	O - Re - N(1)	74.3(2)		
	O - Re - N(3)	175.2(3)		
	Cl(1)—Re—O	83.2(2)		
	Cl(2)—Re—O	83.9(2)		
	P-Re-O	90.6(2)		
	N(1) - N(2) - C(30)	109.7(7)		
	N(2) - N(1) - C(20)	111.1(7)		
	Cl(1)— Re — $N(1)$	84.5(2)		
	Cl(1)—Re—N(3)	94.3(2)		
	Cl(1)—Re—P	89.28(7)		
	Cl(2)—Re—N(1)	85.8(2)		
	Cl(2)—Re—P	97.22(8)		

Table 3. Selected bond lengths (Å) and bond angles (°)



Fig. 5. Cyclic voltammograms for $[ReCl(NC_6H_4Me-4) (OMe)({}^{BuNC})_2(PPh_3)][BPh_4]$ (1) and $[ReCl(NC_6H_4Me-2)(OMe)({}^{BuNC})_2(PPh_3)][BPh_4]$ (2). Recorded at room temperature in CH_2Cl_2 at a platinum wire auxiliary electrode and silver wire pseudo-reference electrode.

Table 4. Cyclic voltammetry data for $[ReCl(NC_6H_4Me-4)(OMe)({}^{BuNC})_2 (PPh_3)][BPh_4]$ (2)

Process	$i_{ m pa}/i_{ m pc}$	$E_{ m pa}({ m V})^a$	$E_{\rm pc}({f V})^a$	$\Delta E_{\rm p}(m{ m V})$	$E_{1,2}(\mathbf{V})$
[ReCl(NC ₆ H ₄ M	e-4)(OMe)((BuNC) ₂ (PPl	$[1_3)][BPh_4] (1$.)	
Oxidation		0.56			_
Reduction 1	0.95	-1.25	-1.34	90	-1.29
Reduction 2		-2.01		11-m x	
[ReCl(NC ₆ Me ₂ -2	2,6)(OMe)('BuNC)2(PPh	n ₃)][BPh ₄] (2	.)	
Oxidation		0.55			
Reduction 1	0.90	-1.24	-1.35	110	-1.29
Reduction 2		-2.05			•

"All potentials are quoted relative to the ferrocenium/ferrocene couple taken as 0.0 volts. Ferrocene was added to cell for each measurement. Scan rate 0.2 Vs⁻¹.

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indicated the reversibility of the first reduction process and that one electron is involved.

CONCLUSIONS

We have demonstrated the synthesis and properties of some new rhenium imido- complexes. [ReCl(NAr)(OMe)(PPh₃)('BuNC)₂][BPh₄] where NAr = NC₆H₄Me-4(1) or NC₆H₃Me₂-2,6 (2) represent a new class of complex containing both the imido- and isonitrile ligand. The arylhydrazono- complexes [ReCl₂(NC₆H₄Me-4)(PPh₃){Ar(O) CNNCRR'-O,N}], where Ar = Ph; R' = Me (3) or C₆H₄Cl-4; R = H, R' = Ph (4) represent a new class of complex containing the rhenium imidocore with chelating hydrazone- ligands. Further studies of the substitution chemistry of representative complexes of these types will be reported at a later date.

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