# Selective Substitution of an Imido Ligand in Alkyl- and Arylimido Rhenium(VII) Complexes; Crystal Structures of (2,6-Dimethylphenyl)ammonium Trichlorobis(2,6-dimethylphenylimido)methylrhenate(VII) and Bis(2,6-dimethylphenylimido)methylbis(neopentyl)rhenium(VII) †‡

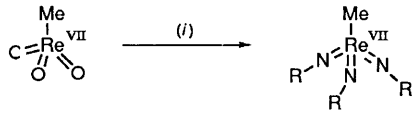
**Malcolm R. Cook, Wolfgang A. Herrmann,* Paul Kiprof and Janos Takacs**
*Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching bei München, Germany*

Reaction of $ReMeO_3$ and 2,6-dimethylphenyl isocyanate gives the imido complex $[ReMe(NR)_3]$ (R = 2,6-$Me_2C_6H_3$). Complexes of the type $[ReMe(NR)_3]$ or $[ReMe(NBu^t)_3]$ undergo selective substitution of only one imido ligand to form bis(imido) derivatives. Thus, $[ReMe(NBu^t)_3]$ reacts with the weak acid catechol *via* protonation of one imido ligand to form a stable five-co-ordinate complex $[ReMe(NBu^t)_2(O_2C_6H_4)]$. In contrast, $[ReMe(NR)_3]$ forms a complex which can only be isolated in a pure state by the addition of pyridine (py) to give the six-co-ordinate $[ReMe(NR)_2(O_2C_6H_4)(py)]$. The complex $[ReMe(NR)_3]$ also reacts with thiophenol to give five-co-ordinate $[ReMe(NR)_2(SPh)_2]$. Reaction of $[ReMe(NR)_3]$ with HCl gives the ionic complex $[NH_3R][ReMeCl_3(NR)_2]$. The crystal structure of this complex was determined by X-ray crystallography. The neutral dihalide complexes $[ReMe(NR)_2X_2(py)]$ (X = Cl or Br) are prepared from $[ReMe(NR)_3]$ by the addition of 2 equivalents of pyridinium halide. Alkylation of the dichloro or dibromo derivative with neopentylmagnesium chloride gives the novel mixed-alkyl complex $[ReMe(CH_2Bu^t)_2(NR)_2]$ as a mixture of two isomers, the structure of one of which was determined by X-ray crystallography.

Over the past few years we have developed synthetic and structural aspects, as well as catalytic applications, of high-oxidation-state rhenium compounds.[2] As part of our on-going studies into this chemistry we are interested in high-oxidation-state rhenium imido complexes.

Recently we reported on the synthesis of alkyltris(imido)-rhenium complexes, $[ReR(NR')_3]$, by two routes.[3] The first route involved alkylation of the tris(imido) compound, $[Re(NBu^t)_3(OSiMe_3)]$,[4] by organolithium or Grignard reagents (methyl, ethyl, σ-allyl, or σ-phenylacetylide). This method had previously been used to prepare other complexes of the general formula $[ReR(NBu^t)_3]$ (R = $CH_2Bu^t$,[5] *o*-tolyl, xylyl, or mesityl[6]). The second route we used was the deoxygenation of the readily accessible rhenium oxo complex $ReMeO_3$ **1**[7] with 2,6-diisopropylphenyl isocyanate. This route utilises the reaction between a metal oxide and an isocyanate which has been well documented for the preparation of other organoimido complexes.[8] This allowed the preparation of complexes containing an arylimido group. Previous methods of synthesis were prepared by deoxygenation of $[ReO_3(OSiMe_3)]$[9] by aryl isocyanates then alkylation of the trimethylsiloxotris-(arylimido) complexes using neopentyllithium, neopentylmagnesium chloride, or bis(neopentyl)zinc. This led to complexes of the general formula $[Re(CH_2Bu^t)(NR)_3]$ (R = 2,6-dimethyl-, 2,6-diisopropyl-, or 2,6-dichloro-phenyl[10]).

As part of our work on tris(imido) complexes we are particularly interested in those of general formula $[ReMe(NR)_3]$ because they allow a direct comparison of their chemistry with that of $ReMeO_3$ **1**. We have previously shown that the deoxygenation of $ReMeO_3$ **1** with 2,6-diisopropylphenyl isocyanate gives the tris(imido) complex $[ReMe(NR)_3]$ (R = 2,6-diisopropylphenyl).[3] By analogy, we have prepared the sterically less hindered complex $[ReMe(NR)_3]$ **2a** (R = 2,6-dimethylphenyl) and studied its reactivity.



**1** **2a**

**Scheme 1** R = 2,6-$Me_2C_6H_3$. (*i*) RNCO, toluene, 110 °C

## Results and Discussion

*Imido Complexes* $[ReMe(NR)_3]$.—The tris(imido) complex **2a** was prepared by complete deoxygenation of $ReMeO_3$ **1** according to Scheme 1. It is available in 94% isolated yield as a red, moisture-sensitive solid which is soluble in all common organic solvents. The IR spectrum has ν(C–H) bands centred at 3060 and 2973 $cm^{-1}$, and bands typical of aromatic δ(C–H) at 763 and 725 $cm^{-1}$. Additionally, a strong band appears at 1313 $cm^{-1}$ which may be attributable to the ν(M–N) stretching mode. However, Nugent and Mayer[8c] warn of the uncertainty in assigning the ν(M–N) band in the IR spectra of many imido complexes. Definitive IR studies of imido complexes in which the bands due to M=NR can be positively assigned have involved the preparation of $^{15}N$ complexes and comparison of their spectra with the $^{14}N$ complexes.[11] In general, these imido complexes show a band in the region 1310–1360 $cm^{-1}$ which moves *ca.* 20–30 $cm^{-1}$ to lower frequency upon $^{15}N$ substitution. However, it is not clear whether this band is due to a

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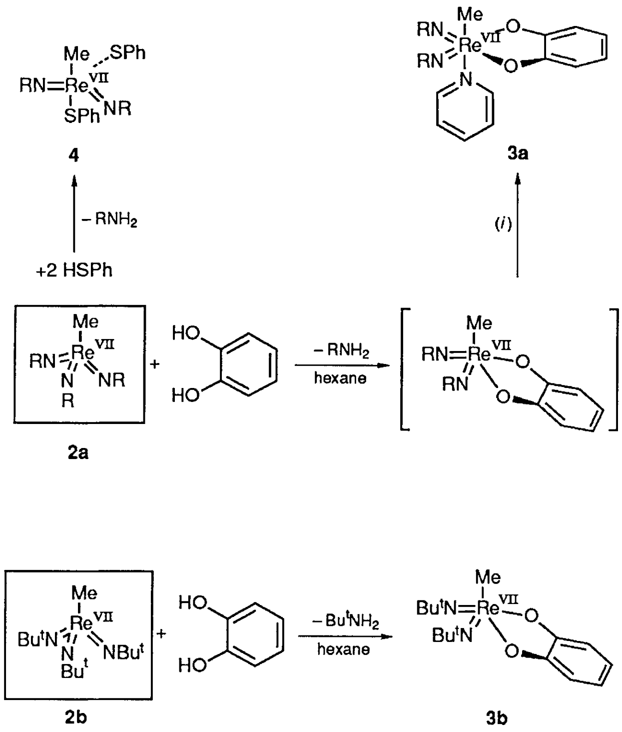
† To be regarded as Part 88[1] of the series Multiple Bonds between Main Group Elements and Transition Metals.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



**Scheme 2** R = 2,6-$Me_2C_6H_3$. (*i*) Pyridine

M–N or C–N stretching mode or some combination of the two. Additionally, this region of the IR spectrum often contains other bands which may be attributable to other functionalities so assignment of the IR spectra of imido complexes must be, at best, tentative. This means that NMR and mass spectroscopy (together with crystallographic studies if available) are generally more useful in the characterisation of imido complexes.

The mass spectrum of complex **2a** shows the molecular ion ($m/z$ = 559, $^{187}$Re) and the fragmentation pattern shows the loss of one methyl ($m/z$ = 544) and of an aryl group from an imido ligand ($m/z$ = 455). The $^1$H NMR spectrum shows singlets at δ 2.29 and 2.56 (ratio 18:3) which can be assigned to the six methyl groups of the three imido ligands and the methyl ligand at the rhenium, respectively. The aromatic protons of the imido ligands give rise to a doublet at δ 7.05 and a triplet δ 6.90 (ratio 6:3). The simplicity of the $^1$H NMR and mass spectra suggest that the complex is monomeric and because of the equivalence of the three imido groups in solution it is probable that it has a tetrahedral arrangement of the ligands around the rhenium.

Additionally, [ReMe($NBu^t$)$_3$] **2b** was prepared according to the literature method[3] to allow a comparison of its reactivity to that of **2a**.

In accordance with the 18-electron rule, only two of the three imido nitrogen atoms in complexes **2a** and **2b** can simultaneously donate their lone pair to rhenium. This implies that the nitrogen atoms should retain some of their nucleophilic character. This is consistent with their pronounced sensitivity to hydrolysis.

*Catecholato*-O,O′ *Complexes*.—In order to utilise the observation that complexes **2a** and **2b** are sensitive to hydrolysis, we studied their reactions with various proton sources. Complex **2a** reacts with catechol with the loss of one imido ligand as its corresponding free amine to give a catecholato complex which cannot be isolated in a pure state unless pyridine is added to form the six-co-ordinate complex **3a** according to Scheme 2.

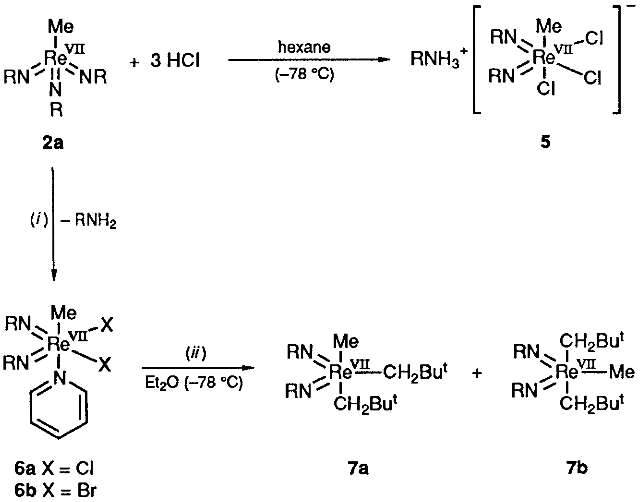
The $^1$H NMR spectrum shows singlets at δ 2.15 and 2.40 (ratio 3:12) due to the methyl ligand and the methyl groups of two equivalent imido ligands respectively. The signals for the catechol ligand appear as two multiplets centred at δ 6.63 and 6.80 whose pattern corresponds to that for a 1,2-disubstituted aromatic ring. The aromatic protons of the imido groups give a triplet and a doublet (ratio 2:3) at δ 7.04 and 7.10, respectively. The co-ordinated pyridine ligand (py) gives the expected pattern of two triplets and a doublet (ratio 2:1:2) at δ 7.28, 7.73, and 8.45, respectively. The mass spectrum of this complex shows the molecular peak ($m/z$ = 627) and a peak corresponding to loss of pyridine ($m/z$ = 548). The catecholato complex **3a** corresponds directly to the product prepared by reaction of **1** and catechol which cannot be isolated in a pure state but requires the presence of pyridine to give [$ReMeO_2(O_2C_6H_4)$(py)] whose structure was determined by X-ray crystallography.[12] As is the case for this complex, the data for **3a** suggest that it is monomeric with an octahedral arrangement of the ligands around the rhenium. From the $^1$H NMR spectrum the imido ligands are equivalent and they are probably mutually *cis* to minimise competition as π ligands. As is the case in the oxo complex, the catecholato ligand may occupy the other two positions in the equatorial plane with the methyl ligand and the pyridine ligand occupying the axial positions. The absence of further signals in the $^1$H NMR spectrum (particularly for the methyl ligand) suggests that only one isomer is formed during this reaction.

In contrast to **3a**, no stabilising donor ligand is required for the isolation of the catecholato complex **3b** obtained from [ReMe($NBu^t$)$_3$] **2b** and catechol according to Scheme 2. The $^1$H NMR spectrum of **3b** shows only one type of signal at δ 1.48 for two equivalent $NBu^t$ ligands. The signal for the methyl ligand appears at δ 1.86. The signals for the catecholato ligand appear as two distinct multiplets (δ 6.61 and 6.74) typical for a 1,2-disubstituted aromatic ring. The mass spectrum shows the molecular peak ($m/z$ = 452) and peaks due to loss of the methyl ligand ($m/z$ = 437) and for the loss of one and two $Bu^t$ groups from the imido ligands ($m/z$ = 396 and 338, respectively). These data suggest that **3b** is monomeric with two equivalent imido ligands but the absolute structural geometry cannot be ascertained in the absence of a crystallographic study.

*Thiophenolato Complexes*.—Complex **2a** reacts with thiophenol to give the bis(thiolato) complex **4** according to Scheme 2. No suitable single crystals of **4** could be obtained for an X-ray structural determination so the structure of this complex remains unresolved. However, the $^1$H NMR spectrum shows a complex set of signals (δ 6.69–7.60) indicating more than one type of thiolato ligand. Within this region the aromatic protons from the two imido ligands are clearly defined at δ 6.99(d) and 7.17(t) (ratio 4:2). At higher field there are only two singlets at δ 2.11 and 2.26 (ratio 3:12) assignable to the methyl ligand attached to the rhenium and the methyl groups of the imido ligands, respectively. This is consistent with the presence of two inequivalent thiolato ligands and two equivalent imido ligands. The mass spectrum of **4** shows only the molecular ion ($m/z$ = 658). These results agree with a trigonal-bipyramidal structure with one thiolato ligand and the methyl ligands occupying the axial positions. A trigonal-bipyramidal structure has been previously determined by X-ray crystallography for several five-co-ordinate rhenium(VII) imido complexes[13] (see also the structure of **7b** below).

*Halide Complexes*.—Treatment of **2a** with hydrogen chloride in diethyl ether results in the immediate precipitation of the dark purple complex **5** even when only 2 equivalents of HCl are used. This product is obtained almost quantitatively by the addition of 3 equivalents of HCl to a hexane solution of **2a** at −78 °C (Scheme 3). It is soluble in $CH_2Cl_2$, but insoluble in ether, hexane, or pentane. Single crystals of **5**, suitable for X-ray diffraction, were obtained by slow diffusion from a $CH_2Cl_2$–hexane mixture.

The crystal structure of complex **5** shows a distorted octahedral arrangement of the ligands around the rhenium in the anion (Figs. 1 and 2). The two imido ligands are



Scheme 3 R = 2,6-$Me_2C_6H_3$. (*i*) $2[C_5H_5NH]X$; (*ii*) $2Mg(CH_2Bu^t)Cl$

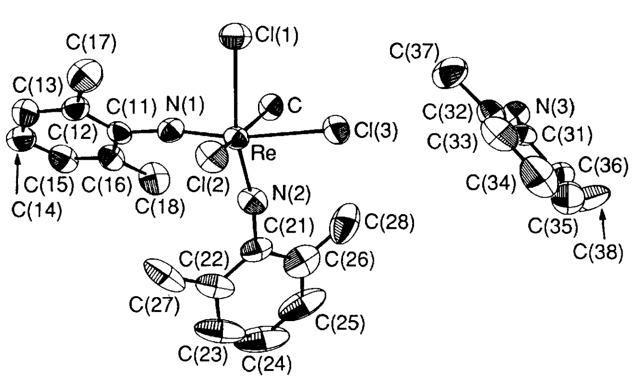


**Fig. 1** The molecular structure of $[NH_3(C_6H_3Me_2\text{-}2,6)][ReCl_3Me(NC_6H_3Me_2\text{-}2,6)_2]$ **5** (hydrogen atoms not shown)

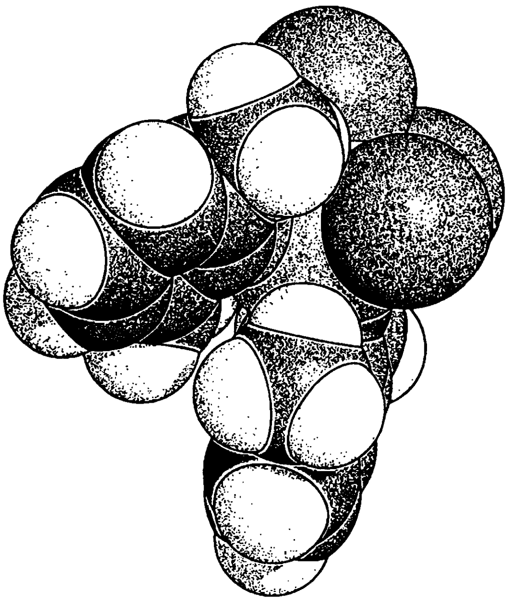


**Fig. 2** Space-filled diagram of the molecular structure of complex **5**

*cis* to each other as is expected for a $d^0$ system containing two multiply bonded ligands. They have bond angles of 170.5(5) [Re–N(1)–C(11)] and 169.2(5)° [Re–N(2)–C(21)] (Table 1). The Re–N bond lengths are 1.723(4) Å [Re–N(1)] and 1.724(5) Å [Re–N(2)] respectively and the values agree well with those in similar rhenium imido complexes containing *cis* imido ligands.[8,14] The imido ligands in the anion of **5** can formally be either 2π- or 4π-electron donors (bond order 2 or 3, respectively). If the imido ligand acts as a four (2π)-electron donor this means that rhenium has access to 16 electrons. Conversely, if both imido ligands act as formal six (4π)-electron donors rhenium can obtain 20 electrons. Clearly for the rhenium to obtain an 18-electron system only one of the imido ligands is required to act as a formal six (4π)-electron donor, but in reality an average bond order of 2.5 is observed which results in similar Re–N–C bond angles and Re–N bond lengths. This averaging is a common process in complexes having access to more than 18 electrons. In fact, there are only a few known examples of complexes having two dissimilar imido ligands with the classic example being $[Mo(NPh)_2(S_2CNEt)_2]$ which has Mo–N–C bond angles of 139.4(4) and 169.4(6)°, and Mo–N bond lengths of 1.789(4) and 1.754(4) Å, corresponding formally to a double and a triple bond.[15] The bond angle of 104.0(2)° for N(1)–Re–N(2) is greater than that for an idealised octahedron, whereas the angle of 80.48(6)° for Cl(1)–Re–Cl(3) is smaller. This effect is probably due to a combination of steric and electronic repulsion of the multiply bonded ligands and has been noted in the past for similar systems.[8]

**Table 1** Selected bond distances (Å) and angles (°) of complex **5** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Re–Cl(1) | 2.549(2) | Re–N(1) | 1.723(4) |
| Re–Cl(2) | 2.447(1) | N(1)–C(11) | 1.396(6) |
| Re–Cl(3) | 2.541(1) | N(2)–C(21) | 1.373(7) |
| Re–C | 2.169(5) | N(3)–C(31) | 1.474(6) |
| Re–N(2) | 1.724(5) | | |
| Cl(1)–Re–Cl(2) | 84.67(5) | Cl(3)–Re–N(1) | 168.3(2) |
| Cl(1)–Re–Cl(3) | 80.48(6) | Cl(3)–Re–N(2) | 87.8(2) |
| Cl(1)–Re–N(1) | 87.8(2) | Cl(3)–Re–C | 83.5(2) |
| Cl(1)–Re–N(2) | 167.1(2) | N(1)–Re–N(2) | 104.0(2) |
| Cl(1)–Re–C | 81.9(2) | N(1)–Re–C | 95.1(2) |
| Cl(2)–Re–Cl(3) | 82.75(5) | N(2)–Re–C | 91.5(2) |
| Cl(2)–Re–N(1) | 96.0(1) | Re–N(1)–C(11) | 170.5(5) |
| Cl(2)–Re–N(2) | 99.3(2) | Re–N(2)–C(21) | 169.2(5) |
| Cl(2)–Re–C | 162.2(2) | | |

The two chloro ligands of complex **5** which are *trans* to an imido ligand [Re–Cl(1) and Re–Cl(3)] have similar bond lengths of 2.549(2) and 2.541(1) Å respectively, while the chloro ligand *cis* to both imido ligands [Re–Cl(2)] has a shorter bond length of 2.447(1) Å. This difference (*ca.* 0.1 Å) in the Re–Cl bond lengths may be accounted for by the *trans* influence of the imido ligand. This *trans* influence has been reviewed[16] and discussed several times since.[8] In view of the relatively few structurally characterised rhenium imido complexes with chloro ligands, no direct comparisons of the Re–Cl bond lengths can be made. However, it is of interest that Re–Cl(2) [2.447(1) Å] is slightly longer than the Re–Cl bond lengths found in $[ReCl_3(NBu^t)_2]$[13] (*ca.* 2.35 Å) and $[AsPh_4][ReCl_4(NSH)_2]$[23] (2.38 Å) but both these complexes have special structural considerations. In the former complex the authors were surprised to note no difference in the Re–Cl bond lengths for ligands *cis* or *trans* to the imido groups and in the latter ionic complex the imido ligands are not so straightforward. The Re–C bond length of 2.169(5) Å is in the normal range found in other octahedral methylrhenium(VII) complexes.[12]

The spectral data for complex **5** are consistent with the structure obtained from the X-ray crystallographic study. The IR spectrum shows the bands expected for such a complex. There is a broad band with fine structure in the region 3100–2700 $cm^{-1}$. This may be attributable to the ν(N–H) for the ammonium cation with the fine structure due to the ν(C–H) vibrations of the aliphatic and aromatic protons. The bands in the region 767–780 $cm^{-1}$ are characteristic of those for aromatic δ(C–H) vibrations. The $^1$H NMR spectrum shows a broad signal at δ 9.93 for the protons of the ammonium ion, and a complex set of signals for the aromatic protons at δ 7.11–7.19 (intensity 9) due to the two different groups in the molecule. The high-field region shows a signal at δ 2.35 (intensity 3) for the methyl ligand attached to the rhenium, one at 2.40 (intensity 12) due to the methyl groups of the two equivalent imido ligands, and a signal at 2.60 (intensity 6) for the methyl groups of the ammonium ion. The mass spectrum shows a peak corresponding to the anion ($m/z$ = 545); the signals in this region agree with the calculated isotope pattern for $C_{17}H_{21}Cl_3N_2Re$. Additionally, fragments corresponding to the loss of one and two chlorides ($m/z$ = 510 and 475, respectively) are observed.

The formation of the ionic complex **5** is in contrast to the behaviour of $[Re(CH_2Bu^t)(NR)_3]$ which gives the neutral dichloro complex $[RE(CH_2Bu^t)Cl_2(NR)_2]$ upon treatment with 3 equivalents of HCl.[5] The difference in these two results may be accounted for on steric grounds: the methyl ligand is sterically much less demanding than the neopentyl ligand so the ionic, six-co-ordinate complex is more stable than a neutral, five-co-ordinate complex. This reasoning is supported by the reaction of **5** with $AgBF_4$ to give a pentane-soluble, unstable product which forms a stable adduct **6a** with pyridine. The latter can also be prepared directly from **5** by heating briefly in tetrahydrofuran (thf)–pyridine. A higher-yielding alternative route to **6a** is the reaction of 2 equivalents of pyridinium chloride with **2a** as shown in Scheme 3. In this manner the neutral, six-co-ordinate complex **6a** is obtained in 94% yield. Similarly, the dibromo analogue, **6b**, is prepared in 91% yield using pyridinium bromide. These complexes are soluble in $CH_2Cl_2$, slightly soluble in ether, and insoluble in hexane or pentane.

The IR spectra of the dichloro complex **6a** and the dibromo complex **6b** show essentially the same bands with only slight changes in positions. Similarly, the $^1$H NMR spectra of **6a** and **6b** show the same pattern of signals with only slight variations in the chemical shift. The spectra show signals for co-ordinated pyridine: δ 7.47, 7.92 and 9.11 (ratio 2:1:2) for **6a** and δ 7.62, 8.11 and 9.06 (intensity 2:1:2) for **6b**. The aromatic region of **6a** shows the expected doublet and doublet of doublets at δ 7.05 and 7.12 (intensity 4:2) for the aromatic protons of two equivalent imido groups. By contrast the aromatic region of the spectrum of **6b** is not so well resolved and shows a multiplet at δ 7.13. Both complexes show only two signals in the high-field region of the spectrum, δ 2.23 and 2.37 (intensity 3:12) for **6a** and δ 2.37 and 2.43 (intensity 12:3) for **6b**. It is interesting that the signal for the methyl attached to the rhenium is shifted only 0.2 ppm downfield on going from dichloro to dibromo substitution. The mass spectrum of **6a** shows a peak for the molecular ion ($m/z$ = 589) while that of **6b** shows the loss of pyridine from the molecular ion ($m/z$ = 598) as the base peak and peaks due to the loss of a methyl and a bromide ($m/z$ = 583 and 519 respectively). These results indicate that both complexes have the same basic core geometry around the rhenium and probably have a structure similar to **5** with the halide ligand that is *trans* to the methyl ligand in **5** being replaced by a pyridine in **6a** and **6b**.

*Mixed-alkyl Complexes.*—Alkylation of the dichloro or dibromo complex, **6a** or **6b**, with neopentylmagnesium chloride gives a mixture of isomeric bis(neopentyl) complexes **7a** and **7b** according to Scheme 3. (It is noteworthy that **6a** or **6b** does not react cleanly with neopentyllithium which may be due to reduction of the rhenium centre.)

Recrystallisation of the mixture of isomers obtained from the reaction of **6a** with neopentylmagnesium chloride from pentane at −78 °C gave single crystals of complex **7b** suitable for an X-ray diffraction study. The core geometry of **7b** is best described as trigonal bipyramidal (see Fig. 3). The imido ligands of **7b** are mutually *cis* as is expected in a d$^0$ system containing two multiply bonded ligands and are located in the equatorial plane with the methyl ligand occupying the third position. The two neopentyl ligands are mutually *trans* and occupy the axial positions of the trigonal bipyramid. Electronically, the rhenium centre can achieve 18 electrons if both imido ligands act as 4π electron donors (formal triple bonds). The angle of 175.2(2)° for both Re–N(1)–C(11) and Re–N(2)–C(21) (Table 2) is almost linear and consistent with a structure having a Re≡N bond. The Re–N bond lengths of 1.764(2) [Re–N(1)] and 1.739(3) Å [Re–N(2)] are longer than those found in **5** (*ca.* 1.72 Å) and are in the upper range of known Re–N bond lengths (1.64–1.75 Å) for complexes containing imido ligands.[8,14] This greater than expected Re–N bond length (relative to **5**) may be a result of steric crowding within the molecule. The N(1)–Re–N(2) angle of 130.8(1)° is greater than that of an idealised trigonal bipyramid and is much larger than the N–Re–N angle of 110.5(9) between the *cis* imido ligands in the trigonal-bipyramidal complex $[ReCl_3(NBu^t)_2]$.[13] This may be a result of steric and electronic repulsion of the imido ligands. In particular, steric interactions between the methyl groups, C(18) and C(27), of the imido ligands may also contribute to an increase in the bond angle.

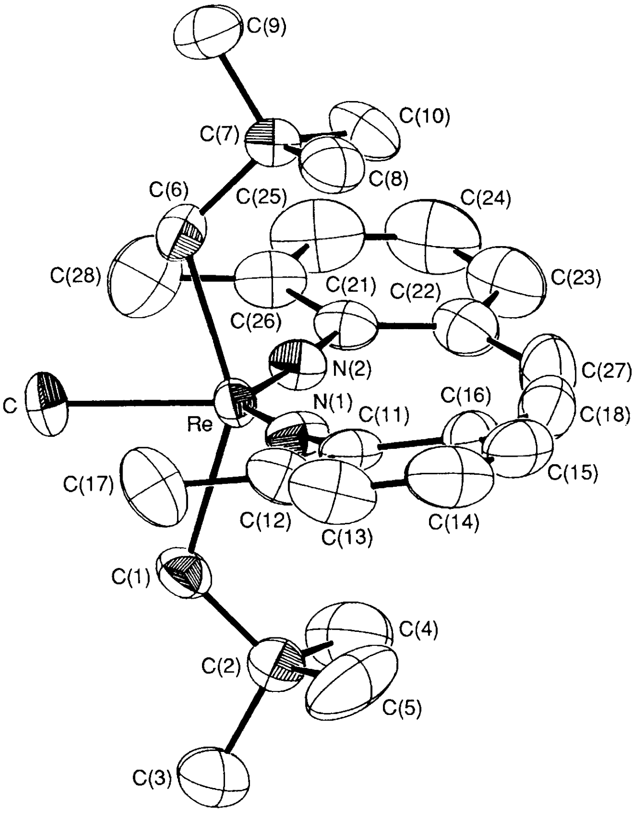


**Fig. 3** The molecular structure of $[ReMe(CH_2Bu^t)_2(NC_6H_3Me_2\text{-}2,6)_2]$ **7b**

**Table 2** Selected bond distances (Å) and angles (°) of complex **7b** with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Re–N(1) | 1.764(2) | Re–C(6) | 2.185(3) |
| Re–N(2) | 1.739(3) | N(1)–C(11) | 1.380(4) |
| Re–C | 2.200(4) | N(2)–C(21) | 1.392(4) |
| Re–C(1) | 2.185(3) | | |
| N(1)–Re–N(2) | 130.8(1) | C–Re–C(1) | 73.6(1) |
| N(1)–Re–C | 114.0(1) | C–Re–C(6) | 74.2(1) |
| N(1)–Re–C(1) | 98.0(1) | C(1)–Re–C(6) | 147.7(1) |
| N(1)–Re–C(6) | 95.6(2) | Re–N(1)–C(11) | 175.2(2) |
| N(2)–Re–C | 115.2(1) | Re–N(2)–C(21) | 175.2(2) |
| N(2)–Re–C(1) | 97.7(1) | Re–C(1)–C(2) | 120.2(3) |
| N(2)–Re–C(6) | 95.2(1) | Re–C(6)–C(7) | 119.9(2) |

The Re–C bond length of 2.200(4) Å for the methyl ligand is slightly longer than that of **5** [2.169(5) Å] and this may be due to a combination of the *trans* influence of the imido ligands and steric effects caused by the methylene protons of the neopentyl ligands.

The ratio of the two isomers, **7a** and **7b**, is dependent upon which dihalide precursor (**6a** or **6b**) is used. If the dichloro complex **6a** is used the formation of **7a** is favoured (**7a**:**7b** is *ca.* 60:40), but if the dibromo complex **6b** is used then formation of **7b** is favoured (**7a**:**7b** is *ca.* 25:75). These ratios are based on $^1$H NMR spectral studies. In both cases the same signals appear in the spectra but the ratios are altered, therefore it is possible clearly to assign the signals in each spectrum to those corresponding to **7a** and those corresponding to **7b**. The $^1$H NMR spectrum of **7b** shows signals at δ 1.00 and 3.32 attributable to Bu$^t$ groups and the methylene protons of two equivalent neopentyl ligands (intensity 18:4). The signal for the methyl ligand comes at δ 1.91 and that for the methyl groups of two equivalent imido ligands at 2.46 (intensity 3:12). (The signals for the aromatic protons of the imido ligands cannot be distinguished from those of **7a**.) The $^1$H NMR spectrum of **7b** shows signals at δ 1.09 and 1.46 (intensity 9:9) attributable to the Bu$^t$ groups of two types of neopentyl ligands. Similarly, the signals at δ 2.85 and 3.42 can be assigned to the methylene groups of two different neopentyl ligands. By comparison with the spectrum of **7a**, the signals at δ 1.09 and 2.85 may be assigned to the neopentyl ligand that occupies the axial position, and the signals at δ 1.46 and 3.42 can be assigned to the neopentyl ligand in the equatorial position. The signal for the methyl ligand comes at δ 2.24 and that for the methyl groups of two equivalent imido ligands at 2.34 (intensity 3:12, respectively). Although the structure of **7b** has been determined crystallographically, the absolute structure of **7a** has not been determined. However, the $^1$H NMR data agree with the proposed trigonal-bipyramidal structure shown in Scheme 3, since a square-based pyramidal structure cannot be drawn in such a manner that both imido ligands are equivalent and both neopentyl ligands are non-equivalent.

The reasons for the difference in the ratio of **7a**:**7b** when the halide of the starting material is changed are not clear. However, since we are dealing with a sterically very hindered system the small difference in size between the chloride and bromide ligands may play a significent part in determining the ratio of **7a**:**7b** in the final product. Attempts to obtain more information about this reaction by preparation of the mononeopentyl derivatives have so far proved unsuccessful, however work is underway to prepare the diiodo analogue of **6a** which should give predominantly **7b** if the size of the halide ligand is in fact significant.

This general reaction sequence (1) promises to be extremely useful and may enable us to prepare and study the reactivity of many high-oxidation-state alkylrhenium imido complexes. Also it will be of interest to see if other Grignard reagents give similar mixtures of isomers on reaction with complex **6a** or **6b** as is the case with neopentyl Grignard.

$$\mathrm{M{=}O} \longrightarrow \mathrm{M{=}NR} \longrightarrow \mathrm{MCl_2} \longrightarrow \mathrm{MR_2} \qquad (1)$$

## Conclusion

Rhenium(VII) aryl- and alkyl-imido complexes of the type [ReMe(NR)$_3$] undergo selective substitution of only one imido ligand upon treatment with protic acids (pyridinium bromide or chloride, HCl, thiols and aromatic diols). Bis(imido) derivatives are thus formed, with their exact composition and stability depending upon the nature of the acid used. *In no case is the methyl–rhenium bond attacked by the acid.* Of particular synthetic use are the dihalide complexes [ReMe(NR)$_2$X$_2$(py)] (X = Cl or Br) as they are precursors to mixed-alkyl derivatives.

We also find that *no reduction of the rhenium* occurs in any of the reactions of these imido complexes with acids. This contrasts with similar reactions of ReMeO$_3$ [12b] which in several cases give reduction to rhenium(V) complexes.

## Experimental

All syntheses and sample manipulations were carried out using standard Schlenk techniques. The solvents were dried by standard methods (pentane, hexane, toluene, ether and thf over sodium–benzophenone; CH$_2$Cl$_2$ over P$_2$O$_5$ then CaH$_2$) and distilled under nitrogen prior to use. Methyltrioxorhenium(VII) [2,22] **1** and methyltris(*tert*-butylimido)rhenium(VII) [3] **2b** were prepared by literature methods. Infrared spectra were recorded on a Nicolet DX 5 FT spectrophotometer, NMR spectra on a JEOL GX 400 MHz FT instrument using the chemical shift of the solvent as the internal standard. Mass spectra were obtained with Finnigan MAT 311 A and MAT 90 spectrometers (data referenced to $^{187}$Re, $^{35}$Cl and $^{79}$Br). Elemental analyses were performed in the Microanalytical Laboratory of this department.

*Tris(2,6-dimethylphenylimido)methylrhenium*(VII) **2a**.—To a stirred solution of ReMeO$_3$ (1.0 g, 4.0 mmol) in toluene (50 cm$^3$) was added 2,6-dimethylphenyl isocyanate (1.88 g, 1.78 cm$^3$, 12.8 mmol) and the mixture was refluxed for 6 h. After cooling to room temperature the red solution was evaporated *in vacuo* and the residue extracted with pentane. The solvent was removed *in vacuo* from the combined extracts to give a red solid. Yield 2.4 g (94%) (Found: C, 53.3; H, 5.5; N, 7.6. C$_{25}$H$_{30}$N$_3$Re requires C, 53.7; H, 5.4; N, 7.6%). IR (KBr): 3060w, 2973w, 1458m, 1347w, 1313s, 1247m, 1095m, 992m, 915w, 763s and 725m cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 2.29 [s, 18 H, 2,6-(C$H_3$)$_2$C$_6$H$_3$], 2.56 (s, 3 H, CH$_3$), 6.90 [t, $^3J$(HH) = 7.5, 3 H, H$^4$ of C$_6$H$_3$Me$_2$] and 7.05 [d, $^3J$(HH) = 7.5 Hz, 6 H, H$^{3,5}$ of C$_6$H$_3$Me$_2$]. Electron-impact (EI) MS: *m/z* 559 ($M^+$, 100), 544 ([$M$ − CH$_3$]$^+$, 10) and 455 ([$M$ − C$_8$H$_8$]$^+$, 30%).

(1,2-*Catecholato*-O,O′)*bis*(2,6-*dimethylphenylimido*)*methyl*(*pyridine*)*rhenium*(VII) **3a**.—To a stirred solution of complex **2a** (300 mg, 0.54 mmol) in pentane (20 cm$^3$) was added catechol (55 mg, 0.50 mmol). After 30 min, pyridine (47.5 mg, 48.5 μl, 0.6 mmol) was added and the mixture stirred for 2 h. Concentration of the solution *in vacuo* and cooling to 0 °C gave a purple, waxy solid which was washed with a little cold pentane and dried *in vacuo* to give a purple, microcrystalline solid. Yield 231 mg (74%) (Found: C, 53.8; H, 4.9; N, 6.8. C$_{28}$H$_{30}$N$_3$O$_2$Re requires C, 53.7; H, 4.8; N, 6.7%). IR (KBr): 3048w, 2970w, 2920m, 2842w, 1621w, 1600w, 1580w, 1469m, 1443s, 1378w, 1312s, 1269s, 1212m, 1163w, 1096w, 1066m, 1033m, 984w, 906w, 810m, 769s, 737s, 696m, 633m, 618m, 532m and 503w cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 2.15 (s, 3 H, CH$_3$), 2.40 [s, 12 H, 2,6-(C$H_3$)$_2$-C$_6$H$_3$], 6.63 (m, 2 H, H$^{4,5}$ of O$_2$C$_6$H$_4$), 6.80 (m, 2 H, H$^{3,6}$ of O$_2$C$_6$H$_4$), 7.04 [t, $^3J$(HH) = 7.4, 2 H, H$^4$ of C$_6$H$_3$Me$_2$], 7.10 [d, $^3J$(HH) = 7.4 Hz, 4 H, H$^{3,5}$ of C$_6$H$_3$Me$_2$], 7.28 (t, 2 H, H$^{3,5}$ of C$_5$H$_5$N), 7.73 (t, 1 H, H$^4$ of C$_5$H$_5$N) and 8.45 (d, 2 H, H$^{2,6}$ of C$_5$H$_5$N). Field desorption (FD) MS: *m/z* 627 ($M^+$, 33) and 548 ([$M^+$ − C$_5$H$_5$N]$^+$, 100%).

(1,2-*Catecholato*-O,O′)*methylbis*(*tert-butylimido*)*rhenium*(VII) **3b**.—To a stirred solution of complex **2b** (298 mg, 0.80 mmol) in hexane (10 cm$^3$) was added catechol (77 mg, 0.70 mmol). The yellow solution turned orange as the catechol reacted and after 15 min the solvent was removed *in vacuo* and the residue extracted with pentane (3 × 10 cm$^3$). The combined extracts were filtered through 0.5 cm of silylated silica gel. Concentration of the filtrate *in vacuo* and cooling to −30 °C gave orange crystals. Yield 241 mg (76%) (Found: C, 39.9; H, 5.7; N, 6.2. C$_{15}$H$_{25}$N$_2$O$_2$Re requires C, 39.9; H, 5.6; N, 6.2%). IR (KBr): 3052w, 2976m, 2925w, 1479s, 1452m, 1361m, 1337m, 1257s, 1204s, 1137m, 1014m, 914w, 814s, 733s, 649s, 621m and

540m cm$^{-1}$. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 1.48 (s, 18 H, $C_4H_9$), 1.86 (s, 3 H, $CH_3$), 6.61 (m, 2 H, $H^{4,5}$ of $O_2C_6H_4$) and 6.74 (m, 2 H, $H^{3,6}$ of $O_2C_6H_4$). EIMS: *m/z* 452 ($M^+$, 38), 437 ($[M - CH_3]^+$, 5), 396 ($[M - C_4H_8]^+$, 20) and 338 ($[M - 2C_4H_9]^+$, 100%).

*Bis*(2,6-*dimethylphenylimido*)*methylbis*(*thiophenolato*)-*rhenium*(VII) **4**.—To a stirred solution of complex **2a** (167 mg, 0.3 mmol) in pentane (10 cm$^3$) was added thiophenol (99 mg, 93 µl, 0.9 mmol). The red solution slowly darkened. After 15 min a red-brown precipitate began to form. The reaction mixture was stirred for 4 h and the solvent removed *in vacuo*. The brown solid was washed with pentane and dried *in vacuo*. Yield 159 mg (80%) (Found: C, 52.5; H, 4.7; N, 4.1. $C_{29}H_{31}N_2ReS_2$ requires C, 52.9; H, 4.75; N, 4.25%). IR (KBr): 3048w, 2976m, 2902w, 1577m, 1468m, 1434m, 1296m, 1248m, 1025m, 781m, 770m, 764m, 744s, 737s, 692s, 685s and 488m cm$^{-1}$. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 2.11 (s, 3 H, $CH_3$), 2.26 [s, 12 H, 2,6-$(CH_3)_2C_6H_3$], 6.69, 6.75, 7.10, 7.27, 7.60 (m, 10 H, $SC_6H_5$), 6.99 [d, $^3J$(HH) = 7.5, 4 H, $H^{3,5}$ of $C_6H_3Me_2$] and 7.17 [t, $^3J$(HH) = 7.5 Hz, 2 H, $H^4$ of $C_6H_3Me_2$]. FDMS ($CH_2Cl_2$): *m/z* 658 ($M^+$, 100%).

(2,6-*Dimethylphenyl*)*ammonium Trichlorobis*(2,6-*dimethylphenylimido*)*methylrhenate*(VII) **5**.—To a stirred solution of complex **2a** (650 mg, 1.16 mmol) in hexane (10 cm$^3$) at −78 °C was added anhydrous HCl (3.49 cm$^3$ of a 1 mol dm$^{-3}$ solution in ether). Immediately a dark purple precipitate began to form. After allowing the mixture to warm to room temperature the precipitate was filtered off, washed well with pentane and dried *in vacuo*. Yield 749 mg (97%) (Found: C, 45.45; H, 5.00; Cl, 15.45; N, 6.10; Re, 28.10. $C_{25}H_{33}Cl_3N_3Re$ requires C, 45.00; H, 5.00; Cl, 15.90; N, 6.30; Re, 27.85%). IR (KBr): 3264w, 2960m, 2920s, 2850w, 1632w, 1580m, 1562m, 1495m, 1475s, 1381w, 1308w, 1247w, 1095m, 1032m, 769s, 727m, 597w, 543w and 493w cm$^{-1}$. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 2.35 (s, 3 H, $CH_3$), 2.40 [s, 12 H, $(CH_3)_2C_6H_3NH_3$], 2.60 [s, 6 H, $(CH_3)_2C_6H_3NH_3$], 7.11–7.19 (m, 9 H, aromatic protons) and 9.93 [br, $(CH_3)_2C_6H_3NH_3$]. FD (negative ion $C_{17}H_{21}Cl_3N_2Re$) MS ($CH_2Cl_2$): *m/z* 545 ($M^-$, 15), 510 ($[M - Cl]^-$, 43) and 475 ($[M - 2Cl]^-$, 100%).

*Dichlorobis*(2,6-*dimethylphenylimido*)*methyl*(*pyridine*)-*rhenium*(VII) **6a**.—To a stirred solution of complex **2a** (465 mg, 0.83 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added pyridinium chloride (180 mg, 1.56 mmol). The mixture was stirred for 1 h at room temperature during which time the colour changed from red to purple. The solvent was concentrated *in vacuo* and hexane added to precipitate a purple, microcrystalline solid. Yield 460 mg (94%) (Found: C, 44.2; H, 4.4; Cl, 12.3; N, 6.9; Re, 31.7. $C_{22}H_{26}Cl_2N_3Re$ requires C, 44.8; H, 4.45; Cl, 12.0; N, 7.1; Re, 31.6%). IR (KBr): 3115w, 3058w, 2953w, 2924m, 1601w, 1581w, 1463m, 1441s, 1375w, 1307s, 1246m, 1206s, 1163w, 1095w, 1070m, 991m, 914m, 785s, 753w, 730w, 694m, 604m and 504w cm$^{-1}$. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 2.23 (s, 3 H, $CH_3$), 2.37 [s, 12 H, $(CH_3)_2C_6H_3$], 7.05 [d, $^3J$(HH) = 7.3, 4 H, $H^{3,5}$ of $C_6H_3Me_2$], 7.12 [dd, $^3J$(HH) = 6.1 Hz, 2 H, $H^4$ of $C_6H_3Me_2$], 7.47 (t, 2 H, $H^{3,5}$ of $C_5H_5N$), 7.92 (t, 1 H, $H^4$ of $C_5H_5N$), and 9.11 (d, 2 H, $H^{2,6}$ of $C_5H_5N$). FDMS ($CH_2Cl_2$): *m/z* 589 ($M^+$, 100%).

*Dibromobis*(2,6-*dimethylphenylimido*)*methyl*(*pyridine*)-*rhenium*(VII) **6b**.—To a stirred solution of complex **2a** (501 mg, 0.90 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added pyridinium bromide (280 mg, 1.75 mmol). The mixture was stirred for 2 h at room temperature during which time it changed from red to purple. The solvent was concentrated *in vacuo* and hexane added to precipitate a purple, microcrystalline solid. Yield 540 mg (91%) (Found: C, 38.7; H, 4.0; N, 6.2. $C_{22}H_{26}Br_2N_3Re$ requires C, 38.9; H, 3.9; N, 6.2%). IR (KBr): 3020w, 2954w, 2922m, 2854w, 1604w, 1580w, 1466m, 1441s, 1378w, 1308s, 1247m, 1210s, 1163w, 1097w, 1070m, 989s, 784s, 756w, 730m, 695m, 605m and 508w cm$^{-1}$. $^{1}$H NMR ($CD_2Cl_2$): $\delta$ 2.37 [s, 12 H, $(CH_3)_2C_6H_3$], 2.43 (s, 3 H, $CH_3$), 7.13 [m, 6 H, $(CH_3)_2C_6H_3$], 7.62 [t, 2 H, $H^{3,5}$ of $C_5H_5N$), 8.11 (t, 1 H, $H^4$ of $C_5H_5N$) and 9.06 (d, 2 H, $H^{2,6}$ of $C_5H_5N$). FDMS ($CH_2Cl_2$): *m/z* 598 ($[M - C_5H_5N]^+$, 100), 583 ($[M - C_5H_5N - CH_3]^+$, 39) and 519 ($[M - C_5H_5N - Br]^+$, 13%).

*Bis*(2,6-*dimethylphenylimido*)*methylbis*(*neopentyl*)*rhenium*-(VII) **7**.—To a stirred solution of complex **6a** (345 mg, 0.59 mmol) in $Et_2O$ (20 cm$^3$) at −78 °C was added neopentylmagnesium chloride (1.06 cm$^3$ of a 1.1 mol dm$^{-3}$ solution in ether, 1.17 mmol). The reaction mixture was allowed to warm slowly to room temperature and then stirred for 2 h. The solvent was removed *in vacuo* and the residue extracted with pentane. The pentane extracts were filtered through silylated silica and the pentane removed *in vacuo* to give an orange solid. Yield 183 mg (53%). Ratio **7a**:**7b** ($^{1}$H NMR spectroscopy) *ca.* 60:40. Similarly, from complex **6b** (210 mg, 0.30 mmol) and neopentylmagnesium chloride (333 µl of a 1.8 mol dm$^{-3}$ solution in ether, 0.6 mmol) was isolated an orange solid. Yield 119 mg (68%). Ratio **7a**:**7b** *ca.* 25:75.

$^{1}$H NMR ($CD_2Cl_2$): **7a**, $\delta$ 1.00 (s, 18 H, $CH_2Bu^t$), 1.91 (s, 3 H, $CH_3$), 2.46 [s, 12 H, $(CH_3)_2C_6H_3$] and 3.32 (s, 4 H, $CH_2Bu^t$); **7b**, 1.09 (s, 9 H, $CH_2Bu^t$), 1.46 (s, 9 H, $CH_2Bu^t$), 2.24 (s, 3 H, $CH_3$), 2.34 [s, 12 H, $(CH_3)_2C_6H_3$], 2.85 (s, 2 H, $CH_2Bu^t$) and 3.42 (s, 2 H, $CH_2Bu^t$); aromatic protons for both isomers $\delta$ 6.76–6.90 (m). FDMS ($CH_2Cl_2$): *m/z* 511 ($[M - C_5H_{11}]^+$, 100%).

*X-Ray Structure Determination of Complex* **5**.—*Crystal data.* $C_{25}H_{33}Cl_3N_3Re$, $M$ 668.1, space group $C2/c$ (no. 15), $a$ = 30.049(3), $b$ = 10.812(<1), $c$ = 16.705(1) Å, $\beta$ = 96.53(<1)°, $U$ = 5392 Å$^3$, $Z$ = 8. $D_c$ = 1.646 g cm$^{-3}$, crystal size 0.17 × 0.15 × 0.13 mm, crystal colour dark purple.

Diffraction data were collected using an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Cu-K$\alpha$ radiation ($2\theta_{max}$ = 130°). The orientation matrix and cell dimensions were obtained from least-squares refinement[17] using a set of 25 reflections, $70.2 \leqslant 2\theta \leqslant 80.8°$. During the data collection only slight decay (5.7%) was observed but not corrected. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction based upon nine reflections was applied ($\mu$ = 114.3 cm$^{-1}$). 4933 Reflections were measured of which 3598 [$I \geqslant 1.0\sigma(I)$] were taken as independent. The rhenium atom position was determined by the heavy-atom method[18] and the remaining atoms located using successive least-squares refinements and Fourier difference syntheses. Refinement minimised the function $\Sigma w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$. Hydrogen atoms were placed in ideal positions (C–H 0.95 Å), and added to the calculations with isotropic displacement parameters, but not refined. Anomalous dispersion corrections were applied to all non-hydrogen atoms.[19] Scattering factors were taken from ref. 20. Refinements converged with unweighted and weighted agreement factors of $R$ = 0.040 and $R'$ = 0.030. Final Fourier difference maps exhibited electron-density maxima and minima of +0.80 and −0.69 e Å$^{-3}$. The calculations were performed on a MicroVAX 3100 computer using the STRUX III[21] and SDP[17] systems. The atomic coordinates are given in Table 3.

*X-Ray Structure Determination of Complex* **7b**.—*Crystal data.* $C_{27}H_{43}N_2Re$, $M$ 577.8, space group $P\bar{1}$ (no. 2), $a$ = 9.378(6), $b$ = 10.668(8), $c$ = 15.255(8) Å, $\alpha$ = 76.61(5), $\beta$ = 80.21(4)°, $\gamma$ = 65.53(5), $U$ = 1346 Å$^3$, $Z$ = 2, $D_c$ = 1.425 g cm$^{-3}$, crystal size 0.50 × 0.50 × 0.25 mm, crystal colour red-brown.

Diffraction data were collected using an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Mo-K$\alpha$ radiation ($2\theta_{max}$ = 50°). The orientation matrix and cell dimensions were obtained from least-squares refinement[17] using a set of 25 reflections, $43.9 \leqslant 2\theta \leqslant 47.9°$. During the data collection no decay was observed. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction based upon nine reflections was applied ($\mu$ = 45.9 cm$^{-1}$). Because of the asymmetric reflection profile and unequal

**Table 3** Fractional atomic coordinates and their e.s.d.s for complex **5**

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Re | 0.369 71(1) | 0.337 63(3) | 0.072 15(2) | C(21) | 0.395 3(2) | 0.132 1(7) | 0.196 8(4) |
| Cl(1) | 0.342 29(6) | 0.524 3(2) | −0.012 7(1) | C(22) | 0.421 8(3) | 0.035 1(7) | 0.173 3(5) |
| Cl(2) | 0.331 37(6) | 0.216 7(2) | −0.038 8(1) | C(23) | 0.439 0(3) | −0.050 8(8) | 0.230 0(6) |
| Cl(3) | 0.291 08(5) | 0.356 3(2) | 0.113 0(1) | C(24) | 0.431 1(3) | −0.041 5(9) | 0.307 5(6) |
| N(1) | 0.419 9(2) | 0.350 4(6) | 0.032 0(3) | C(25) | 0.404 1(3) | 0.055 1(9) | 0.333 1(5) |
| N(2) | 0.379 3(2) | 0.222 1(5) | 0.143 1(3) | C(26) | 0.385 0(2) | 0.139 1(8) | 0.278 7(5) |
| N(3) | 0.246 2(2) | 0.578 9(5) | 0.436 3(3) | C(27) | 0.430 7(3) | 0.024 5(8) | 0.086 0(6) |
| C | 0.385 1(2) | 0.479 4(7) | 0.163 0(4) | C(28) | 0.356 2(3) | 0.242(1) | 0.304 1(5) |
| C(11) | 0.461 7(2) | 0.340 5(7) | 0.003 8(4) | C(31) | 0.222 2(2) | 0.482 6(6) | 0.386 0(4) |
| C(12) | 0.463 7(2) | 0.352 5(7) | −0.080 7(4) | C(32) | 0.224 8(2) | 0.488 0(7) | 0.304 3(4) |
| C(13) | 0.505 7(2) | 0.340 2(8) | −0.107 6(4) | C(33) | 0.200 8(3) | 0.401 8(8) | 0.257 8(5) |
| C(14) | 0.542 8(2) | 0.316 3(8) | −0.054 9(5) | C(34) | 0.176 7(2) | 0.310 9(8) | 0.291 7(5) |
| C(15) | 0.540 2(2) | 0.308 8(7) | 0.026 3(5) | C(35) | 0.177 1(3) | 0.304 8(7) | 0.374 3(5) |
| C(16) | 0.499 7(2) | 0.317 8(7) | 0.057 5(4) | C(36) | 0.200 3(2) | 0.391 9(7) | 0.424 5(5) |
| C(17) | 0.421 4(3) | 0.379 5(8) | −0.137 1(4) | C(37) | 0.252 8(3) | 0.582 5(8) | 0.267 4(5) |
| C(18) | 0.497 6(2) | 0.310 4(8) | 0.146 4(4) | C(38) | 0.201 9(3) | 0.381 8(8) | 0.515 2(5) |

**Table 4** Fractional atomic coordinates and their e.s.d.s for complex **7b**

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Re | 0.088 79(3) | 0.226 96(2) | 0.193 79(1) | C(12) | −0.170 1(7) | 0.600 0(6) | 0.264 8(4) |
| N(1) | −0.050 0(5) | 0.362 5(4) | 0.248 4(3) | C(13) | −0.271 2(8) | 0.703 2(6) | 0.313 8(4) |
| N(2) | 0.139 7(5) | 0.046 9(4) | 0.219 8(3) | C(14) | −0.348 0(8) | 0.667 4(7) | 0.395 6(4) |
| C | 0.226 9(7) | 0.298 1(6) | 0.076 9(4) | C(15) | −0.328 1(7) | 0.529 9(7) | 0.429 4(4) |
| C(1) | −0.037 9(6) | 0.270 0(6) | 0.075 5(3) | C(16) | −0.233 2(6) | 0.424 9(6) | 0.380 8(4) |
| C(2) | −0.195 5(6) | 0.251 1(6) | 0.086 4(4) | C(17) | −0.080 3(8) | 0.635 9(7) | 0.177 9(4) |
| C(3) | −0.258 4(8) | 0.296 5(8) | −0.007 4(5) | C(18) | −0.214 7(7) | 0.274 1(6) | 0.417 4(4) |
| C(4) | −0.173 5(8) | 0.098 5(7) | 0.120 0(6) | C(21) | 0.190 8(6) | −0.097 8(5) | 0.244 2(4) |
| C(5) | −0.315 3(8) | 0.341 0(9) | 0.148 2(5) | C(22) | 0.107 5(7) | −0.161 7(6) | 0.312 9(4) |
| C(6) | 0.293 9(6) | 0.220 6(5) | 0.247 5(4) | C(23) | 0.171 3(8) | −0.308 1(6) | 0.335 0(5) |
| C(7) | 0.312 9(6) | 0.174 6(5) | 0.350 4(4) | C(24) | 0.309 8(9) | −0.384 8(7) | 0.292 5(5) |
| C(8) | 0.194 4(7) | 0.287 0(6) | 0.402 7(4) | C(25) | 0.388 6(8) | −0.322 1(6) | 0.225 7(5) |
| C(9) | 0.478 2(7) | 0.160 7(7) | 0.362 6(4) | C(26) | 0.332 9(7) | −0.178 0(6) | 0.199 7(4) |
| C(10) | 0.297 8(7) | 0.035 0(6) | 0.391 1(4) | C(27) | −0.041 8(8) | −0.076 6(7) | 0.363 0(5) |
| C(11) | −0.153 1(6) | 0.462 0(5) | 0.297 8(3) | C(28) | 0.420 0(8) | −0.110 8(7) | 0.128 0(5) |

background values a background correction was performed. 4928 Reflections were measured of which 4561 [$I > 0.0\sigma(I)$] were taken as independent. The rhenium atom position was determined by the heavy-atom method[18] and the remaining atoms located using successive least-squares refinements and Fourier difference syntheses. Refinement minimised the function $\Sigma w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$. Hydrogen atoms were placed in ideal positions (C–H 0.95 Å), and added to the calculations with isotropic displacement parameters, but not refined. Anomalous dispersion corrections were applied to all non-hydrogen atoms.[19] Scattering factors were taken from ref. 20. Refinements converged with unweighted and weighted agreement factors of $R = 0.037$ and $R' = 0.031$ (without background correction 0.045 and 0.047 respectively). Final Fourier difference maps exhibited electron-density maxima and minima of $+1.77$ and $-1.57$ e Å$^{-3}$ at rhenium. The calculations were performed on a MicroVAX 3100 computer using the STRUX III[21] and SDP[17] systems. The atomic coordinates are given in Table 4.

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

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