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t-BUTYLIMIDO AND *t*-BUTYLIMIDO OXO ARYLS OF RHENIUM. X-RAY CRYSTAL STRUCTURES OF $Re(NBu^t)_2(2,6\text{-}Me_2C_6H_3)_2$, $Re(NBu^t)(2,4,6\text{-}Me_3C_6H_2)(C_{27}H_{32})$, $Re(NBu^t)_3(2,4,6\text{-}Me_3C_6H_2)$, $[(Bu^tN)Br(2,4,6\text{-}Me_3C_6H_2)Re(\mu\text{-}NBu^t)(\mu\text{-}O)Re(OC_6H_2Me_2CH_2)(NBu^t)]$, $[Re(NBu^t)(O)Ar(\mu\text{-}O)]_2$, Ar = 2,6-$C_6H_3$ AND 2,4,6-C_6H_2

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Abstract—The interaction of $Re(NBu^t)_2Cl_3$ with 2,6-xylyl magnesium bromide gives rise to the paramagnetic rhenium(VI) compound, $Re(NBu^t)_2(xyl)_2$, which is readily oxidized to the cation $[Re(NBu^t)_2(xyl)_2]^+$, isolated as its PF_6^- salt; the latter with Bu^tNC gives the iminoacyl cation $[Re(NBu^t)_2(xyl)(Bu^tN{=}Cxyl)]^+$. An unstable rhenium(V) anion, $[Re(NBu^t)_2(xyl)_2]^-$, has been characterized. Interaction of $Re(NBu^t)_2Cl_3$ with excess mesityl Grignard gives a compound of stoichiometry $Re(NBu^t)(mes)(C_{27}H_{32})$ in which three aromatic rings are coupled, the central one comprising a η^5-cyclohexadienyl ring bearing an *exo*-mesityl group in the 1-position and in the 3-position linked by a CH_2 group to an aryl group σ-bonded to the metal, which is formally in the V oxidation state. The compound $Re(NBu^t)_2Cl(o\text{-}tol)_2$ has been synthesized; treatment with $AgPF_6$ produces the salt $[Re(NBu^t)_2(o\text{-}tol)_2]PF_6$. Hydrolysis of $Re(NBu^t)_2ReCl_3$ with LiOH gives $Re(NBu^t)_2Cl(OH)_2$, which on arylation, gives the oxo imido species $Re(NBu^t)_2(O)mes$ and $[(Bu^tN)Br(mes)Re(\mu\text{-}NBu^t)(\mu\text{-}O)Re(OC_6H_2Me_2CH_2)(NBu^t)_2]$. Interaction of excess NO with $Re(NBu^t)_2Ar_2$, Ar = 2,6-xylyl and mesityl, gives the compounds $[Re(NBu^t)(O)(\mu\text{-}O)Ar]_2$; the reaction involves a unique N—N bond formation to give $Bu^tN{=}NAr$. Stoichiometric reactions of $Re(NBu^t)_2(xyl)_2$ and NO lead to the complexes $Re(NBu^t)_2(xyl)_2NO$ and $Re(NBu^t)_2(O)(xyl)$. Mechanisms for the NO reactions are proposed. X-ray structures of the compounds listed in the title have been determined; the compounds $[Re(NBu^t)(O)(\mu\text{-}O)Ar]_2$ have asymmetric oxo bridges.

In previous papers we have described the synthesis and X-ray crystal structures of a number of oxo[1,2] and *t*-butylimido[2,3] aryls of rhenium(V), (VI) and (VII). Extensions of these studies are now reported; Table 1 summarizes present knowledge of the aryl compounds. Table 2 gives analytical and physical data for the new compounds described in this paper.

RESULTS AND DISCUSSION

(1) t-*Butylimido aryls*

(a) 2,6-*Dimethylphenyl compounds*. Although the interaction of $Re(NBu^t)_2Cl_3$ with *o*-tolyl Grignard reagent gives the triaryl,[3] the mesityl Grignard

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Abbreviations used: *o*-tol = 2-MeC_6H_4, xyl = 2,6-$Me_2C_6H_3$, mes = 2,4,6-$Me_3C_6H_2$.

Table 1. *t*-Butylimido, *t*-butylimidoxo and oxo aryls of rhenium[a]

Oxidation state	Compound	X-ray structure
V	$[O_2ReAr_2]_2Mg(THF)_2$; xyl,[b] mes,[c]	
	$(Bu^tN)Re(mes)(\sigma,\eta^5\text{-}C_{27}H_{32})$[d]	[d]
	$(Bu^tN)_2Re(NO)(xyl)_2$[d]	
	$[(Bu^tN)_2Re(xyl)_2]^-$[d]	
VI	$OReAr_4$; mes,[c] *o*-tol,[c] *o*-$MeOC_6H_4$[c]	mes[c]
	$(O)_2ReAr_2$; mes,[c] xyl[b]	mes,[c] xyl[b]
	$Re_2(NBu^t)_2(\mu\text{-}NBu^t)(\mu\text{-}O)Br(mes)(OC_6H_2Me_2CH_2)$[d]	[d]
	$(Bu^tN)_2ReAr_2$; xyl,[d] mes[e]	xyl[d]
VII	O_3ReAr; mes[f,g] and others[g]	mes[g]
	$(Bu^tN)_2(O)ReAr$; xyl,[d] mes[d]	
	$[(Bu^tN)(O)_2ReAr]_2$; xyl,[d] mes[d]	xyl,[d] mes[d]
	$(Bu^tN)_2Re(o\text{-tol})_3$[e]	
	$(Bu^tN)_2ReCl(o\text{-tol})_2$[d]	
	$(Bu^tN)_2ReCl_2Ar$; Ph,[e] *o*-tol,[b] xyl,[b] mes[b]	Ph,[e] *o*-tol[b]
	$[(Bu^tN)_2ReAr_2]^+$; *o*-tol,[d] xyl,[d] mes[e]	
	$\{(Bu^tN)_2ReAr[\eta^2\text{-}RN{=}CAr]\}^+$; xyl,[d] mes[e]	
	$(Bu^tN)_3ReAr$; *o*-tol,[b] xyl,[b] mes[b]	mes[d]

[a] *o*-tol = 2-MeC_6H_4, xyl = 2,6-$Me_2C_6H_3$, mes = 2,4,6-$Me_3C_6H_2$.
[b] Reference 2.
[c] Reference 1.
[d] This paper.
[e] Reference 3.
[f] Reference 11.
[g] W. A. Herrmann *et al.*, *J. Organomet. Chem.* 1989, **371**, C13.

produced the rhenium(VI) compound, $Re(NBu^t)_2(mes)_2$, which was paramagnetic with one unpaired electron and which was readily oxidized to the rhenium(VII) cation $[Re(NBu^t)_2(mes)_2]^+$. The latter gave an iminoacyl cation with Bu^tNC.

The 2,6-dimethylphenyl analogue has now been made in a similar way; it is also oxidized by Ag^+ salts to give the cation $[Re(NBu^t)_2(xyl)_2]^+$ which was isolated as orange PF_6^- or $CF_3SO_3^-$ salts. The ^1H NMR spectrum of the salts in solution shows equivalent *t*-butyl and xylyl groups. This cation, like the mesityl analogue, undergoes insertion with *t*-butylisocyanide to give the iminoacyl cation which was isolated as a white, air-stable PF_6^- salt.

Although a cyclic voltammetry study showed[3] that $Re(NBu^t)_2(mes)_2$ underwent a reversible one-electron reduction, the rhenium(V) anion could not be isolated. Reduction of the xylyl by Na/Hg or Mg in THF gives purple solutions of a very air-sensitive diamagnetic species that is evidently $[Re^V(NBu^t)_2(xyl)_2]^-$. Dark purple, crystalline solids can be isolated from the solution but they are difficult to handle being very readily re-oxidized to the rhenium(VI) precursor. The ^1H NMR spectrum of the anion has signals at 7.24–7.06 (*m*, *p*-$C_6H_3Me_2$), 2.41 (*o*-Me) and 1.49 (Bu^t) ppm that are shifted relative to those in the cation (cf. 7.42–7.21, 2.46, 1.80 ppm); this shift is consistent with the anionic formulation.

The X-ray crystal structure of $Re(NBu^t)_2(xyl)_2$ has been determined and a diagram of the structure is shown in Fig. 1; bond lengths and angles are given in Table 3. The coordination geometry of rhenium is, as expected, very similar to that found for the analogous dioxo complex.[2] The Re—C (xylyl) distances in the imido complex are just slightly larger [*ca* 0.03(1) Å] than those in the oxo complex. The C—Re—C angles are equal within experimental error. The Re=NBu^t distances are *ca* 0.05(1) Å longer than the Re=O distances, consistent with the large covalent radius of N, but the N—Re—N angle at 121.7(6)° is equal, within error, to the O—Re—O angle of 121.3(4)°.

$Re(NBu^t)_2(xyl)_2$ in solution at 295 K has an electron paramagnetic resonance spectrum similar to that for the mesityl analogue;[3] there is again

Table 2. Analytical[a] and physical data for rhenium compounds

Compound	Colour	Melting point (°C)	Analysis (%)[b] C	H	N
$Re(NBu^t)_2(xyl)_2$	Red	117	54.1 (53.4)	6.7 (6.7)	5.2 (5.1)
$[Re(NBu^t)_2(xyl)_2]PF_6$	Orange	161	40.4 (42.1)	5.2 (5.3)	4.2 (4.1)
$Re(NBu^t)_2(xyl)(Bu^tN{=}Cxyl)PF_6$	Colourless	167	43.4 (45.4)	5.7 (5.9)	5.8 (5.5)
$Re(NBu^t)(mes)(C_{27}H_{32})$	Red	205	65.4 (65.6)	7.1 (7.1)	1.8 (1.9)
$Re(NBu^t)_2Cl(o\text{-tol})_2$	Yellow	120	48.1 (48.4)	5.7 (5.8)	5.1 (5.1)
$[Re(NBu^t)_2(o\text{-tol})_2]PF_6$	Yellow	141	40.8 (40.3)	4.6 (4.9)	4.2 (4.3)
$Re(NBu^t)_2Cl(OH)_2$	Yellow	[c]	22.0 (24.1)	5.1 (5.1)	6.8 (7.0)
$Re(NBu^t)_2(O)(mes)$	Yellow	106	45.0 (44.1)	6.1 (6.2)	5.0 (6.0)
$Re_2(NBu^t)_3Br(O)(mes)(CH_2Me_2C_6H_2O)$	Red	d 205	38.6 (38.5)	5.2 (5.2)	4.5 (4.5)
$[Re(NBu^t)(O)_2(xyl)]_2$	Yellow	99	36.2 (36.4)	4.6 (4.6)	3.5 (3.5)
$[Re(NBu^t)(O)_2(mes)]_2$	Orange	97	38.2 (38.1)	5.0 (5.0)	3.4 (3.4)
$Re(NBu^t)_2(xyl)_2NO$	Orange	141	45.8 (50.6)	6.4 (6.3)	7.3 (7.4)
$Re(NBu^t)_2(O)(xyl)$	Dark yellow	144	43.0 (42.6)	6.0 (6.0)	6.2 (6.2)

[a] For mass spectra see Experimental.
[b] Required in parentheses.
[c] Melting point, 134°C, is probably that of $Re(NBu^t)_2Cl(O)$ formed on loss of H_2O.

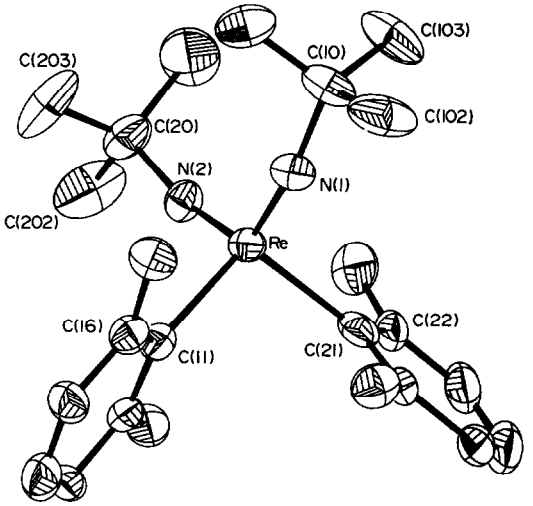
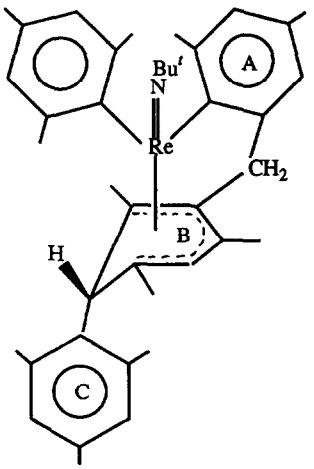


Fig. 1. The structure of $Re(NBu^t)_2(xyl)_2$.

a six-line hyperfine structure with $g_{iso} = 1.934$, $A = 0.0141\ cm^{-1}$. On lowering the temperature the spectrum changes giving a complicated pattern comprising three sets of six rhenium hyperfine lines with uneven spacing. Similar patterns for the mesityl[3] and the related oxo aryls, $Re(O)_2(Ar)_2$,[1,2] were attributed to restriction of rotation of the aryl groups about the Re—C bonds and the same explanation probably holds in the present case.

(b) *The compound* $Re(NBu^t)(mes)(C_{27}H_{32})$. As noted above, interaction of $Re(NBu^t)_3Cl_3$ with mesityl Grignard, in diethyl ether gave $Re(NBu^t)_2(mes)_2$.[3] When this reaction is carried out in THF using a large excess of Grignard reagent (1:5 or more), about 15% of the rhenium can be recovered as a new complex with the structure shown in structure **1** together with $Re(NBu^t)_2(mes)_2$



(1)

and small amounts of bimesityl. The structure was determined by X-ray diffraction and a diagram of the molecule is shown in Fig. 2; selected bond lengths and angles are given in Table 4.

The formulation shown above as **1** was confirmed by experimental location and successful refinement of one hydrogen on each of C(31) and C(33). The bonding of the rhenium atom to the cyclohexadienyl ring is unsymmetrical with the Re—C(31) and Re—C(32) distances of 2.19 and 2.25(1) Å being considerably shorter than Re—C(34), Re—C(35) and Re—C(36) distances, 2.45, 2.44 and 2.39(1) Å, respectively. The shortest C—C distances in the ring are C(34)—C(35) and C(35)—C(36), each at 1.40(1) Å. The five-atom fragment C(31), C(32), C(34), C(35) and C(36) is planar to within 0.05 Å and the envelope fold up to C(33) is 36.7°. The two Re—C(aryl) distances are slightly different with Re—C(21) being the shortest at 2.159(7)°. Interestingly, the Re—C(11) distance, 2.191(8) Å, is very similar to the shortest Re—(dienyl) distance Re—C(31), 2.194(7) Å. The Re≡N distance to the *t*-butylimido ligand lies in the range found for the

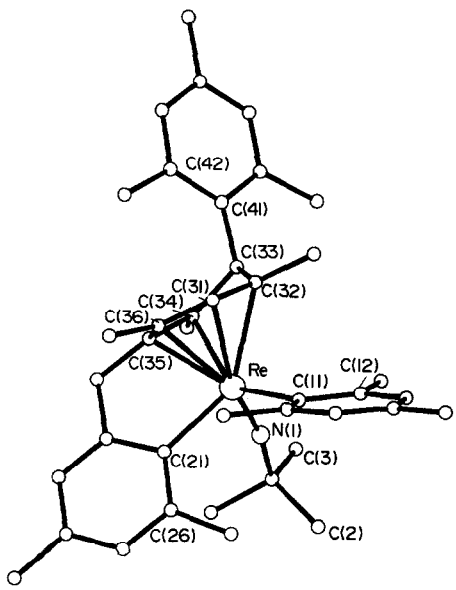


Fig. 2. The structure of the compound Re(Bu^{t}N)(mes) ($C_{27}H_{32}$).

same interaction in other complexes. The compound is diamagnetic having rhenium formally in the V oxidation state. The ^{1}H NMR spectrum shows numerous bands for CH_3, CH_2 and aryl hydrogens and we have not attempted detailed assignment.

The formation of the main product in the reaction, Re(NBu^t)$_2$(mes)$_2$, is presumably an independent reaction involving one-electron reduction by the Grignard of unisolated Re(NBu^t)$_2$(mes)$_2$Cl or of [Re(NBu^t)$_2$(mes)$_2$]$^+$.

The generation of the moiety with rhenium bound to rings **A**, **B** and **C** in structure **1** may be accounted for by the established reactions of cyclometallation[4a] and reductive coupling,[4b,5] followed by nucleophilic attack[4c] by mesitylmagnesium bromide (i.e. by mes$^-$) on a cationic species.

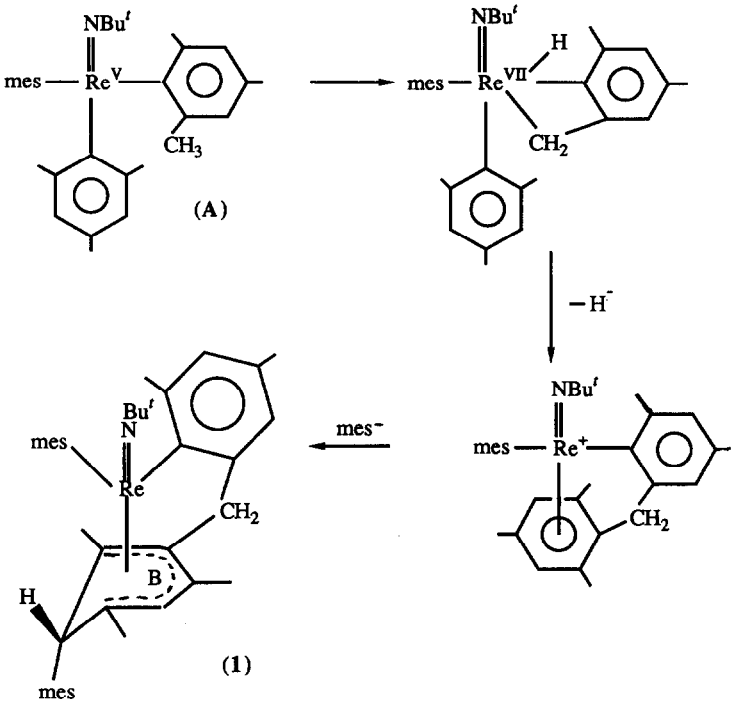
Table 3. Selected bond lengths and bond angles for $C_{24}H_{36}N_2Re$

Bond lengths (Å)			
N(1)—Re(1)	1.737(11)	N(2)—Re(1)	1.738(11)
C(11)—Re(1)	2.105(13)	C(21)—Re(1)	2.096(14)
Bond angles (°)			
N(2)—Re(1)—N(1)	121.7(6)	C(11)—Re(1)—N(1)	110.4(5)
C(11)—Re(1)—N(2)	103.8(5)	C(21)—Re(1)—N(1)	104.8(6)
C(21)—Re(1)—N(2)	112.9(6)	C(21)—Re(1)—C(11)	101.5(5)
C(10)—N(1)—Re(1)	157.7(8)	C(20)—N(2)—Re(1)	160.3(9)
C(12)—C(11)—Re(1)	118.8(10)	C(16)—C(11)—Re(1)	122.4(9)
C(22)—C(21)—Re(1)	123.7(11)	C(26)—C(21)—Re(1)	118.1(10)

Table 4. Selected bond lengths and bond angles for $C_{40}H_{51}NRe$

Bond lengths (Å)			
N(1)—Re(1)	1.715(7)	C(11)—Re(1)	2.191(8)
C(21)—Re(1)	2.159(7)	C(31)—Re(1)	2.194(7)
C(32)—Re(1)	2.253(7)	C(33)—Re(1)	2.864(8)
C(34)—Re(1)	2.451(6)	C(35)—Re(1)	2.443(7)
C(36)—Re(1)	2.389(8)	C(32)—C(31)	1.435(9)
C(36)—C(31)	1.463(10)	C(33)—C(32)	1.530(9)
C(35)—C(34)	1.401(10)	C(36)—C(35)	1.401(9)
C(34)—C(33)	1.503(10)	C(33)—C(41)	1.535(9)
Bond angles (°)			
C(11)—Re(1)—N(1)	100.7(3)	C(21)—Re(1)—N(1)	89.8(3)
C(21)—Re(1)—C(11)	103.1(3)	C(31)—Re(1)—N(1)	119.3(3)
C(31)—Re(1)—C(11)	139.9(2)	C(31)—Re(1)—C(21)	76.6(3)
C(32)—Re(1)—N(1)	99.9(3)	C(32)—Re(1)—C(11)	141.9(2)
C(32)—Re(1)—C(21)	108.7(3)	C(32)—Re(1)—C(31)	37.6(2)
C(33)—Re(1)—N(1)	109.9(3)	C(33)—Re(1)—C(11)	110.2(3)
C(33)—Re(1)—C(21)	136.6(2)	C(33)—Re(1)—C(31)	60.1(3)
C(33)—Re(1)—C(32)	32.0(2)	C(34)—Re(1)—N(1)	130.3(2)
C(34)—Re(1)—C(11)	81.5(3)	C(34)—Re(1)—C(21)	138.7(2)
C(34)—Re(1)—C(31)	74.7(3)	C(34)—Re(1)—C(32)	60.8(3)
C(34)—Re(1)—C(33)	31.6(2)	C(35)—Re(1)—N(1)	163.5(2)
C(35)—Re(1)—C(11)	79.3(3)	C(35)—Re(1)—C(21)	106.4(3)
C(35)—Re(1)—C(31)	63.1(3)	C(35)—Re(1)—C(32)	72.1(3)
C(35)—Re(1)—C(33)	55.8(3)	C(35)—Re(1)—C(34)	33.3(2)
C(36)—Re(1)—N(1)	155.1(2)	C(36)—Re(1)—C(11)	103.2(3)
C(36)—Re(1)—C(21)	78.0(3)	C(36)—Re(1)—C(31)	36.9(2)
C(36)—Re(1)—C(32)	64.7(3)	C(36)—Re(1)—C(33)	68.1(3)
C(36)—Re(1)—C(34)	61.2(3)	C(36)—Re(1)—C(35)	33.7(2)
C(12)—C(11)—Re(1)	117.0(6)	C(16)—C(11)—Re(1)	126.9(5)
C(22)—C(21)—Re(1)	115.7(4)	C(26)—C(21)—Re(1)	128.6(5)
C(33)—C(34)—Re(1)	89.5(4)	C(35)—C(34)—Re(1)	73.1(4)
C(32)—C(31)—Re(1)	73.4(4)	C(36)—C(31)—Re(1)	78.8(4)
C(31)—C(32)—Re(1)	69.0(4)	C(33)—C(32)—Re(1)	96.6(4)
C(41)—C(33)—Re(1)	165.1(4)	C(32)—C(33)—Re(1)	51.4(3)
C(34)—C(33)—Re(1)	58.8(3)	C(34)—C(35)—Re(1)	73.7(4)
C(36)—C(35)—Re(1)	71.0(4)	C(31)—C(36)—Re(1)	64.3(4)
C(35)—C(36)—Re(1)	75.3(4)	C(36)—C(31)—C(32)	118.1(6)
C(33)—C(32)—C(31)	122.3(6)	C(32)—C(33)—C(41)	119.3(6)
C(34)—C(33)—C(41)	120.4(5)	C(34)—C(33)—C(32)	103.8(5)
C(35)—C(34)—C(33)	119.6(6)	C(36)—C(35)—C(34)	123.2(7)
C(35)—C(36)—C(31)	116.4(6)	C(361)—C(36)—Re(1)	135.7(3)
C(221)—C(31)—Re(1)	114.1(4)	C(341)—C(34)—Re(1)	129.8(5)
C(321)—C(32)—Re(1)	119.5(4)		

Thus, assuming an initial rhenium(V) species (**A**), a reasonable sequence for the synthesis of the compound can be envisaged as in Scheme 1. A problem arises in the formation of species **A** from the reaction of $Re(NBu^t)_2Cl_3$ with the Grignard reagent and in the loss of the NBu^t group, as well as in the fate of the hydride ion removed in Scheme 1. In the reaction products we have not been able to identify Bu^tNH_2 or Bu^t(mes)NH, which should arise from attack on the imido group by mes^-. There are precedents for removal of imido groups, e.g. by the attack of H^- on Re≡NPh in reductions of $Re(NPh)Cl_3(PR_3)_2$ by Na in THF.[6a] Interaction of this rhenium compound with excess $Mg(CH_2SiMe_3)_2$ also led to removal of the phenylimido group.[6b] The interaction of $Cr(OR)_2(NBu^t)_2$ with $ZnPh_2$ gave rise to Bu^tNHPh, biphenyl and other products,[7] while another elimination of an NBu^t



Scheme 1. Possible route for linking of mesityl groups with starting compound **A**.

group is that from $Cr(NBu^t)_2(COmes)_2$ to give *t*-butylmesitylamide, probably via acyl transfer to the imido nitrogen atom followed by another hydride transfer, probably from a mesityl group.[8]

(c) *Other aryl compounds.* The interaction of one equivalent of (*o*-tol)MgBr with $Re(NBu^t)_2Cl_3$ gave $Re(NBu^t)_2Cl_2(o\text{-tol})$[2] and three equivalents of $Re(NBu^t)_2(o\text{-tol})_3$.[3] Using two equivalents we obtained $Re(NBu^t)_2Cl(o\text{-tol})_2$ whose NMR spectrum suggests a *tbp* structure with equatorial imido and chlorine ligands (cf. refs 2 and 3). The IR spectrum has a band at 322 cm^{-1} assignable as ν(Re—Cl). The compound reacts with $AgPF_6$ in THF and the salt $[Re(NBu^t)_2(o\text{-tol})_2]PF_6$, which is a 1 : 1 electrolyte in MeCN, can be isolated. The ^1H NMR spectrum of the cation is similar to that of $Mo(NBu^t)_2(xyl)_2$[8] and of the mesityl and xylyl analogues discussed above.

For the molecule $Re(NBu^t)_3mes$, the crystals that could be obtained were not of good quality and this has reduced the precision of the structural determination. A diagram of the molecule is given in Fig. 3, selected bond lengths and angles in Table 5. The geometry is distorted tetrahedral with angles ranging from 95 to 123(1)°. The Re—N—C angles in the imido ligands vary from 142 to

Table 5. Selected bond lengths and bond angles for $C_{21}H_{38}N_3Re$

Bond lengths (Å)			
N(1)—Re(1)	1.738(29)	N(2)—Re(1)	1.657(30)
N(3)—Re(1)	1.769(29)	C(10)—Re(1)	2.097(36)
Bond angles (°)			
N(2)—Re(1)—N(1)	123.1(14)	N(3)—Re(1)—N(1)	109.2(13)
N(3)—Re(1)—N(2)	109.3(14)	C(10)—Re(1)—N(1)	94.8(14)
C(10)—Re(1)—N(2)	113.3(14)	C(10)—Re(1)—N(3)	105.3(14)
C(1)—N(1)—Re(1)	142.4(22)	C(2)—N(2)—Re(1)	161.3(25)
C(3)—N(3)—Re(1)	157.1(27)	C(20)—C(10)—Re(1)	121.7(28)
C(60)—C(10)—Re(1)	126.2(23)		

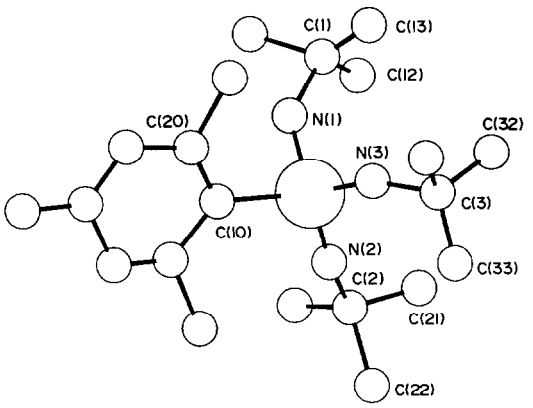


Fig. 3. The structure of $Re(NBu^t)_3(mes)$.

161(1)° and the large deviations from 180° are consistent with the metal electron count exceeding 18 if all three imido groups were to act as 4e ligands.

(2) t-*Butylimido oxo compounds*

A number of compounds having both Bu^tN and oxo groups were obtained either from the hydrolysis product of $(Bu^tN)_2ReCl_3$ or by interaction of nitric oxide with the aryls $(Bu^tN)_2Re(Ar)_2$, Ar = xyl and mes. A bis-imido oxo compound, $ReO[N(2,6\text{-}C_6H_3{}^iPr_2)]_2CH_2Bu^t$, was made[9] by interaction of $Re(NAr)_2(CHBu^t)Cl$ with Me_4NOH in MeOH and characterized spectroscopically; the reaction was proposed to proceed via a hydroxo intermediate; an osmium(VI) compound, $Os(NBu^t)(O)(mes)_2$, has been structurally characterized by X-ray diffraction.[10]

(a) *From hydroxo species.* In a reaction of mesMgBr with a sample of $Re(NBu^t)_2Cl_3$ that had been inadvertently exposed to air for several weeks, work-up gave the two imido oxo aryls described below. In order to obtain a more rational synthesis, the hydroxo compound $Re(NBu^t)_2Cl(OH)_2$ was made by interaction of the trichloride with two equivalents of LiOH. The NMR and IR spectra are consistent with this formula; on heating, loss of water occurs to give $Re(NBu^t)_2Cl(O)$ as shown by the disappearance of OH bands and the appearance of an Re=O band in the IR spectrum. Interaction of the hydroxide in THF with mesMgBr gave products similar to the ones obtained from the aged sample of $Re(NBu^t)_2Cl_3$. These were separated by fractional crystallization and identified as $Re(NBu^t)_2(O)(mes)$, $[(Bu^tN)Br(mes)Re(\mu\text{-}NBu^t)(\mu\text{-}O)\overline{Re(OC_6H_2Me_2CH_2)(NBu^t)}]$, Bu^tNH_3Cl and a magnesium-containing solid. The compound $Re(NBu^t)_2(O)(mes)$ has also been obtained as the sole rhenium-containing product by the reaction

$$Re(NBu^t)_2ReCl_2(mes) \xrightarrow{Ag_2O,\ Et_2O} Re(NBu^t)_2(O)(mes) + 2AgCl.$$

This monomeric compound has a Re=O stretch at 908 cm^{-1} in the IR spectrum, while the mass spectrum shows the parent ion and peaks due to loss of oxygen and NBu^t groups.

The more complicated bridged dimer has been characterized by X-ray diffraction and the structure is shown in Fig. 4; selected bond lengths and angles are given in Table 6.

Neglecting the proposed metal–metal interaction, the coordination geometry at each metal is very distorted trigonal bipyramidal. Thus, for Re(1), O(1) and O(2) define the axis [angle = 149.9(4)°] and for Re(2), N(1) and Br(1) [angle = 158.0(3)°]. The Re—O(1)—Re bridge is close to symmetrical, whereas the two Re—N distances

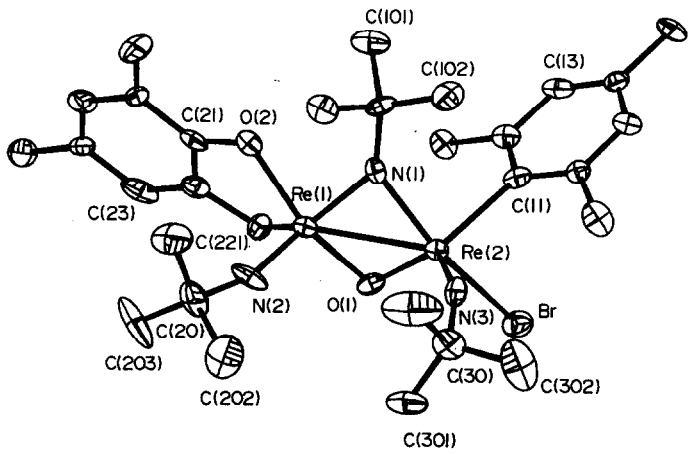


Fig. 4. The structure of $[(Bu^tN)Br(mes)Re(\mu\text{-}NBu^t)(\mu\text{-}O)\overline{Re(OC_6H_2Me_2CH_2)(NBu^t)}]$.

Table 6. Selected bond lengths and bond angles for $C_{30}H_{48}BrN_3O_2Re_2$

Bond lengths (Å)			
O(1)—Re(1)	1.909(11)	N(1)—Re(1)	1.922(13)
O(2)—Re(1)	1.964(12)	C(21)—Re(1)	2.856(19)
C(221)—Re(1)	2.139(17)	N(2)—Re(1)	1.708(14)
Br(1)—Re(2)	2.552(5)	O(1)—Re(2)	1.886(12)
N(1)—Re(2)	1.990(14)	C(11)—Re(2)	2.149(16)
N(3)—Re(2)	1.695(14)		
Bond angles (°)			
N(1)—Re(1)—O(1)	92.5(6)	O(2)—Re(1)—O(1)	149.9(4)
O(2)—Re(1)—N(1)	85.0(5)	C(21)—Re(1)—O(1)	135.9(4)
C(21)—Re(1)—N(1)	108.7(5)	C(21)—Re(1)—O(2)	25.4(4)
C(221)—Re(1)—O(1)	82.2(6)	C(221)—Re(1)—N(1)	131.8(5)
C(221)—Re(1)—O(2)	77.4(6)	C(221)—Re(1)—C(21)	54.7(6)
N(2)—Re(1)—O(1)	108.6(7)	N(2)—Re(1)—N(1)	125.0(6)
N(2)—Re(1)—O(2)	97.2(7)	N(2)—Re(1)—C(21)	90.7(7)
N(2)—Re(1)—C(221)	101.8(7)	N(1)—Re(2)—Br(1)	158.0(3)
N(1)—Re(2)—O(1)	91.1(5)	O(1)—Re(2)—Br(1)	82.0(4)
C(11)—Re(2)—Br(1)	79.6(4)	C(11)—Re(2)—O(1)	127.3(6)
C(11)—Re(2)—N(1)	88.4(6)	N(3)—Re(2)—Br(1)	93.0(5)
N(3)—Re(2)—O(1)	120.9(6)	N(3)—Re(2)—N(1)	108.3(6)
N(3)—Re(2)—C(11)	109.0(7)	Re(2)—O(1)—Re(1)	87.0(5)
Re(2)—N(1)—Re(1)	83.8(6)	C(10)—N(1)—Re(1)	138.1(9)
C(10)—N(1)—Re(2)	137.0(9)	C(16)—C(11)—Re(2)	125.3(11)
C(21)—O(2)—Re(1)	116.7(10)	O(2)—C(21)—Re(1)	37.9(6)
C(22)—C(21)—Re(1)	79.9(10)	C(26)—C(21)—Re(1)	152.7(12)
C(22)—C(221)—Re(1)	109.4(12)	C(30)—N(3)—Re(2)	157.8(11)
C(20)—N(2)—Re(1)	161.9(13)		

in the Re—N(1)—Re bridge differ by *ca* 0.07 Å, with Re(2)—N(1) being the longer. This may be a reflection of N(1) occupying an axial site in the Re(2) coordination. The two imino functions show some bending [Re(1)—$\widehat{N(2)}$—C(20) = 162(1)°, Re(2)—$\widehat{N(3)}$—C(30) = 158(1)°] but both can be considered to act as normal 4e ligands, Re≡N—R.

The rhenium atoms that are bridged by μ-O and μ-NBu^t have formal oxidation state VI; since the compound is diamagnetic there is probably a metal–metal bond as in the homoleptic rhenium(VI) dimer,[3] $Re_2(NBu^t)_4(\mu\text{-}NBu^t)_2$, and the bond distances in the two compounds are 2.61 and 2.70 Å, respectively.

The ^{1}H NMR and IR spectra of the compound can be interpreted in terms of the above structure; the ^{1}H resonance of the *t*-butyl group of μ-NBu^t is at lower field than the terminal ones and the latter appear equivalent.

There must be a complex series of reactions leading to this product probably comprising condensation of Re(OH) groups to give ReORe, and hydrolysis of one imido group, probably via an amido intermediate; the phenolic moiety could arise by a cyclometallation reaction of an *o*-CH_3 group on a mesityl followed by an oxygen atom "insertion" into the Re—C bond.

(b) *From nitric oxide.* When NO is bubbled rapidly through hexane solutions of $Re(NBu^t)_2(Ar)_2$, Ar = xylyl or mesityl, the colour changes almost instantaneously and from the solutions yellow (xyl) or orange (mes) crystals of the dioxoimido compounds, $[Re(NBu^t)(O)_2Ar]_2$, can be isolated in high yield.

The X-ray crystallographic structure determinations of these two complexes have showed them to be dimeric with two oxo bridges. Diagrams of the structures are given in Figs 5 and 6, with selected bond lengths and angles in Table 7. In both cases the geometry about the metal is trigonal bipyramidal with the terminal imido group and a bridging oxygen atom occupying the axial sites. The bridging thus involves one axial and one equatorial site and both dimers are centrosymmetric.

In the mesityl the bridges are quite unsymmetrical, with equatorial and axial Re—O distances of 1.791(7) and 2.364(7) Å, respectively. This is not unexpected and can be ascribed to lengthening of the axial Re—O bond through the *trans* influence of the imido group. It was, therefore, surprising to

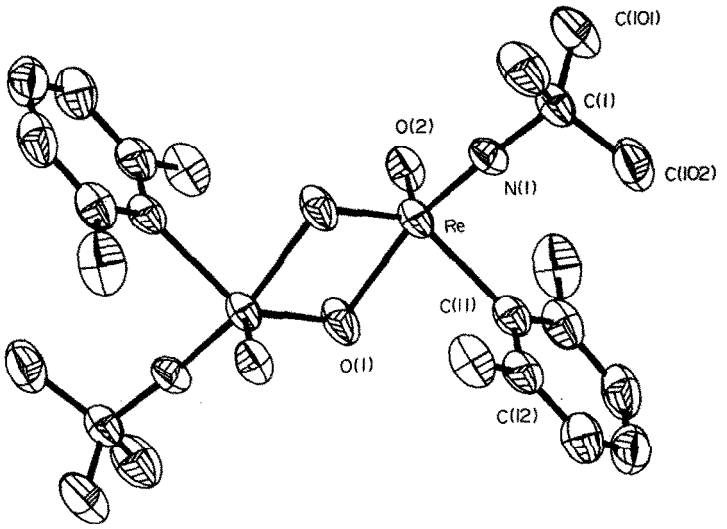


Fig. 5. The structure of $[Re(NBu^t)(O)(\mu\text{-}O)(xyl)]_2$.

find that in the xylyl, the bridge is more symmetrical, with equatorial and axial Re—O distances of 1.867(8) and 2.081(8) Å—a difference of only 0.21 Å compared to 0.57 Å in the mesityl. In all other respects, the geometries of the two compounds are very similar. We find it difficult to explain this major difference. The two compounds differ only in the presence of the extra methyl group in the mesityl complex, and this is most unlikely to affect the geometry of ligands around the metal. It does, however, affect the packing of the molecules in the unit cell, as evidenced by the choice of two quite different unit cells and crystal systems.

Asymmetric M_2O_2 rings have also been found in $Ru_2(\mu\text{-}O)_2(CH_2SiMe_3)_6$,[10a] which has a metal–metal bond and Ru—O distances of 2.208 and 1.733 Å, while $[OsO(o\text{-}OC_6H_{10}O)(quin)]_2$,[10b] quin = quinuclidene, has Os—O distances of 2.22 and 1.78 Å. An unsymmetrical single bridge has been found in a tungsten compound.[10c] For general information on MO and MOM distances see ref. 7(b) Table 5.2, p. 159 and West;[10d] in other compounds with Re_2O_2 rings such as $Re_2O_2(\mu\text{-}O)_2(CH_2CMe_3)_4$,[10e] the Re($\mu$-O) distances are essentially the same (1.967, 1.946 Å) but there is also a Re—Re bond (2.606 Å).

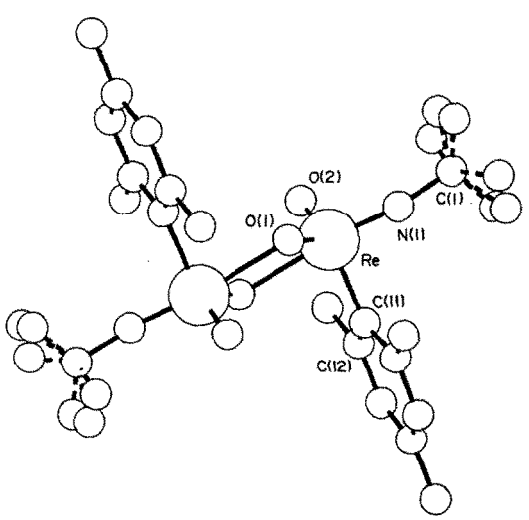


Fig. 6. The structure $[Re(NBu^t)(O)(\mu\text{-}O)(mes)]_2$.

The mass spectra do not show peaks of mass greater than the monomeric parent ions, $Re(NBu^t)_2(O)_2Ar^+$, so that the dimers must dissociate in the gas phase; there are other peaks to lower mass indicating loss of oxo and NBu^t groups.

The IR spectra of these and similar aryls (see Table 1 and ref. 11) show strong aromatic bands in the region associated with metal–oxygen stretching frequencies, and consequently it is not always easy to identify the Re=O or Re—O—Re stretch, and indeed some of these could be obscured. The IR of the xylyl compound shows two Re=O stretches at 952 and 925 cm^{-1} both in the solid state and in hexane solution. The mesityl differs in that only bands at 939 and 830 cm^{-1} in the solid-state spectrum can be identified, while in solution in hexane there are, as in the xylyl, two bands at 956 and 932 cm^{-1}. Oxygen exchange with $^{18}OH_2$ which would have helped identification of ReO bands cannot be done due to hydrolysis of the imido groups. For discussion of IR spectra of MO compounds see refs 7(b) and 10(d) and for compounds with Re_2O_2 (μ-O)$_2$ groups, ref. 10(e).

The other products of the NO reactions were identified as N_2O (by MS) and the unsymmetrical

Table 7. Selected bond lengths and bond angles for $[C_{13}H_{20}NO_2Re]_2$ and $[C_{12}H_{18}NO_2Re]_2$

	$[C_{13}H_{20}NO_2Re]_2$	$[C_{12}H_{18}NO_2Re]_2$
Bond lengths (Å)		
O(1)—Re(1)	1.791(7)	2.081(8)
O(2)—Re(1)	1.704(8)	1.708(9)
O(1a')—Re(1)	2.364(7)	1.867(8)
C(11)—Re(1)	2.090(10)	2.147(10)
N(1)—Re(1)	1.741(8)	1.722(9)
Re(1)—Re(1a)	3.332(4)	3.118(2)
Bond angles (°)		
O(2)—Re(1)—O(1)	119.4(4)	94.2(4)
C(11)—Re(1)—O(1)	115.3(4)	79.4(4)
C(11)—Re(1)—O(2)	112.0(4)	108.7(4)
N(1)—Re(1)—O(1)	105.5(4)	161.0(4)
N(1)—Re(1)—O(2)	105.3(4)	103.9(5)
N(1)—Re(1)—C(11)	95.6(4)	89.4(4)
O(1)—Re(1)—O(1a)	74.2(4)	75.8(4)
O(2)—Re(1)—O(1a)	79.9(4)	113.4(4)
C(11)—Re(1)—O(1a)	79.2(4)	132.1(3)
N(1)—Re(1)—O(1a)	173.8(4)	101.4(5)
Re(1)—O(1)—Re(1a)	105.8(4)	107.7(4)
C(12)—C(11)—Re(1)	121.4(8)	116.9(7)
C(16)—C(11)—Re(1)	116.7(7)	121.9(8)
C(1)—N(1)—Re(1)	153.7(7)	173.8(7)

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z); (a) $-x, 1.0-y, 2.0-z$.

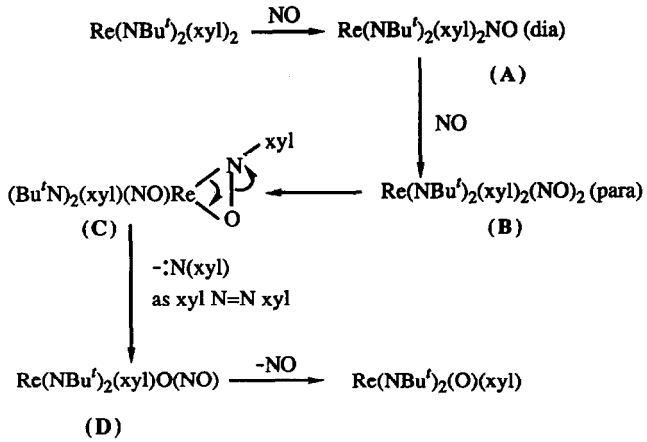
azo compounds, Bu^{t}N=NAr, so that the stoichiometry is that of eq. (1):

$$Re(NBu^t)_2(Ar)_2 + 3\,NO \longrightarrow Re(NBu^t)(O)_2Ar + N_2O + Bu^tN{=}NAr. \quad (1)$$

The reaction of $Re(NBu^t)_2(xyl)_2$ with one equivalent of NO was much slower than when excess NO was bubbled through the solution (*ca* 1 h vs a few seconds) and from the solution the nitrosyl compound, $Re(NBu^t)_2(xyl)_2(NO)$, could be isolated. This compound, formally having rhenium(V), is diamagnetic and the ^1H NMR spectrum shows that the NBu^t and aryl groups have a 1:1 ratio and that the equivalence is maintained to 223 K as there is no broadening or splitting of the peaks. The IR spectrum has a new band at 1639 cm^{-1} assignable as ν(ReNO). The spectra are thus consistent with a *tbp* structure with equatorial NBu^t and axial aryl groups. The mass spectrum shows the parent ion at $m/z = 569$ (Re^{187}) with other peaks due to loss of NO, O, Bu^t, N(xyl) and xylyl. Crystals suitable for X-ray study could not be obtained. The only similar nitrosyl derived by addition to a rhenium(VI) compound is the diamagnetic $ReMe_6(NO)$ which has ν(NO) at 1710 cm^{-1}.[12] The low NO stretches suggest that both species have bent MNO groups.

Treatment of the nitrosyl with slightly less than one equivalent of NO gives, as the final product, the complex $Re(NBu^t)_2(O)(xyl)$, which is the analogue of the tetrahedral $Re(NBu^t)_2(O)(mes)$ obtained by arylation of $Re(NBu^t)_2Cl(OH)_2$ as described above. Hence, there appears to be a substantial difference, presumably due to kinetic factors, between the reactions of the diaryls with stoichiometric amounts of NO and the very rapid reaction found when NO is bubbled through the solution. The final product in both cases has rhenium(VII) and does not react further with NO.

Considering first the stoichiometric reaction, this can be accounted for by well established chemistry as in Scheme 2. The five-coordinate diamagnetic nitrosyl **A** reacts with more NO to give a six-coordinate, paramagnetic dinitrosyl **B**, which would then undergo the well established aryl (or alkyl) transfer reaction[13] (also ref. 4, p. 1210) via an η^2-RNO intermediate leading to an M=O group and RN=NR as found for other paramagnetic compounds[12,13] such as $ReOMe_4$[13c] and

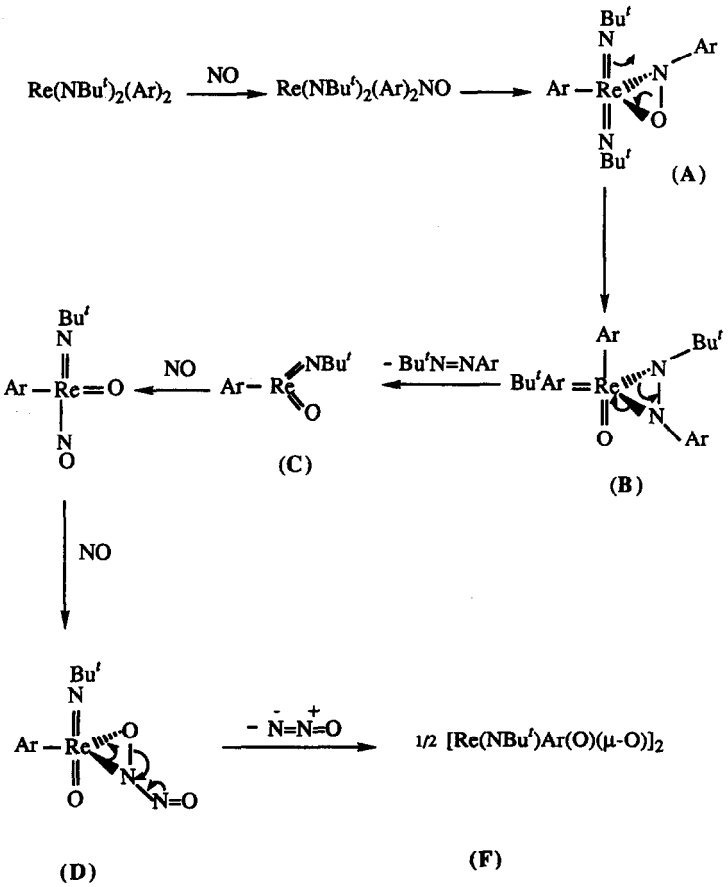


Scheme 2. Stoichiometric reaction of $Re(NBu^t)_2(xyl)_2$ with NO leading to $Re(NBu^t)_2(O)(xyl)_2$ and xylN=Nxyl.

$(C_5H_5)_2NbMe_2$.[13d] The oxo species **D** would doubtless readily lose NO to give the final stable product; the overall reaction is that of eq. (2):

$$Re(NBu^t)_2(xyl)_2 + NO \longrightarrow Re(NBu^t)_2(O)(xyl) + \tfrac{1}{2}(xyl)N{=}N(xyl). \quad (2)$$

The fast reaction presents a different problem since the mixed azo compounds, $Bu^tN{=}NAr$, were isolated. Although mixed azo compounds have been prepared by other methods,[14] these particular ones appear to be new. In Scheme 3 we propose that the ArNO species first formed by aryl migration to



Scheme 3. Interaction of $Re(NBu^t)_2(Ar)_2$, Ar = xyl, mes, with excess NO.

NO (either η^2 as in **A** of Scheme 2, or η^1), instead of giving ArN=NAr, either in an intermolecular reaction or by dimerization of eliminated :NAr, undergoes N—N bond formation to give species **B**. This intermediate could be regarded as an η^2-azo compound of rhenium(V) or more likely as a rhenium(VII) compound with a hydrazido (2−) ligand as drawn in Scheme 3. Examples of metal azo and hydrazido (2−) complexes are well established;[15] the distinction between azo and hydrazido (2−) is a somewhat formal one (cf. alkene and alkyne complexes, ref. 4, p. 71). This species, **B**, then undergoes a cheletropic[16] elimination of the azo compound leaving the coordinately unsaturated species **C** to react successively with two molecules of NO, probably via a dinitrosyl,[17a] to form the hyponitrite **D** which finally eliminates N_2O giving the isolated products **F**. The initial formation of a dinitrosyl as in **B** (Scheme 2) and elimination of N_2O at this point can be ruled out as this would give $Re(NBu^t)_2(Ar)_2O$ with rhenium in the impossible oxidation state of VIII.

While hyponitrites such as **D** have been proposed as intermediates and some examples characterized spectroscopically,[12a,b,17] recent calculations[17b] comparing $Re(NS)_2$ coupling with $Re(NO)_2$ coupling suggest[17b] that the latter "is disfavoured but might occur via N—N bonding". It can be noted regarding the formation of the azo compound that no examples of coupling of $M(NR)_2$ appear to be known (see ref. 7b, p. 273).

Finally, a question arises why in its reactions with NO, $Re(NBu^t)_2(mes)_2$ differs from $Re(O)_2(mes)_2$ which reacts quantitatively[10] as in eq. (3) to give dimesitylamido trioxorhenium(VII) via an η^2-ON(mes) intermediate,

$$Re(O)_2(mes)_2 + NO \longrightarrow O_3Re{=}N(mes)_2. \quad (3)$$

There would seem to be no reason *a priori* why the present reaction should not give $Re(NBu^t)_2O(Nmes_2)$ by the same route, but in order for a second aryl transfer to NAr to occur, the second aryl group would have to be in a position *cis* to the N atom of the η^2-ONAr group. Species **A** hence presumably has a NBu^t group in this position as shown in Scheme 3; *cis* geometry would be preserved even if the molecule is fluxional.

EXPERIMENTAL

Microanalyses were carried out by Imperial College and Pascher, Remagen, Laboratories. The spectrometers and general techniques used have been described.[3] The compounds $Re(NBu^t)_2Cl_3$[18] and $Re(NBu^t)_3Cl$[3] were prepared as described. Nitrogen oxide (British Oxygen Company) was passed through a tube of solid KOH and a copper spiral cooled at −78°C. In mass spectra, the rhenium compounds showed the correct $Re^{185,187}$ patterns for parent ions and fragments. NMR spectra were referenced to Me_4Si and are in ppm; IR spectra in cm^{-1} are in Nujol mulls unless otherwise specified.

(1) *Di*(t-*butylimido*)*di*(2,6-*dimethylphenyl*)*rhenium* (VI)

To $Re(NBu^t)_2Cl_3$ (0.43 g, 1 mmol) in Et_2O (20 cm^3) at −20°C was added 13 cm^3 of a 0.38 M solution of xylylmagnesium bromide in Et_2O. The resulting red solution was then stirred for 15 h at room temperature. After filtration and evaporation of the solution, the residue was extracted with hexane (3×15 cm^3) and the solution filtered through celite; concentration to 20 cm^3 and cooling at −20°C gave large red crystals. Yield: 0.45 g (83%). MS(FAB): 539 (100%), $^{187}M^+$; 537 (58%), $^{185}M^+$; 483 (8%), $M^+ - Bu^t$; 434 (10%), $M^+ - xylyl$; 427 (7%), $M^+ - 2Bu^t$. IR: 3047m, 2969s, 2926s, 1594m, 1456s, 1360s, 1261s, 1210m, 1091w, 1022m, 911vs, 801s, 766s, 716m, 525w. EPR: see text.

(2) *Di*(t-*butylimido*)*di*(2,6-*dimethylphenyl*)*rhenium* (VII) *hexafluorophosphate*

The solids $Re(Bu^tN)_2(xyl)_2$ (0.54 g, 1 mmol) and $AgPF_6$ (0.25 g, 1 mmol) were mixed under nitrogen and 25 cm^3 of THF added. On vigorous stirring the solution became bright orange and a grey precipitate of Ag appeared. After 2 h the solution was filtered and Et_2O (15 cm^3) added; cooling at −20°C gave crystals of the salt. Yield: 0.6 g (88%). MS(FAB): 539 (100%), $^{187}M^+$; 483 (5%), $M^+ - Bu^t$; 434 (6%), $M^+ - xyl$; 427 (5%), $M^+ - 2Bu^t$. IR: 1572w, 1365s, 1302w, 1261m, 1227m, 1173m, 1140w, 1099w, 1026w, 914s, 876w, 840vs, 786m, 739m, 704w, 557s, 471w. NMR: ^1H ($CDCl_3$): 7.42 (1H, m, *p*-$C_6H_3Me_2$); 7.21 (2H, d, *m*-$C_6H_3Me_2$); 2.46 (6H, s, *o*-$C_6H_3Me_2$); 1.80 (9H, s, NBu^t).

The *trifluoromethanesulphonate* was obtained similarly using AgO_3SCF_3 (0.26 g, 1 mmol). Yield: 0.55 g (81%); m.p. 131°C dec. The IR spectrum is the same as for PF_6^- except for anion bands.

(3) *Interaction of* $[Re(NBu^t)_2(xyl)_2]PF_6$ *and* Bu^tNC

To the PF_6^- salt (0.2 g, 0.3 mmol) in THF (15 cm^3) was added Bu^tNC (0.04 cm^3, 0.35 mmol). The solution became pale yellow and after stirring for 1 h, hexane (10 cm^3) was added to precipitate a white solid. Recrystallization from THF gave crystals of

$[Re(NBu^t)_2(xyl)(\eta^2\text{-}Bu^tNC{=}Cxyl)]PF_6$. MS(EI): 513 (1%), $^{187}M^+$, and a variety of peaks from 435 to 131. IR: 2981s, 2935s, 1713s, 1639w, 1459s, 1365m, 1246m, 1215m, 1188s, 1173s, 1093w, 1030w, 911m, 816w, 842vs, 785m, 737w, 710w, 558s, 472w, 360w. NMR: ^1H ($CDCl_3$): 7.34 (2H, m, *p*-$C_6H_3Me_2$); 7.21 (4H, m, *m*-$C_6H_3Me_2$); 2.44 (6H, s, *o*-$C_6H_3Me_2$); 2.32 (6H, s, *o*-$C_6H_3Me_2C{=}NBu^t$); 1.61 (18H, s, NBu^t); 1.14 (9H, s, $C{=}NBu^t$).

(4) $(Bu^tN)(2,4,6\text{-}Me_3C_6H_2)(C_{27}H_{32})Re^V$

To $(Bu^tN)_2ReCl_3$ (0.7 g, 1.6 mmol) in THF at −40°C was added mesMgBr (8 cm^3 of a 1 M solution in THF) and the red solution stirred for 12 h, while warming to room temperature. The solvent was removed, the residue extracted with Et_2O and this solution evaporated and the residue extracted with hexane. The filtered solution on cooling at −20°C yields $Re(NBu^t)_2(mes)_2$[1] in *ca* 65% yield. Dissolution of the residue from the hexane extraction in THF–hexane (2 : 1) and cooling the solution at −20°C gave red crystals. Yield: *ca* 13%. The compound was recrystallized from THF–hexane to give X-ray quality crystals. IR: 2973s, 1638s, 1618, 1505w, 1456w, 1403w, 1385w, 1372w, 1357s, 1256s, 1211s, 1134s, 1010m, 949w, 922w, 844s, 805w, 710m, 669m, 602w, 554w, 511w, 464w. NMR: ^1H (C_6D_6): 6.94 (2H, s, *m*-H); 6.71 (2H, s, *m*-H); 3.98 (1H, s, cyclohexadienyl-H); 2.80 (1H, s, *endo*cyclic H); 2.27 (3H, s, Me); 2.18 (2H, s, CH_2); 2.15 (3H, s, Me); 2.11 (3H, s, Me); 2.06 (3H, s, Me); 2.04 (9H, s, 3Me); 1.98 (12H, s, 4Me); 1.26 (9H, s, Bu^t). Some bimesityl[19] was also isolated from the solution after removal of $Re(NBu^t)_2(mes)_2$.

(5) *Bis*(t-*butylimido*)*chlorobis*(2-*methylphenyl*)*rhenium*(VII)

To $Re(NBu^t)_2Cl_3$ (1.0 g, 2.3 mmol) in Et_2O (10 cm^3) at −25°C was added *o*-tolMgBr (1.5 cm^3 of a 3.3 M solution in Et_2O) and the mixture slowly warmed to room temperature and stirred for 5 h. Removal of solvent, extraction of the residue with hexane (*ca* 10 cm^3) and cooling (−20°C, 3 days) gave crystals. Yield: 0.86 g (68%). MS(FAB): 511 (100%), $^{187}M^+ - Cl$; 437 (53%), $^{187}Re(NBu^t)(o\text{-tol})_2^+$; 420 (16%), $^{187}Re(NBu^t)_2(o\text{-tol})^+$.

(6) *Bis*(t-*butylimido*)(2-*methylphenyl*)*rhenium*(VII) *hexafluorophosphate*

The interaction of equimolar quantities of $Re(NBu^t)_2(o\text{-tol})_2Cl$ (0.464 g) and $AgPF_6$ (0.225 g), each in THF (*ca* 5 cm^3), at room temperature gives a precipitate of AgCl and a yellow solution. After 2 h stirring, the solution was filtered, concentrated (5 cm^3) and hexane (*ca* 3 cm^3) added; cooling at −20°C gave crystals. Yield: 0.43 g (78%). MS(FAB): 511 (85%), $^{187}Re(NBu^t)_2(o\text{-tol})_2^+$; 420 (19%), $^{187}Re(NBu^t)_2(o\text{-tol})^+$; 57 (100%), Bu^{t+}.

(7) *Bis*-t-*butylimido*(*chloro*)(*dihydroxo*)*rhenium*(VII)

To a mixture of $(Bu^tN)_2ReCl_3$ (0.435 g, 1 mmol) and LiOH (0.06 g, 1.5 mmol) was added THF (50 cm^3). The dark red solution slowly turns yellow with a white precipitate (LiCl). After stirring for 1 h the solution was filtered, concentrated (3 cm^3) and hexane (5 cm^3) added to precipitate the yellow solid which was washed with Et_2O (3 × 10 cm^3). Yield: 81%. MS(FAB): 399, (35%) $^{187}M^+$; 74 (100%), $Bu^tNH_3^+$; 57 (100%), Bu^{t+}. MS(EI): 310 (1%), $^{187}Re(NBu^t)OH^{35}Cl^+$; 270 (2%), $^{187}Re(N)(OH)_2{}^{35}Cl^+$; 58 (100%), Bu^tH^+. IR: 3417s(OH), 2966m, 2925w, 1634m, 1455w, 1359w, 1261s, 1219w, 1093s, 1019s, 914s, 879w, 858m, 800m, 454m, 397m, 321m. NMR: ^1H ($CDCl_3$): 5.62 (2H, br, OH); 1.32 (18H, s, Bu^t).

(8) *Reaction of* $Re(NBu^t)_2Cl(OH)_2$ *with mesityl magnesium bromide*

(a) *Bis*(t-*butylimido*)*oxomesitylrhenium*(VII). *Method A*: To $Re(NBu^t)_2Cl(OH)_2$ (0.6 g) in THF (10 cm^3) at −20°C was added mesMgBr (6 cm^3, 1 M solution in Et_2O) and the solution stirred for 12 h at room temperature. Removal of solvent, extraction of the residue into hexane (3 × 15 cm^3), filtration and concentration (5 cm^3) of the dark yellow solution followed by cooling at −20°C gave yellow crystals of $Re(NBu^t)_2(O)(mes)$. Yield: 0.48 g (68%). MS(EI): 464 (29%), $^{187}M^+$; 448 (25%), $^{187}M^+ - O$; 393 (80%), $^{187}M^+ - NBu^t$; 336 (24%), $^{187}Re(N)(O)(mes)^+$; 329 (3%), $^{187}Re(NBu^t)_2^+$; 306 (9%), $^{187}Re(mes)^+$; 58 (100%), Bu^tH^+. IR: 2970s, 2924s, 1597w, 1453m, 1376w, 1359m, 1261s, 1209s, 1094s, 1025s, 908s, 849m, 805s, 706w, 596w, 511w, 462w, 387m.

Method B: A solution of $Re(Bu^tN)_2Cl_2(mes)$[1] (0.26 g) in THF (10 cm^3) was stirred with 0.15 g of moist Ag_2O for 2 h. After filtration the solution was evaporated and the residue extracted into hexane (15 cm^3); concentration (to 3 cm^3), followed by cooling at −20°C gave yellow crystals of $Re(NBu^t)_2(O)mes$. Yield: 0.18 g (73%).

(b) *The bridge species* $(Bu^tN)(Br)(mes)Re(\mu\text{-}NBu^t)(\mu\text{-}O)\overline{ReOC_6H_2Me_2CH_2}(NBu^t)$. The mother liquor from above in method A after removal of $Re(NB^t)_2(O)(mes)$ was evaporated and the residual dark yellow oil allowed to stand at −20°C for *ca* 3

days. The red crystals were collected, washed with Et_2O and dried. Yield: 0.25 g (19%). IR: 2974s, 2924s, 2856m, 1456s, 1385s, 1357s, 1259s, 1200s, 1133m, 1099m, 1018s, 912w, 844s, 805s, 710s, 669s, 513m. NMR: $^1H(C_6D_6)$: 6.87 (1H, s, *m*-H); 6.83 (1H, s, *m*-H); 6.49 (2H, s, *m*-H); 3.01 (3H, s, Me); 1.68 (6H, s, 2Me); 1.07 (9H, s, μ-NBu^t); 0.88 (18H, s, NBu^t).

(9) *Reactions with nitrogen monoxide*

(a) t-*Butylimido(dioxo)(2,6-dimethylphenyl)rhenium*(VII). Nitrogen monoxide was bubbled through a hexane solution of $Re(NBu^t)_2(xyl)_2$ (0.54 g, 1 mmol) until the colour changed to light orange. The solvent was removed and the residue was dissolved in hexamethyldisiloxane (5 cm^3); the solution was filtered, concentrated to 2 cm^3 and cooled to -20°C to give yellow crystals. Yield 0.35 g (90%). MS(EI): 395 (35%), $^{187}M^+$; 393 (21%), $^{185}M^+$; 379 (71%), M^+-O; 339 (85%), M^+-Bu^t; 323 (62%), $^{187}Re(NH)(O)(xyl)^+$; 105 (100%), xyl. IR: 2966s, 1652w, 1575w, 1447m, 1404w, 1379m, 1362m, 1261s, 1130w, 1023m, 952s, 925s, 829s, 805m, 770m, 752w, 707w, 558m, 483w, 391m. NMR: ^1H ($CDCl_3$): 7.31–7.19 (3H, m, *m*, *p*-$C_6H_3Me_2$); 2.55 (6H, s, *o*-$C_6H_3Me_2$) 1.58 (9H, s, Bu^{t}N).

(b) t-*Butylimido(dioxo)(2,4,6-trimethylphenyl) rhenium*(VII). Nitrogen monoxide was bubbled through $(Bu^tN)_2Re(mes)_2$ (0.283 g) in hexane (10 cm^3) at room temperature until the dark red solution became light orange with the appearance of a faint precipitate. The solution was filtered, evaporated and the residue extracted into hexamethyldisiloxane (*ca* 8 cm^3). After concentration (3 cm^3) and cooling (-20°C) the orange crystals were collected. Yield: 0.29 (84%). MS(EI): 409 (40%), $^{187}M^+$; 393 (71%), $^{187}M^+-O$; 377 (4%), M^+-O_2; 353 (73%), $^{187}M^+-Bu^t$; 306 (13%), $^{187}Re(mes)^+$; 119 (90%), $C_9H_{11}^+$. IR: 3016w, 2975s, 2920m, 1589s, 1541w, 1467w, 1448s, 1398w, 1379m, 1362m, 1286m, 1230s, 1033m, 984w, 939s, 857m, 830s, 803m, 706w, 599m, 582m, 565w, 541w, 387w, 329m. NMR: ^1H ($CDCl_3$): 7.14 (2H, s, *m*-H); 2.52 (6H, s, *o*-Me), 2.32 (3H, s, *p*-Me); 1.58 (9H, s, Bu^t).

The hexamethyldisiloxane mother liquor from above was evaporated, the residue dissolved in Et_2O (5 cm^3), the solution filtered, concentrated to 2 cm^3 and cooled at -20°C to give orange crystals of the azo compound Bu^{t}N=Nmes, which were recrystallized from Et_2O. Yield: 0.05 g (70%), m.p. 116°C. [Found (required): C, 74.2 (74.5); H, 9.5 (9.8); N, 13.9 (13.7)%.] NMR: ^1H ($CDCl_3$): 6.98 (2H, s, *m*-$C_6H_2Me_3$); 2.80 (6H, s, *o*-$C_6H_2Me_3$); 2.18 (3H, s, *p*-$C_6H_2Me_3$); 1.60 (9H, s, N*Bu^t*). IR: 2966s, 2921m, 2861m, 1652w, 1610w, 1597w, 1550w, 1465s, 1376w, 1360m, 1261m, 1208w, 910w, 882w, 853m, 801s, 709w.

(c) *Di(t-butylimido)di(2,6-dimethylphenyl)nitrosylrhenium*(V). To a solution of $Re(NBu^t)_2(xyl)_2$ (0.3 g, 0.55 mmol) in hexane (10 cm^3) at -78°C, in a small flask with septum, was injected via a gas syringe NO (11 cm^3, 0.5 mmol). The solution was allowed to warm and was stirred at room temperature until the initial deep red colour changed to light yellow (*ca* 1 h). Evaporation in vacuum, extraction of the residue into $(Me_3Si)_2O$ (2×3 cm^3) and cooling of the solution (-30°C) gave orange crystals. Yield: 0.14 g (45%). MS(EI): 569 (44%), $^{187}M^+$; 567 (26%), $^{185}M^+$; 553 (14%), M^+-O; 539 (10%), M^+-NO; 513 (8%), M^+-Bu^t; 450 (30%), $Re(NBu^t)_2(xyl)O^+$; 434 (51%), $Re(NBu^t)_2(xyl)^+$; 379 (72%), $Re(NBu^t)NH(xyl)^+$; 322 (33%), $Re(NH)_2(xyl)^+$; 105 (100%), xyl^+. IR: 1639m, 1616m, 1575w, 1564w, 1533m, 1439s, 1384w, 1360s, 1286w, 1250m, 1230s. NMR: $^1H(CDCl_3)$: 7.21–7.11 (3H, m, *m*, *p*-$C_6H_3Me_2$); 2.85 (6H, s, *o*-$C_6H_3Me_2$); 1.61 (9H, *s*, NBu^t).

(d) *Interaction of nitrosyl compound with* NO. To a solution of $Re(NBu^t)_2(xyl)_2NO$ (0.1 g, 0.17 mmol) in Et_2O (15 cm^3) was injected slightly less than one equivalent of NO and the solution stirred for *ca* 12 h. No change in colour takes place. Evaporation of the solution, extraction of the residue with $(Me_3Si)_2O$ (5 cm^3) and cooling of the filtered solution (-30°C) affords dark yellow crystals of $Re(NBu^t)_2(O)(xyl)$. Yield: 0.06 g (68%). MS(EI): 450 (30%), $^{187}M^+$; 448 (18%), $^{185}M^+$; other peaks due to M^+-Bu^t and M^+-NBu^t; 338 (21%), $Re(NH)_2(O)(xyl)^+$; 323 (17%), $ReNH(O)(xyl)^+$; 105 (61%), xyl^+; 58 (100%), $C_4H_{10}^+$. IR: Re=O, 912 cm^{-1} and other Bu^{t}N and xylyl bands. NMR: ^1H ($CDCl_3$): 7.37–7.15 (3H, m, *m*, *p*-$C_6H_3Me_2$); 2.78 (6H, s, *o*-$C_6H_3Me_2$); 1.62 (18H, s, *Bu^t*N).

X-ray crystallography

Crystals of all six compounds were sealed under argon in thin-walled glass capillaries for X-ray work. Following preliminary photography, orientation matrices and associated cell dimensions were obtained using a CAD4 diffractometer and standard procedures. Intensity data were recorded[20] using ω–2θ scans and graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), and corrected for Lp effects and for absorption using psi-scan information. Further corrections for absorption were made during the refinement process, using the DIFABS method.[21]

Table 8. Crystal data, details of intensity measurements and structure refinement

Molecular formula	$C_{24}H_{36}N_2Re$	$C_{40}H_{52}NRe$	$C_{21}H_{38}N_3Re$	$C_{30}H_{48}BrN_3O_2Re_2$	$C_{26}H_{40}N_2O_4Re_2$	$C_{24}H_{36}N_2O_4Re_2$
Molecular weight	442.518	732.02	518.74	935.04	816.984	788.926
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
a (Å)	17.576(3)	10.924(1)	9.965(8)	8.952(1)	10.536(3)	8.379(2)
b (Å)	14.342(2)	11.049(3)	11.568(7)	10.685(2)	12.428(1)	12.373(3)
c (Å)	9.946(2)	15.478(3)	11.960(9)	17.785(4)	21.310(4)	6.947(1)
α (°)	90	99.84(3)	75.49(6)	95.93(2)	90	97.23(2)
β (°)	95.21(2)	95.80(4)	106.32(8)	95.02(3)	90	103.49(2)
γ (°)	90	108.80(5)	77.32(6)	99.38(6)	90	93.71(2)
Volume (Å)	2421.47	1717.91	1216.26	1659.92	2790.36	671.07
Space group	$P21/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P\bar{1}$
Z	4	2	2	2	4	1
D_c (g cm^{-3})	1.477	1.415	1.416	1.873	1.944	1.952
μ (cm^{-1})	48.04	39.09	50.68	85.70	44.17	91.38
$F(000)$	1064	746	460	876	1268	372
h, k, l range	$-19 \rightarrow 19$	$0 \rightarrow 13$	$0 \rightarrow 10$	$0 \rightarrow 9$	$0 \rightarrow 12$	$-9 \rightarrow 9$
	$0 \rightarrow 15$	$-13 \rightarrow 13$	$-12 \rightarrow 12$	$-11 \rightarrow 11$	$0 \rightarrow 14$	$-14 \rightarrow 14$
	$0 \rightarrow 10$	$-18 \rightarrow 18$	$-13 \rightarrow 13$	$-19 \rightarrow 19$	$0 \rightarrow 25$	$0 \rightarrow 8$
Total number of reflections	3758	6383	3607	4947	3457	2573
Number of unique reflections	3356	6036	2346	4597	2453	2359
Number of reflections	2219	5069	2346	3537	1308	2182
Significance test	$[F > 3\sigma(F)]$	$[F > 3\sigma(F)]$	$[F > 6\sigma(F)]$	$[F > 3\sigma(F)]$	$[F > 6\sigma(F)]$	$[F > 3\sigma(F)]$
Number of parameters	244	380	196	347	154	145
Weighting scheme parameter g in $w = 1/[\sigma^2(F_o)+gF_o^2]$	0.0008	0.0009	0.00009	0.000002	0.09	0.002
Final R	0.0393	0.0309	0.0885	0.0432	0.0512	0.0474
Final R_w	0.0374	0.0327	0.0885	0.0393	0.0550	0.0469

The structures were solved and developed via the heavy atom method and refined by full-matrix least-squares. The usual difficulties were encountered with disorder of *t*-butyl groups generally, and the crystal quality for $Re(NBu^t)_3(xyl)$ was poor. Otherwise all atoms were refined in the anisotropic displacement mode and no hydrogens were included except for $Re(NBu^t)(mes)(C_{27}H_{32})$.

Details of the crystal data, intensity measurements and refinement are given in Table 8.

Tables of final atomic positional parameters and displacement factor coefficients, bond lengths and angles and F_o/F_c values have been deposited with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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