SYNTHESIS AND REACTIONS OF TERT-BUTYLIMIDO COMPLEXES OF RHENIUM. X-RAY CRYSTAL STRUCTURES OF [(ReNBu^t)₂(OSiMe₃)]₂(μ-O)(μ-OSiMe₃)(μ-O₂CCF₃), Re(NBu^t)₃PPh₂ AND [Re(NBu^t)₃(NH₂Bu^t)]O₃SCF₃

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Abstract—The reactions of Re(NBu^t)₃Cl with NaC₅H₅, AgX (X = BF₄, PF₆ and CF₃CO₂) and with SbCl₅ lead to the loss of an NBu^t group, and the formation of bis tert-butylimido compounds, respectively, [Re(NBu^t)₂(η^1 -C₅H₅)]₂(μ -O)(μ -C₅H₄), [(Bu^tN)₂(Cl)Re(μ -F)(μ -NBu^t)Re(NBu^t)(μ -F)]₂X (X = BF₄ and PF₆), [Re(NBu^t)₂]₂(μ -OSiMe₃)(μ -O₂CCF₃) and [Re(NBu^t)₂Cl₂(MeCN)₂]SbCl₆. The interaction between Re₃(NBu^t)₄(O)₅(OSiMe₃)₃ and AgO₂CCF₃ produces a species, [Re(NBu^t)₂(OSiMe₃)]₂(μ -O)(μ -OSiMe₃)(μ -O₂CCF₃), in which the μ -OReO₃ group in the starting material is replaced by μ -O₂CCF₃. Protonation of Re(NBu^t)₃(NHBu^t) by CF₃SO₃H produces the cation [Re(NBu^t)₃(NH₂Bu^t)]⁺ in which the amine can be replaced by PPh₃. Reactions of Re(NBu^t)₃X, where X = Cl or OSiMe₃ are replaced by NR₂, PR₂, NPPh₃ and C₄H₃N₂, are described. Deprotonation of Re(NBu^t)₃ PH(mes), mes = 2,4,6-Me₃C₆H₂, by Bu^tLi gives the known compound [Re(NBu^t)₂(μ -NBu^t)]₂ and a new cyclotriphosphane, (Pmes)₃.

The structures of compounds listed in the title have been determined by X-ray diffraction. The $[Re(NBu^{t})_{2}(OSiMe_{3})]_{2}(\mu-O)(\mu-OSiMe_{3})(\mu-O_{2}CCF_{3})$ structure has crystallographic C_{s} symmetry with a planar $Re_{2}O_{2}$ ring; $Re \cdots Re$ separation is 3.25 Å. The bridging acetate has a significantly enlarged O—C—O angle of 134°. The $[Re(NBu^{t})_{3}(NH_{2}Bu^{t})]O_{3}SCF_{3}$ structure has tetrahedral geometry at rhenium with noticeably differing Re—N distances which correlate to the Re—N—C angles. The $Re(NBu^{t})_{3}PPh_{2}$ compound has tetrahedral geometry at rhenium and a pyramidal geometry at phosphorus. The Re—P distance is 2.445(2) Å.

In previous papers¹⁻³ on tris tert-butylimido compounds of rhenium(VII) we have characterized the aryls¹ Re(NBu¹)₃Ar, Ar = 2-MeC₆H₄, 2,6-Me₂C₆H₃ and 2,4,6-Me₃C₆H₂(mes) and determined the X-ray crystal structure of the mesityl.² The structures of the compounds Re(NBu¹)₃X, where X = Cl and OSiMe₃, were also determined and the chloride converted to the amido species Re(NBu¹)₃(NHBu¹), which in turn was deprotonated by BuⁿLi to give Li(tmed)Re(NBu¹)₄, where tmed = Me₂NCH₂CH₂NMe₂.³ Recently, the aryl-

imido methyl, Re(NAr)₃CH₃, where Ar = 2,6-Pr'C₆H₃, was synthesized, as were the compounds Re(NBu^t)₃R, where R = Me, Et, σ -C₃H₅ and C=CPh.⁴

We now describe some unusual reactions of $Re(NBu^{1})_{3}X$, where $X = Cl^{3}$ and $OSiMe_{3}{}^{5}$, in which an imido group is removed leading to bis tert-butylimido compounds. Substitution of the siloxide group gives dialkyl- or diarylamido and phosphido species. The amido compound $Re(NBu^{t})_{3}(NHBu^{t})$ on protonation gives the cation $[Re(NBu^{t})_{3}(NH_{2} Bu^{t})]^{+}$ as its trifluoromethane sulphonate.

Analytical and physical data for new compounds are given in Table 1.

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				Analyses ^a		
Compound	Colour	m.p. (°C)	С	Н	N	Other
(1) $\operatorname{Re}_2(\operatorname{NBu}^t)_4(O)(C_5H_5)_2(C_5H_4)$	Orange	104–5	41.0	5.7	6.3	
			(42.9)	(5.9)	(6.4)	
(2) $\text{Re}_2(\text{NBu}^1)_4(\text{O})(\text{OSiMe}_3)_3(\text{O}_2\text{CCF}_3)$	Yellow	113-115	28.2	5.0	5.3	6.0 (F)
			(30.1)	(6.0)	(5.3)	(5.7)
(3) $\operatorname{Re}_2(\operatorname{NBu}^t)_4(\operatorname{OSiMe}_3)(\operatorname{O}_2\operatorname{CCF}_3)$	Yellow	70–72	28.8	5.2	6.2	5.8 (O)
			(29.4)	(5.3)	(6.5)	(5.6)
(4) $[\text{Re}_4(\text{NBu}^{1})_8\text{Cl}_2\text{F}_4]\text{BF}_4$	Yellow	> 200	24.1	4.5	7.1	
			(24.8)	(4.6)	(7.2)	
(5) $[\text{Re}_4(\text{NBu}')_8\text{Cl}_2\text{F}_4]\text{PF}_6$	Yellow	> 200	23.2	4.3	7.5	10.8 (F)
			(23.9)	(4.5)	(7.0)	(11.8)
(6) $[\text{Re}(\text{NBu}^{t})_{2}\text{Cl}_{2}(\text{MeCN})_{2}]\text{SbCl}_{6}$	Orange-red	146 dec.	17.9	3.0	7.0	34.3 (Cl)
			(17.7)	(3.0)	(7.0)	(34.8)
(7) $[\text{Re}(\text{NBu}^{t})_{3}(\text{NH}_{2}\text{Bu}^{t})]O_{3}\text{SCF}_{3}$	Yellow	1458	33.2	6.1	8.9	
	_		(32.9)	(6.1)	(9.0)	
(8) $[\text{Re}(\text{NBu}^{t})_{3}(\text{PPh}_{3})]O_{3}\text{SCF}_{3}$	Orange	158-60	45.5	5.1	4.9	
			(45.9)	(5.2)	(5.2)	
(9) $\operatorname{Re}(\operatorname{NBu})_3(\operatorname{NMe}_2)$	Yellow	oil	38.1	7.5	12.4	
	~	<i></i>	(37.9)	(7.5)	(12.6)	
(10) $\operatorname{Re}(\operatorname{NBu'})_3(\operatorname{NPh}_2)$	Yellow	62-3	52.0	6.6	9.6	
	0		(51.0)	(6.6)	(9.9)	
(11) $\operatorname{Re}(\operatorname{NBu}^{\prime})_{3}(\operatorname{PPh}_{2})$	Orange	50-2	49.3	6.4	7.3	5.5 (P)
		<i></i>	(49.3)	(6.4)	(7.2)	(5.3)
(12) $\operatorname{Re}(\operatorname{NBu})_{3}[\operatorname{P}(\operatorname{SiMe}_{3})_{2}]$	Yellow	65–6	37.8	7.9	7.1	5.5 (P)
		0.5	(37.5)	(7.9)	(7.3)	(5.4)
(13) $\text{Re}(\text{NBu}')_{3}[\text{PH}(\text{mes})]$	Yellow	85	45.5	7.1	7.4	
	T 7 11		(45.8)	(7.1)	(7.6)	
(14) $\operatorname{Re}(\operatorname{NBu}^{\circ})_{3}(\operatorname{NPPh}_{3})$	Yellow	161–3	53.4	6.3	8.2	4.8 (P)
	<u> </u>	100 100	(53.3)	(6.3)	(8.3)	(4.7)
(15) $\text{Ke}(\text{NBu})_3(\text{C}_3\text{H}_3\text{N}_2)$	Orange-red	150-152	37.8	6.5	15.0	
			(38.6)	(6.3)	(15.0)	

Table 1. Analytical and physical data for new compounds

^a Calculated values in parentheses. Mass spectra are given in the Experimental.

RESULTS AND DISCUSSION

(1) Reactions leading to bis tert-butylimido compounds

In attempts to convert $Re(NBu^{t})_{3}(OSiMe_{3})$ to the chloride³ it was observed that interactions with $SOCl_{2}$ and PCl_{3} gave the bis imidotrichloride $Re(NBu^{t})_{2}Cl_{3}$. We now describe other, different reactions leading to the removal of an NBu^t group.

(a) Interaction of Re(NBu¹)₃Cl and NaC₅H₅. It was stated by Herrmann *et al.*⁴ that all attempts to react Re(NBu¹)₃(OSiMe₃) with C₅H₅M (M = Na, Tl, SnBuⁿ₃) or C₅Me₅M (M = K, MgCl, Li) were unsuccessful. The reaction of Re(O)₃OSiMe₃ with C_5H_5Na in THF gives only low yields (*ca* 5%) of Re(O)₃(η^5 -C₅H₅), characterized by analysis and spectra.*

The interaction between Re(NBu^t)₃Cl in Et₂O and NaC₅H₅ in THF leads to air-sensitive crystals from hexane of the orange compound 1, whose X-ray crystal structure has been determined⁶ as that shown in Structure I. The bridging $C_5H_4^{2-}$ group



^{*} P. G. Edwards and G. Wilkinson, unpublished work, 1979.

is unique; other types of μ -C₅H₄ moieties are, however, known (see ref. 6). The ¹H NMR spectra over a certain temperature range confirmed the fluxionality of the η^1 -C₅H₅ groups in 1, although the slow exchange limit could not be reached at -90° C.

Any mechanism for the synthesis of the compound has to account for the loss of a NBu^t group from each metal atom and for the presence of the bridging oxygen. A possibility is given in Scheme 1 where the first step is the formation of a σ -C₅H₅ compound (A). While similar substitution by various Cp nucleophiles in Re(NBu^t)₃(OSiMe₃) has been claimed as impossible on steric and electronic grounds,⁴ it is likely that lowered crowding in the chloride compared to the siloxide, coupled with the formation of NaCl rather than NaOSiMe₃, can drive the substitution to completion. The intermediate A of Scheme 1 could be in a tautomeric equilibrium with the alkylidene B from which the tert-butylimido group can be removed by NaCp to give C and NaNHBut. Reaction (iv) competing with (iii) could be a base-initiated (i.e. NaNHBu^t) cycloelimination reaction of tetrahydrofuran leading to **D** with the loss of tert-butylamine and butadiene. Interaction of C and D would then lead to the isolated species with the μ -C₅H₄ group 1.



Scheme 1. Possible route to synthesis of compound 1.

(b) Interaction of tert-butylimido siloxides with AgO₂CCF₃. The rhenium siloxides, [Re(NBu^t)₂ (OSiMe₃)]₂(μ -OSiMe₃)(μ -O)(μ -OReO₃) (Structure II), together with Re(NBu^t)₃(OSiMe₃) were obtained⁵ from the interaction between ReO₃ (OSiMe₃) and Bu^tNH(SiMe₃), the former on using a deficiency of the amine. The structure of dimer II was earlier determined by X-ray diffraction.⁷ Another dimer,² Re₂(NBu^t)₃Br(O)(mesityl) (CH₂Me₂C₆H₂O) which has μ -O and μ -NBu^t groups, has been characterized crystallographically.



Although first obtained in low yield by interaction of Re(NBu¹)₃Cl and AgO₂CCF₃, compound **2** was subsequently made by the more rational procedure of the interaction between Nugent's triplybridged species and silver trifluoroacetate, which leads to substitution of the μ -OReO₃ group by μ -O₂CCF₃. The orange crystalline compound **2** was shown by X-ray crystallography to have structure **III**. The structure is shown in Fig. 1; data in Table 2.

The molecule has crystallographic C_s symmetry about a plane bisecting the $Re(1) \cdots Re(1')$ vector and passing through the bridging μ -O and the O₂CCF₃ and OSiMe₃ groups. The geometry at each rhenium atom is distorted octahedral with interbond angles in the ranges 73-104° and 151-171°. The angles subtended at rhenium by O(1), O(3) and O(4) are significantly contracted from 90°, whereas those formed by N(1), O(2) and N(2) are noticeably enlarged. The former are a consequence of satisfying the Re...Re separation and ligand bridging constraints and the latter of accommodating the bulky facially-substituted NBu^t and OSiMe₃ groups. The strain of bridging between the two rhenium centres by the O_2CCF_3 ligand is reflected in a significant enlargement of the O(4)—C(14)—



Fig. 1. The structure of $[(Bu^tN)_2(Me_3SiO)Re]_2(\mu-O)(\mu-OSiMe_3)(\mu-O_2CCF_3).$

O(4') angle, $134(2)^{\circ}$. With the exception of the Re(1)—O(4) distance [2.32(1) Å], which is significantly longer than that observed for Re—O in e.g. acetates or formates, the remaining Re—O and Re—N distances are normal. The central Re₂O₂ ring is planar to within 0.007 Å and the transannular Re…Re and O…O distances are 3.25 and 2.41 Å, respectively. The angles at N(1)

and N(2) are both appreciably bent [152.5(12) and 165.4(13)°, respectively] and consistent with two doubly-bound NBu^t groups. There is marked enlargement of the angle at O(2), 145.3(8)°, compared with that to Si at O(1), 131.0(3)°. These values are virtually identical to those reported for the closely related structure by Nugent and Harlow.⁷

It may be noted that structures I, II and III are

Tabl	e 2.	Bond	lengths	(A)) and	angles	(°)	for	(2)	with	e.s.d.s	in	parentheses
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Re(1)-O(1) 2	2.160(11)	Re(1) - O(2) = 1.	935(12)
Re(1)-O(3) 1	.900(10)	Re(1) - O(4) = 2.	322(9)
Re(1) - N(1) = 1	.731(9)	Re(1) - N(2) = 1.	693(14)
Si(1)-O(1) 1	.647(19)	O(3) - Re(1') = 1.	900(10)
Si(2)-O(2) 1	.618(13)		
O(1) - Re(1') = 2	.160(11)		
O(4)-C(14) 1	.232(14)		
O(1)—Re(1)— $O(2)$	85.9(5)	O(1) - Re(1) - O(3)	72.6(6)
O(2)—Re(1)—O(3)	151.0(6)	O(1) - Re(1) - O(4)	79.3(4)
O(2)—Re(1)—O(4)	75.6(4)	O(3) - Re(1) - O(4)	81.4(5)
O(1) - Re(1) - N(1)	93.1(5)	O(2) - Re(1) - N(1)	99.4(5)
O(3) - Re(1) - N(1)	100.9(6)	O(4) - Re(1) - N(1)	171.1(5)
O(1) - Re(1) - N(2)	160.3(5)	O(2)—Re(1)—N(2)	101.0(6)
O(3) - Re(1) - N(2)	94.0(7)	O(4) - Re(1) - N(2)	84.5(5)
N(1) - Re(1) - N(2)	103.8(5)	Re(1) - O(1) - Si(1)	131.0(3)
Re(1)-O(1)-Re(1') 97.4(7)	Re(1) - O(3) - Re(1')	117.3(10)
Re(1) - O(2) - Si(2)	145.3(8)	Re(1) - N(1) - C(6)	152.5(12)
Re(1)-O(4)-C(14)	125.3(12)		
Re(1) - N(2) - C(10)) 165.4(13)		
O(4)C(14)O(4')	133.6(20)		

quite similar being bis-imido species with different bridging groups. The IR and NMR spectra are in accord with the structures. Thus, for 2 the ¹H NMR data indicate terminal NBu¹ groups and both terminal and bridging OSiMe₃ groups with the correct intensity ratios, while there is a single ¹⁹F resonance for the μ -O₂CF₃ group. The IR spectra show typical bands for the μ -carboxylate and the other groups except that the μ -O frequency is uncertain due to other bands in this region.

The interaction between Re(NBu¹)₃(OSiMe₃) and silver trifluoroacetate also leads to a bis imido species, presumably by initial electrophilic attack of Ag⁺ on a bent imido group; the reaction is evidently complicated and the yield is not quantitative. On the basis of analytical and spectroscopic data, product 3 has structure IV; crystals suitable for X-ray study could not be obtained. The compound has rhenium in the V oxidation state corresponding to the loss of an imido group from rhenium(VII). The IR and NMR data are similar to those of 2.



(c) Interaction of $Re(NBu^{t})_{3}Cl$ with $AgBF_{4}$ and $AgPF_{6}$. The interaction between $Re(NBu^{t})_{3}Cl$ and $AgBF_{4}$ (or $AgPF_{6}$) is sensitive to the nature of the solvent used and the order of addition of reactants. Crystalline products (4, 5) were obtained only when the reaction was carried out in $CH_{2}Cl_{2}$ and with the addition of the imido compound to the solvent salt in excess.

The salts thus obtained both have a cation with the tetrameric structure shown in Structure V. This structure is based on analytical and spectroscopic data and an incomplete X-ray study⁸ of the BF₄⁻ salt. The latter confirmed the tetrameric structure with the rhenium atoms having distorted square-pyramidal geometry, but the refinement was hindered by disorder problems.



As in the reaction of the siloxide with AgO_2CCF_3 , reduction occurred since the cation contains rhenium atoms formally in oxidation states IV (inner) and VII (outer). This structure with a linear chain of four metal atoms resembles that of a neutral tert-butylimido(oxo)osmium(VI) compound, $[(Bu^tN)_2Os(\mu-NBu^t)_2Os(NBu^t)(\mu-O)]_2$. Since both 4 and 5 are diamagnetic, metal-metal bonding or electron spin coupling via the bridge groups in the cation is evident. The ¹H NMR spectrum (CD_2Cl_2) of the cation shows two Bu^tN groups in a 1:1 ratio at 25°C, but on cooling there is initial broadening and finally collapse of these peaks at $T_{\rm c} = -70^{\circ}$ C. Further cooling to -90° C does not allow observation of the slow exchange limit. The data suggest that at higher temperatures the two internal NBu^t and μ -NBu^t groups are exchanging positions very rapidly and the two peaks observed are due to "external" and "internal" imido groups. There is only a single ¹⁹F resonance for the bridging fluoride groups at all temperatures.

(d) Interaction of $Re(NBu^{t})_{3}Cl$ and $SbCl_{5}$ in MeCN. This reaction also leads to the loss of an NBu^t group and the formation of the rhenium(VII) complex $[Re(NBu^{t})_{2}Cl_{2}(MeCN)_{2}]SbCl_{6}$ (6). The complex could be formed by chlorination of an NBu^t group by $SbCl_{5}$, similar to the conversion of $Re(NBu^{t})_{3}(OSiMe_{3})$ to $Re(NBu^{t})_{2}Cl_{3}$ noted above [and to the reaction of Cl_{2} with $Cr^{VI}(NBu^{t})_{2}Cl_{2}$ which leads¹⁰ to $Cr^{V}(NBu^{t})Cl_{3}$], and possibly $Bu^{t}NCl_{2}$. An alternative route is the following:

 $Re(NBu^{t})_{3}Cl + SbCl_{5} \longrightarrow Re(NBu^{t})_{3}^{+}SbCl_{6}^{-}$ $Re(NBu^{t})_{3}^{+} + SbCl_{5} + 2MeCN \longrightarrow$ $[Re(NBu^{t})_{2}Cl_{2}(MeCN)_{2}]^{+} + Bu^{t}N \Longrightarrow SbCl_{3}.$

Although $Bu^tN = SbCl_3$ is not known it would be similar to $Bu^tN = TaCl_3$.

Compound 6 is also available essentially quantitatively by chloride abstraction in refluxing MeCN according to the stoichiometry:

$$Re(NBu^{t})_{2}Cl_{3} + 2MeCN + SbCl_{5} \longrightarrow$$
$$[Re(NBu^{t})_{2}Cl_{3}(MeCN)_{2}]SbCl_{4}.$$

The salt crystallizes from MeCN as large, deep orange-red crystals that are soluble in MeCN, THF, CH₂Cl₂ and CHCl₃; it is a 1:1 electrolyte in MeCN. The IR spectrum shows two stretches for the *cis* nitriles at 2292 and 2319 cm⁻¹ that are above the value for free MeCN (2255 cm⁻¹), indicating the absence of M—N π -bonding (which may lower the CN stretching frequency¹³) as can be expected with the high oxidation state of rhenium.

Although an X-ray study confirmed the general features, difficulties in refinement due to disorder

problems preclude detailed discussion. The IR and NMR spectra, which show equivalence of the NBu^t groups, suggest an octahedral structure with *cis*-MeCN and Bu^tN groups and *trans*-chlorines.

Attempts to isolate the triply-coordinated ion $[Re(NBu^{1})_{3}]^{+}$ have been unsuccessful. The interaction between $Re(NBu^{1})_{3}Cl$ in $CH_{2}Cl_{2}$ and $AlCl_{3}$ leads to $Re(NBu^{1})_{2}Cl_{3}$ (cf. above) as the only rhenium-containing product and there is no evidence for $[Re(NBu^{1})_{3}]AlCl_{4}$. An aluminium-containing product appears to be $[AlCl(NBu^{1})]_{n}$ for which analogues, e.g. $[AlCl(NPr^{1})]_{6}$ are known.¹¹ The attempted removal of $Bu^{1}NH_{2}$ from the cation $[(Bu^{1}N)_{3}Re(NH_{2}Bu^{1})]^{+}$ by refluxing its salt (described below) in toluene¹² also failed.

(2) Protonation of Re(NBu^t)₃(NHBu^t)

The interaction of this amide³ with trifluoromethanesulphonic acid leads to the specific protonation of the amido nitrogen atom and the formation of the cation $[(\text{Re}(\text{NBu}^{t})_{3}\text{NH}_{2}\text{Bu}^{t}]^{+}$, which is isolated as the triflate (7). The basicity of the amido nitrogen will be greater than that of the imido nitrogens since the lone pairs on the latter are involved in π -bonding Bu'N=Re to a greater extent than is the case for Bu'HN \Rightarrow Re. Similar behaviour has been observed for W(NBu^t)₂(NHBu^t)₂, where NHBu^t protonation of the amido ligand gives *cis,cis,trans*-W(NBu^t)₂(η^{1} -OTf)₂(NH₂Bu^t)₂.¹⁴ The rhenium compound is a 1:1 electrolyte in CH₂Cl₂ or MeCN, although after ca 5 min reaction with MeCN begins to occur. The cationic nature contrasts with the structure of the tungsten compound, which has oxygen-bound η^{1} -triflate groups, possibly due to the reluctance of rhenium(VII) to be five- or six-coordinate when three bulky NBu^t groups are present. The compound is readily hydrolysed by moisture. The IR spectrum of the solid has a band at 1250 cm⁻¹ assignable to CF₃SO₃⁻¹⁵.

The X-ray crystal structure of the cation is shown in Fig. 2, data is given in Table 3. The geometry at rhenium deviates from tetrahedral with the angles subtended by N(1) and N(2) and by N(3) and N(4), both contracted at 102° whilst the remainder are all slightly enlarged at 113°. There are marked differences in the Re-N bond lengths which range from 1.724(8) Å for N(1) to 1.849(9) Å for N(2). There are concomitant differences in the degree of bending at nitrogen, ranging from 164.6(8)° at N(1) to $139.8(7)^{\circ}$ at N(2). In fact, the relationship between Re-N distance and angle at nitrogen is almost linear. The dominance of the scattering by the rhenium atom coupled with the disorder in the F_3CSO_3 anion prevented the location of the NH₂ hydrogen atoms. However, the length of the Re-N(2) bond and the associated angle at nitrogen indicates N(2) as the most likely site for protonation. This conclusion is further strengthened by inspection of the packing of the anion and cation in the crystal (Fig. 3). Here we see that one of the oxygen atoms [O(2)] of the anion is inserted into a cleft between N(2) and N(1)in the cation at a distance of 3.06 Å from N(2).



Fig. 2. The structure of the $[Re(NBu^{t})_{3}(NH_{2}Bu^{t})]^{+}$ ion in the trifluoromethanesulphonate.

Re-N(1)	1.724(8)	ReN(2)	1.849(9)	
ReN(3)	1.761(10)	Re-N(4)	1.805(10)	
N(1)—Re—N(2)	102.2(4)	N(1)—Re—N(3)	113.0(4)	
N(2)—Re— $N(3)$	113.5(5)	N(1)—Re— $N(4)$	113.2(5)	
N(2)—Re— $N(4)$	113.2(4)	N(3)—Re— $N(4)$	102.1(5)	
Re-N(1)-C(1)	164.6(8)	Re-N(2)-C(2)	139.8(7)	
Re-N(3)-C(3)	152.6(8)	Re-N(4)-C(4)	146.0(8)	

Table 3. Bond lengths (Å) and angles (°) for (7) with e.s.d.s in parentheses

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This is compatible with the formation of a weak cation \cdots anion N—H \cdots O hydrogen bond [the N(1) \cdots O(2) distance is 3.7 Å]; N(3) and N(4) are not approached in this way.

Attempts to substitute the $Bu'NH_2$ ligand with various bases such as PMe_3 or PMe_2Ph by reactions in CH_2Cl_2 solution gave mixtures. However, triphenylphosphine gave the salt [Re(NBu')₃(PPh₃)] O₃SCF₃ (8).

Attempts to obtain the hydride $\text{ReH}(\text{NBu}^{t})_{3}$ by action of NaH or KH on $[\text{Re}(\text{NBu}^{t})_{3}(\text{NH}_{2}\text{Bu}^{t})]^{+}$ in THF gave only the neutral amido complex by deprotonation. Similarly, thermal decompositions of alkyls such as $\text{Re}(\text{NBu}^{t})_{3}\text{Et}^{4}$ or $\text{Re}(\text{NBu}^{t})_{3}(\text{O}^{t}\text{Pr})$ and treatment of $\text{Re}(\text{NBu}^{t})_{3}\text{Cl}$ with various hydrides, boro- and aluminohydrides also failed, as did the reaction of H₂ in the presence of Et₃N in hexane.

(3) Substitution reactions of $Re(NBu^{t})_{3}X$, X = Clor $OSiMe_{3}$

(a) Dialkyl- and arylimido compounds. The interaction of $Re(NBu^{t})_{3}Cl$ and $LiNMe_{2}$ in $Et_{2}O$ leads



Fig. 3. Space-filling representation of the cation and anion in [Re(NBu^t)₃(NH₂Bu^t)]SO₃CF₃.

to the dimethylamido complex 9 as a yellow, highboiling oil. A similar reaction using the siloxide gave a red solution from which no well-defined product could be isolated. However, the siloxide and LiNPh₂ react cleanly to give Re(NBu^t)₃(NPh₂) (10) as yellow crystals. Both amides are moderately airand moisture-sensitive. It is of interest that while the oxo analogue ReO₃[N(mes)₂], whose crystal structure was determined, was formed by interaction of ReO₂(mes)₂ with nitric oxide via an oxygen transfer to rhenium and a double aryl migration to the nitrogen atom,¹⁶ the reaction of Re(NBu^t)₂ (mes)₂ with NO gives [Re(NBu^t)(O)(mes)(μ -O)]₂ and Bu^tN=Nmes.²

In the ¹H NMR spectrum of Re(NBu¹)₃(NPh₂) there are two multiplets for the aromatic protons (centred at 7.00 and 7.23 ppm). There is no temperature dependency from -90 to $+100^{\circ}$ C unlike that found in ReO₃[N(mesityl)₂].¹⁶ For the dimethylamido complex the methyl resonance occurs at 3.35 ppm as a singlet.

(b) Dialkyl and arylphosphido complexes. There is a marked difference between the reactivities of $Re(NBu^{t})_{3}X$ (X = Cl or OSiMe₃) and those of lithium phosphido reagents. Reaction of the chloride with LiPPh₂ gives [Ph₂P]₂ as the only identifiable product; this was characterized by its NMR spectrum $\binom{^{31}P{^{1}H}}{=} 15.12 \text{ ppm in } C_6D_6$ and m.p. (120°C).¹⁷ Re(NBu^t)₃(OSiMe₃) reacts cleanly with $LiPR_2$ (R = Ph, SiMe₃) and LiPH(mes) in Et_2O at 78°C to give the corresponding phosphido complexes: $Re(NBu^{t})_{3}PPh_{2}$ (11), $Re(NBu^{t})_{3}P(SiMe_{3})_{2}$ (12) and Re(NBu^t)₃PH(mes) (13). The diphenylphosphido complex is obtained as an oil from hexane, but can be crystallized from MeCN as a yellow crystalline solid in ca 40% yield. The complexes Re(NBu^t)₃P(SiMe₃)₂ and Re(NBu^t)₃ PH(mes) are obtained as yellow-orange solids from hexane in yields of ca 60 and 45%, respec-



Fig. 4. The structure of Re(NBu^t)₃(PPh₂).

tively. All three compounds have low melting points, are soluble in all common organic solvents, and are moderately air- and moisture-sensitive.

The structure of the diphenylphosphido compound 11 is shown in Fig. 4; data are in Table 4. The compound crystallizes with two crystallographically-independent molecules in the asymmetric unit. Both molecules have nearly identical conformations, the only major difference being in the orientation of one of the tert-butyl groups [C(2)]. The geometry at rhenium is distorted tetrahedral with angles ranging from 99.7(2) to 115.2(3)° in one molecule and from 99.3(3) to 116.2(3)° in the other. The Re—N distances do not differ significantly and are in the range 1.732(7)-1.748(8) Å. The angles at nitrogen reflect an almost equal degree of bending with values between 153.2(6) and 158.7(7)°. It is interesting to note that these values fit the bond length/angle correlation observed above in the [Re(NBu^t)₃(NH₂Bu^t)]⁺

Re(1) - N(1) = 1.743	5(7)	Re(1)— $N(2)$	1.748(8)
Re(1)—N(3) 1.732	2(7)	Re(1) - P(1)	2.446(2)
P(1)-C(46) 1.853	3(8)	P(1)-C(56)	1.852(7)
Re(1') - N(1') = 1.743	3(6)	Re(1') - N(2')	1.744(7)
Re(1')-N(3') 1.732	2(7)	Re(1') - P(1')	2.445(2)
P(1')—C(46') 1.850	5(6)	P(1')—C(56')	1.834(7)
N(1) - Re(1) - N(2)	114.1(4)	N(1)-Re(1)-N(3) 114.8(3)
N(2) - Re(1) - N(3)	115.2(3)	N(1) - Re(1) - P(1)	1) 107.6(2)
N(2) - Re(1) - P(1)	103.2(2)	N(3) - Re(1) - P(1)	1) 99.7(2)
Re(1) - N(1) - C(1)	154.9(7)	Re(1) - N(2) - C(2)	2) 156.1(6)
Re(1) - N(3) - C(3)	157.0(7)	Re(1) - P(1) - C(4)	6) 102.9(2)
Re(1) - P(1) - C(56)	104.6(2)	C(46) - P(1) - C(5)	56) 102.2(3)
N(1') - Re(1') - N(2')	114.5(3)	N(1') - Re(1') - N	1(3') 116.2(3)
N(2') - Re(1') - N(3')	115.3(3)	N(1')— $Re(1')$ — P	(1') 100.8(2)
N(2') - Re(1') - P(1')	107.9(2)	N(3') - Re(1') - P	(1') 99.3(3)
Re(1')-N(1')-C(1')	158.7(7)	Re(1')-N(2')-C	2(2') 153.2(6)
Re(1') - N(3') - C(3')	154.1(7)	Re(1') - P(1') - C	(46') 102.6(2)
Re(1') - P(1') - C(56')	104.2(2)	C(46')P(1')C	(56') 104.4(3)
	and the second s		

Table 4. Bond lengths (Å) and angles (°) for (11) with e.s.d.s in parentheses

cation. The two Re—P distances are 2.446(2) and 2.445(2) Å and the angles at phosphorus are all less than tetrahedral ranging between 102.2(3) and $104.6(2)^{\circ}$. The pyramidal geometry at phosphorus is in agreement with the NMR data given below.

Terminal dialkyl or aryl phosphido complexes are relatively rare;¹⁸ for rhenium there is the homoleptic anion,^{18c} [Re(PCy₂)₄]⁻, where Cy = cyclohexyl. The IR and NMR spectra of 11 are in accord with the structure found in the crystal. The ¹H NMR spectrum shows two multiplets (centred at 7.86 and 7.14 ppm) for the aromatic protons and a singlet for the NBu^t protons (at 1.26 ppm); there is no temperature dependency from -90 to $+100^{\circ}$ C. The ³¹P NMR spectrum shows a quintet centred at -8.78 ppm, due to the coupling of the four *ortho*hydrogen nuclei on the phenyl rings with the ³¹P nucleus $({}^{4}J(P-H) = 7 Hz)$; decoupling the proton resonances gives a sharp singlet at -8.78 ppm. The shifts are in the region characteristic for $M-PR_2$ single-bonded compounds with pyramidal geometry.18e

For Re(NBu¹)₃P(SiMe₃)₂, the SiMe₃ protons are split into a doublet by the phosphorus nucleus $({}^{3}J(P-H) = 4.5 \text{ Hz})$. The ${}^{31}P\{{}^{1}H\}$ NMR spectrum has a singlet at -212.33 ppm. The ${}^{1}H$ NMR spectrum of Re(NBu¹)₃PH(mes) shows a doublet centred at 5.37 ppm for the phosphido proton $({}^{1}J(P-H) = 195 \text{ Hz})$. The same coupling constant is observed in the ${}^{31}P$ NMR spectrum of the complex where the doublet is centred at -153.1 ppm.

Attempts to deprotonate $\text{Re}(\text{NBu}^{t})_{3}P(\text{H})(\text{mes})$ (13) in the hope of obtaining a phosphinidine¹⁹ species, $[(\text{Bu}^{t}\text{N})_{3}\text{Re}=P(\text{mes})]^{-}$, by interaction with Bu^{t}Li in hexane or MeLi in Et_{2}O or by refluxing in toluene with Et_{3}N were unsuccessful. Although deprotonation occurs, other reactions followed and the only rhenium-containing species isolated was the rhenium(VI) dimer $[\text{Re}(\text{NBu}^{t})_{2}(\mu-\text{Bu}^{t}\text{N})]_{2}$, whose structure has been determined.³ From the reaction of 13 with one equiv. of Bu^{n}Li in hexane the only other product that could be isolated was a colourless, crystalline solid that has been found to be the new cyclophosphane $[P(2,4,6-\text{Me}_{3}\text{C}_{6}\text{H}_{2})]_{3}$.

Cyclophosphanes, $(PR)_n$ (n = 3-6), are known.²⁰⁻²² The trimers, with bulky R groups have two of the R groups on one side of the P₃ plane. The ³¹P{¹H} spectrum of (Pmes)₃ has two singlets at -111.20 and -118.35 ppm in a 2 : 1 ratio that are in close agreement with values reported for similar compounds.

The mechanism of this reaction leading to the formation of the rhenium(VI) dimer and the cyclophosphane is not clear. The oily, lithium-containing residue has eluded characterization. It is of interest that phosphinidine intermediates have been proposed²² in the synthesis of metal compounds such as $[(CO)_5Cr]_3(PBu)_3$.

(c) Phosphiniminato compound. The interaction between Re(NBu¹)₃Cl and a slight excess of LiNPPh₃ in refluxing toluene gives the phosphiniminato complex Re(NBu¹)₃(N==PPh₃) (14). The resonance form Re---N==PPh₃ rather than others such as Re⁻==N⁺==PPh₃ appears to be the main contributor since the IR band at 1094 cm⁻¹ is at the lower limit of the ν (P---N) region (1052-1200 cm⁻¹) for such complexes.^{23a} The only other related rhenium(VII) compound is Re[N(2,6-ⁱPr₂C₆H₃)]₃ (N==PPh₃), whose X-ray structure was recently reported: it was made by the interaction between Ph₃PNReO₃ and the aryl isocyanate.^{23b}

(d) Pyrazolate. The interaction of $Re(NBu^{1})_{3}Cl$ with the sodium salt of pyrazole in THF gives $Re(NBu^{1})_{3}(C_{3}H_{3}N_{2})$ (15). The mass spectrum indicates that the compound is monomeric in the gas phase; the ¹H NMR spectra shows a singlet for the NBu^t protons and an ABC pattern for the $C_{3}H_{3}N_{2}$ protons; the ratio is 9:1 as expected.

EXPERIMENTAL

The general techniques and instruments used have been described.^{3,24} All compounds and operations were carried out under purified nitrogen, argon or *in vacuo*. Commercial chemicals were from Aldrich. NMR spectra (250 MHz) are in ppm (δ) in C₆D₆ unless otherwise stated and referenced to Me₄Si (¹H), CFCl₃ (¹⁹F) and external H₃PO₄ (³¹P). IR spectra (in cm⁻¹) are in Nujol mulls. Electron impact mass spectra (*m*/*z*) show isotropic envelopes for the rhenium-containing ions but only peaks corresponding to those with ¹⁸⁷Re (62.5%) are listed.

The compounds $Re(NBu^t)_3(OSiMe_3)^5$ and $Re(NBu^t)_3Cl^3$ were made as described. The previously undescribed tert-butoxide and isopropoxide have been made from the chloride as below.

The reagents LiNMe₂, LiNPh₂, LiPPh₂ and LiPH(mes) were prepared by the standard method of interaction of the corresponding amine or phosphine with one equiv. of BuⁿLi in hexane at -78° C. LiP(SiMe₃)₂ was prepared by the interaction of P(SiMe₃)₃ with BuⁿLi in THF at -40° C. LiN=PPh₃ was prepared from HN=PPh₃²⁵ and one equiv. of BuⁿLi in toluene at -78° C. The sodium salt of pyrazole was made by adding a suspension of NaH in THF to a solution of pyrazole at -78° C; the solution was stirred for 30 min at room temperature, filtered, evaporated and the residue washed with hexane (3 × 30 cm³).

Tris(*tert-butylimido*)*tert-butoxo*)- and -(*isopropoxo*) rhenium(VII)

To a mixture of $\text{Re}(\text{NBu}^{t})_{3}\text{Cl}(0.44 \text{ g}, 1 \text{ mmol})$ and $\text{KOBu}^{t}(0.11 \text{ g}, 1 \text{ mmol})$ at -20°C was added cold $\text{Et}_{2}\text{O}(20 \text{ cm}^{3})$; the yellow solution was allowed to warm and was then stirred for 15 h at ambient temperature. After filtration and removal of the solvent, extraction with hexane (5 cm³) and cooling gave yellow needles. Yield: 0.34 g, 71%; m.p. 55– 56°C. Found: C, 40.7; H, 7.6; N, 9.0%. M.S. 473 (18%), Re(NBu^t)_3(OBu^t); 402 (100%), Re(NBu¹)_2 (OBu^t). NMR: ¹H: 1.34 (s, 27H, OBu^t); 1.25 (s, 9H, OBu^t).

The *isopropoxide* was made similarly. Yield : *ca* 82%, b.p. 100–120° at *ca* 0.15 mm Hg. M.S. 457 (M⁺), 442 (M—Me); 400 (M—Me₂C=CH₂); 386 (M—NBu'). IR : 1220 cm⁻¹, ReNBu'. NMR : ¹H : 1.35 (*s*, 27H, NCMe₃); 1.30 (d, 6H, Me₂CH); 450 (sept., ¹H, CHMe₂).

Bis[bis(tert-butylimido)(η^1 -cyclopentadienyl)rhenium (VII)](μ -oxo)(μ -cyclopentadienylidene) (1)

To ReCl(NBu¹)₃ (0.45 g, 1 mmol) in Et₂O (20 cm³) at -78° C was added a THF solution of NaC₅H₅ (1.12 cm³ of 0.98 M solution, 1.1 mmol) and the mixture was allowed to warm to ambient temperature when the colour changed from orange to brown. After stirring for 1 h the volatiles were removed *in vacuo* and the residue extracted with hexane (3 × 10 cm³); the orange extracts were concentrated and cooled (-20° C, 12h) to give orange prisms. Yield: 0.065 g, 15%. M.S. 736(1), Re₂ (NBu¹)₄(O)(C₅H₅); 458 (45), Re(NBu¹)₂(C₅H₅)₂; 443 (100), Re(NBu¹)(C₅H₅)-CH₃; 410 (32), Re(NBu¹)₂(O)(C₅H₅). NMR: ¹H (20°C, CD₂Cl₂): 1.35 (s, 18H) and 1.32 (s, 18H) NCMe₃; 5.85 (m, 4H, μ -C₅H₄); 6.2 (s, 8H, η ¹-C₅H₅).

Bis[*bis*(*tert* - *butylimido*)(*trimethylsiloxo*)*rhenium*(VII)] (μ-oxo)-(μ-trimethylsiloxo)(μ-trifluoroacetato) (**2**)

To a suspension of AgO₂CCF₃ (0.11 g, 0.5 mmol) in THF (30 cm³) at -78° C was added a solution of Re₃(NBu¹)₄(O)₅(OSiMe₃)₃⁵ (0.45 g, 0.38 mmol) in THF (20 cm³). After stirring at room temperature (12 h) the solution was evaporated and extracted with hexane (2 × 20 cm³). Concentration (10 cm³) and cooling (-20° C) gave yellow crystals, some of X-ray quality. Yield: 0.18 g (44%). IR: 1682 (ν_{asym} OCO); 1454 (ν_{sym} OCO); 1203 (NBu¹). The values of the symmetric and asymmetric carboxylate stretches and the separation $\Delta = 228$ cm⁻¹ are similar to those in other bridged trifluoroacetates.²⁶ NMR (CDCl₃): ¹H: 1.42 (s, 26H, NBu^t); 0.25 (s, 9H, μ -OSiMe₃); 0.13 (s, 18H, OSiMe₃). ¹⁹F: 57.72 (s).

Bis[bis(tert-butylimido)rhenium(V)](μ -trimethylsiloxo) (μ -trifluoroacetato) (3)

To a suspension of AgO₂CCF₃ (0.2 g, 1.27 mmol) in THF (30 cm³) at -78° C was added a solution of Re(NBu^t)₃(OSiMe₃) (0.5 g, 1.02 mmol) in THF (10 cm³). After warming and stirring at room temperature for *ca* 18 h, the solution was evaporated *in vacuo* and the residue extracted with hexane (2 × 20 cm³). Concentration (to 10 cm³) of the filtered extract and cooling (-20° C) gave a yellow crystalline solid. Yield: 0.57 g, 65%. IR : 1674, 1450 cm⁻¹ (asym and sym vOCO, $\Delta = 224$ cm⁻¹); 1208 (NBu^t). NMR (CDCl₃): ¹H : 1.44 (s, 36H, NBu^t); 0.13 (s, 9H, OSiMe₃). ¹⁹F : 60.18 (s).

 $Bis[bis(tert-butylimido)chlororhenium(VII)(\mu-tert$ $butylimido)(\mu-fluoro)(tert-butylimido)rhenium(IV)(\mu$ fluoro)]tetrafluoroborate (4) and hexafluorophosphate (5)

To a solution of $AgBF_4$ (0.15 g, 0.76 mmol) or AgPF₆ (0.19 g, 0.75 mmol) in CH₂Cl₂ (15 cm³) was added Re(NBu^t)₃Cl (0.3 g, 0.7 mmol) in CH₂Cl₂ (20 cm³) when a white precipitate (AgCl) formed immediately. After stirring in the dark for 4 h, the volatiles were removed in vacuo and the residue washed with Et₂O (3×20 cm³). Extraction of the residue with CH_2Cl_2 (2 × 10 cm³) and concentration to 2-3 cm³, followed by layering with Et_2O gave yellow prisms after ca 24 h at room temperature. Yield: ca 20%. NMR (CDCl₃): ¹H: 1.65 (terminal NBu^t); 1.61 (internal and bridge NBu^t). ${}^{19}F: BF_4^$ salt, $-150 (BF_4^{-})$; $-126 (\mu$ -F). ¹⁹F: PF₆⁻ salt, $-75 (d, J(P-F) = 713 Hz, equatorial F of PF_6^-);$ $-80 (d, J(P-F) = 986 Hz, axial F of PF_6); -135$ (μ-F).

Bis(tert-butylimido)dichlorobis(acetonitrile)rhenium (VII)hexachloroantimonate(V) (**6**)

To Re(NBu¹)₃Cl (0.4 g, 0.92 mmol) in MeCN (30 cm³) was added SbCl₅ (1 cm³ of 1 M solution in CH₂Cl₂) and the solution refluxed (*ca* 12 h) and evaporated. The residue was washed with Et₂O (2 × 30 cm³) and extracted into MeCN (2 × 10 cm³); concentration and cooling gives bright orange-red crystals. Further crops may be obtained from the supernatant. Overall yield: 0.54 g (72%). Conductivity (MeCN): $\Lambda_{\rm M} = 111 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$. IR :

2319, 2292 (MeCN); 1200 (NBu^t); 337 vs (SbCl₆⁻). NMR : ¹H : 1.64 (s, Bu^tN); 2.22 (s, MeCN).

The compound is obtained similarly from stoichiometric amounts of $\text{Re}(\text{NBu}^t)_2\text{Cl}_3^{27}$ and SbCl_5 in MeCN with an essentially quantitative yield.

Tris(tert-butylimido)(tert-butylamine)rhenium(VII) *trifluoromethanesulphonate* (7)

To a solution of Re(NBu^t)₃(NHBu^t)³ (0.5 g, 1.05 mmol) in Et₂O (30 cm³) at -78° C was added dropwise with stirring a pre-cooled solution of CF₃SO₃H (0.1 cm², 1.17 mmol in 20 cm³ Et₂O). The yellow solution was stirred for 1 h and then allowed to warm slowly. The yellow precipitate was collected, washed with Et₂O (2×10 cm³) and crystallized from CH₂Cl₂-Et₂O (1:2) at -20° C as yellow prisms. Yield: 0.29 g, 45%. IR: 3177 (*H*₂NBu^t); 1250 (CF₃SO₃⁻); 1210 (NBu^t). NMR (CDCl₃): ¹H: 1.45 (s, 27H, NBu^t); 1.39 (s, 9H, H₂NBu^t). ¹⁹F: -82.0. Conductivity (CH₂Cl₂): $\Lambda_{\rm M} = 141 \,\Omega^{-1} \, {\rm cm}^2 \, {\rm mol}^{-1}$ (cf. Buⁿ₄NPF₆ under the same conditions, $\Lambda_{\rm M} = 145 \,\Omega^{-1} \, {\rm cm}^2 \, {\rm mol}^{-1}$.

Tris(tert-butylimido)(triphenylphosphine)rhenium (VII)trifluoromethanesulphonate (8)

To a solution of the above amine complex (0.2 g, 0.32 mmol) in CH₂Cl₂ (20 cm³) was added PPh₃ (0.1 g, 0.4 mmol) when the colour changed from yellow to orange. After stirring for 2 h the volatiles were moved *in vacuo* and the residue washed with Et₂O (3×30 cm³) and recrystallized as orange needles from CH₂Cl₂ after addition of Et₂O at -20° C. Yield: 0.14 g, 55%. IR: 1255 (CF₃SO₃); 1210 (NBu¹). NMR (CDCl₃): ¹H: 1.25 (s, 27H, NBu¹); 7.3 (m, 15H, PPh₃). ³¹P{¹H}: 34.83. ¹⁹F: -79.0.

Tris(tert-butylimido)(dimethylamido)rhenium(VII) (9)

To a solution of Re(NBu¹)₃Cl (0.45 g, 1.03 mmol) in Et₂O (20 cm³) at -78° C was added a cold suspension of LiNMe₂ (0.07 g, 1.4 mmol) in Et₂O (30 cm³). After warming and stirring at room temperature for 5 h the solution was evaporated and the residue extracted with hexane (2 × 5 cm³). Evaporation of the extract left a yellow oil which was distilled under high vacuum at *ca* 150°C. Yield: 0.16 g, 35%. M.S. 444 (M); 429 (M—Me); 373 (M—NBu¹). IR: 1211 (NBu¹). NMR: ¹H: 3.35 [s, 6H, N(Me)₂], 1.37 (s, 27H, NBu¹).

Tris(tert-butylimido)(diphenylamido)rhenium(VII)(10)

As above but using Re(NBu^t)₃(OSiMe₃) (0.42 g, 0.86 mmol) in Et₂O (20 cm³) and LiNPh₂ (0.19 g, 1.10 mmol) in Et₂O (30 cm³). Concentration of the hexane extract and cooling (-20° C) gave yellow crystals. Yield: 0.26 g, 53%. M.S. 568 (M); 553 (M—Me); 497 (M—Bu^tN). IR: 1200 (NBu^t). NMR: ¹H: 7.00–7.23 (m, 10H, NPh₂); 1.29 (s, 27H, NBu^t).

Tris(tert-butylimido)(diphenylphosphido)rhenium(VII) (11)

As above but using Re(NBu^t)₃(OSiMe₃) (0.51 g, 1.04 mmol) in Et₂O (20 cm³) and LiPPh₂ (0.25 g, 1.30 mmol) in Et₂O (30 cm³). The hexane extracted (30 cm³) was evaporated and the residue crystallized from MeCN to give an orange–yellow crystalline solid. Yield: 0.24 g, 40%. M.S. 585 (M); 570 (M—Me); 555 (M-2Me); 514 (M—Bu^tN). IR: 1211 (NBu^t). NMR : ¹H : 7.14, 7.86 (m, 10H, PPh₂); 1.26 (s, 27H, NBu^t). ³¹P: -8.78 [quin. ⁴J(P—H) = 7 Hz; coupling to four *o*-H on C₆H₅ rings]. ³¹P{¹H}: -8.78 (s).

Tris(tert - butylimido)[bis(trimethylsilyl)phosphido]rhenium(VII) (12)

As above from Re(NBu¹)₃(OSiMe₃) (0.55 g, 1.13 mmol) in Et₂O (20 cm³) and Li[P(SiMe₃)₂] (0.26 g, 1.41 mmol) in Et₂O (20 cm³). Concentration of the hexane extract (20 cm,³) and work-up gave a yellow crystalline solid. Yield : 0.28 g, 43%. M.S. 577 (M); 562 (M—Me); 520 (M—Bu¹); 504 (M—SiMe₃); 406 (M—3 × Bu¹); 333 (M—3 × Bu¹SiMe₃). IR : 1211 (NBu¹). NMR : ¹H : 1.37 (s, 27H, NBu¹); 0.49 (d, 18H, SiMe₃, ³J(P—H) = 4.5 Hz). ³¹P{¹H}: -212.33 (s).

Tris(tert-butylimido)(mesitylphosphido)rhenium(VII) (13)

As above from Re(NBu^t)₃(OSiMe₃) (0.639 g, 1.29 mmol) but using LiPH(mesityl) (6.25 g, 1.58 mmol). The product is obtained from hexane as yellow crystals. Yield : 60%. M.S. 551 (M); 536 (M—Me); 478 (M—Me, HBu^t); 463 (M—2Me, Bu^t, H); 431 (M—mesityl, H). IR : 2328 (P—H), 1211 (NBu^t). NMR : ¹H : 1.27 (s, 27H, NBu^t); 2.16 (s, 3H, *p*-CH₃); 2.65 (s, 6H, *o*-CH₃); 5.37 [d, 1H, P—H, ¹J(P—H) = 195 Hz]; 6.78 (s, 2H, C₆H₂). ³¹P{¹H} : -153.16 (s). ³¹P : -153.1, 155.79 (d, J(P—H) = 195 Hz).

The interaction of stoichiometric amounts of 13

and BuⁿLi in hexane gave yellow $[(\text{Re}(\text{NBu}^{t})_{2}(\mu-\text{NBu}^{t})]_{2}$, ³ identified by m.p. and ¹H NMR spectrum, and colourless (Pmesityl)₃, which crystallized first, in yields 10–20%. Found : C, 71.5; H, 8.0; P, 20.5. Calc. for C₂₇H₃₃P₃: C, 72.0; H, 7.4; P, 20.6%. M.S. 450 (M); 330 (M—mesityl—H); M 302 [M—(mesP)₂]. For NMR see text.

Tris(tert-butylimido)(triphenylphosphineiminato)rhenium(VII) (14)

To Re(NBu^t)₃Cl (0.38 g, 0.87 mmol) in toluene (20 cm³) was added LiN=PPh₃ (0.30 g, 1.06 mmol) in toluene (20 cm³) and the solution refluxed for 12 h. After evaporation the residue was extracted into hexane (2 × 30 cm³) which was filtered, concentrated and cooled to give an orange-brown powder. Recrystallization from Et₂O gave a yellow crystalline solid. Yield: 0.2 g, 33%. M.S. 676 (M); 661 (M-Me); 646 (M-2Me); 605 (M-Bu^t); 400 (M-NPPh₃). IR: 1206 (NBu^t). NMR: ¹H: 7.02, 7.44 (m, 15H, Ph); 1.44 (s, 27H, NBu^t). ³¹P{¹H}: 15.28 (s).

Tris(tert-butylimido)pyrazolatorhenium(VII) (15)

To a solution of Re(NBu¹)₃Cl (0.56 g, 1.29 mmol) in THF (20 cm³) at -78° C was added a cold solution of sodium pyrazolate (from pyrazole and NaH in THF; 0.15 g, 1.67 mmol) in THF (30 cm³). After warming and stirring at room temperature (18 h) the solution was evaporated and extracted with hexane (2 × 20 cm³). Concentration (to 5 cm³), filtration and cooling (-20° C) gave orange-red crystals. Yield: 0.19 g, 32%. M.S. 464 (M—3H), 449 (M—3H—CH₃); 393 (M—3H—NBu¹). NMR (CDCl₃): ¹H: 7.18 (m, 1H, C₄H₃N); 7.59 (m, 1H, C₄H₃N); 5.95 (m, 1H, C₄H₃N); 1.53 (s, 27H, NBu¹).

X-ray crystallography

All three compounds were air-sensitive and were sealed in Lindemann glass capillaries under argon. Crystal data: (2) $C_{27}H_{63}F_3N_4O_6Re_2Si_3$, M =1053.5, monoclinic, a = 9.895(1), b = 22.603(4), c = 10.383(1) Å, $\beta = 109.77(1)^{\circ}$, V = 2185 Å³, space group $P2_1/m$, Z = 2 (the complex has crystallographic C_s symmetry), $D_c = 1.60$ g cm⁻³, copper radiation, $\lambda = 1.54178$ Å, $\mu(Cu-K_a) =$ 115 cm⁻¹, F(000) = 1040. Data were measured on a Nicolet R3m diffractometer with Cu- K_{α} radiation (graphite monochromator) using ω -scans. A crystal of dimensions $0.03 \times 0.18 \times 0.38$ mm was used. 3046 independent reflections ($2\theta \leq 116^{\circ}$) were measured, of which 2252 had $|F_0| > 3\sigma(|F_0|)$, and were considered to be observed. The data were corrected for Lorentz and polarization factors; a numerical absorption correction (face-indexed crystal) was applied; maximum and minimum transmission factors were 0.677 and 0.141. The structure was solved by the heavy-atom method. The nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized, C-H = 0.96 Å, assigned isotropic thermal parameters, U(H) = 0.08, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by fullmatrix least-squares to R = 0.064, $R_w = 0.058$ $[w^{-1} = \sigma^2(F) + 0.00050F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 2.32 and -1.87 e Å⁻³, respectively. The mean and maximum shift/errors in the final refinement were 0.000 and 0.000, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system and on an IBM 386 PC using SHELXTL PC.

Crystal data: (7) $C_{17}H_{38}F_{3}N_{4}O_{3}ReS$, M =621.8, monoclinic, a = 15.495(5), b = 11.208(5), c = 16.034(11) Å, $\beta = 105.48(4)^{\circ}$, V = 2684 Å³ space group $P2_1/a$, Z = 4, $D_c = 1.54$ g cm⁻³, copper radiation, $\lambda = 1.54178$ Å, $\mu(Cu-K_{\alpha}) = 96$ cm^{-1} , F(000) = 1240. Data were measured as above for a crystal of dimensions $0.17 \times 0.20 \times$ 0.33 mm. 3625 independent reflections ($2\theta \le 116^\circ$) were measured, of which 2969 had $|F_{o}| >$ $3\sigma(|F_0|)$, and were considered to be observed. The data were corrected for Lorentz and polarization factors; an empirical absorption correction (ellipsoidal) based on 309 azimuthal measurements was applied; maximum and minimum transmission factors were 0.367 and 0.206. The structure was solved by the heavy-atom method. The non-hydrogen atoms were refined anisotropically. The triflate ion was disordered about the C-S axis and was refined with two rigid body orientations for both the CF₃ and SO₃ groups. The amine hydrogen atoms could not be located. The positions of the idealized. hydrogen atoms were remaining C-H = 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by blockcascade full-matrix least-squares to R = 0.046, $R_{\rm w} = 0.045 \ [{\rm w}^{-1} = \sigma^2(F) + 0.00054F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 0.75 and -0.61 e Å⁻³, respectively. The mean and maximum shift/error in the final refinement were 0.047 and 0.465, respectively. Computations were carried out as above.

Crystal data: (11) $C_{24}H_{37}N_3PRe$, M = 584.8, triclinic, a = 10.430(2), b = 10.319(3), c = 26.227(10)Å, $\alpha = 91.23(3)$, $\beta = 94.23(3)$, $\gamma = 99.30(2)^\circ$, V = 2776 Å³, space group $P\overline{1}$, Z = 4 (2 crystallo-

graphically-independent molecules), $D_c = 1.40$ g cm⁻³, copper radiation, $\lambda = 1.54178$ Å, μ (Cu- K_{α}) $= 90 \text{ cm}^{-1}$, F(000) = 1168. Data were measured as above on a crystal of dimensions $0.17 \times$ 0.23×0.26 mm. 7485 independent reflections ($2\theta \leq$ 116°) were measured, of which 5868 had $|F_o| >$ $3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; a numerical absorption correction (face-indexed crystal) was applied; maximum and minimum transmission factors were 0.352 and 0.105. The structure was solved by the heavy-atom method. The non-hydrogen atoms were refined anisotropically. The phenyl rings together with their hydrogen atoms were refined as idealized rigid bodies. The methyl groups were also refined as idealized rigid bodies with a common refined-free variable isotropic thermal parameter for each tertbutyl group. Refinement was by blocked full-matrix least-squares to R = 0.043, $R_w = 0.047$ [w⁻¹ = σ^2 $(F) + 0.00147F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.89 and -0.79 e Å⁻³, respectively. The mean and maximum shift/error in the final refinement were 0.000 and 0.000, respectively. Computations were carried out as above.

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