The First d^0 Organoimido Complexes of Rhenium. *X*-Ray Crystal and Molecular Structure of μ-Oxo-μ-trimethylsilyloxo-μ-perrhenato-bis-(di-t-butylimidotrimethylsilyloxorhenium)

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Summary The novel complexes $Re(NBu^t)_3(OSiMe_3)$ and $Re_3(NBu^t)_4O_5(OSiMe_3)_3$ have been prepared and characterized; an *X*-ray crystal structure of the latter compound has been determined.

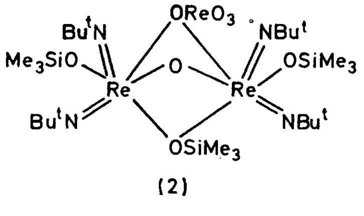
While d^0 organoimido complexes of the early third-row transition metals are known[1] for Hf, Ta, W, and Os, such derivatives have not been reported for rhenium. In contrast, examples of d^2 organoimido complexes containing Re^V abound.[2] We now report the preparation and characterization of the first Re^{VII} organoimido complexes.

Trimethylsilyl perrhenate[3] was treated with excess of butyltrimethylsilylamine[4] in hexane (48 h; 25 °C) [reaction (1)]. Solvent was distilled off, and the resultant yellow oil

$$Me_3SiOReO_3 + 3\ Bu^tNHSiMe_3 \rightarrow Me_3SiORe(NBu^t)_3 + 3\ Me_3SiOH \quad (1)$$

(1)

was distilled *in vacuo* then redissolved in hexamethyldisiloxane. Cooling to −40 °C afforded yellow needles of trimethylsilyloxotris-(*N*-t-butylimido)rhenium (**1**): (64%); m.p. 36—38 °C; δ (C_6D_6) 0·23 (9H, s) and 1·36 (27H, s). Compound (**1**) oxidizes trimethylphosphine to Me_3PO (toluene, 80 °C); treatment of (**1**) with aqueous NBu_4OH leads to gradual precipitation of $(NBu_4)(ReO_4)$ (0·5 h; 25 °C).



(2)

Reaction of trimethylsilyl perrhenate with an insufficient amount of $Bu^tNH(SiMe_3)$ afforded a yellow, low-melting solid (**2**) analysing for $Re_3(NBu^t)_4O_5(OSiMe_3)_3$. Compound (**2**) has been characterized by an *X*-ray crystal structure (Figure). Although the mechanism of its formation is not known, (**2**) may be rationalized as the product of silylation of the dimer $[(Me_3SiO)Re(NBu^t)_2O]_2$ by $Me_3SiOReO_3$.

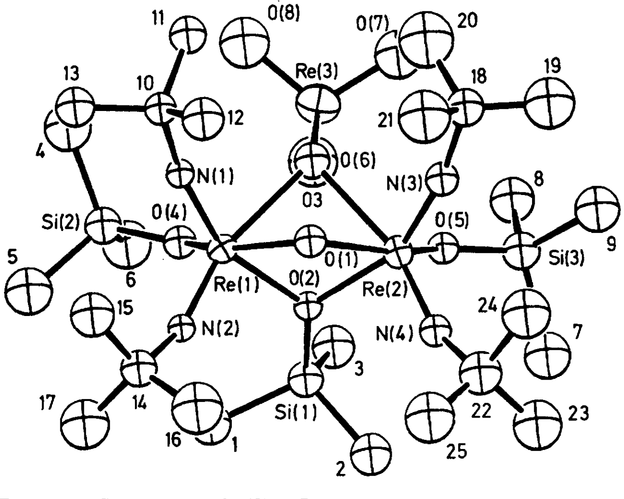


Figure. Structure of (**2**). Important bond distances and angles in the molecule are: Re(1)–N(1), 1·70(1); Re(1)–N(2), 1·72(1); Re(1)–O(1), 1·92(1); Re(1)–O(2), 2·12(1); Re(1)–O(3), 2·47(1); Re(1)–O(4), 1·93(1); Re(2)–N(3), 1·70(1); Re(2)–N(4), 1·69(1), Re(2)–O(1), 1·92(1), Re(2)–O(2), 2·15(1); Re(2)–O(3), 2·46(1); Re(2)–O(5), 1·91(1); Re(3)–O(3), 1·80(1); Re(3)–O(6), 1·74(1); Re(3)–O(7), 1·68(1); Re(3)–O(8), 1·70(1); and Re(1)–Re(2), 3·165(1) Å; ∠Re(1)–O(1)–Re(2), 110·8(5); ∠Re(1)–O(2)–Re(2), 95·6(4); ∠Re(1)–O(3)–Re(2), 80·0(3); ∠Re(1)–N(1)–C(10), 166·0(12); ∠Re(1)–N(2)–C(14), 152·6(12); ∠Re(1)–O(4)–Si(2), 144·3(7); ∠Re(2)–N(3)–C(18), 167·8(13); ∠Re(2)–N(4)–C(22), 154·9(13); and ∠Re(2)–O(5)–Si(3), 145·6(7)°.

The average Re–N bond length of 1·70(1) Å is close to the average Re–N distance (1·69 Å) for the four Re^{V} organoimido complexes which have been structurally characterized.[5] Although both Re(1) and Re(2) exhibit one markedly bent (av. 153·8°) and one more nearly linear (av. 166·9°) Re–N–C angle, all the t-butyl groups are apparently equivalent at 25 °C on the n.m.r. time scale.[6]

Crystal Data: $C_{25}H_{63}N_4O_8Re_3Si_3$, $M = 1190{\cdot}7$, orthorhombic, space group *Pbca*, at -47 °C, $a = 23{\cdot}489(6)$, $b = 19{\cdot}960(6)$, $c = 18{\cdot}269(6)$ Å, $Z = 8$, $D_c = 1{\cdot}847$ g cm^{-3}; Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å, $\mu = 5{\cdot}1$ cm^{-1}). Data were collected on a Syntex P3 diffractometer ($4° < 2\theta < 45°$) using the ω-scan technique. The structure was solved by direct methods and refined by the full-matrix least-squares technique. The positions of the hydrogen atoms were not located. The refinement of 203 variables (anisotropic thermal parameters for Re and Si, isotropic thermal parameters for O, N, and C) using 2520 reflections for which $I > 3{\cdot}0\ \sigma(I)$ yielded a conventional R index of 0·048. The ten largest peaks in the final difference-Fourier (0·79—0·94 e Å^{-3}) are associated with Re atoms or indicate a small amount of disorder among the various methyl groups.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 22721 (19 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* or *II*, Index Issues.

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[2] See for instance: J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012; R. Shandles and R. K. Murmann, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1869; J. F. Rowbottom and G. Wilkinson, *J.C.S. Dalton*, 1972, 826.

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