Synthesis and X-Ray Crystal Structure of the Rhenium(VII) *tert*-Butylimido Compound, $[Re(NBu^t)_2(\eta^1\text{-}C_5H_5)]_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$

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The interaction of NaC_5H_5 in tetrahydrofuran with a diethyl ether solution of $Re(NBu^t)_3Cl$ gives rise to a compound $[Re(NBu^t)_2(\eta^1\text{-}C_5H_5)]_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$ that has fluxional $\eta^1\text{-}C_5H_5$ groups, non-equivalent Bu^tN groups and a unique bridging C_5H_4 group; the structure has been elucidated by X-ray crystallography.

The reactions of alkyl, aryl and similar compounds of Li, Na, Mg, *etc.*, with transition metal halides, complex halides, alkoxides or oxides are often capricious. There are cases where there is no reaction, reduction occurs, reactions are solvent dependent, or influenced by trace impurities or oxygen; unexpected products may arise.

A recent example is the failure of Herrmann *et al.*[1] to obtain productive reactions of $Re(NBu^t)_3(OSiMe_3)$ with $C_5H_5^-$ (Na, Tl, $SnBu^n_3$) or $C_5Me_5^-$ (Li, K, MgCl). Using the chloride,[2] $Re(NBu^t)_3Cl$, in diethyl ether with NaC_5H_5 in tetrahydrofuran (THF) under argon at ambient temperature a facile reaction occurred but the anticipated[1] product $Re(\eta^5\text{-}C_5H_5)(NBu^t)_3$ was not formed. The air-sensitive orange crystals (m.p., 104–105 °C) isolated are of the compound **1** where a NBu^t group has been lost from Re, a μ-O bridge formed, probably by oxygen abstraction from THF, fluxional $\eta^1\text{-}C_5H_5$ groups[3] are bound to rhenium, and finally a unique $C_5H_4^{2-}$ group bridges the Re atoms. The latter can be regarded as a μ-alkylidene as in other $\mu\text{-}CR_2$ cases;[4] both hydrogens of the methylene group in cyclopentadiene are thus substituted by metal. Some $\mu\text{-}C_5H_4$ groups of different types are known with $\mu\text{-}\eta^5$ **2**[5a] or μ_3 **3**[5b] groups and bonding as in **4**.[5c] A compound with a μ-fluorenyl $(C_{13}H_8)$ ligand, $[\{Mo(\mu\text{-}C_{13}H_{18})(CO)(Cp)\}_2]$[5d] provides the closest analogue to the present $\mu\text{-}C_5H_4$ group.

The X-ray structure† of the rhenium compound is shown in Fig. 1. The molecule adopts non-crystallographic C_s symmetry with the plane of the bridging cyclopentadienylidene (C_5H_4) ring lying perpendicular to the Re(1)···Re(2) axis. The geometry at each 5-coordinate Re atom can probably best be described as distorted trigonal bipyramidal with the C(6)···C(7) and C(5)···C(7) vectors forming the principal axes.‡ The central $Re_2(C)(O)$ ring is folded with a dihedral

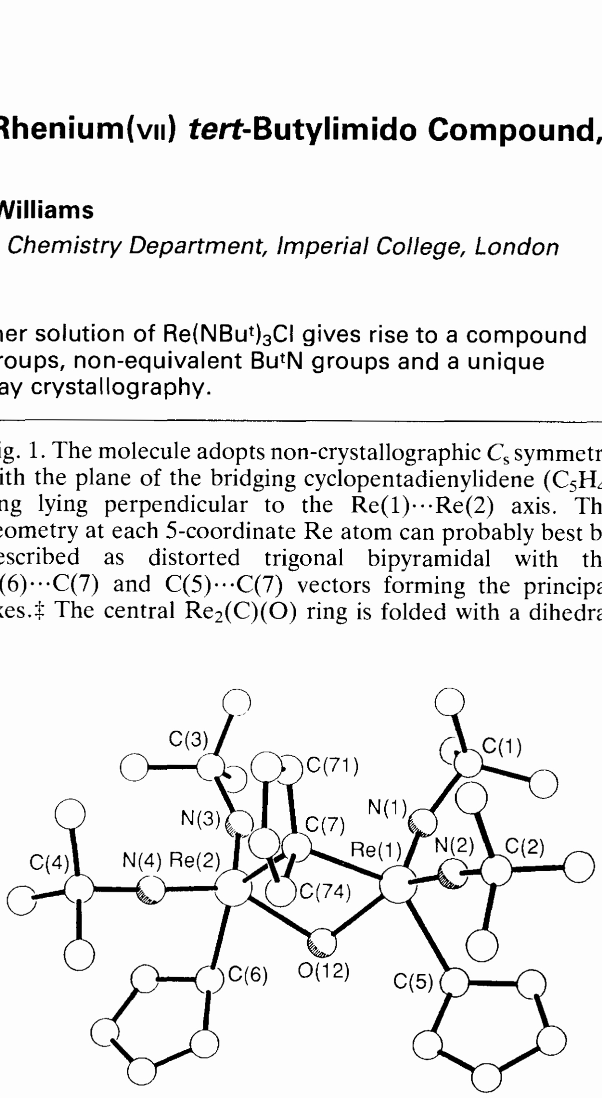

Fig. 1 Perspective view of $[Re(NBu^t)_2(\eta^1\text{-}C_5H_5)]_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$. Selected bond lengths (Å) and angles (°): Re(1)–N(1) 1.716(11), Re(1)–N(2) 1.715(12), Re(1)–C(5) 2.218(15), Re(1)–C(7) 2.155(13), Re(1)–O(12) 1.965(10), Re(2)–N(3) 1.692(11), Re(2)–N(4) 1.715(12), Re(2)–C(6) 2.210(16), Re(2)–C(7) 2.162(13), Re(2)–O(12) 1.979(10); Re(1)C(7)Re(2) 95.8(5), Re(1)O(12)Re(2) 108.7(5), C(7)Re(1)O(12) 72.8(5), C(7)Re(2)O(12) 72.4(5), N(1)Re(1)O(12) 108.0(5), N(3)Re(2)O(12) 110.2(5), N(2)Re(1)O(12) 142.9(5), N(4)Re(2)O(12) 136.8(6), C(5)Re(1)C(7) 142.8(5), C(6)Re(2)C(7) 145.1(5).

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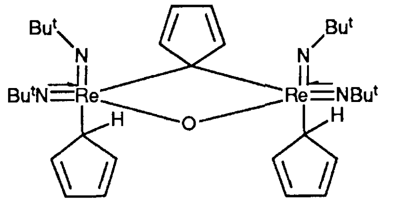
† *Crystal data* for $[Re(NBu^t)_2(\eta^1\text{-}C_5H_5)]_2(\mu\text{-}C_5H_4)(\mu\text{-}O)$: $C_{31}H_{50}N_4ORe_2$, $M = 867.2$, orthorhombic, $a = 12.873(2)$, $b = 14.955(2)$, $c = 17.711(3)$ Å, $V = 3410$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $\mu = 134$ cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy atom method and refined anisotropically using absorption corrected data to give $R = 0.042$, $R_w = 0.042$ for 2369 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \le 116°]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, issue No. 1.

‡ Re(1) lies 0.01 Å from the N(1)N(2)O(12) plane and Re(2) 0.02 Å from the N(3)N(4)O(12) plane.



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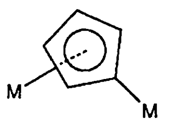

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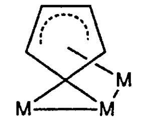

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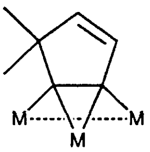

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angle of 30° about the C(7)···O(12) direction and 39° about Re(1)···Re(2). The transannular Re···Re and C···O distances are 3.20 and 2.45 Å respectively. The bonds from each Re atom to their pendant σ-Cp ring carbon atom are of the same length [2.218(15) and 2.210(16) Å to C(5) and C(6) respectively] and slightly longer than those to the bridging C_5H_4 carbon C(7) [2.155(13) and 2.162(13) Å respectively]. There are marked departures from tetrahedral geometry at C(7) with both the Re(1)C(7)Re(2) and C(71)C(7)C(74) angles noticeably contracted at 95.8(5) and 101.7(12)° respectively. All three C_5 rings have conventional localised diene bonding. Although all four rhenium to nitrogen bonds are of the same length [range 1.692(11) to 1.716(11) Å] there are marked differences in the angles at nitrogen.[6] These fall into two groups with those at N(2) and N(4) nearly linear [173.4(11) and 176.2(12)° respectively], and those at N(1) and N(3) appreciably bent [146.1(10) and 152.5(12)° respectively] with their N–C bonds oriented in an *anti* geometry with respect to the Re–O bridge bonds. The rhenium atom thus has an 18e configuration assuming one linear, triply and one bent, doubly bound NBu^t group (ref. 6 p. 22).

The ^1H NMR spectra§ of the compound over the range 20 to −70 °C show that the multiplet at δ 5.85 due to μ-C_5H_4 and also the two inequivalent NBu^t resonances are temperature independent but that the δ 6.2 signal starts to broaden at −30 °C; the slow exchange limit lies below −70 °C.

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6 See W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, John Wiley, New York, 1988, chap. 5.

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§ 250 MHz, CD_2Cl_2, 20 °C, δ 1.35 (s, 18H) and 1.32 (s, 18H) $NCMe_3$; 5.85 (m, 4H, μ-C_5H_4); 6.2 (s, 8H, η^1-C_5H_5).