Imido Analogues of the Tungstate(vi) and Perrhenate(vii) Ions. X-Ray Crystal Structures of Li$_2$W(NBu^t)$_4$ and Li(tmed)Re(NBu^t)$_4$†

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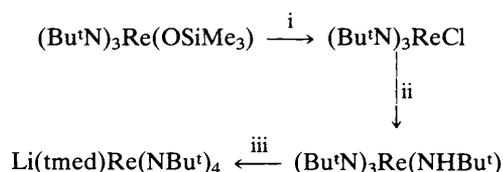
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The first homoleptic imido compounds of transition metals, namely the imido analogues of the tungstate, WO$_4^{2-}$, and perrhenate, ReO$_4^-$, anions have been obtained as the lithium salts, Li$_2$W(NBu^t)$_4$ and Li(tmed)Re(NBu^t)$_4$; the structure of the tungsten compound contains two W(NBu^t)$_4$ units linked by N $\cdots$ Li $\cdots$ N bridges while that of the rhenium compound shows the lithium co-ordinated to N atoms of tetramethylethylenediamine and to two N atoms of the anion.

Main group homoleptic compounds, M$_x$(NR)$_y$, can be regarded as imido or, if they have pyramidal N forming three single bonds, as amido compounds; examples are P$_4$(NR)$_6$,[1] S(NR)$_3$,[1] Sn$_4$(NBu^t)$_4$,[2a] Li$_4$[(Bu^{t}N)$_2$Si(μ-NBu^t)]$_2$ and (μ-M)$_2$[(Bu^{t}N)$_2$Si(μ-NBu^t)]$_2$, M = Ge^{II}, Sn^{II}.[2b] No transition metal homoleptic imido compounds are known; the closest approach is Os(NBu^t)$_3$(NSO$_2$Ar), details of which have never been published.[3]

We have now synthesised the t-butylimido analogues of the tungstate(vi) and perrhenate(vii) ions as the lithium salts Li$_2$W(NBu^t)$_4$ (**1**) and Li(tmed)Re(NBu^t)$_4$ (**2**). The former is obtained as colourless crystals by deprotonation of (Bu^{t}NH)$_2$W(NBu^t)$_2$[4] with methyl-lithium in diethyl ether/hexane; X-ray quality crystals were obtained from toluene containing pentamethyldiethylenetriamine. Compound (**2**) is

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† Dilithium tetra(t-butylimido)tungstate(vi); lithium(tetramethylethylenediamine)tetra(t-butylimido)rhenate(vii).

$$(Bu^tN)_3Re(OSiMe_3) \xrightarrow{\text{i}} (Bu^tN)_3ReCl$$

$$\downarrow \text{ii}$$

$$Li(tmed)Re(NBu^t)_4 \xleftarrow{\text{iii}} (Bu^tN)_3Re(NHBu^t)$$

Scheme 1. *Reagents and conditions*: i, PhICl$_2$ in toluene; ii, LiNHBu^t in tetrahydrofuran (thf); iii, LiMe·tmed in Et$_2$O.

obtained in low yield by the sequence in Scheme 1, as orange coloured, air and moisture sensitive prisms from hexane at $-78\,^\circ$C.

The ^{1}H n.m.r. spectrum of (**1**) has bands at δ 1.48 (27H), assignable to bent W–NBu^t groups, and at δ 1.67 (9H), assignable to a linear W–NBu^t group, and is unchanged up to 283 K, whereas for (**2**) there is only a peak at δ 1.58 (36H) and tmed peaks at δ 1.88 and 1.99 at 25 °C.
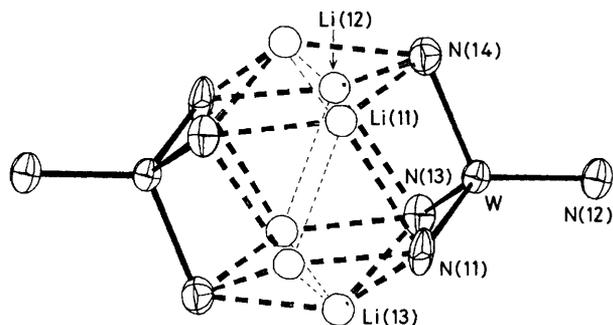
Figure 1. A representation of the $[W_2(NBu^t)_8Li_4]$ dimer showing all lithium sites (2/3 occupied). The Bu^t carbons have been omitted for clarity. Some geometry parameters are as follows (equivalent values for the second dimer are given in brackets). W(1)–N(12) 1.723(8) [1.770(9)]; W(1)–N(11), N(13), N(14) 1.869—1.883(8) [1.866—1.887(9)]; Li–N 1.89—2.23(3) Å; W(1)–N(12)–C(12) 176.6(6) [178.5(7)°]; W(1)–N(11), N(13), N(14)–C 134.4—139.6(5)° [135.1(5)—138.4(6)°].
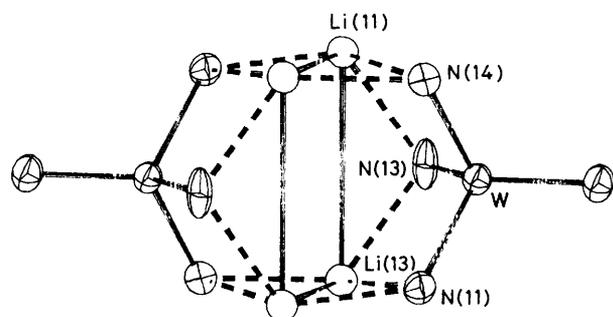

Figure 2. A representation of the $[W_2(NBu^t)_8Li_4]$ dimer showing proposed occupancy of lithium sites in one unit.

The crystal structure‡ of the tungsten compound contains two crystallographically independent centrosymmetric dimers in which the two $W(NBu^t)_4$ units are linked by N ⋯ Li ⋯ N bridges. The linking occurs between an N_3 face of each of the two WN_4 tetrahedra. Although the bridging lithium atoms are found to occupy six sites in the form of a cyclohexane-type ring (Figure 1), the sites are only partially occupied and we propose that this averaged structure is derived by disorder of a unique structure in which only four positions are occupied (Figure 2). These four sites form a rectangle in which the shorter edge, at least, corresponds to strong Li ⋯ Li interactions. The distances of 2.10—2.22 Å are similar to those found[5] in the cluster $[o\text{-}LiC_6H_4CH_2\cdot NLiCH_2CH_2NMe_2]_4$. The

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‡ *Crystal data*: (1), $C_{32}H_{72}Li_4N_8W_2$, $M = 964.54$, triclinic, $a = 10.244(2)$, $b = 13.871(2)$, $c = 15.860(4)$ Å, $\alpha = 92.45(2)$, $\beta = 99.52(4)$, $\gamma = 90.86(2)°$, $U = 2220.0$ Å^3, space group $P\bar{1}$, $Z = 2$ (two independent centrosymmetric dimers), $D_c = 1.44$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 53.1$ cm^{-1}, $F(000) = 840$. 6128 Observed reflections $[F_o > 3\sigma(F_o)]$ from 7799 independent measured (CAD4 diffractometer, graphite monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å), $R = 0.039$, $R_w = 0.044$, 403 parameters.

Crystal data: (2), $C_{22}H_{52}N_6ReLi$, $M = 593.84$, orthorhombic, $a = 16.907(4)$, $b = 15.752(4)$, $c = 11.364(4)$ Å, $U = 3026.4$ Å^3, space group $Pnn2$, $Z = 4$ (molecule has C_2 symmetry), $D_c = 1.303$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 40.64$ cm^{-1}, $F(000) = 1216$. 1560 Observed reflections $[F_o > 6\sigma(F_o)]$ from 2809 measured, $R = 0.045$, $R_w = 0.064$, 265 parameters. Atomic parameters, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
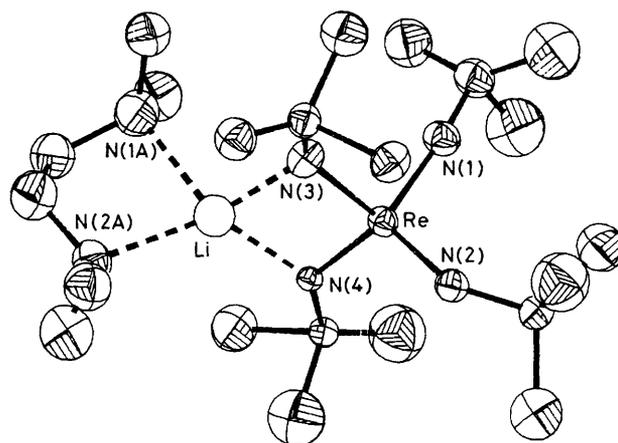

Figure 3. A molecule of $[Re(Bu^t)_4\cdot Li(tmed)]$. Important geometry parameters are as follows. Re–N(1) 1.78(2); Re–N(2) 1.77(2); Re–N(3) 1.87(3); Re–N(4) 1.80(2); Li–N(3) 1.92(6); Li–N(4) 2.19(6) Å. Li–N(14) 2.26(5); Li–N(24) 2.19(5) Å. Re–N(1)–C(1) 161(3), Re–N(2)–C(2) 150(1), Re–N(3)–C(3) 135(2), Re–N(4)–C(4) 131(2). N(1)–Re–N(2) 107.9(9), N(3)–Re–N(4) 98.8(8), N(3)–Li–N(4) 85(2), N(14)–Li–N(24) 84(2)°.

nitrogens involved in N ⋯ Li ⋯ N bridging are four-co-ordinate and this corresponds to bent, 2e imido ligands. This is consistent with the 18e rule since the species $W(NBu^t)_4^{2-}$ requires only one formal triple bond, and this occurs in the bond to the 'terminal' imido ligand.

The structure of the rhenium compound‡ contains isolated molecular 'ion pairs' in which the $[(tmed)Li]^+$ unit bonds along one edge of the ReN_4 tetrahedron (Figure 3). Bending occurs at the bridged nitrogens as for the tungsten complex, but in contrast, the 'non-bridging' or terminal NBu^t groups are also non-linear. Again, this can be ascribed to the 18e rule since the $[Re(NBu^t)_4]^-$ unit requires only one triple bond, and this can be considered to be averaged over the two terminal ligands (Re–N–C 150, 161° compared with 130, 134° for the bridged nitrogens).

Attempts to make $[M(PR)_4]^{n-}$ mixed ions such as $[W(S)_2(NR)_2]^{2-}$ and imido analogues of other oxoanions are in progress. Complexes with $W(NBu^t)_4^{2-}$ as ligand have been made, an example being $[(Me_2Al)(\mu\text{-}NBu^t)_2]_2W$ which has been structurally characterised.

It may be noted that a homoleptic compound of different type, $(Bu^tN)_2Re^{VI}(\mu\text{-}NBu^t)_2Re^{VI}(NBu^t)_2$, has been made by reduction of $(Bu^tN)_3Re(OSiMe_3)$ with sodium in hexane; it is diamagnetic with an Re–Re bond.[6]

References

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