

tert-Butoxylimido derivatives of niobium

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The synthesis and crystal structure of the η -cyclopentadienylniobium compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2(\text{NOBu}^t)]$, which contains the first example of the terminal transition metal–alkoxyimido ligand system $\text{M}=\text{N}-\text{OR}$, is reported along with some preliminary reactivity studies.

The chemistry of transition-metal imido compounds $\text{M}=\text{N}-\text{R}$, where R is an alkyl or aryl group, is a very rapidly expanding field. Imido complexes have been utilised in alkene metathesis reactions,¹ MOCVD processes,² C–H activation^{3,4} and organic transformations⁵ as well as being of considerable fundamental interest.^{6,7} The field has recently been extensively reviewed.⁸ We have been interested in the substitution of the organic group in imido compounds for a heteroatom in an attempt to understand the changes such substitution will have on bonding and reactivity. Heteroatom-substituted analogues such as hydrazido(2–) compounds $\text{M}=\text{N}-\text{NR}_2$ are known, and there has been a brief reference to the sulfonylimido system $\text{M}=\text{N}-\text{SR}$.⁹ Here we report the synthesis of a new alkoxy-substituted imido ligand system and some preliminary investigations of its reactivity.

Treatment of a dichloromethane suspension of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_4]$ with a mixture of *O*-tert-butylhydroxylamine hydrochloride and triethylamine in dichloromethane gave a red solution from which red–orange crystals of the *tert*-butoxylimido derivative $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2(\text{NOBu}^t)]$ **1** were isolated by crystallisation from pentane at -20°C . The compound $[\text{Nb}(\eta\text{-C}_5\text{H}_4\text{Me})\text{Cl}_2(\text{NOBu}^t)]$ **2** was similarly prepared from $[\text{Nb}(\eta\text{-C}_5\text{H}_4\text{Me})\text{Cl}_4]$ as a red oil at room temperature.

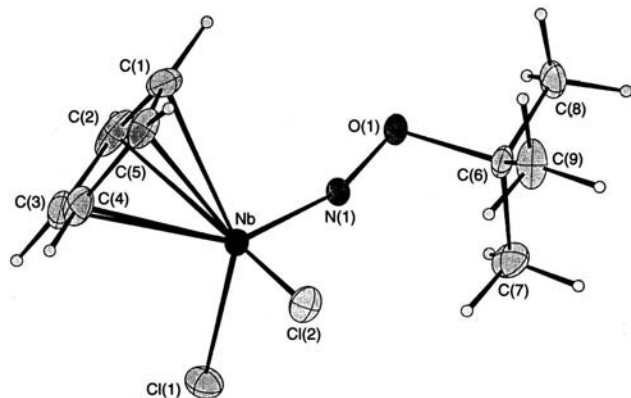
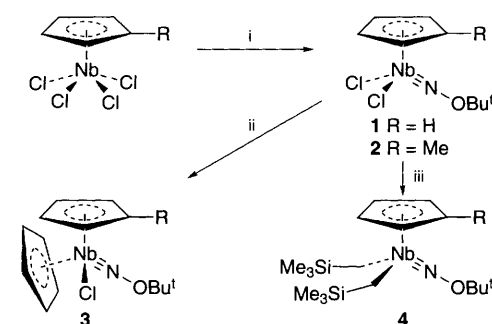


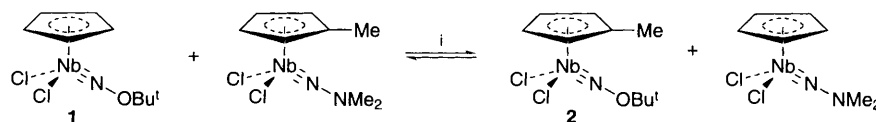
Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Nb–N 1.769(3), N–O 1.342(5), Nb–Cl(1) 2.358(1), Nb–Cl(2) 2.369(1), Nb–Cl(1) 2.372(5), Nb–C(2) 2.381(5), Nb–C(3) 2.421(5), Nb–C(4) 2.487(5), Nb–C(5) 2.451(5); Nb–N–O 162.5(3), N–O–C(6) 111.7(3).

Crystals of **1** were grown by slowly cooling an octane solution from 100°C to room temperature. The crystal structure has been determined[†] and the molecular structure is shown in Fig. 1 together with selected bond lengths and angles. Compound **1** is a monomer in the solid state. The Nb–N–O angle is $162.5(3)^\circ$ and the N–O–C(6) angle is $111.7(3)^\circ$, consistent with *sp* hybridisation at the nitrogen atom and *sp*³ hybridisation at the oxygen atom. The Nb–N distance [1.769(3) Å] and N–O distance [1.342(5) Å] are consistent with a triple and a single bond respectively. The Nb–N distance is similar to the value of 1.752(2) Å found in the analogous imido compounds $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{NOBu}^t)]$.¹⁰ The Nb–Cl bond lengths in **1** are 2.358(1) and 2.369(1) Å, similar to those found in $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{NOBu}^t)]$ [2.355(1) Å] but considerably shorter than the average distances of 2.496(2) and 2.484(2) Å found for the two crystallographically independent molecules of the 18-electron compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{NOBu}^t)(\text{PMe}_3)]$.¹⁰ This indicates that **1** relieves its electron deficiency at the niobium centre by extensive Nb–Cl $d_{\pi}-p_{\pi}$ bonding. In common with many other η -cyclopentadienylniobium compounds^{10–12} the cyclopentadienyl ligand in **1** is considerably distorted away from η^5 geometry towards η^3 geometry. Thus there are two short, two medium and one long Nb–C bond lengths. The bonding in the new ligand thus appears to be similar to that found in analogous *tert*-butyl imido groups.

Treatment of compound **1** with LiC_5H_5 gives the formally 20-electron compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{NOBu}^t)]$ **3**. Also, **1** reacts with $\text{LiCH}_2\text{SiMe}_3$ to form the dialkyl derivative $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{CH}_2\text{SiMe}_3)_2(\text{NOBu}^t)]$ **4**. The alkoxyimido ligand can also undergo ligand-exchange reactions as exemplified by the reaction between **1** and the hydrazido compound $[\text{Nb}(\eta\text{-C}_5\text{H}_4\text{Me})\text{Cl}_2(\text{NNMe}_2)]$ which gives **2** and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2(\text{NNMe}_2)]$. These reactions are summarised in Schemes 1 and 2.



Scheme 1 Reagents and conditions: i, $[\text{H}_3\text{NOBu}^t]\text{Cl}$, 3 equiv. NEt_3 , CH_2Cl_2 , 3 h; ii, LiC_5H_5 , thf, 20 min; iii, 2 equiv. $\text{LiCH}_2\text{SiMe}_3$, THF, 20 min



Scheme 2 Reagents and conditions: i, CD_2Cl_2 , 48 h

The new compounds **1–4**† are, to our knowledge, the first examples of terminal alkoxyimido derivatives. A triply bridging alkoxyimido ligand has been reported to be formed by the methylation of a nitrosyl group to yield $[\{\text{Ru}(\text{CO})_3\}_3(\mu^3\text{-CO})\mu^3\text{-NOMe}]^{13}$ and a sulfur analogue $[\text{Mo}(\text{S}_2\text{CNEt}_2)_3\text{Cl}(\text{NSAr})]$ was also synthesised by the action of ArSCl on a terminal molybdenum nitride species.⁹

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Footnotes

† *Crystal data for 1*: red crystal of dimensions $0.28 \times 0.14 \times 0.11$ mm, $\text{C}_9\text{H}_{14}\text{Cl}_2\text{NNbO}$, $M = 316.03$, monoclinic, space group = $P2_1/n$, $a = 6.762(2)$ Å, $b = 18.710(2)$ Å, $c = 9.913(1)$ Å, $\beta = 91.08(2)^\circ$, $U = 1253.9(4)$ Å³, $Z = 4$, $\text{Mo-K}\alpha$ ($\lambda = 0.71069$ Å), $D_c = 1.68$ g cm⁻³, $T = 150$ K. Of the 5270 reflections measured, 1606 were unique with $I > 3\sigma(I)$. Data were corrected for Lorentz and polarisation effects and the Chebychev weighting scheme¹⁴ was applied. The structure was solved by SIR92¹⁵ using CRYSTALS¹⁶ to yield final $R = 0.059$, $R_w = 0.063$ for 127 least-squares parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/79.

‡ *Characterising data for 1–4*. Satisfactory microanalytical data were obtained for compounds **1–3**. All NMR data are reported in CD_2Cl_2 at 300 MHz (¹H) or 75.4 MHz (¹³C{¹H}) unless otherwise stated. EIMS data are reported for the ³⁵Cl isotopomer where appropriate: correct isotope envelopes were observed.

Compound **1**: ¹H NMR, δ 6.51 (s, 5 H, C₅H₅), 1.34 [s, 9 H, C(CH₃)₃]; ¹³C{¹H} NMR (C₆D₆), δ 112.22 (C₅H₅), 90.64 [C(CH₃)₃], 26.79 [C(CH₃)₃]. EIMS, m/z 317 (M)⁺ 8%. Compound **3**: ¹H NMR, δ 6.11 (s, 10 H, C₅H₅), 1.16 [s, 9 H, C(CH₃)₃]; ¹³C{¹H} NMR, δ 112.0 (C₅H₅), 87.4 [C(CH₃)₃], 27.0 [C(CH₃)₃]. EIMS, m/z 349 (M)⁺ 4%. Compound **4**: ¹H NMR (C₆D₆) δ 5.71 (s, 5 H, C₅H₅), 1.40 (d, 2 H, J_{HH} 10.4 Hz, CH₂), 1.29 [s, 9 H, NOC(CH₃)₃], 0.24 [s, 18 H, Si(CH₃)₃], 0.14 (d, 2 H, J_{HH} 10.4 Hz,

CH₂); ¹³C{¹H} NMR (CD₂Cl₂) δ 106.8 (C₅H₅), 84.36 [NOC(CH₃)₃], 50.9 (b, CH₂), 26.93, [NOC(CH₃)₃], 2.21 [Si(CH₃)₃]. EIMS m/z 420 (M)⁺ 2%.

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