Schiff-base chemistry of niobium: unexpected products of radical elimination and diastereoselective addition

Letter

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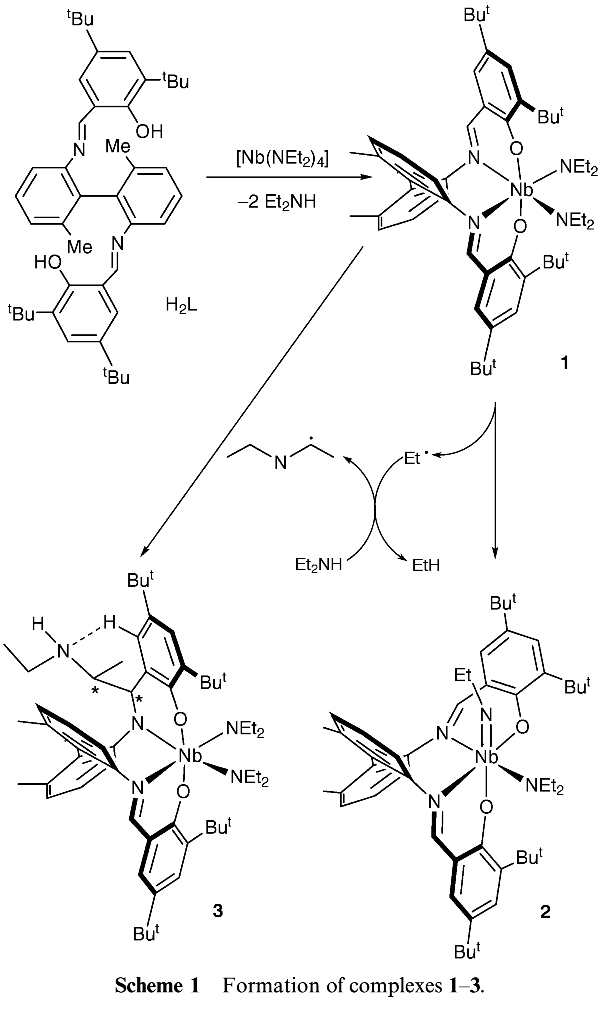
The two main products from the reaction of a chiral Schiff-base proligand H_2L with $[Nb^{IV}(NEt_2)_4]$ are the amidoimido species $[LNb^{V}(NEt)(NEt_2)]$ and the highly unusual $[L'Nb^{V}(NEt_2)_2]$ in which a 1-ethylaminoethyl radical has undergone highly diastereoselective addition to one of the coordinated imine groups.

Our current work on the development of synthetic routes to chiral multidentate Schiff-base complexes of the transition metals is inspired by the success of this type of compound in the mediation of enantioselective catalytic processes.[1] We note that while there is an extensive chemistry of achiral Schiff-base vanadium compounds,[2] there is a paucity of such complexes of the heavier Group 5 congeners niobium and tantalum.[3,4] This might be blamed on the apparent ease with which the latter elements may move between closely spaced oxidation states, but is no doubt also caused in part by the inherent reactivity of the imine ligand.[5] Not unexpectedly then, attempts to extend our work on zirconium complexes of a biphenyl bridged quadridentate Schiff-base system[6] to niobium were initially plagued by complex side-reactions, but we are now able to report a reliable route to such complexes of this element. The highly unexpected products formed cast light on the type of side reactions which have prevented the development of this chemistry in the past.

We have prepared zirconium diamides in good yield *via* a protonolysis reaction between H_2L with metal amides $[Zr(NR_2)_4]$.[6] Accordingly, reaction of H_2L (Scheme 1) with $[Nb(NEt_2)_4]$ was examined. Unexpectedly the target molecule, green $[NbL(NEt_2)_2]$ **1** (identified by its mass spectrum and EPR signal) was produced in only trace quantities. The two main products formed in this reaction, the (diethylamido)(ethylimido) complex $[NbL(NEt)(NEt_2)]$ **2** (43%) and $[NbL'(NEt_2)_2]$ **3** (16%) contain pentavalent niobium centres. The compounds were readily separated by crystallisation.†

We propose a simple mechanism for the formation of **2** and **3** (Scheme 1). The reaction of H_2L and $[Nb^{IV}(NEt_2)_4]$ gives $[Nb^{IV}L(NEt_2)_2]$ **1** and two equivalents of diethylamine as expected. Loss of an ethyl radical from **1** to give **2** is driven by the concomitant oxidation Nb^{IV} to Nb^{V} and formation of the strong bond Nb=N. The ethyl radical is rapidly quenched by the two-fold excess of diethylamine present in the reaction mixture to produce the more stable 1-ethylaminoethyl radical which adds in an intermolecular fashion to one of the two equivalent imine groups of further **1** to give **3** directly.

Pure yellow **2** is obtained by recrystallisation of the reaction mixture from pentane, and single crystals were obtained by allowing acetonitrile to diffuse slowly into a concentrated solution of the compound in dichloromethane–pentane. The molecular structure as determined by X-ray diffraction‡ (Fig. 1) is a rare example of the *cis–trans* N_2O_2 structure (class II)[6] in which the two imine nitrogen atoms N(1) and N(2), one phenoxide oxygen atom O(1) and the amido nitrogen atom N(3) form the plane of a distorted octahedron. The second phenoxide oxygen atom O(2) and the imido ligand nitrogen atom N(4) occupy mutually *trans* sites with O(2)–Nb–N(4) of 168.4(2)°. The angle at niobium between the amido and imido ligands is 96.1(2)°. The three types of Nb–N bond are clearly distinguishable in this structure; the Nb–N(imine) bond lengths are 2.388(5) Å and 2.240(6) Å, the Nb–N(amido) length is 2.012(5) Å and the Nb–N(imido) bond is 1.786(7) Å. The imido linkage C(49)–N(4)–Nb is almost linear at 172.2(5)°, as is common in early transition metal imido chemistry.[7] The amido nitrogen atom N(3) is coplanar with Nb, C(46) and



Scheme 1 Formation of complexes **1**–**3**.

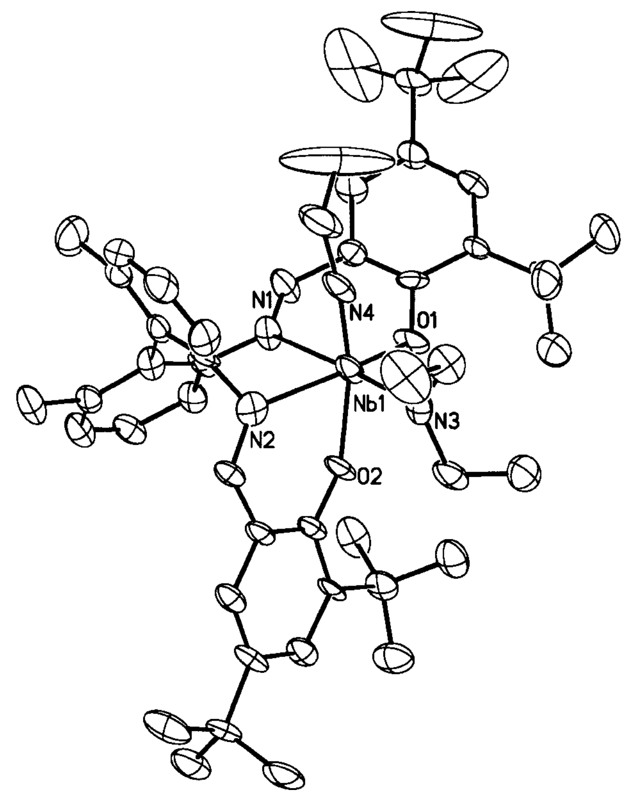


Fig. 1 Thermal ellipsoid plot of the molecular structure of **2**; hydrogen atoms omitted.

C(47) (sum of angles = 359.9°) indicating normal sp^2 amido–metal bonding.[8]

The ^{1}H NMR spectrum of **2** contains four resonances assigned to *tert*-butyl groups and two resonances assigned to aromatic methyl groups, as expected for an unsymmetric complex containing L. It is interesting to note that all four methylene protons of the diethylamido group are inequivalent, indicating that rotation about the Nb–NEt$_2$ bond is slow compared to the ^{1}H NMR chemical shift timescale.

Although the formation of complex **2** under these mild conditions is quite unexpected, mixed amido–imido complexes of the Group 5 metals are known. For example [Ta(=NEt)(NEt$_2$)$_3$] is a product of the thermolysis of [Ta(NEt$_2$)$_5$],[9] and [MCl$_2$(NBu^t)(NHBu^t)(NH$_2$Bu^t)]$_2$ (M = Nb, Ta) results from the reaction of MCl$_5$ with Bu^{t}NH$_2$.[10] However, these reactions proceed without change in oxidation state at the metal centre; to our knowledge **2** is the first such complex produced by an oxidative process from an amido precursor.

The third product of the reaction between H$_2$L and [Nb(NEt$_2$)$_4$], *i.e.* [NbL′(NEt$_2$)$_2$] **3** is obtained from the pentane mother-liquor of **2** above after exposing the solution briefly to air in order to decompose any Nb^{IV} species.

Single crystals of **3** were grown from a saturated solution of the pure compound in a pentane–acetonitrile mixture and the molecular structure was determined by X-ray diffraction.‡ The niobium atom is in a distorted octahedral environment (Fig. 2) with the diethylamido ligands occupying mutually *cis* co-ordination sites. The Nb–N(2) and Nb–N(1) distances for the chelate ligand nitrogen atoms of 2.336(3) Å and 2.032(3) Å are indicative of imino and amido functionality respectively. All three dialkylamido(niobium) fragments are essentially planar and have bond angles consistent with sp^2 hybridisation. The structural parameters within the diethylamine fragment which has become bonded to C(7) do not show any peculiarities. Nevertheless, the pendant amine nitrogen N(5) makes a close approach (*ca.* 3.05 Å) to the phenolic carbon C(5). Although the hydrogen atom at C(5) was not located, its calculated position is *ca.* 2.34 Å from N(5), commensurate with the presence of an intramolecular C–H→N hydrogen bond. This is highlighted in Scheme 1.

The ^{1}H and ^{13}C NMR spectra of **3** have been fully assigned by standard two-dimensional methods and are consistent with the observed solid state structure. For example, the unusually low field ^{1}H NMR resonance of one of the phenolic aromatic protons (δ 8.45) is assigned to the hydrogen-bonded C–H group (see above). Also, the protons of the diastereotopic

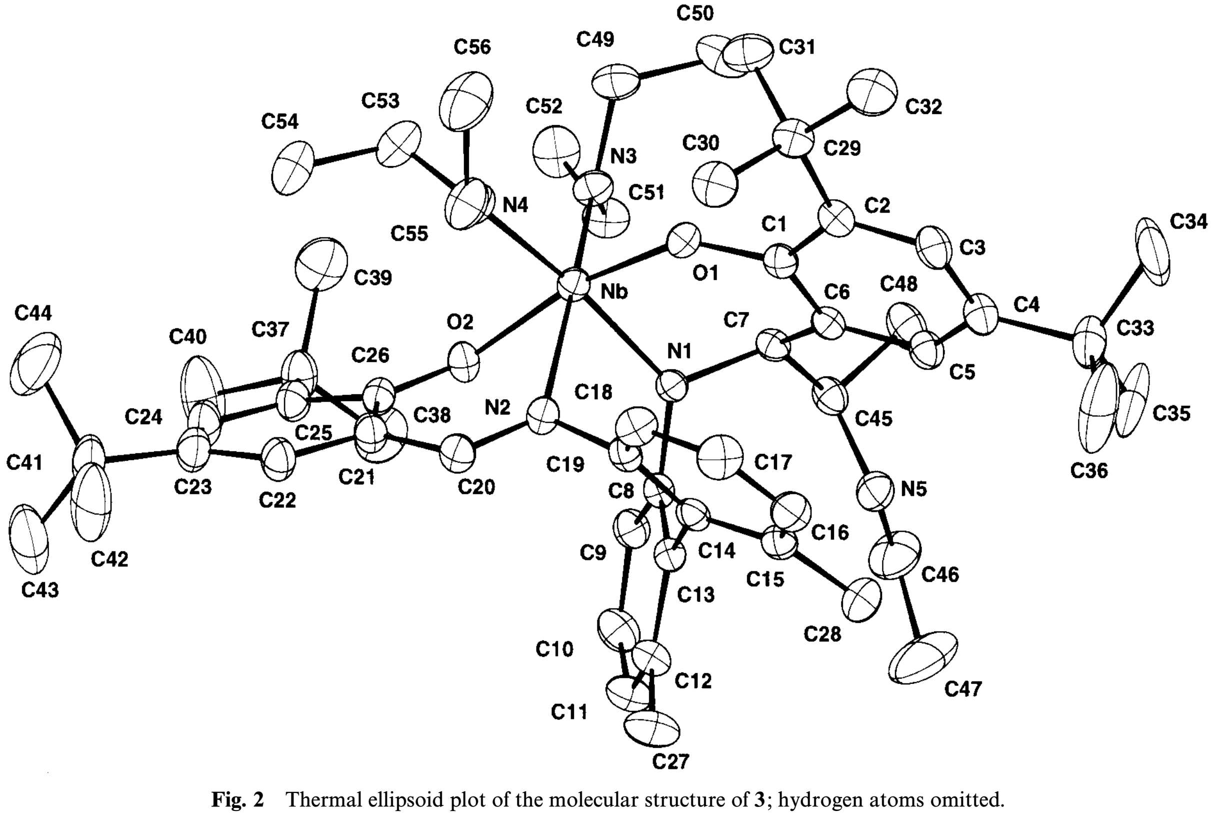


Fig. 2 Thermal ellipsoid plot of the molecular structure of **3**; hydrogen atoms omitted.

methylene group C(46) adjacent to the amine group are separated by an unusually large chemical shift difference (0.68 ppm), suggesting that the rotation of the diethylamine fragment is restricted by the hydrogen bond.

The highly unusual trianionic quadridentate ligand L′ in **3** contains three elements of chirality: the two stereogenic centres marked * (Scheme 1) and the biaryl group. Despite this, close examination of the ^{1}H and ^{13}C NMR spectra of the crude reaction mixture provided no evidence for the presence of significant amounts of more than one diastereomer (d.e. >95%). The configurations of the stereogenic centres in **3** are readily explained. Intermolecular attack of the radical at the imine carbon from the side opposite to the metal leads to the observed stereochemistry of C(7). That of C(45) is determined by the close proximity of the biaryl group below and a vacant space above the nascent C(7)–C(45) vector as drawn in Fig. 2. It is possible also that one of these interactions ultimately controls the stereochemistry at both carbon centres. The above mentioned hydrogen bond also may have had a part to play in the highly diastereoselective formation of **3**.

The chiral pentavalent complex $[\mathrm{NbL(NEt)(NEt_2)}]$ **2** and the fascinating diastereomerically pure $[\mathrm{NbL'(NEt_2)_2}]$ **3** are thus shown to have been formed from the reaction of $\mathrm{H_2L}$ and $[\mathrm{Nb(NEt_2)_4}]$. The Nb(IV/V) radical redox processes which gave rise to these species are probably characteristic of the kinds of side reactions which have beleaguered earlier attempts to synthesise Schiff-base complexes of the heavier Group 5 metals. Notably, the complexes $[\mathrm{LNbCl_2}]$ and $[\mathrm{LNb(NMe_2)_2}]$ are readily accessible, and we will report their chemistry in due course.

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Notes and references

† Experimental: $[\mathrm{NbL(NEt_2)(NEt)}]$ **2**. A solution of $\mathrm{H_2L}$ (1.00 g, 1.55 mmol) in diethyl ether (30 ml) was added dropwise to a solution of $[\mathrm{Nb(NEt_2)_4}]$ (0.60 g, 1.57 mmol) also in diethyl ether (10 ml). The mixture was stirred for 12 h to give a green solution from which the volatile components were removed under reduced pressure. The solid remaining was extracted into pentane and cooled to −30 °C to give a dark green solid and yellow-brown supernatant liquor. The solid was collected and dried *in vacuo*, then dissolved in the minimum quantity of diethyl ether, briefly exposed to air to turn the solution orange, and cooled to −30 °C to give yellow crystals (570 mg, 43%). Found (Calculated for $\mathrm{C_{50}H_{69}N_4O_2Nb}$): C, 70.44 (70.57); H, 8.24 (8.17); N, 6.68 (6.58)%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 8.08 (s, 1H, N=CH), 7.74 (s, 1H, N=CH), 7.69 (d, 1H, phenolic), 7.57 (d, 1H, phenolic), 7.43 (d, 1H, biaryl), 7.18 (t, 1H, biaryl), 7.02 (d, 1H, phenolic), 6.85 (d, 1H, biaryl), 6.70 (d, 1H, phenolic), 6.65 (t, 1H, biaryl), 6.53 (d, 1H, biaryl), 6.47 (d, 1H, biaryl), 4.58 (sextet, 1H, Nb–$\mathrm{NCH_2}$), 4.07 (sextet, 1H, Nb–$\mathrm{NCH_2}$), 3.91 (sextet, 1H, Nb–$\mathrm{NCH_2}$), 3.65 (sextet, 1H, Nb–$\mathrm{NCH_2}$), 2.76 (sextet, 1H, Nb=$\mathrm{NCH_2}$), 2.56 (sextet, 1H, Nb=$\mathrm{NCH_2}$), 1.95 (s, 3H, Me), 1.79 (s, 9H, Bu^t), 1.71 (s, 9H, Bu^t), 1.70 (s, 3H, Me), 1.45 (t, 3H, Nb–$\mathrm{NCH_2}CH_3$), 1.27 (s, 9H, Bu^t), 1.16 (s, 9H, Bu^t), 1.02 (t, 3H, Nb–$\mathrm{NCH_2}CH_3$), 0.34 (t, 3H, Nb=$\mathrm{NCH_2}CH_3$). ^{13}C-{^{1}H}NMR ($\mathrm{C_6D_6}$): δ 167.95 (N=C), 166.67, 166.25 (aromatic), 164.88 (N=C), 154.49, 151.90, 140.98, 138.86, 138.66, 138.01, 136.93, 136.05, 131.94, 131.26, 131.12, 129.06, 128.30, 128.11, 127.87, 127.61, 127.01, 124.18, 123.75, 120.55, 118.87, 115.26 (aromatic), 59.48, 52.71, 48.02 ($\mathrm{N}C\mathrm{H_2CH_3}$), 35.89, 35.74, 34.14, 33.86 ($C\mathrm{Me_3}$), 31.66, 31.37, 30.28, 30.15 ($\mathrm{C}Me_3$), 19.92 (Me), 18.09, 16.60, 16.52 ($\mathrm{NCH_2}C\mathrm{H_3}$). IR (Nujol) cm^{-1}: 1612 (m), 1595 (m), 1551, 1530, 1321, 1302, 1259 (m), 1199, 1169, 1067, 1005, 970, 886, 841, 825, 789, 774, 722 (m), 610, 561, 547. MS (EI): *m*/*z* 850 [M$^+$], 813, 778 [M$^+$ − $\mathrm{NEt_2}$]

$[\mathrm{NbL'(NEt_2)_2}]$ **3**. The yellow-brown supernatant liquor from the above experiment was evaporated to dryness and the solid remaining was washed with pentane (3 × 2 cm^3). These portions of pentane were combined and briefly exposed to air. The solution became dark red. Acetonitrile was added until solids began to precipitate. The solution was then cooled to −30 °C to give red crystalline **3** (240 mg, 16%). Found (Calculated for $\mathrm{C_{56}H_{84}N_5O_2Nb}$): C, 70.70 (70.64); H, 8.99 (8.89); N, 7.21 (7.35)%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 8.45 (d, 1H, phenolic), 7.64 (s, 1H, N=CH), 7.51 (d, 1H, phenolic), 7.26 (d, 1H, phenolic), 7.07 (d, 1H, biaryl), 7.04 (d, 1H, biaryl), 6.87 (t, 1H, biaryl), 6.84 (t, 1H, biaryl), 6.73 (d, 1H, phenolic), 6.63 (d, 1H, biaryl), 6.44 (d, 1H, biaryl), 5.56 (d, 1H, N–$\mathrm{C}H\mathrm{C_6H_2}$), 4.50 (sextet, 2H, Nb–$\mathrm{NCH_2}$), 4.19 (sextet, 2H, Nb–$\mathrm{NCH_2}$), 3.86 (sextet, 2H, Nb–$\mathrm{NCH_2}$), 3.80 (sextet, 2H, Nb–$\mathrm{NCH_2}$), 3.50 (q of d, 1H, diethylamino $\mathrm{NC}H\mathrm{CH_3}$), 2.56 (m, 1H, $\mathrm{N}CH_2\mathrm{CH_3}$), 2.16 (s, 3H, Me), 1.88 (m, 1H, $\mathrm{NC}H_2\mathrm{CH_3}$) 1.73 (s, 18H, 2Bu^t), 1.68 (s, 3H, Me), 1.47 (s, 9H, Bu^t), 1.38 (d, 3H, N–$\mathrm{CHC}H_3$), 1.08 (s and t, 15H, Bu^t and Nb–$\mathrm{NCH_2}CH_3$), 0.75 (t, 6H, Nb–$\mathrm{NCH_2}CH_3$), 0.69 (t, 3H, $\mathrm{NCH_2}CH_3$). ^{13}C-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 165.79 (N=C), 161.50, 159.67, 152.Z, 148.17, 139.44, 139.31, 138.07, 137.11, 136.74, 134.73, 133.31, 129.74, 127.8, 127.67, 127.59, 127.36, 126.88, 126.18, 123.98, 123.51, 122.51, 119.11, 115.26, 112.64, 105.57 (aromatic), 68.58, 58.97, 45.97, 45.20, 43.20, 35.57, 35.43, 34.67, 33.93 ($C\mathrm{Me_3}$), 32.32, 31.82, 31.29, 30.55 ($\mathrm{C}Me_3$), 21.10, 20.07, 18.83, 15.61, 13.78, 13.31 (Me). IR (Nujol) cm^{-1}: 3331, 1618, 1551, 1538, 1299, 1257, 1231, 1201, 1172, 1145, 1124, 1100, 1037, 1004, 949, 915, 875, 837, 824, 797, 772, 735, 722, 685, 668, 592, 547, 534.4, 502, 473. MS (EI): *m*/*z* 879 [M$^+$ − $\mathrm{NEt_2}$], 807 [M$^+$ − 2$\mathrm{NEt_2}$], 735 [M$^+$ − 3$\mathrm{NEt_2}$].

‡ Crystal data for $\mathrm{C_{51.5}H_{69}N_4NbO_2}$ **2**: $M = 869.02$, triclinic, $a = 12.5569(10)$, $b = 13.0513(5)$, $c = 16.5008(5)$ Å, $\alpha = 80.481(5)$, $\beta = 92.26(3)$, $\gamma = 82.328(5)°$, $U = 2511.7(2)$ Å^3, $T = 180(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu = 0.279$ mm^{-1}, 14 770 reflections collected, 10 931 independent ($R_{\mathrm{int}} = 0.1857$). Final R indices $[I > 2\sigma(I)]$ were $R_1 = 0.0939$, $wR_2 = 0.2028$. For $\mathrm{C_{56}H_{84}N_5NbO_2}$ **3**: $M = 952.2$, monoclinic, $a = 13.670(2)$, $b = 20.289(14)$, $c = 19.765(11)$ Å, $\beta = 92.26(3)°$, $U = 5478(5)$ Å^3, $T = 293(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu = 0.26$ mm^{-1}, 10 018 reflections collected, 9597 independent ($R_{\mathrm{int}} = 0.0456$). Final R indices $[I > 2\sigma(I)$, 6753 reflections] were $R_1 = 0.048$, $wR_2 = 0.117$. The structures were solved using full-matrix least squares on F^2. Crystals of **2** desolvated rapidly and consequently diffracted weakly, leading to a high R value. A disordered solvent molecule (presumably pentane) was modelled as three 0.5 occupancy C atoms near to an inversion centre. CCDC reference number 440/122. See http://www.rsc.org/suppdata/nj/1999/815/ for crystallographic files in .cif format.

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