C–H Activation and Nitrile Insertion Reactions of a Cationic Niobium Alkylidene Complex

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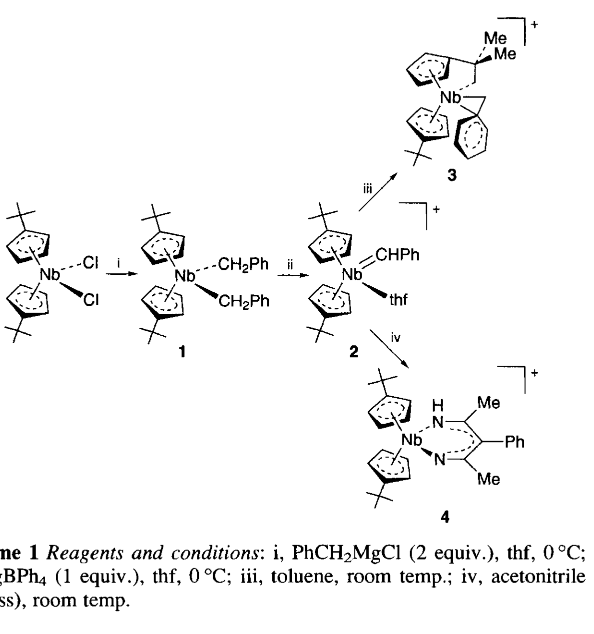
Oxidation of [Nb(η^5-$C_5H_4Bu^t$)$_2$(CH_2Ph)$_2$] yields the stable cationic benzylidene complex [Nb(η^5-$C_5H_4Bu^t$)$_2$(CHPh)(thf)]BPh_4, which readily loses thf to form the C–H activation product [Nb(η^5-$C_4H_4Bu^t$)(η^5:η^1-$C_5H_4CMe_2CH_2$)(η^2-CH_2Ph)]BPh_4 and reacts with acetonitrile to give the double-insertion product [Nb(η^5-$C_5H_4Bu^t$)$_2${η^2-NC(Me)C(Ph)C(Me)NH}]BPh_4.

The synthesis and reactivity of early transition-metal alkylidene complexes is an area of considerable interest at present.[1] Recent reports include the use of such complexes for alkene metathesis and ROMP applications,[2–4] and for the stereoselective synthesis of metal–alkene complexes.[5] While the addition of heteroatom–H bonds to metal–alkylidene complexes has been demonstrated,[6–9] the corresponding addition of sp^3 C–H bonds across the M=CR$_2$ bond is much rarer; examples are largely confined to spectroscopically characterised Group 4 examples.[10–13] Here we describe the synthesis of the first cationic niobium benzylidene complex and demonstrate its high reactivity by structural characterisation of products resulting from C–H bond activation and nitrile 'double insertion' reactions.

[Nb(η^5-$C_5H_4Bu^t$)$_2$(CH_2Ph)$_2$] **1** can be isolated from the reaction of the corresponding dichloride with $PhCH_2MgCl$ as thermally stable dark red crystals.† Upon oxidation of **1** with $AgBPh_4$ in thf a grey precipitate of metallic silver is deposited and the cationic benzylidene complex [Nb(η^5-$C_5H_4Bu^t$)$_2$(CHPh)(thf)]BPh_4 **2** is formed in good yield (Scheme 1). The presence of toluene, the α-elimination by-product, in the reaction mixture was demonstrated by GC–MS. The ^{1}H and ^{13}C NMR spectra of **2** show resonances at δ 13.79 and 295.4, assigned to the H and C of the Nb=CH group.[1,14] Simple Nb alkylidene complexes are rare,[15] and the route described to **2** is a straightforward, direct preparation of a thermally stable example. While **2** is reasonably air-stable and may be stored at 5 °C for weeks, the Nb=CHPh bond is highly reactive towards a range of substrates including sp^3 C–H bonds and nitriles.

Removal of the coordinated thf of **2** by stirring in toluene leads, upon work-up, to orange crystals of the intramolecular C–H activation product **3**. The asymmetry of the metal centre of **3** is clearly demonstrated by the appearance of the ^{1}H NMR spectrum which shows resonances at δ 3.37 and 3.17, assigned to the diastereotopic CH_2Ph group, and at δ −0.29 and −5.58, assigned to the diastereotopic CH_2CMe_2 group. The high-field shift of the latter resonances is due to the ring current of the phenyl group, towards which one H points directly (H···phenyl centroid 2.25 Å), and the other obliquely (3.67 Å). The corresponding methylene C resonances are observed at δ 40.8 and 15.3, respectively. The *ipso*-C resonance of the phenyl group, at δ 137.2, is at a somewhat higher field than expected for a conventional η^1-benzyl group.[16,17]



Scheme 1 *Reagents and conditions*: i, $PhCH_2MgCl$ (2 equiv.), thf, 0 °C; ii, $AgBPh_4$ (1 equiv.), thf, 0 °C; iii, toluene, room temp.; iv, acetonitrile (excess), room temp.

The molecular structure of the cation of **3** is shown in Fig. 1.‡ The electron-deficient niobium centre draws in the benzyl ligand in an η^2-fashion with a short Nb–CH_2 bond length of 2.271(6) Å, a longer Nb–C_{ipso} bond length of 2.620(6) Å and an acute Nb–C(19)–C(20) angle of 85.8(3)°. The *ipso* carbon C(20) lies very close to the plane described by C(18)C(9)Nb (deviation 0.16 Å). Complex **3** is the first Group 5 representative of a small family of structurally characterised η^2-benzyl complexes.[18–21] The geometry of the η^2-benzyl group, *viz.* the elongated C(19)–C(20) bond [1.483(9) Å] and elongated C_{ipso}–C_{ortho} bonds (average 1.407 Å compared with the average of 1.385 Å for the remaining phenyl C–C bond lengths) is consistent with the other known η^2-benzyl complexes. The hydrogen atoms of the CH_2 groups attached to the niobium were located in the latter stages of the refinement and their positions refined; no agostic interactions were noted.[22] A thf molecule is contained as an 'innocent bystander' within the lattice, being too far from the cation (> 5 Å from the niobium) to interact in any way.

Dissolution of **2** in acetonitrile results initially in an orange solution which gradually darkens to deep red before finally becoming forest green. Recrystallisation from acetonitrile–diethyl ether afforded dark green crystals of **4** in essentially quantitative yield. The ^{1}H NMR spectrum clearly indicates that **4** contains two equivalent η^5-$C_5H_4Bu^t$ ligands, and two inequivalent Me groups at δ 1.85 and 1.73, one of which is observed as a doublet with a small coupling (J_{HH} = 0.8 Hz). A

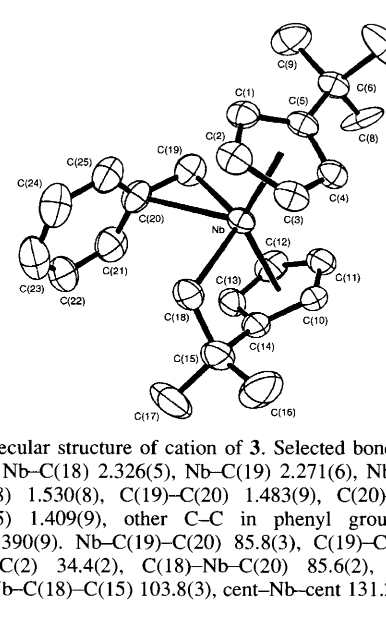


Fig. 1 Molecular structure of cation of **3**. Selected bond lengths (Å) and angles (°): Nb–C(18) 2.326(5), Nb–C(19) 2.271(6), Nb–C(20) 2.620(6), C(15)–C(18) 1.530(8), C(19)–C(20) 1.483(9), C(20)–C(21) 1.406(9), C(20)–C(25) 1.409(9), other C–C in phenyl group in the range 1.377(9)–1.390(9). Nb–C(19)–C(20) 85.8(3), C(19)–C(20)–Nb 59.8(3), C(19)–Nb–C(2) 34.4(2), C(18)–Nb–C(20) 85.6(2), C(18)–Nb–C(19) 119.7(2), Nb–C(18)–C(15) 103.8(3), cent–Nb–cent 131.2.

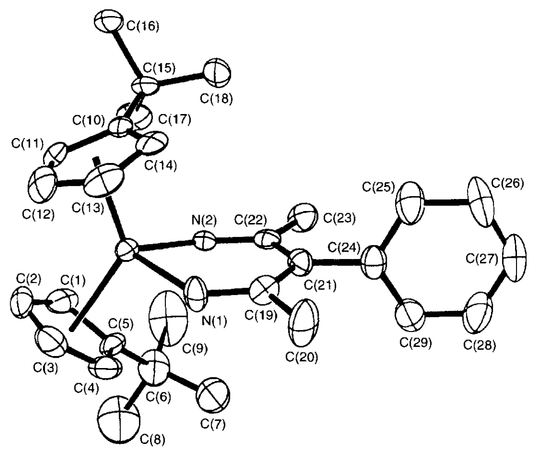
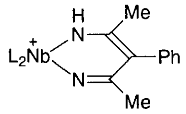


Fig. 2 Molecular structure of cation of **4**. Selected bond lengths (Å) and angles (°): Nb–N(1) 2.140(4), Nb–N(2) 1.846(4), N(1)–C(19) 1.336(6), N(2)–C(22) 1.320(6), C(19)–C(21) 1.401(7), C(21)–C(22) 1.423(7), C(21)–C(24) 1.480(7); Nb–N(1)–C(19) 130.1(4), Nb–N(2)–C(22) 145.9(4), N(1)–Nb–N(2) 78.4(2), N(1)–C(19)–C(21) 124.2(5), N(2)–C(22)–C(21) 118.3(5), C(19)–C(21)–C(22) 120.7(5), cent–Nb–cent 129.6.



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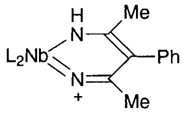

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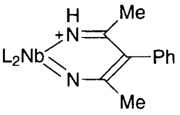

C

L = η-$C_5H_4Bu^t$

broad resonance at δ 8.12 is attributable to the NH group. The ^{13}C NMR spectrum shows resonances at δ 172.2 and 168.5, due to the C(Me) quaternary carbon atoms, and at δ 149.2 due to the C(Ph) carbon, consistent with an sp^2 system in which the carbons are not bound to the niobium. The IR spectrum of **4** shows bands at 3308 and 1548 cm^{-1}, assigned to ν(NH) and ν(CN) stretching modes, respectively.

The structure of **4** as determined by NMR and IR spectroscopy has been confirmed by X-ray crystallography. The molecular structure of the cation of **4** is shown in Fig. 2. The niobium centre is in a pseudo-tetrahedral environment in which the sp^2-like nitrogen and carbon centres constrain the diazapentadiendiyl moiety of **4** to be essentially flat, although the niobium is displaced from this plane [dihedral angle of NbN(1)N(2) and N(1)C(19)C(21)C(22)N(2) plane = 12.5°]. While the Nb–N(2) bond [1.846(4) Å] is much shorter than the Nb–N(1) bond [2.140(4) Å] and clearly indicates some double bond character, it is somewhat longer than comparable bonds in typical terminal Nb^V=NR imido complexes.[23] The angle Nb–N(2)–C(22) of 145.9(4)° is more open than the Nb–N(1)–C(19) angle [130.1(4)°].

The bonding in **4** may be represented by the structures **A**–**C**. Structure **B** is the most consistent with the structural data, although all three forms probably contribute to the overall structure. The electron-deficient nature of the nitrogen atoms results in a significant shortening of the N(1)–C(19) and N(2)–C(22) bonds. The double insertion of nitriles into $M{=}CR_2$ bonds is unusual, and **4** represents the first structurally characterised example of such a compound.[24] We are presently investigating the mechanism of this reaction.

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Footnotes

† Satisfactory analytical and spectroscopic (^1H, ^{13}C NMR and IR) data have been obtained for all compounds.

‡ *Crystal data* for **3**: $C_{53}H_{60}BNbO$, M = 816.73, orthorhombic, space group $Pbca$, a = 20.565(8), b = 20.360(7), c = 20.941(6) Å, U = 8768 Å^3, Z = 8, D_c = 1.237 g cm^{-3}, $F(000)$ = 3456, T = 200 K. 7732 reflections were measured on a Siemens R3m diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2θ < 50°, μ = 0.31 mm^{-1}). Data were corrected for absorption and extinction. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 0.225 (7732 independent reflections), $R = \Sigma|F_o - F_c|/\Sigma F_o$ = 0.068 [5579 reflections with $I/2\sigma(I) > 2.0$], S = 0.982. For **4**: $C_{53}H_{58}BN_2Nb$, M = 826.73, monoclinic, $P2_1/c$, a = 17.706(6), b = 13.176(3), c = 19.134(3) Å, U = 4416 Å^3, Z = 4, D_c = 1.244 g cm^{-3}, $F(000)$ = 1744, T = 150 K. 19818 reflections were measured with a FAST area detector on a CAD4 diffractometer using Mo-Kα radiation. Data were uncorrected for absorption and extinction. $wR2$ = 0.099 (7042 independent reflections), R = 0.046 [3110 reflections with $I/2\sigma(I) > 2.0$], S = 0.712. Details in common: the niobium atoms were located using the Patterson interpretation of SHELXTL.[25] Refinements were by full-matrix least squares on F^2. Anisotropic thermal parameters were used for all non-H atoms. H-atoms were given fixed isotropic thermal parameters, and most were constrained (all for **4**); the CH_2 groups attached to the Nb in **3** were located in the difference map and their positions successfully refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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