η²-Benzyne and η¹-Benzylidene Complexes of Niobium with Ancillary Imido Ligands

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Rare η²-benzyne and benzylidene complexes of niobium have been synthesised from [Nb(C₅R₅)(NR')Cl₂] (R = H, Me; R' = 2,6-Pr^{i}₂C₆H₃) *via* intermediate diphenyl and dibenzyl species and their molecular structures have been determined: these complexes are analogues of well-established zirconocene derivatives.

Recently, we described a series of half-sandwich imido complexes of niobium of the general type [Nb(C₅R₅)-(NR')]Cl₂] (R = H, Me; R' = 2,6-Pr^{i}₂C₆H₃, Bu^t, Me),[1] and noted the similarities between the shapes and energies of the frontier orbitals of the [Nb(C₅R₅)(NR')] fragment with those of the bent metallocene unit [Zr(C₅R₅)₂]. This is a potentially

useful relationship since zirconocene reagents are widely exploited in organic synthesis[2] and polymerisation catalysis.[3] Herein, we report the synthesis and characterisation of rare examples of benzyne and benzylidene complexes of niobium which are direct analogues of synthetically useful zirconocene derivatives.

R = 2,6-Pr^{i}₂C₆H₃
R' = H, Me
R" = CH₂CMe₃
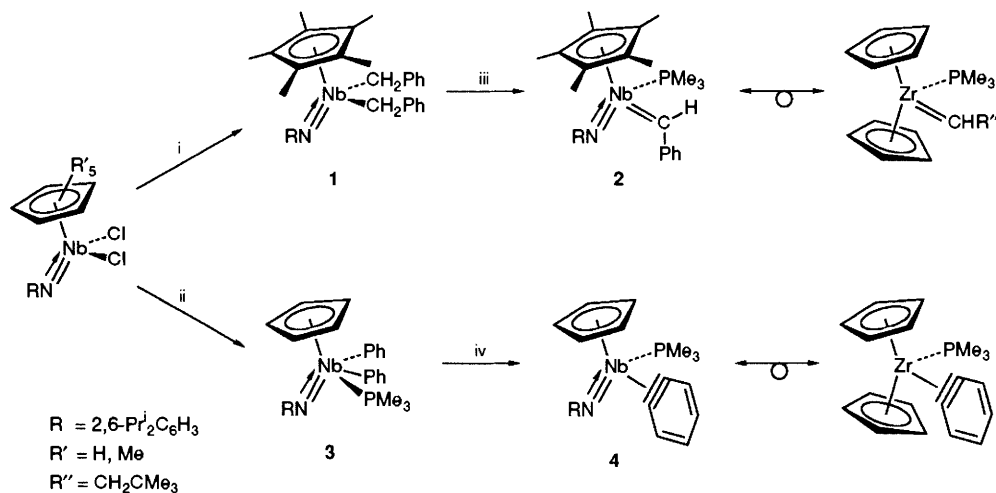
Scheme 1 *Reagents and conditions*: i, 2KCH₂Ph, Et₂O, 25 °C, 18 h; ii, 2PhMgCl, Et₂O, PMe₃, 25 °C, 4 h; iii, PMe₃, n-heptane, 65 °C, 14 days; iv, n-heptane, 60 °C, 3 days

Both complexes are prepared *via* closely related method-ologies according to Scheme 1.† This involves the synthesis of the dibenzyl and diphenyl intermediates 1 and 3 *via* treatment
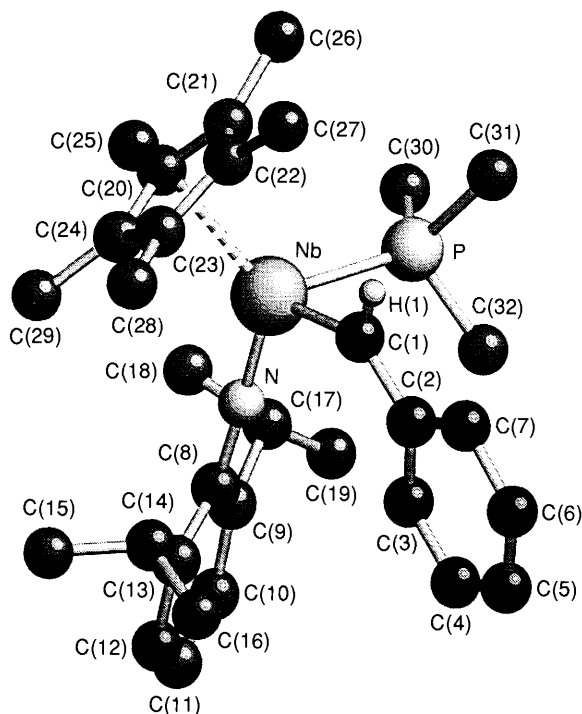
Fig. 1 Molecular structure of **2**. Key interatomic distances (Å) and angles (°): Nb–P 2.578(1), Nb–N 1.812(3), Nb–C(1) 2.026(4); P–Nb–N 99.3(1), P–Nb–C(1) 83.6(1), N–Nb–C(1) 103.4(2), Nb–C(1)–C(2) 136.3(4), Nb–C(1)–H(1) 111.4(33), Nb–N–C(8) 175.6(2), P–Nb–X 117.8, N–Nb–X 128.1, C(1)–Nb–X 115.0 (X = C₅Me₅ ring centroid).

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† Satisfactory elemental analyses have been obtained. *Selected spectroscopic data* for **1**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 1.29 (d, 12H, ³J_HH 6.8 Hz, CH*Me*₂), 1.61 (s, 15H, C₅*Me*₅), 2.18 (d, 2H, ²J_HH 10.8 Hz, C*H*₂C₆H₅), 2.45 (d, 2H, ²J_HH 10.8 Hz, C*H*₂C₆H₅), 3.89 (sept, 2H, ³J_HH 6.8 Hz, C*H*Me₂), 6.84–7.11 (aromatic ring hydrogens). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 10.96 (s, C₅*Me*₅), 25.00 (s, CH*Me*₂), 27.48 (s, C*H*Me₂), 57.68 (br, C*H*₂C₆H₅), 115.48 (s, C₅*Me*₅), 122.92 (s, *m*-C₆H₃), 124.09 (s, *p*-C₆H₃), 124.53 (s, *ipso*-C₆H₅), 128.51 (s, *m*-C₆H₅), 130.73 (s, *p*-C₆H₅), 143.15 (s, *o*-C₆H₃), 145.54 (s, *o*-C₆H₅), 150.55 (s, *ipso*-C₆H₃). For **2**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 0.85 (d, 9H, ²J_PH 7.6 Hz, P*Me*₃), 1.21, 1.32 (d, 12H, ³J_HH 6.7 Hz, CH*Me*₂), 1.96 (s, 15H, C₅*Me*₅), 4.21 (sept, 2H, ³J_HH 6.7 Hz, C*H*Me₂), 6.91 (t, 1H, ³J_HH 7.2 Hz, *p*-C₆H₃), 6.95–7.18 (*m*-C₆H₃, *m*-C₆H₅, *p*-C₆H₅), 7.75 (d, 2H, ³J_HH 8.3 Hz, *o*-C₆H₅), 11.23 (d, 1H, ³J_PH 5.4 Hz, C*H*C₆H₅). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 11.52 (s, C₅*Me*₅), 16.75 (d, J_CP 24 Hz, P*Me*₃), 24.76 (s, CH*Me*₂), 26.93 (s, C*H*Me₂), 112.38 (s, C₅Me₅), 121.58 (d, *m*-C₆H₃), 122.69, 127.54, 127.80 (*o*, *m*, *p*-C₆H₅), 124.24 (s, *p*-C₆H₃), 143.20 (s, *o*-C₆H₃), 148.20 (s, *ipso*-C₆H₅), 150.50 (s, *ipso*-C₆H₃), 268.60 (br, CHC₆H₅). For **3**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 0.60 (d, 9H, ²J_PH 5.9 Hz, P*Me*₃), 1.32 (d, 12H, ³J_HH 6.8 Hz, CH*Me*₂), 4.19 (sept, 2H, ³J_HH 6.8 Hz, C*H*Me₂), 5.72 (s, 5H, C₅*H*₅), 6.97 (t, 1H, ³J_HH 7.2 Hz, *p*-C₆H₃), 7.08 (t, 2H, ³J_HH 6.0 Hz, *p*-C₆H₅), 7.09 (d, 2H, ³J_HH 7.2 Hz, *m*-C₆H₃), 7.21 (t, 4H, ³J_HH 7.2 Hz, *m*-C₆H₅), 7.56 (br, 4H, *o*-C₆H₅). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 14.78 (d, J_CP 17 Hz, P*Me*₃), 25.07 (s, CH*Me*₂), 27.15 (s, C*H*Me₂),108.90 (s, C₅*H*₅), 123.52 (s, *m*-C₆H₃), 124.01 (s, *p*-C₆H₃), 124.46 (s, *p*-C₆H₅), 126.95 (s, *m*-C₆H₅), 137.86 (s, *o*-C₆H₅), 142.44 (br, *o*-C₆H₃), 154.17 (br, *ipso*-C₆H₃), 177.62 (br, *ipso*-C₆H₅). For **4**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 0.97, 1.16 (d, 12H, ³J_HH 6.8 Hz, CH*Me*₂), 1.13 (d, 9H, ²J_PH 8.0 Hz, P*Me*₃), 3.56 (sept, 2H, ³J_HH 6.8 Hz, C*H*Me₂), 5.67 (d, 5H, ³J_PH 1.2 Hz, C₅*H*₅), 6.89 (t, 1H, ³J_HH 7.2 Hz, *p*-C₆H₅), 6.99 (d, 2H, ³J_HH 7.2 Hz, *m*-C₆H₃), 7.35, 7.60, 7.71, 8.29 (m, 4H, C₆*H*₄). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 17.93 (d, J_CP 25 Hz, P*Me*₃), 23.52, 24.00 (s, CH*Me*₂), 27.35 (s, C*H*Me₂), 103.37 (s, C₅*H*₅), 122.21 (s, *m*-C₆H₃), 122.87 (s, *p*-C₆H₃), 130.16, 130.63, 130.83, 132.10, 153.73, 162.67 (*C*₆H₄), 143.74 (s, *o*-C₆H₃), 152.05 (br, *ipso*-C₆H₃).

of [Nb(C₅R₅)(NR′)Cl₂] (R = H, Me; R′ = 2,6-Pr^i₂C₆H₃) with two equivalents of KCH₂Ph and PhMgCl, respectively. Trimethylphosphine is required to stabilise the diphenyl complex **3** but this phosphine does not coordinate to the sterically more hindered niobium centre of the C₅Me₅ derivative **1**.

Upon warming to 60 °C, **3** eliminates benzene *via* a β-hydrogen abstraction process to give the green η²-benzyne complex **4**. The reaction is slowed dramatically in the presence of an excess of PMe₃ indicating that PMe₃ loss from **3** is rate limiting. The dibenzyl species **1** undergoes a related α-abstrac-tion process at 65 °C, with elimination of toluene, to afford the orange benzylidene product **2**. However, by contrast the α-abstraction reaction is *phosphine assisted*, **1** being stable indefinitely at 100 °C in the absence of PMe₃. This is most readily explained due to the PMe₃ interacting with the laterally projecting LUMO¹ which forces the two benzyl groups together thus facilitating the α-hydrogen abstraction. Such an interaction clearly does not favour the conversion of **3** into **4** but here the transition state for β-hydrogen abstraction is likely to be substantially different, requiring more space in the immediate vicinity of the metal if the hydrogen transfer process is mediated by the niobium.
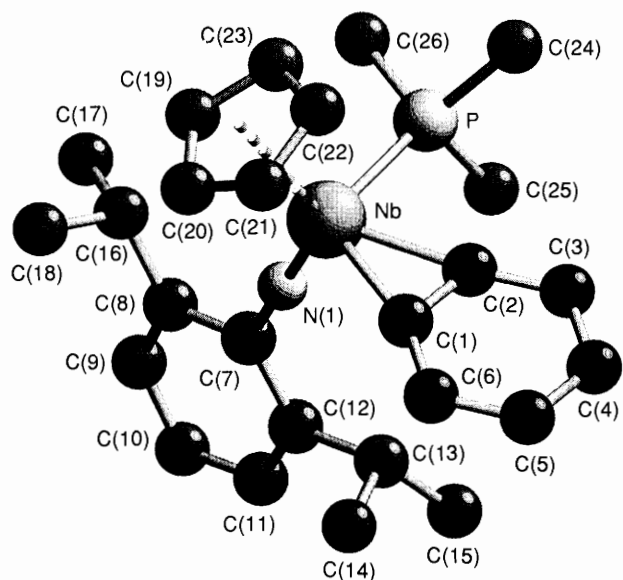
A doublet resonance at δ 11.23 (J_PH 5.4 Hz) in the ¹H NMR spectrum of **2** is attributable to the α-benzylidene hydrogen and is indicative of the presence of a single alkylidene rotamer. Difference nuclear Overhauser effect experiments indicate that the α-hydrogen projects towards the C₅Me₅ ring, and this is also found to be the case in the solid state structure‡ (Fig. 1). In general, thermally robust niobium alkylidenes are rare, especially by comparison with their tantalum counter-parts⁴ and, to our knowledge, **2** is the first simple niobium alkylidene to be structurally characterised; two other struc-tures have been reported but these contain relatively unusual alkylidene ligand arrangements.⁵,⁶ The Nb–C(1) distance of 2.026(4) Å is consistent with a niobium–carbon double bond and compares favourably with related tantalocene deriva-tives,⁷ as expected for the similarly sized Nbⱽ and Taⱽ centres. The orientation of the benzylidene hydrogen and phenyl substituents, lying perpendicular to the P–Nb–C(1) plane, is consistent with the p orbital of the benzylidene carbon interacting with the metallocene-like π-symmetry orbitals of the [Nb(C₅Me₅)(NR)] fragment lending support to the metal-locene analogy. Thus, **2** may be regarded as a direct analogue of the zirconocene complex [Zr(η-C₅H₅)₂(=CHCH₂CMe₃)-(PPh₃)] described by Schwartz and coworkers.⁸

The molecular structure of the benzyne complex **4** is shown in Fig. 2. The benzyne ligand interacts with the niobium 'end-on' in an analogous fashion to that observed in the zirconocene derivative [Zr(η-C₅H₅)₂(η²-C₆H₄)(PMe₃)].⁹

Fig. 2 Molecular structure of **4**. Key interatomic distances (Å) and angles (°): Nb–C(1) 2.138(7), Nb–C(2) 2.190(8), Nb–N(1) 1.809(6), Nb–P 2.528(3), C(1)–C(2) 1.342(11), C(2)–C(3) 1.394(12), C(3)–C(4) 1.393(13), C(4)–C(5) 1.357(15), C(5)–C(6) 1.384(14); P–Nb–N(1) 90.7(2), P–Nb–X 109.7, N–Nb–X 129.0, P–Nb–Y 95.8, N–Nb–Y 105.8, X–Nb–Y 117.2 [X = C_5H_5 ring centroid; Y = C(1)–C(2) centroid].

There are also similarities in the structural parameters associated with the metal–benzyne moieties in these two complexes. For example, the C(1)–C(2) bond length in **4** [1.342(11) Å] is comparable with the distance of 1.364(8) Å found in the zirconocene complex, and the C–C distances within the benzyne rings of both complexes are equivalent within experimental error, consistent with a delocalised aromatic structure arising from electron pair donation from the in-plane π-orbital of the C_6 ring coupled with a high degree of back-donation from the metal to the benzyne π* orbital. Thus, the benzyne unit in **4** may be regarded as a 2 electron ligand resulting in an overall 18 electron count for the complex. Contrastingly, the benzyne ligand in [Ta(η-C_5Me_5)-(η²-C_6H_4)Me₂][10] possesses alternating C–C bond lengths most likely reflecting electron pair donation from both of the filled orthogonal π-orbitals of the benzyne ligand (*i.e.* a 4 electron donor situation). For **4**, of particular significance is the alignment of C(1)–C(2) in the plane containing the Nb–P vector in accordance with metallocene-like frontier orbitals for the [Nb(η-C_5H_5)(N-2,6-$Pr^i_2C_6H_3$)] fragment. The only other structurally characterised niobium benzyne is the unusual lithiated species [Nb(C_6H_4)₂Ph₃(LiPh·thf)-(Li·thf)₄]·0.5thf·0.5C_6H_{14} (thf = tetrahydrofuran) derived from the reaction of NbCl₅ with an excess of PhLi in thf.[11]

The benzyne and benzylidene complexes reported here lend strong support to the analogy between half-sandwich niobium imido species and zirconocene derivatives and provide access to compounds of potential utility in organic synthesis.

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