Observing and modelling energetically close α- and β-carbon–hydrogen agostic interactions in an isopropyl tris(pyrazolyl)boratoniobium complex

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An equilibrium between α- and β-agostic interactions has been observed in Tp*Nb(Cl)(CHMe$_2$)(PhC≡CMe) 1 [Tp* = hydridotris(3,5-dimethylpyrazolyl)borate] while only α-agostic interactions have been observed for the analogous ethyl complex; calculations using the hybrid QM/MM method IMOMM (B3LYP:mm3) methodology properly account for the experimental results, and suggest that steric effects are responsible for the presence of distinct minima in the isopropyl complex.

Agostic interactions have been found to play an important role in the olefin polymerization reactions and also in the isomerization and dynamics of alkyl groups.[1–5] One of the central issues has been the competition between α- and β-agostic interactions. While theoretical studies have suggested that the two situations could correspond to stable minima, the β-agostic interaction has always been calculated to be energetically favored.[6] To our knowledge, the two types of agostic interactions have never been observed in any single system, since fast rotation of alkyl chain makes characterization of secondary minima unlikely on the NMR time scale. We report here the first observation of an equilibrium between α-C–H and β-C–H agostic forms of an isopropyl group in the formally d^2 complex Tp*Nb(Cl)(CHMe$_2$)(PhC≡CMe) **1** [Tp* = hydridotris(3,5-dimethylpyrazolyl)borate]. We have previously shown that *n*-alkyl complexes such as Tp*Nb(Cl)(CH$_2$R)(PhC≡CMe) exhibit only α-agostic interaction.[7]

The isopropyl complex Tp*Nb(Cl)(CHMe$_2$)(PhC≡CMe) **1** has been isolated in 75% yield from the reaction of Tp*NbCl$_2$(PhC≡CMe)[8] with 1 equiv. of (CHMe$_2$)MgCl.[9] X-Ray diffraction[10] on a single crystal at 160 K reveals a β-agostic structure as shown in Fig. 1. Interaction of one β-H with Nb results in a pronounced distortion of both the alkyl ligand and the metal coordination sphere. An acute Nb–Cα–Cβ angle, a shortened Cα–Cβ bond, a close Nb–Hβ contact and a markedly obtuse Cα–Nb–Cl angle are noteworthy data.[1] The conformation of the isopropyl group is such that the non-agostic Me sits in the wedge formed by two *cis*-pyrazole rings, as do the R groups in Tp*Nb(Cl)(CH$_2$R)(PhC≡CMe) complexes, all of which exhibit α-agostic structures.[7] NMR studies on **1**, however, reveal a more complex situation in solution.

The ^{1}H NMR spectra of **1** in CD$_2$Cl$_2$ indicate dynamic behavior due to an unprecedented equilibrium between a β- and an α-agostic form, **1β** and **1α** respectively (Scheme 1). In the slow exchange regime (193 K), the equilibrium constant measured as the ratio **1β** : **1α** is 3.9 ($\Delta G°_{193} = -2.2$ kJ mol^{-1}). **1β** is characterized by isopropyl methyls at δ 1.29 and 0.05 (both d, J 7 Hz) and a methine proton at δ 2.10. The 'in-plane' rotation of the agostic Me is not frozen out as observed in other β-agostic complexes of the early transition metals. Evidence for the β-agostic interaction thus comes from the ^{13}C NMR data which are consistent with the rehybridization of Cα towards sp^2(δ 72.0, $^1J_{CH}$ 141 Hz). Spectroscopic data for **1α**, including a shielded Hα at δ −1.13 and a broad deshielded Cα at δ 126.4 with a reduced $^1J_{CH}$ (100 ± 5 Hz), testify to the α-agostic interaction. Significantly, there is no NMR evidence for a putative third Nb–C rotamer, which might or might not have a β-agostic interaction, namely that with Hα in the wedge formed by the two *cis* pyrazole rings (see discussion of the X-ray data).

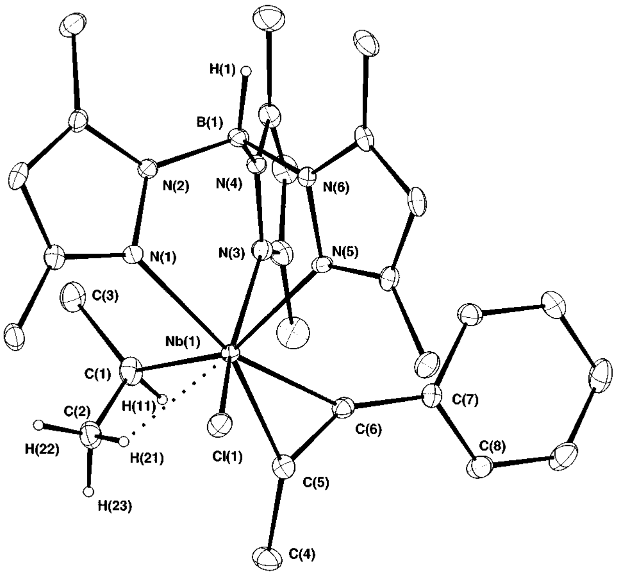
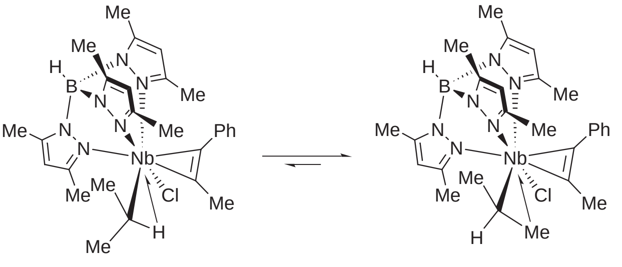


Fig. 1 Plot of the molecular structure of **1**. Located and refined H are shown. Selected bond lengths (Å): Nb(1)–C(1), 2.228(4); Nb(1)···C(2), 2.608(4); C(1)–C(2), 1.476(7); C(1)–C(3), 1.535(6); Nb(1)–H(21), 2.17(5). Selected bond angles (°): Nb(1)–C(1)–C(2), 87.0(3); Nb(1)–C(1)–C(3), 121.2(3); Cl(1)–Nb(1)–C(1), 122.1(1); C(2)–C(1)–C(3), 115.3(4); Cl(1)–Nb(1)–C(1)–C(2), 5.3; Nb(1)–C(1)–C(2)–H(21), 2.4.

The synthesis of Tp*Nb(Cl)[CH(CD$_3$)$_2$](PhC≡CMe) (**1**-d_6), selectively deuterated at the isopropyl methyls, has been achieved.[9] Owing to the preference for H rather than D to occupy an agostic position,[1,11] a thermodynamic isotope effect



1α

1β

Scheme 1

should lead to an equilibrium shift towards the formation of **1α**-d_6, *i.e.* to a smaller equilibrium constant. An isotopic perturbation of the equilibrium is indeed observed. At 193 K the ratio **1β**-d_6 : **1α**-d_6 is 3.2 ($\Delta G^\circ_{193} = -1.9$ kJ mol^{-1}), which translates to a $\Delta\Delta G^\circ_{193}$ of 0.3 kJ mol^{-1} in favor of **1α**, giving further evidence for the proposed equilibrium between β- and α-agostic forms of the isopropyl group.

The electronic structure of the isopropyl complex **1**, along with that of the ethyl complex,[7b] were examined using the integrated molecular orbitals and molecular mechanics (IMOMM) methodology,[12,13] which has recently been used successfully to model agostic interactions.[15] Only one minimum was located for the ethyl complex, corresponding to the structurally characterized α-agostic isomer.[7b] In contrast, two minima are obtained for the isopropyl complex, one corresponding to the β-agostic structure described above, and the other, 9.3 kJ mol^{-1} higher in energy, to an α-agostic isomer related to the first by rotation of 120° about the Nb–CH(CH$_3$)$_2$ bond. All three minima show features typical of agostic interactions, namely short Nb···H distances (2.35–2.58 Å), long agostic C–H bonds (1.112–1.116 Å), obtuse Cl–Nb–Cα angles (110.8–126.9°) and angles substantially less than 109.5° (86.3–92.4°) between the Nb–Cα bond and the agostic group (H or CH$_3$).

The location of two distinct minima for the isopropyl system, lying very close in energy, raises the question of the origin of the barrier to rotation about the Nb–C bond. The absence of a β-agostic minimum for the ethyl complex suggests that the barrier is not caused by the intrinsic stability of the agostic interactions themselves. The hindered rotation may be thus caused by the steric constraints of the Tp* ligand. The most sterically favorable conformation for the alkyl chain places one Me group along a wedge defined by two *cis*-pyrazole rings, where the pendant methyl groups of Tp* present a significant barrier to rotation about the Nb–C bond. This ‘locking’ of the non-agostic Me group leaves an α-C–H bond and a Me group to compete for the electron deficient Nb centre in the isopropyl complex, but only two α-C–H groups in the ethyl analogue, thereby accounting for the presence of two distinct isomers in the former, but only one in the latter.

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Notes and References

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9 Complex **1** like its dichloro precursor[8] exists as a mixture of discrete rotamers depending on the orientation of PhC≡CMe with respect to the organometallic moiety. Data are discussed and depicted for the major alkyne rotamer but all conclusions are valid for the other rotamer. Full analytical and spectroscopic data are available from the authors.

10 *Crystal data* for **1**: $C_{27}H_{37}BClN_6Nb$, M = 584.8, monoclinic, $P2_1/n$, a = 15.169(2), b = 10.7604(7), c = 16.886(2) Å, β = 98.43(1)°, V = 2726(1) Å^3, Z = 4, T = 160 K, μ = 5.47 cm^{-1}, R = 0.0289, Rw = 0.0281 for 2412 reflections [$I > 2\sigma(I)$] and 342 parameters. CCDC 182/966.

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13 IMOMM calculations were performed on the experimental complex replacing Ph of alkyne by H. The QM part of the calculation was performed on the model system $[Nb(NH{=}CH_2)_3Cl\{CH(CH_3)_2\}(HCCH)]^+$ with Gaussian 92/DFT,[14a] using the B3LYP density functional. A pseudopotential was used for the internal electrons of niobium, and a valence double-ζ basis set for all atoms, with the addition of a polarisation d shell on Cl. The positive charge in the QM part, which arises because the negatively charged Tp* ligand is replaced by three neutral NH=CH$_2$ groups, should not influence the relative energies of the two minima. The molecular mechanics (MM) part was performed using mm3(92).[14b]

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