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An unprecedented α-C–C agostic interaction in a cyclopropyl tris(pyrazolyl)boratoniobium complex†

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Structural, spectroscopic and theoretical evidence indicate that an unusual α-C–C agostic interaction is preferred over both α- and β-C–H agostic alternatives in the title compound, $Tp^{Me2}NbCl(c\text{-}C_3H_5)(MeCCMe)$.

Since the earliest reports of C–H agostic interactions,[1] much effort has been expended on developing an understanding of what was, at the time of its discovery, an entirely new type of chemical bond.[2] Of the multitude of agostic complexes that have been characterised in the intervening period, the vast majority involve a β-C–H bond although, in the absence of such groups, α-C–H agostic species have also been observed. Very recently, it has been shown that steric factors can overcome the intrinsic electronic preference for the β-agostic structure, leading, in certain circumstances, to equilibria between α- and β-agostic isomers.[3] In marked contrast to the plethora of well-characterised C–H agostic bonds, examples where a metal centre interacts with a saturated C–C, rather than C–H, bond are extremely rare, and have only been observed in systems where no viable C–H agostic alternative is available.[4] In this paper, we report the synthesis, structure and spectroscopic properties of the cyclopropyl Nb^{III} complex, $Tp^{Me2}NbCl(c\text{-}C_3H_5)(MeCCMe)$ (**1**). Remarkably, despite the presence of both α and β hydrogens, this system shows no sign of C–H agostic interactions of any kind, but instead adopts the rare α-C–C agostic structure. Hybrid density functional/molecular mechanics calculations reveal that the unique electronic properties of the cyclopropyl ligand, rather than the steric constraints of the Tp^{Me2} ligand, are responsible for the adoption of the unusual α-C–C structure.

The molecular structure of **1** (Fig. 1)[5] reveals many of the features exhibited by its straight-chain analogues (R = Et, ^{i}Pr, *sec*-Bu), but also some remarkable differences. In the straight chain alkyl complexes,[3a,b] the typical structural indicator of an agostic C–H interaction is an opening of the Cl–Nb–Cα angle and a tilting of the alkyl group to place the agostic C–H bond (either α or β) approximately in the Cl–Nb–Cα plane. The opening of the Cl–Nb–C(1) angle is clearly discernable in **1** (110.85(8)°), but, remarkably, the cyclopropyl group itself shows no evidence for a C–H agostic interaction of any kind. The orientation of the cyclopropyl group is such that Hα (which has been located) is directed away from the metal centre (Nb···H(11) = 2.72(4) Å), effectively precluding an α agostic interaction. Moreover, although the cyclopropyl group is tilted towards the Cl ligand (Nb–C(1)–C(2) = 131.4(2)°, Nb–C(1)–C(3) = 109.7(2)°), the restricted rotation about C(1)–C(2) prevents either of the β-C–H bonds (hydrogens have been located) from lying in the Cl–Nb–Cα plane. The temperature-independent solution ^{1}H and ^{13}C NMR spectra of **1** are entirely consistent with the absence of C–H agostic interactions; the cyclopropyl protons resonate as complex multiplets between δ 0.95 and 2.24 (the shielded signal is tentatively assigned to Hα) while the ^{13}C spectrum shows a doublet ($^{1}J_{CH}$ 139 Hz) for Cα at δ 75.3 and triplets for Cβ at δ 23.2 and 13.8. Although Cα is slightly deshielded, and its $^{1}J_{CH}$ reduced compared to Cβ, no C–H agostic interaction is apparent from the data.[6]

The properties of **1** therefore pose an intriguing paradox: whilst the first coordination sphere shows clear evidence for donation of an electron pair from the cyclopropyl group to the formally 16-electron Nb centre, there is no evidence to suggest that this electron pair comes from a C–H bond. The structure of the cyclopropyl ring does, however, offer an alternative explanation. The C(1)–C(3) bond also lies approximately in the Cl–Nb–Cα plane (Cl(1)–Nb(1)–C(1)–C(3) = 336°), and the C(1)–C(3) bond length of 1.539(4) Å is some 0.05 Å greater than either of the other C–C bonds in the ring. This elongation is quite distinct from the contraction typically observed in β-C–H agostic systems, and strongly suggests that it is the C–C, rather than the C–H, bond that is donating an electron pair to the Nb^{III} centre. In general terms, of course, the adoption of a β-C–H agostic structure will necessarily place the α-C–C bond in a position where it could also interact with the metal centre. In the case of compound **1**, and very unusually, it appears that the α-C–C bond is a more effective donor than its β-C–H counterpart. Remarkably, all of these distinctive features are also apparent in the bromo analogue of **1**, $Tp^{Me2}NbBr(c\text{-}C_3H_5)(MeCCMe)$ (**2**).[5]

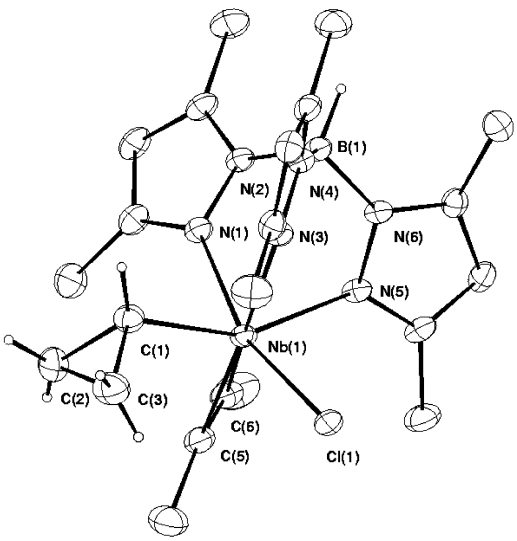

Fig. 1 Plot of the molecular structure of (**1**). Selected bond lengths (Å): Nb(1)–Cl(1), 2.4465(6); Nb(1)–C(1), 2.159(3); C(1)–C(3), 1.539(4); C(1)–C(2), 1.490(4); C(2)–C(3), 1.478(5); Nb(1)–C(2), 3.336(3); Nb(1)–C(3), 3.045(3). Selected bond angles (°): Nb(1)–C(1)–C(3), 109.7(2); Nb(1)–C(1)–C(2), 131.4(2); Cl(1)–Nb(1)–Cl(1), 110.85(8); Cl(1)–Nb(1)–C(1)–C(3), 24.

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b3/b300324h/

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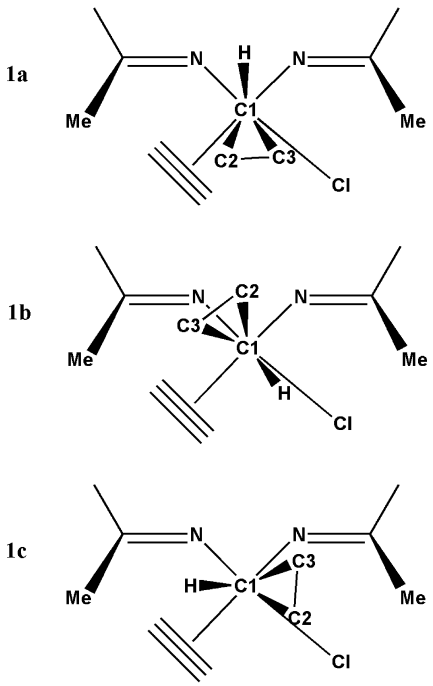
These observations have prompted us to conduct a detailed examination of the electronic structure of **1** using a hybrid density functional/molecular mechanics methodology.[7] Similar techniques were employed in our analysis of the related straight-chain alkyl complexes,[3a,b] where we showed that rotation about the Nb–Cα bond can, in principle, yield three distinct rotamers, each with a different substituent in the 'agostic' position in the Cl–Nb–Cα plane. The corresponding three rotamers of **1** are shown in Scheme 1, and their relative energies and optimised structural parameters are summarised in Table 1. The structure of the most stable of the three, **1a**, is very similar to the crystal structure of **1**. Most importantly, the distinct elongation of the C(1)–C(3) bond is accurately reproduced, and the C(3)–H bonds show no sign of the lengthening that would be expected if the β-C–H bond was involved in an agostic bond.[3a,b] In the other two rotamers, **1b** and **1c**, the bond in the agostic position [C(1)–H(11) and C(1)–C(2), respectively] is similarly elongated. Both **1b** and **1c**, however, lie significantly higher in energy than **1a**, consistent both with the observed structure of **1** and also the temperature independence of the NMR spectra.

Whilst the experimental and computational results clearly indicate that an α-C–C agostic is present in the ground state of **1**, we have not yet established the reasons why a C–H agostic alternative (either α or β) is not observed. One possible explanation is that the steric demands of the pendant methyl groups in the Tp^{Me2} ligand preferentially destabilise one or both of the C–H agostic alternatives, as has been shown to be the case in the acyclic analogues. The hypothesis can be probed in a computational experiment, by removing the three pendant methyl groups, thereby relieving the steric crowding around the cycloalkyl ligand. In this case, and in complete contrast to the straight-chain analogues, the relief of the steric strain causes only minimal changes in the structure of the three rotamers, and their energetic order (**1a** < **1b** < **1c**) remains the same. The limited impact of the pendant methyl groups probably reflects the fact that the cyclopropyl group occupies less space than its acyclic analogue, and is therefore less constrained by the steric pocket defined by the Tp^{Me2} ligand.



Scheme 1 The three rotamers of **1**, viewed along the Nb–C(1) axis.

Table 1 Optimised structural parameters and relative energies of the three rotamers of $Tp^{Me2}NbCl(c\text{-}C_3H_5)(MeCCMe)$

	X-ray	**1a**	**1b**	**1c**
Nb–C(1)/Å	2.159(3)	2.156	2.159	2.177
C(1)–C(2)/Å	1.490(4)	1.514	1.513	1.534
C(1)–C(3)/Å	1.539(4)	1.550	1.506	1.515
C(1)–H(11)/Å	0.97(4)	1.091	1.106	1.086
C(3)–C(1)–Nb–Cl/°	336.0	330.4	208.3	65.8
Energy/kcal mol^{-1}		0.0	6.2	8.2

The calculations described in the preceding paragraph prove conclusively that the preference for the unusual structure of **1** has an electronic, rather than steric, origin. It is less straightforward, however, to identify the precise nature of the interaction between the metal and the cyclopropyl group. The most obvious difference between the cyclopropyl system and its straight chain analogues, where C–H agostic interactions always dominate, is the very small C–C–C angles, which lead to less than optimal overlap of the hybrid orbitals on the carbon atoms (so-called 'banana bonds'). Calculations performed at the same level of theory used for the complexes (B3LYP/6-31G**) confirm that, whilst the HOMO of propane has dominant C–H bonding character, the corresponding orbital in cyclopropane is localised between the carbon centres, and orbitals with dominant C–H character lie some 2 eV lower in energy. The relative destabilisation of the C–C σ orbitals naturally makes them more able to interact with the metal centre. Thus, although the preferred conformation places both the α-C–C and β-C–H bonds close to the agostic bonding position, the unusually high energy of the C–C σ orbitals in the cyclopropyl ligand dictates the preference for the C–C, rather than C–H, agostic structure.

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Notes and references

1 M. Brookhart, M. L. H. Green and L. L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

2 (*a*) A. Demolliens, Y. Jean and O. Eisenstein, *Organometallics*, 1986, **5**, 1457; (*b*) A. Haaland, W. Scherer, K. Ruud, G. S. McGrady, A. J. Downs and O. Swang, *J. Am. Chem. Soc.*, 1998, **120**, 3762.

3 (*a*) J. Jaffart, R. Mathieu, M. Etienne, J. E. McGrady, O. Eisenstein and F. Maseras, *Chem. Commun.*, 1998, 2011; (*b*) J. Jaffart, M. Etienne, F. Maseras, J. E. McGrady and O. Eisenstein, *J. Am. Chem. Soc.*, 2001, **123**, 6000; (*c*) R. H. Grubbs and G. W. Coates, *Acc. Chem. Res.*, 1996, **29**, 85; (*d*) M. D. Fryzuk, S. A. Johnson and S. J. Rettig, *J. Am. Chem. Soc.*, 2001, **123**, 1602; (*e*) F. M. Alias, M. L. Poveda, M. Sellin and E. Carmona, *J. Am. Chem. Soc.*, 1998, **120**, 5816.

4 (*a*) A. Vigalok and D. Milstein, *Acc. Chem. Res.*, 2001, **34**, 798; (*b*) G. Lanza, I. L. Fragalia and T. J. Marks, *J. Am. Chem. Soc.*, 2000, **122**, 12764; (*c*) R. Tomaszewski, I. Hyla-Kryspin, C. L. Mayne, A. M. Arif, R. Gleiter and R. D. Ernst, *J. Am. Chem. Soc.*, 1998, **120**, 2960.

5 Crystal data for **1: $C_{22}H_{33}NbClN_6B$,** M = 520.7, triclinic, $P1$, a = 10.697(2), b = 10.755(2), c = 13.164(2) Å, α = 96.58(2), β = 106.87(2), γ = 118.49(2)°, V = 1215(1) Å^3, Z = 2, T = 160 K, μ = 0.63 cm^{-1}, R = 0.0277 (on F), Rw = 0.0346 for 3195 reflections with $I > 2\sigma(I)$. For **2: $C_{22}H_{33}NbBrN_6B$,** M = 565.17, triclinic, $P1$, a = 10.747(2), b = 10.852(2), c = 13.211(2) Å, α = 96.16(2), β = 106.91(2), γ = 119.21(2)°, V = 1228(1) Å^3, Z = 2, T = 160 K, μ = 2.10 cm^{-1}, R = 0.0393 (on F), Rw = 0.0316 for 5785 reflections with $I > 3\sigma(I)$. CCDC 201292 and 201293. See http://www.rsc.org/suppdata/cc/b3/b300324h/ for crystallographic data in CIF or other electronic format.

6 C. P. Schaller, C. P. Cummins and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1996, **118**, 591.

7 Calculations were performed using the ONIOM option within Gaussian 98. The quantum mechanical partition, $[Nb(NH{=}CH_2)_3Cl(C_3H_5)(HCCH)]^+$, was treated using the B3LYP functional. The LANL2DZ basis set was used for Nb and Cl, augmented by a d polarisation function in the latter case. The three N atoms, along with all atoms in the cyclopropyl unit, were described with the 6-31G** basis, with 6-31G* on the remainder of the atoms. A pseudopotential (LANL2) was used for the inner electrons of Nb. The universal force field (UFF) was used to describe the molecular mechanics partition.