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Steric and Electronic Probes for α-Agostic Interaction in a Niobium Ethyl Complex

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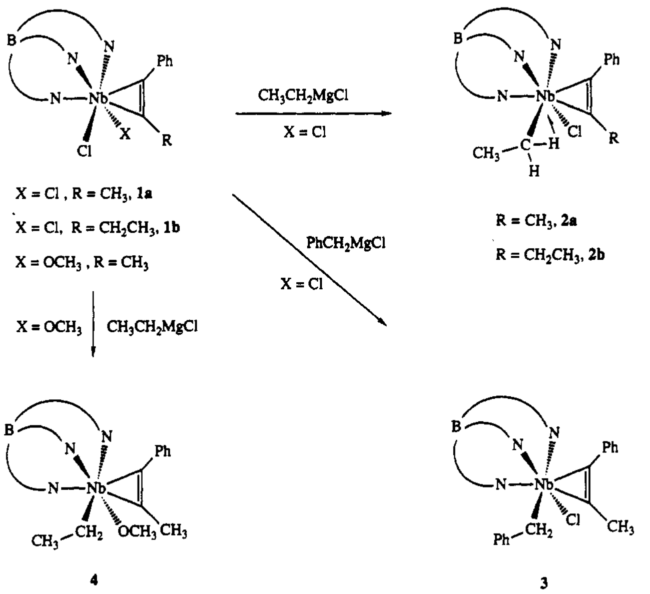
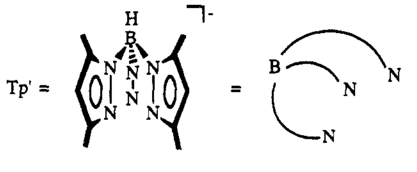
Summary: The new ethyl complexes $Tp'Nb(Cl)(CH_2CH_3)(PhC{\equiv}C{-}R)$ *(Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate; R =* CH_3*,* ***2a****; R =* CH_2CH_3*,* ***2b****) are shown to exhibit an α-hydrogen agostic interaction. The reason why the α-agostic interaction is preferred over a more conventional β-agostic interaction is proposed to lie on steric grounds. Accordingly, the bulkier benzyl ligand in* $Tp'Nb(Cl)(CH_2Ph)(PhC{\equiv}CCH_3)$ *(****3****) coordinates in an* η^1 *fashion, whereas the good π-donor methoxy ligand in* $Tp'Nb(OCH_3)(CH_2CH_3)(PhC{\equiv}CCH_3)$ *(****4****) weakens the α-agostic bond.*

Alkyl complexes exhibiting β-hydrogen agostic interaction are much more numerous than those with α-hydrogen agostic bonds.[1] Similarly, β-hydride elimination is generally more facile than α-hydrogen elimination.[2] This is particularly the case for the heavier group 5 metals niobium and tantalum.[3] A recent example[4] is found in the reaction of the imido complex $CpNb(NR)Cl_2$ with ethylmagnesium chloride that leads to an ethene complex via β-hydride elimination. A rare case of competition between α- and β-hydrogen elimination[5] results in an equilibrium between a tantalum neopentyl ethene complex and a tantalum neopentylidene ethyl complex. We describe herein the synthesis and characterization of stable *α-agostic ethyl* complexes of niobium together with some preliminary observations on the occurrence of such a system (see Scheme 1). As far as we are aware, only one example of a very weak α-agostic interaction in an 18 electron ethyl complex has been reported.[6] α-Agostic alkyls have recently been identified as intermediates or transition states during Ziegler-Natta type polymerization of olefins.[7]

Scheme 1





Addition of 1 equiv of ethylmagnesium chloride to a toluene solution of $Tp'NbCl_2(PhC{\equiv}C{-}R)$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate; R = CH_3, **1a**; R = CH_2CH_3, **1b**)[8] affords the orange chloro ethyl derivatives $Tp'Nb(Cl)(CH_2CH_3)(PhC{\equiv}C{-}R)$ (R = CH_3, **2a**; R = CH_2CH_3, **2b**) in greater than 80% yield (Scheme 1). Prominent ^1H NMR data include an AM_3X pattern for the niobium bound ethyl group of **2a** and **2b**.[9] One of the diastereotopic methylene protons H_A is deshielded [for **2a**, δ 3.84 (dq, J_{AX} = 12.8 Hz, J_{AM} = 7.7 Hz, 1H, NbHC*H*CH$_3$); for **2b**, δ 4.02 (dq, J_{AX} = 12.6 Hz, J_{AM} = 7.8 Hz, 1H, NbHC*H*CH$_3$)] and the other one H_X is conspicuously shielded [for **2a**, δ 0.37 (dq, J_{AX} = 12.4 Hz, J_{MX} = 6.2 Hz, 1H, Nb*H*CHCH$_3$); for **2b**, δ 0.37 (dq, J_{AX} = 12.7 Hz, J_{MX} = 6.3 Hz, 1H, Nb*H*CHCH$_3$)], whereas the methyl group appears as a doublet of doublets [for **2a**, δ 1.15, J_{AM} = 7.6 Hz, J_{MX} = 6.1 Hz; for **2b**, δ 1.13, J_{AM} = 7.6 Hz, J_{MX} = 6.2 Hz]. These

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(9) All the complexes described here exist as mixtures of two isomers differing in the alkyne orientation with respect to the Tp′ ligand.[8] Only data for the major isomer are reported but all observations and conclusions are also valid for the minor isomers. Full data are available in the supplementary material. All complexes were synthesized following the same procedure described in detail for $Tp'Nb(Cl)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (**2a**). To a vigorously stirred toluene (30 mL) solution of $Tp'NbCl_2(PhC{\equiv}CCH_3)$ (**1a**) (0.840 g, 1.45 mmol) cooled to −25 °C is added dropwise under dinitrogen an ethereal solution of ethylmagnesium chloride (0.8 mL of a 2.0 M solution). The temperature is maintained at −20 °C for 1 h. The resulting orange slurry is further stirred for 1 h at room temperature. The solvent is partially evaporated under vacuum to *ca.* 20 mL, and an equal volume of hexanes is added. The slurry is filtered through a pad of Celite that is washed several times with hexanes. The clear orange solution is evaporated to dryness to give either an orange oil or powder. Recrystallization from toluene (minimum amount)/hexane mixtures gives orange microcrystals of **2a** in 86% yield (0.720 g, 1.25 mmol).

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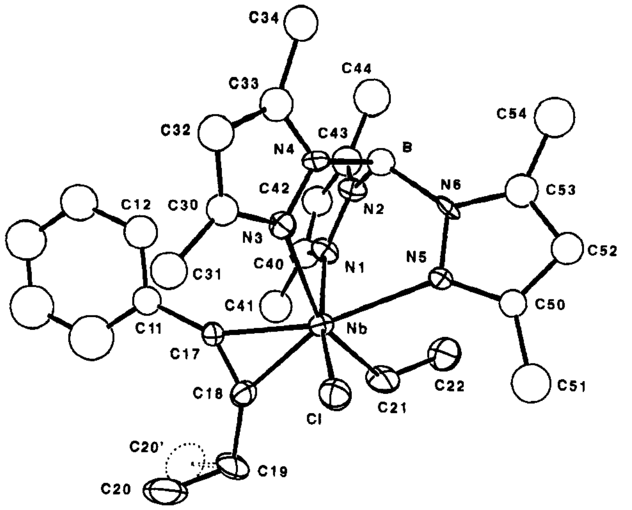

Figure 1. ORTEP plot of $Tp'Nb(Cl)(CH_2CH_3)(PhC{\equiv}C{-}CH_2CH_3)$ (**2b**).

spectral features are temperature independent in the 213–323 K range. In the ^{13}C NMR spectrum, the methylene carbon bound to niobium gives a broadened (due to coupling to the niobium nucleus) doublet of doublets [for **2a**, δ 86.5 (dd, $w_{1/2}$ = 12 Hz, J_{CH} = 108, 129 Hz, $NbHCHCH_3$); for **2b**, δ 86.3 (dd, J_{CH} = 108, 130 Hz, $NbHCHCH_3$)]. Both of these ^1H and ^{13}C NMR features are characteristic of a static α-hydrogen (H_X) agostic interaction.[1,10,11]

The molecular structure of **2b** determined by X-ray diffraction[15] is shown in Figure 1. The overall geometry is that observed previously[8] for $Tp'NbCl_2(PhC{\equiv}C{-}CH_3)$: the alkyne bisects the $Cl{-}Nb{-}CH_2CH_3$ angle (vertical geometry), the niobium being in a roughly octahedral environment if the alkyne is considered to occupy one coordination site. Evidence for an α-agostic interaction in the crystal comes from the following data: the $Nb{-}C_\alpha$ bond length (Nb—C21 = 2.17 (2) Å) is significantly shorter than a simple niobium—carbon single bond and the $Nb{-}C_\alpha{-}C_\beta$ angle is more obtuse (Nb—C21—C22 = 126(1)°) than that observed in anagostic[12] or even very weak[6] α-agostic complexes ($Cp_2Nb(CH_2CH_3)(C_2H_4)$,[12] $Nb{-}C_\alpha$ = 2.316(8) Å, $Nb{-}C_\alpha{-}C_\beta$ = 118.6(7) °; $Cp_2Nb(CH_2CH_3)(CH_3C{\equiv}CCH_3)$,[6] $Nb{-}C_\alpha$ = 2.31(1) Å, $Nb{-}C_\alpha{-}C_\beta$ = 121(1)°; typical niobium—carbon double bonds: $C_5Me_5Nb({=}CHPh)(NR)(PMe_3)$,[16] 2.026(4) Å; $Tp'(CH_3O)\overline{Nb[{=}C(Ph)C(CH_3)C(CH_3)O}]$,[17] 1.983(5) Å). The data for our complex compare well with those of a tantalum α-agostic complex $[\eta^5\text{-}C_5(tBu)(CH_2tBu)_2(CH_2CMe_2CH_2)_2]TaCl_2$ ($Ta{-}C_\alpha$ = 2.176(7) Å, $Ta{-}C_\alpha{-}C_\beta$ = 128.6(4)°),[13] and with those of the recently described α-agostic neopentylniobium complex $CpNb(N\text{-}2,6\text{-}C_6H_3iPr_2)(CH_2tBu)_2$ ($Nb{-}C_\alpha$ = 2.174(3) and 2.215(3) Å, $Nb{-}C_\alpha{-}C_\beta$ = 131.2(2) and 132.5(3)°).[14] Similar geometric trends have been observed in neopentylthorium[18] and benzyltitanium[19] α-agostic complexes.

We have started to systematically probe the factors that could lead to such an interaction. The benzyl derivative $Tp'Nb(Cl)(CH_2Ph)(PhC{\equiv}CCH_3)$ (**3**) obtained by treatment of **1a** with benzylmagnesium chloride (Scheme 1) definitely has a normal η^1-benzyl group, as revealed by spectroscopic data. The methylene protons give an AB quartet in the ^1H NMR spectrum [δ 3.95 and 3.21 (d, J = 9.5 Hz)] and in the ^{13}C spectrum, the methylene carbon bound to niobium resonates at δ 89.6 (br t, J_{CH} = 120 Hz), the *ipso*-carbon of the benzyl group being observed around δ 153.[20] Interestingly, the case of the methoxy ethyl complex $Tp'Nb(OCH_3)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (**4**) (Scheme 1) is a not a clear cut situation. The ^1H and ^{13}C NMR data [^1H NMR (unchanged between 193 and 323 K in toluene-d_8) δ 2.69 (dq, J = 14.0, 7.1 Hz, 1H) and 1.60 (dq (pseudosextet), J = 7.0, 14.0 Hz, 1H) $NbCH_2CH_3$, 1.09 (t, J = 7.4 Hz, $NbCH_2CH_3$); ^{13}C NMR δ 51.8 (br t, J_{CH} = 116 Hz, $NbCH_2CH_3$); at 183 K, the triplet pattern is no longer resolved, the signal being exceedingly broad] cannot be taken as evidence for an α-agostic interaction in **4**: the difference between the ^1H NMR chemical shifts of the methylene protons is between those of **2a** and **3**, and chemical shifts themselves are only marginally exceptional in **4**. Also the $^1J_{CH}$ value is "normal" but might well be an average for a "low" and a "high" value (see data for **2**) for a fluxional system, so that if there is any α-interaction it is much weaker than that in **2a** and **2b**. Presumably, the methoxide ligand being a better π-donor than chloride more efficiently competes with one of the $C_\alpha{-}H$ bonds of the ethyl group for donation into a vacant niobium orbital.

Complexes of the type $Tp'Nb(X)(Y)(PhC{\equiv}CR)$ are formally 16 electron species, the metal being either Nb(III), d^2, or Nb(V), d^0, if the alkyne is considered substantially reduced. The availability of the LUMO in the Cp series $CpNb(X)(Y)(PhC{\equiv}CR)$ is hampered by a large HOMO–LUMO gap,[21] although reactions with isonitriles and carbon monoxide have been observed in both the Cp and Tp' series.[17,22] Thus there is an empty orbital available for interaction with one of the $C_\alpha{-}H$ bonds and, again, the case of complex **4** containing a good π-donor methoxide ligand is significant in this respect. Work is in progress to understand the bonding in our Tp' complexes. Finally, recall that a β-agostic interaction is much

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(10) More precisely in the case of group 5 alkyl complexes, these data significantly differ from those for the nonagostic ethyl ethene complex[12] $Cp_2Nb(CH_2CH_3)(C_2H_4)$ and compare well with those of the α-agostic tantalum complex[13] $[\eta^5\text{-}C_5(tBu)(CH_2tBu)_2(CH_2CMe_2CH_2)_2]TaCl_2$ and with those of the recently described α-agostic neopentylniobium[14] complex $CpNb(N\text{-}2,6\text{-}C_6H_3iPr_2)(CH_2tBu)_2$.

(11) Comparison of the solid state infrared spectra of **2a** and **2b** with those of other $Tp'NbXY(PhC{\equiv}CR)$ complexes, including **3** and **4**, in the 3000–2000-cm^{-1} region does not securely allow any reduced carbon—hydrogen stretch assignment. Note that the boron—hydrogen stretch from the Tp' ligand is observed around 2550 cm^{-1}.

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(15) Crystal data: orthorhombic, D_{2h}^{15}–*Pbca*, a = 16.272(3) Å, b = 17.663(2) Å, c = 19.802(3) Å, V = 5690(2) Å, Z = 8, λ(Mo Kα_1) = 0.7093 Å, ρ_{calcd} = 1.365 g·cm^{-3}, μ = 5.24 cm^{-1}. The final residuals for 218 variables refined against 1663 unique data with $F_o^2 > 5\sigma(F_o^2)$ were R = 0.067 and R_w = 0.075. Full details of the structure are available as supplementary material.

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more sterically demanding than an α-agostic interaction[1] and that steric properties are part of the unique ligating characteristics of the Tp′ ligand.[23] Shielding of the metal by the Tp′ ligand prevents the bending of the ethyl group necessary for a β-agostic interaction. The fact that the bulkier benzyl ligand in **3** coordinates in an η^1 fashion corroborates this idea.

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Supplementary Material Available: A textual presentation of full analytical and spectroscopic data for complexes **2a**, **2b**, **3**, and **4**, photocopies of the ^{13}C and $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b**, and X-ray structural parameters for **2b** including tables of experimental data, atomic coordinates, thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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