Alkyne[hydrotris(pyrazolyl)borato]tantalum Complexes – An Ethyl Group is a Better α-Agostic Donor Than a Methyl Group

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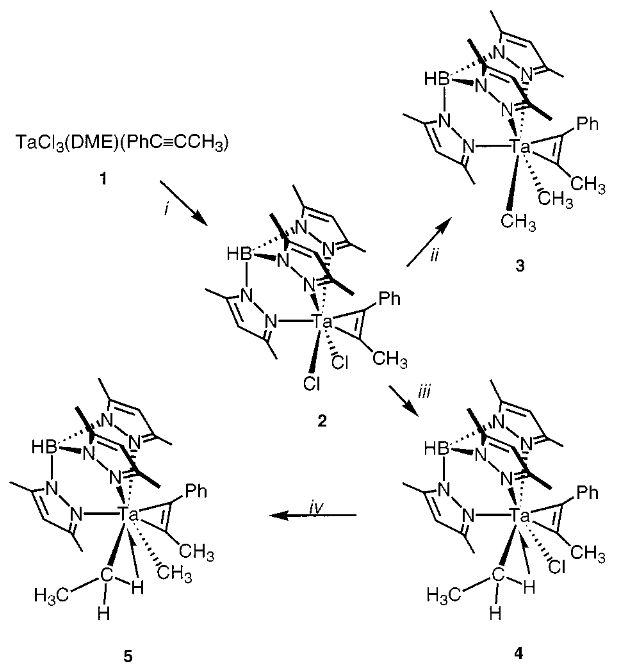
The synthesis of unprecedented alkyne hydrotris(3,5-dimethylpyrazolyl)borato (Tp^{Me2}) tantalum(III) complexes is reported. The parent dichloro complex $Tp^{Me2}TaCl_2(PhC{\equiv}CCH_3)$ (**2**) is obtained from $TaCl_3(DME)(PhC{\equiv}CCH_3)$ and KTp^{Me2}. **2** reacts with methyllithium to give the dimethyl complex $Tp^{Me2}Ta(CH_3)_2(PhC{\equiv}CCH_3)$ (**3**) and with ethylmagnesium chloride to give the X-ray characterized α-agostic ethyl complex $Tp^{Me2}Ta(Cl)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ (**4**). Reaction of **4** with methyllithium generates the mixed methyl ethyl complex $Tp^{Me2}Ta(CH_3)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ (**5**) in solution. Spectroscopic data indicate that **5** is α-agostic at the ethyl group only.

Whereas β-agostic interactions in alkyl complexes are electronically favored,[1] steric constraints may induce a preference for an α-agostic interaction even though β-hydrogen atoms are available.[2] Competition between the two effects allowed us to observe the only example of an equilibrium between α- and β-agostic rotamers of an isopropyl group in $Tp^{Me2}Nb(Cl)(iPr)(PhC{\equiv}CCH_3)$ [Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate].[3] The steric pressure that causes α-agostic interaction is obviously weaker when the alkyl group is methyl and ascertaining the presence of these interactions then remains a challenge.[4] Together with the synthesis of unprecedented trivalent $Tp^{Me2}Ta$ complexes,[5] we herein provide evidence that the mixed ethyl methyl complex $Tp^{Me2}Ta(CH_3)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ is α-agostic at the ethyl group selectively. This unprecedented situation is brought about by the efficient steric control exerted by Tp^{Me2}.

The chemistry we report is summarized in Scheme 1. Addition of one equivalent of KTp^{Me2} to in situ generated[6a][6b] $TaCl_3(DME)(PhC{\equiv}CCH_3)$ (**1**) (DME = 1,2-dimethoxyethane) affords orange crystals of $Tp^{Me2}TaCl_2(PhC{\equiv}CCH_3)$ (**2**) in 40% yield. Just like during the synthesis of $Tp^{Me2}TaCl_2(=N\text{–}tBu)$,[7] the formation of the byproduct $[HB(C_3N_2Me_2H)_3BH][TaCl_6]$ lowers the yield. Addition of KTp^{Me2} to successfully isolated[6c] **1** only improves the yield slightly. $Tp^{Me2}SnCl_3$ does not react with **1**, although this reagent is efficient in the synthesis of tetra- and pentavalent $Tp^{Me2}Ta$ derivatives.[8] **2** has spectroscopic and structural properties akin to those of $Tp^{Me2}NbCl_2(PhC{\equiv}CCH_3)$.[9] Thus, the 4e-alkyne sits in the molecular mirror plane, and two discrete alkyne rotamers, depending on the orientation of the alkyne with respect to Tp^{Me2} are observed up to 373 K (^{1}H NMR, [D$_8$]toluene). The X-ray structure will be described elsewhere.

Both mono- and dialkyl derivatives have been synthesized. Treatment of **1** with two equivalents of methyllithium



Scheme 1. (i) KTp^{Me2}, toluene/DME; (ii) 2 $LiCH_3$, diethyl ether; (iii) CH_3CH_2MgCl, diethyl ether; (iv) $LiCH_3$, diethyl ether

gives $Tp^{Me2}Ta(CH_3)_2(PhC{\equiv}CCH_3)$ (**3**) in 70% yield. Here the yield is only limited by the high solubility of **3** in alkanes. The equivalent Ta-bound methyl groups of **3** give a singlet at δ = 0.76 in the ^{1}H-NMR spectrum, and a quadruplet centered at δ = 59.9 ($^1J_{CH}$ = 114 Hz) in the ^{13}C-NMR spectrum. These data are similar to those for $Tp^{Me2}Nb(CH_3)_2(PhC{\equiv}CCH_3)$[9] and $CpTa(CH_3)_2(ArC{\equiv}CAr)$,[10] and suggest the lack of any significant agostic interaction. The thermally stable $Tp^{Me2}Ta(Cl)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ (**4**) is obtained in 80% yield from the reaction between **1** and one equivalent of CH_3CH_2MgCl. A crystal structure analysis (Figure 1) reveals the α-agostic interaction through the distortion of the ethyl group with a very obtuse Ta–Cα–Cβ angle [Ta(1)–C(1)–C(2)= 123.5(3)°]. The Ta–Cα bond [Ta(1)–C(1) =

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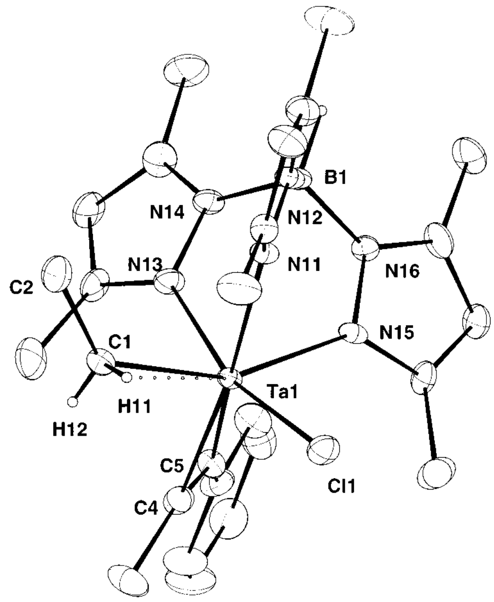

Figure 1. Plot of the molecular structure of $Tp^{Me2}Ta(Cl)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ (**4**); selected bond lengths [Å] and angles [°]: Ta(1)–Cl(1) 2.407(1), Ta(1)–C(1) 2.234(5), Ta(1)–C(4) 2.061(5), Ta(1)–C(5) 2.063(5), Ta(1)–H(11) 2.37(6), C(4)–C(5) 1.322(7); Cl(1)–Ta(1)–C(1) 104.4(2), Ta(1)–C(1)–C(2) 123.5(3), Ta(1)–C(1)–H(1) 88.6(43)

2.234(5) Å] remains normal. X-ray data collected at 160 K with an image plate detector combined with absorption corrections allowed the location of the methylene hydrogen atoms. The α-agostic interaction with H(11) is thus further substantiated by the observation of a short Ta···H contact [Ta(1)–H(11) = 2.37(6)°, Ta(1)–C(1)–H(11) = 88.6(43)°]. This interaction is the result of the steric locking of the ethyl group between two adjacent pyrazolyl groups which directs the methylene hydrogen atom in the appropriate location. ^{1}H- and ^{13}C-NMR-spectroscopies also give evidence for the α-agostic interaction in solution. In the room temperature ^{1}H-NMR spectrum, the entire ethyl group yields an AM_3X pattern with one shielded proton [δ = 0.59 (dq, J = 14.6, 6.6 Hz, 1 H, Ta(μ-*H*)CHCH$_3$), 1.40 (dd, J = 7.2, 6.7 Hz, 3 H, TaCH$_2$C*H*$_3$), 3.02 (dq, J = 14.6, 7.5 Hz, 1 H, Ta(μ-H)C*H*CH$_3$]. In the ^{13}C-NMR spectrum, the signal of the Ta-bound carbon atom appears as a doublet of doublets with one low and one high $^1J_{CH}$ [δ = 78.4 (dd, $^1J_{CH}$ = 102, 122 Hz)]. Similar X-ray and spectroscopic data characterize the analogous α-agostic ethyl- and related *n*-alkylniobium derivatives.[2a][2c]

Owing to the increased kinetic stability brought about by tantalum, **4** is thermally stable (373 K, toluene, 24 h) when the niobium analog readily rearranges to $Tp^{Me2}Nb(Cl)(CH_3)(PhC{\equiv}CCH_2CH_3)$ at 343 K (k = 3.0 10^{-5} s^{-1}).[2a] However, this kinetic stability allows the generation of the *unsymmetrical* dialkyl complex $Tp^{Me2}Ta(CH_3)(\mu\text{-}H\text{–}CHCH_3)(PhC{\equiv}CCH_3)$ (**5**) in quantitative yield from **4** and methyllithium in diethyl ether. Although **5** is thermally stable, it slowly decomposes upon attempted isolation. Attempts to synthesize such unsymmetrical niobium complexes lead to alkyl exchange and only dimethyl- and dibenzylniobium complexes have been obtained.[9] ^{1}H- and ^{13}C-NMR data obtained at room temperature on the crude reaction mixture are in favor of a single α-agostic interaction occurring exclusively with the ethyl group. The Ta-bound methyl group of **5** gives a ^{1}H-NMR singlet at δ = 0.68 and a ^{13}C-NMR quadruplet at δ = 55.2 ($^1J_{CH}$ = 116 Hz). In the ^{1}H-NMR spectrum, the diastereotopic methylene protons give a shielded and deshielded doublet of quadruplets at δ = –0.25 (J = 7.4, 15.0 Hz) and 2.46 (J = 7.2, 14.8 Hz). In the ^{13}C-NMR spectrum, the tantalum-bound carbon atom of the ethyl group is characterized by a doublet of doublets centered at δ = 78.0 ($^1J_{CH}$ = 105, 116 Hz). These data, compared to those for the dimethyl complex **3** and for the chloro(ethyl) complex **4**, indicate an α-agostic interaction with the ethyl group selectively. The strength of this interaction cannot be traced from the data: The ^{1}H-NMR chemical shift difference between the signals of the agostic and non-agostic methylene protons is slightly smaller in **4** (2.40 ppm) than in **5** (2.70 ppm) whereas the $^1J_{CH}$ differences are smaller for **5** (10 Hz) than for **4** (20 Hz). The agostic proton is also slightly more shielded in **5**. The ^{1}H-NMR data for **4** do not vary in the temperature range 193–363 K.

Whereas multiple agostic interactions are known, either from a single alkyl group[11a] or from two identical alkyl groups,[11b] it is the first time to our knowledge that two different alkyl groups compete for an agostic bonding. Here, the situation is dominated by the steric demand and directing properties of Tp^{Me2} both of which have little effect, if any, on a methyl group as compared to an ethyl group. The exclusive preference for agostic interaction with the ethyl group is a direct consequence of these properties. This is the main conclusion of this work in addition to the syntheses of the first trivalent $Tp^{Me2}Ta$ complexes.

Experimental Section

All reactions and workup procedures were performed under dry dinitrogen using conventional vacuum-line and Schlenk tube techniques. Toluene, DME, dichloromethane, pentane and *n*-hexane were dried and distilled by refluxing over calcium dihydride under dinitrogen. Diethyl ether was dried and distilled by refluxing over sodium benzophenone under dinitrogen. Tantalum pentachloride, zinc powder, 1-phenyl-1-propyne, methyllithium (1.6 M in diethyl ether) and ethylmagnesium chloride (2.0 M in diethyl ether) were used as received from commercial sources. [D$_6$]Benzene (degassed and stored over molecular sieves under dinitrogen) was used for NMR studies unless stated otherwise. ^{1}H- and ^{13}C-NMR data were acquired with Bruker AC 200, AM 250 or DPX 300. Elemental analyses were performed in the Analytical Service of our laboratory.

$Tp^{Me2}TaCl_2(PhC{\equiv}CCH_3)$ (2): A toluene/DME solution of $TaCl_3(DME)(PhC{\equiv}CCH_3)$, generated from $TaCl_5$ (2.15 g, 6.0 mmol), zinc powder (0.60 g, 9.0 mmol) and $PhC{\equiv}CCH_3$ (0.70 g, 6.0 mmol),[6] was filtered into a suspension of degassed KTp^{Me2} (2.02 g, 6.0 mmol) in DME (10 mL). The slurry was stirred for 5 h and then filtered through Celite to give a bright orange solution. The volatiles were removed under vacuum. The residue was extracted with toluene, filtered and dried under vacuum. This process was repeated three times to separate the less soluble [HB($C_3N_2Me_2H$)$_3$BH][$TaCl_6$]. $Tp^{Me2}TaCl_2(PhC{\equiv}CCH_3)$ was then obtained as an orange powder (1.60 g, 2.4 mmol, 40% yield). It can be recrystallized from a dichloromethane/hexane (1:1) mixture to give an analytical sample. $C_{24}H_{30}BCl_2N_6Ta$ (665.2): calcd. C 43.4, H 4.4, N 12.7; found C 43.1, H 4.1, N 12.7. – ^{1}H NMR: major isomer: δ = 1.82, 1.96, 2.08, 2.98 (all s, 6, 6, 3, 3 H, $Tp^{Me2}CH_3$), 4.22 (s, 3 H, ≡CCH_3), 5.35, 5.62 (both s, 2, 1 H, Tp^{Me2}CH), 6.83–7.00 (m, 5 H, C_6H_5); minor isomer (some resonances obscured): δ = 1.93, 2.71, 3.00 (all s, 6, 3, 3 H, $Tp^{Me2}CH_3$), 5.44, 5.68 (both s, 2, 1 H, Tp^{Me2}CH), 7.19 (t, J = 7.4 Hz, 1 H, p-C_6H_5), 7.5 (t, J = 7.7 Hz, 2 H, m-C_6H_5), 8.37 (d, J = 7.7 Hz, 2 H, o-C_6H_5); isomer ratio 7:1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): major isomer: δ = 12.6, 13.0, 15.3, 15.9 ($Tp^{Me2}CH_3$), 25.7 (≡CCH_3), 108.2, 108.6 (Tp^{Me2}CH), 128.6, 128.9, 130.5, 142.4 (C_6H_5), 144.2, 144.5, 153.4, 154.0 ($Tp^{Me2}CCH_3$), 226.8, 269.3 ($CH_3C{\equiv}CPh$).

[HB($C_3N_2Me_2H$)$_3$BH][$TaCl_6$]: $C_{15}H_{23}B_2Cl_6N_6Ta$ (702.7): calcd. C 25.6, H 3.3, N 11.9; found C 25.6, H 3.8, N 11.3. – ^{1}H NMR (CD_2Cl_2): δ = 2.42 (s, 6 H, CH_3), 6.07 (s, 1 H, CH).

$Tp^{Me2}Ta(CH_3)_2(PhC{\equiv}CCH_3)$ (3): Methyllithium (3.7 mmol, 2.3 mL of a 1.6 M ethereal solution) was added dropwise via syringe at –70 °C to a vigorously stirred suspension of $Tp^{Me2}TaCl_2$-($PhC{\equiv}CCH_3$) (1.00 g, 1.4 mmol) in diethyl ether (40 mL). The cooling bath was then removed and the orange suspension slowly turned to pale yellow. The mixture was stirred for 4 h and a white precipitate formed. The solvent was stripped off under vacuum and the residue was extracted three time in a mixture of pentane/diethyl ether (5:1). $Tp^{Me2}Ta(CH_3)_2(PhC{\equiv}CCH_3)$ was obtained as a spectroscopically pure yellow powder after the volatiles were removed. Crystallization from a minimum of pentane gave bright yellow needles (0.66 g, 1.0 mmol, 71% yield). $C_{26}H_{36}BN_6Ta$ (624.4): calcd. C 50.0, H 5.8, N 13.5; found C 50.2, H 5.8, N 13.6. – ^{1}H NMR: major isomer: δ = 0.76 (s, 6 H, $TaCH_3$), 1.71, 2.05, 2.21, 2.52 (all s, 6, 6, 3, 3 H, $Tp^{Me2}CH_3$), 3.86 (s, 3 H, ≡CCH_3), 5.48, 5.79 (both s, 2, 1 H, $Tp^{Me2}CH$), 7.05–8.13 (m, 5 H, C_6H_5); minor isomer (some resonances obscured): δ = 0.83 (s, 6 H, $TaCH_3$), 1.92, 2.04, 2.20, 2.53 (all s, 6, 6, 3, 3 H, $Tp^{Me2}CH_3$), 5.51, 5.78 (both s, 2, 1 H, $Tp^{Me2}CH$), 7.50 (t, J = 7.7 Hz, 2 H, C_6H_5), 8.10 (d, J = 7.7 Hz, 2 H, C_6H_5); isomer ratio 5:1. – ^{13}C NMR: major isomer: δ = 12.8, 12.7, 15.0, 15.4 ($Tp^{Me2}CH_3$), 25.2 (≡CCH_3), 59.9 (q, J = 114 Hz, $TaCH_3$), 107.5, 108.6 (Tp^{Me2}CH), 143.5, 143.8, 151.7, 151.9 ($Tp^{Me2}CCH_3$), 234.7, 262.3 ($CH_3C{\equiv}CPh$); minor isomer: δ = 60.7 ($TaCH_3$).

$Tp^{Me2}Ta(Cl)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (4): An ethereal solution of ethylmagnesium chloride (1.0 mmol, 0.5 mL of a 2.0 M solution) was added via syringe to a vigorously stirred suspension of Tp^{Me2}-$TaCl_2(PhC{\equiv}CCH_3)$ (0.53 g, 0.8 mmol) in diethyl ether (30 mL). The orange suspension slowly turned to a brownish yellow slurry. After filtration, the solution was concentrated to dryness and the residue was extracted with toluene and filtered through a pad of Celite. Concentration of the bright yellow solution to an oil (ca 2 mL) and addition of pentane (10 mL) led to immediate precipitation of golden yellow plates. $Tp^{Me2}Ta(Cl)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (0.26 g, 0.4 mmol, 80% yield) was recovered after filtration and drying under vacuum. – $C_{26}H_{35}BClN_6Ta$ (658.8): calcd. C 47.4, H 5.4, N 12.8; found C 47.4, H, 5.3, N 12.7. – ^{1}H NMR: major isomer: δ = 0.59 [dq, J = 14.6, 6.6 Hz, 1 H, Ta(μ-H)$CHCH_3$], 1.40 (dd, J= 7.2, 6.7 Hz, 3 H, $TaCH_2CH_3$), 1.62, 1.90, 2.02, 2.03, 2.15, 2.77 (all s, 3 H each, $Tp^{Me2}CH_3$), 3.02 [dq, J = 14.6, 7.5 Hz, 1 H, Ta(μ-H)$CHCH_3$], 3.91 (s, 3 H, ≡CCH_3), 5.41, 5.52, 5.70 (all s, 1 H each, $Tp^{Me2}CH$), 6.93–7.09 (m, 5 H, C_6H_5); minor isomer (some resonances obscured): δ = 0.92 [m, 1 H, Ta(μ-H)$CHCH_3$], 1.81, 1.99, 2.07, 2.13, 2.75, 2.79 (3 H each $Tp^{Me2}CH_3$), 3.15 [m, 1 H, Ta(μ-H)$CHCH_3$], 5.49, 5.57, 5.69 (all s, 1 H each, $Tp^{Me2}CH$), 7.17 (t, J= 7.7 Hz, 1 H, p-C_6H_5), 7.49 (t, J= 7.7 Hz, 2 H, m-C_6H_5), 8.24 (dd, J = 8.0, 1.1 Hz, 2 H, o-C_6H_5); isomer ratio 4:1. – ^{13}C NMR: major isomer: δ = 12.7, 12.9, 13.2, 14.8, 15.7, 15.9, 16.0 ($TaCH_2CH_3$, $Tp^{Me2}CH_3$), 25.2 (≡CCH_3), 78.4 (dd, $w_{1/2}$ = 12 Hz, J = 122, 103 Hz, $TaCH_2CH_3$), 108.0, 108.1, 108.8 ($Tp^{Me2}CH$), 129.1, 130.9, 132.5 (C_6H_5), 144.0, 144.2, 144.3, 151.2, 153.6, 153.9 ($Tp^{Me2}CCH_3$), 227.3, 261.9 ($CH_3C{\equiv}CPh$); minor isomer: δ = 79.9 ($TaCH_2CH_3$).

$Tp^{Me2}Ta(CH_3)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (5): To an ice/water-cooled (5 °C) suspension of $Tp^{Me2}Ta(Cl)(CH_2CH_3)(PhC{\equiv}CCH_3)$ (0.15 g, 0.23 mmol) in diethyl ether (80 mL) was added via syringe an excess of methyllithium (0.4 mmol, 0.25 mL). The pale yellow mixture turned into a golden yellow solution after ca 15 min. The solution was then stirred for 1 h at room temperature. Various attempts to extract the product using toluene and/or pentane led to rapid decomposition. NMR data were obtained after removing the volatiles under vacuum. – ^{1}H NMR: major isomer: δ = –0.25 [dq, J = 7.2, 14.8 Hz, 1 H, Ta(μ-H)$CHCH_3$], 0.68 (s, 3 H, $TaCH_3$) 1.42 (t, J = 7.2 Hz, 3 H, $TaCH_2CH_3$), 1.71, 1.72, 2.04, 2.07, 2.21, 2.51 (all s, 3 H each, $Tp^{Me2}CH_3$), 2.46 [dq, J = 15.0, 7.4 Hz, 1 H, Ta(μ-H)$CHCH_3$], 3.79 (s, 3 H, ≡CCH_3), 5.47, 5.58, 5.80 (all s, 1 H each, $Tp^{Me2}CH$), 6.94–7.24 (m, C_6H_5); minor isomer (some resonances obscured): δ = 0.74 (s, 3 H, $TaCH_3$), 1.91, 1.92, 2.03, 2.06, 2.19, 2.53 (all s, 3 H, $Tp^{Me2}CH_3$), 5.53, 5.62, 5.78 (all s, 1 H, $Tp^{Me2}CH$), 7.52 (t, J = 7.0 Hz, 2 H, m-C_6H_5), 8.08 (dd, J = 1.5, 8.0 Hz, 2 H, o-C_6H_5); isomer ratio 5:1. – ^{13}C NMR: major isomer: δ = 12.9, 13.0, 13.1, 14.7, 15.2, 15.3, 15.7 ($TaCH_2CH_3$, $Tp^{Me2}CH_3$), 25.0 (≡CCH_3), 55.2 (q, J = 116 Hz, $TaCH_3$), 78.0 (dd, $w_{1/2}$ = 12 Hz, J = 116, 105 Hz, $TaCH_2CH_3$), 107.5, 107.6, 108.7 ($Tp^{Me2}CH$), 129.1, 130.9, 132.5 (C_6H_5), 143.9 ($ipso$-C_6H_5), 143.8, 144.0, 144.7, 151.5, 152.1, 152.2 ($Tp^{Me2}CCH_3$), 231.8, 260.2 ($CH_3C{\equiv}CPh$); minor isomer: δ = 55.4 ($TaCH_3$), 79.3 ($TaCH_2CH_3$).

Crystallographic Study: Single crystals of **4** were obtained from a toluene/pentane solution. Crystal data: $C_{26}H_{35}TaClN_6B$ (571.8), orthorhombic, $Pbca$, a = 15.995(4), b = 19.458(4), c = 17.259(4) Å, V = 5371(1) Å^3, Z = 8, T = 160 K, D = 1.63 Mg m^{-3}, μ = 4.21 mm^{-1}. Data collection was performed with a STOE IPDS diffractometer (Imaging Plate Device) using a graphite- monochromatized Mo-K_α radiation. The structure was solved by direct methods using SIR92.[12] Absorption corrections were applied (min/max trans. 0.5395/0.8161).[13] The refinement was carried out with the CRYSTALS package.[14] 36121 reflections were collected and 5225 found unique (R_{int} = 0.0605). All non-hydrogen atoms were anisotropically refined. Several hydrogen atoms were located from a difference Fourier map but only H(1), H(11) and H(12) were refined with an isotropic thermal parameter [equivalent parameter for H(11) and H(12)]. All the others were included in the calculations in idealized positions (C–H = 0.96 Å) with an isotropic thermal parameter 1.2 times that of the atom to which they were attached. Full-matrix least-square refinements were carried out by minimizing the function $\Sigma w(||F_o| - ||F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was introduced[15] with $w = w'\{1 - [\Delta F/6\sigma(F)]^2\}^2$. Final $R = \Sigma(||F_o| - ||F_c|)/\Sigma|F_o|$, $Rw = [\Sigma w(||F_o| - ||F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$ were 0.0196 and 0.0190, respectively [2820 reflections with $I > 2\sigma(I)$, 328 parameters, gof = 1.099, Δρ(min/max) = –0.73/0.54, max ls/esd shift 0.0051]. The plot of the molecular structure was performed with the software CAMERON.[16] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number No. CCDC-138605.

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] M. Brookhart, M. L. H. Green, L.-L. Wong, *Prog. Inorg. Chem.* **1988**, *36*, 1–124. Y. Han, L. Deng, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 5939–5945. D. G. Musaev, R. D. J. Froese, M. Svensson, K. Morokuma, *J. Am. Chem. Soc.* **1997**, *119*, 367–374. A. Haaland, W. Scherer, K. Ruud, G. S. McGrady, A. J. Downs, O. Swang, *J. Am. Chem. Soc.* **1998**, *120*, 3762–3772.

[2] [2a] M. Etienne, R. Mathieu, B. Donnadieu, *J. Am. Chem. Soc.* **1997**, *119*, 3218–3228. – [2b] Z. Guo, D. C. Swenson, R. F. Jordan, *Organometallics* **1994**, *13*, 1424–1432. – [2c] M. Etienne, *Organometallics* **1994**, *13*, 410–412.

[3] J. Jaffart, R. Mathieu, M. Etienne, J. E. McGrady, O. Eisenstein, F. Maseras, *Chem. Commun.* **1998**, 2011–2012.

[4] Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, K. Prout, A. J. Schultz, J. M. Williams, T. F. Koetzle, *J. Chem. Soc., Dalton Trans.* **1986**, 1629–1637. M. L. H. Green, A. K. Hugues, N. A. Popham, A. H. H. Stephens, L. L. Wong, *J. Chem. Soc., Dalton Trans.* **1992**, 3077–3082. D. C. Maus, V. Copié, B. Sun, J. M. Griffiths, R. G. Griffin, S. Luo, R. R. Schrock, A. H. Lûu, S. W. Seidel, W. M. Davis, A. Groham, *J. Am. Chem. Soc.* **1996**, *118*, 5665–5671. J. M. Cole, V. C. Gibson, J. A. K. Howard, G. J. McIntyre, G. L. P. Walker, *Chem. Commun.* **1998**, 1829–1830.

[5] General reviews: S. Trofimenko, *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**. S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943–980. Review on Group-5 metals: M. Etienne, *Coord. Chem. Rev.* **1996**, *156*, 201–236. For *organo*tantalum(V) complexes with Tp′ ligands: D. L. Reger, C. A. Swift, L. Lebioda, *Inorg. Chem.* **1984**, *23*, 349–354. J. M. Boncella, M. L. Cajigal, K. A. Abboud, *Organometallics* **1996**, *15*, 1905–1912. G. Rodriguez, J. P. Graham, W. D. Cotter, C. K. Sperry, G. C. Bazan, B. E. Bursten, *J. Am. Chem. Soc.* **1998**, *120*, 12512–12523.

[6] [6a] K. Takai, Y. Kataoka, K. Utimoto, *J. Org. Chem.* **1990**, *55*, 1707–1708. – [6b] Y. Kataoka, K. Takai, K. Oshima, K. Utimoto, *J. Org. Chem.* **1992**, *57*, 1615–1618. – [6c] (alkyne)(DME)-$TaCl_3$ complexes were not isolated by these authors. We have successfully isolated crystals of $TaCl_3$(DME)(PhC≡CCH_3) after addition of *n*-hexane to the crude DME/toluene reaction mixture and cooling to –20 °C (44% yield). – $C_{13}H_{18}Cl_3O_2Ta \cdot 1/4\ C_4H_{10}O_2$ (516.1): calcd. C 32.6, H 4.0; found C 33.0, H 3.5. – ^{1}H NMR ([D$_6$]benzene): δ = 3.01, 3.57, 3.65 (all s, 3 H, TaOCH_3 and ≡CCH_3), 3.03 (m, 4 H, CH_2), 3.11 (s, ca. 1.5 H, free CH_2OCH_3), 3.31 (s, 1 H, free CH_2OCH_3), 7.05–7.95 (m, 5 H, ≡C$C_6$$H_5$).

[7] J. M. Boncella, M. L. Cajigal, A. S. Gamble, K. A. Abboud, *Polyhedron* **1996**, *15*, 2071–2078.

[8] K. Mashima, T. Oshiki, K. Tani, *Organometallics* **1997**, *16*, 2760–2762.

[9] M. Etienne, F. Biasotto, R. Mathieu, J. L. Templeton, *Organometallics* **1996**, *15*, 1106–1112.

[10] M. D. Curtis, J. Real, W. Hirpo, W. M. Butler, *Organometallics* **1990**, *9*, 66–74.

[11] [11a] J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz, J. M. Williams, *J. Am. Chem. Soc.* **1986**, *108*, 40–56. – [11b] A. D. Poole, D. N. Williams, A. M. Kenwright, V. C. Gibson, D. C. R. Hockless, P. A. O'Neil, *Organometallics* **1993**, *12*, 2549–2555.

[12] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guargliardi, M. C. Burla, G. Polidori, M. Camalli, "SIR 92, A program for automatic solution of crystal structures by direct methods", *J. Appl. Crystallogr.* **1994**, *27*, 435.

[13] *X-SHAPE, Crystal Optimisation for Numerical Absorption Correction*, Revision 1.01, STOE and Cie GmbH, Darmstadt, **1996**.

[14] D. J. Watkin, C. K. Prout, R. J. Carruthers, P. Betteridge, *Crystals*, University of Oxford, **1996**, issue 10.

[15] R. J. Carruthers, D. J. Watkin, *Acta Crystallogr.* **1979**, *A35*, 698.

[16] D. J. Watkin, C. K. Prout, L. J. Pearce, *CAMERON*, University of Oxford, Oxford, **1996**.

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