Formation and Reactivity of a Tantalocene Trihydride Containing an Aminoethyl-Functionalised Ligand

Cyril Poulard,[a] Danièle Perrey,[a] Gilles Boni,*[a] Estelle Vigier,[a] Olivier Blacque,[a] Marek M. Kubicki,[a] and Claude Moïse[a]

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The complex [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}$TaCl_2$] (**1**) was synthesised by reaction of the lithium salt $LiC_5H_4(CH_2CH_2NMe_2)$ with the tantalum compound [Cp*$TaCl_3(PMe_3)$]. Reduction of **1** with $NaAl(H)_2(OCH_2CH_2OMe)_2$ leads to the trihydride derivative [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_3] (**2**). The oxidation of **2** in THF with ferrocenium ion leads to a cationic dihydride intermediate [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]PF_6 (**3**) with an intramolecular stabilization by the aminoethyl side-chain of the cyclopentadienyl ligand. The hemilabile character of the functionalised cyclopentadienyl ligand was checked by treating **3** with electron-donating ligands (e.g. phosphanes, sulfides, anions); in all cases, no displacement of the amino group was observed. When treated with HBF_4, **2** undergoes a loss of the hydride and the resulting cation can be isolated as a solvento adduct by carrying out the reaction in dimethyl sulfide. Acidolysis of **2** in the presence of an excess of trifluoroacetic acid affords the compound [Cp*{$C_5H_4(CH_2CH_2NHMe_2)$}$TaH(OCOCF_3)_2$](CF_3COO) (**5**). Microanalytical and NMR spectroscopic data for these complexes are given. The X-ray crystal structures are reported for [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]PF_6 (**3**) and [Cp*{$C_5H_4(CH_2CH_2NHMe_2)$}$TaH(OCOCF_3)_2$](CF_3COO) (**5**).

Introduction

The cyclopentadienyl group has become one of the most important ligands in organo-transition-metal chemistry.[1] Variation in the ring substituents results in important changes in steric and electronic properties of this type of ligands.[2] In the last few years a wide range of functionalised cyclopentadienyl ligands, where a donor group (NR_2, OR, PR_2) is connected to the Cp ring by a suitable spacer, has been investigated.[3] Interest in such organometallic systems lies in the fact that the Cp ring binds strongly to the metal atom, whereas the donor atom interacts only when necessary. This concept of a hemilabile ligand has been used for the stabilisation of reactive intermediates and for catalytic processes.[4]

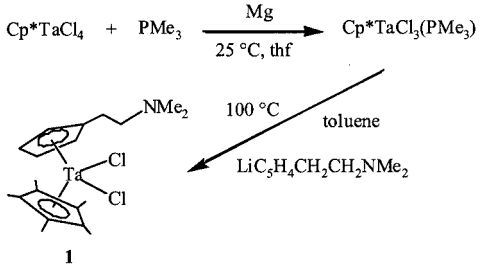
Following our studies on tantalocene complexes,[5] we have synthesised a new tantalocene dichloride and a trihydride incorporating the aminoethyl-functionalised cyclopentadienyl ligand [$C_5H_4(CH_2CH_2NMe_2)$]. The oxidation behaviour of the trihydride compound has been studied. It undergoes a loss of hydrogen atom upon reaction with ferrocenium ion leading to a cationic dihydride intermediate that is intramolecularly stabilized by the aminoethyl side-chain of the cyclopentadienyl ring.

[a] Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (UMR, 5632), Université de Bourgogne, 2100 Dijon, France

Results and Discussion

Synthesis of [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}$TaCl_2$] (1) and [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_3] (2)

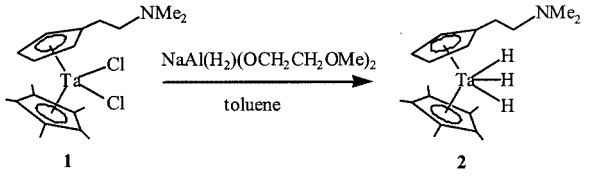
The synthesis of the tantalocene dichloride **1** was adapted from Bercaw's method[6] as outlined in Scheme 1. Complex **1** is isolated in good yield (80%) as a green solid soluble in halogenated solvents. It displays the eight-line ESR spectrum characteristic of bis(cyclopentadienyl)tantalum(IV) derivatives.



Scheme 1

Treatment of **1** with $NaAl(H)_2(OCH_2CH_2OMe)_2$ in toluene over a period of 3 h affords a red solution which, on hydrolysis, gives the trihydridometallocene **2** (Scheme 2). The ^1H NMR spectrum of **2** has the characteristic pattern of tantalocene trihydride:[7] a doublet ($\delta = -1.24$ ppm) and

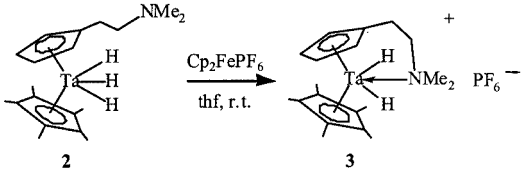
a triplet (δ = 0.46 ppm) ($^2J_{H,H}$ = 12.7 Hz) corresponding to the central and lateral hydride ions respectively.



Scheme 2

Formation and Stabilization of the Cationic Dihydride Species "[Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]$^+$"

It has been shown by our group that chemical oxidation of tantalocene trihydride [(η^5-tBuC_5H_4)$_2$TaH_3] by ferrocenium ion leads to the formation of the reactive species [(η^5-tBuC_5H_4)$_2$TaH_2]$^+$;[5c] this cationic intermediate can be stabilized and isolated as a solvento adduct when the reaction is carried out in a potentially coordinating solvent like dimethyl sulfide or tetrahydrothiophene. In contrast, when an amine is added to the reaction mixture, no stabilization is observed and no well-defined product could be isolated. In this context, it was interesting to oxidize the trihydride complex **2** and to test the intramolecular stabilization abilities of the pendant aminoethyl chain. Treatment of a THF solution of **2** with 1 equiv. of [Cp_2Fe]PF_6 at room temperature results in the formation of [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]PF_6 (**3**) and ferrocene, while a vigorous gas evolution is observed (Scheme 3).



Scheme 3

The ^{1}H and ^{13}C NMR spectroscopic data for **3** show some remarkable differences compared with the data of **2**. The most significant change in the ^{1}H NMR spectra is the low-field shift for the signal of the methylene hydrogen atoms adjacent to the nitrogen atom of the side chain. While for complex **2** this signal is observed at δ = 2.67 ppm, the signal appears at δ = 3.20 ppm for **3**. In addition, the signals for the methyl group at the nitrogen atom are shifted downfield (Δδ = 0.57 ppm with respect to the tantalocene trihydride **2**). Corresponding downfield shifts for the signals of the methylene and methyl groups adjacent to the nitrogen atom are also observed in the ^{13}C NMR spectra. The signal for the NMe_2 group is shifted downfield by 32 ppm for complex **3** (δ = 77.9 ppm) relative to that in **2** (δ = 45.6 ppm). These NMR spectroscopic data agree with the intramolecular coordination of the amino group.[8] Moreover, the ^{1}H NMR spectrum of **3** displays one low-field singlet at δ = 6.71 ppm for the hydrido ligands (the value usually observed for cationic tantalocene species), suggesting their lateral positions and, consequently, the central position of the coordinated amino arm of the side chain. Such a description of the molecular structure of the cation in **3** has been confirmed by an X-ray diffraction study. The crystal structure of **3** is built up of discrete organometallic cations and PF_6 anions. The geometry of the cation is typical of bent tantalocenes (Ta^V, Figure 1). The intramolecular Ta−N bond of 2.430(3) Å observed in the cation corresponds well to the value expected for a single bond between the large metallic centre and the tertiary amine.

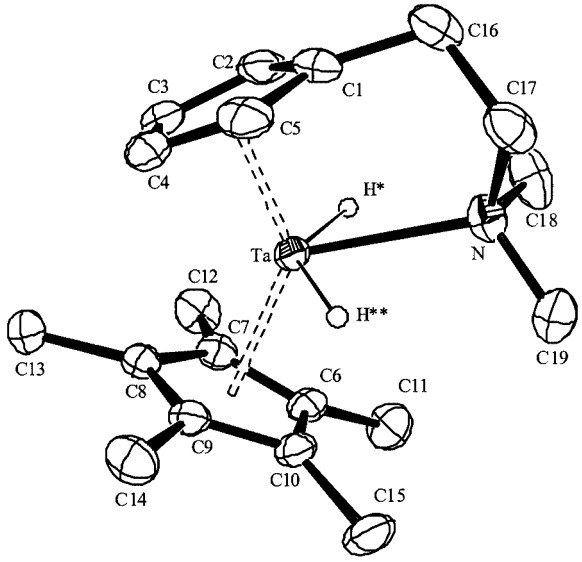
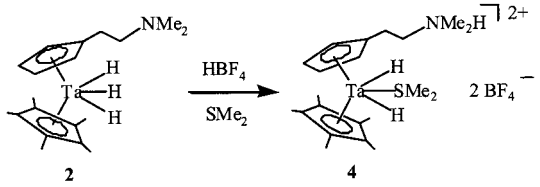


Figure 1. ORTEP drawing (50% probability displacement ellipsoids) of the cation in **3**; selected bond lengths [Å] and angles [°]: Ta−CP1 (geometrical centre of C1...C5 ring) 2.05, Ta−CP2 (geometrical centre of C6...C10 ring) 2.08, Ta−N 2.430(4), Ta−H* 1.71(5), Ta−H** 1.74(6); CP1−Ta−CP2 134.9, CP1−Ta−N 101.2, CP2−Ta−N 123.9, H*−Ta−H** 137(3), H*−Ta−N 67(2), H**−Ta−N 72(2)

In order to check the hemilabile properties of the aminoethyl arm, complex **3** was treated with electron-donating species. When **3** is heated at 80 °C in toluene in the presence of a phosphane (PMe_3, PMe_2Ph, PPh_2H) or a sulfur donor (Me_2S) no reaction occurs and the starting material is recovered. Reactions with anions (BuLi, PPh_2Li) also failed and degradation products were obtained. Thus, the aminoethyl chain coordinates strongly to the tantalum atom and cannot be displaced.

However, an acidolysis-type reaction may generate the cationic species "[Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]$^+$".[5c] The addition of 2 equiv. of HBF_4·Et_2O to a dimethyl sulfide solution of **2** results, as expected, in the evolution of dihydrogen and the formation of the dicationic solvento adduct [Cp*{$C_5H_4(CH_2CH_2NHMe_2)$}TaH_2(SMe_2)](BF_4)$_2$ (**4**) (Scheme 4). The ^{1}H NMR spectrum of **4** shows two signals at δ = 5.36 and 5.89 ppm for the cyclopentadienyl protons together with one singlet at δ = 2.38 ppm for the two hydride ions, characteristic of a symmetrical structure. Deprotonation of the ammonium group with several different bases (NEt_3, NaOH, EtONa) was carried out. These reactions give degradation products and the displacement of the di-

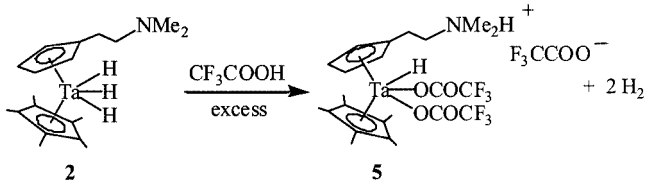
methyl sulfide ligand by the amino group could not be studied.



Scheme 4

Reaction of [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_3] (2) with Carboxylic Acids

Complex **2** reacts rapidly with trifluoroacetic acid (4 equiv.) in toluene at room temperature leading to the protonation of the amino group and the formation of the tantalum(v) dicarboxylate complex **5** as a white solid, with evolution of dihydrogen (Scheme 5).



Scheme 5

The loss of two hydrido ligands is accompanied by the monodentate coordination of two carboxylate ions at the tantalum centre. As previously observed for the parent complex [$(\eta^5$-tBu$C_5H_4)_2TaH_3$],[5c] an excess of trifluoroacetic acid does not lead to the trisubstituted derivative. Complex **5** has been characterised by spectroscopic and analytical methods. Four signals are observed for the cyclopentadienyl protons in the ^{1}H NMR spectrum of **5** (δ = 4.99, 5.17, 6.06, 6.24 ppm), indicating an unsymmetrical structure due to the lateral position of the tantalocene hydride. The spectrum also contains a downfield singlet (δ = 12.58 ppm) for the residual hydride ion, consistent with the strong electron-withdrawing properties of the carboxylato ligands. In order to deprotonate the ammonium group, compound **5** was treated with MeLi, EtONa, or Et_3N. All attempts failed and no defined products were formed. X-ray diffraction experiment confirmed the proposed structure of the cation in **5** (Figure 2).

The asymmetric unit of the triclinic ($P\bar{1}$) unit cell of **5** contains one metal-containing cation, one trifluoroacetate anion and two chloroform solvent molecules. There is strong hydrogen bonding[9] between the ammonium end of the substituted cyclopentadienyl ligand and the anion [N···O5 = 2.732(4) Å]. The acetato ligands coordinated to Ta do not seem to participate in secondary interactions. For steric reasons their noncoordinated oxygen atoms (O2 and O4) lie on the less-hindered side of the C1...C5 ring.

Experimental Section

General: All manipulations were carried out under argon using standard Schlenk line techniques and conventional glass vessels. The solvents were dried with suitable reagents and freshly distilled under argon before use. [Cp*$TaCl_4$],[6] Li[$C_5H_4(CH_2CH_2NMe_2)$],[10] and ferrocenium salts[11] were prepared according to literature methods. NMR spectra were recorded with Bruker AC 200 or DRX 300 spectrometers for ^{1}H, ^{13}C, and ^{31}P NMR, with $SiMe_4$ and H_3PO_4 as references. Elemental analyses were performed with an EA 1108 CHNS-O FISONS Instruments apparatus.

[Cp*{$C_5H_4(CH_2CH_2NMe_2)$}$TaCl_2$] (1): Compound **1** was synthesised according to Bercaw's method reported for [Cp*$CpTaCl_2$][6] with minor modifications. [Cp*$TaCl_4$] (4.58 g, 10 mmol) was reduced with magnesium (0.12 g, 5 mmol) in THF

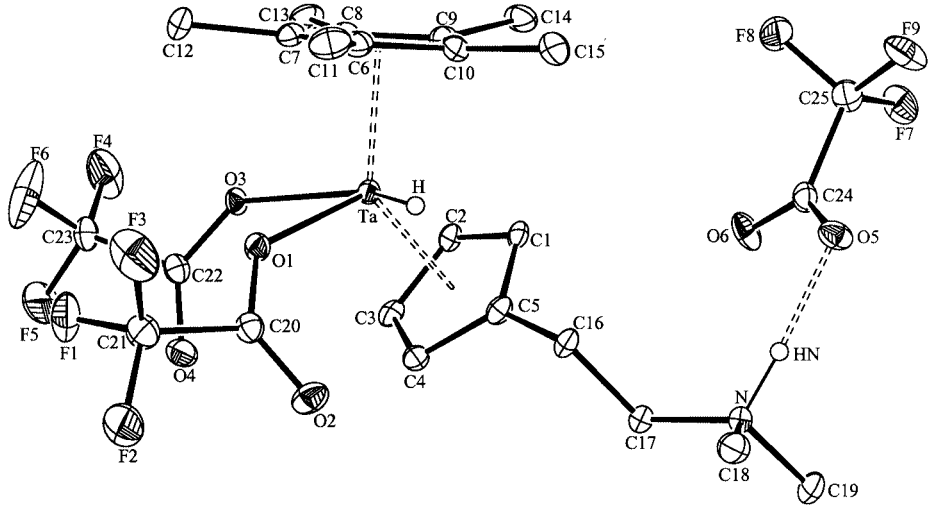


Figure 2. ORTEP drawing (30% probability displacement ellipsoids) of the cation in **5** showing the hydrogen bond between the ammonium group of the Cp ligand and the trifluoroacetate anion; selected bond lengths [Å] and angles [°]: Ta−CP1 (C1...C5 ring) 2.08, Ta−CP2 (C6...C10 ring) 2.095, Ta−H 1.48(4), Ta−O1 2.131(2), Ta−O3 2.162(2), CP1−Ta−CP2 132.8, H−Ta−O1 71(1), H−Ta−O3 143(1), O1−Ta−O3 72.2(1), N−HN 1.02(4), HN···O5 1.74(4), N···O5 2.732(4), N−HN···O5 166

(50 mL) in the presence of PMe_3 (0.76 g, 10 mmol). Removal of the solvent afforded a red residue which was treated with $Li[C_5H_4(CH_2CH_2NMe_2)]$ (1.43 g, 10 mmol) in toluene (50 mL) at 100 °C. After 12 h of stirring, extraction and crystallisation from acetone afforded the green paramagnetic product **1** (4.20 g, 80% yield). $C_{19}H_{29}Cl_2NTa$ (523.3): calcd. C 43.61, H 5.59, N 2.68; found C 44.16, H 5.74, N 2.47. The ESR spectrum in toluene showed an eight-line spectrum: g_{iso} = 1.9336; $A_{Ta,iso}$ = 103.54 G.

[Cp*{$C_5H_4CH_2CH_2NMe_2$)}TaH_3] (2): Complex **1** (2.62 g, 5 mmol) was reduced by $NaAlH_2(OCH_2CH_2OMe)_2$ (5 mL, 2 M in toluene, 10 mmol) in toluene (50 mL) at 0 °C. After 3 h of stirring, the brown-red solution was hydrolysed slowly with degassed water (10 mL). The organic layer was decanted and extracted. Evaporation of the solvent, followed by washing with pentane gave complex **2** (1.48 g, 65% yield). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = −1.24 (d, J = 12.7 Hz, 2 H), 0.46 (t, J = 12.7 Hz, 1 H), 1.99 (s, 15 H, Cp*), 2.06 (s, 6 H, NMe_2), 2.39 (t, J = 6.8 Hz, 2 H, CH_2), 2.67 (t, J = 6.8 Hz, 2 H, CH_2N), 4.53 (t, J = 2.4 Hz, 2 H, C_5H_4), 4.80 (t, J = 2.4 Hz, 2 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, 25 °C): δ = 12.8 (CH_3 of Cp*), 29.3 (CH_2), 45.6 (NMe_2), 62.2 (CH_2N), 88.7 (ring C), 89.1 (ring C), 102.8 (ring Cp*), 113.8 (ring C) ppm. $C_{19}H_{32}NTa$ (455.42): calcd. C 50.11, H 7.08, N 3.08; found C 49.69, H 6.79, N 3.35.

[Cp*($C_5H_4CH_2CH_2NMe_2$)TaH_2][PF_6] (3): A solution of **2** (0.10 g, 0.22 mmol) in THF (10 mL) was treated at room temperature with $[Cp_2Fe][PF_6]$ (0.08 g, 0.22 mmol). The solution was stirred for an additional 0.5 h. During this time, a white precipitate formed; it was filtered off and washed with pentane. The crude reaction product was crystallised from chloroform (0.12 g, 90% yield). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.11 (s, 15 H, Cp*), 2.56 (t, J = 2.6 Hz, 2 H, CH_2), 2.63 (s, 6 H, NMe_2), 3.20 (t, J = 2.6 Hz, 2 H, CH_2-N), 4.14 (t, J = 2.6 Hz, 2 H, C_5H_4), 6.71 (s, 2 H, Ta−H), 7.14 (t, J = 2.6 Hz, 2 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C): δ = 12.3 (CH_3 of Cp*), 24.1 (CH_2), 58.7 (CH_2), 77.9 (NMe_2), 93.3 (ring C), 100.2 (ring C), 111.6 (ring Cp*), 126.3 (ring C) ppm. $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$, 25 °C): δ = −153.8 (sept, J = 712 Hz) ppm. $C_{19}H_{31}F_6NPTa$ (599.38): calcd. C 38.07, H 5.21, N 2.34; found C 38.08, H 5.30, N 2.56.

[Cp*($C_5H_4CH_2CH_2NHMe_2$)TaH_2SMe_2][BF_4)$_2$ (4): A solution of **2** (0.105 g, 0.23 mmol) in dimethyl sulfide (10 mL) was treated at room temperature with 0.1 mL of HBF_4·Et_2O (54 wt% in Et_2O); the solution was stirred for an additional 0.5 h. After evaporation of the solvents, the crude solid was washed with diethyl ether and the complex was recrystallised from chloroform/pentane (2:1). Yield: 0.127 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.19 (s, 15 H, Cp*), 2.38 (s, 2 H, TaH), 2.70 (s, 6 H, SMe_2 or NMe_2),

Table 1. Crystallographic data for [Cp*{$C_5H_4(CH_2CH_2NMe_2)$}TaH_2]PF_6 (**3**) and [Cp*{$C_5H_4(CH_2CH_2NHMe_2)$}-$TaH(OCOCF_3)_2$](CF_3COO) (**5**)

Compound	**3**	**5**
Colour	colourless	pale yellow
Shape	prism	irregular
Size [mm]	0.15 × 0.12 × 0.08	0.20 × 0.13 × 0.10
Empirical formula	$C_{19}H_{31}F_6NPTa$	$C_{27}H_{33}Cl_6F_9NO_6Ta$
Formula mass	599.37	1032.19
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (2)	$P\bar{1}$ (2)
T [K]	293	120
a [Å]	8.7546(7)	12.2794(2)
b [Å]	10.4533(10)	12.6826(2)
c [Å]	13.0578(8)	13.7804(3)
α [°]	73.150(6)	68.159(1)
β [°]	72.048(5)	72.982(1)
γ [°]	86.452(7)	87.595(1)
V [Å^3]	1087.50(15)	1899.39(6)
Z	2	2
$D_{calcd.}$ [g·cm^{-3}]	1.830	1.805
μ (Mo-$K_α$) [Mm^{-1}]	5.182	3.399
λ (Mo-$K_α$) [Å]	0.71073	0.71073
F(000)	588	1012
θ range [°]	4.8; 18.6	1.018; 30.508
hkl ranges	−10; 0/ −13; 12/ −16; 15	−17; 17/ −17; 17/ −18; 15
Collected reflections, Unique reflections, Measured reflections, R_{int}	4699, 4401, 4122, 0.0112	13088, 9731, 7660, 0.0338
Reflections/parameters/restraints	4401/268/0	9731/459/0
Goodness-of-fit on F^2	1.086	0.999
$R(F)$, $Rw(F^2)$[a] [$I > 2σ(I)$]	0.0246, 0.0647	0.0417, 0.0709
$R(F)$, $Rw(F^2)$[a] (all data)	0.0279, 0.0661	0.0664, 0.0778
w:[b] a, b	0.0421, 0.8624	0.0268, 0.0000
$ρ_{max}$, $ρ_{min}$ [e·Å^{-3}]	0.409, −1.526	0.982, −1.673

[a] $R(F) = Σ||F_o| - |F_c||/Σ|F_o|$, $Rw(F^2) = [Σw(F_o^2 - F_c^2)^2/Σ[w(F_o^2)^2]^{1/2}$. [b] $w = 1/[σ^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

2.95 (m, 2 H, CH_2), 3.11 (s, 6 H, NMe_2 or SMe_2), 3.52 (m, 2 H, CH_2), 5.36 (t, J = 2.5 Hz, 2 H, C_5H_4), 5.89 (t, J = 2.5 Hz, 2 H, C_5H_4) ppm. $C_{21}H_{38}B_2F_8NSTa$ (691.16): calcd. C 36.49, H 5.54, N 2.03; found C 35.98, H 1.71, N 5.45.

[Cp*($C_5H_4CH_2CH_2NHMe_2$)TaH($OCOCF_3$)$_2$][CF_3COO] (5): A toluene (20 mL) solution of **2** (2.28 g, 5 mmol) was treated at room temperature with an excess of trifluoroacetic acid (0.176 g, 2 mmol). The colourless solution turned pale yellow, and gas evolution was observed. The solution was stirred for an additional 30 min, and the volatiles were then removed in vacuo. Recrystallisation from chloroform gave white crystals (3.17 g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.10 (s, 15 H, Cp*), 2.82 (d, J = 23.5 Hz, 6 H, NMe_2), 3.23 (m, 2 H, CH_2), 3.89 (m, 2 H, CH_2), 4.99 (br. s, 1 H, C_5H_4), 5.17 (br. s, 1 H, C_5H_4), 6.06 (br. s, 1 H, C_5H_4), 6.24 (br. s, 1 H, C_5H_4), 12.58 (s, 2 H, TaH), 13.20 (s, 1 H, $HNMe_2$) ppm. $C_{25}H_{31}F_9NO_6Ta$ (793.46): calcd. C 37.84, H 3.94, N 1.77; found C 37.89, H 4.19, N 2.07.

X-ray Structure Analyses: Crystals of **3** and **5** suitable for X-ray studies were grown from acetone and chloroform solutions, respectively. The intensities were measured at room temperature (298 K) for **3** with an Enraf Nonius CAD4 and at 120 K for **5** with a Nonius Kappa CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The measured intensities were reduced with MolEN of Enraf Nonius[12] for **3** and with the DENZO program[13] for **5**. The structures were solved by direct methods and Patterson syntheses with SHELXS-97. All models were further refined with full-matrix least-squares methods (SHELXL-97) based on $|F^2|$.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrido ligands in both structures as well as the hydrogen atom of the ammonium group in **5** were located from difference Fourier maps and refined isotropically. Other hydrogen atoms were included in calculated positions and refined with a riding model. Crystallographic data and refinement parameters are gathered in Table 1. CCDC-190157 (**3**) and -190158 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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