Formation and Reactivity of the [Cp'₂Ta(H)₂]⁺ Cation $(\mathbf{Cp}' = \eta^{5} \cdot \mathbf{BuC}_{5}\mathbf{H}_{4})$

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The complex $Cp'_2Ta(H)(OCOCF_3)_2$ (2) is synthesized by the acidolysis of Cp'_2TaH_3 (1) (Cp' $= \eta^{5}$ -'BuC₅H₄) in the presence of an excess of trifluoroacetic acid. **1** undergoes a loss of H⁻ upon the reaction of electrophile (H⁺ or CPh₃⁺). The resulting cation $[Cp'_2Ta(H)_2]^+$ ([**3**]⁺) can be isolated as a solvento adduct $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (4·BF₄) by carring out the reaction in dimethyl sulfide. Oxidation of 1 by means of ferrocenium hexafluorophosphate gives 4. PF₆. Coordination of various neutral two-electron-donor L ligands affords the corresponding cationic species $[Cp'_{2}Ta(H)_{2}(L)]^{+}$ as BF₄ or PF₆ salts with L = tetrahydrothiophene (5), CN-^tBu (6), PMe₂Ph (8), and CO (9). Microanalytical, mass spectrometric, and infrared and NMR (¹H, ¹⁹F, ³¹P) spectroscopic data for the complexes are reported, along with the X-ray crystal structure of $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (4·BF₄). The structural and spectroscopic properties of the dihydride complexes (4-8, 12, and 13) are consistent with a central position of the ligand at the tantalum center. The oxidation of **1** in the presence of acetonitrile results in the formation of the two isomeric azaalkenylidene complexes [Cp'₂Ta(H)(NCHMe)]PF₆ (9/9'· PF_{6}), but only one isomer, **10**·PF₆, is obtained with pivalonitrile. By heating in acetonitrile, complex $4 \cdot BF_4$ loses a molecule of dimethyl sulfide and is transformed to the mixture $9/9' \cdot$ PF₆. The cationic heterobimetallic µ-hydrido complex [Cp'₂Ta(H)₂(µ-H)Nb(CO)Cp₂]PF₆ (11· PF_6) is synthesized by reaction of $[3]^+$ with $Cp_2Nb(CO)H$. The neutral dihydride complexes $Cp'_{2}Ta(H)_{2}(X)$, with X = SEt (12), CN (13), are formed by treatment of $[3]^{+}$ with the corresponding anionic species. The central position of the ligand X is proposed from ¹H NMR spectroscopic data. When treated with potassium hydroxide, $[3]^+$ leads to the formation of the known oxo complex $Cp'_2Ta(=O)H$.

Introduction

Organotransition metal polyhydride complexes have received considerable attention because of their great reactivity¹ and their involvement in a number of stoichiometric and catalytic hydrogenations.² An important step in such processes occurs via an intra- or intermolecular tranfer of hydrogen from transition metal hydride complexes as a hydride, a hydrogen atom, or a proton.³

The reactivity of group 5 transition metal polyhydride complexes, especially those with formal d⁰ configuration as such Cp₂MH₃ is an area of continuous interest. The loss of molecular hydrogen on heating⁴ and the insertion reactions into the M-H bond⁵ are outstanding features

exhibited by these complexes. Even when acidic⁶ and nucleophilic⁷ properties have been reported, studies showing a somewhat hydridic character are rather scarce.8

Following our recent studies on tantalocene hydride complexes,⁹ we show now that the tantalocene $Cp'_{2}TaH_{3}$

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(1) (Cp' = $\eta^{5_{-t}}BuC_5H_4$) undergoes a loss of hydrogen atom by oxidation with ferrocenium ion but behaves as a hydride donor toward Lewis acid reagents (proton and trityl cation). The electrophilic nature of the cationic dihydride complex is confirmed by reactions with various nucleophiles, leading to several new complexes of tantalocene.

Results and Discussion

Reaction of Cp'_2TaH_3 with Carboxylic Acids. Treatment of 1 with trifluoroacetic acid (3 equiv) in toluene at ambient temperature rapidly leads to the formation of dicarboxylate tantalum(V) complex 2 as a white solid with evolution of dihydrogen (eq 1):

$$\begin{array}{c} Cp'_{2}Ta \overset{H}{\underset{H}{\leftarrow}} H \xrightarrow{CF_{3}COOH} Cp'_{2}Ta \overset{H}{\underset{OCOCF_{3}}{\leftarrow}} 2H_{2} \\ 1 & 2 \end{array}$$

The loss of two hydride ligands is accompanied by the monodentate coordination of two carboxylate ions at the tantalum center. The excess of trifluoroacetic acid leads neither to the trisubstituted derivative nor to a cyclopentadienyl ligand substitution as observed in the zirconocene series.¹¹ From a mechanistic point of view, we believe that the first step of the reaction path may consist in the protonation of **1**. Because **1** is a d^0 coordinatively saturated complex, the protonation cannot occur at the metal but must operate at the M-H bond, affording a two-electron three-center cationic intermediate [Ta- - -H- - -H]+. Such a pathway has already been proposed for protonation of polyhydride complexes of sixth-row transition metals.¹⁰ Complex 2 has been characterized by analytical and spectral methods. Four signals observed for the cyclopentadienyl protons in its ¹H NMR spectrum indicate an unsymmetrical distribution of the three σ -bonds. The low-field resonance of residual hydride ($\delta = 12.17$ ppm) on Ta agrees with strong electron-withdrawing properties of the carboxylate ligands. Such a reaction fails with weak carboxylic acids such as CH₃COOH but works with other strong monoacids (e.g., HCl): acidolysis takes place upon the treatment of 1 with a toluene solution of hydrochloric acid, giving the known Cp'2TaCl2H dichloro complex.12

Synthesis of [Cp'₂Ta(H)₂(SMe₂)]BF₄ (4·BF₄). We thought that some intermediates in acidolysis could be characterized by the use of other strong acids with weakly coordinating anions. Thus, the addition of an excess (1.5 equiv) of HBF₄·Et₂O to a toluene solution of 1 results, as expected, in evolution of dihydrogen, but no well-defined product could be extracted from the

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yellow pale solution. However, the cationic intermediate $[Cp'_2Ta(H)_2]^+$ ([**3**]⁺) could be isolated as a solvento adduct **4**·BF₄ (72% yield) by carrying out the reaction in dimethyl sulfide (route *i*; eq 2).



The analytical and spectroscopic data are consistent with the formula shown in eq 2. The ¹H NMR spectrum of **4**·BF₄ in the cyclopentadienyl region displays only two signals at δ 5.84 and 4.95; the singlet at δ 1.70 is assigned to the two equivalent (symmetrically distributed) metal hydrides.

Two other synthetical approaches of $[Cp'_2Ta(H)_2-(SMe_2)]^+$ have been checked starting from a mixture of **1** with SMe₂. The first one consists once more in the hydride abstraction reaction that occurs when a dimethyl sulfide solution of **1** is treated with an organic Lewis acid species such as trityl cation (*ii*; Scheme 1).

4•BF₄ is formed in good yield (90%), and triphenylmethane is the only organic product detected. A hydrid transfer mechanism through a cationic inner-sphere intermediate [Ta- - -H- - -CPh₃]⁺ can be suggested to account for the formation of complex [**4**]⁺. However, the alternative electron transfer/H atom transfer mechanism cannot be definitively ruled out but seems less favorable in view of the redox potentials of **1** (+0.5 V vs SCE)¹⁴ and Ph₃C⁺ (-0.32 V vs FC).^{13a}

The second one (*iii*; Scheme 1) arises from a chemical oxidation with ferrocenium ion. Room-temperature treatment of a dimethyl sulfide solution of **1** with 1 equiv of $Cp_2Fe\cdot PF_6$ immediately leads to the formation of **4**·PF₆ (ca. 80–85%) and ferrocene, while a vigorous gas evolution is observed. Ferrocenium ion operates the clean one-electron outer-sphere oxidation and converts

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1 into the corresponding $[\mathbf{3}]^+$ cation by dihydrogen elimination. Formation of dihydrogen apparently contrasts with oxidations of metal hydrides studied by M. Tilset^{13a-e} and Y. Mugnier,^{13f} but could arise from the protonation of Cp'₂TaH₃ by the strong Brønsted-acidic cation radical [Cp'₂TaH₃]*⁺ (route *i*, vide supra). The electrochemical oxidation of a thf solution (0.2 M Bu₄NPF₆) of **1** in the presence of SMe₂ is a one-electron process and leads to formation of complex **4**·PF₆ in quantitative yield.

Structural Characterization of [Cp'2Ta(H)2(SMe2)]-**BF**₄. Coordination of the solvent molecule in **4**·BF₄ at tantalum in a central position has been confirmed by an X-ray structure analysis. There are three independent cations and anions in the noncentrosymmetric triclinic cell. One of them is depicted in Figure 1. The cations 1 and 2 have rougly the same geometries with a slightly staggerred conformation of the rings. The cation 3 may be considered as an optical isomer of 1 and 2 because it is a mirror plane image of 1 and 2. The Ta-S bond length (mean 2.558(6) Å) falls in the upper range of values (2.417-2.567 Å) observed for tantalocenes with a single Ta-S bond.^{12,15} It is, however, much shorter than those reported by Cotton et al. (2.698–2.730 Å)¹⁶ for Ta(III) inorganic complexes with terminal dimethyl sulfide.

Reaction of $[Cp'_2Ta(H)_2]^+$ with Other Neutral **Two-Electron-Donor Ligands.** The electrophilic nature of $[Cp'_2Ta(H)_2]^+$ [3]⁺ is confirmed by the adduct formation with other ligands (alkyl sulfide, isocyanide, phosphines, and carbon monoxide) as reported in eq 3.



Stirring a solution of Cp'_2TaH_3 in a toluene/tetrahydrothiophene (10/1) mixture with CPh_3BF_4 results in the formation of $[Cp'_2Ta(H)_2(tht)][BF_4]$ (5·BF₄) in 85% yield. Spectroscopic data of 5·BF₄ are similar to those of complex 4·BF₄.

Addition of trityl hexafluorophosphate to a solution of Cp'₂TaH₃ in the presence of a slight excess of *tert*butyl isocyanide results in an immediate coordination of isocyanide at the tantalum leading to complex **6**·PF₆. The infrared spectra exhibits a strong ν (NC) stretching absorption at 2210 cm⁻¹.

The metallophosphonium complex $7 \cdot PF_6$ is obtained by addition of 1.2 equiv of PMe_2Ph to a thf solution of $[3]^+$ prepared in situ (Scheme 1, *iii*). The spectroscopic data of this complex are very similar to those of the



Figure 1. ORTEP drawing of one (2) of the three cations in the structure of $4 \cdot BF_4$. Selected bond distances (Å) and angles (deg) for 2: Ta(2)-S(2) 2.55(1), S(2)-C(39) 1.69(2), S(2)-C(40) 1.76(2), Ta(2)-S(2)-C(39) 115.3(9), Ta(2)-S(2)-C(40) 113.3(8), C(39)-S(2)-C(40) 103(1).



symmetrical isomer obtained by protonation of the Cp₂Ta(H)(PMe₂Ph) metallophosphine:^{9d} the ¹H NMR spectrum of **7**·PF₆ displays one doublet (²J_{H,P} = 71.2 Hz) at -0.52 ppm for the two equivalent hydride ligands, and the ³¹P{¹H} NMR exhibits a signal at -16.5 ppm for the metallophosphonium nucleus.

In addition to sulfide, isocyanide, and phosphine, carbon monoxide also adds to $[3]^+$. When a sample of $[Cp'_2Ta(H)_2][PF_6]$ is exposed in toluene to a CO atmosphere, selective formation of the trans $[Cp'_2TaH_2(CO)]$ - $[PF_6]$ (8) is observed and identified by its spectroscopic properties similar to the complex previously characterized.¹⁷

When carried out in acetonitrile, the oxidation reaction of Cp'₂TaH₃ with ferrocenium ion leads to a mixture of isomeric azaalkenylidene complexes **9**•PF₆ and **9**′•PF₆. The formulation of these two inseparable isomers is based on their analytic and spectroscopic data. The infrared spectrum shows a weak absorption at 1892 cm⁻¹, which is characteristic of the Ta–H vibration and the ν (CN) stretching absorption at 1714 cm⁻¹. The ¹H NMR spectrum of the mixture indicates a 2/1 ratio for the two isomers and gives rise for each isomer to the four signals expected for protons of the two equivalent cyclopentadienyl ligands.

A probable mechanism for their formation (Scheme 2) may involve a rapid rearrangement of the initially formed nitrile cationic adduct consisting of a hydride migration (in the bisecting plane of the Cp'-Ta-Cp'

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angle) from tantalum to the electrophilic carbon atom of the nitrile ligand.

Recently Grimes et al. reported insertion reactions of nitriles with tantalum(V) carborane alkyl complexes; however these reactions lead to a unique azaalkenvlidene isomer.18

The existence of the two isomers $9 \cdot PF_6$ and $9' \cdot PF_6$ could result from a probably linear heteroallene TaNC arrangement (Scheme 3) where the azaalkenylidene group acts as a three-electron-donor ligand to form an 18-electron Ta(V) complex, as observed for the titanocene, zirconocene, scandocene, and tungsten complexes.¹⁹ The stereostability of these isomers at room temperature indicates a restricted rotation about the Ta-N bond.

In a fashion analogous to that for isomers $9 \cdot PF_6$ and **9'**·PF₆, complex $[Cp'_2Ta(H)(N=CH^{-t}Bu)]$ ·PF₆ is isolated by using the hindered pivalonitrile and exists as one stereoisomer, 10·PF₆. The "tBu-outside" assignment for complex $10 \cdot PF_6$ is based on an NOE experiment. Selective irradiation of the hydride signal (at 6.01 ppm) leads to an expressed NOE of 4.5% on the CH-tBu proton at 8.20 ppm.

Both azaalkenylidene isomers $9 \cdot PF_6$ and $9' \cdot PF_6$ are also formed by heating the dimethyl sulfide adduct 4. PF_6 in acetonitrile (Scheme 2), suggesting the lability of the coordinated solvent molecule (SMe₂). Note, however, that the displacement of the SMe₂ ligand by NCMe does not operate with the stoichiometric ratio in thf at room temperature.

The similar reactivity observed for Cp*₂ZrH₂^{19d} and $[Cp'_{2}Ta(H)_{2}]^{+}$ toward nitriles does not recur in the reaction with the carbonyl-niobium Cp₂Nb(CO)H complex. Whereas Cp*₂ZrH₂ leads to the formation of the zirconoxy carbene complex Cp₂(H)Nb=CHOZr(H)Cp*₂,²⁰ $[3]^+$ reacts with Cp₂Nb(CO)H to form in good yield (75%) the heterodinuclear cationic complex $11 \cdot PF_6$ (eq 4).



The pronounced Lewis acid character of $[Cp'_2Ta(H)_2]^+$ is emphasized by the formation of complex $11 \cdot PF_6$ due to coordination of the donor hydrido-niobocene complex. **11**·PF₆ is a stable brown-red solid soluble in thf and acetone, but slow decomposition is observed in solution. The high-field proton resonance at -19.08 ppm and the presence of two equivalent Cp' ligands confirm that the



two metal centers are connected in a central position via a hydrido bridge.²¹ The IR ν (CO) stretching band in the cation $11 \cdot PF_6$ exhibits a blue shift of 25 cm⁻¹ with respect to the parent Cp₂Nb(CO)H complex.

The positive charge can be delocalized onto both metallic nuclei since complex 11.PF₆ can also be considered as the adduct of Cp'₂TaH₃ to the Lewis acid $[Cp_2Nb(CO)]^+$ niobium moiety. It is worth noting that $[Cp'_{2}TaH_{2}]^{+}$ remains unreactive in the presence of the chloro Cp₂Nb(CO)Cl complex.

Reaction of [Cp'₂Ta(H)₂]⁺ with Anionic Species. Neutral tantalocene complexes 12 and 13 (eq 5) are formed by reaction of $[Cp'_2Ta(H)_2]^+$ with sodium ethanethiolate (in thf) and with sodium cyanide (in thf/water), respectively. These compounds are soluble in benzene, toluene, and chloroform but insoluble in aliphatic solvents and can be isolated as white solids after chromatographic workup, to principally eliminate a small amount of the oxo complex 14 (cf. experimental).

Spectroscopic and analytic characterizations confirm the formulas of these materials. In particular, the two compounds exhibit similar ¹H NMR spectra with a single resonance for the two hydride ligands and two resonances for the cyclopentadienyl protons. On the basis of these ¹H NMR data, we provide the $C_{2\nu}$ symmetric strutures for these complexes shown in eq 5.

Attempt to prepare the hydroxido derivative Cp'₂Ta-(H)₂(OH) by reaction of complex $[3]^+$ prepared in thf with a large excess of a 10 M solution of KOH in water was unsuccessful; however, this reaction leads to the known oxo complex 14 in nearly quantative yield (eq 6) and provides a convenient route to the preparation of this complex.

While the mechanistic details of the formation of 14 are unknown, this reaction clearly involves nucleophilic attack which would lead to the unstable hydroxide complex; the analogous sulfur Cp'₂Ta(H)₂(SH) complex, which is accessible by a different route,²² is less sensitive but decomposes slowly when heated in solution and reverts to the starting sulfido complex $Cp'_2Ta(=S)H$.

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Conclusion

In conclusion, the tantalocene trihydrides are amphoteric compounds exhibiting both the protic (acid) and hydride (base) reactivity. They can be deprotonated with strong bases leading to the $[Cp_2Ta(H)_2]^-$ anions⁶ or may undergo acidolysis with strong acids, as shown here. The cationic intermediate $[Cp'_2Ta(H)_2]^+$ has been characterized as a solvento complex. It behaves as a versatile Lewis acid toward various inorganic, organic, and organometallic nucleophiles and can be used as a reducing agent of nitriles. Generation of this coordinatively and electronically unsaturated species is of synthetic interest for building extended molecular systems, and forthcoming studies will address its utilization as a reactive precursor.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. Dimethyl sulfide (99%, Sigma-Aldrich) was degassed and stored under argon. Except for PMe₂Ph (Strem) all chemicals were purchased either from Janssen Chimica or from Sigma-Aldrich. Ethanethiol (98%, Sigma-Aldrich) was distilled before use and stored over 4 Å molecular sieves under argon. Column chromatography was performed under argon with silica gel (70–230 mesh, Merck).

The following compounds were prepared as described elsewhere: Cp'_2TaH_3 (1), 23a $Cp_2Nb(CO)H, ^{23b}$ and ferrocenium salts. 23c

¹H, ¹⁹F, and ³¹P spectra were recorded at ambient temperature on a Bruker AC200 spectrometer. Infrared spectra were obtained on a Bruker IFS 66v spectrophotometer. The molecular weights were determined by field desorption (FD) mass spectra on a Finnigan MAT 311A instrument. Elemental analyses were carried out using an EA 1108 Fisons instrument.

Preparation of Cp'₂**Ta(H)(OCOCF**₃)₂ (2). A toluene (20 mL) solution of 1 (0.200 g, 0.47 mmol) was treated at room temperature with an excess of trifluoroacetic acid (0.132 g, 1.5 mmol). The colorless solution turned pale yellow, and gas evolution was observed. The solution was stirred for an additional 30 min, and the volatiles were removed in vacuo. Recrystallization from diethyl ether gave white crystals. Yield: 250 mg (82%).

¹H NMR (200 MHz, C₆D₆, 20 °C, TMS): δ = 12.17 (s, 1H, TaH), 6.02 (m, 2H, C₅H₄), 5.90 (m, 2H, C₅H₄), 4.83 (m, 2H, C₅H₄), 3.92 (m, 2H, C₅H₄), 1.02 (s, 18H, C(CH₃)₃). ¹⁹F NMR (188.33 MHz, C₆D₆, 20 °C, CFCl₃): δ = -75.2, -76.0. IR (KBr,

cm ^1): ν (C=O) 1716 br. Anal. Calcd for C₂₂H₂₇F₆O₄Ta: C, 40.63; H, 4.18. Found: C, 40.43; H, 4.26.

Preparation of $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (4·BF₄). Method i. A solution of 1 (0.100 g, 0.23 mmol) in dimethylsulfide (10 mL) was treated at room temperature with 0.1 mL of HBF₄· Et₂O (54 wt % in Et₂O); the solution was stirred for an additional 0.5 h. After evaporating, the crude solid was washed with ether and the complex was recrystallized from thf. Yield: 120 mg (90%).

Method ii. A solution of **1** (0.100 g, 0.23 mmol) in dimethylsufide (10 mL) was treated at room temperature with [Ph₃C]-BF₄ (0.077 g, 0.23 mmol); the solution was stirred for an additional 0.5 h. After evaporating, the crude solid was washed with pentane and the complex was recrystallized from thf. Yield: 120 mg (90%).

Method iii. A solution of **1** (0.100 g, 0.23 mmol) in dimethylsufide (10 mL) was treated at room temperature with $[Cp_2Fe][BF_4]$ (0.064 g, 0.23 mmol); the solution was stirred for an additional 0.5 h. After evaporating, the crude solid was washed with pentane and the complex was recrystallized from thf. Yield: 120 mg (90%).

4·BF₄: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) $\delta = 5.84$ (m, 4H, C₅*H*₄), 4.95 (m, 4H, C₅*H*₄), 2.54 (s, 6H, SMe₂), 1.70 (s, 2H, Ta*H*), 1.31 (s, 18, C(C*H*₃)₃); MS (FD) *m*/*z* 487.2 [M⁺] ([C₂₀H₃₄STa⁺] requires 487.18). Anal. Calcd for C₂₀H₃₄BF₄-STa: C, 41.83; H, 5.97. Found: C, 41.76; H, 5.87.

Preparation of [Cp'₂Ta(H)₂(tht)]PF₆ (5·PF₆). To a solution of **1** (0.100 g, 0.23 mmol) in 11 mL of 10/1 toluene tht was added 1 equiv of [Ph₃C]PF₆ (0.77 g, 0.23 mmol). After stirring 45 min, the solvent was eliminated under reduced pressure and the crude material was washed with pentane to give a white solid (ca. 85% yield). Recrystallization from thf/pentane gave white crystals.

5·PF₆: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) $\delta = 5.83$ (m, 4H, C₅*H*₄), 4.86 (m, 4H, C₅*H*₄), 2.96 (m, 4H, tht), 1.97 (m, 4H, tht), 1.90 (s, 2H, Ta-*H*), 1.32 (s, 18H, C(*CH*₃)₃); MS (FD) *m*/*z* 513.3 [M⁺] ([C₂₂H₃₆STa⁺] requires 513.2). Anal. Calcd for C₂₂H₃₆PF₆STa: C, 40.13; H, 5.51. Found: C, 40.06; H, 5.49.

Preparation of [Cp'₂Ta(H)₂(CN-^tBu)]PF₆ (6·PF₆). To a solution of **1** (0.100 g, 0.23 mmol) in thf (10 mL) were added [Ph₃C]PF₆ (0.091 g, 0.23 mmol) and a slight excess of CN-^tBu (0.029 g, 0.35 mmol). After stirring 30 min, the volatiles were removed in vacuo and the crude material was washed with pentane to give **6**·PF₆ in good yield (90%). Recrystallization from chloroform/ether gave white crystals.

6·PF₆: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) δ = 5.69 (m, 4H, C₅*H*₄), 4.89 (m, 4H, C₅*H*₄), 1.46 (s, 9H, CN-'Bu), 1.26 (s, 18H, C(C*H*₃)₃), -0.86 (s, 2H, Ta*H*); IR (KBr, cm⁻¹) ν (Ta-H) 1910 w, ν (C=N) 2210 s; MS (FD) *m*/*z* 508.3 [M⁺] ([C₂₃H₃₇-NTa⁺] requires 508.2). Anal. Calcd for C₂₃H₃₇PF₆NTa: C, 42.28; H, 5.71. Found: C, 41.97; H, 5.78.

Preparation of $[Cp'_2Ta(H)_2(PMe_2Ph)]PF_6$ (7·PF₆). To a solution of 1 (0.100 g, 0.23 mmol) in thf (10 mL) were added $[Cp_2Fe][PF_6]$ (0.093 g, 0.23 mmol) and a slight excess of PMe₂-Ph (0.038 g, 0.28 mmol). After stirring 10 min, the volatiles were removed in vacuo and the crude material was washed with pentane to give 7·PF₆ with a good yield (90%). Recrystallization from thf/ether gave white crystals.

7 PF₆: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) δ = 7.50– 7.30 (m, 5H, C₆H₅), 5.53 (m, 4H, C₅H₄), 4.64 (m, 4H, C₅H₄), 1.88 (d, ²J_{H,P} = 8.8 Hz, 6H, P*Me*₂), 1.18 (s, 18H, C(CH₃)₃), -0.52 (d, ²J_{H,P} = 71.2 Hz, 2H, Ta-*H*); ³¹P {¹H} NMR (81 MHz, CDCl₃, 20 °C, H₃PO₄) δ = -16.5 (s), -146.1 (hep, ¹J_{F,P} = 713 Hz). Anal. Calcd for C₂₆H₃₉P₂F₆Ta: C, 44.08; H, 5.55. Found: C, 44.49; H, 5.81.

Preparation of [Cp'₂Ta(H)₂(CO)]PF₆ (8·PF₆). To a solution of **1** (0.100 g, 0.23 mmol) in thf (10 mL) was added [Cp₂Fe]-[PF₆] (0.091 g, 0.23 mmol) under CO atmosphere. After stirring 10 min, the volatiles were removed in vacuo and the crude material was washed with pentane to give a white powder. Compound **7** was identified by its ¹H NMR data.¹⁷

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8 PF₆: ¹H NMR (200 MHz, thf- d_8 , 20 °C, TMS) $\delta = 6.13$ (t, 4H, C₅H₄), 5.56 (m, 4H, C₅H₄), 1.38 (s, 18H, C(CH₃)₃), -1.62 (s, 2H, Ta-H).

Preparation of [Cp'₂Ta(H)(N=CHMe)]PF₆ (9·PF₆/9'-**PF**₆). A solution of [Cp₂Fe][PF₆] (0.078 g, 0.33 mmol) in acetonitrile (5 mL) was added to a solution of **1** (0.100 g, 0.33 mmol) in acetonitrile (10 mL). The mixture was stirred at room temperature for 30 min. The solvent was removed under vacuum and the residue washed with pentane (overall yield about 80%). The ¹H NMR spectrum of the mixture indicates a 2/1 ratio for the isomers **9**·PF₆/**9**'·PF₆, respectively. Beige microcrystals were obtained by crystallization from chloroform/ pentane (unchanged ratio). MS (FD): m/z 466.3 [M⁺] ([C₂₀H₃₁-NTa] requires 466.19. IR (KBr, cm⁻¹): ν (Ta–H) 1892 w, ν (C=N) 1714 s. Anal. Calcd for C₂₀H₃₁NPF₆Ta: C, 39.29; H, 5.11. Found: C, 38.73; H, 5.00.

9·PF₆: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) δ = 8.36 (dq, ⁴*J*_{H,H} = 3.3 Hz, ³*J*_{H,H} = 5,5 Hz, 1H,N=C*H*Me), 6.15 (m, 2H, C₅*H*₄), 6.11 (m, 3H, C₅*H*₄ and TaH), 5.61 (m, 2H, C₅*H*₄), 5.37 (m, 2H, C₅*H*₄), 1.90 (d, ³*J*_{H,H} = 5.5 Hz, 3H, N=CH*Me*), 1.27 (s, 18H, C(C*H*₃)₃).

9'·PF₆: ¹H NMR (200 MHz, CDCl₃, 20 °C, TMS) δ = 8.19 (dq, ⁴*J*_{H,H} = 3.0 Hz, ³*J*_{H,H} = 5,5 Hz, 1H, N=C*H*Me), 6. 28 (m, 2H, C₅*H*₄), 6.11 (d, 1H, Ta*H*), 6.04 (m, 2H, C₅*H*₄), 5.56 (m, 2H, C₅H₄), 5.48 (m, 2H, C₅H₄), 2.10 (d, ³*J*_{H,H} = 5.5 Hz, 3H, N=CH*Me*), 1.27 (s, 18H, C(C*H*₃)₃).

By heating at 60 °C, a solution of $4 \cdot PF_6$ in acetonitrile leads to the formation of $9 \cdot PF_6$ and $9' \cdot PF_6$ (2/1 ratio).

Preparation of [Cp'₂**Ta(H)(N=CH-'Bu)]PF**₆ (10·PF₆). To a solution of 1 (0.120 g, 0.28 mmol) in thf (10 mL) were added [Cp₂Fe][PF₆] (0.093 g, 0.28 mmol) and 2 equiv of 'Bu-CN (0.040 g, 0.056 mmol). After stirring 30 min, the volatiles were removed in vacuo and the crude material was washed with pentane to give 10·PF₆ with a good yield (ca. 90%). White analytically pure microcrystals were obtained by crystallization from chloroform/pentane.

10•PF₆: ¹H NMR (200 MHz, CDCl₃ 20 °C, TMS) $\delta = 8.20$ (d, ⁴ $J_{H,H} = 3.3$ Hz, 1H, N=CH(^tBu)), 6.42 (m, 2H, C₅ H_4), 6.01 (d, ⁴ $J_{H,H} = 3.3$ Hz, Ta-H), 5.99 (m, 2H, C₅ H_4), 5.51 (m, 2H, C₅ H_4), 5.19 (m, 2H, C₅ H_4), 1.29 (s, 18H, C(CH₃)₃), 0.98 (s, 9H, N=C(H)-^tBu). MS (FD) m/z 508.3 [M⁺] ([C₂₃H₃₇NTa⁺] requires 508.2); IR (KBr, cm⁻¹) ν (Ta-H) 1910 w, ν (C=N) 1703 s. Anal. Calcd for C₂₃H₃₇NTaPF₆: C, 42.28; H, 5.71. Found: C, 42.42; H, 5.90.

Preparation of [Cp'_2Ta(H)_2(\mu-H)Nb(CO)Cp_2]PF_6 (11·**PF_6).**To a solution of**1**(0.100 g, 0.23 mmol) in thf (10 mL) were added [Ph₃C]PF₆ (0.77 g, 0.23 mmol) and a slight excess of Cp₂Nb(CO)H (0.071 g, 0.028 mmol) in thf (8 mL). After stirring 15 min, the volatiles were removed in vacuo and the crude material was washed with toluene to give**11**·PF₆ in good yield (ca. 75%). Brown-red analytically pure microcrystals were obtained by a rapid crystallization from acetone/pentane.

11•PF₆: ¹H NMR (200 MHz, CD₃COCD₃, 20 °C, TMS) $\delta = 5.79$ (m, 4H, C₅*H*₄), 5.60 (s, 10H, C₅*H*₅), 5.10 (m, 4H, C₅*H*₄), 1.34 (s, 18H, C(C*H*₃)₃), 0.70 (d, 2H, ²*J*_{H,H} = 10.5 Hz, Ta(*H*)₂), -19.08 (broad t, 1H, ²*J*_{H,H} = 10.5 Hz, μ -*H*); IR (thf, cm⁻¹) ν (C=O) 1930 s. Anal. Calcd for C₂₉H₃₉OTaNbPF₆: C, 42.35; H, 4.78. Found: C, 42.68; H, 4.83.

Preparation of Cp'₂**Ta(H)**₂**(SEt) (12).** To a solution of **1** (0.100 g, 0.23 mmol) in thf (15 mL) was added 1 equiv of $[Cp_2Fe][PF_6]$ (0.078 g, 0.23 mmol). After stirring 5 min, a large excess (100 equiv) of a freshly prepared solution of sodium thioethanolate in thf was added. The solvent was evaporated in vacuo, and the crude material was purified by column chromatography ($h = 12 \text{ cm}, \emptyset = 2.5 \text{ cm}$). Elution with toluene eliminated ferrocene and elution with 9/1 toluene/thf furnished compound **12** in good yield (80%). Recrystallization from thf/ pentane gave white needles.

Traces of water in the solvent are responsible for the formation of the oxo complex **14** that could be easely eliminated by the chromatographic workup.

12: ¹H NMR (200 MHz, C₆D₆, 20 °C, TMS) δ = 5.05 (m, 4H, C₅*H*₄), 4.33 (m, 4H, C₅*H*₄), 2.80 (q, ³*J*_{H,H} = 7.3 Hz, 2H, C*H*₂-Me), 2.73 (s, 2H, Ta-*H*), 1.45 (t, 3H, ³*J*_{H,H} = 7.3 Hz, CH₂-*Me*), 1.34 (s, 18H, C(C*H*₃)₃); MS (FD) *m*/*z* 486.3 [M⁺] ([C₂₀H₃₃STa⁺] requires 486.2); IR (KBr, cm⁻¹) ν (Ta-H) 1801 w. Anal. Calcd for C₂₀H₃₃STa: C, 49.38; H, 6.84. Found: C, 49.58; H, 6.79.

Preparation of Cp'₂**Ta(H)**₂**(CN) (13).** To a solution of **1** (0.100 g, 0.23 mmol) in thf (10 mL) was added 1 equiv of [Ph₃C]-PF₆ (0.091 g, 0.23 mmol). After stirring 5 min, a large excess of potassium cyanide (0.130 g, 2 mmol) in solution in water was added. The solvent was eliminated under reduced pressure to give a mixture of **13** and **14**. The crude material was purified by column chromatography (h = 9 cm, $\emptyset = 2.5$ cm). Elution with toluene eliminated triphenylmethane, and elution with 9/1 toluene/thf furnished compound **13**. Recrystallization from chloroform/ether gave pale green crystals.

The presence of OH^- in the aqueous solution of potassium cyanide leads to the formation of **14** and gave a large range of yield (40–90%).

13: ¹H NMR (200 MHz, C₆D₆, 20 °C, TMS) $\delta = 4.76$ (m, 4H, C₅*H*₄), 4.31 (m, 4H, C₅*H*₄), 1.23 (s, 18H, C(C*H*₃)₃), -0.14 (s, 2H, Ta*H*); IR (KBr, cm⁻¹) ν (Ta-H) 1802 w, ν (C=N) 2109 w. Anal. Calcd for C₁₉H₂₈NTa: C, 50.56; H, 6.25. Found: C, 50.41; H, 6.16.

Preparation of [Cp'₂Ta(=O)(H)] (14). To a solution of **1** (0.260 g, 0.61 mmol) in thf (15 mL) was added 1 equiv of $[Cp_2Fe][PF_6]$ (0.202 g, 0.61 mmol). After stirring 5 min, a large excess of KOH (0.5 g, 8.9 mmol) in water (1 mL) was added, and the solution was evaporated in vaccuo. The pale pink residue was extracted with toluene to give, after elimination of the solvent, a white solid. Compound **13** was identified by its ¹H NMR data.¹²

14: ¹H NMR (200 MHz, C_6D_6 , 20 °C, TMS) $\delta = 7.35$ (s, 1H, Ta-*H*), 5.82 (m, 2H, C_5H_4), 5.43 (m, 2H, C_5H_4), 5.33 (m, 2H, C_5H_4), 5.03 (m, 2H, C_5H_4), 1.37 (s, 18H, C(*CH*₃)₃).

Crystal Data for [Cp'₂Ta(H)₂(SMe₂)]BF₄. C₂₀H₃₄BF₄STa, M = 574.3, colorless prisms (0.20 × 0.45 × 0.65 mm), triclinic, P1 (No. 1), a = 10.305(2) Å, b = 10.601(2) Å, c = 17.272(2) Å, $\alpha = 77.28(2)^{\circ}$, $\beta = 75.77(2)^{\circ}$, $\gamma = 75.23(2)^{\circ}$, V = 1743.4(7) Å³, Z = 3, $d_{calc} = 1.64$ g/cm³, $\mu = 4.85$ mm⁻¹, F(000) = 852, empirical absorption correction 8 reflections 7.0° < 2 θ < 46.0°, transmission factor (min/max) 0.55/1.00, Syntex R3 diffractometer, Mo Kα radiation, T = 296 K, 7042 unique reflections, 5930 with $I > 2.5 \sigma(I)$; structure solution by Patterson– difference Fourier (SHELXTL Plus), 728 parameters, hydride ligands not found, other H atoms in calculated positions, R =0.041, $R_w = 0.036$, GOF = 1.68. Residual electron density max/ min 1.49/-1.19 e/Å³. CCDC 101073.

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Supporting Information Available: Tables of crystallographic data for **4**·BF₄, including bond distances, bond angles, atomic parameters, and isotropic and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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