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Formation and Reactivity of the $[Cp'_2Ta(H)_2]^+$ Cation ($Cp' = \eta^5\text{-}^tBuC_5H_4$)

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The complex $Cp'_2Ta(H)(OCOCF_3)_2$ (**2**) is synthesized by the acidolysis of Cp'_2TaH_3 (**1**) ($Cp' = \eta^5\text{-}^tBuC_5H_4$) in the presence of an excess of trifluoroacetic acid. **1** undergoes a loss of H^- upon the reaction of electrophile (H^+ or CPh_3^+). The resulting cation $[Cp'_2Ta(H)_2]^+$ ($[\mathbf{3}]^+$) can be isolated as a solvento adduct $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (**4**·BF_4) by carring out the reaction in dimethyl sulfide. Oxidation of **1** by means of ferrocenium hexafluorophosphate gives **4**·PF_6. Coordination of various neutral two-electron-donor L ligands affords the corresponding cationic species $[Cp'_2Ta(H)_2(L)]^+$ as BF_4 or PF_6 salts with L = tetrahydrothiophene (**5**), CN-^{t}Bu (**6**), PMe_2Ph (**8**), and CO (**9**). Microanalytical, mass spectrometric, and infrared and NMR (^1H, ^{19}F, ^{31}P) spectroscopic data for the complexes are reported, along with the X-ray crystal structure of $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (**4**·BF_4). 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 $[Cp'_2Ta(H)(NCHMe)]PF_6$ (**9**/**9′**·PF_6), but only one isomer, **10**·PF_6, is obtained with pivalonitrile. By heating in acetonitrile, complex **4**·BF_4 loses a molecule of dimethyl sulfide and is transformed to the mixture **9**/**9′**·PF_6. The cationic heterobimetallic μ−hydrido complex $[Cp'_2Ta(H)_2(\mu\text{-}H)Nb(CO)Cp_2]PF_6$ (**11**·PF_6) is synthesized by reaction of $[\mathbf{3}]^+$ with $Cp_2Nb(CO)H$. The neutral dihydride complexes $Cp'_2Ta(H)_2(X)$, with X = SEt (**12**), CN (**13**), are formed by treatment of $[\mathbf{3}]^+$ with the corresponding anionic species. The central position of the ligand X is proposed from ^1H NMR spectroscopic data. When treated with potassium hydroxide, $[\mathbf{3}]^+$ 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 reactivity[1] 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 d^0 configuration as such Cp_2MH_3 is an area of continuous interest. The loss of molecular hydrogen on heating[4] and the insertion reactions into the M−H bond[5] are outstanding features exhibited by these complexes. Even when acidic[6] and nucleophilic[7] 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'_2TaH_3

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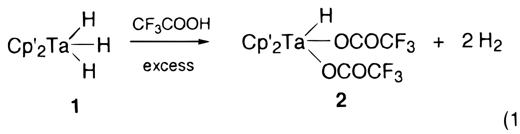
(**1**) ($Cp' = \eta^5\text{-}^tBuC_5H_4$) undergoes a loss of hydrogen atom by oxidation with ferrocenium ion but behaves as a hydride donor toward Lewis acid reagents (proton and trityl cation). The electrophilic nature of the cationic dihydride complex is confirmed by reactions with various nucleophiles, 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):

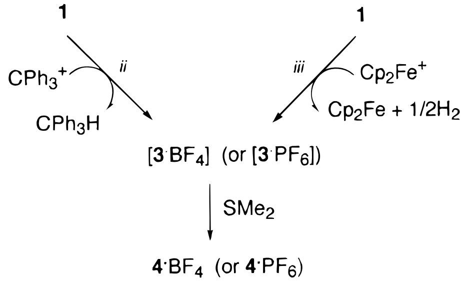


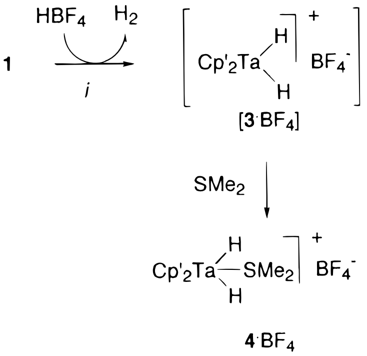
(1)

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 $[Ta\text{---}H\text{---}H]^+$. 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 CH_3COOH 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'_2TaCl_2H dichloro complex.[12]

Synthesis of $[Cp'_2Ta(H)_2(SMe_2)]BF_4$ (4·BF_4). 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 $HBF_4\cdot Et_2O$ to a toluene solution of **1** results, as expected, in evolution of dihydrogen, but no well-defined product could be extracted from the yellow pale solution. However, the cationic intermediate $[Cp'_2Ta(H)_2]^+$ ([**3**]$^+$) could be isolated as a solvento adduct **4**·BF_4 (72% yield) by carrying out the reaction in dimethyl sulfide (route *i*; eq 2).

Scheme 1





(2)

The analytical and spectroscopic data are consistent with the formula shown in eq 2. The ^1H NMR spectrum of **4**·BF_4 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 SMe_2. 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**·BF_4 is formed in good yield (90%), and triphenylmethane is the only organic product detected. A hydrid transfer mechanism through a cationic inner-sphere intermediate $[Ta\text{---}H\text{---}CPh_3]^+$ 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 Ph_3C^+ (−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**·PF_6 (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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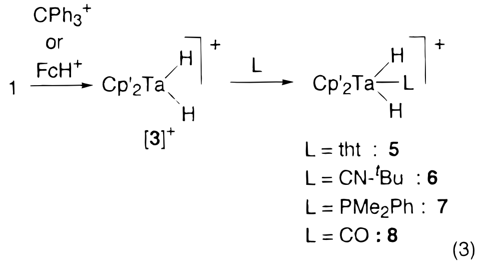
1 into the corresponding $[\mathbf{3}]^+$ cation by dihydrogen elimination. Formation of dihydrogen apparently contrasts with oxidations of metal hydrides studied by M. Tilset[13a–e] and Y. Mugnier,[13f] but could arise from the protonation of Cp'_2TaH_3 by the strong Brønsted-acidic cation radical $[Cp'_2TaH_3]^{\bullet+}$ (route *i*, vide supra). The electrochemical oxidation of a thf solution (0.2 M Bu_4NPF_6) of **1** in the presence of SMe_2 is a one-electron process and leads to formation of complex **4**·PF_6 in quantitative yield.

Structural Characterization of $[Cp'_2Ta(H)_2(SMe_2)]BF_4$. Coordination of the solvent molecule in **4**·BF_4 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.



(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**·BF_4) in 85% yield. Spectroscopic data of **5**·BF_4 are similar to those of complex **4**·BF_4.

Addition of trityl hexafluorophosphate to a solution of Cp'_2TaH_3 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**·PF_6. The infrared spectra exhibits a strong ν(NC) stretching absorption at 2210 cm^{-1}.

The metallophosphonium complex **7**·PF_6 is obtained by addition of 1.2 equiv of PMe_2Ph to a thf solution of $[\mathbf{3}]^+$ prepared in situ (Scheme 1, *iii*). The spectroscopic data of this complex are very similar to those of the symmetrical isomer obtained by protonation of the $Cp_2Ta(H)(PMe_2Ph)$ metallophosphine:[9d] the ^1H NMR spectrum of **7**·PF_6 displays one doublet ($^2J_{H,P} = 71.2$ Hz) at −0.52 ppm for the two equivalent hydride ligands, and the $^{31}P\{^1H\}$ NMR exhibits a signal at −16.5 ppm for the metallophosphonium nucleus.

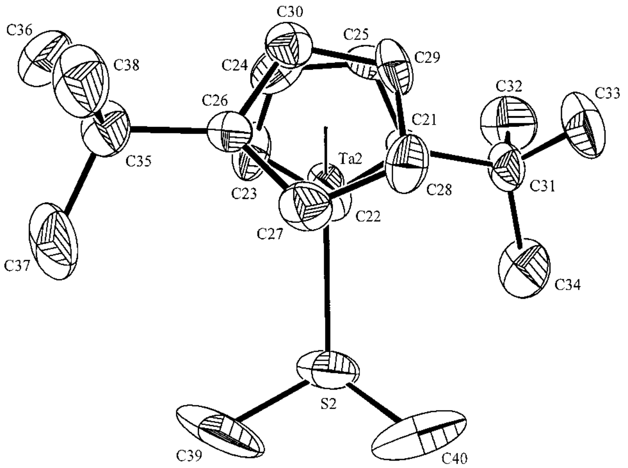
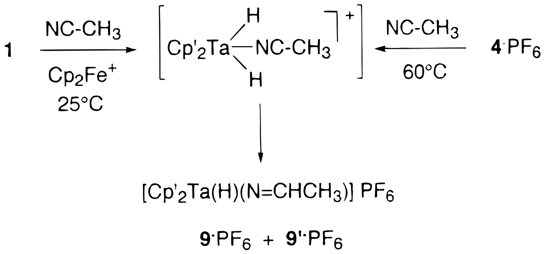


Figure 1. ORTEP drawing of one (2) of the three cations in the structure of **4**·BF_4. Selected bond distances (Å) and angles (deg) for 2: Ta(2)–S(2) 2.55(1), S(2)–C(39) 1.69(2), S(2)–C(40) 1.76(2), Ta(2)–S(2)–C(39) 115.3(9), Ta(2)–S(2)–C(40) 113.3(8), C(39)–S(2)–C(40) 103(1).

Scheme 2



In addition to sulfide, isocyanide, and phosphine, carbon monoxide also adds to $[\mathbf{3}]^+$. 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'_2TaH_3 with ferrocenium ion leads to a mixture of isomeric azaalkenylidene complexes **9**·PF_6 and **9′**·PF_6. 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.

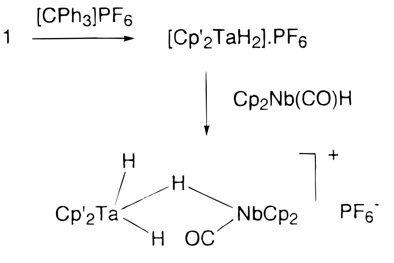
Recently Grimes et al. reported insertion reactions of nitriles with tantalum(V) carborane alkyl complexes; however these reactions lead to a unique azaalkenylidene isomer.[18]

The existence of the two isomers **9**·PF_6 and **9′**·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**·PF_6 and **9′**·PF_6, complex $[Cp'_2Ta(H)(N{=}CH\text{-}{}^tBu)]\cdot PF_6$ is isolated by using the hindered pivalonitrile and exists as one stereoisomer, **10**·PF_6. The "^{t}Bu-outside" assigment for complex **10**·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 C*H*-^{t}Bu proton at 8.20 ppm.

Both azaalkenylidene isomers **9**·PF_6 and **9′**·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 (SMe_2). Note, however, that the displacement of the SMe_2 ligand by NCMe does not operate with the stoichiometric ratio in thf at room temperature.

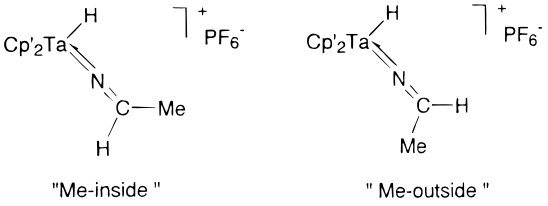
The similar reactivity observed for $Cp^*_2ZrH_2$[19d] and $[Cp'_2Ta(H)_2]^+$ toward nitriles does not recur in the reaction with the carbonyl−niobium $Cp_2Nb(CO)H$ complex. Whereas $Cp^*_2ZrH_2$ leads to the formation of the zirconoxy carbene complex $Cp_2(H)Nb{=}CHOZr(H)Cp^*_2$,[20] [**3**]$^+$ reacts with $Cp_2Nb(CO)H$ to form in good yield (75%) the heterodinuclear cationic complex **11**·PF_6 (eq 4).



11.PF_6 (4)

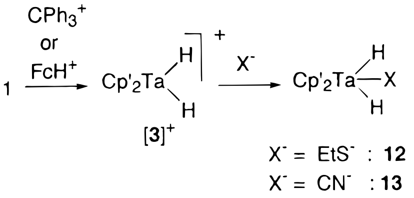
The pronounced Lewis acid character of $[Cp'_2Ta(H)_2]^+$ is emphasized by the formation of complex **11**·PF_6 due to coordination of the donor hydrido−niobocene complex. **11**·PF_6 is a stable brown-red solid soluble in thf and acetone, but slow decomposition is observed in solution. The high-field 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**·PF_6 exhibits a blue shift of 25 cm^{-1} with respect to the parent $Cp_2Nb(CO)H$ complex.

Scheme 3



The positive charge can be delocalized onto both metallic nuclei since complex **11**·PF_6 can also be considered as the adduct of Cp'_2TaH_3 to the Lewis acid $[Cp_2Nb(CO)]^+$ niobium moiety. It is worth noting that $[Cp'_2TaH_2]^+$ remains unreactive in the presence of the chloro $Cp_2Nb(CO)Cl$ 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).



(5)

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_{2v} 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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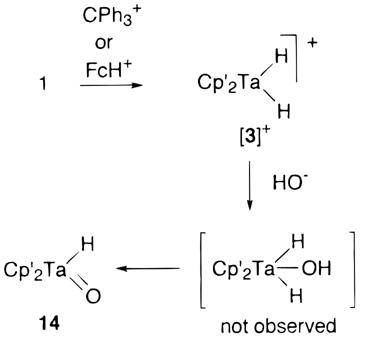

(6)

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 $[Cp_2Ta(H)_2]^-$ anions[6] 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 PMe_2Ph (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, ^{19}F, and ^{31}P 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 $Cp'_2Ta(H)(OCOCF_3)_2$ (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, C_6D_6, 20 °C, TMS): $\delta = 12.17$ (s, 1H, TaH), 6.02 (m, 2H, C_5H_4), 5.90 (m, 2H, C_5H_4), 4.83 (m, 2H, C_5H_4), 3.92 (m, 2H, C_5H_4), 1.02 (s, 18H, $C(CH_3)_3$). ^{19}F NMR (188.33 MHz, C_6D_6, 20 °C, $CFCl_3$): $\delta = -75.2, -76.0$. IR (KBr, cm^{-1}): ν(C=O) 1716 br. Anal. Calcd for $C_{22}H_{27}F_6O_4Ta$: 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 $HBF_4 \cdot Et_2O$ (54 wt % in Et_2O); 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 $[Ph_3C]BF_4$ (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·BF_4: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS) $\delta = 5.84$ (m, 4H, C_5H_4), 4.95 (m, 4H, C_5H_4), 2.54 (s, 6H, SMe_2), 1.70 (s, 2H, TaH), 1.31 (s, 18, $C(CH_3)_3$); MS (FD) m/z 487.2 [M^+] ([$C_{20}H_{34}STa^+$] requires 487.18). Anal. Calcd for $C_{20}H_{34}BF_4STa$: C, 41.83; H, 5.97. Found: C, 41.76; H, 5.87.

Preparation of $[Cp'_2Ta(H)_2(tht)]PF_6$ (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 $[Ph_3C]PF_6$ (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·PF_6: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS) $\delta = 5.83$ (m, 4H, C_5H_4), 4.86 (m, 4H, C_5H_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^+] ([$C_{22}H_{36}STa^+$] requires 513.2). Anal. Calcd for $C_{22}H_{36}PF_6STa$: C, 40.13; H, 5.51. Found: C, 40.06; H, 5.49.

Preparation of $[Cp'_2Ta(H)_2(CN\text{-}{}^tBu)]PF_6$ (6·PF6). To a solution of **1** (0.100 g, 0.23 mmol) in thf (10 mL) were added $[Ph_3C]PF_6$ (0.091 g, 0.23 mmol) and a slight excess of CN-^{t}Bu (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**·PF_6 in good yield (90%). Recrystallization from chloroform/ether gave white crystals.

6·PF_6: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS) $\delta = 5.69$ (m, 4H, C_5H_4), 4.89 (m, 4H, C_5H_4), 1.46 (s, 9H, CN-^{t}Bu), 1.26 (s, 18H, $C(CH_3)_3$), −0.86 (s, 2H, TaH); IR (KBr, cm^{-1}) ν(Ta−H) 1910 w, ν(C=N) 2210 s; MS (FD) m/z 508.3 [M^+] ([$C_{23}H_{37}NTa^+$] requires 508.2). Anal. Calcd for $C_{23}H_{37}PF_6NTa$: 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 PMe_2Ph (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**·PF_6 with a good yield (90%). Recrystallization from thf/ether gave white crystals.

7 PF_6: ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS) $\delta = 7.50-7.30$ (m, 5H, C_6H_5), 5.53 (m, 4H, C_5H_4), 4.64 (m, 4H, C_5H_4), 1.88 (d, $^2J_{H,P} = 8.8$ Hz, 6H, PMe_2), 1.18 (s, 18H, $C(CH_3)_3$), −0.52 (d, $^2J_{H,P} = 71.2$ Hz, 2H, Ta-H); ^{31}P {^1H} NMR (81 MHz, $CDCl_3$, 20 °C, H_3PO_4) $\delta = -16.5$ (s), −146.1 (hep, $^1J_{F,P} = 713$ Hz). Anal. Calcd for $C_{26}H_{39}P_2F_6Ta$: C, 44.08; H, 5.55. Found: C, 44.49; H, 5.81.

Preparation of $[Cp'_2Ta(H)_2(CO)]PF_6$ (8·PF6). To a solution of **1** (0.100 g, 0.23 mmol) in thf (10 mL) was added $[Cp_2Fe][PF_6]$ (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 PF$_6$: ^{1}H NMR (200 MHz, thf-d_8, 20 °C, TMS) $\delta = 6.13$ (t, 4H, C$_5H_4$), 5.56 (m, 4H, C$_5H_4$), 1.38 (s, 18H, C(CH_3)$_3$), −1.62 (s, 2H, Ta-H).

Preparation of [Cp′$_2$Ta(H)(N═CHMe)]PF$_6$ (9·PF$_6$/9′·PF$_6$). A solution of [Cp$_2$Fe][PF$_6$] (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 ^{1}H NMR spectrum of the mixture indicates a 2/1 ratio for the isomers **9**·PF$_6$/**9′**·PF$_6$, respectively. Beige microcrystals were obtained by crystallization from chloroform/pentane (unchanged ratio). MS (FD): m/z 466.3 [M$^+$] ([C$_{20}$H$_{31}$NTa] requires 466.19. IR (KBr, cm^{-1}): ν(Ta−H) 1892 w, ν(C═N) 1714 s. Anal. Calcd for C$_{20}$H$_{31}$NPF$_6$Ta: C, 39.29; H, 5.11. Found: C, 38.73; H, 5.00.

9·PF$_6$: ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS) $\delta = 8.36$ (dq, $^4J_{\mathrm{H,H}} = 3.3$ Hz, $^3J_{\mathrm{H,H}} = 5{,}5$ Hz, 1H,N═CHMe), 6.15 (m, 2H, C$_5H_4$), 6.11 (m, 3H, C$_5H_4$ and TaH), 5.61 (m, 2H, C$_5H_4$), 5.37 (m, 2H, C$_5H_4$), 1.90 (d, $^3J_{\mathrm{H,H}} = 5.5$ Hz, 3H, N═CHMe), 1.27 (s, 18H, C(CH_3)$_3$).

9′·PF$_6$: ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS) $\delta = 8.19$ (dq, $^4J_{\mathrm{H,H}} = 3.0$ Hz, $^3J_{\mathrm{H,H}} = 5{,}5$ Hz, 1H, N═CHMe), 6. 28 (m, 2H, C$_5H_4$), 6.11 (d, 1H, TaH), 6.04 (m, 2H, C$_5H_4$), 5.56 (m, 2H, C$_5$H$_4$), 5.48 (m, 2H, C$_5$H$_4$), 2.10 (d, $^3J_{\mathrm{H,H}} = 5.5$ Hz, 3H, N═CHMe), 1.27 (s, 18H, C(CH_3)$_3$).

By heating at 60 °C, a solution of **4**·PF$_6$ in acetonitrile leads to the formation of **9**·PF$_6$ and **9′**·PF$_6$ (2/1 ratio).

Preparation of [Cp′$_2$Ta(H)(N═CH-^{t}Bu)]PF$_6$ (10·PF$_6$). To a solution of **1** (0.120 g, 0.28 mmol) in thf (10 mL) were added [Cp$_2$Fe][PF$_6$] (0.093 g, 0.28 mmol) and 2 equiv of ^{t}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**·PF$_6$ with a good yield (ca. 90%). White analytically pure microcrystals were obtained by crystallization from chloroform/pentane.

10·PF$_6$: ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS) $\delta = 8.20$ (d, $^4J_{\mathrm{H,H}} = 3.3$ Hz, 1H, N═CH(^{t}Bu)), 6.42 (m, 2H, C$_5H_4$), 6.01 (d, $^4J_{\mathrm{H,H}} = 3.3$ Hz, Ta-H), 5.99 (m, 2H, C$_5H_4$), 5.51 (m, 2H, C$_5H_4$), 5.19 (m, 2H, C$_5H_4$), 1.29 (s, 18H, C(CH_3)$_3$), 0.98 (s, 9H, N═C(H)-^{t}Bu). MS (FD) m/z 508.3 [M$^+$] ([C$_{23}$H$_{37}$NTa$^+$] requires 508.2); IR (KBr, cm^{-1}) ν(Ta−H) 1910 w, ν(C═N) 1703 s. Anal. Calcd for C$_{23}$H$_{37}$NTaPF$_6$: C, 42.28; H, 5.71. Found: C, 42.42; H, 5.90.

Preparation of [Cp′$_2$Ta(H)$_2$(μ-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 [Ph$_3$C]PF$_6$ (0.77 g, 0.23 mmol) and a slight excess of Cp$_2$Nb(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**·PF$_6$ in good yield (ca. 75%). Brown-red analytically pure microcrystals were obtained by a rapid crystallization from acetone/pentane.

11·PF$_6$: ^{1}H NMR (200 MHz, CD$_3$COCD$_3$, 20 °C, TMS) $\delta =$ 5.79 (m, 4H, C$_5H_4$), 5.60 (s, 10H, C$_5H_5$), 5.10 (m, 4H, C$_5H_4$), 1.34 (s, 18H, C(CH_3)$_3$), 0.70 (d, 2H, $^2J_{\mathrm{H,H}} = 10.5$ Hz,Ta(H)$_2$), −19.08 (broad t, 1H, $^2J_{\mathrm{H,H}} = 10.5$ Hz, μ-H); IR (thf, cm^{-1}) ν(C═O) 1930 s. Anal. Calcd for C$_{29}$H$_{39}$OTaNbPF$_6$: 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$_2$Fe][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 ($h = 12$ cm, Ø = 2.5 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: ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C, TMS) $\delta = 5.05$ (m, 4H, C$_5H_4$), 4.33 (m, 4H, C$_5H_4$), 2.80 (q, $^3J_{\mathrm{H,H}} = 7.3$ Hz, 2H, CH_2-Me), 2.73 (s, 2H, Ta-H), 1.45 (t, 3H, $^3J_{\mathrm{H,H}} = 7.3$ Hz, CH$_2$-Me), 1.34 (s, 18H, C(CH_3)$_3$); MS (FD) m/z 486.3 [M$^+$] ([C$_{20}$H$_{33}$STa$^+$] requires 486.2); IR (KBr, cm^{-1}) ν(Ta−H) 1801 w. Anal. Calcd for C$_{20}$H$_{33}$STa: 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 [Ph$_3$C]-PF$_6$ (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, Ø = 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: ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C, TMS) $\delta = 4.76$ (m, 4H, C$_5H_4$), 4.31 (m, 4H, C$_5H_4$), 1.23 (s, 18H, C(CH_3)$_3$), −0.14 (s, 2H, TaH); IR (KBr, cm^{-1}) ν(Ta−H) 1802 w, ν(C═N) 2109 w. Anal. Calcd for C$_{19}$H$_{28}$NTa: C, 50.56; H, 6.25. Found: C, 50.41; H, 6.16.

Preparation of [Cp′$_2$Ta(═O)(H)] (14). To a solution of **1** (0.260 g, 0.61 mmol) in thf (15 mL) was added 1 equiv of [Cp$_2$Fe][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 ^{1}H NMR data.[12]

14: ^{1}H NMR (200 MHz, C$_6$D$_6$, 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′$_2$Ta(H)$_2$(SMe$_2$)]BF$_4$. C$_{20}$H$_{34}$BF$_4$STa, $M = 574.3$, colorless prisms ($0.20 \times 0.45 \times 0.65$ mm), triclinic, $P1$ (No. 1), $a = 10.305(2)$ Å, $b = 10.601(2)$ Å, $c = 17.272(2)$ Å, $\alpha = 77.28(2)°$, $\beta = 75.77(2)°$, $\gamma = 75.23(2)°$, $V = 1743.4(7)$ Å^3, $Z = 3$, $d_{\mathrm{calc}} = 1.64$ g/cm^3, $\mu = 4.85$ mm^{-1}, $F(000) = 852$, empirical absorption correction 8 reflections $7.0° < 2\theta < 46.0°$, 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, $R = 0.041$, $R_{\mathrm{w}} = 0.036$, GOF = 1.68. Residual electron density max/min 1.49/−1.19 e/Å^3. CCDC 101073.

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Supporting Information Available: Tables of crystallographic data for **4**·BF$_4$, 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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