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New insights into the reactivity of the tantalocene hydride Cp'_2TaH_3 ($Cp' = \eta^5\text{-}{}^tBuC_5H_4$). Synthesis and characterisation of cationic Ta(V) complexes with 0,0 and *S*,*N* chelating ligands

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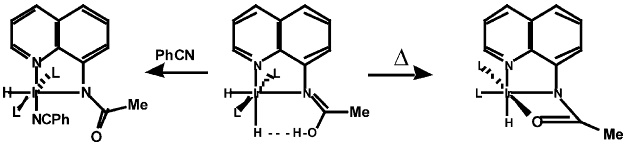
Abstract

Reaction of various neutral L–XH bidentate ligands (2-aminobenzoïc acid, acetylacetone, dibenzoylmethan and 2-aminobenzenethiol) with $[Cp'_2TaH_2]^+$, obtained in situ from Cp'_2TaH_3 treated with triphenylmethan cation, affords after dihydrogen elimination the corresponding cationic species $[Cp'_2Ta(H)(L\text{–}X)]^+$ in BF_4 or PF_6 salts. Complexes $[Cp'_2TaH(\eta^2\text{-}O_2CC_6H_4\text{-}o\text{-}NH_2\text{–}O,O')]PF_6$ (**3**), $\{Cp'_2Ta[\eta^2\text{-}OC(Me)CHC(Me)O\text{–}O,O']\}BF_4$ (**4a**), $\{Cp'_2TaH[\eta^2\text{-}OC(Ph)CHC(Ph)O\text{–}O,O']\}BF_4$ (**4b**) and $[Cp'_2TaH(\eta^2\text{-}SC_6H_4\text{-}o\text{-}NH_2\text{–}S,N)]PF_6$ (**5**) are characterised by analytical and spectroscopic methods. With thiopyridine, the kinetic (**6**) and the thermodynamic (**6′**) isomers $[Cp'_2TaH(\eta^2\text{-}2\text{-}SC_5H_4N\text{–}S,N)]PF_6$ are identified. Crystal structures are reported for complexes **3**, **5** and **6′**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tantalocene hydrides; Carboxylato–; Acetylacetonato–; 2-Aminobenzenethiolato–; Pyridine-2-thiolato complexes; Crystal structures

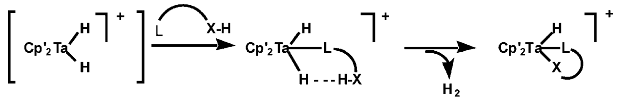
1. Introduction

An unconventional hydrogen bond M–H···H–X, where the hydride atom of a transition metal behaves as proton acceptor, has recently attracted attention. Several examples of intramolecular hydrogen bonds of this type involving electron rich transition metal hydrides (Groups 7–9) [1] or main group element hydrides (e.g. B [2] and Ga [3]) have been reported. The O–H and N–H bonds can act therein as usual acidic components. These interactions, observed as well in the solid state as in solution, can be easily broken by coordination of a good hydrogen-bond acceptor like an oxygenated solvent [1e]. In some cases, the dihydrogen molecule can be displaced by the own complex ligand as reported for iridium compound [1j].



However, to the best of our knowledge, no report on early-transition metal complex of this type is known.

We have recently found a new entry into the tantalocene hydride chemistry by reaction of Cp'_2TaH_3 (**1**) ($Cp' = \eta^5\text{-}{}^tBuC_5H_4$) with strong electrophiles (H^+ or CPh_3^+) or by its oxidation with ferrocenium ion that give rise in situ to the formation of a cationic dihydride complex $[Cp'_2TaH_2]^+$ ($\mathbf{2}^+$) [4]. Following our interest in the chemistry of this cationic complex towards one and two electron donor ligands, we consider now its behaviour against bidentate ligands L–XH such as 2-aminobenzoïc acid, β-diketones, 2-aminothiophenol and pyridine-2-thiol. The overall reaction pathway is depicted below.



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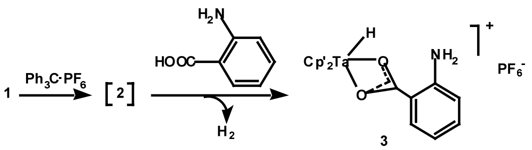
Crystal structures of ionic Ta(V) complexes $[\mathrm{Cp}'_2\mathrm{TaH}(\eta^2\text{-}\mathrm{O_2CC_6H_4}\text{-}o\text{-}\mathrm{NH_2}\text{-}O,O')]\mathrm{PF_6}$, $[\mathrm{Cp}'_2\mathrm{TaH}(\eta^2\text{-}\mathrm{SC_6H_4}\text{-}o\text{-}\mathrm{NH_2}\text{-}S,N)]\mathrm{PF_6}$ and $[\mathrm{Cp}'_2\mathrm{TaH}(\eta^2\text{-}2\text{-}\mathrm{SNC_6H_4}\text{-}S,N)]\mathrm{PF_6}$ are reported.

2. Results and discussion

2.1. 2-aminobenzoïc acid

The addition of $\mathrm{Ph_3C{\cdot}PF_6}$ and 2-aminobenzoïc acid (abaH) to a solution of $\mathrm{Cp}'_2\mathrm{TaH_3}$ (**1**) promptly affords the formation of the carboxylato complex $[\mathrm{Cp}'_2\mathrm{Ta(H)(a\text{-}aba)}]\mathrm{PF_6}$ (**3**) with evolution of dihydrogen (Eq. (1)). Complex **3** is obtained in good yield (80%) in analytically pure form.



(1)

In principle **3**, may exhibit several isomers according to the central or lateral position of potentially coordinating atoms (O and N).

The structure proposed for compound **3** in Eq. (1) is based on its IR spectroscopic data. The spectrum shows two bands at 3505 and 3397 cm^{-1} for the uncoordinated amino group and two bands at 1627 and 1500 cm^{-1} corresponding to $\nu_{(\mathrm{sym})}(\mathrm{COO})$ and $\nu_{(\mathrm{asym})}(\mathrm{COO})$, respectively, characteristic of the bidentate mode of coordination of the carboxylato ligand [5].

This structure is confirmed by X-ray analysis. An ORTEP view of the cation $[\mathrm{Cp}'_2\mathrm{Ta(H)(aba)}]^+$ is shown on Fig. 1. The non-coordination of the amino group at tantalum centre is confirmed by this study.

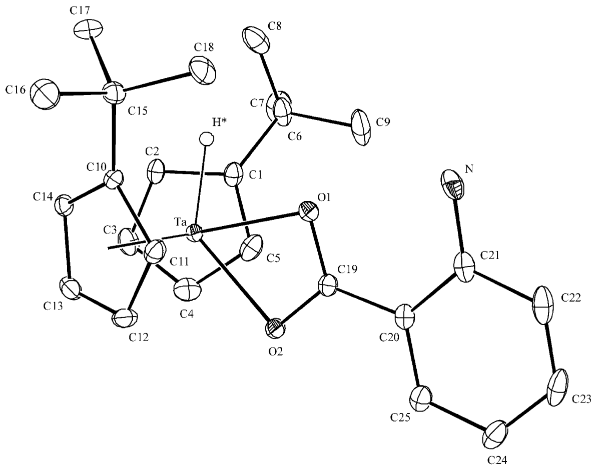
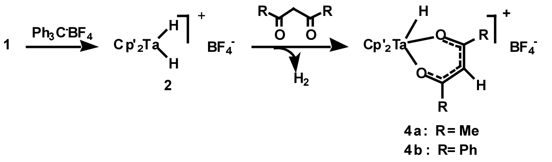


Fig. 1. ORTEP drawing of the cation $[\mathrm{Cp}'_2\mathrm{Ta(H)(aba)}]^+$ in **3**. Hydrogen atoms, except the hydride (H*), are omitted for clarity. Selected bond distances (Å) and angles (°): Ta–CP1 2.082, Ta–CP2 2.070, Ta–H* 1.65(4), Ta–O1 2.168(2), Ta–O2 2.177(2), CP1–Ta–CP2 132.7, O1–Ta–O2 59.47(7), O1–Ta–H* 70(1), O2–Ta–H* 129(1); CP1 and CP2 are the geometrical centers of C1–C5 and C10–C14 rings, respectively.

Consequently, one may assume that the formation of complex **3** results from an initial co-ordination of one of the two oxygen atoms of carboxylic group of the ligand at the central site of cationic intermediate $[\mathrm{Cp}'_2\mathrm{Ta(H)_2}]^+$ followed by immediate elimination of dihydrogen. The central site at the metal corresponds to the central lobe of empty Ta(V) $\mathrm{a_1}$ (in C_{2v} symmetry) molecular orbital (LUMO) of dihydride cation [6]. Formally, the cation in **3** may be also formed by a similar attack on one of the external (lateral) lobes of this orbital. However, a central co-ordination may be preferred for steric reasons.

2.2. β-diketone

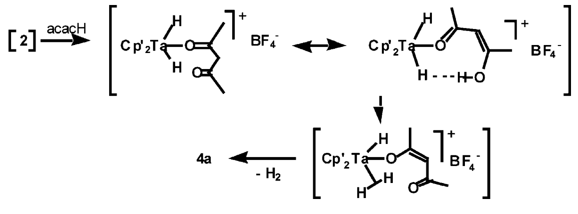
When complex **1** is treated with one equivalent of $\mathrm{Ph_3C{\cdot}BF_4}$ in presence of an excess of acetylacetone (acacH) or dibenzoylmethan (dbmH) for some minutes, pale yellow solutions are obtained. Colourless crystals of complexes **4a** and **4b**, respectively, are obtained by recrystallisation from $\mathrm{CHCl_3}$–ether. The analytical and spectroscopic data are consistent with the proposed structure **4** (Eq. (2)).



(2)

FD mass spectra (field desorption) and elemental analyses of the products indicate their composition to be $[\mathrm{Cp}'_2\mathrm{Ta(H)(acac)}]\mathrm{BF_4}$ and $[\mathrm{Cp}'_2\mathrm{Ta(H)(dbm)}]\mathrm{BF_4}$ and a loss of dihydrogen in the reaction of **2** with the corresponding β-diketon. Four signals observed for the cyclopentadienyl protons in their ^{1}H-NMR spectrum confirm a disymmetrical distribution of the three σ-bonds.The low-field resonance of the residual hydride ($\delta = 13.36$ and 13.58 ppm for **4a** and **4b**) on Ta agrees with strong electron-withdrawing properties of the dicarbonyl ligand coordinated in these cationic Ta(V) complexes. Moreover, a weak coupling constant ($^5J_{\mathrm{H-H}} = 0.8$ Hz) is observed for **4a** between the Ta–H and the methinic proton.

As proposed on Scheme 1, the formation of **4** may involve in the first step the co-ordination of the carbonyl group at the metal, probably in central position. The

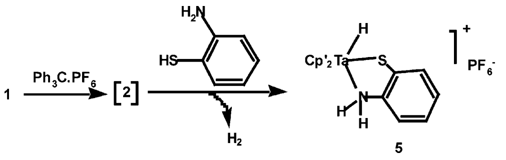


Scheme 1. Proposed mechanism of formation of **4**.

generated enol group would then take part in a Ta–H···H–O hydrogen bond that induce a dihydrogen elimination.

2.3. 2-Aminobenzenethiol

Compound **5** (Eq. (3)) is obtained in good yield as a yellow solid by reaction of an excess of 2-aminobenzenethiol (abtH) with the cationic dihydride tantalocene complex **2**·PF_6. The formulation $[Cp_2'Ta(H)(abt)]PF_6$ is consistent with its analytical and mass spectrometric FD data.



(3)

The two low $\nu(NH_2)$ frequencies at 3306 and 3260 cm^{-1} observed in the IR spectrum of compound **5** suggest the existence of a coordinated NH_2-group at tantalum atom. However, the coordination regioselectivity of the aminobenzenethiolato ligand could not be inferred from the spectroscopic data, so an X-ray diffraction study of **5** has been carried out. The structure of the cation is shown on Fig. 2.

The molecular structure of **5** reveals that the bidentate ligand forms a five-membered ring in which the NH_2-group lies on the opposite side with respect to the hydride ligand. The Ta–S bond length of 2.5160(7) Å falls in the typical range of values observed for tantalocene sulfur complexes with a single Ta–S bond [7].

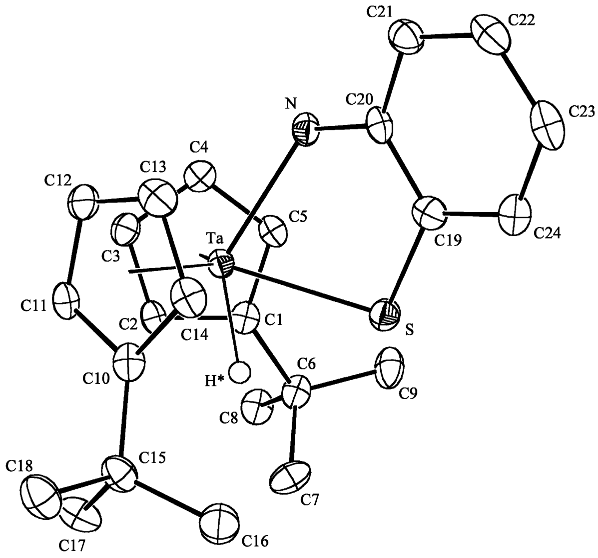
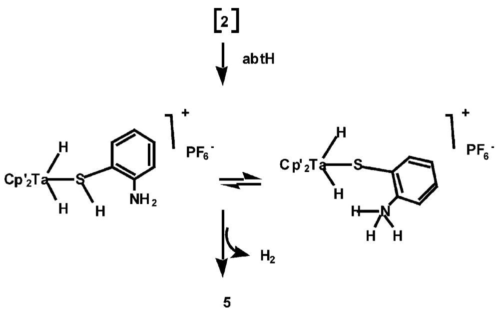


Fig. 2. ORTEP drawing of the cation $[Cp_2'Ta(H)(abt)]^+$ in **5**. Hydrogen atoms, except hydride (H*), are omitted for clarity. Selected bond distances (Å) and angles (°): Ta–CP1 2.102, Ta–CP2 2.087, Ta–H* 1.53(4), Ta–S 2.516(1), Ta–N 2.282(3), CP1–Ta–CP2 132.0, S–Ta–N 72.94(6), S–Ta–H* 64(1), N–Ta–H* 136(1).



Scheme 2. Proposed mechanism of formation of **6**.

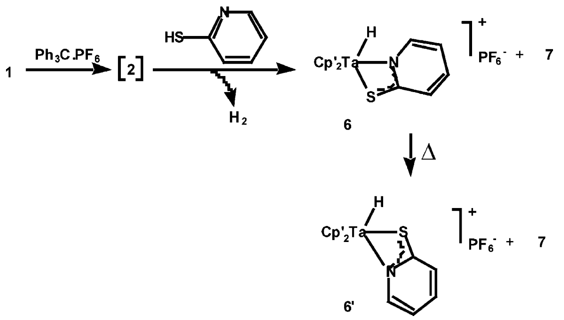
The mechanism of formation of **5** (Scheme 2) may involve an initial coordination of the sulfur atom (SH) on the central lobe of a_1 molecular orbital resulting in formation of sulphonium unit bearing an acidic hydrogen. The next step may consist either in a direct elimination of H_2 (interaction of this acidic hydrogen with one of the two hydrides) and co-ordination of the amine on liberated metallic site, or in an intra-ligand migration of this hydrogen from sulfur to nitrogen (formation of ammonium group) followed by elimination of H_2 and formation of Ta–N bond. On the other hand, an initial attack of amine function on lateral lobe of a_1-orbital seems to be not plausible, because the formation of **5** in that case should involve an interaction of the Ta–*H* hydride with a hydrogen from the less polarised *H*–S bond.

2.4. 2-Thiopyridine

In recent years, several examples of dihydrogene complexes [8] and those with unconventional hydrogen bond 1d1h derived from 2-thiopyridine (pySH) as basic ancillary ligand and late-transition metal hydrides have been reported. It was of interest to examine the reactivity of such ligand with early-transition metal complexes such as tantalocene hydride.

Addition at 0 °C of pySH to a solution of $Cp_2'TaH_3$ (**1**) in THF in presence of $Ph_3C·PF_6$ rapidly results in the formation of the two major products **6** and **7** in 60/40 ratio, together with traces of the isomer **6′**, as observed by ^1H-NMR analysis. Only the isomer **6** has been obtained in analytically pure form by re-crystallisation of the crude material at low temperature (−30 °C). By heating the solution of the mixture up to 30 °C, kinetically controlled complex **6** undergoes fast and quantitative rearrangement leading to the thermodynamically controlled isomer **6′** and unchanged compound **7** (Eq. (4)). Re-crystallisation of their mixture again only leads to the pure complex **6′**.

Analytical, mass spectroscopic FD and ^1H-NMR spectroscopic data are in agreement with a common formulation $[Cp_2'Ta(H)(pyS)]PF_6$ for two isomeric complexes **6** and **6′**, but the stereochemistry of the two isomers can not be readily deduced from these data. However, an X-ray diffraction study recovered the structure of **6′** (Fig. 3) and consequently allowed to propose that of the isomer **6** shown in Eq. (4).



(4)

This study confirms the presence of an anionic (pyS^-) ligand that functions as a *N*,*S*-donor chelate with sulfur atom located in central position in the structure of **6′**. The ^{t}Bu substituents on C_5 rings in this structure, as well as in those of **3** and **5**, span the space over the hydride ligand, and lie on the same side (with respect to the plane defined by the centers of the rings and tantalum atom) of the molecule. The dihedral angles (taken as measure of conformation) between the planes C6,CP1,CP2/C15,CP2,CP1 are equal to 23.2, 37.7 and 29.4° for cations **3**, **5** and **6′**, respectively. Such conformations are not current for this family of $(C_5H_4'Bu)_2M$ metallocenes. An inspection of Cambridge Crystallographic Data Base shows that only some 7% of complexes adopt the conformation with dihedral angles defined above in the range of 20–40°. In a large majority of complexes (more than 55%) these angles span a range of 160–200°. This crystallochemical topic will be discussed elsewhere.

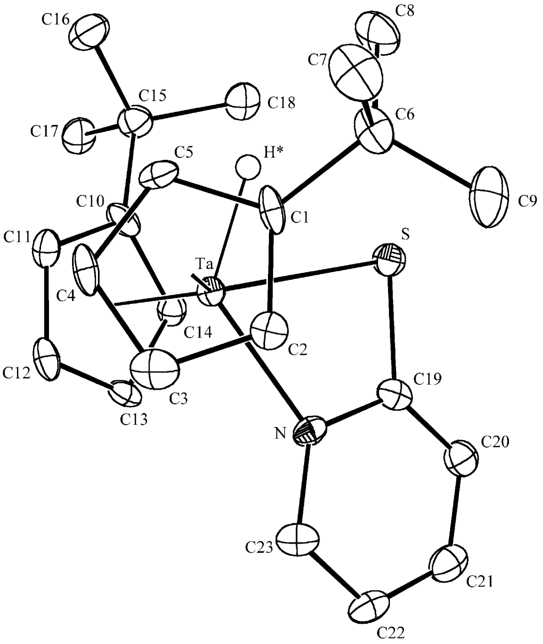


Fig. 3. ORTEP drawing of the cation $[Cp_2'Ta(H)(pyS)]^+$ in **6′**. Hydrogen atoms, except hydride (H*), are omitted for clarity. Selected bond distances (Å) and angles (°): Ta–CP1 2.091, Ta–CP2 2.121, Ta–H* 1.58(6), Ta–S 2.509(2), Ta–N 2.196(6), CP1–Ta–CP2 130.4, S–Ta–N 64.1(2), S–Ta–H* 67(5), N–Ta–H* 131(5).

Our attempts to isolate compound **7** were unsuccessful. The structure of **7** cannot be clearly deduced on the basis of ^{1}H-NMR data of mixtures **6**+**7** (or **6′**+**7**). Nevertheless, some characteristic data (see experimental part) can be pointed out: in CD_3COCD_3 solution, spectrum of **7** (in presence of **6**) shows a singlet at 1.93 ppm (2H) and two multiplets at 5.03 (4H) and 6.05 ppm (4H) in the typical region for hydrides and cyclopentadienyl protons, respectively, characteristic of a high symmetry structure, e.g. C_{2v}, around the metal. Moreover, coordination of a thiopyridine ligand on the tantalocene moiety can be proposed according to the presence of signals at 7.41 (1H), 8.05 (2H) and 8.44 ppm (1H). In this way, the speculative formulations either as a neutral complex $[Cp_2'Ta(H)_2(\eta^1\text{-S–}C_5H_4N)]$ or as an ionic one $[Cp_2'Ta(H)_2(\eta^1\text{-S–}C_5H_4NH)]PF_6$ may be proposed for complex **7**.

3. Conclusions

Although we showed that the bidentate L–XH ligands easily coordinate to $[Cp_2'TaH_2]^+$ cation, we were not able to detect clearly an intramolecular proton–hydride interaction. The unstable intermediate $[Cp_2'Ta(H)_2(L\text{–}XH)]^+$ liberates rapidly the dihydrogen molecule and gives rise to formation of new (*O*,*O′*)– or (*N*,*S*)–bidentate cationic Ta(V) complexes **3**, **4**, **5**, **6** and **6′**. Work is currently in progress to investigate a specific synthesis of **7** in order to examine properties and structural parameters of this complex.

4. Experimental

All reactions were performed under an argon atmosphere by using Schlenk techniques. Solvents were distilled from sodium benzopohenone ketyl. The following instruments were used in this work: Bruker AC 200 (RMN); Bruker IFS 66v spectrophotometer (IR); Finnigan MAT 311 (field desorption mass spectra); 1108 CHNS-O FISONS Instruments (elemental analysis).

NMR spectra were recorded in $CDCl_3$ (otherwise stated), and chemical shifts are reported in ppm from tetramethylsilane.

The tantalocene hydride $Cp_2'TaH_3$ [9] and the ferricinium [10] salts were prepared by published procedures. Other reagents were degassed and stored under argon.

4.1. $[Cp'_2Ta(H)(\eta^2\text{-}OOC\text{–}C_6H_4\text{-}o\text{-}NH_2)]PF_6$ (**3**)

A solution of Cp'_2TaH_3 (0.12 g, 0.28 mmol) in THF (10 ml) was treated with one equivalent of $Ph_3C{\cdot}PF_6$ (0.11 g, 0.28 mmol) and 2-aminobenzoïc acid (39 mg, 0.28 mmol). The volatiles were removed in vacuo and the residue was washed with pentane (yield: 80%). An analytically pure sample was obtained by recrystallisation from THF–ether.

Elemental Anal. Found: C, 42.81; H, 4.56; N, 2.60. Calc. for $C_{25}H_{33}TaNO_2PF_6$: C, 42.56; H, 4.72; N, 1.99%. ^{1}H-NMR, δ: 1.35 (s, 18H, ^{t}*Bu*), 5.30 (m, 2H, C_5H_4), 5.78 (m, 2H, C_5H_4), 6.08 (m, 2H, C_5H_4), 6.6 (m, 2H, C_5H_4 and m, 2H, *Ph*), 7.3 (m, 1H, *Ph*), 7.48 (m, 1H, *Ph*), 13.10 (s, 1H, Ta*H*) (N*H*$_2$: not observed). IR (KBr pellet, cm^{-1}): 1627s, $\nu_{(sym)}$(COO); 1500 s, $\nu_{(asym)}$(COO); 3505s, 3397s, ν(NH$_2$). FDMS (CHCl$_3$): *m*/*z* 560.2.

4.2. $[Cp'_2Ta(H)(acac)]BF_4$ (**4a**)

One equivalent of $Ph_3C{\cdot}BF_4$ (0.14 g, 0.35 mmol) and two equivalents of acetylaceton (70 µl, 0.7 mmol) were added to a solution of Cp'_2TaH_3 (0.15 g, 0.35 mmol) in THF (10 ml). After stirring 15 min, the solvent was removed in vacuo and the crude material was washed with toluene and pentane to give a pale yellow solid in good yield (75%). Recrystallisation from chloroform–ether gave white microcrystals.

Elemental Anal. Found: C, 44.43; H, 5.85. Calc. for $C_{23}H_{34}TaO_2BF_4$: C, 45.27; H, 5.69%. ^{1}H-NMR, δ: 1.36 (s, 18H, ^{t}*Bu*), 1.98 (s, 3H, CO*Me*), 2.09 (s, 3H, CO*Me*), 5.67 (m, 2H, C_5H_4), 5.88 (d, $^5J_{HH} = 0.8$ Hz, 1H, CO–C*H*–CO), 5.91 (m, 2H, C_5H_4), 6.27 (m, 2H, C_5H_4), 6.39 (m, 2H, C_5H_4), 13.36 (d, $^5J_{HH} = 0.8$ Hz, 1H, Ta*H*). IR (KBr pellet, cm^{-1}): 1588s, 1536s, ν(CO). FDMS (CHCl$_3$): *m*/*z* 523.3.

4.3. $[Cp'_2Ta(H)(dbm)]BF_4$ (**4b**)

One equivalent of $Ph_3C{\cdot}BF_4$ (0.14 g, 0.35 mmol) and two equivalents of dibenzoylmethane (0.16 g, 0.7 mmol) were added to a solution of Cp'_2TaH_3 (0.15 g, 0.35 mmol) in THF (10 ml). After stirring for 15 min, the solvent was eliminated under reduced pressure and the yellow residue was washed with toluene (2 × 5 ml) and pentane (5 ml) (75% yield). Recrystallisation from chloroform–ether gave white crystals.

Elemental Anal. Found: C, 53.69; H, 4.96. Calc. for $C_{33}H_{38}TaO_2BF_4$: C, 53.97; H, 5.22%. ^{1}H-NMR, δ: 1.30 (s, 18H, ^{t}*Bu*), 5.44 (m, 2H, C_5H_4), 5.57 (m, 2H, C_5H_4), 6.33 (m, 2H, C_5H_4), 6.53 (m, 2H, C_5H_4), 7.01 (s, 1H, CO–C*H*–CO), 13.58 (s, 1H, Ta*H*). IR (KBr pellet, cm^{-1}): 1592s, 1528s, ν(CO). FDMS (CHCl$_3$): *m*/*z* 647.3.

4.4. $[Cp'_2Ta(H)(\eta^2\text{-}o\text{-}S\text{–}C_6H_4\text{–}NH_2)]PF_6$ (**5**)

One equivalent of $Ph_3C{\cdot}PF_6$ (55 mg, 0.14 mmol) and an excess of 2-aminobenzenethiol (40 µl, 0.28 mmol) were added to a solution of Cp'_2TaH_3 (60 mg, 0.14 mmol) in THF (10 ml). The solvent was eliminated under reduced pressure after 10 min stirring, and the yellow residue was washed with pentane (yield: 85%). Yellow crystals were obtained by recrystallisation from CHCl$_3$–ether.

Elemental Anal. Found: C, 41.57; H, 4.63; N, 2.21. Calc. for $C_{24}H_{33}TaNSPF_6$: C, 41.57; H, 4.80; N, 2.02%. ^{1}H-NMR, δ: 1.38 (s, 18H, ^{t}*Bu*), 4.81 (m, 2H, C_5H_4), 5.42 (m, 2H, C_5H_4), 5.90 (m, 2H, C_5H_4), 6.17 (m, 2H, C_5H_4), 6.7–7.4 (m, 4H, Ph), 8.30 (s, 1H, TaH) (N*H*$_2$: not observed). IR (KBr pellet, cm^{-1}): 3306s, 3260s, ν(NH$_2$). FDMS (CHCl$_3$): *m*/*z* 548.2.

4.5. $[Cp'_2Ta(H)(\eta^2\text{-}2\text{-}SC_5H_4N)]PF_6$ (**6** and **6′**)

One equivalent of $Ph_3C{\cdot}PF_6$ (73 mg, 0.19 mmol) and of 2-mercaptopyridine (21 mg, 0.19 mmol) were added to a solution of **1** (0.8 g, 0.19 mmol). After stirring 5 min at 0 °C, the volatiles were eliminated under reduced pressure to give a mixture of **6** and **7** (with trace of **6′**) in 75% overall yield. After washing with ether, a few white crystals of **6** can be isolated by fractional crystallisation (CHCl$_3$–ether).

Carried out at 40–45 °C, the same reaction leads to the formation of a mixture containing only **6′** and **7**. Complex **6′** is obtained as a white microcrystalline solid by slow recrystallisation of the crude material in a CHCl$_3$–ether mixture at low temperature (−30 °C).

4.5.1. Isomer **6**

Elemental Anal. Found: C, 40.72; H, 4.33; N, 2.51. Calc. for $C_{23}H_{31}TaNSPF_6$: C, 40.66; H, 4.60; N, 2.06%. ^{1}H-NMR, δ: 1.29 (s, 18H, ^{t}*Bu*), 5.25 (m, 2H, C_5H_4), 5.36 (m, 2H, C_5H_4), 5.82 (m, 2H, C_5H_4), 6.56 (m, 2H, C_5H_4), 6.72 (m, 1H, C_5H_4N), 6.93 (m, 1H, C_5H_4N), 7.49 (m, 1H, C_5H_4N), 8.02 (m, 1H, C_5H_4N), 8.48 (s, 1H, Ta*H*). FDMS (CHCl$_3$): *m*/*z* 534.2.

4.5.2. Isomer **6′**

Elemental Anal. Found: C, 40.84; H, 4.56; N, 2.55. Calc. for $C_{23}H_{31}TaNSPF_6$: C, 40.66; H, 4.60; N, 2.06%. ^{1}H-NMR, δ: 1.35 (s, 18H, ^{t}*Bu*), 4.69 (m, 2H, C_5H_4), 5.48 (m, 2H, C_5H_4), 6.01 (m, 4H, C_5H_4), 6.62 (m, 1H, C_5H_4N), 7.18 (m, 1H, C_5H_4N), 7.56 (m, 1H, C_5H_4N), 8.52 (m, 1H, C_5H_4N), 9.06 (s, 1H, Ta*H*). FDMS (CHCl$_3$): *m*/*z* 534.2.

Characteristic ^{1}H-NMR spectroscopic data for compound **7**: (CD$_3$)$_2$CO, δ: 1.31 (s, 18H, ^{t}Bu), 1.93 (s, 2H, TaH), 5.03 (m, 4H, C_5H_4), 6.08 (m, 4H, C_5H_4), 7.13 (m, 1H, C_5H_4N), 8.05 (m, 2H, C_5H_4N), 8.44 (m, 1H, C_5H_4N); in CDCl$_3$, the two Cp′ protons are observed

Table 1
Crystallographic data for complexes **3** [$Cp'_2TaH(\eta^2\text{-}O_2CC_6H_4\text{-}o\text{-}NH_2\text{-}O,O')][PF_6]$, **5** [$Cp'_2TaH(\eta^2\text{-}SC_6H_4\text{-}o\text{-}NH_2\text{-}S,N)][PF_6][THF]$ and **6′** [$Cp'_2TaH(\eta^2\text{-}2\text{-}SCC_6H_4N\text{-}S,N)][PF_6]$

Compound	**3**	**5**	**6′**
Empirical formula	$C_{25}H_{33}F_6NO_2PTa$	$C_{28}H_{41}F_6NOPSTa$	$C_{23}H_{31}F_6NPSTa$
M	705.44	765.60	679.47
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Orthorhombic, $P2cb$
a (Å)	12.2340(3)	10.2570(2)	8.3450(2)
b (Å)	16.6050(4)	11.5110(3)	16.6690(3)
c (Å)	12.9860(2)	13.9940(3)	17.4100(3)
α (°)		109.2100(14)	
β (°)	94.7430(13)	91.3820(14)	
γ (°)		106.3741(12)	
V (Å^3)	3324.0(4)	1744.30(6)	2216.4(2)
Z	4	2	4
D_{calc} (Mg m^{-3})	1.782	1.713	1.864
Lin. Absorption coefficient (mm^{-1})	4.308	3.887	4.749
$F(000)$	1700	754	1310
Crystal size (mm^3)	0.40 × 0.35 × 0.2	0.15 × 0.15 × 0.03	0.12 × 0.12 × 0.12
θ range (°) for collection	2.07–30.09	1.97–27.48	2.34–27.45
hkl/ranges	$0 \le h \le 17$, $0 \le k \le 23$, $l \le \pm 18$	± 13, $-14k \le +13$, $-18 \le l \le 16$	$0 \le h \le 10$, $0 \le k \le 21$, $0 \le l \le 22$
Data/restraints/parameters	7624/0/329	6779/0/356	2947/1/318
Goodness-of-fit on F^2	1.042	1.060	1.060
Final R indices [$I > 2\sigma(I)$]	R_1 [a] $= 0.0268$, wR_2 [b] $= 0.0581$	$R_1 = 0.0273$, $wR_2 = 0.0614$	$R_1 = 0.0252$, $wR_2 = 0.0581$
R indices (all data)	R_1 [a] $= 0.0330$, wR_2 [b] $= 0.0608$	$R_1 = 0.0308$, $wR_2 = 0.0632$	$R_1 = 0.0273$, $wR_2 = 0.0595$
Absolute structure, Flack			0.07(1)
w [c]/a, b	0.0165, 4.1865	0.0211, 0.7748	0.0204, 8.5496
ρ_{max}, ρ_{min} (e Å^{-3})	0.57, −1.35	0.78, −1.37	0.91, −1.135

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$.
[c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

at 4.75 (m, 4H) and near 5.8 ppm (very broad signal, 4H) at 293 K.

4.5.3. X-ray structure analyses

Crystals of **3, 5** and **6′** suitable for X-ray studies were mounted on a Nonius Kappa CCD diffractometer. The unit cell determinations and data collections were carried out with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at low temperature (110 K). The measured intensities were reduced with DENZO program [11]. The structures were solved via direct methods and Patterson syntheses with SHELXS-97. All models were further refined with full-matrix least-squares methods (SHELXL-97) based on $|F^2|$ [12]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligands in these three complexes were located from difference Fourier maps and isotropically refined. Other hydrogen atoms were included in calculated positions and refined with a riding model. The three compounds studied are the PF_6 salts of organometallic cations that lie in general positions. The anions in **3** and **5** also occupy the general positions, whereas in **6′** they are placed on two-fold axes. Some disorder of F atoms is observed in the structure of **6′**, but it has no influence on metric parameters of the cation. There is one solvent molecule (THF) per one cation and one anion in the lattice of **5**. Crystallographic data and refinement parameters are gathered in Table 1.

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 174347 for compound **3**, no. 174348 for compound **5** and no. 174349 for compound **6′**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http//www.ccdc.cam.ac.uk).

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