Metallocenes of Nb and Ta with η^2-Se_2H, SeH, and Se Ligands – Crystal Structures of $[Cp'_2Ta(SeH)H_2]$ and $[Cp'_2Ta(=Se)H \cdot W(CO)_5]$ ($Cp' = tBuC_5H_4$)

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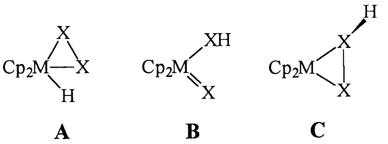
The reactions of $[Cp^{\#}_2NbBH_4]$ (**1**) [$Cp^{\#} = C_5Me_5$ (Cp^*) or C_5Me_4Et] and $[Cp'_2TaH_3]$ ($Cp' = tBuC_5H_4$) with elemental selenium give complexes of the general composition $[Cp_2MSe_2H]$. These exist in three isomeric forms, **A–C**, depending on the metal and the chalcogen. $[Cp^{\#}_2NbSe_2H]$ (**2**) incorporates the novel η^2-Se_2H ligand (**C**), which is labile when exposed to light. Solutions of **2**(Cp^*) can be converted into $[Cp^*_2NbSe_2H]$ (**3**), which exists in two isomeric forms **A** or **B**, along with $[Cp^*_2NbSe_3H]$ (**4**) and $[Cp^*_2NbO_2H]$ (**5**). $[Cp'_2Ta(\eta^2\text{-}Se_2)H]$ (**6**) is the only isomer found for the Ta system. Se abstraction by means of $P(OEt)_3$ gives $[Cp'_2Ta(=Se)H]$ (**7**). Complex **7** can be reduced with Na/Hg and subsequently hydrolysed to give $[Cp'_2Ta(SeH)H_2]$ (**8**), which has also been observed during the formation of **6**. Coordination of $[W(CO)_5THF]$ at the Se lone pair of **7** affords the heterobimetallic complex **9**. All compounds have been characterized by means of ^1H- and, in some cases, ^{77}Se-NMR spectroscopy. Products **8** and **9** have also been subjected to X-ray diffraction analysis.

Introduction

Metallocenes of the early transition metals are excellent reagents for the stabilization of chalcogenido ligands.[1] However, only a few comparative studies have been carried out, in which the coordination behavior of various chalcogens has been studied at a specific transition metal.[2] Compounds of the class $[Cp_2MX_2H]$ (Cp = any substituted cyclopentadienyl) are predominant in Nb and Ta chalcogen chemistry. They occur as isomers **A−C**, where the form adopted depends on the combination of substituted cyclopentadienyl ligands [$Cp' = tBuC_5H_4$; $Cp^{\#} = C_5Me_5$ (Cp^*) or C_5Me_4Et] with the appropriate metals (M = Nb, Ta) and chalcogens (X = S, Se, Te). Examples existing as isomeric form **A** are $[Cp^{\#}_2NbS_2H]$,[3] $[Cp'_2TaS_2H]$,[3] and $[Cp^*_2TaX_2H]$ (X = S,[4] Se,[5] Te[6]). The chemistry of this isomeric form is characterized by the nucleophilic behavior of the free electron pairs of the dichalcogenido ligands, which can ultimately lead to the formation of polymetallic compounds.[7] Another feature is the photolytic rupture of its X−X bond, giving isomers of type **B** (M = Nb, Ta: X = S;[8] M = Ta: X = Se[5]). Only one example (M = Nb: X = Te) corresponding to isomer form **C** has been reported, which involves a chiral X atom: $[Cp^{\#}_2Nb(\eta^2\text{-}Te_2H)]$ serves as a reagent for the transfer of Te^0[9] or Te^{2-} ligands[10] to other organometallic complexes.

Whereas peralkylated tantalocene compounds of type **A** are well established for X = S, Se, and Te, the corresponding niobocene selenides are not known. Therefore, we decided to investigate the reactions of $[Cp^{\#}_2NbBH_4]$ and of $[Cp'_2TaH_3]$ with elemental selenium. The latter was employed because sulfido compounds containing the Cp'_2Ta fragment exhibit striking relationships in their chemical behavior when compared to sulfido compounds involving the $Cp^{\#}_2Nb$ fragment.[11]



Scheme 1. Isomeric forms of Cp_2MX_2H (M = Nb, Ta; X = S, Se, Te)

Results

The $Cp^{\#}_2Nb$/Se System

Reaction of $[Cp^{\#}_2NbBH_4]$ **1** with 2.3 equivalents of red selenium in the dark at ambient temperature gives the green compounds **2** in 85−89% yields (Equation 1). The reaction of **1** with grey Se requires a temperature of at least 40°C. FD mass spectra and elemental analyses of the products indicate their composition to be $[Cp^{\#}_2NbSe_2H]$. The ^1H-NMR spectra of compounds **2** invariably exhibit a high-field resonance at $\delta = -0.90$, surrounded by ^{77}Se satellites. ^{77}Se-NMR spectra feature resonances at $\delta = -210$ and 230, respectively, the latter exhibiting a $^{77}Se-^1H$ coupling of 34 Hz. The absence of a highly deshielded resonance rules out the presence of double-bonded Se.[5][12] The ^1H-NMR spectrum of $[(C_5Me_4Et)_2Nb(Se_2H)]$ (Figure 1) features a

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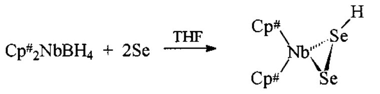
multiplet attributable to the CH_2 protons. A similar NMR pattern has been observed for [$(C_5Me_4Et)_2Nb(\eta^2\text{-}Te_2H)$], the structure of which has been determined by X-ray crystallography.[9] On this basis, compounds **2** are assigned the isomeric form **C**.



1 **2**

(1)

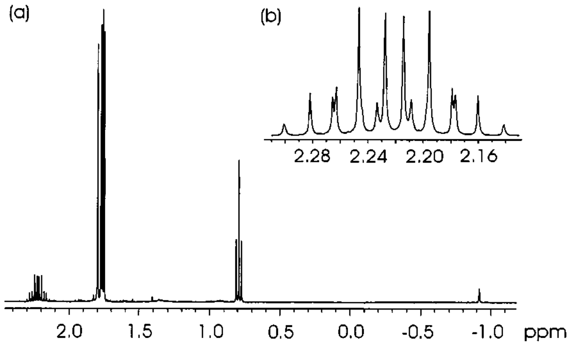


Figure 1. ^{1}H-NMR spectrum (400 MHz, C_6D_6) of [$(C_5Me_4Et)_2Nb(\eta^2\text{-}Se_2H)$] (Figure 1a) and CH_2 resonances of the C_5Me_4Et ligands (· 5; Figure 1b)

The green solutions of **2** slowly become orange when exposed to light. This process was studied by ^{1}H-NMR spectroscopy in the case of **2**(Cp*) in C_6D_6 solution. The signals at $\delta = 1.73$ (CH_3) and $\delta = -0.89$ (SeH) disappear as new signals develop (Figure 2), the latter being attributable to the compounds [$Cp^*_2NbSe_2H$] (**3**), [$Cp^*_2NbSe_3H$] (**4**), and [$Cp^*_2NbO_2H$] (**5**) (Equation 2). The products were identified, after partial chromatographic separation, on the basis of their mass-spectrometric and ^{1}H-NMR-spectroscopic data, following irradiation of a solution of **2**(Cp*) on a preparative scale. Separation into discrete compounds could not be achieved, and consequently there is some scatter in the C,H elemental analysis data for **3** and **4**. In the ^{1}H-NMR spectrum of **3**, the "hydride" resonance is flanked by two pairs of ^{77}Se satellites (Figure 2b). A structural assignment to one of the two isomers **A** or **B** (Scheme 1) is not yet possible because the low solubility of **3** does not allow a ^{77}Se-NMR spectrum of sufficient quality to be recorded. IR spectra are of little use in assigning the isomeric form as the only significant absorptions are those of the ν(C−H) vibrations of the Cp# rings. Irradiation of the C_5Me_4Et derivative of **2** proceeds in a similar manner, but separation into discrete complexes proved even more difficult, thus preventing clear assignments of signals in the NMR spectra. Although an unambiguous assignment of the structures of **3** and **4** is not yet possible, further support for the proposed isomeric forms is provided by the thermolysis of [$Cp^*_2NbS_2H$]. Here, isomer **A** is converted to isomer **B** in the formation of [$Cp^*_2NbS_3H$], and both structures have been confirmed by X-ray studies.[3][8]

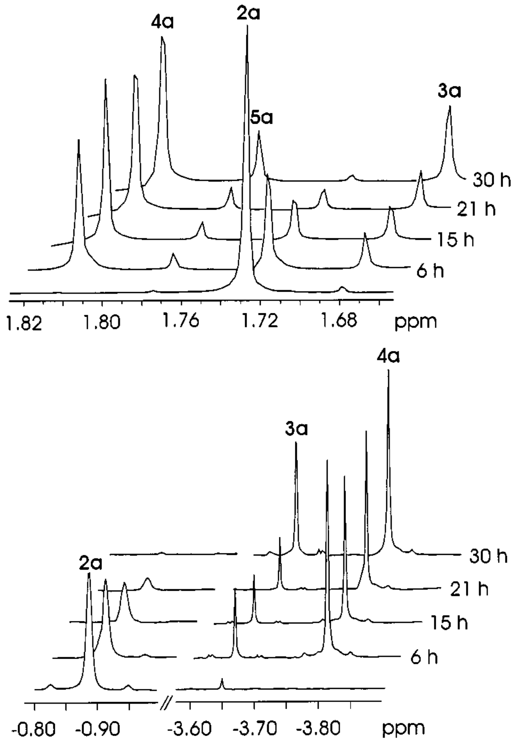
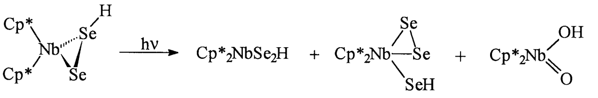


Figure 2. ^{1}H-NMR investigation of the isomerization of [$Cp^*_2Nb(\eta^2\text{-}Se_2H)$] [**2**(Cp*)] during irradiation (400 MHz, C_6D_6); methyl resonances of the Cp* ligands of **2**(Cp*), [$Cp^*_2NbSe_2H$] (**3**), [$Cp^*_2Nb(Se_2)SeH$] (**4**), and [$Cp^*_2Nb(O)OH$] (**5**) (see text; Figure 2a); high-field region (· 20; Figure 2b)

The formation of **5** may be rationalized in terms of the substitution of selenide ligands by traces of oxygen. In a control experiment, a solution of **2**(Cp*) produced bright-yellow [$Cp^*_2NbO_2H$] (**5**) along with red selenium when exposed to air. Complex **5** belongs to the class of oxonio-bocenes of the type [$Cp^*_2Nb(=O)R$] (R = H, Cl, OCH_3, etc.).[13]



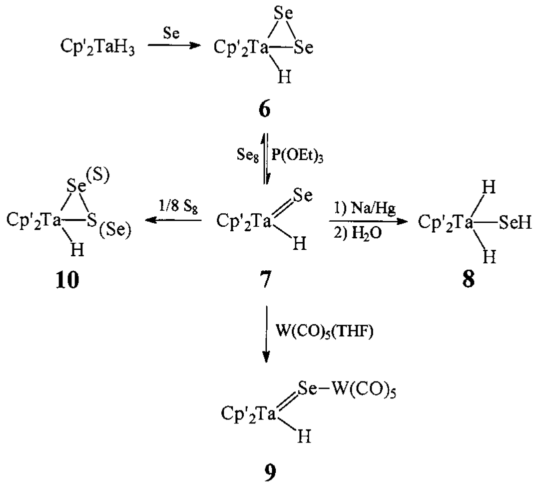
2(Cp*) **3A,B** **4** **5**

(2)

The Cp′$_2$Ta/Se System

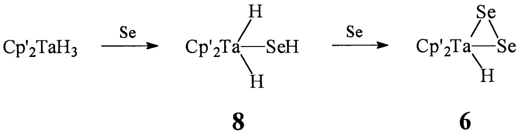
Stirring of a toluene solution of [Cp'_2TaH_3] with an excess of grey selenium (12 h, 25 °C) leads to the formation of the red complex [Cp'_2TaSe_2H] (**6**) (Scheme 2). The isomeric form **A** can be proposed on the basis of spectroscopic data. The IR spectrum of **6** shows an absorption at 1710 cm^{-1} characteristic of ν(Ta−H), and the ^{1}H-NMR spectrum exhibits a singlet at $\delta = 1.11$ for the TaH proton and a set of four resonances ($\delta = 3.81$, 4.21, 4.34, and 6.15) due to the cyclopentadienyl protons. Two resonances ($\delta = -251$ and -571) are observed for the two non-equivalent chalcogen atoms in the ^{77}Se-NMR spectrum. In contrast to the analogous [$Cp^*_2Ta(\eta^2$-$Se_2)H$],[5] no $^{77}Se-^{1}H$ coupling is observed.

Treatment of a toluene solution of **6** with triethyl phosphite (4 h, reflux) leads to formation of the monoselenido complex [$Cp'_2Ta(=Se)H$] (**7**). The ^{77}Se-NMR spectrum of **7** exhibits a deshielded signal at $\delta = 2303$, which is typical for doubly bonded Se.[5][12] The signal at $\delta = 7.52$ in the ^{1}H-NMR spectrum, attributable to the TaH group, is suggestive of a protic rather than a hydridic nature of the hydrogen ligand.[14] [$Cp'_2Ta(\eta^2$-$Se_2)H$] (**6**) is regenerated upon addition of an excess of Se_8 to solutions of **7** (Scheme 2).



Scheme 2

Like the related tantalocene sulfide,[14][15] the Ta=Se bond in **7** can be expected to exhibit an interesting reaction potential. Thus, when a pale-blue THF solution of **7** is treated with sodium amalgam and then with a few drops of water, rapid decolouration of the reaction mixture occurs, from which the white complex **8** can subsequently be isolated. Analytical data for **8** are consistent with the composition [Cp'_2TaSeH_3]. In this context, it is of interest that the FD mass spectrum of **8** features the parent ion peak, whereas that of its precursor **7** shows only the peak of **6**, which is richer in Se. The ^{1}H-NMR spectrum of **8** exhibits two multiplets at $\delta = 4.91$ and $\delta = 4.37$ for the Cp protons, and a singlet at $\delta = 1.29$ for the *t*Bu group. This is in accord with the presence of two equivalent cyclopentadienyl rings. The "hydride" resonances appear as a doublet at $\delta = 2.43$ and a triplet at $\delta = -4.86$ (ratio 2:1). The ^{77}Se-NMR spectrum shows a triplet at $\delta = -570$ with $^{2}J(^{77}Se-^{1}H) =$ 23 Hz. The same coupling is found for the doublet, whereas the aforementioned high-field triplet does not exhibit any SeH coupling, even upon irradiation of the doublet. The high-field resonance disappears in D_2O as [$Cp'_2Ta(SeD)H_2$] is formed. As in the case of the related [$Cp'_2Ta(SD)H_2$], which shows a similar spectrum,[16] no evidence for Ta–D bond formation could be detected. This is in contrast to the exchange process hydrochalcogenido vs. hydrido ligands observed by Bergman et al. in the case of [$Cp^*_2Ti(SH)H$].[17] Complex **8** is also observed in the course of formation of **6**, so that it may be considered as the first relatively stable intermediate product in the activation of elemental selenium by [Cp'_2TaH_3] (Equation 3).



(3)

In order to gain further insight into the structure of **8**, a single-crystal X-ray analysis was carried out. This revealed the typical bent metallocene structure (Figure 3), with the Se atom located in the plane defined by the centers of the Cp ligands and the Ta atom. The final difference Fourier map exhibits several positive peaks close (< 1.5 Å) to the Ta and Se atoms. However, none of them could be refined as a bona fide hydrogen atom. Thus, even though we were unable to locate the hydrogen atoms, the overall metallocene geometry[18] of **8**, together with a long Ta–Se bond of 2.646(1) Å {some 0.3 Å longer than the Ta=Se bond in [$Cp^*_2Ta(=Se)H$][5]}, are clearly indicative of the presence of a hydroselenide ligand. Complex **8** is one of the few examples containing this ligand.[5][19]

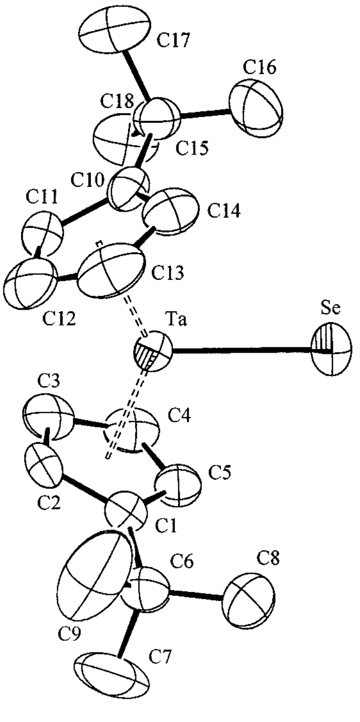


Figure 3. Molecular structure (ORTEP drawing at 50% probability level) of [Cp'_2TaH_2SeH] (**8**); selected bond lengths [Å] and angles [°]: Ta–Se 2.646(1), Ta–Cp1 2.09, Ta–Cp2 2.08 (Cp1 and Cp2 are the centers of the rings C1–C5 and C10–C14, respectively); Cp1–Ta–Cp2 136.9; the H atoms attached to Ta and Se could not be localized

The selenido complex **7** reacts with [$W(CO)_5(THF)$] to afford the brown, heterobimetallic compound **9** in 65% yield (Scheme 2). This complex has been characterized by both spectroscopic and crystallographic measurements. The IR spectrum of **9** exhibits the typical absorption pattern for the coordinated $W(CO)_5$ moiety and the ^{1}H-NMR spectrum features one signal for the *t*Bu protons. The molecular structure of **9** is shown in Figure 4. It may be classified as being of the pseudotetrahedral metallocene-type,[18] with the Se atom located 0.86 Å from the central Cp−Ta−Cp plane (cf. the "in-plane" position of Se in the structure of **8**). The Ta−Se distance [2.422(2) Å] is only slightly longer than that of other Ta=Se bonds.[5][20] The orientation of the W(CO)$_5$ group towards one of the Cp rings in the solid state should be of no relevance in solution. As in the related [Cp′$_2$Ta(S)H · W(CO)$_5$], a low barrier to rotation about the metal−selenium bond may be expected.[15]

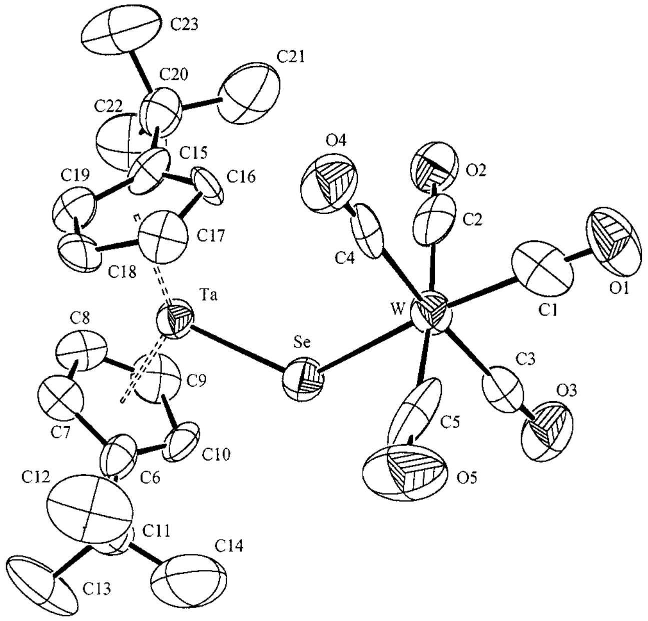


Figure 4. Molecular structure (ORTEP drawing at 50% probability level) of [Cp′$_2$TaSeH·W(CO)$_5$] (**9**); selected bond lengths [Å] and angles [°]: Ta−Se 2.422(4), Ta−Cp1 2.09, Ta−Cp2 2.09 (Cp1 and Cp2 are the centers of the rings C6−C10 and C15−C19, respectively), W−Se 2.672(2); Ta−Se−W 130.92(8), Cp1−Ta−Cp2 134.8; the H atom attached to Ta could not be localized

Another aspect of the reactivity of **7** is illustrated by its behavior towards S$_8$. When a toluene solution of **7** is treated with an excess of elemental sulfur, there is an immediate colour change from blue to dark-brown. After chromatographic work-up, a brown band is obtained, which consists mainly of the mixed complex [Cp′$_2$Ta(SeS)H] (**10**), as established by mass spectrometry. The ^{1}H-NMR spectrum shows the presence of two isomers, arising from different orientations of the (η^2-SeS) ligands, besides ca. 10% of [Cp′$_2$Ta(η^2-S$_2$)H].[3] Unfortunately, full chromatographic separation could not be achieved, precluding the analytical characterization of these isomers. However, dechalcogenation of the mixture with P(OEt)$_3$ appears to be chemoselective, since it affords exclusively [Cp′$_2$Ta(=S)H][3] along with Se=P(OEt)$_3$. The same reactivity is observed in the cross-reaction when [Cp′$_2$Ta(=S)H] is exposed to an excess of Se$_8$.

Conclusions

Transition metal complexes with hydroselenido ligands are still rare. In this paper, we have reported the facile syntheses of two different ligand types containing Se−H bonds. The results show that Cp$^{\#}_2$Nb fragments play a particular role in the activation of elemental selenium as opposed to other chalcogens. Like its Te congener [Cp$^{\#}_2$Nb(Te$_2$H)], which has already been successfully employed in the synthesis of telluride clusters,[9][10] the novel hydroselenido ligand in **2** merits attention as a potential source of reactive Se. On the other hand, the ligand arrangements in complexes **3** and **4** show similarities to niobocene−sulfide chemistry. The Se coordination chemistry induced by the Cp′$_2$Ta fragment closely resembles that observed for the systems Cp′$_2$Ta/S$_8$ and Cp*$_2$Ta/X (X = Se, Te). The crucial difference is the stabilization of the dihydrido−hydroselenido complex **8** as an intermediate product during activation of elemental selenium. Another complex typical of tantalocene−selenium chemistry is **7**, for which a series of novel reactions have been described.

Experimental Section

General: All procedures were carried out under N$_2$ using dry solvents. − Elemental analyses (C,H) were performed at the Mikroanalytisches Laboratorium, Universität Regensburg. − IR spectra were obtained with a Perkin−Elmer 580 B instrument. − Molecular masses were determined by field desorption (FD) mass spectrometry (toluene solutions) using a Finnigan MAT 95 instrument. − ^{1}H- and ^{77}Se-NMR (standard: external Me$_2$Se) spectra were recorded with Bruker AC 200, WM 250, and WM 400 instruments. − [(C$_5$Me$_5$)$_2$NbBH$_4$],[21] [(C$_5$Me$_4$Et)$_2$NbBH$_4$],[22] and [Cp′$_2$TaH$_3$][23] were prepared according to literature procedures. − ***Note:*** Work should be carried out in a well-ventilated fume hood because of the possible evolution of H$_2$Se.

Preparation of [Cp$^{\#}_2$NbSe$_2$H] (2): It was essential that all operations were carried out in the absence of light. A mixture of 1.50 mmol of **1**, 373 mg (4.7 mmol) of red amorphous selenium,[24] and 70 mL of THF was stirred for 20 h at room temperature. After evaporation of the solvent, chromatography of the residue on SiO$_2$ (column 25 cm, Ø 5 cm) gave upon elution with toluene a green band containing [Cp$^{\#}_2$NbSe$_2$H] (**2**) in 85−89% yield. − **2**: C$_{20}$H$_{31}$NbSe$_2$ (522.3): calcd. C 45.99, H 5.98; found C 45.71, H 6.01. − Mol. mass 519.1 (FD-MS, ^{78}Se). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.72 (s, 30 H, CH$_3$), −0.90 [s, 1 H, SeH, ^1J(H−Se) = 33.9 Hz]. − ^{77}Se NMR (76 MHz, C$_6$D$_6$): δ = 236.7 [d, 1 Se, ^1J(Se−H) = 34 Hz], −209.0 (s, 1 Se). − C$_{22}$H$_{35}$NbSe$_2$ (550.3): calcd. C 48.01, H 6.41; found C 48.00, H 6.40. − Mol. mass 547.0 (FD-MS, ^{78}Se). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.74 (s, 6 H, CH$_3$), 1.76 (s, 6 H, CH$_3$), 1.77 (s, 6 H, CH$_3$), 1.78 (s, 6 H, CH$_3$), 0.86 (t, 6 H, CH$_3$), 2.22 (m, 4 H, CH$_2$), −0.92 [s, 1 H, SeH, ^1J(H−Se) = 34.4 Hz]. − ^{77}Se NMR (76 MHz, C$_6$D$_6$): δ = 223.2 [d, 1 Se, ^1J(Se−H) = 33.6 Hz], −217.4 (s, 1 Se).

Irradiation of [Cp*$_2$NbSe$_2$H] [2(Cp*)]: A green solution of 1.5 g (2.87 mmol) of **2**(Cp*) in 150 mL of toluene was stirred for 7 d at room temperature and exposed to daylight. During this time the colour slowly changed to brown-orange. After evaporation of the solvent, the brown residue was dissolved in 20 mL of toluene and then chromatographed on SiO$_2$ (column 25 cm, Ø 5 cm). Elution with toluene/pentane (2:1) gave a broad yellow band containing 80 mg of product. Further elution with toluene/pentane (3:1) gave two very broad bands containing 420 and 850 mg, respectively. On the basis of mass-spectrometric and ^{1}H-NMR investigations, the first band was found to consist of 68% [Cp*$_2$NbSe$_2$H] (**3**), 8% [Cp*$_2$NbSe$_3$H] (**4**), and 13% [Cp*$_2$NbO$_2$H] (**5**). The second band was shown to contain these compounds in a ratio of 21:68:9, while the third band consisted almost exclusively of **5**, which exhibited the same properties as an independently prepared sample (see below). − **3**: $C_{20}H_{31}NbSe_2$ (522.3): Mol. mass 519.1 (FD-MS, ^{78}Se). − ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.67$ (s, 30 H, CH$_3$), −3.67 [s, 1 H, *J*(H−Se) = 20.9, 25.5 Hz]. − **4**: $C_{20}H_{31}NbSe_3$ (601.3): Mol. mass 598.1 (FD-MS, ^{78}Se). − ^{1}H NMR (400 MHz, C_6D_6): $\delta =$ 1.82 (s, 30 H, CH$_3$), −3.84 [s, 1 H, SeH, ^1J(H−Se) = 21.2 Hz].

Reaction of [Cp*$_2$NbSe$_2$H] [2(Cp*)] with Air: A solution of 300 mg (0.575 mmol) of **2**(Cp*) in 100 mL of THF was stirred for 12 h in the dark in an open flask. After filtration of the precipitated amorphous selenium, the solvent was evaporated from the yellow filtrate to give 200 mg (88% yield) of a pale-yellow powder. Recrystallization from toluene/pentane (1:2) gave analytically pure **5**. − **5**: $C_{20}H_{31}NbO_2$ (396.0): calcd. C 60.61, H 7.83; found C 60.12, H 7.71. − Mol. mass 396.0 (FD-MS). − IR (KBr): $\tilde{\nu} = 3470$ cm^{-1} m [ν(OH)], 843 cm^{-1} s [ν(Nb=O)]. − ^{1}H NMR (250 MHz, C_6D_6): $\delta = 1.77$ (s, 30 H, CH$_3$), 2.11 (s, 1 H, OH).

Synthesis of [Cp′$_2$TaSe$_2$H] (6): A mixture of 100 mg (0.23 mmol) of [Cp′$_2$TaH$_3$], 100 mg (1.26 mmol) of grey selenium, and 10 mL of toluene was stirred for 18 h at 25°C (when red selenium was used, the reaction was complete within 3 h). The solvent was subsequently removed in vacuo and the dark residue was purified by chromatography on SiO$_2$ (column 12 cm, Ø 2.5 cm). Elution with toluene/THF gave a red band containing 67 mg (49% yield) of **6**. Recrystallization from toluene/pentane gave red crystals. − **6**: $C_{18}H_{27}TaSe_2$ (582.3): calcd. C 37.13, H 4.67; found C 36.84, H 4.77. − Mol. mass 580.0 (FD-MS, ^{78}Se). − IR (CsI): $\tilde{\nu} = 1710$ cm^{-1} w [ν(Ta−H)]. − ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.11$ (s, 1 H, TaH), 1.23 (s, 18 H, CH$_3$), 3.81 (m, 2 H, C$_5$H$_4$R), 4.21 (m, 2 H, C$_5$H$_4$R), 4.34 (m, 2 H, C$_5$H$_4$R), 6.15 (m, 2 H, C$_5$H$_4$R). − {^{1}H}^{77}Se NMR (95 MHz, C_6D_6): $\delta = -251, -571$.

Synthesis of [Cp′$_2$TaSeH] (7): A solution of 90 mg (0.15 mmol) of **6** and 0.5 mL (excess) of P(OEt)$_3$ in 12 mL of toluene was refluxed for 4 h. After cooling, the solvent was removed under reduced pressure and the residual solid was washed with pentane. After drying in vacuo, 55 mg (70% yield) of crude **7** was obtained as a blue solid. Recrystallization from toluene/pentane gave an analytically pure sample, the FD-MS spectrum of which showed exclusively the more Se-rich peak of the precursor **6**. − **7**: $C_{18}H_{27}TaSe$ (503.3): calcd. C 42.95, H 5.41; found C 42.69, H 5.47. − IR (CsI): $\tilde{\nu} =$ 1862 cm^{-1} w [ν(Ta−H)]. − ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.29$ (s, 18 H, CH$_3$), 4.76 (m, 2 H, C$_5$H$_4$R), 5.10 (m, 2 H, C$_5$H$_4$R), 5.42 (m, 2 H, C$_5$H$_4$R), 5.82 (m, 2 H, C$_5$H$_4$R), 7.52 (s, 1 H, TaH). − {^{1}H}^{77}Se NMR (95 MHz, C_6D_6): $\delta = 2303$.

Synthesis of [Cp′$_2$Ta(H)$_2$SeH] (8): A solution of 70 mg (0.14 mmol) of **7** in 8 mL of THF was stirred with excess sodium amalgam for 20 min and then 3−4 drops of water were added. After decantation of the organic layer and washing of the amalgam residue with THF, the solvent was evaporated to leave crude **8** as a white solid (53 mg, 75% yield). Recrystallization from toluene/pentane gave white needles. − **8**: $C_{18}H_{29}TaSe$ (505.3): calcd. C 42.78, H 5.78; found C 42.83, H 5.71. − Mol. mass 504.2 (FD-MS, ^{78}Se). − ^{1}H NMR (200 MHz, C_6D_6): $\delta = -4.86$ [t, 1 H, SeH, ^3J(H−H) = 8.3 Hz], 1.29 (s, 18 H, CH$_3$), 2.43 [d, 2 H, TaH, ^3J(H−H) = 8.3 Hz, ^2J(Se−H) = 22.6 Hz], 4.37 (m, 4 H, C$_5$H$_4$R), 4.91 (m, 4 H, C$_5$H$_4$R) [^1J(Se−H) not observed]. − {^{1}H}^{77}Se NMR (95 MHz, C_6D_6): $\delta =$ −570 [t, 1 Se, ^2J(Se−H) = 23 Hz].

Synthesis of [Cp′$_2$TaSeH · W(CO)$_5$] (9): A mixture of 90 mg (0.18 mmol) of **7**, 0.22 mmol of [W(CO)$_5$(THF)], and 15 mL of THF was stirred at room temperature for 30 min. After evaporation of the solvent, the residue was chromatographed on SiO$_2$ (column 10 cm, Ø 2.5 cm). Eluting with toluene, a red-brown band was obtained, which was found to contain 100 mg (65% yield) of **9**. Recrystallization from toluene/pentane gave dark-brown crystals. − **9**: $C_{23}H_{27}O_5SeTaW$ (827.2): calcd. C 33.40, H 3.29; found C 33.77, H 3.27. − Mol. mass 828 (FD-MS; calcd. 828.0 for $C_{23}H_{27}TaO_5{}^{78}Se^{184}W$). − IR (THF): $\tilde{\nu} = 2061$ s, 1928 s, 1918 sh, 1894 m cm^{-1} [ν(CO)]. − ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.06$ (s, 18 H, CH$_3$), 4.32 (m, 2 H, C$_5$H$_4$R), 4.81 (m, 2 H, C$_5$H$_4$R), 5.43 (m, 2 H, C$_5$H$_4$R), 5.81 (m, 2 H, C$_5$H$_4$R), 7.36 (s, 1 H, TaH).

Synthesis of [Cp′$_2$TaSeSH] (10): To a solution of 60 mg (0.12 mmol) of **7** in 10 mL of toluene, 5 equiv. of sulfur were added. The mixture was stirred for 5 min. The solvent was then evaporated and the residual brown solid was chromatographed on SiO$_2$ (column 10 cm, Ø 2.5 cm). Eluting with toluene/THF (9:1), a brown band was obtained, which was found to contain **10** as a mixture of two isomers and an inseparable small amount (15%) of [Cp′$_2$TaS$_2$H] (overall yield 65%). − **10**: $C_{18}H_{27}TaSSe$ (536.1): Mol. mass 536.1 (FD-MS). − ^{1}H NMR (200 MHz, C_6D_6): Major isomer (60%): $\delta = 1.23$ (s, 18 H, CH$_3$), 2.28 (s, 1 H, TaH), 3.86 (m, 2 H, C$_5$H$_4$R), 4.37 (m, 2 H, C$_5$H$_4$R), 4.43 (m, 2 H, C$_5$H$_4$R), 5.91 (m, 2 H, C$_5$H$_4$R). − Minor isomer (40%): $\delta = 1.24$ (s, 18 H, CH$_3$), 1.52 (s, 1 H, TaH), 3.92 (m, 2 H, C$_5$H$_4$R), 4.37 (m, 4 H, C$_5$H$_4$R), 6.15 (m, 2 H, C$_5$H$_4$R).

X-ray Structure Determinations[25] of Complexes 8 and 9. − [Cp′$_2$Ta(H)$_2$SeH] (8): Yellow prisms (0.4 × 0.3 × 0.2 mm), monoclinic $P2_1/n$ (no. 14); cell: $a = 8.036(1)$, $b = 18.255(2)$, $c = 12.666(2)$ Å, $\beta = 97.77(1)°$; $V = 1840.9$ Å^3, $Z = 4$; $d_{\text{calcd.}} = 1.823$ gcm^{-3}; absorption correction (ψ scan): 73.64/99.86. Linear absorption $\mu =$ 79.38 cm^{-1}; $F(000) = 976$. Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation, graphite monochromator, 3240 unique observed reflections; 2603 independent reflections [$I > 2\sigma(I)$]. Structure solution by means of direct methods and subsequent Fourier syntheses using the SHELX97 package. Refinement on F^2 with 181 variables; $R = 0.036$, $wR = 0.093$, GoF = 1.039; residual electron density (max./min.): 1.23 (close to the Ta atom)/−1.74 e/Å^3. − **[Cp′$_2$TaSeH·W(CO)$_5$]** (9): Red-brown plates (0.15 × 0.10 × 0.05 mm), monoclinic $P2_1/n$ (no. 14); cell: $a = 13.321(2)$, $b = 18.418(4)$, $c = 12.792(3)$ Å, $\beta = 116.39(2)°$; $V = 2600.3$ Å^3, $Z = 4$; $d_{\text{calcd.}} =$ 2.113 gcm^{-3}; absorption correction (ψ scan): 71.98/99.80. Linear absorption $\mu = 100.53$ cm^{-1}; $F(000) = 1544$. Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation, graphite monochromator, 5505 unique observed reflections; 2212 independent reflections [$I > 2\sigma(I)$]. Structure solution by means of direct methods and subsequent Fourier syntheses using the SHELX97 package. Refinement on F^2; number of variables = 280; $R = 0.056$, $wR = 0.098$, GoF = 0.952; residual electron density (max./min.): 1.99 (close to the Ta atom)/−2.04 e/Å^3.

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