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ARTICLE

To Coordinate or not to Coordinate: The Special Role of Chalcogen Ether Functionalities in the Design of Twofold Functionalized Cyclopentadienyl Ligands [Cp,O,*Ch* (*Ch* = S, Se)]

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Abstract. The solvent- and catalyst free synthesis of two β-thio ketones **L1a** and **L1b** is reported. **L1a**, **L1b**, and a β-seleno ketone **L1c** were successfully employed as ligand precursors in the synthesis of a novel series of cationic titanium complexes **4a**–**4c** via a well-established reaction sequence: insertion of the carbonyl functional group into the polarized Ti–$C_{q,exo}$ bond of the monopentafulvene complex Cp*Ti(Cl)(π-η^5:σ–η^1-C_5H_4=CR_2) (**1**) (CR_2 = adamantylidene), subsequent methylation, and final activation with $B(C_6F_5)_3$. The cationic titanium complexes **4a**–**4c** bear twofold functionalized cyclopentadienyl [Cp,O,*Ch* (*Ch* = S, Se)] ligand frameworks built directly in the coordination sphere of the metal, in which the chalcogen ether functionalities do not coordinate to the central metal atoms as demonstrated by NMR experiments. Consequently, Cp,O σ,π chelating ligand systems are formed with free coordination sites at the central titanium atoms and pendant chalcogen ether moieties.

Introduction

Ligand design is the key to organometallic chemistry and requires intensive studies because even small variations in designing appropriate ligands can have a tremendous effect on enabling subsequent reactions, especially when taking the main field of application, the homogeneous (asymmetric) catalysis, into account.[1]

Tridentate ligands have risen in popularity mostly due to their versatility, and so called pincer ligands have become the most employed representatives.[2a–2f] Although the definition of pincer ligands has broadened after the first description by *van Koten* in 1989,[3] the term now generally refers to tridentate ligands, that occupy adjacent binding sites in a metal complex with a strong preference of adopting a meridional arrangement.[2a–2f] In this context, the seminar studies of *Shaw* et al. reported one of the first Pincer complexes (PCP)NiCl via orthometalation of $NiCl_2(H_2O)_6$ with 1,3-$(CH_2PtBu_2)_2C_6H_4$.[28] Since *van Koten*, a multitude of different pincer ligands have been studied, synthesized, and reviewed in several books[4,5] and articles,[2a–2f] demonstrating their high impact as platforms for homogeneous catalysis. The key factors for the success of pincer ligands to be mentioned are their ability of effectively controlling and tuning steric and electronic properties by introducing hard or soft donor sites in conjunction with aspects of hemilability,[6] noninnocence,[7] variations of bite angles, and ring size effects.

Another interesting and important, but less developed tridentate ligand platform is based on η^5-cyclopentadienyls, which are usually synthesized by multistep syntheses followed by subsequent coordination to the metal fragments.[8]

We have recently addressed the synthesis of such ligands and established a convenient, flexible, and high-yielding synthesis of novel types of tridentate ligands with a cyclopentadienyl basis by directly building such ligands in the coordination spheres of the central metal atoms, thus distinguished from the classic approach. Starting with monopentafulvene complexes of group 4 metals, the umpolung of the exocyclic quaternary carbon atom ($C_{q,exo}$) of the ligated pentafulvene ligand enabled the insertion of various bidentate ligand precursors. Subsequent methylation and final activation with the strong Lewis acid $B(C_6F_5)_3$ yielded cationic d^0 complexes of group 4 metals bearing Cp,*X*,*Y* ligand frameworks (Scheme 1, top).

Complexes with a Cp,O,P ligand set were synthesized, and their possible modifications and limitations with regard to this special ligand set were pointed out.[9,10] Further studies dealt with the corresponding Cp,N,P and Cp,O,N ligand systems and their respective titanium complexes. They proved to be rare examples of titanium based frustrated Lewis pairs, hence they were able to activate acetone, phenylacetylene, dihydrogen, or, in the case of the Cp,O,N congeners they were even capable of activating carbon–halogen bonds (Scheme 1, middle).[11,12] These recent examples have already shown the high versatility of this approach, which might offer tuning potentials comparable to those of the ubiquitous and comprehensively analyzed class of pincer ligands (Scheme 1, middle). To further address and verify the influence of the hemilabile donor site and its donor strength, we herein present a series of cationic titanium complexes with twofold functionalized cyclopentadienyl li-

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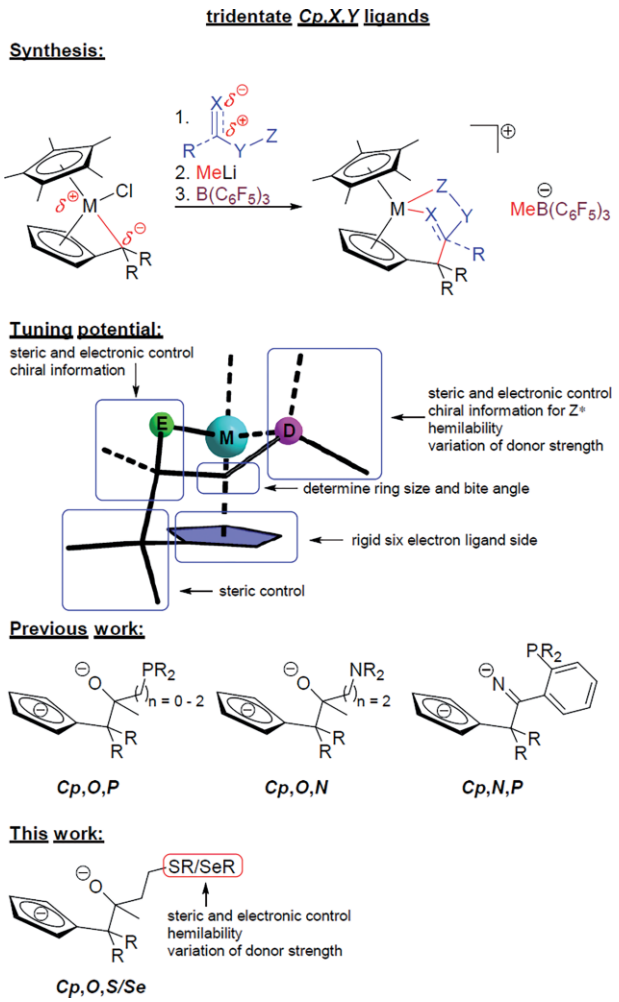


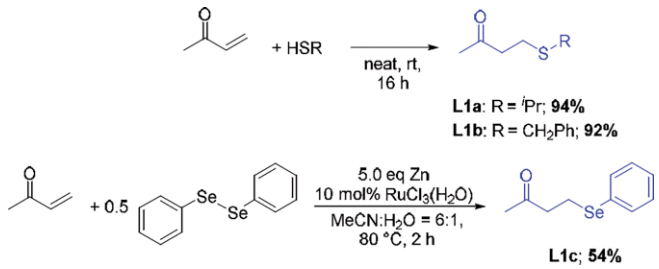
Scheme 1. Overview of tridentate Cp,X,Y ligands built directly in the coordination sphere of the metal; synthesis, tuning potential, previous examples, and attempted synthesis of Cp,O,*Ch* ligands (*Ch* = S, Se).

gands [Cp,O,*Ch* (Ch = S, Se)]. These complexes are bearing bidentate π,σ Cp,O chelating ligands with unoccupied chalcogen ether functionalities, showing no interaction to the central titanium atom in the final cationic complexes.

Results and Discussion

Synthesis of the O,Ch-Ligand Precursor Compounds L1a–c (Ch = S, Se)

Inspired by pioneering work concerning the solvent- and catalyst free synthesis of various β-substituted diphenylphosphino ketones[10,13] and β-amino ketones,[12] which are accessible without any further purification steps starting from methyl vinyl ketone and appropriate secondary amines and phosphines, the analogous synthesis of β-thio ketones was targeted. The reactions of methyl vinyl ketone with propane-2-thiol and benzylthiol resulted in clean conversions (shown by ^{1}H NMR analysis) to the corresponding 1,4-addition products **L1a** and **L1b** within 16 h of vigorous stirring at room temperature (Scheme 2).



Scheme 2. Solvent- and catalyst-free synthesis of the β-thio ketones **L1a**,**b**, and synthesis of the β-seleno ketone **L1c**.[14]

Removal of slight excess of the starting materials under reduced pressure yielded **L1a** and **L1b** as yellow (**L1a**) and colorless (**L1b**) oils respectively in very good isolated yields and adequate purity without the requirement of further purification steps. Previous efforts to synthesize β-thio ketones by 1,4-addition mention the employment of strong bases[15] or the use of Lewis acids[16a–16c] in organic solvents. These strong acidic or basic conditions are often accompanied by the formation of undesired byproducts. More recent improvements describe the synthesis of β-thio ketones catalyst-free in water with the employment of micellar solutions[17] or ionic liquids.[18] Our approach appears far more efficient.

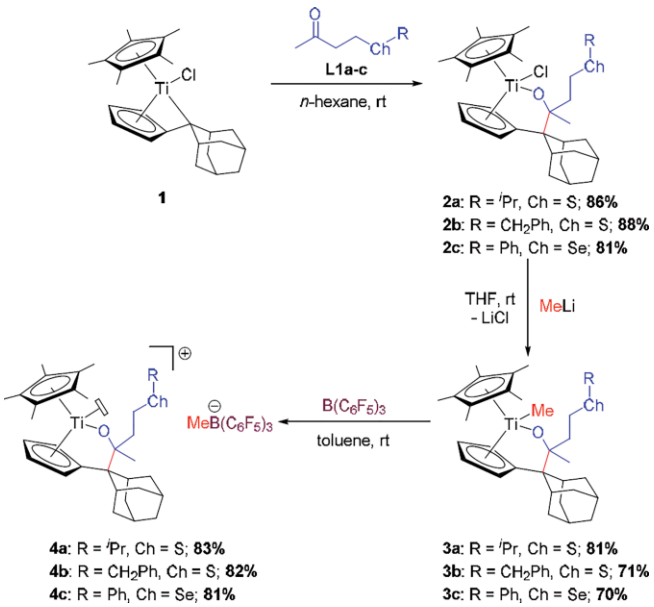
In addition to the β-thio ketones **L1a** and **L1b**, the β-seleno ketone **L1c** was synthesized following a procedure reported by *Tatar* et al.,[14] and NMR spectroscopic data of **L1c** was recollected in C_6D_6 for reasons of comparison (Scheme 2). The introduction of selenium provides further derivatization prospects and an additional NMR active nucleus for characterization.

L1a–c feature carbonyl functional groups, which are suitable for the targeted insertion reaction into the polarized bond between the titanium atom and the quaternary exocyclic carbon atom ($C_{q,exo}$) of the pentafulvene ligand of **1**, and chalcogen ether units connected and spaced from the carbonyl group by two methylene groups.

Synthesis of Cationic Titanium Complexes with Tridentate Cp,O,Ch (Ch = S, Se) Ligands

The reactions of the titanium monopentafulvene complex **1** with the bidentate O,*Ch*-ligand precursors **L1a–c** in *n*-hexane at room temperature were accompanied by color changes from yellow-brown to yellow-orange and yielded the titanium complexes **2a–2c** in good isolated yields of 86 % (**2a**), 88 % (**2b**), and 81 % (**2c**). All complexes show good (**2a**, **2b**) or moderate (**2c**) solubilities in *n*-hexane, benzene, toluene, and tetrahydrofuran. The insertion reactions lead to the formation of Cp,O π,σ-chelating ligands due to the formation of new C–C bonds (Scheme 3).

The subsequent exchange of the chlorido ligand by a methyl group was performed with methyllithium in tetrahydrofuran at room temperature to give complexes **3a–3c** in good yields of up to 81 % after removal of lithium chloride and all volatiles. **3a–3c** show the same solubility properties as **2a–2c**.



Scheme 3. Three-/two-step synthesis of cationic titanium complexes **4a**–**4c** with twofold functionalized cyclopentadienyl ligands.

Compounds **2a**–**2c** and **3a**–**3c** were fully characterized by NMR analyses, and, in the case of **2a**, **2c**, and **3c** crystals for single-crystal X-ray diffraction were obtained either from saturated solution in *n*-hexane at –26 °C (**2a**, **3c**) or by recrystallization in *n*-hexane at room temperature (**2c**). The molecular structures of **2a**, **2c**, and **3c** are shown in Figure 1, Figure 2, and Figure 3.

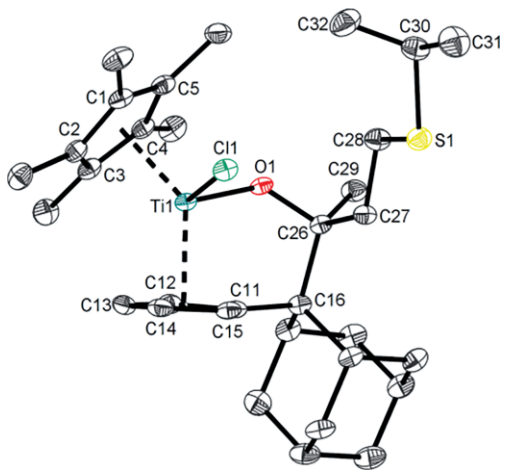


Figure 1. Molecular structures of **2a** in the crystal. Thermal ellipsoids are drawn at the 50 % probability level (hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Ti1–Cl1 2.3734(8), Ti1–O1 1.854(2), O1–C26 1.430(3), S1–C28 1.819(3), C11–C16 1.523(4), C16–C26 1.630(4), C26–C27 1.543(4), C26–C29 1.529(4), C27–C28 1.536(4), Cl1–Ti1–O1 99.32(6), Ct1–Ti1–Ct2 134.0, Σangles C26 321.2 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29) (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

Complex **2a** crystallizes in the monoclinic space group *C*2/*c* and displays the expected pseudotetrahedral coordination environment at the central titanium atom as represented by the Cl1–Ti1–O1 and Ct1–Ti1–Ct2 angles of 99.32(6) and 134.0°,

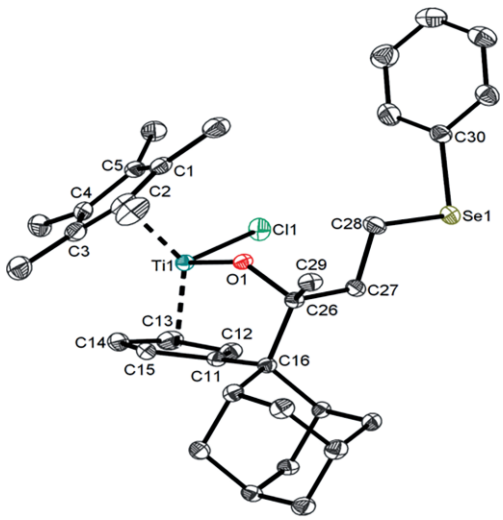


Figure 2. Molecular structure of **2c** in the crystal. Thermal ellipsoids are drawn at the 50 % probability level (hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Ti1–Cl1 2.3759(5), Ti1–O1 1.8584(9), O1–C26 1.4310(16), Se1–C28 1.9620(15), C11–C16 1.5178(18), C16–C26 1.6229(19), C26–C27 1.5439(19), C26–C29 1.5325(18), Cl1–Ti1–O1 98.51(3), Ct1–Ti1–Ct2 134.0, Σ∠C11 359.5, Σangles C26 320.9 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29) (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

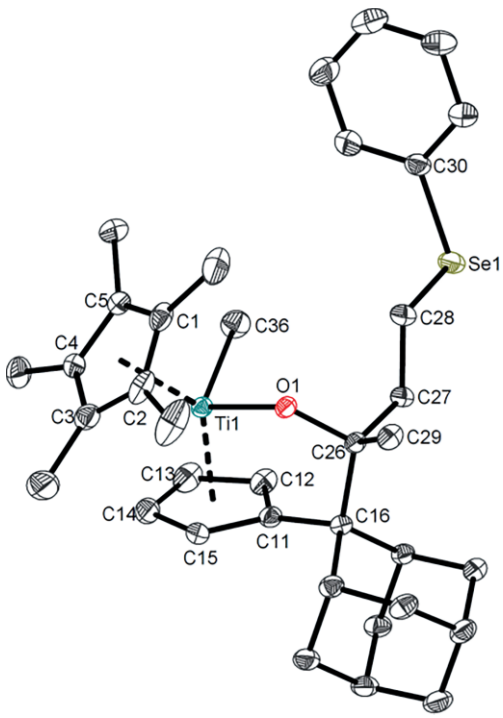


Figure 3. Molecular structure of **3c** in the crystal. Thermal ellipsoids are drawn at the 50 % probability level (hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: Ti1–C36 2.1794(17), Ti1–O1 1.8653(10), O1–C26 1.4275(17), Se1–C28 1.9690(16), C11–C16 1.527(2), C16–C26 1.6236(19), C26–C27 1.551(2), C26–C29 1.536(2), C36–Ti1–O1 98.62(6), Ct1–Ti1–Ct2 134.9, Σangles C11 359.5, Σangles C26 320.7 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29) (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

respectively. Whereas the newly formed bond Ti1–O1 with a bond length of 1.854(2) Å constitutes a typical single bond,[19,20] the second newly formed bond C16–C26 with a bond length of 1.630(4) Å is significantly elongated compared to typical C(sp^3)–C(sp^3) single bonds.[21] This elongation of the Cp,O σ,π-chelating ligand framework is comparable to sterically crowded alkanes,[22] and also characteristic for complexes derived from insertion reactions of carbonyl compounds into the polarized *M*–$C_{q,exo}$ bond of monopentafulvene complexes.[9,10,12,23] The former carbonyl carbon atom C26 is sp^3-hybridizied as shown by the sum of angles around C26 (e.g. O1–C26–C27 + O1–C26–C29 + C27–C26–C29 = 321.2°). The C11–C16 bond length of 1.523(4) Å constitutes now a C(sp^2)–C(sp^3) single bond.[21] This elongation compared to **1**[24] confirms the transition from the pentafulvene ligand in **1** to a substituted cyclopentadienyl ligand in **2a**. The sulfur–carbon bond lengths [e.g. S1–C28 1.819(3) Å], and the Ti1–Cl1 bond length of 2.3734(8) Å are also typical of single bonds.[19–21] Complexes **2c** and **3c** are isostructural and crystallize in the monoclinic space group $P2_1/c$. The structural parameters are comparable to those of **2a**. The selenium–carbon bonds in **2c** and **3c** are typical of Se–C(sp^3) single bonds [e.g. Se1–C28 1.9620(15) Å (**2c**), 1.9690(16) Å (**3c**)], and the Ti1–C36 bond length of 2.1794(17) Å is typical of Ti–C(sp^3) single bonds.[21]

The NMR spectroscopic data of **2a**–**2c** and **3a**–**3c** show a double set of signals in some cases. This is caused by the insertion of the carbonyl functional group of the prochiral O,*Ch*-ligand precursors **L1a**–**c** into the polarized Ti–$C_{q,exo}$ bond, which lead, in addition to the titanium atoms, to the generation of second stereogenic centers at the former carbonyl carbon atoms. Thus, **2a**–**2c** and **3a**–**3c** are obtained as mixtures of diastereoisomers. The ratios of the diastereoisomers were determined by integration of appropriate signals in the ^{1}H NMR spectra and lie between 4:1 and 15:1. The formations of diastereoisomers in similar ratios was also observed previously by our group for cationic group 4 complexes with tridentate Cp,O,P or Cp,O,N-ligand systems.[9,10,12] The most characteristic NMR spectroscopic data of **2a**–**2c** and **3a**–**3c** are summarized in Table 1 and compared with the NMR spectroscopic data of **Ia**, **Ib** and **IIa**, **IIb**, which feature amine or phosphine moieties instead of the chalcogen ether functional groups.

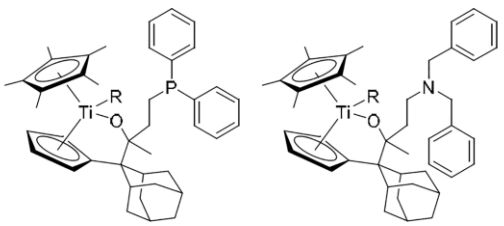
As can be gathered from Table 1, the chemical shifts of **2a**–**2c** and **3a**–**3c** are in excellent agreement with the previously reported complexes **Ia**, **Ib** and **IIa**, **IIb**, which were synthesized by the same reaction sequence, thus being highly characteristic for the whole compound class bearing bidentate Cp,O chelating ligands with a donor functional group in the ligand backbone.[9,10,12]

According to the established reaction pathway, **3a**–**3c** were finally reacted with the strong Lewis acid $B(C_6F_5)_3$ in toluene at room temperature. After a few minutes of vigorous stirring these reactions were accompanied by the development of two phases as soon as the stirring processes were stopped, which is already indicative for the formation of the envisaged ionic species. After purification the corresponding cationic d^0 titanium complexes **4a**–**4c**, now diastereomerically pure, were obtained in good isolated yields (Scheme 3).

The fact that they are diastereomerically pure is clearly verified by single set of signals in the NMR spectroscopic data. In addition, high-resolution ESI mass spectrometry provides clean detection of the M^+ signals of the cationic moieties of **4a**–**4c**.[25] Compounds **4a**–**4c** are insoluble in aliphatic and aromatic hydrocarbons such as *n*-hexane, benzene, and toluene, which proved ideal for purification purposes. Noteworthy, **4a**–**4c** are consistently stable and excellently soluble in deuterated dichloromethane, which was therefore chosen for measuring

Table 1. Selected NMR parameters of complexes **2a**–**2c**, **3a**–**3c**, **Ia**, **Ib**, and **IIa**, **IIb** [a].

	δ^1H / δ^{13}C{^{1}H} MCH_3	δ^{13}C{^{1}H} OC_q	δ^1H / δ^{13}C{^{1}H} OC_qCH_3	δ^{13}C{^{1}H} $C_{q,exo}/C_{q,ipso}$	δ = ^{77}Se
2a [b]	–	111.7	1.35/31.1	54.6/156.8	–
2b [b]	–	111.5	1.24/31.0	54.6/156.7	–
2c	–	111.7	1.32/30.9	54.6/156.5	307.8
3a [b]	0.22/34.4	107.3	1.28/30.9	54.9/151.4	–
3b [b]	0.13/34.5	107.1	1.18/30.8	54.8/151.3	–
3c	0.17/34.6	107.5	1.23/30.7	54.9/151.3	301.9
Ia [10]	–	111.7	1.39/31.0	54.7/156.7	–
Ib [10]	0.26/35.3	107.4	1.32/30.8	54.9/151.4	–
IIa [12]	–	112.1	1.29/31.2	54.8/156.9	–
IIb [12] [b]	0.10/34.8	107.6	1.24/31.1	55.0/151.5	–

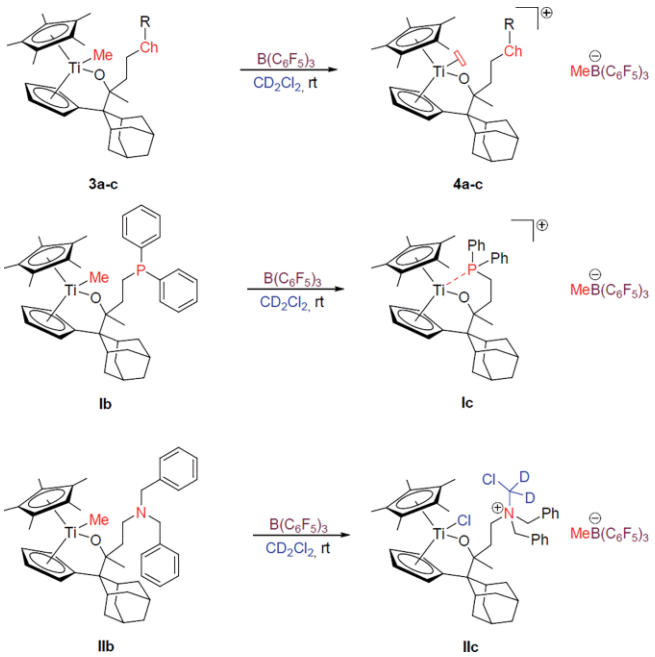


Ia: R = Cl
Ib: R = Me

IIa: R = Cl
IIb: R = Me

a) The δ values are given in ppm. Measurements were carried out in C_6D_6 at room temperature. b) Product is a mixture of diastereoisomers; therefore, only clearly assignable signals of the main diastereoisomer are given.

the 1D and 2D NMR spectra. The stability towards dichloromethane is in stark contrast to the analogous cationic titanium complexes with amine moieties obtained after methyl group abstraction. For instance **IIb** reacts readily and cleanly with CD_2Cl_2 to give $R_3NCD_2Cl^+$ and Ti–Cl functional groups (Scheme 4, bottom).[12]



Scheme 4. Unique features of cationic titanium complexes with different Cp,O,X ligand frameworks and their reactivity toward CD_2Cl_2 (top: X = S, Se, middle: representative example for X = PR_2[10], bottom: representative example for X = NR_2[12]).

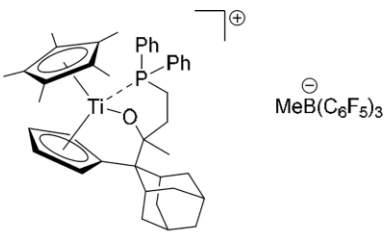
The NMR spectroscopic data are exemplary discussed for the selenium congener **4c** and summarized for all in Table 2. They are compared with the previously reported phosphine substituted cationic complex **Ic**.[10] The methyl borate anion $MeB(C_6F_5)_3^-$ shows the typical chemical shifts in the NMR spectra, e.g. $\delta^1H/\delta^{13}C\{^1H\}(BCH_3)$ = 0.49 s(br) / 9.9 ppm, $\delta^{11}B\{^1H\}$ = –14.8 ppm, and $\delta^{19}F\{^1H\}$ = –167.9 (*m*-$F_{Ar}B$), –165.4 (*p*-$F_{Ar}B$), –133.0 (*o*-$F_{Ar}B$) ppm. The Horton parameter $\Delta\delta(m,p\text{-F})$ of $\Delta\delta(m,p\text{-F})$ = 2.5 ppm for **4c** shows, that the $MeB(C_6F_5)_3^-$ anion is noncoordinating.[26a–26c] This is in good agreement with other cationic group 4 complexes with this specific borate anion.[9–11]

Of high diagnostic value, and particularly useful for determining the connectivity of **4c** is the ^{77}Se NMR spectroscopy. In comparison to the precursor complexes **2c**, **3c**, and the free ligand precursor **L1c** with ^{77}Se NMR chemical shifts of $\delta^{77}Se$ = 309.4 ppm (**L1c**), 307.8 ppm (**2c**), and 301.9 ppm (**3c**) respectively, the chemical shift in **4c** remains nearly unchanged ($\delta^{77}Se$ = 316.1 ppm).[27] This parameter is not only indicative for same chemical environments at the selenium atom in this series, but shows that the selenium atom also has no interaction with the titanium atom in **4c** after abstraction of the methyl group with $B(C_6F_5)_3$ (Scheme 4, top). Consequently, **4c** features a free coordination site at the central titanium atom. This is further supported by the analytical data of the cationic titanium complexes bearing phosphine functional groups, reported recently.[9,10] Here, the phosphorus shows a persistent titanium–phosphorus bond after activation of **Ib** with $B(C_6F_5)_3$ as verified by a significant shift toward lower field by comparison of the $^{31}P\{^1H\}$ NMR chemical shifts of **Ib** and **Ic**, respectively [$\Delta\delta^{31}P\{^1H\}$ = 41.3 ppm ($\delta^{31}P\{^1H\}$ = –12.7 ppm for **Ib**, and 28.6 ppm for **Ic**)] (Scheme 4, middle). All other chemical shifts are in the expected ranges and fit well into the series of cationic titanium complexes derived from monopentafulvene complexes and bidentate ligand precursors with a carbonyl unit and an additional donor functional group (Table 2).

Based on the results from the ^{77}Se NMR in the series **2c**, **3c**, **4c**, it is very likely, that complexes **4a** and **4b** with the thioether functional groups also show no interactions between the central titanium atoms and the sulfur, which we attribute to thioether and selenoethers generally being weaker Lewis bases than phosphine or amine functionalities. Although clear evidence is missing due to poor crystallization properties of **4a**–**4c**[29] and nearly identical NMR spectroscopic data in com-

Table 2. Selected NMR parameters of complexes **4a**–**4c**, and **Ic** [a].

	δ^1H / $\delta^{13}C\{^1H\}$ BCH_3	δ^1H / $\delta^{13}C\{^1H\}$ OC_qCH_3	$\delta^{13}C\{^1H\}$ OC_q	$\delta^{13}C\{^1H\}$ $C_{q,exo}/C_{q,ipso}$	$\delta^{11}B\{^1H\}$
4a	0.49/10.0	1.51/32.5	111.2	55.4/157.3	–14.9
4b	0.50/10.3	1.51/35.1	112.4	55.4/156.1	–14.9
4c	0.50/9.9	1.58/32.8	112.2	55.6/157.8	–14.8
Ic [10]	0.48/12.8	1.70/34.3	113.9	55.0/155.6	–15.5



Ic

a) The δ values are given in ppm. Measurements were carried out in CD_2Cl_2 at room temperature.

parison to the cationic titanium complex **Ic** with a persistent Ti/P interaction, a further reason might be the overall high similarity of thioethers and selenoethers.

In summary, the implementation of chalcogen ether functional groups into the design of twofold functionalized Cp,O,*X* based ligand frameworks leads to the maintenance of a bidentate Cp,O ligand system after activation with $B(C_6F_5)_3$. Hence a free coordination site at the central titanium atom, and also a pendant and unoccupied chalcogen ether moiety are present in **4a**–**4c**, clearly emphasizing the unique characteristics of this explicit substitution pattern, especially when compared to the Cp,O,P and Cp,O,N congeners.

Conclusions

A high-yielding, solvent- and catalyst free synthesis of the β-thio ketones **L1a** and **L1b** is described, starting from the commercially available methyl vinyl ketone and selected thiols. The synthesized β-thio ketones **L1a**, **L1b**, and the β-seleno ketone **L1c** were successfully employed as ligand precursors in the established three-step synthesis of the cationic titanium complexes **4a**–**4c** by insertion, subsequent methylation and activation with the strong Lewis acid $B(C_6F_5)_3$. **4a**–**4c** were obtained in good isolated yields under mild reaction conditions. The analytical data show that the corresponding methyl borate anion $MeB(C_6F_5)_3^-$ is noncoordinating in all cases. ^{77}Se NMR spectroscopy of derivative **4c** showed, that in contrast to the previously reported cationic titanium complexes with tridentate Cp,O,P ligands,[9,10] the respective chalcogen atoms of the chalcogen ether functionalities do not coordinate to the central titanium atoms in **4a**–**4c**. Thus **4a**–**4c** are bearing bidentate Cp,O chelating ligands with unoccupied chalcogen ether functionalities in the ligands backbone, and free coordinate sites at the central titanium atoms, clearly distinguishing this series of cationic d^0 titanium complexes from the previously reported ones. These findings underline the flexibility in tuning electronic and steric properties of tridentate and bidentate ligands, which are built directly in the coordination sphere of the central metal atom. Due to the missing interaction between the central Lewis acidic titanium atom and the pendant chalcogen ether functionalities, it might be challenging to find metal-ligand cooperative activations of substrates, which has been key to success in the previous reported systems with Ti···N and Ti–N functionalities.[11,12] Nevertheless, the free coordination site might open up novel subsequent reactions and applications, which are currently subject to investigation in our group.

Experimental Section

General: All air- and moisture-sensitive reactions were carried out in an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents and liquid starting materials were dried according to standard procedures and/or freeze-pump-thaw degassed three times prior to use. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 in a nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. The methyllithium was used as a 1.6 M solution in diethyl ether. The pentafulvene complex **1** was synthesized according to a literature procedure.[24] Methyl vinyl ketone, propane-2-thiol, and benzylthiol were purchased from commercial sources, freshly distilled over $CaCl_2$, freeze-pump-thaw degassed three times prior to use, and stored under nitrogen. Diphenyl diselenide, ruthenium(III)chloride hydrate, and zinc dust were purchased from commercial sources and used as received. Thin-layer chromatography was performed using commercially available Alugram SIL/G UV254 sheets with fluorescent indicator (254 nm) from Macherey–Nagel. Silica gel from Grace (particle size 40–63 μm) was used for column chromatography. High-resolution mass spectra of **4a**–**4c** were measured with a Finnigan-MAT95 spectrometer using ESI (solvent: dichloromethane). Infrared spectra were performed with a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system. NMR spectra were recorded with Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. ^{1}H NMR spectra were referenced to the residual solvent resonance as internal standard ([D$_6$]benzene (C_6D_6): $\delta^1H(C_6D_5H)$ = 7.16 ppm, [D$_2$]dichloromethane (CD_2Cl_2): $\delta^1H(CDHCl_2)$ = 5.32 ppm) and $^{13}C\{^1H\}$ spectra were referenced by using the central line of the solvent signal ([D$_6$]benzene (C_6D_6): $\delta^{13}C\{^1H\}(C_6D_6)$ = 128.06 ppm, [D$_2$]dichloromethane (CD_2Cl_2): $\delta^{13}C\{^1H\}(CD_2Cl_2)$ = 53.84 ppm). $^{11}B\{^1H\}$ NMR, $^{19}F\{^1H\}$ NMR, and ^{77}Se NMR spectra were referenced against external standards [BF_3·OEt_2 ($\delta^{11}B\{^1H\}(BF_3{\cdot}OEt_2)$ = 0.0 ppm); $CFCl_3$ ($\delta^{19}F\{^1H\}(CFCl_3)$ = 0.0 ppm); Me_2Se ($\delta^{77}Se(Me_2Se)$ = 0.0 ppm)]. Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer. The carbon and hydrogen values in the elemental analysis are found in some times higher, which we attribute to residue of solvents. Melting points were determined with a "Mel-Temp" apparatus by Laboratory Devices, Cambridge, U·K. Single crystal X-ray data were measured with a Bruker AXS diffractometer with Apex II CCD detector and graphite monochromated Mo-$K_{\alpha1}$ radiation with λ = 0.71073 Å.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1886225, CCDC-1886226, and CCDC-1886227. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Synthesis of L1a: Propane-2-thiol (2.2 mL, 23.68 mmol) was slowly added to freshly condensed methyl vinyl ketone (2.0 mL, 23.68 mmol) at room temperature. The solution was stirred for 16 h at room temperature to yield **L1a** as slightly yellow oil in quantitative yield and was used without further purification steps. Yield: 3.256 g (22.26 mmol; 94 %). **^{1}H NMR** (500 MHz, C_6D_6, 300 K): δ = 1.10 [d, ^3J(H,H) = 6.7 Hz, 6 H, CH(CH_3)$_2$], 1.57 (s, 3 H, O = C$_q$CH_3), 2.17 (t, $^3J_{H,H}$ = 7.4 Hz, SCH_2CH$_2$), 2.60 (t, $^3J_{H,H}$ = 7.4 Hz, SCH$_2$CH_2), 2.64 [hept, $^3J_{H,H}$ = 6.8 Hz, CH(CH$_3$)$_2$] ppm. **^{13}C{^{1}H} NMR** [126 MHz, C_6D_6, 300 K): δ = 23.5 [CH(*C*H$_3$)$_2$], 24.7 (S*C*H$_2$CH$_2$), 29.4 (O=C$_q$*C*H$_3$), 35.3 [*C*H(CH$_3$)$_2$], 43.6 (SCH$_2$*C*H$_2$), 204.7 (O=*C*$_q$CH$_3$) ppm.

Synthesis of L1b: Benzylthiol (2.8 mL, 23.68 mmol) was slowly added to freshly condensed methyl vinyl ketone (2.0 mL, 23.68 mmol) at room temperature. The solution was stirred for 16 h at room temperature to yield **L1b** as colorless oil in quantitative yield and was used without further purification steps. Yield: 4.223 g (21.74 mmol; 92 %). **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 1.51 (s, 3 H, O=C$_q$CH$_3$), 2.05 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, SCH$_2$CH_2), 2.48 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, SCH_2CH$_2$), 3.41 (s, 2 H, SCH_2Ph), 7.00–7.05 (m, 1 H,

p-C*H*$_{Ph}$CH$_2$S), 7.08–7.11 (m, 2 H, 2 × *m*-C*H*$_{Ph}$CH$_2$S), 7.16–7.18 (m, 2 H, 2 × *o*-C*H*$_{Ph}$CH$_2$S)* ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 25.6 (S*C*H$_2$CH$_2$), 29.3 (O=C$_q$*C*H$_3$), 36.9 (S*C*H$_2$Ph), 43.2 (SCH$_2$*C*H$_2$), 127.2 (*p*-*C*H$_{Ph}$CH$_2$S), 128.7 (2 × *m*-*C*H$_{Ph}$CH$_2$S), 129.2 (2 × *o*-*C*H$_{Ph}$CH$_2$S), 139.1 (C$_{q,Ph}$), 204.5 (O=*C*$_q$CH$_3$) ppm. * = overlap with C_6D_6 signals.

Synthesis of L1c: L1c was synthesized according to a literature procedure.[14] Diphenyl diselenide (0.400 g, 1.282 mmol), zinc dust (0.450 g, 6.883 mmol), and ruthenium(III)chloride hydrate (30 mg, 0.133 mmol) were suspended in 12 mL of acetonitrile and 2 mL of water. The reaction mixture was stirred for 1 h at 80 °C, followed by the addition of methyl vinyl ketone (0.22 mL, 2.563 mmol) and further stirring at 80 °C for 1 h. The solution was filtered, all volatile components were removed under vacuum, and the crude product was purified by column chromatography (SiO_2; hexane:EE = 4:1). **L1c** was obtained as slightly yellow oil. R_f = 0.30 (SiO_2; hexane:EE = 4:1). Yield: 0.312 g (1.373 mmol; 54 %). **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 1.48 (s, 3 H, OC$_q$CH$_3$), 2.25 (t, $^3J_{H,H}$ = 7.3 Hz, SeC*H*$_2$CH$_2$), 2.86 (t, $^3J_{H,H}$ = 7.2 Hz, SeCH$_2$C*H*$_2$), 6.96–7.00 (m, 3 H, 3 × CH$_{Ph}$), 7.37–7.39 (m, 2 H, 2×CH$_{Ph}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 20.8 (SeCH$_2$CH$_2$), 29.2 (OC$_q$*C*H$_3$), 43.8 (Se*C*H$_2$CH$_2$), 127.1 (CH$_{Ph}$), 129.4 (2 × CH$_{Ph}$), 130.9 (C$_{q,Ph}$), 132.9 (2 × CH$_{Ph}$), 204.7 (O*C*$_q$CH$_3$) ppm. **^{77}Se NMR** (95 MHz, C_6D_6, 305 K): δ = 309.4 ppm.

Synthesis of 2a: In a glove box compound **L1** (0.211 g, 1.439 mmol) in toluene (3 × 2 mL) was added to a solution of complex **1** (0.600 g, 1.439 mmol) in 8 mL of toluene. The reaction mixture was stirred for 16 h at room temperature. All volatile components were removed under vacuum to give **2a** as a yellow-orange solid as a mixture of both diastereoisomers (ratio: approximately 5:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.696 g (1.236 mmol, 86 %). Melting point: 71–73 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2902, 2855, 1714, 1481, 1450, 1374, 1245, 1186, 1167, 1148, 1098, 1073, 1063, 1022, 998, 982, 969, 954, 874, 849, 812, 790, 771, 692, 683, 658, 634 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 299 K): δ = 1.35 (s, 3 H, OC$_q$CH$_3$), 1.37 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.42 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.77 (s, 15 H, C$_5$Me$_5$), 3.20 [hept, $^3J_{H,H}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 5.03–5.04 (m, 1 H, C$_5$H$_4$), 5.38–5.40 (m, 1 H, C$_5$H$_4$), 5.44–5.46 (m, 1 H, C$_5$H$_4$), 6.41–6.43 (m, 1 H, C$_5$H$_4$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 299 K): δ = 12.6 (C$_5$*Me*$_5$), 24.1 [CH(*C*H$_3$)$_2$], 24.6 [CH(*C*H$_3$)$_2$], 25.9 (CH$_2$), 27.5 (CH$_{Ad}$), 28.0 (CH$_{Ad}$), 31.1 (OC$_q$*C*H$_3$), 32.7 (CH$_{Ad}$), 32.9 (CH$_{Ad}$), 33.6 (CH$_2$), 34.8 (CH$_2$), 35.8 [*C*H(CH$_3$)$_2$], 37.2 (CH$_2$), 37.3 (CH$_2$), 39.4 (CH$_2$), 40.4 (CH$_2$), 54.6 (C$_{q,exo}$), 104.5 (C$_5$H$_4$), 111.66 (O*C*$_q$CH$_3$), 111.7 (C$_5$H$_4$), 112.7 (C$_5$H$_4$), 120.0 (C$_5$H$_4$), 123.7 (*C*$_5$Me$_5$), 156.8 (C$_{q,ipso}$) ppm. $C_{32}H_{47}ClOSTi$: calcd. C 68.26; H 8.41 %; found: C 68.19; H 8.59 %.

Synthesis of 2b: In a glove box compound **L1** (0.248 g, 1.276 mmol) in toluene (3 × 2 mL) was added to a solution of complex **1** (0.532 g, 1.439 mmol) in 8 mL of toluene. The reaction mixture was stirred for 16 h at room temperature. All volatile components were removed under vacuum to give **2b** as a yellow-brown solid as a mixture of both diastereoisomers (ratio: approximately 4:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.687 g (1.124 mmol, 88 %). Melting point: 64–68 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2901, 2852, 1711, 1493, 1481, 1451, 1374, 1223, 1186, 1167, 1148, 1098, 1064, 1023, 970, 955, 875, 849, 812, 791, 770, 701, 658, 634 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 1.24 (s, 3 H, OC$_q$CH$_3$), 1.74 (s, 15 H, C$_5$Me$_5$), 2.77–2.85 (m, 2 H, SCH$_2$CH$_2$), 3.89 (s, 2 H, SC*H*$_2$Ph), 5.01–5.02 (m, 1 H, C$_5$H$_4$), 5.38–5.40 (m, 1 H, C$_5$H$_4$), 5.44–5.46 (m, 1 H, C$_5$H$_4$), 6.39–6.41 (m, 1 H, C$_5$H$_4$), 7.06–7.10 (m, 1 H, *p*-C*H*$_{Ph}$CH$_2$S), 7.18–7.21 (m, 2 H, 2 × *m*-C*H*$_{Ph}$CH$_2$S), 7.50–7.51 (m, 2 H, 2 × *o*-C*H*$_{Ph}$CH$_2$S) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 12.5 (C$_5$*Me*$_5$), 27.5 (CH$_{Ad}$), 28.0 (CH$_{Ad}$), 31.0 (OC$_q$*C*H$_3$), 32.7 (CH$_{Ad}$), 32.9 (CH$_{Ad}$), 33.7 (CH$_{2,Ad}$), 34.8 (CH$_{2,Ad}$), 37.2 (CH$_{2,Ad}$), 37.3 (CH$_{2,Ad}$), 37.6 (CH$_{2,Ad}$), 37.7 (S*C*H$_2$Ph), 39.4 (SCH$_2$*C*H$_2$), 40.3 (SCH$_2$*C*H$_2$), 54.6 (C$_{q,exo}$), 104.5 (C$_5$H$_4$), 111.5 (O*C*$_q$CH$_3$), 111.7 (C$_5$H$_4$), 112.8 (C$_5$H$_4$), 120.0 (C$_5$H$_4$), 123.8 (*C*$_5$Me$_5$), 126.7 (*p*-*C*H$_{Ph}$CH$_2$S), 128.5 (2 × *m*-*C*H$_{Ph}$CH$_2$S), 129.5 (2 × *o*-*C*H$_{Ph}$CH$_2$S), 140.8 (C$_{q,Ph}$), 156.7 (C$_{q,ipso}$) ppm. $C_{36}H_{47}ClOSTi$: calcd. C 70.75; H 7.75 %; found: C 71.51; H 7.88 %.

Synthesis of 2c: In a glove box compound **L1c** (0.250 g, 1.101 mmol) in *n*-hexane (3 × 2 mL) was added to a solution of complex **1** (0.459 g, 1.101 mmol) in 12 mL of *n*-hexane. The reaction mixture was stirred for 16 h at room temperature. All volatile components were removed under vacuum, and the residue was recrystallized from *n*-hexane to give **2c** as an orange solid as a mixture of both diastereoisomers (ratio approximately 10:1). Yield: 0.576 g (0.894 mmol, 81 %). Melting point: 154–156 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2950, 2912, 2850, 1717, 1577, 1476, 1449, 1435, 1375, 1329, 1300, 1208, 1197, 1173, 1144, 1099, 1060, 1021, 981, 947, 914, 875, 847, 817, 744, 691, 670, 644, 631, 616 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 1.32 (s, 3 H, OC$_q$CH$_3$), 1.39–1.43 (m, 1 H, CH$_{Ad}$/CH$_{2,Ad}$), 1.52–1.73 (m, 8 H, CH$_{Ad}$/CH$_{2,Ad}$), 1.77 (s, 15 H, C$_5$*Me*$_5$), 2.06–2.16 (m, 3 H, CH$_{Ad}$/CH$_{2,Ad}$, OC$_q$C*H*$_2$C*H*$_2$Se), 2.28–2.28 (m, 1 H, CH$_{Ad}$/CH$_{2,Ad}$), 2.36–2.45 (m, 2 H, CH$_{Ad}$/CH$_{2,Ad}$), 2.98–3.04 (m, 2 H, OC$_q$C*H*$_2$C*H*$_2$Se), 3.19–3.23 (m, 1 H, OC$_q$C*H*$_2$C*H*$_2$Se), 5.02–5.03 (m, 1 H, C$_5$H$_4$), 5.36–5.37 (m, 1 H, C$_5$H$_4$), 5.46–5.48 (m, 1 H, C$_5$H$_4$), 6.39–6.40 (m, 1 H, C$_5$H$_4$), 6.99–7.02 (m, 1 H, *p*-CH$_{Ph}$), 7.08–7.11 (m, 2 H, 2 × *m*-CH$_{Ph}$), 7.69–7.71 (m, 2 H, 2 × *o*-CH$_{Ph}$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 12.6 (C$_5$*Me*$_5$), 23.4 (OC$_q$*C*H$_2$*C*H$_2$Se), 27.5 (CH$_{Ad}$), 28.0 (CH$_{Ad}$), 30.9 (OC$_q$*C*H$_3$), 32.7 (CH$_{Ad}$), 32.9 (CH$_{Ad}$), 33.5 (CH$_{2,Ad}$), 34.8 (CH$_{2,Ad}$), 37.2 (CH$_{2,Ad}$), 37.3 (CH$_{2,Ad}$), 39.4 (CH$_{2,Ad}$), 40.3 (OC$_q$*C*H$_2$*C*H$_2$Se), 54.6 (C$_{q,exo}$), 104.6 (C$_5$H$_4$), 111.4 (C$_5$H$_4$), 111.7 (O*C*$_q$CH$_3$), 113.0 (C$_5$H$_4$), 120.3 (C$_5$H$_4$), 123.9 (*C*$_5$Me$_5$), 126.3 (*p*-CH$_{Ph}$), 129.2 (2 × CH$_{Ph}$), 132.7 (2 × CH$_{Ph}$), 132.9 (C$_{q,Ph}$), 156.5 (C$_{q,ipso}$) ppm. **^{77}Se NMR** (95 MHz, C_6D_6, 305 K): δ = 307.8 ppm. $C_{35}H_{45}ClOSeTi$: calcd. C 65.28; H 7.04 %; found: C 64.94; H 7.00 %.

Synthesis of 3a: To a solution of complex **2a** (0.600 g, 1.066 mmol) in 10 mL of tetrahydrofurane was added a methyllithium solution (0.7 mL, 1.066 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 12 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 12 mL). All volatile components were removed under vacuum to give complex **3a** as a pale yellow solid as a mixture of both diastereoisomers (ratio: approximately 7:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.471 g (0.868 mmol, 81 %). Melting point: 74–76 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2901, 2855, 1638, 1480, 1450, 1374, 1329, 1244, 1205, 1182, 1167, 1148, 1117, 1097, 1072, 1062, 1022, 969, 961, 874, 849, 809, 684, 659, 634 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 0.22 (s, 3 H, TiCH$_3$), 1.28 (s, 3 H, OC$_q$CH$_3$), 1.30 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.31 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.70 (s, 15 H, C$_5$Me$_5$), 2.92 [hept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 4.85–4.86 (m, 1 H, C$_5$H$_4$), 5.07–5.09 (m, 1 H, C$_5$H$_4$), 5.28–5.29 (m, 1 H, C$_5$H$_4$), 6.15–6.16 (m, 1 H, C$_5$H$_4$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 11.9 (C$_5$*Me*$_5$), 23.9 [CH(*C*H$_3$)$_2$], 24.1 [CH(*C*H$_3$)$_2$], 25.8 (CH$_2$), 27.8 (CH$_{Ad}$), 28.2 (CH$_{Ad}$), 30.9 (OC$_q$*C*H$_3$), 32.9 (CH$_{Ad}$), 33.0 (CH$_{Ad}$), 33.9 (CH$_2$), 34.4 (TiCH$_3$), 35.0 (CH$_2$), 35.7 [*C*H(CH$_3$)$_2$], 37.38 (CH$_2$), 37.4 (CH$_2$), 39.6 (CH$_2$), 40.5 (CH$_2$), 54.9 (C$_{q,exo}$), 103.5 (C$_5$H$_4$), 107.3 (O*C*$_q$CH$_3$), 108.1 (C$_5$H$_4$), 108.7 (C$_5$H$_4$), 116.3 (C$_5$H$_4$), 118.6 (*C*$_5$Me$_5$), 151.4 (C$_{q,ipso}$) ppm. $C_{33}H_{50}OSTi$: calcd. C 73.06; H 9.29 %; found: C 71.97; H 8.49 %.

Synthesis of 3b: To a solution of complex **2b** (0.370 g, 0.605 mmol) in 10 mL of tetrahydrofurane was added a methyllithium solution (0.4 mL, 0.605 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 8 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 10 mL). All volatile components were removed under vacuum to give complex **3b** as an orange solid as a mixture of both diastereoisomers (ratio: approximately 10:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.253 g (0.428 mmol, 71 %). Melting point: 81–83 °C. **IR** (ATR): $\tilde{\nu}$ = 2901, 2852, 1493, 1480, 1451, 1373, 1331, 1261, 1235, 1206, 1182, 1168, 1147, 1098, 1063, 1023, 971, 961, 876, 849, 808, 697, 658, 634 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 0.13 (s, 3 H, $TiCH_3$), 1.18 (s, 3 H, OC_qCH_3), 1.65 (s, 15 H, C_5Me_5), 3.66–3.67 (m, 2 H, SCH_2Ph), 4.83–4.85 (m, 1 H, C_5H_4), 5.07–5.08 (m, 1 H, C_5H_4), 5.24–5.26 (m, 1 H, C_5H_4), 6.12–6.13 (m, 1 H, C_5H_4), 7.06–7.09 (m, 1 H, *p*-$CH_{Ph}CH_2S$), 7.16–7.19 (m, 2 H, 2 × *m*-$CH_{Ph}CH_2S$)*, 7.34–7.36 (m, 2 H, 2 × *o*-$CH_{Ph}CH_2S$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 11.9 (C_5Me_5), 27.2 (CH_2), 27.8 (CH_{Ad}), 28.2 (CH_{Ad}), 30.8 (OC_qCH_3), 32.7 (CH_2), 32.8 (CH_{Ad}), 33.0 (CH_{Ad}), 33.9 (CH_2), 34.5 ($TiCH_3$), 35.0 (CH_2), 37.4 (SCH_2Ph), 37.7 (CH_2), 39.6 (CH_2), 40.3 (CH_2), 54.8 ($C_{q,exo}$), 103.4 (C_5H_4), 107.1 (OC_qCH_3), 108.0 (C_5H_4), 108.7 (C_5H_4), 116.2 (C_5H_4), 118.6 (C_5Me_5), 126.9 (*p*-$CH_{Ph}CH_2S$), 128.6 (2 × *m*-$CH_{Ph}CH_2S$), 129.3 (2 × *o*-$CH_{Ph}CH_2S$), 140.0 ($C_{q,Ph}$), 151.3 ($C_{q,ipso}$) ppm. $C_{37}H_{50}OSTi$: calcd. C 75.23; H 8.53 %; found: C 74.02; H 8.16 %.

Synthesis of 3c: To a solution of complex **1** (0.200 g, 0.311 mmol) in 8 mL of tetrahydrofurane was added a methyllithium solution (0.2 mL, 0.311 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 8 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 8 mL). All volatile components were removed under vacuum to give complex **3c** as a pale yellow solid as a mixture of both diastereosiomers (ratio: approximately 15:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.136 g (0.218 mmol, 70 %). Melting point: 58–60 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2900, 2853, 1579, 1477, 1450, 1436, 1373, 1324, 1301, 1207, 1166, 1146, 1119, 1097, 1061, 1022, 998, 982, 957, 912, 872, 849, 809, 732, 690, 670, 631, 618 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 0.18 (s, 3 H, $TiCH_3$), 1.23 (s, 3 H, OC_qCH_3), 1.42–1.49 (m, 2 H, $CH_{Ad}/CH_{2,Ad}$), 1.55–1.60 (m, 3 H, $CH_{Ad}/CH_{2,Ad}$), 1.66–1.68 (m, 3 H, $CH_{Ad}/CH_{2,Ad}$), 1.68 (s, 15 H, C_5Me_5), 1.77–1.78 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 1.92–1.95 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.06–2.12 (m, 1 H, $SeCH_2CH_2$), 2.18–2.19 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.28–2.29 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.45–2.54 (m, 2 H, $SeCH_2CH_2$, $CH_{Ad}/CH_{2,Ad}$), 2.68–2.71 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.75–2.81 (m, 1 H, $SeCH_2CH_2$), 2.92–2.97 (m, 1 H, $SeCH_2CH_2$), 4.85–4.86 (m, 1 H, C_5H_4), 5.05–5.07 (m, 1 H, C_5H_4), 5.26–5.27 (m, 1 H, C_5H_4), 6.13–6.14 (m, 1 H, C_5H_4), 6.98–7.01 (m, 1 H, *p*-$CH_{Aryl}Se$), 7.05–7.08 (m, 2 H, 2 × *m*-$CH_{Aryl}Se$), 7.60–7.62 (m, 2 H, 2 × *o*-$CH_{Aryl}Se$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 11.9 (C_5Me_5), 23.4 ($SeCH_2CH_2$), 27.7 (CH_{Ad}), 28.2 (CH_{Ad}), 30.7 (OC_qCH_3), 32.8 (CH_{Ad}), 33.0 (CH_{Ad}), 33.7 (CH_2), 34.6 ($TiCH_3$), 35.0 (CH_2), 37.35 (CH_2), 37.38 (CH_2), 39.6 (CH_2), 41.0 ($SeCH_2CH_2$), 54.9 ($C_{q,exo}$), 103.5 (C_5H_4), 107.5 (OC_qCH_3), 107.9 (C_5H_4), 108.8 (C_5H_4), 116.3 (C_5H_4), 118.7 (C_5Me_5), 126.6 (*p*-$CH_{Aryl}Se$), 129.2 (2 × *m*-$CH_{Aryl}Se$), 132.4 ($C_{q,Ph}$), 132.8 (2 × *o*-$CH_{Aryl}Se$), 151.3 ($C_{q,ipso}$) ppm. **^{77}Se NMR** (95 MHz, C_6D_6, 305 K): δ = 301.9 ppm. $C_{36}H_{48}OSeTi$: calcd. C 69.34; H 7.76 %; found: C 69.40; H 8.02 %.

Synthesis of 3b: To a solution of complex **2b** (0.370 g, 0.605 mmol) in 10 mL of tetrahydrofurane was added a methyllithium solution (0.4 mL, 0.605 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 8 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 10 mL). All volatile components were removed under vacuum to give complex **3b** as an orange solid as a mixture of both diastereoisomers (ratio: approximately 10:1). NMR spectroscopic data is given for the clearly assignable signals of the main diastereoisomer. Yield: 0.253 g (0.428 mmol, 71 %). Melting point: 81–83 °C. **IR** (ATR): $\tilde{\nu}$ = 2901, 2852, 1493, 1480, 1451, 1373, 1331, 1261, 1235, 1206, 1182, 1168, 1147, 1098, 1063, 1023, 971, 961, 876, 849, 808, 697, 658, 634 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 305 K): δ = 0.13 (s, 3 H, $TiCH_3$), 1.18 (s, 3 H, OC_qCH_3), 1.65 (s, 15 H, C_5Me_5), 3.66–3.67 (m, 2 H, SCH_2Ph), 4.83–4.85 (m, 1 H, C_5H_4), 5.07–5.08 (m, 1 H, C_5H_4), 5.24–5.26 (m, 1 H, C_5H_4), 6.12–6.13 (m, 1 H, C_5H_4), 7.06–7.09 (m, 1 H, *p*-$CH_{Ph}CH_2S$), 7.16–7.19 (m, 2 H, 2 × *m*-$CH_{Ph}CH_2S$)*, 7.34–7.36 (m, 2 H, 2 × *o*-$CH_{Ph}CH_2S$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 305 K): δ = 11.9 (C_5Me_5), 27.2 (CH_2), 27.8 (CH_{Ad}), 28.2 (CH_{Ad}), 30.8 (OC_qCH_3), 32.7 (CH_2), 32.8 (CH_{Ad}), 33.0 (CH_{Ad}), 33.9 (CH_2), 34.5 ($TiCH_3$), 35.0 (CH_2), 37.4 (SCH_2Ph), 37.7 (CH_2), 39.6 (CH_2), 40.3 (CH_2), 54.8 ($C_{q,exo}$), 103.4 (C_5H_4), 107.1 (OC_qCH_3), 108.0 (C_5H_4), 108.7 (C_5H_4), 116.2 (C_5H_4), 118.6 (C_5Me_5), 126.9 (*p*-$CH_{Ph}CH_2S$), 128.6 (2 × *m*-$CH_{Ph}CH_2S$), 129.3 (2 × *o*-$CH_{Ph}CH_2S$), 140.0 ($C_{q,Ph}$), 151.3 ($C_{q,ipso}$) ppm. $C_{37}H_{50}OSTi$: calcd. C 75.23; H, 8.53 %; found: C 74.02; H, 8.16 %.

Synthesis of 4a: A mixture of complex **3a** (0.150 g, 0.276 mmol) and $B(C_6F_5)_3$ (0.142 g, 0.276 mmol) was stirred in 8 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **4a**. The solvent was decanted, the residue was washed with *n*-hexane (3 × 5 mL), and dried under vacuum to give complex **4a** as an orange solid. Yield: 0.243 g (0.230 mmol, 83 %). Melting point: 58–60 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2913, 2861, 1638, 1509, 1455, 1380, 1267, 1081, 979, 965, 950, 934, 891, 824, 757, 705, 659, 603, 565 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 305 K): δ = 0.49 (s(br), 3 H, BCH_3), 1.01 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$], 1.51–1.52 [m, 6 H, OC_qCH_3, $CH(CH_3)_2$], 1.64–1.79 (m, 9 H, $CH_{Ad}/CH_{2,Ad}$), 1.89–1.97 (m, 3 H, $CH_{Ad}/CH_{2,Ad}$), 2.02 (s, 15 H, C_5Me_5), 2.23–2.26 (m, 1 H, NCH_2CH_2), 2.33–2.38 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$)*, 2.54–2.55 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.63–2.66 (m, 1 H, NCH_2CH_2), 2.79–2.85 (m, 1 H, NCH_2CH_2), 2.95–2.99 (m, 1 H, NCH_2CH_2), 3.09 [hept, $^3J_{H,H}$ = 6.5 Hz, 1 H, $CH(CH_3)_2$], 5.12–5.13 (m, 1 H, C_5H_4), 5.34–5.35 (m, 1 H, C_5H_4), 6.34–6.35 (m, 1 H, C_5H_4), 6.65–6.66 (m, 1 H, C_5H_4) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 305 K): δ = 10.0 (BCH_3)**, 12.9 (C_5Me_5), 22.2 [$CH(CH_3)_2$], 22.7 [$CH(CH_3)_2$], 27.4 (CH_{Ad}), 28.0 (CH_{Ad}), 32.5 (OC_qCH_3), 32.9 (CH_2), 33.0 (CH_2), 33.8 (CH_{Ad}), 34.1 (CH_{Ad}), 34.3 (CH_2), 36.4 (CH_2), 36.9 (CH_2), 37.5 (CH_2), 39.2 (CH_2), 39.8 [$CH(CH_3)_2$], 55.4 ($C_{q,exo}$), 107.3 (C_5H_4), 111.2 (OC_qCH_3), 113.5 (C_5H_4), 113.6 (C_5H_4), 119.1 (C_5H_4), 128.2 (C_5Me_5), 128.7 ($C_{q,Ar}B$)**, 136.8 (dm, $^1J_{C,F}$ = 237.2 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 243.5 Hz, $C_{q,Ar}F$), 148.7 (dm, $^1J_{C,F}$ = 236.0 Hz, $C_{q,Ar}F$), 157.3 ($C_{q,ipso}$) ppm. * = overlay with the signals of residue of toluene. ** = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra. **^{11}B{^{1}H} NMR** (160 MHz, CD_2Cl_2, 305 K): δ = –14.9 ppm. **^{19}F{^{1}H} NMR** (470 MHz, CD_2Cl_2, 305 K): δ = –167.9 (m, 6F, *m*-$F_{Ar}B$), –165.3 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), –133.1 (m, 6F, *o*-$F_{Ar}B$) ppm; $\Delta\delta^{19}F_{m,p}$ = 2.6 ppm. **HR/MS**: calculated: *m/z* = 527.2827 [M$^+$]; measured (ESI): *m/z* = 527.2831. $C_{51}H_{50}BF_{15}OSTi$: calcd. C 58.08; H, 4.78 %; found: C 57.06; H, 4.87 %.

Synthesis of 4b: A mixture of complex **3b** (0.105 g, 0.178 mmol) and $B(C_6F_5)_3$ (0.091 g, 0.178 mmol) was stirred in 8 mL of toluene. By stopping the stirring process after a few minutes, the development of

two phases can be observed due to the formation of **4b**. The solvent was decanted, the residue was washed with *n*-hexane (3 × 5 mL), and dried under vacuum to give complex **4b** as an orange solid. Yield: 0.160 g (0.146 mmol, 82 %). Melting point: 77–79 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2914, 1640, 1509, 1450, 1379, 1267, 1081, 951, 934, 900, 826, 765, 732, 701, 659, 643, 603 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 305 K): δ = 0.50 [s(br), 3 H, BCH_3], 1.51 (s, 3 H, OC_qCH_3), 1.74–1.96 (m, 10 H, $CH_{Ad}/CH_{2,Ad}/SCH_2CH_2$), 2.03 (s, 15 H, C_5Me_5), 2.06–2.19 (m, 3 H, $CH_{Ad}/CH_{2,Ad}$), 2.57–2.58 (m, 2 H, $CH_{Ad}/CH_{2,Ad}$), 2.68–2.72 (m, 1 H, SCH_2CH_2), 2.78–2.89 (m, 2 H, SCH_2CH_2), 3.63–3.71 (m, 2 H, SCH_2Ph), 5.06–5.07 (m, 1 H, C_5H_4), 5.39–5.40 (m, 1 H, C_5H_4), 6.43–6.44 (m, 1 H, C_5H_4), 6.65–6.66 (m, 1 H, C_5H_4), 7.31–7.33 (m, 2 H, 2×CH_{Ph}), 7.43–7.44 (m, 3 H, 3×CH_{Ph}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 305 K): δ = 10.3 (BCH_3)*, 12.7 ($C_5\mathit{Me}_5$), 27.2 (CH_{Ad}), 27.9 (CH_{Ad}), 33.3 (CH_{Ad}), 33.46 (CH_{Ad}), 33.51 (CH_2), 34.4 (CH_2), 34.9 (CH_2), 35.1 ($OC_q\mathit{C}H_3$), 36.6 (CH_2), 37.3 (CH_2), 37.6 (CH_2), 39.0 (CH_2), 41.7 (SCH_2Ph), 55.4 ($C_{q,exo}$), 106.2 (C_5H_4), 112.4 (OC_qCH_3), 113.4 (C_5H_4), 115.8 (C_5H_4), 119.5 (C_5H_4), 127.7 (C_5Me_5), 128.9 ($C_{q,Ar}B$)*, 129.7 (3×CH_{Ph}), 130.0 (2×CH_{Ph}), 133.0 ($C_{q,Ph}$), 136.8 (dm, $^1J_{C,F}$ = 243.5 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 243.1 Hz, $C_{q,Ar}F$), 148.8 (dm, $^1J_{C,F}$ = 243.1 Hz, $C_{q,Ar}F$), 156.1 ($C_{q,ipso}$) ppm. * = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra. **^{11}B{^{1}H} NMR** (160 MHz, CD_2Cl_2, 305 K): δ = –14.9 ppm. **^{19}F{^{1}H} NMR** (470 MHz, CD_2Cl_2, 305 K): δ = –167.9 (m, 6F, *m*-$F_{Ar}B$), –165.3 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), –133.0 (m, 6F, *o*-$F_{Ar}B$) ppm; $\Delta\delta^{19}F_{m,p}$ = 2.6 ppm. **HR/MS**: calculated: *m/z* = 575.2827 [M$^+$]; measured (ESI): *m/z* = 575.2821. $C_{55}H_{50}BF_{15}OSTi$: calcd. C 59.91; H, 4.57 %; found: C 58.76; H, 4.43 %.

Synthesis of 4c: A mixture of complex **1** (0.100 g, 0.160 mmol) and $B(C_6F_5)_3$ (0.082 g, 0.160 mmol) was stirred in 5 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **4c**. The solvent was decanted, the residue was washed with *n*-hexane (2 × 5 mL), and dried under vacuum to give complex **4c** as a pale orange solid. Yield: 0.146 g (0.129 mmol, 81 %). Melting point: 46–48 °C (dec.). **IR** (ATR): $\tilde{\nu}$ = 2915, 2861, 1640, 1509, 1451, 1380, 1267, 1212, 1081, 1022, 980, 964, 948, 934, 887, 834, 805, 786, 765, 734, 690, 659, 642 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 305 K): δ = 0.50 (s(br), 3 H, BCH_3), 1,49–1.52 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 1.58 (s, 3 H, OC_qCH_3), 1.64–1.80 (m, 7 H, $CH_{Ad}/CH_{2,Ad}$), 1.92–1.95 (m, 2 H, $CH_{Ad}/CH_{2,Ad}$), 2.06–2.07 (m, 2 H, $CH_{Ad}/CH_{2,Ad}$), 2.12 (s, 15 H, C_5Me_5), 2.19–2.22 (m, 1 H, $SeCH_2CH_2$), 2.41–2.42 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.60–2.63 (m, 1 H, $CH_{Ad}/CH_{2,Ad}$), 2.90–2.97 (m, 1 H, $SeCH_2CH_2$), 3.04–3.09 (m, 1 H, $SeCH_2CH_2$), 3.51–3.55 (m, 1 H, $SeCH_2CH_2$), 4.84–4.86 (m, 1 H, C_5H_4), 5.39–5.40 (m, 1 H, C_5H_4), 5.70–5.71 (m, 1 H, C_5H_4), 6.59–6.61 (m, 1 H, C_5H_4), 7.07–7.09 (m, 2 H, 2×CH_{Ph}), 7.49–7.52 (m, 3 H, 3×CH_{Ph}) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 305 K): δ = 9.9 (BCH_3)*, 13.0 ($C_5\mathit{Me}_5$), 27.3 (CH_{Ad}), 27.9 (CH_{Ad}), 31.2 ($SeCH_2CH_2$), 32.8 ($OC_q\mathit{C}H_3$), 33.3 ($CH_{2,Ad}$), 33.8 (CH_{Ad}), 34.3 (CH_{Ad}), 34.4 ($CH_{2,Ad}$), 36.4 ($CH_{2,Ad}$), 36.9 ($SeCH_2CH_2$), 37.5 ($CH_{2,Ad}$), 39.0 ($CH_{2,Ad}$), 55.6 ($C_{q,exo}$), 108.2 (C_5H_4), 112.2 (OC_qCH_3), 113.6 (C_5H_4), 116.4 (C_5H_4), 119.1 (C_5H_4), 126.9 ($C_{q,Ph}$), 127.7 (C_5Me_5), 128.6 (2×CH_{Ph}), 129.0 ($C_{q,Ar}B$)*, 130.4 (CH_{Ph}), 131.4 (2×CH_{Ph}), 136.9 (dm, $^1J_{C,F}$ = 246.7 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 237.0 Hz, $C_{q,Ar}F$), 148.8 (dm, $^1J_{C,F}$ = 233.5 Hz, $C_{q,Ar}F$), 157.8 ($C_{q,ipso}$) ppm. * = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra. **^{11}B{^{1}H} NMR** (160 MHz, CD_2Cl_2, 305 K): δ = –14.8 ppm. **^{19}F{^{1}H} NMR** (470 MHz, CD_2Cl_2, 305 K): δ = –167.9 (m, 6F, *m*-$F_{Ar}B$), –165.4 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), –133.0 (m, 6F, *o*-$F_{Ar}B$) ppm; $\Delta\delta^{19}F_{m,p}$ = 2.5 ppm. **^{77}Se NMR** (95 MHz, C_6D_6, 305 K): δ = 316.1 ppm. **HR/MS**: calculated: *m/z* = 609.2115 [M$^+$]; measured (ESI): *m/z* = 609.2113. $C_{54}H_{48}BF_{15}OSeTi$: calcd. C 57.12; H, 4.26 %; found: C 57.55; H, 3.73 %.

Supporting Information (see footnote on the first page of this article): The general considerations, the synthesis and characterization of the compounds **L1a**, **L1b**, **L1c**, **2a**, **2b**, **2c**, **3a**, **3b**, **3c**, **4a**, **4b**, **4c**, the Crystallographic Data of **2a**, **2c**, **3c**, and the ^{1}H-, ^{13}C{^{1}H}-, ^{77}Se-, ^{11}B{^{1}H}-, ^{19}F{^{1}H}-NMR-Spectra can be found in the electronic supporting information (ESI).

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Keywords: Pentafulvene; Titanium; Cationic complex; Ligand design; NMR spectroscopy

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