A New Route into Single-Crystalline Partially Oxidized Cobalt Compounds: Reactions with Zintl-Type Hexaselenodistannate(III) $K_6Sn_2Se_6$ as Mild Oxidant

Stefanie Dehnen* and Christian Zimmermann[a]

Abstract: Reactions of $K_6Sn_2Se_6$ (**1**) with $[Cp^*CoCl]_2$ were investigated in order to probe the stability of the formal +3 oxidation state at Sn and possible ligand properties of heteroatomic zintl-type anion "$Sn_2Se_6^{6-}$". From these experiments, we obtained the following compounds that are oxidized to different extent as a result of the reaction with Sn^{III}: $[Cp^*_2Co][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**2**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2]$ (**3**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**4**), and $[(Cp^*Co)_4(\mu_3\text{-}Se)_4]$ (**5**). These compounds were structurally characterized by single-crystal X-ray diffractometry. It shows that the reaction conditions strongly affect the type and oxidation state of the isolated product. Two of the observed compounds, **3** and **4**, are closely related both structurally and electronically; this is discussed and further illustrated by cyclovoltammetric measurements. The choice of the terminal Cp* ligand attached to the transition metal in the reactand complex is assumed to be basically dependent for the alignment of unexpected structural details when compared with known compounds of similar compositions. In conclusion, **1** is observed to act as mild oxidant as well as selenide donor, but is not in the position to keep its Sn–Se framework under the given reaction conditions.

Keywords: binary polyanions · cobalt · selenium · structure elucidation · tin

Introduction

Very little is known about the chemical behavior of binary zintl polyanions or binary alloys towards transition metal complexes. Some reactions of Group 15/16 binary species with transition metal carbonyl complexes or chalcogenolates have been described that lead to the coordination of binary aggregates to the metal complexes.[1] The complexes are treated with anions such as $As_4Se_6^{2-}$ or $P_2Se_8^{2-}$, or with alloys like As_4Se_4 or P_4S_3. For reactions of carbonyl complexes with polyanions, large counterions are usually added to equalize the introduced charge and to support crystallization. The coordination of carbonyl complexes by mixed element ligands can also be provoked by heating the first with binary alloys under emission of CO. Examples for product complexes are $[Et_4N]_2[W(CO)_2(As_3Se_3)_2]$,[2a] $[Ph_4P]_2[Fe_2(CO)_4(PSe_5)_2]$,[2b] $[Ph_4P]_2[W_2(\mu\text{-}Se)_3(AsSe_5)_2]$,[2c] or $[(CO)_5Mo(P_4S_3)]$.[2d] In the first compound cited, the anionic ligand is attached to the transition metal center through atoms of both main-group elements. In contrast, either selenium or phosphorus atoms act as donor centers in the other examples. However, corresponding experiments that consider Group 14/16 mixed element anions have not yet been documented.

Recently, we reported the synthesis and crystal structure of hexaselenodistannate(III) $K_6Sn_2Se_6$ (**1**).[3] Containing a Sn–Sn single bond, the compound exhibits tin atoms in the formal oxidation state +3, which is rather uncommon for inorganic compounds. In order to check the chemical stability of this oxidation state in the presence of ligated transition metal centers and to further probe whether **1**—or at least its fragment—is able to act as ligand, we are currently investigating reactions of **1** with transition metal complexes. Herein we present the results of experiments that employ **1** and $[Cp^*CoCl]_2$, formed in situ from $CoCl_2$ and $LiCp^*$, as starting compounds (Cp* = pentamethylcyclopentadiene).

Results and Discussion

Depending on the reaction temperature, solvent, or molar ratio of the reactants, one obtains compounds $[Cp^*_2Co][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**2**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2]$ (**3**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**4**), or $[(Cp^*Co)_4(\mu_3\text{-}Se)_4]$ (**5**), which were structurally characterized by single-crystal X-ray diffractometry.[4] Scheme 1 shows an overview of the reactions that lead to the products **2**–**5**.

An oxidative effect of **1** can be recognized for all investigated reactions. Although we were not yet in the position to identify all reaction byproducts with high certainty, one further hint exists for the reduction of Sn^{III} to Sn^{II} rather

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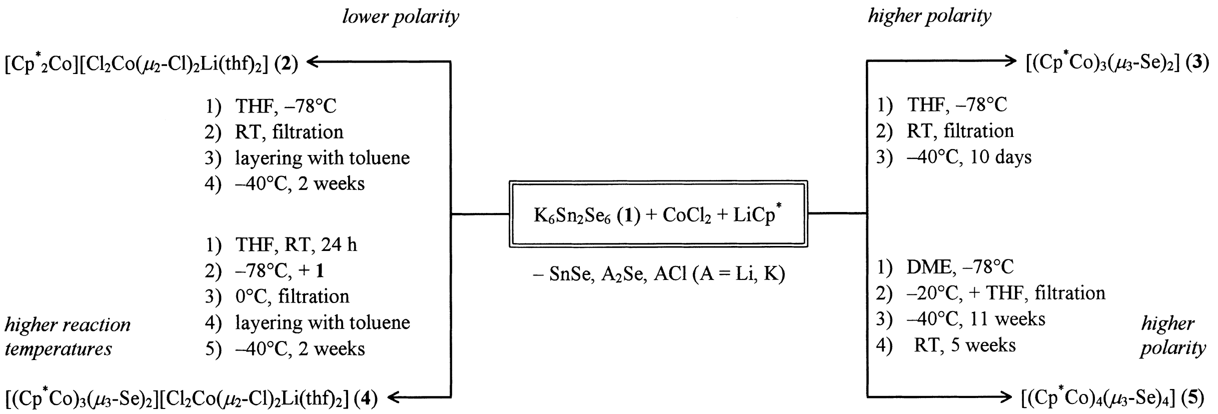


Scheme 1. Reactions of $K_6Sn_2Se_6$ with $CoCl_2$ and LiCp* under different reaction conditions.

than for an oxidation to Sn^{IV}. Small $SnSe^+$ peaks are always found in the mass spectra of the primary reaction precipitates, whereas no further Sn products—such as $SnCl_4$ or $SnSe_2$ or even $SnCl_2$—are observed in the mass spectrum nor in an NMR measurement of the reaction solution. Moreover, unwanted oxidation of Co^{II} by vestiges of oxygen in the reaction mixture can be excluded as the products are not formed in reactions with pure selenide donors such as K_2Se or $Se(SiMe_3)_2$. The occurring redox processes are facilitated by ligation of the Co^{II} centers by Cp*; this decreases the redox potential for the oxidation to Co^{III}.[5] From Scheme 1, one gathers the importance of the reaction conditions, especially the polarity of the solvent used. The latter first of all controls the isolation of ionic or uncharged compounds. Secondly, fairly good solubility of the products or at least of possible intermediates give the oxidant **1** the time it needs for successive oxidation of Co^{II} centers to Co^{III}. A correlation between reaction time and the Co^{III}:Co^{II} ratio is clearly observed.

Abstract in German: *Reaktionen von $K_6Sn_2Se_6$ (**1**) mit $[Cp^*CoCl]_2$ wurden durchgeführt, um die Stabilität der formalen Oxidationsstufe +3 am Zinn sowie potentielle Ligandeneigenschaften des heteroatomaren Zintl-Anions „$Sn_2Se_6^{6-}$“ zu untersuchen. Man erhielt hierbei die folgenden Verbindungen, die infolge der Reaktion mit Sn^{III} unterschiedlich stark oxidiert sind: $[Cp^*_2Co][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**2**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2]$ (**3**), $[(Cp^*Co)_3(\mu_3\text{-}Se)_2][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (**4**) bzw. $[(Cp^*Co)_4(\mu_3\text{-}Se)_4]$ (**5**). Verbindungen **1**–**5** wurden mit Hilfe der Einkristall-Röntgenstrukturanalyse charakterisiert. Es zeigt sich, dass die Reaktionsbedingungen einen entscheidenden Einfluss auf die Natur und den Oxidationszustand des zu isolierenden Produkts ausüben. Zwei der vorgestellten Verbindungen, **3** und **4**, sind strukturell und elektronisch eng verwandt. Dies wird diskutiert und mittels cyclovoltammetrischer Messungen genauer beleuchtet. Die Wahl des Cp*-Liganden führt ganz offensichtlich zu strukturellen Unterschieden im Vergleich zu bekannten Verbindungen ähnlicher Zusammensetzung. Zusammenfassend lässt sich feststellen, dass **1** als mildes Oxidationsmittel und als Selenid-Donor fungiert, dass es jedoch unter den gegebenen Reaktionsbedingungen nicht möglich ist, das Sn-Se-Gerüst zu erhalten.*

Compound **2** does not contain any atomic components of **1**, but is a product of its oxidation effect. Besides the 18 electron cobaltocene(III) cation $[Cp^*_2Co]^+$ species,[6] compound **2** features a binuclear anion that has not been reported yet (Figure 1).

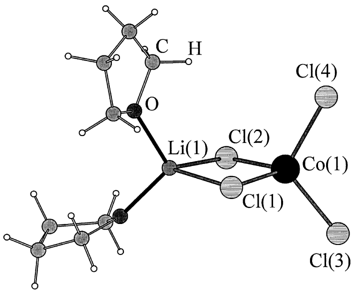


Figure 1. Molecular structure of the anion in **2** in the crystal. Selected bond lengths [pm] and angles [°]: Co(1)–Cl 225.6(2)–232.4(2), Li(1)–Cl 238.2(11)–238.3(9), Li(1)–O 190.8(11)–191.2(12); Cl-Co(1)-Cl 99.49(6)–113.08(7), (O,Cl)-Li(1)-(O,Cl) 96.2(4)–120.9(5).

The total charge of a primary $[CoCl_4]^{2-}$ anion, which is often observed as counterion in reactions of $CoCl_2$ or related complexes,[7] is formally reduced by means of a $[Li(thf)_2]^+$ unit attached to the complex anion through two of the chlorine ligands. Both metal centers show slightly distorted tetrahedral coordination. By sharing one edge formed by the μ_2-bridging atoms Cl(1) and Cl(2), the two tetrahedra are conjoined.

The reactions yielding **3** or **4** also involve redox processes. However, in contrast to **2**, compounds **3** and **4** exhibit Co^{II} and Co^{III} side by side in one molecule. Additionally, they contain selenide ligands that descend from **1**. According to the X-ray structural analyses, both **3** and **4** contain differently distorted $[Co_3Se_2]$ trigonal bipyramids that bind one Cp* group per cobalt atom. The Cp* rings surround the equatorial plane of the cluster in such a way that the methyl groups interdigitate with each other as would the teeth of three cogwheels. Figure 2 shows the molecular structure of **3** that topologically equals the cluster cation in **4**; analogue distances for compound **4** are given in the figure caption.

Formally, compound **3** exhibits one Co^{III} and two Co^{II} centers to be neutral. Thus, the total number of valence electrons within the cluster amounts to 50. Pursuant the Wade–Mingos rules,[8] one would therefore expect a *nido-*

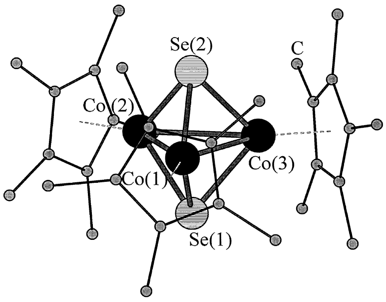
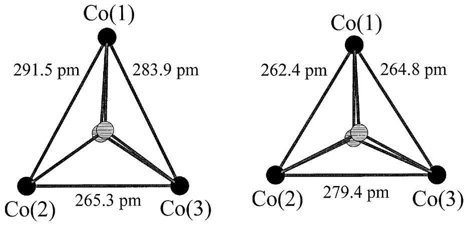


Figure 2. Molecular structure of **3** in the crystal. Selected bond lengths [pm] and angles [°]: Co(1)–Co(2) 291.5(1), Co(1)–Co(3) 283.9(1), Co(2)–Co(3) 265.3(1), Co–Se: 229.7(1)–230.7(1); Se-Co-Se 90.32(3)–90.48(3), Co-Se-Co: 70.52(3)–78.78(3). Analogue bond lengths [pm] and angles [°] in **4**: Co(1)–Co(2) 262.4(3), Co(1)–Co(3) 264.8(2), Co(2)–Co(3) 279.4(3), Co–Se 226.9(2)–228.3(3); Se-Co-Se 93.69(10)–93.91(9), Co-Se-Co 70.28(8)–75.94(9).

type cluster core. However, a square pyramid, corresponding to five cluster atoms, is not formed. The distorted trigonal bipyramid realized instead rather represents a variant of the *closo*-type cage that should be observed for a total electron number of 48. The equatorial Co_3 unit features one short and two long Co–Co bond lengths. Due to a difference of 7.6 pm for the long intermetallic distances, an isoceles triangle is not observed.

In fact, most clusters which contain 50 valence electrons that were reported in the past are of the type $[(L_nM)M'_2(CO)_6(\mu_3\text{-}E)_2]$ (L = (substituted) Cp group ($n = 1$), PR_3 ($n = 2$), CO ($n = 3$); M = Group 8–10 metal or W; M' = Group 8–10 metal; E = S, Se, Te, CO, NO, NR; R = organic group) and fulfill the normal structural requirements.[9–15] In contrast, only a few 50 electron pentanuclear clusters exhibit a cluster core similar to that of **3**, for example, $[(CpCo)_3(\mu_3\text{-}S)_2]$,[16, 17] $[(CpNi)_3(\mu_3\text{-}CO)_2]^-$,[18] or $[\{(C_5H_4CO_2Me)Co\}_3(\mu_3\text{-}S)(\mu_3\text{-}N\mathit{t}Bu)]$.[19] Theoretical treatment of M_2E_3 clusters generally explains the enlargement of M–M distances by the occupation of antibonding molecular orbitals (MOs) when going from 48 through 49 to 50 valence electrons.[9c, 19, 20] However, the reason for a preference of either one or the other structural isomer for both 49 or 50 electron compounds was not been cleared up yet. From our point of view, for a given μ_3-bridging ligand the steric influence of the terminal, non-bridging ligand is mainly responsible for the experimentally observed structure type. Considering the known examples, one perceives a deviation from Wade–Mingos rules—at least for compounds that contain two or three 3d metal atoms—if sterically demanding ligands are present. An exception from this tendency is $[(Cp'Co)_3(\mu_3\text{-}S)_2]$,[9c] which unlike $[(CpCo)_3(\mu_3\text{-}S)_2]$ or $[(CpNi)_3(\mu_3\text{-}CO)_2]^-$ exhibits a square pyramidal cluster shape despite being ligated by somewhat more bulky Cp' groups (Cp' = methylcyclopentadiene). Nevertheless, assuming that apart from any steric restraints caused by its ligands a 50 electron *nido*-type compound would represent the thermodynamically advantaged species, the described trend, except for $[(Cp'Co)_3(\mu_3\text{-}S)_2]$, gives evidence for the two following possible explanations. Either sterical demanding terminal ligands facilitate the isolation of kinetically controlled reaction products, since a rearrangement that pursues "half a Berry-type rotation"[21] and thereby forms the thermodynamically preferred isomer is hindered under the given reaction conditions, or the energetic order of the respective pair of isomers is inverted as a result of the forced enlargement of the interatomic distances due to large ligating groups. Preliminary results of a comprehensive theoretical study into this subject,[22] evidence the second explanation to be more likely.

In compound **4**, $[Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]^-$ acts as counterion as in **2**; this indicates a close relationship of the reactions that lead to **2** and **4**. Actually, both compounds show the same Co^{III}:Co^{II} ratio and are formed within the same reaction time under slightly differing temperature programs. For electroneutrality, the cluster unit in **4** is positively charged. Thus, it formally contains one Co^{II} and two Co^{III} centers; this correlates with a longer reaction time and the larger molar amount of **1** in the reaction mixture that yields **4** compared with the time and the **1**:$CoCl_2$ ratio for the synthesis of **3**. Since the total electron count in compound **4** amounts to 49 valence electrons, the cage cannot be structurally treated by means of Wade–Mingos rules. One can only claim those clusters with an odd electron number to obtain a medium structure that eventually resembles one of the extremes more than the other. Accordingly, the cluster core can be viewed as a "hybrid" that lies between a trigonal bipyramidal and a square pyramidal arrangement of the five atoms. Which one of the isomeric structure types is preferred, if a structural tendency towards one of them is found, should again be closely related to the steric properties of the ligand sphere. Hence, for compound **4** ligated by Cp*, a rather trigonal bipyramidal arrangement is observed. In contrast to **3**, compoud **4** exhibits one longer and two shorter Co–Co contacts in accordance with one electron less occupying antibonding MOs. Consequently, also the Co–Se bonds are somewhat shorter than in **3**. A comparison of the two Co_3Se_2 cluster cores of **3** or **4** is illustrated in Figure 3.



3 **4**

Figure 3. Comparison of the Co_3Se_2 cluster cores of **3** or **4** viewed down the Se–Se axis.

Unlike for the 50 electron species, there are a significant number of clusters that contain 49 valence electrons whose pentanuclear structural unit can be derived from a trigonal bipyramid,[9c, 10c, 20a, 23] and only very few 49 electron compounds that show a structure closer to a square pyramid. For example, the structure of the dianion in $[Ph_4P]_2[\{Mn(CO)_3\}_3(\mu_3\text{-}Se)_2]$[24] is based on a square-pyramidal Mn_3Se_2 aggregate. As it is ligated by relatively small CO ligands, the compound again underlines the correlation between steric demand of the terminal ligands and the observed structure type.

Vahrenkamp,[25] Dahl,[9c] and Rauchfuss[10c] have reported reversible electron transfer processes in pentanuclear cluster systems containing 48 to 50 valence electrons. Cyclovoltammetric measurements of a solution of single crystals of **4** in THF give similar results (Figure 4).

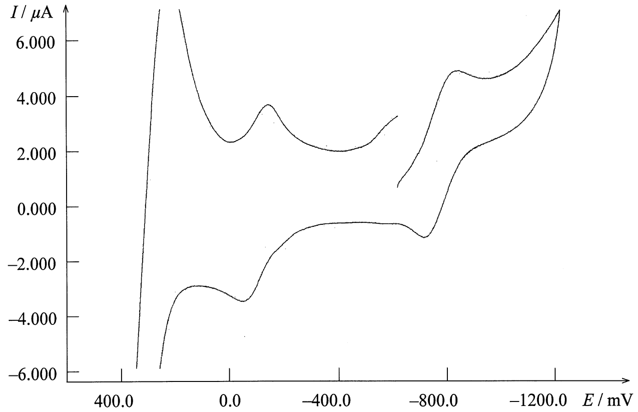


Figure 4. Cyclic voltammogram of a solution of **4** in THF. Specification of the cyclovoltammetric measurement: electrolyte: [nBu$_4$N][PF$_6$] (c = 0.1 mol L^{-1}); scan rate: 200 mV s^{-1}; measured against standard calomel electrode (SCE; $E_{SCE} = 560$ mV); the experiments are referenced to Cp$_2$Fe/Cp$_2$Fe$^+$ (observed: $E_{Fc/Fc^+} = 325$ mV; correction increment: $E_{SCE} - E_{Fc/Fc^+} = 235$ mV); $I_{peak,a}/I_{peak,c}$ ratios: 1.22 or 0.94; ΔE_{peak} values: 74 or 94 mV.

A reversible[26] single-electron oxidation and a reversible single-electron reduction are observed at potential values +0.132 and −0.538 V, respectively. The latter corresponds with the formation of compounds **3** from **4**; the first value belongs to an oxidation process that produces a 48 valence electron compound which contains three Co^{III} centers within the cluster. However, this compound could not yet be isolated within the scope of our experiments. Comparing the potentials for the 49 to 48 electron oxidation steps of electrochemically investigated [(CpCo)$_3$(μ_3-S)$_2$] (+0.57 V)[25] and [(Cp′Co)$_3$(μ_3-S)$_2$] (+0.52 V),[9c] one perceives a slight decrease. The continuation of this trend by the presented Cp* clad species (+0.132 V) illustrates the effect of increasingly steric demanding Cp^R groups (Cp^R = Cp, Cp′, Cp*) on the oxidation sensibility of the ligated Co^{II} center, in addition to the effect of substitution of μ_3-Se for μ_3-S. By the same token, further reduction to a—theoretically disadvantaged[22]—51 electron cluster that was observed in the above-cited experiments is evidently suppressed here.

A reaction of **1** with CoCl$_2$/LiCp* carried out in DME apparently follows the same course, but does not produce crystalline products over a long period. However, after four months, black crystals of compound **5** can be isolated. The molecular structure of **5** is given in Figure 5.

Four Cp*Co units and four μ_3-bridging selenide ligands form a heterocubane that formally displays exclusively Co^{III} metal centers. The experimental observations reported herein give evidence for quite a small rate constant for the oxidation of Cp*-ligated Co^{II} centers by **1**. Hence, in the case of **5**, only good solubility of possible intermediate reaction products might have enabled **1** to oxidize *all* Co^{II} centers before partially oxidized reaction products could precipitate and be removed from the reaction mixture. Accordingly, the above described reactions and their products may be claimed to be the result of incomplete turnover due to solvents causing lower solubility.

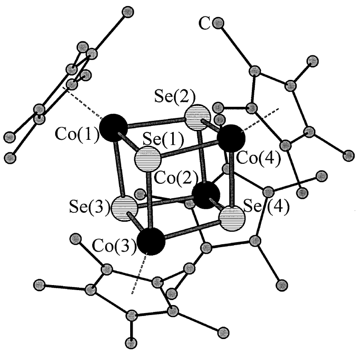


Figure 5. Molecular structure of **5** in the crystal; only one of the two split positions is shown for the twofold disordered Cp* group attached to Co(4). Selected bond lengths [pm] and angles [°]: Co–Se 235.2(3)–239.1(4), Co–Co 349.6(7)–357.0(6); Se-Co-Se 82.76(1)–84.58(1), Co-Se-Co 94.55(1)–97.16(1).

Heterocubane-type aggregates such as **5** are common for the combination of numerous transition metal elements (e.g., Ti, V, Cr, Group 8–10 metals) and Group 15 or 16 non-metal atoms. Famous examples are synthetic analogues of the active sites in iron–sulfur proteins such as [{(RS)Fe}$_4$S$_4$]$^{2-}$ (R = cysteinyl for biological systems; R = alkyl or aryl for synthetic analogues).[27] Of the multitude of further similar systems, the following compounds that are related to **5** are given as examples: [(CpCo)$_4$S$_4$]$^{n+}$ (n = 0, 1),[28] [{(Ph$_3$P)Co}$_4$Se$_4$],[29] and [{(tBuSe)Co}$_4$Se$_4$]$^-$.[30] However, compound **5** is the first cobalt–selenide heterocubane ligated by a Cp derivate. This ligand helps the cobalt atoms to achieve an 18 electron configuration. Accordingly, no Co–Co interactions are observed with Co–Co distances in the range of 349.6(7)–357.0(6) pm. As expected, the Co–Co distances in [(CpCo)$_4$S$_4$] (Co-Co: 323.6(1)–334.2(1) pm) are somewhat shorter due to a smaller μ_3-bridging ligand. The other quoted compounds show electron defects to different extents that are frustrated by formation of an accordant number of intermetallic bonds with bond lengths in the range of 262—277 pm. Compared with the equally μ_3-bridging situation in **3** or **4**, one finds an elongation of the Co–Se bond lengths of about 5-10 pm and somewhat obtuse Co-Se-Co angles instead of acute ones. This correlates with the significantly larger Co–Co distances of the four bridged Co$_3$ triangles in **5** (i.e., the faces of the Co$_4$ tetrahedron formally inscribed in the heterocubane) when compared with the triangles in **3** or **4**. The heterocubane unit is slightly distorted in a trigonal fashion and exhibits somewhat acute Se-Co-Se angles besides the obtuse angles around Se. However, the near D_{3d} symmetry of the Co$_4$Se$_4$ core is not realized for the complete molecule owing to the symmetry and orientation of the Cp* groups.

Conclusion

The presented and discussed experiments and their products show that compound **1** acts as mild oxidant and Se^{2-} donor in the investigated systems. Presupposition or at least facilitation for the formation of the reported compounds is a suitable redox potential of the employed transition metal complex as well as a strong preference for the formation of metal–selenium bonds compared with the preservation of the Sn–Se bond in **1**. Due to these properties of $[Cp^*CoCl]_2$ under the given reaction conditions, a pure coordinative ligand activity of **1** is inhibited. The experimental observations give evidence for a fairly small rate constant for the oxidation of Cp*-ligated Co^{II} centers by **1**. Hence, reaction times in the order of magnitude of weeks or months produce Co^{III}:Co^{II} ratios of 0.5, 1 or finally ∞ in the products. The polarity of the solvent also plays a major role. Firstly, it discriminates the crystallization of ionic versus neutral products (c.f. **2** or **4** vs. **3** or **5**, respectively). Secondly, even a slight increase in the solubility of possible reaction products leads to significantly larger reaction times that gives compound **1** the chance to increase its oxidation turnover (c.f. **5** vs. **3**). The choice of the reaction temperature also seems to be fundamental. An increased rate constant and thus acceleration of the reaction, besides adverse crystallization conditions, suppress the isolation of an intermediate or previous product (c.f. **4** vs. **2**). By carfully choosing the reaction conditions, the products with different solubilities can thus be individually isolated.

Besides variation of the reaction conditions future experiments shall probe whether modification of the transition metal complex, with regard to both ligands or central atom/ion, further influences the course and results of reactions with **1**.

Experimental Section

General: All reaction steps were carried out under exclusion of air and moisture either in a dry nitrogen atmosphere or under argon (glovebox). All solvents were dried and freshly destilled prior to use. For reactions with **1**, $CoCl_2$ (0.078 g, 0.6 mmol) and LiCp* (0.085 g, 0.6 mmol) were stirred in THF (2 mL; **2**, **3** or **4**) or DME (3 mL; **5**) for 20 min at room temperature, resulting in the formation of brownish-black solutions of $[Cp^*CoCl]_2$.

$[Cp^*_2Co][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (2): The $[Cp^*CoCl]_2$ solution was cooled down to −78 °C, whereupon **1** (0.095 g, 0.1 mmol) was added. On warming to room temperature, the color changed to deep black. After removal of an insoluble black precipitate the filtrate was layered with toluene (10 mL). The solution was stored at −40 °C and light green, rhombic crystals of **2** were isolated after two weeks. Yield: 0.031 g (0.045 mmol, 15 %); elemental analysis calcd (%) for $C_{28}H_{46}Co_2Cl_4LiO_2$: C 49.36, H 6.81; found C 49.21, H 6.78.

$[(Cp^*Co)_3(\mu_3\text{-}Se)_2]$ (3): The $[Cp^*CoCl]_2$ solution was cooled down to −78 °C whereupon **1** (0.095 g, 0.1 mmol) was added. On warming to room temperature, the color changed to deep black. After removal of an insoluble black precipitate the filtrate was stored at −40 °C. Large black crystals of **3** with a trapezoidal-type shape formed within 10 days. Yield: 0.116 g (0.156 mmol, 78 %); MS (70 eV): m/z (%): 742 (100) $[M]^+$, 605 (8) $[M-Cp^*]^+$, 470 (20) $[M-2Cp^*]^+$, 371 (15) $[M]^{2+}$, 335 (20) $[M-3Cp^*]^+$; elemental analysis calcd (%) for $C_{30}H_{45}Co_3Se_2$: C 48.67, H 6.13; found C 48.85, H 6.15.

$[(Cp^*Co)_3(\mu_3\text{-}Se)_2][Cl_2Co(\mu_2\text{-}Cl)_2Li(thf)_2]$ (4): Compound **1** (0.095 g, 0.1 mmol) was added to the $[Cp^*CoCl]_2$ solution and the resulting solution was stirred for 24 h. The deep black reaction mixture was then cooled down to −78 °C and **1** (0.095 g, 0.1 mmol) was added again. After warming to 0 °C and removal of an insoluble black precipitate, the filtrate was layered with toluene (10 mL). The solution was stored at −40 °C, and thin black crystalline needles of **4** were isolated after two weeks. Yield: 0.073 g (0.068 mmol, 45 %); elemental analysis calcd (%) for $C_{38}H_{61}Co_4Cl_4LiO_2Se_2$: C 41.78, H 5.63; found C 41.66, H 5.59.

$[(Cp^*Co)_4(\mu_3\text{-}Se)_4]$ (5): The $[Cp^*CoCl]_2$ solution was cooled down to −78 °C whereupon **1** (0.095 g, 0.1 mmol) was added. After warming to −20 °C, THF (1 mL) was added. An insoluble black precipitate was removed, and the filtrate was stored at −40 °C for 11 weeks. The solution was stored at room temperature for a further 5 weeks and black crystals of **5** were isolated. Yield: 0.118 g (0.108 mmol, 72 %); MS (70 eV): m/z (%): 1094 (83) $[M]^+$, 957 (23) $[M-Cp^*-2H]^+$, 743 (15) $[M-2Cp^*-Se-H]^+$, 604 (10) $[M-2Cp^*-Co-2Se-2H]^+$, 546 (32) $[M-2H]^{2+}$; elemental analysis calcd (%) for $C_{40}H_{60}Co_4Se_4$: C 43.98, H 5.54; found C 43.82, H 5.51.

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[4] Data of the X-ray structure analyses. $Mo_{K\alpha}$ radiation, graphite monochromator, imaging plate diffractometer STOE IPDS, for **2**–**4** with a rotating anode (SCHNEIDER); structure solution by direct methods and full-matrix least-squares refinement on F^2; programs used: SHELXS-86,[31] SHELXL-97.[32] Compound **2**: triclinic, space group $P1$, $Z=2$, $a=942.0(2)$, $b=1305.1(3)$, $c=1448.4(2)$ pm, $\alpha=91.13(3)$, $\beta=108.17(3)$, $\gamma=104.83(3)^\circ$, $V=1625.9(6)\times10^6$ pm^3, $\rho_{calcd}=1.392$ g cm^{-3}, $2\theta=4.2-50.0^\circ$, 6539 reflections measured, 4656 independent reflections [$R_{int}=0.067$], 3144 with $I>2\sigma(I)$, $\mu(Mo_{K\alpha})=1.372$ cm^{-1}, 344 parameters (positions of all non-hydrogen atoms were refined by employing anisotropic displacement parameters; H atoms were calculated for idealized positions and were not refined), maximum peak: 0.426 e Å^{-3}, $R_1=0.051$, $wR_2=0.121$; Compound **3**: orthorhombic, space group Pbca, $Z=8$, $a=1535.4(3)$, $b=1785.9(4)$, $c=2206.0(4)$ pm, $V=6049.0(6)\times10^6$ pm^3, $\rho_{calcd}=1.626$ g cm^{-3}, $2\theta=4-50^\circ$, 16709 reflections measured, 4965 independent reflections [$R_{int}=0.064$], 3772 with $I>2\sigma(I)$, $\mu(Mo_{K\alpha})=4.050$ mm^{-1}, 331 parameters (positions of all non-hydrogen atoms were refined by employing anisotropic displacement parameters; H atoms at the Cp* rings were calculated for idealized positions and were not refined; three twofold disordered methyl C atoms were refined assuming split positions), maximum peak: 0.992 e Å^{-3}, $R_1=0.044$, $wR_2=0.105$; Compound **4**: triclinic, space group $P1$, $Z=2$, $a=865.1(2)$, $b=1640.6(3)$, $c=1650.3(3)$ pm, $\alpha=99.70(3)$, $\beta=102.82(3)$, $\gamma=99.46(3)^\circ$, $V=2201.2(8)\times10^6$ pm^3, $\rho_{calcd}=1.648$ g cm^{-3}, $2\theta=4-46^\circ$, 7189 reflections measured, 4993 independent reflections [$R_{int}=0.071$], 3107 with $I>2\sigma(I)$, $\mu(Mo_{K\alpha})=3.409$ mm^{-1}, 353 parameters (positions of all heavy atoms and of the C atoms of two Cp* rings were refined by employing anisotropic displacement parameters, all remaining non-hydrogen atoms were refined by employing isotropic displacement parameters; for a twofold disordered Cp* ring adequate split positions were assigned; all Cp* rings were refined as rigid groups; atoms of the THF molecules of the anion that showed to be twofold disordered were refined assuming according split positions; for one of the THF molecules, only one O and two C atoms could be localized; H atoms at the not disordered Cp* rings were calculated for idealized positions and were not refined), maximum peak: 0.702 e Å^{-3}, $R_1=0.076$, $wR_2=0.221$; Compound **5**: triclinic, space group $P1$, $Z=2$, $a=1114.8(2)$, $b=1124.4(2)$, $c=1866.0(4)$ pm, $\alpha=82.90(3)$, $\beta=82.73(3)$, $\gamma=65.78(3)^\circ$, $V=2109.4(7)\times10^6$ pm^3, $\rho_{calcd}=1.720$ g cm^{-3}, $2\theta=4-52^\circ$, 12683 reflections measured, 7538 independent reflections

[$R_{\text{int}} = 0.057$], 3476 with $I > 2\sigma(I)$, $\mu(\text{Mo}_{\text{K}\alpha}) = 5.023\ \text{mm}^{-1}$, 273 parameters (positions of all non-hydrogen atoms despite the C atoms of a twofold disordered Cp* ring and those of eight twofold disordered methyl C atoms at other Cp* rings were refined by employing anisotropic displacement parameters; for the disordered groups, adequate split positions were assigned and the C atoms were refined by using isotropic displacement parameters; H atoms were calculated for idealized positions except for the completely disordered Cp* ring and were not refined), maximum peak: 1.803 e Å^{-3}, $R_1 = 0.087$, $wR_2 = 0.217$. It was not possible to find a higher metric symmetry for the observed crystallographic data of compounds **4** or **5**, even though the equality of two axes and two angles is astonishing; a twinning problem cannot be excluded; however, preliminary twin refinement did not lead to better results in R_1 or wR_2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135478–135480 and CCDC-138625. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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