Reductive Activation of tripod Metal Compounds: Preparative Application

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In memoriam Dr. Laszlo Zsolnai

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The tripodnickel(0) species $[tripod_4Ni_3]$ (1) $\{tripod =$ CH₃C(CH₂PPPh₂)₃) is shown to undergo oxidative addition with disulfides or diselenides REER ($E = S_t$, S_t , R = tBu, Ph) to produce [tripodNi(ER)] (2). Compounds 2 show pseudo tetrahedral coordination. They are paramagnetic with one unpaired electron per molecule. Their magnetic behaviour is almost that of an ideal Curie-type magnet down to temperatures of 2 K. They undergo reversible one electron oxidation to the 16 valence electron species [tripodNi(ER)]⁺. The isoelectronic pseudo tetrahedral 16 valence electron cobalt species [tripodCo(ER)] (3) are obtained by reduction of $CoCl_2$ with KC₈ in the presence of tripod and subsequent reaction with REER (E = S, Se; R = tBu, Ph). They are paramagnetic with two unpaired electrons per molecule. They can be reversibly oxidised to the 15 valence electron compounds [tripodCo(ER)]⁺ while their reduction to the 17 valence electron species [tripodCo(ER)]⁻, which would be isoelectronic to the stable compounds 2_{1} is not observed. Under appropriate conditions the reactions with REER do not result in the formation of **3** but yield [tripodCoECotripod] (**4**) by extrusion of sulfur and selenium from the substrate. Compounds 4 show a linear Co-E-Co framework with very short Co-E bonds (E = S: 205 pm; E = Se: 216 pm). They are members of a family of dimetallaheterocumulenic compounds $[L_n MEML_n]$ (E = main group element of groups III to VI) with a valence electron count of 36 electrons. Quantum chemistry predicts that the HOMO of such compounds should be a degenerated pair of mainly metal centred orbitals. Electrochemistry of 4a, [tripodCoSCotripod], shows three quasi-reversible oxidation steps in the range of -700 mV vs. SCE to 570 mV vs. SCE, which can be understood as metal centred oxidations. Three different types of crystals have been obtained for different types of pseudopolymorphs 4a. The geometric parameters of the coordination compounds are almost equal in these pseudopolymorphic crystals. The real difference is the content of solvent molecules and, hence, the packing of the molecules. In the crystals of 4a containing no solvent the coordination compounds form close packed layers stacked on each other in an oblique way. In the crystals containing 4a.DME a layer of solvent molecules separates each pair of layers of close packed molecules. In the crystal of 4a·3DME a cuboctahedral cage of solvent molecules embedding each coordination compound separates the complex molecules from each other. The different types of crystals observed underpin the globular shape of 4 and the effective shielding power of the tripod ligand.

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Introduction

The metal(II) halides of cobalt and nickel in the presence of *tripod* {*tripod* = CH₃C(CH₂P')₃; P' = PPh₂} have been shown to produce highly reactive *tripod*cobalt(0)^[1] and -nickel(0)^[2] species upon their activation with KC₈ in THF solutions. The composition of the reactive *tripod*nickel(0) species has been elucidated to be [*tripod*₄Ni₃] (1) (Scheme 1).^[2] 1 has been shown to react with two-electron donors L (L = PPh₃, AsPh₃, cHexNC *t*BuNC, C₂H₄) to give the *tripod*nickel(0) compounds [*tripod*NiL].^[2] Oxidative addition to 1 in its reactions with disulfides RSSR and diselenides RSeSeR is analysed in this paper.





The reduction of CoCl_2 with KC₈ in the presence of *tripod* in THF in an argon atmosphere likewise produces a reactive species ["*tripod*Co⁰"] (A).^[1,2] Oxidative addition of the same reagents to A was found to be rather analogous to the one observed for 1. In addition it is observed that the thiophilicity of A is high enough to split C–S bonds, extracting sulfur from different organic sources to produce the dinuclear compound [*tripod*CoSCo*tripod*] (4a).



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The aim of the work reported here was to further elucidate the reactivity of the species $[tripod_4Ni_3]$ (1) and its co-balt(0) analogue **A**.

Results and Discussion

THF solutions of $[tripod_4Ni_3]$ react with dichalgogenides REER (E = S, Se, R = tBu, Ph) to produce the tripod-nickel(I) species **2a–2c** (Scheme 2).



Scheme 2.

Compounds 2 are isolated as red crystals in analytically pure form in yields between 60% and 80%. Their coordination geometry is pseudo-tetrahedral as verified by X-ray structure analyses of 2a–2c. As an example of their geometry, sketches of the structure of 2b are shown in Figure 1. Characteristic geometric parameters of all three compounds 2a–2c are summarised in Table 1.

Ni–P distances in 2a-2c vary from 218 pm to 226 pm, somehow reflecting the steric congestion by the ER ligands imposed on the individual phosphorus atoms. Thus, for instance, in 2b, the distance Ni1–P1 (226 pm) is distinctly larger than the distances Ni1–P2 and Ni1–P3 (221 pm). In 2b the Ni1–P1 bond is eclipsed to the S1–C6 bond (Figure 1) such that P1 will feel the steric load imposed by the *tert*-butyl group. In consequence the Ni1–P1 bond is lengthened and the P1–Ni1–S1 angle (127°) is increased compared to the angles P2–Ni1–S1 (121°) and P3–Ni1–S1 (119°), respectively. The skew of the *tripod* metal scaffolding ex-

Table 1. Selected bond lengths [pm], bond angles [°] and torsion angles [°] in **2a–c**.

| 2.a[a.c] | e 1 [] | |
|---------------------|---|---|
| 2a ^[-,-] | $2\mathbf{b}^{[a,c]}$ | 2c ^[b] |
| 222.7(2) | 226.0(1) | 221.5(1) |
| 221.2(2) | 221.3(2) | 218.1(2) |
| 221.5(2) | 220.6(1) | 220.3(1) |
| 221.2(2) | 219.1(1) | 230.1(1) |
| 99.2(1) | 95.6(2) | 93.3(2) |
| 92.7(1) | 93.8(1) | 98.0(1) |
| 88.7(1) | 91.8(1) | 91.9(1) |
| 127.7(1) | 127.0(1) | 130.6(1) |
| 111.7(1) | 121.0(1) | 115.7(1) |
| 127.6(1) | 119.4(1) | 118.6(1) |
| 34.5 | 32.1 | 9.3 |
| 18.5 | 27.9 | 10.7 |
| 27.9 | 39.2 | 19.5 |
| 32.4 | 39.4 | -45.6 |
| 70.8 | 60.9 | 21.8 |
| 27.7 | 3.1 | 16.7 |
| 5.7 | -10.0 | 32.0 |
| 10.0 | 42.6 | 32.8 |
| 2.5 | 0.0 | 9.8 |
| | 222.7(2) 221.2(2) 221.5(2) 221.2(2) 99.2(1) 92.7(1) 88.7(1) 127.7(1) 111.7(1) 127.6(1) 34.5 18.5 27.9 32.4 70.8 27.7 5.7 10.0 2.5 | $2a^{(ne)}$ $2b^{(ne)}$ 222.7(2)226.0(1)221.2(2)221.3(2)221.5(2)220.6(1)221.2(2)219.1(1)99.2(1)95.6(2)92.7(1)93.8(1)88.7(1)91.8(1)127.7(1)127.0(1)111.7(1)121.0(1)127.6(1)119.4(1)34.532.118.527.927.939.232.439.470.860.927.73.15.7-10.010.042.62.50.0 |

[a] **2a**, **2b** with E = S. [b] **2c** with E = Se. [c] The values in parentheses are standard deviations in units of the last decimals listed. [d] τ = torsion angles within the chelate cage: τ_1 = C4–C1–P1–Ni, τ_2 = C4–C2–P2–Ni, τ_3 = C4–C3–P3–Ni. [e] The torsion angles *f* involving Hz are defined as follows: f_1 = Hz1–P1–C100–C101, f_2 = Hz1–P1–C106–C107, f_3 = Hz2–P2–C200–C201, f_4 = Hz2–P1–C206–C207, f_5 = Hz3–P3–C300–C301, f_6 = Hz3–P3–C306–C307; Hz–P designates a vector that is vertical to the plane formed by the three *tripod* phosphorus donor atoms and points towards the observer when, in a projection onto this plane, the vector Co–C4 points away from the observer, such that C4 lies below this plane.^[3]

pressed by the torsion angles τ (Table 1) is larger for the sulfur derivatives **2a** and **2b** ($\tau = 30^{\circ}$ in the mean) than for the selenium derivative **2c** ($\tau = 13^{\circ}$ in the mean).

There is only one mononuclear coordination compound of the type [*tripod*Ni(SR)] reported to compare with: in [*tripod*Ni(SH)], characterised by Sacconi and his group,^[4] the Ni–S distance is found to be 217 pm, close to the values of about 220 pm as observed for **2a** and **2b**. As expected, due



Figure 1. The molecular structure of **2b** in the crystal. Left: general view; right: projection onto the plane defined by the three *tripod* phosphorus atoms.

to the difference in atomic radii, the Ni–Se distance in **2c** is some 10 pm larger than the Ni–S distances in **2a** and **2b**.

The nickel(I) complexes 2 are paramagnetic species. The pseudo tetrahedral coordination geometry and the d⁹ electron count lead one to expect one unpaired electron per complex entity. Magnetic measurements in solution by the Evans Method^[5] show magnetic moments μ_{eff} close to the spin-only value corresponding to one unpaired electron. SQUID measurements of 2 in the temperature range 2–300 K show almost perfect Curie behaviour with Curie constants *C* from 0.370 cm³ K mol⁻¹ to 0.394 cm³ K mol⁻¹ and Weiss constants Θ of only $\Theta = -1$ K, indicating that there is almost no magnetic interaction between the individual molecules. The magnetic moments extracted from SQUID measurements in the solid state are well in agreement with the ones obtained by the Evans Method in solution (Table 2).

Table 2. Magnetic and EPR data of 2a-2c.

| | Evans Method: μ_{eff} (300 K) [μ_{B}] | SQUID: $\mu_{\rm eff}$ (300 K) [$\mu_{\rm B}$], C [cm ³ K mol ⁻¹], Θ [K] | EPR: $A_{iso}(P)$ [G] |
|----|--|---|---|
| 2a | $\mu_{\rm eff} = 1.68$ | $ \mu_{\rm eff} = 1.63 $ C = 0.394 $ \Theta = -1 $ | $g_{iso} = 2.1263$ $A_{iso}(P) = 60$ |
| 2b | $\mu_{\rm eff} = 1.57$ | $ \mu_{\rm eff} = 1.74 $ C = 0.370 $ \Theta = -1 $ | $g_{iso} = 2.1110$ $A_{iso}(P) = 61$ |
| 2c | $\mu_{\rm eff} = 1.77$ | $\mu_{\rm eff} = 1.74$ C = 0.374 $\Theta = -1$ | $g_{\rm iso} = 2.1156$ $A_{\rm iso}(P) = 60$ |

EPR spectra of THF solutions of complexes 2 show a quartet in each case with a single coupling constant A(P) to the phosphorus nuclei of around 60 Gauss (Table 2) as shown for 2b as an example (Figure 2). The spectrum is well in agreement with its simulation, as shown by the bottom line in Figure 2. The g values in the range of $g_{iso} = 2.1110$ to $g_{iso} = 2.1263$ are somewhat larger than $g_e = 2.0023$ indicating that there is some spin-orbit coupling present in complexes 2 (Table 2), as expected for a pseudo tetrahedral d⁹-system.



Figure 2. EPR spectrum of **2b** (295 K, 9.44 GHz) (middle trace), simulation [top trace; parameters: $g_{iso} = 2.1110$, A(P) = 61 G, line width = 38×10^{-4} cm⁻¹] and residual (bottom trace).

Cyclovoltammetric experiments show that the 17 electron compounds 2a and 2b undergo reversible one-electron oxidation to give the 16 electron species $2a^+$ and $2b^+$

(Scheme 3). With **2c** one-electron oxidation is observed as well, which, however, is only quasi-reversible at room temperature under the conditions applied. Oxidation of compounds **2** occurs between $E_{1/2} = -180 \text{ mV}$ (**2c**) and $E_{1/2} =$ -470 mV (**2b**) vs. SCE (Scheme 3), demonstrating that there is no strong influence on the oxidation potential neither of the substituent linked to sulfur nor of the nature of the ligating chalcogen element. This means that the orbital involved in the redox process is mainly metal in character. No attempt has been made to characterise the nickel(II) species **2**⁺. It has been reported that nickel in the oxidation state +II forms both mononuclear and dinuclear complexes containing thiolate groups and tripodal ligands: stable mononuclear compounds of the general formula [LM(SR)]⁺ {L = P(CH₂CH₂PPh₂)₃, N(CH₂CH₂PPh₂)₃; M = Co, Ni} have

been described by Sacconi and his group,^[6] dinuclear complexes of the composition $[(tripodNiSR)_2]^{2+}$ (R = Ph) were characterised in our group;^[7] in this type of compounds the *tripod* ligand is only coordinated with two of his phosphane donor entities.^[7] The reversibility of the oxidation process observed for **2a** and **2b** tends to indicate that the Scheme 3



Scheme 3.

Repeating the experiments described for nickel using the reactive solution obtained by the reduction of $CoCl_2$ in THF by KC_8 in the presence of *tripod* under an argon atmosphere gives rather similar results even though the electron count differs by one electron: with disulfides RSSR the neutral cobalt(I) compounds [*tripod*Co(SR)] (**3a**: R = Ph; **3b**: R = tBu) are formed, the diselenide PhSeSePh forms the analogue complex [*tripod*Co(SePh)] (**3c**) (Scheme 4).



Scheme 4.

The pseudo-tetrahedral coordination of the metal in 3a-3c has been confirmed by the X-ray crystal structure analyses. The mean value of the Co–P distances in all three compounds is 222 pm and individual Co–P distances do not

differ significantly from this mean value (Table 3). The close to trigonal local symmetry of the CoP_3 fragment is as well documented by the P–Co–P angles which differ by only 1.5° from the mean value of 91.5° at most. In all compounds **3** the residues ER in [*tripod*Co(ER)] are arranged such as to occupy the space between two Co–P bonds, corresponding to a close to staggered conformation of the bond S1–C6 with respect to the CoP₃ entity (Figure 3). The ER ligands

Table 3. Selected bond lengths [pm], bond angles [°] and torsion angles [°] in $3a{\rm -}c.$

| | 3a ^[a,c] | 3b ^[a] | 3c ^[b] |
|-------------------------------|----------------------------|--------------------------|--------------------------|
| Co1–P1 | 222.7(2) | 222.9(1) | 220.6(1) |
| Co1–P2 | 223.5(2) | 222.8(1) | 221.7(1) |
| Co1–P3 | 222.3(2) | 224.2(1) | 219.7(1) |
| Co1–E | 224.2(2) | 223.2(1) | 236.2(1) |
| P1-Co1-P2 | 93.5(1) | 91.7(1) | 91.4(1) |
| P1-Co1-P3 | 90.3(1) | 90.4(1) | 91.4(1) |
| P2-Co1-P3 | 90.8(1) | 93.0(1) | 91.4(1) |
| P1–Co1–E | 123.6(1) | 107.2(1) | 112.3(1) |
| P2–Co1–E | 134.3(1) | 127.8(1) | 130.5(1) |
| P3–Co1–E | 112.3(1) | 133.6(1) | 128.1(1) |
| $\tau_1^{[d]}$ | 31.2 | 26.0 | 18.2 |
| $\tau_2^{[d]}$ | 23.3 | 28.3 | 16.1 |
| $\tau_{3}^{[d]}$ | 23.0 | 24.5 | 19.0 |
| $f_1^{[e]}$ | -6.7 | 1.6 | 10.2 |
| $f_2^{[e]}$ | 18.9 | 20.0 | 35.3 |
| $f_{3}^{[e]}$ | -42.3 | 21.6 | 11.8 |
| $f_4^{[e]}$ | -50.2 | 96.7 | 31.7 |
| f ₅ ^[e] | -20.4 | 15.2 | 19.4 |
| $f_{\epsilon}^{[e]}$ | 20.8 | 24.1 | 42.4 |

[a] E = S. [b] E = Se. [c] The values in parentheses are standard deviations in units of the last decimals listed. [d] τ = torsion angles within the chelate cage: $\tau_1 = C4-C1-P1-Ni$, $\tau_2 = C4-C2-P2-Ni$, $\tau_3 = C4-C3-P3-Ni$. [e] The torsion angles *f* involving Hz are defined as follows: $f_1 = Hz1-P1-C100-C101$, $f_2 = Hz1-P1-C106-C107$, $f_3 = Hz2-P2-C200-C201$, $f_4 = Hz2-P1-C206-C207$, $f_5 = Hz3-P3-C300-C301$, $f_6 = Hz3-P3-C306-C307$; Hz-P designates a vector that is vertical to the plane formed by the three *tripod* phosphorus donor atoms and points towards the observer when, in a projection onto this plane, the vector Co-C4 points away from the observer, such that C4 lies below this plane.^[3]

therefore have only less immediate steric influence on the geometric parameters of the CoP_3 tripod, quite different from the case of **2b** in which the bond S1–C6 and the bulky *tert*-butyl group, respectively, is in eclipsed position to the bond Ni1–P1 (Figure 1). The steric load, nevertheless present, mirrors itself in the direction of the deviation of the chalcogen atom from the pseudotrigonal axis: the angles P–Co–E fall in two classes throughout. There are two large angles close to the mean of 130° and one small angle again close to the respective mean value of 111° (Table 3). The small P–Co–E angle is found for the one phosphorus atom which is opposite to the sector occupied by the substituent R. Compressing this angle alleviates the steric repulsion between the group R and the two other phosphorus atoms and their substituents.

The skew of the *tripod*Co scaffolding which is documented by the torsion angles τ (Table 3) is similar to the one observed for compounds 2. As in the case of the nickel complexes 2 the torsion angles are larger for the sulfur compounds ($\tau = 26^{\circ}$ mean value) than for the selenium complex ($\tau = 18^{\circ}$ mean value). As expected, the Co–E distances are slightly larger than the ones observed for the analogous nickel compounds 2 (see Tables 1 and 3). The Co–Se distance in 3c is around 10 pm larger than the metal sulfur distances in 3a and 3b as already observed for the analogous nickel compounds 2.

The pseudo tetrahedral 16 electron species 3 with a d⁸configuration of the metal should be paramagnetic due to the presence of two unpaired electrons. Magnetic measurements by the Evans Method give magnetic moments between $\mu_{eff} = 3.1 \,\mu_B$ and $\mu_{eff} = 3.3 \,\mu_B$ well in agreement with the spin-only value of $\mu_{eff} = 2.83 \,\mu_B$ for two unpaired electrons. The deviation from the spin-only value is due to spinorbit coupling.

Compounds **3** are isoelectronic analogues to [*tripod*-Ni(ER)]⁺ (**2**⁺). Therefore, it is expected that they could be reduced in a one electron step to produce isoelectronic analogues of the stable compounds [*tripod*Ni(ER)] (**2**). By cy-



Figure 3. The molecular structure of **3b** in the crystal. Left: general view; right: projection onto the plane defined by the three *tripod* phosphorus atoms.

clic voltammetry it is found, however, that reduction processes are irreversible throughout. In contrast, reversible oxidation is observed for the sulfur derivatives 3a and 3b (Scheme 5). Oxidation occurs as a fully reversible process at $E_{1/2} = -240 \text{ mV}$ vs. SCE for **3a** and $E_{1/2} = -280 \text{ mV}$ vs. SCE for 3b. The small difference between the redox potentials of 3a and 3b is again indicative of the metal character of the orbital involved. The selenium species 3c shows an oxidation peak at $E_p^A = -310 \text{ mV}$ vs. SCE, which, even though the process is irreversible under the conditions applied, indicates that the nature of the chalcogen atom of the coligand does not strongly affect the oxidation potential. It has not been attempted to isolate the cationic compounds 3^+ . It is known, however, that the dinuclear complex [(tripod- $CoSR)_2]^{2+}$ (R = Me) is a stable entity.^[8] It has been characterised by the group of Sacconi and has been found to be structurally rather similar to the analogous nickel compound $[(tripodNiSR)_2]^{2+}$ (R = Ph).^[7] The reversibility of the oxidation of 3a and 3b, similar to the case discussed for the nickel complexes 2a and 2b suggests that the monomeric species [(tripodNiSR)]⁺ are intrinsically stable under the conditions applied.





In the synthesis of compounds **3**, a minor green by-product was sometimes observed. The nature of this by-product became clear when dibenzyl disulfide was used as the substrate expected to undergo oxidative addition with "*tripod*Co⁰". In this case the green compound was the main product and no species of type **3** could be isolated. It was characterised as **4a**, a dinuclear compound containing two *tripod*cobalt entities linked by a sulfur atom (Scheme 6).



Scheme 6.

The structure of **4a** was determined for crystals containing solely **4a** and also for crystals containing **4a** and different amounts of solvent (Figure 5, Table 5). In all of the three pseudopolymorphs **4a**, **4a**·DME and **4a**·3DME (Table 5) the Co–S–Co axis is strictly linear. In all cases but one this linearity corresponds to crystallographic symmetry requirements. In the case of the two crystallographically independent molecules in the cell of 4a.DME only one is restricted to be linear by an inversion centre at the position of the sulfur atom; for the other one, not restricted by crystal symmetry, a Co-S-Co angle of very close to 180° is observed (176.4°). The two Co-S distances within each molecule in all three crystal variants of 4a are either exactly equal by crystal symmetry or are so within the limits of error (4a·3DME). They are very short with an average value of 205.3 pm. Similarly short M-S distances have already been observed in a few other coordination compounds containing a linear M-S-M entity (Table 4). The bonding situation in this type of complexes has already been analysed by different quantum chemical approaches^[9,10] with the unequivocal result that the bond order of the M-S bond is at least two.

Table 4. Selected bond lengths [pm] in complexes $[L_nMSML_n]^{m+}$ with linear M–S–M fragments.

| т | М | d(M–S) | d(M-P) | L_nM |
|-----|----------|----------------|----------------|--|
| 000 | Co Co | 205.3 212.8 | 216.9 228.5 | [CH ₃ C(CH ₂ PPh ₂) ₃ Co] (4a) [N(CH ₂ CH ₂ PPh ₂) ₃ Co] ^[11] |
| 2 | Ni | 203.4 | 223.6 | $[CH_{3}C(CH_{2}PPh_{2})_{3}Ni]^{2+[11]}$ |
| 0 | V | 217.2 | 248.8 | $[(CP)(CO)_2C1]^{[13]}$ $[(dppe)(CO)_3V]^{[13]}$ |

All the compounds containing a linear M–S–M entity so far described (Table 4) have in common that the valence electron count of the $[L_n MSML_n]^{m+}$ species corresponds to 36 electrons; the L_nM fragments in these compounds are 15 electron species throughout (Table 4). The principle that the 36 electron count of a linear M-E-M entity appears to be a precondition for its formation is further exemplified by the existence of a series of compounds containing a linear L_nMEL_nM framework with E ranging from main group III (Ga,^[14a] In,^[14b] Tl^[14c]) over main group IV (Ge,^[15a-15c] Sn,^[15c] Pb^[15d,15e]) to main group V (P,^[16a] As,^[16b-16d] $Sb^{[16b, 16e]}$). The L_nM entities are organometallic throughout in all these cases. The valence electron count of 16 electrons $\{ [Cp(CO)_2Mn], [(CO)_5Cr], [(C_6Me_6)(CO)_2Cr] \}$ leads to neutral compounds with main group IV, cationic ones with main group V and anionic species with main group III elements.^[14c,15,16] The 16 valence electron species {[(Cp*)-(CO)₂Fe]} accordingly forms cationic compounds with Indium and Gallium.^[14a,14b] All these compounds, hence, have a 36 valence electron count. Quantum chemical calculations on the EHT level^[17] indicate that the HOMO in compounds of this type should be a degenerate pair of metal orbitals. More recent density functional calculations^[18] are in agreement with these early results. If the highest orbital occupied is metal centred with no contribution to M-E bonding one might expect that compounds with linear M-E-M entities might as well exist with an electron count of less than 36 electrons. While compounds of this type have not yet been described, cyclovoltammetric analysis of 4a reveals three oxidation peaks in the range of -1000 mV to +800 mV vs. SCE (Figure 4).



Figure 4. Cyclic voltammogramm of 4a.

The first oxidation wave is fully reversible with $E_{1/2}$ = -700 mV vs. SCE, the following two oxidation steps are only quasi-reversible and occur at $E_p^A = -40 \text{ mV}$ vs. SCE and $E_p^A = +570 \text{ mV}$ vs. SCE, respectively (Figure 4). The phenotype of the cyclic voltammogramm is well in agreement with the quantum chemically supported assumption of a pair of metal centred orbitals at the HOMO level in 4a. The neutral compound 4a with the degenerate pair of HOMO orbitals completely filled should be diamagnetic as is in fact found. ¹H and ¹³C NMR spectra show the signals characteristic of *tripod* metal entities (see Exp. Section). The peculiarity of the bonding situation in 4a is, on the other hand, reflected by its behaviour in ³¹P NMR spectroscopic experiments: in the temperature range of 303 K to 203 K no ³¹P NMR signal can be observed at all. Only at 193 K, the lowest accessible temperature in the solvent used, a very broad signal starts to appear with a full width at half maximum of 400 Hz. The origin of this strange behavior is not clear. A similar type of behavior has already been described for the diamagnetic compounds [tripodCo(C₆O₄X₂)Cotri $pod[(PF_6)_2 (X = H, Cl, Br, I, NO_2, Me),^{[19]} where a {}^{31}P$ NMR signal only appears below 200 K.^[19] Just one sharp singlet is observed in this case, which makes clear that the tripod ligands are still free to rotate at these low temperatures, excluding any process of hindered rotation as an explanation for the observed behavior. No rationale has been found to explain the observed behaviour. As both types of compounds are dinuclear with the *tripod*Co entities coupled by a strong π -type interaction with the bridging ligand, the yet unknown explanation might rest on the same type of arguments for both classes of compounds.

The synthesis of **4a** with $(PhCH_2S)_2$ as the source of sulfur points to some thiophilicity of the "*tripod*Co⁰" species **A**, as does the generation of **4a** as a by-product in the synthesis of **3a** and **3b**. Even reacting **A** with DMSO yields **4a** in minor amounts. All this points to a high potential of "*tripod*Co⁰" (**A**) to extrude sulfur out of organic sulfur compounds. As a sulfur source which is more resistant to desulfurisation than (PhCH₂S)₂, dibenzothiophene was therefore treated with "*tripod*Co⁰" (**A**). Clean desulfurisation was observed with **4a** as the cobalt compound and biphenyl as the organic product (Scheme 7).

The extrusion of selenium out of organic selenium compounds is as well possible. Treating "*tripod*Co⁰" (A) with PhSeSePh in a ratio of 4:1, in addition to 3c, the olive green



Scheme 7.

compound **4b** is obtained in crystalline form as **4b**·3DME (Scheme 8). The structure of **4b**·3DME resembles that of **4a**·3DME in all comparable details (Figure 5, Table 5). The Co–Se bond has a length of 216.3 pm and is the shortest Co–Se bond reported so far.^[20]





As already mentioned, four different types of crystals of 4a were obtained, depending on the conditions of crystallisation and the solvent employed (see Exp. Section). The structure of the coordination compound was found to be principally the same in all four types of crystals as far as scalar entities (distances, angles) are concerned (Table 5). The different types of solvation present in the different types of crystals of 4a do not markedly affect distances and angles within the coordination compound but they do affect the rotational position of the *tripod* metal entities as a whole as well as the skew of the *tripod* metal cage and the rotational position of its phenyl rings. In all but one crystal the rotation of the tripod metal cages with respect to the Co-S-Co axis corresponds to a staggered arrangement corresponding to the position of the sulfur atom at a crystallographic centre of inversion. In the triclinic unit cell of 4a·DME one of the two crystallographically independent molecules shows a staggered arrangement as well, corresponding to its location at a crystallographic centre of inversion, while the other one, not restricted by crystallographic symmetry requirements, reveals an eclipsed arrangement of the two tripodcobalt entities with respect to the Co-S-Co axis. This indicates that rotation of the tripod cobalt entities around the Co-S-Co axis has a rather low rotation barrier.

The kind of packing of **4** in three types of crystals is interesting in itself: in the triclinic structure of **4a**, which is free of solvate molecules, the basic motif of packing in two dimensions is that of a centred hexagon. Within the (011) plane the centres of the molecules (represented by the sulfur atoms), approach the pattern of planar close packing. The distances within the hexagons are almost equal (1285– 1335 pm), the angles are close to 60° throughout (57.9– 61.6°). The formation of this quite regular arrangement is



Figure 5. The molecular structure of **4a**·3DME in the crystal (hydrogen and DME omitted for clarity). Left: general view; right: projection onto the defined by the three *tripod* phosphorus atoms.

Table 5. Selected bond lengths [pm], bond angles [°] and torsion angles [°] in $4a,\,4b.$

| | $4a \cdot DME^{[a,b,g]}$ | 4a ^[a,c] | 4a·3solv. ^[a,d,e] | 4b·3DME ^{[d,} |
|-------------------------------|--------------------------|----------------------------|------------------------------|------------------------|
| Co1–P1 | 215.8(2) | 217.0(2) | 217.2(1) | 216.3(1) |
| Co1–P2 | 218.1(2) | 216.9(2) | 217.2(1) | 216.3(1) |
| Co1–P3 | 216.2(2) | 216.5(2) | 217.2(1) | 216.3(1) |
| Co1–E | 204.5(2) | 205.5(1) | 205.9(1) | 216.3(1) |
| P1–Co1–P2 | 90.1(2) | 90.7(1) | 91.7(1) | 92.5(1) |
| P1–Co1–P3 | 93.0(2) | 95.4(1) | 91.7(1) | 92.5(1) |
| P2–Co1–P3 | 94.4(2) | 91.7(1) | 91.7(1) | 92.5(1) |
| Co1–E–Co2 | 180.0 | 180.0 | 180.0 | 180.0 |
| P1–Co1–E | 119.4(2) | 120.9(1) | 124.1(1) | 123.5(1) |
| P2–Co1–E | 128.7(2) | 127.2(1) | 124.1(1) | 123.5(1) |
| P3–Co1–E | 122.3(2) | 122.2(1) | 124.1(1) | 123.5(1) |
| $\tau_1^{[h]}$ | 28.4 | 3.6 | 24.6 | 23.4 |
| $\tau_2^{[h]}$ | 25.0 | 10.3 | 24.6 | 23.4 |
| $\tau_{3}^{[h]}$ | 31.8 | 17.1 | 24.6 | 23.4 |
| $f_1^{[i]}$ | 39.2 | 27.6 | 28.5 | 27.0 |
| $f_2^{[i]}$ | 0.2 | 25.9 | 3.8 | 4.7 |
| f ₃ ^[i] | 44.1 | 32.1 | 28.5 | 27.0 |
| $f_4^{[i]}$ | 4.0 | 31.7 | 3.8 | 4.7 |
| f ₅ ^[i] | 24.1 | 20.8 | 28.5 | 27.0 |
| $f_{6}^{[i]}$ | 16.4 | 19.7 | 3.8 | 4.7 |

[a] E = S. [b] Two symmetrically independent molecules, the values are given for the one located at a special position. [c] Two symmetrically independent molecules; both located at a crystallographic centre of inversion. [d] Identical values are obtained as a consequence of the cubic space group $Ia\bar{3}$. [e] Depending on the conditions of crystallisation crystals with DME and THF as solvate (solv.) were obtained.^[22] [f] E = Se. [g] The values in parentheses are standard deviations in units of the last decimals listed. [h] $\tau =$ torsion angles within the chelate cage: $\tau_1 = C4-C1-P1-Ni$, $\tau_2 =$ C4–C2–P2–Ni, $\tau_3 = C4$ –C3–P3–Ni. [i] The torsion angles f involving Hz are defined as follows: $f_1 = Hz1-P1-C100-C101$, $f_2 = Hz1-P1-C100-C101$ P1-C106-C107, $f_3 = Hz2-P2-C200-C201$, $f_4 = Hz2-P1-C206-C201$ C207, $f_5 = Hz3-P3-C300-C301$, $f_6 = Hz3-P3-C306-C307$; Hz-P designates a vector that is vertical to the plane formed by the three tripod phosphorus donor atoms and points towards the observer when, in a projection onto this plane, the vector Co-C4 points away from the observer, such that C4 lies below this plane.^[3]

astonishing at first glance since the molecules within each hexagon show two different kinds of orientation: in one kind the Co–S–Co axis of the molecules is oriented close to

vertical, in the other one close to parallel with respect to the (011) plane. If almost regular hexagons are nevertheless formed, this must mean that the molecules "see" each other as circles of similar radii within the plane, irrespective of their orientation. Constructing the van der Waals surface or as well the solvent accessible surface of the molecules, it is observed that – in contrast to what the view of the ball and stick model (Figure 5) suggests at first glance - the molecules are close to globular in effect. To illustrate this observation, a view of a space-filling model of 4 embedded in a sphere is shown in Figure 6. The van der Waals surface of the molecule is not really spherical of course such that the packing in the molecular structure of 4a in the crystal in the third dimension does not conform to either a hexagonal AB- (hcp) or a cubic ABC-type (fcc) of arrangement. The centres of the molecules of the second layer are somewhat displaced from the position they would occupy in a hexagonal packing, leading to an arrangement as if the hexagonal columns would have undergone a shear motion.



Figure 6. View of the space-filling model of **4** embedded in a sphere. Left: view along Co–S–Co axis; right: view perpendicular to Co– S–Co axis.

4a•DME, containing one solvent molecule per complex entity crystallises in a triclinic space group as well. There are two crystallographically independent molecules in the cell, which arrange themselves in such a way that they again form the pattern of planar hexagonal close packing in the

(011) plane. The Co–S–Co axes of the molecules show two different types of orientation relative to this plane. As described above in the case of **4a**, a close to spherical boundary surface of the molecules allows for this regular arrangement, irrespective of the orientation of the molecules. The distances within the centred hexagons span the narrow range from 1280 pm to 1354 pm, the angles differ only slightly from the ideal value of 60° (57.1°–63.5°). The stacking of these planes is such that a pair of layers is interspersed with a layer of solvent molecules. The layers of the solvent molecules show the same type of planar hexagonal close packing as is observed for the molecules of the coordination compound. The type of stacking is close to the one characteristic of a tetragonally deformed, body-centred cubic pattern (bcc).^[21]

4a·3DME crystallises in the space group $Ia\bar{3}$ and contains layers of complex molecules with a planar hexagonal close packed arrangement as required by symmetry. The stacking sequence is that of an exact ABC pattern, also as required by crystal symmetry. The close packed layers in 4a·3DME are, however, different from the ones observed in the structures of 4a and 4a·DME (see above). In 4a·3DME there is no direct contact between the complex molecules as was found for 4a and 4a. DME, but all pairs of molecules are separated by a solvent molecule with the centre of the solvent molecule in the middle of the vector, connecting the centres of the coordination compounds. The distance between the centres of the coordination compounds, which is at the same time the distance within the hexagons, is around 1820 pm. The corresponding distance in 4a and 4a·DME, where there is a direct contact between the coordination compounds themselves, while the solvent molecules, if present (4a·DME), occupy the space between the layers, amounts to around 1300 pm (see above). The solvent molecules in 4a·3DME hence separate the coordination compounds by around 500 pm. Principally the same type of layers and packing is observed for 4b·3DME, the selenium analogue of 4a·3DME. The distance between the centres of the coordination compounds is 1890 pm in this case (4a·3DME: 1820 pm), reflecting the larger size of selenium as compared to sulfur.^[22]

The arrangement of the solvent molecules thus far described with the focus on close packed planes corresponds



Figure 7. Cuboctahedral cage of DME molecules (symbolised by small balls) surrounding the complex molecule (symbolised by big ball) in the molecular structure of **4**·3DME in the crystal.

to a complete shielding of the coordination compounds by a cuboctahedral cage of solvent molecules (Figure 7). The radius of this cage is 910 pm in $4a \cdot 3DME$ and 945 pm in $4b \cdot 3DME$, of course corresponding exactly to one half of the distance between the centres of the coordination molecules (see above). The fact that regular cuboctahedra are formed as the solvent cages of molecules of 4 is a clear indication of the close to spherical surface of the molecules (Figure 6) and of the outstanding shielding properties of the *tripod* ligand.

Conclusions

The nickel(0) compound [*tripod*₄Ni₃] (1) obtained by KC₈ reduction of THF solutions of [(DME)NiBr₂] and *tripod* undergoes oxidative addition with dichalcogenides REER (E = S, Se; R = *t*Bu, Ph) to produce the nickel(I) species [*tripod*Ni(ER)] (2). Compounds 2 are pseudo tetrahedral 17 valence electron molecules with magnetic moments corresponding to one unpaired electron per molecule. They are reversibly oxidised to 16 valence electron species [*tripod*Ni(ER)]⁺ (2⁺).

Cobalt(I) compounds [*tripod*Co(ER)] (3) isoelectronic to the nickel(II) species [*tripod*Ni(ER)]⁺ (2⁺) are obtained by treating solutions prepared from [*tripod*CoCl₂] in THF and KC₈ under an argon atmosphere with dichalcogenides REER (E = S, Se; R = *t*Bu, Ph). Compounds 3 are pseudo tetrahedral 16 valence electron species with magnetic moments corresponding to two unpaired electrons per molecule. They are reversibly oxidised to 15 valence electron species [*tripod*Co(ER)]⁺ (3⁺).

Depending on the reaction conditions and on the type of dichalcogenide employed the reaction, which normally leads to the formation of 3, may be biased to produce [tripodCoECotripod], 4 (E = S, Se), instead. Compounds 4 contain a linear tripodCo-E-Cotripod dumbbell with very short Co-E distances (Co-S: 205.4 pm; Co-Se: 216.3 pm), the corresponding bond order being at least two in each case. Compounds 4 are members of a family of isoelectronic species containing dumbbell shaped M-E-M entities with short M–E bonds; all these complexes $[L_n MEML_n]$ are 36 valence electron compounds; the difference in electron count of E (E may be an element of group III to group VI) is compensated for by the appropriate electron count of the L_nM entity and the overall charge of the complex in each case. Quantum chemical models suggest that the HOMO in such compounds corresponds to a degenerate pair of metal orbitals. The fact, that [tripodCoSCotripod] (4a) shows three reversible or quasi-reversible oxidation waves supports this suggestion.

Compounds **4** crystallise in four different pseudopolymorphs differing in the content and kind of solvate molecules. In all these pseudopolymorphs hexagonally closed packed planes are a characteristic basic pattern. In one type of pseudopolymorph each coordination compound is embedded in a cuboctahedral cage of solvate molecules. This rather unconventional pattern of molecular packing is a consequence of the close to spherical shape of coordination compounds 4.

Experimental Section

General: All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or by working in a glove box. Solvents were dried with potassium (THF, DME) or CaH₂ (CH₂Cl₂, Et₂O, PE 40/60), distilled, and thoroughly degassed prior to use. Deuterated solvents were dried with potassium ([D₈]THF) or CaH₂ (CD₂Cl₂), vacuum distilled, degassed by three successive "freeze-pump-thaw" cycles and stored in Teflon valve ampoules under argon.

NMR: Bruker Avance DPX 200 at 200.120 MHz (1H), 50.323 MHz $({}^{13}C{}^{1}H{})$, 81.015 MHz $({}^{31}P{})$; T = 303 K unless stated otherwise; chemical shifts (δ) in ppm referenced to (residual proton) peaks of CD_2Cl_2 (¹H: δ = 5.32; ¹³C: δ = 53.8 ppm) and [D₈]THF (¹H: δ = 1.73, 3.58; ¹³C: δ = 25.5, 67.7) as internal standards; ³¹P chemical shifts (δ) in ppm with respect to 85% H₃PO₄ (³¹P: δ = 0 ppm) as external standard. FAB-/HR-FAB-MS: Finnigan MAT 8400 spectrometer, xenon, matrix: 4-nitrobenzyl alcohol. LIFDI-MS: JEOL JMS-700 double-focusing magnetic sector mass spectrometer.^[23] IR: BioRad Excalibur FTS 3000 spectrometer using CsI discs. UV/ Vis: Perkin-Elmer Lambda 19; 0.2 cm cells (Hellma, suprasil). Cyclic Voltammetry (CV): Metrohm "Universal Meß- und Titriergefäß", Metrohm GC electrode RDE 628, platinum electrode, SCE electrode, EG&G Princeton Applied Research potentiostate Model 273, potentials in mV vs. SCE at 25 °C, sample 10⁻³ M in 0.1 M nBu₄NPF₆/CH₂Cl₂. Differential Scanning calorimetry (DSC): Mettler DSC 30, argon, 30-600 °C, heating rate: 10 K min⁻¹. Thermogravimetric Analysis (TGA): Mettler TC 15, argon, 30-600 °C, heating rate: 10 K min⁻¹. EPR: Bruker ELEXSYS E500; X-band; v = 9.44 GHz; external standard diphenylpicrylhydrazyl. All measurements were carried out at 293 K in a standard cavity ER 4102St. Xsophe, version 1.0.2ß was used for simulation of the spectra using the following parameters: ⁵⁸Ni (I = 0; 100%); g- and A-strain Gaussian line shape model. Elemental analyses were recorded by the analytical service of the Department of Chemistry Heidelberg.

Materials: 1,1,1-Tris[(diphenylphosphanyl)methyl]ethane (*tripod*), was prepared according to a literature procedure.^[24] All other reagents were obtained from commercial sources and used as received unless explicitly stated. Silica gel (Kieselgel z. A., 0.06–0.20 mm, J. T. Baker Chemicals B. V.) used for chromatography and kieselgur (Erg. B.6, Riedel-de Haën AG) used for filtration were degassed at 10^{-2} mbar for 48 h and saturated with argon.

General Procedure for the Synthesis of Solutions Containing A or 1: KC₈ (297 mg, 2.2 mmol), prepared by heating potassium (86 mg, 2.2 mmol) with graphite (211 mg, 17.6 mmol) was added to a solution of [*tripod*CoCl₂]^[25] (754 mg, 1 mmol) or [*tripod*NiBr₂] (840 mg, 1 mmol), respectively, in THF (20 mL), prepared by treating either [CoCl₂] (130 mg, 1 mmol) or [(DME)NiBr₂] (309 mg, 1 mmol) with equimolar amounts of *tripod* (625 mg, 1 mmol). The resulting suspension was sonicated until the colour changed to orange brown in the case of A ["*tripod*Co⁰"] and yellow brown in the case of 1 ([*tripod*₄Ni₃]). The reduction was monitored by UV/Vis spectroscopy until the spectra indicated completeness of the reaction showing a strong band at $\lambda_{max} = 680$ nm (A) and $\lambda_{max} = 380$ nm (1), respectively. The reaction mixture was then filtered through kieselgur by means of a syringe to remove the remaining graphite.



Synthesis of [tripodNi(ER)] (2a-c): To a THF solution containing 1, prepared from [tripodNiBr₂] (840 mg, 1 mmol) and KC₈ (297 mg, 2.2 mmol) (see above) a solution of either $(PhS)_2$ (109 mg, (153 mmol), $(t\text{BuS})_2$ (89 mg, (153 mmol)) or $(t\text{PhSe})_2$ (153 mg, 0.5 mmol) in THF (10 mL) was added. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40-60 °C) and transferred to a column containing silica gel ($\emptyset = 3 \text{ cm}, l = 5 \text{ cm}$), conditioning with petroleum ether (boiling range 40-60 °C) via a cannula. After elution by 50 mL of petroleum ether (boiling range 40-60 °C) and 50 mL of diethyl ether, the products were eluted with 50 mL of dichloromethane (for 2a, 2c) or 50 mL of DME (for 2b) as orange to dark red coloured bands. Having removed the solvent in vacuo, red microcrystalline powders were obtained. Red crystals, suitable for X-ray structural analysis, were obtained by layering saturated dichloromethane solutions (2a, 2c) and DME solutions (2b) with diethyl ether. Yields for 2a: 640 mg, 0.81 mmol, 81%; 2b: 455 mg, 0.59 mmol, 59%; 2c: 545 mg, 0.65 mmol, 65%.

2a: $C_{47}H_{44}NiP_3S \cdot 0.35CH_2Cl_2$ (822.24): calcd. C 69.16, H 5.48, P 11.30, S 3.90; found C 69.16, H 5.76, P 11.06, S 3.82. MS (HR-FAB⁺); *m*/*z* [fragment]: 791.1723 [M⁺, ⁵⁸Ni], 793.1674 [M⁺, ⁶⁰Ni] (calcd. *m*/*z*: 791.1730, 793.1685). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹cm⁻¹]: 390 (sh, 4200), 500 (sh, 1420), 950 (160). CV: $E_{1/2} = -290$ mV (rev. ox., $\Delta E = 140$ mV), $E_p^A = 850$ mV, $E_p^C = -1560$ mV. DSC/TGA: endothermic melting process (m.p. 220 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 13.8%; calcd. final weight [Ni₂P₃]: 12.8%. For magnetic and EPR data see Table 2.

2b:^[26] C₄₅H₄₈NiP₃S (772.56): calcd. C 69.96, H 6.26; found C 68.54, H 6.07. MS (HR-FAB⁺); *m*/*z* [fragment]: 771.2043 [M⁺, ⁵⁸Ni], 773.2022 [M⁺, ⁶⁰Ni] (calcd. *m*/*z*: 771.2043, 773.2024). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹ cm⁻¹]: 380 (sh, 3350). CV: $E_{1/2} = -470$ mV (rev. ox., $\Delta E = 140$ mV), $E_p^A = -200$ mV (irreversible; reverse scan: -950 mV), $E_p^A = 1030$ mV. DSC/TGA: endothermic melting process (m.p. 210 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 10.1%; calcd. final weight [Ni₂P₃]: 13.5%. For magnetic and EPR data see Table 2.

2c: $C_{47}H_{44}NiP_3Se$ (839.44): calcd. C 67.25, H 5.28, P 11.07; found C 69.02, H 5.36, P 11.05. MS (HR-FAB⁺); *m/z* [fragment]: 839.1244 [M⁺, ⁵⁸Ni], 841.1170 [M⁺, ⁶⁰Ni] (calcd. *m/z*: 839.1177, 841.1165). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹ cm⁻¹]: 520 (1900), 900 (320). CV: $E_{1/2} = -180$ mV (qrev. ox., $\Delta E = 140$ mV), $E_P^A = 800$ mV, $E_P^A = 1540$ mV. DSC/TGA: endothermic melting process (m.p. 230 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 16.8%; calcd. final weight [Ni₂P₃]: 12.5%. For magnetic and EPR data see Table 2.

Synthesis of [tripodCo(ER)] (3a-c): To a THF solution containing A, prepared from [tripodCoCl₂]^[25] (754 mg, 1 mmol) and KC₈ (297 mg, 2.2 mmol) (see above) a solution of either (PhS)₂ (109 mg, 0.5 mmol), (tBuS)₂ (89 mg, 0.5 mmol) or (PhSe)₂ (153 mg, 0.5 mmol) in THF (10 mL) was added. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40-60 °C) and transferred to a column containing silica gel ($\emptyset = 3 \text{ cm}, l = 5 \text{ cm}$), conditioning with petroleum ether (boiling range 40-60 °C) via a cannula. After elution by 50 mL of petroleum ether (boiling range 40-60 °C) and 50 mL of diethyl ether, the products were eluted as brown bands by 50 mL of DME (3a, 3b) or by 50 mL of a 1:1 mixture of DME and diethyl ether (3c). Having removed the solvent in vacuo, brown microcrystalline powders were obtained. Dark brown crystals, suitable for X-ray structural analysis, were obtained by layering saturated DME solutions with diethyl ether. Yields for 3a: 340 mg,

0.43 mmol, 43%; **3b**: 365 mg, 0.47 mmol, 47%; **3c**: 380 mg, 0.45 mmol, 45%.

3a: $C_{47}H_{44}CoP_3S$ (792.79): calcd. C 71.21, H 5.59, P 11.72, S 4.04; found C 71.28, H 5.59, P 11.53, S 4.16. MS (HR-FAB⁺); *m/z* [fragment]: 792.1691 [M⁺] (calcd. *m/z*: 792.1709). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹ cm⁻¹]: 320 (6600), 360 (4780), 650 (150), 760 (150), 900 (130), 1170 (300), 1320 (sh, 260). CV: $E_{1/2} = -240$ mV (rev. ox., ΔE = 120 mV), $E_{1/2} = 500$ mV (rev. ox., $\Delta E = 120$ mV), $E_P^A = 1600$ mV. μ_{eff} (300 K) [μ_B] = 3.31. DSC/TGA: endothermic melting process (m.p. 270 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 19.8%; calcd. final weight [Co₂P₃]: 13.3%.

3b: C₄₅H₄₈CoP₃S (772.80): calcd. C 69.94, H 6.26, P 12.02, S 4.15; found C 70.08, H 6.31, P 11.85, S 4.44. MS (HR-FAB⁺); *m/z* [fragment]: 772.2025 [M⁺] (calcd. *m/z*: 772.2022). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹cm⁻¹]: 320 (6100), 360 (6700), 740 (130), 920 (170), 1170 (380), 1350 (sh, 310). CV: $E_{1/2} = -280$ mV (rev. ox., $\Delta E = 120$ mV), $E_{\rm p}^{\rm A} = 810$ mV, $E_{\rm p}^{\rm A} = 1210$ mV, $E_{\rm p}^{\rm A} = 1510$ mV. $\mu_{\rm eff}$ (300 K) [$\mu_{\rm B}$] = 3.12. DSC/TGA: endothermic melting process (m.p. 240 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 17.8%; calcd. final weight [Co₂P₃]: 13.6%.

3c: $C_{47}H_{44}CoP_3Se DME$ (929.80): calcd. C 65.88, H 5.85, P 9.99; found C 65.42, H 5.65, P 10.02. MS (HR-FAB⁺); *m/z* [fragment]: 838.1207 [M⁺, ⁷⁸Se], 840.1188 [M⁺, ⁸⁰Se], 842.1201 [M⁺, ⁸²Se] (calcd. *m/z*: 838.1187, 840.1159, 842.1184). UV/Vis (THF), λ_{max} [nm] (ε) [M⁻¹cm⁻¹]: 310 (6900), 370 (4440), 770 (150), 760 (150), 1170 (320), 1360 (sh, 280). CV: $E_{\rm p}^{\rm A}$ = -310 mV, $E_{\rm p}^{\rm C}$ = -760 mV. $\mu_{\rm eff}$ (300 K) [$\mu_{\rm B}$] = 3.17. DSC/TGA: endothermic melting process (m.p. 260 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 15.3%; calcd. final weight [Co_2P_3]: 11.3%. Synthesis of [tripodCoSCotripod] (4a): To a THF solution containing A, prepared from [tripodCoCl2][25] (754 mg, 1 mmol) and KC_8 (297 mg, 2.2 mmol) (see above) a solution of either PhCH₂SSCH₂Ph (44 mg, 0.25 mmol) or dibenzothiophene (92 mg, 0.5 mmol) in THF (10 mL) was added. Within two hours the colour of the solution changes to a brownish green. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40-60 °C) and transferred to a column containing silica gel ($\emptyset = 3 \text{ cm}, l = 5 \text{ cm}$), conditioning with petroleum ether (boiling range 40-60 °C) via a cannula. After elution by 50 mL of petroleum ether (boiling range 40-60 °C) and 50 mL of diethyl ether, the product was eluted by 50 mL of DME as a dark green band. Having removed the solvent in vacuo, a green microcrystalline powder is obtained. Depending on the conditions of crystallisation different kinds of crystals, suitable for X-ray structural analysis, could be obtained. Storing a concentrated solution of 4a in THF or DME at -10 °C yields crystals of 4a·3THF and 4a·3DME respectively. By layering saturated DME solutions with diethyl ether crystals of 4a. DME were obtained, using petroleum ether (boiling range 40-60 °C) instead leads to the crystallisation of 4a. Yield (calcd. for 4a·DME): 410 mg, 0.30 mmol, 60%. Correct analytical data was obtained for C82H78P6SCo2·DME (see 4a) while for the other polymorphs, the microanalytical data always indicated a loss of solvent during the preparation of samples for microanalysis.

4a: $C_{82}H_{78}Co_2P_6S$ ·DME (1489.42): calcd. C 69.35, H 5.96, P 12.48, S 2.15; found C 69.11, H 5.95, P 12.35, S 2.30. ¹H NMR ([D₈]-THF): $\delta = 1.53$ (s, 6 H, *tripod*-CH₃), 2.71 (s, 12 H, *tripod*-CH₂), 3.39 (s, 6 H, O-CH₃), 3.55 (s, 4 H, O-CH₂), 6.79–7.79 (m, 60 H, arom. *H*) ppm. ³¹P{¹H} NMR ([D₈]THF): $\delta = 33.2$ (br. s) ppm. ¹³C{¹H} NMR ([D₈]THF): $\delta = 28.9$ (br. s, *tripod*-CH₂), 36.8 (s, CH₃-C_q), 37.3 (s, *tripod*-CH₃), 59.0 (s, O-CH₃), 72.2 (s, O-CH₂), 128.0 (s, arom. *tripod*-C_p), 129.6 (m, arom. *tripod*-C_m), 139.2 (m,

Table 6. Crystal data for 2a-c and 3a-c.

| Compound | 2a | 2b | 2c | 3a | 3b | 3c |
|--|--|--|--|--|--|---|
| Empirical formula | C47H44P3SNi 0.35CH2 | ClC ₄₅ H ₄₈ P ₃ SNi | C47H44P3SeNi | C47H44P3SCo | C45H48P3SCo | C ₄₇ H ₄₄ P ₃ SeCo·DMI |
| Molecular mass | 822.24 | 772.56 | 839.44 | 792.79 | 772.80 | 929.80 |
| Crystal size [mm] | $0.20 \times 0.20 \times 0.15$ | $0.20 \times 0.20 \times 0.10$ | $0.20 \times 0.20 \times 0.10$ | $0.25 \times 0.20 \times 0.10$ | $0.25 \times 0.20 \times 0.20$ | $0.25 \times 0.20 \times 0.10$ |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic | monoclinic | monoclinic |
| Space group (No.) | $P2_{1}/c$ (14) | $P2_1/c$ (14) | Pn (7) | $P\overline{1}(2)$ | $P2_1/c$ (14) | $P2_1/n(14)$ |
| Lattice constants: | | | | | | |
| <i>a</i> [pm] | 991.1(2) | 1965.0(4) | 1289.9(3) | 1514.3(3) | 1280.5(3) | 1988.9(4) |
| <i>b</i> [pm] | 1682.2(3) | 1034.0(2) | 3525.1(7) | 1708.9(3) | 1540.2(3) | 969.2(2) |
| <i>c</i> [pm] | 2520.1(5) | 2100.1(4) | 1825.0(4) | 1843.3(4) | 2038.8(4) | 2344.6(5) |
| a [°] | 90 | 90 | 90 | 72.87(3) | 90 | 90 |
| β[°] | 94.11(3) | 115.81(3) | 109.44(3) | 67.36(3) | 95.61(3) | 97.81(3) |
| γ [°] | 90 | 90 | 90 | 64.84(3) | 90 | 90 |
| $V[10^{6} \text{ pm}^{3}]$ | 4191 | 3841 | 7825 | 3936 | 4002 | 4478 |
| Ζ | 4 | 4 | 8 | 4 | 4 | 4 |
| $d_{\text{calcd.}} [\text{g cm}^{-3}]$ | 1.303 | 1.336 | 1.425 | 1.338 | 1.283 | 1.379 |
| T [K] | 200 | 200 | 200 | 200 | 200 | 200 |
| Scan range | $2.9^{\circ} \le 2\theta \le 53.6^{\circ}$ | $2.3^\circ \le 2\theta \le 55.1^\circ$ | $2.6^{\circ} \le 2\theta \le 55.0^{\circ}$ | $2.4^{\circ} \le 2\theta \le 54.9^{\circ}$ | $3.2^{\circ} \le 2\theta \le 55.0^{\circ}$ | $2.5^{\circ} \leq 2\theta \leq 55.0^{\circ}$ |
| Method | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ |
| Scan speed [s frame ⁻¹] | 10 | 20 | 10 | 8 | 8 | 15 |
| No. of reflections measured | 15998 | 13903 | 23350 | 23706 | 16517 | 17878 |
| No. of unique reflections | 8722 | 8441 | 23110 | 16475 | 9098 | 10211 |
| No. of reflections observed | 4828 | 4473 | 14773 | 7824 | 6611 | 5603 |
| Observation criterion | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ |
| No. of parameters refined | 481 | 459 | 618 | 979 | 492 | 532 |
| Residial electron density | 2.01 | 0.46 | 1.19 | 1.21 | 0.43 | 0.43 |
| 10^{-6} [e pm ⁻³] | | | | | | |
| R_1/R_w (%) F^2 refinement | 8.8/27.3 | 6.9/16.0 | 7.7/17.5 | 8.8/27.2 | 4.3/9.8 | 5.5/10.8 |

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| Table 7. C | rystal data | for 4a, | 4a·DME, | 4a·3DME, | 4a·3THF | and | 4b·3DME |
|------------|-------------|---------|---------|----------|---------|-----|---------|
|------------|-------------|---------|---------|----------|---------|-----|---------|

| Compound | 4a | 4a·DME | 4a·3DME | 4a·3THF | 4b·3DME |
|--|---|--|---|---|--|
| Empirical formula | C ₈₂ H ₇₈ P ₆ SCo ₂ | C ₈₂ H ₇₈ P ₆ SCo ₂ ·DME | C ₈₂ H ₇₈ P ₆ SCo ₂ ·3DME | C ₈₂ H ₇₈ P ₆ SCo ₂ ·3THF | C ₈₂ H ₇₈ P ₆ SeCo ₂ ·3DME |
| Molecular mass [g] | 1399.30 | 1489.42 | 1669.66 | 1615.62 | 1716.56 |
| Crystal size [mm] | $0.20 \times 0.10 \times 0.10$ | $0.20 \times 0.10 \times 0.10$ | $0.10 \times 0.10 \times 0.10$ | $0.25 \times 0.25 \times 0.25$ | $0.25 \times 0.25 \times 0.20$ |
| Crystal system | triclinic | triclinic | cubic | cubic | cubic |
| Space group (No.) | <i>P</i> 1 (2) | P1 (2) | Ia3 (206) | Ia3 (206) | Ia3 (206) |
| Lattice constants: | | | | | |
| <i>a</i> [pm] | 1284.1(3) | 1286.4(3) | 2575.0(3) | 2598.1(3) | 2575.8(3) |
| <i>b</i> [pm] | 1515.0(3) | 2086.8(4) | 2575.0(3) | 2598.1(3) | 2575.8(3) |
| <i>c</i> [pm] | 1778.4(4) | 2269.5(5) | 2575.0(3) | 2598.1(3) | 2575.8(3) |
| a [°] | 90.85(3) | 69.31(3) | 90 | 90 | 90 |
| β [°] | 90.88(3) | 80.25(3) | 90 | 90 | 90 |
| γ [°] | 90.03(3) | 80.05(3) | 90 | 90 | 90 |
| V [10 ⁶ pm ³] | 3459 | 5575 | 17074 | 17537 | 17090 |
| Ζ | 2 | 3 | 8 | 8 | 8 |
| $d_{\text{calcd.}} [\text{g cm}^{-3}]$ | 1.343 | 1.331 | 1.299 | 1.114 | 1.334 |
| <i>T</i> [K] | 200 | 200 | 200 | 200 | 200 |
| Scan range | $2.3^{\circ} \le 2\theta \le 55.0^{\circ}$ | $1.9^{\circ} \le 2\theta \le 55.6^{\circ}$ | $3.9^{\circ} \le 2\theta \le 55.0^{\circ}$ | $3.8^{\circ} \le 2\theta \le 53.5^{\circ}$ | $3.9^\circ \le 2\theta \le 54.9^\circ$ |
| Method | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ | ω scan, $\Delta \omega = 1^{\circ}$ |
| Scan speed [s frame ⁻¹] | 10 | 8 | 10 | 10 | 20 |
| No. of reflections measured | 20368 | 35483 | 6559 | 6255 | 6556 |
| No. of unique reflections | 15210 | 23916 | 3278 | 3127 | 3278 |
| No. of reflections observed | 9733 | 14234 | 2454 | 1865 | 2554 |
| Observation criterion | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ | $I \ge 2\sigma$ |
| No. of parameters refined | 828 | 1335 | 172 | 145 | 163 |
| Residial electron density | 0.46 | 3.32 | 1.18 | 1.07 | 0.80 |
| $10^{-6} [e pm^{-3}]$ | | | | | |
| R_1/R_w (%) F^2 refinement | 5.4/11.3 | 7.3/23.4 | 4.8/14.9 | 8.1/30.1 | 3.9/11.5 |

arom. *tripod*- C_0), 159.0 (m, arom. C_q) ppm. ¹³C DEPT NMR ([D₈]-THF): $\delta = 28.9$ (br. s, *tripod*-CH₂), 37.3 (s, *tripod*-CH₃), 59.0 (s, O-CH₃), 72.2 (s, O-CH₂), 127.9 (s, arom. *tripod*- C_p), 129.7 (m, arom. *tripod*- C_m), 139.6 (m, arom. *tripod*- C_o) ppm. MS (HR-FAB⁺); *m/z* [fragment]: 1398.3027 [M⁺] (calcd. *m/z*: 1398.2914). UV/Vis (THF), λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 420 (24650), 640 (7500). CV: $E_{1/2} = -700$ mV (rev. ox., $\Delta E = 110$ mV), $E_{1/2} = -40$ mV (qrev. ox., $\Delta E = 120$ mV). DSC/TGA: endothermic melting process (m.p. 350 °C) initiates exothermic decomposition. Decomposition is complete at 600 °C; exp. final weight: 16.7%; calcd. final weight [Co₂P₃]: 14.2%.

Synthesis of [*tripod*CoSeCotripod] (4b): To a THF solution containing A, prepared from [*tripod*CoCl₂]^[25] (754 mg, 1 mmol) and KC₈ (297 mg, 2.2 mmol) (see above) a solution of PhSeSePh (77 mg, 0.25 mmol) in THF (10 mL) was added. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40–60 °C) and transferred to a column containing silica gel ($\emptyset = 3 \text{ cm}$, l = 5 cm), conditioning with petroleum ether (boiling range 40–60 °C) via a cannula. After elution by 50 mL of petroleum ether (boiling range 40–60 °C) and 50 mL of diethyl ether, **3c** was eluted by 50 mL of a 1:1 mixture of DME and diethyl ether (see above). Small amounts of a dark solid remained on top of the column, which could be eluted with DME as an olive green coloured band. Dark green crystals of **4a**·3DME, suitable for X-ray structural analysis, could be obtained by storing a concentrated solution of **4b** in DME at –10 °C.

4b: MS (HR-FAB⁺); *m/z* [fragment]: 1444.2371 [M⁺, ⁷⁸Se], 1446.2424 [M⁺, ⁸⁰Se], 1448.2469 [M⁺, ⁸²Se] (calcd. *m/z*: 1444.2400, 1446.2376, 1448.2409).

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius-Kappa CCD diffractometer with a low-temperature unit

using graphite-monochromated Mo- K_a radiation. The data collected were processed using the standard Nonius software^[27] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[28,29] Graphical handling of the structural data during solution and refinement was performed with XPMA.^[30] Structural representations were generated using Winray 32.^[31] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. Data relating to the structure determinations are compiled in Tables 6 and 7.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-657989 (for 2c), -657990 (for 4a·3THF), -657991 (for 4a·3DME), -657992 (for 4a·DME), -657993 (for 3c), -657994 (for 3b), -657995 (for 3a), -657996 (for 4a), -657997 (for 2b), -657998 (for 2a), -657999 (for 4b·3DME). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk.

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