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Synthesis and reactivity of half-sandwich type cobalt, rhodium and iridium complexes containing trithiocarbonate, dithiocarbonate, *N*-cyanodithiocarbimate, 1,1-dicyanoethylene-2,2-dithiolate and 1,1-dicyanoethylene-2,2-diselenolate as chelating ligands

Helmut Werner *, Lothar Scheller

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Dedicated to Professor Malcolm Green on the occasion of his 75th birthday, to commemorate the golden years of the fierce Fischer/Wilkinson competition

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ABSTRACT

A series of half-sandwich type complexes with $[(C_5R_5)Co(L)]$ (R = H, Me; L = PR_3, $P(OR)_3$, CNR), $[(C_5R_5)RhPR'_3]$ (R = H, Me) and $[(C_5H_5)Ir(PiPr_3)]$ as building blocks and trithiocarbonate, dithiocarbonate, *N*-cyanodithiocarbimate, 1,1-dicyanoethylene-2,2-dithiolate and 1,1-dicyanoethylene-2,2-diselenolate as chelating ligands was prepared. They were characterized by mass spectrometry and IR, UV, and NMR spectroscopic techniques. The trithiocarbonate derivatives $[(C_5R_5)Co(PMe_3)(S_2C{=}S)]$ (R = H, Me) were oxidized with $[Fe(C_5H_5)_2]X$ (X = BF_4, PF_6) to the cationic compounds $[(C_5R_5)Co(PMe_3)(S_2C{=}S)]X$. The oxidation potentials of the half-sandwich type complexes were determined by cyclovoltammetry. The reaction of $[(C_5Me_5)Co(PMe_3)(S_2C{=}S)]$ with tetracyanoethylene (TCNE) led to a ligand fragment exchange and gave the cobalt 1,1-dicyanoethylene-2,2-dithiolate $[(C_5Me_5)Co(PMe_3)\{S_2C{=}C(CN)_2\}]$ in good yield.

1. Introduction

Following our work on half-sandwich type cobalt and rhodium complexes formed from CS_2, CSe_2 and related heteroallenes [1,2], we were interested to find out whether dinuclear compounds of the general composition $[(C_5R_5)(L)M(S_2C{=}CS_2)M(L)(C_5R_5)]$ could be prepared and, if they could, whether they would behave as electron donor molecules similar to tetrathiofulvalenes [3]. In 2000, Rauchfuss and co-workers disclosed that the dechlorination of the tetrathiooxalato complex $[\{(C_5Me_5)(Cl)Rh\}_2(\mu\text{-}S_2S_4)]$ led to the formation of the ethylenetetrathiolato compound $[\{(C_5Me_5)Rh\}_2(\mu\text{-}C_2S_4)]$ of type **A** (Scheme 1) [4]. Earlier, Dahl and co-workers described the high-yield synthesis and molecular structure of $[\{(C_5Me_5)Ni\}_2(\mu\text{-}C_2S_4)]$, being the first example of a type **A** complex [5]. More recently, Guyon et al. reported that the reaction of $[(C_5Me_5)Co(CO)_2]$ with CS_2 gave an isomeric mixture of the cobalt compound $[\{(C_5Me_5)Co\}_2(\mu\text{-}C_2S_4)]$ containing both type **A** and type **B** derivatives [6]. In addition, with ML_n building blocks other than $[(C_5Me_5)M]$ other complexes of type **A** were obtained and investigated for their optical and electrochemical properties [7].

The aim of this study was to prepare complexes of type **B** on a route as straightforward as possible. In order to reach this goal, we decided to use trithiocarbonato, dithiocarbonato and *N*-cyanodithiocarbimato complexes containing the molecular unit $[(C_5R_5)M(L)]$ (M = Co, Rh, Ir; R = H, Me) as starting materials. By applying established procedures to convert compounds with the fragments $S_2C{=}S$, $S_2C{=}O$ and $S_2C{=}NR$ by methylation to the corresponding cationic species, we hoped that by subsequent abstraction of SMe, OMe and NR_2 the target molecules could be obtained.

2. Results and discussion

The cyclopentadienyl cobalt diiodides **1a**, **1f** and **1g** reacted with equimolar amounts of K_2CS_3 in CH_2Cl_2 at room temperature to give the corresponding trithiocarbonates **4a**, **4f** and **4g** in good yields (Scheme 2). Prior to our work, Manning and co-workers prepared the analogues **4b–4e** on a similar route [8]. In contrast to Manning's synthetic protocol, we found that K_2CS_3 is more favourable than Na_2CS_3 as the precursor for the trithiocarbonato ligand because it is less sensitive to hydrolysis.

* Corresponding author. Tel.: +49 931 31 85270; fax: +49 931 84623.
E-mail address: helmut.werner@mail.uni-wuerzburg.de (H. Werner).

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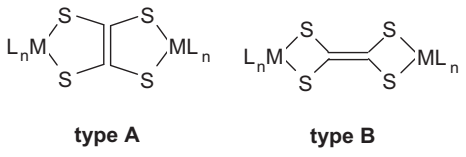
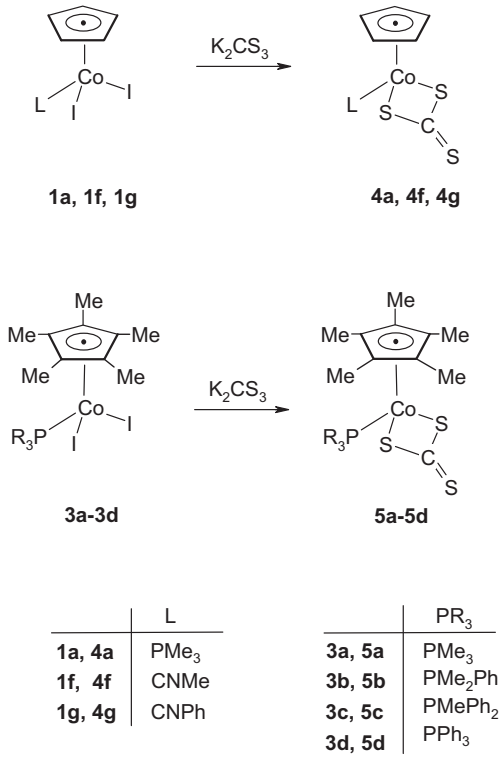


Scheme 1.



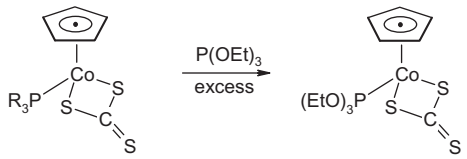
	L
1a, 4a	PMe_3
1f, 4f	CNMe
1g, 4g	CNPh

	PR_3
3a, 5a	PMe_3
3b, 5b	PMe_2Ph
3c, 5c	$PMePh_2$
3d, 5d	PPh_3

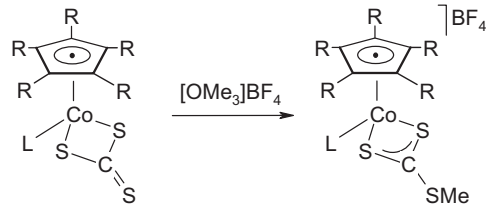
Scheme 2. Complex **4b**: $[(C_5H_5)Co(PMe_2Ph)(S_2C{=}S)]$; **4c**: $[(C_5H_5)Co(PMePh_2)(S_2C{=}S)]$; **4d**: $[(C_5H_5)Co(PPh_3)(S_2C{=}S)]$; **4e**: $[(C_5H_5)Co\{P(OPh)_3\}(S_2C{=}S)]$.

With **3a**–**3d** as starting materials, the pentamethylcyclopentadienyl complexes **5a**–**5d** were obtained (Scheme 2) and, similar to **4a**, **4f**, **4g**, characterized by elemental analysis and spectroscopic techniques. The diiodides **3a** and **3c** were prepared by ligand displacement from $[(C_5Me_5)Co(CO)I_2]$ and PR_3 using the synthetic procedure described by Fairhurst and White [9]. In contrast to King's work [10], the triphenylphosphine derivative **3d** was obtained as the sole product in high yield from $[(C_5Me_5)CoI_2]_2$ and PPh_3 by cleavage of the iodide bridges. With regard to the IR spectra of **4a**, **4f**, **4g** and **5a**–**5d** we note that neither the ring ligand nor the phosphine has a significant influence on the frequency of the C=S stretching mode. The same is true for the band in the UV spectra of **4a** and **5a**–**5d** at λ 356–362 nm, which is assigned to a $\pi \rightarrow \pi^*$ interligand transition of the $S_2C{=}S$ ligand [11].

Attempts to abstract the exocyclic sulfur atom of the $MS_2C{=}S$ unit in the **4a**–**4g** and the **5a**–**5d** series failed. The reactions of **4a**, **4b** and **4d** with an excess of $P(OEt)_3$ in benzene at room temperature or under reflux only led to a phosphine/phosphite exchange and gave the substitution product **4h** in moderate to good yield (Scheme 3). Under similar conditions, tetrathiofulvalene derivatives were obtained from five-membered 1,3-dithio-2-thiones and $P(OEt)_3$ [12]. Similar attempts with **4a** or **4e** and P*n*Bu$_3$ as starting materials also gave the substitution product $[(C_5H_5)Co(P\textit{n}Bu_3)(S_2C{=}S)]$, which was already known [8].



Scheme 3.



	R	L
6a	H	PMe_3
6b	H	PMe_2Ph
6c	H	$PMePh_2$
6d	H	PPh_3
6e	H	CHMe

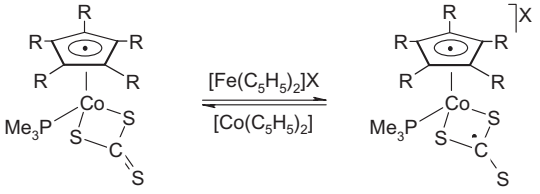
	R	L
6f	H	CNPh
7a	Me	PMe_3
7b	Me	PMe_2Ph
7c	Me	$PMePh_2$
7d	Me	PPh_3

Scheme 4.

Treatment of **5a** or **5c** with $P(OEt)_3$ (ratio 1:5) in benzene at 40 °C under UV irradiation afforded mixtures of $[(C_5Me_5)Co\{P(OEt)_3\}(S_2C{=}S)]$ and **5a** or **5c**, which could not be separated either by fractional crystallization or column chromatography. In the presence of the distannane $Sn_2\textit{n}Bu_6$, which was used by Ueno et al. for the preparation of a variety of tetrathiofulvalenes from 1,3-dithio-2-thiones probably via 1,3-dithiocarbenes [13], **4b** and **4c** proved to be inert, even under photochemical conditions. Other attempts with $Co_2(CO)_8$ as sulfur abstracting reagent [14] and either the cyclopentadienyl or the pentamethylcyclopentadienyl cobalt trithiocarbonates as precursors also remained unsuccessful.

To find out whether the desired tetrathiofulvalene analogues of type **B** were accessible via the methylated derivatives of the cobalt trithiocarbonates, the two series of compounds **6a**–**6f** and **7a**–**7d** were prepared (Scheme 4). In contrast to Manning's and Bianchini's work [8,15], we used instead of methyl iodide Meerwein's reagent $[OMe_3]BF_4$ as methyl source and, in CH_2Cl_2 at room temperature, obtained the tetrafluoroborates **6a**–**6f** and **7a**–**7d** in 80–92% yield. Typical spectroscopic data of the methylthioxanthate complexes are the singlet for the SCH_3 protons at δ 2.4–2.8 in the ^{1}H NMR and the C–SCH_3 stretching mode at 980–990 cm^{-1} in the IR spectra. The lowering of the ν(C–SCH_3) mode by only ca. 40–50 cm^{-1} compared with the ν(C=S) mode in the spectra of **4a, 4f**, **4g** and **5a–5d** indicates that the C–S bond in **6a**–**6f** and **7a**–**7d** retains some double bond character. This is in agreement with previous results reported by Roper's group [16] and by others [17].

Despite the weakening of the C–SCH_3 bond in **6a**–**6f** and **7a**–**7d** compared with the C=S bond in **4a, 4f**, **4g** and **5a–5d**, all attempts to abstract the SCH_3 fragment of the methylthioxanthate ligand failed. In contrast to studies by Fanghänel et al., which showed that



4a, 5a 8a,b; 9a,b

	R	X
8a	H	BF_4
8b	H	PF_6
9a	Me	BF_4
9b	Me	PF_6

Scheme 5.

tetrathiofulvalenes can be prepared on treating 2-alkylthio- or 2-arylthio-1,3-dithiolium salts with phosphines or phosphites [18], the cobalt compounds **6a**–**6f** and **7a**–**7d** were inert in the presence of PMe_3, PPh_3 and $P(OEt)_3$. Moreover, attempts to cleave the C–SCH_3 bond on a reductive route, as used for the synthesis of tetrathiofulvalenes from 2-alkylthio-1,3-dithiolium salts [18,19], remained unsuccessful. Although the reduction potential of the complexes **6a**–**6f** and **7a**–**7d**, determined by cyclovoltammetry (see below), indicated that reagents such as $[Co(C_5H_5)_2]$ or Zn [20] should be suitable to reduce the cationic cobalt methylthioxanthates, we observed only decomposition by reacting **6a**–**6f** and **7a**–**7d** with cobaltocene, sodium naphthalide, magnesium and zinc either in CH_2Cl_2 or acetonitrile.

Since the electroanalytical data of **4a, 4f**, **4g** and **5a** revealed that the cobalt trithiocarbonates could be easily oxidized, we reacted **4a** and **5a** with $[Fe(C_5H_5)_2]BF_4$ and $[Fe(C_5H_5)_2]PF_6$ in CH_2Cl_2 at room temperature. After evaporation of the solvent and extraction of ferrocene from the residue, red brown solids were obtained. They analyzed as the BF_4 and PF_6 salts of the radical cations $[(C_5R_5)Co(PMe_3)(S_2CS)]^+$ (**8a**,**b** and **9a**,**b**; see Scheme 5). In contrast to **4a** and **5a**, the dark brown solids **8a**,**b** and **9a**,**b** are air-sensitive and readily soluble only in nitromethane. They are almost insoluble in acetone, CH_2Cl_2 and THF. The conductivity of **8a**,**b** and **9a**,**b** in nitromethane corresponds to that of 1:1 electrolytes. Unexpectedly, the ^1H and ^{31}P NMR spectra of **8a**,**b** and **9a**,**b** displayed rather sharp signals, despite the presence of one unpaired electron in the formally cobalt(IV) cation. Even the ^1H,^{31}P coupling for the resonance of the PCH_3 protons could be determined. We note that paramagnetic sandwich compounds of cobalt(II) show also relatively sharp lines in the ^1H and ^{13}C spectra, which has been explained by spin delocalization of the unpaired electron in the metallocene frontier orbitals [21]. In the case of **8a**,**b** and **9a**,**b** we assume, that the unpaired electron is mainly localized in the trithiocarbonate ligand and much less at the metal atom. The reactions of **8b** and **9b** with cobaltocene in the ratio of 1:1 resulted in the quantitative reformation of the cobalt(III) complexes **4a** and **5a**, which is consistent with the proposed structure of the cationic species.

Our attempts to use the cobalt dithiocarbonates **10a–c** and **11a**,**b** as precursors to obtain tetrathiofulvalene analogues of type **B** equally failed. Similar to the procedure developed by Manning and co-workers [8], **10a–c** and **11a**,**b** were prepared from the diiodides **1a,f,g** and **3a**,**b** and isolated in good yields (Scheme 6). In contrast to Manning's results [8], the deeply coloured, air-stable solids did not contain solvent molecules and analyzed as calculated for **10a–c** and **11a**,**b**. The IR spectra of **10a–c** and **11a**,**b** showed two strong absorption bands at, respectively, 1580–1590 cm^{-1} and 1680–1700 cm^{-1}, of which the first is assigned to the ν(C=O) vibration. The second band at higher frequencies has been proposed to be due to Fermi resonance between the carbon–oxygen stretching mode and the first overtone band of the carbon–sulfur asymmetric stretching mode [22]. This mode was also observed in other metal dithiocarbonates [8,23]. From the experiments carried out to abstract the oxygen atom of the S_2C=O ligand, mention should be made of the reactions of **10b** and **11a** with an excess of $P(OEt)_3$ or $P(OMe)_3$, which gave the corresponding cobalt derivatives **12** and **13** by phosphine/phosphite exchange. Under similar conditions, tetrathiofulvalenes were obtained by treatment of 1,3-dithiol-2-ones and $P(OEt)_3$ or $P(OMe)_3$ [12c–f]. Attempts to oxidize **10a** and **11a** with $[Fe(C_5H_5)_2]PF_6$ in CH_2Cl_2, similar as carried out with **4a** and **5a** to afford **8b** and **9b** (see Scheme 5), failed. It should also be noted that the reactions of **10a** and **11a** with Meerwein's reagent $[OMe_3]BF_4$ gave a mixture of products, while treating **10a** and **11a** with two equivalents of Me_3SiCl led to the displacement of the dithiocarbonate ligand and the formation of **14a** [24] and **14b**.

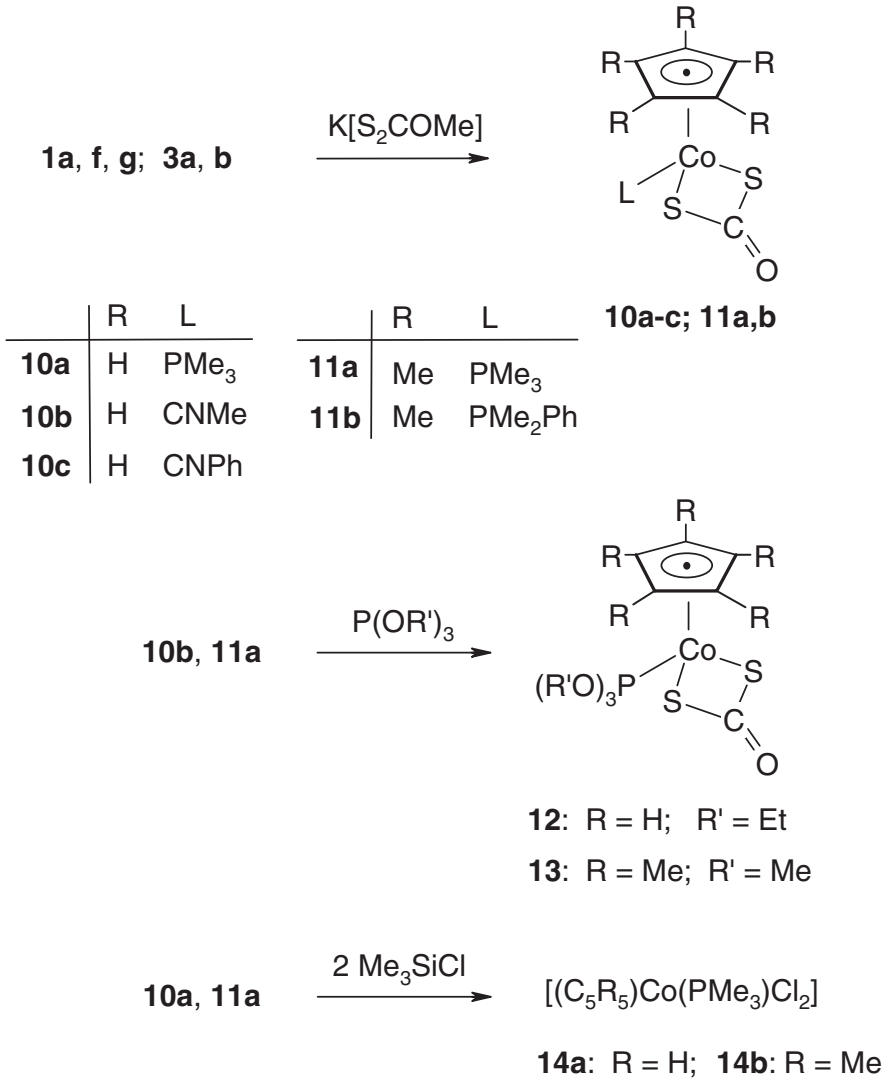
The X-ray diffraction analysis of **11b** confirmed the structural proposal shown in Scheme 6 [25].[1] The planar cyclopentadienyl ring is slightly unsymmetrically coordinated to the cobalt atom with Co–C distances lying between 2.063(3) and 2.116(3) Å. The bond angles between cobalt and the phosphorus and the sulfur atoms, which occupy the three legs of the pianostool configuration, are P–Co–S(1) = 93.98(3)°, P–Co–S(2) = 89.01(4)° and S(1)–Co–S(2) = 77.24(4)°, the latter being determined by the relatively small bite angle of the dithiocarbonate ligand. The bond lengths Co–S(1) = 2.241(1) Å and Co–S(2) = 2.252(1) Å are almost identical to the Co–S bond lengths in $[(C_5H_5)Co(CNtBu)(S_2C{=}S)]$ (2.235(3) and 2.252(3) Å) [8] and $[(C_5H_5)Co(PMe_3)(\eta^2\text{-}CS_2)]$ (2.24(0) Å) [2a]. The Co–S distances in cobalt dithiolene complexes are significantly shorter than in **11b** and lie between 2.12 and 2.14 Å [6,26]. The bond length C–O of 1.211(5) Å corresponds to a carbon–oxygen double bond and is agreement with data of other dithiocarbonato metal compounds [27].

The *N*-cyanodithiocarbimate complexes **15a** and **15b**, which compared with **10a–c** and **11a**,**b** contain an exocyclic NCN unit instead of the oxygen atom at the four-membered ring, were prepared from **1c**, **3c** and $K_2[S_2C{=}NCN]$ (Scheme 7). After separation of by-products by column chromatography, they were isolated as dark violet, air-stable solids in 67% and 76% yield. The most typical spectroscopic data of **15a** and **15b** are the C≡N and C=N stretching modes at, respectively, 2170 and 1440–1445 cm^{-1} in the IR and the absorption at 518 nm in the UV spectra, the latter being somewhat shifted to higher wavelengths compared with **10a** and **11a**.

The synthesis of the 1,1-dicyanoethylene-2,2-dithiolate cobalt compounds **16a–e**, of which some isomers with maleonitriledithiolate as chelating ligand were known [28], and of **17a–d** occurred on a similar route as used for **15a** and **15b** (Scheme 7). The deeply coloured solids are air-stable and soluble in chlorinated hydrocarbons; the pentamethylcyclopentadienyl derivatives **17a–d** are better soluble than their cyclopentadienyl counterparts **16a–e**. Similar to some 1,1-dicyanoethylene-2,2-dithiolate palladium and platinum complexes [27a], the IR spectra of **16a–e** and **17a–d** display a strong ν(C≡N) mode at 2200 cm^{-1} and a ν(C=C) mode at 1400–1410 cm^{-1}. The characteristic UV band appears at 512–535 nm and thus at similar wavelengths as for the analogous trithiocarbonates **4a** and **5a–d**.

In the course of attempting to obtain 1:1 adducts between **5a** as an electron donor and tetracyanoethylene (TCNE) as an electron acceptor, we found that both starting materials reacted in CH_2Cl_2 to give **17a** in 81% yield (Scheme 8). The same complex was obtained from **7a** and $CH_2(CN)_2$ in the presence of NaOMe. A similar

[1] Tables with selected bond distances and bond angles, the atomic parameters *x*, *y*, *z*, the isotropic temperature factors *U*(eq), and the anisotropic temperature factors *U*11, *U*22, *U*33, *U*12, *U*13, *U*23 are available on request from the corresponding author.



	R	L
10a	H	PMe_3
10b	H	CNMe
10c	H	CNPh

	R	L
11a	Me	PMe_3
11b	Me	PMe_2Ph

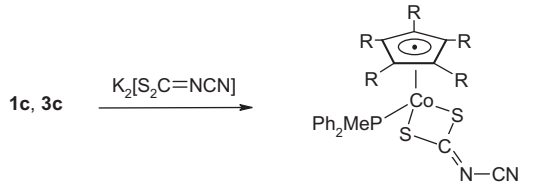
Scheme 6.

procedure was used by Yonemoto and co-workers for the preparation of dicyanomethylene-1,4,2-dithiazoles from 1,4,2-dithiazolium perchlorates [29]. With regard to the formation of **17a** from **5a** and TCNE, we assume that the reaction proceeds by a [2+2] cycloaddition via a four-membered thietane intermediate **I**. Previously, intermediates of this type have been observed on treating thioketones or thioketenes with electron poor olefins [30].

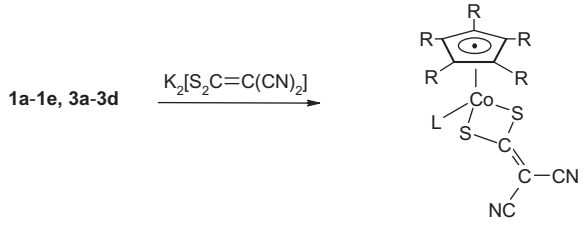
The preparation of the cobalt 1,1-dicyanoethylene-2,2-diselenolates **18a** and **18b** occurred analogously as reported for **16a** and **16b** (Scheme 9). The chemical properties as well as the spectroscopic data of **18a** and **18b** revealed only minor differences to those of the 2,2-dithiolates **16a** and **16b**. We note that whereas some square-planar silver(I), nickel(II), palladium(II) and platinum(II) complexes with $[Se_2C{=}C(CN)_2]^{2-}$ were described [31,32], related half-sandwich type compounds with this dianion as chelating ligand, to the best of our knowledge, were unknown.

To compare the reactivity of the cobalt trithiocarbonates **4** and **5** with some rhodium and iridium counterparts, we prepared the model compounds **20a,b** and **22** as shown in Scheme 10. As expected for complexes of the 4d and 5d elements, they are less deeply coloured than the 3d analogues, but air-stable too. The spectroscopic data are similar to those of **4a** and **5d**. The same is true for the methylated species **23a,b** and **24**, which were obtained from **20a,b** and **22** and Meerwein's reagent $[OMe_3]BF_4$. The reactions of **20a,b** and **23a,b** with $P(OEt)_3$ and zinc did not lead to tetrathiofulvalene analogues of type **B**; only decomposition was observed.

The oxidation potentials of most of the half-sandwich type complexes reported in this study were determined by cyclovoltammetry. All compounds showed irreversible oxidation waves in acetonitrile at room temperature. As summarized in Table 1, the E_{pa} values for the cyclopentadienyl cobalt trithiocarbonates $[(C_5H_5)Co(L)(S_2C{=}S)]$ (**4a,f,g**) increase in the order L = PMe_3 < CNMe < CNPh, which is in agreement with the decreasing donor and increasing acceptor character of L. The same tendency is perceptible for the dithiocarbonates **10a** and **10b**. By comparing the analogues **4a** and **5a**, **10a** and **11a**, **15a** and **15b**, **16a** and **17a**, **18a** and **18b**, the E_{pa} values for the pentamethylcyclopentadienyl compounds are always lower than those of the cyclopentadienyl counterparts. This is in agreement with the increasing donor strength by substituting hydrogen for methyl at the five-membered ring. The tertiary phosphine ligand has only a minor influence on the oxidation potentials, as is illustrated by the E_{pa} values for **16a–d** and **17a–d**. As expected, the E_{pa} value of the triphenylphosphite derivative **16e** is significantly higher than that of the triphenylphosphine analogue **16d**. If we accept that the donor ability of the trialkylphosphines PMe_3 and $PiPr_3$ is nearly the same, the E_{pa} values of **4a** and **22** point to an increase from the 3d to the 5d element. We finally note



15a: R = H; **15b:** R = Me

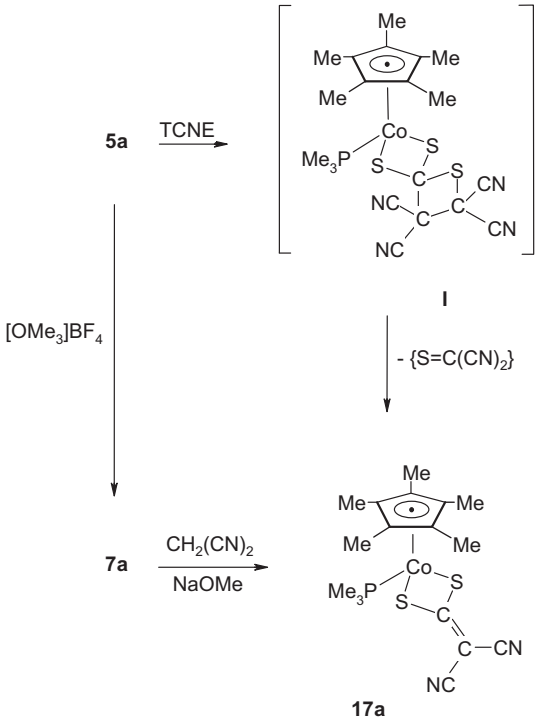


	R	L
16a	H	PMe_3
16b	H	PMe_2Ph
16c	H	$PMePh_2$
16d	H	PPh_3
16e	H	$P(OPh)_3$

	R	L
17a	Me	PMe_3
17b	Me	PMe_2Ph
17c	Me	$PMePh_2$
17d	Me	PPh_3

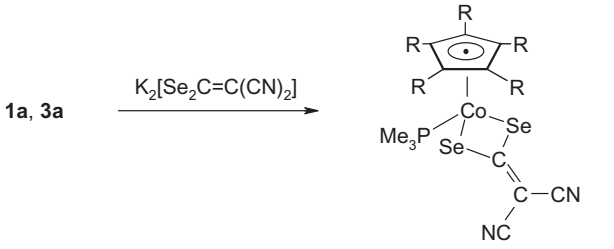
16a-16e, **17a-17d**

Scheme 7.



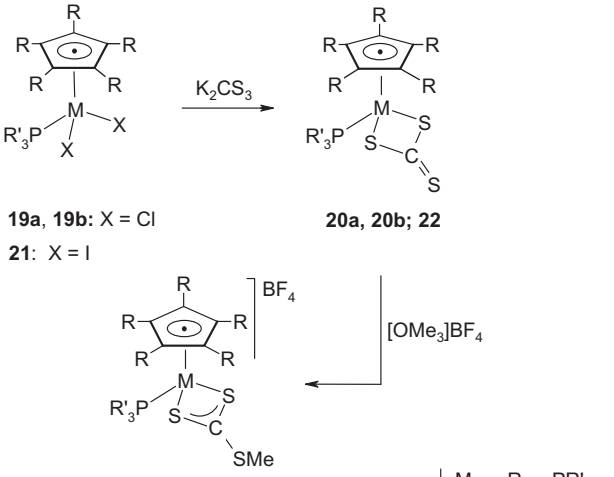
Scheme 8.

that the 1,1-dicyanoethylene-2,2-diselenolates **18a** and **18b** exhibit lower oxidation potentials than the 1,1-dicyanoethylene-2,2-dithiolates **16a** and **17a**, which can be rationalized by the lower σ-donating capabilities of the dianion $[Se_2C_2(CN)_2]^{2-}$ compared with the sulfur analogue $[S_2C_2(CN)_2]^{2-}$. The trend is the same, although less significant, for the nickel and platinum complexes $[M\{Se_2C_2(CN)_2\}]^{2-}$ and $[M\{S_2C_2(CN)_2\}]^{2-}$ (M = Ni, Pt) [32c].



18a; R = H; **18b**: R = Me

Scheme 9.



19a, **19b:** X = Cl

21: X = I

20a, 20b; 22

23a, **23b**; **24**

	M	R	PR'_3
19a, 20a, 23a	Rh	H	$PiPr_3$
19b, 20b, 23b	Rh	Me	PPh_3
21, 22, 24	Ir	H	$PiPr_3$

Scheme 10.

In summarizing, the present work revealed that, in addition to Manning's half-sandwich type cyclopentadienyl cobalt complexes with trithiocarbonate as chelating ligand [8], related compounds with dithiocarbonate, *N*-cyanodithiocarbimato, 1,1-dicyanoethylene-2,2-dithiolate and 1,1-dicyanoethylene-2,2-diselenolate were also accessible. While attempts to convert the complexes with $[(C_5R_5)Co(L)]$ (R = H, Me; L = PR_3, $P(OR)_3$, CNR) as molecular unit and $[S_2C{=}S]^{2-}$, $[S_2C{=}O]^{2-}$, $[S_2C{=}NR]^{2-}$ as ligands either directly or via the methylated cationic species to metalated analogues of tetrathiofulvalenes failed, the trithiocarbonate derivatives $[(C_5R_5)Co(PMe_3)(S_2C{=}S)]$ could be oxidized with ferricinium salts to the cationic compounds $[(C_5R_5)Co(PMe_3)(S_2CS)]X$. Cyclic voltammetry showed that the oxidation potentials of the title complexes with L = PR_3 depend only slightly on the donor capability of the phosphine ligand. Increasing the donor strength of either the five-membered ring or the monodentate ligand L led to a decrease in the oxidation potential which is consistent with the generally accepted bonding concepts [33].

3. Experimental

3.1. General considerations

All experiments were carried out under an atmosphere of argon using Schlenk techniques. Solvents were purified and degassed by

Table 1
Oxidation potentials of cyclopentadienyl and pentamethylcyclopentadienyl metal complexes with trithiocarbonate, dithiocarbonate, *N*-cyanodithiocarbimate, 1,1-dicyanoethylene-2,2-dithiolate and 1,1-dicyanoethylene-2,2-diselenolate as chelating ligands (in acetonitrile, referenced to the ferrocene/ferricinium redox couple).

Compound	E_{pa} (V_{Fc})	Compound	E_{pa} [V_{Fc}]	Compound	E_{pa} [V_{Fc}]	Compound	E_{pa} [V_{Fc}]
4a	+0.56	**11a**	+0.84	**16c**	+1.20	**17d**	+1.13
4f	+0.74	**11b**	+0.89	**16d**	+1.25	**18a**	+1.09
4g	+0.62	**15a**	+1.25	**16e**	+1.37	**18b**	+0.95
5a	+0.46	**15b**	+1.12	**17a**	+1.05	**20b**	+0.90
10a	+1.01	**16a**	+1.21	**17b**	+1.07	**22**	+0.66
10b	+1.29	**16b**	+1.21	**17c**	+1.06		

standard procedures. The starting materials **1a** [34], **1b,c** [35], **1d** [36], **1e,f** [37], **1g** [38], **2a** [36,39], **2b** [40], **3b** [9], **4b–4e** [8], **17a** [41], **17b** [42], and **19** [43] were prepared as described in the literature. NMR spectra were recorded on Bruker WH 90 and AC 200 instruments, IR spectra on a Perkin-Elmer 1420, and UV spectra on a Hitachi 340 spectrometer. For the X-ray analysis an Enraf Nonius CAD4 diffractometer with Mo Kα radiation (0.70930 Å), a graphite monochromator and a zirconium filter (factor 16.55) were used. Melting points were determined by Differential Thermal Analysis (DTA). The mass spectra were measured on a Varian MAT instrument (electron energy 70 eV). Conductivity measurements were carried out in nitromethane with a Schott Konduktometer CG 851. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants *J* and *N* [$N = {}^3J(P,H) + {}^5J(P,H)$] in Hz.

3.2. General procedure for the preparation of $[(C_5Me_5)Co(PR_3)I_2]$ (**3a–3c**)

A solution of **2a** (476 mg, 1.00 mmol) in 40 ml of CH_2Cl_2 was treated dropwise with a solution of 1.10 mmol of PR_3 in 20 ml of CH_2Cl_2 and stirred for 6 h at r.t. The solution was concentrated to 10 ml in vacuo, and then layered with 60 ml of diethyl ether. After the mixture was stored for 12 h at −20 °C, a microcrystalline solid precipitated. The mother liquor was decanted, the residue washed twice with 5 ml of diethyl ether and dried in vacuo. The time of reaction for **3c** was 16 h.

3a: Dark brownish solid; yield 461 mg (88%), m.p. 120 °C (dec.). *Anal.* Calc. for $C_{13}H_{24}CoI_2P$: C, 29.79; H, 4.62; Co, 11.25. Found: C, 30.12; H, 4.99; Co, 11.05%. MS (70 eV) *m/z* 524 (M^+), 397 (M^+-I), 194 ($C_5Me_5Co^+$). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.89 [d, $^4J(PH) = 1.5$, 15H, C_5Me_5], 1.83 [d, $^2J(PH) = 11.0$, 9H, PMe_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 8.8 (s).

3b: Black solid, yield 492 mg (84%), m.p. 75 °C (dec.). *Anal.* Calc. for $C_{18}H_{26}CoI_2P$: C, 36.89; H, 4.47; Co, 10.05. Found: C, 37.44; H, 4.69; Co, 9.89%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.38–8.32 (br m, 5H, C_6H_5), 2.08 [d, $^2J(PH) = 10.3$, 6H, PCH_3], 1.68 [d, $^4J(PH) = 1.5$, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 12.2 (s).

3c: Dark greenish solid, yield 551 mg (85%), m.p. 79 °C (dec.). *Anal.* Calc. for $C_{23}H_{28}CoI_2P$: C, 42.62; H, 4.35; Co, 9.09. Found: C, 43.04; H, 4.49; Co, 8.72%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.33–8.08 (br m, 10H, C_6H_5), 2.34 [d, $^2J(PH) = 9.8$, 3H, PCH_3], 1.68 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 25.5 (s).

3.3. Preparation of $[(C_5Me_5)Co(PPh_3)I_2]$ (**3d**)

A solution of **2b** (515 mg, 1.15 mmol) in 40 ml of CH_2Cl_2 was treated under stirring with PPh_3 (603 mg, 2.30 mmol), which led to a quick change of colour from black to green. The solution was continuously stirred for 5 min at r.t., then filtered and the filtrate was brought to dryness in vacuo. The remaining green microcrystalline solid was washed three times with 3 ml of a mixture of hexane/diethyl ether (3:1) and dried in vacuo: yield 1.57 g (96%), m.p. 112 °C (dec.). *Anal.* Calc. for $C_{28}H_{30}CoI_2P$: C, 47.35; H, 4.26; Co, 8.30. Found: C, 47.43; H, 4.18; Co, 8.14%. The NMR spectroscopic data were identical with those described by King et al. [10].

3.4. Preparation of $[(C_5H_5)Co(PMe_3)(S_2C{=}S)]$ (**4a**)

A solution of **1a** (136 mg, 0.30 mmol) in 25 ml of CH_2Cl_2 was treated with K_2CS_3 (56 mg, 0.30 mmol) and stirred for 16 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The remaining red-violet microcrystalline solid was washed twice with 3 ml of diethyl ether and dried in vacuo: yield 64 mg (69%), m.p. 89 °C (dec.). *Anal.* Calc. for $C_9H_{14}CoPS_3$: C, 35.06; H, 4.58; S, 31.20; Co, 19.11. Found: C, 35.34; H, 4.65; S, 30.65; Co, 18.91%. IR (KBr): ν(C=S) 1030 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 356, 512 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.08 (s, 5H, C_5H_5), 1.56 [d, $^2J(PH) = 11.0$, 9H, PMe_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 20.7 (s).

3.5. Preparation of $[(C_5H_5)Co(CNMe)(S_2C{=}S)]$ (**4f**)

This compound was prepared as described for **4a**, with 63 mg (0.15 mmol) of **1b** and 56 mg (0.30 mmol) of K_2CS_3 as starting materials; reaction time 3 h. Red brown solid, yield 28 mg (68%), m.p. 144 °C (dec.). *Anal.* Calc. for $C_8H_8CoNS_3$: C, 35.16; H, 2.95; N, 5.13; S, 35.20; Co, 21.56. Found: C, 34.84; H, 2.90; N, 4.90; S, 35.22; Co, 21.20%. IR (KBr): ν(C≡NMe) 2220, ν(C=S) 1035 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 340, 492 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.28 (s, 5H, C_5H_5), 3.52 (s, 3H, NCH_3).

3.6. Preparation of $[(C_5H_5)Co(CNPh)(S_2C{=}S)]$ (**4g**)

This compound was prepared as described for **4a**, with 72 mg (0.15 mmol) of **1c** and 56 mg (0.30 mmol) of K_2CS_3 as starting materials; reaction time 3 h. Red brown solid, yield 31 mg (62%), m.p. 78 °C (dec.). *Anal.* Calc. for $C_{13}H_{10}CoNS_3$: C, 46.56; H, 3.01; N, 4.18; S, 19.12; Co, 17.57. Found: C, 46.46; H, 2.87; N, 3.99; S, 19.21; Co, 16.94%. IR (KBr): ν(C≡NMe) 2175, ν(C=S) 1030 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 339, 494 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.38 (br m, 5H, C_6H_5), 5.40 (s, 5H, C_5H_5).

3.7. Preparation of $[(C_5H_5)Co\{P(OEt)_3\}(S_2C{=}S)]$ (**4h**)

(a) A solution of **4b** (109 mg, 0.22 mmol) in 25 ml of benzene was treated with $P(OEt)_3$ (382 μl, 2.20 mmol) and stirred for 2 d at 40 °C. After the solution was cooled to r.t., it was filtered and the filtrate was brought to dryness in vacuo. The remaining red microcrystalline solid was washed three times with 3 ml of a mixture of hexane/diethyl ether (3:1) and dried in vacuo: yield 47 mg (54%). (b) A suspension of **4a** (65 mg, 0.21 mmol) in 10 ml of benzene was treated with $P(OEt)_3$ (1.00 ml, 6.30 mmol) and stirred for 3 d at 70 °C. After the solution was cooled to r.t., it was worked up as described for (a): yield 38 mg (46%). (c) A solution of **4d** (52 mg, 0.19 mmol) in 20 ml of benzene was treated with $P(OEt)_3$ (0.33 ml, 1.90 mmol) and stirred for 18 h at r.t. It was then worked up as described for (a): yield 61 mg (81%), m.p. 86 °C (dec.). *Anal.* Calc. for $C_{12}H_{20}CoO_3PS_3$: C, 36.18; H, 5.06; S, 24.15; Co, 14.79. Found: C,

36.29; H, 5.03; S, 23.82; Co, 14.51%. IR (KBr): ν(C═S) 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 5.15 (s, 5H, C_5H_5), 4.05 [dq, $^3J(PH) = {}^3J(HH) = 7.1$, 6H, CH_2], 1.29 [t, $^3J(HH) = 7.1$, 9H, CH_3].

3.8. Preparation of [(C_5Me_5)Co(PMe_3)(S_2C═S)] (**5a**)

A solution of **3a** (131 mg, 0.25 mmol) in 25 ml of CH_2Cl_2 was treated with K_2CS_3 (93 mg, 0.50 mmol) and stirred for 5 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The remaining dark red microcrystalline solid was washed three times with 3 ml of diethyl ether and dried in vacuo: yield 62 mg (66%), m.p. 133 °C (dec.). *Anal.* Calc. for $C_{14}H_{24}CoPS_3$: C, 44.43; H, 6.39; S, 25.42; Co, 15.57. Found: C, 43.97; H, 6.51; S, 25.08; Co, 14.97%. MS (70 eV) *m/z* 378 (M^+), 194 ($C_5Me_5Co^+$). IR (KBr): ν(C═S) 1030, 1020 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 361, 502 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.57 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5], 1.42 [d, $^2J(PH) = 10.0$, 9H, PMe_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 13.2 (s).

3.9. Preparation of [(C_5Me_5)Co(PMe_2Ph)(S_2C═S)] (**5b**)

This compound was prepared as described for **5a**, with 147 mg (0.25 mmol) of **3b** and 93 mg (0.50 mmol) of K_2CS_3 as starting materials; reaction time 6 h. Red violet solid, yield 77 mg (70%), m.p. 86 °C (dec.). *Anal.* Calc. for $C_{14}H_{24}CoPS_3$: C, 51.81; H, 5.95; S, 21.84; Co, 13.38. Found: C, 51.34; H, 6.09; S, 22.09; Co, 12.89%. IR (KBr): ν(C═S) 1030, 1020 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 362, 512 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.40–7.55 (br m, 5H, C_6H_5), 1.42 [d, $^2J(PH) = 9.8$, 6H, CH_3], 1.30 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 23.2 (s).

3.10. Preparation of [(C_5Me_5)Co($PMePh_2$)(S_2C═S)] (**5c**)

This compound was prepared as described for **5a**, with 162 mg (0.25 mmol) of **3c** and 93 mg (0.50 mmol) of K_2CS_3 as starting materials; reaction time 8 h. Dark violet solid, yield 92 mg (73%), m.p. 73 °C (dec.). *Anal.* Calc. for $C_{24}H_{28}CoPS_3$: C, 57.36; H, 5.62; S, 19.14; Co, 11.73. Found: C, 57.11; H, 5.70; S, 18.75; Co, 11.37%. IR (KBr): ν(C═S) 1035, 1020 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 361, 516 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.45–7.85 (br m, 10H, C_6H_5), 1.60 [d, $^2J(PH) = 8.3$, 3H, CH_3], 1.26 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 41.2 (s).

3.11. Preparation of [(C_5Me_5)Co(PPh_3)(S_2C═S)] (**5d**)

This compound was prepared as described for **5a**, with 178 mg (0.25 mmol) of **3d** and 93 mg (0.50 mmol) of K_2CS_3 as starting materials; reaction time 10 h. Red violet solid, yield 45 mg (32%), m.p. 156 °C (dec.). *Anal.* Calc. for $C_{29}H_{30}CoPS_3$: C, 61.69; H, 5.36; S, 17.04; Co, 10.44. Found: C, 62.13; H, 5.28; S, 16.68; Co, 10.35%. IR (KBr): ν(C═S) 1030, 1020 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 360, 524 nm. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.25–7.65 (br m, 15H, C_6H_5), 1.30 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 49.6 (s).

3.12. General procedure for the preparation of [(C_5H_5)Co(L)(S_2CSMe)BF_4 (**6a–6f**) and [(C_5Me_5)Co(PR_3)(S_2CSMe)BF_4 (**7a–7d**)

A solution of 0.35 mmol of **4a–4d, 4f, 4g, 5a–5d** in 25 ml of CH_2Cl_2 was treated under stirring with $[Me_3O]BF_4$ (52 mg, 0.35 mmol) and continuously stirred for 3 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The residue was washed three times with 5 ml of diethyl ether and dried in vacuo.

6a: Red brown solid, yield 126 mg (88%), m.p. 123 °C (dec.), Λ = 71 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{10}H_{17}BCoF_4PS_3$: C, 29.28; H, 4.18; S, 23.45; Co, 14.37. Found: C, 29.34; H, 4.53; S, 23.19; Co, 13.91%. IR (KBr): ν(C═S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 568 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 5.57 [d, $^3J(PH) = 0.7$, 5H, C_5H_5], 2.76 (s, 3H, SCH_3), 1.71 [d, $^2J(PH) = 11.7$, 9H, PMe_3]. ^{13}C NMR (CD_3NO_2, 50.3 MHz): δ 88.7 (s, C_5H_5), 17.1 (s, SCH_3), 16.6 [d, $^1J(PC) = 34.7$, PMe_3], signal of S_2C carbon atom not exactly located. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 22.8 (s).

6b: Dark brown solid, yield 139 mg (84%), m.p. 102 °C (dec.), Λ = 74 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{15}H_{19}BCoF_4PS_3$: C, 38.15; H, 4.06; S, 20.37; Co, 12.48. Found: C, 38.30; H, 3.93; S, 20.61; Co, 12.13%. IR (KBr): ν(C═S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 574 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.37–7.68 (br m, 5H, C_6H_5), 5.49 [d, $^3J(PH) = 0.7$, 5H, C_5H_5], 2.60 (s, 3H, SCH_3), 2.08 [d, $^2J(PH) = 10.5$, 6H, PCH_3]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 27.0 (s).

6c: Dark brown solid, yield 166 mg (89%), m.p. 150 °C (dec.), Λ = 73 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{20}H_{21}BCoF_4PS_3$: C, 44.96; H, 3.96; S, 18.00; Co, 11.03. Found: C, 44.81; H, 4.14; S, 18.31; Co, 10.66%. IR (KBr): ν(C═S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 572 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.52–7.71 (br m, 10H, C_6H_5), 5.59 [d, $^3J(PH) = 0.5$, 5H, C_5H_5], 2.60 [d, $^2J(PH) = 10.5$, 3H, PCH_3], 2.40 (s, 3H, SCH_3). ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 36.4 (s).

6d: Dark brown solid, yield 182 mg (87%), m.p. 54 °C (dec.), Λ = 81 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{25}H_{23}BCoF_4PS_3$: C, 48.33; H, 3.89; S, 16.13; Co, 9.88. Found: C, 48.68; H, 3.66; S, 16.37; Co, 9.57%. IR (KBr): ν(C═S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 574 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.48–7.93 (br m, 15H, C_6H_5), 5.49 (s, 5H, C_5H_5], 2.37 (s, 3H, SCH_3). ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 46.4 (s).

6e: Red brown solid, yield 113 mg (86%), m.p. 94 °C (dec.), Λ = 80 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_9H_{11}BCoF_4NS_3$: C, 28.82; H, 2.96; N, 3.73; S, 25.64; Co, 15.71. Found: C, 29.04; H, 2.78; N, 3.97; S, 25.44; Co, 15.41%. IR (KBr): ν(C≡NMe) 2240, ν(C═S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 576 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 5.80 (s, 5H, C_5H_5), 2.80 (s, 3H, SCH_3), 3.70 (br s, 3H, NCH_3).

6f: Dark brown solid, yield 122 mg (80%), m.p. 144 °C (dec.), Λ = 78 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{14}H_{13}BCoF_4NS_3$: S, 22.00; Co, 13.48. Found: S, 21.78; Co, 13.51%. IR (KBr): ν(C≡NPh) 2180, ν(C═S) 990 cm^{-1}. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.40–7.68 (br m, 15H, C_6H_5), 5.91 (s, 5H, C_5H_5), 2.81 (s, 3H, SCH_3).

7a: Red brown solid, yield 145 mg (86%), m.p. 97 °C (dec.), Λ = 73 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{15}H_{27}BCoF_4PS_3$: C, 37.51; H, 5.67; S, 20.03; Co, 12.27. Found: C, 38.06; H, 5.80; S, 20.59; Co, 12.00%. IR (KBr): ν(C═S) 980 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 580 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 2.77 (s, 3H, SCH_3), 1.66 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5], 1.56 [d, $^2J(PH) = 10.5$, 9H, PMe_3]. ^{13}C NMR (CD_3NO_2, 50.3 MHz): δ 97.1 (s, C_5Me_5), 17.1 (s, SCH_3), 13.9 [d, $^1J(PC) = 31.6$, PMe_3], 9.3 (s, CCH_3), signal of S_2C carbon atom not exactly located. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 11.1 (s).

7b: Dark brown solid, yield 156 mg (82%), m.p. 99 °C (dec.), Λ = 64 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{20}H_{29}BCoF_4PS_3$: C, 44.29; H, 5.39; S, 17.74; Co, 10.87. Found: C, 44.63; H, 5.46; S, 18.01; Co, 10.84%. IR (KBr): ν(C═S) 980 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 580 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.48–7.65 (br m, 5H, C_6H_5), 2.75 (s, 3H, SCH_3), 1.77 [d, $^2J(PH) = 10.0$, 6H, PMe_2], 1.45 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 20.2 (s).

7c: Dark brown solid, yield 195 mg (92%), m.p. 138 °C (dec.), Λ = 65 $cm^2\,\Omega^{-1}\,mol^{-1}$. *Anal.* Calc. for $C_{25}H_{31}BCoF_4PS_3$: C, 49.68; H, 5.17; S, 15.91; Co, 9.75. Found: C, 50.29; H, 5.35; S, 16.16; Co, 9.76%. IR (KBr): ν(C═S) 985 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 580 nm. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.42–7.63 (br m, 10H, C_6H_5), 2.47 [d, $^2J(PH) = 9.5$, 3H, PCH_3], 2.39 (s, 3H, SCH_3), 1.50 [d, $^4J(PH) = 1.7$, 15H, C_5Me_5]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 31.1 (s).

7d: Dark brown solid, yield 196 mg (84%), m.p. 113 °C (dec.), $\Lambda = 63\ cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{30}H_{33}BCoF_4PS_3$: C, 54.06; H, 4.99; S, 14.43; Co, 8.84. Found: C, 54.07; H, 5.11; S, 14.39; Co, 9.20%. IR (KBr): ν(C═S) 985 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 590$ nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 7.37–7.82 (br m, 15H, C_6H_5), 2.37 (s, 3H, SCH_3), 1.33 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 47.9 (s).

3.13. General procedure for the preparation of $[(C_5H_5)Co(PMe_3)(S_2CS)]X$ (**8a**, **8b**) and $[(C_5Me_5)Co(PMe_3)(S_2CS)]X$ (**9a**, **9b**)

A suspension of **4a** (80 mg, 0.26 mmol) or **5a** (98 mg, 0.26 mmol) and $[Fe(C_5H_5)_2]BF_4$ (71 mg, 0.26 mmol) in 15 ml of CH_2Cl_2 was stirred for 1 h at r.t. The solvent was evaporated in vacuo and the dark brown solid was extracted twice with 10 ml of benzene. The residue was washed three times with 5 ml of diethyl ether and dried. The PF_6^- salts were prepared analogously with $[Fe(C_5H_5)_2]PF_6$ (86 mg, 0.26 mmol) as oxidans.

8a: Red brown solid, yield 88 mg (86%), m.p. 151 °C (dec.), $\Lambda = 83\ cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_9H_{14}BCoF_4PS_3$: C, 27.36; H, 3.57; S, 24.35; Co, 14.91. Found: C, 26.81; H, 3.58; S, 24.07; Co, 14.51%. IR (KBr): $\nu(BF_4)$ 1050 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 590$ nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 5.64 (s, 5H, C_5H_5), 1.71 [d, ^2J(PH) = 11.7, 9H, PMe_3]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 19.0 (s).

8b: Red brown solid, yield 95 mg (81%), m.p. 126 °C (dec.), $\Lambda = 69\ cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_9H_{14}CoF_6P_2S_3$: C, 23.85; H, 3.11; S, 21.22; Co, 13.00. Found: C, 24.24; H, 3.18; S, 20.96; Co, 12.66%. IR (KBr): $\nu(PF_6)$ 835, ν(CS) 1010 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 590$ nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 5.65 (s, 5H, C_5H_5), 1.73 [d, ^2J(PH) = 11.8, 9H, PMe_3]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 19.2 (s, PMe_3), −146.4 (sept, PF_6).

9a: Red brown solid, yield 108 mg (89%), m.p. 56 °C (dec.), $\Lambda = 74\ cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{14}H_{24}BCoF_4PS_3$: C, 36.15; H, 4.20; S, 20.68; Co, 12.69. Found: C, 36.26; H, 4.15; S, 20.41; Co, 12.52%. IR (KBr): $\nu(BF_4)$ 1055 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 590$ nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 1.68 (s, 15H, C_5Me_5), 1.58 [d, ^2J(PH) = 10.5, 9H, PMe_3]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 8.0 (s).

9b: Red brown solid, yield 120 mg (88%), m.p. 108 °C (dec.), $\Lambda = 91\ cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{14}H_{24}CoF_6P_2S_3$: C, 32.13; H, 4.62; S, 18.38; Co, 11.26. Found: C, 32.23; H, 4.65; S, 18.51; Co, 10.88%. IR (KBr): $\nu(PF_6)$ 835, ν(CS) 1020 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 590$ nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 1.68 (s, 15H, C_5Me_5), 1.58 [d, ^2J(PH) = 10.6, 9H, PMe_3]. ^{31}P NMR [$(CD_3)_2CO$, 36.2 MHz]: δ 8.1 (s, PMe_3), −154.9 (sept, PF_6).

3.14. General procedure for the preparation of $[(C_5H_5)Co(L)(S_2C{=}O)]$ (**10a–10c**) and $[(C_5Me_5)Co(PR_3)(S_2C{=}O)]$ (**11a**, **11b**)

A suspension of 0.30 mmol of **1a–1c** or **3a, 3b** and $K[S_2COMe]$ (48 mg, 0.33 mmol) in 25 ml of CH_2Cl_2 was intensively stirred for 1 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The residue was washed three times with 3 ml of diethyl ether and dried in vacuo.

10a: Dark red solid, yield 63 mg (72%), m.p. 65 °C (dec.). *Anal.* Calc. for $C_9H_{14}CoOPS_2$: C, 36.99; H, 4.83; S, 21.94; Co, 20.16. Found: C, 36.80; H, 4.63; S, 22.21; Co, 19.78%. IR (KBr): ν(C═O) 1590, 1690 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 396$, 494 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.08 s, 5H, C_5H_5), 1.54 [d, ^2J(PH) = 11.0, 9H, PMe_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 21.4 (s).

10b: Red violet solid, yield 53 mg (69%), m.p. 64 °C (dec.). *Anal.* Calc. for $C_8H_8CoNOS_2$: C, 37.36; H, 3.13; N, 5.45; S, 24.93; Co, 22.91. Found: C, 37.08; H, 3.27; N, 5.69; S, 24.61; Co, 22.99%. IR (KBr): ν(C≡N) 2230, ν(C═O) 1590, 1700 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 406$, 506 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.28 (s, 5H, C_5H_5), 3.51 (s, 3H, NCH_3).

10c: Red violet solid, yield 65 mg (68%), m.p. 67 °C (dec.). *Anal.* Calc. for $C_{13}H_{10}CoNOS_2$: C, 48.90; H, 3.16; N, 4.39; S, 20.08; Co, 18.46. Found: C, 48.87; H, 3.17; N, 4.39; S, 19.91; Co, 18.36%. IR (KBr): ν(C≡N) 2170, ν(C═O) 1580, 1695 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 408$, 506 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 6.38 (m, 5H, C_6H_5), 5.39 (s, 5H, C_5H_5).

11a: Red violet solid, yield 85 mg (78%), m.p. 158 °C (dec.). *Anal.* Calc. for $C_{14}H_{24}CoOPS_2$: C, 46.40; H, 6.68; S, 17.70; Co, 16.26. Found: C, 46.76; H, 6.83; S, 17.93; Co, 15.88%. MS (70 eV) *m/z* 362 (M^+), 286 (M^+-PMe_3), 194 ($C_5Me_5Co^+$). IR (KBr): ν(C═O) 1585, 1700 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 382$, 504 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.57 [d, ^4J(PH) = 1.5, 15H, C_5Me_5], 1.41 [d, ^2J(PH) = 9.8, 9H, PMe_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 21.4 (s).

11b: Dark violet solid, yield 98 mg (77%), m.p. 86 °C (dec.). *Anal.* Calc. for $C_{19}H_{26}CoOPS_2$: C, 53.77; H, 6.17; S, 15.11; Co, 13.88. Found: C, 53.75; H, 6.40; S, 15.15; Co, 13.38%. IR (KBr): ν(C═O) 1590, 1685 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 376$, 506 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.38–7.89 (br m, 5H, C_6H_5), 1.58 [d, ^2J(PH) = 9.8, 6H, PMe_2], 1.30 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 21.4 (s).

3.15. Preparation of $[(C_5H_5)Co\{P(OEt)_3\}(S_2C{=}O)]$ (**12**)

A solution of **10b** (48 mg, 0.19 mmol) in 20 ml of benzene was treated with $P(OEt)_3$ (330 μl, 1.90 mmol) and stirred for 3 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The remaining red microcrystalline solid was washed three times with 3 ml of a mixture of hexane/diethyl ether (3:1) and dried in vacuo: yield 58 mg (81%), m.p. 103 °C (dec.). *Anal.* Calc. for $C_{12}H_{20}CoO_4PS_2$: C, 37.70; H, 5.27; S, 16.77; Co, 15.41. Found: C, 38.04; H, 5.09; S, 16.79; Co, 14.94%. IR (KBr): ν(C═O) 1585 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.16 (s, 5H, C_5H_5), 4.10 [dq, ^3J(PH) = ^3J(HH) = 7.0, 6H, CH_2], 1.31 [t, ^3J(HH) = 7.0, 9H, CH_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 135.4 (br s).

3.16. Preparation of $[(C_5Me_5)Co\{P(OMe)_3\}(S_2C{=}O)]$ (**13**)

A solution of **11a** (87 mg, 0.24 mmol) in 20 ml of benzene was treated with $P(OMe)_3$ (0.90 ml, 7.20 mmol) and stirred for 3 h under reflux. After the solution was cooled to r.t., the solvent was evaporated in vacuo. The residue was dissolved in 3 ml of CH_2Cl_2 and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With CH_2Cl_2 a dark red fraction was eluted, from which the solvent was removed. The red microcrystalline solid was washed three times with 3 ml of a mixture of hexane/CH_2Cl_2 (3:1) and dried in vacuo: yield 60 mg (61%), m.p. 121 °C (dec.). *Anal.* Calc. for $C_{14}H_{24}CoO_4PS_2$: C, 40.98; H, 5.89; S, 15.63; Co, 14.36. Found: C, 40.49; H, 5.85; S, 15.11; Co, 14.44%. IR (KBr): ν(C═O) 1590, 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.67 [d, ^3J(PH) = 10.2, 9H, POH_3], 1.58 [d, ^4J(PH) = 1.5, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 146.7 (br s).

3.17. Preparation of $[(C_5Me_5)Co(PMe_3)Cl_2]$ (**14b**)

A solution of **11a** (91 mg, 0.25 mmol) in 15 ml of CH_2Cl_2 was treated with Me_3SiCl (0.63 μl, 0.50 mmol) and stirred for 4 h at r.t. The solution was filtered, and the filtrate was brought to dryness in vacuo. The residue was worked up as described for **13**. Red violet solid, yield 47 mg (55%), m.p. 98 °C (dec.). *Anal.* Calc. for $C_{13}H_{24}Cl_2CoP$: C, 45.77; H, 7.09; Co, 17.27. Found: C, 45.66; H, 6.86; Co, 17.00%. MS (70 eV) *m/z* 340 (M^+), 305 (M^+-Cl), 200 (M^+-2Cl). UV (CH_2Cl_2, 10^{-6} mol/l): $\lambda = 546$ nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.58 [d, ^2J(PH) = 11.0, 9H, PMe_3] 1.39 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 14.3 (s).

3.18. Preparation of [(C_5H_5)Co($PMePh_2$)(S_2C=NCN)] (**15a**)

A solution of **1c** (127 mg, 0.22 mmol) in 35 ml of THF was treated with $K_2[S_2C{=}NCN]$ (86 mg, 0.44 mmol) and stirred for 3 h at 70 °C. After the solution was cooled to r.t., it was filtered and the filtrate was brought to dryness in vacuo. The residue was dissolved in 5 ml of CH_2Cl_2 and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With CH_2Cl_2 a violet fraction was eluted, from which the solvent was evaporated. The dark violet microcrystalline solid was washed three times with 3 ml of a mixture of hexane/CH_2Cl_2 (3:1) and dried in vacuo: yield 65 mg (67%), m.p. 208 °C (dec.). *Anal.* Calc. for $C_{20}H_{18}CoN_2PS_2$: C, 54.54; H, 4.12; N, 6.36; S, 14.56; Co, 13.38. Found: C, 54.30; H, 4.21; N, 6.08; S, 14.30; Co, 13.06%. IR (KBr): ν(C≡N) 2170, ν(C=N) 1445 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 518 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.31–7.89 (br m, 10H, C_6H_5), 5.01 (s, 5H, C_5H_5), 1.77 [d, ^2J(PH) = 10.6, 3H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 38.1 (s).

3.19. Preparation of [(C_5Me_5)Co($PMePh_2$)(S_2C=NCN)] (**15b**)

This compound was prepared as described for **15a**, with 143 mg (0.22 mmol) of **3c** and 86 mg (0.44 mmol) of $K_2[S_2C{=}NCN]$ as starting materials. Dark violet solid, yield 85 mg (76%), m.p. 148 °C (dec.). *Anal.* Calc. for $C_{25}H_{28}CoN_2PS_2$: C, 58.81; H, 5.53; N, 5.49; S, 12.56; Co, 11.54. Found: C, 58.64; H, 5.44; N, 5.03; S, 12.63; Co, 11.32%. IR (KBr): ν(C≡N) 2170, ν(C=N) 1440 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 518 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.28–7.76 (br m, 10H, C_6H_5), 1.76 [d, ^2J(PH) = 9.8, 3H, CH_3], 1.30 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 36.7 (s).

3.20. General procedure for the preparation of [(C_5H_5)Co(PR_3){S_2C=C(CN)$_2$}] (**16a–16e**) and [(C_5Me_5)Co(PR_3){S_2C=C(CN)$_2$}] (**17a–17d**)

A suspension of 0.19 mmol of [(C_5H_5)Co(PR_3)I_2] (**1a–1e**) or [(C_5Me_5)Co(PR_3)I_2] (**3a–3d**) in 25 ml of a mixture of CH_2Cl_2/THF (3:1) was treated with $K_2[S_2C{=}C(CN)_2]$ (83 mg, 0.38 mmol) and stirred for 2 h at r.t. The solution was filtered and the filtrate was worked up as described for **15a**.

***16a**:* Red violet solid; yield 36 mg (56%), m.p. 266 °C (dec.). *Anal.* Calc. for $C_{12}H_{14}CoN_2PS_2$: C, 42.35; H, 4.15; N, 9.21; S, 18.85; Co, 17.32. Found: C, 42.41; H, 4.01; N, 9.42; S, 18.58; Co, 17.53%. MS (70 eV) *m/z* 340 (M^+), 200 ($C_5H_5Co(PMe_3)^+$). IR (KBr): ν(C≡N) 2200, ν(C=N) 1405 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 513 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.10 (s, 5H, C_5H_5), 1.75 [d, ^2J(PH) = 10.8, 9H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 21.1 (s).

***16b**:* Red violet solid; yield 59 mg (77%), m.p. 136 °C (dec.). *Anal.* Calc. for $C_{17}H_{16}CoN_2PS_2$: C, 50.75; H, 4.01; N, 6.96; S, 15.94; Co, 14.65. Found: C, 50.17; H, 3.93; N, 6.88; S, 16.02; Co, 14.25%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 519 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.41–7.62 (br m, 5H, C_6H_5), 4.94 (s, 5H, C_5H_5), 1.81 [d, ^2J(PH) = 10.8, 6H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 25.6 (s).

***16c**:* Dark violet solid; yield 70 mg (79%), m.p. 206 °C (dec.). *Anal.* Calc. for $C_{22}H_{18}CoN_2PS_2$: C, 56.89; H, 3.91; N, 6.03; S, 13.81; Co, 12.69. Found: C, 56.90; H, 3.97; N, 5.84; S, 13.68; Co, 12.49%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 530 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.39–7.80 (br m, 10H, C_6H_5), 5.00 (s, 5H, C_5H_5), 1.92 [d, ^2J(PH) = 10.6, 3H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 37.1 (s).

***16d**:* Red solid; yield 62 mg (62%), m.p. 206 °C (dec.). *Anal.* Calc. for $C_{27}H_{20}CoN_2PS_2$: C, 61.59; H, 3.83; N, 5.32; S, 12.18; Co, 11.19. Found: C, 61.51; H, 3.79; N, 5.56; S, 12.11; Co, 11.28%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 530 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.36–7.76 (br m, 15H, C_6H_5), 5.01 (s, 5H, C_5H_5). ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 46.4 (s).

***16e**:* Red violet solid; yield 83 mg (76%), m.p. 182 °C (dec.). *Anal.* Calc. for $C_{27}H_{20}CoN_2O_3PS_2$: C, 56.45; H, 3.51; N, 4.88; S, 11.16; Co, 10.26. Found: C, 56.51; H, 3.51; N, 4.86; S, 11.03; Co, 10.10%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 518 nm. ^{1}H NMR (CD_2Cl_2, 90 MHz): δ 7.08–7.50 (br m, 15H, C_6H_5), 4.85 [d, ^3J(PH) = 1.7, 5H, C_5H_5]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 132.5 (s).

***17a**:* Red violet solid; yield 57 mg (73%), m.p. 115 °C (dec.). *Anal.* Calc. for $C_{17}H_{24}CoN_2PS_2$: C, 49.75; H, 5.89; N, 6.83; S, 15.63; Co, 14.36. Found: C, 50.39; H, 6.07; N, 6.98; S, 15.58; Co, 14.21%. MS (70 eV) *m/z* 410 (M^+), 194 ($C_5Me_5Co^+$). IR (KBr): ν(C≡N) 2200, ν(C=N) 1400 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 512 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.54 [d, ^4J(PH) = 1.7, 15H, C_5Me_5], 1.46 [d, ^2J(PH) = 10.0, 9H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 12.4 (s).

***17b**:* Violet solid; yield 66 mg (74%), m.p. 124 °C (dec.). *Anal.* Calc. for $C_{22}H_{26}CoN_2PS_2$: C, 55.92; H, 5.55; N, 5.93; S, 13.57; Co, 12.47. Found: C, 56.09; H, 5.55; N, 6.08; S, 13.40; Co, 12.75%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1405 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 512 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.40–7.70 (br m, 5H, C_6H_5), 1.62 [d, ^2J(PH) = 10.0, 6H, PCH_3], 1.28 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 21.1 (s).

***17c**:* Violet solid; yield 81 mg (80%), m.p. 173 °C (dec.). *Anal.* Calc. for $C_{27}H_{28}CoN_2PS_2$: C, 60.67; H, 5.28; N, 5.24; S, 12.00; Co, 11.02. Found: C, 60.42; H, 5.46; N, 5.18; S, 11.97; Co, 10.79%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 530 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.32–7.70 (br m, 10H, C_6H_5), 1.91 [d, ^2J(PH) = 9.4, 3H, PCH_3], 1.32 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 32.0 (s).

***17d**:* Red solid; yield 69 mg (61%), m.p. 198 °C (dec.). *Anal.* Calc. for $C_{32}H_{30}CoN_2PS_2$: S, 10.75; Co, 9.88. Found: S, 10.88; Co, 9.78%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1410 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 535 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.27–7.66 (br m, 15H, C_6H_5), 1.21 [d, ^4J(PH) = 1.7, 15H, C_5Me_5]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 46.3 (s).

3.21. Preparation of **17a** with **5a** or **7a** as starting material

(a) A solution of **5a** (102 mg, 0.27 mmol) in 25 ml of CH_2Cl_2 was treated with $C_2(CN)_4$ (35 mg, 0.27 mmol) and stirred for 1 h at r.t. The solution was filtered and the filtrate was worked up as described for **15a**; yield 90 mg (81%). (b) A solution of **7a** (115 mg, 0.24 mmol) in 25 ml of CH_2Cl_2 was stepwise treated with $CH_2(CN)_2$ (48 mg, 0.72 mmol) and NaOMe (39 mg, 0.72 mmol). After the reaction mixture was stirred for 24 h at r.t., it was filtered and the filtrate was worked up as described for **15a**; yield 76 mg (77%).

3.22. Preparation of [(C_5H_5)Co(PMe_3){Se_2C=C(CN)$_2$}] (**18a**)

This compound was prepared as described for **15a**, with 118 mg (0.26 mmol) of **1a** and 162 mg (0.52 mmol) of $K_2[Se_2C{=}C(CN)_2]$ as starting materials. Dark brown solid, yield 71 mg (63%); m.p. 176 °C (dec.). *Anal.* Calc. for $C_{12}H_{14}CoN_2PSe_2$: C, 33.20; H, 3.25; N, 6.45; Co, 13.58. Found: C, 32.96; H, 3.11; N, 6.18; Co, 13.31%. MS (70 eV) *m/z* 436 (M^+), 280 ($M^+ - SeC_2(CN)_2$), 200 ($C_5H_5Co(PMe_3)^+$). IR (KBr): ν(C≡N) 2200, ν(C=N) 1405 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 534 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.07 (s, 5H, C_5H_5), 1.73 [d, ^2J(PH) = 10.6, 9H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 17.3 (s).

3.23. Preparation of [(C_5Me_5)Co(PMe_3){Se_2C=C(CN)$_2$}] (**18b**)

This compound was prepared as described for **15a**, with 136 mg (0.26 mmol) of **3a** and 162 mg (0.52 mmol) of $K_2[Se_2C{=}C(CN)_2]$ as starting materials. Brown solid, yield 93 mg (71%); m.p. 113 °C

(dec.). *Anal.* Calc. for $C_{17}H_{24}CoN_2PSe_2$: C, 40.50; H, 4.80; N, 5.56; Co, 11.69. Found: C, 40.22; H, 4.55; N, 5.19; Co, 11.73%. IR (KBr): ν(C≡N) 2200, ν(C=N) 1400 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 524 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.62 [d, ^4J(PH) = 1.6, 15H, C_5Me_5], 1.55 [d, ^2J(PH) = 9.7, 9H, PCH_3]. ^{31}P NMR [$CDCl_3$, 36.2 MHz]: δ 13.3 (s).

3.24. Preparation of [(C_5H_5)Rh($PiPr_3$)(S_2C=S)] (**20a**)

A solution of **19a** (120 mg, 0.30 mmol) in 25 ml of CH_2Cl_2 was treated with K_2CS_3 (61 mg, 0.33 mmol) and stirred for 24 h at r.t. The solution was filtered and the filtrate was worked-up as described for **16a**. Orange-yellow solid; yield 77 mg (59%), m.p. 79 °C (dec.). *Anal.* Calc. for $C_{15}H_{26}PRhS_3$: C, 41.28; H, 6.00; S, 22.04; Rh, 23.58. Found: C, 41.47; H, 5.86; S, 22.29; Rh, 23.13%. IR (KBr): ν(C=S) 1030 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 470 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.56 [dd, ^2J(RhH) = 0.5, ^3J(PH) = 1.8, 5H, C_5H_5], 2.35 (br m, 3H, PCH), 1.26 [dvt, N = 14.0, ^3J(PH) = 7.0, 18H, PCHCH_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 63.0 [d, ^1J(RhP) = 143.6].

3.25. Preparation of [(C_5Me_5)Rh(PPh_3)(S_2C=S)] (**20b**)

This compound was prepared as described for **20a**, with 171 mg (0.30 mmol) of **19b** and 61 mg (0.33 mmol) of K_2CS_3 as starting materials; reaction time 18 h. Orange-yellow solid, yield 115 mg (63%); m.p. 201 °C (dec.). *Anal.* Calc. for $C_{29}H_{30}PRhS_3$: C, 57.23; H, 4.97; S, 15.81; Rh, 16.91. Found: C, 56.61; H, 5.13; S, 15.52; Rh, 16.28%. IR (KBr): ν(C=S) 1035 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 472 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.28–7.78 (br m, 15H, C_6H_5), 1.47 [dd, ^3J(RhH) = 0.5, ^4J(PH) = 3.1, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 39.7 [d, ^1J(RhP) = 151.8].

3.26. Preparation of [(C_5H_5)Ir($PiPr_3$)(S_2C=S)] (**22**)

This compound was prepared as described for **20a**, with 171 mg (0.30 mmol) of **21** and 61 mg (0.33 mmol) of K_2CS_3 as starting materials; reaction time 18 h. Yellow-green solid, yield 60 mg (41%); m.p. 120 °C (dec.). *Anal.* Calc. for $C_{15}H_{26}IrPS_3$: C, 34.20; H, 4.98; S, 18.26. Found: C, 34.00; H, 5.14; S, 18.01%. IR (KBr): ν(C=S) 1035 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 469 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 5.59 [d, ^3J(PH) = 1.2, 5H, C_5H_5], 2.52 (br m, 3H, PCH), 1.25 [dvt, N = 14.0, ^3J(PH) = 7.0, 18H, PCHCH_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 20.3 (s).

3.27. General procedure for the preparation of [(C_5R_5)Rh(PR_3)(S_2CSMe)BF_4 (**23a**, **23b**) and [(C_5H_5)Ir($PiPr_3$)(S_2CSMe)BF_4 (**24**)

A solution of **20a** (87 mg, 0.20 mmol), **20b** (122 mg, 0.20 mmol) or **22** (84 mg, 0.16 mmol) in 30 ml of CH_2Cl_2 was treated under stirring with an equimolar amount of [Me_3O]BF_4 (30 mg, 0.20 mmol or 24 mg 0.16 mmol, respectively) and continuously stirred for 4 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. The residue was washed three times with 10 ml of diethyl ether and dried in vacuo.

23a: Orange-yellow solid, yield 86 mg (80%), m.p. 189 °C (dec.), Λ = 72 $cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{16}H_{19}BF_4PRhS_3$: C, 35.74; H, 3.56; S, 17.89; Rh, 19.14. Found: C, 35.49; H, 3.38; S, 17.50; Rh, 18.99%. IR (KBr): ν(C=S) 995 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 486 nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 5.98 [dd, ^2J(RhH) = 0.4, ^3J(PH) = 1.5, 5H, C_5H_5], 2.78 (s, 3H, SCH_3), 2.57 (br m, 3H, PCH), 1.34 [dvt, N = 14.2, ^3J(PH) = 7.1, 18H, PCHCH_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 64.4 [d, ^1J(RhP) = 131.0].

23b: Orange-yellow solid, yield 119 mg (84%); m.p. 228 °C (dec.), Λ = 66 $cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{30}H_{33}PBF_4PRhS_3$: C, 50.72; H, 4.68; S, 13.54; Rh, 14.48. Found: C, 50.14; H, 4.51; S, 13.16; Rh, 14.24%. IR (KBr): ν(C=S) 990 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 488 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.53–7.91 (br m, 15H, C_6H_5), 2.39 (s, 3H, SCH_3), 1.60 [dd, ^3J(RhH) = 0.4, ^4J(PH) = 3.3, 15H, C_5Me_5]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 38.4 [d, ^1J(RhP) = 142.2].

24: Yellow-green solid, yield 79 mg (79%), m.p. 144 °C (dec.), Λ = 77 $cm^2\ \Omega^{-1}\ mol^{-1}$. *Anal.* Calc. for $C_{16}H_{19}BF_4IrPS_3$: C, 30.62; H, 4.66; S, 15.33. Found: C, 30.40; H, 4.91; S, 15.36%. IR (KBr): ν(C=S) 995 cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/l): λ = 483 nm. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 6.04 [d, ^3J(PH) = 1.1, 5H, C_5H_5], 2.76 (br m, 3H, PCH), 2.70 (s, 3H, SCH_3), 1.32 [dvt, N = 14.4, ^3J(PH) = 7.2, 18H, PCHCH_3]. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 23.7 (s).

Cyclic voltammetry: In a glovebox [N(nBu)$_4$]PF_6 and the electroactive species were placed into a thoroughly dried CV cell. At a high purity argon line acetonitrile was added through a gastight syringe. Then a platinum disk working electrode, a platinum wire counter electrode, and a Hg/$HgCl_2$ reference electrode were placed into the solution. The cyclic voltammograms were recorded at scan rates between 50 and 200 mV/s using different starting and switching potentials. For the determination of the oxidation potentials, ferrocene ($E_{1/2}$ = +0.40 V versus SCE) [44] was added as the internal standard. Cyclic voltammograms were recorded using a Potentioscan Wenking POS 73 model of Bank Electronics with an XY recorder as described by Feldmann and Koberstein [45].

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