Mono- and Bicyclic Organometallic Ring Systems with Exocyclic C=C and C=S Bonds[☆]

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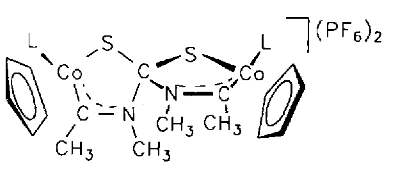
Received March 6, 1997

Keywords: Cobalt / Cyclopentadienyl complexes / Heterocycles / Electrophilic addition / Insertion reaction

The cobaltaheterocycles [$C_5H_5Co\{\kappa^2(C,S)$-$C(=CH_2)$-$N(R)C(=S)S\}(PMe_2Ph)$] (**5**−**7**), which contain both an exocyclic C=C and C=S bond, were prepared from the iminoacylcobalt compounds [$C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_2Ph)$]I (**2**−**4**) on treatment with either $CS_2/NaOCH_3$ or K[S_2CNMe_2], respectively. While protonation of **5** (R = CH_3) and **7** (R = CH_2Ph) with HBF_4 occurs at the exocyclic $C=CH_2$ bond to give cations containing a $CoC(CH_3)N(R)C(=S)S$ ring, the methylation of **5** and **7** with [OMe_3]BF_4 takes place at the exocyclic C=S bond and generates five-membered heterocycles with an SCH_3 substituent. The reaction of **5**−**7** with S_8 leads to the elimination of the phosphane ligand and affords the bicyclic dithiolenecobalt complexes **14**−**16** in moderate to good yields. On treatment of **5**−**7** with $C_2(CO_2R')_2$ (R′ = Me, Et), an insertion of the alkyne into the $C=CH_2$ bond occurs and five-membered ring systems **19**−**22** with an unsaturated exocyclic $=C(CO_2R')-C(CO_2R')=CH_2$ group are formed. As in the case of **5** and **7**, protonation and methylation reactions of **19** also take place at different sites leading to cations with either a delocalized CoCN or NCS unit.

In continuation of our work on d^8 halfsandwich-type complexes, which behave as Lewis bases[1], we have recently shown that isocyanidocobalt(I) as well as iminoacylcobalt(III) compounds on treatment with C−X double- or triple-bond systems readily undergo [2 + 2] and [3 + 2] cycloaddition reactions to give four- or five-membered cobaltaheterocycles[2]. By usig [$C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_3)$]I as the starting material and CS_2 as the substrate, in the presence of a PF_6 salt instead of a mononuclear cobalt complex the binuclear spirocyclic compound **1** is formed[3].



1 (L = PMe_3)

When we extended these studies to analogous iminoacylcobalt derivatives with phosphane ligands other than PMe_3, we found that the cationic species [$C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_2Ph)$]$^+$ reacts with CS_2 in the presence of $NaOCH_3$ to yield a neutral mononuclear product with a CoCNCS five-membered ring[4]. The remarkable reactivity of this compound towards S_8 prompted us to further develop the chemistry of sulfur-containing cobaltaheterocycles and to investigate in particular their behavior towards electrophilic substrates.

In this paper we describe a new route to metal-containing ring systems with both exocyclic $C=CH_2$ and C=S bonds, the conversion of these species to bicyclic dithiolenecobalt complexes, and the formal insertion of activated alkynes into the $C=CH_2$ bond. We furthermore illustrate that protonation and methylation reactions of both the initially formed heterocycles and the insertion products occur at different sites of the molecules, probably due to the hardness and softness of the reacting centres.

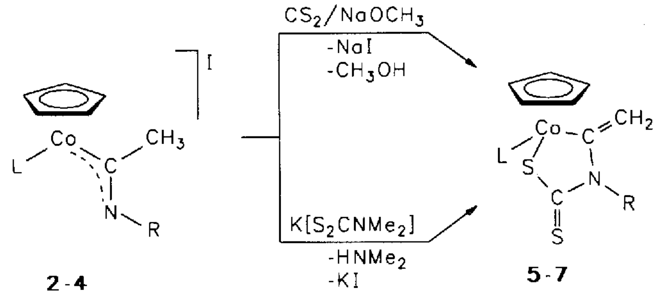
Results and Discussion

Preparation and Electrophilic Addition Reactions of the CoCNCS Heterocycles

We have already reported that the heterocyclic complex **5** is formed from **2** after stepwise reactions with CS_2 and $NaOCH_3$ in dichloromethane[4]. The iminoacylcobalt(III) compounds **3** and **4** behave similarly (see Scheme 1) and upon treatment with CS_2 and $NaOCH_3$ give the uncharged metallaheterocycles **6** and **7** in ca. 60% yield. An alternative route to **5**−**7** consists of the reaction of the starting materials **2**−**4** with the dithiocarbamate K[S_2CNMe_2] in CH_2Cl_2 at room temp. which, after chromatographic workup and recrystallization from CH_2Cl_2/ether, affords the target complexes in excellent yield.

The IR- and NMR-spectroscopic data of **6** and **7** are quite similar to those of compound **5**, the molecular structure of which has been determined by X-ray crystallography[4]. Characteristic features of the ^1H-NMR spectra of **6** and **7** (in $CDCl_3$) are the two resonances for the chemically different protons of the exocyclic $=CH_2$ group, which − due to P−H and H−H coupling − appear as doublets of doublets, and also the two signals for the CH_3 protons of the phosphane ligand, diagnostic for the chirality of the molecules. The ^{13}C-NMR spectrum of **7** (in $CDCl_3$) displays a singlet at $\delta = 210.3$ for the C=S and a broadened doublet at $\delta = 157.5$ for the *C*=CH_2 carbon atoms, the broadening being due to the quadrupole moment of cobalt.

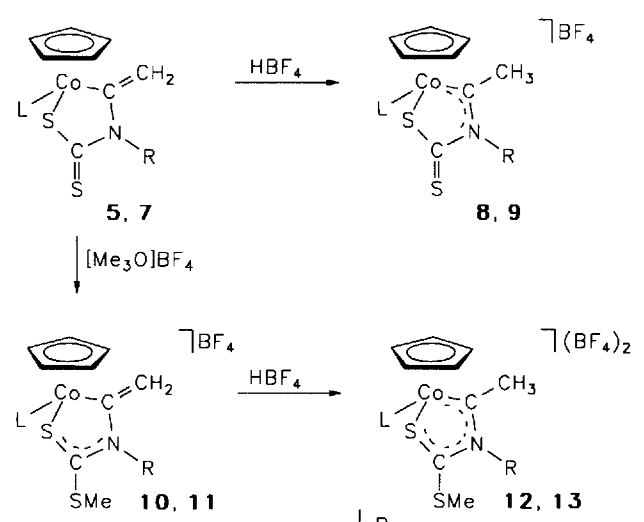
Scheme 1. L = PMe_2Ph



	R
2, 5	CH_3
3, 6	C_6H_5
4, 7	CH_2Ph

The protonation reactions of **5** and **7** with HBF_4 in CH_2Cl_2/ether lead to the formation of cationic cobaltaheterocycles, in which the metal-bonded carbon atom carries instead of a methylene a CH_3 group. The BF_4 salts **8** and **9** (Scheme 2), that have been isolated as red microcrystalline solids, are practically air-stable and soluble in polar solvents such as CH_2Cl_2, $CHCl_3$ or nitromethane. The ^{1}H-NMR spectra of **8** and **9** display instead of two signals for the =CH_2 protons (as observed for the precursor compounds **5** and **7**) a doublet at $\delta = 3.41$ (**8**) or 3.40 (**9**) with the relative intensity of 3H for the CCH_3 group. The ^{13}C-NMR spectrum of **9** exhibits resonances at $\delta = 157.0$ for the *C*CH_3 and at $\delta = 9.7$ for the C*C*H_3 carbon atoms, which supports the structural proposal.

Scheme 2. L = PMe_2Ph



	R
8, 10, 12	CH_3
9, 11, 13	CH_2Ph

In contrast to HBF_4, Meerwein's reagent $[OMe_3]BF_4$ does not attack the C=CH_2 but the C=S bond leading to a five-membered ring with an exocyclic SCH_3 unit. The cationic complexes **10** and **11** (Scheme 2) are – like the related species **8** and **9** – red, air-stable solids which were characterized by elemental analysis and spectroscopic techniques. Due to the methylation of the C=S moiety, the signal of the respective carbon atom in the ^{13}C-NMR spectrum is shifted from $\delta = 210.3$ (for **7**) to $\delta = 196.8$ (for **10**) and 200.2 (for **11**), which is in agreement with a partial decrease of the C–S bond order.

While attempts to methylate the C=S bond of the cationic species **8** and **9** with $[OMe_3]BF_4$ failed, the synthesis of the wanted dicationic metallaheterocycles **12** and **13** was achieved by treatment of **10** and **11** with HBF_4 in nitromethane/ether. The protonation appears to be reversible since during chromatography of solutions of **12** and **13** in CH_2Cl_2 or CH_3NO_2 on neutral Al_2O_3 the starting materials **10** and **11** are reformed. Owing to the doubly positive charge of the complexes, the ^{1}H-NMR signals of the C_5H_5 and PCH_3 protons of **12** and **13** are shifted, compared to **10** and **11**, to significantly lower fields. The orange-yellow solids **12** and **13** are only sparingly soluble in CH_3NO_2 or CH_2Cl_2 and in solution slowly loose HBF_4 to regenerate **10** and **11**.

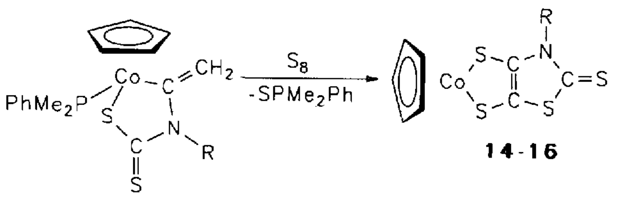
Bicyclic Dithiolenecobalt Complexes by Addition of Sulfur

The reaction of compounds **5**, **6** and **7** with sulfur, originally aimed to prepare $[C_5H_5CoS_5(PMe_2Ph)]$ and the four-membered heterocycles $SC(=S)N(R)C(=CH_2)$, unexpectedly leads to the formation of the novel bicyclic dithiolenecobalt complexes **14–16** (Scheme 3) in 40–50% yield. In the course of the reaction, the phosphane ligand is eliminated and reacts with S_8 to give $SPMe_2Ph$ as a byproduct. Monocyclic relatives of **14–16** of the general composition $[C_5H_5Co\{\kappa^2(S,S')\text{-}S_2C_2RR'\}]$ are already known and have been obtained either from mononuclear C_5H_5Co derivatives[5] or from Co_3 clusters[6] as starting materials.

The neutral complexes **14–16** form green crystals which are only slightly air-sensitive and easily soluble in chlorinated hydrocarbons such as CH_2Cl_2 or $CHCl_3$. As the X-ray crystal-structure analysis of **14** showed[4], the bicyclic fragment is almost exactly planar, the dihedral angle between the CoS_2C_2 and C_2SCN planes being 2.7 and 1.7°, respectively. The two C–S distances of the cobalt-containing ring are somewhat shorter (by ca. 0.05 Å) than the two C–S bond lengths in the second ring, which points to partial electron delocalization of the CoS_2C_2 unit.

The interesting question of how the novel dithiolenecobalt complexes **14–16** are formed from the monocyclic precursors **5–7** and sulfur cannot be answered conclusively. A labeling experiment, in which isotopically pure $^{12}CH_3I$ was used for the preparation of **5**, revealed that one of the central carbon atoms of the bicyclic system, which is connected to two S and one C atom, stems from the exocyclic =CH_2 unit[4]. However, despite this information it is not clear what the initial step of the reaction is and which intermediates are involved in the rearrangement from the original metal-

Scheme 3



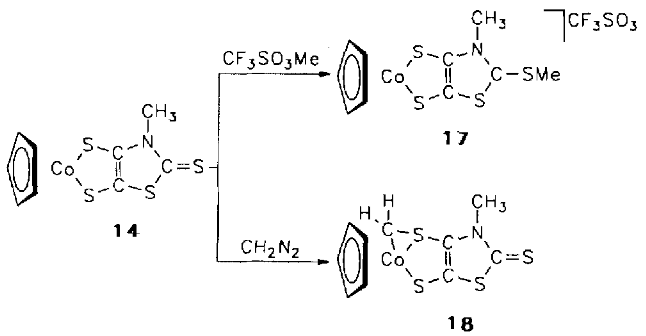
5-7 **14-16**

	R
14	CH_3[4]
15	C_6H_5
16	CH_2Ph

laheterocycle to the bicyclic dithiolenes. It should be mentioned that the starting materials **5–7** are quite inert towards selenium and do not react even upon stirring at 70°C in benzene for 3 days.

In order to find out whether the bicyclic dithiolenes like the monocyclic precursors **5–7** are also attacked by electrophiles, the reactivity of compound **14** towards $CF_3SO_3CH_3$ and CH_2N_2 was investigated. The results are outlined in Scheme 4. Methyl triflate reacts with the exocyclic C=S bond of **14** and affords the ionic complex **17** in ca. 65% yield. Treatment of **14** with diazomethane in CH_2Cl_2/ether at −30°C leads to the formation of a CH_2 adduct **18**, which is probably related in structure to a corresponding species obtained by Sugimori et al. from the monocyclic dithiolene-cobalt complex $[C_5H_5Co\{\kappa^2(S,S)\text{-}S_2C_2(CN)_2\}]$ and CH_2N_2[7]. The ^1H-NMR spectrum of **18** (in $CDCl_3$) displays besides the resonances for the C_5H_5 and the NCH_3 protons two doublets at δ = 3.88 and 1.94 which are assigned to the two stereochemically different protons of the CH_2 group. The signal for the CH_2 carbon atom appears in the ^{13}C-NMR spectrum (in $CDCl_3$) at δ = 27.0, which is in agreement with Sugimori's results[7]. From the spectroscopic data of **18**, however, and also from the fragmentation pattern in the mass spectrum we can not decide, whether the addition of the CH_2 moiety takes place at the Co–S bond in *cis* or in *trans* disposition to the NCH_3 substituent at the central C=C bond of **14**.

Scheme 4



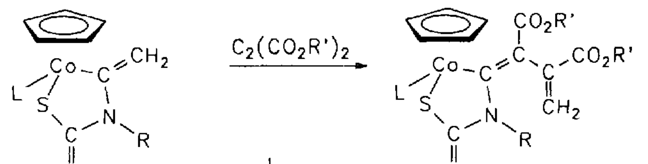
14 **17** **18**

Alkyne Insertion into the Exocyclic C=CH₂ Bond

The reaction of the monocyclic compounds **5–7** with activated alkynes $C_2(CO_2R')_2$ (R′ = Me, Et) follows an unexpected route. Since it is known that various five-membered metallacycles react with alkynes by ring expansion and, after elimination of the metal–ligand fragment to form six-membered rings[8], we anticipated that on treatment of **5–7** with $C_2(CO_2R')_2$ a similar process could occur. However, instead of an insertion of the alkyne into the Co–C bond of the starting material a formal insertion into the exocyclic C=C bond takes place (Scheme 5). After chromatographic workup and recrystallization from CH_2Cl_2/ether, the complexes **19–22** are isolated in 60–70% yield. They form brown crystals which are quite stable both in the solid state and in solution. The ^{13}C-NMR spectra of **19–22** (in $CDCl_3$) display two signals for the carbon atoms which are connected to a CO_2R' group at $\delta \approx$ 167 and 140 and a resonance for the $=CH_2$ carbon atom at $\delta \approx$ 127. The assignment of the latter has been confirmed by DEPT measurements. The signals of the $=CH_2$ protons appear in the ^1H-NMR spectra of the insertion products in the region between δ = 5.3 and 6.3 and are thus shifted by ca. 1.0–1.5 ppm downfield compared to those of **5–7**.

With regard to the mechanism of formation of **19–22** we assume that in the initial step the electrophilic alkyne attacks the exocyclic $C=CH_2$ bond of **5–7** to generate, possibly via a zwitterionic intermediate, a heterocycle with a fused four-membered ring. The opening of this ring at the $C_{sp3}-C_{sp3}$ bond could lead to the product carrying a $=C(CO_2R')-C(CO_2R')=CH_2$ substituent at the α-carbon atom of the metallacycle. Precedence for this mechanistic scheme stems from the work by Fischer and Dötz who studied the insertion of alkynes such as $MeC{\equiv}CNEt_2$ into the M=C bond of carbenechromium and -tungsten derivatives[9].

Scheme 5. L = PMe_2Ph

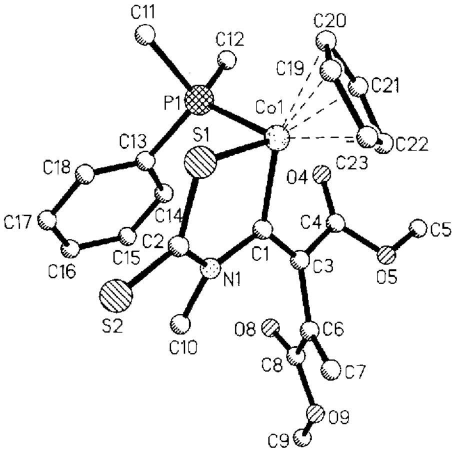


5-7 **19-22**

	R	R'
19	CH_3	CH_3
20	C_6H_5	CH_3
21	CH_2Ph	CH_3
22	CH_3	C_2H_5

The result of the X-ray crystal-structural analysis of **19** is shown in Figure 1. The five-membered heterocycle is nearly coplanar with the largest deviation from the [Co,C1,N1,C2,S1] plane observed for S2 (0.082 Å). Both the bond lengths and angles of the CoCNCS ring of **19** and of the precursor complex **5**[4] are quite similar which indicates that the two different substituents $=CH_2$ (in **5**) and $=C(CO_2Me)-C(CO_2Me)=CH_2$ (in **19**) are only of minor importance for the bond situation of the heterocycle. The distances C1–C3, C3–C6 and C6–C7 are alternating from 137.3(4) to 149.4(4) and 132.8(4) Å which is in agreement with the presence of a butadien-like fragment. It should be noted that the two CO_2Me groups prefer an *anti*-type arrangement at the C–C bond which probably minimizes the steric repulsion between these two units.

Figure 1. Molecular structure of **19**[a]



[a] Selected bond lengths [Å] and angles [°]: Co–P 2.185(1), Co–S1 2.184(1), Co–C1 1.944(3), Co–C19 2.093(3), Co–C20 2.093(3), Co–C21 2.091(3), Co–C22 2.103(3), Co–C23 2.102(3), C1–N1 1.424(3), C2–N1 1.367(4), C2–S1 1.697(3), C2–S2 1.673(3), N1–C10 1.474(4), C1–C3 1.373(4), C3–C4 1.480(4), C3–C6 1.494(4), C6–C7 1.328(4), C6–C8 1.490(4), C4–O4 1.198(4), C4–O5 1.355(4), C8–O8 1.202(4), C8–O9 1.329(4); P–Co–S1 91.2(1), P–Co–C1 92.2(1), S1–Co–C1 86.7(1), Co–S1–C2 101.1(1), S1–C2–S2 120.2(2), S1–C2–N1 116.1(2), S2–C2–N1 123.7(2), C1–N1–C2 119.8(2), C1–N1–C10 122.2(2), C2–N1–C10 117.1(2), N1–C1–C3 117.4(2), Co–C1–N1 115.8(2), Co–C1–C3 126.4(2), C1–C3–C4 121.3(3), C1–C3–C6 124.6(2), C4–C3–C6 114.0(2), C3–C6–C7 122.4(3), C3–C6–C8 115.9(2), C7–C6–C8 121.7(3), C3–C4–O4 127.5(3), C3–C4–O5 110.0(2), O4–C4–C5 122.4(3), C6–C8–O8 124.3(3), C6–C8–O9 112.6(3), O8–C8–O9 123.1(3).

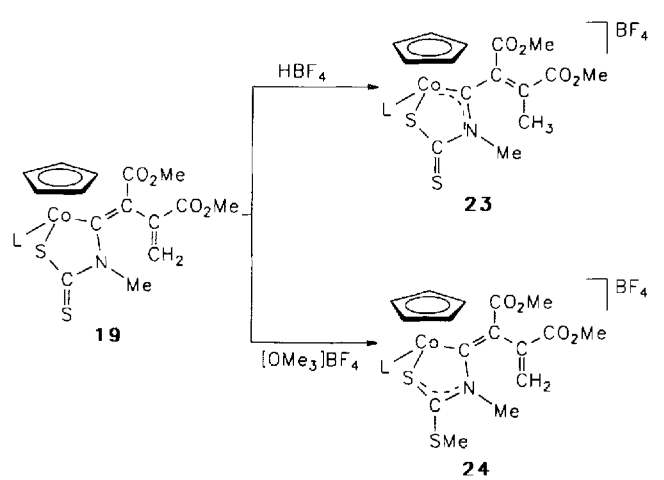
The behavior of the insertion product **19** towards HBF_4 and $[OMe_3]BF_4$ is quite similar to that of complex **5**. Whilst the Broensted acid reacts with the $C{=}CH_2$ bond to form a cationic metallaheterocycle containing a vinylic unit $-C(CO_2Me){=}C(CO_2Me)CH_3$ at the α-carbon atom of the ring, Meerwein's reagent $[OMe_3]BF_4$ attacks the exocyclic C=S bond and affords a derivative with a SCH_3 substituent. Both **23** and **24** (Scheme 6) are red or red-brown, air-stable solids, which in nitromethane reveal a conductivity corresponding to a 1:1 electrolyte. Particularly diagnostic in the ^{1}H-NMR spectrum of **24** (CD_3NO_2) are the two signals for the protons of the terminal $=CH_2$ group, which appear as doublets at δ = 6.22 and 5.30.

This work was supported by the *Ministry of Education of the People's Republic of China* and the *Stiftung Volkswagenwerk*. We thank Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses and DTA measurements, Dr. *W. Buchner* for recording NMR spectra, and Dr. *G. Lange* and Mr. *F. Dadrich* for mass-spectroscopic measurements.

Experimental Section

All operations were carried out under argon with the Schlenk technique. $[C_5H_5Co(PMe_2Ph)_2]$ was prepared as described in the literature[10]. A preparative procedure for the starting material **2** and compound **14** was already given[4,11]. The alkynes $C_2(CO_2R')_2$ and the isocyanides were commercial products from Aldrich. – IR: Perkin-Elmer 1420. – NMR: Jeol FX 90 Q and Bruker AC 200. – MS: Varian MAT CH7.

Scheme 6. L = PMe_2Ph



1. *Preparation of* $[C_5H_5Co\{C(CH_3){=}NR\}(PMe_2Ph)]I$ (**3**, **4**): A solution of 175 mg (0.43 mmol) of $[C_5H_5Co(PMe_2Ph)_2]$ in 6 ml of benzene was treated with an equimolar amount of CNR (R = Ph, CH_2Ph) and stirred for 10 min at room temp. The solvent was removed in vacuo, and the brownish oily residue was extracted with 5 ml of pentane. The extract (containing the isocyanide complex $[C_5H_5Co(CNR)(PMe_2Ph)]$) was treated at –30°C with 80 μl (1.30 mmol) of CH_3I and stirred for 5 min. A yellow solid precipitated, which was separated from the mother liquor, washed twice with 3-ml portions of pentane (–30°C) and dried; yield 75–80%. Due to the lability and air sensitivity of the product it was only characterized by IR and ^{1}H-NMR spectroscopy. **3**: IR (KBr): $\tilde{\nu}$ = 1625 cm^{-1} [ν(C=N)]. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.1–7.6 (m, 10H, C_6H_5), 5.40 [d, *J*(PH) = 0.4 Hz, 5H, C_5H_5], 3.28 [d, *J*(PH) = 2.5 Hz, 3H, CCH_3], 2.20 [d, *J*(PH) = 11.0 Hz, 3H, PCH_3], 2.05 [d, *J*(PH) = 11.4 Hz, 3H, PCH_3]. – **4**: IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} [ν(C=N)]. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.2–7.8 (m, 10H, C_6H_5), 5.28 [d, *J*(PH) = 0.5 Hz, 5H, C_5H_5], 4.90 (br. s, 2H, NCH_2), 3.40 [d, *J*(PH) = 2.2 Hz, 3H, CCH_3], 2.15 [d, *J*(PH) = 10.8 Hz, 3H, PCH_3], 2.07 [d, *J*(PH) = 10.5 Hz, 3H, PCH_3].

2. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C({=}CH_2)N(CH_3)\text{-}C({=}S)S\}(PMe_2Ph)]$ (**5**): The synthesis of compound **5** from **2** and CS_2 had already been reported[4]. An alternative preparative procedure is as follows: A solution of 250 mg (0.56 mmol) of **2** in 10 ml of CH_2Cl_2 was treated with 267 mg (1.68 mmol) of $K[S_2CNMe_2]$ at room temp. After the reaction mixture had been stirred for 4 h, the solvent was removed, the residue was dissolved in 2 ml of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). With CH_2Cl_2/pentane (10:1) a brown fraction was eluted which was brought to dryness in vacuo. Recrystallization from CH_2Cl_2/ether gave brown crystals; yield 170 mg (77%). The product was characterized by comparison of the IR and NMR data with those of an authentic sample[4].

3. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C({=}CH_2)N(C_6H_5)C\text{-}({=}S)S\}(PMe_2Ph)]$ (**6**). – (a) A solution of 250 mg (0.49 mmol) of **3** in 10 ml of CH_2Cl_2 was treated dropwise with 0.1 ml (1.60 mmol) of CS_2 at room temp. After the solution had been stirred for 1 h, 30 mg (0.55 mmol) of $NaOCH_3$ was added, and the reaction mixture was stirred again for 3 h. The solvent was removed, and the residue was worked up as described for **5**. Upon recrys-

tallization from CH_2Cl_2/ether brown crystals were obtained; yield 155 mg (68%). – (b) Compound **6** was also prepared analogously as described for **5**, by using 250 mg (0.49 mmol) of **3** and a threefold excess of $K[S_2CNMe_2]$ as starting materials; yield 173 mg (76%); m.p. 193°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1160 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.2–7.8 (m, 10H, C_6H_5), 4.77 [d, *J*(PH) = 0.4 Hz, 5H, C_5H_5], 4.60 [dd, *J*(PH) = 2.4, *J*(HH) = 1.2 Hz, 1H, 1H of $=CH_2$], 4.43 [dd, *J*(PH) = 3.6, *J*(HH) = 1.2 Hz, 1H, 1H of $=CH_2$], 1.72 [d, *J*(PH) = 10.6 Hz, 3H, PCH_3], 1.61 [d, *J*(PH) = 10.4 Hz, 3H, PCH_3]. – $C_{22}H_{23}CoNPS_2$ (455.2): calcd. C 58.00, H 5.09, N 3.08; found C 58.12, H 5.11, N 3.30.

4. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=CH_2)N(CH_2Ph)C(=S)S\}(PMe_2Ph)]$ (**7**): This compound was prepared analogously as described for **5** and **6** by using either (a) 260 mg (0.50 mmol) of **4**, 0.1 ml (1.60 mmol) of CS_2 and 30 mg (0.55 mmol) of $NaOCH_3$, or (b) 260 mg (0.50 mmol) of **4** and 240 mg (1.50 mmol) of $K[S_2CNMe_2]$ as starting materials. Recrystallization from CH_2Cl_2/ether gave brown crystals; yield 152 mg (63%) for (a) and 189 mg (80%) for (b); m.p. 202°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1165 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.3–7.9 (m,10H, C_6H_5), 5.41 (br. s, 2H, NCH_2), 5.32 [dd, *J*(PH) = 2.3, *J*(HH) = 2.0 Hz, 1H, 1H of $=CH_2$], 4.93 [d, *J*(PH) = 0.3 Hz, 5H, C_5H_5], 4.85 [dd, *J*(PH) = 2.5, *J*(HH) = 2.0 Hz, 1H, 1H of $=CH_2$], 1.80 [d, *J*(PH) = 10.6 Hz, 3H, PCH_3], 1.61 [d, *J*(PH) = 10.8 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 210.3 (s, C=S), 157.5 [br. d, *J*(PC) = 38.7 Hz, CoC], 137.4 [d, *J*(PC) = 42.3 Hz, *ipso*-C of PC_6H_5], 137.0, 130.4 (2 s, C_6H_5), 129.1 [d, *J*(PC) = 7.7 Hz, *meta*-C of PC_6H_5], 128.6 [d, *J*(PC) = 9.5 Hz, *ortho*-C of PC_6H_5], 128.2, 126.8, 126.6 (3 s, C_6H_5), 108.9 [d, *J*(PC) = 4.3 Hz, $=CH_2$], 89.1 [d, *J*(PC) = 2.6 Hz, C_5H_5], 56.0 (br. s, NCH_2), 13.9 [d, *J*(PC) = 37.7 Hz, PCH_3], 12.7 [d, *J*(PC) = 34.9 Hz, PCH_3]. – $C_{23}H_{25}CoNPS_2$ (469.3): calcd. C 58.82, H 5.37, N 2.98; found C 59.27, H 5.46, N 3.03.

5. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(CH_3)N(CH_3)C(=S)S\}(PMe_2Ph)]BF_4$ (**8**): A solution of 395 mg (1.00 mmol) of **5** in 10 ml of CH_2Cl_2 was treated dropwise with a 54% solution of HBF_4 in ether at room temp. After the reaction mixture had been stirred for 3 min, it was filtered, and the filtrate was concentrated in vacuo to ca. 1 ml. Addition of 10 ml of ether led to the precipitation of a red solid, which was filtered, repeatedly washed with ether and pentane and dried; yield 355 mg (74%); m.p. 216°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1150 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, CD_2Cl_2): δ = 7.5 (m, 5H, C_6H_5), 5.59 [d, *J*(PH) = 0.7 Hz, 5H, C_5H_5], 3.44 (br. s, 3H, NCH_3), 3.41 [d, *J*(PH) = 2.2 Hz, 3H, CCH_3], 2.09 [d, *J*(PH) = 11.3 Hz, 3H, PCH_3], 2.05 [d, *J*(PH) = 11.5 Hz, 3H, PCH_3]. – $C_{17}H_{22}BCoF_4NPS_2$ (481.1): calcd. C 42.41, H 4.61, N 2.91; found C 42.13, H 4.35, N 2.57.

6. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(CH_3)N(CH_2Ph)C(=S)S\}(PMe_2Ph)]BF_4$ (**9**): This compound was prepared analogously as described for **8** by using 470 mg (1.00 mmol) of **7** and a 54% solution of HBF_4 in ether as starting materials. Red microcrystalline solid; yield 389 mg (70%); m.p. 204°C (dec.) – IR (KBr): $\tilde{\nu}$ = 1155 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, CD_2Cl_2): δ = 7.2–7.7 (m, 10H, C_6H_5), 5.62 [d, *J*(PH) = 0.7 Hz, 5H, C_5H_5], 4.75 (br. s, 2H, NCH_2), 3.40 [d, *J*(PH) = 2.2 Hz, 3H, CCH_3], 2.11 [d, *J*(PH) = 11.4 Hz, 3H, PCH_3] 2.08 [d, *J*(PH) = 11.1 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 219.1 (s, C=S), 157.0 [br. d, *J*(PC) = 46.2 Hz, CoC], 144.2, 141.9, 139.7, 139.4, 139.1, 139.0, 137.8, 135.7 (8 s or overlapping d, C_6H_5), 97.7 (s, C_5H_5), 59.1 (br. s, NCH_2), 11.6 [d, *J*(PC) = 31.4 Hz, PCH_3], 10.9 [d, *J*(PC) = 34.9 Hz, PCH_3], 9.7 (s, CCH_3). – $C_{23}H_{26}BCoF_4NPS_2$ (557.1): calcd. C 49.55, H 4.70, N 2.51; found C 49.26, H 4.44, N 2.33.

7. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=CH_2)N(CH_3)C(SCH_3)S\}(PMe_2Ph)]BF_4$ (**10**): A solution of 395 mg (1.00 mmol) of **5** in 10 ml of CH_3NO_2 was treated with small portions of 177 mg (1.20 mmol) of $[OMe_3]BF_4$ and stirred for 30 min at room temp. The solution was filtered, the filtrate was concentrated in vacuo to ca. 1 ml, and 10 ml of ether was added. An orange-yellow solid precipitated which was separated from the mother liquor, repeatedly washed with ether and pentane and dried; yield 400 mg (81%); m.p. 197°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.5 (m, 5H, C_6H_5), 5.50 [dd, *J*(PH) = 2.8, *J*(HH) = 2.2 Hz, 1H, 1H of $=CH_2$], 5.22 [d, *J*(PH) = 0.3 Hz, 5H, C_5H_5], 5.20 [dd, *J*(PH) = 2.7, *J*(HH) = 2.2 Hz, 1H, 1H of $=CH_2$], 3.06 (s, 3H, SCH_3), 2.81 (br. s, 3H, NCH_3), 1.97 [d, *J*(PH) = 11.1 Hz, 3H, PCH_3], 1.81 [d, *J*(PH) = 11.0 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 196.8 (s, SCN), 159.4 [br. d, *J*(PC) = 40.2 Hz, CoC], 132.7 [d, *J*(PC) = 49.8 Hz, *ipso*-C of PC_6H_5], 130.7 [d, *J*(PC) = 2.7 Hz, *para*-C of PC_6H_5], 129.6 [d, *J*(PC) = 7.0 Hz, *meta*-C of PC_6H_5], 128.1 [d, *J*(PC) = 9.8 Hz, *ortho*-C of PC_6H_5], 113.4 [d, *J*(PC) = 5.0 Hz, $=CH_2$], 91.6 [d, *J*(PC) = 2.5 Hz, C_5H_5], 36.6 (br. s, NCH_3), 17.8 (s, SCH_3), 15.0 [d, *J*(PC) = 33.3 Hz, PCH_3], 13.4 [d, *J*(PC) = 35.1 Hz, PCH_3]. – $C_{18}H_{24}BCoF_4NPS_2$ (495.0): calcd. C 43.64, H 4.89, N 2.83; found C 43.85, H 5.01, N 2.65.

8. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=CH_2)N(CH_2Ph)C(SCH_3)S\}(PMe_2Ph)]BF_4$ (**11**): This compound was prepared analogously as described for **10** by using 470 mg (1.00 mmol) of **7** and 177 mg (1.20 mmol) of $[OMe_3]BF_4$ as starting materials. Orange-yellow crystals; yield 422 mg (74%); m.p. 206°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.2–7.7 (m, 10H, C_6H_5), 5.40 [dd, *J*(PH) = 2.8, *J*(HH) = 2.1 Hz, 1H, 1H of $=CH_2$], 5.25 [d, *J*(PH) = 0.3 Hz, 5H, C_5H_5], 5.17 [dd, *J*(PH) = 2.2, *J*(HH) = 2.1 Hz, 1H, 1H of $=CH_2$], 4.75 (br. s, 2H, NCH_2), 2.83 (s, 3H, SCH_3), 1.97 [d, *J*(PH) = 10.9 Hz, 3H, PCH_3], 1.85 [d, *J*(PH) = 10.8 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 200.2 (s, SCN), 160.5 [br. d, *J*(PC) = 41.8 Hz, CoC], 134.5 [d, *J*(PC) = 49.2 Hz, *ipso*-C of PC_6H_5], 131.5 [d, *J*(PC) = 6.8 Hz, *meta*-C of PC_6H_5], 129.6 [d, *J*(PC) = 9.6 Hz, *ortho*-C of PC_6H_5], 135.4, 132.2, 130.3, 129.1, 127.5 (5 s, C_6H_5), 115.3 (br. s, $=CH_2$), 91.8 (s, C_5H_5), 54.3 (br. s, NCH_2), 18.5 (s, SCH_3), 15.8 [d, *J*(PC) = 33.1 Hz, PCH_3], 14.2 [d, *J*(PC) = 35.9 Hz, PCH_3]. – $C_{24}H_{28}BCoF_4NPS_2$ (571.1): calcd. C 50.44, H 4.94, N 2.45; found C 50.61, H 5.18, N 2.59.

9. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(CH_3)N(CH_3)C(SCH_3)S\}(PMe_2Ph)](BF_4)_2$ (**12**): A solution of 340 mg (0.70 mmol) of **10** in 10 ml of CH_3NO_2 was treated with a large excess (ca. 1 ml) of a 54% solution of HBF_4 in ether. After the reaction mixture had been stirred for 1 h at room temp., the solvent was removed. The residue was dissolved in 2 ml of methanol, and 10 ml of ether was added to the solution. An orange-yellow solid precipitated, which was separated from the mother liquor and washed three times with 10-ml portions of ether. Recrystallization from CH_2Cl_2/ether gave orange-yellow air-stable crystals; yield 334 mg (82%); m.p. 184°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.5 (m, 5H, C_6H_5), 6.02 [d, *J*(PH) = 1.0 Hz, 5H, C_5H_5], 3.64 [d, *J*(PH) = 2.5 Hz, 3H, CCH_3], 3.51 (br. s, 3H, NCH_3), 3.14 (s, 3H, SCH_3), 2.39 [d, *J*(PH) = 11.8 Hz, 3H, PCH_3], 2.26 [d, *J*(PH) = 11.6 Hz, 3H, PCH_3]. – $C_{18}H_{25}B_2CoF_8NPS_2$ (582.8): calcd. C 37.07, H 4.32, N 2.40; found C 37.29, H 4.41, N 2.44.

10. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(CH_3)N(CH_2Ph)C(SCH_3)S\}(PMe_2Ph)](BF_4)_2$ (**13**): This compound was prepared analogously as described for **12** by using 400 mg (0.70 mmol) of **11** and HBF_4 as starting materials. Orange-yellow air-stable crystals; yield 354 mg (77%); m.p. 164°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.2–7.7 (m, 10H, C_6H_5), 6.12 [d, *J*(PH) = 1.1 Hz,

5H, C_5H_5], 5.20 (br. s, 2H, NCH_2), 3.68 [d, J(PH) = 3.4 Hz, 3H, CCH_3], 3.14 (s, 3H, SCH_3), 2.40 [d, J(PH) = 11.2 Hz, 3H, PCH_3], 2.35 [d, J(PH) = 11.0 Hz, 3H, PCH_3]. – $C_{24}H_{29}B_2CoF_8NPS_2$ (658.8): calcd. C 43.72, H 4.44, N 2.13; found C 43.15, H 4.66, N 2.10.

11. *Preparation of* $[C_5H_5Co\{\kappa^2(S,S)\text{-}S_2C_2(SC(=S)NC_6H_5)\}]$ (**15**): A suspension of 228 mg (0.50 mmol) of **6** in 10 ml of benzene was treated with an excess (ca. 100 mg) of sulfur, and the reaction mixture was stirred for 48 h at 65°C. A change of color from brown to green occurred. After the mixture had been cooled to room temp., the solvent was removed. The residue was dissolved in 2 ml of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 6 cm). With CH_2Cl_2/pentane (10:1), first a colorless fraction (containing $SPMe_2Ph$) and then a green fraction was eluted. The latter was concentrated in vacuo to ca. 4 ml, and 20 ml of pentane was added. Upon cooling to −78°C, green crystals precipitated which were separated from the mother liquor, repeatedly washed with pentane and dried; yield 88 mg (45%); m.p. 226°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1165 cm^{-1} [ν(C=S)]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.34 (m, 5H, C_6H_5), 5.28 (s, 5H, C_5H_5). – $C_{14}H_{10}CoNS_4$ (379.3): calcd. C 44.30, H 2.67, N 3.39; found C 44.45, H 2.46, N 3.40.

12. *Preparation of* $[C_5H_5Co\{\kappa^2(S,S)\text{-}S_2C_2(SC(=S)NCH_2Ph)\}]$ (**16**): This compound was prepared analogously as described for **15** by using 235 mg (0.50 mmol) of **7** and ca. 100 mg of sulfur as starting materials. Green microcrystalline solid; yield 75 mg (40%); m.p. 213°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1160 cm^{-1} [ν(C=S)]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.38 (m, 5H, C_6H_5), 5.30 (s, 5H, C_5H_5), 5.02 (br. s, 2H, NCH_2). – MS (70 eV): *m/z* (%) = 393 (13) [M^+], 317 (1) [$M^+ - CS_2$], 276 (4) [$M^+ - CNCH_2Ph$], 212 (5) [$C_5H_5CoS_2C_2^+$]. – $C_{15}H_{12}CoNS_4$ (393.3): calcd. C 45.77, H 3.08, N 3.56; found C 45.56, H 3.17, N 3.55.

13. *Preparation of* $[C_5H_5Co\{\kappa^2(S,S)\text{-}S_2C_2(SC(SCH_3)NCH_3\}](CF_3SO_3)$ (**17**): A solution of 98 mg (0.31 mmol) of **14** in 5 ml of CH_2Cl_2 was treated at 0°C with 50 mg (0.31 mmol) of CF_3SO_3Me. A rapid change of color from green to blue occurred. After the solution had been stirred for 5 min, the solvent was removed, and the residue was repeatedly washed with ether. Upon recrystallization from CH_2Cl_2/ether, blue air-stable crystals were obtained; yield 94 mg (63%); m.p. 180°C (dec.). – ^1H NMR (90 MHz, $CDCl_3$): δ = 5.70 (s, 5H, C_5H_5), 4.25 (br. s, 3H, NCH_3), 3.15 (s, 3H, SCH_3). – $C_{11}H_{11}CoF_3NO_3S_5$ (481.3): calcd. C 27.43, H 2.30, N 2.91; found C 27.86, H 2.41, N 2.77.

14. *Preparation of* $[C_5H_5Co\{\kappa^3(C,S,S)\text{-}CH_2S_2C_2(SC(=S)NCH_3\}]$ (**18**): A solution of 260 mg (0.82 mmol) of **14** in 8 ml of CH_2Cl_2 was treated at −30°C with 0.40 ml (0.82 mmol) of a 2.0 M solution of CH_2N_2 in ether. A change of color from green to red-brown occurred. After the solution had been warmed to room temp., the solvent was removed 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 III, height of column 5 cm). With CH_2Cl_2 a brown fraction was eluted which was brought to dryness in vacuo. Recrystallization from CH_2Cl_2/ether (5:1) at −78°C gave a redbrown microcrystalline solid; yield 65 mg (24%); m.p. 139°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1180 cm^{-1} [ν(C=S)]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 5.12 (s, 5H, C_5H_5), 3.88 [d, J(HH) = 3.3 Hz, 1H, 1H of CH_2], 3.56 (br. s, 3H, NCH_3), 1.94 [d, J(HH) = 3.3 Hz, 1H, 1H, of CH_2]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 190.4 (s, C=S), 162.5, 144.8 (2 s, C=C), 83.5 (s, C_5H_5), 35.7 (br. s, NCH_3), 27.0 (s, CH_2). – MS (70 eV): *m/z* (%) = 331 (1) [M^+], 317 (33) [$M^+ - CH_2$], 266 (0.3) [$M^+ - C_5H_5$], 202 (29) [$C_5H_5CoCH_2S_2^+$]. – $C_{10}H_{10}CoNS_4$ (331.3): calcd. C 36.22, H 5.15, N 2.10; found C 35.88, H 5.10, N 2.13.

15. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=C(CO_2Me)C(CO_2Me)=CH_2)N(CH_3)C(=S)S\}(PMe_2Ph)]$ (**19**): A solution of 275 mg (0.70 mmol) of **5** in 10 ml of benzene was treated with 200 mg (1.40 mmol) of $C_2(CO_2Me)_2$ and stirred for 18 h under reflux. After the solution had been cooled to room temp., the solvent was removed 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 6 cm). With CH_2Cl_2/pentane (10:1) a brown fraction was eluted which was brought to dryness in vacuo. Recrystallization from CH_2Cl_2/ether gave brown crystals; yield 251 mg (67%); m.p. 160°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1090 cm^{-1} [ν(C=S)]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.45 (m, 5H, C_6H_5), 6.31 [d, J(HH) = 1.5 Hz, 1H, 1H of $=CH_2$], 5.36 (br., 1H, 1H of $=CH_2$), 5.19 (s, 5H, C_5H_5), 3.97, 3.90 (2 s, 3H each, CO_2CH_3), 2.69 (br. s, 3H, NCH_3), 2.28 [d, J(PH) = 10.6 Hz, 3H, PCH_3], 2.16 [d, J(PH) = 10.2 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 213.0 (s, C=S), 192.1 [br. d, J(PC) = 38 Hz, CoC], 170.5, 169.8 (2 s, CO_2CH_3), 167.5 (s, 1 C of =CC=), 140.6 [d, J(PC) = 2.4 Hz, 1C of =CC=], 135.1 [d, J(PC) = 55.4 Hz, *ipso*-C of PC_6H_5], 130.0 [d, J(PC) = 7.7 Hz, *meta*-C of PC_6H_5], 129.8 [d, J(PC) = 2.8 Hz, *para*-C of PC_6H_5], 128.1 [d, J(PC) = 9.3 Hz, *ortho*-C of PC_6H_5], 126.6 (s, $=CH_2$), 90.0 (s, C_5H_5), 51.9, 51.3 (2 s, OCH_3), 47.7 (br. s, NCH_3), 17.9 [d, J(PC) = 34.5 Hz, PCH_3], 17.2 [d, J(PC) = 31.8 Hz, PCH_3]. – MS (70 eV): *m/z* (%) = 535 (4) [M^+], 370 (3) [$C_5H_5Co(PMe_2Ph)S_2CS^+$], 306 (2) [$C_5H_5Co(PMe_2Ph)CS^+$], 189 (5) [$(C_5H_5)_2Co^+$]. – $C_{23}H_{27}CoNO_4PS_2$ (535.3): calcd. C 51.56, H 5.08, N 2.62; found C 51.49, H 5.17, N 2.53.

16. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=C(CO_2Me)C(CO_2Me)=CH_2)N(C_6H_5)C(=S)S\}(PMe_2Ph)]$ (**20**): This compound was prepared analogously as described for **19** by using 320 mg (0.70 mmol) of **6** and 200 mg (1.41 mmol) of $C_2(CO_2Me)_2$ as starting materials. Brown microcrystalline solid; yield 250 mg (60%); m.p. 156°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1100 cm^{-1} [ν(C=S)]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.25–7.65 (m, 10H, C_6H_5), 6.27 [d, J(HH) = 1.2 Hz, 1H, 1H of $=CH_2$], 5.30 (br., 1H, 1H of $=CH_2$), 5.12 (s, 5H, C_5H_5), 3.98, 3.92 (2 s, 3H each, CO_2CH_3), 2.07 [d, J(PH) = 10.3 Hz, 3H, PCH_3], 1.98 [d, J(PH) = 10.2 Hz, 3H, PCH_3]. – $C_{28}H_{29}CoNO_4PS_2$ (597.3): calcd. C 56.31, H 4.89, N 2.34; found C 56.32, H 4.94, N 2.28.

17. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=C(CO_2Me)C(CO_2Me)=CH_2)N(CH_2Ph)C(=S)S\}(PMe_2Ph)]$ (**21**): This compound was prepared analogously as described for **19** by using 330 mg (0.70 mmol) of **7** and 200 mg (1.41 mmol) of $C_2(CO_2Me)_2$ as starting materials. Brown microcrystalline solid; yield 278 mg (65%); m.p. 184°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1095 cm^{-1} [ν(C=S)]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 214.1 (s, C=S), 194.1 [br. d, J(PC) = 36 Hz, CoC], 170.1, 168.4 (2 s, CO_2CH_3), 167.5, 139.6 (2 s, =CC=), 136.9 [d, J(PC) = 43.6 Hz, *ipso*-C of PC_6H_5], 130.0 [d, J(PC) = 7.5 Hz, *meta*-C of PC_6H_5], 128.4 [d, J(PC) = 8.7 Hz, *ortho*-C of PC_6H_5], 138.4, 129.1, 128.6, 127.9, 125.4 (5 s, C_6H_5), 127.3 (s, $=CH_2$), 88.8 (s, C_5H_5), 58.5 (br. s, NCH_2), 52.0, 51.2 (2 s, OCH_3), 17.2 [d, J(PC) = 28.3 Hz, PCH_3], 15.5 [d, J(PC) = 32.7 Hz, PCH_3]. – MS (70 eV); *m/z* (%) = 611 (10) [M^+], 494 (2) [$M^+ - CNCH_2Ph$], 370 (2) [$C_5H_5Co(PMe_2Ph)S_2CS^+$], 306 (4) [$C_5H_5Co(PMe_2Ph)CS^+$], 189 (2) [$(C_5H_5)_2Co^+$]. – $C_{29}H_{31}CoNO_4PS_2$ (611.4): calcd. C 56.93, H 5.11, N 2.29; found C 57.14, H 4.93, N 2.27.

18. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(=C(CO_2Et)C(CO_2Et)=CH_2)N(CH_3)C(=S)S\}(PMe_2Ph)]$ (**22**): This com-

pound was prepared analogously as described for **19** by using 275 mg (0.70 mmol) of **5** and 238 mg (1.40 mmol) of $C_2(CO_2Et)_2$ as starting materials. Brown air-stable crystals; yield 228 mg (58%); m.p. 153°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1090 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.5 (m, 5H, C_6H_5), 6.05 [d, *J*(HH) = 1.7 Hz, 1H, 1H of $=CH_2$], 5.43 (br., 1H, 1H of $=CH_2$), 4.95 (s, 5H, C_5H_5), 4.16, 4.12 [2 q, *J*(HH) = 7.1 Hz, 2H each, OCH_2], 2.42 (br. s, 3H, NCH_3), 1.28, 1.23 [2 t, *J*(HH) = 7.1 Hz, 3H each, $OCH_2C\mathit{H}_3$], 2.01 [d, *J*(PH) = 11.1 Hz, 3H, PCH_3], 1.98 [d, *J*(PH) = 10.4 Hz, 3H, PCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 212.7 (s, C=S), 191.0 [br. d, *J*(PC) = 36.5 Hz, CoC], 169.3, 168.5 (2 s, $\mathit{C}O_2Et$), 167.0, 140.9 (2 s, =CC=), 135.0 [d, *J*(PC) = 50.8 Hz, *ipso*-C of PC_6H_5], 129.9 [d, *J*(PC) = 7.9 Hz, *meta*-C of PC_6H_5], 129.6 [d, *J*(PC = 2.1 Hz, *para*-C of PC_6H_5], 128.0 [d, *J*(PC) = 10.2 Hz, *ortho*-C of PC_6H_5], 126.2 (s, $=CH_2$), 90.0 (s, C_5H_5), 60.5, 59.7 (2 s, OCH_2), 47.6 (br. s, NCH_3), 17.9, 17.2 [2 d, *J*(PC) = 34.5 Hz, PCH_3], 14.2, 14.1 (2 s, $OCH_2\mathit{C}H_3$). – $C_{25}H_{31}CoNO_4PS_2$ (563.3): calcd. C 53.26, H 5.55, N 2.49; found C 53.43, H 5.45, N 2.49.

19. *Preparation of* $[C_5H_5Co\{\kappa^2(C,S)\text{-}C(C(CO_2Me){=}C(CO_2Me)CH_3)N(CH_3)C({=}S)S\}(PMe_2Ph)]BF_4$ (**23**): A solution of 268 mg (0.50 mmol) of **19** in 10 ml of CH_2Cl_2 was treated with an excess (ca. 0.5 ml) of a 54% solution of HBF_4 in ether. After the reaction mixture had been stirred for 20 min at room temp., the solvent was removed, and the residue was dissolved in 3 ml of CH_2Cl_2. Upon addition of 25 ml of pentane, a red solid precipitated which was filtered off and recrystallized from CH_2Cl_2/ether. Red air-stable crystals; yield 249 mg (80%); m.p. 143°C (dec.). Equiv. conductivity (in CH_3NO_2): Λ = 65 cm^{2}Ω^{-1}mol^{-1}. – IR (KBr: $\tilde{\nu}$ = 1070 cm^{-1} [ν(C=S)]. – ^{1}H NMR (90 MHz, CD_3NO_2): δ = 7.6 (m, 5H, C_6H_5), 5.70 [d, *J*(PH) = 0.7 Hz, 5H, C_5H_5], 4.10, 3.89 (2 s, 3H each, OCH_3) 3.37 (br. s, 3H, NCH_3), 2.23, 2.01 [2 d, *J*(PH) = 11.3 Hz, 3H each, PCH_3], 1.85 (s, 3H, CCH_3). – $C_{23}H_{28}BCoF_4NO_4PS_2$ (623.1): calcd. C 44.30, H 4.53, N 2.25; found C 44.12, H 4.65, N 2.21.

20. Preparation of $[C_5H_5Co\{\kappa^2(C,S)\text{-}C({=}C(CO_2Me)C(CO_2Me){=}CH_2)N(CH_3)C(SCH_3)S\}(PMe_2Ph)]BF_4$ (**24**): A solution of 268 mg (0.50 mmol) of **19** in 10 ml of CH_2Cl_2 was treated at 0°C with 104 mg (0.70 mmol) of $[OMe_3]BF_4$ and stirred for 30 min. After the reaction mixture had been warmed to room temp., the solvent was removed. 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 6 cm). With CH_2Cl_2/pentane (10:1), a brown fraction was eluted, which was concentrated in vacuo to ca. 4 ml. Addition of 20 ml of ether led to the formation of red-brown precipitate which was filtered, repeatedly washed with ether and pentane and dried; yield 244 mg (64%); m.p. 163°C (dec.). Equiv. conductivity (in CH_3NO_2): Λ = 72 cm^{2}Ω^{-1}mol^{-1}. – ^{1}H NMR (90 MHz, CD_3NO_2): δ = 7.5 (m, 5H, C_6H_5), 6.22 [d, *J*(HH) = 1.2 Hz, 1H, 1H of $=CH_2$], 5.34 (s, 5H, C_5H_5), 5.30 [d, *J*(HH) = 1.2 Hz, 1H, 1H of $=CH_2$], 3.97, 3.76 (2 s, 3H each, OCH_3), 2.92 (br. s, 3H, NCH_3), 2.67 (s, 3H, SCH_3), 2.33, 2.17 [2 d, *J*(PH) = 10.7 Hz, 3H each, PCH_3]. – $C_{24}H_{30}BCoF_4NO_4PS_2$ (637.1): calcd. C 45.20, H 4.74, N 2.20; found C 45.11, H 5.00, N 2.24.

21. *Determination of the X-ray Crystal Structure of* **19**[12]: Single crystals were grown by slow diffusion of ether into a solution of **19** in CH_2Cl_2. Crystal data: orthorhombic, space group *Pbca*, a = 12.777(1), b = 25.127(5), c = 16.119(2) Å, V = 5175.0(6) Å^3, Z = 8, $d_{\text{calcd.}}$ = 1.374 g cm^{-3}, μ(Mo-K_α) = 0.91 mm^{-1}; crystal size 0.4 × 0.6 × 0.1 mm; STOE-Stadi4 diffractometer, Mo-K_α radiation, graphite monochromator; Θ/Θ-scan, $2\Theta_{\max}$ = 50°; 6186 reflections scanned, 4531 unique reflections, 3646 reflections with $F > 3\sigma(F)$. Intensity data were corrected for Lorentz and polarization effects and a geometrical absorption correction was applied. The structure was solved by direct methods (SHELXTL PLUS). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and refined by the riding method with fixed isotropic U values. R = 0.042, R_w = 0.028 [weighting scheme $w = 1/\sigma^2(F)$]; reflections-to-parameter ratio 12.57; residual electron density +0.53/–0.42 e Å^{-3}.

☆ Dedicated to Professor *Joachim Strähle* on the occasion of his 60th birthday.

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[12] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100239. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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