$HOCH_2CH_2Co(D_2H_2)OH_2$ could be detected during the decomposition of $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ and $C_6H_5OCH_2CH_2Co(D_2H_2)OH_2$ and could be purified from reaction mixtures in which the (alkoxyethyl)cobaloximes were partially decomposed. Similar experiments were consequently attempted for the β-$ROCH_2CH_2Cbl$'s. Each of the six compounds (**1a–f**) was decomposed for 1 halftime in 1.0 M HCl, neutralized with K_2HPO_4, desalted by chromatography on Amberlite XAD resin, and analyzed by HPLC, as all six of the complexes are cleanly separated by the HPLC methodology described above. The chromatograms from each sample contained peaks for the unreacted starting material and for H_2OCbl, but no β-$HOCH_2CH_2Cbl$ (**1a**) could be detected in the samples from any of the other five β-$ROCH_2CH_2Cbl$'s (**1b–1f**). By overinjection of the samples resulting from the partial decomposition of **1b–f** and comparison of the chromatograms to those of samples which were spiked with varying amounts of **1a**, a detection limit of 0.05% could be set for **1a** in such mixtures of **1b–f** and H_2OCbl. Thus, if **1a** is formed during the decomposition of **1a–f**, it is present at less than 0.05% of the total cobamide during these reactions.

In the absence of any evidence whatsoever for the formation of an intermediate in the acid-induced decomposition of the $ROCH_2CH_2Cba$'s, the simplest mechanism which accounts for all of the observations is a concerted elimination of the alcohol, ROH, and the dealkylated cobalt corrinoid from the β-oxygen-protonated species formed in a rapid preequilibrium. For such a mechanism, achievement of equilibrium β-oxygen protonation (i.e., a leveling of the *H*–rate profiles) would be expected to occur at some acidity. Our failure to observe such a leveling of the *H*–rate profiles of representative β-$ROCH_2CH_2Cbl$'s at *H* values as low as −3.0 (Figure 5) indicates that the β-oxygens of the (alkoxyethyl)cobalt corrinoids are very weak bases indeed.

Summary. An extensive series of (alkoxyethyl)cobalt corrinoids has been prepared, including the α- and β-diastereomers of the cobalamins and cobinamides as well as the deuterated analogue of (2-hydroxyethyl)cobalamin and the ^{13}C-enriched analogues of the four (hydroxyethyl)cobalt corrinoids. These complexes have been thoroughly characterized by ^1H, ^2H, ^{13}C, ^{19}F, and ^{13}C edited ^1H NMR spectroscopy, UV–visible spectroscopy, and mass spectrometry. As was the case with the analogous (hydroxyethyl)cobaloximes, these complexes undergo an acid-induced decomposition to yield a cobalt(III) product, ethylene, and the alcohol derived from the alkoxy moiety. However, unlike the cobaloximes, which decompose via a two-step mechanism involving a σ-bonded ethylcobaloxime carbonium ion intermediate which accumulates in strongly acidic media and has been directly observed by ^1H and ^{13}C NMR spectroscopy, the (alkoxyethyl)cobalt corrinoids appear to decompose via a concerted elimination from the β-oxygen-protonated species.

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Synthesis and Structure of a Novel Bicyclic Cobalt Dithiolene: Formation of a Five-Membered CoS_2C_2 Ring from a CoSCNC Precursor and Elemental Sulfur as a Substrate[1]

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The cobalt isocyanide complex $C_5H_5Co(PMe_2Ph)(CNMe)$ (**3**), prepared from $C_5H_5Co(PMe_2Ph)_2$ (**2**) and CNMe by ligand exchange, reacts with methyl iodide to form the imidoylcobalt compound $[C_5H_5Co(PMe_2Ph)(CH_3CNMe)]I$ (**4**), which on further treatment with CS_2 in the presence of sodium methoxide gives the metallaheterocycle $C_5H_5(PMe_2Ph)\overline{CoC({=}CH_2)N(CH_3)C({=}S)S}$ (**5**). The X-ray crystal structure of **5** has been determined: monoclinic, space group $P2_1/n$ (No. 14), a = 8.461 (1) Å, b = 13.885 (3) Å, c = 15.187 (1) Å, β = 93.57 (1)°, Z = 4. The reaction of **5** with S_8 leads to the elimination of the phosphine ligand and affords the novel bicyclic cobalt dithiolene complex $C_5H_5Co[\eta^2\text{-}S_2C_2(SC({=}S)NCH_3)]$ (**6**) in 50% yield. The X-ray structure analysis of **6** (monoclinic, space group $P2_1/n$ (No. 14), with a = 13.757 (4) Å, b = 12.614 (2) Å, c = 14.555 (4) Å, β = 112.69 (1)°, and Z = 8) reveals an almost exactly planar bicyclic system in which partial electron delocalization is to be expected. From labeling studies with $^{12}CH_3I$ it is found that the second carbon atom of the C=C bond in **6** stems from the exocyclic CH_2 group of the heterocyclic ring system in **5**.

The reactivity of transition-metal complexes toward small molecules containing a carbon-to-element double bond or triple bond continues to arouse much attention.[2] We have recently shown that cyclopentadienylcobalt

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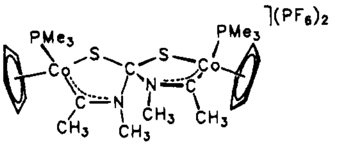
cations of general composition $[C_5H_5(PMe_3)Co(CH_3C{=}NR)]^+$ behave as 1,3-dipoles and react with ketones, aldehydes, nitriles, and isothiocyanates by [3 + 2] cycloaddition to form five-membered cobaltaheterocycles.[3] By using CS_2 as a substrate, the binuclear spirocyclic compound 1 has been obtained.[4]



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In this paper we describe that an imidoylcobalt derivative which is an analogue of the starting material used for the synthesis of 1 but contains PMe_2Ph instead of PMe_3 as phosphine ligand reacts with CS_2 to give a *mononuclear* $\overline{\text{CoCNCS}}$ heterocycle. Treatment of the neutral compound with elemental sulfur affords a bicyclic organometallic product of unprecedented structure, resembling in parts the bicyclic precursors for the preparation of TTF (tetrathiafulvalene) and related derivatives.[5]

Experimental Section

All reactions were carried out under argon by using Schlenk tube techniques. The starting material **2** was prepared as described in the literature.[6] NMR spectra were recorded on JEOL FX 90 Q and Bruker AC 200 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, UV spectra on a Hewlett-Packard 8452 A diode array spectrophotometer, and mass spectra on a Varian MAT CH 7 instrument.

Preparation of $C_5H_5Co(PMe_2Ph)(CNMe)$ (3). A solution of 177 mg (0.44 mmol) of **2** in 8 mL of benzene was treated with 25 μL (0.44 mmol) of methyl isocyanide and the mixture stirred for 5 min at room temperature. The solvent was removed in vacuo, and the oily residue was extracted with 5 mL of pentane. The extract was filtered over cotton wool and the filtrate cooled to −78 °C. A brown, oily, very air-sensitive precipitate was obtained; yield 116 mg (87%). Anal. Calcd for $C_{15}H_{19}CoNP$: C, 59.42; H, 6.32; N, 4.62. Found: C, 59.52; H, 6.41; N, 4.34. ^1H NMR (C_6D_6): δ 7.4 (m, C_6H_5), 5.00 (d, $J(PH) = 0.5$ Hz, C_5H_5), 2.85 (d, $J(PH) = 2.2$ Hz, $CNCH_3$), 1.80 (d, $J(PH) = 8.0$ Hz, PCH_3).

Preparation of $C_5H_5(PMe_2Ph)\overline{CoC(=CH_2)N(CH_3)C(=S)S}$ (5). A solution of 143 mg (0.47 mmol) of **3** in 20 mL of pentane was treated at −30 °C with 83 μL (1.34 mmol) of methyl iodide. A yellow solid precipitated, which was separated from the mother liquor, washed with pentane (at −30 °C), and dried in vacuo; yield 172 mg (82%). The freshly prepared, thermolabile solid **4** was dissolved in 10 mL of dichloromethane, and 0.1 mL (1.6 mmol) of CS_2 was added dropwise to the solution. After it was stirred for 1 h at room temperature, the solution was treated with 27 mg (0.5 mmol) of $NaOCH_3$ and continuously stirred for 3 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). With CH_2Cl_2/pentane (20:1) a brown fraction was eluted, which was brought to dryness in vacuo. After recrystallization from CH_2Cl_2/ether brown crystals were obtained: yield 118 mg (64% from **3**); mp 175 °C dec. Anal. Calcd for $C_{17}H_{21}CoNPS_2$: C, 51.91; H, 5.38; N, 3.56; M_r, 393.4. Found: C, 51.73; H, 5.22; N, 3.41; M_r, 393 (MS). IR (KBr): ν(C=S) 1160 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5), 5.00 (dd, $J(PH) = 3.2$, $J(HH) = 2.0$ Hz, one H of $=CH_2$), 4.53 (dd, $J(PH) = 2.8$, $J(HH) = 2.0$ Hz, one H of $=CH_2$), 4.53 (s, C_5H_5), 3.60 (s, NCH_3), 1.38 and 1.18 (both d, $J(PH) = 10.1$ Hz, PCH_3). ^{13}C NMR ($CDCl_3$): δ 209.0 (s, C=S), 159.0 (d, br, $J(PC) = 39.7$ Hz, Co—C=CH_2), 136.9 (d, $J(PC) = 42$ Hz, C^1 from C_6H_5), 130.3 (s, C^4 from C_6H_5), 129.0 (d, $J(PC) = 7.1$ Hz, C^3 and C^5 from C_6H_5), 128.5 (d, $J(PC) = 9.5$ Hz, C^2 and C^6 from C_6H_5), 106.8 (d, $J(PC) = 4.2$ Hz, C=CH_2), 89.1 (d, $J(PC) = 2.2$ Hz, C_5H_5), 39.7 (s, NCH_3), 14.3 (d, $J(PC) = 37.9$ Hz, PCH_3), 13.5 (d, $J(PC) = 35.2$ Hz, PCH_3).

Table I. Selected Bond Distances and Angles with Esd's for 5

Bond Distances (Å)

Co–S1	2.198 (1)	Co–C8	2.052 (5)	C4–N	1.341 (6)
Co–P	2.174 (1)	Co–C9	2.089 (5)	C1–C2	1.263 (6)
Co–C1	1.923 (5)	S1–C4	1.722 (5)	P–C10	1.829 (5)
Co–C5	2.117 (5)	S2–C4	1.678 (5)	P–C11	1.832 (5)
Co–C6	2.103 (5)	C1–N	1.433 (6)	P–C12	1.815 (5)
Co–C7	2.075 (5)	C3–N	1.475 (6)		

Bond Angles (deg)

S1–Co–P	91.96 (5)	Co–C1–N	116.5 (3)
S1–Co–C1	87.0 (1)	Co–C1–C2	123.6 (4)
C1–Co–P	87.8 (1)	S1–C4–S2	118.5 (3)
Co–S1–C4	99.9 (2)	S1–C4–N	116.4 (3)
C1–N–C3	118.9 (4)	S2–C4–N	125.0 (4)
C1–N–C4	120.2 (4)	Co–P–C10	112.9 (2)
C3–N–C4	120.9 (4)	Co–P–C11	113.8 (2)
C2–C1–N	119.9 (4)	Co–P–C12	117.5 (1)

Preparation of $C_5H_5Co[\eta^2\text{-}S_2C_2(SC(=S)NCH_3)]$ (6). A suspension of 196 mg (0.50 mmol) of **5** in 10 mL of benzene was treated with 80 mg (2.50 mmol) of sulfur and the mixture stirred for 24 h at 65 °C. A color change from brown to green occurred. 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). With CH_2Cl_2/pentane (10:1), first a colorless fraction (which contained $SPMe_2Ph$) and then a green fraction was eluted. The green fraction was concentrated to ca. 4 mL in vacuo, and 25 mL of pentane was added. After the mixture was cooled to −78 °C, green crystals precipitated, which were filtered off, washed with pentane, and dried in vacuo: yield 160 mg (51%); mp 177 °C dec. Anal. Calcd for $C_9H_8CoNS_4$: C, 34.06; H, 2.54; N, 4.41; M_r, 317.3. Found: C, 34.21; H, 2.56; N, 4.53; M_r, 317 (MS). IR (KBr): ν(C=S) 1170 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.30 (s, C_5H_5), 3.80 (s, NCH_3). ^{13}C NMR ($CDCl_3$): δ 193.6 (s, C=S), 162.6 (s, =C(S)N), 146.6 (s, =C(S)S), 78.9 (s, C_5H_5), 35.1 (s, NCH_3). UV (CH_2Cl_2): λ_{max} (log ϵ) 708 (7.22), 334 (7.25), 284 (7.46), 240 (7.45), 208 (6.91) nm.

Crystal Structure Analysis. Single crystals of **5** and **6** were grown from dichloromethane/pentane at room temperature. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 94.9% for **5** and 90.3% for **6**. The structures were solved by direct methods (SHELXS-86). The crystals of **6** contain two almost identical molecules in the asymmetric unit. Atomic coordinates and 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 and were refined using the riding method. For other details see the supplementary material.

Results and Discussion

The (isocyanide)(phosphine)cobalt(I) compound **3**, which has been prepared nearly quantitatively from the bis(phosphine) derivative **2** and $CNCH_3$ by ligand exchange, behaves as a metal base[3,7] and reacts with methyl

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(1) Cycloaddition Reactions of Organometallic Compounds. 15. Part 14: Strecker, B.; Werner, H. *Z. Anorg. Allg. Chem.*, in press.

(2) See, for example: (a) Elschenbroich, C.; Salzer, A. *Organometallchemie*; Teubner Studienbücher: Stuttgart, Germany, 1988. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

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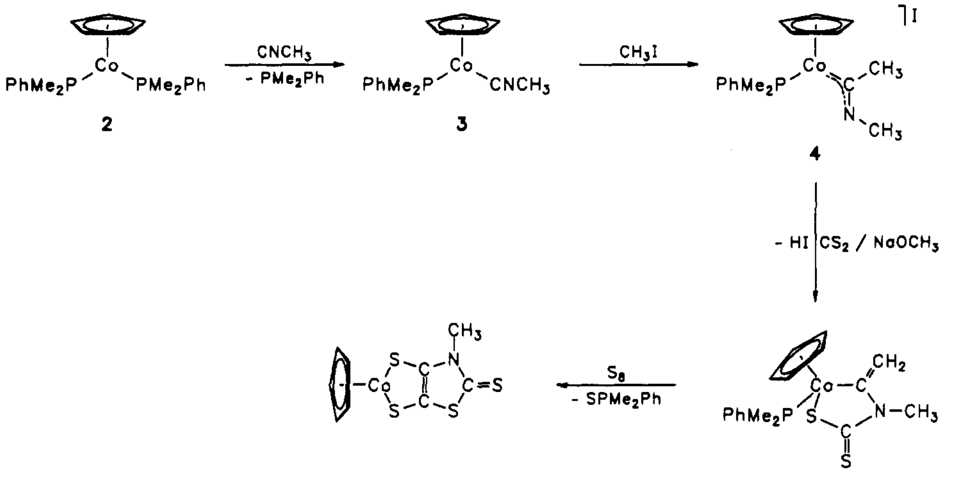
Table II. Selected Bond Distances and Angles with Esd's for 6[a]

			Bond Distances (Å)				
Co–S1	2.128 (1)	Co*–S1*	2.139 (1)	S2–C2	1.703 (4)	S2*–C2*	1.711 (4)
Co–S2	2.138 (1)	Co*–S2*	2.140 (1)	S3–C1	1.743 (4)	S3*–C1*	1.746 (4)
Co–C5	2.038 (4)	Co*–C5*	2.021 (5)	S3–C3	1.740 (5)	S3*–C3*	1.751 (4)
Co–C6	2.049 (5)	Co*–C6*	2.039 (5)	S4–C3	1.654 (4)	S4*–C3*	1.647 (4)
Co–C7	2.033 (5)	Co*–C7*	2.040 (4)	N–C2	1.399 (5)	N*–C2*	1.394 (5)
Co–C8	2.037 (4)	Co*–C8*	2.033 (5)	N–C3	1.353 (5)	N*–C3*	1.356 (5)
Co–C9	2.035 (5)	Co*–C9*	2.027 (5)	N–C4	1.441 (5)	N*–C4*	1.422 (5)
S1–C1	1.690 (4)	S1*–C1*	1.693 (4)	C1–C2	1.352 (5)	C1*–C2*	1.352 (6)
			Bond Angles (deg)				
S1–Co–S2	93.63 (5)	S1*–Co*–S2*	93.79 (5)	C2–C1–S3	110.1 (3)	C2*–C1*–S3*	110.4 (3)
Co–S1–C1	102.2 (1)	Co*–S1*–C1*	102.1 (2)	C1–S3–C3	92.0 (2)	C1*–S3*–C3*	91.8 (2)
Co–S2–C2	101.7 (1)	Co*–S2*–C2*	101.3 (2)	C2–N–C3	114.7 (4)	C2*–N*–C3*	115.2 (4)
S1–C1–C2	121.3 (3)	S1*–C1*–C2*	121.1 (3)	C2–N–C4	122.8 (4)	C2*–N*–C4*	121.8 (4)
S1–C1–S3	128.5 (2)	S1*–C1*–S3*	128.4 (3)	C3–N–C4	122.5 (4)	C3*–N*–C4*	122.9 (4)
S2–C2–C1	121.1 (3)	S2*–C2*–C1*	121.6 (3)	S3–C3–S4	123.2 (3)	S3*–C3*–S4*	123.5 (3)
S2–C2–N	125.3 (3)	S2*–C2*–N*	124.9 (3)	S3–C3–N	109.6 (3)	S3*–C3*–N*	109.1 (3)
C1–C2–N	113.6 (4)	C1*–C2*–N*	113.5 (4)	S4–C3–N	127.2 (4)	S4*–C3*–N*	127.4 (3)

[a] Atoms marked with an asterisk are those of the second independent molecule in the unit cell.

Scheme I



2 3 4 6 5

iodide at low temperature to form the imidoylcobalt complex 4 (Scheme I). Owing to conductivity measurements ($\Lambda = 72$ cm^2 Ω^{-1} mol^{-1}, in CH_3NO_2), there is no doubt that the yellow, very air-sensitive solid is ionic in nature. We have previously shown that whereas $C_5H_5Co(PMe_3)(CNPh)$ reacts with methyl iodide to give the neutral compound $C_5H_5Co[\eta^1\text{-}C(CH_3){=}NPh](PMe_3)I$, the corresponding methyl and *tert*-butyl isocyanide complexes $C_5H_5Co(PMe_3)(CNR)$ ($R = CH_3$, $t\text{-}C_4H_9$) on treatment with CH_3I afforded ionic products of different structure.[8]

In contrast to what we anticipated, the reaction of compound 4 with CS_2 does not give an analogue of 1 but instead leads to the uncharged metallaheterocycle 5. As HI is formed as a byproduct in this process, the yield increases significantly (up to 80%) if the cycloaddition is performed in the presence of $NaOCH_3$. Compound 5 is a brown crystalline solid that for short times can be handled in air. The composition has been confirmed by elemental analysis, mass spectrometry, and X-ray crystallography. As far as the spectroscopic data are concerned, the most characteristic feature in the ^{1}H NMR spectrum is the presence of two signals for the chemically different protons of the exocyclic $=CH_2$ group, which appear as doublets of doublets at δ 5.00 and 4.53. There are also two signals for the methyl protons of the phosphine ligand, in accordance with the chirality of the molecule. In the ^{13}C

Table III. Crystallographic Data for Complexes 5 and 6

	5	6
formula	$C_{17}H_{21}CoN_2PS_2$	$C_9H_8CoNS_4$
fw	393.39	317.34
cryst size, mm	0.6 × 0.4 × 0.4	0.3 × 0.3 × 0.4
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
cell dimens determn	25 rflns, $11° < \theta < 14°$	23 rflns, $11° < \theta < 14°$
a, Å	8.461 (1)	13.757 (4)
b, Å	13.885 (3)	12.614 (2)
c, Å	15.187 (1)	14.555 (4)
β, deg	93.57 (1)	112.69 (1)
V, Å^3	1780.8	2330.2
Z	4	8
d_{calc}, g cm^{-3}	1.47	1.81
diffractometer	Enraf-Nonius CAD4	
radiation (graphite monochromator)	Mo Kα (0.709 30 Å)	
temp, °C	20 ± 1	
μ, cm^{-1}	12.7	21.2
scan method	ω/θ	$\omega/2\theta$
2θ(max), deg	44	46
total no. of rflns scanned	2474	3564
no. of unique rflns	2293	3404
no. of obsd rflns ($F_o > 3\sigma(F_o)$)	1771	2298
no. of params refined	199	271
R	0.043	0.031
R_w	0.046	0.032
rfln/param ratio	8.83	8.48
residual electron density, e Å^{-3}	+0.50/−0.34	+0.37/−0.27

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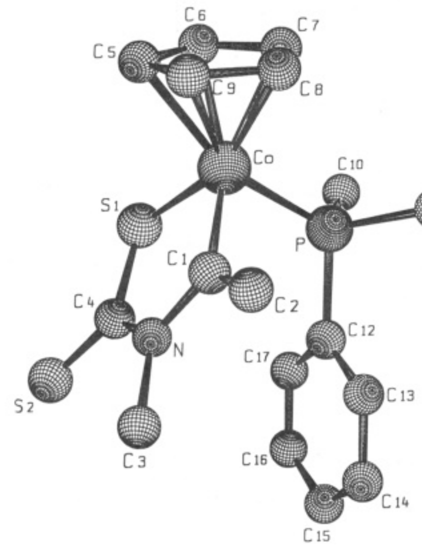

Figure 1. SCHAKAL drawing of complex **5**.

NMR spectrum of **5**, the absorbances of the C=S and the $C{=}CH_2$ carbon atoms are found at δ 209.0, 159.0 (broad, owing to the quadrupole moment of cobalt), and 106.8; the assignment of the last resonance as belonging to the methylene carbon has been confirmed by DEPT measurements.

The molecular structure of **5** is shown in Figure 1. The five-membered heterocycle is planar within experimental error, with the largest deviation of the Co–S1–C4–N–C1 plane shown by C4 (−0.014 Å). Whereas the Co–S1 distance (2.198 (1) Å) is identical to that in complex **1** (2.195 (5) Å), the Co–C1 bond length in **5** is significantly longer (1.923 (5) Å, compared with 1.87 (2) Å in **1**), which is in agreement with the partial double-bond character of Co–C bond in the spirocyclic compound.[4] We note that the two C–S distances in **5** differ only by 0.044 Å, which together with the bond angles S1–C4–S2, S1–C4–N, and S2–C4–N (see Table I) point to some electron delocalization in the SC(S)N unit.

The reaction of **5** with sulfur, originally intended to generate $C_5H_5(PMe_2Ph)CoS_5$[9] together with the four-membered heterocycle $\overline{\mathrm{SC}(=\mathrm{S})\mathrm{N}(\mathrm{CH_3})\mathrm{C}}(=\mathrm{CH_2})$, surprisingly leads to the formation of the novel, non-phosphine-containing complex **6** in ca. 50% yield. Although numerous metallo dithiolenes have been described in the literature,[10] to the best of our knowledge there is only one group of compounds known which is related in structure to the bicyclic product **6** shown in Scheme I. Vollhardt and Walborsky have reported that the trinuclear cobalt complexes $(C_5H_5Co)_3(\mu_3\text{-}CR^1)(\mu_3\text{-}CR^2)$ react with S_8 in boiling chloroform by degradation of the cluster to give nearly quantitatively the cobalt mono(dithiolenes) $C_5H_5Co(S_2C_2R^1R^2)$.[11]

The bicyclic compound **6** forms intense green crystals which are moderately stable in air and easily soluble in chlorinated hydrocarbons such as CH_2Cl_2 and $CHCl_3$. The ^{13}C NMR spectrum reveals three signals at δ 193.6, 162.6, and 146.6, which are assigned to the ring carbon atoms of the C_3NS system. By using isotopically pure $^{12}CH_3I$ for the preparation of **5**, we found that the ^{13}C NMR spectrum of the product obtained upon treatment of this precursor complex with sulfur shows only absorptions at δ 193.6 and 162.6, and thus, the signal at δ 146.6 is assigned to the atom C^1 originating from the former exocyclic CH_2 group.

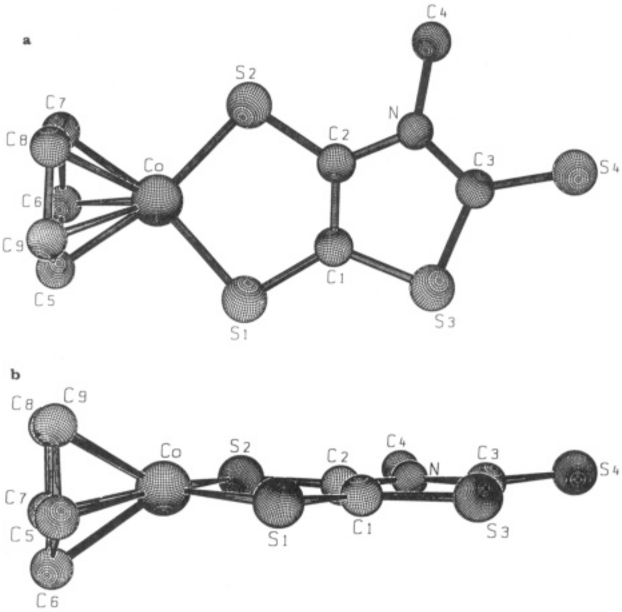

Figure 2. SCHAKAL drawings of complex **6**, with the bicyclic system in the drawing plane (a) and perpendicular to that plane (b).

Two perspectives of the molecular structure of compound **6** are shown in Figure 2. The bicyclic system 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 bond lengths of the metal-containing ring are significantly shorter (1.69 and 1.70 Å) than the C–S distances in the second cycle (1.74 and 1.75 Å), which is indicative of partial electron delocalization in the cobalt dithiolene unit. In contrast, the distance C3–S4 (1.65 Å) corresponds to that of a normal C=S double bond.[12]

Concluding Remarks

The most remarkable result of the present work concerning the synthesis of new cobaltaheterocycles is the formation of the bicyclic system **6**. It is to some extent structurally related to precursor compounds of tetrathiafulvalenes (e.g., 4,5-(ethylenedithio)-1,3-dithiole-2-thione[5c]) and, therefore, might offer the possibility of preparing organometallic TTF analogues. At this stage, the actual question is *how* the bicyclic product is formed. As there is no doubt that the second carbon atom C^1 of the C=C bond in **6** stems from the formerly exocyclic CH_2 group, the sulfur is not only needed to build up the cobalt dithiolene moiety but also to abstract the two hydrogen atoms from the methylene unit. The exposed carbon obviously is then reactive enough to become incorporated (possible stepwise) into the ring system.

As there is no precedence for the formation of a metallo dithiolene derivative such as **6**, we are presently attempting to prepare similar bicyclic compounds on treatment of **5** and the C_5Me_5 analogue with selenium instead of sulfur, and furthermore, to use starting materials such as $C_5H_5(PMe_3)\overline{\mathrm{CoSC}(=\mathrm{NR})\mathrm{N}(\mathrm{R}')\mathrm{C}}(=\mathrm{CH_2})$[13] and C_5H_5-

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[9] For the preparation and crystal structure of $C_5H_5(PMe_3)CoS_5$, see: Burschka, C.; Leonhard, K.; Werner, H. *Z. Anorg. Allg. Chem.* **1980**, *464*, 30.

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$(P\mathit{i}Pr_3)\overline{RhOC(Ph)NC}(=CH_2)$,[14] which, like **5**, also contain a five-membered metallaheterocycle with an exocyclic $=CH_2$ group.

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Supplementary Material Available: Additional drawings and tables of all bond distances and angles, positional and thermal parameters, and least-squares planes and deviations for compounds **5** and **6** (18 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Oxidation of *syn*-Dirhodium Complexes of Cyclohepta- and Cyclooctatriene: Influence of C–H Bond Activation in Multiple Electron-Transfer Reactions

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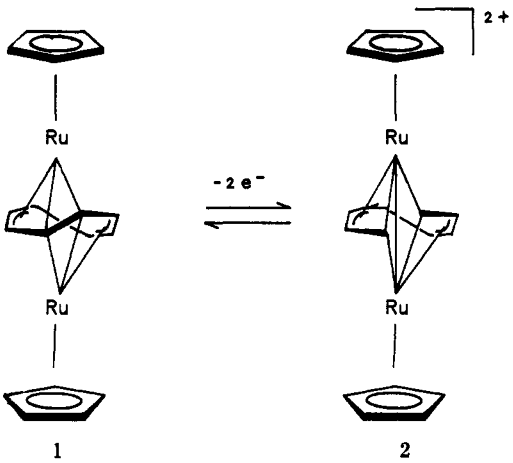
The oxidation of dinuclear complexes $Cp_2Rh_2(\mu\text{-}C_7H_8)$ (**3**) and $Cp_2Rh_2(\mu\text{-}C_8H_{10})$ (**6**) has been examined in dichloromethane and acetone solutions. Complex **3** undergoes one-electron oxidation to $\mathbf{3}^+$ ($E° = -0.04$ V vs SCE), which is further oxidized to highly unstable $\mathbf{3}^{2+}$ at $E_p = +0.34$ V (CH_2Cl_2). Bulk electrolysis of **3** gave a mixture of the tropylium complex $[Cp_2Rh_2(\mu\text{-}C_7H_7)]^+$ (**4**) and the μ-hydrido complex $[Cp_2Rh_2(\mu\text{-}H)(\mu\text{-}C_7H_8)]^+$ (**5**), the relative amounts depending on the electrolysis potential. Complex **6** gave the persistent cation radical $\mathbf{6}^+$ ($E° = +0.14$ V) and underwent oxidation to a transient dication ($E° = +0.45$ V). Both $\mathbf{6}^+$ and $\mathbf{6}^{2+}$ eventually form complex **7**, characterized in situ by NMR spectroscopy as $[Cp_2Rh_2\{\mu\text{-}(1,2,5,6\text{-}\eta{:}2\text{-}\sigma,3,4\text{-}\eta)\text{-}C_8H_9\}]^+$, in which one of the sp^2 ring carbons has lost an H atom and become σ bonded to a Rh atom. Complex **7** was reduced back to **6** electrochemically. The *one*-electron processes seen for these syn-dinuclear complexes, in contrast with the *two*-electron processes observed for anti analogues, and the differences are rationalized in terms of the type of structural rearrangements available to the one-electron intermediates in the two cases. The one-electron intermediates with syn-dinuclear metals enjoy greater thermodynamic stability compared to their anti counterparts since C–H bond cleavage is required to produce multielectron processes in the former.

Introduction

We report the electrochemical oxidation of two complexes in which two CpRh (Cp = η^5-cyclopentadienyl) moieties are bonded to the same face of an unsaturated C_7 or C_8 polyolefin and joined by a metal–metal bond. Interest in these systems derives from two viewpoints. First, dinuclear Rh and Ru complexes in which the metals are aligned on the *opposite* sides of a bridging C_8H_8 ligand (an anti arrangement) have been shown to undergo novel structural rearrangements when oxidized by two electrons,[1–6] leading ultimately to efficient reversible insertion of metals into the C–C framework of the hydrocarbon. The anti-dinuclear pseudo-triple-decker complex $Cp_2Ru_2(\eta^5,\eta'^5\text{-}C_8H_8)$ (**1**) forms the flyover complex **2** in an overall $2e^-$ process via an ECE mechanism.[3,6] An important structural feature of **2** is its M–M bond, which allows each metal to achieve an $18e^-$ configuration. Metal–metal bonds are a common feature of syn-dinuclear complexes of bridging cyclic polyolefins.[7] This stands in contrast to their anti analogues, raising the question of how metal–metal bonding might influence insertion of electron-deficient metals into the C–C bonds of oxidized syn com-



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