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# Reactions of metallocenes during intercalation into the layered $TiSe_2$ lattice

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The intercalation of metallocenes ($Cp_2Co$, $Cp_2Fe$, and $Cp_2Ni$, where Cp is $\eta^5$-$C_5H_5$) from the gas phase into the $TiSe_2$ lattice and of cobaltocene from solutions in acetonitrile, carbon tetrachloride, and chloroform into $TiSe_2$ was studied. The insertion of metallocenes from the gas phase into the $TiSe_2$ lattice gives rise to the $TiSe_2(Cp_2M)_{0.3}$ compounds (M = Co or Fe) having the same stoichiometry. The reactions with the use of acetonitrile as the solvent for metallocenes, which facilitates the insertion, afford not only the intercalation complex but also the reaction product of metallocene and acetonitrile, *viz.*, ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CH_2CN$) (**1**). In the reactions of cobaltocene with chloroform or carbon tetrachloride in the presence of titanium diselenide, only the addition product, *viz.*, ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CCl_3$) (**2**), was isolated. The structures of complexes **1** and **2** were studied by X-ray diffraction.

**Key words:** intercalation, metallocene, titanium diselenide, complex.

Layered inorganic compounds having highly anisotropic physical properties can be used for the preparation of hybrid organo-inorganic composite materials by inserting various organo-inorganometallic compounds into a matrix lattice. Upon intercalation, the integrity of the host crystal structure is retained, and only a slight increase in the interlayer distance and the lattice parameters is observed. First intercalation compounds of metallocenes with metal dichalcogenides were synthesized in 1975.[1] Since that time, the area of chemistry concerned with intercalation compounds of organometallic molecules into layers of inorganic solid compounds has received strong impetus.[2—8] The insertion of metallocenes into lattices of transition metal dichalcogenides has attracted interest in connection with changes in the electrical and magnetic characteristics of the starting crystals and the appearance of low-temperature superconductivity in the resulting intercalation complexes.[2—5]

In the present study, we investigated the chemical features of the intercalation process depending on the reaction conditions with the use of direct intercalation of metallocenes into the $TiSe_2$ lattice from the gas phase and from solutions in $CH_3CN$, $CHCl_3$, and $CCl_4$.

## Results and Discussion

In the present study, using X-ray powder diffraction and elemental analysis, we showed for the first time that the insertion of ferrocene and cobaltocene from the gas phase into the lattice of titanium diselenide afforded the intercalation complexes $TiSe_2(Cp_2Fe)_{0.27}$ and $TiSe_2(Cp_2Co)_{0.3}$. Under analogous reaction conditions, the intercalation of nickelocene into the $TiSe_2$ lattice does not occur. The intercalation of metallocenes is accompanied by a change from the violet color of titanium diselenide to the black color and decomposition of a pressed pellet of $TiSe_2$ because of crystal lattice strains induced by the insertion of a metallocene molecule. Upon intercalation of metallocenes, the hexagonal system of $TiSe_2$ crystals changes to the monoclinic system of the intercalation compounds $(Cp_2M)_{0.3}TiSe_2$ (M = Fe or Co).[9] The X-ray powder study of $TiSe_2(Cp_2Fe)_{0.27}$ and $TiSe_2(Cp_2Co)_{0.3}$ demonstrated that the intercalation of metallocenes into the $TiSe_2$ lattice led to an approximately equal increase in the interlayer distance,[9] close to 5.5 Å, which is observed upon the insertion of various metallocenes into layered transition metal dichalcogenides.[3—5] This value is comparable with the sizes of metallocene molecules. The main lattice parameters and physical characteristics of the resulting intercalation compounds have been published earlier.[9]

The intercalation is facilitated with the use of acetonitrile or THF as solvents for metallocenes.[10,11] The intercalation of cobaltocene from a solution in acetonitrile into the titanium diselenide lattice is accompanied by the chemical reaction of cobaltocene with acetonitrile on the surface of titanium diselenide.

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$$\mathrm{CoCp_2 + TiSe_2} \xrightarrow{\mathrm{MeCN,\ 20\ ^\circ C}}$$
$$\longrightarrow \mathrm{(CoCp_2)_{0.3}TiSe_2 + \underset{\mathbf{1}}{(C_5H_5)Co(C_5H_5CH_2CN)}}.$$

As a result, we isolated the intercalation complex $TiSe_2(Cp_2Co)_{0.3}$ and the reaction product of cobaltocene and acetonitrile, *viz.*, $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CH_2CN)$ (**1**) (X-ray powder and elemental analysis data). Compound **1** was not detected in the reaction performed in the absence of $TiSe_2$ under vacuum. Complex **1** has been synthesized earlier[12] by the reaction of cobaltocene with acetonitrile in the presence of oxygen.

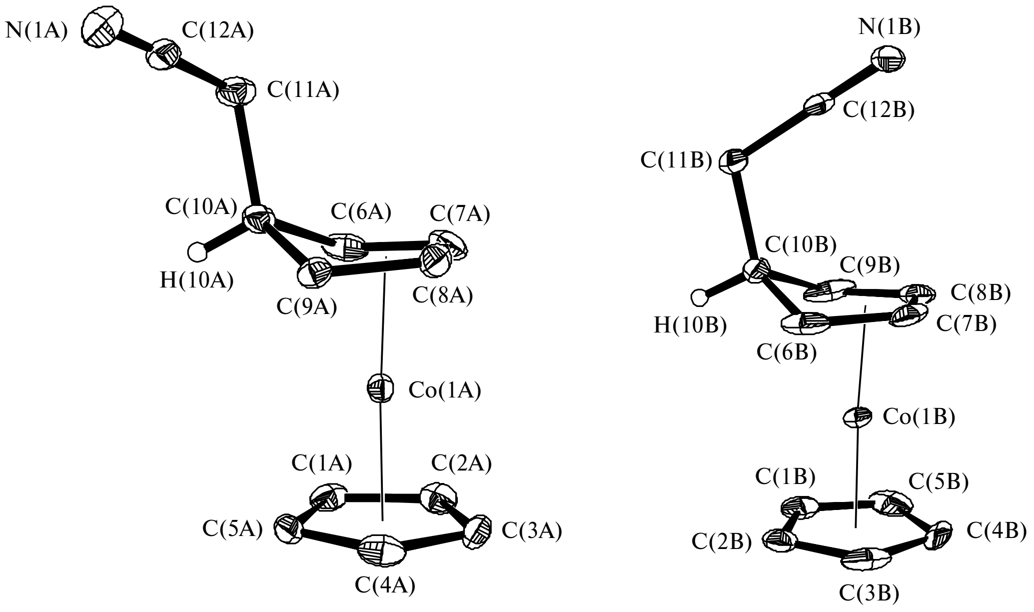
(π-Cyclopentadienyl)(1-*endo*-cyanomethylcyclopentadiene)cobalt (**1**) is a red crystalline compound, which is readily soluble in hexane and acetonitrile and stable in air over a short period of time. The crystal structure of complex **1** was established by X-ray diffraction (Fig. 1, Table 1). The X-ray diffraction study of **1** showed that the acetonitrile molecule is bound only to one Cp ring, resulting in violation of its aromaticity (see Fig. 1). The C(10)—C(9) (1.508(3) and 1.486(5) Å) and C(10)—C(6) (1.494(4) and 1.492(5) Å) distances are comparable with the C—C single bond length, whereas the C—C distances in the C(6), C(7), C(8), C(9) fragment reflect the electron density delocalization in this fragment (1.385(5)—1.413(4) Å). The dihedral angles between the planes of the C(6)—C(9)—C(10) and C(6)—C(7)—C(8)—C(9) fragments are 32.8 and 32.3°, respectively. The Co—C($\eta^5$-Cp) distances are in the range of 2.047(2)—2.093(3) Å and are somewhat longer than the Co—C($\eta^4$-Cp) distances (1.955(3)—2.022(3) Å).

**Table 1.** Selected bond lengths (*d*) and bond angles (ω) in the structure of **1**

| Parameter | A | B |
|---|---|---|
| Bond | *d*/Å | |
| C(6)–C(10) | 1.494(4) | 1.492(5) |
| C(8)–C(9) | 1.413(4) | 1.385(5) |
| C(9)–C(10) | 1.508(3) | 1.486(5) |
| C(10)–C(11) | 1.559(3) | 1.565(4) |
| C(11)–C(12) | 1.460(4) | 1.461(4) |
| N(1)–C(12) | 1.145(4) | 1.131(3) |
| Angle | ω/deg | |
| C(8)C(9)C(10) | 109.2(2) | 110.1(3) |
| C(6)C(10)C(9) | 95.3(2) | 94.6(2) |
| C(9)C(10)C(11) | 115.2(2) | 116.3(3) |
| C(12)C(11)C(10) | 112.3(2) | 112.3(2) |
| N(1)C(12)C(11) | 177.0(3) | 179.4(3) |

The structures of independent molecules **A** and **B** are radically different in the mutual arrangement of the H(10) atom and the acetonitrile fragment relative to the C(10)—C(11) bond. In molecule **A**, the ligands are in *cis* positions, whereas the ligands in molecule **B** are in *trans* positions. It should be noted that the *cis* and *trans* conformations have no significant effect on the geometry of the C(10)—C(11)—C(12)—N(1) fragment (see Table 1). Apparently, free rotation of the acetonitrile fragment about the C(10)—C(11) bond can occur in solution.

According to the X-ray powder data, ferrocene intercalated from a solution in acetonitrile forms an intercala-



**A** **B**

**Fig. 1.** Molecular structure of compound **1**. The conformations of two independent molecules **A** and **B** are shown.

tion complex identical to the complex isolated upon intercalation of ferrocene from the gas phase into the $TiSe_2$ lattice. According to the results of X-ray spectral analysis,**[9]** the stoichiometric composition of intercalation compounds is independent of the mode of intercalation of organometallic compounds and the nature of metallocene. The $Cp_2Fe$ to $TiSe_2$ or $Cp_2Co$ to $TiSe_2$ molar ratio in intercalation compounds is ~0.3.**[9]** The intercalation of nickelocene into the $TiSe_2$ lattice from a solution in acetonitrile cannot be performed because nickelocene, unlike cobaltocene and ferrocene, is readily involved in the replacement of the Cp ring.

The intercalation of cobaltocene into the $TiSe_2$ lattice from a solution in $CCl_4$ at room temperature and from $CHCl_3$ in evacuated tubes does not give rise to intercalation compounds. In both cases, we isolated the same product of the chemical reaction of cobaltocene with the corresponding solvent, *viz.*, $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CCl_3)$ (**2**) (Scheme 1).

**Scheme 1**

$$\mathrm{CoCp_2} \longrightarrow \mathrm{(C_5H_5)Co(C_5H_5CCl_3)}$$

**2**

**Reagents and conditions:** $TiSe_2$, 20 °C, $CHCl_3$ or $CCl_4$.

The reactions of cobaltocene with organic halides (RX) in an inert atmosphere or under vacuum produce two complexes, $(\eta^4\text{-}C_5H_5R)(\eta^5\text{-}C_5H_5)Co$ and $(\eta^5\text{-}C_5H_5)_2Co^+X^-$.**[16,17]** Complex **2** and its synthesis from cobaltocene and $CCl_4$ in an inert atmosphere were documented.**[18,19]** The reaction of cobaltocene with chloroform under air-free conditions gives the $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CHCl_2)$ (see Refs 16 and 17) and $Cp_2Co^+Cl^-$ compounds rather than complex **2**. In an oxygen atmosphere, the reaction of cobaltocene with chloroform yields complex **2**.**[12]** In the present study, we demonstrated that the reaction of cobaltocene with chloroform in the presence of $TiSe_2$ under vacuum also affords compound **2**.

(π-Cyclopentadienyl)(1-*endo*-trichloromethylcyclopentadiene)cobalt (**2**) is an orange-red crystalline compound, which is readily soluble in pentane, hexane, chloroform, and carbon tetrachloride and unstable in air. Crystals of compound **2**, which was synthesized by the reactions of $CoCp_2$ with $CHCl_3$ or $CCl_4$, were grown from a solution in hexane by slow solvent evaporation. The crystal structure of complex **2** was established by X-ray diffraction (Fig. 2, Table 2). As in the case of compound **1**, the attachment of the chloroform molecule to one Cp ring in complex **2** causes violation of its aromaticity (Fig. 2). The C(10)—C(6) (1.510(2) Å) and C(10)—C(9) (1.502(2) Å) distances are substantially longer than the C—C bonds in the C(6)—C(7)—C(8)—C(9) fragment (1.411(3)—1.421(2) Å). The folding angle along the C(6)...C(9) line in complex **2** (29.9°) is somewhat smaller than that in compound **1**. The $Co—C(\eta^5\text{-}Cp)$ distances are in the range of 2.016(3)—2.107(3) Å and slightly overlap with the range of the $Co—C(\eta^4\text{-}Cp)$ distances (1.961(2)—2.024(2) Å). The $Cp_{center}—Co—(C(6)—C(7)—C(8)—C(9))_{center}$ angles have similar values in both complexes (176.7(1)° and 177.4(1)° in complex **1** and 174.1(1)° in complex **2**). Data on analogous cobalt complexes, whose geometric characteristics are similar to those of compounds **1** and **2**, are scarce.**[13—15]**

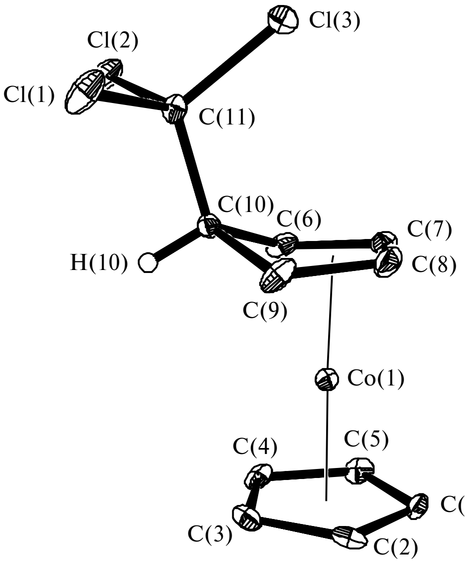


**Fig. 2.** Molecular structure of compound **2**.

Therefore, the nature of the solvent has a decisive effect on the intercalation process. The use of such solvents as chloroform or carbon tetrachloride decreases the possibility of the formation of intercalation complexes because of the immediate formation of the reaction product with cobaltocene, *viz.*, ($\eta^4$-alkylcyclopentadiene)($\eta^5$-cyclopentadienyl)cobalt.

**Table 2.** Selected bond lengths (*d*) and bond angles (ω) in the structure of **2**

| Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|
| C(6)—C(10) | 1.510(2) | C(9)—C(10)—C(6) | 95.77(1) |
| C(9)—C(10) | 1.502(2) | C(9)—C(10)—C(11) | 116.24(1) |
| C(10)—C(11) | 1.549(2) | C(11)—C(10)—Co(1) | 158.74(1) |
| Cl(1)—C(11) | 1.7815(1) | C(10)—C(11)—Cl(3) | 113.30(1) |
| Cl(2)—C(11) | 1.7775(1) | C(10)—C(11)—Cl(2) | 109.61(1) |
| Cl(3)—C(11) | 1.7616(1) | C(10)—C(11)—Cl(1) | 108.92(1) |
| | | Cl(3)—C(11)—Cl(2) | 107.74(8) |
| | | Cl(3)—C(11)—Cl(1) | 108.86(9) |
| | | Cl(2)—C(11)—Cl(1) | 108.29(8) |

## Experimental

All reactions were carried out in evacuated tubes. The metallocene : titanium diselenide molar ratio for the reactions in the gas phase was 0.6 : 1; for the reactions in solution, 0.45 : 1. The intercalation of metallocenes from the gas phase into the $TiSe_2$ lattice was performed at 170—180 °C for 30 days. The reactions of metallocenes in solution in the presence of $TiSe_2$ were carried out at 20 °C. The products were isolated under vacuum or in argon. The starting $TiSe_2$ and $TiTe_2$ compounds were synthesized in the Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences (Ekaterinburg); ferrocene was recrystallized from hexane; nickelocene and cobaltocene were synthesized according to a known procedure.[20] The solvents were prepared according to a procedure described earlier.[21]

X-ray powder studies for the $TiSe_2(Cp_2Fe)_{0.27}$ and $TiSe_2(CoCp_2)_{0.3}$ intercalates were performed on a DRON-3M diffractometer ($CuK_\alpha$ radiation, Ni filter). The IR spectra were recorded on an FSM 1201 Fourier transform spectrometer in Nujol mulls. The UV spectra were measured on a Perkin Elmer Lambda 25 spectrophotometer.

**Intercalation of ferrocene from the gas phase into the $TiSe_2$ lattice.** Polycrystalline $TiSe_2$ (1.6 g, 7.8 mmol) as a pressed pellet and ferrocene (0.9 g, 4.8 mmol) were mixed and sealed in an evacuated tube. Then the tube was opened under argon, and $TiSe_2(Cp_2Fe)_{0.27}$ was washed with hexane to separate from unconsumed ferrocene and dried under a stream of argon. Found (%): C, 12.26; H, 1.08; Se, 61.41. $TiSe_2 \cdot 0.27(FeCp_2)$. Calculated (%): C, 12.67; H, 1.06; Se, 61.68.

**Intercalation of ferrocene from a solution in acetonitrile into the $TiSe_2$ lattice.** Polycrystalline titanium diselenide as a pressed pellet (0.62 g, 3.0 mmol) and a solution of ferrocene (0.25 g, 1.3 mmol) in acetonitrile were placed in a tube. The tube was evacuated, sealed, and kept for 20 days. Then the tube was opened under argon, $TiSe_2(Cp_2Fe)_{0.27}$ was washed with hexane, which was degassed and saturated with argon, and then the product was dried under a stream of argon.

**Intercalation of cobaltocene from the gas phase into the $TiSe_2$ lattice.** Polycrystalline $TiSe_2$ as a pressed pellet (0.6 g, 2.9 mmol) and cobaltocene (0.33 g, 1.7 mmol) were mixed and sealed in an evacuated tube. The tube was opened under argon. The reaction product was washed with THF, which was deaerated and saturated with argon, and dried under a stream of argon. Found (%): C, 13.54; H, 1.10; Se, 59.29. $TiSe_2 \cdot 0.3(CoCp_2)$. Calculated (%): C, 13.72; H, 1.15; Se, 60.15. Heating and storage of $TiSe_2 \cdot 0.3(CoCp_2)$ at 300 °C for 2—3 h afforded $CoSe_2$ with a cubic system in the $TiSe_2$ lattice.

**Reaction of cobaltocene with acetonitrile in the presence of $TiSe_2$.** Powdered polycrystalline $TiSe_2$ (0.87 g, 4.2 mmol) and a solution of cobaltocene (0.36 g, 1.9 mmol) in acetonitrile were mixed in a tube. The tube was evacuated, sealed, and kept for 20 days. Then the tube was opened under vacuum, and $TiSe_2(CoCp_2)_{0.3}$ was separated from the reaction solution, washed with acetonitrile, and dried under a stream of argon. Found (%): C, 13.48; H, 1.12; Se, 59.72. $TiSe_2 \cdot 0.3(CoCp_2)$. Calculated (%): C, 13.72; H, 1.15; Se, 60.15. Acetonitrile was removed from the solution under vacuum, and the reaction product was extracted with hexane. The red crystalline compound was isolated in a yield of 0.04 g (9%), m.p. 58 °C (*cf.* lit. data[12]: m.p. 58 °C). Found (%): C, 63.59; H, 5.54; Co, 25.05. $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CH_2CN)$ (**1**). Calculated (%): C, 62.89; H, 5.29; Co, 25.71; N, 6.11. UV (hexane), $\lambda_{max}$/nm: 327, 395, 505. IR (Nujol mulls), $\nu$/cm$^{-1}$: 2234 (C≡N); 1615 (C=C); 1008, 765, 431 (Co—Cp). In the absence of $TiSe_2$, compound **1** was not detected.

**Reaction of cobaltocene with carbon tetrachloride in the presence of $TiSe_2$.** Powdered polycrystalline $TiSe_2$ (0.51 g, 2.5 mmol) was added to a solution of cobaltocene (0.21 g, 1.1 mmol) in $CCl_4$ and the mixture was sealed in an evacuated tube. The reaction proceeded very vigorously for 1 h. Then the tube was opened under vacuum, after which $TiSe_2$ was separated from the solution and dried under a stream of argon. Carbon tetrachloride was removed from the reaction solution under vacuum, and the reaction product was extracted with hexane. The orange-red product $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CCl_3)$ (**2**) was isolated from the hexane solution in a yield of 0.025 g (7%), m.p. 79 °C (*cf.* lit. data[18,19]: m.p. 79—80 °C). Found (%): C, 43.20; H, 3.58; Cl, 33.89; Co, 18.67. $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5CCl_3)$. Calculated (%): C, 42.96; H, 3.28; Cl, 34.59; Co, 19.17. UV (hexane), $\lambda_{max}$/nm: 270, 328, 400. IR (Nujol mulls), $\nu$/cm$^{-1}$: 1615 (C=C); 430, 473 (Co—Cp); 1007, 1107, 988 ($C_5H_5$).

**Reaction of cobaltocene with chloroform in the presence of $TiSe_2$.** A solution of cobaltocene (0.23 g, 1.2 mmol) in chloroform and powdered polycrystalline $TiSe_2$ (0.56 g, 2.7 mmol) were mixed and sealed in an evacuated tube. The reaction was carried out at room temperature for 4 day. Then the tube was opened under vacuum, after which $TiSe_2$ was separated from the

**Table 3.** Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **1** and **2**

| Compound | **1** | **2** |
|---|---|---|
| Molecular formula | $C_{12}H_{12}CoN$ | $C_{11}H_{10}Cl_3Co$ |
| Molecular weight/g mol$^{-1}$ | 229.16 | 307.47 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P*2(*1*)/*c*, | *P*2(*1*)/*c* |
| *T*/K | 100 | 100 |
| *a*/Å | 5.7227(3) | 7.5920(6) |
| *b*/Å | 23.852(1) | 10.0080(8) |
| *c*/Å | 14.6290(9) | 15.273(1) |
| $\beta$/deg | 92.398(1) | 98.138(2) |
| *V*/Å$^3$ | 1995.1(2) | 1148.8(2) |
| *Z* | 8 | 4 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.526 | 1.778 |
| *F*(000) | 944 | 616 |
| $\mu(MoK_\alpha)$/mm$^{-1}$ | 1.674 | 2.151 |
| Scan range, $\theta$/deg | 25.1 | 27.5 |
| Number of measured reflections | 10874 | 10465 |
| Number of independent reflections ($R_{int}$) | 3551<br>(0.0207) | 2626<br>(0.0369) |
| Number of parameters in refinement | 349 | 185 |
| *R* factors | | |
| $R_1$ based on $I \geq 2\sigma(I)$ | 0.0342 | 0.0441 |
| $wR_2$ based on all reflections | 0.0754 | 0.0713 |
| $S(F^2)$ | 1.086 | 1.012 |
| Residual electron density ($\rho_{min}/\rho_{max}$)/e Å$^{-3}$ | 0.468/–0.249 | 0.506/–0.774 |

reaction solution and dried under a stream of argon. Chloroform was removed from the solution under vacuum, and the reaction product was extracted with hexane. The orange-red crystalline compound ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CCl_3$) (**2**) was isolated from the hexane solution in a yield of 0.05 g (13%), m.p. 79 °C (*cf.* lit. data[18,19]: m.p. 79—80 °C). Found (%): C, 43.10; H, 3.43; Cl, 33.75; Co, 18.56. ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CCl_3$). Calculated (%): C, 42.96; H, 3.28; Cl, 34.59; Co, 19.17. UV (hexane), $\lambda_{max}$/nm: 270, 328, 400. IR (Nujol mulls), $\nu$/cm$^{-1}$: 1615 (C=C); 430, 473 (Co—Cp); 1007, 1107, 988 ($C_5H_5$).

**X-ray diffraction study of compounds 1 and 2.** Crystals were grown from a solution in hexane by slow solvent evaporation. The crystals of compound **2** were prepared by the reaction of cobaltocene with $CHCl_3$ or $CCl_4$. The X-ray diffraction data for ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CH_2CN$) (**1**) and ($\eta^5$-$C_5H_5$)Co($\eta^4$-$C_5H_5CCl_3$) (**2**) were collected at 100 K on a Bruker AXS SMART APEX diffractometer ($\varphi$—$\omega$ scanning technique, Mo-K$\alpha$ radiation, $\lambda$ = 0.71073 Å, graphite monochromator). The structures were solved by direct methods and refined by the least-squares method on $F^2_{hkl}$ with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXTL program package.[22]

The absorption correction was applied using the SADABS program.[23] The hydrogen atoms in compounds **1** and **2** (except for the H atoms of the Cp ligand in **2**) were revealed in difference electron density maps and refined isotropically. The cyclopentadienyl ligand in compound **2** was disordered over two positions, and the hydrogen atoms of this fragment were positioned geometrically and refined using a riding model. The crystallographic parameters and the X-ray data collection and refinement statistics for compounds **1** and **2** are given in Table 3.

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