Organometallic Chemistry

Interaction between cobaltocenium and decamethylcobaltocenium salts and Ph_3ELi (E = Si, Ge, Sn)

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Reactions of cobaltocenium salts $[(C_5R_5)_2Co]PF_6$ (R = H, Me) with Ph_3ELi (E = Si, Ge, Sn) and with Ph_2SbLi mainly follow two pathways (nucleophilic addition and one-electron reduction), yielding cobalt cyclopentadiene-cyclopentadienyl complexes $(\eta^4\text{-}Ph_3EC_5R_5)(\eta^5\text{-}C_5R_5)Co$ (R = H, E = Si, Ge, Sn; R = Me, E = Si) and cobaltocenes $(C_5R_5)_2Co$ (R = H, Me), respectively. The contribution of nucleophilic addition of Ph_3ELi decreases in the order of elements Si > Ge > Sn and when hydrogen atoms are replaced by methyl groups in the initial cobaltocenium salt. Thermal decomposition of cobalt cyclopentadiene-cyclopentadienyl complexes results in substituted cobaltocenes.

Key words: cobaltocene, cobaltocenium, silicon, germanium, tin.

Cobalt cyclopentadiene-cyclopentadienyl complexes are key compounds in the cobaltocene-cobaltocenium system. They are used to prepare substituted cobaltocenes and substituted cobaltocenium salts.[1–4] Cobalt cyclopentadiene-cyclopentadienyl complexes with bulky organoelement groups are of special interest. Previously, radical addition to cobaltocene derivatives was used to introduce bulky organoelement groups into the cyclopentadienyl ring. For example, the complexes $(\eta^4\text{-}R\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Co$[5,6] were synthesized by the reaction of Cp_2Co with R_2M (R = $GeEt_3$, CH_2SiMe_3, M = Cd, Hg).

In this work, reactions of $[(C_5R_5)_2Co]PF_6$ (R = H, Me) with Ph_3ELi (E = Si, Ge, Sn) and with Ph_2SbLi were investigated in order to obtain cobalt derivatives containing organoelement groups. The reactions were carried out over a period of 3 h in THF solution in the temperature range from −40 to 20 °C with an excess of lithium derivative. The reaction products (complexes **1a—d**) were isolated as red-brown crystals. The reaction of $[(C_5Me_5)_2Co]PF_6$ with Ph_3SnLi resulted unexpectedly in complex **2** in 14% yield (Table 1). We obtained an analogous complex by the reaction of $[(C_5Me_5)_2Co]PF_6$ with $LiAlH_4$.[7]

Compounds **1**,**2** were characterized by elemental analysis and the ^1H NMR spectra, which are similar to those of the known complexes containing alkyl and aryl groups.[3,8,9]

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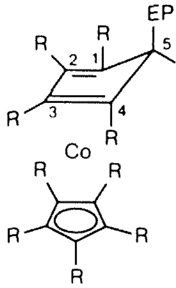
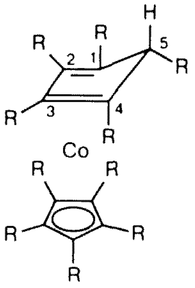


1a—d



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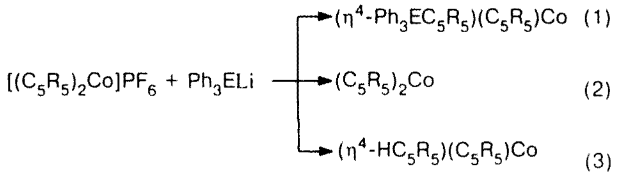
1: R = H, E = Si (**a**); Ge (**b**); Sn (**c**); R = Me, E = Si (**d**) **2**: R = Me

An analysis of the composition and yields of the reaction products of $[(C_5R_5)_2Co]PF_6$ (R = H, Me) with Ph_3ELi (E = Si, Ge, Sn) (see Table 1) shows that nucleophilic addition to the cobaltocenium cation (reaction (1)) is accompanied by one-electron reduction (reaction (2)), resulting in the formation of cobaltocene and reductive addition of hydrogen (reaction 3). The contribution of a particular reaction depends both on the element E in Ph_3ELi salt and the presence of a substituent in the cyclopentadienyl ligand.



$$[(C_5R_5)_2Co]PF_6 + Ph_3ELi \longrightarrow \begin{cases} (\eta^4\text{-}Ph_3EC_5R_5)(C_5R_5)Co & (1) \\ (C_5R_5)_2Co & (2) \\ (\eta^4\text{-}HC_5R_5)(C_5R_5)Co & (3) \end{cases}$$

R = H, Me; E = Si, Ge, Sn

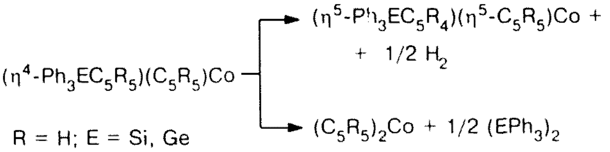
The highest yields of complexes **1a—c** (and minimum yields of cobaltocene) are observed in the reaction of $[(C_5H_5)_2Co]PF_6$ with Ph_3SiLi. The replacement of the nucleophilic agent by Ph_2SbLi abruptly changes the ratio of the products of nucleophilic addition and one-electron reduction: the only reaction product is cobaltocene.

When $[(C_5H_5)_2Co]PF_6$ reacts with Ph_3ELi, the increase in the contribution of reaction (2) as compared to that of reaction (1) matches the increasing tendency of the Ph_3E^- anion toward one-electron transfer in the order of the elements: Si < Ge < Sn.

The ratio of the contributions of nucleophilic addition and one-electron reduction is determined by several factors. For example, on the one hand, the replacement of hydrogen atoms by methyl groups in the cyclopentadienyl ligand leads to an increase in the basicity of the cobalt atom (increase in the redox potentials of the cobaltocene—cobaltocenium system[10]), which hampers reaction (2). On the other hand, the introduction of methyl groups in the ring results in steric hindrances to the entering of an attacking group in the cyclopentadienyl ring.

The increasing contribution of one-electron reduction as compared to that of nucleophilic addition on going from cobaltocenium to decamethylcobaltocenium for any RLi (R = Alk, Ph, EPh_3) is evidence that the steric effect of methyl substituents is manifested itself to a greater extent than the electronic effect. The reaction of $[(C_5Me_5)_2Co]PF_6$ with Ph_3ELi (E = Ge, Sn) does not result in addition products due to steric hindrances and the increasing tendency of Ph_3E^- anion toward one-electron transfer. When $[(C_5Me_5)_2Co]PF_6$ reacts with Ph_3SnLi, a new pathway arises, reductive addition of hydrogen (reaction (3)), where the steric hindrances are less important due to the small bulk of the entering group, whereas the Ph_3Sn- group favors electron transfer.

Thermal decomposition of complexes **1a** and **1b** was investigated in order to obtain cobaltocenes containing an organoelement group in the ring. Thermolysis was carried out *in vacuo* at 140 °C for 1 h. It was established that the decomposition of complexes **1a** and **1b** results in cobaltocenes $(C_5H_4EPh_3)(C_5H_5)Co$ (E = Si, Ge) and $(C_5H_5)_2Co$ in 3 : 2 ratio, respectively.



$$(\eta^4\text{-}Ph_3EC_5R_5)(C_5R_5)Co \longrightarrow \begin{cases} (\eta^5\text{-}Ph_3EC_5R_4)(\eta^5\text{-}C_5R_5)Co + 1/2\,H_2 \\ (C_5R_5)_2Co + 1/2\,(EPh_3)_2 \end{cases}$$

R = H; E = Si, Ge

Table 1. Reaction of $[(C_5R_5)_2Co]PF_6$ (R = H, Me) with Ph_3ELi (E = Si, Ge, Sn) and with Ph_2SbLi

Initial reagents		Reaction products, mol/mol of initial salt		
$[(C_5R_5)_2Co]PF_6$	Ph_3ELi	$(C_5R_5EPh_3)(C_5R_5)Co$	$(C_5R_5)_2Co$	$(C_5R_5)(C_5R_5H)$ Co
$(Cp_2Co)PF_6$	Ph_3SiLi	0.72 (**1a**)	0.25	—
$(Cp_2Co)PF_6$	Ph_3GeLi	0.70 (**1b**)	0.23	—
$(Cp_2Co)PF_6$	Ph_3SnLi	0.42 (**1c**)	0.57	—
$(Cp_2Co)PF_6$	Ph_2SbLi	—	0.80	—
$[(C_5Me_5)_2Co]PF_6$	Ph_3SiLi	0.45 (**1d**)	0.52	—
$[(C_5Me_5)_2Co]PF_6$	Ph_3GeLi	—	0.90	—
$[(C_5Me_5)_2Co]PF_6$	Ph_3SnLi	—	0.82	0.14 (**2**)

Thus, one can obtain cobalt cyclopentadiene-cyclopentadienyl complexes with bulky organoelement groups using cobaltocenium salts as the starting compounds. Thermal decomposition of these complexes can result in substituted cobaltocenes.

Experimental

The starting compounds of composition $[(C_5R_5)_2Co]PF_6$ (R = H, Me) and Ph_3ELi (E = Si, Ge, Sn) were prepared by known procedures.[1,11] The reactions were carried out in evacuated ampules. NMR spectra were recorded on a Bruker WP 200-SY spectrometer (^1H, 200 MHz).

Reaction of $[Cp_2Co]PF_6$ with Ph_3ELi (E = Si, Ge, Sn) and with Ph_2SbLi. A solution of Ph_3ELi salt in THF (1.3—2.0 mmol) was added to a suspension of $[(C_5H_5)_2Co]PF_6$ (0.3—0.5 g, 1.0—1.6 mmol) in THF (30 mL) at −20 °C. The reaction mixture was stirred for 30 min at 0 °C and then for an additional 2 h at 20 °C. The solvent was removed *in vacuo*, and then water (5 mL) and CH_2Cl_2 (15 mL) were added to the residue. The aqueous layer was separated from the organic layer. The yellow residue of the cobaltocenium salt was filtered off and dried. The organic solution was concentrated to 3 mL and passed through a column with Al_2O_3. Removal of the solvent gave crystals of $(C_5H_5EPh_3)(C_5H_5)Co$ (**1a—c**) (the yields are given in Table 1). All compounds were recrystallized from a benzene—hexane mixture. Complex **1a**. Found (%): C, 73.70; H, 5.65. $C_{28}H_{25}CoSi$. Calculated (%): C, 73.28; H, 5.62. ^1H NMR (acetone-d_6), δ: 2.53 (m, H(5)); 2.72 (m, H(1,4)); 4.71 (s, H(Cp)); 5.29 (t, H(2,3)); 6.8—7.6 (m, H(Ph)). Complex **1b**. Found (%): C, 68.40; H, 5.20. $C_{28}H_{25}CoGe$. Calculated (%): C, 68.21; H, 5.11. ^1H NMR (acetone-d_6), δ: 2.59 (m, H(5)); 2.74 (m, H(1,4)); 4.65 (s, H(Cp)); 5.35 (t, H(2,3)), 6.8—7.6 (m, H(Ph)). Complex **1c**. Found (%): C, 62.00; H, 4.75. $C_{28}H_{25}CoSn$. Calculated (%): C, 62.38; H, 4.61. ^1H NMR (acetone-d_6), δ: 2.51 (m, H(5)); 2.71 (m, H(1,4)); 4.75 (s, H(Cp)); 5.21 (t, H(2,3)); 6.8—7.6 (m, H(Ph)).

Reaction of $[(C_5Me_5)_2Co]PF_6$ with Ph_3SiLi. A 0.18 *M* solution of Ph_3SiLi in THF (5.4 mL) was added to a suspension of $[(C_5Me_5)_2Co]PF_6$ (0.23 g, 0.48 mmol) in THF (25 mL) at −20 °C. The temperature of the reaction mixture was raised to 20 °C, and the mixture was stirred for 2 h. The solvent was removed *in vacuo*, and then Et_2O (15 mL) and H_2O (3 mL) were added at 0 °C. The aqueous layer was separated from the organic layer. The ethereal layer was passed through a column with Al_2O_3, and the solvent was removed *in vacuo*. The red-brown residue was dissolved in C_6H_6 (3 mL), passed through a column with Al_2O_3 (with hexane as the eluent), and after removal of the solvent *in vacuo*, red-brown crystals of $(\eta^4\text{-}Ph_3SiC_5Me_5)(\eta^5\text{-}C_5Me_5)Co$ (**1d**) (0.13 g, 45%) were obtained. The compound was recrystallized from a toluene—hexane mixture. ^1H NMR (C_6D_6), δ: 1.67 (s, Me(Cp)); 1.74 (s, 2-Me, 3-Me); 0.67 (s, 1-Me, 4-Me); 1.40 (s, 5-Me_{endo}); 6.9—7.5 (m, Ph). The column with Al_2O_3 was eluted with a methanol—acetone mixture (1 : 1). Yellow crystals of $[(C_5Me_5)_2Co]PF_6$ (0.12 g, 52%) were obtained after evaporation of the solvent.

Reaction of $[(C_5Me_5)_2Co]PF_6$ with Ph_3GeLi. A 0.20 *M* solution of Ph_3GeLi in THF (4.6 mL) was added to a suspension of $[(C_5Me_5)_2Co]PF_6$ (0.22 g, 0.46 mmol) in THF (25 mL) at −20 °C. The temperature of the reaction mixture was raised to 20 °C, and the mixture was stirred for 2 h. The solvent was removed *in vacuo*, and then Et_2O (15 mL) and H_2O (3 mL) were added at 0 °C. The aqueous layer was separated from the organic layer, and the latter was passed through a column with Al_2O_3 (with methanol—acetone (1 : 1) as the eluent). Yellow crystals of $[(C_5Me_5)_2Co]PF_6$ (0.20 g, 90%) were obtained after evaporation of the solvent.

Reaction of $[(C_5Me_5)_2Co]PF_6$ with Ph_3SnLi. A 0.26 *M* solution of Ph_3SnLi in THF (5.8 mL) was added to a suspension of $[(C_5Me_5)_2Co]PF_6$ (0.36 g, 0.76 mmol) in THF (30 mL) at −20 °C. The temperature of the reaction mixture was raised to 20 °C, and the solution was stirred for 2 h. Then it was cooled to 0 °C, and water (2 mL) was added. The solvent was removed *in vacuo*, and the residue was extracted with hexane (10 mL). The solution was concentrated *in vacuo* to 2 mL and passed through a column with Al_2O_3. Evaporation of the solvent gave bright-red crystals of $(\eta^4\text{-}H_{exo}\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_5)Co$ (**2**) (0.035 g, 14%). Found (%): C, 73.00; H, 9.60; Co, 17.50. $C_{20}H_{31}Co$. Calculated (%): C, 72.70; H, 9.46; Co, 17.84. ^1H NMR (C_6D_6), δ: 1.73 (s, Me(Cp)); 1.95 (s, 2-Me, 3-Me); 0.79 (d, 1-Me, 4-Me, $J_{1,4-5}$ = 1 5 Hz); 1.50 (d, 5-Me, J_{5-Me} = 7.0 Hz); 2.20 (dd, H(5)). After extraction with hexane, the residue was dissolved in acetone and passed through a column with Al_2O_3. Evaporation of the solvent gave $[(C_5Me_5)_2Co]PF_6$ (0.29 g, 82%).

Thermal decomposition of 1a. Complex **1a** (0.35 g, 0.78 mmol) was heated in an evacuated ampule at 140 °C for 1 h, and H_2 (0.21 mmol) evolved. The residue in the ampule was dissolved in hexane, and a solution of bromine in hexane was added dropwise until precipitation ceased. The residue was filtered off, dried, and dissolved in water (15 mL) with addition of several drops of HCl. Then a solution of Ph_4BNa was added to the transparent solution, and a yellow precipitate formed. It was filtered off, dried, dissolved in acetone, and then the solution was chromatographed on a column with Al_2O_3 (with acetone—methanol (1 : 1) as the eluent). A mixture of cobaltocenium salts $[Cp_2Co]BPh_4$ and $[(C_5H_4SiPh_3)CpCo]BPh_4$ (0.36 g) was obtained as yellow crystals after evaporation of the solvent. ^1H NMR spectrum of the mixture (acetone-d_6), δ: 5.87 (s, H(Cp), Cp_2Co^+); 5.57 (s, H(Cp), $Cp(C_5H_4SiPh_3)Co^+$); 5.68 and 6.10 (m, (H(C_5H_4)). The ratio of the substitution products was determined on the basis of the integrated intensities of protons in the cyclopentadienyl rings in substituted and unsubstituted cobaltocenium.

Thermal decomposition of 1b. Complex **1b** (0.30 g, 0.61 mmol) was heated in an evacuated ampule at 140 °C for 1 h, and H_2 (0.17 mmol) evolved. The reaction mixture was treated analogously to the preceding experiment. A mixture of cobaltocenium salts $[Cp_2Co]BPh_4$ and $[(C_5H_4GePh_3)CpCo]BPh_4$ (0.28 g) was obtained. ^1H NMR spectrum of the mixture (acetone-d_6), δ: 5.87 (s, H(Cp), Cp_2Co^+); 5.56 (s, H(Cp), $Cp(C_5H_4GePh_3)Co^+$); 5.60 and 6.23 (m, H(C_5H_4)).

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References

1. E. V. Leonova and V. Kh. Syundyukova, in *Metody elementoorganicheskikh soedinenii. Kobal't, nikel', platinovye metally* [*Methods of Organoelement Compounds. Cobalt, Nickel, and Platinum Metals*], Nauka, Moscow, 1978, 45 (in Russian).
2. E. V. Leonova, A. V. Malkov, N. S. Kochetkova, and V. A. Sergeev, *Metalloorg. Khim.*, 1988, **1**, 137 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].

3. A. V. Malkov, E. V. Leonova, N. S. Kochetkova, and V. A. Sergeev, *Metalloorg. Khim.*, 1988, **1**, 357 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
4. V. P. Maryin and P. V. Petrovskii, *J. Organomet. Chem.*, 1992, **441**, 125.
5. A. V. Malkov, P. V. Petrovskii, E. I. Fedin, and E. V. Leonova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1270 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].
6. G. A. Razuvaev, V. P. Maryin, Yu. A. Andrianov, L. I. Vyshinskaya, and O. N. Druzhkov, *J. Organomet. Chem.*, 1988, **346**, 403.
7. V. P. Maryin, *Abstracts XVth Int. Conf. on Organomet. Chem.*, Warsaw, 1992, 86.
8. H. Lehmkul and H. F. Nehl, *Chem. Ber.*, 1984, **117**, 3443.
9. G. A. Razuvaev, V. P. Maryin, L. I. Vyshinskaya, G. Ya. Mal'kova, Yu. A. Andrianov, and O. N. Druzhkov, *Dokl. Akad. Nauk SSSR*, 1987, **294**, 614 [*Dokl. Chem*, 1987, **294** (Engl. Transl.)].
10. U. Kolle and F. Khouzami, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 640.
11. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, *Metody elementoorganicheskikh soedinenii. Germanii, olovo, svinets* [*Methods of Organoelement Compounds. Germanium, Tin, and Lead*], Nauka, Moscow, 1968, 702 pp. (in Russian).

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