Oxidative Addition of Hydrosilanes, Hydrogermane, and Hydrostannane to Cyclopentadienylcobalt(I) Bearing a Pendant Phosphane Ligand: Cyclopentadienylhydridocobalt(III) Chelate Complexes with Silyl, Germyl, and Stannyl Ligands

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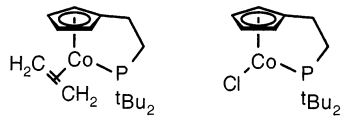
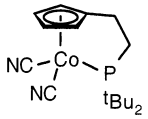
Oxidative addition of hydrosilanes, a hydrogermane, and a hydrostannane to the ((cyclopentadienylalkyl)phosphane)cobalt(I) chelate **1** results in the formation of cyclopentadienylhydridocobalt(III) complexes having a tethered phosphorus ligand and silyl (*rac*-**4**−*rac*-**8**), germyl (*rac*-**10**), and stannyl substituents (*rac*-**11**). The pseudo-four-coordinate complexes are chiral. The X-ray structures of **5** and **7** have been determined. Variable-temperature NMR spectra indicate racemization in solution due to reversible dissociation of the phosphorus ligand. The barrier of this process has been estimated to be in the range of 13−16 kcal/mol.

Oxidative addition of hydrosilanes at vacant coordination sites of transition metals is considered a key step in the transition-metal-catalyzed hydrosilylation of alkenes, alkynes, aldehydes, and ketones.[1] While hydrosilylation and in particular silylcarbonylation reactions catalyzed by cobalt(0) carbonyl complexes have been widely investigated, this is not the case for cyclopentadienylcobalt(I) complexes. Recently Brookhart reported on 2-fold oxidative addition reactions at pentamethylcyclopentadienylcobalt(I) (Cp^*Co^I) starting from bis(alkene) complexes. This sequence of reactions led to the formation of remarkable cobalt(V) complexes bearing two hydrido and two silyl ligands at Cp^*Co.[2] As the first step after an alkene decomplexation the authors propose an oxidative addition leading to a Cp^*Co^{III} silyl hydride intermediate, which was, however, not isolated.

While some complexes have been stabilized by the steric and the electronic effects of the pentamethylcyclopentadienyl ligand as compared to those of the unsubstituted cyclopentadienyl ligand, stabilization of cyclopentadienyl complexes can also be achieved by chelation when cyclopentadienyl ligands with an attached donor tether are used. In this context nitrogen,[3−8] oxygen,[3,9] phosphorus,[3,8,10,11] and other donors[10] have been connected to cyclopentadienyl ligands, making chelation possible when a sufficiently long tether is given. We have focused on phosphanylalkyl-substituted cyclopentadienylcobalt complexes, and particularly the di-*tert*-butylphosphanylethylcyclopentadienylcobalt ($Cp^{\#}$-Co) chelates, which favorably combine good yields and crystallization properties. In this context we prepared rare vinylidene, vinylcarbene, Arduengo type carbene,[12] cobaltacyclobutenone,[13] and cyclopropene complexes starting either from the cobalt(II) chloride **2** in the



1 **2**



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presence of sodium amalgam or from the ethene cobalt(I) chelate **1**. Remarkably, the reaction of **2** with *tert*-

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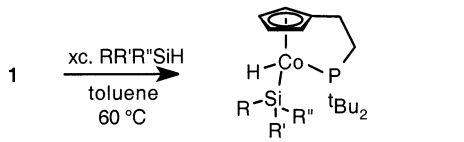
butylphosphaethyne in the presence of sodium amalgam at low temperature resulted in a cleavage of the P−C triple bond.[14]

Recently we reported on reactions of **1** with silyl compounds such as trimethylsilyl chloride, azide, isocyanate, isothiocyanate, and cyanide. While in the first four cases cobalt(II) chelate complexes with chloro, azido, isocyanato, and isothiocyanato ligands such as **2** were obtained, trimethylsilyl cyanide gave the dicyanocobalt(III) chelate **3**.[15] These observations suggest reaction sequences involving oxidative additions of the silyl reagents and possibly the formation of radical intermediates. A reaction involving an oxidative addition of a carbon−silicon bond was also envisaged to explain the isomerization of the bis(trimethylsilyl)ethyne complex to the bis(trimethylsilyl)vinylidene complex.[12] To better understand the chemistry of silyl compounds and related substrates and the Cp#Co system, we investigated some reactions of **1** with hydrosilanes. In addition, a hydrogermane and a hydrostannane were included in this study. We found that hydrosilanes, a hydrogermane, and a hydrostannane readily oxidatively add to the cobalt(I) chelate to give stable cobalt(III) silyl, germyl, and stannyl hydrides.

The silylhydridocobalt(III) chelate *rac*-**4** formed quickly in 85% yield upon treatment of the ethene complex **1** with phenylsilane in toluene at 60 °C. In contrast, the



rac-**4**: R = Ph, R' = R" = H (85 %)
rac-**5**: R = R' = Ph, R" = H (79 %)
rac-**6**: R = R' = R" = Ph (54 %)

reaction with triphenylsilane required, presumably as a result of the steric bulk of the silane, a longer reaction time. Chelates *rac*-**4**−*rac*-**6** were characterized spectroscopically. In the IR spectra the Co−H vibrations gave rise to diagnostic absorption bands around 2060 cm^{-1}.[16,17] Particularly indicative are the ^1H NMR signals around δ −16 showing coupling to the phosphorus ligand ($^2J_{P,H}$ = 44 Hz), which are assigned to the hydrido ligands. The ^{31}P NMR chemical shifts between δ 110 and 120 are somewhat higher than in chelates with a phosphane ligand coordinated at Co(I).[15]

A detailed inspection of the ^1H NMR spectra of *rac*-**4**−*rac*-**6** shows an interesting phenomenon. For *rac*-**6** the signal assigned to the cobalt hydride proton (δ −16.53), a doublet ($^2J_{P,H}$ = 47.6 Hz), is observed as a consequence of the coupling to the phosphorus ligand. The cobalt hydride signal of *rac*-**5** (δ −17.02) also is a doublet ($^2J_{P,H}$ = 46.5 Hz); in the normal spectrum as well as in an H,H COSY spectrum, *no* coupling to the silyl hydride proton is observed. In contrast to the other two complexes the cobalt hydride signal of *rac*-**4** (δ −16.89) is a doublet of doublets. A H,H COSY spectrum clearly shows that in addition to the coupling to the phosphorus atom ($^2J_{Co-H,P}$ = 44.8 Hz) only *one* coupling from the cobalt hydride to a silyl hydride exists ($^3J_{Si-H,Co-H}$ = 3.8 Hz), which was measured from the signal of Si−*H*. Obviously the two diastereotopic silyl hydride substituents show clearly different NMR properties. When spectra were measured with ^{31}P decoupling, it was possible to observe the missing couplings, indicating the phosphane ligand being the cause of the phenomenon. The interesting point is, however, that only one of the two diastereotopic silyl hydrides in *rac*-**4** is affected.

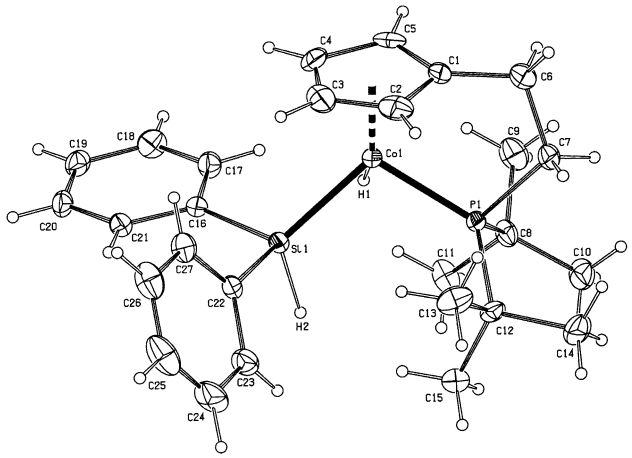


Figure 1. Structure of one molecule of **5** in the crystal. The unit cell contains four molecules, in space group $P2_12_12_1$. Selected bond lengths (Å), angles (deg), and dihedral angle (deg): Co1−H1 = 1.51(3), Co1−Si1 = 2.236(2), Co1−P1 = 2.174(2), Co1−C1 = 2.056(3), Si1−H2 = 1.48(2), Si1−C22 = 1.909(3), Si1−C16 = 1.897(3); C(16)−Si(1)−C(22) = 104.8(1), C(16)−Si(1)−Co(1) = 114.4(1), C(22)−Si(1)−Co(1) = 117.6(1), P(1)−Co(1)−Si(1) = 104.60(4); H1−Co1−Si1−H2 = 54(1).

To get a deeper insight into the conformation of *rac*-**5** with respect to this bond, the compound was crystallized from toluene at −25 °C in order to perform an X-ray crystal structure analysis. The unit cell contains four symmetry-equivalent molecules of equal chirality, one of which is shown in Figure 1. A crystal containing the other enantiomer was found as well. The analysis confirmed the constitution already assigned on the basis of the spectroscopic data. It was possible to locate either hydrogen atom, the one bound at cobalt (H1) and that bound at silicon (H2), in the difference Fourier synthesis, and to refine both as independent atoms. To our knowledge this is the first time that a cobalt hydride bond distance (1.51(3) Å) has been determined in a cyclopentadienylcobalt system. The dihedral angle H1−Co1−Si1−H2 is 54(1)°, corresponding to a nearly staggered conformation. However, it is difficult to correlate this value with that observed for the $^3J_{Si-H,Co-H}$ NMR coupling observed for *rac*-**4**, as it is not clear to which of the silyl hydrides the coupling corresponds. In addition, the conformation observed for solid *rac*-**5** is not necessarily that of *rac*-**4** in solution.

While the starting material and the silanes used are achiral, the oxidative addition products *rac*-**4**−*rac*-**6** show cobalt-centered chirality. As no chiral information was given, they are of course formed as racemates. However, use of either chiral or prochiral hydrosilanes

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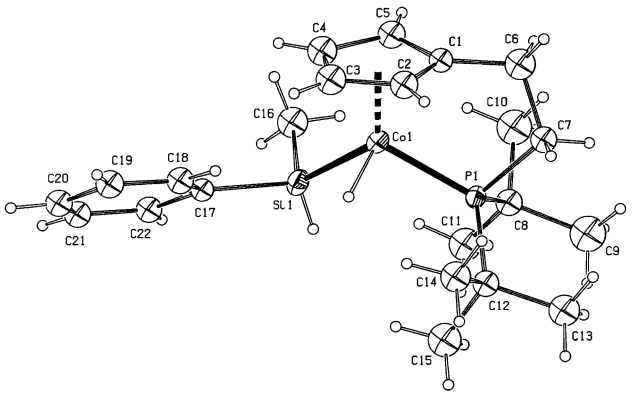
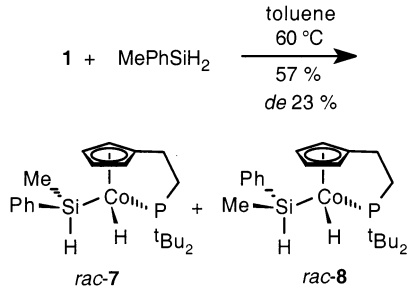


Figure 2. Structure of *rac*-**7** in the crystal. Selected bond lengths (Å) and angles (deg): Co1−C1 = 2.015(8), Co−C2 = 2.086(10), Co1−C3 = 2.060(11), Co1−C4 = 2.014(10), Co1−C5 = 2.055(9), Co1−Si1 = 2.246(3), Co1−P1 = 2.171(3); P1−Co1−Si1 = 105.4(1).

should cause additional silicon-centered chirality, thus resulting in the formation of diastereoisomers. To check the possible diastereoselectivity of such a process, **1** was treated with methylphenylsilane. The reaction with the prochiral methylphenylsilane gave the oxidative-addition products *rac*-**7** (*RS*/*SR*) and *rac*-**8** (*SS*/*RR*) as a diastereomeric mixture. The ^{1}H NMR signals of the

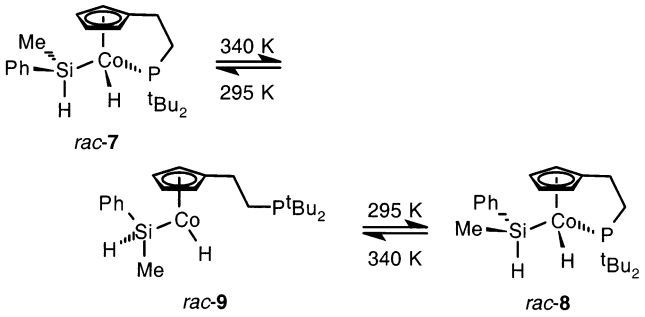


hydrido ligands were sufficiently separated to allow the determination of the diastereomeric ratio to be 16:10 (de 23%). The P−H,Si−H coupling between the two hydride protons is observed only in the P-decoupled ^{1}H NMR spectrum; Si−H,Co−H coupling is not observed.

Crystallization of *rac*-**7**/*rac*-**8** from hexane/toluene (10:1) gave crystals suitable for an X-ray crystal structure analysis. Figure 2 displays the structure of *rac*-**7**. In contrast to the analysis of *rac*-**5** the hydrogen atom connected to the cobalt atom could not be detected and therefore had to be calculated.

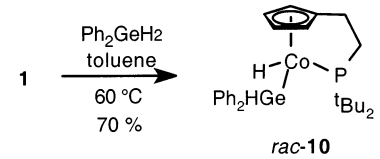
When the hydridocobalt chelates *rac*-**4**, *rac*-**5**, and *rac*-**7**/*rac*-**8** were more deeply investigated by NMR, an interesting dynamic behavior was observed. As all of them are chiral, the *tert*-butyl groups at the phosphorus atoms are diastereotopic and give rise to two ^{1}H NMR and two ^{13}C NMR signals for the *tert*-butyl methyl groups ([D_8]toluene). This is indeed the case at 300 K for *rac*-**4**, at 295 K for *rac*-**5**, and at 240 K for *rac*-**7**/*rac*-**8**. However, with rising temperature a coalescence is observed, finally resulting in one signal for these methyl groups in the ^{1}H as well as in the ^{13}C NMR spectrum. In a similar way the differentiation of the cyclopentadienyl protons is lost at elevated temperature. Control measurements below the coalescence temperature after heating gave the same spectra as before. These observations were made with all three compounds investigated. Clearly, the diastereotopicity of the *tert*-butyl groups is lost with respect to the NMR time scale at elevated temperature. The free enthalpies of activation for this process are estimated to be 16.3, 15.4, and 14.9 kcal/mol, respectively.[18] The process was verified by numerous measurements using a variety of NMR techniques such as H,H COSY, HSQC, HMBC, P,H correlated spectroscopy, ^{31}P{^{1}H}, and ^{1}H{^{31}P} NMR. Remarkably the diastereomeric ratio of *rac*-**7** to *rac*-**8**, which was observed at 295 K, was the same before and after the coalescence, suggesting that it reflects the thermodynamically favored composition of the diastereomeric mixture.

An interpretation of the observed process involves a temporary decomplexation of the phosphane sidearm, thereby generating a vacant coordination site in *rac*-**9**.



This might facilitate a racemization by allowing the hydride (more likely) or the silyl ligand to change its place followed by recomplexation of the phosphane sidearm. As ^{31}P NMR measurements at temperatures below as well as above the coalescence temperature did not indicate a decoordinated sidearm,[10] this process has to be rapid relative to the NMR time scale. The ability to decoordinate and subsequently to recoordinate facilitates this unique process and clearly distinguishes the chelates discussed here from the respective non-chelate cyclopentadienylcobalt complexes. Alternatively, one might envisage a sequence of reductive elimination of hydrosilane followed by oxidative readdition. However, as treatment of *rac*-**4** with triphenylsilane at temperatures up to 340 K did not result in any formation of *rac*-**6**, we consider this possibility less likely.

Having shown the possibility of silane oxidative additions at Cp$^{\#}$Co, we became interested in the question if a hydrogermane behaved similarly. Treatment of **1** with diphenylgermane in toluene at 60 °C indeed resulted in the desired oxidative addition, giving *rac*-**10** in 70% yield. *rac*-**10** appears to be more stable (heat, air) than the silicon derivatives. To our knowledge *rac*-**10** is the first cyclopentadienylcobalt complex with a cobalt−germanium bond. Like its homologue *rac*-**5**, in the ^{1}H NMR spectrum a doublet is observed for the



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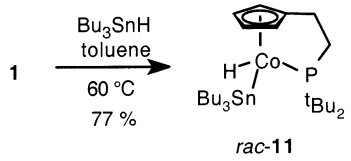
cobalt hydride (δ −16.11), the coupling to the phosphorus atom being somewhat larger ($^2J_{P,H}$ = 56.7 Hz). As with *rac*-**5** no coupling to the silyl hydride is observed.

Next an oxidative addition of a stannane was tried. **1** was treated with tributylstannane in toluene at 60 °C. The reaction indeed resulted in the formation of the stannyl cobalt chelate *rac*-**11** in 77% yield. The hydride



rac-**11**

proton gives rise to a doublet signal at δ −17.17 ($^2J_{P,H}$ = 54.5 Hz). The signal shows ^{119}Sn satelites ($^2J_{Sn,H}$ = 149.4 Hz).

In conclusion, we have shown that hydrosilanes, -germanes, and -stannanes are able to undergo oxidative additions with **1**, resulting in the formation of the respective cobalt(III) silyl hydrides. At elevated temperatures an equilibration of the configurations at the asymmetric cobalt atom takes place, as shown by NMR. We are currently investigating the chemistry of these complexes with particular emphasis on catalytic reactions such as hydrosilylation and hydrostannylation.

Experimental Section

General Considerations. All operations involving air-sensitive materials were performed under argon using standard Schlenk techniques. Diethyl ether, THF, benzene, and toluene were dried over and distilled from Na/K−benzophenone. Silica gel was heated at reduced pressure and then put under normal pressure with argon. This was repeated five times. Starting materials were either purchased or prepared according to literature procedures. IR: Bruker ISS 25, Perkin-Elmer FT 580, FT 1710. ^{1}H NMR: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz), AVB 500 (500.1 MHz). Chemical shifts refer to δ_{TMS} or to residual solvent peaks. Coupling constants indicated as *J* were obtained only in the P-decoupled spectrum; ^{29}Si,H coupling constants were determined from the ^{29}Si satellites in the ^{1}H NMR spectrum. ^{13}C NMR: Bruker AVS 200 (50.3 MHz), AVS 400 (100.6 MHz). Spectra were obtained with the DEPT and with the APT techniques. + and − indicate positive (C, CH_2) and negative phase (CH, CH_3), respectively. Chemical shifts refer to δ_{TMS} or to residual solvent peaks. ^{31}P NMR: H decoupled, Bruker AVS 400 (161.9 MHz), 85% aqueous H_3PO_4 as external standard. MS, FAB-MS, HRMS: Finnigan AM 400, Fisons VG Autospec. Elemental analyses: Haeraeus CHN-Rapid. Melting points: Büchi apparatus according to the method of Dr. Tottoli, uncorrected.

General Procedure (GP) for Oxidative Addition of Hydrosilane, -germane, and -stannane at Cp$^{\#}$Co. In a 20 mL Schlenk flask 158 mg (0.49 mmol) of **1** and 1.47 mmol of the hydrosilane, -germane, or -stannane in 5 mL of toluene was stirred at 60 °C for 10 h. After the mixture was cooled to 25 °C, the excess hydride and the solvent were removed into a old trap at reduced pressure. The solid product was recrystallized from toluene at −20 °C.

***rac*-[((Di-*tert*-butylphosphanyl)ethyl)cyclopentadienyl-*P*]hydrido(phenylsilyl)cobalt(III) (*rac*-4):** GP, 158 mg (0.30 mL, 1.5 mmol) of phenylsilane; 168 mg (0.4 mmol, 85%) of *rac*-**4**, yellow crystals (mp 122−123 °C). IR (film, cm^{-1}): $\tilde{\nu}$ 3062 (w), 2960 (w), 2897 (m), 2864 (w), 2049 (s, Co−H), 1941 (w, Si−H), 1475 (m), 1427 (m), 1183 (w), 1102 (m), 948 (m), 833 (s, Si−H), 822 (s, Si−H), 729 (m), 701 (m), 581 (m, Co−H). ^{1}H NMR (500 MHz, $C_6D_5CD_3$): δ −16.89 (dd, 1H, $^2J_{P,H}$ = 43.6 Hz, Co−H), 1.06 (d, 9H, $^3J_{P,H}$ = 12.6 Hz, $C(CH_3)_3$), 1.14 (d, 9H, $^3J_{P,H}$ = 12.6 Hz, $C(CH_3)_3$), 1.75−1.88 (m, 2H, CH_2), 1.96−2.12 (m, 2H, CH_2), 3.49 (s, 1H, H_{Cp}), 4.31 (s, 1H, H_{Cp}), 4.66 (s, 1H, H_{Cp}), 5.06 (s, 1H, H_{Cp}), 5.10 (ddd, 1H, $^2J_{Si-H,Si-H}$ = 6.8 Hz, $^3J_{Si-H,Co-H}$ = 3.8 Hz, $^3J_{Si-H,P}$ = 3.8 Hz, $^1J_{Si,H}$ = 86.6 Hz , Si−H), 5.50 (dd, 1H, $^3J_{Si-H,Co-H}$ = 12.6 Hz, $^2J_{Si-H,Si-H}$ = 6.8 Hz, $^1J_{Si,H}$ = 79.2 Hz, Si−H), 7.18−7.23 (m, 1H, H_{Ph}), 7.24−7.27 (m, 2H, H_{Ph}), 7.28−7.31 (m, 2H, H_{Ph}). ^{13}C NMR (50.3 MHz, C_6D_6): δ 25.1 (+, d, $^2J_{C,P}$ = 4.7 Hz, C-6), 29.1 (−, d, $^2J_{C,P}$ = 3.2 Hz, $C(CH_3)_3$), 29.8 (−, d, $^2J_{C,P}$ = 4.1 Hz, $C(CH_3)_3$), 35.6 (+, d, $J_{C,P}$ = 15.1 Hz, $C(CH_3)_3$), 36.3 (+, d, $J_{C,P}$ = 15.3 Hz, $C(CH_3)_3$), 40.6(+, d, $J_{C,P}$ = 18.5, C-7), 73.9 (−, d, $^4J_{C,P}$ = 4.3 Hz, C-2 or C-5), 78.6 (−, C-4 or C-3), 85.2 (−, d, $^4J_{C,P}$ = 2.8 Hz, C-5 or C-2), 85.6 (−, C-4 or C-3), 116.4 (+, d, $^3J_{C,P}$ = 8.2 Hz, C-1), 127.4 (−, C_{Ph}), 127.6 (−, C_{Ph}), 135.2 (−, C_{Ph}), 145.6 (+, *ipso*-C_{Ph}). ^{31}P NMR (121.5 MHz, C_6D_6): δ =118.9. MS (70 eV): *m*/*z* (%) 404 (19) [M$^+$], 296 (100) [M$^+$ − $SiPhH_2$ − H], 237 (36) [M$^+$ − $SiPhH_2$ − H − Co], 184 [M$^+$ − $SiPh_2H$ − H − 2 C_4H_8], 137 (32), 107 (96). Anal. Calcd for $C_{21}H_{34}CoPSi$ (404.5): C, 62.36; H, 8.74. Found: C, 62.39; H, 8.28. HRMS: $C_{21}H_{34}CoPSi$ calcd *m*/*z* 404.1501, found 404.1499.

***rac*-[((Di-*tert*-butylphosphanyl)ethyl)cyclopentadienyl-*P*]hydrido(diphenylsilyl)cobalt(III) (*rac*-5):** GP, 270 mg (0.27 mL, 1.5 mmol) of diphenylsilane; 186 mg (0.4 mmol, 79%) of *rac*-**5**, orange crystals (mp 142 °C dec). IR (film, cm^{-1}): $\tilde{\nu}$ 3061 cm^{-1} (w), 2963 (w), 2897 (m), 2862 (w), 2060 (w, Co−H), 2001 (w, Si−H), 1472 (m), 1423 (m), 1178 (w), 1094 (m), 918 (m), 807 (s, Si−H), 730 (s), 698 (s), 580 (m, Co−H). ^{1}H NMR (500 MHz, $C_6D_5CD_3$): δ −17.02 (d, 1H, $^2J_{P,H}$ = 46.5 Hz, Co−H), 0.90 (d, 9H, $^3J_{P,H}$ = 12.5, $C(CH_3)_3$), 1.16 (d, 9H, $^3J_{P,H}$ = 12.2 Hz, $C(CH_3)_3$), 1.70−1.85 (m, 2H, CH_2), 1.96−2.06 (m, 2H, CH_2), 3.67 (s, 1H, H_{Cp}), 4.49 (s, 1H, H_{Cp}), 4.90 (s, 1H, H_{Cp}), 5.04 (s, 1H, H_{Cp}), 5.73 (dd, 1H, $^3J_{Si-H,P}$ = 5.0 Hz, $^3J_{Si-H,Co-H}$ = 1.6 Hz, $^1J_{Si,H}$ = 89.3 Hz, Si−H), 7.06−7.37 (m, 6H, H_{Ph}), 7.82−7.84 (m, 2H, H_{Ph}), 8.05−8.06 (m, 2H, H_{Ph}). ^{13}C NMR (50.3 MHz, C_6D_6): δ 25.0 (+, d, $^2J_{C,P}$ = 4.7 Hz, C-6), 29.5 (−, br, $C(CH_3)_3$), 29.8 (−, br, $C(CH_3)_3$), 36.0 (+, br, $C(CH_3)_3$), 40.4 (+, br, $C(CH_3)_3$), 40.6 (+, br, C-7), 75.2 (−, C-2 or C-5), 78.7 (−, C-4 or C-3), 82.6 (−, C-5 or C-2), 85.2 (−, C-4 or C-3), 116.7 (+, d, $^3J_{C,P}$ = 8.2 Hz, C-1), 127.4 (−, C_{Ph}), 128.5 (−, C_{Ph}), 135.4 (−, C_{Ph}), 136.3 (−, C_{Ph}), 146.1 (+, *ipso*-C_{Ph}), 147.7 (+, *ipso*-C_{Ph}). ^{31}P NMR (121.5 MHz, C_6D_6): δ 117.2. MS (70 eV), *m*/*z* (%) 480 (17) [M$^+$], 423 (17) [M$^+$ − Ph], 296 (98) [M$^+$ − $SiPh_2H$ − H], 184 [M$^+$ − $SiPh_2H$ − H − 2 C_4H_8], 137 (32), 106 (96). Anal. Calcd for $C_{27}H_{38}CoPSi$ (480.7): C, 67.47; H, 7.98. Found: C, 67.05; H, 7.87. HRMS: $C_{27}H_{38}CoPSi$ calcd *m*/*z* 480.1816, found 480.1812.

Crystal Structure Analysis of One Enantiomer of 5:[19] $C_{27}H_{38}CoPSi$, molecular weight 480.56, crystal system orthorhombic, space group $P2_12_12_1$, a = 10.00(1) Å, b = 14.52(1) Å, c = 17.28(2) Å, α = 90°, β = 90°, γ = 90°, V = 2509(4) Å^3, Z = 4, d_{calcd} = 1.272 g cm^{-3}, $F(000)$ = 1024 e, μ = 0.81 mm^{-1}, crystal color red, crystal size 0.15 × 0.15 × 0.17 mm, Stoe IPDS (area detector) diffractometer, T = 300 K, λ(Mo Kα) = 0.710 73 Å, θ_{min} = 2.35°, θ_{max} = 26.06°, no absorption correction, no extinction correction, refinement program SHELXL-93, refinement by least-squares methods (F^2), $R(F)$ = 0.0334, $R_w(F^2)$ = 0.0597, 279 parameters, minimum/maximum residual electron density −0.35/0.26 e Å^{-3}, Flack parameter x = 0.02(1).

***rac*-[((Di-*tert*-butylphosphanyl)ethyl)cyclopentadienyl-*P*]hydrido(triphenylsilyl)cobalt(III) (*rac*-6):** GP, 382 mg (1.5 mmol) of triphenylsilane; 147 mg (0.3 mmol, 54%) of *rac*-**6**, deep red crystals (mp 138 °C dec). IR (film, cm^{-1}): $\tilde{\nu}$ 3066 cm^{-1} (w), 2959 (s), 2924 (s), 2867 (s), 2341 (s, Co−H), 1465 (s),

(19) The crystallographic data (without structure factors) of the structures described in this publication were deposited as Supplementary Publication Nos. CCDC 215326 (**5**), 215327 (*ent*-**5**), and 215328 (*rac*-**7**) at the Cambridge Crystallography Data Centre. Copies of the data can be obtained at no charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (telefax, Int. + 1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

1428 (s), 1119 (m), 1096 (m), 998 (s), 803 (s), 771 (s), 514 (s, Co−H). ^{1}H NMR (400 MHz, C_6D_6): δ −16.53 (d, 1H, Co−H, J = 47.6 Hz), 0.78−0.80 (s, 9H, $C(CH_3)_3$), 0.83−0.86 (s, 9H, $C(CH_3)_3$), 1.64−1.73 (m, 2H, CH_2), 1.92−1.98 (m, 2H, CH_2), 3.41 (s, 1H, H_{Cp}), 4.31 (s, 1H, H_{Cp}), 4.97 (s, 1H, H_{Cp}), 5.01 (s, 1H, H_{Cp}), 7.18−7.20 (m, 3H, H_{Ph}), 7.24−7.28 (m, 6H, H_{Ph}), 8.08−8.10 (m, 6H, H_{Ph}). ^{13}C NMR (50.3 MHz, C_6D_6): δ 24.4 (+, d, $^2J_{C,P}$ = 5.2 Hz, C-6), 29.7 (−, d, $^2J_{C,P}$ = 3.7 Hz, $C(CH_3)_3$), 29.8 (−, d, $^2J_{C,P}$ = 4.1 Hz, $C(CH_3)_3$), 34.9 (+, d, $J_{C,P}$ = 14.0 Hz, $C(CH_3)_3$), 41.6 (+, br, $C(CH_3)_3$), 41.8 (+, br, C-7), 76.9 (−, br, C-2 or C-5), 80.1 (−, C-4 or C-3), 84.1 (−, br, C-5 or C-2), 85.4 (−, C-4 or C-3), 118.2 (+, d, $^3J_{C,P}$ = 7.6 Hz, C-1), 127.0 (−, C_{Ph}), 127.3 (−, C_{Ph}), 137.4 (−, C_{Ph}), 146.6 (+, *ipso*-C_{Ph})). ^{31}P NMR (121.5 MHz, C_6D_6): δ 110.2. MS (70 eV): *m*/*z* (%) 557 (2) [M^+ + 1], 556 (4) [M^+], 555 (7) [M^+ − 1], 533 (90) [M^+ − 2Me], 296 (3) [M^+ − $SiPh_2H$ − H], 260 (79), 182 (100) [M^+ − $SiPh_2H$ − H − 2 C_4H_8], 183 (65), 137 (32), 105 (42). HRMS: $C_{27}H_{38}PCoSi$ *m*/*z* calcd 556.2274, found 556.2471.

***rac*-[(Di-*tert*-butylphosphanyl)ethylcyclopentadienyl-*P*](hydrido)(methylphenylsilyl)cobalt(III) (*rac*-7/*rac*-8):** GP, 179 mg (0.20 mL, 1.5 mmol) of methylphenylsilane; 117 mg (0.3 mmol, 57%) of *rac*-**7**/*rac*-**8** (mixture of diastereomers, 8:5, NMR), orange crystals. IR (film, cm^{-1}): $\tilde{\nu}$ 3067 cm^{-1} (w), 3028 (w), 3005 (w), 2963 (s), 2898 (s), 2862 (s), 2052 (s, Co−H), 1931 (s, Si−H), 1463 (s), 1425 (s), 1172 (m), 1020 (m), 932 (s), 816 (s, Si−H), 730 (s), 585 (s, Co−H). ^{1}H NMR (400 MHz, 295 K, C_6D_6): *rac*-**7**, δ −17.12 (d, 1H, Co−H, $^2J_{P,H}$ = 46.7 Hz), 0.68 (s, br, 3H, CH_3), 1.13−1.32 (m, 18H, $C(CH_3)_3$), 1.85−1.93 (m, 2H, CH_2), 2.01−2.21 (m, 2H, CH_2), 3.59, 3.90, 4.45, 4.69, 4.93, 5.07, 5.17 (7 s, in total 4H, H_{Cp}), 5.35−5.43 (m, br, 1H, $^3J_{Si-H,C-H}$ = 3.7 Hz, $^3J_{Si-H,\ Co-H}$ = ca. 3.7 Hz, $^1J_{Si,H}$ = 82.7 Hz, $^2J_{Si,C-H}$ = 6.4 Hz, $^3J_{Si-H,P}$ not resolved, Si−H), 7.29−7.32 (m, 1H, H_{Ph}), 7.36−7.38 (m, 2H, H_{Ph}), 7.43−7.48 (m, 2H, H_{Ph}); *rac*-**8**, δ −17.28 (d, $^2J_{P,H}$ = 47.3 Hz), other signals covered by those of *rac*-**7**. ^{13}C NMR (50.3 MHz, C_6D_6, only one set of signals is observed): δ 15.3 (+, $SiCH_3$), 26.0 (+, d, $^2J_{C,P}$ = 4.8 Hz, C-6), 30.3 (−, br, $C(CH_3)_3$), 30.9 [−, br, $C(CH_3)_3$], 35.7 (+, br, $C(CH_3)_3$), 36.5 (+, br, $C(CH_3)_3$), 41.63 (+, d, $J_{C,P}$ = 18.6, C-7), 75.7 (−, br, C-2 or C-5), 79.4 (−, C-4 or C-3), 84.9 (−, br, C-5 or C-2), 85.9 (−, C-4 or C-3), 117.1 (+, br, C-1), 128.5 (−, C_{Ph}), 129.3 (−, C_{Ph}), 135.4 (−, C_{Ph}), 146.7 (+, *ipso*-C_{Ph}). ^{31}P NMR (121.5 MHz, C_6D_6): δ 117.9, 118.1. MS (70 eV): *m*/*z* (%) 418 (41) [M^+], 296 (100) [M^+ − SiPhMeH − H], 184 (77) [M^+ − SiPhMeH − H − 2(C_4H_8)], 121 (80), 79 (25). Anal. Calcd for $C_{22}H_{36}PCoSi$ (418.2): C, 63.16; H, 8.61. Found: C, 63.01; H, 8.60.

Crystal Structure Analysis of *rac*-7:[19] $C_{22}H_{36}CoPSi$, molecular weight 418.50, crystal system monoclinic, space group $P2_1/c$, a = 13.569(4) Å, b = 10.350(3) Å, c = 15.735(4) Å, α = 90°, β = 98.30(3)°, γ = 90°, V = 2186.7(11) Å^3, Z = 4, d_{calcd} = 1.271 g cm^{-3}, $F(000)$ = 896 e, μ = 0.916 mm^{-1}, crystal color orange-red, crystal size 0.26 × 0.18 × 0.15 mm, Stoe IPDS (area detector) diffractometer, T = 300 K, λ(Mo Kα) = 0.710 73 Å, 17804 measured, 3467 unique, and 793 observed ($I > 2\sigma_I$) reflections (R_{int} = 0.109), θ_{min} = 2.36°, θ_{max} = 24.27°, no absorption correction, no extinction correction, refinement program SHELXL-93, refinement by least-squares methods (F^2), $R(F)$ = 0.0667, $R_w(F^2)$ = 0.1313, 119 parameters, minimum/maximum residual electron density −0.34/0.40 e Å^{-3}.

***rac*-[((Di-*tert*-butylphosphanyl)ethyl)cyclopentadienyl-*P*]hydrido(diphenylgermyl)cobalt(III) (*rac*-10):** GP, 335 mg (0.36 mL, 1.5 mmol) of diphenylgallane; 180 mg (0.3 mmol, 70%) of *rac*-**10**, orange crystals, mp 164 °C dec. IR (film, cm^{-1}): $\tilde{\nu}$ 3060 cm^{-1} (w), 3028 cm^{-1} (w), 3005 cm^{-1} (w), 2989 cm^{-1} (w), 2962 (s), 2897 (s), 2861 (s), 2052 (s, Co−H), 1949 (s, Ge−H), 1472 (s), 1425 (s), 1260 (m), 1078 (m), 935 (s), 813 (s), 718 (s), 584 (s, Co−H). ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ −16.11 (d, 1H, Co−H, $^2J_{P,H}$ = 56.7 Hz), 0.97 (d, $^3J_{P,H}$ = 12.7 Hz, 9H, $C(CH_3)_3$), 1.14 (d, $^3J_{P,H}$ = 12.5 Hz, 9H, $C(CH_3)_3$), 1.71−1.82 (m, 2H, CH_2), 1.99−2.06 (m, 2H, CH_2), 3.78 (s, 1H, H_{Cp}), 4.56 (s, 1H, H_{Cp}), 4.94 (s, 1H, H_{Cp}), 4.98 (s, 1H, H_{Cp}), 5.35−5.39 (m, 1H, Si−H), 7.25 (s, 2H, H_{Ph}), 7.48−7.54 (m, 3H, H_{Ph}), 7.62−7.92 (m, 2H, H_{Ph}), 8.01 (m, 3H, H_{Ph}). ^{13}C NMR (50.3 MHz, C_6D_6): δ 24.9 (+, d, $^2J_{C,P}$ = 4.7 Hz, C-6), 29.2 (−, d, $^2J_{C,P}$ = 3.2 Hz, $C(CH_3)_3$), 29.9 (−, d, $^2J_{C,P}$ = 3.9 Hz, $C(CH_3)_3$), 35.8 (+, d, $J_{C,P}$ = 16.3 Hz, $C(CH_3)_3$), 36.0 (+, d, $J_{C,P}$ = 12.3 Hz, $C(CH_3)_3$), 40.2 (+, d, $^2J_{C,P}$ = 19.2, C-7), 73.0 (−, d, $^4J_{C,P}$ = 4.7 Hz, C-2 or C-5), 79.4 (−, C-4 or C-3), 84.4 (−, C-4 or C-3), 84.8 (−, d, $^4J_{C,P}$ = 2.5 Hz, C-5 or C-2), 115.1 (+, d, $^3J_{C,P}$ = 8.1 Hz, C-1), 128.7 (−, C_{Ph}), 129.3 (−, C_{Ph}), 135.5 (−, C_{Ph}), 148.5 (+, *ipso*-C_{Ph}), 149.8 (+, *ipso*-C_{Ph}). ^{31}P NMR (121.5 MHz, C_6D_6): δ 117.7. MS (70 eV): *m*/*z* (%) 527 (8), 526 (11) [M^+], 525 [M^+ − 1], 479 (11), 423 (13), 375 (12), 331 (11), 296 (100) [M^+ − $GePh_2H$ − H], 183 (35) [M^+ − $GePh_2H$ − 2 C_4H_8], 121 (46), 91 (42), 71 (22). Anal. Calcd for $C_{27}H_{38}CoGeP$ (526.12): C, 61.64; H, 7.28. Found: C, 61.38; H, 7.02. HRMS: $C_{27}H_{38}CoGeP$ *m*/*z* calcd 526.1229, found 526.1255.

***rac*-[((Di-*tert*-butylphosphanyl)ethyl)cyclopentadienyl-*P*]hydrido(tributylstannyl)cobalt(III) (*rac*-11):** GP, 156 mg (0.54 mmol) of tributylstannane; 226 mg (0.39 mmol, 77%) of *rac*-**11**, orange crystals (mp 126 °C, dec). IR (film, cm^{-1}): $\tilde{\nu}$ 3036 cm^{-1} (w), 2955 (s), 2920 (s), 2871 (s), 2852 (s), 2440 (m, Co−H), 1807 (s), 1531 (s), 1643 (s), 1417 (m), 1375 (m), 1291(m), 1260 (m), 1145 (m), 1072 (m), 1019 (m), 960 (s, Sn−C), 815 (s, Sn−C), 674 (s), 517 (s, Co−H). ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ −17.17 (d, 1H, Co−H, $^2J_{P,\ H}$ = 54.6 Hz), 0.65−0.73 (m, 9H, CH_3), 0.78−0.80 (m, 9H, $C(CH_3)_3$), 0.83−0.86 (m, 9H, $C(CH_3)_3$), 0.89−0.93 (m, 6H, CH_2), 1.03−1.07 (m, 6H, CH_2), 1.53−1.61 (m, 6H, CH_2), 2.66−2.84 (m, 4H, CH_2), 3.88 (s, 1H, H_{Cp}), 4.43 (s, 1H, H_{Cp}), 4.99 (s, 1H, H_{Cp}), 5.01 (s, 1H, H_{Cp}). ^{13}C NMR (100.6 MHz, C_6D_6): δ 10.3 (+, CH_2), 13.9 (−, CH_3), 16.6 (+, CH_2), 26.5 (+, d, $^2J_{C,P}$ = 5.9 Hz, C-6), 27.1 (−, d, $^2J_{C,P}$ = 4.4 Hz, C-9, C-10, C-11), 28.2 (+, CH_2), 29.2 (+, CH_2), 31.5 (−, d, $^2J_{C,P}$ = 4.8 Hz, C-13, C-14, C-15), 31.7 (+, C-7), 36.1 (+, d, $J_{C,P}$ = 14.0 Hz, C-8), 36.7 (+, C-12), 78.1 (−, C-2 or C-5), 79.2 (−, C-4 or C-3), 82.9 (−, C-5 or C-2), 84.5 (−, C-4 or C-3), 116.1 (+, d, $^3J_{C,P}$ = 7.6 Hz, C-1). ^{31}P NMR (121.5 MHz, C_6D_6): δ 122.2. MS (70 eV; $C_{27}H_{54}PCoSn$ (587)): *m*/*z* (%) 587 (6) [M^+], 586 (3) [M^+ − 1], 546 (56) [M^+ − C_3H_7 + 1], 545 (17) [M^+ − C_3H_7], 544 (77) [M^+ − C_3H_7 − 1], 540 (100) [M^+ − 3CH_3 − 2], 539 (81) [M^+ − 3CH_3 − 3], 530 (23) [M^+ − C_4H_9 − 1], 484 (78) [M^+ − C_4H_9 − 3CH_3 − 1], 415 (20) [M^+ − 3 C_4H_9 −1], 317 (11) [M^+ − 3 C_4H_9 − CH_2CH_2 - 3CH_3 − 1], 296 (5) [M^+ − $Sn(C_4H_9)_3$], 254 (46), 251 (78), 182 (79) [M^+ − $Sn(C_4H_9)_3$ − H − 2 C_4H_8], 183 (61), 137 (32), 105 (44). HRMS: $C_{27}H_{54}PCoSn$ *m*/*z* calcd 588.2317, found 588.2310.

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Supporting Information Available: Tables of X-ray crystallographic data for **5,** *ent*-**5**, and *rac*-**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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