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PAPER

New cyclopentadienylethylphosphane chelate complexes with unsymmetrical phosphane substitution†‡

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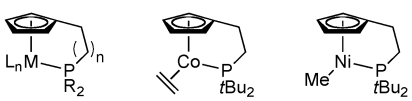
The syntheses, characterization, and some reactions of (phosphanylethyl)cyclopentadienyl chelate complexes of cobalt, rhodium, iridium, nickel, and chromium with unsymmetrical substitution at the phosphorus atom are described. The ligand systems were prepared by nucleophilic ring opening of spiro[2.4]hepta-4,6-diene with lithium *tert*-butylphenylphosphide or lithium *tert*-butylcyclohexylphosphide. The anionic ligands give the respective chelate complexes by treatment with metal halide reagents. In three cases it was possible to obtain X-ray crystal structure analyses. The cobalt chelate complex undergoes oxidative addition with a dihydrosilane, the reaction results in the formation of products with three stereogenic centers at phosphorus, cobalt, and silicon, which show dynamic behavior as indicated by VTNMR. The rhodium chelate complex undergoes oxidative addition of iodomethane with diastereoselective formation of the respective Rh(III) chelate. While diastereoselectivity caused by a planar chiral indenyl ligand or by a stereogenic carbon center in the chelate backbone has earlier been observed, this is the first case of a stereoinduction by the stereogenic phosphorus ligand. Activation energies for the rotation of cobalt and rhodium chelates have also been determined by VTNMR.

Introduction

Cyclopentadienyl (Cp) complexes are among the most common ones in organometallic chemistry and have found various applications in fields such as catalysis,[1] synthesis,[2] materials sciences,[3,4] medicinal chemistry[3–6] and many more.[7–11] One characteristic feature of cyclopentadienyl ligands is their facile rotation around the axis between the center of the Cp ligand and the metal atom.[12] Such a rotation is impossible in Cp chelate complexes, in which the Cp ligand is connected to other coordinated moieties. The chemistry of Cp complexes with heteroatomic tethers, *e.g.* phosphane complexes such as **1** has been reviewed some time ago, and complexes with an ethylene tether ($n = 1$) are the most prominent representatives of this class of chelates.[13,14] Most complexes of this kind have two identical substituents at the phosphorus atom. This includes a number of cobalt and nickel complexes reported by our group, which have a di-*tert*-butyl substitution pattern, such as complexes **2** and **3**.[13,15–30]



1 **2** **3**

Complexes with two different substituents at phosphorus are comparatively rare. The few, in some cases rather special examples of such complexes, have been reported by Nakazawa and Miyoshi *et al.* (Zr, Hf),[31–33] Hey-Hawkins *et al.* (Ti, Zr),[34] Ganter *et al.* (Mn, Ru),[35–37] and Saunders *et al.* (Rh).[38–41] Different substituents at phosphorus render the complexes less symmetric and are expected to affect the chemical and spectroscopic properties of the complexes as well as the energy of activation of an ethene rotation, which has earlier been reported for **2**.[27] In order to get a deeper insight into these aspects we prepared the first cyclopentadienylethylphosphane chelates of cobalt, rhodium, iridium, nickel, and chromium with *tert*-butyl and phenyl or with *tert*-butyl and cyclohexyl substituents at phosphorus. Three of these complexes were characterized by crystal structure analyses.

Results and discussion

As first shown by Kauffmann *et al.*, spiro[2.4]hepta-4,6-diene (**4**) is the superior starting material for the synthesis of cyclopentadienylethylphosphane ligands.[42] The ligands, which

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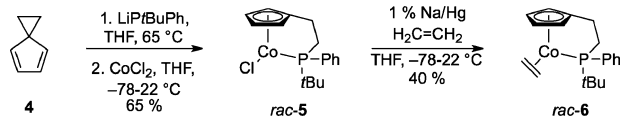
are obtained by treatment of **4** with the respective phosphide, are treated with metal halides to form the respective cyclopentadienyl complexes.

Reaction of **4** with lithium *tert*-butylphenylphosphide followed by addition of $CoCl_2$, chromatographic product isolation and recrystallization from *tert*-butyl methyl ether (TBME)/petroleum ether (PE) at −25 °C gave paramagnetic chloro chelate *rac*-**5** as purple crystals in 65% yield. *rac*-**5** was characterized spectroscopically by the IR and MS data obtained in addition to an elemental analysis. The data obtained resemble those of the closely related di-*tert*-butyl substituted complex.[28,29] Subsequent treatment of *rac*-**5** with sodium amalgam (1%) and ethene in THF at −78 °C followed by warming to 25 °C gave ethene chelate complex *rac*-**6** in 40% yield.



As a consequence of the asymmetric substitution pattern at phosphorus the ^{1}H NMR spectrum of *rac*-**6** is more complicated than that of **2**. The cyclopentadienyl protons give rise to a ABCD line system, and the diastereotopic methylene protons 6-H give rise to two signals, which appear as multiplets. The ethene ligand shows three clearly separated ^{1}H NMR signals at δ = 2.05 (m, 2H), 2.44 (m, 1H), and 2.73 (m, 1H) ppm, whereas the corresponding signals of **2** are observed at δ = 1.87 (2H) and 2.27 (m, 2H) ppm. This clearly attests for the asymmetry of the compound and for the profound difference of the electronic environment of the ethene protons as a result of the magnetic anisotropy of the phenyl substituent. Remarkably, a corresponding difference is not observed for the ^{13}C NMR signal assigned to the ethene carbon atoms, which give rise to only one signal at δ = 22.9 ppm, a value very close to the corresponding one observed for **2** (δ = 22.4 ppm).[27] Dynamic ^{1}H NMR measurements allowed for the determination of the activation energy of the hindered rotation of the ethene ligand around the ethene-cobalt axis in **2**, which was found to be 62 kJ mol^{-1}.[29] For **6** the respective coalescence was observed at 350 K (400 MHz) corresponding to an estimated activation energy of 68.7 kJ mol^{-1}.[43] This value is somewhat higher than that obtained for **2**, $CpNi(C_2H_4)CH_3$, and $CpRh(C_2H_4)_2$, but significantly lower than that for $CpCo(C_2H_4)_2$.[43,44]

Crystallization from hexane at −25 °C afforded crystals, which were suitable for an X-ray crystal structure analysis (Fig. 1). The structure shows a torsion of the ethylene bridge, which is typical for this class of complexes and allows a minimization of H–H interactions in the bridge. Remarkably, the cyclopentadienyl ring and the phenyl substituent adopt an almost coplanar orientation. In contrast to the NMR investigation the asymmetry of the phosphane substitution is not structurally reflected in the ethene ligand, both carbon atoms show almost identical distances to the cobalt atom.

Chelate **2** has been shown to undergo oxidative addition reactions with hydrosilanes resulting in hydridosilylcobalt(III) chelates.[18] When a dihydrosilane was used the process generates a new stereogenic center at silicon as well as at cobalt.

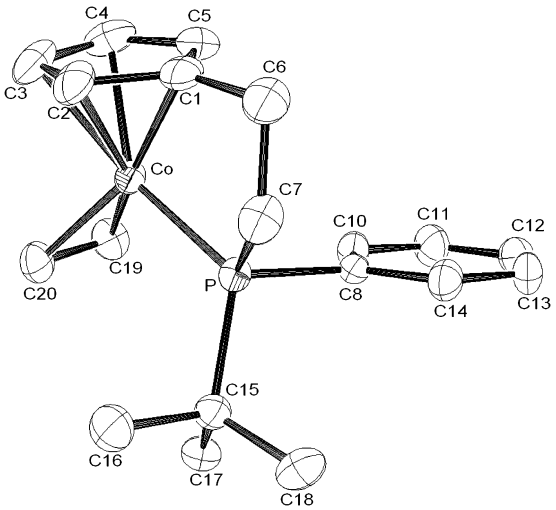
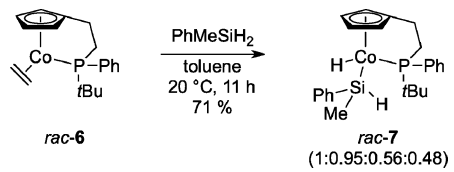


Fig. 1 Structure of *rac*-**6** in the crystal.[45] Displacement ellipsoids correspond to the 50% probability level. Selected bond lengths [pm] and angles [°]: Co1–P1 215.76(9), Co1–C1 205.2(3), Co1–C2 208.3(3), Co1–C3 207.4(3), Co1–C4 209.1(3), Co1–C5 208.8(3), Co1–C19 200.8(3), Co1–C20 200.8(3), C1–C6 150.8(4), C6–C7 152.7(4); C1–C6–C7 109.9(2), C6–C7–P1 105.43(19), Co1–P1–C7 103.08(10).

However, the diastereomeric excess was only 23% in the reported case. In contrast to **2** chelate *rac*-**6** has an additional stereocenter at the phosphorus atom. Consequently, the respective reaction of *rac*-**6** with methylphenylsilane was expected to give four diastereomers. The experiment showed that this was indeed the case, addition of methylphenylsilane to *rac*-**6** afforded complex *rac*-**7** in 71% yield as a mixture of diastereomers in the ratio 1.00 : 0.95 : 0.56 : 0.48 as determined by deconvolution calculations from the 500 MHz ^{1}H NMR spectrum at 280 K. The ratio clearly shows that two out of four diastereomers are predominantly formed. Although attempts to obtain crystals suitable for structure analyses failed, we speculate that diastereomers with the cobalt hydride ligand being located closely to the *tert*-butyl group are favored for obvious steric reasons.



The diastereomeric mixture was fully characterized by IR and NMR spectroscopy including DEPT, HMQC, H–H-COSY and NOE experiments allowing assignments of all observed signals. The Co–H absorptions are observed at 2043 cm^{-1} in contrast to 2052 cm^{-1} for the corresponding di-*tert*-butylphosphanyl complex.[18] The ^{31}P NMR signals for the two dominant diastereomers appear at δ = 93.7 and 95.5 ppm. The ^{1}H NMR spectrum, which was obtained at 294 K, shows the four Co–H doublet signals at −16.89, −16.85, −16.58 and −16.50 ppm with $^2J_{H,P}$ coupling constants in the range of 45.1–53.8 Hz. Variable temperature measurements in 5 K steps up to 350 K show coalescence resulting in two doublets (approx. ratio 1 : 1.5) with a coalescence temperature

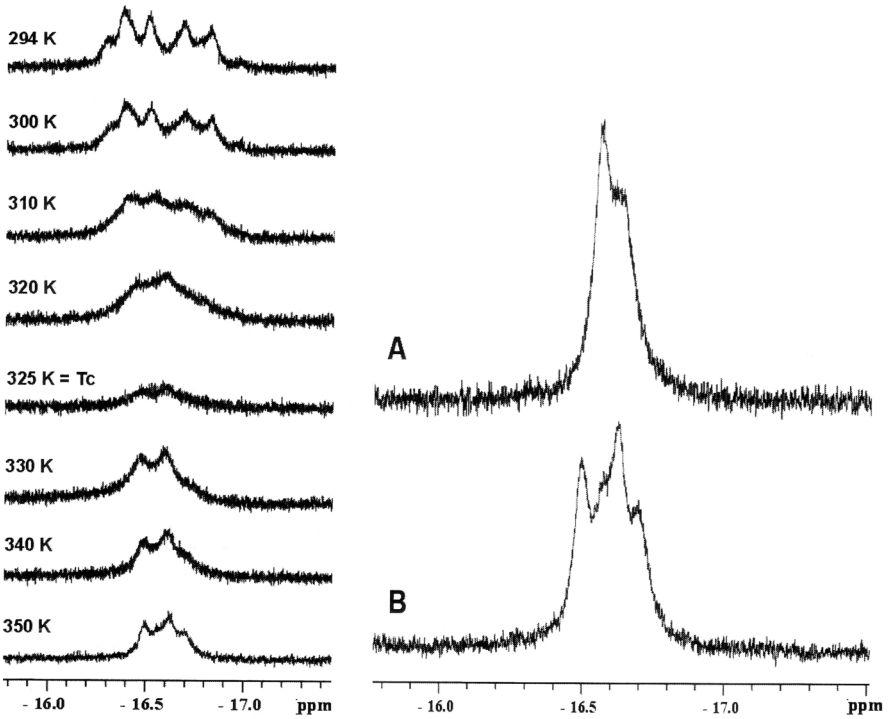


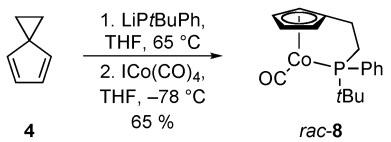
Fig. 2 Coalescence of the Co–*H* signals in the ^{1}H NMR spectrum of *rac*-**7**. Left: variable temperature measurements. Right: signal at 350 K with P decoupling (A) and with P coupling (B).

of T_c = 325 K, which corresponds to an estimated free enthalpy of activation of 64.9 kJ mol^{-1}, which is well in the range observed for related cases.[18] Fig. 2 shows the coalescence as well as the signals observed at 350 K.

The diastereoisomerization process causing the coalescence is presumably closely related to the configurational instability of the cobalt stereogenic center in cyclopentadienylcobalt systems, which has been the subject of theoretical investigations recently published by Gandon and Aubert *et al.*[46] According to these calculations a reductive elimination of the hydrosilane with formation of an intermediate η^2 Si–H system has to be invoked, which undergoes a change in conformation followed by oxidative re-addition. Alternatively, one might discuss a temporary decomplexation of the phosphane tether with formation of a vacant coordination site facilitating the diastereoisomerization process. The activation energies of both processes are in the same order of magnitude.[46,47]

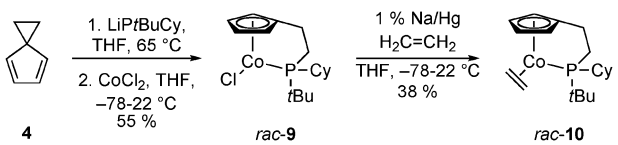
The carbonylcobalt complex *rac*-**8** corresponding to *rac*-**6** was obtained in 65% yield by the procedure of Pályi by treatment of spiro[2.4]hepta-4,6-diene (**4**) with lithium *tert*-butylphenylphosphide followed by a THF solution of $Co(CO)_4I$.[48] *rac*-**8** complements a series of complexes with phenyl, isopropyl and *tert*-butyl substituents at the phosphorus atom[28,30] and is the first representative with two different substituents at this position. The carbonyl absorption of *rac*-**8** is observed at 1894 cm^{-1}, a value similar to that for the diphenyl (1897 cm^{-1}) and the di-*tert*-butyl derivative (1898 cm^{-1}).[49]

Similar to the formation of *rac*-**5** and *rac*-**6** the corresponding *tert*-butyl(cyclohexyl) substituted complexes *rac*-**9** and *rac*-**10** are obtained in moderate yields from spiro[2.4]hepta-4,6-diene



4 *rac*-**8**

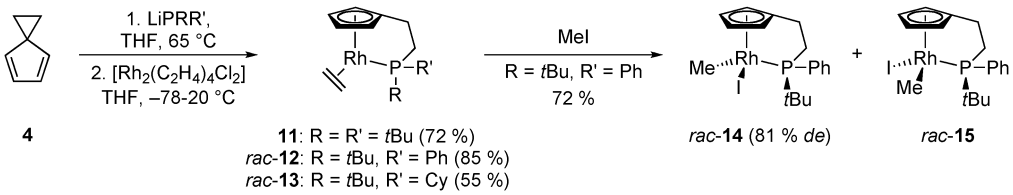
(**4**) by treatment with lithium *tert*-butylcyclohexylphosphide followed by $CoCl_2$ and subsequent reduction with sodium amalgam in the presence of ethene. The complexes were characterized spectroscopically. According to HMQC measurements ^{1}H NMR signals at δ = 2.34 (m, 1H) and 2.64 (m, 1H) ppm are assigned to the ethene ligand. In addition, resonances of two other ethene protons are unresolved in a broad signal at δ = 1.87 ppm overlapping with signals derived from the cyclohexyl substituent. The ^{31}P NMR signal at δ = 93.2 ppm is in accord with a completely aliphatic substitution pattern at phosphorus and resembles that of **2** (δ = 96.4 ppm).



4 *rac*-**9** *rac*-**10**

The syntheses as well as reactions of cyclopentadienyl or indenyl rhodium chelate complexes bearing a phosphane tether have been reported by Poilblanc *et al.*,[50] Tani *et al.*,[51–56] Nelson *et al.*,[57,58] Saunders *et al.*,[38–40,59–61] Hidai *et al.*,[62] Jones *et al.*,[63] Green *et al.*,[64] Salzer *et al.*,[65–68] Cole-Hamilton *et al.*,[69] Lalinde *et al.*,[70] and Whitby *et al.*[71] In most cases the phosphane tether bears phenyl substituents, however, there are also some in which alkyl, pentafluorophenyl

or more complicated substituents are present. To our knowledge there are no examples with *tert*-butyl substituents, which, according to our experience with cobalt complexes, increase the stability of the complexes and improve their crystallization properties. Therefore, and for the possibility of comparison, the di-*tert*-butyl substituted rhodium(I) chelate **11** was prepared by treatment of spiro[2.4]hepta-4,6-diene (**4**) with lithium di-*tert*-butylphosphide followed by $[Rh_2(C_2H_4)_4Cl_2]$. **11** was obtained in 72% yield as a brown oil, which is less air sensitive than the corresponding cobalt chelate **2**. The unsymmetric chelates *rac*-**12** and *rac*-**13** with *tert*-butylphenyl and *tert*-butylcyclohexyl substitution at phosphorus were prepared accordingly in 85% and 55% yield, respectively, and are also brown oils.



Chelates **11**–*rac*-**13** were characterized spectroscopically. The symmetric complex **11** shows two ^{1}H NMR signals for the ethene ligand, which appear at δ = 2.40 (m, 2H) ppm and at δ = 2.78 (m, 2H) ppm [**2**:[29] 1.87 (m, 2H), 2.27 (m, 2H) ppm]. The less symmetric complex *rac*-**12** with a phenyl group at the phosphorus atom shows four signals for the ethene ligand, which appear at δ = 2.31 (m, 1H), 2.50 (m, 1H), 2.93 (m, 1H), 3.11 (m, 1H) ppm. The cyclohexyl substituted chelate *rac*-**13** shows a ^{1}H NMR signal at δ = 2.86 (m, 2H) for the ethene ligand. The resonances for the other two ethene protons overlap with a large multiplet caused by the cyclohexyl protons as well as by the ethylene bridge between the cyclopentadienyl group and the phosphorus atom. The data show that the phenyl substituent has a significantly larger influence on the magnetic behavior of the ethene protons than that of the aliphatic *tert*-butyl or cyclohexyl substituents, an effect, which we attribute to the magnetic anisotropy of the phenyl group. The clear separation of the signals in *rac*-**12** made it possible to determine the energy of activation of the ethene rotation by temperature dependent ^{1}H NMR spectroscopy (Fig. 3). At 400 MHz the coalescence was observed at T_c = 330 K in d_6-benzene and at T_c = 325 K

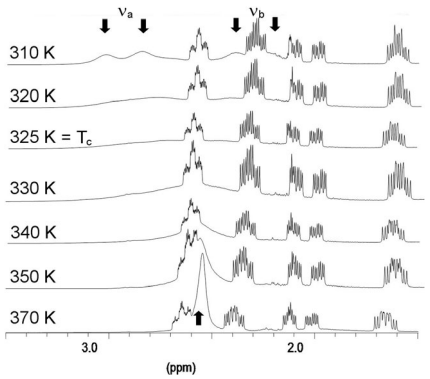


Fig. 3 ^{1}H NMR coalescence of *rac*-**12** (400 MHz, C_6D_6).

in d_8-toluene, corresponding to energies of activation E_a of 63.0 kJ mol^{-1} and 62.5 kJ mol^{-1}, respectively.[43] These values are rather similar to those observed for the di-*tert*-butyl substituted cobalt complex **2** but significantly smaller than those observed for the *tert*-butylphenyl substituted cobalt analog *rac*-**7** of *rac*-**12**.

Treatment of *rac*-**13** with iodomethane resulted in an oxidative addition with formation of a diastereomeric mixture of *rac*-**14** and *rac*-**15** in 72% yield. The diastereomeric excess (de) was 81% (^{1}H NMR) and could be improved to de of 95% by recrystallization from dichloromethane/hexane. Diastereoselective oxidative additions to (cyclopentadienylethyl)phosphane rhodium chelates have been investigated by the group of Kataoka and Tani, as well as by the group of Salzer. Kataoka and Tani prepared planar chiral carbonyl[1-(diphenylphosphanylethyl)indenyl]rhodium chelates and methylated these with formation of the respective acetyliodo chelates possessing metal centered chirality in addition to the planar chirality caused by the indenyl ligand. These reactions proceeded with high diastereoselectivity.[54–56,72,73] The Salzer group prepared a [(diphenylphosphanyl)ethylcyclopentadienyl]-ethenerhodium(I) chelate with a methyl substituent at the carbon atom next to phosphorus in enantiomerically pure form. In addition, the corresponding indenyl and fluorenyl complexes were reported. Reaction with iodomethane resulted in highly diastereoselective oxidative additions with formation of the respective iodomethyl chelate complexes.[65,67,74] While Kataoka and Tani reported a stereoinduction from the planar chiral indenyl ligand to the metal center, the results of Salzer include a stereoinduction from an asymmetric carbon atom in the chelate backbone to rhodium. To our knowledge, the formation of *rac*-**14** and *rac*-**15** is the first case in the chemistry of cyclopentadienylalkylphosphane chelate complexes involving a stereoinduction from the asymmetric phosphorus atom to rhodium. The assignment of *rac*-**14** as the major diastereomer is the result of NOE measurements and is in accord with an X-ray crystal structure analysis (Fig. 4).

Although the quality of the analysis is limited, the data clearly show that cyclopentadienyl carbon atoms C1 and C2 are bound significantly closer to the rhodium atom as compared to the other three cyclopentadienyl carbon atoms. This observation presumably reflects the asymmetric ligand environment around the rhodium atom and is detectable clearly, because the usual rotation around the cyclopentadienyl-rhodium axis is impossible in *rac*-**14**.

We recently reported that the nucleophilic ring opening of [4,5]benzospiro[2.4]heptadiene (**16**) proceeds rather slowly with LiP*t*Bu$_2$ (reflux in THF for 12 h or microwave heating at 150 °C for 40 min) as compared to less bulky nucleophiles LiPR$_2$ (R = Ph, Cy, iBu, Et).[15] In the context of the present work **16** was treated with LiP*t*BuPh in THF at reflux for 3 d resulting in

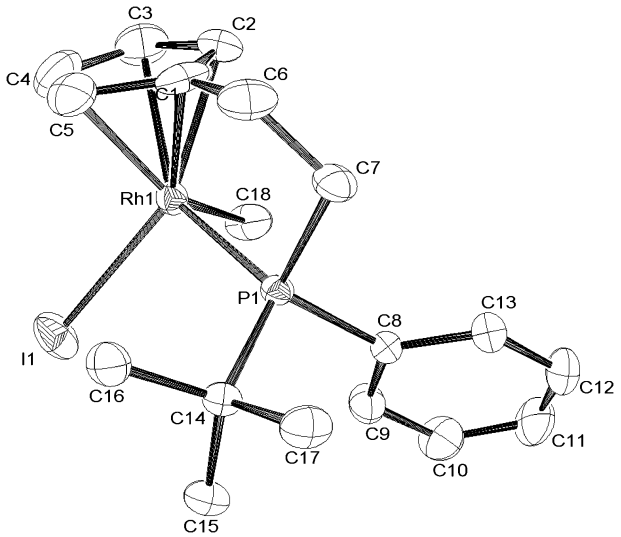
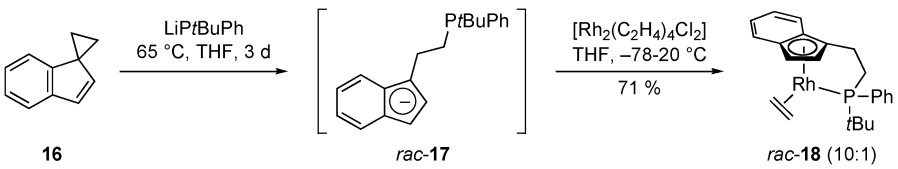


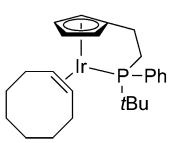
Fig. 4 Structure of *rac*-**14** in the crystal.[45] There are two similar molecules of *rac*-**14** in the asymmetric unit, only one molecule is shown. Displacement ellipsoids correspond to the 50% probability level. Selected bond lengths [pm] and angles [°]: Rh1–I1 268.59(9), Rh1–P1 227.39(14), Rh1–C1 216.7(6), Rh1–C2 214.8(5), Rh1–C3 222.8(6), Rh1–C4 226.1(7), Rh1–C5 225.0(6), Rh1–C18 217.4(5), P1–C7 185.7(5), P1–C8 181.4(5), P1–C14 188.9(5), C1–C2 142.7(9), C1–C5 143.8(10), C1–C6 149.5(9), C2–C3 139.0(10), C3–C4 133.1(11), C4–C5 138.4(11), C6–C7 150.3(9); I1–Rh1–P1 101.52(4), I1–Rh1–C18 84.26(19), P1–Rh1–C18 97.7(2), Rh1–P1–C7 100.53(19), Rh1–P1–C8 119.14(16), C7–P1–C14 105.7(2), C8–P1–C14 104.7(2).

the formation of *rac*-**17**. Subsequent addition of $[Rh_2(C_2H_4)_4Cl_2]$ gave the indenyl chelate *rac*-**18** as a diastereomeric mixture (10 : 1) in 71% yield. *rac*-**18** is more air-sensitive as compared to the cyclopentadienyl chelate *rac*-**12**, so that attempts to remove a minor amount of the uncoordinated ligand were only partly successful. *rac*-**18** was characterized spectroscopically, the NMR data reflect the asymmetry of the compound.



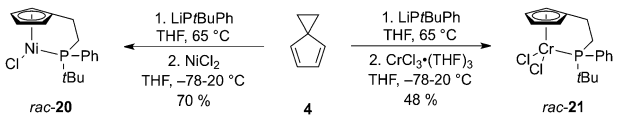
16 *rac*-**17** *rac*-**18** (10:1)

As early as 1994 Poilblanc *et al*. reported the first synthesis of an iridium chelate with the [2-(diphenylphosphanyl)ethyl]cyclopentadienyl ligand.[50] The ethene complex decomposed readily, but corresponding carbonyl or cyclooctene (coe) complexes have been isolated.[75] Therefore, the iridium chelate *rac*-**19** was prepared by reaction of the anionic ligand system with $[IrCl(coe)]_2$. *rac*-**19** was obtained in only 21% yield in addition to the residual uncoordinated ligand and was characterized spectroscopically.



rac-**19**

Nickel chelate complexes with cyclopentadienylalkylphosphane ligands have been unknown until we recently reported on the synthesis and reactivity of a number of examples with the di-*tert*-butyl substitution pattern at the phosphorus atom.[15,16] With the new *tert*-butylphenyl substituted ligand in hand, we prepared the respective nickel chelate *rac*-**20** in 70% yield. *rac*-**20** was characterized spectroscopically, all data are in accord with related complexes.[15,16]



rac-**20** **4** *rac*-**21**

Jolly *et al*. reported the synthesis of cyclopentadienylchromium dichloride chelates with a phosphane tether and their application as catalysts in alkene oligo- and polymerization reactions.[76] The complexes reported bear identical substituents at phosphorus, crystal structure analyses of the diphenyl and the dicyclohexyl complexes were included. We succeeded in the synthesis of the *tert*-butylphenyl substituted derivative, which was obtained in 48% yield by treatment of the anionic ligand with $CrCl_3 \cdot 3THF$ as blue needles from toluene. The paramagnetic complex was characterized by IR spectroscopy, mass spectrometry (including HRMS), and by an elemental analysis. These data are in accord with those obtained by Jolly for related complexes. In addition, it was possible to obtain an X-ray crystal structure analysis (Fig. 5).

The difference in Cr–Cl bond lengths reflects the asymmetry of the complex. In this context a comparison with the closely related structures of the dicyclohexyl and the diphenyl substituted complexes is instructive. Those Cr–Cl bond lengths are 227.53(8) and 227.86(8) pm for the dicyclohexyl but 228.37(12) and 228.44(11) pm for the diphenyl substituted complex, and the Cr–P bond lengths also differ considerably [PCy_2: 245.9(1), PPh_2: 244.7(1) pm].[76] In *rac*-**21** both features are present, and consequently differences in the Cr–Cl bond lengths are observed. The shorter bond is next to the *tert*-butyl group [Cr1–Cl1, 227.4(1) pm] and the longer one next to the phenyl substituent [Cr1–Cl2, 228.7(1) pm]. The Cr–P bond length in *rac*-**21** [246.1(1) pm] resembles more that of the dicyclohexyl [245.9(1) pm] than that of the diphenyl compound [244.7(1) pm]. It seems reasonable that these data reflect the steric bulk of the *tert*-butyl substituent as compared to that of the phenyl group.

In conclusion, we have reported the first chelate complexes with the [2-(*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl ligand system, in which the phosphorus atom is a center of chirality. This asymmetry is reflected in the structures of the complexes, three of which have been determined, as well as in the diastereoselectivity of the reaction of rhodium chelate *rac*-**12** with iodomethane. While stereoinduction from an

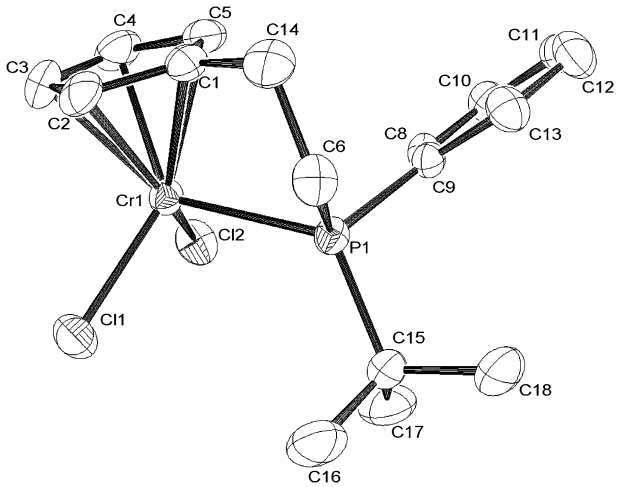


Fig. 5 Structure of *rac*-**21** in the crystal.[45] There are two similar molecules of *rac*-**21** in the asymmetric unit, only one molecule is shown. Displacement ellipsoids correspond to the 50% probability level. Selected bond lengths [pm] and angles [°]: Cr1–Cl1 227.39(10), Cr1–Cl2 228.71(11), Cr1–P1 246.13(11), Cr1–C1 224.5(3), Cr1–C2 222.3(4), Cr1–C3 222.6(4), Cr1–C4 222.3(3), Cr1–C5 222.4(3), P1–C6 182.9(3), P1–C9 181.5(3), P1–C15 186.1(3), C1–C2 138.8(4), C1–C5 141.9(4), C1–C14 150.2(4), C2–C3 138.7(5), C3–C4 137.4(5), C4–C5 141.0(4), C6–C14 152.6(5); Cl1–Cr1–Cl2 98.27(4), Cl1–Cr1–P1 98.91(4), Cl2–Cr 101.18(4).

indenyl ligand or an asymmetric carbon atom in the chelate backbone has earlier been reported, this is the first case that the asymmetric phosphorus atom causes this diastereoselectivity.

Experimental section

General: All manipulations involving air sensitive material were performed in flame-dried reaction vessels in an argon or nitrogen atmosphere using vacuum line and standard Schlenk techniques. Spiro[2.4]hepta-4,6-diene (**4**) and [4,5]benzospiro[2.4]-hepta-4,6-diene (**16**) were prepared according to published procedures.[53,77] Diethyl ether (EE), and THF were distilled from sodium benzophenone ketyl. Hexane, pentane and dichloromethane were dried with calcium hydride and freshly distilled before use. Petroleum ether (PE) was dried with calcium chloride. All the solvents were purged with nitrogen before use. Column chromatography was carried out by flash chromatography.[78] Silica gel (J. T. Baker, 40 μm) was degassed three times by heating it with a flame at reduced pressure followed by setting it at normal pressure with nitrogen. *IR-Spectra*: Bruker FT-IR spectrometer Vektor 22 (ATR). *Mass spectra*: Finnegan MAT 112 and MAT 312. *HRMS* (*ESI*): Micromass LCT with a lock spray ion source combined with a Water Alliances 2695 HPLC unit; VG autospec (peak-matching method, PFK). *^{1}H NMR*: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz) and DRX 500 (500.1 MHz). *^{13}C NMR*: Bruker AVS 200 (50.3 MHz) and AVS 400 (100.6 MHz). Signal multiplicities were determined with ATP and DEPT techniques. *^{31}P NMR*: Bruker AVS 400 (161.9 MHz). *Melting points*: Electrothermal IA9000 Series Digital Melting Point Apparatus. *Elemental analyses*: Elementar Vario EL.

Chloro-{η^5:η^1[2-(*tert*-butylphenylphosphanyl)ethyl]-cyclopentadienyl}cobalt(II) (*rac*-5)

At −78 °C butyllithium in hexane (19.4 mL, 31.2 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (4.314 g, 25.9 mmol) in THF (100 mL). After stirring for 2 h at 20 °C spiro[2.4]hepta-4,6-diene (**4**, 2.484 g, 27.0 mmol) was added, and after stirring for 4 h at 65 °C the mixture was cooled to −78 °C, and $CoCl_2$ (4.050 g, 31.2 mmol) was added. The mixture was slowly warmed to 20 °C and stirred for another 1 h. After solvent removal at reduced pressure the residue was taken up with diethyl ether (25 mL) and filtered through a 3 cm thick layer of Celite. After solvent removal the product was isolated by column chromatography (3 × 20 cm, TBME) to give **5** (5.960 g, 16.9 mmol, 65%) as a purple solid, mp 106.1 °C.

IR: $\tilde{\nu}$ = 3406 (w), 3078 (m), 2940 (s, C-H), 2863 (w, C-H), 2360 (w), 1630 (m), 1473 (w), 1461 (m), 1437 (w, P-Ph), 1365 (w, *t*-Bu), 1183 (m), 1163 (w), 1101 (w), 1035 (m), 1023 (s, *t*-Bu), 934 (m), 848 (w), 806 (s, Cp), 755 (m), 700 (s), 621 (m) cm^{-1}. MS: *m*/*z* (%) = 351 (20) [M$^+$], 259 (54) [M$^+$ − CoCl], 182 (17), 160 (40), 126 (65), 110 (62), 79 (76), 57 (19) [*t*-Bu$^+$]. HRMS (M$^+$ = $C_{17}H_{22}ClCoP$) calcd 351.0482, found 351.0479. Anal. ($C_{17}H_{22}ClCoP$) calcd C 50.01; H 7.27, found C 50.14; H 7.19.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]cyclopentadienyl}-(η^2-ethen)-cobalt(I) (*rac*-6)

At −78 °C sodium amalgam (1%, 3.2 mL, 2.1 mmol) was added to chlorocobalt complex *rac*-**5** (0.765 g, 4.3 mmol) in THF (15 mL), and ethene was purged through the mixture. After 1 h the mixture was slowly warmed to 20 °C and stirred for another 4 h. After separation of the organic layer from the amalgam the solvent was removed at reduced pressure, and the residue was taken up with hexane (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. After concentration at reduced pressure the filtrate was cooled to −25 °C affording complex *rac*-**6** (1.19 g, 3.5 mmol, 40%) as brown-black crystals (mp 73.0 °C), purity (^{1}H NMR) ≥ 95%.

IR: $\tilde{\nu}$ = 3052 (m, C_2H_4), 2959 (s, C-H), 2862 (m, C-H), 2364 (w), 1474 (m, C-H), 1461 (m), 1434 (m, P-Ph), 1362 (m, *t*-Bu), 1261 (m, C_2H_4), 1164 (m), 1095 (m), 1027 (m, *t*-Bu), 895 (w), 800 (s, Cp-R), 745 (m), 699 (s) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.76 (d, $^3J_{H,P}$ = 12.7 Hz, 9H, CH_3), 1.46 (m, 1H, PCH_2CH_2), 1.79–1.96 (m, 1H, PCH_2CH_2), 2.03 (m, 2H, PCH_2), 2.05 (m, 2H, $CH_2{=}CH_2$), 2.44 (m, 1H, $CH_2{=}CH_2$), 2.73 (m, 1H, $CH_2{=}CH_2$), 3.54 (s, 1H, PCH_2CH_2CCHCH), 3.81 (s, 1H, PCH_2CH_2CCH), 5.05 (s, 1H, PCH_2CH_2CCH), 5.55 (s, 1H, $PCH_2CH_2CCHCHCH$), 7.15 (d, $^2J_{H,P}$ = 6.0 Hz, 3H, *o*-, *p*-CH), 7.98 (t, $^3J_{H,P}$ = 7.5 Hz, 2H, *m*-CH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 22.1 (d, $^2J_{C,P}$ = 5.5 Hz, PCH_2CH_2), 22.9 ($=CH_2$), 26.5 (d, $^2J_{C,P}$ = 3.7 Hz, CH_3), 31.2 (d, $^1J_{C,P}$ = 14.1 Hz, $PCCH_3$), 38.8 (d, $^1J_{C,P}$ = 24.9 Hz, PCH_2), 77.7 (PCH_2CH_2CCHCH), 79.1 (d, $^4J_{C,P}$ = 5.1 Hz, PCH_2CH_2CCH), 82.4 (PCH_2CH_2CCHCH), 83.0 (d, $^4J_{C,P}$ = 5.3 Hz, PCH_2CH_2CCH), 108.8 (d, $^3J_{C,P}$ = 6.3 Hz, PCH_2CH_2C), 127.6 (d, $^2J_{C,P}$ = 8.3 Hz, *o*-CH), 129 (*p*-CH), 134.0 (d, $^3J_{C,P}$ = 9.1 Hz, *m*-CH), 135.4 (d, $^1J_{C,P}$ = 20.3 Hz, $PCCH$) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 79.9 ppm.

MS: m/z (%) = 344 [M^+] (11), 316 [$M^+ - CH_2{=}CH_2$] (100), 259 (86), 180 (43), 136 (61), 91 (24), 57 (41). HRMS (M^+ = $C_{19}H_{26}CoP$) calcd 344.1104, found 344.1102. T_c = 350 K (d_8-toluene, 400 MHz), $\Delta G^{\ddagger} \approx 68.7$ kJ mol^{-1}.

Crystal structure analysis of *rac*-**6**:[45] empirical formula $C_{19}H_{26}CoP$, molecular weight 344.30, crystal system monoclinic, space group $P2_1/n$, a = 11.070(5), b = 11.504(4), c = 14.202(6) Å, α = 90.00°, β = 104.47(5)°, γ = 90.00°, V = 1751.3(12) Å^3, Z = 4, d_{calcd} = 1.306 g cm^{-1}, $F(000)$ = 728, μ = 1.063 mm^{-1}, Stoe IPDS diffractometer, T = 294 K, MoK_α (λ = 0.71073 Å), θ_{min} = 2.10°, θ_{max} = 26.23°, 24 177 measured reflections ($-13 \le h \le 13$, $-14 \le k \le 14$, $-17 \le l \le 17$), 3479 independent, 2070 observed reflections, R_{int} = 0.089, R = 0.0301, wR = 0.0534, residual electron density 0.244 and −0.286 e Å^{-3}, Gof = 0.803, refinement program SHELXL-97, N_{ref} = 3479, N_{par} = 202.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]cyclopentadienyl}-(hydrido)(methylphenylsilyl)cobalt(III) (*rac*-7)

Methylphenylsilane (0.5 mL, 4.0 mmol) was added to ethene-cobalt chelate *rac*-**6** (465 mg, 1.4 mmol) in toluene (14 mL). After stirring for 11 h at 60 °C the solvent was removed at reduced pressure, and the residue was taken up with hexane (5 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. The solvent was removed at reduced pressure to give *rac*-**7** (420 mg, 1.35 mmol, 71%) as a yellow oil as a mixture of four diastereomers [1.00 : 0.95 : 0.56 : 0.48, purity ≥ 95% (^{1}H NMR)].

IR: $\tilde{\nu}$ = 3060 (w), 2956 (m, C-H), 2043 (m, Co-H), 1946 (w, Si-H), 1461 (w, C-H), 1426 (m, P-Ph), 1392 (w), 1363 (w, *t*-Bu), 1310 (w), 1260 (m), 1232 (w), 1181 (w), 1123 (w), 1095 (m, C-H), 1014 (s), 996 (m), 878 (m), 816 (s, Si-H), 730 (m), 696 (s) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = −16.89 (d, $^2J_{H,P}$ = 53.8 Hz, 1/4H, 14-H), −16.85 (d, $^2J_{H,P}$ = 45.1 Hz, 1/4H, 14-H), −16.58 (d, $^2J_{H,P}$ = 53.1 Hz, 1/4H, 14-H), −16.50 (d, $^2J_{H,P}$ = 46.1 Hz, 1/4H, 14-H), 0.37 (s, 3H, $SiCH_3$), 0.87 (m, 9H, CCH_3), 1.66–2.07 (m, 2H, PCH_2CH_2), 1.42–2.58 (m, 2H, PCH_2), 4.26–5.15 (m, 4H, Cp-H), 5.59 (s, 1H, Si-H), 7.07–7.58 (m, 10H, Ph-H) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6, main product): δ = 1.4 ($SiCH_3$), 22.5 (d, $^2J_{C,P}$ = 5.2 Hz, PCH_2CH_2), 26.5 (d, $^2J_{C,P}$ = 3.6 Hz, CCH_3), 31.9 (d, $^1J_{C,P}$ = 9.5 Hz, CCH_3), 40.5 (d, $^1J_{C,P}$ = 24.7 Hz, PCH_2), 80.2 ($C_{Cp}CH$), 80.8 ($C_{Cp}CH$), 80.9 ($C_{Cp}CH$), 84.2 ($C_{Cp}CH$), 116.0 (d, $^3J_{C,P}$ = 6.7 Hz, $C_{Cp}CH_2$), 127.6 (d, $^2J_{C,P}$ = 5.3 Hz, P-*o*-$C_{Ph}H$), 127.9 (Si-$C_{Ph}H$), 129.4 (P-*p*-$C_{Ph}H$), 132.7 (Si-$C_{Ph}H$), 133.5 (d, $^3J_{C,P}$ = 9.1 Hz, P-*m*-$C_{Ph}H$), 134.7 (Si-$C_{Ph}H$), 135.0 (PC_{Ph}C), 148.6 (SiC_{Ph}C) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 93.7, 95.5 ppm. MS: m/z (%) = 437 (32) [$M^+ - H$], 436 (100) [$M^+ - 2H$], 358 (31), 258 (42), 121 (58), 105 (39), 78 (70), 57 (78) [*t*-Bu$^+$]. HRMS ($M^+ - 2H$ = $C_{24}H_{30}CoPSi$) calcd 436.1186, found 436.1182.

Carbonyl{η^5:η^1[2-(*tert*-butylphenylphosphanyl)ethyl]-cyclopentadienyl}cobalt(I) (*rac*-8)

A solution of $ICo(CO)_4$ was prepared by addition of $Co_2(CO)_8$ (1.000 g, 2.9 mmol) in THF (15 mL) to I_2 (0.740 g, 2.9 mmol) in THF (25 mL) at −78 °C and subsequent stirring for 1 h at −78 °C.[48] A solution of the anionic ligand was prepared by addition at −78 °C of butyllithium in hexane (3.2 mL, 5.1 mmol, 1.6 M) to *tert*-butylphenylphosphane (0.719 g, 4.3 mmol) in THF (15 mL), followed by stirring for 2 h at 20 °C and addition of spiro[2.4]hepta-4,6-diene (**4**, 0.45 mL, 4.5 mmol). This solution was added to the $ICo(CO)_4$ solution at −78 °C, and the mixture was stirred for 1 h at −78 °C and then for 4 h at 20 °C. After solvent removal at reduced pressure the residue was taken up with hexane (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. Solvent removal from the filtrate afforded complex *rac*-**8** (0.667 g, 1.9 mmol, 45%) as a brown-black oil (purity ≥ 90%, ^{1}H NMR).

IR: $\tilde{\nu}$ = 2961 (m, C-H), 2077 (w), 2015 (s, impur.), 1946 (s, impur.), 1894 (CO, s), 1620 (w), 1474 (w, C-H), 1435 (w, P-Ph), 1166 (w), 1099 (w), 1015 (w, *t*-Bu), 815 (w, Cp), 746 (w), 697 (m) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.9 (d, $^3J_{H,P}$ = 14.3 Hz, CH_3), 1.37 (m, 1H, PCH_2CH_2), 1.72 (m, 1H, PCH_2CH_2), 2.30 (m, 2H, PCH_2), 4.62 (s, 1H, PCH_2CH_2CCHCH), 4.89 (s, 1H, PCH_2CH_2CCHCH), 4.97 (s, 1H, PCH_2CH_2CCH), 5.81 (s, 1H, PCH_2CH_2CCH), 7.08 (m, 3H, *o*-CH, *p*-CH), 7.79 (t, $^3J_{H,P}$ = 9.5 Hz, 2H, *m*-CH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 23.2 (d, $^2J_{C,P}$ = 6.5 Hz, PCH_2CH_2), 26.7 (d, $^2J_{C,P}$ = 4.7 Hz, CH_3), 32.1 (d, $^1J_{C,P}$ = 25.1 Hz, CCH_3), 39.5 (d, $^1J_{C,P}$ = 24.7 Hz, PCH_2), 78.6 (d, $^4J_{C,P}$ = 3.6 Hz, PCH_2CH_2CCH), 80.5 (d, $^5J_{C,P}$ = 1.1 Hz, PCH_2CH_2CCHCH), 81.1 (d, $^4J_{C,P}$ = 3.6 Hz, PCH_2CH_2CCH), 83.8 (d, $^5J_{C,P}$ = 1.1 Hz, PCH_2CH_2CCHCH), 108.7 (d, $^3J_{C,P}$ = 6.5 Hz, PCH_2CH_2C), 127.8 (d, $^2J_{C,P}$ = 5.1 Hz, *o*-CH), 129.7 (d, $^4J_{C,P}$ = 2.3 Hz, *p*-CH), 133.7 (d, $^3J_{C,P}$ = 10.1 Hz, *m*-CH), 134.2 (d, $^1J_{C,P}$ = 31.2 Hz, PCCH), 207.1 (CO) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 108.7 ppm. MS: m/z (%) = 344 (34) [M^+], 316 (96) [M^+ − CO], 260 (100), 259 (65), 180 (28), 136 (44), 58 (24). HRMS (M^+ = $C_{18}H_{22}CoOP$) calcd 344.0740, found 344.0741.

Chloro-{η^5:η^1[2-(*tert*-butylcyclohexylphosphanyl)ethyl]-cyclopentadienyl}cobalt(II) (*rac*-9)

At −78 °C butyllithium in hexane (6.4 mL, 10.2 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (1.489 g, 8.7 mmol) in THF (30 mL). After stirring for 2 h at 20 °C spiro[2.4]hepta-4,6-diene (**4**, 0.9 mL, 9.0 mmol) was added, and after stirring for 2 h at 65 °C the mixture was cooled to −78 °C, and $CoCl_2$ (1.350 g, 10.4 mmol) was added. The mixture was slowly warmed to 20 °C and stirred for another 2 h. After solvent removal at reduced pressure the residue was taken up with diethyl ether (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. The filtrate was concentrated and cooled at −25 °C affording complex *rac*-**9** (1.717 g, 4.8 mmol, 55%) as a purple solid (mp 113 °C).

IR: $\tilde{\nu}$ = 2922 (s, C-H), 2851 (m, C-H), 2357 (w), 1693 (w), 1446 (m), 1394 (w), 1365 (m, *t*-Bu), 1262 (w), 1103 (m), 1031 (m), 1016 (m, *t*-Bu), 936 (w), 888 (w), 851 (w), 828 (m), 796 (s, Cp), 735 (w) cm^{-1}. MS: m/z (%) = 357 (100) [M^+], 263 (82) [M^+ − CoCl], 258 (49), 182 (90), 163 (44), 57 (34). HRMS (M^+ = $C_{17}H_{28}ClCoP$) calcd 357.0949, found 357.0949.

{η^5:η^1[2-(*tert*-Butylcyclohexylphosphanyl)ethyl]-cyclopentadienyl}-(η^2-ethen)-cobalt(I) (*rac*-10)

At −78 °C sodium amalgam (1%, 6.3 mL, 3.7 mmol) was added to chlorocobalt complex *rac*-**9** (1.171 g, 4.8 mmol) in THF (80 mL), and ethene was purged through the mixture.

After 1 h the mixture was slowly warmed to 20 °C and stirred for another 6 h. After separation of the organic layer from the amalgam the solvent was removed at reduced pressure, and the residue was taken up with hexane (30 mL) and filtered through a frit covered with a 3 cm thick layer of alumina. After solvent removal at reduced pressure complex *rac*-**10** [0.637 g, 1.8 mmol, 38%, purity (^{1}H NMR) ≥ 95%] was obtained as a red oil.

IR: $\tilde{\nu}$ = 2921 (s, C-H), 2850 (s, C-H), 1447 (m, C-H), 1364 (w, *t*-Bu), 1266 (w, C_2H_4), 1161 (m), 1013 (w, *t*-Bu), 890 (w), 816 (m), 793 (m, Cp), 681 (m) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.02 (d, $^3J_{H,P}$ = 12.1 Hz, 9H, CH_3), 1.87 (m, 17H, 7 CH_2, =CH_2, PCH), 2.34 (m, 1H, =CH_2), 2.64 (m, 1H, =CH_2), 3.36 (s, 1H, PCH_2CH_2CCHCH), 4.29 (s, 1H, PCH_2CH_2CCH), 5.47 (s, 1H, PCH_2CH_2CCHCH), 5.54 (s, 1H, PCH_2CH_2CCH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 22.5 (=CH_2), 23.5 (d, $^4J_{C,P}$ = 4.6 Hz, $PCHCH_2CH_2CH_2$), 25.1 (d, $^2J_{C,P}$ = 6.9 Hz, PCH_2CH_2), 27.5 (d, $^3J_{C,P}$ = 6.3 Hz, $PCHCH_2CH_2$), 28.7 (d, $^4J_{C,P}$ = 3.4 Hz, CH_3), 29.4 (d, $^2J_{C,P}$ = 5.9 Hz, $PCHCH_2$), 31.0 (d, $^4J_{C,P}$ = 12.4 Hz, $PCCH_3$), 34.8 (d, $^4J_{C,P}$ = 10.5 Hz, PCH), 36.2 (d, $^4J_{C,P}$ = 21.2 Hz, PCH_2), 77.2 (d, $^4J_{C,P}$ = 6.5 Hz, PCH_2CH_2CCH), 79.2 (PCH_2CH_2CCHCH), 80.9 (PCH_2CH_2CCHCH), 83.5 (d, $^4J_{C,P}$ = 4.6 Hz, PCH_2CH_2CCH), 109.3 (d, $^3J_{C,P}$ = 6.7 Hz, PCH_2CH_2CCH) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 93.2 ppm. MS: *m*/*z* (%) = 350 (10) [M$^+$], 322 (59) [M$^+$ − CH_2 = CH_2], 263 (73) [M$^+$ − CH_2=CH_2-Co], 240 (30), 183 (69), 136 (55), 83 (61), 57 (100) [*t*-Bu$^+$], 55 (73). HRMS (M$^+$ = $C_{19}H_{32}CoP$) calcd 350.1573, found 350.1571.

{η^5:η^1[2-(Di-*tert*-butylphosphanyl)ethyl]cyclopentadienyl}-(η^2-ethen)-rhodium(I) (*rac*-11)

At −78 °C butyllithium in hexane (2.9 mL, 4.6 mmol, 1.6 M) was added dropwise to di-*tert*-butylphosphane (0.610 g, 4.2 mmol) in THF (15 mL). After stirring for 2 h at 21 °C spiro[2.4]hepta-4,6-diene (**4**, 0.5 mL, 5.0 mmol) was added, and after stirring for 2 h at 65 °C the mixture was cooled to −78 °C, and $[Rh_2(C_2H_4)_4Cl_2]$ (0.982 g, 2.5 mmol) was added. The mixture was slowly warmed to 20 °C and stirred for another 2 h. After solvent removal at reduced pressure the residue was taken up with pentane (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. The solvent was removed at reduced pressure affording *rac*-**11** [1.120 g, 3.0 mmol, 72%, purity ≥ 95% (^{1}H NMR)] as a brown oil.

IR: $\tilde{\nu}$ = 2958 (m, C-H), 2896 (m, C-H), 1471 (m, C-H), 1386 (w), 1366 (m, *t*-Bu), 1167 (s), 1019 (m, *t*-Bu), 928 (w), 809 (m), 772 (m), 661 (w) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.06 (d, 18H, $^3J_{H,P}$ = 12.2 Hz, CH_3), 1.88 (m, 2H, PCH_2CH_2), 2.02 (m, 2H, PCH_2), 2.40 (m, 2H, CH_2=CH_2), 2.78 (m, 2H, CH_2=CH_2), 4.72 (m, 2H, PCH_2CH_2CCHCH), 5.51 (m, 2H, PCH_2CH_2CCH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 25.5 (dd, $^2J_{C,P}$ = 15.1 Hz, $^3J_{C,Rh}$ = 2.4 Hz, PCH_2CH_2), 30.1 (d, $^2J_{C,P}$ = 4.9 Hz, CH_3), 35.5 (dd, $^1J_{C,P}$ = 9.5 Hz, $^2J_{C,Rh}$ = 2.4 Hz, $PCCH_3$), 37.9 (dd, $^2J_{C,P}$ = 13.4 Hz, $^1J_{C,Rh}$ = 2.1 Hz, H_2C=CH_2), 42.4 (d, $^1J_{C,P}$ = 19.5 Hz, PCH_2), 82.9 (dd, $J_{C,P}$ = 4.0 Hz, $^1J_{C,Rh}$ = 3.0 Hz, PCH_2CH_2CCHCH or PCH_2CH_2CCH), 86.2 (dd, $J_{C,P}$ = 8.4 Hz, $^1J_{C,Rh}$ = 2.8 Hz, PCH_2CH_2CCHCH or PCH_2CH_2CCH), 113.6 (dd, $J_{C,P}$ = 6.4 Hz, $^1J_{C,Rh}$ = 4.2 Hz, PCH_2CH_2C) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 99.3 (d, $^1J_{P,Rh}$ = 211.7 Hz) ppm. MS: *m*/*z* (%) = 368 (18) [M$^+$], 340 (60) [M$^+$ − CH_2=CH_2], 284 (100), 227 (45), 224 (56), 180 (30), 57 (76) [*t*-Bu$^+$]. HRMS (M$^+$ = $C_{17}H_{30}RhP$) calcd 368.1137, found 368.1140.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]cyclopentadienyl}-(η^2-ethen)-rhodium(I) (*rac*-12)

At −78 °C butyllithium in hexane (6.4 mL, 10.2 mmol, 1.6 M) was added dropwise to di-*tert*-butylphosphane (1.438 g, 8.7 mmol) in THF (30 mL). After stirring for 2 h at 21 °C spiro[2.4]hepta-4,6-diene (**4**, 0.9 mL, 9.0 mmol) was added, and after stirring for 2 h at 65 °C the mixture was cooled to −78 °C, and $[Rh_2(C_2H_4)_4Cl_2]$ (2.020 g, 5.2 mmol) was added. The mixture was slowly warmed to 20 °C and stirred for another 2 h. After solvent removal at reduced pressure the residue was taken up with pentane (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. The solvent was removed at reduced pressure and the residue was taken up with 3 mL of toluene. As attempts to crystallize the product at −25 °C failed, the solvent was removed at reduced pressure affording *rac*-**12** (2.850 g, 7.7 mmol, 85%) as a brown oil, purity ≥ 95% (^{1}H NMR).

IR: $\tilde{\nu}$ = 3045 (w, C_2H_4), 2941 (m, C-H), 2861 (w, C-H), 1474 (w, C-H), 1433 (m, P-Ph), 1416 (w), 1390 (w), 1362 (m, *t*-Bu), 1308 (m), 1266 (w, kompl. C_2H_4), 1167 (w), 1095 (s), 1028 (m, *t*-Bu), 1013 (w), 929 (w), 841 (m, Cp), 809 (s, Cp), 772 (m), 744 (m), 697 (s), 668 (m), 620 (s) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.87 (d, $^3J_{H,P}$ = 13.6 Hz, 9H, CH_3), 1.59 (m, 1H, PCH_2CH_2), 2.03 (dddd, $^2J_{H,P}$ = 45.6, $J_{H,H}$ = 13.5, 6.6, 2.4 Hz, 1H, PCH_2CH_2), 2.24 (m, 1H, PCH_2), 2.31 (m, 1H, =CH_2), 2.50 (m, 1H, =CH_2), 2.54 (m, 1H, PCH_2), 2.93 (m, 1H, =CH_2), 3.11 (m, 1H, =CH_2), 4.70 (d, $^4J_{H,P}$ = 2.7 Hz, 1H, PCH_2CH_2CCH), 4.99 (d, $^3J_{H,P}$ = 2.0 Hz, 1H, PCH_2CH_2CCH), 5.23 (d, $^5J_{H,P}$ = 1.0 Hz, 1H, PCH_2CH_2CCHCH), 5.60 (d, $^5J_{H,P}$ = 1.3 Hz, 1H, PCH_2CH_2CCHCH), 7.17 (m, 3H, *o*-CH, *p*-CH), 7.89 (m, 2H, *m*-CH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 22.7 (d, $^2J_{C,P}$ = 2.6 Hz, PCH_2CH_2), 25.9 (dd, $^2J_{C,P}$ = 15.1 Hz, $^1J_{C,Rh}$ = 2.4 Hz, =CH_2), 26.5 (d, $^2J_{C,P}$ = 4.7 Hz, CH_3), 32.0 (d, $^1J_{C,P}$ = 16.7 Hz, $^2J_{C,Rh}$ = 2.7 Hz, $PCCH_3$), 42.2 (d, $^1J_{C,P}$ = 24.5 Hz, PCH_2), 80.8 (dd, $^5J_{C,P}$ = 4.2 Hz, $^1J_{C,Rh}$ = 2.6 Hz, PCH_2CH_2CCHCH), 84.8 (dd, $^5J_{C,P}$ = 3.8 Hz, $^1J_{C,Rh}$ = 3.0 Hz, PCH_2CH_2CCHCH), 85.3 (dd, $^4J_{C,P}$ = 8.8 Hz, $^1J_{C,Rh}$ = 2.8 Hz, PCH_2CH_2CCH), 88.9 (dd, $^4J_{C,P}$ = 8.4 Hz, $^1J_{C,Rh}$ = 2.7 Hz, PCH_2CH_2CCH), 112.0 (dd, $^3J_{C,P}$ = 5.5 Hz, $^1J_{C,Rh}$ = 4.2 Hz, PCH_2CH_2C), 127.5 (d, $^2J_{C,P}$ = 8.8. Hz, *o*-CH), 129.4 (d, $^4J_{C,P}$ = 2.3 Hz, *p*-CH), 134.1 (d, $^3J_{C,P}$ = 10.5 Hz, *m*-CH), 136.3 (dd, $^1J_{C,P}$ = 25.1 Hz, $^2J_{C,Rh}$ = 1.5 Hz, PCCH) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 79.7 (d, $^1J_{P,Rh}$ = 215 Hz) ppm. MS: *m*/*z* (%) = 388 (47) [M$^+$], 360 (99) [M$^+$ − CH_2=CH_2], 304 (100) [M$^+$ − C_4H_8], 223 (34), 180 (50), 57 (39) [*t*-Bu$^+$]. HRMS (M$^+$ = $C_{19}H_{26}RhP$) calcd 388.0827, found 388.0828. T_c = 330 K (d_6-benzene). $\Delta G^{\ddagger}$ = 62.98 kJ mol^{-1}. T_c = 325 K (d_8-toluene), $\Delta G^{\ddagger}$ = 62.5 kJ mol^{-1}.

{η^5:η^1[2-(*tert*-Butylcyclohexylphosphanyl)ethyl]-cyclopentadienyl}-(η^2-ethen)rhodium(I) (*rac*-13)

At −78 °C butyllithium in hexane (2.9 mL, 4.6 mmol, 1.6 M) was added dropwise to *tert*-butylcyclohexylphosphane

(0.726 g, 4.2 mmol) in THF (15 mL). After stirring for 2 h at 20 °C spiro[2.4]hepta-4,6-diene (**4**, 0.9 mL, 9.0 mmol) was added, and after stirring for 2 h at 65 °C the mixture was cooled to −78 °C, and $[Rh_2(C_2H_4)_4Cl_2]$ (0.982 g, 2.5 mmol) was added. The mixture was slowly warmed to 20 °C and stirred for another 2 h. After solvent removal at reduced pressure the residue was taken up with pentane (15 mL) and filtered through a frit covered with a 3 cm thick layer of Celite. The solvent was removed at reduced pressure affording *rac*-**13** (0.910 g, 2.3 mmol, 55%) as a brown oil.

IR: $\tilde{\nu}$ = 2920 (s, C-H), 2849 (s, C-H), 1944 (m), 1782 (w), 1447 (m, C-H), 1415 (w), 1391 (w), 1363 (m, *t*-Bu), 1268 (w, C_2H_4), 1184 (m), 1168 (s), 1026 (m), 1012 (m, *t*-Bu), 930 (m), 887 (w), 850 (w), 810 (m), 769 (s, Cp), 730 (m) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.94 (d, $^3J_{H,P}$ = 12.1 Hz, 9H, CH_3), 1.81 (m, 17H, 7 CH2, =CH_2), 2.86 (m, 2H, =CH_2), 4.71 (d, $^4J_{H,P}$ = 2.4 Hz, 1H, PCH_2CH_2CCHCH), 5.00 (s, 1H, PCH_2CH_2CCH), 5.54 (d, $^5J_{H,P}$ = 1.0 Hz, 1H, PCH_2CH_2CCH), 5.60 (d, $^5J_{H,P}$ = 1.4 Hz, 1H, PCH_2CH_2CCHCH) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 25.3 (d, $^2J_{C,P}$ = 2.8 Hz, PCH_2CH_2), 26.6 (d, $^4J_{C,P}$ = 1.3 Hz, $PCHCH_2CH_2CH_2$), 27.6 (d, $^3J_{C,P}$ = 8.0 Hz, $PCHCH_2CH_2$), 28.0 (d, $^2J_{C,P}$ = 13.2 Hz, =CH_2), 28.4 (d, $^2J_{C,P}$ = 4.2 Hz, CH_3), 29.3 (d, $^2J_{C,P}$ = 3.2 Hz, $PCHCH_2$), 32.1 (dd, $^1J_{C,P}$ = 15.5 Hz, $^2J_{C,Rh}$ = 2.3 Hz, $PCCH_3$), 35.8 (dd, $^1J_{C,P}$ = 13.3 Hz, $^2J_{C,Rh}$ = 2.0 Hz, PCH), 41.1 (d, $^1J_{C,P}$ = 21.0 Hz, PCH_2), 81.7 (dd, $^5J_{C,P}$ = 4.1 Hz, $^1J_{C,Rh}$ = 2.5 Hz, PCH_2CH_2CCHCH), 82.6 (dd, $^5J_{C,P}$ = 4.0 Hz, $^1J_{C,Rh}$ = 3.0 Hz, PCH_2CH_2CCHCH), 85.2 (dd, $^4J_{C,P}$ = 9.2 Hz, $^1J_{C,Rh}$ = 2.6 Hz, PCH_2CH_2CCH), 88.1 (dd, $^4J_{C,P}$ = 7.4 Hz, $^1J_{C,Rh}$ = 2.8 Hz, PCH_2CH_2CCHCH), 113.1 (dd, $^3J_{C,P}$ = 6.3 Hz, $^1J_{C,Rh}$ = 4.2 Hz, PCH_2CH_2C) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 91.5 (d, $^1J_{P,Rh}$ = 209.6 Hz) ppm. MS: *m*/*z* (%) = 394 (12) [M^+], 366 (41) [$M^+ - CH_2$=CH_2], 284 (34), 224 (33), 166 (24), 82 (100) [$C_6H_{10}^+$], 57 (57) [*t*-Bu^+]. HRMS ($M^+ = C_{19}H_{32}RhP$) calcd 394.1296, found 394.1298.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]-cyclopentadienyl}iodomethyl-rhodium(II) (*rac*-14 and *rac*-15)

At 22 °C iodomethane (0.6 mL, 9.0 mmol) was added to rhodium(I) complex *rac*-**11** (767 mg, 1.9 mmol) in THF (120 mL). After stirring at 22 °C for 24 h the solvent was removed at reduced pressure, and the residue was taken up with dichloromethane (20 mL). The mixture was filtered through a frit covered with a 3 cm thick layer of Celite. The filtrate was concentrated and the product was crystallized from dichloromethane/hexane at −25 °C. The product was obtained as a diastereomeric mixture of *rac*-**14** and *rac*-**15** (100 : 0.7, ^{1}H NMR) as a red solid (593 mg, 1.2 mmol, 60%).

IR (95% de): $\tilde{\nu}$ = 2958 (m, C-H), 2893 (m, C-H), 1460 (m, C-H), 1432 (m, P-Ph), 1260 (m), 1168 (w), 1125 (m), 1096 (s), 1015 (s, *t*-Bu), 840 (m, Cp), 797 (s, Cp), 746 (m), 698 (s) cm^{-1}. *rac*-**14**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.06 (dd, *J* = 5.4, 2.3 Hz, 3H, $RhCH_3$), 1.15 (d, $^3J_{H,P}$ = 14.8 Hz, 9H, CCH_3), 2.17 (d, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,P}$ = 34.7 Hz, $^2J_{H,H}$ = −14.1 Hz, 1H, PCH_2CH_2), 2.32 (d, 1H, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,P}$ = 20.6 Hz, $^2J_{H,H}$ = −14.1 Hz, PCH_2CH_2), 2.84 (d, $^3J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 6.9 Hz, $^2J_{H,P}$ = 9.8 Hz, $^3J_{H,H}$ = −14.2 Hz, $^3J_{H,Rh}$ = 0.6 Hz, 1H, PCH_2), 3.23 (d, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 6.0 Hz, $^2J_{H,P}$ = 9.0 Hz, $^3J_{H,H}$ = −14.2 Hz, $^3J_{H,Rh}$ = 1.2 Hz, 1H, PCH_2), 4.50 (m, 1H, PCH_2CH_2CCH), 5.15 (m, 1H, PCH_2CH_2CCHCH), 5.40 (m, 1H, PCH_2CH_2CCH), 5.89 (m, 1H, PCH_2CH_2CCHCH), 7.28 (m, 5H, Ph-H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = −13.5 (dd, $^2J_{C,P}$ = 20.9 Hz, $^1J_{C,Rh}$ = 10.4 Hz, $RhCH_3$), 23.3 (d, $^2J_{C,P}$ = 1.3 Hz, PCH_2CH_2), 27.9 (d, $^2J_{C,P}$ = 3.4 Hz, CCH_3), 35.0 (d, $^1J_{C,P}$ = 19.1 Hz, $^2J_{C,Rh}$ = 0.5 Hz, CCH_3), 42.5 (d, $^1J_{C,P}$ = 24.9 Hz, PCH_2), 81.7 (dd, $J_{C,P}$ = 6.9 Hz, $^1J_{C,Rh}$ = 3.1 Hz, PCH_2CH_2CCH), 84.9 (dd, $J_{C,P}$ = 3.2 Hz, PCH_2CH_2CCH), 87.2 (dd, $J_{C,P}$ = 11.3 Hz, $J_{C,Rh}$ = 3.6 Hz, PCH_2CH_2CCHCH), 102.7 (dd, $J_{C,P}$ = 5.7 Hz, $J_{C,Rh}$ = 2.3 Hz, PCH_2CH_2CCHCH), 118.3 (dd, $^3J_{C,P}$ = 7.7 Hz, $J_{C,Rh}$ = 5.0 Hz, PCH_2CH_2C), 127.8 (d, $^2J_{C,P}$ = 9.0 Hz, *o*-CH), 130.0 (d, $^4J_{C,P}$ = 2.4 Hz, *p*-CH), 132.9 (d, $^3J_{C,P}$ = 7.2 Hz, *m*-CH), 133.9 (dd, $^1J_{C,P}$ = 8.4 Hz, PCCH) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 75.7 (d, $^1J_{P,Rh}$ = 167 Hz) ppm. MS (95% de): *m*/*z* (%) = 501 (14) [M^+], 486 (61) [$M^+ - CH_3$], 360 (61) [$M^+ - CH_3 - I$], 302 (100), 180 (40), 68 (24), 57 (40) [*t*-Bu^+]. HRMS ($M^+ = C_{18}H_{25}PRhI$) calcd 501.9793, found 501.9791.

Crystal structure analysis of *rac*-**14**:[45] empirical formula $C_{18}H_{25}IPRh$, molecular weight 502.16, crystal system orthorhombic, space group *Pbca*, *a* = 21.093(9) Å, *b* = 16.109(5) Å, *c* = 21.823(6) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 7415(4) Å^3, *Z* = 16, d_{calcd} = 1.799 g cm^{-1}, *F*(000) = 3936.0, μ = 2.665 mm^{-1}, Stoe IPDS diffractometer, *T* = 297 K, MoK_α (λ = 0.71073 Å), θ_{min} = 1.93°, θ_{max} = 26.15°, 1 02 298 measured reflections ($-26 \le h \le 25$, $-19 \le k \le 19$, $-26 \le l \le 26$), 7303 independent, 4923 observed reflections, R_{int} = 0.0967, *R* = 0.0361, w*R* = 0.0881, residual electron density 1.195 and −1.055 e Å^{-3}, Gof = 0.950, refinement program SHELXL-97, N_{ref} = 7303, N_{par} = 376.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]indenyl}-(η^2-ethen)rhodium(I) (*rac*-18)

At −78 °C butyllithium in hexane (2.3 mL, 3.7 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (0.159 g, 3.1 mmol) in THF (15 mL). After stirring for 2 h at 20 °C [4.5]benzospiro[2.4]hepta-4,6-diene (**16**, 0.440 g, 3.1 mmol) was added. After stirring for 3 d at 65 °C the mixture was cooled to −78 °C, and $[Rh_2(C_2H_4)Cl_2]$ (0.720 g, 1.9 mmol) was added, and the solution was warmed to 20 °C. After 2 h the solvent was removed at reduced pressure, and the residue was taken up with diethyl ether (5 mL). After filtration through a frit covered with a 3 cm thick layer of Celite the solvent was removed at reduced pressure, and the residue was taken up with pentane (5 mL). Another filtration through a frit covered with a 3 cm thick layer of Celite afforded after solvent removal rhodium(I) chelate *rac*-**18** [0.963 g, 2.2 mmol, 71%, diastereomeric mixture (10 : 1, ^{1}H NMR), purity ≥ 95% (^{1}H NMR)] as a brown oil.

IR (de 82%): $\tilde{\nu}$ = 3050 (w, C_2H_4), 2961 (m, C-H), 2356 (w), 2130 (w), 1948 (w), 1592 (w), 1430 (w, P-Ph), 1327 (w), 1260 (s, C_2H_4), 1124 (m), 1091 (s), 1017 (s, *t*-Bu), 922 (w), 842 (m, Cp), 797 (s, Cp), 731 (m), 697 (s) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, major diastereomer): δ = 0.74 (d, $^3J_{H,P}$ = 13.3 Hz, 9H, CH_3), 2.11 (m, 2H, PCH_2CH_2), 2.47 (d, $^3J_{H,H}$ = 6.1 Hz,

2H, =CH_2), 2.75 (m, 2H, PCH_2), 3.02 (dt, $^3J_{H,H}$ = 7.9, 2.0 Hz, 2H, =CH_2), 5.36 (d, $^3J_{H,H}$ = 2.9 Hz, 1H, PCH_2CH_2-CCHC*H*), 6.13 (d, $^3J_{H,H}$ = 2.6 Hz, 1H, PCH_2CH_2CCH), 6.41 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, PCH_2CH_2CCCH or PCH_2CH_2CCH), 6.77 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, $PCH_2CH_2CCCHCH$ or PCH_2CH_2-CCHC*H*), 6.93 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, PCH_2CH_2CCCH or PCH_2CH_2CCH), 7.03 (t, $^3J_{H,H}$ = 7.2 Hz, 1H, PCH_2CH_2-CCCHC*H* or PCH_2CH_2CCHCH), 7.19 (m, 3H, *o*-, *p*-CH), 7.52 (m, 2H, *m*-H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 19.3 (d, $^2J_{C,P}$ = 2.4 Hz, PCH_2CH_2), 26.3 (d, $^2J_{C,P}$ = 4.7 Hz, CH_3), 32.0 (d, $^1J_{C,P}$ = 16.7 Hz, $^2J_{C,Rh}$ = 3.7 Hz, CCH_3), 35.2 (dd, $^2J_{C,P}$ = 13.9 Hz, $^1J_{C,Rh}$ = 1.3 Hz, =CH_2), 42.5 (d, $^1J_{C,P}$ = 23.7 Hz, PCH_2), 77.0 (dd, $^5J_{C,P}$ = 13.2 Hz, $^1J_{C,Rh}$ = 2.6 Hz, PCH_2CH_2CCHCH), 90.2 (dd, $^5J_{C,P}$ = 5.7 Hz, $^1J_{C,Rh}$ = 3.2 Hz, PCH_2CH_2CCH), 102.6 (dd, $^4J_{C,P}$ = 6.3 Hz, $^1J_{C,Rh}$ = 4.7 Hz, PCH_2CH_2CC or PCH_2CH_2CCC), 109.2 (d, $^3J_{C,P}$ = 2.5 Hz, PCH_2CH_2C), 113.6 (d, $^4J_{C,P}$ = 2.1 Hz, PCH_2CH_2CC or PCH_2CH_2CCC), 115.9 (PCH_2CH_2CCCH or PCH_2CH_2-CCCCH), 118.0 (PCH_2CH_2CCCH or PCH_2CH_2CCCCH), 119.3 ($PCH_2CH_2CCCHCH$ or $PCH_2CH_2CCCCHCH$), 123.4 ($PCH_2CH_2CCCHCH$ or $PCH_2CH_2CCCCHCH$), 127.7 (d, $^2J_{C,P}$ = 9.2 Hz, *o*-CH), 129.5 (d, $^4J_{C,P}$ = 2.1 Hz, *p*-CH), 133.9 (dd, $^1J_{C,P}$ = 22.2 Hz, $PCCH$), 134.1 (d, $^3J_{C,P}$ = 11.3 Hz, *m*-CH) ppm. ^{31}P-NMR (162 MHz, C_6D_6): δ = 84.0 (d, $^1J_{P,Rh}$ = 227.7 Hz) ppm. MS (de 82%): *m*/*z* (%) = 438 (16) [M^+], 410 (100) [$M^+ - CH_2{=}CH_2$], 354 (62), 231 (18), 197 (25), 135 (30), 57 (12) [*t*-Bu^+]. HRMS (M^+ = $C_{23}H_{28}PRh$) calcd 438.0984, found 438.0987.

{η^5:η^1[2-(*tert*-Butylphenylphosphanyl)ethyl]cyclopentadienyl}-(η^2-cycloocten)iridium(I) (*rac*-19)

At −78 °C butyllithium in hexane (1.1 mL, 1.7 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (0.269 g, 1.6 mmol) in THF (15 mL). After stirring at 22 °C for 2 h spiro[2.4]hepta-4,6-diene (**4**, 0.15 mL, 1.6 mmol) was added, and the solution was stirred at 65 °C for 2 h. Then the mixture was cooled to −78 °C, and $[Ir(coe)_2Cl]_2$ (0.871 g, 1.0 mmol, coe = cyclooctene) was added, and the mixture was slowly warmed to 20 °C. After stirring for 12 h the solvent was removed at reduced pressure, and the residue was taken up with diethyl ether (5 mL). After filtration through a frit covered with a 3 cm thick layer of Celite *rac*-**19** (0.187 g, 0.3 mmol, 21%) was isolated as a yellow oil. Residual cyclooctene could not be removed.

IR: $\tilde{\nu}$ = 3055 (w), 2918 (s, C-H), 2855 (m, C-H), 2321 (w), 2104 (w), 1947 (w), 1623 (m), 1463 (m, C-H), 1435 (s, P-Ph), 1392 (w), 1361 (w, *t*-Bu), 1261 (m), 1156 (w), 1100 (s), 1015 (s, *t*-Bu), 920 (w), 805 (s, Cp), 745 (s, Cp), 687 (s) cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.93 (d, $^2J_{H,P}$ = 13.0 Hz, 9H, CH_3), 1.23–2.07 (m, 14H, coe-H), 2.64 (m, 2H, PCH_2CH_2), 2.86 (m, 2H, PCH_2), 4.70 (d, $J_{H,P}$ = 2.4 Hz, 1H, PCH_2CH_2CCHCH), 4.86 (s, 1H, PCH_2CH_2CCH), 5.02 (s, 1H, PCH_2CH_2CCHCH), 5.28 (s, 1H, PCH_2CH_2CCH), 7.14 (m, 3H, *o*-, *p*-H), 7.93 (t, $^3J_{H,P}$ = 8.2 Hz, 2H, *m*-H) ppm. ^{13}C-NMR (100.6 MHz, C_6D_6): δ = 21.6 (d, $^2J_{C,P}$ = 0.7 Hz, PCH_2CH_2), 27.0 (d, $^2J_{C,P}$ = 4.0 Hz, CH_3), 31.6 (d, $^1J_{C,P}$ = 23.9 Hz, CCH_3), 33.2 (coe-C), 34.8 (coe-C), 36.6 (coe-C), 36.8 (coe-C), 46.4 (d, $^1J_{C,P}$ = 46.5 Hz, PCH_2), 72.0 (d, $J_{C,P}$ = 1.9 Hz, PCH_2CH_2-CCHCH), 76.8 (d, $J_{C,P}$ = 2.4 Hz, PCH_2CH_2CCHCH), 83.7 (d, $J_{C,P}$ = 9.5 Hz, PCH_2CH_2CCH), 89.8 (d, $J_{C,P}$ = 8.2 Hz, PCH_2CH_2CCH), 105.1 (d, $^3J_{C,P}$ = 5.9 Hz, PCH_2CH_2C), 127.4 (d, $^2J_{C,P}$ = 9.0 Hz, *o*-CH), 129.3 (d, $^4J_{C,P}$ = 2.3 Hz, *p*-CH), 134.4 (d, $^3J_{C,P}$ = 9.7 Hz, *m*-CH), 136.5 (d, $^1J_{C,P}$ = 34.1 Hz, $PCCH$) ppm. ^{31}P NMR (162 MHz, C_6D_6): δ = 35.3 ppm. MS: *m*/*z* (%) = 560 (12) [M^+], 450 (12) [M^+ − coe], 392 (47), 366 (100), 257 (19) [M^+ − Ir − coe]. HRMS (M^+ = $C_{25}H_{36}IrP$) calcd 560.2184, found 560.2180.

Chloro-{η^5:η^1[2-(*tert*-butylphenylphosphanyl)ethyl]-cyclopentadienyl}-nickel(II) (*rac*-20)

At −78 °C butyllithium in hexane (6.4 mL, 10.2 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (1.438 g, 8.7 mmol) in THF (30 mL). After stirring at 20 °C for 2 h spiro[2.4]hepta-4,6-diene (**4**, 0.9 mL, 9.0 mmol) was added, and the solution was stirred at 65 °C for 2 h. Then the mixture was cooled to −78 °C, and $NiCl_2$ (1.350 g, 10.3 mmol) was added, and the mixture was slowly warmed to 20 °C. After stirring for 1 h the solvent was removed at reduced pressure, and the residue was taken up with diethyl ether (5 mL). After filtration through a frit covered with a 3 cm thick layer of Celite, solvent removal at reduced pressure, and purification of the residue by column chromatography (3 × 20 cm, SiO_2, TBME) *rac*-**20** [2.122 g, 6.1 mmol, 70%, purity ≥ 95% (^{1}H-NMR)] was isolated as a purple solid, mp 105.5 °C.

IR: $\tilde{\nu}$ = 3077 (w), 2945 (m, C-H), 2916 (m), 2862 (m, C-H), 1610 (w), 1460 (m, C-H), 1437 (m, P-Ph), 1394 (w), 1361 (m, *t*-Bu), 1183 (m), 1162 (m), 1102 (m), 1022 (m, *t*-Bu), 847 (m, Cp), 785 (s, Cp), 755 (s), 688 (s), 617 (m) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.43 (d, $^3J_{H,P}$ = 15.1 Hz, 9H, CH_3), 1.39 (m, 1H, PCH_2CH_2), 1.45 (m, 2H, PCH_2CH_2), 2.44 (m, 1H, PCH_2), 2.69 (m, 1H, PCH_2), 5.55 (dd, $^3J_{H,P}$ = 1.3, 2.2 Hz, 1H, PCH_2CH_2CCH), 5.76 (d, $^3J_{H,P}$ = 2.1 Hz, 1H, PCH_2CH_2CCH), 5.82 (dt, $^3J_{H,P}$ = 1.5, 3.3 Hz, 1H, PCH_2CH_2-CCHC*H*), 5.96 (t, $^3J_{H,P}$ = 1.7 Hz, 1H, PCH_2CH_2CCHCH), 7.62 (t, $^2J_{H,P}$ = 2.6 Hz, 3H, *o*-, *p*-H), 8.30 (ddd, $^3J_{H,P}$ = 1.6, 7.9, 10.1 Hz, 2H, *m*-H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 22.2 (d, $^2J_{C,P}$ = 4.4 Hz, PCH_2CH_2), 25.5 (d, $^2J_{C,P}$ = 3.8, CH_3), 30.7 (d, $^1J_{C,P}$ = 21.2 Hz, $PCCH_3$), 33.4 (d, $^1J_{C,P}$ = 27.0, PCH_2), 93.7 (PCH_2CH_2CCHCH), 94.6 (d, $^3J_{C,P}$ = 7.0 Hz, PCH_2CH_2C), 96.6 (d, $^4J_{C,P}$ = 6.3 Hz, PCH_2CH_2CCH), 98.1 (PCH_2CH_2CCHCH), 99.6 (d, $^4J_{C,P}$ = 5.5 Hz, PCH_2CH_2CCH), 127.4 (d, $^2J_{C,P}$ = 9.3 Hz, *o*-CH), 127.8 (d, $^1J_{C,P}$ = 32.5, $PCCH$), 130.0 (d, $^4J_{C,P}$ = 2.3 Hz, *p*-CH), 132.6 (d, $^3J_{C,P}$ = 10.1 Hz, *m*-CH) ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 99.3 ppm. MS: *m*/*z* (%) = 350 (76) [M^+], 358 (100) [M^+ − NiCl], 182 (50), 126 (59), 91 (11), 79 (10), 57 (13) [*t*-Bu^+]. HRMS (M^+ = $C_{17}H_{22}NiPCl$) calcd 350.0501, found 350.0499.

Dichloro{η^5:η^1[2-(*tert*-butylphenylphosphanyl)ethyl]-cyclopentadienyl}-chromium(III) (*rac*-21)

At −78 °C butyllithium in hexane (2.9 mL, 3.7 mmol, 1.6 M) was added dropwise to *tert*-butylphenylphosphane (0.518 g, 3,1 mmol) in THF (15 mL). After stirring at 20 °C for 2 h spiro[2.4]hepta-4,6-diene (**4**, 0.3 mL, 3.3 mmol) was added, and the solution was stirred at 65 °C for 2 h. Then the mixture

was cooled to −78 °C, and $Cr(THF)_3Cl_3$ (1.16 g, 3.1 mmol) was added, and the mixture was slowly warmed to 20 °C. After stirring for 12 h the solvent was removed at reduced pressure, and the residue was washed with pentane and then taken up with boiling toluene (10 mL). After filtration through a frit covered with a 3 cm thick layer of Celite, the solution was concentrated and cooled to −25 °C. *rac*-**21** (0.570 g, 1.5 mmol, 48%) was obtained as a blue solid, mp 239.9 °C.

IR: $\tilde{\nu}$ = 3092 (w), 3055 (w), 2959 (w, C-H), 2361 (w), 1474 (m, C-H), 1435 (m, P-Ph), 1366 (m, *t*-Bu), 1172 (m), 1100 (m), 1053 (w), 892 (w), 819 (m), 810 (s, Cp), 747 (s, Cp), 699 (s) cm^{-1}. MS: *m*/*z* (%) = 379 (30) [M^+], 288 (54), 286 (100), 202 (44), 124 (26), 109 (37), 91 (36), 57 (76) [*t*-Bu^+]. HRMS (M^+ = $C_{17}H_{22}Cl_2CrP$) calcd 379.0241, found 379.0242. Anal. ($C_{17}H_{22}Cl_2CrP$) calcd C 52.86; H 7.30, found C 52.90; H 7.03.

Crystal structure analysis:[45] empirical formula $C_{17}H_{22}Cl_2CrP$, molecular weight 380.22, crystal system monoclinic, space group $P2_1/c$, a = 15.428(3) Å, b = 16.376(5) Å, c = 15.847(3) Å, α = 90.00°, β = 115.182(19)°, γ = 90.00°, V = 3623.3(14) $Å^3$, Z = 8, d_{calcd} = 1.394 g cm^{-1}, $F(000)$ = 1576.0, μ = 1.006 mm^{-1}, Stoe IPDS diffractometer, T = 297 K, MoK_α (λ = 0.71073 Å), θ_{min} = 1.92°, θ_{max} = 26.14°, 50 517 measured reflections ($-18 \le h \le 18$, $-20 \le k \le 20$, $-19 \le l \le 19$), 7080 independent, 3591 observed reflections, R_{int} = 0.1203, R = 0.0343, wR = 0.0558, residual electron density 0.366 and −0.237 e $Å^{-3}$, Gof = 0.841, refinement program SHELXL-97, N_{ref} = 3591, N_{par} = 379.

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