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Syntheses and Structures of Sterically Congested Linear and Branched Cobalta[*n*]triangulanes**

Sergei I. Kozhushkov,[a] Jan Foerstner,[b] Alf Kakoschke,[b] Dirk Stellfeldt,[b] Li Yong,[b] Rudolf Wartchow,[c] Armin de Meijere,*[a] and Holger Butenschön*[b]

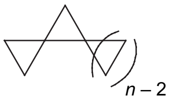
Dedicated to Professor K. Peter C. Vollhardt on the occasion of his 60th birthday

Abstract: Treatment of {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}cobalt(I) chloride (**5**) with methylenecyclopropane (**3**) or bicyclopropylidene (**4**), as well as with their spirocyclopropanated analogues methylenespiropentane (**7**), cyclopropylidenespiropentane (**10**), or 7,7′-bi(dispiro[2.0.2.1]heptylidene) (**15**) in the presence of sodium amalgam at −50 °C, furnished the stable cobalt complexes **6**, **9**, **8**, **11**, and **16**, respectively, in 72, 83, 84, 86, and 54 % isolated yield, respectively. The complexes **14** and **16** were also obtained by ligand exchange of the ethene complex {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-ethene)cobalt(I) (**12**) with **13** and **15** in 79 and 52 % yield, respectively. The X-ray crystal-structure analyses of complexes **9**, **14**, and **16**, as well as the NMR-spectroscopic data of all complexes, reveal that they can be regarded as linear and branched cobalta[*n*]triangulanes. The thermal stability of complexes **6**, **8**, and **9** up to 109, 145, and 160 °C was determined by differential thermal analysis-thermogravimetry (DTA-TG) analysis.

Keywords: cobalt · spiro compounds · strained molecules · structure elucidation · triangulanes

Introduction

Among the inherently strained[1] oligocycles with embedded cyclopropane moieties, linear (**1**) and branched (**2**) [*n*]triangulanes,[2] that is, hydrocarbons that consist of spiroannelated cyclopropane rings only, are of special interest: in spite of their high strain, which in each case significantly exceeds that of the sum of the separate three-membered rings,[3] these hydrocarbons are surprisingly stable.



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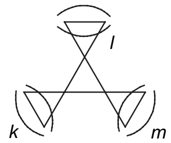

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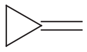

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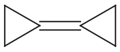

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Relative to the meanwhile reasonably large number of all carbon-based triangulanes, with the current records being a linear[4] as well as a branched[5] [15]triangulane, far fewer heterocyclic triangulanes are known, and this certainly reflects enhanced reactivity of the three-membered heterocycles.[2a,6] Almost nothing is known about metalla[*n*]triangulanes because the organometallic chemistry of cyclopropane derivatives is dominated by ring-opening reactions.[1b,7] However, metal-mediated substitutions on vinylcyclopropane derivatives[8] and cycloadditions with the simplest methylene-

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[a] Dr. S. I. Kozhushkov, Prof. Dr. A. de Meijere
Institut für Organische und Biomolekulare Chemie der
Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen (Germany)
Fax: (+49) 551-399-475
E-mail: Armin.deMeijere@chemie.uni-goettingen.de

[b] Dr. J. Foerstner, Dr. A. Kakoschke, D. Stellfeldt, Dr. L. Yong,
Prof. Dr. H. Butenschön
Institut für Organische Chemie der Universität Hannover
Schneiderberg 1B, 30167 Hannover (Germany)
Fax: (+49) 511-762-4616
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de

[c] Dr. R. Wartchow
Institut für Anorganische Chemie der Universität Hannover
Callinstraße 9, 30167 Hannover (Germany)

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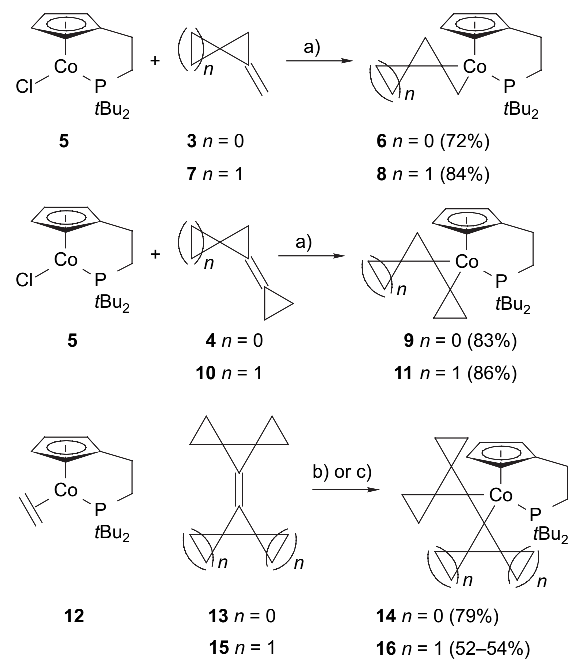
triangulane, methylenecyclopropane (**3**), and its derivatives[9] as well as bicyclopropylidene (**4**)[10] can be achieved with retention of one or both of the rings, respectively. In particular, strained alkenes have an increased ability to accept back-bonding and are, therefore, coordinated preferentially to transition metals.[11] It is this feature that is used frequently to stabilize otherwise unstable alkenes and alkynes by complexation.[12] In view of their high-lying HOMOs,[13,14] methylenecyclopropane (**3**) and especially bicyclopropylidene (**4**)[15] should be strong π-bases capable of efficiently donating electron density into the vacant orbitals of transition metals. Indeed, complexes of a few transition metals, including cobalt and titanium, with methylenecyclopropane (**3**) and bicyclopropylidene (**4**) have been reported.[9a,b,16] From the structural and electronics point of view, such complexes can be considered as metallaspiropentane and metalladispiro[2.0.2.1]heptane derivatives.[17] Here, we report the synthesis and structural characterization of some cobalt complexes of **3** and **4**, as well as of higher methylenetriangulanes and bicyclopropylidenes. These complexes can be considered as higher linear and branched cobalta[*n*]triangulanes.

Results and Discussion

One of the reliable methods to prepare cobalt complexes of sensitive ligands is complexation with the {[2-(di-*tert*-butylphosphanyl-*P*)ethyl]-η^5-cyclopentadienyl}cobalt(I) fragment (CoCp#), in which the cyclopentadienyl ligand and the pendant phosphane side-arm coordinate at the metal to form a rather stable chelate.[18] A convenient route to such complexes is the reductive complexation starting from the paramagnetic chloro complex **5** in the presence of sodium amalgam and the new ligand.[19] This method was selected for the preparation of linear cobalta[*n*]triangulanes from carbocyclic methylenetriangulanes and spirocyclopropanated bicyclopropylidenes (Scheme 1).

Thus, by treating **5** with methylenecyclopropane **3** or its spirocyclopropanated analogue **7** in the presence of sodium amalgam at −50 °C, the cobalt complexes **6** and **8** were isolated after recrystallization as red-brown crystals in 72 and 84 % yield, respectively (Scheme 1). Under the same conditions, bicyclopropylidene (**4**) and monospirocyclopropanated bicyclopropylidene **10** gave the corresponding products **9** and **11** in even higher yields (83 and 87 %, respectively). The former was obtained in the form of large brown crystals with edge length of up to 7 mm after crystallization from diethyl ether. Alternatively, this type of compound may be prepared by ligand exchange of the ethene complex {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-ethene)cobalt(I) (**12**).[18b] This approach was tested for the more sterically demanding dispirocyclopropanated bicyclopropylidene **13**. Indeed, the corresponding complex **14** was isolated in comparable yield (79 %). However, this method appeared to have no advantages, as the complex **16** from the tetraspirocyclopropanated bicyclopropylidene **15** was obtained in very similar (and lower, in accord with increased steric-demand problems) yields by both methods (Scheme 1).



Scheme 1. Preparation of linear cobaltatriangulanes **6**, **8** and **9**, **11** as well as branched cobaltatriangulanes **14**, **16**. Reagents and conditions: a) Na/Hg, THF, −50 to 20 °C; b) **5**, Na/Hg, THF, −50 to 20 °C; c) **12**, THF, −50 °C, 3–6 h.

All of the prepared complexes were characterized by recording adequate IR, NMR, and mass spectra; the base peak in the latter corresponds to the CoCp# fragment resulting from complete decomplexation (see Experimental Section). The NMR spectra of complexes **9** and **16** indicate a plane of symmetry through the cobalt atom and the center of the former double bond, whereas NMR spectra of the other complexes disclose their asymmetric structure and, therefore, exclude any low-barrier rotation around one of the C−Co bonds.[19] This indicates a large back-bonding effect accepted by methylenetriangulanes as well as bicyclopropylidenes, and these complexes should be considered as cobalta[*n*]triangulanes containing cobaltacyclopropane moieties. To confirm this, suitable crystals of compounds **9**,[16b] **14**, and **16** were subjected to X-ray structural analyses (Figure 1).

According to the results, the carbocyclic three-membered rings in the 7-cobaltadispiro[2.0.2.1]heptane moiety in all three cases have undergone remarkable out-of-plane bending by 40 (**9**), 42 (**14**), and 40° (**16**) at both termini of the former double bond, whereas in carbocyclic[3]triangulane this angle is only 30°. This fact, and also the lengthening of the coordinated former double bonds, which were found to be 1.401(5) (**9**), 1.420(2) (**14**), and 1.435(4) Å (**16**), indicates a large back-bonding effect increasing in parallel with ligand strain. In the free-ligand bicyclopropylidenes **4** (1.304(2) Å,[15b,21]), **13** (1.309(1) Å[22]), and **15** (1.305(4) Å[23]), the double-bond lengths are shorter by 7.4, 8.5, and 10.0 %,

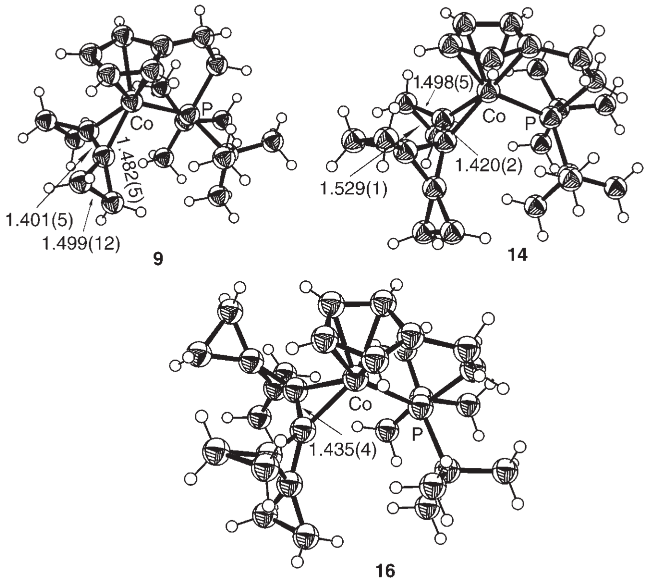


Figure 1. Molecular structures of {η^5:η^1[2-di(*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-bicyclopropylidene)cobalt(I) (**9**), {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2–7-cyclopropylidenedispiro-[2.0.2.1]heptane)cobalt(I) (**14**), and {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}{η^2–7,7′-bi(dispiro[2.0.2.1]heptylidene)}cobalt(I) (**16**) in the crystal.[20] Selected bond lengths [Å] shown represent mean values; thermal ellipsoids are shown at the 50 % probability level.

respectively. For comparison, an analogous complexation of ethene as in **12** (1.330 Å) expanded its double-bond length by 5 % only (from 1.330 to 1.396 Å).[18b] The change in hybridization upon coordination of the double-bond carbon atoms in the bicyclopropylidenes leads to a dramatic decrease in strain energy due to a decrease in the endocyclic interorbital angles. This, along with the electron-withdrawing properties of a cobaltacyclopropane ring,[24] leads to the observed shortening of the distal bonds (with respect to the metallacycle) in the cyclopropane rings (1.499(12) vs 1.539(2) Å for **9** and 1.529(1) vs 1.538(1) Å for **14**), and lengthening of the proximal bonds (1.482(5) vs 1.467(2) Å for **9** and 1.498(5) vs 1.465(1) Å for **14**) in contrast to the uncomplexed bicyclopropylidenes **4** and **13**.

Similar to the carbocyclic [*n*]triangulanes, the newly prepared cobalta[*n*]triangulanes **6**, **8**, **9**, **11** and **14**, **16** all demonstrate remarkable thermal stabilities. A differential thermal analysis-thermogravimetry (DTA-TG) analysis revealed that compounds **6**, **8**, and **9** can be heated up to 109, 145, and 160 °C, respectively, without decomposition. At 109, 145, and 168 °C a strongly exothermic reaction takes place, for which $\Delta H = -34.3$, -41.0, and $-52.1\,\mathrm{kcal\,mol^{-1}}$, respectively, with a relative loss of mass of 4.6 (**6**) and 11.5 % (**9**). The TG curve of **8** was not resolved sufficiently clearly to allow the data for this compound to be determined. The decrease in mass corresponds to a loss of 16 (**6**) and 40 $\mathrm{g\,mol^{-1}}$ (**9**), resembling the loss of methylene from **6** and cyclopropylidene from **9**. This suggests that at elevated temperatures, both the cobalta[2]triangulane **6** with a terminal cobaltacyclopropane and the cobalta[3]triangulane **9** with an internal cobaltacyclopropane moiety undergo fragmentation in terms of a [2+1] cycloreversion, leaving behind 1′-cobaltamethylenecyclopropanes, that is, cyclopropylidenecobalt complexes. After DTA-TG analysis of **9**, the residual material was also analyzed by FAB-MS. The results indicate a molecular ion peak at $m/z = 1304$ and fragment peaks corresponding to the loss of CoCp# ($m/z = 296$) and cyclopropylidene ($m/z = 40$) units. This hints towards the formation of a $(\mathrm{CoCp\#})_4$ cluster involving three cyclopropylidene rings upon thermal decomposition of **9**. However, all attempts to isolate this product in pure form for subsequent characterization failed. In contrast to the tetraspirocyclopropanated bicyclopropylidene **15**, octamethylbicyclopropylidene could not be transformed at all into an analogous cobalt complex. This is probably due to the steric encumbrance of the double bond in the latter, as well as the fact that ring strain is released in **15** upon progression to complex **16**. Furthermore, the steric strain would even increase upon progression from octamethylbicyclopropylidene to its complex.

With regard to the remarkable stability of the complexes prepared, one might ask whether this is a consequence of the chelate nature of the CoCp# system, which, in addition, causes conformational rigidity, or rather of the steric shielding by the di-*tert*-butylphosphanyl group, which makes the coordinated methylenecyclopropane and bicyclopropylidene ligands less accessible. To gain further insight, similar complexes with less sterically demanding substituents attached to the phosphorus tether ought to be prepared.

In conclusion, cyclopentadienylcobalt chelate complexes of highly strained methylenecyclopropane and bicyclopropylidene, as well as their sterically congested spirocyclopropanated derivatives, were prepared and structurally characterized. The complexes are remarkably stable, no metal insertions into the highly strained cyclopropane bonds were observed. This behavior is in contrast to that of related cyclopropene-derived complexes.[25] In the current complexes, the coordinated double bonds undergo a significant out-of-plane bending, thus, these complexes are more suitably described as cobalta|*n*]triangulanes rather than as alkene complexes.

Experimental Section

General: Methylenecyclopropane (**3**),[26] methylenespiropentane (**7**),[27] and bicyclopropylidenes **4**,[28] **10**,[29] **13**,[29] and **15**[5b] were prepared according to previously published procedures. All operations in anhydrous solvents were performed under argon in flame-dried glassware. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl under an atmosphere of argon, pentane was distilled from sodium. All other chemicals were used as commercially available. NMR spectra were recorded by using Bruker AC 200 (200 MHz for ^{1}H and 81 MHz for ^{31}P NMR), AVS 200 (200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C NMR), and AVS 400 (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C NMR, and 161.9 MHz for ^{31}P NMR) instruments in C_6D_6. Multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements, if not otherwise specified. Chemical shifts are refer to $\delta_{\mathrm{TMS}} = 0.00$ ppm according to the chemical shifts of residual C_6D_5H signals. IR spectra were recorded by using a Bruker ISS 25, a Perkin–Elmer FT 580, and a FT 1710 with KBr pellets, capillary film, as a chloroform solution, or as ATR spectra. Mass spectra were measured by using Finnigan AM 400 (EI and HREI, at 70 eV, preselected ion-peak-matching at $R \gg 10000$ to be within ±2 ppm of the exact masses) and Fisons VG Autospec (CI, at 70 eV) spectrometers.

Crystal-structure determinations: Suitable crystals of the compounds were obtained by recrystallization from diethyl ether (**9**), pentane at −28 °C (**14**) and −25 °C (**16**). The data were collected by using a Stoe IPDS (imaging plate) diffractometer (graphite monochromator, $\mathrm{Mo}_{K\alpha}$ radiation, ω-scan). The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The treatment of hydrogen atoms varied for the different structures, but in most cases the hydrogen atoms were located in the difference Fourier map and were refined isotropically. The parameters of crystal data collections and structure refinements are presented in Table 1.[20]

Table 1. Crystal and data-collection parameters for compounds **9**, **14**, and **16**.

Compound	**9**	**14**	**16**
formula	$C_{21}H_{34}CoP$	$C_{25}H_{38}CoP$	$C_{29}H_{42}CoP$
M_r	376.38	428.48	480.53
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
crystal size [mm]	0.70 × 0.60 × 0.60	0.30 × 0.06 × 0.15	0.41 × 0.37 × 0.28
a [Å]	9.658(1)	17.166(2)	8.696(2)
b [Å]	14.731(2)	15.676(2)	10.200(2)
c [Å]	21.282(4)	18.850(3)	15.613(4)
α [°]	84.21(2)	90	73.55(3)
β [°]	80.64(1)	113.79(2)	79.24(3)
γ [°]	88.46(1)	90	77.93(3)
V [Å^3]	2972.1(8)	4641.4(13)	1286.8(5)
Z	3	8	2
F(000)	1212	1840	516
ρ [g cm^{-3}]	1.262	1.226	1.240
μ [mm^{-1}]	0.945	0.082	0.743
T [K]	153(2)	300(2)	300(2)
θ_{max} [°]	25.06	24.35	26.13
reflns collected	17372	38099	18405
reflns independent	10.506	7350	4706
R_{int}	0.0248	0.0316	0.0364
R_1 [$I = 2\sigma(I)$]	0.0544	0.0334	0.0462
wR_2 (all data)	0.1208	0.0938	0.1160
no. of parameters refined	401	487	245
GoF	1.030	0.45	1.111
largest diff. peak, hole [e Å^{-3}]	1.304, −1.304	0.17, −0.31	0.711, −0.565

Preparation of compounds 6, 8, 9, and 11: General procedure (GP) 1

The respective alkene was added dropwise at −50 °C to a stirred solution of {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}cobalt(I) chloride (**5**) in anhydrous THF under an atmosphere of argon, and the resulting solution was stirred at this temperature for 5 min. After this, sodium amalgam (1 % Na) was added dropwise, the reaction mixture was allowed to warm up slowly to −45 °C (melting point of sodium amalgam), and was then stirred vigorously at this temperature for an additional 10 min. The reaction mixture was allowed to warm up slowly to 25 °C and was stirred at this temperature for an additional 1 h. The solvent was condensed off under reduced pressure into a cold trap. The residue was taken up with anhydrous diethyl ether, filtered through a pad of Celite under an atmosphere of argon, and the Celite was washed with Et_2O until the filtrate was completely colorless. The solvent from the combined ethereal filtrates was condensed off under reduced pressure to a cold trap, and the residue was purified by recrystallization.

{η^5:η^1[2-Di(*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-methylenecyclopropane)cobalt(I) (6): From **5** (110 mg, 0.33 mmol), methylenecyclopropane (**3**) (72 mg, 1.33 mmol), and Na/Hg (7.3 g) in anhydrous THF (30 mL), compound **6** (84 mg, 72 %) was obtained according to GP 1 after recrystallization from diethyl ether as a deep-red-brown microcrystalline powder. M.p.: exothermal decomposition at 109 °C with 4.6 % loss of the mass, as determined by DTA-TG; ^{1}H NMR (400 MHz, C_6D_6): δ = 3.88 (br s, 3 H; Cp-H), 3.65 (br s, 1 H; Cp-H), 2.45 (d, $^3J_{P,H}$ = 2.0 Hz, 1 H; $=CH_2$), 1.95–1.75 (m, 4 H; 2 CH_2), 1.74 (d, $^3J_{P,H}$ = 8 Hz, 1 H; $=CH_2$), 1.17 (d, $^3J_{P,H}$ = 12.0 Hz, 9 H; 3 CH_3), 1.05 (d, $^3J_{P,H}$ = 12.0 Hz, 9 H; 3 CH_3), 1.05–0.85 ppm (m, 4 H; *c*Pr-H); ^{13}C NMR (50 MHz, C_6D_6, APT): δ = 110.4 (d, $^3J_{C,P}$ = 6.9 Hz, C), 86.7 (d, $^2J_{C,P}$ = 5.5 Hz, CH), 80.9 (CH), 80.7 (d, $^2J_{C,P}$ = 6.2 Hz, CH), 80.3 (CH), 38.4 (d, $^1J_{C,P}$ = 19.4 Hz, CH_2), 35.0 (d, $^1J_{C,P}$ = 8.4 Hz, C), 33.7 (d, $^1J_{C,P}$ = 6.5 Hz, C), 31.7 (br d, $^2J_{C,P}$ = 6.8 Hz, C), 31.2 (d, $^2J_{C,P}$ = 3.7 Hz, 3 CH_3), 30.2 (d, $^2J_{C,P}$ = 5.2 Hz, 3 CH_3), 25.0 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 15.7 (d, $^2J_{C,P}$ = 6.3 Hz, CH_2), 13.7 (CH_2), 13.4 ppm (d, $^3J_{C,P}$ = 1.5 Hz, CH_2); ^{31}P NMR (81 MHz, C_6D_6): δ = 97.2 ppm; IR (KBr): $\tilde{\nu}$ = 3092 (w), 3036 (m), 2964 (s, $-CH_2-$, CH_3), 2896 (s, $-CH_2-$, CH_3), 1560 (w), 1472 (s), 1416 (m), 1388 (s, *t*Bu), 1364 (s, *t*Bu), 1264 (w), 1232 (w), 1116 (m), 1092 (s), 1016 (m), 880 (m), 796 (s), 736 (w), 664 (w), 620 (m), 572 (m), 480 (s), 436 cm^{-1} (m); MS (EI, 70 eV, 50 °C): *m*/*z* (%): 350 (19) [M^+], 295 (100) [$M^+ - C_4H_7$], 240 (34) [$M^+ - 2\,C_4H_7$], 184 (87) [$M^+ - 2\,C_4H_7 - C_4H_8$], 137 (40), 91 (37), 74 (20); HRMS: *m*/*z* calcd for $C_{19}H_{32}CoP$: 350.1576; found: 350.1575.

{η^5:η^1[2-Di(*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-methylenespiro[2.2]pentane)cobalt(I) (8): From **5** (534 mg, 1.62 mmol), methylenespiropentane (**7**) (130 mg, 1.62 mmol), and Na/Hg (30.0 g) in anhydrous THF (50 mL), compound **8** (505 mg, 84 %) was obtained according to GP 1 after recrystallization from Et_2O as brown crystals. M.p.: exothermal decomposition at 144.9 °C, as determined by DTA-TG; ^{1}H NMR (400 MHz, C_6D_6): δ = 5.31 (br s, 2 H; Cp-H), 4.29 (br s, 1 H; Cp-H), 3.74 (br s, 1 H; Cp-H), 2.29 (d, $^3J_{P,H}$ = 2.0 Hz, 1 H; $=CH_2$), 2.50–1.65 (m, 6 H; 3 CH_2), 1.24 (d, $^3J_{P,H}$ = 11.4 Hz, 9 H; 3 CH_3), 1.20 (d, $^3J_{P,H}$ = 11.8 Hz, 9 H; 3 CH_3), 0.98 (d, $^3J_{P,H}$ = 7.0 Hz, 1 H; $=CH_2$), 0.79 ppm (m, 4 H; *c*Pr-H); ^{13}C NMR (100 MHz, C_6D_6): δ = 111.0 (C), 80.9 (2 CH), 79.9 (d, $^2J_{C,P}$ = 6.0 Hz, CH), 78.5 (d, $^2J_{C,P}$ = 5.2 Hz, CH), 38.2 (d, $^1J_{C,P}$ = 22.7 Hz, CH_2), 34.9 (d, $^1J_{C,P}$ = 8.4 Hz, C), 33.7 (d, $^1J_{C,P}$ = 6.8 Hz, C), 31.7 (br d, $^2J_{C,P}$ = 6.8 Hz, C), 30.8 (d, $^2J_{C,P}$ = 4.0 Hz, 3 CH_3), 30.6 (d, $^2J_{C,P}$ = 5.2 Hz, 3 CH_3), 24.9 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 21.9 (CH_2), 21.5 (C), 13.4 (d, $^2J_{C,P}$ = 6.8 Hz, CH_2), 9.9 (CH_2), 6.6 ppm (CH_2); IR (KBr): $\tilde{\nu}$ = 3112 (w), 3052 (m), 3024 (w), 2952 (s, $-CH_2-$, CH_3), 2900 (s, $-CH_2-$, CH_3), 2868 (s, $-CH_2-$, CH_3), 1684 (w), 1628 (w), 1560 (w), 1472 (s), 1392 (m, *t*Bu), 1368 (w, *t*Bu), 1260 (w), 1140 (s, alkene compl.), 1052 (w, Cp-R), 1020 (m, Cp-R), 976 (w), 936 (w), 816 (s, Cp), 796 (m), 660 (w), 576 (w), 572 (w), 492 (w), 464 cm^{-1} (w); HRMS: *m*/*z* calcd for $C_{21}H_{34}CoP$: 376.1730; found: 376.1743; elemental analysis calcd (%) for $C_{21}H_{34}CoP$ (376.41): C 67.01, H 9.10; found: C 66.13, H 8.68.

{η^5:η^1[2-Di(*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-bicyclopropylidene)cobalt(I) (9): From **5** (1.02 g, 3.08 mmol), bicyclopropylidene (**4**) (246 mg, 3.1 mmol), and Na/Hg (40.0 g) in anhydrous THF (50 mL), compound **9** (961 mg, 83 %) was obtained according to GP 1 after recrystallization from Et_2O as brown crystals. M.p.: exothermal decomposition at 168 °C with 11.5 % loss of the mass, as determined by DTA-TG; ^{1}H NMR (200 MHz, C_6D_6): δ = 5.09–4.00 (m, AA′BB′, ΣJ = 4.0 Hz, 4 H; Cp-H), 2.10–1.75 (m, 4 H; 2 CH_2), 1.20 (d, $^3J_{P,H}$ = 11.5 Hz, 18 H; 6 CH_3), 1.00 (br d, J = 9.0 Hz, 4 H; *c*Pr-H), 0.55 ppm (br s, 4 H; *c*Pr-H); ^{13}C NMR (50 MHz, C_6D_6, APT): δ = 112.2 (d, $^3J_{C,P}$ = 6.9 Hz, C), 86.9 (d, $^2J_{C,P}$ = 6.9 Hz, 2 CH), 80.6 (2 CH), 38.6 (d, $^1J_{C,P}$ = 19.3 Hz, CH_2), 33.8 (d, $^1J_{C,P}$ = 8.2 Hz, 2 C), 30.6 (d, $^2J_{C,P}$ = 4.8 Hz, 6 CH_3), 24.9 (d, $^2J_{C,P}$ = 6.3 Hz, CH_2), 23.8 (br d, $^2J_{C,P}$ = 11.0 Hz, 2 C), 12.0 (2 CH_2), 11.4 ppm (d, $^3J_{C,P}$ = 2.4 Hz, 2 CH_2); IR (KBr): $\tilde{\nu}$ = 3073 (w, Cp-H), 2950 (s, $-CH_2-$, CH_3), 2903 (s, $-CH_2-$, CH_3), 2870 (s, $-CH_2-$, CH_3), 1634 (w), 1473 (s), 1393 (w), 1369 (w, *t*Bu), 1261 (w), 1180 (w, alkene compl.), 1142 (br s), 1020 (w, Cp-R), 936 (w), 817 (s, Cp), 727 (w), 634 (w), 494 (w), 436 cm^{-1} (w); MS (EI, 70 eV, 50 °C): *m*/*z* (%): 376 (27) [M^+], 295 (100) [$M^+ - C_6H_9$], 254 (15), 240 (46) [$M^+ - C_4H_8 - C_6H_8$], 184 (74) [$M^+ - C_6H_8 - 2\,C_4H_8$], 137 (35), 106 (22), 91 (21), 79 (77) [C_6H_7]$^+$; HRMS: *m*/*z* calcd for $C_{21}H_{34}CoP$: 376.17300; found: 376.17280; elemental analysis calcd (%) for $C_{21}H_{34}CoP$ (376.41): C 67.01, H 9.10; found: C 66.85, H 8.82.

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{η^5:η^1-[2-Di(*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}[(η^2-(cyclopropylidenespiropentane)]cobalt(I) (11): From **5** (170 mg, 0.51 mmol), cyclopropylidenespiropentane (**10**) (54 mg, 0.51 mmol), and Na/Hg (10.0 g) in anhydrous THF (30 mL), compound **11** (177 mg, 86 %) was obtained according to GP 1 after recrystallization from Et_2O as deep-red crystals; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.21$ (br s, 1 H; Cp-H), 4.93 (br s, 1 H; Cp-H), 3.95 (br s, 1 H; Cp-H), 3.89 (br s, 1 H; Cp-H), 2.01–1.67 (m, 4 H; 2 CH_2), 1.18 (d, $^3J_{P,H} = 11.8$ Hz, 9 H; 3 CH_3), 1.09 (d, $^3J_{P,H} = 11.8$ Hz, 9 H; 3 CH_3), 0.88–0.76 (m, 6 H; *c*Pr-H), 0.69 (d, $^4J_{P,H} = 2.9$ Hz, 2 H; *c*Pr-H), 0.57–0.52 ppm (m, 2 H; *c*Pr-H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 112.4$ (C), 90.0 (d, $^2J_{C,P} = 5.1$ Hz, CH), 82.0 (CH), 81.7 (CH), 76.8 (d, $^2J_{C,P} = 6.4$ Hz, CH), 39.0 (d, $^1J_{C,P} = 19.7$ Hz, CH_2), 34.9 (d, $^1J_{C,P} = 8.3$ Hz, C), 34.8 (d, $^1J_{C,P} = 8.3$ Hz, C), 34.0 (br d, $^2J_{C,P} = 7.6$ Hz, C), 31.9 (d, $^2J_{C,P} = 5.1$ Hz, 3 CH_3), 30.8 (d, $^2J_{C,P} = 5.1$ Hz, 3 CH_3), 27.9 (br d, $^2J_{C,P} = 8.9$ Hz, C), 25.6 (d, $^2J_{C,P} = 5.7$ Hz, CH_2), 21.3 (CH_2), 18.9 (d, $^3J_{C,P} = 3.2$ Hz, CH_2), 11.6 (CH_2), 11.1 (d, $^3J_{C,P} = 2.5$ Hz, C), 7.9 (CH_2), 5.2 ppm (CH_2); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 96.5$ ppm; IR (KBr): $\tilde{\nu} = 3084$ (w, Cp-H), 3052 (w, Cp-H), 2960 (s, *sp*^{3}-C-H), 2900 (s, *sp*^{3}-C-H), 2864 (s, *sp*^{3}-C-H), 1472 (m), 1416 (m), 1384 (m, *t*Bu), 1364 (m, *t*Bu), 1304 (w), 1260 (m), 1176 (m), 1120 (m), 1072 (s), 1012 (s), 932 (w), 892 (m), 796 (s), 664 (m), 620 (w), 600 (w), 572 (w), 496 (w), 468 (m), 432 cm^{-1} (w); MS (EI, 70 eV, 100 °C): *m*/*z* (%): 402 (8) [M^+], 345 (5) [$M^+ - C_4H_9$], 296 (100) [$M^+ - C_8H_{10}$], 254 (17), 240 (57) [$M^+ - C_8H_{10} - C_4H_8$], 184 (88) [$\mathrm{M}^+ - C_8H_{10} - 2\,C_4H_8$], 137 (32) [$Co(Cp)CH_2^+$], 106 (5) [$C_8H_{10}^+$], 105 (11) [$C_8H_9^+$], 91 (40) [$C_7H_7^+$], 79 (14), 57 (29) [$C_4H_9^+$]; HRMS: *m*/*z* calcd for $C_{23}H_{36}CoP$: 402.1887; found: 402.1885.

Preparation of compounds 14, 16: General procedure (GP) 2: The respective alkene was added dropwise at −50 °C to a vigorously stirred solution of {η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2-ethene)cobalt(I) (**12**)[18b] in anhydrous THF under an atmosphere of argon, and the resulting solution was stirred at this temperature for the indicated time. The solvent was condensed off under reduced pressure into a cold trap. The residue was taken up with anhydrous pentane, filtered through a pad of Celite under an atmosphere of argon, and the Celite was washed with the same solvent until the filtrate was completely colorless. The solvent from the combined filtrates was condensed off under reduced pressure to a cold trap, and the residue was purified by triturating with pentane at low temperature followed by filtration.

{η^5:η^1[2-(Di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}(η^2–7-cyclopropylidenedispiro[2.0.2.1]heptane)cobalt(I) (14): From **12** (500 mg, 1.54 mmol) and 7-cyclopropylidenedispiro[2.0.2.1]heptane (**13**) (205 mg, 1.55 mmol) in anhydrous THF (50 mL), compound **14** (521 mg, 79 %) was obtained according to GP 2 (3 h of stirring) as a red-brown air-sensitive solid. M.p. 106 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.71$ (s, 1 H; Cp-H), 4.15 (s, 1 H; Cp-H), 3.91 (s, 1 H; Cp-H), 3.56 (br s, 1 H; Cp-H), 2.38 (m, 2 H; CH_2), 1.81 (m, 2 H; CH_2), 1.23 (d, $^3J_{P,H} = 8.2$ Hz, 4 H; *c*Pr-H), 1.06 (d, $^3J_{P,H} = 11.4$ Hz, 9 H; 3 CH_3), 1.00 (d, $^3J_{P,H} = 12.0$ Hz, 9 H; 3 CH_3), 0.92–0.41 ppm (m, 8 H; *c*Pr-H); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 110.6$ (d, $^3J_{P,C} = 12.6$ Hz, C), 87.5 (d, $^2J_{C,P} = 5.6$ Hz, CH), 82.6 (d, $^2J_{P,C} = 14.8$ Hz, CH), 80.8 (d, $^2J_{P,C} = 6.0$ Hz, CH), 78.5 (d, $^2J_{C,P} = 5.6$ Hz, CH), 39.2 (d, $^3J_{C,P} = 20.5$ Hz, C), 38.9 (d, $^3J_{C,P} = 19.7$ Hz, C), 35.5 (d, $^4J_{C,P} = 6.8$ Hz, 2 CH_2), 34.6 (d, $^1J_{C,P} = 10.0$ Hz, CH_2), 33.8 (d, $^4J_{C,P} = 6.4$ Hz, 2 CH_2), 33.0 (d, $^1J_{C,P} = 4.0$ Hz, C), 32.9 (d, $^1J_{C,P} = 4.0$ Hz, C), 31.8 (d, $^2J_{C,P} = 4.8$ Hz, 3 CH_3), 31.1 (d, $^2J_{C,P} = 4.4$ Hz, 3 CH_3), 27.4 (d, $^2J_{C,P} = 10.8$ Hz, C), 25.7 (d, $^2J_{C,P} = 6.8$ Hz, CH_2), 22.9 (d, $^2J_{C,P} = 10.6$ Hz, C), 9.7 (d, $^3J_{C,P} = 3.6$ Hz, CH_2), 4.0 ppm (d, $^3J_{C,P} = 4.0$ Hz, CH_2); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 94.5$ ppm; IR (KBr): $\tilde{\nu} = 2964$ (s, $-CH_2-$, CH_3), 2872 (m, $-CH_2-$, CH_3), 1600 (m), 1472 (m), 1392 (m), 1368 (m), 1136 (m, alkene compl.), 1016 cm^{-1} (w); MS (EI, 70 eV, 180 °C): *m*/*z* (%): 428 (5) [M^+], 401 (6) [$M^+ - C_2H_3$], 387 (13) [$M^+ - C_2H_3 - CH_2$], 312 (52), 297 (100), 240 (59), 184 (100), 137 (46), 115 (20), 91 (44), 77 (21); elemental analysis calcd (%) for $C_{25}H_{38}CoP$ (428.48): C 70.08, H 8.94; found: C 69.17, H 8.68.

{η^5:η^1[2-(Di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl}{η^2–7,7′-bi(dispiro[2.0.2.1]heptylidene)}cobalt(I) (16):

a) From **5** (360 mg, 1.09 mmol), 7,7′-bi(dispiro[2.0.2.1]heptylidene) (**15**) (200 mg, 1.09 mmol), and Na/Hg (20.5 g) in anhydrous THF (50 mL), compound **16** (285 mg, 54 %) was obtained according to GP 1 after recrystallization from Et_2O as a red-brown air-sensitive solid.

b) From **12** (359 mg, 1.11 mmol) and 7,7′-bi(dispiro[2.0.2.1]heptylidene) (**15**) (204 mg, 1.11 mmol) in anhydrous THF (50 mL), compound **16** (279 mg, 52 %) was obtained according to GP 2 (6 h stirring) as a red-brown air-sensitive solid.

16: M.p. 113 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.20$ (s, 2 H; Cp-H), 4.22 (s, 2 H; Cp-H), 2.05 (m, 2 H; CH_2), 1.82 (m, 2 H; CH_2), 1.25 (mc, 8 H; *c*Pr-H), 1.03 (d, $^3J_{P,H} = 12.4$ Hz, 18 H; 6 CH_3), 0.69 ppm (mc, 8 H; *c*Pr-H); ^{13}C NMR (100.6 MHz, C_6D_6, APT): $\delta = 111.7$ (d, $^3J_{P,C} = 6.9$ Hz, C), 82.5 (2 CH), 79.1 (d, $^2J_{P,C} = 5.3$ Hz, 2 CH), 38.3 (d, $^2J_{C,P} = 19.9$ Hz, 4 C), 33.2 (d, $^1J_{C,P} = 7.7$ Hz, 2 C), 30.5 (d, $^2J_{C,P} = 5.0$ Hz, 6 CH_3), 25.7 (CH_2), 24.8 (br d, $^2J_{C,P} = 8.6$ Hz, 2 C), 23.0 (CH_2), 7.5 (d, $^3J_{C,P} = 3.0$ Hz, 4 CH_2), 7.2 ppm (d, $^3J_{C,P} = 4.2$ Hz, 4 CH_2); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 93.8$ ppm; IR (KBr): $\tilde{\nu} = 3067$ (m), 2986 (s, $-CH_2-$, $-CH_3$), 1736 (w), 1560 (w), 1475 (m), 1450 (m), 1365 (w), 1130 (w, alkene compl.), 1098 (m), 1039 (s), 1020 (s, Cp-R), 933 (m), 888 (m), 803 (m), 686 (w), 494 cm^{-1} (w); MS (EI, 70 eV, 120 °C): *m*/*z* (%): 482/481/480 (1/6/15) [M^+], 423 (3) [$M^+ - C_4H_9^+$], 333 (3), 296 (100) [$M^+ - C_{14}H_{16}$], 240 (34), 184 (44), 153 (15), 128 (21), 91 (20), 71 (4); HRMS: *m*/*z* calcd for $C_{29}H_{42}CoP$: 480.235613; found: 480.235443.

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