Reactions of Cyclopropenone Derivatives with a Cyclopentadienylcobalt(I) Chelate: Formation of a Cobaltacyclobutenone and a Transformation of 2,2-Dimethoxycyclopropenone to Methyl Acrylate at Cobalt

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Reactions of cyclopropenone derivatives with the [2-(di-*tert*-butylphosphanyl)ethyl]cyclopentadienylcobalt(I) chelate system were investigated. Ethene complex **2** reacts with diphenylcyclopropenone under cobalt insertion to give cobaltacyclobutenone chelate complex **6** in 91% yield. **6** was characterized crystallographically and shows a structure similar to that of a known platinacyclobutenone. Thermoanalysis of **6** indicated a reaction at elevated temperature, which was shown to be a cycloreversion at 60 °C leading to known diphenylethyne and carbonyl complexes **7** and **9**. Attempts to reduce the metallacyclobutenone with lithium tetrahydridoaluminate resulted in the cycloreversion reaction at a temperature as low as −100 to −90 °C, the lithium cation acting as a Lewis acid. The reaction of dimethoxycyclopropene complex **4** with zinc triflate unexpectedly resulted in the formation of methyl acrylate complex **13**, which was characterized crystallographically.

Introduction

Transition metal complexes with cyclopropene ligands are rare due to frequent ring-opening reactions of the strained three-membered rings, usually leading to the formation of oligomers or vinylcarbene complexes.[1−5] Recently we reported reactions of cyclopentadienyl chelates **1** and **2** with 3,3-diphenylcyclopropene, 3,3-dimethylcyclopropene, and 3,3-dimethoxycyclopropene.[6] Whereas the reaction with 3,3-diphenylcyclopropene gave the corresponding 3,3-diphenylvinylcarbene complex in high yield, it was possible to isolate cyclopropene complexes **3** and **4** as stable complexes in 71% and 93% yield, respectively.[6] In continuation of this research we were interested to use the strained, readily accessible diphenylcyclopropenone (**5**) as a possible ligand.[7] Cyclopropenones, mostly **5**, have been used in reactions with some metal complexes.[8,9] Visser observed complexation of methylcyclopropenone to platinum at −65 °C; upon warming to −30 °C an insertion of the metal into the strained ring occurred.[10] Baddley observed the formation of a platinacyclobutenone, which was structurally characterized, upon treatment of Pt(PPh$_3$)$_4$ with **5**.[11]

Results and Discussion

Treatment of ethene complex **2** with diphenylcyclopropenone (**5**) in THF at 20 °C for 3 days gave a 91% yield of cobaltacyclobutenone **6**, which was characterized spectroscopically. In the IR spectrum the carbonyl absorption was observed at 1660 cm^{-1} and compares well with a value of 1652 cm^{-1}, which had been observed for a platinacyclobutenone.[11] In the ^{13}C NMR spectrum the signal assigned to the carbonyl carbon atom is found at $\delta = 205.3$ ($^2J_{C,P} = 18.5$ Hz).[11] It was possible to obtain crystals of **6**, which were suitable for an X-ray crystal structure analysis (Figure 1).

The structure of cobaltacyclobutenone **6** is rather similar to that of the known platinacyclobutenone. The metallacyclobutene ring is almost planar, and the bond lengths and angles do not deviate much in both structures. As a consequence of the different atomic radii, the bonds involving cobalt in **6** are somewhat shorter than the corresponding ones in the platinacyclobuten-

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10.1021/om0000818 CCC: $19.00

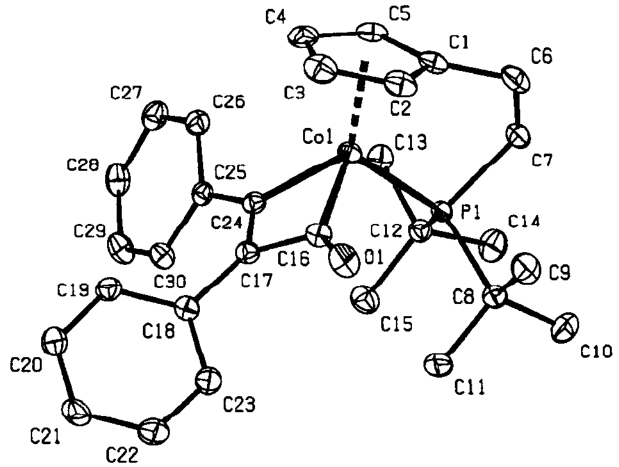
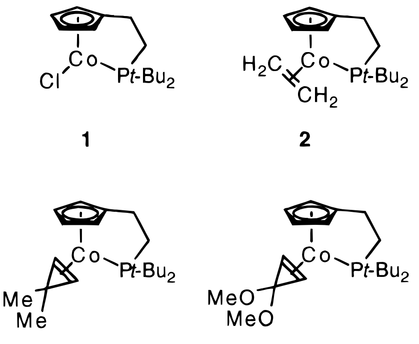
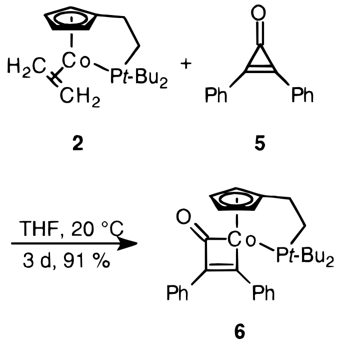


Figure 1. Structure of **6** in the crystal. Selected bond lengths (Å), bond and dihedral angles (deg): Co1−C1 2.112(2), Co1−C2 2.089(2), Co1−C3 2.089(2), Co1−C4 2.123(2), Co1−C5 2.153(2), Co1−C16 1.936(2), Co1−C24 1.966(2), Co1−P1 2.246(1), C16−C17 1.459(3), C17−C24 1.364(3), C16−O1 1.214(2), C1−C2 1.413(3), C1−C5 1.426(3), C1−C6 1.494(3), C2−C3 1.403(3), C3−C4 1.409(3), C4−C5 1.400(3), C6−C7 1.521(3), C7−P1 1.849(2); C24−Co1−C16 67.3(1), Co1−C16−C17 95.2(1), C17−C16−O1 131.0(2), O1−C16−Co1 133.4(2), C16−C17−C24 100.0(2), C17−C24−Co1 97.2(1), C24−Co1−P1 103.0(1), C16−Co1−P1 100.8(1), C1−C6−C7 111.4(2), C6−C7−P1 111.9(1); Co1−C24−C17−C16 3.6(2), C1−C6−C7−P1 36.9(2).

Scheme 1



Scheme 2



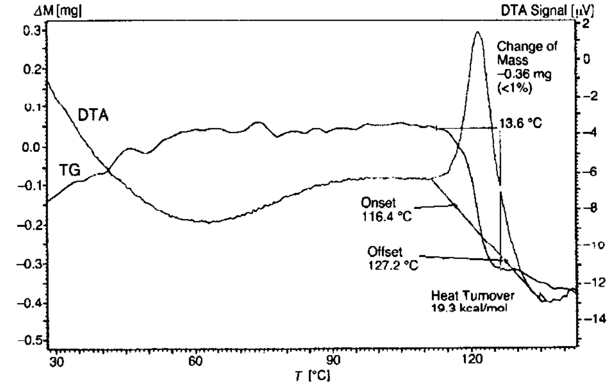
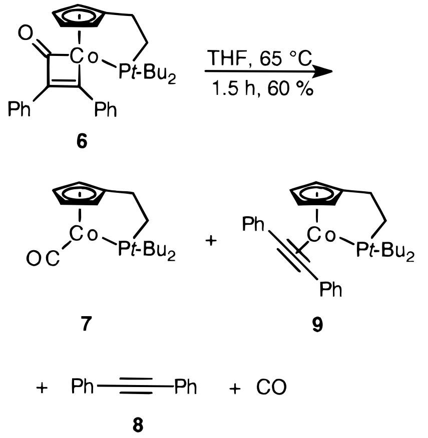
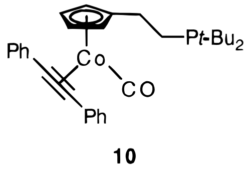


Figure 2. DTA/TG plot of **6**.

Scheme 3



Scheme 4



one: Co1−C16 is 1.936(2) Å, as compared to 2.08(6) Å in the platinum compound, and Co1−C24 is 1.966(2) Å, as compared to 2.09(4) Å in the platinum complex. Consequently the intracyclic angle at Co is somewhat larger in **6** than in the platinacyclobutenone [67.3(1)° vs 62°]. The bond length of the carbonyl group and the intracyclic angle at C17 are almost equal in both cases. As usual in chelate complexes like **6**, the ethylene bridge between the cyclopentadienyl and the phosphane ligands shows some torsion.[12−15]

Stang reported the reaction of (PPh$_3$)$_3$RhCl with **5** at 80 °C in benzene to give (PPh$_3$)$_2$RhCl(CO) and diphenylethyne. The intermediate rhodacyclobutenone, which was not isolated, was supposed to decompose with formation of diphenylethyne and the observed carbonyl complex.

A DTA/TG measurement of **6** indicates a reaction with less than 1% loss of mass above 116 °C (Figure 2). It was found that this reaction corresponds to the cycloreversion of **6** to the known carbonyl complex **7**[13,16] and diphenylethyne (**8**). When thermolysis of **6** was carried out in THF at 65 °C, a 60% yield of a mixture of carbonyl and diphenylethyne complexes **7** and **9**[13,14,16] in addition

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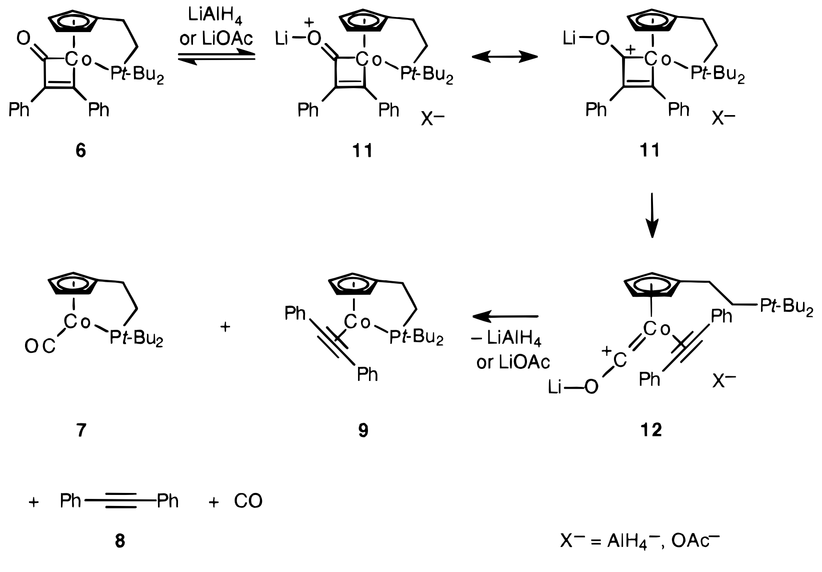
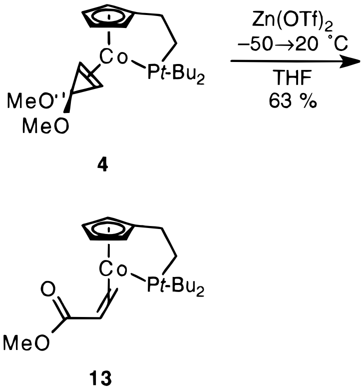
Scheme 5



Scheme 6



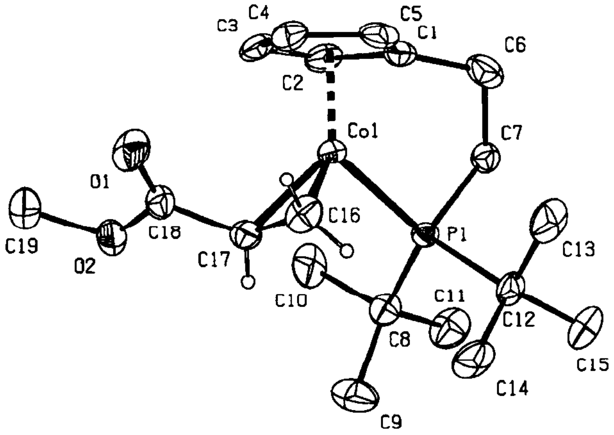


Figure 3. Structure of **13** in the crystal. Selected bond lengths (Å), bond and dihedral angles (deg): Co1–C1 2.033(4), Co1–C2 2.098(4), Co1–C3 2.100(4), Co1–C4 2.063(4), Co1–C5 2.064(4), Co1–C16 1.965(6), Co1–C17 2.000(5), Co1–P1 2.217(1), C1–C2 1.406(6), C1–C5 1.414(6), C1–C6 1.477(6), C2–C3 1.400(5), C3–C4 1.398(6), C4–C5 1.422(6), C6–C7 1.546(5), C7–P1 1.855(4), C16–C17 1.393(7), C17–C18 1.446(6); Co1–C16–C17 70.8(3), Co1–C17–C16 68.1(3), C16–C17–C18 120.6(5); C1–C6–C7–P1 40.3(5), C16–C17–C18–O1 8.4(9), C16–C17–C18–O2 173.1(5).

to some diphenylethyne (**8**) was obtained. The ratio of **7** and **9** varied within a number of experiments. The formation of diphenylethyne complex **9** is remarkable because it is known that carbonyl complex **7** does not undergo a thermal ligand exchange process with diphenylethyne (**8**) to give **9**.[13,16] Therefore the formation of **9** has to be regarded as a direct result of the cycloreversion of **6**. An intermediate to be considered in this reaction is **10**, with a decoordinated phosphane sidearm. **10** could be the direct product of the cycloreversion process. Recomplexation of the sidearm would liberate either CO or diphenylethyne (**8**), possibly depending on the degree of bond rotation around the cyclopentadienyl–cobalt bond, which results in different directions for the phosphorus atom to approach the metal. This line of thought implies an associative intramolecular ligand exchange reaction at cobalt. In a first attempt to investigate its chemical behavior **6** was treated with lithium tetrahydridoaluminate in THF at −78 → 20 °C. Surprisingly, instead of a reduction of the carbonyl group the cycloreversion to a mixture of **7** and **9** occurred. In another experiment **6** was treated with LiAlH$_4$ at −100 → −90 °C with a similar result. This is remarkable because of the low reaction temperature and the unclear role of the LiAlH$_4$. Could it be that the lithium cation was active instead of the tetrahydridoaluminate anion? This would imply LiAlH$_4$ unusually acting as a Lewis acid. To test this, solid lithium acetate was added to a solution of **6** in THF at −78 to −25 °C, followed by quenching with ethanol. Again **7** and **9** were obtained as the only isolated products. A possible route from **6** to **7** and **9** involves an attack of Li$^+$ at the carbonyl oxygen atom to give **11**, whose carbonyl carbon atom apparently is sterically shielded to such an extent, that the cycloreversion is faster than an AlH$_4^-$ attack, which would induce the reduction in the case of LiAlH$_4$. Whereas the role of the cation as a Lewis acid assisting the reduction process has been investigated to some extent for borohydride reductions,[17–21] this is much less the case for aluminohydride reductions.[18,19]

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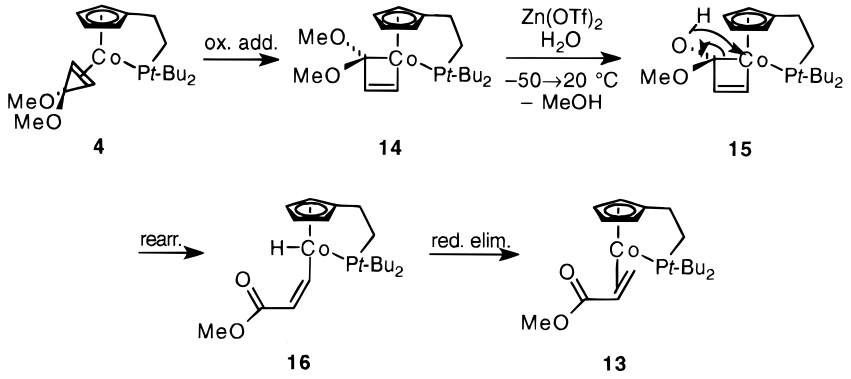
Scheme 7



As it was not possible to obtain a cyclopropenone complex by treatment of **2** with **5**, we tried to prepare such a complex starting from acetal complex **4**. So far, attempts to hydrolyze the acetal moiety with formation of the cyclopropenone ligand failed. However, when **4** was treated with zinc triflate at low temperature, a new product was obtained in 63% yield, which was identified as methyl acrylate complex **13**. **13** was completely characterized, including an X-ray structure analysis depicted in Figure 3. The structure shows only a slight distortion of the conjugated olefinic ligand out of the planarity of the π system.[22] The orientation of the alkene moiety is almost perpendicular as compared to that in a cationic molybdenum acrylate complex.[23] Similar to the structures of similar chelate complexes, **13** shows some torsion around the ethylene bridge between the cyclopentadienyl and the phosphane parts of the ligand system.

There is some evidence that in **4** cobalt inserts into one of the strained cyclopropene single bonds with formation of cobaltacyclobutene **14**. In some expriments this intermediate was observed and shown to react forming the corresponding vinylcarbene complex. However, because these were only incompletely characterized, and because the reactions lacked reproducibility, we refrained from publishing these results so far. We think that in the following step the Lewis acid zinc triflate causes partial acetal hydrolysis with formation of hemiacetal **15**, presumably by an onium cation intermediate with a small amount of water present.[24,25]

In the next step a hydride shift in combination with a ring opening would give vinyl hydride **16**. This step could also be formulated with reversed arrows, then being a proton shift along with a ring opening. A final reductive elimination leads to the methyl acrylate complex **13**. This mechanism is similar to the one proposed for the rerrangement of 3,3-dimethylcyclopropene to isoprene, which we reported earlier.[6] In this context a recent communication by Nakamura deserves interest, in which the reaction of a cyclopropenone acetal to an α,β-unsaturated ester is described to take place in the presence of copper or silver triflate, presumably also via a vinylmetal intermediate.[26] Both cases contrast with the known reaction of diphenylcyclopropene to *cis*-1,2-diphenylacrylic acid, which takes place under basic reaction conditions.[7]

Experimental Section

General Procedures. All operations were performed in flame-dried reaction vessels in an argon atmosphere using the Schlenk technique. Diethyl ether and THF were distilled from sodium−potassium alloy/benzophenone. Pentane was distilled from calcium hydride. ^{1}H NMR: Bruker WP 200 SY (200.1 MHz), AM 400 (400.1 MHz). ^{13}C NMR: Bruker WP 200 SY (50.3 MHz), AM 400 (100.1 MHz). Signal multiplicities were determined with APT and DEPT techniques. The phase of the signals is marked by (+) or (−), where the (+) indicates a positive phase for C and CH$_2$ and a (−) a negative phase for CH and CH$_3$. Chemical shifts refer to $\delta_{TMS} = 0$ or to residual solvent signals.[27,28] ^{31}P NMR: Bruker AM 400 (162 MHz), 85% aqueous H$_3$PO$_4$ as external standard. IR: Perkin-Elmer FT-IR 580 and 1710. MS: Finnigan MAT 112, 312 at 70 eV. HRMS: Finnigan MAT 312, VG Autospec, peak matching with PFK. Combustion analyses: Heraeus CHN Rapid. DTA/TG: Linseis Thermobalance L 81, inert gas argon. Melting points (uncorrected) were determined in sealed glass tubes with an apparatus according to Dr. Tottoli. Column chromatography: silica gel (J. T. Baker, 40 μm) was degassed by heating it with a heat gun at reduced pressure followed by setting it under normal pressure with argon. This sequence was repeated five times. Separations were performed using flash chromatography.[29]

Cobaltacyclobutenone 6. A solution of 142 mg (0.44 mmol) of ethene complex **2**[14] and 90 mg (0.44 mmol) of diphenylcyclopropenone (**5**) in 15 mL of THF was stirred for 3 days at 20 °C. After solvent removal at reduced pressure crystallization from diethyl ether at 7, −20, and −78 °C gave 202 mg (0.4 mmol, 91%) of **6** as red-brown crystals [mp 117 °C (DTA/TG)]. Suitable crystals for structure analysis were obtained from diethyl ether at −28 °C over 3 days.

IR (KBr): $\tilde{\nu} = 3076$ cm^{-1} (w), 3052 (w), 3004 (w), 2960 (w, −CH$_2$−, CH$_3$), 2900 (m, −CH$_2$−, CH$_3$), 2864 (m, −CH$_2$−, CH$_3$), 1660 (s, C═O), 1592 (m), 1572 (w), 1544 (m), 1476 (m), 1440 (m), 1388 (w, *t*-Bu), 1368 (w, *t*-Bu), 1256 (w), 1176 (m), 1056 (m, Cp−R), 1056 (m, Cp−R), 812 (m, Cp), 780 (m), 748 (m), 692 (m), 668 (w), 560 (m), 504 (w), 464 (w). ^{1}H NMR (200 MHz, [D$_6$]-benzene): $\delta = 1.05$ (d, 9H, 9(10,11)-H or 13(14,15)-H, $^3J_{P,H} = 12.4$ Hz), 1.38 (d, 9H, 9(10,11)-H or 13(14,15)-H, $^3J_{P,H} = 12.5$

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Hz), 1.58−1.81 (m, 2H, 6-H), 2.00−2.19 (m, 2H, 7-H), 4.48 (m, 1H, 2-H or 3-H or 4-H or 5-H), 4.63 (m, 1H, 2-H or 3-H or 4-H or 5-H), 4.63 (m, 1H, 2-H or 3-H or 4-H or 5-H), 6.95−7.06 [m, 2H, 21-H, 28-H], 7.12−7.24 [m, 4H, 19(23)-H or 26(30)-H], 7.67−7.58 [m, 4H, 20(22)-H or 27(29)-H]. ^{13}C NMR (100 MHz, [D$_6$]-benzene): δ = 24.4 (d, C-6, $^2J_{\mathrm{P,C}}$ = 4.0 Hz), 29.5 (d, C-9(10,11) or C-13(14,15), $^2J_{\mathrm{P,C}}$ = 2.8 Hz), 30.1 (d, C-9(10,11) or C-13(14,15), $^2J_{\mathrm{P,C}}$= 4,0 Hz), 35.6 (d, C-8 or C-10, $^1J_{\mathrm{P,C}}$ = 10.0 Hz), 37.4 (d, C-8 or C-10, $^1J_{\mathrm{P,C}}$ = 12.5 Hz), 39.3 (d, C-7, $^1J_{\mathrm{P,C}}$ = 20.5 Hz), 79.0 (C-2 or C-3 or C-4 or C-5), 82.6 (d, C-2, or C-3 or C-4 or C-5, $^2J_{\mathrm{P,C}}$ = 1.2 Hz), 86.1 (d, C-2 or C-3 or C-4 or C-5, $^2J_{\mathrm{P,C}}$ = 6.0 Hz), 88.4 (d, C-2 or C-3 or C-4 or C-5, $^2J_{\mathrm{P,C}}$ = 5.6 Hz), 120.8 (d, C-1, $^3J_{\mathrm{P,C}}$ = 9.3 Hz), 125.9 [C-19(23), C-26(30) or C-20(22), C-27(29) or C-21, C-28], 128.4 [C-19(23), C-26(30) or C-20(22), C-27(29) or C-21, C-28], 128.53 [C-19(23), C-26(30) or C-20(22), C-27(29) or C-21, C-28], 131.7 (d, C-25, $^4J_{\mathrm{C,P}}$ = 0.8 Hz), 156.9 (d, C-17, $^3J_{\mathrm{P,C}}$ = 2.81 Hz), 170.3 (br.d, C-24, $^2J_{\mathrm{P,C}}$ = 20.1 Hz), 205.3 (d, C-16, $^2J_{\mathrm{P,C}}$ = 18.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]-benzene): δ = 94.8. MS (70 eV, 80 °C) *m/z* (%): 324 (8) [M$^+$ − C$_{14}$H$_{10}$], 296 (14) [M$^+$ − C$_{15}$H$_{10}$O], 240 (9) [M$^+$ − C$_{15}$H$_{10}$O − C$_4$H$_8$], 185 (18) [M$^+$ − C$_{15}$H$_{10}$O − C$_4$H$_8$ − C$_4$H$_7$], 178 (100) [C$_{14}$H$_{10}$$^+$], 152 (9), 137 (9), 89 (9), 76 (8). Anal. Calcd for C$_{30}$H$_{36}$OPCo (502.5): C, 71.71; H, 7.71. Found: C, 71.76; H, 7.50.

Crystal Structure Analysis of 6: C$_{30}$H$_{36}$OPCo, fw 502.49 g mol^{-1}, color red-brown, crystal size 1.04 × 0.78 × 1.85 mm, crystal system monoclinic, space group $P2_1/c$ (no. 14), a = 11.445(2) Å, b = 13.275(2) Å, c = 17.294(2) Å, α = 90°, β = 99.50(2)°, γ = 90°, V = 2591.5(7) Å^3, Z = 4, ρ_{calc} = 1.288 g cm^{-3}, $2\theta_{\mathrm{min}}$ = 3.6°, $2\theta_{\mathrm{max}}$ = 48.1°, Mo Kα, λ = 0.71073 Å, T = 300(2) K, μ = 7.4 cm^{-1}, F(000) = 1064 e, Stoe IPDS (imaging plate), 18 166 measured reflections (±13; ±15; −18−19), 3894 unique [$R(I)_{\mathrm{int}}$ = 0.044] and 3194 observed reflections [$I > 2\sigma(I)$], 298 refined parameters, transmission factors min, max 0.4618, 0.4687, spherical absorption correction (μR = 0.53), no extinction correction, structure solution with direct methods with SHELX-86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, R = 0.0265, R_{w} = 0.0656 [$w = 1/\sigma^2F_o{}^2 + (0.03P)^2$], P = [max ($F_o{}^2 + 2F_o{}^2$)]/3, minimal and maximal residual eletron density −0.19, 0.24 e Å^{-3}. The crystallographic data (without structure factors) of the structure were deposited at the Cambridge Crystallographic Data Centre (CCDC-137406). Copies of the data can be obtained from the following address in Great Britain: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + 44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk).

Thermolysis of 6. A 1360 mg (2.76 mmol) sample of **6** was heated in 50 mL of THF for 90 min at 65 °C. The color of the solution changed from brown-red to green-brown. The solvent was removed at reduced pressure into a cold trap, and the residue was taken up with 40 mL of diethyl ether and filtered through a P4 frit covered with a 1 cm thick layer of Celite. After solvent removal 816 mg (60%) of a green-brown oil was obtained, which was identified as a mixture of **7** and **9** (ca. 1:1) by comparison of the spectroscopic data (IR, NMR).[13]

Reaction of 6 with Lithium Tetrahydridoaluminate. (a) A 87 mg (0.17 mmol) sample of **6** and 1.6 mg (0.043 mmol) of lithium tetrahydridoaluminate in 10 mL of THF were stirred at −78 °C for 30 min. The mixture was allowed to warm to 25 °C over 3 h, was again cooled to −78 °C, and was quenched by addition of 0.2 mL of methanol. After solvent removal at reduced pressure the residue was taken up with 20 mL of diethyl ether and filtered through a P4 frit covered with a 2 cm thick layer of Celite. After solvent removal 37 mg of a red-brown powder was obtained, which was identified as a 1:1 mixture of **7** and **9** by comparison of the spectroscopic data (IR, NMR).[13,14,16]

(b) A 5 mg (0.001 mmol) sample of lithium tetrahydridoaluminate was added to a solution of 25 mg (0.05 mmol) of **6** in 10 mL of THF at −100 °C. Over 3 h the cooling bath temperature was allowed to increase to −90 °C. A 0.2 mL portion of ethanol was added, and the mixture was warmed to 25 °C. After removal of the volatiles at reduced pressure, the residue was taken up with 20 mL of diethyl ether and then filtered through a P4 frit covered with a 1 cm thick layer of Celite. After solvent removal at reduced pressure 11 mg of a red-brown powder was obtained, which was identified as a 1:1 mixture of **7** and **9** by comparison of the spectroscopic data (IR, NMR).[13,14,16]

Reaction of 6 with Lithium Acetate. At −78 °C 50 mg (0.08 mmol) of lithium acetate was added to 41 mg (0.08 mmol) of **6** in 10 mL of THF. Over 3 h the temperature rose to −25 °C. After cooling the soution again to −78 °C 0.2 mL of ethanol was added. After warming to 25 °C and removal of all volatiles in vacuo, a brownish powder was obtained, which was taken up with 20 mL of diethyl ether and filtered through a P4 frit covered with a 1 cm thick layer of Celite. After solvent removal at reduced pressure 18 mg of a red-brown powder was obtained, which was identified as a 1:1 mixture of **7** and **9** by comparison of the spectroscopic data (IR, NMR).[13,14,16]

Reaction of 4 with Zinc Triflate. A 100 mg (0.25 mmol) sample of **4** and 92 mg (0.25 mmol) of zinc triflate in 50 mL of THF were stirred at −50 °C for 30 min. Then the solution was allowed to warm to 25 °C over 12 h. After removal of volatiles at reduced pressure, the residue was taken up with 50 mL of a 1:1 mixture of pentane and diethyl ether. After filtration through a P4 frit covered with a 3 cm thick layer of Celite and washing with 10 mL of pentane, all solvents were evaporated to dryness at reduced pressure to give 61 mg (0.16 mmol; 63%) of **13** as a red-brown powder (mp 54 °C). Suitable crystals were obtained from a 1:1 mixture of diethyl ether and pentane at −28 °C over 14 days.

IR (CHCl$_3$): $\tilde{\nu}$ = 2963 cm^{-1} (s, −CH$_2$−, CH$_3$), 2904 (m, −CH$_2$−, CH$_3$), 1725 (s, ester C═O), 1454 (s), 1412 (m), 1024-(s, Cp−R), 866 (s, Cp), 819 (s). ^{1}H NMR (400 MHz, [D$_6$]-benzene): δ = 0.87 (d, 9H, 9(10,11)-H or 13(14,15)-H, $^3J_{\mathrm{P,H}}$ = 11.3 Hz), 1.11 (d, 9H, 9(10,11)-H or 13(14,15)-H, $^3J_{\mathrm{P,H}}$ = 11.5 Hz), 1.26 (m, 2H, 6-H or 7-H), 1.75 (m, 2H, 6-H or 7-H), 2.24 (dd, 1H, 16-H, $^3J_{\mathrm{H,H}\,(cis)}$ = 6.0 Hz, $^2J_{\mathrm{H,H}}$ = 1.5 Hz), 2.87 (m, 1H, 16-H), 3.17 (dt, 1H, 17-H, $^3J_{\mathrm{H,H}\,(trans)}$ = 9.0 Hz, $^3J_{\mathrm{H,H}}$ = 2.0 Hz), 3.59 (s, 3H, 19-H), 3.91 (m, 1H, 3-H or 4-H, $^4J_{\mathrm{P,H}}$ = 2.4 Hz), 4.00 (m, 1H, 3-H or 4-H, $^4J_{\mathrm{P,H}}$ = 2.6 Hz), 5.13 (m, 1H, 2-H or 5-H, $^4J_{\mathrm{P,H}}$ = 1.5 Hz), 5.31 (m, 1H, 2-H or 5-H, $^4J_{\mathrm{P,H}}$ = 1.0 Hz). ^{13}C NMR (100 MHz, [D$_6$]-benzene, APT): δ = 24.8 (+, d, C-6 or C-7, $^2J_{\mathrm{P,C}}$ = 6.1 Hz), 25.1 (+, d, C-16, $^2J_{\mathrm{P,C}}$ = 7.7 Hz), 29.5 (−, d, C-17, $^2J_{\mathrm{P,C}}$ = 1.1 Hz), 29.9 (−, d, C-9(10,11), $^2J_{\mathrm{P,C}}$ = 3.9 Hz), 30.7 (−, d, C-13(14,15), $^2J_{\mathrm{P,C}}$ = 3.9 Hz), 35.0 (+, d, C-8, $^1J_{\mathrm{P,C}}$ = 6.6 Hz), 35.3 (+, d, C-12, $^1J_{\mathrm{P,C}}$ = 9.1 Hz), 36.6 (+, d, C-6 or C-7, $^2J_{\mathrm{P,C}}$ = 5.0 Hz), 50.3 (−, s, C-19), 79.9 (−, d, C-2 or C-3 or C-4 or C-5, $^3J_{\mathrm{P,C}}$ = 6.6 Hz), 80.8 (−, d, C-2 or C-3 or C-4 or C-5, $^3J_{\mathrm{P,C}}$ = 1.0 Hz), 80.9 (−, d, C-2 or C-3 or C-4 or C-5, $^3J_{\mathrm{P,C}}$ = 1.4 Hz), 89.0 (−, d, C-2 or C-3 or C-4 or C-5, $^3J_{\mathrm{P,C}}$ = 5.0 Hz), 109.8 (+, d, C-1, $^3J_{\mathrm{P,C}}$ = 7.5 Hz), 180.3 (+, d, C-18, $^3J_{\mathrm{P,C}}$ = 1.4 Hz). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]-benzene): δ = 93.5 (s). MS (70 eV, 100 °C): *m/z* (%) 382 (3) [M$^+$], 381 (14) [M$^+$ − H], 324 (1) [M$^+$ − C$_4$H$_6$O$_2$], 296 (100) [M$^+$ − C$_4$H$_6$O$_2$ − C$_2$H$_3$], 240 (33) [M$^+$ − C$_4$H$_6$O$_2$ − C$_2$H$_3$ − ^{t}Bu], 184 (62) [M$^+$ − C$_4$H$_6$O$_2$ − C$_2$H$_3$ − ^{t}Bu − ^{t}Bu], 137 (23), 106 (5), 85 (3). HRMS: calcd for (C$_{19}$H$_{32}$O$_2$PCo) 382.147034; found 382.147192.

Crystal Structure Analysis of 13: C$_{19}$H$_{32}$CoO$_2$P, fw 382.35 g mol^{-1}, red-brown plate II (001) size 0.44 × 0.31 × 0.03 mm, crystal system monoclinic, space group $P2_1/a$ (no. 14), a = 17.748(2) Å, b = 13.011(2) Å, c = 17.979(2) Å, α = 90°, β = 108.66(1)°, γ = 90°, V = 3933.5(9) Å^3, Z = 8, ρ_{calc} = 1.291 g cm^{-3}, $2\theta_{\mathrm{min}}$ = 3.9°, $2\theta_{\mathrm{max}}$ = 48.3°, Mo Kα, λ = 0.71073 Å, T = 300(2) K, μ = 9.6 cm^{-1}, F(000) = 1632 e, Stoe IPDS (imaging plate), 24 070 measured reflections (±18; ±14; ±20), 5871 unique [$R(I)_{\mathrm{int}}$ = 0.100] and 2520 observed reflections [$I > 2\sigma(I)$], 439 refined parameters, transmission factors min, max 0.7081, 0.9714, numerical absorption correction, no extinction correction, structure solution with direct methods with SHELX-

86, refinement with SHELXL-93, hydrogen atoms in geometrically calculated positions, but H27, H28, H29, H27′, H28′, and H29′ free, $R = 0.0331$, $R_w = 0.0529$ [$w = 1/\sigma^2(F_o{}^2)$], R is based on F of 2520 reflections with $F_o > 4\sigma(F_o)$, R_w is based on F^2 of all 5871 independent reflections, $S = 0.63$, minimal and maximal residual eletron density −0.29, 0.26 e Å^{-3}. The crystallographic data (without structure factors) of the structure were deposited at the Cambridge Crystallographic Data Centre (CCDC-137405). Copies of the data can be obtained from the following address in Great Britain: CCDC, 12 Union Road, Cambrige CB2 1EZ, UK (fax: int. code + 44−1223/336−033, e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic thermal parameters, hydrogen atom positions, anisotropic thermal parameters, bond distances, bond angles, and torsional angles for **6** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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