# (Bicyclo[3.2.0]hepta-1,3-dienyl)cobalt(I) Complexes

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Three isomeric bicyclo[3.2.0]heptadienes **1**–**3** are compared by semiempirical calculations. Experimental attempts directed to the synthesis of derivatives of **1** are described. The synthesis, properties and some reactions of ($\eta^5$-bicyclo[3.2.0]hepta-1,3-dienyl)($\eta^4$-cycloocta-1,5-diene)cobalt(I) (**22**), including an X-ray crystal structure determination of the reaction product with diphenylethyne, the tetraphenylcyclobutadiene complex **30**, are presented.

Although numerous $\eta^5$-cyclopentadienyl and $\eta^6$-arene transition-metal complexes are known[1], only few containing a small ring anellated to the coordinated $\pi$ system have been prepared[2,3]. Small-ring anellated complexes differ from species with larger anellated rings (e.g. indane and tetralin complexes[3a,4]) in that the ligands are rigid, and this may preclude the adoption of a preferred conformation in the course of a reaction.

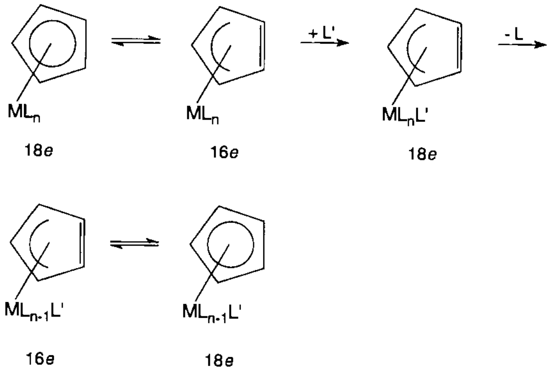
Complexes with a cyclopropane ring anellated to a complexed cyclopentadienyl or arene system are unknown[5a]; complexes of polycyclic cyclopropa-arenes with the metal coordinated to a ring further away from the site of anellation have, however, been reported[5b–d]. Benzocyclobutene complexes have been studied by us[3f–h,6] and others[3a–e], the first example having been described by Jackson et al.[3a]. At the start of our work only one example of a bicyclo[3.2.0]hepta-1,3-dienyl complex had been reported[2].

Basolo[7] was the first to show that ligand exchange reactions at transition-metal complexes may proceed by dissociative or associative paths. Associative reactions are preferentially observed for cyclopentadienyl complexes and have been suggested to occur by a so-called "ring-slippage reaction"[8] involving a reversible change in hapticity from $\eta^5$ to $\eta^3$, which allows the system to avoid a 20-electron intermediate. In the course of such a ring-slippage reaction the original cyclopentadienyl ligand changes its identitiy to an "allyl-ene". One may envision a corresponding process for $\eta^6$-arene complexes, which should proceed via a "diene-ene" intermediate.

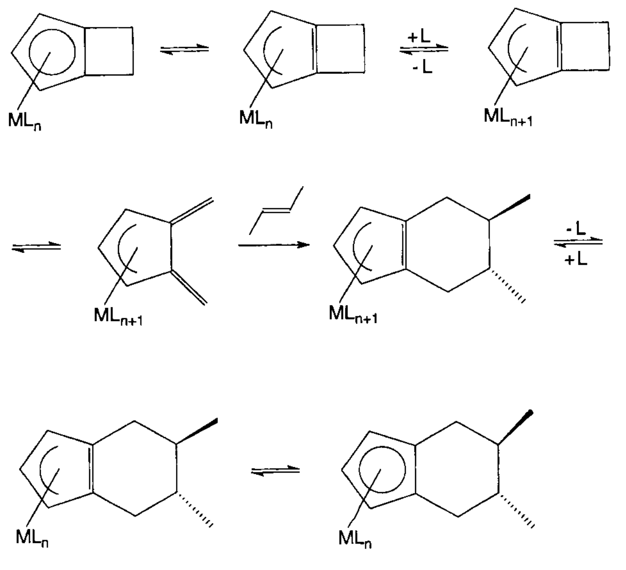
We are interested in finding reactions involving the uncomplexed double bond in such an allyl-ene intermediate. Are there reactions, which would not take place, if the temporarily decomplexed double bond were not present? Of course, such reactions would be preferred, if at the end of a reaction sequence a stable cyclopentadienyl or arene complex would be reformed.

The sequence we had in mind includes a ring-opening reaction of a bicyclo[3.2.0]hepta-1,3-dienyl complex yielding a 4,5-dimethylenecyclopentenyl intermediate, which may be regarded as a lower homolog of an *o*-quinodimethane complex. Subsequent [4 + 2] cycloaddition with a dienophile regenerates the stable cyclopentadienyl system. The driving force of the sequence would be the strain relief and the conversion of two $\pi$ bonds into two $\sigma$ bonds, which is characteristic of all [4 + 2] cycloadditions. Reaction sequences like this have recently been realized[6d,9].

Scheme 1. Associative ligand exchange by a *ring-slippage* reaction ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$); L = 2*e* donor; M = metal



Scheme 2. Projected reaction sequence; L = 2*e* donor; M = metal



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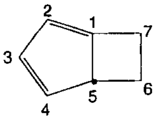
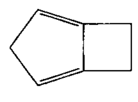
To test this idea, it was neccessary to synthesize suitable bicyclo[3.2.0]hepta-1,3-dienyl complexes. This paper describes attempts directed to the synthesis of (bicyclo[3.2.0]hepta-1,3-dienyl)cobalt(I) complexes, and the synthesis, characterization and chemistry of cycloocta-1,5-diene complex **22**. The realization of a ring-opening reaction cycloaddition sequence will soon be reported in a detailed paper. Some of the material has been the subject of preliminary communications[10].

## Results and Discussion

The structures of dienes **1**–**3**, anion **4**, and **5** were calculated[11] by using the MOPAC[12] program. The results are summarized in Table 1.



**1**



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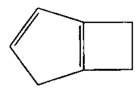

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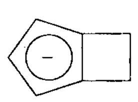
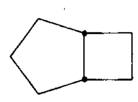


**4**



**5**

Table 1. Results obtained by a geometrical optimization with the MOPAC[12] program

| | Heat of formation[a] | Energy of HOMO[b] | Energy of LUMO[b] | Plane angle[c] |
|---|---|---|---|---|
| **1** | 77.6 | −8.8 | 0.4 | 39 |
| **2** | 76.5 | −9.1 | 0.6 | 0 |
| **3** | 87.4 | −8.6 | 0.3 | 0 |
| **4** | 69.1 | −2.2 | 7.5 | 0 |
| **5** | −10.5 | −10.9 | 3.4 | 66 |

[a] In kcal/mol. — [b] In eV. — [c] Angle between the mean planes through the carbon atoms of the four-membered and of the five-membered ring in °.

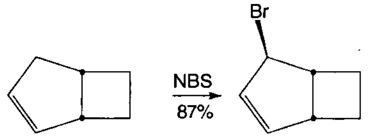
The data obtained reveal **3** as the most strained isomer. Its energy (heat of formation) is ca. 10–11 kcal/mol higher than those of **1** and **2**. The main origin is found in the contribution made by the elongated double bonds (C1–C5 1.39 Å, C2–C3 1.37 Å) and by the bending of the valence angles at the bridgehead carbon atoms (C4–C5–C6 156°, C2–C1–C7 156°). The energies of dienes **1** and **2** are almost equivalent. While the double bonds in **2** have standard bond lengths (C4–C5 1.34 Å, C1–C2 1.34 Å) the bending of the valence angles at the bridging carbon atoms is slightly increased (C4–C5–C6 159°, C2–C1–C6 159°) as compared to **3**.

The bridgehead $sp^3$ carbon atom in diene **2** decreases these values significantly (C4–C5–C6 130°, C2–C1–C7 143°) but simultaneously causes a bending of ca. 39° of the angle between the mean plane defined by all carbon atoms of the five-membered ring and all carbon atoms of the four-membered ring, respectively (0° in **2** and in **3**). This in turn forces (i) a twist of the double bond (C1–C2 (1.35 Å, C7–C1–C2–C3 56°) which has its equivalent in a reduction of the corresponding bond order and (ii) an elongation of the bond C3–C4 (1.37 Å) comparable to the bond C2–C3 in **3**. The results summarized in Table 1 show that the amount of energy gained by diene **1** by bending the molecular plane seems to almost level out the loss caused by the reduction of the sterical strain of **2**.

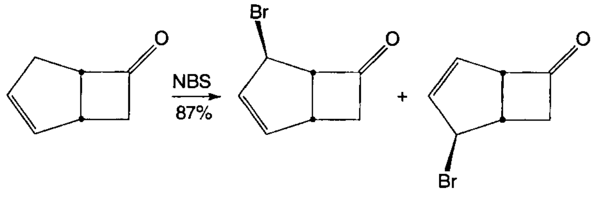
If we assume thermodynamical control the probability of the formation of the dienes **1**–**3** should decrease in the order **2** ≈ **1** > **3**. While anion **4** was prepared by Oda and Breslow in 1972[2], dienes **1**–**3** are unknown.

Bicyclo[3.2.0]hept-2-ene (**6**)[14] and bicyclo[3.2.0]hept-2-en-6-one (**8**)[15] are easily obtained by reduction of the [2 + 2] cycloadduct of cyclopentadiene and dichloroketene. Allylic bromination of **6** gives *exo*-bromide **7** (87%) which has been obtained earlier by bromination of the corresponding alcohol with $Br_2PPh_3$, however, without assignment of the relative configuration at C-4[16]. Bromination of **8** yields a 1:2 mixture of regioisomers **9** and **10**.

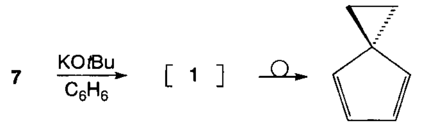
Hamer and Stubbs attempted the dehydrobromination of **7** with potassium *tert*-butoxide in benzene and observed that the elimination product **1** rapidly rearranges to spiro[2.4]hepta-4,6-diene (**11**)[16].



**6** **7**



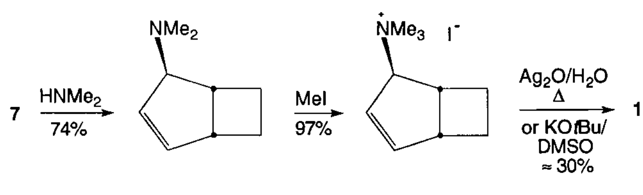
**8** **9** *1:2* **10**



**11**

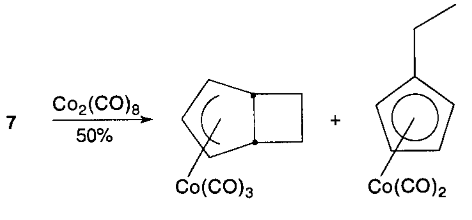
In order to test whether this rearrangement is a characteristic feature of the strained olefin **1** itself or a result of the reaction conditions applied by Hamer and Stubbs, a Hofmann elimination via **12** and **13** was attempted. Both thermolysis (120–180°C) of the ammonium hydroxide and treatment of **13** with potassium *tert*-butoxide in dimethyl sulfoxide resulted in the formation of **11** as the only identified product (ca. 30%). This is interesting in connection with results obtained by Kloosterziel et al.[17], who found that the pyrolysis of **11** at 345–400°C gave among other products 3,4-di-methylenecyclopentene which presumably originated from **1**. The rearrangement to the spiro[2.4]hepta-4,6-diene system might not take place with the dehydrohalogenation products obtained from **9** and **10**[18]. However, experiments performed with weak bases gave no reaction, with stronger bases polymeric material was formed.

A preliminary experiment showed that the reaction of 3-bromocyclopentene with $Co_2(CO)_8$ yields dicarbonyl(cyclo-

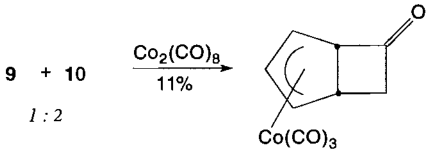


**12** **13**

pentadienyl)cobalt(I). Therefore, we expected that the corresponding reaction of **7** should result in the formation of a bicyclo[3.2.0]hepta-1,3-dienyl complex. A rearrangement to a spiro[2.4]hepta-4,6-diene derivative could be avoided by coordination of the double bond in **7** to the cobalt atom prior to the elimination step. However, instead of the desired complex the reaction of **7** with $Co_2(CO)_8$ gave **14** in 50% yield in addition to some dicarbonyl($\eta^5$-ethylcyclopentadienyl)cobalt(I) (**15**). The corresponding reaction of **9** and **10** resulted in **16** (11%).

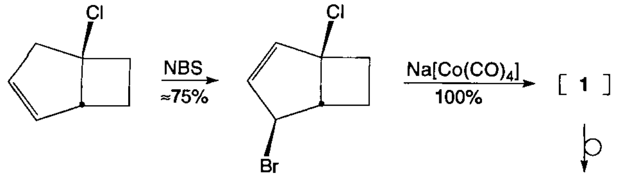


**14** **15**



**16**

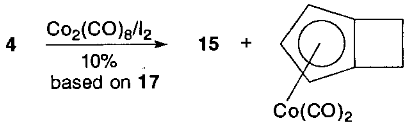
Bromination of known 5-chlorobicyclo[3.2.0]hept-2-ene (**17**)[2] with NBS gave **18** in ca. 75% yield. Attempts to prepare an allyl complex similar to **14** by reaction of **18** with $Co_2(CO)_8$ with the additional possibility of a subsequent dehydrohalogenation failed. The reaction with the more nucleophilic[19] $Na[Co(CO)_4]$[20] gave a quantitative yield of **11**. Therefore, the formation of an allyl complex seems unlikely. Instead, a σ-bound tetracarbonylcobalt species is formed by nucleophilic substitution, and this either eliminates $ClCo(CO)_4$ or reacts with additional $Na[Co(CO)_4]$ to form the corresponding disubstitution product which might then eliminate $Co_2(CO)_8$[20,21]. Bicyclo[3.2.0]hepta-1,3-diene (**1**) formed would rapidly rearrange to **11**.



**17** **18** **11**

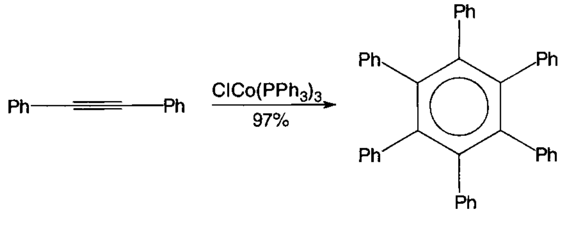
Oda and Breslow used **17** to prepare the bicyclo[3.2.0]hepta-1,3-dienyl anion (**4**)[2] by reaction with lithium diethylamide at −20°C. Their route is at present the only one which leads to the desired ligand. However, there is no obvious way to prepare substituted derivatives by this route. These are desirable, because the activation energy of ring-opening reactions in bicyclo[3.2.0]hepta-1,3-dienyl complexes is expected to be strongly influenced by the substitution pattern at the four-membered ring. Attempts to synthesize substituted bicyclo[3.2.0]hepta-1,3-dienyl anions are under way[22]. To prepare bicyclo[3.2.0]hepta-1,3-dienyl complexes, anion **4** was allowed to react with halide complexes of cobalt(I). Cobalt was chosen, because the chemistry of cyclopentadienylcobalt(I) complexes is well-known[23], and because there are ligand-exchange reactions of cyclopentadienylcobalt(I) complexes, which proceed by associative paths[7,24,25].

Cyclopentadienyl anions react with $Co_2(CO)_8$ and $I_2$ in THF[26a] with the formation of the corresponding dicarbonylcobalt(I) complexes[26b]. The reaction with anion **4** yielded a mixture of **19** and the ring-opened product **15** in the ratio 81:19. A pure sample of **19** was isolated by column chromatography and its identity established spectroscopically.



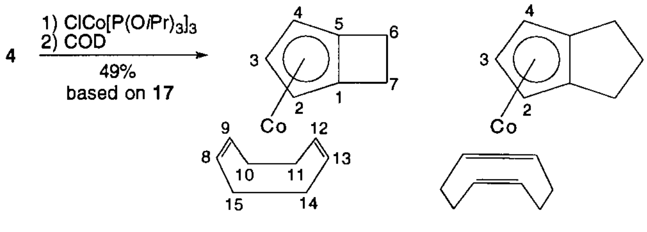
**19**

Reaction attempts of **4** with $Co(PPh_3)_3Cl$[27a] failed. Besides decomposition products only triphenylphosphane was obtained. Addition of an excess of diphenylethyne (**20**) to facilitate the formation of a presumably more stable tetraphenylcyclobutadiene complex resulted in alkyne trimerization. Further investigations revealed that the reaction of $Co(PPh_3)_3Cl$ with eight equivalents of **20** in boiling *ortho*-xylene affords hexaphenylbenzene (**21**) in a stoichiometric reaction in 97% yield besides five equivalents of **20**. The chemistry of $Co(PPh_3)_3Cl$ is well investigated: this compound catalyzes the dimerization of ethene[27b] and the cyclodimerization of butadiene to cycloocta-1,5-diene and 4-ethenylcyclohexene[27c] as well as the hydrodimerization of methyl acrylate to dimethyl adipate[27d]. To our knowledge the alkyne trimerization with $Co(PPh_3)_3Cl$ has not been reported.



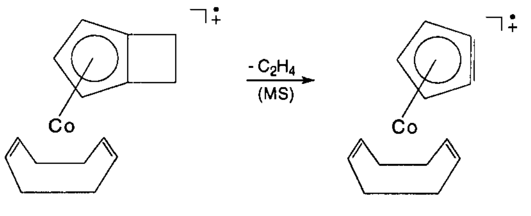
**20** **21**

While no reaction took place with $Co[P(OMe)_3]_3Br$[28], the reaction with chlorotris(triisopropyl phosphite)cobalt(I)[29] was successful, if the reaction product was not subjected to column chromatography but treated directly with an excess of cycloocta-1,5-diene (COD)[30]. Compound **22** was obtained in 49% yield (based on **17**). In addition to **22**, a small amount of the next higher homolog, the corresponding bicyclo[3.3.0]octa-1,3-diene complex **23**, was present in the crude product mixture. Its formation by reactions of COD with cobalt reagents has been reported earlier by Lehmkuhl et al[31].



**22** **23**

Compound **22** was fully characterized by including an X-ray crystal structure determination[10a]. The mass spectrum contains a signal for the molecular ion [$m/z$ (%) = 258 (13)] in addition to peaks at $m/z$ (%) = 230 (15) and 229 (22). A comparison with the fragmentation patterns of 12 compounds of the ($\eta^5$-cyclopentadienyl)($\eta^4$-cycloocta-1,5-diene)cobalt(I) type[32] shows that the appearance of these peaks is a special feature of **22**, and we believe that it is due to a [2 + 2] cycloreversion with ethene elimination to give a (cycloocta-1,5-diene)(cyclopentenynyl)cobalt radical cation $\mathbf{24}^{+\cdot}$.



$\mathbf{22}^{\cdot+}$ $\mathbf{24}^{\cdot+}$

Remarkably, in the $^1$H-NMR spectrum of **22** the difference in the chemical shifts of the 3-H and 2(4)-H signals ($\Delta\delta$ = $-1.67$) is more than ten times higher than that of the corresponding next higher homolog **23** ($\Delta\delta$ = 0.14). In addition, for **22** the resonance line of 2(4)-H appears at lower field than that of 3-H, while the order is reversed in **23**. The resonance lines of 3-H and 2(4)-H in **22** are unusually temperature-dependent (see Table 2), at 170°C the chemical shift of the 3-H signal is $\delta$ = 3.45, and $\Delta\delta$ is reduced to 1.15. The fact that $\Delta\delta$ values of similar magnitude are not observed for other bicyclo[3.2.0]hepta-1,3-dienyl complexes (e.g. **19**, **25**, **30**) shows that the large $\Delta\delta$ value observed for **22** is *not* characteristic of the bicyclo[3.2.0]hepta-1,3-dienyl ligand (e.g. a result of strain), but appears to be an anisotropy effect of the COD ligand. Apparently, at higher temperatures conformations other than the energetically most favored are more highly populated, thus reducing the anisochrony of 3-H and 2(4)-H.

Table 2. Temperature dependence of $\Delta\delta = \delta_3 - \delta_{2(4)}$ in **22**[a]

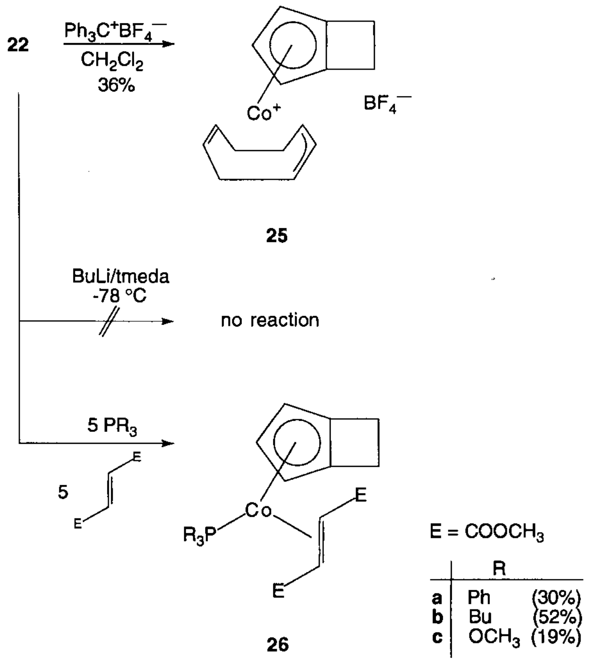
| Temp. [°C] | $\Delta\delta$ |
|---|---|
| 43 | 1.62 |
| 98 | 1.35 |
| 122 | 1.31 |
| 131 | 1.27 |
| 141 | 1.25 |
| 151 | 1.21 |
| 170 | 1.15 |

[a] 80 MHz; [$D_{10}$]*p*-xylene; temperature determined by measurement of the signal difference of the resonance frequencies of ethane-1,2-diol in [$D_6$]DMSO.

Bönnemann found a direct relation between the $^{59}$Co-NMR chemical shift of substituted (cyclopentadienyl)cobalt(I) complexes and their catalytic activity in the synthesis of pyridines[33]. As **22** is the first small-ring-anellated complex of this kind the $^{59}$Co-NMR spectrum was recorded ($\delta$ = $-1274.4$). The resonance lines of ($\eta^4$-cycloocta-1,5-diene)($\eta^5$-cyclopentadienyl)cobalt(I) and of **23**, ($\delta$ = $-1176$ and $-1268$)[34] are within the range of the width at half height; therefore one would expect a catalytic activity for **22** similar to that of these two compounds.

The crystal structure analysis of **22** has been reported in a preliminary communication[10a] and shows that not only in solution but also in the solid state a conformation different from the one adopted by **23** is preferred: while in **23** the double bonds of the COD ligand are oriented almost parallel to the bonds of the anellated ring, which start from C-1 and C-5[34,35], the orientation is almost perpendicular in **22**. The consequence is a rather close proximity of 3-H and one of the COD double bonds, presumably causing the anisotropy effect observed in the $^1$H-NMR spectra. In addition to the COD orientation, the crystal structure of **22** is of interest because of the distorted coordination of the bicyclic ligand: bonds C1–C2 and C4–C5 are significantly shorter than in **23**, bonds C2–C3 and C3–C4 are slightly longer. The bond Co–C3 is shorter than all other Co–C bonds in **22** or **23**.

To test a deprotonation, **22** was treated with butyllithium/tmeda followed by chlorotrimethylsilane. All experiments ended up with the isolation of starting material; apparently, there is no increased acidity of the protons bound to the four-membered ring. This is in accord with similar experiments carried out with ($\eta^6$-benzocyclobutene)tricarbonylchromium[3c,f,h]. A quasi-benzylic carbanion generated from **22** cannot adopt a favorable alignment of the doubly occupied $sp^3$ orbital of an anion parallel to the cyclopentadienyl π system, a consequence of the rigidity of the system. If a hydride anion instead of a proton was abstracted from the four-membered ring a mesomeric interaction of the cation formed ($sp^2$) with the arene π system could be possible. Therefore, **22** was treated with $Ph_3C^+BF_4^-$. The result was indeed a hydride abstraction, which, however, did not take place at the bicyclic ligand but at the COD ligand, and the cationic complex **25** was obtained in 36% yield[36].

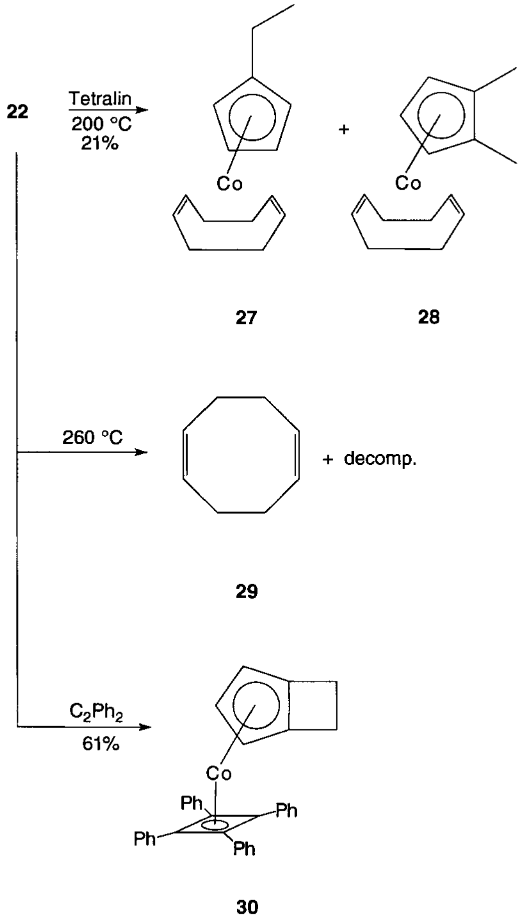


First attempts to open the four-membered ring in the course of a ring-slippage reaction were undertaken with several dienophiles in the presence of phosphanes in order to trap an intermediate 4,5-dimethylenecyclopentenyl complex. The use of tetracyanoethene and (*E*)-dicyanoethene caused decomposition of **22**. The use of maleic anhydride was unsuitable because of the formation of 1:1 adducts with phosphanes[37]. Finally, dimethyl fumarate was selected. The (*E*) dienophile was initially preferred because its successful reaction would result in the formation of enantiomers, whereas the application of dimethyl maleate would lead to a pair of diastereomers, which would be more difficult to analyze.

Treatment of **22** with a fivefold molar excess of triphenylphosphane, tri-*n*-butylphosphane or trimethyl phosphite and a fivefold molar excess of dimethyl fumarate in boiling *o*-xylene (144°C) did not, however, result in an opening of the four-membered ring; instead a ligand displacement of the COD ligand with the formation of complexes **26** occured. Similar reactions at 190°C in tetralin yielded only decomposition products.

The reaction of **22** with a fivefold excess of dimethyl maleate in the presence of a fivefold of triphenylphosphane led to dimethyl fumarate complex **26a** whereby the excess of dimethyl maleate isomerized to dimethyl fumarate[38]. Photochemical reaction conditions caused a (*E*)-(*Z*) isomerization of dimethyl fumarate only[39].

Besides the endothermal melting the DSC[40] analysis of **22** shows that a first-order reaction occurs above ca. 200°C (curve analysis)[41]. To investigate this process in more detail some thermolysis experiments were carried out with **22**. Compound **22** was recovered unchanged after heating a solution of it in diglyme at 162°C for 16 h. Treatment in tetralin at 170°C for 16 h furnished small amounts (<10%) of **27**[42] and **28**, and at 200°C a mixture of **27** and **28** was obtained in 21% yield besides decomposition products. We suggest that the solvent tetralin is the source of the additional hydrogen atoms. Short heating of **22** at 260°C – the temperature of the maximum heat flow in the DSC analysis – yields cycloocta-1,5-diene (**29**) as the only characterized product in addition to decomposed material. The experiments undertaken so far show that the activation energy of the opening of the four-membered ring is apparently higher than that of the dissociation of the electroneutral ligand.



The problem could be resolved in two ways: (i) Replacement of the cycloocta-1,5-diene by a ligand which is less easily dissociated or (ii) reduction of the activation energy of the ring opening by use of bicyclo[3.2.0]hepta-1,3-dienyl complexes with substituents at the four-membered ring. It is known that substituents stabilizing an *o*-quinodimethane intermediate are especially suitable for this purpose.

A replacement of COD[23] by a ligand which would be less easily dissociated, thus allowing the complex to be heated to temperatures neccessary to open the four-membered ring, was tested. Since a suitable ligand has to be electroneutral, the possiblities are limited. Phosphanes and olefins other than COD are usually dissociated at temperatures below 200°C[43,44].

Cyclopentadienylcobalt(I) complexes bearing a cyclobutadiene ligand are stable thermally and on exposure to air. They have been extensively investigated[44] and are frequently formed as undesired products from cyclopentadienylcobalt(I) complexes by treatment with alkynes in the synthesis of [2 + 2 + 2] cycloadducts[33,45,46]. However, recent results obtained by Gleiter show that in special cases complexes of this type can take part in the formation of [2 + 2 + 2] cycloadducts under more forcing reaction conditions[47].

Treatment of cycloocta-1,5-diene complex **22** with a tenfold excess of diphenylethyne in boiling *o*-xylene leads to the formation of the corresponding tetraphenylcyclobutadiene complex **30** in 61% yield. Compound **30** can easily be separated from unreacted **22** by column chromatography. Recrystallization of **30** from diethyl ether yields brown, air-stable crystals.

In the $^1$H-NMR spectrum of **30** the chemical shift difference of the 2(4)-H and 3-H signals is only $\Delta\delta = 0.12$, which is more than ten times less than the corresponding value in the spectrum of **22** and rather close to the value for **23**. This confirms that the unusual $^1$H-NMR data of **22** are associated with the COD ligand and not with the bicyclic system.

The structure of **30** in the crystal is given in Figure 1 (for atomic fractional coordinates see Table 3). There are two molecules of **30** and one molecule of diethyl ether in the asymmetric unit. In contrast to **22** the bond lengths in the cyclopentadienyl ring are nearly equal. The bicyclic ligand is planar, and the coordination not distorted, indicating that in **22** the strained nature of the bicyclic ligand is not the cause of its distorted coordination.

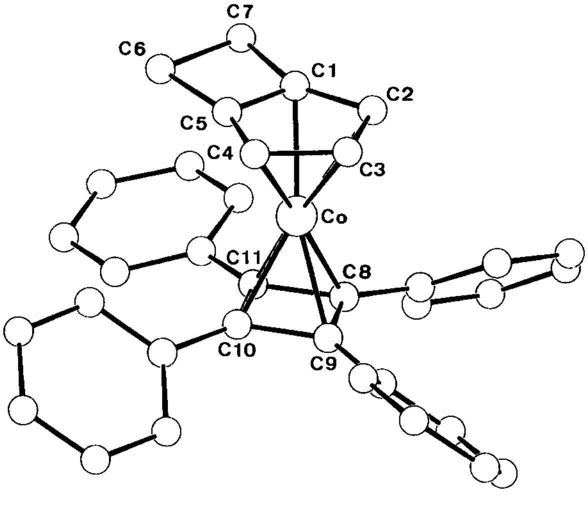


Figure 1. Crystal structure of **30**[48]; one asymmetric unit contains two independent molecules of **30** and one molecule of diethyl ether; selected bond lengths averaged over two molecules [Å]: C1−C2 1.42(2), C2−C3 1.41(1), C3−C4 1.41(2), C4−C5 1.38(5), C5−C1 1.394(8), C5−C6 1.51(4), C6−C7 1.58(3), C1−C7 1.50(3), Co−C1 2.062(7), Co−C2 2.074(5), Co−C3 2.043(5), Co−C4 2.059(7), Co−C5 2.043(7), Co−C8 1.988(13), Co−C9 1.987(4), Co−C10 1.971(4), Co−C11 1.979(4), C8−C9 1.463(6), C9−C10 1.463(6), C10−C11 1.474(6), C8−C11 1.46(2)

With the synthesis of **30** the stage was set for the successful execution of the ring opening reaction followed by a cycloaddition. This has already been reported in a preliminary communication[9a], full details will be published soon.

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## Experimental

Unless otherwise indicated, all operations were performed under Ar in flame-dried vessels. Starting materials were purchased and used without further purification. Dimethyl sulfoxide (DMSO) was dried with calcium hydride; dichloromethane, tetrachloromethane, and acetone were distilled from $P_4O_{10}$. Pentane, hexane, benzene, toluene, *o*-xylene, tetrahydronaphthalene, diethyl ether, and tetrahydrofuran (THF) were dried with sodium tetraethylaluminate and distilled from sodium-potassium alloy/benzophenone before use. − UV: Varian CARY-2300. − IR: Nicolet 7199 FT-IR. − $^1$H NMR: Bruker WH 400-FT (400.1 MHz), AM 200, AC 200 (200.1 MHz), WP 80 (80 MHz). − $^{13}$C NMR: Bruker AM 200 (50.3 MHz), WM 300 (75.5 MHz). Signal multiplicities were determined either by inspection of gated spectra or by application of the DEPT technique. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shift of residual solvent signals. − $^{31}$P NMR: Bruker WP 80 (32.4 MHz), AM 200, AC 200 (81.0 MHz) with $H_3PO_4$ as external standard. − MS: Varian 311A. − GC-MS: Finnigan CH 7A + Perkin-Elmer GCF 22. − HR MS: Finnigan MAT 820. − Anal. GC: BP 427 (GC 3), Dani 3800 (GC 2), Carlo Erba Mega (GC 1), Becker-Packard 417, Shimadzu GC-8AX, FID, glass capillary columns 15−40 m, PS 240 or PS 345.5 and 40 m OV-1, carrier gas $H_2$. − Prep. GC: AMPG-60, Gerstel, Mülheim, carrier gas $N_2$. − Anal. HPLC: Varian 5560, Gyncotec M300C + Shimadzu CT06A + SPDa + FCV-100B, UV detection (200−254 nm), and Hewlett-Packard HP 1090. − Prep. HPLC: DuPont/Shimadzu SPD-6A prep., LiChrospher Si 100, 10 µm, column 250 mm, ∅ 8 mm, UV detection (254 nm). − DSC: DuPont 9900. − Melting points (uncorr.): Büchi SMP-20. − Elemental analyses: Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr. − The descriptor *exo* refers to that configuration in which the senior substituent is on the same side of the reference plane as the substituents at the bridgehead atoms. The description *syn* refers to that configuration in which the senior substituent is on the same side of the reference plane as the metal atom.

*exo-4-Bromobicyclo[3.2.0]hept-2-ene* (**7**): A mixture of 10.0 g (106 mmol) of **6**[14], 20.8 g (117 mmol) of *N*-bromosuccinimide (NBS) and 0.40 g (1.70 mmol) of dibenzoyl peroxide in 300 ml of tetrachloromethane was refluxed in a 500-ml round-bottom flask for 4 h. After cooling to room temp. (25°C), the flask was stored at 2°C for 14 h. After filtration, the solvent was condensed into a cold trap, and the residue was condensed into another flask at 0.001 mbar/25°C; 16.1 g (87%) of **7** was obtained as a bright yellow oil, which decomposed in the air and in the presence of water and mineral acids. An analytical sample was purified by prep. GC (3 m SE-30 + 2 m DC 200 on Volaspher A4, 60−80 mesh, ∅ 14 mm, 120°C, cold trap −35°C).

IR (film): $\tilde{\nu}$ = 3047 cm$^{-1}$ (m), 2982 (s), 2937 (s), 2895 (m, sh), 2859 (m), 1710 (w), 1593 (m), 1451 (w), 1435 (m), 1352 (m), 1320 (w), 1275 (w), 1235 (m), 1163 (s), 1102 (w), 1069 (w), 1038 (w), 1027 (w), 925 (w), 850 (w), 781 (s), 761 (s), 659 (s). − $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.49 (m, 1H, *endo*-7-H, $^3J_{1,endo\text{-}7} = 2.2$ Hz, $^4J_{5,endo\text{-}7} = 0.7$ Hz, $^3J_{exo\text{-}6,endo\text{-}7} = 3.3$ Hz, $^3J_{endo\text{-}6,endo\text{-}7} = 9.6$ Hz, $^2J_{endo\text{-}7,exo\text{-}7} = -11.4$ Hz), 1.63 (m, 1H, *endo*-6-H, $^3J_{5,endo\text{-}6} = 7.1$ Hz, $^4J_{1,endo\text{-}6} = 0.5$ Hz, $^2J_{endo\text{-}6,exo\text{-}6} = -12.2$ Hz, $^3J_{endo\text{-}6,exo\text{-}7} = 9.1$ Hz), 2.20 (m, 1H, *exo*-6-H, $^3J_{5,exo\text{-}6} = 9.6$ Hz, $^3J_{exo\text{-}6,exo\text{-}7} = 9.6$ Hz, $^4J_{1,exo\text{-}6} = 1.8$ Hz), 2.37 (m, 1H, *exo*-7-H, $^3J_{1,exo\text{-}7} \approx 8.7$ Hz), 3.23 (m, 1H, 5-H, $^3J_{1,5} \approx 6.1$ Hz), 3.49 (m, 1H, 1-H, $^4J_{1,4} = 2.7$ Hz), 4.89 (m, 1H, *endo*-4-H, $^3J_{3,4} = 1.7$ Hz), 6.06 (m, 2H, 2-H, 3-H, $^3J_{2,3} \approx 5.2$ Hz). − $^{13}$C NMR (50 MHz, CDCl$_3$)[49]: $\delta$ = 23.1 (t, C-7, $^1J_{C,H} = 137$ Hz), 24.8 (t, C-6, $^1J_{C,H} = 137$ Hz), 45.1 (d, C-1, $^1J_{C,H} = 144$ Hz), 46.2 (d, C-5, $^1J_{C,H} = 147$ Hz), 61.4 (d, C-4, $^1J_{C,H} = 162$ Hz), 132.4

(d, C-3, $^{1}J_{\mathrm{C,H}}$ = 170 Hz), 138.8 (d, C-2, $^{1}J_{\mathrm{C,H}}$ = 164 Hz). – MS (70 eV): *m/z* (%) = 174 (4.5) [M$^{+}$], 172 (4.8) [M$^{+}$], 146 (9) [M$^{+}$ – $C_2H_4$], 144 (9) [M$^{+}$ – $C_2H_4$], 93 (100) [M$^{+}$ – Br], 92 (29) [M$^{+}$ – HBr], 91 (86) [$C_7H_7^+$], 79 (21) [$C_6H_7^+$], 78 (9) [$C_6H_6^+$], 77 (43) [$C_6H_5^+$], 66 (12) [$C_5H_6^+$], 65 (42) [$C_5H_5^+$], 63 (10), 51 (11), 41 (7), 39 (32), 38 (6), 28 (5), 27 (11).

$C_7H_9Br$ (173.1) Calcd. C 48.58 H 5.24 Br 46.17
Found C 48.65 H 5.20 Br 46.28

*exo-4-Bromobicyclo[3.2.0]hept-2-en-6-one* (**9**) *and exo-4-Bromobicyclo[3.2.0]hept-2-en-7-one* (**10**): A mixture of 5.00 g (46.3 mmol) of **8**[15], 9.07 g (51.0 mmol) of NBS, and 0.30 g (1.2 mmol) of dibenzoyl peroxide in 150 ml of tetrachloromethane was refluxed for 5 h. After cooling to room temp. (25 °C), the mixture was stored at 2 °C for 15 h and filtered. The residue was washed with two portions of 50 ml of tetrachloromethane. The solvent was condensed into a cold trap, and 9.80 g of a viscous oil remained, which was condensed into another flask at 0.001 mbar/45 °C; 8.06 g (93%) of a mixture of **9** and **10** (1:2) was obtained as a bright yellow liquid, which became darker upon standing. The material decomposed slowly when heated; above 100 °C spontaneous decomposition occured. Anal. GC led to decomposition.

IR (KBr): $\tilde{\nu}$ = 3066 cm$^{-1}$ (w), 2966 (w), 2923 (w), 1782 (s, C=O), 1743 (w), 1591 (w), 1389 (w), 1347 (w), 1261 (w), 1218 (m), 1171 (m), 1101 (m), 1077 (m), 1024 (w), 996 (m), 953 (w), 850 (w), 789 (m), 774 (s), 719 (w), 664 (w), 608 (w). – $^{1}$H NMR (200 MHz, $CDCl_3$): **9**: δ = 2.61 (ddd, 1H, *endo*-7-H, $^{2}J_{exo\text{-}7,endo\text{-}7}$ = –17.5 Hz, $^{3}J_{1,endo\text{-}7}$ = 2.6 Hz, $^{4}J_{5,endo\text{-}7}$ = 2.9 Hz), 3.39 (m, 1H, *exo*-7-H, $^{3}J_{1,exo\text{-}7}$ = 8.9 Hz, $^{4}J_{5,exo\text{-}7}$ = 2.2 Hz), 3.76 (m, 1H, 1-H, $^{3}J_{1,5}$ = 6.2 Hz, $^{3}J_{1,2}$ = 2.4 Hz), 4.20 (m, 1H, 5-H), 5.12 (m, 1H, *endo*-4-H), 6.09 (s, 2H, 1-H, 2-H); **10**: δ = 2.86 (m, 1H, *endo*-6-H?), 3.26 (m, 1H, *exo*-6-H?), 3.30 (m, 1H, 1-H?, $^{4}J_{1,4}$ = 3.4 Hz, $^{4}J_{1,3}$ = 2.1 Hz, $^{3}J_{1,2}$ = 2.9 Hz), 4.50 (m, 1H, 5-H?, $^{3}J_{1,5}$ > 0 Hz, $^{3}J_{endo\text{-}4,5}$ > 0 Hz), 5.04 (m, 1H, *endo*-4H, $^{4}J_{2,endo\text{-}4}$ = –0.8 Hz, $^{3}J_{3,endo\text{-}4}$ = 2.3 Hz), 5.90 (m, 1H, 2-H, $^{3}J_{2,3}$ = 5.3 Hz), 6.16 (m, 1H, 3-H). – $^{13}$C NMR (50 MHz, $C_6D_6$): **9**: δ = 36.7 (d, C-1, $^{1}J_{\mathrm{C,H}}$ = 152 Hz), 50.9 (t, C-7, $^{1}J_{\mathrm{C,H}}$ = 133.8 Hz), 52.5 (d, C-5, $^{1}J_{\mathrm{C,H}}$ = 143.9 Hz), 72.3 (d, C-4, $^{1}J_{\mathrm{C,H}}$ = 150.4 Hz), 135.1 (d, C-3, $^{1}J_{\mathrm{C,H}}$ = 172.4 Hz), 137.2 (d, C-2, $^{1}J_{\mathrm{C,H}}$ = 165.6 Hz), 204.3 (s, C-6); **10**: δ = 37.0 (d, C-5, $^{1}J_{\mathrm{C,H}}$ = 152.3 Hz), 50.1 (t, C-6, $^{1}J_{\mathrm{C,H}}$ = 135.8 Hz), 58.9 (d, C-1, $^{1}J_{\mathrm{C,H}}$ = 161.2 Hz), 73.2 (d, C-4, $^{1}J_{\mathrm{C,H}}$ = 147.2 Hz), 130.2 (d, C-3, $^{1}J_{\mathrm{C,H}}$ = 173 Hz), 135.0 (d, C-2, $^{1}J_{\mathrm{C,H}}$ = 170.5 Hz), 201.4 (s, C-7). – MS (70 eV): *m/z* (%) = 188 (0.6) [M$^{+}$], 186 (0.5) [M$^{+}$], 146 (14) [M$^{+}$ – $CH_2CO$], 144 (10) [M$^{+}$ – $CH_2CO$], 107 (62) [M$^{+}$ – Br], 105 (3), 81 (3), 80 (100), 79 (25), 77 (60), 74 (3), 66 (4), 65 (39), 63 (10), 62 (4), 54 (5), 52 (10), 51 (16), 50 (15), 39 (29), 27 (15), 26 (10).

$C_7H_7BrO$ (187.0) Calcd. C 44.95 H 3.77 Br 42.72
Found C 44.81 H 3.77 Br 42.62

*exo-4-Dimethylaminobicyclo[3.2.0]hept-2-ene* (**12**): A solution of 3.00 g (17.3 mmol) of **7** in 20 ml of pentane was added dropwise to a solution of 7.50 ml (113 mmol) of diethylamine in 40 ml of pentane. The mixture was stirred at 0 °C for 3 h. Precipitated ammonium salt was removed by filtration. Highly volatile material was condensed into a cold trap at 10 mbar/25 °C. The residue was condensed into another flask at 0.1 mbar/25 °C; 1.77 g (74%) of **12** was obtained as a colorless oil.

IR (film): $\tilde{\nu}$ = 3043 (m, =C–H), 2969 (s), 2934 (s), 2857 (s), 2814 (s), 2773 (s), 1604 (w, C=C), 1456 (s), 1437 (m), 1363 (s), 1322 (w), 1277 (m), 1261 (m), 1234 (w), 1214 (w), 1184 (m), 1155 (m), 1103 (m), 1069 (m), 1044 (m), 1037 (m), 1019 (m), 956 (w), 923 (w), 866 (m), 796 (m), 771 (m), 731 (s), 658 (w). – $^{1}$H NMR (200 MHz, $C_6D_6$): δ = 1.5 [m, 2H, *endo*-6(7)-H], 2.07 (s, 6H, $CH_3$), 2.1 [m, 2H, *exo*-6(7)-H, $^{3}J_{1,endo\text{-}7}$ = 2.3 Hz], 2.69 (m, 1H, 5-H), 3.02 (m, 1H, 1-H, $^{3}J_{1,2}$ = 0.6 Hz, $^{4}J_{1,3}$ = 1.1 Hz), 3.35 (m, 1H, *endo*-4-H, $^{4}J_{2,endo\text{-}4}$ = –1.5 Hz, $^{3}J_{3,endo\text{-}4}$ = 2.5 Hz), 5.79 (m, 1H, 3-H, $^{3}J_{2,3}$ = 2.5 Hz), 5.91 (m, 1H, 2-H). – $^{13}$C NMR (50 MHz, $C_6D_6$): δ = 24.9 (t, C-6, $^{1}J_{\mathrm{C,H}}$ = 134 Hz), 25.7 (t, C-7, $^{1}J_{\mathrm{C,H}}$ = 135 Hz), 36.7 (d, C-1, $^{1}J_{\mathrm{C,H}}$ = 138 Hz), 41.1 (q, $CH_3$, $^{1}J_{\mathrm{C,H}}$ = 132 Hz), 46.0 (d, C-5, $^{1}J_{\mathrm{C,H}}$ = 136 Hz), 78.8 (d, C-4, $^{1}J_{\mathrm{C,H}}$ = 138 Hz), 130.8 (d, C-2, $^{1}J_{\mathrm{C,H}}$ = 162 Hz), 137.5 (d, C-3, $^{1}J_{\mathrm{C,H}}$ = 160 Hz). – MS (70 eV): *m/z* (%) = 138 (7), 137 (65) [M$^{+}$], 136 (98), 122 (51) [M$^{+}$ – $CH_3$], 110 (14), 109 (43), 108 (42) [M$^{+}$ – 2 $CH_3$], 107 (12), 96 (11), 95 (18), 94 (67), 92 (27), 91 (100) [$C_7H_7^+$], 84 (14), 82 (40), 81 (18), 79 (27), 78 (12), 77 (69), 71 (28), 70 (25), 68 (18), 67 (19), 66 (13), 65 (39) [$C_5H_5^+$], 58 (28), 56 (12), 55 (12), 53 (28), 51 (12), 46 (24), 45 (12), 44 (65), 43 (14), 42 (95), 41 (27), 39 (40), 27 (22).

$C_9H_{15}N$ (137.2) Calcd. C 78.78 H 11.02 N 10.21
Found C 78.80 H 10.97 N 10.26

*(Bicyclo[3.2.0]hept-2-en-exo-4-yl)trimethylammonium Iodide* (**13**): At 25 °C 10.0 ml (161 mmol) of iodomethane was added to a solution of 1.00 g (7.30 mmol) of **12** in 50 ml of diethyl ether. After 3 min, a colorless precipitate formed, and 10 min later another 10 ml of diethyl ether was added. After stirring for 4 h, the solvent and unreacted iodomethane were removed into a cold trap at 0.1 mbar/25 °C. The bright yellow residue was dried at 0.001 mbar/25 °C; 1.97 g (97%) of **13** was obtained as a bright yellow solid.

IR (KBr): $\tilde{\nu}$ = 3050 cm$^{-1}$ (m, =C–H), 3006 (s), 2992 (s), 2980 (s), 2971 (s), 2939 (s), 2925 (s), 2858 (m), 1604 (m, C=C), 1471 (s, $^{+}NMe_3$), 1439 (m), 1417 (m), 1405 (m), 1379 (m), 1242 (m), 1130 (w), 1124 (w), 1106 (w), 1067 (w), 1038 (m), 1000 (m), 980 (m), 971 (m), 943 (m), 872 (s), 853 (m), 803 (s), 732 (m), 559 (m). – $^{1}$H NMR (200 MHz, $CDCl_3$): δ = 1.7 + 2.4 (2 m, 2 × 2H, *endo*-6-H, *exo*-6-H, *endo*-7-H, *exo*-7-H), 3.25 (s, 9H, 8-H), 3.4 (m, 2H, 1-H, 5-H, $^{3}J_{1,2}$ = 2.3 Hz, $^{4}J_{1,3}$ = 1.5 Hz), 4.67 (m, 1H, *endo*-4-H, $^{3}J_{3,endo\text{-}4}$ = 2.3 Hz, $^{3}J_{endo\text{-}4,5}$ = 3.1 Hz, $^{4}J_{2,endo\text{-}4}$ = 1.3 Hz), 6.05 (m, 1H, 3-H, $^{1}J_{2,3}$ = 5.6 Hz), 6.68 (m, 1H, 2-H). – $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 23.5 (t, C-6, $^{1}J_{\mathrm{C,H}}$ = 139 Hz), 23.8 (t, C-7, $^{1}J_{\mathrm{C,H}}$ = 139 Hz), 36.8 (d, C-1, $^{1}J_{\mathrm{C,H}}$ = 140 Hz), 45.9 (d, C-5, $^{1}J_{\mathrm{C,H}}$ = 145 Hz), 50.9 (q, $CH_3$, $^{1}J_{\mathrm{C,H}}$ = 145 Hz), 86.7 (d, C-4, $^{1}J_{\mathrm{C,H}}$ = 151 Hz), 122.7 (d, C-2, $^{1}J_{\mathrm{C,H}}$ = 167 Hz), 148.8 (d, C-3, $^{1}J_{\mathrm{C,H}}$ = 166 Hz). – MS (FAB, propane-1,2,3-triol): *m/z* (%) = 431 (1), 152 (100) [$C_{10}H_{18}N^+$].

$C_{10}H_{18}IN$ (279.2)
Calcd. C 43.02 H 6.50 I 45.46 N 5.02
Found C 42.98 H 6.46 I 45.54 N 4.88

*Treatment of* **13** *with Wet Silver Oxide:* 300 mg (1.10 mmol) of **13** and 225 mg (1.10 mmol) of silver oxide were stirred in 4 ml of water at 25 °C for 14 h. After filtration, the volume of the mixture was reduced to 0.5 ml at 0.1 mbar/25 °C. The residue was thermolyzed at 10 mbar/120–180 °C, and volatile products were directly condensed into another flask, which was cooled to –78 °C; 1 ml of [D$_6$]benzene was added to the condensed mixture. According to the $^{1}$H-NMR spectrum **11** was formed as the main reaction product. Anal. GC (GC 2, 36 m PS 240, 60–280 °C, 2 min isothermal, then 8 °C/min): I (rel. retention time 1.00): 27.2% of **11**, II (2.37): 15.1%; III (2.94): 28.2%; IV (3.29): 4.7% of **12**; V (5.69): 11.0%. Extraction with water/pentane gave ca. 60 mg of a colorless oil. GC (GC 2, 36 m PS 240, 60–280 °C, 2 min isothermal, then 8 °C/min): I (rel. retention time 0.28): 49.1% of pentane; II (1.00): 7.6% of **11**, III (2.38): 5.6%; IV (2.57): 3.6%; V (2.97): 11.7%; VI (3.30): 1.8% of **12**.

*Treatment of* **13** *with Potassium tert-Butoxide in DMSO:* A mixture of 558 mg (2.00 mmol) of **13** and 246 mg (2.20 mmol) of freshly sublimed potassium *tert*-butoxide in 5 ml of DMSO for 14 h was stirred at 10 mbar/50 °C in a flask connected to a cold trap. Volatile reaction products were collected in the cold trap at –78 °C. Within 2 h, 1.97 g of volatile material containing some DMSO was obtained and extracted with water/pentane. After drying of the organic layer with $MgSO_4$ and removal of the solvent in vacuo, 10.0 mg of a colorless oil remained which was identified as **11** by a comparison of the $^{1}$H-NMR spectrum with that of an authentic sample. The reaction mixture which had not been condensed into the cold trap was also extracted with water/pentane. After drying the organic layer with $MgSO_4$ and solvent removal in vacuo, 50.0 mg of a colorless oil remained. GC (GC 1, 36 m, PS 240, 80–280 °C, 4 min isotherm, then 8 °C/min): I (rel. retention time 1.00): 60.0% of **11**; II (3.15): 12.3%; III (3.25): 17.1%. The overall yield of **11** was 40.0 mg (22%).

*Reaction of 3-Bromocyclopentene with Octacarbonyldicobalt:* At 25 °C a solution of 1.00 g (6.80 mmol) of 3-bromocyclopentene[50] in 20 ml of THF was added dropwise to a solution of 3.49 g (10.2

mmol) of octacarbonyldicobalt in 50 ml of THF. An immediate gas evolution was observed. After 3 h, the solvent was condensed into a cold trap at 10 mbar/25 °C. The residue was condensed into another flask at 0.01 mbar; 0.12 g (10%) of dicarbonyl($\eta^5$-cyclopentadienyl)cobalt(I) was obtained (identified by a comparison of the $^1$H-NMR and IR spectra with those of an authentic sample).

*(2—4-$\eta^3$-bicyclo[3.2.0]hept-2-enyl)tricarbonylcobalt(I)* (**14**): A solution of 4.40 g (12.8 mmol) of octacarbonyldicobalt in 200 ml of THF was added over a period of 15 min to a solution of 2.10 g (12.1 mmol) of **7** in 300 ml of THF. A gas evolution occurred, and the color of the mixture became green. The mixture was stirred at 25 °C for 18 h, then the solvent was condensed into a cold trap at 1 mbar. Residual THF was removed at 0.01 mbar within 5 min. The residue was condensed into another flask at 0.001 mbar/25 °C three times; 1.42 g (50%) of **14** was obtained as a volatile dark red oil. In some experiments varying amounts of **15** (max. 10%) were obtained besides **14**.

IR (film): $\tilde{\nu}$ = 3033 cm$^{-1}$ (w), 2980 (m), 2941 (m), 2476 (w), 2056 (s, C=O), 1954 (br. s, C=O), 1954 (s, C=O), 1431 (w), 1302 (m), 1222 (m), 1108 (m), 1062 (m), 1010 (w), 937 (w), 649 (w), 635 (w), 617 (w), 547 (s), 528 (s), 503 (s), 468 (m), 417 (m). — $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 1.03 + 1.55 [m, 2 × 2H, *exo*-6(7)-H, AA′BB′ line system], 2.23 [m, 2H, 1(5)-H, $\Sigma J_{1(5),2(4)}$ = 1.7 Hz, $\Sigma J_{1(5),3}$ = 0.9 Hz], 4.12 [m, 2H, 2(4)-H, $^3J_{2(4),3}$ = 3.1 Hz], 4.38 (m, 1H, 3-H). — $^{13}$C NMR (50 MHz, $C_6D_6$): $\delta$ = 22.8 [t, C6(7), $^1J_{C,H}$ = 137 Hz], 43.9 [d, C-1(5), $^1J_{C,H}$ = 145 Hz], 75.5 (d, C-3, $^1J_{C,H}$ = 178 Hz), 80.0 [d, C-2(4), $^1J_{C,H}$ = 165 Hz], 203.8 (s, C=O). — MS (70 eV): *m/z* (%) = 236 (2.7) [M$^+$], 208 (23) [M$^+$ − CO], 180 (25) [M$^+$ − 2 CO], 152 (36) [M$^+$ − 3 CO], 151 (10) [M$^+$ − 3 CO − H], 150 (100) [M$^+$ − 3 CO − 2H], 137 (10), 125 (6), 124 (64) [M$^+$ − 3 CO − $C_2H_4$], 98 (16), 91 (38) [$C_7H_7^+$], 87 (10) [CoCO$^+$], 77 (6), 65 (7) [$C_5H_5^+$], 59 (16) [Co$^+$].

| | | |
|---|---|---|
| $C_{10}H_9CoO_3$ (236.1) | Calcd. | C 50.87 H 3.84 Co 24.96 |
| | Found | C 50.76 H 3.90 Co 24.84 |

*Treatment of* **9** *and* **10** *with Octacarbonyldicobalt:* At 25 °C a solution of 3.00 g (16.0 mmol) of a mixture of **9** and **10** (1:2) in 50 ml of THF was added dropwise to a solution of 6.84 g (20.0 mmol) of octacarbonyldicobalt in 150 ml of THF. A gas evolution was observed, and the mixture was stirred for 24 h. The solvent was evaporated into a cold trap at 10 mbar, and the residue was exposed to 10 mbar/25 °C for 2 h. From the residue 0.44 g (11%) of **16** was condensed into another flask at 0.001 mbar/25 °C [red oil, purity ca. 85% ($^1$H NMR), containing some ($\eta^5$-acetylcyclopentadienyl)dicarbonylcobalt(I)].

IR (film): $\tilde{\nu}$ = 3058 cm$^{-1}$ (w), 2956 (m), 2924 (m), 2854 (m), 2017 (s, CO), 1952 (s, CO), 1781 (s, C=O), 1710 (w, impur.), 1445 (w), 1070 (w), 925 (w), 823 (w), 746 (w), 721 (m), 704 (m), 620 (m), 610 (m), 563 (m), 542 (m). — $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 1.81 (dt, 1H, *endo*-7-H, $^2J_{endo\text{-}7,exo\text{-}7}$ = −17.3 Hz, $^3J_{1,endo\text{-}7} \approx$ 3.0 Hz, $^4J_{5,endo\text{-}7} \approx$ 3.0 Hz), 1.91 (m, 1H, 1-H, $^3J_{1,2} \approx$ 0.8 Hz, $^3J_{1,5}$ = 4.9 Hz), 2.08 (ddd, 1H, *exo*-7-H, $^3J_{1,exo\text{-}7}$ = 7.9 Hz, $^4J_{5,exo\text{-}7}$ = 2.9 Hz), 2.79 (m, 1H, 5-H, $^3J_{4,5} \approx$ 0.6 Hz), 3.70 (m, 1H, 2-H or 4-H), 3.73 (m, 1H, 2-H or 4-H), 4.17 (dd, 1H, 3-H, $^3J_{2,3} \approx {}^3J_{3,4}$ = 3.1 Hz). — MS (70 eV): *m/z* (%) = 194 (16) [M$^+$ − 2 CO], 166 (16) [M$^+$ − 3 CO], 138 (39) [M$^+$ − 4 CO], 137 (23) [M$^+$ − 3 CO − HCO], 108 (9) [$C_7H_8O$], 79 (23) [$C_6H_7^+$], 77 (14) [$C_6H_5^+$], 66 (100) [$C_5H_6^+$], 59 (14) [Co$^+$], 41 (11) [HCO$^+$], 39 (16), 27 (11).

*Treatment of 5-Chlorobicyclo[3.2.0]hept-2-ene* (**17**) *with NBS:* 1.00 g (7.80 mmol) of **17** 1.66 g (9.30 mmol) of NBS and 0.10 g (0.40 mmol) of dibenzoyl peroxide in 100 ml of tetrachloromethane were heated under reflux for 2 h. Then the mixture was stored at 2 °C for 16 h. After filtration, the solvent was removed at 10 mbar into a cold trap. The residue was filtered through a column of Florisil (30 × 2 cm) with pentane. After solvent removal, 2.01 g of a product mixture was obtained with **18** as the main component (ca. 75%) and some *exo*-4-bromo-5-chlorobicyclo[3.2.0]hept-2-ene.

$^1$H NMR (200 MHz, $CDCl_3$, signal assignment by NOE): $\delta$ = 1.37 (m, 1H, *endo*-7-H?), 2.34 (m, 2H, *endo*-6-H, *exo*-7-H?), 2.68 (m, 1H, *exo*-6-H?), 3.40 (m, 1H, 5-H, $^3J_{4,5} \approx$ 0.7 Hz, $^4J_{3,5}$ = 1.1 Hz, $^4J_{2,5}$ = 1.0 Hz), 4.71 (m, 1H, *endo*-4-H, $^4J_{2,endo\text{-}4}$ = −0.7 Hz, $^3J_{3,endo\text{-}4}$ = 2.6 Hz, $^4J_{endo\text{-}4,exo\text{-}6}$ = 0.6 Hz?), 6.02 (m, 1H, 2-H, $^3J_{2,3}$ = 5.3 Hz), 6.13 (m, 1H, 3-H). — $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 21.9 (t, C-6), 34.9 (t, C-7), 54.5 (d, C-4 or C-5), 55.5 (d, C-4 or C-5), 72.4 (s, C-1), 133.5 (d, C-2 or C-3), 136.6 (d, C-2 or C-3).

*Treatment of* **18** *with Sodium Tetracarbonylcobaltate(−II):* A solution of 410 mg (1.20 mmol) of octacarbonyldicobalt in 20 ml of diethyl ether was stirred for 20 h over 30 g of 1% sodium amalgam. The colorless solution of Na[Co(CO)$_4$][20,21] was filtered and then added dropwise at −78 °C to a solution of 250 mg (1.20 mmol) of **18** in 30 ml of diethyl ether. The mixture was allowed to warm up to 25 °C over a period of 14 h and turned red during this time. The solvent was condensed into a cold trap at 10 mbar, and the residue was transferred into another flask at 0.01 mbar. We obtained 110 mg (100%) of **11**, identified by a comparison of the $^1$H-NMR spectral and GC data with those of an authentic sample.

*Preparation of a Solution of the Bicyclo[3.2.0]hepta-1,3-dienyl Anion* (**4**)[2]: At −25 °C 385 mg (3.00 mmol) of **17** was rapidly added to a solution of 642 mg (6.00 mmol) of lithium diisopropylamide[51] (LDA) in 3 ml of THF. A yellow color appeared, which did not become more intense after 1 h.

*Treatment of the Bicyclo[3.2.0]hepta-1,3-dienyl Anion* (**4**) *with $Co_2(CO)_8/I_2$:* 1.53 g (12.0 mmol) of iodine was added in small portions to a solution of 2.07 g (6.10 mmol) of octacarbonyldicobalt in 150 ml of THF. During this addition the mixture assumed a green color with evolution of some gas. After stirring for 1 h, the mixture was slowly added at −30 °C to a solution of **4**, which had been prepared from 0.64 g (6.00 mmol) of LDA and 0.39 g (3.00 mmol) of **17**. The mixture was allowed to warm to 25 °C over a period of 3 h and was then stirred at this temperature for 16 h. The solvent was evaporated into a cold trap at 1 mbar. Filtration through a silica gel column (20 × 2 cm) with diethyl ether gave a red oil, which was condensed into another flask at 25 °C/0.001 mbar with some losses; 0.10 g (17%) of a mixture of **19** and **15** in a ratio of 81:19 was obtained. Column chromatography (silica gel, column 40 × 1 cm) with pentane led to some decomposition and gave 0.01 g (1.6%) of **19**.

IR ($C_6D_6$): $\tilde{\nu}$ = 1954 cm$^{-1}$ (C=O), 2017 (C=O). — $^1$H NMR (80 MHz, $C_6D_6$): 2.4 [AA′BB′ system, 4H, *syn*-6(7)-H, *anti*-6(7)-H], 3.90 [t, 1H, 3-H, $^3J_{3,2(4)}$ = 2.2 Hz], 4.52 [d, 2H, 2(4)-H]. — MS (70 eV): *m/z* (%) = 206 (26) [M$^+$], 178 (36) [M$^+$ − CO], 150 (76) [M$^+$ − 2 CO], 91 (100) [$C_7H_7^+$], 59 (62) [Co$^+$].

*Treatment of the Bicyclo[3.2.0]hepta-1,3-dienyl Anion* (**4**) *with $Co(PPh_3)_3Cl$:* To a solution of **4**, prepared from 0.77 g (6.00 mmol) of **17** and 1.27 g (12.0 mmol) of LDA in 6 ml of THF at −20 °C, a slurry of 5.28 g (6.00 mmol) of chlorotris(triphenylphosphane)cobalt[27a] in 50 ml of THF was added; during this addition the color changed to red. After 15 min, the THF was removed into a cold trap at 1 mbar, and the residue was mixed with 50 ml of diethyl ether. The mixture was filtered through a P4 frit covered with a layer (1 cm) of alumina. Removal of some of the solvent followed by crystallization at −30 °C gave 1.47 g of triphenylphosphane, identified by a comparison of the NMR spectra ($^1$H, $^{13}$C, $^{31}$P) with those of an authentic sample. Repeated crystallization at −78 °C gave additional 2.24 g of triphenylphosphane (overall yield 79%).

*Treatment of $ClCo(PPh_3)_3$ with Diphenylethyne* (**20**): 0.88 g (1.00 mmol) of chlorotris(triphenylphosphane)cobalt(I)[27a] and 1.42 g (8.00 mmol) of **20** in 25 ml of *o*-xylene were heated under reflux for 16 h. After cooling to 25 °C, 0.52 g (97%) of crystalline **21** was filtered off (identified by a comparison of the IR spectrum with that of an authentic sample). Column chromatography of the filtrate (silica gel, column 30 × 2 cm) with pentane gave 0.90 g (63%) of diphenylethyne.

*Bromotris(trimethyl phosphite)cobalt(I):* 21.9 g (0.10 mol) of cobalt(II) bromide, 74.4 g (0.60 mol) of trimethyl phosphite and 4.91 g (75.0 mmol) of zinc dust were stirred in 900 ml of THF at 25°C for 24 h. After filtration, the solvent and unreacted trimethyl phosphite were condensed into a cold trap at 1 mbar/25°C. The yellow residue was collected in a small volume of THF and precipitated by the addition of pentane at −20°C; 42.7 g (83%) of bromotris(trimethyl phosphite)cobalt(I) was obtained as a yellow-green solid (m.p. 149.5°C).

IR (KBr): $\tilde{\nu}$ = 2990 (m), 2948 (s), 2842 (m), 1461 (m), 1179 (m), 1036 (s), 768 (s), 706 (s), 540 (m). − $^1$H NMR (200 MHz, $CDCl_3$): δ = 3.63 (br. s). − $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 52.8. − $^{31}$P NMR (81 MHz, $CDCl_3$): δ = 148.5. − MS (70 eV): *m/z* (%) = 512 (0.6) [$M^+$], 510 (0.7) [$M^+$], 481 (0.2) [$M^+ - OCH_3$], 479 (0.2) [$M^+ - OCH_3$], 388 (2) [$M^+ - P(OCH_3)_3$], 386 (2) [$M^+ - P(OCH_3)_3$], 307 (1) [$M^+ - P(OCH_3)_3 - Br$], 264 (2) [$M^+ - 2\,P(OCH_3)_3$], 262 (2) [$M^+ - 2\,P(OCH_3)_3$], 140 (2) [$CoBr^+$], 125 (2) [$HP(OCH_3)_3^+$], 124 (57) [$P(OCH_3)_3^+$], 110 (10) [$P(OCH_3)_2OH^+$], 109 (59) [$PO(OCH_3)_2^+$], 96 (4), 95 (3), 94 (35) [$HP(OCH_3)_2^+$], 93 (100) [$P(OCH_3)_2^+$], 80 (12) [$HP(OH)(OCH_3)^+$], 79 (26) [$HPO(OCH_3)^+$], 72 (7), 71 (6), 63 (47) [$HPOCH_3^+$], 47 (19) [$PO^+$], 42 (13).

$C_9H_{27}BrCoO_9P_3$ (511.1)
Calcd. C 21.15 H 5.33 Br 15.63 Co 11.53 P 18.18
Found C 20.51 H 4.76 Br 15.29 Co 11.26 P 17.64

*Treatment of the Bicyclo[3.2.0]hepta-1,3-dienyl Anion* (**4**) *with Co[P(OMe)$_3$]$_3$Br:* At −20°C a slurry of 1.83 g (3.00 mol) of bromotris(trimethyl phosphite)cobalt(I) in 25 ml of THF was added to a solution of **4**, prepared from 0.39 g (3.00 mmol) of **17** and 1.27 g (12.0 mmol) of LDA in 6 ml of THF. The mixture became darker over a period of 7 d. After solvent removal, $Co[P(OMe)_3]_3Br$ remained as a yellow solid beside some **11** (identified by a comparison of the $^1$H-NMR spectrum with those of authentic samples).

*($\eta^5$-Bicyclo[3.2.0]hepta-1,3-dienyl)($\eta^4$-cycloocta-1,5-diene)cobalt(I)* (**22**): A solution of 17.6 g (24.5 mmol) of $ClCo[P(OiPr)_3]_3$[29] in 100 ml of THF was cooled to −20°C and then added during 30 min to a −20 to −30°C cold solution of **4**, prepared from 2.45 g (12.0 mmol, purity 63%) of **17** and 2.57 g (24.0 mmol) of LDA in 12 ml THF. The mixture was stirred at −20 to −30°C for 30 min and then allowed to warm to 25°C during 16 h. The solvent and all other volatile components were condensed into a cold trap at 0.1 mbar. The residue was dissolved in 50 ml of cycloocta-1,5-diene and stirred at 110°C for 6 h. After cooling to 25°C, unreacted cycloocta-1,5-diene and all other volatile products were condensed into a cold trap at 0.1 mbar. The residue was chromatographed on silica gel (column 40 × 3 cm) to yield a yellow-orange oil, which was crystallized from diethyl ether at −78°C; 1.53 g (49%) of **22** was obtained as brick-red crystals (m.p. 113.5°C).

IR (KBr): $\tilde{\nu}$ = 3094 cm$^{-1}$ (w), 3074 (w), 2990 (m), 2973 (m), 2928 (s), 2904 (w, sh), 2866 (m), 2819 (s), 1467 (w), 1449 (m), 1424 (w), 1371 (m), 1319 (m), 1296 (w), 1234 (w), 1219 (m), 1204 (w), 1175 (w), 1146 (w), 1072 (w), 1037 (w), 989 (m), 943 (m), 920 (w), 886 (m), 857 (s), 824 (w), 803 (s), 487 (m). − UV (cyclohexane): λ (lg ε) = 213 nm (5.244), 237 (5.171), 274 (5.116), 359 (3.325), 424 (3.344). − $^1$H NMR (200 MHz, $C_6D_6$): δ = 1.7 (m, 4H), 1.98 + 2.36 [AA′BB′, 2 × 2H, *syn*-6(7)-H, *anti*-6(7)-H], 2.5 (m, 4H), 3.1 (m, 4H), 3.16 (t, 3-H, $^3J_{3,2(4)}$ = 2.2 Hz), 4.83 [d, 2H, 2(4)-H]. − $^{13}$C NMR (50 MHz, $C_6D_6$): δ = 26.3 [t, C-6(7), $^1J_{C,H}$ = 140.2 Hz], 32.6 [t, C-10(11,14,15), $^1J_{C,H}$ = 126.7 Hz], 67.2 [d, C-8(9,12,13), $^1J_{C,H}$ = 155.0 Hz], 77.8 [d, C-2(4), $^1J_{C,H}$ = 178.5 Hz], 81.5 (d, C-3, $^1J_{C,H}$ = 171.1 Hz), 105.4 [s, C-1(5)]. − $^{59}$Co NMR (94.8 MHz, $C_6D_6$, 310 K): δ = −1274.4 ($w_{1/2}$ = 11700 Hz). − MS (70 eV): *m/z* (%) = 258 (13) [$M^+$], 230 (15), 229 (22), 152 (18), 151 (12), 150 (27) [$CoC_7H_7^+$], 138 (13), 137 (25) [$CoC_6H_6^+$], 125 (15), 124 (25) [$CoC_5H_5^+$], 113 (35), 105 (6), 98 (11), 91 (58) [$C_7H_7^+$], 85 (12), 79 (18), 77 (14), 65 (40) [$C_5H_5^+$], 63 (19), 59 (100) [$Co^+$], 53 (13), 51 (20), 41 (30), 39 (69), 29 (10), 27 (33).

$C_{15}H_{19}Co$ (258.2) Calcd. C 69.76 H 7.42 Co 22.82
Found C 69.84 H 7.10 Co 22.96

*Treatment of* **22** *with Butyllithium/Tetramethylethylenediamine (tmeda).* − a) At −78°C 16.0 mg (0.14 mmol) of tetramethylethylenediamine (tmeda) and then 0.10 ml of a 1.4 M solution of *n*-butyllithium in hexane were added with a syringe to a solution of 30.0 mg (0.12 mmol) of **22** in 2 ml of THF. After stirring at −78°C for 1 h, 45.0 mg (0.42 mmol) of chlorotrimethylsilane was added, and the mixture was warmed to 25°C during 16 h. Then 5 ml of water was added, and the mixture was extracted three times with 3 ml of diethyl ether each. The collected organic layers were dried with $MgSO_4$, filtered, and the solvent was condensed into a cold trap at 0.1 mbar. Column chromatography (silica gel, column 30 × 1 cm) of the residue with pentane gave 12.0 mg (39%) of **22**. No more products were obtained by elution with diethyl ether.

b) At −78°C 16.0 mg (0.14 mmol) of tmeda and then 0.10 ml of a 1.4 M solution of *n*-butyllithium in hexane were added with a syringe to a solution of 30.0 mg (0.12 mmol) of **22** in 2 ml of THF. The mixture was slowly warmed. At −70°C a clouding was observed with some precipitation. The precipitate redissolved at −30°C. At −10°C 45.0 mg (0.42 mmol) of chlorotrimethylsilane was added. For workup see a); 15.0 mg (50%) of **22** was obtained.

*Treatment of* **22** *with Triphenylcarbenium Tetrafluoroborate:* At 25°C a solution of 40.0 mg (0.12 mmol) of triphenylcarbenium tetrafluoroborate in 2 ml of dichloromethane was added to a solution of 30.0 mg (0.12 mmol) of **22** in 2 ml of dichloromethane. The color of the mixture immediately became red. The mixture was extracted six times with 2 ml of water each. The aqueous layers were separated from the $CH_2Cl_2$ layer with a pipette and washed twice with 5 ml of diethyl ether each. After separation of the organic layer, the water was evaporated from the collected aqueous layers at 0.1 mbar. The red residue was dried at 0.001 mbar/25°C for 16 h; 15.0 mg (36%) of **28** was obtained as a red solid (m.p. 169.5−170.5) which was soluble in acetone.

IR (KBr): $\tilde{\nu}$ = 3527 cm$^{-1}$ (m, $H_2O$), 3110 (w, coord. cyclopentadienyl), 2962 (w), 2933 (w), 2895 (w), 2844 (w), 1632 (m, $H_2O$), 1482 (w, C=C, π-allyl), 1446 (m), 1375 (m), 1282 (m, grease?), 1221 (w), 1057 (s, $BF_4^-$), 918 (w), 900 (w), 860 (w), 849 (w), 805 (m), 586 (w), 521 (m). − $^1$H NMR (400 MHz, [D$_6$]acetone): δ = 1.28 (m, 1H, *syn*-15-H, $^3J_{8,syn\text{-}15}$ = 7.3 Hz, $^3J_{anti\text{-}14,syn\text{-}15}$ ≈ 7.3 Hz, $^3J_{syn\text{-}14,syn\text{-}1,5}$ ≈ 13.3 Hz, $^2J_{syn\text{-}15,anti\text{-}15}$ ≈ −13.3 Hz), 1.9−2.2 (m, 4H, *syn*-11-H, *anti*-14-H, *syn*-14-H, *anti*-15-H, $^3J_{10,syn\text{-}11}$ = 5.8 Hz, $^2J_{anti\text{-}11,syn\text{-}11}$ ≈ −13.2 Hz, $^3J_{syn\text{-}11,12}$ ≈ 8.6 Hz, $^4J_{12,anti\text{-}14}$ ≈ −1.5 Hz, $^3J_{13,anti\text{-}14}$ ≈ 7.3 Hz), 2.78 (m, 1H, 6-H or 7-H), 2.9−3.1 (m, 3H, 6-H, 7-H), 3.32 (m, 1H, *anti*-11-H, $^3J_{10,anti\text{-}11}$ = 9.5 Hz, $^3J_{anti\text{-}11,12}$ ≈ 8.6 Hz), 3.61 (ddd, 1H, 12-H, $^3J_{12,13}$ = 8.5 Hz), 4.31 (dd, 1H, 9-H, $^3J_{8,9}$ = 7.9 Hz, $^3J_{9,10}$ = 7.9 Hz), 5.40 (m, 1H, 13-H), 5.44 (t, 1H, 3-H, $^3J_{2,3}$ = 2.3 Hz, $^3J_{3,4}$ = 2.3 Hz), 5.48 (m, 1H, 10-H, $^4J_{8,10}$ = 1.2 Hz), 5.52 (d, 1H, 2-H), 5.56 (d, 1H, 4-H), 5.99 (dd, 1H, 8-H). − MS (70 eV): Decomposition.

$C_{15}H_{18}BCoF_4$ (344.0) Calcd. C 52.37 H 5.27 B 3.14
Found C 52.42 H 5.25 B 3.29

*Reaction of* **22** *with Triphenylphosphane/Dimethyl Fumarate:* 109 mg (0.42 mmol) of **22**, 508 mg (1.94 mmol) of triphenylphosphane, and 308 mg (2.14 mmol) of dimethyl fumarate in 20 ml of *o*-xylene were heated under reflux for 24 h. The solvent and all other volatile components were condensed into a cold trap at 0.001 mbar/25°C, and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane 60.0 mg (55%) of **22** was eluted. Unreacted dimethyl fumarate and triphenylphosphane were eluted with pentane/diethyl ether (30:1). With diethyl ether 70.0 mg [30%, purity ca. 90% (NMR)] of **26a** was obtained as dark red microcrystals (m.p. 50.6°C).

IR (KBr): $\tilde{\nu}$ = 3060 cm$^{-1}$ (w, coord. cyclopentadienyl), 2950 (w), 1735 (m, C=O), 1690 (s, C=O), 1465 (w), 1458 (w), 1435 (m, $PPh_3$), 1292 (m), 1260 (m), 1150 (s, C−O), 1090 (w), 1038 (m), 805 (w, 1,2-disubst. cyclopentadienyl), 747 (m), 695 (s, $PPh_3$), 542 (w), 535 (m, $PPh_3$), 515 (w). − $^1$H NMR (400 MHz, $C_6D_6$): δ = 2.27 (m, 1H, 6-H or 7-H), 2.63 (m, 1H, 6-H or 7-H), 2.70 (dd, 1H, 10-H, $^3J_{9,10}$ = 10.4 Hz, $J_{10,P}$ = 11.6 Hz), 2.71 (m, 1H, 6-H or 7-H), 2.94 (s, 3H, 12-H or 13-H), 3.35 (m, 1H, 6-H or 7-H), 3.55 (s + dd, 4H, 12-H or 13-H, 9-H, $J_{9,P}$ > 0 Hz), 3.83 (br. s, 1H, 3-H), 4.25 (br. s, 2H, 2-H, 4-H), 7.03 (m, 3H, *p*-H), 7.10 (m, 6H, *m*-H), 7.76 (m, 6H, *o*-H). − $^{13}$C NMR (50 MHz,

$C_6D_6$): $\delta$ = 27.3 (t, C-6 or C-7), 27.9 (t, C-6 or C-7), 35.8 (d, C-9 or C-10), 42.1 (d, C-9 or C-10), 50.1 (q, C-12 or C-13), 50.9 (q, C-12 or C-13), 77.3 (d, C-2 or C-3 or C-4), 80.7 (d, C-2 or C-3 or C-4), 85.3 (d, C-2 or C-3 or C-4), 104.0 (s, C-1 or C-5), 109.9 (s, C-1 or C-5), 127.9 (dd, C-15 or C-16, $J_{C,P}$ = 9.3 Hz), 129.4 (dd, C-17, $J_{C,P}$ = 1.9 Hz), 134.8 (dd, C-15 or C-16, $J_{C,P}$ = 10.6 Hz), 134.8 (d, C-14, $^{1}J_{C,P}$ = 39.0 Hz), 177.4 (s, C-8 or C-11), 178.6 (s, C-8 or C-11). – $^{31}P$ NMR (81 MHz, $C_6D_6$): $\delta$ = 62.1. – MS (70 eV): *m/z* = 438 (0.4) [$M^+ - 2\,COOCH_3$], 294 (13) [$M^+ - PPh_3$], 263 (19) [$HPPh_3^+$], 262 (100) [$PPh_3^+$], 261 (16) [$PPh_3^+ - H$], 234 (5), 185 (8) [$PPh_2^+$], 184 (15) [$PPh_2^+ - H$], 183 (58) [$PPh_2^+ - 2H$], 176 (4), 175 (3), 174 (3), 173 (3), 158 (3), 157 (4), 152 (9), 151 (5), 150 (17) [$C_7H_7Co^+$], 145 (4), 144 (7) [$C_6H_8O_4^+$], 141 (4), 115 (5), 114 (3), 113 (12), 108 (37) [$PPh^+$], 107 (12), 105 (4), 91 (33) [$C_7H_7^+$], 85 (5), 65 (5) [$C_5H_5^+$], 59 (10) [$Co^+$], 51 (5), 40 (3), 39 (4).

*Reaction of* **22** *with Tributylphosphane/Dimethyl Fumarate:* 120 mg (0.47 mmol) of **22**, 336 mg (2.33 mmol) of dimethyl fumarate, and 606 mg (3.00 mmol) of tri-*n*-butylphosphane in 30 ml of *o*-xylene were heated under reflux for 16 h. The solvent and all other volatile material was condensed into a cold trap at 0.001 mbar/25°C, and the residue was chromatographed on silica gel (column 40 × 2 cm). With pentane 30.0 mg (25%) of **22** was eluted. With diethyl ether 160 mg (69%) of **26b** was obtained. Recrystallization from diethyl ether at –25°C gave 90.0 mg (52% rel. to converted starting compound) of **26b** as dark red crystals (m.p. 87°C).

IR (KBr): $\tilde{\nu}$ = 2957 $cm^{-1}$ (s), 2954 (s), 2872 (m), 2858 (m), 1740 (w), 1697 (s, C=O), 1672 (s, C=O), 1471 (m), 1455 (m), 1435 (m), 1295 (s, coord. dimethyl fumarate), 1169 (s, C–O), 1152 (s, C–O), 1094 (m), 1039 (m), 907 (m), 883 (m), 860 (w), 802 (m), 785 (w), 774 (w), 763 (w), 721 (w), 684 (w), 558 (w). – $^{1}H$ NMR (200 MHz, $C_6D_6$): $\delta$ = 0.92 (m, 3H, 10-H), 1.2–1.6 (m, 6H, 8-H, 9-H, 10-H), 2.51 (m, 1H, *syn*-6-H), 2.77 (dd, 1H, 12-H or 13-H, $^{3}J_{12,13}$ = 10.3 Hz, $J_{12,P}$ = 2.2 Hz, $J_{13,P}$ = 10.3 Hz), 2.7–2.9 (m, 2H, *anti*-6-H, *syn*-7-H), 3.36 (m, 1H, *anti*-7-H), 3.45 (s, 3H, 16-H or 17-H), 3.50 (dd, 1H, 12-H or 13-H), 3.56 (s, 3H, 16-H or 17-H), 4.01 (dd, 1H, 2-H or 4-H, $^{3}J_{2,3}$ = 2.5 Hz, $^{3}J_{3,4}$ = 2.0 Hz, $J_{2,P} > 0$ Hz, $J_{4,P}$ = 1.7 Hz), 4.27 (dd, 1H, 2-H or 4-H), 4.66 (ddd, 1H, 3-H, $J_{3,P}$ = 1.2 Hz). – $^{13}C$ NMR (50 MHz, $C_6D_6$): $\delta$ = 14.1 (q, C-17), 23.5 (td, C-14, $^{1}J_{C,P}$ = 22.1 Hz), 24.7 (td, C-15, $^{2}J_{C,P}$ = 11.8 Hz), 26.2 (t, C-16), 27.0 (t, C-6 or C-7), 28.7 (t, C-6 or C-7), 32.4 (d, C-9 or C-10), 35.2 (d, C-9 or C-10), 50.4 (q, C-12 or C-13), 50.6 (q, C-12 or C-13), 75.0 (d, C-3), 80.2 (d, C-2 or C-4), 80.9 (d, C-2 or C-4), 100.3 (s, C-1 or C-5), 111.2 (s, C-1 or C-5), 178.6 (s, C-8 or C-11), 179.3 (s, C-8 or C-11). – $^{31}P$ NMR (81 MHz, $C_6D_6$): $\delta$ = 32.7. – MS (70 eV): *m/z* (%) = 497 (1) [$M^+ + 1$], 496 (4) [$M^+$], 352 (22) [$M^+ + 1 - C_6H_8O_4$], 352 (100) [$M^+ - C_6H_8O_4$], 351 (14) [$M^+ - C_6H_8O_4 - H$], 350 (64) [$M^+ - C_6H_8O_4 - 2H$], 296 (19) [$M^+ - PnBu_3 + 2H$], 295 (7) [$M^+ - PnBu_3 + H$], 294 (29) [$M^+ - PnBu_3$], 240 (17), 238 (10), 237 (5), 235 (12), 207 (21), 206 (54), 205 (5), 204 (11), 203 (8), 202 (7) [$PnBu_3^+$], 184 (9), 175 (5), 173 (15), 161 (6), 150 (16) [$C_7H_7CO^+$], 147 (10), 146 (7), 145 (7), 144 (7), 131 (7), 119 (8), 118 (11), 113 (14), 104 (14), 91 (25) [$C_7H_7^+$], 89 (5), 85 (6), 76 (39), 62 (23), 61 (10), 59 (10) [$Co^+$], 55 (8), 41 (11), 39 (5), 29 (15).

$C_{25}H_{42}CoPO_4$ (496.5)
Calcd. C 60.48 H 8.53 Co 11.87 P 6.24
Found C 60.39 H 8.48 Co 11.76 P 6.25

*Reaction of* **22** *with Trimethyl Phosphite/Dimethyl Fumarate:* 258 mg (1.00 mmol) of **22**, 590 mg (5.00 mmol) of trimethyl phosphite and 720 mg (5.00 mmol) of dimethyl fumarate in 120 ml of *o*-xylene were heated under reflux for 16 h. The solvent and all other volatile products were condensed into a cold trap. Column chromatography on silica gel [column 60 × 2 cm, pentane/diethyl ether (10:1 → 1:1)] gave some unreacted dimethyl fumarate, **22** and finally 80.0 mg (19%) of **26c** as a red oil, which became solid upon standing.

IR (film): $\tilde{\nu}$ = 3095 $cm^{-1}$ (w), 2980 (m), 2946 (s), 2907 (w), 2840 (m), 1698 (s, C=O), 1459 (s), 1434 (s), 1295 (s), 1260 (s), 1152 (s), 1016 (s, $OCH_3$), 883 (w), 798 (s), 782 (s), 744 (s), 686 (w), 544 (m). – $^{1}H$ NMR (400 MHz, $C_6D_6$): $\delta$ = 2.50 (m, 1H, *syn*-6-H, $^{2}J_{anti\text{-}6,syn\text{-}6}$ = –13.4 Hz, $^{3}J_{syn\text{-}6,anti\text{-}7}$ = 3.0 Hz, $^{3}J_{syn\text{-}6,syn\text{-}7}$ = 6.0 Hz, $J_{syn\text{-}6,P}$ = 6.2 Hz), 2.73 (m, 1H, *syn*-7-H, $^{3}J_{anti\text{-}6,syn\text{-}7}$ = 2.7 Hz, $^{2}J_{anti\text{-}7,syn\text{-}7}$ = –12.8 Hz, $J_{syn\text{-}7,P}$ = 2.0 Hz), 2.85 (m, 1H, *anti*-6-H, $^{3}J_{anti\text{-}6,anti\text{-}7}$ = 5.0 Hz, $J_{anti\text{-}6,P}$ = 3.2 Hz), 3.11 (dd, 1H, 11-H or 10-H, $^{3}J_{10,11}$ = 10.4 Hz, $J_{11,P}$ = 11.8 Hz, $J_{10,P}$ = 3.2 Hz), 3.28 (d, 9H, 8-H, $J_{8,P}$ = 11.6 Hz), 3.3 (m, 1H, *anti*-7-H, $J_{anti\text{-}7,P} > 0$ Hz), 3.40 (s, 3H, 11-H or 12-H), 3.43 (dd, 1H, 10-H or 11-H), 3.49 (s, 3H, 13-H or 14-H), 4.20 (dd, 1H, 4-H or 2-H, $^{3}J_{2,3}$ = 2.5 Hz, $^{3}J_{3,4} \approx 2.2$ Hz, $J_{4,P} \approx 1$ Hz), 4.35 (d, 1H, 2-H or 4-H), 4.65 (dd, 1H, 3-H). – $^{31}P$ NMR (81 MHz, $C_6D_6$): $\delta$ = 168.2. – MS (70 eV): *m/z* (%) = 418 (32) [$M^+$], 294 (11) [$M^+ - P(OCH_3)_3$], 275 (11), 274 (100) [$M^+ - C_2H_2(COOCH_3)_2$], 259 (18), 183 (15), 168 (26), 164 (32), 153 (14), 152 (11), 151 (40), 150 (43) [$C_7H_7Co^+$], 138 (19), 93 (38) [$C_7H_9^+$], 91 (44) [$C_7H_7^+$], 63 (13), 59 (17) [$Co^+$].

$C_{16}H_{24}CoO_7P$ Calcd. 418.05916 Found 418.05939 (HR MS)

*Reaction of* **22** *with Triphenylphosphane/Dimethyl Maleate:* 30.0 mg (0.12 mmol) of **22**, 152 mg (0.58 mmol) of triphenylphosphane and 91.0 mg (0.58 mmol) of dimethyl maleate in 10 ml of *o*-xylene were heated under reflux for 2 d. The solvent and all other volatile products were condensed into a cold trap, and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane 10.0 mg (32%) of **22** was eluted. With pentane/diethyl ether (30:1) 30.0 mg of a mixture of dimethyl fumarate ($^{1}H$ NMR) and triphenylphosphane was eluted. With diethyl ether 10.0 mg (25% rel. to converted starting compound) of **26a** was obtained and identified by a comparison of the $^{1}H$-NMR spectrum with that of an authentic sample.

*Thermolysis of* **22** *at 162°C in Diethylene Glycol Dimethyl Ether (diglyme):* 30.0 mg (0.12 mmol) of **22** in 3 ml of diglyme was heated to 162°C for 16 h. The solvent was condensed into a cold trap at 0.001 mbar/25°C, and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane 20.0 mg (66%) of **22** was eluted.

*Thermolysis of* **22** *at 170°C in Tetralin:* 25.0 mg (0.10 mmol) of **22** in 2 ml of tetralin was heated to 170°C for 16 h. The solvent was condensed into a cold trap at 0.001 mbar/25°C, and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane 19.0 mg of a mixture (12:1, $^{1}H$ NMR) of the starting compound **22** and the products **27**[42] and **28** were eluted.

*Thermolysis of* **22** *at 200°C in Tetralin:* 60.0 mg (0.23 mmol) of **22** in 3 ml of tetralin (98.0% purity, 0.95% naphthalene) was heated at 200°C for 17 h. The solvent and all other volatile components were condensed into a cold trap at 0.001 mbar/25°C (98.0% tetralin, 0.97% naphthalene), and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane as the eluent 12.6 mg (ca. 21%) of a mixture (ca. 1:1) of **27**[19] and **28** was isolated. With diethyl ether 5.00 mg of a brown unidentified material was eluted.

$^{1}H$ NMR (200 MHz, $C_6D_6$): **28**[53]: $\delta$ = 1.50 [s, 6H, 6(7)-H], 1.74 (m, 4H, aliph. COD-H), 3.91 (t, 1H, 4-H, $^{3}J_{4,3(5)}$ = 2.7 Hz), 4.35 [d, 2H, 3(5)-H]. – MS (70 eV): **27** + **28**: *m/z* (%) = 261 (16) [$M^+ + 1$], 260 (100) [$M^+$], 259 (9) [$M^+ - H$], 258 (37) [$M^+ - 2H$], 257 (13) [$M^+ - 3H$], 256 (9) [$M^+ - 4H$], 245 (9) [$M^+ - CH_3$], 244 (8) [$M^+ - CH_3 - H$], 243 (35) [$M^+ - CH_3 - 2H$], 231 (25) [$M^+ + 1 - 2\,CH_3$ or $M^+ - C_2H_5$], 230 (98) [$M^+ - 2\,CH_3$], 229 (37) [$M^+ - 2\,CH_3 - H$], 217 (13), 216 (8), 206 (11), 165 (13), 164 (22), 152 (62) [$M^+$ – COD], 151 (21) [$M^+$ – COD – H], 150 (51) [$M^+$ – COD – 2H], 138 (19), 137 (37), 125 (11), 124 (23), 113 (13), 98 (7), 93 (7), 91 (23) [$C_7H_7^+$], 85 (5), 79 (8), 77 (8), 59 (67) [$Co^+$], 41 (9), 39 (8).

*Thermolysis of* **22** *at 260°C:* 20.0 mg (0.08 mmol) of **22** in a 10-ml Schlenk flask was placed into a 260°C hot oil bath for 5 min. Some white smoke developed and was condensed into another flask. The material was identified as **29** ($^{1}H$ NMR, GC). The residue was insoluble in all common solvents.

*($\eta^5$-Bicyclo[3.2.0]hepta-1,3-dienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt(I)* (**30**): A solution of 0.15 g (0.58 mmol) of **22** and 1.03 g (5.80 mmol) of diphenylethyne in 20 ml of *o*-xylene was heated at reflux for 20 h.The solvent and all other volatile products were condensed into a cold trap at 0.1 mbar/25°C, and the residue was chromatographed on silica gel (column 30 × 1 cm). With pentane a small amount of unreacted **22** was eluted. With diethyl ether 0.18 g (61%) of **30** was eluted and crystallized from diethyl ether at –78°C (m.p. 180°C, DSC, red-brown crystals).

IR (KBr): $\tilde{\nu}$ = 3077 $cm^{-1}$ (w), 3056 (w), 3024 (w), 2969 (w), 2930 (m), 2031 (w), 1595 (m), 1571 (w), 1498 (s), 1442 (m), 1378 (m), 1176 (w), 1153 (w), 1118 (m), 1072 (m), 1024 (m), 1007 (w), 807 (m), 782 (m), 740 (m), 698 (s), 697 (s), 618 (m), 589 (m), 565 (s), 541 (w). – UV (methanol): $\lambda_{max}$ (lg $\varepsilon$) = 243 nm (4.450), 256 (4.454), 292 (4.392). – $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.30 + 2.68 [AA'BB', 4H, *syn*-6(7)-H, *anti*-6(7)-H, $\sum J_{syn\text{-}6(7),anti\text{-}6(7)}$ = 9.6 Hz], 4.34 (t, 1H, 3-H, $^3J_{2(4),3}$ = 2.2 Hz), 4.48 [d, 2H, 2(4)-H], 7.23 (m, 12H, *m*-, *p*-H), 7.44 (m, 8H, *o*-H). – $^{13}C$ NMR (50 MHz, $C_6D_6$): $\delta$ = 26.1 [t, C-6(7), $^1J_{C,H}$ = 141.9 Hz], 75.4 (s, C-8), 77.3 [d, C-2(4), $^1J_{C,H}$ = 177.2 Hz], 82.9 (d, C-3, $^1J_{C,H}$ = 174.3 Hz), 103.1 [s, C-1(5)], 126.4 (d, C-12, $^1J_{C,H}$ = 162 Hz), 128.4 [d, C-10 or C-11, $^1J_{C,H}$ = 160 Hz], 129.1 [d, C-10 or C-11, $^1J_{C,H}$ = 161 Hz], 136.9 (s, C-6). – MS (70 eV): *m*/*z* (%) = 508 (14) $[M^+ + 2]$, 507 (37) $[M^+ + 1]$, 506 (100) $[M^+]$, 505 (11) $[M^+ - H]$, 415 (7) $[M^+ - C_7H_7]$, 329 (8) $[M^+ + 1 - C_2Ph_2]$, 328 (36) $[M^+ - C_2Ph_2]$, 327 (28) $[M^+ - H - C_2Ph_2]$, 326 (48) $[M^+ - 2H - C_2Ph_2]$, 267 (7), 265 (12), 253 (11), 250 (6), 239 (19), 238 (10), 237 (52) $[CoC_2Ph_2^+]$, 179 (9) $[C_2Ph_2H^+]$, 178 (52) $[C_2Ph_2^+]$, 176 (7), 152 (7) $[C_7H_9Co^+]$, 150 (21) $[C_7H_7Co^+]$, 91 (31) $[C_7H_7^+]$, 59 (33) $[Co^+]$.

$C_{35}H_{27}Co \cdot 0.5\ C_4H_{10}O$ (543.6) Calcd. C 81.75 H 5.93 Co 10.84
Found C 81.57 H 6.10 Co 10.68

*Crystal Structure Analysis of* **30**: 2 independent molecules of **30** and 1 molecule of diethyl ether per asymmetric unit; crystal size: 0.22 × 0.50 × 0.29 mm; color: brown; $a$ = 11.355(1), $b$ = 14.745(2), $c$ = 18.338(2) Å; $\alpha$ = 101.77(1), $\beta$ = 105.79(1), $\gamma$ = 100.41(1)°; $V$ = 2799.9 $Å^3$; $d_{calcd.}$ = 1.29 $gcm^{-3}$; $\mu$ = 6.35 $cm^{-1}$, Mo-$K_\alpha$ radiation; $\lambda$ = 0.71069 Å; $F(000)$ = 1140; crystal system: triclinic; space group: $P\bar{1}$, Nonius CAD-4 diffractometer; scan mode: $\omega$-2$\Theta$; $\sin\Theta/\lambda_{max.}$ = 0.65; 12729 measured reflections ($\pm h$, $\pm k$, $+l$); 12727 independent reflections; 6869 observed reflections $[I > 2\sigma(I)]$ for 694 refined parameters; $R$ = 0.063, $R_w$ = 0.046 $[w = 1/\sigma^2(F_o)]$; EOF = 1.51; residual electron density: 0.48 $eÅ^{-3}$.

Table 3. Atomic fractional parameters for **30**; $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Co(1) | 0.1232(1) | 0.3078(1) | 0.0702(1) | 0.033(1) |
| C(1) | 0.2625(4) | 0.4349(3) | 0.1165(3) | 0.047(3) |
| C(2) | 0.2384(5) | 0.4000(3) | 0.1781(3) | 0.057(4) |
| C(3) | 0.1092(5) | 0.3939(3) | 0.1681(3) | 0.061(4) |
| C(4) | 0.0528(4) | 0.4238(3) | 0.1011(3) | 0.054(4) |
| C(5) | 0.1519(4) | 0.4486(3) | 0.0699(2) | 0.044(4) |
| C(6) | 0.2182(5) | 0.4914(3) | 0.0176(3) | 0.064(4) |
| C(7) | 0.3423(4) | 0.4777(3) | 0.0716(3) | 0.067(4) |
| C(8) | 0.1570(3) | 0.1787(3) | 0.0452(2) | 0.032(3) |
| C(9) | 0.0268(3) | 0.1727(3) | 0.0448(2) | 0.031(3) |
| C(10) | 0.0009(3) | 0.2121(3) | −0.0234(2) | 0.031(3) |
| C(11) | 0.1316(3) | 0.2179(3) | −0.0234(2) | 0.032(3) |
| C(12) | 0.2612(3) | 0.1452(3) | 0.0894(2) | 0.033(3) |
| C(13) | 0.2868(4) | 0.1563(3) | 0.1697(3) | 0.048(3) |
| C(14) | 0.3842(4) | 0.1241(3) | 0.2113(3) | 0.058(4) |
| C(15) | 0.4568(4) | 0.0807(3) | 0.1735(3) | 0.059(4) |
| C(16) | 0.4307(4) | 0.0666(3) | 0.0944(3) | 0.055(4) |
| C(17) | 0.3323(4) | 0.0977(3) | 0.0517(2) | 0.043(3) |
| C(18) | −0.0497(3) | 0.1306(3) | 0.0883(2) | 0.034(3) |
| C(19) | −0.0308(4) | 0.0494(3) | 0.1123(2) | 0.044(3) |
| C(20) | −0.1019(5) | 0.0119(3) | 0.1550(3) | 0.056(4) |
| C(21) | −0.1930(5) | 0.0526(4) | 0.1723(3) | 0.066(4) |
| C(22) | −0.2150(4) | 0.1325(4) | 0.1484(3) | 0.065(4) |
| C(23) | −0.1433(4) | 0.1709(3) | 0.1063(2) | 0.047(3) |
| C(24) | −0.1148(3) | 0.2250(3) | −0.0752(2) | 0.032(3) |
| C(25) | −0.2306(4) | 0.1611(3) | −0.0907(2) | 0.042(3) |
| C(26) | −0.3406(4) | 0.1733(3) | −0.1394(3) | 0.052(4) |
| C(27) | −0.3364(4) | 0.2472(3) | −0.1742(2) | 0.048(4) |
| C(28) | −0.2231(4) | 0.3109(3) | −0.1607(2) | 0.043(3) |
| C(29) | −0.1132(4) | 0.3007(3) | −0.1104(2) | 0.038(3) |
| C(30) | 0.2050(4) | 0.2443(3) | −0.0737(2) | 0.033(3) |
| C(31) | 0.1466(4) | 0.2506(3) | −0.1492(2) | 0.042(3) |
| C(32) | 0.2185(4) | 0.2786(3) | −0.1954(2) | 0.053(4) |
| C(33) | 0.3483(4) | 0.2979(3) | −0.1673(3) | 0.057(4) |
| C(34) | 0.4069(4) | 0.2895(3) | −0.0938(3) | 0.054(4) |
| C(35) | 0.3363(4) | 0.2643(3) | −0.0468(2) | 0.043(3) |
| Co(2) | 0.8801(1) | 0.7443(1) | 0.5708(1) | 0.038(1) |
| C(36) | 0.7871(5) | 0.6791(5) | 0.6353(4) | 0.079(6) |
| C(37) | 0.9076(5) | 0.7391(3) | 0.6858(3) | 0.062(4) |
| C(38) | 0.9953(4) | 0.7010(4) | 0.6564(3) | 0.062(4) |
| C(39) | 0.9354(7) | 0.6235(4) | 0.5907(4) | 0.086(6) |
| C(40) | 0.8100(7) | 0.6106(4) | 0.5792(4) | 0.085(6) |
| C(41) | 0.6782(8) | 0.5527(5) | 0.5374(4) | 0.138(7) |
| C(42) | 0.6509(6) | 0.6287(8) | 0.6029(5) | 0.16(1) |
| C(43) | 0.8416(4) | 0.8617(3) | 0.5449(2) | 0.035(3) |
| C(44) | 0.9661(4) | 0.8537(3) | 0.5406(2) | 0.036(3) |
| C(45) | 0.9068(3) | 0.7691(3) | 0.4740(2) | 0.032(3) |
| C(46) | 0.7815(3) | 0.7787(3) | 0.4782(2) | 0.034(3) |
| C(47) | 0.7949(4) | 0.9363(3) | 0.5873(2) | 0.037(3) |
| C(48) | 0.8372(4) | 0.9700(3) | 0.6681(3) | 0.058(4) |
| C(49) | 0.7917(6) | 1.0404(4) | 0.7062(3) | 0.076(5) |
| C(50) | 0.7033(5) | 1.0772(3) | 0.6633(4) | 0.072(5) |
| C(51) | 0.6615(5) | 1.0467(3) | 0.5835(3) | 0.070(5) |
| C(52) | 0.7072(4) | 0.9765(3) | 0.5451(3) | 0.053(4) |
| C(53) | 1.0953(4) | 0.9132(3) | 0.5816(2) | 0.036(3) |
| C(54) | 1.1184(4) | 1.0104(3) | 0.6161(3) | 0.050(3) |
| C(55) | 1.2402(5) | 1.0654(3) | 0.6551(3) | 0.065(4) |
| C(56) | 1.3408(5) | 1.0253(4) | 0.6603(3) | 0.067(4) |
| C(57) | 1.3208(4) | 0.9297(4) | 0.6254(3) | 0.062(4) |
| C(58) | 1.1993(4) | 0.8738(3) | 0.5865(3) | 0.051(4) |
| C(59) | 0.9533(3) | 0.7125(3) | 0.4169(2) | 0.033(3) |
| C(60) | 1.0434(4) | 0.7576(3) | 0.3886(2) | 0.043(3) |
| C(61) | 1.0840(4) | 0.7053(3) | 0.3322(3) | 0.055(4) |
| C(62) | 1.0351(5) | 0.6077(4) | 0.3039(3) | 0.060(4) |
| C(63) | 0.9464(5) | 0.5618(3) | 0.3313(3) | 0.059(4) |
| C(64) | 0.9065(4) | 0.6137(3) | 0.3881(3) | 0.049(4) |
| C(65) | 0.6501(4) | 0.7296(3) | 0.4314(2) | 0.035(3) |
| C(66) | 0.6184(4) | 0.6633(3) | 0.3591(2) | 0.046(3) |
| C(67) | 0.4939(5) | 0.6146(3) | 0.3175(3) | 0.056(4) |
| C(68) | 0.3979(4) | 0.6325(3) | 0.3469(3) | 0.058(4) |
| C(69) | 0.4271(4) | 0.6989(4) | 0.4171(3) | 0.058(4) |
| C(70) | 0.5510(4) | 0.7468(3) | 0.4598(3) | 0.050(4) |
| O | 0.6752(5) | 0.3688(4) | 0.2491(4) | 0.138(6) |
| C(71) | 0.6151(8) | 0.3679(6) | 0.3030(6) | 0.14(1) |
| C(72) | 0.6790(8) | 0.3403(7) | 0.3684(6) | 0.18(1) |
| C(73) | 0.6153(9) | 0.3892(8) | 0.1841(7) | 0.17(1) |
| C(74) | 0.6772(8) | 0.3953(8) | 0.1293(6) | 0.18(1) |

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