Ring Opening of (η^5-Bicyclo[3.2.0]hepta-1,3-dienyl)-(η^4-tetraphenylcyclobutadiene)cobalt(I) Followed by Cycloaddition

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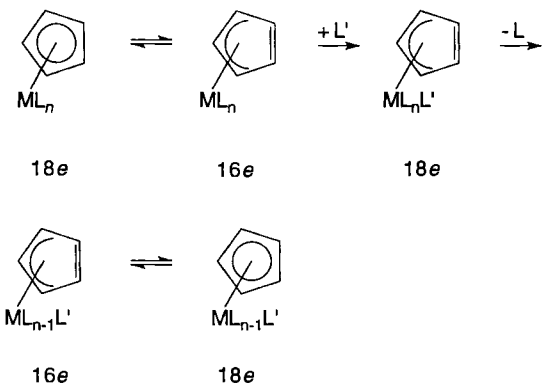
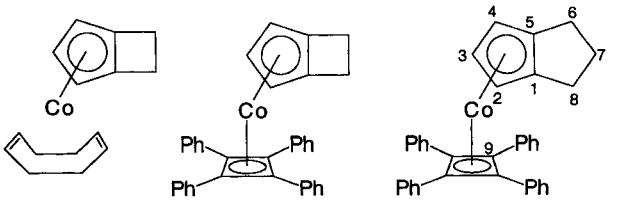
The title reaction, which was detected by a comparison of the DSC analysis of title compound **2** with that of the corresponding bicyclo[3.3.0]octa-1,3-dienyl complex **3**, takes place at 200°C with various dienophiles (dimethyl fumarate, dimethyl maleate, diphenylethyne, *N*-methylmaleinimide). 3,4-Dimethylenecyclopentenyl complex **12** most likely is the key intermediate of the reaction.

Ring slippage reactions[1] of cyclopentadienyl complexes, this means a reversible change in hapticity from η^5 to η^3, are frequently used to explain the mechanism of associative ligand exchange reactions of cyclopentadienyl complexes[2]. Scheme 1 demonstrates such a reaction sequence, which essentially is a sequence of conventional dissociative ligand exchange reactions. However, the sequence is consistent with kinetic measurements indicating a second-order reaction[1], because the decomplexed double bond does not leave the molecule as a whole.

Scheme 1



One question of interest in this context is, in how far chemical reactions involving a temporarily decomplexed double bond of an η^3-cylcopentadienyl intermediate may be possible. The concept of testing this possibility by using bicyclo[3.2.0]hepta-1,3-dienyl complexes, in which the η^3-intermediate might thermally open the cyclobutene ring with the formation of a 4,5-dimethylenecyclopentenyl[3] intermediate has recently been published[4]. However, the 1,5-cyclooctadiene (COD) complex **1** was unsuitable for this purpose, because the activation energy of an opening of the four-membered ring exceeds that of a decomplexation of the electroneutral COD ligand. Therefore the COD was replaced by tetraphenylcyclobutadiene. (η^4-Cyclobutadiene)(η^5-cyclopentadienyl)cobalt(I) complexes are known to be extremely stable against oxidation and heat[5]. Here the successful execution of a reaction sequence involving a ring opening to a 4,5-dimethylenecyclopentenyl intermediate followed by its trapping with dienophiles is described starting from cobalt complex **2**[4]. Some of the results reported were the subject of a preliminary communication[6].



1 **2** **3**

For comparison purposes, the next higher homologue **3** was prepared, which contains an anellated five-membered ring instead of the cyclobutane fragment present in **2**. Complex **3** was obtained in 13% yield by treating the corresponding COD complex[7] with diphenylethyne in boiling *o*-xylene. The DSC analysis (DSC = *D*ifferential *S*canning *C*alorimetry) of **3** shows the compound to be a typical representative of its class (Figure 1 A): After melting at 174°C **3** can be heated to temperatures as high as 400°C without decomposition. Above 400°C a decomposition reaction is detected, the base line of the plot becomes uneven.

The DSC analysis of **2** (Figure 1 B) contrasts with that of **3**. The process detected between 70 and 90°C can be attributed to the thermal loss of solvating diethyl ether[4]. **2** melts at 180°C, and above 200°C a reaction can be observed. This is not a thermal decomposition, the base line remains even. This behaviour is completely untypical of a (η^4-cyclobuta-

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diene)(η^5-cyclopentadienyl)cobalt(I) complexes and clearly has its origin in the presence of the anellated four-membered ring, presumably in a ring-opening reaction.

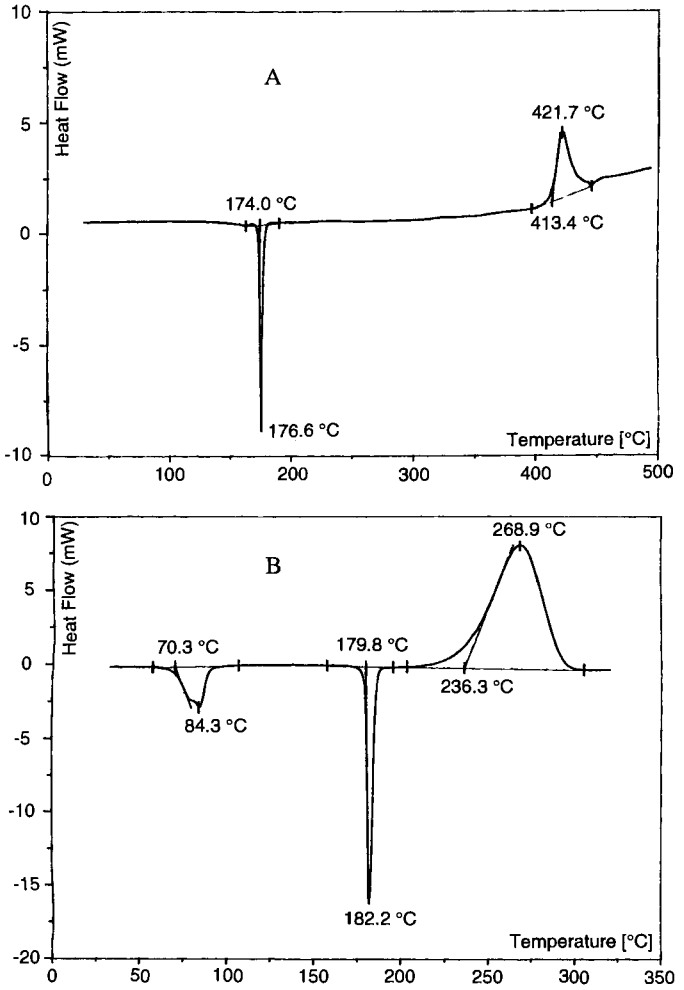
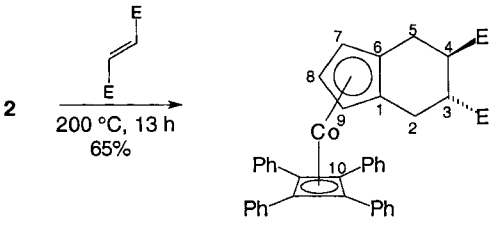


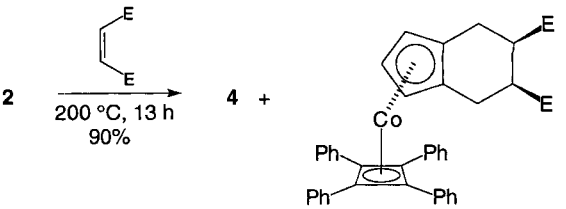
Figure 1. A. DSC plot of **3** (2.31 mg, 25–500 C, 10 K/min); B. DSC plot of **2** (5.71 mg, 25–400 °C, 10 K/min)

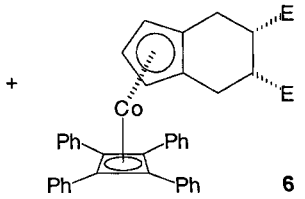
It should be pointed out that this information was obtained by using 2.31 mg of **3** and 5.71 mg of **2**. These are amounts normally needed to obtain a ^{1}H-NMR spectrum. The information obtained includes physical data like the melting point and information of the thermal reactivity of the compound under investigation. The DSC analysis allows computerised curve analyses providing kinetic data of processes observed[8]. We think that this analytical method, which is frequently used in polymer chemistry, metallurgy, and material sciences, is completely underrepresented in the fields of organic and organometallic chemistry.

To test the suggestion that the process detected by thermal analysis could be the desired ring-opening reaction, **2** was heated with a 100fold excess of neat dimethyl fumarate at 200 °C for 13 h. Air-stable [η^5-*trans*-3,4-bis(methoxycarbonyl)bicylco[4.3.0]nona-6,8-dienyl]cobalt(I) complex **4** was indeed formed in 65% yield as brick-red crystals. **4** was characterised by its consistent spectroscopic data and the correct elemental analysis. The formation of **4** proves the opening of the distal bond of the anellated four-membered ring in **2**. The reaction conditions for **2** (200 °C, 13 h) are somewhat more rigorous than those for the corresponding reaction of benzocyclobutene (180 °C, 10 h)[9].



To assess the stereoselectivity of the reaction it is insufficient to perform it with the (*Z*)-dienophile only. Therefore the reaction was repeated by using dimethyl maleate instead of dimethyl fumarate. A mixture of diastereomeric products **4**, **5**, and **6** (0.9:0.5:1.0) was obtained in 90% yield by applying the same reaction conditions. Besides the fact that isomerisation takes place to some extent, it appears remarkable that the *syn-cis*-cycloadduct **6** and not the presumably less crowded *anti-cis*-isomer **5** is the main product of the reaction. **5** and **6** were characterised spectroscopically by taking into account the different signal intensities in the NMR spectra and including NOE experiments. These showed an NOE for the *o*-phenyl protons of the *syn*-product **6** upon irradiation at the resonance frequency of the methyl ester protons.



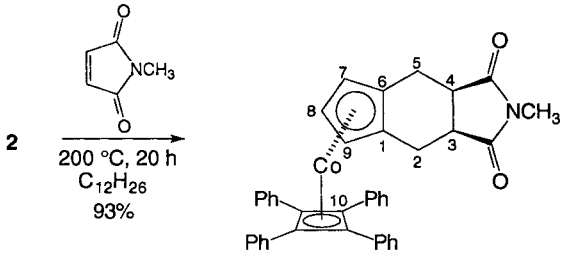


Some additional observations have to be included in the assessment of the reaction: The dimethyl maleate used contained 0.3% of dimethyl fumarate before the reaction. After the reaction this content had increased to 3.9%. Apparently, an isomerisation had taken place. To further investigate this observation, some control experiments were performed, which led to the following results: In the absence of **2** no comparable isomerisation was observed under otherwise identical reaction conditions. The presence of (η^5-cyclopen-

tadienyl)(η^4-tetraphenylcyclobutadiene)cobalt(I)[10], this is the compound corresponding to **2** lacking the anellated ring, did not cause a comparable isomerisation under otherwise unchanged reaction conditions. The presence of **3** caused an isomerisation only to a low extent. In the presence of **2** up to 180°C, this is below the ring-opening temperature determined by DSC, no comparable isomerisation was found.

The higher yield of the reaction with dimethyl maleate as compared to the reaction with dimethyl fumarate presumably has its origin in a practical reason: At room temperature dimethyl fumarate is a solid; in the course of the reaction some of it sublimed into the reflux condenser and was brought back into the reaction mixture by melting it. In contrast, dimethyl maleate is a liquid and gently refluxed during the reaction effecting a more homogeneous reaction mixture.

Because the reaction is strongly influenced by the isomerisation of the dimethyl maleate, cyclic dienophiles were tested. Attempts to perform the reaction with maleic acid anhydride as the dienophile failed: Only decomposition products and oligomers of maleic acid anhydride (MS) were detected. Possibly maleic acid anhydride is coordinated during the reaction, giving rise to oligomerisation and/or decomposition reactions. The reaction with *N*-methylmaleinimide was more successful: Cycloadduct **7** was obtained in 93% yield, when the dienophile was treated with **2** at 200°C for 20 h in dodecane. Only the *anti*-diastereomer **7** was detected. **7** was characterised by its spectroscopic data and the correct elemental analysis. The *anti*-configuration was determined by NOE measurements: Irradiation at the resonance frequency of the phenyl *ortho*-protons resulted in NOEs at the *syn*-methylene and the methine protons of the tricyclic ligand. Very recently, Trahanovsky et al.[11] reported a similar reaction starting from (η^5-bicyclo[3.2.0]hepta-1,3-dienyl)(η^5-cyclopentadienyl)iron(II) and *N*-phenylmaleinimide. Their reaction resulted in the formation of the cycloadduct corresponding to **7** in 13% yield (the absolute amount was 2.1 mg) besides a small amount which was believed to be the *syn*-isomer (*anti*:*syn* = 11:1). However, the *syn*-isomer was only insufficiently characterised by ^{1}H-NMR spectroscopy, some signals being obscured by those of the major *anti*-isomer[12].



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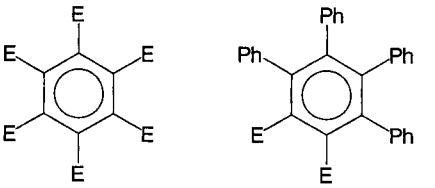
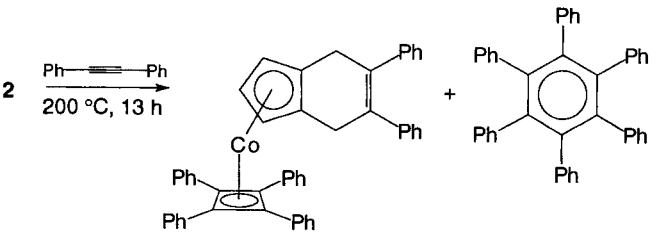
Treatment of **2** with a 100fold excess of dimethyl butynedioate at 200°C for 13 h resulted in the formation of a viscous syrup. In spite of work-up problems a main fraction was isolated by column chromatography. This predominantly consisted of **8**, the cyclotrimer of the alkyne. In addition GC-MS measurements indicated the presence of some methyl tetraphenylbenzenedicarboxylate (m/z = 498), most likely **9**. Diester **9** is the product of a cocyclisation process with participation of the tetraphenylcyclobutadiene ligand of **2** and one molecule of dimethyl butynedioate. Recently Gleiter et al. reported the first case of a cycloaddition reaction with CpCo-stabilised cyclobutadiene derivatives[13].



8 **9**

E = C(O)OCH$_3$

The reaction of **2** with diphenylethyne at 220°C results in a 36% yield of cycloadduct **10** beside hexaphenylbenzene (**11**). The lower yield of **10** might be the result of the lower dienophile reactivity of the alkyne and some difficulties in the separation of the reaction products. Treatment of **2** with benzonitrile resulted in starting material isolation only.

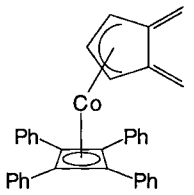


10 **11**

The mechanistic interpretation of the results obtained so far rests on product analysis only. Stereochemical and isotope labeling experiments are highly desirable, however, so far the unsubstituted bicyclo[3.2.0]hepta-1,3-dienyl anion is the only ligand available. The observed alkyne trimerisation[14] suggests the formation of a vacant coordination site in connection with the ring-opening reaction. The isomerisation experiments support this, because isomerisation is found only in the presence of the anellated cyclobutane ring and only above the ring-opening temperature as determined by DSC. Such a vacant coordination site would be formed if in the course of a ring-slippage reaction an "allyl-ene" intermediate opened the cyclobutene ring with formation of **12**, which we believe to play the role of a key intermediate in the reaction sequence. **12** might be stabilised by coordination of dienophile, which is present in excess and which could undergo an isomerisation in the case of dimethyl maleate. The fact that in the reaction with dimethyl maleate **6** is formed as the main product instead of **5** might indicate

some kind of precomplexation of the dienophile at the metal followed by a cycloaddition from the coordinated face of the diene. Due to the steric bulk of the $Co(C_4Ph_4)$ a direct cycloaddition from the coordinated face of the diene seems less likely as compared to an attack from the uncoordinated face. The idea of some kind of precomplexation is supported by the experiment using *N*-methylmaleinimide as the dienophile: Maleinimide derivatives are known to be poor ligands, only very few maleinimide complexes are known[15]. That **4** is formed to a considerable extent besides **5** and **6** might be explained either by a non-concerted cycloaddition mechanism[16] or by a cycloaddition with the dimethyl fumarate present in the reaction mixture. Sauer et al.[17] had earlier found that in Diels-Alder reactions dimethyl fumarate is 80–100 times as reactive as dimethyl maleate.

12



In conclusion, it was shown that **2** thermally opens the anellated four-membered ring with the formation of an intermediate, which undergoes [4 + 2]-cycloadditions with some dienophiles. The results indicate that the intermediate has a vacant coordination site and most likely is 4,5-dimethylenecyclopentenyl complex **12**.

Although it was shown that the reaction takes place, more general applications are somewhat limited by the high reaction temperature (200°C). Therefore, possibilities of decreasing the activation energy of the ring-opening reaction by the introduction of appropriate substituents into the four-membered ring are currently under investigation[18].

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Experimental

General: See ref.[4]

(η^5-Bicyclo[3.3.0]octa-1,3-dienyl)(η^4-tetraphenylcyclobutadiene)cobalt(I) (**3**): A solution of 1.00 g (3.68 mmol) of (η^5-bicyclo[3.3.0]octa-1,3-dienyl)(η^4-cycloocta-1,5-diene)cobalt(I)[7] and 6.54 g (36.8 mmol) of diphenylethyne in 100 ml of *o*-xylene was heated at reflux for 16 h. The solvent was removed into a cold trap at 0.1 mbar/25°C, and the residue was chromatographed on silica gel (column 30 × 2 cm). With pentane, a small amount of **3** was eluted beside unreacted diphenylethyne, then with diethyl ether 300 mg of crude **3** was eluted, which was crystallised from diethyl ether at −78°C to yield 250 mg (0.48 mmol, 13%) of **3** as russet crystals (m.p. 174°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} (w), 3057 (m), 3026 (w), 2968 (w), 2951 (m), 2844 (m), 1596 (s), 1573 (w), 1535 (w), 1498 (s), 1443 (m), 1368 (w), 1275 (w), 1242 (w), 1206 (w), 1177 (w), 1153 (w), 1066 (m), 1024 (m), 907 (w), 884 (w), 815 (m), 778 (s), 764 (s), 698 (s), 619 (w), 588 (m), 563 (s). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.4 (m, 2H, *syn*-7-H, *anti*-7-H), 2.0 [m, 4H, *syn*-6(8)-H, *anti*-6(8)-H], 4.40 [d, 2H, 2(4)-H, $^3J_{2(4),3}$ = 2.4 Hz], 4.49 (d, 1H, 3-H), 7.2 (m, 12H, *m*-, *p*-H), 7.42 (m, 8H, *o*-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.2 [t, C-6(8), $^1J_{C,H}$ = 129.9 Hz], 28.6 (t, C-7, $^1J_{C,H}$ = 129.9 Hz), 74.1 (s, C-9), 76.0 [d, C-2(4), $^1J_{C,H}$ = 175.3 Hz], 84.2 (d, C-3, $^1J_{C,H}$ = 173.5), 106.5 [s, C-1(5)], 125.9 (d, *p*-C, $^1J_{C,H}$ = 160.4), 127.9 (d, *o*-C or *m*-C, $^1J_{C,H}$ = 163.1), 128.5 (d, *o*-C or *m*-C, $^1J_{C,H}$ = 159.6), 136.6 (s, *ipso*-C). – MS (70 eV), *m/z* (%): 522 (7) [M^+ + 2], 521 (38) [M^+ + 1], 520 (100) [M^+], 415 (4) [$CoC_4Ph_4^+$], 342 (19) [$M^+ - C_2Ph_2$], 239 (25) [$CoC_2H_2Ph_2^+$], 178 (11) [$C_2Ph_2^+$], 162 (11), 59 (4) [Co^+]. – $C_{36}H_{29}Co$ (520.6): calcd. C 83.06, H 5.62, Co 11.32; found C 82.56, H 5.66, Co 11.82.

Reaction of **2** *with Dimethyl Fumarate:* In a Schlenk flask equipped with a reflux condenser 0.350 g (0.69 mmol) of **2** and 9.960 g (69 mmol) of dimethyl fumarate were heated at 200°C for 13 h. Dimethyl fumarate, which sublimed to the wall of the flask, was melted by heating with a fan. After cooling to room temp. unreacted dimethyl fumarate was sublimed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W). The residue was chromatographed on silica gel (column 40 × 1 cm). Elution with pentane/diethyl ether (30:1) gave 30 mg of **2**. Then elution with pentane/diethyl ether (6:1) gave 290 mg (0.45 mmol, 65%) of *{η^5-trans-3,4-bis(methoxycarbonyl)bicyclo[4.3.0]nona-6,8-dienyl}(η^4-tetraphenylcyclobutadiene)cobalt(I)* (**4**). Crystallisation from diethyl ether gave 90 mg of **4** as russet crystals (m.p. 197°C, DSC). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 3057 (w), 3025 (w), 2972 (w), 2950 (w), 2934 (w), 2849 (w), 1730 (s, C=O), 1596 (m), 1574 (w), 1498 (s), 1441 (m), 1380 (m), 1352 (m), 1304 (m), 1270 (w), 1238 (m), 1198 (m), 1168 (s), 1149 (m), 1115 (w), 1074 (w), 1025 (m), 1004 (m), 920 (w), 910 (w), 808 (w), 783 (m), 747 (m), 698 (s), 586 (m), 562 (s). – ^{1}H NMR (200 MHz, C_6D_6): δ = 2.08 (m, 1H, *anti*-5-H, $^2J_{syn\text{-}5,anti\text{-}5}$ = −15.9, $^3J_{4,anti\text{-}5}$ = 12.4 Hz), 2.20 (m, 1H, *syn*-2-H, $^2J_{syn\text{-}2,anti\text{-}2}$ = −15.8, $^3J_{syn\text{-}2,3}$ = 11.9 Hz), 2.38 (m, 1H, *anti*-2-H, $^3J_{anti\text{-}2,3}$ = 6.1 Hz), 2.54 (m, 2H, 4-H, *syn*-5-H, $^3J_{4,syn\text{-}5}$ = 4.9, $^3J_{anti\text{-}3,syn\text{-}4}$ = 11.6 Hz), 2.76 (m, 1H, *anti*-3-H), 3.27 [s, 3H, $C(O)OCH_3$], 3.29 [s, 3H, $C(O)OCH_3$], 4.24 (dd, 1H, 7-H or 9-H, $^3J_{7,8}$ = 2.5, $^4J_{7,9}$ = 1.5 Hz), 4.30 (dd, 1H, 7-H or 9-H), 4.36 (dd, 1H, 8-H, $^3J_{8,9}$ = 2.5 Hz), 7.1 (m, 12H, *m*-, *p*-H), 7.56 (m, 8H, *o*-H); signal assignment by NOE of the *o*-H. – ^{13}C NMR (50 MHz, C_6D_6): δ = 23.0 (t, C-2 or C-5), 25.5 (t, C-2 or C-5), 42.1 (d, C-3 or C-4), 42.8 (d, C-2 or C-4), 51.2 [q, $C(O)OCH_3$], 51.3 [q, $C(O)OCH_3$], 74.8 (s, C-10), 79.6 (d, C-8), 81.2 (d, C-7 or C-9), 81.7 (d, C-7 or C-9), 92.4 (s, C-1 or C-6), 94.5 (s, C-1 or C-6), 126.7 (d, *p*-C), 128.7 (d, *o*-C or *m*-C), 129.2 (d, *o*-C or *m*-C), 136.4 (s, *ipso*-C), 174.3 [s, $C(O)OCH_3$], 174.7 [s, $C(O)OCH_3$]. – MS (70 eV), *m/z* (%): 652 (10) [M^+ + 2], 651 (46) [M^+ + 1], 650 (100) [M^+], 416 (8) [$CoC_4Ph_4H^+$], 415 (13) [$CoC_4Ph_4^+$], 295 (6) [$CoC_{13}H_{16}O_4^+$], 294 (44) [$CoC_{13}H_{15}O_4^+$], 264 (15), 237 (7) [$CoC_2Ph_2^+$], 234 (10) [$M^+ - CoC_4Ph_4$], 206 (5), 179 (6), 178 (44) [$C_2Ph_2^+$], 175 (10), 174 (17), 143 (7), 91 (5), 59 (6) [Co^+]. – $C_{41}H_{35}CoO_4$ (650.1): calcd. C 75.68, H 5.42, Co 9.06; found C 75.55, H 5.55, Co 8.98.

Reaction of **2** *with Dimethyl Maleate:* In a Schlenk flask equipped with a reflux condenser 0.20 g (0.40 mmol) of **2** and 5.70 g (40 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 99.3%, contents of dimethyl fumarate 0.32%] were heated at 200°C for 13 h. After cooling to room temp. unreacted dimethyl maleate was condensed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W) [purity determined by GC (as above) 95.3%, contents of dimethyl fumarate 3.87%]. The residue was chromatographed on silica gel (column 40 × 1 cm). With pentane/diethyl ether (1:1) 230 mg (0.35 mmol, 90%) of a mixture of **4**, *{η^5-*

anti-cis-3,4-bis(methoxycarbonyl)bicyclo[4.3.0]nona-6,8-dienyl}(η^4-tetraphenylcyclobutadiene)cobalt(I) (**5**), and *{η^5-syn-cis-3,4-bis(methoxycarbonyl)bicyclo[4.3.0]nona-6,8-dienyl}(η^4-tetraphenylcyclobutadiene)cobalt(I)* (**6**) in a ratio of 0.9:0.5:1.0 (^{1}H, ^{13}C NMR) was obtained. – IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} (w), 3056 (w), 3023 (w), 2948 (m), 2854 (w), 1735 (s, C=O), 1596 (m), 1573 (w), 1538 (w), 1498 (s), 1434 (m), 1349 (m), 1197 (m), 1170 (w), 1152 (w), 1114 (w), 1067 (w), 1025 (m), 912 (m), 812 (m), 781 (m), 742 (m), 696 (s), 617 (w), 586 (m), 560 (s), 543 (w), 506 (w). – ^{1}H NMR (**5**)[19] (400 MHz, $CDCl_3$): δ = 2.06–2.88 [m, 6H, *syn*-2(5)-H, *anti*-2(5)-H, *syn*-3(4)-H], 3.56 [s, 6H, C(O)OCH$_3$], 4.39 [t, 1H, 8-H, $^3J_{7(9),8}$ = 2.5 Hz), 4.59 [d, 2H, 7(9)-H], 7.2 (m, 12H, *m*-, *p*-H), 7.41 (m, 8H, *o*-H); irradiation at the resonance frequency of *o*-H gave no NOE for 12(13)-H. – ^{13}C NMR (**5**)[19] (50 MHz, C_6D_6): δ = 22.4 [t, C-2(5)], 40.4 [d, C-3(4)], 51.3 [q, C(O)OCH$_3$], 74.9 (s, C-10), 80.9 [d, C-7(9)], 82.0 (d, C-8), 93.7 [s, C-1(6)], 128.0 (d, *p*-C), 128.3 (d, *o*-C or *m*-C), 128.8 (d, *o*-C or *m*-C), 136.5 (s, *ipso*-C), 172.9 [s, C(O)OCH$_3$]. – ^{1}H NMR (**6**)[19] (400 MHz, $CDCl_3$): δ = 2.06–2.88 [m, 6H, *syn*-2(5)-H, *anti*-2(5)-H, *anti*-3(4)-H], 3.42 [s, 6H, C(O)OCH$_3$], 4.37 [d, 2H, 7(9)-H, $^3J_{7(9),8}$ = 2.5 Hz], 4.43 (t, 1H, 8-H), 7.2 (m, 12H, *m*-, *p*-H), 7.32 (m, 8H, *o*-H); irradiation at the resonance frequency of *o*-H gave an NOE for 12(13)-H and vice versa. – ^{13}C NMR (**6**)[19] (50 MHz, C_6D_6): δ = 21.0 [t, C-2(5)], 40.4 [d, C-3(4)], 51.5 [q, C(O)OCH$_3$], 74.6 (s, C-10), 80.4 (d, C-8), 80.9 [d, C-7(9)], 95.4 [s, C-1(6)], 126.3 (d, *p*-C), 128.3 (d, *o*-C or *m*-C), 129.0 (d, *o*-C or *m*-C), 136.7 (s, *ipso*-C), 172.8 [s, C(O)OCH$_3$]. – MS (70 eV): Identical with that of **4**.

Behaviour of Dimethyl Maleate under the Conditions of its Reaction with **2**: – a) 2 ml (16.1 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 99.3%, contents of dimethyl fumarate 0.32%] was heated at 200°C for 13 h and then analysed by GC (as above): Purity 93.0%, contents of dimethyl fumarate 0.36%. – b) 2 ml (16.1 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 99.1%, contents of dimethyl fumarate 0.36%] was condensed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W) and then analysed by GC (as above): Purity 99.2%, contents of dimethyl fumarate 0.36%).

Treatment of Dimethyl Maleate with (η^5-Cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt(I): 480 mg (1.0 mmol) of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt(I)[10] and 14.4 g (100.0 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 97.2%, contents of dimethyl fumarate 2.30%] were heated at 200°C for 13 h. After cooling to room temp. the dimethyl maleate was condensed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W), and analysed by GC (as above): Purity 91.7%, contents of dimethyl fumarate 1.85%.

Treatment of Dimethyl Maleate with **3**: 20 mg (0.045 mmol) of **3** and 653 mg (4.5 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 98.6%, contents of dimethyl fumarate 0.85%] were heated at 200°C for 13 h. After cooling to room temp. the dimethyl maleate was condensed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W) and analysed by GC: Purity 92.3%, contents of dimethyl fumarate 2.72%.

Treatment of **2** *with Dimethyl Maleate at 180°C:* 20 mg (0.04 mmol) of **2** and 569 mg (3.95 mmol) of dimethyl maleate [purity determined by GC (50 m PS 240, FS 376, 100–280°C, 2 min isothermal, then 8°C/min) 96.5%, contents of dimethyl fumarate 2.88%] were heated at 180°C for 13 h. After cooling to room temp. the dimethyl maleate was condensed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W) and analysed by GC: Purity 96.4%, contents of dimethyl fumarate 3.13%.

Reaction of 2 with N-Methylmaleinimide: 0.300 g (0.59 mmol) of **2** and 3.330 g (30 mmol) of *N*-methylmaleinimide in 25 ml of dodecane were heated at 200°C for 20 h. After cooling to room temp. the reaction mixture was chromatographed on silica gel (column 40 × 2 cm). With pentane the dodecane was eluted, with diethyl ether unreacted *N*-methylmaleinimide and a red-orange product were eluted. From this fraction the *N*-methylmaleinimide was sublimed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W). The residue (380 mg) was crystallised from diethyl ether to yield 340 mg (0.55 mmol, 93%) of *(N-methyl-η^5-bicyclo[4.3.0]nona-6,8-dienyl-syn-cis-3,4-dicarboximide)}(η^4-tetraphenylcyclobutadiene)cobalt(I)* (**7**). – IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1} (w), 3024 (w), 2960 (w), 2925 (w), 2854 (w), 1775 (m), 1701 (s, C=O), 1596 (m), 1573 (w), 1498 (s), 1442 (m), 1433 (m), 1382 (m), 1320 (m), 938 (w), 866 (w), 765 (m), 696 (s), 618 (w), 588 (m), 562 (m). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 [m, 2H, *syn*-2(5)-H, $J_{syn\text{-}2(5),3(4)} \approx 7.3$, $^2J_{syn\text{-}2(5),anti\text{-}2(5)} = -15.1$ Hz], 2.60 [m, 2H, *anti*-2(5)-H, $J_{anti\text{-}2(5),3(4)} \approx 3.1$ Hz], 2.73 [m, 2H, 3(4)-H], 2.76 (s, 3H, 12-H), 4.32 (t, 1H, 8-H, $^3J_{7(9),8}$ = 2.6 Hz), 7.23 (m, 12H, *m*-, *p*-H), 7.41 (m, 8H, *o*-H); irradiation at the resonance frequency of *o*-H gives a NOE for *syn*-2(5)-H and 3(4)-H. – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2 [t, C-2(5), $^1J_{C,H}$ = 132.1 Hz], 24.7 (q, CH$_3$, $^1J_{C,H}$ = 141.3 Hz), 39.7 [d, C-3(4), $^1J_{C,H}$ = 136.1 Hz], 74.9 (s, C-10), 80.9 [d, C-7(9), $^1J_{C,H}$ = 176.1 Hz], 81.1 (d, C-8, $^1J_{C,H}$ = 175.3 Hz), 92.5 [s, C-1(6)], 126.3 (d, *p*-C, $^1J_{C,H}$ = 161.3), 128.0 (d, *o*-C or *m*-C, $^1J_{C,H}$ = 160.4), 128.5 (d, *o*-C or *m*-C, $^1J_{C,H}$ = 159.6), 135.8 (s, *ipso*-C), 179.5 [s, C=O]. – MS (70 eV), *m/z* (%) = 619 (9) [$M^+ + 2$], 618 (42) [$M^+ + 1$], 617 (100) [M^+], 439 (5) [$M^+ - C_2Ph_2$], 261 (7) [$M^+ - C_4Ph_4$], 178 (3) [$C_2Ph_2^+$], 174 (7) [$C_{11}H_{10}O_2^+$], 59 (1) [Co^+]. – $C_{40}H_{32}CoNO_2$ (617.0): calcd. C 77.79, H 5.22, Co 9.54, N 2.27; found C 77.54, H 5.46, Co 9.29, N 2.00.

Reaction of **2** *with Dimethyl Butynedioate:* 0.170 g (0.36 mmol) of **2** and 5.160 g (36 mmol) of dimethyl butynedioate were heated at 200°C for 13 h. The mixture soon became dark and viscous. After cooling to room temp. unreacted dimethyl butynedioate was in part sublimed into a cold trap at 0.001 mbar by irradiation with an infrared lamp (Osram Siccatherm, 250 W). The viscous residue was dissolved in a small amount of dichloromethane and the solution filtered through a silica gel column (20 × 2 cm) by eluting with diethyl ether. 2.0 g of a product mixture was obtained, which was chromatographed on silica gel (column (30 × 2 cm).

Fraction I (pentane/diethyl ether, 1:1): 910 mg of a viscous oil; GC (28 m PS 428, FS 467, 100–300°C, 8°C/min): ret. time (% peak area): I: 13.59 (7.45), *M* = 446 or 402 (GC-MS); II: 13.92 (33.7), *M* = 370 (GC-MS); III: 14.75 (5.04), *M* = 368 (GC-MS); IV: 15.24 (15.4), *M* = 398 (GC-MS); V: 16.33 (10.3), *hexakis(methoxycarbonyl)benzene* (**8**) (GC-MS); VI: 22.40 (3.44), similar *1,2-bis(methoxycarbonyl)-3,4,5,6-tetraphenylbenzene* (**9**), *M* = 498 (GC-MS). – Fraction II (diethyl ether): 340 mg of a viscous oil; *M* = *710 possible* (MS).

Reaction of **2** *with Diphenylethyne:* 102 mg (0.20 mmol) of **2** and 3.517 g (20 mmol) of diphenylethyne were heated at 220°C for 13 h. After cooling to room temp. the reaction mixture was chromatographed on silica gel (column 30 × 2 cm). With pentane unreacted diphenylethyne was eluted. Elution with diethyl ether gave a red product besides *hexaphenylbenzene* (**11**). The red product was crystallised from diethyl ether at –78°C over 7 d. 50 mg (0.073 mmol, 36%) of a red crystalline powder of *{1,6,7,8,9-η^5-3,4-diphenylbicy-*

clo[4.3.0]nona-3,6,8-trienyl}(η⁴-tetraphenylcyclobutadiene)cobalt-(I) (**10**) containing impurities of **11** was obtained. – IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} (w), 3056 (m), 3026 (w), 1597 (s), 1573 (w), 1498 (s), 1443 (m), 1175 (w), 1155 (w), 1067 (w), 1026 (w), 911 (w), 808 (m), 779 (m), 763 (m), 745 (m), 698 (s), 618 (w), 588 (w), 562 (m). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.03 [*AA'BB'*, 2H, *anti*-2(5)-H, $^2J_{syn\text{-}2(5),anti\text{-}2(5)} = -21.2$, $^5J_{syn\text{-}2,anti\text{-}5} = 4.2$, $^5J_{anti\text{-}2,anti\text{-}5} = 5.1$ Hz], 3.26 (AA'*BB'*, 2H, $^5J_{syn\text{-}2,syn\text{-}5} = 5.1$ Hz), 4.53 [d, 2H, 7(9)-H, $^3J_{7(9),8} = 2.5$ Hz], 4.63 (t, 1H, 8-H), 6.67 [m, 4H, *o*-H of 3(4)-Ph], 7.04 [m, 4H, *m*-H of 3(4)-Ph], 7.2 [m, 14H, *p*-H of 3(4)-Ph, *m*-, *p*-H of C_4Ph_4], 7.39 (m, 8H, *o*-H of C_4Ph_4). – MS (70 eV), *m/z* (%): 687 (11) [$M^+ + 3$], 686 (30) [$M^+ + 2$], 685 (55) [$M^+ + 1$], 684 (100) [M^+], 418 (6), 417 (22) [$CoC_4Ph_4H_2^+$], 416 (12) [$CoCPh_4H^+$], 415 (19) [$CoC_2Ph_2^+$], 339 (12), 328 (9) [$M^+ - C_4Ph_4$], 327 (29) [$M^+ - C_4Ph_4H$], 326 (24) [$M^+ - C_4Ph_4H_2$], 279 (7), 265 (8), 239 (7) [$CoC_2Ph_2H_2^+$], 237 (9) [$CoC_2Ph_2^+$], 178 (20) [$C_2Ph_2^+$]. – $C_{49}H_{37}Co$ (684.8): calcd. C 85.95, H 5.45, Co 8.61; found C 84.26, H 5.43, Co (not det.).

Thermolysis of **2**: A solution of 102 mg (0.2 mmol) of **2** in 3 ml of dodecane was heated at 220°C for 48 h. The reaction mixture was chromatographed on silica gel (column 30 × 1 cm). Dodecane was eluted with pentane, then with pentane/diethyl ether 120 mg of an orange product mixture was eluted which did not contain **2**. – MS (70 eV), Evaporation temp. 120°C, *m/z*: 506 [M^+, main fraction]; 170°C: 562 [M^+]; 240°C: 676, 862 [M^+]; 280°C: 1012, 1068, 1104 [M^+] (trace).

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