Reactions of 1,8-Diheterocyclotetradeca-4,11-diynes with (η^4-Cycloocta-1,5-diene)(η^5-cyclopentadienyl)cobalt

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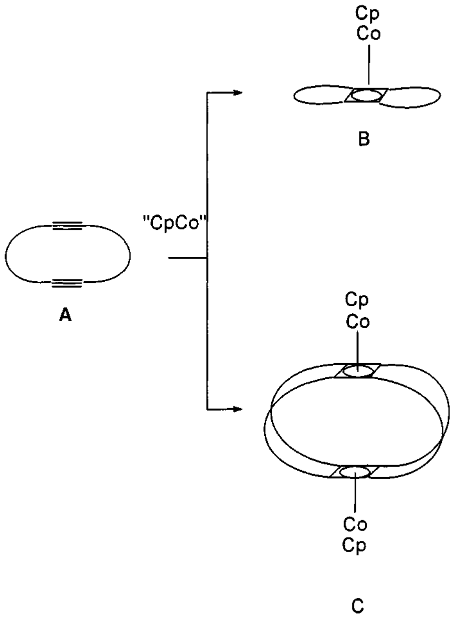
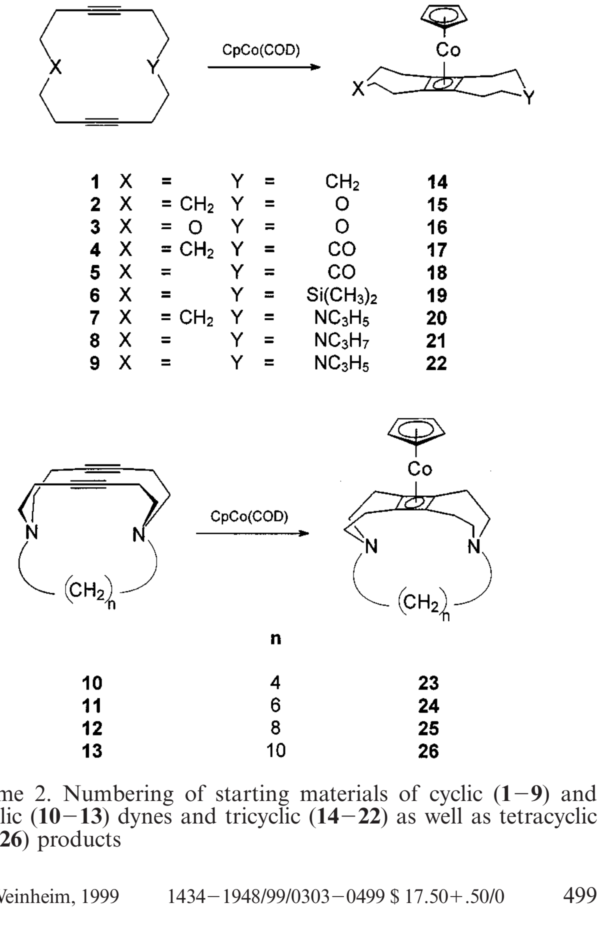
The following monocyclic and bicyclic 14-membered diynes were treated with [CpCo(cod)]: 1-oxacyclotetradeca-4,11-diyne (**2**), 1,8-dioxacyclotetradeca-4,11-diyne (**3**), cyclotetradeca-4,11-diynone (**4**), cyclotetradeca-4,11-diyne-1,8-dione (**5**), 1,1,8,8-tetramethyl-1,8-disilacyclotetradeca-4,11-diyne (**6**), 1-allyl-1-azacyclotetradeca-4,11diyne (**7**), 1,8-dipropyl-1,8-diazacyclotetradeca-1,11-diyne (**8**), 1,8-diallyl-1,8-diazacyclotetradeca-4,11-diyne (**9**), 1,8-diazabicyclo[6.6.4]-octadeca-4,11-diyne (**10**), 1,8-diazabicyclo[6.6.6]eicosa-4,11-diyne (**11**), 1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (**12**) and 1,12-diazabicyclo[10.6.6]tetracosa-15,21-diyne (**13**). In all cases we obtained an intramolecular cyclobutadiene complex stabilized with a CpCo fragment (**15**–**26**). For **3** we could isolate, besides the cyclobutadiene complex **16**, the trimerization product **28**. In the cases of **15**, **16**, **18**, **20**, **23**, **25**, and **26** the structure of the cylobutadiene complexes could be confirmed by X-ray studies. Common to all structures is a boat-like conformation of the tricyclic unit containing the cyclobutadiene ring. The two cycloheptene units adopt a chair conformation in which the heteroatom is removed from the metal center.

The cobalt-mediated cycloaddition of alkynes proceeds either in a [2+2] fashion to yield cyclobutadiene (Cbd) complexes or in a [2+2+2] fashion to give aromatic systems.[1−7] In the case of cyclic diynes the cyclobutadiene complexes dominate.[5−7] Depending on the length of the chain between the triple bonds one obtains either the tricyclic intramolecular cyclobutadiene complexes **B** or the superphanes **C** which are generated in an intermolecular pathway.[6,7] The latter path was preferred in the case of 1,6-cyclodecadiyne and in disilabridged cyclic diynes, while larger rings favored the intramolecular path.[6,7]

In order to extend our knowledge to the 14-membered rings we synthesized a number of hetero derivatives of 1,8-



Scheme 1. Possible reaction paths between cycloalkynes and a CpCo fragment



1 X = Y = CH_2 **14**
2 X = CH_2 Y = O **15**
3 X = O Y = O **16**
4 X = CH_2 Y = CO **17**
5 X = Y = CO **18**
6 X = Y = $Si(CH_3)_2$ **19**
7 X = CH_2 Y = NC_3H_5 **20**
8 X = Y = NC_3H_7 **21**
9 X = Y = NC_3H_5 **22**

	n	
10	4	**23**
11	6	**24**
12	8	**25**
13	10	**26**

Scheme 2. Numbering of starting materials of cyclic (**1**−**9**) and bicyclic (**10**−**13**) dynes and tricyclic (**14**−**22**) as well as tetracyclic (**23**−**26**) products

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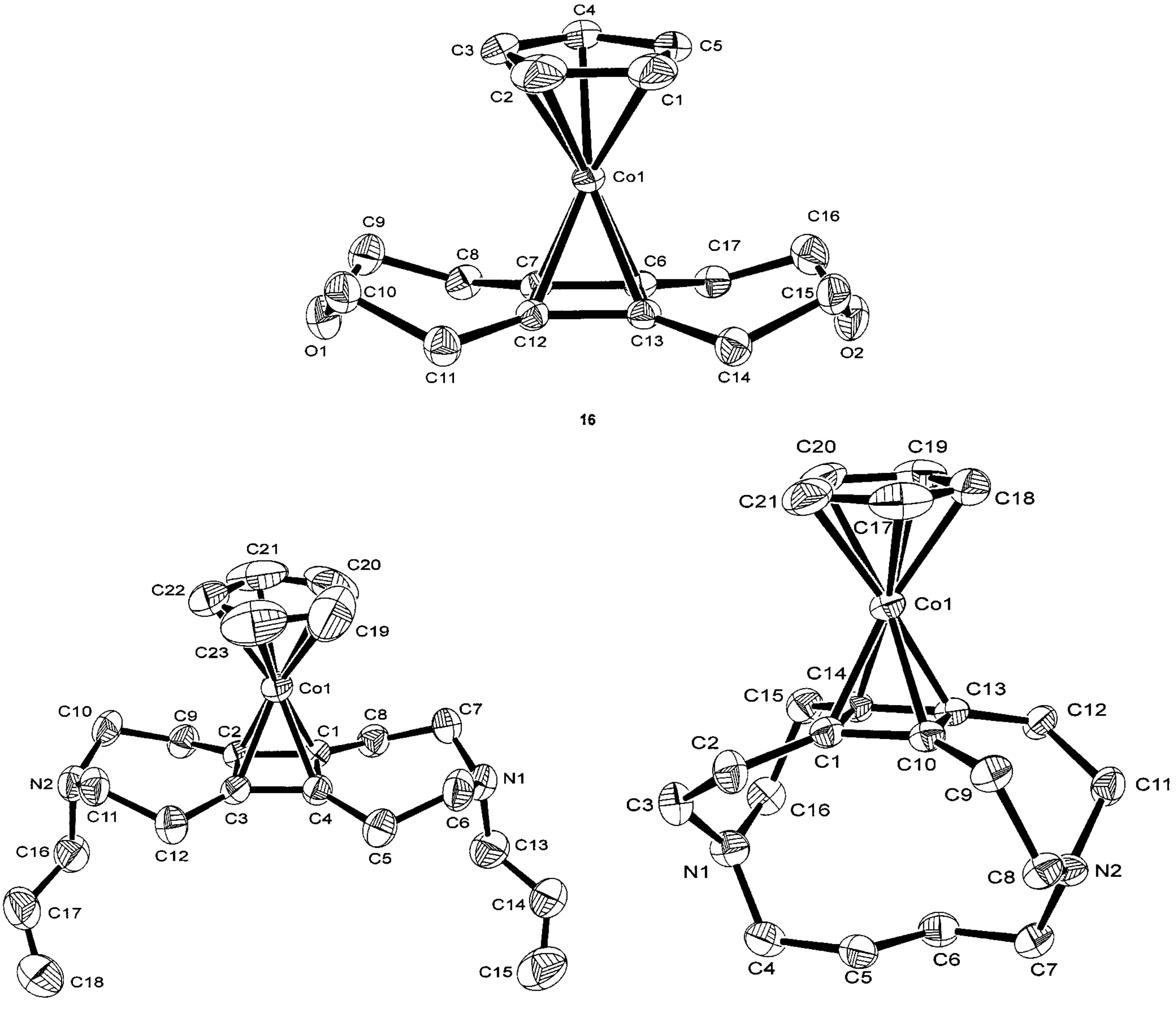
cyclotetradecadiyne (**1**) and explored their reaction with (η^4-cycloocta-1,5-diene)(η^5-cyclopentadienyl)cobalt ([CpCo(cod)]). As model systems we either chose monocyclic systems with O and NR as electron-donating heteroatoms and dimethylsilyl groups as bulky substituents, or we chose bicyclic 1,8-diaza-substituted systems. By varying the chain length we were able to influence the conformation of the 14-membered ring system.

We chose the following congeners of **1**: 1-oxacyclotetradeca-4,11-diyne (**2**),[8] 1,8-dioxacyclotetradeca-4,11-diyne (**3**),[8] cyclotetradeca-4,11-diynone (**4**),[8] cyclotetradeca-4,11-diyne-1,8-dione (**5**),[8] 1,1,8,8-tetramethyl-1,8-disilacyclotetradeca-4,11-diyne (**6**),[9] 1-allyl-1-azacyclotetradeca-4,11-diyne (**7**),[10] 1,8-dipropyl-1,8-diazacyclotetradeca-4,11-diyne (**8**),[10] 1,8-diallyl-1,8-diazacyclotetradeca-4,11-diyne (**9**),[10] 1,8-diazabicyclo[6.6.4]octadeca-4,4-diyne (**10**),[10] 1,8-diazabicyclo[6.6.6]eicosa-4,11-diyne (**11**),[10] 1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (**12**)[10] and 1,12-diazabicyclo[10.6.6]tetracosa-15,20-diyne (**13**)[10] (see Scheme 2).

Results and Discussion

The reactions of **2**−**13** were carried out by heating the diynes in nonane with [CpCo(cod)] until no starting material could be detected. In most cases we could only observe the corresponding intramolecular products **15**−**26** in yields



16

22

23

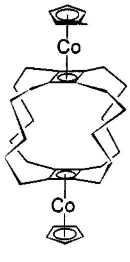
Figure 1. Molecular structure of **16**, **22** and **23**; selected bond lengths [Å] and angles [°]: **16**: Co−C6 1.980(2), Co−C7 1.991(2), Co−C1 2.058(2), Co−C3 2.082(2), C6−C7 1.462(2), C7−C12 1.463(2); C7−C8 1.485(2), C9−O1 1.433(2), C9−O1−C10 115.2(2), C8−C9−O1 113.4(2); **22**: Co−C1 1.977(3), Co−C2 1.983(3), Co−C19 2.035(5), Co−C20 2.041(5), C1−C2 1.466(4), C2−C3 1.452(4), C1−C8 1.477(4), C7−N1 1.459(5), N1−C13 1.448(5), C13−C14 1.493(6), C14−C15 1.298(6); C6−N1−C7 116.9(3), C6−N1−C13 115.0(3), C13−C14−C15 125.6(5); **23**: Co−C1 1.983(3), Co−C10 1.978(3), Co−C19 2.058(3), Co−C20 2.065(4), C1−C10 1.465(5), C1−C14 1.448 (5), C1−C2 1.495(5), C3−N1 1.441(4), N1−C4 1.448(4); C3−N1−C16 118.8(2), C3−N1−C4 119.0(3)

between 3 and 70% (see Table 1). The exceptions were the parent system **1**, in which besides the intramolecular product **14** a superphane **27** could be observed in 7% yield,[11] and **3**, for which in addition to **16** the trimer **28** was obtained in 6% yield. In the case of **15**, **16**, **18**, **22**, **23**, **25**, and **26** we were able to grow single crystals which allowed the study of the molecular structure of these molecules in the solid state. In Figure 1 we show the X-ray-structures of **16**, **22**, and **23** as examples. In all cases we observed that together with the two carbon atoms of the cyclobutadiene unit the bridges with five main-group atoms between the former triple bonds adopt a chair conformation in which the heteroatom is removed from the metal center. This holds whether the heteroatoms are tethered with a short (C_4 in **23**), a long (C_{10} in **26**) or no chain (**15**, **16**, **18**, **22**). The substituents at the nitrogen atoms adopt the axial position whether they are tethered (**23**, **25**, **26**) or not (**22**).

Table 1. Yields of the intramolecular cyclobutadiene complexes **14**–**26** by treating **1**–**13** with [CpCo(cod)]

starting material		**1**	**2**	**3**	**4**	**5**	**6**
product		**14**	**15**	**16**	**17**	**18**	**19**
yield (%)		29	11	14	48	60	68
starting material	**7**	**8**	**9**	**10**	**11**	**12**	**13**
product	**20**	**21**	**22**	**23**	**24**	**25**	**26**
yield (%)	5	39	3	71	25	38	50

The chair conformation is expected because for cycloheptene systems a chair conformation **29** is reported in the literature.[12] The axial position of the allylic groups in **22** we ascribe to packing effects in the crystal because there are clearly two 1,3 interactions in the chair form.



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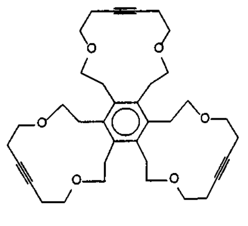

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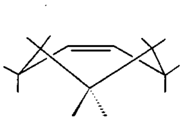
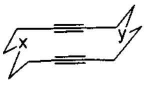
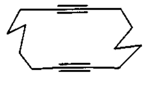


29

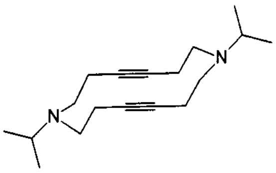
The uniformity of the conformations of the products is contrasted by a variety of conformations of the starting diynes. The structures of **1**, **3**–**5**,[8] 1,8-diisopropyl-1,8-diazacyclotetradeca-4,11-diyne (**30**),[10] **10**,[10] and **12**[10] have been studied in the solid state by means of X-ray techniques. For **3**–**5** the 14-membered ring adopts a chair conformation with a zig-zag arrangement of the chains between the triple bonds. This gives rise to two *anti* and two *gauche* interactions in the chain (**D**). In the case of **1**[8,13] an arrangement of the methylene groups with three *gauche* and one *anti* interaction is found (**E**). AM1[14] and MNDO[15] calculations show only a small energy difference (2 kcal/mol) between the two conformations. In the case of **30** a chair conformation was found in which the chains adopt a half-envelope conformation (**F**). In this conformation there are two *gauche* and two *eclipsed* interactions. The energy difference between conformations **F** and **D** was calculated (AM1, MNDO) to be 20 kcal/mol. In the cases of the bicyclic diynes **10** and **12** a twist-boat conformation was encountered.



D



E



F

X = Y = O
X = Y = CO
X = CO Y = O

The different conformations provide different transannular distances between the triple bonds: **1**: 4.64 Å; **3**: 4.71 Å; **5**: 5.20 Å; **29**: 3.85 Å; **10**: 4.19 Å; **12**: 3.77 Å. Our experiments provide no correlation between conformations of the starting material and yield of the products. This can be interpreted by assuming either that steric effects are important at a later stage of the multi-step reaction, or that at the reaction temperature all conformations mentioned above interconvert rapidly.

Experimental Section

General Methods: Reactions were conducted in oven-dried (150 °C) glassware under argon. Solvents were distilled and dried under argon before use: *n*-nonane and cyclooctane from sodium, DME from potassium. – Melting points: Dr. Tottoli apparatus (Büchi), uncorrected values. – Materials used for column chromatography: Neutral alumina (Aldrich, Macherey-Nagel), Kieselgel 60 (Merck, Macherey-Nagel), Florisil (Acros). GLC: HP 5890A instrument connected to a Shimadzu C-R3A integrator. A capillary column Ultra 2 (PhMeSilicone, 25 m × 0.32 mm × 0.52 µm) was used with nitrogen carrier gas and a flame-ionization detector (FID). – ^{1}H and ^{13}C NMR: Bruker WH 300 (^{1}H at 300 MHz and ^{13}C at 75.47 MHz) and Bruker WH 200 (^{1}H at 200 MHz and ^{13}C at 50.33 MHz) by using the solvent as internal standard. If not otherwise mentioned spectra were determined at 300 MHz and 75.47 MHz, respectively. – IR: Perkin Elmer 580B, Bruker IFS 66, Bruker IFS 88 and Bruker Vector 22. – UV: Hewlett Packard HP 8452A. – High-resolution MS: ZAB high-resolution mass spectrometer (Fa. Vacuum Generators). – Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg.

General Procedure for the Reactions of the Cyclic and Bicyclic Diynes 2–13 with [CpCo(cod)]: If not otherwise mentioned the diynes and [CpCo(cod)] were dissolved in *n*-nonane and the mixtures were heated under reflux. When the diyne could not be detected any more by TLC the mixture was cooled. In the case of the carbocyclic cobalt complexes **17** and **18** the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, adsorbed on Al_2O_3 (neutral, 6% H_2O) and chromatographed on Al_2O_3 (neutral, 6% H_2O). For the other cobalt complexes excess [CpCo(cod)] and *n*-nonane were removed by flash chromatography on Al_2O_3 (neutral, 6% H_2O) with petroleum ether as solvent. Afterwards the cobalt complex was eluted with petroleum ether or petroleum ether/diethyl ether mixtures as eluent.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-5-oxatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}cobalt (15): To a refluxing solution of 800 mg (5.0 mmol) of 1-oxacyclotetradeca-4,11-diyne (**2**) in 80 mL of *n*-nonane 1.66 g (10.0 mmol) of [CpCo(cod)] in 20 mL of *n*-nonane was added within 60 min and refluxing was continued for 4 h. Column chromatography of the cooled mixture with petroleum ether/pentane (5:1) as eluent yielded 330 mg, (21%) of **15** as orange crystals, m.p. 143°C. − ^{1}H NMR ($CDCl_3$): δ = 4.72 (s, 5 H, H_{Cp}), 4.19 (m, ^2J = 12.5 Hz, 2 H, $CH_2{-}O$), 3.42 (m, 2 H, $CH_2{-}O$), 1.97 (m, 4 H, $C_{Cbd}{-}CH_2$, 1.58 (m, 5 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 79.9 (C_{Cbd}), 78.8 (C_{Cp}), 76.8 (C_{Cbd}), 74.4 ($CH_2{-}O$), 30.4, 30.2, 30.0, 27.8 (CH_2). − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1}, 3094, 2922, 2860, 2811, 1112, 1002, 809. − UV (CH_2Cl_2): λ_{max} (lg ε) = 292 nm (3.09), 272 (4.35), 222 (4.05). − $C_{18}H_{23}CoO$ (314.31): calcd. C 68.78, H 7.38; found C 68.67, H 7.45.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-5,12-dioxatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}cobalt (16): Starting material: 800 mg (4.2 mmol) of 1,8-dioxacyclotetradeca-4,11-diyne (**3**) and 966 mg (4.2 mmol) of [CpCo(cod)] in 50 mL of *n*-nonane. Reaction time: 4 h. The warm reaction mixture was chromatographed with petroleum ether/diethyl ether (1:1) to yield the intramolecular complex **16** (180 mg, 14%). Afterwards the trimerization product **28** (51 mg, 6%) could be isolated by using diethyl ether as eluent. − **16**: Yellow-orange crystals, m.p. 193°C. − ^{1}H NMR (CD_2Cl_2): δ = 4.70 (s, 5 H, H_{Cp}), 4.15 (m, 4 H, $CH_2{-}O$), 3.63 (m, 4 H, $CH_2{-}O$), 1.94 (m, 8 H, $C_{Cbd}{-}CH_2$). − ^{13}C NMR (CD_2Cl_2): δ = 79.3 (C_{Cp}), 30.6 ($C_{Cbd}{-}CH_2$), 77.8 ($CH_2{-}O$), 74.5 (C_{Cbd}). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 2938, 2866, 2816, 1632, 1108. − UV (CH_2Cl_2): λ_{max} (lg ε) = 386 nm (2.35), 298 (2.87), 266 (4.37), 222 (4.04). − HRMS (EI, 70 eV): $C_{17}H_{21}CoO_2$: calcd. 316.0874, found 316.0841. − **28**: Colorless needles. − ^{1}H NMR ($CDCl_3$): δ = 3.71 (t, 12 H, $CH_2{-}O$), 3.62 (t, 12 H, $CH_2{-}O$), 3.08 (t, 12 H, $CH_2{-}Ph$), 2.40 (t, 12 H, $CH_2{-}C{\equiv}$). − ^{13}C NMR ($CDCl_3$): δ = 135.5 (C_{ar}), 79.5 ($C{\equiv}C$), 20.8 ($CH_2{-}C{\equiv}C$), 71.4 ($CH_2{-}O$), 69.0 ($CH_2{-}O$), 31.5 ($CH_2{-}Ph$). − IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1}, 2864, 1632, 1483, 1365, 1131, 799. − UV (CH_2Cl_2): λ_{max} (lg ε): 232 nm (3.3). − HRMS (EI, 70 eV): $C_{36}H_{48}O_6$: calcd. 576.3451, found 576.3465.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-dien-5-one}cobalt (17): Starting material: 400 mg (2.0 mmol) of cyclotetradeca-4,11-diynone (**4**) and 504 mg (2.2 mmol) of [CpCo(cod)] in 30 mL of *n*-nonane. Reaction time: 3 d. The reaction mixture was chromatographed with *n*-hexane/diethyl ether (8:1). For elemental analysis it was necessary to subject **17** to further column chromatography on silica gel with the solvent mixture mentioned above. Yield: 314 mg (48%) of **16** as yellow crystals, m.p. 124°C. − ^{1}H NMR ($CDCl_3$): δ = 4.80 (s, 5 H, H_{Cp}), 2.98 (td, ^2J = $^3J_1$ = 11.3, $^3J_2$ = 5.2 Hz, 2 H, $O{=}C{-}CH_2$), 2.54 (d, 2 H, $O{=}C{-}CH_2$, ^2J = 11.3 Hz), 2.12−1.80 (m, 10 H, CH_2), 1.58 (m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 214.4 (CO), 80.7 (C_{Cbd}), 79.2 (C_{Cp}), 76.4 (C_{Cbd}), 44.1, 30.4, 30.3, 27.5, 22.4 (CH_2). − IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 2821, 2812, 1701, 1444, 1321, 1295, 798. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.05), 266 (4.29). − $C_{19}H_{23}CoO$ (326.32): calcd. C 69.93, H 7.11; found C 69.84, H 7.10.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-tricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene-5,12-dione}cobalt (18): Starting material: 500 mg (2.3 mmol) of cyclotetradeca-4,11-diyne-1,8-dione (**5**) and 580 mg (2.5 mmol) of [CpCo(cod)] in 35 mL of *n*-nonane. Reaction time: 5 d. The reaction mixture was chromatographed with $CHCl_3$/ethyl acetate (20:1). For elemental analysis it was necessary to subject **18** to further column chromatography on silica gel with the solvent mixture mentioned above. Yield: 470 mg (60%) of **18** as yellow crystals, m.p. 177°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.85 (s, 5 H, H_{Cp}), 2.95 (td, ^2J = $^3J_1$ = 11.6, $^3J_2$ = 5.2 Hz, 4 H, $O{=}C{-}CH_2$,), 2.57 (m, 4 H, $O{=}C{-}CH_2$), 2.12 (ddd, 4 H, $C_{Cbd}{-}CH_2$, ^2J = 15.9, $^3J_1$ = 5.2, $^3J_2$ = 4.2 Hz), 1.88 (ddd, 4 H, $C_{Cbd}{-}CH_2$, ^2J = 15.9, $^3J_1$ = 11.6, $^3J_2$ = 4.3 Hz). − ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 208.7 (CO), 79.8 (C_{Cp}), 77.7 (C_{Cbd}), 44.0, 22.1 (CH_2). − IR (KBr): $\tilde{\nu}$ = 1695 cm^{-1}, 1321, 1295, 1165, 1104, 803. − UV/VIS (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.03), 268 (4.26). − $C_{19}H_{21}CoO_2$ (340.31): calcd. C 67.06, H 6.22; found C 66.75, H 6.25.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-5,5,12,12-tetramethyl-5,12-disilatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}cobalt (19): Starting material: 106 mg (0.38 mmol) of 1,1,8,8-tetramethyl-1,8-disilacyclotetradeca-4,11-diyne (**6**) and 159 mg (0.69 mmol) of [CpCo(cod)] in 25 mL of *n*-nonane. Reaction time: 130 h. The reaction mixture was poured on a column, which was filled with 5 cm of Al_2O_3 (neutral, 6% water) and SiO_2 on top. Quick flash chromatography, with petroleum ether as eluent, yielded **19** (105 mg, 68%) as yellow crystals, m.p. 120°C (dec.). − ^{1}H NMR (C_6D_6): δ = 4.92 (s, 5 H, H_{Cp}), 2.25−1.86 (m, 8 H, $C_{Cbd}{-}CH_2$), 1.07−0.88 (m, 8 H, $Si{-}CH_2$), 0.12 (s, 6 H, $Si{-}CH_3$), −0.02 (s, 6 H, $Si{-}CH_3$). − ^{13}C NMR (C_6D_6): δ = 81.4 (C_{Cbd}), 79.2 (C_{Cp}), 21.0 (CH_2), 16.9 ($Si{-}CH_2$), −1.6 ($Si{-}CH_3$), −6.2 ($Si{-}CH_3$). − IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1}, 3101, 3080, 2947, 2915, 2893, 2874, 2821, 1622, 1439, 1394, 1246, 1001, 834, 679. − UV (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.01), 266 (4.29), 296 (3.15), 362 (2.60). − HRMS (EI, 70 eV): $C_{21}H_{33}CoSi_2$: calcd. 400.14527, found 400.14529.

{(η^4-1,2,8,9)-*N*-Allyl-5-azatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}-(η^5-cyclopentadienyl)cobalt (20): Starting material: 800 mg (3.5 mmol) of *N*-allyl-1-azacyclotetradeca-4,11-diyne (**7**) and 810 mg (3.5 mmol) of [CpCo(cod)] in 40 mL of *n*-nonane were heated at reflux for 4 h. After 10 h of additional stirring at room temperature (r.t.), the mixture was subjected to column chromatography with petroleum ether/diethyl ether (3:1) as eluent. Yield: 60 mg (5%) of **20** as orange crystals, m.p. 102°C. − ^{1}H NMR ($CDCl_3$): δ = 5.83 (m, 1 H, $CH_2{=}CH{-}$), 5.13 (m, 2 H, $CH_2{=}CH{-}$), 4.78 (s, 5 H, H_{Cp}), 3.28−2.95 (m, 4 H, $CH_2{-}N$), 2.13−1.57 (m, 8 H, $C_{Cbd}{-}CH_2$, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 136.6 ($CH_2{=}CH$), 116.7 ($CH_2{=}CH{-}$), 79.5 (C_{Cbd}), 78.9 (C_{cp}), 78.0 (C_{Cbd}), 55.5, 54.7 ($CH_2{-}N$), 30.6, 30.4, 28.0, 26.9, 26.2, 24.6 (CH_2). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3074, 2913, 1636, 1442, 1351, 1112, 1000, 803, 566. − UV (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (4.1), 266 (4.37), 300 (3.07). − $C_{20}H_{28}CoN$ (353.39): calcd. C 71.37, H 7.99; N 3.96; found C 71.42, H 7.86, N 3.77.

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-*N*,*N*′-di-*n*-propyl-5,12-diazatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}cobalt (21): Starting material: 850 mg (3.7 mmol) of [CpCo(cod)] in 50 mL of *n*-nonane, which was refluxed for 45 min; 945 mg (3.45 mmol) of *N*,*N*′-di-*n*-propyl-1,8-diazacyclotetradeca-4,11-diyne (**8**) was added. The mixture was heated to 160°C for 20 h. After cooling to r.t., column chromatography of the reaction mixture on Al_2O_3 [neutral, 6% water, petroleum ether/diethyl ether (5:1)] gave 537 mg, (39%) of **21** as orange crystals, m.p. 40°C. − ^{1}H NMR ($CDCl_3$): δ = 4.75 (s, 5 H, H_{Cp}), 3.24−3.00 (m, 8 H, $CH_2{-}N$), 2.44 (m, 4 H, $CH_2{-}N$), 2.04 (m, 4 H, $C_{Cbd}{-}CH_2$), 1.75−1.70 (m, 4 H, $C_{Cbd}{-}CH_2$),1.44 (m, 4 H, CH_2), 0.86 (t, ^3J = 7.4 Hz, 6 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 79.0 (C_{Cp}), 77.9 (C_{Cbd}), 55.4 ($CH_2{-}N$), 52.4 ($CH_2{-}N$), 26.1, 20.6 (CH_2), 11.9 (CH_3). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3094, 3066, 2952, 2899, 2869, 2828, 1624, 1449, 1348, 1117, 1091, 1024, 999, 807, 587, 438. − UV (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (4.3), 266 (4.4), 294 (3.5), 358 (3.2). − HRMS (EI, 70 eV): $C_{23}H_{36}CoN_2$: calcd. 398.2148, found 398.2132.

Table 2. Crystallographic data of **15**, **16**, **18**, **22**, **23**, **25** and **26**

	15	**16**	**18**	**22**	**23**	**25**	**26**
Empirical formula	$C_{18}H_{23}CoO$	$C_{17}H_{21}CoO_2$	$C_{19}H_{21}CoO_2$	$C_{23}H_{31}CoN_2$	$C_{21}H_{29}CoN_2$	$C_{25}H_{37}CoN_2$	$C_{27}H_{41}CoN_2$
Molecular mass [g/mol]	314.29	316.27	340.29	394.43	368.40	424.50	452.56
Crystal size [mm]	0.5 × 0.35 × 0.2	0.38 × 0.27 × 0.21	0.95 × 0.90 × 0.35	0.8 × 0.2 × 0.05	0.15 × 0.4 × 0.55	0.32 × 0.25 × 0.9	0.25 × 0.35 × 0.8
Crystal color	orange-yellow	yellow-orange	orange	yellow-orange	yellow	orange-yellow	yellow
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	triclinic
Space group	$P\,2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a [Å]	13.601(2)	7.7984(2)	8.235(2)	6.912(3)	8.686(4)	16.004(3)	10.281(3)
b [Å]	8.9720(10)	11.1670(1)	11.243(2)	9.844(4)	9.529(5)	11.725(3)	10.682(2)
c [Å]	13.688(2)	16.1573(3)	16.800(3)	15.067(7)	11.359(6)	12.533(3)	12.307(3)
α [°]	90	90	90	96.42(4)	86.91(2)	90	75.04(2)
β [°]	115.320(10)	90	90	92.29(4)	85.77(3)	109.40(3)	78.58(2)
γ [°]	90	90	90	96.34(4)	69.64(2)	90	72.63(2)
V [Å^3]	1509.9(4)	1407.05(5)	1555.4(5)	1011.1(8)	878.6(8)	2218.3(8)	1235.5(5)
$D_{calcd.}$ [g/cm^3]	1.383	1.493	1.453	1.296	1.392	1.271	1.217
Z	4	4	4	2	2	4	2
$F(000)$	664	664	712	420	392	912	488
T [K]	293(2)	200(2)	293(2)	293(2)	293(2)	293(2)	293(2)
μ [mm^{-1}]	1.130	1.218	1.107	0.857	0.980	0.786	0.710
Refl. collected	3778	6452	5259	4627	4595	2888	4351
Refl. unique	3641	2365	4775	4627	4595	2888	4351
Refl. observed [$I > 2\sigma(I)$]	2740	2229	3940	3438	3234	2107	3191
Variables $(\Delta/\sigma)_{max}$	273	265	261	360	333	191	417
$R1$ [$I > 2\sigma(I)$]	0.052	0.020	0.053	0.058	0.041	0.042	0.057
$wR2$	0.127	0.0499	0.1386	0.115	0.1103	0.1042	0.1232
S (Gof)	1.131	1.056	1.045	1.112	1.021	1.022	1.110
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.547	0.181	0.589	0.409	0.739	0.805	0.250
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.382	−0.284	−0.404	−0.261	−0.564	−0.504	−0.206

(η^5-Cyclopentadienyl){(η^4-1,2,8,9)-*N*,*N'*-diallyl-5,12-diazatricyclo[7.5.0.0^{2,8}]tetradeca-1,8-diene}cobalt (22): 1.0 g (3.7 mmol) of *N*,*N'*-diallyl-1,8-diazacyclotetradeca-4,11-diyne (**9**) and 860 mg (3.7 mmol) of [CpCo(cod)] in 20 mL of *n*-nonane were heated at reflux for 3 h. After 10 h of additional stirring at r.t., the mixture was subjected to column chromatography with petroleum ether/diethyl ether (3:1) as eluent. Yield: 50 mg (3%) of **22** as orange crystals, m.p. 102 °C. − ^{1}H NMR ($CDCl_3$): δ = 5.83 (m, 2 H, $CH_2{=}CH{-}$), 5.13 (m, 4 H, $CH_2{=}CH{-}$), 4.77 (s, 5 H, H_{Cp}), 3.24 (m, 4 H, CH_2N), 3.17 (m, 4 H, $CH_2{-}N$), 2.98 (dt, 4 H, ^3J = 16 Hz, $CH_2{-}N$), 1.90 (m, 8 H, $C_{Cbd}{-}CH_2$). − ^{13}C NMR ($CDCl_3$): δ = 136.5 ($CH_2{=}CH{-}$), 116.8 ($CH_2{=}CH{-}$), 79.0 (C_{Cp}), 77.9 (C_{Cbd}), 55.5 ($CH_2{-}N$), 54.0 ($CH_2{-}N$), 26.4 (CH_2). − IR (KBr): $\tilde{\nu}$ = 3431 cm^{-1}, 3073, 3004, 2906, 2868, 2818, 1639. − UV (CH_2Cl_2): λ_{max} (lg ε) = 382 nm (1.70), 300 (2.72), 266 (4.18), 224 (3.97). − $C_{23}H_{31}CoN_2$ (394.44): calcd. C 70.04, H 7.92; N 7.10; found C 69.57, H 8.15, N 6.86.

(η^5-Cyclopentadienyl){(η^4-4,5,11,12)-1,8-diazatetracyclo[6.6.4.0^{4,12}.0^{5,11}]octadeca-4,11-diene}cobalt (23): Starting material: 168 mg (0.69 mmol) of 1,8-diazabicyclo[6.6.4]octadeca-4,11-diyne (**10**) and 176 mg (0.76 mmol) of [CpCo(cod)] in 80 mL of *n*-nonane. Reaction time: 66 h. The reaction mixture was chromatographed with petroleum ether/diethyl ether (5:2). Yield: 187 mg (71%) of **23** as a yellow-orange solid, decomposition at 205 °C. − ^{1}H NMR: ($CDCl_3$): δ = 4.63 (s, 5 H, H_{Cp}), 2.84 (t, 8 H, $CH_2{-}N$), 2.75 (t, 4 H, $CH_2{-}N$), 2.30−1.98 (m, 8 H, $C_{Cbd}{-}CH_2$), 1.39 (q, 4 H, CH_2). − ^{13}C NMR: ($CDCl_3$): δ = 79.1 (C_{Cp}), 74.1 (C_{Cbd}), 55.4, 48.7 ($CH_2{-}N$), 27.7, 25.7 (CH_2). − IR (KBr): $\tilde{\nu}$ = 2903 cm^{-1}, 2827, 2225, 2044, 2014, 1620, 1427, 1357, 1159, 1128, 1031, 740. − UV (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.25), 274 (4.36), 312 (960), 392 (2.60). − HRMS (EI, 70 eV): $C_{21}H_{29}CoN_2$: calcd. 369.1741; found 369.1799.

(η^5-Cyclopentadienyl){(η^4-4,5,11,12)-1,8-Diazatetracyclo[6.6.6.0^{4,12}0^{5,11}]eicosa-4,11-diene}cobalt (24): Starting material: 440 mg (1.6 mmol) of 1,8-diazabicyclo[6.6.6]eicosa-4,11-diyne (**11**) and 400 mg (1.7 mmol) of [CpCo(cod)] in 100 mL of cyclooctane at 150 °C. Reaction time: 6 d. The reaction mixture was chromatographed with petroleum ether/diethyl ether (10:1). Yield: 160 mg (25%) of **24** as yellow-orange colored solid, m.p. > 250 °C. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.60 (s, 5 H, H_{Cp}), 2.64 (m, 8 H, $CH_2{-}N$), 2.10 (m, 8 H, CH_2), 1.33 (m, 8 H, $C_{Cbd}{-}CH_2$). − ^{13}C NMR (50.33 MHz, CD_2Cl_2): δ = 79.3 (C_{Cp}), 79.3 (C_{Cbd}), 58.4, 53.3 ($CH_2{-}N$), 29.8, 29.3, 27.6 (CH_2). − IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2848, 1631, 1371, 1349, 1105, 797. − UV (CH_2Cl_2): λ_{max} (lg ε) = 222 nm (4.2), 273 (4.3). − $C_{23}H_{33}CoN_2$ (396.46): calcd. C 69.68, H 8.39; N 7.07; found C 69.21, H 8.41, N 6.62.

(η^5-Cyclopentadienyl){(η^4-13,14,19,20)-1,10-diazatetracyclo[8.6.6.0^{13,20}.0^{14,19}]docosa-13,19-diene}cobalt (25): Starting material: 370 mg of (1.2 mmol) 1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (**12**) and 280 mg (1.2 mmol) of [CpCo(cod)] in 100 mL of *n*-nonane. Reaction time: 35 h. The reaction mixture was chromatographed with petroleum ether/diethyl ether (5:1). Yield: 194 mg (38%) of **25** as yellow crystals m.p. 120 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.67 (s, 5 H, H_{Cp}), 2.95 (m, 8 H, $CH_2{-}N$), 2.73 (m, 4 H, $CH_2{-}N$), 2.00 (m, 8 H, $C_{Cbd}{-}CH_2$), 1.27 (m, 12 H, CH_2). − ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 79.0 (C_{Cp}), 76.3 (C_{Cbd}), 55.5, 53.4 ($CH_2{-}N$), 30.6, 29.3, 29.1, 26.8 (CH_2). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3089, 2895, 1602, 1442, 1375, 1344, 1144, 1125, 798. − UV (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.31), 268 (4.41), 300 (3.24), 378 (3.02). − HRMS (EI, 70 eV): $C_{25}H_{37}CoN_2$: calcd. 425.2367; found 425.2330.

(η^5-Cyclopentadienyl){(η^4-15,16,21,22)-1,12-diazatetracyclo[10.6.6.0^{15,22}0^{16,21}]tetracosa-15,21-diene}cobalt (26): Starting material: 126 mg (0.38 mmol) of 1,12-diazabicyclo[10.6.6]tetracosa-15,21-diyne (**13**) and 89 mg (0.38 mmol) of [CpCo(cod)] in 50 mL of *n*-nonane. Reaction time: 5 d. The reaction mixture was chromatographed with petroleum ether/diethyl ether (5:2). Yield: 85 mg

(50%) of **26** as yellow solid, m.p. 130°C. − ^{1}H NMR (CDCl$_3$): δ = 4.71 (s, 5 H, H_{Cp}), 3.25−2.95 (m, 8 H, CH_2-N), 2.65 (t, 4 H, CH_2-N), 2.15−1.81 (m, 8 H, $C_{Cbd}-CH_2$), 1.44−1.21 (m, 16 H, CH_2). − ^{13}C NMR (CDCl$_3$): δ = 79.0 (C_{Cp}), 76.7 (C_{Cbd}), 55.4, 52.2 (CH_2-N), 29.4, 29.3, 29.2, 28.9, 27.0 (CH_2). − IR (KBr): $\tilde{\nu}$ = 3091 cm^{-1}, 2925, 2898, 2848, 1597, 1442, 1361, 1136, 799. − UV (CH_2Cl_2): λ_{max} (lg ε) = 224 nm (4.18), 266 (4.36), 304 (2.98). − $C_{27}H_{41}CoN_2$ (452.56): calcd. C 71.66, H 9.13, N 6.19; found C 71.29, H 9.15, N 6.19.

X-ray Crystallographic Studies: Crystal data are given in Table 2. Intensity data were collected for **16** at −73°C with a Siemens CCD system, for all other compounds with a Syntex R3 diffractometer (Mo-K_α radiation, graphite monochromator, ω scan). Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied. All structures were solved by direct methods (SHELXS-86)[16] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[17] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in difference Fourier maps and refined isotropically. The cyclopentadienyl rings in **18** and **25** were disordered. The positions of the Cp hydrogen atoms in the latter compounds and in **26** were calculated and not refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103160 (**15**), -103161 (**16**), -103162 (**18**), -103163 (**22**), -103164 (**23**), -103165 (**25**), -103166 (**26**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-0335, E-mail: deposit@ccdc.cam.uc.uk].

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