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FULL PAPER

Reaction of N,N′-bridged 1,10-diazacyclooctadeca-5,14-diynes with [CpCo(cod)]: a new type of superphane

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The reaction of N,N′-bridged 1,10-diazacyclooctadeca-5,14-diynes **1a–d** with [CpCo(cod)] (**2**) leads to both intra- (**3**) and inter-molecular (**4**) CpCo–cyclobutadiene complexes. The yield of intramolecular complex decreases and the yield of intermolecular complex increases with growing length of the alkane bridge. X-Ray investigations on single crystals of **3a**, **3d** and **4d** reveal that the repulsions between the Cp ring and two CH_2-groups in β-position to the cyclobutadiene ring increase from **3a** to **3d**. Such steric repulsions are not found in **4d**.

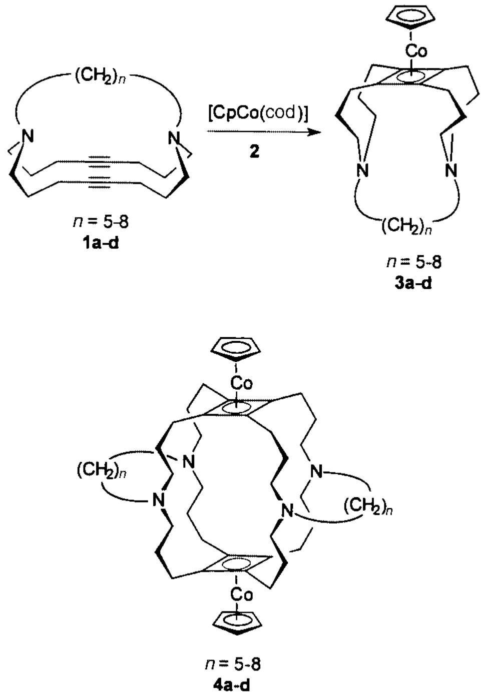
Since 1956 when Longuet-Higgins and Orgel predicted the stability of cyclobutadiene coordinated to a transition metal[1] a great variety of these compounds has been synthesized. In particular (η^5-cyclopentadienyl)cobalt (CpCo) was found to be a good stabilizing transition metal fragment and the resulting cyclobutadiene (Cbd) complexes are legion by now.[2] Cobalt initiated dimerization of alkynes occurs either thermally or photochemically.[3,4]

Early investigations by King *et al.*[5] have shown that cyclic diynes of medium ring size yield the intramolecular cyclobutadiene complex stabilized either with the CpCo or the $Fe(CO)_3$ fragment. More detailed investigations showed that also an intermolecular route can be followed.[6,7] In this case dimeric,[6,7] trimeric and tetrameric[8] superphanes result. These studies show that the resulting products depend mainly on steric effects.[6,7]

For 1,10-cyclooctadecadiyne the reaction with (η^4-cycloocta-1,5-diene)(η^5-cyclopentadienyl)cobalt [CpCo(cod)] **2** afforded only an intermolecular complex, a superphane, in low yield besides material of higher molecular weight.[9] This was rationalized by assuming that in the 18-membered ring the transannular distance (7.12 Å) of the triple bonds prevents an intramolecular dimerization.[6,7] In the related bicyclic system of N,N′-bridged 1,10-diazacyclooctadeca-5,14-diynes **1** the additional bridge forces a folding of the 18-membered diyne cycle which leads to a shorter transannular distance of the π-systems[10] compared to the carbocyclic compound so that an intramolecular reaction might be possible. Here, we report on the complexation of a series of bicyclic diynes **1a–d**, the dependence of the distribution of products on the length of the third bridge and the solid state structures of the complexes.

Table 1 Isolated yields (%) of intra- and inter-molecular complexes

$(CH_2)_n$	Intra	Inter
5	29.3 (**3a**)	Trace (**4a**)
6	13.6 (**3b**)	FAB-MS (**4b**)
7	6.6 (**3c**)	FAB-MS (**4c**)
8	9.4 (**3d**)	10.7 (**4d**)



Scheme 1

Heating of **1a–d** with **2** yields two types of products (Scheme 1, Table 1). For **1a** only the intramolecular complex **3a** was found in almost 30% yield. The yield of the intramolecular complex decreases with growing length of the alkane bridge whereas the formation of the intermolecular complex **4** increases in the same manner so that **4d** could be isolated in nearly 11% yield. The increase in the yields of **4b** and **4c** was observed in the mass spectra (FAB^+) of the reaction mixture but they could not be successfully isolated. The reason for the decreasing yield of the intramolecular complex from **1a** to **1d** can be seen by comparing the solid state structures of **3a** and **3d** (Fig. 1). In **3a** the planes of the cyclopentadienyl and cyclobutadiene rings are arranged almost parallel whereas a bending of the cyclopentadienyl ring is found in **3d** (the angles between the least-squares-planes are 1.7° in **3a** *cf.* 5.2° in **3d**) leading also to a slight downfield shift of the cyclopentadienyl protons from δ 4.61 for **3a** to δ 4.74 for **3d** so that packing effects in the crystal can be excluded as the reason for the bending. The long -$(CH_2)_8$- bridge in **3d** forces a conformation of the molecule in which steric hindrance between the hydrogen atoms of two β-methylene groups of the cyclobutadiene ligand and the hydrogen atoms of the cyclopentadienyl ring leads to the bending. For the corresponding intermolecular complex **4d** a parallel arrangement of the rings in the solid state (Fig. 2) and a

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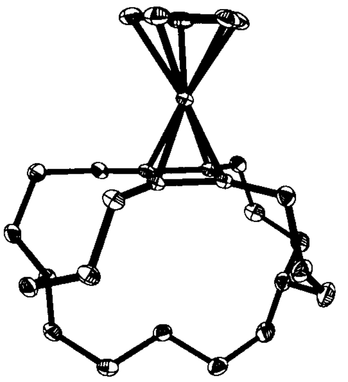
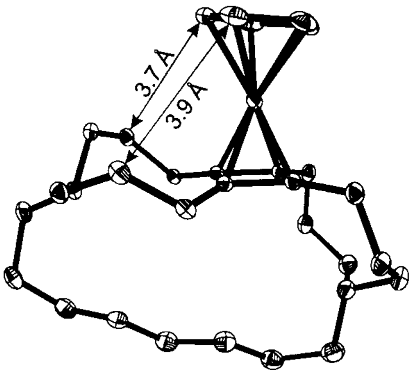


3a



3d

Fig. 1 Molecular structure of **3a** and **3d** in solid state. The thermal ellipsoids are of 25% probability and the hydrogen atoms have been omitted for clarity.

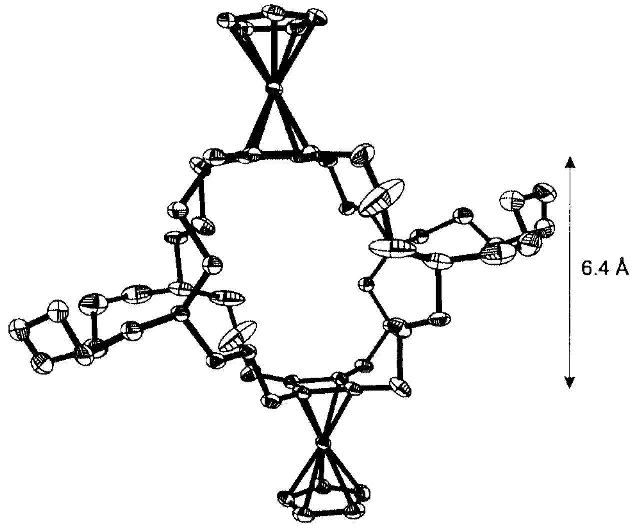


Fig. 2 Molecular structure of **4d** in the solid state. The thermal ellipsoids are of 10% probability and the hydrogen atoms have been omitted for clarity.

normal ^{1}H-shift for the cyclopentadienyl protons of δ 4.63 was found.

Conclusions

The shorter transannular distance of the π-systems in the bicyclic system of N,N′-bridged 1,10-diazacyclooctadeca-5,14-diynes compared to 1,10-cyclooctadecadiyne leads preferably to intramolecular cyclobutadiene complexes. The increasing steric hindrance with growing length of the alkane bridge is avoided by formation of the intermolecular complex. The superphane **4d** represents a new type of superphane in so far as the chains interconnecting the two π-systems are tethered.

Experimental

General

All reactions were carried out under argon atmosphere with magnetic stirring in sodium-dried and oxygen-free *n*-nonane. ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 with Bruker AC 300 and Avance 500 instruments, respectively. High resolution (HR) mass spectra were obtained with a JEOL JMS 700 high-resolution mass spectrometer. The UV/VIS spectrum of **3a** was recorded on a Hewlett-Packard HP 8452 diode array spectrometer in CH_2Cl_2 and the microanalysis was performed at the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

General procedure for preparation of the complexes

A solution of bicyclic diyne **1a**–**d** (0.6 mmol) and of **2** (140 mg, 0.6 mmol) in *n*-nonane (60 ml) was refluxed for four days. Solvent and unreacted **2** were then removed by chromatography (Al_2O_3 with 6% water) using light petroleum (bp 30–40 °C) as solvent. The intramolecular complexes **3a**–**d** were obtained using light petroleum-diethyl ether (10 : 1) while **4d** was eluted upon increasing the polarity of the eluent (light petroleum-diethyl ether (5 : 1)). The intramolecular complexes **3a**–**d** were recrystallized from pentane while **4d** was recrystallized from C_6D_6. In all cases, polymeric material remains as a yellow band on the head of the column.

{(5,6,14,15-η)-1,10-Diazatetracyclo[8.8.5.0^{5,15}.O^{6,14}]tricosa-5(6),14(15)-diene}(η^5-cyclopentadienyl)cobalt 3a

Yield: 77 mg (0.17 mmol), 29.3% (orange crystals (mp 164 °C)) (Calc. for $C_{26}H_{39}CoN_2$: C, 71.21; H, 8.96; N, 6.39. Found: C, 71.31; H, 8.89; N, 6.35%). HRMS, FAB: *m*/*z* 438.2469, calc. for $C_{26}H_{39}CoN_2$ (M$^+$): *m*/*z* 438.2445. UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 222 (4.33), 266 (4.48), 300 (3.12), 384 (2.39). IR (KBr)/cm^{-1} 3447br, 3093w, 2903vs, 2846s, 2800vs, 1651w, 1460m. ^{1}H NMR (C_6D_6, 500 MHz) δ 1.16–1.24 (m, 4H), 1.32–1.57 (m, 10H), 2.10–2.18 (m, 4H), 2.22–2.40 (m, 12H), 2.48–2.55 (m, 4H) (CH_2); 4.61 (s, 5H, CpH). ^{13}C NMR (C_6D_6, 125.76 MHz) δ 27.64 (CH_2), 28.39 (CH_2-Cbd); 29.60, 30.74 (CH_2); 61.14, 61.88 (CH_2N); 80.04 (CpC), 81.15 (Cbd C).

{(5,6,14,15-η)-1,10-Diazatetracyclo[8.8.6.0^{5,15}.0^{6,14}]tetracosa-5(6),14(15)-diene}(η^5-cyclopentadienyl)cobalt 3b

Yield: 37 mg (0.08 mmol), 13.6% (orange crystals). HRMS, FAB: *m*/*z* 452.2607, calc. for $C_{27}H_{41}CoN_2$ (M$^+$): *m*/*z* 452.2602. ^{1}H NMR (C_6D_6, 500 MHz) δ 1.27–1.43 (m, 8H), 1.43–1.63 (m, 8H), 2.02–2.33 (m, 16H), 2.44–2.56 (m, 4H) (CH_2); 4.65 (s, 5H, Cp–H). ^{13}C NMR (C_6D_6, 125.76 MHz) δ 27.42, 28.34, 29.07, 29.27 (CH_2); 58.79, 60.19 (CH_2N); 79.68 (CpC); 80.91 (Cbd C).

{(5,6,14,15-η)-1,10-Diazatetracyclo[8.8.7.0^{5,15}.0^{6,14}]pentacosa-5(6),14(15)-diene}(η^5-cyclopentadienyl)cobalt 3c

Yield: 18 mg (0.04 mmol), 6.6% (orange crystals). HRMS, FAB: *m*/*z* 466.2777, calc. for $C_{28}H_{43}CoN_2$ (M$^+$): *m*/*z* 466.2758. ^{1}H NMR (C_6D_6, 500 MHz) δ 1.24–1.47 (m, 10H), 1.47–1.67 (m, 8H), 1.94–2.10 (m, 8H), 2.21–2.31 (m, 4H), 2.37–2.60 (m, 8H) (CH_2); 4.71 (s, 5H, CpH). ^{13}C NMR (C_6D_6, 125.76 MHz) δ 26.01, 26.37, 28.35, 29.16, 29.41 (CH_2); 57.98, 59.19 (CH_2N); 78.38 (CpC); 81.33 (Cbd C).

{(5,6,14,15-η)-1,10-Diazatetracyclo[8.8.8.0^{5,15}.0^{6,14}]hexacosa-5(6),14(15)-diene}(η^5-cyclopentadienyl)cobalt 3d

Yield: 29 mg (0.06 mmol), 9.4% (orange crystals). HRMS, FAB: *m*/*z* 480.2923, calc. for $C_{29}H_{45}CoN_2$ (M$^+$): *m*/*z* 480.2915.

Table 2 Crystallographic data for **3a**, **3d** and **4d**

	3a	**3d**	**4d**
Empirical formula	$C_{26}H_{39}CoN_2$	$C_{29}H_{45}CoN_2$	$C_{58}H_{90}Co_2N_4$
Formula weight	438.52	480.60	961.20
T/K	200(2)	200(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
Z	2	4	4
a/Å	7.6567(1)	8.5424(1)	23.9708(2)
b/Å	9.7915(2)	29.0936(3)	9.4887(7)
c/Å	16.0835(3)	10.9486(1)	23.9264(2)
α/°		87.261(1)	
β/°	77.433(1)	110.090(1)	98.214(1)
γ/°		75.054(1)	
V/Å^3	1137.04(3)	2555.55(5)	5386.3(7)
μ/mm^{-1}	0.769	0.690	0.655
Reflections collected	8530	18908	19435
Independent reflections	3796	4439	4623
R_{int}	0.0143	0.0242	0.0648
Final R indices			
($I > 2\sigma(I)$) $R(F)$	0.028	0.031	0.069
$R_w(F^2)$	0.083	0.082	0.160

^{1}H NMR (C_6D_6, 500 MHz) δ 1.33–1.62 (m, 20H), 1.82–1.92 (m, 4H), 1.99–2.09 (m, 4H), 2.22–2.29 (m, 4H), 2.38–2.50 (m, 8H) (CH_2); 4.74 (s, 5H, Cp H); ^{13}C NMR (C_6D_6, 125.76 MHz) δ 25.14, 27.51, 28.81,[11] 30.22 (CH_2); 56.30, 56.76 (CH_2N); 79.30 (Cp C), 80.79 (Cbd C).

{(5,6,48,49-η)(23,24,40,41-η)-1,10,19,28-Tetraazaheptacyclo[16.16.8^{1,10}.8^{19,28}.0^{5,49}.0^{6,48}.0^{23,41}.0^{24,40}]dopentaconta-5(49),6(48),23(41),24(40)-tetraene}bis[(η^5-cyclopentadienyl)cobalt] 4d

Yield: 33 mg (0.03 mmol), 10.7% (orange crystals). HRMS, FAB: *m*/*z* 960.5873, calc. for $C_{58}H_{90}Co_2N_4$ (M^+): *m*/*z* 960.5829. ^{1}H NMR (C_6D_6, 500 MHz) δ 1.30–1.80 (m, 20H), 1.93–2.08 (m, 4H), 2.20–2.49 (m, 16H) (CH_2), 4.63 (s, 5H, Cp H); ^{13}C NMR (C_6D_6, 125.76 MHz) δ 25.24, 27.87, 28.28,[11] 29.84 (CH_2); 54.60, 55.38 (CH_2N); 79.00 (Cp C); 80.55 (Cbd C).

X-Ray structural analysis of 3a, 3d and 4d

The measurements were performed on a Bruker SMART CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The SMART software package[12] was used for data collection as well as frame integration. Structure solution was carried out using the SHELXTL V5.10 software package.[13] Intensities were corrected for Lorentz and polarisation effects. All structures were solved by direct methods. Full-matrix least-squares refinement was carried out against F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were taken into account at calculated positions. The crystallographic data are listed in Table 2.

CCDC reference number 186/1806.

See http://www.rsc.org/suppdata/dt/a9/a909482b/ for crystallographic files in .cif format.

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