

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

Rolf Gleiter,\* Thomas von Hirschheydt, Volker Wolfart and Frank Rominger

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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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<sub>2</sub>-groups in  $\beta$ -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<sup>1</sup> a great variety of these compounds has been synthesized. In particular ( $\eta^5$ -cyclopentadienyl)cobalt (CpCo) was found to be a good stabilizing transition metal fragment and the resulting cyclobutadiene (Cbd) complexes are legion by now.<sup>2</sup> Cobalt initiated dimerization of alkynes occurs either thermally or photochemically.<sup>3,4</sup>

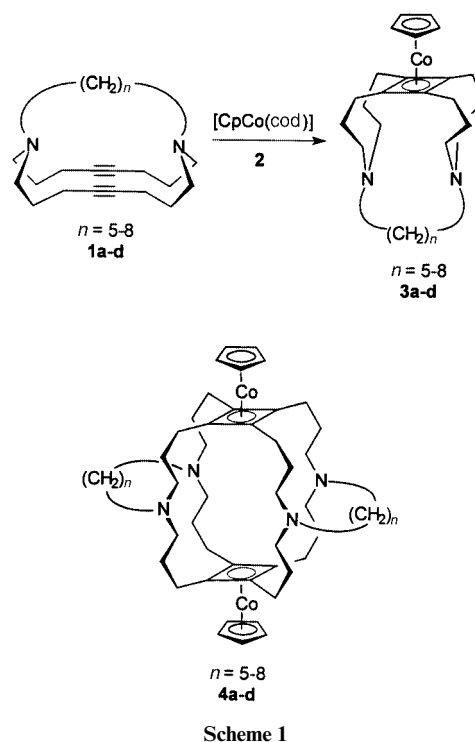
Early investigations by King *et al.*<sup>5</sup> have shown that cyclic diynes of medium ring size yield the intramolecular cyclobutadiene complex stabilized either with the CpCo or the Fe(CO)<sub>3</sub> fragment. More detailed investigations showed that also an intermolecular route can be followed.<sup>6,7</sup> In this case dimeric,<sup>6,7</sup> trimeric and tetrameric<sup>8</sup> superphanes result. These studies show that the resulting products depend mainly on steric effects.<sup>6,7</sup>

For 1,10-cyclooctadecadiyne the reaction with ( $\eta^4$ -cycloocta-1,5-diene)( $\eta^5$ -cyclopentadienyl)cobalt [CpCo(cod)] **2** afforded only an intermolecular complex, a superphane, in low yield besides material of higher molecular weight.<sup>9</sup> 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.<sup>6,7</sup> 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  $\pi$ -systems<sup>10</sup> 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.

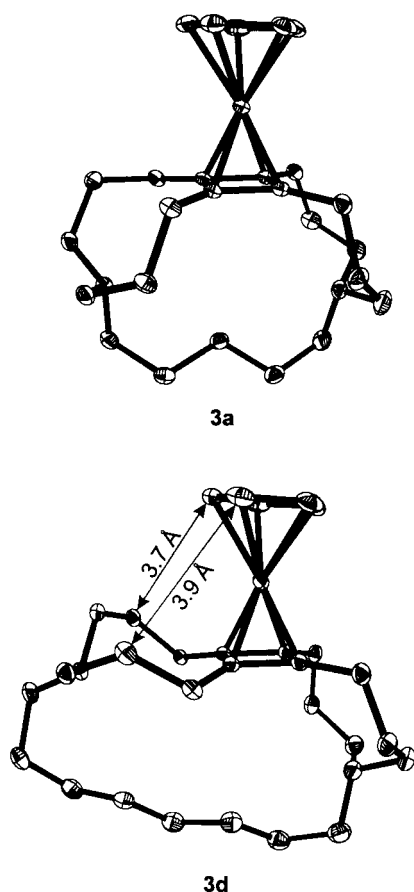
Heating of **1a–d** with **2** yields two types of products (Scheme 1, Table 1). For **1a** only the intramolecular complex **3a** was found in almost 30% yield. The yield of the intramolecular complex decreases with growing length of the alkane bridge whereas the formation of the intermolecular complex **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<sup>+</sup>) 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

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

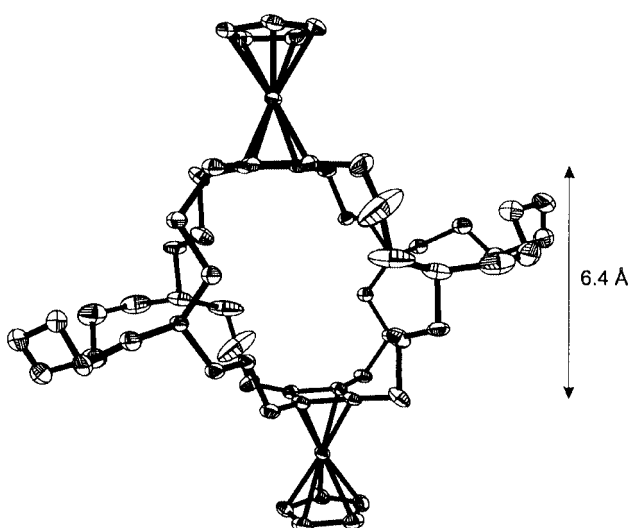
(CH <sub>2</sub> ) <sub>n</sub>	Intra	Inter
5	29.3 ( <b>3a</b> )	Trace ( <b>4a</b> )
6	13.6 ( <b>3b</b> )	FAB-MS ( <b>4b</b> )
7	6.6 ( <b>3c</b> )	FAB-MS ( <b>4c</b> )
8	9.4 ( <b>3d</b> )	10.7 ( <b>4d</b> )



to a slight downfield shift of the cyclopentadienyl protons from  $\delta$  4.61 for **3a** to  $\delta$  4.74 for **3d** so that packing effects in the crystal can be excluded as the reason for the bending. The long -(CH<sub>2</sub>)<sub>8</sub>- bridge in **3d** forces a conformation of the molecule in which steric hindrance between the hydrogen atoms of two  $\beta$ -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



**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  $^1\text{H}$ -shift for the cyclopentadienyl protons of  $\delta$  4.63 was found.

## Conclusions

The shorter transannular distance of the  $\pi$ -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  $\pi$ -systems are tethered.

## Experimental

### General

All reactions were carried out under argon atmosphere with magnetic stirring in sodium-dried and oxygen-free *n*-nonane.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$  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  $\text{CH}_2\text{Cl}_2$  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 ( $\text{Al}_2\text{O}_3$  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  $\text{C}_6\text{D}_6$ . In all cases, polymeric material remains as a yellow band on the head of the column.

#### **{(5,6,14,15- $\eta$ )-1,10-Diazatetracyclo[8.8.5.0<sup>5,15</sup>.0<sup>6,14</sup>]tricoso-5(6),14(15)-diene} $\{\eta^5$ -cyclopentadienyl}cobalt **3a****

Yield: 77 mg (0.17 mmol), 29.3% (orange crystals (mp 164 °C)) (Calc. for  $\text{C}_{26}\text{H}_{39}\text{CoN}_2$ : 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  $\text{C}_{26}\text{H}_{39}\text{CoN}_2$  ( $\text{M}^+$ ):  $m/z$  438.2445. UV–VIS ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 222 (4.33), 266 (4.48), 300 (3.12), 384 (2.39). IR (KBr)/ $\text{cm}^{-1}$  3447br, 3093w, 2903vs, 2846s, 2800vs, 1651w, 1460m.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\delta$  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) ( $\text{CH}_2$ ); 4.61 (s, 5H, CpH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 125.76 MHz)  $\delta$  27.64 ( $\text{CH}_2$ ), 28.39 ( $\text{CH}_2$ -Cbd), 29.60, 30.74 ( $\text{CH}_2$ ); 61.14, 61.88 ( $\text{CH}_2\text{N}$ ); 80.04 (CpC), 81.15 (Cbd C).

#### **{(5,6,14,15- $\eta$ )-1,10-Diazatetracyclo[8.8.6.0<sup>5,15</sup>.0<sup>6,14</sup>]tetracosa-5(6),14(15)-diene} $\{\eta^5$ -cyclopentadienyl}cobalt **3b****

Yield: 37 mg (0.08 mmol), 13.6% (orange crystals). HRMS, FAB:  $m/z$  452.2607, calc. for  $\text{C}_{27}\text{H}_{41}\text{CoN}_2$  ( $\text{M}^+$ ):  $m/z$  452.2602.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\delta$  1.27–1.43 (m, 8H), 1.43–1.63 (m, 8H), 2.02–2.33 (m, 16H), 2.44–2.56 (m, 4H) ( $\text{CH}_2$ ); 4.65 (s, 5H, Cp–H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 125.76 MHz)  $\delta$  27.42, 28.34, 29.07, 29.27 ( $\text{CH}_2$ ); 58.79, 60.19 ( $\text{CH}_2\text{N}$ ); 79.68 (CpC); 80.91 (Cbd C).

#### **{(5,6,14,15- $\eta$ )-1,10-Diazatetracyclo[8.8.7.0<sup>5,15</sup>.0<sup>6,14</sup>]pentacosa-5(6),14(15)-diene} $\{\eta^5$ -cyclopentadienyl}cobalt **3c****

Yield: 18 mg (0.04 mmol), 6.6% (orange crystals). HRMS, FAB:  $m/z$  466.2777, calc. for  $\text{C}_{28}\text{H}_{43}\text{CoN}_2$  ( $\text{M}^+$ ):  $m/z$  466.2758.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\delta$  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) ( $\text{CH}_2$ ); 4.71 (s, 5H, CpH).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 125.76 MHz)  $\delta$  26.01, 26.37, 28.35, 29.16, 29.41 ( $\text{CH}_2$ ); 57.98, 59.19 ( $\text{CH}_2\text{N}$ ); 78.38 (CpC); 81.33 (Cbd C).

#### **{(5,6,14,15- $\eta$ )-1,10-Diazatetracyclo[8.8.8.0<sup>5,15</sup>.0<sup>6,14</sup>]hexacosa-5(6),14(15)-diene} $\{\eta^5$ -cyclopentadienyl}cobalt **3d****

Yield: 29 mg (0.06 mmol), 9.4% (orange crystals). HRMS, FAB:  $m/z$  480.2923, calc. for  $\text{C}_{29}\text{H}_{45}\text{CoN}_2$  ( $\text{M}^+$ ):  $m/z$  480.2915.

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

	<b>3a</b>	<b>3d</b>	<b>4d</b>
Empirical formula	C <sub>26</sub> H <sub>39</sub> CoN <sub>2</sub>	C <sub>29</sub> H <sub>45</sub> CoN <sub>2</sub>	C <sub>58</sub> H <sub>90</sub> Co <sub>2</sub> N <sub>4</sub>
Formula weight	438.52	480.60	961.20
<i>T</i> /K	200(2)	200(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	4	4
<i>a</i> /Å	7.6567(1)	8.5424(1)	23.9708(2)
<i>b</i> /Å	9.7915(2)	29.0936(3)	9.4887(7)
<i>c</i> /Å	16.0835(3)	10.9486(1)	23.9264(2)
$\alpha$ /°		87.261(1)	
$\beta$ /°	77.433(1)	110.090(1)	98.214(1)
$\gamma$ /°		75.054(1)	
<i>V</i> /Å <sup>3</sup>	1137.04(3)	2555.55(5)	5386.3(7)
$\mu$ /mm <sup>-1</sup>	0.769	0.690	0.655
Reflections collected	8530	18908	19435
Independent reflections	3796	4439	4623
<i>R</i> <sub>int</sub>	0.0143	0.0242	0.0648
Final <i>R</i> indices			
( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <i>R</i> ( <i>F</i> )	0.028	0.031	0.069
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.083	0.082	0.160

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)  $\delta$  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<sub>2</sub>); 4.74 (s, 5H, Cp H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.76 MHz)  $\delta$  25.14, 27.51, 28.81,<sup>11</sup> 30.22 (CH<sub>2</sub>); 56.30, 56.76 (CH<sub>2</sub>N); 79.30 (Cp C), 80.79 (Cbd C).

**{(5,6,48,49- $\eta$ )(23,24,40,41- $\eta$ )-1,10,19,28-Tetraazaheptacyclo-[16.16.8<sup>1,10</sup>.8<sup>19,28</sup>.0<sup>5,49</sup>.0<sup>6,48</sup>.0<sup>23,41</sup>.0<sup>24,40</sup>]dopentaconta-5(49),6(48),23(41),24(40)-tetraene}bis[( $\eta^5$ -cyclopentadienyl)cobalt] **4d****

Yield: 33 mg (0.03 mmol), 10.7% (orange crystals). HRMS, FAB: *m/z* 960.5873, calc. for C<sub>58</sub>H<sub>90</sub>Co<sub>2</sub>N<sub>4</sub> (M<sup>+</sup>): *m/z* 960.5829. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)  $\delta$  1.30–1.80 (m, 20H), 1.93–2.08 (m, 4H), 2.20–2.49 (m, 16H) (CH<sub>2</sub>), 4.63 (s, 5H, Cp H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.76 MHz)  $\delta$  25.24, 27.87, 28.28,<sup>11</sup> 29.84 (CH<sub>2</sub>); 54.60, 55.38 (CH<sub>2</sub>N); 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-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The SMART software package<sup>12</sup> was used for data collection as well as frame integration. Structure solution was carried out using the SHELXTL V5.10 software package.<sup>13</sup> 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*<sup>2</sup>. 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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