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1,2-Azaborolyl complexes XXXI. Cyclooligomerization of alkynes at the 1,2-azaborolylcobalt moiety *

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Abstract

1-tert-Butyl-2-methyl-η^5-1*H*-1,2-azaborolyl-bis(η^2-ethene)cobalt (AbCo(C_2H_4)$_2$) (**1**) reacts with 2-butyne to give AbCo(η^4-1,2,3,4-tetramethyl-1,3-cyclohexadiene) (**2**) and catalytically generated free hexamethylbenzene. With diphenylethyne, 3-hexyne and 4-octyne the formation of 1,3-cyclohexadiene complexes **3**, **5** and **7** is observed as well as the cyclodimerization of the alkynes with formation of cyclobutadiene complexes **4**, **6** and **8**. The separation of corresponding cyclohexadiene and cyclobutadiene complexes is possible by high performance liquid chromatography, as is exemplified with the combination **3**–**4**. Two-dimensional NMR techniques enable the characterization of the product mixtures **5**–**6** and **7**–**8**.

Keywords: Cyclotrimerization; Cyclodimerization; Alkynes; Cobalt; 1,2-azaborolyl complexes

1. Introduction

In contrast with Co(0), which forms numerous alkyne complexes, Co(I) is known to bind alkynes as η^2-coordinated ligands in only a few cases [2]. Usually contact of alkynes with the CpCo fragment results in their oligomerization. The use of CpCo(CO)$_2$ as a catalyst precursor is the most common compound to inhibit cyclization reactions of alkynes. Numerous examples have been described during the last two decades [3]. Bercaw and coworkers [4] discussed mechanistic effects including CpCo as the catalytic active spezies for the cyclotrimerization of acetylenes. Recently, supercritical water has been found to be a good solvent for alkyne trimerizations by CpCo(CO)$_2$ as a catalyst precursor [5].

The 1,2-azaborolylcobalt moiety (AbCo) is isoelectronic with CpCo. However, a decisive property compared with CpCo is its chiral character (see Fig. 1.)

In combination with a second prochiral Ab ring, pairs of diastereoisomer sandwich complexes are formed. Such bis(1,2-azaborolyl)metal complexes have been investigated by us in detail [6]. It is the chiral character of AbCo which makes this complex fragment an interesting object for the study of stereoselectivity. As has been shown in a number of cases, racemization of enantiomers does not occur because of the strong covalent bonds. Only in ionic systems with very electropositive metals, such as beryllium, has racemization been observed [7].

The present report describes the first reactions of the AbCo unit with alkynes to give cyclobutadiene, cyclohexadiene and arene derivatives.

2. Results and discussion

The most reactive of the AbCo complexes is AbCo(η^2-C_2H_4)$_2$ (**1**). The dicarbonyl compound, frequently used in Cp chemistry, is unreactive towards

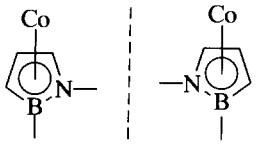

Fig. 1. η^5-1,2-azaborolylcobalt moieties as a pair of enantiomers.

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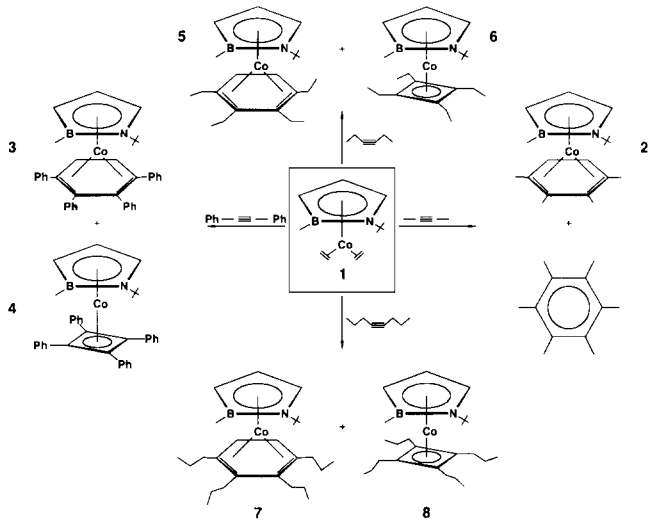
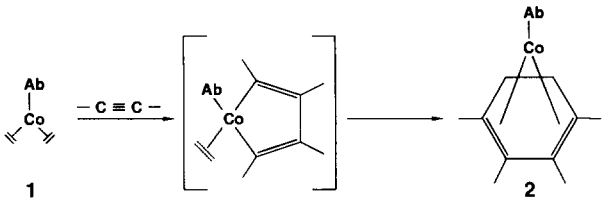


Scheme 1.

alkynes, even at elevated temperatures. 1-tert-Butyl-2-methyl-η^5-1*H*-1,2-azaborolyl-bis(η^2-ethene)-cobalt (**1**), available from $AbCo(CO)_2$ and ethene under photolytic conditions [8] reacts with various alkynes to give **2–8**. In every case the cobalt complex **1** and the corresponding alkyne react under mild conditions at room temperature in pentane or benzene (Scheme 1).

All reactions of **1** with the various alkynes result in the formation of 1,3-cyclohexadiene complexes (**2**, **3**, **5** and **7**) by cyclotrimerization of two equivalents of the alkyne and one ethene molecule of **1**. The first 1,3-cyclohexadiene–cobalt-Ab complex has recently been described by us [9]. A second type of AbCo complex is formed by cyclodimerization of the alkynes, namely the novel cyclobutadiene complexes **4**, **6** and **8**. As an exception, 2-butyne gives only the 1,3-cyclohexadiene complex **2** and catalytically formed free hexamethylbenzene. This cyclotrimerization product is probably generated via an unstable 20-electron 1,2-azaborolylhexamethylbenzene–cobalt complex which, however, could not be isolated or detected. The amount of hexamethylbenzene depends only on the amount of excess 2-butyne. The electronic situation in the supposed unstable 20-electron complex is obviously the reason for the loss of the arene, hence starting the catalytic process.

Mechanisms for the formation of arenes from alkynes at the CpCo moiety have been discussed by Bercaw and coworkers [4]. Metalacyclopentadienes are formulated as intermediates, followed by the insertion of a third alkyne and elimination of the arene molecule. The formation of the corresponding metalaazaborole intermediates explains not only the generation of hexamethylbenzene but also that of the η^4-1,2,3,4-tetramethyl-1,3-cyclohexadienecobalt complex **2** formation by insertion of an ethene ligand instead of a third 2-butyne (Scheme 2). The orange–red 18-electron com-



Scheme 2.

plex **2** is stable so that the 1,3-cyclohexadiene molecule has no tendency to dissociate.

The cyclobutadiene complexes **4**, **6** and **8** may also be formed via metalaazaborole intermediates; however, for steric reasons a third alkyne molecule can obviously not be coordinated additionally to give six-membered arenes. The geometric situation at the cobalt atom using, ethyl, n-propyl and phenyl substituents enables only coordination and insertion of the small ethene ligand to give the 1,3-cyclohexadiene complexes **3**, **5** and **7**.

The separation of the corresponding cyclohexadiene and cyclobutadiene complexes is only possible by means of high performance liquid chromatography (HPLC). As the complexes can be identified by two-dimensional (2D) NMR spectroscopy even as mixtures, only **3** and **4** were separated exemplarily by HPLC to identify the pure compounds by NMR spectroscopy beyond doubt.

The UV spectrum of a **3–4** mixture in hexane : dioxane (100 : 1) shows two maxima at $\lambda = 278$ and 296 nm. The maximum at 278 nm was used for detection. The preparative separation succeeded on a Nucleosil 100/10 μm column using a pressure of 1.3 MPa, and a flow rate of 16 ml min^{-1}. Under these conditions the retention times were 8.5 min for **4** and 11.6 min for **3**. Using five runs with 500 μl each time, 20 mg of **3** and 80 mg of **4** could be isolated.

Fig. 2 shows the ^1H NMR spectra of the HPLC-separated **3** and **4** in the region between 3.5 and 5.5 ppm, showing the typical signals for the Ab ring protons. Using the HH COSY technique, the ^1H NMR signals for **3** and **4** could already be detected before HPLC

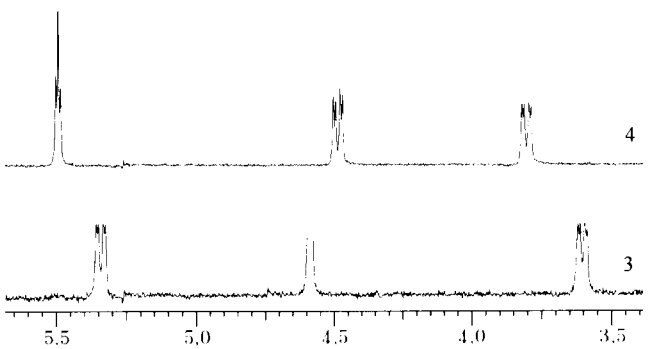


Fig. 2. ^1H NMR spectra of HPLC-separated **3** and **4** in the 3.5–5.5 ppm region.

separation as shown in Fig. 3. Based on these findings, the NMR spectroscopic identification of **5–6** and **7–8** respectively could be performed with the mixtures.

Table 1 contains the ^{1}H, ^{11}B and ^{13}C NMR data of **2–8**. The discussion of the NMR data can be reduced to the comparison of the cyclohexadiene complexes

Table 1
^{1}H, ^{11}B and ^{13}C chemical shifts δ and coupling constants J for **2–8**

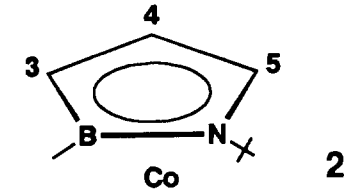
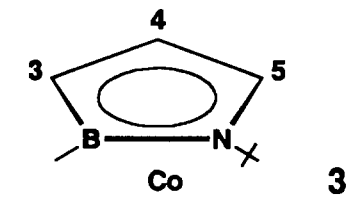
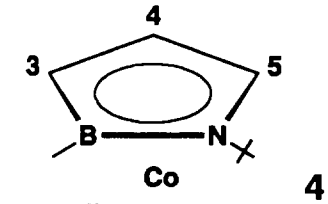
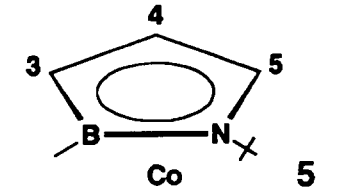
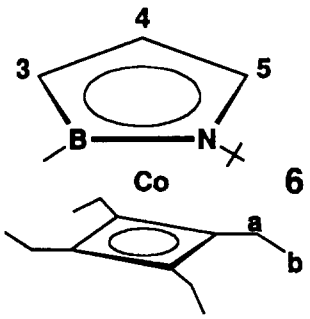
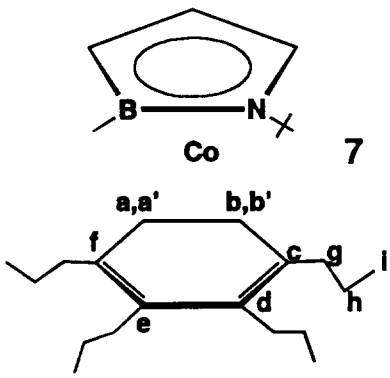
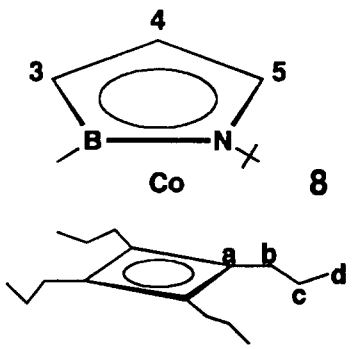
	^{1}H	^{11}B	$^{13}C\{^{1}H\}$
 **2**	0.61 (s, 3H, B–CH_3), 1.20 (s, 9H, C(CH_3)$_3$), 2.93 (s, br, 1H, H^3), 4.11 (dd, $^3J_{H^4H^5}$ = 1.1 Hz, $^3J_{H^3H^4}$ = 3.8 Hz, 1H, H^4), 4.51 (s, br, 1H, H^5),	17.7	−3 (B–CH_3) 31.11 (*C*(CH_3)$_3$), 55.22), (C(*C*H_3)$_3$, 75 (br, C^3), 84, 57 (C^4), 88.35 (C^5),
	0.77, 1.42 (2m, 2×1H, H^a, $H^{a'}$), 0.93, 1.61 (2m, 2×1H, H^b, $H^{b'}$), 1.39, 1.56, 1.72, 1.77 (4s, 4×3H, H^g, H^h, H^i, H^k)		24.72 (C^a), 25.05 (C^b), 53.71 (C^c), 79.72 (C^d), 78.33 (C^e), 52.79 (C^f), 15.14, 15.34, 26.02, 26.16 (C^g, C^h, C^i, C^k)
 **3**	0.83 (s, 3H, B–CH_3), 0.82 (s, 9H, C(CH_3)$_3$), 360 (dd, $^3J_{H^3H^5}$ = 1.5 Hz, $^3J_{H^3H^4}$ = 4.8 Hz, 1H, H^3), 5.35 (dd, $^3J_{H^4H^5}$ = 1.5 Hz, $^3J_{H^3H^4}$ = 4.8 Hz, 1H, H^4), 4.57 (dd, $^3J_{H^4H^5}$ = 1.5 Hz, $^3J_{H^5H^3}$ = 1.5 Hz, 1H, H^5);	19, br	−0.6 (B–CH_3), 30.43 (*C*(CH_3)$_3$), 56.60 (C(*C*H_3)$_3$), 72 (br, C^3), 87.49 (C^4), 93.50 (C^5),
	1.56, 2.32 (2m, 2×1H, H^a, $H^{a'}$), 1.89, 2.63 (2m, 2×1H, H^b, $H^{b'}$), 6.9–7.7 (m, 20H, C_6H_5)		28.16 (C^a), 28.49 (C^b), 62.91 (C^c), 101.17 (C^d), 100.29 (C^e), 59.94 (C^f), 126.29, 148.09 (C_6H_5)
 **4**	0.01 (s, 3H, B–CH_3), 0.84 (s, 9H, C(CH_3)$_3$), 3.79 (dd, $^3J_{H^3H^5}$ = 1.6 Hz, $^3J_{H^3H^4}$ = 4.8 Hz, 1H, H^3), 4.85 (dd, $^3J_{H^4H^5}$ = 1.6 Hz, $^3J_{H^3H^4}$ = 4.8 Hz, 1H, H^4), 5.50 (dd, $^3J_{H^4H^5}$ = 1.6 Hz, $^3J_{H^3H^5}$ = 1.6 Hz, 1H, H^5),	19, br	−1.3 (B–CH_3), 30.77 (*C*(CH_3)$_3$), 56.29 (C(*C*H_3)$_3$), 79 (br, C^3), 85.37 (C^4), 89.30 (C^5),
	7.03–7.78 (m, 20H, C_6H_5)		74.16 (*C*–Ph), 137.68 (C_6H_5)
 **5**	0.66 (s, 3H, B–CH_3), 1.22 (s, br, 9H, C(CH_3)$_3$), 3.33 (s, br, 1H, H^3), 4.32 (s, br, 1H, H^4), 4.54 (s, br, 1H, H^5),	17.7	−1 (B–CH_3), 31.31 (*C*(CH_3)$_3$), 54.98 (C(*C*H_3)$_3$), 76 (br, C^3), 84.64 (C^4), 87.66 (C^5),
	1.17, 1.57 (2m, 2×1H, H^a, $H^{a'}$), 0.77, 1.42 (2m, 2×1H, H^b, $H^{b'}$), 2.0–2.2 (m, 8H, H^g, H^h, H^i, H^k), 1.1–1.4 (m, 12H, H^l, H^m, H^n, H^o)		28.43 (c^a), 28.70 (c^b), 66.26 (C^c), 95.20 (C^d), 94.54 (C^e), 65.16 (C^f), 33.08, 33.33 (C^g), 13.47, 14.06 (C^h)

Table 1 (continued)

 6	0.45 (s, 3H, B–CH_3), 1.22 (s, 9H, $C(CH_3)_3$), 3.66 (s, br, 1H, H^3), 4.60 (s, br, 1H, H^4), 5.64 (s, br, 1H, H^5), 2.3–2.5 (m, 8H, H^a), 1.3–1.5 (m, 12H, H^b)	17.7	−1 (B–CH_3), 31.18 ($C(CH_3)_3$), 55.23 ($C(CH_3)_3$), 73 (s, br, C^3), 84.90 (s, C^4), 80.72 (s, C^5), 77.98 (*C*–Et), 29–32 (C^a), 16.66, 16.79 (C^b)
 7	0.75 (s, 3H, B–CH_3), 1.27 (s, 9H, $C(CH_3)_3$), 3.71 d, $^3J_{H^3H^4}$ = 3.8 Hz, 1H, H^3), 4.61 (s, 1H, H^4), 5.39 (s, 1H, H^5) H^a, $H^{a'}$, H^b, $H^{b'}$ not detectable, 2.4–2.7 (m, 8H, H^g), 1.9–2.2 (m, 8H, H^h), 0.8–1.0 (m, 12H, H^i)	18, br	−1 (B–CH_3), 32.57 ($C(CH_3)_3$), 54.94 ($C(CH_3)_3$), 77 (br, C^3), 85.14 (C^4), 86.46 (C^5), C^a, C^b not detectable, 65.63 (C^c), 94.22 (C^d), 93.47 (C^e), 64.39 (C^f), 31.1–32.7 (C^g), 22.6–25.2 (C^h), 14.2–15.2 (C^i)
 8	0.40 (s, 3H, B–CH_3), 1.34 (s, 9H, $C(CH_3)_3$), 3.61 (d, $^3J_{H^3H^4}$ = 4.8 Hz, 1H, H^3), 4.30 (s, br, 1H, H^4), 5.53 (s, br, 1H, H^5), 2.4–2.7 (m, 8H, H^b), 2.0–2.2 (m, 8H, H^c), 0.5–1.0 (m, 12H, H^d)	18, br	−1 (B–CH_3), 32.57 ($C(CH_3)_3$), 54.58 ($C(CH_3)_3$), 71 (br, C^3), 80.98 (C^4), 87.93 (C^5), 7.16 (*C*-Prop), 30.1–32.7 (C^b), 22.6–25.7 (C^c), 14.2–15.2 (C^d)

with the cyclobutadiene compounds, as the typical ^1H and ^{13}C NMR signals of the Ab rings do not differ significantly within one class of compounds. The most sensitive group with respect to the electronic conditions at the cobalt atom is the B–CH_3 moiety. As can be seen from Table 1, the ^1H NMR signals of the cyclobutadiene complexes are shifted characteristically to a high field compared with the cyclohexadiene compounds, owing to the increased electron density of the four-membered rings.

On the contrary, the boron atom itself, which is in a direct bonding interaction with the cobalt atom, does not reflect this sensitive electronic changes by its chemical shift. In all three pairs of cyclohexadiene–cyclobutadiene complex the ^{11}B NMR signals cannot be differentiated. However, as is known, the ^{11}B nucleus does not react very sensitively to small electronic changes in its coordination sphere.

The other data in Table 1 look more or less as could be expected and will not be discussed in detail. It should be mentioned again that the assignments of most of the signals could be made without doubt by means of the 2D NMR technique.

3. Experimental part

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. The solvents were dried and saturated with nitrogen by the usual methods. The NMR spectra were recorded on a

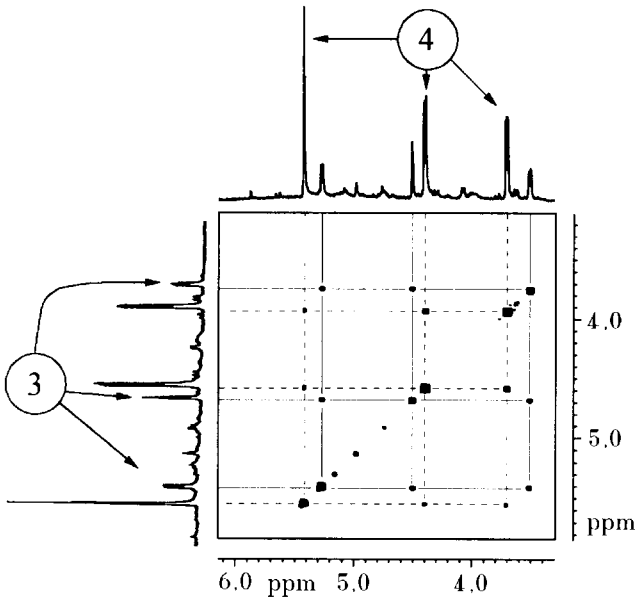


Fig. 3. ^{1}H NMR spectra obtained by HH COSY technique before HPLC separation.

Bruker AM 300 instrument in C_6D_6 solution. The mass spectra were measured on a Finnigan MAT 312 (electron impact, 70 eV). For UV spectra a Perkin–Elmer 550 S spectrometer has been used. HPLC experiments were performed using a Knauer pump 364.00, a Rheodyne Incorporated injection velve 7125 and a Knauer photometer 731.87. $AbCo(C_2H_4)_2$ (**1**) was prepared as described in the literature [8]. All other reagents were commercially available.

3.1. Reaction of 1 with excessive 2-butyne

In a typical experiment, 0.25 g (1.0 mmol) of **1** and 3 ml (38 mmol) of 2-butyne are dissolved in 25 ml of pentane with stirring at room temperature. After a few minutes, gas evolution starts. The reaction is stopped after 24 h. A greenish-brown pyrophoric solid together with parts of the catalytically formed hexamethylbenzene is separated by filtration. The separation of the hexamethylbenzene succeeds by extraction with a few millilitres of benzene. Concentration of the filtrate containing **2** leads to precipitation of further hexamethylbenzene (total yield, 1.9 g (92%, related to 2-butyne)). ^{1}H NMR: δ 2.2 ppm [10].

2: ($C_{18}H_{32}BCoN$), mass spectrum: m/z 331 [M^+].

3.2. Reactions of 1 with diphenylethyne, 3-hexyne and 4-octyne

0.30 g (1.2 mmol) of **1** and the equivalent amount of the corresponding alkyne is dissolved in benzene (diphenylethyne) and pentane respectively at room temperature with stirring. After 24 h, column chromatography on silylated silica was used to purify the orange–red reaction mixtures. The HPLC separation of **3** and **4** is described in Section 2. The mixtures of **5–6** and **7–8** were used after chromatography for the NMR spectroscopy.

3: ($C_{38}H_{39}BCoN$), mass spectrum: m/z 579 [M^+].
4: ($C_{36}H_{35}BCoN$), mass spectrum: m/z 551 [M^+].
5: ($C_{22}H_{39}BCoN$), mass spectrum: m/z 387 [M^+].
6: ($C_{20}H_{35}BCoN$), mass spectrum: m/z 359 [M^+].
7: ($C_{26}H_{47}BCoN$), mass spectrum: m/z 442 [M^+].
8: ($C_{24}H_{43}BCoN$), mass spectrum: m/z 414 [M^+].

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