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Cobalt 1,2-Azaborolyl Diene Complexes[1]

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The reaction of (1-*tert*-butyl-2-methyl-1*H*-η^5-1,2-azaborolyl)dicarbonylcobalt [AbCo(CO)$_2$] (1) with various di-, tri-, and tetraolefins under photolytic conditions at −40 °C in pentane solution gives AbCo(η^4-diene) complexes (diene = 1,3-butadiene (2), 2-methyl-1,3-butadiene (**3a**, **3b**), 2,3-dimethyl-1,3-butadiene (4), 1,5-hexadiene (5), six isomers of octadiene (**6a–6f**), cyclopentadiene (7), 1,3-cyclohexadiene (8), norbornadiene (9), 1,3,5-cycloheptatriene (**10a**, **10b**), 1,3,5,7-cyclooctatetraene (11)). Due to the chiral AbCo moiety, the use of prochiral olefins leads to diastereoisomers, as observed in the case of **3**, **6**, and **10**. The use of 1,7-octadiene could lead to an immense number of isomeric complexes. Only six can be observed in the ^{13}C NMR spectrum. ^{1}H, ^{13}C, and ^{11}B NMR spectra of all compounds in combination with 2D and NOE techniques enable reliable structure determinations.

Introduction

The 1,2-azaborolyl ring system has not only been shown to have ligand behavior comparable to that of the isoelectronic cyclopentadienyl ring but, due to the BN perturbation of the aromatic ring, it also creates special structural details in transition-metal complexes.[2] Furthermore, its prochiral character leads to chiral systems if it is combined with a metal atom. This property is used to induce stereoselective reactions at the metal center.[3] Recently, we described the synthesis of AbCo(C$_2$H$_4$)$_2$(Ab = 1-*tert*-butyl-2-methyl-1*H*-1,2-azaborolyl), a highly reactive compound, which can be used for the synthesis of various AbCo cluster compounds and substitution products, as the ethylene ligands can easily be eliminated or substituted.[1] AbCo(COD) (COD = 1,5-cyclooctadiene), the second Ab olefin complex described up to now,[4] was shown to be much more stable than the ethylene complex, probably because of the chelating character of the COD ligand. It seemed of interest to synthesize and to investigate AbCo(diene) complexes more systematically, especially to use prochiral olefins, which would generate chiral centers if coordinated to the metal. This paper describes the preparation and characterization of AbCo(η^4-diene) complexes with various acyclic and cyclic olefins with at least two double bonds. Some of these are prochiral and so would generate diastereoisomers. The stability of the AbM moiety prevents racemization, which might occur if coordinatively unsaturated transition states are formed in the course of substitution reactions at the metal center. Therefore AbCo complexes containing prochiral olefins might be interesting systems for synthesizing chiral molecules. Corresponding but not-chiral CpCo(η^4-diene) complexes have been described in the literature extensively and will be referred to at the appropriate points.

Results and Discussion

The route to various AbCo(η^4-diene) complexes is very simple: AbCo(CO)$_2$ (1)[4] together with an excess of the corresponding olefin is irradiated with UV radiation for several hours. The yields in most cases lie above 50%.

$$\mathrm{AbCo(CO)_2 + diene \rightarrow AbCo(\eta^4\text{-diene}) + 2CO} \quad (1)$$

The diene complexes are orange or red, volatile, oily liquids. In cases where prochiral olefins are used, two or more diastereoisomers are formed. They can be observed by ^{1}H and ^{13}C NMR spectroscopy but could not be identified in every case.

Another route to the olefin complexes is possible using the ethylene complex, AbCo(C$_2$H$_4$)$_2$. Although the yields are higher in some cases, this method is less favorable, as AbCo(C$_2$H$_4$)$_2$ must be synthesized from 1 in a first step. Table I summarizes the complexes prepared from 1 and various acyclic and cyclic olefins. Table II contains the ^{1}H, ^{11}B, and ^{13}C NMR data for compounds 2–11.

The 1,3-butadiene complex 2 forms NMR spectroscopically nondistinguishable enantiomers. Besides the Ab ring protons, all six H atoms of the butadiene ligand can be observed as individual signals. The four H atoms of the two CH$_2$ groups all differ markedly in their chemical shifts. In particular, the difference between the chemical shifts for the H atoms a′, d′ (−0.35, 0.12) versus a, d (2.02, 2.19) is caused by the closeness of H$^{a'}$ and H$^{d'}$ to the cobalt atom. The difference between H$^{a'}$ and H$^{d'}$ must be due to the fact that they are influenced by the B and the N atoms, respectively.

The prochiral 2-methyl-1,3-butadiene forms diastereoisomers **3a** and **3b**. Consequently, all ^{1}H and ^{13}C NMR signals are observed twice, but in the ratio 1:2. Interpretation of the ^{1}H and ^{13}C NMR data is readily effected and is supported by 2D experiments (HH COSY, CH COSY). However, it cannot be decided which of the two isomers is **3a** or **3b**. As in the case of 2, two of the H atoms of the CH$_2$ groups adjacent to the metal atom show significant high field shifts. The use of the symmetrical 2,3-dimethyl-1,3-butadiene ligand, as expected, results in only one compound, 4.

When 1,5-hexadiene is used in the CpCo chemistry, the formation of the *EE* and *EZ* 2,4-diene complexes is observed during the course of 90 days at 20 °C. The AbCo system differs to some extent from this behavior, as the 1,5-hexadiene complex 5 is not converted into the 2,4-diene isomers. This observation is confirmed by the unsuccessful attempt to prepare these complexes from 1 and 2,4-hexadiene. These compounds show no tendency to react under photolytic conditions.

The use of 1,7-octadiene as a ligand leads to much more complicated systems. However, of the immense number of different octadiene complexes including numerous diastereoisomers, which in principle could be formed, only six can be observed by ^{13}C NMR spectroscopy. It is impossible to characterize these isomers, but probably the 2,4 and the 3,5 family should be formed preferably. The

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[1] 1,2-Azaborolyl Complexes. 26. Part 25: Schmid, G.; Boutrid, A. K.; Kreuzer, E. M. *Z. Naturforsch.* **1990**, *45B*, 1235.

[2] Schmid, G. *Comments Inorg. Chem.* **1985**, *4*, 17.

[3] Schmid, G.; Rohling, T. *J. Organomet. Chem.* **1989**, *375*, 21.

[4] Schmid, G.; Schmidt, F. *Chem. Ber.* **1986**, *119*, 1766.

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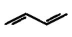
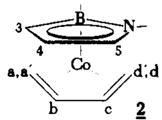
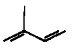
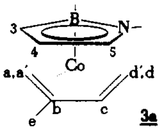
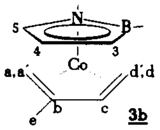
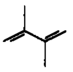
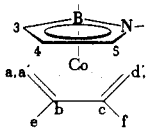
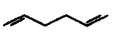
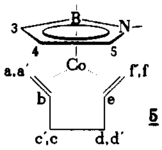
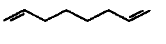
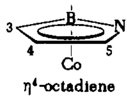
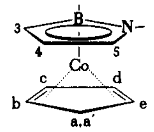
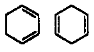
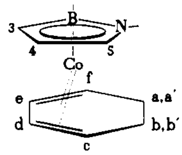
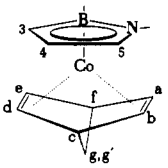
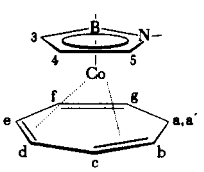
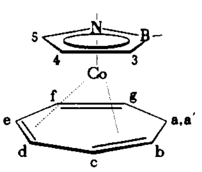
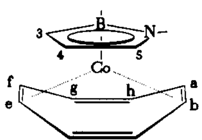
Table I. Synthesized AbCo(η^4-olefin) Complexes 2–11 with Olefins Used for the Synthesis and Yields[a]

olefin	products	yield, %
	 **2**	68
	 **3a**  **3b**	70
	 **4**	78
	 **5**	52
	 **6a**-**6f**	47
	 **7**	36
	 **8**	90
	 **9**	87
	 **10a**  **10b**	70
	 **11**	71

[a] The numbers on the Ab rings and the letters on the olefins mark H and C atoms, respectively.

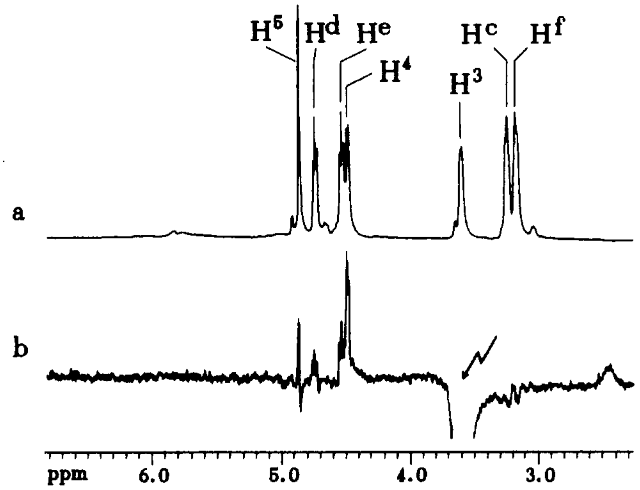


Figure 1. ^1H NMR spectrum of 8 in the region between 3 and 6 ppm (a) and NOE difference spectrum (b) in the same region. The signals for H^4, H^d, and H^e show a NOE, thus H^d and H^e must be positioned below H^3 whose frequency has been irradiated.

^1H NMR spectrum of this mixture of isomers is too complicated to be analyzed. However, the ^{13}C NMR spectrum can be interpreted to result from six isomers, as signals for the $C(CH_3)_3$ group and additionally for the ring atoms C^4 and C^5 can be observed six times each. Of course, it is not possible to identify the individual compounds **6a**–**6f**. This observation can be compared with that made in the case of CpCo(1,6-heptadiene),[5] which is rearranged in the course of 90 min at 40 °C into the 1,5-heptadiene isomer. After an additional 20 h at 50 °C a mixture of the 2,4-heptadiene compounds with *EE* and *EZ* configuration results, whereas the *ZZ* configuration could not be observed.

Cyclic diolefins and the AbCo moiety usually form complexes which are more stable than those of acyclic olefins. **1** and cyclopentadiene react under photolytic conditions to give AbCo(C_5H_6) (**7**), a complex which also has been found recently as a byproduct of the reaction of AbCo(C_2H_4)$_2$ with CpCo(C_2H_4)$_2$.[6] The homologous cyclopentadienyl–cyclopentadiene complex is well-known and was first prepared by reduction of the cobaltocenium cation with $LiAlH_4$.[7] Attempts to coordinate 1,4-cyclohexadiene failed. It is isomerized to 1,3-cyclohexadiene, forming AbCo(1,3-cyclohexadiene) (**8**). The yield of 80% is almost as high as that obtained with 1,3-cyclohexadiene (90%). The isomerization is a stoichiometric process. The HH COSY and CH COSY NMR spectra allow assignment of all signals of the 1,3-cyclohexadiene ligand. The evaluation of the NOE difference ^1H NMR spectrum even enables a rather reliable structure determination. The NOE difference spectrum of **8** in the region between 3 and 5 ppm is shown in Figure 1.

We used the resonance frequency for H^3 to irradiate the Ab ring. The difference spectrum in Figure 1 indicates that three protons are involved in the NOE, namely H^4 as a neighboring atom of H^3 and, additionally, H^d and H^e of the hexadiene ligand. This signifies that H^d and H^e must be positioned under the C^3 moiety of the Ab ring, as shown in Table I.

Norbornadiene (nor) is a cyclic 1,4-diene, which cannot isomerize like 1,4-cyclohexadiene. Its reactions with **1** at −40 °C with irradiation consequently leads to orange-red AbCo(nor) (**9**) in 87% yield. 1,3,5-Cycloheptatriene and

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[5] Chibura, K. Thesis, University of Bochum, Germany, 1985.
[6] Boutrid, A. K. Thesis, University of Essen, Essen, Germany, 1990.
[7] Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753.

Table II. ^{1}H, ^{11}B, and ^{13}C Chemical Shifts (δ) and Coupling Constants (J) for the AbCo(η^4-olefin) Complexes 2–11

	^{1}H	^{11}B	^{13}C{^{1}H}
2	5.01 (s, 1 H, H^5) 4.77 (dd, 1 H, H^b, $^3J_{H^aH^b}$ = 4.2 Hz, $^3J_{H^{a'}H^b}$ = 6.4 Hz) 4.53 (dd, 1 H, H^c, $^3J_{H^dH^c}$ = 4.0 Hz, $^3J_{H^{d'}H^c}$ = 6.4 Hz) 4.32 (s, 1 H, H^4) 3.09 (s, 1 H, H^3) 2.19 (d, 1 H, H^d, $^3J_{H^dH^c}$ = 4.0 Hz) 2.02 (d, 1 H, H^a, $^3J_{H^aH^b}$ = 4.2 Hz) 1.23 (s, 9 H, $C(CH_3)_3$) 0.80 (s, 3 H, B–CH_3) 0.12 (d, 1 H, $H^{d'}$, $^3J_{H^{d'}H^c}$ = 6.4 Hz) −0.35 (d, 1 H, $H^{a'}$, $^3J_{H^{a'}H^b}$ = 6.4 Hz)	18.6	84.30 (C^5) 83.39 (C^4) 80.97 (C^b) 80.63 (C^c) 70–72 (C^3) 55.58 (N–$\mathit{C}(CH_3)_3$) 35.96 (C^d) 33.09 (C^a) 31.22 (N–$C(\mathit{C}H_3)_3$) 1 (B–CH_3)
3a	4.96 (dd, 1 H, H^c, $^3J_{H^cH^d}$ = 6.6 Hz, $^3J_{H^cH^{d'}}$ = 9.6 Hz) 4.86 (s, 1 H, H^5) 4.35 (d, 1 H, H^4, $^3J_{H^3H^4}$ = 4.3 Hz) 2.68 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 4.3 Hz) 2.22 (d, 1 H, H^d, $^3J_{H^cH^d}$ = 6.6 Hz) 1.92 (s, 1 H, H^a) 1.72 (s, 3 H, H^e) 1.26 (s, 9 H, $C(CH_3)_3$) 0.93 (s, 3 H, B–CH_3) 0.19 (d, 1 H, $H^{d'}$, $^3J_{H^cH^{d'}}$ = 9.6 Hz) −0.50 (s, 1 H, $H^{a'}$)	18.5	95.25 (C^b) 83.66 (C^4) 82.59 (C^5) 81.82 (C^c) 70–72 (C^3) 55.42 (N–$\mathit{C}(CH_3)_3$) 35.83 (C^a) 35.12 (C^d) 31.26 (N–$C(\mathit{C}H_3)_3$) 23.91 (C^e) 0 (B–CH_3)
3b	4.99 (s, 1 H, H^5) 4.43 (dd, 1 H, H^c, $^3J_{H^cH^d}$ = 6.1 Hz, $^3J_{H^cH^{d'}}$ = 9.6 Hz) 3.97 (d, 1 H, H^4, $^3J_{H^3H^4}$ = 4.1 Hz) 3.14 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 4.1 Hz) 2.19 (d, 1 H, H^d, $^3J_{H^cH^d}$ = 6.1 Hz) 1.86 (s, 1 H, H^a) 1.60 (s, 3 H, H^e) 1.29 (s, 9 H, $C(CH_3)_3$) 0.93 (s, 3 H, B–CH_3) 0.06 (d, 1 H, $H^{d'}$, $^3J_{H^cH^{d'}}$ = 9.6 Hz) 0.36 (s, 1 H, $H^{a'}$)	18.5	96.19 (C^b) 86.81 (C^4) 83.66 (C^5) 81.08 (C^c) 73–74 (C^3) 55.42 (N–$\mathit{C}(CH_3)_3$) 38.39 (C^a) 31.72 (C^d) 31.26 (N–$C(\mathit{C}H_3)_3$) 23.37 (C^e) 0 (B–CH_3)
4	4.97 (dd, 1 H, H^5, $^3J_{H^4H^5}$ = 1.6 Hz, $^4J_{H^3H^5}$ = 1.3 Hz) 3.99 (dd, 1 H, H^4, $^3H_{H^4H^5}$ = 1.6 Hz, $^3J_{H^3H^4}$ = 4.9 Hz) 2.77 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 4.9 Hz) 2.15 (s, 1 H, H^d) 2.00 (s, 1 H, H^a) 1.88 (s, 3 H, H^f) 1.74 (s, 3 H, H^e) 1.28 (s, 9 H, $C(CH_3)_3$) 0.92 (s, 3 H, B–CH_3) 0.04 (s, 1 H, $H^{d'}$) −0.50 (s, 1 H, $H^{a'}$)	18.5	94.43 (C^b) 94.33 (C^c) 86.73 (C^5) 82.94 (C^4) 74–76 (C^3) 55.61 (N–$\mathit{C}(CH_3)_3$) 39.62 (C^d) 36.54 (C^a) 31.59 (N–$C(\mathit{C}H_3)_3$) 20.76 (C^e, C^f) 0 (B–CH_3)
5	5.05 (s, 1 H, H^5) 4.2 (m, 2 H, H^d, $H^{d'}$) 4.0 (m, 2 H, H^b, H^e) 3.98 (s, 1 H, H^4) 2.71 (s, 1 H, H^3) 2.7 (m, 2 H, H^c, $H^{c'}$) 2.15 (s, 1 H, H^a) 2.03 (s, 1 H, H^f) 1.33 (s, 1 H, $H^{a'}$) 1.24 (s, 9 H, $C(CH_3)_3$) 1.23 (s, 1 H, $H^{f'}$) 0.35 (s, 3 H, B–CH_3)	18.6	89.40 (C^5) 86.97 (C^4) 80–83 (C^3) 66.96 (C^b, C^e) 55.88 (N–$\mathit{C}(CH_3)_3$) 47.46 (C^d) 42.73 (C^c) 34.40 (C^a) 33.30 (C^f) 31.70 (N–$C(\mathit{C}H_3)_3$) −1.4 (B–CH_3)
6a–6f	4.7 (s, br, 1 H, H^5) 4.5–5.5 (m, CH) 4.2 (s, br, 1 H, H^4) 3.5 (s, br, 1 H, H^3) 2.5–4.5 (m, CH_2, CH_3) 1.5–2.0 (m, CH_2, CH_3) 1.24 (s, 9 H, $C(CH_3)_3$) 1.23 (s, br CH_2) 0.15 (s, 3 H, B–CH_3)	17.6	80.13, 80.23, 80.87, 80.99, 81.26, 81.42, 84.37, 84.49, 84.74, 84.85, 85.02, 85.08 (C^4, C^5) 80–82 (C^3) 55.24, 55.35, 55.63, 55.70, 56.11, 56.21 (N–$\mathit{C}(CH_3)$ 51–55 (C^b, C^g) 32.2–38.9 (CH_2, CH) 31.51 (N–$C(\mathit{C}H_3)_3$)
7	5.05 (s, 1 H, H^5) 4.85 (s, 1 H, H^4) 4.47 (m, 2 H, H^c, H^d) 4.06 (s, 1 H, H^3) 1.52–1.95 (m, 4 H, H^a, $H^{a'}$, H^b, H^e) 1.19 (s, 9 H, $C(CH_3)_3$) 0.99 (s, 3 H, B–CH_3)	22.0	
8	4.88 (s, 1 H, H^5) 4.73 (m, 1 H, H^d) 4.52 (m, 1 H, H^e) 4.48 (s, 1 H, H^4) 3.57 (s, 1 H, H^3) 3.22 (m, 1 H, H^c) 3.16 (m, 1 H, H^f) 1.51 (m, 2 H, H^a, H^b) 1.14 (s, 9 H, $C(CH_3)_3$) 0.96 (m, 2 H, $H^{a'}$, $H^{b'}$) 0.88 (s, 3 H, B–CH_3)	18.2	85.59 (C^5) 81.24 (C^4) 79.72 (C^d) 78.33 (C^e) 72–74 (C^3) 55.20 (N–$\mathit{C}(CH_3)_3$) 53.71 (C^c) 52.79 (C^f) 30.91 (N–$C(\mathit{C}H_3)_3$) 25.05 (C^b) 24.72 (C^a) −1 (B–CH_3)
9	5.16 (dd, 1 H, H^4, $^3J_{H^4H^5}$ = 1.0 Hz, $^3J_{H^3H^4}$ = 4.3 Hz) 4.02 (dd, 1 H, H^5, $^3J_{H^4H^5}$ = 1.0 Hz, $^4J_{H^3H^5}$ = 1.0 Hz) 3.90 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 4.3 Hz) 3.23 (s, 2 H, H^c, H^f) 3.04 (s, 2 H, H^a, H^b) 3.01 (s, 2 H, H^d, H^e) 1.33 (s, 9 H, $C(CH_3)_3$) 1.02 (s, 2 H, H^g, $H^{g'}$) 0.38 (s, 3 H, B–CH_3)	16.1	86.62 (C^5) 82.52 (C^4) 72–74 (C^3) 56.56 (C^g) 55.53 (N–$\mathit{C}(CH_3)_3$) 45.44 (C^c, C^f) 33.14 (C^a, C^b) 31.86 (C^d, C^e) 31.86 (N–$C(\mathit{C}H_3)_3$) −2 (B–CH_3)
10a	5.66 (m, 1 H, H^f) 5.15 (m, 1 H, H^g) 4.83 (dd, 1 H, H^5, $^3J_{H^4H^5}$ = 1.7 Hz, $^4J_{H^3H^5}$ = 1.7 Hz) 4.71 (m, 1 H, H^e) 4.31 (dd, 1 H, H^4, $^3J_{H^4H^5}$ = 1.7 Hz, $^3J_{H^3H^4}$ = 5.5 Hz) 4.21 (m, 1 H, H^d) 3.61 (m, 1 H, H^b) 3.45 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 5.5 Hz) 3.21 (m, 1 H, H^e) 2.10 (m, 1 H, $H^{a'}$) 1.27 (m, 1 H, H^a) 1.16 (s, 9 H, $C(CH_3)_3$) 1.01 (s, 3 H, B–CH_3)	18.8	131.4 (C^f) 123.58 (C^g) 88.89 (C^d) 85.88 (C^4) 82.63 (C^5) 82.50 (C^c) 72–74 (C^3) 55.52 (N–$\mathit{C}(CH_3)_3$) 52.38 (C^b) 47.09 (C^f) 32.18 (C^a) 30.75 (N–$C(\mathit{C}H_3)_3$) 0 (B–CH_3)
10b	5.85 (m, 1 H, H^f) 5.15 (m, 1 H, H^g) 5.12 (dd, 1 H, H^5, $^3J_{H^4H^5}$ = 1.9 Hz, $^4J_{H^3H^5}$ = 1.9 Hz) 4.58 (m, 1 H, H^d) 4.47 (m, 1 H, H^e) 4.34 (dd, 1 H, H^4, $^3J_{H^4H^5}$ = 1.9 Hz, $^3J_{H^3H^4}$ = 5.7 Hz) 3.45 (m, 1 H, H^b) 3.40 (m, 1 H, H^e) 3.07 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 5.7 Hz) 2.00 (m, 1 H, $H^{a'}$) 1.22 (s, 9 H, $C(CH_3)_3$) 1.07 (m, 1 H, H^a) 0.98 (s, 3 H, B–CH_3)	18.8	131.5 (C^f) 123.21 (C^g) 88.25 (C^d) 86.32 (C^4) 85.88 (C^c) 83.62 (C^5) 70–72 (C^3) 55.73 (N–$\mathit{C}(CH_3)_3$) 50.05 (C^b) 48.98 (C^f) 32.62 (C^a) 30.04 (N–$C(\mathit{C}H_3)_3$) 0 (B–CH_3)
11 (20 °C)	5.27 (m, 4 H, H^c, H^d, H^g, H^h) 5.13 (d, 1 H, H^4, $^3J_{H^4H^5}$ = 1.1 Hz) 4.24 (d, 1 H, H^3, $^3J_{H^3H^4}$ = 5.2 Hz) 3.89 (dd, 1 H, H^5, $^3J_{H^4H^5}$ = 1.1 Hz, $^4J_{H^3H^5}$ = 1.2 Hz) 3.66 (s, 2 H, H^e, H^f) 3.63 (s, 2 H, H^a, H^b) 1.36 (s, 9 H, $C(CH_3)_3$) 0.19 (s, 3 H, B–CH_3)	18.3	135.93 (C^g, C^h) 135.79 (C^c, C^d) 90.98 (C^5) 86.75 (C^4) 84–86 (C^3) 72–74 (C^a, C^b, C^e, C^f) 56.77 (N–$\mathit{C}(CH_3)_3$) 31.52 (N–$C(\mathit{C}H_3)_3$) −2 (B–CH_3)
11 (−50 °C)			138.55 (C^g, C^h) 137.13 (C^c, C^d) 91.81 (C^5) 87.94 (C^4) 86.84 (C^3) 77.40 75.34 72.96 70.14 (C^a, C^b, C^e, C^f) 57.68 (N–$\mathit{C}(CH_3)_3$) 32.53 (N–$C(\mathit{C}H_3)_3$) −1 (B–CH_3)

1 react at −40 °C under photolytic conditions to give the orange-red azaborolyl(η^4-cycloheptatriene)cobalt complexes **10a** and **10b**, two diastereoisomers, which can be distinguished by ^{1}H and ^{13}C NMR spectroscopy. By means of a 2D ^{1}H NMR spectrum the eight multiplets caused by the eight different kinds of protons in the cycloheptatriene ligand for each of the diastereoisomers could be separated and analyzed. Two coupling systems, each consisting of

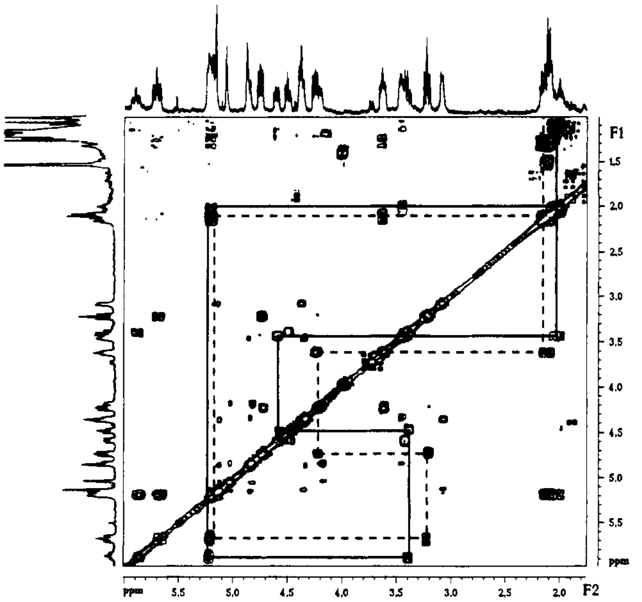

Figure 2. HH COSY of **10a**/**10b** showing the two independent coupling systems. The dotted line indicates the proton correlations of **10a**; the straight line indicates that of **10b**.

eight protons, are observed. To separate the superimposing signals (Figure 2), the F1 or the F2 axis of the 2D data set is scanned where coupling of the corresponding proton is observed. From this a one-dimensional data set is calculated. The FID resolution for the F1 axis in Figure 2 is 11.48 Hz; for the F2 axis it is 1.43 Hz. Together with a 2D Jresolv spectrum (F1 axis proton-coupled, F2 axis proton-decoupled proton signal) the coupling constants for the Ab systems have been determined.

Cyclooctatetraene (COT) acts as a diolefin in AbCo(COT) (**11**). The brown oil is formed in 71% yield from **1** and an excess of COT at −40 °C with irradiation. At 20 °C the four coordinated C atoms C^a, C^b, C^e, and C^f cause one very broad ^{13}C NMR signal (72–74 ppm), which indicates fluxional behavior of the COT ligand at this temperature. Temperature-dependent ^{13}C NMR studies show that at −30 °C the mobility of the COT molecule stops, observable by four separated signals for C^a, C^b, C^e, and C^f. The uncoordinated atoms C^c, C^d, C^g, and C^h seem not to be involved significantly in this thermal motion process, as at 20 °C as well as at −50 °C each of the atomic pairs C^c, C^d and C^g, C^h causes one sharp signal. However, at −50 °C these signals at 138.55 and 137.13 ppm are better separated than at 20 °C (135.93 and 135.79 ppm). This can easily be understood, as the coordinated atoms are highly influenced by the prochiral Ab ring system. We believe that the fluxionality of the COT ligand only consists of a pendulum motion, as previously observed in the similar system AbCo(1,5-COD).[4] However, a slow rotation cannot be excluded. Under these conditions the positions a and e, b and f, c and g, and d and h are interconverted. In the case of CpCo(COT) interconversion processes between 1,5- and 1,3-COT have been described in the literature.[8-10] In spite of the fact that the 1,3 isomer could not be observed by NMR spectroscopy at low temperature, its existence cannot be excluded completely since its concentration may be below the detection limit. Two relatively sharp ^{1}H NMR signals for H^a, H^b, and H^e, H^f, respectively, at 20 °C indicate that these hydrogen atoms are better differentiated compared with the corresponding C atoms and herewith support the presumption of a "wobbling" ligand.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. The solvents were deoxygenated and dried by standard methods. IR spectra were recorded on Perkin-Elmer spectrophotometers 597 and 283B. The mass spectra were measured on a Finnigan MAT CH5 (EI, 70 eV) at the Max-Planck-Institut für Kohlenforschung, Mülheim, Germany. NMR spectra (^{1}H, ^{13}C, ^{11}B), in C$_6$D$_6$ solution, were recorded on a Bruker AC 80, Bruker AM 300, or Varian Gemini 200 instrument. Chemical analyses were performed by the Mikroanalytisches Laboratorium des Fachbereichs Chemie der Universität Essen. For UV irradiations a 150-W quartz mercury high-pressure burner (NORMAG, TQ 150) has been used.

AbCo(CO)$_2$ (**1**) was prepared by literature methods from 1-*tert*-butyl-2,5-dihydro-2-methyl-1*H*-1,2-azaborole and Co$_2$(CO)$_8$.[5] All other reagents were commercial grade and were used as obtained.

Synthesis of the AbCo(η^4-diene) Complexes 2–11. A sample (1–2 mmol) of AbCo(CO)$_2$ (**1**) was dissolved in 250 mL of pentane, and the solution was cooled to −40 °C. The 2-fold amount of the stoichiometrically required quantity of the corresponding olefin was added, followed by 2–4 h of UV irradiation. The duration of irradiation depends on the olefin used and can be followed by the disappearance of the ν(CO) frequencies of **1** at 2020 and 1955 cm^{-1}. The orange-red solutions then were warmed to room temperature and concentrated to a volume of about 20 mL under reduced pressure. Column chromatography on silylated silica gel with pentane as an eluant gave the orange-red or red oils of **2**-**11**.

2: mass spectrum, *m/z* 249 [M]$^+$. Anal. Calcd for C$_{12}$H$_{21}$BCoN: C, 57.87; H, 8.05; N, 5.62. Found: C, 57.88; H, 8.37; N, 5.50.

3: mass spectrum, *m/z* 263 [M]$^+$. Anal. Calcd for C$_{13}$H$_{23}$BCoN: C, 59.35; H, 8.81; N, 5.32. Found: C, 59.84; H, 8.85; N, 5.05.

4: mass spectrum, *m/z* 277 [M]$^+$. Anal. Calcd for C$_{14}$H$_{25}$BCoN: C, 60.68; H, 9.09; N, 5.05. Found: C, 60.67; H, 9.74; N, 4.73.

5: mass spectrum, *m/z* 277 [M]$^+$. Anal. Calcd for C$_{14}$H$_{25}$BCoN: C, 60.68; H, 9.09; N, 5.05. Found: C, 60.74; H, 9.58; N, 4.61.

6: mass spectrum, *m/z* 305 [M]$^+$. Anal. Calcd for C$_{16}$H$_{29}$BCoN: C, 62.93; H, 9.58; N, 4.59. Found: C, 62.12; H, 10.33; N, 4.57. The unsatisfactory agreement of the C and H values is due to the extreme sensitivity of the compound.

7: The complex was identified by comparison of its NMR data with literature values.[6]

8: mass spectrum, *m/z* 275 [M]$^+$. Anal. Calcd for C$_{14}$H$_{23}$BCoN: C, 61.12; H, 8.42; N, 5.09. Found: C, 61.45; H, 8.41; N, 5.28.

9: mass spectrum, *m/z* 287 [M]$^+$. Anal. Calcd for C$_{15}$H$_{23}$BCoN: C, 62.75; H, 8.07; N, 4.87. Found: C, 63.18; H, 7.51; N, 4.95.

10: mass spectrum, *m/z* 287 [M]$^+$. Anal. Calcd for C$_{15}$H$_{23}$BCoN: C, 62.75; H, 8.07; N, 4.87. Found: C, 62.46; H, 8.68; N, 5.36.

11: mass spectrum, *m/z* 299 [M]$^+$. Anal. Calcd for C$_{16}$H$_{24}$BCoN: C, 64.25; H, 7.75; N, 4.68. Found: C, 64.61; H, 7.94; N, 4.52.

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Registry No. **1**, 131283-20-0; **2**, 139732-91-5; **3a**, 139894-19-2; **3b**, 139732-99-3; **4**, 139732-92-6; **5**, 139732-93-7; **7**, 139732-94-8; **8**, 139732-95-9; **9**, 139732-96-0; **10a**, 139732-97-1; **10b**, 140148-32-9; **11**, 139732-98-2; 1,3-butadiene, 106-99-0; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,5-hexadiene, 592-42-7; 1,7-octadiene, 3710-30-3; cyclopentadiene, 542-92-7; 1,4-cyclohexadiene, 592-57-4; norbornadiene, 121-46-0; 1,3,5-cycloheptatriene, 544-25-2; 1,3,5,7-cyclooctatetraene, 629-20-9.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra and HH COSY spectra of compounds **2**, **4**, **6**, and **8** (12 pages). Ordering information is given on any current masthead page.

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