ORGANOMETALLICS

Volume 6, Number 3, March 1987

Dihydroazaborolyl Complexes. 21. Syntheses and Investigations of Bis(1-*tert*-butyldihydro-2-methyl-1*H*-azaborolyl)beryllium and (1-*tert*-Butyldihydro-2-methyl-1*H*-azaborolyl)cyclopentadienylberyllium: A Contribution to the Beryllocene Problem

Günter Schmid,* Ottmar Boltsch, and Roland Boese

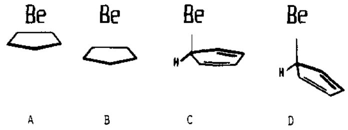
Institut für Anorganische Chemie der Universität Essen, D-4300 Essen 1, Federal Republic of Germany

Received June 16, 1986

(1-*tert*-Butyldihydro-2-methyl-1*H*-azaborolyl)lithium (AbLi) and $BeCl_2$ react to give the beryllocene analogue Ab_2Be. This complex has been characterized by a single-crystal X-ray diffraction study at −150 °C. It crystallizes in the space group $P2_1/c$ with a = 8.606 (8) Å, b = 10.121 (9) Å, c = 20.582 (20) Å, $\alpha = \gamma = 90°$, β = 92.78 (7)°, V = 1163 $Å^3$, and Z = 4; μ(Mo Kα, graphite monochromator) = 1.0 cm^{-1}. The structure refined to R = 0.077 and R_w = 0.078. The molecule shows one η^1- and one η^5-coordinated Ab ring and so far agrees with the low-temperature structure of Cp_2Be, but without a disorder of the Be atom. In solution Ab_2Be gives only NMR signals for η^5-coordinated rings. The prochirality of Ab causes two diastereoisomers of Ab_2Be with equivalent or different ring sites coordinated to beryllium. The isomers can be distinguished by ^1H NMR spectroscopy. On dissolving one isomer in benzene, the other one is formed again within a few days. This suggests a dissociation of one ring enabling the flip. More details on the structural and fluxional behavior of Be sandwiches can be learned from the mixed-complex AbCpBe that is easily prepared from Ab_2Be and Cp_2Be. AbCpBe is, in contrast to Ab_2Be and Cp_2Be, stable in THF solution. The solution shows a remarkable conductivity in accord with the ring flip, observed in Ab_2Be solution. As can be seen from NMR measurements, the η^5-coordinated Cp ring dissociates, whereas the η^1-bonded Ab ring remains bonded to Be. Temperature-dependent ^1H NMR studies show that with increasing temperatures the Ab ring becomes more and more η^5-coordinated; i.e., the fluxionality becomes similar to that in Ab_2Be at room temperature.

Introduction

Since the discovery of beryllocene by Fischer and Hofmann in 1959[1] the controversy concerning its structural behavior could not be resolved till today. The unusual dipole moment of 2.24 D in cyclohexane and 2.46 D in benzene suggested a structure different from the usual symmetrical sandwich type A.



Electron diffraction data from gaseous beryllocene is compatible with both structure B and with a slipped arrangement of the rings.[2] IR spectroscopic investigations of beryllocene in solution supported an η^5/η^1-coordination as found in C.[3]

Other authors again concluded structure B from ^1H NMR and IR data.[4] A first X-ray structure of beryllocene at −120 °C supported the η^5/η^1-type C with coplanar rings but showed disordered Be atoms.[5] A reinvestigation at room temperature suggested that Be is π-bonded to one ring and electrostatically bonded to the second ring.[6] As

---

(1) Fischer, E. O.; Hofmann, H. P. *Chem. Ber.* **1959**, *92*, 482.

(2) Drew, D. A.; Haaland, A. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 3671. Almenningen, A.; Bastiansen, O.; Haaland, A. *J. Chem. Phys.* **1964**, *49*, 3434. Haaland, A. *Acta Chem. Scand.* **1968**, *22*, 3030.

(3) Pratten, S. J.; Cooper, M. K.; Aroney, M. J. *Polyhedron* **1984**, *3*, 1347.

(4) McVicker, G. B.; Morgan, H. L. *Spectrochim. Acta, Part A* **1970**, *A26*, 23. Morgan, G. L.; McVicker, G. B. *J. Am. Chem. Soc.* **1968**, *90*, 2789.

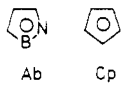
(5) Wong, C. H.; Lee, T. Y.; Chao, F. J.; Lee, S. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*. 1662.

(6) Wong, C. H.; Lee, T. Y.; Wang, T. W.; Liu, C. S. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 667.

0276-7333/87/2306-0435$01.50/0

the ^1H NMR spectra between −135 and +50 °C showed only one sharp singlet, it has been assumed that the cyclopentadienyl rings rotate relative to each other and that the Be oscillates between the alternate positions. The last X-ray structure determination was carried out at −150 °C and again confirmed the η^5/η^1-structure type C with disordered Be atoms.[7] Numerous semiempirical and ab inito calculations on beryllocene gave results varying between the ferrocene-like structure A and type D with an angled η^1-bonded ring.[8] The most recent contribution to the beryllocene problem dates from 1986 and describes a microwave dielectric loss study favoring the η^5/η^1-configuration with nonparallel rings of type D and oscillating Be atoms.[9]

Dihydro-1*H*-azaborolyl rings (Ab) are isostructural and isoelectronic with the cyclopentadienyl system and act as



ligands in numerous sandwich and half-sandwich compounds.[10] Concerning the coordination chemistry of the Ab rings, there are two very important distinctive points to note: due to the different electronegativities of B and N, the metal atom can interact in a variable manner with the Ab ligands. Electron-poor metals try to get closer contact to the nitrogen and electron-rich metal atoms prefer stronger bonds to the boron, whereas, e.g., Fe prefers equivalent interactions to all five ring atoms to achieve the noble-gas configuration. Secondly, the prochirality of the Ab ligand leads to diastereomerism for sandwich complexes Ab_2M and to enantiomerism only for half sandwich compounds $AbML_n$. These two features cause a structural variety that is, compared with cyclopentadienyl complexes, much more instructive for studies of structural and electronic problems found for compounds such as beryllocene than the cyclopentadienyl system can do.

Experimental Section

All reactions were performed in an atmosphere of pure nitrogen and in freshly distilled and absolutely dry solvents. ^1H, ^{11}B, and ^{13}C NMR spectra were obtained with a Varian XL 200 instrument. Mass spectra were carried out with a Varian MAT 312 spectrometer. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Institut für Anorganische Chemie, Universität Essen.

X-ray Crystallography Procedures. Crystals of Ab_2Be have monoclinic symmetry, space group $P2_1/c$. The crystal selected at −20 °C was irregularly shaped (approximately 0.25 × 0.16 × 0.15 mm^3) with some satellites that could not be removed. On warming the crystals above −20 °C, they become soft and do not give any diffraction pattern, so without interrupting the cooling, the crystal was mounted on a Nicolet R3 four-circle diffractometer and cooled to −150 °C. No phase transition could be detected by comparing the preliminary cell dimensions at −20 °C and later on at −150 °C. These were refined from the setting angles of 25 reflections ($20° \geq 2\theta \leq 25°$): a = 8.606 (8) Å, = b = 10.121 (9) Å, c = 20.582 (20) Å, $\alpha = \gamma = 90°$, β = 92.78 (7)°, V = 1163 $Å^3$, Z = 4, D_{calcd} = 1.61 g/cm^{-3}, μ(Mo Kα, graphite monochromator) = 1.0 cm^{-1}. With a total of 4121 unique reflections, recorded by ω scan techniques with $2\theta_{max}$ = 55°, data reduction was performed. No absorption correction was applied. The structure was solved by direct methods. Successive difference Fourier maps and least-squares refinement cycles processes revealed the positions of all non-hydrogen atoms.

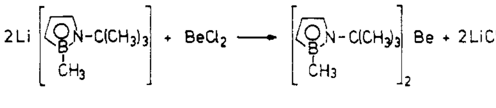
All non-hydrogen atoms were refined anisotropically; methyl hydrogen atoms were included as rigid groups (C–H = 0.96 Å; H–C–H = 109°) and given the 1.2-fold isotropic temperature factor of the corresponding C atom. The ring hydrogen atoms were located on a difference Fourier map and refined with no constraints on the positional parameters with an unique isotropic temperature factor of U = 0.027 (3) $Å^2$. The atomic scattering factors were those incorporated in SHELXTL;[11] scattering factors for beryllium were taken from Cromer and Mann.[12] The final block-cascade least-squares refinement converged to $R = \sum||F_o - F_c||/\sum|F_o| = 0.077$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o{}^2]^{1/2} = 0.078$, $w^{-1} = (\sigma(F_o)^2 + 5 \times 10^{-4}F_o{}^2)$ with 3000 unique observed reflections ($F_o \geq 4.5\sigma(F_o)$) and 233 parameters. The maximum height of the final difference Fourier was 0.54 e/$Å^3$ between B(2/1) and C(6/1). No significant residual electron density could be detected between C(3/2) and the center of the σ-bonded ring, indicating no disorder of the beryllium atom.

Preparation of Ab_2Be. A mixture of AbLi[13] (5.00 g, 34.97 mmol) and 1.40 g $BeCl_2$ (1.40 g, 17.48 mmol) was treated slowly with 200 mL of diethyl ether of −100 °C. After being warmed to room temperature, the reaction mixture was heated at reflux for 24 h after which the white precipitate was filtered. The filtrate was evaporated and the residue extracted with petroleum ether (~50 mL). The solution then was evaporated to half the volume and again filtered. Evaporation to dryness yielded 4.86 g of oily Ab_2Be (99%). Crystals of the BN/NB isomer were obtained by cooling a diethyl ether solution to −30 °C. The BN/BN isomer remained dissolved. BN/BN: ^1H NMR ($CDCl_3$) δ 0.60 (s, 6 H, BCH_3), 1.46 (s, 18 H, $NC(CH_3)_3$), 3.20 (dd, J(H3H5) = 4.2 Hz, J(H3H4) = 1.3 Hz, 2 H, H3), 5.78 (dd, J(H5H4) = J(H5H3) = 3.7 Hz, 2 H, H4), 6.47 (dd, J(H4H5) = 3.3 Hz, J(H4H3) = 1.6 Hz, 2 H, H5); ^{11}B NMR ($CDCl_3$) δ 34.2; ^{13}C NMR (C_6D_6) δ 31.5 ($C(CH_3)_3$), 55.1 ($C(CH_3)_3$), 61.9 (C3), 112.2 (C4), 116.7 (C5). BN/NB: ^1H NMR ($CDCl_3$) δ 0.68 (s, 6 H, BCH_3), 1.47 (s, 18 H, $NC(CH_3)_3$), 3.16 (dd, J(H3H5) = 4.1 Hz, J(H3H4) = 1.4 Hz, 2 H, H3), 5.65 (dd, J(H5H4) = J(H5H3) = 3.8 Hz, 2 H, H5), 6.40 (dd, J(H4H5) = 3.3 Hz, J(H4H3) = 1.6 Hz, 2 H, H4); ^{11}B NMR ($CDCl_3$) δ 34.2; ^{13}C NMR (C_6D_6) δ 31.5 ($C(CH_3)_3$), 55.2 ($C(CH_3)_3$), 61.9 (C3), 111.5 (C4), 116.6 (C5). Anal. Calcd for $C_{16}H_{30}B_2BeN_2$: C, 68.39; H, 10.76; N, 9.97. Found: C, 68.29; H, 10.62; N, 10.08.

Preparation of AbCpBe. Cp_2Be[1] (139 mg, 1.0 mmol) and Ab_2Be (281 mg, 1.0 mmol) were stirred for 30 min in 50 mL of diethyl ether at room temperature. CpAbBe was isolated quantitatively as a yellow oil by evaporation of the solvent: ^1H NMR ($CDCl_3$) δ 0.52 (s, 3 H, BCH_3), 1.41 (s, 9 H, $NC(CH_3)_3$), 2.04 (s, 1 H, H3), 5.37 (dd, J(H5H4) = J(H5H3) = 3.4 Hz, 1 H, H4), 6.01 (s, 5 H, C_5H_5), 6.40 (d, J(H4H5) = 3.5 Hz, 1 H, H5); ^{11}B NMR ($CDCl_3$) δ 40.5; ^{13}C NMR (C_6D_6) δ 2.8 (BCH_3), 32.1 ($C(CH_3)_3$, 37.2 (C3), 53.3 ($C(CH_3)_3$), 103.6 (C_5H_5), 115.3 (C4), 128.3 (C5); mass spectrum, m/e 210 (M^+). Anal. Calcd for $C_{13}H_{20}BBeN$: C, 74.31; H, 9.59; N, 6.67. Found: C, 72.36; H, 8.04; N, 6.88.

Results and Discussion

Syntheses. Bis(1-*tert*-butyldihydro-2-methyl-1*H*-azaborolyl)beryllium (Ab_2Be) is obtained quantitatively when LiAb is reacted with $BeCl_2$ in refluxing diethyl ether for about 24 h (eq 1).



(1)

---

(7) Nugent, K. W.; Beattie, J. K.; Hambley, T. W.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1601.

(8) Marynick, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 1436. Gleiter, R.; Böhm, M. C.; Haaland, A.; Johansen, R. *J. Organomet. Chem.* **1979**, *170*, 285. Demuynck, J.; Rohmer, M. M. *Chem. Phys. Lett.* **1978**, *54*, 567. Jemmis, E. D.; Alexandratos, S.; Schleyer, P. v. R.; Streitwieser, A., Jr.; Schaeffer H.-F., III *J. Am. Chem. Soc.* **1978**, *100*, 5695. Chiu, N. S.; Schäfer, L. *J. Am. Chem. Soc.* **1978**, *100*, 2604. Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 777.

(9) Pratten, S. J.; Cooper, M. C.; Aroney, M. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1761.

(10) Schmid, G. *Comments Inorg. Chem.* **1985**, *4*, 17.

(11) Sheldrick, G. M. *SHELXTL*, a complete program system to solve, refine and to plot crystal structures from diffraction data; Universität Göttingen, 1981.

(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(13) Schmid, G.; Amirkhalili, S.; Höhner, U.; Kampmann, D.; Boese, R. *Chem. Ber.* **1982**, *115*, 3830.

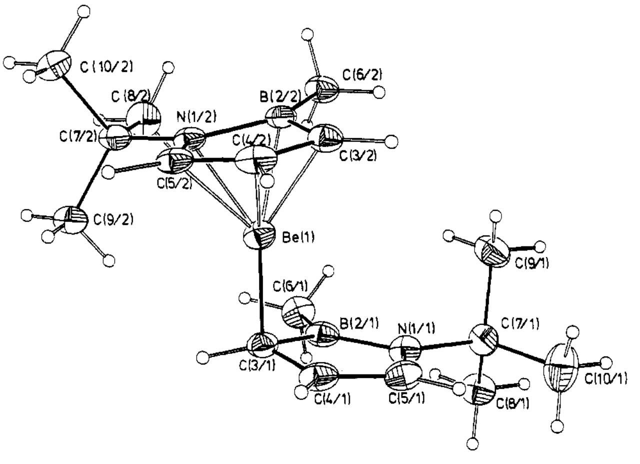


Figure 1. Molecular structure of Ab_2Be. The vibrational ellipsoids have been drawn at the 50% probability level. The size of the hydrogen atoms is arbitrary.

Due to the prochiral character of the Ab ligand, two diastereoisomers are formed: if the two rings in one molecule use the same site for the coordination, the atomic sequence is BN/NB; different sites cause the BN/BN isomer. Both isomers can be distinguished by their ^1H NMR data, as the ring protons give different signals. The separation of Ab_2M isomers sometimes succeeds by fractionating crystallization. In the case of Ab_2Be, the BN/NB isomer crystallizes at −30 °C from diethyl ether, whereas the BN/BN isomer remains in solution and is oily when the solvent is evaporated.

The mixed-sandwich complex AbCpBe is easily formed in Cp_2Be and Ab_2Be are dissolved in a 1:1 ratio in diethyl ether at room temperature. The yellow oil could not be crystallized. Nevertheless, structural details can be cleared up by NMR investigations.

X-ray Structure of Ab_2Be (BN/NB) Isomer. The X-ray structure analysis was carried out at −150 °C. As can been seen from Figure 1, the Be atom is η^5-coordinated by one Ab ring and η^1-bonded to the second ligand. So far, the structure corresponds to that found for Cp_2Be in the solid state, but without any disorder of the Be atom. As the three ring C atoms are inequivalent, it may be of interest which of them binds to the metal. It is the B-neighboring carbon atom. This atom is the most reactive too if LiAb reacts with different kinds of non-metal and metal halides such as $(CH_3)_3ECl$ (E = C, Si, Ge, Sn, Pb).[14] A comparision of the bond distances in both rings shows that the η^1-coordinated ring behaves like a diene, as the C3–B and C3–C4 distances are longer than in the η^5-ring but C4–C5 and B–N are significantly shorter. In contrast to Cp_2Be, but in agreement with theoretical calculations on beryllocene, the Ab rings are not coplanar. The interplanar angle is 14.5°. There is no disorder to be expected for Ab_2Be because of the noncoplanarity of the Ab rings. The distance of Be to the η^5-ring center is 1.47 Å and somewhat shorter than in Cp_2Be (1.505 Å). Also the Be–C(3/1) distance (1.755 Å) is significantly shortened compared with Cp_2Be (1.826 Å) and agrees better with the gas-phase value of 1.706 Å.[2] The bond angles at the C(3/1) atom (96.4° for Be–C(3/1)–C(4/1), 97.3° for Be–C(3/1)–B(2/1), and 102.4° for Be–C(3/1–H(3/1)) characterize it as not fully sp^3-hydridized. The investigated BN/NB diastereoisomer should exist in enantiomeric forms (*R,R* and *S,S*). The crystal structure indeed shows the two forms alternating in the unit cell (Figure 2).

Table I. Atomic Coordinates ($\times 10^4$) for Ab_2Be

atom	x	y	z
Be(1)	9462 (4)	3300 (3)	3427 (2)
N(1/1)	7576 (2)	659 (2)	3257 (1)
B(2/1)	9244 (4)	884 (3)	3278 (1)
C(3/1)	9481 (3)	2068 (2)	2828 (1)
C(4/1)	7911 (3)	2341 (2)	2537 (1)
C(5/1)	6852 (3)	1548 (2)	2811 (1)
C(6/1)	10553 (3)	93 (3)	3680 (1)
C(7/1)	6640 (3)	−257 (2)	3652 (1)
C(8/1)	7221 (4)	−1666 (2)	3562 (1)
C(9/1)	6838 (4)	146 (3)	4367 (1)
C(10/1)	4909 (4)	−215 (3)	3452 (2)
N(1/2)	10975 (2)	4209 (2)	3978 (1)
B(2/2)	9734 (3)	3673 (3)	4397 (1)
C(3/2)	8258 (3)	4129 (2)	4041 (1)
C(4/2)	8682 (3)	5013 (2)	3525 (1)
C(5/2)	10275 (3)	5033 (2)	3488 (1)
C(6/2)	9897 (3)	2755 (3)	5013 (1)
C(7/2)	12725 (3)	4124 (2)	4013 (1)
C(8/2)	13278 (3)	3165 (3)	4544 (1)
C(9/2)	13321 (3)	3663 (3)	3363 (1)
C(10/2)	13384 (3)	5496 (3)	4180 (1)

Table II. Selected Bond Lengths (Å) and Angles (deg) for Ab_2Be

	Bond Lengths		
Be(1)–C(3/1)	1.755 (4)	C(7/1)–C(8/1)	1.527 (3)
Be(1)–N(1/2)	1.918 (4)	C(7/1)–C(9/1)	1.527 (4)
Be(1)–C(2/2)	2.032 (4)	C(7/1)–C(10/1)	1.526 (4)
Be(1)–C(3/2)	1.873 (4)	N(1/2)–B(2/2)	1.507 (3)
Be(1)–C(4/2)	1.876 (4)	B(2/2)–C(3/2)	1.507 (4)
Be(1)–C(5/2)	1.892 (4)	C(3/2)–C(4/2)	1.449 (3)
N(1/1)–B(2/1)	1.452 (4)	C(4/2)–C(5/2)	1.377 (4)
B(2/1)–C(3/1)	1.534 (4)	N(1/2)–C(5/2)	1.419 (3)
C(3/1)–C(4/1)	1.476 (4)	B(2/2)–C(6/2)	1.573 (4)
C(4/1)–C(5/1)	1.359 (4)	N(1/2)–C(3/2)	1.507 (3)
N(1/1)–C(5/1)	1.408 (3)	C(7/2)–C(8/2)	1.520 (4)
N(1/1)–C(7/1)	1.495 (3)	C(7/2)–C(9/2)	1.529 (4)
B(1/2)–C(6/1)	1.582 (4)	C(7/2)–C(10/2)	1.534 (4)
	Bond Angles		
Be(1)–C(3/1)–H(3/1)	102.4 (16)	C(5/1)–C(4/1)–C(3/1)	109.9 (2)
Be(1)–C(3/1)–C(4/1)	96.4 (2)	C(4/1)–C(3/1)–B(2/1)	104.1 (2)
Be(1)–C(3/1)–B(2/1)	97.3 (2)	C(3/1)–B(2/1)–N(1/1)	105.5 (2)
H(3/1)–C(3/1)–B(2/1)	121.5 (16)	B(2/2)–N(1/2)–C(5/2)	109.3 (2)
H(3/1)–C(3/1)–C(4/1)	127.1 (16)	N(1/2)–C(5/2)–C(4/2)	109.2 (2)
C(4/1)–C(3/1)–B(2/1)	104.1 (2)	C(5/2)–C(4/2)–C(3/2)	109.7 (2)
B(2/1)–N(1/1)–C(5/1)	108.8 (2)	C(4/2)–C(3/2)–B(2/2)	107.9 (2)
N(1/1)–C(5/1)–C(4/1)	111.4 (2)	C(3/2)–B(2/2)–N(1/2)	102.5 (2)

Interplanar Angle Ring(1)–Ring(2) = 14.5

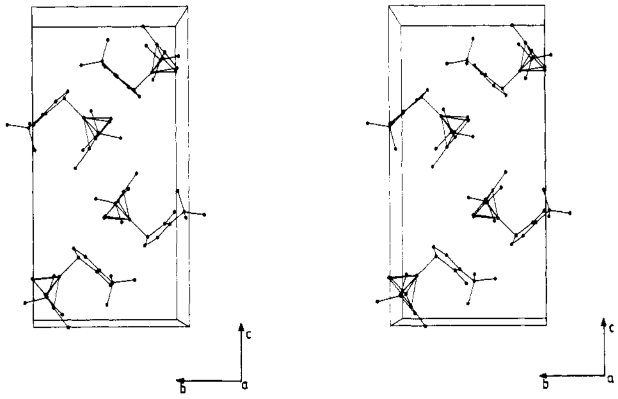


Figure 2. Stereoview of the crystal structure of Ab_2Be.

NMR Investigations. The ^1H NMR spectrum of Ab_2Be as a mixture of BN/BN and BN/NB isomer in $CDCl_3$ or toluene-d_8 at room temperature shows the signals of both compounds simultaneously. The ring protons cause double doublets, each due to the coupling with the other two protons. As the BN/NB isomer could be iso-

---

[14] Schmid, G.; Zaika-Meyer, D., unpublished results.

lated in a crystalline form, the signals can be assigned to each isomer. The protons of the *tert*-butyl and the BCH_3 groups also appear twice. The range of the chemical shifts for H3, H4, and H5 is typical for Ab_2M sandwich complexes. The room-temperature spectrum of Ab_2Be gives no indication of a σ-bonded C3 atom. ^1H NMR experiments between +20 and −55 °C in $CDCl_3$ and −70 °C in toluene-d_8 showed no change in the spectra.

Solutions of the structurally characterized BN/NB isomer in C_6D_6 or in toluene-d_8 show, as expected, only three signals for the ring protons in the ^1H NMR spectrum at room temperature. But after 5 days, the original 1:1 mixture of BN/NB and BN/BN isomer is formed back, producing 2 × 3 signals. This is a very important observation, as in the Cp_2Be case this effect cannot be observed. The flip of one Ab ring should only be possible if at least a small amount of the molecule is dissociated:

$$Ab_2Be \rightleftharpoons AbBe^+ + Ab^-$$

In benzene, toluene, chloroform, petroleum ether, and diethyl ether no remarkable conductivity is found. More basic solvents like THF decompose the complex. So, the ionic part may be very small but large enough to form back the second isomer over a period of 5 days.

More detailed studies can be performed with the mixed complex AbCpBe, as it is much more stable in THF. A 0.004 M solution of AbCpBe in THF shows a conductivity of 0.077×10^{-6} S. This is more than found for LiBr. A 0.004 M solution of LiBr shows no measurable conductivity and a 0.04 M solution only a conductivity of 0.114×10^{-6} S. A flip of Ab and/or Cp in AbCpBe solutions, of course, is not observable by ^1H NMR, as only enantiomers are present.

The ^1H NMR spectrum of AbCpBe at room temperature in $CDCl_3$ shows, as expected, a double doublet for H4 at 5.37 ppm, but only a doublet for H5 at 6.40 ppm and a singlet for H3 at 2.04 ppm. The Cp signal appears as a singlet at 6.01 ppm. The H3 singlet at 2.04 ppm leaves no doubt that C3 is σ-bonded to beryllium, whereas the Cp ring is η^5-coordinated. In contrast to Cp_2Be and Ab_2Be, the presence of Ab and Cp rings in the molecule enables the metal atom to differentiate. The Ab ring is elected for η^1-binding and the Cp ring for η^5-binding.

Temperature-dependent ^1H NMR studies give very interesting information on the fluxional properties of AbCpBe. Figure 3 shows five spectra in the range from −50 to +90 °C in toluene-d_8 between 7 and 2 ppm.

At −50 °C the spectrum corresponds to that found in $CDCl_3$ at room temperature. The signal at 5.67 ppm for H4 consists of a double doublet (pseudotriplet), due to coupling with H3 and H5, with identical coupling constants. At −20 °C broad resonances at 6.5 and 3.8 ppm begin to get visible, whereas the H4 signal has shifted from 5.67 to 5.59 ppm. This tendency has increased at +20 °C, the H4 signal now appears at higher field (5.49 ppm) than the Cp signal (5.61 ppm). At +90 °C the intensities of the new and the old signals are equal. The new signals, especially that at 3.8 ppm clearly shows the presence of η^5-coordinated Ab rings, whereas the intensity of the signals for the original η^1-rings decreases.

The stability of AbCpBe in THF allows NMR investigations in this solvent that possibly help to understand the observed flip in the Ab_2Be case. The spectrum at room temperature shows signals for the ring protons that agree with those in other solvents; i.e., the Ab ring is essentially η^1-coordinated. However, the Cp signal is shifted from 5.61 ppm in toluene-d_8 to 6.00 ppm, suggesting an uncoordinated Cp ring: THF molecules coordinate instead to the metal. So, the observed conductivity in THF is to be explained by a dissociation of the Cp ring only, the Ab ring remaining σ-bonded! Cooling down to −50 °C the THF solution contains a new species. At 6.36, 5.40, and 1.93 ppm new signals for H5, H4, and H3 are observed, however, the Cp signal is shifted to high field (5.44 ppm); e.g., at −50 °C the Cp ring is coordinated to the beryllium with substitution of the THF molecules. These results are formulated in Scheme I.

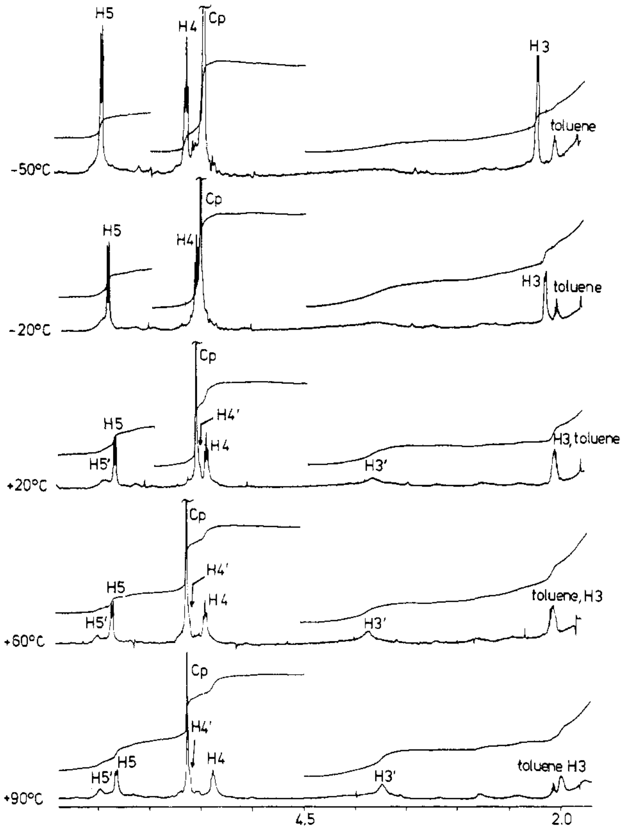
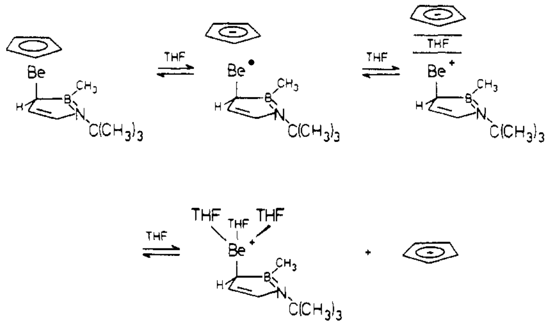


Figure 3. ^1H NMR spectra of AbCpBe in the temperature range of −50 to +90 °C. H3, H4, and H5 are caused by the η^1-coordinated Ab ring; H3′, H4′, and H5′ are due to the η^5-bonded ligand.

Scheme I



The ^{11}B NMR spectra of Ab_2Be and AbCpBe are in agreement with the ^1H NMR results. Ab_2Be gives a signal at 34.2 ppm in $CDCl_3$ and 32.4 ppm in toluene-d_8. As $(\eta^5\text{-}Ab)_2M$ complexes cause signals in the range of 12–15 ppm,[13] $(\eta^3\text{-}Ab)_2Ni$[15] causes a signal at 27 ppm, and C3-substituted Ab rings cause signals at 44–50 ppm,[14] the chemical shift for Ab_2Be indicates a state between σ- and π-bonding. AbCpBe shows its ^{11}B NMR signal a 40.5 ppm in different solvents as toluene-d_8 or $CDCl_3$; i.e., the Ab ring is σ-bonded independently on dissociation of the Cp ligand.

---

(15) Schmid, G.; Kampmann, D.; Höhner, U.; Boese, R. *Chem. Ber.* 1984, *117*, 1052.

Conclusions

Ab_2Be and AbCpBe help to solve some of the remaining problems in the structural and electronic behavior of beryllocene. The fact that Ab_2Be forms diastereoisomers enables the observation of ring flips in solution. The more stable AbCpBe shows a remarkable conductivity in THF, supporting the suggested dissociation. This is a condition for the observed flip. NMR studies of the mixed complex additionally show that the Cp ring dissociates whereas the Ab ligand remains η^1-coordinated.

It seems reasonable to apply this knowledge to beryllocene. Consequently, Cp_2Be in solution should exist in an equilibrium with $CpBe^+$ and Cp^-. The rate of dissociation depends on the solvent. The fact that in AbCpBe the η^5-bonded Cp ring dissociates whereas the Ab ring remains η^1-bonded shows that the η^1-coordination is stronger than the η^5-coordination. It agrees with the ^1H NMR results that only at about +90 °C half of the molecules show η^5-coordinated Ab rings. The result that the ^1H NMR spectra of AbCpBe at higher temperatures show separated η^5- and η^1-coordinated Ab rings proves a temperature-dependent equilibrium of two species. So, an oscillation of beryllium is to be excluded. Concerning Ab_2Be and Cp_2Be it can be concluded that also in these compounds two η^5-coordinated rings exist instead of an oscillation of Be between η^5- and η^1-coordinated rings.

Registry No. Ab_2Be (BN/NB), 106420-41-1; Ab_2Be (BN/BN), 106420-42-2; AbCpBe, 106420-43-3; AbLi, 84356-32-1; Cp_2Be, 12083-43-1.

Supplementary Material Available: Tables of atom coordinates, hydrogen atom coordinates, anisotropic temperature factors, bond lengths, and bond angles (5 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

$Ph_2AsCH_2CH_2PPh_2$ (arphos) and $Ph_2PCH_2CH_2PPh_2$ (diphos) Complexes of $Co_2(CO)_6MCCO_2$-*i*-Pr [M = $Co(CO)_3$, $(C_5Me_5)Mo(CO)_2$]: X-ray Crystal Structure and NMR Fluxionality

Karen A. Sutin,[†] Joseph W. Kolis,[†] Michael Mlekuz,[†] Peter Bougeard,[†] Brian G. Sayer,[†]
Michael A. Quilliam,[†] Romolo Faggiani,[‡] Colin J. L. Lock,[‡] Michael J. McGlinchey,*[†] and
Gérard Jaouen*[§]

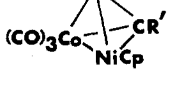
Department of Chemistry and Institute for Materials Research, McMaster University,
Hamilton, Ontario, L8S 4M1, Canada, and Ecole Nationale Supérieure de Chimie, 75231 Paris Cedex, France

Received November 18, 1985

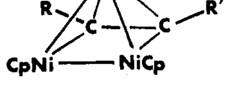
The tetrahedral clusters $Co_2(CO)_6MCR$, where R = CO_2CHMe_2 and M = $Co(CO)_3$ or $(C_5Me_5)Mo(CO)_2$, react with $Ph_2PCH_2CH_2PPh_2$ (diphos) and $Ph_2AsCH_2CH_2PPh_2$ (arphos). The molecule $Co_3(CO)_7$(arphos)CR crystallizes in space group *Pbca* with $a = 17.845$ (4) Å, $b = 19.630$ (4) Å, $c = 22.426$ (3) Å, and $Z = 8$. The structure has been solved by direct and Fourier methods and refined by full-matrix least squares to R_1 and R_2 values of 0.075 and 0.092, respectively, for 2317 observed reflections. The structure reveals that the arphos ligand spans equatorial positions on adjacent cobalts, thus forming a six-membered ring in a half-chair conformation. ^1H and ^{13}C NMR studies show that, in the Co_3(arphos) complex, the molecule loses its stereochemical integrity via migration of the arsenic terminus between cobalt atoms. In contrast, the Co_3(diphos) system and both of the Co_2Mo complexes retain their configurations. However, the $(C_5Me_5)Mo(CO)_2$ vertex can rotate with respect to the cluster, and two orientations are detectable at low temperature. Concomitantly, carbonyl migrations occur and the various mechanistic possibilities are discussed.

Introduction

With the ultimate goal of using organo-transition-metal clusters in asymmetric catalysis,[1] attention has been focused on synthetic routes to chiral clusters.[2] Among the plethora of systems now available are those in which each vertex of the polyhedron bears a different transition metal or main group element. Nevertheless, molecules such as 1 and 2, which fulfill the classic criteria for chirality, exhibit fluxional behavior and so racemize even on the NMR time scale.



1



2

[†] Department of Chemistry, McMaster University.

[‡] Institute for Materials Research, McMaster University.

[§] Ecole Nationale Supérieure de Chimie.

(1) Bosnich, B. *Chem. Brit.* 1984, *20*, 808. (b) Pittman, C. U., Jr.; Richmond, M. G.; Absi-Halabi, M.; Beurich, H.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 786.

0276-7333/87/2306-0439$01.50/0