The remarkable finding of kinetic and thermodynamic structures for the copolymers between olefins and carbon monoxide[12,13] will surely awake new interest and stimulate research in the apparently neglected subject[17,18] of cationic carbene complexes of platinum and palladium.

Acknowledgment. We are very grateful to F. Hoffman-La Roche AG (Dr. E. Broger) for a generous gift of (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine).

Registry No. Pd($CH_3COO)_2$, 3375-31-3; $NiClO_4$, 13637-71-3; CO, 630-08-0; propylene, 115-07-1; (carbon monoxide)(propylene) (copolymer), 29612-55-3; (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine), 123790-92-1.

OM920023P

Bis(fluorenyl)barium–Tetrakis(ammonia), The First Structurally Characterized Alkaline-Earth-Metal Fluorenyl Complex. Are BaX_2 Structures Inherently Bent?

Gabriele Mösges,[†] Frank Hampel, and Paul von Ragué Schleyer*

Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, West Germany

Received December 26, 1991

Summary: Reaction of 2 equiv of fluorene with barium in liquid ammonia provides the orange air- and moisture-sensitive $(C_{13}H_9)_2Ba(NH_3)_4$ (**1**) in 87% yield. The X-ray structure of crystalline **1** reveals two different monomeric conformers exhibiting bent-sandwich structures with an average Ba–C distance of 2.94 Å to the five-membered rings of the fluorenyl anion moieties and ring centroid–Ba–ring centroid angles of 112.3 and 116.4°. Four ammonia molecules complete the coordination sphere of barium. This supports the general preference of $BaX_2{\cdot}L_n$ compounds (X = anionic ligand, L = neutral ligand) for bent rather than linear arrangements of the $X^-Ba^{2+}X^-$ moieties.

Alkaline-earth-metal compounds are dominated by their highly ionic character. Due to their involatility and insolubility in common organic solvents, only a few derivatives of "true" calcium, strontium, and barium organometallics have been investigated.[1] $Ba(Me_5C_5)_2$, the first structurally characterized organobarium complex,[2] has a "quasipolymeric" structure with bent metallocenes (the ring centroid–metal–ring centroid angle is 131°). A similar structure was obtained for $[(C_3H_7)_4C_5H]_2Ba$.[3] Here, two crystallographically independent but nearly identical molecules are present in the asymmetric unit. The ring centroid–metal–ring centroid angle of 154.3° is significantly larger than that in $Ba(Me_5C_5)_2$.

We now report on the X-ray structure of bis(fluorenyl)barium–tetrakis(ammonia) (**1**), the first X-ray structure of an alkaline-earth-metal fluorene complex. In solution, $Ba(Fl)_2$ (Fl = fluorene) has been studied by electronic, spectroscopic, and conductometric methods.[4] Absorption and emission spectra were interpreted to suggest the existence of triple ion pairs with mutually tilted fluorenyl units. This feature would allow additional external coordination of Ba^{2+} by solvent molecules.[4b,c] The X-ray structure presented here agrees with this analysis.

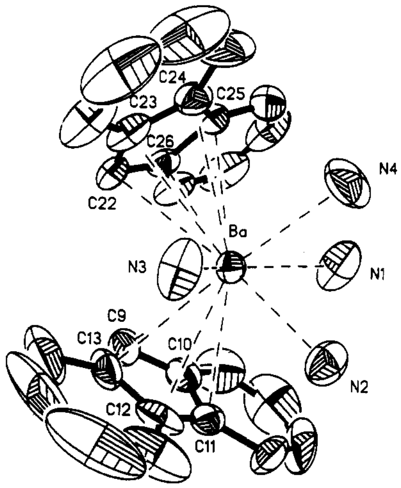


Figure 1. Ortep plot for bis(fluorenyl)barium–tetrakis(ammonia) (**1**), giving the numbering scheme used in Table I.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 1A and 1B

	1A	1B
	Bond Lengths	
Ba–C9	3.151	3.107
Ba–C10	3.180	3.099
Ba–C11	3.189	3.098
Ba–C12	3.171	3.120
Ba–C13	3.160	3.141
Ba–C22	3.071	3.100
Ba–C23	3.223	3.048
Ba–C24	3.249	3.300
Ba–C25	3.226	3.570
Ba–C26	3.077	3.441
Ba–N1	2.887	2.873
Ba–N2	2.882	2.924
Ba–N3	2.839	2.854
Ba–N4	2.942	2.864
Ba–X1A	2.936	2.870
Ba–X1B	2.940	3.069
	Bond Angles	
X1A–Ba–X1B	112.3	116.4

First obtained as an orange-yellow microcrystalline powder from the reaction of barium and fluorene in liquid ammonia at −80 °C,[5,6] **1** was dissolved in THF, from which

---

[†] In memoriam, Feb 21, 1964–Feb 16, 1992.

(1) (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, G., Eds.; Pergamon: Oxford, U.K., 1982; Vol. I, Chapter 4. (b) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345.

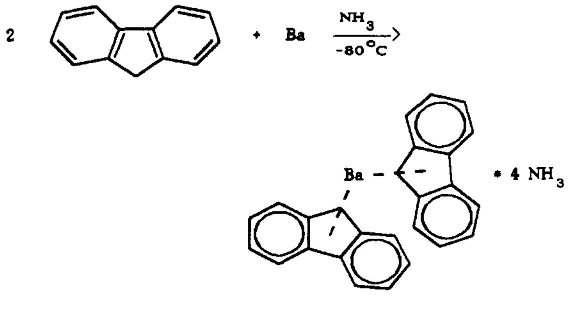
(2) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045.

(3) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843.

(4) (a) Pascault, J.-P.; Golé J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 449. (b) Hogen-Esch, T. E.; Plodinec, M. J. *J. Phys. Chem.* **1976**, *80*, 1085. (c) Hogen-Esch, T. E.; Smid, J. *J. Phys. Chem.* **1975**, *79*, 233. (d) Takaki, U.; Smid, J. *J. Am. Chem. Soc.* **1974**, *96*, 2588.

0276-7333/92/2311-1769$03.00/0

yellow needles suitable for single-crystal X-ray crystallography could be isolated.[7] The very air- and mois-



(1)

1

ture-sensitive 1 crystallizes with two crystallographically independent but essentially identical molecules in the unit cell. The X-ray structure reveals monomers with bent-metallocene geometries. Figure 1 shows one of the two independent conformers of 1 (A). Selected bond lengths and bond angles of the two conformers are summarized in Table I.

Both fluorenyl anions coordinate in a η^5 fashion to the Ba^{2+} dication. The major difference between the two conformers—denoted A and B—is the manner in which the five-membered rings of the fluorene moieties are joined to the metal center. In conformer A, Ba^{2+} exhibits nearly symmetric interactions with both five-membered rings of the two fluorenyl moieties. The Ba–C(ring) distances range from 3.151 to 3.189 Å in one fluorenyl group and 3.071–3.295 Å in the other. A comparable η^5 coordination was also observed in Na(fluorenide)·PMDTA (PMDTA = $Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2$)[8] but not in Li(fluorenide)$(NC_7H_{13})_2$, which is closer to a η^3 coordination.[9a] In confomer B the metal center is coordinated symmetrically to the five-membered ring of one fluorenyl moiety, with Ba–C(ring) distances between 3.908 (8) and 3.141 (9) Å, but unsymmetrically to the five-membered ring of the second fluorenyl moiety.

The distances between Ba^{2+} and C25/C26 are 3.44 and 3.57 Å, respectively, somwhat longer than those between Ba^{2+} and C22/C23/C24 (3.05, 3.10, 3.30 Å). We attribute the fact that two different bonding modes—η^3 vs η^5—are observed to a very shallow potential energy surface for the interaction of the metal cation with the fluorenyl moiety. This is also indicated by MNDO studies on (fluorenyl)lithium with various donor ligands which predict energy differences of less than 6 kJ/mol for these different bonding modes.[9b] The average Ba–C(ring) distance of 2.94 Å is comparable with that in $[(C_3H_7)_4C_5H]_2Ba$ (2.94 Å) and somewhat shorter than that in $Ba(Me_5C_5)_2$ (2.99 Å). The four ammonia molecules, which complete the coordination sphere of the metal center, have Ba–N distances of 2.84–2.94 Å for conformer A and 2.85–2.92 Å for conformer B. It should be noted that 1 coordinates exclusively to NH_3, although it was crystallized from a THF solution. This testifies to a strong Ba···N interaction and might also reflect the fact that the interaction of the metal with the NH_3 ligands is sterically more favorable than it would be with THF.

The available X-ray structures of bis(cyclopentadienyl) compounds of the heavier group 2 metals (Ca, Sr, Ba) all disclose bent arrangements of the Cp rings around the metal.[1b] MX_2 compounds of barium generally tend to be nonlinear, more so than CaX_2 or SrX_2 species. Theoretical studies[10,11] have shown this to be due to d-orbital participation in small covalent bonding contributions and to the polarization of the metal cation by the anions.[10a-c] Moreover, ligand–ligand repulsion is much smaller in barium compounds than, for example, in corresponding CaX_2 or SrX_2 species due to the larger distances involved.[10b] The recent X-ray structure of a barium carbazole complex also features a bent arrangement of the anionic ligands, in contrast to the corresponding calcium and strontium systems.[12] While a recent theoretical investigation of MCp_2 shows the degree of bending to be much smaller with these π-ligands, $BaCp_2$ exhibits a shallow minimum with a ring centroid—M—ring centroid angle of ca. 150°.[11] Hence, the bending effects in barium coordination chemistry might be a general "inherent" phenomenon, although structure-determining factors induced by the solvating NH_3 ligands cannot be excluded. The bending observed in the solid-state structure of 1 will result from a combination of two effects: d-orbital participation and polarization effects as well as the stereochemical influence of the NH_3 ligands.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagenstiftung. We thank Martin Kaupp for his comments and interest.

Supplementary Material Available: Tables of crystallographic details, positional parameters, isotropic and anisotropic thermal parameters, and all bond distances and angles (10 pages). Ordering information is given on any current masthead page.

OM910801Y

---

(5) All manipulations were carried out under an argon atmosphere by using Schlenk techniques. THF was freshly distilled from potassium under an argon atmosphere. Barium was used as dendritic pieces received from Strem Chemicals. Barium (0.48 g, 3.5 mmol) was dissolved in 100 mL of liquid ammonia at −80 °C, and fluorene (1.16 g, 7.0 mmol) was added to the dark blue solution while stirring the mixture. When it was warmed to −70 °C, the mixture changed color to orange-brown. A 30-mL portion of THF was added. After evaporation of the ammonia an orange suspension formed, which was filtered. The clear orange filtrate was carefully covered with a layer of hexane. After 3 days at room temperature orange-yellow needles of X-ray quality were obtained.

(6) Spectroscopic data for 1: ^1H NMR (400 MHz, THF-d_8, 28 °C) δ −0.27 (s, 12 H, NH_3), 5.96 (s, 2 H, C9), 6.73 (t, 4 H, C3,6), 7.03 (t, 4 H, C2,7), 7.39 (d, 4 H, C1,8), 7.91 (d, 4 H, C4,5); ^{13}C NMR (100.6 MHz, THF-d_8, 28 °C) δ 85.42 (C9), 112.82 (C2,7), 118.81 (C4,5), 121.04 (C1,8), 122.30 (C3,6), 127.42 (C4a,5a), 136.01 (C8a,9a).

(7) The data set was collected at 200 K on a yellow crystal of monoclinic space group $P2_1/n$ with the following unit cell parameters: a = 10.155 (3) Å, b = 18.000 (9) Å, c = 27.364 (6) Å, β = 94.45 (2)°, V = 4987 (2) Å^3, Z = 8, and D_{calcd} = 1.428 g/cm^3. Full-matrix least-squares refinements of 1 converged at R = 0.0540 and R_w = 0.0416 for observed ($F > 4.0\sigma(F)$) reflections. The structure was solved by direct methods implemented in the program package SHELXTL-PLUS (Sheldrick, G. M. Structure Determination Software Programs; Siemens Analytical X-ray Instruments, Inc.).

(8) Corbelin, S.; Kopf, J.; Weiss, E. *Chem. Ber.* **1991**, *124*, 2417.

(9) (a) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339. (b) Hoffmann, D.; Schleyer, P. v. R. Unpublished results.

(10) (a) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360. (b) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* **1991**, *113*, 6012. (c) Seijo, L.; Barandiaran, Z.; Huzinaga, S. *J. Chem. Phys.* **1991**, *94*, 3762. (d) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 491.

(11) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.*, in press.

(12) Mösges, G.; Hampel, F.; Kaupp, M.; Schleyer, P. v. R. Submitted for publication in *J. Am. Chem. Soc.*