

## Theoretical Study of Structure, Bonding, and Electronic Behavior of Low-Valent Bismuth Cyclopentadienyl and Pentamethylcyclopentadienyl Half-Sandwich Compounds

Kirill Yu. Monakhov and Gerald Linti\*

*Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

Received March 31, 2009

The correlations between structural and electronic properties of the bismuth cyclopentadienyl complexes of the types  $[(C_5R_5)_nBi_n]^{q+}$  (where R = H, Me;  $n = 1, q = 2; n = 1-4, q = 0$ ) and  $(C_5R_5)BiX_2$  (where R = H, Me; X = Cl, Br, I) were studied with quantum-chemical calculations. The influence of the ligand, significant variations in the Bi–C bond lengths, haptotropic shifts with distortion of the  $C_5R_5$  ring, Jahn–Teller splitting, interstabilization effects, and the role of the lone pairs on p-block element—unalkylated or peralkylated cyclopentadienyl ring interactions were examined to obtain qualitative and quantitative pictures of the intramolecular  $C_5R_5$ –Bi interactions. Our theoretical investigations of monovalent and trivalent bismuth cyclopentadienyl complexes give an insight into the geometric and electronic structures, the relative stabilities and further behavior of this kind of compounds.

### Introduction

The synthesis, characterization, and theoretical study of inorganic and organometallic compounds of the group 13–15 p-elements are an interesting area and target of chemistry, not at least because of their suitability as single source precursors to the production of thin films by chemical vapor deposition (CVD).<sup>1</sup> Potentially leaving groups in this process can be  $\pi$ -coordinated ligands. These can be separated into two general classes, cyclopentadienyl- and arene-type derivatives. However, usually only the compounds containing cyclopentadienyl rings can give a variety of metal oxidation states and consequently many variations in electronic structure and behavior. The cyclopentadienyl ligand can act as a potential leaving group making this chemistry an object of intensive studies.<sup>1f,2</sup>

In the cyclopentadienyl chemistry of p-block elements we want to focus on bismuth half-sandwich cyclopentadienyl

complexes with R = H and R = Me substituents at the  $C_5R_5$  ring, because the metal complexes with the strong  $\pi$ -electron donating cyclopentadienyl ligand (R = H) and the more bulky but even stronger donor pentamethylcyclopentadienyl (R = Me) ligand show different properties and behavior (thermal stability, intermolecular interactions, solubility, tendency to form polymeric structures, etc.).

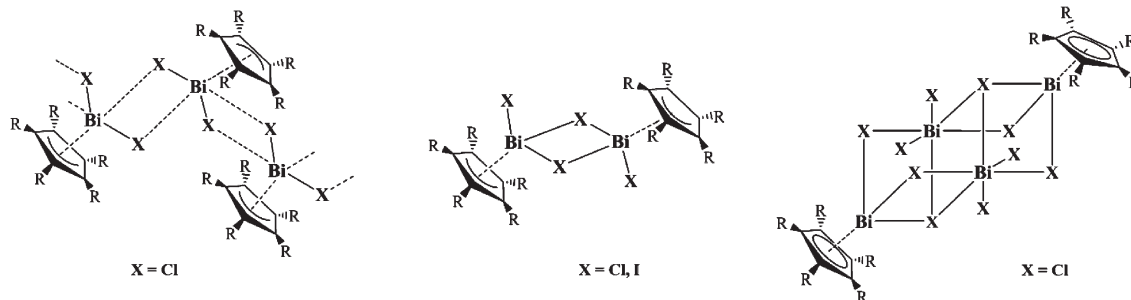
Bismuth ( $[Xe] 4f^{14}5d^{10}6s^26p^3$ ) is known to display various oxidation states, the most common being +3 and +5, but formal +1 and 0 are also known.<sup>3</sup> However, in its cyclopentadienyl chemistry bismuth has only displayed +3 oxidation state. Bismuth species containing cyclopentadienyl units  $M(\eta^x-C_5R_5)_{3-n}X_n$  (where M = Bi<sup>III</sup>;  $x = 1, 2, 3, 5$ ;  $C_5R_5 = C_5H_5, C_5Me_5, C_5^iPr_3Me_2, C_5^iPr_4H$ , or  $C_5^iBu_3H_2$ ; X = Cl, Br, I;  $n = 0-2$ ) with highly variable  $C_5R_5$ –bismuth interactions have been characterized by X-ray diffraction in the solid

\*To whom correspondence should be addressed. E-mail: gerald.linti@aci.uni-heidelberg.de. Phone: +49-6221-548468. Fax: +49-6221-546617.

(1) (a) Dahlhaus, J.; Jutzi, P.; Fienck, H. J.; Kulisch, N. *Adv. Mater.* 1993, 5, 377. (b) Scherer, M.; Kruck, T. *Chem. Vap. Deposition* 1999, 3, 33. (c) Bensiak, S.; Bangel, M.; Jutzi, P. *Organometallics* 2000, 19, 1292. (d) Klipp, A.; Hamelmann, F.; Haindl, G.; Hartwich, J.; Kleineberg, U.; Jutzi, P.; Heinzmann, U. *Chem. Vap. Deposition* 2000, 6, 63. (e) Dittmar, K.; Jutzi, P.; Schmalhorst, J.; Reiss, G. *Chem. Vap. Deposition* 2001, 7, 193. (f) Jutzi, P. *Pure Appl. Chem.* 2003, 75, 483–494.

(2) (a) Bartlett, R. A.; Cowley, A.; Jutzi, P.; Olmstead, M. M.; Stammer, H. G. *Organometallics* 1992, 11, 2837–2840. (b) Jutzi, P.; Burford, N. *Chem. Rev.* 1999, 99, 969–990. (c) Jutzi, P.; Reumann, G. *J. Chem. Soc., Dalton Trans.* 2000, 2237–2244. (d) Sapunov, V. N.; Kirchner, K.; Schmid, R. *Coord. Chem. Rev.* 2001, 214, 143–185.

(3) (a) Becker, G.; Mundt, O. In *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente*; VCH: Weinheim, 1992; p 199. (b) Wallenhauer, S.; Leopold, D.; Seppelt, K. *Inorg. Chem.* 1993, 32, 3948–3951. (c) Wallenhauer, S.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* 1994, 33, 976–978. (d) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* 1997, 277, 78–81. (e) Breunig, H. J.; Rösler, R.; Lork, E. *Angew. Chem., Int. Ed.* 1998, 37, 3175–3177. (f) Silvestru, C.; Breunig, H. J.; Althaus, H. *Chem. Rev.* 1999, 99, 3277–3327. (g) Hardman, N. J.; Twamley, B.; Power, P. P. *Angew. Chem., Int. Ed.* 2000, 39, 2771–2773. (h) Linti, G.; Köstler, W. *Z. Anorg. Allg. Chem.* 2002, 628, 63–66. (i) Linti, G.; Köstler, W.; Pritzkow, H. *Eur. J. Inorg. Chem.* 2002, 2643–2647. (j) Balázs, G.; Balázs, L.; Breunig, H. J.; Lork, E. *Organometallics* 2003, 22, 2919–2924. (k) Balázs, L.; Breunig, H. J.; Lork, E. *Z. Anorg. Allg. Chem.* 2004, 630, 1937–1940. (l) Breunig, H. J.; Balázs, L.; Philipp, N.; Soran, A.; Silvestru, C. *Phosphorus, Sulfur Silicon Relat. Elem.* 2004, 179, 853–857.



**Figure 1.** Half-sandwich polymeric (left), dimeric (center), and tetrameric (right) bismuth cyclopentadienyl compounds bridged by halide atoms, where  $C_5R_5 = \eta^2/\eta^3-C_5H_5$ ,  $\eta^3-C_5Pr_4H$ , and  $\eta^2-C_5Pr_4H$ , respectively.

state.<sup>4</sup> Monomer, dimeric, and tetrameric molecules associated via Bi–X–Bi bridges, as well as polymeric chains, were obtained (Figure 1). For all these compounds, information about the nature of the  $C_5R_5$ –Bi bonding and the intermolecular interactions based on electron diffraction, photoelectron spectra, and quantum chemical calculations in the gas phase have not been available up to now. By contrast, isoelectronic fragments of the groups 13–14 elements of type  $(C_5R_5)_aE^{q+}X_b$  ( $E = Al, Ga, In, Tl, Si, Ge, Sn, Pb; a = 1–2; b = 0, 2, 3; q = 0–1$ )<sup>5</sup> have been studied more extensively. In addition, such compounds of the groups 13–15 elements are valuable starting material for different synthetic reactions and their applications: cluster synthesis, Diels–Alder or heterometallic addition, disproportionation, exchange or electron transfer reactions, and as Metalorganic Vapor phase

Epitaxy (MOVPE) sources.<sup>1f,2c,6</sup> These compounds can be used as an alternative to the metal halides, too.<sup>6a,6h</sup>

In this paper, we describe a computational study on the nature of the chemical bonding and the electronic structures in cyclopentadienyl derivatives of bismuth. Here, gas phase model structures of the monomeric trivalent bismuth cyclopentadienyl complexes of two types,  $(C_5R_5)Bi^{2+}$  (where  $R = H, Me$ ) and  $(C_5R_5)BiX_2$  (where  $R = H, Me; X = Cl, Br, I$ ) along with an experimentally unknown family of the monovalent bismuth cyclopentadienyl complexes  $[(C_5R_5)Bi]_n$  (where  $R = H, Me; n = 1–4$ ) are investigated with several goals. One is to predict their further synthetic strategies (donor–acceptor properties, etc.), another to give useful information to the understanding of structures and the qualitative and quantitative description of bonding modes and electronic ligand effects. Thus, an effective adjustment of electronic and bonding situations can open a way to a manipulation of the bismuth-cyclopentadienyl bonds.

### Computational Details and Theory

The electron structure calculations were performed by means of density functional theory (DFT) based on Kohn–Sham theory and Møller–Plesset perturbation theory based on Rayleigh–Schrödinger perturbation theory (RS-PT), and using Hartree–Fock (HF) theory.

The initial geometries were fully optimized with the hybrid exchange–correlation functional PBE0<sup>7</sup>, which uses a 1:3 mixture of DFT, 25% of the exact exchange from Hartree–Fock, and 75% correlation weighting from PBE for the exchange part with a generalized-gradient approximation:  $E_{XC} = 0.25E_X(HF) + 0.75E_X(PBE) + E_C(mPW91)$ . DFT structure optimizations were performed with the Turbomole program,<sup>8</sup> adopting the multiple “M3” grid size for the density fitting and a self-consistent field (SCF) convergence criterion of  $1 \times 10^{-7} E_h$ . Coulomb interactions were considered within the resolution of the identity (RI) approximation. As Gaussian AO basis for all atoms, large all-electron triple  $\zeta$  split valence (TZVP) sets of def2-type<sup>9</sup> were employed (Basis Set System I, which is denoted BS-I). In standard notation these are [6s,5p,3d,2f] for Bi, [5s,3p,2d,1f] for C, [5s,5p,2d,1f] for Cl, [6s,5p,4d,1f] for Br, [6s,5p,3d,2f] for I, and [3s,1p] for H.

The post-Hartree–Fock ab initio methods of second- and fourth-order Møller–Plesset perturbation theory [MP2 and MP4(SDQ), respectively] were presented to account for high electron correlation effects in molecules and to obtain more

(4) (a) Frank, W. *J. Organomet. Chem.* **1990**, *386*, 177–186. (b) Sitzmann, H.; Wolmershäuser, G. *Chem. Ber.* **1994**, *127*, 1335–1342. (c) Lorberth, J.; Massa, W.; Wocadlo, S.; Sarraje, I.; Shin, S.-H.; Li, X.-W. *J. Organomet. Chem.* **1995**, *485*, 149–152. (d) Sitzmann, H.; Wolmershäuser, G. *Z. Naturforsch.* **1997**, *52b*, 398. (e) Sitzmann, H.; Wolmershäuser, G.; Boese, R.; Bläser, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2103–2107. (f) Üffing, C.; Ecker, A.; Baum, E.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1354–1356.

(5) (a) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757. (b) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *Chem. Commun.* **1981**, 925. (c) Haaland, A.; Schilling, B. E. R. *Acta Chem. Scand.* **1984**, *38A*, 217. (d) Lattman, M.; Cowley, A. H. *Inorg. Chem.* **1984**, *23*, 241–247. (e) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164. (f) Beachley, O. T. Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051–1059. (g) Beachley, O. T. Jr.; Blom, R.; Churchill, M. R.; Faegri, K. Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346–356. (h) Loos, D.; Schnöckel, H.; Gauss, J.; Schneider, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1362–1364. (i) Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860. (j) Armstrong, D. R.; Duer, M. J.; Davidson, M. G.; Moncrieff, D.; Russell, C. A.; Stourton, C.; Steiner, A.; Stahlke, D.; Wright, D. S. *Organometallics* **1997**, *16*, 3340–3351. (k) Winter, J. G.; Portius, P.; Kociok-Kohn, G.; Steck, R.; Filippou, A. C. *Organometallics* **1998**, *17*, 4176. (l) Smith, J. D.; Hanusa, T. P. *Organometallics* **2001**, *20*, 3056–3062. (m) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238–239*, 55–82. (n) Jones, J. N.; Moore, J. A.; Cowley, A. H.; Macdonald, C. L. B. *Dalton Trans.* **2005**, 3846. (o) Schenk, C.; Schnepf, A. *Organometallics* **2006**, *25*, 2378.

(6) (a) Wiberg, N.; Blank, T.; Nöth, H.; Ponikvar, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 839–841. (b) Wiberg, N.; Blank, T.; Purath, A.; Stösser, G.; Schnöckel, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2563–2565. (c) Fischer, R. A.; Weiss, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2830–2850. (d) Kühler, T.; Jutzi, P.; Stämmler, A.; Stämmler, H. G. *Chem. Commun.* **2001**, 539–540. (e) *Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley-VCH: Weinheim, **2004**; pp 1–444. (f) Joudat, M.; Castel, A.; Delpech, F.; Riviere, P.; Mcheik, A.; Gornitzka, H.; Massou, S.; Sourmia-Saquet, A. *Organometallics* **2004**, *23*, 3147. (g) Steinke, T.; Gemel, C.; Winter, M.; Fischer, R. A. *Chem.—Eur. J.* **2005**, *11*, 1636–1646. (h) Bühler, M.; Linti, G. *Z. Anorg. Allg. Chem.* **2006**, *632*, 2453–2460. (i) Schulz, S.; Kuczkowski, A.; Schuchmann, D.; Flörke, U.; Nieger, M. *Organometallics* **2006**, *25*, 5487–5491. (j) Grachova, E. V.; Linti, G. *Eur. J. Inorg. Chem.* **2007**, 3561–3564.

(7) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

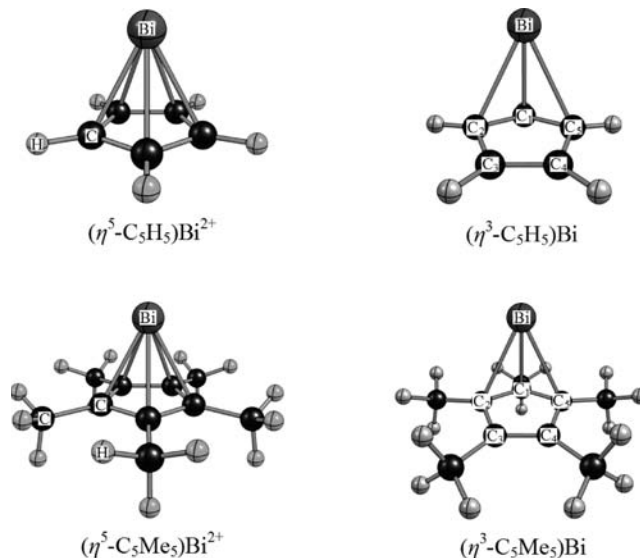
(8) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.

(9) (a) Metz, B.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2000**, *113*, 2563–2569. (b) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7/18*, 3297–3305.

accurate energies and charges. Los Alamos National Laboratory 2 (LANL2) relativistic effective core potentials (ECPs) were used to describe the core electrons of Bi, Cl, Br, and I atoms and split-valence (double- $\zeta$ ) basis sets were used to describe s- and p-valence electrons of Bi, Cl, Br, and I. The LANL2DZ basis set was augmented by adding one set of polarization functions on all atoms and one set of diffuse functions on all non-hydrogen atoms.<sup>10</sup> For C and H atoms all-electron split-valence 6-31 + G(d,p) basis sets supplemented with a single set of diffuse functions on carbon atoms were employed.<sup>11</sup> The combination of LANL2DZdp and 6-31 + G(d,p) is denoted Basis Set System II (BS-II). The vibrational frequencies were evaluated on all DFT-optimized geometries using the HF method to verify their status as true local minima on the potential energy surface and to obtain zero-point corrections to the energies (ZPE) without scaling. The nature of the chemical bonding was analyzed by the Natural Bond Orbital (NBO) approach with the second-order Møller–Plesset perturbation theory, including all valence electrons in the configuration space [MP2(full)/BS-II]. The atomic charges were computed within the Natural Population Analysis (NPA). Second order perturbative analysis of donor–acceptor interactions is available, labeled as  $E(2)$  energies. Wiberg indexes were evaluated and used as bond strength indicators. NBO analysis was performed with NBO Version 3.1<sup>12</sup> incorporated in the Gaussian 03 program. The vertical singlet electronic states were studied using the extended Koopman's theorem with time-dependent PBE0 density functional method (TD-PBE0/BS-II). Energies and dipole moments reported herein were evaluated using the second- and fourth-order Møller–Plesset perturbation theory [MP2(full)/BS-II or MP4(SDQ)/BS-II] in combination with PBE0 parametrization [PBE0/BS-I]. All of these computations were carried out using the Gaussian 03 program package.<sup>13</sup>

## Results and Discussion

**Compounds of the Types  $(C_5R_5)Bi^{2+}$  and  $[(C_5R_5)Bi]_n$  ( $n = 1-4$ ).** DFT structure optimizations of molecules of type  $[(C_5R_5)Bi]^{q+}$  ( $R = H, Me; q = 2, 0$ ) were performed. The cationic  $(C_5R_5)Bi^{2+}$  complexes display a half-sandwich “open-faced” structure where the pentagonal ligand



**Figure 2.** PBE0/BS-I optimized geometries of  $[(C_5R_5)Bi]^{q+}$  ( $R = H, Me; q = 2, 0$ ) molecules where the bismuth atom is bonded to the  $C_5R_5$  ring in a  $\eta^5$ - and  $\eta^3$ -fashion, respectively. Selected computed bond lengths [pm] and angles [deg] of  $(C_5H_5)Bi^{2+}$ : Bi–Z 212.3,  $(C_5Me_5)Bi^{2+}$ : Bi–Z 211.7.  $(C_5H_5)Bi$ : Bi–Z 254.8, Bi–C<sub>1</sub> 232.7, Bi–C<sub>2</sub> 259.7, Bi–C<sub>3</sub> 260.4, Bi–C<sub>4</sub> 322.4, Bi–C<sub>5</sub> 322.7, C<sub>1</sub>–C<sub>2</sub> 143.4, C<sub>2</sub>–C<sub>3</sub> 143.6, C<sub>1</sub>–C<sub>5</sub> 143.4, C<sub>4</sub>–C<sub>5</sub> 143.5, C<sub>3</sub>–C<sub>4</sub> 136.6, Bi–C<sub>2</sub>–C<sub>3</sub> 102.3, Bi–C<sub>5</sub>–C<sub>4</sub> 102.2, Bi–C<sub>1</sub>–Z 85.6.  $(C_5Me_5)Bi$ : Bi–Z 250.5, Bi–C<sub>1</sub> 233.3, Bi–C<sub>2</sub> 256.8, Bi–C<sub>5</sub> 256.7, Bi–C<sub>3</sub> 317.3, Bi–C<sub>4</sub> 317.3, C<sub>1</sub>–C<sub>2</sub> 144.2, C<sub>2</sub>–C<sub>3</sub> 145.5, C<sub>1</sub>–C<sub>5</sub> 144.2, C<sub>4</sub>–C<sub>5</sub> 145.5, C<sub>3</sub>–C<sub>4</sub> 136.6, Bi–C<sub>2</sub>–C<sub>3</sub> 100.5, Bi–C<sub>5</sub>–C<sub>4</sub> 100.5, Bi–C<sub>1</sub>–Z 82.9.

$C_5R_5$  is  $\eta^5$ -coordinated to the bismuth center (Figure 2). The carbon–carbon bond lengths in the  $C_5R_5$  ring are 143.4 pm for  $R = H$  and 145.1 pm for  $R = Me$ . The ring-centroid to metal bond distance (Bi–Z) for  $(C_5H_5)Bi^{2+}$  is slightly longer than that for the  $(C_5Me_5)Bi^{2+}$  complex. Compared to isoelectronic groups 13 and 14 cyclopentadienyl compounds of the types  $(C_5R_5)E$  and  $(C_5R_5)E^+$ , respectively, this distance is slightly longer than in the germanium, aluminum, gallium, and tin compounds ( $Ge^+$ : 189.7 pm for  $R = Me$ ; Al: 203.7 pm for  $R = H$ , 206.3 pm for  $R = Me$ ; Ga: 209.6 pm for  $R = H$ , 208.1 pm for  $R = Me$ ; Sn<sup>+</sup>: 211.4 pm for  $R = Me$ ) but shorter than in the indium, thallium, and lead derivatives (In: 232.2 pm for  $R = H$ , 228.8 pm for  $R = Me$ ; Tl: 241.0 pm for  $R = H$ , 237.2 pm for  $R = Me$ ; Pb<sup>+</sup>: 244.4 pm for  $R = Me$ ).<sup>5a,5d–5i,5k,5n</sup> This indicates that the distances metal–centroid (El–Z) are sensitive to the nature of metal, its environment and type of ligand, thereby the El–Z distance clearly elongates down on the group and shortens left to right on the period, as is expected.

The structure optimizations of  $(C_5R_5)Bi$  molecules with bismuth in oxidation state +I reveal distorted half-sandwich structures (bent-conformation) where the  $C_5R_5$  rings exhibit  $\eta^3$ -coordination and monoene distortion  $C_3-C_4$  (Figure 2). The shortest Bi–C distances are  $d_{Bi-C_1} = 232.7$  pm for  $R = H$  and 233.3 pm for  $R = Me$ , respectively. The C<sub>1</sub> carbon atom is slightly displaced from the ring plane toward the bismuth atom. The bond length in the monoene fragment  $d_{C_3-C_4}$  of the  $C_5R_5$  ring is similar for  $R = H$  and  $R = Me$  (136.6 pm). Other carbon–carbon distances (C<sub>1</sub>–C<sub>2</sub>, C<sub>1</sub>–C<sub>5</sub>, C<sub>2</sub>–C<sub>3</sub>, C<sub>4</sub>–C<sub>5</sub>) in the  $C_5R_5$  ring are in the region of ~144 pm for  $R = H$  and ~145 pm for  $R = Me$ . The angle between the

(10) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (d) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111.

(11) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Clark, T.; Chandrasekhar, J.; Schleyer, P.v.R. *J. Comput. Chem.* **1983**, *4*, 294.

(12) (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO program*, version 3.1. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, M.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, B. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, **2004**.

**Table 1.** Important Calculated Values for the Complexes Obtained from the NBO Analysis at the MP2(full)/BS-II//PBE0/BS-I Level

parameter	$(C_5R_5)Bi^{2+}$		$(C_5R_5)Bi$	
	R = H	R = Me	R = H	R = Me
$nVE^a$	8	8	10	10
NEC <sup>b</sup> of Bi	6s <sup>1.93</sup> 6p <sup>1.34</sup>	6s <sup>1.91</sup> 6p <sup>1.50</sup>	6s <sup>1.93</sup> 6p <sup>2.65</sup>	6s <sup>1.92</sup> 6p <sup>2.71</sup>
$Q_{NPA}^c$ on Bi	+1.728	+1.587	+0.414	+0.365
$i_{CSR_5-Bi}^d$	57.6	52.9	41.4	36.5
LP <sub>1</sub> NHO <sup>e</sup> at Bi	s <sup>95.92%</sup> p <sup>4.07%</sup>	s <sup>94.95%</sup> p <sup>5.05%</sup>	s <sup>95.50%</sup> p <sup>4.50%</sup>	s <sup>94.73%</sup> p <sup>5.26%</sup>
occupancy <sup>f</sup>	1.998	1.997	1.999	1.997
LP <sub>2</sub> NHO at Bi			s <sup>0.24%</sup> p <sup>99.74%</sup>	s <sup>0.58%</sup> p <sup>99.40%</sup>
occupancy			1.893	1.865
$\rho_L^g$	97.1	97.6	98.5	98.7

<sup>a</sup> Number of valence electrons. <sup>b</sup> Natural electron configuration. <sup>c</sup> Natural charge. <sup>d</sup> Degree of ionicity of C<sub>5</sub>R<sub>5</sub>-Bi bonding [%]. <sup>e</sup> Lone pair natural hybrid orbital. <sup>f</sup> Occupancy of lone pair orbital [e]. <sup>g</sup> Accuracy of calculation model [%].

Bi-C<sub>1</sub> bond and the center of the C<sub>5</sub>R<sub>5</sub> ring (Bi-C<sub>1</sub>-Z) is 85.6° for R = H and 82.9° for R = Me. This means, the bismuth atom in the (C<sub>5</sub>H<sub>5</sub>)Bi complex is shifted from the central axes of the C<sub>5</sub>R<sub>5</sub> ring and loses strength of  $\pi$ -bonding to the cyclopentadienyl ring.

The natural population analysis (NPA) shows that the bismuth atom does not have an idealized electronic configuration 6s<sup>2</sup>6p<sup>0</sup> (in the <sup>1</sup>S ground state) in (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> and 6s<sup>2</sup>6p<sup>2</sup> (in the <sup>3</sup>P ground state) in (C<sub>5</sub>H<sub>5</sub>)Bi complexes, but a partial occupied s<sup>a</sup>p<sup>b</sup>-hybrid (a, b > 1 and a > 1, b > 2, respectively) with increased electron density in the 6p orbitals. In accordance with the natural electronic configuration (NEC) (Table 1) the 6s electrons of both complexes (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> and (C<sub>5</sub>R<sub>5</sub>)Bi are almost completely localized; therefore it may be expected that the 6p orbital will give the major contribution to covalent bonding.

The positive partial charge is located on the bismuth atom; it is less than the chemical valence of Bi in the ionic model (+3 and +1, respectively). In the (C<sub>5</sub>R<sub>5</sub>)Bi complexes, most negative charges in the C<sub>5</sub>R<sub>5</sub> ring are located on the carbon atom C<sub>1</sub> [-0.46 (R = H), -0.21 (R = Me)]. The charges on the C<sub>2</sub> and C<sub>5</sub> carbons are -0.38 for R = H, and -0.15 for R = Me. The carbon atoms C<sub>3</sub> and C<sub>4</sub> in the monoene fragment have -0.26 for R = H and -0.04 for R = Me.

The NPA reveals a predominantly ionic character of the Bi-C bonds in ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> complexes for R = H (57.6%, ionic participation) and R = Me (52.9%), and a predominantly covalent character of the Bi-C bonds in ( $\eta^3$ -C<sub>5</sub>R<sub>5</sub>)Bi complexes for R = H (41.4%) and R = Me (36.5%). The charge on the metal atoms in the bismuth pentamethylcyclopentadienyl complexes is less than in the bismuth cyclopentadienyl complexes. This is in line with better donor properties of the C<sub>5</sub>Me<sub>5</sub> ligand compared to those of the C<sub>5</sub>H<sub>5</sub> ligand. The localized NBO Lewis-description ( $\rho_L$ ) illustrates the high accuracy of the calculation models.

On the basis of NBO analysis, the space-filling lone pair localized on bismuth in the (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> complexes mainly has s-like-character. In (C<sub>5</sub>R<sub>5</sub>)Bi one of the lone pairs (LP) is of s-type, while the second one has predominantly p-character. The orbital occupancy of the LP with the

**Table 2.** Selected Computed Orbital Energies and Dipole Moments at the MP4 (SDQ)/BS-II//PBE0/BS-I Level

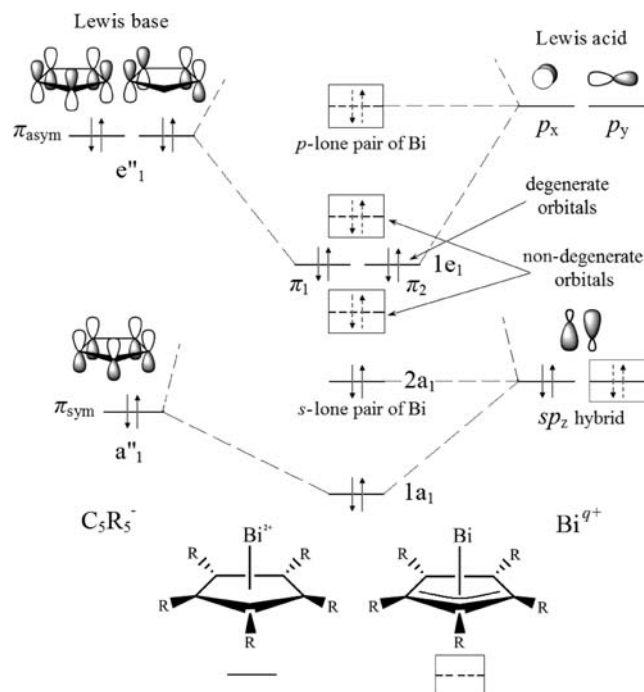
parameter	$(C_5R_5)Bi^{2+}$		$(C_5R_5)Bi$	
	R = H	R = Me	R = H	R = Me
LUMO	-9.46 (2e <sub>1</sub> )	-8.04 (2e <sub>1</sub> )	0.19	0.51
HOMO	-20.60 (1e <sub>1</sub> )	-18.15 (1e <sub>1</sub> )	-6.06 (p-LP)	-5.67 (p-LP)
HOMO-1	-23.46 (2a <sub>1</sub> )	-20.60 (2a <sub>1</sub> )	-8.80 ( $\pi_1$ )	-7.94 ( $\pi_1$ )
HOMO-2			-9.16 ( $\pi_2$ )	-8.36 ( $\pi_2$ )
HOMO-3			-13.12 (s-LP)	-11.77 (s-LP)
$\Delta E_{HOMO-LUMO}$	11.14	10.11	6.25	6.18
$\mu$	4.63	4.92	0.23	1.46

s-main contribution is higher than the occupancy of the LP with a more p-like character. The larger contributions of the s- and p-orbital parts in the lone pairs of (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> and (C<sub>5</sub>R<sub>5</sub>)Bi complexes indicate that such compounds have a relatively low Lewis basicity. Besides, the acceptor ability of the (C<sub>5</sub>R<sub>5</sub>)Bi complexes is expressed to a lesser degree compared to (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup>, but the donor ability is stronger. Consequently, the (C<sub>5</sub>R<sub>5</sub>)Bi complexes might act as ditopic ligands.

In NBO evaluations, described above, hybrid orbitals are used, which are not eigenfunctions. In an alternative concept canonical molecular orbitals are taken in account to obtain an insight into ligand metal interaction for [(C<sub>5</sub>R<sub>5</sub>)Bi]<sup>q+</sup> (R = H, Me; q = 2, 0). Thus, for the MO construction (Table 2, Figure 3) between the C<sub>5</sub>R<sub>5</sub>  $\pi$ -system and the {s, p} bismuth set in the ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> complexes an approximation in the Lewis structures was used. The  $\pi_{sym}(a_2'')$  orbital of C<sub>5</sub>R<sub>5</sub> ring interacts with the bismuth s and p<sub>z</sub> atomic orbitals (AOs) forming three centrosymmetric MOs: 1a<sub>1</sub>, 2a<sub>1</sub>, and 3a<sub>1</sub> (high-lying anti-bonding MO). The bonding 1a<sub>1</sub> orbital is formed as an approximation  $\langle s, p_z | a_2'' \rangle$ : 1a<sub>1</sub> = ( $\langle s | a_1'' \rangle, \langle p_z | a_1'' \rangle$ ) =  $\langle s, p_z | a_1'' \rangle_{bonding}$ . The non-bonding 2a<sub>1</sub> MO is classical metal sp<sub>z</sub> (2a<sub>1</sub> =  $\langle s, p_z \rangle_{non-bonding}$ ).

The two filled  $\pi_{asym}(e_1'')$  orbitals of C<sub>5</sub>R<sub>5</sub> ring interact with the p<sub>x</sub> and p<sub>y</sub> bismuth AOs forming two bonding 1e<sub>1</sub> and two anti-bonding 2e<sub>1</sub> molecular orbitals. The two bonding 1e<sub>1</sub> orbitals are formed by the non-axial  $\langle p_x, p_y | e_1'' \rangle$  interaction 1e<sub>1</sub> = ( $\langle p_x | e_1'' \rangle, \langle p_y | e_1'' \rangle$ ) =  $\langle p_x, p_y | e_1'' \rangle_{bonding}$ . Thus, the (C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> compounds have 8 valence electrons; all 5 C<sub>5</sub>R<sub>5</sub> electrons are involved in bonding to the bismuth center. A similar MO scheme was observed for cyclopentadienyl complexes of the group 13 elements in their oxidation state +I.<sup>5d,5h,5m</sup>

The results of the MO approximation indicate that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Bi<sup>2+</sup> complexes are doubly degenerate (e<sub>1</sub> and e<sub>2</sub> symmetries, respectively). The HOMO contains the main contribution of the  $\pi(C_5R_5)$ - $\pi(Bi)$  interaction. The HOMO-3 (a<sub>1</sub> symmetry) corresponds to the sp<sub>z</sub>-hybridized bismuth lone pair with the major contribution from the bismuth 6s-orbital. In the bismuth(I) cyclopentadienyl complexes the electronic situation changes from 8 to 10 VEs [isoelectronic to groups 13 and 14 cyclopentadienyl compounds of the types (C<sub>5</sub>R<sub>5</sub>)EX<sub>2</sub> and (C<sub>5</sub>R<sub>5</sub>)EX, respectively] and the degeneracy of the HOMO disappears (non-degenerate  $\pi$ -orbitals) and these orbitals become HOMO-1 and HOMO-2, accordingly. The new HOMO is metal centered (LP of p<sub>y</sub> type) and has a major



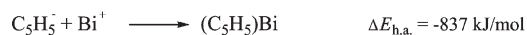
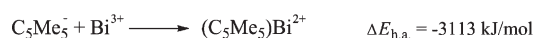
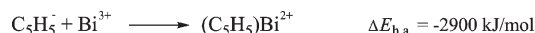
**Figure 3.** Slice from the qualitative correlation MO-diagram of the filled valence orbital interactions of  $C_5R_5-Bi$  in the  $(\eta^3-C_5R_5)Bi^{2+}$  and  $(\eta^3-C_5R_5)Bi$  complexes upon bending. The MO scheme shows the interaction of  $a''_1$  of  $C_5R_5$  with the  $s$  and  $p_z$  bismuth AOs and the interaction of  $e''_1$  of  $C_5R_5$  with the  $p_x$  and  $p_y$  bismuth AOs. For  $(\eta^3-C_5R_5)Bi$  the degeneration of the HOMO  $1e_1$  orbital is repealed, resulting in a new non-degenerate HOMO.

contribution from the bismuth  $6p$ -orbital. The  $sp_2$ -lone pair of Bi in the  $(\eta^3-C_5R_5)Bi$  complexes lies, similar to that in the  $(\eta^5-C_5R_5)Bi^{2+}$  complexes, under the  $\pi_1$  and  $\pi_2$  orbitals. These changes are in line with the haptotropic shifts and a change of coordination of the  $C_5R_5$  ring from  $\eta^5$  to  $\eta^3$  (Figure 3). As can be seen, the interpretation via canonical MO theory is in line with the results obtained by the NBO approach with hybridized molecular orbitals for the  $[(C_5R_5)Bi]^{q+}$  complexes.

The heterolytic association energies ( $\Delta E_{h.a.}$ ) of the  $[(C_5Me_5)Bi]^{q+}$  compounds are slightly more exothermic than  $\Delta E_{h.a.}$  of  $[(C_5H_5)Bi]^{q+}$  (Scheme 1).

Time-dependent (TD) DFT computations of vertical electronic transitions in the  $(C_5R_5)Bi$  complexes show three main excited electronic states  $S_1$ ,  $S_2$ , and  $S_3$ . Thus, for the  $(C_5R_5)Bi$  bismuth complexes the lowest energy  $S_0 \rightarrow S_1$  transition can be described as a HOMO  $\rightarrow$  LUMO excitation (2566 nm for  $R = H$ ; 1929 nm for  $R = Me$ ) from the lone pair of  $p$ -type localized on bismuth toward its lowest unoccupied  $p$ -MO ( $n_{Bi(p)} \rightarrow n_{Bi(p)^*}$ ). This transfer of electrons is the most intense energy transition. The  $S_0 \rightarrow S_2$  transition is a HOMO  $\rightarrow$  LUMO + 1 excitation with  $n_{Bi(p)} \rightarrow n_{Bi(p)^*}$  character, whereas the  $S_0 \rightarrow S_3$  transition is mainly a  $\pi \rightarrow n_{Bi(p)^*}$  excitation (from a predominantly ligand  $\pi$ -orbital toward the LUMO of metal). The very low energy values ( $< 1$  eV) of the HOMO  $\rightarrow$  LUMO excitation for both derivatives of the  $(C_5R_5)Bi$  complexes and low values of  $\Delta E$  ( $E_{HOMO} - E_{LUMO}$ ), which are about 1.5 times lower than these of the  $(C_5R_5)BiX_2$  complexes (will be discussed later) indicate that the cyclopentadienyl compounds of monovalent bismuth are much less kinetically stable than these of

**Scheme 1.** Heterolytic Association Energies of the  $[(C_5R_5)Bi]^{q+}$  Compounds Calculated at the MP4(SDQ)/BS-II//PBE0/BS-I Level

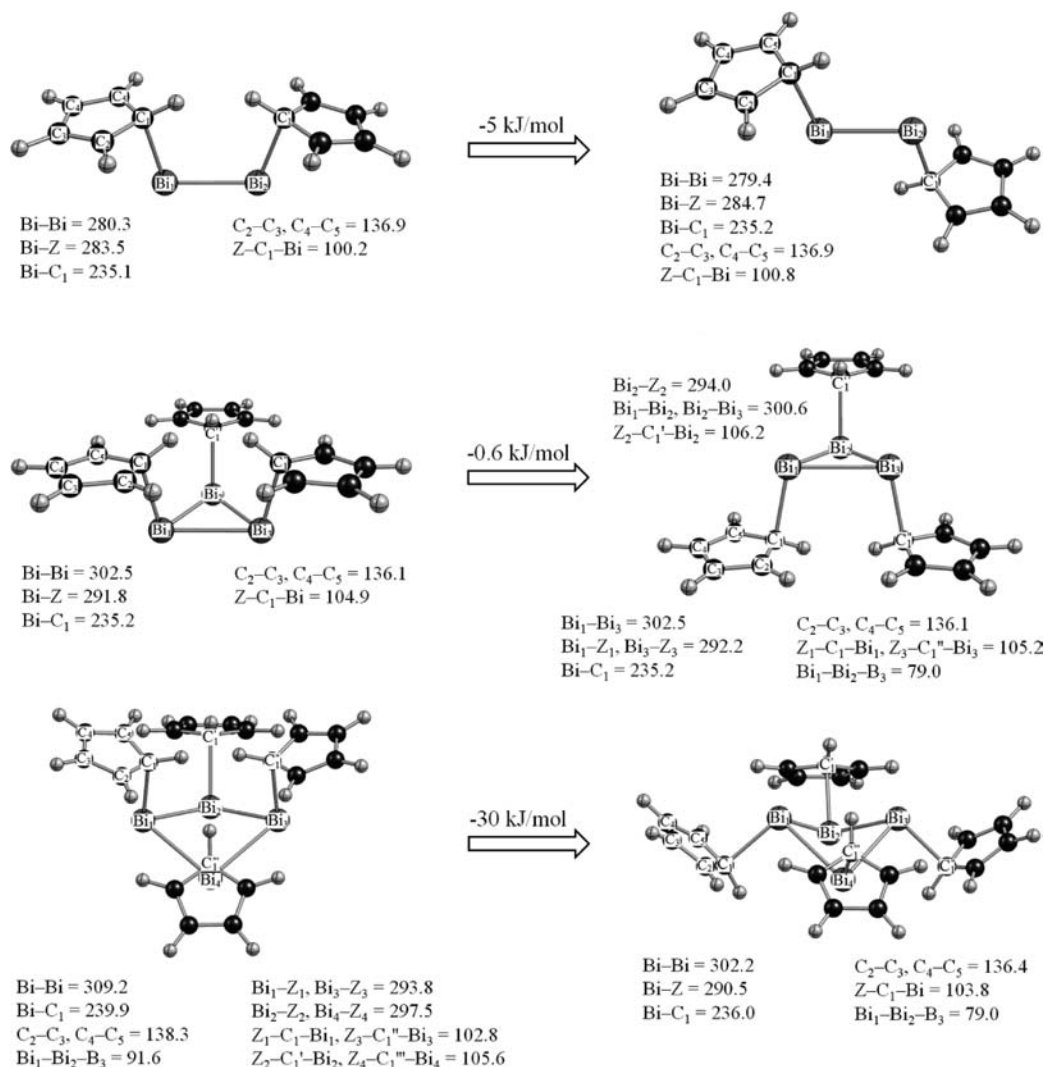


trivalent bismuth. Finally, the low values of the first ionization potential ( $-IP_1 = -E_{HOMO}$ ) indicate that  $(C_5R_5)Bi$  can be easily oxidized. This also explains why the monovalent Bi cyclopentadienyl compounds can hardly exist in their monomer state. The kinetically much more stable group 13 cyclopentadienyl compounds  $(C_5R_5)E$ , which have the larger HOMO-LUMO-gap and higher energy values for the HOMO  $\rightarrow$  LUMO excitation, are only monomers in gas phase and solution.<sup>5d,5f-5i</sup>

Can the cyclopentadienyl complexes of bismuth be stabilized in its low-oxidation state +I in spite of this? In our opinion, such stabilization might come from the formation of homonuclear systems (clusters) of  $n$ -bonded Bi-Bi atoms or heteronuclear systems in the form of bismuth-metal adducts, when the  $p$ -lone pair of bismuth will be localized at one of these bonds. Therefore, we have studied simple “ $n$ -merized” models of the bismuth cyclopentadienyl complexes of type  $[(C_5H_5)Bi]_n$  ( $n = 2-4$ ) in their *cis*- and *trans*-configurations (Figure 4). DFT structural simulations of molecules show that all of these have bent core geometry with pure  $\eta^1(\sigma)$ -coordination modes of the  $C_5H_5$  ring. The results from MP2 calculations suggest that *trans*-optimized structures are more stable than *cis* isomers. Therefore, in the following we consider only *trans*-geometries of the  $[(C_5H_5)Bi]_n$  complexes.

Thus, the Bi-Bi distance in the dimeric molecule  $[(C_5H_5)Bi]_2$  is of double bond character (279.4 pm). The molecule shows a *trans*-geometry (*anti*-periplanar) of the  $C_{ipso}-Bi_1-Bi_2-C_{ipso}$  core (torsion angle  $-179.9^\circ$ ) or  $LP_1-Bi_1-Bi_2-LP_2$ , where the lone pairs ( $LP_1$  and  $LP_2$ ) localized on the bismuth atoms are of a predominantly  $s$ -type ( $\sim 86\%$ ). This distance corresponds to the Wiberg bond index (WBI) of 1.83, which describes the bond order and can be used as indicator of bond strength. Besides, the value of the Bi=Bi double bond distance indicates that a cyclopentadienyl dibismuthene has more electronic repulsion of the metal centers than the aryl dibismuthene  $\{trans-[(C_6H_5)Bi]_2: d_{Bi-Bi} = 277.1 \text{ pm}\}$ .<sup>14</sup> The C-Bi-Bi bond angle of  $95.8^\circ$  deviates from the ideal  $sp^2$  hybridized bond angle ( $120^\circ$ ), which is connected with the “inert  $s$ -pair effect”. This “non-hybridization effect” was also observed in aryl dibismuthenes obtained.<sup>3d,3g</sup> The Bi-Bi distances in the tribismuthane  $[(C_5H_5)Bi]_3$  with a *trans*-bent, nonplanar conformation ( $C_{ipso}-Bi-Bi-C_{ipso}$  torsion angle of  $-167.6^\circ$ ) and in the folded four-membered bismuth ring  $[(C_5H_5)Bi]_4$  with a *trans*-geometry ( $C_{ipso}-Bi-Bi-C_{ipso}$  torsion angle of  $\pm 118.6^\circ$ ) are of single bond character ( $d_{Bi-Bi}$ : over 300 pm; WBI values are approximately 0.95). Examples of a zirconocene-complexed

(14) The *trans*- $[(C_6H_5)Bi]_2$  molecule was optimized at the PBE0/def2-TZVP level of theory using the Turbomole program.



**Figure 4.** *cis*-bent core (left) and *trans*-bent core (right) optimized structures of the  $[(C_5H_5)Bi]_n$  ( $n = 2-4$ ) complexes and total energy differences between them calculated at the MP2(full)/BS-II//PBE-0/BS-I level. Selected important bond lengths and angles are given in [pm] and [deg], respectively.

dibismuthene trimeric<sup>15</sup> and tetrameric bismuthanes with alkyl or silyl substituents<sup>3e,3h-3j</sup> have been reported with similar bonding parameters.

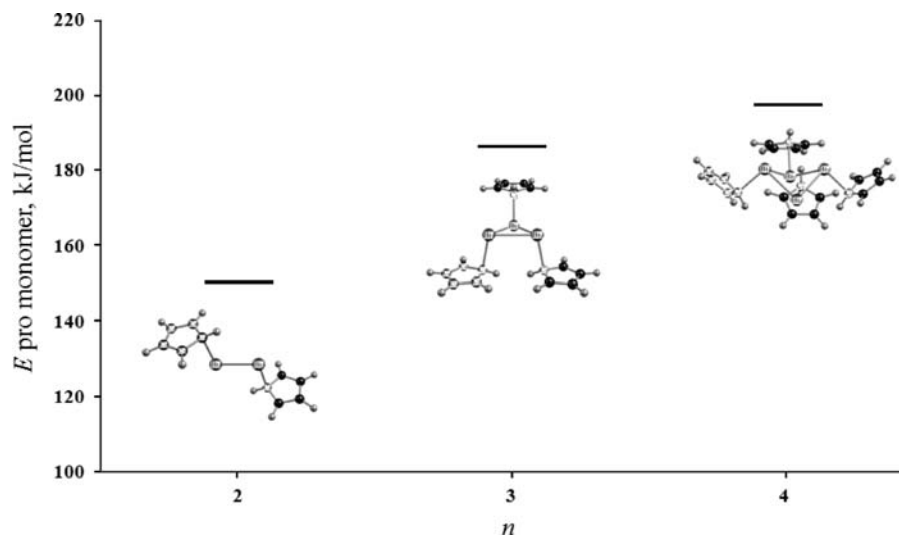
Thus, the *s*-character of the lone pairs at bismuth in  $[(C_5H_5)Bi]_n$  decreases with “*n*-merization” of the Bi atoms (~96% for  $n = 1$ , ~86% for  $n = 2$ , ~85% for  $n = 3$ , ~83% for  $n = 4$ ). This leads to an increase of the Lewis basicity. The ionic character of the Bi-C bonds, which are polarized toward carbons (~71%), decreases from  $n = 2$  (45.6%) via  $n = 3$  (44.0%) to  $n = 4$  (43.7%). Besides, “*n*-merization” leads to an increase of the kinetic stability ( $\Delta E_{HOMO-LUMO}$ : 6.24 for  $n = 1$ , 6.35 for  $n = 2$ , 7.79 for  $n = 3$ , 7.78 for  $n = 4$ ) and the first ionization potential. Consequently, the result is a decrease of the ability for oxidation (−6.06 for  $n = 1$ , −6.54 for  $n = 2$ , −7.19 for  $n = 3$ , −7.45 for  $n = 4$ ). Thus, the  $S_0 \rightarrow S_1$  transition for  $[(C_5H_5)Bi]_n$ , describing a HOMO  $\rightarrow$  LUMO excitation with  $n_{Bi(p)} \rightarrow n_{Bi(p)^*}$  character, has now relatively high energies (> 2 eV: 512 nm for  $n = 2$ , 471 nm for  $n = 3$ , 476 nm for  $n = 4$ ). The increase in the “*n*-merization” energies and the energy expenses *pro*

monomer unit  $(C_5H_5)Bi$  result from the increased stabilization of corresponding molecules (Scheme 2, Figure 5).

To understand the preferred coordination modes of the  $C_5R_5$  ring to Bi in trivalent bismuth cyclopentadienyl complexes, we have studied haptotropic rearrangement processes using the example of the cationic  $(C_5R_5)Bi^{2+}$  complexes and calculated the relative energies of the haptotropic shifts for variable bonding modes ( $\eta^3$ ,  $\eta^2$ ,  $\eta^1$ ) of the  $C_5R_5$  ring to the metal center with regard to the  $\eta^5$ -coordinated  $(C_5R_5)Bi^{2+}$  ( $R = H, Me$ ) molecules (Figure 6). The reaction path clearly shows that  $\eta^1(\pi)$ -bonded  $C_5R_5$  rings (when Bi resides inside the cylinder) possess the lowest energy barriers (120 kJ/mol for  $R = H$ , 118 kJ/mol for  $R = Me$ ). Such bonding is energetically more favorable than the  $\eta^1(\sigma)$ - (when Bi resides outside the cylinder; 205 kJ/mol for  $R = H$ , 218 kJ/mol for  $R = Me$ ),  $\eta^2$ - (192 kJ/mol for  $R = H$ , 268 kJ/mol for  $R = Me$ ) or  $\eta^3$ -coordinated modes (142 kJ/mol for  $R = H$ , 153 kJ/mol for  $R = Me$ ). Thus, the MP4(SDQ) calculations suggest that the structures of  $(C_5R_5)Bi^{2+}$  are more stabilized in the series  $(\eta^5-C_5R_5)Bi^{2+} > [\eta^1(\pi)-C_5R_5]Bi^{2+} > (\eta^3-C_5R_5)Bi^{2+} > [\eta^2/\eta^1(\sigma)-C_5R_5]Bi^{2+}$ .

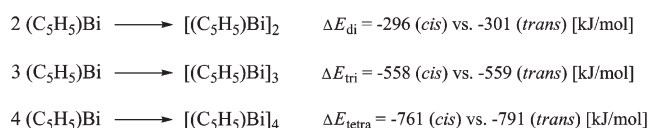
**Cyclopentadienyl Bismuth(III) Dihalides of the Type  $(C_5R_5)BiX_2$  ( $X = \text{Halogen}$ ).**  $(C_5R_5)BiX_2$  compounds

(15) Wang, Y.; Quillian, B.; Yang, X. J.; Wei, P.; Chen, Z.; Wannere, C. S.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 7672–7673.



**Figure 5.** Energy expenses of the *trans*-[(C<sub>5</sub>H<sub>5</sub>)Bi]<sub>n</sub> (*n* = 2–4) complexes *pro* monomer unit calculated at the MP2(full)/BS-II//PBE-0/BS-I level.

**Scheme 2.** Di-, Tri-, and Tetramerization Energies of Monovalent Bismuth Cyclopentadienyl Complexes [(C<sub>5</sub>H<sub>5</sub>)Bi]<sub>n</sub> (*n* = 2–4) Calculated at the MP2(full)/BS-II//PBE-0/BS-I Level



usually are oligomers via Bi–Bi bridges. Here, we examine only monomers. The molecular views resulting from the DFT local minima structures indicate that the bismuth atom in the (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> (R = H, Me; X = Cl, Br, I) complexes display a pyramidal coordination environment (Table 3, Figure 7). The distance of the metal atom to the carbon C<sub>1</sub> is longer than the sum of the covalent Bi–C radii ( $\Delta \sum r_{\text{cov}} = 223$  pm). Thus, the Bi–C<sub>1</sub> distances are elongated in the row of the (C<sub>5</sub>Me<sub>5</sub>)BiX<sub>2</sub> compounds from X = Cl via X = Br to X = I. For the (C<sub>5</sub>H<sub>5</sub>)BiX<sub>2</sub> complexes such elongation is expressed very weakly. For both rows of the (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> compounds an elongation of the Bi–X distances, an increase of the sum of angles at the bismuth center (Bi<sup>sum</sup>), and an increase in pyramidalization with increasing ring and halogen sizes are observed. The elongation of the Bi–Z distance with increasing halogen size for complexes with R = H in the C<sub>5</sub>R<sub>5</sub> ring leads to an increase in the β angle (Table 3) and thus, to a lower (π)-coordination mode ( $\eta^1$ ). For the (C<sub>5</sub>Me<sub>5</sub>)BiX<sub>2</sub> complexes such regularity is expressed weakly. Thus, the dihalides show a different bismuth-ring coordination than the related dications.

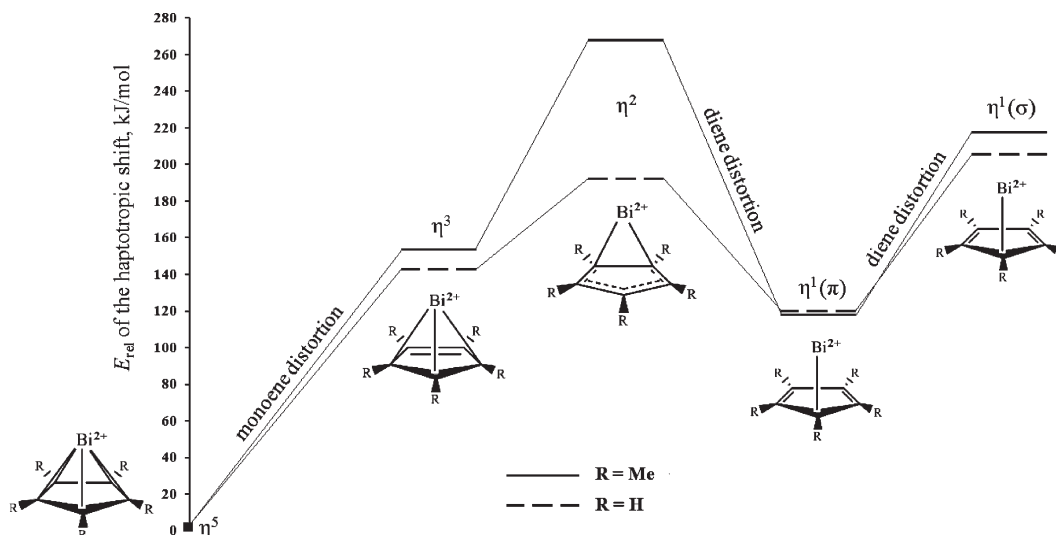
The interactions of the bismuth atom with the C<sub>2</sub> and C<sub>5</sub> carbons are not regarded as bonding. The distances of C<sub>2</sub>–C<sub>3</sub> and C<sub>4</sub>–C<sub>5</sub> show a slight diene distortion of the C<sub>5</sub>R<sub>5</sub> ring. The C<sub>5</sub>R<sub>5</sub> rings are attached via a  $\eta^1(\pi)$ -bonding mode, Bi–C<sub>1</sub>. To answer the question “what kind of type is the Bi–C<sub>1</sub> bond: ionic, covalent, or non-bonded?”, to obtain an insight into the electronic influence of halide ions on the bismuth–cyclopentadienyl bonds, and to evaluate the nature of these bonds, the natural bond orbital (NBO) analysis was performed (Table 4).

The natural population analysis (NPA) of the cyclopentadienyl bismuth(III) dihalides shows that the bismuth atom does not have an idealized 6s<sup>2</sup>6p<sup>0</sup> electronic configuration (in the <sup>1</sup>S ground state) but has a partial occupied s<sup>a</sup>p<sup>b</sup>-hybrid (*a*, *b* > 1) with increased electron density in the 6p orbitals. In accordance with the NEC (Table 4) the 6s electrons of Bi are almost completely localized; therefore, the contribution to covalent attraction is mainly due to participation of its 6p orbitals.

The positive partial charge is located on the bismuth atom and is far less than its chemical valence of +3 in the ionic model. Most of the negative charges in C<sub>5</sub>R<sub>5</sub> ring are located on the C<sub>1</sub> carbon (~−0.55 [R = H], ~−0.30 [R = Me]). It makes the charge transfer between the C<sub>1</sub> carbon atom and the bismuth ion and proves the existence of the sole Bi–C<sub>1</sub> coordination bond. In addition, the natural population analysis reveals a predominantly ionic character of the Bi–C<sub>1</sub> bond for (C<sub>5</sub>R<sub>5</sub>)BiCl<sub>2</sub> (~54% ionic character according to NPA charges) and a predominantly covalent character of the Bi–C<sub>1</sub> bond for the (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> compounds (~47% [X = Br], ~40% [X = I]).

A bonding population analysis displays overlap populations of approximately 0.35 between the bismuth center and the C<sub>1</sub> carbon atom in these compounds. WBI values for the Bi–C<sub>1</sub> bond indicate the single bond character and comparatively weak covalent interactions (accordingly a weak overlap population) for the (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> (X = Cl, Br) compounds. Accordingly, stronger interactions are observed for X = I. Since, the Bi–C<sub>1</sub> bond is polar and strongly polarized toward the C<sub>1</sub> carbon atom (~70%), the bond order should have a value less than one. The localized NBO Lewis-description ( $\rho_L$ ) illustrates the high accuracy of the calculation models.

On the basis of natural hybrid orbitals (NHO), the Bi–C<sub>1</sub> bond mainly forms from p-orbitals of both atoms. The NBO analysis for (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> finds the voluminous sp<sub>y</sub>-hybridized lone pair orbital localized at the bismuth atom. This lone pair is mostly of s-type and has a high orbital occupancy. The large contribution of the s-orbital in the lone pair indicates that compounds of type (C<sub>5</sub>R<sub>5</sub>)

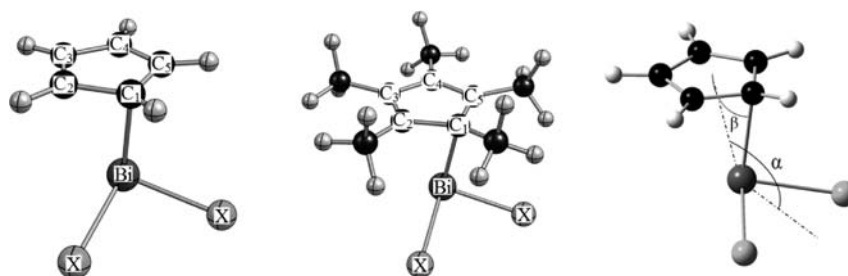


**Figure 6.** Relative energies of the  $C_5R_5$ -Bi bond hapticity changes ( $\eta^3 \rightarrow \eta^2 \rightarrow \eta^1$ ) in the model compounds  $(C_5R_5)Bi^{2+}$  ( $R = H, Me$ ) relative to  $\eta^5$ -bonded ring  $C_5R_5$  ( $R = H, Me$ ) to the bismuth center [MP4(SDQ)/BS-II//PBE0/BS-I].

**Table 3.** Selected Geometrical Parameters of  $(C_5R_5)BiX_2$  ( $R = H, Me; X = Cl, Br, I$ ) Optimized at the PBE0/BS-I Level of Theory<sup>a</sup>

complex	Bi-Z	Bi-C <sub>1</sub>	Bi-C <sub>2,5</sub>	C <sub>1</sub> -C <sub>2</sub> , C <sub>1</sub> -C <sub>5</sub>	C <sub>2</sub> -C <sub>3</sub> , C <sub>4</sub> -C <sub>5</sub>	C <sub>3</sub> -C <sub>4</sub>	Bi-X	Bi <sup>sum</sup>	$\alpha$	$\beta$
$(C_5H_5)BiCl_2$	253.0	237.0	270.1	144.4	138.5	141.9	247.4	293.3	132.2	83.1
$(C_5Me_5)BiCl_2$	247.5	237.3	267.7	145.8	139.3	143.3	250.1	293.5	133.8	80.1
$(C_5H_5)BiBr_2$	253.6	237.1	270.7	144.5	138.4	142.1	263.3	295.7	133.3	83.4
$(C_5Me_5)BiBr_2$	247.2	238.3	267.8	145.8	139.3	143.4	266.4	297.1	135.9	79.5
$(C_5H_5)BiI_2$	256.5	237.1	272.7	144.6	138.2	142.3	284.2	297.5	134.0	84.8
$(C_5Me_5)BiI_2$	248.7	239.2	269.2	145.9	139.2	143.5	287.6	299.1	137.3	79.8

<sup>a</sup> Bond lengths [pm], angles [deg].



**Figure 7.** PBE0/BS-I optimized structures of the complexes  $(C_5H_5)BiX_2$  (left) and  $(C_5Me_5)BiX_2$  (center) in bent conformation where the bismuth atom is bonded to the  $C_5R_5$  ring in a "monohapto" fashion. Right, the angles  $\alpha$  and  $\beta$  are mapped on the  $(C_5R_5)BiX_2$  complex.

$BiX_2$  have a relatively low Lewis basicity. In addition, the Lewis base strength slightly increases in the  $(C_5Me_5)BiX_2$  complexes from  $X = I$  via  $X = Br$  to  $X = Cl$  with a decrease of the s-character of the bismuth's lone pair. For the  $(C_5H_5)BiX_2$  complexes such regularity is not obvious. Also, the lone pair of p-type ( $\sim 95\%$ ) can be found on the  $C_1$  carbon atom for a predominantly ionic character of the Bi-C<sub>1</sub> bond (lone pairs of halogen atoms we do not discuss here). The exception is  $(C_5Me_5)BiBr_2$  with a more covalent character of the Bi-C<sub>1</sub> bond. Here, according to a NBO analysis, there is also the lone pair of p-type on the  $C_1$  carbon atom.

In this Bi-C<sub>1</sub> interaction these lone pairs contribute differently. Thus, the lone pair of the  $C_1$  carbon atom interacts with anti-bonding orbitals located at the metal center, which makes the main contribution to the Bi-C<sub>1</sub> interaction: delocalization  $\{E(2)\}$  from the lone pair orbital of  $C_1$  into Bi unoccupied 6p-orbitals. Another, more important delocalization could be obtained from

the interaction between lone pairs of the bismuth center and the  $C_1$  carbon atom. Other delocalizations have only minor contributions.

Here, the behavior of valence and frontier MOs was examined by the canonical MO theory. In this way, the MO construction of some important orbitals was performed and the interelectronic effects in the  $(C_5R_5)BiX_2$  complexes ( $R = H, Me; X = Cl, Br, I$ ) were studied (Table 5, Figure 8). The results of MO approximation indicate that the non-degenerate bonding D and C types of orbitals representing HOMO and HOMO-1 are of  $\pi$ -type. They are formed from the contributions of AOs of the  $C_5R_5-X_2$  system and the bismuth valence 6p<sub>x,z</sub> set. The bonding HOMO-3 (denoted B) corresponds to the space-filling sp<sub>y</sub>-hybridized bismuth's lone pair. The major contribution to this comes from the bismuth 6s-MO. The bonding A MO is formed from the contributions of the  $C_5R_5-X_2$  AOs and the bismuth valence 6s AO. The bonding MOs, in which two electrons, each, are



**Table 4.** Important Calculated Values for the Complexes Obtained from the NBO Analysis at the MP2(full)/BS-II//PBE0/BS-I Level

parameter	(C <sub>5</sub> H <sub>5</sub> )BiX <sub>2</sub>			(C <sub>5</sub> Me <sub>5</sub> )BiX <sub>2</sub>		
	Cl	Br	I	Cl	Br	I
<i>n</i> VE <sup>a</sup>	12	12	12	12	12	12
NEC of Bi <sup>b</sup>	6s <sup>1.86</sup> 6p <sup>1.49</sup>	6s <sup>1.87</sup> 6p <sup>1.68</sup>	6s <sup>1.87</sup> 6p <sup>1.90</sup>	6s <sup>1.86</sup> 6p <sup>1.50</sup>	6s <sup>1.88</sup> 6p <sup>1.67</sup>	6s <sup>1.89</sup> 6p <sup>1.87</sup>
<i>Q</i> <sub>NPA</sub> <sup>c</sup>						
on Bi	+1.618	+1.420	+1.189	+1.614	+1.423	+1.203
on C <sub>1</sub>	-0.549	-0.543	-0.544	-0.312	-0.296	-0.284
<i>i</i> <sub>C<sub>5</sub>R<sub>5</sub>-Bi</sub> <sup>d</sup>	53.9	47.3	39.6	53.8	47.4	40.1
overlap/WBI <sup>e</sup>	0.370/0.476	0.345/0.487	0.352/0.510	0.342/0.490	0.340/0.494	0.337/0.509
NHO at Bi-C <sub>1</sub> <sup>f</sup>						
Bi		s <sup>5.39%</sup> p <sup>94.18%</sup>	s <sup>5.54%</sup> p <sup>94.03%</sup>			s <sup>5.61%</sup> p <sup>94.03%</sup>
C <sub>1</sub>		s <sup>6.60%</sup> p <sup>93.34%</sup>	s <sup>7.01%</sup> p <sup>92.94%</sup>			s <sup>5.77%</sup> p <sup>94.18%</sup>
occupancy		1.626	1.651			1.637
100 C <sub>Bi</sub>   <sup>2g</sup>		27.03	28.26			29.77
LP NHO <sup>h</sup> at Bi		s <sup>90.16%</sup> p <sup>9.83%</sup>	s <sup>90.24%</sup> p <sup>9.75%</sup>	s <sup>90.13%</sup> p <sup>9.86%</sup>	s <sup>90.60%</sup> p <sup>9.39%</sup>	s <sup>91.09%</sup> p <sup>8.91%</sup>
occupancy		1.997	1.997		1.995	1.995
LP NHO at C <sub>1</sub>		s <sup>4.60%</sup> p <sup>95.33%</sup>		s <sup>4.86%</sup> p <sup>95.08%</sup>	s <sup>5.05%</sup> p <sup>94.89%</sup>	
occupancy		1.211		1.203	1.189	
<i>E</i> (2) <sup>i</sup>	273.28		277.77	310.58		
<i>E</i> (2) <sup>j</sup>	8.02		7.70	7.51		
<i>ρ</i> <sub>L</sub> <sup>k</sup>	99.0	99.4	99.5	99.0	99.2	99.4

<sup>a</sup> Number of valence electrons. <sup>b</sup> Natural electron configuration. <sup>c</sup> Natural charges. <sup>d</sup> Degree of ionicity of C<sub>5</sub>R<sub>5</sub>-Bi bonding [%]. <sup>e</sup> Atom-atom overlap-weighted NAO bond order and Wiberg bond index for the Bi-C<sub>1</sub> interaction. <sup>f</sup> Natural hybrid orbital at the Bi-C<sub>1</sub> bond. <sup>g</sup> Polarization toward Bi [%]. <sup>h</sup> Lone pair natural hybrid orbital. <sup>i</sup> Delocalization energy of LP<sub>C<sub>1</sub></sub> into bismuth 6p-orbital [kcal/mol]. <sup>j</sup> Delocalization energy of LP<sub>Bi</sub> into carbon (C<sub>1</sub>) LP-orbital [kcal/mol]. <sup>k</sup> Accuracy of calculation model [%].

**Table 5.** Selected Important Calculated Values for the Complexes Obtained at the MP4(SDQ)/BS-II//PBE0/BS-I Level

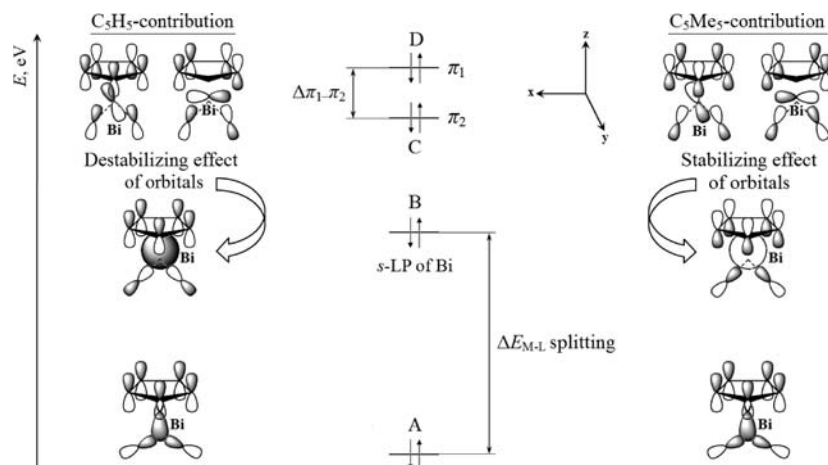
parameter	(C <sub>5</sub> H <sub>5</sub> )BiX <sub>2</sub>			(C <sub>5</sub> Me <sub>5</sub> )BiX <sub>2</sub>		
	Cl	Br	I	Cl	Br	I
<i>E</i> (LUMO)	0.48	0.38	0.12	0.74	0.64	0.40
<i>D</i> (HOMO)	-9.48	-9.34	-9.15	-8.60	-8.54	-8.44
<i>C</i>	-9.80	-9.63	-9.31	-8.93	-8.83	-8.67
<i>B</i>	-11.02	-10.29	-9.57	-10.48	-9.81	-9.12
<i>A</i>	-15.09	-14.85	-14.63	-13.53	-13.33	-13.16
<i>d</i> <sub>C<sub>5</sub>R<sub>5</sub>-X<sub>2</sub></sub> <sup>a</sup>	385.9	396.1	411.0	386.2	397.6	414.2
<i>Δ</i> <sub>LUMO-B</sub> <sup>b</sup>	11.50	10.67	9.69	11.23	10.45	9.52
<i>Δ</i> <sub>E<sub>HOMO</sub>-LUMO</sub> <sup>c</sup>	9.96	9.72	9.27	9.34	9.18	8.84
<i>Δ</i> <sub>E<sub>M-L</sub></sub> <sup>d</sup>	4.07	4.56	5.06	3.05	3.52	4.04
<i>Δ</i> <sub>π<sub>1</sub>-π<sub>2</sub></sub> <sup>e</sup>	0.32	0.29	0.16	0.33	0.29	0.23
<i>Δ</i> <sub>E<sub>h,a</sub></sub> <sup>f</sup>	-824	-792	-753	-878	-847	-805
<i>λ</i> <sup>g*</sup>	290	310	351	324	344	372
<i>μ</i> <sup>h</sup>	5.50	5.04	4.65	7.05	6.98	6.97

<sup>a</sup> Interplane distance between the C<sub>5</sub>R<sub>5</sub> plane and X-X line [pm]. <sup>b</sup> Stabilization energy between LUMO and B MO [eV]. <sup>c</sup> Energy of the HOMO-LUMO-gap [eV]. <sup>d</sup> Splitting energy with metal contribution [eV]. <sup>e</sup> Stabilization energy between D and C MOs [eV]. <sup>f</sup> Heterolytic association energy [kJ/mol]. <sup>g\*</sup> Values of the S<sub>0</sub> → S<sub>1</sub> transition (HOMO → LUMO excitation) [nm] computed at the TD-PBE0/BS-II//PBE0/BS-I level. <sup>h</sup> Dipole moment [Debye].

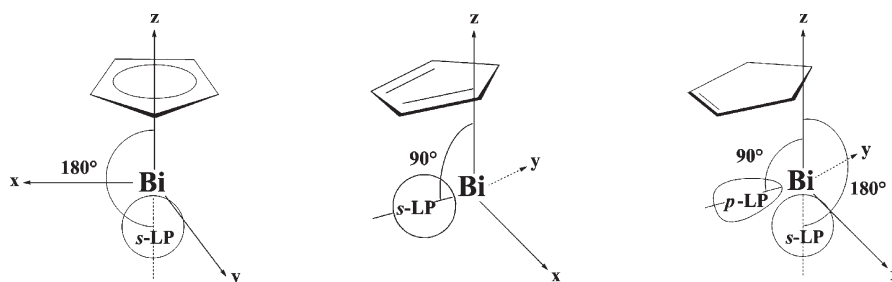
donated from halogen groups are not discussed by us and not shown in Figure 8. As a result, the (C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> compounds with a realized 12 valence electron situation are isoelectronic to groups 13 and 14 cyclopentadienyl compounds of the types (C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>E<sup>+</sup> and (C<sub>5</sub>R<sub>5</sub>)EX<sub>3</sub>, respectively. In addition, the canonical MO theory here evidence results of the NBO analysis for the [(C<sub>5</sub>R<sub>5</sub>)Bi]<sup>q+</sup> complexes.

The testing of the interelectronic behavior of the (η<sup>1</sup>-C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> complexes starts with an examination of the interactions of important bonding orbitals (*A*, *B*, *C*, and *D*; Table 5). Thus, the interplane distances *d*<sub>C<sub>5</sub>R<sub>5</sub>-X<sub>2</sub></sub> are much longer than the corresponding sums of van der Waals (vdW) radii in the (η<sup>1</sup>-C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> complexes, that is, vdW repulsion outweighs vdW attraction. The first

type of stabilization can be found from the examination of LUMO-B interactions, that is, a low-lying π\* orbital of ligands and a MO with metal s-like character, respectively. We can see (Table 5) that compounds with more covalent Bi-C<sub>1</sub> bonds have a smaller energy difference, which means a stronger mixing and more stabilized B MO (LP of Bi). The B MO is more destabilized in compounds having lone pairs at the Bi and the C<sub>1</sub> carbon atom, which can participate in different delocalizations among themselves. The Δ*E* (*E*<sub>HOMO</sub> - *E*<sub>LUMO</sub>) values of the (η<sup>1</sup>-C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> complexes, resulting from the Koopman's free-electron molecular-orbital approximation (FE-MO) approach, show the general kinetic stabilization of molecules, which decreases with increasing halogen size. The energy of metal-ligand splitting Δ*E*<sub>M-L</sub>, which can be denoted the energy of Jahn-Teller splitting, characterizes vdW repulsion energy in molecule. The higher this energy is, the less stable the compound is. The repulsion energy increases with increasing halogen size and decreases with increasing ring size. The different orbital orientation in the (η<sup>1</sup>-C<sub>5</sub>R<sub>5</sub>)BiX<sub>2</sub> complexes with R = H and R = Me clearly expresses this regularity and confirms that the compounds with the sterically better protected C<sub>5</sub>Me<sub>5</sub> ligand have less repulsion forces and are more stabilized (Figure 8). Besides, the electrostatic attraction between bismuth and the C<sub>5</sub>Me<sub>5</sub> ring obtained from the electric charge differences provides a stronger stabilizing force than for the unalkylated cyclopentadienyl ring. The smaller energy difference between C and D π-orbitals indicates that these MOs have stronger covalent attraction of the π(C<sub>5</sub>R<sub>5</sub>)-π(Bi) interaction. The corresponding decrease of Δπ<sub>1</sub>-π<sub>2</sub> values in a direction of the compounds with a predominantly covalent Bi-C<sub>5</sub>R<sub>5</sub> bonding can be observed. Thus, the heterolytic association energies decrease with increasing halogen size and increase with increasing ring size. The dipole moment decreases with increasing halogen size. The peralkylated cyclopentadienyl derivatives of the complexes are more polar than unalkylated ones.



**Figure 8.** Slice from the qualitative correlation MO-diagram of the filled valence orbital interactions of  $X_2\text{Bi}-\text{C}_5\text{R}_5$  in the  $(\eta^1-\text{C}_5\text{R}_5)\text{BiX}_2^{2+}$  complexes.



**Figure 9.** Orientations of the lone pairs in  $x, y, z$  dimension coordinates for  $(\eta^5-\text{C}_5\text{R}_5)\text{Bi}^{2+}$  (left),  $(\eta^1-\text{C}_5\text{R}_5)\text{BiX}_2$  (center;  $X_2$  part is not shown), and  $(\eta^3-\text{C}_5\text{R}_5)\text{Bi}$  (right). The lone pairs show the main contribution in their orbitals.

TD-PBE0 calculations for the  $(\text{C}_5\text{R}_5)\text{BiX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) complexes having the sole hybridized lone pair of  $s$ -type localized on bismuth show that the most intense  $S_0 \rightarrow S_1$  transition corresponds to a  $\text{HOMO} \rightarrow \text{LUMO}$  excitation with  $\pi \rightarrow n_{\text{Bi}(p)}$  character. This lowest energy transition can be described as ligand–metal charge transfer (LMCT excitation) arising from the electron move from a predominantly ligand  $\pi$ -orbital to a predominantly metal  $p$ -orbital. Such a type of transition promotes the reduction of the bismuth center and a formation of a new type of the lowest-valent bismuth compounds in further synthetic reactions. In addition, the energy of the  $S_0 \rightarrow S_1$  transition decreases with increasing ring and halogen sizes.

### Summary and Outlook

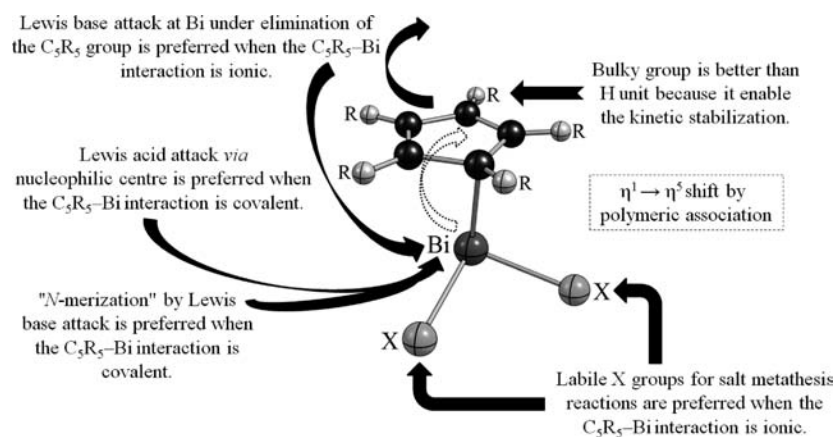
The orientation of the  $s$ - and  $p$ -lone pairs on the bismuth center in regard to the cyclopentadienyl ring, as well as the valence electron number, is responsible for the  $\eta^x$ -hapticity of the  $\text{C}_5\text{R}_5$  ligand and determines the structure and stability of the complexes (Figure 9).

Here, we find that 12 and 8 VE situations correspond to the compounds of type  $(\eta^1-\text{C}_5\text{R}_5)\text{BiX}_2$  and  $(\eta^5-\text{C}_5\text{R}_5)\text{Bi}^{2+}$ , respectively, whereas the 10 VE situation corresponds to the kinetically less stable  $(\eta^3-\text{C}_5\text{R}_5)\text{Bi}$  compounds. Besides, the  $\eta^1(\pi)$ -coordination (LP is of  $90^\circ$  to  $z$ -axes) of the  $\text{C}_5\text{R}_5$  ring to Bi in the cyclopentadienyl bismuth(III) dihalides (12 VEs) should be realized mainly in solution, whereas in solid state such compounds should associate. A haptotropic rearrangement in the  $\eta^5$ -coordination (LP is of

$180^\circ$  to  $z$ -axes) is possibly due to an equilibrium distribution of electronic density on the metal center (Figure 9, Scheme 3).

The complexes of type  $(\text{C}_5\text{R}_5)\text{BiX}_2$  enable three potential regions for an attack: the bismuth center, the halogen  $X$  groups, and the  $\text{C}_5\text{R}_5$  ring (Scheme 3). The reactivity of complexes of this type depends strongly on the nature of both the  $\text{C}_5\text{R}_5$  and  $X$  ligands and the nature of the  $\text{C}_5\text{R}_5\text{-Bi}$  bonding. First, the  $(\text{C}_5\text{R}_5)\text{BiX}_2$  complexes may react via a space-filling lone pair orbital of  $s$ -type localized at the bismuth atom as Lewis base ( $\sigma$ -donor), donating electrons to the empty  $p$ -orbitals of trigonal-planar molecules of the group 13  $p$ -elements ( $\text{EIR}_3$ ) or to the empty  $d$ -orbitals of transition metal complex fragments, to form Lewis acid–base adducts of type  $[(\text{C}_5\text{R}_5)\text{BiX}_2]\text{-LA}$  ( $\text{LA} = \text{Lewis acid}$ ). Here, the covalent  $\text{C}_5\text{R}_5\text{-Bi}$  bonding with only one LP on Bi looks more reasonable. By Lewis base attack on such covalent bonded molecules “ $N$ -merization” of the bismuth center can be preferred, resulting, for example, in the dipnictene compounds of type  $[(\text{C}_5\text{R}_5)\text{Bi}]_n$ . Corresponding terphenyl derivatives have already been characterized.<sup>16</sup> Second, the  $(\text{C}_5\text{R}_5)\text{BiX}_2$  complexes may react via valence  $p$ -orbitals as Lewis acids ( $\pi$ -acceptor), exchanging the chlorine electrons for the electrons of the incoming groups (salt metathesis reactions), to form the molecules of type  $(\text{C}_5\text{R}_5)\text{Bi}(\text{IG})_2$  ( $\text{IG} = \text{incoming group}$ ). The alkyl or silyl ligands of the

(16) (a) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357–3367. (b) Wolf, R.; Fischer, J.; Fischer, R. C.; Fettingner, J. C.; Power, P. P. *Eur. J. Inorg. Chem.* **2008**, 2515–2521.

Scheme 3. Further Behavior and Capabilities of the  $(C_5R_5)BiX_2$  Complexes

alkali metal (M) coordination compounds  $[MR_a(R_b)_3]$ , where  $R_a = C, Si, Ge$ ;  $R_b =$  organic group] can act as incoming groups. For these aims, the ionic  $C_5R_5$ -Bi bonding with two LPs localized on bismuth and  $C_1$  carbon of the  $C_5R_5$  ring looks more reasonable. Besides, here the  $C_5R_5$ -group allows for a possibility of its exchange  $[-(C_5R_5)M, -MX]$  for the nucleophilic incoming group of the Lewis base to form the compounds of type  $Bi_x(IG)_y$ . Finally, it is necessary to remark that the ionic  $C_5R_5$ -Bi bonding can work as one of the reasons of forming associated structures.

**Acknowledgment.** We are grateful to the Graduate College 850 Molecular Modeling of the German Research Foundation (DFG) for financial support. We also thank Junior Prof. Dr. A. Auer, TU Chemnitz, for helpful discussions.

**Supporting Information Available:** Zero-point corrections to the energies (ZPE) computed at the HF/BS-II//PBE0/BS-I level and vertical excitation energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.