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[10] a) Crystallographic data for **2** ($C_{26}H_{58}Cu_2Li_2N_2O_4$, $M_r = 603.7$): monoclinic, space group $P2_1/n$, $a = 1208.7(1)$, $b = 1497.9(1)$, $c = 1941.8(2)$ pm, $\beta = 91.10(1)^\circ$, $V = 3515.1(5) \times 10^{-30}$ m^3, $Z = 4$, $\rho_{calcd} = 1.141$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.237$ mm^{-1}. Data were collected with a STOE IPDS array detector with $Mo_{K\alpha}$ radiation and a graphite monochromator at $T = 120(2)$ K. Of 27 126 reflections measured ($2 < \theta < 26^\circ$), 6427 were independent ($R_{int} = 0.0803$). The structure was solved by direct methods (SHELXS-97)[10c] and refined against F^2 with all reflections (SHELXL-97).[10d] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined with isotropic temperature factors. Parameters of the weighting scheme calculated by the program: 0.0449, 33.6513; $wR2 = 0.2052$, $R1 = 0.0756$ (for 4128 reflections with $I > 2\sigma(I)$), GOF = 1.073; in total 339 refined parameters; b) crystallographic data for **3** ($C_{35}H_{80}CuLi_2N_7O_2$, $M_r = 708.48$): monoclinic, space group $P2_1/c$, $a = 916.9(1)$, $b = 1498.5(1)$, $c = 1661.8(2)$ pm, $\beta = 100.95(1)^\circ$, $V = 2241.8(3) \times 10^{-30}$ m^3, $Z = 2$, $\rho_{calcd} = 1.050$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.521$ mm^{-1}. Data were collected with a STOE IPDS array detector with $Mo_{K\alpha}$ radiation and a graphite monochromator at $T = 190(2)$ K. Of 17 246 reflections measured ($2 < \theta < 26^\circ$), 4324 were independent ($R_{int} = 0.0443$). The structure was solved by direct methods (SIR92)[10e] and refined against F^2 with all reflections (SHELXL-97).[10d] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined with isotropic temperature factors. Parameters of the weighting scheme calculated by the program: 0.1576, 0.4352; $wR2 = 0.2553$, $R1 = 0.0787$ (for 2804 reflections with $I > 2\sigma(I)$), GOF = 1.093; in total 242 refined parameters. The CN group is disordered about the center of symmetry. The disordered *tert*-butyl group was refined in two positions in the ratio 62:38. Unrefined disorder in the atoms of the solvent molecules is reflected in large thermal ellipsoids. All calculations were made on a DEC Alpha Station with the VMS operating system;[10f–h] c) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, **1997**; d) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen **1997**; e) M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389–393; f) A. L. Spek, Platon 94, Program for Geometrical Analysis of Crystal Structures, Utrecht, **1994**; g) E. Keller, SCHAKAL-88B, A FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models, Freiburg, **1988**; h) crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 103. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Unusual Five-Center, Four-Electron Bonding in a Rhodium–Bismuth Complex with Pentagonal-Bipyramidal Geometry**

Zhitao Xu and Zhenyang Lin*

Pentagonal coordinated molecules always provide very interesting bonding features. For example, in $[In\{Mn(CO)_4\}_5]^{2-}$ (**1**),[1] the indium atom and five manganese atoms lie almost in a plane. The bonding was elegantly described as an In^{3+} ion that binds the pentagonal Mn_5 ring.[2] In the pentagonal ring there are five two-center, two-electron bonds. Each manganese center satisfies the 18-electron rule. In the recently synthesized pentagonal $[Ni_5(\mu_5\text{-}S)(\mu_2\text{-}S\mathit{t}Bu)_5]^-$ cluster (**2**),[3] the bonding has been described as having a six-center, ten-electron bond in the central $Ni_5(\mu_5\text{-}S)$ unit.[4] The cluster has a total of 70 valence electrons and actually conforms to the 16-electron rule. Very recently Ruck reported the synthesis and structural characterization of, and calculations on, a structurally remarkable ternary subhalide of bismuth containing the discrete rhodium–bismuth molecular complex $[\{RhBi_7\}Br_8]$ (**3**).[5] In this complex the seven bismuth atoms are bonded to the central rhodium atom in a regular pentagonal-bipyramidal arrangement. The eight bromine atoms bridge the apical and equatorial bismuth atoms in a

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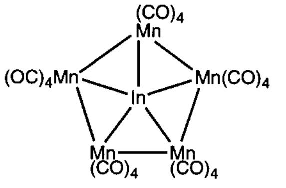

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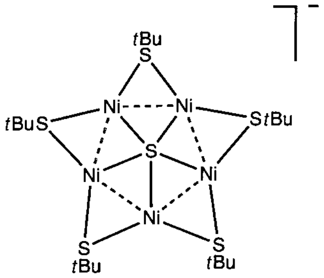

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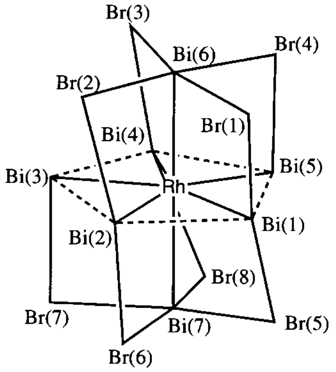

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μ_2-mode in which four are above the equatorial plane and the other four below the plane. In such an arrangement, two of the five equatorial bismuth atoms are coordinated to only one Br atom.

The results of band-structure calculations by Ruck[5] show that the interactions between the central Rh atom and the coordinated Bi atoms are almost exclusively bonding, the Bi–Bi interactions between the equatorial atoms are all bonding while those between the equatorial and the apical Bi atoms are non-bonding. It was also noted that the Rh–Bi bonds within the equatorial plane are weaker than those along the axis. These weaker Rh–Bi bonds are compensated by an additional, homoatomic bond in the five-membered ring. Indeed, the average Bi–Bi nearest-neighbor distance of 3.22 Å in the Bi_5 ring is longer than the sum of two covalent radii (2.92 Å) but shorter than the recently reviewed closed-shell Bi–Bi interaction distances (3.50–3.80 Å).[6] This bonding feature is very intriguing. What does this additional homoatomic bond look like? What is the overall electronic structure of this molecular cluster complex? In this communication we attempt to provide a clearer picture of the bonding based on the simple orbital interaction concept to describe the intriguing electronic structure of this molecular complex with the aid of ab initio molecular orbital calculations.

Full geometry optimizations were performed at both the HF and B3LYP levels (see Experimental Section for details). The optimized structural parameters are listed in Table 1, and where reported, experimental values are included for comparison. In view of the size of the metal cluster, the calculated structural parameters agree reasonably well with the experimental values. Overall, it seems that the B3LYP results agree better. The agreement could be improved if we increased the size of the basis sets by adding polarization functions for the Br atoms. It should also be noted that our calculation is for an isolated cluster. The close packing effect, as noted by Ruck,[5] certainly influences the geometry of the cluster. An exact comparison is therefore not possible. However, our aim is to provide a qualitative bonding picture to understand the intriguing feature of the electronic structure.

Table 1. Selected bond lengths [Å] and bond angles [°] of the $[\{RhBi_7\}Br_8]$ molecular complex from both calculation and experimental results.

	HF	B3LYP	EXP
Rh–Bi(1)	2.734	2.735	2.732
Rh–Bi(2)	2.734	2.735	2.738
Rh–Bi(3)	2.751	2.743	2.749
Rh–Bi(4)	2.719	2.732	2.742
Rh–Bi(5)	2.751	2.743	2.719
Rh–Bi(6)	2.831	2.793	2.735
Rh–Bi(7)	2.831	2.793	2.719
Bi(1)–Bi(2)	3.256	3.285	3.266
Bi(2)–Bi(3)	3.183	3.171	3.228
Bi(3)–Bi(4)	3.235	3.232	3.191
Bi(4)–Bi(5)	3.235	3.232	3.203
Bi(5)–Bi(1)	3.183	3.171	3.194
Bi(1)–Bi(6)	3.950	3.913	3.813
Bi(1)–Bi(7)	3.934	3.898	3.882
Bi(6)–Br(1)	3.175	3.077	2.897
Bi(6)–Br(2)	2.796	2.871	2.876
Bi(6)–Br(3)	2.900	2.949	2.962
Bi(6)–Br(4)	3.332	3.197	3.010
Bi(1)-Rh-Bi(2)	73.10	73.80	73.32
Bi(2)-Rh-Bi(3)	70.95	70.74	71.08
Bi(3)-Rh-Bi(4)	72.50	72.36	71.05
Bi(4)-Rh-Bi(5)	72.50	72.36	71.81
Bi(5)-Rh-Bi(1)	70.95	70.74	71.73
Bi(6)-Rh-Bi(7)	179.49	179.67	178.91

Before continuing our discussion of the calculation results, we examine the relevant electron count of the complex. In the molecular complex, none of the seven Bi atoms has a terminal ligand. One can assume that each Bi atom has one lone pair of electrons whose maximum electron density is pointing away from the central Rh atom. In other words, each Bi atom has a lone pair (two electrons) that is not involved in the Rh–Bi or Bi–Bi bonding. The assumption should be reasonable in view of the fact that many naked Bi clusters (e.g., Bi_5^{3+} and Bi_8^{2+}),[7] which conform to Wade's electron counting rules, have this feature in their electronic structures. Excluding these lone pair electrons and those electrons involved in the metal–bromide bonding, we can immediately have a valence electron count of 22 for the metal complex. These 22 metal electrons are responsible for the Rh–Bi and Bi–Bi interactions.

For a Rh complex in a three-dimensional ligand environment, one would expect it to conform to the 18-electron rule. An 18-electron regular ML_7 pentagonal-bipyramidal transition metal complex would normally have seven metal–ligand bonds (14 electrons) and two non-bonding d electron pairs (4 electrons in the d_{xz} and d_{yz} orbitals if the axis of the pentagonal-bipyramid is defined as the z axis). In the Rh complex, we would expect a similar bonding picture in which fourteen electrons are required to form the seven Rh–Bi σ-bonds (two axial and five equatorial bonds) and four electrons occupy the two non-bonding d_{xz} and d_{yz} orbitals. The remaining four electrons can be considered to be involved in the Bi–Bi interactions. Since the distances between the apical Bi and the equatorial Bi atoms are significantly longer than those between the adjacent Bi atoms in the equatorial plane, the remaining 4 electrons can be assigned to the Bi–Bi bonding among the 5 equatorial Bi atoms. This unprecedented five-center, four-electron bond is thus responsible for the observed Bi–Bi bonding in Ruck's band structure calculations.

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At this stage, one would ask how the five-center, four-electron bond is formed. Examining carefully the local coordination environment of each Bi center in the equatorial plane, we find that each Bi atom has one p orbital not used in the Bi–Br and Bi–Rh bonding. This unused p orbital is lying on the equatorial plane and is tangential to the pentagonal ring. The symmetry-adapted linear combinations of five such tangential p orbitals (each Bi atom contributes one) can be easily derived from group theory.[8] A pictorial illustration of the five symmetry-adapted linear combinations is shown in Figure 1. One can see that there are two bonding and three antibonding orbitals in the five linear combinations. Occupation of the two bonding orbitals (e_2 in a five-fold rotational point group) gives the five-center, four-electron bonding picture.

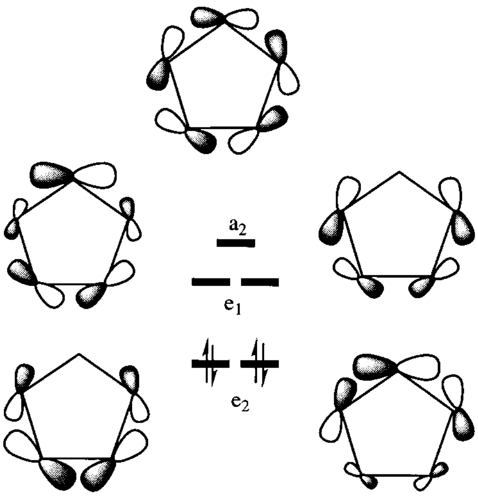

Figure 1. Schematic illustration of the five symmetry-adapted linear combinations based on the five tangential p orbitals of the Bi atoms. The relative locations of the MO energy levels are given.

Indeed, the two tangential Bi–Bi bonding molecular orbitals (e_2 in a five-fold rotational point group) are found from our ab initio molecular orbital calculations. Based on the B3LYP results, they are in the region of highest occupied molecular orbitals (HOMOs). Other molecular orbitals in the HOMO region also include those involving the seven Bi lone pairs pointing away from the Rh center. Figure 2 shows the spatial plots[9] of the two Bi–Bi bonding molecular orbitals obtained from the B3LYP calculations. These two molecular orbitals are mainly derived from the tangential p orbitals of the five equatorial Bi atoms, and the electron density is maximized between Bi–Bi bonds in the equatorial pentagonal ring. Slight mixings with orbitals from Br atoms and Rh can also be seen. The mixings are desirable, because Br atoms are π-donating ligands and Rh–Bi bonding orbitals (containing metal d orbitals) are low-lying and fully occupied. Ignoring the mixings, the overall features of these two Bi–Bi bonding molecular orbitals resemble the e_2 representations shown in Figure 1.

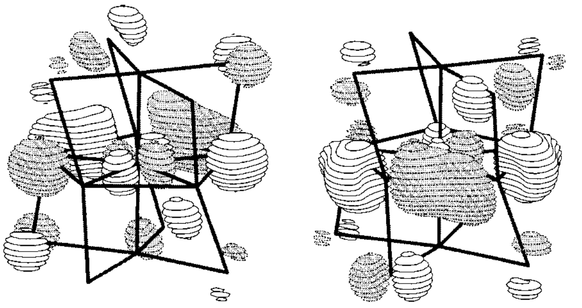

Figure 2. Spatial plots of the two Bi–Bi bonding molecular orbitals of the $[\{RhBi_7\}Br_8]$ molecular complex obtained from the results of B3LYP calculations.

A preliminary examination of the Laplacian of electron density ($\nabla^2\rho$) on the equatorial plane indicates that all Bi atoms have maximum electron density pointing away from the central Rh atom. This result gives support for the assumption that each Bi atom has one lone pair of electrons not participating in metal–metal bonding. Since the Laplacian plot gives the overall feature of the electron density, it does not correlate directly with the five-center, four-electron bond discussed above.

In summary, the bonding in the $[\{RhBi_7\}Br_8]$ complex can be described as follows: The complex has 22 valence electrons available for Rh–Bi and Bi–Bi bonding interactions. The Rh center satisfies the 18-electron closed-shell electronic requirement. The remaining four electrons are mainly responsible for the Bi–Bi bonding among the five Bi atoms in the equatorial plane. An unusual five-center, four-electron bond is discovered in this complex. The approach here is to consider the Rh–Bi interactions first. The Bi–Bi bonding interactions are then derived from the available orbitals of individual Bi fragments from their local metal–ligand coordination. This kind of "local metal frontier orbital" approach has proved extremely successful in understanding the metal–metal interactions of transition metal cluster complexes containing mainly π-donating ligands.[4, 10]

Experimental Section

Quasi-relativistic pseudopotentials of Stuttgart-type[11] were employed in our ab initio calculations. Full geometry optimizations were performed at both HF and B3LYP levels with the Gaussian 94 suite of programs.[12] The pseudopotential basis sets of the central Rh atom were described with (8s7p6d)/[6s5p3d], corresponding to a triple-ζ representation for the metal d orbitals. For the Bi atoms, basis sets with the polarized functions (4s4p1d)/[2s2p1d] were used, while for the Br atoms, basis sets of (4s5p)/[2s3p] were used. The total number of basis set functions used in the calculations was 215.

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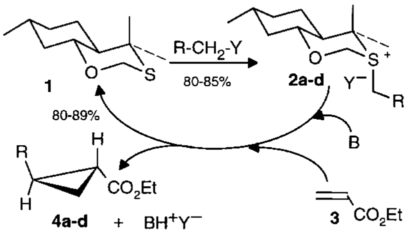
Two-Step Synthesis of *trans*-2-Arylcyclopropane Carboxylates with 98–100% *ee* by the Use of a Phosphazene Base

Arlette Solladié-Cavallo,* Ahn Diep-Vohuule, and Thomas Isarno

We found recently that oxathiane **1** (see Scheme 1) is a very efficient chiral auxiliary that allows the preparation of various pure *trans*-diarylepoxides in high yields (≈85%) and with high enantiomeric purities (98.5–99.9%).[1] We report here the extension of this method to the synthesis of disubstituted cyclopropanes.

Since the first Simmons–Smith reaction in 1958,[2] extensive work has been devoted to the synthesis of enantiomerically enriched polysubstituted cyclopropanes. Pure *trans*- (or pure *cis*-) disubstituted cyclopropanes with levels of enantioselectivity up to 93% have been obtained from *trans*- (or *cis*-) olefins by the use of stoichiometric quantities of an external chiral promoter and an excess of the preformed $Zn(CH_2I)_2 \cdot$ DME complex.[3] However, with catalytic amounts of a chiral promoter only 90% *ee* could be achieved.[4] Although styrene was converted into a *trans*-alkoxycarbonyl-substituted cyclopropane with 99% *ee* by adding only 1 mol% of a chiral copper catalyst,[5] an exotic and very hindered ester had to be used to obtain a *trans*/*cis* ratio of 94/6. Starting from the inexpensive and commercially available ethyl ester, low *trans*/*cis* diastereoselectivities (*trans*/*cis* ≈ 70/30) are obtained. Further difficulties arise from the fact that diazo reagents have to be used and that they have to be added slowly (over about 16 h for 0.02 mol) to avoid the formation of side products.[6, 7] Therefore, for large-scale preparations the sulfur ylide method might be more promising, as already stated by Corey.[8] However, until now the chirality had only been located on the olefinic moiety, and either yields[9] or diastereomeric excesses[10] were low. In the method described here the chirality is located at the sulfur center of the reagent, which is recoverable and can thus be reused (Scheme 1).



Scheme 1. Synthesis of cyclopropanes **4a–d**. **2a**: R = Ph, Y = TfO; **2b**: R = *p*-NCC_6H_4, Y = TfO; **2c**: R = *p*-*t*BuC_6H_4, Y = BF_4; **2c'**: R = *p*-*t*BuC_6H_4, Y = TfO; **2d**: R = 2-naphthyl, Y = BF_4; **4a**: R = Ph; **4b**: R = *p*-NCC_6H_4; **4c**: R = *p*-*t*BuC_6H_4; **4d**: R = 2-naphthyl. B = NaH, Et–P_2.[13]

(Arylmethyl)sulfonium salts **2a–d** were prepared in about 80–85% yield from RCH_2OH, Tf_2O, and pyridine in CH_2Cl_2[11] or from RCH_2Br $AgBF_4$. Only one diastereomer was detected by ^1H and ^{13}C NMR spectroscopy, and the axial position was assigned for the arylmethyl group in **2b–d** based on a comparison with spectra of the known **2a**.[12] The corresponding ylides were generated in situ with either NaH or $EtN{=}P(NMe_2)_2{-}N{=}P(NMe_2)_3$ ("Et–P_2")[13] as base (Tables 1 and 2). With NaH in THF at −30 °C full conversions were achieved, as seen from the ^1H NMR spectra of the crude product, but 24 to 76 hours were required. Whereas cyclopropane **4a** was isolated in high yield (83%) and with complete enantioselectivity (100% *ee*), **4b** and **4d** were obtained with slightly lower enantioselectivities (≈96% for **4b** and ≈95% for **4d**, Table 1). Only traces of the *cis* isomer of crude **4d** were detected, but about 15% of the *cis* isomer was observed for **4b**. Surprisingly, in the case of **4c**, although

Table 1. Synthesis of cyclopropanes **4a–d** from **2a–d** in THF at −30 °C with NaH as base.

4	R	c_{ylide} [M]	*t* [h]	Crude product *trans*/*cis*[a]	*trans*-**4** yield [%][b]	*trans*-**4** *ee* [%][c]	Reisolated **1** [%]
a	C_6H_5	0.22	24	95/5	83	**100**	89
b	*p*-NCC_6H_4	0.23	48	80/20	62	95.8	89
c	*p*-*t*BuC_6H_4	0.23	72	≥99/1	50	60.8	80
d	2-naphthyl	0.19	6	95/5	78	94.8	80

[a] Determined by ^1H NMR spectroscopy (200 MHz). [b] Not optimized. [c] Determined by chromatography on a chiral phase (see ref. [16] and the supporting information).

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