sistent with the solid-state structure. The downfield region of the $^{13}C\{^1H\}$ NMR spectrum consists of four signals at δ 161.9 (C2), 144.4 and 142.7 (C3 and C4), and 120.6 (C1). C2 appears as a doublet (J = 76.7 Hz) of triplets (J = 14.2 Hz), due to phosphorus coupling. The $^{31}P\{^1H\}$ NMR spectrum is an AX_2 (triplet/doublet) pattern, as expected for a planar metallacycle with a *mer* arrangement of phosphine ligands.

A comparison of the (oxapentadienyl)iridium chemistry (Schemes I and II) with that of the analogous (thiapentadienyl)iridium system (Schemes III and IV) reveals some interesting differences. The oxapentadienyl chemistry appears to be driven by the favorable thermodynamics of forming C–O double bonds; hence, the final products are carbonyl-containing ring compounds. In contrast, C–S double bonds are relatively weak[21] and, as a result, all of the products in the (thiapentadienyl)iridium reaction systems contain C–S single bonds.[22] In both systems, however, five-membered rings are thermodynamically preferred over six-membered rings.

In summary, we have shown that treatment of (Cl)Ir(PR_3)$_3$ (R = Me, Et) with potassium thiapentadienide leads to the production of ((1,2,5-η)-5-thiapentadienyl)Ir(PR_3)$_3$ complexes. While the PMe_3 compound is stable in solution, its PEt_3 analogue undergoes intramolecular C–H bond activation processes, producing five- and six-membered thiairidacycles. The further reactivity of these novel species is currently under investigation in our laboratories.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8520680 and CHE-9003159) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of $IrCl_3\cdot 3H_2O$ from Johnson-Matthey Alfa/Aesar is gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456). The High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Supplementary Material Available: Structure determination summaries for 1 and 4, listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for 1 and 4, and ORTEP drawings of both independent molecules of 4 (19 pages). Ordering information is given on any current masthead page.

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[21] Typical bond energies for C=O and C=S are 799 and 573 kJ/mol, respectively: Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1972; Appendix F and references therein.

[22] In addition, the "soft" sulfur center of the thiapentadienyl ligand interacts more strongly with the Ir(PR_3)$_3$ moiety than does the "harder" oxygen center of oxapentadienyl.

Secondary Bonding in Organobismuth Compounds. Comparison of the Structures of 2,2′,5,5′-Tetramethyl-1,1′-dibismaferrocene and 2,2′,5,5′-Tetramethylbibismole

Arthur J. Ashe, III,* Jeff W. Kampf, and Dhananjay B. Puranik
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Samir M. Al-Taweel
The Chemistry Department, Mu'tah University, Al Karak, Jordan

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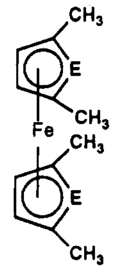
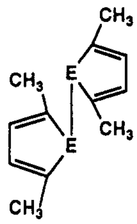
Summary: **The reaction of 1-phenyl-2,5-dimethylbismole (5) with lithium in THF followed by $FeCl_2$ gave red-black crystals of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (3), while the reaction of 5 with sodium in liquid ammonia followed by 1,2-dichloroethane gave green crystals of 2,2′,5,5′-tetramethylbibismole (4). Single-crystal X-ray diffraction studies show that 3 adopts a ferrocene-like arrangement with a close (3.688 (1) Å) inter-ring Bi···Bi contact, while 4 has a zigzag chain of Bi atoms with close intermolecular contacts of 3.6595 (5) Å.**

The structures of many main-group compounds exhibit short contacts between formally nonbonded atoms, which indicate a secondary bonding.[1,2] We recently reported the crystal structure of the distibaferrocene 1, which shows an inter-ring Sb···Sb contact that is well below the van der Waals distance.[3] The corresponding thermochromic bistibole 2 crystallizes so that Sb atoms are aligned in chains with a similar short intermolecular separation.[4,5] Since secondary bonding is generally more important for heavier atoms,[1] it is of interest to examine the corresponding bismuth compounds. We report here on the synthesis of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (3) and on a comparison of its crystal structure with that of 2,2′,5,5′-tetramethylbibismole (4).



1 E = Sb

3 E = Bi



2 E = Sb

4 E = Bi

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[1] Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

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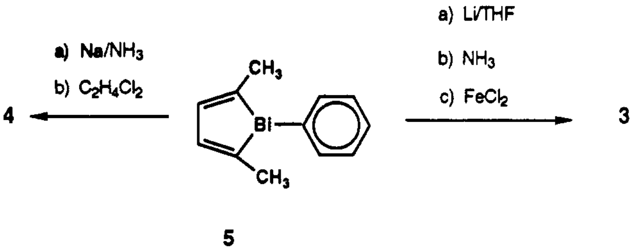
Both dibismaferrocene 3 and bibismole 4 have been prepared from 1-phenyl-2,5-dimethylbismole (5).[6] The



reaction of 5 with lithium in THF at 25 °C gave a deep green solution of (2,5-dimethylbismolyl)lithium and phenyllithium, which on sequential reaction with NH_3, followed by $FeCl_2$, afforded 3 in 37% yield. The reaction of 5 with Na in liquid NH_3 at −30 °C followed by reaction with 1,2-dichloroethane gave 61% of 4. Compound 3 forms red-black crystals, while 4 forms green crystals which have a metallic luster. Both 3 and 4 are only mildly air-sensitive and are thermally stable to 100 °C. These compounds have been characterized by X-ray crystallography.[7]

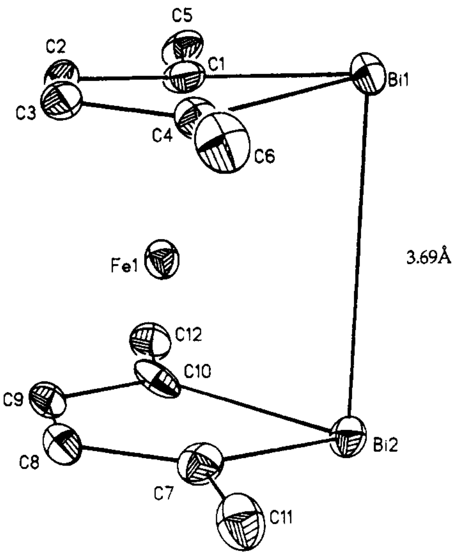


Figure 1. ORTEP drawing of the solid-state structure of 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (3), with thermal ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg) are as follows: Bi(1)–Bi(2) 3.688 (1); Fe–Bi(av), 2.677 (4); Fe–C_α(av), 2.12 (2); Fe–C_β(av), 2.05 (2); Bi–C_α(av), 2.22 (2); C_α–C_β(av), 1.40 (3); C_β–$C_{\beta'}$(av), 1.43 (3); C_α–Bi–$C_{\alpha'}$(av), 76.4 (12). C_α = C(1), C(4), C(7), C(10); C_β = C(2), C(3), C(8), C(9).

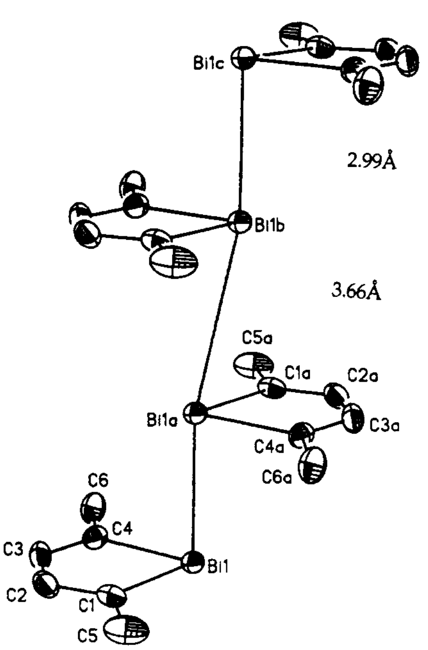


Figure 2. ORTEP drawing of the solid-state structure of 2,2′,5,5′-tetramethylbibismole (4) showing the relationship of two molecules along the *a* axis. Selected interatomic distances (Å) and angles (deg) are as follows: Bi(1)–Bi(1a), 2.9902 (5); Bi(1a)–Bi(1b), 3.6595 (5); Bi(1)–C(1), 2.23 (1); Bi(1)–C(4), 2.24 (1); C(1)–C(2), 1.35 (2); C(3)–C(4), 1.34 (2); C(2)–C(3), 1.44 (2); Bi(1)–Bi(1a)–Bi(1b), 166.53 (2); C(1)–Bi(1)–C(4), 79.3; C(1)–Bi(1)–Bi(1a), 88.8 (3); C(4)–Bi(1)–Bi(1a), 90.0 (3).

The molecular structure of the dibismaferrocene 3, illustrated in Figure 1, shows the iron atom π-bonded to the two eclipsed η^5-dimethylbismolyl rings. The overall geometry of the bismolyl ligands is similar to that observed for monobismaferrocene 6.[8] The intra-ring bond lengths

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[6] (a) Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495. (b) 1-Phenyl-2,5-dimethylbismole (5): A hexane solution of 2.7 M butyllithium (2.8 mL, 7.56 mmol) was added dropwise over 10 min with stirring to a solution of 2,5-diiodo-2,4-hexadiene (1.20 g, 3.60 mmol) in 20 mL of ether at −35 °C. After 30 min a precipitate had formed. The mixture was warmed to 25 °C and was stirred for 2.5 h. The solution of 2,5-dilithio-2,4-hexadiene was cannulated into a suspension of diiodophenylbismuthine (2.00 g, 3.71 mmol) in 80 mL of ether at −35 °C. The red color was discharged over a period of 30 min, leaving a yellow-orange suspension, which was stirred for an additional 3.5 h at −10 °C. The solvent was evaporated in vacuo, and the residue was extracted with 50 mL of pentane at 0 °C. After filtration the pentane was removed by evaporation to a yellow semisolid. The pentane extraction was repeated, and on evaporation 1.0 g (80%) of 1-phenyl-2,5-dimethylbismole (5) was obtained as a yellow viscous oil. Because of its lability 5 was not subjected to further purification. (c) 2,2′,5,5′-Tetramethyl-1,1′-dibismaferrocene (3): An excess (0.5 g) of lithium wire cut into small pieces was added to a solution of 1-phenyl-2,5-dimethylbismole (1.0 g, 2.9 mmol) in 20 mL of THF at 0 °C. The color changed to green-brown, and stirring was continued for 4 h. The solution was decanted from the excess lithium and cooled to −35 °C, and gaseous NH_3 was bubbled through for 5 min to remove the phenyllithium. The deep blue solution was stirred for 10 min and warmed to 0 °C. Excess NH_3 was removed by bubbling N_2 through the solution, and 10 mL of THF was added. The solution was then cooled to −78 °C and cannulated into a suspension of $FeCl_2$ (0.45 g, 3.54 mmol) in 20 mL of THF at −73 °C. The brown solution was stirred at −78 °C for 4 h and then warmed to 0 °C for 1 h. After removal of the solvent the residue was extracted with 70 mL of pentane. Cooling to −78 °C gave 0.35 g (37%) of 3 as black shiny needles; mp 124–125 °C. Anal. Calcd for $C_{12}H_{16}Bi_2Fe$: C, 22.73; H, 2.54. Found: C, 22.29; H, 2.39, ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 12 H), 7.51 (s, 4 H). ^{1}H NMR (C_6D_6): δ 2.09 (s, 12 H), 7.35 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 29.1 (CH_3), 109.6 (CH). CBi not observed. MS (EI): *m/e* (intensity) 634 (M^+, for $C_{12}H_{16}Bi_2Fe$). MS exact mass (EI): Calcd for $C_{12}H_{16}Bi_2Fe$ 634.0209, found 634.0199. (d) 2,2′,5,5′-Tetramethylbibismole (4): Excess sodium (0.09 g, 3.90 mmol) was added to a solution of 1-phenyl-2,5-dimethylbismole (0.7 g, mmol) in 40 mL of hexane at −31 °C. Gaseous ammonia was bubbled into the solution for 10 min, during which time the reaction mixture turned red. The solution was stirred for 2 h at −31 °C with NH_3 bubbling every hour for 5 min. After addition of 1,2-dichloroethane (0.5 g, 5 mmol), the solution was warmed to 0 °C and the excess NH_3 was removed with a nitrogen gas purge. Hexane (10 mL) was added. After filtration and cooling 0.34 g (61%) of metallic green 4 was obtained. X-ray-quality crystals were obtained by slow vacuum sublimation (0.01 Torr, 45–52 °C); mp 101–102 °C dec. Anal. Calcd for $C_{12}H_{10}Bi_2$: C, 24.93; H, 2.79. Found: C, 24.81; H, 2.77. ^{1}H NMR (C_7D_8): δ 2.41 (s, 12 H), 8.43 (s, 4 H). ^{13}C NMR (C_7D_8): δ 28.5 (CH_3), 152.3 (CH), 162.6 (CBi). MS (CI-CH_4): *m/e* (intensity) 579 (0.5) (M^+ + 1, for $C_{12}H_{16}Bi_2$), 160 (100). UV (c-C_6H_{12}): nm (ϵ 14 700), 320 sh (5600), low-intensity tail to 700. Diffuse reflectance (solid): λ_{max} 690 nm.

[7] 3: monoclinic, space group $P2_1/c$ (No. 14), with a = 8.187 (2) Å, b = 12.208 (7) Å, c = 13.103 (4) Å, β = 93.81 (2)°, V = 1306.7 (7) Å^3, and Z = 4 (d_{calc} = 3.223 g cm^{-3}); μ (Mo Kα) = 93.18 cm^{-1} absorption corrected by ψ scans; 2321 unique reflections; 1881 reflections with $F_o \geq 0.6\sigma(F)$ were used in refinement; R = 6.10%, R_w = 7.66%, GOF = 2.12. 4: triclinic, space group $P\bar{1}$ (No. 2), with a = 6.0673 (9) Å, b = 7.044 (1) Å, c = 7.576 (2) Å, α = 80.54 (2)°, β = 88.11 (2)°, γ = 89.09 (1)°, V = 347.6 (1) Å^3, and Z = 1 (d_{calc} = 2.762 g cm^{-3}); μ(Mo Kα) = 93.18 cm^{-1} absorption corrected by ψ scans; 1230 unique reflections; 1228 reflections with $F_o \geq$ $0.6\sigma(F)$ were used in refinement; R = 3.62%, R_w = 4.89%, GOF = 0.83.

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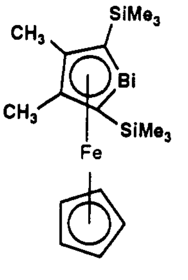
[9] Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 1491.



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indicate that the bismolyl groups of 3 are π-complexed heteroaromatic rings. As had previously been found for other group 15 heteroferrocenes,[3,8–11] the heteroatoms are displaced out of the ring planes away from iron. Since the average displacement (0.28 Å) is smaller than the 0.39 Å found for the monobismaferrocene 6, the Bi atoms are closer than anticipated. In fact, the 3.69-Å interannular separation of the Bi atoms is nearly 1 Å below the van der Waals distance of 4.6 Å. Therefore, the structural data give evidence of a direct inter-ring Bi⋯Bi bond. If the primary π-bonding of the Bi atoms of 3 involves the Bi(6p$_z$) orbitals, these orbitals are aligned so that the inter-ring Bi⋯Bi bond is likely due to p–p σ-overlap.

For comparison we have also obtained a structure of the green thermochromic bibismole 4.[6] The molecular structure of 4, as shown in Figure 2, has a staggered trans conformation as is the case for all reported distibines[2,4,12] and dibismuthines.[13,14] The Bi–Bi bond distance of 2.990 Å is identical with that found for the nonthermochromic tetraphenyldibismuthine[13] but somewhat shorter than the 3.04 Å reported for the thermochromic tetrakis(trimethylsilyl)dibismuthine (7).[14] The crystal packing of bibismole 4 shows the Bi atoms are aligned in zigzag chains[15] with alternating intramolecular Bi–Bi bonds (2.99 Å) and slightly longer intermolecular Bi⋯Bi contacts (3.66 Å). All structures of thermochromic distibines and dibismuthines contain similar metal atom chains which are associated with their intense solid-phase colors.[2,5] However, the intermolecular contacts of 4 are distinctly shorter than the 3.80 Å found for the sterically congested 7. Unfortunately, there are no other reported structures for thermochromic dibismuthines.[16]

$$(SiMe_3)_2Bi\text{-}Bi(SiMe_3)_2$$

7

The comparison of the juxtaposition of Bi atoms in 3 and 4 suggests a similar origin for the secondary bonding. For structure 4 the CBiC and CBiBi bond angles are significantly smaller than tetrahedral angles, implying that the Bi atoms are p^3-hybridized. Since the Bi(6p$_z$) orbitals are approximately aligned with the metal chain, the intermolecular bonding is likely due to p–p overlap. Indeed, the intermolecular Bi(6p$_z$)–Bi(6p$_z$) overlap integral (0.252) is 60% as large as the intramolecular overlap integral (0.417).[17] Pseudopotential calculations which may provide an estimate of the strength of this bonding are now in progress and will be communicated elsewhere in detail.

Acknowledgment. We are grateful to the Research Corp., to NATO Scientific Affairs, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also wish to thank Professor S. L. Buchwald for informing us of his results prior to publication and Professor L. L. Lohr for stimulating discussions.

Supplementary Material Available: Tables of crystal data and data collection and solution and refinement details, bond lengths and angles, and positional and thermal parameters and packing diagrams for 3 and 4 and a table of least-squares planes for 3 (13 pages). Ordering information is given on any current masthead page. Tables of calculated and observed structure factors are available from A.J.A. on request.

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Homogeneous Catalysis. $[Ti(Cp)_2(CF_3SO_3)_2]$ and $[Zr(Cp)_2(CF_3SO_3)_2THF]$, Efficient Catalysts for the Diels–Alder Reaction

T. Keith Hollis, N. P. Robinson, and B. Bosnich*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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Summary: The readily prepared species $[Ti(Cp)_2(CF_3SO_3)_2]$ and $[Zr(Cp)_2(CF_3SO_3)_2THF]$ are efficient catalysts for the Diels–Alder reaction at very low catalyst loadings, giving accelerations of between 10^3 and $>10^5$ over the corresponding thermal reactions.

The classical Diels–Alder reaction is promoted by a variety of Lewis acids, most commonly by the halides of tervalent boron and aluminum and tetravalent titanium and tin. These traditional Lewis acids present a number of difficulties when they are modified for enantioselection by incorporation of chiral ligands. The problems that arise are dependent on the Lewis acidic element and on the ligand chosen, but in general, the difficulties are associated with the tendency of these chelated species to oligomerize, to exchange their ligands rapidly, and to produce a variety of species. As a consequence there can exist a complex equilibrium, making identification of the catalytic species

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