The two new indium hydrides K{H[In(CH_2CMe_3)$_3$]$_2$} and K[HIn(CH_2CMe_3)$_3$] are inert to decomposition reactions in benzene solution over long periods of time. Neopentane (CMe_4) was not observed to be present in benzene solutions of the compounds, even after 3 months of standing at room temperature. In contrast, the closely related compound K[HIn(CH_2SiMe_3)$_3$][3] was observed to decompose in benzene solution to form indium metal, $SiMe_4$, biphenyl, and varying amounts of H_2. All CH_2SiMe_3 groups were converted to $SiMe_4$ within 2 months at room temperature.[3] These decomposition reactions of K[HIn(CH_2SiMe_3)$_3$] were proposed to be related to the formation of KCH_2SiMe_3 by the dissociation of $CH_2SiMe_3^-$. Thus, the stability of the neopentyl derivatives suggests increased inertness to dissociative reactions, a property which might be related to the Lewis acidity of trineopentylindium.[4] It is noteworthy that the reagents, 1 mmol of $InMe_3$ and excess KH, formed 0.159 mmol of CH_4 and indium metal in 12 h at 25 °C.[15]

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Registry No. K[HIn(CH_2CMe_3)$_3$], 139408-74-5; In(CH_2CMe_3)$_3$, 106136-98-5; K[DIn(CH_2CMe_3)$_3$], 139408-76-7; K{H[In(CH_2CMe_3)$_3$]$_2$}, 139408-75-6; K{D[In(CH_2CMe_3)$_3$]$_2$}, 139408-77-8.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms for K{H[In(CH_2CMe_3)$_3$]$_2$} (10 pages); F_o/F_c list (18 pages). Ordering information is given on any current masthead page.

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Conformations of Heteroferrocenes. Synthesis and Crystal and Dynamic Solution Behavior of 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene

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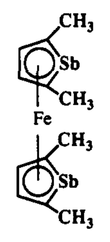
2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (2) as been obtained from the reaction of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylstibole with lithium followed by $FeCl_2$. In a similar manner 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-dibismaferrocene (3) was obtained from 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismole. Dark red crystals of 2 form in the $P\bar{1}$ (No. 2) space group with $Z = 2$, $a = 9.243$ (2) Å, $b = 11.310$ (2) Å, $c = 17.345$ (3) Å, $\alpha = 76.51$ (1)°, $\beta = 79.23$ (2)°, and $\gamma = 73.18$ (1)°. A full structure has been determined and shows a ferrocene-like arrangement in which the trimethylsilyl groups are arranged in a staggered fashion. In solution a barrier to ring rotation for both 2 and 3 of $\Delta G^{\ddagger} = 13$ kcal/mol can be estimated from variable-temperature ^{1}H-NMR spectroscopy.

We recently reported the crystal structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene (1), which adopts a totally eclipsed ferrocene-like conformation with a short separation between the Sb atoms in each ring.[1] The inter-ring Sb⋯Sb contact (3.68 Å) is 0.72 Å shorter than the van der Waals radius separation (4.4 Å), which seems indicative of secondary bonding between the Sb atoms. Formally similar secondary bonding has been found for a number of compounds of antimony and other heavy main group elements.[2,3] In order to examine this phenomenon further, we have prepared the highly substituted distibaferrocene and the analogous dibismaferrocene 3. We report here on the X-ray structure of 2 and dynamic behavior of 2 and 3 in solution.



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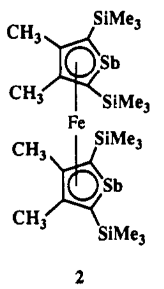

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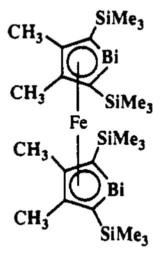

3

Results and Discussion

Synthesis. Distibaferrocene 2 was prepared by a route similar to that which we have recently reported for bismaferrocenes.[4] See Scheme I. 1-(Trimethylsilyl)-1-propyne (4) reacts with zirconocene dichloride and magnesium amalgam to give 1,1-bis(η^5-cyclopentadienyl)zirconacyclopentadiene (5).[4] The direct exchange of 5 with

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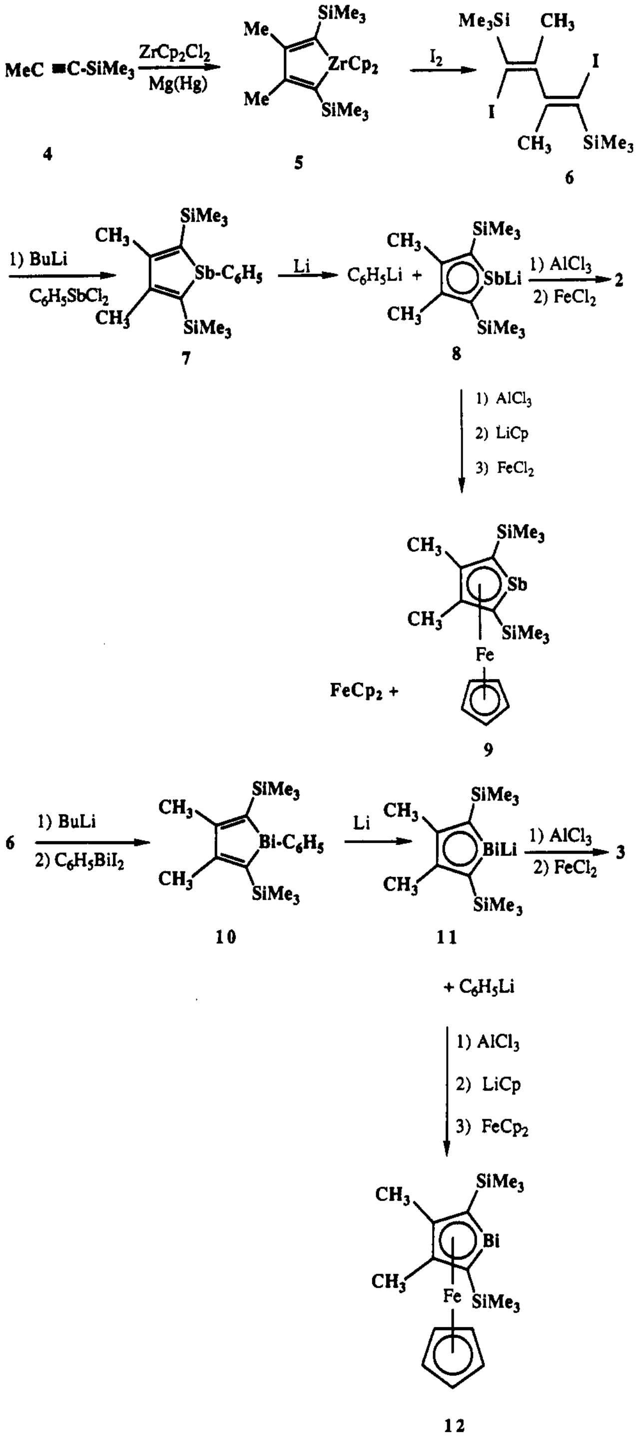
Scheme I. Preparation of 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (2) and 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-dibismaferrocene (3)



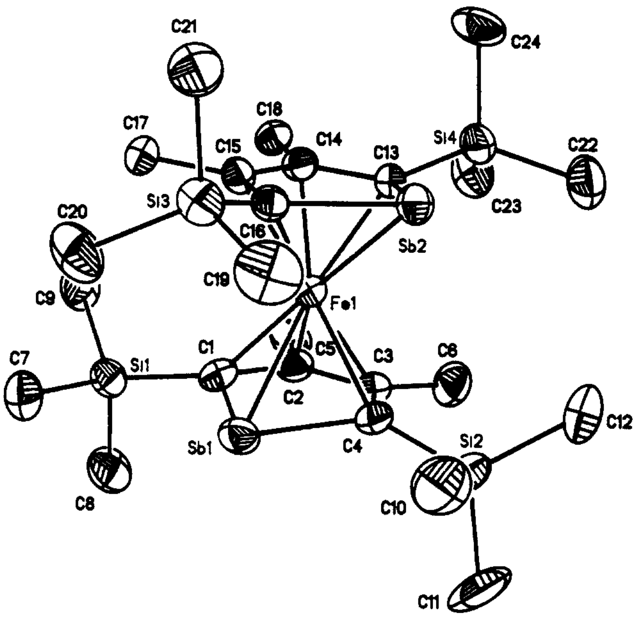


Figure 1. ORTEP drawing of the solid-state structure of 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (2), with thermal ellipsoids at the 50% probability level.

phenylantimony dichloride using the Fagan–Nugent procedure gives stibole 7 and zirconocene dichloride.[5] However, an indirect approach affords the product in higher yield and better purity. Thus, iodonolysis of 5 gives 86% of the easily purified crystalline diiodide 6.[4] Lithiation of 6 with butyllithium followed by treatment with phenylantimony dichloride gives an 82% yield of the desired stibole. Stibole 7 reacts with lithium metal in THF to give a deep blue solution of the corresponding stibolyl anion 8 and phenyllithium.[1,6] Following a procedure used by Mathey to prepare phosphaferrocenes,[7] the phenyllithium is first converted to triphenylaluminum by treatment with $AlCl_3$. Subsequent reaction with $FeCl_2$ gave distibaferrocene 2 in 20% yield. A modification of this procedure allows preparation of the monostibaferrocene 9. Thus, treating 8 with 1 equiv of LiCp prior to reaction with $FeCl_2$ gives a mixture of ferrocene and 9. After sublimation of the ferrocene from the less volatile product, 9 may be obtained in 30% yield. Interestingly very little 2 is found in the product mixture. Apparently, the formation of the less hindered 9 must be faster.

An analogous route has been used to prepare dibismaferrocene 3 and bismaferrocene 12. Thus, dilithiation of 6 with butyllithium in ether followed by treatment with a suspension of phenylbismuth diiodide gave a nearly quantitative yield of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismole (10). Because of its lability, the bismole was used directly without extensive purification. Reaction of 10 with lithium metal in THF at 0 °C for 3 h gave a deep red solution of bismolyl anion 11 and phenyllithium. Addition of $^1/_3$ equiv of $AlCl_3$, followed by treatment with $FeCl_2$, afforded the dibismaferrocene 3 in 17% yield. Alternatively, addition of LiCp to 11 prior to reaction with $FeCl_2$ gave bismaferrocene 12 in 25% yield.

Structure. The molecular structure of 2 illustrated in Figure 1 shows a ferrocene-like arrangement in which the iron atom is sandwiched between two η^5-stibolyl rings. This structure is very similar to that shown by 1 except that the Sb atoms are not eclipsed. Each ring is rotated relative to the other so that its Sb atom eclipses the carbon adjacent to the Sb atom of the second ring. This allows the four bulky Me_3Si groups to interlock in a gearlike manner. In this respect the structure resembles that of 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene (13).[9]

The overall geometry of the stibolyl ligands conforms closely to the pattern observed for 1. The four carbon

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atoms of each stibolyl ring lie in parallel planes 3.27 Å apart. As had previously been found for 1[1] and from other group 15 heterometallocenes,[4,10,11] the heteroatoms are displaced out of the carbon planes away from iron. The average displacement is slightly larger (0.23 (1) Å) for 2 than had been found for 1 (0.18 (2) Å).[12] Otherwise there are no significant differences between the intra-ring bond angles and lengths and the Fe–ring distances of distibaferrocenes 1 and 2. These structural parameters have previously been discussed in detail for 1.[1] They indicate the stibolyl groups of both 1 and 2 are π-complexed heteroaromatic rings.

The inter-annular separation of the Sb atoms of 2 is 4.29 Å. This value is comparable with the van der Waals radius separation (4.4 Å) and is similar to the closest intermolecular approach found in normal antimony compounds, e.g. 4.28 Å for Ph_4Sb_2.[9] There can be no inter-annular Sb···Sb bonding. Clearly a closer approach is prevented by the bulky Me_3Si groups. Thus, a relative rotation of the stibolyl ligands to bring the Sb atoms into a fully eclipsed arrangement would also bring two pairs of the Me_3Si groups into an eclipsed arrangement. On this basis, we can conclude that the Me_3Si steric repulsion must exceed the inter-annular Sb···Sb bond energy.

^{1}H-NMR Studies. In order to investigate further the conformational properties of 2 we have examined its temperature dependent H-NMR spectrum in $CDCl_3$ and CD_2Cl_2 solution.[14] Energy barriers for several ferrocenes carrying bulky substituents have been evaluated from NMR coalescence studies.[9,15–19] There is no prior experimental report of the rotational barrier of a heteroferrocene,[20] although calculations on phosphaferrocenes have been published.[21]

At 30 °C the H-NMR spectrum (300 MHz) of 2 consists of a single Me_3Si resonance ($\delta = 0.233$) and a single ring methyl resonance ($\delta = 2.061$) indicating rapid ring rotation on the NMR time scale. On cooling to −40 °C two distinct Me_3Si signals are observed at $\delta = 0.180$ and $\delta = 0.265$ and two ring methyl signals at $\delta = 2.103$ and $\delta = 1.986$. Taking the coalesence temperature at −5 °C, the ΔG^* for ring rotation is 13.3 ± 0.5 kcal/mol.[22]

The low-temperature NMR spectrum indicates the population of a conformation of C_2 symmetry in which the two Me_3Si groups as well as the two vicinal Me groups on the same ring are nonequivalent. This is consistent with crystallographic conformation A (and its enantiomer A′). The ring rotations which interconvert A and A′ thereby making the Me_3Si and Me groups equivalent are illustrated in Figure 2. This may be accomplished by either a clockwise rotation via conformation B or counterclockwise rotation via conformations C and C′. Experimental data do not allow a distinction to be made.

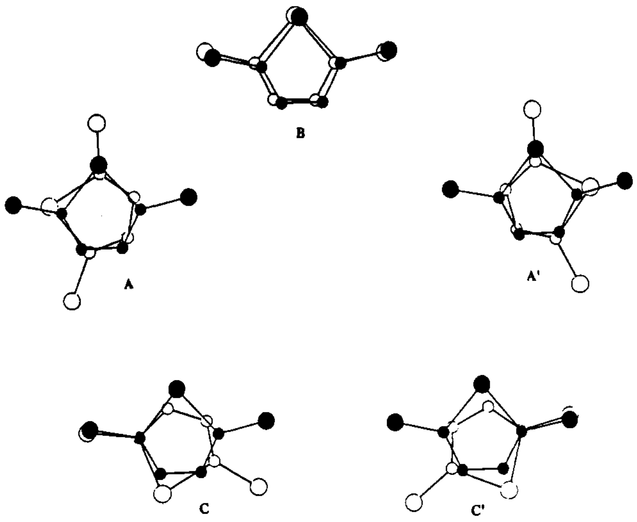

Figure 2. Schematic representations of the five eclipsed (A, A′, B, C, C′) conformations of 2, showing interconversion pathways resulting from relative ring rotation. The shaded atoms represent the stationary upper ring, while the lighter atoms belong to the rotating lower ring. Methyl groups have been omitted for clarity.

The rotational barrier of 2 can be compared with that measured for 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene (13).[8,10] An X-ray crystal structure of 13 showed that it adopted a C_2 conformation, which is almost identical to that of 2, while analysis of the temperature-dependent H-NMR spectrum in toluene-d_8 solution gave a value of 11.0 kcal/mol as the barrier to ring rotation. This barrier is likely to involve a rotation through conformations analogous to C and C′ in which two Me_3Si groups pass each other in the transition states.[23] The alternative roation through conformation analogous to B would involve the two pairs of Me_3Si groups simultaneously passing each other. On the simplistic but plausible assumption that the Me_3Si interactions are additive, we might assign this barrier height as 22 kcal/mol.

Since both ring geometries and substitution patterns of 2 and 13 are different, comparison of their rotational barriers can be only approximate. However, in the case of various tetra-*tert*-butylmetallocenes a clear inverse relationship has been found between the inter-ring distance and the rotational barriers.[15] The inter-ring distances of 3.32 Å for 13 and 3.27 Å for 2 are rather close, while the rotational barriers are similar. This suggests that the barrier in 2, like that of 13, is dominated by the passing of two Me_3Si groups. Therefore, we assign conformation C(C′) as the transition state for interconversion of A and A′. Again assuming an additivity of repulsive effects, conformation B would be destabilized by 22–26 kcal/mol. However, conformation B will be lowered from this maximum value by the bonding energy of the Sb···Sb interaction. On the other hand, the energy of B cannot be lower than the observed barrier height of 13.0 kcal/mol. On this basis, it can be argued that the maximum value for the inter-ring Sb···Sb bonding is approximately 13 kcal/mol.

For comparison we have also examined the temperature-dependent H-NMR spectrum of 3 and find that is completely analogous to that of 2. At room temperature the ^{1}H-NMR spectrum of 3 consists of two sharp singlets in the ratio of 3:1 assignable to the Me_3Si- and ring-Me groups, respectively. On cooling, both singlets separate into two well-separated singlets. The coalescence tem-

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(12) The value quoted in ref 1 is wrong.

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(14) No solvent effects were noted on T_c.

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(20) However, there is an unpublished report of a study of 2,2′,5,5′-tetra-*tert*-butyl-1,1′-diazaferrocene: Kuhn, N.; Jendral, K.; Boese, R.; Bläser, D. *Chem. Ber.* **1991**, *124*, 89.

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(22) Coalescence of the Me and Me_3Si singlets occurred at the same temperature.

(23) However, the transition state may be the symmetrical staggered conformation between C and C′. See refs 9 and 15.

perature of −7 °C was not noticeably different from either set of singlets. This allows the $\Delta G^{\ddagger}$ for the dynamic process to be estimated at 13.1 ± 0.5 kcal/mol.

The low-temperature H-NMR spectrum of **3** requires the population of a conformation with C_2 symmetry. Although no solid-state structure of **3** has been determined, the structure reported for **12** indicates that the bismolyl ligand of **12** is very similar to the corresponding stibolyl ligand of **2**. Thus, **3** probably adopts conformation A (A′). Interconversion of A and A′ is likely to occur via C and C′ for both **2** and **3**. The identity of the $\Delta G^{\ddagger}$ values for the rotational barriers for **2** and **3** argues strongly against conformation B as the observed transition state. Thus, the relative energy of B for **2** and **3** should be the sum of similar steric interactions and (presumably) different Sb···Sb and Bi···Bi interactions.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of argon. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Brucker WH-360 or AM-300 spectrometer, on solutions in $CDCl_3$ or C_6D_6. The ^{1}H-NMR and ^{13}C-NMR spectra were calibrated by using signals from the solvents referenced to Me_4Si. The combustion analyses were determined by Galbraith Laboratories, Knoxville, TN.

1,1-Bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethyl-1-zircona-2,4-cyclopentadiene (5). Magnesium turnings (3.2 g, 133 mmol) and mercuric chloride (3.6 g, 13.3 mmol) were stirred for 20 min in 100 mL of THF, after which a solution of zirconocene dichloride (7.2 g, 25 mmol) and 1-trimethylsilyl-1-propyne (4.4 g, 40 mmol) in 50 mL of THF was added dropwise over 7 min. After being stirred at 25 °C for 24 h, the mixture had become yellow in color. The solution was then decanted from the excess magnesium, and the solvent was removed under reduced pressure. The dark green residue was extracted with 150 mL of pentane. After filtration the solvent was removed in vacuo, affording 8.5 g (96%) of a yellow solid, mp 167 °C dec. Anal. Calcd for $C_{22}H_{34}Si_2Zr$: C, 59.26; H, 7.69. Found: C, 58.94; H, 7.57. H-NMR (C_6D_6): δ 6.00 (s, 10 H), 1.83 (s, 6 H), 0.15 (s, 18 H). C-NMR (C_6D_6): δ 202 (CZr), 146.6 (CCH$_3$), 111.0 (Cp), 25.9 (CCH_3), 2.6 (SiCH_3).

(1*Z*,3*Z*)-1,4-Bis(trimethylsilyl)-1,4-diiodo-2,3-dimethyl-1,3-butadiene (6). Iodine (2.3 g, 9 mmol) was added portionwise to a solution of 1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethyl-1-zircona-2,4-cyclopentadiene (2.0 g, 4.5 mmol) in 100 mL of THF at −78 °C with stirring. Stirring was continued for 30 min at −78 °C, after which the solution was allowed to warm to 25 °C. Solvent was removed under reduced pressure leaving a dark brown residue, which was extracted with 3 × 100 mL of pentane. The combined extracts were washed successively with a saturated aqueous solution of $Na_2S_2O_3$ (3 × 30 mL), and water (3 × 50 mL) and then dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a creamy-white solid, which was recrystallized from methanol to give 1.85 g (86%) of product as shiny white crystals, mp 48 °C. Anal. Calcd for $C_{12}H_{24}I_2Si_2$: C, 30.13; H, 5.06. Found: C, 30.24; H, 4.98. H-NMR ($CDCl_3$): δ 1.95 (s, 6 H), 0.3 (s, 18 H). C-NMR ($CDCl_3$): δ 162 (CCH$_3$), 103 (CI), 19.5 (CCH$_3$), 1.50 (SiCH_3).

1-Phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylstibole (7). A solution of 2.5 N butyllithium in hexane (3.35 mL, 8.4 mmol) was added slowly to a solution of (1*Z*,3*Z*)-1,4-bis(trimethylsilyl)-1,4-diiodo-2,3-dimethyl-1,3-butadiene (2.0 g, 4.2 mmol) in 70 mL of ether at −78 °C with stirring. Stirring was continued at −78 °C for 2 h, after which the solution was allowed to warm to 25 °C for 5 min. After being recooled to −78 °C, this solution was added to a solution of phenyldichlorostilbine (1.2 g, 4.2 mmol) in 30 mL of ether at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and then allowed to warm to 25 °C. After the solvent was removed under reduced pressure, the residue was extracted with 2 × 50 mL of pentane. Removal of the pentane under reduced pressure gave a yellow semisolid mass which could be recrystallized from pentane at −78 °C to give 2.15 g (82%) of yellow crystals, mp 65 °C. Anal. Calcd for $C_{18}H_{29}SbSi_2$: C, 51.07; H, 6.90. Found: C, 50.89; H, 6.74. H-NMR ($CDCl_3$): δ 0.08 (s, 18 H), 2.17 (s, 6 H), 7.23 (m, 3 H), 7.42 (m, 2 H). MS (EI) [*m/e* (intensity)]: 424 (13, M$^+$ for $C_{18}H_{29}{}^{123}SbSi_2$), 422 (15) 336 (21), 334 (26), 73 (100).

Lithium 2,5-Bis(trimethylsilyl)-3,4-dimethyl-1-stibacyclopentadienide (8). An excess of lithium wire cut into pieces approximately 2 mm in diameter was added with stirring at 25 °C to a solution of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylstibole (1.75 g, 4.1 mmol) in 40 mL of THF. The initial color of yellow changed to red-violet within 30 min, and stirring was continued for 3 h at 25 °C. The reaction mixture was cooled to −78 °C, decanted from the excess lithium, and added to $AlCl_3$ (0.18 g, 1.4 mmol) with stirring and allowed to warm to 0 °C for 5 min.

a. 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-distibaferrocene (2). The solution of **8** prepared above was recooled to −78 °C and added to $FeCl_2$ (0.53 g, 2.1 mmol) in 15 mL of THF. After warming to 25 °C, stirring was continued for 24 h. Removal of the solvent under reduced pressure left a dark residue which was extracted with pentane (3 × 50 mL). Dark red crystals (0.3 g, 20%) were obtained on cooling to −78 °C. ^{1}H-NMR ($CDCl_3$) (at 30 °C): δ 0.233 (s, 36 H), 2.061 (s, 12 H). ^{1}H-NMR (at −40 °C): δ 0.180 (s, 18 H), 0.265 (s, 18 H), 1.986 (s, 6 H), 2.103 (s, 6 H). T_c = −5 ± 5 °C. Anal. Calcd for $C_{24}H_{48}FeSb_2Si_4$: C, 38.52; H, 6.47. Found: C, 38.27; H, 6.57. MS (EI) exact mass: calcd for $C_{24}H_{48}FeSb_2Si_4$, *m/e* 748.0263; found; *m/e* 748.0249.

b. 2,5-Bis(trimethylsilyl)-3,4-dimethyl-1-stibaferrocene (9). Lithium cyclopentadienide (4.1 mmol) in 20 mL of THF was added to the solution of **8** prepared above. The combined solution was cooled to −78 °C and then added to a solution of $FeCl_2$ (0.52 g, 4.1 mmol) in 30 mL of THF at −78 °C with stirring. The reaction mixture was allowed to warm to 25 °C and was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was extracted with pentane (3 × 75 mL). After removal of the solvent under reduced pressure the residue was subject to sublimation (0.05 Torr, 60 °C) to remove the ferrocene. The residue was then extracted with pentane. The extracts were filtered and cooled to −78 °C affording 0.5 g (30%) of dark red crystals of **9**, mp 132 °C. ^{1}H NMR ($CDCl_3$): δ 4.20 (s, 5 H), 2.25 (s, 6 H), 0.18 (s, 18 H). Anal. Calcd for $C_{17}H_{29}FeSbSi_2$: C, 43.71; H, 6.26. Found: C, 43.61; H, 6.12. MS (EI) exact mass: calcd for $C_{17}H_{29}FeSbSi_2$, *m/e* 466.0195; found, *m/e* 466.0193. UV (C_6H_{12}) [$\lambda_{\max,\,\mathrm{nm}}$ (ϵ)]: 520 (240), 452 (425), 362 (16000), 314 (4600), 222 (31000).

1-Phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismole (10). To a solution of (1*Z*,3*Z*)-1,4-bis(trimethylsilyl)-1,4-diiodo-2,3-dimethyl-1,3-butadiene (1.0 g, 2.1 mmol) in 40 mL of ether at −78 °C was added 1.7 mL of 2.5 M butyllithium (4.2 mmol) in hexane with stirring. Stirring was continued at −78 °C for 2 h, after which the solution was allowed to warm to 0 °C for 5 min. After recooling to −78 °C, this solution was added to a stirred suspension of phenyldiiodobismuthine (1.12 g, 2.1 mmol) in 30 mL of ether. The reaction mixture was allowed to warm to 0 °C and was stirred at this temperature for 10 min. Removal of solvent at 0 °C under reduced pressure left a yellow residue, which was extracted with 2 × 50 mL of pentane at 0 °C. Removal of pentane under reduced pressure left 1.05 g (100%) of a yellow solid. The bismole was not subject to further purification because of its lability. ^{1}H-NMR ($CDCl_3$): δ 8.00 (m, 2 H), 7.35 (m, 3 H), 2.04 (s, 6 H), 0.20 (s, 18 H). C-NMR ($CDCl_3$): δ 170 (C, Sb), 167 (CCH$_3$), 137.4 (C_i), 137.5 (C_o), 130, 127 (C_m, C_p), 29.7 (CCH_3), 2.7 (SiCH_3). MS (EI) exact mass: calcd for $C_{18}H_{29}BiSi_2$, *m/e* 510.1611; found, *m/e* 510.1596. Anal. Calcd for $C_{18}H_{29}BiSi_2$: C, 42.34; H, 5.73. Found: C, 41.83, H, 5.80.

Lithium 2,5-Bis(trimethylsilyl)-3,4-dimethylbismacyclopentadienide (11). A solution of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismole (2.14 g, 4.2 mmol) in 40 mL of THF was added at 0 °C to an excess of lithium wire which had been cut into pieces approximately 2 mm in diameter. The color changed from yellow to red-violet within 30 min. Stirring was continued at 0 °C for 3 h. The solution was decanted from the excess lithium, cooled to −78 °C, added to anhydrous $AlCl_3$ (0.18 g, 1.4 mmol), and allowed to stir for 5 min at 0 °C.

a. 2,5-Bis(trimethylsilyl)-3,4-dimethyl-1-bismaferrocene (12). A solution of lithium cyclopentadienide (4.2 mmol) in 15

Table I. Structure Determination Summary[a]

	Crystal Data
compd	**2**
empirical formula	$C_{24}H_{48}Si_4Fe_1Sb_2$
fw	748.33_9
cryst color and habit	dark red, irregular, platelike
cryst dimens, mm	0.28 × 0.34 × 0.16
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
Z	2
unit cell dimens from 25 reflcns (4.1° ≤ 2θ ≤ 25.9°)	
a, Å	9.243 (2)
b, Å	11.310 (2)
c, Å	17.345 (3)
α, deg	76.51 (1)
β, deg	79.23 (2)
γ, deg	73.18 (1)
V, Å^3	1674.0 (5)
D(calcd), g cm^{-3}	1.48_4
F(000), e	536
linear abs coeff (μ), cm^{-1}	21.89
	Data Collection
diffractometer	Siemens R3m/v
radiation type (λ, Å)	Mo K$\bar{\alpha}$ (0.71073) (Lp corr, graphite monochromator)
temp, °C	23
scan type	$\theta/2\theta$ scan
2θ scan range, deg	5–50
octants used	$+h,\pm k,\pm l$ (h, 0/11, k, $\overline{14}$/14, l, $\overline{21}$/21)
scan rate, deg min^{-1}	5–8, variable
scan width	0.8° below Kα_1 to 0.8° above Kα_2
bkgd/scan ratio	0.5
std reflcns	3 measd every 97 reflcns, linear decay ~45%
no. of data collcd	6719
no. of unique reflcns	5920 (R_{int} = 0.0472)
abs corr	empirical, ψ scans
R merge before/after corr	0.0820/0.0227
max/min transm	0.711/0.406
	Solution and Refinement
system used	Siemens SHELXTL PLUS VAXStation 3500
solution	Patterson
refinement method	full-matrix least squares
function minimized	$\Sigma w(\|F_o - F_c\|)^2$
H atoms	riding model, d_{C-H} = 0.96 Å, common isotropic *U*(H) refined to 0.150 (8) Å^2
no. of refined reflcns with $F_o \geq 0.6\sigma(F)$	5105
no. of params refined	282
data/param ratio	18.1
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.0793
$R_w = [\sum(w\|F_o - F_c\|)^2/\sum w(F_o)^2]^{1/2}$ ($w^{-1} = \sigma^2(F_o) + 0.001228(F_o)^2$	0.0832
GOF	1.47
mean shift/error	<0.001
max shift/error	0.001
secondary extinction	1.3 (2) × 10^{-7}, plus 6 reflcns excluded
resid electron density, e/Å^3	+1.41/−1.30 near Sb

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, *U*(eq), defined as $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table II. Positional Parameters and Isotropic Equivalent Thermal Parameters (Å^2) of 2

atom	*x*	*y*	*z*	*U*(eq)
Sb(1)	0.03777 (8)	0.25977 (6)	0.33813 (4)	0.0616 (3)
Sb(2)	0.52423 (8)	0.11885 (5)	0.30105 (4)	0.0563 (3)
Fe(1)	0.2837 (2)	0.2591 (1)	0.24079 (6)	0.0432 (4)
Si(1)	−0.0626 (3)	0.5361 (2)	0.2060 (2)	0.060 (1)
Si(2)	0.1888 (4)	−0.0498 (3)	0.3267 (3)	0.092 (2)
Si(3)	0.3757 (4)	0.3310 (3)	0.4252 (2)	0.066 (1)
Si(4)	0.6373 (4)	0.1367 (3)	0.1006 (2)	0.066 (1)
C(1)	0.058 (1)	0.3716 (8)	0.2222 (5)	0.052 (3)
C(2)	0.123 (1)	0.2965 (8)	0.1612 (5)	0.055 (4)
C(3)	0.175 (1)	0.1637 (8)	0.1885 (5)	0.056 (4)
C(4)	0.162 (1)	0.1163 (8)	0.2729 (6)	0.061 (4)
C(5)	0.131 (1)	0.354 (1)	0.0751 (5)	0.070 (4)
C(6)	0.239 (1)	0.0758 (9)	0.1312 (7)	0.082 (5)
C(7)	−0.126 (1)	0.5918 (9)	0.3035 (6)	0.083 (5)
C(8)	−0.236 (1)	0.531 (1)	0.1687 (7)	0.093 (6)
C(9)	0.022 (1)	0.6570 (9)	0.1318 (7)	0.087 (5)
C(10)	0.190 (2)	−0.057 (1)	0.4358 (9)	0.135 (8)
C(11)	0.017 (2)	−0.099 (1)	0.313 (1)	0.17 (1)
C(12)	0.367 (2)	−0.167 (1)	0.293 (1)	0.134 (8)
C(13)	0.511 (1)	0.2150 (7)	0.1811 (5)	0.048 (3)
C(14)	0.451 (1)	0.3485 (7)	0.1763 (5)	0.049 (3)
C(15)	0.395 (1)	0.3916 (7)	0.2493 (5)	0.050 (3)
C(16)	0.403 (1)	0.3004 (7)	0.3225 (5)	0.049 (3)
C(17)	0.337 (1)	0.5299 (7)	0.2515 (5)	0.060 (4)
C(18)	0.449 (1)	0.4374 (8)	0.0970 (5)	0.058 (4)
C(19)	0.360 (2)	0.188 (1)	0.4994 (6)	0.110 (7)
C(20)	0.208 (1)	0.459 (1)	0.4518 (6)	0.100 (6)
C(21)	0.554 (1)	0.369 (1)	0.4348 (7)	0.093 (6)
C(22)	0.683 (2)	−0.038 (1)	0.1320 (8)	0.100 (6)
C(23)	0.570 (1)	0.176 (1)	−0.0005 (6)	0.093 (6)
C(24)	0.818 (1)	0.184 (1)	0.0879 (8)	0.101 (6)

Table III. Selected Bond Distances (Å) for 2

Sb(1)–Fe(1)	2.565 (2)	Si(2)–C(11)	1.89 (2)
Sb(1)–C(1)	2.12 (1)	Si(2)–C(12)	1.88 (2)
Sb(1)–C(4)	2.13 (1)	Si(3)–C(16)	1.85 (1)
Sb(2)–Fe(1)	2.570 (2)	Si(3)–C(19)	1.84 (2)
Sb(2)–C(13)	2.12 (1)	Si(3)–C(20)	1.86 (1)
Sb(2)–C(16)	2.12 (1)	Si(3)–C(21)	1.87 (1)
Fe(1)–C(1)	2.15 (1)	Si(4)–C(13)	1.86 (1)
Fe(1)–C(2)	2.10 (1)	Si(4)–C(22)	1.87 (1)
Fe(1)–C(3)	2.10 (1)	Si(4)–C(23)	1.88 (2)
Fe(1)–C(4)	2.14 (1)	Si(4)–C(24)	1.86 (1)
Fe(1)–C(13)	2.131 (9)	C(1)–C(2)	1.45 (2)
Fe(1)–C(14)	2.10 (1)	C(2)–C(3)	1.43 (2)
Fe(1)–C(15)	2.09 (1)	C(2)–C(5)	1.48 (2)
Fe(1)–C(16)	2.15 (1)	C(3)–C(4)	1.43 (2)
Si(1)–C(1)	1.86 (1)	C(3)–C(6)	1.49 (2)
Si(1)–C(7)	1.87 (2)	C(13)–C(14)	1.44 (1)
Si(1)–C(8)	1.86 (1)	C(14)–C(15)	1.42 (2)
Si(1)–C(9)	1.89 (1)	C(14)–C(18)	1.50 (2)
Si(2)–C(4)	1.86 (1)	C(15)–C(16)	1.44 (2)
Si(2)–C(10)	1.88 (2)	C(15)–C(17)	1.51 (1)

mL of THF was added to the solution of 11. The combined mixture was cooled to −78 °C and added to $FeCl_2$ (0.55 g, 4.2 mmol) in 15 mL of THF. The reaction mixture was warmed to 25 °C and allowed to stir for 24 h. The solvent was removed under reduced pressure, and the residue was extracted with 3 × 100 mL of pentane. Removal of the pentane under reduced pressure gave a dark residue which was subject to sublimation (50–60 °C/0.05 Torr) to remove ferrocene. The residue was taken up in pentane, which on cooling to −78 °C gave 0.6 g (25%) of dark red crystals, mp 190 °C. Anal. Calcd for $C_{17}H_{29}BiFeSi_2$: C, 36.83; H, 5.27. Found: C, 36.82; H, 5.10. ^{1}H-NMR ($CDCl_3$): δ 4.18 (s, 5 H), 2.03 (s, 6 H), 0.18 (s, 18 H). C-NMR ($CDCl_3$): δ 129 (*C*Bi), 119 (*C*CH_3), 71.6 (Cp), 30.7 (C*CH_3*), 3.72 (Si*CH_3*). MS (EI) exact mass: calcd for $C_{17}H_{29}BiFeSi_2$, *m/e* 554.0961; found, *m/e* 554.0957. UV (cyclohexane) [λ, nm (ϵ)]: 538 (324), 401 (1220), 319 (3150), 277 (5710), 274 (6040), 262 (7470), 228 (24700).

b. 2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-dibismaferrocene (3). The solution of 11 prepared above was recooled to −78 °C and added to $FeCl_2$ (0.29 g, 2.1 mmol) in 30 mL of THF. After warming of the solution to 25 °C, stirring was continued for 24 h. Removal of solvent under reduced pressure left a dark residue, which was extracted with pentane (3 × 50 mL). Solvent was removed from the extracts, and the residue was recrystallized from CH_2Cl_2 at −78 °C to give 0.32 g (17%) of dark red crystals, mp ~205 °C dec. ^{1}H-NMR ($CDCl_3$) (30 °C): δ 0.21 (s, 36 H), 1.85 (s, 12 H). ^{1}H-NMR (CD_2Cl_2) (30 °C): δ 0.237 (s, 36 H), 1.88 (s, 12 H). ^{1}H NMR (CD_2Cl_2) (−38 °C): 0.122 (s, 18 H), 0.227 (s, 18 H), 1.747 (s, 6 H), 1.881 (s, 6 H). T_c = −7 ± 5 °C. MS (EI) [m/e (intensity)]: 922 (34, M$^+$, calcd for $C_{24}H_{48}Bi_2FeSi_4$), 73 (100). Anal. Calcd for $C_{24}H_{48}Bi_2FeSi_4$: C, 31.24; H, 5.24. Found: C, 30.99; H, 5.20.

X-ray Structure Determination. Crystallographic data are collected in Table I. Crystals of 2 suitable for X-ray diffraction were obtained by recrystallization from pentane. Laue symmetry indicated that the space group was $P1$ or $P\bar{1}$, and it was shown

Table IV. Selected Bond Angles (deg) for 2

Sb(1)–C(1)–Si(1)	118.2 (6)	C(1)–C(2)–C(3)	116 (1)
Sb(1)–C(1)–C(2)	112.3 (8)	C(1)–C(2)–C(5)	122 (1)
Sb(1)–C(4)–Si(2)	117.5 (7)	C(2)–C(3)–C(4)	118 (1)
Sb(1)–C(4)–C(3)	111.6 (8)	C(2)–C(3)–C(6)	121 (1)
Sb(2)–C(13)–Si(4)	117.9 (5)	C(3)–C(2)–C(5)	122 (1)
Sb(2)–C(13)–C(14)	111.5 (8)	C(4)–C(3)–C(6)	120 (1)
Sb(2)–C(16)–Si(13)	118.7 (6)	C(13)–Sb(2)–C(16)	81.1 (4)
Sb(2)–C(16)–C(15)	111.0 (8)	C(13)–C(14)–C(15)	117 (1)
Si(1)–C(1)–C(2)	125.8 (9)	C(13)–C(14)–C(18)	121 (1)
Si(2)–C(4)–C(3)	128 (1)	C(14)–C(15)–C(16)	118.4 (9)
Si(3)–C(16)–C(15)	127.2 (8)	C(14)–C(15)–C(17)	121 (1)
Si(4)–C(13)–C(14)	125.7 (8)	C(15)–C(14)–C(18)	122.0 (9)
C(1)–Sb(1)–C(4)	80.8 (5)	C(16)–C(15)–C(17)	120 (1)

to be the latter by structural solution and refinement. An ORTEP plot of the molecular structure of 2 that shows the numbering scheme used in the refinement is illustrated in Figure 1. Table II gives the positional values, while Tables III and IV give the more important distances and the bond angles for the non-hydrogen atoms. Table VI, a list of observed and calculated structure factors, is available in the supplementary material.

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Registry No. 2, 139426-50-9; 3, 139426-51-0; 5, 137594-89-9; 6, 137594-87-7; 7, 139426-49-6; 8, 139408-78-9; 9, 139426-52-1; 10, 137594-88-8; 11, 139408-79-0; 12, 139426-53-2; zirconocene dichloride, 1291-32-3; 1-trimethylsilyl-1-propyne, 6224-91-5; phenyldichlorostibine, 5035-52-9; phenyldiiodobismuthine, 39110-03-7.

Supplementary Material Available: Figure 1a, showing an ORTEP plot from a different perspective, and Table V, listing hydrogen atomic parameters for 2 (3 pages); Table VI, listing observed and calculated structure factors for 2 (22 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Rhodium Complexes Containing a Photolabile η^2-Carbodiimide Ligand. 1,3-Dipolar Cycloaddition of Phenyl Azide to Tp′Rh(CNR)$_2$ (Tp′ = Hydrotris(3,5-dimethylpyrazolyl)borate)

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The 1,3-dipolar cycloaddition of phenyl azide to the metal-coordinated isocyanide ligands in Tp′Rh(CNR)$_2$ (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate, R = neopentyl, methyl, 2,6-xylyl; **1a–c**) or Cp*Rh(CN-neopentyl)$_2$ (Cp* = η^5-1,2,3,4,5-pentamethylcyclopentadienyl; **3**) in hexane produces the complexes Tp′Rh(CNR)(η^2-PhN=C=NR) (R = neopentyl, methyl, 2,6-xylyl; **2a–c**) and Cp*Rh(CNR)(η^2-PhN=C=N-neopentyl) (**4**), respectively, in high yield. The reaction is regiospecific with respect to coordination of the unsymmetrical carbodiimide ligand. Reaction of 2,4-xylyl azide with Tp′Rh(CN-2-tolyl)$_2$ (**1d**) gives Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl) (**2d**), for which the solid-state structure has been obtained by X-ray diffraction. Complex **2d** crystallizes from toluene in the triclinic space group $P\bar{1}$ with a = 10.962 (6) Å, b = 11.238 (4) Å, c = 8.691 (14) Å, α = 96.95 (5)°, β = 104.02 (5)°, γ = 101.00 (4)°, V = 2159 (5) Å^3, and Z = 2. The structure of **2d** confirms the bidentate bonding of the carbodiimide and shows that the nitrogen of the carbodiimide arising from the azide is coordinated to rhodium. Photolysis of **2a** in benzene produces Tp′Rh(H)(Ph)(CN-neopentyl) (**5**) along with free PhN=C=N-neopentyl with a quantum yield of 1.0 ± 0.3, whereas complex **4** is photochemically unreactive in benzene solution. The conversion of **2a** to **5** can also be effected thermally, although the rate is slow at 100 °C. Photolysis of **2a** in the solid state results in an intramolecular reaction to give Tp′Rh(H)(2-(N=C=N-neopentyl)C$_6$H$_4$)(CN-neopentyl) (**7**). Addition of excess neopentyl isocyanide to **2a** gives the azametallacyclobutane complex Tp′RhC(=N-neopentyl)N(Ph)C(=N-neopentyl)(CN-neopentyl) (**8**).

Introduction

The chemistry relating to the coordination of heterocumulenes to transition metals is extensive and can be viewed as having an important relationship to the activation and reduction of carbon dioxide.[1] Many stable transition-metal complexes containing such ligands as allenes,[2] isocyanates,[3] ketenes,[4] ketenimines,[5] carbon disulfide,[6] and carbon diselenide[7] as well as carbon dioxide[1] itself have been characterized. Stable complexes of carbodiimides have also been reported.[8] Isolation of complexes in which the carbodiimide is bound in an η^2 mode are uncommon, however, and there exists only one crystallographically characterized example to date.[8a] As is typical of most cumulenes, carbodiimides only form stable

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