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Secondary Bonding in Organopnicogen Compounds. Comparison of the Structures of Octamethyl-1,1′-distibaferrocene and Octamethyl-1,1′-diarsaferrocene

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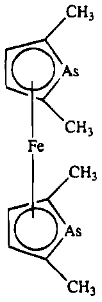
2,2′,3,3′,4,4′,5,5′-Octamethyl-1,1′–diarsaferrocene (**6**) and 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-distibaferrocene (**7**) were obtained from the reactions of the corresponding 1-phenyl-2,3,4,5-tetramethylheteroles with lithium followed by $FeCl_2$. Red-black crystals of **7** form in space group $P2_1/n$ with $Z = 4$, $a = 7.346(2)$ Å, $b = 14.357(2)$ Å, $c = 15.927(3)$ Å, and $\beta = 101.17(2)°$, while red-brown crystals of **6** form in space group $C2/c$ with $Z = 4$, $a = 14.416(3)$ Å, $b = 12.829(2)$ Å, $c = 8.982(2)$ Å, and $\beta = 103.94(2)°$. Full structures have been determined and show a close (3.58 Å) inter-ring Sb···Sb contact for **7**, but no close As···As contact is found for **6**. Extended Hückel MO calculations have been performed on the family of diheteroferrocenes $(C_4H_4E)_2Fe$ (E = P, As, Sb, Bi).

In the solid state several derivatives of the heavier group 15 element diheteroferrocenes $Fe(C_4H_4E)_2$ adopt structures with short interannular separations between the heteroatoms. Thus, the 2,2′,5,5′-tetramethyl-1,1′-diheteroferrocenes **1**,[1] **2**,[2] and **3**[3] all have totally eclipsed structures with E···E contacts less than 3.7 Å, where E = As, Sb, Bi. Since these distances are shorter than the van der Waals radius separation, they seem indicative of secondary bonding.[4] However, not all diheteroferrocenes have these short E···E contacts. The closely related 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**4**) adopts a different conformation with a much longer P···P separation.[5] Similarly, the more crowded distibaferrocene **5** does not have a short Sb···Sb contact.[6] In order to explore this phenomonon further, we have prepared octamethyl-1,1′-diarsaferrocene (**6**) and octamethyl-1,1′-distibaferrocene (**7**). We report here on their crystal structures and on extended Hückel calculations of the conformations of the family of diheteroferrocenes $(C_4H_4E)_2Fe$, where E = P, As, Sb, Bi.



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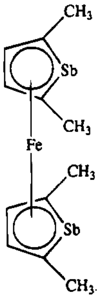

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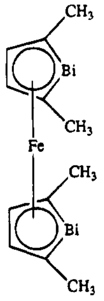

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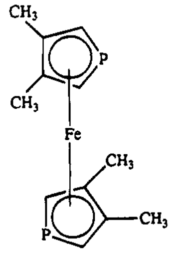

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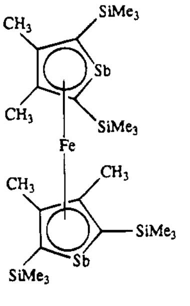

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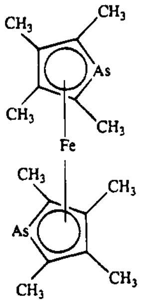

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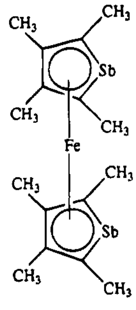

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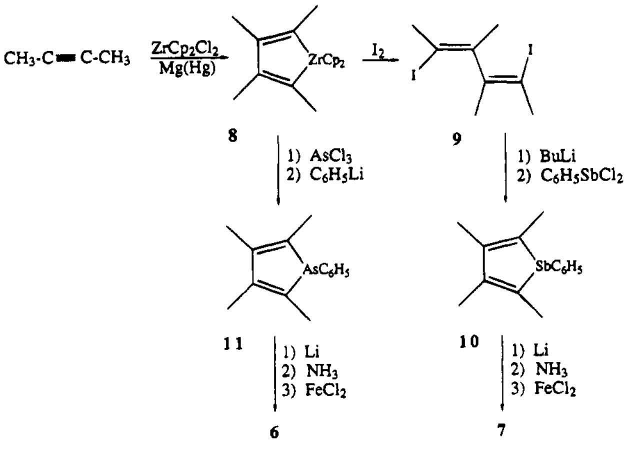
Results and Discussion

Syntheses. The octamethyldiheteroferrocenes **6** and **7** were prepared from 2-butyne by adaption of Fagan and Nugent heterole synthesis:[7]



The reaction of zirconacycle **8** with iodine to give the diodide **9**, followed by sequential treatment with butyl-

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[4] A secondary bond may be defined as a covalent bond with fractional bond order which involves interatomic distances significantly longer than normal bonds but shorter than van der Waals separation. For a more detailed discussion see: Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972,** *15,* 1.

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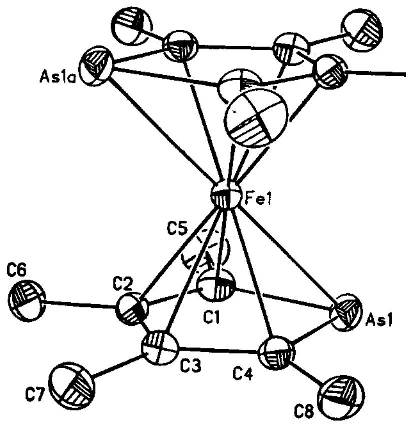
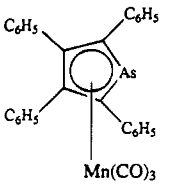


Figure 1. ORTEP drawing of the solid-state structure of 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-diarsaferrocene (**6**), with thermal ellipsoids at the 50% probability level.

lithium and phenylantimony dichloride, affords stibole **10** in satisfactory yield. On the other hand, arsole **11** is prepared using the procedure of Theopold et al.[8] Reaction of these heteroles with lithium metal gives unisolated lithium heterocyclopentadienides and phenyllithium. After removal of the phenyllithium by its reaction with ammonia, the diheteroferrocenes are formed in good yield by treatment with ferrous chloride.

Structures. The molecular structure of **6** is illustrated in Figure 1. Octamethyldiarsaferrocene has a ferrocene-like structure in which the iron atom is sandwiched between the two tetramethyl-η^5-arsolyl rings. The structure of **6** is very similar to that of **1**, except that the As atoms are trans-anti to each other rather than cis-eclipsed. Thus, **6** has C_{2h} symmetry rather than the C_{2v} symmetry shown by **1**.

The geometry of the tetramethyl-η^5-arsolyl ligands of **6** closely resembles those of the dimethyl-η^5-arsolyl ligands of **1** and the tetraphenyl-η^5-arsolyl ring of **12**.[9]



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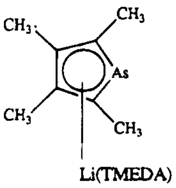

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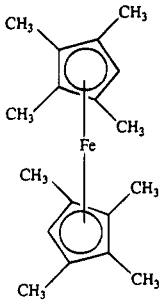

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The four C atoms of each arsolyl ring lie in parallel planes 3.30 Å apart and 1.65 Å from the Fe atom. The As atoms are displaced out of these planes away from Fe by 0.086 Å. Compound **1** and other group 15 heteroferrocenes show similar displacements.[10] This displacement appears to be a consequence of the need of the Fe to simultaneously maintain π-bonding to the small C and the large As atoms. In this respect it is instructive to compare the geometry of the tetramethylarsolyl ring of **6** with that shown by the lithium tetramethylethylenediamine salt of the same ligand, **13**.[8] While the corresponding bond lengths and angles of **13** are nearly the same as those of **6**, the As atom of **13** is displaced out of the plane of the four C atoms toward the small Li by 0.024 Å.

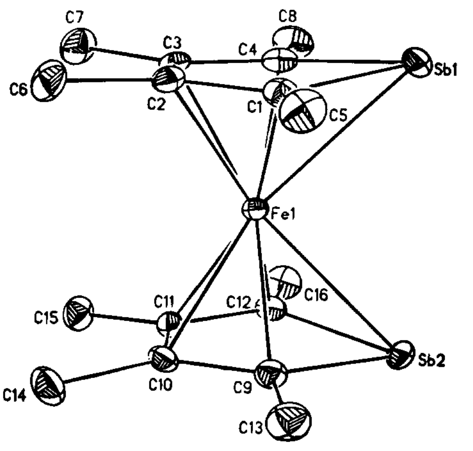

Figure 2. ORTEP drawing of the solid-state structure of 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-distibaferrocene (**7**), with thermal ellipsoids at the 50% probability level.

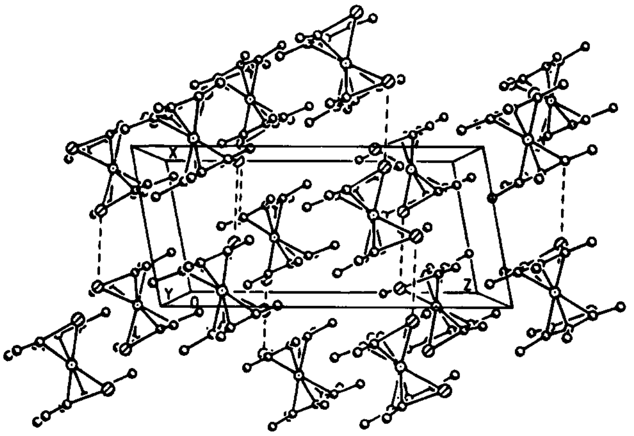

Figure 3. Crystal packing diagram of 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-distibaferrocene (**7**). The short (3.95 Å) intermolecular Sb—Sb contact is shown by a dashed line.

The molecular structure of octamethyldistibaferrocene (**7**) is illustrated in Figure 2. As can be seen, the compound adopts the C_{2v} conformation, which is very similar to that reported for **2**. Indeed, all of the structural parameters of **2** and **7** are nearly identical. However, the inter-ring Sb••Sb separation in **7** is 0.10 Å shorter than in **2**, while the Fe—Sb distances are somewhat longer. In addition there is also an intermolecular Sb••Sb contact at 3.95 Å, while **2** has no intermolecular Sb••Sb distances shorter than 4.2 Å (see Figure 3). Thus, the secondary bonding involving Sb is more pronounced in the octamethyldistibaferrocene. In contrast, the secondary bonding involving As is totally absent in the octamethyldiarsaferrocene.

The crystallographic C_{2h} conformation found for **6** is analogous to the crystallographic conformation observed for the corresponding octamethylferrocene (**14**).[11] Molecular mechanics calculations on **14** indicate that this C_{2h} conformation is a global minimum[12] but that the

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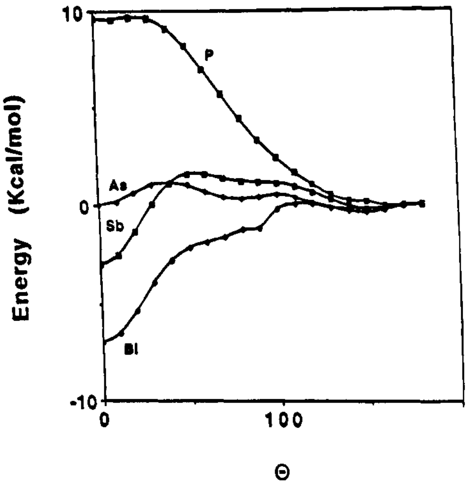


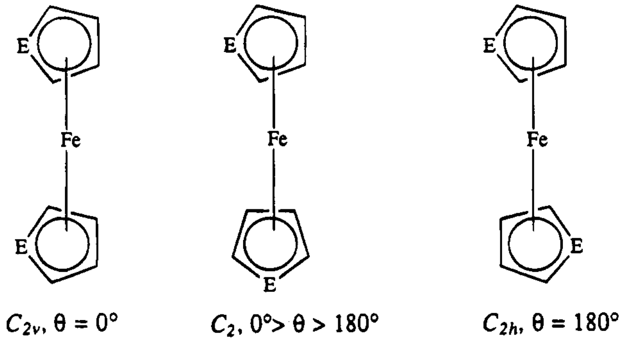
Figure 4. Relative energies of the 1,1′-diheteroferrocenes $(C_4H_4E)_2Fe$, where E = P, As, Sb, Bi, as a function of the angle θ.

barrier to ring rotation is modest (2–3 kcal/mol).[13] Similarly, gas-phase electron diffraction studies on decamethylferrocene give an internal rotational barrier of only 1 kcal/mol.[14] Thus, it seems likely that conformation preferences of polymethylferrocenes are small. The ferrocene conformational results are particularly relevant to the heteroferrocenes since the inter-ring distances are nearly the same.

The observation that the tetramethyl- and the octamethyldiarsaferrocenes adopt different conformations suggests that the conformational preferences of polymethyldiarsaferrocenes are also small. Thus, if the C_{2v} conformation observed for **1** is stabilized by a secondary As···As bonding, the bond strength must be quite small. Since both distibaferrocenes **2** and **7** adopt C_{2v} conformations, there must be a larger conformational preference which may indicate stronger secondary Sb···Sb bonding. We also note that many distibines (R_4Sb_2) show similar secondary bonding which is absent in the corresponding diarsines (R_4As_2).[15] Indeed, it is a general observation that secondary bonding is more important for the heavier main-group elements.[4]

Calculations. The conformation properties of 1,1′-diphosphaferrocene have been studied theoretically using extended Hückel (EH)[16,17] and Fenske–Hall methods.[18] A recent EH study of the conformations of heterocyclic transition-metal complexes treats diphosphaferrocene and diarsaferrocene in some detail but gives only a more cursory treatment of distibaferrocene.[17] Unfortunately, this study is somewhat compromised by the use of incorrect bond lengths and unrealistic geometries. For this reason we have performed an EH study of the family of diheteroferrocenes ($(C_4H_4E)_2Fe$, where E = P, As, Sb, Bi) using molecular parameters derived from X-ray diffraction structures of derivatives **1**–**7**. The usual values of electronic parameters were used,[19] except in the case of Bi, where relativistically corrected parameters were employed.[20,21]

We have chosen to hold the relative geometry of each C_4H_4E ring and the C–Fe and E–Fe distances constant. The sole conformational variable (θ) is the relative orientation of the two C_4H_4E rings. When the atoms E are cis-eclipsed (C_{2v} symmetry), $\theta = 0°$. When the E atoms are trans-anti (C_{2h} symmetry), $\theta = 180°$, while the intermediate C_2 symmetry conformations have $0° > \theta > 180°$.



The total energies of the four diheteroferrocenes were determined as a function of angle θ. Since only the relative conformational energies are of interest, the C_{2h} conformation of each diheteroferrocene was arbitarily set at zero energy. Figure 4 gives the relative conformational energy as a function of θ.

The behavior of all of the diheteroferrocenes is very similar in the region near the C_{2h} conformation. There is little energy change (±2 kcal/mol) as θ varies from 100 to 180°. However, the relative energies diverge markedly as the C_{2v} conformation is approached. Diphosphaferrocene is destabilized by 9.6 kcal/mol at $\theta = 0°$, in good qualitative agreement with the prior EH treatments.[16,17] Diarsaferrocene is found to be equienergetic at $\theta = 0$ and 180°. The C_{2v} conformations of distibaferrocene and dibismaferrocene are the global mimima. Relative to the C_{2h} conformations, the C_{2v} eclipsed conformations of distibaferrocene and dibismaferrocene are stabilized by 3 and 7 kcal/mol, respectively.

Paradoxically the relative conformational energies of the C_{2v} conformation of $(C_4H_4E)_2Fe$ become more favorable as E becomes larger. The source of this stabilization must be due to direct through-space bonding involving overlap of the pnicogen p orbitals. To test this conclusion, we have performed calculations with the overlap integrals involving the two heteroatoms set equal to zero. The stabilization of the C_{2v} conformation vanishes. For all $(C_4H_4E)_2Fe$ compounds the C_{2v} conformation becomes the global maximum, while the C_{2h} conformation becomes the global minimum. Thus, the secondary inter-ring bonding must dominate the conformational properties of the heavier diheteroferrocenes.

Our calculations are consistent with the observed crystallographic conformations of **1**–**7**. The X-ray structure of **4** has $\theta = 140°$.[5] While the computational global minimum occurs for $\theta = 160°$, the observed $\theta = 140°$ has an insignificantly higher value (0.25 kcal/mol). The conformational energies of diarsaferrocene vary by only 1.4 kcal/mol over the full range of θ values. Thus, it is not surprising that different conformations are populated by **1** and **6**. In contrast, the C_{2v} conformation of

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Table 1. Structure Determination Summary[a]

	7	6[b]
	Crystal Data	
empirical formula	$C_{16}H_{24}FeSb_2$	$C_{16}H_{24}As_2Fe$
fw	515.72	422.060
cryst color and habit	red-black needles	red-brown rectangular plate
cryst dimens, mm	0.18 × 0.22 × 0.32	0.40 × 0.38 × 0.14
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
Z	4	4
unit cell dimens from 27 rflns: 2θ range, deg	$15.1 \le 2\theta \le 28.6$	$21.5 \le 2\theta \le 34.6$
a, Å	7.346(2)	14.416(3)
b, Å	14.357(2)	12.829(2)
c, Å	15.927(3)	8.982(2)
β, deg	101.17(2)	103.94(2)
V, Å^3	1648.0(5)	1612.0(5)
D(calcd), g cm^{-3}	2.07_9	1.73_9
F(000), e	992	848
linear abs coeff (μ), cm^{-1}	41.3	49.87
	Data Collection	
diffractometer	Siemens R3m/v, equipped with LT-2	Siemens R3m/v, equipped with LT-2
radiation type (λ, Å)	Mo Kα (0.710 73) (Lp cor, graphite monochromator)	Mo Kα (0.710 73) (Lp cor, graphite monochromator)
temp, °C	−140	−95
scan type	$\theta/2\theta$ scan	$\theta/2\theta$ scan
2θ scan range, deg	5−55	5−55
octants used	$+h,+k,\pm l$ (h, 0 to 10; k, 0 to 19; l, −19 to +19) plus Friedel pairs	$+h,+k,\pm l$ (h, 0 to 19; k, −17 to +17; l, −12 to +12) plus Friedel pairs
scan rate, deg min^{-1}	3.5−9.0, variable	3−8, variable
scan width, deg	0.9 below Kα_1 to 0.9° above Kα_2	0.9 below Kα_1 to 0.9 above Kα_2
bdgd scan ratio	0.5	0.5
std rflns	3 measd every 97 rflns, random variations <2%	3 measd every 97 rflns, random variations <2%
no. of rflns collected	8769	4019
no. of rflns used	3801 ($R_{int} = 0.0208$)	1855 ($R_{int} = 0.0197$)
abs cor	empirical	empirical
	Solution and Refinement	
system used	Siemens SHELXTL PLUS, VAXStation 3500	Siemens SHELXTL PLUS, VAXStation 3500
soln	direct methods	direct methods
refinement method	full-matrix least squares	full-matrix least squares
function minimized	$\Sigma w(\lvert F_o - F_c\rvert)^2$	$\Sigma w(\lvert F_o - F_c\rvert)^2$
H atoms	individual isotropic refinement	individual isotropic refinement
refined rflns with $F_o \ge 4\sigma(F)$	3392	1798
no. of params refined	270	138
data/param ratio	12.6	13.0
$R = \Sigma(\lvert F_o - F_c\rvert)/\Sigma\lvert F_o\rvert$	0.0244	0.0316
$R_w = [\Sigma(w\lvert F_o - F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2}$	0.0247	0.0442
w^{-1}	$\sigma^2(F_o) + 0.000089(F_o)^2$	$\sigma^2(F_o) + 0.001085(F_o)^2$
GOF	1.46	1.18
mean shift error	<0.001	<0.001
max shift/error	0.001	0.002
secondary extinction	no cor applied	$[5.0(9)] \times 10^{-8}$
resid electron density, e/Å^3	+0.61/−0.55	+0.68/−0.71

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, U(eq), defined as $^1/_3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. [b] The molecule lies on a special position in the crystal lattice with the Fe atom on an inversion center.

distibaferrocene is favored over the C_{2h} conformation by 3 kcal/mol. Thus, both **2** and **7** crystallize with C_{2v} conformations. However, distibaferrocene derivative **5** shows a crystallographic conformation with $\theta \approx 70°$,[5] which is close to the calculated global maximum energy of 4.5 kcal/mol. In this case the conformation must be controlled by the gear locking of the large trimethylsilyl groups[6,22] rather than any electronic preference of the distibaferrocene system. Indeed, it has been estimated that the electronically favorable C_{2v} conformation will be sterically destabilized by the two pairs of trimethylsilyl interactions to the extent of 22 kcal/mol.[6] The C_{2v} conformation is calculated to be most favorable for dibismaferrocene. This conformation is populated in the only crystallographically characterized dibismaferrocene, **3**.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen. 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 Bruker WH-360 or AM-300 spectrometer, on solutions in $CDCl_3$ or C_6D_6. The ^1H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me_4Si. The combustion analyses were determined by the Analytical Services Department of the Department of Chemistry, University of Michigan.

(1Z,3Z)-1,4-Diiodo-1,2,3,4-tetramethyl-1,3-butadiene (9). Iodine (44 g, 173 mmol) was added portionwise to a solution of 1,1-bis(η^5-cyclopentadienyl)-1,2,3,4-tetramethyl-1-zircona-2,4-cyclopentadiene[7] (29.8 g, 91 mmol) in 200 mL of THF at −78 °C with stirring. Stirring was continued for 30 min at −78 °C, after which time the solution was warmed to 25 °C. Solvent was removed in vacuo, leaving a tarry residue which was extracted with pentane (3 × 100 mL). The combined extracts were washed successively with a saturated aqueous solution of $Na_2S_2O_3$ (3 × 100 mL) and water (2 × 100 mL) and then dried over anhydrous Na_2SO_4. Solvent was removed in vacuo, leaving a semisolid brown oil, which was recrystallized from pentane to give 22.5 g of white crystals with a yellow

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

atom	*x*	*y*	*z*	*U*(eq)
		Compound **7**		
Sb(1)	0.11012(3)	0.18515(1)	0.27942(1)	0.01450(7)
Sb(2)	0.55914(3)	0.17823(1)	0.22308(1)	0.01421(6)
Fe(1)	0.42240(6)	0.26883(3)	0.33631(3)	0.0094(1)
C(1)	0.1588(4)	0.3297(2)	0.2938(2)	0.0140(9)
C(2)	0.2356(4)	0.3570(2)	0.3789(2)	0.0144(9)
C(3)	0.2897(4)	0.2828(2)	0.4392(2)	0.0141(9)
C(4)	0.2574(4)	0.1911(2)	0.4064(2)	0.0154(9)
C(5)	0.0880(5)	0.3967(2)	0.2227(2)	0.020(1)
C(6)	0.2561(5)	0.4576(2)	0.4056(2)	0.020(1)
C(7)	0.3679(5)	0.3027(3)	0.5321(2)	0.022(1)
C(8)	0.2985(5)	0.1050(2)	0.4614(2)	0.023(1)
C(9)	0.5638(4)	0.3234(2)	0.2437(2)	0.0147(9)
C(10)	0.6516(4)	0.3505(2)	0.3272(2)	0.0137(9)
C(11)	0.7050(4)	0.2763(2)	0.3874(2)	0.0123(8)
C(12)	0.6618(4)	0.1850(2)	0.3562(2)	0.0147(9)
C(13)	0.5036(5)	0.3916(2)	0.1718(2)	0.021(1)
C(14)	0.6938(5)	0.4511(2)	0.3512(2)	0.020(1)
C(15)	0.8081(5)	0.2941(3)	0.4773(2)	0.019(1)
C(16)	0.7154(5)	0.0991(2)	0.4098(2)	0.021(1)
		Compound **6**		
As(1)	0.34808(2)	0.28810(2)	0.25016(2)	0.0228(1)
Fe(1)	0.25000	0.25000	0.00000	0.0143(1)
C(1)	0.2128(2)	0.2730(2)	0.2111(3)	0.0215(7)
C(2)	0.1620(2)	0.3425(2)	0.0976(2)	0.0191(6)
C(3)	0.2233(2)	0.4068(2)	0.0295(3)	0.0202(6)
C(4)	0.3217(2)	0.3879(2)	0.0897(3)	0.0206(6)
C(5)	0.1668(2)	0.1986(2)	0.3011(3)	0.0342(9)
C(6)	0.0555(2)	0.3513(2)	0.0558(3)	0.0292(8)
C(7)	0.1835(2)	0.4869(2)	−0.0922(3)	0.0317(8)
C(8)	0.4011(2)	0.4446(2)	0.0400(3)	0.0300(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 7 and 6

	Compound **7**		
Sb(1)−Fe(1)	2.5926(5)	Fe(1)−C(9)	2.113(3)
Sb(1)−C(1)	2.110(3)	Fe(1)−C(10)	2.080(3)
Sb(1)−C(4)	2.102(3)	Fe(1)−C(11)	2.080(3)
Sb(2)−Fe(1)	2.5797(4)	Fe(1)−C(12)	2.104(3)
Sb(2)−C(9)	2.109(3)	C(1)−C(2)	1.419(4)
Sb(2)−C(12)	2.110(3)	C(2)−C(3)	1.438(4)
Fe(1)−C(1)	2.113(3)	C(3)−C(4)	1.420(4)
Fe(1)−C(2)	2.075(3)	C(9)−C(10)	1.416(4)
Fe(1)−C(3)	2.073(3)	C(10)−C(11)	1.436(4)
Fe(1)−C(4)	2.118(3)	C(11)−C(12)	1.416(4)
Sb(1)−C(1)−C(2)	113.8(2)	C(1)−C(2)−C(3)	116.2(3)
Sb(1)−C(4)−C(3)	114.2(2)	C(2)−C(3)−C(4)	115.8(2)
Sb(2)−C(9)−C(10)	114.1(2)	C(9)−Sb(2)−C(12)	78.9(1)
Sb(2)−C(12)−C(11)	114.0(2)	C(9)−C(10)−C(11)	116.0(3)
C(1)−Sb(1)−C(4)	79.1(1)	C(10)−C(11)−C(12)	116.0(2)
	Compound **6**		
As(1)−Fe(1)	2.3984(2)	Fe(1)−C(3)	2.077(2)
As(1)−C(1)	1.907(3)	Fe(1)−C(4)	2.109(2)
As(1)−C(4)	1.896(2)	C(1)−C(2)	1.418(3)
Fe(1)−C(1)	2.112(2)	C(2)−C(3)	1.447(3)
Fe(1)−C(2)	2.080(2)	C(3)−C(4)	1.413(3)
As(1)−C(1)−C(2)	113.4(2)	C(1)−As(1)−C(4)	85.43(9)
As(1)−C(4)−C(3)	113.9(1)	C(1)−C(2)−C(3)	113.6(2)
C(2)−C(3)−C(4)	113.6(2)		

cast, mp 40.5−42 °C. The diiodide could be stored in the freezer but slowly decolorized at 25 °C. Anal. Calcd for $C_8H_{12}I_2$: C, 26.54; H, 3.34. Found: C, 26.37; H, 3.47. ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 6H), 2.47 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 15.8, 29.1, 94.2, 146.4 MS (EI, 70 eV; *m/z* (intensity)): 362 (1, M$^+$ for $C_8H_{12}I_2$), 235 (100 M + − I). MS (EI) exact mass: calcd for $C_8H_{12}I_2$ 361.9029, found 361.9035.

1-Phenyl-2,3,4,5-tetramethylstibole (10). To a solution of (1*Z*,3*Z*)-1,4-diiodo-1,2,3,4-tetramethyl-1,3-butadiene (2.4 g, 6.6 mmol) in 50 mL of ether at −78 °C was added with stirring 9.2 mL of 1.44 N butyllithium (13.2 mmol) in hexane. This solution was stirred at −78 °C for 1.5 h, after which time the solution was warmed to 25 °C for 15 min. After the mixture was recooled to −78 °C, the dilithio compound was added via a cannula to a solution of phenylantimony dichloride (1.9 g, 7.1 mmol) in 40 mL of ether. There was an immediate color change to gray-brown. The reaction mixture was warmed to 25 °C over a period of 1 h. Removal of solvent under reduced pressure left a tar which was extracted with pentane (2 × 50 mL). The extracts were filtered, giving a bright yellow filtrate. Removal of solvent left 2.0 g (99%) of a golden brown oil which showed ^{1}H NMR and ^{13}C NMR spectra identical with those reported by Fajan and Nugent.[7]

2,2′,3,3′,4,4′,5,5′-Octamethyl-1,1′-distibaferrocene (7). Lithium wire (2% sodium; 1.0 g, excess) was cut into pieces approximately 2 mm in diameter and placed in 50 mL of THF. 1-Phenyl-2,3,4,5-tetramethylstibole (1.0 g, 3.3 mmol) was added. After about 5 min the color darkened, ultimately becoming red-brown. The solution was stirred for 20 h, after which time it was decanted from the excess lithium. After it was cooled to −78 °C, the solution was flushed with dry NH_3 gas for 5 min and then warmed to 25 °C to remove the excess NH_3. At this point the solution was a dirty green. After the temperature was lowered to −78 °C, $FeCl_2$ (1.0 g, 7.9 mmol) was added, and the reaction mixture was warmed to 25 °C and was stirred for 20 h. Solvent was removed to leave a dark residue, which was extracted with 50 mL of hexane. When the temperature was lowered to −78 °C, the red-brown extracts deposited 500 mg (59%) of red-brown crystals, mp ~280 °C. ^{1}H NMR (C_6D_6): δ 1.65 (s, 12H), 1.50 (s, 12H). ^{13}C NMR (C_6D_6): δ 14.8, 20.9, 103.9, 105.6. MS (EI; *m/z* (intensity)): 516 (100, M$^+$ for $C_{16}H_{24}{}^{121}Sb^{123}Sb^{56}Fe$). MS exact mass: calcd for $C_{16}H_{24}{}^{121}Sb_2{}^{56}Fe$ 513.9304, found 513.9313.

2,2′,3,3′,4,4′,5,5′-Octamethyl-1,1′-diarsaferrocene (6). In the same manner 6 was prepared from 1-phenyl-2,3,4,5-tetramethylarsole[7] (1.8 q, 6.9 mmol), lithium wire (0.5 g, 70 mmol), and ferrous chloride (0.44 g, 3.45 mmol). The product (1.2 g, 82%) was isolated as dark red crystals, mp 260 °C. Anal. Calcd for $C_{16}H_{24}As_2Fe$: C, 45.53; H, 5.61. Found: C, 45.61; H, 5.62. ^{1}H NMR (C_6D_6): δ 1.67 (s, 12H), 1.73 (s, 12H). ^{13}C NMR (C_6D_6): δ 13.9, 17.0, 97.2, 103.8. MS (EI; *m/z* (intensity)): 422 (100, M$^+$ for $C_{16}H_{24}As_2Fe$). MS exact mass: calcd for $C_{16}H_{24}As_2{}^{56}Fe$ 421.9659, found 421.9663.

X-ray Structure Determinations. Crystals of **6** and **7** suitable for X-ray diffraction were obtained by recrystallization from pentane. Crystallographic data are collected in Table 1. ORTEP plots of the molecular structures of **6** and **7** showing the numbering scheme used in the refinement are illustrated in Figures 1 and 2, respectively. Table 2 gives the positional values, while Table 3 gives the more important distances and bond angles for the non-hydrogen atoms. A list of observed and calculated structure factors is available from A.J.A. on request.

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Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms, positional parameters of the hydrogen atoms, and planes of ring carbon atoms for **6** and **7**, a packing diagram of **6**, and tables and a figure giving coordinates of atoms of $(C_4H_4E)_2Fe$ used in EH calculations and relative energies from EH calculations (12 pages). Ordering information is given on any current masthead page.

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