Synthesis, Characterization, and Reactivity of Iron–Dienyl Complexes

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A series of complexes of the type $CpFe(CO)_2(\eta^1$-R) [R = pd (1); R = hd (4); Cp = C_5H_5, pd = 2,4-pentadien-1-yl, hd = 2,4-hexadien-1-yl], $CpFe(CO)(\eta^3$-R) [R = pd (2); R = hd (5)], and $CpFe(\eta^5$-R) [R = pd (3); R = hd (6)] has been prepared and characterized with appropriate physical methods. Among these complexes, an X-ray diffraction study of 5 is reported; crystallographic data: space group $P2_1/c$, a = 7.648 (7) Å, b = 9.743 (3) Å, c = 14.664 (5) Å, β = 97.45 (5)°, V = 1083 (8) Å^3, and Z = 4. The structure parameters are refined to convergence with R = 0.034 and R_w = 0.030 for 890 reflections having $I > 3\sigma(I)$. The coordination geometry about the iron atom approximates a trigonal plane with carbonyl, Cp, and allyl groups occupying three coordination sites. Attempts to characterize the half-open sandwich compound 3 by an X-ray diffraction study were prevented by its highly disordered structure. The reaction of HPF_6 with 2 and 5 in ether respectively yields the cations $CpFe(CO)(\eta^4$-pentadiene)PF_6 (7) and $CpFe(CO)(\eta^4$-2,4-hexadiene)PF_6 (8). The structure of 8 has been solved by an X-ray diffraction study with the following parameters: space group $Ia3$, $a = b = c$ = 26.023 (4) Å, V = 17623 (8) Å^3, and Z = 48. The structural parameters are refined to convergence with R = 0.060 and R_w = 0.043 for 1364 reflections having $I > 3\sigma(I)$. The coordination geometry about the iron center approximates a distorted tetrahedron with the carbonyl, the Cp group, and the olefin occupying the four coordination sites. In the reaction of HPF_6 with η^1-dienyl complexes 1 and 4, the proton directly attacks on the γ- and ϵ-carbons of the ligand to give the corresponding η^2-diene cations in various amounts.

Introduction

The chemistry of transition-metal–pentadienyl complexes has become a subject of intensive studies in recent years.[1] One of the intriguing features of these complexes is the variety of geometries for the pentadienyl group bound to the metal center as depicted below. The
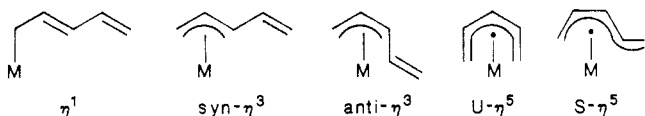
availability of appropriate reagents such as the pentadienyltin compound $(C_5H_7)Sn(CH_3)_3$[2] and the pentadienyl alkaline-metal salts[3] [2,4-$(CH_3)_2C_5H_5$]M (M = Na, K) has led to the rapid development of this area. In our laboratory,[4] we have used 1-halo-2,4-pentadienes for the preparation of such metal compounds because it reacts with metal carbonyl anions[4b-e] to give η^1-pentadienyl derivatives, which subsequently can be converted to the syn-η^3 and η^5 forms by thermal or photochemical activation as depicted in Scheme I.

In our earlier communication,[4d] we have used this method to prepare $CpFe(CO)_2(\eta^1$-pentadienyl) (1) (Cp = C_5H_5), $CpFe(CO)(syn$-η^3-pentadienyl) (2), and $CpFe(\eta^5$-pentadienyl) (3). Herein, in addition to the synthesis of their hexadienyl analogues, we also describe the crystal
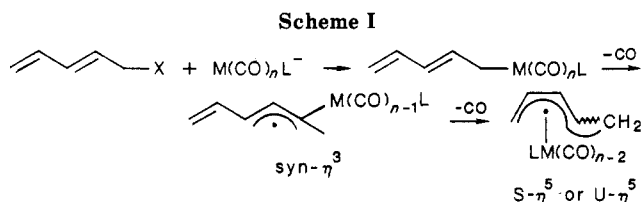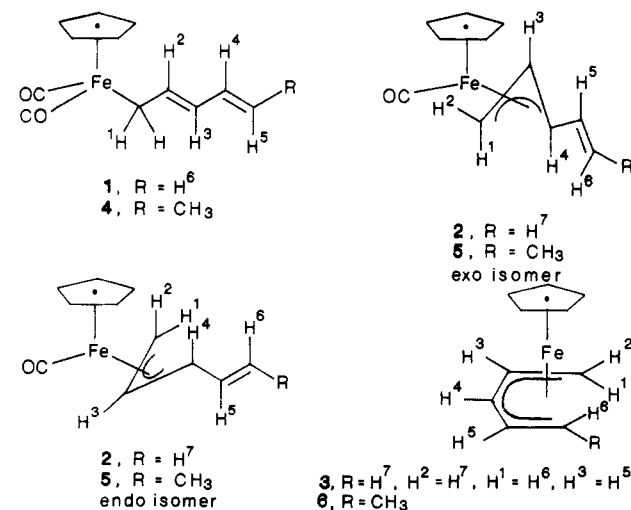
Scheme I

Chart I⁻

structures and reaction chemistry of these complexes and an X-ray diffraction study of a novel Fe(II) diene resulting from the reaction.

Results and Discussion

Previously, we have reported[4d] the synthesis of $CpFe(CO)_2(\eta^1$-pentadienyl) (1) by the reaction between $CpFe(CO)_2Na$ and *trans*-1-chloropenta-2,4-diene. Photolysis of 1 in ether at –20 °C leads to successive loss of CO ligands and yields $CpFe(CO)(\eta^3$-pentadienyl) (2) and $CpFe(\eta^5$-

(1) For recent reviews of acyclic pentadienyl complexes see: (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15.

(2) (a) Seyferth, D.; Goldman, E. W.; Pornet, J. J. *J. Organomet. Chem.* **1981**, *208*, 189. (b) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1981**, *219*, 81. (c) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1983**, *252*, 205.

(3) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuda, M.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089.

(4) (a) Cheng, C.-H.; Liu, R.-S., *J. Organomet. Chem.* **1986**, *308*, 237. (b) Lee, G.-H.; Peng, S.-M.; Liao, M. Y.; Liu, R.-S. *Ibid.* **1986**, *312*, 113. (c) Lee, T.-W.; Liu, R.-S. *Ibid.*, in press. (d) Lush, S.-F.; Liu, R.-S. *Organometallics* **1986**, *5*, 1908. (e) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Ibid.* **1986**, *5*, 2378.
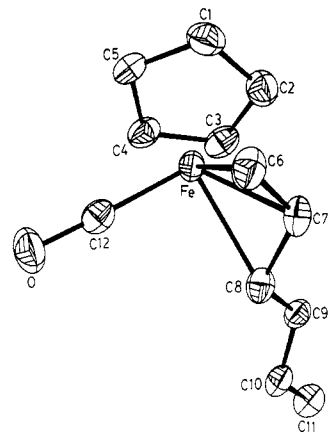
Figure 1. ORTEP drawing of CpFe(CO)(η^3-2,4-hexadien-1-yl) (5) Ellipsoids are scaled to represent the 50% probability Surface.

Table I. Atomic Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of CpFe(CO)(η^3-2,4-hexadien-1-yl) (5)

	x	y	z	B(iso), Å^2
Fe	0.15067 (11)	0.10502 (10)	0.16560 (6)	4.16 (5)
C(1)	0.2511 (10)	0.3004 (8)	0.1538 (5)	6.9 (4)
C(2)	0.3723 (9)	0.2045 (8)	0.1292 (5)	6.4 (4)
C(3)	0.2930 (9)	0.1299 (7)	0.0559 (5)	6.3 (4)
C(4)	0.1225 (9)	0.1769 (7)	0.0331 (5)	6.1 (4)
C(5)	0.0961 (9)	0.2854 (7)	0.0929 (5)	6.4 (4)
C(6)	0.1875 (8)	1.0888 (8)	0.3079 (4)	5.9 (4)
C(7)	0.2923 (8)	0.9986 (8)	0.2665 (4)	5.2 (4)
C(8)	0.2201 (7)	0.8981 (7)	0.2053 (4)	4.7 (3)
C(9)	0.3251 (8)	0.8203 (6)	0.1487 (4)	4.4 (4)
C(10)	0.2732 (7)	0.7053 (7)	0.1061 (4)	4.7 (3)
C(11)	0.3741 (9)	0.6275 (8)	0.0444 (5)	6.2 (4)
C(12)	-0.0674 (8)	0.0622 (7)	0.1643 (4)	5.0 (3)
O	-0.2169 (5)	0.0374 (5)	0.1615 (3)	7.4 (3)

a Estimated standard deviations are in parentheses.

pentadienyl) (3), respectively. Complex 2 exists as two stereoisomers, the endo and exo isomers (Chart I). The endo isomer undergoes facile isomerization to the exo isomer at ambient temperatures.

Following the work in synthesis of 1, CpFe(CO)$_2$(η^1-2,4-hexadien-1-yl) (4) was obtained in moderate yields (43%) from the reaction between CpFe(CO)$_2$Na and (E,E)-1-chlorohexa-2,4-diene in tetrahydrofuran at -78 °C. Similar to 2, photolysis of 4 in ether at -20 °C gave a mixture of CpFe(CO)(*syn*-η^3-2,4-hexadien-1-yl) (5) and CpFe(η^5-2,4-hexadien-1-yl) (6). Compound 5 was separated from 6 by column chromatography and recrystallized from pentane at -25 °C to give dark red crystals in moderate yield (39%). Stirring of a dichloromethane solution of 4 with anhydrous trimethylamine oxide at 0 °C for 6 h produced only 5 in a better yield (67%). The ^{1}H NMR spectrum of 5 reveals that only the exo isomer is present in solution. The NMR spectrum of the exo isomer is characterized by the more upfield resonances of H^1 and H^4 than that of H^{2}.[4d] We believe that the absence of endo isomer is due to its rapid isomerization to the exo isomer during preparation of the compounds. Complex 2 melts around room temperatures (mp 21 °C), and the crystal structure for a compound of this class therefore was undertaken for 5. An ORTEP drawing is shown in Figure 1. Atomic coordinates for the non-hydrogen atoms are listed in Table I. Selected bond distances and angles are reported in Table II.
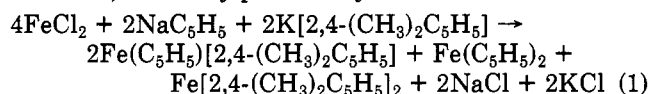
The coordination geometry about the iron atom approximates that of a trigonal plane with carbonyl, cyclopentadienyl, and allyl groups occupying three coordination sites.[5] The mouth of the allyl moiety faces away from the

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) of CpFe(CO)(η^3-2,4-hexadien-1-yl) (5)

Bond Distances					
Fe–C(1)	2.069 (7)	Fe–C(2)	2.082 (7)	Fe–C(3)	2.070 (6)
Fe–C(4)	2.049 (6)	Fe–C(5)	2.070 (6)	Fe–C(6)	2.075 (6)
Fe–C(7)	2.006 (6)	Fe–C(8)	2.145 (7)	Fe–C(12)	1.717 (6)
C(1)–C(2)	1.40 (1)	C(1)–C(5)	1.396 (9)	C(2)–C(3)	1.37 (1)
C(3)–C(4)	1.381 (9)	C(4)–C(5)	1.405 (9)	C(6)–C(7)	1.382 (9)
C(7)–C(8)	1.393 (9)	C(8)–C(9)	1.443 (8)	C(9)–C(10)	1.318 (9)
C(10)–C(11)	1.473 (9)	C(12)–O	1.164 (7)		

Bond Angles			
C(6)–Fe–C(7)	39.5 (2)	C(6)–Fe–C(8)	70.1 (2)
C(6)–Fe–C(12)	89.9 (2)	C(7)–Fe–C(8)	39.0 (2)
C(7)–Fe–C(12)	108.3 (2)	C(8)–Fe–C(12)	88.9 (2)
Fe–C(6)–C(7)	67.5 (3)	Fe–C(7)–C(6)	72.9 (3)
Fe–C(7)–C(8)	75.9 (3)	Fe–C(8)–C(7)	65.1 (3)
Fe–C(8)–C(9)	118.3 (4)	C(6)–C(7)–C(8)	121.7 (5)
C(7)–C(8)–C(9)	122.4 (5)	C(8)–C(9)–C(10)	124.3 (5)
C(9)–C(10)–C(11)	125.3 (5)	Fe–C(12)–O	177.5 (5)
C(2)–C(1)–C(5)	107.6 (6)	C(1)–C(2)–C(3)	108.4 (6)
C(2)–C(3)–C(4)	108.7 (6)	C(3)–C(4)–C(5)	107.8 (6)
C(1)–C(5)–C(4)	107.4 (6)		

cyclopentadienyl group and is aligned with the CO group. The structure of the hexadienyl ligand closely resembles that of pentadienyl ligands in (*syn*-η^3-pentadienyl)Co-(CO)$_2$(PPh$_3$),[4b] CpMo(CO)$_2$(*syn*-pentadienyl),[4e] bis(*syn*-η^3-pentadienyl)Fe[P(CH$_3$)$_3$]$_2$,[6a] and (*syn*-η^3-pentadienyl)-Mn(dmpe)$_2$.[6b] The hexadienyl ligand is bonded to the iron atom in an unsymmetric fashion with Fe–C(6) = 2.075 (6) Å, Fe–C(7) = 2.006 (6) Å, and Fe–C(8) = 2.145 (7) Å. The methylvinyl group of the hexadienyl ligand points away from the rest of the complex, minimizing the steric hindrance. The dihedral angle between methylvinyl plane (C(9),C(10),C(11)) and allylic plane (C(6),C(7),C(8)) is 27.2 (1)°.

Analogous to 2, photolysis of 5 in benzene for 24 h gave rise to a complete conversion to CpFe(η^5-2,4-hexadien-1-yl) (6). This *syn*-$\eta^3 \rightarrow \eta^5$ process is not achievable by thermal activation. Both 2 and 5 are thermally stable even at reflux in toluene for 24 h. A half-open sandwich structure is assigned to these compounds based on their ^{1}H and ^{13}C NMR data. Further characterization of 3 by an X-ray diffraction study is plagued by its highly disordered structure.[7] Ernst and co-workers[8] recently have reported a similar half-open compound CpFe[2,4-(CH$_3$)$_2$C$_5$H$_5$], prepared by reaction 1. Although this synthetic method appears to be more convenient and direct, it only works for the 2,4-dimethylpentadienyl salt.

$$4FeCl_2 + 2NaC_5H_5 + 2K[2,4\text{-}(CH_3)_2C_5H_5] \rightarrow$$
$$2Fe(C_5H_5)[2,4\text{-}(CH_3)_2C_5H_5] + Fe(C_5H_5)_2 +$$
$$Fe[2,4\text{-}(CH_3)_2C_5H_5]_2 + 2NaCl + 2KCl \quad (1)$$

Protonation of 2 and 5 gave a class of iron(II)–diene cations.[9] Slow addition of aqueous HPF$_6$ solution to 2 in ether formed a yellow precipitate. Recrystallization from dichloromethane/hexane gave air-stable, orange crystals
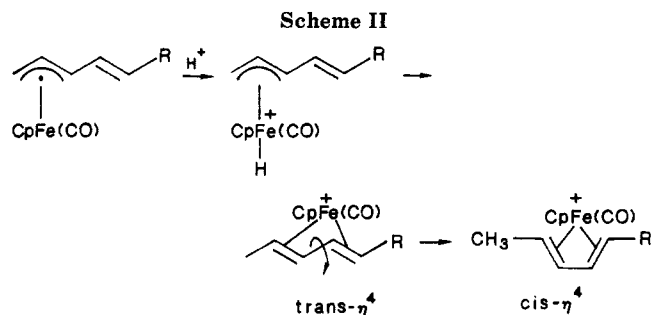
(5) The allyl and cyclopentadienyl groups are treated as monodentate ligands. The L–Fe–L angles are 127 (3)°, 124.4 (3)°, and 108.3 (3)° for Cp–Fe–C(7), Cp–Fe–C(12), and C(7)–Fe–C(12), respectively. The Cp is the centroid of cyclopentadienyl group.

(6) (a) Bleeke, J. R.; Hays, M. K. *Organometallics* 1984, 3, 506. (b) Bleeke, J. R.; Kotyk, J. J. *Ibid.* 1985, 4, 194.

(7) Compound 3 crystallizes in the space group P2$_1$/n with a = 6.251 (2) Å, b = 7.603 (3) Å, c = 9.132 (3) Å, β = 93.55 (3)°, V = 433.11 Å^3, and Z = 2. The structure can be refined with a highly disordered model. No useful information can be abstracted from the structural result.

(8) An X-ray crystallographic structure of Fe(C$_5$H$_5$)[2,4-(CH$_3$)$_2$C$_5$H$_5$] was published in a recent review of metal pentadienyl complexes by R. D. Ernst.[1a]

(9) There are a few reports on Fe(II)–diene complexes; see: (a) Ashley-Smith, J.; Howe, D. V.; Johnson, B. F. G.; Lewis, J.; Ryder, I. E. *J. Organomet. Chem.* 1974, 269.

Scheme II

Table III. Atomic Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of the CpFe(CO)(η^4-2,4-hexadiene)$^+$ Cation[a]

	x	y	z	B(iso), Å²
Fe	0.15689 (5)	0.12237 (5)	0.89553 (5)	4.26 (6)
C(1)	0.2204 (6)	0.1682 (8)	0.8927 (5)	10.2 (10)
C(2)	0.2262 (4)	0.1371 (6)	0.9312 (7)	8.5 (8)
C(3)	0.1871 (7)	0.1453 (7)	0.9643 (5)	10.0 (10)
C(4)	0.1552 (6)	0.1817 (10)	0.9457 (10)	15.5 (17)
C(5)	0.1790 (9)	0.1955 (6)	0.9030 (10)	13.9 (16)
C(6)	0.2129 (4)	0.0691 (4)	0.7970 (4)	8.3 (7)
C(7)	0.1699 (4)	0.0646 (4)	0.8344 (4)	6.6 (6)
C(8)	0.1777 (4)	0.0470 (4)	0.8833 (4)	6.8 (6)
C(9)	0.1400 (4)	0.0508 (4)	0.9226 (4)	6.4 (6)
C(10)	0.0927 (4)	0.0731 (4)	0.9146 (4)	5.9 (5)
C(11)	0.0583 (4)	0.0864 (4)	0.9570 (4)	7.6 (6)
C(12)	0.1134 (4)	0.1448 (3)	0.8504 (3)	5.4 (5)
O	0.0842 (3)	0.1607 (3)	0.8213 (3)	8.6 (4)
P(1)	0.11763 (10)	0.11763	0.11763	4.60 (6)
P(2)	0.04391 (13)	0	3/4	4.49 (18)
P(3)	1/4	1/4	1/4	5.73 (11)
F(11)	0.14844 (25)	0.16317 (24)	0.0973 (3)	12.8 (5)
F(12)	0.07169 (23)	0.1375 (3)	0.0872 (3)	12.0 (5)
F(21)	0.0874 (3)	0.0296 (3)	0.7240 (3)	13.0 (5)
F(22)	0.04394 (23)	0.0382 (3)	0.7938 (3)	13.8 (5)
F(23)	0.0011 (3)	−0.0298 (3)	0.7764 (3)	13.3 (5)
F(3)	0.2569 (13)	0.2170 (11)	0.2970 (10)	14.6 (12)
F(3')	0.21679 (25)	0.21679	0.21679	14.6 (3)

[a] Occupancy of F(3) = $^2/_3$; occupancy of F(3') = 1. B(iso) is the mean of the principal axes of the thermal ellipsoid.

of [CpFe(CO)(η^4-(*E*)-pentadiene)]PF$_6$ (7) in good yield (81%). The reaction between HPF$_6$ and 5 gave [CpFe-

7, R = H^5
8, R = CH$_3$, H^1 = H^4, H^2 = H^3

(CO)(η^4-(*E,E*)-hexadiene)]PF$_6$ (8), which showed the addition of hydrogen to the less substituted end of allyl moiety. Use of DBF$_4$ further confirmed this protonation site and showed no hydrogen scrambling within the dienyl ligand from its ^{2}H NMR spectrum. Our results are relevant to the work of Bleeke et al.,[6b] who previously reported that protonation of (*syn*-η^3-pentadienyl)Mn(dmpe)$_2$ with NH$_4$PF$_6$ gave Mn(dmpe)$_3^+$ and free pentadiene. In the latter case, the reaction is believed to proceed by initial protonation at the metal center, followed by hydride migration to the η^3-pentadienyl ligand. The resulting weakly bound η^2-pentadiene ligand is then displaced by dmpe. It is noteworthy that in our earlier attempts the reaction of HPF$_6$ with BrFe(CO)$_3$(*syn*-η^3-pentadienyl),[4a] Co(CO)$_3$-(η^3-pentadienyl),[4b] and CpMo(CO)$_2$(*syn*-η^3-pentadienyl)[4e] in ether failed to give the expected isolable diene cations[10] but gave rather a mixture of free pentadiene and uncharacterized species. Clearly, the stabilizing effect of Cp group and metal electron density of iron are key factors which allow preparation of stable η^4-diene cations. A proposed mechanism is depicted in Scheme II, which involves the formation of a 18e *trans*-η^4 diene intermediate by hydride migration to the allyl moiety. We believe that a 18e *trans*-η^4-diene is more stable than a 16e species to which the other olefin is unbound. The strong electron-donating property of the cyclopentadienyl group enables the iron atom to offer stabilization of such an intermediate and allows it to further undergo σ-C–C bond rotation to become the more stable *cis*-η^4-diene complex. Isolable *trans*-η^4-diene metal complexes have recently been described.[11] In addition to this mechanism, direct protonation at the allyl end is not excluded.
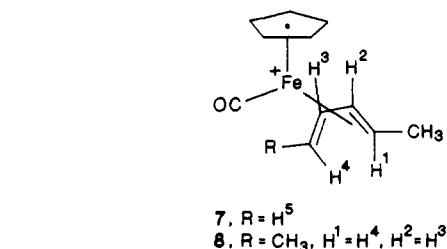
In contrast to its iron(0)–diene counterpart, no satisfactory iron(II)–diene structure has been reported.[12] The following crystallographic data of 8 enables one to look into

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) of the CpFe(CO)(η^4-2,4-hexadiene) Cation

Bond Distances

Fe–C(1)	2.04 (1)	Fe–C(2)	2.06 (1)
Fe–C(3)	2.04 (1)	Fe–C(4)	2.02 (1)
Fe–C(5)	2.00 (1)	Fe–C(7)	2.22 (1)
Fe–C(8)	2.06 (1)	Fe–C(9)	2.040 (9)
Fe–C(10)	2.164 (9)	Fe–C(12)	1.733 (9)
C(1)–C(2)	1.30 (3)	C(1)–C(5)	1.32 (3)
C(2)–C(3)	1.35 (2)	C(3)–C(4)	1.35 (4)
C(4)–C(5)	1.32 (4)	C(6)–C(7)	1.49 (2)
C(7)–C(8)	1.37 (2)	C(8)–C(9)	1.42 (2)
C(9)–C(10)	1.38 (1)	C(10)–C(11)	1.46 (2)
C(12)–O	1.15 (1)	P(1)–F(11)	3 × 1.526 (8)
P(1)–F(12)	3 × 1.524 (8)	P(2)–F(21)	2 × 1.527 (6)
P(2)–F(22)	2 × 1.511 (6)	P(2)–F(23)	2 × 1.521 (6)
P(3)–F(3)	6 × 1.50 (4)	P(3)–F(3')	2 × 1.50 (1)

Bond Angles

C(7)–Fe–C(8)	37.1 (4)	C(7)–Fe–C(9)	70.2 (4)
C(8)–Fe–C(9)	40.5 (5)	C(8)–Fe–C(10)	70.9 (4)
C(8)–Fe–C(12)	112.8 (4)	C(9)–Fe–C(10)	38.1 (4)
C(9)–Fe–C(12)	113.6 (4)	C(10)–Fe–C(12)	81.4 (4)
C(2)–C(1)–C(5)	106 (2)	C(1)–C(2)–C(3)	108 (1)
C(2)–C(3)–C(4)	110 (2)	C(3)–C(4)–C(5)	102 (2)
C(1)–C(5)–C(4)	114 (2)	C(6)–C(7)–C(8)	121.5 (9)
C(7)–C(8)–C(9)	123.0 (9)'	C(8)–C(9)–C(10)	122.6 (9)
C(9)–C(10)–C(11)	122.2 (9)	Fe–C(12)–O	178.2 (8)
F(11)–P(1)–F(11a)	92.5 (4)	F(21)–P(2)–F(21c)	84.4 (4)
F(11)–P(1)–F(12)	88.2 (4)	F(21)–P(2)–F(22)	90.1 (4)
F(11)–P(1)–F(12a)	87.3 (3)	F(21)–P(2)–F(22c)	89.9 (4)
F(11)–P(1)–F(12b)	179.3 (4)	F(21)–P(2)–F(23c)	94.9 (4)
F(12)–P(1)–F(12a)	92.0 (4)	F(21)–P(2)–F(23)	179.2 (4)
F(3)–P(3)–F(3')	102.1 (7)	F(20)–P(2)–F(22c)	179.8 (1)
F(3)–P(3)–F(3d)	180	F(22)–P(2)–F(23)	89.7 (4)
F(3)–P(3)–F(3f)	116 (2)	F(22)–P(2)–F(23c)	90.3 (4)
F(3)–P(3)–F(3e)	64 (2)	F(23)–P(2)–F(23c)	85.8 (4)
F(3)–P(3)–F(3'd)	77.9 (7)	F(3')–P(3)–F(3'd)	180

(10) The expected dienes Co(CO)$_3$(η^4-diene)$^+$ and CpMo(CO)$_2$(η^4-diene)$^+$ are known to be isolable and stable; see: (a) Charudhary, F. M.; Pauson, P. L. *J. Organomet. Chem.* 1974, 69, C31. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* 1977, 99, 4858.

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the nature of the Fe(II)–diene bonding. The unit cell contains one independent (C$_5$H$_5$)Fe(CO)(diene)$^+$ cation and three independent PF$_6^-$ anions, one of which is located on a 2-fold axis, the second one lies on a 3-fold axis, and the third one is at the $\bar{3}$-position (disorder). An ORTEP drawing of the cation is shown in Figure 2, and atomic
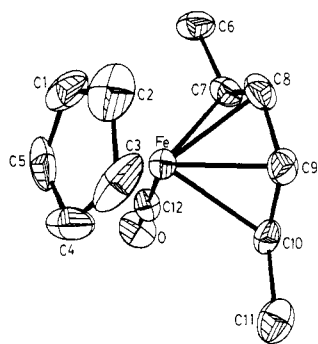
Figure 2. ORTEP drawing of the CpFe(CO)(η^4-2,4-hexadiene)$^+$ cation. Ellipsoids are scaled to encompass the 50% probability surface.

coordinates for the non-hydrogen atoms are listed in Table III. Selected bond distances and angles are given in Table IV.

Unlike its molybdenum analogue, CpMo(CO)$_2$(diene)$^+$,[13] complex 8 crystallizes in exo form; i.e., the mouth of the diene moiety lies away from the Cp group. The coordination geometry about the iron atom approximates a distorted tetrahedron with the carbonyl, the Cp group and the olefin occupying the four coordination sites.[14] The geometry of the diene moiety closely relates to those of iron(0)–diene complexes:[12,15] the carbon atoms C(7), C(8), C(9), and C(10) of the diene ligand form a perfect least-square plane with deviations within 0.01 Å; the distance of the iron atom to the inner carbon atoms (2.05 (1) Å) is shorter than that to the outer atoms (2.19 (1) Å). The syn-methyl group of the diene moiety exhibits twisting around the double bond, and the displacements of the Fe, C(6)(syn), and C(11)(syn) atoms from the diene plane are +1.63, +0.27, and +0.27 Å, respectively (+ indicates toward Fe atom).

The important difference between the structures of the iron(II)–diene and iron(0)–diene complexes is the bond lengths of the diene group. For 8, the outer C–C lengths are 1.37 (2) (C(7)–C(8)) and 1.38 (1) Å (C(9)–C(10)) and the inner C–C length is 1.42 (2) Å (C(8)–C(9)). This short–long–short pattern indicates the diene moiety is in its ground-state configuration[16] (bond lengths for ground-state butadiene: 1.36 Å for outer atoms and 1.45 Å for inner atoms). This contrasts with the long–short-long pattern observed for most iron(0)–diene complexes[15] (1.42 Å for outer C–C length, and 1.40 Å for inner C–C length). It suggests that the degree of the transfer of filled d electron density into the LUMO π^*-orbital of the diene group will be less for the Fe(II) than for Fe(0) complexes.

Protonation of η^1-dienyl ligand gave a class of η^2-diene cations of various forms. The reaction between HPF$_6$ and 1 in ether yielded a mixture of [CpFe(CO)$_2$(η^2-1,3-pentadiene)]PF$_6$ (9) and [CpFe(CO)$_2$(η^2-1,4-pentadiene)]PF$_6$ (10) in 8:2 ratio after workup and crystallization from CH$_2$Cl$_2$/hexane. The evidence for the direct proton attack on the C(3) and C(5) of the dienyl ligand was seen from
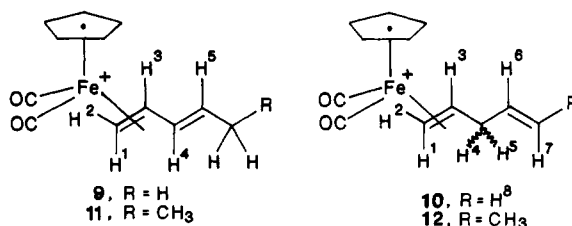
the protonation of 4 with HPF$_6$, which gave a mixture of [CpFe(CO)$_2$(η^2-1,3-hexadiene)]PF$_6$ (11) and [CpFe(CO)$_2$-(η^2-1,4-hexadiene)]PF$_6$ (12) in 3:7 ratio. Both 9 and 11 exist in trans form as inferred from the coupling constant J_{45} = 14–15 Hz. Compounds 10 and 12 are characterized by the nonequivalent ^{1}H NMR resonances of H^4 and H^5 at δ 2.3–3.0. Likewise, these protonation sites were also confirmed by reaction with DBF$_4$ and the ^{2}H NMR spectrum of product of D$^+$ addition. For 10 and 12, deuterium was found equally at H^4 and H^5.

Our study presents regioselective chemistry in protonation of a dienyl ligand bound to metal in the η^1 and η^3 forms. In η^1-dienyl complexes, the bulky CpFe(CO)$_2$ groups impose steric hinderance for α-addition, and the selectivity at γ- and ϵ-positions is greatly affected by the presence of substituents at carbon. In contrast, the dominant α-addition for vinylallyl complexes is assisted either by initial protonation of iron, followed by migration to the allyl moiety, or by direct attack on the less substituted end of the allyl ligand. Direct pentadienylation[17] of electrophiles with pentadienyl anions is an important reaction in organic synthesis for extension of carbon chains. This process, however, suffers a disadvantage in that the reaction results in a complex mixture of regioisomers by uncontrolled attack at α-, γ-, and ϵ-positions.[18] In order to circumvent this, Seyferth[19] and Sakurai[20] have recently developed the use of Lewis acid to increase regiocontrolled pentadienylation with 2,4-pentadienylsilane. The regiochemical control by metal coordination might be valuable in organic synthesis if the scope of electrophilic reaction of these η^1- and η^3-dienyl complexes is expanded. Progress in this direction is currently underway.

Experimental Section

(13) For (C$_5$H$_5$)Mo(CO)$_2$(η^4-diene)$^{+ \, 10b}$ and its homologues, the endo isomer is the major species in equilibrium with the exo isomer in solution. For 7 and 8, only the exo isomer is present in solution as shown by their ^{1}H NMR spectrum at –60 °C in acetone-d_6.

(14) The L–Fe–L angles are 132.2 (5)°, 132.9 (5)°, 118.6 (5)°, 65.2 (5)°, 96.3 (4)°, and 97.2 (4)° for Cp–Fe–C(7.5), Cp–Fe–C(9.5), Cp–Fe–C(12), C(7.5)–Fe–C(9.5), C(7.5)–Fe–C(12), and C(9.5)–Fe–C(12), respectively; Cp, C(7.5), and C(9.5) are the centers of the cyclopentadienyl group, the C(7)–C(8) double bond, and the C(9)–C(10) double bond, respectively.

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AM-400 spectrometer. ¹H, ²H, and ¹³C spectra were referenced to tetramethylsilane. Infrared spectra were recorded on a Perken-Elmer 781 spectrophotometer. Microanalyses were performed by Microanalytic Laboratory at National Taiwan University.

A. Synthesis of CpFe(CO)₂(η¹-2,4-hexadien-1-yl) (4). (E,E)-1-Chlorohexa-2,4-diene (1.3 g, 11.2 mmol) was added dropwise to 50 mL of tetrahydrofuran solution containing CpFe(CO)₂Na (1.5 g, 8.4 mmol) at -78 °C and stirred for 3 h. After the insoluble sodium chloride was filtered off at -78 °C, the solution was warmed to 0 °C and evaporated to dryness to give a dark red residue. The residue was extracted with 20 mL of pentane twice, filtered, and evaporated to dryness. With pentane as the eluting solvent, the residue was chromatographed on a neutral alumina column (50 g, Merck) at 23 °C. In addition to an immobile band of Cp₂Fe₂(CO)₄, a gold-yellow band was eluted rapidly and collected. After the solution was removed, followed by vacuum distillation (4.2 × 10⁻³ torr, 26 °C) of the residues, an orange oil of 4 (094 g, 3.65 mmol) was obtained. Anal. Calcd for C₁₃H₁₄FeO₂: C, 60.46; H, 5.43. Found: C, 60.78; H, 5.57. Mass spectrum (12 eV): m/e 258 (M⁺), 230 (M – CO)⁺, 202 (M – 2CO)⁺, 177 (M – C₆H₉)⁺. IR (pentane): ν(CO) 2009 (s) and 1955 (s) cm⁻¹; ν(C=C) 1622 (w) cm⁻¹. ¹H NMR (100 MHz, C₆D₆): δ 1.64 (3 H, d, CH₃, J = 6.5 Hz), 2.23 (2 H, d, Fe–CH₂, J = 7.7 Hz), 3.96 (5 H, s, C₅H₅), 5.3–6.2 (4 H, complex m, ²H + ³H + ⁴H + ⁵H). ¹³C{H} NMR: δ 4.9 (Fe–CH₂), 18.3 (CH₃), 68.2, 123.8, 133.8, 143.2 (CH₂ + CH₃ + CH₄ + CH₅), 217.4 (CO).

B. Synthesis of CpFe(CO)(η³-2,4-hexadien-1-yl) (5). Method a. A 25-mL ether solution of 4 (0.60 g, 2.33 mmol) in a vacuum-sealed tube was irradiated by a 400-W mercury lamp at -20 °C for 2 h. After removal of the solvent under reduced pressure, the residue was chromatographed through a neutral alumina column (150 g, Merck) at 0 °C with pentane as the eluting solvent. An orange band, which was eluted first, was identified as 6 and collected. A second orange band was collected, and the solvent was removed under reduced pressure. A purple band of (C₅H₅)₂Fe₂(CO)₄ which remained on the top portion of the column was not collected. The dark residues from the second band were dissolved in pentane and cooled to -25 °C to yield dark red crystals of 5 (0.21 g, 0.91 mmol). The purification of 6 from the first orange band was conducted by a similar procedure, and dark red crystals (0.10 g, 0.47 mmol) of 6 were obtained. Anal. Calcd for C₁₂H₁₄FeO: C, 62.61; H, 6.08. Found: C, 62.64; H, 6.23. Mass spectrum (12 eV): m/e 230 (M⁺), 202 (M – CO)⁺. IR spectrum (pentane): ν(C=C) 1617 (w) cm⁻¹; ν(CO) 1950 (s) cm⁻¹. ¹H NMR (400 MHz, C₆D₆): δ 0.62 (1 H, dd, H¹), 1.53 (3 H, d, CH₃), 2.15 (1 H, dd, H⁴), 2.51 (1 H, dd, H²), 4.00 (¹H, s, C₅H₅), 4.22 (1 H, ddd, H³), 5.58–5.64 (2 H, m, H⁵ + H⁶), J_{13} = 10.9 Hz, J_{23} = 6.8 Hz, J_{34} = 10.4 Hz, J_{45} = 10.4 Hz, J_{56} = 13.5 Hz, J_{12} = 1.2 Hz, J_{CH_3-6} = 6.2 Hz. ¹³C{H} NMR (101 MHz, C₆D₆): δ 18.5 (CH₃), 30.1 (CH¹H²), 57.9 (CH⁴), 73.2 (CH³), 79.5 (C₅H₅), 122.3 (CH⁶), 137.0 (CH⁵), 222.8 (CO).

Method b. A 25-mL tetrahydrofuran solution of 4 (0.42, 1.62 mmol) was stirred with trimethylamine oxide (0.50 g, 6.55 mmol) at 0 °C for 6 h. After the solvent was removed in vacuo, the residues were chromatographed through neutral alumina (50 g, Merck). With pentane as the eluting solvent, an orange band was developed and collected. After removal of the solvent, the red residues were recrystallized from pentane at -25 °C to give red plates of 5 (0.25 g, 1.08 mmol).

C. Synthesis of CpFe(η⁵-2,4-hexadien-1-yl) (6). A 20-mL benzene solution of 5 (0.26 g, 1.09 mmol) in a vacuum-sealed Pyrex tube was irradiated by a 400-W mercury lamp at 23 °C for 24 h. After the solvent was removed under reduced pressure, the red residue was sublimed (4.7 × 10⁻³ torr) at 28 °C into a -25 °C cold trap to yield a crystalline solid, 6 (0.20 g, 0.99 mmol). Anal. Calcd for C₁₁H₁₄Fe: C, 65.34; H, 6.93. Found: C, 65.20; H, 6.81. Mass spectrum (12 eV): m/e 202 (M⁺). ¹H NMR (400 MHz, C₆D₆): δ -0.62 (1 H, dd, H¹), -0.04 (1 H, m, H⁶), 1.42 (3 H, d, CH₃), 2.53 (1 H, dd, H²), 4.21 (1 H, ddd, H³), 4.07 (1 H, dd, H⁵), 5.20 (1 H, dd, H⁴), 3.96 (5 H, s, C₅H₅), J_{12} = 2.6 Hz, J_{23} = 8.6 Hz, J_{34} = 6.2 Hz, J_{45} = 6.0 Hz, J_{56} = 8.6 Hz, J_{13} = 9.3 Hz, J_{6-CH_3} = 6.1 Hz. ¹³C{H} NMR (101 MHz, C₆D₆): δ 22.7 (CH₃), 41.6 (CH¹H²), 56.3 (CH⁶), 74.6 (C₅H₅), 79.8 (CH³), 84.7 (CH⁵), 87.6 (CH⁴).

D. Preparation of [CpFe(CO)(η⁴-pentadiene)]PF₆ (7). Aqueous HPF₆ (0.4 mL, 75%) was slowly added to 2 (0.45 g, 2.08 mmol) in 20 mL of ether with rapid stirring. An orange precipitate

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was produced immediately. The precipitate was redissolved in a mixture of dichloromethane and hexane (3:1) and slowly evaporated under argon, yielding orange blocks (0.61 g, 1.68 mmol) of [CpFe(CO)(η⁴-pentadiene)]PF₆. Anal. Calcd for C₁₁H₁₃FeOPF₆: C, 36.48; H, 3.59; P, 8.57. Found: C, 36.24; H, 3.59; P, 8.14. IR (Nujol): ν(CO) 2030 (s) cm⁻¹. ¹H NMR (400.1 MHz, CD₃COCD₃, 23 °C): δ 0.72 (dd, 1 H, H⁴), 1.68 (d, 3 H, CH₃), 1.80 (m, 1 H, H¹), 3.25 (dd, 1 H, H⁵), 5.37 (s, 5 H, C₅H₅), 6.24 (m, 2 H, H² + H³), J_{CH_3-1} = 4.8 Hz, J_{12} = 12.1 Hz, J_{35} = 9.1 Hz, J_{34} = 10.6 Hz, J_{45} = 2.1 Hz. ¹³C{H} NMR (100.2 MHz, CD₃COCD₃): δ 19.8 (CH₃), 50.6 (CH⁴H⁵), 78.6 (CH¹), 85.18 (C₅H₅), 89.1 and 85.4 (CH³ + CH²).

E. Preparation of [CpFe(CO)(η⁴-2,4-hexadiene)]PF₆ (8). Aqueous HPF₆ (0.4 mL, 75%) was slowly added to 5 (0.41 g, 1.70 mmol) in 20 mL of ether with rapid stirring. An orange precipitate was produced immediately. The precipitate was dissolved in a mixture of dichloromethane and hexane and slowly evaporated under argon, yielding orange blocks (0.54 g, 1.50 mmol) of [CpFe(CO)(η⁴-2,4-hexadiene)]PF₆. Anal. Calcd for C₁₂H₁₅FeOPF₆: C, 38.31; H, 3.99; P, 8.25. Found: C, 38.51; H, 3.90; P, 8.61. IR (Nujol): ν(CO) 2028 cm⁻¹. ¹H NMR (400.1 MHz, CD₃COCD₃): δ 1.64 (d, 3 H, CH₃). 1.89 (m, 1 H, H¹), 6.54 (d, 1 H, H²). J_{12} = 11.8 Hz, J_{1-CH_3} = 6.2 Hz.

F. Protonation of CpFe(CO)₂(η¹-pentadien-1-yl) (1). Aqueous HPF₆ (2 mL, 75%) solution was slowly added to 1 (0.45 g, 1.74 mmol) in 20 mL of ether with rapid stirring. After the addition was complete, the resulting yellow plates were collected by filtration and washed with 20 mL of ether. ¹H NMR spectrum showed that the plates were a mixture of [CpFe(CO)₂(η²-1,3-pentadiene)]PF₆ (9) and [CpFe(CO)₂(η²-1,4-pentadiene)]PF₆ (10) in a molar ratio about 4:1. Further crystallization from dichloromethane/hexane (2:1) at -20 °C gave orange plates of compounds (0.44 g, 1.19 mmol). Anal. Calcd for C₁₂H₁₃FeO₂PF₆: C, 36.92; H, 3.33; P, 7.95. Found: C, 36.85; H, 3.62; P, 7.74. IR spectrum (Nujol): ν(CO) 2083(s) and 2036(s) cm⁻¹; ν(C=C) 1634 (w) cm⁻¹. ¹H NMR (400 MHz, acetone-d_6): 9, δ 1.84 (d, 3 H, CH₃), 3.69 (dd, 1 H, H¹), 3.84 (dd, 1 H, H²), 5.51 (s, 5 H, C₅H₅), 5.61 (t, 1 H, H⁴), 6.01 (m, 1 H, H³), 6.62 (m, 1 H, H⁵), J_{13} = 14.5 Hz, J_{23} = 8.0 Hz, J_{12} = 1.5 Hz, J_{34} = 14.8 Hz, J_{45} = 14.8 Hz, J_{5-CH_3} = 6.2 Hz; 10, δ 2.35 (m, 1 H, H⁴), 3.05 (m, 1 H, H⁵), 3.40 (dd, 1 H, H¹), 3.87 (dd, 1 H, H²), 4.95 (m, 1 H, H³), 5.19 (dd, 1 H, H⁸), 5.20 (dd, 1 H, H⁷), 5.53 (s, 5 H, C₅H₅), 5.85 (m, 1 H, H⁶), J_{13} = 14.7 Hz, J_{23} = 8.3 Hz, J_{12} = 1.5 Hz, J_{67} = 16.5 Hz, J_{68} = 11.0 Hz, J_{78} = 1.2 Hz.

G. Protonation of CpFe(CO)₂(η¹-2,4-hexadien-1-yl) (4). Aqueous HPF₆ (2 mL, 75%) solution was slowly added to 4 (0.23 g, 0.85 mmol) in 20 mL of ether with rapid stirring. Orange plates of [CpFe(CO)₂(η²-1,3-hexadiene)]PF₆ (11) and CpFe(CO)₂(η²-1,4-hexadiene)PF₆ (12) were obtained after workup. The mixture (0.26 g, 0.70 mmol) consisted of 11 and 12 in a molar ratio of 3:7,

respectively. Anal. Calcd for $C_{13}H_{15}FeO_2PF_6$: C, 38.61; H, 3.96; P, 7.67. Found: C, 38.85; H, 4.34; P, 7.55. IR spectrum (Nujol): ν(CO) 2078 (s) and 2032 (s) cm^{-1}; ν(C=C) 1637 (w) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): 11, δ 1.00 (t, 3 H, CH$_3$), 2.27 (m, 2 H, CH$_2$), 3.42 (dd, 1 H, H^1), 3.75 (dd, 1 H, H^2), 5.4–5.5 (m, 2 H, H^3 + H^4), 5.53 (s, 5 H, C$_5$H$_5$), 6.57 (m, 1 H, H^5), J_{13} = 14.7 Hz, J_{12} = 1.4 Hz, J_{23} = 8.3 Hz, J_{45} = 14.5 Hz, J_{5-CH_3} = 6.1 Hz, $J_{CH_2CH_3}$ = 6.4 Hz; 12, δ 1.65 (d, 3 H, CH$_3$), 2.50 (m, 1 H, H^4), 2.95 (m, 1 H, H^5), 3.36 (dd, 1 H, H^1), 3.82 (dd, 1 H, H^2), 4.92 (m, 1 H, H^3), 5.30 (m, 1 H, H^7), 5.51 (s, 5 H, C$_5$H$_5$), 5.61 (m, 1 H, H^6), J_{13} = 14.7 Hz, J_{12} = 1.5 Hz, J_{23} = 8.5 Hz, J_{67} = 15.2 Hz, J_{7-CH_3} = 6.2 Hz.

X-ray Diffraction Study of 5 and 8. Data were collected at room temperature on a CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were performed by using the NRCC-SDP-PDP-11 and NRCC-SDP-VAX packages (ORTEP from the Enraf-Nonius PDP 11/23 computer). Crystal data, details of data collection, and structural analysis are summarized in Table V.

The structure of two compounds were solved by Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

Reactions of (Me₃SiCH₂)₂AsSiMe₃ with Gallium Halides. Crystal Structure and Dynamic NMR Study of the Dimer {[(Me₃SiCH₂)₂As]₂GaBr}₂

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(Me$_3$SiCH$_2$)$_2$AsSiMe$_3$ reacted with the gallium halides GaBr$_3$, MeGaCl$_2$, and PhGaCl$_2$ to produce the (arsino)gallanes [(Me$_3$SiCH$_2$)$_2$AsGaBr$_2$]$_3$, {[(Me$_3$SiCH$_2$)$_2$As]$_2$GaBr}$_2$, [(Me$_3$SiCH$_2$)$_2$AsGaMeCl]$_n$ (n = 2, 3), and [(Me$_3$SiCH$_2$)$_2$AsGaClPh]$_n$ (n = 2, 3), which were characterized by elemental analysis (C and H), ^{1}H and ^{13}C NMR spectroscopy, and cryoscopic molecular weight determinations. A single-crystal X-ray diffraction study of {[(Me$_3$SiCH$_2$)$_2$As]$_2$GaBr}$_2$ was carried out. Crystal data are as follows: triclinic, space group $P\bar{1}$, a = 11.892 (2) Å, b = 12.492 (2) Å, c = 11.515 (1) Å, α = 98.24 (1)°, β = 113.57 (1)°, γ = 84.21 (1)°, V = 1549.9 Å^3, Z = 1. The centrosymmetric, dimeric molecule crystallizes in the trans configuration, with unequal endocyclic Ga–As distances [2.513 (1) Å and 2.521 (1) Å] and very significantly different bond angles [84.37 (1)° and 95.63 (2)°, respectively, at Ga and As] in the planar (Ga–As)$_2$ ring. The Ga-exo-As distance of 2.437 (1) Å is the shortest yet measured in an organogallium–arsenic compound. A ^{13}C{^{1}H} dynamic NMR study of {[(Me$_3$SiCH$_2$)$_2$As]$_2$GaBr}$_2$ revealed that both an interchange of the (Me$_3$SiCH$_2$)$_2$As groups [$\Delta H^{\ddagger}$ = 18.7 ± 0.3 kcal/mol; $\Delta S^{\ddagger}$ = 4.5 ± 1.0 cal/(mol K)] and a trans–cis isomerization [$\Delta H^{\ddagger}$ = 17.4 ± 0.7 kcal/mol; $\Delta S^{\ddagger}$ = -2.2 ± 2.1 cal/(mol K)] take place.

Introduction

Prior to our recent studies,[1] the only method of preparing organogallium–arsenic compounds was that reported by Coates et al.[2] These authors prepared two mono(arsino)gallanes by the cleavage of a single Ga–C bond in Me$_3$Ga with the As–H bond of a secondary arsine. In our hands, this reaction not only suffered a reduction in efficiency but also eventually failed to yield the desired products as the substituents on Ga and As increased in size.[1a] Moreover, the fact that bis- and tris(arsino)gallanes could not be made by this route[1a] led us to examine alternative methods of forming the Ga–As bond, viz., the coupling of gallium chlorides with lithium arsenides[1e,g] or silyl arsines.[1a] Others have since reported the use of the lithium arsenide method.[3] There is ample precedent for the reaction of silyl-substituted main-group elements (E–SiMe$_3$) with covalent halides MCl$_x$, to yield an E–M bond and Me$_3$SiCl.[4] Our previous communication[1a] revealed that secondary trimethylsilylarsines, R$_2$AsSiMe$_3$, readily

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