Regio- and Diastereoselective Addition of Alkyl Anions to Electron-Rich (η^5-Pentadienyl)iron Complexes[1]

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Abstract: Treatment of (η^5-pentadienyl)(η^3-pentadienyl)Fe(PEt_3) (**1**) with $Ag^+PF_6^-$ and PEt_3 or with $HPEt_3^+PF_6^-$ produces (η^5-pentadienyl)Fe$(PEt_3)_2^+PF_6^-$ (**2**), a $16e^-$ paramagnetic complex. Compound **2** crystallizes in the monoclinic space group $C2/c$ (no. 15) with a = 20.556 (6) Å, b = 7.894 (2) Å, c = 15.000 (4) Å, β = 103.80 (2)°, V = 2363.9 (11) Å^3, and Z = 4. The two phosphine ligands reside in inequivalent environments, one under the open "mouth" of the η^5-pentadienyl ligand and the other under the pentadienyl "backbone". The electronic origins of compound **2**'s ligand orientation and paramagnetism have been probed by performing Fenske–Hall molecular orbital calculations on a model complex. Treatment of **2** with 1 equiv of carbon monoxide or *tert*-butylisonitrile (L) leads to the production of (η^5-pentadienyl)Fe$(PEt_3)_2(L)^+PF_6^-$ (L = CO, **3a**; L = $CNCMe_3$, **3b**). These complexes adopt unsymmetrical three-legged piano stool structures, wherein one PEt_3 ligand and L reside under the pentadienyl backbone, while the other PEt_3 ligand resides under the pentadienyl mouth. Complexes **3a,b** possess stereogenic centers at iron by virtue of the fact that the two PEt_3 ligands are inequivalent. Treatment of **3a** or **3b** with methyllithium at −78 °C results in exo nucleophilic attack at C2 of the pentadienyl ligand, producing (2-methyl-1,3,4,5-η-pentenediyl)Fe$(PEt_3)_2$(L) (L = CO, **4a**; L = $CNCMe_3$, **4b**). The analogous reactions involving *tert*-butyllithium produce (2-*tert*-butyl-1,3,4,5-η-pentenediyl)Fe$(PEt_3)_2$(L) (L = CO, **5a**; L = $CNCMe_3$, **5b**). In each case, attack occurs with >85% diastereoselectivity on the "L-side" of the pentadienyl ligand, i.e., at the internal pentadienyl carbon which resides above ligand L and opposite the bulky PEt_3 ligand. Compound **5b** crystallizes in the triclinic space group P1 (no. 2) with a = 9.433 (2) Å, b = 9.849 (2) Å, c = 18.015 (4) Å, α = 100.98 (2)°, β = 93.51 (2)°, γ = 111.44 (2)°, V = 1513.6 (6) Å^3, and Z = 2. The solid-state structure shows the attacked carbon, C2, to be displaced 0.59 Å out of the C1/C3/C4/C5 plane. Bond distances within the pentenediyl ligand are consistent with its σ,π-allyl character.

Introduction

During the past two decades, there has been increasing interest in the reactions of acyclic pentadienyl ligands with nucleophiles.[2] However, virtually all of these studies have involved electron-poor complexes in which the pentadienyl group is bonded to an iron–tricarbonyl moiety and, with few exceptions, have resulted in nucleophilic attack at a terminus (C1/C5) of the pentadienyl ligand.[3] Furthermore, reactions involving hard carbon nucleophiles (e.g., alkyl Grignards) have been plagued by competitive reductive coupling processes.[2d]

We are interested in promoting nucleophilic addition to the *internal* carbons (C2/C4) of pentadienyl ligands in order to produce (pentenediyl)metal complexes, a relatively unexplored compound class[4] with potential applications to organic synthesis. Following the thesis of Davies, Green, and Mingos, which asserts that electron-rich ML_n moieties will promote nucleophilic attack at the even-numbered carbon atoms of odd open polyenyl ligands (i.e., C2/C4 in pentadienyl ligands),[5] we have begun to investigate the synthesis and reactivity of electron-rich (η^5-pentadienyl)FeL_3^+ complexes.

In a preliminary communication,[1k] we reported that one such electron-rich complex, (η^5-pentadienyl)Fe$(PMe_3)_3^+$, reacts cleanly with 2,4-dimethylpentadienide to produce the C2 addition product. We now report the synthesis of two new electron-rich (η^5-pentadienyl)FeL_3^+ complexes, (η^5-pentadienyl)Fe$(PEt_3)_2(CO)^+$ and (η^5-pentadienyl)Fe$(PEt_3)_2(CNCMe_3)^+$, and describe the regio- and diastereoselective nucleophilic addition of alkyl anions to the C2 position of the pentadienyl ligands in these species.[6]

Results and Discussion

A. Synthesis of (η^5-Pentadienyl)Fe$(PEt_3)_2^+PF_6^-$ (2), a Precursor to (η^5-Pentadienyl)FeL_3^+ Complexes. (η^5-Pentadienyl)(η^3-pentadienyl)Fe(PEt_3) (**1**), which is obtained in high yield upon treatment of $FeCl_2(PEt_3)_2$ with 2 equiv of potassium pentadienide·tetrahydrofuran,[10] serves as a convenient starting material for the synthesis of a large family of electron-rich (η^5-pentadienyl)FeL_3^+ complexes. In an earlier paper,[10] we reported that treatment of **1** with 1 equiv of $Ag^+PF_6^-$ and 1 equiv of PEt_3 resulted in the production of a red, paramagnetic intermediate, **2**, which could be treated in situ with a series of small phosphorus-based ligands to produce $18e^-$ (η^5-pentadienyl)$FeL_3^+PF_6^-$ complexes. At that time, we speculated that the red intermediate

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† Pew Postdoctoral Fellow.

(1) Pentadienyl–Metal–Phosphine Chemistry. 20. The previous papers in this series are the following: (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (e) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1986**, *5*, 635. (f) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (g) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522. (h) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401. (i) Bleeke, J. R.; Hays, M. K. *Ibid.* **1987**, *6*, 486. (j) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417. (k) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367. (l) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1987**, *6*, 1576. (m) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Ibid.* **1988**, *7*, 33. (n) Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Ibid.* **1987**, *6*, 2614. (o) Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Ibid.* **1988**, *7*, 1417. (p) Bleeke, J. R.; Donaldson, A. J. *Ibid.* **1988**, *7*, 1588. (q) Bleeke, J. R.; Rauscher, D. J. *Ibid.* **1988**, *7*, 2328. (r) Bleeke, J. R.; Earl, P. L. *Ibid.* **1989**, *8*, 2735. (s) Bleeke, J. R.; Rauscher, D. J. *J. Am. Chem. Soc.* **1989**, *11*, 8972.

(2) (a) Maglio, G.; Musco, A.; Palumbo, R. *J. Organomet. Chem.* **1971**, *32*, 127. (b) Maglio, G.; Palumbo, R. *Ibid.* **1974**, *76*, 367. (c) Bonner, T. G.; Holder, K. A.; Powell, P. *Ibid.* **1974**, *77*, C37. (d) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. I* **1976**, 954. (e) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63. (f) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* **1978**, *150*, 75. (g) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *Ibid.* **1979**, *174*, 297. (h) Powell, P. *Ibid.* **1979**, *165*, C43. (i) Pearson, A. J.; Roy, T. *Tetrahedron* **1985**, *41*, 5765. (j) Gree, R.; Laabassi, M.; Mosset, P.; Carrie, R. *Tetrahedron Lett.* **1985**, *26*, 2317. (k) Uemura, M.; Minami, T.; Yamashita, Y.; Hiyoshi, K.; Hayashi, Y. *Ibid.* **1987**, *28*, 641. (l) Semmelhack, M. F.; Park, J. *J. Am. Chem. Soc.* **1987**, *109*, 935. (m) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1988**, *29*, 1343. (n) Donaldson, W. A.; Ramaswamy, M. *Ibid.* **1989**, *30*, 1339. (o) Donaldson, W. A.; Ramaswamy, M. *Ibid.* **1989**, *30*, 1343. (p) Pinsard, P.; Lellouche, J.-P.; Beaucourt, J.-P.; Toupet, L.; Schio, L.; Gree, R. *J. Organomet. Chem.* **1989**, *371*, 219.

(3) Exceptions are reported in refs 2e, 2o, and 2p (C2/C4 attack) and in ref 2h (C3 attack).

(4) The first (pentenediyl)metal complexes were obtained by Aumann via metal-centered vinyl cyclopropane ring opening: (a) Aumann, R. *J. Organomet. Chem.* **1973**, *47*, C29. (b) Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631.

(5) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (b) This thesis is particularly applicable to nucleophilic additions involving hard nucleophiles where charge control is anticipated.

(6) In related work, Pearson has reported nucleophilic attack at C2 of the dienyl moiety in (η^5-cycloheptadienyl)Fe$(CO)_2(L)^+$ (L = PPh_3 and $P(OPh)_3$) complexes. See: Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

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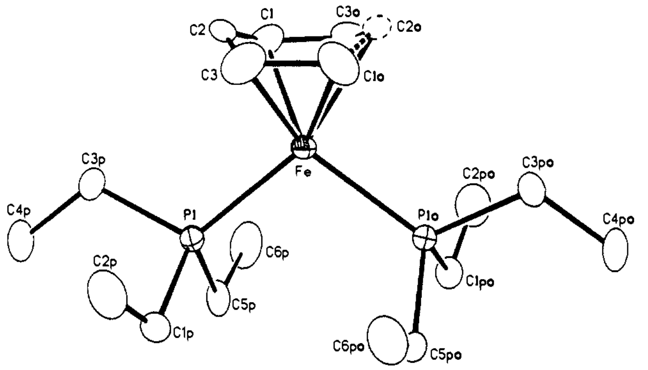

Figure 1. ORTEP drawing of the cation in (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (**2**). The cation resides on a crystallographically imposed 2-fold rotation axis. As a result, the pentadienyl ligand exhibits a 2-fold rotational disorder, and atom C2 was refined at a multiplicity of 0.5.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-Pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (**2**)

Bond Distances

Fe–P1	2.296 (2)	C2–C3	1.514 (28)	C3P–C4P	1.511 (15)
Fe–C1	2.126 (12)	P1–C1P	1.833 (10)	C5P–C6P	1.473 (18)
Fe–C2	2.140 (15)	P1–C3P	1.832 (9)	P2–F1	1.580 (6)
Fe–C3	2.150 (11)	P1–C5P	1.808 (11)	P2–F2	1.571 (8)
C1–C3a	1.353 (18)	C1P–C2P	1.522 (14)	P2–F3	1.587 (10)
C1–C2	1.491 (25)				

Bond Angles

P1–Fe–P1a	103.7 (1)	C1–C2–C3	134.7 (13)
P1–Fe–C1	99.3 (3)	C2–C1–C3a	108.6 (13)
P1–Fe–C2	95.4 (4)	C2–C3–C1a	108.7 (11)
P1–Fe–C3	101.4 (3)	Fe–P1–C1P	116.7 (3)
P1–Fe–C1a	133.7 (3)	Fe–P1–C3P	115.4 (3)
P1–Fe–C3a	131.5 (4)	Fe–P1–C5P	113.2 (3)
P1a–Fe–C2	160.9 (5)	C1P–P1–C3P	103.8 (4)
C1–Fe–C2	40.9 (7)	C1P–P1–C5P	102.3 (5)
C1–Fe–C3	80.9 (5)	C3P–P1–C5P	103.9 (5)
C1–Fe–C1a	92.9 (6)	P1–C1P–C2P	113.8 (7)
C1–Fe–C3a	36.9 (5)	P1–C3P–C4P	117.0 (8)
C2–Fe–C3	41.3 (8)	P1–C5P–C6P	115.4 (9)
C2–Fe–C3a	65.2 (6)	F1–P2–F2	90.8 (4)
C2–Fe–C1a	66.3 (7)	F1–P2–F3	88.5 (4)
C3–Fe–C3a	91.8 (6)	F2–P2–F3	90.2 (5)

was a 17e$^-$ bis(pentadienyl) complex of formula (η-pentadienyl)$_2$Fe(PEt$_3$)$_x$$^+PF_6$$^-$. We now report that the correct formulation for **2** is actually 16e$^-$ (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$.[7] The solid-state structure of this compound, as determined by an X-ray diffraction study, is described in section **B**.

The reaction of **1** with Ag$^+$PF$_6$$^-$ probably involves initial 1e$^-$ oxidation to yield 17e$^-$ (η^5-pentadienyl)(η^3-pentadienyl)Fe(PEt$_3$)$^+$PF$_6$$^-$, which then loses pentadienyl radical[8] and adds PEt$_3$, producing **2**. The pentadienyl radical abstracts hydrogen from CH$_2$Cl$_2$ solvent, producing *trans*-1,3-pentadiene.[9] Complex **2** can also be generated by treating **1** with 1 equiv of protonated triethylphosphine (HPEt$_3$$^+PF_6$$^-$). The mechanism of this protonation reaction probably involves initial H$^+$ attack at the iron center, migration of the "hydride" ligand to the η^3-pentadienyl group, and displacement of the resulting η^2-pentadiene ligand by incoming PEt$_3$.[10]

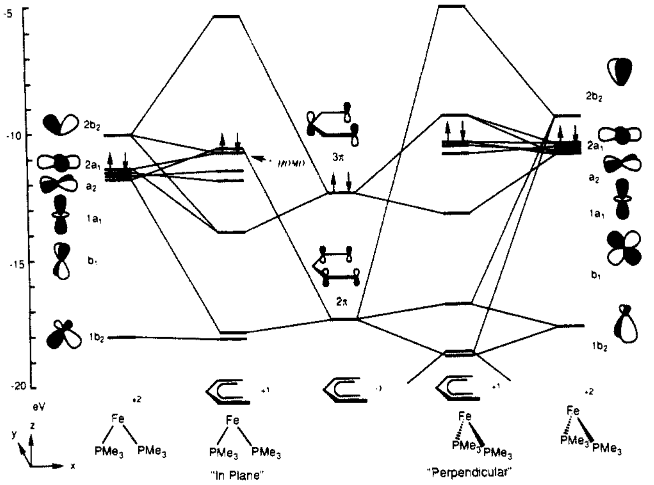

Figure 2. Molecular orbital diagram for (η^5-pentadienyl)Fe(PMe$_3$)$_2$$^+$ showing the interaction of the pentadienide ligand with a Fe(PMe$_3$)$_2$$^{2+}$ fragment in the in-plane and perpendicular geometries.

B. Characterization of (η^5-Pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (2). The solid-state structure of (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (**2**), produced by reacting(η^5-pentadienyl)(η^3-pentadienyl)Fe(PEt$_3$) (**1**) with Ag$^+$PF$_6$$^-$ and PEt$_3$, has been determined by X-ray crystallography (see ORTEP drawing, Figure 1). Selected bond distances and angles are given in Table I. The molecule resides on a crystallographically imposed 2-fold rotation axis, which results in a 2-fold rotational disorder of the pentadienyl group. Hence, the central carbon atom of the pentadienyl group (C2 in Figure 1) was refined at a multiplicity of 0.5. Carbons C1 and C3 have large thermal parameters because they represent average positions of terminal and internal pentadienyl carbon atoms. The PEt$_3$ ligands adopt an "in-plane" orientation, i.e., they reside on the symmetry plane of the pentadienyl ligand. Their environments are chemically inequivalent, one under the open mouth of the η^5-pentadienyl ligand and one under the pentadienyl backbone.

Perhaps the most striking feature of the structure is the *apparent* nonplanarity of pentadienyl carbon C2 with respect to the rest of the pentadienyl group. This ostensible out-of-plane displacement of C2 is probably an artifact of the 2-fold rotational disorder and can be explained by postulating a nearly planar pentadienyl ligand which is *tilted toward the mouth phosphine*. A 2-fold rotation of a planar tilted pentadienyl ligand would give rise to the boat-shaped ligand which we observe. Consistent with this model are (a) the size and orientation of the thermal ellipsoids on C1 and C3 and (b) the fact that C2 resides as close to the iron center as do C1 and C3. Strong support for this model also comes from the structures of two closely related cobalt complexes, 18e$^-$ (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$ and 17e$^-$ (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$$^+BF_4$$^-$, which we reported earlier.[1c,e] In each of these structures (which are *not* disordered), the pentadienyl ligand is nearly planar and tilted toward the mouth phosphine ligand. As a result of the tilting, the mouth phosphorus atom resides substantially closer to the pentadienyl plane than does the backbone phosphorus atom.[11]

Compound **2** is paramagnetic, and, as a result, NMR signals are extremely broad and shifted. The effective magnetic moment, determined by the Evans method, is 2.85 (3) μ_B. This corresponds to two unpaired electrons per cation.

C. Fenske–Hall Molecular Orbital Calculations on (η^5-Pentadienyl)Fe(PMe$_3$)$_2$$^+$. In order to probe the electronic origins of the observed in-plane geometry of **2** and its paramagnetism, we have performed Fenske–Hall molecular orbital calculations[12] on a model system, (η^5-pentadienyl)Fe(PMe$_3$)$_2$$^+$. We have examined the interaction of the pentadienide fragment with a Fe(PMe$_3$)$_2$$^{2+}$

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[7] Our initial incorrect formulation of **2** as a bis(pentadienyl) complex was based on the observation that treatment of **2** with sodium naphthalenide converted it back to **1**. Apparently, this reaction involves reduction of **2** to 17e$^-$ (η^5-pentadienyl)Fe(PEt$_3$)$_2$, which then undergoes ligand scrambling to produce **1** in ~50% yield.

[8] Extrusion of pentadienyl radical from a paramagnetic 17e$^-$ (pentadienyl)metal complex has precedent in cobalt chemistry.[1e]

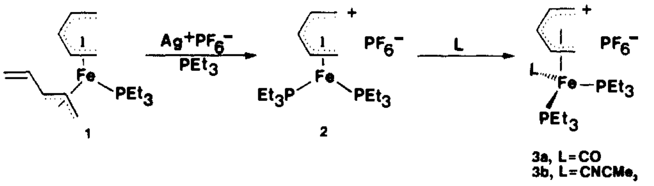
[9] This product was detected by gas chromatography.

[10] Similarly, treatment of (η^3-pentadienyl)$_2$Fe(PMe$_3$)$_2$ with HPMe$_3$$^+$ leads to loss of 1,3-pentadiene and production of (η^5-pentadienyl)Fe(PMe$_3$)$_3$$^+$.[1k]

[11] The actual distances of the mouth and backbone phosphorus atoms from the pentadienyl plane are 2.43 and 3.24 Å, respectively, in (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$ and 2.46 and 3.33 Å, respectively, in (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$$^+BF_4$$^-$.

[12] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

Scheme I



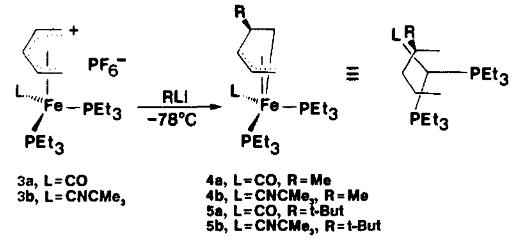
fragment in two geometries, the observed in-plane geometry and the 90°-rotated "perpendicular" geometry. We find that Fenske–Hall calculates a lower energy for the observed in-plane geometry (−65 005.5 eV) than for the perpendicular geometry (−65 001.6 eV).[13] This result contrasts with an Extended Hückel MO calculation on the analogous 16e⁻ (η^5-pentadienyl)Fe(CO)$_2$ cation performed by Hoffmann et al.,[14] which predicts that the perpendicular geometry will be favored.[15]

Shown in Figure 2 are the important orbitals which result from the interaction of the pentadienide ligand with a Fe(PMe$_3$)$_2$$^{2+}$ fragment in the in-plane and perpendicular geometries. The preference for the observed in-plane structure apparently derives from the variable interaction of the filled pentadienide π orbitals with the energetically low-lying, unfilled 2b$_2$ fragment orbital of Fe(PMe$_3$)$^{2+}$. In the in-plane geometry, the 2b$_2$ orbital has the proper symmetry and is energetically proximite with the pentadienide 3π orbital, resulting in a strong bonding interaction. In the perpendicular structure, on the other hand, the 2b$_2$ orbital is symmetry matched with the pentadienide 2π orbital but is energetically far removed from this orbital and thus interacts only weakly. Mulliken population analysis shows that the overlap population for the 2b$_2$ and 3π orbitals in the in-plane geometry is significantly greater than that for the 2b$_2$ and 2π orbitals in the perpendicular geometry (0.270 e⁻ vs 0.209 e⁻). The electronic preference for the in-plane geometry is reinforced by steric interactions between the pentadienide and the phosphine ligands, which are minimized when one of the phosphines resides under the open mouth of the pentadienide.

An unusual feature of the orbital interaction diagram for the in-plane geometry of (η^5-pentadienyl)Fe(PMe$_3$)$_2$$^+$ is the extremely small calculated HOMO–LUMO gap of 0.10 eV (see Figure 2). This is normally a predictor of "instability" for closed shell MO calculations and might be expected to lead to a change in geometry, relieving the near degeneracy of the HOMO and LUMO.[16] For the steric and electronic reasons cited above, such a geometry change does not occur; rather, the molecule adopts the observed high-spin electronic configuration which corresponds in a formal sense to an occupation of one unpaired electron in both the HOMO and the LUMO.

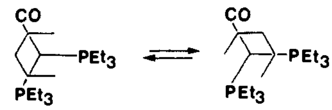
D. Synthesis of (η^5-Pentadienyl)Fe(PEt$_3$)$_2$(CO)$^+$PF$_6$$^-$ (3a) and (η^5-Pentadienyl)Fe(PEt$_3$)$_2$(CNCMe$_3$)$^+$PF$_6$$^-$ (3b). As we reported earlier,[10] compound **2** reacts with small phosphorus-based ligands to produce 18e⁻ (η^5-pentadienyl)FeL$_3$$^+PF_6$$^-$ complexes. For example, treatment of **2** with PMe$_3$, (Me$_2$PCH$_2$)$_3$CMe, or P(OMe)$_3$ leads to the production of (η^5-pentadienyl)Fe(PMe$_3$)$_3$$^+PF_6$$^-$, ($\eta^5$-pentadienyl)Fe[(Me$_2PCH_2$)$_3$CMe]$^+PF_6$$^-$, or ($\eta^5$-pentadienyl)Fe[P(OMe)$_3$]$_2$(PEt$_3$)$^+PF_6$$^-$, respectively.[10] However, **2** is unreactive toward additional PEt$_3$ or other large (cone angle > 130°)[17] phosphines.

Scheme II



We now report that compound **2** reacts cleanly with 1 equiv of carbon monoxide or *tert*-butylisonitrile to produce (η^5-pentadienyl)Fe(PEt$_3$)$_2$(CO)$^+$PF$_6$$^-$ (**3a**) or (η^5-pentadienyl)Fe(PEt$_3$)$_2$(CNCMe$_3$)$^+$PF$_6$$^-$ (**3b**) (Scheme I). Unlike the reactions reported earlier, these reactions are simple ligand additions, not accompanied by ligand exchange. In solution, compounds **3a** and **3b** adopt the unsymmetrical three-legged piano stool structures shown in Scheme I, wherein one PEt$_3$ ligand and L reside under the pentadienyl backbone and the other PEt$_3$ ligand resides under the open pentadienyl mouth.[18] This unsymmetrical ligand orientation is clear from the ^{31}P{^{1}H} NMR spectra of **3a** and **3b**, which exhibit distinct signals for the inequivalent PEt$_3$ ligands. As a consequence of the inequivalence of the two PEt$_3$ ligands, compounds **3a** and **3b** possess stereogenic centers at iron.

As compound **3a** is heated in solution, its η^5-pentadienyl ligand begins to rotate with respect to the Fe(PEt$_3$)$_2$(CO) fragment, causing exchange of the two phosphine ligands and, ultimately, coalescence of their NMR signals. Line shape simulations of the variable-temperature ^{31}P{^{1}H} NMR spectra of **3a** (0–90 °C) yield a $\Delta G^‡$ of 14.7 ± 0.2 kcal/mol for this exchange process. Compound **3b** exhibits no broadening of its NMR signals up to 35 °C, where it begins to decompose. This establishes a lower limit of ~17 kcal/mol for the $\Delta G^‡$ associated with pentadienyl ligand rotation in **3b**. It should be noted that pentadienyl ligand rotation in **3a,b** has the effect of racemizing the two enantiomers.



The rotameric preference exhibited by compounds **3a,b** is not fully understood but apparently derives, in part, from an electronic preference for an electron-donating ligand (i.e., PEt$_3$) to reside under the pentadienyl mouth or an electron-accepting ligand (i.e., L) to reside under the pentadienyl backbone. A similar preference is exhibited by the closely related ruthenium complexes, (η^5-pentadienyl)Ru(PMe$_3$)(PPh$_3$)(CO)$^+$ and (η^5-pentadienyl)Ru(PMe$_3$)(PPh$_3$)(CNCMe$_3$)$^+$.[18]

E. Reactions of Compounds 3a,b with Alkyl Anions. Treatment of **3a,b** with methyllithium or *tert*-butyllithium at −78 °C leads cleanly to exo attack at C2 of the pentadienyl ligands and production of (2-methyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$(L) (L = CO, **4a**; L = CNCMe$_3$, **4b**) or (2-*tert*-butyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$(L) (L = CO, **5a**; L = CNCMe$_3$, **5b**), respectively (see Scheme II). In each case, attack occurs with >85% diastereoselectivity on the "L-side" of the pentadienyl ligand, i.e., at the internal pentadienyl carbon which resides above ligand L and opposite the PEt$_3$ ligand.

The observed L-side attack (at C2 rather than C4) was unanticipated on electronic grounds, because C2 resides roughly trans to an electron-donating ligand (PEt$_3$), while C4 resides roughly trans to an electron-withdrawing ligand (CO or CNCMe$_3$);

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[13] Total energy as calculated by the Fenske–Hall approach produces energies and energy differences which are too large to be realistic but provides a reliable indication of relative energetics. For a discussion and application of total energy calculated by the Fenske–Hall MO method, see: Milletti, M. C.; Fenske, R. F. *Organometallics* **1989**, *8*, 420.

[14] Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812.

[15] It appears that the difference between the Fenske–Hall and Extended Hückel calculations for these systems arises primarily from higher calculated metal based orbital energies generated by the Fenske–Hall calculations. In the Extended Hückel calculations, the b$_1$ ML$_2$ fragment orbital and the pentadienide 2π participate in a 4e⁻–2 orbital interaction that destabilizes the in-plane conformation. Fenske–Hall calculates a higher energy for the b$_1$ orbital thus removing it from energetic proximity with the 2π and diminishing the importance of the destabilizing interaction. This effect derives in part from the stabilization of the b$_1$ orbital in the Extended Hückel calculation by the strongly π accepting CO ligands relative to the σ donating PMe$_3$ ligands utilized in the Fenske–Hall calculation. In addition, differences in the choice of metal basis function and the placement of the metal atom relative to the pentadienide ligand probably contribute to the contrasting results produced by Fenske–Hall.

[16] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.

[17] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

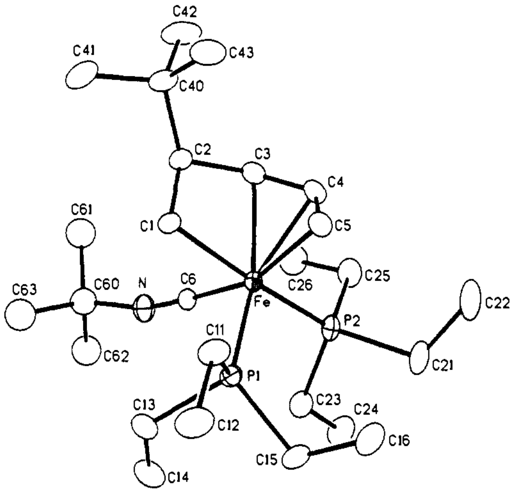

Figure 3. ORTEP drawing of (2-*tert*-butyl-1,3,4,5-η-pentenediyl)Fe$(PEt_3)_2(CNCMe_3)$ (**5b**).

therefore, C2 was expected to be more negative than C4. However, the PEt_3 ligand (with its relatively diffuse orbitals) may polarize the molecule's electronic distribution so that the whole "PEt_3-side" of the molecule becomes more negative than the L-side, thereby directing L-side (C2) attack. An alternative explanation is that the site of nucleophilic addition is determined by steric factors, with the attack occurring preferentially on the side of the pentadienyl ligand opposite the bulky PEt_3 ligand. We have recently observed analogous L-side attack of methyl anion on two closely related (η^5-pentadienyl)ruthenium cations, (η^5-pentadienyl)Ru$(PMe_3)(PPh_3)(CO)^+$ and (η^5-pentadienyl)Ru$(PMe_3)(PPh_3)(CNCMe_3)^+$.[18]

The solid-state structure of **5b**, derived from a single-crystal X-ray diffraction study, is shown in Figure 3. Selected bond distances and angles are given in Table II. The attacked pentadienyl carbon atom, C2, is displaced 0.59 Å out of the C1/C3/C4/C5 plane; C2 resides 2.66 Å from the Fe atom. The dihedral angle between plane C1/C3/C4/C5 and plane C1/C2/C3 is 38.1°. Within the 1,3,4,5-η-pentenediyl ligand, carbon–carbon bonds C1–C2 and C2–C3 exhibit normal single bond lengths, while C3–C4 and C4–C5 exhibit typical allylic bond lengths (see Table II). The C1–C3 and C1–C5 nonbonding distances are 2.36 and 2.79 Å, respectively.

The NMR spectra of **4a**, **4b**, and **5a** are very similar to those of **5b**, strongly suggesting that all four compounds are isostructural. Particularly diagnostic of L-side attack is a $^{13}C\{^1H\}$ NMR signal for pentenediyl carbon C1 which exhibits relatively strong P–C coupling (>20 Hz) to *both* phosphine ligands, the mouth phosphine and the backbone phosphine which resides roughly trans to C1. In contrast, the pentenediyl C1 atom in the minor PEt_3-side attack product exhibits strong P–C coupling only to the mouth phosphine.

Experimental Section

General Comments. All manipulations were carried out under inert atmosphere, by using either drybox or Schlenk techniques. Diethyl ether and tetrahydrofuran (THF) were dried with sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Dichloromethane was dried over magnesium sulfate and distilled. $HPF_6 \cdot OEt_2$ (Columbia), $AgPF_6$ (Aldrich), PEt_3 (Pressure), CO (Air Products), $CNCMe_3$ (Aldrich), methyllithium (Aldrich), and *tert*-butyllithium (Aldrich) were used without further purification. $HPEt_3^+PF_6^-$ was prepared by treating PEt_3 with $HPF_6 \cdot OEt_2$ in diethyl ether, followed by filtering the precipitated product. (η^5-Pentadienyl)(η^3-pentadienyl)-Fe(PEt_3) was synthesized as reported earlier.[10]

NMR experiments were performed on a Varian XL-300 or Gemini 300 (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz) NMR spectrometer. ^1H and ^{13}C spectra were referenced to tetramethylsilane. ^{31}P spectra were referenced to external H_3PO_4. In general, ^1H connectivities were determined from ^1H–^1H shift-correlated (COSY) 2D spectra; ^1H and ^{13}C peak assignments were made by using the ^{13}C gated-decoupled spectra and ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. Reported ^1H–^1H and some ^1H–^{31}P coupling constants were determined by using ^1H J-resolved (HOM2DJ) spectra.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (2-*tert*-Butyl-1,3,4,5-η-pentenediyl)Fe$(PEt_3)_2(CNCMe_3)$ (**5b**)[a]

Bond Distances

Fe–P1	2.194 (1)	P2–C25	1.848 (4)	C23–C24	1.531 (5)
Fe–P2	2.261 (1)	N–C6	1.158 (4)	C25–C26	1.526 (6)
Fe–C1	2.098 (3)	N–C60	1.457 (4)	C40–C41	1.512 (8)
Fe–C3	2.139 (4)	C1–C2	1.516 (5)	C40–C42	1.535 (7)
Fe–C4	2.058 (4)	C2–C3	1.508 (6)	C40–C43	1.519 (5)
Fe–C5	2.135 (3)	C2–C40	1.557 (5)	C60–C61	1.528 (6)
Fe–C6	1.791 (3)	C3–C4	1.392 (5)	C60–C62	1.527 (5)
P1–C11	1.845 (3)	C4–C5	1.410 (5)	C60–C63	1.527 (7)
P1–C13	1.846 (4)	C11–C12	1.525 (6)	C60–C61′	1.527 (7)
P1–C15	1.847 (4)	C13–C14	1.517 (5)	C60–C62′	1.527 (6)
P2–C21	1.845 (5)	C15–C16	1.541 (6)	C60–C63′	1.528 (5)
P2–C23	1.842 (4)	C21–C22	1.544 (7)		

Bond Angles

P1–Fe–P2	102.1 (1)	C1–C2–C40	120.2 (3)
P1–Fe–C1	88.6 (1)	C3–C2–C40	116.5 (4)
P2–Fe–C1	167.5 (1)	C2–C3–C4	126.8 (3)
P1–Fe–C3	153.0 (1)	C3–C4–C5	126.5 (4)
P2–Fe–C3	103.0 (1)	Fe–C6–N	175.8 (3)
C1–Fe–C3	67.7 (2)	P1–C11–C12	119.3 (3)
P1–Fe–C5	93.2 (1)	P1–C13–C14	115.9 (3)
P2–Fe–C5	103.1 (1)	P1–C15–C16	113.1 (3)
C1–Fe–C5	82.4 (1)	P2–C21–C22	115.5 (4)
C3–Fe–C5	71.7 (1)	P2–C23–C24	120.0 (3)
P1–Fe–C6	97.7 (1)	P2–C25–C26	115.1 (4)
P2–Fe–C6	89.8 (1)	C2–C40–C41	108.6 (4)
C1–Fe–C6	82.3 (1)	C2–C40–C42	108.1 (3)
C3–Fe–C6	92.0 (1)	C41–C40–C42	110.3 (4)
C5–Fe–C6	161.0 (1)	C2–C40–C43	112.1 (3)
Fe–P1–C11	114.8 (1)	C41–C40–C43	109.4 (3)
Fe–P1–C13	115.3 (1)	C42–C40–C43	108.4 (4)
C11–P1–C13	99.6 (2)	N–C60–C61	109.4 (3)
Fe–P1–C15	122.9 (1)	N–C60–C62	109.5 (3)
C11–P1–C15	100.0 (1)	C61–C60–C62	109.4 (4)
C13–P1–C15	100.6 (2)	N–C60–C63	109.5 (3)
Fe–P2–C21	124.6 (1)	C61–C60–C63	109.5 (5)
Fe–P2–C23	114.7 (1)	C62–C60–C63	109.5 (4)
C21–P2–C23	98.9 (2)	N–C60–C61′	109.5 (4)
Fe–P2–C25	114.6 (1)	N–C60–C62′	109.5 (3)
C21–P2–C25	98.9 (2)	C61′–C60–C62′	109.5 (4)
C23–P2–C25	101.5 (2)	N–C60–C63′	109.4 (3)
C6–N–C60	163.2 (3)	C61′–C60–C63′	109.4 (5)
C1–C2–C3	102.7 (3)	C62′–C60–C63′	109.4 (5)

[a] The methyl groups of the *tert*-butylisonitrile ligand were rotationally disordered. Two independent sets were located in the electron-difference maps. The first set (C61/C62/C63) was refined at multiplicity 0.55, while the second set (C61′/C62′/C63′) was refined at multiplicity 0.45.

Infrared spectra were recorded on a Perkin-Elmer 283B or Mattson Polaris FT-IR spectrometer. Microanalyses of compounds **2a**, **3a**, **3b**, and **5b** were performed by Galbraith Laboratories, Inc., Knoxville, TN. Compounds **4a**, **4b**, and **5a** were oils; therefore, their elemental composition was determined by mass spectrometry, by using a Finnegan 3200 GC/MS.

Paramagnetic Susceptibility Measurements. Paramagnetic susceptibility was determined by using the methods of Evans.[19] The paramagnetic sample was dissolved in dichloromethane. A portion of this solution was placed in an NMR tube, and an insert containing pure dichloromethane was added. The mass susceptibility, x_g, of the complex was determined by using the expression

$$x_g = \frac{3\Delta f}{4\pi f m} + x_0$$

where Δf is the frequency separation between the shifted and unshifted CH_2Cl_2 signals, f is the spectrometer frequency, m is the mass of the complex contained in 1 mL of solution, and x_0 is the mass susceptibility (-0.549×10^{-6}). The molar susceptibility, x_M, was then calculated, and a correction for the diamagnetic contribution of the complex was applied. From the corrected x_M, the effective magnetic moment, μ_{eff}, was determined.

Dynamic NMR Studies. Determination of $\Delta G^{\ddagger}$. The $\Delta G^{\ddagger}$ value for pentadienyl ligand rotation in **3a** was determined by NMR line shape simulation. The variable-temperature $^{31}P\{^1H\}$ NMR spectra were matched against theoretical line shapes, calculated by using the method of C. S. Johnson.[20,21] In this way, exchange rate constants were determined for each temperature. These exchange rate constants, k, were then used to calculate the free energy of activation, $\Delta G^{\ddagger}$, at each temperature, T, by using the Eyring equation.[22] The reported $\Delta G^{\ddagger}$ is the average value over all the temperatures in the simulation, and the uncertainty is the estimated standard deviation.

(η^5-Pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$, 2. Method A. PEt$_3$ (0.118, 1.00×10^{-3} mol) was added to a cold (−30 °C) stirred solution of (η^5-pentadienyl)(η^3-pentadienyl)Fe(PEt$_3$)[1c] in 75 mL of dichloromethane. The solution was allowed to stir for 10 min before AgPF$_6$ (0.253 g, 1.00×10^{-3} mol) in 25 mL of dichloromethane was added. A Ag^0 precipitate and a Ag^0 mirror on the walls of the flask were immediately observed. The solution was then stirred for 10 min at −78 °C before warming to room temperature and stirring for an additional hour. The solution was filtered through Celite on a course glass frit, and the solvent was removed under vacuum leaving a red powder. The powder was washed with diethyl ether and extracted with a minimal amount of dichloromethane. The extract was filtered through Celite on a course frit. The filtrate was concentrated and cooled to −30 °C causing the product to crystallize as dark red plates: yield of crystalline product, 0.35 g (69%).

Method B. HPEt$_3$$^+PF_6$$^-$ (0.264 g, 1.00×10^{-3} mol) and (η^5-pentadienyl)(η^3-pentadienyl)Fe(PEt$_3$)[1c] (0.308 g, 1.00×10^{-3} mol) were stirred at room temperature in 50 mL of dichloromethane for 4 h. The solvent was then removed under vacuum, leaving a red powder. The powder was washed with diethyl ether and collected on a fine frit: yield of product, 0.450 g (89%); $\mu_{\mathrm{eff}} = 2.85 \pm 0.03\ \mu_B$. Anal. Calcd for $C_{17}H_{37}FeP_3F_6$: C, 40.49; H, 7.40. Found: C, 40.59; H, 7.45.

(η^5-Pentadienyl)Fe(PEt$_3$)$_2$($C\equiv O$)$^+$PF$_6$$^-$, 3a. An unmeasured volume of $C\equiv O$ gas was bubbled through a slurry of (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (0.504 g, 1.00×10^{-3} mol) in 50 mL of THF for 1 min. The slurry was then stirred until dissolution of the sparingly soluble (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ and production of a bright yellow solution were observed. At this point the flask was immediately placed under vacuum, and the volatiles were removed leaving a yellow oil. The oil was extracted with a minimal quantity of THF and filtered through a course frit packed with Celite and alumina. The THF solution was then reduced in volume to ca. 10 mL under reduced pressure. Diethyl ether was added until the solution became turbid, at which point the solution was cooled to −30 °C where the product crystallized as yellow microcrystals: yield of crystalline product, 0.431 g (81%); ^{1}H NMR (−10.0 °C, dichloromethane-d_2) δ 5.85 (apparent t, $J_{\mathrm{H-H}} = 6.1$ Hz, 1, H3), 5.33 (apparent quar, $J_{\mathrm{H-H}} = 8.5$ Hz, 1, H2), 5.18 (apparent quin, $J_{\mathrm{H-H}} = 7.8$ Hz, 1, H4), 3.02 (br s, 1, H5$_{\mathrm{outer}}$), 2.60 (br s, 1, H1$_{\mathrm{outer}}$), 2.02 (apparent quin, $J_{\mathrm{H-H}} = 7.0$ Hz, $J_{\mathrm{H-P}} = 7.0$ Hz, 6, phosphine CH$_2$'s), 1.72 (apparent sextet, $J_{\mathrm{H-H}} = 7.8$ Hz, $J_{\mathrm{H-P}} = 15.7$ Hz, 3, phosphine CH$_2$'s), 1.46 (apparent sextet, $J_{\mathrm{H-H}} = 7.2$ Hz, $J_{\mathrm{H-P}} = 12.3$, 3, phosphine CH$_2$'s), 1.16 (apparent quin, $J_{\mathrm{H-H}} = 7.5$ Hz, $J_{\mathrm{H-P}} = 15.2$ Hz, 9, phosphine CH$_3$'s), 1.02 (apparent quin, $J_{\mathrm{H-H}} = 7.4$ Hz, $J_{\mathrm{H-P}} = 14.7$ Hz, 9, phosphine CH$_3$'s), 0.64 (br s, 1, H5$_{\mathrm{inner}}$), 0.20 (br s, 1, H1$_{\mathrm{inner}}$); ^{13}C{^{1}H} NMR (−10.0 °C, dichloromethane-d_2) δ 212.6 (d of d, $J_{\mathrm{C-P}} = 39.5$ Hz, $J_{\mathrm{C-P}} = 20.1$ Hz, $C\equiv O$), 103.8 (s, C4), 99.3 (s, C2), 92.6 (s, C3), 56.6 (d, $J_{\mathrm{C-P}} = 6.7$ Hz, C5), 55.7 (t, $J_{\mathrm{C-P}} = 8.4$ Hz, C1), 23.2 (d, $J_{\mathrm{C-P}} = 27.3$ Hz, phosphine CH$_2$'s), 18.9 (d, $J_{\mathrm{C-P}} = 24.6$ Hz, phosphine CH$_2$'s), 8.7 (d, $J_{\mathrm{C-P}} = 5.6$ Hz, phosphine CH$_3$'s), 8.0 (d, $J_{\mathrm{C-P}} = 4.4$ Hz, phosphine CH$_3$'s); ^{31}P{^{1}H} NMR (−10.0 °C, dichloromethane-d_2) δ 44.3 (d, $J_{\mathrm{P-P}} = 34.2$ Hz), 42.4 (d, $J_{\mathrm{P-P}} = 34.2$ Hz); IR (KBr pellet; selected peak) 1958.6 cm^{-1} (carbonyl $C\equiv O$ stretch). Anal. Calcd for $C_{18}H_{37}FeP_3F_6O$: C, 40.62; H, 7.01. Found: C, 40.24; H, 6.99.

(η^5-Pentadienyl)Fe(PEt$_3$)$_2$($C\equiv NCMe_3$)$^+$PF$_6$$^-$, 3b. $C\equiv NCMe_3$ (0.083 g, 1.00×10^{-3} mol) was added to (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ (0.504 g, 1.00×10^{-3} mol) in 50 mL of THF. The solution immediately turned bright yellow, and the sparingly soluble (η^5-pentadienyl)Fe(PEt$_3$)$_2$$^+PF_6$$^-$ was quickly taken into solution. The solution was filtered through Celite and concentrated to ca. 10 mL under reduced pressure. Thirty milliliters of diethyl ether was then added slowly causing the product to crystallize as bright yellow microcrystals: yield of crystalline product, 0.546 g (93%); ^{1}H NMR (20.0 °C, dichloromethane-d_2) δ 5.85 (apparent t, $J_{\mathrm{H-H}} = 6.4$ Hz, 1, H3), 4.92 (m, 2, H2 and H4), 2.56 (br m, 1, H5$_{\mathrm{outer}}$), 2.31 (br m, 1, H1$_{\mathrm{outer}}$), 2.08 (apparent quin, 6, $J_{\mathrm{H-H}} = 7.5$ Hz, $J_{\mathrm{H-P}} = 7.5$ Hz, phosphine CH$_2$'s), 1.66 (m, 3, phosphine CH$_2$'s), 1.45 (m, 3, phosphine CH$_2$'s), 1.38 (s, 9, $C\equiv NCMe_3$), 1.25 (apparent quin, $J_{\mathrm{H-H}} = 7.2$ Hz, $J_{\mathrm{H-P}} = 14.6$ Hz, 9, phosphine CH$_3$'s), 1.08 (apparent quin, $J_{\mathrm{H-H}} = 7.8$ Hz, $J_{\mathrm{H-P}} = 14.2$ Hz, 9, phosphine CH$_3$'s), 0.00 (br s, 1, H5$_{\mathrm{inner}}$), −0.28 (br m, 1, H1$_{\mathrm{inner}}$); ^{13}C{^{1}H} NMR (20.0 °C, dichloromethane-d_2) δ 101.3 (s, C4), 98.0 (s, C2), 91.1 (s, C3), 58.9 (s, $C\equiv NCMe_3$), 51.6 (t, $J_{\mathrm{C-P}} = 9$ Hz, C1), 50.8 (d, $J_{\mathrm{C-P}} = 11$ Hz, C5), 30.6 (s, $C\equiv NCMe_3$), 23.6 (d, $J_{\mathrm{C-P}} = 25$ Hz, phosphine CH$_2$'s), 19.3 (d, $J_{\mathrm{C-P}} = 22$ Hz, phosphine CH$_2$'s), 9.1 (d, $J_{\mathrm{C-P}} = 5$ Hz, phosphine CH$_3$'s), 8.8 (d, $J_{\mathrm{C-P}} = 4$ Hz, phosphine CH$_3$'s); ^{31}P{^{1}H} NMR (20.0 °C, dichloromethane-d_2) δ 47.6 (d, $J_{\mathrm{P-P}} = 35.4$ Hz), 42.1 (d, $J_{\mathrm{P-P}} = 35.4$ Hz); IR (KBr pellet; selected peak) 2125.4 cm^{-1} ($C\equiv N$ stretch). Anal. Calcd for $C_{22}H_{46}FeNP_3F_6$: C, 45.01; H, 7.90. Found: C, 45.07; H, 7.47.

(2-Methyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$($C\equiv O$), 4a. Methyllithium (0.71 mL, 1.4 M in diethyl ether, 1.00×10^{-3} mol) was added to a cold (−78 °C) stirred solution of (η^5-pentadienyl)Fe(PEt$_3$)$_2$($C\equiv O$)$^+$PF$_6$$^-$ (0.53 g, 1.00×10^{-3} mol) in 50 mL of tetrahydrofuran. The mixture was warmed to room temperature and stirred for 1 h, yielding a clear dark orange solution. ^{31}P{^{1}H} NMR of an aliquot of the reaction solution indicated a 85:15 mixture of a major product (isolated) and minor products. The solution was filtered through Celite on a course frit, and the solvent was removed under reduced pressure to yield an orange-yellow oil. The oil was dissolved in 50 mL of pentane and filtered through Celite on a course frit, and the solvent was removed under vacuum yielding an orange-yellow oil: yield of product, 0.25 g (62.1%); MS (low resolution, electron impact, solid probe, 35 eV) M$^+$ at 402; ^{1}H NMR (benzene-d_6, 17 °C) δ 3.71 (m, 1, H4), 3.46 (apparent t, $J_{\mathrm{H-H}} = 6.7$ Hz, 1, H3), 3.33 (m, 1 H5$_{\mathrm{outer}}$), 2.76 (apparent quin, $J_{\mathrm{H-H}} = 7.8$ Hz, 1, H2), 1.68 (m, 3, phosphine CH$_2$'s), 1.57 (m, 3, phosphine CH$_2$'s), 1.44 (m, 7, H5$_{\mathrm{inner}}$ and phosphine CH$_2$'s), 1.00 (d of t, $J_{\mathrm{H-H}} = 7.4$ Hz, $J_{\mathrm{H-P}} = 11.4$ Hz, 9, phosphine CH$_3$'s), 0.90 (d, $J = 5.5$ Hz, 3, pentenediyl CH$_3$'s), 0.81 (m, 9, phosphine CH$_3$'s), 0.28 (m, 1, H1$_{\mathrm{outer}}$), −2.12 (m, 1, H1$_{\mathrm{inner}}$); ^{13}C{^{1}H} NMR (benzene-d_6, 17 °C) δ 226.1 (d of d, $J_{\mathrm{C-P}} = 18.1$ Hz, $J_{\mathrm{C-P}} = 12.1$ Hz, $C\equiv O$), 94.8 (s, C4), 58.0 (s, C2), 49.6 (d of d, $J_{\mathrm{C-P}} = 9.6$ Hz, $J_{\mathrm{C-P}} = 1.2$ Hz, C5), 36.7 (s, C3), 28.8 (d, $J_{\mathrm{C-P}} = 8.5$ Hz, pentenediyl CH$_3$'s), 21.3 (d of d, $J_{\mathrm{C-P}} = 20.1$ Hz, $J_{\mathrm{C-P}} = 3.1$ Hz, phosphine CH$_2$'s), 19.9 (d, $J_{\mathrm{C-P}} = 14.3$ Hz, phosphine CH$_2$'s), 8.5 (d, $J_{\mathrm{C-P}} = 2.2$ Hz, phosphine CH$_3$'s), 8.0 (d, $J_{\mathrm{C-P}} = 2.6$ Hz, phosphine CH$_3$'s), 4.8 (apparent t, $J_{\mathrm{C-P}} = 23.9$ Hz, C1); ^{31}P{^{1}H} NMR (benzene-d_6, 17 °C) δ 51.5 (d, $J_{\mathrm{P-P}} = 22.3$ Hz), 34.9 (d, $J_{\mathrm{P-P}} = 22.3$ Hz).

(2-Methyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$($C\equiv NCMe_3$), 4b. Methyllithium (0.71 mL, 1.4 M in diethyl ether, 1.00×10^{-3} mol) was added to a cold (−78 °C) stirred solution of (η^5-pentadienyl)Fe(PEt$_3$)$_2$($C\equiv NCMe_3$)$^+$PF$_6$$^-$ (0.58 g, 1.00×10^{-3} mol) in 50 mL of tetrahydrofuran. The mixture was warmed to room temperature and stirred for 1 h yielding a clear dark orange solution. ^{31}P{^{1}H} NMR of an aliquot of the reaction solution indicated a 85:15 mixture of a major product (isolated) and minor products. The solution was filtered through Celite on a course frit, and the solvent was removed under reduced pressure to yield an orange-yellow oil. The oil was dissolved in 50 mL of pentane and filtered through Celite on a course frit, and the solvent was removed under vacuum yielding an orange-yellow oil: yield of product, 0.27 g (59.0%); MS (low resolution, electron impact, solid probe, 35 eV) M$^+$ at 457; ^{1}H NMR (benzene-d_6, 17 °C) δ 3.89 (m, 1, H4), 3.31 (apparent t, $J_{\mathrm{H-H}} = 6.0$ Hz, 1, H3), 3.18 (m, 1, H5$_{\mathrm{outer}}$), 2.79 (apparent quin, $J_{\mathrm{H-H}} = 7.5$ Hz, 1, H2), 1.90–1.48 (complex overlapping m, 12, phosphine CH$_2$'s), 1.39 (m, 1, H5$_{\mathrm{inner}}$), 1.32 (s, 9, $C\equiv NCMe_3$), 1.09 (m, 9, phosphine CH$_3$'s), 0.95 (d, $J = 6.8$ Hz, 3, pentenediyl CH$_3$'s), 0.91 (m, 9, phosphine CH$_3$'s), 0.23 (m, 1, H1$_{\mathrm{outer}}$), −2.09 (m, 1, H1$_{\mathrm{inner}}$); ^{13}C{^{1}H} NMR (benzene-d_6, 17 °C) δ 196.7 (d of d, $J_{\mathrm{C-P}} = 20.4$ Hz, $J_{\mathrm{C-P}} = 15.3$ Hz, $C\equiv NCMe_3$), 92.9 (s, C4), 54.9 (s, $C\equiv NCMe_3$), 54.3 (s, C2), 45.4 (d, $J_{\mathrm{C-P}} = 9.3$ Hz, C5), 37.4 (s, C3), 32.1 (s, $C\equiv NCMe_3$), 29.6 (d, $J_{\mathrm{C-P}} = 8.4$ Hz, pentenediyl CH$_3$'s), 21.4 (d of d, $J_{\mathrm{C-P}} = 17.8$ Hz, $J_{\mathrm{C-P}} = 3.0$ Hz, phosphine CH$_2$'s), 20.0 (d, $J_{\mathrm{C-P}} = 12.1$ Hz, phosphine CH$_2$'s), 8.9 (s, phosphine CH$_3$'s), 8.5 (d, $J_{\mathrm{C-P}} = 2.4$ Hz, phosphine CH$_3$'s), 4.8 (d of d, $J_{\mathrm{C-P}} = 26.1$ Hz, $J_{\mathrm{C-P}} = 22.7$ Hz, C1); ^{31}P{^{1}H} NMR (benzene-d_6, 17 °C) δ 53.1 (d, $J_{\mathrm{P-P}} = 19.9$ Hz), 36.3 (d, $J_{\mathrm{P-P}} = 19.9$ Hz).

(2-*tert*-Butyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$($C\equiv O$), 5a. *tert*-Butyllithium (0.59 mL, 1.7 M in pentane, 1.00×10^{-3} mol) was added to a cold (−78 °C) stirred solution of (η^5-pentadienyl)Fe(PEt$_3$)$_2$($C\equiv O$)$^+$PF$_6$$^-$ (0.53 g, 1.00×10^{-3} mol) in 50 mL of tetrahydrofuran. The mixture was warmed to room temperature and stirred for 1 h, yielding a clear dark orange solution. ^{31}P{^{1}H} NMR of an aliquot of the reaction solution indicated a 95:5 mixture of a major product (isolated) and minor products. The solution was filtered through Celite on a course frit, and the solvent was removed under reduced pressure to yield an orange-yellow oil. The oil was dissolved in 50 mL of pentane and filtered through Celite on a course frit, and the solvent was removed under vacuum yielding an orange-yellow oil: yield of product 0.32 g (72.0%); MS (low resolution,

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(18) If other rotamers are present, they must represent <1% of the mixture.

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electron impact, solid probe, 35 eV) M^+ at 444; ^{1}H NMR (benzene-d_6, 17 °C) δ 3.74 (m, 1, H4), 3.40 (apparent t, J_{H-H} = 7.0 Hz, 1, H3), 3.18 (m, 1, H5$_{outer}$), 2.52 (apparent quar, J_{H-H} = 9.0 Hz, 1, H2), 1.61–1.03 (complex overlapping m, 13, H5$_{inner}$ and phosphine CH$_2$'s), 0.99 (d of t, J_{H-H} = 7.5 Hz, J_{H-P} = 13.2 Hz, 9, phosphine CH$_3$'s), 0.82 (br s, 9, pentenediyl *tert*-butyl CH$_3$'s), 0.81 (m, 9, phosphine CH$_3$'s), 0.06 (m, 1, H1$_{outer}$), −1.94 (m, 1, H1$_{inner}$); ^{13}C{^{1}H} NMR (benzene-d_6, 17 °C) δ 225.5 (d of d, J_{C-P} = 18.0 Hz, J_{C-P} = 12.3 Hz, C≡O), 96.8 (s, C4), 58.0 (s, C2), 54.7 (s, C3), 49.7 (d of d, J_{C-P} = 9.8 Hz, J_{C-P} = 2.4 Hz, C5), 36.4 (d, J_{C-P} = 5.9 Hz, pentenediyl *tert*-butyl quaternary C), 27.0 (s, pentenediyl *tert*-butyl CH$_3$'s), 21.3 (d of d, J_{C-P} = 20.3 Hz, J_{C-P} = 3.2 Hz, phosphine CH$_2$'s), 19.8 (d, J_{C-P} = 14.6 Hz, phosphine CH$_2$'s), 8.5 (d, J_{C-P} = 7.3 Hz, phosphine CH$_3$'s), 8.0 (d, J_{C-P} = 5.8 Hz, phosphine CH$_3$'s), 1.1 (apparent t, J_{C-P} = 23.9 Hz, C1); ^{31}P{^{1}H} NMR (benzene-d_6, 17 °C) δ 52.4 (d, J_{P-P} = 22.4 Hz), 34.6 (d, J_{P-P} = 22.4 Hz).

(2-*tert*-Butyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$(C≡NCMe$_3$), 5b. *tert*-Butyllithium (0.59 mL, 1.7 M in pentane, 1.00 × 10^{-3} mol) was added to a cold (−78 °C) stirred solution of (η^5-pentadienyl)Fe(PEt$_3$)$_2$(C≡NCMe$_3$)$^+$PF$_6^-$ (0.59 g, 1.00 × 10^{-3} mol) in 50 mL of tetrahydrofuran. The mixture was warmed to room temperature and stirred for 1 h yielding a clear dark orange solution. ^{31}P{^{1}H} NMR of an aliquot of the reaction solution indicated a 95:5 mixture of a major product (isolated) and minor products. The solution was filtered through Celite on a course frit, and the solvent was removed under reduced pressure to yield an orange-yellow oil. The oil was dissolved in 50 mL of pentane, filtered through Celite on a course frit, and reduced in volume to ca. 10 mL. The solution was then cooled to −30 °C where the product crystallized as large orange-yellow blocks: yield of crystalline product, 0.30 g (60.0%, two crops). MS (low resolution, electron impact, solid probe, 35 eV) M^+ at 499; ^{1}H NMR (benzene-d_6, 17 °C) δ 3.90 (m, 1, H4), 3.20 (apparent t, J_{H-H} = 7.0 Hz, 1, H3), 3.02 (m, 1 H5$_{outer}$), 2.45 (apparent t of d, J_{H-H} = 9.9 Hz, J_{H-H} = 6.7 Hz, 1, H2), 1.59 (m, 6, phosphine CH$_2$'s), 1.32 (br s, 10, H5$_{inner}$ and C≡NC*Me*$_3$), 1.26 (m, 3, phosphine CH$_2$'s), 1.08 (d of t, J_{H-P} = 12.7 Hz, J_{H-H} = 7.5 Hz, 9, phosphine CH$_3$'s), 1.20–0.97 (m, 3, phosphine CH$_2$'s), 1.01 (s, 9, pentenediyl *tert*-butyl CH$_3$'s), 0.89 (d of t, J_{H-P} = 11.5 Hz, J_{H-H} = 7.6 Hz, 9, phosphine CH$_3$'s), −0.08 (m, 1, H1$_{outer}$), −1.99 (m, 1, H1$_{inner}$); ^{13}C{^{1}H} NMR (benzene-d_6, 17 °C) δ 195.2 (d of d, J_{C-P} = 20.9 Hz, J_{C-P} = 14.4 Hz, *C*≡NCMe$_3$), 95.1 (s, C4), 55.8 (s, C2), 54.9 (s, C≡N*C*Me$_3$), 54.2 (s, C3), 45.6 (d of d, J_{C-P} = 10.9 Hz, J_{C-P} = 1.8 Hz, C5), 36.4 (d, J_{C-P} = 5.9 Hz, pentenediyl *tert*-butyl quaternary C), 32.1 (s, C≡NC*Me*$_3$), 27.2 (s, pentenediyl *tert*-butyl CH$_3$'s), 21.6 (d of d, J_{C-P} = 17.7 Hz, J_{C-P} = 3.1 Hz, phosphine CH$_2$'s), 20.0 (d, J_{C-P} = 12.2 Hz, phosphine CH$_2$'s), 8.9 (d, J_{C-P} = 2.0 Hz, phosphine CH$_3$'s), 8.5 (d, J_{C-P} = 2.8 Hz, phosphine CH$_3$'s), 2.4 (apparent t, J_{C-P} = 25.0 Hz, C1). ^{31}P{^{1}H} NMR (benzene-d_6, 17 °C) δ 54.1 (d, J_{P-P} = 20.2 Hz), 36.2 (d, J_{P-P} = 20.2 Hz). Anal. Calcd for $C_{26}H_{55}NP_2Fe$: C, 62.52; H, 11.10. Found: C, 62.80; H, 11.04.

Single-Crystal X-ray Diffraction Studies of 2 and 5b. Suitable crystals of **2** and **5b** were mounted in glass capillaries under inert atmosphere. Data were collected at room temperature by using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 50 (for **5b**) or 100 (for **2**) events as check reflections for crystal deterioration and/or misalignment. Data reduction and refinement were done by using the Siemens SHELXTL PLUS package on a MicroVAX II computer.[23] Crystal data and details of data collection and structure analysis are summarized in Table III.

The positions of most of the non-hydrogen atoms in **2** and **5b** (including the iron and phosphorus atoms) were obtained by using direct methods. The structures were completed by successive full-matrix least-squares refinements and difference Fourier map calculations.

The cation in **2** resided on a 2-fold rotation axis, which resulted in a 2-fold rotational disorder of the pentadienyl group. Hence, C2 (the central carbon on the pentadienyl group) was included at a multiplicity of 0.5. All other non-hydrogen atoms in the cation were included with multiplicities of 1.0. The PF$_6^-$ group in **2** was situated on an inversion center, and it too was disordered. Three sets of independent fluorine atoms (F2/F3, F2′/F3′, and F2″/F3″) were located in the equatorial plane of the PF$_6$ anion. The multiplicities of these sets, as determined by refinement and normalization to 1.0, were 0.62 for F2/F3, 0.20 for F2′/F3′, and 0.18 for F2″/F3″. The positional parameters of F2/F3 were refined, while those of F2′/F3′ and F2″/F3″ were held fixed. Thermal parameters for all three sets were refined isotropically. The axial fluorine atom of the PF$_6$ anion, F1, was not disordered and was included in the model with a multiplicity of 1.0. Its position was refined, and its thermal parameters were refined isotropically. An ORTEP drawing of the disordered PF$_6$ anion, showing all three sets of equatorial fluorine atoms, is included in Supplementary Material. Hydrogen atoms on the phosphine ligands were located in difference Fourier maps and included in the model. Their positions were refined, and a common thermal parameter was refined isotropically. Hydrogens on the disordered pentadienyl group were not included.

Table III. X-ray Diffraction Structure Summary

Crystal Parameters and Data Collection Summary		
compd	**2**	5b
formula	$C_{17}H_{37}FeP_2PF_6$	$C_{26}H_{55}FeNP_2$
formula weight	504.2	499.5
crystal system	monoclinic	triclinic
space group	*C*2/*c* (no. 15)	*P*1 (no. 2)
a, Å	20.556 (6)	9.433 (2)
b, Å	7.894 (2)	9.849 (2)
c, Å	15.000 (4)	18.015 (4)
α, deg	90.0	100.98 (2)
β, deg	103.80 (2)	93.51 (2)
γ, deg	90.0	111.44 (2)
V, Å^3	2363.9 (11)	1513.6 (6)
Z	4	2
crystal dimensions, mm	0.08 × 0.18 × 0.50	0.68 × 0.75 × 0.88
crystal color	red	orange-yellow
density$_{calcd}$, g/cm^3	1.417	1.096
diffractometer model	Siemens R3m/V	Siemens R3m/V
radiation, Å	Mo Kα, 0.71069	Mo Kα, 0.71069
scan type	θ:2θ	ω
scan rate, deg/min	variable; 3.0–14.6	variable; 4.88–14.65
scan range	1.2° 2θ below Kα_1 to 1.2° 2θ above Kα_2	1.2° ω
2θ range, deg	3.5–50.0	3.5–60.0
data collected	*h* (0–24), *k* (0–9), *l* (−17 to 17)	*h* (−13 to −4 and 0–11) *k* (−11 to 13) *l* (−23 to 24)
total decay	none detected	none detected
Treatment of Intensity Data and Refinement Summary		
no. of data collected	2163	10893
no. of unique data	1939	7742
no. of data with *I* > 3σ (I)	1137	5229
Mo Kα linear abs. coeff., cm^{-1}	8.83	6.13
abs. correction applied	ψ scans	ψ scans
data to parameter ratio	6.9:1	18.6:1
R^a	0.0580	0.0496
R$_w$^{a}	0.0654	0.0731
GOF^b	1.71	1.49
largest residual peak in diff. Fourier, e/Å^3	0.60	0.80

[a] $R = \|F_o| - |F_c\|/|F_o|$. $R_w = [w^*(|F_o| - |F_c|)^2/w^*|F_o|^2]^{1/2}$. For **2**, $w = 1/[\sigma^2(|F_o|) + 0.0005(|F_o|)^2]$. For **5b**, $w = 1/[\sigma^2(|F_o|) + 0.0013(|F_o|)^2]$. [b] $GOF = [w^*(|F_o| - |F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$

All of the non-hydrogen atoms in **5b**, except for the carbons in the *tert*-butyl group of the *tert*-butylisonitrile ligand, were refined anisotropically. Two sets of independent methyl groups (C61/C62/C63 and C61′/C62′/C63′) were located in the region of the *tert*-butylisonitrile ligand. The multiplicities of these sets, as determined by refinement and normalization to 1.0, were 0.55 for C61/C62/C63 and 0.45 for C61′/C62′/C63′. The positional parameters of both sets were refined within a constrained tetrahedral geometry; thermal parameters were held fixed at U = 0.09 Å^{-2}. The quaternary carbon atom of the *tert*-butylisonitrile ligand (C60) was refined isotropically. All of the hydrogen atoms in the pentenediyl ligand, except for those on the *tert*-butyl substituent, were located in electron-difference maps, and their positions were refined. All other hydrogens in the molecule, except for those on the disordered *tert*-butylisonitrile ligand, were placed at idealized positions, riding upon their respective carbon atoms. A common isotropic temperature factor was assigned to all hydrogen atoms and refined.

Fenske–Hall Molecular Orbital Calculations. Molecular orbital calculations were carried out on a Micro VAX II computer system by using the Fenske–Hall nonempirical approximate MO method.[12] In calculations of (η^5-pentadienyl)Fe(PMe$_3$)$_2^+$, the geometry was based upon the X-ray crystal structure of (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$,[1c,24] and all structures were optimized to C_s symmetry. The geometry of the PMe$_3$ ligands was generated by using the bond distances and angles reported by Hall and optimized to local C_{3v} symmetry.[25]

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(23) Atomic scattering factors were obtained from the following: *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, 1974; Vol. IV.

(24) We chose not to base the calculations on the structure of **2**, because it exhibits a 2-fold rotational disorder.

(25) Yarbrough, L, W., II; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269.

All atomic wave functions were generated by the method of Bursten, Jensen, and Fenske.[26] Contracted double-ζ representations were used for the Fe 3d, P 3p, and C 2p AO's. The hydrogen 1s AO utilized an exponent of 1.16.[27] The basis functions for Fe were derived for the +1 oxidation state with fixed 5s and 5p exponents of 2.0. The P basis functions were derived for the +0.45 oxidation state.

Summary

In order to study nucleophilic attack at internal carbons (C2/C4) of pentadienyl ligands, a family of electron-rich (η^5-pentadienyl)FeL$_3^+$ complexes has been synthesized. These complexes are obtained by treating (η^5-pentadienyl)Fe(PEt$_3$)$_2^+$PF$_6^-$ (**2**) with a series of 2e$^-$ donor ligands, L. In this paper, we report the synthesis of (η^5-pentadienyl)Fe(PEt$_3$)$_2$(L)$^+$PF$_6^-$ (L = CO, **3a**; L = CNCMe$_3$, **3b**), which are single rotamers (PEt$_3$ resides under the open pentadienyl mouth) and are chiral (the Fe atom is a stereogenic center).

Cations **3a** and **3b** undergo regioselective attack by alkyl anions at internal carbon C2 of the pentadienyl ligand. In particular, treatment of **3a,b** with methyllithium leads to the clean production of (2-methyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$(L) (L = CO, **4a**; L = CNCMe$_3$, **4b**), while treatment with *tert*-butyllithium generates (2-*tert*-butyl-1,3,4,5-η-pentenediyl)Fe(PEt$_3$)$_2$(L) (L = CO, **5a**; L = CNCMe$_3$, **5b**). In each case, the Fe(PEt$_3$)$_2$(L)$^+$ fragment serves as an effective chiral auxiliary, directing diastereoselective addition to the less-hindered L-side of the pentadienyl ligand.

Work currently in progress is directed toward effecting further transformations of the pentenediyl ligands. Results of these studies will be reported in the future.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's X-ray Crystallographic Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456). The High Resolution NMR Service Facility was funded in part by the National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from the Monsanto Company. The Washington University Mass Spectrometry Resource is supported by a grant from the National Institutes of Health (RR00954).

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes for **2** and **5b** and an ORTEP drawing of the disordered PF$_6^-$ group in **2**, showing all three sets of equatorial fluorine atoms (14 pages); listings of observed and calculated structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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Bis(η^6-hexamethylbenzene)(η^6,η^6-[2$_n$]cyclophane)diruthenium(II,II) Complexes and Their Two-Electron Reduction to [2$_n$]Cyclophane Derivatives Having Two Cyclohexadienyl Anion Decks Joined by an Extremely Long Carbon–Carbon Bond

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Received January 8, 1990

Abstract: A series of bis(η^6-hexamethylbenzene)(η^6,η^6-[2$_n$]cyclophane)diruthenium(II,II) tetrakis(tetrafluoroborate) complexes, **4**, **5**, **9**, **10**, and **11**, has been prepared, where the [2$_n$]cyclophanes are [2$_2$](1,4)cyclophane, [2$_2$](1,3)cyclophane, 4,7,13,16-tetramethyl-[2$_2$](1,4)cyclophane, 4,5,7,8-tetramethyl-[2$_2$](1,4)cyclophane, and [2$_3$](1,3,5)cyclophane, respectively. These 4+ diruthenium complexes undergo two-electron reduction to give **7**, **8**, **12**, **13**, and **14**, respectively, in which each of the cyclophane ligands now has two cyclohexadienyl anion decks connected by a new carbon–carbon bond. The assignment of structures to these two-electron reduction products is based on ^{1}H and ^{13}C NMR spectral analyses, electrochemical studies, and X-ray photoelectron data. A single-crystal X-ray analysis confirmed the structure assigned to the [2$_2$](1,4)cyclophane derivative **7** and showed that the carbon–carbon bond connecting the two cyclohexadienyl anion decks in **7** is 1.96 (3) Å in length, an extremely long carbon–carbon bond. A theoretical analysis of these 2+ diruthenium complexes and their formation is presented.

Recently we described a synthesis of bis(η^6-hexamethylbenzene)(η^6,η^6-[2$_4$](1,2,4,5)cyclophane)diruthenium(II,II) tetrakis(tetrafluoroborate), **1**, and its reduction to the corresponding 2+ ion, **2**, and the neutral species, **3**.[2] A study of the 2+ ion **2** showed it to be a mixed-valence ion (class II), exhibiting a net two-electron intervalence transfer. Although the ^{1}H and ^{13}C NMR spectra of **2** are symmetrical at room temperature, indicating the same environment for each of the two ruthenium atoms, cooling of these NMR solutions leads to a coalescence of signals and, below −45 °C, the two ruthenium atoms have different environments,

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