to prepare the appropriate concentration by dilution with pure methanol or water followed by a small pH readjustment.

The 25 mM alkylammonium/20 mM citrate solutions were made similarly, except that the pH was adjusted to 6.5 by using a 4 M $NH_4^+OH^-$ solution.

Instrumentation. A Varian 5000 chromatograph was used throughout this work. Samples were injected with a 10-μL loop injector, and sample detection employed a Varian VARI-CHROM variable-wavelength detector, 0.005–2 absorbance units, with a 1.0 mm diameter, 10 mm path length flow cell, volume 7.9 μL. A 4.6 mm diameter and 25 cm length C18 (10-μm particle size) reversed-phase column (Scientific Products and Equipment Ltd.) was used and was protected by an Upchurch Scientifics guard column packed with Perisorb RP-18 30–40-μm particles. The eluent flow rate read a nominal 2 mL min^{-1}, but calibration showed that this was closer to 1.4 mL min^{-1} and somewhat variable. Similarly, it was found that the proportioning pump on the instrument was inaccurate. For this reason, and also because of column variability, the nominal percentages of methanol and flow rates given in the following should be used only as a guide to establishing the conditions on other systems. *In general, the retention times were found to be quite sensitive to the exact percentage of MeOH. They will also likely vary significantly from column to column.*

Chromatographic Procedure. Before each set of injections, the column was prepared by washing with pure HPLC grade methanol, followed by equilibration for 15 min with the appropriate eluent composition. Eluent concentrations were always changed by using a gradient, to avoid column shock and to allow time for reequilibration. When not in use, the column was thoroughly cleaned and stored filled with pure methanol. Experiments were carried out with either isocratic or gradient elution, depending on the range of analyte retentivities present in the sample. Peaks were detected by their UV absorbance at appropriate wavelengths, given in the figure captions.

Samples (0.01–1.0 mM) for injection were dissolved in unbuffered water. Early experiments (prior to the ^{51}V NMR control experiments) gave evidence of thermal decomposition for some of the species on standing over periods of a few hours *at room temperature*, so that in the later work all samples were kept on ice, a procedure that seemd to completely eliminate the problem (as subsequently verified via the ^{51}V NMR control experiments). [For samples that degrade at higher pH values (at or above the present operating pH = 6.5) or samples of unknown pH stability, the literature[14] suggests that dissolving them *initially* in organic cosolvents (e.g. $MeOH/H_2O$) and in the presence of the ion-interaction reagent ($R_{4-x}NH_x^+$) could be used to inhibit their degradation, although this was not necessary and thus was not confirmed as part of the present studies.]

Acknowledgment. Work at Victoria was supported by NSERC Grant A1291 and by the University of Victoria Faculty Research Fund, while work at Oregon was supported by NSF Grant CHE-861924. We are indebted to Dr. Peter Domaille for his generous gift of the $PW_{12-x}V_xO_{40}^{-3-x}$ samples.

Supplementary Material Available: Figure A, spectra for the ^{51}V NMR control experiments, and Figure B, chromatogram of the effect of pH on chromatographic efficiencies and the efficiency of the competing ion citrate (3 pages). Ordering information is given on any current masthead page.

Notes

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Synthesis and Chemistry of (η^3-Pentadienyl)iron Tricarbonyl Halides

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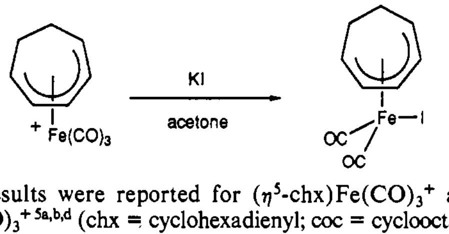
There are now many compounds of the general form $(ped)_xML_y$ ($x = 1, 2$; $y = 0$–4; ped = pentadienyl), where L is a neutral donor ligand and M may be any of a number of transition or rare-earth elements.[2-4] In contrast, there are few pentadienyl complexes that also contain ligands such as halogen or hydrocarbyl.[5,6] Insofar as the significance of pentadienyl complexes will depend upon the degree to which chemistry can be carried out at the metal center, the synthesis of metal-functionalized pentadienyl complexes becomes important. In this regard, we are studying the chemistry of (η^5-chp)$Fe(CO)_2I$[6] (chp = cycloheptadienyl), a species prepared by reaction of (η^5-C_7H_9)$Fe(CO)_3^+$ with KI:[5a,b]



Similar results were reported for (η^5-chx)$Fe(CO)_3^+$ and (η^5-coc)$Fe(CO)_3^+$[5a,b,d] (chx = cyclohexadienyl; coc = cyclooctadienyl). Recently, Ernst used this synthesis to prepare (η^5-2,4-Me_2-ped)$Fe(CO)_2I$.[5e] In contrast, we find that halide addition to other acyclic cationic iron dienyl complexes follows a different path. In these cases, halide ion induces an isomerization of the pentadienyl ligand in preference to displacement of carbon monoxide.

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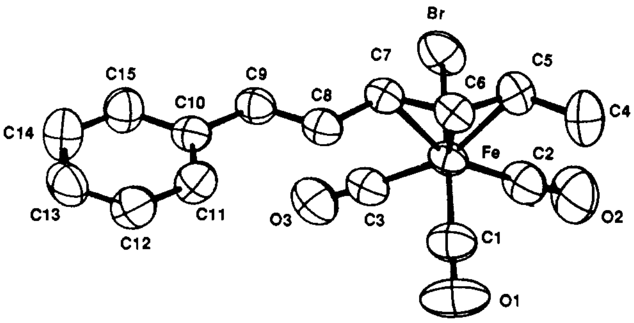


Figure I. ORTEP diagram of (η^3-1-Me-5-Ph-ped)Fe(CO)$_3$Br (**5b**).

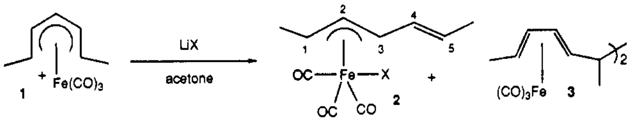
Table I. Atomic Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in Compound **5b**

atom	x	y	z
C1	0.2427 (5)	0.0139 (4)	0.9346 (5)
C2	0.1659 (5)	0.1833 (4)	0.9969 (5)
C3	0.4101 (5)	0.1295 (3)	0.9901 (4)
C4	0.0467 (5)	0.1279 (5)	0.7104 (6)
C5	0.1692 (4)	0.1578 (3)	0.7156 (4)
C6	0.2547 (4)	0.0898 (3)	0.6924 (4)
C7	0.3732 (4)	0.1084 (3)	0.7023 (4)
C8	0.4541 (4)	0.0284 (3)	0.6919 (4)
C9	0.5661 (4)	0.0396 (3)	0.6782 (4)
C10	0.6506 (4)	−0.0399 (3)	0.6627 (4)
C11	0.6187 (4)	−0.1378 (3)	0.6461 (5)
C12	0.7026 (5)	−0.2101 (4)	0.6302 (5)
C13	0.8156 (5)	−0.1871 (4)	0.6323 (5)
C14	0.8474 (4)	−0.0890 (5)	0.6459 (6)
C15	0.7666 (5)	−0.0175 (4)	0.6603 (5)
O1	0.2192 (5)	−0.0632 (3)	0.9696 (5)
O2	0.0904 (4)	0.2131 (3)	1.0546 (4)
O3	0.4961 (3)	0.1243 (3)	1.0444 (4)
Br	0.33354 (5)	0.31407 (3)	0.8739 (1)
Fe	0.2786 (1)	0.13634 (4)	0.8915 (1)

The resulting η^3-pentadienyl complexes are direct analogues of (π-all)Fe(CO)$_3$X (all = allyl).

Discussion

When (1,5-Me$_2$-ped)Fe(CO)$_3^+$ (**1**)[7] is treated with LiX in acetone (1.05 equiv, 25 °C; X = Cl, Br, I), the η^3-pentadienyl complexes **2a–c** are formed in varying yields. There is no evidence for an η^5-pentadienyl complex. The reaction also produces an η^4-diene dimer, **3**, which we collect by chromatography as a nonpolar band contaminated by small amounts of organic materials believed to be noncomplexed dienes arising from decomposition of the organoiron compounds.



The syn η^3-pentadienyl complex **2a** (X = Cl) is easily characterized by NMR spectroscopy. Most telling are two downfield multiplets (6.29 and 5.89 ppm) assigned to H4 and H5. The coupling constant for these two hydrogens (15.2 Hz) establishes trans stereochemistry. Also present in the ^{1}H NMR spectrum are three multiplets whose chemical shifts and coupling interactions are consistent with the central and anti hydrogens of an η^3-allyl group. Assignment of the syn configuration for both methyl and vinyl groups rests upon the coupling constants for H1 and H3 to the central dienyl hydrogen, H2. The values are 12.2 and 12.6 Hz, respectively. The two methyl groups appear as expected. The bromo and iodo analogues **2b,c** show similar coupling interactions but different chemical shifts. For example, the signals for H1 and H3 shift smoothly downfield as the halide is varied from chloride to iodide; there is a concomitant upfield shift of H2. Similar observations were made by Faller and Adams for (η^3-all)Fe(CO)$_3$X.[8] Formulation of **2a–c** as syn η^3-pentadienyls is also in complete accord with the ^{13}C NMR spectra.

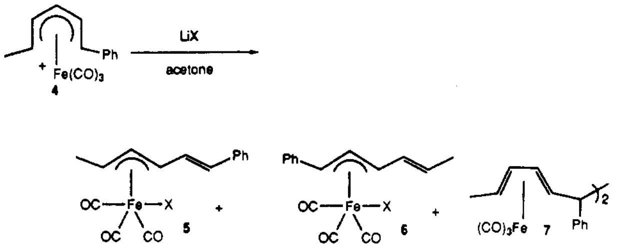
Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for Compound **5b**

	Bond Distances		
Fe–C1	1.771 (5)	C5–C6	1.385 (6)
Fe–C2	1.816 (6)	C6–C7	1.414 (6)
Fe–C3	1.819 (5)	C7–C8	1.448 (6)
Fe–C5	2.179 (4)	C8–C9	1.330 (6)
Fe–C6	2.100 (4)	C9–C10	1.476 (6)
Fe–C7	2.235 (4)	C10–C11	1.392 (6)
Fe–Br	2.509 (1)	C10–C15	1.394 (7)
C1–O1	1.140 (6)	C11–C12	1.399 (7)
C2–O2	1.137 (6)	C12–C13	1.361 (7)
C3–O3	1.140 (6)	C13–C14	1.391 (8)
C4–C5	1.492 (7)	C14–C15	1.366 (7)
	Bond Angles		
O1–C1–Fe	176.17 (50)	C4–C5–C6	120.66 (44)
O2–C2–Fe	174.94 (47)	C5–C6–C7	125.52 (41)
O3–C3–Fe	175.61 (44)	C6–C7–C8	120.88 (40)
C1–Fe–C2	90.75 (25)	C7–C8–C9	124.71 (42)
C1–Fe–C3	91.33 (24)	C8–C9–C10	126.26 (41)
C2–Fe–C3	108.79 (22)	C9–C10–C11	122.25 (43)
C1–Fe–Br	169.95 (17)	C10–C11–C12	119.75 (49)
C2–Fe–Br	83.72 (18)	C11–C12–C13	121.57 (49)
C3–Fe–Br	82.57 (15)	C12–C13–C14	118.69 (47)
C1–Fe–C6	85.28 (21)	C13–C14–C15	120.50 (50)
C1–Fe–C5	100.52 (21)	C14–C15–C10	121.59 (48)
C1–Fe–C7	99.66 (20)	C15–C10–C9	119.86 (42)
C2–Fe–C5	89.70 (20)	C15–C10–C11	117.87 (44)
C2–Fe–C6	124.43 (21)	C6–C5–Fe	68.05 (24)
C2–Fe–C7	157.26 (19)	C4–C5–Fe	123.13 (38)
C3–Fe–C5	157.98 (19)	C6–C7–Fe	65.87 (24)
C3–Fe–C6	126.68 (20)	C8–C7–Fe	121.40 (29)
C3–Fe–C7	91.26 (19)	Fe–C5–C7	56.75 (14)
C5–Fe–Br	87.87 (12)	C5–Fe–C7	68.62 (16)
C6–Fe–Br	104.77 (13)	C7–Fe–Br	88.50 (11)

Table III. Crystallographic Data for the X-ray Diffraction Study of **5b**

	A. Crystal Data		
formula	$C_{15}H_{13}O_3BrFe$	c, Å	9.978 (2)
fw	377.02	β, deg	90.79 (2)
space group	$P2_1/n$, monoclinic	V, Å^3	1588.73
a, Å	11.709 (3)	Z	4
b, Å	13.598 (4)	density (calc), g cm^{-3}	1.576
	B. Collection Data		
radiation	Mo Kα		
λ(Kα), Å	0.709 30		
temp, °C	22		
scan rate, deg min^{-1}	variable, 4–16		
2θ(max), deg	50		
no. of data collected	3991		
no of data with $F_o^2 > 3\sigma(F_o^2)$	1996		

The 1-methyl 5-phenyl cation **4** reacts with LiX to give two η^3-pentadienyl products, **5** and **6**. The major product, **5**, as well as **6**, can be characterized by spectroscopic techniques.



The proposed structure for these η^3-pentadienyl complexes was confirmed by a single-crystal X-ray diffraction study on **5b**; an

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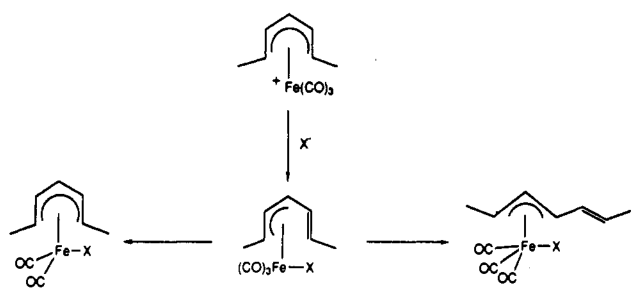
Scheme I



ORTEP drawing appears in Figure 1. Positional parameters of non-hydrogen atoms and selected bond distances and angles are listed in Tables I and II; crystal data and collection data are presented in Table III. The metal adopts pseudooctahedral geometry, with C5 and C7 of the pentadienyl ligand occupying two positions in the equatorial plane. The axial bromine atom is bent away from the pentadienyl ligand with a Br–Fe–C1 angle of 169.9°. The pentadienyl ligand is the endo configuration (C6 is oriented away from the bromine atom). Both substituents (methyl and styryl) are in the syn configuration. Bond lengths and angles are all as expected for W-shaped η^3-pentadienyl complexes.[9] Specifically, C8 is displaced toward the iron atom, 0.12 Å out of the plane containing the "allyl" carbons C5, C6, and C7. The angle between the plane containing C5, C6, and C7 and the plane containing C7, C8, and C9 is 16.6°; the vinyl group is lifted away from the metal center. The structure of **5b** is quite similar to that of its isoelectronic analogue (η^3-all)Fe(CO)$_3$Br.[10]

Although **5b** crystallizes as the endo conformer, a mixture of the endo and exo isomers is established in solution (8:1 mixture in CDCl$_3$). The two isomers have similar ^{1}H NMR coupling patterns, but the minor component shows greater dispersion of chemical shifts, with H1 and H3 appearing over 1 ppm upfield of their positions in the major isomer. For the iodo complex **5c**, the endo:exo ratio is 2.5:1, while for the chloride **5a** the same ratio is 15:1. The dimethyl analogues **2a–c** also establish equilibria between exo and endo forms. Similar behavior was observed for (all)Fe(CO)$_3$X,[8] and by analogy with detailed ^{1}H NMR studies of these compounds, we suggest that the endo conformers of both **5a–c** and **2a–c** predominate in solution and that rotation of the pentadienyl ligand interconverts the two isomers.

The minor pentadienyl products of the 1-Me 5-Ph system (cation **4**) are **6a–c**. Although **6** can be isolated with difficulty by column chromatography, it is an unstable oil. In the process of decomposing to uncharacterized paramagnetic materials, **6** can be seen to rearrange (at least in part) to **5**. The half-life of **6c** is approximately 2 h in CDCl$_3$.

We have also examined (1-Me-5-^{i}Pr-ped)Fe(CO)$_3^+$ and find results similar to those obtained for cation **4**. For each of the lithium halides we isolated a mixture of (η^3-1-Me-5-^{i}Pr-ped)Fe(CO)$_3$X and (η^3-1-^{i}Pr-5-Me-ped)Fe(CO)$_3$X as an unstable oil. Complete separation of the two isomers was precluded by their facile interconversion. Treatment of (1-Me-ped)Fe(CO)$_3^+$, (1,4-Me$_2$-ped)Fe(CO)$_3^+$, or (1-Ph-3-Me-ped)Fe(CO)$_3^+$ failed to provide tractable quantities of the desired η^3-pentadienyl compounds. In each case we were able to identify the η^3 species by NMR spectroscopy, but the compounds were all too unstable for proper characterization.

These pentadienyl products are formed by halide-ion-induced isomerization of the pentadienyl ligand in the same manner that phosphines can react with neutral η^5-pentadienyl complexes (Scheme I).[4a,h] The initial product of halide coordination leaves the vinyl group in the anti position of the η^3-pentadienyl species, an unfavorable conformation for this ligand.[9] Isomerization through an η^1-pentadienyl intermediate gives the preferred syn (W-shaped) η^3-pentadienyl complex.[3c] For cyclic dienyl cations such as (η^5-C$_7$H$_9$)Fe(CO)$_3$, anti–syn isomerization is prohibited by conformational constraints imposed by the ring. Here, dissociation of a neutral ligand with concomitant η^3 to η^5 ligand slip becomes the logical consequence of halide coordination. Recently, Ernst found that the (2,4-Me$_2$-ped)Fe(CO)$_3$ cation gives the η^5 species (C$_7$H$_{11}$)Fe(CO)$_2$I.[5e] In this case, formation of a syn η^3 species would lead to an unfavorable 1,3-arrangement of the methyl groups. Again, loss of carbon monoxide becomes the most favored course of action.

Limited reactivity studies on these pentadienyliron compounds reveal a propensity for coupling of the dienyl ligand, presumably via radical processes. For example, treatment of **5c** with MeMgCl at −78 °C under an atmosphere of CO leads to the isolation of a yellow crystalline solid, which we formulate as the acetyl-substituted η^4-diene complex **8** (Scheme II). Compound **8** is characterized by spectroscopic techniques. The ^{1}H NMR spectrum of **8** exhibits a pair of four-line multiplets for the inner diene hydrogens (δ 5.79, 5.19), as well as a doublet for H1 (δ 2.14) and a triplet for H4 (δ 1.41). The methyl group appears as a doublet at δ 1.33, and the acetyl singlet is observed at δ 2.24. The ^{13}C NMR spectrum displays a signal at 51.8 ppm that is assigned to C5, the carbon bearing the acetyl and methyl groups. The coupling constant for this methine signal is 126 Hz, consistent with our assignment of an acyl group bound to an sp^3-hybridized carbon atom. The stretching frequency of the diene carbonyl is 1716 cm^{-1}. We suggest that methylation of **5** takes place at the metal, followed by CO insertion to give an intermediate η^1-acyl complex. Reductive migration to the endo face of the pentadienyl ligand provides the coupled product. Direct interaction of the Grignard reagent with the *exo* face of the pentadienyl ligand would most likely lead to an *alkyl*-coupled product rather than the isolated acyl species. We isolate the identical complex, **8**, by reduction of **5c** with Na/Hg in THF, followed by reaction with acetyl chloride at −78 °C. Here, reduction of **5c** provides an organoiron anion; acylation at the metal center followed by reductive coupling gives the final product. Unfortunately, the yield is quite low in both cases (<25%). The predominant species along both pathways is the dimer **7**. Similar results were obtained for **5a,b**. Apparently, the stability of the (η^4-diene)Fe(CO)$_3$ fragment dominates the chemistry of these η^3-pentadienyl complexes. Nevertheless, Scheme II illustrates two interesting points. First, reductive coupling from the presumed η^1-acyl intermediate is completely regiospecific. Second, the new carbon–carbon bond has been constructed on the bottom or endo face of the coordinated ligand. We are working to develop new systems that incorporate these attractive features without the complications of one-electron coupling.

Experimental Section

General Comments. All operations except chromatography were carried out under an atmosphere of N$_2$ using drybox or Schlenk techniques; flash chromatography was conducted on the bench top under ambient conditions. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl; all other reagents and solvents were distilled from calcium hydride and were deoxygenated by freeze–pump–thaw methods. The (dienyl)Fe(CO)$_3$ cations, all BF$_4^-$ salts, were prepared by using known procedures.[7] Magnetic resonance spectra were obtained on a Bruker WM-250, a General Electric QE-300, or a General Electric GN-500 spectrometer. Spectra are reported in ppm from (CH$_3$)$_4$Si; coupling constants are given in Hz. Mass spectra were recorded on a Finnagan 9610 spectrometer at 70 eV. Infrared spectra were obtained with a Perkin-Elmer 283 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Compound **5** is a crystalline solid, and it is the only product of this series that is stable for long periods of time. All of the other η^3-pentadienyl complexes mentioned herein are oils that decompose if they are not absolutely pure. All of the products are air-sensitive in solution, and they are somewhat unstable in halogenated solvents. We find that these pentadienyl complexes decompose rapidly in the presence of excess halide, giving the coupled η^4-diene dimers and significant quantities of paramagnetic byproducts.

General Synthesis of (η^3-ped)Fe(CO)$_3$X (2a–c, 5a–c). In each case ca. 1 g of the appropriate cation was added to a Schlenk flask along with 1.05 equiv of LiX. Acetone (50 mL) was added at room temperature, and the mixture was stirred for 1 h. The reaction mixture was evaporated

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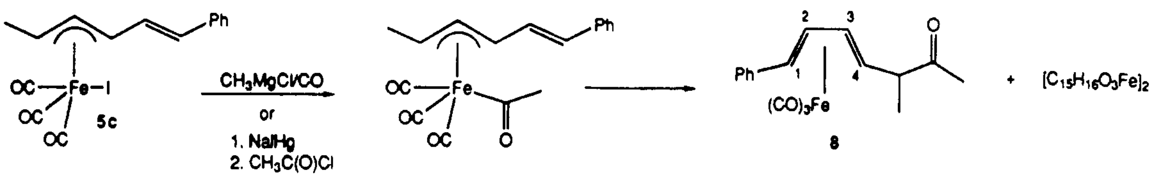
(9) Ernst, R. D. *Struct. Bonding* **1984**, *57*, 1.

(10) Simon, F. E.; Lauer, J. *Inorg. Chem.* **1980**, *19*, 2238.

Scheme II



to dryness, and the residue was purified by chromatography on silica gel using petroleum ether–ether.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$Cl (2a): yield 26%; orange-red oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.29 (sext, H5, $J_{5,\mathrm{Me}}$ = 6.5, $J_{4,5}$ = 15.2), 5.89 (m, H4, $J_{4,\mathrm{Me}}$ = 1.5), 4.99 (t, H2, $J_{1,2}$ = 12.2, $J_{2,3}$ = 12.6), 4.68 (t, H3, $J_{3,4}$ = 10.5), 4.03 (sext, H1, $J_{1,\mathrm{Me}}$ = 6.3), 2.00 (d, Me at C1), 1.80 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 207.9, 205.4, 204.2 (CO's), 133.1, 131.1 (C4,5), 101.2, 90.5, 82.2 (C1–3), 20.1, 18.7 (Me's); IR (CHCl$_3$) 2084, 2035, 2000 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeCl$ (M$^+$) requires 269.9746 (not observed), $C_{10}H_{11}O_3Fe$ (M – Cl) requires 235.0058 (found 235.0052), $C_9H_{11}O_2Fe$ (M – Cl – CO) requires 207.0108 (found 207.0074), $C_9H_{11}O_2Fe$ (M – Cl – 2 CO) requires 179.0159 (found 179.0156). The dimer $[C_7H_{11}Fe(CO)_3]_2$ (**3**) was isolated in 50% yield from this reaction.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$Br (2b): yield 74%; red-brown oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.26 (sext, H5, $J_{5,\mathrm{Me}}$ = 6.8, $J_{4,5}$ = 15.3), 5.81 (m, H4, $J_{4,\mathrm{Me}}$ = 1.5), 4.88 (t, H3, $J_{3,4}$ = 9.5, $J_{2,3}$ = 12.3), 4.76 (t, H2, $J_{1,2}$ = 11.3), 4.19 (sext, H1, $J_{1,\mathrm{Me}}$ = 6.3), 1.94 (d, Me at C1), 1.78 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 209.6, 205.5, 204.3 (CO's), 132.9, 131.1 (C4,5), 100.7, 87.6, 79.1 (C1–3), 20.2, 18.7 (Me's); IR (CHCl$_3$) 2076, 2029, 2001 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeBr$ (M$^+$) requires 313.9240 + 315.9219 (found 313.9267 + 315.9234), $C_9H_{11}O_2FeBr$ (M – CO) requires 285.92921 + 287.9270 (found 2852.9275 + 287.9281), C_8H_{11}-OFeBr (M – 2 CO) requires 257.9342 + 259.9321 (found 257.9359 + 259.9339). The dimer **3** was isolated in 14% yield from this reaction.

(η^3-1,5-Me$_2$ped)Fe(CO)$_3$I (2c): yield 76%; red-brown oil; ^{1}H NMR (CDCl$_3$; 250 MHz) 6.23 (sext, H5, $J_{5,\mathrm{Me}}$ = 6.6, $J_{4,5}$ = 15.3), 5.78 (m, H4, $J_{4,\mathrm{Me}}$ = 1.5), 5.19 (t, H3, $J_{3,4}$ = 10.1, $J_{2,3}$ = 12.6), 4.45 (m, H1,2), 1.90 (d, Me at C1, $J_{1,\mathrm{Me}}$ = 5.5), 1.79 (dd, Me at C5); ^{13}C NMR (CDCl$_3$, 75.5 MHz) 210.8, 206.8, 205.5 (CO's), 132.3, 131.1 (C4,5), 995, 82.4, 73.6 (C1–3), 20.3, 18.5 (Me's); IR (CHCl$_3$) 2067, 2018, 2000 cm^{-1}; HRMS, $C_{10}H_{11}O_3FeI$ (M$^+$) requires 361.9102 (found 361.9089), C_9-$H_{11}O_2FeI$ (M – CO) requires 333.9153 (found 333.9146), $C_8H_{11}OFeI$ (M – 2 CO) requires 305.9204 (found 305.9204). The dimer **3** was isolated in 9% yield from this reaction.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$Cl (5a): yield 32%; orange-brown crystals; ^{1}H NMR (CDCl$_3$; 250 MHz) 7.40 (m, Ph), 7.14 (d, H5, $J_{4,5}$ = 15.5), 6.60 (dd, H4, $J_{3,4}$ = 10.3), 5.21 (t, H2, $J_{2,3}$ = 12.6, $J_{1,2}$ = 11.6), 4.91 (t, H3), 4.18 (sext, H1, $J_{1,\mathrm{Me}}$ = 6.4), 2.06 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 207.9, 205.3, 203.7 (CO's), 136.5, 135.0, 129.5, 128.9, 128.7, 126.6 (C4,5, Ph), 102.2, 90.3, 83.1 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2085, 2039, 2003 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3ClFe$: C, 54.17; H, 3.94; Cl, 10.66. Found: C, 53.89; H, 3.96; Cl, 10.47. This reaction also produced 46% of the dimer $[C_{15}H_{13}O_3Fe]_2$ (**7**) and 13% of the 1-phenyl 5-methyl isomer **6a**.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$Br (5b): yield 56%; red-brown crystals; ^{1}H NMR (CDCl$_3$; 250 MHz) 7.40 (m, Ph), 7.12 (d, H5, $J_{4,5}$ = 15.5), 6.56 (dd, H4, $J_{3,4}$ = 10.0), 5.12 (t, H3, $J_{2,3}$ = 12.1), 5.01 (t, H2, $J_{1,2}$ = 11.5), 4.38 (sext, H1, $J_{1,\mathrm{Me}}$ = 6.5), 2.02 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 209.4, 205.4, 203.8 (CO's), 136.5, 134.7, 128.9, 128.7, 128.5, 126.6 (C4,5 Ph), 101.6, 87.2, 79.9 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2079, 2033, 2001 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3BrFe$: C, 47.49; H, 3.48; Br, 21.20. Found: C, 47.81; H, 3.46; Br, 21.41. This reaction also produced 21% of the dimer **7** and 9% of the 1-phenyl 5-methyl isomer **6a**.

(η^3-1-Me-5-Ph-ped)Fe(CO)$_3$I (5c): yield 49%; red-brown crystals; ^{1}H NMR (C$_6$D$_6$; 250 MHz) 7.21 (m, Ph), 6.82 (d, H5, $J_{4,5}$ = 15.5), 6.11 (dd, H4, $J_{3,4}$ = 10.5), 5.40 (t, H3, $J_{2,3}$ = 12.5), 4.46 (sext, H1, $J_{1,\mathrm{Me}}$ = 6.3), 3.75 (t, H2, $J_{1,2}$ = 12.0), 1.30 (d, Me); ^{13}C NMR (CDCl$_3$, 62.9 MHz) 206.7, 205.1, 203.3 (CO's), 136.5, 134.2, 128.9, 128.8, 128.4, 126.65 (C4,5, Ph), 100.6, 81.9, 74.5 (C1–3), 20.2 (Me); IR (CHCl$_3$) 2069, 2023, 2000 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_3IFe$: C, 42.49; H, 3.09; I, 29.93. Found: C, 42.03; H, 3.43; I, 30.18. This reaction also produced 11% of the dimer **7** and 27% of the 1-phenyl 5-methyl isomer **6a**.

Synthesis of (η^4-1-Ph-5-Ac-1,3-hxd)Fe(CO)$_3$ (8). a. Via Reduction of 5c with Na/Hg. **5b** (0.15 g, 0.46 mmol) was dissolved in 15 mL of THF. Na–Hg was added to the mixture, and the reaction mixture was stirred at room temperature for 3 h. The resulting solution was filtered through Celite and then added to a solution of acetyl chloride (0.28 mL, 3.86 mmol) at –78 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 15 h. Filtration through Celite and removal of solvent left an oil that was purified by column chromatography on silica gel. The desired product, **8**, was isolated as a yellow solid in 21% yield: ^{1}H NMR (CDCl$_3$; 500 MHz) 7.20 (m, Ph), 5.79 (dd, H2, $J_{1,2}$ = 9.2), 5.19 (dd, H3, $J_{3,4}$ = 8.7), 2.59 (m, H5, $J_{5,\mathrm{Me}}$ = 6.8), 2.24 (s, acetyl Me), 2.14 (d, H1), 1.41 (br t, H4, $J_{4,5}$ = 9.3), 1.33 (d, Me at C5); ^{13}C NMR (CDCl$_3$; 125.8 MHz) 211.3 (CO), 209.2 (C=O), 139.2, 128.2, 127.7, 126.0 (Ph), 82.1, 80.2 (C2,3), 61.2, 60.8 (C1,4), 51.7 (C5), 28.4 (Ac Me), 21.5 (Me at C5); IR (CHCl$_3$) 2047, 1993, 1716 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_4Fe$: C, 60.03; H, 4.74. Found: C, 60.05; H, 5.01. The reaction also gave a 37% yield of the dimer $[(C_{15}H_{13})FeO_3]_2$ (**7**).

b. Via Reaction of 5c with CH$_3$MgCl and CO. A solution of **5b** (0.18 g, 0.54 mmol) in 20 mL of THF was cooled to –78 °C. CH$_3$MgCl (0.20 mL of a 3.0 M solution) was added dropwise by syringe. The vessel was placed under an atmosphere of CO, and the mixture was warmed to room temperature and stirred for 15 h. After filtration through Celite, the solvent was removed. Purification by chromatography on silica gel gave an 8% yield of **8** along with a 50% yield of **7**.

Structure Determination of 5b. Red-brown needles of $C_{15}H_{13}O_3BrFe$ were grown in petroleum ether–diethyl ether. Properties of the crystal and details of structure collection are provided in Table III. Three-dimensional intensity data were collected on a Syntex P2$_1$ automated diffractometer with a graphite detector. A combination of Patterson and difference Fourier techniques provided the locations of all non-hydrogen atoms, which were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The hydrogen atoms were included in the refinement at fixed idealized positions and were treated isotropically. The refinement converged to conventional factors R_1 = 0.035 and R_2 = 0.046.

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Supplementary Material Available: Tables of analytical data for **3**, **6a–c**, **7**, and the 1-methyl-5-isopropylpentadienyl system and anisotropic and isotropic temperature factors for **5b** (4 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Air-Stable Chromium(II) Complexes with 1,4,8,11-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane

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Recently, Kida et al. prepared the octadentate ligand 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) together with several of its metal complexes.[2-7] All the

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