intensity for Rh{331} is reduced to 79 ± 2% of that found for Rh{111}. The LEED I-V[9] calculations and EELS[8] measurements suggest that ethylidyne binds to three-fold sites on the {111} plane. The observed decrease in C 1s intensity on Rh{331} scales precisely as the decrease in the number of three-fold holes available for binding. Note from Figure 2 that the presence of the step removes 20%[14] of these sites. Although it is not yet possible to identify the overlayer structure on Rh{331}, we note that it is possible to construct the same zig-zag geometry postulated for Rh{111} without steric interference from the step itself.

In summary, we have performed accurate carbon coverage measurements for CO and C_2H_4 adsorption on Rh{111} and Rh{331}. The results suggest that a very stable structure with interlocking hydrogen atoms is formed on the {111} plane and that the presence of the step on the {331} surface inhibits ethylidyne formation by reducing the number of active sites. It is of interest that the high site specificity of this reaction may provide a selective titrant for threefold sites on polycrystalline surfaces.

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(14) The surface atom density ratio for Rh{331}/Rh{111} is 1.2, including step atoms (or step sites). Removing the step atoms (or step sites), covering $^1/_3$ of the Rh{331} surface leaves a ratio of 0.80 or 80%.

Unprecedented Bonding of a Coordinated Polyenyl Ligand. Synthesis and Molecular Structures of *fac*-Trialkyltricarbonyliron Compounds Containing the η^3-Nonafluorocycloocta-2,5-diene-1,4,7-triyl Ligand and Its Derivatives

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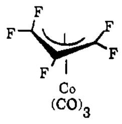
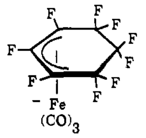
While hydrocarbon enyl and polyenyl ligands are ubiquitous in organotransition metal chemistry, (η^3-pentafluoroallyl)tricarbonylcobalt **1**[2] and the (η^3-nonafluorocyclohexenyl)tricarbonyliron anion **2**[3] appear to be the only reported examples of complexes containing perfluorinated enyl ligands. No compounds containing perfluoropolyenyl ligands have been reported. We now report that the perfluorocycloocta-2,5-diene-1,4,7-triyl ligand and its derivatives can be prepared by nucleophilic attack on coordinated octafluorocyclooctatetraene. These perfluoropolyenyl ligands bind to the metal via three σ-bonds rather than through the π-system of the polyenyl ring, affording the first examples of trialkyltricarbonylmetal complexes.



1



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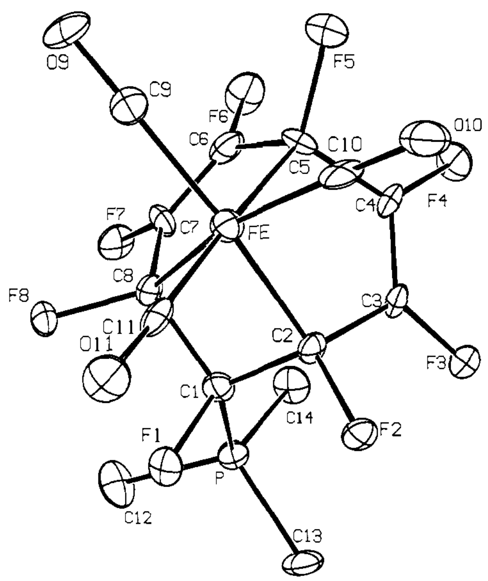
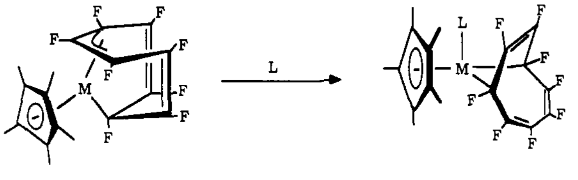


Figure 1. ORTEP drawing and numbering scheme for **6**. Selected bond distances (Å) and bond angles (deg) are as follows: Fe–C(2), 2.006 (8); Fe–C(5), 2.058 (11); Fe–C(8), 2.013 (8); Fe–C(9), 1.833 (9); Fe–C(10), 1.821 (8); Fe–C(11), 1.797 (11); P–C(1), 1.854 (9); P–C(12), 1.810 (10); P–C(13), 1.788 (8); P–C(14), 1.784 (13); C(1)–C(2), 1.519 (11); C(1)–C(8), 1.536 (10); C(2)–C(3), 1.487 (14); C(3)–C(4), 1.324 (12); C(4)–C(5), 1.448 (12); C(5)–C(6), 1.475 (10); C(6)–C(7), 1.315 (14); C(7)–C(8), 1.465 (13); C(9)–O(9), 1.129 (10); C(10)–O(10), 1.139 (11); C(11)–O(11), 1.1709 (13); C(2)–Fe–C(5), 83.8 (4); C(5)–Fe–C(8), 83.3 (4); C(8)–Fe–C(9), 94.7 (3); C(9)–Fe–C(10), 98.3 (4); C(10)–Fe–C(11), 94.8 (5); C(11)–Fe–C(2), 92.3 (4).

We have shown previously that the Co and Rh complexes **3**[4] undergo thermal reaction with *t*-BuNC or PMe_3 at the metal center, affording the octafluorocycloocta-2,5,7-triene-1,4-diyl complexes **4**[5] as the initial products. In contrast, reaction of the corresponding iron complex **5**[6] with PMe_3 yielded white crystals of a 1:1 adduct **6**.[7] Retention of the $Fe(CO)_3$ moiety was confirmed by the IR spectrum, and the ^{19}F NMR spectrum exhibited five resonances of relative intensity 2:2:1:1:2, indicating retention



3 M = Co, Rh

4 M = Co, Rh
L = t-BuNC, PMe_3

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(1) (a) Dartmouth College. (b) University of Texas at Austin.

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(7) **6**: 44%; mp 144–146 °C dec; IR (CH_2Cl_2) ν_{CO} 2100, 2080, 2005, $\nu_{C=C}$ 1717 cm^{-1}; ^{19}F NMR ($CDCl_3$, shifts upfield from internal $CFCl_3$, see drawing for numbering) δ 113.9 (m, F_4), 126.6 (m, F_3), 155.5 (m, F_1, $J_{P\text{-}F}$ = 138 Hz), 176.4 (m, F_5), 187.8 (m, F_2); ^1H NMR ($CDCl_3$) δ 1.86 (d, $J_{P\text{-}H}$ = 14 Hz, PMe_3); ^{31}P NMR ($CDCl_3$, shifts upfield from external H_3PO_4) δ 17.7, d, $J_{P\text{-}F}$ = 138 Hz). Calcd for $C_{14}H_9F_8FeO_3P$: C, 36.24; H, 1.95. Found: C, 36.12; H, 1.78. Crystal data: orthorhombic, $P2_1/c$, a = 13.652 (3) Å, b = 10.228 (2) Å, c = 13.132 (5) Å, β = 116.65 (2)°, Z = 4. The structure solved by heavy atom methods and refined by full-matrix least-squares procedures to final agreement factors $R = \sum|(|F_o| - |F_c|)|/\sum|F_o| = 0.0755$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0740$, by using 2401 reflections with $F_o \geq 4.0\ \sigma(F_o)$. X-ray experimental procedures, data processing, and principal computer programs were essentially as described previously by Riley and Davis (Riley, P. E.; Davis, R. *Acta Crystallogr., Sect B: Struct. Crystallogr.* **1976**, *B32*, 381–386). Full details are provided as Supplementary Material (see paragraph at end of text).

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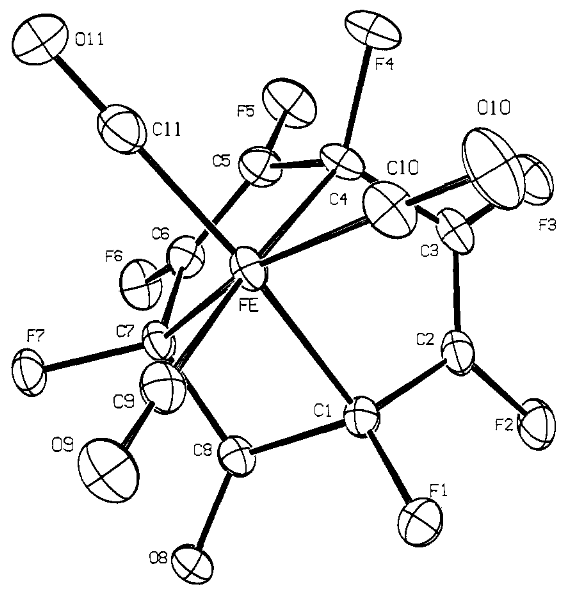
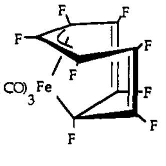


Figure 2. ORTEP drawing and numbering scheme for the K(18-crown-6)$^+$ salt of anion **8**. Selected bond distances (Å) and bond angles (deg) are as follows: C(1)–Fe, 2.036 (2); C(4)–Fe, 2.058 (2); C(7)–Fe, 2.039 (2); C(9)–Fe, 1.826 (2); C(10)–Fe, 1.801 (2); C(11)–Fe, 1.805 (2); C(1)–C(2), 1.474 (3); C(1)–C(8), 1.492 (2); C(2)–C(3), 1.316 (3); C(3)–C(4), 1.474 (3); C(4)–C(5), 1.486 (3); C(5)–C(6), 1.317 (3); C(6)–C(7), 1.471 (3); C(7)–C(8), 1.486 (3); C(8)–O(8), 1.230 (2); C(9)–O(9), 1.130 (2); C(10)–O(10), 1.136 (2); C(1)–Fe–C(4), 83.75 (9); C(4)–Fe–C(7), 83.17 (7); C(7)–Fe–C(9), 97.32 (8); C(9)–Fe–C(10), 92.87 (8); C(10)–Fe–C(11), 101.35 (9); C(11)–Fe–C(1), 163.64 (8).

of the original symmetry plane. A large phosphorus coupling to one of the unit intensity fluorine resonances indicated that PMe$_3$ was bound to the fluorinated ring rather than to the metal.[7] The regio- and stereochemistry of phosphine attack were unambiguously defined by a single-crystal X-ray diffraction study, which characterized the zwitterionic structure **6**;[7] an ORTEP is shown in Figure 1, with selected bond distances and angles. Compound **6** apparently arises by exo attack of PMe$_3$ on the internal allylic carbon of **5**,[8] generating two new iron–carbon σ-bonds to give an octahedral coordination geometry. Analogous attack by anionic nucleophiles at cationic η^3-allylic complexes is precedented, though rare.[9] Formation of **6** represents the first example of two neutral molecules undergoing such a reaction and also provides the first example of a *fac*-trialkyltricarbonylmetal complex.



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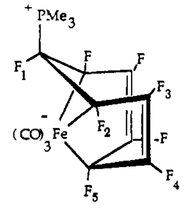
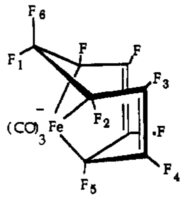


6

The previously reported reaction of [Fe(1-4η-octafluorocyclohexadiene)(CO)$_3$] with fluoride ion to yield **2**[3] suggested that anionic nucleophiles might react similarly with **5**. Treatment of **5** with [(Me$_2$N)$_3$S]$^+$[Me$_3$SiF$_2$]$^-$ [10] afforded the anionic η^3-nonafluorocycloocta-2,5-diene-1,4,7-triyl complex **7** as a pale yellow oil whose ^{19}F NMR spectrum exhibited resonances due to nine fluorines, including a geminal CF$_2$ group.[11] In contrast to **2**, which is reported to be stable in aqueous solution,[3] **7** reacted with traces of moisture to afford the [(Me$_2$N)$_3$S]$^+$ salt of the anionic 8-oxoheptafluorocycloocta-2,5-diene-1,4,7-triyl complex **8**.[12] The same anion, together with HF, is produced by the reaction of **5** with H$_2$O in THF solution. The (18-crown-6)potassium salt of **8** could also be synthesized directly from **5** by reaction with KOH in DMSO; crystals of this salt proved suitable for X-ray diffraction, and the resultant ORTEP is shown in Figure 2, along with selected bond distances and angles.[12]



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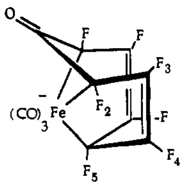

8

The most unusual feature of this new family of organometallic complexes is that the polyenyl ligands bind to the iron via three σ-bonds rather than through the π-system of the ring. The known compounds **1**[2] and **2**[3] indicate that this latter bonding mode is feasible. Therefore, compounds **6**–**8** can formally be considered as iron(II) derivatives of the cycloocta-2,5-diene-1,4,7-triyl trianion. The unusually high values for ν_{CO} (>2000 cm^{-1}) in compounds with a formally anionic metal center is also noteworthy, as is the unusually low value for the ketonic stretching frequency in compounds **8**. Finally we note that both hard and soft nucleophiles apparently attack **5** at the internal allylic carbon.[8] Further studies of reactions of nucleophiles with coordinated octafluorocyclooctatetraene and the chemistry of these novel trialkyltricarbonyliron complexes are in progress.

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Supplementary Material Available: Tables of crystallographic summaries, fractional coordinates and isotropic thermal parameters for non-hydrogen and hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles for **6** and **8** (14 pages); tables of observed and calculated structure factor amplitudes for **6** and **8** (49 pages). Ordering information is given on any current masthead page.

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(8) Initial attack at another ring site followed by rearrangement to give a thermodynamically favorable structure **6** cannot be excluded on the basis of our data.

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(11) **7**: 60%; IR (CH$_2$Cl$_2$) ν_{CO} 2071, 2002 cm^{-1}; ^{19}F NMR (CDCl$_3$, shifts upfield from internal CFCl$_3$, see drawing for numbering) δ 61.8 (m, F$_1$, J_{1-6} = 189 Hz), 119.6 (m, F$_4$), 126.3 (m, F$_6$, J_{1-6} = 189 Hz), 128.3 (m, F$_3$), 173.2 (m, F$_5$), 195.9 (m, F$_2$). Due to the moisture sensitivity of this compound satisfactory microanalysis results could not be obtained. Proof of structure rests in spectroscopic data and chemical derivatization to give **8**.

(12) **8**: [(Me$_2$N)$_3$S]$^+$ salt from hydrolysis of **7**: yellow crystals, 28%; mp 178–180 °C dec; IR (CH$_2$Cl$_2$) ν_{CO} 2076, 2009, $\nu_{C=C}$ 1728, $\nu_{C=O}$ 1608 cm^{-1}; ^{19}F NMR (CDCl$_3$, shifts upfield from internal CFCl$_3$, see drawing for numbering) δ 120.0 (dt, F$_4$), 126.4 (dd, F$_3$), 169.1 (dd, F$_2$), 173.1 (m, F$_5$); $J_{2,4}$ = 5, $J_{2,3}$ = 26, $J_{3,5}$ = 8, $J_{4,5}$ = 17; ^{1}H NMR (CDCl$_3$) δ 2.96 (s, [Me$_2$N]$_3$S). **8**: (18-crown-6)K$^+$ salt: yellow crystals, 13%; mp 191–193 °C dec; IR (CH$_2$Cl$_2$) ν_{CO} 2076, 2011, $\nu_{C=C}$ 1730, $\nu_{C=O}$ 1611 cm^{-1}; ^{19}F NMR (CDCl$_3$, shifts upfield from internal CFCl$_3$, see drawing for numbering) δ 119.7 (dt, F$_4$), 126.7 (dd, F$_3$), 168.6 (dd, F$_2$), 173.0 (m, F$_5$); $J_{2,4}$ = 5, $J_{2,3}$ = 26, $J_{3,5}$ = 8, $J_{4,5}$ = 17; ^{1}H NMR (CDCl$_3$) δ 3.62 (s, CH$_2$). Molecular composition was verified by a single-crystal X-ray diffraction study. Crystal data: orthorhombic, $P2_1/n$, a = 13.403 (6) Å, b = 20.157 (7) Å, c = 10.716 (5) Å, β = 94.62 (5)°, Z = 4. The structure was solved by heavy atom methods and refined by full-matrix least-squares procedures to final agreement factors $R = \sum|(|F_o| - |F_c|)|/\sum|F_o| = 0.0325$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0338$, by using 5465 reflections with $F_o \geq 4.0\ \sigma(F_o)$. X-ray experimental procedures, data processing, and principal computer programs were essentially as described previously by Riley and Davis (Riley, P. E.; Davis, R. *Acta Crystallogr., Sect B: Struct. Crystallogr.* **1976**, *B32*, 381–386). Full details are provided as Supplementary Material (see paragraph at end of text).