

Coordination Chemistry of Fluorinated Allenes

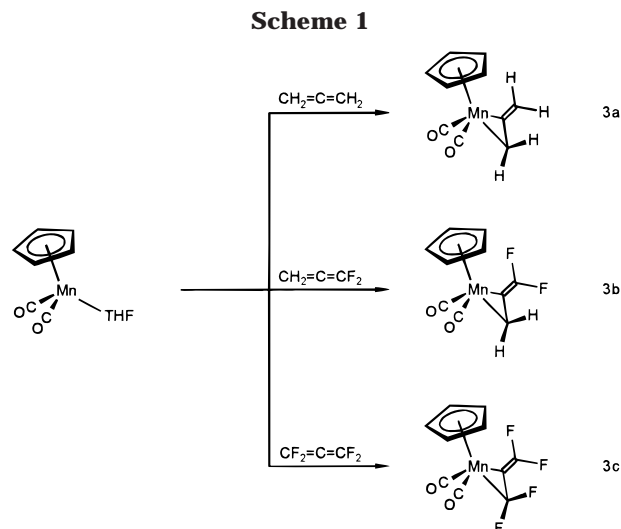
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Summary: The synthesis, spectroscopic data, and structure determinations of the allene complexes $\text{CpMn}(\text{CO})_2\text{L}$ **3a–c** (**a**, $\text{L} = \text{C}_3\text{H}_4$; **b**, $\text{C}_3\text{H}_2\text{F}_2$; **c**, C_3F_4) are described. The analysis of the IR spectroscopic data revealed increasing acceptor properties on increasing the number of fluorine substituents, making tetrafluoroallene a better π -acceptor ligand than CO.

Despite the great technological importance of fluorinated alkenes,¹ their coordination chemistry is by far less developed than that of alkenes. This fact is even more astonishing in light of the fact that most metal-catalyzed reactions of alkenes require the coordination of the alkene.² Among the 20 complexes of noncyclic fluorinated alkenes structurally characterized by X-ray crystallography, so far there have been 16 compounds containing the tetrafluoroethene ligand.³ During our studies on fluorination effects on small organic molecules we have started to investigate the coordination chemistry of 1,1-difluoropropadiene and tetrafluoropropadiene. According to ab initio calculations 1,1-difluoropropadiene has a very interesting frontier orbital situation, with the HOMO localized at the fluorine-substituted double bond and the LUMO at the hydrogen-substituted double bond, respectively,⁴ giving raise to the question which double bond will be coordinated to



a metal complex fragment. The two-component interaction originally proposed by Dewar, Chatt, and Duncan⁵ is still the best way of picturing the interaction of an alkene with a transition metal.⁶ To get information about the σ -donor and π -acceptor properties of these allene ligands, we have chosen the $\text{CpMn}(\text{CO})_2$ fragment for our studies, as it allows an easy calculation of the force constant $k(\text{CO})$.⁷

Reaction of $\text{CpMn}(\text{CO})_2(\text{THF})$ (**1**) with the propadienes $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, $\text{H}_2\text{C}=\text{C}=\text{CF}_2$, and $\text{F}_2\text{C}=\text{C}=\text{CF}_2$ (**2a–c**) gave good yields of the manganese complexes **3a–c** (Scheme 1).⁸ Compound **3a** was previously synthesized by a different method.⁹ The X-ray crystal structure analyses of **3a–c** (Figure 1 and Table 1)¹⁰ show similar coordinations of one double bond to the metal center. Whereas the Mn–C bond lengths to the central carbon atom are alike in the compounds **3b** and **3c**, the Mn–C distance is significantly shorter for **3c**, in which the coordination occurs via the fluorinated double bond. The C–C bond lengths of the noncoordinated double bonds are comparable to those of the free propadiene molecules,¹¹ in contrast to the coordinated ones, which are lengthened by 8–9 pm. Due to coordination, the propadiene unit is strongly bent at the central carbon atom C2; C1 has a pyramidal and C3 a trigonal-planar configuration. The bending at C2 increases strongly with the number of fluorine substituents.

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From the structure determination of **3a–c** steric hindrance can be excluded as the reason for the preferred coordination of the hydrogen-substituted double bond in **3b**. This makes it even more astonishing that NMR spectra of **3b** between -80 and 80 °C exhibit signals of a single isomer. Whereas the ^{19}F NMR spectra of **3b** exhibit no changes as the temperature is varied, the ^1H NMR spectra depend on the temperature. The signals of the chemically nonequivalent protons of the allene ligand get broad on warming, showing coalescence at -5 °C and exhibiting a sharp signal at 30 °C. The NMR spectra can be analyzed in terms of a propeller rotation of the coordinated allene at the d^6 metal center with free activation enthalpies of 37 ± 1 kJ mol^{-1} ($T_c = -75$ °C) for **3a**, 52 ± 1 kJ mol^{-1} ($T_c = -5$ °C) for **3b**, and 53.4 ± 0.2 kJ mol^{-1} ($T_c = -5$ °C) for **3c**, comparable with the values for other $\text{CpMn}(\text{CO})_2$ - (alkene) complexes.¹² The value of **3c** seems to be rather low for a coordinated fluorinated alkene.^{3j} However, as emphasized by others,⁶ there should be no correlation between acceptor properties of an alkene and the activation energy of the propeller rotation. The low free activation enthalpy for the propeller rotation in $\text{Cp}^*\text{Ru}(\text{acac})(\text{C}_2\text{F}_4)$ was attributed to the d^6 electron configu-

(8) $\text{H}_2\text{C}=\text{C}=\text{CH}_2$,¹⁵ $\text{H}_2\text{C}=\text{C}=\text{CF}_2$,¹⁶ and $\text{F}_2\text{C}=\text{C}=\text{CF}_2$ ¹⁷ were prepared by literature methods. $\text{CpMn}(\text{CO})_2(\eta^2\text{-CH}_2=\text{C}=\text{CH}_2)$ (**3a**): Tricarbonyl(η^5 -cyclopentadienyl)manganese (600 mg, 2.9 mmol) was dissolved in dry THF. After irradiation with UV light for about 4 h allene (9.5 mmol) was added via a glass vacuum line. The solution was stirred at ambient temperature. After the color changed from red to yellow, the solution was stirred for an additional 1 h. The solvent was removed under vacuum. The residue was dissolved in *n*-pentane and purified by chromatography (silica, *n*-pentane, $45 \text{ cm} \times 4 \text{ cm}^2$) followed by vacuum sublimation (25 °C, 10^{-3} mbar), yielding 320 mg (50%) of yellow crystals, mp 27 °C. ^1H NMR (d_8 -toluene, 30 °C): δ 6.31 (1H, td, $^2J_{\text{HH}} = 1.8$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, CH_2), 5.71 (1H, td, $^2J_{\text{HH}} = 1.8$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, CH_2), 3.9 (5H, s, Cp), 1.59 (2H, t, $^2J_{\text{HH}} = 1.8$ Hz, CH_2) [1.73 (1H, -100 °C), 1.35 (1H, -100 °C), CH_2]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 231.9 (s, CO), 169.5 (s, $\text{C}-\text{CH}_2$), 105.9 (s, CH_2), 85.5 (s, Cp), 5.8 (s, CH_2). ^{13}C NMR (d_8 -toluene): δ 231.2 (CO), 168.8 (s, $\text{C}-\text{CH}_2$), 105.0 (dd, $^1J_{\text{CH}} = 160$ Hz, CH_2), 84.5 (dm, $^1J_{\text{CH}} = 178$ Hz, Cp), 6.4 (dd, $^1J_{\text{CH}} = 160$ Hz, CH_2). IR (*n*-pentane): $\tilde{\nu}$ 1989 s (CO), 1934 s (CO) cm^{-1} . MS (70 eV): m/z 216 (M^+), 188 ($\text{M}^+ - \text{CO}$), 160 ($\text{M}^+ - 2\text{CO}$), 148 (CpMnCO^+), 120 (CpMn^+). Anal. Calcd: C, 55.58; H, 4.20. Found: C, 55.00; H, 4.20. $\text{CpMn}(\text{CO})_2(\eta^2\text{-CH}_2=\text{C}=\text{CF}_2)$ (**3b**): preparation analogous to that for **3a** as described above. Purification by chromatography (silica, *n*-pentane, $50 \text{ cm} \times 4 \text{ cm}^2$) followed by vacuum sublimation yielded 361 mg (42.1%) of yellow crystals, mp 39 °C. ^1H NMR ($\text{CD}_2\text{-Cl}_2$, 20 °C): δ 2.16 (2H, s, CH_2), 4.82 (5H, s, Cp). ^1H NMR (d_8 -toluene, 20 °C): δ 1.70 (2H, s, CH_2), 3.92 (5H, s, Cp). ^1H NMR (d_8 -toluene, -80 °C): δ 1.30 (1H, s, CH_2), 1.81 (1H, s, CH_2), 3.57 (5H, s, Cp). ^{19}F NMR (d_8 -toluene, 20 °C, CFCl_3): δ -99.57 (1F, d, $^2J_{\text{FF}} = 89.4$ Hz, CF_2), -63.83 (1F, d, $^2J_{\text{FF}} = 89.4$ Hz, CF_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 230.9 (CO), 150.8 (dd, $^1J_{\text{CF}} = 256.6$, 283.9 Hz, CF_2), 99.8 (dd, $^2J_{\text{CF}} = 20.3$, 49.0 Hz, $\text{C}-\text{CH}_2$), 86.4 (s, Cp), 13.2 (s, CH_2). $^{13}\text{C}\{^{19}\text{F}\}$ NMR (CD_2Cl_2): δ 230.3 (CO), 151.1 (s, CF_2), 99.8 (s, $\text{C}-\text{CF}_2$), 85.7 (dm, $^1J_{\text{CH}} = 179.1$ Hz, Cp), 12.9 (t, $^1J_{\text{CH}} = 166.7$ Hz, CH_2). IR (*n*-pentane): $\tilde{\nu}$ 2012 vs (CO), 1962 s (CO), 1819 m ($\text{C}=\text{CF}_2$) cm^{-1} . MS (70 eV): m/z 252 (M^+), 224 ($\text{M}^+ - \text{CO}$), 196 ($\text{M}^+ - 2\text{CO}$), 148 (CpMnCO^+), 120 (CpMn^+). Anal. Calcd: C, 47.64; H, 2.80. Found: C, 47.58; H, 3.11. $\text{CpMn}(\text{CO})_2(\eta^2\text{-CF}_2=\text{C}=\text{CF}_2)$ (**3c**): preparation analogous to that for **3a**. Purification by chromatography (silica, *n*-pentane, $50 \text{ cm} \times 4 \text{ cm}^2$) followed by vacuum sublimation yielded 312 mg (34%) of yellow crystals, mp 46 °C. ^1H NMR (CDCl_3 , 25 °C): δ 4.90 (5H, s, Cp). ^{19}F NMR (CDCl_3 , -27 °C): δ -94.76 (1F, d, $^2J_{\text{FF}} = 53.6$ Hz, CF_2), -87.91 (1F, d, $^2J_{\text{FF}} = 117.1$ Hz, MnCF_2), -73.6 (1F, d, $^2J_{\text{FF}} = 117.1$ Hz, MnCF_2), -38.62 (1F, d, $^2J_{\text{FF}} = 53.6$ Hz, CF_2). ^{19}F NMR (d_8 -toluene, 80 °C): δ -95.3 (1F, CF_2), -80.3 (2F, MnCF_2), -39.7 (1F, CF_2). ^{13}C NMR (CDCl_3): δ 225.6 (s, CO), 150.9 (dd, $^1J_{\text{CF}} = 275$ Hz, $^1J_{\text{CF}} = 302$ Hz, CF_2), 134.5 (dd, $^1J_{\text{CF}} = 311$ Hz, $^1J_{\text{CF}} = 330$ Hz, MnCF_2), 87.9 ($^1J_{\text{CH}} = 181$ Hz, Cp), 66.7 (t, $^2J_{\text{CF}} = 124$ Hz, $\text{C}=\text{CF}_2$). The assignment of the CF_2 -groups is obtained from a ^{19}F - ^{13}C correlation (HMQC) spectrum. IR (*n*-pentane): $\tilde{\nu}$ 2029 vs (CO), 1980 s (CO), 1799 m ($\text{C}=\text{CF}_2$) cm^{-1} . MS (70 eV): m/z 288 (M^+), 232 ($\text{M}^+ - 2\text{CO}$), 148 (CpMnCO^+), 120 (CpMn^+). Anal. Calcd: C, 41.69; H, 1.74. Found: C, 41.63; H, 2.53.

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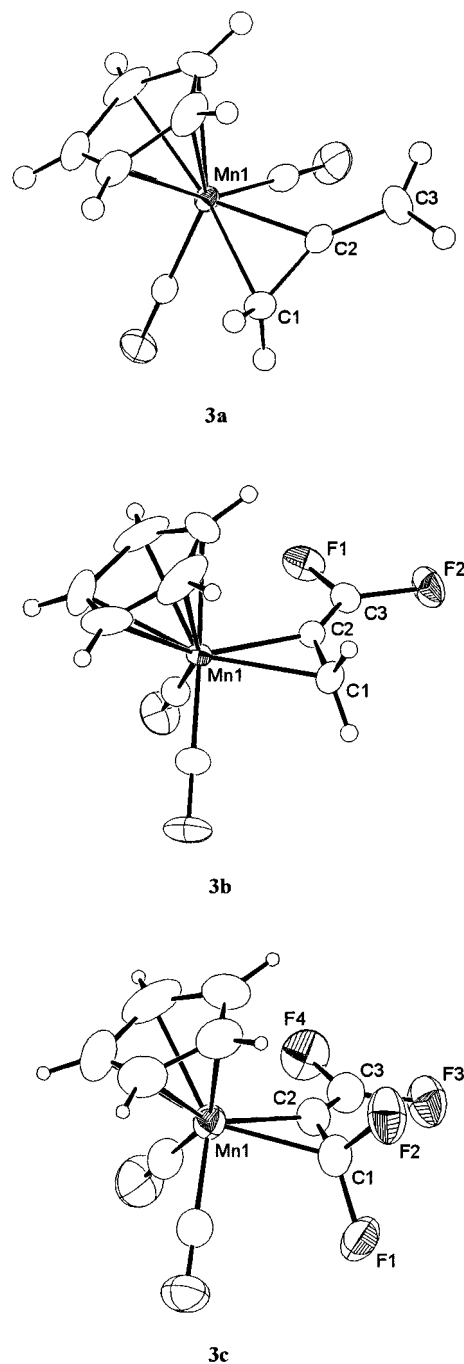


Figure 1. Structure plots (ORTEP¹⁸) of **3a–c**.

Table 1. Important Bond Lengths (pm) and Angles (deg) in $\text{CpMn}(\text{CO})_2\text{L}$ (**3a–c**)

L	Mn–C1	Mn–C2	C1–C2	C2–C3	C1–C2–C3
$\text{CH}_2=\text{C}=\text{CH}_2^a$	213.8(5)	203.2(5)	137.8(8)	132.0(8)	148.6(5)
$\text{CH}_2=\text{C}=\text{CF}_2$	213.5(3)	199.1(2)	138.9(3)	129.4(3)	143.8(2)
$\text{CF}_2=\text{C}=\text{CF}_2$	205.1(3)	198.8(3)	138.1(4)	128.9(4)	141.3(2)

^a The asymmetric unit consists of two molecules. Only the data for one molecule are given.

ration of the metal center.^{3j} A change of the coordination site as in $\text{Fe}(\text{CO})_4[(\text{CH}_3)_2\text{C}=\text{C}=\text{C}(\text{CH}_3)_2]$ ¹³ or $[\text{CpFe}(\text{CO})_2(\text{allene})][\text{BF}_4]$ (allene = $\text{C}_3\text{H}_3\text{Me}$, $\text{C}_3\text{H}_2\text{Me}_2$, $\text{C}_3\text{-Me}_4$)¹⁴ was not observed up to 80 °C. The ^{13}C NMR spectra of **3a–c**, exhibiting three resonances for the three chemically nonequivalent carbon atoms of the propadiene ligands, are in perfect agreement with these

findings. The signals of the coordinated carbon atoms are shifted to lower frequencies (-5.0 ppm for $F_2C=C=CF_2$ (**3c**) to -90.7 ppm for $H_2C=C=CF_2$ (**3b**)) in comparison to the free propadiene molecules. Significant changes in the chemical shift values of the noncoordinated alkene unit have been observed solely for **3a** (32 ppm).

Important information on the ligand properties of the allenes can be extracted from the CO force constants of the molecules listed in Table 2 in comparison with $CpMn(CO)_3$ and $CpMn(CO)_2(\eta^2-cis-cyclooctene)$. The force constant $k(CO)$ increases, and thus the relative

Table 2. Force Constants $k(CO)$ in **3a–c, $CpMn(CO)_3$, and $CpMn(CO)_2(\eta^2-cis-C_8H_{14})$**

$CpMn(CO)_2L$	$\nu(CO)$ (cm^{-1})	$k(CO)$ ($N\ cm^{-1}$)
$CpMn(CO)_2(\eta^2-cis-cyclooctene)$	1948, 1888	14.86
$CpMn(CO)_2(\eta^2-CH_2-CH_2=C=CH_2)$ (3a)	1989, 1934	15.54
$CpMn(CO)_3$	2029, 1949	15.77
$CpMn(CO)_2(\eta^2-CH_2=C=CF_2)$ (3b)	2012, 1962	15.93
$CpMn(CO)_2(\eta^2-CF_2=C=CF_2)$ (3c)	2029, 1980	16.23

π -acceptor ability of the coordinated alkene increases dramatically on going from *cis*-cyclooctene, propadiene, CO, and 1,1-difluoropropadiene to tetrafluoropropadiene, which turned out to be a very strong π -accepting ligand, even stronger than the carbonyl ligand. The important role of π back-bonding in the coordination of fluorinated allenes might be an explanation for the preferred coordination of the hydrogen-substituted double bond in **3b**, as the LUMO is located there.

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, bond distances and angles, and thermal parameters for **3a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Crystal structures are as follows. **3a**: monoclinic, $P2_1/n$, $a = 1032.1(2)$ pm, $b = 739.7(2)$ pm, $c = 2388.5(4)$ pm, $\beta = 99.10(2)^\circ$, $V = [1.8005(7)] \times 10^9$ pm³, $Z = 8$, $\rho_{\text{calcd}} = 1.594$ Mg/m³, 3238 measured reflections, 3159 crystallographically unique reflections, 2140 reflections with $I > 2\sigma(I)$, Mo K α , $\lambda = 71.069$ pm, $2\theta_{\text{max}} = 50^\circ$, $\omega-2\theta$ scan, 113 K, no absorption correction ($\mu = 1.424$ mm⁻¹), $R(F)_{\text{obsd}} = 0.0535$, $R_w(F^2)_{\text{all}} = 0.1621$, $w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 5.0707P]$ with $P = [F_o^2 + 2F_c^2]/3$, anisotropic temperature factors for C, F, O, and Mn, H atoms refined isotropically, solution by direct methods (SHELXS-90),¹⁸ full-matrix least-squares refinement on F^2 (SHELXL-97),¹⁹ 250 refined parameters, $\rho_{\text{max/min}} = +1.709/-0.951$ e Å⁻³. **3b**: triclinic, $P1$, $a = 668.25(5)$ pm, $b = 817.76(6)$ pm, $c = 900.73(14)$ pm, $\alpha = 90.633(9)^\circ$, $\beta = 96.430(9)^\circ$, $\gamma = 104.234(7)^\circ$, $V = [473.73(9)] \times 10^8$ pm³, $Z = 2$, $\rho_{\text{calcd}} = 1.767$ Mg/m³, 2974 measured reflections, 2755 unique, 2397 reflections with $I > 2\sigma(I)$, Mo K α , $\lambda = 71.069$ pm, $2\theta_{\text{max}} = 60^\circ$, $\omega-2\theta$ scan, 113 K, absorption correction ψ scan ($\mu = 1.396$ mm⁻¹), $R(F)_{\text{obsd}} = 0.0318$, $R_w(F^2)_{\text{all}} = 0.0801$, $w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.4548P]$ with $P = [F_o^2 + 2F_c^2]/3$, anisotropic temperature factors for C, F, O, and Mn, H atoms refined isotropically, solution by direct methods (SHELXS-90),¹⁸ full-matrix least-squares refinement on F^2 (SHELXL-97),¹⁹ 164 refined parameters, $\rho_{\text{max/min}} = +0.665/-0.426$ e Å⁻³. **3c**: triclinic, $P1$, $a = 666.56(8)$ pm, $b = 718.14(8)$ pm, $c = 1180.28(15)$ pm, $\alpha = 81.32(1)^\circ$, $\beta = 84.44(1)^\circ$, $\gamma = 71.330(9)^\circ$, $V = [5.2841(11)] \times 10^8$ pm³, $Z = 2$, $\rho_{\text{calcd}} = 1.811$ Mg/m³, 3541 measured reflections, 3092 unique reflections, 2530 reflections with $I > 2\sigma(I)$, Mo K α , $\lambda = 71.069$ pm, $2\theta_{\text{max}} = 60^\circ$, $\omega-2\theta$ scan, 293 K, absorption correction ψ scan ($\mu = 1.290$ mm⁻¹), min/max transmission 0.801/0.974,²⁰ $R(F)_{\text{obsd}} = 0.0309$, $R_w(F^2)_{\text{all}} = 0.0871$, $w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.4548P]$ with $P = [F_o^2 + 2F_c^2]/3$, anisotropic temperature factors for C, F, O, and Mn, H atoms were refined isotropically on calculated positions, structure solution by direct methods (SHELXS-90),¹⁸ full-matrix least-squares refinement on F^2 (SHELXL-97),²⁰ 155 refined parameters, $\Delta\rho_{\text{max/min}} = +0.304/-0.249$ e Å⁻³.

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