Organometallic Chemistry of Fluorinated Allenes

Dieter Lentz,* Natascha Nickelt, and Stefan Willemsen[a]

Abstract: Reaction of 1,1-difluoroallene and tetrafluoroallene with a series of transition metal complex fragments yields the mononuclear allene complexes [CpMn(CO)$_2$(allene)] (**1**), [(CO)$_4$Fe(allene)] (**2**), [(Ph$_3$P)$_2$Pt(C$_3$H$_2$F$_2$)] (**4**), [Ir(PPh$_3$)$_2$(C$_3$H$_2$F$_2$)$_2$Cl] (**5**), and the dinuclear complexes [(μ-η^1-η^3-C$_3$H$_2$F$_2$)Fe$_2$(CO)$_7$] (**3**), [Ir(PPh$_3$)(C$_3$H$_2$F$_2$)$_2$Cl]$_2$ (**6**), and [(μ-η^2-η^2-C$_3$H$_2$F$_2$){CpMo(CO)$_2$}$_2$] (**9**), respectively. In attempts to synthesize cationic complexes of fluorinated allenes [CpFe(CO)$_2$(C(CF$_3$)=CH$_2$)] (**7a**), [CpFe(CO)$_2$(C(CF$_3$)=CF$_2$)] (**7b**) and [μ-I-{CpFe(CO)$_2$}$_2$][B{C$_6$H$_3$-3,5-(CF$_3$)$_2$}$_4$] were isolated. The spectroscopic and structural data of these complexes revealed that the 1,1-difluoroallene ligand is coordinated exclusively with the double bond containing the hydrogen-substituted carbon atom. 1,1-Difluoroallene and tetrafluoroallene proved to be powerful π acceptor ligands.

Keywords: allenes · coordination compounds · fluorinated ligands · organometallic chemistry

Introduction

Fluorinated alkenes are important starting materials for the industrial synthesis of polymers like polytetrafluroethylene (PTFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), polychlorotrifluoroethylene (PCTFE), poly(vinylidene difluoride) (PVDF)[1] and therefore have been extensively studied.[2] The principal method for synthesizing organic fluoropolymers is free-radical polymerization. Coordination catalysts[3] do not effect polymerization of fluoroalkenes. That might be one reason for the fact that the organometallic chemistry of fluoroalkenes is much less developed than that of alkenes. Nevertheless, this fact still is astonishing in the view that most metal-catalyzed reactions of alkenes require the coordination of the alkene.[4] Among the 20 complexes of noncyclic fluorinated alkenes structurally characterized by X-ray crystallography so far, there are 16 compounds containing the tetrafluoroethene ligand.[5] However, in recent years there has been a growing interest in fluorine organometallic chemistry[6] focusing on C–F bond activation[7] and the fluorous biphase system.[8] Although 1,1-difluoroallene has been known since 1957,[9] its chemistry remained nearly unexplored until an efficient synthesis was described by Dolbier Jr. et al. in 1982.[10] During the subsequent years, the organic chemistry of fluorinated allenes has been studied in detail mainly by those workers.[11] The structures of fluoroallene[12] and 1,1-difluoroallene[13] in the gas phase were determined by microwave spectroscopy, and the photoelectron spectrum of 1,1-difluoroallene was recorded in 1978.[14] Tetrafluroallene, first prepared by Jacobs and Bauer in 1959, has been even less studied.[15] Again, that might be due to the lack of an efficient synthesis[16, 17] until 1995 when Burton et al. published an easy high-yield synthesis from a commercially available starting material.[18] During our studies on the fluorination effects on small organic molecules,[19] we have started to investigate the chemistry of 1,1-difluoroallene and tetrafluoroallene. According to ab initio calculations, 1,1-difluoroallene has a very interesting frontier orbital situation with the HOMO localized at the fluorine-substituted and the LUMO at the hydrogen-substituted double bond, respectively.[20] The energy gap between the LUMO and the NLUMO of 2.0 eV, and between the HOMO and NHOMO of 1.3 eV, are large. In the view of the two-component interaction originally proposed by Dewar, Chatt and Duncanson,[21] which is still the best way of picturing the interaction of an alkene with a transition metal,[22] the question arises of which double bond will be coordinated to a metal complex fragment. Preliminary results from this work have been published in a recent communication.[23] Herein, we report on the synthesis, spectroscopic, and structural properties of 1,1-difluoroallene and tetrafluoroallene complexes.

Results and Discussion

Syntheses: The syntheses of the allene complexes are outlined in Schemes 1 and 2. The manganese half-sandwich complexes **1** are best prepared by reaction of the photolytically generated

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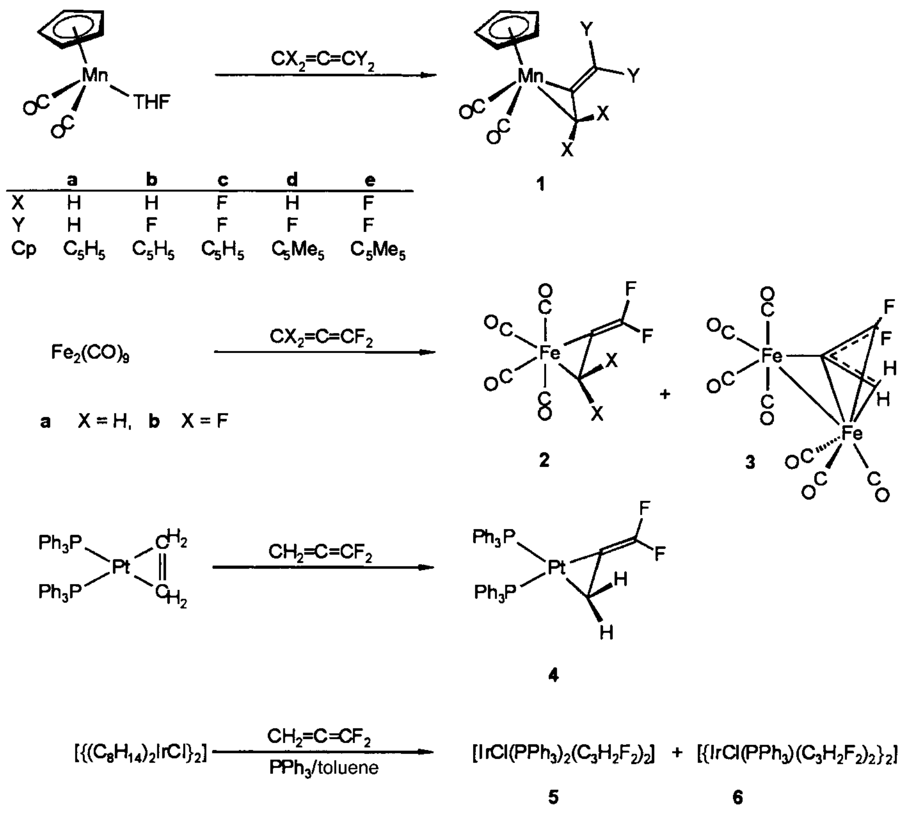
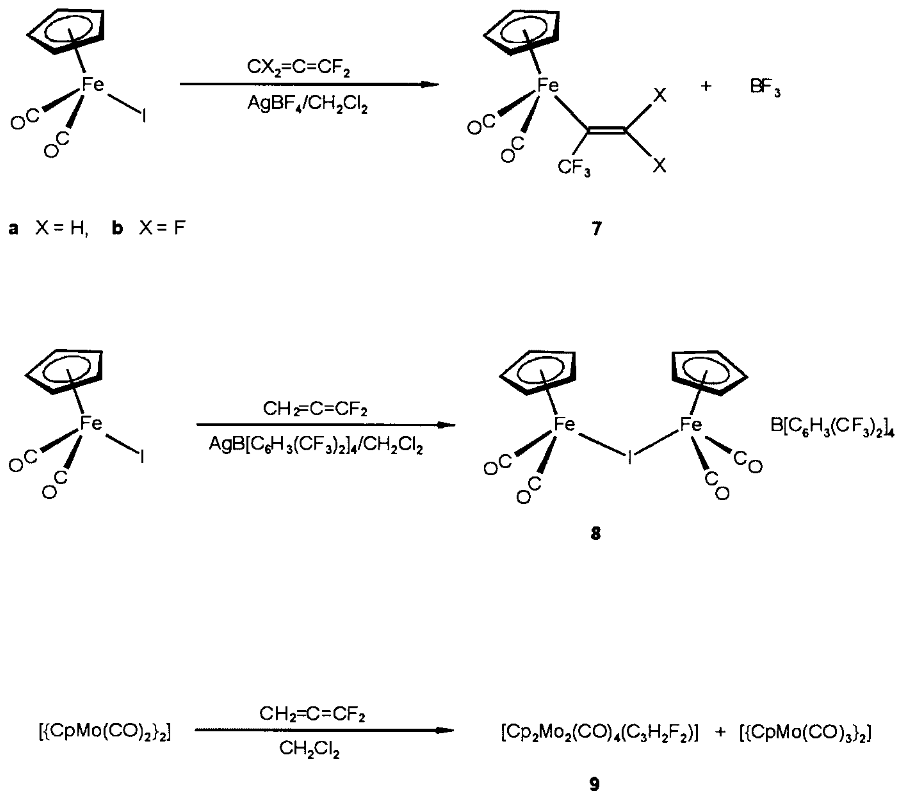


Scheme 1. Synthesis of allene complexes **1**–**6**.



Scheme 2. Synthesis of allene complexes **7**–**9**.

solvent-stabilized complexes [CpMn(CO)$_2$(thf)][24] (Cp = C$_5$H$_5$, C$_5$Me$_5$) with allene, difluoroallene or tetrafluoroallene, respectively. The allene complex **1a** was synthesized earlier from [CpMn(CO)$_2$(thf)] and diketene.[25] The compounds **1** were obtained as yellow crystalline solids after chromatography and crystallization from pentane. Eneacarbonyldiiron can be used as a source for a Fe(CO)$_4$ fragment resulting in the complexes **2**, which were isolated as yellow oils after purification by fractional condensation under vacuum. Longer reaction times result in the formation of the by-product **3** in low yield. Replacement of the ethene ligand in ethenebis(triphenylphosphane)platinum occurs easily at ambient temperature, yielding the colorless crystalline complex **4**. Two products **5** and **6** could be isolated in low yields from the reaction of bis[chlorobis(*cis*-cyclooctene)iridium] with difluoroallene and triphenylphosphane. Reaction of dicarbonyl(cyclopentadienyl)(iodo)iron with difluoroallene and tetrafluoroallene in the presence of silver tetrafluorborate did not result in the expected allene complexes. Dicarbonyl(η^5-cyclopentadienyl)(η^1-3,3,3-trifluoroprop-1-en-2-yl)iron (**7a**) and dicarbonyl(η^5-cyclopentadienyl)(η^1-1,1,3,3,3-pentafluoroprop-1-en-2-yl)iron (**7b**) could be isolated as final products, although cationic dicarbonyl(η^5-cyclopentadienyl)iron complexes of methyl-substituted allenes could be prepared.[26] Evidently, the cationic allene complexes which might be formed as intermediate species are stronger Lewis acids than boron trifluoride and abstract a fluoride ion from the anion BF$_4^-$. On using the silver salt of the weakly coordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[27] to prevent the reaction of intermediate allene complexes with the anion tetracarbonylbis(cyclopentadienyl)(μ-iodo)diiron tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**8**) was isolated as the only product. Reaction of bis[dicarbonyl(η-cyclopentadienyl)molybdenum] with 1,1-difluoroallene resulted in large amounts of a brown amorphous insoluble solid that was not further characterized, together with low yields of the dinuclear molybdenum complex **9** and bis[tricarbonyl(η-cyclopentadienyl)molybdenum].

Crystal structures: The structures of **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **4**, **5**, **6**, **8**, and **9**, were elucidated by X-ray crystallography. The crystallographic data of **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **4**, **5**, **6**, **8**, and **9** are summarized in Tables 1 and 2. Selected bond lengths and angles of **1a–d** are listed in Table 3 for comparison. ORTEP drawings of the molecules are given in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6. In all of compounds **1b**, **1d**, **2a**, **4**, **5**, and **6** the 1,1-difluorallene ligands are exclusively coordinated by the double bonds bearing the hydrogen-substituted carbon atom. Steric reasons for the preference can be excluded as tetrafluoroallene forms the similar complexes **1c** and **2b**, respectively, which have even shorter metal-to-carbon distances.

The manganese compounds **1a–d** all possess the same principal piano-chair geometry (Figure 1) with an η^2-coordinated allene ligand. Whereas the Mn–C2 bond lengths to the central carbon atom vary only between 1.988(2) Å for **1c** to 2.032(5) Å for **1a**, the Mn–C1 distance is significantly shorter for **1c** compared to **1a**, **b**, and **d**, demonstrating the strong effect of fluorine substitution. The C–C bond lengths of the noncoordinated double bonds are comparable to those of the free allene molecules[19a] in contrast to the coordinated ones, which are lengthened by 0.08 to 0.09 Å. Because of coordination, the allene 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 significantly with the number of fluorine substituents. Manganese–carbon distances to the carbonyl and cyclopentadienyl ligands show no significant variation with fluorine substitution.

Crystals of **2a** and **b** were obtained by sublimation at −30 °C in an ampoule sealed under vacuum. As both compounds are liquid at ambient temperature the crystals were mounted at low temperature. In both compounds the allene ligands occupy an equatorial position of the distorted trigonal-bipyramidal coordination polyhedra with the allene carbon atoms (Figure 2), the iron atom and the equatorial carbonyl ligand in one plane. This principal geometry is also found in all other tetracarbonyl(alkene)iron complexes[28] including tetracarbonyl(ethene)iron[29] and tetracarbonyl-(tetrafluoroethene)iron,[30] which were structurally studied by electron diffraction and microwave spectroscopy. The only cumulene tetracarbonyliron complex studied by X-ray crystallography is tetracarbonyl(tetraphenylbutatriene)iron.[31] Again, the metal–carbon bond to the central carbon atom of the allene ligands (1.972(3) **2a** and 1.958(4) Å **2b**) is shorter than the one to the CH_2 and CF_2 groups (2.107(3) **2a** and 1.997(4) Å **2b**), respectively. Fluorine substitution results in a 0.11 Å shrinkage of the metal–carbon bond, a greater lengthening of the coordinated C–C bond and a smaller

Table 1. Crystal data and structure refinement for**1a**, **1b**, **1c**, **1d**, **2a**, and **2b**.

	1a	**1b**	**1c**	**1d** mod. 1	**1d** mod. 2	**2a**	**2b**
empirical formula	$C_{10}H_9MnO_2$	$C_{10}H_7F_2MnO_2$	$C_{10}H_5F_4MnO_2$	$C_{15}H_{17}F_2MnO_2$	$C_{15}H_{17}F_2MnO_2$	$C_7H_2F_2FeO_4$	$C_7F_4FeO_4$
M_r	216.11	252.10	288.08	322.23	322.23	243.94	279.92
T [K]	133(2)	113(2)	293(2)	293(2)	293(2)	133(2)	133(2)
λ [Å]	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a [Å]	10.321(2)	6.6825(5)	6.6656(8)	6.7585(7)	10.822(3)	7.134(2)	6.559(2)
b [Å]	7.397(2)	8.1776(6)	7.1814(8)	12.479(2)	10.303(3)	10.423(2)	678.2(2)
c [Å]	23.885(4)	9.0073(14)	11.8028(15)	8.9460(10)	13.314(4)	11.709(2)	20.805(5)
α [°]	90	90.633(9)	81.320(10)	90	90	90	90
β [°]	99.10(2)	96.430(9)	84.440(10)	94.040(10)	90.86(3).	92.53(2)	90
γ [°]	90	104.234(7)	71.330(9)	90	90	90	90
volume [Å^3]	1800.5(7)	473.73(9)	528.41(11)	752.62(17)	1484.3(7)	869.8(3)	925.5(5)
Z	8	2	2	2	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.594	1.767	1.811	1.422	1.442	1.863	2.009
μ [mm^{-1}]	1.424	1.396	1.290	0.896	0.908	1.750	1.688
F(000)	880	252	284	332	664	480	544
crystal size [mm^3]	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.1	0.4 × 0.3 × 0.1	0.85 × 0.3 × 0.12	0.5 × 0.1 × 0.05	0.4 × 0.4 × 0.1
θ_{max} [°]	24.97.	29.96	30.03	25.0	27.00	24.98	29.96
index ranges	$-12 \leq h \leq 12$	$0 \leq h \leq 9$	$-9 \leq h \leq 9$	$0 \leq \mathrm{h} \leq 8$	$-13 \leq h \leq 13$	$0 \leq h \leq 8$	$0 \leq \mathrm{h} \leq 9$
	$-8 \leq k \leq 0$	$-11 \leq k \leq 11$	$-10 \leq k \leq 6$	$-14 \leq k \leq 14$	$-13 \leq k \leq 13$	$-12 \leq \mathrm{k} \leq 0$	$0 \leq k \leq 9$
	$0 \leq l \leq 28$	$-12 \leq l \leq 12$	$-16 \leq l \leq 16$	$-10 \leq l \leq 10$	$-17 \leq l \leq 0$	$-13 \leq l \leq 13$	$-29 \leq l \leq 0$
reflections collected	3238	2974	3541	2884	6534	1655	1584
independent reflections/R_{int}	3159/0.0461	2755/0.0214	3092/0.0178	2649/0.0263	3226/0.059	1526/0.0284	1584
completeness to θ_{max} [%]	99.9	99.9	99.8	100.0	99.7	99.9	99.9
absorption correction	none	psi-scan	psi-scan	none	none	psi-scan	psi-scan
max./min. transmission		0.965/0.756	0.974/0.801			0.930/0.697	0.970/0.857
refinement method	Full-matrix least-squares on F^2						
data/restraints/parameters	3159/0/249	2755/0/164	3092/0/155	2649/1/131	3226/0/189	1526/0/135	1584/145
goodness-of-fit on F^2	1.098	1.077	1.042	1.084	1.096	1.145	1.019
R_1/wR_2 [$I > 2\sigma(I)$]	0.0535/0.1420	0.0318/0.0761	0.0309/0.0816	0.0674/0.1766	0.0653/0.1892	0.0269/0.0671	0.0343/0.718
R_1/wR_2 (all data)	0.0964/0.1620	0.0440/ 0.0801	0.0433/0.0871	0.1148/0.2092	0.1038/02121	0.0407/0.0723	0.0791/0.814
extinction coefficient	none	none	0.022(3)	none	none	none	none
$\Delta\rho_{max}/\Delta\rho_{min\ e Å^{-3}}$	1.709/ − 0.951	0.665/ − 0.426	0.304/ − 0.249	0.553/ − 0.347	0.990/ − 0.514	0.316/ − 0.418	0.478/ − 0.486

Table 2. Crystal data and structure refinement for **4**, **5**, **6**, **8**, and **9**.

	4	**5**	**6**	**8**	**9**
empirical formula	$C_{39}H_{32}F_2P_2Pt$	$C_{44}H_{36}Cl_7F_4P_2Ir \cdot 2\,CHCl_3$	$C_{48}H_{38}Cl_2F_8Ir_2P_2$	$C_{93}H_{45}B_2Cl_3F_{48}Fe_4I_2O_8$	$C_{17}H_{12}F_2Mo_2O_4$
M^r	795.68	1143.02	1284.02	2807.46	510.15
T [K]	138(2)	153(2)	173(2)	143(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71069
crystal system	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P2_{1/n}$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_{1/n}$
a [Å]	11.5066(9)	11.8519(11)	11.4480(6)	13.7170(10)	8.032(3)
b [Å]	19.6942(15)	17.6285(16)	13.7452(7)	14.0222(14)	12.061(2)
c [Å]	14.2538(11)	21.5189(17)	15.3140(8)	31.008(2)	17.558(2)
α [°]	90	90	89.4600(10)	100.474(2)	90
β [°]	91.583(2)	90	80.9590(10	92.491(2)	99.61(3)
γ [°]	90	90	77.4500(10)	119.2810(10)	90
volume [Å^3]	3228.9(4)	4496.0(7)	2322.2(2)	5054.1(7)	1677.0(7)
Z	4	4	2	2	4
ρcalcd [Mg m^{-3}]	1.637	1.689	1.836	1.845	2.021
μ [mm^{-1}]	4.483	3.505	5.974	1.397	1.535
F(000)	1568	2248	1232	2740	992
crystal size [mm^3]	0.24 × 0.08 × 0.04	0.4 × 0.1 × 0.1	0.4 × 0.2 × 0.1	0.35 × 0.25 × 0.23	0.5 × 0.4 × 0.1
θ_{max} [°]	31.63	30.54	30.05	25.03	27.03
index ranges	$-16 \leq h \leq 16$	$-16 \leq h \leq 16$	$-16 \leq h \leq 16$	$-16 \leq h \leq 16$	$-5 \leq h \leq 10$
	$-29 \leq k \leq 29$	$-24 \leq k \leq 25$	$-19 \leq k \leq 19$	$-16 \leq k \leq 16$	$-13 \leq k \leq 15$
	$-21 \leq l \leq 20$	$-30 \leq l \leq 30$	$-21 \leq l \leq 21$	$-36 \leq l \leq 26$	$-21 \leq l \leq 22$
reflections collected	38850	53457	27519	39115	3945
independent reflections/R_{int}	10095/0.0602	13514/0.0556	13273/0.0478	17744/0.0504	3554/0.0670
completeness to θ_{max} [%]	93.0	99.2	97.4	99.3	96.3
absorption correction	empirical SADABS	empirical SADABS	empirical SADABS	empirical SADABS	none
max./min. transmission	0.7679/0.5642	0.695/0.500	1.00/0.73	0.813/0498	
refinement method			full-matrix least-squares on F^2		
data/restraints/parameters	10095/0/405	13514/0/551	13273/0/591	17744/0/1441	3554/0/ 226
goodness-of-fit on F^2	0.977	1.084	0.829	1.024	1.095
R_1/wR_2 [$I > 2\sigma(I)$]	0.0314/0.0415	0.0384/0.0859	0.0335/0.0586	0.0503/ 0.1346	0.0592/0.1549
R_1/wR_2 (all data)	0.0623/0.0444	0.0541/0.0908	0.0666/0.0630	0.0656/ 0.1453	0.0847/0.1685
extinction coefficient			none		
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	1.748/ – 1.407	1.556/ – 1.233	1.454/ – 1.866	1.272/ – 1.451	2.111/ – 2.029

Table 3. Selected bond lengths [Å] and angles [°] of **1a–d**.

	Mn–C1	Mn–C2	C1–C2	C2–C3	C1-C2-C3
1a, molecule 1	2.138(5)	2.032(5)	1.378(8)	1.320(8)	148.6(5)
1b	2.135(3)	1.991(2)	1.389(3)	1.294(3)	143.8(2)
1c	2.051(2)	1.988(2)	1.381(3)	1.289(3)	141.3(2)
1d (modification 2)	2.133(7)	1.995(6)	1.394(9)	1.284(9)	142.9(6)

C-C-C angle. The F–C distances of the coordinated CF_2 group are significantly longer than those to the noncoordinated CF_2 group of **2b**. Comparing the metal-carbon distances to the axial and equatorial carbonyl ligands, there seems to exist no obvious influence of the fluorine substitution.

The platinum complex **4** (Figure 3) possesses the expected trigonal planar coordination sphere of alkene-bis(triphenylphosphane)platinum complexes,[32] allene-bis(triphenylphosphane)platinum[33] and 1,1-dimethylallene-bis(triphenylphosphane)platinum.[34] The coordination of the 1,1-difluoroallene ligand occurs by the hydrogen-substituted double bond. The allene ligand is strongly bent at the central carbon atom C2 and the carbon–metal bond lengths show the same characteristics observed for the other 1,1-difluoroallene complexes. The Pt–P distances are equal within 3σ.

Both iridium complexes **5** and **6** crystallize with solvent molecules, which gives raise to disorder problems. Compound **5** crystallizes orthorhombic $P2_12_12_1$ with one molecule **5** and two chloroform molecules in the asymmetric unit. The solvent molecules (Figure 4) occupy channels with a maximum diameter of 11 Å parallel to the crystallographic a axis. In the mononuclear complex **5** (Figure 5) the two phosphane ligands occupy the axial positions (P1-Ir1-P2 176.17(4)°) of a distorted trigonal bipyramid and the two allene ligands and the chloro ligand are in the equatorial positions. Alkene complexes containing the $IrCl(PPh_3)_2$ fragment usually possess a square-planar *trans*-$[IrCl(PPh_3)_2(alkene)]$ structure (alkene = C_2H_4, C_3H_4, C_2F_4).[35] The ethene complex *trans*-$[IrCl(PPh_3)_2(C_2H_4)]$ was structurally characterized by X-ray crystallography.[36] *trans*-$[IrCl(\eta^2\text{-}H_2C{=}C{=}CPh_2)(P\mathit{i}Pr_3)_2]$ was prepared by reaction of *trans*-$[IrCl({=}C{=}C{=}CPh_2)(P\mathit{i}Pr_3)_2]$ with H_2 and the structure elucidated by X-ray diffraction.[37] The five-coordinate ethene complex $[IrCl(PPh_3)_2(C_2H_4)_2]$ can be prepared at low temperature but it looses ethene above –50 °C.[35] The only other example of a iridium complex of the type $[IrCl(PR_3)_2(alkene)_2]$ structurally characterized was recently reported by Milstein et al.[38] However, $[IrCl(C_2H_4)_2(PEt_3)_2]$ contains a more electron-rich iridium center due to the triethylphosphine ligands. The structure of **5** (Figure 5) differs significantly from $[IrCl(C_2H_4)_2(PEt_3)_2]$, in which the chloro ligand and one of the two phosphane ligands occupy the axial position of the trigonal bipyramid, whereas the second phosphane ligand occupies the equatorial position. According to the ^{31}P NMR spectra, which exhibits two signals

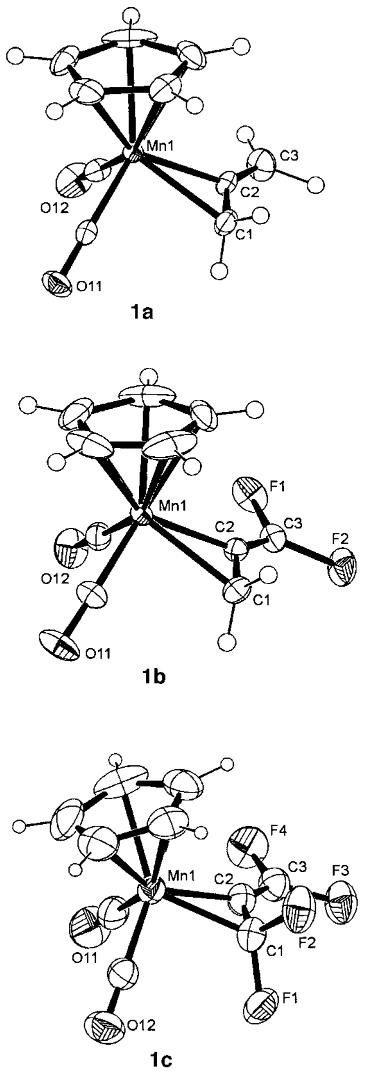


Figure 1. Molecular structures (ORTEP[64]) of **1a–c** (50 % ellipsoids **1a**,**b**; 30 % ellipsoids **1c**).

for the inequivalent phosphane ligands, this structure is also maintained in solution.[38] The cationic pentacoordinate allene complex of iridium $[Ir(C_3H_4)_2(PMe_2Ph)_3][BF_4]$ was isolated and structurally characterized by Caulton et al.[39] As in **5**, the two allene ligands occupy equatorial positions of a distorted trigonal bipyramid. As observed for the other 1,1-difluoroallene complexes, the allene ligands are coordinated through the hydrogen-substituted double bond with shorter Ir–C distances to the central carbon atom. The two allene ligands are not related by symmetry. Due to the greater steric demand of the CF_2 substituent at C5 compared to the hydrogen substituents at C1 the Cl1-Ir1-C1 and Cl1-Ir1-C5 bond angles differ by more than 10°. This might be a reason for the great difference in bond length of similar Ir–C bonds (Ir1–C1 2.181(5), Ir1–C4 2.139(4) and Ir1–C2 2.049(4), Ir1–C5 2.102(4) Å). These differences are reflected in a different lengthening of the coordinated carbon-carbon bond (C1–C2 1.386(6) versus C4–C5 1.425(6) Å) and bond angles at the central carbon atom (C1-C2-C3 143.2(4) versus C4-C5-C6 134.8(4)°). The iridium atom, the chlorine atom and all carbon atoms of the allene ligands are almost within one plane.

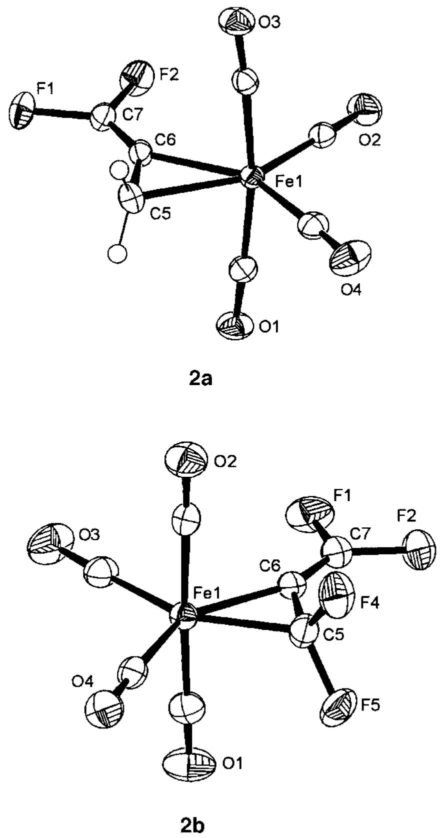


Figure 2. Molecular structures (ORTEP[64] 50 % ellipsoids) of **2a**,**b**. Selected bond lengths [Å] and angles [°] for **2a** [**2b**]: Fe1–CO 1.811(3)–1.821(3) [1.810(5)–1.840(4)], Fe1–C5 2.107(3) [1.997(4)], Fe1–C6 1.972(3) [1.957(4)], C5–C6 1.408(4) [1.397(6)], C6–C7 1.287(4) [1.282(6)], C7–F(av) 1.338 [1.327], C5–F(av) [1.358(5)]; C7-C6-C5 144.8(3) [137.3(4)].

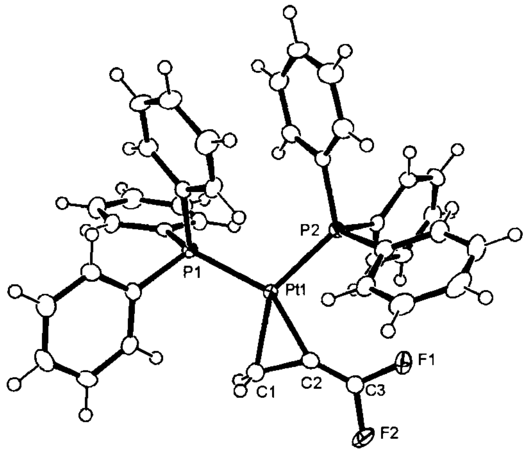


Figure 3. Molecular structure (ORTEP[64] 50 % ellipsoids) of **4**. Selected bond lengths [Å] and angles [°]: Pt1–C1 2.110(4), Pt1–C2 2.019(3), Pt1–P1 2.293(1), Pt1–P2 2.296(1), C1–C2 1.418(5), C2–C3 1.286(4), C3–F(av) 1.348, C1-C2-C3 138.9(3).

The dinuclear iridium complex **6** (Figure 5) crystallizes triclinic $P\bar{1}$ with one molecule **6** and one disordered solvent molecule in the asymmetric unit. To the best of our knowledge the structure of **6** is unique. Again, the coordination polyhedra of the iridium atoms are distorted trigonal bipyramids that share a common edge resulting in a C_2-symmetric molecule. As is obvious from the bond angles, the phosphorous atoms

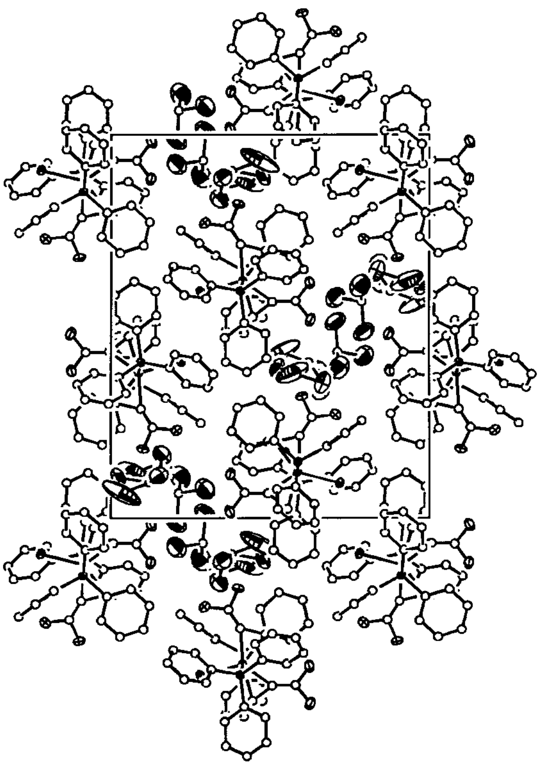


Figure 4. Unit cell (ORTEP[64] 50% ellipsoids) of **5**. View along the *a* axis.

and the chlorine atom Cl1 are in the axial positions. The allene ligands and Cl2 occupy the equatorial ones. The Ir–Cl distances vary from 2.464(2) to 2.484(2) Å. The Ir–C distances to the allene ligands show the same effects observed in **5** demonstrating that the strikingly different bond lengths are due to the different coordination of the allene ligands.

The structure determination of **7b** is hindered by a disorder of the CF_2 and CF_3 moiety that does not allow a discussion of the important structural parameters. An X-ray crystal structure determination of the undesired product **8** proves the formation of a tetracarbonyl-bis(cyclopentadienyl)(*μ*-iodo)-diiron cation that has been structurally characterized before with the BF_4^- ions.[40] Compound **8** crystallizes with two crystallographically independent $[\mu\text{-I-}\{CpFe(CO)_2\}_2][B\{C_6H_3(CF_3)_2\}_4]$ molecules and one chloroform molecule in the asymmetric unit.

Compound **9** consists of two $CpMo(CO)_2$ units bridged by the 1,1-difluoroallene ligand (Figure 6). The metal–metal distance of 3.162(1) Å is similar to that of $[Cp_2Mo_2(CO)_2(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-}H_2C{=}C{=}CH_2)]$.[41] Whereas related Mo–C distances to the allene ligand are equal for $[Cp_2Mo_2(CO)_2(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-}H_2C{=}C{=}CH_2)]$ (Mo1–C1 2.23(2), Mo2–C3 2.23(2), Mo1–C2 2.11(1), Mo2–C1 2.13(1) Å) the fluorine substitution results in an unsymmetrical situation with shorter distances to the fluorine-substituted double bond and longer distances to the hydrogen-substituted one. However, both C–C bonds have equal bond lengths.

Spectroscopic data: All compounds were fully characterized by spectroscopic methods. Selected spectroscopic data are summarized in Tables 4 and 5.

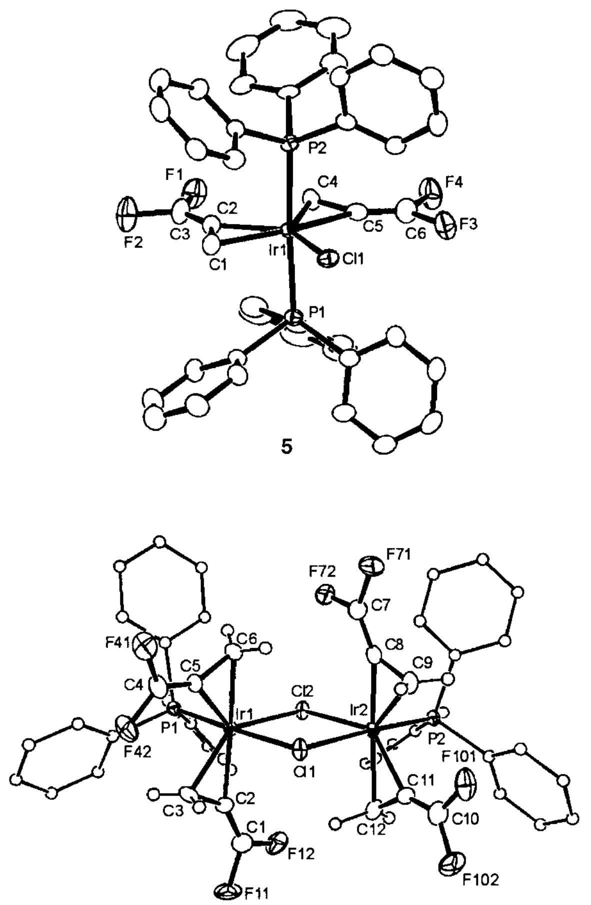


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Figure 5. Molecular structures (ORTEP[64] 50% ellipsoids) of **5** and **6**. Selected bond lengths [Å] and angles [°]: For **5**: Ir1–C1 2.182(5), Ir2–C2 2.041(5), Ir1–C4 2.162(5), Ir1–C5 2.108(5), C1–C2 1.401(8), C2–C3 1.293(8), C4–C5 1.439(8), C5–C6 1.268(8); C1-C2-C3 142.9(5), C4-C5-C6 135.1(5), Cl1-Ir1-C2 127.4(2), Cl1-Ir1-C5 102.3(2), P1-Ir1-P2 176.08(5); for **6**: Ir1–C2 2.084(5), Ir1–C3 2.128(5), Ir1–C5 2.039(5), Ir1–C6 2.1739(5), Ir1–Cl1 2.466(1), Ir1–Cl2 2.476(1), Ir2–C8 2.080(5), Ir2–C9 2.137(5), Ir2–C11 2.033(5), Ir2–C12 2.163(6), Ir2–Cl1 2.483(1), Ir2–Cl2 2.484(1); Cl1-Ir1-P1 176.71(4), Cl1-Ir2-P2 175.64(4), P1-Ir1-Cl2 94.37(4), Cl1-Ir1-Cl2 82.47(4), P2-Ir2-Cl2 96.42(4), Cl1-Ir2-Cl2 81.99(4).

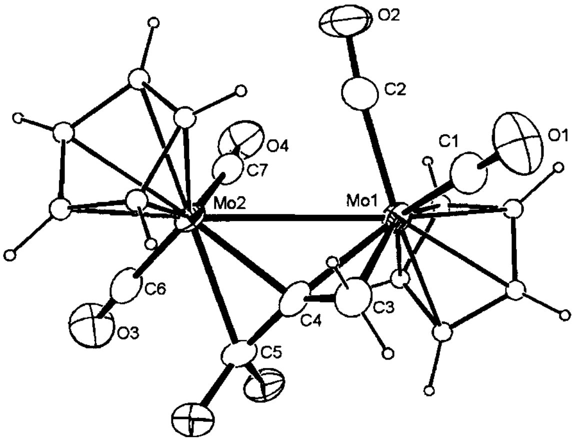

Figure 6. Molecular structures (ORTEP[64] 50% ellipsoids) of **9**. Selected bond lengths [Å] and angles [°] for **9**: Mo1–Mo2 3.162(1), Mo1–C3 2.312(8), Mo1–C4 2.120(8), Mo2–C4 2.118(7), Mo2–C5 2.244(7); C3-C4-C5 142.3(8).

Table 4. Spectroscopic data of **1a–e**, **2a**, **b**, and **3** in comparison to allene, 1,1-difluoroallene and tetrafluoroallene.

Compound	IR [cm^{-1}]	^1H NMR	^{19}F NMR	^{13}C NMR
$H_2C{=}C{=}CH_2$				73.8 (CH_2), 212.5 (=C=)
$H_2C{=}C{=}CF_2$				103.7 (CH_2), 154.7 (CF_2), 179.9 (=C=)
$F_2C{=}C{=}CF_2$				139.5 (CF_2), 117.4 (=C=)
1a	1989 s (CO), 1934 s (CO)	30 °C 6.31, (1H, td, CH_2); $^2J_{H,H} = 1.8$ Hz; $^4J_{H,H} = 3.4$ Hz 5.71, (1H, td, CH_2) $^2J_{H,H} = 1.8$ Hz, $^4J_{H,H} = 3.4$ Hz 3.9 (5H, s, Cp) 1.59 (2H, t, CH_2), $^4J_{H,H} = 3.4$ Hz changes at – 100 °C, 1.73 (1H, $MnCH_2$), 1.35 (1H, $MnCH_2$)		231.2 (CO), 168.8 (s, *C*-CH_2) 105.0 (dd, CH_2), $^1J_{C,H} = 160, 164$ Hz, 84.5 (dm, Cp) $^1J_{C,H} = 178$ Hz, 6.4 (dd, CH_2) $^1J_{C,H} = 160$ Hz
1b	2012 vs (CO), 1962 s (CO) 1819 m ($C{=}CF_2$)	20 °C, CD_2Cl_2 2.16 (2H, s, CH_2) 4.82 (5H, s, Cp); 20 °C ([D_8]toluene) 1.70 (2H, s, CH_2) 3.92 (5H, s, Cp) – 80 °C ([D_8]toluene) 1.30 (1H, s, CH_2) 1.81 (1H, s, CH_2) 3.57 (5H, s, Cp)	– 99.57 (1F, d, CF_2), – 63.83 (1F, d, CF_2) $^2J_{F,F} = 89.4$ Hz	230.9 (CO), 150.8 (dd, CF_2) $^1J_{C,F} = 256.6, 283.9$ Hz 99.8 (dd, =C=) $^2J_{C,F} = 20.3, 49.0$ Hz 86.4 (dm, Cp) $^1J_{C,H} = 179.1$ Hz 13.2 (t, CH_2) $^1J_{C,H} = 166.7$ Hz
1c	2029 vs (CO) 1980 s (CO) 1799 m ($C{=}CF_2$)	25 °C, $CDCl_3$ 4.90 (5H, s, Cp)	– 27 °C ($CDCl_3$) – 94.76 (1F, d, CF_2) $^2J_{F,F} = 53.6$ Hz; – 87.91(1F, d, $MnCF_2$) $^2J_{F,F} = 117.1$ Hz , – 73.6 (1F, d, $MnCF_2$), $^2J_{F,F} = 117.1$ Hz; – 38.62 (1F, d, CF_2) $^2J_{F,F} = 53.6$ Hz; 80 °C, [D_8]toluene – 95.3 (1F, CF_2) – 80.3 (2F, $MnCF_2$), – 39.7 (1F, CF_2)	25 °C ($CDCl_3$): 225.6 (s, CO) 150.9 (dd, CF_2), $^1J_{C,F} = 274, 297$ Hz, 134.5 (dd, $MnCF_2$) $^1J_{C,F} = 302, 316$ Hz, 87.9 (Cp) $^1J_{C,H} = 181$ Hz, 66.7 (d, =*C*=) $^2J_{C,F} = 60$ Hz
1d	1988 vs (CO), 1933 s (CO) 1809 m ($C{=}CF_2$)	1.74 (s, CH_3) 4.41 (s, CH_2)	– 65.16 (d, CF_2) – 100.62 (d, CF_2) $^2J(^{19}F,^{19}F) = 91$ Hz	9.4 (s, CH_3), 18.6 (d, CH_2) $^3J(^{19}F,^{13}C) = 7$ Hz), 97.2 (s, Cp*) 105.1 (dd, $F_2C = C$), $^2J(^{19}F,^{13}C) = 14$ Hz $^2J(^{19}F,^{13}C) = 39$ Hz 152.2 (dd, CF_2) $^1J(^{13}C,^{19}F) = 260$ Hz $^1J(^{13}C,^{19}F) = 289$ Hz 233.5 (CO)
1e	2011 s (CO), 1961 s (CO), 1787 m ($C{=}CF_2$)	1.80 (s, CH_3)	– 95.26 (1F, d, CF_2), $^2J_{F,F} = 58$ Hz; – 92.91 (1F, d, $MnCF_2$), $^2J_{F,F} = 122$ Hz – 86.33 (1F, d, $MnCF_2$), $^2J_{F,F} = 122$ Hz; – 40.84 (1F, d, CF_2),$^2J_{F,F} = 58$ Hz	
2a	2110 s (CO), 2035 vs (CO), 2010 vs (CO), 1814 m ($C{=}CF_2$)	2.33 (s, CH_2)	– 62.12 (d, CF_2) – 95.82 (d, CF_2) $^2J(^{19}F,^{19}F) = 82$ Hz	12.6 (d, CH_2) $^3J(^{19}F,^{13}C) = 7$ Hz) 92.7 (dd, $F_2C{=}C$) $^2J(^{19}F,^{13}C) = 20, 53$ Hz 151.0(dd, CF_2) $^1J(^{13}C,^{19}F) = 260, 289$ Hz 206.2 (CO)
2b	2129 vs (CO) 2106 s (CO) 2062 vs (CO) 2039 vs (CO) 1787 s ($C{=}CF_2$)		– 39.8 (d, 1F) – 79.2 (s, 2F) – 91.8 (d, 1F) $^2J(^{19}F,^{19}F) = 44$ Hz	63.3 (dd, $C{=}CF_2$) $^2J(^{19}F,^{13}C) = 13, 57$ Hz 129.0 (dt, CF_2Fe) $^1J(^{19}F,^{13}C) = 326$ Hz $^3J(^{19}F,^{13}C) = 21$ Hz 150.6 (dd, CF_2) $^1J(^{19}F,^{13}C) = 277, 302$ Hz 200.1 (Co_{ax}), 201.7 (CO_{eq}) 204.2 (CO_{eq})
3	2104 m 2074 m 2049 vs 2029 vs 2018 vs 1994 m 1986 m	3.54 (d, 1H), $J = 2.6$ Hz 2.96 (s, 1H)	74.0 (d, 1F) 86.2 (d, 1F) $^2J(^{19}F,^{19}F) = 79$ Hz	64.4 (t; $C{=}CF_2$) $^2J(^{19}F,^{13}C) = 7$ Hz 149.9 (dd, CH_2) $^3J(^{19}F,^{13}C) = 8, 29$ Hz 153.2 dd, CF_2) $^1J(^{19}F,^{13}C) = 307, 331$ Hz 205.2 (br, CO), 211.2 (br, CO)

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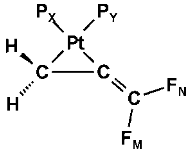
Table 5. NMR data of **4**. One possible assignment of the signals is depicted.



δ		^1H	$^{19}F_M$	$^{19}F_N$	$^{31}P_X$	$^{31}P_Y$	^{195}Pt
^1H	1.978		3				50
$^{19}F_M$	−82.3	3		84	3	45	319
$^{19}F_N$	−89.0		84		11	4	53
$^{31}P_X$	32.3		3	4		27	3304
$^{31}P_Y$	28.9		45	11	27		3557
^{195}Pt	−473.8	50	319	53	3303	3357	

The half-sandwich manganese complexes **1** exhibit two very strong absorptions in the IR spectrum at around 2000 cm^{-1}, due to CO stretching vibrations, besides one absorption around 1800 cm^{-1} that can be assigned to the C–C stretching mode of the noncoordinated C–C double bond. Important information on the ligand properties of the allenes in comparison with other ligands can be extracted from the CO force constants[42] of **1a–c**, $[CpMn(CO)_2(\eta^2\text{-}cis\text{-cyclooctene})]$ and $[CpMn(CO)_3]$. The force constant $k(CO)$ increases, and thus the relative π-acceptor ability of the coordinated alkene increases strongly on going from *cis*-cyclooctene ($k(CO) = 14.86\,N\,cm^{-1}$), allene ($k(CO) = 15.54\,N\,cm^{-1}$), CO ($k(CO) = 15.77\,N\,cm^{-1}$), 1,1-difluoroallene ($k(CO) = 15.93\,N\,cm^{-1}$) to tetrafluoroallene ($k(CO) = 16.23\,N\,cm^{-1}$). Tetrafluoroallene turned out to be a very strong π-accepting ligand, even stronger than the carbonyl ligand.

The iron complexes **2a** and **2b** possess noncrystallographic C_s symmetry. Thus, four infrared CO stretching vibrations should be observed as is found for **2b**. The observation of only three CO vibrations for **2a** is due to an accidental overlap. All CO stretching vibrations are observed well above 2000 cm^{-1}, again demonstrating the high π-acceptor abilities of the fluorinated allene ligands. The C–C stretching mode of the noncoordinated double bond is observed at 1814 (**2a**) and 1787 cm^{-1} (**2b**), respectively. The infrared spectrum of the dinuclear iron complex **3** exhibits seven absorptions between 1950 and 2150 cm^{-1} but none in between 1700 and 1950 cm^{-1} excluding structures with a bridging carbonyl ligand. The dinuclear molybdenum complex **9** exhibits the four expected carbonyl stretching modes between 1850 and 1970 cm^{-1}.

The manganese complexes **1** possess C_1 symmetry and should exhibit four signals for the chemically inequivalent allene protons and fluorine substituents in the ^1H and ^{19}F NMR spectra. However, only three signals were observed for **1a**, **b**, and **d** at ambient temperature (see Table 4). Compound **1c** exhibits two well-resolved signals besides two broad signals in its ^{19}F NMR spectrum, whereas **1e** exhibits four well-resolved signals. These observations can be easily explained by a propeller rotation[43] of the coordinated allene ligands that has a different activation barrier depending on the cyclopentadienyl ligand and allene ligand, and interconverts one enantiomer into the other. The ^1H and ^{19}F NMR spectra of **1a–e** vary strongly with the temperature. At low temperature the four expected signals are observed. On warming the samples, two of the signals get broad. The coalescence temperature depends on the allene and the cyclopentadienyl ligand. The free enthalpies of activation of the propeller rotation of the coordinated allene at the d^6 metal center were determined as $37 \pm 1\,kJ\,mol^{-1}$ ($T_c = -75\,°C$) for **1a**, $52 \pm 1\,kJ\,mol^{-1}$ ($T_c = -5\,°C$) for **1b**, and $53.4 \pm 0.2\,kJ\,mol^{-1}$ ($T_c = 45\,°C$) for **1c**, respectively, comparable with the values for other other $[CpMn(CO)_2(alkene)]$ complexes.[44] The value of **1c** seems to be rather low for a coordinated fluorinated alkene.[5j] However, as emphasized by others,[22] there should be no correlation between acceptor properties of an alkene and the activation energy of the propeller rotation. The low free activation for the propeller rotation in $[Cp^*Ru(acac)(C_2F_4)]$ (acac = acetylacetonate) was attributed to the d^6 electron configuration of the metal center.[5j] A change of the coordination site as in $[Fe(CO)_4\{(CH_3)_2C{=}C{=}C(CH_3)_2\}]$[45] or $[CpFe(CO)_2(allene)][BF_4]$ (allene = C_3H_3Me, $C_3H_2Me_2$, C_3Me_4)[26] was not observed up to 80 °C. The ^{13}C NMR spectra of **1a–c** exhibiting three resonances for the three chemically nonequivalent carbon atoms of the allene ligands are in perfect agreement with these findings. The signals of the coordinated carbon atoms are shifted to lower frequencies ($\delta = -5.0$ $F_2\mathit{C}{=}C{=}CF_2$ **1c** to -90.7 $H_2\mathit{C}{=}C{=}CF_2$ **1b**) in comparison to the free allene molecules. Significant changes in the chemical shift values of the noncoordinated alkene unit have been observed solely for **1a** ($\delta = 32$).

In accordance with the C_s symmetry, **2a** exhibits a singlet at $\delta = 2.33$ in the ^1H NMR spectrum and two doublets at -62.1 and -95.8 ($^2J(^{19}F,^{19}F) = 82$ Hz). The $^{13}C\{^1H\}$ NMR spectrum taken at ambient temperature consists of three signals for the allene ligand and only one for the CO ligands. Thus there exists a process that makes the axial and equatorial carbonyl ligands equivalent on the NMR time scale, which is most probably the Berry pseudorotation process. However, again there is no indication of a change of the coordination site as has been observed for $[Fe(CO)_4\{(CH_3)_2C{=}C{=}C(CH_3)_2\}]$[45] or $[CpFe(CO)_2(allene)][BF_4]$ (allene = C_3H_3Me, $C_3H_2Me_2$, C_3Me_4).[26] The ^{19}F NMR spectrum of **2b** exhibits three signals for the three chemically inequivalent fluorine atoms in accordance with the C_s symmetry of the molecule. Three signals for the allene carbon atoms and three signals for the chemically inequivalent carbonyl carbon atoms are observed in the ^{13}C NMR spectrum taken at ambient temperature. The assignment of the signals of the carbon atoms of the allene ligand is straight forward due to characteristic coupling to the fluorine atoms. Only one signal of the carbonyl ligands can be assigned to the chemically equivalent axial carbonyl carbon atoms due to its much higher intensity. An assignment of the remaining two signals seems not to be possible. Substitution of two hydrogen atoms by fluorine in going from **2a** to **2b** results in a rigid structure of **2b** on the NMR time scale at ambient temperature.

The structure of the dinuclear iron complex **3** is based solely on the spectroscopic data. The mass spectrum exhibits a signal m/z 384 that corresponds to $Fe_2(CO)_7(H_2C{=}C{=}CF_2)$. The ^1H and ^{19}F NMR spectra exhibit AB patterns, and the ^{13}C NMR spectrum and the IR spectrum of **3** are consistent with the structure drawn in Scheme 1. The allene is η^3- coordinated to a

$Fe(CO)_3$ moiety and η^1-coordinated to a $Fe(CO)_4$ group and can be regarded as a 2-ferraallyl ligand. Thus the structure of **3** corresponds to that of the complex synthesized from $Fe_2(CO)_9$ and allene,[46] whose triphenylphosphane derivative was structurally characterized by X-ray crystallography.[47]

The ^1H, ^{19}F, ^{31}P, and ^{195}Pt NMR spectra of the platinum complex **4** depicted in Figure 7 are nicely resolved. The ^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ spectra exhibit the expected multiplicity for an A_2MNRSX-type spectrum and can be reproduced by simulation using LAOCOON.[48] The NMR spectroscopic data that can be extracted from the spectra are summarized in Table 5. Although differences in chemical shift values and coupling constants are large, the assignment of the ^{19}F and ^{31}P resonances to the individual atoms is not possible without ambiguity. Various platinum alkene and alkyne complexes with different substituents were reported but no assignment of the phosphorus resonances to the chemically inequivalent phosphane ligands were made.[49, 50]

The NMR spectra unambiguously demonstrate that the solid-state structure is also maintained in solution as the two protons are chemically equivalent and the fluorine and phosphorus atoms are nonequivalent. There is no evidence at all for another isomer. The $^{31}P\{^1H\}$ NMR spectrum of **4** remains unchanged up to 80 °C. At 100 °C, new signals of so far not characterized decomposition products appear. However, no broadening of the resonances of **4** could be observed and the spectrums remains nicely resolved. Thus **4** is rigid on the NMR time scale, even at 100 °C, both to propeller rotation and slipping of the metal complex fragment along the orthogonal π system of the allene.

In accordance with the solid state structures of **5** and **6** their ^{19}F NMR spectra exhibit two AB spectra for the four chemically nonequivalent fluorine atoms. Thus again no propeller rotation and no Berry pseudorotation is observed on the NMR time scale.

The mass spectrum of **7a** and **7b** show the signals of the molecular ions at m/z 272 and m/z 308, respectively. The ^1H NMR spectrum of **7a** exhibits a singlet at $\delta = 4.88$ for the cyclopentadienyl ligand, and signals at $\delta = 5.48$(s) and 6.23 (qua, $^4J(^1H,^{19}F) = 2$ Hz) for the methylene group. The ^{19}F NMR spectrum consists of a single resonance at $\delta = -60.7$ for the CF_3 group. The ^{13}C NMR spectrum exhibits signals for the cyclopentadienyl ligand ($\delta = 85.4$), the carbonyl ligands ($\delta = 214.7$) and the 3,3,3-trifluoroprop-1-en-2-yl ligand ($\delta = 127.8$, CF_3, $^1J(^{19}F,^{13}C) = 274$ Hz, $^3J(^1H,^{13}C) = 7.8$ Hz, $^3J(^1H,^{13}C) = 16.1$ Hz; 133.1, CH_2, $^3J(^{19}F,^{13}C) = 9.6$ Hz, $^1J(^1H,^{13}C) = 154.6$ Hz, $^1J(^1H,^{13}C) = 159.7$ Hz); 140.6 (C, $^2J(^{19}F,^{13}C) = 29.8$ Hz, $^2J(^1H,^{13}C) = 8.3$ Hz). Similarly, the 1,1,3,3,3-pentafluoroprop-1-en-2-yl ligand of **7b** gave rise to three signals in the ^{19}F NMR spectrum at $\delta = -50.0$ (dd, CF_3, $^4J(^{19}F,^{19}F) = 12$ Hz, $^4J(^{19}F,^{19}F) = 23$ Hz), -52.6 (CF_2, $^2J(^{19}F,^{19}F) = 47$ Hz, $^4J(^{19}F,^{19}F) = 23$ Hz) and -69.7 (CF_2, $^2J(^{19}F,^{19}F) = 47$ Hz, $^4J(^{19}F,^{19}F) = 12$ Hz), and in the ^{13}C NMR spectrum at $\delta = 66.2$ (C, $^2J(^{13}C,^{19}F) = 20$ Hz, $^2J(^{13}C,^{19}F = 35$ Hz, $^2J(^{19}F,^{13}C) = 81$ Hz), 128.5 (CF_3, $^1J(^{19}F,^{13}C) = 270$ Hz, $^3J(^{19}F,^{13}C) = 24$ Hz), 150.5 (CF_2, $^1J(^{19}F,^{13}C) = 266$ Hz, $^1J(^{19}F,^{13}C) = 315$ Hz,

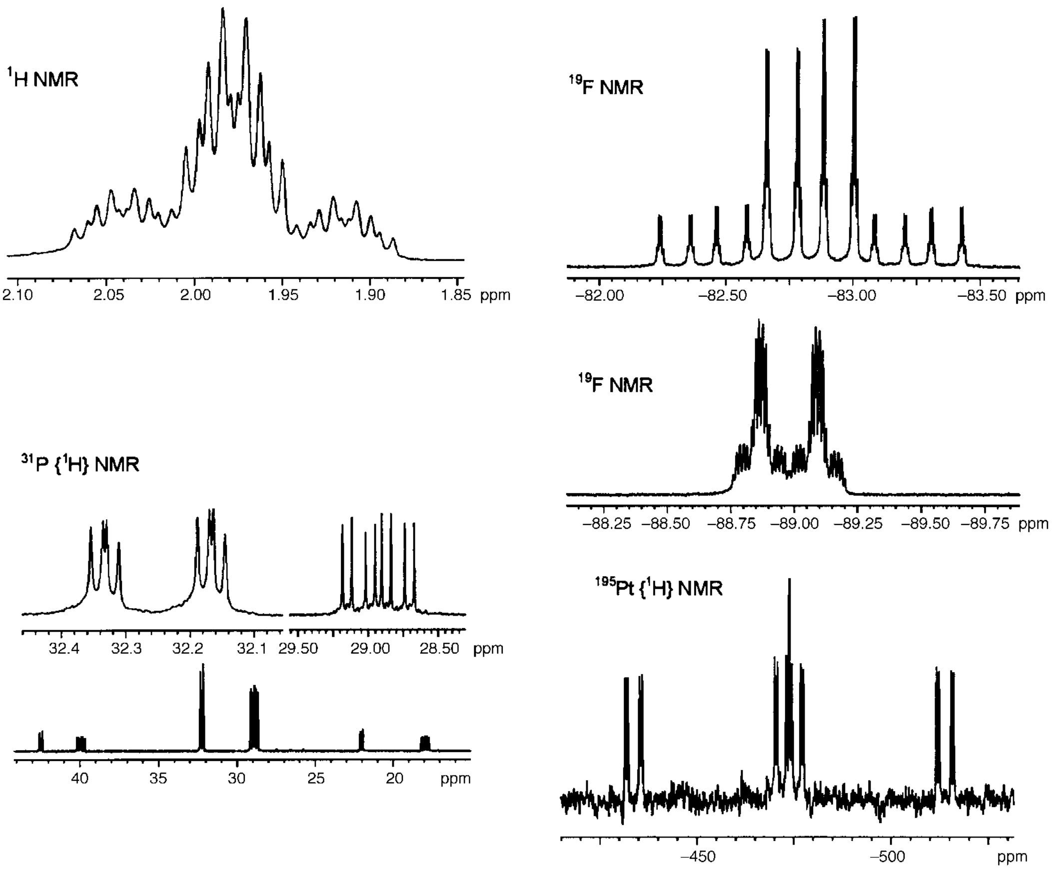


Figure 7. NMR spectra for **4**.

$^3J(^{19}F,^{13}C) = 9$ Hz), respectively. Signals of the cyclopentadienyl ligand and carbonyl ligand are observed at $\delta = 85.2$ and 213.2 in the ^{13}C NMR spectrum and at $\delta = 4.95$ in the ^1H NMR spectrum.

In accordance with the molecular structure the dinuclear molybdenum complex **9** exhibits four signals in the ^1H NMR spectrum ($\delta = 5.13$, 5H, Cp; 5.06, 5H, Cp; 4.15, 1H, CH_2, $^2J(^1H,^1H) = 3$ Hz and 2.72, 1H, CH_2, $^2J(^1H,^1H) = 3$ Hz, $^4J(^1H,^{19}F) = 3$ Hz) and an AB spectrum in the ^{19}F NMR spectrum ($\delta = -50.3$, 1F, CF_2; -93.6, 1F, CF_2, $^2J(^{19}F,^{19}F) = 138$ Hz).

Conclusion

The structural and spectroscopic data of the 1,1-difluoroallene complexes synthesized so far clearly demonstrate that the 1,1-difluoroallene ligand is solely coordinated to the metal center at the double bond substituted by the hydrogen atoms. With electron-rich metal-complex fragments, very stable complexes both with 1,1-difluoroallene and tetrafluoroallene were formed. An analysis of the vibrational spectroscopic data revealed that 1,1-difluoroallene and tetrafluorallene are stronger π-accepting ligands than the carbonyl ligand. Any attempt to coordinate the fluorine-substituted double bond to electron-poor metal-complex fragments has so far failed.

Experimental Section

General: All reactions were carried out under dry argon using standard Schlenk and vacuum techniques. Volatile materials were handled in a conventional glass vacuum line and amounts were determined by PVT techniques. Moisture-sensitive compounds were handled in an automatic dry box (Braun) under dry argon. ^1H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR spectra were recorded using a JEOL FX 90Q or JEOL LAMBDA 400 instrument with TMS or solvent signals (^1H, ^{13}C), $CFCl_3$ (^{19}F), H_3PO_4 (^{31}P) as standards. The ^{195}Pt NMR spectra were referenced equivalent to a frequency of 21.4 MHz with 100 MHz ^1H resonance frequency for TMS. Infrared spectra were taken on a Perkin Elmer 883, Nicolet 5SXC or a Bruker Vector 22 instrument. Raman spectra were recorded using a Bruker RFS 100. Mass spectra were obtained on a Varian MAT 711 (80 eV). $H_2C{=}C{=}CH_2$,[51] $H_2C{=}C{=}CF_2$,[10] $F_2C{=}C{=}CF_2$,[16] $[Cp^*Mn(CO)_3]$,[52] $[CpMn(CO)_3]$,[53] $[Fe_2(CO)_9]$,[54] $[(Ph_3P)_2Pt(C_2H_4)]$,[54] $[(cis\text{-}C_8H_{14})_2IrCl]_2$,[55] $[CpFe(CO)_2I]$,[54] $Ag[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$,[56] and $[CpMo(CO)_2]_2$[57] were prepared according to literature methods.

$[CpMn(CO)_2(\eta^2\text{-}CH_2{=}C{=}CH_2)]$ (1a): 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 using 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 hour. The solvent was removed under vacuum. The residue was dissolved in *n*-pentane and purified by chromatography (silica, *n*-pentane, 45 cm × 4 cm^2) followed by vacuum sublimation (25 °C, 10^{-3} mbar) to yield **1a** (320 mg; 50 %) as yellow crystals. M.p. 27 °C; MS (70 eV): *m*/*z*: 216 $[M]^+$, 188 $[M-CO]^+$, 160 $[M-2CO]^+$, 148 $[CpMnCO]^+$, 120 $[CpMn]^+$; elemental analysis calcd (%) for $C_{10}H_9MnO_2$ (216.1): C 55.58, H 4.20; found: C 55.00, H 4.20.

$[CpMn(CO)_2(\eta^2\text{-}CH_2{=}C{=}CF_2)]$ (1b): Preparation was analogous to **1a** as described above. Purification by chromatography (silica, *n*-pentane, 50 cm × 4 cm^2) followed by vacuum sublimation yielded **1a** (361 mg; 42.1 %) as yellow crystals. M.p. 39 °C; MS (70 eV): *m*/*z*: 252 $[M^+]$, 224 $[M-CO]^+$, 196 $[M-2CO]^+$, 148 $[CpMnCO]^+$, 120 $[CpMn]^+$; elemental analysis calcd (%) for $C_{10}H_7F_2MnO_2$ (252.1): C 47.64, H 2.80; found: C 47.58, H 3.11.

$[CpMn(CO)_2(\eta^2\text{-}CF_2{=}C{=}CF_2)]$ (1c): Compound **1c** was prepared in an analogous manner to **1a**. Purification by chromatography (silica, *n*-pentane, 50 cm × 4 cm^2) followed by vacuum sublimation yielded **1c** (312 mg; 34 %) as yellow crystals. M.p. 46 °C; ^{13}C NMR ($CDCl_3$): $\delta = 225.6$ (s, CO), 150.9 (dd, $^1J(C,F) = 274$ Hz, $^1J(C,F) = 297$ Hz; CF_2), 134.5 (dd, $^1J(C,F) = 302$ Hz, $^1J(C,F) = 316$ Hz; $MnCF_2$), 87.9 ($^1J(C,H) = 181$ Hz, Cp), 66.7 (d, $^2J(C,F) = 124$ Hz; $C = CF_2$), the assignment of the CF_2 groups is obtained from a ^{19}F-^{13}C correlation (HMQC) spectrum; MS (70 eV): *m*/*z*: 288 $[M]^+$, 232 $[M-2CO]^+$, 148 $[CpMnCO]^+$, 120 $[CpMn]^+$; elemental analysis calcd (%) for $C_{10}H_5F_4MnO_2$ (288.11): C 41.69, H 1.74; found: C 41.63, H 2.53.

$[Cp^*Mn(CO)_2(\eta^2\text{-}CH_2{=}C{=}CF_2)]$ (1d): Compound was prepared in an analogous manner to **1a**. Purification by chromatography (silica, *n*-pentane, 45 cm × 4 cm^2) followed by vacuum sublimation yielded **1d** (204 mg; 19.6 %) as yellow crystals. M.p. 63–64 °C (decomp); IR (KBr): $\tilde{\nu} = 2962$ m, 2926 w, 2340 w, 1976 s (CO), 1919 s (CO), 1847 w, 1813 m ($C{=}CF_2$), 1722 w, 1603 m, 1425 m, 1381 m, 1261 m, 1170 m, 1097 m, 1025 m, 935 w, 844 m, 803 m, 648 w, 639 w, 600 m, 581 w, 536 w, 475 w, 459 w, 387 w, 302 w cm^{-1}; MS (70 eV): *m*/*z* (%): 322 (22) $[M]^+$, 294 (21) $[M-CO]^+$, 266 (27) $[M-2CO]^+$, 190 (100) $[Cp^*Mn]^+$, 135 (76) $[Cp^*]^+$; elemental analysis calcd (%) for $C_{10}H_{17}F_2MnO_2$ (322.23): C 55.91, H 5.32; found: C 54.49, H 5.31.

$[Cp^*Mn(CO)_2(\eta^2\text{-}CF_2{=}C{=}CF_2)]$ (1e): Compound **1e** was prepared in a manner analogous to **1a**. Purification by chromatography (silica, *n*-pentane, 45 cm × 4 cm^2) followed by vacuum sublimation yielded **1e** (66 mg; 5.74 %) as yellow crystals. M.p. 81 °C (decomp); MS (70 eV): *m*/*z* (%): 358 (21) $[M]^+$, 302 (22) $[M-2CO]^+$, 246 (7) $[Cp^*Mn(CO)_2]^+$, 218 (25) $[Cp^*MnCO]^+$, 190 (100) $[Cp^*Mn]^+$, 135 (93) $[Cp^*]^+$.

$[(CO)_4Fe(\eta^2\text{-}CH_2{=}C{=}CF_2)]$ (2a): Nonacarbonyldiiron (1380 mg, 5.66 mmol) was suspended in dry dichloromethane (50 mL). 1,1-Difluoroallene (22.5 mmol) was condensed onto this mixture using a glass vacuum line. The suspension was stirred at ambient temperature until all of the enneacarbonyldiiron was dissolved. After the solution had been stirred for an additional 30 min, the compound was purified by fractional condensation under vacuum (10^{-3} mbar) through traps kept at 0, −25, and −196 °C. Compound **2a** (220 mg; 15.9 %) was collected in the trap kept at −25 °C as a yellow oil at ambient temperature. m.p. −12 °C; MS (70eV): *m*/*z*: 244 $[M]^+$, 216 $[M-CO]^+$, 188 $[M-2CO]^+$, 160 $[M-3CO]^+$, 132 $[M-4CO]^+$, 75 $[F_2C{=}C{=}CH]^+$, 65 $[Fe]^+$; Raman: $\tilde{\nu} = 2110$ m, 2042 w, 2005 w, 1814 vw cm^{-1}.

$[Fe_2(CO)_7(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_3H_2F_2)]$ (3): When a mixture such as that used for the synthesis of **2a** was allowed to react for three days, a further compound could be isolated by chromatography (silica/*n*-pentane). After removing most of the solvent of the second fraction under vacuum, crystallization at −78 °C yielded **3** (72 mg, 3 %) as orange crystals. MS (70 eV): *m*/*z* (%): 384 (1) $[M]^+$, 356 (3) $[M-CO]^+$, 328 (0.5) $[M-2CO]^+$, 300 (0.5) $[M-3CO]^+$, 244 (1) $[M-5CO]^+$, 216 (2) $[M-6CO]^+$, 188 (12) $[M-7CO]^+$, and smaller fragment ions.

$[(CO)_4Fe(\eta^2\text{-}CF_2{=}C{=}CF_2)]$ (2b): Compound **2b** was prepared in a manner analogous to that for **2a**. Purification by fractional condensation (10^{-3} mbar, 0 °C, −30 °C, −196 °C) yielded **2b** (130 mg; 16.3 %) as pale yellow crystals in the trap kept at −30 °C. M.p. −8 °C; $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, −40 °C): $\delta = 204.7$ (s; CO), 202.3 (s; CO), 200.6 (s; CO), 150.8 (s; CF_2), 129.8 (s; $FeCF_2$), 63.8 (s; $C{=}CF_2$); MS (70 eV): *m*/*z*: 280 (6) $[M]^+$, 252 (49) $[M-CO]^+$, 224 (22) $[M-2CO]^+$, 196 (34) $[M-3CO]^+$, 168 (100) $[M-4CO]^+$; elemental analysis calcd (%) for $C_7F_4FeO_4$ (279.92): C 30.04; found C 28.41.

$[(PPh_3)_2Pt(\eta^2\text{-}CH_2{=}C{=}CF_2)]$ (4): η^2-Ethenebis(triphenylphosphane)platinum (115 mg, 0.154 mmol) was dissolved in dichloromethane (20 mL). 1,1-Difluoroallene was added by condensation using a glass vacuum line. After stirring for 12 h at ambient temperature most of the solvent was removed under vacuum and n-pentane was added. Crystallization at −30 °C yielded **4** (23 mg, 19 %) as colorless crystals. M.p. >135 °C (decomp); MS (70 eV): *m*/*z*: 795 $[M]^+$, 719 $[M-C_3H_2F_2]^+$, and smaller fragment ions; IR (KBr): $\tilde{\nu} = 3052$ w, 2936 w, 1817 s, 1770 vs, 1586 w, 1571 vw, 1478 s, 1434 vs, 1325 vw, 1306 w, 1186 s, 1178 s, 1158 m, 1148 s, 193 s, 1071 w, 1028 w, 998 w, 914 w, 860 s, 854 s, 748 s, 742 s, 693 vs, 619 vw, 537 m, 511 vs, 448 m, 422 w cm^{-1}; elemental analysis calcd (%) for $C_{39}H_{32}F_2P_2Pt$ (795.68): C 58.87, H 4.05; found: C 57.86, H 3.81.

$[(PPh_3)_2IrCl(\eta^2\text{-}CH_2{=}C{=}CF_2)_2]$ (5) and $[(PPh_3)IrCl(\eta^2\text{-}CH_2{=}C{=}CF_2)_2]_2$ (6): $[(C_8H_{14})_2Ir(\mu_2\text{-}Cl]_2$ (500 mg, 0.56 mmol) and triphenylphosphane (292 mg, 1.11 mmol) were dissolved in dry toluene (50 mL) and stirred for an hour at ambient temperature. 1,1-Difluoroallene (18.3 mmol) was added by condensation using a glass vacuum line and the solution stirred for additional 16 h. After filtration through a short pad of silica the compounds were separated by a preparative TLC (n-pentane/dichloromethane 2:1). Crystallization of the second fraction at $-30\,^{\circ}C$ yielded **6** (18 mg, 2.5 %) as pale yellow crystals: ^{19}F NMR ($CDCl_3$): $\delta = -68.40$ (d, $^2J(F,F) = 79.5$ Hz, 2F; CF_2), -72.23 (d, $^2J(F,F) = 84.5$ Hz, 2F; CF_2), -89.15 (d, $^2J(F,F) = 79.5$ Hz, 2F; CF_2), -97.71 (d, $^2J(F,F) = 84.5$ Hz, 2F; CF_2).

Crystallization of the third fraction yielded **5** (27 mg, 2.7 %) as colorless crystals: ^{19}F NMR ($CDCl_3$): $\delta = -71.51$ (d, $^2J(F,F) = 79.5$ Hz, 1F; CF_2), -75.18 (d, $^2J(F,F) = 84.5$ Hz, 1F; CF_2), -92.28 (d, $^2J(F,F) = 79.5$ Hz, 1F; CF_2), -100.83 (d, $^2J(F,F) = 84.5$ Hz, 1F; CF_2); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$): $\delta = 150.4$ (s; CF_2), 145.6 (s; CF_2), 135.0, 133.3, 130.9, 129.3, 128.1, 127.1, 126.6 (m; PPh_3), 91.4 (t, $^3J(C,H) = 7.0$ Hz; $C{-}CF_2$), 87.4 (t, $^3J(C,H) = 4.8$ Hz; $C{-}CF_2$), 53.0 (t, $^1J(C,H) = 177.4$ Hz; CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -8.7$ (s; PPh_3).

Dicarbonyl(η^5-cyclopentadienyl)(η^1-3,3,3-trifluoroprop-1-en-2-yl)iron (7a): $[CpFe(CO)_2I]$ (959 mg, 3.15 mmol) and $AgBF_4$ (638 mg, 3.28 mmol) were dissolved in CH_2Cl_2 (40 mL). 1,1-Difluoroallene (9.4 mmol) was added by condensation using a glass vacuum line. The solution was stirred for two hours. The precipitate was removed by filtration and the solution was concentrated under vacuum. Purification by chromatography (n-pentane/silica 20 cm × 4 cm^2) and vacuum sublimation (10^{-3} mbar at $40\,^{\circ}C$) gave **7a** (312 mg, 36.2 %) as a deep yellow oil: ^1H NMR ($CDCl_3$): $\delta = 4.88$ (5H, s; Cp), 5.48 (1H, s; CH_2), 6.23 (1H, qua, $^4J(H,F) = 2$ Hz; CH_2); ^{19}F NMR ($CDCl_3$): $\delta = -60.72$ (CF_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 85.4$ (s; Cp), 127.8 (q, $^1J(C,F) = 274.2$ Hz; CF_3), 133.1 (q, $^3J(C,F) = 9.6$ Hz; CH_2), 140.6 (q, $^2J(C,F) = 29.8$ Hz; $C{=}CH_2$), 214.7 (s; CO); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$): $\delta = 214.8$ (s; CO), 140.6 (d, $^2J(C,H) = 8.6$ Hz; $C{=}CH_2$), 133.2 (dd, $^1J(C,H) = 154.6$, 159.6 Hz; CH_2), 127.8 (dd, $^3J(C,H) = 7.8$, 16.1 Hz; CF_3), 85.1(dm, $^1J(C,H) = 180.7$Hz; Cp); IR (KBr): $\tilde{\nu} = 3124$ w, 3065 w, 2957 w, 2922 w, 2853 w, 2029 vs (CO), 1974 vs (CO), 1863 w, 1793 w, 1706 w, 1624 w, 1587 m ($C{=}CH_2$), 1432 m, 1421 m, 1408 m, 1395 m, 1263 m, 1242 s, 1136 s, 1102 s, 1076 s, 1017 w, 1003 w, 921 m, 846 m, 837 m, 813 m, 735 m, 672 m, 630 s, 607 m, 590 m, 571 m, 504 w, 463 w cm^{-1}; IR (*n*-pentane): $\tilde{\nu} = 2037$ vs (CO), 1987 vs (CO), 1589 ($C{=}CH_2$) cm^{-1}; MS (70 eV): m/z (%): 272 (73) $[M]^+$, 244 (59) $[M - CO]^+$, 216 (90) $[M - 2CO]^+$, 177 (14) $[CpFe(CO)_2]^+$, 149 (9) $[CpFeCO]^+$; elemental analysis calcd (%) for $C_{10}F_3FeH_7O_2$ (272.01): C 44.16, H 2.59; found: C 41.77, H 3.05.

Dicarbonyl(η^5-cyclopentadienyl)(η^1-1,1,3,3,3-pentafluoroprop-1-en-2-yl)iron (7b): Compound **7b** was prepared in an analogous manner to **7a**. Purification by chromatography (*n*-pentane/silica 20 cm × 4 cm^2) and vacuum sublimation (10^{-3} mbar at $60\,^{\circ}C$) yielded **7b** (329 mg; 40.6 %) as yellow crystals. M.p. $74\,^{\circ}C$; ^1H NMR ($CDCl_3$): $\delta = 4.95$ (Cp); ^{19}F NMR ($CDCl_3$): $\delta = -50.03$ (dd, $^4J(F,F) = 12$ Hz, $^4J(F,F) = 23$ Hz, 3F; CF_3), -52.60 (qd, $^4J(F,F) = 23$ Hz, $^2J(F,F) = 47$ Hz, 1F; CF_2), -69.73 (qd, $^4J(F,F) = 12$ Hz, $^2J(F,F) = 47$ Hz, 1F; CF_2); ^{13}C NMR ($CDCl_3$): $\delta = 213.3$ (s; CO), 150.5 (ddq, $^1J(C,F) = 266$ Hz, $^1J(C,F) = 315$ Hz, $^3J(C,F) = 8.9$; CF_2), 128.5 (dq, $^1J(C,F) = 270$ Hz, $^3J(C,F) = 24$ Hz; CF_3), 85.2 (dm, $^1J(C,H) = 182$ Hz; Cp), 66.2 (ddq, $^2J(C,F) = 80$ Hz, $^2J(C,F) = 35$ Hz, $^2J(C,F) = 20$ Hz; $C - CF_2$); $^{13}C\{^{19}F\}$ NMR ($CDCl_3$): $\delta = 213.2$ (s; CO), 150.7 (s; CF_2), 128.5 (s; CF_3), 85.2 (dm, $^1J(C,H) = 182$ Hz; Cp), 66.2 (s; $C - CF_3$); IR (KBr): $\tilde{\nu} = 3218$ w, 2037 vs (CO), 1989 vs (CO), 1812 m, 1679 s ($C{=}CF_2$), 1360 m, 1307 m, 1263 vs, 1213 s, 1157 w, 1119 s, 1096 s, 1019 w, 1006 w, 967 vs, 906 s, 852 s, 717 m, 654 w, 615 m, 601 m, 586 m, 556 m, 498 w, 454 cm^{-1} w; IR (CH_2Cl_2): $\tilde{\nu} = 2042$ vs (CO), 1992 vs (CO), 1681 s ($C{=}CF_2$) cm^{-1}; IR (n-pentane): $\tilde{\nu} = 2047$ vs (CO), 2002 vs (CO), 1685 m ($C{=}CF_2$) cm^{-1}; MS (70 eV): m/z: 308 (12) $[M]^+$, 280 (9) $[M - CO]^+$, 252 (21) $[M - 2CO]^+$, 187 (21) $[FeC_3F_5]^+$, 177 (12) $[CpFe(CO)_2]^+$, 140 (100) $[CpFeF]^+$; elemental analysis calcd (%) for $C_{10}H_5F_5FeO_2$ (307.99): C 39.00, H 1.64; found: C 38.83, H 2.58.

$[Cp_2Mo_2(CO)_4(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-}C_3H_2F_2)]$ (9): An ampoule (outer diameter 9 mm) was charged with bis[dicarbonyl(η^5-cyclopentadienyl)molybdenum] (110 mg, 0.253 mmol). Dichloromethane (5 mL) and 1,1-difluoroallene were added by condensation using a glass vacuum line. The ampoule was flame sealed under vacuum. After the ampoule had been allowed to warm to ambient temperature, the progress of the reaction was monitored by ^{19}F NMR spectroscopy. After about 60 min by-products started to be formed and the ampoule was kept at $-78\,^{\circ}C$ for 12 h. The crystals were seperated by centrifugation keeping the low temperature. The ampoule was placed upside down into liquid nitrogen to freeze the remaining solvent. After the ampoule had been opened, crystals (42 mg) of different shapes were isolated. The needle-shaped crystals were found to be bis[tricarbonyl(η^5-cyclopentadienyl)molybdenum] by comparison with IR data, whereas the hexagonal platelets were compound **9**. By sorting the crystals using a microscope a few mg of **9** could be isolated which were sufficient to obtain the spectroscopic data. ^1H NMR ($CDCl_3$): $\delta = 2.72$ (dd, $^2J(H,H) = 3$ Hz, $^4J(H,F) = 3$ Hz, 1H; CH_2), 4.15 (d, $^2J(H,H) = 3$ Hz, 1H; CH_2), 5.06 (s, 5H; Cp), 5.13 (s, 5H; Cp); ^{19}F NMR ($CDCl_3$): -50.3 (d, $^2J(F,F) = 138$ Hz, 1F; CF_2), -93.6 (d, $^2J(F,F) = 138$ Hz, 1F; CF_2); IR (KBr): $\tilde{\nu} = 1966$ s, 1927 vs, 1889 vs, 1860 cm^{-1} s; MS (70 eV): m/z: 514 $[M]^+$, 458 $[M - 2CO]^+$, 430 $[M - 3CO]^+$, 402 $[M - 4CO]^+$ and smaller fragment ions; elemental analysis calcd (%) for $C_{17}H_{12}F_2Mo_2O_4$ (510.16): C 39.45, H 2.52; found: C 40.02, H 2.37.

Crystallography: Crystal data and details of the structure determinations are presented in Tables 1 and 2. The intensity data were collected using a Bruker AXS Smart (**4, 5**, **6** and **8**), STOE (**1c**, **1d**), ENRAF NONIUS CAD4 (**1a**, **1b**) and Siemens (**9**) diffractometer, respectively. Corrections for Lorentz polarization and absorption effects[58, 59] were applied to the data. The structures were solved by Patterson and direct methods (SHELXS-97)[60], respectively. Details on the data collection structure refinement are summarized in Tables 1 and 2. Hydrogen atoms of the allene ligand were found in subsequent difference Fourier maps for **1a**, **b, 1d** (modification 2), **2a**, **4**, and **6**, and refined isotropically. Further hydrogen atoms were refined in calculated positions using isotropic thermal parameter (1.2 U_{eq}(C) and 1.5 U_{eq}(C) for methyl). Anisotropic thermal parameters were applied to all non hydrogen atoms. Refinement for all structures on F^2 were achieved using the SHELXL-97 system.[60] Crystals of **6** contain a solvent accessible area of about 166 Å^3, which is filled by an unknown disordered solvent molecule. The squeeze option of the program PLATON[61] indicates 55 electrons in this area that could correspond to dichloromethane or chloroform. The structure factors of the reflections were corrected using the sqeeze option. This allowed the detection of the hydrogen atoms of the allene ligand in the difference Fourier map and an isotropic refinement. The program packages SHELXTL[62] and WINGX[63] were used during the structure determinations. Plots of the molecules were made using ORTEP for Windows.[64] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-117442 (**1a**), CCDC-117443 (**1b**), CCDC-117444 (**1c**), CCDC-168925 (**1d**) (modification 1), CCDC-168926 (**1d**) (modification 2), CCDC-168927 (**2a**), CCDC-168928 (**2b**), CCDC-168929 (**4**), CCDC-168930 (**5**), CCDC-168931 (**6**), CCDC-168932 (**8**), and CCDC-168933 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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