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ORIGINAL PAPER

Molecular and Crystal Structures of Some Fluorocymantrenes

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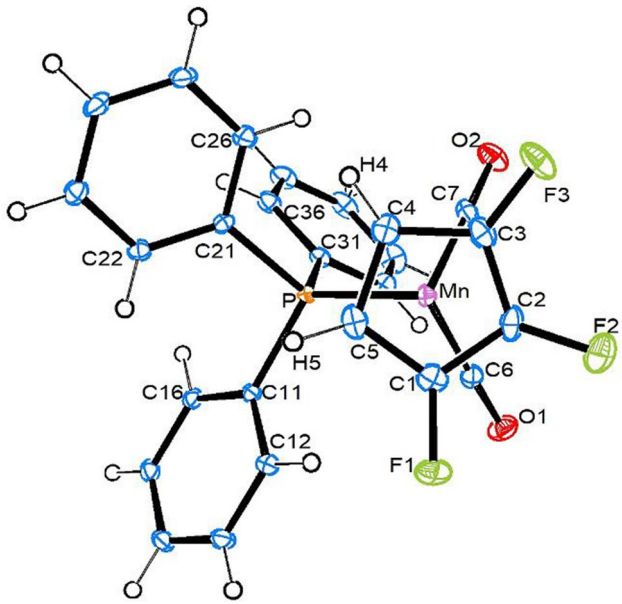
Abstract

The crystal and molecular structures of the fluorocymantrenes $[(C_5H_4F)Mn(CO)_3]$ and $[(C_5H_{5-n}F_n)Mn\ (CO)_2(PPh_3)]$ (n = 1–3) have been studied. The influence of the phosphine for carbonyl substitution on the bond parameters is larger than the influence of the increasing fluorine content. In most cases the Mn → P vector is in a transoid position relative to the fluorine substituents, and therefore the conformational parameters of the PPh_3 propeller are in these cases very similar. The crystal structures show many intermolecular C–H···O hydrogen bonds and only very few C–H···F hydrogen bonds.

Graphic Abstract

The influence of the phosphine for carbonyl substitution on the bond parameters of the fluorocymantrenes $[(C_5H_4F)Mn(CO)_3]$ and $[(C_5H_{5-n}F_n)Mn\ (CO)_2(PPh_3)]$ (n = 1–3) is larger than the influence of the increasing fluorine content.



Keywords Cymantrene · Fluorocyclopentadienyl complexes · Triphenylphosphine · Conformational analysis

Introduction

Fluoroorganic compounds continue to be of great importance in many areas of modern applied chemistry, e.g. materials chemistry [1], biomolecular chemistry [2] or medicinal chemistry [3, 4]. At the same time, metallocenes and related organometallic compounds have left the labs of

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fundamental research and dived into the realm of applied chemistry, particularly medicinal chemistry [5–7]. Thus, it was not surprising that recently the idea was born, to join these two important areas [8]. This became possible (at least for the compounds bearing a fluorine atom bound directly to the cyclopentadienyl ring) with our introduction of *N*-fluorobenzenesulfonimide (NFSI) as electrophilic fluorination reagent in ferrocene chemistry 10 years ago [9]. Before 2011, fluorometallocenes were not more than a lab curiosity, being obtainable either only in very low yields [10, 11] or by experimental techniques unavailable to most labs [12–14]. Most of the experimental work on fluorometallocenes after 2011 was done with the ferrocene system, mainly by the group of Erb at the University of Rennes [8, 15, 16]. Although fluorocymantrene was the very first fluorometallocene prepared [10], there were no other reports on it until very recently [17]. This seems astonishing, considering the still active research on cymantrene derivatives in cancer research on one hand [18, 19], and the importance of ^{18}F-labeled arenes in Positron Emission Tomography (PET) [4]. This imbalance in general research is also mirrored in the crystal structure domain. There are 43 entries of fluorometallocenes in the Cambridge Structure Database [20] (CSD-version 5.42, accessed on June 10, 2021), of which 39 are derivatives of ferrocene (all studied between 2011 and 2020) and three of ruthenocene (all reported in the 1990s). Here we report our crystal structure determinations of $[(C_5H_4F)Mn(CO)_3]$ (**1**) and $[(C_5H_{5-n}F_n)Mn(CO)_2(PPh_3)]$ (n = 1–3; **2–4**).

Experimental

The synthesis and characterization of all compounds was published elsewhere recently [17]. Although the spectroscopic data have already been reported, the NMR data are collected here once again:

^{1}H-NMR

1: δ = 4.71 m, 4.45 m; **2**: δ = 7.46–7.33 m, 4.23 m, 3.94 m; **3**: δ = 7.66–7.20 m, 4.31 m, 3.48 m; **4**: δ = 3.44 m.

^{19}F-NMR

1: δ = − 165.0; **2**: δ = − 171.1; **3**: δ = − 188.0; **4**: δ = − 187.8 (d, 18 Hz), − 203.7 (td, 18 Hz/4 Hz).

^{31}P-NMR

2: δ = 91.6; **3**: δ = 88.50; **4**: δ = 87.8.

^{13}C-NMR

1: δ = 223.9, 143.9 (d, 276 Hz), 75.9 (d, 4 Hz), 66.8 (d, 13 Hz).

2: δ = 231.4, 142.9 (d, 271 Hz), 137.7 (d, 41 Hz), 133.1 (d, 11 Hz), 128.3 (d, 9 Hz), 129.8, 76.1 (d, 4 Hz), 67.5 (d, 13 Hz).

3: δ = 230.5, 137.1 (d, 42 Hz), 133.1 (d, 10 Hz), 128.4 (d, 9 Hz), 129.9, 127.6 (dd, 272 and 11 Hz), 67.7, 62.7.

4: δ = 229.0, 136.6 (d, 42 Hz), 133.1 (d, 11 Hz), 128.5 (d, 10 Hz), 130.1 (d, 2 Hz), 123.8 (ddd, 276/8/4 Hz), 114.7 (dt, 274/11 Hz), 53.2 (dd, 8/5 Hz).

The pre-purified compounds obtained after column chromatography were dissolved at r.t. in the minimum amount of an 85:15 mixture of petroleum ether/diethyl ether and transferred in an open vial to a refrigerator operating at + 5 °C. After standing for several days and slow evaporation of the solvent, yellow crystals were obtained.

Crystals of **1** and **3** were measured on an Oxford XCALIBUR 2 diffractometer and crystals of **2** and **4** on a Bruker D8 Venture diffractometer. The obtained datasets were examined by the WINGX program suite [21–24]. The structure of **1** was solved with SIR97 and the others with SHELXT. Refinements of all structures were performed with SHELXL 2018/3. Table 1 presents general experimental details of the structure determinations.

Special Remarks on the Structure Refinements

The four hydrogen atoms of compound **1** were localized on difference Fourier maps. Their positions were refined, with U_{iso} values fixed at 1.2 times the equivalent U_{iso} values of the attached carbon atoms, and restrained to be all of the same CH bond length.

All hydrogen atoms of compound **2** were geometrically positioned, using the standard riding model with all U_{iso} fixed at 1.2 times the equivalent U_{iso} values of the attached carbon atoms. In both independent molecules there was found additional electron density next to one cyclopentadienyl C–H bond, each. In both molecules this occurred in relative 3-position to the first F-atom (hydrogen H5 in molecule A and H35 in molecule B). It was possible to refine a H/F disorder model for the atom pair H5/F1A to a relative occupancy 0.869/0.131, and for the pair H35/F2A to a relative occupancy 0.97/0.03 (and vice versa for H3/F1 and H33/F2, respectively; see also "Discussion" section on this issue).

The original data collection of compound **3** was performed on a monoclinic *I* cell with $a = 17.1994(5)$, $b = 13.4797(4)$, $c = 18.5495(5)$ Å and $\beta = 100.184(3)°$. Examination by PLATON suggested transfer to space group

Table 1 Experimental data of the crystal structure determinations

	1	2	3	4
Empirical formula	$C_8H_4FMnO_3$	$C_{25}H_{19}FMnO_2P$	$C_{25}H_{18}F_2MnO_2P$	$C_{25}H_{17}F_3MnO_2P$
Formula weight	222.05	456.31	474.30	492.29
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$C2/c$
Temperature (K)	123	100	173	100
Crystal size (mm)	0.22 × 0.21 × 0.12	0.10 × 0.07 × 0.04	0.43 × 0.30 × 0.23	0.10 × 0.07 × 0.04
a (Å)	10.8503 (6)	9.3676 (15)	22.9584 (9)	22.7937 (6)
b	6.9206 (3)	13.524 (2)	13.4797 (4)	13.6951 (3)
c	11.5547 (7)	17.103 (3)	17.1994 (5)	18.4224 (4)
α (°)		85.847 (6)		
β	114.182 (7)	74.738 (5)	127.323 (2)	132.255 (1)
γ		89.055 (6)		
V (Å^3)	791.51 (8)	2084.8 (6)	4232.8 (3)	4256.49 (18)
Z	4	4	8	8
μ (mm^{-1})	1.65	0.74	0.74	0.74
T_{min}, T_{max}	0.973, 1	0.698, 0.746	0.964, 1	0.707, 0.746
Measured/independent reflect	4864/1797	26,490/12,714	15,135/5244	32,941/4873
R_{int}	0.031	0.032	0.029	0.028
Observed reflect. [I > 2σ(I)]	1567	10,079	3940	4387
Data/restraints/parameters	1797/18/130	12,714/7/549	5244/4/285	4873/1/290
GOOF	1.08	1.10	1.04	1.10
R1, wR2 [I > 2σ(I)]	0.062, 0.174	0.058, 0.182	0.037, 0.089	0.032, 0.080
R1, wR2 [all data]	0.070, 0.182	0.080, 0.251	0.056, 0.102	0.036, 0.082
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, − 2.19	1.02, − 1.99	0.49, − 0.43	0.83, − 0.49
CCDC-#	2,090,559	2,090,560	2,090,561	2,090,562

C2/c with the cell parameters given in Table 1. All hydrogen atoms were geometrically positioned, using the standard riding model with all U_{iso} fixed at 1.2 times the equivalent U_{iso} values of the attached carbon atoms. One fluorine atom was disordered over the two α positions and this was refined as a 75:25 disorder on F2A/F5B (and on the H atoms H2/H5 vice versa, using some length fixing restraints. (see also "Discussion" section on this issue).

All hydrogen atoms of compound **4** were geometrically positioned, using the standard riding model with all U_{iso} fixed at 1.2 times the equivalent U_{iso} values of the attached carbon atoms.

Results and Discussion

Molecular Structure of [(C_5H_4F)Mn(CO)$_3$], 1

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Figure 1 shows the molecular structure. Important bond lengths and angles are collected in Table 2. The C1–F bond is in an eclipsed position to the C7–O2 carbonyl group, while the carbonyl group C6–O1 bisects the ring C2–C3 bond. This situation is very similar to the situation found in [(C_5H_4I)Mn(CO)$_3$] [25]. There are three structure reports on compounds containing a C_5H_4F ligand: [(C_5H_4F)Fe(C_5H_5)]

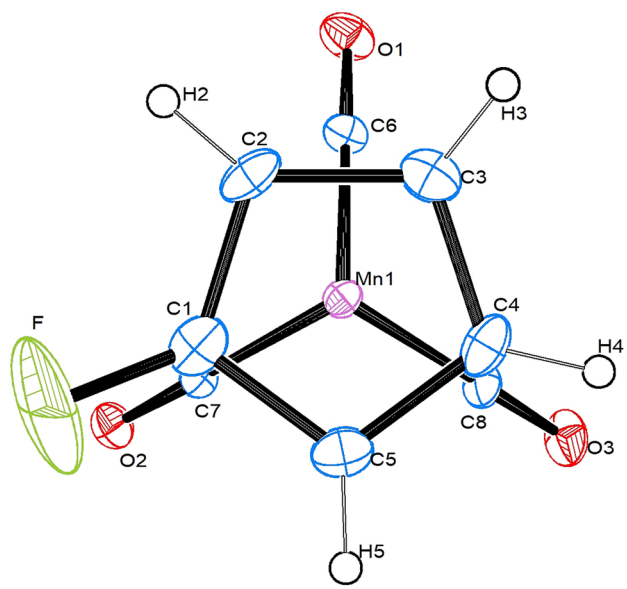


Fig. 1 Top view of compound **1**. 30% probability ellipsoids

Table 2 Important bond parameters of 1–4 and some related compounds

compd	C–F [Å]	Mn–P [Å]	Mn–Ct [Å]	OC–Mn–CO [°]	DCp-F [Å]	Reference
1	1.280(11)	–	1.768(3)	92.5(2) 92.8(3) 91.9(2)	0.038(9)	This work
2 (mol. A)	1.326(4) {1.260(15)}	2.2352(8)	1.7734(17)	90.93(13)	0.100(3)	This work
2 (mol.B)	1.322(5) {1.30(5)}	2.2454(9)	1.7742(19)	92.01(13)	0.091(3)	This work
3	1.342(4) 1.303(3)	2.2375(8)	1.7677(11)	93.59(10)	0.067(2) 0.090(2)	This work
4	1.373(3) 1.364(4) 1.334(2)	2.2396(7)	1.7638(9)	93.86(9)	0.091(1) 0.080(1) 0.088(1)	This work
$CpMn(CO)_3$	–	–	1.772	91.85(11) 92.63(11) 91.94(12)	–	[34]
$CpMn(CO)_2PPh_3$	–	2.236(3)	1.775	92.42(41)	–	[35]

"Ct" is the centroid of the cyclopentadienyl ring. DCp-F is the distance of the fluorine atoms from the plane of the cyclopentadienyl ring

[16, 26], $[(C_5H_4F)_2Fe]$ [23] and $[(C_5H_4F)Ru(C_5Me_5)]$ [14]. The two reports on monofluoroferrocene have two different monoclinic unit cells. Whereas Inkpen et. al. report on a highly disordered structure, which prevented any meaningful geometric analysis, the report by Tazi et al. contains no structure discussion at all (however, inspection of the cif-file that can be obtained from the Cambridge Structural Database shows also severe disorder problems). In addition, the ruthenium compound shows severe disorder with the fluorine atom spread over three positions. Apparently the only compound without any structure solution problems is the 1,1′-difluoroferrocene. A C–F bond length of 1.357(3) Å is reported for this compound, while for the major components of the two mentioned disordered structures C–F bond lengths of 1.344 Å and 1.265(8) Å are given. Thus the C–F bond in **1** is at the shorter end of the observed distances. There are three intermolecular C–H···O bonds: all three carbonyl oxygen atoms accept hydrogen bonds from H atoms H4 (O1 and O3) and H2 (O2). The individual molecules are linked in all directions via these interactions (Figure S1 and Table S1 of the Supporting information).

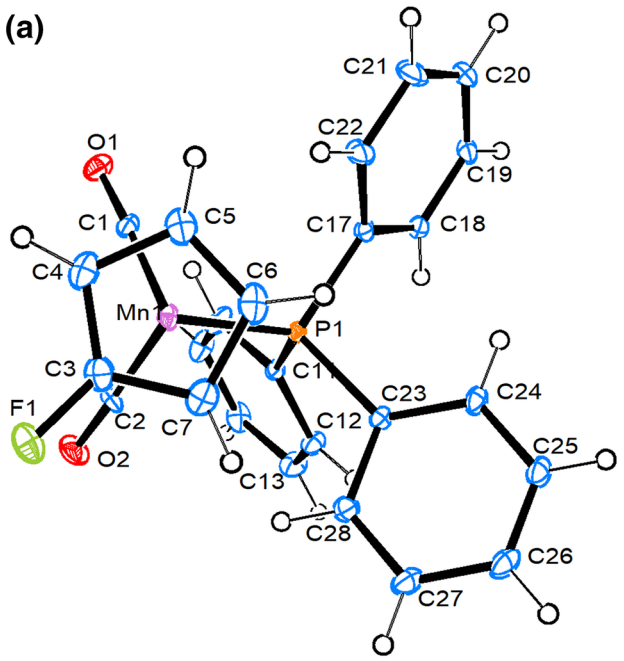
Molecular Structure of $[(C_5H_4F)Mn(CO)_2(PPh_3)]$, 2

Compound **2** crystallizes in the triclinic space group $P^{-}1$ with two independent molecules in the unit cell. Figure 2 shows a top view of both molecules.

In both molecules the fluorine atom is disordered over two positions at C3/C6 and C33/C35, with one orientation clearly dominating (87% in A, 97% in B). An alternative interpretation (and quite possible regarding the contamination of **2** with **3** even after chromatography, [17] of the disorder would be co-crystallization of **2** and **3**. Refinement of such a situation gave slightly worse R-values. However, this interpretation was discarded because of the fact, that **3** crystallizes in a different Bravais lattice. The two independent molecules could be transferred into each other by a cyclopentadienyl ring rotation of ca. 210° around an axis through the cyclopentadienyl centroid and the manganese atom. Thus while the C3–F1 bond is nearly eclipsed with the C2–O2 carbonyl bond (torsion C3–Ct1–Mn1–C2 = − 11.43°) in **A**, the C33–F2 bond in **B** is eclipsed with the Mn2–P bond (torsion C33–Ct2–Mn2–P2 = 6.96°). In molecule **A**, the Mn1–P1 bond is nearly eclipsed with the C6–H6 bond (torsion C6–Ct1–Mn1–P = 13.00°). The C–F bonds in both molecules are identical within 1σ and substantially longer than in compound **1**. The distances from manganese to the cyclopentadienyl ring centroids are also identical in both molecules and slightly longer (ca. 2σ) than in **1**. However, the Mn2–P2 bond is significantly longer (> 10σ) than Mn1–P1, which is most likely due to the eclipsed C–F bond. Both molecules form a large number of C–H···F (two, both involving atom F2) and C–H···O (nine, with O1 accepting even four and O31 three) hydrogen bonds (Figure S2 and Table S1 of the Supporting information). The conformational analysis of the PPh_3 "propeller" will be discussed below.

Molecular Structure of $[(C_5H_3F_2)Mn(CO)_2(PPh_3)]$, 3

Compound **3** crystallizes in the monoclinic space group *C*2/*c* with one independent molecule in the asymmetric unit. Figure 3 shows a top view of the structure.



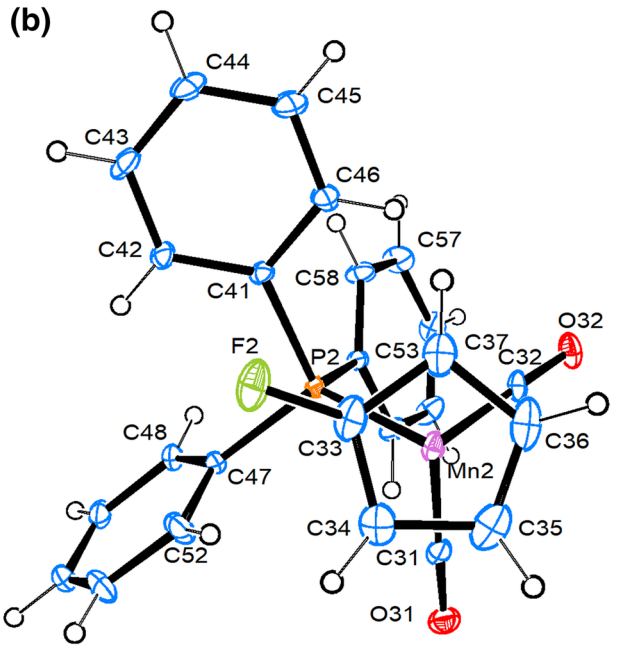


Fig. 2 **a** (left) Top view of compound **2**, molecule A; **b** (right) top view of compound **2** molecule B. 30% probability ellipsoids

Fluorine atom F2 is disordered over two positions (at carbon atoms C2 and C5), with relative populations of 75 and 25%. An alternative interpretation of this disorder would be co-crystallization of **3** and **4**, which should be possible, since both compounds crystallize in the same space group with very similar cell parameters. Refinement under this assumption gave an approximate 2:1 ratio of **3** and **4**, but also worse

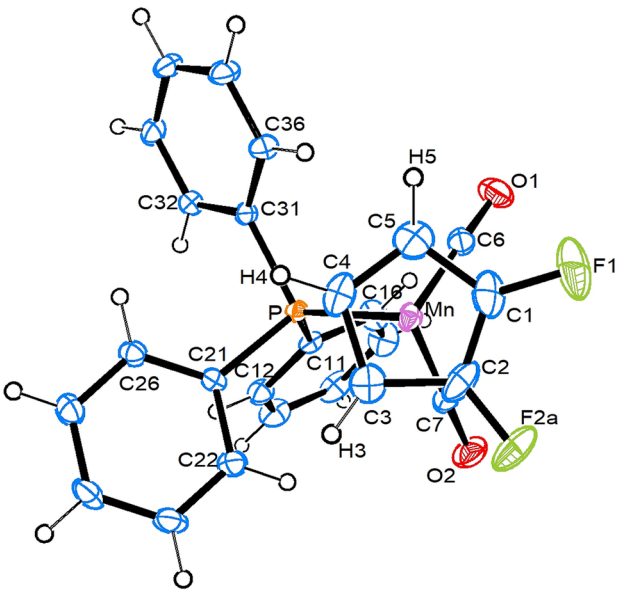


Fig. 3 Top view of the molecular structure of compound **3**. 30% probability ellipsoids

R1 and wR2 values. This model was therefore discarded. One C–F bond (C1–F1) is nearly in trans position to the Mn–P vector (torsion C1–Ct–Mn–P = – 159.63°), while the other C–F bond (major orientation) nearly eclipses with the C7–O2 bond (torsion C2–Ct–Mn–C7 = 11.91°). The C1–F1 bond is significantly longer (> 10σ) than C2–F2A. Although it cannot be excluded, that this effect is "real", it might just be an artefact of an improperly treated disorder F2A/H2 (at the same time, the C5–F5B bond is much too short, which is certainly due to the disorder F5B/H5). There is only one other structure report of a compound containing a $C_5H_3F_2$ ligand, i.e. $[(C_5H_3F_2)Ru(C_5Me_5)]$ [14]. In this compound the two C–F bond lengths were also very different, showed however relatively large standard deviations: 1.311(14) and 1.227(18) Å. No discussion/ interpretation of this difference was presented.

In the crystal structure, molecules of **3** form sheets parallel to the *ab* plane via C34–H34···F1 and C13–H13···F2A hydrogen bonds. These sheets are connected in *b* and *c* direction via three C–H···O hydrogen bonds. (Table S1 and Figure S3 of the Supporting Information). The conformational analysis of the PPh_3 "propeller" can be found below.

Molecular Structure of $[(C_5H_2F_3)Mn(CO)_2(PPh_3)]$, 4

As mentioned above, compound **4** also crystallizes in the monoclinic space group *C*2/*c* with one molecule in the asymmetric unit. Figure 4 shows a top view of the structure.

The structure is rather similar to the structure of **3**. The bond C2–F2 is nearly in trans-position to the Mn–P bond (torsion C2–Ct–Mn–P = 161.75°), while C3–F3 eclipses

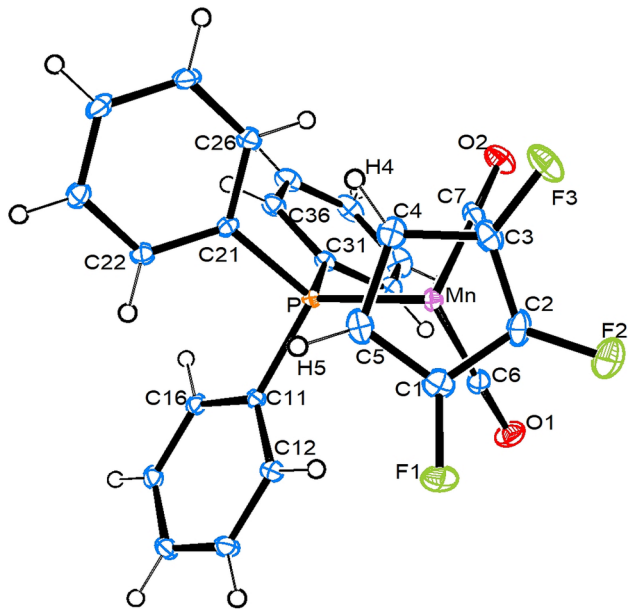


Fig. 4 Top view of compound **4**. 30% probability ellipsoids

the C7–O2 bond (torsion C3–Ct–Mn–C7 = − 9.10°). The Mn–C6–O1 bond bisects the C1–C2 bond of the cyclopentadienyl ring. The bonds C1–F1 and C2–F2 are identical within 2σ and the longest C–F bonds observed in this study. The third bond is substantially shorter, as was also observed in the structure of **3** for the C–F bond eclipsed to a C–O bond.

All C–F bonds are involved in hydrogen bonding (intermolecular C15–H15···F1, C14–H14···F2, C35–H35···F3 and intramolecular C12–H12···F1), creating chains along the *bc* diagonal that are cross-linked perpendicular to this direction (Table S1 and Fig. 5). Additionally, there is also a system of C–H···O hydrogen bonds that connects the molecules in *b* direction (Table S1 and Fig. S4).

Although there are apparently "channels" in this structure, careful analysis by PLATON shows that there are no solvent accessible voids. The discussion of the conformational analysis of the PPh_3 ligand can be found in the next chapter.

Conformational Analysis of the PPh_3 Ligands in 2–4

There has been a controversy for quite a long time about which parameters are the most important for the conformational parameters in [(Arene)LL'M(PPh_3)] complexes [27–33]. For the following discussion, we follow the definitions and arguments of the Brunner group. For better understanding, Fig. 6 shows a wireframe projection down the P → Mn vector in compound **4** (corresponding presentations of the other compounds can be found in the Supporting Information).

The "propeller angle" τ_j is defined by the absolute value of the torsion angle $^{out}C_o(j)$–$C_i(j)$–P–Mn; the "gauche angle" ρ_j by the absolute value of the torsion angle Ct–Mn–P–$C_i(j)$

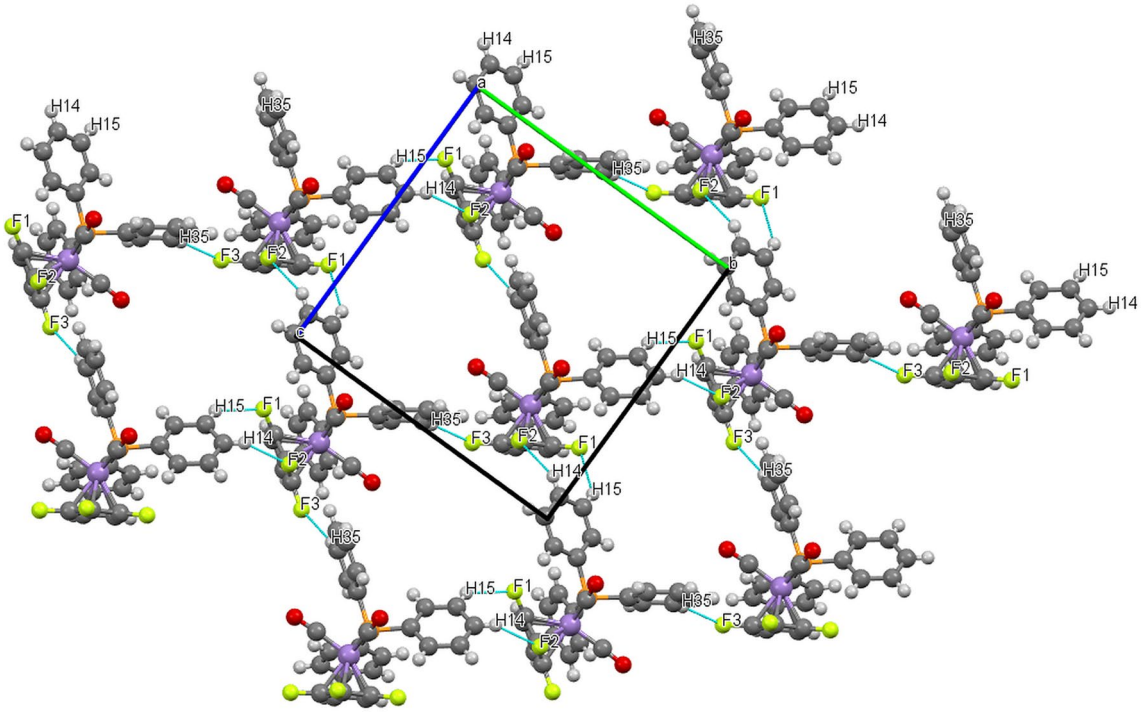


Fig. 5 Packing diagram (MERCURY) of **4** viewed along *a*

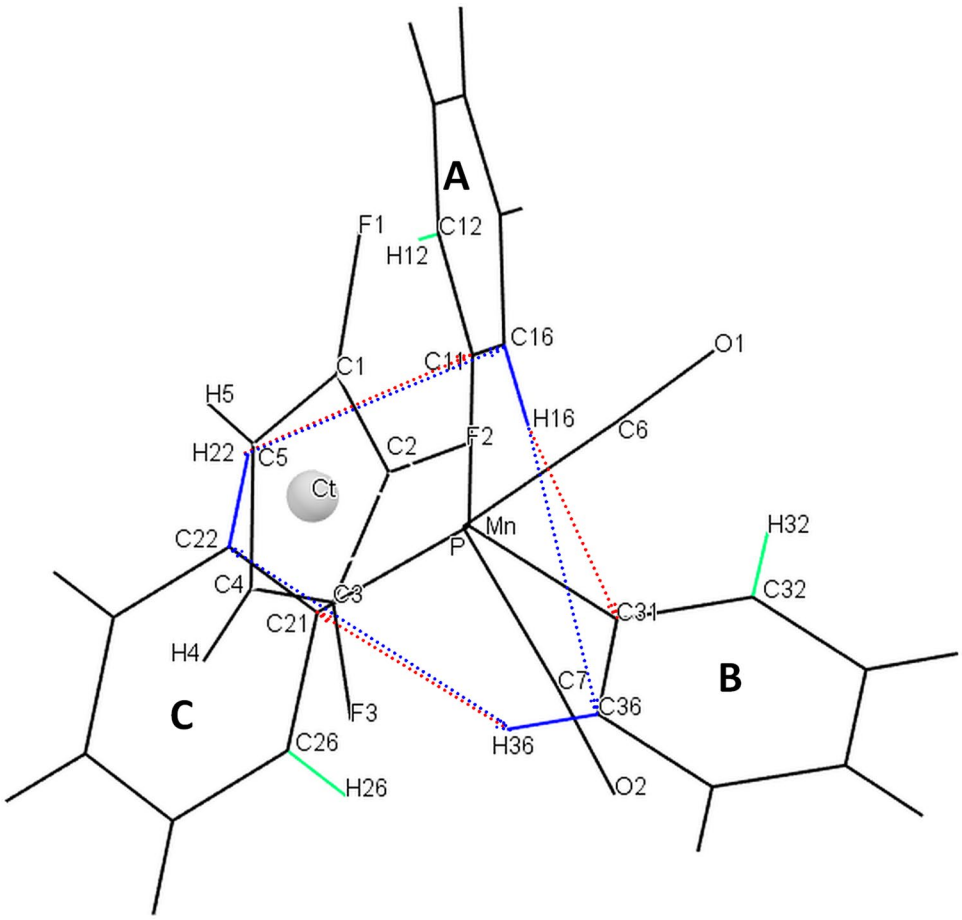


Fig. 6 Wireframe projection along the P → Mn vector in compound **4**

and φ_j is the interplanar angle between the plane of the cyclopentadienyl ring and phenyl ring "j". "j" stands either for "A", "B" or "C". For every phenyl ring there is one ipso carbon $C_i(j)$ and two ortho carbons, $^{out}C_o(j)$ and $^{in}C_o(j)$. "out" and "in" refer to the relative positions of these carbon atoms towards the plane of the three ipso carbon atoms: "in" lies between the three phenyl rings of the propeller, "out" on the side closer to the metal atom. In Fig. 6, the three $^{in}C_o$–H bonds are marked blue and the three $^{out}C_o$–H bonds are green. The red arrows represent the $^{in}C_oH(j) \rightarrow C_i(j')$ distances and the blue arrows the $^{in}C_oH(j) \rightarrow {}^{in}C_o(j')$. The assignment of the letters A, B, C is based on the following rule: ring A is the ring with the smallest "propeller angle" τ. Ring B is that ring for which $^{in}C_oH(A) \rightarrow C_i(j') < 2.9$ Å, and ring C is, of course, the only ring left. For compound **4** (Fig. 5) ring A corresponds to C11–C16 ring B to C31–C36 and ring C to C21–C26. With these definitions, the parameter list shown in Table 3 can be collected.

When looking at the propeller angles of ring A, one sees that they are rather small except for molecule B of compound **2**. Inspection of Fig. 2 immediately shows the reason for this: The bond C33–F2 eclipses the Mn → P vector, while in all other cases (at least in the major orientations) the CF groups

Table 3 Typical conformational parameters of the PPh_3 ligands in **2**–**4**

Angle [°]/distance [Å]	**2**/mol. A	**2**/mol. B	**3**	**4**
τ_A	20.45	32.50	13.38	15.01
τ_B	60.41	56.88	46.33	46.86
τ_C	51.84	46.91	43.42	54.69
ρ_A	80.51	82.43	76.77	78.53
ρ_B	159.89	158.4	160.67	159.04
ρ_C	41.43	40.81	43.42	41.31
φ_A	57.59	70.1	51.24	51.17
φ_B	70.59	62.3	69.56	68.08
φ_C	20.05	18.6	17.87	20.26
$^{in}C_oH(A) \rightarrow C_i(B)$	2.661	2.6223	2.809	2.799
$^{in}C_oH(A) \rightarrow {}^{in}C_o(B)$	3.055	2.988	2.964	2.964
$^{in}C_oH(B) \rightarrow C_i(C)$	2.573	2.564	2.541	2.554
$^{in}C_oH(B) \rightarrow {}^{in}C_o(C)$	3.330	3.804	3.146	3.205
$^{in}C_oH(B) \rightarrow {}^{out}C_o(C)$	2.668	2.605	2.794	2.773
$^{in}C_oH(C) \rightarrow C_i(A)$	2.648	2.636	2.591	2.582
$^{in}C_oH(C) \rightarrow {}^{in}C_o(A)$	2.843	2.908	2.651	2.664

Definitions of angles τ, ρ, φ and "in" and "out" see text. C_i is the ipso carbon, C_o are the ortho carbon atoms of the phenyl ring

have P–Mn–Ct–C_F torsions >> 90°. Because of this, the other angles ρ and φ apparently show no correlation with the number of fluorine substituents on the cyclopentadienyl ring. Most of the $^{in}C_oH \rightarrow C_i$ distances are around 2.60 ± 0.05 Å and hint therefore to rather strong C–H–π interactions. The only exemptions are the $^{in}C_oH(A) \rightarrow C_i(B)$ distances for **3** and **4**, which are about 0.20 Å longer. However, also these values still are below the some of the van-der-Waals radii.

The appearance of rather small φ angles for ring C in all compounds hint on the existence of the bonding motif "Ph_{PPh3}-Face-On-π Aryl" [27–30], however, the rather large distances C_{cp}–C_i (ring C) show that this interaction is here rather unimportant.

Conclusions

Replacing one carbonyl ligand of compound **1** for one PPh_3 ligand leads to an increase of the C–F bond length by 0.04 Å. Successive introduction of fluorine substituents leads to further lengthening of the C–F bonds by ca. 0.02 Å for each fluorine. The lengths of the Mn–P bonds and the distances from Mn to the cyclopentadienyl ring centroid are not affected by the increasing fluorine content. Nearly always, the Mn → P vector is in a transoid orientation relative to the C–F bonds, and therefore the conformations of the PPh_3 propellers are hardly influenced by increasing fluorine content. However, when the Mn–P bond eclipses with a C–F bond, it becomes significantly longer, and the propeller angles "flatten". This mutual "avoiding" of Mn–P and C–F bonds would become impossible, when a further fluorine substituent should be introduced. This might be an explanation, why, at least up to now, it was not possible to prepare fluorocymantrenes with a higher fluorine content.

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Declarations

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

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