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# X-RAY CRYSTAL STRUCTURES OF ($\eta^5$-CYCLOPENTADIENYL)-($\eta^1$-CYMANTRENYL)IRON DICARBONYL AND ($\eta^5$-CYCLOPENTADIENYL)-($\eta^1$-CYMANTRENYL)(TRIPHENYLPHOSPHINE)IRON CARBONYL

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## Summary

The complexes $(OC)_3MnC_5H_4Fe(C_5H_5)(CO)L$ (L = CO and $PPh_3$) were studied by X-ray crystallography. The $C_5H_4$ moiety of cymantrenyl is an $\eta^5$-ligand for Mn and an $\eta^1$-ligand for the Fe atom, forming, with the latter, $\sigma$-bonds of normal length (2.001 and 1.99 Å, respectively).

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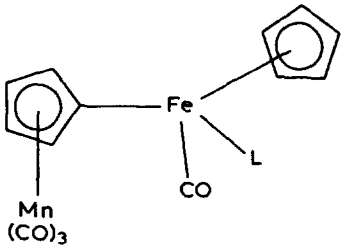
## Introduction

In the course of a structural investigation of cymantrenyl derivatives with a metallated $\pi$-cyclopentadienyl ring [1,2], we carried out an X-ray study of the title complexes I and II, prepared by Perevalova and coworkers [3,4].



(I : L = CO ;
II : L = $PPh_3$)

## Results and discussion

The molecular structures of I and II are shown in Figs. 1 and 2. The relevant bond distances and angles are listed in Tables 1 and 2 (the atomic numbering schemes in I and II are the same, except for the $PPh_3$ ligand).

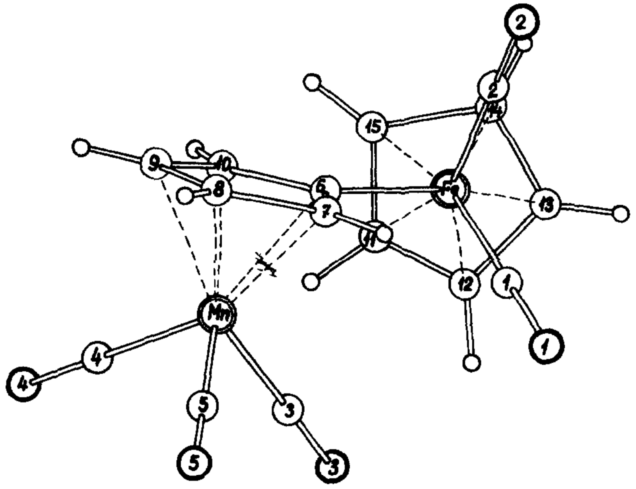


Fig. 1. Molecular structure of I (projection on the mean plane of the Cp ring C(11)...C(15)).

In both complexes the iron atom is coordinated by a planar $\eta^5$-$C_5H_5$ ligand (Cp), two two-electron donors (CO or phosphine) and a $\sigma$-bonded C(6) atom of the cymantrenyl moiety in a usual "piano stool" arrangement. The bond angles between the two-centre bonds at the Fe atom exhibit small deviations from the ideal value of 90°. Surprisingly, the replacement of a CO group by a bulky $PPh_3$ ligand in II even decreases these deviations.

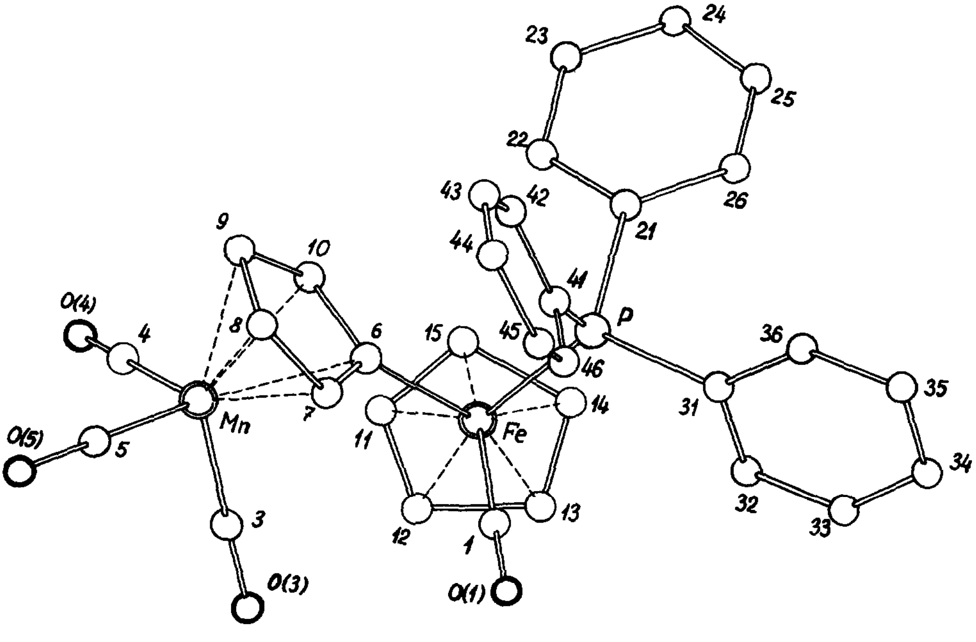


Fig. 2. Molecular structure of II (projection on the mean plane of the Cp ring C(11)...C(15)). The hydrogen atoms are omitted.

TABLE 1

BOND DISTANCES (Å) IN THE STRUCTURES OF I AND II

| Bond | I | II | Bond | I | II |
|---|---|---|---|---|---|
| Fe-P | - | 2.201(5) | P-C(21) | - | 1.85(2) |
| Fe-C(1) | 1.745(7) | 1.70(2) | P-C(31) | - | 1.80(2) |
| Fe-C(2) | 1.767(7) | - | P-C(41) | - | 1.83(2) |
| Fe-C(6) | 2.001(6) | 1.99(1) | C(1)-O(1) | 1.15(1) | 1.20(2) |
| Fe-C(11) | 2.110(7) | 2.16(1) | C(2)-O(2) | 1.14(1) | - |
| Fe-C(12) | 2.102(8) | 2.11(2) | C(3)-O(3) | 1.15(1) | 1.16(2) |
| Fe-C(13) | 2.104(7) | 2.13(2) | C(4)-O(4) | 1.15(1) | 1.23(2) |
| Fe-C(14) | 2.091(9) | 2.10(1) | C(5)-O(5) | 1.15(1) | 1.18(2) |
| Fe-C(15) | 2.092(8) | 2.08(2) | C(6)-C(7) | 1.43(1) | 1.44(2) |
| Fe-Cp(2) [a] | 1.730 | 1.73 | C(7)-C(8) | 1.42(1) | 1.37(3) |
| Mn-C(3) | 1.790(8) | 1.78(2) | C(8)-C(9) | 1.39(1) | 1.44(3) |
| Mn-C(4) | 1.787(7) | 1.70(2) | C(9)-C(10) | 1.44(1) | 1.45(3) |
| Mn-C(5) | 1.792(8) | 1.73(2) | C(10)-C(6) | 1.43(1) | 1.39(2) |
| Mn-C(6) | 2.216(6) | 2.25(2) | C(11)-C(12) | 1.39(1) | 1.40(2) |
| Mn-C(7) | 2.144(7) | 2.14(2) | C(12)-C(13) | 1.40(1) | 1.48(3) |
| Mn-C(8) | 2.129(8) | 2.16(2) | C(13)-C(14) | 1.39(1) | 1.42(2) |
| Mn-C(9) | 2.130(8) | 2.13(2) | C(14)-C(15) | 1.40(1) | 1.50(3) |
| Mn-C(10) | 2.155(7) | 2.16(2) | C(15)-C(11) | 1.41(1) | 1.39(2) |
| Mn-Cp(1) [a] | 1.783 | 1.80 | C-C(Ph), average | - | 1.38(5) |

[a] Cp(1) and Cp(2) are the centroids of the C(6)...C(10) and C(11)...C(15) cyclopentadienyl rings, respectively.

The Fe-C(6) $\sigma$-bond lengths in I (2.001(6) Å) and II (1.99(1) Å) are essentially equal. According to Churchill [5], the M-C($sp^2$) bonds (M = transition metal) with the unsaturated ligand should be longer if the latter acts as a $\pi,\sigma$-bridge. In this case

TABLE 2

BOND ANGLES (°) IN I AND II

| Angle | I | II | Angle | I | II |
|---|---|---|---|---|---|
| C(1)FeX [a] | 94.2(3) | 90.7(6) | FeC(1)O(1) | 178.9(7) | 177(1) |
| C(1)FeC(6) | 90.8(3) | 92.8(7) | FeC(2)O(2) | 179.6(7) | - |
| C(1)FeCp(2) | 124.2 | 125.5 | MnC(3)O(3) | 178.1(7) | 177(2) |
| XFeC(6) | 86.8(3) | 90.3(4) | MnC(4)O(4) | 178.5(7) | 173(2) |
| XFeCp(2) | 125.7 | 124.7 | MnC(5)O(5) | 178.5(7) | 176(2) |
| C(6)FeCp(2) | 124.5 | 122.8 | FeC(6)C(7) | 126.3(5) | 129(1) |
| C(3)MnC(4) | 91.3(4) | 93.9(9) | FeC(6)C(10) | 127.4(5) | 127(1) |
| C(3)MnC(5) | 92.3(4) | 90.6(8) | C(7)C(6)C(10) | 106.1(6) | 104(1) |
| C(3)MnCp(1) | 124.8 | 122.4 | C(6)C(7)C(8) | 109.3(6) | 110(1) |
| C(4)MnC(5) | 92.8(4) | 94.9(9) | C(7)C(8)C(9) | 108.3(7) | 111(2) |
| C(4)MnCp(1) | 123.4 | 121.8 | C(8)C(9)C(10) | 107.8(7) | 101(2) |
| C(5)MnCp(1) | 123.1 | 124.9 | C(9)C(10)C(6) | 108.4(6) | 114(1) |
| FePC(21) | - | 112.3(5) | C(12)C(11)C(15) | 108.0(7) | 105(1) |
| FePC(31) | - | 116.0(5) | C(11)C(12)C(13) | 108.6(7) | 112(1) |
| FePC(41) | - | 116.8(5) | C(12)C(13)C(14) | 107.3(8) | 107(1) |
| C(21)PC(31) | - | 103.0(7) | C(13)C(14)C(15) | 109.0(8) | 104(1) |
| C(21)PC(41) | - | 106.5(7) | C(14)C(15)C(11) | 107.0(8) | 113(1) |
| C(31)PC(41) | - | 100.7(7) | | | |

[a] X = C(2) in I, and P in II.

the $p$-orbital of $C(sp^2)$ is involved in the $\pi$-interaction with the $d$-orbitals of the other metal atom, hence its interaction with M (responsible for the contraction of $\sigma$-bonds $M-C(sp^2)$ vs. $M-C(sp^3)$) is weakened. However, in disagreement with these considerations, the Fe–C $\sigma$-bond distances in I and II are close to the value most common for terminal unsaturated ligands (1.98 Å), i.e. they are much shorter than the $Fe-C(sp^3)$ bond distances (ca. 2.11 Å) [6]. In the complex $(PhNCH_2C_6H_4)Fe_3(CO)_8$ with an $\eta^6:\eta^1$-bridging benzene ring, the Fe–C(benzene) $\sigma$-bond is still shorter (1.969(6) Å). This is probably due to an increase in bond order [7].

The geometry of the cymantrenyl moiety in I and II is similar to that observed in cymantrene [8,9], but the Mn atom is further away from C(6) (bonded to Fe) than from the other ring carbons. Thus, the Mn–C(6) distances are 2.216(6) Å in I and 2.25(2) Å in II vs. the average of the other four Mn–C(Cp) distances, which are equal to 2.14(1) and 2.15(2) Å, respectively. Such non-equivalence is not observed in cymantrenyl derivatives of non-transition metals, viz. Sn and Bi [1,2]. The C(6)...C(10)-cyclopentadienyl ring is planar, the iron atom is tilted by 0.25 Å (in I) and 0.19 Å (in II) out of its plane to the side opposite to Mn. This tilting and the large Fe...Mn distances (3.861(2) Å in I, 3.852(3) Å in II) indicate the absence of metal–metal bonding interaction.

The differences in the bond distances and angles between I and II are not statistically significant. Conformational differences due to the replacement of CO by the bulky $PPh_3$ ligand are more pronounced. Thus the dihedral angle between the planes of the Cp rings is 81.3° in I vs. 66° in II. The orientation of the $Mn(CO)_3$ moiety relative to the Cp ring is also changed. In I, the carbonyl group atom C(3) is, in fact, eclipsed with C(6), the C(6)–Cp(1)–Mn–C(3) torsion angle being 1.4° (Cp(1) is the centroid of the Cp ring C(6)...C(10)). Such a conformation is generally uncommon for derivatives of cymantrene [10] and its analogue pyrrolyltricarbonylmanganese [11] with bulky substituents in the $\eta^5$-ring. More often these derivatives exhibit a staggered conformation of CO groups with respect to the substituent-carrying atom of the ring. The unusual conformation of I is probably due to crystal packing. In II, the torsion angle of $-26°$ for C(6)–Cp(1)–Mn–C(3) corresponds to a skew conformation.

The geometry of the $PPh_3$ ligand in II is unexceptional. All the phenyl rings are planar, but the P–C(Ph) bonds are bent out of their planes by 7.5, 4.4 and 4.8° (for the C(21)...C(26), C(31)...C(36) and C(41)...C(46) rings, respectively).

The intermolecular distances in the structures of I and II are consistent with Van der Waals interactions [12], with the exception of a single, shortened contact C(8)...C(8)$(1-x,\ -y,\ 1-z)$ of 3.25(1) Å in the structure of I. In both I and II there are some short intramolecular (non-bonding) contacts, mainly due to overcrowding in the coordination sphere of the iron atoms, viz. C(1)...C(3), 3.33(1), C(1)...C(7) 3.04(1), C(2)...C(7) 3.16(1), C(10)...C(15) 3.29(1) Å in I; C(1)...C(7) 3.04(3), C(10)...C(11) 3.16(3), C(7)...C(41) 3.24(3) Å in II.

## Experimental

X-Ray experiments were performed with a Syntex $P2_1$ four-circle autodiffractometer at room temperature, using graphite-monochromated Mo-$K_\alpha$ radiation. Calculations were carried out with an Eclipse S/200 computer using INEXTL programs [13]. The structure of I was solved by a heavy atom method; the structure of II by a

TABLE 3

CRYSTAL DATA AND EXPERIMENTAL DETAILS

| | I | | II |
|---|---|---|---|
| Symmetry | Monoclinic | | Monoclinic |
| $a$ (Å) | 8.592(2) | | 10.783(2) |
| $b$ (Å) | 13.521(2) | | 14.294(4) |
| $c$ (Å) | 12.481(3) | | 18.105(4) |
| $\beta$ (°) | 94.92(2) | | 92.77(2) |
| $V$ (Å$^3$) | 1444.6(9) | | 2788 (2) |
| $d_{\text{meas}}$(flotation) (g cm$^{-3}$) | 1.74 | | 1.46 |
| $d_{\text{calcd}}$ (g cm$^{-3}$) | 1.75 | | 1.46 |
| $Z$ | 4 | | 4 |
| Space group | $P2_1/c$ | | $P2_1/c$ |
| Scan technique | | $\theta/2\theta$, $2\theta_{\text{max}} = 50°$ | |
| No. of reflections ($I > 2\sigma(I)$) | 1546 | | 2053 |
| Weighting scheme | | $W = [\sigma_F^2 + (k\|F_o\|)^2]^{-1}$ | |
| $k$ | 0.01 | | 0.03 |
| $R$ | 0.057 | | 0.098 |
| $R_w$ | 0.045 | | 0.117 |

direct method using the MULTAN program. All non-hydrogen atoms in both I and II were refined by full matrix least-squares with anisotropic thermal factors. All the hydrogen atoms were placed in calculated positions and were included in the

TABLE 4

ATOMIC COORDINATES ($\times 10^4$) AND $B_{\text{iso}}^{\text{eq}}$ IN THE STRUCTURE OF I

| Atom | $x$ | $y$ | $z$ | $B_{\text{iso}}^{\text{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| Fe | 1032(1) | 794(1) | 2654(1) | 2.00(3) |
| Mn | 4795(1) | 2265(1) | 3485(1) | 3.54(3) |
| O(1) | −133(6) | 2342(4) | 3977(4) | 5.0(3) |
| O(2) | 683(6) | −769(4) | 4219(4) | 4.9(3) |
| O(3) | 2482(7) | 3516(4) | 2252(5) | 6.7(3) |
| O(4) | 7226(6) | 2950(4) | 2139(5) | 5.6(3) |
| O(5) | 5495(8) | 3796(5) | 5127(5) | 6.8(3) |
| C(1) | 337(8) | 1721(6) | 3460(6) | 3.3(3) |
| C(2) | 815(8) | −153(5) | 3604(6) | 3.3(3) |
| C(3) | 3367(9) | 3020(6) | 2745(7) | 4.3(3) |
| C(4) | 6286(8) | 2682(5) | 2679(6) | 3.8(3) |
| C(5) | 5221(9) | 3208(6) | 4475(7) | 4.3(3) |
| C(6) | 3200(8) | 974(5) | 3350(5) | 2.9(3) |
| C(7) | 3612(8) | 1239(5) | 4443(6) | 3.5(3) |
| C(8) | 5257(9) | 1147(6) | 4671(7) | 4.4(3) |
| C(9) | 5899(8) | 863(6) | 3730(7) | 4.7(3) |
| C(10) | 4638(8) | 767(6) | 2895(6) | 3.7(3) |
| C(11) | 1700(9) | 1169(7) | 1117(6) | 4.2(4) |
| C(12) | 222(11) | 1549(6) | 1242(6) | 4.6(4) |
| C(13) | −789(8) | 761(8) | 1415(6) | 4.8(4) |
| C(14) | 81(13) | −107(7) | 1402(6) | 5.5(4) |
| C(15) | 1629(11) | 131(7) | 1231(6) | 4.8(4) |

TABLE 5

ATOMIC COORDINATES ($\times 10^4$) AND $B_{\text{iso}}^{\text{eq}}$ IN THE STRUCTURE OF II

| Atom | $x$ | $y$ | $z$ | $B_{\text{iso}}^{\text{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| Fe | 7506(2) | 1621(2) | 4655(1) | 2.48(6) |
| Mn | 5071(3) | 1546(2) | 3029(1) | 3.51(7) |
| P | 8762(4) | 2835(3) | 4697(2) | 2.7(1) |
| O(1) | 9210(13) | 562(9) | 3784(8) | 7.1(5) |
| O(3) | 5804(14) | −382(8) | 3407(7) | 6.6(5) |
| O(4) | 2546(14) | 1388(11) | 3536(9) | 8.1(6) |
| O(5) | 4254(16) | 900(12) | 1556(7) | 8.7(6) |
| C(1) | 8504(12) | 1021(12) | 4130(9) | 3.8(5) |
| C(3) | 5516(17) | 383(13) | 3277(9) | 4.7(6) |
| C(4) | 3634(18) | 1443(13) | 3368(10) | 5.3(6) |
| C(5) | 4617(15) | 1177(14) | 2144(10) | 4.8(6) |
| C(6) | 6588(14) | 2155(10) | 3775(7) | 3.0(4) |
| C(7) | 6899(17) | 2127(13) | 3014(9) | 4.9(6) |
| C(8) | 6112(17) | 2698(14) | 2602(9) | 5.3(6) |
| C(9) | 5130(22) | 3037(12) | 3039(10) | 5.3(7) |
| C(10) | 5520(16) | 2696(11) | 3765(9) | 3.8(5) |
| C(11) | 5735(13) | 1218(11) | 5061(8) | 3.3(5) |
| C(12) | 6562(16) | 467(12) | 5090(8) | 4.5(5) |
| C(13) | 7683(19) | 674(11) | 5566(9) | 4.2(6) |
| C(14) | 7555(20) | 1610(13) | 5815(8) | 4.7(6) |
| C(15) | 6315(14) | 1911(11) | 5492(8) | 3.5(5) |
| C(21) | 8221(15) | 3769(10) | 5308(8) | 2.8(4) |
| C(22) | 7086(17) | 4188(11) | 5145(10) | 4.4(5) |
| C(23) | 6590(17) | 4808(15) | 5639(11) | 5.9(6) |
| C(24) | 7248(20) | 4976(13) | 6312(11) | 6.1(7) |
| C(25) | 8331(21) | 4581(14) | 6468(11) | 6.2(7) |
| C(26) | 8866(17) | 3957(11) | 5964(9) | 4.4(6) |
| C(31) | 10321(13) | 2617(11) | 5055(8) | 3.0(4) |
| C(32) | 10663(14) | 1778(10) | 5438(8) | 3.1(4) |
| C(33) | 11818(17) | 1660(12) | 5765(9) | 4.7(5) |
| C(34) | 12734(18) | 2333(13) | 5720(10) | 4.8(6) |
| C(35) | 12347(21) | 3142(12) | 5319(11) | 5.4(7) |
| C(36) | 11315(16) | 3311(12) | 5014(10) | 4.4(5) |
| C(41) | 9068(16) | 3394(11) | 3813(8) | 3.6(5) |
| C(42) | 8471(17) | 4180(12) | 3537(10) | 4.8(6) |
| C(43) | 8696(22) | 4472(14) | 2810(10) | 7.1(8) |
| C(44) | 9535(21) | 4012(16) | 2405(9) | 7.1(8) |
| C(45) | 10146(24) | 3240(15) | 2669(10) | 6.5(8) |
| C(46) | 9903(17) | 2917(12) | 3369(9) | 4.0(5) |

refinement as fixed contributions. The crystal data of I and II and the experimental details are listed in Table 3; the atomic coordinates and $B_{\text{iso}}^{\text{eq}} = 1/3\Sigma_{ij}B_{ij}a_i^\star a_j^\star(a_i a_j)$ are given in Tables 4–6.

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TABLE 6

COORDINATES ($\times 10^3$) OF THE HYDROGEN ATOMS

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| *Structure I* | | | | | | | |
| H(7) | 286 | 146 | 497 | H(11) | 265 | 156 | 97 |
| H(8) | 585 | 127 | 538 | H(12) | −7 | 227 | 121 |
| H(9) | 703 | 75 | 365 | H(13) | −193 | 81 | 153 |
| H(10) | 475 | 59 | 213 | H(14) | −33 | −79 | 150 |
| | | | | H(15) | 251 | −35 | 120 |
| *Structure II* | | | | | | | |
| H(7) | 759 | 175 | 281 | H(25) | 878 | 472 | 695 |
| H(8) | 621 | 286 | 207 | H(26) | 969 | 366 | 608 |
| H(9) | 438 | 341 | 288 | H(32) | 1004 | 126 | 547 |
| H(10) | 506 | 284 | 422 | H(33) | 1201 | 107 | 605 |
| H(11) | 491 | 125 | 479 | H(34) | 1359 | 226 | 595 |
| H(12) | 642 | −14 | 482 | H(35) | 1299 | 364 | 528 |
| H(13) | 839 | 24 | 569 | H(36) | 1117 | 391 | 474 |
| H(14) | 816 | 198 | 613 | H(42) | 789 | 454 | 385 |
| H(15) | 594 | 254 | 558 | H(43) | 823 | 502 | 259 |
| H(22) | 662 | 404 | 467 | H(44) | 971 | 425 | 190 |
| H(23) | 578 | 513 | 552 | H(45) | 1076 | 291 | 236 |
| H(24) | 689 | 540 | 668 | H(46) | 1033 | 234 | 356 |

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