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REACTION OF $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}HC{\equiv}CCOOCH_3)$ WITH $Fe_2(CO)_9$ AND X-RAY CRYSTAL STRUCTURE OF (1-η^5-CYCLOPENTADIENYL)(1,2;1,3-μ-DICARBONYL)(1-η^2;2,3-σ-METHYLACRYLATE)(2,2,2,3,3,3-HEXACARBONYL)-*triangulo*-1-MANGANESE-2,3-DIIRON

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Summary

The reaction of $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}HC{\equiv}CCOOCH_3)$ with $Fe_2(CO)_9$ yields the title complex characterized by an X-ray structural study as a cluster containing a Fe_2Mn three-membered cycle and a bridging $\pi,2\sigma$-olefin ligand.

Introduction

Methylacetylene and transition metal σ-acetylenides react with iron carbonyls forming cluster systems [1,2]. Thus it seemed interesting to find out whether transition metal π-acetylene complexes can also form clusters on interaction with iron carbonyls. In this paper we describe the reaction between the manganese π-acetylene complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}HC{\equiv}CCOOCH_3)$ (I) and $Fe_2(CO)_9$.

Results and discussion

Recently we have reported [3] that the reaction of I with $Fe_2(CO)_9$ in hexane yields, besides two isomeric binuclear μ-vinylidene complexes IIa,b, two other products III and IV.

$$\text{I} + Fe_2(CO)_9 \xrightarrow[\text{n-hexane}]{40^\circ\text{C, 45 min}} Cp(CO)_2Mn(\mu\text{-}C{=}CHCOOMe)Fe(CO)_4 + \text{III} + \text{IV}$$

III is a yellow-green oil which we could not characterize due to its thermal and oxidative instability. IV is a black crystalline non-melting substance, poorly soluble in alkanes and readily soluble in polar solvents. Its IR spectrum (in CCl_4) shows 7 absorption bands in the range 1800—2000 cm^{-1} (1977vs, 1940vs,

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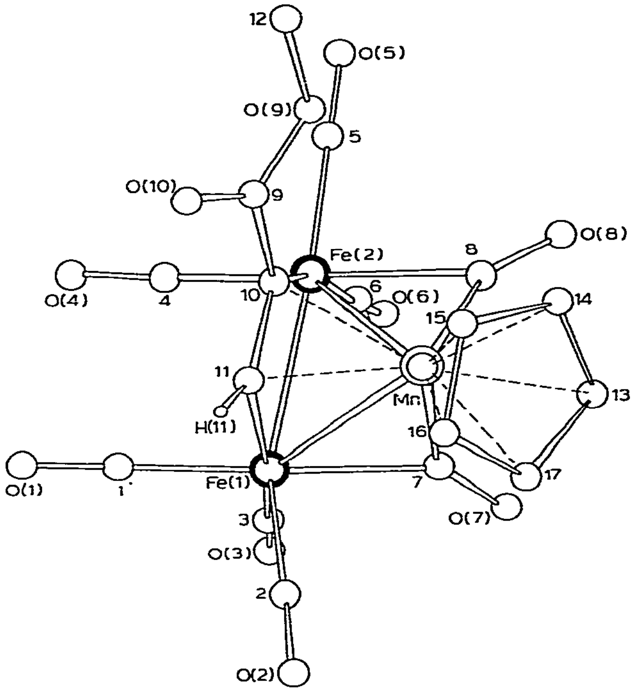

Fig. 1. Molecular structure of IV. Methyl and cyclopentadienyl hydrogens are omitted.

1925vs, 1905s, 1895s, 1855s, 1820m cm^{-1}). The former five bands can be attributed to terminal carbonyls and the latter two to bridging ones. The band at 1700m cm^{-1} can be assigned to ν(C═O) of the COOMe moiety. The mass spectrum of IV exhibits peaks with the masses 511 and 511 $- n$(CO) ($n = 1$, 4—7), as well as 56 $[Fe]^+$ and 55 $[Mn]^+$.

The molecular structure of IV, established by X-ray crystallography, is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The two iron and one manganese atoms form a three-membered metallocycle and are bridged by the former π-methylpropiolate ligand of I. This bridging ligand is σ-bonded to Fe(1) and Fe(2) via C(11) and C(10), respectively, the average σ-bond length, 1.970(3) Å, being slightly shorter than the Fe—C(sp^2) bond in *trans*-$[Cp(CO)_2$-$FeCH{=}CH—]_2$ (1.987(5) Å) [4]. The C(10)—C(11) multiple bond of 1.362(4) Å in length is somewhat longer than the normal double bond (1.337 Å [5]). The geometry of C(10) and C(11) is planar trigonal (neglecting the Mn atom). Thus, the bridging ligand can be ascribed as an olefin, nearly symmetrically π-bonded to the manganese atom (the Mn—C(10) and Mn—C(11) distances are 2.094(3) and 2.063(3) Å, respectively), and IV can be formulated as:

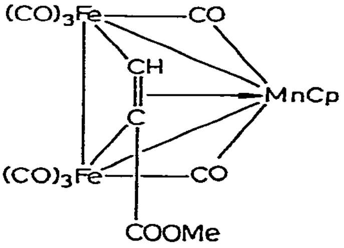

TABLE 1

BOND LENGTH (Å) AND ANGLES (°) [a]

Bond		Bond		Bond	
Mn—Fe(1)	2.561(1)	Mn—C(10)	2.094(3)	C(8)—O(8)	1.165(4)
Mn—Fe(2)	2.577(1)	Mn—C(11)	2.063(3)	C(9)—O(9)	1.324(3)
Fe(1)—Fe(2)	2.679(1)	Mn—C(13)	2.122(3)	C(9)—O(10)	1.207(4)
Fe(1)—C(1)	1.805(3)	Mn—C(14)	2.143(3)	C(9)—C(10)	1.493(4)
Fe(1)—C(2)	1.820(3)	Mn—C(15)	2.157(3)	C(10)—C(11)	1.362(4)
Fe(1)—C(3)	1.808(3)	Mn—C(16)	2.150(4)	C(11)—H(11)	0.91(3)
Fe(2)—C(4)	1.791(3)	Mn—C(17)	2.136(4)	O(9)—C(12)	1.446(4)
Fe(2)—C(5)	1.814(3)	Mn—X	1.777	C(12)—H	Av.0.91(5)
Fe(2)—C(6)	1.821(3)	C(1)—O(1)	1.136(4)	C(13)—C(14)	1.415(5)
Mn—C(7)	1.922(3)	C(2)—O(2)	1.132(4)	C(13)—C(17)	1.410(5)
Fe(1)—C(7)	2.034(3)	C(3)—O(3)	1.146(4)	C(14)—C(15)	1.393(5)
Mn—C(8)	1.877(3)	C(4)—O(4)	1.142(4)	C(15)—C(16)	1.410(6)
Fe(2)—C(8)	2.123(3)	C(5)—O(5)	1.135(4)	C(16)—C(17)	1.400(6)
Fe(1)—C(11)	1.973(3)	C(6)—O(6)	1.139(4)	C(Cp)—H	Av.0.91(4)
Fe(2)—C(10)	1.967(3)	C(7)—O(7)	1.164(4)		
Angle		Angle		Angle	
Fe(1)MnFe(2)	62.84(2)	C(1)Fe(1)C(3)	96.2(2)	C(6)Fe(2)C(10)	166.2(1)
MnFe(1)Fe(2)	58.86(2)	C(1)Fe(1)C(7)	176.0(1)	C(8)Fe(2)C(10)	87.0(1)
MnFe(2)Fe(1)	58.31(2)	C(1)Fe(1)C(11)	79.4(1)	FeCO (terminal)	Av. 176.8(1.7)
Fe(1)MnC(7)	51.6(1)	C(2)Fe(1)C(3)	97.4(1)	Fe(1)C(7)Mn	80.7(1)
Fe(1)MnC(8)	106.7(1)	C(2)Fe(1)C(7)	89.5(1)	Fe(1)C(7)O(7)	136.2(3)
Fe(1)MnX	136.4(1)	C(2)Fe(1)C(11)	99.1(1)	MnC(7)O(7)	143.1(3)
Fe(1)MnZ	59.5(1)	C(3)Fe(1)C(7)	83.7(1)	Fe(2)C(8)Mn	79.9(1)
Fe(2)MnC(7)	80.4(1)	C(3)Fe(1)C(11)	163.2(1)	Fe(2)C(8)O(8)	130.5(2)
Fe(2)MnC(8)	54.2(1)	C(7)Fe(1)C(11)	99.7(1)	MnC(8)O(8)	149.5(3)
Fe(2)MnX	160.4(1)	MnFe(2)C(4)	132.0(1)	Fe(1)C(11)C(10)	110.9(2)
Fe(2)MnZ	58.2(1)	MnFe(2)C(5)	117.3(1)	Fe(1)C(11)H(11)	125(2)
C(7)MnC(8)	83.3(1)	MnFe(2)C(6)	115.6(1)	C(10)C(11)H(11)	123(2)
C(7)MnX	114.1(1)	MnFe(2)C(8)	45.8(1)	Fe(2)C(10)C(11)	108.2(2)
C(7)MnZ	110.1(1)	MnFe(2)C(10)	52.8(1)	Fe(2)C(10)C(9)	129.0(2)
C(8)MnX	112.3(1)	Fe(1)Fe(2)C(4)	82.4(1)	C(9)C(10)C(11)	122.1(2)
C(8)MnZ	107.1(1)	Fe(1)Fe(2)C(5)	169.0(1)	C(10)C(9)O(9)	113.0(2)
XMnZ	122.9(1)	Fe(1)Fe(2)C(6)	96.4(1)	C(10)C(9)O(10)	123.8(3)
MnFe(I)C(I)	130.8(1)	Fe(1)Fe(2)C(8)	95.9(1)	O(9)C(9)O(10)	123.2(3)
MnFe(1)C(2)	100.6(1)	Fe(1)Fe(2)C(10)	71.3(1)	C(9)O(9)C(12)	116.3(2)
MnFe(1)C(3)	127.3(1)	C(4)Fe(2)C(5)	95.9(1)	O(9)C(12)H	Av. 110(3)
MnFe(1)C(7)	47.8(1)	C(4)Fe(2)C(6)	93.6(1)	HC(12)H	Av. 109(6)
MnFe(1)C(11)	52.2(1)	C(4)Fe(2)C(8)	177.8(1)	C(14)C(13)C(17)	107.5(3)
Fe(2)Fe(1)C(1)	100.0(1)	C(4)Fe(2)C(10)	91.1(1)	C(13)C(14)C(15)	108.1(3)
Fe(2)Fe(1)C(2)	159.5(1)	C(5)Fe(2)C(6)	94.5(1)	C(14)C(15)C(16)	108.4(3)
Fe(2)Fe(1)C(3)	95.5(1)	C(5)Fe(2)C(8)	85.5(1)	C(15)C(16)C(17)	107.9(3)
Fe(2)Fe(1)C(7)	76.1(1)	C(5)Fe(2)C(10)	97.9(1)	C(13)C(17)C(16)	108.2(3)
Fe(2)Fe(1)C(11)	69.7(1)	C(6)Fe(2)C(8)	88.0(1)	CCH(Cp)	Av. 126(2)
C(1)Fe(1)C(2)	94.5(1)				

[a] X is the centroid of the Cp ring; Z is the midpoint of the C(10)—C(11) bond.

Such a bridging coordination of the acetylene ligand to a three-membered metallocycle has been reported earlier, e.g. in $Os_3(CO)_{10}(PhC_2Ph)$ [6] and $Fe_3(CO)_8(PhC_2Ph)_2$ [7], wherein the bond order of the acetylenic bonds is also less than 2.

The olefinic moiety of IV (containing C(10), C(11) and the directly bonded

TABLE 2

ATOMIC COORDINATES (Fe, Mn $\times 10^5$; O, C $\times 10^4$) AND ANISOTROPIC THERMAL FACTORS IN THE FORM $T = \exp[-0.25(B_{11}a^{*2}h^2 + \ldots + 2B_{12}a^*b^*hk + \ldots)]$ (Fe, Mn $\times 10^2$; O, C $\times 10$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	10260(3)	7415(4)	25113(3)	121(2)	200(2)	162(2)	3(1)	−3(1)	11(1)
Fe(2)	−11620(3)	12236(4)	20442(3)	130(2)	185(2)	119(2)	−16(1)	−26(1)	16(1)
Mn	−721(3)	23814(4)	33556(3)	137(2)	156(2)	153(2)	0(1)	−42(1)	1(1)
O(1)	935(2)	−1859(2)	2724(2)	26(1)	21(1)	58(2)	1(1)	1(1)	0(1)
O(2)	3284(2)	964(2)	3482(2)	17(1)	34(1)	37(1)	−2(1)	−7(1)	7(1)
O(3)	1845(2)	782(3)	560(2)	42(1)	61(2)	22(1)	6(1)	11(1)	2(1)
O(4)	−1259(2)	−1302(2)	1530(2)	31(1)	22(1)	32(1)	−3(1)	−5(1)	−7(1)
O(5)	−3659(2)	1552(2)	1832(2)	17(1)	36(1)	24(1)	1(1)	−6(1)	3(1)
O(6)	−812(2)	1971(3)	73(2)	40(1)	53(2)	19(1)	−11(1)	0(1)	12(1)
O(7)	1457(2)	3237(2)	1894(2)	25(1)	28(1)	35(1)	−5(1)	4(1)	10(1)
O(8)	−1565(2)	3870(2)	2138(2)	27(1)	20(1)	30(1)	4(1)	−8(1)	4(1)
O(9)	−2932(2)	1223(2)	3857(1)	15(1)	25(1)	21(1)	5(1)	2(1)	4(1)
O(10)	−1916(2)	−76(2)	4722(2)	19(1)	46(1)	24(1)	6(1)	2(1)	18(1)
C(1)	951(3)	−858(3)	2612(2)	15(1)	27(2)	30(2)	0(1)	−1(1)	−1(1)
C(2)	2419(3)	857(3)	3111(2)	18(1)	20(1)	22(1)	1(1)	3(1)	4(1)
C(3)	1525(3)	766(3)	1316(2)	21(1)	32(2)	26(2)	2(1)	1(1)	0(1)
C(4)	−1178(2)	−322(3)	1733(2)	18(1)	29(2)	13(1)	−1(1)	−3(1)	2(1)
C(5)	−2701(3)	1430(3)	1948(2)	21(1)	21(1)	13(1)	−1(1)	−4(1)	3(1)
C(6)	−907(3)	1712(3)	844(2)	19(1)	27(1)	21(1)	−4(1)	−3(1)	4(1)
C(7)	996(3)	2541(3)	2358(2)	16(1)	20(1)	24(1)	−1(1)	−6(1)	3(1)
C(8)	−1103(2)	3039(3)	2460(2)	18(1)	19(1)	18(1)	−1(1)	−2(1)	1(1)
C(9)	−1995(2)	603(3)	4064(2)	14(1)	19(1)	14(1)	0(1)	−3(1)	−1(1)
C(10)	−1055(2)	825(2)	3394(2)	14(1)	16(1)	13(1)	1(1)	−1(1)	1(1)
C(11)	60(2)	581(3)	3623(2)	17(1)	15(1)	13(1)	1(1)	−3(1)	2(1)
C(12)	−3907(3)	997(4)	4437(3)	17(1)	37(2)	25(2)	5(1)	7(1)	2(1)
C(13)	270(3)	4161(3)	3779(3)	30(2)	17(1)	29(2)	−2(1)	−7(1)	−5(1)
C(14)	−738(3)	3773(3)	4217(2)	26(1)	25(1)	24(1)	4(1)	−4(1)	−9(1)
C(15)	−454(4)	2809(3)	4796(2)	47(2)	29(2)	14(1)	−7(1)	−1(1)	−8(1)
C(16)	729(4)	2589(3)	4729(3)	47(2)	27(2)	22(1)	8(1)	−20(1)	−8(1)
C(17)	1175(3)	3428(3)	4109(3)	24(1)	26(2)	37(2)	−1(1)	−12(1)	−14(1)

Fe(1), Fe(2), C(9) and H(11)) is planar within 0.07 Å. Its mean plane forms a dihedral angle of 60.2° with the plane through the three metal atoms (hereafter referred to as TM), and an angle 67.0° with the line through Mn and the midpoint of the C(10)—C(11) bond. The latter angle is rather far from the ideal value of 90° [8], which is most favourable for π-bonding, but would require a severe distortion of certain bond lengths. The planar COOMe group is rotated with respect to the olefinic moiety, the torsion angle C(11)C(10)C(9)O(10) being −20.9(3)°.

The complex IV is closely related to $(\eta\text{-}C_5H_5)Mn(CO)_2Fe_2(CO)_6\cdot(\mu_3\text{-}PPh)$ (V) [9], the only difference being a replacement of the μ_3-bridging phosphorous atom by the π,2σ-olefin, which strongly affects the Fe—Mn bond lengths (average 2.747 Å in V vs. 2.659 Å in IV), but does not affect the Fe—Fe bond length (2.686 Å in V vs. 2.679(1) Å in IV). Both latter values are within the range 2.666—2.711 Å typical for non-bridged Fe—Fe bonds in *triangulo*-triiron complexes [10], i.e. both olefin and μ_3-PPh bridges induce no metal—metal bond shortening.

The conformation of the Cp ligand in IV differs from that in V and its triiron analogues $(\eta^5\text{-}C_5H_2Me_2C_2H_3)Fe_3(CO)_8(\mu_3\text{-}CEt)$ [1], $(\eta^5\text{-}C_5H_5)Fe_3(CO)_8\text{-}(\mu_3\text{-}CCH{=}CH_2)$ [2] and $(\eta^5\text{-}C_5H_5)Fe_3(CO)_8(\mu_3\text{-}CMe)$ [11]. In IV the cyclopentadienyl ligand is almost normal to the TM plane (dihedral angle 87.4°), while in the latter complexes it is inclined at 72.7—74.7° to TM, and its centroid is bent out of this plane towards the μ_3-bridging ligand. Furthermore, in IV the COOMe moiety destroys a local mirror symmetry plane (through the Mn or Fe atom ligated by Cp and the midpoint of the opposite Fe—Fe bond) which is present in all other complexes mentioned above. The Cp ligand is rotated from the COOMe moiety (see Fig. 1) and bridging carbonyls are unequally tilted out of the TM plane (the MnFe(1)C(7)O(7) and MnFe(2)C(8) O(8) planes are inclined to the latter by 79.8 and 40.3°, respectively), probably to avoid short contacts with the Cp ligand, as the angles C(7)MnX and C(8)MnX (X is the Cp centroid) remain almost equal (114.1(1)° vs. 112.3(1)°). The conformational non-equivalence of the bridging carbonyls is also evidenced by the IR spectrum, viz. the $\nu(\mu_2\text{-}CO)$ values are 1855 and 1820 cm^{-1}.

The carbonyl bridges in IV, similar to its analogues [1,2,9,11], are remarkably unsymmetrical. The Mn—C(7) and Mn—C(8) bond distances are shorter

TABLE 3

COORDINATES ($\times 10^3$) AND B_{iso} ($Å^2$) OF H ATOMS

Atom	x	y	z	B_{iso}
H(11)	29(3)	27(3)	419(2)	2.2(7)
H(12)	−450(3)	142(3)	421(3)	3.2(8)
H′(12)	−375(4)	126(4)	508(3)	4.6(10)
H″(12)	−403(3)	24(4)	449(3)	4.2(10)
H(13)	35(3)	478(4)	333(3)	3.6(9)
H(14)	−141(3)	411(3)	417(2)	1.6(7)
H(15)	−96(3)	238(3)	513(3)	2.6(8)
H(16)	106(3)	196(4)	502(3)	3.6(9)
H(17)	192(4)	347(4)	394(3)	4.5(10)

than Fe(1)—C(7) and Fe(2)—C(8), respectively, by 0.11 and 0.25 Å, though the Mn covalent radius is somewhat greater than that of Fe (e.g., 1.25 and 1.24 Å [12]).

Experimental

All operations were performed under nitrogen using absolute solvents saturated with nitrogen. IR spectra were measured on an UR-20 Zeiss spectrometer, and mass spectra on an AEI-MS-30 mass spectrometer with a DS-50 data processing system (ionizing energy 70 eV).

An X-ray study of IV was performed with a four-circle computer-controlled Syntex P2$_1$ diffractometer and computations were made with an Eclipse S/200 computer using EXTL programmes modified in our laboratory by A.I. Yanovskii and R.G. Gerr.

Crystal data

$C_{17}H_9Fe_2MnO_{10}$, mol. wt. 539.9, monoclinic, at —120°C a = 11.686(3), b = 11.234(2), c = 14.182(2) Å, β = 91.62(2)°, V = 1860.9(6) Å^3, $d_{\text{calcd.}}$ = 1.93 g cm^{-1}, Z = 4, space group $P2_1/n$.

Intensities of 3581 independent reflections were measured at —120°C (graphite-monochromated Mo-K_α radiation, $\theta/2\theta$ scan, $2° \leqslant 2\theta \leqslant 54°$). 3161 reflections with $I \geqslant 2\sigma$ were used in calculations. The structure was solved by a direct method with the MULTAN programme and refined by full matrix least squares using weights $w = [\sigma_F^2 + (0.01|F_0|)^2]^{-1}$ and a correction for anomalous dispersion of Fe and Mn. All hydrogen atoms were revealed in a difference synthesis. The refinement (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) converged at R = 0.032 and R_w = 0.037. Final positional and thermal atomic parameters are listed in Tables 2 and 3.

Reaction of I with $Fe_2(CO)_9$

1.6 g (4.40 mmol) of $Fe_2(CO)_9$ was added to a solution of 1.0 g (3.84 mmol) of I in 70 ml of hexane. After stirring for 45 min at 40°C, a dark brown precipitate consisting of unreacted $Fe_2(CO)_9$ and III was formed. The solution was decanted from the precipitate, and the solvent was removed under vacuum. The residue was chromatographed on SiO_2 at 4°C, giving three fractions, viz. red, eluted by petroleum ether/ether (3/1) and yielding 0.28 g of IIa,b (characterized by m.p. and IR spectra), yellow-green (0.09 g of III) and brown, eluted by petroleum ether/ether (1/1). The latter one gave 0.18 g (9.23%) of black crystalline IV, decomposing above 300°C (from the n-hexane/ether, 3/1, mixture). Found: C, 38.05; H, 1.47; Fe, 21.03; Mn, 10.39. $C_{17}H_9Fe_2MnO_{10}$ calcd.: C, 37.82; H, 1.68; Fe, 20.69; Mn, 10.18%. Mass spectrum (m/e): 511 $[M - CO]^+$ (0.1%); 483 $[M - 2\ CO]^+$ (0.2%); 400 $[M - 5\ CO]^+$; (1.2%); 372 $[M - 6\ CO]^+$ (3.0%); 344 $[M - 7\ CO]^+$ (2.7%); 316 $[M - 8\ CO]^+$ (4.1%); 148 $[Cp(CO)Mn]^+$ (7.3%); 121 $[CpFe]^+$ (25.2%); 120 $[CpMn]^+$ (24.0%); 56 $[Fe]^+$ (20.9%); 55 $[Mn]^+$ (20.3%).

References

1 S. Aime, L. Milone, E. Sappa and A. Tiripicchio, J. Chem. Soc., Dalton, (1977) 227.
2 G.G. Aleksandrov, V.V. Skripkin, N.E. Kolobova and Yu.T. Struchkov, Koord. Khimiya, 5 (1979) 1479.
3 N.E. Kolobova, L.L. Ivanov and O.S. Zhvanko, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1435.
4 M.R. Churchill and J. Wormald, Inorg. Chem., 8 (1969) 1936.
5 L.E. Sutton (Ed.), Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement, Chemical Society, Special Publication, No. 18, London, 1965.
6 C.G. Pierpont, Inorg. Chem., 16 (1977) 636.
7 R.P. Dodge and V. Schomaker, J. Organometal. Chem., 3 (1965) 274.
8 I. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.
9 G. Huttner, A. Frank and G. Nohr, Z. Naturforsch., 31b (1976) 1161.
10 F.H. Herbstein, Acta Cryst. B, 37 (1981) 339.
11 (a) P. Brun, G.M. Dawkins, M. Green, R.M. Mills, J.-Y. Salaün, F.G.A. Stone, P. Woodward, J. Chem. Soc. Chem. Commun., (1981) 966;
(b) L.V. Rybin, E.A. Petrovskaya, Yu.T. Struchkov, A.S. Batsanov and M.I. Rybinskaya, J. Organometal. Chem., 226 (1982) 63.
12 L. Pauling, Proc. Nat. Acad. Sci. USA, 72 (1975) 3799.