PROTONATION OF ALLENYLIDENE- AND VINYLIDENE-MANGANESE COMPLEXES. CRYSTAL AND MOLECULAR STRUCTURE OF [Cp(CO)₂Mn≡C–CH=CPh₂]⁺ BF₄⁻

N.E. KOLOBOVA*, L.L. IVANOV, O.S. ZHVANKO, O.M. KHITROVA, A.S. BATSANOV and
Yu.T. STRUCHKOV

Nesmeyanov Institute of Organoelement Compounds, U.S.S.R. Academy of Sciences, 28 Vavilov Str., Moscow B-334 (U.S.S.R.)

Summary

The cyclopentadienylmanganese carbonyl complexes with terminal allenylidene ligands, $Cp(CO)_2Mn=C=C=CR_2$ (R = Bu^t, Ph), are protonated by HX acids (X = Cl, BF_4, CF_3COO) yielding cationic vinylcarbyne complexes of the type $[Cp(CO)_2Mn\equiv C-CH=CR_2]^+X^-$. One of these, with R = Ph, X = BF_4, was characterized by X-ray crystallography. The Mn–C bond of 1.665 Å in it is the shortest one known to date. The binuclear μ-vinylidene complexes, $[Cp(CO)_2Mn]_2C=CHR'$ (R' = Ph, COOMe) are also protonated at the β-carbon atom of the vinylidene ligand.

Introduction

The reactivity of metal carbonyl complexes with terminal unsaturated carbene ligands, e.g. $Cp(CO)_2Mn=C=CRR'$ and $Cp(CO)_2Mn=C=C=CR_2$, is insufficiently studied to date. These complexes are known to react with $Fe_2(CO)_9$ giving binuclear complexes with metallated trimethylenemethane [1], μ-vinylidene and μ-allenylidene ligands [2].

The interaction of $Cp(CO)_2Mn=C=CRR'$ and $Cp(CO)_2Mn=C=C=CR_2$ with $Cp(CO)_2MQ$ (M = Mn, Re; Q = Et_2O, THF) yields binuclear cumulidene complexes [3–6]:

In the case M = Re the η^1-vinylidene ligand migrates from the manganese to the rhenium atom, through the intermediate formation of the unstable intermediate μ-vinylidene Mn–Re complex. Their reactions with nucleophiles, such as RLi [6–8],

LiOMe, NaNH$_2$, NaSBu^t, PR$_3$ [9–11], have also been studied.

On the other hand, the reactions with electrophilic reagents remain practically uninvestigated. The only example known is the interaction of the unsubstituted μ-vinylidenemanganese complex [Cp(CO)$_2$Mn]$_2$C=CH$_2$ with CF$_3$COOH, which yields a binuclear carbyne compound [12]. In the present paper we report protonation of manganese carbonyl complexes with terminal allenylidene and bridging vinylidene ligands by protic acids (HCl, HBF$_4$, CF$_3$COOH). The preliminary communication was published earlier [13].

Results and discussion

The molecules of allenylidene- and vinylidene-manganese complexes contain several reaction centers which can be attacked by a proton, i.e. the metal atom, a carbonyl oxygen and carbon atoms of the cumulidene chain. It was found that the allenylidene complexes I and II readily react with protic acids (HCl, HBF$_4$ and CF$_3$COOH). A proton is added to the β-carbon atom of the allenylidene ligand and thus cationic vinylcarbyne manganese complexes are formed:

$$Cp(CO)_2Mn=C=C=CR_2 + HX \xrightarrow[\text{ether}]{20°C} \left[Cp(CO)_2Mn\equiv C-CH=CR_2 \right]^+ X^-$$
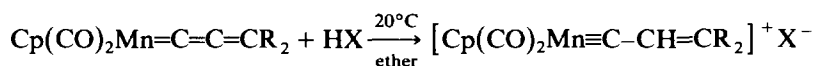
(I: R = Bu^t;   (III: R = Bu^t, X = CF$_3$COO;

  II: R = Ph)   IV: R = Ph, X = Cl;

                V: R = Ph, X = CF$_3$COO;

                VI: R = Ph, X = BF$_4$)

The complexes prepared are orange crystalline (IV, VI) or oily (III, V) substances. They are sensitive to oxygen and moisture, are poorly soluble in aliphatic hydrocarbons and ether but are readily soluble in CH$_2$Cl$_2$. In basic solvating solvents (THF, H$_2$O) they dissociate into the initial allenylidene complexes (I or II) and the corresponding acids.

The molecular structures of III and IV were studied by IR and ^{1}H NMR spectroscopy. The IR spectra of I–VI each contain two absorption bands ν(C≡O) of equal intensity (see Table 1). The carbonyl group bands of the protonated compounds III–VI are shifted by 80–100 cm^{-1} to shorter wavelengths with respect to the parent complexes I and II. The shift is due to a decrease in electron density on

TABLE 1

IR SPECTRA OF THE COMPLEXES I–VI (ν, cm^{-1})

Compound	ν(C≡O)	ν(C=C=C)	Solvent
I	1955, 1940	1925	Cyclohexane
II	2000, 1950	1915	Cyclohexane
III	2090, 2050	–	CH$_2$Cl$_2$ + CF$_3$COOH
IV	2076, 2036	–	CH$_2$Cl$_2$
V	2086, 2046	–	CH$_2$Cl$_2$ + CF$_3$COOH
VI	2090, 2048	–	CH$_2$Cl$_2$

TABLE 2

^{1}H NMR SPECTRA OF I AND III (δ, ppm, TMS)

Compound	Bu^t	Cp	CH	Solvent
I	1.33	4.75	–	CD$_2$Cl$_2$
III ^{a}	0.88	5.05	6.85	CF$_3$COOH
	1.27			

^{a} TMS as an external standard.

the metal atom on passing from the neutral allenylidene- to cationic vinylcarbyne-manganese complexes.

It is noteworthy that the ν(C≡O) values observed for III and IV are similar to those of the previously studied manganese and rhenium carbyne complexes, viz. 2088, 2047 cm^{-1} for [Cp(CO)$_2$Mn≡CPh]$^+$BCl$_4$$^-$ [14] and 2089, 2038 cm^{-1} for [Cp(CO)$_2$Re≡CPh]$^+$BCl$_4$$^-$ [15]. The absence of the characteristic frequencies of the allenylidene moiety in spectra of III–VI is consistent with the proposed structures of the complexes.

Additional structural information about the protonated complexes was obtained from their ^{1}H NMR spectra, presented in Table 2. The spectrum of the parent allenylidene complex I contains only a singlet of protons of two equivalent Bu^t groups and a singlet of the Cp ring. In the spectrum of the protonated product III two signals of Bu^t group protons are present, the Cp signal is shifted to a low field, and a signal of a vinyl group proton appears. Such difference between the NMR spectra of I and III can be explained by protonation of the β-carbon atom of the allenylidene ligand and formation of the vinyl moiety: -CH=CBu$^t_2$. Thus the Bu^t groups become magnetically non-equivalent, while the manganese atom acquires positive charge.

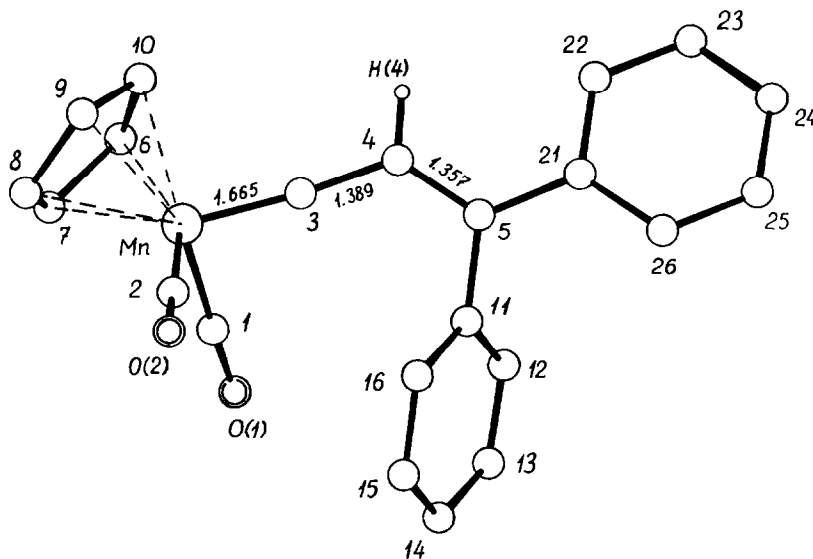Fig. 1. The structure of the [Cp(CO)$_2$Mn≡C-CH=CPh$_2$]$^+$ cation in crystals of VI (phenyl and cyclopentadienyl hydrogen atoms are omitted).

TABLE 3

BOND LENGTHS (Å)

Bond		Bond		Bond	
Mn–C(1)	1.838(6)	C(4)–H(4)	0.91	C(24)–C(25)	1.374(8)
Mn–C(2)	1.816(5)	C(5)–C(11)	1.480(7)	C(25)–C(26)	1.381(7)
Mn–C(3)	1.665(5)	C(5)–C(21)	1.463(7)	C(26)–C(21)	1.390(7)
Mn–C(6)	2.132(6)	C(11)–C(12)	1.394(7)	C(6)–C(7)	1.408(9)
Mn–C(7)	2.163(6)	C(12)–C(13)	1.378(7)	C(7)–C(8)	1.384(9)
Mn–C(8)	2.162(6)	C(13)–C(14)	1.379(8)	C(8)–C(9)	1.412(9)
Mn–C(9)	2.120(6)	C(14)–C(15)	1.382(7)	C(9)–C(10)	1.417(9)
Mn–C(10)	2.116(6)	C(15)–C(16)	1.387(7)	C(10)–C(6)	1.412(9)
C(1)–O(1)	1.134(7)	C(16)–C(11)	1.391(7)	B–F(1)	1.331(9)
C(2)–O(2)	1.132(6)	C(21)–C(22)	1.412(7)	B–F(2)	1.334(9)
C(3)–C(4)	1.389(7)	C(22)–C(23)	1.373(7)	B–F(3)	1.333(9)
C(4)–C(5)	1.357(7)	C(23)–C(24)	1.389(8)	B–F(4)	1.28(1)

A more detailed structural study of the vinylcarbyne complex VI was performed by X-ray crystallography. The crystal structure of VI consists of discrete $[Cp(CO)_2Mn\equiv C-CH=CPh_2]^+$ cations (Fig. 1) and BF_4^- anions. Bond lengths and angles are listed in Tables 3 and 4.

The Mn atom is bonded to the planar η^5-cyclopentadienyl ring (the Mn to Cp mean plane distance is 1.772 Å), two linear carbonyls and the C(3) atom of the carbyne ligand, and has a "piano stool" environment. C(3) eclipses C(10) of the Cp ring, thus the cation (except its $C(5)Ph_2$ moiety) has an approximate non-crystallographic mirror plane (through Mn, C(3), C(4), C(10) and the midpoint of the C(7)–C(8) bond). The C(4)–C(5) bond forms an angle of 24° with this plane.

The Mn–C(3) bond is the shortest one known till now. The Mn–C(sp) double bonds are of 1.806 Å in $Cp(CO)_2Mn=C=C=C(C_6H_{11}\text{-}cyclo)_2$ [10] and of 1.79 Å in $(C_5H_4Me)(CO)_2Mn=C=CMe_2$ [8], while the triple bonds (on which no information is available) must be slightly shorter than the Cr–C(carbyne) bonds of 1.68–1.76 Å [16], as the Pauling single-bond covalent radii of Cr and Mn are 1.26 and 1.25 Å, respectively [17]. Thus, the Mn–C(3) bond length of 1.665 Å reflects its strong

TABLE 4

BOND ANGLES (°)

Angle		Angle		Angle	
C(1)MnC(2)	95.0(2)	C(5)C(11)C(16)	120.5(4)	C(24)C(25)C(26)	120.1(5)
C(1)MnC(3)	93.9(3)	C(12)C(11)C(16)	119.2(4)	C(21)C(26)C(25)	120.6(5)
C(2)MnC(3)	93.1(2)	C(11)C(12)C(13)	120.3(5)	C(7)C(6)C(10)	107.1(5)
MnC(1)O(1)	177.9(5)	C(12)C(13)C(14)	120.2(5)	C(6)C(7)C(8)	109.3(5)
MnC(2)O(2)	176.8(5)	C(13)C(14)C(15)	120.2(5)	C(7)C(8)C(9)	108.1(5)
MnC(3)C(4)	174.6(4)	C(14)C(15)C(16)	120.0(5)	C(8)C(9)C(10)	107.5(5)
C(3)C(4)C(5)	124.2(5)	C(11)C(16)C(15)	120.1(5)	C(6)C(10)C(9)	108.0(5)
C(3)C(4)H(4)	115.6	C(5)C(21)C(22)	120.6(4)	F(1)BF(2)	108.0(6)
C(5)C(4)H(4)	119.9	C(5)C(21)C(26)	120.4(4)	F(1)BF(3)	109.9(6)
C(4)C(5)C(11)	119.6(4)	C(22)C(21)C(26)	119.0(4)	F(1)BF(4)	108.0(7)
C(4)C(5)C(21)	122.4(5)	C(21)C(22)C(23)	119.6(5)	F(2)BF(3)	110.4(6)
C(11)C(5)C(21)	118.0(4)	C(22)C(23)C(24)	120.5(5)	F(2)BF(4)	109.9(7)
C(5)C(11)C(12)	120.3(4)	C(23)C(24)C(25)	120.2(5)	F(3)BF(4)	110.6(7)

triple character. On the other hand, the C(3)–C(4) bond of 1.389 Å is shorter than the standard length of the $C(sp)$–$C(sp^2)$ single bond of 1.426 Å [18], and the C(4)–C(5) bond of 1.357 Å is longer than the standard length of the double bond of 1.333 Å [19], indicating that the carbyne structure (A) of VI is stabilized by a contribution from the carbene structure (B):

$$Mn^+\equiv C-CH=CPh_2 \leftrightarrow Mn=C=CH-C^+Ph_2$$
$$\quad (A) \qquad\qquad\qquad (B)$$

Coordination of the C(4) and C(5) atoms is planar trigonal. The corresponding coordination planes C(3), C(4), C(5), H(4) and C(4), C(5), C(11), C(21) form an angle of 10.7°. The Mn–C(3) bond is tilted out of the C(4) coordination plane by 4.5°. Such non-planarity of the π-delocalized system MnC(3)C(4)C(5), too small to prevent such delocalization, is due to the bulky phenyl substituents C(11) · · · C(16) and C(21) · · · C(26). These phenyls form large angles (54.8° and 29.2°, respectively) with the C(5) coordination plane, due to the same steric overcrowding.

The BF_4^- anion has the usual tetrahedral geometry and undergoes strong libration, indicated by large thermal factors of its fluorine atoms.

The ions are separated from each other by normal Van der Waals distances [20,21], the shortest of which are C(7) · · · C(13) $(x - 1, y, z)$ of 3.28, C(8) · · · C(14) $(x - 1, y, z)$ of 3.32, F(3) · · · H(10) $(x, 1/2 - y, 1/2 + z)$ of 2.25 Å.

We have also studied the action of protic acids on the binuclear complexes VII and VIII containing μ-vinylidene ligands. It was found that under identical conditions both complexes were protonated at the β-carbon atom of the vinylidene ligand:

$$\left[Cp(CO)_2Mn\right]_2 C=CHR \xrightarrow[\quad]{HX, \; 20°C} \left[Cp(CO)_2Mn-\!\!\!-\!\!\!-Mn(CO)_2Cp\right]^+ X^-$$

(VII   R = COOMe ;
  VIII · R = Ph)

(VIIa   R = COOMe ,
  VIIIa   R = Ph)

The resulting complexes VIIa and VIIIa are unstable and therefore were not isolated. They were characterized by ^{1}H NMR spectroscopy (see Table 5).

As shown in Table 5, the NMR spectra of the protonated complexes VIIa and

TABLE 5

^{1}H NMR SPECTRA OF COMPLEXES VII, VIII, VIIa AND VIIIa (δ, ppm, TMS)

Compound	Cp	R	CH	CH$_2$	Solvent
VII	4.60	3.64	7.64	–	CDCl$_3$
	4.70	(OCH$_3$)			
VIII	4.72	7.0–8.3	8.46	–	CS$_2$
	4.79	(Ph)	–		
VIIa	4.8	3.26	–	4.8	CF$_3$COOH
		(OCH$_3$)			
VIIIa	4.62	7.0–7.6	–	4.56	CDCl$_3$
	4.71	(Ph)			

TABLE 6. ATOMIC COORDINATES ($\times 10^4$, for Mn $\times 10^5$) AND ANISOTROPIC THERMAL FACTORS IN THE FORM $T = \exp[-0.25(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	19683(8)	23643(5)	4552(6)	1.57(3)	1.43(3)	2.11(3)	−0.13(3)	0.47(3)	0.00(3)
O(1)	3578(4)	853(3)	−3(4)	3.2(2)	2.0(2)	7.4(3)	0.2(2)	1.6(2)	−1.8(2)
O(2)	3325(4)	2530(3)	2720(3)	4.1(2)	3.3(2)	2.1(2)	−0.4(2)	−0.2(2)	0.7(2)
C(1)	2961(6)	1422(4)	189(5)	2.4(3)	1.8(3)	3.5(3)	−0.7(2)	0.6(3)	−0.7(2)
C(2)	2807(5)	2441(3)	1853(4)	2.2(3)	1.4(2)	3.1(3)	0.0(2)	1.0(2)	0.9(2)
C(3)	2991(5)	3097(3)	101(4)	1.1(2)	2.1(2)	1.4(2)	0.5(2)	0.1(2)	−0.2(2)
C(4)	3750(5)	3719(3)	−282(4)	1.8(2)	1.5(2)	1.9(3)	0.1(2)	0.5(2)	−0.2(2)
C(5)	5023(5)	3583(3)	−401(4)	1.9(2)	1.1(2)	1.3(2)	−0.3(2)	0.2(2)	−0.6(2)
C(6)	259(6)	2125(4)	−820(5)	2.1(3)	4.5(4)	2.4(3)	−0.4(2)	0.2(2)	0.0(3)
C(7)	183(6)	1553(4)	15(5)	1.8(3)	3.3(3)	3.4(3)	−1.0(2)	0.0(2)	0.0(3)
C(8)	111(6)	2036(4)	903(5)	2.0(3)	4.1(3)	2.8(3)	−0.8(2)	1.0(2)	0.1(2)
C(9)	137(6)	2932(4)	641(5)	1.4(3)	3.4(3)	4.4(4)	0.3(2)	0.9(3)	−1.1(3)
C(10)	208(6)	2986(4)	−436(6)	1.7(3)	2.8(3)	5.0(4)	0.5(2)	0.0(3)	1.5(3)
C(11)	5761(5)	2783(3)	44(4)	1.4(2)	1.3(2)	1.7(2)	0.0(2)	0.0(2)	0.2(2)
C(12)	6275(5)	2218(3)	−609(4)	1.6(2)	1.5(2)	2.5(3)	−0.2(2)	0.4(2)	0.0(2)
C(13)	6906(5)	1452(3)	−206(4)	1.7(2)	1.5(2)	2.8(3)	−0.2(2)	0.8(2)	−0.2(2)
C(14)	7056(5)	1247(3)	851(4)	1.5(2)	1.6(2)	2.8(3)	0.3(2)	0.3(2)	0.5(2)
C(15)	6581(5)	1810(3)	1514(4)	2.2(3)	2.3(3)	2.0(3)	0.3(2)	0.6(2)	0.8(2)
C(16)	5931(5)	2578(3)	1113(4)	1.9(2)	1.5(2)	2.1(2)	−0.1(2)	0.7(2)	0.0(2)
C(21)	5693(5)	4190(3)	−986(4)	1.8(2)	0.8(2)	1.7(2)	0.2(2)	0.7(2)	−0.2(2)
C(22)	4930(5)	4702(3)	−1821(4)	1.7(2)	1.5(2)	1.7(2)	0.2(2)	0.5(2)	0.1(2)
C(23)	5582(5)	5245(3)	−2382(4)	2.7(3)	1.7(2)	1.8(2)	0.7(2)	0.6(2)	0.5(2)
C(24)	6983(6)	5301(3)	−2126(4)	3.0(3)	1.3(2)	2.9(3)	−0.2(2)	1.6(2)	0.0(2)
C(25)	7732(5)	4812(3)	−1307(4)	2.2(3)	1.4(2)	2.9(3)	−0.3(2)	0.9(2)	−0.3(2)
C(26)	7094(5)	4260(3)	−736(4)	1.7(2)	1.0(2)	2.3(3)	0.0(2)	0.6(2)	−0.3(2)
B	931(7)	−101(5)	2431(6)	2.8(4)	3.5(4)	2.8(4)	−0.6(3)	0.7(3)	−0.8(3)
F(1)	1671(4)	−30(3)	1714(3)	6.0(2)	8.0(3)	6.3(3)	−1.7(2)	3.7(2)	−2.0(2)
F(2)	−339(4)	−274(4)	1919(4)	2.5(2)	14.0(4)	12.3(4)	−1.1(2)	1.6(2)	−10.3(3)
F(3)	986(5)	643(3)	2975(4)	8.3(3)	9.2(3)	8.8(3)	−1.6(2)	2.2(3)	−6.7(3)
F(4)	1405(8)	−737(4)	3052(5)	20.4(7)	12.0(5)	11.0(5)	−1.1(4)	−1.2(4)	8.9(4)

VIIIa exhibit no signal of a vinyl proton, but show a signal of CH_2 group protons. In the spectrum of VIIa the latter signal overlaps that of the Cp ligand. The ratio between the intensities of singlets at 4.8 ppm (2 Cp, 10 H + CH_2, 2 H) and 3.26 ppm (OCH_3, 3 H) is 4:1, i.e. it is consistent with such an overlap. The magnetic equivalence of both Cp ligands in VIIa can be explained by free rotation of the CH_2COOMe group. In VIIIa such rotation is probably hindered due to the presence of a more bulky Ph substituent and, as a result, the signals of Cp rings from both rotamers are present. Thus, the NMR data give evidence that in the case of complexes VII and VIII the proton is added to the β-carbon atom of the vinylidene ligand.

The protonation of both the E and Z isomers of the binuclear Fe–Mn complex IX (prepared earlier [2]) probably proceeds similarly, i.e. a reversible addition of a proton to the β-carbon of the vinylidene ligand takes place:
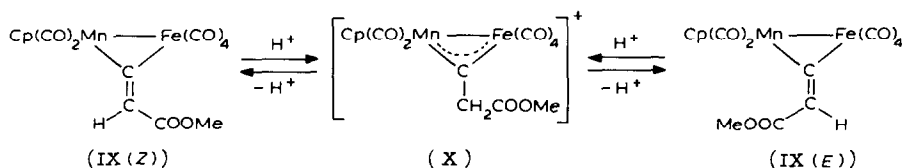
In the unstable intermediate complex X the rotation of the CH_2COOMe group is probably free, and so deprotonation of X gives a mixture of equal amounts of the E and Z isomers of IX.

Experimental

All operations were performed in a nitrogen atmosphere using absolute solvents. The original vinylidene and mononuclear allenylidene complexes were prepared according to reported procedures [3,7,22,23]. Photochemical reactions were run in a water-cooled quartz apparatus using a PRK-7 lamp (1000 W) for irradiation. Chromatography was performed on SiO_2 (100 × 160 μ, Chemapol, Czechoslovakia). IR spectra were recorded with an UR-20 Zeiss spectrometer, and NMR spectra with a R-20 Perkin Elmer spectrometer (60 MHz).

The X-ray study of VI was performed with a Syntex $P2_1$ autodiffractometer (graphite-monochromated Mo-K_α radiation) at $-120°C$. Crystal data of VI: $C_{22}H_{16}BF_4MnO_2$, monoclinic, $a = 10.179(3)$; $b = 15.286(4)$, $c = 12.961(4)$ Å, $\beta = 103.57(3)°$, $V = 1960.4(1.1)$ Å^3, $Z = 4$, $D_{calcd} = 1.54$ g cm^{-3}, space group $P2_1/c$. 2103 independent reflections with $I \geqslant 2\sigma$ and $2\theta \leqslant 49°$ were measured by $\theta/2\theta$ scan technique. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares, using the weighting scheme $W = \sigma_F^{-2}$ and an anomalous dispersion correction in the Mn scattering curve. The anisotropic refinement of all non-hydrogen atoms converged at $R = 0.073$. Then all hydrogen atoms were included as fixed contributions (H(4) located from the difference Fourier synthesis, others in calculated positions) with assumed B_{iso} 1 Å^2 larges than the B_{iso}^{eq} of the corresponding (linked) carbon atoms. The final refinement gave $R = 0.054$, $R_w = 0.044$. The corresponding atomic coordinates and thermal factors are listed in Tables 6 and 7.

Calculations were performed with an Eclipse S/200 computer using EXTL

programmes modified and expanded in our laboratory by A.I. Yanovskii and R.G. Gerr [24].

Preparation of III

0.1 g (0.31 mmol) of $Cp(CO)_2Mn=C=C=C(Bu^t)_2$ (I) was dissolved in 2 ml of CH_2Cl_2. After addition of 1 ml CF_3COOH the solution changed colour from brown to orange. In the IR spectrum two $\nu(C≡O)$ bands at 2090 and 1950 cm^{-1} were found. The solvent was removed in vacuo, the remaining orange oil was washed with pentane (3 × 3 ml) and dried in vacuo, yielding 0.14 g (93%) of III.

Preparation of V

0.15 g (0.41 mmol) of II was treated by the same procedure as I, yielding 0.11 g (55%) of V. IR: $\nu(C≡O)$ 2086, 2046 cm^{-1} (in CH_2Cl_2/CF_3COOH, 2:1).

Preparation of IV

0.33 g (0.81 mmol) of II was dissolved in 20 ml of ether. Then 4.0 ml of a 3.56 N solution of HCl in Et_2O was added. The solution changed colour from dark red to dark brown and an orange crystalline precipitate was formed. The solution was decanted off, and the precipitate was washed with ether (3 × 3 ml) and dried in vacuo, yielding 0.11 g (33%) of IV (orange crystals, decomposing without melting at 150°C).

Preparation of VI

After addition of 15 ml of a 0.31 N ether solution of HBF_4 to a solution of 0.26 g (0.71 mmol) of II in 20 ml of ether, an orange oil was formed. The solution was decanted off, and the oil was washed with ether (3 × 3 ml) and crystallized on drying in vacuo. Recrystallization from CH_2Cl_2 gave 0.25 g (78.1%) or orange crystalline VI, m.p. 109–110°C (dec.). The quality of crystals was sufficiently good for a single crystal X-ray study. Found: C, 55.75; H, 3.52; F, 16.60. $C_{22}H_{16}BF_4MnO_2$, calcd.: C, 58.19; H, 3.55; F, 16.74%.

Preparation of VIIa

0.1 g (0.23 mmol) of VII was dissolved in 3 ml of CF_3COOH. NMR ^1H (δ, ppm, TMS): 3.26 s (OCH_3, 3 H); 4.8 s (2 Cp, 10 H + CH_2, 2 H).

TABLE 7

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

Atom	x	y	z	Atom	x	y	z
H(4)	331	422	−52	H(14)	751	69	114
H(6)	34	194	−155	H(15)	670	167	228
H(7)	17	90	−2	H(16)	558	298	159
H(8)	5	179	161	H(22)	392	467	−201
H(9)	12	344	113	H(23)	505	561	−297
H(10)	22	354	−84	H(24)	745	569	−255
H(12)	619	237	−138	H(25)	874	486	−112
H(13)	726	104	−68	H(26)	765	391	−13

Preparation of VIIIa

0.1 g (0.22 mmol) of VIII was dissolved in 3 ml of CF_3COOH. NMR ^1H (δ, ppm, TMS): 4.62 s (Cp, 5 H); 4.56 s (CH_2, 2 H); 7.00–7.60 (Ph, 5 H).

Interaction of Z-IX with HCl / Et$_2$O

0.43 g (1.00 mmol) of Z-IX was dissolved in 30 ml of ether. 5 ml of 3.56 N HCl/Et_2O solution was added and the mixture stirred for 30 min at 20°C. The solvent was removed in vacuo and the residue was chromatographed. A bright red zone eluted by petroleum ether/ether (9/1) yielded 0.16 g (37%) of *E*-IX, and a dark-red zone eluted by petroleum ether/ether (4/1) yielded 0.20 g (46%) of *Z*-IX, identified by IR spectra [2].

References

1 V.G. Andrianov, Yu.T. Struchkov, N.E. Kolobova, A.B. Antonova and N.S. Obesyuk, J. Organomet. Chem., 122 (1976) C33.

2 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, G.G. Aleksandrov and Yu.T. Struchkov, J. Organomet. Chem., 228 (1982) 265.

3 A.B. Antonova, N.E. Kolobova, P.V. Petrovsky, B.V. Lokshin and N.S. Obesyuk, J. Organomet. Chem., 137 (1977) 55.

4 N.E. Kolobova, A.B. Antonova and O.M. Khitrova, J. Organomet. Chem., 146 (1978) C17.

5 H. Berke, J. Organomet. Chem., 185 (1980) 75.

6 H. Berke, Z. Naturforsch., 35b (1980) 86.

7 N.E. Kolobova, L.L. Ivanov and O.S. Zhvanko, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 478.

8 H. Berke, G. Huttner and J. Seyerl, J. Organomet. Chem., 218 (1981) 193.

9 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, V.F. Sizoy and Yu.S. Nekrasov, Izv. Akad. Nauk. SSSR, Ser. Khim., (1979) 2393.

10 H. Berke, G. Huttner and J. Seyerl, Z. Naturforsch., 36b (1981) 1277.

11 H. Berke, P. Härter, G. Huttner and L. Szolnai, Z. Naturforsch., 36b (1981) 929.

12 L.N. Lewis, J.C. Huffman and K.O. Caulton, J. Amer. Chem. Soc., 102 (1980) 403.

13 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, A.S. Batsanov and Yu.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2632.

14 E.O. Fischer, E.W. Meineke and F.R. Kreissl, Chem. Ber., 110 (1977) 1140.

15 E.O. Fischer, R.L. Clough, G. Besl and F.R. Kreissl, J. Organomet. Chem., 120 (1976) C6.

16 A. Frank, U. Shubert and G. Huttner, Chem. Ber., 110 (1977) 3020.

17 L. Pauling, Acta Crystallogr. B, 34 (1978) 746.

18 H.J. Bernstein, Trans. Faraday Soc., 57 (1961) 1649.

19 A.I. Kitaigorodsky, Molecular Crystals and Molecules. Academic Press Inc., New York, London, 1973.

20 Yu.V. Zefirov and P.M. Zorkii, Zh. Strukt. Khim., 15 (1974) 118.

21 Yu.V. Zefirov and M.A. Porai-Koshits, Zh. Strukt. Khim., 21 (1980) 150.

22 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko and P.V. Petrovskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 432.

23 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, I.N. Chechulina and V.V. Derunov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2632.

24 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, Kristallografiya, 28 (1983) 1029.