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CYCLOPENTADIENYLDICARBONYLMANGANESE PHOSPHONIUM YLIDE COMPLEXES. X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta\text{-}C_5H_5)(CO)_2Mn^- \ C(P^+Ph_3)=C=CPh_2 \cdot CH_2Cl_2$

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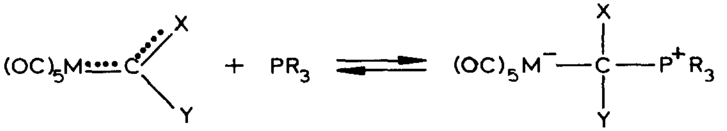
Summary

Unsaturated carbene complexes of manganese, $Cp(CO)_2Mn{=}C{=}CHR$ and $Cp(CO)_2Mn{=}C{=}C{=}CR'_2$ ($Cp = \eta\text{-}C_5H_5$, R = Ph, CO_2Me, $C(t\text{-}Bu)_2OH$; R′ = t-Bu, Ph), add phosphines to the α-carbon atom of a cumulidene ligand to yield the phosphonium ylide complex $Cp(CO)_2Mn^- \ C(P^+Ph_2R'')=CHR$ (R″ = Ph, Me) or $Cp(CO)_2Mn^- \ C(P^+Ph_3)=C=CR'_2$. The latter complex (with R′ = Ph) was studied by X-ray crystallography as a 1 : 1 solvate with CH_2Cl_2.

Introduction

Carbene complexes, $(OC)_nM\overset{\cdots}{-}C(-Y)\overset{\cdots}{-}X$, bearing an electophilic α-carbon atom in the carbene ligand [1] react with various nucleophilic reagents [2]. In particular, such complexes of the Group VIA metals (M = Cr, Mo, W) add phosphines to the α-carbon atom to yield phosphonium ylide complexes [3]:



(1)

These ylide complexes are usually unstable, their stability depending on the nature of the metal, the X and Y substituents, and the basicity of the phosphine [4]. In solution the Cr, Mo and W complexes dissociate into the initial compounds. The equilibrium (1) is shifted towards the initial components when X and Y are heteroatomic substituents, and when the electrophilicity of the carbene ligand is reduced by conjugation effects [4]. On the contrary, diphenylcarbenepentacarbonyl-

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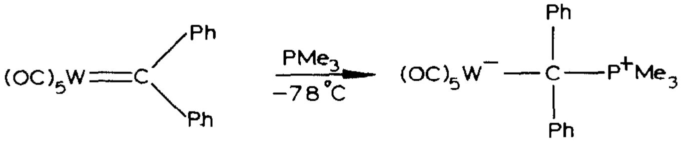
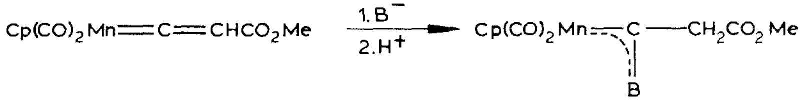
tungsten, which has a more electrophilic α-carbon atom due to the absence of heteroatomic substituents, reacts readily with PMe_3 at low temperatures [5]:



(2)

Metal carbonyl complexes with unsaturated carbene ligands, in contrast to Fischer carbene complexes, have several reaction centres. Vinylidene complexes of the type $Cp(CO)_2Mn{=}C(1){=}C(2)HR$ have two: viz. the electrophilic C(1) and the nucleophilic C(2). Accordingly, $Cp(CO)_2Mn{=}C{=}CHCO_2Me$ reacts with MeOLi in methanol and with $NaNH_2$ in liquid NH_3 [6], adding a MeO^- or an $NH_2{}^-$ anion to C(1) and a proton to C(2) of the carbene ligand:



(3)

Manganese carbene complexes with allenylidene ligands have been predicted (by MO calculations of the idealized model $Cp(CO)_2Mn{=}C(1){=}C(2){=}C(3)H_2$) to have two electrophilic centres, viz. C(1) and C(3) [7,8].

We established the nucleophilic character of the C(2) atom in the complexes $Cp(CO)_2Mn{=}C{=}C{=}CR_2$ (where R = Ph, t-Bu) by studying their protonation, which gives cationic vinylcarbyne complexes [9]:

$$Cp(CO)_2Mn{=}C{=}C{=}CR_2 \xrightarrow{H^+} [Cp(CO)_2Mn{\equiv}C{-}CH{=}CR_2]^+X^- \qquad (4)$$

$$(X = Cl, BF_4, CF_3CO_2)$$

Berke et al. [7] investigated the interaction of allenylidene manganese complexes with Lewis bases, and found that hard bases (MeO^-, Me_2N^-) add to C(1) while soft ones (PPh_3, PEt_3) add to C(3) of the unsaturated carbene ligand. Moreover, the methoxy group attached to C(1) participates in the conjugation with the vinyl group. Therefore a methoxyvinyl moiety is more stable than that of a phosphonium ylide.

The reaction of $(\eta\text{-}MeC_5H_4)(CO)_2Mn{=}C{=}C{=}CR_2$ (R = Ph, t-Bu) with phosphines, studied by the same authors, yielded crystalline substances, which on the basis of their ^1H, ^{13}C and ^{31}P NMR spectra were considered to be betaine compounds with a tetracoordinated phosphorus atom bonded to C(3).

It should be noted, however, that the allenylidene chromium complex reacts with PPh_3, producing an adduct with the phosphine moiety bonded to C(1) [10]. The structure of I was unambiguously established by X-ray crystallography.

$$(OC)_5Cr{=}C{=}C{=}C(i\text{-}Pr)_2 \xrightarrow{PPh_3} \underset{(I)}{(OC)_5Cr^-C(P^+Ph_3){=}C{=}C(i\text{-}Pr)_2} \qquad (5)$$

We have already reported [11,12] the preparation of some phosphonium ylide derivatives from vinylidene and allenylidene manganese complexes and PPh_3.

In the present paper we report the synthesis of phosphonium ylide manganese derivatives, their structure and their reactivity.

Results and discussion

In the course of our investigation of unsaturated carbene manganese complexes, we prepared several vinyl- and allenyl-phosphonium ylide manganese derivatives (reactions 6 and 7):

$$\mathrm{Cp(CO)_2Mn{=}C{=}CHR} \xrightarrow{\mathrm{PPh_2R'}} \mathrm{Cp(CO)_2Mn^-C(P^+Ph_2R'){=}CHR} \tag{6}$$

$(R = R' = Ph$ (II), $R = Ph$, $R' = Me$ (III);
$R = CO_2Me$, $R' = Ph$ (IV);
$R = C(t\text{-}Bu)_2OH$, $R' = Ph$ (V))

$$\mathrm{Cp(CO)_2Mn{=}C{=}C{=}CR_2} \xrightarrow{\mathrm{PPh_3}} \mathrm{Cp(CO)_2Mn^-C(P^+Ph_3){=}C{=}CR_2} \tag{7}$$

$(R = t\text{-}Bu$ (VI); $R = Ph$ (VII))

Some properties, IR and ^{31}P NMR spectral data of complexes II–VII are presented in Table 1. These complexes are intensely coloured crystalline substances, poorly soluble in hydrocarbons but readily soluble in CH_2Cl_2. In polar solvents (THF, $CHCl_3$, Et_2O) they readily dissociate into the initial compounds. In the range 1600–2000 cm^{-1} of their IR spectra, complexes II–VII exhibit two $\nu(C{\equiv}O)$ bands of equal intensity at 1810–1900 cm^{-1}. These bands are shifted to longer wavelengths relative to $\nu(C{\equiv}O)$ of the initial compounds [14,15]. No $\nu(Mn{=}C{=}C)$ or $\nu(Mn{=}C{=}C{=}C)$ stretching bands are observed.

The ^{31}P NMR spectra of complexes II–VII exhibit signals of ^{31}P in the range 12–15 ppm, characteristic of a tetracoordinated, positively charged phosphorus atom. The mass spectra of these complexes, except III, show no molecular ion signals. The most typical peaks correspond to the fragments $[Cp(CO)_2MnPPh_3]^+$, $[CpMnPPh_3]^+$, $[CpMn]^+$, $[PPh_3]^+$, $[Mn]^+$, $[Cp(CO)_2MnL]^+$ and $[CpMnL]^+$ ($L = C{=}CHPh$, $C{=}C{=}CPh_2$, $C{=}C{=}C(t\text{-}Bu)_2$).

The spectroscopic data reveal that molecules of II–VII involve tetracoordinated phosphorus atoms bonded to one of carbon atoms of the unsaturated moiety. For vinylidene manganese complexes, the ylide structure is unquestionable, because only the α-carbon atom of that ligand is electrophilic. Allenylidene manganese complexes, according to MO calculations [7], have two electrophilic centres, C(1) and C(3). Thus, on the basis of the spectral data alone, the position of the PR_3 substituent in the ligand could not be unambiguously established. Therefore a complete X-ray structural study of VII was performed.

Crystals of VII grown from CH_2Cl_2 turned out to be a 1:1 solvate, designated below as VIII. The molecular structure of VII is shown in Fig. 1; bond lengths and angles are listed in Tables 2 and 3. As seen from Fig. 1, the C(1) atom of the allene moiety is bonded to the Mn and P atoms, i.e. addition of PPh_3 to the η^1-allenylidene ligand occurs at position 1, just as in I [10] and in $[Cp(CO)_2FeC(P^+Ph_3){=}CHPh]BF_4^-$ (IX), with a vinylidene ligand instead of an allenylidene ligand [15].

The manganese atom in VIII has a slightly distorted "three-legged piano stool" coordination. The η^5-cyclopentadienyl ring is planar with the Mn–C and C–C distances averaging 2.153(8) and 1.410(5) Å, respectively. The C(4)O(1) carbonyl group is significantly non-linear due to intramolecular steric overcrowding revealed

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF COMPLEXES II–VII

Complex	M.p. (°C)	Colour	IR spectra ν(C≡O) (cm^{-1})[a]	^{31}P NMR spectra (δ, ppm, H_3PO_4, in CH_2Cl_2 at −70°C)[b]
$Cp(CO)_2Mn^- C(P^+Ph_3)$=CHPh (II)	113–114	orange	1900, 1830 (CH_2Cl_2) 1890, 1820 (KBr)	14.64
$Cp(CO)_2Mn^- C(P^+Ph_2Me)$=CHPh (III)	147 (dec.)	orange	1900, 1825 (CH_2Cl_2) 1885, 1812 (KBr)	13.94
$Cp(CO)_2Mn^- C(P^+Ph_3)=CHCO_2Me$ (IV)	85–87 (dec.)	brown	1910, 1827 (KBr) 1710 (ν(C=O))	13.87
$Cp(CO)_2Mn^- C(P^+Ph_3)$=CHC $(t\text{-}Bu)_2OH$ (V)	100–105 (dec.)	yellow	1890, 1818 (KBr) 3200–3400 (ν(OH))	
$Cp(CO)_2Mn^- C(P^+Ph_3)=C=C(t\text{-}Bu)_2$ (VI)	126–127	yellow	1895, 1825 (CH_2Cl_2) 1880, 1810 (KBr)	12.33
$Cp(CO)_2Mn^- C(P^+Ph_3)=C=CPh_2$ (VII)	>100 (dec.)	yellow	1895, 1825 (CH_2Cl_2) 1895, 1825 (KBr)	15.91

[a] ν(C≡O) of the corresponding parent complexes (cm^{-1}, in cyclohexane): $Cp(CO)_2Mn$=C=CHPh, 2009, 1955 [13]; $Cp(CO)_2Mn=C=CHCO_2Me$, 2030, 1975 [15]; $Cp(CO)_2Mn=C=CHC(t\text{-}Bu)_2(OH)$, 2010, 1950 [14]; $Cp(CO)_2Mn=C=C=C(t\text{-}Bu)_2$, 1955, 1940; $Cp(CO)_2Mn=C=C=CPh_2$, 2000, 1948 [14]. [b] ^{31}P NMR spectra (δ, ppm): PPh_3, −8 [26]; PPh_2Me, −28 [27]; Ph_4P^+ Br^-, +20.8 [28]; $(MeC_5H_4)(CO)_2MnC_3Ph_2PPh_3$ (H_3PO_4, in CS_2, at −30°C), 14.3 [8].

by the short contacts P ⋯ C(4) 3.352(2), C(4) ⋯ C(31) 3.084(3), and O(1) ⋯ C(36) 3.174(3) Å. The manganese-allene Mn–C(1) bond distance of 2.065(2) Å in VIII is characteristic of a single bond (Mn–C(phenyl) bond lengths usually vary in the range 2.04–2.08 Å [16–18]), like the corresponding bonds in I and IX. The P–C(1) bond length in VIII (1.779(2) Å) is only slightly shorter than the P–C(Ph) distances (average 1.808(5) Å) and somewhat longer than typical ylide P–C bonds (1.68–1.75 Å [19]). Hence it can be considered a single bond. In I the relationship of the

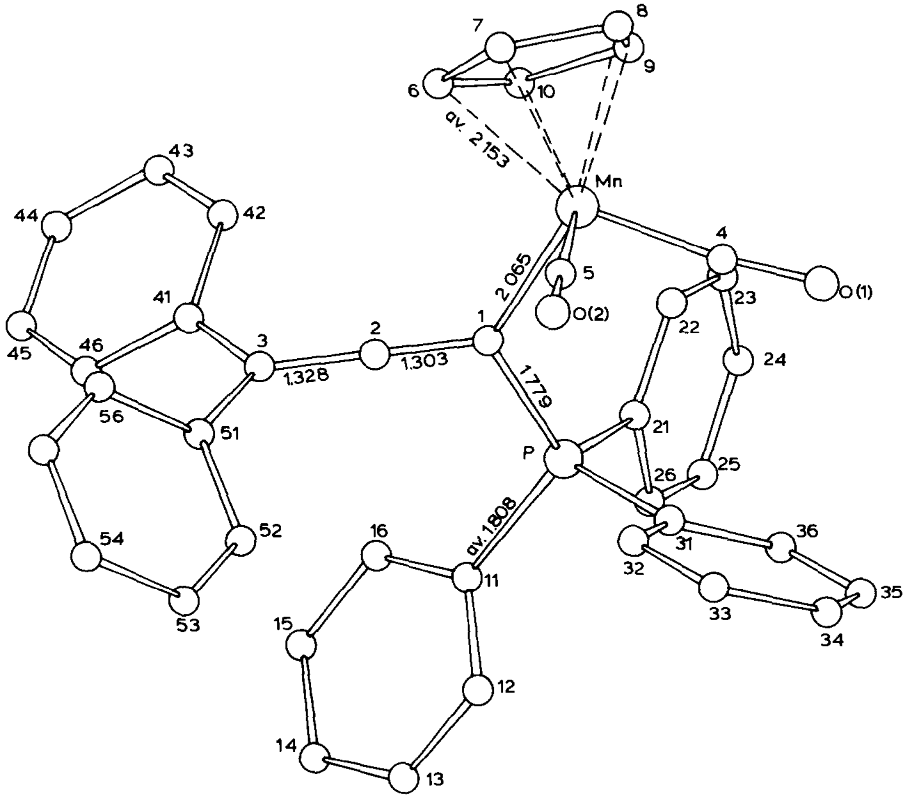


Fig. 1. Molecular structure of $Cp(CO)_2Mn^-$ $C(P^+Ph_3)$=C=CPh$_2$ in VIII. (The hydrogen atoms have been omitted.)

P–C(allene) and average P–C(Ph) bond distances of 1.779(6) and 1.801(4) Å, respectively, is the same as that in VIII, while in IX the P–C(vinyl) and P–C(Ph) bond lengths are essentially equal (1.799(6) and 1.801(6) Å, respectively). The double-bond distances C(1)–C(2) of 1.303(3) and C(2)–C(3) of 1.328(3) Å in the allene moiety of VIII are comparable to those in the free allene molecule (1.308 Å)

TABLE 2

BOND DISTANCES (Å)

Mn–C(1)	2.065(2)	C(5)–O(2)	1.170(3)	C(7)–C(8)	1.407(3)
Mn–C(4)	1.763(2)	P–C(1)	1.779(2)	C(8)–C(9)	1.416(3)
Mn–C(5)	1.766(2)	P–C(11)	1.812(2)	C(9)–C(10)	1.407(3)
Mn–C(6)	2.163(2)	P–C(21)	1.810(2)	C(10)–C(6)	1.415(3)
Mn–C(7)	2.149(2)	P–C(31)	1.801(2)	C–Cl(1)	1.763(2)
Mn–C(8)	2.140(2)	C(1)–C(2)	1.303(3)	C–Cl(2)	1.762(3)
Mn–C(9)	2.156(2)	C(2)–C(3)	1.328(3)	Average	
Mn–C(10)	2.156(2)	C(3)–C(41)	1.493(3)	C–C(Ph)	1.388(6)
Mn–Cp [a]	1.788	C(3)–C(51)	1.493(3)	C(sp^2)–H	0.96(4)
C(4)–O(1)	1.174(3)	C(6)–C(7)	1.403(3)	C(sp^3)–H	1.00(2)

[a] Cp is the centroid of the cyclopentadienyl ring.

TABLE 3

BOND ANGLES (°)

C(1)MnC(4)	100.6(1)	MnC(1)P	122.2(1)	C(12)C(11)C(16)	119.3(2)
C(1)MnC(5)	91.8(1)	MnC(1)C(2)	125.7(2)	PC(21)C(22)	122.1(2)
C(4)MnC(5)	90.4(1)	PC(1)C(2)	112.1(2)	PC(21)C(26)	118.1(2)
CpMnC(1)	120.3	C(1)C(2)C(3)	178.6(2)	C(22)C(21)C(26)	119.7(2)
CpMnC(4)	122.5	C(2)C(3)C(41)	120.7(2)	PC(31)C(32)	117.7(2)
CpMnC(5)	123.6	C(2)C(3)C(51)	120.0(2)	PC(31)C(36)	121.9(2)
C(1)PC(11)	113.2(1)	C(41)C(3)C(51)	119.3(2)	C(32)C(31)C(36)	120.4(2)
C(1)PC(21)	113.1(1)	C(7)C(6)C(10)	107.6(2)	C(3)C(41)C(42)	121.7(2)
C(1)PC(31)	109.4(1)	C(6)C(7)C(8)	108.6(2)	C(3)C(41)C(46)	120.2(2)
C(11)PC(21)	104.5(1)	C(7)C(8)C(9)	107.8(2)	C(42)C(41)C(46)	118.1(2)
C(11)PC(31)	107.0(1)	C(8)C(9)C(10)	107.7(2)	C(3)C(51)C(52)	121.3(2)
C(21)PC(31)	109.4(1)	C(9)C(10)C(6)	108.3(2)	C(3)C(51)C(56)	120.3(2)
MnC(4)O(1)	172.4(2)	PC(11)C(12)	122.2(2)	C(52)C(51)C(56)	118.3(2)
MnC(5)O(2)	176.1(2)	PC(11)C(16)	118.6(2)	Cl(1)CCl(2)	111.7(1)

[20] and those in I (both 1.301 Å). Thus, to satisfy the EAN rule, the Mn and P atoms have to carry charges of -1 and $+1$, respectively, the allene moiety taking no part in their delocalization.

However, no direct interaction exists between the oppositely-charged metal and phosphonium centres, as the Mn $\cdots$ P distance of 3.369(1) Å is approximately 1 Å greater than usual Mn–P bond lengths [17,18], and the coordination geometries of Mn (octahedral), P (tetrahedral) and C(1) (planar trigonal) exhibit no significant distortion.

The coordination planes of the C(1) and C(3) atoms form a dihedral angle of 90.2° in agreement with π-bonding in allene. All the phenyl cycles are planar. The P and C(3) substituents are coplanar with the latter within 0.03 Å. The C(2)C(3)C(41)C(42) and C(2)C(3)C(51)C(52) torsion angles are $-31.1(3)$ and $-44.1(3)°$, respectively.

The packing of molecules of VII in the crystal of VIII leaves infinite channels (along the line $[x\ 1/2\ 0]$ and its symmetrical equivalents) occupied by CH_2Cl_2 molecules. Contact between the CH_2Cl_2 molecules by their Cl atoms, and the intermolecular distances Cl(1) $\cdots$ Cl(1) $(-x, 1-y, -z)$ 4.340(1) Å and Cl(2) $\cdots$ Cl(2)$(1-x, 1-y, -z)$ 3.563(1) Å are comparable with the double Van der Waals radius of chlorine (which is estimated as 1.80 [21], 1.78 [22], 1.75 [23], and 1.90 Å [24]). Rapid amorphization of crystalline VIII on storage (without chemical decomposition of VII) is probably due to the easy loss of solvent from these channels.

When studying the reactivity of II we observed that PPh_3 can be substituted in the ylide complex by a stronger Lewis base, such as PPh_2Me, under mild conditions:

$$\underset{\text{(II)}}{Cp(CO)_2Mn^-C(P^+Ph_3){=}CHPh} \xrightarrow[0.5\ \text{h},\ 20°\text{C}]{PPh_2Me,\ \text{pentane}} \underset{\text{(III)}}{Cp(CO)_2Mn^-C(P^+Ph_2Me){=}CHPh} \qquad (8)$$

Complex III, similar to its PPh_3 analogue II, is a red crystalline substance that is moderately soluble in non-polar solvents. In polar solvents (Et_2O, THF) it dissociates into the initial compounds.

The IR spectrum of III exhibits no significant changes in $\nu(\mathrm{C{\equiv}O})$ with respect to that of II, as the substitution of one phenyl group for a methyl group probably does not significantly increase the electron density on the metal atom.

In the ^{31}P NMR spectra of III, the signal of a phosphorus atom is shifted somewhat to a lower field (by 0.7 ppm) compared to II, but the difference is also very small.

Earlier some of us found that in a photochemical reaction $\mathrm{PPh_3}$ can substitute one of the carbonyl groups in the phenylvinylidene manganese complex:

$$\mathrm{Cp(CO)_2Mn{=}C{=}CHPh} \xrightarrow[\text{1 h, pentane}]{\mathrm{PPh_3},\,h\nu} \underset{\text{(X)}}{\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}CHPh}} \qquad (9)$$

A more-detailed study of this reaction revealed the first step to be the addition of $\mathrm{PPh_3}$ to the α-carbon atom of the vinylidene ligand, i.e. the formation of II. Only then does UV irradiation of II in the presence of free $\mathrm{PPh_3}$ give the phosphine-substituted complex X:

$$\underset{\text{(II)}}{\mathrm{Cp(CO)_2Mn^{-}C(P^{+}Ph_3){=}CHPh}} \xrightarrow[\text{1 h, pentane}]{\mathrm{PPh_3},\,h\nu}$$

$$\left[\mathrm{Cp(CO)(PPh_3)Mn^{-}C(P^{+}Ph_3){=}CHPh}\right] \rightarrow \underset{\text{(X)}}{\mathrm{Cp(CO)(PPh_3)Mn{=}C{=}CHPh}} \qquad (10)$$

Experimental

All operations were performed under nitrogen, using absolute solvents saturated with nitrogen. IR spectra were recorded with a UR 20 Zeiss spectrometer, ^{31}P NMR spectra with a Bruker HX 90 spectrometer (36.4 MHz) and mass spectra with an MS 30 spectrometer (ionizing potential 70 V, temperature of ion source 200°C and of injection system 20–50°C).

X-Ray experiments were performed with a Syntex $P2_1$ autodiffractometer (temperature −120°C, graphite-monochromated Mo-K_α radiation, $\theta/2\theta$ scan, $2\theta \leqslant 50°$, 5126 independent reflections with $I \geqslant 2\sigma$). The structure was solved by the standard heavy-atom method, and refined by block-diagonal least-squares. Non-hydrogen atoms were refined using anisotropic temperature factors; hydrogen atoms were first placed in calculated positions and then refined isotropically. The refinement gave $R = 0.031$ and $R_w = 0.027$ (weighting scheme $w = \sigma_F^{-2}$). All calculations were performed with an Eclipse S/200 computer using INEXTL programs [25]. The positional and thermal atomic parameters are listed in Tables 4 and 5.

Crystal data of VIII: $\mathrm{C_{40}H_{30}MnO_2P \cdot CH_2Cl_2}$, triclinic, at −120°C, a 10.266(2), b 10.603(2), c 16.320(4) Å, α 79.22(2), β 84.30(2), γ 74.70(2)°, V 1680.8(6) Å^3, $Z = 2$, $d_{\text{calc.}}$ 1.41 g cm^{-1}, space group $P\bar{1}$.

Preparation of complexes II–VII

$\mathrm{Cp(CO)_2Mn^{-}\,C(P^{+}Ph_3){=}CHPh}$ (II)

$\mathrm{PPh_3}$ (0.9 g; 3.44 mmol) dissolved in 100 ml of pentane was added, at 20°C, to a solution of 0.3 g (1.08 mmol) of $\mathrm{Cp(CO)_2Mn{=}C{=}CHPh}$ in 50 ml of pentane and

(Continued on p. 280)

TABLE 4

ATOMIC COORDINATES ($\times 10^4$; for Mn, P and Cl $\times 10^5$) AND B_{iso}^{eq} ($Å^2$)

Atom	x	y	z	B_{iso}^{eq}	Atom	x	y	z	B_{iso}^{eq}
Mn	40006(3)	51148(3)	70849(2)	1.12(1)	C(23)	4989(2)	8272(2)	4503(1)	1.89(6)
P	20571(5)	81540(5)	63876(3)	1.09(1)	C(24)	4459(2)	9481(2)	4009(1)	1.86(6)
Cl(1)	12518(7)	43160(7)	10703(4)	3.08(2)	C(25)	3223(2)	10268(2)	4233(1)	1.89(6)
Cl(2)	37036(6)	41721(7)	−145(4)	3.40(2)	C(26)	2507(2)	9851(2)	4950(1)	1.65(6)
O(1)	2933(2)	4731(2)	5575(1)	2.42(5)	C(31)	826(2)	7372(2)	6132(1)	1.20(2)
O(2)	1859(2)	4115(2)	8114(1)	2.43(5)	C(32)	129(2)	6744(2)	6791(1)	1.50(6)
C(1)	3076(2)	7068(2)	7179(1)	1.07(5)	C(33)	−820(2)	6119(2)	6622(1)	1.78(6)
C(2)	3112(2)	7640(2)	7814(1)	1.25(5)	C(34)	−1066(2)	6113(2)	5804(1)	1.87(6)
C(3)	3154(2)	8195(2)	8473(1)	1.35(6)	C(35)	−379(2)	6747(2)	5148(1)	1.70(6)
C(4)	3303(2)	4969(2)	6173(1)	1.55(6)	C(36)	576(2)	7375(2)	5309(1)	1.41(6)
C(5)	2687(2)	4558(2)	7705(1)	1.58(6)	C(41)	4223(2)	8899(2)	8514(1)	1.45(6)
C(6)	5636(2)	5071(2)	7838(1)	1.81(6)	C(42)	5504(2)	8516(2)	8134(1)	1.91(6)
C(7)	5459(2)	3786(2)	7910(1)	1.96(6)	C(43)	6493(2)	9178(2)	8176(2)	2.34(7)
C(8)	5681(2)	3412(2)	7115(2)	2.03(6)	C(44)	6201(3)	10242(2)	8603(2)	2.50(7)
C(9)	6017(2)	4473(2)	6542(1)	2.02(6)	C(45)	4937(3)	10639(2)	8976(2)	2.79(8)
C(10)	5975(2)	5499(2)	6988(1)	1.81(6)	C(46)	3947(2)	9978(2)	8935(1)	2.22(7)
C(11)	1129(2)	9709(2)	6703(1)	1.33(6)	C(51)	2102(2)	8154(2)	9172(1)	1.42(6)
C(12)	−274(2)	10099(2)	6744(1)	1.90(6)	C(52)	740(2)	8416(2)	9018(1)	1.85(6)
C(13)	−947(2)	11296(2)	6986(2)	2.64(7)	C(53)	−228(2)	8349(2)	9676(1)	2.26(7)
C(14)	−222(3)	12112(2)	7184(1)	2.98(8)	C(54)	153(2)	8021(2)	10492(1)	2.26(7)
C(15)	1172(3)	11734(2)	7152(1)	2.66(8)	C(55)	1509(2)	7755(2)	10651(1)	2.24(7)
C(16)	1858(2)	10541(2)	6909(1)	1.95(6)	C(56)	2473(2)	7828(2)	9999(1)	1.83(6)
C(21)	3028(2)	8633(2)	5448(1)	1.15(5)	C	1922(2)	4572(2)	33(1)	2.45(7)
C(22)	4273(2)	7835(2)	5220(1)	1.58(6)					

TABLE 5

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

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
H(6)	550(2)	555(2)	829(1)	2.5(5)	H(7)	522(2)	332(2)	838(1)	2.1(5)
H(8)	570(2)	261(2)	701(1)	3.0(6)	H(9)	622(2)	448(2)	596(1)	3.2(6)
H(10)	609(2)	635(2)	673(1)	3.0(6)	H(12)	−78(2)	957(2)	660(1)	3.0(6)
H(13)	−197(2)	1159(2)	703(1)	3.7(6)	H(14)	−68(2)	1293(2)	734(1)	3.4(6)
H(15)	168(2)	1226(2)	729(1)	3.0(6)	H(16)	290(2)	1023(2)	689(1)	2.7(5)
H(22)	463(2)	697(2)	558(1)	1.3(4)	H(23)	583(2)	767(2)	438(1)	2.3(5)
H(24)	494(2)	977(2)	354(1)	1.8(5)	H(25)	288(2)	1108(2)	388(1)	2.6(5)
H(26)	163(2)	1043(2)	511(1)	1.7(5)	H(32)	28(2)	675(2)	737(1)	1.2(4)
H(33)	−125(2)	567(2)	708(1)	2.2(5)	H(34)	−176(2)	567(2)	570(1)	3.0(6)
H(35)	−53(2)	675(2)	459(1)	1.8(5)	H(36)	105(2)	781(2)	485(1)	1.2(4)
H(42)	571(2)	784(2)	787(1)	2.0(5)	H(43)	742(2)	884(2)	792(1)	3.1(6)
H(44)	690(2)	1068(2)	864(1)	3.4(6)	H(45)	470(2)	1138(2)	931(1)	3.6(6)
H(46)	312(2)	1024(2)	919(1)	2.0(5)	H(52)	44(2)	861(2)	846(1)	1.9(5)
H(53)	−122(2)	858(2)	953(1)	3.3(6)	H(54)	−52(2)	798(2)	1096(1)	2.8(5)
H(55)	178(2)	753(2)	1120(1)	2.6(5)	H(56)	339(2)	765(2)	1010(1)	2.1(5)
H	158(2)	552(2)	−21(1)	3.4(6)	H′	168(2)	398(2)	−31(2)	3.8(6)

stirred for 1 h at 30–40°C. The bright-orange precipitate obtained was isolated, washed with pentane (7 × 10 ml) and dried in air, yielding 0.42 g (72.4%) of orange crystalline II (m.p. 113–114°C). Found: C, 73.36; H, 4.95; Mn, 9.69; P, 5.89. $C_{33}H_{26}MnO_2P$ calcd.: C, 73.33; H, 4.85; Mn, 10.46; P, 5.73%. Mass spectrum (*m/z*): 382 $[CpMnPPh_3]^+$; 278 $[Cp(CO)_2Mn{=}C{=}CHPh]^+$; 262 $[PPh_3]^+$; 222 $[CpMn{=}C{=}CHPh]^+$; 157 $[MnC_2PhH]^+$; 120 $[CpMn]^+$; 108 $[PhP]^+$.

$Cp(CO)_2Mn^- C(P^+Ph_2Me){=}CHPh$ *(III)*

PPh_2Me (0.5 ml; 0.6 g or 2.8 mmol) was added to a solution of 0.4 g (1.4 mmol) of $Cp(CO)_2Mn{=}C{=}CHPh$ in 60 ml of hexane on stirring at 20°C. A red precipitate was formed. The mixture was stirred for another 2 h, then the solution was decanted, and the precipitate was washed with hexane (4 × 10 ml) and dried in vacuo. 0.37 g (60%) of orange, crystalline III was obtained (m.p. 147°C). Found: C, 70.21; H, 5.07; Mn, 11.46; P, 6.45. $C_{28}H_{24}MnO_2P$ calcd.: C, 70.33; H, 5.01; Mn, 11.49; P, 6.46%.

$Cp(CO)_2Mn^- C(P^+Ph_3){=}CHCO_2Me$ *(IV)*

A solution of 1.24 g (4.73 mmol) of PPh_3 in 100 ml of pentane was added to a solution of 0.41 g (1.58 mmol) of $Cp(CO)_2Mn{=}C{=}CHCO_2Me$ in 80 ml of pentane at 35°C. The solvent was evaporated to half the initial volume, and the dark-brown crystalline precipitate that formed was isolated, washed with pentane (7 × 10 ml) and dried in vacuo, yielding 0.42 g (51%) of IV, m.p. 85–87°C (dec.). Found: C, 66.29; H, 4.56; P, 5.89. $C_{29}H_{24}MnO_4P$ calcd.: C, 66.67; H, 4.63; P, 5.93%. Mass spectrum (*m/z*): 438 $[Cp(CO)_2MnPPh_3]^+$; 382 $[CpMnPPh_3]^+$; 262 $[PPh_3]^+$; 120 $[CpMn]^+$; 108 $[PhP]^+$.

$Cp(CO)_2Mn^- C(P^+Ph_3){=}CHC(t\text{-}Bu)_2OH$ *(V)*

0.17 g (65%) of yellow crystalline V (m.p. 65–100°C (dec.)) was obtained from 0.2 g (0.58 mmol) of $Cp(CO)_2Mn{=}C{=}CH(t\text{-}Bu)_2OH$ and 0.35 g (1.33 mmol) of PPh_3 by the same procedure as for II. Found: C, 71.04; H, 6.58; Mn, 8.76; P, 5.01. $C_{36}H_{40}MnO_3P$ calcd.: C, 71.28; H, 6.64; Mn, 9.056; P, 5.1%. Mass spectrum (*m/z*); 434 $[Cp(CO)_2MnPPh_3]^+$; 382 $[CpMnPPh_3]^+$; 262 $[PPh_3]^+$; 120 $[CpMn]^+$.

$Cp(CO)_2Mn^- C(P^+Ph_3){=}C{=}C(t\text{-}Bu)_2$ *(VI)*

0.2 g (0.61 mmol) of $Cp(CO)_2Mn{=}C{=}C{=}C(t\text{-}Bu)_2$ and 0.8 g (3.05 mmol) of PPh_3 were treated as in the preparation of II, yielding 0.3 g (83.3%) of yellow crystalline VI, m.p. 126–127°C (dec.). Found: C, 73.41; H, 6.93; Mn, 9.38; P, 5.95. $C_{36}H_{38}MnO_2P$ calcd.: C, 73.46; H, 6.51; Mn, 9.33; P, 5.26%. Mass spectrum (*m/z*): 326 $[Cp(CO)_2MnC_3(t\text{-}Bu)_2]^+$; 270 $[CpMnC_3(t\text{-}Bu)_2]^+$; 213 $[CpMnC_3(t\text{-}Bu)]^+$; 182 $[PPh_2]^+$; 148 $[CpMn(CO)]^+$; 120 $[CpMn]^+$; 57 $[t\text{-}Bu]^+$; 55 $[Mn]^+$.

$Cp(CO)_2Mn^- C(P^+Ph_3){=}C{=}CPh_2$ *(VII)*

0.42 g (99.5%) of yellow crystalline VII (m.p. 100°C (dec.)) was obtained from 0.24 g (0.66 mmol) of $Cp(CO)_2Mn{=}C{=}C{=}CPh_2$ and 0.72 g (2.74 mmol) of PPh_3 by the same procedure as for II. Found: C, 76.30; H, 5.10; Mn, 8.04; P, 4.94. $C_{40}H_{30}MnO_2P$ calcd.: C, 76.43; H, 4.81; Mn, 8.74; P, 4.93%. Mass spectrum (*m/z*): 366 $[Cp(CO)_2MnC_3Ph_2]^+$; 310 $[CpMnC_3Ph_2]^+$; 262 $[PPh_3]^+$.

Reaction of II with PPh_2Me

PPh_2Me (0.1 ml; 0.12 g or 0.56 mmol) was added to a suspension of 0.13 g (0.24

mmol) of $Cp(CO)_2Mn^- C(P^+Ph_3)$=CHPh (II) in pentane. The colour of the mixture changed to bright orange. The solution was decanted, and the precipitate was washed with pentane and dried in vacuo, yielding 0.1 g (87%) of orange crystalline III, characterized by m.p. and IR spectrum.

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