Journal of Organometallic Chemistry, 244 (1983) 35–45
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHEMISTRY OF VINYLIDENE COMPLEXES

I. CONVERSION OF VINYLIDENE MANGANESE COMPLEXES INTO π-OLEFINIC COMPLEXES BY ACTION OF PHOSPHITES. CRYSTAL AND MOLECULAR STRUCTURE OF η^5-CYCLOPENTADIENYLDICARBONYL-(η^2-*trans*-1-DIETHYLPHOSPHONATO-2-PHENYLETHYLENE)MANGANESE, η^5-$C_5H_5(CO)_2Mn[\eta^2$-$PhCH{=}CHP(O)(OEt)_2]$

A.B. ANTONOVA*, S.V. KOVALENKO, E.D. KORNIYETS, A.A. JOHANSSON,

Institute of Chemistry and Chemical Technology, Siberian Branch of Academy of Sciences of the U.S.S.R., K. Marx St. 42, Krasnoyarsk 660097 (U.S.S.R.)

Yu.T. STRUCHKOV*, A.I. AHMEDOV and A.I. YANOVSKY

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov St. 28, Moscow B-312, 117813 (U.S.S.R.)

(Received September 23rd, 1982)

Summary

The novel reaction of the manganese vinylidene complex $Cp(CO)_2Mn{=}C{=}CHPh$ with $P(OR)_3$ (R = Et or Ph) affords the olefinic complexes of the type $Cp(CO)_2Mn[PhCH{=}CHP(O)(OR)_2]$ under mild conditions. This conversion may be interpreted as an unusual variant of the Arbuzov reaction occurring in the coordination sphere of a transition metal atom which is accompanied by an n–π rearrangement of the organic ligand. The X-ray study of the complex $Cp(CO)_2Mn[PhCH{=}CHP(O)(OEt)_2]$ shows that the phosphonatoethylene ligand is coordinated by the manganese atom as an η^2-olefin and that the substituents at the C=C bond are in *trans* positions. IR and ^1H NMR spectra of the complexes are discussed. A probable mechanistic scheme for the reaction is proposed.

Introduction

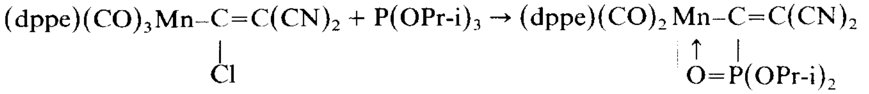
The vinylidene complexes of transition metals, whose syntheses, structures and some properties we have described previously [1–3], are very reactive compounds. The variety of chemical behaviour of these complexes is determined by the characteristic electronic and steric features of their molecules. The X-ray analysis [1,2] and IR

0022-328X/83/0000–0000/$03.00 © 1983 Elsevier Sequoia S.A.

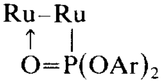
and ^{13}C NMR study [3] of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) have shown that (1) the vinylidene group, $C{=}CHPh$, is only slightly shielded by other ligands attached to manganese atom and has an essentially electron-withdrawing character and (2) the electron density on the vinylidene α-carbon atom is significantly decreased. The first feature provides the weakening of Mn–CO bonds and facilitates the substitution of CO by other neutral nucleophiles; the second one makes possible the addition of nucleophiles to the α-carbon atom of the $C{=}CHPh$ group.

When we studied the reactions of compound I with trivalent phosphorus compounds, we found that, due to the presence of both of these features in molecule I, rather small changes of the reaction conditions or the nature of reagents cause a great change of reaction pathways. Earlier, we reported [3,4] that the reactions of I with phosphines or phosphites lead to the substitution of one of CO groups to form the vinylidene complexes $Cp(CO)(L)Mn{=}C{=}CHPh$ (II) where $L = PPh_3$ or $P(OPh)_3$. Herein we have established that phosphites may react with I in another way to produce complexes containing the phosphonate group $P(O)(OR)_2$ bonded to the α-carbon atom of the organic ligand.

Only few examples of formation of a phosphonate group in reactions between trialkylphosphites and transition metal carbonyl complexes are known. Thus, the compounds $Cp(CO)_2[P(OR)_3]MoP(O)(OR)_2$ and $Cp(CO)_2FeP(O)(OR)_2$ containing phosphorus–metal σ-bonds were prepared by reactions of alkylphosphites with $[Cp(CO)_3Mo]_2$ and $Cp(CO)_2FeCl$, respectively [5]. The σ-vinyl manganese complex containing a chelate phosphonate ligand was prepared [6] by photochemical reaction:



$$\underset{\displaystyle Cl}{(dppe)(CO)_3Mn{-}C}{=}C(CN)_2 + P(OPr\text{-}i)_3 \rightarrow (dppe)(CO)_2\underset{\displaystyle \uparrow\quad |\ \ \ \atop \displaystyle O{=}P(OPr\text{-}i)_2}{Mn{-}C}{=}C(CN)_2$$

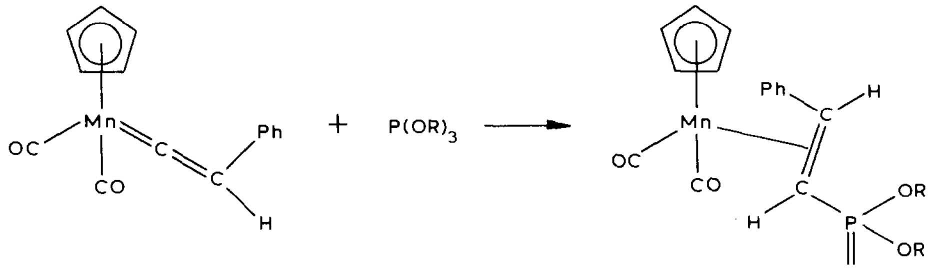
This interpretation of these reactions suggests an analogy with the Arbuzov-Michaelis reaction [7]. As far as we know, no similar transformations of arylphosphites have as yet been described. The only exception was the preparation of binuclear ruthenium complexes involving the moiety  $\underset{\displaystyle \uparrow\ \ | \atop \displaystyle O{=}P(OAr)_2}{Ru{-}Ru}$ by thermolysis of the trinuclear clusters $Ru_3(CO)_9L_3$ ($L = P(OPh)_3$ or $P(OC_6H_4Me\text{-}p)_3$) at 165–190°C [8]. In this case the conversion of the arylphosphite ligand into the arylphosphonate moiety is probably favoured by the presence of neighbouring metal centers in the cluster molecule.

In this paper we report the preparation of the complexes $Cp(CO)_2Mn[PhCH{=}CHP(O)(OR)_2]$, where R = Et or Ph, by reactions of triethyl- or triphenylphosphites with $Cp(CO)_2Mn{=}C{=}CHPh$ (I) under mild conditions. The formation of these phosphonatoethylene compounds is apparently a result of an unusual Arbuzov reaction in the coordination sphere of the transition metal atom followed by an n–π rearrangement of the organic ligand.

Results and discussion

In our study of the reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with $Pt[P(OEt)_3]_4$ we have found [9] that, in addition to the heteronuclear complex $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)[P(OEt)_3]_2$, a novel cyclopentadienylmanganese dicarbonyl complex containing an organic ligand involving the $P(OEt)_2$ group is produced in good yield. In order to establish the nature of this compound an X-ray study was performed which showed that the complex represents the π-olefinic cymantrene derivative $Cp(CO)_2Mn[PhCH{=}CHP(O)(OEt)_2]$ (IIIa) containing *trans*-1-diethylphosphonato-2-phenylethylene as a ligand. It is probably the first example of the transition metal phosphonatoethylene π-complex.

It was quite reasonable to suggest that the formation of IIIa was a result of reaction between I and $P(OEt)_3$ produced by dissociation of $Pt[P(OEt)_3]_4$ in solution. To prove this suggestion we carried out the direct reactions of I with phosphites in the absence of complexes of platinum(0). It was found that I rapidly reacts with both triethyl- and triphenyl-phosphite in non-polar solvents at 20°C without UV-irradiation as follows:



(I)

(III)

(IIIa : R = Et ; IIIb : R = Ph)

Following the course of these reactions by IR spectroscopy showed that formation of IIIa in cyclohexane solution was complete after 1 h, and IIIb after 5 h. The yields of the complexes were practically quantitative; only trace amounts of the compounds $Cp(CO)[P(OR)_3]Mn{=}C{=}CHPh$ (II) were obtained from the reaction mixtures. Previously, the complexes II had been prepared in reactions of I with $P(OR)_3$ in

TABLE 1

IR AND ^{1}H NMR DATA FOR THE COMPLEXES $Cp(CO)_2Mn[PhCH^B{=}CH^AP(O)(OR)_2]$

Complex	R	IR spectra ν (cm^{-1})		^{1}H NMR spectra, δ (ppm), J (Hz) [c]			
		C≡O [a]	P=O [b]	H^A	H^B	C_5H_5	Other groups
IIIa	Et	1988 1933	1227	2.60 br		4.70 br	1.21 br CH_3 1.40 br CH_3 4.07 br CH_2 7.16 br C_6H_5
IIIb	Ph	1990 1937	1255	2.86 dd $J(H^AH^B)$ 12.7 $J(PH^A)$ 6.1	4.52 dd $J(H^BH^A)$ 12.7 $J(PH^B)$ 18.6	4.67 s	7.07–7.36 m C_6H_5

[a] Cyclohexane solutions. [b] KBr pellets. [c] $CDCl_3$ solutions.

yields of ca. 14% [3,4]. The difference in the yields of II may be rationalised as being due to non-identical light conditions.

The complexes III are yellow solids, fairly stable under normal conditions and readily soluble in organic solvents. The spectral data given in Table 1 indicate that compounds IIIa and IIIb have similar structures.

The infrared spectra of III show two bands of $\nu(C\equiv O)$ with equal intensities. The increase in frequencies of these bands by 15–20 cm^{-1} compared with those of many known π-olefinic cymantrene derivatives of the type $Cp(CO)_2Mn(\eta^2\text{-}RCH{=}CHR')$ [10] indicates a rather strong electron-withdrawing capacity of the $PhCH{=}CHP(O)(OR)_2$ ligands, similar to that of such olefins as $CH_2{=}CPh(OCOMe)$ [3] and $PhCH{=}CHC(O)Me$ [11]. The $\nu(P{=}O)$ band in the spectrum of IIIa is decreased by 13 cm^{-1} compared with that of a free phosphonatoethylene, $PhCH{=}CHP(O)(OEt)_2$ [12].

Since compound IIIa is unstable in solutions all signals in its ^1H NMR spectrum are somewhat broadened and the fine structure of the lines due to the spin-spin coupling is not resolved. The broad signals at δ 1.21 and 1.40 ppm correspond to the hydrogen atoms of two non-equivalent methyl groups and one broad resonance centered at δ 4.07 ppm is observed for CH_2 groups. The broad line at δ 2.60 ppm corresponds to one of the olefinic hydrogens, the resonance of the second one seems to be coincident with the signals of methylene and cyclopentadienyl hydrogen atoms.

All signals in the ^1H NMR spectrum of complex IIIb are significantly sharper. Both signals of the olefinic hydrogen atoms at δ 2.86 and 4.52 ppm form a doublet of doublets with the same value of the spin-spin coupling constant $J(H^AH^B)$ equal to 12.7 Hz. It is known that the value of $J(H^AH^B)$ in olefins is decreased when an olefin forms π-complex with a transition metal atom. Thus, in the ^1H NMR spectrum of the closely related complex $Cp(CO)_2Mn[\textit{trans}\text{-}PhCH{=}CHC(O)Me]$ $J(H^AH^B)$ is 12 Hz, compared with that of a free olefin, 16 Hz [11]. Therefore, the value $J(H^AH^B) = 12.7$ Hz in the ^1H NMR spectrum of IIIb proves the *trans* configuration of the hydrogen atoms at the C=C bond, as was found for IIIa by an X-ray study. This conclusion is supported also by analysis of the spin-spin coupling

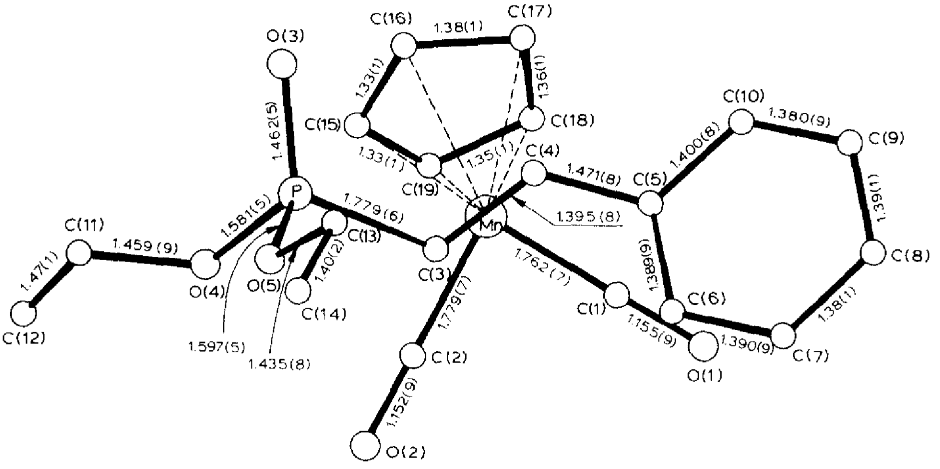


Fig. 1. The molecular structure of $\eta^5\text{-}C_5H_5(CO)_2Mn[\eta^2\text{-}PhCH{=}CHP(O)(OEt)_2]$ (IIIa) projected onto the plane perpendicular to that of the MnC(3)C(4) triangle.

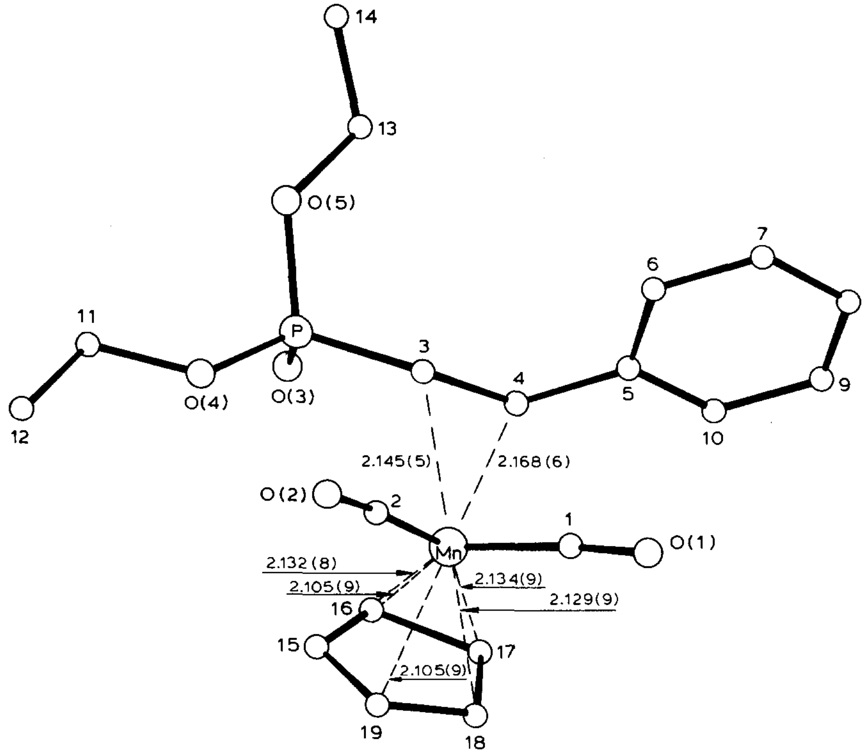


Fig. 2. ORTEP drawing of the molecule IIIa showing the arrangement of the ligands around Mn with selected Mn–C distances.

constants on the ^{31}P nucleus (see Table 1); the values of these constants are characteristic of *gem* and *cis* arrangements of the coupled nuclei. Since it is known [12,13] that *J*(PH-*cis*) is greater than *J*(PH-*gem*), the signal at δ 2.86 ppm may be assigned to the H^A hydrogen, and that at δ 4.52 ppm to the H^B hydrogen atom.

The crystals of the compound $Cp(CO)_2Mn[PhCH{=}CHP(O)(OEt)_2]$ (IIIa) (from hexane solution, −20°C) are triclinic, at 20°C $a = 10.578(2)$, $b = 11.120(2)$, $c = 18.069(4)$ Å, $\alpha = 72.42(1)$, $\beta = 84.46(1)$, $\gamma = 88.02(1)°$, $V = 2017.3$ Å^3, $D_c = 1.344$ g/cm^3, $Z = 4$, space group $P\bar{1}$, two independent molecules. The structure was refined to $R = 0.060$ ($R_w = 0.058$) for 5664 independent reflexions with $F^2 \geqslant 2\sigma$. The coordinates of non-hydrogen atoms are given in Table 2.

Both independent molecules in the unit cell of IIIa have the same structure. Two projections of one of the molecules with average values of bond lengths are given in Figs. 1 and 2. The individual values of bond lengths and bond and torsion angles are summarized in Tables 3, 4 and 5, respectively.

The manganese atom has a distorted octahedral configuration. It is coordinated with an η^5-cyclopentadienyl ligand, two carbonyl groups and an η^2-olefinic fragment of diethyl-*trans*-2-phenylvinylphosphonate occupying one coordination site.

As a result of the π-coordination with the Mn atom the olefinic C(3)=C(4) bond (1.395(8) Å) * is lengthened significantly; it should be noted that the C=C distance

---

* Throughout this paper the average values of geometrical parameters and the larger of the standard deviations for the two independent molecules are given.

TABLE 2

COORDINATES OF NON-HYDROGEN ATOMS ($\times 10^4$) IN THE STRUCTURE OF IIIa

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Mn	3710(1)	3382(1)	6931(1)	1509(1)	1467(1)	3515(1)
P	6690(2)	2886(2)	7430(1)	4183(1)	2222(1)	2336(1)
O(1)	1676(5)	4931(6)	7361(3)	−565(5)	−226(5)	3545(3)
O(2)	4862(5)	5705(4)	5885(3)	2970(5)	−811(4)	4222(3)
O(3)	6709(4)	1511(4)	7652(3)	4073(4)	3595(4)	2150(3)
O(4)	7148(4)	3591(4)	6548(3)	4930(4)	1540(4)	3062(2)
O(5)	7673(4)	3492(5)	7837(3)	4986(4)	1774(4)	1675(2)
C(1)	2510(6)	4313(7)	7212(4)	258(6)	447(6)	3505(4)
C(2)	4420(6)	4790(6)	6307(4)	2413(6)	85(6)	3929(4)
C(3)	5199(5)	3597(5)	7609(3)	2725(5)	1399(5)	2509(3)
C(4)	4233(5)	2880(5)	8117(3)	1617(5)	2033(5)	2253(3)
C(5)	3427(5)	3279(5)	8705(3)	668(5)	1545(5)	1866(3)
C(6)	3629(6)	4403(6)	8862(4)	805(5)	423(5)	1680(4)
C(7)	2852(7)	4727(6)	9436(4)	−89(6)	27(6)	1287(4)
C(8)	1867(7)	3936(7)	9859(4)	−1140(6)	757(6)	1072(4)
C(9)	1689(6)	2804(7)	9710(4)	−1335(6)	1870(6)	1266(4)
C(10)	2446(6)	2496(6)	9143(4)	−425(5)	2269(6)	1656(4)
C(11)	8416(7)	3365(8)	6218(5)	6225(6)	1881(8)	3123(5)
C(12)	8452(9)	3998(9)	5392(6)	6475(7)	1321(8)	3957(5)
C(13)	7610(9)	3123(10)	8667(5)	4590(7)	2132(8)	897(4)
C(14)	8540(11)	3744(10)	8894(6)	5076(9)	1254(10)	514(5)
C(15)	4281(8)	2375(8)	6135(5)	412(7)	2143(8)	4340(5)
C(16)	4171(8)	1543(6)	6835(5)	1548(8)	1914(7)	4575(4)
C(17)	2898(9)	1574(8)	7128(5)	2391(6)	2664(7)	4041(5)
C(18)	2349(7)	2459(9)	6510(7)	1816(9)	3387(6)	3453(4)
C(19)	3245(9)	2887(8)	5959(5)	520(9)	3100(8)	3619(5)

TABLE 3

BOND LENGTHS *d*(Å) IN THE STRUCTURE OF IIIa

Bond	Molecule A	Molecule B	Bond	Molecule A	Molecule B
Mn–C(1)	1.745(7)	1.778(7)	O(5)–C(13)	1.43(1)	1.440(8)
Mn–C(2)	1.773(7)	1.784(7)	C(3)–C(4)	1.399(8)	1.391(7)
Mn–C(3)	2.148(5)	2.141(5)	C(4)–C(5)	1.462(8)	1.480(7)
Mn–C(4)	2.167(6)	2.168(5)	C(5)–C(6)	1.390(9)	1.387(8)
Mn–C(15)	2.109(9)	2.101(9)	C(5)–C(10)	1.396(8)	1.403(8)
Mn–C(16)	2.139(8)	2.124(7)	C(6)–C(7)	1.386(9)	1.393(9)
Mn–C(17)	2.130(9)	2.137(8)	C(7)–C(8)	1.39(1)	1.370(9)
Mn–C(18)	2.119(9)	2.139(7)	C(8)–C(9)	1.39(1)	1.39(1)
Mn–C(19)	2.097(9)	2.113(9)	C(9)–C(10)	1.358(9)	1.401(9)
P–O(3)	1.460(5)	1.464(5)	C(11)–C(12)	1.44(1)	1.49(1)
P–O(4)	1.585(5)	1.576(4)	C(13)–C(14)	1.38(2)	1.41(1)
P–O(5)	1.602(5)	1.591(5)	C(15)–C(16)	1.32(1)	1.31(1)
P–C(3)	1.784(6)	1.774(5)	C(15)–C(19)	1.24(1)	1.41(1)
O(1)–C(1)	1.160(9)	1.150(9)	C(16)–C(17)	1.40(1)	1.35(1)
O(2)–C(2)	1.154(8)	1.149(8)	C(17)–C(18)	1.41(1)	1.31(1)
O(4)–C(11)	1.460(9)	1.457(8)	C(18)–C(19)	1.30(1)	1.40(1)

TABLE 4

BOND ANGLES ω (degrees) IN THE STRUCTURE OF IIIa

Angle	Molecule A	Molecule B	Angle	Molecule A	Molecule B
C(1)MnCp[a]	122.3(3)	123.2(2)	C(4)C(5)C(6)	122.0(5)	124.0(5)
C(1)MnA[a]	94.3(2)	94.5(2)	C(4)C(5)C(10)	119.5(5)	118.6(5)
C(2)MnCp	117.9(2)	118.4(2)	C(6)C(5)C(10)	118.5(5)	117.5(5)
C(2)MnA	97.0(2)	97.1(2)	C(5)C(6)C(7)	119.7(5)	122.0(6)
O(3)PO(4)	115.8(3)	115.8(2)	C(6)C(7)C(8)	120.7(7)	119.8(6)
O(3)PO(5)	114.9(3)	113.4(3)	C(7)C(8)C(9)	119.2(7)	120.2(6)
O(3)PC(3)	116.0(3)	115.5(3)	C(8)C(9)C(10)	119.8(7)	119.7(6)
O(4)PO(5)	98.5(3)	100.6(2)	C(5)C(10)C(9)	122.0(6)	120.8(6)
O(4)PC(3)	105.0(3)	104.5(2)	O(4)C(11)C(12)	106.2(7)	106.5(6)
O(5)PC(3)	104.5(3)	105.3(2)	O(5)C(13)C(14)	109.4(8)	109.4(7)
PO(4)C(11)	120.7(4)	122.1(4)	C(16)C(15)C(19)	111.2(9)	107.6(8)
PO(5)C(13)	118.5(5)	119.9(4)	C(15)C(16)C(17)	106.7(8)	110.7(7)
MnC(1)O(1)	175.9(6)	176.0(6)	C(16)C(17)C(18)	108.9(8)	110.7(7)
MnC(2)O(2)	178.1(6)	177.5(6)	C(17)C(18)C(19)	107.6(9)	106.5(8)
PC(3)C(4)	120.4(4)	120.3(4)	C(15)C(19)C(18)	111.5(9)	106.0(8)
C(3)C(4)C(5)	125.5(5)	124.5(5)			

[a] Cp and A are the centeroids of the cyclopentadienyl ring and the C(4)=C(5) bond, respectively.

in the parent complex I is 1.34 Å[1,2] and practically coincides with the standard value of 1.337 Å [14]. The distances between Mn and olefinic carbon atoms, Mn–C(3) (2.145(5) Å) and Mn–C(4) (2.168(6) Å), are close to those found in related manganese complexes, e.g. 2.162 Å in Cp(CO)$_2$Mn[CH$_2$=CHC(O)Me] [15], and 2.20 Å in Cp(CO)$_2$Mn[CH$_2$=CPh(OCOMe)] [16]. The Mn–C(CO) (1.762(7) and 1.779(7) Å) and Mn–C(Cp) (2.105–2.134 Å) bond lengths only differ slightly from the corresponding values in the molecule of cymantrene, where, as shown by the recent

TABLE 5

TORSION ANGLES ω (degrees) IN THE STRUCTURE OF IIIa

Angle	Molecule A	Molecule B
C(12)C(11)O(4)P	172(1)	164(1)
C(14)C(13)O(5)P	180(1)	−156(1)
C(11)O(4)PO(3)	−58.2(9)	−55.8(8)
C(13)O(5)PO(3)	−57(1)	−59.0(8)
C(11)O(4)PC(3)	172.5(9)	175.9(8)
C(13)O(5)PC(3)	72(1)	68.3(8)
O(4)PO(5)C(13)	180(1)	176.7(8)
O(3)PC(3)C(4)	16.8(7)	18.7(6)
O(4)PC(3)C(4)	146.1(8)	147.2(7)
O(5)PC(3)C(4)	−110.8(7)	−107.2(7)
C(11)O(4)PO(5)	65.0(7)	66.9(8)
PC(3)C(4)C(5)	136.7(8)	136.3(8)
C(3)C(4)C(5)C(6)	−5.8(8)	3.3(8)
C(3)C(4)C(5)C(10)	176(1)	178(1)

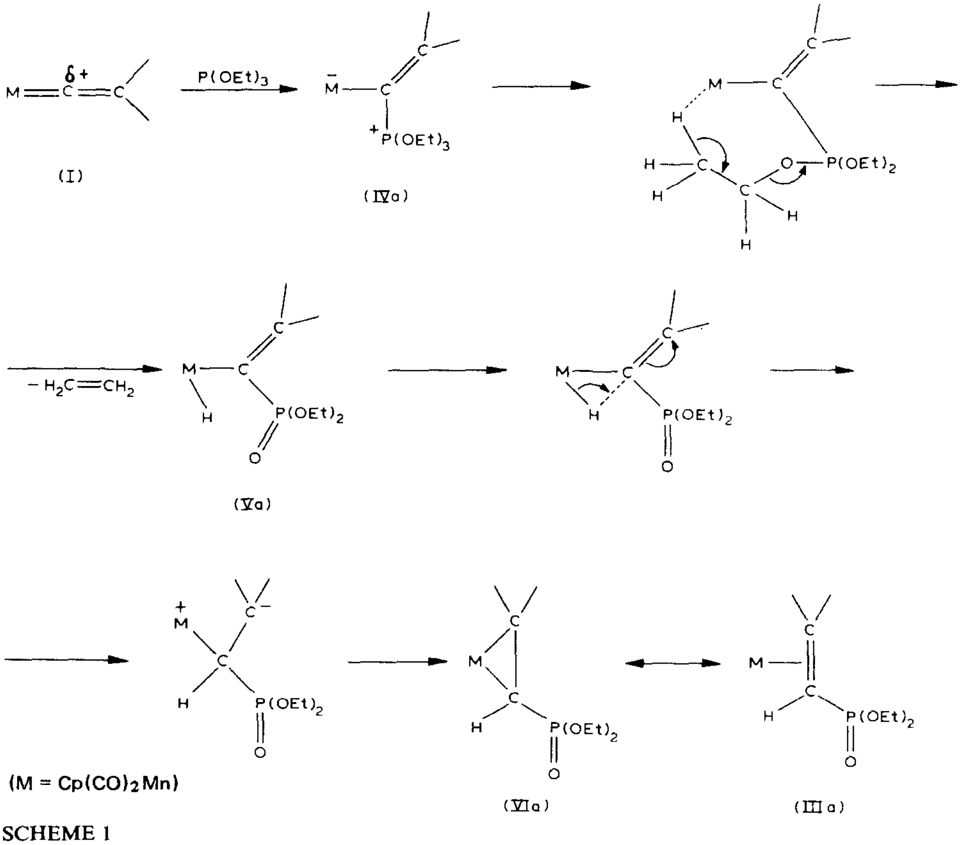
accurate X-ray study [17], Mn–C(CO) and Mn–C(Cp) bond lengths are 1.772–1.786 and 2.120–2.131 Å, respectively.

The phosphonatoethylene ligand in IIIa has a *trans* configuration, but the torsion angle PC(3)C(4)C(5) (136.5(8)°) differs considerably from the ideal value of 180° due to coordination. The repulsion of the *ipso*-atom C(5) of the phenyl ring from the carbon atom of the carbonyl group C(1)O(1) (the distance C(5)···C(1) is 2.843(9) Å) causes the increase of the bond angle C(3)C(4)C(5) to 125.0(5)°, as compared with the ideal value of 120°. At the same time the bond angle C(4)C(3)P (120.3(3)°) is very close to the ideal value. The diethylphosphonate group has a usual geometry, bond lengths P=O (1.462(5) Å) and P–O (1.581(5) and 1.597(5) Å) resemble closely those found in the structures of other phosphonates, e.g. 3-hydroxy-3-diphenylphosphono-2,2,5,5-tetramethyltetrahydrofuran (P=O 1.471 Å, P–O 1.580 and 1.582 Å) [18] and 7-dimethoxyphosphoryl-1,7-phenylnorcaradiene (P=O 1.456 Å, P–O 1.562 and 1.574 Å) [19].

In contrast to the phosphonato-σ-dicyanovinyl ligand in:

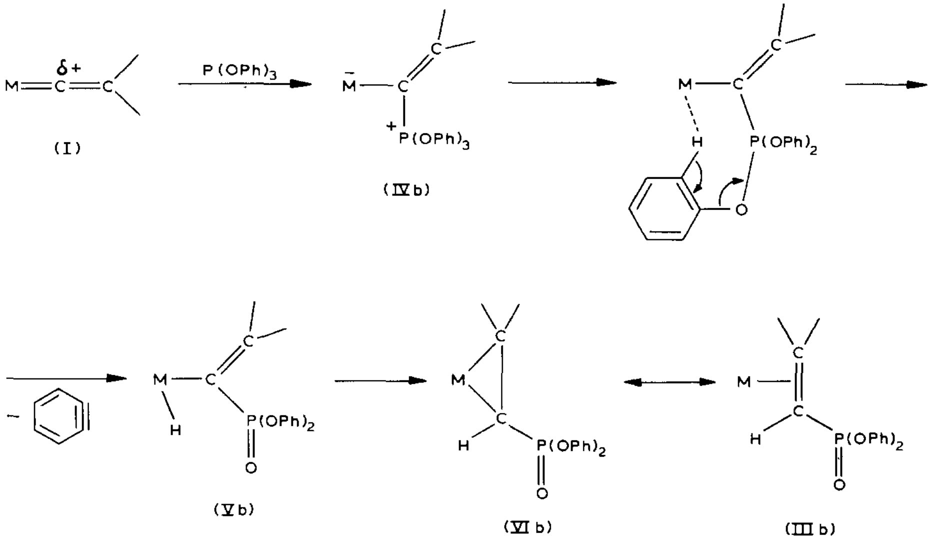
$$\begin{array}{l}(\mathrm{dppe})(\mathrm{CO})_2\mathrm{Mn{-}C{=}C(CN)_2}\\ \qquad\qquad\quad\uparrow\quad |\\ \qquad\qquad\quad \mathrm{O{=}P(OPr\text{-}i)_2}\end{array}$$

[6], the phosphonatoethylene ligand in IIIa is not chelated, and the non-bonding Mn···P and Mn···O distances are 3.343(2) and 3.839(5) Å, respectively.



(M = Cp(CO)2Mn)

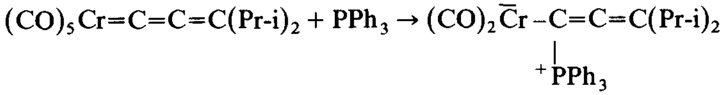
SCHEME 1



(M = Cp(CO)$_2$Mn)

SCHEME 2

The possible mechanisms of the formation of complexes IIIa and IIIb are represented in Schemes 1 and 2. It is most probable that the first stage of both reactions is the addition of phosphite to the electrophilic α-carbon atom of vinylidene complex I, yielding the intermediate bipolar adducts IV. The smaller rate of the reaction between I and P(OPh)$_3$, as compared to the reaction with P(OEt)$_3$, may be explained by the lower nucleophility and the greater size of P(OPh)$_3$ [20]. Recently, the formation of such bipolar complexes as a result of the addition of PPh$_3$ to an electrophilic carbon atom in M=C=C and M=C=C=C systems has been demonstrated [21,22], e.g.:



$$(CO)_5Cr{=}C{=}C{=}C(Pr\text{-}i)_2 + PPh_3 \rightarrow (CO)_2\overline{Cr}-\underset{^{+}PPh_3}{\overset{}{C}}{=}C{=}C(Pr\text{-}i)_2$$

It is known [23] that the tendency to delocalization of charges in bipolar intermediates formed by the addition of triethylphosphite to *sp*-hybridized carbon atoms in acetylenes or allenes results in the rearrangement of the adducts to yield ethylene and vinylphosphonates. The analogous conversions may also take place in the case of the complexes of type IV. The stabilization of the intermediates IV may be achieved via internal proton transfer influenced by the basicity of the manganese atom, by a cyclic *cis*-β-elimination process to yield ethylene in the case of R = Et or dehydrobenzene when R = Ph, and the formation of a double P=O bond. The rearrangement of the intermediate σ-vinyl complex V may occur via the transfer of a hydrogen atom from manganese to the neighbouring carbon atom followed by the formation of a metal–β-carbon bond. The resulting metallacyclopropane compounds VI may be regarded as resonance forms of the isolated π-olefinic complexes

III. The formation of the complexes III with *trans*-β-phenylvinylphosphonate ligands confirms the cyclic *cis*-β-elimination process.

Thus, the reaction described here represents a novel variant of the Arbuzov reaction, occurring in the coordination sphere of a transition metal atom. It consists of a nucleophilic addition of $P(OR)_3$ to an electron-deficient carbon atom, followed by the cleavage of one of the phosphite R-O bonds and the formation of a phosphonate group, as in the classic Arbuzov reaction. The distinctive features of this novel reaction are the probable "ricochet" transfer of the hydrogen atom from the eliminating alkyl or aryl moiety through a transition metal atom to the α-carbon vinylidene atom and the n–π rearrangement of the unsaturated ligand.

Experimental

Argon-saturated dry solvents were used. All operations were carried out under argon. Chromatography was performed on a column packed with neutral alumina.

IR spectra were registered on a Specord IR-75 spectrometer. ^1H NMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) at 20°C, the internal standard was TMS.

X-ray crystal structure determination

The parameters of the unit cell and intensities of reflections were measured with an automatic four-circle Sintex $P2_1$ diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan., $2\theta \leqslant 50°$). The structure was solved by the standard heavy-atom method. Coordinates of the two independent manganese atoms were determined from the three-dimensional Patterson function, and all other non-hydrogen atoms were located by successive syntheses of electron density. The structure was refined by the full-matrix least-squares technique at first in the isotropic and then in the anisotropic approximation. All calculations were performed with an Eclipse S/200 mini-computer with modified * EXTL programs.

Synthesis of $Cp(CO)_2Mn[PhCH{=}CHP(O)(OEt)_2]$ (IIIa)

To a solution of 0.14 g (0.5 mmol) of $Cp(CO)_2MnC_2HPh$ (I) in 15 ml of hexane was added 0.10 g (0.6 mmol) of $P(OEt)_3$ and the mixture was stirred at 20°C for 1 h. The solution was then concentrated in vacuo to 2 ml and chromatographed on an alumina column. Hexane/ether mixture (5/1) eluted narrow yellow and light red bands which were united in a fraction (1), and ether brought down a broad yellow band (2). After evaporation of the fraction (1) 0.008 g of an orange oil containing $CpMn(CO)_3$, $CpMn(CO)_2P(OEt)_3$, $CpMn(CO)[P(OEt)_3]_2$ and $Cp(CO)$-$[P(OEt)_3]MnC_2HPh$ (IIa), identified by IR spectra, was produced. Removal of the solvent from fraction (2) rendered 0.20 g (96%) of IIIa. Recrystallization of IIIa from hexane/ether mixture yielded dark yellow crystals, m.p. 102°C. (Found: C, 55.24; H, 5.25. $C_{19}H_{22}PO_5Mn$ calcd.: C, 54.81; H, 5.29%).

Synthesis of $Cp(CO)_2Mn[PhCH{=}CHP(O)(OPh)_2]$ (IIIb)

A solution of 0.14 g (0.5 mmol) of I and 0.25 g (0.75 mmol) of $P(OPh)_3$ in 15 ml

---

* The modification of the programs was carried out in the Laboratory of X-ray analysis of the Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R. by A.I. Yanovsky and R.G. Gerr.

of hexane was stirred at 20°C for 5 h. The dark brown oil obtained after evaporation of the solvent was chromatographed on an alumina column. With hexane/ether mixtures (10/1 and then 5/1) sharp yellow and light red bands were eluted, containing traces of $CpMn(CO)_2P(OPh)_3$, $CpMn(CO)[P(OPh)_3]_2$ and $Cp(CO)[P(OPh)_3]MnC_2HPh$ (IIb) identified by IR spectra. With ether a broad yellow zone was eluted which after evaporation gave a yellow oil purified by filtration of its solution in ether through a 2 cm alumina pad. After evaporation of the solvent, 0.24 g (95%) of the yellow amorphous product IIIb was obtained. (Found: C, 63.80, H, 4.56. $C_{27}H_{22}PO_5Mn$ calcd.: C, 63.31; H, 4.30%).

Acknowledgements

The authors are grateful to Mrs. N.I. Pavlenko for measurement of IR spectra, and to Professor R.A. Cherkasov and Drs. M.A. Pudovik, and A.G. Ginsburg for helpful discussions.

References

1 A.N. Nesmeyanov, G.G. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, J. Organometal. Chem., 110 (1976) C36.

2 G.G. Aleksandrov, A.B. Antonova, N.E. Kolobova and Yu.T. Struchkov, Koord. Khimiya, 2 (1976) 1684.

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

4 A.N. Nesmeyanov, N.E. Kolobova, A.B. Antonova, N.S. Obezyuk and K.N. Anisimov, Izv. Akad Nauk SSSR, Ser. Khim., (1976) 948.

5 R.J. Haines and C.R. Nolte, J. Organometal. Chem., 24 (1970) 725; R.J. Haines, A.L. du Preez and J.L. Marais, J. Organometal. Chem., 28 (1971) 97, 405, 413.

6 M.G. Newton, N.S. Pantaleo, R.B. King and S.P. Diefenbach, J. Chem. Soc., Chem. Commun., (1979) 55.

7 B.A. Arbuzov, Reaktsii i metody issledovaniya organicheskich soyedineniy (Reactions and methods of investigation of organic compounds), Goskhimizdat, Moscow, 3 (1954) 7.

8 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton, (1973) 1667.

9 A.B. Antonova, S.P. Gubin and S.V. Kovalenko, Izv. Akad. Nauk. SSSR, Ser. Khim., (1982) 953.

10 M. Herberhold, Metal π-Complexes Vol. II, Complexes with monoolefinic ligands, Elsevier, Amsterdam, London, New York, 1972.

11 M. Giffard and P. Dixneuf, J. Organometal. Chem., 85 (1975) C26.

12 P. Tavs and H. Weitkamp, Tetrahedron, 26 (1970) 5529.

13 T.N. Timofeeva, B.I. Ionin, Yu.L. Klejman, N.V. Morkovin and A.A. Petrov, Zh. Obshch. Khim., 38 (1968) 1255.

14 L.E. Sutton (Ed.), Tables of interatomic distances and configurations in molecules and ions. Supplement, Chemical Society, Special Publication No. 18, London, 1965.

15 P.G. Borgne, E. Gentric and D. Grandjean, Acta Crystallogr. B, 31 (1975) 2824.

16 G.G. Aleksandrov, A.B. Antonova, N.E. Kolobova, N.S. Obezyuk and Yu.T. Struchkov, Koord. Khimiya, 5 (1979) 279.

17 P.J. Fitzpatrick, V. Le Page, J. Sedman and I.S. Butler, Inorg. Chem., 20 (1981) 2852.

18 G. Samuel and R. Wess, Tetrahedron, 26 (1970) 2995.

19 G. Mass and K. Fischer, Acta Crystallogr. B, 30 (1974) 1140.

20 C.A. Tolman, Chem. Rev., 77 (1977) 313.

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

22 H. Berke, P. Härter, G. Huttner, L. Zsolnai, Z. Naturforsch., 36b (1981) 929.

23 C.E. Griffin and T.D. Mitchell, J. Org. Chem., 30 (1965) 1935.