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REACTION OF (η-C_5H_5)$(CO)_2$Mn(η^2-HC≡CCO_2Me) WITH PHOSPHINES. CRYSTAL AND MOLECULAR STRUCTURE OF (η-C_5H_5)$(CO)_2Mn^-$—C(CO_2Me)=CHP^+Ph_3

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Summary

Reaction of Cp$(CO)_2$Mn(η^2-HC≡CCO_2Me) (I) with PPh_3 or $(Ph_2PCH_2—)_2$ gives rise to π—σ-rearrangement of the methylpropiolate ligand in I, yielding the phosphonium ylide complexes Cp$(CO)_2Mn^-$C(CO_2Me)=CHP^+Ph_2R, where R = Ph or $CH_2CH_2PPh_2$. The structure of II was established by X-ray crystallography.

Introduction

As we have reported recently [1], Cp$(CO)_2$Mn(η^2-HC≡CCO_2Me) (I) adds PPh_3 under mild conditions (20—40°C, in pentane), giving the complex Cp$(CO)_2$Mn(HC_2CO_2Me)PPh_3 (II), isolated as red air-stable crystals, insoluble in alkanes, moderately soluble in benzene and ether, and readily soluble in $CHCl_3$ and CH_2Cl_2. In solution II is sensitive to atmospheric oxygen. The IR spectra of II show two absorption bands for terminal carbonyls (1910 and 1835 cm^{-1}) and a band for the methoxycarbonyl group (1680 cm^{-1}), but no band for the coordinated triple bond. These data together with mass spectra and elemental analysis results led us to the conclusion [1] that PPh_3 induces a rearrangement of I into a vinylidene complex, Cp$(CO)_2$Mn=C=$CHCO_2$Me (III), and then adds to the α-carbon atom of the vinylidene ligand, i.e. II has the structure Cp$(CO)_2Mn^-$—C(P^+Ph_3)=$CHCO_2$Me, similar to that of the previously reported Cr and W complexes of phosphonium ylide [2,3].

Surprisingly, an attempt to obtain II from III and PPh_3 under the same conditions gave a brown substance with the same composition as II, but different IR spectra and melting point. The structure of this product is now under investigation. To establish the structure of II unambiguously we performed its X-ray analysis.

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Results and discussion

The molecular geometry of II is shown in Fig. 1, bond lengths and angles are listed in Table 1.

The Mn atom has a "piano stool" environment of the planar cyclopentadienyl moiety (Mn···C(Cp) distances are essentially equal, averaging 2.158(5) Å), two linear carbonyls and the σ-bonded C(4) atom. The C(2)MnC(4) angle is increased (95.7°) and the C(1)MnC(4) angle is, on the contrary, decreased (85.5°) in comparison with the ideal value of 90°, due to bulky CO_2Me substituent at C(4).

The Mn—C(4) bond of 1.985 Å is longer than double Mn=C bonds in carbene complexes $Cp(CO)_2Mn{=}CRR'$ (1.86—1.89 Å) [4—6], but shorter than single Mn—C(sp^2) bonds (e.g. 2.03—2.07 Å in mononuclear σ-arene manganese complexes [7] and 2.026 Å in the σ-carbamoyl complex Cp(CO)(NO)MnC(=O)NH_2 [8]). The latter bonds are still shorter than the sum of covalent radii of Mn (1.39 [9] or 1.38 Å [10]) and C(sp^2) (0.74 Å [11]), as usual for transition metal—sp^2-carbon bonds [12]. In the binuclear complexes $[Cp(CO)_2Mn]_2$(μ_2-C=CRR') the bridging Mn—C(vinylidene) distances are 1.94—1.99 Å [13].

The C(4)—C(5) bond, of 1.361 Å, is somewhat longer than the normal double bond, of 1.337 Å [14]. The essentially equal P—C(Ph) bond distances (mean value 1.806(3) Å) lie in the range 1.78—1.82 Å common for carbon—tetrahedral phosphorous bonds [15]. The P—C(5) bond length of 1.761 Å is significantly shorter and close to the values typical of partially double P—C bonds in phosphonium ylides (1.68—1.75 Å), usually interpreted in terms of the resonance [15]:

$$\geqslant P{=}C\leqslant \leftrightarrow \geqslant P^{+}{-}C\leqslant .$$

The distortion of the tetrahedral P atom geometry agrees with the multiple

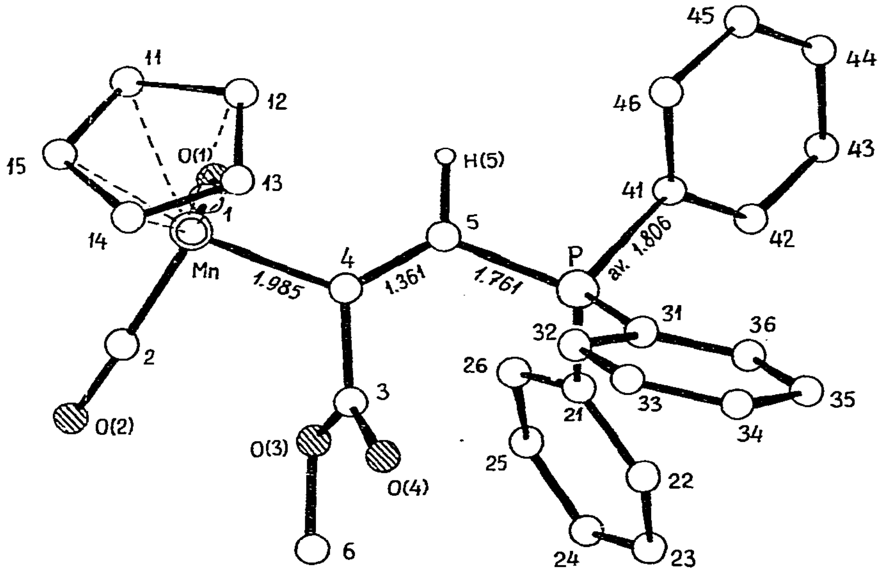


Fig. 1. Molecular structure of II. Hydrogen atoms, except H(5), are omitted.

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°)

Bond		Bond		Bond	
Mn—C(1)	1.770(4)	C(2)—O(2)	1.174(4)	P—C(31)	1.804(3)
Mn—C(2)	1.760(3)	C(3)—C(4)	1.486(4)	P—C(41)	1.810(3)
Mn—C(4)	1.985(3)	C(3)—O(3)	1.350(4)	C(11)—C(12)	1.428(5)
Mn—C(11)	2.155(3)	C(3)—O(4)	1.213(4)	C(12)—C(13)	1.417(5)
Mn—C(12)	2.156(3)	O(3)—C(6)	1.447(4)	C(13)—C(14)	1.419(5)
Mn—C(13)	2.154(3)	C(6)—H, av.	0.95(4)	C(14)—C(15)	1.420(5)
Mn—C(14)	2.163(3)	C(4)—C(5)	1.361(4)	C(15)—C(11)	1.405(5)
Mn—C(15)	2.164(3)	C(5)—H(5)	0.95(4)	C—C(Ph)	1.372(5)—1.398(4)
Mn—Cp [a]	1.790	C(5)—P	1.761(3)		av. 1.387(7)
C(1)—O(1)	1.166(4)	P—C(21)	1.805(3)		
Angle		**Angle**		**Angle**	
C(1)MnC(2)	91.7(2)	C(3)O(3)C(6)	115.4(3)	C(12)C(13)C(14)	108.2(3)
C(1)MnC(4)	85.5(1)	O(3)C(6)H, av.	107	C(13)C(14)C(15)	108.0(3)
C(2)MnC(4)	95.7(1)	HC(6)H, av.	112	C(11)C(15)C(14)	107.9(3)
CpMnC(1) [a]	127.8	C(4)C(5)P	126.9(2)	PC(21)C(22)	122.8(2)
CpMnC(2) [a]	123.8	C(4)C(5)H(5)	112(2)	PC(21)C(26)	117.0(2)
CpMnC(4) [a]	122.1	PC(5)H(5)	121(2)	C(22)C(21)C(26)	119.9(3)
MnC(1)O(1)	177.6(3)	C(5)PC(21)	110.9(1)	PC(31)C(32)	120.6(2)
MnC(2)O(2)	177.4(3)	C(5)PC(31)	113.8(1)	PC(31)C(36)	119.5(2)
MnC(4)C(3)	115.2(2)	C(5)PC(41)	109.3(1)	C(32)C(31)C(36)	119.9(3)
MnC(4)C(5)	126.9(2)	C(21)PC(31)	110.1(1)	PC(41)C(42)	119.5(2)
C(3)C(4)C(5)	118.0(3)	C(21)PC(41)	105.2(1)	PC(41)C(46)	120.9(2)
C(4)C(3)O(3)	113.0(3)	C(31)PC(41)	107.1(1)	C(42)C(41)C(46)	119.5(3)
C(4)C(3)O(4)	124.3(3)	C(12)C(11)C(15)	108.6(3)	CCC in Ph	119.4(3)—121.3(3)
O(3)C(3)O(4)	122.6(3)	C(11)C(12)C(13)	107.3(3)		av. 120.0(5)

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

character of the P—C(5) bond, as the mean C(5)PC(Ph) angle, 111(2)°, is greater than the mean C(Ph)PC(Ph) angle, 107(2)°, though the tendency is not very pronounced, probably due to steric hindrance.

Thus, the bond distances observed in the MnC(4)C(5)P moiety can be represented by two resonance forms, viz. a zwitter-ionic "σ-vinyl-carbene" form $Cp(CO)_2Mn^-—C(CO_2Me)=CHP^+Ph_3$, and a "carbene-ylide" form $Cp(CO)_2$-

TABLE 2

PROPERTIES OF II AND IV

Complex	Appearance, m.p. (°C)	IR spectra (cm^{-1}) (in CH_2Cl_2)		^{31}P NMR spectra (H_3PO_4 internal standard, in CH_2Cl_2), δ (ppm) $J(^{31}P—^{31}P)$ (Hz) in parenthesis	
		ν(C≡O)	ν(C=O)	P (phosphonium)	P (phosphine)
II	Red crystals, 175 (dec.)	1910 1835	1680	—3.82	—
IV	Red powder, 75 (dec.)	1920 1845	1680	—4.34 (47.61)	—14.37 (41.50)

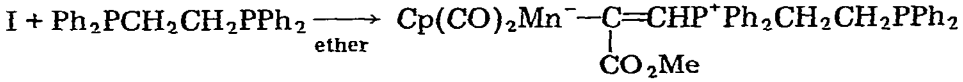
Mn=C(CO$_2$Me)—CH=PPh$_3$ without separate charges. II resembles the anion of the complex (NMe$_4$)[Cp(CO)$_2$MnCOPh], in which the bond distances Mn—C of 1.96(2) Å (the same as in II within e.s.d.) and C—O of 1.28 Å are consistent with two resonance forms, Cp(CO)$_2$Mn$^-$—C(=O)Ph and Cp(CO)$_2$Mn=C(—O$^-$)Ph, contributing to delocalization of the negative charge [16].

Atoms C(3), C(4), C(5), Mn and P are coplanar within 0.02 Å. H(5) is displaced by 0.06 Å, or less than 2σ, out of their best-fit plane. This plane forms an angle of 106.5° with the plane of C(4), C(3), O(3), O(4), C(6) (indicating no conjugation between the carboxyl π-system and MnC(4)C(5)P moiety) and an angle of 134° with the Cp plane.

The phenyl groups have normal geometry. The P atom is tilted by 0.18 Å out of the C(21)···C(26) phenyl plane (i.e. the P—C(21) bond is bent out of this plane by 5.6°) in the direction opposite to the CO$_2$Me moiety, probably in order to minimize steric hindrance with the latter, indicated by the short intramolecular distances: C(3)···C(21) of 3.070, C(3)···C(26) of 3.287 Å. No abnormally short intermolecular contacts are observed.

The structure of II confirms that PPh$_3$ addition induces not an acetylene—metalloallene transformation, but a previously unknown π—σ rearrangement of the methylpropiolate ligand in I.

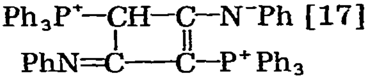
Diphosphine Ph$_2$PCH$_2$CH$_2$PPh$_2$ reacts with I in the same way as PPh$_3$, yielding complex IV:



$$\mathrm{I} + \mathrm{Ph_2PCH_2CH_2PPh_2} \xrightarrow[\text{ether}]{} \mathrm{Cp(CO)_2Mn^-}\!-\!\underset{\mathrm{CO_2Me}}{\underset{|}{\mathrm{C}}}\!=\!\mathrm{CHP^+Ph_2CH_2CH_2PPh_2}$$

(IV)

The properties of II and IV are summarized in Table 2. The ^{31}P NMR spectrum of II exhibits one singlet at —3.82 ppm which compares with the signal at —4.08 ppm observed for the Ph$_3$P$^+$—C$\lessgtr$ moiety in Ph$_3$P$^+$—CH—C—N$^-$Ph [17].



PhN=C——C—P$^+$Ph$_3$

The ^{31}P NMR spectrum of IV exhibits two doublets at —4.34 and —14.37 ppm. The former signal can be attributed to the tetracoordinate P atom, and the latter one to the tricoordinate P (uncomplexed Ph$_2$PCH$_2$CH$_2$PPh$_2$ exhibits a singlet at —13.2 ppm [18]). These data and the similarity between the IR spectra of II and IV allow us to ascribe to IV a structure similar to II.

Experimental

All synthetic operations were performed in an argon stream, using absolute solvents saturated with argon. IR spectra were recorded on a Zeiss UR-20 spectrometer, and ^{31}P NMR spectra on a Bruker HX-98 spectrometer (36.44 MHz).

An X-ray experiment was performed with a Syntex P2$_1$ four-circle computer-controlled diffractometer at —120°C using graphite-monochromated Mo-K_α radiation.

Crystal data: C$_{29}$H$_{24}$MnO$_4$P, F.W. 522.4, monoclinic, at —120°C a = 14.74(1), b = 10.91(1), c = 15.57(1) Å, β = 100.57(5)°, V =2461(3) Å^3, $d_{\mathrm{calcd.}}$ = 1.41 g cm^{-3}, Z = 4, space group $P2_1/a$.

TABLE 3

ATOMIC COORDINATES ($\times 10^5$ for Mn and P, $\times 10^4$ for C and O) AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^2$ for Mn and P, $\times 10$ for C and O) IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	10261(3)	6069(4)	32124(3)	164(2)	112(2)	147(2)	11(2)	46(2)	17(2)
P	5972(6)	47957(7)	25912(5)	140(4)	106(3)	145(4)	5(3)	35(3)	−3(3)
O(1)	−834(2)	845(2)	3615(2)	17(1)	41(1)	25(1)	−4(1)	8(1)	−8(1)
O(2)	348(2)	−847(2)	1641(2)	35(1)	18(1)	22(1)	8(1)	1(1)	−7(1)
O(3)	−311(1)	1803(2)	1380(1)	18(1)	16(1)	16(1)	−2(1)	−1(1)	0(1)
O(4)	1071(2)	2547(2)	1218(1)	24(1)	20(1)	18(1)	−2(1)	10(1)	3(1)
C(1)	−95(2)	725(3)	3460(2)	24(2)	16(1)	11(1)	−4(1)	1(1)	−1(1)
C(2)	612(2)	−241(3)	2259(2)	21(2)	11(1)	22(2)	8(1)	7(1)	5(1)
C(3)	544(2)	2237(3)	1691(2)	17(2)	4(1)	20(2)	4(1)	1(1)	0(1)
C(4)	775(2)	2242(3)	2661(2)	10(1)	14(1)	15(1)	0(1)	4(1)	3(1)
C(5)	830(2)	3344(3)	3077(2)	19(2)	12(1)	13(2)	1(1)	3(1)	1(1)
C(6)	−565(3)	1750(4)	438(3)	36(2)	31(2)	19(2)	−7(2)	−6(2)	1(2)
C(11)	1651(2)	−21(3)	4498(2)	17(2)	25(2)	18(2)	3(1)	1(1)	10(1)
C(12)	1979(2)	1184(3)	4361(2)	14(2)	24(2)	17(2)	5(1)	−4(1)	0(1)
C(13)	2448(2)	1117(3)	3646(2)	14(2)	23(2)	20(2)	1(1)	3(1)	6(1)
C(14)	2412(2)	−114(3)	3346(2)	17(2)	23(2)	23(2)	8(1)	6(1)	1(1)
C(15)	1915(2)	−812(3)	3875(2)	25(2)	17(1)	25(2)	6(1)	4(1)	9(1)
C(21)	−402(2)	4739(3)	1727(2)	14(1)	9(1)	16(1)	2(1)	6(1)	−3(1)
C(22)	−462(2)	5393(3)	955(2)	21(2)	16(1)	17(2)	0(1)	6(1)	−2(1)
C(23)	−1291(2)	5412(3)	355(2)	28(2)	24(2)	13(1)	8(1)	2(1)	2(1)
C(24)	−2039(2)	4767(3)	533(2)	19(2)	27(2)	22(2)	7(1)	0(1)	−7(1)
C(25)	−1983(2)	4095(3)	1295(2)	15(2)	22(2)	24(2)	0(1)	3(1)	−4(1)
C(26)	−1166(2)	4084(3)	1894(2)	20(2)	16(1)	15(2)	2(1)	5(1)	−2(1)
C(31)	1563(2)	5457(3)	2192(2)	14(1)	14(1)	15(1)	0(1)	3(1)	−2(1)
C(32)	2327(2)	4745(3)	2113(2)	17(2)	14(1)	16(1)	2(1)	1(1)	−1(1)
C(33)	3059(2)	5268(3)	1801(2)	14(1)	25(2)	18(1)	1(1)	2(1)	−4(1)
C(34)	3028(2)	6493(3)	1555(2)	18(2)	22(2)	19(2)	−8(1)	5(1)	−5(1)
C(35)	2278(2)	7207(3)	1640(2)	27(2)	15(1)	22(2)	−6(1)	6(1)	1(1)
C(36)	1543(2)	6699(3)	1968(2)	21(2)	11(1)	23(2)	1(1)	7(1)	−1(1)
C(41)	291(2)	5851(3)	3388(2)	14(1)	13(1)	15(1)	−3(1)	6(1)	−1(1)
C(42)	−415(2)	6691(3)	3135(2)	21(2)	15(1)	18(2)	2(1)	2(1)	−2(1)
C(43)	−642(2)	7531(3)	3729(2)	17(2)	19(1)	27(2)	4(1)	4(1)	−5(1)
C(44)	−170(2)	7528(3)	4575(2)	21(2)	24(2)	26(2)	−1(1)	10(1)	−10(1)
C(45)	533(2)	6693(3)	4836(2)	24(2)	30(2)	18(2)	0(1)	0(1)	−6(1)
C(46)	777(2)	5864(3)	4242(2)	18(2)	20(2)	22(2)	1(1)	1(1)	−3(1)

TABLE 4

COORDINATES ($\times 10^3$) AND ISOTROPIC B (Å^2) OF H ATOMS [a]

Atom	x	y	z	B_{iso}
H(5)	101(2)	339(3)	369(2)	1.7(7)
H(6)	−52(3)	253(4)	19(3)	5(1)
H(6)	−12(3)	120(4)	22(3)	4(1)
H″(6)	−117(3)	153(4)	35(3)	5(1)
H(11)	129	−26	496	
H(12)	189	193	471	
H(13)	275	182	340	
H(14)	269	−43	285	
H(15)	178	−171	382	
H(22)	9	585	83	
H(23)	−134	589	−20	
H(24)	−263	478	10	
H(25)	−253	362	141	
H(26)	−112	361	245	
H(32)	235	386	228	
H(33)	361	476	175	
H(34)	355	686	132	
H(35)	226	809	147	
H(36)	101	722	204	
H(42)	−76	669	252	
H(43)	−115	814	354	
H(44)	−33	813	500	
H(45)	87	669	546	
H(46)	130	528	443	

[a] Atoms from H(11) to H(46) have fixed coordinates corresponding to C—H distances 1.0 Å and sp^2 geometry of C atoms, and isotropic B of 3 Å^2.

Of 3190 independent reflections collected by the $\theta/2\theta$ scan technique in the range $2\theta \leqslant 45°$, 2593 having $I \geqslant 2\sigma$ were used in calculations. The structure was solved by Patterson and Fourier methods, and refined by full matrix least squares. Non-hydrogen atoms were refined with anisotropic temperature factors; methyl group hydrogen atoms and H(5) were located from a difference Fourier map and refined with isotropic temperature factors; other (Ph and Cp groups) hydrogen atoms were included in F_c as fixed contributions at calculated positions with isotropic B = 3 Å^2. Refinement converged at R = 0.035, or, after discarding strong, extinction-affected 001 and 002 reflections, to R = 0.033 and R_w = 0.031. Relative weights $w = [\sigma_F^2 + (0.005|F_o|)^2]^{-1}$ were used. Calculations were performed on an Eclipse S/200 computer using EXTL programmes modified in this laboratory by A.I. Yanovskii and R.G. Gerr. Final atomic parameters are listed in Tables 3 and 4.

Reaction of I with PPh$_3$

0.7 g (2.67 mmol) of PPh_3 in 50 ml pentane was added to a solution of 0.3 g (1.15 mmol) of I in 50 ml pentane. The mixture was stirred for 3.5 hours, yielding a red crystalline precipitate. The solution was poured off, the precipitate was washed with pentane (6 × 10 ml) and dried in vacuo, yielding 0.51 g (85%) of pure II. Found: C, 66.67; H, 4.81; Mn, 11.06; P, 5.91. $C_{29}H_{24}MnO_4P$ calcd.: C, 66.67; H, 4.63; Mn, 10.52; P, 5.93%.

Reaction of I with $Ph_2PCH_2CH_2PPh_2$

0.55 g (1.38 mmol) of $Ph_2PCH_2CH_2PPh_2$ in 50 ml ether was added to a solution of 0.36 g (1.38 mmol) of I in 50 ml ether. The mixture was boiled for 2.5 hours, the solvent was removed in vacuo and the residue was chromatographed on SiO_2 (Chemapol, Czechoslovakia, 100 × 160 μ). The red-orange zone eluted with ether gave after removal of the solvent 0.55 g (60%) of IV. Found: C, 68.19; H, 5.37; Mn, 8.16; P, 9.91. $C_{37}H_{33}MnO_4P_2$ calcd.: C, 66.51; H, 5.05; Mn, 8.34; P, 9.41%.

References

1 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, V.F. Sizoy and Yu.S. Nekrasov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2393.
2 F.R. Kreissl, C.G. Kreiter and E.O. Fischer, Angew. Chem. Int. Ed., 11 (1972) 643.
3 F.R. Kreissl and W. Held, J. Organometal. Chem., 86 (1975) C10.
4 A.D. Redhouse, J. Organometal. Chem., 99 (1975) C29.
5 P. Friedrich, G. Besl, E.O. Fischer and G. Huttner, J. Organometal. Chem., 139 (1977) C68.
6 W.A. Herrmann, J. Plank, M.L. Zigler and K. Weidenhammer, Angew. Chem., 90 (1978) 817.
7 R.J. Doedens, J.T. Veal and R.G. Little, Inorg. Chem., 14 (1975) 1138.
8 D. Messer, G. Landgraf and H. Behrens, J. Organometal. Chem., 172 (1979) 349.
9 F.A. Cotton and D.C. Richardson, Inorg. Chem., 5 (1966) 1851.
10 V.G. Andrianov, B.P. Biryukov and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 1129.
11 L. Pauling, The Nature of the Chemical Bond, 3rd. ed., Cornell Univ. Press, Ithaca, New York, 1960.
12 M.R. Churchill, Perspectives in Struct. Chem., 3 (1970) 91.
13 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, G.G. Aleksandrov and Yu.T. Struchkov, J. Organometal. Chem., 228 (1982) 265.
14 L.E. Sutton (Ed.), Tables of interatomic distances and configurations in molecules and ions, Suppl. 1956—1959, Chem. Soc., Special Publication, No. 18, London, 1965.
15 N.G. Bokii, Yu.T. Struchkov, A.E. Kalinin, V.G. Andrianov and T.N. Sal'nikova, in Itogi Nauki, Ser. Kristallokhimiya, Vol. 12, Ed. VINITI, Moscow, 1977, p. 56.
16 E. Hadice and W. Hoppe, Acta Crystallogr. B, 27 (1971) 760.
17 H.S. Bestmann, G. Schmid, D. Sandmeier and L. Kiselowski, Angew. Chem. Int. Ed., 16 (1977) 268.
18 G.M. Kosolapoff and L. Maier, Organic Phosphorous Compounds, Vol. 1. Wiley-Interscience, New York, 1972, p. 203.