Journal of Organometallic Chemistry 696 (2011) 3408–3414

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Protonation of manganese phosphonioallenyl complexes

Kamil I. Utegenov, Vasily V. Krivykh, Ivan V. Glukhov, Pavel V. Petrovskii, Nikolay A. Ustynyuk*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 22 June 2011
Received in revised form
21 July 2011
Accepted 25 July 2011

Keywords:
Allenylidene complexes
Nucleophilic addition
Phosphonioallenyl complexes
Protonation
Phosphonioallene complexes

ABSTRACT

The addition of phosphines to the manganese allenylidene complexes $Cp(CO)_2Mn{=}C{=}C{=}C(Ph)R$ (R = H, Ph) proceeds selectively at the C_α atom to result in the α-phosphonioallenyl complexes $Cp(CO)_2Mn^-{-}C(^+PR^1_3){=}C{=}C(Ph)R$. The protonation of the latter affords the η^2-(1,2)-phosphonioallenes $Cp(CO)_2Mn\{\eta^2\text{-}(1,2)\text{-}H\boldsymbol{C}(^+PR^1_3){=}\boldsymbol{C}{=}C(Ph)R\}$, rather than the phosphoniovinylcarbenes $Cp(CO)_2Mn{=}C(^+PR^1_3){-}HC{=}C(Ph)R$. All complexes obtained are stereochemically rigid and do not isomerize into the η^2-(2,3)-phosphonioallene isomers.

1. Introduction

Transition metal allenylidene complexes $[M]{=}C_\alpha{=}C_\beta{=}C_\gamma R_2$ attract attention as efficient building blocks for the selective carbon–heteroatom and carbon–carbon bond formation [1] and as alkene metathesis catalyst precursors [2]. Thanks to the presence of the electrophilic (C_α and C_γ) and nucleophilic (C_β) sites, these compounds can react with both nucleophiles and electrophiles, but their rich reactivity is primarily related to their reactions with nucleophiles. Protic nucleophiles, such as secondary amines and phosphines, alcohols, and thiols, add to allenylidene complexes at the $C_\alpha{=}C_\beta$ bond [1]. The analogous reactions involving protic *N*,*N*- and *N*,*S*-dinucleophiles are accompanied by cyclization to form the unusual heterocycles, wherein one of the carbon atoms is linked to the transition metal *via* the ordinary or double metal–carbon bond [1]. The addition of tertiary phosphines to allenylidene complexes proceeds reversibly at the C_α or C_γ atoms to afford the α-phosphonioallenyl $[M]^-{-}C(^+PR_3){=}C{=}CR_2$ [3a–f] or γ-phosphonioalkynyl $[M]^-{-}C{\equiv}C{-}CR_2(^+PR_3)$ [3h–j] adducts, respectively, and, in some cases, a mixture of both adducts [3h]. There are also reports on the initial phosphine attack at the C_γ atom followed by the rearrangement into the α-phosphonioallenyl adducts [4]. Whether the reaction proceeds at the C_α or C_γ atom is defined by a delicate balance of various factors, such as the nature of the metal atom, electronic and steric properties of ancillary ligands and substituents at the C_γ atom of the allenylidene ligand.

Despite the formation of the zwitter-ionic C_α adducts $[M]^-{-}C(^+L){=}C{=}CR_2$ and C_γ adducts $[M]^-{-}C{\equiv}C{-}CR_2(^+L)$ (L = PR_3, NR_3, and SR_2) determines the course of many reactions of allenylidene complexes, the reactions of these adducts remain virtually unexplored and deserve careful study. We started a systematic study of the reactions of the adducts of phosphorus nucleophiles with vinylidene and allenylidene complexes [5]. In particular, the protonation of manganese and rhenium phosphoniovinyl complexes **A** was found to proceed at the metal atom *via* the intermediate hydride **B** and affords phosphonioalkenes **C**, rather than phosphoniocarbenes **D** [5b] (Scheme 1).

In order to determine the generality of the reactions shown in Scheme 1, in the present work we studied the protonation of the manganese zwitter-ionic α-phosphonioallenyl complexes $Cp(CO)_2Mn{-}C(^+PR^1_3){=}C{=}C(Ph)R$ and found that these reactions also afforded the η^2-(1,2)-phosphonioallenes $Cp(CO)_2Mn(\eta^2\text{-}H(R^1_3P^+))\boldsymbol{C}{=}\boldsymbol{C}{=}CPhR$, rather than the (phosphonio)vinylcarbenes $Cp(CO)_2Mn{=}C(^+PR^1_3)CH{=}C(Ph)R$. Previously, the manganese α-phosphonioallenyl adducts of the type $Cp(CO)_2Mn{-}C(PPh_3){=}C{=}CR_2$ (R = Ph, t-Bu) [3c] have been synthesized for only one phosphine (PPh_3), one adduct (R = Ph) having been characterized by X-ray diffraction. However, their protonation has not been studied.

2. Results and discussion

2.1. Manganese 1-phosphonio-3,3-diphenylallenyl complexes

The reactions of complex **1** with tertiary phosphines (PPh_2Me (**a**), $PPhMe_2$ (**b**), and PMe_3 (**c**)) proceed at the C_α atom to result in the zwitter-ionic adducts **2a**–**c** (Scheme 2).

* Tel.: +7 (499) 135 50 64; fax: +7 (499) 135 50 85.
E-mail address: ustynyuk@ineos.ac.ru (N.A. Ustynyuk).

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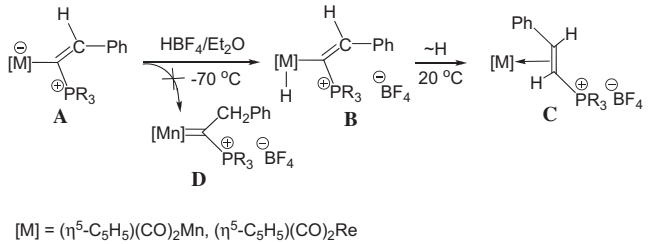
doi:10.1016/j.jorganchem.2011.07.034



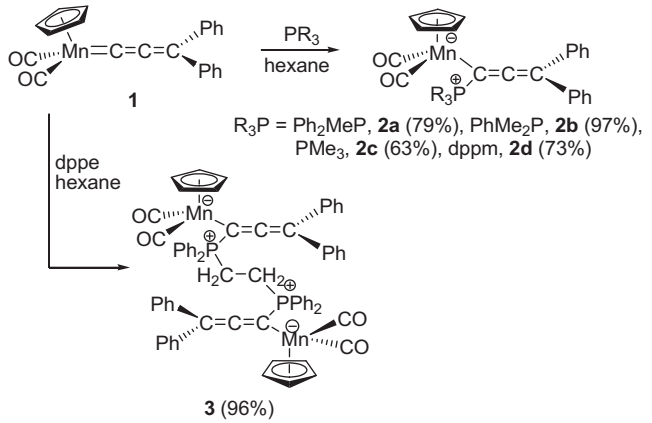
Scheme 1.

Contrary to our expectations, the reaction products of complex **1** with diphosphines dppm and dppe were different: the mononuclear adduct **2d** formed in the reaction with dppm, while the reaction with dppe afforded the binuclear adduct **3** even if the reagent ratio was 1:1.

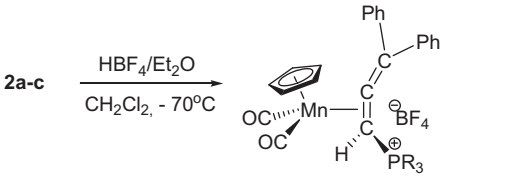
The spectral characteristics of complexes **2** and **3** agree quite well with their structure. Their IR spectra contain two carbonyl bands (ν_{CO} 1894, 1824 cm^{-1}), which are very close to those observed earlier for the analogous phosphonioallenyl complex $Cp(CO)_2M^-–C(^+PPh_3)=C=CPh_2$ [3c] and phosphoniovinyl complexes $Cp(CO)_2M^-–C(^+PR_3)=C(H)Ph$ [5b] and expectedly shifted to low frequencies compared to those of **1** (ν_{CO} 1994, 1940 cm^{-1}). The signals for the cyclopentadienyl protons appear in the region of δ 4.2–4.5; the methyl protons of phosphorus bonded methyl groups in **2a,c** are clearly seen as doublets at δ 1.93 ($^2J_{PH} = 8.3$ Hz) and 0.92, ($^2J_{PH} = 11.3$ Hz), respectively, while the signal for the methyl protons in **2b** appears as a broad singlet at δ 1.42. The phenyl protons appear as multiplets in the region of δ 6.9–7.5. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** contain the signals for the phosphonium nucleus in the narrow region of δ 12.5–18.0 typical of the previously reported phosphonioallenyl [3c] and phosphoniovinyl complexes [5b].

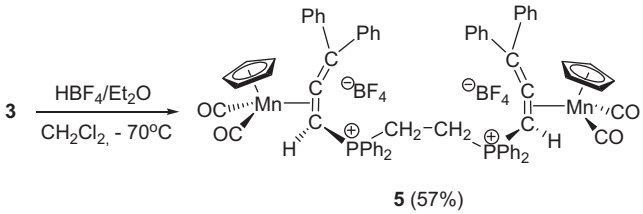
2.2. Protonation of the manganese 1-phosphonio-3,3-diphenylallenyl complexes

As stated above (see Scheme 1), the protonation of manganese and rhenium phosphoniovinyl complexes $Cp(CO)_2M^-–C(^+PR_3)=C(H)Ph$ (M = Mn, Re) proceeds at the metal atom to form the phosphonioalkene complexes, rather than the phosphoniocarbene ones. We showed that the protonation of the phosphonioallenyl complexes **2a–c** and **3** proceeded similarly to result in the phosphonioallenes, rather than the (phosphonio)vinylcarbenes (Scheme 3). The course of the reaction was monitored by IR spectroscopy and



Scheme 2.





Scheme 3.

the structures of the products were confirmed by ^1H and ^{31}P NMR spectroscopy and, in some cases, by ^{13}C NMR spectroscopy.

Unlike the reactions shown in Scheme 3, the protonation of the dppm adduct **2d** afforded exclusively the phospine complex **6** containing the allenylphosphonium fragment in the side chain (Scheme 4). We failed to detect the intermediate η^2-phosphonioallene complex of type **4**.

We assume that the initially formed η^2-allene complex undergoes intramolecular substitution of the free phosphine fragment of dppm for the allene ligand, which is presumably promoted by an easy accessibility of the chelate five-membered ring in the transition state. The structure of complex **6** was proposed based on the IR, ^1H, and ^{31}P NMR spectral data and finally confirmed by X-ray diffraction (Fig. 1).

2.3. Manganese 1-phosphonio-3-phenylallenyl complex and protonation thereof

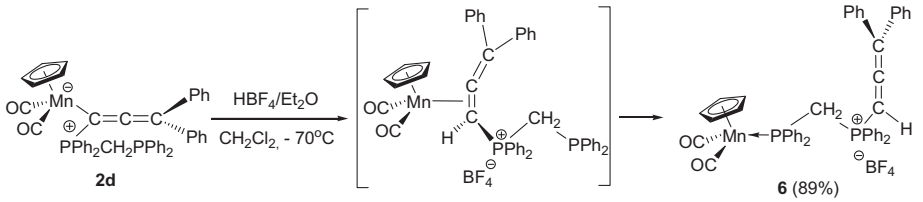
We tried to extend these reactions to adduct **8** formed by the addition of methyldiphenylphosphine to the monophenylallenylidene complex **7** (Scheme 5). Complex **7** was found to be unstable and decomposed on attempting to isolate it [6]. Therefore, the desired adduct **8** was prepared by the addition of phosphine to complex **7** generated *in situ* (see Scheme 5).

The acid treatment of **8** under the same conditions as for **2** resulted in the corresponding phosphonioallene **9** (Scheme 6).

The structure of **9** was established by X-ray diffraction (Fig. 2).

2.4. Isomerism of phosphonioallene complexes

Thus, the protonation of the manganese α-phosphonioallenyl complexes $Cp(CO)_2Mn^-–C(^+PR^1_3)=C=C(Ph)R$ affords the η^2-1,2-phosphonioallenes $[(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}H\mathbf{C}(^+PR^1_3)=\mathbf{C}=CHPh)]BF_4$, which allows one to assume proceeding of the reaction along the same pathway as for the protonation of the structurally close phosphoniovinyl adducts $Cp(CO)_2Mn-–C(^+PR_3)=C(H)Ph$ (Scheme 1) [5b], *i.e.*, through the proton addition to the metal atom followed by the C,H-reductive elimination in the intermediate hydrides $Cp(CO)_2(H)Mn–C(^+PR^1_3)=C=C(Ph)R$. It is very likely that the protonation of the zwitter-ionic α-phosphonioallenyl complexes of other transition metals will occur in the same way to result in the corresponding η^2-1,2-phosphonioallenyl structures as the primary reaction products. Similarly, the protonation of the γ-phosphonioallenyl compounds should afford the corresponding η^2-2,3-phosphonioallene complexes. This is in good accordance with the



Scheme 4.

protonation of the rhenium γ-phosphonio-α-tolylallenyl complex $Cp(CO)_2Re{-}C(Tol){=}C{=}C(Ph)PPh_2Me$ with TfOD, which was reported to give $Cp(CO)_2Re\{\eta^2\text{-}(2,3)\text{-}DC(Tol){=}C{=}C(Ph)PPh_2Me\}$ (**10**) [7]. It should be noted that the η^2-(1,2)-phosphonioallene complexes are known only by solitary examples [8].

The transition metal monosubstituted allene complexes can exist as three isomers, namely, η^2-(1,2)-isomer (**E**) and *syn*- and *anti*-η^2-(2,3)-isomers (**F** and **G**, respectively) (Chart 1). For example, the cationic iron methylallene complex exists as a mixture of isomers **F** and **G** ([M] = $[Cp(CO)_2Fe]^+$, R = Me) as identified by NMR spectroscopy [9], while the manganese methoxyallene and hydroxamethylallene complexes exist as a mixture of all three possible isomers ([M] = $Cp(CO)_2Mn$, R = OMe and CH_2OH) [10].

Almost all known transition metal complexes with the unsymmetrically substituted allenes represent one isomer [11], which is usually the *anti*-η^2-(2,3)-isomer **G** in the case of donor (methyl) substituents or the η^2-(1,2)-isomer **E** in the case of acceptor substituents. As mentioned above, all manganese phosphonioallene complexes (**4a**–**c**, **5**, and **9**) obtained in this work are the η^2-(1,2)-isomers of type **E**.

Among the synthetic approaches to the alternative η^2-(2,3)-isomers, we would like to point out first of all the photochemical reaction of the transition metal half-sandwich carbonyls with propargyl alcohol followed by the treatment of the *in situ* generated η^2-alkyne complexes with triphenylphosphine and tetrafluoroboric acid [8]. In the case of cymantrene, $[Cp(CO)_2Mn(\eta^2\text{-}2,3\text{-}H_2\boldsymbol{C}{=}\boldsymbol{C}{=}C(^+PPh_3)H)]BF_4$ **10** was obtained as the only product [8a], while, in the case of chromium and molybdenum arenetricarbonyl complexes, the η^2-2,3-phosphonioallene complexes $(\eta^6\text{-}C_6H_{6-n}Me_n)(CO)_2M(\eta^2\text{-}2,3\text{-}H_2\boldsymbol{C}{=}\boldsymbol{C}{=}C(^+PPh_3)H]BF_4$ (M = Cr, n = 3,5; M = Mo, n = 5, 6) formed first and then isomerized slowly into the corresponding η^2-1,2 isomers of type **E** [8a,b] at room temperature in CD_2Cl_2 or CD_3NO_2. Besides the above-mentioned rhenium η^2-(2,3)-phosphonioallene complex [7], the ruthenium η^2-(2,3)-phosphonioallene complex $[Ru(\eta^2\text{-}H_2C{=}C{=}CHPPh_3)(CO)_2(PPh_3)_2]Br$ has been prepared recently by the reaction of $Ru(CO)_2(PPh_3)_3$ with $[HC{\equiv}CCH_2PPh_3]Br$ [12].

On keeping in solutions (acetone, dichloromethane) at room temperature, the manganese complexes **4a**–**c**, **5**, and **9** do not undergo the η^2,η^2-haptotropic rearrangement into the corresponding η^2-(2,3)-phosphonioallene isomers. The similar structural rigidity has been noted earlier for all three possible isomers of the manganese methoxyallene and hydroxymethylallene complexes [10]. As mentioned above, the structurally similar chromium and molybdenum complexes $(\eta^6\text{-}C_6H_{6-n}Me_n)(CO)_2M(\eta^2\text{-}2,3\text{-}H_2\boldsymbol{C}{=}\boldsymbol{C}{=}C(^+PPh_3)H)]BF_4$ (M = Cr, n = 3, 5; M = Mo, n = 5, 6) isomerize slowly into the corresponding η^2-1,2 isomers of the type **E** [8a,b] at room temperature in CD_2Cl_2. It follows from these data that the ability of η^2-phosphonioallene complexes to undergo the haptotropic isomerization depends largely on the metal nature [13]. Presumably, this is due to a lower kinetic barrier for the rearrangement of chromium and molybdenum complexes as compared with the analogous complexes of manganese and other metals.

2.5. Molecular structures of $(\eta^5\text{-}C_5H_5)(CO)_2Mn{-}PPh_2CH_2(^+PPh_2C(H){=}C{=}CPh_2)$ (**6**) and $[(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}HC(^+PPh_2Me){=}C{=}C(H)Ph)]BF_4$ (**9**)

The molecular geometries of **6** and **9** are shown in Figs. 1 and 2, respectively. Complex **6** is the first structurally characterized compound, wherein the phosphonioallene fragment is remote from the metal atom. The double-bond distances C(33)–C(34) of 1.307(3) and C(34)–C(35) of 1.314(3) Å in the allene moiety of **6** are comparable to those in the free allene molecule (1.308 Å) [14] and those in $Cp(CO)_2Mn{-}C(PPh_3){=}C{=}CPh_2$ [3c] (1.303(3) and 1.328 (3) Å, respectively). The allene carbon atoms in **6** deviate slightly from linearity (the angle C(33)–C(34)–C(35) is 172.2(3)°).

The allene moiety of **9** is bonded to the manganese atom of the $Cp(CO)_2Mn$ fragment through C(8) and C(9). The Mn–C distance to

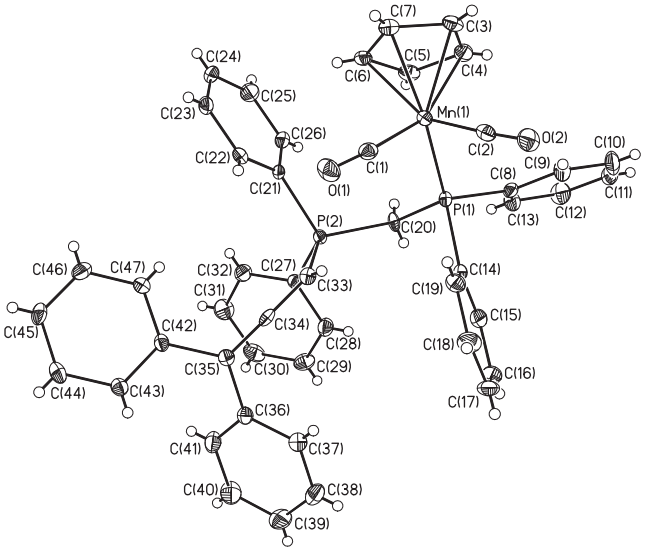
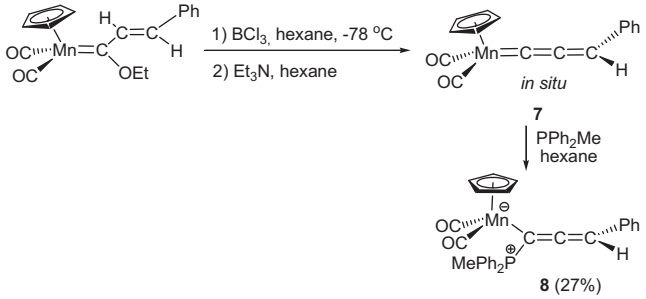
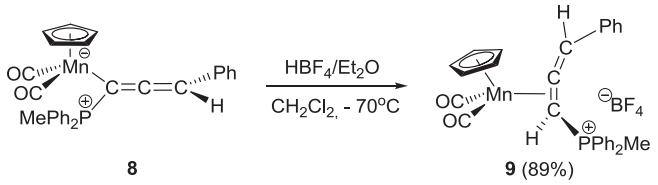


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{-}PPh_2CH_2(^+PPh_2CH{=}C{=}CPh_2)]BF_4^-$ (**6**) (50% probability displacement thermal ellipsoids). BF_4^- anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)–C(1) 1.768(2), Mn(1)–C(2) 1.772(2), Mn(1)–P(1) 2.2118(7), C(33)–C(34) 1.307(3), C(34)–C(35) 1.315(3), C(1)–Mn(1)–C(2) 91.6(1), C(1)–Mn(1)–P(1) 97.9(1), C(2)–Mn(1)–P(1) 92.1(1), C(33)–C(34)–C(35) 172.2(2).

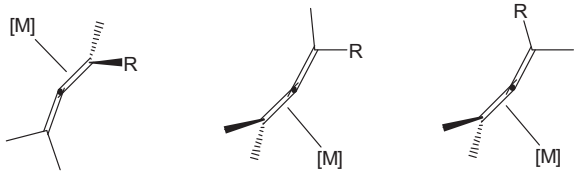


Scheme 5.



8 9 (89%)

Scheme 6.



E F G

Chart 1. Possible isomers of a monosubstituted allene complex.

the carbon atom bearing the $PMePh_2$ group Mn–C(8) = 2.1282(16) Å is significantly greater than that to the central carbon atom Mn–C(9) = 2.0263(16) Å. A similar effect occurs in the parent allene complex $Cp(CO)_2Mn(\eta^2\text{-}CH_2{=}C{=}CH_2)$ [15] and phosphinoallene complex $C_5H_4Me(CO)_2Mn(\eta^2\text{-}Ph_2P\boldsymbol{C}(Ph){=}\boldsymbol{C}{=}C(Tol)H)$ [16], in which the metal–carbon distances are very close to those in **9**. The coordinated C=C bond C(8)–C(9) = 1.412(2) Å is longer than the uncoordinated C=C bond C(9)–C(10) = 1.331(2) Å, these values being similar to those found in the allene manganese complexes [15,16] or phosphonioallene complexes of other metals [8c–d,12]. The coordination causes the usually linear allene to bend away from the metal centre, the angle C(8)–C(9)–C(10) (144.82(16)) falls in the range of angles for η^2-coordinated allenes (140–158°) [11c,12: Table S1].

Thus, we proposed a convenient entry to the manganese η^2-1,2-phosphonioallene complexes, which consists of the protonation of the α-phosphonioallenyl adducts. It is thought to be applicable for the preparation of the η^2-1,2- or 2,3-phosphonioallene complexes of other metals from the corresponding α- or γ-phosphonioallenyl derivatives.

3. Conclusions

In the present work, we showed that the addition of phosphines to the manganese allenylidene complexes $Cp(CO)_2Mn{=}C{=}C{=}C(Ph)R$ (R = H, Ph) proceeds selectively at the C_α atom to form the α-phosphonioallenyl complexes $Cp(CO)_2Mn^-\text{–}C(^+PR^1_3){=}C{=}C(Ph)R$. The protonation of the latter affords the phosphonioallene complexes $Cp(CO)_2Mn\{\eta^2\text{-}(1,2)\text{-}H\boldsymbol{C}(^+PR^1_3){=}\boldsymbol{C}{=}C(Ph)R\}$, rather than the phosphoniovinylcarbene ones $Cp(CO)_2Mn{=}C(^+PR^1_3)\text{–}HC{=}C(Ph)R$. All complexes obtained are stereochemically rigid and do not isomerize into the corresponding η^2-(1,2)-phosphonioallene isomers under ambient conditions.

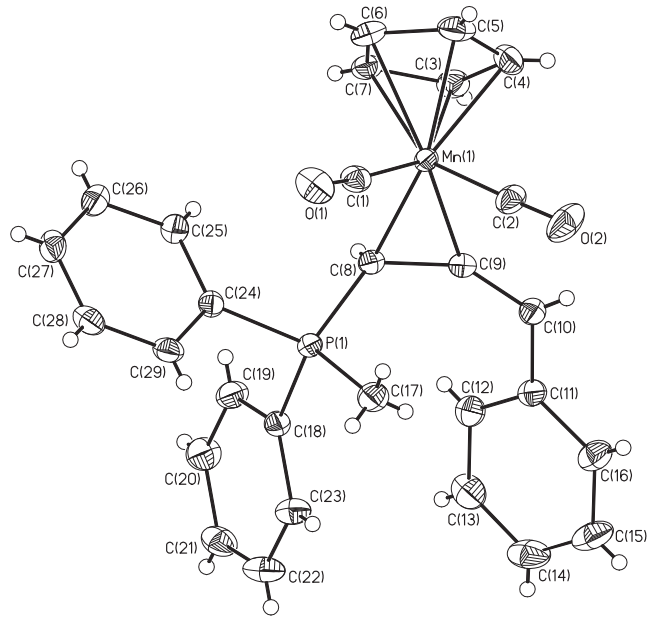


Fig. 2. Molecular structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Mn(\eta^2\text{-}HC(^+PPh_2Me){=}C{=}CHPh)]BF_4^-$ (**9**) (50% probability displacement thermal ellipsoids). BF_4^- anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)–C(1) 1.8042(18), Mn(1)-C(2) 1.7830(17), Mn(1)–C(8) 2.1282(16), Mn(1)–C(9) 2.0263(16), C(8)–C(9) 1.412(2), C(9)–C(10) 1.331(2), C(2)–Mn(1)–C(1) 86.07(8), C(8)–C(9)–C(10) 144.82(16).

4. Experimental

4.1. General

All operations were carried out under an argon atmosphere using the standard Schlenk techniques. Solvents were purified according to the standard procedures and distilled under argon prior to use. IR spectra were recorded on Specord 75 and Specord M80 IR (Carl Zeiss, Jena) spectrophotometers. ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 400 instruments at 25 °C and referenced to the residual deuterated solvent signals and external 85% H_3PO_4, respectively. Elemental analysis was performed on a Carlo Erba-1106 analyzer (C, H) and VRA-30 (Carl Zeiss, Jena) X-ray fluorescence spectrometer (Mn) in the Microanalysis Laboratory of the Institute of Organoelement Compounds of the RAS. Complex **1** was prepared according to the modified procedure of Kolobova et al. [17]. PPh_2Me [18], $PPhMe_2$ [19], PMe_3 [20], and 1-phenyl-propynol [21] were prepared according to known procedures. $PPh_2CH_2PPh_2$, $PPh_2CH_2CH_2PPh_2$, and $HBF_4{\cdot}OEt_2$ were purchased from Aldrich and used as received.

4.2. Synthesis of the manganese 1-phosphonioallenyl complexes

4.2.1. Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_2Mn^-\text{–}C(P^+Ph_2Me){=}C{=}CPh_2$ (**2a**)

To a solution of complex **1** (366 mg, 1.0 mmol) in *n*-hexane (25 mL), methyldiphenylphosphine (0.19 mL, 1.021 mmol) was added with stirring. The resulted mixture was stirred for 1 h at room temperature. The orange precipitate formed was filtered off, washed with *n*-hexane, and dried by an argon stream to yield complex **2a** (445 mg, 79%). Found (%): C, 74.28; H, 5.01. $C_{35}H_{28}MnO_2P$. Calculated (%): C, 74.21; H, 4.98. IR, ν/cm^{-1}: 1894s, 1824s (CO). ^1H NMR (C_6D_6), δ: 1.93 (d, 3H, J_{PH} = 8.3 Hz, Me), 4.41 (s, 5H, Cp), 6.90–7.31 (m, 20H, Ph). ^{31}P NMR (C_6D_6), δ: 15.08 (s).

4.2.2. Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_2Mn^-\text{–}C(P^+PhMe_2){=}C{=}CPh_2$ (**2b**)

To a solution of complex **1** (110 mg, 0.3 mmol) in CH_2Cl_2 (2 mL), phenyldimethylphosphine (0.042 mL, 0.3 mmol) was added with stirring. The resulted mixture was stirred for 30 min and then evaporated to dryness. The oily residue was washed with *n*-hexane (2 × 2 mL) and dried *in vacuo* to yield compound **2b** (147 mg, 97%) as a deep-brown oil. IR, ν/cm^{-1}: 1898s, 1828s (CO). ^1H NMR (C_6D_6), δ: 1.42 (br.s, 6H, Me), 4.50 (br.s, 5H, Cp), 7.05–7.54 (m, 15H, Ph). ^{31}P NMR (C_6D_6), δ: 12.48 (s).

*4.2.3. Synthesis of (η^5-C_5H_5)$(CO)_2Mn^-$–$C(P^+Me_3)$=C=CPh_2 (**2c**)*

To a solution of complex **1** (146.5 mg, 0.4 mmol) in *n*-hexane (10 mL), a solution of trimethylphosphine in diethyl ether (0.092 M, $c = 7$ mg/mL, 5 mL, 0.46 mmol) was added with stirring. The reaction mixture was stirred for 1 h at room temperature and then evaporated. The residue was washed with *n*-hexane, filtered off, and dried by an argon stream. Complex **2c** (110.8 mg, 63%) was obtained as an orange powder. Found (%): C, 67.69; H, 5.41; Mn, 12.30. $C_{25}H_{24}MnO_2P$. Calculated (%): C, 67.88; H, 5.47; Mn, 12.42. IR, ν_{CO}/cm^{-1} (CH_2Cl_2): 1898s, 1828s. ^{1}H NMR (C_6D_6), δ: 0.92 (d, 9H, $J_{PH} = 11.8$ Hz, Me), 4.44 (s, 5H, Cp), 7.07–7.51 (m, 10H, Ph). ^{31}P NMR (C_6D_6), δ: 12.45 (s).

*4.2.4. Synthesis of (η^5-C_5H_5)$(CO)_2Mn^-$–$C(^+PPh_2CH_2PPh_2)$=C=CPh_2 (**2d**)*

To a solution of bis(diphenylphosphino)methane (461.3 mg, 1.2 mmol) in *n*-hexane (75 mL), a solution of complex **1** (366 mg, 1.0 mmol) in *n*-hexane (12 mL) was added with stirring. The reaction mixture was stirred for 2 h at room temperature. The orange precipitate formed was filtered off, washed with *n*-hexane, and dried by an argon stream to yield complex **2d** (546 mg, 73 %). Found (%): C, 75.35; H, 5.01; P, 8.64. $C_{47}H_{37}MnO_2P_2$. Calculated (%): C, 75.20; H, 4.97; P, 8.25. IR, ν/cm^{-1} (CH_2Cl_2): 1894s, 1820s (CO). ^{1}H NMR (C_6D_6), δ: 4.01 (d, 2H, $J_{PH} = 13.6$ Hz, CH_2), 4.44 (s, 5H, Cp), 6.92–7.67 (m, 30H, Ph). ^{31}P NMR (C_6D_6), δ: −27.04 (d, 1P, $J_{PP} = 58.5$ Hz, PPh_2CH_2), 16.38 (d, 1P, $J_{PP} = 58.5$ Hz, $P^+Ph_2CH_2$).

*4.2.5. Synthesis of [(η^5-C_5H_5)$(CO)_2Mn^-$–$C(=C=CPh_2)$–$P^+Ph_2CH_2]_2$ (**3**)*

To a solution of complex **1** (309.3 mg, 0.844 mmol) in *n*-hexane (150 mL), a solution of bis(diphenylphosphino)ethane (155 mg, 0.389 mmol) in *n*-hexane (50 mL) was added with stirring. The reaction mixture was stirred for 2 h at room temperature. The orange precipitate formed was filtered off, washed with *n*-hexane, and dried by an argon stream to yield complex **5e** (423.5 mg, 96% based on dppe). Found (%): C, 73.91; H, 4.54; P, 5.24. $C_{70}H_{54}Mn_2O_4P_2$. Calculated (%): C, 74.34; H, 4.81; P, 5.48. IR, ν/cm^{-1} (CH_2Cl_2): 1892s, 1820s (CO). ^{1}H NMR (C_6D_6), δ: 3.54 (s, 4H, CH_2), 4.22 (s, 10H, Cp), 7.0–8.02 (m, 40H, Ph). ^{31}P NMR (C_6D_6), δ: 17.72 (s).

*4.2.6. Synthesis of (η^5-C_5H_5)$(CO)_2Mn^-$–$C(P^+Ph_2Me)$=C=C(H)Ph (**8**)*

To a cooled (−70 °C) solution of the ethoxystyrylcarbene complex (η^5-C_5H_5)$Mn(CO)_2$=C(OEt)–(H)C=C(H)Ph (145.6 mg, 0.45 mmol), 1 M BCl_3 in *n*-hexane (1.13 mL, 1.12 mmol) was added dropwise with vigorous stirring. (The mixture became lighter and an orange precipitate formed.) The resulted mixture was stirred for 3 h at −50 °C and then triethylamine (1.5 mL, 10.76 mmol) was added (the mixture darkened immediately and gained a dark-brown color; the IR spectrum displayed the absorption bands ν_{CO} 1994, 1940, $\nu_{C=C=C}$ 1904 that correspond to the allenylidene complex **7**). When the temperature rose to −20 °C, degassed water was added and the mixture was stirred for additional 20 min. The aqueous layer was separated and the organic layer was washed twice with degassed water and dried over $MgSO_4$. After filtration, methyldiphenylphosphine (0.084 mL, 0.45 mmol) was added. The mixture was stirred for 1 h. The yellow precipitate formed was filtered off, washed twice with *n*-hexane, and dried *in vacuo* to yield complex **8** (60 mg, 27%). IR, ν/cm^{-1} (*n*-hexane): 1894s, 1824s (CO).

4.3. Protonation of the manganese 1-phosphonioallenyl complexes

*4.3.1. [(η^5-C_5H_5)$(CO)_2Mn$\{η^2-$CH(P^+Ph_2Me)$=C=CPh_2\}]BF_4^- (**4a**)*

To a cooled (−70 °C) solution of complex **2a** (113 mg, 0.2 mmol) in dichloromethane (4 mL), $HBF_4 \cdot OEt_2$ (0.03 mL, 0.220 mmol) was added with stirring. The reaction mixture was stirred for 30 min on cooling (dry-ice/ethanol bath) and then diethyl ether (20 mL) was added. The precipitate formed was filtered off, washed with diethyl ether, dried by an argon stream, and chromatographed on a silica gel column at −20 to −40 °C. The light-yellow fraction was eluted with a CH_2Cl_2–acetone (10:1) mixture. After concentration of the eluate and reprecipitation with diethyl ether, complex **4a** (96.2 mg, 74 %) was obtained as a yellow powder. Found (%): C, 64.24; H, 4.46; P, 4.48. $C_{35}H_{29}BF_4MnO_2P$. Calculated (%): C, 64.25; H, 4.47; P, 4.73. IR, ν/cm^{-1} (CH_2Cl_2): 2002s, 1950s (CO). ^{1}H NMR (acetone-d_6), δ: 2.08 (d, 3H, $J_{PH} = 13.7$ Hz, Me), 4.16 (d, 1H, $J_{PH} = 6.7$ Hz, =CH), 5.10 (s, 5H, Cp), 7.08–7.87 (m, 20H, Ph). ^{31}P NMR (acetone-d_6) δ: 27,04 (s). MS (ESI), *m*/*z*: 566.866.

*4.3.2. [(η^5-C_5H_5)$(CO)_2Mn$\{η^2-$CH(P^+PhMe_2)$=C=CPh_2\}]BF_4^- (**4b**)*

To a cooled (−70 °C) solution of HBF_4 (0.066, 0.480 mmol) in Et_2O (10 mL), complex **2b** (69 mg, 0.137 mmol) was added. The reaction mixture was stirred until the temperature rose to 25 °C. The precipitate formed was filtered off, washed with diethyl ether, and dried by an argon stream to yield complex **4b** (55.3 mg, 68 %) as a yellow powder. IR, ν/cm^{-1} (CH_2Cl_2): 2000s, 1950s (CO). ^{1}H NMR (acetone-d_6), δ: 1.70 (br.s, 6H, Me), 3.71 (br.s, 1H, =CH), 4.98 (br.s, 5H, Cp), 7.00–8.00 (m, 15H, Ph). ^{31}P NMR (acetone-d_6), δ: 29.95 (s).

*4.3.3. [(η^5-C_5H_5)$(CO)_2Mn$\{η^2-$CH(P^+Me_3)$=C=CPh_2\}]BF_4^- (**4c**)*

To a cooled (−70 °C) solution of complex **1** (183 mg, 0.5 mmol) in dichloromethane (10 mL), a solution of trimethylphosphine in diethyl ether (0.092 M, $c = 7$ mg/mL, 6 mL, 0.55 mmol) was added with stirring. The mixture was warmed slowly. At −30 °C, a violet color disappeared and the IR spectrum displayed the absorption bands of complex **2c** (1898s, 1828s (CO)). $HBF_4 \cdot OEt_2$ (0.16 mL, mmol) was added to the resulted mixture at −30 °C and the mixture was stirred on cooling (dry-ice/ethanol bath) for 20 min. Then diethyl ether (30 mL) was added. The yellow precipitate formed was filtered off and chromatographed on a silica gel column at −40 to 20 °C. The light-yellow fraction was eluted with a CH_2Cl_2–acetone (1:10) mixture. After evaporation and reprecipitation with diethyl ether, complex **4c** (156 mg, 59 %) was obtained as a yellow powder. Found (%): C, 56.41; H, 4.71. $C_{25}H_{25}BF_4MnO_2P$. Calculated (%): C, 56.64; H, 4.75. IR, ν/cm^{-1}: 2000s, 1950s (CO). ^{1}H (acetone-d_6), δ: 1.58 (d, 9H, $J_{PH} = 13.6$ Hz, Me), 3.42 (br.s, 1H, =CH), 5.07 (s, 5H, Cp), 7.26–7.66 (m, 10H, Ph). ^{13}C NMR (acetone-d_6), δ: 2.88 (d, $^1J_{PC} = 76.0$ Hz, Me), 9.30 (d, $^1J_{PC} = 55.6$ Hz, =CHP), 86.96 (s, C=*C*=CPh_2), 89.11 (s, Cp), 127.41, 127.48, 128.36, 128.40, 128.56, 129.78 (s, Ph), 141.35 (d, $^2J_{PC} = 7.4$ Hz, =*C*=CPh_2), 141.35 (d, $^3J_{PC} = 3.3$ Hz, =CPh_2), 157.98 (d, $^3J_{PC} = 5.7$ Hz), 227.93 (s, CO), 233.70 (s, CO). ^{31}P NMR (acetone-d_6), δ: 33.99 (s).

*4.3.4. [(η^5-C_5H_5)$Mn(CO)_2$–$PPh_2CH_2P^+Ph_2$–$C(H)$=C=CPh_2]BF_4^- (**6**)*

To a cooled (−70 °C) solution of complex **2d** (75.4 mg, 0.1 mmol) in dichloromethane (2 mL), $HBF_4 \cdot OEt_2$ (0.023 mL, 0.167 mmol) was added with stirring. The reaction mixture was stirred on cooling (dry-ice/ethanol bath) for 30 min and then diethyl ether (15 mL) and *n*-hexane (10 mL) were added subsequently. The dark-yellow crystalline precipitate was filtered off, washed with diethyl ether, and dried by an argon stream to yield complex **6** (75 mg, 89%). IR, ν/cm^{-1} (CH_2Cl_2): 1940s, 1866s (CO). ^{1}H NMR (acetone-d_6), δ: 4.28 (s, 5H, Cp), 4.80 (dd, 2H, $J_{P1,H} = 7.8$ Hz, $J_{P2,H} = 15.9$ Hz, CH_2), 6.79 (d, 1H, $J_{PH} = 10.3$ Hz, =CH), 6.84–7.80 (m, 30H, Ph). ^{31}P NMR (acetone-d_6), δ: 18.33 (s, 1P, $P^+Ph_2CH_2$), 84.82 (s, 1P, P–Mn).

*4.3.5. [{(η^5-C_5H_5)$Mn(CO)_2$(η^2-Ph_2C=C=$C(H)P^+Ph_2CH_2$)}$_2$]$(BF_4^-)_2$ (**5**)*

To a cooled (−70 °C) solution of complex **3** (250 mg, 0.221 mmol) in dichloromethane (8 mL), $HBF_4 \cdot OEt_2$ (0.037 mL,

0.265 mmol) was added with stirring. The reaction mixture was stirred on cooling (dry-ice/ethanol bath) for 30 min and then diethyl ether (5 mL) and *n*-hexane (20 mL) were added. The precipitate formed was filtered off, washed with diethyl ether, dissolved in dichloromethane (1 mL), and chromatographed on a silica gel column at −20 to −40 °C. The light-yellow fraction was eluted with a CH_2Cl_2–acetone (10:1) mixture. After concentration of the eluate *in vacuo* and reprecipitation with diethyl ether, complex **5** (165.1 mg, 57%) was obtained as a yellow powder. Found (%): C, 64.81; H, 4.29; Mn, 8.40; P, 4.81. $C_{70}H_{56}B_2F_8Mn_2O_4P_2$. Calculated (%): C, 64.35; H, 4.32; Mn, 8.41; P, 4.74. IR, ν/cm^{-1} (CH_2Cl_2): 2002s, 1950s (CO). ^{1}H NMR (acetone-d_6), δ: 2.8–3.0 (CH_2, overlapped with the H_2O signals), 3.95 (m, 2H, $J_{PH} = 4.20$ Hz, =CH), 4.93 (s, 10H, Cp), 6.92–8.20 (m, 40H, Ph). ^{31}P NMR (acetone-d_6), δ: 35.10 (s).

4.3.6. $[(\eta^5\text{-}C_5H_5)(CO)_2Mn\{\eta^2\text{-}CH(P^+Ph_2Me)=C=C(H)Ph\}]BF_4^-$ (**9**)

To a cooled (−70 °C) solution of complex **8** (60 mg, 0.12 mmol) in dichloromethane (4 mL), $HBF_4 \cdot OEt_2$ (0.028 mL, 0.2 mmol) was added with stirring. The reaction mixture was stirred on cooling (dry-ice/ethanol bath) for 30 min and then diethyl ether (20 mL) was added. The precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo* to yield complex **9** (62 mg, 89%). IR, ν/cm^{-1} (CH_2Cl_2): 2000 (v.s, CO), 1950 (v.s, CO).

4.4. X-ray crystal structure determination of compounds **6** and **9**

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX2 CCD area detector diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å, ω-scans) at 100 K. Low temperature of the crystals was maintained with a Cobra (Oxford Cryosystems) N_2 gas cryostat. Reflection intensities were integrated using the SAINT software [22,23] and semi-empirical method SADABS [24]. The structures were solved by the direct method and refined by the full-matrix least-squares against F^2 in the anisotropic (for non-hydrogen atoms) approximation. All H(C) atoms were placed in the geometrically calculated positions and refined in isotropic approximation in riding model with Uiso(H) parameters equal to 1.2 Ueq(Ci) for CH and CH_2 groups and 1.5 Ueq(Cii), where U(Ci) and U(Cii) are, respectively, the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed on an IBM PC/AT using the SHELXTL software [25]. The crystallographic details are given in Table 1.

Table 1
Crystallographic details for **6** and **9**.

Compound	**6**	**9**
Chemical formula	$C_{47}H_{38}BF_4MnO_2P_2$	$C_{29}H_{25}BF_4MnO_2P$
Formula weight	838.46	578.21
Crystal system	Triclinic	Monoclinic
Space group	P −1 (no. 2)	P 2(1)/c (no. 14)
Crystal color and shape	Dark-yellow, prism	Yellow, prism
Crystal size	0.21 × 0.16 × 0.14	0.31 × 0.28 × 0.14
a (Å)	10.6943(5)	10.146(3)
b (Å)	13.4105(7)	16.387(3)
c (Å)	15.2331(8)	16.272(3)
α (°)	98.5720(10)	90.00
β (°)	110.0960(10)	97.619(11)
γ (°)	94.1250(10)	90.00
V (Å^3)	2010.83(18)	2681.4(10)
Z	2	4
T (K)	100	100
Dc (g cm^{-3})	1.385	1.432
μ (mm^{-1})	0.466	0.605
Scan range (°)	$1.91 < \theta < 28.0$	$1.77 < \theta < 30.3$
Unique reflections	9710	7839
Reflections used $\|I > 2\sigma(I)\|$	6683	6363
R_{int}	0.0578	0.0258
Final *R* indices $\|I > 2\sigma(I)\|$	0.0456, w$R_2 = 0.0972$	0.0372, w$R_2 = 0.0719$
R indices (all data)	0.0794, w$R_2 = 0.1106$	0.0508, w$R_2 = 0.0770$
Goodness-of-fit	0.984	1.011
Max, Min $\Delta\rho/e$ (Å^{-3})	0.500, −0.402	0.641, −0.475

Acknowledgments

Financial support from the Russian Foundation for Basic Research (Grants No. 08-03-00846 and 11-03-00819) and from the Presidium of the Russian Academy of Sciences (Subprogram "Development of organic synthesis methodology and design of compounds with valuable applied properties") is gratefully acknowledged.

Appendix. Supplementary data

CCDC 830693 and 830694 contain the crystallographic data for compounds **6** and **9**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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[6] Complex 7 was generated in situ from the ethoxycarbene complex $Cp(CO)_2Mn{=}C(OEt){-}C(H){=}C(H)Ph$ in two steps: in the first step, addition of BCl_3 to the carbene complex results in the elimination of the ethoxy group to form the carbyne complex $[Cp(CO)_2Mn{\equiv}C{-}C(H){=}C(H)Ph]BCl_4$ (*cf.*, for example, E.O. Fischer, H.-J. Kalder, A. Frank, F.H. Köhler, G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 623); in the second step, deprotonation of the latter with Et_3N affords the allenylidene complex 7.

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