Chemistry of vinylidene complexes 15.* Transmetallation of μ -vinylidene MnPd complexes. Synthesis, X-ray diffraction analysis, and mass spectrometric study of the (η^5 -C₅H₅)MnFe₂(μ_3 -C=CHPh)(CO)₈ cluster^{**}

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The reaction of $Cp(CO)_2Mn=C=CHPh$ (1) with $Pd(PPh_3)_4$ followed by the replacement of the PPh₃ ligands by diphosphines $Ph_2P(CH_2)_2PPh_2$ (dppc) or $Ph_2P(CH_2)_3PPh_2$ (dppp) (where dppe is bis(diphenylphosphino)ethane and dppp is 1,3-bis(diphenylphosphino)propane) afforded the binuclear complexes $Cp(CO)_2MnPd(\mu-C=CHPh)(dppe)$ (2a) and $Cp(CO)_2MnPd(\mu-C=CHPh)(dppp)$ (2b), respectively. The reactions of 2a and 2b with $Fe_2(CO)_9$ gave the trinuclear complex $CpMnFe_2(\mu_3-C=CHPh)(CO)_8$ (3). Competitive transmetallation took the second pathway to yield clusters containing the $PdFe_3$ and $PdFe_2$ cores. Complex 3 was also formed in the thermal reaction of compound 1 with $Fe_2(CO)_9$. Complex 3 was studied by IR spectroscopy, ¹H and ¹³C NMR spectroscopy, massspectrometry, and X-ray diffraction analysis.

Key words: vinylidene complexes, heterometallic clusters, manganese, iron, palladium, mass spectrometry, X-ray diffraction analysis.

Heterometallic complexes containing the bridging vinylidene ligands μ_n -C=CRR' (n = 2-4; R and R' = H, alkyl, aryl, *etc.*) attract attention as models of catalytic systems and as starting compounds for the preparation of new polymetallic materials.^{2,3}

Over a period of years we performed systematic studies of processes of successive assembly of hetero-

metallic μ -vinylidene clusters from mononuclear (A) and binuclear (B) precursors (Scheme 1).²



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^{**} In this country, the chemistry of vinylidene complexes originated at the laboratory headed by K. N. Anisimov with the encouragement and active assistance of A. N. Nesmeyanov. At this laboratory, the acetylene-vinylidene rearrangement, which is presently a general procedure for the synthesis of vinylidene complexes of Groups IV-X transition metals, has been discovered, the ability of the metallaallenic M=C=C system to add the second metal atom has been found, and heterometallic µ-vinylidene complexes have been prepared for the first time. The development of this field of chemistry would be impossible without stimulating interest in vinylidene compounds expressed by Yu. T. Struchkov. At the laboratory headed by him, the structures of new complexes have been unambiguously established, and these investigations are being continued. The chemistry of vinylidene complexes has been further developed at the laboratory headed by A. A. loganson at the Krasnoyarsk Institute of Chemistry. The present work was dedicated to the blessed memory of these outstanding scientists

Starting from the phenylvinylidene derivative of cimanthrene, viz., $Cp(CO)_{2}Mn=C=CHPh$ (1),⁴ a series of complexes of type **B**, which contain the vinylidene bridge incorporated into the three-membered cyclic group $Mn-M'(\mu-C=CHPh)$ (where $M' = Mn.^{4.5}$ Re,⁶ Rh,⁷ Pd.⁸ or Pt⁹) were prepared. The general character of reaction *I* (Scheme 1) was confirmed by many examples of the addition of M'-containing species to the metalfaallenic M=C=C system (A) (M = Mn, Rh, or Os; M' = Cr, Mo, W, Fe, or Cu).^{2,3} Generally, complexes of type **B** are stable and are formed from complexes of type **A** in high yields. The exception is complex **6a**, which is spontaneously converted into the isomeric compound η^4 -[Cp(CO)₂MnC(CO)CHPh]Fe(CO)₃ (**6**) of the "trimethylenemethane type" (Scheme 2).¹⁰

Further metallation of binuclear MnPt complexes (reaction 2, Scheme 1) afforded trimetallic μ_3 -vinylidene complexes of types C (the MnFePt triangular core) and C' (the MnFePt chain).^{11,12} The chain of conversions $A \rightarrow B \rightarrow C$ was performed for complexes containing ligands, such as CO. PPh₃, phosphites, or dppm (dppm is bis(diphenylphosphino)methane), with M' = Pt atoms.

Transmetallation reactions in which the third M" metal atom replaces either the Mn atom (reaction 3, Scheme 1) or the M' atom (reaction 4) are more typical of MnM' complexes of type **B**. Thus the reaction of $Cp(CO)_2MnPt(\mu-C=CHPh)(P-P)$ (P-P = dppe¹³ or dppp, ¹⁴ where dppe is bis(diphenylphosphino)ethane and dppp is 1,3-bis(diphenylphosphino)propane) with $Fe_2(CO)_9$ afforded the (P-P)PtFe_3(μ_4 -C=CHPh)(CO)₉ clusters (reactions 3 and 5), whereas transmetallation of $Cp(CO)_2MnRh(\mu-C=CHPh)(Acac)(CO)$ under the action of $Fe_2(CO)_9^7$ took pathway 4 (see Scheme 1) to form MnFe complex **6**.

Several examples of transmetallation of μ -vinylidene complexes were reported in the literature.^{2,3} The formation of the tetranuclear CpFeCo₃(μ_4 -C=CH₂)(μ -CO)₂(CO)₇ cluster from [Cp(CO)Fe]₂(μ -C=CH₂)(μ -CO) and Co₂(CO)₈ involves the replacement of one of the Fe-containing fragments by the carbonylcobalt moiety.^{15,16} The ability of the μ_3 -vinylidene complexes FeCo₂(μ_3 -C=CHR)(CO)₉ to undergo transmetallation was used in the synthesis of the trimetallic clusters L_nMFeCo(μ_3 -C=CHR)(CO)₆ (M = Mo, W, or Ni; R = alkyl or Ph) and Cp₂Ni₂Fe(μ_3 -C=CHR)(CO)₃.^{17,18}

We chose palladium-containing complexes \mathbf{B} as objects of further studies devoted to the regularities of metallation and transmetallation processes.

Two competitive directions of transmetallation, viz., the replacement of Mn by Fe (reaction 3) and the replacement of Pd by Fe (reaction 4), were observed for the first time in the reaction of Cp(CO)₂MnPd(μ -C=CHPh)(dppe) (2a) with Fe₂(CO)₉ (see Schemes 1 and 2).¹⁹ In both cases, transmetallation is accompanied by the attachment of additional Fe-containing groups (reactions 5 and 6, respectively). Processes I, 3, and 5 result in the transfer of the vinylidene ligand from the Mn atom to the PdFe₃ cluster system to form $(dppe)PdFe_3(\mu_4-C=CHph)(CO)_9$ (4a).^{1,19} The predominating sequence of reactions 4 and 6 affords the CpMnFe₃(μ_3 -C=CHPh)(CO)₈ complex (3).

The behavior of complex 2a, which has no analogy in the chemistry of vinylidene complexes, raises a number of questions. It was of interest to find out how a change in the ligand environment about the Pd atom affects the direction of further conversions of MnPd complexes of type **B** as well as to examine the possibility of the synthesis of MnFe₂-containing complex **3** from **1** or **6** without participation of palladium compounds. The present work was devoted to elucidation of these questions. The structure and the properties of the CpMnFe₂(μ_3 -C=CHPh)(CO)₈ complex (**3**) have been briefly reported previously.^{1,19} In this work, the mass spectrum and the crystal and molecular structure of this complex are discussed in detail.

Results and Discussion

With the aim of revealing the effect of the nature of the ligands at the Pd atom on the direction of further conversions of complexes containing the Mn-Pd bond, we studied the reaction of $Cp(CO)_2MnPd(\mu$ -C=CHPh)(dppp) (2b) with $Fe_2(CO)_9$. The brown $CpMnFe_2(\mu_3-C=CHPh)(CO)_8$ complex (3) along with two new complexes, viz., the dark-green (dppp)PdFe_3(\mu_4- $C=CHPh)(CO)_9$ complex (4b) and the violet (dppp)PdFe_2(CO)_8 complex (5b), were isolated from a mixture of the reaction products by chromatography on a column with Al₂O₃ (Scheme 2). This reaction shows a general resemblance to the reaction of $Cp(CO)_2MnPd(\mu$ -C=CHPh)(dppe) (2a) with $Fe_2(CO)_9^{1.19}$ and gives products of the same three structural types.

The above-mentioned reactions differ in the ratio of the yields of the products. In the reaction of compound **2a** with Fe₂(CO)₉, the ratio between the yields of the PdFe₃ (**4a**) and MnFe₂ (**3**) clusters was at most 1 : 6 throughout the range of the variable conditions (the ratio of the initial reagents, the temperature, and the reaction time). In the reaction of complex **2b** with Fe₂(CO)₉, an increase in the temperature to 50–70 °C led to an increase in this ratio to 1 : 1.5, *i.e.*, reactions 3 and 4 (Scheme 1) became virtually equially probable. Whatever conditions were used, the yields of PdFe₂containing complexes **5a** and **5b** were low (<5%).

On the whole, it can be stated that the replacement of the dppe ligand by the more electron-donor dppp ligand results in the strengthening of the palladiummanganese and palladium-vinylidene bonds in the MnPd complex.

The compositions and structures of complexes 4b and 5b were established by elemental analysis and IR and NMR spectroscopy. A detailed comparison of the spectral parameters of complexes 4a and 5a with the characteristics of the (dppe)PtFe₃(μ_4 -C=CHPh)(CO)₉ and (dppe)PtFe₂(CO)₈ complexes, respectively, whose

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Scheme 2



structures have been established by X-ray diffraction analysis,¹³ led to the conclusion that the structures of the palladium complexes and of the corresponding platinum complexes are identical.¹ The fact that the region of stretching vibrations of the carbonyl groups in the IR spectrum of complex **4b** is very similar to that of complex **4a** as well as the fact that the spectra of complexes **5b** and **5a** are identical (see the Experimental section) provide convincing proof that the structures of the pair of homologs **4a** and **4b** as well as of the pair of compounds **5a** and **5b** are the same.

The CpMnFe₂(μ_3 -C=CHPh)(CO)₈ complex (3) was crystallized from hexane as brown needles stable under ambient conditions. Compound 3 was studied by X-ray diffraction analysis, IR spectroscopy. ¹H and ¹³C{¹H} NMR spectroscopy, and mass spectrometry.

of the CpMnFe₂(u₃-The IR spectrum $C=CHPh)(CO)_8$ complex (3) in C_6H_{12} has seven v(CO) bands in the region of 2073-1875 cm⁻¹, which is indicative of a low symmetry of the molecule. Two weak bands at 1913 and 1875 cm⁻¹ can be assigned to vibrations of the semibridging and bridging CO groups (see below). The frequency of the latter is close to the frequencies of the µ-CO groups in the spectra of the CpMnFePt(µ3u₃-phenylvinylidene complexes $C=CHPh)(CO)_6[\eta^1-Ph_2PCH_2P(=O)Ph_2]$ (7, 1870 cm⁻¹)¹² and $Fe_3(\mu_3-C=CHPh)(CO)_{10}$ (8, 1892 cm⁻¹).²⁰ In the $-CpMnFe_2(\mu_3 -$ 1Rspectrum of the HC≡CCOOMe)(CO)₈ complex (9).²¹ the frequencies of the bridging CO groups (1855 and 1820 cm⁻¹) are substantially lower due to the weaker electron-withdrawing effect of methyl propiolate compared to that of vinylidene.

The proton resonance of the =C<u>H</u>Ph group in the ¹H NMR spectrum of complex 3 is manifested as a low-field singlet at δ 7.85, which is typical of complexes with bridging vinylidene ligands.^{2,3}

In the ¹³C{¹H} NMR spectrum of compound **3**, signals for the C(1) and C(2) atoms are observed in the regions (at δ 306.18 and 97.01, respectively) typical of trinuclear complexes with μ_3 -C(1)=C(2)HR ligands (R = H or Ph).^{2,3} One singlet signal at δ 211.64 corresponds to the CO groups at the Fe atoms, and the signals at δ 232.86 and 237.04 correspond to the μ -CO groups. In the ¹³C{¹H} NMR spectrum of complex **8**, ten carbonyl groups give one broad singlet at δ 210.40.²⁰

It was of considerable interest to elucidate the question of whether the CpMnFe₂(μ_3 -C=CHPh)(CO)₈ cluster (3) can be prepared directly from Cp(CO)₂Mn=C=CHPh (1) by adding two carbonyliron fragments to the latter as well as from the η^4 -[Cp(CO)₂MnC(CO)CHPh]Fe(CO)₃ complex (6).

The existence of equilibrium between two isomeric forms. vic., "trimethylenemethane" form 6 and μ -vinylidene form 6a (see Scheme 2), in solutions of complex 6 gave impetus to a search for the possibility of the conversion of 6 into 3. The existence of this equilibrium is evidenced by the presence of several additional strong v(CO) bands in the 1R spectrum of a solution of complex 6 as well as by additional signals in the ¹H and ¹³C NMR spectra in the regions corresponding to the μ -C=CHPh and Cp ligands. However, attempts to synthesize compound 3 from complex 6 failed.

With the aim of converting complex 1 into compound 3, various carbonyliron complexes were examined. It appeared that complex 1 did not react with

 $Fe_3(CO)_{12}$. The reaction of complex 1 with $Fe(CO)_4(THF)$ in THF was terminated at the stage of formation of complex 6 and did not proceed further. The addition of catalytic amounts of Pd(PPh₃)₄ or $Cp(CO)_2MnPd(\mu-C=CHPh)(PPh_3)_2$ did not change the situation. We succeeded in preparing complex 3 in low yield only in the reaction of complex 1 with an excess of $Fe_2(CO)_9$ in boiling heptane (see the Experimental section).

Mass-spectrometric study of complex 3

The mass spectrum of the CpMnFe₂(μ_3 - $C=CHPh)(CO)_8$ complex (3) has a molecular ion peak M^+ at m/z 558. Further decomposition of this molecular ion upon electron impact occurs with successive elimination of eight CO groups to form the corresponding ions.

Elimination of the manganese atom and then the iron atom from the $[C_5H_5MnFe_2(C_8H_6)]^+$ ion with m/z334 affords ions with m/z 279 and 223, respectively. Further decomposition of the $[C_5H_5(C_8H_6)Fe_2]^{T}$ ion with m/z 279 proceeds with elimination of acetylene and then of the $[C_5H_5]$ fragment to form ions with m/z 253 and 188, respectively. Fragmentation of the $[C_5H_5Fe(C_8H_6)]^{\pm}$ ion with m/z 223 proceeds with elimination of either the $[C_5H_5]$ species or the $[C_8H_6]$ species to form ions with m/z 158 or 121, respectively.

The most intense peak in the spectrum of complex 3 belongs to the phenylvinylidene (or phenylacetylene) ion $[C_8H_6]^+$ with m/z 102 (100%). It should be noted that the spectrum has also an intense (92%) peak of the ferrocene ion $[(C_5H_5)_2Fe]^+$ with m/z 186 due, apparently, to thermal decomposition of the compound in the vicinity of the ionization chamber of the mass spectrometer.

X-ray diffraction study of $(\eta^5 - C_5 H_5) Mn Fe_2(\mu_3 - C = CHPh)(CO)_8$ (3)

The molecular structure of complex 3 is shown in Fig. 1. The principal geometric parameters are given in Tables 1 and 2. The structure of compound 3 was compared with the structures of the known complexes $CpMnFePt(\mu_3-C=CHPh)(CO)_6[\eta^1-Ph_2PCH_2P(=O)Ph_2]$ (7),¹² Fe₃(μ_3 -C=CHPh)(CO)₁₀ (8), 20and $(9)^{21}$ $(\eta^5 - C_5 H_5) Mn Fe_2(\mu_3 - HC = CCOOMe)(CO)_8$ (Scheme 3).

Two iron atoms and the manganese atom in complex 3 form an isosceles triangle (Mn(1)-Fe(1), 2.653(2) Å; Mn(1) = Fe(2), 2.669(2) Å; and Fe(1) = Fe(2), 2.569(2)Å). Recently, we have found¹² the similar Mn—Fe bond lengths (2.676 and 2.692 Å for two independent molecules) in complex 7 containing the Mn-Fe-Pt chain as the central fragment. Fe-Fe distances similar to the Fe(1)—Fe(2) distance in complex 3 were observed in



Fig. 1. Structure of the CpMnFe₂(μ_3 -C=CHPh)(CO)₈ complex (3): a, the overall view of the molecule; b, the projection onto the plane of the MnFe₂ triangle. The second position of the μ_2 -C=CHPh ligand is indicated by double lines.

Table 1. Principal bond lengths (d) in molecule 3

Table 2. Bond angles (w) in molecule 3

Bond	d/Λ	Bond	d/Λ
Fe(1)-Fe(2)	2.569(2)	Fe(1)-Mn(1)	2.653(2)
Fe(2) - C(9)	1.756(11)	Fe(2) - C(10)	1.775(10)
Fe(2)Mn(1)	2.669(2)	Mn(1) - C(1)	1.939(9)
Fe(1) - C(1)	1.877(11)	Mn(1) - C(3)	1.779(10)
Fe(1) - C(2')	2,45(2)	Mn(1) - C(4)	1.783(9)
Fe(1) - C(3)	2.444(12)	Mn(1) - C(Cp)	2.13(1) -
Fe(1) - C(5)	1.790(10)		2.17(1)
Fe(1) - C(6)	1.798(12)	C0	1.11(1)-
Fe(1) - C(7)	1.777(13)		1.15(1)
Fe(2) - C(1)	1.896(10)	C(1) - C(2)	1.26(2)
Fe(2) - C(2)	2.35(2)	C(1) - C(2')	1.35(2)
Fe(2) - C(4)	2.478(10)	C(2) = C(11)	1.51(2)
Fe(2) - C(8)	1.794(9)	C(2') - C(11')	1.44(3)

Angle	₀⁄deg	Angle	₀/deg
$\overline{Fe(2)-Fe(1)-Mn(1)}$	61.45(5)	Fe(1) - C(1) - Mn(1)	88.1(5)
Fe(1) - Fe(2) - Mn(1)	60.82(5)	Fe(2) = C(1) = Mn(1)	88.2(4)
Fe(1) - Mn(1) - Fe(2)	57.73(5)	C(1) - C(2) - C(11)	134(2)
C(1) - Fe(1) - Fe(2)	47.4(3)	C(1)-C(2')-C(11')	135(2)
C(1) - Fe(1) - Mn(1)	46.9(3)	C(3) - Fe(1) - Mn(1)	40.6(2)
C(1) - Fe(2) - Fe(1)	46.8(3)	C(4) - Fe(2) - Mn(1)	40.3(2)
C(1) - Fe(2) - Mn(1)	46.6(3)	C(3) - Mn(1) - Fe(1)	63.4(4)
C(1) - Mn(1) - Fe(1)	. 45.0(3)	C(4) - Mn(1) - Fe(2)	64.1(3)
C(1) - Mn(1) - Fe(2)	45.3(3)	O(3) - C(3) - Mn(1)	163.7(12)
C(2) - C(1) - Fe(1)	134.4(9)	O(3) - C(3) - Fe(1)	120.3(10)
C(2') = C(1) = Fe(1)	97.4(9)	Mn(1) - C(3) - Fe(1)	76.0(4)
C(2) - C(1) - Fe(2)	93.9(10)	O(4) - C(4) - Mn(1)	164.6(9)
C(2') - C(1) - Fe(2)	133.5(9)	O(4) - C(4) - Fe(2)	119.7(7)
Fe(1) = C(1) = Fe(2)	85.8(4)	Mn(1) - C(4) - Fe(2)	75.6(3)
$C(2) \rightarrow C(1) \rightarrow Mn(1)$	137.5(10)	O-C-Fe	177(1)-
$C(2^{+})-C(1)-Mn(1)$	138.1(9)		179(2)

 μ_3 -vinylidene complex **8** (2.597, 2.584, and 2.562 Å).²⁰ In the complex with the methyl propiolate ligand **9**,²¹ both Mn—Fe bond lengths (2.561 and 2.577 Å) are -0.1 Å smaller than those in molecule **3**, and, on the contrary, the Fe—Fe bond length (2.679 Å) is -0.1 Å larger.

Scheme 3



The phenylvinylidene ligand C=CHPh in molecule 3 is located above the MnFe₂ triangle and is disordered over two positions with equal occupancies, *viz.*, C(2)-C(11)...C(16) and C(2')-C(11')...C(16') (the latter is indicated by double lines in Fig. 1). Hence, molecule 3 in the crystal can be considered as a superposition of two molecules. In the first of them, the vinylidene fragment

forms σ -bonds with the Mn(1) and Fe(1) atoms and a π -bond with the Fe(2) atom, whereas this fragment in the second molecule forms σ -bonds with the Mn(1) and Fe(2) atoms and a π -bond with the Fe(1) atom (Mn(1)-C(1), 1.939(9) Å; Fe(1)-C(1), 1.877(11) Å; Fe(2)-C(1), 1.896(10) Å; Fe(1)-C(2'), 2.45(2) Å; and Fe(2)-C(2), 2.35(2) Å).

The Mn–C(1) σ -bond length in compound 3 is close to the length of the corresponding bond in complex 7¹² (1.95 and 1.96 Å for two independent molecules). Similar Fe–C(1) σ -bond lengths were observed in complex 8 (1.92 and 1.91 Å).²⁰

A distinguishing feature of the structure of complex 3 is that the interaction of the metal atom, which is η^2 -coordinated by the C(1)=C(2) bond of the vinylidene ligand, with the C(2) atom is substantially weaker than the interaction with the C(1) atom (the average difference between the Fe-C(1) and Fe-C(2) distances is 0.5 Å). In other μ_3 -vinylidene complexes, the η^2 -bonding is more symmetrical. For example, in complex 8²⁰ as well as in the ruthenium complex Ru₃(μ_3 -C=CHPh)(μ -H)₂(CO)₉, which have been studied recently,²² the differences between the corresponding distances are 0.22 and 0.25 Å, respectively.

The lengths of the C(1)=C(2) double bond in two molecules 3 (1.26(2) and 1.35(2) Å) are somewhat smaller than the usual bond lengths in μ_3 -vinylidene complexes (1.37-1.43 Å).^{2,3} In complexes 7¹² and 8,²⁰ the C(1)=C(2) bond lengths are typical of this mode of coordination of the vinylidene ligand (1.42 and 1.38 Å, respectively).

In complex 3, the angle between the plane of the phenyl substituent and the plane passing through the C(1), C(2), and C(11) atoms is 40° (for the second orientation of the phenylvinylidene ligand, this angle is 34°).

Each iron atom in complex 3 is coordinated by three terminal CO ligands. Both carbonyl groups (C(3)O(3))

and C(4)O(4)) at the manganese atom act as semibridging ligands. The Mn-CO distances (the average value is 1.78(1) Å) are substantially shorter than the Fe-CO distances (Fe(1)...C(3) and Fe(2)...C(4) are 2.44(1) and 2.48(1) Å, respectively). The Mn(1)-C(3)-O(3) and Mn(1)-C(4)-O(4) bond angles are 164(1) and 165(1)°, respectively.

Apparently, the presence of two semibridging CO groups (instead of one bridging group and one semibridging group according to the requirements of the electroneutrality of the complex) in molecule **3** is a consequence of a superposition of two molecules containing the phenylvinylidene ligand in different orientations. Attempts to reveal the disordered positions of these carbonyl groups in the course of structure refinement failed.

The parameters of the bond between the Cp ring and the Mn atom are typical of cimanthrene derivatives. The distance from the Mn(1) atom to the centroid of the C(17)-C(21) ring is 1.79 Å. The angle between the plane of the MnFe₂ triangle and the plane of the C(17)-C(21) ring is 63°.

Therefore, a new type of the chemical behavior of complexes **B** (two competitive pathways of transmetallation are realized) is observed in the reactions of the CpMnPd(μ -C=CHPh)(CO)₂(P-P) compounds (P-P = dppe (2a) or dppp (2b)) with Fe₂(CO)₉. In the first pathway, the vinylidene ligand retains the bond with the Mn atom, whereas in the second pathway the bond with the Pd atom is retained. The replacement of the dppe ligand by the more electron-donor dppp ligand results in the strengthening of the Mn-Pd and Pd-vinylidene bonds, which is reflected in the ratio between the contributions of the competitive processes but does not change the overall picture of the reaction.

Apparently, the mechanism of formation of the CpMnFe₂(μ_3 -C=CHPh)(CO)₈ complex is more complicated than that represented by the formal sequence of reactions *I*, *4*, and *6* in Scheme 1. Even under severe conditions, complex **3** is formed from compound **1** and Fe₂(CO)₉ in low yield and is not formed from compound **6**, which indicates that palladium plays a specific role in the synthesis of this compound. The unusual behavior of palladium-containing complexes **B** in processes of the block synthesis of clusters is still not completely understood and calls for further investigation.

Experimental

All operations were carried out under an argon atmosphere. Anhydrous solvents saturated with argon were used. $Cp(CO)_2MnPd(\mu-C=CHPh)(dppe)$ The (2a)and $Cp(CO)_{3}MnPd(\mu-C=CHPh)(dppp)$ (2b) complexes were prepared by the reactions of $Cp(CO)_2MnPd(\mu-C=CHPh)(PPh_3)_2$ with dppe and dppp, respectively, according to a procedure reported previously.¹ The synthesis and the characteristics of $(dppe)PdFe_3(\mu_4-C=CHPh)(CO)_9$ the (4a) and (dppe)PdFe₂(CO)₈ (5a) complexes have been described previously.¹ Chromatography was performed with the use of neutral aluminum oxide (Brockman II). The course of the reaction was monitored by TLC on Silufol plates.

The 1R spectra were recorded on a Specord IR-75 instrument. The ¹H (400.13 MHz), ¹³C{¹H} (100.61 MHz), and ³¹P{¹H} (161.98 MHz) NMR spectra were measured on a Bruker AMX-400 spectrometer. The mass spectra were obtained on an MS-890 instrument (KRATOS); the ionizing voltage was 70 V; the temperature of the inlet system was 150 °C.

The reaction of η^5 -cyclopentadienyldicarbonyl(μ^2 -(phenyl)ethenvlidene)bis(diphenvlphosphinopropane)manganesepalladium, $Cp(CO)_2MnPd(\mu-C=CHPh)dppp$ (2b), with nonacarbonyldiiron, Fe2(CO)9. Fe2(CO)9 (2.565 g, 7.05 mmol) was added to a solution of compound 2b (0.935 g, 1.17 mmol) in benzene (40 mL). The reaction mixture was heated with stirring at 70 °C for 30 min, filtered through an -0.5-cm Al₃O₃ layer, and concentrated in vacuo. The oily residue was dissolved in a 1:1 hexane-benzene mixture (5 mL) and chromatographed on a column with Al₂O₃. The vellow fraction containing dppp and CpMn(CO)₃ was eluted with a 3 : 1 hexane-benzene mixture. Then the brown (hexane-benzene, 3 : 1), violet (hexanebenzene, 1 : 1), and green (hexane-benzene, 1 : 3) fractions were successively eluted. After removal of the solvent and recrystallization from hexane, brown crystals of CpMnFe2(µ3- $C=CHPh)(CO)_8$ (3) were obtained from the brown zone in a yield of 0.350 g (53%). Found (%): C, 40.91; H, 1.84; Mn. 9.85; Fe, 20.02. C₁₉H₁₀Fe₂MnO₆. Calculated (%): C, 40.86; H. 1.79; Mn. 9.86; Fe. 20.07. IR (C_6H_{12}), v/cm⁻¹: 2073 s, 2032 v.s. 2010 s. 1995 m. 1973 m, 1913 w, 1875 w (CO). ¹H NMR ((CD₃)₂CO), δ: 5.68 (s, 5 H, C₅H₅); 7.74 (t, 1 H, p-H, $C_{b}H_{5}$, $J_{HH} = 7.6$ Hz); 7.85 (t, 2 H, m-H, $C_{6}H_{5}$, $J_{HH} =$ 6.8 Hz); 7.86 (s, 1 H. C=C<u>H</u>C₆H₅); 8.19 (d, 2 H, o-H, C₆H₅, $J_{\rm HH} = 7.6$ Hz). ¹³C{¹H} NMR ((CD₃)₂CO), δ : 91.79 (s. C_5H_5 ; 97.01 (s, C=C(2)HC₆H₅); 127.80, 128.51, and 129.31 (all s. p-C, m-C, and o-C, C₆H₅); 143.42 (s. ipso-C, C₆H₅); 211.64 (s, Fe+CO); 232.86 and 237.04 (both s, µ-CO); 306.18 (s. $\underline{C}(1) = CHC_6H_5$). MS (E1, 70 eV), m/z (I_{rel} (%)): 558 [M]⁺ (0.3), 530 $[M - CO]^+$ (0.1), 502 $[M - 2 CO]^+$ (0.3), 474 $[M - 3 CO]^+$ (0.1), 446 $[M - 4 CO]^+$ (0.2), 418 [M - $5 \text{ CO}^+(2.4)$, 390 [M - 6 CO]⁺(2.4), 362 [M - 7 CO]⁺(1.4), 334 $[M - 8 CO]^{+} = [C_5H_5Mn(C_8H_6)Fe_2]^{+}$ (3.4), 279 $[C_5H_5Fe_2C_8H_6]^{+}$ (2.4), 253 $[C_5H_5(C_6H_4)Fe_2]^{+}$ (0.6), 223 $[C_5H_5FeC_3H_6]^+$ (4.1), 188 $[(C_6H_4)Fe_2]^+$ (1.2), 158 $[FeC_8H_6]^+$ $(2.1), 121 [C_5H_5Fe]^+ (24.1), 102 [C_8H_6]^+ (100.0).$

The violet zone was concentrated to 2 mL. After reprecipitation with hexane, the violet complex (1,1,1,1,2,2,2,2-octacarbonyl)-[3-n²-bis(diphenylphosphino)propane-*PP'*]-*triangulo*diironpalladium(*2Fe*-*Pd*,*Fe*-*Fe*), (dppp)PdFe₂(CO)₈ (**5b**), was obtained in a yield of 0.005 g (<1%). Compound **5b** was identified by IR spectroscopy (CH₂Cl₂), v/cm⁻¹: 2049 s, 2000 v.s. 1964 s, 1945 sh, 1885 w.br (CO). (IR of (dppe)PdFe₂(CO)₈ (**5a**), v/cm⁻¹: 2052 s, 2002 v.s, 1969 s, 1955 s, 1909 w.br (CO).¹)

After reprecipitation with hexane, dark-green crystals of (1,1,1,2,2,2,3,3,3-nonacarbonyl)- μ_{4} - $(1-\eta^2,2,3,4-\eta^1-(phenyl)-ethenylidenc]-[4-\eta^2-bis(diphenylphosphino)propane-$ *PP'*]-bis(*triangulo*)-triironpalladium(*2Fe-Pd,2Fe-Fe,Fe-Fe* $), (dppp)PdFe₃(<math>\mu_4$ -C=CHPh)(CO)₉ (**4b**), were obtained in a yield of 0.339 g (28%). Found (%): C, 50.23; H, 2.99; P, 6.02, C₄₄H₃₂Fe₃O₉P₂Pd, Calculated (%): C, 50.77; H, 3.08; P, 5.96. IR (CH₂Cl₂), v/cm⁻¹: 2050 s, 1998 sh, 1989 s, 1933 w.br (CO). (1R of (dppe)PdFe₃(μ_4 -C=CHPh)(CO)₉ (**4a**) (CH₂Cl₂), v/cm⁻¹: 2049 s, 2002 sh, 1988 s, 1929 w.br (CO).¹). ³¹P(¹H) NMR (CD₂Cl₁), δ : -4.23 (d, 1 P, ⁴J_{PP} = 158 Hz); -2.08 (d, 1 P, ⁴J_{PP} = 158 Hz).

The reaction of $(\eta^5$ -cyclopentadienyldicarbonyl(phenyl)ethenylidene)manganese, $Cp(CO)_2Mn=C=CHPh$ (1), with **Fe₂(CO)**₉. Compound 1 (0.200 g, 0.72 mmol) and Fe₂(CO)₉ (0.968 g, 2.66 mmol) were mixed with heptane (20 mL), which was warmed to 50 °C. The reaction mixture was refluxed with stirring for 1 h and then filtered. The filtrate was chromatographed on a column with Al₂O₃. The yellow zone containing CpMn(CO)₅ (0.039 g, 20%) and two yellow-green zones containing small amounts of unidentified products were successively eluted with a 5 : 1 hexane—benzene mixture. Then the brown zone was eluted with a 3 : 1 hexane—benzene mixture. The latter was concentrated. After recrystallization from hexane, brown crystals were obtained in a yield of 0.040 g (10%). These crystals were identified as CpMnFe₂(μ_3 -C=CHPh)(CO)₈ (3) based on the IR spectral data.

X-ray diffraction study of the complex (1,1,2,2,2,3,3,3)octacarbonyl)- $(1-\eta^5$ -cyclopentadienyl)- μ_3 - $[1,2-\eta^1,3-\eta^2$ -(phenyl)ethenylidene]-*triangulo*-manganesediiron(2Fe-Mn,Fe-Fe) (3). Black needle-like crystals of CpMnFe₂(μ_3 -C=CHPh)(CO)₈ obtained by crystallization from CCl₄ as well as from CCl₄-hexane (1 : 1) or pentane-ether-dioxane (5 : 4 : 1) mixtures were identical. A well-faceted single crystal obtained from a CCl₄-hexane mixture was chosen for X-ray diffraction study.

Crystals of C₂₁H₁₁O₅FeMn₂ (M = 557.94) are orthorhombic, at 20 °C a = 13.492(4), b = 15.110(7), c = 10.309(4) Å, V = 2102(2) Å³, space group *Pna*2₁, Z = 4, $d_{calc} = 1.763$ g cm⁻³.

Intensities of 2338 independent reflections were measured on an automated Siemens P3/PC diffractometer at 20 °C (λ Mo-K α radiation, graphite monochromator, $\theta_{max} = 28^\circ$). Absorption was ignored (μ (Mo-K α) = 20.0 cm⁻¹). The structure was solved by the direct method. The coordinates and anisotropic thermal parameters of all nonhydrogen atoms (except for the carbon atoms of the disordered fragment, which were refined isotropically) were refined by the least-squares method based on F_{hkl}^2 . The hydrogen atoms were placed in calculated positions and refined using the riding model.

The final values of the *R* factors were as follows: $R_1 = 0.048$ (calculated based on F_{hk1} using 1423 reflections with $l \ge 2\sigma(l)$), $wR_2 = 0.1355$ based on F^2_{hk1} for all 2285 reflections used at the final stage of the refinement. All calculations were performed on a PC with the use of the SHELXTL PLUS 5 program package.²³

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