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Chemistry of vinylidene complexes. XIII. The reaction between $Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(\eta^2\text{-dppm})$ and $Fe_2(CO)_9$: simultaneous formation of the μ_3-vinylidene MnFePt and μ_4-vinylidene $PtFe_3$ clusters. Crystal structure of $(\eta^5\text{-}C_5H_5)MnFePt(\mu_3\text{-}C{=}CHPh)(CO)_6[\eta^1\text{-}Ph_2PCH_2P({=}O)Ph_2]$[☆,☆☆]

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Abstract

The reaction between $[Cp(CO)_2MnPt(\mu\text{-}C{=}CHPh)(\eta^2\text{-dppm})]$[1] (**1**) and $[Fe_2(CO)_9]$ gives heterometallic MnFePt and $PtFe_3$ vinylidene clusters **2**–**4**, in which diphosphine ligands are coordinated to metal cores in three different modes. In $[(\eta^2\text{-dppm})PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9]$ (**2**) the Pt atom is chelated by dppm while in $[CpMnFePt(\mu_3\text{-}C{=}CHPh)(\mu\text{-dppm})(CO)_5]$ (**3**) dppm bridges the Pt–Fe bond. Complex **3** was shown to exist in two isomeric forms. The novel complex $\{CpMnFePt(\mu_3\text{-}C{=}CHPh)(CO)_6[\eta^1\text{-}Ph_2PCH_2P({=}O)Ph_2]\}$ (**4**), characterized by X-ray diffraction study, possesses a trimetallic chain core. The diphosphine ligand in **4** links to platinum by only one of phosphorus atoms whereas the second P atom is uncoordinated and oxidized to the phosphineoxide group. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vinylidene complexes; Manganese; Iron; Platinum; Clusters; X-ray diffraction

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1. Introduction

Tens of heterometallic clusters containing M_2M', $MM'M''$, M_3M' cores and μ_3- or μ_4-vinylidene $C{=}CRR'$ have been described up to the present [2,3]. Most of them were synthesized by transformations of unsaturated organic ligands, more often $\mu\text{-}C{\equiv}CR$ or $\mu\text{-}HC{\equiv}CR$, linked to the already formed framework and only a few were prepared from metalvinylidene precursors (see, for instance [4–6]).

We have recently demonstrated for the first time [7] that μ_3-vinylidene clusters of the **C** type may be prepared by the consecutive assembling of the $MM'M''$ core starting from the mononuclear vinylidene complex **A** (Scheme 1).

The addition of the carbenoide $[PtL_2]$ units ($L = PPh_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OPh)_3$) to $[Cp(CO)_2\text{-}Mn{=}C{=}CHPh]$ (**A**) results in the formation of bimetallic

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[☆] For part XII see [1].

[☆☆] Dedicated to the memory of Professor Yury T. Struchkov. Deceased August 16, 1995.

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[✠] This study was started in the laboratory of Professor Alfred A. Johansson with his active participation. He passed away untimely on December 2, 1996.

[1] $Dppm = Ph_2PCH_2PPh_2$; $dppe = Ph_2PCH_2CH_2PPh_2$; $dppp = Ph_2PCH_2CH_2CH_2PPh_2$.

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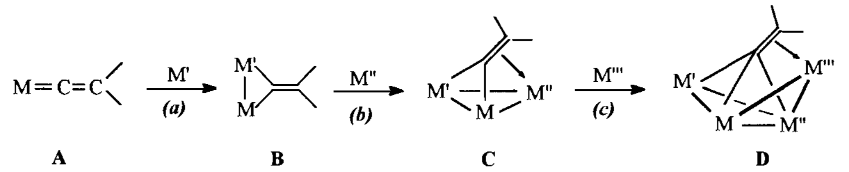


Scheme 1.

complexes [Cp(CO)$_2$MnPt(μ-C=CHPh)L$_2$] (**B**) [8], which react further with [Fe$_2$(CO)$_9$] to give a series of trimetallic clusters [CpMnFePt(μ$_3$-C=CHPh)(CO)$_6$L] (**C**) [7]. In the case of L=PPh$_3$, the (a) and (b) reactions proceed in quantitative yields. On the contrary, the action of [Fe$_2$(CO)$_9$] on [Cp(CO)$_2$MnPt(μ-C=CHPh)(η^2-$\widehat{PP}$)], where $\widehat{PP}$ = dppe, dppp [9], gives only transmetallation products, [(η^2-dppe)PtFe$_3$(μ$_4$-C=CHPh)(CO)$_9$] (**5**) (crystallographically characterized) [10] and [(η^2-dppp)PtFe$_3$(μ^4-C=CHPh)(CO)$_9$] (**6**) [1], having the **D** structure of the central fragments.

2. Results and discussion

Developing vinylidene complexes chemistry, we carried out the reaction of complex **1** [9] and [Fe$_2$(CO)$_9$]. The tetranuclear PtFe$_3$ cluster **2** and trinuclear MnFePt complexes **3** and **4** were isolated from the reaction mixture (Scheme 2).

The structures proposed for compounds **2** and **3** are based on the interpretation of the IR and NMR spectra. The principal spectral characteristics of [(η^2-dppm)PtFe$_3$(μ$_4$-C=CHPh)(CO)$_9$] (**2**), in particular, its IR and ^{1}H-NMR data, are very close to those found for **5** [10] and **6** [1]. The ^{31}P-NMR spectrum of **2** confirms the chelate coordination of dppm to the Pt atom (compare with Ref. [11]).

The major product isolated is [CpMnFePt(μ$_3$-C=CHPh)(μ-dppm)(CO)$_5$] (**3**). The signals of the C^1 (δ 311.70) and C^2 (δ 94.17) nuclei in the ^{13}C-NMR spectrum of **3** are located in the δ region typical for the known clusters containing the μ$_3$-C^1=C^{2}HR (R = H, Ph) ligands [2,3,7,12]. The large J(PtC^1) and J(PtC^2) constant values correspond with the η^2-coordination of vinylidene to the Pt atom. The ^{1}H-NMR spectrum of **3** contains two complete signal sets with intensity ratio of 9:1 indicating that this compound exists in solution as a mixture of two isomers, **3a** and **3b**. According to the ^{31}P-NMR spectrum, in both **3a** and **3b**, the P^1 atom is bound to Pt and the P^2 to Fe. Similar δ and J(PtP) values were found earlier [11a,b] for complexes in which dppm bridged the Fe–Pt bond. Due to the presence of two isomers the IR spectrum of **3** exhibits nine bands in the ν(CO) region. The strong band at 2053 cm^{-1} with the shoulder at 2061 cm^{-1} belongs to the CO(Pt) vibration, the broadened weak band at 1875 cm^{-1} belongs to the μ-CO group.

These data suggest that complex **3** is of type **C** with both isomers having the same central [MnFePt(μ$_3$-C=CHPh)] fragment, which probably differ by the arrangement of dppm with respect to the MnFePt triangle plane (on the same plane or perpendicular to it). In other words, in these isomers, the diphosphine ligand is either *cis* or *trans* with respect to the vinylidene ligand.

The novel complex {CpMnFePt(μ$_3$-C=CHPh)-(CO)$_6$[η^1-Ph$_2$PCH$_2$P(=O)Ph$_2$]} (**4**) has been investigated by X-ray diffraction (Fig. 1).

The central fragment of **4** is a metall chain: the Pt(1)...Mn(1) distance is 3.512(3) and 3.718(3) Å (for two independent molecules). The μ$_3$-C=CHPh ligand is η^1-bound to the Mn and Fe atoms and η^2-coordinated to the Pt atom. The semi-bridging CO group C(3)O(3) supports the Mn–Fe bond. The diphosphine ligand is η^1-coordinated to the Pt atom and the uncoordinated P(2) atom is oxidized to P=O group.

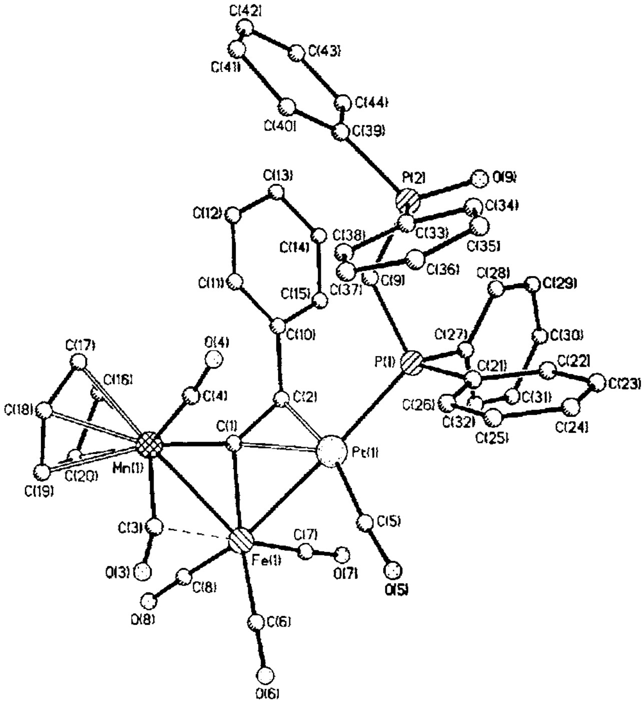
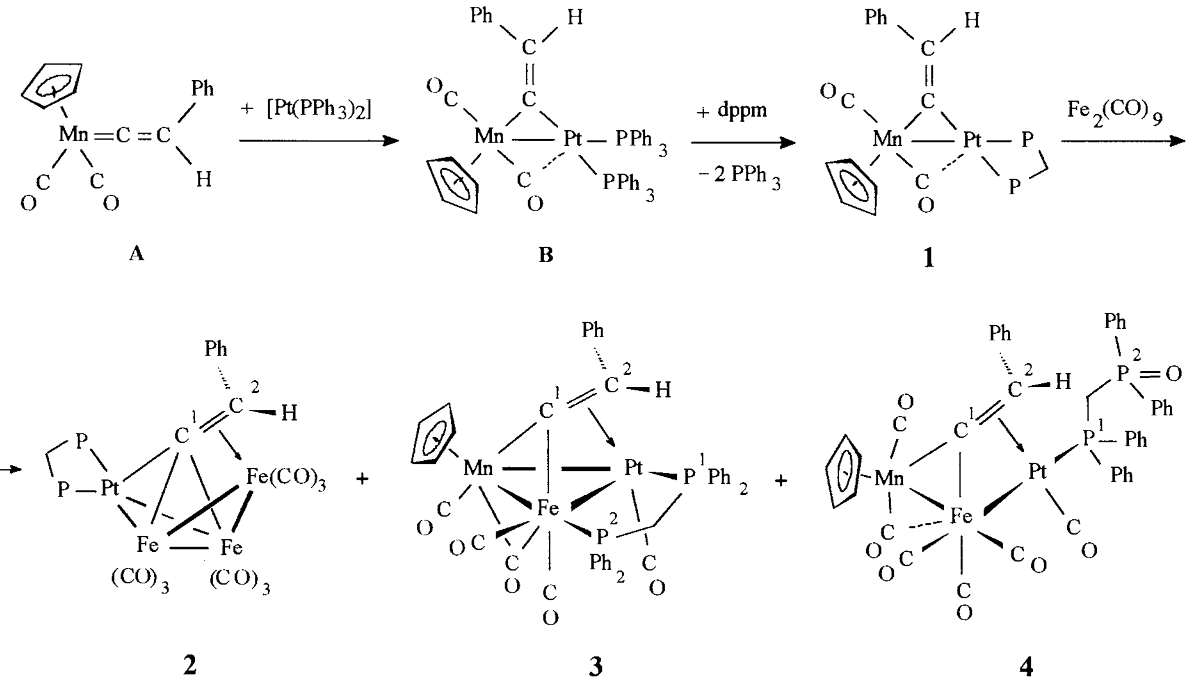


Fig. 1. Molecular structure of complex **4**. Selected interatomic distances (Å) and bond angles (°) for two independent molecules: Pt(1)–Fe(1) 2.617(3) 2.632(3); Pt(1)–C(1) 2.24(1) 2.23(1); Pt–C(2) 2.24(1) 2.18(1); Fe(1)–Mn(1) 2.676(3) 2.692(3); Fe(1)–C(1) 1.88(1) 1.84(1); Mn(1)–C(1) 1.95(1) 1.96(1); C(1)–C(2) 1.42(2) 1.42(1); P(2)–O(9) 1.481(8) 1.486(8); Pt(1)–Fe(1)–Mn(1) 83.14(9) 88.57(9); Fe(1)–C(1)–Mn(1) 88.5(5) 90.2(5).



Scheme 2.

In the IR spectrum of **4** the band at 2053 cm^{-1} is assigned to the CO(Pt) and the band at 1870 cm^{-1} is assigned to the μ-CO group. The $^{31}P\{^1H\}$-NMR spectrum shows the signal of the P^1 nucleus at δ 11.88 ppm. The constant of $J(PtP^1) = 3536.0$ Hz is close to the constant $J(PtP^1)$ found for **3a** and **3b**, while the P^2 signal at δ 22.39 has a $J(PtP^2)$ coupling constant of only 33.7 Hz. The =C*H*Ph resonance in the ^1H-NMR spectrum of **4** is slightly lower than that for **3a** and **3b**, but the J(PtH) constant values for **3a**, **3b** and **4** (52–55 Hz) are nearly the same indicating the η^2-coordination of the C=CHPh ligand to the Pt atom.

In summary, the nature of the products indicates that the reaction between **1** and $[Fe_2(CO)_9]$ proceeds in two parallel directions. The tetranuclear $PtFe_3$ cluster **2** results from the replacement of the $[Cp(CO)_2Mn]$ fragment in **1** by $[Fe(CO)_4]$ followed by addition of two further iron-carbonyl units. The η^2-coordination of dppm remains intact. The triangular MnFePt complex **3** is the result of a joining of the $[Fe(CO)_4]$ unit with **1** accompanied by a change of the dppm ligand from a chelate to a bridging position. The complex **4**, having a trimetallic MnFePt chain, is formed from **3** by a cleavage of the Mn–Pt and Fe–P bonds and oxidation of the uncoordinated P atom of dppm.

3. Experimental

All synthetic manipulations were carried out under an argon atmosphere. Absolute solvents saturated with argon were used. The course of reaction was followed by means of TLC on Silufol plates and IR spectroscopy. Chromatographic separation of the complexes was performed on a column of alumina (Brockman activity II). IR spectra were recorded on a Specord IR-75 instrument. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra (acetone-d_6 solutions) were obtained using Bruker AMX-400 (400.13, 100.61 and 161.98 MHz, respectively) spectrometer.

*3.1. Reaction of [Cp(CO)$_2$MnPt(μ-C=CHPh)(dppm)] (**1**) with [Fe$_2$(CO)$_9$]*

A mixture of **1** (978 mg, 1.1 mmol) and $Fe_2(CO)_9$ (245 mg, 3.4 mmol) in benzene (50 ml) was stirred at 20°C for 20 h. The reaction mixture was filtered, concentrated to a volume of ~ 5 ml and chromatographed on an alumina column. Green complex of $[CpMnFePt(\mu_3\text{-}C{=}CHPh)(\mu\text{-dppm})(CO)_5]$ (**3**) (589 mg, 46%) and black–green cluster $[(\eta^2\text{-dppm})PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9]$ (**2**) (57 mg, 4%) were isolated with hexane–benzene (1:2) mixture. Further elution with benzene–ether (1:1) afforded $\{CpMnFePt(\mu_3\text{-}C{=}CHPh)(\mu\text{-}CO)(CO)_5[\eta^1\text{-}Ph_2\text{-}PCH_2P({=}O)Ph_2]\}$ (**4**) (26 mg, 2%) as dark-green crystals.

For **2**. Anal. Found: C, 46.11; H, 2.69. $C_{42}H_{28}O_9P_2Fe_3Pt$. Anal. Calc.: C, 45.77; H, 2.54%. IR (CH_2Cl_2) ν(CO) 2042s, 1992sh, 1985vs, 1935m,br cm^{-1}. ^1H-NMR δ: 4.82 [dt, 1H, $^2J(H^1H^2)$ 16.2 Hz, $^2J(P^1H^2)$ 10.6 Hz, $^2J(P^2H^2)$ 10.6 Hz, H^2 of dppm]; 5.41 [dt, 1H, $^2J(H^1H^2)$ 16.2 Hz, $^2J(P^1H^1)$ 10.6 Hz, $^2J(P^2H^1)$ 10.6 Hz, H^1 of dppm]; 6.27 [t, 1H, $^2J(P^1H)$ 3.4 Hz, $^2J(P^2H)$ 3.4 Hz, $^3J(PtH) \leq 19$ Hz, =C*H*Ph]; 6.83–7.69

(m, 25H, C_6H_5). $^{31}P\{^1H\}$-NMR δ: -19.54 [d*[2], $J(P^1P^2)$ 122.3 Hz, $^1J(PtP^1)$ 3198.2 Hz, P^1]; -15.77 [d*, $^2J(P^1P^2)$ 122.3 Hz, $^1J(PtP^2)$ 3150.4 Hz, P^2].

For **3**. Anal. Found: C, 51.81; H, 3.29. $C_{43}H_{33}O_5P_2MnFePt$. Anal. Calc.: C, 51.75; H, 3.3%. IR (C_6H_{12}) ν(CO) 2061sh, 2053vs, 2018s, 1982m, 1966s, 1948vs, 1936vs, 1920m, 1875w,br cm^{-1}. ^1H-NMR δ. Isomer **3a**: 3.97 [dt, 0.9H, $^2J(H^1H^2)$ 14.4 Hz, $^2J(P^1H^2)$ and $^2J(P^2H^2)$ 10.0 Hz, H^2 of dppm]; 4.20 [dt, 0.9H, $^2J(H^1H^2)$ 14.4 Hz, $^2J(P^1H^1)$ and $^2J(P^2H^1)$ 9.2 Hz, H^1 of dppm]; 4.49 (s, 4.5H, C_5H_5); 6.49 [s*, 0.9H, $^2J(PtH)$ 55.1 Hz, $^3J(PH)$ ≤ 3 Hz, =C*H*Ph]; 6.75–7.50 (m, 22.5H and 4.5H, C_6H_5 of dppm and =CHC_6H_5); isomer **3b**: 3.97 (m, 0.2H, H^1 and H^2 of dppm); 4.80 (s, 0.5H, C_5H_5); 6.23 [s*, 0.1H, $^2J(PtH)$ 54.3 Hz, $^3J(PH)$ ≤ 3 Hz, =C*H*Ph]; 6.75–7.50 (m, 2.5H and 0.5H, C_6H_5 of dppm and =CHC_6H_5). $^{13}C\{^1H\}$-NMR δ. Isomer **3a**: 30.06 [t, $^1J(P^1C)$ and $^1J(P^2C)$ 8.6 Hz, CH_2]; 88.25 (s, C_5H_5); 94.17 [d*, $^3J(P^1C^2)$ 3.4 Hz, $^2J(PtC^2)$ 169.6 Hz, C=C^2HPh]; 126.4–134.5 (m, C_6H_5); 145.00 [s*, $^2J(PtC)$ ≤ 30 Hz, C_{ipso} of =CHC_6H_5]; 187.46 [d*, $^2J(P^1C)$ 4.9 Hz, $^2J(PtC)$ 83.3 Hz, Pt–*C*O]; 213.18 [d, $^3J(P^1C)$ 18.5 Hz, Fe–*C*O]; 214.26 [s*, $^2J(PtC)$ 30.2 Hz, Fe–*C*O]; 234.05 [s*, $^2J(PtC)$ ≤ 17 Hz, Mn–*C*O]; 238.75 (s, Mn–*C*O); 311.70 [s*, $^2J(PC^1)$ ≤ 4 Hz, $^1J(PtC^1)$ 68.5 Hz, C^1=CHPh]; isomer **3b**: 88.46 (s, C_5H_5), 214.83 [s*, $^2J(PtC)$ 21.3 Hz, Fe–*C*O]. $^{31}P\{^1H\}$-NMR δ. Isomer **3a**: 17.84 [d*, $J(PtP^1)$ 3439 Hz, $^2J(P^1P^2)$ 31 Hz, P^1Pt]; 65.96 [d*, $J(PtP^2)$ 96 Hz, $^2J(P^1P^2)$ 31 Hz, P^2Fe]; isomer **3b**: 12.89 [d*, $J(PtP^1)$ 3346 Hz, $^2J(P^1P^2)$ 29 Hz, P^1Pt]; 68.74 [d*, $J(PtP^2)$ 58 Hz, $^2J(P^1P^2)$ 29 Hz, P^2Fe].

For **4**. Anal. Found: C, 50.84; H, 3.26. $C_{44}H_{33}O_7P_2MnFePt$. Anal. Calc.: C, 50.72; H, 3.17%. IR (C_6H_{12}) ν(CO) 2053s, 2018vs, 1965s, 1947vs, 1917m, 1870w,br cm^{-1}. ^1H-NMR δ: 3.19 [td, 1H, $^2J(H^1H^2)$ 14.4 Hz, $^2J(P^1H^2)$ 14.4 Hz, $^2J(P^2H^2)$ 9.8 Hz, H^2 of dppm]; 3.90 [td, 1H, $^2J(H^1H^2)$ 14.4 Hz, $^2J(P^1H^1)$ 14.4 Hz, $^2J(P^2H^1)$ 9.8 Hz, H^1 of dppm]; 4.44 (s, 5H, C_5H_5); 6.73 [s*, 1H, $^2J(PtH)$ 52.0 Hz, =C*H*Ph]; 6.80–7.90 (m, 25H, C_6H_5). $^{31}P\{^1H\}$-NMR δ: 11.88 [d*, $^2J(P^1P^2)$ 7.5 Hz, $^1J(PtP^1)$ 3536.0 Hz, P^1]; 22.39 [d*, $^2J(P^1P^2)$ 7.5 Hz, $^3J(PtP^2)$ 33.7 Hz, P^2=O].

3.2. X-ray diffraction studies of **4**

$C_{44}H_{33}O_7P_2MnFePt\cdot 0.5$ n-C_5H_{12}, M = 1077.60, dark-green crystal, triclinic, $P\bar{1}$, at 293 K: $a = 13.646(9)$, $b = 18.496(8)$, $c = 19.099(9)$ Å, $\alpha = 76.55(3)$, $\beta = 70.96(3)$, $\gamma = 73.33(3)°$, $V = 4314(4)$ Å^3, $Z = 4$, $D_{calc.} = 1.659$ g cm^{-3}. The experiment was carried out with a CAD4 Enraf Nonius diffractometer (graphite-monochromated Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å, θ-5/3θ scan technique, $\theta \leq 24°$); 12 400 independent reflections were obtained. The structure was solved by direct methods and refined by full-matrix least-squares on F^2, using SHELXTL PLUS 5 program [13] (PC version). Absorption correction (μ(Mo–K$_\alpha$) = 39.8 cm^{-1}) was not applied. Hydrogen atoms were included in calculated positions and taken into account in the final stages of refinement in the riding model approximation. Refinement converged at a final $R^1 = 0.0497$ (on F for 7338 reflections observed with $I \geq 2\sigma(I)$) and $\omega R_2 = 0.1505$ (on F^2 for all 12 310 reflections used in refinement, 1054 parameters). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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[2] d*, s* are doublet and singlet, respectively, with ^{195}Pt satellites.

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