Simultaneous formation of new $PdFe_3$ and $MnFe_2$ clusters in the reaction of $Cp(CO)_2MnPd(\mu\text{-}C=CHPh)(Ph_2PCH_2CH_2PPh_2)$ with $Fe_2(CO)_9$

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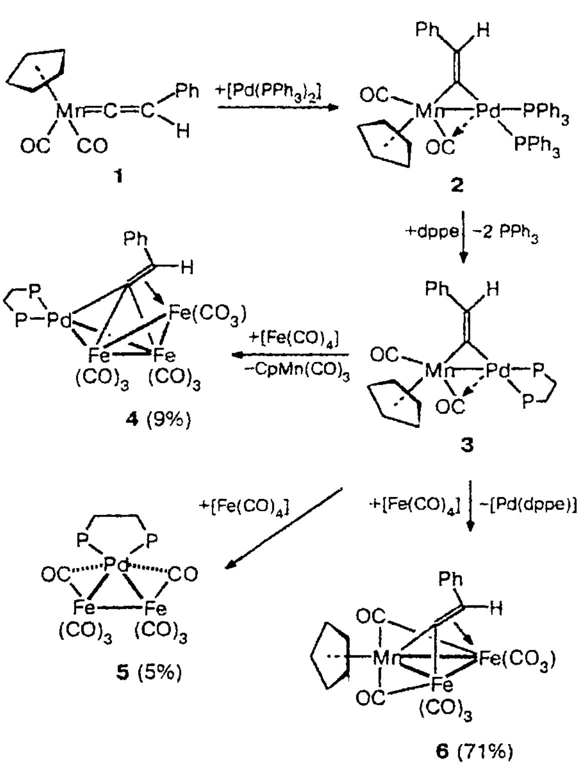
We have shown previously[1,2] that reactions of μ-vinylidene complexes $Cp(CO)_2MnPt(\mu\text{-}C=CHPh)L_2$ with iron nonacarbonyl can occur *via* two alternative routes depending on the nature of ligands L. When L = PPh_3, the addition of the $[Fe(CO)_4]$ to vinylidene results in the formation of the trinuclear MnFePt μ_3-vinylidene cluster.[1] When $L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe), the $[Mn(CO)_2Cp]$ fragment is replaced by $[Fe(CO)_4]$ to form the tetranuclear $PtFe_3$-μ_4-vinylidene cluster.[2] In continuation of the systematic studies in this area, we synthesized the first μ-vinylidene complex with the Mn—Pd bond (**2**) from $Cp(CO)_2Mn=C=CHPh$ (**1**) and $Pd(PPh_3)_4$. (1,1-Dicarbonyl)(1-η^5-cyclopentadienyl)(1,2-μ-phenylvinylidene)[2-η^2-bis(diphenylphosphino)ethane]manganesepalladium (**3**) was obtained by the replacement of the PPh_3 ligand by dppe.[3] In this work, we report on the results of studying the reaction of **3** with $Fe_2(CO)_9$.

The reaction of cluster **3** with $Fe_2(CO)_9$ (benzene, 20 °C, 4 h) results in a mixture of products, which were isolated and characterized by the elemental analysis data and IR and NMR spectra. Three new clusters were obtained: (1,1,1,2,2,2,3,3,3-nonacarbonyl)-μ_4-[1-η^2,2,3,4-η^1-(phenyl)ethenylidene]-[4-η^2-bis(diphenylphosphino)ethane-*PP'*]-bis(*triangulo*)-triironpalladium(*2Fe—Pd, 2Fe—Fe, Fe—Fe*) (**4**) (green crystals, yield 9%), (1,1,1,1,2,2,2,2-octacarbonyl)-[3-η^2-bis(diphenylphosphino)ethane-*PP'*]-*triangulo*-diironpalladium(*2Fe—Pd, Fe—Fe*) (**5**) (violet crystals, yield 5%) and (1,1,2,2,2,3,3,3-octacarbonyl)-(1-η^5-cyclopentadienyl)-μ_3-[1,2-η^1,3-η^2-(phenyl)ethenylidene]-*triangulo*-manganesediiron(*2Fe—Mn, Fe—Fe*) (**6**) (brown crystals, yield 71%) (Scheme 1).

Scheme 1



The IR and ^1H and $^{31}P\{^1H\}$ NMR spectra of compounds **4** and **5** are very close to those of the $(dppe)PtFe_3(\mu_4\text{-}C=CHPh)(CO)_9$ (**7**) and $(dppe)PtFe_2(CO)_8$ (**8**) clusters, respectively.[2] For example, the IR spectrum of **4** (in CH_2Cl_2) in the ν(CO) region at 2049 (s), 2002 (sh), 1988 (s), and 1929 cm^{-1} (w.br) almost coincide with that of **7**, and the spectrum of compound **5** (2052 (s), 2002 (v.s), 1969 (s), 1955 (s), and 1909 cm^{-1} (w.br)) is almost identical to the spectrum of **8**. All the data obtained indicate that clusters **4** and **5** are isostructural to the corresponding platinum analogs **7** and **8**, whose structures were established by the X-ray diffraction method.[2]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 549—550, March, 1998.

The main reaction product was unexpectedly $\mathrm{CpMnFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8}$ (**6**). The mass spectrum (EI, 70 eV) of complex **6** contains a peak of the molecular ion with *m/z* 558 $[\mathrm{M}]^+$ and peaks of the $[\mathrm{M} - n(\mathrm{CO})]^+$ (n = 1—8) ions; further fragmentation of the ion with *m/z* 334 $[\mathrm{CpMnFe_2(C_8H_6)}]^+$ consists in loss of the Mn atom and then of the Fe atom; the most intensive peak with *m/z* 102 corresponds to phenylvinylidene $[\mathrm{C_8H_6}]^+$. The signals of the C(1) (δ 306.18) and C(2) (δ 97.01) nuclei in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum and that of the proton of $=\mathrm{C\underline{H}Ph}$ (δ 7.86) in the ^{1}H NMR spectrum are located in the δ regions standard for trinuclear complexes with the μ_3-C(1)=C(2)HR (R = H, Ph) ligands.[4] The IR spectrum of complex **6** contains in the 2069—1871 cm^{-1} range seven ν(CO) bands, the lowest frequency of which corresponds to the bridging CO group. The suggested structure of complex **6** was confirmed by the preliminary X-ray diffraction data (λ(Mo-K), 7447 reflections with $I > 2\sigma(I)$, triclinic crystals, at 20 °C a = 12.268(4) Å, b = 14.093(3) Å, c = 19.810(4) Å, α = 90.62(2)°, β = 102.43(2)°, γ = 101.89(2)°, d_{calc} = 1.701 g cm^{-3}, Z = 6, space group $P\bar{1}$, 11572 independent reflections, refinement to R = 0.0625).

The sequence of successive transformations **1** → **2** → **3** → **4** resulting in the transfer of vinylidene from the Mn atom to the cluster $\mathrm{PdFe_3}$ system is similar to the transformations **1** → **7**.[2] The **3** → **6** direction predominant in this reaction has no analogs in the chemistry of complexes containing the Mn—Pt bond.

Thus, in the reaction studied, we observed for the first time two parallel directions of transmetallation of the methylenedimetallocyclopropane system: with cleavage of the $\overline{\mathrm{MnPd}(\mu\text{-}\mathrm{C}}(1){=}\mathrm{C}(2)\mathrm{HPh})$ cycle at the Mn—C(1) bond and at the Pd—C(1) bond.

This work was financially supported by the Krasnoyarsk District Science Foundation (Grant 6F0177).

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Received December 26, 1997