Molecular structure of a new palladium-containing vinylidene cluster $[\eta^2\text{-}Ph_2P(CH_2)_3PPh_2]PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$

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The structure of the vinylidene cluster $[\eta^2\text{-}Ph_2P(CH_2)_3PPh_2]PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ was established by X-ray diffraction analysis. The metal core of the molecule has a butterfly shape with the Pd atom occupying a wingtip position. The C(1)=C(2)HPh ligand is σ-bound to three atoms of the Fe_2Pd triangle through the C(1) atom and is η^2-coordinated to the Fe atom located in the second wingtip position *via* the C(1)=C(2) double bond. The Pd atom is chelated by the diphosphine ligand.

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

One of the most important characteristic features of transition-metal complexes containing vinylidene ligands C=CHR (R = H, Alk, Ar, *etc.*) is their ability to be involved in reactions resulting in a successive increase in the size of the metal core.[1—3] This ability allows the synthesis of heteropolynuclear compounds with particular compositions and structures with the aim of using these compounds in metal-complex catalysis and preparing polymetallic materials.[3,4]

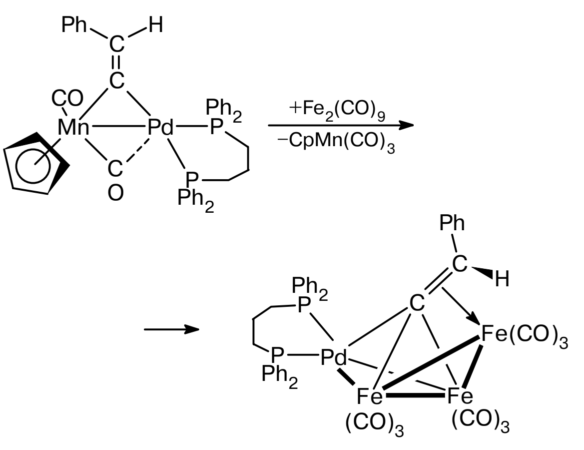
Recently,[2,5,6] we have prepared the first vinylidene palladium-containing clusters $(\eta^2\text{-}P{-}P)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (P—P = dppe (**1**) or dppp (**2**))* and characterized them by IR and NMR spectral data. Previously,[7] a platinum-containing analog of these compounds, *viz.*, $(\eta^2\text{-dppe})PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**3**), has been synthesized and studied by X-ray diffraction analysis. However, although about fifteen polynuclear complexes containing the μ_4-vinylidene ligands C=CRR′ (R and R′ = H, Alk, Ar, *etc.*) were structurally studied, data on palladium-containing compounds are lacking.[8]

In the present work, we studied the cluster $(\eta^2\text{-dppp})PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**2**) by X-ray diffraction analysis and compared its structural characteristics with those of other μ_4-vinylidene clusters.

Results and Discussion

The compound $(\eta^2\text{-dppp})PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**2**) was isolated from a mixture of products formed (Scheme 1) in the reaction of $Fe_2(CO)_9$ with the μ-vinylidene complex $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)(\eta^2\text{-dppp})$ (benzene, 60 °C, 0.5 h, the yield was 30%).[6]

Scheme 1



2

The molecular structure of complex **2** is shown in Fig. 1. The metal core of **2** consisting of the Pd(1)—Fe(2)—Fe(3) and Fe(1)—Fe(2)—Fe(3) triangles adopts a butterfly shape. The Fe(2)—Pd(1)—Fe(3) bond angle at the palladium atom is 55.96(1)°. The dihedral angle between the planes of the "butterfly wings" is 119.0°. Similar values of the corresponding dihedral angles (116—124°) were found in all known complexes with the "butterfly" MM'_3 [9] or $M_2M'_2$ [10] cores. To the contrary, this dihedral angle in the homometallic cluster $Ru_4(\mu_4\text{-}C{=}CHPr^i)(\mu\text{-}PPh_2)(\mu_3\text{-}OH)(CO)_{10}$ characterized by the absence of the bond between the Ru atoms of the "butterfly base" is substantially larger (143.7°).[11]

In complex **2**, the carbene C(1) atom of the μ_4-C(1)=C(2)H(1)Ph ligand forms σ-bonds with the

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* dppe = $Ph_2P(CH_2)_2PPh_2$ and dppp = $Ph_2P(CH_2)_3PPh_2$.

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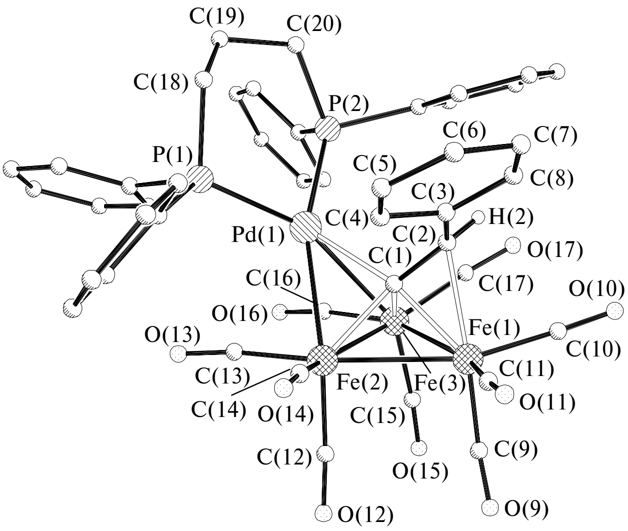

Fig. 1. Structure of molecule **2**.

Pd(1), Fe(2), and Fe(3) atoms and deviates insignificantly (by 0.07 Å) from the mirror symmetry plane of the $PdFe_3$ core passing through the Pd(1) and Fe(1) atoms and the midpoint of the Fe(2)—Fe(3) bond. The Pd(1)—C(1) distance in complex **2** is substantially larger than those in binuclear complexes of the $PdM(\mu\text{-}C{=}CCl_2)(\mu\text{-dppm})_2Cl_2$ type (M = Ni or Pd) in which these values are, on the average,[12,13] equal to 1.97 Å. The lengths of the Pt—C(1) σ-bonds in μ_4-vinylidene clusters **3**[7] and $(\eta^2\text{-dppe})Ru_3Pt(\mu_4\text{-}C{=}CHBu^t)(CO)_9$[9] are 2.10 and 2.12 Å, respectively.

The Fe(1) atom is η^2-coordinated by the vinylidene ligand through the C(1)=C(2) bond. The difference between the Fe(1)—C(2) and Fe(1)—C(1) distances is 0.236 Å. Such substantial differences between the corresponding M—C(2) and M—C(1) distances were observed only in the structures of the closest analogs of complex **2**, *viz.*, in compound **3** (0.202 Å)[7] and in $(dppe)Ru_3Pt(\mu_4\text{-}C{=}CHBu^t)(CO)_9$ (0.174 Å).[9] To the contrary, almost symmetrical η^2-coordination of the C(1)=C(2) fragment (the difference between the M—C(2) and M—C(1) bond lengths is nearly 0.1 Å[4]) is typical of μ_4-vinylidene clusters.

The C(1)=C(2) bond length in cluster **2** (1.403(3) Å) is somewhat smaller than the corresponding values in the majority of other μ_4-vinylidene complexes.[4] Thus, the corresponding distance (1.422 Å) in the complex $(\eta^2\text{-dppe})PtFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**3**) is typical of compounds belonging to this structural type. However, the C=C bond in $(\eta^2\text{-dppe})PtRu_3(\mu_4\text{-}C{=}CHBu^t)(CO)_9$[9] is even shorter (1.391(16) Å) than that in complex **2**.

The angles between the C(1)—C(2) bond and the Pd(1)Fe(2)Fe(3) and Fe(1)Fe(2)Fe(3) planes are 77.7 and 39.8°, respectively. The C(2) atom lies in the symmetry plane of the metal core (the deviation from the plane is 0.02 Å).

The Pd atom is chelated by the bis(diphenylphosphino)propane ligand. The coordination environment about the Pd atom without considering the bond with the C(1) atom is nearly square-planar (the dihedral angle between the Pd(1)Fe(2)Fe(3) and Pd(1)P(1)P(2) planes is 13.3°). The P(1)—Pd(1)—P(2) bond angle (92.69(2)°) is comparable with the corresponding angles in the dication $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}$ (90.92° and 92.02°).[14]

The Fe atoms in cluster **2** have a distorted octahedral coordination. These atoms each are bound to three carbonyl groups. The C(13)—O(13) group at the Fe(2) atom and the C(16)—O(16) group at the Fe(3) atom are somewhat semibridging in character with respect to the Pd atom: the Fe(2)—C(13)—O(13), Pd(1)—C(13)—O(13), Fe(3)—C(16)—O(16), and Pd(1)—C(16)—O(16) bond angles are 173.1(2)°, 116.6(1)°, 172.7(2)°, and 115.2(1)°, respectively; the Pd(1)...C(13) and Pd(1)...C(16) distances are 2.713(3) and 2.652(3) Å, respectively.

The data of ^1H (δ 6.62, 1 H, =CH), $^{13}C\{^1H\}$ (δ 329.95, C(1); and δ 91.51, C(2)), and $^{31}P\{^1H\}$ NMR spectroscopy (AB quadruplet, δ −1.89 (A), −0.03 (B), $^2J_{PP}$ = 129.7 Hz) are consistent with the structure established.

In conclusion, it should be noted that the initial complexes $Cp(CO)_2MnPd(\mu\text{-}C{=}CHPh)(\eta^2\text{-}P\text{—}P)$ (P—P = dppe or dppp) were prepared based on $Cp(CO)_2Mn{=}C{=}CHPh$. Therefore, the conversions giving rise to compounds **1** and **2** can be considered as the first examples of transfer of the vinylidene ligand from one transition-metal atom (Mn) to the cluster moiety containing the palladium atom ($PdFe_3$).

Experimental

The synthesis of the complex (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)propane-*PP*′]-bis(*triangulo*)triironpalladium, $(dppp)PdFe_3(\mu_4\text{-}C{=}CHPh)(CO)_9$ (**2**), and its IR and $^{31}P\{^1H\}$ NMR spectra have been published previously.[6] The ^1H (400.13 MHz) and $^{13}C\{^1H\}$ NMR (100.61 MHz) spectra were recorded on a Bruker AMX-400 spectrometer relative to Me_4Si.

Table 1. Principal bond lengths (*d*) in complex **2**

Bond	*d*/Å	Bond	*d*/Å
Pd(1)—Fe(2)	2.6859(4)	Fe(2)—C(12)	1.783(3)
Pd(1)—Fe(3)	2.6504(4)	Fe(2)—C(13)	1.776(3)
Fe(1)—Fe(2)	2.6538(5)	Fe(2)—C(14)	1.793(3)
Fe(1)—Fe(3)	2.6272(5)	Fe(3)—C(15)	1.783(3)
Fe(2)—Fe(3)	2.5036(5)	Fe(3)—C(16)	1.777(3)
Pd(1)—C(1)	2.134(2)	Fe(3)—C(17)	1.808(3)
Fe(1)—C(1)	1.946(2)	P(1)—C(18)	1.831(3)
Fe(1)—C(2)	2.182(3)	P(2)—C(20)	1.839(3)
Fe(2)—C(1)	1.925(3)	O(13)—C(13)	1.155(3)
Fe(3)—C(1)	1.967(2)	O(16)—C(16)	1.163(3)
Pd(1)—P(1)	2.3155(7)	O—C	1.138(3)—1.158(3)
Pd(1)—P(2)	2.3319(7)	C(1)—C(2)	1.403(3)
Fe(1)—C(9)	1.799(3)	C(2)—C(3)	1.481(3)
Fe(1)—C(10)	1.788(3)	C(18)—C(19)	1.524(4)
Fe(1)—C(11)	1.794(3)	C(19)—C(20)	1.518(4)

Table 2. Principal bond angles (ω) in complex **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Fe(3)—Pd(1)—Fe(2)	55.956(12)	C(1)—Pd(1)—Fe(2)	45.30(7)	C(1)—Pd(1)—P(2)	119.64(7)
Fe(3)—Fe(1)—Fe(2)	56.597(13)	C(1)—Pd(1)—Fe(3)	47.04(6)	C(18)—P(1)—Pd(1)	113.91(10)
Fe(1)—Fe(2)—Pd(1)	98.103(15)	C(1)—Fe(1)—Fe(2)	46.38(7)	C(20)—P(2)—Pd(1)	115.00(9)
Fe(3)—Fe(2)—Pd(1)	61.305(12)	C(1)—Fe(1)—Fe(3)	48.17(7)	C(2)—C(1)—Pd(1)	116.96(17)
Fe(3)—Fe(2)—Fe(1)	61.164(14)	C(1)—Fe(2)—Pd(1)	51.99(7)	C(1)—Fe(1)—C(2)	39.21(9)
Fe(1)—Fe(3)—Pd(1)	99.671(14)	C(1)—Fe(2)—Fe(1)	47.05(7)	C(1)—C(2)—Fe(1)	61.27(14)
Fe(2)—Fe(3)—Pd(1)	62.738(13)	C(1)—Fe(2)—Fe(3)	50.71(7)	C(2)—C(1)—Fe(1)	79.52(15)
Fe(2)—Fe(3)—Fe(1)	62.239(14)	C(1)—Fe(3)—Pd(1)	52.54(7)	C(3)—C(2)—Fe(1)	119.10(17)
P(1)—Pd(1)—Fe(2)	106.81(2)	C(1)—Fe(3)—Fe(1)	47.49(7)	C(2)—C(1)—Fe(3)	131.49(19)
P(2)—Pd(1)—Fe(3)	105.156(19)	C(1)—Fe(3)—Fe(2)	49.22(7)	O(13)—C(13)—Fe(2)	173.1(2)
Fe(1)—C(1)—Pd(1)	162.66(13)	C(13)—Fe(2)—Pd(1)	71.62(8)	O(16)—C(16)—Fe(3)	172.7(2)
Fe(2)—C(1)—Pd(1)	82.71(9)	C(16)—Fe(3)—Pd(1)	70.48(8)	O—C—Fe	174.1(2)—177.3(2)
Fe(3)—C(1)—Pd(1)	80.42(8)	C(14)—Fe(2)—Fe(3)	155.55(9)	C(1)—C(2)—C(3)	128.8(2)
Fe(1)—C(1)—Fe(3)	84.34(9)	C(17)—Fe(3)—Fe(2)	147.47(8)	C(19)—C(18)—P(1)	113.79(18)
Fe(2)—C(1)—Fe(1)	86.57(10)	P(1)—Pd(1)—P(2)	92.69(2)	C(19)—C(20)—P(2)	118.96(19)
Fe(2)—C(1)—Fe(3)	80.07(9)	C(1)—Pd(1)—P(1)	131.35(7)	C(20)—C(19)—C(18)	114.0(2)

^{1}H NMR (($(CD_3)_2CO$), δ: 2.35—2.65 (m, 2 H, CH_2); 2.90—3.02 (m, 4 H, PCH_2); 6.62 (t, 1 H, $=C\underline{H}C_6H_5$, $^4J_{PH}$ = 4.3 Hz); 6.80—7.70 (m, 25 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 30.06 (m, CH_2); 91.51 (t, $C=C(2)HC_6H_5$, $^3J_{PC}$ = 2.1 Hz); 126.97, 127.29, and 128.38 (all s, *p*-C, *o*-C, *m*-C, $=CH\underline{C}_6H_5$); 128.16—135.75 (m, PC_6H_5); 144.96 (s, *ipso*-C, $=CH\underline{C}_6H_5$); 211.31, 215.16, and 215.90 (all s, Fe—CO); 329.95 (dd, $\underline{C}(1)=CHC_6H_5$, $^2J_{PC}$ = 9.0 and 9.7 Hz).

X-ray diffraction study. Crystals of complex **2**, which were grown from a 1 : 1 CH_2Cl_2—ether mixture, are monoclinic; at T = 100 K, a = 10.9265(3) Å, b = 16.2393(5) Å, c = 22.6431(6) Å, β = 91.606(1)°, V = 4016.2(2) Å^3, Z = 4, d_{calc} = 1.721 g cm^{-3}, space group $P2_1/n$. The intensities of 12545 independent reflections were measured on an automated Bruker SMART CCD 1000 diffractometer (Mo-Kα radiation, λ = 0.71073 Å, T = 100 K, $2\theta_{max}$ = 63°, the ω scan step was 0.3°, the time per scan step was 20 s). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms were revealed from the difference Fourier synthesis and included in the refinement with isotropic thermal parameters. The final R factors were as follows: R_1 = 0.0367 (based on F for 7903 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.0694 (based on F^2 for all reflections). The atomic coordinates were deposited with the Cambridge Structural Database. The principal bond lengths and bond angles of complex **2** are given in Tables 1 and 2, respectively. The experimental data were processed and all subsequent calculations were carried out with the use of the SAINT [15] and SHELXTL-97 [16] program packages.

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