

Synthesis and Characterization of the Heterobinuclear μ -Methylene Complex $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$

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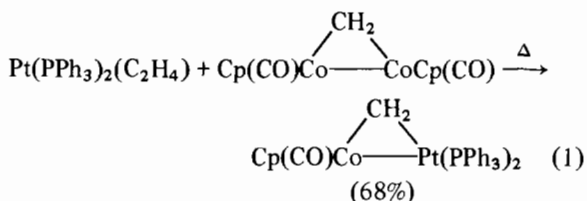
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Abstract

The new bridging methylene complex $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ has been prepared by the reaction of $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ with $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$ and has been crystallographically characterized: $P2_1/c$, $a = 10.338(2)$, $b = 19.604(5)$, $c = 18.422(4)$ Å, $\beta = 105.30(2)$, $D_c = 1.65$, $Z = 4$, $R = 3.54$, $R_w = 3.64$ for 4052 reflections with $F_o \geq 5\sigma(F_o)$. The iron atom has a distorted octahedral geometry defined by the four carbonyl ligands, the platinum atom, and the methylene ligand, whereas the platinum center has a distorted square planar geometry.

Introduction

We recently described the synthesis and characterization of the $\mu\text{-CH}_2$ complex $\text{CoPtCp}(\text{CO})(\text{PPh}_3)_2(\mu\text{-CH}_2)$ that was prepared via the reaction of $[\text{CpCo}(\text{CO})]_2(\mu\text{-CH}_2)$ with $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, eqn. (1). In an effort to determine the generality of this type of reaction for the synthesis of complexes with bridging



methylene ligands, the reaction of $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ with $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ has been subsequently examined. As described herein, this reaction does indeed lead to the formation of the desired complex $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3) which has been spectroscopically and structurally characterized. A review of bridging methylene complexes is given in ref. 1.

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Experimental

General

The complexes $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ [2] and $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ [3] were prepared by literature procedures. Solvents used were dried and degassed by standard methods, and all manipulations were conducted under prepurified N_2 using standard Schlenk techniques. Infrared spectra were obtained on an IBM FTIR/32 spectrometer with 0.5 mm NaCl solution cells, and NMR spectra were recorded on a Bruker WH-300 Fourier Transform spectrometer. Field desorption mass spectra were obtained by Dr Guy Steinmetz and R. J. Hale at the Tennessee Eastman Co., Kingsport, TN, and elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3)

The complexes $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ (0.206 g, 0.589 mmol) and $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ (0.413 g, 0.553 mmol) were combined in a 100 ml two-necked flask equipped with an N_2 inlet and a reflux condenser to which THF (60 ml) was added. The yellow mixture was refluxed for 50 min followed by cooling to 22 °C to give a dark red solution. Removal of solvent by evaporation left a dark red solid which was dissolved in a minimum amount of hexane and chromatographed on silica gel. Elution with hexane yielded two yellow fractions which gave $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ (0.101 g, 0.236 mmol, 40% yield, IR: (pentane) 2053(m), 1978(s), 1942(m) cm^{-1}), a trace of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ (0.002 g, 0.006 mmol, 1% yield, IR: (pentane) 1892(vs) cm^{-1}) and a small amount of an unidentified yellow material. Further elution with hexane yielded another yellow fraction which gave complex 3 (0.132 g, 0.147 mmol, 25% yield) as a yellow crystalline solid upon solvent evaporation. Still further elution with CH_2Cl_2 as eluent gave a red band of an unidentified compound which showed the

TABLE 1. Crystal, data collection and refinement parameters for $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3)

Crystal parameters	
Formula	$\text{C}_{41}\text{H}_{32}\text{O}_4\text{P}_2\text{FePt}$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.388(2)
b (Å)	19.604(5)
c (Å)	18.422(4)
α (°)	90
β (°)	105.30(2)
γ (°)	90
V (Å ³)	3618(1)
Z	4
D (calc) (g cm ⁻³)	1.654
μ (cm ⁻¹)	46.0
Temperature (°C)	23
Size (mm)	0.28 × 0.30 × 0.38
Color	yellow
$T_{(\text{max})}/T_{(\text{min})}$	1.287
Data collection	
Diffractometer	Nicolet R3m/μ
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Monochromator	graphite
Scan method	Wyckoff
Scan limits (°)	4–48
Scan speed (° min ⁻¹)	6–20
Standard reflections	3 std/197 reflns
Decay	<2%
Reflections collected	6070
Independent reflections	5676
$R(\text{int})$ (%)	2.31
Observed reflections	4052 ($F_o \geq 5\sigma(F_o)$)
Data solution and refinement	
Solution method	Patterson
Anisotropic refinement	all non-H
Hydrogen atoms	calculated
R_f (%) ^a	3.54
R_{wt} (%) ($g = 0.001$) ^a	3.64
GOF	0.961
$\Delta(\rho)$ (e Å ⁻³)	0.773
$\Delta/\sigma(\text{max.})$	0.016
Data/parameter	10.9

$$^a R(F) = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; \quad R(wF) = \frac{\sum(w^{1/2}(|F_o| - |F_c|))}{\sum(w^{1/2}|F_o|)}; \quad GOF = \left[\frac{\sum w(|F_o| - |F_c|)^2}{N_o - N_v} \right]^{1/2}$$

following spectroscopic properties, *Anal.* Found: C, 39.04; H, 2.19%. IR (CH_2Cl_2): $\nu(\text{CO}) = 2020(\text{m}), 1990(\text{s}), 1950(\text{s}), 1898(\text{s}), 1855(\text{m}), 1794(\text{m}) \text{ cm}^{-1}$. ¹H NMR (CD_2Cl_2): δ 7.65–7.00 (m, Ph). ³¹P NMR (C_6D_6): δ 34.02.

3: *Anal.* Calc. for $\text{C}_{41}\text{H}_{32}\text{FeO}_4\text{P}_2\text{Pt}$: C, 54.62; H, 3.58. Found: C, 54.93; H, 3.46%. IR (CH_2Cl_2): $\nu(\text{CO}) = 2029(\text{m}), 1954(\text{vs}), 1920(\text{sh}) \text{ cm}^{-1}$. m/z (FD) = 901 (M^+). ¹H NMR (C_6D_6): δ 7.67–6.91 (m, Ph), 3.66 (dd, $J(\text{P-H}) = 3.0, 0.75 \text{ Hz}$; $\mu\text{-CH}_2$). ³¹P

NMR (CD_2Cl_2): δ 31.99 (d, $J(\text{P-P}) = 2.04 \text{ Hz}$, $J(\text{P-Pt}) = 4303 \text{ Hz}$), 30.68 (d, $J(\text{P-Pt}) = 2703 \text{ Hz}$).

Crystallographic Characterization of Complex 3

Crystals were grown from a CH_2Cl_2 /hexane solution by slow evaporation. A specimen mounted on a glass fiber was uniquely identified as belonging to the monoclinic space group, $P2_1/c$. Table 1 provides the crystal parameters as well as details of data collection and refinement. The data were empirically corrected for absorption. The metal atoms were located by heavy-atom methods, and the structure was completed by difference Fourier syntheses. Phenyl rings were constrained to rigid, planar hexagons ($d(\text{C-C})$ 1.395 Å) and hydrogen atoms were treated as idealized, updated isotropic contributions. All non-hydrogen atoms were refined anisotropically. All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

Results and Discussion

Synthesis and Spectroscopic Characterization of $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3)

The complexes $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ and $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ reacted upon heating to yield the new heterobinuclear complex 3 along with the known mononuclear complexes $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, eqn. (2). Also isolated in low yield was a red compound that was not fully characterized. Complex 3 was isolated as a moderately air-stable microcrystalline solid in modest yield and has been characterized spectroscopically and by an X-ray diffraction study, the results of which are shown in Fig. 1. Its field desorption mass spectrum showed a parent ion peak

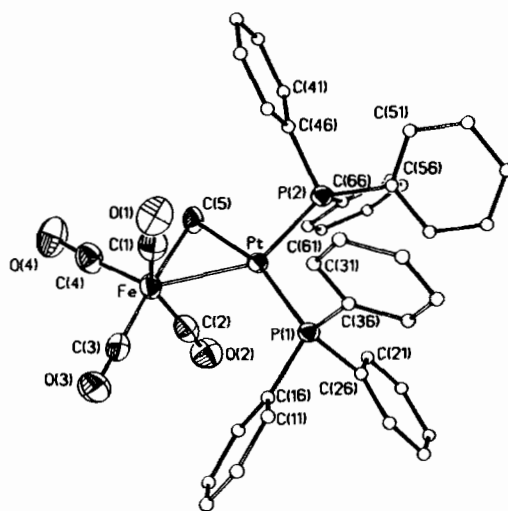
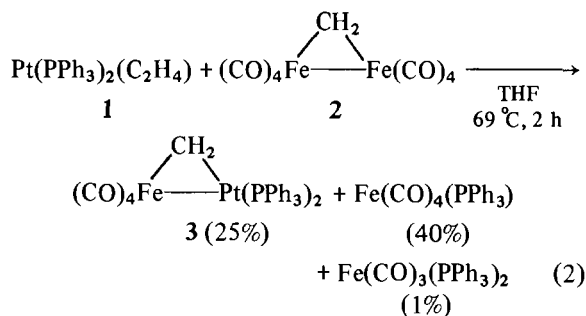
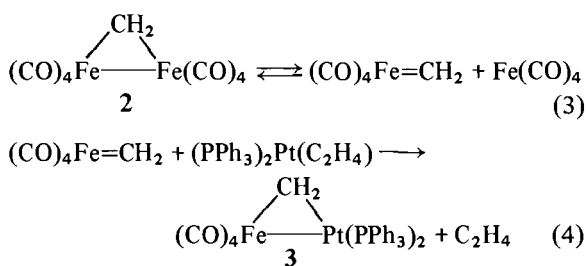


Fig. 1. An ORTEP drawing of $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3) giving the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.



at m/z 901, and three $\nu(\text{CO})$ bands were observed in its IR spectrum at 2029, 1954 and 1920 cm^{-1} . The crystal structure shows the methylene protons to be equivalent, and this is reflected in the ^1H NMR spectrum of **3** which shows a single resonance for these protons at δ 3.66 ($J(\text{P-H}) = 3.0, 0.75$ Hz) which appears as a doublet of doublets due to coupling to two inequivalent phosphorus atoms. The ^{31}P NMR spectrum of **3** showed two separate PPh_3 resonances at δ 31.99 ($J(\text{P-P}) = 2.04$ Hz) and 30.68 ppm with $J(\text{P-Pt})$ values of 4303 and 2703 Hz, respectively.

The mechanism by which complex **3** forms is unknown, although it is tempting to suggest a parallel between this reaction and that outlined in eqn. (2) which gave the related compound $\text{CoPtCp}(\text{CO})(\text{PPh}_3)_2(\mu\text{-CH}_2)$. This latter species was proposed to form by the addition of ' $\text{Pt}(\text{PPh}_3)_2$ ' to mononuclear $\text{Cp}(\text{CO})\text{Co}=\text{CH}_2$ that resulted from the reversible dissociation of $[\text{Cp}(\text{CO})\text{Co}]_2(\mu\text{-CH}_2)$ into $\text{Cp}(\text{CO})\text{Co}$ and $\text{Cp}(\text{CO})\text{Co}=\text{CH}_2$ fragments as originally proposed by Theopold and Bergman [4]. We accordingly suggest that under our reaction conditions $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$ reversibly dissociates into $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CH}_2)(\text{CO})_4$ fragments, eqn. (3), and that the latter



is scavenged by $\text{Pt}(\text{PPh}_3)_2$ produced from ethylene dissociation from $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, eqn. (4). The reaction shown in eqn. (3) is similar to that known to occur with the isostructural complex $\text{Fe}_2(\text{CO})_9$ in coordinating solvents [5] and also accounts for the formation of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in significant yield as a by-product in the synthesis of **3**.

Crystal and Molecular Structure of Complex 3

An ORTEP drawing of complex **3** is shown in Fig. 1 and pertinent crystallographic details are given in Tables 1–3. The methylene ligand of **3** bridges the

TABLE 2. Atomic coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$) for $(\text{CO})_4\text{FePt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (**3**)

	x	y	z	U^a
Pt	31.8(3)	890.2(1)	2168.3(2)	34.0(1)
Fe	-1850(1)	300.5(6)	1179.3(7)	50.2(4)
P(1)	-441(2)	2035.3(9)	2235(1)	33.5(6)
P(2)	2108(2)	737(1)	2926(1)	38.2(7)
C(1)	-776(10)	600(5)	629(5)	70(4)
O(1)	-73(8)	780(4)	284(4)	90(4)
C(2)	-2421(8)	368(4)	2026(5)	62(4)
O(2)	-2795(7)	401(4)	2547(4)	82(3)
C(3)	-3243(10)	757(5)	612(5)	74(4)
O(3)	-4154(8)	1025(5)	228(4)	122(4)
C(4)	-2251(10)	-542(5)	821(6)	71(4)
O(4)	-2434(9)	-1080(4)	585(5)	109(4)
C(5)	-119(8)	-114(4)	1841(5)	53(3)
C(11)	-2076(4)	2092(3)	1120(3)	47(3)
C(12)	-3309	3158	715	64(4)
C(13)	-4485	2882	820	66(4)
C(14)	-4427	2350	1330	63(4)
C(15)	-3193	2094	1736	53(3)
C(16)	-2018	2370	1631	39(3)
C(21)	-467(5)	1883(2)	3734(3)	44(3)
C(22)	-725	2086	4407	60(4)
C(23)	-1184	2745	4479	58(4)
C(24)	-1385	3200	3878	52(3)
C(25)	-1127	2997	3204	46(3)
C(26)	-669	2338	3132	37(3)
C(31)	1176(5)	2387(2)	1342(3)	52(3)
C(32)	2033	2799	1066	68(4)
C(33)	2516	3406	1433	75(5)
C(34)	2142	3601	2076	77(5)
C(35)	1284	3189	2353	54(3)
C(36)	801	2581	1986	37(3)
C(41)	3571(5)	-458(3)	2783(3)	53(3)
C(42)	4263	-871	2398	67(4)
C(43)	4401	-671	1696	68(4)
C(44)	3847	-57	1378	70(4)
C(45)	3155	357	1763	56(3)
C(46)	3017	157	2465	41(3)
C(51)	4592(5)	1403(3)	3139(3)	66(4)
C(52)	5505	1921	3426	85(5)
C(53)	5132	2467	3812	73(4)
C(54)	3847	2495	3911	75(4)
C(55)	2935	1976	3624	65(4)
C(56)	3308	1430	3238	41(3)
C(61)	1046(4)	-60(3)	3875(3)	57(4)
C(62)	1031	-378	4550	69(4)
C(63)	2109	-300	5182	72(4)
C(64)	3203	96	5139	67(4)
C(65)	3218	414	4464	54(3)
C(66)	2140	336	3832	43(3)

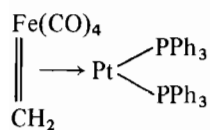
^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fe-Pt bond with the Fe atom further coordinated by four CO ligands and the Pt center by two PPh_3 ligands. The coordination geometry about Pt can be described as a distorted square plane defined by the

TABLE 3. Selected bond lengths and angles for (CO)₄FePt(PPh₃)₂(μ-CH₂) (3)

Bond lengths (Å)			
Pt-Fe	2.569(1)	Pt-P(1)	2.308(2)
Pt-P(2)	2.259(2)	Pt-C(5)	2.054(8)
Fe-C(1)	1.793(11)	Fe-C(2)	1.814(11)
Fe-C(3)	1.785(9)	Fe-C(4)	1.787(11)
Fe-C(5)	2.056(8)	P(1)-C(16)	1.841(4)
P(1)-C(26)	1.829(6)	P(1)-C(36)	1.826(6)
P(2)-C(46)	1.824(6)	P(2)-C(56)	1.832(6)
C(2)-O(2)	1.127(13)	C(1)-O(1)	1.143(14)
C(4)-O(4)	1.137(13)	C(3)-O(3)	1.149(12)
Bond angles (°)			
Fe-Pt-P(1)	110.0(1)	Fe-Pt-P(2)	143.3(1)
P(1)-Pt-P(2)	106.2(1)	Fe-Pt-C(5)	51.3(2)
P(1)-Pt-C(5)	161.4(2)	P(2)-Pt-C(5)	92.3(2)
Pt-Fe-C(1)	77.5(3)	Pt-Fe-C(2)	73.6(3)
C(1)-Fe-C(2)	148.8(4)	Pt-Fe-C(3)	122.5(3)
C(1)-Fe-C(3)	92.0(5)	C(1)-Fe-C(3)	93.9(4)
Pt-Fe-C(4)	137.5(3)	C(1)-Fe-C(4)	102.3(5)
C(2)-Fe-C(4)	106.7(5)	C(3)-Fe-C(4)	100.0(4)
Pt-Fe-C(5)	51.3(2)	C(1)-Fe-C(5)	83.5(4)
C(2)-Fe-C(5)	87.3(4)	C(3)-Fe-C(5)	173.0(4)
C(4)-Fe-C(5)	86.3(4)	Pt-P(1)-C(16)	118.8(2)
Pt-P(1)-C(26)	116.4(2)	C(16)-P(1)-C(26)	97.1(2)
Pt-P(1)-C(36)	112.5(2)	C(16)-P(1)-C(36)	102.4(2)
C(26)-P(1)-C(36)	107.8(2)	Pt-P(2)-C(46)	108.8(2)
Pt-P(2)-C(56)	123.7(2)	C(46)-P(2)-C(56)	102.5(3)
Pt-P(2)-C(66)	113.8(2)	C(46)-P(2)-C(66)	105.6(2)
C(56)-P(2)-C(66)	100.6(3)	Fe-C(1)-O(1)	178.6(8)
Fe-C(2)-O(2)	178.6(6)	Fe-C(3)-O(3)	177.0(9)
Fe-C(4)-O(4)	176.0(10)	Pt-C(5)-Fe	77.4(3)
P(1)-C(16)-C(11)	123.2(2)	P(1)-C(16)-C(15)	116.7(2)
P(1)-C(26)-C(21)	118.8(1)	P(1)-C(26)-C(25)	121.0(1)
P(1)-C(36)-C(31)	115.3(2)	P(1)-C(36)-C(35)	124.5(2)
P(2)-C(46)-C(41)	123.4(2)	P(2)-C(46)-C(45)	116.6(2)
P(2)-C(56)-C(51)	121.7(2)	P(2)-C(56)-C(55)	118.2(2)
P(2)-C(66)-C(61)	118.0(1)	P(2)-C(66)-C(65)	122.0(1)

two phosphines, the iron and the methylene ligand. Alternatively, the Pt may be viewed as having a trigonal planar geometry with a π -bonded Fe=CH₂ unit sketched below.



The latter structure is similar to that found for Pt(PPh₃)₂(CH₂=CH₂) [6] and is reflected in the isolobal relationship between CH₂=CH₂ and (CO)₄-Fe=CH₂. The 106.2(1)° P(1)-Pt-P(2) bond angle is closer to the 120° trigonal planar angle than it is to the 90° square planar angle and is only slightly less than the corresponding P-Pt-P angle of 111.5° found in Pt(PPh₃)₂(CH₂=CH₂) [6]. The coordination geometry about the iron atom is best described as a

distorted octahedron defined by the four carbonyls, the platinum atom and the methylene ligand.

Although no other complexes that possess methylene ligands bridging Fe-Pt bonds have been reported, a comparison to other compounds which contain Fe-CH₂ and Pt-CH₂ linkages indicates normal M-C single bonds for 3. The Fe-CH₂ bond length of 2.056(8) in 3 is only slightly longer than the Fe-CH₂ bond lengths in 2 (1.920(2), 1.925(2) Å) [7], and the Pt-CH₂ distance of 2.054(8) Å for 3 compares well to the Pt-CH₂ distances in Os₃Pt(μ-CH₂)(CO)₁₁-(PPh₃)₂ (1.95(6) Å) [8], Pt₂Cl₂(μ-CH₂)(dppm)₂ (2.01(2) Å) [9] and [Pt₂Cl(CH₂PPh₃)(μ-CH₂)(μ-dppm)₂][PF₆] (2.13(3) Å) [9]. The Fe-Pt bond length of 2.569(1) Å compares well to the Fe-Pt bond length of 2.564 Å in (Ph₃P)(CO)PtFe₂(CO)₈ [10] and the Pt-C(5)-Fe angle of 77.4(3)° is within the usual 74.0–87.4° range found for methylene ligands bridging metal-metal bonds [1].

Supplementary Material

Hydrogen atom coordinates with isotropic thermal parameters, anisotropic thermal parameters and structure factor tables are available from A. L. Rheingold.

Acknowledgements

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