

Bis(alkoxycarbonyl) complexes of platinum: preparation, reactivity and their role in carbonylation reactions *

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Abstract

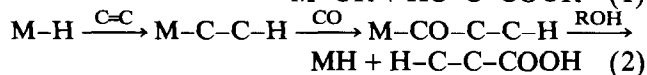
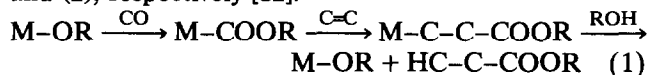
bis(alkoxycarbonyl) complexes of platinum of the type $[\text{Pt}(\text{COOR})_2\text{L}]$ [$\text{L} = 1,2$ -bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,1'-bis(diphenylphosphino)ferrocene (dppf) or 1,2-bis(diphenylphosphino)benzene (dppb); $\text{R} = \text{CH}_3$, C_6H_5 or C_2H_5] were obtained by reaction of $[\text{PtCl}_2\text{L}]$ with carbon monoxide and alkoxides. Palladium and nickel complexes gave only carbonyl complexes of the type $[\text{M}(\text{CO})\text{L}]$ or $[\text{M}(\text{CO})_2\text{L}]$. The new complexes were characterized by chemical and spectroscopic means. The X-ray structure of $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})] \cdot \text{CH}_3\text{OH}$ is also reported. The reactivity of some alkoxycarbonyl complexes was also investigated.

Key words: Platinum; Phosphines; X-ray structure; Carbonylation; Alkoxycarbonyls

1. Introduction

There is considerable interest in alkoxycarbonyl complexes of transition metals owing to their recognition as intermediates in several important catalytic processes, such as carbonylation of alcohols, hydrocarboxylation of olefins to saturated and unsaturated esters, single and double carbonylation of alkyl halides, carbon monoxide–olefin copolymerization to polyketones and synthesis of alkyl carbonates and oxalates esters [1–11]. The supposed intermediates in these reactions are very different. For example, in the carbonylation of olefins to esters catalysed by $[\text{PdCl}_2(\text{PPh}_3)_2]$, two different intermediates are postulated, an alkoxycarbonyl complex $[\text{PdCl}(\text{COOMe})(\text{PPh}_3)_2]$ (A)

and an acyl complex $[\text{PdCl}(\text{COR}')(\text{PPh}_3)_2]$ (B) ($\text{R}' =$ radical arising from the olefin), related to reactions (1) and (2), respectively [12].



When carbonylation is carried out in presence of MeOH, both complexes A and B can be isolated and when the reaction is carried out in the presence of EtOH, BuOH (or a higher alkanol) only complex B can be isolated.

Alkoxycarbonyl complexes of transition metals have usually been prepared by reaction of a variety of metal carbonyl complexes in the presence of alkoxides or tertiary amines [13] and complexes of the type $[\text{PdCl}(\text{COOR})\text{L}_2]$ can also be easily prepared by oxidative addition of ethyl or phenyl chloroformate to Pd^0 as in $[\text{Pd}(\text{PPh}_3)_4]$ [14].

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* Dedicated to Professor Adziano Sacco. He made great contributions to organometallic chemistry and we learned a great deal from him.

TABLE 1. Analytical data for bis(alkoxycarbonyl) complexes

Compound	Analysis: found (calc.) (%)		
	C	H	P
[Pt(COOCH ₃) ₂ (dppf)]	52.22 (52.61)	3.98 (3.95)	7.05 (7.14)
[Pt(COOCH ₃) ₂ (dppp)]	49.90 (51.33)	4.22 (4.40)	8.33 (8.54)
[Pt(COOCH ₃) ₂ (dppb)]	52.39 (51.98)	4.70 (4.60)	8.27 (8.38)
[Pt(COOCH ₃) ₂ (dpb)]	53.40 (53.78)	4.01 (3.95)	8.20 (8.16)
[Pt(COOC ₆ H ₅) ₂ (dppf)]	57.20 (58.13)	3.77 (3.81)	6.00 (6.20)
[Ni(CO) ₂ (dppf)]	63.58 (64.62)	4.60 (4.22)	9.30 (9.12)
[Pt(CO) ₂ (dppf)]	54.50 (53.68)	3.81 (3.50)	7.99 (7.69)
[(dppf)Pt(μ-CO)(μ-H)Pt(dppf)](BF ₄)	52.00 (51.32)	3.69 (3.55)	7.10 (7.67)

We have also described recently some new routes to carbamoyl and alkoxycarbonyl complexes of palladium (II) together with the preparation of the bis(alkoxycarbonyl) complex [Pt(COOCH₃)₂(dppf)] [15]. We also showed that the 2,6-bis(diphenylphosphinomethyl)pyridine complex of Ni^{II} reacts with carbon monoxide at room temperature and atmospheric pressure to give a nickel(0) carbonyl complex and carbon dioxide in water-ethanol solutions (the reaction does not occur in anhydrous ethanol) and this suggests a nucleophilic attack on a very labile carbonyl intermediate of nickel(II) [16].

In this paper, we describe the synthesis and the characterization, by chemical and spectroscopic means, of bis(alkoxycarbonyl) complexes of platinum, together with the X-ray structure of [Pt(COOCH₃)₂(dppf)], to study their role in alkoxycarboxylation reactions and the influence of the chelating ligands.

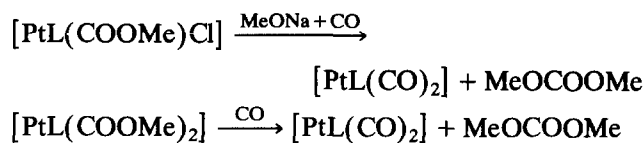
2. Results and discussion

2.1. Synthesis of bis(alkoxycarbonyl) complexes of platinum, palladium and nickel

Complexes [Pt(COOCH₃)₂L] are prepared in good yield by reaction of [PtCl₂L] (L = dppf, dppp, dppb or dpb) with sodium methoxide (or phenoxide in the case of [Pt(COOC₆H₅)₂(dppf)]) in the molar ratio 1:2 in methanol under carbon monoxide at ambient temperature. The reaction, which gives first the intermediate monoalkoxycarbonyl complexes [PtCl(COOCH₃)L] (detected by IR spectroscopy and easily isolable), is complete within 24 h. The compounds obtained were characterized by elemental analysis (Table 1) and IR and ¹H NMR spectra (Table 2 and 3).

The IR spectra (Table 2) show absorption bands in the regions 1672–1608 and 1068–1012 cm⁻¹ assignable, to the C=O and C–O–C stretches, respectively. The ¹H NMR spectra of the complexes show singlets in the region 2–3 ppm due to the protons of the CH₃ group of the methoxycarbonyl group and of the phenyl protons of the phosphine. We observe that reaction of [PtCl₂(dppf)] and sodium methoxide (1:2) in methanol

under carbon monoxide for 5 d yields [Pt(CO)₂(dppf)] instead of the bis(alkoxycarbonyl) complex. It is likely that reduction to Pt⁰ (accompanied by dimethylcarbonate or dimethyloxalate formation) occurs first via mono- or bis-(methoxycarbonyl) complexes ([PtCl(COOME)L] or [Pt(COOME)₂L]), according to the following schemes:



This mechanism has been proposed for the formation of dimethylcarbonate and dimethyloxalate from [Pd(OAc)(COOME)L₂] and [Pd(COOME)₂L₂], respectively (L = triphenylphosphine) [17,18].

We were not able to obtain the corresponding bis(alkoxycarbonyl) complexes for palladium and nickel; only mono- or bis-carbonyl complexes were obtained (see Experimental section).

2.2. Reactions of the bis(alkoxycarbonyl) complexes

The alkoxycarbonyl complexes of platinum react readily at ambient temperature with HCl, HBF₄ or HClO₄, carbon monoxide, to give methylformate or other compounds depending on the experimental conditions. They react also with amines in the presence of CuCl₂ or FeCl₃ to give carbamate and urea (see Experimental).

TABLE 2. IR data for bis(alkoxycarbonyl) complexes

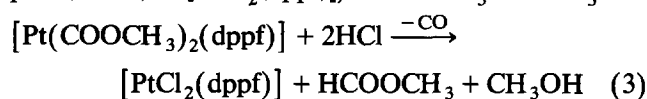
Compound	$\nu(\text{CO})$ (cm ⁻¹)	$\nu(\text{O}-\text{C}-\text{O})$ (cm ⁻¹)
[Pt(COOCH ₃) ₂ (dppf)]	1672, 1645	1056, 1012
[Pt(COOCH ₃) ₂ (dppp)]	1620	1042, 1068
[Pt(COOCH ₃) ₂ (dppb)]	1608, 1639	1040, 1098
[Pt(COOCH ₃) ₂ (dpb)]	1630, 1648	1038, 1060
[Pt(COOC ₆ H ₅) ₂ (dppf)]	1612, 1650	1049, 1092
[Ni(CO) ₂ (dppf)]	1945, 2002	
[Pt(CO) ₂ (dppf)]	1984, 1943	
[(dppf)Pt(μ-CO)(μ-H)Pt(dppf)](BF ₄)	1770	

TABLE 3. ^1H NMR data for bis(alkoxycarbonyl) complexes

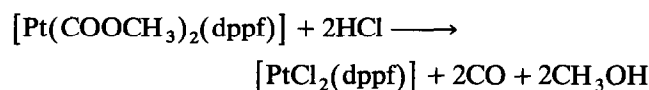
Compound	Phosphine			CH_3
	Ph	C_5H_4	CH_2	
$[\text{Pt}(\text{dppf})(\text{COOCH}_3)_2]$	7.77 (m)	4.25(d)	–	2.94(s)
$[\text{Pt}(\text{dppp})(\text{COOCH}_3)_2]$	7.8–7.3(m)	–	2.58(m)	3.45(s)
$[\text{Pt}(\text{dppb})(\text{COOCH}_3)_2]$	7.70–7.26(m)	–	1.9(m)	3.46(s)
$[\text{Pt}(\text{dpb})(\text{COOCH}_3)_2]$	7.81–7.20(m)	–	2.55(m)	1.8(m)
			–	3.5(s)

2.2.1. Reaction with HCl

The methoxycarbonyl complex $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ in CH_2Cl_2 at room temperature decomposes in part (< 5%) to $[\text{PtCl}_2(\text{dppf})]$, HCOOCH_3 and CH_3OH :

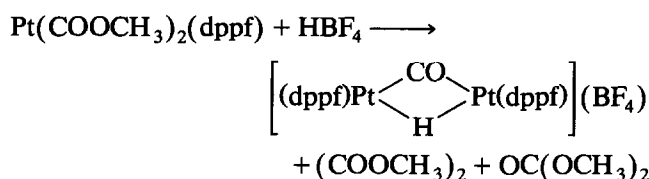


The principal reaction with HCl is as follows:



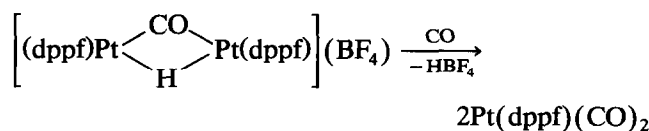
2.2.2. Reaction with aqueous HBF_4

$[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ and aqueous HBF_4 (50%) in the molar ratio 1:1 in dichloromethane give a yellow compound identified as $[(\text{dppf})\text{Pt}(\mu\text{-CO})(\mu\text{-H})\text{Pt}(\text{dppf})]\text{BF}_4$, perhaps according to the following scheme:



Unfortunately, we detected methyloxalate and methylcarbonate in only trace amounts.

When the reaction is performed at a molar ratio of 1:5 under carbon monoxide $[\text{Pt}(\text{CO})_2(\text{dppf})]$ is obtained. Probably the $[(\text{dppf})\text{Pt}(\mu\text{-CO})(\mu\text{-H})\text{Pt}(\text{dppf})]\text{BF}_4$ reacts with carbon monoxide as follows:



2.2.3. Reaction with *n*-butylamine

$[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ reacts with *n*-butylamine in the presence of CuCl_2 to give $^n\text{BuNHCOOCH}_3$ and BuNHCONHBu .

2.3. X-Ray structure of $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})] \cdot \text{CH}_3\text{OH}$

The molecular structure is shown in Fig. 1. Selected bond distances and angles are given in Table 4. The

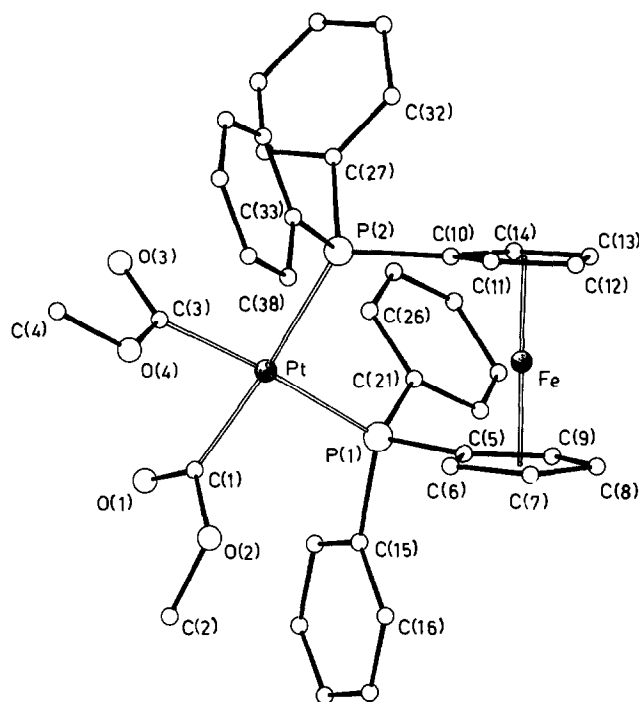


Fig. 1. View of the structure of the complex $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ with the atomic labelling scheme.

coordination around the Pt atom, involving the two P atoms of the dppf and two C methoxycarbonyl atoms, is distorted square planar (the angle values range from $85.1(7)$ to $97.4(2)^\circ$). C(1) and C(3) are above the

TABLE 4. Selected bond distances (\AA) and angles ($^\circ$) with e.s.d.s in parentheses for the complex $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})] \cdot \text{CH}_3\text{OH}$

Pt–P(1)	2.310(5)	P(2)–C(10)	1.830(2)
Pt–P(2)	2.331(5)	P(2)–C(27)	1.866(19)
Pt–C(1)	1.992(22)	P(2)–C(33)	1.833(19)
Pt–C(3)	2.016(22)	O(1)–C(1)	1.231(30)
Fe–CE(1)	1.632(20)	O(2)–C(1)	1.428(27)
Fe–CE(2)	1.640(22)	O(2)–C(2)	1.450(26)
P(1)–C(5)	1.768(20)	O(3)–C(3)	1.233(26)
P(1)–C(15)	1.831(17)	O(4)–C(3)	1.315(26)
P(1)–C(21)	1.859(18)	O(4)–C(4)	1.429(27)
P(1)–Pt–P(2)	97.4(2)	Pt–C(1)–O(2)	111.3(13)
P(1)–Pt–C(1)	89.2(6)	Pt–C(1)–O(1)	130.8(18)
P(1)–Pt–C(3)	173.5(7)	O(3)–C(3)–O(4)	117.8(18)
P(2)–Pt–C(1)	172.8(7)	Pt–C(3)–O(4)	119.2(15)
P(2)–Pt–C(3)	88.5(5)	Pt–C(3)–O(3)	122.8(16)
C(1)–Pt–C(3)	85.1(7)	P(1)–C(5)–C(9)	134.1(15)
CE(1)–Fe–CE(2)	179.1(10)	P(1)–C(5)–C(6)	119.2(14)
Pt–P(1)–C(5)	114.2(7)	C(6)–C(5)–C(9)	106.7(16)
Pt–P(2)–C(10)	120.5(6)	P(2)–C(10)–C(14)	123.6(16)
C(1)–O(2)–C(2)	116.4(15)	P(2)–C(10)–C(11)	126.9(15)
C(3)–O(4)–C(4)	120.9(17)	C(11)–C(10)–C(14)	109.4(18)
O(1)–C(1)–O(2)	117.9(20)		

CE(1) and CE(2) are the centroids of the C(5)...C(9) and C(10)...C(14) cyclopentadienyl rings, respectively.

weighted least-squares coordination plane P(1)P(2)-C(1)C(3) by 0.11(2) and $-0.08(2)$ Å and the Pt atom is only 0.005(1) Å away from it. The C(5) and C(10) cyclopentadienyl carbon atoms and the O(2), C(2), O(4) and C(4) atoms of the two methoxycarbonyl moieties are on the same side of the coordination plane and are displaced from it by 1.32(2), 0.72(2), 1.44(1), 1.61(3), 0.99(2), 0.99(3) Å, respectively.

The two methoxycarbonyl groups are roughly orthogonal ($92.9(11)^\circ$) and the dihedral angles between them and the coordination plane are similar ($78.8(8)^\circ$ for O(1)C(1)O(2)C(2) and $77.2(6)^\circ$ for O(3)C(3)-O(4)C(5)).

The two staggered cyclopentadienyl rings (mean torsion angle value $35(2)^\circ$) and at $3.5(9)^\circ$ to each other, make angles of $70.2(6)$ and $66.8(7)^\circ$ with the mean coordination plane (the first value refers to the C(5)...C(9) Cp ring and the second to the C(10)...C(14) ring). The centroids CE(1) and CE(2) of the Cp rings and the Fe atom are displaced by 2.31(2), 1.13(2) and 1.734(3) Å from the coordination plane. The platinum-phosphinofero-cenyl moiety has an envelope conformation with the P(1) atom out of the mean plane PtP(2)CE(1)CE(2) by 1.204(5) Å.

The only significant differences in the $(\text{Pt}(\text{dppf}))^{2+}$ fragment of the complex with regard to the bond distances observed in complexes $[(\text{dppf})\text{Pt}(1\text{-MeTy}(\text{-H})(\text{DMF}))\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ (1-MeTy(-H) = 1-methylthyminato- N^3), $[(\text{dppf})\text{Pt}(1\text{-MeTy}(\text{-H})(1\text{-MeCy}))\text{BF}_4$ (1-MeCy = 1-methylcytosine- N^3) [19] and $[\text{PtCl}_2(\text{dppf})]$ [20] are the lengthening of the Pt-P bond distances, probably owing to the *trans* effect of the methoxycarbonyl groups. The Pt...Fe distance (4.223(4) Å) is similar to that found in the first complex mentioned above (4.202(3) Å) but shorter than those found in the other two (4.310(2) and 4.278(2) Å).

3. Experimental section

All preparations were carried out in deoxygenated solvents and all operations performed under carbon monoxide using standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 577 instrument. ^1H NMR spectra (at 200 MHz) were recorded with a Varian XL 200 pulsed Fourier transform spectrometer.

The complexes $[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ and $[\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ and the phosphines dppf, dppd, dpb, dppe and dppp were purchased and used without purification.

3.1. Preparation of $[\text{PtCl}_2\text{L}]$, $[\text{PdCl}_2\text{L}]$ and $[\text{NiCl}_2\text{L}]$

Only the preparation of $[\text{PtCl}_2(\text{dppf})]$ is reported, following the method of refs. 15 and 20. The other complexes were prepared similarly. A solution of dppf

(0.25 mmol) in 10 ml of dichloromethane was added to 200 mg (0.24 mmol) of $[\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ in 5 ml of dichloromethane. The solution was stirred at room temperature for 1 h then concentrated to 10 ml. The yellow crystalline precipitate was washed with diethyl ether and dried *in vacuo* (yield = 66%).

3.2. Preparation of the bis(alkoxycarbonyl) complexes of platinum

We report only the preparation of $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$. The other complexes were prepared similarly. A solution of sodium methoxide (0.82 mmol) in 10 ml of methanol was added to a stirred solution of $[\text{PtCl}_2(\text{dppf})]$ (0.4 mmol) in 10 ml of methanol under carbon monoxide. The resulting solution was stirred for 24 h at room temperature. The solvent was evaporated *in vacuo* and the residue extracted with benzene. Addition of hexane and cooling to -30°C produced a crystalline product, which was filtered, washed with hexane and dried *in vacuo* (yield = 44%).

When the reaction mixture was stirred with 0.4 mmol of sodium methoxide only $[\text{PtCl}(\text{COOCH}_3)(\text{dppf})]$ was isolated (yield = 75%).

3.3. Reaction of $[\text{PdCl}_2(\text{dppf})]$ with sodium methoxide under carbon monoxide

A solution of sodium methoxide (0.41 mmol) in 10 ml of methanol was added to a stirred solution of $[\text{PdCl}_2(\text{dppf})]$ (0.2 mmol) in 10 ml of methanol under carbon monoxide. The resultant solution was stirred at room temperature for 2 h. Work-up of the solution as for platinum complexes produced compounds identified by IR spectroscopy as a mixture of $[\text{Pd}(\text{CO})_2(\text{dppf})]$ ($\nu(\text{CO}) = 1825, 1890 \text{ cm}^{-1}$) and $[[\text{Pd}(\text{CO})(\text{dppf})]_2]$ ($\nu(\text{CO}) = 1710 \text{ cm}^{-1}$) (total yield = 59%).

3.4. Reaction of $[\text{NiCl}_2(\text{dppf})]$ with sodium methoxide under carbon monoxide

A solution of sodium methoxide (0.41 mmol) in 10 ml of methanol was added to a stirred solution of $[\text{NiCl}_2(\text{dppf})]$ (0.2 mmol) in 10 ml of methanol under carbon monoxide. The resultant solution was stirred at room temperature for 0.5 h. Work-up of the solution as above produced $[\text{Ni}(\text{CO})_2(\text{dppf})]$ ($\nu(\text{CO}) = 1945, 2002 \text{ cm}^{-1}$) (yield = 32%). A better yield can be obtained from $[\text{NiCl}_2(\text{dppf})]$ in methanol under carbon monoxide in the presence of *n*-butylamine.

3.5. Reactivity of the alkoxycarbonyl complexes

Only the reactivity of $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ is described. The other complexes react very similarly.

(a) A mixture of $[\text{Pt}(\text{COOCH}_3)_2(\text{dppf})]$ (100 mg, 0.11 mmol) and aqueous 10 M HCl (1 drop) in 5 ml of dichloromethane was stirred at room temperature for 2

h. GC-MS analysis of the solution showed a small amount of CH₃OH (5%) together with trace of methyloxalate and HCOOCH₃ (identified by GC-MS).

(b) A mixture of [Pt(COOCH₃)₂(dppf)] (100 mg, 0.11 mmol) and aqueous (50%) HBF₄ (1:1) in dichloromethane (4 ml) was stirred under dinitrogen at ambient temperature for 3 h. The solution obtained was concentrated *in vacuo* and addition of diethyl ether gave a yellow compound identified as [(dppf)Pt(μ-CO)(μ-H)Pt(dppf)]BF₄ (yield = 58%) from analytical data and the IR spectrum ($\nu(\text{CO}) = 1770 \text{ cm}^{-1}$) and also by comparison of the data with those of the compound described by Bandini *et al.* [21].

(c) A mixture of [Pt(COOCH₃)₂(dppf)] (100 mg, 0.11 mmol) and aqueous (50%) HBF₄ (1:5) in dichloromethane (4 ml) was stirred under carbon monoxide at ambient temperature for 3 h. The solution obtained was concentrated *in vacuo* and addition of diethyl ether gave compound identified as [Pt(CO)₂(dppf)] from analytical data and the IR spectrum ($\nu(\text{CO}) = 2120 \text{ cm}^{-1}$) (yield = 48%).

(d) A 100 mg (0.11 mmol) amount of [Pt(COOCH₃)₂(dppf)] in 4 ml of dichloromethane were stirred at ambient temperature under carbon monoxide for 3 h. The solution was concentrated *in vacuo* and addition of diethyl ether gave the compound [Pt(CO)₂(dppf)] (yield = 71%).

The same compound was obtained on reaction of [PtCl₂(dppf)] and sodium methoxide in methanol under carbon monoxide for 5 d.

(e) A 100 mg (0.11 mmol) amount of [Pt(COOCH₃)₂(dppf)] suspended in 4 ml of methanol was stirred at room temperature under carbon monoxide for 3 h in presence of CuCl₂ (0.3 mmol) and n-butylamine (0.5 mmol) at 50°C. GL-MS analysis of the solution showed a stoichiometric amount of BuNHCOOCH₃ (0.10 mmol) together with a trace of BuNHCONHBu.

3.6. Determination of the crystal structure of [Pt(COOCH₃)₂(dppf)] · CH₃OH

Crystal data for C₃₈H₃₄FeO₄P₂Pt · CH₃OH, $M = 899.61$, monoclinic, space group $P2_1/a$, $a = 17.410(8)$, $b = 21.093(9)$, $c = 9.497(5)$ Å, $\beta = 94.51(2)^\circ$, $V = 3477(3)$ Å³; $Z = 4$, $D_c = 1.719 \text{ g cm}^{-3}$, $F(000) = 1784$, $\mu(\text{Mo K}\alpha) = 45.73 \text{ cm}^{-1}$, crystal size $0.16 \times 0.19 \times 0.25 \text{ mm}^3$.

The intensity data were collected at ambient temperature (22°C) on a Siemens AED diffractometer, using niobium-filtered Mo K α radiation ($\lambda = 0.71073$ Å) and the θ - 2θ scan technique; 6154 unique reflections were measured ($3^\circ < \theta < 25^\circ$) with a scan width of $(1.20 + 0.346 \tan \theta)^\circ$ and a scan speed in the range 3 - $12^\circ \text{ min}^{-1}$; 2394 reflections with $I \geq 2\sigma(I)$ were used in the refinement. One standard reflection was

monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analysed following Lehmann and Larsen [22]. Intensities were corrected for Lorentz and polarization effects and a correction for absorption

TABLE 5. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of complex [Pt(COOCH₃)₂(dppf)] · CH₃OH

Atom	x	y	z	U
Pt	3046.0(4)	529.9(4)	2264.5(9)	313(2) ^a
Fe	1963(2)	943(1)	-1767(3)	379(11) ^a
P(1)	1785(3)	333(2)	1436(5)	303(18) ^a
P(2)	3221(3)	1446(2)	955(6)	360(19) ^a
O(1)	2932(8)	-354(7)	4641(17)	609(63) ^a
O(2)	3131(8)	-810(6)	2526(17)	520(56) ^a
O(3)	4274(9)	1025(7)	4156(22)	839(77) ^a
O(4)	4677(8)	277(8)	2808(18)	737(69) ^a
C(1)	3040(10)	-267(10)	3392(27)	425(80) ^a
C(2)	3048(15)	-1423(9)	3192(31)	824(124) ^a
C(3)	4120(13)	646(8)	3185(22)	453(83) ^a
C(4)	5453(13)	366(15)	3385(32)	1092(146) ^a
C(5)	1640(10)	275(8)	-423(21)	322(65) ^a
C(6)	2276(12)	35(9)	-1238(21)	378(75) ^a
C(7)	1987(15)	67(11)	-2645(23)	551(96) ^a
C(8)	1205(15)	319(11)	-2853(24)	620(99) ^a
C(9)	1024(11)	416(9)	-1408(20)	404(72) ^a
C(10)	2665(11)	1573(8)	-738(21)	373(72) ^a
C(11)	2928(12)	1490(10)	-2112(20)	429(76) ^a
C(12)	2308(18)	1637(13)	-3077(32)	871(130) ^a
C(13)	1654(16)	1861(10)	-2283(32)	675(107) ^a
C(14)	1886(12)	1801(9)	-865(29)	517(92) ^a
C(15)	1324(9)	-385(7)	2051(20)	275(45)
C(16)	1248(11)	-932(9)	1186(23)	460(55)
C(17)	894(12)	-1444(11)	1759(27)	610(67)
C(18)	672(13)	-1457(12)	3099(28)	664(72)
C(19)	746(12)	-957(11)	3938(27)	594(66)
C(20)	1111(11)	-387(10)	3402(24)	519(61)
C(21)	1118(10)	946(8)	2038(20)	310(45)
C(22)	323(12)	883(10)	1679(24)	497(58)
C(23)	-161(12)	1296(10)	2287(24)	521(60)
C(24)	119(12)	1768(10)	3196(24)	528(61)
C(25)	900(12)	1811(10)	3457(25)	529(61)
C(26)	1415(12)	1400(9)	2956(23)	470(56)
C(27)	3066(10)	2204(8)	1905(20)	304(52)
C(28)	3162(11)	2185(9)	3321(23)	388(56)
C(29)	3025(12)	2746(10)	4026(28)	564(63)
C(30)	2809(12)	3289(10)	3330(25)	531(61)
C(31)	2743(12)	3305(11)	1929(26)	554(63)
C(32)	2872(11)	2737(9)	1184(25)	441(56)
C(33)	4222(10)	1467(9)	486(21)	370(49)
C(34)	4711(12)	1983(10)	830(24)	521(61)
C(35)	5466(17)	1937(14)	545(32)	924(95)
C(36)	5745(15)	1418(12)	-104(28)	744(78)
C(37)	5296(16)	937(14)	-436(31)	879(91)
C(38)	4492(13)	942(10)	-148(24)	556(64)
C(39)	-226(25)	3164(21)	6737(49)	1892(184)
O(5)	53(18)	2987(15)	5564(38)	2048(127)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_i tensor.

effects [23] was applied (maximum and minimum values for the transmission factors were 1.2754 and 0.8736, respectively).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, with anisotropic thermal parameters in the last cycles of refinement only for the two metal atoms, the two P atoms, the methoxycarbonyl group atoms and the carbon atoms of the ferrocenyl group. All hydrogen atoms (excluding those of the molecule of solvation) were placed at their calculated positions ($C-H = 1.00 \text{ \AA}$) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried on the basis of 306 variables; after the last cycles, no parameters shifted by more 0.50 times their e.s.d. The biggest remaining peak (close to the platinum atom) in the final difference map was equivalent to about 0.96 e \AA^{-3} . A weighting scheme, $w = K[\sigma(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the K and g values were 0.3831 and 0.0034, respectively. The final R and R_w were 0.0542 and 0.0610, respectively. The SHELX-76 and SHELXS-86 computed programs were used [24]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 25. Final atomic coordinates for the non-hydrogen atoms are given in Table 5. All calculations were carried out with the Gould Povernode 6040 and Encore 91 computers of the Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma. Additional data are available from the authors, or from the Cambridge Crystallographic Data Centre.

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