Journal of Organometallic Chemistry, 356 (1988) 397–409
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Syntheses and structures of 2-diphenylphosphinomethylenide-6-diphenylphosphinomethylenepyridine complexes of palladium(II) and platinum(II); crystal structures of [PtCl{2-($CHPPh_2$)-6-(CH_2PPh_2)pyridine}] and [Pd(COOMe){2-($CHPPh_2$)-6-(CH_2PPh_2)pyridine}]

Adriano Sacco, Giuseppe Vasapollo, Cosimo F. Nobile, Angela Piergiovanni

Dipartimento di Chimica, Centro di Studio sulle Metodologie Innovative di Sintesi Organiche del C.N.R., Università di Bari, via Amendola 173, Bari (Italy)

Maria A. Pellinghelli and Maurizio Lanfranchi

Istituto di Chimica Generale e Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, Parma (Italy)

(Received April 13th, 1988)

Abstract

The reactions of the palladium(II) and platinum(II) complexes of formula $M(pnp)Cl_2$ (M = Pd, Pt; pnp = 2,6-bis(diphenylphosphinomethyl)pyridine) and $Pt(dppf)Cl_2$ (dppf = 1,1′-bis(diphenylphosphinomethyl)ferrocene) with NaOMe in methanol under CO at room temperature and atmospheric pressure has been investigated.

In contrast with the behaviour of the $Pt(dppf)Cl_2$ complex, which gives the corresponding bis-methoxycarbonyl compound, the terdentate ligand of the $M(pnp)Cl_2$ complexes is nucleophilically attacked by the methoxide ion to lose a proton and yield complexes of formula $[MX\{C_5H_3N(CHPPh_2)(CH_2PPh_2)\}]$ (M = Pt, X = Cl, COOMe; M = Pd, X = COOMe), which have been characterized by chemical and spectroscopic means. The crystal structures of [PtCl{2-($CHPPh_2$)-6-(CH_2PPh_2)pyridine] (**1**) and [Pd(COOMe){2-($CHPPh_2$)-6-(CH_2PPh_2)pyridine}] (**2**) have been determined by X-ray diffraction. In both complexes the terdentate anionic ligand chelates the metal to form two five-membered rings, and the P–C and C–C bond lengths in one of the chelate rings is in agreement with an sp^2 hybridization of the formally anionic methylenidic carbon and with a large delocalization in the ring.

0022-328X/88/$03.50

Introduction

In pursuit of our interest [1] in the study of the factors which influence the reactions of the metal center during catalysis, we recently described [2] the preparation of alkoxycarbonyl and carbamoyl complexes of palladium(II) and platinum(II) with the terdentate ligand pnp (pnp = 2,6-bis(diphenylphosphinomethyl)pyridine). Such complexes are of value in improving our understanding of the mechanism of important processes, such as the palladium-catalyzed oxalate ester synthesis [3].

Further studies on the properties and the reactions of the alkoxycarbonyl compounds showed, however, that the compound previously formulated as $Pd(pnp)(COOMe)_2$ is actually a complex of the anionic terdentate ligand 2-diphenylphosphinomethylenide-6-diphenylphosphinomethylenepyridine, of formula $[Pd(COOMe)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)pyridine\}]$.

In this paper we describe the synthesis and the characterization, by chemical and spectroscopic means, of palladium(II) and platinum(II) complexes containing the anionic terdentate ligand $2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)pyridine$, and the crystal structures of $[PtCl\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)pyridine\}]$ and $[Pd(COOMe)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)pyridine\}]$.

Results and discussion

Preparation and spectral properties of the complexes

As previously reported reaction of $M(pnp)Cl_2$ (M = Pd, Pt) with methoxide ion in molar ratio 1/1 in dry methanol under a carbon monoxide atmosphere proceeds rapidly at room temperature and atmospheric pressure to give the corresponding methoxycarbonyl complexes [M(pnp)(COOMe)]Cl in good yield. The same reaction but with a 2/1 molar ratio of methoxide ion and metal complex under the same conditions gives good yields of complexes which contain, besides the tridentate ligand, only one methoxycarbonyl ligand, and no chloride ion. The stoichiometry of the reaction, which requires one mole of carbon monoxide and two moles of methoxide ion per mole of metal, has been confirmed experimentally by monitoring the absorption of the carbon monoxide by a gas-volumetric apparatus and determining the amount of residual methoxide by acidimetric titration at the end of the reaction.

The same products, in the form of red microcrystals with elemental analyses in good agreement with the formula M(pnp)COOMe, were obtained by treating the methoxycarbonyl compounds of Pd^{II} and Pt^{II}, of formula [M(pnp)(COOMe)]Cl, with methoxide ion under either carbon monoxide or dinitrogen.

Table 1 gives the relevant infrared data for the compounds discussed.

A similar compound, of apparent formula Pt(pnp)Cl, was obtained in the form of red microcrystals from $Pt(pnp)Cl_2$ and methoxide ion in methanol under dinitrogen.

Since these compounds are diamagnetic, and monomeric in solution, they are obviously not Pd^I and Pt^I derivatives. Their ^1H NMR spectra in $CDCl_3$ (Table 2) show, besides the resonances of the phenyl protons, two sets of signals assignable to the methylenic protons of the terdentate ligand, in contrast to the spectra of the free ligand, of $M(pnp)Cl_2$ and of [M(pnp)(COOMe)]Cl, which show identical resonances for these protons. The 2/1 integration ratio of the signals (Fig. 1) clearly indicates

Table 1

IR data (Nujol mulls) for the complexes [a]

Compound	ν(C–O) (cm^{-1})	ν(ClO$_4$) (cm^{-1})	ν(C–O–C) (cm^{-1})
Pd(pnp)(COOCH$_3$)Cl	1665,1600		1065
Pt(pnp)(COOCH$_3$)Cl	1620,		1028
Pd(pnp)(COOCH$_3$)ClO$_4$	1663,1601	1090	
[Pd(COOCH$_3$){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}]	1638,1603		1048
[Pt(COOCH$_3$){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}]	1612,1570		1026
Pt(dppf)(COOCH$_3$)$_2$	1672,1645		1056,1012

that one of carbon atoms of the methylenic groups has undergone nucleophilic attack by methoxide ion to lose a proton and form a carbanion (see below). Moreover, the ^{31}P NMR spectra of these complexes show (Table 3) two signals of equal intensity assignable to two different phosphorous atoms. It was concluded that the red complexes must be formulated as [MX{C$_5$H$_3$N(CHPPh$_2$)(CH$_2$PPh$_2$)}] (M = Pd, Pt; X = Cl, COOMe), and the X-ray diffraction studies (see below) confirmed this formulation.

The rigid pnp skeleton of the terdentate pnp ligand and the presence both of the hard N-donor atom, which enhances the electron-donating ability of the metal center, and of the soft P-acceptor/donor atom confer unusual properties on the complexes of formula M(pnp)Cl$_2$. Thus, while the reaction of (dppe)PtCl$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) with sodium methoxide yields (dppe)Pt(OMe)$_2$, which subsequently reacts with carbon monoxide to give the corresponding bis-methoxycarbonyl compound [4], the metal center in the M(pnp)Cl$_2$ complexes cannot undergo a similar nucleophilic attack: in absence of carbon monoxide, they undergo proton abstraction from the carbon in the β-position from the metal center, and so in this case no chloride–methoxide exchange occurs.

In the presence of carbon monoxide, the attack of the latter on the metal occurs more quickly than that of the nucleophilic on the carbon in the β-position, and the reaction proceeds, exclusively in the case of the palladium compound and predominantly (ca. 85%) in the case of the platinum compound, by pathway A of Scheme 1.

Table 2

^{1}H NMR data (in ppm) for the complexes

Compound	pnp				CH$_3$
	Ph,Py	CH$_2$		CH	
pnp	7.5–6.9(m)	3.25(s)	–	–	
Pd(pnp)Cl$_2$	8.0–7.3(m)	4.48(t) J(P–H) 4.6 Hz			
Pd(pnp)(COOCH$_3$)Cl	7.8–7.5(m)	4.6(t) J(P–H) 4.6 Hz		3.55(s)	
[Pd(COOCH$_3$){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}]	8.59–7.0(m)	3.58(d,2H) (J 9.5 Hz)		4.38 (broad d)	3.93(s)
[Pt(COOCH$_3$){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}]	8.3–6.6(m)	3.04(d asym,5H)		4.22 (1H)	–
Ni(pnp)(CO)$_2$	7.64–7.15	3.68(d,4H)	(J 8 Hz)		

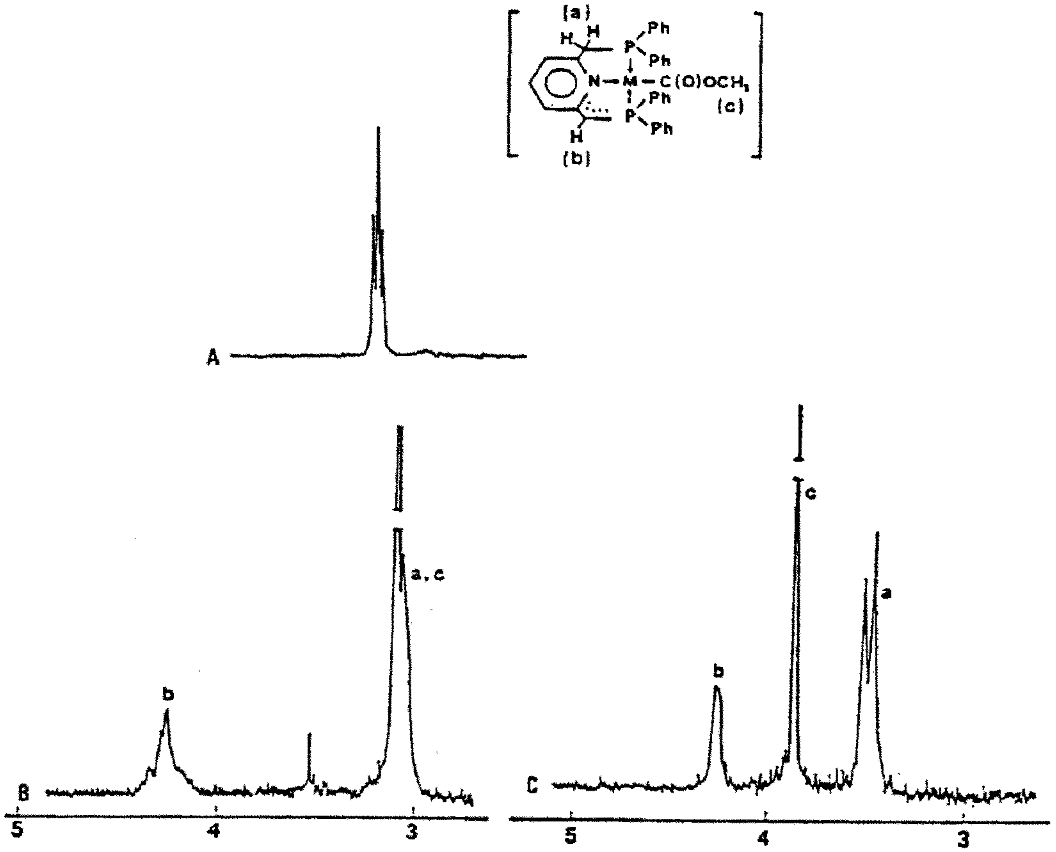
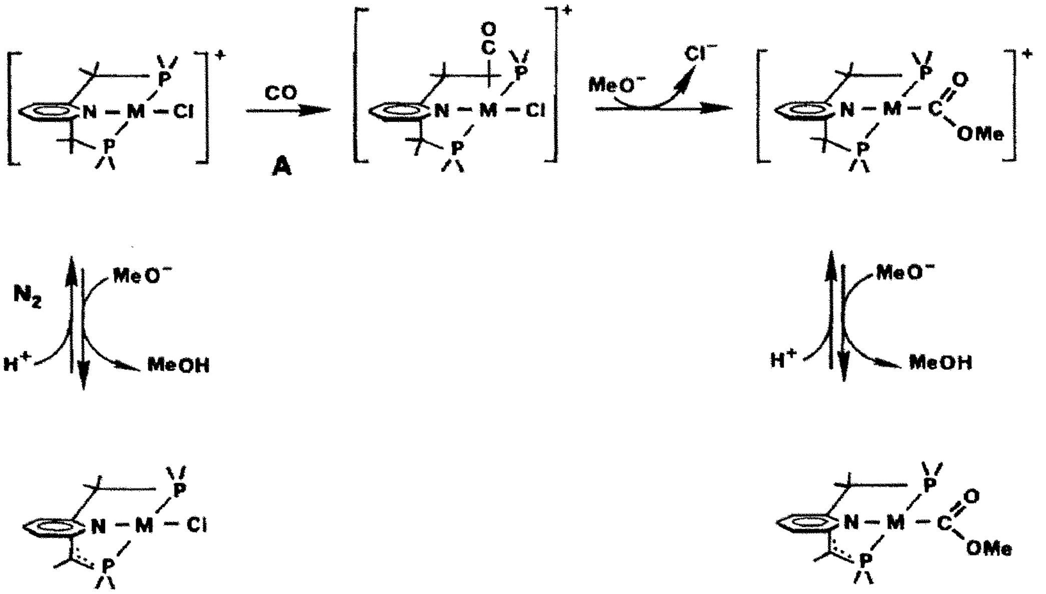


Fig. 1. ^{1}H NMR spectra showing the pnp methylene region of: (A) Pd(pnp)Cl(COOMe); (B) [Pt(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}]; (C) [Pd(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)C$_5$H$_3$N}].



Scheme 1

Table 3

^{31}P NMR data for the complexes [a]

Compound	$^{31}P\{^1H\}$ NMR
pnp	−11.13
$Pd(pnp)Cl_2$	24.35
$[Pd(COOCH_3)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)C_5H_3N\}]$	17.47; 18.42
$[PtCl\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)C_5H_3N\}]$	20.5; 28.4
$Pt(dppf)(COOCH_3)_2$	13.13

[a] In CD_2Cl_2; chemical shift in ppm relative to 85% H_3PO_4.

The structure of the coordinate terdentate ligand favours the formation of the carbanion, the negative charge of which is delocalized (see Scheme 2) leading to a strongly stabilized ylide. The free ligand does not undergo attack by the methoxide ion under the same conditions.

Treatment of $[MX\{C_5H_3N(CHPPh_2)(CH_2PPh_2)\}]$ (M = Pd, X = COOMe; M = Pt, X = Cl, COOMe) with an aqueous solution of HCl or $HClO_4$ results in protonation of the carbanion to give the complexes $[MX\{C_5H_3N(CH_2PPh_2)(CH_2\text{-}PPh_2)\}]$ (M = Pd, X = COOMe; M = Pt, X = Cl, COOMe).

The bis-methoxycarbonyl complex of platinum(II) containing the rigid chelating ligand dppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene] was readily obtained from $Pt(dppf)Cl_2$ and methoxide ion in methanol under CO at room temperature and atmospheric pressure.

Solid state structure of [PtCl{2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}] (1) and [Pd(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}] (2)

The molecular structures of **1** and **2** are shown in Fig. 2 and 3, respectively (Fig. 2 depicts the Pt complex in the equivalent position $-x$, $-y$, $-z$ in order to facilitate

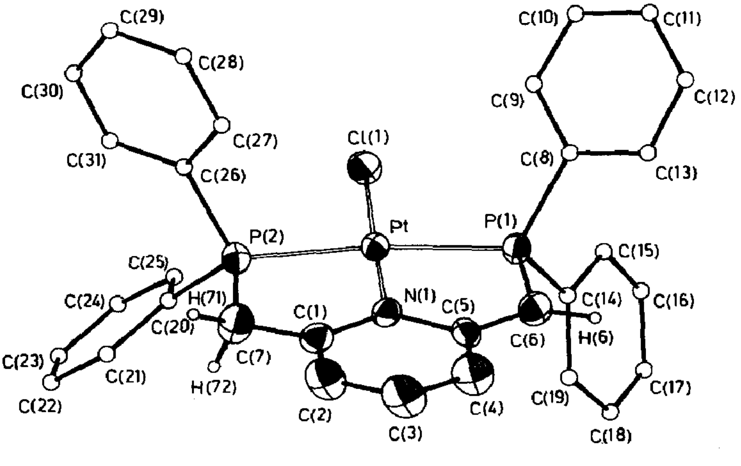


Fig. 2. View of the $[PtCl\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)pyridine\}]$ complex with the atomic numbering scheme. Thermal parameters are drawn at the 30% probability level.

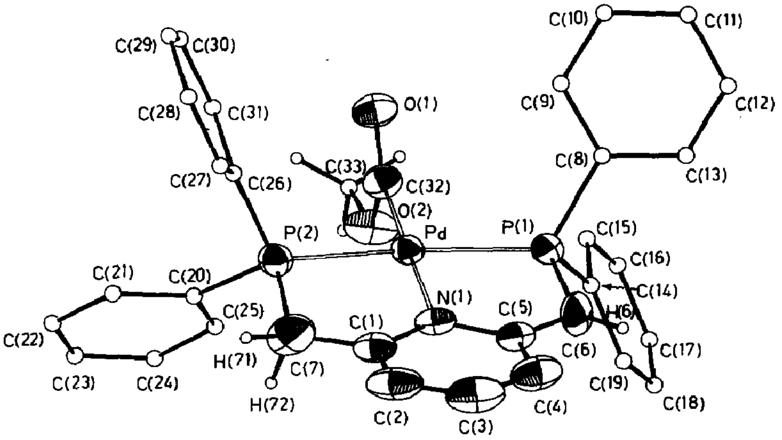
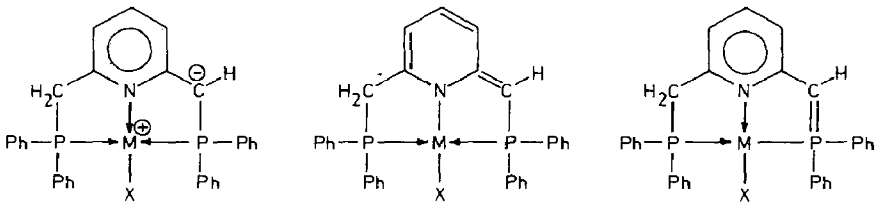


Fig. 3. View of the [Pd(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}] complex with the atomic numbering scheme. Thermal parameters are drawn at the 30% probability level.

comparison with **2**). Selected bond distances and angles are listed in Table 4. The terdentate pnp anionic ligand chelates the metal to form two five-membered rings: one of these, that including the carbanionic moiety, is almost planar (the maximum deviation being 0.04(1) Å in **1** and 0.09(1) Å in **2** for C(6)), whereas the other has an "envelope" conformation at C(7). The P(1)–C(6) and C(5)–C(6) bonds (1.77(1), 1.37(1) in **1** and 1.77(1), 1.41(1) Å in **2**) are shorter than the corresponding P(2)–C(7) and C(1)–C(7) bonds (1.83(1), 1.44(1) and 1.80(1), 1.44(2) Å). The range of P–C and C–C bond lengths in similar Ph$_2$PCCOM fragments are 1.742(18)–1.80(3) and 1.347(23)–1.46(3) Å [5,6]. These results are consistent with sp^2 hybridization of the formally anionic C(6) and with a large charge delocalization in one of the chelate rings (Scheme 2):



Scheme 2

In **2** the methoxycarbonyl is planar (the maximum deviation is 0.003(18) Å for C(33)) and is quite perpendicular to the coordination plane (93.1(3)°). Apart from the methyl group of the methoxycarbonyl and the methylenic and methylenidic hydrogens, the complex **2** presents a pseudo C_2 symmetry with the pseudo two-fold axis passing through the Pd and N(1) atoms. **1** does not show this symmetry as a result of the different phenyl orientation.

In the two square-planar complexes the Pt–P(1), Pt–P(2), Pd–P(1), Pd–P(2) bond lengths (2.284(3), 2.286(3), 2.286(2), 2.290(3) Å, respectively) are very similar, while the Pt–N(1) (2.008(7) Å) is much shorter than the Pd–N(1) (2.073(8) Å) bond distance, in keeping with the strong *trans* effect of the COOMe group. The Pd–C(32) distance of 1.991(10) Å) is not significantly different from that in

Table 4

Selected bond distances (Å) and angles (°) in the complexes **1** and **2** (with e.s.d.'s in parentheses)

1		**2**	
Pt–P(1)	2.284(3)	Pd–P(1)	2.286(2)
Pt–P(2)	2.286(3)	Pd–P(2)	2.290(3)
Pt–N(1)	2.008(7)	Pd–N(1)	2.073(8)
Pt–Cl(1)	2.312(3)	Pd–C(32)	1.991(10)
P(1)–C(6)	1.77(1)	P(1)–C(6)	1.77(1)
P(1)–C(8)	1.84(1)	P(1)–C(8)	1.81(1)
P(1)–C(14)	1.85(1)	P(1)–C(14)	1.81(1)
P(2)–C(7)	1.83(1)	P(2)–C(7)	1.80(1)
P(2)–C(20)	1.79(1)	P(2)–C(20)	1.82(1)
P(2)–C(26)	1.83(1)	P(2)–C(26)	1.80(1)
N(1)–C(1)	1.39(1)	N(1)–C(1)	1.37(1)
N(1)–C(5)	1.40(1)	N(1)–C(5)	1.36(1)
C(1)–C(2)	1.38(2)	C(1)–C(2)	1.39(2)
C(1)–C(7)	1.44(1)	C(1)–C(7)	1.44(2)
C(2)–C(3)	1.38(2)	C(2)–C(3)	1.35(2)
C(3)–C(4)	1.36(2)	C(3)–C(4)	1.36(2)
C(4)–C(5)	1.43(2)	C(4)–C(5)	1.41(2)
C(5)–C(6)	1.37(1)	C(5)–C(6)	1.41(1)
		C(32)–O(1)	1.20(2)
		C(32)–O(2)	1.35(2)
		C(33)–O(2)	1.44(2)
P(1)–Pt–N(1)	84.2(2)	P(1)–Pd–N(1)	84.2(3)
P(1)–Pt–Cl(1)	94.6(1)	P(1)–Pd–C(32)	95.3(3)
P(2)–Pt–N(1)	84.9(2)	P(2)–Pd–N(1)	83.6(2)
P(2)–Pt–Cl(1)	96.3(1)	P(2)–Pd–C(32)	97.0(4)
Pt–P(1)–C(6)	100.3(4)	Pd–P(1)–C(6)	99.1(4)
Pt–P(1)–C(8)	117.3(3)	Pd–P(1)–C(8)	117.8(3)
Pt–P(1)–C(14)	116.9(3)	Pd–P(1)–C(14)	120.2(4)
C(6)–P(1)–C(8)	109.6(5)	C(6)–P(1)–C(8)	107.6(6)
C(6)–P(1)–C(14)	108.2(5)	C(6)–P(1)–C(14)	109.7(6)
C(8)–P(1)–C(14)	104.3(4)	C(8)–P(1)–C(14)	101.9(5)
Pt–P(2)–C(7)	100.4(4)	Pd–P(2)–C(7)	99.4(5)
Pt–P(2)–C(20)	121.4(3)	Pd–P(2)–C(20)	120.1(4)
Pt–P(2)–C(26)	115.3(3)	Pd–P(2)–C(26)	117.3(4)
C(7)–P(2)–C(20)	108.3(5)	C(7)–P(2)–C(20)	107.5(7)
C(7)–P(2)–C(26)	105.7(5)	C(7)–P(2)–C(26)	107.2(6)
C(20)–P(2)–C(26)	104.6(5)	C(20)–P(2)–C(26)	104.4(5)
P(1)–C(6)–C(5)	115.9(7)	P(1)–C(6)–C(5)	118.1(9)
P(2)–C(7)–C(1)	113.6(8)	P(2)–C(7)–C(1)	116.2(9)
N(1)–C(1)–C(7)	119.7(9)	N(1)–C(1)–C(7)	116.8(9)
N(1)–C(1)–C(2)	120.5(9)	N(1)–C(1)–C(2)	120.8(11)
C(2)–C(1)–C(7)	119.9(10)	C(2)–C(1)–C(7)	122.5(11)
N(1)–C(5)–C(6)	120.7(9)	N(1)–C(5)–C(6)	118.2(10)
N(1)–C(5)–C(4)	117.5(9)	N(1)–C(5)–C(4)	120.2(10)
C(4)–C(5)–C(6)	121.7(9)	C(4)–C(5)–C(6)	121.6(11)
C(1)–N(1)–C(5)	120.2(8)	C(1)–N(1)–C(5)	119.3(8)
Pt–N(1)–C(1)	120.9(6)	Pd–N(1)–C(1)	121.1(7)
Pt–N(1)–C(5)	118.9(6)	Pd–N(1)–C(5)	119.3(6)
		Pd–C(32)–O(1)	128.6(9)
		Pd–C(32)–O(2)	111.1(7)
		O(1)–C(32)–O(2)	120.3(9)
		C(32)–O(2)–C(33)	118.0(11)

trans-acetato(methoxycarbonyl)bis(triphenylphosphine)palladium (II) (1.984(4) Å) [7].

In both complexes there are intra- and intermolecular interactions of type $C-H_{phenyl} \cdots Cl$ or $C-H_{phenyl} \cdots O$ (Table 5).

Experimental

All preparations were carried out in deoxygenated solvents, and all operations were performed under carbon monoxide or dinitrogen by standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer 577 instrument. ^1H NMR spectra (at 200 MHz) and ^{31}P NMR spectra (at 81 MHz) were recorded with a Varian XL 200 pulsed Fourier transformer spectrometer. For ^{31}P NMR spectra the reference was external 85% phosphoric acid.

The Pt(dppf)Cl_2 was prepared by a published method [8].

Preparation of [Pd(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}]

(a) A solution of sodium methoxide (0.93 mmol) in 8 ml of methanol was added to a stirred solution of Pd(pnp)Cl_2 (0.46 mmol) in 10 ml of anhydrous methanol under carbon monoxide at atmospheric pressure. The mixture was stirred for 10 h at room temperature then filtered, and the filtrate was evaporated in vacuo and the residue extracted with benzene (10 ml). The extract was concentrated to 5 ml in vacuo and hexane (5 ml) added to produce red crystals, which were filtered off, washed with hexane, and dried in vacuo. Yield 95%. Analysis: Found: C, 62.2; H, 4.22; N, 2.0; P, 9.5. $C_{33}H_{29}NO_2P_2Pd$ calcd.: C, 61.94; H, 4.57;N, 2.19; P, 9.68%.

A crystal suitable for X-ray analysis was obtained by slow diffusion of hexane into a concentrated benzene solution of the complex.

(b) The same compound was obtained in a similar manner from [Pd(pnp)COOMe]Cl and sodium methoxide in a 1/1 molar ratio, either under dinitrogen or carbon monoxide.

Preparation of [Pt(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}]

A solution of sodium methoxide (0.85 mmol) in 10 ml of methanol was added to a stirred solution of Pt(pnp)Cl_2 (0.40 mmol) in 10 ml of anhydrous methanol under carbon monoxide at atmospheric pressure, and the mixture was stirred for 18 h at room temperature then filtered. The filtrate was evaporated in vacuo and the residue extracted with benzene (10 ml). Addition of hexane (15 ml) to the extract produced a crude dark red crystalline product (yield 87%), which was taken up in benzene and small amounts of hexane were successively added. The first crystals that separated contained some of the chloride complex, and the pure methoxycarbonyl complex (yield 70%) separated out. Analysis: Found: C, 54.6; H, 3.75; N, 2.0; P, 8.47%. $C_{33}H_{28}NO_2P_2Pt$ calcd.: C, 54.40; H, 4.01; N, 1.92; P, 8.50%.

Preparation of [PtCl{2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}]

A solution of sodium methoxide (0.52 mmol) in 10 ml of methanol was added to a stirred solution of Pt(pnp)Cl_2 (0.38 mmol) in 10 ml of methanol under dinitrogen, and the mixture was stirred for 16 h at room temperature, then filtered. The extract was evaporated in vacuo and the residue extracted with benzene. Addition of hexane to the extract produced red crystals, which were filtered off, washed with hexane, and dried in vacuo. Yield 94%. Analysis: Found: C, 52.0; H, 3.90; Cl, 5.0; N, 2.0; P, 9.0%. $C_{31}H_{26}ClNP_2Pt$ calcd.: C, 52.81; H, 3.72; Cl, 5.03; N, 1.99; P, 8.79%.

A crystal suitable for X-ray analysis was obtained by slow diffusion of hexane into a concentrated benzene solution of the complex.

Reaction of [Pd(COOMe){2-(CHPPh$_2$)-6-(CH$_2$PPh$_2$)pyridine}] with acids

Aqueous perchloric acid (0.026 ml of an 11.7 *M* solution) was added to a suspension of the complex (0.22 mmol) in diethyl ether (10 ml), and the mixture was stirred at room temperature under dinitrogen for 3 h. The pale-yellow solid precipitate was filtered off, washed with diethyl ether, and dried in vacuo. Analysis: Found: C, 52.8; H, 4.1; N, 2.0; Cl, 5.0%. $C_{33}H_{30}NO_6ClP_2Pd$ calcd.: C, 53.53; H, 4.08; N, 1.89; Cl, 4.79%. The known [Pd(pnp)COOMe]Cl was obtained similarly by using hydrochloric acid (0.025 ml of a 12 *M* solution) and was identified by its IR spectrum and elemental analysis (Found: C, 58.3; H, 4.7; Cl, 5.1; P, 9.0%).

Preparation of Pt(dppf)(COOMe)$_2$

A solution of sodium methoxide (0.70 mmol) in methanol (8 ml) was added to a suspension of $Pt(dppf)Cl_2$ (0.30 mmol) in methanol (10 ml) under carbon monoxide at atmospheric pressure, and the mixture was stirred for 24 h at room temperature. After evaporation of the solvent in vacuo, the residue was extracted with benzene (15 ml).The extract was concentrated in vacuo (to 7 ml) and hexane (5 ml) added to produce a yellow precipitate (yield 95%), which was recrystallized from benzene/hexane. Analysis: Found: C, 53.0; H, 4.0; P, 7.05%. $C_{38}H_{34}O_4P_2FePt$ calc.: C, 52.61; H, 3.95; P, 7.14%.

X-Ray data collections, structure solutions and refinements

Crystal data and data collection parameters for the two complexes are given in Table 6. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. A correction for absorption effects was applied to the data for **1** and **2** [9,10] (maximum and minimum transmission factor values: 1.3140 and 0.8346 for **1**, 1.4218 and 0.6254 for **2**). Both structures were solved by Patterson and

Table 5

Most significant contacts involving phenyl ligands

	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
Complex 1				
C(9)–H(9)...Cl(1)	1.04	3.57(1)	2.69	142
C(25)–H(25)...Cl(1)	1.04	3.59(1)	2.67	147
C(4)–H(4)...Cl(1) [a]	0.97(12)	3.68(1)	2.88(12)	140(9)
C(28)–H(28)...Cl(1) [b]	0.92(11)	3.67(1)	2.97(12)	135(9)
Complex 2				
C(9)–H(9)...O(1)	0.76(11)	3.43(1)	2.70(13)	161(12)
C(25)–H(25)...O(2)	1.03	3.25(2)	2.44	135
C(2)–H(2)...O(1) [c]	1.03(12)	3.47(1)	2.62(13)	140(9)
C(22)–H(22)...O(1) [d]	0.80(12)	3.40(1)	2.62(13)	160(15)
C(24)–H(24)...O(2) [e]	0.93(16)	3.38(3)	2.70(16)	130(9)

[a] $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$. [b] $x, y, z-1$. [c] $x, 1+y, z$. [d] $-x, \frac{1}{2}+y, -\frac{1}{2}-z$. [e] $-x, -y, -z$.

Table 6

Crystal data and details of data collection

	1	**2**
Formula	$C_{31}H_{26}ClNP_2Pt$	$C_{33}H_{29}NO_2P_2Pd$
M.W.	705.044	639.945
Space group	$P2_1/n$	$P2_1/c$
a (Å)	15.915(5)	17.838(6)
b (Å)	19.337(8)	10.182(6)
c (Å)	8.861(6)	18.008(5)
β (°)	98.94(2)	115.99(2)
V (Å^3)	2695(2)	2940(2)
Z	4	4
D_c (Mg m^{-3})	1.738	1.446
Reflection for lattice parameters number	30	30
θ-range (°)	21–32	24–42
Radiation	Cu-K_α (Ni-filtered)	Cu-K_α (Ni-filtered)
Wavelength (Å) ($\bar{\lambda}$)	1.541838	1.541838
$F(000)$	1376	1304
Temperature (K)	295	295
Crystal size (mm^3)	0.05×0.24×0.16	0.14×0.61×0.63
Colour	red	red
Diffractometer	Siemens AED	Siemens AED
μ (mm^{-1})	12.081	6.491
θ-range (°)	3–70	3–70
h-range	−19/19	−21/19
k-range	0/23	0/12
l-range	0/10	0/19
Standard reflection checked after every 50	−4 8 2	−13 0 12
Intensity variation	none	none
Scan speed (° s^{-1})	0.20–0.10–0.05	0.20–0.10–0.05
Scan width (°)	1.20+0.142tg θ	1.20+0.142tg θ
No. of measured reflections	5513	5616
Condition for observed reflections	$I \geqslant 2\sigma(I)$	$I \geqslant 3\sigma(I)$
No. of reflections used in the refinement	3338	3088
No. of refined parameters	393	456
$R = \Sigma\|\Delta F\|/\Sigma\|F_0\|$ (%)	4.18	6.63
$R_w = [\Sigma w(\Delta F)^2/\Sigma wF_0^2]^{1/2}$ (%)	4.83	8.44
k, g ($w = k[\sigma^2(F_0) + gF_0^2]^{-1}$)	$k = 0.6435$, $g = 0.001253$	$k = 1.1720$, $g = 0.003735$

Fourier techniques and refined by full-matrix least-squares using the SHELX system of programs [11] with initially isotropic and then anisotropic thermal parameters. In both complexes all the hydrogen atoms were clearly localized from a difference Fourier synthesis and were allowed to vibrate isotropically in the last full-matrix least-squares cycle (except the phenyl H(9), H(15), H(22), H(24), H(25), H(27), H(29) and H(30) ones in **1**, and the phenyl H(16), H(25) and methylenic H(333) ones in **2** which were placed in their found positions and included as fixed contributions with isotropic thermal parameters $U = 0.10$ Å^2). The atomic scattering factors, corrected for anomalous dispersion, were taken from International Tables for X-Ray Crystallography [12]. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first stages of the refinements, and subsequently weights were applied according to the scheme $w = k[\sigma^2(F_0) + g \cdot$

Table 7

Fractional atomic coordinates ($\times 10^4$) (with esd in parentheses) for the non-hydrogen atoms of complex **1**

Atom	*x*	*y*	*z*
Pt	2527(1)	681(1)	2636(1)
Cl(1)	1848(2)	−304(1)	3306(3)
P(1)	1546(2)	1424(1)	3358(3)
P(2)	3624(2)	124(1)	1760(3)
N(1)	3080(5)	1548(4)	2017(8)
C(1)	3822(6)	1518(5)	1366(11)
C(2)	4170(7)	2114(6)	867(14)
C(3)	3795(8)	2749(6)	1028(16)
C(4)	3083(8)	2794(6)	1705(15)
C(5)	2709(5)	2189(5)	2261(10)
C(6)	1988(6)	2225(5)	2923(12)
C(7)	4238(7)	866(5)	1252(14)
C(8)	451(6)	1357(5)	2354(11)
C(9)	152(7)	788(7)	1625(18)
C(10)	−662(8)	777(9)	834(21)
C(11)	−1152(8)	1339(10)	701(17)
C(12)	−872(10)	1895(9)	1418(28)
C(13)	−59(8)	1929(6)	2291(20)
C(14)	1431(6)	1429(5)	5408(11)
C(15)	764(7)	1117(7)	5929(12)
C(16)	717(9)	1149(9)	7469(18)
C(17)	1309(11)	1488(9)	8453(15)
C(18)	1950(10)	1797(7)	7933(14)
C(19)	2052(7)	1770(6)	6413(12)
C(20)	4325(6)	−436(5)	2968(11)
C(21)	5204(6)	−425(7)	3013(13)
C(22)	5745(7)	−874(8)	3831(16)
C(23)	5386(8)	−1367(8)	4709(15)
C(24)	4534(9)	−1396(7)	4710(15)
C(25)	4005(7)	−915(6)	3843(13)
C(26)	3332(6)	−365(5)	−6(11)
C(27)	2822(6)	−23(6)	−1185(12)
C(28)	2601(8)	−368(9)	−2566(13)
C(29)	2882(8)	−1023(9)	−2777(14)
C(30)	3384(7)	−1359(6)	−1582(14)
C(31)	3615(6)	−1028(5)	−225(12)

$F_0^2]^{-1}$ and the final *k* and *g* values as well as the final *R* are given in Table 6. Final ΔF maps showed no unusual features and the minimum and maximum heights were -1.11 and 1.22 e Å^{-3} in **1** and -1.81, 1.35 e Å^{-3} in **2** (maxima close to the metal atoms).

Most significant contact distances involving Ph ligands in complexes 1 and 2 are given in Table 5 and final atomic coordinates for the non-hydrogen atoms in Table 7 and 8, respectively. List of atomic coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors for both structures can be obtained from the authors on request.

All calculations were performed on the CRAY X-MP/48 computer of the "Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario

Table 8

Fractional atomic coordinates ($\times 10^4$) (with esd in parentheses) for the non-hydrogen atoms of complex **2**

Atom	x	y	z
Pd	2544(1)	847(1)	−89(1)
P(1)	3705(2)	328(3)	1090(2)
P(2)	1535(2)	1803(3)	−1247(2)
O(1)	2281(5)	−1767(7)	−794(5)
O(2)	1642(5)	−1331(7)	−8(6)
N(1)	2965(5)	2761(7)	210(5)
C(1)	2554(7)	3785(9)	−295(7)
C(2)	2911(11)	5033(11)	−165(9)
C(3)	3666(11)	5232(13)	481(10)
C(4)	4067(9)	4244(12)	1020(9)
C(5)	3702(7)	2987(10)	883(7)
C(6)	4086(7)	1931(11)	1423(8)
C(7)	1751(10)	3504(12)	−960(8)
C(8)	4523(6)	−584(9)	986(6)
C(9)	4389(7)	−1232(10)	264(7)
C(10)	5036(8)	−1919(11)	207(8)
C(11)	5820(8)	−1932(12)	863(9)
C(12)	5954(7)	−1265(14)	1562(8)
C(13)	5318(7)	−609(11)	1630(7)
C(14)	3606(6)	−551(11)	1918(7)
C(15)	3451(8)	−1849(13)	1848(9)
C(16)	3339(10)	−2559(18)	2462(13)
C(17)	3371(12)	−1927(29)	3129(15)
C(18)	3550(11)	−620(27)	3206(10)
C(19)	3638(8)	88(16)	2613(8)
C(20)	437(6)	1519(12)	−1520(7)
C(21)	−193(8)	1911(13)	−2252(8)
C(22)	−1020(8)	1698(13)	−2422(9)
C(23)	−1200(9)	1106(15)	−1845(11)
C(24)	−592(10)	707(20)	−1122(11)
C(25)	241(8)	896(18)	−962(9)
C(26)	1614(6)	1586(10)	−2205(6)
C(27)	1843(8)	2541(12)	−2601(8)
C(28)	1903(10)	2293(18)	−3323(10)
C(29)	1719(13)	1100(22)	−3655(10)
C(30)	1485(16)	121(18)	−3309(12)
C(31)	1444(12)	353(14)	−2572(10)
C(32)	2144(7)	−996(10)	−364(7)
C(33)	1276(11)	−2619(14)	−171(11)

dell'Italia Nord-Orientale (Cineca, Casalecchio, Bologna)" with the financial support from the University of Parma, and on the GOULD-SEL 32/77 computer of the "Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma". The program PARST [13] and ORTEP [14] were also used.

Acknowledgement

The authors thank the C.N.R. (Rome) and the Ministero della Pubblica Istruzione for a financial support, Prof. G. Predieri and Mr. S. Creti for experimental NMR assistance, Mr. U. Farella for the drawings.

References

1 P. Giannoccaro, G. Vasapollo and A. Sacco, J. Chem. Soc. Chem. Comm., (1980) 1136; P. Giannoccaro, G. Vasapollo, C.F. Nobile and A. Sacco, Inorg. Chim. Acta, 61 (1982) 69; A. Sacco, P. Giannoccaro and G. Vasapollo, ibid., 83 (1984) 125.

2 G. Vasapollo, C.F. Nobile and A. Sacco, J. Organomet. Chem., 296 (1985) 435.

3 F. Rivetti and U. Romano, Chim. Ind., 62 (1980) 7.

4 H.E. Bryndza, S.A. Kretchmar and T.H. Tulip, J. Chem. Soc. Chem. Comm., (1985) 977.

5 H. Qichen, X. Minzhi, Q. Yanlong, X. Weihus, S. Meicheng and T. Youqi, J. Organomet. Chem., 287 (1985) 419.

6 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, J. Am. Chem. Soc., 103 (1981) 5115.

7 G. Del Piero and M. Cesari, Acta Cryst., B, 35 (1979) 2411.

8 A.L. Bandini, G. Banditelli, G. Minghetti and G. Sana, in M. di Pula (Ed.), Abstr. XIX Congresso Nazionale di Chimica Inorganica, Cagliari, A22 (1986) 75.

9 N. Walker and D. Stuart, Acta Cryst., A, 39 (1983) 158.

10 F. Ugozzoli, Comp. Chem., 11 (1987) 109.

11 G.M. Sheldrick, System of Crystallographic Computer Programs, University of Cambridge, 1976.

12 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, Vol. IV, p. 99, p. 149, 1974.

13 M. Nardelli, Comp. Chem., 7 (1985) 95.

14 C.K. Johnson, ORTEP, Report ORNL-3794, revised, Oak Ridge National Laboratory, Tennessee, 1965.