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The reactivity of the dinuclear halo-bridged cycloplatinated complex [Pt(μ-Cl){(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}]$_2$ towards neutral ligands

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ABSTRACT

The reactivity of (*cis*- + *trans*-)[Pt(μ-Cl){(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}]$_2$ (**1**) towards several ligands L (L = RCN, P(OMe)$_3$, DMSO, NHEt$_2$, py, CO, C$_2$H$_4$, C$_8$H$_{16}$) has been studied. Ethylene and 1-octene do not react while the other reactions proceed with cleavage of the halide bridge and formation of one or both geometrical isomers of [PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}L] (**2**–**8**) depending on the nature of the entering ligand. In some cases equilibrium reactions (L = RCN, DMSO, CO, py) were observed. The structures of [SP4-3]-[PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}(S)DMSO] ([SP4-3]-**4**) and [SP4-4]-[[PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}py] ([SP4-4]-**6**) are reported.

1. Introduction

Cyclometalated complexes have been successfully used in organic synthesis, catalysis and photochemistry, so their chemistry has attracted a considerable attention as evidenced by the number of reviews on this topic [1]. In this field, platinum group metals have been largely studied, especially palladium derivatives. Orthometallated arylphosphite derivatives of palladium and platinum of the type [M(μ-Cl){(κ^2-P,C)P(OC$_6$H$_3$X)(OR)$_2$}]$_2$ are known since the seventies of last century [2] and recently, they have been successfully used as catalysts in several organic reactions [3]. Moreover, their synthesis and spectroscopic features have been re-examined [4,5] and the crystal and molecular structure of *trans*-[Pt(μ-Cl){(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}]$_2$ (*trans*-**1**) has been reported [5]. Furthermore, the reactivities of μ-chloro bridged dinuclear cyclometalated Pd(II) complexes [Pd{(4-R)C$_6$H$_3$CH]N–C$_6$H$_3$–2,6-^{i}Pr$_2$}(μ-Cl)]$_2$ (R = H, OMe) with mono-, bi- and tridentate ligands (aromatic *N*-heterocycles) [6] and of the cycloplatinated dichloro-bridged complex of the 2-tolylpyridine, [(2-Tolpy)Pt(μ-Cl)]$_2$, with monodentate ligands [7] have been recently studied. In view of the multidisciplinary interest towards these derivatives and due to our previous experience in the synthesis, characterization and reactivity of halo-bridged dinuclear platinum complexes [5,8], we have undertaken the study of the reactions of **1** with several neutral ligands. Such reactions were expected to afford the mononuclear complexes [PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}L] through the chloride bridge splitting of Eq. (1).

$$2L + \left[Pt(\mu - Cl)\left\{\left(\kappa^2 - P, C\right)P(OC_6H_4)(OPh)_2\right\}\right]_2 \rightarrow 2\left[PtCl\left\{\left(\kappa^2 - P, C\right)P(OC_6H_4)(OPh)_2\right\}L\right] \quad (1)$$

This paper reports the reactions of **1** (as the mixture of its geometrical isomers) with C$_2$H$_4$, C$_8$H$_{16}$ (1-octene), RCN (R = Me, Et), CO, Me$_2$SO (DMSO), P(OMe)$_3$, C$_5$H$_5$N (py) and NHEt$_2$.

A few reactions do not proceed, some are well displaced to the right, and others are easily reversed equilibria.

2. Results and discussion

[Pt(μ-Cl){(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}]$_2$, **1**, is usually obtained [2,4,5] as the mixture of its geometrical isomers, *cis* and *trans*, the latter prevailing in both chloroform and toluene.

In the course of this work the reactions of **1** with a series of neutral ligands have been studied. It was expected, as usual for complexes with bridging halogens, that bridge cleavage occurred with formation of one or both the geometrical isomers of the mononuclear complexes [PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}L]. As a matter of fact, the complexes **2**–**7** were readily obtained (see Scheme 1). Nevertheless, equilibrium reactions were observed not only for the "weak" ligands RCN and DMSO, but also for the relatively "robust" ligands CO and pyridine. Moreover, terminal alkenes unexpectedly did not react.

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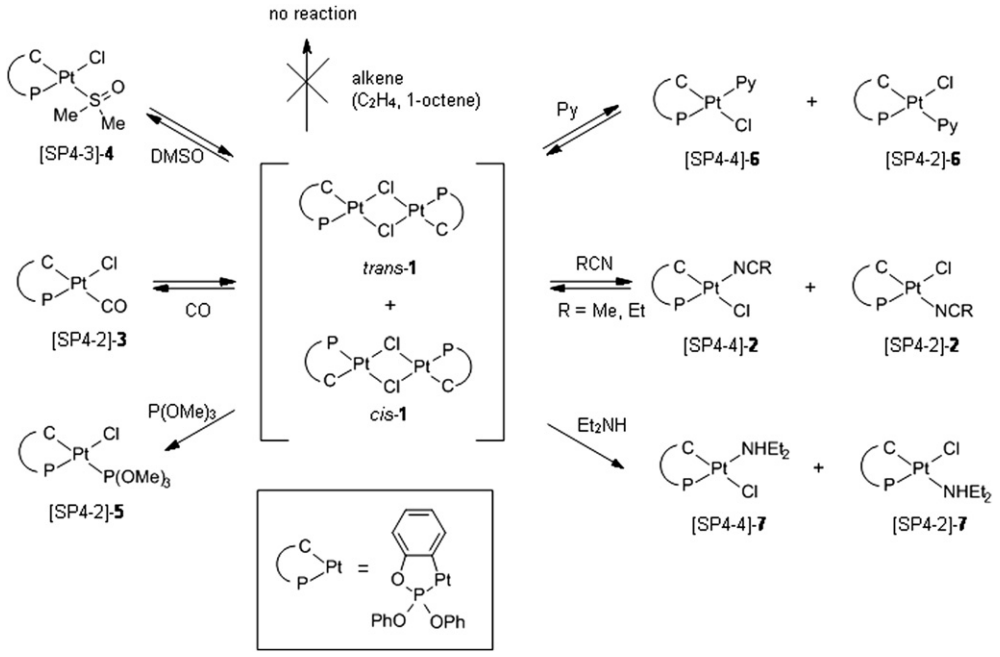

Scheme 1. Reactivity of **1** towards neutral ligands.

The reactions have been monitored by ^{31}P and ^{195}Pt NMR (see Table 1).

A solution of **1** in MeCN at about 50 °C yields [SP4-2]- and [SP4-4]-**2a**. Similarly, the reaction of **1** with EtCN afforded the mixture of the two geometrical isomers of **2b**. Both **2a** and **2b** promptly release the coordinated nitrile when the concentration of free nitrile decreases (Scheme 1) thus reverting to **1**. ^{31}P and ^{195}Pt NMR data are reported in Table 1. Although [SP4-2]-**2b** had been previously isolated and structurally characterized in the solid state [5], its rapid isomerisation in solution prevented the definition of its spectroscopic features, consequently the assignment of the signals to the different isomers was not possible.

In view of the reactivity with alkylnitrile reported above, we expected **1** to react with ethylene with formation of [PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}(C$_2$H$_4$)], possibly through an equilibrium reaction. Such a hypothesis stemmed from the results of studies on the CO/alkylnitriles [9] and CO/alkenes [10] competition towards the {PtCl$_2$(CO)} fragment, showing that the coordination ability of EtCN was similar to that of alkenes (1-octene, cyclohexene), terminal alkene being slightly preferred. Surprisingly, no reaction between **1** and C$_2$H$_4$ ($P_{C_2H_4}$ = 1 atm, room temperature) in 1,2-dichloroethane (1,2-DCE) was observed: ^{31}P NMR spectra of the mixture recorded after 1, 5, 12, 24 h showed no signals in addition to those of the precursor. In order to force the reaction to the right by increasing the alkene concentration without involving superatmospheric pressure, a liquid terminal alkene (1-octene) was used. The reaction was carried out with a large excess of the alkene with the addition of some 1,2-DCE to increase the solubility of the metal complex.

By monitoring the reaction by ^{31}P NMR it was inferred that no reaction occurred from room temperature to about 90 °C. The {[PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}]} fragment appears to prefer the chloro-bridged dinuclear arrangement rather than the alkene coordination.

Unlike alkenes, CO reacted smoothly with **1**. The resulting product, **3**, has already been reported in the literature and the assignment of its geometry ([SP4-2], CO *trans* to C) was done on the basis of the ^{31}P- and ^{13}C NMR parameters [4]. We have confirmed that CO was absorbed by a solution of **1** in CH$_2$Cl$_2$ ($P_{CO} \approx 1$ atm, $T = 25$ °C) with the exclusive production of only one geometrical isomer (Scheme 1), as inferred by monitoring the reaction via ^{31}P NMR [4]. In addition, ^{195}Pt NMR spectra of the reaction mixture were recorded immediately after the introduction of CO into the reactor and regularly every 2 h for one day. Only one resonance was observed (see Table 1). Consistently, the IR spectrum of the solution showed only one CO stretching band at 2125 cm^{-1}. Thus, under CO the system appears to contain only the complex [SP4-2]-**3**. However, it was observed that the evaporation of the solution at room temperature under reduced pressure caused the release of CO with formation of **1**, thus proving that we were dealing with an easily displaceable equilibrium reaction. In the platinum(II) chlorocarbonyl chemistry, spontaneous dimerization in mild conditions by release of CO and formation of chloride bridges are rare [11].

The reaction of **1** with neat DMSO rapidly led to a solution containing only one isomer of the mononuclear product **4** (Scheme

Table 1
^{31}P and ^{195}Pt NMR data for **1** and [PtCl{(κ^2-P,C)P(OC$_6$H$_4$)(OPh)$_2$}L].

	L	^{31}P δ/ppm	^{195}Pt δ/ppm	$^1J_{P-Pt}$/Hz	Solvent	Ref.
trans-**1**		88.4	−4144	7760	$CDCl_3$	[4]
cis-**1**		85.8	−4038	7860	$CDCl_3$	[4]
2a	MeCN	100.5		6700	MeCN	This
[SP4-4]+[SP4-2]		94.6		7469		work
2b	EtCN	101.2		6750	$MeNO_2$	This
[SP4-4]+[SP4-2]		95.8		6806		work
[SP4-2]-**3**[a]	CO	105.6	−4518	5949	CH_2Cl_2	This work
[SP4-3]-**4**	DMSO	99.6	−4331	6681	DMSO	This work
[SP4-3]-**5**[a]	$P(OMe)_3$	128.8[b]	−4547	3168[b]	$CDCl_3$	This
		105.7		6398		work
[SP4-4]-**6**	py	95.4	−4197	6602	$CDCl_3$	This
[SP4-2]-**6**		95.5	−4128	7063		work
7	$NHEt_2$	102.0		6501	1,2-DCE	This
[SP4-4]+[SP4-2]		92.0		7276		work

[a] See also Ref. [4].
[b] Coordinated $P(OMe)_3$ ($^2J_{P-P}$ 32 Hz).

1), as revealed by ^{31}P and ^{195}Pt NMR spectra of the reaction mixture (see Table 1) recorded shortly after the addition. After 24 h, the spectra were unchanged, showing that no isomerisation had occurred. The product was recovered by evaporating the solvent under vacuum at room temperature. The IR spectrum of the product in the solid state showed a band at 1119 cm^{-1}, due to the SO stretching vibration of coordinated DMSO. The position of this band suggests that the sulfoxide is S-coordinated: in fact free DMSO absorbs at 1050 cm^{-1}, while the band shifts to lower or higher wavenumbers for the O- or S-coordinated ligand, respectively [12]. ^{13}C- and ^{1}H NMR spectra confirmed this hypothesis. The resonances of the sulphur-bonded carbon atom in dialkylsulfoxides are up- or downfield shifted in the complexes with respect to the free ligand when O- or S-coordination is adopted, respectively [13]. The ^{13}C NMR spectrum of our compound in $CDCl_3$ showed the methyl signal at 43.3 ppm, to be compared with 41.0 ppm of the free ligand in the same solvent, which suggests S-coordination. Moreover, the ^{1}H NMR spectrum of the complex (in $CDCl_3$) showed a relatively high coupling constant of the methyl protons with the active platinum nucleus (9.5 Hz), consistent with a $^{3}J_{Pt-H}$ of a S-coordinated sulfoxide rather than with a $^{4}J_{Pt-H}$ of a O-coordinated ligand.

The NMR spectra of chloroform solution of **4** showed, besides the product signals, additional resonances due to **1** and to free DMSO, suggesting that the ligand is rather easily released. A confirm came from the reaction of **1** with 2 equivalents of DMSO in $CDCl_3$: NMR spectra of the reaction mixture showed the presence of **1**, **4** and free DMSO, with about 20% of platinum in the form of **1**. Moreover, starting from chloroform solution of **4**, complete conversion to **1** was obtained by operating under vacuum at about 90 °C.

X-Ray diffraction studies on single crystals of **4** confirmed that the complex contained S-coordinated DMSO and allowed to define the geometry around platinum as [SP4-3], *i.e.* with S *trans* to C (see Fig. 1). Selected bond lengths and angles are reported in Table 2.

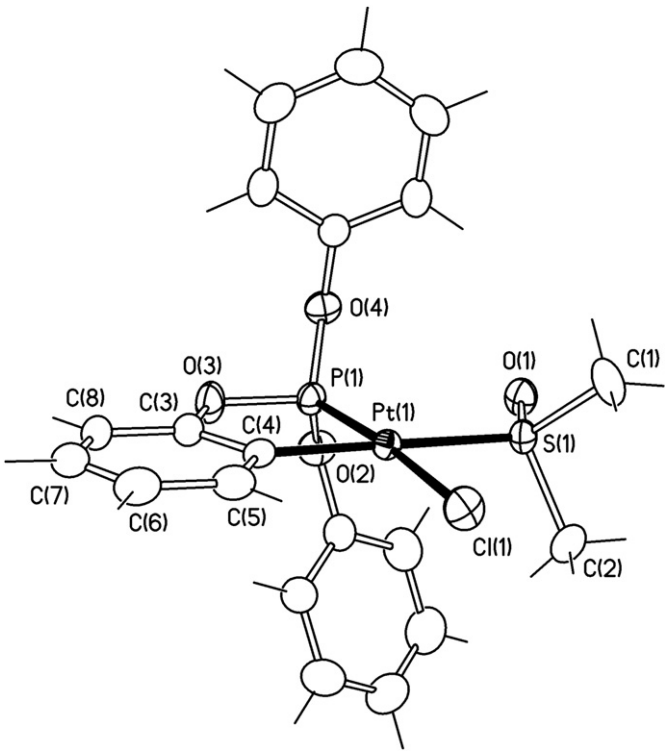

Fig. 1. View of the molecular structure [SP4-3]-**4**. Thermal ellipsoids are at 30% probability.

Table 2
Selected bond lengths (Å) and angles (°) for [SP4-3]-**4**.

Pt(1)–C(4)	2.041(3)	Pt(1)–S(1)	2.3260(9)
Pt(1)–P(1)	2.1578(9)	Pt(1)–Cl(1)	2.3427(9)
C(4)–Pt(1)–Cl(1)	93.25(10)	P(1)–Pt(1)–S(1)	96.38(3)
C(4)–Pt(1)–P(1)	81.88(10)	S(1)–Pt(1)–Cl(1)	88.43(4)
P(1)–Pt(1)–Cl(1)	174.39(4)	C(4)–Pt(1)–S(1)	177.94(10)

The platinum coordination is square planar with a maximum deviation of 0.03 Å. The orthometalation of a phenyl group of the triphenylphosphite ligand produces a planar $OPPtC_2$ five membered ring. This feature is also observed in the other platinum orthometalated triarylphosphite structurally characterized [5,14]. Within the five membered ring the greater lengths of the Pt–P and Pt–C bonds with respect to the C–C and C–O ones causes a decrease of P(1)–Pt(1)–C(4) angle from the ideal value for a pentagon (108°) to about 82°. The narrowing of this angle is the more relevant deviation from the ideal square coordination around the metal. While Pt–Cl, Pt–C and Pt–S bond lengths are as expected, Pt–P bond is slightly shorter than the mean value, 2.23 Å, normally found in similar compounds, as results from a rapid survey on the CCDC database [15].

The reaction of **1** with $P(OMe)_3$ has already been reported and the assignment of the product geometry, [SP4-2], *i.e.* with $P(OMe)_3$ *trans* to C, has been proposed on the basis of NMR data [4].

We have confirmed that by reacting **1** with the stoichiometric amount of $P(OMe)_3$ in $CDCl_3$ only one isomer of **5** is obtained, corresponding to that reported in the literature [4], as inferred by comparison of the NMR data (see Table 1). To compare this reaction with the others discussed so far, we controlled the possibility to convert **5** to **1** by operating under vacuum at relatively high temperature (up to 120 °C, a temperature higher than the b.p. of $P(OMe)_3$). In the course of these experiments **5** remained unchanged and no formation of **1** was noticed. At variance with the other mononuclear complexes **2**–**4**, the trimetylphosphite complex [SP4-2]-**5** appears to be stable with respect to ligand release, in spite of the strong *trans*-effect of the aryl group [16].

By monitoring the reaction of **1** with the stoichiometric amount of pyridine (in $CDCl_3$) via ^{31}P NMR, the disappearance of the precursor was observed and the mixture of the two geometrical isomers of **6** [Scheme 1] was obtained. The molar ratio between the two isomers was constant with time, thus preventing the possibility to detect the kinetic product. The reaction can be reversed by operating under vacuum at relatively high temperatures ($T = 60$–90 °C).

Single crystals of [SP4-2]-**6** separated out from 1,2-DCE/pentane ($v/v = 1$) and the molecular and crystal structure of the complex was studied by X-Ray diffraction methods. Fig. 2 shows a view of the molecular structure and selected bond lengths and angles are reported in Table 3.

A comparison with the molecular structure of [SP4-3]-**4** shows that the substitution of the DMSO with the pyridine leaves unaltered the coordination geometry around the metal. Due to the different encumbrance of the coordinated pyridine with respect to DMSO the C_6H_5 groups of the phosphite are differently oriented.

The assignment of the NMR signal to the two geometrical isomers of **6** was achieved by recording a ^{31}P NMR spectrum of a freshly prepared solution ($CDCl_3$) of [SP4-2]-**6**: the spectrum showed the resonance at 96.0 ppm ($^{1}J_{P-Pt} = 7063$ Hz) only. After a few hours, the equilibrium mixture of the two isomers was present.

When **1** was treated with the stoichiometric amount of $NHEt_2$ in 1,2-DCE as solvent, a ^{31}P NMR spectrum, recorded 30 min after the amine addition, showed the absence of the signals due to the precursor and the presence of two resonances attributable to the

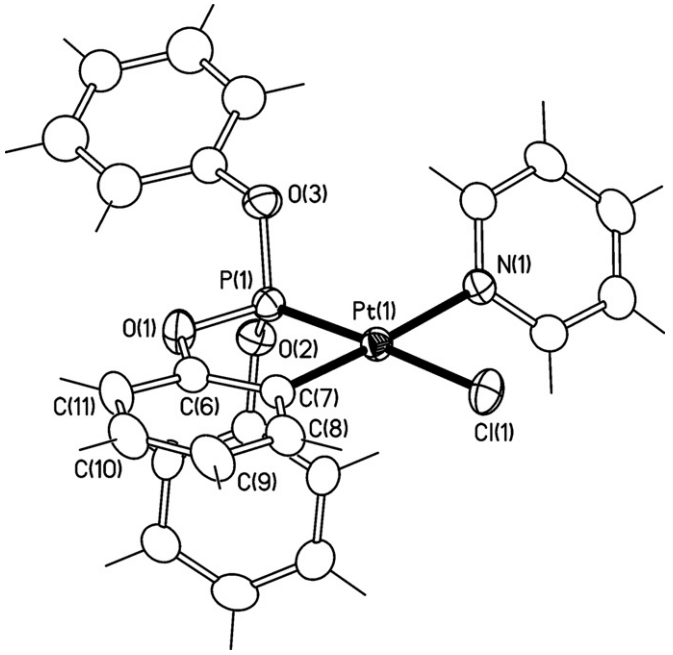

Fig. 2. View of the molecular structure of [SP4-2]-**6**. Thermal ellipsoids are at 30% probability. The less populated position of the disordered phenyl group has been omitted for clarity.

two geometrical isomers of **7** (Scheme 1): the ratio between the main signal (101.9 ppm) and the other (92.1 ppm) was 93:7. After 24 h, a new ^{31}P NMR spectrum presented the same signals but the ratio was changed to 40:60. Therefore, the kinetic product of the reaction, associated to the resonance at 101.9 ppm, slowly isomerises until the equilibrium mixture is obtained. A strong *trans*-effect is associated with both triarylphosphite and aryl ligands [13]; thus, it is not easy to predict the geometry of the kinetic product by exploiting this effect. Nevertheless, we suggest that the kinetic product is the [SP4-2] isomer where $NHEt_2$ is *trans* to C. Our proposal is supported by the finding that the reactions of **1** with CO, DMSO, $P(OMe)_3$ (Scheme 1) afford the isomer with L *trans* to C (products **3**, **4**, **5**, respectively), as observed immediately after the reagent mixing, corresponding to the fast formation of the thermodynamic product.

In summary, the reactions of **1** with the carbon-based ligands CO, C_2H_4, 1-octene, the group 15 ligands MeCN, EtCN, Py, $NHEt_2$, $P(OMe)_3$ and with DMSO have been examined. For each ligand except alkenes, chloro-bridge cleavage was observed. Of the two possible geometrical isomers both were obtained with the nitrogen-based ligands, while only the isomers with L *trans* to C were observed with the ligands CO, $P(OMe)_3$ and the S-ligated DMSO. It is reasonable to suggest that ligands with a strong π-acid character prefer the position *trans* to the good σ-donor C- rather than to the π-acid P coordination site of the orthometalated phosphite. Moreover, only the products obtained with $NHEt_2$, **7**, and $P(OMe)_3$, **5**, turned out to be stable in solution in the absence of the free ligand even *in vacuo* at relatively high temperature (30–90 °C).

Table 3
Selected bond lengths (Å) and angles (°) for [SP4-2]-**6**.

Pt(1)–C(7)	2.018(3)	Pt(1)–N(1)	2.131(2)
Pt(1)–P(1)	2.1424(8)	Pt(1)–Cl(1)	2.3411(7)
C(7)–Pt(1)–Cl(1)	93.85(8)	P(1)–Pt(1)–N(1)	97.18(7)
C(7)–Pt(1)–P(1)	81.68(8)	N(1)–Pt(1)–Cl(1)	87.27(7)
P(1)–Pt(1)–Cl(1)	175.54(3)	C(7)–Pt(1)–N(1)	176.60(10)

On the other hand, the complexes with the other ligands, **2** (L = RCN), **3** (L = CO), **4** (L = DMSO), **6** (L = Py) were found to revert to **1**, their stability depending on the nature of L increasing in the order: RCN < CO < DMSO < py.

It is known that alkylnitriles and dialkylsulphoxide are easily displaceable ligands, commonly used for this reason also in catalysis [17]. Although CO and pyridine are not usually so easily displaced, we have to conclude that their bond to platinum is not sufficiently strong to prevent (when the free ligand concentration decreases) the shift to the left side of the entropically disfavoured equilibrium 1. On the other hand, the more basic $NHEt_2$ [18] and the trimethylphosphite produce more stable complexes, so that reaction **1** becomes irreversible.

3. Experimental section

3.1. General comments

All manipulations were performed under a dinitrogen atmosphere, if not otherwise stated. Solvents and liquid reagents were dried according to reported procedures [19].

^{1}H-, ^{13}C-, ^{31}P and ^{195}Pt NMR spectra were recorded with a Bruker "Avance DRX 400" spectrometer, in $CDCl_3$ solution if not otherwise stated. Chemical shifts were measured in ppm (δ) from TMS by residual solvent peaks for ^{1}H and ^{13}C, from aqueous (D_2O) H_3PO_4 (85%) for ^{31}P and from aqueous (D_2O) hexachloroplatinic acid for ^{195}Pt. A sealed capillary containing C_6D_6 was introduced in the NMR tube to lock the spectrometer when non-deuterated solvents were used. FTIR spectra in the solid state were recorded with a Perkin–Elmer "Spectrum One" spectrometer, with the ATR technique. FTIR spectra in solution were recorded with a Perkin–Elmer "Spectrum 100" spectrometer. Intensity of bands: w = weak, m = medium, s = strong. A 0.1 mm cell supplied with CaF_2 windows was used. Elemental analyses (C, H, N) were performed at Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine. The products undergoing conversion to **1** under vacuum were not analysed.

{Pt(μ-Cl)[(κ^2-P,C)P(OC_6H_4)(OC_6H_5)$_2$]}$_2$, **1**, [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(EtCN)], **2b**, [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(CO)], **3**, and [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}($P(OMe)_3$)], **5**, were prepared according to the literature [4,5].

3.2. Reaction of *1* with alkenes (ethylene and 1-octene)

In a 50 mL reactor, 193.0 mg (1.8×10^{-1} mmol) of **1** were treated with C_2H_4 ($P = 1$ atm) in 1,2-DCE. No gas uptake was observed. A ^{31}P NMR spectrum of the yellow solution recorded after 24 h stirring showed only the signals due to **1**. From the reaction mixture **1** was recovered unchanged.

In a 25 mL reactor 152.9 mg (1.4×10^{-1} mmol) of **1** were suspended in a mixture of 1-octene (7.0 mL) and 1,2-DCE (2.0 mL). The suspension was stirred at room temperature (48 h). A ^{31}P NMR spectrum showed the signals due to **1** only. The suspension, heated at 90 °C, turned into a yellow solution. A ^{31}P NMR spectrum of the solution showed the signals due to **1** only.

3.3. Formation of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(DMSO)], *4*

In a 50 mL Schlenk tube, 5 mL of DMSO were added to 92.4 mg (8.5×10^{-2} mmol) of **1**. A yellow solution was obtained. NMR spectra were recorded on the reaction mixture. ^{31}P NMR: 99.6 ($^{1}J_{P-Pt}$ = 6681 Hz) ppm; ^{195}Pt NMR: −4331 (d, $^{1}J_{Pt-P}$ = 6681 Hz) ppm. The solution was evaporated to dryness: the pale yellow solid residue was stored in vials under dinitrogen (about 84% yield). The product was contaminated by **1**. ^{31}P NMR ($CDCl_3$): 98.4 ($^{1}J_{P-Pt}$ = 6629 Hz) ppm due to **4**, 88.4 ($^{1}J_{P-Pt}$ = 7760 Hz) and 85.8

($^1J_{P-Pt}$ = 7860 Hz) ppm due to **1**; ^{1}H NMR ($CDCl_3$): 8.05 (d, 1H, Pt–C–C*H*, $^2J_{H-H}$ = 7.4 Hz, $^3J_{H-Pt}$ = 52.2 Hz), 7.40–6.89 (m, 13H, aromatic protons), 2.95 (s, 6H, coordinated DMSO CH_3, $^3J_{H-Pt}$ = 9.5 Hz), 2.66 (s, free DMSO CH_3, about 15% with respect to the coordinated DMSO signal), and minor signals due to **1**; ^{13}C NMR ($CDCl_3$): 158.0, 150.2, 135.8, 129.9, 128.7, 126.1, 123.0, 121.4, 111.2 (aromatic nuclei), 43.3 (coordinated DMSO), 41.0 (free DMSO) and minor signals due to **1**.

^{1}H NMR (d_6-DMSO): 7.74 (d, 1H, Pt–C–C*H*, $^2J_{H-H}$ = 7.7 Hz, $^3J_{H-Pt}$ = 47.8 Hz), 7.44–6.89 (m, 13H). ^{13}C NMR (d_6-DMSO): 158.3, 149.8, 136.0 ($^2J_{C-P}$ = 89 Hz), 135.9, 130.9, 129.1, 127.0, 123.0, 121.5, 111.6. IR (ATR, selected bands): 1585 m, 1483 s, 1174 ms, 1155 s, 1119 s, 1022 s, 938 ms, 900 ms, 803 s, 786 s, 767 s, 748 f, 726 m, 686 s cm^{-1}.

When chloroform solutions of **4** were evaporated to dryness at about 60 °C under stirring, the ^{31}P NMR recorded on $CDCl_3$ solutions of the residue showed extensive or even complete conversion of **4** to **1**.

3.4. Preparation of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}py], 6

In a NMR tube, 40.3 mg (3,73 × 10^{-2} mmol) of **1**, 1.0 mL of $CDCl_3$ and 6 μL (7.5 × 10^{-2} mmol) of pyridine were introduced. NMR spectra were recorded. ^{31}P NMR: 95.4 ($^1J_{P-Pt}$ = 6602 Hz), 95.5 ($^1J_{P-Pt}$ = 7063 Hz) ppm. ^{195}Pt NMR ($CDCl_3$): −4128 (d, $^1J_{Pt-P}$ = 7063 Hz), −4197 (d, $^1J_{Pt-P}$ = 6602 Hz) ppm. Crystals of [SP4-2]-**6** (see X-ray diffraction) were obtained by slow diffusion of pentane vapours into the solution. ^{31}P NMR on a freshly prepared $CDCl_3$ solution of [SP4-2]-**6** showed the signal at 95.5 ppm ($^1J_{P-Pt}$ = 7063 Hz) only. Both isomers were observed (^{31}P NMR) after 48 h.

A solution of **6** in chloroform was subjected to evacuation at 60 °C and the resulting residue was dissolved in $CDCl_3$. In the ^{31}P NMR spectrum, besides the resonances due to the two isomers of **6**, a minor signal at 88.2 ppm was observed, due to **1**. The sample was treated a second time under vacuum at a higher temperature (90 °C). The residue was dissolved in $CDCl_3$ and a ^{31}P NMR spectrum showed a nearly quantitative conversion to **1**.

3.5. Preparation of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(NHEt$_2$)], 7

In a 50 mL reactor 141.9 mg (1.31 × 10^{-1} mmol) of **1** were reacted with 30 μL of $NHEt_2$, (2.90 × 10^{-1} mmol) in 1,2-DCE as solvent (5 mL). A pale yellow solution was obtained. After 40 min stirring, a ^{31}P NMR spectrum was recorded: 102.0 (main signal, $^1J_{P-Pt}$ = 6501 Hz), 92.0 ($^1J_{P-Pt}$ = 7276 Hz) ppm, integral ratio 93:7. After 24 h stirring, a new ^{31}P NMR spectrum was recorded: 102.0 ($^1J_{P-Pt}$ = 6501 Hz), 92.0 (main signal, $^1J_{P-Pt}$ = 7276 Hz) ppm, integral ratio 40:60. The solution was evaporated to dryness under vacuum and the pale-yellow residue was dissolved in toluene (5 mL) and heptane (2 mL) was added to the solution. After 3 d, the microcrystalline solid which precipitated out was collected by filtration. A second crop of crystals was obtained from the filtrate. Both fractions were washed with heptane and dried under vacuum. The two fractions showed analogous analytical results. Anal. Calcd for $C_{23}H_{19}ClNO_3PPt$: C, 43.1; H, 4.1; N, 2.3. Found C, 43.2; H, 4.2; N, 2.1.

First fraction: ^{1}H NMR ($CDCl_3$): 8.24 (d, 1H, Pt–C–C*H*, $^3J_{H-Pt}$ = 50 Hz), 7.48–6.89 (m, 13H, aromatic protons), 3.26–3.02 (m, 5H, N*H* and N–CH_2), 1.21 (t, 6H, N–CH_2–CH_3, $^2J_{H-H}$ = 7.4 Hz) ppm; ^{31}P NMR ($CDCl_3$): 101.0 ($^1J_{P-Pt}$ = 6516 Hz) and 92.1 (main signal, $^1J_{P-Pt}$ = 7330 Hz) ppm, integral ratio 20:80; IR (ATR, selected bands): 3299 mw, 3210 w, 1597 m, 1585 m, 1484 s, 1435 m, 1381 m, 1209 m, 1172 s, 1155 s, 1110 m, 1062 m, 1026 m, 1006 m, 950 s, 924 ms, 889 ms, 803 s, 764 m, 749 s, 687 s cm^{-1}. Second fraction: ^{1}H NMR ($CDCl_3$): 8.24 (d, 1H, Pt–C–C*H*, $^2J_{H-H}$ = 8.5 Hz $^3J_{H-Pt}$ = 50 Hz), 7.38–6.90 (m, 13H), 3.21–2.99 (m, 5H, N*H* and N–CH_2), 1.21 (t, 6H, N–CH$_2$–CH_3, $^2J_{H-H}$ = 7.0 Hz) ppm; ^{31}P NMR ($CDCl_3$): 92.1 ($^1J_{P-Pt}$ = 7292 Hz) ppm. IR (ATR, selected bands): 3210 m, 1587 m, 1486 s, 1435 m, 1380 m, 1209 m, 1163 ms, 1110 m, 1062 m, 1026 s, 948 ms, 926 ms, 889 ms, 806 s, 764 ms, 751 ms, 687 m cm^{-1}.

3.6. Attempted thermal conversion of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(P(OMe)$_3$)], 5, to 1

A solution of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(P(OMe_3))], **5**, was prepared by reacting **1** with P(OMe)$_3$ (molar ratio 1:2) in $CDCl_3$. The solution was treated under vacuum at 60 °C. The colourless residue was dissolved in $CDCl_3$ and the ^{31}P NMR spectrum of the solution showed the signals to [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(P(OMe_3)] only. The same result was obtained by analogous treatments carried out at 90 °C and at 120 °C.

3.7. Conversion of [PtCl{(κ^2-P,C)P(OC_6H_4)(OPh)$_2$}(CO)], 3, to 1

A solution of **3** obtained by reacting **1** with CO (P = 1 atm) in a 1:1 mixture of CH_2Cl_2 and heptane was evaporated to dryness under vacuum at room temperature. The colourless residue was dissolved in $CDCl_3$ and the ^{31}P NMR of the resulting solution showed the signals attributed to **1** only.

3.8. Crystal structure of complexes [SP4-3]-4 and [SP4-2]-6

The X-ray diffraction experiments were carried out at room temperature (T = 293 K) by means of a Bruker Smart Breeze CCD diffractometer operating with graphite-monochromated Mo-K_α radiation. The sample of [SP4-3]-**4** was sealed in a glass capillary under N_2 atmosphere, while that of [SP4-2]-**6** was glued at the end of a glass fibre. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a multi-scan method [20]. Some relevant crystal parameters are listed in Table 4.

The structure solution of [SP4-3]-**4** has been obtained by the automatic direct methods contained in SHELXS97 [21]. The hydrogen atoms have been introduced in calculated positions and have been refined following the method of riding motion. The final refinement cycles gave the reliability factors listed in Table 4.

Table 4
Crystal data and selected structure refinements details.

Compound	[SP4-3]-**4**	[SP4-2]-**6**
Chemical formula	$C_{20}H_{20}ClO_4PPtS$	$C_{23}H_{19}ClNO_3PPt$
Formula mass (g mol^{-1})	617.93	618.90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$(n. 14)	$P2_1/n$(n. 14)
a (Å)	9.449(2)	9.6272(2)
b (Å)	16.028(3)	15.1925(4)
c (Å)	15.245(3)	15.2288(4)
β (°)	105.921(3)	98.0390(10)
Volume (Å^3)	2220.3(8)	2205.49(9)
Z	4	4
Temperature	296(2)	296(2)
Density (calculated)/g cm^{-3})	1.849	1.864
Absorption coefficient (mm^{-1})	6.628	6.580
θ (°) Min Max	3.89–32.73	3.00–36.53
Reflections collected	27,746	27,268
Independent reflections [R_{int}]	8148 [0.0265]	10,551 [0.0221]
Data/restraints/parameters	8148/0/255	10551/0/236
R_{all}, R_{gt} [a]	0.0506, 0.0275	0.0695, 0.0328
$wR(F_o^2)_{all}$, $wR(F_o^2)_{gt}$ [a]	0.0654, 0.0571	0.0994, 0.0841
Goodness-of-fit [a]	0.987	0.892

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2,0) + 2F_c^2]/3$; Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively.

The structure solution of [SP4-2]-**6** has been obtained by the automatic direct methods contained in SIR92 program [22]. During the first stages of the refinement the thermal ellipsoids of a phenyl group of the phosphine appeared excessively elongated with a disposition suggesting the presence of disorder in the position of this moiety. This phenyl group was then introduced in the model as distributed in two different positions, fixing to one the total occupancy of the site. After the introduction of the hydrogen atoms in calculated positions, the refinement was completed. The disordered phenyl groups were refined with a fixed idealized geometry and with isotropic thermal parameters. The distribution on the two positions refined to an almost statistical value: 0.54 and 0.46, respectively. The more relevant reliability parameters of the refinement are listed in Table 4. In addition to the aforementioned software, other control calculations and preparation of publication material were performed with the programs contained in the suite WINGX [23].

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Appendix A. Supplementary Material

CCDC 916573 and 916574 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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