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PAPER

A convenient route to dinuclear chloro-bridged platinum(II) derivatives *via* nitrile complexes†

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The syntheses of the complexes $[PtCl_2(NCR)L]$ [R = Me, Et; L = PPh_3; R = Et, L = Py, CO] and $[PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}(NCEt)]$ are described starting from the easily available $[PtCl_2(NCR)_2]$. The stability of the products under different experimental conditions is discussed as well as their use as precursors to dinuclear complexes $[Pt(\mu\text{-}Cl)ClL]_2$. The crystal and molecular structures of *cis*-$[PtCl_2(NCEt)(PPh_3)]$, [SP-4-2]-$[PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}(NCEt)]$ and *trans*-$[Pt(\mu\text{-}Cl)\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}]_2$ are reported.

Introduction

Organonitrile ligands are moderate σ-donors and weak π-acceptors towards metal centers. Consequently, their easy replacement by other ligands makes organonitrile complexes useful intermediates in coordination chemistry.[1]

As for the platinum(II) species $[PtCl_2(NCR)_2]$, some substitution reactions lead to displacement of both nitrile ligands, affording mixtures of *cis*- and *trans*-$[PtCl_2L_2]$ (L = PR_3,[2,3] or AsR_3[4]). In other cases equilibrium reactions are encountered: for instance, the study of the system $[PtCl_2(NCEt)_2]$/CO in $CDCl_3$ has revealed that reaction 1 is completely displaced to the right, while reaction 2 shows an equilibrium constant $K_2 = 48 \pm 6$ (23.4 °C).[5]

$$[PtCl_2(NCEt)_2] + CO \rightarrow [PtCl_2(CO)(NCEt)] + EtCN \quad (1)$$

$$[PtCl_2(CO)(NCEt)] + CO \overset{K_2}{\rightleftharpoons} cis\text{-}[PtCl_2(CO)_2] + EtCN \quad (2)$$

Moreover, for the competition between nitrile and alkenes approximate values of the equilibrium constant for reaction 3 (RCN = EtCN; alkene = cyclohexene $K_3 \approx 1 \times 10^{-1}$, alkene = 1-octene $K_3 \approx 1$) can be indirectly obtained by the combination of the equilibrium constants of eqn (2) and (4) [$K_4 = (4.1 \pm 0.5) \times 10^2$ and 36 ± 5 for cyclohexene and 1-octene, respectively, in 1,2-dichloroethane (1,2-DCE), 21 °C].[6,7]

$$cis,trans\text{-}[PtCl_2(CO)(NCEt)] + \text{alkene} \overset{K_3}{\rightleftharpoons} cis\text{-}[PtCl_2(CO)(\text{alkene})] + EtCN \quad (3)$$

$$cis,trans\text{-}[PtCl_2(CO)(\text{alkene})] + CO \overset{K_4}{\rightleftharpoons} cis\text{-}[PtCl_2(CO)_2] + \text{alkene} \quad (4)$$

Platinum(II) organonitrile complexes appear to be suitable precursors not only of a variety of derivatives through substitution reactions, but also of dinuclear complexes, by releasing of the coordinated nitrile. For instance, the equilibrium constant of reaction 5 has been determined[8] [$K_5 = 3601 \pm 215$ mol^{-1}dm^3, 25 °C, solvent = CH_2Cl_2] and its value suggests that the reverse reaction can be easily forced.

$$trans\text{-}[Pt(\mu\text{-}Cl)Cl(\eta^2\text{-}C_2H_4)]_2 + 2\ MeCN \overset{K_5}{\rightleftharpoons} 2\ trans\text{-}[PtCl_2(\eta^2\text{-}C_2H_4)(NCMe)] \quad (5)$$

It has been also observed[9,10] that *cis*-$[PtX_2(R_2SO)(NCMe)]$[10] (X = Cl, Br; R = Me, Et, Ph) and *cis*-$[PtCl_2(Py)(NCMe)]$[9] lose the coordinated nitrile upon heating in the solid phase (120–145 °C), affording the corresponding dinuclear derivatives $[Pt(\mu\text{-}X)XL]_2$. Moreover, *cis*-$[PtCl_2(NCMe)_2]$ reacts with Et_2SO in hot nitromethane producing $[Pt(\mu\text{-}Cl)Cl(Et_2SO)]_2$:[10] this last outcome suggests the intermediate formation of $[PtCl_2(Et_2SO)(NCMe)]$, followed by nitrile elimination.

It is then reasonable to suppose that similar reactions (see eqn (6)) can be exploited for the preparation of a series of dinuclear derivatives.

$$2\ [PtCl_2L(NCR)] \rightleftarrows [Pt(\mu\text{-}Cl)ClL]_2 + 2\ RCN \quad (6)$$

Halo-bridged derivatives $[Pt(\mu\text{-}X)X(L)]_2$ are key intermediates in platinum coordination chemistry,[11] allowing the easy preparation of complexes containing two different types of neutral ligands of general formula $[PtX_2(L)(L')]$. Among the many examples described, the following can be mentioned: L = PR_3 and L′ = CO,[12] C_2H_4,[12c] R_2S,[13] R_2SO,[14] amines,[12b,15,16] PhCN;[17] L = amine and L′ = alkenes, nitrogen and sulphur nucleophiles, nitrogen unsaturated nucleophiles;[18] L = $P(OR)_3$ and L′ = amine,[16] CO, $P(OMe)_3$.[19] The preparation of dinuclear complexes of phosphines and

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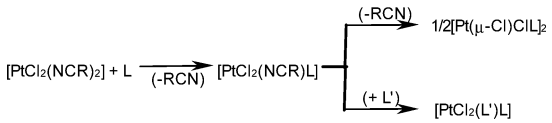
phosphites is usually carried out by reacting at high temperature the suitable $[PtCl_2(L)_2]$ systems with equimolar amounts of $PtCl_2$ in high boiling solvents,[12,20,21] although for some PR_3 derivatives syntheses starting from the Zeise's salt[13] or the Zeise's dimer[22] are also described. Some preparations of dinuclear complexes of amines, $[Pt(\mu\text{-}Cl)Cl(amine)]_2$, are carried out by photochemical decomposition of $[PtCl_2(\eta^2\text{-}C_2H_4)(amine)]$[23] or by addition of $HClO_4$ to $K[PtCl_3(amine)]$.[24]

Although the lability of nitrile complexes is exploited in several syntheses, a systematic study of RCN substitution on platinum(II) is not present. Since dichlorobisorganonitrile complexes $[PtCl_2(NCR)_2]$ are easily prepared,[25] we have considered that they could be good precursors of $[PtCl_2(NCR)L]$ derivatives by reaction with various type of ligands L in suitable molar ratios. Moreover, the above described lability of coordinated nitrile suggested that $[PtCl_2(NCR)L]$ complexes could generate families of mononuclear compounds of the type $[PtCl_2LL']$ or dinuclear derivatives $[Pt(\mu\text{-}Cl)ClL]_2$ (Scheme 1).



Scheme 1

In order to define the right conditions for the synthesis of $[PtCl_2(NCR)L]$, we have reacted $[PtCl_2(NCR)_2]$ with PPh_3, $P(OPh)_3$, py, CO and checked the effects of solvent, temperature and reagent molar ratio on the outcome of the reactions. The results obtained for the different incoming ligands is described here, together with the dimerization of the obtained complexes to chloro-bridged derivatives *via* nitrile release.

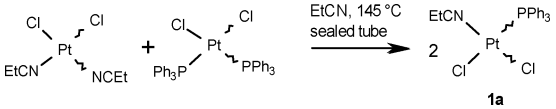
Results and discussion

The $PPh_3/[PtCl_2(NCR)_2]$ system

The formation of $[PtCl_2(PR_3)(NCR)]$ complexes has been observed, beyond the already mentioned[17] bridge-splitting reaction between $[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ and benzonitrile, as a result of the accidental substitution of ethylene by acetonitrile during the attempted purification of $[PtCl_2(PPh_3)(\eta^2\text{-}C_2H_4)]$ (eqn (7)),[26] but the procedure is not described in detail.

$$[PtCl_2(PPh_3)(\eta^2\text{-}C_2H_4)] + MeCN\ (excess) \rightarrow [PtCl_2(PPh_3)(NCMe)] + C_2H_4 \quad (7)$$

In order to find more convenient conditions for the preparation of $[PtCl_2(PPh_3)(NCR)]$ (**1**) derivatives, we have treated a CH_2Cl_2 solution of the mixture of the two geometrical isomers of $[PtCl_2(NCEt)_2]$ (*cis*/*trans* molar ratio ≈ 6)[25] with a solution of PPh_3 in the same solvent at room temperature (Pt/PPh_3 molar ratio = 1). A pale yellow solid immediately formed, identified as *trans*-$[PtCl_2(PPh_3)_2]$,[2b] while the analysis of the liquid phase showed the presence of unreacted $[PtCl_2(NCEt)_2]$.[25] In a further experiment, propionitrile was used as solvent and the reaction mixture was refluxed (97 °C). Under these conditions a yellow suspension was obtained, the liquid phase of which was analysed by ^{31}P NMR spectroscopy. Two signals were observed due to *cis*-$[PtCl_2(PPh_3)_2]$ (16.9 ppm, $^1J_{P\text{-}Pt}$ = 3660 Hz)[2b] and to a new compound (6.0 ppm, $^1J_{P\text{-}Pt}$ = 3560 Hz). Their relative intensities slowly varied with the progress of the reaction in favour of the signal at 6.0 ppm. Since conversion was scarce after a relatively long reaction time (28 h), it was supposed that more drastic conditions were necessary: the reaction mixture was thus heated at 145° C in a sealed tube (Scheme 2).



Scheme 2

After 12 h a yellow, homogeneous solution was obtained and its ^{31}P NMR spectrum showed the absence of the *cis*-$[PtCl_2(PPh_3)_2]$ signal. The solution, upon cooling, separated out pale yellow crystals of *cis*-$[PtCl_2(PPh_3)(NCEt)]$ (*cis*-**1a**) in 68% yield. The presence of coordinated nitrile was confirmed by ^1H and ^{13}C NMR analyses on $CDCl_3$ solutions of the recovered solid and by IR spectroscopy. Single crystal X-ray diffraction analysis confirmed the *cis* stereochemistry of the complex. The ^{31}P NMR spectrum of the liquid phase of the reaction mixture showed, besides the signal of *cis*-(**1a**) (6.0 ppm, $^1J_{P\text{-}Pt}$ = 3560 Hz), a less intense signal (3.4 ppm, $^1J_{P\text{-}Pt}$ = 4100 Hz) ascribed to *trans*-(**1a**).[27] The prevalence of the *cis*-isomer in propionitrile and its low solubility allows its clean recovery by crystallization. In platinum(II) complexes, *trans–cis* isomerization in solution is commonly observed and examples where the *cis* isomer appears to be more stable, independently of the solvent, are for example $[PtCl_2(PPh_3)(CO)]$[28] and $[PtCl_2(CO)_2]$.[29]

The molecular structure of *cis*-(**1a**) is reported (Fig. 1), together with a selection of bond lengths and angles (Table 1).

Crystallographic data are in good agreement with the structure of the analogous *cis*-$[PtCl_2(PPh_3)(NCMe)]$[26] (*cis*-**1b**) and show terminal coordination of propionitrile, with a linear geometry involving platinum, coordinated nitrogen, nitrile carbon and methylene carbon, [Pt–N–C(19)–C(20)]. Of the two Pt–Cl bond distances, Pt–Cl(2), *trans* to PPh_3, is significantly longer than Pt–Cl(1), *trans* to NCEt.

The synthesis of *cis*-(**1b**) was carried out by the same procedure, starting from the mixture of the two geometrical isomers of $[PtCl_2(NCMe)_2]$.[25] The reaction was slightly slower and the complete conversion was reached after 24 h at 150 °C. The product crystallized out of the reaction mixture and was obtained in 77% yield as a single isomer. Although *cis*-(**1b**) has been described,[26] its spectroscopic data are not reported. We assigned the *cis* configuration to our product on the basis of its ^{31}P NMR spectrum, which showed strong analogies with the ^{31}P NMR spectrum of the propionitrile derivative *cis*-(**1a**) (5.4 ppm, $^1J_{P\text{-}Pt}$ = 3530 Hz). Also in this case the ^{31}P NMR spectrum of the liquid phase of the reaction

Table 1 Bond lengths [Å] and angles [°] around Pt atoms in *cis*-(**1a**)

Pt–N	1.976(6)	N–C(19)	1.120(10)
Pt–P	2.2355(19)	C(19)–C(20)	1.464(11)
Pt–Cl(1)	2.2832(19)	C(20)–C(21)	1.451(13)
Pt–Cl(2)	2.342(2)		
N–Pt–P	92.9(2)	P–Pt–Cl(2)	178.70(8)
N–Pt–Cl(1)	176.7(2)	Cl(1)–Pt–Cl(2)	90.10(8)
P–Pt–Cl(1)	89.24(7)	C(19)–N–Pt	174.3(6)
N–Pt–Cl(2)	87.8(2)	N–C(19)–C(20)	177.6(9)

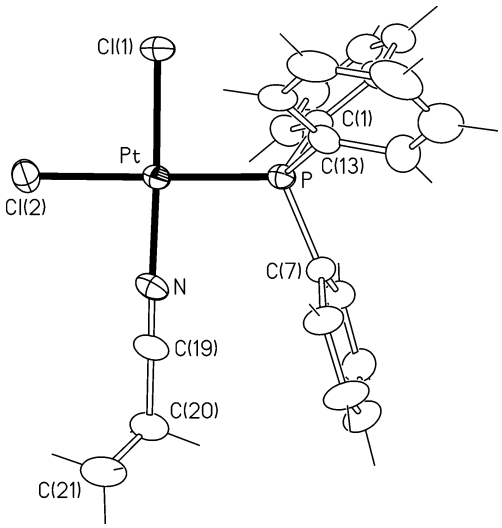
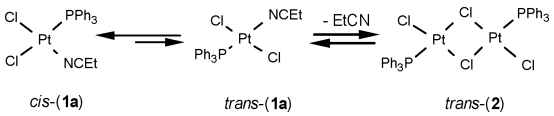


Fig. 1 View of the molecular structure of *cis*-[$PtCl_2(PPh_3)(NCEt)$] (*cis*-(**1a**)). Thermal ellipsoids are at 30% probability.

mixture showed, besides the already mentioned signal of the main product, another signal (3.2 ppm, $^1J_{P\text{-}Pt} = 4110$ Hz), ascribable to minor amounts of *trans*-(**1b**).

Solutions of pure *cis*-(**1a**) in EtCN and pure *cis*-(**1b**) in MeCN were prepared and analysed by ^{31}P NMR spectroscopy at room temperature. In both cases signals of the *trans* isomer were observed after about 48 h and equilibrium between the two isomers was reached after about 7 days. In both cases the *cis* isomer appeared to be more stable than the *trans* one, being the main component of the equilibrium mixtures (about 90% for both derivatives, on the basis of the relative intensities of the ^{31}P NMR signals).

When *cis*-(**1a**) was dissolved in $CDCl_3$ and analysed by ^{31}P NMR at room temperature, the appearance of the resonance of *trans* isomer was followed by the precipitation of an orange solid, which was identified as *trans*-[$Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ (*trans*-**2**).[21,22,26] In the ^1H NMR spectrum, besides signals due to coordinated EtCN of the two geometrical isomers of **1a**, signals of free EtCN were observed. These data show that, in the absence of excess EtCN, coordinated nitrile is promptly released from *trans*-(**1a**) with formation of the corresponding dinuclear derivative **2** (Scheme 3).

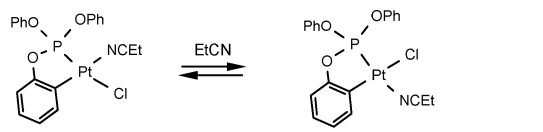


Scheme 3

The synthesis of *trans*-(**2**) was optimized in toluene as solvent at the reflux temperature. Isomerization from *cis*- to *trans*-(**1a**) was much faster and, due to the low solubility of the dinuclear complex in toluene, equilibrium reactions (Scheme 3) were completely displaced to the right. Under these conditions pure *trans*-(**2**) was prepared in 80% yield. Analogous results were obtained when *cis*-(**1b**) was used as precursor. By ^{31}P NMR spectroscopy it is observed that the partial isomerisation of *cis*-**1b** to *trans*-**1b** in $CDCl_3$ is followed by precipitation of *trans*-**2**. The difference in the nitrile alkyl group (Me or Et) does not differentiate the reactivity of the complexes.

The $P(OPh)_3/[PtCl_2(NCEt)_2]$ system

$[PtCl_2(NCEt)_2]$ was reacted with $P(OPh)_3$ under experimental conditions analogous to those used for the preparation of *cis*-(**1a**) (EtCN as solvent, sealed tube, $T = 125$ °C, $Pt/P(OPh)_3$ molar ratio = 1). As analogously observed in the case of triphenylphosphine, addition of triphenylphosphite caused the immediate conversion of half the precursor into *cis*-$[PtCl_2(P(OPh)_3)_2]$,[30] identified *via* ^{31}P NMR spectroscopy on a sample of the reaction mixture. The reaction of this intermediate with the residual unreacted bis-nitrile precursor proceeded quite slowly: the maximum conversion (85%, checked by ^{31}P NMR) was reached after 48 h at 150 °C. The ^{31}P NMR spectrum of the reaction mixture showed two signals (relative intensity 85/15) due to the products, the main one at 99.6 ppm ($^1J_{P\text{-}Pt}$ = 6728 Hz) and the other at 92.7 ppm ($^1J_{P\text{-}Pt}$ = 7550 Hz). White crystals separated out of the mixture upon cooling and X-ray diffraction analysis showed we had obtained the *ortho*-metalated product [SP-4-2]-[PtCl{(κ^2-*P*,*C*)$P(OC_6H_4)(OPh)_2$}(NCEt)] ([SP-4-2]-(**3**)), 40% yield). Activation of C–H bonds leading to *ortho*-metalation products of aryl-phosphite halo-complexes of palladium and platinum has been already described[19,31] under rather drastic experimental conditions (boiling decalin). Yields of *ortho*-metalation products starting from halo-complexes are generally enhanced by working in the presence of flushing dinitrogen to help hydrogen halide removal.[19] In our case, the choice of a sealed tube as reactor prevents HCl from being removed and explains why the conversion is not complete. The two ^{31}P NMR signals observed in the reaction mixture could be reasonably ascribed to the [SP-4-2] and [SP-4-4] isomers of the *ortho*-metalation product **3**, in equilibrium in propionitrile solution (Scheme 4). It is reasonable that $[PtCl_2(P(OPh)_3)(NCEt]$ is an intermediate of the reaction and that, once formed, it is rapidly converted to the products; nevertheless, at the temperatures we have used, there was no evidence of its presence in the reaction mixture.



[SP-4-2]-(**3**): 99.6 ppm ($^1J_{P\text{-}Pt}$ = 6728 Hz) [SP-4-4]-(**3**): 92.7 ppm ($^1J_{P\text{-}Pt}$ = 7550 Hz)

Scheme 4

The molecular structure of [SP-4-2]-(**3**) is reported in Fig. 2, together with a selection of bond lengths and angles (Table 2).

As can be seen in Fig. 2, the metal, P, O(1) and Cl atoms, phenyl ring C(1P) > C(6P) and the propyl group C(1) > C(3) make an almost ideal plane, the maximum deviation being 0.06 Å for C(6) atom. The Pt–C(2P) bond distance, 2.010 Å, is within the range reported for similar compounds,[32] whereas the Pt–P distance, 2.156 Å, is shorter than the range 2.26–2.19 Å normally found in the mononuclear *ortho*-metalated Pt–phosphito derivatives.[32] The Pt–Cl distance is slightly longer than that we have found for chlorine *trans* to phosphine in *cis*-(**1a**), but is however in the range normally found in similar compounds.[33] The nitrile coordination is very similar to that found in *cis*-(**1a**). The Pt–N bond distance in [SP-4-2]-(**3**) is remarkably long (2.08 Å), being well above the average value (1.98 Å) of the Pt–N bond lengths in

Table 2 Bond lengths [Å] and angles [°] around Pt atoms in [SP-4-2]-(**3**)

Pt–C(2P)	2.010(7)	P–O(1)	1.577(6)
Pt–N	2.077(8)	P–O(3)	1.587(5)
Pt–P	2.1557(17)	P–O(2)	1.593(5)
Pt–Cl	2.3506(18)	O(1)–C(1P)	1.422(7)
N–C(1)	1.126(11)	C(2P)–C(3P)	1.410(9)
C(1)–C(2)	1.468(13)	O(2)–C(7P)	1.398(8)
O(3)–C(13P)	1.408(9)		
C(2P)–Pt–N	178.8(3)	C(1)–N–Pt	175.2(8)
C(2P)–Pt–P	82.18(18)	N–C(1)–C(2)	178 (1)
N–Pt–P	96.6(2)	O(1)–P–Pt	108.1(2)
C(2P)–Pt–Cl	94.32(19)	O(3)–P–Pt	121.0(2)
N–Pt–Cl	86.9(2)	O(2)–P–Pt	121.8(2)
P–Pt–Cl	176.47(9)	C(1P)–O(1)–P	114.5(4)

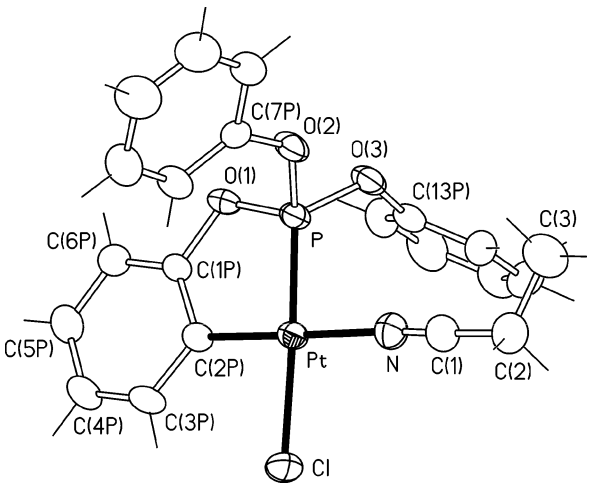


Fig. 2 View of the molecular structure of [SP-4-2]-(**3**). Thermal ellipsoids are at 30% probability.

square planar platinum(II) nitrile complexes.[34] In effect there is a bimodal distribution of the Pt–NCR bond distances: a rather large group of compounds exhibits distances centered around 1.98 Å, while a restricted group shows distances of about 2.07 Å. The complexes of the former group contain several types of ligands *trans* to the nitrile: examples are *cis*-(**1a**) (1.98 Å, see Table 1); *cis*-[$PtCl_2(NCEt)_2$] (1.96 and 1.99 Å);[35] *cis*-[$PtCl_2(CO)(NCEt)$] (1.99 Å);[5] *trans*-[$PtCl_2Py(NCMe)$] (1.98 Å)[36] and, on the borderline, *trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)(NCMe)$] (2.02 Å).[8] The latter group is formed by a few complexes that have strong σ-donor ligands (alkyl, aryl, phosphide), *trans* to the nitrile. Examples of this type are: [1,4-{$Pt(MeCN)$}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}](BPh_4)$_2$ (2.09 Å);[37] [$(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(NCMe)_2$] (2.07 and 2.08 Å);[38] [PtMe-{(R)-$C_{10}H_7CHMeNCHC_4H_2S$}(NCMe)] (2.05 Å);[39] [Pt{C(E)═C(E)–C(E)═C(E)}(*N*,*N*′-dimethylbenzimidazol-2-ylidene)(NCMe)] (E = CO_2Me) (2.06 Å).[40]

While the presence of coordinated nitrile in [SP-4-2]-(**3**) was observed by IR spectroscopy (ATR on solid sample: $\tilde{\nu}_{CN}$ at 2295 cm^{-1}), it was not possible to obtain the direct ^{1}H NMR characterization of the derivative. As a matter of fact, pure [SP-4-2]-(**3**), when dissolved in $CDCl_3$, promptly released coordinated nitrile (eqn (8)), and hydrogen resonances due to the free ligand were observed.

$$2\ [PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}(NCEt)] \underset{(3)}{\rightleftarrows} [Pt(\mu\text{-}Cl)\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}]_2 + 2\ EtCN \quad (8)$$
(4)

The existence of equilibrium (8) in $CDCl_3$ solution was confirmed by ^{31}P NMR spectroscopy, where signals ascribable to *cis*- and *trans*-[$Pt(\mu\text{-}Cl)\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OC_6H_5)_2\}]_2$[19] (**4**) were observed (85.1 ppm [$^1J_{P\text{-}Pt}$ = 7864 Hz] and 87.7 ppm [$^1J_{P\text{-}Pt}$ = 7770 Hz], respectively), while the signals of the two geometrical isomers of the mononuclear precursor showed a relatively weak intensity. The same behaviour was observed in toluene. In this case, slow evaporation of the solvent afforded the pure dinuclear derivative in 70% yield. The overall preparation procedure of **4** could be optimized by carrying out the reaction between [$PtCl_2(NCEt)_2$] and $P(OPh)_3$ at 160 °C in benzonitrile (b.p. 191 °C). In this case the use of a sealed vessel could be avoided, thus making the elimination of $HCl_{(g)}$ easier. After 48 h, a ^{31}P NMR spectrum on a sample of the reaction mixture revealed the complete disappearance of the intermediate [$PtCl_2\{P(OPh)_3\}_2$] and the formation of two main products, with resonances at 98.8 ppm ($^1J_{P\text{-}Pt}$ = 6709 Hz) and 96.4 ppm ($^1J_{P\text{-}Pt}$ = 7223 Hz), with 3/1 molar ratio, according to the relative intensities of the observed signals. We suggest the formation of [SP-4-2]- and [SP-4-4]-[$PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}(NCPh)$] in view of the strong analogies with the previously described spectrum of the propionitrile derivatives **3**, which in this case were observed in traces (signals at 98.7 and 91.9 ppm). The dinuclear derivative **4** was finally obtained in 65% overall yield upon slow evaporation of excess benzonitrile. A sample of the mixture of the two geometrical isomers of **4** was recrystallized from 1,2-dichloroethane/pentane and the molecular structure of the *trans* isomer could be determined by single crystal X-ray diffraction methods (Fig. 3).

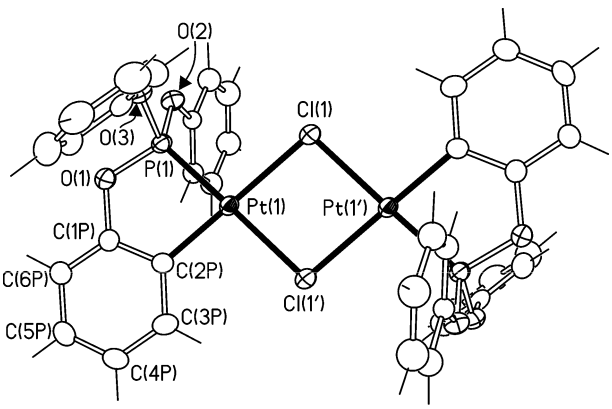


Fig. 3 View of the molecular structure of *trans*- **4**. Thermal ellipsoids are at 30% probability. ′ = 1 – *x*, 1 – *y*, 1 – *z*. For sake of clarity only one of the two conformations of the disordered rings has been represented.

Table 3 reports some geometrical details of the coordination around the metal.

As shown in Fig. 3, the molecule is centrosymmetric and, as the moiety Pt(1), Cl(1), P(1), O(1) and the ring C(1P) > C(6P) are almost perfectly planar, the symmetry related atoms lie on the same plane. Such a feature is not present in the analogous derivative [$Pt(\mu\text{-}Cl)\{(\kappa^2\text{-}P,C)P(OC_6H_2$-2,4-*t*-$Bu_2)\}$((*R*)-binolate)]$_2$,[41] where the Pt coordination planes are tilted

Table 3 Bond lengths [Å] and angles [°] around Pt atoms in *trans*-**4**

Pt(1)–C(2P)	2.018(8)	P(1)–O(2)	1.576(5)
Pt(1)–P(1)	2.1449(18)	P(1)–O(1)	1.583(6)
Pt(1)–Cl(1′)	2.4054(18)	P(1)–O(3)	1.589(5)
Pt(1)–Cl(1)	2.439(2)		
C(2P)–Pt(1)–P(1)	81.8(2)	P(1)–Pt(1)–Cl(1)	97.69(7)
C(2P)–Pt(1)–Cl(1′)	97.0(2)	Cl(1′)–Pt(1)–Cl(1)	83.53(6)
P(1)–Pt(1)–Cl(1′)	177.42(7)	Pt(1′)–Cl(1)–Pt(1)	96.47(6)
C(2P)–Pt(1)–Cl(1)	179.2(2)	O(2)–P(1)–O(3)	94.4(3)

around the Cl(1)···Cl(1′) axis making a Pt(1)–Cl(1)···Cl(1′)–Pt(1′) torsion angle of 163°. The analogies concern, instead, the rather short Pt–P bond: 2.12 vs. 2.14 Å, and the different Pt–Cl distances relative to the Cl(1) and Cl(1′) bridging chlorine atoms. In both cases the Pt–Cl bond *trans* to the phenyl group are longer than those *trans* to phosphorus. The M–Cl bonds show instead the same length in the analogous *cis* derivative known for palladium,[42] disregarding the position of bridging chlorine *trans* with respect to C or P.

The Py/[$PtCl_2(NCEt)_2$] system

The reaction between pyridine and a mixture of *cis*- and *trans*-[$PtCl_2(NCEt)_2$] (Pt/Py = 1/1 molar ratio) was initially carried out in EtCN at 130 °C in a sealed tube. A unique product was obtained in 63% yield, identified as $PtCl_2(NCEt)(Py)$ (**5**). The presence of coordinated propionitrile was observed by both ^{1}H NMR and IR spectroscopy. Since in this case no traces of the disubstituted product [$PtCl_2Py_2$] were observed, in a further experiment the reaction was carried out at room temperature. The outcome of the reaction was essentially the same. A single isomer was always observed in solution (^{1}H and ^{195}Pt NMR) and we propose that we are dealing with the *trans*-isomer. Isomerization from *cis* to *trans* isomers is described for analogous [$PtCl_2(NCMe)(Am)$] complexes (Am = amine) in organic solvents,[36,43] where free MeCN catalyzes the process. The complex is stable in solution at room temperature in chlorinated or aromatic solvents, nevertheless coordinated nitrile was released when a toluene solution of *trans*-(**5**) was heated (75 °C) and slowly evaporated under vacuum. The conversion to a brown, scarcely soluble material was complete only after several evaporation cycles. Unfortunately, the low solubility of the product prevented its ^{195}Pt NMR characterization, but the absence of coordinated nitrile could be verified by ^{1}H NMR. The IR spectrum, which shows the presence of bands due to the coordinated pyridine and the absence of bands attributable to EtCN, is in agreement with that reported in the literature for $Pt_2Cl_4py_2$.[44] Moreover, addition of propionitrile to a $CDCl_3$ suspension of the product caused its slow conversion to the original *trans*-(**5**), thus supporting the hypothesis of the chloro-bridged nature of the product.

The CO/[$PtCl_2(NCEt)_2$] system

As already mentioned, the reaction between [$PtCl_2(NCEt)_2$] and CO affording a mixture of monosubstitution and disubstitution products had been already studied.[5] The preparation of the monosubstitution product was optimized in the course of this work by a modification of the reported[5] procedure and *cis*-[$PtCl_2(NCEt)(CO)$] (*cis*-**6**) was obtained in 70% yield (see Experimental section).

With the aim of obtaining [Pt(μ-Cl)Cl(CO)]$_2$ (**7**), a sample of *cis*-**6** was dissolved in dry mesitylene and the solution was heated (75 °C) and slowly evaporated under vacuum. The outcome of the reaction was followed by ^{195}Pt NMR. The analysis of the residue, dissolved in $CDCl_3$, showed a signal due to *trans*-(**6**),[5] and two more signals due to *trans*-(**7**).[29] The presence of two ^{195}Pt resonances for this dinuclear complex has been already observed and discussed.[29a] The heating/evaporation cycle was repeated and afforded an orange residue, whose ^{195}Pt NMR analysis in $CDCl_3$ showed the complete conversion of the precursor into **7**. The formation of the dinuclear carbonyl derivative was confirmed by IR spectroscopy.[29] The observed data suggest that isomerization from *cis*- to *trans*-(**6**) takes place easily in mesitylene solution upon heating. This observation is in good agreement with the known behaviour of *cis*-(**6**), which is completely isomerized to *trans* isomer in chlorinated solvents at room temperature in 24 h.[5] On the basis of our results, it seems reasonable that *trans*-(**6**) is the isomer which releases coordinated nitrile in an equilibrium reaction leading to the formation of the chloro-bridged dimer (eqn (9)).

$$2\ \underset{trans\text{-}\mathbf{6}}{trans\text{-}[PtCl_2(NCEt)(CO)]} \rightleftarrows \underset{\mathbf{7}}{[Pt(\mu\text{-}Cl)Cl(CO)]_2} + 2\,EtCN \quad (9)$$

At room temperature, equilibrium (9) is completely displaced to the left and the removal of nitrile under vacuum at relatively high temperature is necessary to obtain the dinuclear derivative.

The *trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)(NCEt)$]/[$Pt(\mu\text{-}Cl)Cl(\eta^2\text{-}C_2H_4)]_2$ system

As already mentioned, for L = C_2H_4 the reverse of reaction 6 has been reported (see eqn (5)).[8] We have observed that the treatment of *trans*-[$PtCl_2(\eta^2\text{-}C_2H_4)(NCEt)$] (*trans*-**8**) under vacuum at 25 °C afforded the corresponding dinuclear derivative [$Pt(\mu\text{-}Cl)Cl(\eta^2\text{-}C_2H_4)]_2$ (**9**) in essentially quantitative yield.

Conclusions

Starting from the easily available [$PtCl_2(NCEt)_2$], the syntheses of [$PtCl_2(NCEt)(L)$] (L = PPh_3 (**1a**), Py (**5**)), [$PtCl_2(NCMe)(PPh_3)$] (**1b**) and [SP-4-2]-[$PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}(NCEt)$] ([SP-4-2]-**3**) have been carried out in moderate to good yields and the preparation of [$PtCl_2(NCEt)(CO)$][5] (**6**) has been optimized. While for L = Py the stoichiometric substitution reaction (L/Pt molar ratio = 1, eqn (10)) can be carried out at room temperature in propionitrile and affords the *trans*-isomer of the expected **5**, in the case of PPh_3 and $P(OPh)_3$ the analogous reactions carried out at room temperature afford mixtures containing the starting platinum complex and the double substitution product, [$PtCl_2L_2$], probably because the strong *trans*-effect of these ligands makes the second substitution reaction (eqn (11)) faster than the former (eqn (10)).

$$[PtCl_2(NCR)_2] + L \rightarrow [PtCl_2L(NCR)] + RCN \quad (10)$$

$$[PtCl_2L(NCR)] + L \rightarrow [PtCl_2L_2] + RCN \quad (11)$$

Suitable conditions for the conversion of the obtained mixtures into the desired products have been found. In the case of L = $P(OPh)_3$ the procedure afforded the *ortho*-metalated product **3**.

Although **1a**, **1b** and **3** are stable in RCN solution, in other solvents the formation of dinuclear species upon release of coordinated nitrile (Scheme 3 and eqn (8)) is observed. In $CDCl_3$ **3** is rapidly and extensively converted into the soluble dinuclear $[Pt(\mu\text{-}Cl)\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OPh)_2\}]_2$ (**4**) at room temperature. In the case of **1a** the dinuclear derivative **2** produced according to Scheme 3 is scarcely soluble either in toluene or $CDCl_3$ and slowly separates out of the solution, thus displacing equilibrium to the right. On the other hand, *trans*-(**6**) and *trans*-(**8**), in spite of the strong *trans* effect of CO and C_2H_4, need relatively more severe conditions to release the coordinated nitrile.

Release of nitrile appears particularly easy for **3** and we suppose that the process involves the [SP-4-2]-isomer, where the ligand is *trans* to the phenyl group. The presence of strong σ-donors in platinum(II) square planar complexes has been associated to dissociative paths according to kinetic data regarding substitution reactions.[45] We can reasonably suppose that a dissociative route is followed by this complex to form the dinuclear species, this hypothesis being indirectly corroborated by the rather long Pt–NCR bond distance observed in its structure.

Experimental section

General procedures

All manipulations were performed under a dinitrogen atmosphere, unless otherwise stated. Solvents and liquid reagents were dried according to reported procedures.[46] Triphenylphosphine (Aldrich, Steinheim-Westfalia, DE) was recrystallized from ethanol before use. $[PtCl_2(NCEt)_2]$ and $[PtCl_2(NCMe)_2]$ were prepared (both as the mixture of the two geometrical isomers) according to reported procedures.[25] *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(NCEt)]$ (*trans*-**8**) was prepared from $[Pt(\mu\text{-}Cl)Cl(\eta^2\text{-}C_2H_4)]_2$ (**9**) according to the procedure described for *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(NCMe)]$.[8]

^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer (^1H 401.36 MHz, ^{13}C 100.93 MHz, ^{31}P 162.49 MHz and ^{195}Pt 86.02 MHz operating frequencies). Solvent was $CDCl_3$ if not otherwise stated. Chemical shifts were measured in ppm (δ) from TMS by residual solvent peaks for ^1H 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 into the NMR tube to lock the spectrometer to the deuterium signal when non-deuterated solvents were used. FTIR spectra in the solid phase were recorded with a Perkin–Elmer Spectrum One spectrometer, with ATR technique. FTIR spectra in solution were recorded with a Perkin–Elmer Paragon 500 or a Perkin–Elmer Spectrum 100 spectrometer. A 0.1 mm cell supplied with CaF_2 windows was used. Elemental analyses (C, H, N) were performed by Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine.

Synthesis of *cis*-$[PtCl_2(PPh_3)(NCEt)]$ (1a)

A mixture of $[PtCl_2(NCEt)_2]$ (1.18 g, 3.13 mmol), PPh_3 (0.819 g, 3.12 mmol) and propionitrile (8.0 mL) was heated (145 °C) in a sealed tube (total volume ≈ 100 mL) until a yellow solution was obtained (12 h). Heating was stopped and the solution was slowly cooled to room temperature (25 °C). Light yellow crystals were filtered and dried under vacuum (1.24 g, 68% yield). Anal. Calcd. for $C_{21}H_{20}Cl_2NPPt$: C 43.2; H 3.5; N 2.4%. Found: C 43.1; H 3.6; N 3.3%.[47] A single crystal was selected for X-ray analysis, which confirmed the *cis* stereochemistry. ^1H NMR: δ 7.78–7.45 (m, 15H, aromatic hydrogens); 2.14 (q, 2H, $^2J_{H\text{-}H}$ = 7.5 Hz, CH_2); 0.87 (t, 3H, $^2J_{H\text{-}H}$ = 7.5 Hz, CH_3). ^{13}C NMR: δ 134.6 (d, $J_{C\text{-}P}$ = 10 Hz), 131.5, 128.4 (d, $J_{C\text{-}P}$ = 11 Hz), 126.3 (d, $J_{C\text{-}P}$ = 67 Hz), 118.0, 12.3, 8.8. ^{31}P NMR: δ 5.8 ($^1J_{P\text{-}Pt}$ = 3560 Hz) ^{195}Pt NMR: δ –3595 (d, $^1J_{Pt\text{-}P}$ = 3560 Hz). FTIR (ATR): ($\tilde{\nu}_{CN}$) 2312 cm^{-1}.

Synthesis of *cis*-$[PtCl_2(NCMe)(PPh_3)]$ (1b)

A mixture of $[PtCl_2(NCMe)_2]$ (1.41 g, 4.06 mmol), PPh_3 (1.06 g, 4.05 mmol) and acetonitrile (8.0 mL) was heated (150 °C) in a sealed tube (total volume ≈ 100 mL), until a yellow solution was obtained (18 h). Heating was stopped and the solution was slowly cooled to room temperature (25 °C). Light yellow crystals were filtered and dried under vacuum (1.82 g, 77% yield). Anal. Calcd. for $C_{20}H_{18}Cl_2NPPt$: C, 42.2; H, 3.2; N, 2.5%. Found: C, 42.5; H, 3.3; N, 3.3%.[47] ^1H NMR: δ 7.84–7.46 (m, 15H, aromatic hydrogens); 1.80 (s, 3H, CH_3). ^{13}C NMR: δ 134.7 (d, $J_{C\text{-}P}$ = 11 Hz), 131.6, 128.6 (d, $J_{C\text{-}P}$ = 12 Hz), 127.6 (d, $J_{C\text{-}P}$ = 65 Hz), 114.4, 3.5. ^{31}P NMR: δ 4.8 ($^1J_{P\text{-}Pt}$ = 3530 Hz). ^{195}Pt NMR: δ –3606 (d, $^1J_{Pt\text{-}P}$ = 3530 Hz). FTIR (ATR): ($\tilde{\nu}_{CN}$) 2327 cm^{-1}.

Synthesis of *cis*-$[PtCl_2(CO)(NCEt)]$[5] (6)

A solution of 0.474 g of $[PtCl_2(NCEt)_2]$ (1.26 mmol) in 9.0 mL of 1,2-DCE was treated with 1.0 mL of propionitrile (14.0 mmol, EtCN/Pt molar ratio = 11) in a 80 mL Carius tube under CO. The mixture was heated (65 °C) under stirring until the ^{195}Pt NMR signals of precursors (–2253 and –2342 ppm of *cis*-and *trans*-$[PtCl_2(NCEt)_2]$, respectively) disappeared and signals at –3280, –3430 and –3910 ppm (*cis*-(**6**), *trans*-(**6**) and *cis*-$[PtCl_2(CO)_2]$, respectively) were observed (48 h). The mixture was then cooled to room temperature, CO was replaced with Ar and solvents were eliminated under vacuum. Residual solid was dissolved in 1,2-DCE (8.0 mL), 1.0 mL of propionitrile were added and solvents were eliminated under vacuum. Light-orange crystals of *cis*-(**6**) were obtained (0.346 g, 79% yield). ^1H NMR: δ 2.95 (q, $^2J_{H\text{-}H}$ = 7.7 Hz, CH_2) and 1.50 (t, $^2J_{H\text{-}H}$ = 7.7 Hz, CH_3). ^{195}Pt NMR: δ –3285. FTIR (ATR): ($\tilde{\nu}_{CN}$) 2325; ($\tilde{\nu}_{CO}$) 2125 cm^{-1}.

Synthesis of $[PtCl\{(\kappa^2\text{-}P,C)P(OC_6H_4)(OC_6H_5)_2\}(NCEt)]$ (3)

A solution of 0.620 g (1.65 mmol) of $[PtCl_2(NCEt)_2]$ in 4.0 mL of EtCN was treated with 0.500 g (1.63 mmol) of $P(OPh)_3$ and heated (150 °C) under stirring (44 h) in a sealed tube (total volume ≈ 100 mL). The hot solution was filtered and then cooled (–30 °C). Crystals were filtered and dried under vacuum. A single crystal was selected for X-ray diffraction studies. A second crop of crystals was obtained from the mother liquor. The overall yield (0.330 g) of (**3**) was 40%. ^1H NMR: δ 7.29 (m), 7.10 (m), 6.88 (m), 2.38 (q) and 1.33 (t) (coordinated and free nitrile). ^{31}P NMR: δ 97.2 ($^1J_{P\text{-}Pt}$ = 6853 Hz) [SP-4-2]-(**3**); 89.7 ($^1J_{P\text{-}Pt}$ = 7575 Hz) [SP-4-4]-(**3**); 87.7($^1J_{P\text{-}Pt}$ = 7770 Hz) (*trans*-**4**)); 85.1 ($^1J_{P\text{-}Pt}$ = 7864 Hz) (*cis*-(**4**)). ^{195}Pt: δ –4038 d ($^1J_{Pt\text{-}P}$ = 7864 Hz) (*cis*-(**4**)), –4142 d ($^1J_{Pt\text{-}P}$ = 7770 Hz) (*trans*-(**4**)), –4272 d ($J_{Pt\text{-}P}$ = 6853 Hz) ([SP-4-2] -(**3**)), –4329 d ($J_{Pt\text{-}P}$ = 7575 Hz) ([SP-4-4]-(**3**)). FTIR (ATR): ($\tilde{\nu}_{CN}$) 2295 cm^{-1}.

Synthesis of *trans*-[PtCl$_2$(NCEt)(Py)] (5)

A solution of 0.540 g (1.44 mmol) of [PtCl$_2$(NCEt)$_2$] in 4.0 mL of EtCN was treated with 0.117 mL (1.44 mmol) of pyridine and stirred in a sealed tube (total volume ≈ 100 mL) initially at room temperature (3 h) and then at 130 °C (5 h). The yellow solution was then cooled (25 °C) to afford yellow crystals, which were filtered and dried under vacuum. A second crop of crystals was obtained from the cooled (–30 °C) mother liquor (0.370 g, 63.3% overall yield). An analogous experiment carried out at room temperature afforded similar results. ^{1}H NMR: δ 9.06 (m, 2H); 7.89 (m, 1H); 7.46 (m, 2H); 2.89 (q, 2H); 1.39 (t, 3H). ^{13}C NMR: δ 153.6, 138.7, 125.2, 12.6, 9.6. ^{195}Pt NMR: δ –2139. FTIR (ATR): ($\tilde{\nu}_{CN}$) 2310 cm^{-1}.

Synthesis of *trans*-[Pt(μ-Cl)Cl(η^2-C$_2$H$_4$)]$_2$ (9)

A solution of 1.13 mmol of *trans*-(**8**) in toluene (50.0 mL) was slowly evaporated under vacuum at 25 °C and the solid residue was dried under vacuum (9 h). *trans*-(**9**) was obtained in essentially quantitative yield. ^{195}Pt NMR (CH_2Cl_2): δ –2498.[48]

Synthesis of *trans*-[Pt(μ-Cl)Cl(PPh$_3$)]$_2$ (2)

A suspension of 0.292 g of *cis*-(**1a**) (0.501 mmol) in 20.0 mL of toluene was refluxed (110 °C) until the complete precipitation of an orange solid was achieved and the ^{31}P NMR signal of the precursor disappeared (2 h). The orange crystals were filtered, washed with toluene (3.0 mL) and dried under vacuum (0.217 g, 82% yield). Anal. Calcd. for $C_{36}H_{30}Cl_4P_2Pt_2$: C, 40.9; H, 2.9%. Found: C, 40.6; H 2.8%. ^{31}P NMR: δ 5.1 ($^1J_{P\text{-}Pt}$ = 4100 Hz). ^{195}Pt NMR: δ –3322 (d, $^1J_{Pt\text{-}P}$ = 4100 Hz).

Synthesis of [Pt(μ-Cl){(κ^2-*P*,*C*)P(OC$_6$H$_4$)$_2$(OPh)$_2$}]$_2$[19] (4)

In a round-bottomed flask, equipped with magnetic stirrer and condenser, a solution of 1.06 g (2.81 mmol) of [PtCl$_2$(NCEt)$_2$] in 10.0 mL of benzonitrile was treated with a solution of 0.864 g of triphenylphosphite in 4.0 mL of the same solvent (Pt/P molar ratio = 1). The yellow solution was heated (160 °C) under stirring (48 h) and turned reddish. The mixture was cooled, filtered and excess benzonitrile was eliminated under vacuum. The solid residue was washed with diethylether (15.0 mL) and filtered. The light-brown product was obtained as the mixture of the two geometrical isomers (0.958 g, 63% yield). ^{31}P NMR:[19] δ 87.7 ($^1J_{P\text{-}Pt}$ = 7770 Hz), 85.1 ($^1J_{P\text{-}Pt}$ = 7864 Hz). ^{195}Pt NMR: δ –4144 (d, $^1J_{Pt\text{-}P}$ = 7770 Hz); –4038 (d, $^1J_{Pt\text{-}P}$ = 7864 Hz). Molar ratio between the two isomers, according to the relative intensity of ^{31}P NMR signals, was about 4/1. A small sample of the mixture was recrystallized (1,2-DCE/pentane) and a single crystal was selected for X-ray analysis, which showed the *trans* stereochemistry of the selected product.

Synthesis of [Pt(μ-Cl)Cl(CO)]$_2$[29] (7)

A solution of 45.0 mg (0.13 mmol) of *cis*-(**6**) in 2.0 mL of mesitylene was heated (75 °C) and slowly evaporated to dryness. The dissolution–evaporation cycle was repeated twice. The product was recovered in essentially quantitative yield. ^{195}Pt NMR:[29] δ –3019; –3034. FTIR ($CDCl_3$): ($\tilde{\nu}_{CO}$) 2136 cm^{-1}.

X-ray structure determinations

The X-ray diffraction experiments were carried out at room temperature (T = 293 K) by means of a Bruker P4 diffractometer operating with graphite-monochromated Mo-Kα radiation. The samples were sealed in a glass capillary under a dinitrogen atmosphere. The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check the sample decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a integration method based on the crystal faces[49] in the case of the well shaped crystal of [SP-4-2]-(**3**) and by a semiempirical method in the case

Table 4 Crystal data and structure refinements

	cis-(1a)	[SP-4-2]-(3)	*trans*-(4)
Empirical formula	$C_{21}H_{20}Cl_2NPPt$	$C_{21}H_{19}ClNO_3PPt$	$C_{36}H_{28}Cl_2O_6P_2Pt_2$
Formula weight	583.34	594.88	1079.60
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	14.8678(19)	9.1034(10)	8.910(2)
b/Å	8.9329(9)	9.8626(16)	9.699(1)
c/Å	17.2269(18)	12.6092(12)	10.987(2)
α/°	—	80.004(9)	96.04(1)
β/°	112.879(8)	75.284(7)	106.00(1)
γ/°	—	79.865(10)	105.80(1)
U/Å^3	2108.0(4)	1068.0(2)	861.4(3)
Z	4	2	1
D_{calc}/g cm^{-3}	1.838	1.850	2.081
μ/mm^{-1}	6.991	6.790	8.406
No. measured	5508	5294	4244
No. unique [R_{int}]	4351 [0.0368]	4427 [0.0279]	3527 [0.0318]
No. parameters	236	254	182
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0390, 0.0853	0.0389, 0.0822	0.0380, 0.0898
R_1, wR_2 [all data][a]	0.0593, 0.0935	0.0554, 0.0885	0.0459, 0.0934
Goodness of fit[a] on F^2	1.029	1.033	1.062

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

of the other two samples. The structure solutions were obtained by means of the automatic direct methods contained in SIR-92[50] for [SP-4-2]-(**3**) and by means of the direct methods contained in SHELXS97[51] for the other two compounds. The refinement, based on full-matrix least-squares on F^2, was done by means of the SHELXL97[51] programme. Some other utilities contained in the WINGX suite[52] were also used. The more relevant crystal parameters for the three compounds are listed in Table 4.

In the refinement of the centrosymmetric structure of *trans*-(**4**) the thermal ellipsoids of carbon atoms of one of independent phenyl rings of the phosphite ligand appeared abnormally prolate. The orientation of their main axes suggested the presence of a conformational disorder of the phosphite, characterized by two slight different P–O–phenyl angles for the same phenyl ring. Thus a model with two different orientations for that ring was introduced in the calculations, the total occupancy of each corresponding carbon atoms being fixed to 1. The following refinement cycles showed some reduction in the reliability factor calculating the occupancy of each position at about 50%.

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