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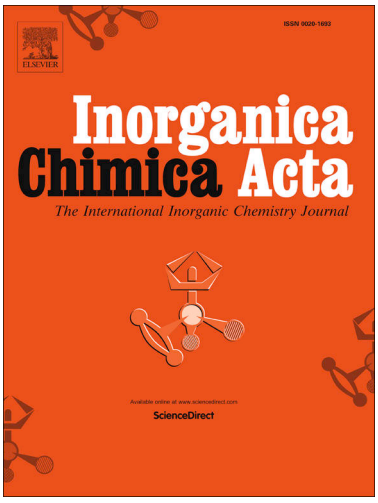

Research paper

Facile nucleophilic substitution of coordinated acetonitrile in *trans*-[$PtCl_4(NCMe)(PPh_3)$]

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Author Statement

In quality of corresponding author of the present paper, I state that all the Authors (Laura Agnarelli, David Fioco, Daniela Belli Dell' Amico, Luca Labella, Fabio Marchetti and Simona Samaritani) equally contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

Prof. Simona Samaritani

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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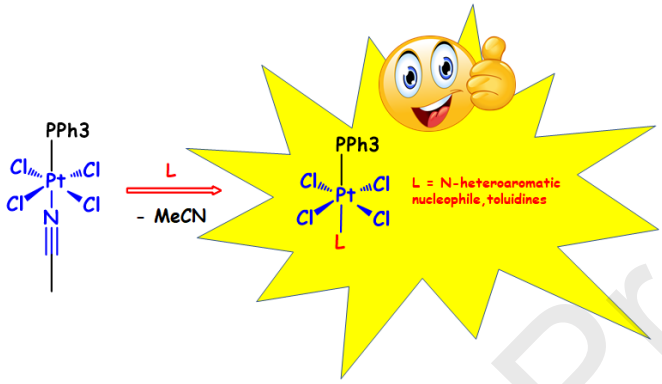

Trans-[$PtCl_4(NCMe)(PPh_3)$] promptly reacts with nucleophiles L (L = pyridine, quinoline, isoquinoline, benzothiazole, o-, m-, p-toluidine) affording the corresponding acetonitrile substitution products.

Even when protic o-, m- and p-toluidines were used, chemoselectivity towards substitution was observed, with addition products formed in less than 10% extent.

Facile nucleophilic substitution of coordinated acetonitrile in *trans*-[$PtCl_4(NCMe)(PPh_3)$]

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Dedicated to Dr Maurizio Peruzzini on occasion of his 65th birthday

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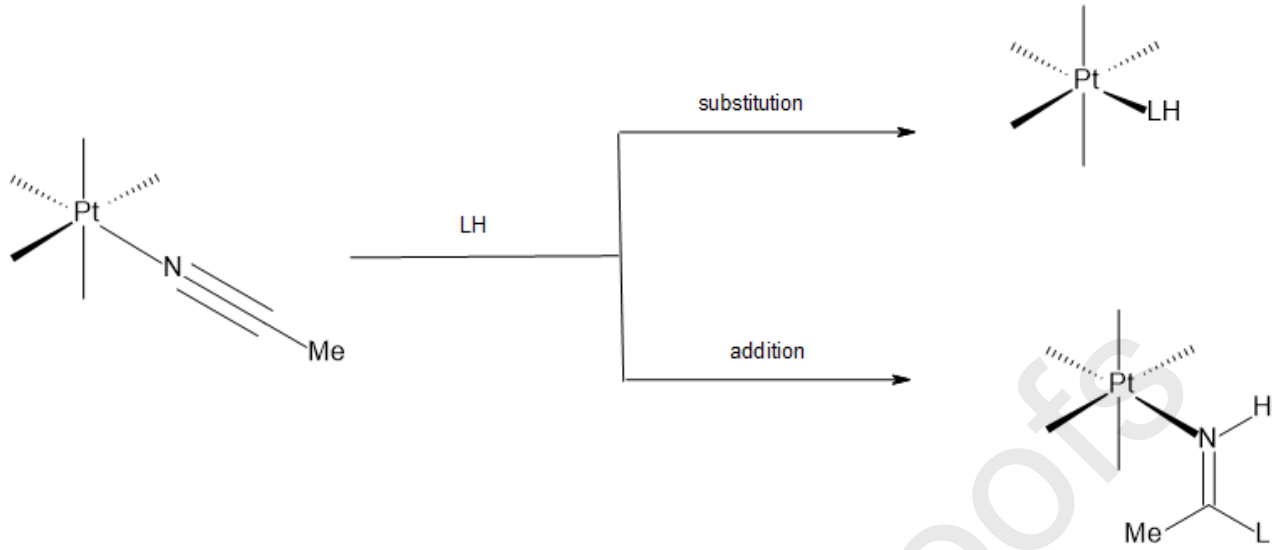
Abstract: Despite the generally accepted inertness of platinum(IV) complexes towards nucleophilic substitution, the title compound promptly reacts with nucleophiles L (L = pyridine, quinoline, isoquinoline, benzothiazole, o-, m-, p-toluidine) affording the corresponding acetonitrile substitution products. To follow the reaction spectroscopically, a series of platinum(IV) standards were prepared by bridge splitting of *trans*-$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$, followed by oxidation by $PhICl_2$. All the new platinum(II) and platinum(IV) complexes were fully characterized, and, in some cases, the structure was studied by single crystal X-ray diffraction. Even when protic o-, m- and p-toluidines were used, chemoselectivity towards substitution was observed, with addition products formed in less than 10% extent.

Keywords: platinum(IV) complexes; substitution reactions; triphenylphosphine; trans effect

1. **Introduction**

Platinum(IV) complexes find several applications in the fields of catalysis [i]and anticancer prodrugs [ii]. Among platinum(IV) species, those containing phosphine ligands [ia,e] are particularly interesting, since they are often involved in C-H and C-C activation processes. Most of these complexes are characterized by the presence of at least one σ-donating anionic aryl- or alkyl coordinated residue, enhancing the electronic density of the metal center and its interaction with π-acid phosphine ligand. In the absence of stabilizing aryl- or alkyl groups, it is quite common to observe decomposition of platinum(IV) phosphine complexes, especially in the presence of water, with formation of platinum(II) species and phosphine oxides [iii]. As a matter of fact, for $[PtX_4(L)(PR_3)]$ and $[PtX_5(PR_3)]^-$ systems (X=halogen, L= neutral ligand) only few data are present in the literature [iv]. It must be underlined that oxidation of platinum(II) precursors is the generally accepted approach to platinum(IV) species. As a matter of fact, apart from the pioneering studies by Chernyaev in aqueous media, [v] very few examples of substitution reactions in Pt(IV) species are described, since platinum(IV) metal centers are slow in this kind of transformation. This behavior clearly appears when considering the reactivity of platinum(IV) nitrile complexes with protic LH nucleophiles. Although both substitution and addition pathways are theoretically possible (Scheme 1), the reaction with LH nucleophiles, such as amidoaldoximes [vi], diamines [vii], oximehydroxamic acid [viii], hydroxylaminoximes [ix], phosphorus imines [x], sulfimidosulfides [xi] usually affords addition products.



Scheme 1. Substitution and addition pathways in the reaction between platinum(IV) nitrile complexes and protic nucleophiles LH.

This reactivity is also evident when considering that platinum(IV) nitrile complexes are moisture sensitive. It is reported, indeed, that they are subject to two step hydration, to give platinum-bound ammonia and uncomplexed acetic acid. [xii] In the slow (2-3 d) reaction of *trans*-[$PtCl_4(NCMe)_2$] with some nitroanilines [xiii], the formation of substitution products has been observed to be dependent on the reaction conditions as well as on the structure (ortho, meta or para) of the nitroaniline. Moreover, only with the less basic ortho- and para-nitroanilines, the yields in the substitution products were good, while in the case of the meta-aniline the addition products were observed. In the context of our studies about anticancer platinum complexes containing PPh_3 ligand, [xiv] we recently described a clean protocol to oxidize [$PtCl_2(L)(PPh_3)$] systems to the corresponding [$PtCl_4(L)(PPh_3)$] species [iva], using $PhICl_2$ under anhydrous conditions. Despite the already mentioned inertness of Pt(IV) species, for L = MeCN a fast exchange of the coordinated MeCN in acetonitrile solution was observed *via* ^1H NMR spectroscopy for the *trans* isomer, but not for the *cis* one, suggesting a different reactivity of the two isomers towards nucleophilic substitution. [iva] The studies of the reaction of *trans*-[$PtCl_4(NCMe)(PPh_3)$] with different nucleophiles are presented in this paper.

2. Experimental

2.1. Materials and methods

Reactions were carried out in Ar atmosphere, if not otherwise stated. Solvents were purified and dried according to reported procedures.[xv] Solid reagents were used with no further purification. Samples of cis,trans-$[PtCl_2(NCMe)_2]$,[xvi] *trans*-$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$,[xvii] were prepared from K_2PtCl_4 and $[PtCl_2(NCMe)_2]$ respectively, according to reported procedures. Complexes $[PtCl_2(L)(PPh_3)]$ were prepared by bridge splitting of *trans*-$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ according to a described procedure.[xiv] Samples of $[PtCl_4(NCMe)(PPh_3)]$[iva], $[PtCl_4(Py)(PPh_3)]$[iva], $[PtCl_4(p\text{-toluidine})(PPh_3)]$[iva], $[PtCl_4(NHBz_2)(PPh_3)]$[iva] $[PtCl_2(Py)(PPh_3)]$[xviii] and $[PtCl_2(p\text{-toluidine})(PPh_3)]$[xivc] were prepared according to reported procedures. Iodobenzene dichloride was prepared according to literature[xix] and stored at -20 °C, shielded from light. Elemental analyses were carried out by an elemental analyzer "vario MICRO CUBE" CHNOS. IR spectra were recorded by a Perkin Elmer "Spectrum One" spectrometer, equipped with an ATR accessory; the following abbreviations were used to describe absorption peaks intensities and shapes: s= strong; m= medium; w= weak; br= broad; sh= shoulder. ^{1}H-, ^{13}C-, ^{31}P- e ^{195}Pt NMR spectra were recorded on a Bruker "Avance DRX 400" 400 MHz spectrometer, in $CDCl_3$ solution (Sigma-Aldrich, stored over Ag), if not otherwise stated. When NMR analyses were recorded using the reaction mixture, a sealed capillary containing C_6D_6 was inserted into the sample to allow the instrument lock. Chemical shifts (δ ppm) are referred to $Si(CH_3)_4$ for ^{1}H and ^{13}C, H_3PO_4 (85% in D_2O) for ^{31}P and H_2PtCl_6 for ^{195}Pt. The following abbreviations were used to describe spectra: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quadruplet, m = multiplet. The following abbreviations were used: tol (toluidine); quino (quinoline); isoquino (isoquinoline); bzthia (benzothiazole); py (pyridine); $NHBz_2$ (dibenzylamine).

2.2. General procedure for the synthesis of Pt(II) complexes from *trans*-$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$.

A sample of *trans*-$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ (≈0.300 g, ≈0.28 mmol), was introduced in a Schlenk tube and suspended in 10 mL of $CHCl_3$. The suitable ligand L was dissolved in $CHCl_3$ (1-3 mL) and added to the suspension ([L]/[Pt]=1 molar ratio). The suspension turned to a yellow, clear solution and was analyzed (^{31}P NMR); when the complete conversion was observed (1-2 h) the solution was concentrated under vacuum up to ¼ of the starting volume and n-heptane (10-15 mL) was added. The solid was isolated by filtration, washed with n-heptane (2-5 mL), dried under vacuum (6-8 h) and stored in sealed glass vials. Products were characterized by ^{31}P-, ^{1}H-,

^{13}C-, ^{195}Pt NMR, IR (ATR) and elemental analysis. *Cis, trans* equilibria in solution for all samples were studied by ^{31}P NMR spectroscopy.(cfr. Table 1)

2.2.1. *Trans*-[$PtCl_2$(isoqui)(PPh_3)]. A sample of 0.3018 g of dinuclear precursor (0.286 mmol) and 0.0739 g of isoquinoline (0.5722 mmol) were used. Conversion was complete (^{31}P NMR: 2.79, $^1J_{P\text{-}Pt}$=3568 Hz) in 1 h: *trans*-[$PtCl_2$(isoqui)(PPh_3)] (0.340g, 89% isolated yield). $C_{27}H_{22}Cl_2NPPt$: requires C 49.33, H 3.37, N 2.13 %. Found: C 48.97, H 3.50, N 1.96 %. IR (ATR), cm^{-1}: 3057br w, 2998m, 1634m, 1597s, 1435s, 1391br m, 1276m, 1211br m, 1098s, 865m, 826m, 740br s, 690s. ^{1}H NMR: 9.72 (s, 1H, C<u>H</u>N, $^3J_{H\text{-}Pt}$ = 30 Hz); 8.87 (br s, 1H, H_{arom}); 8.08 (br s, 1H, H_{arom}); 7.87 (m, 10H, H_{arom}); 7.49 (m, 9H, H_{arom}). ^{13}C NMR: 154.9; 142.9; 136.0; 134.9 (d, $J_{C\text{-}P}$=10.2 Hz); 132.7; 130.8; 129.0; 128.7; 128.4; 128.7 (d, $^1J_{C\text{-}P}$=65 Hz); 128.0 (d, $J_{C\text{-}P}$= 11.3 Hz); 126.3; 122.4 ^{31}P NMR: 2.79 (d, $^1J_{P\text{-}Pt}$= 3568 Hz). ^{195}Pt NMR: -3532 (d, $^1J_{Pt\text{-}P}$= 3568 Hz)

2.2.2. *Trans*-[$PtCl_2$(quino)(PPh_3)]. A sample of 0.3040 g of dinuclear precursor (0.288 mmol) e 0.0750 g of quinoline (0.578 mmol) were used. After ligand addition a light-yellow solid formed in 30 minutes. The mixture was mildly heated to solubilize the solid and the yellow solution was analyzed (^{31}P NMR): 2.22, $^1J_{P\text{-}Pt}$=3642 Hz. *trans*-[$PtCl_2$(quino)(PPh_3)] (0.354 g, 94% isolated yield). Soluble in hot $CHCl_3$. $C_{27}H_{22}Cl_2NPPt\cdot H_2O$ requires C 47.98, H 3.26, N 2.07 %. Found: C 47.36, H 3.16, N 1.94 %. IR (ATR), cm^{-1}: 3050br w, 2999 br w, 2896 br w, 1622w, 1508s, 1483m, 1435s, 1207br w, 1186br w, 1155w, 1027br w, 999w, 807s, 776m, 692s. ^{1}H NMR: 9.57 (d, 1H, C<u>H</u>N); 9.30 (br s, 1H, H_{arom}); 8.33 (d, 1H, NCHC<u>H</u>); 7.90 (m, 7 H, H_{arom}); 7.66 (m, 2 H, H_{arom}); 7.50 (m, 10H, H_{arom}). ^{13}C NMR (50° C): 152.7; 146.2; 138.8; 134.9 (d, $J_{C\text{-}P}$=10 Hz); 130,8; 130,1; 129.1; 128.8; 128.5; 127.9 (d, $J_{C\text{-}P}$=11 Hz); 127.7; 125.6 (d, $^1J_{C\text{-}P}$= 67 Hz); 121.5. ^{31}P NMR: 2.35 ($^1J_{P\text{-}Pt}$= 3634 Hz). ^{195}Pt NMR: -3510 (d, $J_{Pt\text{-}t}$= 3634 Hz).

2.2.3. *Trans*-[$PtCl_2$(m-tol)(PPh_3)]. A sample of 0.3014 g of dinuclear precursor (0.285 mmol) and 0.0612 g of m-toluidine (0.571 mmol) were used. Conversion was complete (^{31}P NMR: 3.60, $^1J_{P\text{-}Pt}$=3775 Hz) in 3 h: *trans*-[$PtCl_2$(m-tol)(PPh_3)] (0.2688 g, isolated yield 74%). $C_{25}H_{24}Cl_2NPPt\cdot H_2O$ requires C 45.94, H 3.98, N 2.14 %. Found: C 45.36, H 3.29, N 2.20 %. IR (ATR), cm^{-1}: 3278br m, 3206br m, 3127br m, 3058br m, 1615br m, 1593br m, 1575br m, 1495m, 1435s, 1121br s, 1096s, 1028br m, 919m, 786m, 747br

m, 707m, 690s.^{1}H NMR: 7.71 (m, 6H, H_{arom}); 7.41 (m, 8H, H_{arom}); 7.22 (m, 4H, H_{arom}); 7.02 (m, 1H, H_{arom}); 5.34 (m, 2H, NH_2); 2.38 (s, 3H, CH_3). ^{13}C NMR: 139.4; 134.8 (d, $^{3}J_{C-P}$= 10.4 Hz); 130.9 (d, $^{4}J_{C-P}$= 2.0 Hz); 129.1; 128.7; 128.0 (d, $^{2}J_{C-P}$= 11.3 Hz); 126.7 ($^{1}J_{C-P}$=64 Hz); 126.4; 122.3; 118.8; 21.2. ^{31}P NMR: 3.63 (J_{P-Pt}=3782 Hz). ^{195}Pt NMR: -3614 ($^{1}J_{Pt-P}$= 3782 Hz).

2.2.4. *Trans*-[$PtCl_2$(o-tol)(PPh_3)]. A sample of 0.3013 g of dinuclear precursor (0.285 mmol) and 0.0617 g of o-toluidine (0.576 mmol) were used. Conversion was complete (^{31}P NMR: 3.65, $^{1}J_{P-Pt}$=3808 Hz) in two hours: *trans*-[$PtCl_2$(o-tol)(PPh_3)] (0.3002 g, 83% yield). $C_{25}H_{24}Cl_2NPPt\cdot H_2O$ requires: C 45.94, H 3.98, N 2.14 %. Found: C 45.48, H 3.30, 2.10%. IR (ATR) cm^{-1}: 3280 bm, 3197 m, 3116 bw, 3055 bw, 1573 m, 1553 m, 1493 m, 1464 m, 1429 bm, 1124 bm, 1092 bm, 1044 m, 1023 m, 995 m, 745 s, 691 s. ^{1}H NMR: 7.36 (bs, 6H, H_{arom}); 7.43 (m, 9 H, H_{arom}); 7.21 (m, 4H, H_{arom}); 5.27 (2, 2H, NH_2); 2.58 (s, 3H, CH_3). ^{13}C NMR: 138.2; 134.8 (d, $^{3}J_{C-P}$=10 Hz); 131.1; 130.9 (d, $^{2}J_{C-P}$=17 Hz); 128.9; 128.4 ($^{1}J_{C-P}$= 63Hz); 127.9 (d, $^{3}J_{C-P}$= 11 Hz); 126.6; 125.7; 123.2; 18.8. ^{31}P NMR: 3.78 ($^{1}J_{P-Pt}$=3813 Hz). ^{195}Pt NMR: -3615 ($^{1}J_{Pt-P}$=3813 Hz).

2.3. *Study of the system "trans-[Pt(μ-Cl)Cl(PPh_3)]$_2$ + benzothiazole" in $CDCl_3$.* A sample of 35.9 mg (0.034 mmol) of dinuclear precursor were weighed into an NMR test tube, suspended in $CDCl_3$, and treated with benzothiazole (bzthia, 14 μL, 0.128 mmol, bzthia/Pt = 1.88 molar ratio). The suspension turned into a yellow solution in minutes and was analyzed (^{1}H-, ^{31}P-, ^{13}C- and ^{195}Pt NMR). The following signals (signals of free benzothiazole are omitted) were ascribed to *trans*-[$PtCl_2$(bzthia)(PPh_3)]. ^{1}H NMR: 9.52 (d, $^{4}J_{H-P}$ = 2.2 Hz, 1H, SCHN); 8.95 (d, J = 8.3 Hz, 1H, S(N)CCH); 7,90-7,80 (m, 7H, PPh_3 + N(S)CCH); 7.7 (t, 1H, CH_{bzthia}); 7.60-7.40 (m, 10H PPh_3 + CH_{bzthia}). ^{31}P NMR = 2.50 ($^{1}J_{P-Pt}$ = 3740 Hz). ^{13}C NMR: 158.2; 148.8; 134.8 ($^{3}J_{C-P}$ = 10.3 Hz); 133.7; 130.9 ($^{4}J_{C-P}$ = 2.6 Hz); 128.3 ($^{1}J_{C-P}$ = 65.5 Hz); 127.9 ($^{2}J_{C-P}$ = 11.4 Hz); 127.1; 126.8; 124.4; 122.1. ^{195}Pt NMR: -3528 ($^{1}J_{P-Pt}$ = 3740 Hz). The mixture was analyzed (^{1}H- and ^{31}P NMR) after three hours: a mixture of *trans*-[$PtCl_2$(PPh_3)(bzthia)] (70%) and *cis*-[$PtCl_2$(bzthia)(PPh_3)] (30%) was present. Selected signals for *cis*-[$PtCl_2$(PPh_3)(bzthia)]: ^{1}H NMR: 9.1 (s, 1H, SCHN); 8.72 (d, 1H, S(N)CCH); 7.70-7.60 (m, 6H, PPh_3); 7.50-7.40 (m, 3H, N(S)CCH, CHC<u>H</u>C<u>H</u>CH); 7.31 (m, 3H, PPh_3); 7.24 (m, 6H, PPh_3). ^{31}P NMR: 6.53 ($^{1}J_{P-Pt}$ = 3790 Hz). After 96 hours a colorless solid was present in the NMR tube, which was identified as *cis*-[$PtCl_2$(bzthia)(PPh_3)], while ^{1}H NMR analysis of the liquid phase evidenced only the presence of excess free benzothiazole.

2.4. Synthesis of cis-[$PtCl_2$(bzthia)(PPh_3)]. A sample of 0,0804 g (0,0761 mmol) of dinuclear precursor was introduced into a Schlenk tube, with 20 µL of bzthia (bzthia/Pt = 1.10 molar ratio), and 5 mL of 1,2-dce The mixture was refluxed (84 °C, 96h). A yellow solution formed in 3h and, upon heating, a colorless, crystalline solid formed. Crystals of *cis*-[$PtCl_2$(bzthia)(PPh_3)] ·$C_2H_4Cl_2$ were filtered and dried (0,1010 g, 87% yield). $C_{25}H_{20}Cl_2NPPtS\cdot C_2H_4Cl_2$ requires: C 42.53, H 3.17, 1.84%. Found: C 42.61, H 3.03, N 1.92%. IR (ATR) cm^{-1}: 3041m, 1480s, 1307m, 1097s, 940s, 750m, 688m. A crystal was selected for the determination of the structure *via* single crystal X-ray diffraction, which confirmed N-coordination and *cis* geometry.

2.5. Synthesis of Pt(IV) complexes starting from trans-[Pt(µ-Cl)Cl(PPh_3)]$_2$. General procedure.

Intermediate Pt(II) complexes were obtained from *trans*-[Pt(µ-Cl)Cl(PPh_3)]$_2$ according to the procedure described in section 2. When the complete conversion into *trans*-[$PtCl_2$(L)(PPh_3)] was reached (^{31}P NMR), a stoichiometric amount of $PhICl_2$ was added [Pt(II)/oxidant=1 molar ratio]. The solution turned to a darker yellow color; the reaction was monitored through ^{31}P NMR. When the maximum conversion was obtained (1-3 h), the solution was concentrated under vacuum and treated with n-heptane. Solid products were isolated by filtration under argon atmosphere, washed with n-heptane, dried under vacuum (6-7 h) and stored under argon atmosphere in sealed glass vials in the dark. Products were characterized by ^{31}P-, ^{1}H-, ^{13}C-, ^{195}Pt NMR ($CDCl_3$), IR (ATR) and elemental analysis. Geometrical equilibria in $CHCl_3$ solutions were studied through ^{31}P NMR for all the reported species (cfr. Table 3).

2.5.1. *Trans-[$PtCl_4$(isoqui)(PPh_3)].* A sample of 0.3020 g (0.2859 mmol) of dinuclear precursor and 0.0741 g (0.5714 mmol) of isoquinoline (isoqui) were used. $PhICl_2$ (0.1970 g, 0.7166 mmol) was dissolved in chloroform and added. *Trans*-[$PtCl_4$(isoqui)(PPh_3)]: 0.3040g (73% yield). $C_{27}H_{22}Cl_4NPPt$ requires: C 44.52, H 3.04, N 1.92 %. Found: C 44.31, H 2.84, N 1.90%. IR (ATR), cm^{-1}: 3058bm, 1633m, 1462w, 1435s, 1387m, 1324bm, 1279m, 1211bs, 1195bm, 1179m, 1087m, 1048m, 999m, 864 m, 818s, 740bs, 686 s. ^{1}H NMR: 9.94 (d, $^{4}J_{H\text{-}P}$ = 5,9 Hz, $^{3}J_{H\text{-}Pt}$= 26 Hz, 1H, isoqui CHN); 9.13 (dd, J= 6.5 Hz, $^{4}J_{H\text{-}P}$ = 5.9 Hz, $^{3}J_{H\text{-}Pt}$= 26 Hz , 1H, isoqui CHN); 8.09 (m, 7H, PPh_3); 7.88 (m, 3H isoqui H_{arom}); 7.72 (t, 1H, isoqui H_{arom}); 7.57 (m, 3H PPh_3); 7.48 (m, 6H, PPh_3). ^{13}C NMR: 155.0; 141.5; 136.6; 136.1 (d, $^{3}J_{C\text{-}P}$=8.8 Hz); 133.6; 132.2; 129.4; 128.5; 127.7 (d, $^{2}J_{P\text{-}C}$=12.2 Hz); 126.2, 125.6 (d, $^{1}J_{C\text{-}P}$= 69 Hz); 122.2 (2C). ^{31}P NMR: -2.38 ($^{1}J_{P\text{-}Pt}$=2169 Hz). ^{195}Pt NMR: -1479 ($^{1}J_{Pt\text{-}P}$=2169 Hz).

2.5.2. *Trans-[$PtCl_4$(quino)(PPh_3)].* A sample of 0.3038 g (0.288 mmol) of dinuclear precursor and 0.0746 g (0.578 mmol) of quinoline (quino) were used. $PhICl_2$ (0.2976 g, 1.08 mmol) was dissolved in chloroform and added. *Trans*-[$PtCl_4$(quino)(PPh_3)] (yellow solid, sparingly soluble in chloroform: 0.2209 g, 53% yield). $C_{27}H_{22}Cl_4NPPt$ requires: C 44.52, H 3.04, N 1.92 %. Found: C 44.48, H 2.97, N 1.76 %. IR (ATR); cm^{-1}: 3148 w, 3115 w, 3067w, 3026 w, 2963 bw, 1620 m, 1585 m, 1513s, 1435s, 1403 m, 1366 m, 1310 m, 1233 m, 1211bs, 1195 m, 1096 m, 1086 m, 1073 m, 998 m, 808 m, 771 m, 740bs, 686 s. ^{1}H NMR: 9.92 (s, 1H); 8.37 (m, 1H); 8.14 (m, 7H); 8.06 (m, 1H); 7.84 (m, 2H); 7.54 (m, 11 H);. ^{31}P NMR: 0.72 ($^1J_{P\text{-}Pt}$= 2215 Hz). ^{195}Pt NMR : -1299 ($^1J_{Pt\text{-}P}$= 2215 Hz).

2.5.3. *[$PtCl_4$(m-tol)(PPh_3)].* A sample of 0.2965 g (0.281 mmol) of dinuclear precursor and 0.0600 g (0.560 mmol) of m-toluidine were used. $PhICl_2$ (0.1964g, 0.714 mmol) was dissolved in chloroform and added to the yellow solution. *Trans*-[$PtCl_4$(m-tol)(PPh_3)] (yellow-brown solid, 0.2965g, 74% yield). $C_{25}H_{24}Cl_4PNPt \cdot H_2O$ requires: C 41.45, H 3.61, N 1.95 %. Found: C 40.96, H 3.21, N 1.98 %. IR (ATR), cm^{-1}: 3257 m, 3202 m, 3114 w, 3059 w, 1570 m, 1483 s, 1435 s, 1258 m, 1132 m, 1088 s, 998 m, 898 m, 746 m, 686 s. ^{1}H NMR: 7.94 (m, 6H, H_{arom}); 7.53 (3H, m, 7.53 H_{arom}); 7.43 (6H, m, H_{arom}); 7.23 (3H, m, H_{arom}); 7.12 (1H, m, H_{arom}); 6.24 (2H, bs, $^1J_{H\text{-}Pt}$=45 Hz, NH_2); 2.34 (3H, s, CH_3); ^{13}C NMR: 138.9; 135.8 (d, $^3J_{C\text{-}P}$=9 Hz); 132.3 (d, $^4J_{C\text{-}P}$=3 Hz); 129.1; 129.0; 128.7; 127.8 (d, $^2J_{C\text{-}P}$=12 Hz); 125.2 (d, $^1J_{C\text{-}P}$= 68 Hz); 123.8; 120.3; 21.4. ^{31}P NMR ($CDCl_3$): 3.83 ($^1J_{P\text{-}Pt}$= 2268). ^{195}Pt NMR ($CDCl_3$): -1607 (d, $^1J_{Pt\text{-}P}$=2268).

2.5.4. *[$PtCl_4$(o-tol)(PPh_3)]* A sample of 0.2982 g (0.2822 mmol) of dinuclear precursor and 0.0605 g (0.565 mmol) of o-toluidine were used. $PhICl_2$ (0.1552g, 0.565 mmol) was dissolved in chloroform and added to the yellow solution. *Trans*-[$PtCl_4$(o-tol)(PPh_3)] (dark-orange solid, 0.3419 g, 86% yield). $C_{25}H_{24}Cl_4PNPt \cdot H_2O$ requires: C 41.45, H 3.61, N 1.95 %. Found: C 41.32, H 3.28, N 2.00 %. IR (ATR), cm^{-1}: 3300 m, 3228 m, 3059 w, 1585 w, 1494 m, 1466 m, 1437 s, 1191 m, 1159 m, 1100 s, 1087 s, 1047 m, 1032 m, 998 m, 767 m, 686s.^{1}H NMR: 7.96 (m, 6H, H_{arom}); 7.50 (m, 8H, H_{arom}); 7.25 (m, 5H, H_{arom}) 6.27 (bs, 2H, NH_2); 2.55 (s, 3H, CH_3). ^{13}C NMR: 135.9 (d, $^3J_{C\text{-}P}$=9 Hz); 135.6; 132.3 (d, $^4J_{C\text{-}P}$=2 Hz); 131.4; 130.8; 127.8 (d, $^2J_{C\text{-}P}$= 12 Hz); 126.9; 126.6; 125.2 (d, $^1J_{C\text{-}P}$=68 Hz); 124.30, 19.37. ^{31}P NMR: 4.4 ($^1J_{P\text{-}Pt}$= 2266 Hz). ^{195}Pt NMR: -1580 (d, $^1J_{Pt\text{-}P}$=2266 Hz).

2.5.5. *Trans-[$PtCl_4$(bzthia)(PPh_3)]* A sample of 0.3013g (0.285 mmol) of dinuclear precursor and 0.0779 g (0.576 mmol) of benzothiazole were used. A clear yellow

solution formed in minutes, showing (^{31}PNMR, C_6D_6) a single signal at 2.44 ppm ($J_{P\text{-}Pt}$=3744). An equimolar amount of $PhICl_2$ (0.1568g, 0.5704 mmol) was added and a yellow solid formed, showing (^{31}P NMR) a single signal at -1.17 ($^1J_{P\text{-}Pt}$=2280 Hz). Trans-[$PtCl_4$(bzthia)(PPh_3)] (yellow solid, 0.3527g, 84% yield). Yellow crystals were obtained from a diluted $CHCl_3$ solution. Single crystal X-ray diffraction confirmed the *trans* geometry of the complex. $C_{25}H_{20}Cl_4NPSPt \cdot ½\ CHCl_3$ requires: C 38.57, H 2.60, N 1.76 %. Found: C 38.14, H 2.52, N 1.74 %. ^{1}H NMR : 10.02 (d, $^3J_{H\text{-}Pt}$=18 H, 1H, SC<u>H</u>N); 9.38 (d, 1H, C<u>H</u>SCHN); 8.09 (m, 6H, H_{arom}); 7.95 (m, 1H, H_{arom}); 7.59 (m, 4 H, H_{arom}); 7.50 (m, 7H H_{arom}). ^{31}P NMR: -1.17 ($^1J_{P\text{-}Pt}$= 2280 Hz). ^{195}Pt NMR: -1398 ($^1J_{Pt\text{-}P}$= 2280 Hz). IR (ATR), cm^{-1}: 3114 w, 2998 w, 1465 m, 1455 m 1434 m 1411 m, 1272 m, 1211bs, 1195 m, 1096 m, 1087 m, 926 s, 740bs, 729 m, 705 m, 686 s.

2.6. *Synthesis of Pt(IV) complexes by substitution reaction of [$PtCl_4$(NCMe)(PPh_3)] with nucleophiles. General procedure.*

A sample of [$PtCl_4$(NCMe)(PPh_3)] was placed in a Schlenk tube under Ar atmosphere with 10 mL of acetonitrile. The yellow suspension was heated (70°C) until complete dissolution of the solid (1h); the clear yellow solution was treated with ligand L (molar ratio [L]/[Pt]=1) under vigorous stirring and the reaction was monitored by ^{31}P NMR spectroscopy until maximum conversion. The mixture was concentrated under vacuum and treated with diethyl ether, affording a solid product that was isolated by filtration under Ar atmosphere, washed with diethyl ether, and dried under vacuum (6-7 h). The characterization was carried out by elemental analysis and comparison of NMR spectroscopic data with those of authentic samples.

2.6.1. Trans-[$PtCl_4$(isoquino)(PPh_3)]. A sample of 0.2438g (0.3808 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.0492g isoquinoline (0.3808 mmol) were used. A yellow solid precipitated out of the reaction mixture in 3.5 h, was isolated by filtration, washed, and dried under vacuum. *Trans*-[$PtCl_4$(isoquino)(PPh_3)] (0.1186 g, yellow solid, 43% yield) was identified by comparison of ^{31}P NMR data (-2.37 ($^1J_{P\text{-}Pt}$= 2166 Hz), cfr. 4.1. Crystals were obtained by slow diffusion of pentane vapors into a chloroform solution and single crystal X-ray diffraction analysis confirmed the trans stereochemistry for the complex.

2.6.2. Trans-[$PtCl_4$(quino)(PPh_3)]. A sample of 0.2893g (0.4521 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.0584g isoquinoline (0.4521 mmol) were used. A yellow solid precipitated out of the reaction mixture in 3.5 h, was isolated by filtration,

washed, and dried under vacuum. *Trans*-[$PtCl_4$(isoquino)(PPh_3)] (0.2332 g, yellow solid, 70% yield) was identified by comparison of ^{31}P NMR data (0.72 ($^1J_{P\text{-}Pt}$= 2217 Hz), cfr. 4.2.

2.6.3. *Trans-[$PtCl_4$(bzthia)(PPh_3)].* A sample of 0.2730g (0.5481 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.07399g benzothiazole (0.5481 mmol) were used. A yellow solid precipitated out of the reaction mixture in 2 h, was isolated by filtration, washed, and dried under vacuum. *Trans*-[$PtCl_4$(bzthia)(PPh_3)] (0.1854 g, yellow solid, 57% yield) was identified by comparison of ^{31}P NMR data (-1.17 ($^1J_{P\text{-}Pt}$= 2280 Hz), cfr. 4.5.

2.6.4. *Trans-[$PtCl_4$(py)(PPh_3)].* A sample of 0.1108 g (0.173 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.0137g of pyridine (0.173 mmol) were used. *Trans*-[$PtCl_4$(py)(PPh_3)] (0.0795 g, 68 % yield) was identified by comparison with reported data [iva].

2.6.5. *[$PtCl_4$(p-tol)(PPh_3)].* A sample of 0.0685 g (0.109 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.0117g of p-toluidine (0.109 mmol) were used. [$PtCl_4$(p-tol)(PPh_3)] (0.0545 g, 72 % yield as mixture of isomers) was identified by comparison with reported data [iva]

2.6.6. *[$PtCl_4$(o-tol)(PPh_3)].* A sample of 0.2430 g (0.380 mmol) of [$PtCl_4$(NCMe)(PPh_3)] and 0.0408g of o-toluidine (0.381 mmol) were used. [$PtCl_4$(o-tol)(PPh_3)] (0.1476 g, 55 % yield) was identified by comparison of ^{31}P NMR data ($CDCl_3$): 4.38 ($J_{P\text{-}Pt}$= 2263 Hz, 70%); 5.65 ($J_{P\text{-}Pt}$=2262 Hz, 25%) (cfr. 4.4). In ^{31}P spectrum a signal at 4.58 ppm ($J_{P\text{-}Pt}$=2130 Hz, 5 %) was ascribed to a product arising from the addition of toluidine to coordinated acetonitrile.

2.6.7. *[$PtCl_4$(m-tol)(PPh_3)].* A sample of 0.1904 g (0.297 mmol) of [$PtCl_4$(PPh_3)(NCMe)] and 0.0319 g of m-toluidine (0.298 mmol) were used. [$PtCl_4$(m-tol)(PPh_3)] (0.1560 g, 73 % yield as mixture of isomers) was identified by comparison of ^{31}P NMR data ($CDCl_3$): 3.88 ($^1J_{P\text{-}Pt}$= 2265 Hz, 73%); 4.59 ($^1J_{P\text{-}Pt}$= 2135 Hz, 22%), cfr. 4.3. In ^{31}P spectrum a signal at 4.89 ppm ($J_{P\text{-}Pt}$ not detected, 5 %) was ascribed to a product arising from the addition of toluidine to coordinated acetonitrile.

2.7. X-Ray determinations

Crystals described in paragraphs 2.4, 2.1.5 and 2.6.1 were selected at room temperature (296 K), glued to glass fibers and analyzed with a Bruker "Smart Breeze" CCD diffractometer. Table 1 summarizes the lattice parameters and the relatives space groups. Intensity data were collected in the range of 2ϑ angles

reported in Table 1. After correction for Lorentz and polarization effects and for absorption, the structure solution was obtained using the direct methods contained in SHELXS program. [xx] Crystals of compounds 4.1 and 5.5 were found to contain one solvent molecule for each molecule of the complex: dichloroethane and chloroform, respectively. The final reliability factors of the refinement procedure obtained using SHELXL program,[xxi] are listed in Table 1. Other control calculations were performed with the programs contained in the WINGX suite.[xxii]

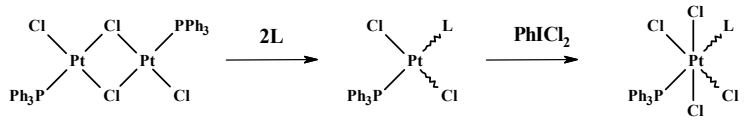
CCDC 2032590-2032592 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table 1. Crystal data and refinement summaries for compounds described in 2.4, 2.1.5 and 2.6.1

Identification code	*cis*-[$PtCl_2$(bzthia)(PPh_3)]·· dce	*trans*-[$PtCl_4$(bzthia)(PPh_3)]·· $CHCl_3$	*trans*-[$PtCl_4$(isoqui)(PPh_3)]
CCDC number	2032590	2032591	2032592
Empirical formula	$C_{27}H_{24}Cl_4NPPtS$	$C_{26}H_{21}Cl_7NPPtS$	$C_{27}H_{22}Cl_4NPPt$
Formula weight	762.39	853.71	728.31
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ 2_1/c$
a (Å)	11.1792(2)	10.009(2)	19.0004(11)
b (Å)	11.2980(2)	11.196(2)	8.9958(5)
c (Å)	11.8469(2)	14.965(3)	15.4543(9)
α (°)	98.6010(10)	79.890(3)	-
β (°)	99.9220(10)	85.039(3)	96.2710(10)
γ (°)	98.8750(10)	67.456(3)	-
Volume (Å^3)	1432.22(4)	1524.4(5)	2625.7(3)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.768	1.860	1.842
μ (mm^{-1})	2.426	5.355	5.829
F(000)	740	824	1408
ϑ range (°)	2.8 to 34.1	2.8 to 26.0	1.1 to 30.5
Reflections collected	42201	15390	63294
Independent reflections	11630	5782	7971
Goodness-of-fit on F^2	1.055	1.187	1.106
Final R_1 [$I \geq 2\sigma(I)$]	0.0248	0.0433	0.0312
Final wR_2 [$I \geq 2\sigma(I)$]	0.0645	0.1010	0.0594
Final R_1 [all data]	0.0311	0.0470	0.0371
Final wR_2 [all data]	0.0682	0.1031	0.0613
Largest peak/hole (e Å^{-3})	1.286, −0.872	1.843, −1.620	1.268, −0. 684

3. Results and Discussion

The reaction between *trans*-[$PtCl_4(NCMe)(PPh_3)$] and suitable nucleophiles can be conveniently followed by ^{31}P NMR spectroscopy. To have suitable standard compounds, a series of [$PtCl_4(L)(PPh_3)$] were necessary. The complexes were prepared by oxidation of the corresponding platinum(II) complexes, according to the procedure already described[iva] for the preparation of [$PtCl_4(Py)(PPh_3)$], [$PtCl_4(p\text{-}tol)(PPh_3)$] and [$PtCl_4(NHBz_2)(PPh_3)$] (Scheme 2).



L = Pyridine; isoquinoline; quinoline; o-toluidine; m-toluidine; p-toluidine; benzothiazole; dibenzylamine

Scheme 2. General procedure for the synthesis of [$PtCl_4(L)(PPh_3)$] complexes

3.1. Preparation of [$PtCl_2(L)(PPh_3)$] complexes

The bridge-splitting reaction of *trans*-[$Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ by neutral nucleophiles L (L/Pt = 1 molar ratio) is a well consolidated procedure driven by the strong trans effect of the PPh_3 group yielding *trans*-[$PtCl_2(L)(PPh_3)$] systems. These kinetic products can isomerize in solution, affording mixtures with a molar ratio between *cis* and *trans* isomers dependent by the nature of L and with isomerization equilibria easily monitorable in solution by ^{31}P NMR spectroscopy (Table 2). In this work, some new complexes were isolated and characterized, *cis* and *trans* configurations were assigned by comparison of NMR data with those of similar species.

Table 2. Main ^{31}P- and ^{195}Pt NMR data for complexes [$PtCl_2$(**L**)(PPh_3)]

	^{31}P NMR (ppm, coupling constant $^1J_{P\text{-}Pt}$ Hz)	**^{195}Pt NMR (ppm, coupling constant $^1J_{P\text{-}Pt}$ Hz)**	**Trans/cis % molar ratio in solution after reaching equilibrium**	**Ref.**
[$PtCl_2$(**Py**)(PPh_3)]	2,59 ($^1J_{P\text{-}Pt}$= 3583) *trans* isomer. 7,24 ($^1J_{P\text{-}Pt}$= 3902) *cis* isomer	-3379 (d, $^1J_{Pt\text{-}P}$= 3902), *cis* isomer -3540 ($^1J_{P\text{-}Pt}$= 3583), *trans* isomer	50/50	Ref. [xviii]
[$PtCl_2$(**isoqui**)(PPh_3)]	2.79 ($^1J_{P\text{-}Pt}$= 3568) *trans* isomer. 7.66 (undetected J) *cis* isomer	-3532 (d, $^1J_{Pt\text{-}P}$= 3568), *trans* isomer	88/12	This work
[$PtCl_2$(**quino**)(PPh_3)]	2.35 ($^1J_{P\text{-}Pt}$= 3634) *trans* isomer. 6.53 ($^1J_{P\text{-}Pt}$=3882) *cis* isomer	-3510 (d, $^1J_{Pt\text{-}P}$= 3634)	77/23	This work
[$PtCl_2$(**o-tol**)(PPh_3)]	3.78 ($^1J_{P\text{-}Pt}$=3813) *trans* isomer. 6.10 (traces) *cis* isomer	-3615 ($^1J_{Pt\text{-}P}$=3813)	99/1	This work
[$PtCl_2$(**m-tol**)(PPh_3)]	3.63 ($^1J_{P\text{-}Pt}$= 3782) *trans* isomer. 3.42 *cis* isomer	-3614 ($^1J_{P\text{-}Pt}$= 3782)	90/10	This work
[$PtCl_2$(**p-tol**)(PPh_3)]	3.63 ($^1J_{P\text{-}Pt}$= 3773 Hz)	-3614 ($^1J_{P\text{-}Pt}$= 3773)	100/0	Ref. [xivb]
[$PtCl_2$(bzthia)(PPh_3)]	2.50 ($^1J_{P\text{-}Pt}$=3740) *trans* isomer.	-3528 ($^1J_{Pt\text{-}P}$ =3740), *trans* isomer	0/100[a]	This work

	6.53 ($^1J_{P-Pt}$=3790 Hz) *cis* isomer.			
[$PtCl_2$(**$NHBz_2$**)(PPh_3)]	4.13 ($^1J_{P-Pt}$=3633 Hz) *trans* isomer.	-3631 ($^1J_{Pt-P}$= 3633 Hz)	100/0	Ref. [xivc]

a) Equilibrium was not reached in solution, but 100% pure cis isomer precipitated out of the solution in 24h.

It is worth to notice that for L = benzothiazole, only N-coordination was observed, even when L/Pt molar ratio used was 0.5. The initial formation of the kinetic *trans* product (100%), which was completely characterized in solution (^{1}H-, ^{13}C-, ^{31}P- and ^{195}Pt NMR), was followed by a slow isomerization to *cis* complex. In this case, due to the very low solubility of *cis*-[$PtCl_2$(bzthia)(PPh_3)] in most organic solvents, the process was complete in 24 h and it was possible to recover the pure product, which was characterized by single crystal X-ray diffraction confirming the assigned stereochemistry. The structure of the complex is reported in figure 1, while the most significant geometric parameters are reported in Table 3.

Table 3: Selected bond distances (Å) and angles (°) in cis-[$PtCl_2$(bzthia)(PPh_3)]

Pt1–Cl1	2.3547(6)	Cl1–Pt1–N1	87.15(5)
Pt1–N1	2.0362(19)	N1–Pt1–P1	94.78(5)
Pt1–P1	2.2346(5)	P1–Pt1–Cl2	88.89(2)
Pt1–Cl2	2.2942(6)	Cl1–Pt1–Cl2	89.17(3)

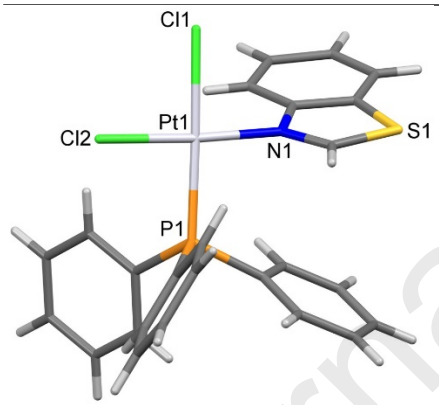


Figure 1. Molecular structure of *cis*-[$PtCl_2$(bzthia)(PPh_3)]

The coordination around platinum is square planar, with N-coordinated benzothiazole plane nearly orthogonal to the coordination plane. The Pt(1)-N(1) bond distance is in good agreement with that observed in analogous complexes [xxiii], while the Pt(1)-Cl(1) bond distance is significantly longer than the Pt(1)-Cl(2) one (2,3547(6) vs 2,2942(6) respectively), as expected due to the presence of PPh_3 ligand in trans position to Cl(1). The five-term benzothiazole ring forms a 26.9° dihedral angle with one of the triphenylphosphine phenyl rings, with a measured 3.87 Å distance between the centroids.

3.2. Preparation of [$PtCl_4$(L)(PPh_3)] complexes

According to the procedure described in Scheme 1, the synthesis of platinum(IV) phosphine complexes was carried out by a two-step process, where the bridge-splitting of *trans*-[Pt(μ-Cl)Cl(PPh_3)]$_2$ by ligand L

was followed by the *in situ* addition of an equimolar amount of $PhICl_2$ oxidant. The reactions were carried out in anhydrous solvents under argon, to minimize decomposition products and the oxidation was monitored by ^{31}P- and ^{195}Pt NMR spectroscopy. Both analyses afford useful information to check the conversion into products. As a matter of fact, in the oxidation of $[PtCl_2(L)(PPh_3)]$ to the corresponding $[PtCl_4(L)(PPh_3)]$ complexes, ^{195}Pt NMR signals move towards lower field, with $\Delta\delta \approx +2000$ ppm, while observed $^1J_{PPt}$ (≈ 2000 Hz) are significantly smaller than those measured (over 3500 Hz) for platinum(II) similar species. In all cases, the oxidant was added as soon as the orange suspension of the dinuclear platinum(II) precursor turned into a clear, yellow solution and the ^{31}P NMR signal of platinum(II) intermediate was observed. Reactions were complete in 2-3 h and products were isolated after elimination of most solvent under vacuum and addition of anhydrous heptane. In all cases, complexes prepared by this approach were obtained as pure, yellow-orange solids in moderate to good yields (63-89 %). The complexes, scarcely soluble in most organic solvents, were characterized by NMR spectroscopy in $CDCl_3$. The most significant NMR data for $[PtCl_4(L)(PPh_3)]$complexes are reported in Table 4. In particular, the *cis/trans* composition in solution was estimated by ^{31}P NMR, by the integration of signals attributed to each isomer. For L = pyridine, quinoline, o-, p- and m-toluidine a mixture of *cis*- and *trans*-complexes was observed in solution, in the cases of isoquinoline, benzothiazole and dibenzylamine only the trans isomer was obtained, which was stable in chloroform. As a representative example, the ^1H NMR spectrum of *trans*-$[PtCl_4$(isoquinoline)$(PPh_3)]$ can be briefly discussed (Figure S1). Hydrogen atoms in *alfa* position to coordinated isoquinoline nitrogen afford two well separated signals (H_a at 9.94 and H_b at 9.13 ppm respectively), characterized by coupling to phosphorus ($^4J_{H\text{-}P}$ = 5,9 Hz) and to platinum ($^3J_{H\text{-}Pt}$ = 26 Hz in both cases). These signals are shifted towards low fields with respect to those shown by the same hydrogen atoms in the platinum(II) counterpart (9.72 and 8.87 ppm respectively), as expected due to the enhanced oxidation state of the metal center. For L = benzothiazole and L = isoquinoline good quality crystals were obtained and the determination of the structure *via* single crystal X-ray diffraction was possible (Figures 2 and 3. The most significant bond lengths and angles are reported in Tables 5 and 6). The coordination around platinum is octahedral and for both complexes Pt-N and Pt-P, as well as Pt-Cl bond lengths, are in good agreement with those reported by Navarro-Ranninger et al. for complexes *trans*-$[PtCl_4(NHMe_2)(PPh_3)]$ and *trans*-$[PtCl_4$(i-$PrNH_2)(PPh_3)]$. [ivb]

Table 4. Most significant NMR data for $[PtCl_4(L)(PPh_3)]$ complexes[a]

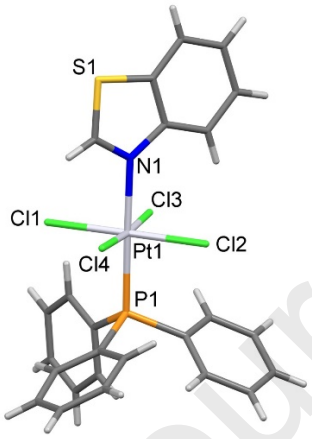
	^{31}P NMR Pt(IV) (ppm, coupling constant $^1J_{P\text{-}Pt}$ Hz)	**^{195}Pt NMR Pt(IV) (ppm, coupling constant $^1J_{P\text{-}Pt}$ Hz)[b]**	**Trans/cis % molar ratio in solution**
$[PtCl_4$(**py**)$(PPh_3)]$ [iv]a]	-2.5 ($^1J_{P\text{-}Pt}$= 2176) *trans* isomer. 1.10 ($^1J_{P\text{-}Pt}$= 2083) *cis* isomer.	-1484 ($^1J_{Pt\text{-}P}$= 2176) *trans* isomer.	(*trans*)/(*cis*)=70/30
$[PtCl_4$(**isoquino**)$(PPh_3)]$	-2.38 ($^1J_{P\text{-}Pt}$= 2169) *trans* isomer.	-1479 ($^1J_{Pt\text{-}P}$= 2169) *trans* isomer.	(*trans*)/(*cis*)=100/0
$[PtCl_4$(**quino**)$(PPh_3)]$	0.72 ($^1J_{P\text{-}Pt}$= 2215) *trans* isomer. 4.37 ($^1J_{P\text{-}Pt}$= 2280) *cis* isomer	-1299 ($^1J_{Pt\text{-}P}$= 2215) *trans* isomer.	(*trans*)/(*cis*)=86/14

[$PtCl_4$(**o-tol**)(PPh_3)]	4.4 ($^1J_{P\text{-}Pt}$= 2266) *trans* isomer. 5.34 ($^1J_{P\text{-}Pt}$= 2259) *cis* isomer.	-1580 ($^1J_{Pt\text{-}P}$=2266) *trans* isomer.	(*trans*)/(*cis*)=90/10
[$PtCl_4$(**m-tol**)(PPh_3)]	3.83 ($^1J_{P\text{-}Pt}$= 2268) *trans* isomer; -0.97($^1J_{P\text{-}Pt}$= 2142) *cis* isomer.	-1607 ($^1J_{Pt\text{-}P}$=2268) *trans* isomer.	(*trans*)/(*cis*)=84/16
[$PtCl_4$(**bzthia**)(PPh_3)]	-1.17 ($^1J_{P\text{-}Pt}$= 2280)	-1398 ($^1J_{Pt\text{-}P}$= 2280) *trans* isomer.	(*trans*)/(*cis*)=100/0
[$PtCl_4$(**$NHBz_2$**)(PPh_3)]	4.1 ($^1J_{P\text{-}Pt}$= 2144)	-1498 ($^1J_{Pt\text{-}P}$= 2144) *trans* isomer.	(*trans*)/(*cis*)=100/0

a) Solvent used: $CDCl_3$; b) due to the low concentration of the mixture, caused by the scarce solubility of the complexes, ^{195}Pt NMR signal of the minor component of the mixture was not observed.

Pt1–N1	2.177(5)	Cl3–Pt1–Cl1	90.09(7)
Pt1–Cl3	2.3205(17)	Cl4–Pt1–Cl1	87.33(7)
Pt1–Cl4	2.3260(17)	N1–Pt1–Cl2	90.91(15)
Pt1–Cl1	2.3289(18)	Cl3–Pt1–Cl2	93.56(7)
Pt1–Cl2	2.3289(17)	Cl4–Pt1–Cl2	88.98(7)
Pt1–P1	2.3444(17)	Cl3–Pt1–P1	87.97(6)
N1–Pt1–Cl3	89.45(14)	Cl4–Pt1–P1	95.53(6)
N1–Pt1–Cl4	87.07(14)	Cl1–Pt1–P1	92.10(7)
N1–Pt1–Cl1	88.33(15)	Cl2–Pt1–P1	88.82(6)

Table 5. Most significant bond distances (Å) and angles (°) for *trans*-[$PtCl_4$(bzthia)(PPh_3)]



Pt1–N1	2.155(3)	Cl3–Pt1–N1	86.09(8)
Pt1–Cl3	2.3130(9)	Cl2–Pt1–Cl3	87.87(4)
Pt1–Cl4	2.3130(9)	Cl3–Pt1–Cl4	90.91(15)
Pt1–Cl1	2.3365(9)	Cl1–Pt1–Cl2	90.49(4)
Pt1–Cl2	2.3133(9)	Cl4–Pt1–Cl1	92.87(4)
Pt1–P1	2.3396(8)	Cl2–Pt1–P1	91.51(3)
N1–Pt1–Cl2	89.79(8)	Cl3–Pt1–P1	94.61(3)
N1–Pt1–Cl4	88.61(8)	Cl4–Pt1–P1	90.14(3)
N1–Pt1–Cl1	88.38(8)	Cl1–Pt1–P1	90.96(3)

Figure 2. Molecular structure of *trans*-[$PtCl_4$(bzthia)(PPh_3)]

Table 6. Most significant bond distances (Å) and angles (°) for *trans*-[$PtCl_4$(isoqui)(PPh_3)]

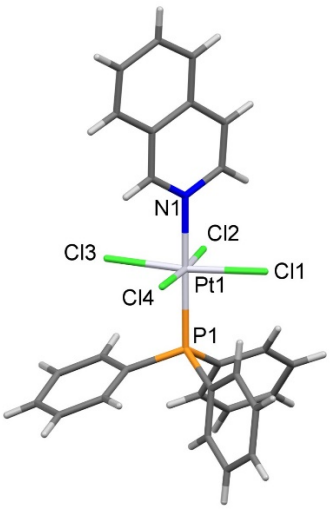
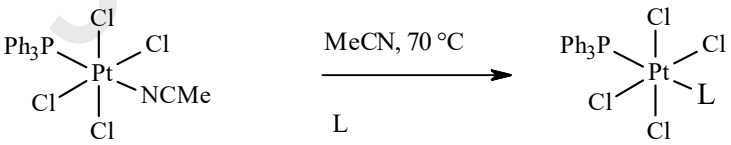


Figure 3. Molecular structure of *trans*-[$PtCl_4$(isoqui)(PPh_3)]

3.3. Substitution reaction on trans-[$PtCl_4$(NCMe)(PPh_3)].

A sample of [$PtCl_4$(NCMe)(PPh_3)] was prepared, as previously described,[iva] by $PhICl_2$ oxidation of [$PtCl_2$(NCMe)(PPh_3)] in MeCN. Under these experimental conditions, a mixture of *cis*- and *trans*- isomers is obtained, but the equilibrium can be conveniently displaced to the *trans*- isomer by heating the solution at 70 °C. The precursor is scarcely soluble in other organic solvents; thus, the experiments were carried out *in situ* at 70 °C, soon after the isomerization step. Thus, in a typical experiment, a solution of [$PtCl_4$(NCMe)(PPh_3)] in acetonitrile was heated at 70 °C and treated with a solution of the chosen nucleophile in the same solvent (Scheme 3). The outcome of the reaction was followed by ^{31}P NMR spectroscopy.

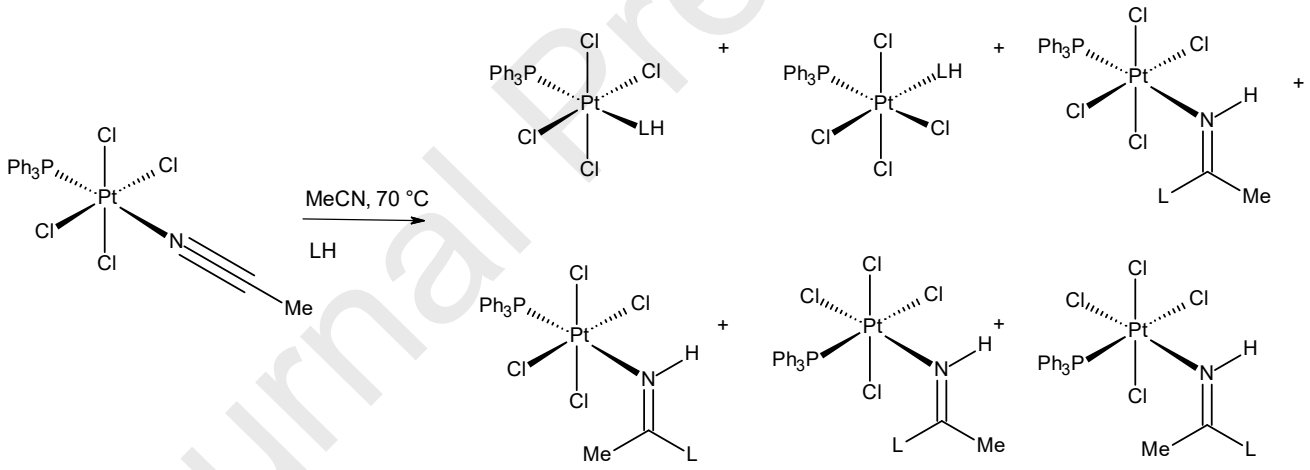


L = Pyridine, isoquinoline, m-toluidine, o-toluidine, p-toluidine, benzothiazole

Scheme 3. Substitution reaction on *trans*-[$PtCl_4$(NCMe)(PPh_3)]

In the cases of N-heterocyclic nucleophiles (isoquinoline, pyridine and benzothiazole), the reaction afforded (2-3 h) a single compound which was identified (^{31}P NMR) as the trans isomer of the

substitution product. The complexes were scarcely soluble in acetonitrile and precipitated out of the reaction mixture, being isolated in generally good yields. It has to be underlined that this synthetic pathway allowed the selective preparation of pure *trans*-[$PtCl_4(PPh_3)(Py)$], at variance with the oxidation of the corresponding Pt(II) system affording a cis/trans mixture of isomers. The reactivity towards protic nucleophiles was then tested, considering that Pt(IV) nitrile complexes usually afford addition reactions on the coordinated nitrile, while substitution reactions are very rare. In the already mentioned literature example [xiii], only weakly nucleophilic ortho- and para-nitroanilines react with trans-[$PtCl_4(NCEt)_2$] to give the substitution products in good yields, while the meta isomer affords the usual addition derivative. In the same work, the Authors report that unsubstituted aniline could not be used in the study, because it is promptly oxidized by the platinum complex. At first, the reactivity of our system with meta-toluidine was checked. As shown in Scheme 4, up to six products could theoretically form in the reaction of *trans*-[$PtCl_4(NCMe)(PPh_3)$] with a protic nucleophile, because, besides the *cis*- and *trans*-substitution products, addition to coordinated nitrile can occur, giving rise to *cis*- and *trans*- amidino derivatives, each presenting (E)/(Z) isomerism as well.



Scheme 4. Possible products of the reaction between *trans*-[$PtCl_4(NCMe)(PPh_3)$] and LH.

In the reaction with meta-toluidine, that was followed, as usual, *via* ^{31}P NMR spectroscopy, three new signals were observed after the precursor disappeared. Two of them (3.88 and 4.59 ppm), accounting for about the 95% composition of the mixture, were assigned by comparison to *cis*- and *trans*-substitution products [$PtCl_4$(m-toluidine)(PPh_3)]. The third signal (4.79 ppm, ≈ 5%) was attributed to a single amidino compound arising from the addition of meta-toluidine to coordinated nitrile, on the basis of two characteristic singlet signals (9.72 and 4.17 ppm) appearing in the ^1H NMR spectrum of the reaction mixture and ascribable [xiii] to NH hydrogen atoms of the $NHC(CH_3)NH$ functional group of

amidino ligand. Moreover, a weak absorption band at 1484 cm^{-1} (N=C stretching) due to traces of the amidino derivative was observed in the IR spectrum of the solid residue obtained after the reaction quenching. Similar results were obtained with ortho- and para-toluidines. No byproducts arising from the oxidation of the nucleophile were ever observed. The reaction was attempted with dialkylamines R_2NH (R = Et, -Bz) as well, but in both cases neither the substitution nor the addition products were obtained. In repeated experiments, the fast disappearance of the precursor was accompanied by the formation of *trans*-[$PtCl_2(NHR_2)(PPh_3)$] [xiva], besides variable amounts of Ph_3PO and R_2NH_2Cl. The presence of the Pt(II) compound bearing the coordinated dialkylamine suggests that the initial substitution of the coordinated nitrile on the Pt(IV) species takes place and is followed by a formal elimination of chlorine, previously observed in solution for similar species, [iva] that is strongly accelerated in the presence of sufficiently basic nucleophiles. Indeed, these considerations can be supported observing the reported pKa values in DMSO solution for the conjugated acids of some amines of interest for this study. As a matter of fact, pKas of pyridinium and anilinium ions are 3.4 and 3.8 respectively, [xxiv] while pKas for benzylammonium and piperidinium ions are 10.2 and 10.9 respectively [xxiv].

4. Conclusions

It was shown that the species *trans*-[$PtCl_4(NCMe)(PPh_3)$] reacts promptly with heteroaromatic nucleophiles with substitution of the coordinated nitrile. When pyridine was used the substitution was stereoselective and gave *trans*-[$PtCl_4(Py)(PPh_3)$] as a single product. The reaction with o-,m- and p-toluidines was chemoselective towards nitrile substitution and in each of the tested cases, only traces of addition byproducts were observed. The reaction is complete in only 2-3 hours. Considering that substitution reactions at platinum(IV) centers are extremely rare and limited to very weak protic nucleophiles such as nitroanilines, this behavior is noteworthy and must be ascribed to the presence of the triphenylphosphine. As a matter of fact, this ligand is at the same time σ-donating and π-acceptor and in many octahedral complexes causes moderate structural trans influence, that can be observed when analyzing bond lengths. [xxv] Experiments showed that the substitution of coordinated nitrile occurs also with dialkylamines (Et_2NH and Bz_2NH), but in this case the stronger basic character of the nucleophile assists a collateral decomposition process that had been already observed in solution, [iva] thus the process is not synthetically useful. In conclusion, the collected data suggest that the reaction between *trans*-[$PtCl_4(NCMe)(PPh_3)$] and protic nucleophiles is selective towards nitrile substitution and that its successful outcome can be correlated with the weak basicity of the used nucleophile.

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Inorganica Chimica Acta

Facile nucleophilic substitution of coordinated acetonitrile in *trans*-$[PtCl_4(NCMe)(PPh_3)]$

Highlights

- MeCN in the title Pt(IV) compound is promptly substituted by N-nucleophiles
- N-heteroaromatic nucleophiles were successfully used in the substitution reaction
- The reaction with toluidines was chemoselective towards substitution products

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