A sound sequence to triphenylphosphino dibromoplatinum(II) complexes. Solvothermal preparation of *trans*-[PtBr(μ-Br)(PPh_3)]$_2$

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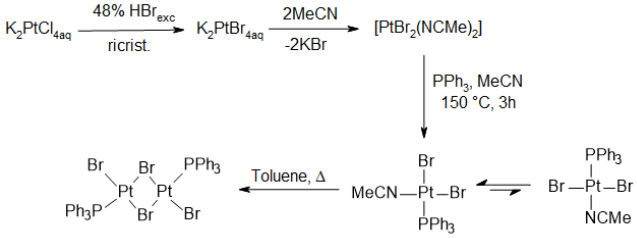
Abstract: A sound synthetic procedure for the preparation of *trans*-[PtBr(μ-Br)(PPh_3)]$_2$ is described. The species was fully characterized and used to obtain [$PtBr_2$(PPh_3)(L)] complexes (L = DMSO, p-toluidine, pyridine) by a bridge-splitting reaction. All products were fully characterized by NMR spectroscopy, together with *cis*-[$PtBr_2$(PPh_3)($NCCH_3$)], obtained as an intermediate in the synthesis of the dinuclear precursor. *Cis*-[$PtBr_2$(PPh_3)($NCCH_3$)] was also studied by x-ray diffraction.

Introduction

Phosphane complexes of platinum find application in many fields of inorganic chemistry, from catalysis[1] to bioactive compounds.[2] Among the last compounds, dichlorotriphenylphosphino derivatives [$PtCl_2$(PPh_3)(L)] have found interesting applications in the field of anticancer compounds.[2a-g,j] Since anticancer properties can be modulated changing the coordination sphere of the metal, besides varying L, we have been interested in varying the nature of the coordinating halide from chloride to bromide. In general, [PtX_2(L)(PR_3)] complexes (X = Cl, Br can be readily obtained by bridge splitting reactions of the suitable dinuclear precursors [PtX(μ-X)(PR_3)]$_2$.[3] Some years ago a convenient synthetic procedure for *trans*-[PtCl(μ-Cl)(PPh_3)]$_2$ was described, making this chlorinated dinuclear derivative formally accessible from commercial K_2PtCl_4 aqueous solution.[4] For the corresponding bromoderivative, *trans*-[PtBr(μ-Br)(PPh_3)]$_2$, there is a lack of data in the literature and its molecular structure was determined only recently[5] by single-crystal X-ray diffraction. In this literature paper, the complex formed from $PtBr_2$ and PPh_3 in the presence of an excess of Bu_4PBr, a system catalyzing a hydroamination reaction, but its isolated yield was not reported. From a synthetic point of view, literature usually refers[6] to the reaction of PtX_2 with [PtX_2(PR_3)$_2$] in high boiling solvents, mostly for chlorinated dinuclear complexes.[7] Moreover these reactions usually report good isolated yields but long purification workups to eliminate byproducts formed at high temperature. As an alternative route, [PtBr(μ-Br)(C_2H_4)]$_2$ has been proposed as precursor in exchange reactions with PR_3,[8] but sterically demanding phosphines often afford mononuclear bridge-splitting products. Moreover, Gilchrist et al.[9] observed the formation of [PtBr(μ-Br)(PPh_3)]$_2$ by decomposition of a reaction intermediate, but the compound was not characterized. Considering the existing literature and the importance of the product as precursor in the high yield synthesis of mixed ligand dibromide platinum(II) complexes, we describe here a high yield convenient preparation of *trans*-[PtBr(μ-Br)(PPh_3)]$_2$ from [$PtBr_2$($NCMe$)$_2$] and triphenylphosphine, in solvothermal conditions. The synthetic sequence is described starting from commercial K_2PtCl_4. Furthermore, in this text, considerable attention has been paid to differences in the reactivity of bromide/chloride analogues.

Results and Discussion

The synthesis of the brominated dinuclear complex (Scheme 1) has been optimized exploiting the consolidated procedure[4,10] employed for the analogous chlorinated derivative.



Scheme 1. Synthesis of $Pt_2Br_4(PPh_3)_2$.

Step1: K_2PtBr_4 can be prepared by an exchange reaction from the commercially available K_2PtCl_4. Since the commonly used preparation[11,12] that involves the treatment of aqueous solutions of K_2PtCl_4 with excess KBr, often yields an anionic bromo complex contaminated with KBr, we preferred to follow another procedure,[13] where the exchange reaction is carried out using aqueous HBr (48%). Since experimental details were not previously reported, we have to mention here that although the procedure is very simple, consisting in mixing two aqueous solutions, great care has to be taken in excluding atmospheric O_2, which can oxidize the bromide ion to bromine, leading to non-negligible amounts of K_2PtBr_6. The oxidation byproduct is recognizable by ^{195}Pt-NMR, affording a singlet signal at -1860 ppm (solvent: H_2O)[14]. Anyway, if the reaction is carried out under nitrogen with deoxygenated reagents, potassium tetrabromoplatinate(II) is obtained as a single product, affording a singlet signal at -2700ppm (in H_2O).[12] The product was recovered by removing the solvent under reduced pressure and further recrystallization from 0.5 M HBr[13].

Step 2: Preparation of [$PtBr_2$($NCMe$)$_2$], obtained from K_2PtBr_4 in acetonitrile, has also been already described[13, 15] but we would

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like to add some important synthetic and spectroscopic details. Compared to the chlorinated species the product is more soluble in water and requires a larger excess of acetonitrile. To push the reaction forward after roughly 50% of the product has been collected the solution needs to be concentrated by removing the solvent and restoring the acetonitrile lost during the process. Collecting a few fractions of the product an overall yield of 81% was achieved. The complex (yellow crystalline powder) was characterized by spectroscopy (IR and NMR) and elemental analysis. As for IR (ATR) spectroscopy, coordinated nitrile afforded a weak, but visible absorption band at 2340 cm^{-1}, while ^{1}H-NMR in CD_3NO_2 allowed us to detect a single singlet signal at 2.67 ppm, with satellites ($^4J_{H\text{-}Pt}$ = 15 Hz), which could be ascribed to methyl group of coordinated acetonitrile. This data indicates the preferential formation of one isomer as confirmed by a single signal registered in the ^{195}Pt-NMR spectrum (-2800 ppm).

$[PtBr_2(NCMe)_2]$ could also be obtained by halogen exchange reaction between the corresponding chlorinated compound and a tenfold excess of *t*BuBr in acetonitrile solution (eq. 1) The reaction is quite slow and solvothermal conditions are required (120 °C in Carius tube, 24h).

$$[PtCl_2(NCMe)_2] + t\text{BuBr(exc)} \rightarrow [PtBr_2(NCMe)_2] + t\text{BuCl} \quad (1)$$

When prepared by this method, the product was recovered as a poorly soluble orange powder, which turned yellow when it was washed with water. Its elemental analysis, IR and ^{1}H NMR spectra were in good agreement with those shown by the product recovered from the aqueous synthesis, for an overall yield of 67 %.

Step 3: For the synthesis of $[PtBr_2(PPh_3)(NCMe)]$, $[PtBr_2(NCMe)_2]$ was reacted with a stoichiometric amount of PPh_3, in acetonitrile solution and in solvothermal conditions (150 °C in a Carius tube) (Scheme 1). Compared to the analogous chlorinated species[4] this reaction is much faster requiring only 3 hours to react $[PtBr_2(NCMe)_2]$ with PPh_3, compared to the 120 hours required by $[PtCl_2(NCMe)_2]$.

^{31}P-NMR analysis was carried out on the solution, showing no residual PPh_3 and two new signals at 5.34 ($^1J_{P\text{-}Pt}$ = 3457Hz) and 1.73 ($^1J_{P\text{-}Pt}$ = 3944Hz) ppm. The two signals were assigned to *cis* and *trans* isomers respectively by comparison with the chlorinated species[4]. In the ^{195}Pt-NMR spectrum of the mixture, two resonances were observed at -3924 ($^1J_{P\text{-}Pt}$ = 3467Hz) and -4143 ($^1J_{P\text{-}Pt}$ = 3944Hz) for *cis* and *trans* isomers respectively, with an expected upfield shift[14] due to the Br/Cl substitution. The crystalline *cis* product forms by slowly cooling the solution to room temperature. Its molecular structure was confirmed by single crystal X-ray diffraction (Figure 1).
It is also possible to prepare $[PtBr_2(PPh_3)(NCMe)]$ using 1 equivalent of $[PtBr_2(NCMe)_2]$ and 1 equivalent of $[PtBr_2(PPh_3)_2]$[15a]. The last compound is readily accessible by the synthetic sequence depicted in eq 2-3 and it involves: preliminary extraction of platinum into dichoromethane solution as $[TBA]_2[PtBr_4]$ (TBA = tetrabutylammonium; DCM = dichloromethane)[16] followed by a reaction with PPh_3 (phosphine/Pt = 2 in moles)

$$K_2PtCl_{4aq} + 4TBABr_{(DCM)} \rightarrow [TBA]_2[PtBr_4]_{(DCM)} + 2TBACl + 2KCl \quad (2)$$

$$[TBA]_2[PtBr_4] + 2PPh_3 \rightarrow [PtBr_2(PPh_3)_2] + 2TBABr \quad (3)$$

When a sample of pure cis-$[PtBr_2(PPh_3)(NCMe)]$ (0.100g) was dissolved in CH_3CN (10 mL) equilibrium was reached in 24 h (^{31}P NMR) and the mixture contained 68% of cis- and 32% of trans isomers. $[PtBr_2(PPh_3)(NCMe)]$ is stable in CH_3CN diluted solution, while it rapidly releases acetonitrile and affords an orange solid identified as *trans*-$[PtBr(\mu\text{-}Br)(PPh_3)]_2$ when dissolved in other solvents or when heated (60 °C) under vacuum.

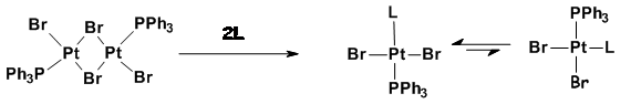
As already described for the acetonitrile complex $[PtBr_2(NCMe)_2]$, the formation of $[PtBr_2(PPh_3)(NCMe)]$ was observed when the corresponding chlorinated compound was reacted with an excess of *t*BuBr in acetonitrile solution (eq. 4, 150 °C in Carius tube, 72h).

$$[PtCl_2(PPh_3)(NCMe)] + t\text{BuBr(exc)} \rightarrow [PtBr_2(PPh_3)(NCMe)] + t\text{BuCl} \quad (4)$$

Nevertheless, in this case it was not possible to isolate the *cis* isomer and the product was obtained as a mixture of *cis*,*trans*-$[PtBr_2(PPh_3)(NCMe)]$ and *trans*-$[PtBr(\mu\text{-}Br)(PPh_3)]_2$.

Step 4:
The final dinuclear product *trans*-$[PtBr(\mu\text{-}Br)(PPh_3)]_2$ was formed refluxing the toluene solution of $[PtBr_2(PPh_3)(NCMe)]$ (Scheme 1). The brominated dinuclear derivative was obtained in high yield (90%) as a light orange solid, sparingly soluble in chlorinated solvents and was characterized by IR (ATR), ^{31}P-NMR and elemental analysis. Due to the scarce solubility of the species, a complete spectroscopic characterization of the dinuclear species was not carried out. Nevertheless, its prompt reactivity towards coordinating solvents could be used to confirm indirectly its nature; as a matter of fact, when a sample of the orange solid was dissolved in acetonitrile, a pale yellow solution was obtained, showing the ^{31}P NMR signals of *cis*- and *trans*-$[PtBr_2(PPh_3)(NCMe)]$ (Table 1). Analogously, the dissolution of the sample in DMSO afforded a colourless solution, showing a single ^{31}P NMR signal, ascribed to *cis*-$[PtBr_2(PPh_3)(DMSO)]$, on the basis of the comparison with the signal of known *cis*-$[PtCl_2(PPh_3)(DMSO)]$[2d] (Table 1). Comparison with the reactivity and the spectroscopic data of *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$ allowed to assign a *trans* configuration to the present brominated system.

As already mentioned for coordinating solvents, the reactivity displayed by *trans*-$[PtBr(\mu\text{-}Br)(PPh_3)]_2$ towards nucleophiles was also remarkably similar to its chlorine bearing counterpart. In all cases tested, a suspension of the dinuclear precursor in chloroform, when treated with a suitable ligand, afforded a clear solution of the product of the bridge-splitting reaction (Scheme 2). As expected, the reaction is directed by the strong *trans*-effect exerted by the phosphine ligand, with the fast formation of the kinetic *trans* product, sometimes followed by isomerization in solution.
Specifically, the product obtained by reaction with p-toluidine was *trans* with no trace of isomerization (^{31}P NMR), while DMSO afforded a stereochemically pure *cis* complex and pyridine yielded a mixture of isomers. ^{31}P- and ^{195}Pt-NMR signals were assigned by comparison with the analogous chlorinated complexes.[10]



Scheme 2. Synthesis of [$PtBr_2(PPh_3)(L)$]

For ease of comparison, the most significant ^{31}P NMR signals in $CDCl_3$ (except for [$PtX_2(PPh_3)(NCMe)$] and [$PtX_2(PPh_3)(DMSO)$] which were registered in MeCN and DMSO respectively) are reported in Table 1 for chlorinated and brominated complexes.

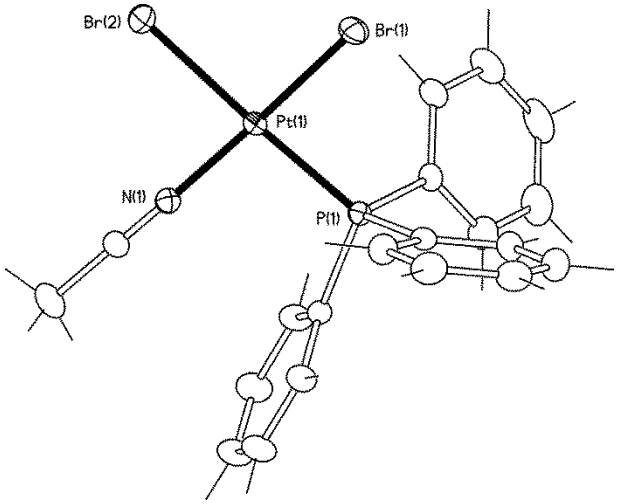


Figure 1. Crystal structure of *cis*-[$PtBr_2(PPh_3)(NCMe)$]. Selected bond lengths (Å): Pt(1)-N(1) 1.986(3); Pt(1)-P(1) 2.2485(9); Pt(1)-Br(1) 2.4096(4); Pt(1)-Br(2) 2.4780(5). Selected bond angles (°): N(1)-Pt(1)-P(1) 92.92(9); N(1)-Pt(1)-Br(1) 174.41(9); P(1)-Pt(1)-Br(1) 90.01(2); N(1)-Pt(1)-Br(2) 87.14(9); P(1)-Pt(1)-Br(2) 174.35(3); Br(1)-Pt(1)-Br(2) 90.412(17).

Table 1. ^{31}P NMR signals in $CDCl_3$ for [$PtX_2(PPh_3)(L)$]: δ ppm ($^1J_{P\text{-}Pt}$ Hz)

L	X = Cl	X= Br[b]
PPh_3	*Cis* 16.9 (3660) *Trans* 21.1 (2615)	*Cis* 13.7 (3610) *Trans* 18.7 (2573)
MeCN[a]	*Cis* 4.8 (3530) *Trans* 1.6 (4100)	*Cis* 5.3 (3467) *Trans* 1.7 (3944)
p-Tol	*Trans* 4.05 (3590)	*Trans* 3.0 (3653)
Py	*Cis* 7.2 (3907) *Trans* 2.6 (3582)	*Cis* 7.8 (3810) *Trans* 0.8 (3458)
DMSO[b]	*Cis* 16.2 (3720)	*Cis* 17.2 (3730)

[a] Solvent: MeCN. [b] Solvent: DMSO

When the preparation of [$PtBr_2(PPh_3)$(amine)] (amine = Py, p-Tol) complexes was attempted by exchange reaction between [$PtCl_2(PPh_3)$(amine)] and excess *t*BuBr, under the same experimental conditions affording [$PtBr_2(NCMe)_2$] (Carius tube, 120 °C), decomposition was observed. In the ^1H-NMR spectrum main signals were attributed to amine·HX species. These data suggest that in the experimental conditions used, *t*BuBr is partially converted into isobutene and HBr. While in the previously discussed cases the presence of hydrogen bromide does not prevent the formation of the desired brominated products, This route cannot be used with acid sensitive complexes.

Conclusions

A stepwise synthetic sequence to prepare *trans*-[$PtBr(\mu\text{-}Br)(PPh_3)]_2$ was described. Solvothermal conditions (Carius tube, acetonitrile at 150 °C) were conveniently used, but in this case the reaction was much faster respect to the analogous chlorinated system. Since *cis,trans*-[$PtBr_2(PPh_3)(NCMe)$] is an intermediate in the formation of the dinuclear compound, it can be reasonably assumed that acetonitrile elimination in the last step proceeds from the trans isomer, which is easily formed due to bromide ion steric hindrance. As a matter of fact, [$PtBr_2(NCMe)(PPh_3)$] is present, in acetonitrile solution, as a mixture of geometric isomers, where the concentration of *trans* complex is much higher than in the chlorinated counterpart (32% *vs* 5% at room temperature, respectively). The possible use of *tB*utyl bromide as exchange brominating agent in non aqueous environment was explored, but its use appears limited to non acid-sensitive complexes. Thus, as exemplified by the reported reactivity, *trans*-[$PtBr(\mu\text{-}Br)(PPh_3)]_2$ is an important precursor to a series of structural analogues of known antiproliferative platinum compounds.

Experimental Section

Reactions were performed under dinitrogen atmosphere. Unless otherwise specified all solvents were previously purified according to reported procedures.[17] Elemental analyses were collected with an Elementar "vario MICRO CUBE" CHNOS elemental analyzer. Solid state IR spectra were collected with Perkin Elmer "Spectrum One" spectrometer outfitted with an Attenuated Total Reflectance (ATR) accessory. Abbreviations used to describe signal shape and intensity: w = weak; m = medium; s = strong; br = broad band. NMR spectra were collected with a Bruker "Avance DRX 400" spectrometer with a 400MHz ^1H frequency and with a Varian "Gemini 200" spectrometer with a 200MHz ^1H frequency. $CDCl_3$ was used, unless otherwise stated. ^{31}P-and ^{195}Pt-NMR spectra were also acquired without deuterated solvents, using a capillary containing C_6D_6 to allow for locking by the spectrometer. Chemical Shifts (ppm) are referenced to $Si(CH_3)_4$ for ^1H and ^{13}C, H_3PO_4 (85% in D_2O) and H_2PtCl_6 were employed for ^{31}P- and for ^{195}Pt-, respectively. Abbreviations used to describe signal multiplicity: s = singlet; d = doublet; t = triplet; td = triple doublet; m = multiplet.

Synthesis of K_2PtBr_4

A sample (1.00 g) of K_2PtCl_4 (2.41 mmol) was dissolved in 250mL of deoxygenated 48%HBr_{aq}. After 24h reaction progress was tested via ^{195}Pt-NMR and found complete (^{195}Pt-NMR: -2662[12]). Solvent was removed under reduced pressure at 40°C and a dark brown solid was obtained, which was recrystallized from aqueous HBr (1.23g, 86% yield).

Synthesis of [$PtBr_2(NCMe)_2$]:

Method A. A sample (1.23 g, 2.08 mmol) of K_2PtBr_4 was dissolved in 80 ml of deoxygenated water and 4 ml of deoxygenated acetonitrile were added, maintaining the system in nitrogen atmosphere. The first greenish/black precipitate was discarded. From the bright red filtrate yellow crystals formed over the course of several days. More crystalline product was collected, through fractional crystallization. The overall yield (0.708 g) was 81%. El. Anal. Calcd. for [$PtBr_2(NCMe)_2$], $C_4H_6Br_2N_2Pt$, %: C=11.0; H=1.4; N=6.4. Found: C=11.3; H=1.4; N=6.6. IR (ATR, cm^{-1}): 2920 w, 2340 m, 1354 m, 1351 m, 1012 m. ^{1}H NMR (CD_3NO_2): 2.67 (s, 3H, $^4J_{H-Pt}$ = 15 Hz, CH_3). ^{13}C-NMR (CD_3NO_2):122.0, 5.0. ^{195}Pt-NMR (CD_3NO_2): -2805.

Method B. A sample (0.267 g, 0.77 mmol) of [$PtCl_2(NCMe)_2$][18] was introduced into a Carius tube, suspended in acetonitrile (5 ml) and *t*Butyl bromide (2 ml) was added. The mixture was stirred at 120 °C (5h), then cooled. An orange precipitate was obtained, which turned yellow upon washing with water. IR (ATR) and elemental analyses were in good agreement with those collected for *Method A* samples. (0.210 g, 67 %)

Synthesis of cis-[$PtBr_2(PPh_3)(NCMe)$]:

In a Carius tube under nitrogen atmosphere, 0,298 g (0.68 mmol) of [$PtBr_2(NCMe)_2$] were added to 3 ml of acetonitrile. The suspension was stirred and a stoichiometric amount of PPh_3 (0.179 g, 0.68 mmol) was added. The tube was sealed and heated (150°C) for 2-3 hours with vigorous stirring. Reaction progress was monitored with ^{31}P-NMR. Once the reaction was found to be complete (5.34, $^1J_{P-Pt}$ 3457Hz, *cis*; 1.72, $^1J_{P-Pt}$ 3944Hz, *trans*), the tube was left overnight to cooldown and yellow crystals of [$PtBr_2(PPh_3)(NCMe)$] were recovered (0.244g, 55%). The crystals were collected for X-ray analysis and found to be in *cis* configuration (see Table 2 for experimental details). Correlation between the crystalline structure and the NMR data was established by comparing the product with its chlorine equivalent. Using the same solvothermal conditions it is possible to obtain *cis*-[$PtBr_2(PPh_3)(NCMe)$] from [$PtBr_2(NCMe)_2$] and [$PtBr_2(PPh_3)_2$] in a 1:1 ratio. The bright yellow solution was evaporated at reduced pressure and afforded a yellow-orange residue (0.201 g). A sample of this solid was dissolved in $CHCl_3$ and analysed (^{31}P-NMR): 5.17 ($^1J_{P-Pt}$ 3480 Hz, 30%), 1.5 ($^1J_{P-Pt}$ not detectable, traces), 7.61 ($^1J_{P-Pt}$ 3940 Hz, 69%). The signal at 7.61 progressively became the only observable signal and an orange solid appeared. The signal at 7.61 ppm was attributed to dinuclear *trans*-[PtBr(μ-Br)(PPh_3)]$_2$ (cfr.*infra*), while the signals at 5.17 and 1.5 were ascribed to *cis*- and *trans*-[$PtBr_2(PPh_3)(NCMe)$] respectively.IR (ATR, cm^{-1}): 3072 w, 3061 w, 3045 w, 2909 w, 2355 w, 2323 w, 1588 w, 1574 w, 1482 m, 1433 s, 1357 m, 1100 s, 993 m, 744 s, 684 s. Isomer *cis*: ^{31}P-NMR (CH_3CN): 5.34 ($^1J_{P-Pt}$ 3457Hz); ^{195}Pt-NMR: -3924 ($^1J_{P-Pt}$ 3457Hz). Isomer *trans*: ^{31}P-NMR (CH_3CN): 1.73 ($^1J_{P-Pt}$ 3940Hz); ^{195}Pt-NMR: -4143 ($^1J_{P-Pt}$ 3940Hz).

Synthesis of [PtBr(μ-Br)(PPh_3)]$_2$:

A sample of *cis*-[$PtBr_2(PPh_3)(NCMe)$] (0.130 g 0.19 mmol) was heated in refluxing toluene (110 °C) for about 3 h, under stirring. The initially yellow suspension turned to orange. Reaction was followed by ^{31}P-NMR, showing the disappearance, in the liquid phase, of the signal of precursor (5.34 ($^1J_{P-Pt}$ 3457Hz)). The orange precipitate was filtered and washed with pentane, then dried under reduced pressure. Yield: 0.109 g (90%). El. Anal. Calcd. for [$Pt_2Br_4(PPh_3)_2$], $C_{36}H_{30}Br_4P_2Pt_2$, %: C 35.0, H 2.5. Found: C 35.4, H 2.4%. IR (ATR, cm^{-1}): 3077 w, 3063 w, 3041, 2913 m, 2363 w, 2322 w, 1583 w, 1571 w, 1481 m, 1433 s, 1094 s, 1000 m, 741 s, 690 s. Due to the very limited solubility, only ^{31}P-NMR is reported. ^{31}P-NMR(CD_2Cl_2): 7.7 ($^1J_{P-Pt}$ 3906Hz). When a sample of the orange solid was dissolved in acetonitrile, a pale yellow solution was obtained. ^{31}P NMR: 5.34 ($^1J_{P-Pt}$ 3457Hz, *cis*-[$PtBr_2(PPh_3)(NCMe)$], 68%); 1.73 ($^1J_{P-Pt}$ 3940Hz, *trans*-[$PtBr_2(PPh_3)(NCMe)$], 32%).

Synthesis of [$PtBr_2(PPh_3)_2$]:[11]

This product was synthesized from 1.034 g ($1.034x10^{-3}$ mol) of [$TBA]_2$[$PtBr_4$] [8] by adding triphenylphosphine (0.542 g, $2.066x10^{-3}$ mol) in dichloromethane at room temperature and with magnetic stirring (PPh_3/Pt = 2 in moles). The system was maintained in nitrogen atmosphere for the duration of the synthesis. The solution changed from a dark reddish brown to a very pale yellow. Reaction progress was monitored by ^{31}P-NMR and found to have reached completeness in 12h. The product was precipitated by removing most of the solvent under reduced pressure and adding heptane. The precipitate was then filtered and dried in vacuum. Yield: 0.861 g (95%) El. Anal. Calcd. for [$PtBr_2(PPh_3)_2$], $C_{36}H_{30}Br_2PPt$, %: C 51.0, H 3.6 %. Found: C 50.2, H 3.6%. IR (ATR, cm^{-1}): 3045 w, 1482 m, 1433 s, 1265 m, 1091 s, 730 s, 689 s. ^{31}P-NMR for *cis* isomer: 13.7 ($^1J_{P-Pt}$=3610Hz).[11] ^{31}P-NMR for *trans* isomer: 18.7 ($^1J_{P-Pt}$=2573Hz).[11]

Bridge-splitting examples of [$Pt_2Br_4(PPh_3)_2$].

All reactions were carried out in NMR test tubes using $CDCl_3$ as a solvent. [$Pt_2Br_4(PPh_3)_2$] precursor (10-20 mg) was suspended in $CDCl_3$ (1 ml) and the suitable ligand was added (Ligand /Pt = 1.0 in moles). The system turned clear yellow in most cases in a 5 minutes time span. A micro syringe was used to add the reagents as the quantities involved were in the range of 3 to 10μl. Products were not isolated. Spectroscopic NMR characterizations is reported.

trans-[$PtBr_2(PPh_3)$(p-Toluidine)]: The reaction was complete (^{31}P-NMR) after half an hour later and displayed only one signal, attributable to kinetic *trans* product. ^{1}H-NMR: 7.72 (m, 6H, H_{arom}), 7.41 (m, 11H, H_{arom}), 7.14 (m, 2H, H_{arom}), 5.14 (m 2H, $^2J_{H-Pt}$ = 36Hz, NH_2), 2.35 (s, 3H, CH_3). ^{13}C-NMR: 136.7, 135.4, 135.0 (d, J_{C-P} =10Hz), 130.8 (d, J_{C-P} =2Hz), 129.8, 126.9 (d, $^1J_{C-P}$= 66Hz), 127.8 (d, J_{C-P} =11Hz), 122.0, 21.0. ^{31}P-NMR: 3.0 ($^1J_{P-Pt}$ = 3653Hz). ^{195}Pt-NMR: -4106 (d, $^1J_{P-Pt}$= 3653Hz).

[$PtBr_2(PPh_3)(Py)$]: The reaction was complete (^{31}P-NMR) after half an hour later and displayed two signals, attributable to a mixture of *cis* and *trans* products. Configuration was assigned comparing ^{31}P-NMR chemical shift and coupling constants data with those of the chlorinated isomers.[10] Isomer *cis*: ^{31}P-NMR: 7.8 ($^1J_{P-P\ t}$= 3810Hz). ^{195}Pt-NMR: -3721 (d $^1J_{P-Pt}$ = 3810Hz). Isomer *trans*: ^{31}P-NMR: 0.8 ($^1J_{P-Pt}$ = 3458Hz). ^{195}Pt-NMR: -4008 (d $^1J_{P-Pt}$ = 3458Hz).

cis-[$PtBr_2(PPh_3)DMSO$]: $Pt_2Br_4(PPh_3)_2$ is dissolved in d^6-DMSO, the reaction was complete (^{31}P-NMR) in a few minutes and displayed only one signal, attributable to isomer *cis*. Configuration was assigned comparing ^{31}P-NMR chemical shift and coupling constants data with those of the known *cis*-[$PtCl_2(PPh_3)(DMSO)$].[2d] ^{31}P-NMR: 17.1 ($^1J_{P-Pt}$ = 3730Hz). ^{195}Pt-NMR: -4162 ($^1J_{P-Pt}$ = 3730Hz).

Table 2. Crystal data and structure refinement for *cis*-[$PtBr_2(PPh_3)(NCMe)$]**.**

Compound	*cis*-[$PtBr_2(PPh_3)(NCMe)$]	
Empirical formula	$C_{20}H_{18}Br_2NPPt$	
Formula weight	658.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.8719(10) Å	α= 90°.
	b = 8.9060(5) Å	β= 114.827(2)°.
	c = 17.3852(11) Å	γ = 90°.

Volume	2089.8(2) $Å^3$
Z	4
Density (calculated)	2.092 Mg/m^3
Absorption coefficient	10.617 mm^{-1}
F(000)	1232
Crystal size	0.155 x 0.155 x 0.095 mm^3
Theta range for data collection	2.381 to 32.504°.
Index ranges	-14<=h<=22, -12<=k<=13, -26<=l<=24
Reflections collected	26438
Independent reflections	7371 [R(int) = 0.0234]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7371 / 0 / 227
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0634
R indices (all data)	R1 = 0.0469, wR2 = 0.0689
Extinction coefficient	n/a
Largest diff. peak and hole	1.549 and -1.275 $e.Å^{-3}$

CCDC 1937596 (for *cis*-[$PtBr_2(PPh_3)$(NCMe)]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

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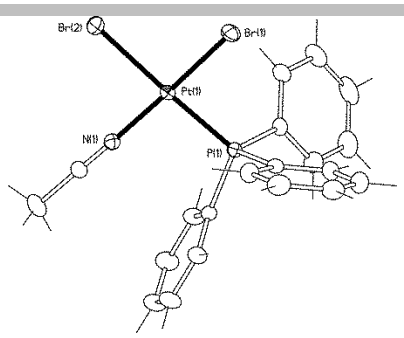
Keywords: platinum, exchange reactions, dinuclear bromocomplexes, solvothermal synthesis.

Table of Contents

FULL PAPER

A sound synthetic procedure for the preparation of *trans*-[PtBr(μ-Br)(PPh_3)]$_2$ is described. The species was fully characterized and used to obtain [$PtBr_2$(PPh_3)(L)] complexes (L = DMSO, p-toluidine, pyridine) by a bridge-splitting reaction. All products were fully characterized by NMR spectroscopy, together with *cis*-[$PtBr_2$(PPh_3)($NCCH_3$)], obtained as an intermediate in the synthesis of the dinuclear precursor. *Cis*-[$PtBr_2$(PPh_3)($NCCH_3$)] was also studied by X-ray diffraction.



Pt(II) bromo complexes

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A sound sequence to triphenylphosphino dibromoplatinum(II) complexes. Solvothermal preparation of *trans*-[PtBr(μ-Br)(PPh_3)]$_2$

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