A sound sequence to triphenylphosphino dibromoplatinum(II) complexes. Solvothermal preparation of \textit{trans-[PtBr}(\textit{μ-Br})(\textit{PPh}_3))_2

David Fioco,\textsuperscript{[a]} Daniela Belli Dell’Amico,\textsuperscript{[a]} Luca Labella,\textsuperscript{[a]} Fabio Marchetti\textsuperscript{[a]} and Simona Samaritani*\textsuperscript{[a]}

\textbf{Abstract:} A sound synthetic procedure for the preparation of trans-[PtBr(μ-Br)(PPh3)]2 is described. The species was fully characterized and used to obtain [PtBr2(PPh3)2(L)] complexes (L = DMSO, p-toluidine, pyridine) by a bridge-splitting reaction. All products were fully characterized by NMR spectroscopy, together with cis-[PtBr2(PPh3)(NCCH3)], obtained as an intermediate in the synthesis of the dinuclear precursor. Cis-[PtBr2(PPh3)(NCCH3)] was also studied by x-ray diffraction.

\textbf{Introduction}

Phosphane complexes of platinum find application in many fields of inorganic chemistry, from catalysis\textsuperscript{1} to bioactive compounds.\textsuperscript{2} Among the last compounds, dichlorotriphenylphosphino derivatives [PtCl2(PPh3)L] have found interesting applications in the field of anticancer compounds.\textsuperscript{2a-9} 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, [PtX2(L)(PR3)] complexes (X = Cl, Br can be readily obtained by bridge splitting reactions of the suitable dinuclear precursors [PtX2(μ-X)(PR3)]\textsuperscript{2-3} Some years ago a convenient synthetic procedure for trans-[PtCl(μ-Cl)(PPh3)]\textsubscript{2} was described, making this chlorinated dinuclear derivative formally accessible from commercial K2PtCl4 aqueous solution.\textsuperscript{4} For the corresponding bromoderivative, trans-[PtBr(μ-Br)(PPh3)]\textsubscript{2}, there is a lack of data in the literature and its molecular structure was determined only recently\textsuperscript{2} by single-crystal X-ray diffraction. In this literature paper, the complex formed from PtBr2 and PPh3 in the presence of an excess of Bu4PBr, a system catalyzing a hydrosplamination reaction, but its isolated yield was not reported. From a synthetic point of view, literature usually refers\textsuperscript{5} to the reaction of PtX2 with [PtCl2(PR3)2] in high boiling solvents, mostly for chlorinated dinuclear complexes.\textsuperscript{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)(C6H4)]\textsubscript{2} has been proposed as precursor in exchange reactions with PR3,\textsuperscript{8} but sterically demanding phosphines often afford mononuclear bridge-splitting products. Moreover, Gilchrist et al.\textsuperscript{9} observed the formation of [PtBr(μ-Br)(PPh3)]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 \textit{trans-[PtBr(μ-Br)(PPh3)]2} from [PtBr2(NCMe)]\textsubscript{3} and triphenylphosphine, in solvothermal conditions. The synthetic sequence is described starting from commercial K2PtCl4.

\textbf{Results and Discussion}

The synthesis of the brominated dinuclear complex (Scheme 1) has been optimized exploiting the consolidated procedures\textsuperscript{4,10} employed for the analogous chlorinated derivative.

\begin{figure}

\centering

\includegraphics[width=\textwidth]{Scheme1}

\caption{Synthesis of PtBr2(PPh3)2.}

\end{figure}

\textbf{Step 1:} K2PtBr4 can be prepared by an exchange reaction from the commercially available K2PtCl4. Since the commonly used preparation\textsuperscript{11,12} that involves the treatment of aqueous solutions of K2PtCl4 with excess KBr, often yields an anionic bromo complex contaminated with KBr, we preferred to follow another procedure,\textsuperscript{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 O2, which can oxidize the bromide ion to bromine, leading to non-negligible amounts of K2PBr6. The oxidation byproduct is recognizable by 195Pt-NMR, affording a singlet signal at -1860 ppm (solvent: H2O).\textsuperscript{14} Anyway, if the reaction is carried out under nitrogen with deoxygenated reagents, potassium tetrabromoplutatinato(II) is obtained as a single product, affording a singlet signal at -2700 ppm (in H2O).\textsuperscript{15} The product was recovered by removing the solvent under reduced pressure and further recrystallization from 0.5 M HBr.\textsuperscript{13}

\textbf{Step 2:} Preparation of [PtBr2(NCMe)]3, obtained from K2PtBr4 in acetonitrile, has also been already described\textsuperscript{13,15} but we would
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 ¹H-NMR in CD₂NO₂ allowed us to detect a single singlet signal at 2.67 ppm, with satellites (ΔJ = 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 ³¹P-NMR spectrum (-2800 ppm).

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

\[
[\text{PtCl}_2(\text{NCMe})_2] + 3 \text{tBuBr(exc)} \rightarrow [\text{PtBr}_2(\text{NCMe})_2] + 3 \text{tBuCl} \tag{1}
\]

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 ¹H NMR spectra were in good agreement with those shown by the product recovered from the aqeous synthesis, for an overall yield of 67%.

**Step 3:** For the synthesis of \([\text{PtBr}_2(\text{PPh}_3)(\text{NCMe})_2] \), \([\text{PtBr}_2(\text{NCMe})_2] \) was reacted with a stoichiometric amount of PPh₃, in acetonitrile solution and in solvothermal conditions (150 °C in a Carius tube) (Scheme 1). Compared to the analogous chlorinated species⁴ this reaction is much faster requiring only 3 hours to react \([\text{PtBr}_2(\text{NCMe})_2] \) with PPh₃, compared to the 120 hours required by \([\text{PtCl}_2(\text{NCMe})_2] \).

³¹P-NMR analysis was carried out on the solution, showing no residual PPh₃ and two new signals at 5.34 (¹P-Br = 3457Hz) and 1.73 (¹P-Br = 3944Hz) ppm. The two signals were assigned to cis and trans isomers respectively by comparison with the chlorinated species⁴. In the ¹⁹⁵Pt-NMR spectrum of the mixture, two resonances were observed at -3924 (¹P-Pt = 3457Hz) and -4143 (¹P-Pt = 3944Hz) for cis and trans isomers respectively, with an expected upfield shift¹⁴ 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 \([\text{PtBr}_2(\text{PPh}_3)(\text{NCMe})_2] \) using 1 equivalent of \([\text{PtBr}_3(\text{NCMe})_2] \) and 1 equivalent of \([\text{PtBr}_2(\text{PPh}_3)_2] \)⁵. The last compound is readily accessible by the synthetic sequence depicted in eq 2-3 and it involves: preliminary extraction of platinum into dichromethane solution as \([\text{TBA}]_2[\text{PtBr}_4] \) (TBA = tetrabutylammonium; DCM = dichromethane)⁶ followed by a reaction with PPh₃ (phosphine/Pt = 2 in moles)

\[
\text{K}_2\text{PtCl}_4 + 4\text{TBABr}_{(\text{DCM})} \rightarrow [\text{TBA}]_2[\text{PtBr}_4]_{(\text{DCM})} + 2\text{TBACl} + 2\text{KCl} \tag{2}
\]

\[
[\text{TBA}]_2[\text{PtBr}_4] + 2\text{PPh}_3 \rightarrow [\text{PtBr}_2(\text{PPh}_3)_2] + 2\text{TBABr} \tag{3}
\]

When a sample of pure cis-[PtBr₂(PPh₃)(NCMe)] (0.100g) was dissolved in CH₃CN (10 mL) equilibrium was reached in 24 h (³¹P NMR) and the mixture contained 68% of cis- and 32% of trans isomers. [PtBr₂(PPh₃)(NCMe)] is stable in CH₃CN diluted solution, while it rapidly releases acetonitrile and affords an orange solid identified as trans-[PtBr(μ-Br)(PPh₃)] when dissolved in other solvents or when heated (60 °C) under vacuum.

As already described for the acetonitrile complex \([\text{PtBr}_2(\text{NCMe})_2] \), the formation of \([\text{PtBr}_2(\text{PPh}_3)(\text{NCMe})] \) was observed when the corresponding chlorinated compound was reacted with an excess of tBuBr in acetonitrile solution (eq. 4, 150 °C in Carius tube, 72h).

\[
[\text{PtCl}_2(\text{PPh}_3)(\text{NCMe})] + 3 \text{tBuBr(exc)} \rightarrow [\text{PtBr}_2(\text{PPh}_3)(\text{NCMe})] + 3 \text{tBuCl} \tag{4}
\]

Nevertheless, in this case it was not possible to isolate the cis isomer and the product was obtained as a mixture of cis,trans-[PtBr₂(PPh₃)(NCMe)] and trans-[PtBr(μ-Br)(PPh₃)]₂.

**Step 4:** The final dinuclear product trans-[PtBr(μ-Br)(PPh₃)]₂ was formed refluxing the toluene solution of \([\text{PtBr}_2(\text{PPh}_3)(\text{NCMe})] \) (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), ³¹P-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 ³¹P NMR signals of cis- and trans-[PtBr₂(PPh₃)(NCMe)] (Table 1). Analogously, the dissolution of the sample in DMSO afforded a colourless solution, showing a single ³¹P NMR signal, ascribed to cis-[PtBr₂(PPh₃)(DMSO)], on the basis of the comparison with the signal of known cis-[PtCl₂(PPh₃)(DMSO)]⁵⁰. The comparison with the reactivity and the spectroscopic data of trans-[PtCl(μ-Cl)(PPh₃)]₂ allowed to assign a trans configuration to the present brominated system.

As already mentioned for coordinating solvents, the reactivity displayed by trans-[PtBr(μ-Br)(PPh₃)]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 (³¹P NMR), while DMSO afforded a stereochemically pure cis complex and pyridine yielded a mixture of isomers. ³¹P- and ¹⁹⁵Pt-NMR signals were assigned by comparison with the analogous chlorinated complexes.⁵⁰
Scheme 2. Synthesis of [PtBr₂(PPh₃)(L)]

For ease of comparison, the most significant ^{31}P NMR signals in CDCl₃ (except for [PtX₂(PPh₃)(NCMe)] and [PtX₂(PPh₃)(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-[PtBr₂(PPh₃)(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); N(1)-Pt(1)-Br(2) 87.14(9); P(1)-Pt(1)-Br(1) 90.01(2); P(1)-Pt(1)-Br(2) 90.412(17).

When the preparation of [PtBr₂(PPh₃)(amine)] (amine = Py, p-Tol) complexes was attempted by exchange reaction between [PtCl₂(PPh₃)(amine)] and excess BuBr, under the same experimental conditions affording [PtBr₂(NCMe)] (Carius tube, 120 °C), decomposition was observed. In the °H-NMR spectrum main signals were attributed to amine-HX species. These data suggest that in the experimental conditions used, 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-[PtBr₂(μ-Br)(PPh₃)] was described. Solvothermal conditions (Carius tube, acetonitrile at 150 °C) were conveniently used, but in this case the reaction was much faster as compared to the analogous chlorinated system. Since cis,trans-[PtBr₂(PPh₃)(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, [PtBr₂(NCMe)](PPh₃) 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 tBuyl 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-[PtBr₂(μ-Br)(PPh₃)] 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.¹¹ 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 also acquired without deuterated solvents, using a capillary containing CDCl₃ to allow for locking by the spectrometer. Chemical Shifts (ppm) are referenced to Si(CH₃)₄ for °H and °C, H₂PO₄ (85% in D₂O) and H₃PO₄ were employed for °P and °Hpt, respectively. Abbreviations used to describe signal multiplicity: s = singlet; d = doublet; t = triplet; dd = double doublet; m = multiplet.

#### Table 1. °P NMR signals in CDCl₃ for [PtX₂(PPh₃)(L)]: δ ppm (°J= n Hz)

<table>
<thead>
<tr>
<th>L</th>
<th>X = Cl</th>
<th>X = Br(^{31})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₃</td>
<td>cis 16.9 (3660)</td>
<td>cis 13.7 (3610)</td>
</tr>
<tr>
<td></td>
<td>Trans 21.1 (2615)</td>
<td>Trans 18.7 (2573)</td>
</tr>
<tr>
<td>MeCN</td>
<td>cis 4.8 (3530)</td>
<td>cis 5.3 (3467)</td>
</tr>
<tr>
<td></td>
<td>Trans 1.6 (4100)</td>
<td>Trans 1.7 (3944)</td>
</tr>
<tr>
<td>p-Tol</td>
<td>Trans 4.05 (3590)</td>
<td>Trans 3.0 (3653)</td>
</tr>
<tr>
<td>Py</td>
<td>cis 7.2 (3907)</td>
<td>cis 7.8 (3810)</td>
</tr>
<tr>
<td></td>
<td>Trans 2.6 (3582)</td>
<td>Trans 0.8 (3458)</td>
</tr>
<tr>
<td>DMSO</td>
<td>cis 16.2 (3720)</td>
<td>cis 17.2 (3730)</td>
</tr>
</tbody>
</table>

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

---

Synthesis of K₂PtBr₄
A sample (1.00 g) of K2PtCl6 (2.41 mmol) was dissolved in 250 mL of deoxygenated 48% HBr. After 24 h reaction progress was tested via 195Pt-NMR and found complete (195Pt-NMR: -2662Hz). Solvent was removed under reduced pressure at 40°C and a dark brown solid was obtained, which was recrystallized from aqueous HBr (1.23 g, 86% yield).

Synthesis of [PtBr2(NCMe)]11

Method A. A sample (1.23 g, 2.08 mmol) of K2PtBr6 was dissolved in 80 mL of deoxygenated water and 4 mL of deoxygenated acetoneitrile 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 [PtBr2(NCMe)]11: C, 12.4; H, 1.4; N, 6.4. Found: C, 12.3; H, 1.4; N, 6.6. IR (ATR, cm-1): 2920 w, 2340 m, 1354 m, 1351 m, 1012 m. 31P-NMR (CDCl3): -2805.

Method B. A sample (0.267 g, 0.77 mmol) of [PtCl(NCMe)]18 was introduced into a Carius tube, suspended in acetoneitrile (5 mL) and tBuBromide (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-[PtBr2(PPh3)](NCMe):

In a Carius tube under nitrogen atmosphere, 0.298 g (0.68 mmol) of [PtBr2(NCMe)]13 were added to 3 mL of acetoneitrile. The suspension was stirred and a stoichiometric amount of PPh3 (0.179 g, 0.68 mmol) was added. The tube was sealed and heated (150°C) for 2.5 h with vigorous stirring. Reaction progress was monitored with 31P-NMR. Once the reaction was found to be complete (5.34, 1Jp-p = 3475 Hz, cis; 1.72, 1Jp-p = 3944 Hz, trans), the tube was left overnight to cool down and yellow crystals of [PtBr2(PPh3)](NCMe)12 were recovered (0.244 g, 55%). The overall yield trans-[PtBr2(PPh3)](NCMe): The reaction was complete (31P-NMR) after half an hour later and displayed only one signal, attributable to kinetic trans. 1H-NMR: 7.72 (m, 6H, arom), 7.41 (m, 11H, arom), 7.14 (m, 2H, arom), 5.14 (m 2H, 2Jp-p = 3610 Hz, NH2), 2.35 (s, 3H, CH3). 13C-NMR: 136.7, 135.4, 135.0 (d, Jp-p = 10Hz), 130.8 (d, Jp-p = 2Hz), 129.8, 126.9 (d, Jp-p = 6Hz), 127.8 (d, Jp-p = 11Hz), 122.0, 21.0. 31P-NMR: 3.0 (d, Jp-p = 3653Hz). 195Pt-NMR: -4106 (d, Jp-p = 3653Hz).

trans-[PtBr2(PPh3)](p-Toluidine): The reaction was complete (31P-NMR) after half an hour later and displayed two signals, attributable to a mixture of cis and trans products. Configuration was assigned comparing 31P-NMR chemical shift and coupling constants data with those of the chlorinated isomers. Isomer cis: 31P-NMR: 7.8 (1Jp-p = 3610Hz), 195Pt-NMR: -3810Hz). Isomer trans: 31P-NMR: 0.8 (1Jp-p = 3458Hz), 195Pt-NMR: -4008 (d, Jp-p = 3458Hz).

cis-[PtBr2(PPh3)(DMSO)]: Pt2Br2(PPh3)12 is dissolved in d6-DMSO, the reaction was complete (31P-NMR) in a few minutes and displayed only one signal, attributable to isomer cis. Configuration was assigned comparing 31P-NMR chemical shift and coupling constants data with those of the known cis-[PtCl2(PPh3)(DMSO)].2 cis-[PtCl2(PPh3)(DMSO)]17: 1Jp-p = 3730Hz), 195Pt-NMR: -4162 (d, Jp-p = 3730Hz).

Table 2. Crystal data and structure refinement for cis-[PtBr2(PPh3)](NCMe).

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis-<a href="NCMe">PtBr2(PPh3)</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Co2Pt4Br11N8P2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>658.23</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 14.8719(10) Å, b = 8.3906(5) Å, c = 17.3852(11) Å, α = 90°, β = 114.827(2)°, γ = 90°</td>
</tr>
</tbody>
</table>

This product was synthesized from 1.034 g (1.034x10-3 mol) of [TBA][PtBr4] (8) by adding triphenylphosphine (0.542 g, 2.06x10-3 mol) in dichloromethane at room temperature and with magnetic stirring (PPh3/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 31P-NMR and found to have reached completeness in 12 h. 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: 0.801 g (95%) El. Anal. Calcd. for [PtBr2(PPh3)]18: C, 12.3; H, 1.4; N, 6.6. IR (ATR, cm-1): 3045 w, 1482 w, 1433 s, 1265 m, 1091 s, 730 s, 889 s. 31P-NMR for cis isomer: 13.7 (1Jp-p = 3610Hz). 195Pt-NMR for trans isomer: 18.7 (1Jp-p = 2573Hz).11

Bridge-splitting examples of [PtBr2(PPh3)]11
CCDC 1937596 (for cis-[PtBr₂(PPh₃)(NCMe)]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

### Acknowledgements

The authors thank the Università di Pisa (Fondi di Ateneo 2017-2018) and Ministero dell'Università e della Ricerca (MIUR) for grant PRIN 2015, “Design of Innovative Metal-Ligand Systems for Catalysis and Energy Applications” as well as the Interuniversity Consortium CHEMICAL REACTIVITY and CATALYSIS (CIRCC) and Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici (C.I.R.C.M.S.B.), for financial support. S. S. is grateful for the financial support provided by Università di Pisa – Progetti di Ricerca di Ateneo 2017 “Composti di metalli di transizione come possibili agenti antitumorali” (PRA_2017_25).

**Keywords:** platinum, exchange reactions, dinuclear bromocomplexes, solvothermal synthesis.
FULL PAPER

A sound synthetic procedure for the preparation of trans-[PtBr(μ-Br)(PPh₃)]₂ is described. The species was fully characterized and used to obtain [PtBr₃(PPh₃)(L)] complexes (L = DMSO, p-toluioide, pyridine) by a bridge-splitting reaction. All products were fully characterized by NMR spectroscopy, together with cis-[PtBr₃(PPh₃)(NCCH₃)] obtained as an intermediate in the synthesis of the dinuclear precursor. Cis-[PtBr(μ-Br)(PPh₃)] was also studied by X-ray diffraction.

Pt(II) bromo complexes


Page No. – Page No.

A sound sequence to triphenylphosphino dibromoplatin(II) complexes.
Solvothermal preparation of trans-[PtBr(μ-Br)(PPh₃)]₂.