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Pt-Catalysed Intermolecular Hydroamination of Non-Activated Olefins Using a Novel Family of Catalysts: Arbuzov-Type Phosphorus Metal Complexes[†]

Mireia Rodriguez-Zubiri,^{*a,1} Stéphane Anguille,^{a,2} Jean-Jacques Brunet^a and Jean-Claude Daran^a

^a CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France

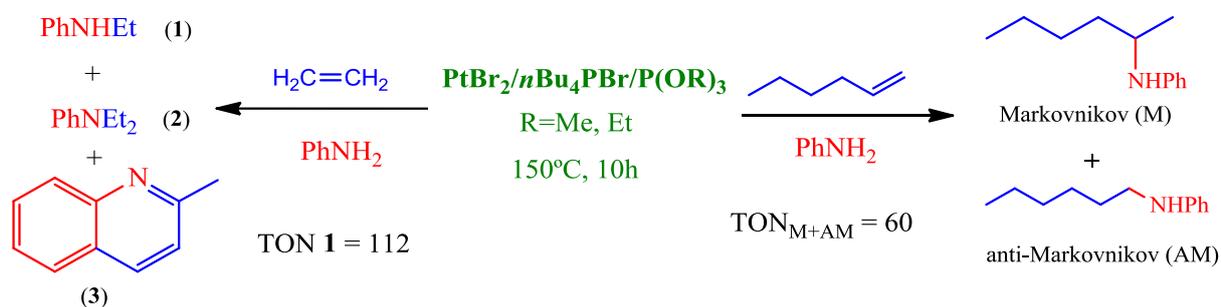
¹ Present address: CNRS, CEISAM, UMR 6230, UFR Sciences et Techniques, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France. Fax: +33 2 5112 5402; Tel: +33 2 5112 5697; e-mail: mireia.rodriquez@univ-nantes.fr.

² Present address: UMR CNRS 7313 iSm2, Aix-Marseille Université, Centre Saint Jérôme, service 531, 13397 Marseille Cedex 20, France.

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ABSTRACT

The catalytic system «PtBr₂(0.3 mol%)/2P(OR)₃/10*n*Bu₄PBr» (R = alkyl) discovered recently in our group, allows good to excellent catalytic activities for the *intermolecular* hydroamination of ethylene and *higher α-olefins* (1-hexene) with aniline type amines to give the expected *N*-ethyl- (1) and *N,N*-diethyl-anilines (2) along with 2-methyl-quinoline (3). A poisoning effect of alkyl and aromatic phosphines has been observed. This effect could be minimized using small amounts of molecular iodide which reacts with phosphorus ligands to form non-coordinating well-described ionic species. Interestingly, beneficial effects of added P(OR)₃ (R = alkyl) have been pointed out and further investigated. In this way, a new potential family of Arbuzov-type phosphorus-metal complexes has been suggested to be responsible for good catalytic activities found when using P(OR)₃ alkyl phosphites rather than PR₃ (R = alkyl, aromatic) and P(OPh)₃ co-catalysts.



KEYWORDS

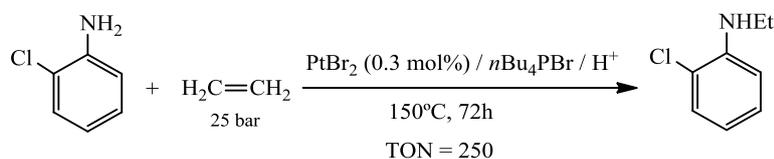
Platinum; phosphorus ligands; Arbuzov; hydroamination; halides.

1. INTRODUCTION

Catalytic hydroamination of alkenes is a practical, economical and sustainable alternative for the preparation of amines and its derivatives. This atom-economic process allows the addition of an N-H bond over an unsaturated carbon-carbon bond to yield a large variety of alkylated amines, very important chemicals in industry and everyday's chemistry. Intense efforts have been devoted to the study and optimisation of this reaction in the past 30 years [1].

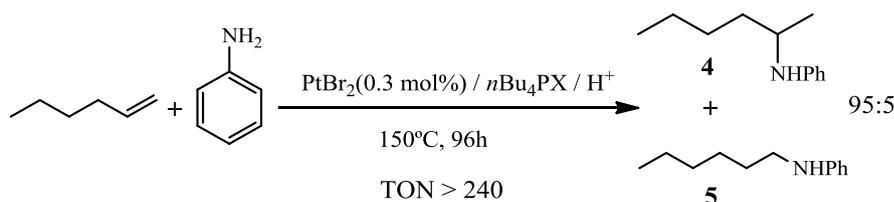
Nowadays, the hydroamination reaction could be classified in three categories: the *intramolecular* hydroamination of olefins [2], the *intermolecular* hydroamination of *activated* olefins and alkynes [3] and, the most challenging, the *intermolecular* hydroamination of *non-activated* olefins [1-4]. The latter has known important improvements with the recently discovered Pt and Rh-based catalytic systems [5].

The Pt-based catalysts have shown to be very efficient systems for the *intermolecular* hydroamination of ethylene (Scheme 1) and 1-hexene (Scheme 2) affording the Markovnikov product with an unprecedented regioselectivity (95%).



Scheme 1. Intermolecular Pt-catalysed hydroamination of ethylene.

This Pt-based system results from the association of PtBr_2 with tetrabutylphosphonium salts.



Scheme 2. Intermolecular Pt-catalysed hydroamination of 1-hexene.

It is also noteworthy that this system proved to be as efficient when reactions were performed under aerobic conditions [5b,5c].

The discovery of an original Rh^{III} -based system, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} / 2\text{PR}_3 / 65n\text{Bu}_4\text{PI} / 2\text{I}_2$, which consists in the association of simple Rh^{III} salts with phosphonium salts and PR_3 ligands (PR_3 = *para* substituted triarylphosphines, $\text{P}(\text{OMe})\text{Ph}_2$, BINAP, dppe) (Scheme 3) was also described recently [5h]. The latter proved to allow the highest catalytic activity for the *intermolecular* hydroamination of ethylene, but also 1-butene and 1-hexene, with aniline type amines (0.3 mol% catalytic precursor) to give the expected *N*-ethyl- (**1**) and *N,N*-diethyl-anilines (**2**) along with 2-methyl-quinoline (**3**) (Scheme 3). This system is particularly efficient in the presence of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, BINAP (CE = 460, CE = Catalytic Efficiency = $\text{TON}_{(1)} + 2\text{TON}_{(2)} + 2\text{TON}_{(3)}$) and tri-*p*-tolylphosphine (CE = 528). Good to excellent activities were also found combining the Wilkinson's catalysts (Rh^{I} complexes) with $n\text{Bu}_4\text{PI}$ and I_2 . Interestingly, the simple association of PPh_3 and I_2 was shown to be an extremely efficient "in situ generated" source of I^- promoters able to substitute preformed $n\text{Bu}_4\text{PI}$. It is important to note that the performance of this Rh-based system depends upon the combination of both PR_3/I^- promoters [5g,5h].

2. EXPERIMENTAL SECTION

2.1. Instrumentation

GC analyses were performed on a Hewlett-Packard HP 4890 (FID) chromatograph (HP 3395 integrator) equipped with a 30 m HP1 capillary column. GC-MS analyses were performed on a Hewlett-Packard HP 6890 apparatus equipped with a HP 5973 M ion detector. NMR analyses were performed on Bruker AM 250 and 400 machines. *J* values are given in Hz. Catalytic experiments were conducted in a 100 mL stainless steel thermoregulated (electric oven) autoclave with a glass liner and a magnetic stirring bar.

2.2. Methods and Materials

Potassium bromide (Aldrich, +99%), 1-iodobutane (Alfa Aesar, 99%), tri-*n*-butylphosphine (Acros Organics, 95%), triphenylphosphine (Aldrich, 99%), triphenylphosphite (Acros, 99%), trimethylphosphite (Strem, 97%), methyl-diphenylphosphinite (Acros, 99%), tris((4-trifluoromethyl)phenyl)phosphine (Avocado, 98%), rac-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (Aldrich, 97%), 1,3-bis(diphenylphosphino)propane (Aldrich, 97%), 1,10-phenanthroline (Aldrich, +99%), potassium tetrachloroplatinate(II) (Aldrich, 98%) and platinum(II) bromide (Strem Chemicals, 98%) were used as received. Tetra-*n*-butylphosphonium bromide (Aldrich, 98%) was stored in a desiccator under vacuum prior to use. Molecular iodine was purchased from Acros Organics.

Aniline (Acros Organics, 99% for analysis ACS), *N*-ethylaniline (Acros Organics, 98%), *N,N*-di-*n*-butylaniline (Aldrich, 97%), 1-hexene (Aldrich, 97%), tri-*t*-butylphosphine (Aldrich, 98%), trimethylphosphine (Aldrich, 97%) tris(dimethylamino)phosphine (Aldrich, 97%) and triethylphosphite (Aldrich, 98%) were distilled before use and stored under argon. Ethylene (N25, +99.5%) was purchased from Air Liquide.

Water was deionised and degassed. All other solvents were of HPLC grade and were degassed prior to use.

cis-Dibromobis(trimethylphosphite)platinum(II) [16a] and *cis*-Dibromobis(triphenylphosphine)platinum(II) [16b] were prepared according to established methods.

Tetra-*n*-butylphosphonium iodide was prepared from *n*Bu₃P and *n*BuI (see below), stored under argon, in a freezer, and protected from light.

Tetra-*n*-butylphosphonium *cis*-dibromo(dimethylphosphonato)(trimethylphosphite)platinum(II), **6**, was prepared from *cis*-dibromobis(trimethylphosphite)platinum(II) and tetra-*n*-butylphosphonium bromide (see below).

2.3. Preparation of tetra(*n*-butyl)phosphonium iodide

Tri(*n*-butyl)phosphine (38 mL, 0.15 mol) was slowly added to 1-iodobutane (40 mL, 0.35 mol) under argon. The mixture was stirred for 1h at RT and then at 100°C for 20h. After cooling, the resulting precipitate was washed with diethylether (4x50 mL) until a white solid was obtained. Evaporation of residual solvent under vacuum overnight afforded pure *n*Bu₄PI as a white powder (55.6 g, 96%), mp = 95-96°C. Anal. Found: C, 49.75; H, 9.57. Calc. for C₁₆H₃₆IP: C, 49.74; H, 9.39. δ_H (250 MHz, acetone-d₆) 0.96 (3H, t, ³*J* 3), 1.55 (2H, m), 1.70 (2H, m), 2.54 (2H, m); δ_P (250 MHz, acetone-d₆) 33.52 (s).

2.4. Preparation of *cis*-[PtBr₂(P(OCH₃)₃)(OP(OCH₃)₂)](*n*Bu₄P), **6**

To a vigorously stirred solution of *cis*-PtBr₂(P(OMe)₃)₂ (243 mg, 0.404 mmol) in acetonitrile (2 mL) placed in to a round-bottom flask at 70°C (oil bath), was dropwise added another solution of *n*Bu₄PBr (137 mg, 0.404 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for further 2h until completion. Solvent removal afforded *cis*-[PtBr₂(P^A(OCH₃)₃)(OP^B(OCH₃)₂)](*n*Bu₄P) quantitatively (340 mg). Anal. Found: C, 29.78; H,

6.25. Calc. for $C_{21}H_{51}O_6P_3Br_2Pt$: C, 29.76; H, 6.07. δ_H (400 MHz, acetone- d_6) 0.97 (3H, t, 3J 3, CH₃ from nBu_4P) 1.55 (2H, m, CH₂ from nBu_4P) 1.7 (2H, m, CH₂ from nBu_4P) 2.54 (2H, m, CH₂ from nBu_4P) 3.5 (6H, d, $^3J_{PH}$ 4.9, P^B-OCH₃); 3.77 (9H, d, $^3J_{PH}$ 4.9, P^A-OCH₃); δ_P (400 MHz, acetone- d_6) 31.06 (m, $^1J_{PB-Pt}$ 4962, P^B) 33.34 (m, $^1J_{PA-Pt}$ 6631, P^A).

2.5. Catalytic reactions

2.5.1. Hydroamination of ethylene: typical procedure.

The autoclave was charged with PtBr₂ (46.2 mg, 0.13 mmol), PPh₃ (2 equiv/Pt, 68.0 mg, 0.26 mmol) and nBu_4PBr (10 equiv/Pt, 441 mg, 1.3 mmol), closed and submitted to several argon-vacuum cycles. Distilled and degassed aniline (4.1 mL, 45 mmol) was then syringed into the autoclave. The ethylene pipe was connected to the autoclave, purged, and the ethylene pressure was adjusted to 25 bars at RT (*ca.* 100 mmol). The temperature was then raised to 150°C. After 10h, the autoclave was allowed to cool to room temperature and slowly vented in a fume cupboard. The reaction mixture was poured into 120 mL of diethylether, stirred for 2h, and then filtered. The external standard (*N,N*-di(*n*-butyl)aniline, *ca.* 0.15 g) was added to the collected ethereal phases and the solution analysed by GC and GC-MS.

2.5.2. Hydroamination of 1-hexene: typical procedure.

The autoclave was charged with PtBr₂ (46.2 mg, 0.13 mmol), and nBu_4PBr (65 equiv/Pt, 2.88 g, 8.45 mmol), closed and submitted to several argon-vacuum cycles. Distilled and degassed aniline (4.1 mL, 45 mmol) along with P(OMe)₃ (1 equiv/Pt, 15.8 mg, 0.13 mmol) and 1-hexene (11.3 mL, 91 mmol) were then syringed sequentially into the autoclave. The temperature was then raised to 150°C. After 10h, the autoclave was allowed to cool down to room temperature and slowly vented in a fume cupboard. The reaction mixture was then poured into 120 mL of diethylether, and stirred for 2h, and then filtered. The external standard (*N,N*-di(*n*-butyl)aniline, *ca.* 0.15 g) was added to the collected ethereal phases and the solution analyzed by GC and GC-MS.

Taking into account the liquid nature of both substrates (aniline and 1-hexene), the hydroamination of 1-hexene by aniline could analogously be carried out using adapted Schlenk glass-ware as follows: A 35 mL Ace Pressure Tube was charged with PtBr₂ (46.2 mg, 0.13 mmol) and nBu_4PBr (65 equiv/Pt, 2.88 g, 8.45 mmol). Distilled and degassed aniline (4.1 mL, 45 mmol) along with P(OMe)₃ (1 equiv/Pt, 15.8 mg, 0.13 mmol) and 1-hexene (11.3 mL, 91 mmol) were then syringed sequentially into the Ace Pressure Tube. The temperature was then raised to 150°C. After 10h, the reaction mixture was allowed to cool down to room temperature and poured into 120 mL of diethylether. The external standard (*N,N*-di(*n*-butyl)aniline, *ca.* 0.15 g) was added to the collected ethereal phases and the solution analysed by GC and GC-MS.

2.6. Study on the coordination chemistry of the PtBr₂/ nBu_4PBr /PR₃ catalytic system.

Typical procedure: PtBr₂ (0.13 mmol, 46.2 mg), nBu_4PBr (65 equiv/Pt, 45 mmol, 2.87 g) and PPh₃ (2 equiv/Pt, 0.26 mmol, 68.0 mg) were weighted and placed in to a 25 mL round-bottom flask. *o*-Dichlorobenzene (5 mL) was added and a reflux condenser adapted to the system. The stirred reaction mixture was heated to 150°C in an oil bath. After 10h, the reaction mixture was allowed to cool down to room temperature, then the solvent was removed under reduced pressure and the crude analysed by ³¹P NMR (250 MHz, CDCl₃, see SI). When PPh₃ and P(OPh)₃ were used, crystals suitable for X-ray diffraction were grown while cooling down the reaction mixture to room temperature (see SI).

2.7. X-ray Structure Determination.

Single crystals of **7**, **8** and **9** were mounted under inert perfluoropolyether at the tip of glass

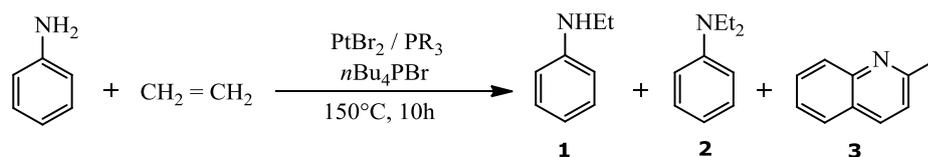
fibre and cooled in the cryostream of the Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the monochromatic MoK α radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SIR97) [17] and refined by least-squares procedures on F² using SHELXL-97 [18]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The drawing of the molecules was realised with the help of ORTEP32 [19]. Crystal data and refinement parameters are shown in Table 3-5 from the SI.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 878731 - 878733. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. RESULTS AND DISCUSSION

3.1. Hydroamination of ethylene by aniline in the presence of phosphorus ligands

Taken the urgency to develop new catalytic systems for the intermolecular hydroamination of *non-activated* olefins and the consolidated reputation of phosphorus ligands to accomplish this type of task for a large range of catalytic reactions (see introduction), we were prompted to investigate the effect of several classical and simple phosphorus ligands in the *intermolecular* hydroamination of *ethylene* by aniline as model reaction (Scheme 4). Aiming to improve the already efficient stable low-loading (0.3 mol%) “one-pot” ready-to-use PtBr₂/*n*Bu₄PBr system recently discovered in our team [5b,5c], we carried some studies to identify a compatible class of ligand able to afford good catalytic activities and capable of playing the role of a potential chiral vector.



Scheme 4. Pt-catalysed *intermolecular* hydroamination of *ethylene* by aniline in the presence of PR₃

In this work, we were led to consider the TON (mol of product formed by mol of catalyst) in order to evaluate the efficiency of the catalyst.

In a previous report, it was briefly pointed out that the catalytic efficiency for the hydroamination of ethylene (Scheme 4) could be dramatically affected by the presence of phosphorus ligands [20]. In order to confirm and generalise our observations, it was decided to investigate the influence of the PR₃/PtBr₂ ratio and the nature of the associated ligand for the hydroamination of *ethylene* with aniline. For this study, experiments were conducted without acid co-catalyst in order to better observe the role of the phosphorus additives. According to previous studies, the selected reaction time was 10h and the chosen reaction temperature was 150°C.

At first, it must be recalled that, in the *absence* of PR₃ ligands, the PtBr₂-based systems exhibit catalytic activity up to TON = 102 (entry 1, Table 1) for the formation of the hydroamination product **1** (Scheme 4).

The influence of the nature of the phosphorus ligands was studied using several types of phosphines containing alkyl, aryl, aryloxy or alkoxy substituents and the results are listed in Table 1.

Table 1. Effect of the amount and nature of the phosphorus ligands used on the PtBr₂-catalysed hydroamination of ethylene by aniline.^a

Entry	Ligand (equiv/Pt)	TON 1 ^b	TON 2 ^b	TON 3 ^b
1	-	102	5	15
2	PPh ₃ (1)	18	-	23
3	PPh ₃ (2)	11	-	19
4	<i>n</i> Bu ₃ P (1)	31	-	6
5	<i>n</i> Bu ₃ P (2)	5	-	4
6	P(OMe) ₃ (1)	98	4	10
7	P(OMe) ₃ (2)	112	6	8
8	P(OPh) ₃ (1)	24	-	-
9	P(OPh) ₃ (2)	<1	-	-

^a Conditions: PtBr₂ (46.1 mg, 0.13 mmol), PR₃, *n*Bu₄PBr (0.4412 g, 1.30 mmol), PhNH₂ (4.1 mL, 45.5 mmol), C₂H₄ (25 bar, *ca.*100 mmol), 150°C, 10h. ^b *N*-ethylaniline (**1**), *N,N*-

diethylaniline (**2**), 2-methyl-quinoline (**3**).

These results showed that to the exception of P(OMe)₃ (entries 6-7, Table 1), phosphorus ligands seem to be inhibitors. It seems that this effect is enhanced when using 2 equiv of ligand/Pt mainly due to a lower production of **1**.

In the case of PPh₃ (entries 2-3, Table 1) the observed catalytic performance is in contrast with our previous results on the Rh^{III}-catalysed reactions of aniline with ethylene [5g,5h], where aromatic phosphorus ligands such as PPh₃ seemed to allow excellent catalytic activities. In the same way, aryloxy-substituted ligands (triarylphosphites) and trialkylphosphines allow the reaction but are inefficient co-catalysts (entries 4-5, 8-9).

Unexpectedly, catalytic activity is fully recovered upon the introduction of alkoxy groups as substituents on the phosphorus atoms. Indeed, results obtained with 2 equiv/Pt of P(OMe)₃ (entries 6-7, Table 1) showed that this ligand *does* afford higher selectivity (less production of **2** and **3** side-products) and catalytic activity for the formation of the desired product, *N*-ethylaniline **1**, than when the reaction is performed in the absence of ligand. Thus, the presence of alkoxy groups in the structure of the phosphorus ligands seems to be a key factor for achieving good catalytic activities.

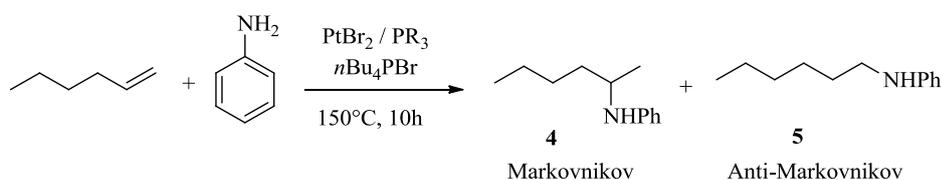
According to results stated in Table 1, alkyl phosphites may represent the only type of phosphorus ligand without an inhibitor effect and thus suitable for the studied reaction.

3.2. Hydroamination of *higher α-olefins* in the presence of phosphorus ligands

In order to potentially widen the scope of this catalytic process, we studied the addition of aniline to *higher α-olefins* such as 1-hexene in the presence of a variety of phosphorus ligands.

The products resulting from these reactions are of great relevance in industry and the transformation of *higher α-olefins* is itself an important scientific challenge [21,15d]. Literature on the *intermolecular* hydroamination of *higher olefins* by simple amines is very scarce and quite recent [2a,5c,15b,22-25]. Marks and co-workers [2a,22] studied the hydroamination of 1-pentene with *n*-propylamine and reported to deal with a challenging reaction, the *intermolecular* hydroamination of *non-activated* alkenes, in comparison to *intramolecular* hydroamination, 350x faster, and alkyne hydroamination, 1400x faster. To the best of our knowledge, only four reports have appointed the use of phosphorus ligands for the *intermolecular* hydroamination of *higher non-activated α-olefins*. First, He *et al.* worked on the addition of TosNH₂ to 1-octene with 5 mol% of Ph₃PAuCl/AgOTf in toluene at 85°C [23]. Later on, Loh and co-workers studied the same reaction in the presence of InBr₃ (20 mol%) in toluene at 120°C [24]. Both groups obtained the desired Markovnikov hydroamination product along with another Markovnikov isomer resulting from the hydroamination of an internal alkene formed by isomerisation of the initial terminal double bond alkene. Next, Agbossou-Niedercorn and Michon (see introduction), used dppe for the hydroamination of 1-hexene by TosNH₂ [15b]. Using AuClPR₃ (PR₃ = P(*t*Bu)₂*o*-biphenyl and 2-di-*tert*-butylphosphino-1,1'-binaphthyl) complexes Widenhoefer and co-workers successfully hydroaminated 1-alkenes with very low basicity amines [25].

As may be seen from literature, only group 11 (Au, Cu, Ag) transition metals have been associated with phosphorus ligands to investigate the title reaction. Thus, the addition of aniline to 1-hexene (Scheme 5) was studied using Pt/P-based catalytic systems.



Scheme 5. Pt-catalysed *intermolecular* hydroamination of *1-hexene* by aniline in the presence of PR_3 .

Catalytic results have revealed that, to the exception of alkyl phosphites ($\text{P}(\text{OEt})_3$ and $\text{P}(\text{OMe})_3$, entries 7-10, Table 1 from SI), the catalytic activity of this reaction seems, once more, inhibited in the presence of phosphorus ligands. As in the case of ethylene, this is true for aromatic phosphines, alkyl phosphines and aromatic phosphites (see Table 1 from SI for further details), confirming our hypothesis on the need of a P-O-C bond in the structure of the ligand to obtain a good catalytic performance.

These results seem to confirm a strong coordination mode between the metal centre and the ligands, completely deactivating the catalytic system by blocking its active sites.

This is somehow confirmed by the results obtained (TON = 1.5) for the hydroamination of *1-hexene* (1.6 mL, 12.73 mmol, 150°C, 144h) by aniline (4.1 mL, 45 mmol) in the presence of preformed *cis*- $\text{PtBr}_2(\text{PPh}_3)_2$ (0.114 g, 0.13 mmol) and *n* Bu_4PBr (6.62 g, 19.5 mmol).

On the basis of previous results on the platinum-catalysed hydroamination of alkenes [5c], the possible role of molecular iodine was also considered. The association of the reported inhibitor systems, *n* $\text{Bu}_4\text{PBr}/\text{dppp}$ (dppp = 1,2-bis(diphenylphosphino)propane) and *n* $\text{Bu}_4\text{PI}/\text{PPh}_3$, with molecular iodine allows to recover the catalytic activity in the presence of PtBr_2 (see Table 2 from SI for further details). These results may be understood as I_2 being an antidote for the poisoning effect of aromatic phosphines by forming $[\text{R}_3\text{PX}]^+\text{X}^-$ salts (Scheme 6) as described in the literature [26].



Scheme 6. Formation of $[\text{R}_3\text{PX}]^+\text{X}^-$ salts from PR_3 and I_2

To confirm this hypothesis, we have studied the ^{31}P NMR (under inert atmosphere) of the reaction mixture of a typical catalytic run in the presence of triphenylphosphine. Two signals were identified: the expected signal corresponding to the phosphonium salt, *n* Bu_4PI , at $\delta_{\text{P}} = 33.1$ ppm, along with another signal ($\delta_{\text{P}} = 26.9$ ppm, major product) that could be attributed to iodotriphenylphosphonium iodide, $[\text{R}_3\text{PI}]^+\text{I}^-$, by correlation with the ^{31}P NMR data obtained from the in situ NMR reaction (at room temperature in acetone- d_6) between PPh_3 and I_2 .

A more detailed discussion about the obtained catalytic results along with literature data for the hydroamination of *1-hexene* in the presence of phosphorus ligands and/or I_2 is available in the supporting information (SI).

It is premature to speculate about the exact role of these phosphorus-containing ligands and mechanistic studies are required to gain full insight into these phenomena. A full mechanistic study on the title reaction is out of the scope of this article and will be addressed in future publications. Although the NMR monitoring of the catalytic process could have provided some important insights on the active catalytic species and on possible intermediates of the catalytic cycle, this study could not be done due to technical difficulties (high temperature, 150 °C, during 10h, and high pressure, 25 bar, in the case of ethylene as starting olefin). As a preliminary alternative we have tried to recover the catalyst at the end of the reaction in order to evaluate, by ^{195}Pt NMR, the absence/presence of phosphorus containing platinum complexes that could explain the observed catalytic results. Decomposition of the active platinum species to black Pt^0 (black precipitate at the end of the catalytic process) did not allow us to observe any platinum containing species by the NMR technique.

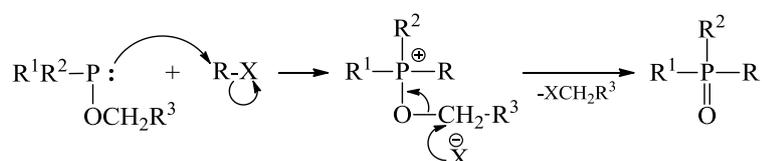
3.3. Hydroamination in the presence of Arbuzov-type phosphorus containing Pt-complexes

On the basis of the good catalytic results obtained with the association of PtBr_2 with *n* Bu_4PI

and alkylphosphites, our next efforts were aimed at investigating the particularly beneficial effect of this unique type of phosphorus ligands in the *intermolecular* Pt-catalysed hydroamination of *ethylene* by aniline.

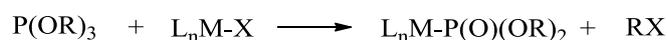
For this study we addressed an important question concerning the fact that alkylphosphites allow high catalytic activities whereas alkyl- and arylphosphines, and even arylphosphites, behave as inhibitors.

Our first hypothesis was based on chemical structural differences between phosphorus promoters and inhibitors: alkylphosphites are the only ones to have O-alkyl substituents on the phosphorus atom. Thus we were prompted to consider an “*in situ*” transformation, under the catalytic conditions, of metal-coordinated alkylphosphites into somehow more active species according to a Michaelis-Arbuzov type reaction. As described by Odinet *et al* [27], the Michaelis-Arbuzov reaction allows the formation of a P=O bond by reaction of an alkylphosphite with an alkylhalide (Scheme 7).



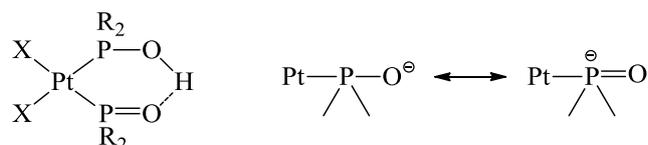
Scheme 7. Michaelis-Arbuzov reaction

Taking a look into literature data we could find several reports on a special type of Michaelis-Arbuzov reaction where, similarly, a metallic complex containing one or more halogen ligands allows the reaction (Scheme 8) [28]. Interestingly, authors report this reaction to take place at moderate to high temperatures when reaction times are prolonged, as in our case.



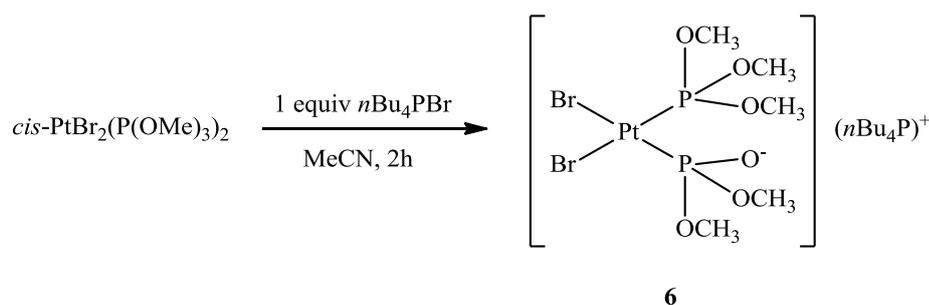
Scheme 8. Michaelis-Arbuzov reaction in metallic complexes

Roundhill and co-workers reported an interesting study on successive Michaelis-Arbuzov reactions on various alkoxy groups from the phosphorus ligand. They succeeded in the formation of transition metal complexes containing different type of phosphorus ligands in equilibrium, when several equivalents of alkylphosphite reacted with a chosen metallic complex (Scheme 9) [29].

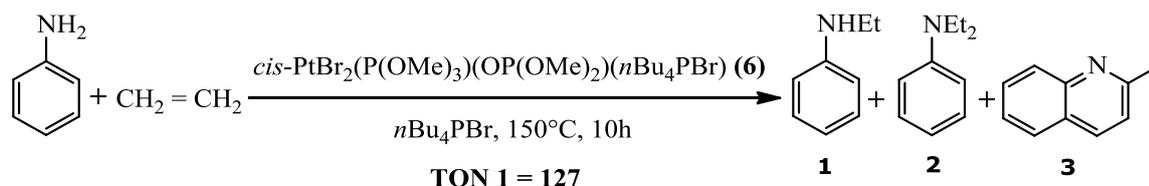


Scheme 9. Transition-metal Michaelis-Arbuzov reaction described by Roundhill and co-workers [29].

Taking into account the state of the art, and in order to confirm our hypothesis on the Michaelis-Arbuzov reaction to be responsible of the particular catalytic effect of alkylphosphites, further catalytic experiments were conducted in the presence of a preformed Pt-complex containing a Michaelis-Arbuzov type phosphorus ligand. Thus, the complex *cis*-[PtBr₂(P(OCH₃)₃)(OP(OCH₃)₂)](*n*Bu₄P) (6) (Scheme 10) was synthesised (see experimental section) and used along with *n*Bu₄PBr for the catalytic hydroamination of ethylene by aniline (Scheme 11).



Scheme 10. Preparation of compound *cis*-[PtBr₂(P(OCH₃)₃)(OP(OCH₃)₂)](*n*Bu₄P) (**6**)



Scheme 11. Catalytic hydroamination of ethylene by aniline in the presence of compound (**6**)

Results in this area were particularly interesting. Indeed, TON up to 127 towards the production of **1** (TON₁ = 127, TON₂ = 5, TON₃ = 4) were obtained using the association of *cis*-[PtBr₂(P(OCH₃)₃)(OP(OCH₃)₂)](*n*Bu₄P) (**6**) (0.3 mol%, 0.13 mmol, 0.110 g) with *n*Bu₄PBr (10 equiv/Pt, 0.4412 g, 1.30 mmol), a particularly efficient system for the hydroamination of ethylene (25 bar, *ca.*100 mmol, 150°C and 10h) by aniline (4.1 mL, 45.5 mmol) and even more active and selective towards the formation of **1**, under comparable conditions, than the platinum system PtBr₂/10*n*Bu₄PBr/2P(OMe)₃ (entry 7, Table 1). It is important to note that no black Pt(0) has been observed at the end of the reaction when performing the catalytic tests in the presence of *cis*-[PtBr₂(P(OCH₃)₃)(OP(OCH₃)₂)](*n*Bu₄P). This seems to point out an important feature of this system: a high stability of the catalytically active species even at high temperature and in a reductive media.

A mechanistic study on the Pt-catalysed hydroamination reaction in the presence of P containing ligands will be addressed in future works.

3.4. Coordination Chemistry of the PtBr₂/*n*Bu₄PBr/PR₃ catalytic systems

As stated above, one of the advantages of the catalytic strategy used in the present study was the possibility to add in a “one-pot” manner the components of the catalytic system. Nevertheless, in order to better understand the coordination abilities of the metal centre towards the added phosphine ligands, we decided to explore a few more experiments on the reactivity of PtBr₂ with some of the phosphine and phosphites used for the hydroamination reaction. Surprisingly, literature data on this subject are still scarce [30].

For this purpose, PtBr₂ was reacted with 1 and 2 equiv/Pt of three different phosphorus ligands (PPh₃, P(OEt)₃ and P(OPh)₃), in the presence of *n*Bu₄PBr.

Surprisingly, the reactivity of PtBr₂ towards aromatic phosphines, aromatic phosphites and alkyl phosphites was found to be quite different under the same reaction conditions.

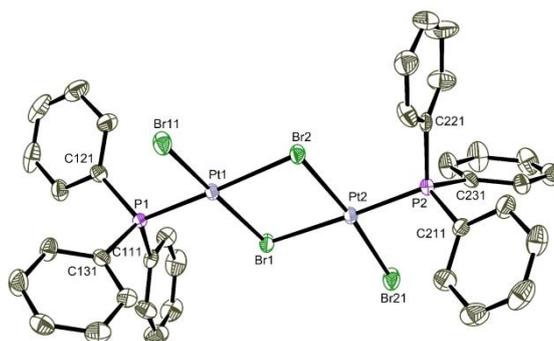


Figure 1. Molecular view of compound **7** $trans$ -[PtBr₂(PPh₃)₂] with the atom-labelling scheme.

As expected, the reaction of PtBr₂ with 1 equiv/Pt of PPh₃ gave a new binuclear complex $trans$ -[PtBr₂(PPh₃)₂] **7** (Figure 1) while 2 equiv/Pt of PPh₃ gave the already known mononuclear complex cis -PtBr₂(PPh₃)₂ **8** (Figure 2).

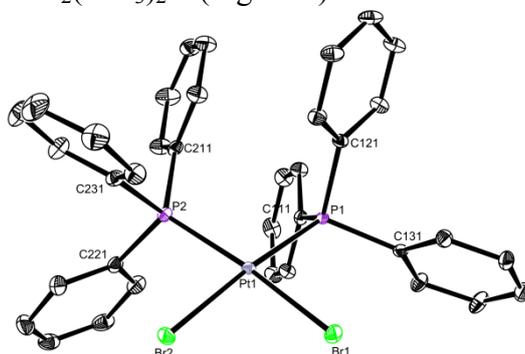


Figure 2. Molecular view of compound cis -PtBr₂(PPh₃)₂, **8**, with the atom-labelling scheme.

Interestingly, the same reaction under the same conditions but using 1 or 2 equiv/Pt of P(OPh)₃ gave only the mononuclear complex cis -PtBr₂(P(OPh)₃)₂ **9** (Figure 3) as stated by a very clean ³¹P NMR spectra.

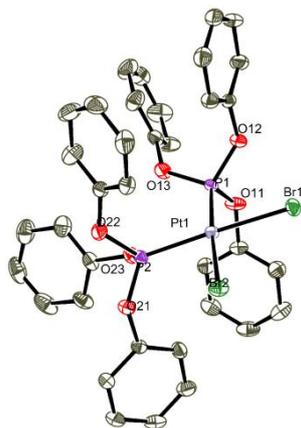


Figure 3. Molecular view of compound cis -PtBr₂(P(OPh)₃)₂, **9**, with the atom-labelling scheme.

Concerning P(OEt)₃ ligand, its coordination chemistry with PtBr₂ seems less straight forward and we tentatively propose the formation of cis -PtBr₂(P(OEt)₃)₂ along with, as expected, platinum complexes containing several Arbusov-type phosphorus ligand according to related literature data.

Single crystals suitable for X-ray diffraction were obtained for compounds **7-9** while cooling down the reaction mixture to room temperature (see experimental section and SI for further details).

A more detailed discussion about the obtained results along with experimental, spectroscopic and crystallographic data for **7-9** complexes and related compounds is available in the supporting information (SI).

4. CONCLUSIONS

An important effect of phosphorus co-catalysts on the *intermolecular* Pt-catalysed hydroamination of ethylene and 1-hexene by aniline has been evidenced. Indeed, although alkyl- and arylphosphines, as well as arylphosphites, inhibit the reaction, alkylphosphites showed to be a unique class of ligands suitable for the title reaction. We have investigated this particular effect of alkylphosphites and found that the association $\text{PtBr}_2(\text{P}(\text{OMe})_3)(\text{OP}(\text{OMe})_2)/10n\text{Bu}_4\text{PBr}$ is a very efficient catalytic system allowing even higher TON than the $\text{PtBr}_2/10n\text{Bu}_4\text{PBr}/2\text{P}(\text{OMe})_3$ catalyst studied in this work and the previously reported $\text{PtBr}_2/10n\text{Bu}_4\text{PBr}$ system [5b].

These results give access to a new broad family of efficient Arbuzov-type ligands for homogeneous catalytic processes. Modulation of their structural properties could provide a large range of new Arbuzov-like phosphoranes. Even more important, these phosphorus containing co-catalysts may represent the first family of ligands suitable for the *intermolecular* Pt-catalysed hydroamination of ethylene and *higher* α -olefins and thus become an important option when considering the enantioselective version of this reaction; an important scientific challenge (see introduction). Indeed, a new series of chiral catalysts could be considered combining, in the coordination sphere of a transition metal centre, different phosphonites $\text{P}(\text{OR}^1)_2\text{R}^2$ and/or phosphinites $\text{P}(\text{OR}^1)\text{R}^2\text{R}^3$ bearing a chiral R^2 and/or R^3 group or, alternatively, 2 different R^2 and R^3 groups.

Furthermore, we have been able to evidence a preventing effect of I_2 towards the poisoning effect of phosphines and arylphosphites on the studied reactions by the formation of $[\text{R}_3\text{PI}]^+\text{I}^-$ type salts.

Investigations on the coordination chemistry of PtBr_2 with PPh_3 , $\text{P}(\text{OPh})_3$ and $\text{P}(\text{OEt})_3$ have revealed an interesting behaviour when using phosphites (only monomers are formed) and provide a new X-ray structure for the dimer complex *trans*- $[\text{PtBr}_2(\text{PPh}_3)]_2$.

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6. SUPPORTING INFORMATION

A detailed discussion about the obtained results on i) the hydroamination of 1-hexene in the presence of phosphorus ligands and/or I₂ along with literature data, and ii) the coordination chemistry of the PtBr₂/*n*Bu₄PBr/PR₃ catalytic systems along with experimental, spectroscopic and crystallographic data for 7-9 complexes and related compounds, is available in the Supporting Information (SI). This material is available free of charge via the Internet.

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