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Convenient high-pressure syntheses of $[\text{PtX}_3(\text{C}_2\text{H}_4)]^-$ ($\text{X} = \text{Cl}, \text{Br}$) salts with a variety of organic cations from PtX_2

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Synthesis

Abstract

Reaction between PtX_2 ($\text{X} = \text{Cl}$ or Br) with an equimolar amount of the appropriate $[\text{Cat}]^+\text{X}^-$ in toluene in an autoclave under 25 bars of C_2H_4 yields the corresponding $[\text{Cat}][\text{PtX}_3(\text{C}_2\text{H}_4)]$ in moderate to excellent isolated yields and high purity ($\text{X} = \text{Cl}$, $\text{Cat} = n\text{Bu}_4\text{P}$; $\text{X} = \text{Br}$, $\text{Cat} = n\text{Bu}_4\text{P}$,

Ph₄P, *n*Bu₄N). The same reaction does not yield any olefin complex if X = I and no reaction also occurs for the PtBr₂+KBr system in water, THF, acetone or toluene.

1. Introduction

The ethylenetrichloroplatinate(II) complex, [PtCl₃(C₂H₄)]⁻, represents a milestone in organometallic chemistry, being the first organometallic complex to be synthesized for a transition metal and isolated as the hydrated potassium salt in 1825 by the Danish chemist Zeise.¹⁻³ The tribromo analogue, [PtBr₃(C₂H₄)]⁻, was introduced by Chojnacki in 1870, and also isolated as the potassium salt.⁴ Until recently, the chemistry of these and other analogous (olefin)trihaloplatinate complexes has been investigated, specifically in terms of ligand exchange kinetics and mechanism,^{5,6} only in combination with potassium or other alkali metals, mostly in water or aqueous methanol. Although a Li⁺ salt was shown to be soluble in THF,^{7,8} salts with bulky organic cations are expected to provide solubility in a broader range of organic solvents and would therefore allow the development of the coordination chemistry of the Zeise, Chojnacki and related anions in these different media.

A compound of stoichiometry [*n*Bu₄N][PtBr₃(C₂H₄)], characterized by IR spectroscopy, was mentioned,⁹ but no detailed synthetic procedure has appeared in the literature to the best of our knowledge. Only recently, motivated by the observation of a remarkable catalytic activity of PtBr₂ in the presence of *n*Bu₄PBr toward the hydroamination of ethylene¹⁰⁻¹² and 1-hexene¹³ by aniline derivatives, we have isolated the [PtX₃(C₂H₄)]⁻ salts (X = Cl, Br) in combination with the *n*Bu₄P⁺ cation. This has allowed us to investigate ligand exchange equilibria in dichloromethane¹⁴ that, in combination with theoretical calculations,¹⁵ have led to the elucidation of the full catalytic cycle for the ethylene hydroamination reaction.^{16,17}

The synthesis of $[n\text{Bu}_4\text{P}][\text{PtX}_3(\text{C}_2\text{H}_4)]$ ($X = \text{Cl}, \text{Br}$) made use of a salt metathesis from Zeise's salt or Chojnacki's salt (the latter being made in situ by halide exchange from Zeise's salt and KBr), respectively. The pure products were obtained in 88 and 61% yield, respectively.¹⁴ Although simple, this synthesis suffers from a relatively high market price of Zeise's salt and the need to use a large amount of KBr (to insure complete halide exchange) for the synthesis of the tribromo analogue, since Chojnacki's salt is not commercially available. In this contribution, we disclose a much simpler and widely applicable synthetic method making use of the less expensive PtCl_2 and PtBr_2 , leading to the isolation in good to excellent yields of salts with a few different organic cations. The method should be easily adaptable to salts with many other cations and different olefins for both halide series.

2. Experimental section

2.1. General. All synthetic procedures were carried out under exclusion of air and using solvents that had been dehydrated by conventional methods. The ^1H , ^{31}P and ^{195}Pt NMR spectra were measured in CD_2Cl_2 or CDCl_3 with Bruker (DPX300, AV400) instruments. The spectra were referenced against the residual solvent resonance for ^1H and against external 85% H_3PO_4 for ^{31}P and $\text{Na}_2[\text{PtCl}_6]$ for ^{195}Pt . Elemental analyses were carried out with a Perkin-Elmer 2400 series II analyzer by the Microanalytical Service of the Laboratoire de Chimie de Coordination. Tetra(*n*-butyl)phosphonium iodide was prepared from $n\text{Bu}_3\text{P}$ and $n\text{BuI}$ according to the literature¹¹ and stored protected from light and under argon in a freezer. All other chemicals were purchased from commercial suppliers and were used as received: PtCl_2 (99.9%, Aldrich), PtBr_2 (99.9%, Aldrich), PtI_2 (Alfa Product), C_2H_4 ($\geq 99.5\%$, Air Liquide), $n\text{Bu}_4\text{PBr}$ (98%, Aldrich), $n\text{Bu}_4\text{PCl}$ (96%, Aldrich), Ph_4PBr (98+%, Avocado), $n\text{Bu}_4\text{NBr}$ ($\geq 98\%$, Aldrich).

2.2. Preparation of $[n\text{Bu}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$. PtBr_2 (100 mg, 0.28 mmol) and one equivalent of $n\text{Bu}_4\text{PBr}$ (95.5 mg, 0.28 mmol) were introduced in a stainless steel autoclave, which was then put under an argon atmosphere after several purges. Toluene (10 mL) was then syringed into the autoclave, followed by pressurization with ethylene (25 bars). After one night (15 h) at 150°C under magnetic stirring, the autoclave was allowed to cool down, depressurized and opened in air. The yellow solution was transferred into a Schlenk flask and the autoclave was washed with toluene, the washings being collected and added to the reaction mixture. A small amount of black residue, probably metallic Pt, remained in the vessel. The collected solution was filtered and evaporated under reduced pressure until appearance of a precipitate (ca. 8 mL). The product precipitation was completed by addition of dry Et_2O (5 mL). The product was recovered by filtration in air and dried under vacuum. Yield 190 mg (94%). ^1H NMR (CD_2Cl_2): δ 4.60 (s+d, $J_{\text{Pt-H}} = 64.3$ Hz, 4H, C_2H_4), 2.30 (m, 8H, PCH_2), 1.60 (m, 16H, CH_2CH_2), 1.05 (m, 12H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 33.11. ^{195}Pt NMR (CD_2Cl_2): -3429 (quint, $J_{\text{Pt-H}} = 64.3$ Hz). Anal. % Calcd. for $\text{C}_{18}\text{H}_{40}\text{Br}_3\text{PPt}$ ($M = 722.283$): C, 29.93; H, 5.58. Found: 30.4; H, 5.6.

2.3. Preparation of $[\text{Ph}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$. The same procedure described above for the preparation of $[n\text{Bu}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$ was adopted, except for the use of PtBr_2 (49.6 mg, 0.140 mmol) and Ph_4PBr (59.0 mg, 0.141 mmol), with the addition of 10 mL of dry toluene. At the end of the reaction, the recovered mixture contained a large amount of yellow-brown precipitate. The autoclave was washed with 5 mL of toluene and the resulting suspension added to the reaction mixture. Then, the autoclave was further washed with 5 mL of CH_2Cl_2 , which completely dissolved the residual precipitate. The combined liquids were evaporated to dryness, The residue was redissolved in 3 mL of CH_2Cl_2 and filtered, leaving behind a small amount of black solid. The product was obtained as a yellow-ocher precipitate after partial solvent evaporation to ca.

0.5 mL and addition of diethyl ether (2 mL). After separation from the mother liquor, the solid was washed twice with Et₂O (2x5mL) and dried. Yield 93 mg (82%). ¹H NMR (CD₂Cl₂): δ 8.0 (m, 4H, Ph), 7.8 (m, 8H, Ph), 7.7 (m, 8H, Ph), 4.52 (s+d, 4H, ²J_{Pt-H} = 65 Hz, C₂H₄). ¹⁹⁵Pt NMR (CD₂Cl₂): δ -3428 (quint, ²J_{Pt-H} = 65 Hz). Anal. % Calcd. for C₂₆H₂₄Br₃PPt (M = 802.242): C, 38.93; H, 3.02. Found: C, 38.8; H, 2.6.

2.4. Preparation of [nBu₄N][PtBr₃(C₂H₄)]. The same procedure described above for the preparation of [nBu₄P][PtBr₃(C₂H₄)] was adopted, except for the use of PtBr₂ (100.7 mg, 0.283 mmol) and nBu₄NBr (90.8mg, 0.282mmol), with the addition of 10 mL of dry toluene. The final mixture consisted of a yellow-orange solution and a small amount of black residue. The autoclave was washed with toluene (10 mL). The combined liquids were evaporated to dryness and the residue was dissolved in CH₂Cl₂ (3 mL) and filtered, leaving behind the black material. The product was obtained as a yellow-ocher precipitate after partial solvent evaporation to less than 1 mL and addition of diethyl ether (ca 5 mL). After separation from the mother liquor, the solid was washed twice with Et₂O (2x5mL) and dried. Yield 62.8 mg (31%). ¹H NMR (CD₂Cl₂): δ 4.59 (s+d, 4H, ²J_{Pt-H} = 64 Hz, C₂H₄), 3.25 (s broad, 8H, CH₂), 1.72 (s broad, 8H, CH₂), 1.53 (s broad, 8H, CH₂), 1.07 (t, 12H, ²J_H : 8Hz, CH₃). ¹⁹⁵Pt NMR (CD₂Cl₂): δ -3430 (quint, ²J_{Pt-H} = 65 Hz). Anal. % Calcd. for C₁₈H₄₀Br₃NPt (M = 705.316): C, 30.65; H, 5.73; N, 1.99. Found: 31.0; H, 5.6; N, 2.2.

2.5. Preparation of [nBu₄P][PtCl₃(C₂H₄)]. The same procedure described above for the preparation of [nBu₄P][PtBr₃(C₂H₄)] was adopted, except for the use of PtCl₂ (100.2 mg, 0.38 mmol) and nBu₄PtCl (102.4 mg, 0.38 mmol), with the addition of 10 mL of dry toluene. Yield: 148.4 mg, 66%. ¹H NMR (CDCl₃): δ 4.48 (s+d, J_{Pt-H} = 64.3 Hz, 4H, C₂H₄), 2.30 (m, 8H, br, PCH₂), 1.60 (m, 4, br, CH₂CH₂), 1.05 (m, 3, br, CH₃). ³¹P{¹H} NMR: δ 33.14. ¹⁹⁵Pt NMR: δ -

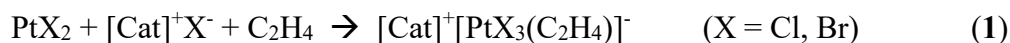
2743 (quint $^2J_{\text{Pt-H}} = 64\text{Hz}$). Anal. % Calcd. for $\text{C}_{18}\text{H}_{40}\text{Cl}_3\text{PPt}$ ($M = 588.930$): C, 36.71; H, 6.85. Found: 37.2; H, 6.9.

2.6. Attempted preparation of $[\text{nBu}_4\text{P}][\text{PtI}_3(\text{C}_2\text{H}_4)]$. The same procedure described above for the preparation of $[\text{nBu}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$ was adopted, except for the use of PtI_2 and nBu_4PI . A pale yellow solution was obtained, together with a red oil and abundant brown precipitate at the bottom of the autoclave. The ^1H NMR spectrum of both fractions did not reveal any resonance indicative of coordinated ethylene. The ^{195}Pt NMR spectrum exhibits a single resonance at $\delta -3691$ with no observable coupling.

3. Results and Discussion

During our recent investigation of the $\text{PtBr}_2/\text{Br}^-$ catalyzed addition of aniline to ethylene, we have been puzzled by the systematic catalyst degradation with generation of Pt^0 .^{18,19} As part of our mechanistic study of this decomposition process, we have carried out tests using the same temperature (150°C) and reaction time (10 h) as the catalytic process, but in the presence of only one or the other of the two reactants. The optimized catalytic conditions for the reaction involved aniline and 25 bars with ethylene ($\text{C}_2\text{H}_2/\text{aniline} = \text{ca. } 2$) in the absence of solvents in a stainless steel autoclave, using 0.3% catalyst and 10 equivalents (3%) of nBu_4PBr relative to the aniline. The test carried out in the absence of aniline, therefore, required the replacement of this component with an inert solvent in order to favour the contact between the two solids (PtBr_2 and $[\text{nBu}_4\text{P}]\text{Br}$) and the gas (C_2H_4). We chose toluene in order to maintain a structural analogy with aniline. This test resulted in the complete dissolution of PtBr_2 to yield a yellow solution and only trace amounts of a black precipitate that may correspond to metallic Pt. While proving the principle that ethylene alone was not the major cause of catalyst decomposition during the hydroamination

process, we also discovered, from the NMR spectra recorded on the crude solution, that a selective reaction resulting in the clean formation of the $[\text{PtBr}_3(\text{C}_2\text{H}_4)]^-$ ion had taken place according to the stoichiometry of equation 1.



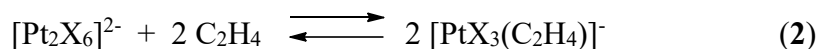
Under the conditions of the above mentioned test, isolation of pure $[\text{nBu}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$ is hampered by the large excess of nBu_4PBr . However, repetition of the same reaction in the presence of the stoichiometric amount of nBu_4PBr still resulted in the selective formation of Chojnacki's anion and in the isolation of the pure nBu_4P^+ salt in nearly quantitative yield.

Encouraged by this result, we have carried out the same reaction using Ph_4PBr and nBu_4NBr , obtaining the corresponding $[\text{Ph}_4\text{P}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$ and $[\text{nBu}_4\text{N}][\text{PtBr}_3(\text{C}_2\text{H}_4)]$ salts in 93 and 31% yield, respectively, also in spectroscopically and analytically pure form. The lower yield obtained for the nBu_4N^+ salt may be related to an insufficient time allowed for the solubilization and reaction of the reagents and/or to a more extensive decomposition to Pt^0 . The ^1H NMR analysis of the residual mother liquor confirms the efficiency of the precipitation step. It may be possible to further optimize this synthesis.

Since all the platinum complexes indicated in this contribution are known as air stable, we also wondered whether the synthesis could be carried out without special precautions to avoid contact with air. We have tested the synthesis of nBu_4P^+ salt under these conditions but only obtained a low yield (ca. 15%) of pure product, the main product being an uncharacterized red oily material. We therefore recommend the use of an inert atmosphere.

Extension of this procedure to the chloride system was tested only for the tetra-*n*-butylphosphonium salt. Compound $[\text{nBu}_4\text{P}][\text{PtCl}_3(\text{C}_2\text{H}_4)]$ could be obtained in pure form and in

66% yield from PtCl₂ and *n*Bu₄PCl. The same procedure was also attempted for the iodide system, reacting PtI₂ and *n*Bu₄PI. However, the solution recovered from the autoclave after depressurization did not show any NMR resonance attributable to coordinated C₂H₄. Analysis of the literature reveals that no stable compound containing the [PtI₃(C₂H₄)]⁻ anion exists. On the other hand, complex [Pt₂I₆]²⁻ is known, obtained by anion metathesis from the reaction of [PtCl₄]²⁻ and excess KI and isolated as the [*n*Pr₄N⁺] salt.²⁰ It seems that ligand addition reactions to [Pt₂X₆]²⁻ to yield [PtX₃L]⁻ (neutral L) or [PtX₃Y]²⁻ (anionic Y⁻) adducts become less and less favourable in the order X = Cl > Br > I. The [PtI₄]²⁻ species has been reported but is described as highly unstable,^{21,22} existing in solution only in the presence of a large excess of I⁻ salts,²³ and apparently no stable salt with this dianion has ever been isolated and characterized. Thus, the equilibrium shown in equation 2 is probably highly shifted to the left hand side for the iodide system and the final product of the reaction between PtI₂ and *n*Bu₄PI in the presence of C₂H₄ could indeed be the [*n*Bu₄P]₂[Pt₂I₆] salt. Although the reaction may well represent a convenient synthetic method for this salt, we have not pursued the isolation and characterization of this product. It is interesting to note that, whereas complex [PtCl₃(C₂H₄)]⁻ is stable toward loss of ethylene, complex [PtBr₃(C₂H₄)]⁻ tends to lose ethylene, because its synthesis by anion exchange from [PtCl₃(C₂H₄)]⁻ was shown to require a protecting C₂H₄ atmosphere to avoid the formation of [Pt₂Br₆]²⁻.²⁴



Finally, the success of the simple ethylene and halide addition to PtX₂ in the presence of various cations made us wonder whether this would also be a simple method for the synthesis of

Chojnacki's salt. However, the reaction of PtBr₂ and KBr using water as solvent and carried out under the same conditions (150°C, 15 h, 25 bars of C₂H₄) did not lead to any dissolution of PtBr₂. Using THF, acetone or toluene instead of water as solvent led to some dissolution as evidenced by the colour of the final liquid but the NMR analysis of the crude solution gave no evidence of the formation of the desired [PtB₃(C₂H₄)]⁻ anion.

4. Conclusions

A simple observation of the behavior of PtBr₂ in toluene in the presence of [*n*Bu₄P]Br and a moderate pressure (25 bars) of C₂H₄ has led us to develop a simple and general method for the synthesis of a variety of [Cat][PtX₃(C₂H₄)] salts for X = Cl and Br. Extension to the preparation of the yet unknown triiodido analogue does not seem possible, at least at the relatively low ethylene pressure used in our study. It is possible that these syntheses may be further optimized by using different solvents, the optimum solvent possibly being cation dependent. It is also possible that the same strategy could lead to a wide variety of similar salts with other coordinated alkenes.

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