Short Communication

A convenient preparation of dinuclear Pt(II) phosphine complexes

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Abstract

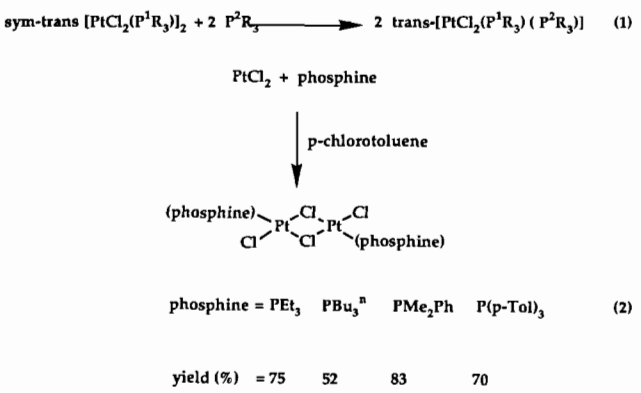
A simple one-step method for the preparation of dinuclear chloro-bridged platinum(II) phosphine complexes, $[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ is reported. The syntheses are carried out in *p*-chlorotoluenc and are reported for the following tertiary phosphines: PMe_2Ph, $P(p\text{-}Tol)_3$, PPh_3, PBu^n_3 and PEt_3.

Introduction

For more than three decades, halogen-bridged dinuclear tertiary phosphine complexes, $[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ (**1**) have proven useful as starting materials in the chemistry of platinum(II) [1]. This results as a consequence of the ease with which nitrogen and phosphorus nucleophiles, amongst others, are able to attack these complexes and split the bridges affording high (frequently quantitative) yields of mononuclear products [2–6]. This simple bridge-splitting reaction is exemplified in eqn. (1) (see Scheme 1) and is a useful method for preparing *trans*-platinum(II) complexes, as these latter are the kinetic products [5] from this reaction.

Use of this simple type of chemistry has led various research groups to successfully prepare nitrogen [2–6] aliphatic and aromatic phosphorous [4a], hydroxo [7], aryl [8], carbonyl [5], trichlorostannato [9, 10] and many other [11] platinum(II) complexes in good-to-excellent yield.

The literature approach to these dinuclear phosphine materials involves the preparation of the bis-phosphine dichloro complex, followed by reaction of this compound with $PtCl_2$ in a suitable high boiling solvent [1]. It is obvious that this disproportionation reaction is successful as the products **1** are thermodynamically more stable than the bis-phosphine starting materials. Equally obvious is that the bis-phosphine complexes form rapidly under mild conditions and this is the basis for their standard preparation [5].



Scheme 1.

Intuitively, it should be possible to prepare the complexes **1** in a single step, thereby avoiding the unnecessary isolation of the bis-phosphine intermediate. The difficulty was one of solubility (contact between the reagents) and we have solved this problem via the use of *p*-chlorotoluene as solvent and summarize our results in Scheme 1. The yields are for isolated complexes which give good microanalytical data (see 'Experimental'). Although not shown, we have used the chlorotoluene approach to prepare the analogous PPh_3 complex. The isolated yield is good (85%); however, the analysis is not completely satisfactory so that we have not included this in the Scheme (although we give a preparation in 'Experimental'). The complexes were readily identified in solution via ^{31}P NMR spectroscopy and specifically via the appearance of the signals at the foot of the main band arising from $^3J(Pt,P)$ (see Fig. 1). The use of the appropriate solvent, e.g. *p*-chlorotoluene, represents a convenient improvement in the synthesis of these very useful molecules.

Experimental

The tertiary phosphines were obtained from Aldrich Chemicals. The solvent, *p*-chlorotoluene, was distilled and kept under nitrogen. The syntheses were carried out under an inert atmosphere. All of the dinuclear complexes are known, or have been mentioned in the literature. The microanalytical data were obtained from the corresponding laboratory of the ETH, Zurich. The

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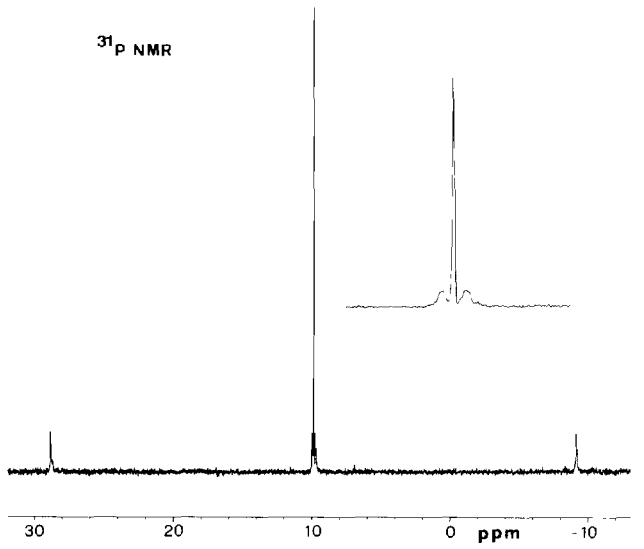

Fig. 1. ^{31}P NMR spectrum of $[Pt(\mu\text{-}Cl)Cl(PEt_3)]_2$. The insert shows the ^{195}Pt satellites which represent $^3J(Pt,P)$

^{31}P NMR spectra were measured using a Bruker-250 MHz NMR spectrometer. Chemical shifts are in ppm, coupling constants in Hz.

Synthesis of $[Pt(\mu\text{-}Cl)Cl(PMe_2Ph)]_2$

$PtCl_2$ (2.01 g, 7.55 mmol) and PMe_2Ph (1.0 ml, 7.03 mmol) were added to 10 ml *p*-chlorotoluene. The resulting suspension was refluxed for 30 min after which time the solvent was removed *in vacuo*. To the remaining dark solid was added 20 ml CH_2Cl_2 and the resulting suspension filtered through celite. The residue was washed with a further 20 ml CH_2Cl_2 until a colorless filtrate appeared. The combined yellow–brown CH_2Cl_2 solution was concentrated to 10 ml and then slowly treated with 40 ml pentane to afford the product as a yellow solid in 83% yield. *Anal.* Found: C, 23.84; H, 2.92. Calc. for $C_{16}H_{22}Cl_4P_2Pt_2$: C, 23.78; H, 2.74%. ^{31}P NMR ($CDCl_3$): -18.65 ($^1J(Pt,P) = 3930$).

Synthesis of $[Pt(\mu\text{-}Cl)Cl(P(p\text{-}tolyl)_3)]_2$

$PtCl_2$ (0.222 g, 0.835 mmol) and $P(p\text{-tolyl})_3$ (0.220 g, 0.723 mmol) were added to 10 ml *p*-chlorotoluene. The resulting suspension was refluxed for 30 min after which time the solvent was removed *in vacuo*. To the remaining brown solid was added 10 ml CH_2Cl_2 and the resulting suspension filtered through celite. The residue was washed with a further 10 ml CH_2Cl_2 until a colorless filtrate appeared. The combined yellow CH_2Cl_2 solution was concentrated to about 7 ml, slowly treated with 25 ml pentane and then concentrated to 10 ml to afford the product as a yellow solid in 70% yield. *Anal.* Found: C, 43.77; H. 3.86. Calc. for $C_{42}H_{42}Cl_4P_2Pt_2$: C, 44.2; H, 3.71%. ^{31}P NMR ($CDCl_3$): 2.8 ($^1J(Pt,P) = 4063$).

Synthesis of $[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$

$PtCl_2$ (0.235 g, 0.882 mmol) and PPh_3 (0.196 g, 0.747 mmol) were added to 10 ml *p*-chlorotoluene. The resulting suspension was refluxed for 2.5 h after which time the solvent was removed *in vacuo*. The remaining brown solid was treated with 30 ml *N,N*-dimethylformamide, and then warmed to about 333 K thereby dissolving most of the solid. The resulting suspension was filtered through celite at room temperature. The solvent was removed and the resulting brown oil was dried *in vacuo* for 30 min. To the oil was added 6 ml CH_2Cl_2 and the brown solution slowly treated with 15 ml n-heptane to afford the product as a yellow solid in 85% yield. *Anal.* Found: C, 40.17; H, 3.13. Calc. for $C_{36}H_{30}Cl_4P_2Pt_2$: C, 40.93; H, 2.86%. ^{31}P NMR ($CDCl_3$): 4.5 ($^1J(Pt,P) = 4100$).

Synthesis of $[Pt(\mu\text{-}Cl)Cl(PBu^n_3)]_2$

$PtCl_2$ (0.228 g, 0.857 mmol) and PBu^n_3 (0.20 ml, 0.794 mmol) were added to 10 ml *p*-chlorotoluene. The resulting suspension was refluxed for 1.5 h, additional $PtCl_2$ (0.032 g, 0.120 mmol) added and then again refluxed for 1.5 h. The brown suspension was filtered through celite and the solvent was removed *in vacuo*. The yellow solid was dissolved in 2 ml CH_2Cl_2, treated with 10 ml pentane and the solution concentrated *in vacuo* to about 5 ml to afford the product as a yellow solid in 52% yield. *Anal.* Found: C, 30.69; H, 5.96. Calc. for $C_{24}H_{54}Cl_4P_2Pt_2$: C, 30.78; H, 5.81%. ^{31}P NMR ($CDCl_3$): 1.8 ($^1J(Pt,P) = 3821$).

Synthesis of $[Pt(\mu\text{-}Cl)Cl(PEt_3)]_2$

$PtCl_2$ (0.460 g, 1.73 mmol) and PEt_3 (1.50 ml solution 1.0 M in THF, 1.50 mmol) were added to 5 ml *p*-chlorotoluene. The resulting suspension was heated to 373 K for 15 min and then the THF removed *in vacuo* at about 373 K for 15 min. The suspension was refluxed for 2 h, additional $PtCl_2$ (0.050 g, 0.19 mmol) added and then again refluxed for 2 h after which time the solvent was removed *in vacuo*. To the remaining dark solid were added 15 ml CH_2Cl_2 and the resulting suspension filtered through celite. The residue was washed with another 10 ml CH_2Cl_2 until a colorless filtrate appeared. The combined yellow CH_2Cl_2 solution was concentrated until the product began to precipitate (about 15 ml) and then slowly treated with 35 ml pentane to afford the product as a yellow solid in 75% yield. *Anal.* Found: C, 19.03; H, 3.80. Calc. for $C_{12}H_{30}Cl_4P_2Pt_2$: C, 18.76; H, 3.94%. ^{31}P NMR ($CDCl_3$): 9.78 ($^1J(Pt,P) = 3845$, $^3J(Pt,P) = 20$).

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