

One-Pot Synthesis of *trans* Mono- or Diarylalkynyl Substituted Platinum(II) Compounds with Tertiary Phosphine or Phosphite Ligands

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Summary: An efficient one-pot synthesis has been developed for preparation of *trans*-mono- or diarylalkynyl bisphosphine or bisphosphite Pt(II) compounds. In the procedure, the alkyne and the tertiary phosphorus ligands are mixed with PtCl₂ in tetrahydrofuran and triethylamine solution. CuI is added for synthesis of disubstituted complexes, but the catalyst is not used for preparation of monosubstituted complexes. Microwave irradiation is preferably employed to give the *trans*-mono- or diarylalkynyl Pt(II) compound in short time and high yield.

Introduction

In the last decade there has been an increased interest in arylalkynyl Pt(II) compounds for construction of stable and rigid systems with nonlinear optical properties that may find use in, for instance, the field of photonics.^{1–7} A typical synthesis of a mono- or diarylalkynyl Pt(II) compound is performed via initial preparation and purification of the *trans*- or *cis*-PtCl₂(PR₃)₂ precursor.^{8–10} The dehydrohalogenation reaction between a PtCl₂(PR₃)₂ complex and an acetylenic compound is often performed with a cuprous halide in the presence of an amine as catalyst.¹¹ Treatment of the platinum complex with ≥2 equiv of the acetylenic compound in the presence of CuI and amine often gives the disubstituted compound in good yield.¹² In the synthesis of the monoaryalkynyl Pt(II) compounds, we previously experienced that both the mono- and diarylalkynyl substituted Pt(II) compounds appear in the product mixture when the PtCl₂(PR₃)₂ complex is treated with 1 equiv of alkynyl compound in the presence of CuI and amine. To obtain monochloro Pt(II) acetylides, D'Amato et al. coupled the acetylide with the *cis*-salt of PtCl₂(PPh₃)₂ in CHCl₃ containing a small amount of diethylamine but no cuprous halide.⁷ After

reflux of the solution for a few hours the major product was the monochloroacetylide.⁷ The same strategy was reported by Schanze et al., who synthesized *trans*-chloro-phenylethynyl-bis-(tri-*n*-butylphosphine)platinum(II) in 88% yield from *cis*-PtCl₂(PBu₃)₂ in DEA.¹³

In this paper we report on the development of a one-pot reaction to synthesize mono- or disubstituted arylalkynyl Pt(II) complexes using microwave irradiation (Scheme 1). The scope of the present work includes a simplification of the synthesis, where prior preparation of the PtCl₂(PR₃)₂ complex is not needed for the coupling of the acetylide. Instead, the mono-aryalkynyl Pt(II) compound is prepared by reaction of the acetylide, tertiary phosphorus ligand, and PtCl₂, while CuI is employed for bis-substitution. The PtCl₂(PR₃)₂ intermediate is formed in situ during the reaction, and the mono- or diarylalkynyl Pt(II) compound is typically obtained in good yield at significantly shorter time in comparison with the more common procedure.

Results and Discussion

The one-pot monoaryalkynyl Pt(II) reaction was optimized for compound **1** (Scheme 2). Initially, 1-ethynyl-4-methoxybenzene (1 equiv), PtCl₂ (1 equiv), and PBu₃ (2 equiv) were allowed to react in a CHCl₃/TEA (48:1 ratio) solution using microwave irradiation at 130 °C for 15 min, resulting in a 25% yield. Changing the solvent to THF/TEA (1:1 ratio) using the same reaction conditions gave the same result. In an attempt to increase the rate of the reaction, it was performed at 160 °C for 1 h, with two different solvent mixtures. When CHCl₃/TEA was used as solvent, compound **1** was collected in 42% yield after full consumption of the acetylenic compound, as determined from ¹H NMR analysis of the crude product. A change of solvent to THF/TEA gave 45% yield of **1** with only half of the amount of alkyne being reacted and with *trans*-PtCl₂(PBu₃)₂ formed as the main byproduct. From these reactions we suspected that CHCl₃ was not a suitable solvent for this high-temperature reaction and that the generation of *trans*-PtCl₂(PBu₃)₂ inhibits the coupling reaction. Kaufmann discovered that the *cis* isomer of PtCl₂(PBu₃)₂ is converted to the thermodynamically more stable *trans* isomer by heating.¹⁰ Grim et al. added PPh₂ to a dichloromethane solution of the *trans* compound to convert *trans*-PtCl₂(PPh₂)₂ to the kinetically favored *cis* isomer.¹⁴ Hence, to achieve a maximum yield of *cis*-PtCl₂(PBu₃)₂ in situ, the concentration of PBu₃ was doubled. This resulted in an increase in yield to 73% after purification. Using the latter reaction conditions we also synthesized compounds **2a** and **2b** (Scheme 3).

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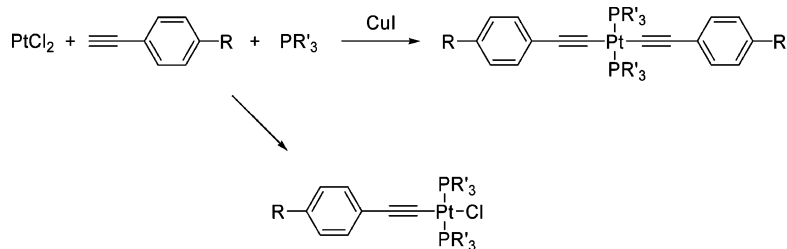
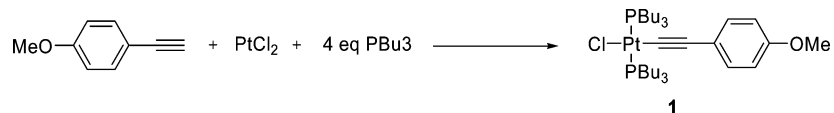
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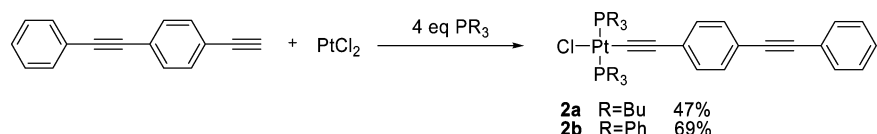
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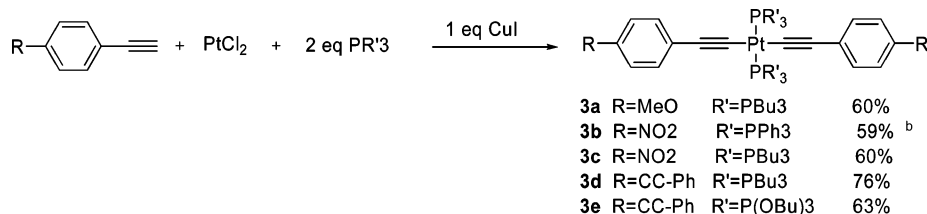
Scheme 1

Scheme 2. One-Pot Synthesis of *trans*-Chloro-[4-methoxyphenylethynyl]bis(tri-*n*-butylphosphine)platinum(II)^a

^a Reaction conditions: TEA and THF (1:1), 160 °C for 1 h using microwave irradiation; 73% yield after purification.

Scheme 3. One-Pot Synthesis of *trans*-Chloro-arylalkynyl Platinum(II) Compounds with Tertiary Phosphine Ligands^a

^a Reaction conditions: TEA and THF (1:1), 160 °C for 1 h using microwave irradiation. The yield (%) is after purification.

Scheme 4. One-Pot Synthesis of *trans*-Diarylalkynyl Platinum(II) Compounds with Tertiary Phosphine or Phosphate Ligands^a

^a Reaction conditions: TEA and THF (1:1), 60 °C for 6 min. The yield (%) is after purification. ^bCHCl₃/TEA (3:1) was used instead of THF/TEA (1:1).

The one-pot reaction of the diarylalkynyl-Pt(II) complexes was performed at 60 °C using alkyne (2.1 equiv), PtCl₂ (1equiv), CuI (2 equiv), and PR₃ (2 equiv) in THF and TEA solution (Scheme 4). Two equivalents of PR₃ was used in order to form more of the *trans*-PtCl₂(PBu₃)₂ in situ. In the synthesis of compound **3b**, CHCl₃ and TEA were used as solvent in order to increase the solubility of PPh₃.

Experimental Section

General Considerations. Compounds **2a**,¹⁵ **3a,c**,¹⁶ **3b**,⁷ and **3d**¹⁷ have been synthesized earlier via initial preparation and purification of the *trans*- or *cis*-PtCl₂(PR₃)₂ precursor. Solvents and chemicals used for synthesis were of reagent grade and used without purification. Microwave synthesis was performed on a monomode reactor: Smith synthesizer (Personal Chemistry AB). Reaction vials: Smith process vials, 2.0–5.0 mL filling volume, sealed with Teflon septa and an aluminum crimp top. TLC was performed on silica gel 60 F₂₅₄ (Merck) with detection by UV light. Flash column chromatography (eluent given in brackets) was performed on silica gel (matrix, 60 Å, 35–70 μm, Grace Amicon). Organic extracts were dried over anhydrous magnesium sulfate prior to solvent concentration. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a

Bruker DRX 400 MHz or Bruker DRX 360 MHz at 298 K. For solution in CDCl₃, ¹H and ¹³C chemical shifts are reported relative to CHCl₃ (δ_H 7.26 ppm) or CDCl₃ (δ_C 77.0 ppm) as internal reference, while ³¹P chemical shifts are given relative to external 0.1 M P(C₆H₅)₃ in CDCl₃ with δ = −4.89, which corresponds to δ = 0 for 85% H₃PO₄. Elemental analyses were performed at Mikrokemi AB, Uppsala, Sweden.

General Procedure for Synthesis of Mono-arylalkynyl Pt(II) Phosphines Exemplified by Compound 1. PtCl₂ (50 mg, 0.19 mmol) and 1-ethynyl-4-methoxybenzene (26 mg, 0.19 mmol) were mixed with THF (2.5 mL) and TEA (2.5 mL). PBu₃ (0.19 mL, 0.75 mmol) was added under stirring, and the solution was heated with microwaves in a monomode instrument at 160 °C for 1 h. The resulting mixture was diluted with CHCl₃ and washed two times with 1 M HCl(aq). The organic extract was dried with anhydrous MgSO₄(s), filtered, and concentrated. Flash chromatography over silica [40:1 heptane/EtOAc] gave **1** as a yellow solid in 73% yield: ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.78 Hz, 2 H), 6.75 (d, *J* = 8.78 Hz, 2 H), 3.77 (s, 3 H), 2.08–1.92 (m, 12 H), 1.63–1.50 (m, 12 H), 1.50–1.37 (12 H), 0.92 (t, *J* = 7.32 Hz, 18 H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 131.8, 121.4, 113.5, 100.2, 80.0 (apparent triplet 14 Hz), 55.2, 26.0, 24.3 (apparent triplet 7 Hz), 21.9 (apparent triplet 17 Hz), 13.8; ³¹P NMR (146 MHz, CDCl₃) δ 7.4 (*J*_{P-Pt} = 2381 Hz).

Compound 2a. Flash chromatography over silica [20:1 heptane/EtOAc] followed by recrystallization from EtOH gave **2a** as colorless crystals in 47% yield: ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.47 (m, 2 H), 7.41–7.29 (m, 5 H), 7.19 (d, *J* = 8.04 Hz, 2 H), 2.10–1.92 (m, 12 H), 1.66–1.51 (m, 12 H), 1.51–1.37 (m, 12

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H), 0.93 (t, $J = 7.32$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 131.5, 131.2, 130.6, 129.0, 128.3, 128.0, 123.5, 119.5, 101.3, 89.9, 89.9, 87.0 (apparent triplet 14 Hz), 26.1, 24.3 (apparent triplet 6.7 Hz), 22.0 (apparent triplet 17 Hz), 13.8; ^{31}P NMR (146 MHz, CDCl_3) δ 7.5 ($J_{\text{P-Pt}} = 2365$ Hz).

Compound 2b. Flash chromatography over silica [200:35 CHCl_3 /heptane] followed by recrystallization from EtOH (99.5%) gave **2b** as yellow crystals in 69% yield: ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.72 (m, 12 H), 7.50–7.35 (m, 20 H), 7.35–7.28 (m, 3 H), 7.04 (d, $J = 8.23$ Hz, 2 H), 6.09 (d, $J = 8.23$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.1 (apparent triplet 6 Hz), 131.4, 130.8, 130.5, 130.3, 130.3, 130.0, 129.7, 128.3, 127.9 (apparent triplet 5 Hz), 123.5, 119.1, 106.2, 90.0, 89.7, 89.6 (apparent triplet 15 Hz); ^{31}P NMR (146 MHz, CDCl_3) δ 22.3 ($J_{\text{P-Pt}} = 2645$ Hz).

General Procedure for Synthesis of Bis-arylalkynyl Pt(II) Phosphines Exemplified by Compound 3a. PtCl_2 (75 mg, 0.28 mmol) and 1-ethynyl-4-methoxybenzene (78 mg, 0.59 mmol) were mixed with THF (2.5 mL) and TEA (2.5 mL). PBu_3 (0.15 mL, 0.56 mmol) was added under stirring, after which a clearer solution appeared, and CuI (107 mg, 0.56 mmol) was added. The solution was heated with microwaves in a monomode instrument at 60 °C for 6 min. The resulting mixture was diluted with CHCl_3 and washed two times with 1 M HCl(aq) . The organic extract was dried with anhydrous $\text{MgSO}_4(\text{s})$, filtered, and concentrated. Flash chromatography over silica [40:1 heptane/EtOAc] and recrystallization from EtOH (99.5%) gave **3a** as colorless crystals in 63% yield: ^1H NMR (360 MHz, CDCl_3) δ 7.20 (d, $J = 7.27$ Hz, 4 H), 6.75 (d, $J = 7.27$ Hz, 4 H), 3.78 (s, 6 H), 2.23–2.04 (m, 12 H), 1.67–1.52 (m, 12 H), 1.52–1.37 (m, 12 H), 0.92 (t, $J = 6.59$ Hz, 18 H); ^{13}C NMR (90 MHz, CDCl_3) δ 157.0, 131.8, 121.7, 113.4, 108.0, 105.3 (apparent triplet 14.8 Hz), 55.2, 26.3, 23.6 (apparent triplet 7 Hz), 21.9 (apparent triplet 17 Hz), 13.8; ^{31}P NMR (146 MHz, CDCl_3) δ 3.5 ($J_{\text{P-Pt}} = 2368$ Hz).

Compound 3b. CHCl_3 was used instead of THF. Recrystallization from CHCl_3 /EtOH gave compound **3b** as yellow crystals in 59% yield: ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.72 (m, 16 H), 7.48–7.34 (m, 18 H), 6.31 (d, $J = 8.73$ Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 135.4, 134.9 (apparent triplet 6 Hz), 131.0, 130.8, 130.6, 130.5, 128.8 (apparent triplet 5.3 Hz), 122.7, 121.5 (apparent triplet 15 Hz), 113.2 (t, 2.3 Hz); ^{31}P NMR (146 MHz, CDCl_3) δ 19.2 ($J_{\text{P-Pt}} = 2599$ Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_4\text{P}_2$: Pt, C, 61.72; H, 3.79; N, 2.77. Found: C, 61.6; H, 3.9; N, 2.7.

Compound 3c. Flash chromatography over silica [15:1 heptane/EtOAc] followed by recrystallization from EtOH (99.5%) gave **3c** as yellow needles in 60% yield: ^1H NMR (360 MHz, CDCl_3) δ 8.09 (d, $J = 8.93$ Hz, 4 H), 7.31 (d, $J = 8.93$ Hz, 4 H), 2.19–1.99 (m, 12 H), 1.67–1.51 (m, 12 H), 1.51–1.36 (m, 12 H), 0.92 (t, $J = 7.31$ Hz, 18 H); ^{13}C NMR (90 MHz, CDCl_3) δ 144.5, 135.9, 130.9, 123.6, 119.1 (apparent triplet 15 Hz), 109.6, 26.3 (apparent triplet 11 Hz), 24.4 (apparent triplet 7 Hz), 24.0 (apparent triplet 17 Hz), 13.7; ^{31}P NMR (146 MHz, CDCl_3) δ 4.3 ($J_{\text{P-Pt}} = 2312$ Hz).

Compound 3d. Flash chromatography over silica [40:1 heptane/EtOAc] and recrystallization from EtOH/ CHCl_3 gave **3d** as yellow crystals in 76% yield: ^1H NMR (360 MHz, CDCl_3) δ 7.55–7.49 (m, 4 H), 7.41–7.27 (m, 10 H), 7.27–7.19 (m, 4 H), 2.19–2.07 (m, 12 H), 1.68–1.55 (m, 12 H), 1.51–1.39 (m, 12 H), 0.93 (t, $J = 7.33$ Hz, 18 H); ^{13}C NMR (90 MHz, CDCl_3) δ 131.5, 131.2, 130.6, 129.0, 128.3, 128.0, 123.5, 119.2, 111.7 (apparent triplet 15 Hz), 109.3, 90.0, 89.8, 26.3, 24.4 (apparent triplet 7 Hz), 23.9 (apparent triplet 17 Hz), 13.8; ^{31}P NMR (146 MHz, CDCl_3) δ 3.7 ($J_{\text{P-Pt}} = 2344$ Hz).

Compound 3e. Flash chromatography over silica [10:1 heptane/EtOAc]. Compound **3e** crystallizes under concentration of solvents. After filtration compound **3e** was recrystallized from EtOH (99.5%) as colorless needles in 63% yield: ^1H NMR (360 MHz, CDCl_3) δ 7.53–7.48 (m, 4 H), 7.39–7.29 (m, 10 H), 7.26–7.21 (m, 4 H), 4.29–4.19 (m, 12 H), 1.75–1.64 (m, 12 H), 1.48–1.35 (m, 12 H), 0.88 (t, $J = 7.27$ Hz, 18 H); ^{13}C NMR (90 MHz, CDCl_3) δ 131.5, 131.1, 128.4, 128.3, 128.0, 123.5, 119.6, 110.6 (apparent triplet 3 Hz), 102.8 (apparent triplet 19 Hz), 89.9, 89.8, 66.3, 32.5 (apparent triplet 3 Hz), 18.9, 13.7; ^{31}P NMR (146 MHz, CDCl_3) δ 99.1 ($J_{\text{P-Pt}} = 4082$ Hz). Anal. Calcd for $\text{C}_{56}\text{H}_{72}\text{O}_6\text{P}_2\text{Pt}$: C, 61.25; H, 6.61. Found: C, 61.0; H, 7.0.

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Supporting Information Available: ^{31}P NMR spectra for all compounds and ^{13}C NMR spectra for compounds **1**, **2b**, and **3e**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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