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

Marcus Carlsson* and Bertil Eliasson

Department of Chemistry, Organic Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Received July 10, 2006

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 $PtCl_2$ 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*-$PtCl_2(PR_3)_2$ precursor.[8−10] The dehydrohalogenation reaction between a $PtCl_2(PR_3)_2$ 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 monoarylalkynyl Pt(II) compounds, we previously experienced that both the mono- and diarylalkynyl substituted Pt(II) compounds appear in the product mixture when the $PtCl_2(PR_3)_2$ 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 $PtCl_2(PPh_3)_2$ in $CHCl_3$ 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*-butylphoshine)platinum(II) in 88% yield from *cis*-$PtCl_2$-$(PBu_3)_2$ 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 $PtCl_2(PR_3)_2$ complex is not needed for the coupling of the acetylide. Instead, the mono-arylalkynyl Pt(II) compound is prepared by reaction of the acetylide, tertiary phosphorus ligand, and $PtCl_2$, while CuI is employed for bis-substitution. The $PtCl_2(PR_3)_2$ 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

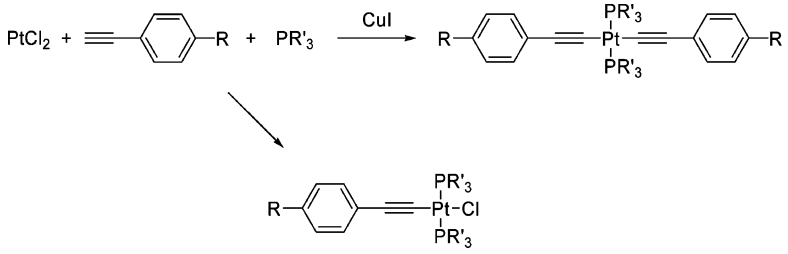
The one-pot monoarylalkynyl Pt(II) reaction was optimized for compound **1** (Scheme 2). Initially, 1-ethynyl-4-methoxybenzene (1 equiv), $PtCl_2$ (1 equiv), and PBu_3 (2 equiv) were allowed to react in a $CHCl_3$/TEA (48:1 ratio) solution using microwave irradiation at 130 °C for 15 min, resulting in 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 $CHCl_3$/TEA was used as solvent, compound **1** was collected in 42% yield after full consumption of the acetylenic compound, as determined from ^{1}H 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*-$PtCl_2(PBu_3)_2$ formed as the main byproduct. From these reactions we suspected that $CHCl_3$ was not a suitable solvent for this high-temperature reaction and that the generation of *trans*-$PtCl_2$-$(PBu_3)_2$ inhibits the coupling reaction. Kaufmann discovered that the *cis* isomer of $PtCl_2(PBu_3)_2$ is converted to the thermodynamically more stable *trans* isomer by heating.[10] Grim et al. added $PPhPr_2$ to a dichloromethane solution of the *trans* compound to convert *trans*-$PtCl_2(PPhPr_2)_2$ to the kinetically favored *cis* isomer.[14] Hence, to achive a maximum yield of *cis*-$PtCl_2(PBu_3)_2$ in situ, the concentration of PBu_3 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).

* Corresponding author. E-mail: Marcus.Carlsson@chem.umu.se. Phone: +46 90 7866286. Fax: +46 90 138885.

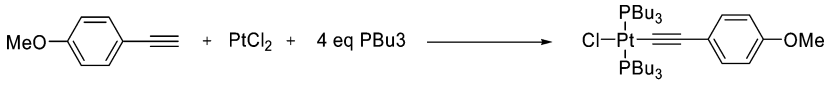
(1) Jiang, H.; Lin, W. *J. Organomet. Chem.* **2005**, *690*, 5159.
(2) Powell, C. E.; Humphrey, M. G. *Coord. Chem. Rev.* **2004**, *248*, 725.
(3) Staromlynska, J.; McKay, T. J.; Wilson, P. *J. Appl. Phys.* **2000**, *88*, 1726.
(4) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K.-Y.; Haskins-Glusac, K.; Schanze, K. S. *Coord. Chem. Rev.* **2005**, *249*, 1491.
(5) Long, N. J.; Wong, C. K.; White, A. J. P. *Organometallics* **2006**, *25*, 2525.
(6) Lewis, J.; Long, N. J.; Raithby, P. R.; Shields, G. P.; Wong, W.-Y.; Younus, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4283.
(7) D'Amato, R.; Furlani, A.; Colapietro, M.; Portalone, G.; Casalboni, M.; Falconieri, M.; Russo, M. V. *J. Organomet. Chem.* **2001**, *627*, 13.
(8) Jensen, K. A. Z. *Anorg. Allg. Chem.* **1936**, *229*, 225.
(9) Jensen, K. A. Z. *Anorg. Allg. Chem.* **1936**, *229*, 265.
(10) Kauffman, G. B.; Teter, L. A. In *Inorganic Syntheses*; Kleinberg, J., Ed.; McGraw Hill: New York, 1963; Vol. 7, p 245.
(11) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101.
(12) Vestberg, R.; Westlund, R.; Eriksson, A.; Lopes, C.; Carlsson, M.; Eliasson, B.; Glimsdal, E.; Lindgren, M.; Malmstroem, E. *Macromolecules* **2006**, *39*, 2238.
(13) Liu, Y.; Jiang, S.; Glusac, K.; Powell, D. H.; Anderson, D. F.; Schanze, K. S. *J. Am. Chem. Soc.* **2002**, *124*, 12412.
(14) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.

10.1021/om060616i CCC: $33.50 © 2006 American Chemical Society
Publication on Web 09/29/2006

Scheme 1



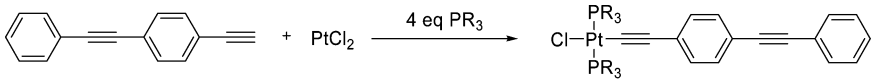
Scheme 2. One-Pot Synthesis of *trans*-Chloro-[4-methoxyphenylethynyl]bis(tri-*n*-butylphosphine)platinum(II)[a]



1

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

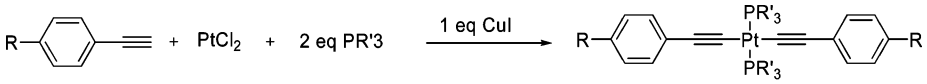
Scheme 3. One-Pot Synthesis of *trans*-Chloro-arylalkynyl Platinum(II) Compounds with Tertiary Phosphine Ligands[a]



2a R=Bu 47%
2b R=Ph 69%

[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]



3a	R=MeO	R'=PBu3	60%	
3b	R=NO2	R'=PPh3	59%	[b]
3c	R=NO2	R'=PBu3	60%	
3d	R=CC-Ph	R'=PBu3	76%	
3e	R=CC-Ph	R'=P(OBu)3	63%	

[a] Reaction conditions: TEA and THF (1:1), 60 °C for 6 min. The yield (%) is after purification. [b] $CHCl_3$/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), $PtCl_2$ (1equiv), CuI (2 equiv), and PR_3 (2 equiv) in THF and TEA solution (Scheme 4). Two equivalents of PR_3 was used in order to form more of the *trans*-$PtCl_2(PBu_3)_2$ in situ. In the synthesis of compound **3b**, $CHCl_3$ and TEA were used as solvent in order to increase the solubility of PPh_3.

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*-$PtCl_2(PR_3)_2$ 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 F_{254} (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. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DRX 400 MHz or Bruker DRX 360 MHz at 298 K. For solution in $CDCl_3$, ^{1}H and ^{13}C chemical shifts are reported relative to $CHCl_3$ (δ_H 7.26 ppm) or $CDCl_3$ (δ_C 77.0 ppm) as internal reference, while ^{31}P chemical shifts are given relative to external 0.1 M $P(C_6H_5)_3$ in $CDCl_3$ with $\delta = -4.89$, which corresponds to $\delta = 0$ for 85% H_3PO_4. Elemental analyses were performed at Mikrokemi AB, Uppsala, Sweden.

General Procedure for Synthesis of Mono-arylalkynyl Pt(II) Phosphines Exemplified by Compound 1. $PtCl_2$ (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). PBu_3 (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 $CHCl_3$ and washed two times with 1 M HCl(aq). The organic extract was dried with anhydrous $MgSO_4$(s), filtered, and concentrated. Flash chromatography over silica [40:1 heptane/EtOAc] gave **1** as a yellow solid in 73% yield: ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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; ^{31}P NMR (146 MHz, $CDCl_3$) 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: ^{1}H NMR (400 MHz, $CDCl_3$) 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

(15) Cooper, T. M.; Krein, D. M.; Burke, A. R.; McLean, D. G.; Rogers, J. E.; Slagle, J. E.; Fleitz, P. A. *J. Phys. Chem. A* **2006**, *110*, 4369.
(16) Sebald, A.; Wrackmeyer, B.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 45.
(17) McKay, T. J.; Bolger, J. A.; Staromlynska, J.; Davy, J. R. *J. Chem. Phys.* **1998**, *108*, 5537.

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 ($J_{P-Pt} = 2365$ 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: ^{1}H 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 ($J_{P-Pt} = 2645$ 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 $MgSO_4$(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: ^{1}H 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 ($J_{P-Pt} = 2368$ Hz).

Compound 3b. $CHCl_3$ was used instead of THF. Recrystallization from $CHCl_3$/EtOH gave compound **3b** as yellow crystals in 59% yield: ^{1}H 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 ($J_{P-Pt} = 2599$ Hz). Anal. Calcd for $C_{52}H_{38}N_2O_4P_2Pt$: 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: ^{1}H 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 ($J_{P-Pt} = 2312$ 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; ^{1}H 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 ($J_{P-Pt} = 2344$ 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: ^{1}H 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 ($J_{P-Pt} = 4082$ Hz). Anal. Calcd for $C_{56}H_{72}O_6P_2Pt$: C, 61.25; H, 6.61. Found: C, 61.0; H, 7.0.

Acknowledgment. This work has been supported by the Swedish Defence Nano Technology Programme managed by the Swedish Defence Research Agency (FOI).

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.

OM060616I