

# Synthesis and Reactivity of ( $\eta^1$ -Alkynyl)diorganoplatinum(IV) Species, Including Structural Studies of PtMe(*p*-Tol)(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) [dmpe = 1,2-bis(dimethylphosphino)ethane] and the Platinum(II) Reagent PtPh<sub>2</sub>(dmpe)

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Synthetic routes to diaryl(alkynyl)platinum(IV) and methyl(aryl)(alkynyl)platinum(IV) motifs are presented, together with studies of selectivity in carbon–carbon coupling by reductive elimination from platinum(IV) centers, and convenient synthetic routes to the platinum(II) reagents PtR<sub>2</sub>(dmpe) [R = Me (**1**), *p*-Tol (**2**), Ph (**3**), dmpe = 1,2-bis(dimethylphosphino)ethane], PtMe(*p*-Tol)(dmpe) (**4**), and PtMe(*p*-Tol)(COD) (COD = 1,5-cyclooctadiene). The hypervalent iodine(III) reagent IPh(C $\equiv$ CSiMe<sub>3</sub>)(OTf) (OTf<sup>−</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>) oxidizes the Pt(II) complexes PtR<sup>1</sup>R<sup>2</sup>(dmpe) [**1**: R<sup>1</sup> = R<sup>2</sup> = Me; **2**: R<sup>1</sup> = R<sup>2</sup> = *p*-Tol; **3**: R<sup>1</sup> = R<sup>2</sup> = Ph; **4**: R<sup>1</sup> = Me, R<sup>2</sup> = *p*-Tol; dmpe = 1,2-bis(dimethylphosphino)ethane] to Pt(IV) complexes that are stable at low temperatures. Those complexes resulting from oxidation of **1** and **4** adopt configurations in which the triflate and  $\eta^1$ -alkynyl ligands are *cis* to each other, Pt(OTf)-R<sup>1</sup>R<sup>2</sup>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) (**1a**, **4a**), with the alkynyl group *trans* to phosphorus, and form equilibria with triflate-free complexes (**1c**, **4c**), assumed to be solvento cations. The mixtures of dimethylplatinum(IV) species (**1a** and **1c**) and of methyl(*p*-tolyl)platinum(IV) species (**4a** and **4c**) react with sodium iodide, acetonitrile, and pyridine to form the *cis*-configured isomers of the complexes PtR<sup>1</sup>R<sup>2</sup>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) (**1b**, **4b**) and [PtR<sup>1</sup>R<sup>2</sup>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe)(L)](OTf) (L = NCMe: **1d**, **4d**; L = py: **1e**, **4e**). The diarylplatinum(II) complexes **2** and **3** are oxidized primarily to species with the triflate and alkynyl groups *trans* to each other, Pt(OTf)Ar<sub>2</sub>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) (**2a**, **3a**). The *trans*-isomers of diaryl(triflate)platinum(IV) complexes do not take part in ligand substitution reactions with sodium iodide, acetonitrile, or pyridine, but minor Pt(IV) complexes in equilibrium with **2a** and **3a** do react with iodide to form Pt[Ar<sub>2</sub>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe)] (**2b**, **3b**). Structural studies of PtPh<sub>2</sub>(dmpe) (**3**) and PtMe(*p*-Tol)(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) (**4b**) reveal square-planar and octahedral geometries, respectively. On warming above −10 °C in acetone, the Pt(IV) triflate stages of all of the systems decompose by reductive elimination via methyl–methyl, methyl–aryl, or aryl–aryl coupling. Similarly, decomposition of PtMe<sub>2</sub>(C $\equiv$ CSiMe<sub>3</sub>)(dmpe) (**1b**) under mild conditions in acetone results in Me–Me coupling. Decomposition of the isolated iodo complexes (**2b**, **3b**, **4b**) at temperatures above 50 °C reveals involvement of the alkynyl group in reductive elimination processes, giving minor quantities of Me<sub>3</sub>SiC $\equiv$ CI and ~1:1 ratios for the dominant products Me<sub>3</sub>SiC $\equiv$ C–Ar and Ar–Ar (**2b**, **3b**), and Me<sub>3</sub>SiC $\equiv$ C–(*p*-Tol) and Me–(*p*-Tol) for **4b**.

## Introduction

$\eta^1$ -Alkynylplatinum(IV) species have been proposed as intermediates in catalytic reactions,<sup>1</sup> and addition of the oxidant iodine promotes the stoichiometric synthesis of macrocycles via carbon–carbon bond formation at the platinum(II) center of  $\eta^1$ -alkynyl complexes.<sup>2</sup> The relatively small number of reported syntheses of  $\eta^1$ -alkynylplatinum(IV) compounds<sup>3,4</sup> has prompted us to investigate methods of preparing new classes of these tetravalent complexes and their decomposition, in particular the potential for carbon–carbon bond formation. In addition,  $\eta^1$ -

alkynylpalladium(IV) species are widely proposed as potential intermediates in stoichiometric and catalytic transformations,<sup>5,6</sup> but to date, the single  $\eta^1$ -alkynylpalladium(IV) complex reported decomposes at −50 °C,<sup>4e</sup> and thus the synthesis of Pt(IV) species more suitable for reactivity studies is desirable.

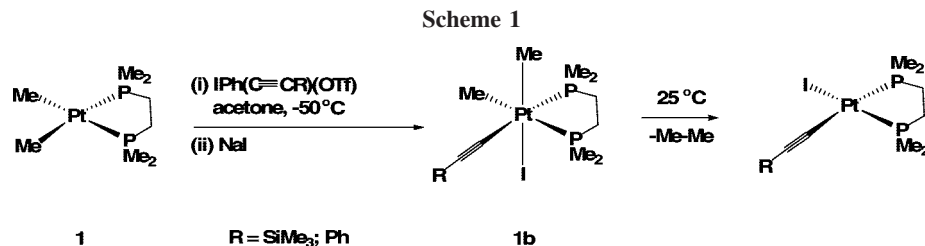
One route to  $\eta^1$ -alkynyl complexes of transition metals involves formal transfer of [C $\equiv$ CR]<sup>+</sup> from the hypervalent iodine(III) reagents IPh(C $\equiv$ CR)(OTf), where R is an organic group and OTf<sup>−</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>, to a metal center that results in overall oxidative addition at the metal and reduction of the iodonium reagent to iodobenzene. The utility of these iodonium reagents in organometallic chemistry and organic synthesis, including proposed mechanisms, has recently been reviewed.<sup>7</sup>

We previously reported reactions of the iodine(III) reagents IPh(C $\equiv$ CR)(OTf) (R = SiMe<sub>3</sub>, Ph) with diorganoplatinum(II) complexes of ligand systems that included the pincer ligands

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[2,6-(dimethylaminomethyl)phenyl-*N,C,M*]<sup>−</sup>, 2,2′-bipyridine, and 1,2-bis(dimethylphosphino)ethane (dmpe).<sup>4e</sup> In these reactions, the platinum(II) starting materials were oxidized to give the first examples of aryl( $\eta^1$ -alkynyl)platinum(IV) and dimethyl(alkynyl)platinum(IV) complexes, where *in situ* ligand exchange of iodide for triflate resulted in characterizable, and in some instances isolable, complexes.

Alkynylplatinum(IV) complexes containing nitrogen donor ligands from the above reactions were found to be thermally stable at room temperature, but for the dmpe complexes reductive elimination occurs under mild conditions in solution to give ethane and the isolable platinum(II) compounds PtI(C≡CR)(dmpe), as shown in Scheme 1. We report herein a study of the iodonium oxidation chemistry of the family of complexes PtR<sup>1</sup>R<sup>2</sup>(dmpe), where R<sup>1</sup> and R<sup>2</sup> are alkyl or aryl groups, in order to probe the behavior of a range of Pt<sup>IV</sup>R<sup>1</sup>R<sup>2</sup>(alkynyl) motifs.

## Experimental Section

Air-sensitive materials were handled under an argon atmosphere using standard Schlenk techniques. All solvents were dried and distilled by conventional methods prior to use. The compounds PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>,<sup>8</sup> Pt(*p*-Tol)<sub>2</sub>(COD) (COD = 1,5-cyclooctadiene),<sup>9</sup> PtClMe(COD),<sup>10</sup> and IPh(C≡CSiMe<sub>3</sub>)(OTf)<sup>11</sup> were prepared as previously reported. NMR spectra were recorded on a Varian

Mercury Plus 300 MHz spectrometer. <sup>1</sup>H NMR spectra were secondary-referenced to residual solvent signals. <sup>31</sup>P NMR spectra were externally referenced to 85% H<sub>3</sub>PO<sub>4</sub>. Microanalyses and LSIMS analyses were performed by the Central Science Laboratory, University of Tasmania. GC-MS analyses were performed using an HP 5890 gas chromatograph equipped with an HP5790 MSD and a 25 × 0.32 mm HP1 column (0.52 μm film thickness, He at 8 psi).

**PtMe<sub>2</sub>(dmpe) (1).** Methylolithium (1.6 M in Et<sub>2</sub>O, 3.2 mL, 5.12 mmol) was added dropwise to a stirred suspension of PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub> (1.01 g, 2.26 mmol) in Et<sub>2</sub>O (40 mL) at −20 °C. After addition was complete, the reaction mixture was allowed to warm to 0 °C and was stirred at this temperature for 2 h. The solution was then quenched by the dropwise addition of saturated NH<sub>4</sub>Cl, and the aqueous phase was extracted with Et<sub>2</sub>O (3 × 20 mL). The combined extracts were dried over MgSO<sub>4</sub> and filtered under argon into a dried flask. 1,2-Bis(dimethylphosphino)ethane (0.38 mL, 2.37 mmol) was added and the solution stirred for 1 h. Removal of the solvent *in vacuo* gave a white solid, which was washed with pentane to afford **1** (0.64 g, 76%). The characterization of this product matched that given in the literature.<sup>11</sup>

**Pt(*p*-Tol)<sub>2</sub>(dmpe) (2).** 1,2-Bis(dimethylphosphino)ethane (15 μL, 0.091 mmol) was added to a stirred solution of Pt(*p*-Tol)<sub>2</sub>(COD) (0.044 g, 0.091 mmol) in Et<sub>2</sub>O (5 mL). A white precipitate formed during the addition. The suspension was stirred for 10 min and the precipitate isolated by filtration to yield **2** (0.026 g, 54%). Anal. Calcd (Found): C, 45.54 (45.26); H, 5.73 (5.49). <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>): δ 7.21 (m, 4 H, *J*<sub>PH</sub> = 57 Hz, *o*-Tol), 6.69 (m, 4 H, *m*-Tol), 2.07 (overlapping with solvent, 6 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.83 (m, 4 H, PCH<sub>2</sub>), 1.29 (m, 12 H, PCH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, acetone-*d*<sub>6</sub>): δ 21.1 (*J*<sub>PIP</sub> = 1674 Hz).

**PtPh<sub>2</sub>(dmpe) (3).** PtPh<sub>2</sub>(dmpe) was prepared by the same procedure as for PtMe<sub>2</sub>(dmpe) (**1**) using the following reagents: phenyllithium (1.8 M in Bu<sub>2</sub>O, 1.4 mL, 2.52 mmol) and PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub> (0.50 g, 1.12 mmol) in Et<sub>2</sub>O (20 mL); dmpe (0.20 mL, 1.25 mmol). The yield of **3** was 0.42 g (76%). The characterization of this product matched that given in the literature.<sup>12a</sup> X-ray quality crystals were grown by layering a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** with pentane.

**PtMe(*p*-Tol)(COD).** A solution of *p*-iodotoluene (1.85 g, 8.49 mmol) in Et<sub>2</sub>O (15 mL) was added dropwise to magnesium metal (0.21 g, 8.6 mmol) to which a crystal of iodine had been added to initiate the reaction. After the addition was complete, the green-gold Grignard system was heated at reflux for 30 min, cooled to room temperature, and added by syringe over 10 min to a precooled (0 °C) solution of PtClMe(COD) (1.5 g, 4.24 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL). During the addition of the Grignard reagent, the solution became cloudy but eventually cleared to a golden-brown color. After addition was complete, the solution was stirred at 0 °C for 30 min and then cooled to −78 °C. Degassed isopropyl alcohol (5 mL) was added at once, the cold bath was removed, and the solution was allowed to warm to 0 °C. Degassed water (100 mL) was then added, and the system was stirred at 0 °C for 1 h. The layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 25 mL). The addition of small amounts of THF aided in this extraction. The combined organic phases were washed with water (100 mL), dried over MgSO<sub>4</sub>, and treated with decolorizing charcoal. Removal of the solvent by rotary evaporation gave a

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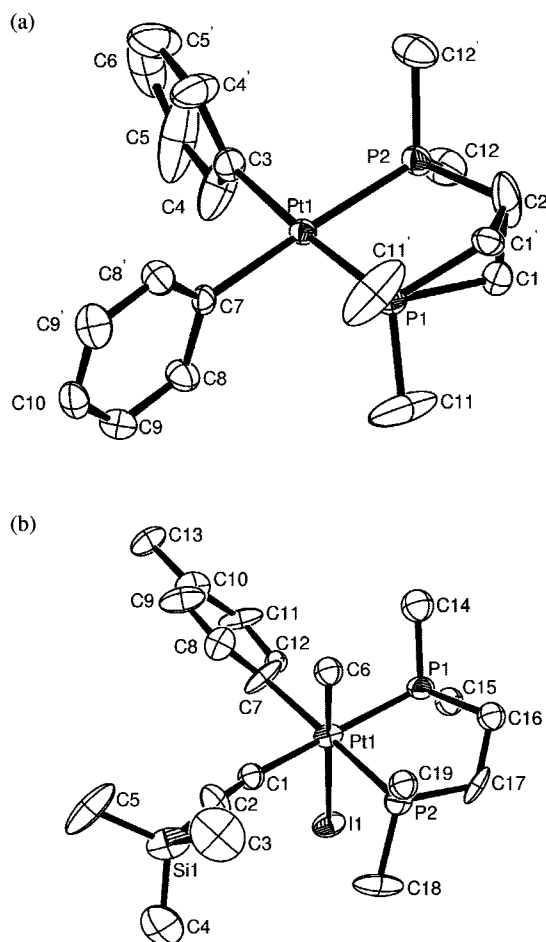
brown solid, which was recrystallized from a minimum of boiling hexanes to give PtMe(*p*-Tol)(COD) (0.88 g, 51%) as brown crystalline flakes. Anal. Calcd (Found): C, 46.94 (46.72); H, 5.42 (5.16). The characterization of this product matched that given in the literature.<sup>13</sup>

**PtMe(*p*-Tol)(dmpe) (4).** 1,2-Bis(dimethylphosphino)ethane (0.20 mL, 1.2 mmol) was added by syringe to a degassed benzene solution (50 mL) of PtMe(*p*-Tol)(COD) (0.50 g, 1.2 mmol). The resulting solution was stirred at room temperature under argon for 1.5 h. The solvent was removed *in vacuo*, affording **4** (0.42 g, 76%), which could be used without further purification. The product could be recrystallized, if necessary, from hot hexanes. Anal. Calcd (Found): C, 37.25 (37.46); H, 5.81 (5.92). <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.17 (t, *J* = 6.9 Hz, *J*<sub>PH</sub> = 56 Hz, 2 H, *o*-Tol), 6.74 (d, *J* = 6.6 Hz, 2 H, *m*-Tol), 2.09 (s, 3 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.80–1.68 (m, 4 H, PCH<sub>2</sub>), 1.47–1.37 (m, 6 H, PCH<sub>3</sub>), 1.28–1.17 (m, 6 H, PCH<sub>3</sub>), 0.31 (t, *J* = 7.8 Hz, *J*<sub>PH</sub> = 69 Hz, 3 H, PtCH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, acetone-*d*<sub>6</sub>):  $\delta$  31.6 (*J*<sub>PP</sub> = 1752), 28.8 (*J*<sub>PP</sub> = 1680). MS ESI(+): *m/z* (rel % abund) [assign]: 474 (10) [M + Na]<sup>+</sup>, 436 (15) [M – CH<sub>3</sub>]<sup>+</sup>, 360 (100) [M – tolyl]<sup>+</sup>.

**Oxidation Studies.** The following procedure was used for the formation and NMR studies of the Pt(IV) complexes PtIR<sup>1</sup>R<sup>2</sup>(C≡CSiMe<sub>3</sub>)(dmpe) [R<sup>1</sup> = R<sup>2</sup> = Me (**1b**); R<sup>1</sup> = R<sup>2</sup> = *p*-Tol (**2b**); R<sup>1</sup> = R<sup>2</sup> = Ph (**3b**); R<sup>1</sup> = Me, R<sup>2</sup> = *p*-Tol (**4b**): A solution of IPh(C≡CSiMe<sub>3</sub>)(OTf) (0.010 g, 0.022 mmol) in acetone-*d*<sub>6</sub> (1 mL) at –50 °C was added to a solution or suspension of PtR<sup>1</sup>R<sup>2</sup>(dmpe) (0.022 mmol) in acetone-*d*<sub>6</sub> (1 mL) at –50 °C, and the mixture was stirred at –50 °C for 30 min (1 h for **2** and **3**) under argon. NMR spectra of an aliquot of this resulting triflate intermediate solution were recorded. To the remaining original solution was added NaI (0.006 g, 0.04 mmol), and the system was stirred at –50 °C for a further 1 h. An aliquot of the resulting solution was then removed and its NMR spectra were recorded.

Reactions involving NaOTf, MeCN, and pyridine were performed as follows: PtR<sup>1</sup>R<sup>2</sup>(dmpe) was treated with IPh(C≡CSiMe<sub>3</sub>)(OTf) and stirred at –50 °C as described above. An excess of NaOTf (20 mg), MeCN (5  $\mu$ L), or pyridine (5  $\mu$ L) was added, and the solution stirred at –50 °C for a further 1 h. The NMR spectra of the resulting solution were then recorded.

**PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (4b).** A solution of IPh(C≡CSiMe<sub>3</sub>)(OTf) (0.051 g, 0.11 mmol) in acetone (25 mL) at –50 °C was added to a solution of PtMe(*p*-Tol)(dmpe) (**4**) (0.051 g, 0.11 mmol) in acetone (25 mL) at –50 °C, and the resulting colorless solution was stirred at –50 °C for 30 min under argon. To this solution was added NaI (0.025 g, 0.17 mmol), and the system was stirred at –50 °C for 1 h, after which time the solution was allowed to warm to room temperature and stirred for a further 16 h. The solvent was removed *in vacuo*, and CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added. The resulting suspension was filtered through Celite/cotton. Pentane (5 mL) was added to the filtrate, giving a fine precipitate, and the system was left at –20 °C for 30 min. The recrystallized product was isolated by suction filtration, washed with pentane, and dried in air, affording **4b** (0.018 g, 24%) as a colorless solid. Anal. Calcd (Found): C, 33.78 (33.96); H, 5.22 (5.47). IR (KBr):  $\nu_{\text{C}\equiv\text{C}}$  = 2100 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.71 (t, *J* = 7.8 Hz, *J*<sub>PH</sub> = 40 Hz, 2 H, *o*-Tol), 6.73 (d, *J* = 6.0 Hz, 2 H, *m*-Tol), 2.48–1.93 (m, PCH<sub>2</sub>, PCH<sub>3</sub>; overlapping singlet at  $\delta$  2.18, PhCH<sub>3</sub>; total integration: 16 H), 1.66–1.46 (m, PCH<sub>3</sub>), 1.38 (t, *J* = 6.6 Hz, *J*<sub>PH</sub> = 34 Hz, PtCH<sub>3</sub>; overlapping with PCH<sub>3</sub>, total integration: 6 H), 0.06 (s, 9 H, SiMe<sub>3</sub>). <sup>31</sup>P NMR (121.4 MHz, acetone-*d*<sub>6</sub>):  $\delta$  3.91 (*J*<sub>PP</sub> = 1088 Hz), –0.20 (*J*<sub>PP</sub> = 1757 Hz). Crystals for a structural analysis were obtained from pentane with the minimum quantity of dichloromethane required to ensure solubility.



**Figure 1.** ORTEP representations of the structures of (a) PtPh<sub>2</sub>(dmpe) (**3**) and (b) PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (**4b**). Displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. (a) PtPh<sub>2</sub>(dmpe) (**3**): atom C(1) is disordered over two positions at half-occupancy. Selected bond lengths (Å) and angles (deg): Pt(1)–C(3, 7) 2.076(7), 2.066(6); Pt(1)–P(1, 2) 2.284(2), 2.279(3); C(3)–Pt(1)–C(7) 92.0(3), C(3)–Pt(1)–P(1, 2) 176.1(2), 91.1(2); P(1)–Pt(1)–P(2) 84.96(9), C(7)–Pt(1)–P(1, 2) 91.87(18), 176.83(16). (b) PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (**4b**): Pt(1)–C(1, 6, 7) 2.04(2), 2.079(19), 2.155(18); Pt(1)–P(1, 2) 2.330(6), 2.380(5); Pt(1)–I(1) 2.757(3), C(1)–C(2) 1.14(3), C(2)–Si(1) 1.89(2), C(1)–Pt(1)–C(6, 7) 88.1(8), 86.3(9); C(6)–Pt(1)–C(7) 90.0(8), C(1)–Pt(1)–P(1, 2) 173.9(5), 92.5(6); C(6)–Pt(1)–P(1, 2) 87.1(7), 88.9(6); C(7)–Pt(1)–P(1, 2) 97.5(7), 178.4(5); I(1)–Pt(1)–C(1, 6, 7) 91.0(5), 177.9(6), 91.8(5); P(1)–Pt(1)–P(2) 83.6(2), Pt(1)–C(1)–C(2) 167.6(19), C(1)–C(2)–Si(1) 169(2).

**Structural Determinations.** Data were collected at 193 K with an Enraf Nonius TurboCAD4 with Mo K $\alpha$  radiation (0.71073 Å) on prismatic crystals of PtPh<sub>2</sub>(dmpe) (**3**) and PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (**4b**), belonging to the space groups *P2<sub>1</sub>/m* (No. 11) and *P2<sub>1</sub>/c* (No. 14), respectively. A summary of crystallographic data, data collection parameters and refinement parameters, and views of molecules of the complexes (Figure 1) are given below. The structures were solved by heavy atom methods with SHELXS-97, refined using full-matrix least-squares routines against *F*<sup>2</sup> with SHELXL-97,<sup>14</sup> and visualized using X-SEED.<sup>15</sup> All non-hydrogen atoms were subsequently refined anisotropically, except for PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe), for which isotropic refinement was neces-

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sary for a number of carbon centers. Hydrogens were included in calculated positions using a riding model, with C–H distances in the range 0.95–0.99 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , except for methyl H atoms, where  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .

The primitive monoclinic unit cell of  $\text{PtPh}_2(\text{dmpe})$  (**3**) contains two molecules, with the asymmetric unit containing one-half of a molecule of **3**. Molecules of **3** lie upon crystallographic mirror planes ( $x$ ,  $3/4$ ,  $z$ ). A disorder in the torsion of the chelating dmpe ligand was apparent in Fourier maps and was modeled as a two-site occupancy disorder across the crystallographic mirror plane for a single methylene carbon center lying off the mirror plane (C1, site occupancy fixed at 0.5). No other resolvable atomic positions as a consequence of this disorder were apparent in the remaining portions of the diphosphine ligand or the phenyl ligands, and they are thus refined with large anisotropic thermal parameters in some cases. Structure refinement in various space groups yielded the same disorder, with no improvements in the disorder model and/or residuals. Thus, refinement in the highest symmetry space group matching the observed systematic data absences is presented. The overall noncrystallographic molecular symmetry of  $\text{PtPh}_2(\text{dmpe})$  is likely to be  $C_2$ , but approximates to  $C_{2v}$  with the exception of the conformation of the diphosphine ligand chelate ring. Crystals of  $\text{PtIme}(p\text{-Tol})(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$  (**4b**) decomposed substantially during data collection, which resulted in a relatively poor refinement model despite data corrections being applied for the decay of the regularly measured intensity standards. Data were collected on several crystals, with similar outcomes.

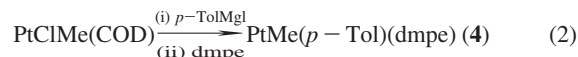
**Crystal Data.** Complex **3**:  $\text{C}_{18}\text{H}_{26}\text{P}_2\text{Pt}$ ,  $M = 499.42$ , monoclinic, space group  $P2_1/m$ ,  $a = 8.624(9)$  Å,  $b = 10.9514(18)$  Å,  $c = 10.323(3)$  Å,  $\beta = 106.99(3)^\circ$ ,  $V = 932.4(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.779$  g cm<sup>-3</sup>,  $\mu = 7.688$  mm<sup>-1</sup>, specimen  $0.20 \times 0.18 \times 0.22$  mm, 1812 measured reflections, 1716 unique reflections,  $R_{\text{int}} = 0.047$ ,  $R^1 = 0.028$  for observed data and  $wR^2 = 0.071$  for all data. Complex **4b**:  $\text{C}_{19}\text{H}_{35}\text{IP}_2\text{PtSi}$ ,  $M = 675.49$ , monoclinic, space group  $P2_1/c$ ,  $a = 16.982(10)$  Å,  $b = 10.492(5)$  Å,  $c = 15.289(12)$  Å,  $\beta = 113.21(8)^\circ$ ,  $V = 2504(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.792$  g cm<sup>-3</sup>,  $\mu = 7.013$  mm<sup>-1</sup>, specimen  $0.43 \times 0.20 \times 0.18$  mm, 4024 measured reflections, 3870 unique reflections,  $R_{\text{int}} = 0.141$ ,  $R^1 = 0.071$  for observed data and  $wR^2 = 0.211$  for all data.

## Results

**Syntheses of Pt(II) Starting Materials.** The complex  $\text{PtMe}_2(\text{dmpe})$  (**1**) has been previously prepared by treating  $\text{PtCl}_2(\text{dmpe})$  with methyllithium or methylmagnesium bromide,<sup>12a,b</sup> or by ligand exchange between  $\text{PtMe}_2(\text{COD})$  and dmpe.<sup>12c,d</sup> The latter route has also been employed for the synthesis of  $\text{PtPh}_2(\text{dmpe})$  (**3**).<sup>12a</sup> Complexes **1** and **3** were prepared in high yield by the alternative route given in eq 1. The reactions of  $\text{PtCl}_2(\text{SEt}_2)_2$  with RLi (R = Me, Ph) afforded the thioether-bridged dimers  $[\text{PtR}_2(\mu\text{-SEt}_2)]_2$ ,<sup>16</sup> which were converted without isolation to the dmpe complexes  $\text{PtR}_2(\text{dmpe})$  by ligand exchange.



The new complex  $\text{Pt}(p\text{-Tol})_2(\text{dmpe})$  (**2**) was also conveniently prepared from  $\text{Pt}(p\text{-Tol})_2(\text{COD})$  by ligand exchange with dmpe. The new methyl/aryl complex  $\text{PtMe}(p\text{-Tol})(\text{dmpe})$  (**4**) was prepared in two steps from  $\text{PtClMe}(\text{COD})$  using *p*-tolylmagnesium iodide to give the isolable complex  $\text{PtMe}(p\text{-Tol})(\text{COD})$ . Subsequent ligand exchange of COD for dmpe yielded **4**. The intermediate  $\text{PtMe}(p\text{-Tol})(\text{COD})$  has been previously prepared using organotin reagents.<sup>13</sup>



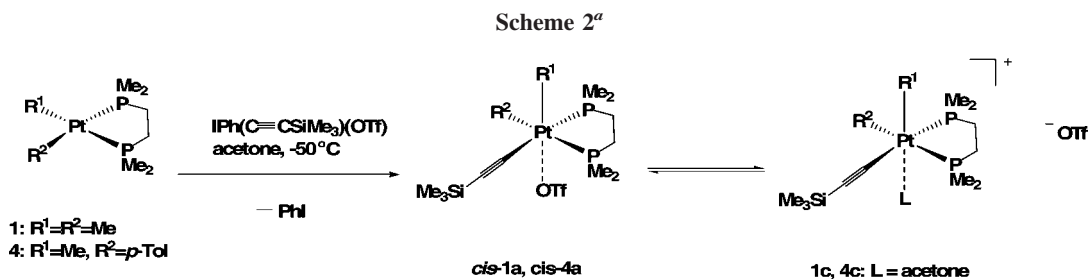
**Syntheses of Pt(IV) Complexes: Triflate Stage.** To better understand the formation of **1b** and its decomposition (Scheme 1), we examined the immediate product resulting from the combination of solutions of  $\text{PtMe}_2(\text{dmpe})$  and  $\text{IPh}(\text{C}\equiv\text{CSiMe}_3)(\text{OTf})$  at  $-50$  °C, yielding the “triflate stage” of the overall reaction in Scheme 1, before addition of NaI. The <sup>31</sup>P NMR spectrum of the triflate stage of **1** at  $-50$  °C displays two dominant signals of equal intensity at 29.4 and 24.7 ppm ( $J_{\text{PtP}} = 1210$  and 1826 Hz, respectively; Table 1). A weaker pair of resonances at 25.3 ( $J_{\text{PtP}} = 1181$  Hz) and 20.7 ( $J_{\text{PtP}} = 1795$  Hz) is also present. In both the major and minor sets, the signal at lower field has the smaller  $J_{\text{PtP}}$ , ca. 1200 Hz, whereas the upfield signal has a  $J_{\text{PtP}}$  of ca. 1800 Hz. The distinct values of the respective coupling constants indicate the two phosphorus nuclei of dmpe in each complex are coupled to groups with disparate *trans* influences, and the spectra are consistent with the presence of two *cis*-configured species (Scheme 2). When a 5-fold excess of NaOTf is added at  $-50$  °C, intensification of the minor set of <sup>31</sup>P signals (**1a**) indicates that the other species (**1c**) may be the solvento cation  $[\text{PtMe}_2(\text{dmpe})(\text{C}\equiv\text{CSiMe}_3)(\text{OCMe}_2)]^+$ . Although the addition of an excess of triflate increases the abundance of **1a** at  $-50$  °C, at  $-20$  °C the species **1c** again predominates. The thermal instability of the triflate stage species prohibits investigations at higher temperatures.

In the corresponding <sup>1</sup>H NMR spectrum of the triflate stage in the dimethylplatinum system (**1a**, **4a**), resonances from the product iodobenzene are observed at low field, while the upfield region displays the complicated overlapping splitting patterns expected from the methyl and methylene groups of the dmpe ligand. The most diagnostic features of the spectrum are the overlapping Pt–CH<sub>3</sub> signals at 1.0–0.8 ppm, accompanied by <sup>195</sup>Pt satellites, which are deshielded relative to the Pt(II) starting material. A dominant trimethylsilyl signal near 0 ppm and

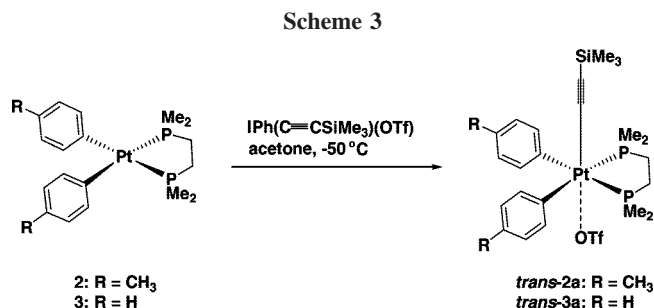
**Table 1.** Observed <sup>31</sup>P NMR Resonances<sup>a</sup> and  $J_{\text{PtP}}$  Coupling Constants<sup>b</sup> for Compounds 1–4

	$\text{Pt}^{\text{II}}\text{R}^1\text{R}^2(\text{dmpe})$	$\text{Pt}^{\text{IV}}\text{R}^1\text{R}^2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$ triflate stage <sup>c</sup>	$\text{Pt}^{\text{IV}}\text{IR}^1\text{R}^2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$
$\text{R}^1 = \text{R}^2 = \text{Me}$	32.4 (1783)	29.4 (1210), 24.7 (1826); 25.3 (1181), 20.7 (1795)	6.3 (1158), 2.1 (1744)
<b>(1)</b>		<b>(1a and 1c)</b>	<b>(1b)</b>
$\text{R}^1 = \text{R}^2 = p\text{-Tol}$	29.0 (1684)	25.5 (1121)	6.8 (1116), 4.0 (1800)
<b>(2)</b>		<b>(2a)</b>	<b>(2b)</b>
$\text{R}^1 = \text{R}^2 = \text{Ph}$	29.1 (1684)	25.8 (1119)	7.0 (1115), 4.3 (1797)
<b>(3)</b>		<b>(3a)</b>	<b>(3b)</b>
$\text{R}^1 = \text{Me}, \text{R}^2 = p\text{-Tol}$	32.0 (1771), 29.6 (1690)	27.5 (1171), 26.0 (1838); 23.7 (1139), 21.4 (1750)	5.8 (1099), 2.5 (1718)
<b>(4)</b>		<b>(4a and 4c)</b>	<b>(4b)</b>

<sup>a</sup>  $\delta$  units,  $-50$  °C, acetone-*d*<sub>6</sub>. <sup>b</sup> In parentheses, Hz. <sup>c</sup>  $\text{Pt}(\text{OTf})\text{R}^1\text{R}^2(\text{dmpe})(\text{C}\equiv\text{CSiMe}_3)$  or  $[\text{PtR}^1\text{R}^2(\text{dmpe})(\text{C}\equiv\text{CSiMe}_3)(\text{OCMe}_2)]\text{OTf}$ .



<sup>a</sup> Configurations at Pt for **4a** and **4c** are unknown.



weaker overlapping trimethylsilyl signals again suggest a mixture of products.

Reactions of Pt(*p*-Tol)<sub>2</sub>(dmpe) (**2**) and PtPh<sub>2</sub>(dmpe) (**3**) with IPh(C≡CSiMe<sub>3</sub>)(OTf) give colorless solutions, whose <sup>31</sup>P NMR spectra show that the single resonance observed at 29 ppm in the Pt(II) starting material is replaced by one dominant signal near 26 ppm (Table 1) and several much weaker signals. Addition of an excess of NaOTf at -50 °C results in the intensification of this dominant signal and the diminution of the weaker ones. At -20 °C, only the dominant signal and its <sup>195</sup>Pt satellites are observed. These NMR data are consistent with the preferred formation of the *trans*-isomers Pt(OTf)(*p*-Tol)<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>) (**2a**) and Pt(OTf)Ph<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>) (**3a**), shown in Scheme 3.

The complex PtMe(*p*-Tol)(dmpe) (**4**) behaves similarly to the dimethylplatinum complex **1** (Scheme 2). Thus, its oxidized triflate stage <sup>31</sup>P NMR spectrum reveals two sets of resonances (Table 1), with the lower field signals dominating, whose chemical shifts and coupling constants are very similar to **1a** and **1c**. The triflate stage of this system is therefore assigned as comprising Pt(OTf)Me(*p*-Tol)(dmpe)(C≡CSiMe<sub>3</sub>) (**4a**) and the solvent-coordinated complex [PtMe(*p*-Tol)(dmpe)(C≡CSiMe<sub>3</sub>)(OCMe<sub>2</sub>)<sub>2</sub>](OTf) (**4c**).

**Syntheses of Pt(IV) Complexes: Ligand Substitutions.** When stoichiometric amounts of acetonitrile are added to the triflate stages of the Pt<sup>IV</sup>Me<sub>2</sub> and Pt<sup>IV</sup>Me(*p*-Tol) systems, (**1a** with **1c**) and (**4a** with **4c**), the adducts [PtMe<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>)(NCMe)](OTf) (**1d**) and [PtMe(*p*-Tol)(dmpe)(C≡CSiMe<sub>3</sub>)(NCMe)](OTf) (**4d**) are formed (Scheme 4), as evidenced by the appearance of two new <sup>31</sup>P signals at 18.2 and 15.4 ppm (*J*<sub>PtP</sub> = 1164 and 1753 Hz, respectively) for **1d** and 17.5 and 16.2 ppm (*J*<sub>PtP</sub> = 1121 and 1763 Hz) for **4d**. Formation of **1d** and **4d** is not quantitative, however, unless a large excess of MeCN is present. At -50 °C, signals from the two platinum-bound methyl groups of **1d** are nearly coincident, but raising the temperature to -10 °C allows the identification of the two nonequivalent groups. The formation of **4d** is markedly slower than that of **1d**. Even when a large excess of

MeCN is used, resonances from triflate stage species persist until the temperature is raised to -20 °C, whereas the formation of **1d** is nearly instantaneous at -50 °C. The corresponding pyridine adducts [PtMe<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>)(py)](OTf) (**1e**; py = pyridine) and [PtMe(*p*-Tol)(dmpe)(C≡CSiMe<sub>3</sub>)(py)](OTf) (**4e**) (Scheme 4) are formed in similar fashion to their MeCN counterparts, giving single sets of <sup>31</sup>P signals at 18.4 and 15.1 ppm (*J*<sub>PtP</sub> = 1135 and 1747 Hz) for **1e** and 17.7 and 17.3 ppm (*J*<sub>PtP</sub> = 1119 and 1765 Hz) for **4e**. Quantitative formation of **1e** and **4e** is slower than for the MeCN analogues, occurring over 1 day at -20 °C. In contrast to the triflate stages, (**1a** with **1c**) and (**4a** with **4c**), the diarylplatinum complexes Pt(OTf)(*p*-Tol)<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>) (**2a**) and Pt(OTf)Ph<sub>2</sub>(dmpe)(C≡CSiMe<sub>3</sub>) (**3a**) do not react with MeCN or pyridine.

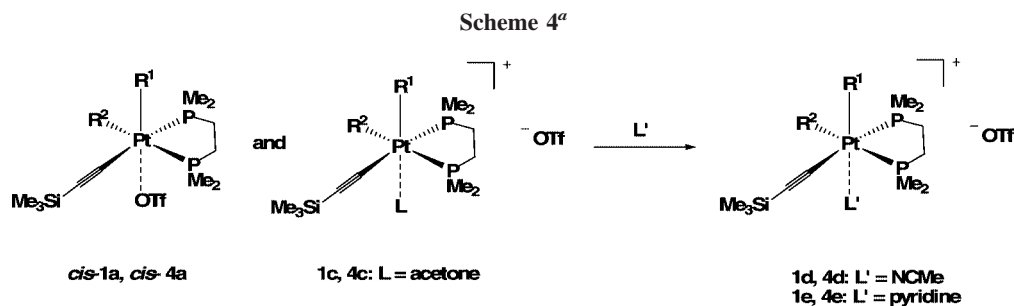
Reaction of the triflate stage equilibrium mixture, **1a** with **1c** (Scheme 2), with NaI results in complete conversion to the iodo complex PtIme<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe) (**1b**, Scheme 1), which decomposes slowly at room temperature to give ethane and the isolable Pt(II) complex PtI(C≡CSiMe<sub>3</sub>)(dmpe).<sup>4e</sup>

The mixed methyl/tolyl triflate stage (**4a** with **4c**) most closely resembles the dimethylplatinum system in its reaction with NaI. Within 30 min, the pairs of resonances in the <sup>31</sup>P NMR spectrum corresponding to the triflate stage species (**4a** with **4c**) are replaced by signals at 5.8 and 2.5 ppm, with *J*<sub>PtP</sub> values similar to PtIme<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe) (Table 1). Residual signals from the triflate stage can still be observed at -50 °C, but at higher temperatures are no longer detected. Thus, the reaction appears to be somewhat slower than in the Pt<sup>IV</sup>Me<sub>2</sub> system. Unlike any of the other Pt(IV) compounds in this study, **4b** can be isolated as a pure solid that is stable for at least two months at -20 °C but shows signs of decomposition after several weeks at room temperature.

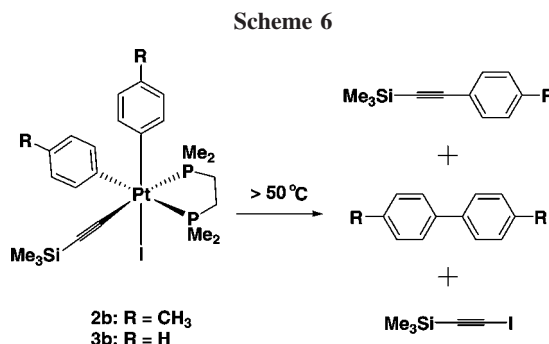
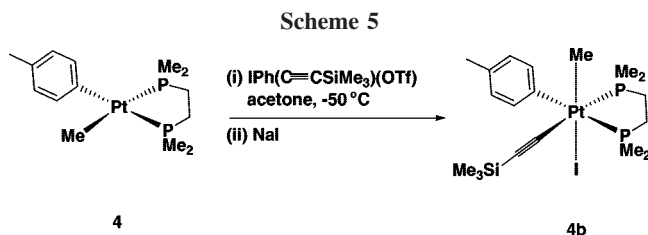
After treatment of the diarylplatinum(IV) triflate species **2a** and **3a** with an excess of NaI, the <sup>31</sup>P NMR spectra exhibit two new signals near 7 and 4 ppm (Table 1), corresponding to the iodo complexes PtI(*p*-Tol)<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe) (**2b**) and PtIPh<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe) (**3b**). Although the *trans*-isomers dominate the triflate stages of the diaryl systems, the pairs of <sup>31</sup>P NMR signals and the presence of nonequivalent tolyl groups for **2b** indicate the formation of the respective *cis*-iodo complexes. Residual resonances of unreacted triflate species gradually disappear as the temperature is raised from -50 °C, and by 10 °C new signals downfield corresponding to Pt(II) decomposition products replace the single resonances for **2a** and **3a**. When an excess of NaOTf is used to eliminate minor Pt(IV) species and form **2a** and **3a** quantitatively as described above, no reaction with NaI is observed, indicating that reaction with iodide occurs via the minor Pt(IV) species rather than **2a** and **3a**.

**Structural Studies of PtPh<sub>2</sub>(dmpe) (**3**) and PtIme(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (**4b**).** The complexes exhibit the expected square-planar (**3**) and octahedral (**4b**) coordination geometries appropriate for Pt(II) and Pt(IV) (Figure 1). The

(16) (a) Kuyper, J.; van der Laan, R.; Jeanneaus, F.; Vrieze, K. *Trans. Met. Chem.* **1976**, *1*, 199. (b) Steele, B. R.; Vrieze, K. *Trans. Met. Chem.* **1977**, *2*, 140.

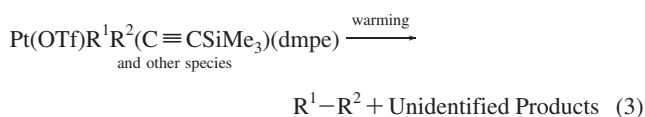


<sup>a</sup> 1a–e: R<sup>1</sup> = R<sup>2</sup> = Me; 4a–e: R<sup>1</sup> = Me, R<sup>2</sup> = *p*-Tol, relative configurations of Me and *p*-Tol at Pt are unknown.



Pt(IV) complex has the *fac*-PtC<sub>3</sub> configuration with *cis*-oriented iodo and alkynyl groups, while the alkynyl group is *trans* to a phosphorus. In both structures the aryl groups form large interplanar angles to the PtC<sub>2</sub>P<sub>2</sub> mean plane [90° for **3**, 49.0(7)° for **4b**], minimizing Ph...Ph interactions in **3** and aryl...PMe<sub>2</sub> interactions in **3** and **4b**; the smaller interplanar angle in **4b** also allows minimization of *p*-Tol...Me and *p*-Tol...I interactions. For related Pt–C(aryl) and Pt–P bonds, longer distances are found in the higher oxidation state, as expected, by ~0.09 Å for Pt–C and ~0.07 Å for Pt–P. For the bidentate phosphine ligand this is reflected in a smaller PtP<sub>2</sub> chelate bite angle in the Pt(IV) complex [84.97(9)° for **3**, 83.6(2)° for **4b**]. The η<sup>1</sup>-alkynylplatinum(IV) complex has Pt–C 2.04(3) Å and C≡C 1.14(3) Å, and the Pt(I)–C(1)–C(2) angle is 167.6(19)°; a similar bending [172.7(3)°] occurs in the pincer complex Pt(O<sub>2</sub>CAr<sub>F</sub>)I(C≡CSiMe<sub>3</sub>)(NCN) (Ar<sub>F</sub> = *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, NCN = [2,6-(dimethylaminomethyl)phenyl-*N,C,N*]<sup>−</sup>).<sup>4e</sup>

**Decomposition of Pt(IV) Complexes.** On warming above −10 °C in acetone, the colorless triflate stage mixtures of all the systems in this study turn dark and opaque. <sup>1</sup>H NMR spectra and GC-MS analyses reveal that decomposition occurs through reductive elimination to give ethane from Pt<sup>IV</sup>Me<sub>2</sub>(C≡CSiMe<sub>3</sub>) species (**1a/1c**), 4,4'-dimethylbiphenyl from Pt<sup>IV</sup>(*p*-Tol)<sub>2</sub>(C≡CSiMe<sub>3</sub>) species (**2a**), biphenyl from Pt<sup>IV</sup>Ph<sub>2</sub>(C≡CSiMe<sub>3</sub>) species (**3a**), and *p*-xylene from Pt<sup>IV</sup>Me(*p*-Tol)(C≡CSiMe<sub>3</sub>) species (**4a** with **4c**) (eq 3). The complex expected from the reductive eliminations, Pt(OTf)(C≡CSiMe<sub>3</sub>)(dmpe), could not be isolated from the dark suspensions. The MeCN and pyridine complexes of systems **1** and **4** decompose in the same manner as their respective triflate stages, thus giving ethane from the mixture of **1d** and **1e** and *p*-xylene from the mixture of **4d** and **4e**, along with unidentified Pt-containing products. The pyridine adducts **1e** and **4e**, however, are thermally more stable than their respective triflate and acetonitrile complexes and persist at room temperature for several days.

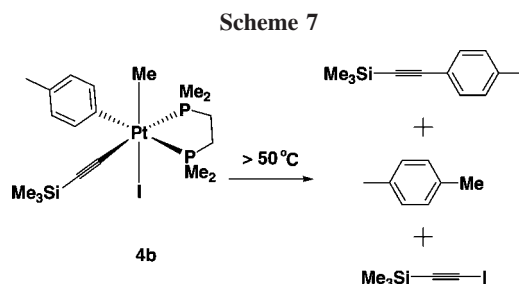


The more stable iodoplatinum(IV) complexes **2b** and **3b**, PtI MeAr<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe), which are isolated accompanied by Pt(II) decomposition products, decompose upon heating

during GC-MS experiments to give Me<sub>3</sub>SiC≡CAr and (Ar)<sub>2</sub> in ~1:1 ratio together with Me<sub>3</sub>SiC≡CI (trace for **2b**, ~0.07 for **3b**) (Scheme 6). Similarly, the methyl/aryl complex PtI Me(*p*-Tol)(C≡CSiMe<sub>3</sub>)(dmpe) (**4b**), which is obtained in pure form, decomposes with heating to form Me<sub>3</sub>SiC≡C(*p*-Tol) and (*p*-Tol)<sub>2</sub> with, in this case, an appreciable quantity of Me<sub>3</sub>SiC≡CI (~0.15 but not reliably quantified due to solid state decomposition in GC-MS) (Scheme 7). The less stable species PtI Me<sub>2</sub>(C≡CSiMe<sub>3</sub>)(dmpe) (**1b**), which cannot be isolated and studied under identical conditions, decomposes in acetone to give ethane and PtI(C≡CSiMe<sub>3</sub>)(dmpe).

## Discussion

The results presented above illustrate a simple route to new diaryl(alkynyl)- and methyl(aryl)(alkynyl)platinum(IV) systems as well as differences in preferred configurations and reactivities of diaryl(alkynyl)platinum(IV) complexes compared to the dimethyl- and methyl(aryl)platinum(IV) complexes, which behave similarly. Thus, although for PtXR<sup>1</sup>R<sup>2</sup>(C≡CSiMe<sub>3</sub>)(dmpe) the triflate stages of the Pt<sup>IV</sup>Me<sub>2</sub> and Pt<sup>IV</sup>MeAr systems (X = OTf: **1a**, **4a**) as well as all iodo species detected (X = I: **1b**, **2b**, **3b**, **4b**) have the alkynyl group *cis* to X, the triflate stages of the Pt<sup>IV</sup>Ar<sub>2</sub> systems (X = OTf: **2a**, **3a**) have the aryl ligands in the square plane containing the dmpe ligand such that the alkynyl and triflate ligands are *trans* to each other. Furthermore, the MeCN and pyridine adducts of the Pt<sup>IV</sup>Me<sub>2</sub> and Pt<sup>IV</sup>MeAr systems (**1d** and **1e**, **4d** and **4e**) form readily, also adopting a *cis*-configuration, whereas the formation of these neutral ligand adducts of the Pt<sup>IV</sup>Ar<sub>2</sub> systems is not observed.



All solutions formed on addition of  $\text{IPh}(\text{C}\equiv\text{CSiMe}_3)(\text{OTf})$  to platinum(II) reagents  $\text{PtR}^1\text{R}^2(\text{dmpe})$  contain species in addition to the major product  $\text{Pt}(\text{OTf})\text{R}^1\text{R}^2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$  that are most likely solvento cations, and only in the case of the  $\text{Pt}^{\text{IV}}\text{Ar}_2$  systems can the equilibria be shifted entirely to the triflate species by addition of  $\text{NaOTf}$ . Only when the equilibrium is shifted in this way to the OTf species does addition of  $\text{NaI}$  not result in formation of  $\text{PtIAR}_2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$ , implying that substitution by  $\text{I}^-$  occurs from the solvento species.

The syntheses reported here have provided an opportunity to examine selectivity in reductive elimination at Pt(IV) centers containing combinations of unidentate, unrestrained methyl, aryl, and alkynyl groups (methyl/alkynyl, aryl/alkynyl, methyl/aryl/alkynyl) together with variation in ancillary ligands (triflate/solvent/iodide).

The preferred decomposition pathways under mild conditions in solution for the triflate stage complexes, as well as the MeCN and pyridine adducts, regardless of configuration (*cis* in Scheme 2; *trans* in Scheme 3), indicate that methyl–aryl and aryl–aryl coupling are more favorable than coupling involving the alkynyl ligands (eq 3). In coupling involving *p*-tolylplatinum(IV) species there is no indication of isomerization of aromatic products, as

only 4,4'-ditolyl and *p*-xylene are observed. No alkynyl coupling products are observed from the triflate systems, and an identical preference is observed for the unstable iodo complex  $\text{PtI}(\text{Me})_2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$  (**1b**), which decomposes under similar conditions to form ethane. In the thermally stable iodo complexes,  $\text{PtI}(\text{Ar})_2(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$  (**2b**, **3b**) and  $\text{PtI}(\text{Me})(p\text{-Tol})(\text{C}\equiv\text{CSiMe}_3)(\text{dmpe})$  (**4b**), heating above 50 °C (solid phase decomposition) results in competitive aryl–alkynyl and aryl–aryl coupling together with minor quantities of  $\text{Me}_3\text{SiC}\equiv\text{CI}$ . Methyl–alkynyl coupling has not been detected in any of the systems examined, indicating that the potential for development of organic synthesis via C–C bond formation at Pt(V) centers involving alkynyl groups may be favored for groups other than alkyl.

**Acknowledgment.** We thank the Australian Research Council for financial support.

**Supporting Information Available:** X-ray crystallographic files in CIF format for **3** and **4b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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