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Synthesis and structure of alkynylplatinum(IV) complexes containing the pincer group [2,6-(dimethylaminomethyl)phenyl-*N*, *C*, *N*]⁻

Allan J. Canty^{a,*}, Thomas Rodemann^a, Brian W. Skelton^b, Allan H. White^b

^a School of Chemistry, University of Tasmania, Private Bag 75, Hobart, TAS 7001, Australia ^b Chemistry M313, University of Western Australia, Crawley, WA 6009, Australia

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Abstract

Reaction of phenyl(trimethylsilylalkynyl)iodine(III) triflate with $Pt^{II}(O_2CAr)(NCN)$ (Ar = Ph, 4-trifluoromethylphenyl (Ar_F); NCN = [C₆H₃(CH₂NMe₂)₂-2,6]) at ambient temperature gives solutions of $Pt^{IV}(O_2CAr)(OTf)(C CSiMe_3)(NCN)$ [Ar = Ph (1a); Ar = Ar_F (1b)]. Addition of sodium iodide (NaI) to 1 results in the isolation of $Pt^{IV}(O_2CAr)I(C CSiMe_3)(NCN)$ [Ar = Ph (2a); Ar = Ar_F (2b)] in >90% yields. In these first examples of alkynyl(pincer)platinum(IV) complexes, the pincer group is present as a *mer*-[NCN]⁻ tridentate donor and the alkynyl group is located *cis* to the pincer carbon donor, and the triflate (1a, 1b) and iodide groups (2a, 2b) are located *trans* to the pincer carbon; an X-ray structural analysis has been completed for 2b. © 2004 Elsevier B.V. All rights reserved.

Keywords: Platinum(IV); Pincer; Intramolecular; Alkynyls; Iodonium; Iodine(III)

There is considerable current interest in alkynylplatinum chemistry [1–4], including for complexes containing intramolecularly coordinating tridentate groups as ancillary ligands [5–10], in particular [NCN][–] pincer groups [5–9]. However, there is a limited range of reported alkynylplatinum(IV) complexes [11–14], and there are no reported examples of platinum(IV) complexes containing [NCN][–] pincer groups. The synthesis of alkynyl(pincer)platinum(IV) complexes appears to have been elusive, e.g. the alkynylplatinum(II) bond in alkynyl(pincer)platinum(II) complexes is not stable to halogen-containing oxidants [6]. Cyclic voltammetry studies for this class of platinum(II) complex [6,7], and related complexes [10], reveal irreversible oxidation processes. We report here a convenient synthetic route to alkynyl(pincer)platinum(IV) complexes employing a readily obtained iodonium reagent [15] as oxidant to transfer $[C \equiv CSiMe_3]^+$ to a platinum(II) substrate containing the archetypal pincer group [2,6-(dimethylaminomethyl)phenyl-*N*, *C*, *N*]⁻ (NCN) [16].

Addition of IPh(C=CSiMe₃)(O₃SCF₃)¹ to Pt(O₂ CAr)(NCN) [Ar = Ph, 4-CF₃C₆H₄ (Ar_F)]^{1,2} in acetone gave complexes **1a** and **1b** as yellow solutions and, on

^{*} Corresponding author. Tel.: +61 3 6226 2162; fax: +61 3 6226 2858.

E-mail address: allan.canty@utas.edu.au (A.J. Canty).

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¹ The reagents IPh(C \equiv CSiMe₃)(OTf) [15] and Pt(O₂CPh)(NCN) [17] were prepared as reported.

² Preparation of Pt(O₂CAr_F)(NCN): silver 4-trifluoromethylbenzoate (9.0 mg, 0.39 m mol) was added to a solution of PtCl(NCN) [18] (16 mg, 0.38 m mol) in acetone (5 mL). The suspension was stirred for 15 h in the absence of light, then filtered through Celite. The solvent was removed in a vacuum to give the product as a white solid (18 mg, 95%). ¹H NMR (acetone-d₆) (300 MHz): δ 8.27 (d, ³*J* = 7.6 Hz, 2H, H2), 7.71 (d, ³*J* = 7.6 Hz, 2H, H3), 6.93 (dd, ³*J* = 6.3, 8.4 Hz, 1H, H4– NCN), 6.80 (d, ³*J* = 7.7 Hz, 2H, H3–NCN), 4.10 (s, ³*J*_{Pt-H} = 47.6 Hz, 4H, NCH₂), 3.04 (s, ³*J*_{Pt-H} = 36.9 Hz, 12H, NCH₃).

addition of sodium iodide, complexes **2a** and **2b** were isolated in 91% and 93% yield, respectively (Scheme 1). ³ The isolated complexes have satisfactory microanalyses (C, H, N), and **1a–2b** exhibit ¹H NMR spectra ^{4,5,6,7} in accord with the configuration revealed by the X-ray structural analysis for **2b**, ⁸ e.g. two *N*-methyl environments consistent with the presence of inequivalent groups above and below the Pt(NCN) coordination plane, and large ²J coupling for the geminal CH₂ groups. Infrared spectra of complexes **2a** and **2b** exhibit v(C==C) of 2078 cm⁻¹. ^{6,7}

In the solid state $Pt(O_2CAr_F)I(C \equiv CSiMe_3)(NCN)$ (2b) has distorted octahedral coordination for platinum

⁴ Pt(O₂CPh)(OTf)(C=CSiMe₃)(NCN) (1a). ¹H NMR (acetone-d₆) (300 MHz): δ 7.85 (d, ³*J* = 8.1 Hz, 2H, H2), 7.59–7.48 (m, 2H, H4, H4–NCN), 7.45–7.36 (m, 2H, H3), 7.24 (d, ³*J* = 8.1 Hz, 2H, H3–NCN), 4.77 (d, ²*J* = 14.8 Hz, ³*J*_{Pt-H} = 30.4 Hz, 2H, NCH₂), 4.61 (d, ²*J* = 14.8 Hz, ³*J*_{Pt-H} = 30.0 Hz, 2H, NCH₂), 3.37 (s, ³*J*_{Pt-H} = 41.7 Hz, 6H, NCH₃), 2.97 (s, ³*J*_{Pt-H} = 24.3 Hz, 6H, NCH₃), 0.08 (s, 9H, Si(CH₃)₃).

⁵ Pt(O₂CAr_F)(OTf) (C=CSiMe₃)(NCN) (**1b**). ¹H NMR (acetoned₆) (300 MHz): δ 8.06 (d, ³*J* = 8.2 Hz, 2H, H2), 7.78–7.72 (m, 2H, H3), 7.40 (t, ³*J* = 7.5 Hz, 1H, H4–NCN), 7.24 (d, ³*J* = 7.8 Hz, 2H, H3– NCN), 4.77 (d, ²*J* = 15.1 Hz, ³*J*_{Pt-H} = 33.0 Hz, 2H, NCH₂), 4.62 (d, ²*J* = 15.1 Hz, ³*J*_{Pt-H} = 37.6 Hz, 2H, NCH₂), 3.37 (s, ³*J*_{Pt-H} = 41.9 Hz, 6H, NCH₃), 2.99 (s, ³*J*_{Pt-H} = 24.0 Hz, 6H, NCH₃), 0.08 (s, 9H, Si(CH₃)₃).

⁶ Pt(O₂CPh)I(C=CSiMe₃)(NCN) (**2a**). ¹H NMR (acetone-d₆) (300 MHz): δ 8.04 (d, ${}^{3}J$ = 8.2 Hz, 2H, H2), 7.46–7.31 (m(b), 4H, H3, H4, H4–NCN), 7.01 (d, ${}^{3}J$ = 7.7 Hz, 2H, H3–NCN), 4.65 (d, ${}^{2}J$ = 14.8 Hz, ${}^{3}J_{\text{Pt-H}}$ = 33.1 Hz, 2H, NCH₂), 4.40 (d, ${}^{2}J$ = 14.8 Hz, ${}^{3}J_{\text{Pt-H}}$ = 35.5 Hz, 2H, NCH₂), 3.41 (s, ${}^{3}J_{\text{Pt-H}}$ = 42.1 Hz, 6H, NCH₃), 3.08 (s, ${}^{3}J_{\text{Pt-H}}$ = 26.4 Hz, 6H, NCH₃), 0.08 (s, 9H, Si(CH₃)₃). IR (KBr disk): ν (C=C) 2078 cm⁻¹.

⁷ Pt(O₂CAr_F)I(C=CSiMe₃)(NCN) (**2b**). ¹H NMR (acetone-d₆) (300 MHz): δ 8.20 (d, ³J = 8.6 Hz, 2H, H2), 7.71 (d, ³J = 8.6 Hz, 2H, H3), 7.41 (t, ³J = 7.6 Hz, 1H, H4–NCN), 7.03 (d, ³J = 7.7 Hz, 2H, H3–NCN), 4.67 (d, ²J = 14.8 Hz, ³J_{Pt-H} = 32.9 Hz, 2H, NCH₂), 4.42 (d, ²J = 14.8 Hz, ³J_{Pt-H} = 35.2 Hz, 2H, NCH₂), 3.41 (s, ³J_{Pt-H} = 42.0 Hz, 6H, NCH₃), 3.08 (s, ³J_{Pt-H} = 25.9 Hz, 6H, NCH₃), 0.08 (s, 9H, Si(CH₃)₃). IR (KBr disk): v (C=C) 2078 cm⁻¹.

⁸ Structure determination for **2b**: C₂₅H₃₂F₃IN₂O₂PtSi, *M* = 799.6, triclinic, space group *P*Ī, *a* = 10.0061(6), *b* = 10.8050(7), *c* = 13.6912(9) Å, α = 85.450(1), β = 70.118(1), γ = 89.947(1), V = 1387.1(2) Å³, D_c (*Z* = 1) = 1.91₄ g cm⁻³, 27502 (=sphere); 2θ_{max} = 75°) CCD diffractometer reflections (absorption corrected) reduced to 14219 unique (*R*_{int} = 0.037), 12056 with *F* > 4σ(*F*) being used in full-matrix leastsquares refinement (anisotropic displacement parameters for nonhydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H constrained), *R* = 0.034, *R*_w (statistical weights) = 0.073.



Scheme 1. Synthesis of alkynyl(pincer)platinum(IV) complexes: (i) IPh(C=CSiMe₃)(O₃SCF₃), acetone, 30 min, 25 °C; (ii) NaI, acetone, 30 min, 25 °C.

(Fig. 1), based on a meridionally coordinated pincer group, an iodo ligand *trans* to the pincer carbon donor, and alkynyl and 4-trifluoromethylbenzoate groups oriented mutually *trans*. One molecule devoid of crystallographic symmetry comprises the asymmetric unit. The C(01)–C(02) distance, 1.205(4) Å, appears to be a normal triple bond. As is often the case with tridentate ligands of this type, the ligand is non-planar, with *quasi*-two symmetry about the metal-central carbon bond, the pendant C–N arrays twisting out of plane to either side of the central aromatic ring. The aroate plane lies *quasi*-normal to the C(01), O(11), N(21,61) coordination plane (C₂O₂/CON₂ interplanar dihedral, 89.1(1)°).

Reactions of alkynyliodine(III) species with soft nucleophiles are believed to occur via Michael addition to the electron-deficient β -carbon, followed by rearrangement to give the alkynyl group bonded to the nucleophile [19]. Organoplatinum(II) species, including pincer complexes, often act as nucleophiles, thus facilitating [C=CSiMe₃]⁺ transfer. Syntheses of the new class of complexes reported here occurs under mild conditions, the exchange of triflate for other groups at the platinum(IV) centre is facile, and the complexes isolated are stable at ambient temperature. Thus, it is anticipated that the synthetic protocol described herein provides the basis for a wider investigation of alkynyl(pincer)platinum(IV) chemistry.

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Appendix A. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. 247684). Copies of the information can be obtained

³ Typical synthesis, where solvents were dried and distilled, and all procedures carried out under argon: phenyl[(trimethylsilyl)ethynyl]iodonium triflate (0.15 m mol) was added to a stirred solution of the platinum(II) reagent (0.15 m mol) in acetone (10 ml) and stirring was continued for another 30 min. For complexes **1a** and **1b** acetone-d₆ was also used as a solvent to allow NMR characterisation. Sodium iodide (0.2 m mol) was added and the solution was stirred for a further 30 min. The solvent was removed in a vacuum and the residue was extracted with a minimum amount of dichloromethane. The suspension was filtered and the solvent removed in a vacuum. The residue was washed with a small amount of cold diethyl ether to give the product. Crystals of **2b** were obtained at 0 °C from a solution of the complex in dichloromethane/diethyl ether.



Fig. 1. Projection of a molecule of $Pt(O_2CAr_F)I(C \equiv CSiMe_3)(NCN)$ (1b), showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (°), Pt-C(1, 01)1.966(3), 1.951(3); Pt-N(21, 61) 2.136(3), 2.125(3); Pt-I 2.7469(3); Pt-O(11) 2.090(2); C(01)-C(02) 1.205(4); C(02)-Si(2) 1.828(3) and C(01)-Pt-C(1) 85.4(1); C(01)-Pt-N(21, 61) 93.5(1), 86.3(1); C(01)-Pt-O(11) 175.7(1); C(01)-Pt-I 90.83(9); Pt-C(01)-C(02) 172.7(3); C(01)-C(02)-Si(2) 165.4(3); C(1)-Pt-N(21, 61) 81.4(1), 81.1(1); C(1)-Pt-O(11) 98.9(1); C(1)-Pt-I 176.09(8); I-Pt-N(21, 61) 97.92(8), 99.58(8); O(11)-Pt-N(21, 61) 87.3(1), 93.4(1); I-Pt-(O11) 84.86(7).

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