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Access to Alkynylpalladium(IV) and -Platinum(IV) Species, Including Triorgano(diphosphine)metal(IV) Complexes and the Structural Study of an Alkynyl(pincer)platinum(IV) Complex, $Pt(O_2CAr_F)I(C\equiv CSiMe_3)(NCN)$ ($Ar_F = 4\text{-}CF_3C_6H_4$, NCN = [2,6-(dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$)

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New classes of alkynylplatinum(IV) complexes are described, and the first examples of alkynylpalladium(IV) complexes have been detected, including a triorganopalladium(IV) diphosphine complex. Alkynyliodine(III) triflate reagents $IPh(C\equiv CR^2)(OTf)$ ($R^2 = SiMe_3$, Ph) are able to transfer alkynyl groups to diorganoplatinum(II) and “pincer” complexes $Pt(O_2CAr)(NCN)$ (NCN = [2,6-(dimethylaminomethyl)-phenyl-*N*,*C*,*N*]$^-$, Ar = Ph, 4-trifluoromethylphenyl (Ar_F)); on addition of iodide ion, complexes with new alkynylplatinum(IV) kernels may be isolated: $PtIMe_2(C\equiv CR^2)(bpy)$ (**1**, **2**, **3a**) (bpy = 2,2′-bipyridine), $PtI(C_4H_8)(C\equiv CSiMe_3)(bpy)$ (**4a**), $PtIPh_2(C\equiv CSiMe_3)(Bu^t{}_2bpy)$ (**5a**), and $PtI(O_2CAr)(C\equiv CR^2)(NCN)$ [Ar = Ph (**14**, **15**), Ar_F (**16**, **17**)]. For the reagent $PtMe_2(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane], the unstable complexes $PtIMe_2(C\equiv CR^2)(dmpe)$ (**6a**, **8a**) are detected prior to reductive elimination of ethane and isolation of $PtI(C\equiv CR^2)(dmpe)$ (**7**, **9**). Isomerism is exhibited by the octahedral *fac*-$Pt^{IV}R_2$-$(C\equiv CR^2)$ complexes, where complexes **1** and **2** form as a mixture of complexes with the alkynyl group opposite the bidentate ligand and *cis* to the iodo ligand (**1a**−**6a**, **8a**), and *cis* to the bidentate ligand and *trans* to the iodo ligand (**1b**, **2b**), complexes **3a**−**5a**, **6a**, and **8a** having R groups mutually *cis*. An X-ray structural analysis for **16** shows distorted octahedral geometry about the metal with the iodo ligand *trans* to the carbon donor of the *mer*-pincer ligand. Studies of the reactivity of related palladium(II) substrates at low temperature allow detection of the pincer complex $Pd(O_2CPh)(OTf)(C\equiv CSiMe_3)(NCN)$ (**19**) and $PdIMe_2(C\equiv CSiMe_3)(dmpe)$ (**18**) as a model for frequently proposed “$Pd^{IV}XR_3P_2$” species in catalytic and stoichiometric reactions.

Introduction

The possible intermediacy of (η^1-alkynyl)palladium(IV) species has been discussed for several catalytic processes,[1,2] but there are no reports of the detection of any type of (η^1-alkynyl)palladium(IV) species, and similarly, there are numerous proposals for the intermediacy of to date undetected “$Pd^{IV}R_nP_2$” ($n = 1$,[3a] 2,[3b,c] 3;[2c,3d−g] P = phosphine donor) species. For the closely related congener platinum, (η^1-alkynyl)platinum(IV) species have been proposed as intermediates in the high-temperature activation of $Pt(C\equiv CR)_2$(1,5-cyclooctadiene) precatalysts for hydrosilation reactions,[4a] and via oxidatively induced reductive elimination, for the synthesis of the macrocycle $\overline{C\equiv C\text{-}X\text{-}C\equiv C\text{-}C\equiv C\text{-}X\text{-}C\equiv C}$ on addition of iodine to $\{CH_2(CH_2PPh_2)_2\text{-}P,P'\}Pt^{II}(\mu\text{-}C\equiv C\text{-}X\text{-}C\equiv C\text{-}C,C)_2Pt\{CH_2(CH_2PPh_2)_2\text{-}P,P'\}$ (X = 3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthiophene).[4b] The limited exploration of (η^1-alkynyl)platinum(IV) chemistry[5,6] includes a single phosphine complex,[6a,7a] and reported synthetic

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(7) (a) 4-Nitrophenyl azide reacts with *trans*-$Pt(C\equiv CPh)_2(PEt_3)_2$ to eliminate dinitrogen and form a complex containing a 2-tetrazene-1,4-diyl group, $Pt(C\equiv CPh)_2(\{N(4\text{-}NO_2C_6H_4)N{=}N{-}N(4\text{-}NO_2C_6H_4)\text{-}N,N'\})(PEt_3)_2$.[6a] (b) $(MeO_2C)C\equiv C(CO_2Me)$ reacts with $PtMe_2\{SnMe_2C(CO_2Me){=}C(CO_2Me)Se\text{-}Sn,Se\}(Bu^t{}_2bpy)$ [$Bu^t{}_2bpy$ = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine] to form a complex containing methyl, alkenyl, and alkynyl groups, $PtMe_2\{C(CO_2Me){=}CH(CO_2Me)\}\{C\equiv C(CO_2Me)\}(Bu^t{}_2bpy)$.[6b,c]

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routes that could be more widely applicable for the synthesis of Pt(IV) species are confined to the oxidation of $Pt^{II}(C{\equiv}CTol\text{-}4)_2(Me_2bpy)$ by iodine to form $Pt^{IV}I_2(C{\equiv}CTol\text{-}4)_2(Me_2bpy)$.[6d] For "pincer" complexes, access to Pt(IV) species has also been elusive.[5] Thus, the alkynylplatinum(II) bond in alkynyl{$C_6H_3(CH_2NMe_2)_2$-2,6-*N*,*C*,*N*′}platinum(II) complexes is not stable to halogen-containing oxidants,[8a] and cyclic voltammetry studies for this class of Pt(II) complex,[8a,b] and related complexes,[9] reveal irreversible oxidation processes.

In a search for routes to new classes of alkynylmetal(IV) (M = Pd, Pt) species, we have noted that alkynyl groups, formally as $[C{\equiv}CR]^+$, are transferred from iodine(III) reagents $IPh(C{\equiv}CR)(O_3SCF_3)$ to rhodium(I) and iridium(I) complexes to form d^6 (η^1-alkynyl)metal(III) complexes with release of iodobenzene.[10] We report here the application of alkynyliodine(III) reagents for the generation of detectable but unstable (η^1-alkynyl)dimethylpalladium(IV) and -platinum(IV) complexes of bidentate bis(dimethylphosphino)ethane (dmpe), the isolation of alkynylplatinum(IV) complexes including moieties $Pt^{IV}R^1_2(C{\equiv}CR^2)$ (R^1 = Me, Ph) and $Pt^{IV}(C{\equiv}CR^2)(NCN)$ ($[NCN]^-$ = [2,6-(dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$), and the detection of an unstable Pd(IV) pincer complex. Preliminary communications of part of this work have appeared.[11]

Experimental Section

The reagents $MMe_2(bpy)$ (M = Pd,[12] Pt[13]), $M(C_4H_8)(bpy)$ (M = Pd,[14] Pt[15]), $PtR_2(Bu^t_2bpy)$ (R = Me,[16] Ph[17]), $MMe_2(dmpe)$ (M = Pd,[18] Pt[19]), MCl(NCN) (M = Pd, Pt),[20] $M(O_2CPh)(NCN)$ (M = Pd, Pt),[21] and $IPh(C{\equiv}CR^2)(O_3SCF_3)$ ($R^2 = SiMe_3$, Ph)[22] were prepared as described; the new complex $Pt(O_2CAr_F)(NCN)$ was prepared by a method similar to that reported for $Pt(O_2CPh)(NCN)$.[21] ^1H NMR spectra were recorded on a Varian Unity Innova 400 MHz wide bore instrument at 399.7 MHz or on a Varian Mercury Plus 300 MHz spectrometer at 299.9 MHz, at room temperature unless indicated otherwise. ^{13}C NMR spectra at 75.4 MHz, ^{31}P NMR at 121.4 MHz (H_3PO_4 external standard), and COSY, HMQC, and HMBC spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. COSY NMR was used to assign all ^1H NMR spectra, and ^1H chemical shifts are given in ppm relative to $SiMe_4$. Microanalyses and LSMIS 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 m × 0.32 mm HP1 column (0.52 μm film thickness, He at 10 psi).

Synthesis of $Pt(O_2CAr_F)(NCN)$. Silver 4-trifluoromethylbenzoate (0.009 g, 0.039 mmol) was added to a solution of PtCl(NCN) (0.016 g, 0.038 mmol) in acetone (5 mL). The suspension was stirred for 15 h in the absence of light, then filtered through Celite. The solvent was removed under a vacuum to give the product as a colorless solid (18 mg, 95%). ^1H NMR (acetone-d_6) (300 MHz): δ 8.27 (d, ^3J = 7.6 Hz, 2H, H2,6), 7.71 (d, ^3J = 7.6 Hz, 2H, H3,5), 6.93 (dd, ^3J = 6.3, 8.4 Hz, 1H, H4-NCN), 6.80 (d, ^3J = 7.7 Hz, 2H, H3,5-NCN), 4.10 (s, $^3J_{Pt-H}$ = 47.6 Hz, ^4H, NCH_2), 3.04 (s, $^3J_{Pt-H}$ = 36.9 Hz, ^{12}H, NCH_3).

Synthesis of Diorgano(alkynyl)platinum(IV) Complexes 1−5a. General Synthesis. The iodine(III) reagent (0.051 mmol) was added to a stirred solution of the Pt(II) reagent (0.051 mmol) in acetone under argon. Stirring was continued for 2 h (2 days for complex **6**). Sodium iodide (9.0 mg, 0.060 mmol) in acetone (1 mL) was added, and the solution stirred for a further 2 h. For complexes **1**, **3a**, and **4a** the solvent was removed under a vacuum and the residue dissolved in the minimum amount of acetone; diethyl ether (5 mL) was added and the precipitated yellow product (**1**) collected by filtration. For the Bu^t_2bpy complexes **2**, **5a**, and **6**, the solvent was removed under a vacuum and the residue dissolved in the minimum amount of diethyl ether; the addition of pentane (5 mL) allowed the isolation of solid products by filtration.

$PtIMe_2(C{\equiv}CSiMe_3)(bpy)$ (1). Yield: 90%. Anal. Found: C, 33.44; H, 3.74; N, 4.78. Calcd for $C_{17}H_{23}N_2IPtSi$: C, 33.72; H, 3.83; N, 4.63. ^1H NMR (acetone-d_6) (400 MHz): *cis*-isomer (**1a**) δ 9.51 (m, 1H, H6-bpy), 8.87 (m, 1H, H6-bpy), 8.25 (m, 2H, H3-bpy), 8.10 (m, 2H, H4-bpy), 7.67 (m, 2H, H5-bpy), 1.76 (s, $^2J_{HPt}$ = 61.2 Hz, 3H, PtMe), 1.08 (s, $^2J_{HPt}$ = 68.8 Hz, 3H, PtMe), 0.20 (s, 9H, $SiMe_3$); *trans*-isomer (**1b**) δ 8.93 (m, 2H, H6-bpy), 8.30 (m, 2H, H3-bpy), 8.13 (m, 2H, H4-bpy), 7.67 (m, 2H, H5-bpy), 2.39 (s, $^2J_{HPt}$ = 73.2 Hz, 6H, PtMe), 0.20 (s, 9H, $SiMe_3$). IR (KBr disk): $\nu(C{\equiv}C)$ 2076 cm^{-1}.

$PtIMe_2(C{\equiv}CSiMe_3)(Bu^t_2bpy)$ (2). Yield: 85%. Anal. Found: C, 41.63; H, 5.33; N, 3.70. Calcd for $C_{25}H_{39}N_2IPtSi$: C, 41.84; H, 5.48; N, 3.90. ^1H NMR (acetone-d_6) (300 MHz): *cis*-isomer (**2a**) δ 9.40 (m, 1H, H6-bpy), 8.89 (m, 1H, H6-bpy), 8.74 (m, 1H, H3-bpy), 1.71 (s, $^2J_{HPt}$ = 68.0 Hz, 3H, PtMe), 1.01 (s, $^2J_{HPt}$ = 69.3 Hz, 3H, PtMe); *trans*-isomer (**2b**) 8.85 (m, 2H, H6-bpy), 2.35 (s, $^2J_{HPt}$ = 72.4 Hz, 3H, PtMe); **2a** and **2b** δ 8.41 (m, 1H, H3-bpy), 7.88 (m, 2H, H5-bpy), 1.49 (s, 3H, Bu^t), 1.48 (s, 9H, Bu^t), 0.15 (s, 9H, $SiMe_3$). IR (KBr disk): $\nu(C{\equiv}C)$ 2075 cm^{-1}.

***cis*-$PtIMe_2(C{\equiv}CPh)(bpy)$ (3a).** Yield: 89%. Anal. Found: C, 39.21; H, 3.18; N, 4.42. Calcd for $C_{20}H_{19}N_2IPt$: C, 39.42; H, 3.14; N, 4.60. ^1H NMR (acetone-d_6) (400 MHz): δ 9.59 (m, 1H, H6-bpy), 9.04 (m, 1H, H6-bpy), 8.93 (m, 2H, H3-bpy), 8.41 (m, 2H, H4-bpy), 7.95 (m, 2H, H5-bpy), 7.40 (d, ^3J = 8.4 Hz, 2H, H2,6-Ph), 7.27 ('t', 2H, H3,5-Ph), 7.15 (t, ^3J = 7.4 Hz, 1H, H4-Ph), 1.85 (s, $^2J_{HPt}$ = 67.6 Hz, 3H, PtMe), 1.12 (s, $^2J_{HPt}$ = 69.2 Hz, 3H, PtMe). IR (KBr disk): $\nu(C{\equiv}C)$ 2145 cm^{-1}.

***cis*-$PtI(C_4H_8)(C{\equiv}CSiMe_3)(bpy)$ (4a).** Yield: 78%. Anal. Found: C, 36.09; H, 3.70; N, 4.60. Calcd for $C_{19}H_{25}N_2IPtSi$: C, 36.14; H, 3.99; N, 4.44. ^1H NMR (acetone-d_6) (400 MHz): δ 9.46 (m, 1H, H6-bpy), 9.10 (m, 1H, H6-bpy), 8.82 (m, 2H, H3-bpy), 8.41 (m, 2H, H4-bpy), 7.95 (m, 2H, H5-bpy), 3.26 [m(b), 1H, CH_2], 2.46 [m(b), 1H, CH_2], 2.28 [m(b), 1H, CH_2], 1.61 [m(b), 1H, CH_2],

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1.34 [m(b), 3H, CH$_2$], 0.61 [m(b), 1H, CH$_2$], 0.11 (s, 9H, SiMe$_3$). IR (KBr disk): ν(C$\equiv$C) 2076 cm^{-1}.

***cis*-PtIPh$_2$(C$\equiv$CSiMe$_3$)(Bu$^t{}_2$bpy) (5a)** (from dichloromethane/diethyl ether). Yield: 82%. Anal. Found: C, 49.86; H, 5.14; N, 3.26. Calcd for $C_{35}H_{43}N_2IPtSi$: C, 49.94; H, 5.15; N, 3.33. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 9.73 (m, 1H, H6-bpy), 9.07 (m, 1H, H6-bpy), 8.73 (d, $^4J = 2.0$ Hz, 1H, H3-bpy), 8.71 (d, $^4J = 1.8$ Hz, 1H, H3-bpy), 8.01 (dd, $^3J = 6.0$ Hz, $^4J = 1.8$ Hz, 1H, H5-bpy), 7.96 (dd, $^3J = 6.2$ Hz, $^4J = 1.8$ Hz, 1H, H5-bpy), 7.67 (d, $^3J_{\mathrm{HPt}} = 45.2$ Hz, $^3J = 8.3$ Hz, 2H, H2,6-Ph), 7.00 (m, 1H, H4$-$Ph), 6.92 (m, 2H), 6.81 (m, 3H), 6.70 (m, 2H), 1.47 (s, 9H, Bu^t), 1.46 (s, 9H, Bu^t), 0.15 (s, 9H, SiMe$_3$). IR (KBr disk): ν(C$\equiv$C) 2079 cm^{-1}.

***cis*-PtIMe$_2$(C$\equiv$CSiMe$_3$)(dmpe) (6a) and PtI(C$\equiv$CSiMe$_3$)(dmpe) (7).** Phenyl{(trimethylsilyl)ethynyl}iodonium triflate (10.0 mg, 0.022 mmol) was added to a stirred solution of PtMe$_2$(dmpe) (8.3 mg, 0.022 mmol) in acetone-*d*$_6$ (1 mL) at -50 °C under argon. Stirring was continued for 30 min. Sodium iodide (4.5 mg, 0.030 mmol) was added, and the solution was stirred for a further 1 h at -50 °C. The NMR spectrum of **6a** was recorded. The solution was warmed to room temperature, and stirring was continued for 15 h. The solvent was removed under a vacuum and the residue dissolved in the minimum amount of dichloromethane. Pentane (5 mL) was added and the precipitate collected by filtration. For complex **6a**, ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 2.10$-$1.70 (m, PCH$_2$ and acetone), 1.65$-$1.37 (m, 6H, PMe, COSY indicates two environments), 1.25$-$1.18 (m, 3H, PMe), 1.15$-$0.95 (m, 6H, PtMe), 0.94$-$0.83 (m, 3H, PMe), 0.00 (s, 9H, SiMe$_3$). ^{31}P NMR (acetone-*d*$_6$) (121.4 MHz): δ 1.35 ($^1J_{\mathrm{PtP}} = 1160$ Hz), -2.81 ($^1J_{\mathrm{PtP}} = 1753$ Hz). For complex **7**, yield: 82%. Anal. Found: C, 22.96; H, 4.53. Calcd for $C_{11}H_{25}P_2IPtSi$: C, 23.21; H, 4.43. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 2.32$-$1.95 (m, PCH$_2$ and acetone), 1.28$-$1.15 (m, 6H, PMe), 1.10$-$0.94 (m, 6H, PMe), 0.05 (s, 9H, SiMe$_3$). ^{31}P NMR (acetone-*d*$_6$) (121.4 MHz): δ 26.8 ($^1J_{\mathrm{PtP}} = 2307$ Hz), 26.3 ($^1J_{\mathrm{PtP}} = 2225$ Hz). IR (KBr disk): ν(C$\equiv$C) 2039 cm^{-1}.

***cis*-PtIMe$_2$(C$\equiv$CPh)(dmpe) (8a) and PtI(C$\equiv$CPh)(dmpe) (9).** The procedure was followed as for **6a** and **7**, using phenyl(phenylethynyl)iodonium triflate. For complex **8a**, ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 7.35 (d, $J = 7.6$ Hz, 2H, H2,6), 7.25 (t, $J = 7.4$ Hz, 2H, H3,5), 7.12 (t, $J = 7.4$ Hz, 1H, H4), 2.13$-$1.75 (m, PCH$_2$ and acetone), 1.69$-$1.36 (m, 6H, PMe, COSY indicates two environments), 1.28$-$1.19 (m, 3H, PMe), 1.23$-$0.91 (m, 6H, PtMe), 1.05$-$0.88 (m, 3H, PMe). ^{31}P NMR (acetone-*d*$_6$) (121.4 MHz): δ 1.47 ($^1J_{\mathrm{PtP}} = 1210$ Hz), -2.08 ($^1J_{\mathrm{PtP}} = 1594$ Hz). For complex **9**, yield: 74%. Anal. Found: C, 29.18; H, 3.43. Calcd for $C_{14}H_{21}P_2IPt$: C, 29.33; H, 3.69. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 7.38 (d, $J = 7.8$ Hz, 2H, H2,6), 7.27 (t, $J = 7.5$ Hz, 2H, H3,5), 7.15 (t, $J = 7.4$ Hz, 1H, H4), 2.27$-$2.04 (m, PCH$_2$ and acetone), 1.33$-$1.19 (m, 6H, PMe), 1.18$-$0.99 (m, 6H, PMe). ^{31}P NMR (acetone-*d*$_6$) (121.4 MHz): δ 27.8 ($^1J_{\mathrm{PtP}} = 2273$ Hz), 26.7 ($^1J_{\mathrm{PtP}} = 2299$ Hz). IR (KBr disk): ν(C$\equiv$C) 2113 cm^{-1}.

General Synthesis of Alkynyl(pincer)platinum(IV) Complexes 10$-$17.** Phenyl{(trimethylsilyl)ethynyl}iodonium triflate (0.15 mmol) was added to a stirred solution of the platinum(II) reagent (0.15 mmol) in acetone (10 mL) under argon, and stirring was continued for another 30 min. For complexes **10** to **13** acetone-*d*$_6$ was also used as a solvent to allow NMR characterization. Sodium iodide (0.2 mmol) was added and the solution stirred for a further 30 min. The solvent was removed under a vacuum and the residue was extracted with a minimum amount of dichloromethane. The suspension was filtered and the solvent removed under a vacuum. The residue was washed with a small amount of cold diethyl ether to give the product. Crystals of **15 were obtained at 0 °C from a solution of the complex in dichloromethane/diethyl ether.

Pt(O$_2$CPh)(OTf)(C$\equiv$CSiMe$_3$)(NCN) (10). ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 7.85 (d, $^3J = 8.1$ Hz, 2H, H2,6), 7.53 (m, 2H, H4, H4-NCN), 7.41 (m, 2H, H3,5), 7.24 (d, $^3J = 8.1$ Hz, 2H, H3,5-NCN), 4.77 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 30.4$ Hz, 2H, NCH$_2$), 4.61 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 39.0$ Hz, 2H, NCH$_2$), 3.37 (s, $^3J_{\mathrm{HPt}} = 41.7$ Hz, 6H, NMe), 2.97 (s, $^3J_{\mathrm{HPt}} = 24.3$ Hz, 6H, NMe), 0.08 (s, 9H, SiMe$_3$).

Pt(O$_2$CPh)(OTf)(C$\equiv$CPh)(NCN) (11). ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 7.96 (d, $^3J = 8.1$ Hz, 2H, H2,6-O$_2$CPh), 7.62$-$7.38 [m(b), 6H], 7.28$-$7.20 (m, 4H), 7.18 (t, $^3J = 7.4$ Hz, 1H, H4$-$C$\equiv$CPh), 4.77 (d, $^2J = 14.9$ Hz, $^3J_{\mathrm{HPt}} = 31.2$ Hz, 2H, NCH$_2$), 4.61 (d, $^2J = 14.9$ Hz, $^3J_{\mathrm{HPt}} = 39.0$ Hz, 2H, NCH$_2$), 3.37 (s, $^3J_{\mathrm{HPt}} = 41.7$ Hz, 6H, NMe), 2.97 (s, $^3J_{\mathrm{HPt}} = 24.2$ Hz, 6H, NMe).

Pt(O$_2$CAr$_F$)(OTf)(C$\equiv$CSiMe$_3$)(NCN) (12). ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.06 (d, $^3J = 8.2$ Hz, 2H, H2,6), 7.75 (m, 2H, H3,5), 7.40 (t, $^3J = 7.5$ Hz, 1H, H4-NCN), 7.24 (d, $^3J = 7.8$ Hz, 2H, H3,5-NCN), 4.77 (d, $^2J = 15.1$ Hz, $^3J_{\mathrm{HPt}} = 33.0$ Hz, 2H, NCH$_2$), 4.62 (d, $^2J = 15.1$ Hz, $^3J_{\mathrm{HPt}} = 37.6$ Hz, 2H, NCH$_2$), 3.37 (s, $^3J_{\mathrm{HPt}} = 41.9$ Hz, 6H, NMe), 2.99 (s, $^3J_{\mathrm{HPt}} = 24.0$ Hz, 6H, NMe), 0.08 (s, 9H, SiMe$_3$).

Pt(O$_2$CAr$_F$)(OTf)(C$\equiv$CPh)(NCN) (13). ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.14 (d, $^3J = 8.2$ Hz, 2H, H2,6-O$_2$CAr$_F$), 7.80$-$7.73 (m, 2H, H3,5-O$_2$CAr$_F$), 7.59$-$7.38 (m, 3H), 7.31$-$7.22 (m, 4H), 7.20 (t, $^3J = 7.5$ Hz, 1H, H4-C$\equiv$CPh), 4.76 (d, $^2J = 15.1$ Hz, $^3J_{\mathrm{HPt}} = 33.2$ Hz, 2H, NCH$_2$), 4.62 (d, $^2J = 15.0$ Hz, $^3J_{\mathrm{HPt}} = 37.6$ Hz, 2H, NCH$_2$), 3.38 (s, $^3J_{\mathrm{HPt}} = 41.9$ Hz, 6H, NMe), 2.99 (s, $^3J_{\mathrm{HPt}} = 24.1$ Hz, 6H, NMe).

Pt(O$_2$CPh)I(C$\equiv$CSiMe$_3$)(NCN) (14). Yield: 93%. Anal. Found: C, 39.28; H, 4.63; N, 3.58. Calcd for $C_{24}H_{33}N_2O_2IPtSi$: C, 39.40; H, 4.55; N, 3.83. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.04 (d, $^3J = 8.2$ Hz, 2H, H2,6), 7.46$-$7.31 [m(b), 4H, H3, H4, H4-NCN], 7.01 (d, $^3J = 7.7$ Hz, 2H, H3,5-NCN), 4.65 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 33.1$ Hz, 2H, NCH$_2$), 4.40 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 35.5$ Hz, 2H, NCH$_2$), 3.41 (s, $^3J_{\mathrm{HPt}} = 42.1$ Hz, 6H, NMe), 3.08 (s, $^3J_{\mathrm{HPt}} = 26.4$ Hz, 6H, NMe), 0.08 (s, 9H, SiMe$_3$). IR (KBr disk): ν(C$\equiv$C) 2078 cm^{-1}.

Pt(O$_2$CPh)I(C$\equiv$CPh)(NCN) (15). Yield: 82%. Anal. Found: C, 44.23; H, 3.75; N, 3.75. Calcd for $C_{27}H_{29}N_2O_2IPt$: C, 44.09; H, 3.97; N, 3.81. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.14 (d, $^3J = 8.1$ Hz, 2H, H2,6-O$_2$CPh), 7.51$-$7.24 [m(b), 8H], 7.15 (t, $^3J = 7.5$ Hz, 1H, H4$-$C$\equiv$CPh), 7.06 (d, $^3J = 7.6$ Hz, 2H, H3,5-NCN), 4.68 (d, $^2J = 14.9$ Hz, $^3J_{\mathrm{HPt}} = 32.8$ Hz, 2H, NCH$_2$), 4.44 (d, $^2J = 14.9$ Hz, $^3J_{\mathrm{HPt}} = 36.2$ Hz, 2H, NCH$_2$), 3.43 (s, $^3J_{\mathrm{HPt}} = 42.3$ Hz, 6H, NMe), 3.13 (s, $^3J_{\mathrm{HPt}} = 26.7$ Hz, 6H, NMe). IR (KBr disk): ν(C$\equiv$C) 2143 cm^{-1}.

Pt(O$_2$CAr$_F$)I(C$\equiv$CSiMe$_3$)(NCN) (16). Yield: 89%. Anal. Found: C, 37.48; H, 3.89; N, 3.48. Calcd for $C_{25}H_{32}N_2O_2IF_3PtSi$: C, 37.55; H, 4.03; N, 3.50. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.20 (d, $^3J = 8.6$ Hz, 2H, H2,6), 7.71 (d, $^3J = 8.6$ Hz, 2H, H3,5), 7.41 (t, $^3J = 7.6$ Hz, 1H, H4-NCN), 7.03 (d, $^3J = 7.7$ Hz, 2H, H3,5-NCN), 4.67 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 32.9$ Hz, 2H, NCH$_2$), 4.42 (d, $^2J = 14.8$ Hz, $^3J_{\mathrm{HPt}} = 35.2$ Hz, 2H, NCH$_2$), 3.41 (s, $^3J_{\mathrm{HPt}} = 42.0$ Hz, 6H, NMe), 3.08 (s, $^3J_{\mathrm{HPt}} = 25.9$ Hz, 6H, NMe), 0.08 (s, 9H, SiMe$_3$). IR (KBr disk): ν(C$\equiv$C) 2078 cm^{-1}.

Pt(O$_2$CAr$_F$)I(C$\equiv$CPh)(NCN) (17). Yield: 78%. Anal. Found: C, 41.69; H, 3.55; N, 3.40. Calcd for $C_{28}H_{28}N_2O_2IF_3Pt$: C, 41.85; H, 3.51; N, 3.49. ^{1}H NMR (acetone-*d*$_6$) (300 MHz): δ 8.25 (d, $^3J = 8.3$ Hz, 2H, H2,6-O$_2$CAr$_F$), 7.74 (d, $^3J = 8.5$ Hz, 2H, H3,5-O$_2$CAr$_F$), 7.45$-$7.26 (m, 5H), 7.15 (t, $^3J = 7.4$ Hz, 1H, H4-C$\equiv$CPh), 7.05 (d, $^3J = 7.7$ Hz, 2H, H3,5-NCN), 4.68 (d, $^2J = 15.0$ Hz, $^3J_{\mathrm{HPt}} = 31.9$ Hz, 2H, NCH$_2$), 4.44 (d, $^2J = 15.0$ Hz, $^3J_{\mathrm{HPt}} = 37.1$ Hz, 2H, NCH$_2$), 3.43 (s, $^3J_{\mathrm{HPt}} = 42.2$ Hz, 6H, NMe), 3.09 (s, $^3J_{\mathrm{HPt}} = 25.3$ Hz, 6H, NMe). IR (KBr disk): ν(C$\equiv$C) 2142 cm^{-1}.

NMR Studies of Reactivity of Palladium(II) Complexes. *cis*-PdIMe$_2$(C$\equiv$CSiMe$_3$)(dmpe) (18). Phenyl[(trimethylsilyl)ethynyl]iodonium triflate (10.0 mg, 0.022 mmol) was added to a stirred solution of PdMe$_2$(dmpe) (6.4 mg, 0.022 mmol) in acetone-*d*$_6$ (1 mL) at -50 °C under argon. Stirring was continued for 1 h. Sodium iodide (4.5 mg, 0.030 mmol) was added, and the solution was stirred for a further 1 h at -50 °C. ^{1}H NMR (acetone-*d*$_6$, -50 °C) (300 MHz): δ 2.80$-$2.21 (m, 4H, PCH$_2$), 2.20 (s, 3H, PdMe), 1.84 (s,

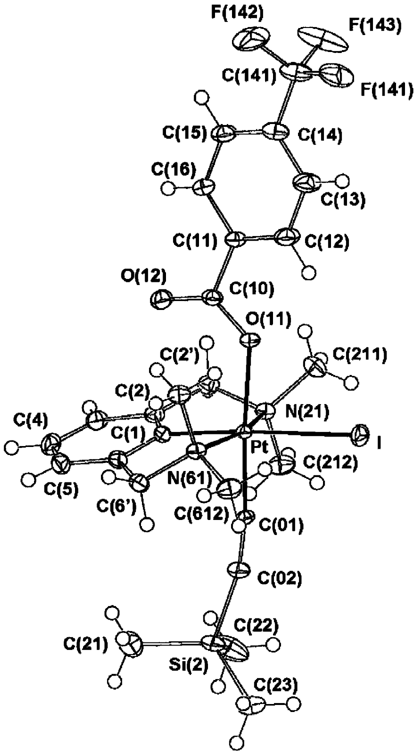

Figure 1. Projection of a molecule of $Pt(O_2CAr_F)I(C{\equiv}CSiMe_3)$-(NCN) (**16**), showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

3H, PdMe), 1.53−1.26 (m, 6H, PMe, COSY indicates two environments), 1.17−0.86 (m, 6H, PMe, COSY indicates two environments), 0.14 (s, 9H, $SiMe_3$. ^{31}P NMR (acetone-d_6, −50 °C) (121.4 MHz): δ 8.2 (d, $^3J_{P-P} = 25.2$ Hz), −16.5 (d, $^3J_{P-P} = 25.5$ Hz). The complex decomposed slowly at −50 °C to give a dark suspension with complex NMR spectra.

$Pd(O_2CPh)(OTf)(C{\equiv}CSiMe_3)(NCN)$ (19). Phenyl[(trimethylsilyl)ethynyl]iodonium triflate (10.0 mg, 0.022 mmol) was added to a stirred solution of $Pd(O_2CPh)(NCN)$ (9.2 mg, 0.022 mmol) in acetone-d_6 (1 mL) at −50 °C under argon. The solution was kept at −80 °C for 1 week. ^1H NMR (acetone-d_6, −50 °C) (300 MHz): δ 7.85 (d, $^3J = 7.5$ Hz, 2H, H2,6), 7.76−7.69 (m, 1H, H4-NCN), 7.55 (t, $^3J = 7.5$ Hz, 1H, H4), 7.38 (d, $^3J = 7.5$ Hz, 2H, H3,5-NCN), 7.32 (d, $^3J = 7.5$ Hz, 2H, H3,5), 5.25 (d, $^2J = 14.5$ Hz, 2H, NCH_2), 4.81 (d, $^2J = 14.5$ Hz, 2H, NCH_2), 3.46 (s, 3H, NMe), 3.43 (s, 3H, NMe), 3.30 (s, 3H, NMe), 3.23 (s, 3H, NMe), 0.48 (s, 9H, $SiMe_3$).

X-ray Data Collection, Structure Determination, and Refinement for $Pt(O_2CAr_F)I(C{\equiv}CSiMe_3)(NCN)$ (16). A crystal of **16** was obtained at 0 °C from a solution of the complex in dichloromethane/diethyl ether. A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS instrument, $2\theta_{max} = 75°$, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K), yielding 27 502 total reflections, merging to 14 219 unique (R_{int} 0.037) after empirical/multiscan absorption correction (proprietary software), 12 056 with $F > 4\sigma(F)$ considered "observed" and used in the full-matrix least squares refinement on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z\ U_{iso})_H$ being constrained. Final residuals on $|F|$ at convergence were $R = 0.034$, R_w [weights: $(\sigma^2(F^2) + 1.2F^2)^{-1}$] = 0.073. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[23] Pertinent results are given in Figure 1 and Table 1. *Crystal data*: $C_{25}H_{32}F_3IN_2O_2PtSi$, $M = 799.6$, triclinic, space group $P\bar{1}$, $a = 10.0061(6)$ Å, $b = 10.8050(7)$ Å, $c = 13.6912(9)$ Å, $\alpha = 85.450(1)°$, $\beta = 70.118(1)°$, $\gamma = 89.947(1)°$, $V = 1387.1(2)$ Å^3, D_c ($Z = 1$) = 1.914 g cm^{-3}, $\mu_{Mo} = 6.3$ mm^{-1}; specimen: 0.25 × 0.15 × 0.08 mm; $T_{min/max} = 0.57$.

Results

Reactivity Studies for Platinum(II) Substrates. The readily prepared reagents $IPh(C{\equiv}CR^2)(OTf)$ ($R^2 = SiMe_3$, Ph)[22] were chosen as representative alkynyliodine(III) reagents, and reactivity studies were initially confined to $PtMe_2(bpy)$ as the Pt(II) substrate. Successful isolation of Pt(IV) complexes encouraged studies of $PtPh_2(Bu^t{}_2bpy)$ [$Bu^t{}_2bpy$ = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine], where the $Bu^t{}_2bpy$ ligand is known to enhance the solubility of diarylplatinum(II) species,[17] the platinacyclopentane complex $Pt(C_4H_8)(bpy)$, the 1,2-bis(dimethylphenylphosphino)ethane complex $PtMe_2(dmpe)$, and the 'pincer' reagents $Pt(O_2CAr)(NCN)$ (Ar = Ph, Ar_F (4-trifluoromethylphenyl); NCN = [2,6-(dimethylaminomethyl)phenyl-*N,C,N*]$^-$). In all cases where reactions occurred, iodobenzene as a product was detected by ^1H NMR spectroscopy.

Diorgano(alkynyl)platinum(IV) complexes of nitrogen donor ligands (**1**−**5**) were isolated in 78−90% yield from reactions at ambient temperature (Scheme 1). The Pt(II) substrates were reacted with phenyl(alkynyl)iodine(III) triflates, followed by addition of iodide as a ligand known to participate in a wide range of stable triorganoplatinum(IV) complexes. Organoplatinum resonances moved downfield on oxidation, e.g., PtMe by 0.1−1.44 for **1**−**3**, and H2,6-Ph by 0.22 for **5a**. Isomerism was readily discernible from ^1H NMR spectra; for example, where *cis*- and *trans*- designate the orientation of alkynyl and iodo ligands (Scheme 1), the *cis*-isomers (**3a**, **4a**, **5a**) exhibit two pyridine environments, **3a** exhibits two methylplatinum environments ($^2J_{HPt} = 61.2−73.2$ Hz), the platinacyclopentane complex **4a** exhibits six methylene multiplets, and integrations are consistent within isomers and between isomers for mixtures of *cis*- and *trans*-isomers (**1a**, **1b**; **2a**, **2b**). Infrared spectra of the isolated complexes **1**, **2**, and **3a**−**5a** exhibit $\nu(C{\equiv}C)$ in the range 2075−2145 cm^{-1}, similar to the range exhibited by other isolated alkynylplatinum complexes described here (**7**, **9**, **15**−**17**) (2039−2145 cm^{-1}).

The phosphine complex $PtMe_2(dmpe)$ reacted rapidly and cleanly with the iodonium reagents, followed by sodium iodide, to give ethane (detected by NMR) and the complexes $PtI(C{\equiv}CR^2)(dmpe)$ [$R^2 = SiMe_3$ (**7**), Ph (**9**)] in 82% and 74% isolated yield, characterized by microanalysis, infrared spectroscopy, and both ^1H and ^{31}P NMR. On examining these reactions at −50 °C, ^1H and ^{31}P NMR spectra revealed the formation of intermediates *cis*-[$PtIMe_2(C{\equiv}CR^2)(dmpe)$)] (**6a**, **8a**). Spectra of the Pt(IV) complexes show four PMe environments and two PtMe environments, consistent with a *cis*-configuration, and as for the nitrogen donor complexes, complexes **6a** and **8a** exhibit PtMe resonances in ^1H NMR spectra downfield from the Pt(II) reagent, in these cases by ~0.8 ppm. The single ^{31}P resonance for $PtMe_2(dmpe)$, at 26.8 ppm, becomes two complex resonances for the Pt(IV) complexes, upfield, at 1.35 and −2.81 ppm (**6a**) and 1.47 and −2.08 ppm (**8a**), exhibiting $^1J_{PtP}$ coupling (1160 and 1753 Hz for **6a**, 1210 and 1594 Hz for **8a**). The isolated Pt(II) complexes $PtI(C{\equiv}CR^2)(dmpe)$ (**7**, **9**) exhibit appropriate integration in the ^1H NMR spectra and two PMe environments, $\nu(C{\equiv}C)$ at 2039 (**7**) and 2113 cm^{-1} (**9**), and ^{31}P resonances are in the same region as the $PtMe_2(dmpe)$ reagent (26.3 and 27.8 for **7**, 26.7 and 27.8 ppm for **9**) and exhibit $^1J_{PtP}$ coupling (2307 and 2225 Hz for **7**, 2273 and 2299 Hz for **9**).

The pincer complexes $Pt(O_2CAr)(NCN)$ (Ar = Ph, Ar_F) also reacted readily with $IPh(C{\equiv}CR^2)(OTf)$ at ambient temperature,

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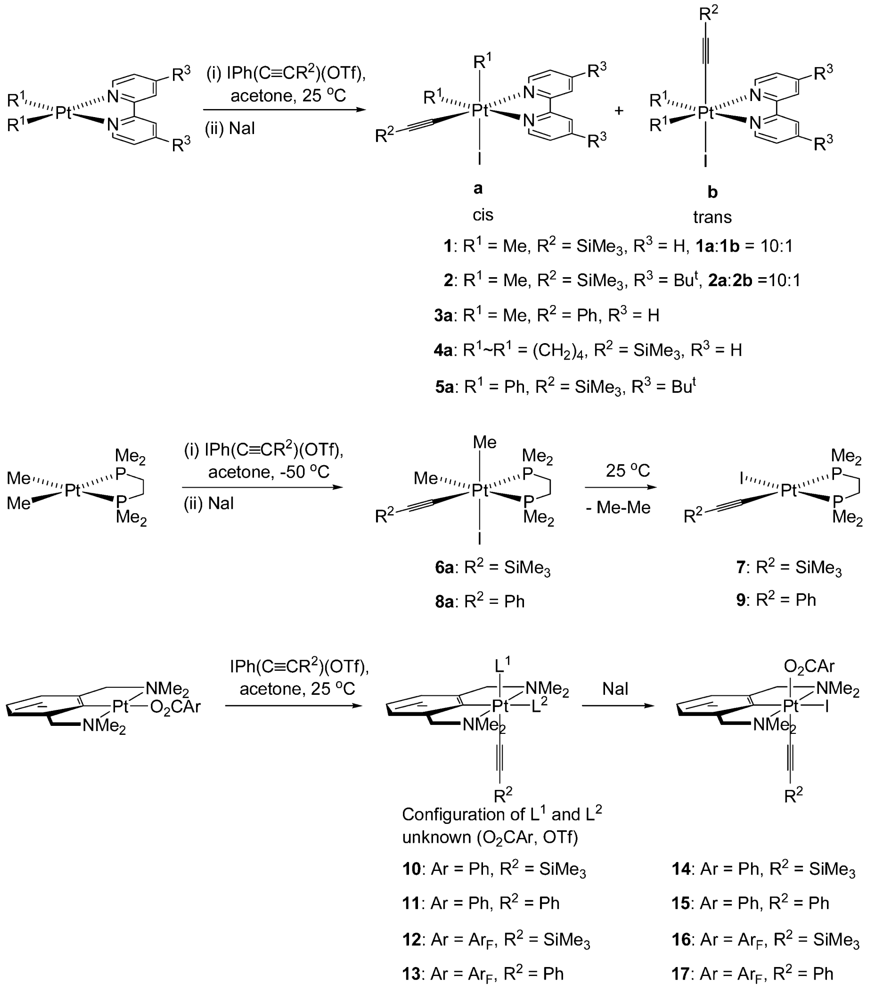
(23) Hall, S. R.; du Boulay, D. J.; Olthoff-Hazekamp, R.; Eds. *The XTAL 3.7 System*; University of Western Australia, 2001.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Pt(O_2CAr_F)I(C\equiv CSiMe_3)(NCN)$ (16)

	Bond Distances		
Pt−C(01, 1)	1.951(3), 1.966(3)	C(01)−C(02)	1.205(4)
Pt−N(21, 61)	2.136(3), 2.125(3)	C(02)−Si(2)	1.828(3)
Pt−O(11)	2.090(2)	C(10)−O(11)	1.275(4)
Pt−I	2.7469(3)	C(10)−O(12)	1.232(4)
	Bond Angles		
C(01)−Pt−C(1)	85.4(1)	I−Pt−O(11)	84.86(7)
C(01)−Pt−N(21, 61)	93.5(1), 86.3(1)	Pt−C(01)−C(02)	172.7(3)
C(1)−Pt−N(21, 61)	81.4(1), 81.1(1)	Pt−C(1)−C(2, 6)	117.5(3), 117.4(3)
N(21)−Pt−N(61)	162.50(11)	Pt−N(21)−C(2′)	106.0(2)
O(11)−Pt−C(01, 1)	175.7(1), 98.9(1)	Pt−N(61)−C(6′)	106.5(2)
I−Pt−C(01, 1)	90.83(9), 176.09(8)	Pt−O(11)−C(10)	132.8(2)
I−Pt−N(21, 61)	97.92(8), 99.58(8)		

Scheme 1



1: R^1 = Me, R^2 = $SiMe_3$, R^3 = H, **1a**:**1b** = 10:1

2: R^1 = Me, R^2 = $SiMe_3$, R^3 = Bu^t, **2a**:**2b** =10:1

3a: R^1 = Me, R^2 = Ph, R^3 = H

4a: R^1~R^1 = $(CH_2)_4$, R^2 = $SiMe_3$, R^3 = H

5a: R^1 = Ph, R^2 = $SiMe_3$, R^3 = Bu^t

6a: R^2 = $SiMe_3$

8a: R^2 = Ph

7: R^2 = $SiMe_3$

9: R^2 = Ph

10: Ar = Ph, R^2 = $SiMe_3$

11: Ar = Ph, R^2 = Ph

12: Ar = Ar_F, R^2 = $SiMe_3$

13: Ar = Ar_F, R^2 = Ph

14: Ar = Ph, R^2 = $SiMe_3$

15: Ar = Ph, R^2 = Ph

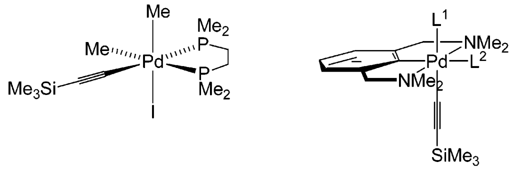
16: Ar = Ar_F, R^2 = $SiMe_3$

17: Ar = Ar_F, R^2 = Ph

and in view of the results reported below for palladium chemistry, the intermediate triflate species (**10**−**13**) were characterized by ^{1}H NMR spectra but not isolated (Scheme 1). The iodo complexes (**14**−**17**) were obtained in 78−93% yield and characterized by microanalysis (CHN) and infrared spectra (ν(C≡C) 2078−2143 cm^{-1}); complex **16** was crystallized for a structural analysis (see below). ^{1}H NMR spectra of **10**−**17** are consistent with the configuration found for the crystal, e.g., two *N*-methyl environments (both exhibiting $^3J_{PtH}$ coupling 24−42.3 Hz), indicating the presence of two inequivalent groups in relation to the Pt(NCN) coordination plane and large ^2J coupling (14.8−15.1 Hz) for the geminal CH_2 groups ($^3J_{PtH}$ 30.4−39 Hz). For those complexes where the H4 resonance (**12**, **16**) and H3,5 resonance (**10**, **12**, **14**, **15**, **17**) are separated from other resonances and readily assigned, they are shifted downfield by 0.47 (H4) and 0.22−0.45 ppm (H3,5). The orientation of the carboxylate and triflate groups in the coordination sphere of **10**−**13** and the Pd(IV) complex **19** (see below) could not be determined. NMR data for **14**, **15**, and **17** indicate that the orientations of carboxylate and iodo groups in these complexes are identical to those determined for **16** (Figure 1); for example, the CH_2 and NMe_2 resonances for the pincer ligand are almost identical for **14**−**17** (within 0.04 ppm), but the alternative configuration (iodo *cis* to the pincer) would place the iodo group much closer to the CH_2 group of the pincer and more distant from one methyl group of the NMe_2 groups.

Reactivity Studies for Palladium(II) Substrates. Initial low-temperature ^{1}H NMR studies indicated that detection of Pd(IV) species was feasible but difficult, so that detailed studies were confined to $IPh(C\equiv CSiMe_3)(OTf)$ as reagent because of the presence of the simple trimethylsilyl NMR singlet. Reaction with $PdMe_2(bpy)$ at −50 °C led to very complex ^{1}H NMR

Scheme 2



18

19: configuration of benzoate and triflate ligands unknown

spectra that could not be interpreted; slow decomposition occurs at this temperature to give a black suspension, and similar results were found for Pd(CH_2)$_4$(bpy).

However, reaction with the phosphine complex PdMe$_2$(dmpe) proceeded cleanly at −50 °C, to give spectra readily interpretable as showing the presence of PdIMe$_2$(C≡CSiMe$_3$)(dmpe) (**18**) with the same configuration as **6a** (Scheme 2). In a manner similar to the Pt(IV) analogue **6a**, the PdMe resonance is shifted downfield by ~0.4 and ~1 ppm, forming two multiplet resonances in 1:1 ratio, four PMe environments (multiplets) are observed, and the single ^{31}P resonance for PdMe$_2$(dmpe) is shifted upfield to form resonances at 8.2 and −16.5 ppm, exhibiting $^3J_{PP}$ 25.3 Hz. The average upfield shift on formation of the Pd(IV) complex (**18**) from PdMe$_2$(dmpe), 26.0 ppm, is almost identical to that for formation of the Pt(IV) analogue (**6a**) from PtMe$_2$(dmpe), 27.5 ppm, and also very similar to that reported for the *mono*-phosphine complex [Pd^{IV}Me$_3$(bpy)(PMe$_2$Ph)][OTf] compared with [Pd^{II}Me(bpy)(PMe$_2$Ph)][OTf], 21.8 ppm [the Pd(IV) cation resonance occurs at −11.3 ppm].[24]

For the pincer system, Pd(O$_2$CPh)(NCN) was found to react slowly with IPh(C≡CSiMe$_3$)(OTf) at −50 °C, and to avoid concurrent decomposition, reaction was completed at −80 °C over 1 week. ^{1}H NMR spectra showed the formation of iodobenzene and, by comparison with changes observed on formation of the Pt(IV) complexes, resonances consistent with the presence of Pd(O$_2$CPh)(OTf)(C≡CSiMe$_3$)(NCN) (**19**), i.e., all environments assigned and exhibiting expected integration, geminal CH$_2$ resonances with ^2J 14.5 Hz, and resonances for the NCN protons H4 and H3,5 that are shifted downfield by 0.79 and 0.59 ppm, respectively. However, four NMe resonances were observed in the ratio 1:1:1:1, although COSY spectra indicated that these resonances belong to the same species; warming the solution to detect assumed fluxional behavior was not possible owing to decomposition, which resulted in a black suspension and complex spectra. As noted for platinum, NMR spectra do not allow confident prediction of the configuration for the six donor atoms at palladium, although the structural analysis for the Pt(IV) complex **16** and low-temperature NMR studies showing a *cis*-PdR$_2$ configuration for the diorganopalladium(IV) complexes PdX$_2$Me$_2$(L$_2$) (L$_2$ = bis(*p*-tolylimino)acenaphthene, bis(phenylimino)camphane)[25a] and PdI$_2$Me(Tol-4)(bpy) [25b] indicate that a "*cis*-Pd(*mer*-NCN)(C≡CSiMe$_3$)" fragment is expected (Scheme 2). Addition of sodium iodide to **19** at −50 °C resulted in extremely complex NMR spectra and a brown suspension indicating general decomposition.

Structural Study of Pt(O$_2$CAr$_F$)I(C≡CSiMe$_3$)(NCN) (16). In the solid state **16** has distorted octahedral geometry for platinum (Figure 1, Table 1), based on a meridionally coordinated pincer group, an iodo ligand *trans* to the pincer carbon donor [176.09(8)°], alkynyl and 4-trifluoromethylbenzoate groups oriented mutually *trans* [175.7(1)°], and a *cis*-PtC$_2$ moiety [85.4(1)°]. One molecule of **16** devoid of crystallographic symmetry comprises the asymmetric unit. The C(01)−C(02) distance and Pt−C(01)−C(02) angle, 1.205(4) Å and 172.7(3)°, are similar to those reported for square-planar Pt(II) pincer complexes, 1.195(10) Å and 170.6(7)° in Pt(C≡CR)(NCN) [R = C$_6$H$_2$(CH$_2$NMe$_2$)-2,6, I-4][28] and 1.200(4) Å and 174.5(2)° in the diimine pincer complex Pt(C≡CSiMe$_3$){C$_6$H$_3$(CHNR)$_2$-2,6} (R = C$_6$H$_3$(Pr^i)$_2$-2,6).[8c] The pincer ligand is nonplanar, with quasi-2 symmetry about the Pt−C(1) 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 [C$_2$O$_2$/CON$_2$ interplanar dihedral, 89.1(1)°].

Discussion

The readily accessible alkynyliodine(III) reagents provide a facile route to new classes of alkynylplatinum(IV) complex for nitrogen and phosphorus donor ancillary ligands, with potential for development of a more extensive chemistry including further studies of reductive elimination, illustrated by **6a** → **7** and **8a** → **9** in Scheme 1, related to the proposed roles of alkynylplatinum(IV) species in organic synthesis and catalysis.[4]

The high reactivity of alkynyliodine(III) reagents at low temperatures has allowed the first spectroscopic detection of alkynylpalladium(IV) complexes, including unstable species containing a bidentate phosphine donor (**18**) and a pincer ligand (**19**) shown in Scheme 2. Organopalladium(IV) species with a single phosphine donor have been reported,[24,26] and in a classic study Gillie and Stille obtained kinetic data suggesting the presence of an undetected *cis*-diphosphine intermediate "PdIMe$_3$(PPh$_2$Me)$_2$" in the reaction of *cis*-PdMe$_2$(PPh$_2$Me)$_2$ with iodomethane.[27a] Complex **18** represents the first example of spectroscopic detection of the "PdC$_3$P$_2$X" donor set frequently proposed as possible intermediates in stoichiometric[27] and catalytic reactions,[2c,3d−g] including for proposed alkynylpalladium(IV) intermediates,[2d] noting that the successful synthetic route to this donor set reported here is different from these proposals.

Supporting Information Available: Atomic parameters, bond distances and angles, and crystallographic details for **16**, a cif file for the structure determination, and projections of the structure of **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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