Reactivity of Diaryliodine(III) Triflates toward Palladium(II) and Platinum(II): Reactions of $C(sp^2)-I$ Bonds to Form Arylmetal(IV) Complexes; Access to Dialkyl(aryl)metal(IV), 1,4-Benzenediyl-Bridged Platinum(IV), and Triphenylplatinum(IV) Species; and Structural Studies of Platinum(IV) Complexes

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Diphenyliodine(III) triflate is able to transfer Ph^+ to Pd(II) and Pt(II) with cleavage of a phenyl−iodine bond and formation of metal(IV) species, leading to the first identified transfer of Ph^+ to Pd(II) from an aryl−halogen bond, and, for platinum, a methodology providing a facile route to dimethyl(aryl)platinum(IV) and 1,4-arenediyl-bridged Pt(IV) species and the first archetypal triarylplatinum(IV) complex. Thus, $[IPh_2][OTf]$ reacts with $PtMe_2(bpy)$ (bpy = 2,2′-bipyridine) at −50 °C to form iodobenzene and the Pt(IV) complex *trans*-$Pt^{IV}(OTf)Me_2Ph(N{\sim}N)$ (**1b**) (Ph trans to OTf), and on addition of NaI, the species $PtIMe_2Ph(bpy)$ (**2a** (Ph cis to I) and **2b** (Ph trans to I) in 2:1 ratio) may be isolated at −20 °C. Similarly, metalla(II)cyclopentane complexes $M(C_4H_8)(bpy)$ react with $[IPh_2][OTf]$ to form *trans*-$Pt(OTf)(C_4H_8)Ph(bpy)$ (**3b**) and a 1:1 ratio of *cis*- (**4a**) and *trans*-$Pd(OTf)(C_4H_8)Ph(bpy)$ (**4b**); addition of halide ion gives *trans*-$PtI(C_4H_8)Ph(bpy)$ (**5b**) and a 1:3 ratio of cis and trans isomers for $PdI(C_4H_8)Ph(bpy)$ (**6a**, **6b**) and $PdCl(C_4H_8)Ph(bpy)$ (**7a**, **7b**). Complex **5b** isomerizes to form a 2:1 mixture of *cis*-$PtI(C_4H_8)Ph(bpy)$ (**5a**) and **5b** at ambient temperature in acetone. Dimethyl(2,2′-bipyridine)palladium(II) reacts with $[IPh_2][OTf]$ to form $Pd(OTf)Me_2Ph(bpy)$, followed by transfer of a methyl group from Pd(IV) to Pd(II), to form trimethylpalladium(IV) species. Dimethyl(2,2′-bipyridine)platinum(II) reacts with $[IPh(C_6H_4\text{-}4\text{-}I)][OTf]$, followed by addition of sodium iodide, to form a 1:1 mixture of *trans*-$PtIMe_2Ph(bpy)$ (**2b**) and *trans*-$PtIMe_2(C_6H_4\text{-}4\text{-}I)(bpy)$ (**8b**), and with $[IPh(C_6H_4\text{-}4\text{-}IPh)][OTf]_2$ to form the 1,4-arenediyl complex *trans*-1,4-$\{PtIMe_2(bpy)\}_2C_6H_4$ (**9b**). Diphenyl{di(*tert*-butyl)-2,2′-bipyridine}platinum(II) reacts with $[IPh_2][OTf]$ at 25 °C over 2 days to form the triphenylplatinum(IV) complex $Pt(OTf)Ph_3(Bu^t{}_2bpy)$ (**10**), and addition of iodide ion results in isolation of $PtIPh_3(Bu^t{}_2bpy)$ (**11**). Structural studies of *trans*-$PtIMe_2Ph(bpy)$ (**2b**) and *trans*-$Pt(C_4H_8)Ph(bpy)$ (**5b**) reveal distorted octahedral geometry and the *fac*-PtC_3 configuration expected for all of the metal(IV) complexes. The compound $[IPh(C_6H_4\text{-}4\text{-}I)][OTf]$ has two sets of cation−anion pairs with a complex array of weak interactions, and the cations have C−I−C angles close to 90°.

Introduction

A key process in reactions catalyzed by palladium complexes is the oxidative addition of $C(sp^2)-X$ bonds to Pd(0) substrates, in particular aryl and alkenyl halides R−X where the organic group is formally transferred as R^+ to give $Pd^{II}R$.[1] Related reactions of Pd(II) substrates with $C(sp^2)-X$ bonds to form Pd(IV) intermediates in catalysis have often been suggested,[2] although there appears to be an absence of reports of "model" oxidative addition reactions involving detected Pd(IV) species to add substance to these suggestions. There are also a range of other possible processes that could be invoked to explain the apparent involvement of Pd(IV) in catalysis, in particular facile exchange of aryl groups between Pd(II) centers or reduction of precatalysts to Pd(0) species that can then act as either heterogeneous or homogeneous catalysts.[3] Reduction to Pd(0) may occur in several ways, e.g., by reaction with the solvent or other reagents, or one-electron oxidation

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by the aryl halide reagent leading to decomposition to Pd(0).[3] Alternatively, it is feasible that oxidative addition reactions of aryl halides to Pd(II) substrates do provide Pd(IV) intermediates that are insufficiently stable to allow their observation.

As part of a search for reactions that could model the addition of C(sp^2)−X bonds to Pd(II) to form Pd(IV) species, we have been attracted by the developing importance of catalytic reactions involving hypervalent iodine(III) reagents [IAr(R)][X] [X usually triflate (OTf) or BF_4] in Pd(0)/Pd(II) cycles.[4,5] These reagents transfer aryl and related groups (R) such as alkenyl and alkynyl to Pd(0) to form Pd^{II}R intermediates, involving cleavage of the R−I bond and elimination of ArI. It has been reported that alkynyl and vinyl groups can be transferred from iodine(III) reagents to Rh(I) and Ir(I) complexes to form M(III) complexes,[4,6] alkynyl groups to Pt(0) to form Pt(II) complexes,[4,7] and possibly phenyl groups to Y(0).[8] Encouraged by these reports we have explored the reactivity of [IPh_2][OTf] toward Pd(II) reagents, and toward Pt(II) in view of the higher reactivity of Pt(II) toward aryl halides demonstrated for some systems to give Pt(IV) species.[9] Although this chemistry does not formally model aryl halide oxidative addition, we report here that transfer of Ar$^+$ to M(II) centers to form M(IV) complexes (M = Pd, Pt) does occur and that this methodology provides a new and facile route to dialkyl(aryl)platinum(IV) complexes, including a 1,4-benzenediyl-bridged complex and the first route to an archetypal triarylplatinum(IV) complex. Preliminary communications of part of this work have appeared.[10]

Experimental Section

The reagents MMe_2(bpy) (M = Pd,[11] Pt[12]) (bpy = 2,2′-bipyridine), M(C_4H_8)(bpy) (M = Pd,[13] Pt[14]), $PtPh_2$(Bu$^t_2$bpy) (Bu$^t_2$bpy = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine),[15] [IPh_2][OTf],[16] and [IPh(C_6H_4-4-IPh)][OTf]$_2$[17] were prepared as described. A preparation of [IPh(C_6H_4-4-I)][OTf] similar to that reported for a successful synthesis[16a,18] was developed, using a longer reaction time and a 0.5:1 mole ratio of trifluoromethanesulfonic anhydride to iodosylbenzene, rather than 1:1 as reported. Solvents were dried and distilled and stored under nitrogen, and all procedures were carried out under nitrogen. ^{1}H 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 and COSY, HMQC, and HMBC spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. 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 Iodo(phenyl)(4-iodophenyl) Triflate. Trifluoromethanesulfonic anhydride (0.25 mL, 1.5 mmol) was added dropwise to a stirred suspension of iodosylbenzene (0.66 g, 3.0 mmol) in dichloromethane (5 mL) at room temperature. Stirring was continued for 48 h, cyclohexene (0.3 mL, 3.0 mmol) was added, and the resulting mixture was stirred for 4 h. The solvent was removed under vacuum, and the residue was treated with diethyl ether (5 mL) to give the product as a white solid collected by filtration (0.53 g, 63%), mp 146−147 °C (lit. 144−148 °C).[16a]

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Synthesis of Pt(IV) and Pd(IV) Complexes. The complexes **2a**, **5b**, **9b**, and **11** and mixtures of **2a** and **2b** and of **2b** and **8b** were isolated as solids; other species were detected by ^{1}H NMR spectroscopy.

***trans*-Pt(OTf)Me$_2$Ph(bpy) (1b).** Diphenyliodonium triflate (3.9 mg, 0.013 mmol) was added to a stirred solution of PtMe$_2$(bpy) (5.0 mg, 0.013 mmol) in $(CD_3)_2CO$ (1 mL) at −50 °C. The mixture was stirred for a further 5 min at −50 °C. ^{1}H NMR (−60 °C): δ 9.39 (m, 2H, H6), 8.72 (m, 2H, H3), 8,43 (m, 2H, H4), 8.08 (m, 2H, H5), 6.80 (m, 5H, Ph), 1.50 (s, $^2J_{HPt}$ = 67.6 Hz, 6H, $PtCH_3$).

***cis*-PtIMe$_2$Ph(bpy) (2a) and *trans*-PtIMe$_2$Ph(bpy) (2b).** Diphenyliodonium triflate (39 mg, 0.13 mmol) was added to a stirred solution of PtMe$_2$(bpy) (50 mg, 0.13 mmol) in acetone (10 mL) at −50 °C. The mixture was stirred for a further 5 min at −50 °C and allowed to warm to room temperature, and sodium iodide (25 mg, 0.17 mmol) was added. The solvent was removed in a vacuum, and dichloromethane (10 mL) was added to the residue. The resulting mixture was stirred for 5 min and filtered. The filtrate was concentrated to half its volume, and small amounts of pentane were added. The solution was kept for several days at −20 °C. The precipitate that formed was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried in a vacuum (69 mg, 91%). ^{1}H NMR spectra indicated a cis:trans isomer ratio of 2:1. The mixture of the two isomers was partially separated by crystal habit to give samples of the cis (**2a**, white powder) and trans isomers (**2b**, yellow crystals). ^{1}H NMR of **2a** ($(CD_3)_2CO$): δ 9.11 (m, 1H, H6), 8.84 (m, 1H, H6′), 8.76 (m, 1H, H3), 8.74 (m, 1H, H3′), 8.37 (m, 1H, H4), 8.32 (m, 1H, H4′), 7.93 (m, 1H, H5), 7.76 (m, 1H, H5′), 7.68 (br m, 2H, H2,6(Ph)), 7.02 (m, 3H, H3−5(Ph)), 1.71 (s, $^2J_{HPt}$ = 71.1 Hz, 3H, $PtCH_3$), 0.99 (s, $^2J_{HPt}$ = 70.7 Hz, 3H, $PtCH_3$). Anal. for **2a**, Calcd for $C_{18}H_{19}N_2PtI$: C, 36.93; H, 3.27; N, 4.79. Found: C, 36.74; H, 3.24; N, 4.88. ^{1}H NMR of **2b** ($(CD_3)_2CO$): δ 9.27 (m, 2H, H6), 8.59 (m, 2H, H3), 8.27 (m, 2H, H4), 7.91 (m, 2H, H5), 7.04 (m, 2H, H2,6(Ph)), 6.73 (m, 3H, H3−5(Ph)), 1.77 (s, $^2J_{HPt}$ = 71.1 Hz, 6H, $PtCH_3$).

***trans*-Pt(OTf)(C$_4$H$_8$)Ph(bpy) (3b).** Diphenyliodonium triflate (3.6 mg, 0.012 mmol) was added to a stirred solution of Pt(C$_4$H$_8$)(bpy) (5.0 mg, 0.012 mmol) in $(CD_3)_2CO$ (1 mL) at −50 °C. The mixture was stirred for a further 5 min at −50 °C. ^{1}H NMR (−50 °C): δ 9.37 (m, 2H, H6), 8.72 (d, ^3J = 8.1 Hz, 2H, H3), 8.44 (‘t’, 2H, H4), 8.06 (m, 2H, H5), 7.15 [m, 2H, H2,6-(Ph)], 6.80 (m, 3H, H3−5(Ph)).

***cis*-Pd(OTf)(C$_4$H$_8$)Ph(bpy) (4a) and *trans*-Pd(OTf)-(C$_4$H$_8$)Ph(bpy) (4b).** Diphenyliodonium triflate (4.7 mg, 0.016 mmol) was added to a stirred solution of Pd(C$_4$H$_8$)(bpy) (5.0 mg, 0.016 mmol) in $(CD_3)_2CO$ (1 mL) at −70 °C. The mixture was stirred for a further 40 min at −70 °C to give a 1:1 mixture of **4a** and **4b**. ^{1}H NMR (−50 °C) of **4a**: δ 9.28 (d, ^3J = 5.1 Hz, 1H, H6), 8.86 (d, ^3J = 7.9 Hz, 1H, H3), 8.82 (d, ^3J = 7.8 Hz, 1H, H3′), 3.76 [m(b), 1H, CH_2]. ^{1}H NMR (−50 °C) of **4b**: δ 9.23 (d, ^3J = 5.2 Hz, 2H, H6), 8.57 (d, ^3J = 8.0 Hz, 2H, H3), 8.30 (‘t’, 2H, H4), 7.95 (‘dd’, 2H, H5), 7.27 (d, ^3J = 7.6 Hz, 2H, H2,6(Ph)), 6.91−6.83 (m, 3H, H3−5(Ph)), 4.15 (m, 2H, CH_2), 3.50 (m, 2H, 2H, CH_2), 1.73 (m, 2H, CH_2), 1.43 (m, 2H, CH_2).

***cis*-PtI(C$_4$H$_8$)Ph(bpy) (5a).** A solution of *trans*-PtI(C$_4$H$_8$)-Ph(bpy) (**5b**) (5.0 mg, 0.0082 mmol) in $(CD_3)_2CO$ (1 mL) was left standing at room temperature for 16 h to give a 2:1 mixture of **5a** and **5b**. ^{1}H NMR (CD_2Cl_2) of **5a**: δ 9.11 (m, 2H, H6), 8.30 (m, 2H, H3), 8.13 (‘t’, 1H, H4), 8.01 (‘t’, 1H, H4′), 7.79 (br m, 2H, H2,6(Ph)), 7.21 (m, 2H, H5), 7.08 (m(b), 3H, H3−H5-(Ph)), 2.91 (m(b), 2H, CH_2), 2.29 (m, 1H, CH_2), 1.72 (m, 1H, CH_2), 1.28 (br, m, 1H, CH_2), 0.98 (br, m, 1H, CH_2), 0.64 (br, m, 1H, CH_2), 0.56 (br, m, 1H, CH_2).

***trans*-PtI(C$_4$H$_8$)Ph(bpy) (5b).** Diphenyliodonium triflate (36 mg, 0.12 mmol) was added to a stirred solution of Pt(C$_4$H$_8$)-(bpy) (50 mg, 0.12 mmol) in acetone (10 mL) at −50 °C. The mixture was stirred for a further 5 min at −50 °C, and sodium iodide (25 mg, 0.17 mmol) was added. The solvent was removed in a vacuum, and dichloromethane (10 mL) was added to the residue at − 50 °C. The mixture was stirred for 5 min at −50 °C and filtered. The filtrate was concentrated to half its volume, and small amounts of pentane were added. The solution was kept for several days at −20 °C. The precipitate that formed was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried in a vacuum (63 mg, 86%). ^{1}H NMR: (CD_2Cl_2, −50 °C): δ 9.06 (m, 2H, H6), 7.94 (m, 4H, H3,4), 7.65 (m, 2H, H5), 6.96 (m, $^3J_{HPt}$ = 54.0 Hz, 2H, H2,6-(Ph)), 6.78 (m, 3H, H3−5(Ph)), 3.63 (m, J_{HPt} = 106.3 Hz, 2H, CH_2), 2.35 (m, J_{HPt} = 54.9 Hz, 2H, CH_2), 1.44 (m, J_{HPt} = 63.6 Hz, 2H, CH_2), 1.10−0.90 (m(b), 2H, CH_2). Anal. Calcd for $C_{20}H_{21}N_2IPt$: C, 39.29; H, 3.46; N, 4.58. Found: C, 39.37; H, 3.26; N, 4.39.

***cis*-PdI(C$_4$H$_8$)Ph(bpy) (6a) and *trans*-PdI(C$_4$H$_8$)Ph(bpy) (6b).** Diphenyliodonium triflate (4.7 mg, 0.016 mmol) was added to a stirred solution of Pd(C$_4$H$_8$)(bpy) (5.0 mg, 0.016 mmol) in $(CD_3)_2CO$ (1 mL) at −50 °C. The mixture was stirred for a further 40 min at −50 °C, and sodium iodide (3.0 mg, 0.020 mmol) was added to give a 1:3 mixture of **6a** and **6b**. ^{1}H NMR (−50 °C) of **6a**: δ 9.22 (d, ^3J = 4.4 Hz, 1H, H6), 8.79 (d, ^3J = 8.0 Hz, 1H, H3), 8.75 (d, ^3J = 8.0 Hz, 1H, H3′), 8.62 (d, ^3J = 4.4 Hz, 1H, H6′), 8.34 (‘t’, 1H, H4), 8.26 (‘t’, 1H, H4′), 7.92 (‘dd’, 1H, H5), 7.70 (‘dd’, 1H, H5′), 7.07 (t, ^3J = 7.0 Hz, 1H, H4(Ph)), 3.98 (‘q’, 1H, CH_2), 3.01 (‘q’, 1H, CH_2), 1.67 (m(b), 1H, CH_2), 1.40 (m(b), 2H, CH_2), 1.22 (m(b), 1H, CH_2), 1.05 (m(b), 2H, CH_2); **6b**: δ 9.15 (d, ^3J = 4.4 Hz, 2H, H6), 8.42 (d, ^3J = 8.0 Hz, 2H, H3), 8.16 (‘t’, 2H, H4), 7.82 (‘dd’, 2H, H5), 7.2 [m, 2H, H2,6(Ph)], 6.88 (‘t’, 2H, H3,5(Ph)), 6.79 (t, ^3J = 7.2 Hz, 1H, H4(Ph)), 4.85 (m, 2H, CH_2), 3.28 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 1.51 (m, 2H, CH_2).

***cis*-PdCl(C$_4$H$_8$)Ph(bpy) (7a) and *trans*-PdCl(C$_4$H$_8$)Ph-(bpy) (7b).** Diphenyliodonium triflate (4.7 mg, 0.016 mmol) was added to a stirred solution of Pd(C$_4$H$_8$)(bpy) (5.0 mg, 0.016 mmol) in $(CD_3)_2CO$ (1 mL) at −50 °C. The mixture was stirred for a further 40 min at −50 °C, and lithium chloride (1.0 mg, 0.024 mmol) was added to give a 1:3 mixture of **7a** and **7b**. ^{1}H NMR (−50 °C) of **7a**: δ 9.15 (d, ^3J = 4.4 Hz, 1H, H6), 8.71 (d, ^3J = 8.4 Hz, 1H, H3), 8.67 (d, ^3J = 8.2 Hz, 1H, H3′), 8.31 (‘t’, 1H, H4), 8.21 (‘t’, 1H, H4′), 7.92 (‘dd’, 1H, H5), 7.09 (d, ^3J = 7.2 Hz, 2H, H2,6(Ph)), 6.98 (t, ^3J = 7.0 Hz, 1H, H4(Ph)), 3.74 (m(b), 1H, CH_2), 2.86 (m(b), 1H, CH_2), 1.21 (m(b), 2H, CH_2); **7b**: δ 9.08 (d, ^3J = 4.4 Hz, 2H, H6), 8.42 (d, ^3J = 8.0 Hz, 2H, H3), 8.15 (‘t’, 2H, H4), 7.81 (‘dd’, 2H, H5), 7.33 (d, ^3J = 8.5 Hz, 2H, H2,6(Ph)), 6.86 (‘t’, 2H, H3,5(Ph)), 6.77 (t, ^3J = 6.8 Hz, 1H, H4(Ph)), 4.38 (m, 2H, CH_2), 3.30 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 1.32 (m, 2H, CH_2).

***trans*-PtIMe$_2$(C$_6$H$_4$-4-I)(bpy) (8b) and *trans*-PtIMe$_2$Ph-(bpy) (2b).** (4-Iodophenyl)(phenyl)iodonium triflate (109.2 mg, 0.20 mmol) was added to a stirred solution of PtMe$_2$(bpy) (75.0 mg, 0.20 mmol) in acetone (10 mL) at −50 °C. The mixture was stirred for 30 min at −50 °C, and sodium iodide (30 mg, 0.20 mmol) was added. The solvent was removed in a vacuum at −50 °C, and dichloromethane (5 mL) at −50 °C was added to the residue. The resulting mixture was stirred for 5 min at −50 °C and filtered, and the solvent removed from the filtrate at −50 °C. The residue was washed with diethyl ether (3 × 5 mL), and the solid dissolved in acetone (10 mL) at −50 °C and kept at −80 °C for 1 week. The solvent was removed at −50 °C under a vacuum to give a yellow solid (118.2 mg, 92%) as a 1:1 mixture of **8b** and **2b**. ^{1}H NMR (−50 °C) of **8b**: δ 9.39 (m, 2H, H6), 8.86 (m, 2H, H3), 8.41 (m, 2H, H4), 7.98 (m, 2H, H5), 7.09 (d, ^3J = 8.4 Hz, 2H, C_6H_4), 6.64 (d, ^3J = 8.4 Hz, 2H, C_6H_4), 1.68 (s, $^2J_{HPt}$ = 69.8 Hz, 6H, Me). HRMS (LSI): calcd for $C_{18}H_{18}N_2{}^{194}PtI$ ($(M - I)^+$) 583.01428, found 583.01395.

***trans*-1,4-{PtIMe$_2$(bpy)}$_2$C$_6$H$_4$ (9b).** 1,4-Bis(phenyliodonium)benzene (121 mg, 0.32 mmol) was added to a stirred solution of PtMe$_2$(bpy) (124 mg, 0.16 mmol) in acetone (15 mL) at −50 °C. The mixture was stirred for 30 min at −50 °C, and sodium iodide (48 mg, 0.32 mmol) was added. The solvent was removed in a vacuum at −50 °C, and dichloromethane (10 mL) at −50 °C was added to the residue. The resulting mixture

Table 1. Selected Bond Distances (Å) and Angles (deg) for *trans*-PtIMe$_2$Ph(bpy) (2b) and *trans*-PtI(C$_4$H$_8$)Ph(bpy) (5b)

	2b	**5b**
	Bond Distances	
Pt−C(1)	2.034(4)	2.04(1)
Pt−C(10a, 10b)	2.060(5), 2.058(5)	2.07(1), 2.05(1)
Pt−N(11a, 11b)	2.151(3), 2.151(3)	2.175(8), 2.158(9)
Pt−I	2.7631(4)	2.759(1)
	Bond Angles	
C(1)−Pt−C(10a, 10b)	89.0(2), 88.9(2)	90.8(5), 89.3(5)
C(1)−Pt−N(11a, 11b)	90.8(1), 90.5(2)	88.5(4), 90.5(4)
C(1)−Pt−I	178.2(1)	179.6(3)
C(10a)−Pt−C(10b)	84.7(2)	83.0(5)
C(10a)−Pt−N(11a, 11b)	175.8(2), 99.4(2)	177.2(4), 101.4(4)
C(10b)−Pt−N(11a, 11b)	99.5(1), 175.9(2)	99.7(4), 175.6(4)
I−Pt−C(10a, 10b)	90.8(1), 92.8(1)	89.5(5), 91.0(5)
I−Pt−N(11a, 11b)	89.18(9), 87.72(9)	91.2(3), 89.2(3)
N(11a)−Pt−N(11b)	76.4(1)	75.9(3)
Pt−C(1)−C(2, 6)	121.9(3), 120.4(3)	120.9(8), 121.7(9)
Pt−N(11a)−C(12a, 16a)	115.8(2), 125.4(3)	124.9(7), 116.4(7)
Pt−N(11b)−C(12b, 16b)	115.9(3), 124.9(3)	125.0(8), 115.5(6)

was stirred for 5 min at −50 °C and filtered, and the solvent removed from the filtrate at −50 °C. Column chromatography (silica, ethyl acetate) of the residue at ambient temperature gave the product (**9b**) ($R_f = 0.65$) as a yellow solid (43 mg, 35%). Other isomers together with **9b** occur in the next fraction as a broad band. ^{1}H NMR of **9b**: δ 9.05 (m, 2H, H6), 8.77 (d, $^3J = 8.3$ Hz, 4H, H3), 8.33 ('td', 4H, H4), 7.91 ('ddd', 4H, H5), 7.55 (s, 4H, C_6H_4), 2.38 (s, $^2J_{HPt} = 73.0$ Hz, 12H, Me). ^{13}C NMR: δ 155.9 (C2), 148.9 (C6), 141.1 (C4), 140.4 (CH(C_6H_4)), 128.2 (C5), 125.4 (C3), 93.9 (C(C_6H_4)), −15.1 (Me). The complex would not ionize satisfactorily to give HRMS (LSI) or ESMS.

PtIPh$_3$(Bu$^t_2$bpy) (11). Diphenyliodonium triflate (13.9 mg, 0.032 mmol) was added to a stirred solution of PtPh$_2$(Bu$^t_2$bpy) (20.0 mg, 0.032 mmol) in acetone (5 mL) at ambient temperature. The mixture was stirred for 2 days, and sodium iodide (5 mg, 0.033 mmol) was added. The solvent was removed in a vacuum, and dichloromethane (5 mL) was added to the residue. The resulting mixture was stirred for 5 min and filtered, and the solvent removed from the filtrate to give a yellow solid (22.3 mg, 85%). A small amount was recrystallized from diethyl ether/pentane for microanalysis. ^{1}H NMR (($CD_3)_2$CO): δ 8.90 (m, 2H, H6), 8.61 (d, $^3J = 1.9$ Hz, 2H, H), 7.86 (d, $^3J_{HPt} = 46.8$ Hz, $^3J = 7.3$ Hz, 4H, H2,6(Ph)), 7.83 ('dd', 2H, H5), 6.94 (m, 2H, H4(Ph)), 6.86 (m, 4H, H3,5(Ph)), 6.72 (m, 2H, H2,6(Ph)), 6.62 (m, 3H, H3−5(Ph)), 1.41 (s, 18H, Me). Anal. Calcd for $C_{36}H_{39}N_2IPt$: C, 52.62; H, 4.78; N, 3.41. Found: C, 52.32; H, 4.86; N, 3.23.

Decomposition of Pallada(IV)cyclopentane Complexes 4, 6, and 7. An acetone solution containing the isomeric mixture of complexes generated in solution at −50 °C, and thus containing excess halide for **6** and **7**, was allowed to warm to ambient temperature and left standing in a sealed flask for 24 h. The organic components were analyzed by GC/MS.

Structure Determinations. Crystals of **2b** and **5b** were obtained at −20 °C from solutions of complexes in dichloromethane/diethyl ether and dichloromethane/pentane, respectively. Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, $2\theta_{max} = 58°$, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding N_t total reflections, merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full-matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z\ U_{iso})_H$ being constrained at estimated values. As modeled, the central atoms of the $(CH_2)_2$ group of **5b** exhibited disorder over two sets of sites with populations of 0.5. Conventional residuals R, R_w on $|F|$ are cited at convergence (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$). Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[19] Table 1 shows selected structural parameters, and Figure 1 depicts non-hydrogen atoms with 50% probability amplitude displacement envelopes, hydrogen atoms having arbitrary radii of 0.1 Å.

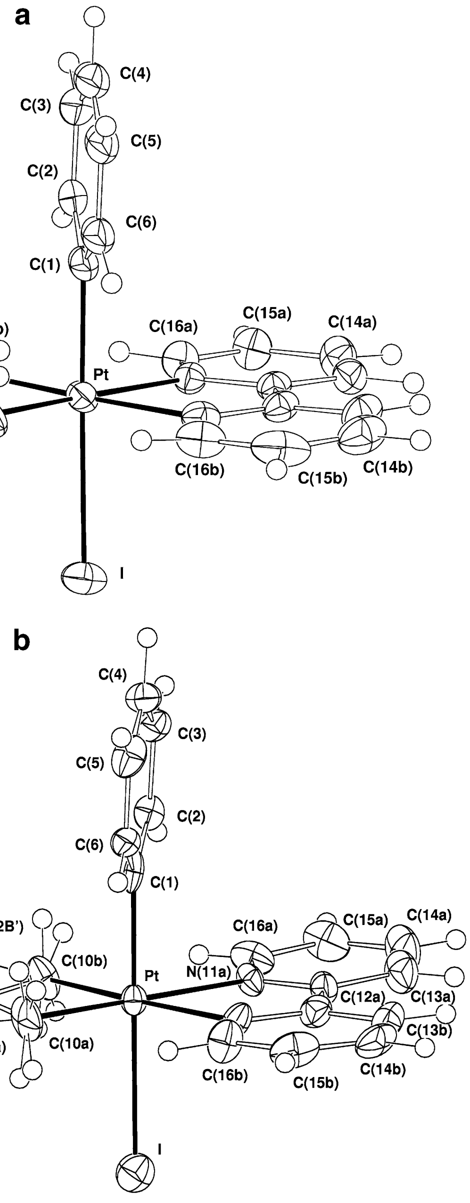

Figure 1. Projections of molecules of (a) *trans*-PtIMe$_2$Ph(bpy) (**2b**) and (b) *trans*-PtI(C$_4$H$_8$)Ph(bpy) (**5b**) showing disorder for the platinacyclopentane ring.

Results

Reactions were studied initially at low temperature by ^{1}H NMR using $(CD_3)_2$CO as a solvent. Although reactivity of Pd(II) species with [IPh$_2$][OTf] was detected, Pd(IV) species could not be isolated owing to very low stability, so that their characterization relied on comparison of spectra with reported palladium complexes prepared by other methods (PdMePh(bpy),[20] PdIMe$_3$(bpy),[21] PdIMe$_2$Ph(bpy),[22] PdI(C_4H_8)Me(bpy)[23]) and more robust Pt(IV) analogues. The isomer designa-

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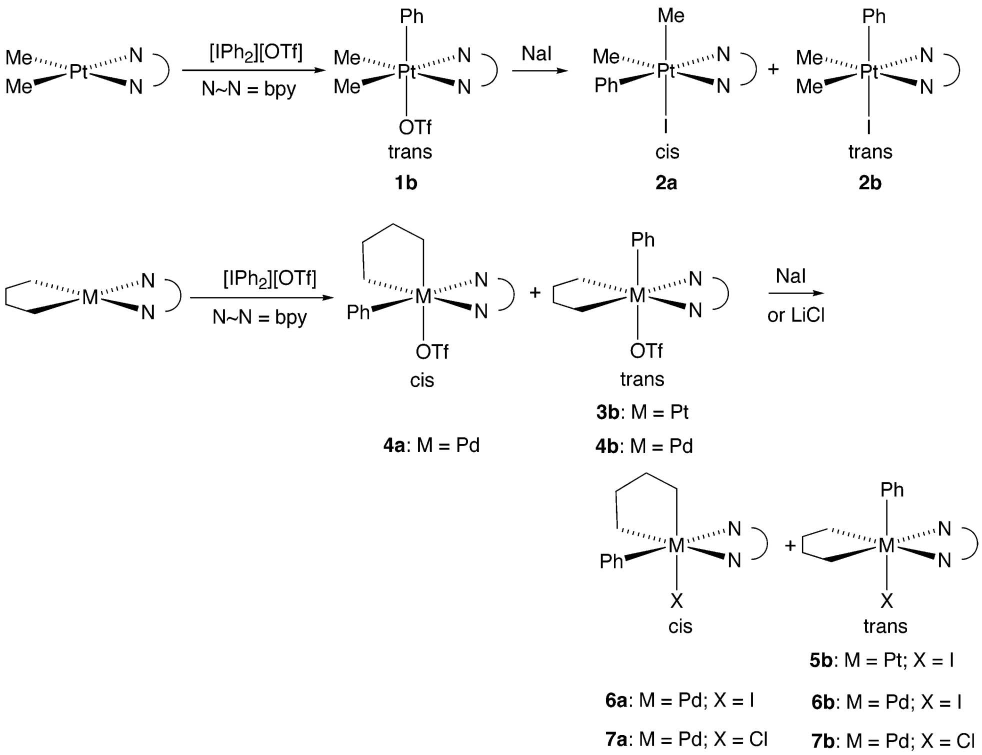
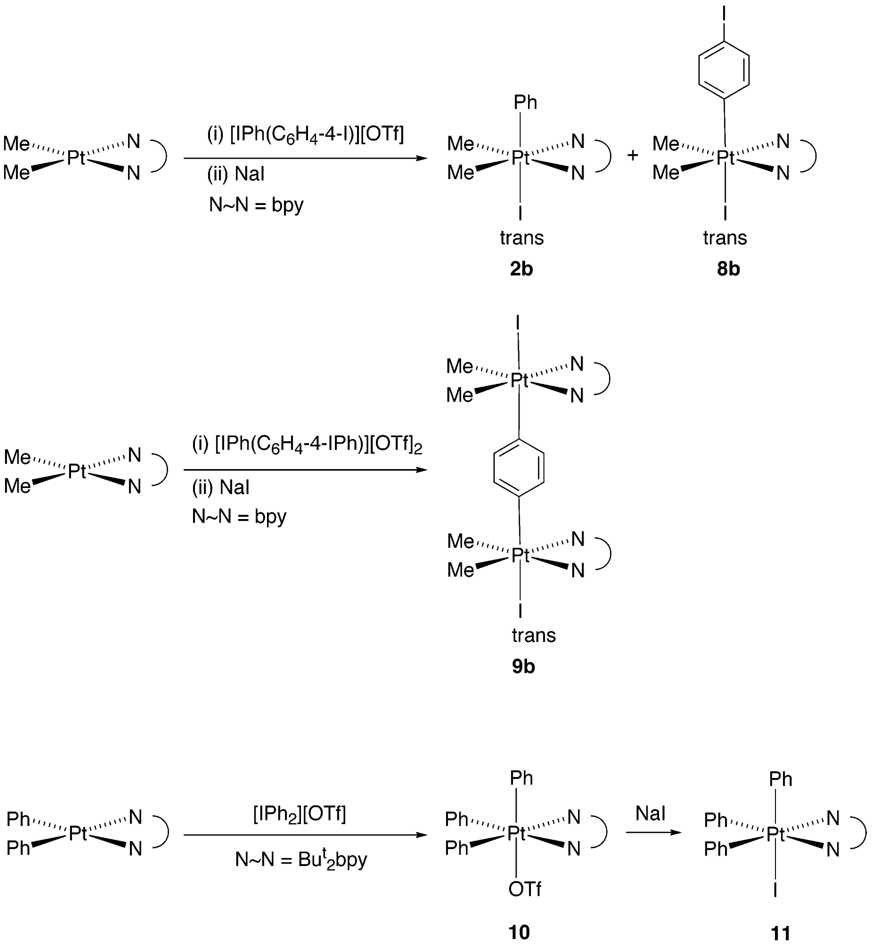
[19] Hall, S. R., Du Boulay, D. J., Olthof-Hazekamp, R., Eds. *The XTAL 3.7 System*; University of Western Australia, 2001.

Scheme 1



Scheme 2



tions cis and trans refer to the disposition of aryl with respect to halogeno or triflate groups (Schemes 1 and 2). Aryl iodide byproducts of aryl group transfer from iodine(III) reagents were detected for all reactions, viz., PhI from [IPh$_2$][OTf] and [IPh(C$_6$H$_4$-4-IPh)][OTf]$_2$, and both PhI and 1,4-C$_6$H$_4$I$_2$ from [IPh(C$_6$H$_4$-4-I)][OTf]$_2$.

Dimethyl(phenyl)metal(IV) Species. The reaction of $PdMe_2(bpy)$ with $[IPh_2][OTf]$ in 1:1 mole ratio at −50 °C gave complex spectra that were difficult to interpret, and only about half of the iodonium reagent was consumed. On addition of sodium iodide to this solution, the species $PdIMe_3(bpy)$, PdMePh(bpy), and a small amount of $PdIMe_2Ph(bpy)$ were detected, where $PdIMe_2Ph(bpy)$ is present as cis and trans isomers in the same ratio (1:1) as reported for its synthesis via the oxidative addition of iodomethane to PdMePh(bpy).[22] Formation of the trimethylpalladium(IV) complex is indicative of transfer of a methyl group between palladium centers, a reaction that is often observed in organopalladium(IV) chemistry; for example, $PdIMe_2Ph(bpy)$ reacts with $PdMe_2(bpy)$ to form PdMePh(bpy) and $PdIMe_3(bpy)$, respectively.[22] Since all of the $PdMe_2(bpy)$ reagent, but not $[IPh_2][OTf]$, is consumed prior to addition of sodium iodide, the NMR observations are consistent with fast methyl group transfer from $Pd(OTf)Me_2Ph(bpy)$ to $PdMe_2(bpy)$. Exchange reactions involving $Pd(OTf)Me_2Ph(bpy)$ are expected to be more facile than those involving $PdIMe_2Ph(bpy)$, as the exchange reaction is favored by weak donor ligands at Pd(IV) and ligand disssociation.

In contrast, $PtMe_2(bpy)$ reacts with $[IPh_2][OTf]$ at −50 °C to give a spectrum consistent with the presence of *trans*-$Pt(OTf)Me_2Ph(bpy)$ (**1b**) (Scheme 1), exhibiting one pyridyl group environment, and for which the triflate group is assumed to be coordinated as reported for the closely related $Pt(OTf)Me_3\{(2,6\text{-}Pr^i{}_2C_6H_3NCH)_2\text{-}N,N'\}$[24] in the solid state and $Pt(OTf)Me_3(tmeda)$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in solution.[25] Complex **1b** reacts with sodium iodide at ambient temperature to give a mixture of cis (**2a**) and trans (**2b**) isomers of $PtIMe_2Ph(bpy)$ in 2:1 ratio (Scheme 1), resulting in isolation of the isomers as a solid mixture in 91% yield from $PtMe_2(bpy)$. The isomers exhibit different crystal habits, allowing separation of a pure sample of the trans isomer (**2b**) suitable for X-ray crystallography and an impure sample of the cis isomer. Solutions of **2a** or **2b** in acetone show isomerization back to the 2:1 ratio of isomers over a period of a few hours at ambient temperature.

The structural analysis of **2b** and partial separation of the cis isomer (**2a**) allow confirmation of ^1H NMR assignments for the isomers; for example, the cis isomer exhibits two pyridyl and methyl group environments and the trans isomer exhibits one environment. Comparison of ^1H NMR spectra for isomers of $MIMe_2Ph(bpy)$ (M = Pd, Pt) confirms the earlier assignments of spectra and isomer ratio for the unstable Pd(IV) complexes for which structural determinations were not feasible.[22]

Metalla(IV)cyclopentane Species. The alkyl group exchange reactions exhibited by $PdIMe_2Ph(bpy)$[22] and $Pd(OTf)Me_2Ph(bpy)$ (see above) are not expected to occur when the methyl groups are replaced by a palladacycle; for example, $PdI(C_4H_8)Me(bpy)$ does not react with $Pd(C_4H_8)(bpy)$.[23] Thus, the reaction of the pallada(II)cyclopentane complex $Pd(C_4H_8)(bpy)$ with $[IPh_2][OTf]$ was studied at −50 °C, resulting in ^1H NMR detection of $Pd(OTf)(C_4H_8)Ph(bpy)$ with a cis (**4a**):trans (**4b**) isomer ratio of 1:1 (Scheme 1). In contrast to the reaction of $PdMe_2(bpy)$ with $[IPh_2][OTf]$ and consistent with the absence of exchange reactions, all of the iodine(III) reagent was consumed in the reaction. Addition of lithium chloride or sodium iodide resulted in formation of $PdX(C_4H_8)Ph(bpy)$ (X = Cl, I), occurring with a cis:trans ratio of 1:3. The Pd(IV) species are unstable. The Pt(IV) complex $Pt(OTf)(C_4H_8)(bpy)$ (**3**) forms as a trans isomer at −50 °C, and addition of sodium iodide and workup at −20 °C allowed the isolation of *trans*-$PtI(C_4H_8)(bpy)$ (**5b**) (Scheme 1), which in solution at ambient temperature isomerizes to form a 2:1 mixture of cis and trans isomers. The trans complex (**5b**) was characterized by X-ray crystallography (see below).

^1H NMR spectra for the metallacyclopentane complexes show broad and/or complex multiplets for methylene protons and in the case of **3b** are too broad to allow confident assignment and are thus not intructive for assignment to isomers. The presence of isomeric mixtures has precluded complete assignment for some of the cis complexes. However, most resonances for the bpy ligand are well resolved and assist with structural assignment; for example, the trans complexes exhibit a single H(6) resonance integrating for two protons (**3b**, **4b**, **5b**, **6b**, **7b**), and the cis complexes exhibit two resonances (**6a**), or one resonance integrating as one proton in those cases where the other resonance is obscured (**4a** and **7a**, which exhibit two H(3) resonances).

The decomposition of a range of isolated pure complexes $PdX(C_4H_8)R(bpy)$ (X = halogen, R = alkyl) has been reported, indicating that reductive elimination via $R-C_4H_8$ coupling occurs followed by decomposition of undetected $Pd^{II}C_4H_8R$ species to give substituted butenes and butanes.[23] The less stable complexes $PdX(C_4H_8)Ph(bpy)$ [X = OTf (**4a**, **4b**), I (**6a**, **6b**), Cl (**7a**, **7b**)] were generated in solution, and their decomposition was examined at ambient temperature and thus in the presence of iodobenzene (quantitatively from $[IPh_2][OTf]$) and, for **6** and **7**, triflate and excess sodium iodide or lithium chloride. Black suspensions were obtained, ^1H NMR spectra revealed traces of butenes and cyclobutane, and some $PdCl_2(bpy)$ could be isolated from the decomposition of **7**. Using iodobenzene as a reference product, GC/MS revealed $Ph\text{-}C_4$ species accounting for 99% of the Pd(IV) complex for X = OTf, 65−80% for X = I, and 49% for X = Cl. The dominant products were phenylbutenes (70% for X = OTf, 50−65% for X = I, 18% for X = Cl), together with butylbenzene (22% for OTf, 15% for I, 4% for Cl) and phenyl(propyl)methanone (7% for OTf, 30% for Cl), where the ketone is assumed to arise from oxidation of alkenes in the presence of palladium species.

para-Iodophenylplatinum(IV) and 1,4-Arenediylplatinum(IV) Species. In view of the facile reac-

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tivity of PtMe$_2$(bpy) with [IPh$_2$][OTf] at low temperatures we have explored its reactivity toward an iodonium reagent containing different aryl groups bonded to iodine(III), [IPh(C$_6$H$_4$-4-I)][OTf], and toward a reagent containing two iodine(III) centers in a search for new routes to bridging 1,4-arenediyl(IV) species (Scheme 2). The reagent [IPh(C$_6$H$_4$-4-I)][OTf], structurally characterized,[26] gave a 1:1 mixture of trans isomers resulting from transfer of phenyl (**2b**) and 4-iodophenyl (**8b**) groups at −50 °C, and on warming to ambient temperature, isomerization occurred to give a 1:1 ratio of cis and trans isomers (**2a**, **2b**) (as expected from Scheme 1) and a 1:1 ratio of cis and trans isomers for PtIMe$_2$(C$_6$H$_4$-4-I)(bpy). The reagent [IPh(C$_6$H$_4$-4-IPh)][OTf]$_2$, containing two iodine(III) centers, gave a 35% yield of a 1,4-benzenediyl-bridged complex (**9b**) in which both Pt(IV) centers have the trans configuration at −50 °C, together with other species that could not be separated by column chromatography. Complex **9b** is stable as the trans isomer at ambient temperature for at least 1 week.

Complex **8b** exhibits the characteristic AB pattern for the *p*-iodo-substituted ring in ^{1}H NMR spectra. A complete ^{1}H and ^{13}C assignment for the 1,4-benzenediyl-bridged complex (**9b**) was ascertained using COSY, HMQC, and HMBC spectra; for example, in the HMBC spectrum two cross-peaks for the 1,4-diylbenzene ^{1}H singlet (δ 7.55) were observed, corresponding to coupling with the *C*(C$_6$H$_4$) and *C*H(C$_6$H$_4$) resonances at δ 93.9 and 141.1, respectively.

Synthesis of a Triphenylplatinum(IV) Complex. In view of the low solubility of PtPh$_2$(bpy), the more soluble species PtPh$_2$(Bu^t$_2$bpy) was used as a reagent, and reaction with [IPh$_2$][OTf], followed by NaI, occurred at ambient temperature to give an isolated yield of 85% for PtIPh$_3$(Bu^t$_2$bpy) (**11**). Complex **11** is stable at ambient temperature. The ^{1}H NMR spectrum shows one pyridyl and two phenyl environments, demonstrating the *fac*-PtR$_3$ environment expected for Pt(IV) and shown crystallographically for **2b** and **5b**.

Structural Studies of 2b and 5b. The complexes exhibit distorted octahedral geometry for platinum(IV) based on the presence of bidentate 2,2′-bipyridine and a *fac*-PtC$_3$ configuration and for which the platinacyclopentane ring exhibits disorder corresponding to the presence of two conformers in 1:1 ratio (Figure 1). With the C(10a)−Pt−C(10b) angle little changed on incorporation into the metallacycle ring, the platinum environments in the complexes are very similar, with only minor deviation from overall m symmetry (the disordered atoms of **5b** excepted).

Discussion

The reactivity of the hypervalent iodine(III) reagent [IPh$_2$][OTf] toward Pd(II), in which a phenyl group is transferred with cleavage of a C(sp^2)−I bond and formation of Pd(IV) products, provides a new pathway to arylpalladium(IV) chemistry. The reactions mirror, for Pd(II)/Pd(IV), the role of iodine(III) reagents in catalysis reactions involving Pd(0)/Pd(II) cycles.

Synthetic routes to dialkyl(aryl)platinum(IV) species reported to date are limited, since aryl−halogen bond oxidative addition to dialkylplatinum(II) substrates appears to require the presence of intramolecular coordination,[9] exemplified by the reaction of 2-(NMe$_2$CH$_2$CH$_2$NCH)C$_6$H$_4$X (X = Cl, Br, I) with [PtMe$_2$(SMe$_2$)]$_2$ to form PtXMe$_2${2-(NMe$_2$CH$_2$CH$_2$NCHC$_6$H$_4$-*C,N,N′*}.[9a] Convenient syntheses of complexes **2**, **5**, and **9b** provide confidence that diaryliodine(III) reagents should provide a general route to other dialkyl(aryl)platinum(IV) complexes. Diaryl(alkyl)platinum(IV) species are readily accessed via oxidative addition of alkyl halides to diarylplatinum(II) substrates, e.g., initial trans oxidative addition of iodomethane to PtPh$_2$(bpy) followed by isomerization to form a 2:1 mixture of *cis*- and *trans*-PtIPh$_2$Me(bpy),[27] exhibiting isomerization behavior similar to that reported here for PtIMe$_2$Ph(bpy) (**2a**, **2b**). In reactions of unsymmetrical species [IArR]$^+$ with organic nucleophiles, the more electron-withdrawing group is eliminated,[28] but in the reaction of PtMe$_2$(bpy) with [IPh(C$_6$H$_4$-4-I)][OTf] this effect is not sufficiently pronounced to give a product distribution different from the statistical 1:1 ratio observed for **2b** and **8b** (Scheme 1).

Construction of simple 1,4-arenediyl bridges between Pt(II) centers that are not stabilized by intramolecular coordination has been achieved via the transmetalation reaction of 1,4-bis(trimethylstannyl)benzene with dichloro(1,4-cyclooctadiene)platinum(II)[29] and the oxidative addition of 1,4-diiodobenzene to tetrakis(triethylphosphine)platinum(0).[30] The synthesis of the diplatinum(IV) complex **9b** using iodine(III) reagents opens a pathway to Pt(IV) complexes containing the archetypal 1,4-benzenediyl bridge.

Triarylplatinum(IV) chemistry involving hydrocarbyl groups appears to be limited to the isolation of *cis*-PtBr{2-(PhCH$_2$N=CH$_2$)C$_6$H$_4$-*C,N*}Ph$_2$(SMe$_2$), formed on the oxidative addition of 2-(benzylimino)bromobenzene to

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[26] [IPh(C$_6$H$_4$-4I)][OTf], C$_{13}$H$_9$F$_3$I$_2$O$_3$S, $M = 556.1$, monoclinic, space group $P2_1/n$ (C_{2h},^{5} No. 14; variant), $a = 9.8845(8)$ Å, $b = 14.898(1)$ Å, $c = 22.312(2)$ Å, $\beta = 95.671(2)°$, $V = 3269$ Å^3, D_c ($Z = 8$) = 2.25$_9$ g cm^{-3}, $\mu_{Mo} = 4.0$ mm^{-1}; specimen 0.35 × 0.25 × 0.17 mm; ‘T’$_{min/max}$ = 0.56. The solid state array is composed of two sets of cation−anion pairs, [IPh(C$_6$H$_4$-4-I)]$^+$ with [O$_3$SCF$_3$]$^-$, with a complex array of weak interactions. The two sets of ion pairs are disposed similarly with the substituted aromatic rings lying approximately parallel to each other and to the *ab* face of the cell, inversion related to generate sheets to either side, while the unsubstituted phenyl rings, approximately parallel to each other, and to the *ac* faces of the cell, lie approximately normal to the *ab* and *bc* faces. Interplanar dihedral angles within the asymmetric unit are as follows: 1/1′,2,2′ 77.9(2)°, 7.4(1)°, 85.8(2)°; 1′/2,2′ 84.9(2)°, 24.5(2)°; 2/2′ 80.0(2)°. The central C−S bonds of the anions lie quasi-parallel to *c*. The unsubstituted phenyl rings and anions, project outward from the *ab* plane, interdigitated with those from the next array disposed to either side of $z = 1/2$. The central, more positively charged, iodine atoms interact with nearby oxygen atoms from their companion anions (I(11)···O(11), I(21)···O(21) 3.028(4), 2.871(3) Å) forming putative ion pairs. However, the pendant/substituent iodine atoms also interact. Thus (I(14)···O(12) (x, $y-1$, z) 3.088(3), I(24)···O(22) (x, $y-1$, z) 3.335(3) Å) linking the pairs into strings; interestingly, despite the seeming noncrystallographic symmetry/equivalence of the two sets of ‘ion pairs’, the latter interaction for the second pair is less clear-cut, albeit still resulting in string formation, the iodine interacting as well with associated fluorines (I(24)···F(21,23), O(22) (x, $y-1$, z) 3.556(4), 3.746(3), Å). As might be expected, there are also numerous other ‘contacts’ from diverse atoms to the iodines at longer distances. The substituted phenyl rings are similarly inclined to the *ac* face, contacting peripherally at typical interplanar spacings. Insofar as intraspecies geometries are concerned, the C−I distances are remarkably similar (av. 2.100(9) Å), the two C−I−C angles both very close to 90°.

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cis-$PtPh_2(SMe_2)_2$.[9h] The facile synthesis and stability at ambient temperature of $PtIPh_3(Bu^t_2bpy)$ (**11**) indicate that it should be possible to develop an extensive chemistry of triarylplatinum(IV) species in the absence of intramolecular coordination by the aryl groups.

Transfer of aryl cations from $[Ar_2I]^+$ to organic and organometallic reagents containing a nucleophilic center most likely occurs via nucleophilic attack at the iodine(III) center followed by Nu−Ar bond formation and release of ArI.[4] In the present case, the nucleophilic metal centers are Pd(II) and Pt(II). Transfer of Ar^+ to metal(II) centers reported here has led us to examination of the reactivity of phenyl triflate toward $PtMe_2(bpy)$ and $M(C_4H_8)(bpy)$ (M = Pd, Pt), indicating an absence of reactivity, thus consistent with the key role of the electrophilic iodine(III) center in the transfer of Ar^+ to these d^8 metal complexes.

Supporting Information Available: Atomic parameters, bond distances and angles, and crystallographic details for **2b**, **5b**, and $[IPh(C_6H_4\text{-}4\text{-}I)][OTf]$, CIF files for the three structure determinations, projections of the structure of $[IPh(C_6H_4\text{-}4\text{-}I)][OTf]$, and a HMBC NMR spectrum for **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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