Organoplatinum(IV) and Palladium(IV) Complexes Containing Intramolecular Coordination Systems Based on the 8-Methylquinolinyl Group (mq), Including Structures of the Cation $[Pt(mq)Me_2(bpy)]^+$ (bpy = 2,2′-bipyridine) and the Palladium(IV) Complexes $Pd(mq)MeR\{(pz)_2BH_2\}$ (R = Me, Ph; $[(pz)_2BH_2]^-$ = Bis(pyrazol-1-yl)borate)

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Oxidative addition of 8-(bromomethyl)quinoline (mqBr) to PdMeR(bpy) (R = Me, Ph; bpy = 2,2′-bipyridine) and $[PdMeR\{(pz)_2BH_2\}]^-$ (R = Me, Ph; $[(pz)_2BH_2]^-$ = bis(pyrazol-1-yl)-borate]) has given the first isolable palladium(IV) complexes containing an intramolecular coordination system, [Pd(mq)MeR(bpy)]Br [R = Me (**1**), Ph (**2**)] and $[Pd(mq)MeR\{(pz)_2BH_2\}]$ [R = Me (**7**), Ph (**8**)]. The pallada(IV)cyclic complex [Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(mq)(bpy)]Br (**6**) has also been isolated. The first structural analysis of an arylpalladium(IV) complex, Pd(mq)MePh$\{(pz)_2BH_2\}$ (**8**), is reported. Complex **8** occurs as two isomers and the one examined by X-ray crystallography has the *fac*-PdC$_3$ configuration with the phenyl group trans to the quinoline nitrogen donor. NMR spectra of **8** indicate that the other isomer has the methyl group trans to the quinoline nitrogen donor. Similar geometric isomerism occurs for [Pd(mq)MePh(bpy)]BF$_4$ (**4**). Structural studies of the dimethylpalladium(IV) complex Pd(mq)Me$_2\{(pz)_2BH_2\}$ (**7**) and the platinum(IV) cation in [Pt(mq)Me$_2$(bpy)]BF$_4$·0.75(CH$_2$Cl$_2$) (**5**) reveal similar structures. The cation $[Pd(mq)Me_2(bpy)]^+$ is less stable than the methyl(phenyl)-palladium(IV) analogue (**2**), decomposing in $(CD_3)_2CO$ by reductive elimination to form ethane and 8-ethylquinoline in ∼1:2 ratio, together with the Pd(II) products [Pd(mq)(bpy)]Br and PdBrMe(bpy). A complex mixture of 8-substituted-quinolines (saturated and unsaturated substituents) were obtained as the major products of decomposition of [Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(mq)(bpy)]Br (**6**), consistent with mq···CH$_2$ coupling to give Pd(II) species that undergo further decomposition.

Introduction

Intramolecular coordination systems have played an important role in the development of organometallic chemistry, and for palladium(II) have led to organic synthesis procedures involving reactions at the metal center.[1] However, for the relatively new oxidation state +IV for organopalladium chemistry,[2] there appear to be only two reports of intramolecular coordination, and in these cases unstable species were detected for which ^{1}H NMR spectra are consistent with presence of Pd(IV).[3,4] Thus, **I** and **II** react with iodomethane, and **III** with chlorine to give unstable products formulated as octahedral Pd(C−N−N)Me$_2$I and Pd(C−N−N)Cl$_3$ from **II** and **III**, respectively.

We have commenced studies aimed at developing the intramolecular coordination chemistry of Pd(IV). Palladium(IV) complexes are usually synthesised from diorganopalladium(II) substrates via oxidative addition chemistry, and for organohalides this has been demonstrated to occur for C(sp^3)−X bonds including benzyl halides[2,5−8] and (halomethyl)naphthalenes.[2,5] Thus, we

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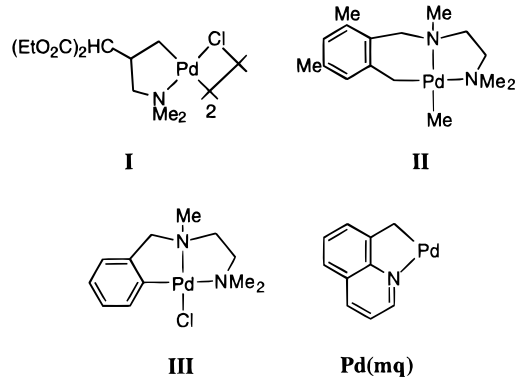

I **II**

III **Pd(mq)**

considered it feasible that 8-(bromomethyl)quinoline (mqBr), which contains a benzylic halide group and which forms Pd(II) intramolecular sytems [**Pd(mq)**][9] with applications including organic synthesis,[1b,10] could potentially react with appropriate Pd(II) substrates to form Pd(IV) intramolecular coordination systems. Organopalladium(II) substrates $PdMe_2$, PdMePh, and Pd(CH$_2$CH$_2$CH$_2$CH$_2$) were chosen in view of their applicability in the synthesis of Pd(IV) complexes,[2,5−8] and in order to explore the potential for selectivity in reductive elimination from anticipated unstable triorganopalladium(IV) species as reported for complexes such as $PdBrMe_2(CH_2Ph)(bpy)$[2,5] and PdBrMePh(CH_2Ph)(bpy) (bpy = 2,2′-bipyridine).[8] We report here the synthesis of new classes of Pd(IV) complex, representative Pt(IV) analogues, the isolation of phenylpalladium(IV) complexes that are stable at ambient temperature, and structural studies including the first analysis of an arylpalladium(IV) complex.

Experimental Section

The reagents bis(pyrazol-1-yl)borate,[11] $PdMe_2(bpy)$,[12] PdMePh(bpy) and PdMePh(tmeda),[13] $[PdMe_2(pyridazine)]_2$,[12,14] $PdMe_2$(tmeda),[14,15] Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(tmeda),[16] $PtMe_2(bpy)$ and $[PtMe_2(SEt_2)]_2$,[17] and 8-(bromomethyl)quinoline[18] were prepared as described. Solvents were dried and distilled, stored under nitrogen and freshly distilled immediately before use, and all procedures were carried out under nitrogen. NMR spectra were recorded on a Varian Unity Innova 400 MHz wide bore instrument, at 399.7 MHz (^{1}H) or 100.5 MHz (^{13}C), and at room temperature unless indicated otherwise. Chemical shifts given in ppm relative to $SiMe_4$. Microanalyses were performed by the Central Science Laboratory, University of Tasmania. GCMS 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). Mass spectra were recorded on a Kratos Concept ISQ mass spectrometer using the LSIMS technique in a *m*-nitrobenzoyl matrix and an *m*/*z* scanning range of 50−1500 with an 8 kV probe.

Synthesis of Complexes. For ^{1}H NMR spectra, primed groups or atoms such as Me′ and H6′(bpy) refer to methyl and pyridine rings that are trans disposed.

[Pd(mq)Me$_2$(bpy)]Br (1). To a solution of $PdMe_2(bpy)$ (0.060 g, 0.21 mmol) in acetone (20 mL) cooled to 0 °C was added 8-(bromomethyl)quinoline (0.046 g, 0.21 mmol), and the resulting solution was stirred for 2 h. The volume was reduced to ∼5 mL in a vacuum, resulting in precipitation of a white solid which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried in a vacuum at 0 °C (0.108 g, ∼100% yield). The complex may be handled for brief periods at ambient temperature. ^{1}H NMR ($CDCl_3$, −20 °C): δ 9.36 (d, ^3J = 8.3 Hz, 1, H3(bpy)), 9.19 (d, ^3J = 8.4 Hz, 1, H3′(bpy)), 8.78 (d, ^3J = 4.1 Hz, 1, H6(bpy)), 8.46 (“t”, 1, H4(bpy)), 8.26 (d, ^3J = 5.4 Hz, 1, H6′(bpy)), 8.16 (m, 2, H5 and H4′(bpy)), 8.06 (d, ^3J = 8.3 Hz, 1, H2), 7.85 (“t”, 1, H5(bpy)), 7.71 (d, ^3J = 7.8 Hz, 1, H7), 7.63 (m, 2, H3,4), 7.43 (m, 1, H5′(bpy)), 7.30 (m, 1, H6), 3.97 (d, ^2J = 13.6 Hz, 1, CH_aH$_b$), 3.69 (d, ^2J = 13.7 Hz, 1, CH$_a$$H_b$), 1.46 (s, 3, Me′), 0.99 (s, 3, Me). Anal. Calcd for $C_{22}H_{22}BrN_3Pd$ C, 51.33; H, 4.31; N, 8.16%. Found: C, 51.09; H, 4.36; N, 7.85%.

[Pd(mq)MePh(bpy)]Br (2). To a solution of PdMePh(bpy) (0.068 g, 0.19 mmol) in acetone (20 mL) at 0 °C was added 8-(bromomethyl)quinoline (0.043 g, 0.19 mmol), and the resulting solution was stirred at 0 °C for 2 h, during which time a white solid product precipitated. The solid was isolated by decantation and recrystallized from dichloromethane/diethyl ether (0.107 g, 98%). The complex may be handled for brief periods at ambient temperature. ^{1}H NMR ($CDCl_3$, −20 °C): δ 9.38 (d, ^3J = 8.4 Hz, 1, H3(bpy)), 9.18 (d, ^3J = 8.0 Hz, 1, H3′(bpy)), 8.95 (d, ^3J = 4.4 Hz, 1, H6(bpy)), 8.51 (“t”, 1, H4(bpy)), 8.45 (d, ^3J = 4.4 Hz, 1, H6′(bpy)), 8.28 (d, ^3J = 8.0 Hz, 1, H5), 8.16 (“t”, 1, H4′(bpy)), 7.93 (“t”, 1, H5(bpy)), 7.88 (d, ^3J = 7.2 Hz, 1, H2), 7.77 (d, ^3J = 8.0 Hz, 1, H4), 7.66 (“t”, 1, H3), 7.58 (d, ^3J = 4.8 Hz, 1, H7), 7.48 (“t”, 1, H5′(bpy)), 7.38 (m, 1, H6), 7.32 and 7.29 (d, ^3J = 4.4 Hz, and m, 3, Ph), 6.78 (d, ^3J = 8.8

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Hz, 1, Ph), 6.61 (d, ^3J = 8.8 Hz, 1, Ph), 4.39 (d, ^2J = 14.0 Hz, 1, CH_aH$_b$), 4.18 (d, ^2J = 13.6 Hz, 1, CH$_a$$H_b$), 1.86 (s, 3, Me′). Anal. Calcd for $C_{27}H_{24}BrN_3Pd$ C, 56.22; H, 4.19; N, 7.28%. Found: C, 56.20; H, 4.11; N, 7.31%.

[Pt(mq)Me$_2$(bpy)]Br (3). To an acetone solution of PtMe$_2$(bpy) (0.075 g, 0.20 mmol) was added 8-(bromomethyl)quinoline (0.050 g, 0.23 mmol). The resulting solution was stirred for 10 min during which time the color changed from bright red to colorless. The solvent was removed in a vacuum and the solid extracted with dichloromethane (3 × 2.5 mL). The dichloromethane solution was filtered through Celite, and the product was obtained as a white solid by addition of diethyl ether (5 mL), cooling to −30 °C overnight, filtering, and drying in a vacuum (0.124 g, 100%). ^{1}H NMR ($CDCl_3$, −20 °C): δ 9.53 (d, ^3J = 8.4 Hz, 1, H3(bpy)), 9.36 (d, ^3J = 8.0 Hz, 1, H3′(bpy)), 8.91 (d, ^3J = 5.6 Hz, 1, H6(bpy)), 8.53 (“t”, 1, H4(bpy)), 8.33 (d, ^3J = 6.8 Hz, 1, H6′(bpy)), 8.27 (d, ^3J = 8.4 Hz, 1, H5), 8.22 (“t”, 1, H4′(bpy)), 7.92 (m, 2, H5′(bpy) and H2), 7.81 (d, ^3J = 6.0 Hz, 1, H7), 7.69 (d, ^3J = 7.2 Hz, 1, H4), 7.63 (“t”, 1, H3), 7.49 (“t”, 1, H5′(bpy)), 7.35 (m, 1, H6), 3.65 (d, ^2J = 16.0 Hz, 1, CH_aH$_b$), 3.51 (d, ^2J = 16.0 Hz, 1, CH$_a$$H_b$), 1.01 ($^2J_{PtH}$ = 68.5 Hz, 3, Me′), 0.54 ($^2J_{PtH}$ = 68.7 Hz, 3, Me). ^{13}C NMR ($CDCl_3$): δ 155.3, 154.6, 148.7, 147.3, 146.1, 145.4, 142.0, 141.2, 139.1, 132.2, 131.6, 131.1, 130.0, 128.8, 128.4, 127.7, 127.6, 127.3, 125.6, 123.0, 17.8 (J_{Ptc} = 690.4 Hz, CH_2), −3.45 (J_{PtC} = 661.8 Hz, Me or Me′), −11.78 (J_{PtC} = 642.0 Hz, Me or Me′). Anal. Calcd for $C_{22}H_{22}BrN_3Pt$ C, 43.79; H, 3.67; N, 6.96%. Found: C, 43.78; H, 3.73; N, 7.11%.

[Pd(mq)MePh(bpy)]BF$_4$ (4). To a solution of **2** in acetone at 0 °C was added a stoichiometric amount of $AgBF_4$, with the immediate precipitation of a white solid (AgBr), which was removed by filtration over celite. The volume of the resulting colorless solution was decreased to approximately 10 mL, and then pentane (10 mL) was added, causing the precipitation of the product in quantitative yield as a white microcrystalline solid. ^{1}H NMR ($CDCl_3$, −20 °C, two isomers denoted A and B, A:B = 60:40): δ 9.01 (d, ^3J = 5.6 Hz, 1, H6(bpy, A)), 8.86 (d, ^3J = 8.4 Hz, 0.7, H3 or 3′(bpy, B)), 8.78 (d, ^3J = 8.4 Hz, 1, H3(bpy, A)), 8.77 (d, ^3J = 8.4 Hz, 0.7, H3 or 3′(bpy, B)), 8.63 (d, ^3J = 8.4 Hz, 1, H3′(bpy, A)), 8.55 (d, ^3J = 5.2 Hz, 0.7, H6 or 6′(bpy, B)), 8.50 (d, ^3J = 4.0 Hz, 1, H6′(bpy, A)), 8.44 (“t”, 1, H4(bpy, A)), 8.39 (“t”, 0.7, H4(bpy, B)), 8.25 (m, 2.4, H5(A) and 2H(B)), 8.16 (“t”, 0.7, H4′(bpy, B)), 8.10 (“t”, 1, H4′(bpy, A)), 8.00 (d, ^3J = 3.2 Hz, 0.7, H(B)), 7.88 (m, 2.7, 2H(A) and H(B)), 7.78 (d, ^3J = 7.6 Hz, 1, H(A)), 7.64 (m, 4.1, 2H(A) and 3H(B)), 7.37 (m, 3.4, 2H(A) and 2H(B)), 7.01 (br, 3.4, Ph(A, B)), 6.96 (m, 5.1, Ph(A, B)), 4.45 (d, ^2J = 13.6 Hz, 1, CH_2(A)), 4.25 (m, 2.4, CH_2(A, B)), 1.94 (s, 3, PdMe(A)), 1.54 (s, 2.1, PdMe(B)). Anal. Calcd for $C_{27}H_{24}BF_4N_3Pd$ C, 55.56; H, 4.14; N, 7.20%. Found: C, 55.70; H, 4.21; N, 7.15%.

[Pt(mq)Me$_2$(bpy)]BF$_4$ (5). To a solution of **3** in acetone (10 mL) was added a stoichiometic amount of $AgBF_4$, and the resulting suspension was stirred for 5 min. A grey solid (AgBr) was removed by filtration, and the volume of the resulting solution was reduced in a vacuum. Addition of diethyl ether and cooling to −30 °C overnight, followed by filtration and drying in a vacuum, afforded a white solid (∼100%). Crystals suitable for X-ray crystallography were obtained from dichloromethane/toluene. ^{1}H NMR ($CDCl_3$): δ 8.93 (d, ^3J = 7.2 Hz, 1, H6(bpy)), 8.84 (d, ^3J = 8.0 Hz, 1, H3(bpy)), 8.72 (d, ^3J = 8.0 Hz, 1, H3′(bpy)), 8.43 (“t”, 1, H4(bpy)), 8.33 (d, ^3J = 5.6 Hz, 1, H6′(bpy)), 8.22 (d, ^3J = 8.4 Hz, 1, H5), 8.14 (“t”, 1, H4′(bpy)), 7.90 (m, 2, H2 and H3(bpy)), 7.84 (d, ^3J = 6.0 Hz, 1, H7), 7.67 (d, ^3J = 8.0 Hz, 1, H4), 7.62 (“t”, 1, H3), 7.45 (“t”, 1, H5′(bpy)), 7.35 (“t”, 1, H6), 3.65 (d, ^2J = 16.0 Hz, $^2J_{PtH}$ = 83.2 Hz, 1, CH_aH$_b$), 3.51 (d, ^2J = 16.4 Hz, $^2J_{PtH}$ = 83.2 Hz, 1, CH$_a$$H_b$), 1.01 (s, $^2J_{PtH}$ = 68.3 Hz, 3, Me′), 0.53 (s, $^2J_{PtH}$ = 69.5 Hz, 3, Me). ^{13}C NMR ($CDCl_3$): δ 155.1, 154.7, 148.7, 147.7, 146.5, 146.4, 146.0, 142.1, 141.4, 139.4, 131.9, 129.0, 128.9, 128.7, 128.0, 126.8, 126.3, 126.0, 123.5, 17.86, −3.40, −11.86. Anal. Calcd for $C_{22}H_{22}BF_4N_3Pt$ C, 43.30; H, 3.63; N, 6.88%. Found: C, 43.25; H, 3.65; N, 6.68%.

[Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(mq)(bpy)]Br (6). The complex was prepared using a similar procedure to that used for **1** (95%). The complex is thermally unstable and decomposes within minutes at ambient temperature, precluding elemental analysis. ^{1}H NMR ($CDCl_3$, −20 °C): δ 9.29 (d, ^3J = 8.2 Hz, 1, H3(bpy)), 9.10 (d, ^3J = 8.2 Hz, 1, H3′(bpy)), 9.03 (d, ^3J = 5.1 Hz, 1, H6(bpy)), 8.51 (“t”, 1, H4(bpy)), 8.31 (d, ^3J = 4.2 Hz, 1, H6′(bpy)), 8.25 (d, ^3J = 8.3 Hz, 1, H5), 8.17 (“t”, 1, H4′(bpy)), 7.99 (“t”, 1, H5(bpy)), 7.89 (d, ^3J = 7.1 Hz, 1, H2), 7.74 (d, ^3J = 8.0 Hz, 1, H7), 7.64 (d, ^3J = 7.6 Hz, 1, H4), 7.60 (m, 1, H3), 7.50 (“t”, 1, H5′(bpy)), 7.31 (m, 1, H6), 3.97 (d, ^2J = 14.2 Hz, 1, CH_aH$_b$), 3.71 (d, ^2J = 14.4 Hz, 1, CH$_a$$H_b$), 3.07 (m, 2, CH_2), 2.73 (m, 2, CH_2), 1.78 (m, 2, CH_2), 1.50 (m, 2, CH_2).

***In Situ* Reactions of PdMe$_2$(tmeda) and PdMePh(tmeda) with 8-(bromomethyl)quinoline. PdMe$_2$(tmeda) + 8-mqBr.** To a $(CD_3)_2CO$ solution of PdMe$_2$(tmeda) (0.020 g, 0.08 mmol) in an NMR tube cooled to −60 °C was added one equiv of 8-mqBr (0.018 g). The solution was thoroughly mixed and inserted into the precooled (−60 °C) probe of the NMR spectrometer. Spectra were recorded immediately, and at 5 min intervals as the temperature was slowly raised to −30 °C, at which point a reaction occurred, as indicated by the appearance of new resonances. The temperature was maintained at −30 °C for 20 min, after which it was slowly raised to room temperature, during which time spectra were recorded every 5 min. The NMR tube was maintained at room temperature for a further 16 h and the ^{1}H NMR spectrum rerecorded. The solution was then analyzed by GCMS and LSIMS. The behavior of PdMe$_2$(tmeda) was examined under identical conditions.

PdMePh(tmeda) + 8-mqBr. To an acetone-d_6 solution of PdMePh(tmeda) (0.023 g, 0.07 mmol) in an NMR tube cooled to −60 °C was added 1 equiv of 8-mqBr 90.016 g). The solution was thoroughly mixed and inserted into the precooled (−60 °C) probe of the NMR spectrometer. Spectra were recorded immediately, and at 5 min intervals as the temperature was slowly raised to 25 °C during which time the ^{1}H NMR spectra showed no evidence of any reaction.

Pd(mq)Me$_2${(pz)$_2$BH$_2$} (7). A mixture of [PdMe$_2$(pyridazine)]$_2$ (0.058 g, 0.135 mmol) and K[(pz)$_2$BH$_2$] (0.075 g, 0.405 mmol) was stirred in acetone (8 mL) at room temperature for 10 min. The solution was cooled to −40 °C and 8-(bromomethyl)quinoline (0.060 g, 0.270 mmol) added. The mixture was allowed to warm to 0 °C over 30 min, after which the solvent removed in a vacuum at 0 °C. To the residue was added cold (0 °C) diethyl ether (20 mL) and water (10 mL), and the mixture was stirred vigorously for 1 min and then cooled to −40 °C. The organic layer was decanted then left to stand over $MgSO_4$ for 10 min at 5 °C. The mixture was filtered through Celite, the Celite washed with diethyl ether (10 mL), the organic extracts were combined, and the solvent was removed in a vacuum. The residue was dissolved in acetone (2 mL), and pentane (10 mL) was added. The solution was cooled to −20 °C and left overnight after which time a small amount of solid had precipitated. The solution was filtered and the solvent removed in a vacuum at 0 °C. The residue was dissolved in diethyl ether (1 mL), and the product crystallized on slow diffusion of pentane into the solution at −20 °C over 24 h (0.059 g, 51%). ^{1}H NMR (CD_2Cl_2): δ 8.19 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 1, H5), 8.10 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1, H2), 7.82 (dd, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1, H7), 7.72 (m, 2, H5(pz)), 7.69 (m, 1, H4), 7.57 (“t”, 1, H3), 7.46 (d, ^3J = 2.0 Hz, 1, H3(pz)), 7.24 (m, 1, H6), 7.07 (d, ^3J = 1.6 Hz, 1, H3(pz)), 6.37 (“t”, 1, H4(pz)), 5.95 (“t”, 1, H4(pz)), 4.10 (d, ^2J = 14.0 Hz, 1, CH_2), 3.43 (d, ^2J = 14.0 Hz, 1, CH_2), 1.41 (s, 3, Me), 1.33 (s, 3, Me). ^{13}C NMR (CD_2Cl_2): δ 149.6, 147.2, 139.4, 138.7, 138.4, 138.5, 137.5, 136.7, 131.0, 130.3, 128.3, 126.0, 122.5, 105.5,

104.9, 36.5, 16.9, 13.3. Anal. Calcd for $C_{18}H_{23}BN_5Pd$: C, 50.68; H, 5.43; N, 16.42. Found: C, 50.82; H, 5.39; N, 16.39%.

Pd(mq)MePh{(pz)$_2$BH$_2$} (8). A mixture of PdMePh(tmeda) (0.059 g, 0.189 mmol) and K[(pz)$_2$BH$_2$] (0.070 g, 0.380 mmol) was stirred in acetone (4 mL) overnight. The solution was cooled to −40 °C and 8-(bromomethyl)quinoline (0.042 g, 0.189 mmol) added. The mixture was allowed to warm to 0 °C over 30 min, after which the solvent removed in a vacuum at 0 °C. To the residue was added cold (0 °C) diethyl ether (8 mL) and water (4 mL), and the mixture was stirred vigorously for 1 min and then cooled to −40 °C. The organic layer was decanted then left to stand over $MgSO_4$ for 10 min at 5 °C. The mixture was filtered through Celite, the Celite was washed with diethyl ether (8 mL), the organic extracts were combined, and the solvent was removed in a vacuum. The residue was dissolved in acetone (2 mL), and pentane (10 mL) was added. The solution was cooled to −20 °C for 1 h, after which time impurities had precipitated as an oil. The solution was decanted, and the product crystallized on slow diffusion of pentane into the solution at −20 °C over 24 h (0.030 g, 33%). ^{1}H NMR (CD_2Cl_2): two isomers, denoted as A and B, A:B = 0.56:0.44, approximated as ∼1:1 elsewhere. δ 8.37 (dd, ^3J = 4.8 Hz, ^4J = 1.5 Hz, 0.44, H2(B)), 8.31 (dd, ^3J = 4.8 Hz, ^4J = 1.5 Hz, 0.56, H2(A)), 8.24 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 0.56, H5(A)), 8.21 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 0.44, H5(B)), 7.85 (m, 1.56, H7), 7.80 (d, ^3J = 1.6 Hz, 0.56, H5(pz, A)), 7.75−7.72 (m, 1.44, H5(pz, B) and H4(A, B)), 7.67 (d, ^3J = 1.6 Hz, 0.56, H5(pz, A)), 7.59 ("t", 1, H3), 7.48 (m, 1, H3(pz)), 7.35 (m, 0.56, H6(A)), 7.30 (m, 0.44, H6(B)), 7.13−7.09 (m, 1, H3(pz)), 6.97−6.85 (m, 3, Ph), 6.59 (d, ^3J = 6.96 Hz, 2, Ph), 6.37 ("t", 0.56, H4(pz, A)), 6.25 ("t", 0.44, H4(pz, B)), 5.95 ("t", 1, H4(pz)), 4.50 (d, ^2J = 14.0 Hz, 0.56, CH_2(A)), 4.24 (d, ^2J = 14.0 Hz, 0.44, CH_2(B)), 3.95 (d, ^2J = 13.6 Hz, 1, CH_2(A)), 1.81 (s, 1.32, Me(B)), 1.80 (s, 1.68, Me(A)). ^{13}C NMR (CD_2Cl_2): δ 150.0, 149.7, 149.42, 148.5, 147.9, 145.7, 141.7, 139.2, 138.5, 138.3, 138.2, 137.9, 137.1, 136.5, 136.3, 135.2, 134.9, 130.4, 129.7, 129.4, 127.9, 127.8, 127.7, 127.5, 125.6, 125.5, 124.6, 124.1, 122.0, 105.0, 104.7, 104.5, 104.3, 43.0, 39.9, 22.2, 20.2. Anal. Calcd for $C_{23}H_{24}BN_5Pd$: C, 56.64; H, 4.96; N, 14.36. Found: C, 56.60; H, 4.94; N, 14.38%.

Pt(mq)Me$_2${(pz)$_2$BH$_2$} (9). A mixture of [PtMe$_2$(SEt$_2$)]$_2$ (0.060 g, 0.095 mmol), K[(pz)$_2$BH$_2$] (0.070 g, 0.380 mmol), and 8-(bromomethyl)quinoline (0.042 g, 0.189 mmol) was stirred at ambient temperature in acetone (4 mL) for 1 h. The solvent was removed in a vacuum and the residue extracted with diethyl ether (8 mL). The organic extract was washed with water (3 × 2 mL) and then dried over $MgSO_4$. The mixture was then filtered through Celite, the Celite was washed with diethyl ether (8 mL), the organic extracts were combined, and the solvent was removed in a vacuum. The residue was dissolved in acetone (1 mL), and pentane (10 mL) was added. The solution was cooled to −20 °C and left overnight, after which time impurities had precipitated as an oil. The solution was decanted, the solvent removed in a vacuum, the residue dissolved in diethyl ether (0.5 mL), and the product crystallized on slow diffusion of pentane into the solution at −20 °C over 24 h (0.052 g, 53%). ^{1}H NMR ($CDCl_3$): δ 8.46 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1, H2), 8.13 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 1, H5), 7.78 (dd, ^3J = 6.8 Hz, ^4J = 1.2 Hz, 1, H7), 7.72 (m, 2, H5(pz)), 7.55 (m, 1, H4), 7.48 ("t", 1, H3), 7.44 (d, ^3J = 2.4 Hz, 1, H3(pz)), 7.35 (d, ^3J = 2.4 Hz, 1, H3(pz)), 7.25 (m, 1, H6), 6.36 ("t", 1, H4(pz)), 6.02 ("t", 1, H4(pz)), 3.77 (d, ^2J = 16.0 Hz, $^2J_{Pt-H}$ = 80.7 Hz, 1, CH_2), 3.20 (d, ^2J = 15.6 Hz, $^2J_{Pt-H}$ = 67.9 Hz, 1, CH_2), 0.85 (s, $^2J_{Pt-H}$ = 68.0 Hz, 3, CH_3), 0.83 (s, $^2J_{Pt-H}$ = 68.8 Hz, 3, Me). ^{13}C NMR ($CDCl_3$) 150.6, 150.5, 149.5, 138.7, 137.0, 131.6, 130.6, 128.7, 125.5, 122.5, 106.0, 105.5, 16.1 ($^1J_{Pt-C}$ = 703.4 Hz), −5.19 ($^1J_{Pt-C}$ = 682.8 Hz), −9.54 ($^1J_{Pt-C}$ = 663.0). Anal. Calcd for $C_{18}H_{23}BN_5Pt$: C, 41.96; H, 4.50; N, 13.59. Found: C, 42.14; H, 4.52; N, 13.52%.

Decomposition Studies. In a typical experiment a Pd(IV) complex (∼10 mg) was dissolved in $(CD_3)_2CO$ at −20 °C and warmed to room temperature overnight. The gas phase and solution were analyzed by GCMS and high resolution LSIMS, and the solution by ^{1}H NMR spectroscopy. Inorganic Pd(II) products were identified by LSIMS.

X-ray Data Collection and Structure Determination, and Refinement for 5, 7, and 8. Crystals of **5** were obtained from dichloromethane/pentane at −30 °C, and crystals of **7** and **8** from the preparation of the complexes. Full spheres of data were measured at room temperature using a Bruker AXS CCD/area detector instrument (monochromatic Mo Kα radiation, λ = 0.710 73 Å; t s frames, 0.4° ω-scan increments, specimen-detector distance 5 cm; T ca. 300 K). N_t total data were merged to N_r unique (R_{int} quoted), N_o of these with $F > 4\sigma(F)$ being considered "observed" and used in the full matrix least squares refinements after preliminary processing, inclusive of "empirical" absorption correction using the proprietary software SAINT, SADABS, XPREP. Anisotropic thermal parameters were refined for the non-hydrogen atoms; for the palladium complex **8** (x,y,z,U_{iso})$_H$ were refined, these parameters being included as constrained estimates for **5** and **7**. In the latter, the solvent molecule was modeled as disordered about sites located on crystallographic 2-axes; "thermal motion" on the tetrafluoroborate anion was also high, and it was incorporated in the model with constrained geometry, the overall consequence being rather lower precision than for **7** and **8**. Conventional R, R_w on $|F|$ are quoted at convergence, statistical weights being employed. Neutral atom complex scattering factors were employed, computation using the Xtal 3.0 program system.[19]

Selected structural data are given in Tables 1 and 2 and views of the complexes are shown in Figures 1 and 2.

Results and Discussion

Synthesis of Complexes. Syntheses were initially confined to the 2,2′-bipyridine complexes [Pd(mq)MeR(bpy)]Br (R = Me, Ph) and [Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(mq)(bpy)]Br (Scheme 1). As these complexes were found to be either unstable (**1**, **6**) or did not yield crystals suitable for X-ray studies (**2**), synthetic studies were extended to include [Pt(mq)Me$_2$(bpy)]Br (**3**) and bis(pyrazol-1-yl)borate complexes because Pt(IV) complexes are expected to be very stable and tris(pyrazol-1-yl)borate forms some of the more stable Pd(IV) complexes such as PdMe$_3${(pz)$_3$BH}.[6] The complex ions [MMeR{(pz)$_2$BH$_2$}]$^-$ (R = Me, Ph) were prepared in a manner similar to [(pz)$_3$BH]$^-$ analogues,[20,21] by addition of K[(pz)$_2$BH$_2$] to [PdMe$_2$(pyridazine)]$_2$, PdMePh(tmeda), or [PtMe$_2$(SEt$_2$)]$_2$. Complex **3** reacts with $AgBF_4$ to give [Pt(mq)Me$_2$(bpy)]BF_4 (**5**) which forms crystals suitable for X-ray diffraction studies, but suitable crystals could not be obtained from the palladium analogue [Pd(mq)Me$_2$(bpy)]BF_4 (**4**). Complexes **1**−**9** were isolable, and all except **6** were sufficiently stable for microanalysis.

^{1}H NMR spectra of the complexes are consistent with structures revealed by X-ray crystallography for **5**, **7**, and **8**, and in the case of bpy complexes assignment of pyridine rings trans to methyl and benzylic groups was possible. Thus, for the very stable Pt(IV) complex **3** a gradient nuclear Overhauser enhancement (gNOESY) experiment revealed a "through-space" interaction for the Me′ and H6(bpy) protons, and for the benzylic proton

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(20)) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 5713.
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Table 1. Specific Crystallographic Details

complex	$[Pt(mq)Me_2(bpy)]BF_4 \cdot 0.75(CH_2Cl_2)$ (**5**)	$Pd(mq)Me_2\{(pz)_2BH_2\}$ (**7**)	$Pd(mq)MePh\{(pz)_2BH_2\}$ (**8**)[a]
formula	$C_{22}H_{22}BF_4N_3Pt \cdot 0.75(CH_2Cl_2)$	$C_{18}H_{22}BN_5Pd$	$C_{23}H_{24}BN_5Pd$
crystal system	monoclinic	monoclinic	triclinic
space group	$C2/c$ (C_{2h},[6] no. 15)	$P2_1/c$ (C_{2h},[5] no. 14)	$P\bar{1}$ (C_i,[1] no. 2)
a (Å)	40.624(4)	16.309(3)	9.2700(9)
b (Å)	12.890(1)	13.198(2)	10.303(1)
c (Å)	19.765(2)	18.549(3)	12.595(2)
β (deg)	91.347(2)	103.792(2)	87.091(1)
V (Å)	10347	3877	1098
Z	16	8	2
mol wt	674.0	425.7	487.7
D_{calcd} (g cm^{-3})	1.730	1.458	1.476
crystal size (mm)	0.20 × 0.12 × 0.10	0.50 × 0.30 × 0.30	0.10 × 0.08 × 0.06
μ (cm^{-1})	56	9.7	8.6
$F(000)$	5208	1728	496
$2\theta_{max}$ (deg)	50	58	58
"T"$_{min,max}$	0.54, 0.75	0.76, 0.89	0.74, 0.93
N_t, N, N_o	60360, 9087, 5982	44409, 9638, 7283	12771, 5354, 4196
R, R_w, R_{int}	0.052, 0.067, 0.030	0.034, 0.044, 0.021	0.029, 0.030, 0.023
n_v	615	451	367
$\lvert\Delta\rho_{max}\rvert$ (e Å^{-3})	2.13(8)	0.83(4)	0.60(6)

[a] $\alpha = 69.576(1)$, $\gamma = 76.927(1)°$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Pt(mq)Me_2(bpy)]BF_4 \cdot 0.75(CH_2Cl_2)$ (5), $Pd(mq)Me_2\{(pz)_2BH_2\}$ (7), and $Pd(mq)MePh\{(pz)_2BH_2\}$ (8)

	5[a,b]		**7**[a,c]		
	molecule 1	molecule 2	molecule 1	molecule 2	**8**[d]
			Bond Distances		
M−C(01)	2.07(1)	2.04(2)	2.038(4)	2.055(4)	2.026(3)
M−C(1)	2.03(1)	2.07(1)	2.035(4)	2.037(4)	2.036(3)
M−C(81)	2.05(1)	2.04(1)	2.030(4)	2.036(3)	2.021(3)
M−N(1)	2.151(9)	2.17(1)	2.170(2)	2.166(2)	2.166(2)
M−N(11)	2.16(1)	2.15(1)	2.189(3)	2.172(3)	2.173(2)
M−N(11′)	2.14(1)	2.12(1)	2.200(2)	2.196(3)	2.182(2)
B−N(12)			1.537(4)	1.547(5)	1.546(4)
B−N(12′)			1.551(5)	1.529(5)	1.548(4)
			Bond Angles		
C(01)−M−C(1)	90.9(5)	90.4(6)	88.5(2)	89.2(2)	89.3(1)
C(01)−M−C(81)	89.9(6)	93.3(6)	88.8(2)	89.1(1)	90.5(1)
C(1)−M−C(81)	87.4(5)	86.1(5)	87.9(2)	87.9(2)	88.0(2)
C(81)−M−N(1)	82.6(5)	82.0(5)	83.1(1)	82.6(1)	82.7(1)
C(81)−M−N(11)	172.9(5)	174.4(5)	178.8(1)	179.3(1)	177.9(1)
C(81)−M−N(11′)	96.8(5)	97.9(5)	91.7(1)	91.6(1)	91.4(1)
C(01)−M−N(1)	172.6(5)	175.1(5)	171.2(2)	170.9(1)	172.3(1)

[a] Two independent molecules; for C(15) read C(16). [b] Distance of Pt from the mq, py and py′ mean planes: molecule 1 (0.04(2), 0.28(2), 0.12(2) Å), molecule 2 (0.01(2), 0.06(2), 0.03(2) Å). Distance of C(81) from mq mean planes 0.04(2), 0.13(2) Å; dihedral angle between py planes 8.4(5), 6.1(5)°. [c] Distance of Pd from the mq, pz, and pz′ mean planes: molecule 1 (0.047(3), 0.271(6), 0.327(6) Å), molecule 2 (0.101(3), 0.408(6), 0.214(6) Å). Distance of C(81) from mq mean planes −0.113(5), −0.169(5) Å; dihedral angle between pz planes 51.1(2), 50.3(2)°. [d] Distance of Pd from the mq, pz, pz′, and Ph mean planes: 0.002(3), 0.545(6), 0.342(5), 0.060(5) Å. Distance of C(81) from the mq mean plane −0.149(5) Å. Dihedral angle between pz planes 52.0(2)°.

H_a and H6′(bpy). A long range gCOSY experiment showed an interaction between the benzylic protons and an aromatic proton at 7.84 ppm, thus confirming the gNOESY assignment for the benzylic proton, allowing assignment of H7(mq) at 7.84 ppm, and thus the remaining mq protons from a short range COSY experiment. Assignment for the palladium complexes was straightforward on comparison with 1D spectra of **3**. All complexes exhibited appropriate integration for the assignments presented in the Experimental Section, and for the Pt(IV) complexes $^2J_{PtH}$ values of 68.0−69.5 Hz for the PtMe groups and 80.2−83.2 Hz for the $PtCH_2$ groups were observed.

Geometrical isomers are indicated from NMR spectra of $[Pd(mq)MePh(bpy)]BF_4$ (**4**) and $Pd(mq)MePh\{(pz)_2BH_2\}$ (**8**), in the ratio 60:40 and ∼1:1 respectively, where the dominant isomer for **4** is as shown in Scheme 1.

Replacement of bromide in **3** by tetrafluoroborate in $[Pt(mq)Me_2(bpy)]BF_4$ (**5**) results in essentially identical spectra, except that the H3(bpy) and H3′(bpy) resonances are shifted upfield by ∼0.7 ppm. Similar effects were observed for [Pd(mq)MePh(bpy)]X (X = Br (**2**), BF_4 (**4**); upfield shifts of ∼0.6 ppm), and have been noted for related trialkylpalladium(IV) complexes $[PdMe_3\{(pz)_3CH\}]X$ (X = I, BF_4; upfield shifts of 3.03 and 0.35 ppm for CH and H(5), respectively)[22] and $[PdMe_2(CH_2Ph)\{(pz)_3CH\}]X$ (X = Br, BF_4; upfield shifts of 3.22 and 1.05 ppm for CH and H(5) respectively),[23] and have been attributed as indicating the site of cation−anion interactions in these complexes.

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(23) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 1231.

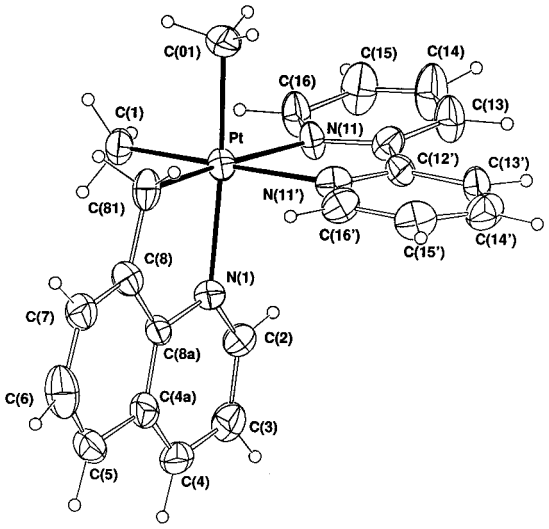


Figure 1. Molecular structure of the cation in [Pt(mq)-Me_2(bpy)]BF_4·0.75(CH_2Cl_2) (**5**). Molecule 1 of two independent molecules is shown. Thermal ellipsoids (20%) are shown for non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

Structural Studies of 5, 7, and 8. The cation [Pt-(mq)Me_2(bpy)]$^+$ and the complexes Pd(mq)MeR{$(pz)_2BH_2$} (R = Me, Ph) have distorted octahedral geometry for the *fac*-MC_3N_3 kernels (Figures 1 and 2, Table 2). The two independent molecules in each of the structures of **5** and **7** are essentially identical. The crystal of **8** that was examined contains the isomer with the configuration shown in Scheme 1. The 8-methylquinolinyl-*N*,*C* groups form essentially planar chelate rings in which the metal and benzylic carbons deviate by 0.001(9)−0.101(3) and 0.04(2)−0.169(5) Å from the mq mean planes. The "M(mq)" motifs exhibit CMN angles of 82.0-(5)−83.1(1)°, intermediate between corresponding angles for the "Pt(bpy)" (NPtN = 76.1(4), 77.3(4)°) and "Pt-{$(pz)_2BH_2$}" motifs (NPdN = 87.2(1), 89.19(8)°).

The phenyl ring plane in **8** bisects the C(1)PdC(81) plane such that the *ortho* protons are positioned between the Me and CH_2 groups, slightly twisted toward the CH_2 group; the torsion angles C(06)−C(01)−Pd−N(11, 11′) are −41.6(2), 47.6(2)°; the H(02)···H(81b) contact as refined is 2.27(5) Å. This slight distortion from the putative mirror plane containing N(1)PdB which bisects the $[(pz)_2BH_2]^-$ ligand may be related to a minor conformational difference between the two molecules of **7**, wherein slight asymmetries in the torsion angles of the $Pd(N_2)_2B$ ring occur in opposite senses in the two molecules (Table 2). The shortness of the H(2)···H(0a) distance (one of the BH_2 hydrogens), refining to 2.34(3) Å, suggests this interaction as a possible determinant, the ring conformation as observed in **8** agreeing closely with one of the conformers of **7**. The variation between equivalent parameters of the Pd environments of the two otherwise "identical" molecules in **7** suggests caution in the interpretation of the generally minor variations observed, although the consistency of the sign of the difference between Pd−N(11, 11′) in **7** and **8** suggests some slight difference in trans effects of the methyl and methylene groups, possible due to the small bite angle of the mq group. The array of (quasi)planar moieties about the periphery of each molecule has implications for crystal packing, the asymmetric units of **5** and **7** having two independent molecules/cations which cluster into aggregates/columns, while in **8** each entity is packed so as to relate to a necessarily parallel inversion image.

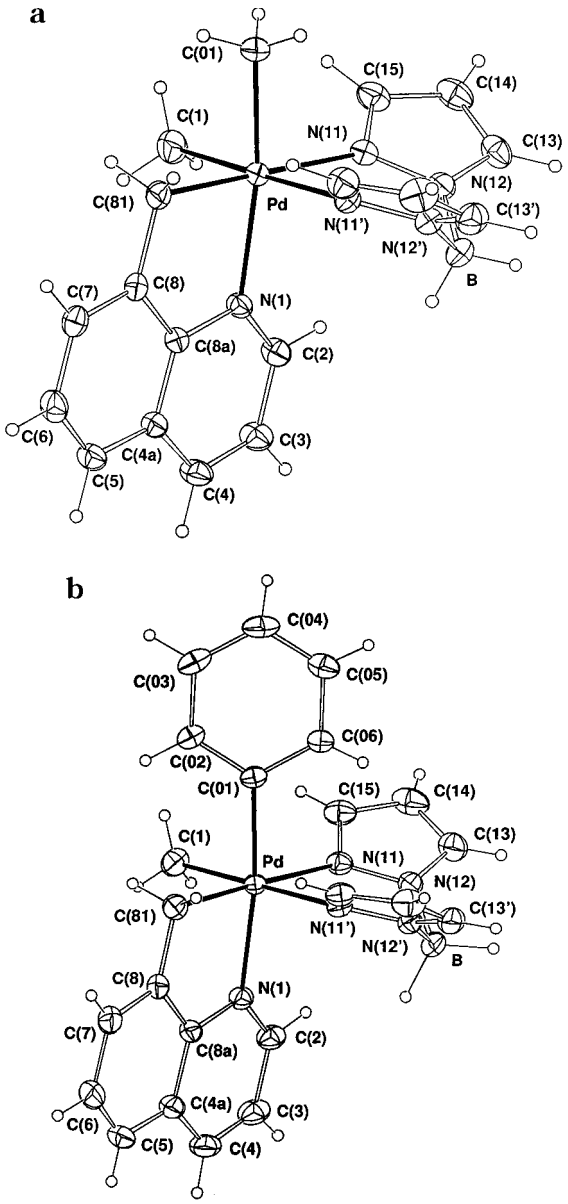
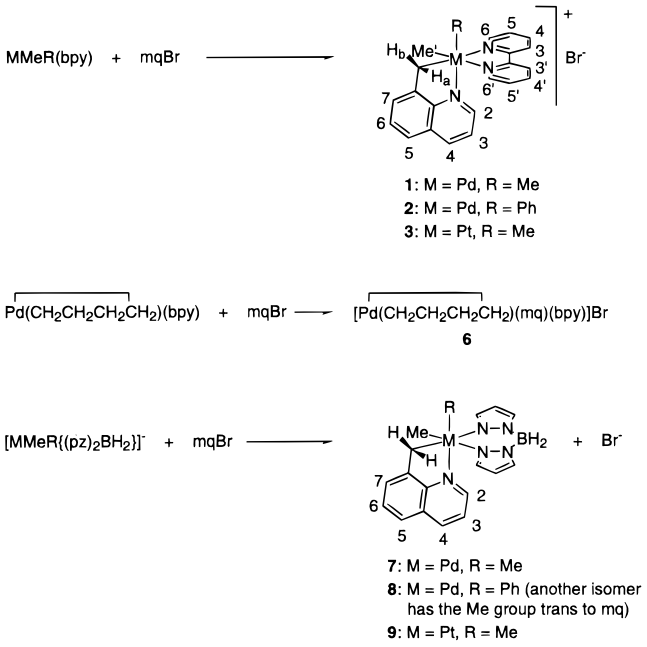


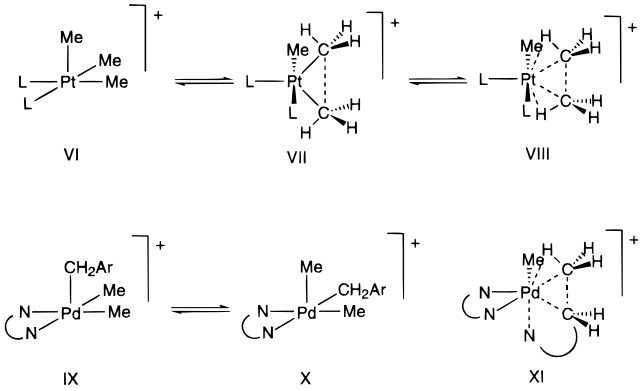
Figure 2. Molecular structure of (a) Molecule 1 of the two independent molecules of Pd(mq)Me_2{$(pz)_2BH_2$} (**7**) and (b) Pd(mq)MePh{$(pz)_2BH_2$} (**8**).

Thermal Decomposition of [Pd(mq)Me_2(bpy)]Br (1) and [Pd($CH_2CH_2CH_2CH_2$)(mq)(bpy)]Br (6). The complexes [Pd(mq)MePh(bpy)]X (X = Br, BF_4) and the $[(pz)_2BH_2]^-$ complexes are stable near ambient temperature, but the remaining Pd(IV) complexes decompose readily and provide opportunities for examination of the influence of intramolecular coordination on decomposition mechanisms. A solution of **1** in $(CD_3)_2CO$ (containing 1,4-dioxane as an internal standard) was sealed in an NMR tube. After 24 h the tube was centrifuged and cooled to −80 °C, giving spectra exhibiting ethane, 8-ethylquinoline, and PdBrMe(bpy) in ∼1:2:2 ratio such that 99% of the methyl groups are accounted for in these products. Mass spectrometry (LSIMS) confirmed the presence of PdBrMe(bpy), together with far less soluble

Scheme 1. Synthesis of Complexes



Scheme 2. Reductive Elimination

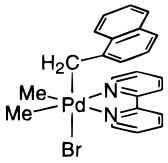


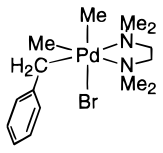
[Pd(mq)(bpy)]$^+$. There was no evidence for the formation of Pd(0), methane, or ethene. Thus, the decomposition reaction is formulated as in eq 1.

$$[Pd(mq)Me_2(bpy)]Br \rightarrow 0.35\ \{Me\text{-}Me + [Pd(mq)(bpy)]Br\} + 0.65\ \{Me\text{-}mq + PdBrMe(bpy)\} \quad (1)$$

Under identical conditions, [Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(mq)(bpy)]Br (**6**) forms 8-substituted quinolines and traces (<5%) of butenes. At least 11 products were detected by GCMS including 8-methylquinoline, 8-C$_5$(unsaturated)quinolines, and 8-C$_5$(saturated)quinolines; quantification of products was not attempted. A similar process has been reported for Pd(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_2$Ph)Br(bpy),[24] consistent with a major pathway involving mq···CH$_2$ coupling followed by decomposition of the organopalladium(II) species thus formed.

The distribution of C···C coupling products from [Pd(mq)Me$_2$(bpy)]Br differs markedly from closely related PdBrMe$_2$(CH$_2$Ar)(bpy) [Ar = Ph, naphthyl (**IV**)][5] and PdBrMe$_2$(CH$_2$Ph)(tmeda) (**V**)[7] which give exclusively ethane and PdBr(CH$_2$Ar)(L$_2$) (L$_2$ = bpy, tmeda).





It has been established that reductive elimination of ethane from PdIMe$_3$(bpy) occurs predominantly via loss of iodide,[25] consistent with experimental studies of closely related trimethylplatinum(IV) complexes PtXMe$_3$(dppe) [dppe = bis(diphenylphosphino)ethane].[26] Recent theoretical studies of reductive elimination from square-pyramidal [PtMe$_3$(PH$_3$)$_2$]$^+$ indicate that elimination of ethane occurs via Me···Me coupling from Me groups in the axial and equatorial sites, and involving close Pt···HC contact (Scheme 2, **VI** → **VIII**).[27] For this approach to apply for PdBrMe$_2$(CH$_2$Ar)(bpy) (**IV**), but not PdBrMe$_2$(CH$_2$Ph)(tmeda) (**V**), to give the observed selective reductive elimination of ethane, an isomerization is required to place methyl groups in axial and equatorial positions (**IX** → **X**). Isomerization is expected to be facile for the cation [PdMe$_2$(CH$_2$Ar)(tmeda)]$^+$ since related species such as [PdMe$_3$(tmeda)(NCCD$_3$)]$^+$ are known to be fluxional ($\Delta G^{\ddagger}$ 53 kJ mol^{-1}).[15]

For [Pd(mq)Me$_2$(bpy)]$^+$, dissociation of the mq nitrogen would give a five-coordinate species with methyl groups in axial and equatorial positions (**X**) so that both Me···Me and Me···mq coupling could compete without a requirement for isomerization. Factors favoring the observed preference for Me···mq coupling (eq 1), compared with Me···Me coupling from **IV** and **V** where closely related Me···CH$_2$Ar coupling is possible, are unclear. One factor that may be excluded is the possibility that the large quinoline group, when dissociated, prevents formation of a species analogous to **VIII** involving Pt···HC interaction, since it is of identical configuration to the naphthyl group. One possibility, if strict five-coordination is not required, is that coordination by nitrogen (perhaps weakly in a transition state) prevents Me···Me coupling and assists Me···mq coupling by correctly orientating the C(sp^3) orbital of the benzylic carbon in a similar manner to that for the methyl groups in **VIII** (as illustrated in **XI**).

Reaction of PdMe$_2$(tmeda) with 8-(Bromomethyl)quinoline. As an auxiliary ligand for palladium, tmeda has played an important role in the early development of Pd(IV) chemistry,[2,7,8a,15] although its Pd(IV) complexes are far less stable than those of bpy[2,5,7,8a] and related ligands.[28] It was found that PdMePh(tmeda) does not react with mqBr up to 25 °C, at which temperature decomposition of PdMe$_2$(tmeda) is known to be significant.[26] However, PdMe$_2$(tmeda) reacts with

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mqBr in $(CD_3)_2CO$ at −20 °C to give complex spectra exhibiting some resonances attributable to Pd(IV) species [AB pattern at 3.6 ppm ($PdCH_2$), singlets at 1.40 and 0.80 ppm (PdMe)]. On gradual warming to room temprature 8-ethylquinoline, 8-methylquinoline, ethane, and methane were detected in the ratio ~42:8:25:25 (low temperature spectrum); GCMS analysis confirmed the presence of these products and showed no trace of ethene. Thus, the major products (arising from C···C coupling) and NMR spectra during reaction are consistent with formation of an unstable Pd(IV) species. However, $PdMe_2$(tmeda) decomposes slowly in the temperature range used in this study to give ethane and methane, and thus caution in interpretation of product ratios is warranted.

Concluding Remarks

Appropriate choice of intramolecular coordination system and synthetic strategy, based on $C(sp^3)$-Br oxidative addition to Pd(II), allows the synthesis of stable Pd(IV) complexes and the first structural analysis of an arylpalladium(IV) complex. Presence of an intramolecular coordination system results in decomposition behavior for [Pd(mq)Me_2(bpy)]Br that differs from closely related and more flexible $PdBrMe_2(CH_2Ph)$(bpy), but which for [Pd($CH_2CH_2CH_2CH_2$)(mq)(bpy)]Br is similar to a related sytem containing a constraining palladacyclic ring, Pd($CH_2CH_2CH_2CH_2$)(CH_2Ph)Br(bpy).

Synthesis and characterization of stable arylpalladium(IV) complexes indicates that species of this type are feasible as intermediates in organic synthesis, in particular where proposed for systems where the individual steps involving Pd(IV) are supported by model reactions for these steps. Representative examples of such syntheses and reports of model reactions for key steps include halogenation of azobenzenes,[29] the synthesis of 2,6-dialkyl-substituted arenes and vinylarenes,[2,8,30] and the acetoxylation of arenes.[31]

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Supporting Information Available: Tables of atom coordinates, thermal parameters, and bond distances and angles for complexes **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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