Organometallics **1996,** *15,* 5713−5722 5713

Oxidation of Diorganopalladium(II) Complexes by Water and Halogens: Reactions Involving Methyl Group Transfer and Structural Studies of Hydrogen-Bonded Adducts Formed by Aryl Alcohols with the Pallada(IV)cyclopentane Complex $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ ($[(pz)_3BH]^- =$ Tris(pyrazol-1-yl)borate)

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Received July 15, 1996⊗

The first observations of oxidation of palladium(II) by water are reported. The pallada(II)cyclic complex ion $[\overline{Pd(CH_2CH_2CH_2C}H_2)\{(pz)_3BH\}]^-$ [$(pz)_3BH$ = tris (pyrazol-1-yl)borate)] is oxidized by water in acetone or tetrahydrofuran to form $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ and hydrogen, and oxidation by hydrogen peroxide gives the same complex. Oxidation by halogens results in the formation of $\overline{Pd(CH_2CH_2CH_2C}H_2)(X)\{(pz)_3BH\}$ (X = Cl, Br, I), and these complexes, together with the hydroxopalladium(IV) complex, represent the first examples of stable dihydrocarbylpalladium(IV) complexes. The octahedral complex $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ forms adducts with phenol, 3-methylphenol, and pentafluorophenol with an overall composition of $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot 2ArOH$ (**5** and **6**) and $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (**7**). Complex hydrogen-bonding interactions occur in the adducts, consistent with the assignment of the phenol and 3-methylphenol adducts as hydroxopalladium(IV) complexes and the pentafluorophenol adduct as an aquapalladium(IV) complex. Complexes **5** and **6** are considered to contain the hydrogen-bonding motifs H−O(Pd)···HO(Ph)···HOPh and Ar(H)O···H−O(Pd)···HOAr, respectively, and **7** to contain an aquapalladium(IV) cation in which both hydrogen atoms of the aqua ligand act as hydrogen-bond donors to pentafluorophenoxide ions in a centrosymmetric dimer, $[\overline{Pd(CH_2CH_2CH_2C}H_2)(OH_2)\{(pz)_3BH\}\cdot C_6F_5O]_2$. The complex ions $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph) react with water or halogens to form the $PdMe_2R\{(pz)_3BH\}$ and $Pd^{II}R$ species, and in the case of water as the oxidant, hydrogen is also formed. These reactions occur via initial oxidation to form undetected palladium(IV) species, presumably $PdMeR(X)\{(pz)_3BH\}$ (X = OH, Cl, Br, I), which undergo rapid methyl group exchange reactions with $[PdMeR\{(pz)_3BH\}]^-$ to form $Pd^{II}R$ species and $PdMe_2R\{(pz)_3BH\}$. The oxidation of palladium(II) by water and the structural analysis of hydroxo- and aquapalladium(IV) complexes represent the first examples of organopalladium(IV) chemistry in aqueous media.

Introduction

Oxidative addition reactions of late transition metal coordination complexes with the d^{10} configuration, such as palladium(0) and platinum(0),[1a,b] and metal−carbon σ-bonded organometallic complexes with the d^8 configuration, such as rhodium(I), iridium(I), platinum(II),[1a,b] and more recently palladium(II),[1c,d] have been studied extensively. For water as the oxidant, reported reactions appear to be limited to studies of d^8 and d^{10} coordination complexes[2−9] that often exhibit reactivity that is relevant to catalytic processes and to reactions of electron rich diorganoplatinum(II) complexes.[10−13]

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⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.

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S0276-7333(96)00583-3 CCC: $12.00

The coordination complexes usually[4] undergo reactions with water that are typical for oxidative addition (eq 1),[2,3,5−9] e.g., reactions of $[Ir(PMe_3)_4]^+$ and $Pt(PEt_3)_3$ to form the hydride complexes *cis*-$[Ir(OH)(H)(PMe_3)_4]^+$ [9a] and $[PtH(PEt_3)_3][OH]$,[5b] respectively.

$$M \xrightarrow{H_2O} M(OH)H \text{ or } [MH]^+ [OH]^- \qquad (1)$$

However, the d^8 diorganoplatinum(II) complexes studied to date react differently with water, such that diorgano(hydroxo)platinum(IV) complexes are formed which do not contain a hydride ligand.[10−13] In addition, there is no evidence for the elimination of alkanes or arenes in these reactions, a potential pathway for the removal of hydride ligands if present in organometallic species, similar to what occurs, for example, in reactions of organoplatinum(II) complexes with acids (eq 2).[13−17] Thus, $PtMe_2(N{\sim}N)$ [$N{\sim}N$ = 2,9-dimethyl-1,10-phenanthroline[14] and 2,2′-bipyridine (bpy)[15]] reacts with aqueous HCl to form chloro(hydrido)dimethylplatinum(IV) species that reductively eliminate methane, and $[PtMe_2\{(pz)_3BH\text{-}N,N'\}]^-$ [$(pz)_3BH$ = tris(pyrazol-1-yl)borate] is protonated by phenol to form $PtHMe_2\{(pz)_3BH\text{-}N,N',N''\}$, which eliminates methane.[17] The different reactivity of diorganoplatinum(II) complexes with water, compared to coordination complexes with water (eq 1) and diorganoplatinum(II) complexes with acids (eq 2), has been attributed to hydrolysis of transient undetected hydridoplatinum(IV) intermediate(s) to give hydrogen, perhaps via eq 3 or 4. This proposal is supported by detection of hydrogen as a product in the closely related reaction of $PtMe_2(bpy)$ with methanol in (almost dry) acetone to give $[PtMe_2(OMe)(bpy)(OH_2)][OH]$.[10] Similar results have been reported for reactions of diorganoplatinum(II) complexes of nitrogen donor tripod ligands, e.g., the reaction of $PtPh_2\{(py)_3COH\text{-}N,N'\}$ [$(py)_3COH$ = tris(pyridin-2-yl)methanol] with water to give $[PtPh_2(OH)\{(py)_3COH\text{-}N,N',N''\}][OH]\cdot 2H_2O$,[12a,c] and of anionic $[PtMe_2\{(pz)_3BH\text{-}N,N'\}]^-$ with water to give $Pt(OH)Me_2\{(pz)_3BH\text{-}N,N',N''\}$ which has been characterized by X-ray crystallography.[12b]

$$\underset{d^8}{PtR_2} \xrightarrow{H^+} \underset{d^6}{[Pt(H)R_2]^+} \xrightarrow{-RH} \underset{d^8}{[PtR]^+} \qquad (2)$$

$$\underset{d^8}{PtR_2} \xrightarrow{H_2O} \underset{d^6}{\underset{\text{(undetected)}}{Pt(OH)(H)R_2}} \xrightarrow[-H_2,\,-OH^-]{H_2O} \underset{d^6}{[Pt(OH)R_2]^+} \qquad (3)$$

$$\underset{d^8}{PtR_2} \xrightarrow[-OH^-]{H_2O} \underset{d^6}{\underset{\text{(undetected)}}{[Pt(H)R_2]^+}} \xrightarrow[-H_2]{H_2O} \underset{d^6}{[Pt(OH)R_2]^+} \qquad (4)$$

An oxidation state of IV for palladium is a relatively new one for hydrocarbylpalladium chemistry.[1c] In view of the exceptional reactivity of the diorganopalladium(II) complex ions $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph) and the pallada(II)cyclopentane species $[\overline{Pd(CH_2CH_2CH_2CH_2})\{(pz)_3BH\}]^-$ toward oxidative addition of organohalides to form organopalladium(IV) complexes of high stability,[18] we have investigated their reactivity toward water. This has resulted in the first examples of the oxidation of palladium(II) by water, the characterization of reactions involving both oxidation and methyl group exchange processes, and the first examples of stable dihydrocarbylpalladium(IV) complexes and of hydroxo and aqua complexes in organopalladium(IV) chemistry. Preliminary reports of parts of this work have appeared.[12ab,19]

Experimental Section

The reagents $K[(pz)_3BH]$,[20] $PhICl_2$,[21] $PdMe_2(tmeda)$,[22] $PdMePh(tmeda)$,[23] and the pallada(II)cyclopentane complex $\overline{Pd(CH_2CH_2CH_2CH_2})(tmeda)$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[24] were prepared as described. Solvents were dried and distilled, and all syntheses were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si.

Syntheses of Pallada(IV)cyclopentane Complexes $\overline{Pd(CH_2CH_2CH_2CH_2})(X)\{(pz)_3BH\}$ [X = OH, Cl, Br, I], $\overline{Pd(CH_2CH_2CH_2CH_2})(OH)\{(pz)_3BH\}$ (1). A solution of $\overline{Pd(CH_2CH_2CH_2CH_2})(tmeda)$ (0.064 g, 0.230 mmol) and $K[(pz)_3BH]$ (0.058 g, 0.230 mmol) in acetone (20 mL) was stirred at 0 °C for 3 h. Distilled water (0.020 mL, 1.10 mmol) was added, and the mixture was stirred at ambient temperature for 20 h. The solvent was evaporated in a vacuum, and the residue was extracted with diethyl ether (4 × 3 mL) and centrifuged to remove a yellow solid. The diethyl ether solution was evaporated in a vacuum to give a pale yellow solid, and on dissolution in acetone (3 mL), a white crystalline solid formed

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(4) The (cyclohexyne)platinum(0) complex $Pt(\eta^2\text{-}C_6H_8)(dppe)$ reacts with water to form the cyclohexenylplatinum(II) complex $Pt(OH)(C_6H_9)(dppe)$ [dppe = bis(diphenylphosphino)ethane]: (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

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on cooling to −20 °C (0.053 g, 59%). ^{1}H NMR, δ ($CDCl_3$): 7.73 (d, ^3J = 2.0 Hz, 1, H 3 or 5 trans to OH), 7.71 (d, ^3J = 2.0 Hz, 2, H 3 or 5), 7.69 (d, ^3J = 2.3 Hz, 1, H 3 or 5 trans to OH), 7.67 (d, ^3J = 2.3 Hz, 2, H 3 or 5), 6.28 (t, 1, H 4 trans to OH), 6.24 (t, 2, H 4), 4.12 (q, 2,, $PdC\mathit{H}_2CH_2$), 3.78 (q, 2, $PdC\mathit{H}_2CH_2$), 1.88 (m, 2, $PdCH_2C\mathit{H}_2$), 1.67 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 139.7, 139.5, 137.2, 135.4, 106.7 (C 4), 106.0 (C 4), 55.1 ($Pd\mathit{C}H_2CH_2$), 33.3 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{13}H_{19}BN_6OPd$: C, 39.8; H, 4.9; N, 21.4. Found: C, 39.9; H, 4.9; N, 21.0. The complex was obtained similarly using hydrogen peroxide (30% aqueous solution, equimolar quantity) as the oxidant, stirring at 0 °C for 1 h, followed by solvent evaporation and recrystallization from acetone/petroleum ether (bp 40−60 °C) to give a white solid (50%).

$Pd(CH_2CH_2CH_2CH_2)(Cl)\{(pz)_3BH\}$ (2). Phenyliodonium dichloride (0.06 g, 0.21 mmol) was added to a solution of $[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^-$ (0.21 mmol) prepared as for the synthesis of **1**, and a white solid formed immediately. The suspension was stirred for 3 h and then evaporated in a vacuum, and the residue was extracted with diethyl ether (3 × 5 mL) and centrifuged to remove a white solid. The pale yellow diethyl ether solution was evaporated, and the resulting white solid was collected and washed with a small amount of diethyl ether at −20 °C (0.072 g, 82%). ^{1}H NMR, δ ($CDCl_3$): 7.87 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to Cl), 7.74 (d, ^3J = 3.0 Hz, 2, H 3 or 5), 7.72 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to Cl), 7.65 (d, ^3J = 3 Hz, 2, H 3 or 5), 6.34 (t, 1, H 4 trans to Cl), 6.23 (t, 2, H 4), 4.64 (q, 2, $PdC\mathit{H}_2CH_2$), 3.87 (q, 2, $PdC\mathit{H}_2CH_2$), 2.05 (m, 2, $PdCH_2C\mathit{H}_2$), 1.69 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 140.5, 139.3, 137.4, 135.3, 107.0 (C 4), 106.2 (C 4), 54.8 ($Pd\mathit{C}H_2CH_2$), 33.7 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{13}H_{18}BClN_6Pd$: C, 38.0; H, 4.4; N, 20.5. Found: C, 38.1; H, 4.6; N, 20.6.

$Pd(CH_2CH_2CH_2CH_2)(Br)\{(pz)_3BH\}$ (3). Bromine (0.084 g, 0.54 mmol) was added to a solution of $[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^-$ (0.54 mmol) prepared as for the synthesis of **1**, and the solution was cooled to −60 °C prior to the addition of bromine. The resulting solution was allowed to warm slowly to 0 °C and was stirred for 2 h at this temperature. The solvent was evaporated in a vacuum, and the residue was extracted with diethyl ether (3 × 5 mL) and centrifuged to remove a yellow solid. The diethyl ether solution was evaporated in a vacuum, and the resulting solid was dissolved in acetone (2 mL) followed by addition of water (10 mL) to precipitate a cream colored solid, which was collected and dried in a vacuum (0.08 g, 33%). ^{1}H NMR, δ ($CDCl_3$): 7.88 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to Br), 7.75 (d, ^3J = 3.0 Hz, 2, H 3 or 5), 7.73 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to Br), 7.65 (d, ^3J = 3.0 Hz, 2, H 3 or 5), 6.34 (t, 1, H 4 trans to Br), 6.22 (t, 2, H 4), 4.79 (q, 2, $PdC\mathit{H}_2CH_2$), 3.77 (q, 2, $PdC\mathit{H}_2CH_2$), 2.10 (m, 2, $PdCH_2C\mathit{H}_2$), 1.83 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 141.1, 139.1, 137.1, 135.4, 106.9 (C 4), 106.2 (C 4), 51.5 ($Pd\mathit{C}H_2CH_2$), 34.4 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{13}H_{18}BBrN_6Pd$: C, 34.3; H, 4.0; N, 18.5. Found: C, 34.5; H, 3.9; N, 18.7.

$Pd(CH_2CH_2CH_2CH_2)(I)\{(pz)_3BH\}$ (4). This complex was prepared following a procedure identical to that for **2**, using iodine as a reagent, to give **4** as a pale orange solid (54%). ^{1}H NMR, δ ($CDCl_3$): 7.90 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to I), 7.80 (d, ^3J = 3.0 Hz, 2, H 3 or 5), 7.65 (d, ^3J = 3.0 Hz, 1, H 3 or 5 trans to I), 7.59 (d, ^3J = 3.0 Hz, 2, H 3 or 5), 6.30 (t, 1, H 4 trans to I), 6.21 (t, 2, H 4), 5.02 (q, 2, $PdC\mathit{H}_2CH_2$), 3.62 (q, 2, $PdC\mathit{H}_2CH_2$), 2.26 (m, 2, $PdCH_2C\mathit{H}_2$), 1.83 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 142.2, 138.7, 136.4, 135.5, 106.4 (C 4), 106.1 (C 4), 44.7 ($Pd\mathit{C}H_2CH_2$), 35.8 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{13}H_{18}BIN_6Pd$: C, 31.1; H, 3.6; N, 16.7. Found: C, 31.3; H, 3.6; N, 16.3.

Synthesis of Hydrogen-Bonded Complexes 5−7 Formed by Interaction of $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}$ (1) with Aryl Alcohols. The complexes were obtained by dissolution of **1** in acetone followed by addition of a 1−2 molar ratio of the aryl alcohol and work up as documented below. The complexes exhibit ^{1}H and ^{13}C NMR resonances that are within 0.05 ppm of the parent complex **1**, except for the $PdCH_2$ resonances of the pallada(IV)cyclopentane group and resonances of the PhOH and 3-MeC_6H_4OH group, and thus resonances of only these groups are recorded below.

$Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2PhOH$ (5). Petroleum ether (bp 60−80 °C) was added until the solution became cloudy, followed by cooling to −20 °C, evaporation to a low volume, filtration, further slow evaporation of the filtrate, filtration, and crystallization from the filtrate (52%). ^{1}H NMR, δ ($CDCl_3$): 7.17 (dd, ^3J = 7.2 Hz, 4, 3,5-Ph), 6.85 (dd, ^3J = 7.2 Hz, 4, 2,6-Ph), 6.82 (t, ^3J = 7.2 Hz, 2, 4-Ph), 4.25 (q, 2, $PdC\mathit{H}_2CH_2$), 3.85 (q, 2, $PdC\mathit{H}_2CH_2$), 1.90 (m, 2, $PdCH_2C\mathit{H}_2$), 1.68 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 158.0 (1-Ph), 141.0 (5-Ph), 140.0, 139.6, 137.4, 135.4, 129.9 (3,5-Ph), 119.8 (2,6-Ph), 116.3 (4-Ph), 106.6 (C 4), 106.1 (C 4), 55.9 ($Pd\mathit{C}H_2CH_2$), 33.2 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{25}H_{31}BN_6O_3Pd$: C, 51.7; H, 5.4; N, 14.5. Found: C, 51.6; H, 5.4; N, 14.9.

$Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_4OH)$ (6). Petroleum ether (bp 60−80 °C) was added until the solution became cloudy, followed by cooling to −20 °C, evaporation to a low volume, filtration, further slow evaporation of the filtrate, filtration, and crystallization from the filtrate (20−40%). ^{1}H NMR, δ ($CDCl_3$): 6.65−7.07 (m, 8, C_6H_4), 4.26 (q, 2, $PdC\mathit{H}_2CH_2$), 3.85 (q, 2, $PdC\mathit{H}_2CH_2$), 2.26 (s, 6, Me), 1.89 (m, 2, $PdCH_2C\mathit{H}_2$), 1.68 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 158.0 (1-Ph), 141.0 (5-Ph), 129.6 (4-Ph), 120.3 and 117.1 (2,6-Ph), 113.4 (3-Ph), 55.8 ($Pd\mathit{C}H_2CH_2$), 33.3 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{27}H_{35}BN_6O_3Pd$: C, 53.3; H, 5.8; N, 13.8. Found: C, 53.3; H, 5.8; N, 13.7.

$Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (7). Subsequent evaporation to dryness and recrystallization from acetone/petroleum ether was required (∼100%). ^{1}H NMR, δ ($CDCl_3$): 4.38 (q, 2, $PdC\mathit{H}_2CH_2$), 3.94 (q, 2, $PdC\mathit{H}_2CH_2$), 1.86 (m, 2, $PdCH_2C\mathit{H}_2$), 1.66 (m, 2, $PdCH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$): 57.6 ($Pd\mathit{C}H_2CH_20$, 32.9 ($PdCH_2\mathit{C}H_2$). Anal. Calcd for $C_{19}H_{18}BF_5N_6OPd\cdot 0.5$(acetone): C, 40.6; H, 3.8; N, 13.9. Found: C, 40.7; H, 4.2; N, 14.1.

Formation of $[PdMe_2\{(pz)_3BH\}]^-$ and $[PdMePh\{(pz)_3BH\}]^-$ in Acetone, and Reactions of the Anions with Water. ^{1}H NMR Studies for the Reaction of $[PdMe_2\{(pz)_3BH\}]^-$ with Water. $K[(pz)_3BH]$ (0.02 g, 0.08 mmol) was added to a solution of $PdMe_2$(tmeda) (0.02 g, 0.08 mmol) and 1,4-dioxane (∼7 μL) in $(CD_3)_2CO$ (0.5 mL). The solution was heated at 30−40 °C for 30 min, and the spectra recorded at 20 °C showed the presence of $[PdMe_2\{(pz)_3BH\}]^-$ (δ(PdMe) +0.14 ppm) together with a minor amount of $PdMe_2$(tmeda) (δ(PdMe) −0.19 ppm). Water (3 μL, 0.17 mmol) was added at ambient temperature, and after 12 h, the slightly cloudy solution gave an NMR spectrum showing the presence of $PdMe_3\{(pz)_3BH\}$ together with a minor amount of unreacted $PdMe_2$(tmeda) and $[PdMe_2\{(pz)_3BH\}]^-$. Addition of PPh_3 gave the same spectrum, together with resonances of $PdMe\{(pz)_3BH\}(PPh_3)$. Analysis of the integrals for 1,4-dioxane and the various methylpalladium species showed that there had been no loss of methyl groups from the palladium species and that the palladium(IV) and palladium(II) products were formed in a 1:1 ratio from palladium(II).

Isolation of Organopalladium Products from the Reaction of $[PdMe_2\{(pz)_3BH\}]^-$ with Water. A solution of $PdMe_2$(tmeda) (0.05 g, 0.20 mmol) and $K[(pz)_3BH]$ (0.05 g, 0.20 mmol) in acetone (10 mL) was stirred at 0 °C for 3 h. Distilled water (0.2 mL, 11 mmol) was added, and the mixture was stirred at ambient temperature for 20 h. The solvent was evaporated in a vacuum, and the residue was extracted with diethyl ether (2 × 3 mL) and filtered. The solvent was evaporated in a vacuum, and the resulting yellow solid was extracted with petroleum ether (bp 40−60 °C, 2 × 5 mL), and on evaporation to low volume, a white crystalline solid was

Table 1. Specific Crystallographic Details

	$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}\mathrm{(OH)\{(pz)_3BH\}}\cdot$ 2(PhOH) (**5**)[a]	$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}\mathrm{(OH)\{(pz)_3BH\}}\cdot$ 2(3-MeC$_6$H$_4$OH) (**6**)	$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}\mathrm{(OH)\{(pz)_3BH\}}\cdot$ C$_6$F$_5$OH (**7**)
formula	$C_{25}H_{31}BN_6O_3Pd$	$C_{27}H_{35}BN_6O_3Pd$	$C_{19}H_{20}BF_5N_6O_2Pd$
space group	$P1$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	12.520(3)	10.945(6)	10.424(3)
b (Å)	11.909(8)	20.07(1)	22.970(15)
c (Å)	10.716(10)	13.359(4)	9.755(3)
β (deg)	112.95(6)	101.17(3)	106.38(2)
V (Å)	1325	2879	2241
Z	2	4	4
M_w	580.8	608.8	576.6
D_{calcd} (g cm^{-3})	1.46	1.40	1.71
cryst size (mm)	0.09 × 0.21 × 0.52	0.22 × 0.34 × 0.09	0.20 × 0.27 × 0.15
μ (cm^{-1})	7.4	6.8	9.0
F(000)	596	1256	1152
$2\theta_{max}$ (deg)	50	50	50
$A^*_{min,max}$	1.06, 1.19	1.07, 1.15	1.13, 1.20
N, N_o	4507, 3885	5056, 2216	3938, 2722
R, R_w	0.029, 0.033	0.055, 0.048	0.038, 0.038

[a] $\alpha = 98.51(7)$, $\gamma = 108.51(4)°$.

obtained and identified as PdMe$_3$\{(pz)$_3$BH\} (45%). The petroleum ether insoluble material was dissolved in dichloromethane (5 mL), and triphenylphosphine was added (0.026 g, 0.10 mmol). After the solution was stirred for 30 min, the solvent was removed in a vacuum, and the resulting solid was recrystallized from diethyl ether/petroleum ether to give a pale yellow solid identified as PdMe\{(pz)$_3$BH\}(PPh$_3$) (42%).

^{1}H NMR Studies for the Reaction of [PdMePh\{(pz)$_3$BH\}]$^-$ with Water. K[(pz)$_3$BH] was added to a solution of PdMePh(tmeda) and 1,4-dioxane in (CD$_3$)$_2$CO as above. The solution was heated at 45 °C for 30 min, and the spectra recorded at 20 °C showed the presence of [PdMePh\{(pz)$_3$BH\}]$^-$ (δ (PdMe) -0.21 ppm) together with a minor amount of PdMePh(tmeda) (δ (PdMe) $+0.30$ ppm). The reaction with water was studied at ambient temperature as for [PdMe$_2$\{(pz)$_3$BH\}]$^-$ but over a longer period (2 days). The clear solution gave a spectrum showing PdMe$_2$Ph\{(pz)$_3$BH\} together with a minor amount of unreacted PdMePh(tmeda) and [PdMePh\{(pz)$_3$BH\}]$^-$. Triphenylphosphine was added, but the presence of any other organopalladium product(s) could not be identified, presumably owing to extensive overlap of the phenyl and pyrazole resonances for the reagents and products. Analysis of the integrals for 1,4-dioxane, PdMe$_2$Ph\{(pz)$_3$BH\}, and unreacted PdMePh(tmeda) and [PdMePh\{(pz)$_3$BH\}]$^-$ showed that the Pd(IV) product is formed from 2 equiv of Pd(II).

Isolation of Products from the Reaction of [PdMePh\{(pz)$_3$BH]$^-$ with Water. A solution of PdMePh(tmeda) (0.062 g, 0.197 mmol) and K[(pz)$_3$BH] (0.063 g, 0.250 mmol) in acetone (5 mL) was heated at 40 °C for 2 h. Water (2 mL) was added, and the solution was refluxed for 2 h and filtered through Celite to remove a brown solid. The solvent was removed from the filtrate, and (CD$_3$)$_2$CO was added to give a spectrum showing PdMe$_2$Ph\{(pz)$_3$BH\} together with broad resonances in the phenyl and tris(pyrazol-1-yl)borate region. Resonances of PdPh\{(pz)$_3$BH\}(PPh$_3$) appeared on addition of triphenylphosphine.

^{1}H NMR Studies of Reactions of [PdMe$_2$\{(pz)$_3$BH]$^-$ or [PdMePh\{(pz)$_3$BH\}]$^-$ with Halogens in (CD$_3$)$_2$CO. With 1,4-dioxane as an internal standard, generation of solutions of the anions in (CD$_3$)$_2$CO as above, addition of halogens (PhICl$_2$, Br$_2$, or I$_2$) in a 1:1 mol ratio at ambient temperature, and addition of PPh$_3$ at the end of the reaction (30 min), NMR spectra showed the formation of PdMe$_3$\{(pz)$_3$BH\} and PdMe\{(pz)$_3$BH\}(PPh$_3$) in a 1:1 ratio with a quantitative yield of methylpalladium groups. Similar experiments with [PdMePh\{(pz)$_3$BH\}]$^-$ gave PdMe$_2$Ph\{(pz)$_3$BH\}, with all of the methyl groups of the reagent appearing in the palladium(IV) product. The complexity of the spectra in the aryl region did not allow identification of other product(s).

Detection of Hydrogen as a Product of the Reactions. Hydrogen was detected as a product in the reactions of [$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$\{(pz)$_3$BH\}]$^-$ and [PdMeR\{(pz)$_3$BH\}]$^-$ (R = Me, Ph) with water in acetone or tetrahydrofuran. In a typical experiment, a solution of [$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$\{(pz)$_3$BH\}]$^-$, prepared from $\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$(tmeda) (0.04 g, 0.14 mmol) and K[(pz)$_3$BH] (0.036 g, 0.14 mmol) in tetrahydrofuran (0.7 mL), was added to a small vial (2 mL) containing 50 μL of water. The vial was then fitted with a septum secured with a Teflon tap. After the vial was allowed to stand for 12 h, the gas phase was sampled using a microsyringe and analyzed by GC−MS using a HP1 column (25 m × 0.32 mm) on a Kratos ISQ mass spectrometer (10 eV ET with helium carrier gas), which showed the presence of hydrogen.

X-ray Structure Determinations. For each complex, a unique data set was measured at 295 K using an Enraf-Nonius CAD-4 diffractometer operating in conventional $2\theta-\theta$ scan mode with monochromatic Mo Kα radiation ($\lambda = 0.710\ 73$ Å), yielding N independent reflections, N_o with $I > 3\sigma(I)$ considered observed and used in the full matrix least-squares refinement after Gaussian absorption correction and solution of the structures by vector methods. Residuals R and R_w are quoted on $|F|$ at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral atom complex scattering factors were used;[25] computation used the XTAL 3.0 program system implemented by Hall.[26] The treatment of the hydrogen atoms is given below.

Crystal data and selected geometries of the complexes are given in Tables 1−3, and views of the complexes are shown in Figures 1−3 and Chart 1.

Results and Discussion

Reactions of Pallada(II)cyclopentane Reagents.

The anionic species [$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$\{(pz)$_3$BH\}]$^-$ was generated from $\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$(tmeda) and K[(pz)$_3$BH] as described.[18] Solutions are stable in the absence of water when studied by ^{1}H NMR spectroscopy, but unlike [PdMeR\{(pz)$_3$BH\}]$^-$ (R = Me, Ph, see below), assignments for [$\overline{\mathrm{Pd(CH_2CH_2CH_2CH_2)}}$\{(pz)$_3$BH\}]$^-$ were not possible, owing to the overlap of the broad palladacyclopentane resonances with those of the reactant and of free and complexed tmeda. Addition of water, in the presence or rigorous exclusion of oxygen, results in a

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(25) *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(26) Hall, S. R.; Stewart, J. M. *The XTAL User's Manual, Version 3.0*; Universities of Western Australia and Maryland, 1990.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(PhOH)$ (5), $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_4OH)$ (6), and $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (7)

	5	6	7
Bond Distances			
Pd−O	1.984(3)	2.011(8)	2.035(4)
Pd−N(2a)	2.195(3)	2.18(1)	2.206(5)
Pd−N(2b)	2.203(3)	2.172(8)	2.168(5)
Pd−N(2c)	2.029(3)	2.036(9)	2.020(4)
Pd−C(1)	2.044(5)	2.04(1)	2.041(7)
Pd−C(4)	2.043(5)	2.02(1)	2.046(8)
C(1)−C(2)	1.476(8)	1.47(2)	1.50(1)
C(2)−C(3)	1.42(2)	1.40(3)	1.49(1)
C(3)−C(4)	1.460(7)	1.48(2)	1.51(1)
B−N(1a)	1.538(7)	1.53(2)	1.534(8)
B−N(1b)	1.534(5)	1.57(1)	1.523(9)
B−N(1c)	1.540(6)	1.52(2)	1.56(1)
O(11)−C(11)	1.366(5)	1.35(2)	1.300(7)
O(21)−C(21)	1.368(5)	1.37(2)	
"Bite Distances" for the Tris(pyrazol-1-yl)borate Ligands			
N(2a)···N(2b)	2.966(5)	2.96(1)	3.017(7)
N(2a)···N(2c)	2.918(5)	2.90(1)	2.863(7)
N(2b)···N(2c)	2.914(4)	2.87(1)	2.944(7)
Bond Angles			
O−Pd−N(2a)	91.2(1)	92.5(4)	95.3(2)
O−Pd−N(2b)	92.3(1)	92.0(3)	88.3(2)
O−Pd−N(2c)	178.4(1)	178.0(3)	177.5(2)
O−Pd−C(1)	89.7(2)	88.9(5)	89.0(2)
O−Pd−C(4)	87.4(2)	89.0(4)	89.8(2)
N(2a)−Pd−N(2b)	84.8(1)	85.7(3)	87.2(2)
N(2a)−Pd−N(2c)	87.3(1)	86.8(4)	85.2(2)
N(2a)−Pd−C(1)	178.8(2)	178.3(4)	175.7(2)
N(2a)−Pd−C(4)	95.1(2)	94.5(5)	94.7(3)
N(2b)−Pd−N(2c)	86.9(1)	86.1(3)	89.3(2)
N(2b)−Pd−C(1)	96.0(2)	95.0(4)	93.0(2)
N(2b)−Pd−C(4)	179.6(2)	178.9(4)	177.5(2)
N(2c)−Pd−C(1)	91.8(2)	91.7(5)	90.5(2)
N(2c)−Pd−C(4)	93.4(2)	92.9(4)	92.6(2)
C(1)−Pd−C(4)	84.1(2)	84.8(5)	85.2(3)
Pd−N(2a)−N(1a)	117.2(3)	117.9(7)	115.2(3)
Pd−N(2a)−C(3a)	136.8(2)	134.7(9)	139.1(5)
Pd−N(2b)−N(1b)	116.8(2)	117.9(6)	117.4(3)
Pd−N(2b)−C(3b)	136.0(2)	136.5(8)	136.1(4)
Pd−N(2c)−N(1c)	118.0(2)	117.2(7)	116.5(4)
Pd−N(2c)−C(3c)	134.7(2)	135.4(9)	135.5(4)
Pd−C(1)−C(2)	109.6(5)	110(1)	109.7(5)
Pd−C(4)−C(3)	109.4(5)	109.1(9)	106.7(5)
C(1)−C(2)−C(3)	115.3(6)	115(2)	110.8(8)
C(2)−C(3)−C(4)	113.9(6)	115(1)	109.9(6)
N(1a)−B−N(1b)	109.0(3)	108.8(9)	110.1(5)
N(1a)−B−N(1c)	108.7(3)	108.6(9)	107.3(5)
N(1b)−B−N(1c)	109.2(3)	107(1)	108.5(6)
O(11)−C(11)−C(12)	122.3(5)	125(1)	122.4(6)
O(11)−C(11)−C(16)	117.8(4)	116(1)	123.5(6)
O(21)−C(21)−C(22)	118.0(4)	119(1)	
O(21)−C(21)−C(26)	121.2(4)	121(1)	

reaction that extends over 20 h to form the hydroxopalladium(IV) complex $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}$ (**1**) which may be isolated in 59% yield. Reactions in tetrahydrofuran also gave the hydroxopalladium(IV) complex. Hydrogen as a product was detected for reactions in both acetone and tetrahydrofuran, and thus the overall reaction is as formulated in eq 5.

$$[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^- + 2H_2O \rightarrow Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\} + H_2 + OH^- \quad (5)$$

Table 3. Deviations (Å) of Atoms from Mean Planes, Angles (deg) Between Pyrazole Mean Planes, and Torsion Angles for the Pallada(IV)cyclic Group in $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(PhOH)$ (5), $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_4OH)$ (6), and $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (7)

	5	6	7
Deviations from "C_3N_2" Mean Planes[a]			
Pd (ring a)	0.080(8)	0.07(2)	0.05(1)
Pd (ring b)	0.269(7)	0.01(2)	0.17(2)
Pd (ring c)	0.025(6)	0.07(2)	0.01(1)
B (ring a)	0.052(8)	0.05(2)	−0.11(1)
B (ring b)	0.158(8)	−0.03(2)	0.12(1)
B (ring c)	−0.007(7)	0.02(2)	0.10(1)
Angles between "C_3N_2" Mean Planes			
rings a/b	71.1(2)	57.7(6)	62.4(3)
rings a/c	57.1(2)	62.6(6)	67.3(3)
rings b/c	51.8(2)	59.2(6)	60.3(3)
Deviations from "PdC_4" Mean Planes			
Pd	0.001(1)	0.000(1)	0.001(1)
C(1)	−0.018(7)	0.00(2)	0.012(9)
C(2)	−0.07(1)	−0.11(2)	−0.18(1)
C(3)	0.27(1)	0.19(2)	0.30(1)
C(4)	−0.073(8)	−0.07(2)	−0.20(1)
Torsion Angles			
Pd−C(1)−C(2)−C(3)	−16.3(8)	−17(2)	−26.5(8)
Pd−C(4)−C(3)−C(2)	−29.0(9)	−24(2)	−41.6(8)
C(1)−Pd−C(4)−C(3)	15.5(6)	11(1)	21.3(5)
C(4)−Pd−C(1)−C(2)	−0.2(5)	3(1)	2.4(5)
C(1)−C(2)−C(3)−C(4)	30.7(10)	28(2)	45.6(10)

[a] χ^2 values for pyrazole rings a−c, respectively: (**5**) 0.4, 0.1, 0.1; (**6**) 0.6, 2.7, 0.6; (**7**) 1.2, 0.2, 1.6.

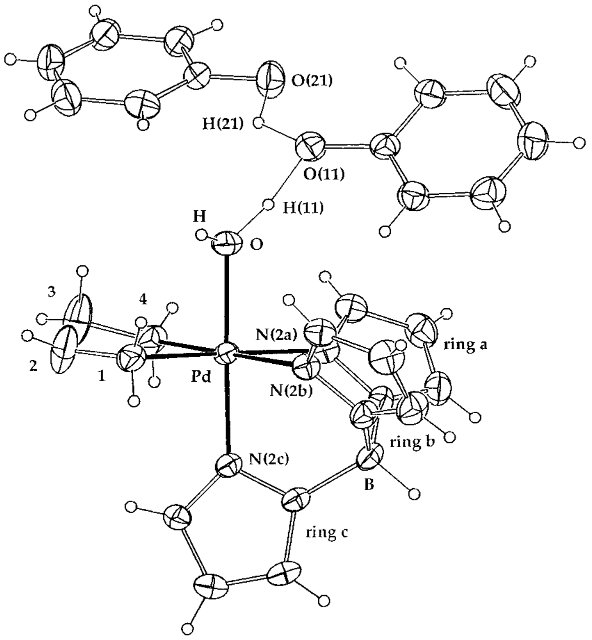

Figure 1. Molecular structure of $Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\}\cdot 2(PhOH)$ (**5**). Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

The oxidation chemistry has been extended to include a range of stronger oxidants (eq 6 and Scheme 1), providing the first examples of diorganopalladium(IV) complexes $Pd(CH_2CH_2CH_2CH_2)(X)\{(pz)_3BH\}$ (X = OH, Cl, Br, I), except for a series of pentafluorophenylpalladium(IV) complexes $PdCl_2(C_6F_5)_2(L_2)$[27] and some un-

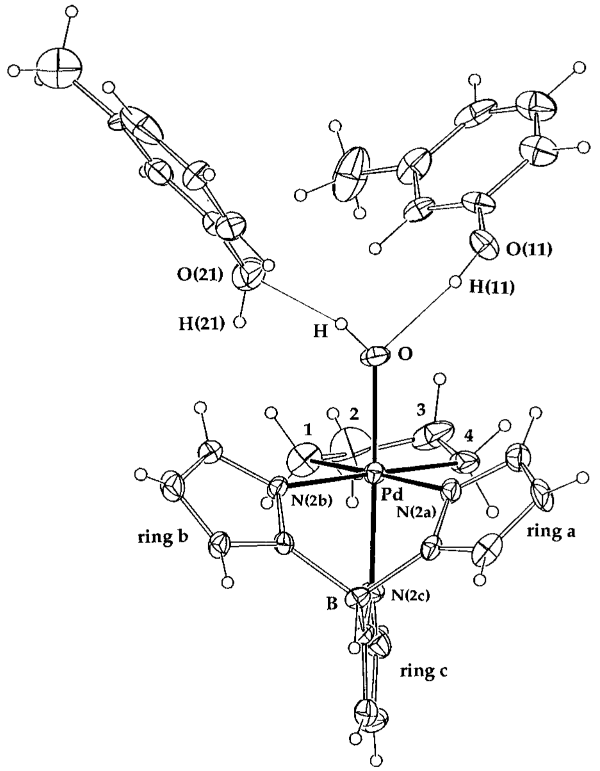

Figure 2. Molecular structure of $\overline{Pd(CH_2CH_2CH_2CH_2)}$-$(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_3OH)$ (**6**).

stable complexes $PdI_2Me_2(L_2)$ (L_2 = bidentate nitrogen donor ligand).[28] Hydrogen peroxide and the halogens reacted instantly with the palladium(II) reagent, in contrast to the slow reaction with water over 20 h. ^1H NMR spectra of the complexes are readily assigned on comparison with spectra of the triorganopalladium(IV) complex $\overline{Pd(CH_2CH_2CH_2CH_2)}(Me)\{(pz)_3BH\}$,[18] e.g., showing two pyrazole ring environments in 2:1 ratio. Assignments for the pallada(IV)cyclopentane group are given in Table 4, illustrating consistent chemical shift trends upfield or downfield as the group X is varied from Cl to Br to I.

$$[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^- + X_2 \rightarrow \overline{Pd(CH_2CH_2CH_2CH_2)}(X)\{(pz)_3BH\} + X^- \; [X_2 = Cl_2 \text{ (as } PhICl_2), Br_2, I_2] \quad (6)$$

Reactions of Dimethylpalladium(II) and Methyl(phenyl)palladium(II) Reagents. Reactions of $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph) are more complex than those of $[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^-$ but are more amenable to ^1H NMR monitoring of reactions owing to the presence of methylpalladium singlets. The anions are readily generated from the tmeda complexes and $K[(pz)_3BH]$ in ~30 min at ambient temperature for $[PdMe_2\{(pz)_3BH\}]^-$ and at ~45 °C for $[PdMePh\{(pz)_3BH\}]^-$,[18] although there is normally some residual unreacted PdMeR(tmeda). ^1H NMR studies using different ratios of reactants allow partial assignment of spectra for the anions, e.g., δ (PdMe) at 0.14 and 0.30 for the anions compared with −0.19 and −0.21 for $PdMe_2$(tmeda) and PdMePh(tmeda), respectively.

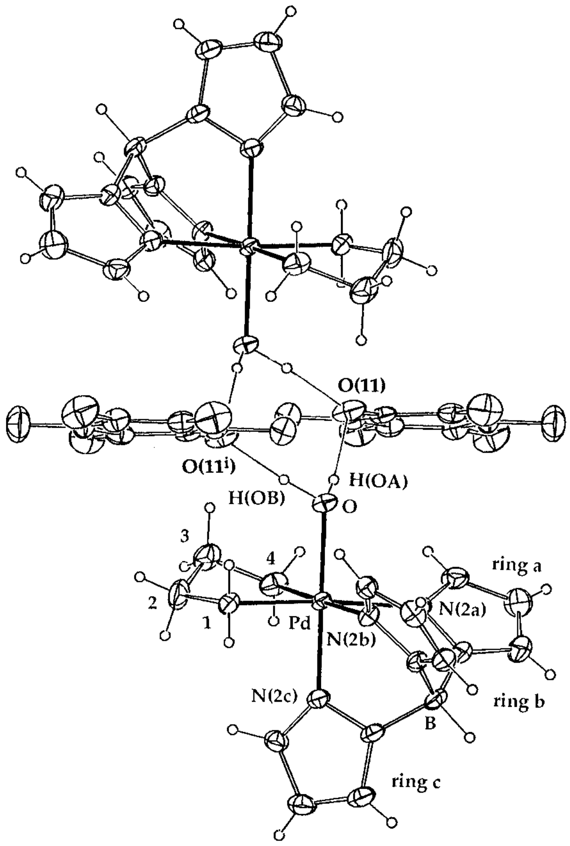

Figure 3. Molecular structure of $\overline{Pd(CH_2CH_2CH_2CH_2)}$-$(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (**7**).

For $[PdMeR\{(pz)_3BH\}]^-$, addition of water to solutions in $(CD_3)_2CO$ results in the detection of palladium(IV) complexes $PdMe_2R\{(pz)_3BH\}$ (R = Me, Ph) by ^1H NMR, and additional studies in acetone and tetrahydrofuran resulted in the detection of hydrogen by GC−MS. On completion of the reaction of $[PdMe_2\{(pz)_3BH\}]^-$ in $(CD_3)_2CO$, addition of triphenylphosphine results in the detection of the palladium(II) derivative $PdMe\{(pz)_3BH\}(PPh_3)$, but the precursor of this derivative, presumably $PdMe\{(pz)_3BH\}(L)$ (L = OH and/or H_2O and/or $(CD_3)_2CO$), could not be detected prior to the addition of PPh_3. Palladium(II) product(s) from the reaction of $[PdMePh\{(pz)_3BH\}]^-$ could not be detected in the NMR studies of the reaction, even on addition of PPh_3, perhaps owing to extensive overlap of PhPd(II), PhPd(IV), and PPh_3 resonances. However, preparative studies of this reaction resulted in the formation of a solid for which NMR spectra showed the presence of both $PdMe_2Ph\{(pz)_3BH\}$ and $PdPh\{(pz)_3BH\}(PPh_3)$. The complexes $PdR\{(pz)_3BH\}(PPh_3)$ (R = Me, Ph)[29] and $PdMe_2R\{(pz)_3BH\}$ (R = Me, Ph)[18] were synthesized independently for comparison of the NMR spectra, and triphenylphosphine does not react with $PdMe_2R\{(pz)_3BH\}$ (R = Me, Ph). No other products could be detected from the reactions, in particular methane, ethane, benzene, or toluene. NMR experiments in the presence of 1,4-dioxane as an internal standard for integration showed that no loss of methylpalladium occurs during the reaction of $[PdMe_2\{(pz)_3BH\}]^-$ with water followed by PPh_3 and permitted an estimation of the reaction

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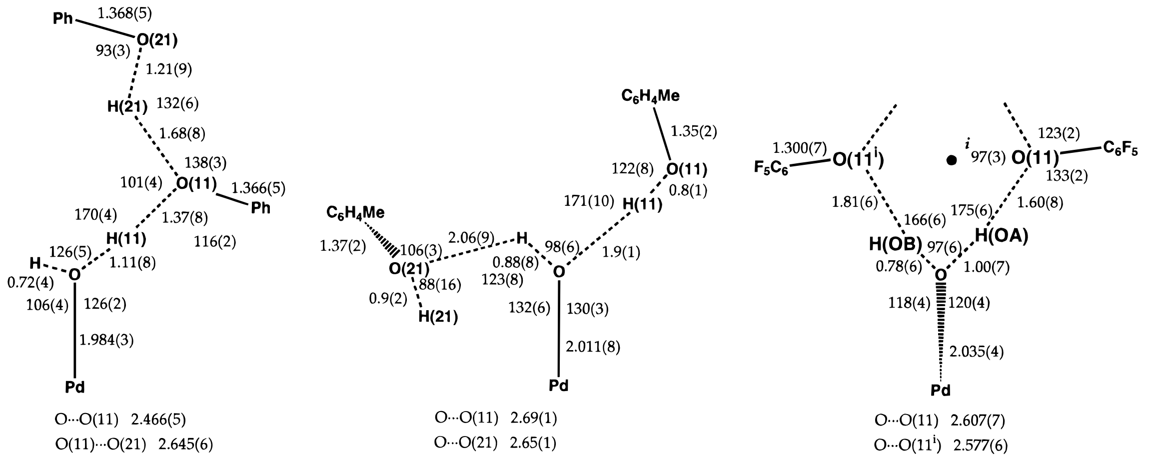
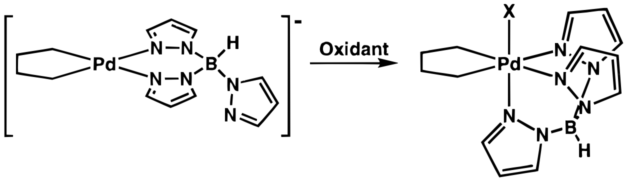
Chart 1. Hydrogen-Bond Geometries for Complexes 5−7



5 6 7

Scheme 1. Synthesis of Pallada(IV)cyclopentane Complexes in Acetone



1-4

Oxidant	H_2O	H_2O_2[a]	Cl_2[b]	Br_2	I_2
X	OH	OH	Cl	Br	I
Complex	**1**	**1**	**2**	**3**	**4**
Yield on isolation	59	50	82	33	54

[a] As 30% aq. solution. [b] As $PhICl_2$

yield as ~100% with a 1:1 ratio of palladium(IV) and palladium(II) products. Thus, the reactions of $[PdMeR\{(pz)_3BH\}]^-$ with water, involving addition of PPh_3 at the end of the reaction, are as shown in eqs 7 and 8.

$$2[PdMe_2\{(pz)_3BH\}]^- + 2H_2O + PPh_3 \rightarrow PdMe_3\{(pz)_3BH\} + PdMe\{(pz)_3BH\}(PPh_3) + H_2 + 2OH^- \quad (7)$$

$$2[PdMePh\{(pz)_3BH\}]^- + 2H_2O + PPh_3 \rightarrow PdMe_2Ph\{(pz)_3BH\} + PdPh\{(pz)_3BH\}(PPh_3) + H_2 + 2OH^- \quad (8)$$

^1H NMR studies of the reactions of $[PdMeR\{(pz)_3BH\}]^-$ with an equimolar amount of the halogens gave similar results, except that reactions were complete within 30 min, giving $PdMe_3\{(pz)_3BH\}$ and $PdMe\{(pz)_3BH\}(PPh_3)$ in 1:1 ratio and 100% yield (based on methyl groups) for R = Me (eq 9) and $PdMe_2Ph\{(pz)_3BH\}$ with a quantitative yield of methyl groups for R = Ph. The complexity of the spectra for the latter reactions did not allow identification of other product(s).

$$2[PdMe_2\{(pz)_3BH\}]^- + X_2 + PPh_3 \rightarrow PdMe_3\{(pz)_3BH\} + PdMe\{(pz)_3BH\}(PPh_3) + 2X^- \; [X_2 = Cl_2 \text{ (as } PhICl_2\text{)}, Br_2, I_2] \quad (9)$$

The reactions of eqs 7−9 require the transfer of a methyl group between palladium centers, and overall, only half of the palladium(II) reagent appears as a palladium(IV) product. Alkyl group transfer from palladium(IV) to platinum(II) and palladium(II) is known to be a facile process, occurring at low temperature for a wide range of reagents, as illustrated in eq 10[30] and eq 11[31] where phen is 1,10-phenanthroline.

$$PdBrMe_2(CH_2Ph)(phen) + PtMe_2(phen) \xrightarrow[20\ °C]{fast} 0.85[PdMe_2(phen) + PtBrMe_2(CH_2Ph)(phen)] + 0.15[PdMe(CH_2Ph)(phen) + PtBrMe_3(phen)] \quad (10)$$

$$PdBrMePh(CH_2Ph)(bpy) + PdMe_2(phen) \xrightarrow[-20\ °C]{fast} [PdMePh(bpy) + PdBrMe_2(CH_2Ph)(phen)] \quad (11)$$

These reactions proceed as shown when the potential platinum(IV) or palladium(IV) product is more stable than the palladium(IV) reactant. Kinetic studies of the reaction of eq 10 show a second-order behavior and activation parameters that are interpreted in terms of the preliminary bromide loss from the palladium(IV) reactant to give a cation, which is thus activated toward nucleophilic attack by the platinum(II) reagent at an alkyl group.[30] This mechanism is consistent with the observed preference for alkyl halide transfer $PhCH_2Br$ > MeBr in the reactions of eqs 10 and 11 since nucleophilic attack on $PhCH_2X$ occurs faster than on MeX by factors as high as 500.[32]

Thus, the different behavior of $[\overline{Pd(CH_2CH_2CH_2CH_2)}\text{-}\{(pz)_3BH\}]^-$ (eqs 5 and 6) and $[PdMeR\{(pz)_3BH\}]^-$ (eqs 7−9), discussed here for reactions of water as the oxidizing agent with considerations similar to those applying for the reactions of halogens, may be explained

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Table 4. ^{1}H and ^{13}C NMR Data for the Pallada(IV)cyclopentane Group in Complexes 1−7[a]

complex	^{1}H NMR: PdCH_2CH$_2$	^{1}H NMR: PdCH$_2$CH_2	^{13}C NMR: PdCH$_2$CH$_2$	^{13}C NMR: PdCH$_2$$CH_2$
1: $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$	4.12 m,[b] 3.78 m	1.87 m, 1.67 m	55.1	33.7
5: $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot 2PhOH$	4.25 m,[b] 3.85 m	1.90 m, 1.68 m	55.9	33.2
6: $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_4OH)$	4.26 m,[b] 3.85 m	1.89 m, 1.68 m	55.8	33.3
7: $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$	4.38 m,[b] 3.94 m	1.86 m, 1.66 m	57.6	32.9
2: $\overline{Pd(CH_2CH_2CH_2C}H_2)(Cl)\{(pz)_3BH\}$	4.64 m,[b] 3.87 m	2.05 m, 1.69 m	54.8	33.7
3: $\overline{Pd(CH_2CH_2CH_2C}H_2)(Br)\{(pz)_3BH\}$	4.79 m,[b] 3.77 m	2.10 m, 1.83 m	51.5	34.4
4: $\overline{Pd(CH_2CH_2CH_2C}H_2)(I)\{(pz)_3BH\}$	5.02 m,[b] 3.62 m	2.26 m, 2.07 m	44.7	35.8

[a] In CDCl$_3$, chemical shifts in ppm relative to Me$_4$Si. [b] Multiplets have the appearance of a quartet.

by (i) the inability of the constrained pallada(IV)cyclic group of $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ to participate in transfer reactions and (ii) for $[PdMeR\{(pz)_3BH\}]^-$ formation of a hydroxo species similar to $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$, e.g., $[Pd(OH)MeR\{(pz)_3BH\}]$ or perhaps the cationic aqua species $[Pd(OH_2)MeR\{(pz)_3BH\}]^+$, followed by methyl group transfer to nucleophilic $[PdMeR\{(pz)_3BH\}]^-$, as shown in eqs 12 and 13 for $Pd(OH)MeR\{(pz)_3BH\}$. Since the oxidation by water is slow for all of the species studied and the transfer reactions of eqs 10 and 11 are rapid, the relative rates shown for reactions 12 and 13 would account for the inability to detect intermediates by ^{1}H NMR spectroscopy (including at low temperature). The palladium(II) product(s) of unknown formulation, represented as $[Pd(OH)R\{(pz)_3BH\}]^-$ in eq 13, could not be detected, but on addition of PPh$_3$, the complexes $PdR\{(pz)_3BH\}(PPh_3)$ were detected in NMR studies (R = Me) and isolated for both R = Me and Ph (see eqs 7 and 8).

$$[PdMeR\{(pz)_3BH\}]^- + 2H_2O \xrightarrow{\text{slow}} Pd(OH)MeR\{(pz)_3BH\} + H_2 + OH^- \quad (12)$$

$$Pd(OH)MeR\{(pz)_3BH\} + [PdMeR\{(pz)_3BH\}]^- \xrightarrow{\text{fast}} [Pd(OH)R\{(pz)_3BH\}]^- + PdMe_2R\{(pz)_3BH\} \quad (13)$$

The proposed mechanism was tested in a series of ^{1}H NMR experiments in $(CD_3)_2CO$. It is known that $[PtMe_2\{(pz)_3BH\}]^-$ reacts with water to form $Pt(OH)Me_2\{(pz)_3BH\}$,[12b] and the absence of methyl group transfer to form $PtMe_3\{(pz)_3BH\}$ in this reaction is in accord with the reports that alkyl transfer from platinum(IV) to platinum(II) does not occur readily.[33] However, transfer from palladium(IV) to platinum(II) is rapid (eq 10), and in the NMR experiments it was found that when $[PtMe_2\{(pz)_3BH\}]^-$ is present with $[PdMe_2\{(pz)_3BH\}]^-$ in the presence of water, $PtMe_3\{(pz)_3BH\}$ is formed as a product in addition to $Pt(OH)Me_2\{(pz)_3BH\}$ and the usual products of reaction of $[PdMe_2\{(pz)_3BH\}]^-$. This observation is consistent with participation of $[PtMe_2\{(pz)_3BH\}]^-$ as a nucleophile in competition with $[PdMe_2\{(pz)_3BH]^-$ in the reaction of eq 13 (R = Me). In addition, $[PtMe_2\{(pz)_3BH\}]^-$ does not react with $PdMe_3\{(pz)_3BH\}$, showing that the methyl transfer to platinum(II) occurs from a palladium(IV) species formed prior to formation of $PdMe_3\{(pz)_3BH\}$. The anions $[MMe_2\{(pz)_3BH\}]^-$ (M = Pd, Pt) do not react with $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$, consistent with the expected inability of the constrained pallada(IV)cyclic ring to participate in a transfer reaction.

Adducts of $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ (1) with Aryl Alcohols. The new pallada(IV)cyclic complexes could not be isolated in a highly crystalline form, although $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}$ was slightly crystalline. This complex was subsequently found to form white solids in the presence of phenol, 3-methylphenol, or pentafluorophenol in acetone, and procedures for the isolation and crystallization of these solids were developed. X-ray structural studies for these solids revealed the compositions $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot 2PhOH$ (**5**), $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot 2(3\text{-}MeC_6H_4OH)$ (**6**), and $\overline{Pd(CH_2CH_2CH_2C}H_2)(OH)\{(pz)_3BH\}\cdot C_6F_5OH$ (**7**). Bulk samples of the crystalline complexes gave microanalyses consistent with the structural results. ^{1}H and ^{13}C NMR spectra of **5**−**7** are very similar to that of the parent complex **1** (within 0.05 ppm), except for the PdCH$_2$ resonances of the pallada(IV)cyclic groups and resonances for aryl alcohols in **5** and **6** (Table 4). The PdCH$_2$ resonances are expected to be most affected by any interaction of the PdOH and/or Pd(OH$_2$) groups with the alcohols and/or aryloxide ions, and thus interactions similar to those in the solid state (see below) appear to occur in solution, although their nature has not been determined.

The results of the single-crystal X-ray studies are shown in Figures 1−3 and Chart 1, illustrating the distorted octahedral geometry for palladium, PdC$_2$ON$_3$. The refined positions for the oxygen atoms and hydroxylic hydrogens (x, y, z, U_{iso}) indicate the presence of hydrogen bonding. Due to the difficulty in locating precise hydrogen atom positions in the absence of neutron diffraction data, all hydrogen atom interactions are indicated O···H in Figures 1−3 and Chart 1, although more precise C−O distances are consistent with the assignment of **5** and **6** as hydroxopalladium(IV) complexes and **7** as an aquapalladium(IV) complex containing pentafluorophenoxide ions. Thus, complex **7** has C−O = 1.300(7) Å, shorter than that for both coordinated $C_6F_5O^-$ [1.314(5) Å] and hydrogen-bonded C_6F_5OH [1.344(4) Å] in the palladium(II) complex *trans*-$PdH(OC_6F_5)(PCy_3)_2\cdot C_6F_5OH$ (O···H−OC$_6$F$_5$ interac-

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[33] Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1990**, *406*, 261.

tion)[34] and shorter than that for hydrogen-bonded C_6F_5OH in $C_6F_5OH \cdots O(CH_2CH_2)_2O \cdots HOC_6F_5$ [1.348(1) Å][35] and $C_6F_5OH \cdots OPPh_3$ [1.348(3) Å].[36] In contrast, the C−O distances in **5** [1.368(6), 1.366(5) Å] and **6** [1.35(2), 1.37(2) Å] are longer than that for **7** and are similar to those of hydrogen-bonded phenol in *trans*-$[PdH(OPh \cdots HOPh)(PCy_3)_2]$ [1.344(4) Å],[34] PdMe(OPh···HOPh)(tmeda) [1.349(3) Å],[37a] PdMe(OPh···HOPh)(P∼N) [P∼N = *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine] [1.354(6) Å],[37b] and Pd{2,6-$(NMe_2CH_2)_2$-C_6H_3-*N*,*C*,*N*}(OPh···HOPh) [1.357(8) Å].[37c] Assignment as hydroxy- (**5** and **6**) and aquapalladium(IV) (**7**) complexes is also in keeping with the higher acidity of pentafluorophenol ($pK_a = 5.49$) compared with phenol (9.95) and 3-methylphenol (10.08),[38] where interaction of $Pd^{IV}OH$ with C_6F_5OH results in protonation to form an aqua complex.

In **7**, all hydrogen atoms were refined in a stable manner in (x, y, z, U_{iso}), modeling the entity coordinated to palladium to be a water molecule with O−H = 1.00(8) and 0.78(6) Å, Pd−O−H = 118(4) and 120(4), and H−O−H = 97(6)°, $\sum$ 336° (Chart 1). The two hydrogen atoms of the aqua ligand contact the two oxygen atoms of a pair of centrosymmetrically related phenol moieties at 1.60(8) and 1.81(6) Å, with O···O = 2.607(7) and 2.577(6) Å, and O−H···O = 175(6) and 166(6)°.

In **6**, for which stable refinement of all tripod ligand and hydroxylic hydrogens (x, y, z, U_{iso}) was achieved (the C_4 and aromatic hydrogens of $2\text{-}MeC_6H_4OH$ were not refined), the results are consistent with approach to the coordinated oxygen by a pair of phenolic oxygen atoms [O···O = 2.69(1) and 2.65(1) Å]. Each phenolic oxygen has a closely affiliated hydrogen [O−H = 0.8(1) and 0.9(2) Å], the former of which approaches the coordinated oxygen at a distance of 1.9(1) Å with O−H···O = 171(10)°, C−O−H being 122(8)°. The other phenolic hydrogen [C−O−H = 140(12)°] is not directed toward the coordinated oxygen, and the single hydrogen associated with the latter [O−H = 0.88(8) Å] is oriented in the general direction of the phenolic oxygen [H···O = 2.1(1) Å] but with O−H···O being 123(8)°.

The parent phenol, PhOH, formed a complex (**5**) for which all hydrogen atoms were refined in (x, y, z, U_{iso}) to give O···H···O geometries intermediate between structures **6** and **7** (Chart 1), but as noted above, a consideration of C−O distances indicates that the complex is most likely a hydroxopalladium(IV) complex containing the motif H−O···H(11)−O(11)···H(21)−O(21). The coordinated oxygen atom has one hydrogen atom closely associated with it [O−H = 0.72(4) Å, Pd−O−H = 106(4)°]. It is approached by one of the phenol moiety oxygen atoms at O···O = 2.466(5) Å; that oxygen, in turn, is being approached by the other phenolic oxygen [O···O = 2.645(6) Å]. The hydrogen-bond acceptor role of the hydroxopalladium(IV) group in **5** and **6**, O···HOAr, is similar to that documented in structural studies of alkoxo- and aryloxopalladium(II) complexes, which often form adducts that exhibit PdOR···HOR′ interactions with O···O = 2.567(6)−2.642(8) Å.[37,39]

Following the usual practice in which, for approximately linear systems O···H···O,[40] hydrogen bond strengths are estimated as "very strong" (O···O < 2.50 Å), "strong" (O···O = 2.50−2.65 Å), "medium" (O···O = 2.65−2.80 Å), or "weak" (O···O > 2.80 Å), then complexes **5** and **6** have one medium−strong interaction for the coordinated oxygen atom and complex **7** has two strong interactions for the $Pd(OH_2)$ group.

The Pd−N(2a, 2b) distances are ∼0.14−0.19 Å longer than Pd−N(2c) in the structures, reflecting the difference in the trans influence of the carbon donors of the pallada(IV)cyclic ring compared with hydroxo and aqua donors (Table 2). Similar differences have been reported for Pt−N distances in related platinum(IV) complexes which contain $PtC_2(OH)N_3$ and $PtC_2(OH_2)N_3$ moieties, $PtMe_2(OH)\{(pz)_3BH\}$ (0.13 Å),[12b] and the tris(pyridin-2-yl)methanol complex $[PtPh_2(OH_2)\{(pz)_3COH\}][NO_3]\cdot H_2O$ (∼0.16 Å).[12c] The Pd−O distances are shorter than those reported for organopalladium(II) complexes containing an aqua ligand trans to groups that have a higher trans influence than nitrogen donors, 2.124(2) Å for an alkyl group[41] and 2.132(3)[42] and 2.20(1)[43] for aryl groups.

The pallada(IV)cyclic groups have PdC_2 chelate angles of 84.1(2)−85.2(3)°, essentially identical to those reported for square planar pallada(II)cyclic complexes $\overline{\mathrm{Pd(CH_2CH_2CH_2C}}\mathrm{H_2)(L_2)}$ (L_2 = bpy[44] 82.2(3)°, L_2 = tmeda[45] 82.5(2)°). The palladium atoms lie within 0.269(7) Å of the pyrazole mean planes, and the puckering of the nonplanar pallada(IV)cyclic rings is such that the outer "deviant" carbon atoms C(2) and C(3) are 0.19(2)−0.30(1) Å from the PdC_4 mean plane (Table 3).

Concluding Remarks

The results reported here show that oxidation of palladium(II) to palladium(IV) by water is a facile process when the palladium(II) reagent is bonded to hydrocarbyl groups and a nitrogen donor ligand and indicate the feasibility of developing aqueous solution organopalladium(IV) chemistry. The complexes also provide structural models that are relevant to the proposals that pallada(IV)cyclic intermediates are involved in organic synthesis.[1c,46]

The formation of hydroxopalladium(IV) complexes upon reaction of water with palladium(II) substrates is assumed to proceed via hydridopalladium(IV) species

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formed by oxidative addition of water. Following our initial report of part of this work,[12a] a similar reaction has been suggested as one step in the decomposition of the acyl complex $[Pd\{2,6(NMe_2CH_2)_2C_5H_3N\text{-}N,N',N''\}(COMe)]^+$ in the presence of water to give acetic anhydride.[47]

Reactions of halogens with organopalladium(II) complexes generally result in Pd–C bond cleavage,[24a,44,48,49] including $\overline{Pd(CH_2CH_2CH_2CH_2})(L_2)$ (L_2 = tmeda, bpy),[24a] in contrast to the facile reactions studied here. Complex reactions of $[PdMeR\{(pz)_3BH\}]^-$ (R = Me, Ph) with water or halogens to give triorganopalladium(IV) and monoorganopalladium(II) products illustrate the importance of facile alkyl group transfer from palladium(IV) to palladium(II) as a general feature in organopalladium chemistry.

Acknowledgment. We thank the Australian Research Council for financial support and Johnson Matthey Ltd. for generous loans of palladium and platinum salts.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, hydrogen atom parameters, and ligand geometry for the complexes (17 pages). Ordering information is given on any current masthead page.

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(49) Exceptions include the stoichiometric reaction of iodine with *trans*-$[PdCl(6\text{-}ClC_5H_3N\text{–}C^2)(PPh_3)_2]$ to replace the chloro ligand,[48h] the oxidation of mono- and bispentafluorophenylpalladium(II) complexes by chlorine to form palladium(IV) complexes,[27,50] the reaction of iodine with $PdMe_2(L_2)$ (L_2 = bis(*p*-tolylimino)acenaphthene or bis(phenylimino)camphane) to form unstable palladium(IV) complexes $PdI_2Me_2(L_2)$,[28] and the reaction of chlorine with cyclopalladated complexes, such as $PdCl\{2\text{-}(NMe_2CH_2CH_2N(Me)CH_2)C_6H_4\text{-}C,N',N''\}$, to form unstable palladium(IV) complexes.[48m]

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