Organometallics **1998,** *17,* 2046−2051

Synthesis and Decomposition Behavior of Pallada(IV)cyclopentane Complexes

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Received January 6, 1998

The octahedral pallada(IV)cyclopentane complexes $PdX(C_4H_8)R(bpy)$ [RX = MeI (**1**), EtI (**2**), $PhCH_2Br$ (**3**), $CH_2{=}CHCH_2Br$ (**4**); bpy = 2,2′-bipyridine] may be isolated on oxidative addition of organohalides to the palladium(II) complex $Pd(C_4H_8)(bpy)$ in acetone at −20 °C. The complex $PdBr(C_4H_8)(CF_3)(bpy)$ (**5**) has been generated in solution but was too unstable to permit isolation as a solid. Complex **1** occurs as a mixture of isomers in a 4:1 ratio, where the dominant isomer has the methyl group trans to bpy and the minor isomer has 2-fold symmetry with the methyl group trans to the iodo ligand. Complexes **2**−**5** adopt only the configuration with R trans to X. The complexes exhibit low stability, allowing studies of decomposition in solution under mild conditions in $CDCl_3$ or CD_2Cl_2. Formation of the major products from $PdI(C_4H_8)Me(bpy)$ (**1**) and $PdI(C_4H_8)Et(bpy)$ (**2**) is assumed to result from $C_4H_8\cdots R$ coupling at Pd(IV) to give undetected $Pd^{II}CH_2CH_2CH_2CH_2R$ species which undergo β-elimination to form alkenes (48% of detected organic products), Pd(0), and HX, with subsequent protonation of $Pd^{II}CH_2CH_2CH_2CH_2R$ to give alkanes (39%). Complexes **1** and **2** also give iodopentane (∼12% from **1**) and iodohexane (∼9% from **2**). The complex $PdBr(C_4H_8)(CH_2Ph)(bpy)$ (**3**) gives phenylpentane (15%), phenylpentenes (66%), toluene (10%), and butenes (8%); $PdBr(C_4H_8)(CH_2CH{=}CH_2)(bpy)$ (**4**) and $PdI(C_4H_8)(CF_3)(bpy)$ (**5**) give predominantly cyclobutane, together with minor amounts of butenes (**4**, **5**) and propene (**4**). Deuteration studies implicate the occurrence of intermolecular hydrogen atom transfer for elimination of alkenes and alkanes, except for cyclobutane.

Introduction

Studies of the decomposition behavior of organometallic compounds are fundamental to the development of organometallic chemistry and to a better understanding of the role of metal complexes in organic synthesis and catalysis.[1] The decomposition chemistry of metallacyclopentane complexes of the nickel triad elements [nickel(II),[2] palladium(II),[3] platinum(II),[4] and platinum(IV)[4b,5]] has been reported, and the relatively recent development of hydrocarbylpalladium(IV) chemistry[6] provides the first opportunity to study palladium(IV) complexes. For palladium, an element of particular importance in organic synthesis and catalysis, decomposition of hydrocarbylpalladium(IV) complexes is characterized by C⋯C bond formation in reductive elimination reactions,[6−8] although detailed mechanistic studies to date have been confined to $PdIMe_3(bpy)$ (bpy = 2,2′-bipyridine), which undergoes facile reductive elimination of ethane.[9] The work reported herein was prompted by several proposals that pallada(IV)cyclic complexes may be involved in catalysis,[10] demonstration of this by detection of a palladium(IV) intermediate for a palladacyclopentadiene system,[11] the remarkable reactivity

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S0276-7333(98)00005-3 CCC: $15.00

of some pallada(II)cyclopentane complexes to reduce water to hydrogen with concomitant oxidation of palladium(II) to palladium(IV),[12] and observations in preliminary studies showing that the decomposition of $Pd^{IV}Br(C_4H_8)(CH_2Ph)(bpy)$ [$Pd(C_4H_8) = \overline{PdCH_2CH_2CH_2CH_2}$] occurs under mild conditions in solution.[13]

Experimental Section

The reagents $C_4D_8Br_2$,[14] $Li_2(C_4R_8)$ (R = H, D),[4a] and $Pd(C_4R_8)(bpy)$,[15] were prepared as previously described. Solvents were dried and distilled, and all procedures were carried out under nitrogen. Microanalyses were performed by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded on a Bruker AM 300 spectrometer with chemical shifts given in ppm relative to $SiMe_4$ or CF_3CO_2H.

Synthesis of Pallada(IV)cyclopentane Complexes $PdX(C_4H_8)R(bpy)$. $PdI(C_4H_8)(CH_3)(bpy)$ (1-d_0). A 10-fold excess of iodomethane was added to an orange solution of $Pd(C_4H_8)(bpy)$ (0.02 g, 0.07 mmol) in acetone (20 mL) at −20 °C, and the resulting solution was stirred for 5 min to give a colorless solution. The solvent and volatiles were removed in a vacuum at −20 °C, and the solid residue was washed with cold diethyl ether and dried in a vacuum at 0 °C to give the product as a white solid in quantitative yield. The complex is unstable at ambient temperature. ^1H NMR ($CDCl_3$, −20 °C): two isomers, δ 9.00 (d, $^3J = 5.2$ Hz, 1, H^{6A}), 8.83 (d, $^3J = 5.3$ Hz, 1, $H^{6'A}$), 8.74 (d, $^3J = 4.8$ Hz, 0.4, H^{6B}), 8.26 (m, 2, $H^{3,3'A}$), 8.19 (d, $^3J = 8.2$ Hz, 0.4, H^{3B}), 7.98 (m, 2.4, $H^{4,4'A}$ and H^{4B}), 7.60 (m, 2.4, $H^{5,5'A}$ and H^{5B}), 4.33 (m, 0.4, CH_2^B), 3.45 (m, 2, CH_2^A), 2.95 (m, 2.4, CH_2^B), 2.68 (m, 1, CH_2^A), 2.47 (m, 1, CH_2^A), 2.14 (m, 0.4, CH_2^B), 1.91 (s, 3, $PdCH_3^A$), 1.85 (m, 0.4, CH_2^B), 1.69 (m, 2, CH_2^A), 1.29 (s, 1.2, $PdCH_3^B$), 1.27 (m, 2, CH_2^A). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −20 °C): δ 152.8, 148.7, 147.6, 147.4, 138.7, 138.5, 126.0, 125.8, 123.3, 123.1, 122.9, 60.8, 50.3, 49.0, 36.0, 34.6, 33.9, 25.6, 18.3. Anal. Calcd for $C_{15}H_{19}N_2IPd$: C, 39.11; H, 4.16; N, 6.08. Found: C, 39.30; H, 4.06; N, 5.83%.

The other complexes were obtained by a similar procedure. All of the complexes are white solids, soluble in dichloromethane and chloroform, sparingly soluble in acetone, and insoluble in pentane or hexane.

$PdI(C_4H_8)Et(bpy)$ (2): iodoethane as reagent. ^1H NMR ($CDCl_3$, −40 °C): δ 8.74 (d, $^3J = 5.0$ Hz, 2, H^6), 8.22 (d, $^3J = 8.4$ Hz, 2, H^3), 8.03 (“t”, 2, H^4), 7.59 (“t”, 2, H^5), 4.26 (m, 2, CH_2), 2.70 (m, 2, CH_2), 2.27 (q, $^3J = 7.4$ Hz, 2, $PdCH_2CH_3$), 2.17 (m, 2, CH_2), 1.89 (m, 2, CH_2), 0.33 (t, $^3J = 7.4$ Hz, 3, CH_3). ^{13}C NMR ($CDCl_3$, −40 °C): δ 153.0, 149.2, 139.1, 126.7, 123.1, 50.8, 40.6, 35.0, 17.6. Thermal instability prevented microanalysis.

$PdBr(C_4H_8)(CH_2Ph)(bpy)$ (3): benzyl bromide as reagent; stable at ambient temperature. ^1H NMR ($CDCl_3$, 20 °C): δ 8.44 (d, $^3J = 5.1$ Hz, 2, H^6), 7.95 (d, $^3J = 7.7$ Hz, 2, H^3), 7.84 (“t”, 2, H^4), 7.34 (“t”, 2, H^5), 6.70 (t, 1, Ph) and 6.59 (d, 2, Ph) overlapping, 6.41 (“t”, 2, Ph), 4.27 (m, 2, CH_2), 3.35 (s, 2, $PdCH_2Ph$), 3.01 (m, 2, CH_2), 2.21 (m, 2, CH_2), 1.90 (m, 2, CH_2). ^{13}C NMR ($CDCl_3$, 20 °C): δ 153.5, 149.3, 145.6, 138.5, 128.2, 126.2 and 122.6 (br), 125.0, 54.3, 43.4, 34.7. Anal. Calcd for $C_{21}H_{23}N_2BrPd$: C, 51.50; H, 4.73; N, 5.72. Found: C, 51.51; H, 4.74; N, 5.68.

$PdBr(C_4H_8)(CH_2CH{=}CH_2)(bpy)$ (4): 2-propenyl bromide as reagent; stable at ambient temperature. ^1H NMR ($CDCl_3$, 20 °C): δ 8.65 (br, 2, H^6), 8.15 (d, $^3J = 8.3$ Hz, 2, H^3), 7.95 (“t”, 2, H^4), 7.51 (“t”, 2, H^5), 5.24 (m, 1, $PdCH_2CH{=}CH_2$), 4.48 (br, 2, $CH{=}CH_2$), 4.21 (m, 2, CH_2), 2.81 (m, 4, CH_2 and $PdCH_2$-$CH{=}CH_2$), 2.08 (m, 2, CH_2), 1.78 (m, 2, CH_2). Anal. Calcd for $C_{17}H_{21}N_2BrPd$: C, 46.44; H, 4.81; N, 6.37. Found: C, 46.26; H, 4.87; N, 5.92.

$PdI(C_4H_8)(CF_3)(bpy)$ (5): iodotrifluoromethane as reagent; thermal instability prevented isolation. ^1H NMR ($CDCl_3$), −40 °C): δ 8.72 (br, 2, H^6), 8.20 (d, $^3J = 6.0$ Hz, 2, H^3), 8.07 (‘t′, 2, H^4), 7.62 (m, 2, H^5), 3.76 (br, 2, CH_2), 1.84 (br, 2, CH_2), 1.26 (br, 1, CH_2), 0.90 (br, 1, CH_2).

The deuterio complexes $PdI(C_4D_8)(CH_3)(bpy)$ (**1**-d_8), $PdI(C_4D_8)(CD_3)(bpy)$ (**1**-d_{11}), $PdBr(C_4D_8)(CH_2Ph)(bpy)$ (**3**-d_8), and $PdBr(C_4D_8)(CH_2CH{=}CH_2)(bpy)$ (**4**-d_8) were also prepared and were used immediately after synthesis in decomposition studies.

Decomposition Studies. GC analyses were performed using an HP 5890 gas chromatograph equipped with an FID and a 25 m × 0.32 mm BP1 column (4 μm film thickness). The carrier gas was nitrogen at 2.0 psi. The oven was programmed to hold at 35 °C for 10 min and then to ramp to 220 °C at 10 deg/min. Data analysis was performed using DAPA software. GCMS analyses for peak identification 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). The oven was programmed to hold at 40 °C for 4 min and then to ramp to 250 °C at 10 deg/min. Mass spectra were recorded over the range *m/z* 10−400. Relative GCMS quantification of deuterated species was performed using an HP5890 gas chromatograph equipped with an HP 5970 MSD and a Chrompak 25 m × 0.32 mm CPSIL5CB column (5 mm film thickness, He at 10 psi). The oven was programmed to hold at 40 °C for 4 min and then to ramp to 200 °C at 10 deg/min. Mass data were collected by selected ion monitoring (SIM) of molecular ions at 1.7 Hz.

In a typical single-component decomposition experiment, a 5 mL septum-sealed gastight tube was charged with a solution (~0.1 mM) of Pd(IV) complex (**1**, **3**, or **4** in $CDCl_3$, **2** in CD_2Cl_2, or **5** in $(CD_3)_2CO$) at 0 °C, together with 0.5 mL of toluene (**1**, **2**, **4**, **5**) or pentane (**3**) as an internal standard for calculation of yields of products. Response factors were determined for iodine-containing products. The tube was warmed to 20 °C for 30 min (**1**, **2**) or 24 h (**3**−**5**) and then cooled to −60 °C. The liquid phase was analyzed by GC/GCMS, and the results are presented in Table 1. Studies of **1**-d_0 and **3**-d_0 show that deuterium incorporation from $CDCl_3$ does not occur. Organic products were examined by ^1H NMR and LSIMS mass spectrometry.

In a typical double-component decomposition experiment, a 5 mL septum-sealed gastight tube was charged with an equimolar mixture of **1**-d_0 and **1**-d_8 or of **1**-d_0 and **1**-d_{11} in $CDCl_3$. The solution was warmed to 20 °C for 30 min and then cooled to −60 °C. The liquid phase was analyzed by GCMS.

Results and Discussion

Synthesis of Pallada(IV)cyclopentane Complexes. The new complexes $PdX(C_4H_8)R(bpy)$ [RX = MeI (**1**-d_0), EtI (**2**), $PhCH_2Br$ (**3**), $CH_2{=}CHCH_2Br$ (**4**), CF_3I (**5**)] formed on oxidative addition of organohalide to $Pd(C_4H_8)(bpy)$ at −20 °C in acetone (eq 1). Complexes **1**

$$Pd(C_4H_8)(bpy) + RX \rightarrow PdX(C_4H_8)R(bpy) \qquad (1)$$

$$\begin{aligned} &\mathbf{1}\text{: } RX = MeI \\ &\mathbf{2}\text{: } RX = EtI \\ &\mathbf{3}\text{: } RX = PhCH_2Br \\ &\mathbf{4}\text{: } RX = CH_2{=}CHCH_2Br \\ &\mathbf{5}\text{: } RX = CF_3I \end{aligned}$$

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Table 1. Organic Products Detected from the Decomposition of Pallada(IV)cyclopentane Complexes $PdX(C_4H_8)R(bpy)$ in Solution at 20 °C

complex	*n*-butane	butenes	cyclobutane	*n*-pentane	*n*-pentenes	*n*-hexane	*n*-hexenes	alkyl iodide	phenylpentane	phenylpentenes	RH
$PdI(C_4H_8)Me(bpy)$ (**1**)	<1[a]	<1[a]		39	48[b]			12[c]			
$PdI(C_4H_8)Et(bpy)$ (**2**)	1.5	3.5[d]				38	48[e]	9[f]			
$PdBr(C_4H_8)(CH_2Ph)(bpy)$ (**3**)	<1[a]	8[g]							15	66[h]	10
$PdBr(C_4H_8)(CH_2CH{=}CH_2)(bpy)$ (**4**)		9[i]	88								3
$PdI(C_4H_8)(CF_3)(bpy)$ (**5**)		12[j]	88								

[a] Traces detected. [b] Ratio pent-1-ene:*trans*-pent-2-ene:*cis*-pent-2-ene = 1:3:1. [c] Iodopentane. [d] Ratio but-1-ene:*trans*-but-2-ene:*cis*-but-2-ene = 25:1:9. [e] Ratio hex-1-ene:*trans*-hex-2-ene:*cis*-hex-2-ene = 1.3:3:1. [f] Iodohexane. [g] Ratio but-1-ene:*trans*-but-2-ene:*cis*-but-2-ene = 3.2:1.3:1. [h] Ratio not determined owing to overlapping peaks. [i] Ratio but-1-ene:*cis*-2-butene = 4.5:1. [j] Ratio of but-1-ene:*cis*-2-butene = 11:1.

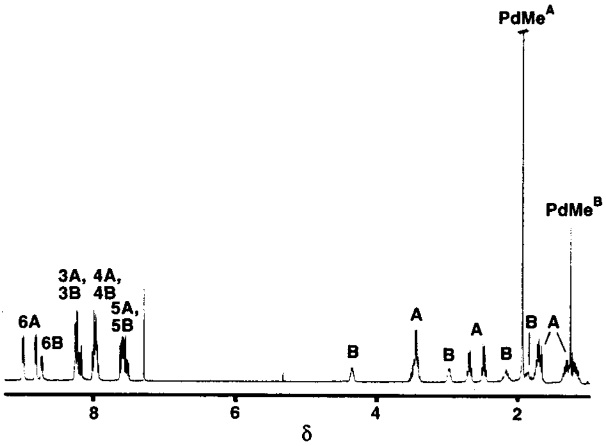
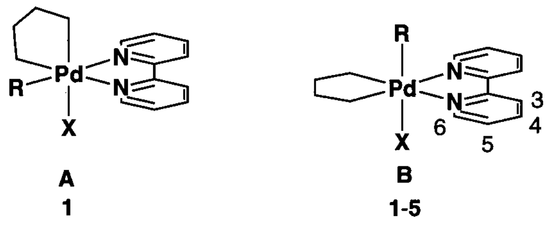


Figure 1. ^1H NMR spectrum of $PdI(C_4H_8)Me(bpy)$ ($\mathbf{1}$-d_0) in $CDCl_3$ at −10 °C, showing assignments of resonances for isomers **A** and **B**.

Scheme 1. Structures of Pallada(IV)cyclopentane Complexes 1−5



1: ratio of isomers = 4:1 for **A**:**B**

and **2** are unstable but may be stored at −20 °C for a few days, complexes **3** and **4** are stable at ambient temperature, and complex **5** was too unstable for isolation. Very rapid handling of complex **1** allowed a microanalysis to be obtained.

All of the complexes exhibit ^1H and ^{13}C NMR spectra consistent with the formulations presented in eq 1, and for complex **1** only, a mixture of isomers (**A**, **B**) in a 4:1 ratio is present (Scheme 1). Complexes **2**−**5** adopt configuration **B** in solution. Configurations **A** and **B** are assignable from integrations and by comparison with spectra of related complexes such as $PdX(C_4H_8)\{(pz)_3BH\}$ (X = Br, I).[12a] ^1H NMR spectra are unaltered over the temperature range −40 to −10 °C. For the ^1H NMR spectrum of $PdI(C_4H_8)Me(bpy)$ (Figure 1), the PdMe resonance for isomer **A** is expected to be upfield from that of isomer **B** since $PdIMe_3(bpy)$ exhibits PdMe resonances in a 2:1 ratio with the upfield resonance being of lower intensity and thus directly assignable to the methyl group trans to the iodo group,[16] and isomer **A** exhibits two H^6 environments for the 2,2′-bipyridyl group. Similar isomerism has been observed for the Pt(IV) analogue $PtI(C_4H_8)Me(bpy)$[5] and the bis(diphenylphosphino)methane complexes $PtX(C_4H_8)Me(dppm)$ (X = Cl, I).[17] None of the complexes could be obtained in a form suitable for X-ray structural studies, although a structural study of a related pallada(IV)cyclic complex, $Pd(C_4H_8)(SePh)_2(bpy)$, has been performed.[18]

Decomposition Studies. Results are given in Tables 1 and 2 and may be summarized according to Scheme 2 for organic products formed in yields >5%. Volatile fluorocarbon products from **5**, if formed, could not be detected, as noted in a previous report of the decomposition of (trifluoromethyl)platinum(IV) complexes.[4b] Some inorganic products were detected by a combination of ^1H NMR and mass spectrometric methods, but trace quantities of other inorganic products (including Pd(0) from **3**−**5**) cannot be excluded.

Alkene products are present as a mixture of isomers, consistent with the occurrence of isomerization processes either during or after decomposition. The absence of branching in alkene and alkane products and of homocoupling of hydrocarbon fragments, e.g. of bibenzyl from **3**, is indicative of the likely absence of free radical processes.

Major Decomposition Pathways for Complexes 1 and 2. Complexes **1** and **2** decompose at 20 °C in CD_2Cl_2 or $CDCl_3$ to give products resulting predominantly from coupling between the pallada(IV)cycle and PdR groups (Table 1): pentenes (~48%) and pentane (~39%) from $PdI(C_4H_8)Me(bpy)$ (**1**); hexenes (~48%) and hexane (~38%) from $PdI(C_4H_8)Et(bpy)$ (**2**). Iodopentane (~12%) and iodohexane (~9%) are also formed from **1** and **2**, respectively.

A mechanism to account for the major hydrocarbon products is shown in Scheme 3. Initial dissociation of iodide (i) to give a five-coordinate (or solvated octahedral) species is as established for reductive elimination of ethane from $PdIMe_3(bpy)$.[9] Dissociation of halide from Pd(IV) is a common feature in the chemistry of this oxidation state.[6,9,16,19−21] Equilibrium between unstable cations **A′** and **B′** is expected to occur since the

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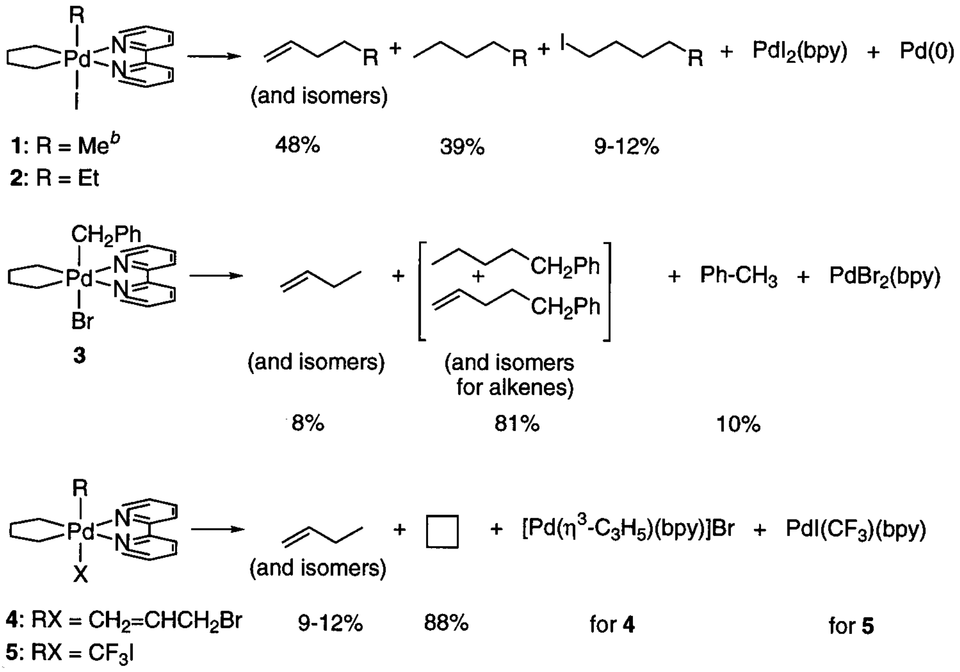
Table 2. Major Organic Products Detected from the Decomposition of Mixtures of Deuterioisomers for Complexes 1 and 4 in Solution at 20 °C

mixture	major hydrocarbon products (mole ratio)[a]
$PdI(C_4H_8)(CH_3)(bpy) + PdI(C_4D_8)(CH_3)(bpy)$ **1**-d_0 **1**-d_8	d_0,d_1,d_8,d_9-pentanes (27:16:35:22) d_0,d_7-pentenes (1:1)
$PdI(C_4H_8)(CH_3)(bpy) + PdI(C_4D_8)(CD_3)(bpy)$ **1**-d_0 **1**-d_{11}	d_0,d_1,d_{11},d_{12}-pentanes (25:18:32:25) d_0,d_{10}-pentenes (1:1)
$PdBr(C_4H_8)(CH_2CH{=}CH_2)(bpy) + PdBr(C_4D_8)(CH_2CH{=}CH_2)(bpy)$ **4**-d_0 **4**-d_8	d_0,d_1-propenes (1:1) d_0,d_8-cyclobutanes (1:1) d_0,d_1,d_7,d_8-butenes[a]

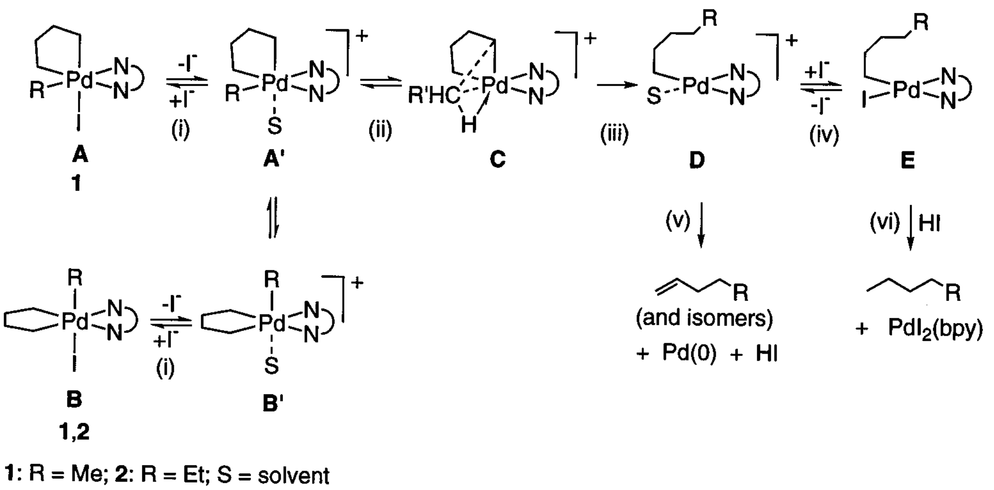
[a] Mole ratios of minor products not reliably determined.

Scheme 2. Major Products Formed on the Decomposition of Pallada(IV)cyclopentane Complexes at 20 °C in Solution[a]



[a] Formation of undetected finely divided Pd(0) from **3**–**5** cannot be excluded. Similarly, small quantities of other inorganic or organometallic products from **1**–**5** cannot be excluded. [b] For simplicity of presentation, only isomer **B** is shown here (see Scheme 1).

Scheme 3. Proposed Mechanism for Formation of Hydrocarbon Products from 1 and 2



cations $[PdMe_2(CD_3)(L_2)\{(CD_3)_2CO\}]^+$ (L_2 = bpy, tetramethylethylenediamine) are fluxional at low temperatures.[16,20] Reductive elimination from **A′** or **B′** appears feasible but may be favored from **A′** (ii and iii) since reductive elimination may involve an agostic interaction (**C**),[9a] and this is expected to be more facile for R in **A′** than for a methylene group in the pallada(IV)cyclic ring of **B′**. In addition, orbital symmetry considerations[22] favor C_4H_8···R reductive elimination from configuration **A** or **A′**, allowing the N–Pd–S angle (N trans to R) to

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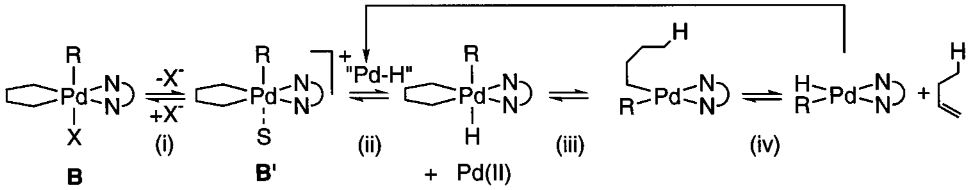
[22] Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1979**, 70.

Scheme 4. Proposed Mechanism for the Formation of Butenes



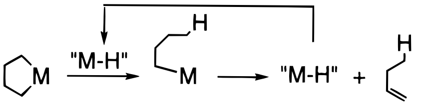
increase from ~90 to ~180° to give the square-planar palladium(II) product **D**.

Reductive elimination is expected to be followed by an equilibrium involving iodide coordination (iv), with β-elimination from the cation to give an alkene and HI, and HI attack (vi) on the neutral complex **E** to give an alkane. Steps iv−vi are by direct analogy with the proposal by Yamamoto et al. for the decomposition of *trans*-$PdX(Et)(PMe_3)_2$ ($X = O_2CCH_2Cl, O_2CCHCl_2, O_2CCl_3$, SPh, SCOMe, Cl, Br, I).[23] Step v involves β-elimination from the methylene group of a (formerly) palladacyclic ring rather than from R, and deuteration studies are consistent with this (Table 2) and also show that alkane formation (step vi) requires intermolecular hydrogen transfer. Thus, the formation of d_0,d_1,d_{11},d_{12}-pentanes from a mixture of $PdI(C_4H_8)(CH_3)(bpy)$ (**1**-d_0) and $PdI(C_4D_8)(CD_3)(bpy)$ (**1**-d_{11}) is consistent with formation of HI and DI from the ring or methyl groups. However, formation of d_0,d_1,d_8,d_9-pentanes from $PdI(C_4H_8)(CH_3)(bpy)$ (**1**-d_0) and $PdI(C_4D_8)(CH_3)(bpy)$ (**1**-d_8) requires formation of DI from the ring to generate the d_1,d_9-pentanes.

The acid formed in β-elimination (step v) could also conceivably cleave Pd−C bonds of **1** or **2** directly (**A**). However, although cleavage of a palladacyclic Pd−C bond to give "$Pd^{IV}R(C_4H_9)$" could lead to reductive elimination of pentane (from **1**) or hexane (from **2**), at least some cleavage of the Pd−R bond is expected to occur to give RH, and this product is not observed in the decomposition of **1** or **2**.

Formation of iodopentane from **1** and iodohexane from **2** may occur via C···I reductive elimination from $PdI(CH_2CH_2CH_2CH_2R)(bpy)$ (**E**). There appear to be few precedents for this; e.g., $[Pd(\mu\text{-}Cl)(CH_2Ph)(PPh_3)]_2$ decomposes in $CDCl_3$ at 65 °C to form $PhCH_2Cl$[24] and C···I reductive elimination occurs for Pt(IV) complexes[5,25] such as the bis(diphenylphosphino)ethane complex $PtIMe_3(dppe)$.[25]

Decomposition of $PdBr(C_4H_8)(CH_2Ph)(bpy)$ (3) and the Formation of Butenes from Complexes 3−5. Formation of phenylpentane and phenylpentenes from the decomposition of **3** is expected to occur via the same mechanism as for C_5 and C_6 hydrocarbons from **1** and **2**, respectively (Scheme 3). Formations of appreciable quantities of butenes from **3**−**5** and very small quantities of butenes from **1** and **2** are assumed to occur via a common mechanism. Deuteration studies show that intermolecular hydrogen transfer from palladacyclic groups occurs in the formation of butenes from **4** (Table 2), in particular the formation of d_1-butenes from a mixture of $PdBr(C_4H_8)(CH_2CH{=}CH_2)(bpy)$ (**4**-d_0) and $PdBr(C_4D_8)(CH_2CH{=}CH_2)(bpy)$ (**4**-d_8). These results are consistent with proposals that elimination of butenes from metallacyclopentanes requires intermolecular hydrogen transfer via "M−H" species because intramolecular β-hydrogen elimination processes are not favored by geometries for this ring size (eq 2).[4d] It has also been



(2)

demonstrated that intramolecular hydride transfer between hydrocarbyl groups occurs in some dimeric Pd(II) complexes.[26]

Unlike the case of "hydrogen transfer" in the form HX to give alkanes from $Pd^{II}CH_2CH_2CH_2CH_2R$ (step vi in Scheme 3), the hydrogen atom transferred to pallada(IV)cyclopentane intermediates is more likely to be hydridic (step ii in Scheme 4). Formation of a transient $Pd^{II}{-}H$ species, e.g. during β-elimination (step v in Scheme 2 and subsequently step iv in Scheme 4), may lead to hydride transfer to the electrophilic Pd(IV) species **A′** or **B′** (**B′** arbitrarily chosen for Scheme 4 since complexes **2**−**5** adopt configuration **B**) giving "$Pd^{IV}H(C_4H_8)R(bpy)$" prior to C···H coupling (step iii in Scheme 4) to give $Pd^{II}(CH_2CH_2CH_2CH_3)R(bpy)$ followed by β-elimination to give butenes (step iv in Scheme 4). Reductive elimination from the latter Pd(II) complex is not expected to occur; e.g., $PdEt_2(bpy)$ decomposes by β-elimination[27] and the electronegative CF_3 group (as R in **5**) is not favored for reductive elimination from Pd(II).[28] A model for "$Pd^{IV}H(C_4H_8)R(bpy)$" is known in Pt(IV) chemistry, where a stable species containing the "$M^{IV}HC_3N_2$" moiety occurs in $[Pt_2(\mu\text{-}H)Me_6(L_2)_2]^+$ (L_2 = 4,4′-di-*tert*-butyl-2,2′-bipyridine).[29]

Major Decomposition Products from Complexes 4 and 5. In addition to butenes as minor products (discussed above), the major organic product is cyclobutane, accompanied by propene (from **4**) and the palladium(II) products $[Pd(\eta^3\text{-}C_3H_5)(bpy)]Br$ (from **4**) and $PdI(CF_3)(bpy)$ (from **5**). Reductive elimination of cyclobutane directly from octahedral species **A** or **A′** is favored over **B** or **B′** on orbital symmetry grounds[22] and is assumed here to most likely occur from a five-coordinate (or solvated) intermediate **A′** in view of the importance of halide dissociation in the decomposition of palladium(IV) complexes. In addition, for the η^1-allyl complex **4**, this may allow concomitant η^3-coordination of the allyl group during elimination.

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Conclusion

The new class of organopalladium(IV) complex reported herein exhibits low stability, ideal for studies of decomposition under mild conditions that demonstrate new decomposition pathways for palladium(IV). Although complexes **1**−**5** exhibit different decomposition products, their decomposition is dominated by C···C reductive elimination as an early step in the process (Scheme 2). Reductive elimination via C_4H_8···R coupling from $PdX(C_4H_8)R(bpy)$ occurs for RX = MeI (**1**), EtI (**2**), and $PhCH_2Br$ (**3**), followed by decomposition from monoalkylpalladium(II) species; for RX = $CH_2{=}CHCH_2Br$ (**4**) and CF_3I (**5**), direct elimination of cyclobutane is the dominant process. This difference in behavior may result from the inability of the latter R groups to form agostic interactions with the vacant site in $[Pd(C_4H_8)R(bpy)]^+$, and/or for R = $CH_2CH{=}CH_2$, an alternative $Pd^{IV}(\eta^3$-allyl) interaction may occur which may disfavor reductive elimination and favor the formation of the $Pd^{II}(\eta^3$-allyl) product.

The deuteration studies provide evidence for intermolecular hydrogen transfer (as "H^+") in the decomposition of monoalkylpalladium(II) complexes to alkanes and for intermolecular hydrogen transfer (as "H^-") in the decomposition of metallacyclopentanes to butenes. The latter concept, pioneered by Whitesides,[4d] deserves wider recognition than appears to be currently given when mechanisms in organic synthesis and catalysis are considered.

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

OM980005T