Involvement of Intramolecular Hydride Transfer in the Formation of Alkanes from Palladium Alkyls

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*Summary: Intramolecular hydride transfer in a dimer between Pd atoms and reductive elimination of H and a benzyl moiety to give $PhCH_2CH_2C_6F_5$ (**3**) is the main decomposition pathway for the hydrido species generated from the η^3-benzylpalladium derivative $[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}CHPhCH_2C_6F_5)_2]$ (**1**). The commonly accepted decomposition of the palladium hydride to give Pd(0) and HX, followed by acid attack on **1** to produce the alkane, is ruled out in this case.*

Hydridopalladium complexes are intermediates in a variety of catalytic processes. Important reactions, such as the Heck functionalization of olefins, involve palladium(II) hydrido derivatives in the final step of the catalytic cycle.[1] Elimination of HX and Pd(0) formation is proposed to explain their decomposition. The acid generated has been held responsible for the formation of alkanes as byproducts in some of these reactions and in the thermolysis of palladium monoalkyl complexes (eqs 1 and 2),[1c,2,3] as well as in the generation of hydrogen in base-free olefin arylation reactions.[4]

$$[Pd(alkyl)XL_2] \rightarrow [PdHXL_2] + \text{alkene} \rightarrow [PdL_2] + HX + \text{alkene} \quad (1)$$

$$[Pd(alkyl)XL_2] + HX \rightarrow [PdX_2L_2] + \text{alkane} \quad (2)$$

Here, we study the decomposition of a benzylic palladium complex which generates hydridopalladium species by β-H elimination. The results show that *intramolecular* hydrido transfer *in a dimer* followed by reductive elimination to generate the alkane is the main decomposition pathway, whereas acid attack is not important in this case. This is a new pathway for the decomposition of Pd−H species that could also be important in other processes.

$[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}CHPhCH_2Pf)_2]$ (**1**, Pf = C_6F_5) was prepared by reacting $[PdPfBr(NCMe)_2]$[5] and a stoichiometric amount of styrene for 5 min in CH_2Cl_2 at room temperature. **1** is only slightly soluble in CH_2Cl_2 and can be easily isolated by cooling and filtration at 0 °C (82% yield). The η^3-benzylic structure (Scheme 1) is supported by the observation of a high-field aromatic resonance (δ = 6.23, H^2) in its room temperature ^1H NMR spectrum in $CDCl_3$. Due to the low solubility of **1** in $CDCl_3$, its ^{13}C NMR spectrum had to be recorded in the presence of MeCN, which increases the solubility but produces the coalescence of the signals for the two ortho and meta C or H atoms (δ = 106.3 for C^2 and C^6; δ = 6.79 for H^2 and H^6; δ = 133.9 for C^3 and C^5; δ = 7.51 for H^3 and H^5).[6] This is due to a rapid $\eta^3 \leftrightarrow \sigma \leftrightarrow \eta^3$ interconversion (**1** ↔ **A**, Scheme 1) exchanging both ortho (and meta) phenyl sites, as reported for other η^3-benzyl complexes.[7]

In the presence of $CDCl_3$ at room temperature, where it is only sparingly soluble, **1** slowly gets in solution and decomposes via Pd−(β-H) elimination, to *E*-PhCH=CHPf (**2**) and an undetected hydrido-containing palladium species. Since it is statistically unlikely that both moieties of the dimer undergo simultaneous H-elimination, the hydrido-containing species is most probably the mixed dimer depicted in Scheme 1.

Complete decomposition of a suspension of **1** in $CDCl_3$ occurs slowly at room temperature, and it was followed by ^{19}F and ^1H NMR. Organic compounds **2**, 2-(pentafluorophenyl)-1-phenylethane (**3**) and 1-bromo-2-(pentafluorophenyl)-1-phenylethane (**4**) are formed in a ratio of 2.3:1.5:1.[8] A mixture of metallic Pd and $PdBr_2$ is also observed. The high amount of saturated compound **3** formed suggested that a mechanism might be operating in this reaction different from that in eqs 1 and 2.[3,4,9] When the reaction was carried out in $CDCl_3$ solution saturated with D_2O, no deuterated compound **3** (neither **4**) was detected. This discounts the involvement of HBr formation in the reaction. Furthermore, the decomposition of **1** in the presence of a strong acid does not increase the amount of saturated derivative **3** formed and the presence of base does not eliminate its formation (Table 1).

These results point to a direct H transfer from a PdHBr fragment to an alkylpalladium moiety. Intermolecular hydride transfer has been proposed in the Pd-

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(6) Data for **1**. Anal. Calcd for $C_{28}H_{16}Br_2F_{10}Pd_2$: C, 36.75; H, 1.76. Found: C, 36.64; H, 1.75. ^1H NMR (300 MHz, δ, $CDCl_3$): 7.6 (m, 1H, H^4), 7.5 (br, 2H, H^3, H^5), 7.35 (br, 1H, H^6), 6.23 (br, 1H, H^2), 3.66 (dd, J = 9.7, 5.6 Hz, 1H, H^α), 3.11 (dd, J = 14.6, 5.6 Hz, 1H, H^β), 3.00 (dd, J = 14.6, 9.7 Hz, 1H, $H^{\beta'}$). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.3 (m, F_{meta}), −156.8 (t, F_{para}), −142.7 (m, F_{ortho}). Data for **1** + CH_3CN (1:4). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.61 (m, 1H, H^4), 7.51 (m, 2H, H^3, H^5), 6.79 (br, 2H, H^2, H^6), 3.65 (dd, J = 9.7, 5.9 Hz, 1H, H^α), 3.10 (dd, J = 15.0, 5.9 Hz, 1H, H^β), 2.98 (dd, J = 15.0, 9.7 Hz, 1H, $H^{\beta'}$). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.3 (m, F_{meta}), −156.8 (t, F_{para}), −142.7 (m, F_{ortho}). ^{13}C NMR (75.4 MHz, δ, $CDCl_3$): 133.9 (d, $^1J_{C-H}$ = 164 Hz, C^3, C^5), 128.8 (d, $^1J_{C-H}$ = 164 Hz, C^4), 114.2 (s, C^1), 106.3 (d, $^1J_{C-H}$ = 164 Hz, C^2, C^6), 58.3 (d, $^1J_{C-H}$ = 157 Hz, C^α), 23.2 (t, $^1J_{C-H}$ = 134 Hz, C^β).

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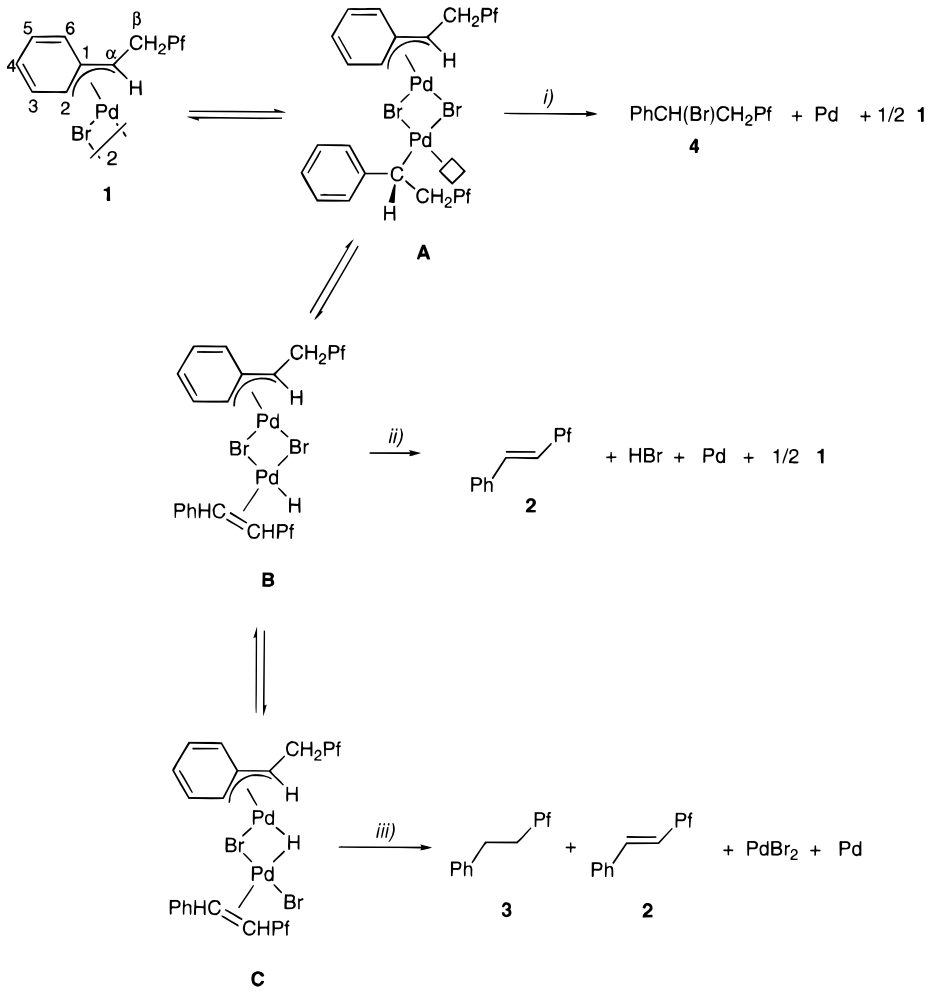
Scheme 1



mediated oxidation of allyl alcohol,[10] but the dimeric nature of **1** provides an easy way for *intramolecular* hydride transfer to Pd−R.[11] The different decomposition pathways and undetected intermediates involved are summarized in Scheme 1.

An $\eta^3 \rightarrow \sigma$ conversion gives **A**, which can produce **4** by reductive elimination of RBr (*i*, Scheme 1). Although the reverse reaction, oxidative addition, is usually observed, it is favored only in the presence of good donors, such as phosphines, that enhance the nucleophilicity of Pd(0) and are absent here. In fact, the formation of **4** is suppressed in the presence of PPh_3 (entries 4 and 5, Table 1).

Table 1. Decomposition Products from 1 in $CDCl_3$ Solution[a]

entry	additive	2	3	4	efficiency[b]
1	no additive	46	33	21	72
2	HBF_4[c]	44	31	25	70
3	proton sponge[d]	71	22	7	31
4	PPh_3[e]	68	31		46
5	PPh_3[f]	96	4		4

[a] Room temperature; reaction time 2 days; percents based on integration of the ^{19}F NMR signals. [b] Efficiency of H-transfer (%) = ratio of **3**/**2**. [c] HBF_4/Et_2O solution. [d] Proton sponge:palladium = 2:1. [e] Pd:PPh_3 = 1:1.1, the reaction is complete in 10 min. [f] Pd:PPh_3 = 1:2.2, the reaction is complete in 10 min.

β-H elimination in **A** gives intermediate **B** containing a Pd−H moiety, from which **2** can be liberated (*ii*, Scheme 1). This corresponds to eq 1 but in a dimer. Hydrogen transfer between the Pd-atoms can occur through an intermediate **C** containing a bridging hydrido ligand. **C** eventually undergoes reductive elimination of R−H (**3**), also giving **2**, $PdBr_2$, and Pd black (*iii*, Scheme 1). The proposed H-transfer can be considered as a variation of the well-documented aryl or alkyl exchange between transition metals. Mechanistic studies on Pt−alkyl or Pd−aryl exchange reveal the intermediacy of binuclear derivatives in such processes.[12] On the other hand, hydrido-bridged binuclear

(8) Decomposition experiments were carried out using a suspension of **1** (15 mg, 0.016 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube at room temperature and monitored by ^1H and ^{19}F NMR. Total decomposition was observed after 7 days, although this time can change in the presence of other additives (see Table 1). Data for **2**. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.5 (m, F_{meta}), −157.0 (t, F_{para}), −143.2 (m, F_{ortho}). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.35−7.55 (m, 5H, Ph), 7.44 (d, J = 16.8 Hz, 1H, PfCH), 6.98 (d, J = 16.8 Hz, 1H, PhCH). MS, EI (70 ev): *m*/*z* (relative intensity) 270 (M^+, 98), 250 (100), 219 (45), 201 (49), 78 (58), 51 (83). Data for **3**. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.5 (m, F_{meta}), −158.0 (t, F_{para}), −144.8 (m, F_{ortho}). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.1−7.8 (m, 5H, Ph), 2.97 (m, 2H, $PfCH_2$), 2.88 (m, 2H, $PhCH_2$). MS, EI (70 ev): *m*/*z* (relative intensity) 272 (M^+, 10), 181 (6), 91 (100), 65 (13), 51 (4). Data for **4**. ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.4 (m, F_{meta}), −155.6 (t, F_{para}), −142.7 (m, F_{ortho}). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.3−7.55 (m, 5H, Ph), 5.17 (dd, J = 8.8, 6.9 Hz, 1H, PhCH, ABX system), 3.65 (ddb, J = 14.3, 8.8 Hz, 1H, PfC*H*H′, ABX system), 3.52 (ddb, J = 14.3, 6.9 Hz, 1H, PfCH*H*′, ABX system). MS, EI (70 ev): *m*/*z* (relative intensity) 352 ($M^+(Br^{81})$, 1), 350 ($M^+(Br^{79})$, 1), 272 (15), 271 (100), 250 (19), 251 (19), 201 (12), 171 (8), 169 (9), 103 (10), 89 (10), 78 (9), 77 (12), 63 (10), 51 (17).

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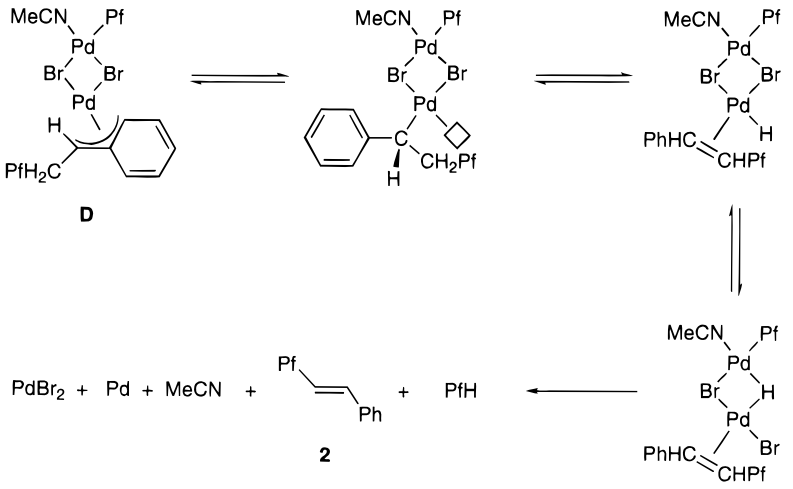
(11) Intramolecular refers here to a process occurring in a dimer. The presence of bridging Br assists the formation of a bridging H needed for a direct Pd to Pd hydride transfer (see main text).

Scheme 2



Pd(II) and Pt(II) complexes are well-known.[13] According to Scheme 1, the amount of **3** cannot exceed the amount of **2**, and the efficiency of *iii* versus *ii* can be calculated from the ratio of **3**:**2**. An efficiency of 72% is found for the decomposition of **1** (Table 1). It does not change when the decomposition occurs in the presence of a strong acid (entry 2, Table 1). The ratio decreases to 31% in the presence of a strong base such as proton sponge (entry 3, Table 1) because the base reacts with the HBr formed in *ii*, favoring the decomposition from **B** over the rearrangement to **C**. Finally, the addition of PPh_3 (entries 4 and 5, Table 1) produces a significant decrease in the efficiency of H-transfer, the higher the concentration of the ligand, the lower the efficiency. This shows that coordinating species hinder the formation of dimers, blocking the intramolecular H-transfer and the formation of alkane, whereas alkene formation from a monomer (as in eq 1) is not affected. In fact when **1** and PPh_3 in a ratio of Pd:PPh_3 = 1:2 are mixed at 213 K, coordination of both phosphine molecules to palladium occurs.[14] Decomposition of this complex is observed at 273 K to form **2** and *trans*-[$PdHBr(PPh_3)_2$].[15]

The direct trapping of hydride by Pd−R was further explored by the reaction of [$Pd(C_6F_5)Br(NCMe)_2$] with styrene in a 2:1 ratio in $CDCl_3$ at room temperature. Besides the products formed in the decomposition of **1** and unreacted pentafluorophenyl starting complex, a new derivative, C_6F_5H, appears. It could be formed from mixed dimers **D** as shown in Scheme 2. Again, the addition of bases does not avoid the formation of **3** and C_6F_5H, and the presence of D_2O does not produce deuterium incorporation in **3** or C_6F_5D, thus ruling out protonation as the mechanism for the formation of **3** and C_6F_5H.

Although under catalytic conditions (usually with large excesses of L) the formation of dimers is unlikely and this intramolecular hydride transfer may be unimportant, whenever the formation of dimeric species is possible (defect of L or L dissociation from a monomer), the H-transfer to a Pd−alkyl or Pd−aryl is fast and could be the main or a competing pathway for the formation of saturated derivatives.

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(14) The species formed is most likely [$Pd(\eta^3$-$CHPhCH_2Pf)(PPh_3)_2$]-Br according to its NMR spectra at 213 K: $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$) 29.2 (d, 1P, J = 52 Hz), 19.4 (d, 1P, J = 52 Hz). $^1H\{^{31}P\}$ NMR (300 MHz, δ, $CDCl_3$) 7.6−6.8 (35H, aromatic), 3.86 (m, 1H, H^{β}), 3.53 (d, 1H, J = 9.8 Hz, H^{α}), 2.95 (d, 1H, J = 13 Hz, $H^{\beta'}$). ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.4 (m, F_{meta}), −157.5 (t, F_{para}), −142.8 (m, F_{ortho}).

(15) *trans*-[$PdHBr(PPh_3)_2$]. $^{31}P\{^1H\}$ NMR (121 MHz, δ, $CDCl_3$, 273 K): 29.18 (s). ^1H NMR (300 MHz, δ, $CDCl_3$, 273 K): 7.9−7.3 (m, 30H, aromatic), −11.82 (t, 1H, J = 9.5 Hz). These data agree with those reported previously for the hydride complex, see: Heaton, B. T.; Hébert, S. P. A.; Iggo, J. A.; Metz, F.; Whyman, R. *J. Chem. Soc., Dalton Trans.* **1993**, 3081.