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Thermal decomposition of palladium-*n*-alkyl complexes by hydrogen elimination

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Abstract

1,1-Dideuterio-1-octyllithium and 2,2-dideuterio-1-octyllithium were allowed to react with palladium complexes of the type L_2PdCl_2 and L_2PdCl_4 ($L = PPh_3$, py; $L_2 =$ bpy, dppe) to form the respective straight-chain alkylpalladate complexes. These complexes were then allowed to decompose thermally and the resulting 1-octene was analyzed. The 1,1-dilabeled alkyl ligand produced 1,1-dideuterio-1-octene, while the 2,2-dilabeled ligand formed 2-deuterio-1-octene. These products indicate that β-hydrogen removal, rather than α-hydrogen removal, is the productive decomposition mode for these *n*-alkylpalladate complexes.

Keywords: Palladium; Alkyl; Mechanism; Decomposition; Alkylpalladate; Beta-elimination

1. Introduction

Thermal decomposition of late transition metal–alkyl complexes yields olefinic products which are generally believed to be the result of β-hydrogen elimination. The alternative α-hydrogen elimination is frequently discounted in late transition metal–alkyl systems bearing both α- and β-hydrogens. However, competitive α-hydrogen elimination pathways have been reported for an alkyliridium complex [1] and several platinacyclobutane complexes [2]. α-Hydrogen elimination produces a carbene or ylide species which cannot be readily stabilized by late transition metals, and may compensate by transferring the hydride back to the α-carbon in an equilibrium step [1], or undergoing a 1,2-hydride shift to form an olefin complex [2]. In the absence of appropriate deuterium labeling, these pathways cannot be distinguished from productive β-hydrogen elimination. With only a few exceptions [3], the necessary labeling studies have not been carried out and, consequently, the occurrence of α-hydrogen elimination in late transition metal complexes may be more common than is generally assumed.

Relatively few decomposition studies have been undertaken with palladium–alkyl complexes to determine which hydrogen is eliminated [4]. Of these, one study involved a labeled palladium–alkyl complex, *trans*-$[Pd(CH_2CD_3)_2(PMePh_2)_2]$, which was shown to decompose via β-hydrogen elimination [5]. We wished to extend this type of study to include an examination of alkylpalladate complexes. Alkylpalladates are frequently encountered species, which form readily when palladium halides are reacted with excess alkyl metals, such as alkyllithiums, and they may be unavoidable in systems where the palladium is limiting.

A series of labeled palladium-*n*-octyl complexes were examined. Octyl ligands were employed to provide easily handled octene and octane products following decomposition. These octyl ligands were labeled in either the α- (1,1-dideuteriooctyl) or β-positions (2,2-dideuteriooctyl). The donor ligands on the initial palladium reagent were varied to examine their impact on the decomposition mechanism.

2. Results and discussion

2.1. Initial palladium complexes

Alkyl palladium species were synthesized by the reaction of palladium chloride complexes with alkyl-

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lithium. The donor ligands on the initial palladium complexes encompassed both monodentate and chelating phenylphosphine-type (PPh_3 and dppe) [6] and pyridine-type (py and bpy) donor ligands. Specifically, the complexes $(PPh_3)_2PdCl_2$, $(dppe)PdCl_2$, *cis*- and *trans*-$(py)_2PdCl_2$, $(bpy)PdCl_2$ and $(bpy)PdCl_4$ were utilized. *Cis*-$(py)_2PdCl_2$ was synthesized for comparison to $(bpy)PdCl_2$, however, the alkyl complexes of both *cis*- and *trans*-$(py)_2PdCl_2$ behaved similarly, so rapid *cis-trans* isomerization prior to or during the reaction could not be ruled out [7].

The related bipyridine complexes $(bpy)PdCl_2$ and $(bpy)PdCl_4$ were examined to determine the effect of the palladium's initial oxidation state on the course of the reaction. However, both $(bpy)PdCl_4$ and $(bpy)PdCl_2$ produced identically labeled octane and 1-octene and 2-octene products. Although bipyridine is generally effective in stabilizing the palladium(IV) oxidation state [8,9], the reduction potential for $(bpy)PdCl_4$ is still well within reach of the octyllithium [10], and the alkyllithium appeared to rapidly reduce the palladium(IV) complex [11]. Therefore, this experiment did not definitively identify the effect of the palladium's oxidation state on the site of hydrogen elimination. Attempts to directly oxidize the palladium(II)-alkyl species to its respective palladium(IV) complex were hindered by decomposition involving the alkyl ligand.

2.2. Octylpalladium complexes

The alkylpalladium complexes were generated in situ by addition of fresh octyllithium solutions [12] to the appropriate palladium dichloride complex suspended in diethyl ether. Palladium–alkyl formation resulted in dissolution of the palladium species and occurred immediately for all complexes except $(dppe)PdCl_2$. Various experiments were run using from 1–10 equivalents of octyllithium per palladium. Decomposition of the resulting complexes occurred only in the presence of more than two equivalents of octyllithium.

The lack of decomposition products observed with 1–2 equivalents of octyllithium supports identification of the decomposing species as a palladate [13]. Nakazawa et al. [14] have shown that excess alkyllithium displaces the original donor ligands (L) from palladium complexes of the type L_2PdCl_2 to form the trialkylpalladate, $Li[PdLR_3]$, instantaneously via a dissociative mechanism. This is followed by slower formation of the tetraalkylpalladate, $Li_2[PdR_4]$, over the course of several hours by an associative mechanism.

The time required for decomposition of the respective octyl palladium complexes to occur was dependent on the nature of the donor ligands (L). The pyridine-type complexes decomposed more rapidly than the phosphine complexes, in concurrence with rate studies reported by Ozawa et al. [5], and the decomposition was slower in the presence of the chelating ligands dppe and bpy. Specifically, the pyridine complexes decomposed immediately following their dissolution, while the bpy and triphenylphosphine complexes decomposed over the course of 1 and 2 h, respectively, and the dppe complex required approximately 8 h to decompose. Addition of 15 equivalents of triphenylphosphine to the $(PPh_3)_2PdCl_2$ prior to addition of the octyllithium also inhibited the decomposition, although no change in volatile products was observed.

This observed donor ligand dependence on the time required for decomposition of the octylpalladium complexes, along with minor differences in the side products obtained, suggest that L is not completely displaced prior to decomposition. Because complexes of the type L_2PdR_2 have been shown to form trialkylpalladates instantaneously, followed by much slower formation of the tetraalkylpalladates, the immediate formation of the initial species followed by slow decomposition even in the presence of up to 10 equivalents of octyllithium suggests that the reaction rapidly forms $Li[PdR_3L]$. The subsequent, slow decomposition is consistent with either decomposition of the trialkylpalladate or slow tetraalkylpalladate formation followed by rapid decomposition. Unfortunately, attempts to follow this reaction by NMR in THF-d_8 were unsuccessful because of instability of the octyllithium in this solvent.

2.3. Side products

The dppe complex was not only anomalous in its slow formation of soluble alkyl products, it was also the only complex to produce significant quantities of hexadecane, (Table 1). This suggests that the chelating dppe does not dissociate as readily as the other ligands and permits reductive elimination from a simple (dioctyl)palladium(II) complex [15]. Dissociation of the more labile PPh_3, py and bpy ligands to form the palladate species would reduce or remove stereochemical effects

Table 1
Relative yields of 1-octene, 2-octene, octane and hexadecane from the reaction of palladium complexes with labelled octyllithiums [a]

L_2PdCl_n	1-octene (%) [b]	2-octene (%)	octane (%)	hexadecane (%)
cis-$(py)_2PdCl_2$	30 [c]	8 [d]	56 [c]	6 [d]
trans-$(py)_2PdCl_2$	26	10	59	5
$(bpy)PdCl_2$	25	8	61	6
$(bpy)PdCl_4$	39	11	46	4
$(PPh_3)_2PdCl_2$	32	11	53	4
$(dppe)PdCl_2$	20	6	37	37

[a] Two to ten equivalents of octyllithium per palladium.
[b] Average of two to five experiments each.
[c] ±10.
[d] ±5.

imposed by these donor ligands, and is consistent with the similar alkyl decomposition products obtained from all three complexes [16], especially the lack of hexadecane from the PPh_3 complex [17,18].

The pyridine and bipyridine ligands each underwent alkylation, producing 2-octyl- and 2,6-dioctylpyridine and 6,6′-dioctyl-2,2′-bipyridine, respectively. This may further support dissociation of the ligands during the reaction. However, Ziegler alkylation [12] of pyridine in the absence of palladium yielded significantly less dioctylpyridine, which suggests that the palladium does play an active role in the alkylation and may be coordinated to the pyridine during the process.

Table 2
Relative yields of 1-octene vs. 2-octene from the reaction of palladium complexes with labelled octyllithiums [a]

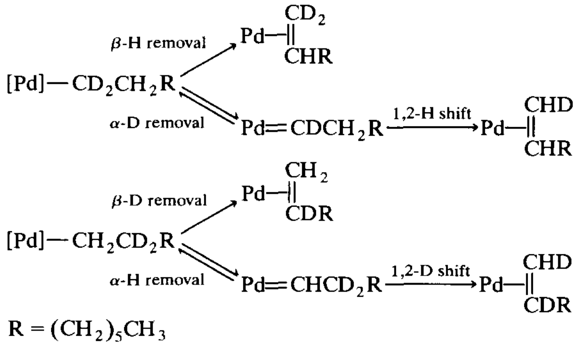
L_2PdCl_n	1-octene (%) [b]	2-octene (%)
cis-$(py)_2PdCl_2$	76 [c]	24
trans-$(py)_2PdCl_2$	74	26
$(bpy)PdCl_2$	74	26
$(bpy)PdCl_4$	75	25
$(PPh_3)_2PdCl_2$	71	29
$(dppe)PdCl_2$	77	23

[a] Two to ten equivalents of octyllithium per palladium.
[b] Average of two to five experiments each.
[c] ±6.

2.4. Hydrocarbon products

Decomposition of the complexes bearing 1,1-dideuteriooctyl ligands produced 1,1-dideuterio-1-octene, 1,1-dideuterio-2-octene and 1,1-dideuteriooctane in all cases. Accordingly, the 2,2-dideuteriooctyl complexes decomposed to 2-deuterio-1-octene, 2-deuterio-2-octene and 1,2,2-trideuteriooctane along with varying amounts of 2,2-dideuteriooctane. The latter dilabeled octane is probably formed as a result of hydrolysis of the octylpalladium complex. Hydrogen–deuterium exchange between alkyl ligands and arylphosphine ligands has been previously observed [17]. However, no deuterium was detected in the aromatic products from this reaction. Product assignments and yields were made by a combination of GC/MS and ^1H and ^2H NMR spectroscopies, (Table 1). The yields did not significantly depend on the reaction stoichiometry (from 2–10 equivalents of octyllithium per palladium) nor on the position of the deuterium label in the octyllithium.

The retention of deuterium on the α-carbon along with loss of deuterium from the β-carbon in the respectively labeled ligands indicates that the decomposition products arose via removal of the β-hydrogen from the alkyl ligand (Scheme 1). Removal of the α-hydrogen follows by a 1,2-hydride shift was not observed with any of the complexes. However, this does not rule out the non-productive equilibrium involving α-hydrogen elimination and reinsertion which requires other methods to detect. The present experiments are unable to distinguish between hydrogen elimination and abstraction.



Scheme 1.

From these reactions 2-octene was obtained as a lesser product (20–35% vs. 1-octene) (Table 2) and was initially thought to arise via secondary isomerization of the 1-octene. However, such an isomerization would have to be irreversible and occur early in the reaction, because no scrambling of the label in the octenes and no change in the relative amounts of the two olefins was observed over 24 h under reaction conditions. The lack of label scrambling also suggests that the hydrogen elimination is irreversible under these conditions [5]. As with formation of the 1-octene and octane, the 2-octene could arise by either hydrogen elimination or abstraction processes and the present experiments are unable to differentiate between these possibilities. However, the process is clearly palladium mediated, since no 2-octene was produced in its absence nor in analogous reactions carried out with iridium complexes [12].

2.5. Conclusions

Thermal decomposition of deuterium-labeled *n*-octyl ligands in a series of octylpalladate complexes formed from 1,1- and 2,2-dideuteriooctyllithium and L_2PdCl_n ($L = py$, PPh_3; $L_2 = bpy$, dppe; $n = 2,4$) yielded products via removal of a β-hydrogen (or deuterium). No evidence for products arising from α-hydrogen removal was observed. The nature of the donor ligands on the initial palladium complexes affected both the time required for decomposition of the octyl palladium complexes and the side products obtained, thus suggesting that these ligands are not completely displaced prior to decomposition of the palladate. Rapid initial formation of $Li[PdR_3L]$ is proposed, followed by either direct decomposition of this species or slow $Li_2[PdR_4]$ formation followed by decomposition.

3. Experimental details

Palladium compounds $PdCl_2$, K_2PdCl_4, $(PPh_3)_2PdCl_2$, (dppe)$PdCl_2$ and (cod)$PdCl_2$ were purchased from Strem Chemicals. Diethyl ether was distilled from sodium-benzophenone ketyl. 1-Bromo-1,1-dideuteriooctane [19], 1-bromo-2,2-dideuteriooctane [20], 1,4-diphenyl-1,4-dithiabutane [21], $(PPh_3)PdCl_4$ [8], *cis*-$(py)_2PdCl_2$ [7], (bpy)$PdCl_2$ [22] and (bpy)$PdCl_4$ [10] were synthesized by literature methods. *Trans*-$(py)_2PdCl_2$ was synthesized by the method of Tayim and Mahmoud [23], with the modification that (1,5-cod)$PdCl_2$ was used in place of (1,4-cod)$PdCl_2$. Other reagents and solvents were purchased from commercial sources and used as received.

Mass spectral analyses were performed on a Hewlett Packard MSD GC/Mass Spectrometer with a 30 m × 0.25 mm SE 30 capillary column. NMR spectra were obtained in $CDCl_3$ or CCl_4 at 25°C on a Bruker AC300 spectrometer. Cyclic voltammograms were determined in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A PAR 273 potentiostat with a platinum-disk working electrode, a platinum-wire auxiliary electrode, and a SCE reference electrode were used. The ferrocene/ferrocenium couple was included as an internal standard.

3.1. General procedure for the synthesis and decomposition of octylpalladium complexes

Freshly prepared 1,1-dideuterio-1-octyllithium or 2,2-dideuterio-1-octyllithium in diethyl ether [12] was cannulated into a suspension of 0.035 mmole of the palladium complex in 1.0 mL diethyl ether at −100–0°C. All reactions were carried out under argon. A dark solution formed immediately and was warmed to room temperature. After 0.1–24 h the volatiles were collected under vacuum and were analyzed by GC/MS. Proton NMR spectra were obtained for the concentrated samples in $CDCl_3$, while ^{2}H NMR spectra were obtained in CCl_4.

3.2. Probe for isomerization of 1-octene to 2-octene

The palladium–alkyl complex was synthesized from $(PPh_3)_2PdCl_2$ and octyllithium, and decomposed in the usual manner. Aliquots were removed after 1, 3, 6, 12 and 24 h and were analyzed by ^{1}H NMR for 1-octene and 2-octene. Relative amounts of the two olefins in these samples remained at 64.6 ± 0.3% 1-octene and 35.4 ± 0.2% 2-octene over the 24 h period.

3.3. Analysis of labeled products

GC/MS analysis of the octene and octane products showed mass peaks consistent with their degree of label incorporation. Resolution of the 2-octene chromatographic peak was hampered by its proximity to the more intense octane peak. The GC/MS product assignments and yields were confirmed by ^{1}H and ^{2}H NMR spectroscopy. Relative amounts of 1- and 2-octene were determined by integrating the olefinic proton resonances (δ 4.92 and δ 5.78 for 1-octene and δ 5.30 for 2-octene) in the proton NMR spectra, while the octane yield was determined by integrating the methyl resonance and subtracting the contributions to it from 1- and 2-octene. Integration of the olefinic protons vs. those of the allylic methylene in each olefin gave evidence for the position of the deuterium label. This comparison was not quantitative, however, because of overlap of the methylene resonances. Final analysis of the position of the deuterium label in the octene and octane products was accomplished by deuterium NMR. The methyl resonances for 2-octene and octane were observed at δ 1.70 and δ 0.96, respectively.

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