ELECTROPHILIC SUBSTITUTION OF STRUCTURALLY RIGID n¹-ALLYLPALLADIUM COMPLEXES

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 η^{\perp} -Allyl(aryl)palladium complexes react with some electrophiles to result in the selective Pd-allyl bond cleavage with 1,3-transposition, while the corresponding η^3 -allyl(aryl)palladiums and the electrophiles give rise to the selective Pd-Ar bond cleavage. The n^{1} -allyl complexes also react with CCl_4 and $CHCl_3$ under very mild conditions to give good yields of CH₂=CHCHR(CR'Cl₂) (R= H, Me; R'= Cl, H).

Much less has been known of the reaction of η^1 -allylpalladium complexes than η^3 -allyl counterparts, even though some examples of the former reaction of potential synthetic significance seem to be emerging only recently.^{1,2)} The lack of such knowledges may in part be attributable to a very limited number of well-characterized, structurally rigid η^{\perp} -allyl complexes of Pd available. We wish to report here some reactions of the rigid η^1 -allylpalladium complexes of type 1^{3} with electrophiles which exhibit different chemo- and regioselectivity from those in the η^3 -allyl counterparts of type 2.



Complexes 1b and 1d were synthesized from 2b and 2d with $Ph_2PCH_2CH_2PPh_2$ (dppe) as described previously for 1a and 1c.³⁾ Notable here is that 1b and 1d exist as only a 2-butenyl isomer (E/Z= ca.2/1 and 3/1), but not as a 1-methyl-2-propenyl isomer, as indicated by ¹H NMR spectroscopy.⁴⁾ 1 was found to react very rapidly with an equimolar quantity of electrophiles (EX= HCl, Br₂, BrNC(0)CH₂CH₂C(0) (NBS)) in chloroform at room temperature to give good yields (≥ 70 %) of the products from the Pd-allyl bond cleavage (Eq. 1).⁵⁾ Importantly, the products from 1b and ld were almost exclusively the isomer of the formula, CH₂=CHCH(E)Me (E= H, Br), demonstrating the direct attack of the electrophile at the C=C bond of the η^2 -Allyl The previous work¹⁾ also assumed the similar electrophilic substitution group.

$$\frac{1}{\omega} + EX \longrightarrow \overset{R}{\longrightarrow} R + PdAr(X) (dppe)$$
(1)
$$\frac{2}{\omega} + EX \longrightarrow Ar-E + Pd(\eta^{3}-allyl)(X) (PPh_{3})$$
(2)

$$EX \longrightarrow Ar-E + Pd(\eta^3-allyl)(X)(PPh_3)$$
(

of n^{\perp} -allylpalladium species, but the position of the attack of the electrophile was not determined.

Quite contrasting to Eq. 1 is the selective $(\geq 75\%)$ Pd-Ar bond cleavage in a reaction of 2a with EX (1:1 ratio) (Eq. 2)⁵⁾ under the similar conditions. The Pd-allyl bond cleavage of 2a occurred only when this was treated with Br₂ or NBS in the presence of more than 5 molar quantities of $[Ph_4P]Br$ (yields of allyl bromide, $\geq 60\%$, and those of C_6F_5Br , $\leq 10\%$). Moreover, the isomer ratio of the allylic bromide from 2b and NBS/Br⁻ (41% CH₂=CHCHMeBr, 17% MeCH=CHCH₂Br) was different from that in Eq. 1. The regioselectivity in the reaction of η^1 -allylpalladium species with, somewhat surprisingly, nucleophiles has been shown to be different from that in the reaction of η^3 -allyl species.⁶⁾ The mechanism of the Pd-allyl bond cleavage of 2 with EX/Br⁻ reagents is currently under investigation.

The complexes <u>lc</u> and <u>ld</u> also underwent formal electrophilic substitution with CCl_4 and $CHCl_3$ (Eq. 1, E= CCl_3 and $CHCl_2$) in dichloromethane solutions under very mild conditions (room temperature, 1-5 h for CCl_4 , 24 h for $CHCl_3$) to give the C-C coupling products in good yields ($\geq 85\%$ with CCl_4 , 70-75\% with $CHCl_3$). <u>la</u> and <u>lb</u> also reacted with CCl_4 similarly (yields, 60-70\%), but their reaction with CHCl_3 afforded no significant amounts of the coupling product under the similar conditions. Nor did <u>2</u> react at all with CCl_4 under the similar conditions.

The coupling products from 1b and 1d again contained only one isomer having the terminal C=C bond. Induction periods were observed in most of the reactions, and propene or 1-butene was the principal by-product (15-25%) from the reaction of 1c or 1d with CHCl₃. Thus, the reaction of 1 with CCl₄ and CHCl₃ may have proceeded through a radical path (S_H^2 ' mechanism), most probably involving the radical chain, similar to that in analogous reactions of allyltin derivatives,⁷) even though the latter required the much more drastic reaction conditions.

The results described in this as well as the previous work¹⁾ strongly suggest the high reactivity of the Pd-bound η^1 -allyl group toward the electrophilic center, thus lending support to the η^1 -allyl participation proposed in the intramolecular reaction of the η^3 -allylpalladium moiety with the C-Cl bond.²⁾ Further studies are in progress toward developing reactions of the η^1 -allylpalladium complexes with other carbon electrophiles.

References

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- 4) For example, $\delta(\text{CDCl}_3)$ of lb: 0.98 (t, $J_H = J_p = 6$), CH_3 (Z-isomer); 1.26 (br), CH_3 (E-isomer); 1.8-2.5 (br,m), PCH₂ and PdCH₂; ca. 4.3 (v br), =CHMe (E); ca. 4.7 (v br), =CHMe (Z); 5.3 (br,m), CH₂CH= (E and Z). The PdCH₂ resonance appeared at δ 2.91 (apparent quartet) in $C_6 D_6$.
- 5) The metallic products were also recovered in comparable yields, and identified by elemental analysis and/or spectral means.
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