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ELECTROPHILIC SUBSTITUTION OF STRUCTURALLY RIGID η^1-ALLYLPALLADIUM COMPLEXES

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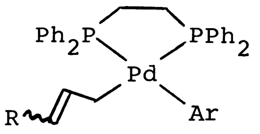
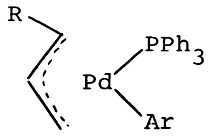
η^1-Allyl(aryl)palladium complexes react with some electrophiles to result in the selective Pd-allyl bond cleavage with 1,3-transposition, while the corresponding η^3-allyl(aryl)palladiums and the electrophiles give rise to the selective Pd-Ar bond cleavage. The η^1-allyl complexes also react with CCl_4 and $CHCl_3$ under very mild conditions to give good yields of CH_2=CHCHR($CR'Cl_2$) (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^1-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.



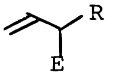
1

	Ar	R
a	C_6F_5	H
b	C_6F_5	Me
c	C_6HCl_4-2,3,5,6	H
d	C_6HCl_4-2,3,5,6	Me



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, Br_2, $BrNC(O)CH_2CH_2C(O)$ (NBS)) in chloroform at room temperature to give good yields ($\geq$ 70%) of the products from the Pd-allyl bond cleavage (Eq. 1).[5] Importantly, the products from 1b and 1d were almost exclusively the isomer of the formula, CH_2=CHCH(E)Me (E= H, Br), demonstrating the direct attack of the electrophile at the C=C bond of the η^1-allyl group. The previous work[1] also assumed the similar electrophilic substitution

1 + EX ⟶  + PdAr(X)(dppe) (1)

2 + EX ⟶ Ar-E + Pd(η^3-allyl)(X)(PPh_3) (2)

of η^1-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 Br_2 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% CH_2=CHCHMeBr, 17% MeCH=$CHCH_2Br$) 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 **1c** and **1d** 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 $CHCl_3$). **1a** and **1b** 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 **2** 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 $CHCl_3$. Thus, the reaction of **1** with CCl_4 and $CHCl_3$ may have proceeded through a radical path (S_H2' 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 work$^{1)}$ 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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2) M. Parra-Hake, M. F. Rettig, and R. M. Wing, Organometallics, 2, 1013 (1983).
3) S. Numata, R. Okawara, and H. Kurosawa, Inorg. Chem., 16, 1737 (1977).
4) For example, $\delta(CDCl_3)$ of **1b**: 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), PCH_2 and $PdCH_2$; ca. 4.3 (v br), =C<u>H</u>Me (E); ca. 4.7 (v br), =C<u>H</u>Me (Z); 5.3 (br,m), CH_2C<u>H</u>= (E and Z). The $PdCH_2$ resonance appeared at δ 2.91 (apparent quartet) in C_6D_6.
5) The metallic products were also recovered in comparable yields, and identified by elemental analysis and/or spectral means.
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