Palladium- and Platinum-catalysed Addition of Aldehydes with Allylstannanes

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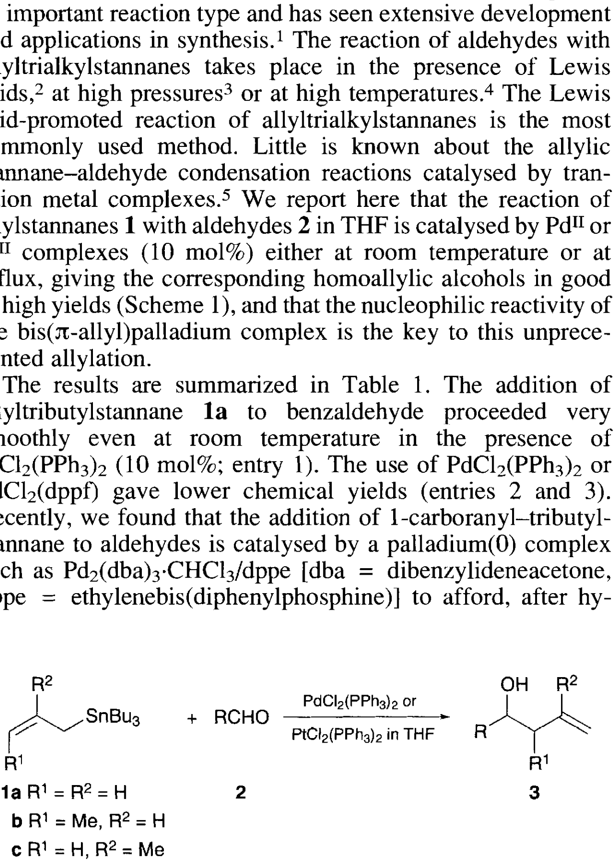
The reaction of allylic stannanes **1** with aldehydes **2** (or a ketone) takes place in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ or $PtCl_2(PPh_3)_2$ to give the corresponding homoallyl alcohols **3** in good to high yields.

The allylation of aldehydes with allylstannanes has emerged as an important reaction type and has seen extensive development and applications in synthesis.[1] The reaction of aldehydes with allyltrialkylstannanes takes place in the presence of Lewis acids,[2] at high pressures[3] or at high temperatures.[4] The Lewis acid-promoted reaction of allyltrialkylstannanes is the most commonly used method. Little is known about the allylic stannane–aldehyde condensation reactions catalysed by transition metal complexes.[5] We report here that the reaction of allylstannanes **1** with aldehydes **2** in THF is catalysed by Pd^{II} or Pt^{II} complexes (10 mol%) either at room temperature or at reflux, giving the corresponding homoallylic alcohols in good to high yields (Scheme 1), and that the nucleophilic reactivity of the bis(π-allyl)palladium complex is the key to this unprecedented allylation.

The results are summarized in Table 1. The addition of allyltributylstannane **1a** to benzaldehyde proceeded very smoothly even at room temperature in the presence of $PtCl_2(PPh_3)_2$ (10 mol%; entry 1). The use of $PdCl_2(PPh_3)_2$ or $PdCl_2(dppf)$ gave lower chemical yields (entries 2 and 3). Recently, we found that the addition of 1-carboranyl–tributylstannane to aldehydes is catalysed by a palladium(0) complex such as $Pd_2(dba)_3{\cdot}CHCl_3$/dppe [dba = dibenzylideneacetone, dppe = ethylenebis(diphenylphosphine)] to afford, after hydrolysis, the corresponding adducts 1-carboranylcarbinols, in good to high yields.[6] We examined palladiun(0) catalysts such as $Pd_2(dba)_3{\cdot}CHCl_3$/dppe and $Pd(PPh_3)_4$ (entry 4), but the allylation product was obtained in lower yield. The use of other transition metal complexes, such as $Rh(H)(CO)(PPh_3)_3$, $RuCl_2(PPh_3)_3$ and $NiCl_2(PPh_3)_2$ afforded the adduct in 10–30% yields. Accordingly, the Pd^{II} complex is a more suitable catalyst for the allylation of aldehydes in comparison with the Pd^0 complexes, and the Pt^{II} complex is the best catalyst of the species examined. Aromatic, α,β-unsaturated and aliphatic aldehydes underwent the allylation reaction in the presence of a $PtCl_2(PPh_3)_2$ catalyst (10 mol%) in THF under reflux to give the corresponding allylation products in good to high yields (entries 5–11). Even cyclohexanone reacted with allyltributylstannane under similar conditions to afford the adduct (43%) along with recovered cyclohexanone (entry 12). The reactions of *Z*-crotyltributylstannane **1b** were slower than those of **1a** (entries 13–15), presumably owing to the γ-methyl substituent of **1b**. The *syn*:*anti* diastereoisomer ratios of the adducts were nearly 1 : 1, and products of allylation at the α-position were not detected.[7] In general, the reaction with methallyltributylstannane **1c** proceeded smoothly in the presence of the $PtCl_2(PPh_3)_2$ catalyst in THF at reflux (entries 16–20). The allylation did *not* take place in the absence of $PtCl_2(PPh_3)_2$ in THF at reflux.



Scheme 1

A typical procedure for the $PtCl_2(PPh_3)_2$-catalysed allylation is as follows. A mixture of 0.2 mmol of an aldehyde, 0.22 mmol of allyltributylstanne and 0.02 mmol of $PtCl_2(PPh_3)_2$ (10 mol%) is dissolved in 1 ml of dried THF under Ar atmosphere. The mixture was stirred either at room temperature or at reflux for an appropriate period of time. The reaction was monitored by TLC. The reaction was quenched by filtering the mixture through a short silica-gel column chromatograph. NMR examination of the reaction mixture prior to the column chromatography indicated the formation of the corresponding stannyloxy

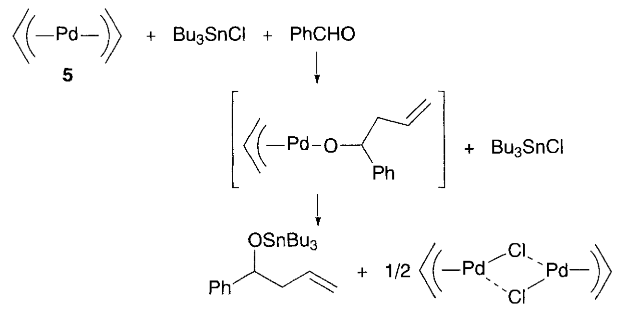
Table 1 Transition metal-catalysed allylation of aldehydes (and a ketone) with allylstannanes[a]

Entry	Allylstannane **1**	Aldehyde **2**	Catalyst (10 mol %)	Reaction temp.[b] (time)	Yield (%) of **3**
1	**1a**	PhCHO	$PtCl_2(PPh_3)_2$	r.t. (4d)	90
2	**1a**	PhCHO	$PdCl_2(PPh_3)_2$	r.t. (4d)	64
3	**1a**	PhCHO	$PdCl_2(dppf)$	r.t. (4d)	59
4	**1a**	PhCHO	$Pd(PPh_3)_4$	r.t. (4d)	40
5	**1a**	*p*-BrC_6H_4CHO	$PtCl_2(PPh_3)_2$	reflux (11 h)	83
6	**1a**	*o*-BrC_6H_4CHO	$PtCl_2(PPh_3)_2$	reflux (8 h)	94
7	**1a**	*p*-$(NO_2)C_6H_4CHO$	$PtCl_2(PPh_3)_2$	reflux (8 h)	70
8	**1a**	*c*-$C_6H_{11}CHO$	$PtCl_2(PPh_3)_2$	reflux (10 h)	99
9	**1a**	*n*-$C_5H_{11}CHO$	$PtCl_2(PPh_3)_2$	50 °C (1 d)	40
10	**1a**	$PhCH_2CH_2CHO$	$PtCl_2(PPh_3)_2$	reflux (8 h)	58
11	**1a**	PhCH=CHCHO	$PtCl_2(PPh_3)_2$	reflux (1 d)	81
12	**1a**	Cyclohexanone	$PtCl_2(PPh_3)_2$	reflux (12 h)	43
13	**1b**	PhCHO	$PtCl_2(PPh_3)_2$	r.t. (4 d)	37
14	**1b**	*p*-$(NO_2)C_6H_4CHO$	$PtCl_2(PPh_3)_2$	reflux (8 h)	65
15	**1b**	*p*-BrC_6H_4CHO	$PtCl_2(PPh_3)_2$	reflux (1 d)	48
16	**1c**	PhCHO	$PtCl_2(PPh_3)_2$	50 °C (1 d)	*ca.* 100
17	**1c**	*p*-$(NO_2)C_6H_4CHO$	$PtCl_2(PPh_3)_2$	reflux (14 h)	71
18	**1c**	*p*-BrC_6H_4CHO	$PtCl_2(PPh_3)_2$	reflux (10 h)	63
19	**1c**	*c*-$C_6H_{11}CHO$	$PtCl_2(PPh_3)_2$	reflux (14 h)	67
20	**1c**	*n*-$C_5H_{11}CHO$	$PtCl_2(PPh_3)_2$	reflux (16 h)	49

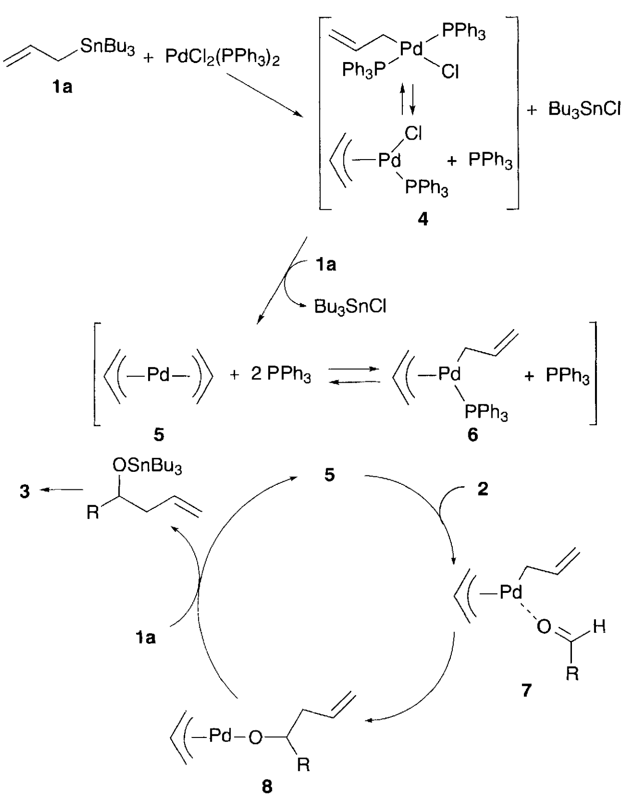
[a] The reaction was monitored by TLC and quenched, after an appropriate period, by fileing the reaction mixture through a short silica gel column chromatograph. In the case of the reactions which gave **3** in low yields, the starting aldehyde was recovered. [b] r.t. = room temp.

derivative. Therefore, hydrolysis of the Sn–O bond must take place during the column chromatography.

In order to clarify the mechanism of the allylation reaction catalysed by PtCl$_2$(PPh$_3$)$_2$ and PdCl$_2$(PPh$_3$)$_2$, we investigated an intermediate produced from a stoichiometric reaction between **1a** and PdCl$_2$(PPh$_3$)$_2$ in [^{2}H$_8$]THF. A 1 : 1 mixture of **1a** and PdCl$_2$(PPh$_3$)$_2$ was heated under reflux for 1 h under an Ar atmosphere. The ^{1}H NMR spectrum of this mixture at 25 °C indicated formation of the π-allylpalladium complex **4**, PPh$_3$ and tributylstannyl chloride: a sharp quintet (δ 5.61, 1 H, *J* 10 Hz) and a broad doublet (δ 3.51, 4 H, *J* 7 Hz) were in good agreement with the signals previously observed by Kurosawa *et al.* for an equilibrium mixture between π and σ-allyl (*cis* and *trans*) palladium species.[8] The π-allylpalladium complex **4** was isolated from a mixture of **4**, PPh$_3$ and Bu$_3$SnCl by column chromatography. Curiously, **4** itself, or a mixture of **4**, PPh$_3$ and Bu$_3$SnCl did not react with benzaldehyde at all. However, if **1a** was added to a mixture of benzaldehyde and **4** (or **4** including PPh$_3$ and Bu$_3$SnCl), the allylation took place immediately. We thought that the bis(π-allyl)palladium complex **5** would be a key intermediate for the allylation. Triphenylphosphine-free bis(π-allyl)palladium complex **5** was prepared from the reaction of π-allylpalladium chloride dimer (1 equiv.) and **1a** (2 equiv.). The ^{1}H NMR spectrum of **5** was in good agreement with the reported spectra.[9] The addition of benzaldehyde to **5** gave the corresponding homoallyl alcohol after hydrolysis. Perhaps, **5** reacted with benzaldehyde to give a π-allyl(alkoxy)palladium complex which would afford the butenyloxystannane *via* redistribution with tributylstannyl chloride (Scheme 2).



Scheme 2



Scheme 3

In conclusion, the catalytic cycle probably proceeds as shown in Scheme 3. The cycle may start from **6** instead of **5**, since triphenylphosphine is involved in the reaction system. The π-allyl-σ-allyl palladium complex **7** may produce the homoallyloxy palladium **8**, which would react with **1a** to give **5** and the homoallyloxystannane derivative. It is clear that the only species which reacts with an aldehyde without any additive is **5**; no reaction takes place between **4** and an aldehyde (even in the presence of Bu$_3$SnCl); the bis(π-allyl)palladium chloride dimer does not react in the presence of additives.

The catalytic reaction enables us to carry out the allylation under essentially neutral conditions either at room temperature or at *ca.* 65 °C. Further, the present findings clarify the nucleophilic reactivity of a bis(π-allyl)palladium complex although it is widely accepted that mono(π-allyl)PdX-type complexes exhibit electrophilic reactivity.

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References

1 Recent reviews: (*a*) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; (*b*) Y. Nishigaichi, A. Takuwa, Y. Narutu and K. Maruyama, *Tetrahedron*, 1993, **49**, 7395; (*c*) J. A. Marshall, *Chemtracts: Biochem. Mol. Biol.*, 1992, **5**, 75; (*d*) W. R. Roush, in *Comprehensive Organic Synthesis*, vol. 2, ed. C. H. Heathcock, Pergamon, Oxford, 1991, pp. 1–53; (*e*) Y. Yamamoto and N. Shida, in *Advances in Detailed Reaction Mechanisms*, ed. J. Coxon, JAI Press, Greenwich, 1994, vol. 3, pp. 1–44.

2 Y. Naruta, S. Ushida and K. Maruyama, *Chem. Lett.*, 1979, 919; A. Hosomi, H. Iguchi, M. Endo and H. Sakurai, *Chem. Lett.*, 1979, 977; Y. Yamamoto, H. Yatagai, Y. Naruta and K. Maruyama, *J. Am. Chem. Soc.*, 1980, **102**, 7107; M. Koreeda and Y. Tanaka, *Chem. Lett.*, 1982, 1297; H. Miyake and K. Yamamura, *Chem. Lett.*, 1992, 2221; A. H. McNeill and E. J. Thomas, *Tetrahedron Lett.*, 1990, **31**, 6239; G. E. Keck, M. B. Andrus and S. Castellino, *J. Am. Chem. Soc.*, 1989, **111**, 8136; A. Gambaro, A. Boaretto, D. Furlani, D. Marton and G. Tagliavini, *J. Organomet. Chem.*, 1986, **299**, 157; S. E. Denmark and S. Hosoi, *J. Org. Chem.*, 1994, **59**, 5133; see also ref. 1.

3 Y. Yamamoto, K. Maruyama and K. Matsumoto, *J. Chem. Soc., Chem. Commun.*, 1983, 489; N. S. Isaacs, R. L. Marshall and D. J. Young, *Tetrahedron Lett.*, 1992, **33**, 3023; Y. Yamamoto and K. Saito, *J. Chem. Soc., Chem. Commun.*, 1989, 1676.

4 C. Servens and M. Pereyre, *J. Organomet. Chem.*, 1972, **35**, C20; C. Hull, S. V. Mortlock and E. J. Thomas, *Tetrahedron*, 1989, **45**, 1007; A. J. Pratt and E. J. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1521; V. J. Jephcote, A. J. Pratt and E. J. Thomas, *J. Chem. Soc. Perkin Trans. 1*, 1989, 1529.

5 J. W. Labadie, D. Tueting and J. K. Stille, *J. Org. Chem.*, 1983, **48**, 4634; B. M. Trost and S. A. King, *J. Am. Chem. Soc.*, 1990, **112**, 408. They suggested that Pd^{II} complexes might act as a Lewis acid or nucleophilic π-allylpalladium complexes might be involved; Y. Masuyama, in *Advances in Metal–Organic Chemistry*, JAI Press, Greenwich, vol. 3, p. 255; Y. Masuyama, J. P. Takahara and Y. Kurusu, *J. Am. Chem. Soc.*, 1988, **110**, 4473; J. P. Takahara, Y. Masuyama and Y. Kurusu, *J. Am. Chem. Soc.*, 1992, **114**, 2577: π-Allylpalladium complexes are converted *in situ* to allyltrichlorostannanes in the presence of SnCl$_2$.

6 H. Nakamura, N. Sadayori, M. Sekido and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1994, 2581.

7 The diastereoisomeric ratio and the γ:α adduct ratio were determined by comparison with the ^{1}H NMR spectra of authentic samples: ref. 1*c* and Y. Yamamoto, H. Yatagai, Y. Ichihara, N. Maeda and K. Maruyama, *Tetrahedron*, 1984, **40**, 2239.

8 S. Numata, R. Okawara and H. Kurosawa, *Inorg. Chem.*, 1977, **16**, 1737; see also J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1967, 1839.

9 J. K. Becconsall, B. E. Job and S. O'Brien, *J. Chem. Soc. (A)*, 1967, 423; B. Henc, P. W. Jolly, R. Salz, G. Wilke, R. Benn, E. G. Hoffmann, R. Mynott, G. Schroth, K. Seevogel, J. C. Sekutowski and C. Krüger, *J. Organomet. Chem.*, 1980, **191**, 425; B. Henc, P. W. Jolly, R. Saltz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard and C. Krüger, *J. Organomet. Chem.*, 1980, **191**, 449.