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Formation of an allyl–tin bond in η^3-allyl(trichlorostannyl)palladium(II) complexes

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Abstract

Attempts were made to find conditions under which formation of the allyl–tin bond takes place efficiently starting from η^3-allylpalladium(II) complexes containing the Pd–$SnCl_3$ bond. Addition of $SnCl_2$ or allylic chloride was effective in this matter, while PPh_3 and maleic anhydride, which had been known before to be good accelerators of couplings between the η^3-allyl ligand and carbon anions on Pd, were totally ineffective for the allyl–$SnCl_3$ coupling. Relative coordination ability of substituted styrenes in a series of complexes, Pd(η^3-CH_2CMeCH_2)(styrene)($SnCl_3$) indicated a highly electron-deficient character of the Pd center. A possible reaction scheme of the Pd-catalyzed formation of allyltin(IV) trichloride from $SnCl_2$ and allylic chloride is discussed in the light of the above findings.

Key words: Palladium complexes; Allyl complexes; Tin complexes

Introduction

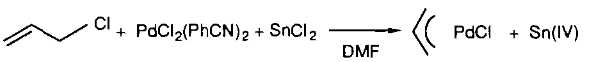
Palladium catalyzed allylic transformations have been among the most successful applications of organometallic reactions to organic synthesis [1]. They are thought to proceed via transfer of a formally electrophilic allylic moiety from palladium to a nucleophilic center. Versatility of allylpalladium chemistry in organic synthesis has recently been widened by generation of nucleophilic allylic intermediates by means of the combination of allylic electrophiles/palladium catalyst and some reducing agents such as Sn(II) or Sm(II) compounds or metallic zinc [2].

Masuyama and co-workers suggested [2a] that allyltin(IV) compounds are key intermediates in the reaction of allylic electrophiles with aldehydes in the presence of Sn(II) reagents and palladium catalysts. However, the way such allyltin(IV) intermediates are generated remained to be established. In this work, we attempted to find conditions under which efficient allyltin(IV) formation takes place starting from η^3-allylpalladium(II) complexes containing the Pd–$SnCl_3$ bond. The objective of the present work is to shed some light on the mechanism of the generation of allyltin(IV) compounds in the related catalytic reactions mentioned above.

Results and discussion

Reaction of $PdCl_2(PhCN)_2$ with $SnCl_2$ and allylic chloride

Masuyama and co-workers observed [2a] the formation of allyltin(IV) species in the reaction of allylic chloride or alcohol with $SnCl_2$ in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ in DMF-d_7. However, the molecular formula of the palladium moiety present during and after the catalysis was not determined. We observed by ^1H NMR the existence of η^3-allylpalladium(II) species in the course of the reaction of allyl chloride (0.1 mol/l) and $SnCl_2$ (0.1 mol/l) in the presence of a deficient amount (0.01 mol/l) of $PdCl_2(PhCN)_2$ in DMF-d_7. Under these reaction conditions an almost quantitative formation of allyltin(IV) trichloride was also confirmed. We also observed that, if the initial amount of $PdCl_2(PhCN)_2$ employed was increased to 0.1 mol/l, i.e. an amount equimolar to both allyl chloride and $SnCl_2$, the formation of allyltin(IV) trichloride was no longer observed, and instead all of the allyl group of the chloride was converted to η^3-allylpalladium(II) chloride (eqn. (1)).



(1)

There are two possible explanations for the absence of allyltin(IV) trichloride as the product in the above

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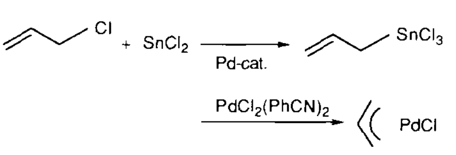
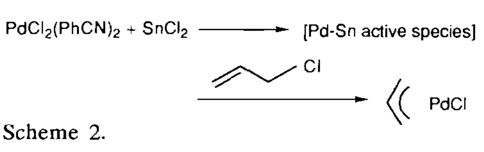
reaction between allyl chloride, $SnCl_2$ and $PdCl_2(PhCN)_2$, each in an equimolar amount; one assumes an initial Pd-catalyzed formation of the allyltin(IV) moiety which subsequently disappears via allyl group transfer from this moiety to $PdCl_2(PhCN)_2$ (Scheme 1), and the other assumes no such allyltin formation but a role of $SnCl_2$ to activate $PdCl_2(PhCN)_2$ toward reaction with allyl chloride[*] to result in η^3-allylpalladium(II) formation (Scheme 2). Although we observed that allyltin(IV) trichloride indeed reacted with $PdCl_2(PhCN)_2$ with considerable ease to give η^3-allylpalladium(II) chloride, we exclude the possibility of Scheme 1 in the above stoichiometric allylpalladium(II) formation shown in eqn. (1) for the following reasons.

We thought that if allyltin(IV) species were formed initially in eqn. (1), they could be trapped by some added electrophiles other than $PdCl_2(PhCN)_2$. In fact, we separately confirmed that when allyltin(IV) trichloride was treated with a mixture of PhCHO and $PdCl_2(PhCN)_2$ (10:1), both $PhCH(OH)CH_2CH{=}CH_2$ and η^3-allylpalladium(II) chloride in a ratio of 13/87 were formed. Thus, we tested the effect of added PhCHO on the reaction of allyl chloride with stoichiometric amounts of $SnCl_2$ and $PdCl_2(PhCN)_2$; i.e. the reaction of allyl chloride with $SnCl_2$ and $PdCl_2(PhCN)_2$ (1:1:1) was carried out in the presence of 10 equiv. of PhCHO in DMF-d_7. Under these conditions we were unable to detect any formation of $PhCH(OH)CH_2CH{=}CH_2$, excluding the possibility of Scheme 1.

We therefore suggest the reaction between allyl chloride, $SnCl_2$ and $PdCl_2(PhCN)_2$ in a 1:1:1 ratio follows Scheme 2. Also in the Pd-catalyzed reaction of allyl chloride and $SnCl_2$, allyl chloride would be first converted to the η^3-allylpalladium(II) complex from which the allyl group is transferred to tin(II) to give allyltin(IV) through a certain mechanism.



Scheme 1.



Scheme 2.

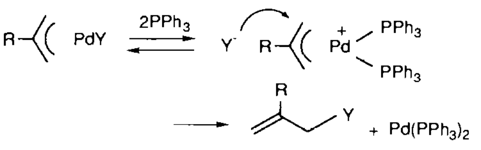
Transfer of allyl group from Pd(II) to Sn(II)

Since the η^3-allylpalladium(II) chloride species formed in eqn. (1) can be converted mostly to a η^3-allyl(trichlorostannyl)palladium(II) moiety in the presence of excess $SnCl_2$ (catalysis condition), we examined the possibility of an allyl–tin bond formation in the complexes $Pd(\eta^3\text{-}CH_2CRCH_2)(styrene)(SnCl_3)$ (**1**) (R = H (**1a**), Me (**1b**) [3]) under various conditions. Allowing **1** to stand in $CDCl_3$ at room temperature caused no allyl–tin bond formation. On the other hand, when dissolved in DMF-d_7 **1** did afford $CH_2{=}CRCH_2SnCl_3$, though in fairly low yields (10–15% after 1 day at room temperature). We next examined the effects of some additives on the allyl–tin coupling.

Addition of excess PPh_3 to **1** was ineffective for allyl–tin bond formation. The ^1H NMR spectra indicated coordination of PPh_3 to palladium [4] since *syn–anti* proton exchange process was induced by addition of PPh_3. It has already been demonstrated [5] that the addition of PPh_3 is quite effective for some allyl–ligand couplings, especially in inducing external nucleophilic attack of the ligand, which was originally bound to palladium, at the η^3-allyl carbon in $[Pd(\eta^3\text{-}CH_2CRCH_2)(PPh_3)_2]^+$ ion; typical examples include conversion of $Pd(\eta^3\text{-}CH_2CRCH_2)[CH(COMe)_2]$ and $[Pd(\eta^3\text{-}CH_2CRCH_2)(SPh)]_2$ to $CH_2{=}CRCH_2Y$ (Y = $CH(COMe)_2$ or SPh) on treatment with excess PPh_3 (Scheme 3). Apparently the $SnCl_3^-$ ion does not undergo a similar external nucleophilic attack.

Addition of maleic anhydride (3 equiv.) to **1** was also ineffective for allyl–tin bond formation. This olefin was previously shown [6] to accelerate the reductive elimination of $Pd(\eta^3\text{-allyl})(aryl)(PR_3)$, through coordination to palladium, resulting in C–C bond formation. It may well be that considerable electron density on palladium is required for maleic anhydride to coordinate because of its electron deficient character. With regard to this point, we propose that the palladium atom in the $Pd(\eta^3\text{-}CH_2CRCH_2)(SnCl_3)$ moiety is so electron-deficient that maleic anhydride can hardly coordinate with this moiety. This notion was supported by the examination of the relative coordination ability of a series of substituted styrenes with the $Pd(\eta^3\text{-}CH_2CRCH_2)(SnCl_3)$ moiety, as shown below.

The equilibrium constants (*K*) of the coordinative equilibrium shown in eqn. (2) (M = Pd) were determined



Scheme 3.

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[*] Treatment of $PdCl_2(PhCN)_2$ with $SnCl_2$ (1:1) in DMF, followed by addition of 4 equiv. PPh_3 afforded a good yield of $Pd(PPh_3)_4$ (65%). Also, allowing a mixture of $PdCl_2(PhCN)_2$ and $SnCl_2$ to stand in the absence of PPh_3 resulted in partial deposition of palladium metal.

TABLE 1. Equilibrium constants (*K*) of eqn. (2)

Complex M	*K*			
	Y = *m*-NO$_2$	*p*-Cl	*p*-Me	*p*-OMe
Pd[a]	0.031	0.36	1.7	5.6
Pt[b]	0.062	0.36	1.2	1.5

[a] In CD_2Cl_2 at −80 °C. [b] In $CDCl_3$ at 25 °C.

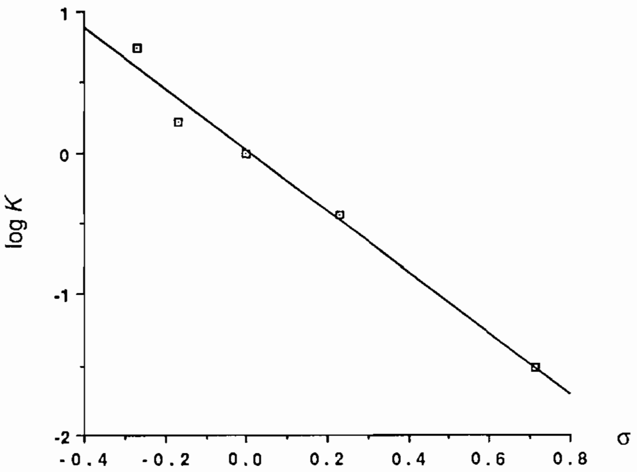
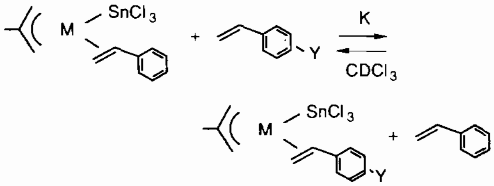


Fig. 1. Hammett plot for equilibrium constants of eqn. (2) (M = Pd) in CD_2Cl_2 at −80 °C.

at −80 °C by ^1H NMR spectral integrations (Table 1). The Hammett plot for the data obtained is shown in Fig. 1. The ρ value (−2.17, r = 0.992) in the plot unambiguously indicates the highly electrophilic character of the palladium atom toward the coordinating olefin. An analogous result was observed for the relative stability of the styrene complexes of the Pt–SnCl$_3$ moiety, Pt(η^3-CH$_2$CMeCH$_2$)(SnCl$_3$)(CH$_2$=CHC$_6$H$_4$Y) (eqn. (2), M = Pt; ρ = −1.45, r = 0.989 at 25 °C).



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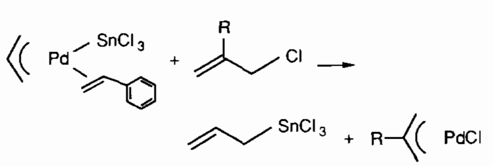


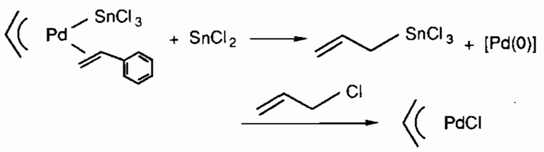
(3)

We found that addition of allylic chloride to **1** was moderately effective in inducing allyl–tin bond formation. Thus, for example, treatment of **1a** (0.02 mmol) with allyl chloride (0.06 mmol) in DMF-d$_7$ or CDCl$_3$ (0.5 ml) afforded allyltin(IV) trichloride in 34 and 52% yields after 2.5 and 1 h, respectively (eqn. (3), R = H). The η^3-allylpalladium(II) moiety is almost quantitatively regenerated simultaneously. Benzyl chloride was not effective in promoting allyl–tin bond formation.

An experiment employing a combination of different allylic groups (eqn. (3), R = Me) afforded CH$_2$=CHCH$_2$SnCl$_3$ almost exclusively at the early stage (25%, after 5 min from 0.04 mmol of **1a** and 0.04 mmol of CH$_2$=CMeCH$_2$Cl in 0.5 ml of CDCl$_3$). At a later stage a small amount of CH$_2$=CMeCH$_2$SnCl$_3$ was also formed (8% after 1 h together with 3% of isobutene which was a hydrolysis product of this tin compound; the yield of CH$_2$=CHCH$_2$SnCl$_3$ increased to 41%). This may be due to a rapid SnCl$_3$–Cl scrambling between the original Pd(η^3-CH$_2$CHCH$_2$) moiety and the newly formed Pd(η^3-CH$_2$CMeCH$_2$) moiety. In other words, the SnCl$_3$ ligand can lie close to both allylic groups on the coordination sphere of Pd. What is deduced from these results is the unlikeliness of the coupling of the SnCl$_3$ group with the incoming substrate (CH$_2$=CMeCH$_2$Cl), e.g. the Heck-type reaction [1b]. This mechanism might have produced CH$_2$=CMeCH$_2$SnCl$_3$, but no CH$_2$=CHCH$_2$SnCl$_3$.

A similar accelerating effect of allylic chlorides in the C–C bond formation in Pd(η^3-allyl)(Ar)(EPh$_3$) (E = P, As) has already been reported [7]. In these reactions the primary role of the allylic chlorides was to oxidatively add to palladium to enhance the allyl–aryl coupling. We also propose a similar role of the allylic chloride in the present allyl–SnCl$_3$ coupling except that no scrambling of the original, Pd-bound allylic and the substrate allylic groups is involved.

In the Pd-catalyzed formation of allyltin(IV) species from allylic chloride and SnCl$_2$, not only allylic chloride but SnCl$_2$ exists in excess amounts relative to the palladium species. Thus, the effect of adding SnCl$_2$ to the η^3-allylpalladium(II) complex was also examined. Interestingly, addition of 3 equiv. SnCl$_2$ to **1a** (0.02 mmol) in DMF-d$_7$ (0.5 ml) caused an effective formation of allyltin(IV) species (61% yield after 0.5 h) (Scheme 4). It is notable that the solution remained homogeneous after completion of the reaction, and addition of allylic chloride to this homogeneous solution resulted in regeneration of a good yield of η^3-allylpalladium(II) species. Furthermore, treatment of the solution with PPh$_3$, instead of allyl chloride, led to isolation of Pd(PPh$_3$)$_4$ (55%). It is assumed from these results as well as the



Scheme 4.

chemical balance that a Pd(0) species is generated in the first step of Scheme 4, even though the exact nature of this species remains to be fully elucidated*.

Conclusions

The formation of allyltin(IV) trichloride from allyl chloride and $SnCl_2$ catalyzed by palladium proceeds via an η^3-allyl(trichlorostannyl)palladium(II) intermediate. This is capable of transferring the allylic group from Pd(II) to Sn(II) to form allyltin(IV) species when interacted with either of the two substrates ($SnCl_2$ and allylic chloride). In either case of the substrate interactions the intermediate η^3-allyl(trichlorostannyl)-palladium(II) complex can be regenerated with great ease through the subsequent action of the other substrate which had not been involved in the initial interaction. Which substrate takes part in the initial and the second interaction remains to be elucidated.

Experimental

^1H NMR spectra were obtained on JEOL GSX-400 and Bruker AM600 spectrometers. Most of the commercially available reagents were used without further purification. $Pd(\eta^3\text{-}CH_2CMeCH_2)(styrene)(SnCl_3)$ (**1b**) and its platinum analog were prepared according to the reported method [3].

Preparation of $Pd(\eta^3\text{-}CH_2CHCH_2)(styrene)(SnCl_3)$ *(1a)*

Under an atmosphere of argon, styrene (0.208 g, 2 mmol) was added to $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$ (0.120 g, 0.33 mmol) dissolved in 5 ml of CH_2Cl_2. After the solution was stirred for 30 min, $SnCl_2$ (0.177 g, 0.97 mmol) was added. After filtration of excess of $SnCl_2$, the filtrate was concentrated, and cooled to −30 °C to give yellow crystals of the desired product (0.208 g, 67%), m.p. 67–70 °C (dec.). *Anal.* Calc. for $C_{11}H_{13}PdSnCl_3$: C, 27.72; H, 2.75. Found: C, 27.35; H, 2.63%.

Reaction of $CH_2{=}CHCH_2SnCl_3$ *with* $PdCl_2(PhCN)_2$ *and PhCHO*

Allyltin(IV) trichloride was generated by the reaction of allyl chloride (3.8 mg, 0.05 mmol) and $SnCl_2$ (9.5 mg, 0.05 mmol) in the presence of $PdCl_2(PhCN)_2$ (1.9 mg, 0.005 mmol) in DMF-d_7 (0.5 ml) and confirmed by the ^1H NMR spectrum [2a]. This spectrum also showed the existence of $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$ in a ~1/10 amount. To this solution was added a DMF-d_7 solution of either $PdCl_2(PhCN)_2$ (19 mg, 0.05 mmol) alone or a mixture of $PdCl_2(PhCN)_2$ (0.05 mmol) and PhCHO (53 mg, 0.5 mmol). The former reaction gave an almost quantitative yield of $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$, and the latter a ~13/87 mixture of $PhCH(OH)CH_2CH{=}CH_2$ and $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$.

Reaction of allyl chloride/$SnCl_2$ *with stoichiometric amount of* $PdCl_2(PhCN)_2$

The reaction was carried out in a manner similar to that described above except that the amount of $PdCl_2(PhCN)_2$ was increased to 0.05 mmol. The ^1H NMR spectrum showed the quantitative formation of $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$, but no formation of allyltin(IV) trichloride. Even when PhCHO (53 mg, 0.5 mmol) was added to the above mixture prior to the start of the reaction, the amount of the η^3-allylpalladium product did not change, and $PhCH(OH)CH_2CH{=}CH_2$ was not detected at all.

General procedure for allyl–tin bond formation from 1

To a DMF-d_7 or $CDCl_3$ solution (0.5 ml) of **1a** (10 mg, 0.02 mmol) was added 0.06 mmol of a given addend, and the reaction process was followed by ^1H NMR measurements at various times. The addends examined in this manner include $SnCl_2$, allyl chloride, methallyl chloride, benzyl chloride, PPh_3 and maleic anhydride.

Solution stability of $M(\eta^3\text{-}CH_2CMeCH_2)(CH_2{=}CHC_6H_4Y)(SnCl_3)$

Substituted styrene complexes $Pd(\eta^3\text{-}CH_2CMeCH_2)(CH_2{=}CHC_6H_4Y)(SnCl_3)$ (Y = *m*-NO_2, *p*-Cl, *p*-Me, *p*-OMe) were generated by adding to a CD_2Cl_2 solution (0.5 ml) of **1b** (0.03 mmol) 5- to 10-fold excess amounts of free styrenes. The NMR tube was set in a probe cooled at −80 °C, and each component involved in eqn. (2) was integrated to give K values. Several measurements with different reagent ratios gave the averaged K values shown in Table 1. The equilibrium measurements for the platinum analogs were carried out in $CDCl_3$ at 25 °C.

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*It was reported before that Pd(0) and Pt(0) complexes are stabilized by coordination of Sn(II) ligands [8].

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