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Synthesis and destannylation of η^3-1-stannylallylpalladium(II) complexes

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Abstract

Reaction of 1-tributylstannyl-3-chloropropene with a $Pd(PPh_3)$ species, generated in situ from $Pd_2(dba)_3$ and two equivalents of PPh_3, afforded $Pd(\eta^3\text{-}Bu_3SnCHCHCH_2)Cl(PPh_3)$ (**1**). Complex **1** underwent PPh_3 promoted protodestannylation with acetic acid or diethyl malonate to give an unsubstituted η^3-allylpalladium moiety as either a detectable product or a reaction intermediate. The reaction of **1** with PPh_3 and 0.5 equivalent of $PdCl_2(PhCN)_2$ afforded the dinuclear complex $(\mu\text{-}1\text{-}3\text{-}\eta^3\text{:}4\text{-}6\text{-}\eta^3\text{-}CH_2CHCHCHCHCH_2)\{PdCl(PPh_3)\}_2$ (**4**) containing a hexatriene ligand, a formal vinylcarbene dimer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Destannylation; η^3-1-Stannylallylpalladium(II) complexes

1. Introduction

Organometallic complexes bearing readily removable functional groups on organic ligands have attracted attention as potential precursors of metal bound reactive intermediates, as exemplified by 1-haloalkyl or 1-alkoxyalkyl metal complexes serving as carbene–metal sources [1,2]. We have been interested in η^3-allylpalladium complexes of the type $Pd\{\eta^3\text{-}CH_2C(CH_2Y)CH_2\}(X)(L)$ as a possible precursor of the trimethylenemethane–palladium intermediate where Y represents an electrophilic (e.g. R_3Sn) [3] or nucleophilic (e.g. Cl, OS(O)Ph) [4] leaving group. Stimulated by a proposal [5], without proof, on the generation of vinylcarbene–palladium species from η^3-1-silylallylpalladium intermediate, we undertook studies of synthesis and reactivities of 1-silylallyl and 1-stannylallyl complexes of palladium.

2. Results and discussion

Initial attempts were made to accomplish desilylation of the known complex $\{Pd(\eta^3\text{-}Me_3SiCHCHCH_2)Cl\}_2$ [6] via, e.g. treatment with excess PPh_3 and/or AgOAc, but no well-characterizable results were obtained. We then turned our attention to stannyl analogs in view of the expected weaker Sn–C bond than the Si–C bond. Indeed, we had found earlier that the stannylmethyl-substituted complex $[Pd\{\eta^3\text{-}CH_2C(CH_2SnMe_3)CH_2\}(PPh_3)_2]Cl$ is a much better trimethylenemethane precursor than the silyl analog [3]. Treatment of 1-tributylstannyl-3-chloropropene with $Pd_2(dba)_3$ and PPh_3 ($Pd/PPh_3 = 1{:}1$) in CH_2Cl_2 at room temperature afforded pale yellow solids of the composition $Pd(\eta^3\text{-}Bu_3SnCHCHCH_2)Cl(PPh_3)$ (**1**) in 21% isolated yield. The ^1H- and ^{31}P-NMR spectra of **1** showed the presence of almost one isomer (Eq. (1)). The resonance of the allylic hydrogen geminal to Sn group (δ 5.06) showed a strong NOE correlation (15%) with the hydrogen at the allylic center (δ 6.27), suggesting the *anti*-Sn configuration. This preferred *anti* configuration is unusual for a η^3-allyl palladium complex, but we cannot give any reason for this [7].

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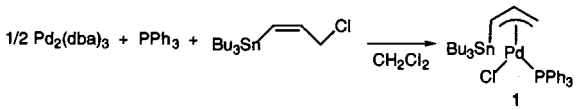
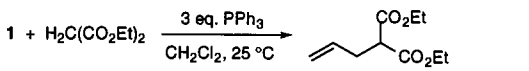


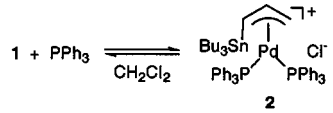
(1)

In view of the previous assumption [5] that the 1-silylallyl–palladium moiety underwent protodesilylation with malonate esters, complex **1** was treated with diethyl malonate in CH_2Cl_2 at 25°C, but no reaction took place. However, addition of excess PPh_3 (three equivalents) to a mixture of **1** and diethyl malonate under the same condition caused the coupling reaction to give diethyl 2-allylmalonate (40%, 46 h) (Eq. (2)).



(2)

In order to clarify the role of PPh_3 in promoting the above coupling, a CD_2Cl_2 solution of **1** and PPh_3 (1:1) was examined by ^{1}H- and ^{31}P-NMR spectroscopy. At room temperature, both ^{1}H- and ^{31}P-NMR spectra showed very broad peaks with small chemical shift changes compared to those of **1** alone, suggesting the occurrence of dynamic movements and/or equilibrium on the NMR time scale. On the other hand, at -60°C, the new allyl proton resonances predominated at δ 2.47 (br t, $J = 12$ Hz, 1H), 4.25 (br, 1H), 4.30 (br d, $J = 8$ Hz, 1H), 6.58 (br, 1H). These chemical shifts are consistent with a η^3-allyl–Pd, but not a η^1-allyl–Pd form; in the latter case the CH_2 protons would have appeared either as a singlet for equivalent two protons ($Bu_3SnCH{=}CHCH_2$–Pd linkage) or as part of terminal olefin proton multiplets ($CH_2{=}CHCH(SnBu_3)$–Pd linkage) [8]. Moreover, these ^{1}H spectral changes were accompanied by the new ^{31}P aspect showing two doublets (δ 21.59, 24.09, $J_{PP} = 38$ Hz), consistent with the *cis* configuration of two PPh_3 groups in η^3-allyl complexes [9]. Almost identical spectral data were observed for a sample prepared by the treatment of the mixture of **1** and PPh_3 with $AgBF_4$ at room temperature. As to the mixture of **1** and PPh_3, we propose the occurrence of the equilibrium (Eq. (3)) where the neutral monophosphine complex **1** dominates at room temperature and the cationic bisphosphine counterpart [Pd(η^3-$Bu_3SnCHCHCH_2$)(PPh_3)$_2$]Cl (**2**) dominates at the lower temperature. Accurate estimation of the degree of ionization at different temperatures was difficult owing to the broadness of the peaks caused by the dynamic movement.



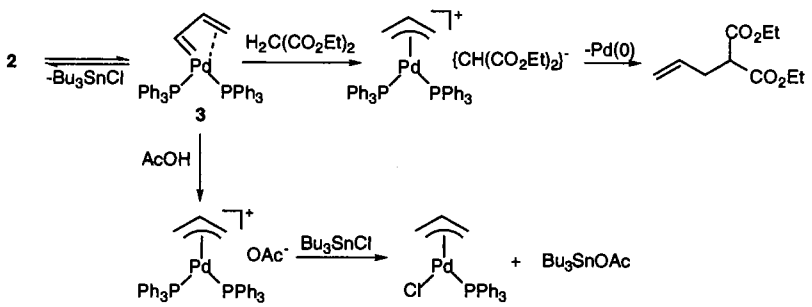
(3)

As expected, addition of CD_3OD to a CD_2Cl_2 solution of the mixture of **1** and PPh_3 (CD_3OD–CD_2Cl_2 = 1:6) led to predominant formation of the cationic complex **2** even at room temperature.

It is to be noted that no protodestannylation occurred in this mixed solvent solution. In contrast, the trimethylenemethane precursor, [Pd{η^3-$CH_2C(CH_2SnMe_3)CH_2$}(PPh_3)$_2$]Cl underwent very facile protodestannylation under the same conditions to give a deuterated η^3-2-methylallyl complex [3]. Addition of acetic acid, instead of methanol, to the mixture of **1** and PPh_3 resulted in protodestannylation to give a quantitative yield (40 h) of Pd(η^3-CH_2CHCH_2)Cl(PPh_3).

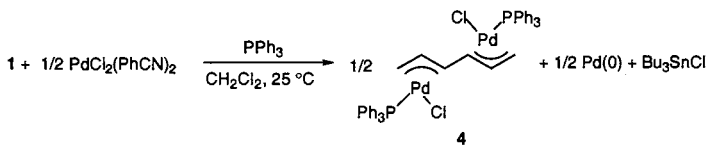
For the PPh_3-promoted destannylation of **1** with diethyl malonate or acetic acid, we suggest a plausible reaction path depicted in Scheme 1 where the Sn atom of the cationic complex **2** is susceptible to the attack of Cl^-, affording the vinylcarbene–palladium intermediate (**3**) which would abstract a proton from the malonate or acetic acid [10]. It should be pointed out here that in the absence of the proton source, the reaction mixture of **1** and PPh_3 underwent a very slow uncharacterizable decomposition path where no evidence for the vinylcarbenepalladium moiety was obtained. An alternative reaction sequence for Eq. (1) involving initial C–C coupling between **2** and $CH_2(COOEt)_2$ to give $CH_2{=}CHCH(SnBu_3)CH(COOEt)_2$ or $Bu_3SnCH{=}CHCH_2CH(COOEt)_2$ followed by their protonolysis seems unlikely, since [Pd(η^3-allyl)(PPh_3)$_2$]Cl does not react with neutral malonate esters.

Attempts were next made to substitute another Pd unit for Sn of **1** by using $PdCl_2(PhCN)_2$ in the hope of obtaining μ-η^3-vinylcarbene dinuclear complexes, since vinylcarbene ligands were known to be stabilized when bridging over the Pd–Pd bond [11]. When the 1:1 mixture of **1** and PPh_3 was treated with an equimolar



Scheme 1.

amount of $PdCl_2(PhCN)_2$, the ^{1}H-NMR analysis indicated the appearance of resonances for some products among which a set of resonances ascribable to a C_3H_4 unit are discerned; δ 2.98 (δ, $J = 12$ Hz, 1H), 3.11 (δ, $J = 7$ Hz, 1H), 4.69 (m, 1H), 5.78 (m, 1H). These peaks became dominant (92%, 40 h) when the amount of $PdCl_2(PhCN)_2$ was decreased to 0.5 equivalent with respect to **1**. The reaction was not so clean in the absence of PPh_3. After several attempts had been made to identify the major product, its structure was determined as **4** (Eq. (4)) having the 1-3-η^3:4-6-η^3-hexadienediyl ligand by synthesizing an authentic sample via an alternative route. This route involved substitution of hexatriene for μ-butadiene in $Pd_2Cl(PPh_3)$(μ-Cl)(μ-butadiene) [12], followed by addition of one equimolar amount of PPh_3. The ^{1}H-NMR data described above are consistent with **4** indicated. Strong NOE correlations were observed between the peaks at δ 4.69 (at C3) and 2.98 (*anti*-H at C1) (3%) as well as those at δ 4.69 and 5.78 (at C2′) (9%) [13].



(4)

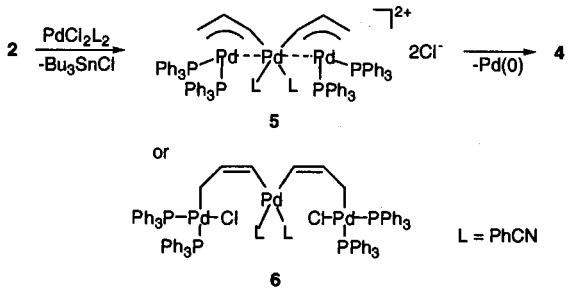
A possible route to **4** is shown in Scheme 2. The electrophilic replacement of the stannyl group in **2** by Pd(II), possibly via the intermediate **3**, would give a trinuclear intermediate (**5**) containing two μ-η^3-vinylcarbene ligands. This would then undergo coupling of two vinylcarbene ligands on the central Pd. The C–C coupling between the vinylcarbene ligand and Ph within the Pd–Pd framework has been known [11b]. An alternative path may be reductive elimination of a diorganopalladium complex (**6**) formed by the attack of Cl^- at **5**.

In conclusion, we succeeded in preparing 1-stannyl-substituted allyl–palladium complexes which served as a formal source of nucleophilic vinylcarbene–palladium intermediate.

3. Experimental

3.1. General procedures and measurements

Most of the commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar by use of standard vacuum line techniques. NMR spectra were obtained on JEOL GSX-270 and JEOL GSX-400 spectrometers. Chemical shifts are given in ppm using TMS or H_3PO_4 as standard.



Scheme 2.

3.2. Preparation of 1-tributylstannyl-3-hydroxypropene [14]

Into a stirred THF suspension (350 ml) of $LiAlH_4$ (4.00 g, 105 mmol) cooled at 0°C was added propargyl alcohol (11.7 g, 209 mmol) drop by drop. Stirring was continued for 17 h at room temperature (r.t.). The mixture was cooled to -60°C, and an Et_2O solution (70 ml) of Bu_3SnOTf (25.9 g, 61.5 mmol) was added. The mixture was stirred further at the same temperature for 4 h. Gaseous ammonia was bubbled through the solution, and 55 ml of methanol, 35 ml of ammonia-saturated aqueous ammonium chloride, and 70 ml of hexane were added successively. After filtration with Celite, the organic solvents were evaporated. The residue was extracted with hexane (50 ml × 3), and subsequent drying ($MgSO_4$) and evaporation gave 13.7 g (67%) of $Bu_3SnCH{=}CHCH_2OH$.

3.3. Preparation of 1-tributylstannyl-3-chloropropene

A THF solution (30 ml) of the 1-tributylstannyl-hydroxypropene (13.7 g, 39.5 mmol), PPh_3 (14.5 g, 55.3 mmol) and 83 ml of CCl_4 was heated at 70°C for 2 h. Pentane (450 ml) was added and the mixture filtered. The solvents were evaporated under vacuum. After addition of another pentane (200 ml), filtration, and evaporation, the residue was dissolved in hexane. Column chromatography (Wako C-200) of the hexane solution gave 9.5 g (65%) of the stannyl–chloropropene. ^{1}H-NMR ($CDCl_3$): δ 0.84–1.57 (m, 27H), 3.97 (d, $J = 7.3$, $J_{Sn} = 7.0$ Hz, 2H), 6.16 (d, $J = 12.2$, $J_{Sn} = 57.3$ Hz, 1H), 6.64 (dt, $J = 12.2$, 7.3, $J_{Sn} = 72.4$ Hz, 1H). Anal. Calc. for $C_{15}H_{31}ClSn$: C, 49.29; H, 8.55. Found: C, 49.17; H, 8.37%.

3.4. Preparation of $Pd(\eta^3\text{-}Bu_3SnCHCHCH_2)(Cl)(PPh_3)$ (1)

To a CH_2Cl_2 solution (5 ml) of $Pd_2(dba)_3$ (414 mg, 0.399 mmol) and PPh_3 (212 mg, 0.808 mmol) was added $Bu_3SnCH{=}CHCH_2Cl$ (300 mg, 0.822 mmol) at r.t. The solution color became deep green after 10 min stirring. The mixture was purified by column chromatography (alumina, CH_2Cl_2) to give a yellow eluent. Evaporation of the solvent, washing with pentane, and filtration gave a yellow solution. Recrystallization from CH_2Cl_2–pentane gave crystalline materials of **1** (125 mg, 21%). ^{1}H-NMR (CD_2Cl_2): δ 0.8–1.6 (m, 27H), 2.63 (bd, $J = 10.8$ Hz, 1H), 3.05 (dd, $J = 7.5$, 2.6 Hz, 1H), 5.06 (m, 1H), 6.27 (m, 1H), 7.45 (m, 9H), 7.6 (m, 6H). ^{31}P-NMR (CD_2Cl_2): δ 21.68 (s, $J_{Sn} = 44$ Hz). Anal. Calc. for $C_{35}H_{46}ClPPdSn$: C, 53.98; H, 6.31. Found: C, 54.08; H, 6.28%.

3.5. Reaction of 1 with PPh_3 and diethyl malonate

To a CD_2Cl_2 solution (0.6 ml) of **1** (10 mg, 0.014 mmol) and PPh_3 (10 mg, 0.039 mmol) in an NMR tube was added diethyl malonate (2.2 mg, 0.014 mmol). The mixture was kept at r.t. for 46 h. ^{1}H-NMR measurements indicated formation of diethyl 2-allylmalonate in 40% yield.

3.6. Reaction of 1 with PPh_3 and acetic acid

To a CD_2Cl_2 solution (0.6 ml) of **1** (9.0 mg, 0.013 mmol) and PPh_3 (3.4 mg, 0.013 mmol) in an NMR tube was added 1 μl of acetic acid. The mixture was kept at r.t. for 40 h. ^{1}H-NMR measurements confirmed almost quantitative formation of $Pd(\eta^3\text{-}CH_2CHCH_2)$–$(Cl)(PPh_3)$.

3.7. Reaction of 1 with PPh_3 and $PdCl_2(PhCN)_2$

To a CD_2Cl_2 solution (0.6 ml) of **1** (9.0 mg, 0.013 mmol) and PPh_3 (3.5 mg, 0.013 mmol) in an NMR tube was added $PdCl_2(PhCN)_2$ (2.7 mg, 0.007 mmol). The solution color changed from pale yellow to orange, and then dark orange. ^{1}H-NMR measurements after 40 h showed a set of four resonances as the major product at δ 2.98 (br d, $J = 12$ Hz, 1H), 3.11 (br d, $J = 7$ Hz, 1H), 4.69 (m, 1H), 5.78 (m, 1H). These data were identical with those of a sample prepared separately. Thus, hexatriene (9 ml) was added to a CH_2Cl_2 solution (10 ml) of 50 mg (0.083 mmol) of $Pd_2Cl(PPh_3)(\mu\text{-}Cl)(\mu\text{-}C_4H_8)$ [12], and then 22 mg of PPh_3 (0.083 mmol) added. Filtration and evaporation of the solvent gave dark yellow solids (30 mg, 41%). Recrystallization from CH_2Cl_2–hexane gave pale yellow solids of $(CH_2CHCHCHCHCH_2)\{PdCl(PPh_3)\}_2 \cdot 1/2CH_2Cl_2$. ^{31}P-NMR ($CDCl_3$): δ 24.02 (s). Anal. Calc. for $C_{42.5}H_{39}Cl_3P_2Pd_2$: C, 54.84; H, 4.22. Found: C, 54.38; H, 4.29%.

Acknowledgements

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