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Intermolecular propargyl/allenyl group transfer from Pd(II) to Pt(0) and Pt(II) to Pd(0). Key reaction in metal-catalyzed isomerization between propargyl and allenyl metal complexes

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Abstract

Isomerization of phenyl-substituted propargylplatinum(II) complex, *trans*-Pt($CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ (**1**) to allenyl complex, *trans*-Pt($CPh{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ (**2**) was found to be catalyzed by zerovalent complex Pd(PPh_3)$_4$. The reaction was proposed to proceed through the transfer of the propargyl/allenyl ligand both from Pt(II) to Pd(0) and Pd(II) to Pt(0). The former transfer, which seemingly has a thermodynamic disadvantage, has unambiguously been confirmed to take place; treatment of **1** with Pd(PPh_3)$_4$ or a mixture of $Pd_2(dba)_3$ and PPh_3 resulted in the formation of Pd(I) complex, Pd_2(μ-PhCCCH$_2$)(μ-Cl)(PPh_3)$_2$ which lies in equilibrium with a mixture of propargyl/allenylpalladium(II) and Pd(0) complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Intermolecular group transfer; Metal-catalyzed isomerization; Propargyl and allenyl metal complexes

1. Introduction

Interconversion between η^1-propargyl and η^1-allenylmetal linkages has received special attention due to its inherent importance in catalytic transformations proceeding through propargyl/allenylmetal intermediates [1,2]. In the course of our recent study on spontaneous reversible isomerization of *trans*-Pt($CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ (**1**) to *trans*-Pt($CPh{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ (**2**) [3a], we found that this isomerization can be catalyzed by Pt(0) complexes with considerable ease [3b]. The catalyzed isomerization may proceed through the transfer of the propargyl/allenyl ligand from Pt(II) to Pt(0) with a concomitant shift of the metal-binding site with regard to this ligand. We describe here a superficially analogous catalyzed isomerization between **1** and **2** in the presence of Pd(0) complexes, which however proceeds much more rapidly than the Pt(0)-catalyzed one, and more surprisingly, could involve a thermodynamically unfavorable [4] redox transmetalation between propargyl/allenylplatinum(II) and Pd(0) complexes. Evidence for occurrence of this unique transmetalation giving the propargyl complex of the Pd(I)–Pd(I) unit will be described. A thermoneutral redox process involving Co(III) to Co(I) transfer of a propargyl ligand accompanying linkage isomerization [2a] and Pd(II) to Pd(0) transfer of an allyl ligand accompanying configurational inversion at the allylic sp^3 carbon [5], or a downhill redox process involving Pd(II) to Pt(0) allyl transfer [5a,b] have been described.

2. Results and discussion

In contrast to the modest acceleration of the isomerization of **1** to **2** on addition of 10 mol% of Pt(PPh_3)$_4$ to a C_6D_6 solution of **1** (rate constant for the catalyzed reaction, $k_{cat} = 1.6 \times 10^{-5}$ s^{-1} at 70°C in C_6D_6; $k_{uncat} = 1.6 \times 10^{-6}$ s^{-1}) [3], the catalytic efficiency of the Pd(0) complex, Pd(PPh_3)$_4$ was much larger. For example, conversion of **1** to an equilibrium mixture

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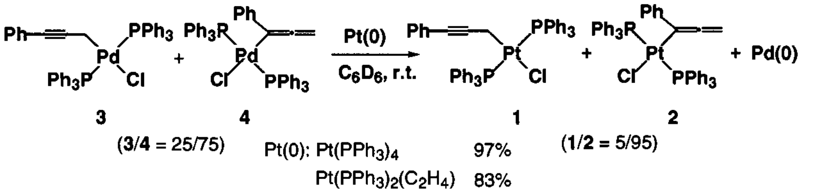
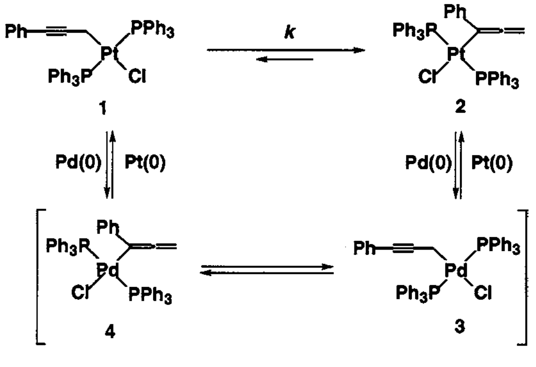
1/**2** = 5/95 was completed within 1 h in C_6D_6 at 70°C in the presence of 10 mol% of $Pd(PPh_3)_4$. This result can be compared with the half-life (120 h) of the uncatalyzed reaction. Moreover, the degree of the acceleration was estimated to amount to ca. 10^4; compare $k_{cat} = 2.8 \times 10^{-4}\ s^{-1}$ in the presence of 5 mol% (5.7×10^{-4} M) of $Pd(PPh_3)_4$ with $k_{uncat} = 6 \times 10^{-8}\ s^{-1}$, both at 40°C in C_6D_6. As shown in Scheme 1, we initially thought that the Pd(0)-catalyzed isomerization of **1** to **2** proceeded via three steps, (1) redox transmetalation between **1** and Pd(0), without regard to the mechanism, to give allenylpalladium(II), *trans*-Pd(CPh=C=CH_2)(Cl)$(PPh_3)_2$ (**4**), (2) interconversion between **4** and propargylpalladium(II), *trans*-Pd($CH_2C{\equiv}CPh$)(Cl)$(PPh_3)_2$ (**3**), and (3) redox transmetalation between **3** and Pt(0) to give allenylplatinum(II).



(1)

Among these three steps, the second and the third ones can be well expected to occur with a sufficiently low activation energy. For example, linkage isomerization in propargyl/allenylpalladium(II) systems is known to be quite rapid [6]. We further confirmed rapid transfer of propargyl/allenyl ligands from Pd(II) to Pt(0); a mixture of **3** and **4** (**3**/**4** = 25/75) was treated with $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$, giving rise to **1**/**2** (5/95) in 97% or 83% yield, respectively, within 5 h at room temperature in C_6D_6 (Eq. (1)). Likewise, treatment of *trans*-Pd(CH=C=CH_2)(Cl)$(PPh_3)_2$ with $Pt(C_2H_4)(PPh_3)_2$ gave 84% yield of *trans*-Pt(CH=C=CH_2)(Cl)$(PPh_3)_2$. These are similar to the allyl group transfer from Pd(II) to Pt(0) [5a,b]. It should also be noted that in contrast to the case of the allyl transfer where cationic η^3-allylpalladium(II) complexes were far more reactive than the neutral analogs [5a,b], cationic η^3-propargylpalladium(II) complex $[Pd(\eta^3\text{-}PhCCCH_2)(PPh_3)_2]BF_4$ [5a,7] failed to undergo clean redox transmetalation with $Pt(C_2H_4)(PPh_3)_2$.



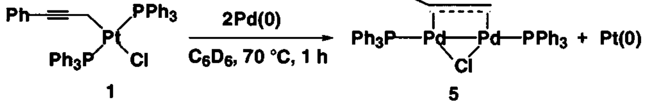
Scheme 1.

In all of the redox transmetalations involving η^1-propargyl or η^1-allenyl ligand described above, the first step would be the π-complexation of the C≡C or C=C bond with Pt(0), followed by the release of Pd(0) which had originally formed the η^1-Pd–C bond. Alternatively, an S_N2' path without the π-complexation could complete the redox transmetalation.

The remaining problem is a feasibility and mechanism of the first step of Scheme 1, i.e. Pt(II)–Pd(0) transmetalation which appears to possess a thermodynamic disadvantage. For example, the cationic η^3-allylplatinum(II) complex, $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]BF_4$ did not react at all with $Pd(PPh_3)_4$ [5b]. Furthermore, theoretical calculations suggested [4] that different ground state electronic configurations of the Pd atom (d^{10}) and Pt atom (d^9s^1) lead to the much larger exothermicity of reductive elimination of $Pd(CH_3)_2$ to Pd(0) and ethane than that of $Pt(CH_3)_2$ to Pt(0) and ethane. Thus, according to these results [4] we can estimate that a hypothetical redox transmetalation between $Pt(CH_3)_2(PH_3)_2$ and $Pd(PH_3)_2$ giving rise to $Pd(CH_3)_2(PH_3)_2$ and $Pt(PH_3)_2$ is an extremely endothermic (-34 kcal mol^{-1}) process. Nevertheless, the following fact encouraged us to carry out a detection or the trapping experiment for propargyl/allenylpalladium(II) species if they formed even in a very small amount in the first step of Scheme 1; that is, in the reaction mixture from **3**/**4** and $Pt(PPh_3)_4$ described above, the propargyl/allenyl ligand still remained associated with Pd in the form of Pd(I) dinuclear complex, $Pd_2(\mu\text{-}PhCCCH_2)(\mu\text{-}Cl)(PPh_3)_2$ (**5**), though in a very small amount, which is known [8] to lie in equilibrium with **3**/**4**. Then, we examined reactions of **1** with some Pd(0) complexes in detail.

When heated in C_6D_6 with two equivalents $Pd(PPh_3)_4$ at 70°C in 2 h, **1** transferred 9% of its organic ligand to palladium to give **5**, with the balance of the ligand remaining in the equilibrium mixture of **1** and **2** (Eq. (2)). The formation of Pt(0) species was confirmed by ^{31}P-NMR measurements in the form of $Pt(PPh_3)_3$. In addition, ^{1}H- and ^{31}P-NMR analysis of the reaction mixture from **1**, $Pd_2(dba)_3$ (one equivalent) and PPh_3 (three equivalents) in C_6D_6 at 70°C revealed the formation of both **5** (33%) and Pt(dba) $(PPh_3)_2$ (50%). The discrepancy between amounts of these two products could have been due to unknown decomposition path(s) of **3**/**4** or **5** under the reaction condition. A total of 43% of the propargyl/allenyl ligand was recovered in **1**/**2**. Unfortunately, in the above two experiments the presence of **3** or **4** was not confirmed. In view of the ready conversion of **3**/**4** to **5** which bears considerably increased thermal stability compared to the former [8], the propargyl/allenylpalladium(II) intermediates **3** and **4**, even if formed from **1** and Pd(0), would have been trapped by another Pd(0) unit rapidly and efficiently to give **5**.

Alternatively, it is possible that the direct ligand transfer from Pt(II) to Pd(0) to give **3** and **4** does not actually take place. In such a case, the formation of **5** in Eq. (2) might have occurred via initial attack of Pd(0) at the Pt atom of **1** affording the Pd–Pt bonded transient intermediate PdPt(μ-PhCCCH$_2$)(μ-Cl)(PPh$_3$)$_2$, followed by replacement of the Pt atom in this complex by another Pd(0). However, we gained no spectral evidence for the existence of such a heterodinuclear complex [9]. In any case, as far as **3** and **4** lie in equilibrium with **5**, though in very small amounts, they could participate as intermediates in Scheme 1. Or it is also possible that the dinuclear complex **5** substitutes for **3** and **4** as intermediate in Scheme 1 since **5** also reacted readily with Pt(PPh$_3$)$_4$ to give the equilibrium mixture of **1** and **2**.



(2)

In summary, we have demonstrated facile transfer of propargyl/allenyl ligands not only between Pd(II) and Pt(0), but Pt(II) and Pd(0) (two equivalents). The redox transmetalation is expected to be more commonly encountered during zerovalent metal-catalyzed transformations of propargyl and allenyl substrates and its facility might have a crucial influence on the regiochemical and stereochemical outcome of the catalytic reactions [10]. Further efforts related to this problem are under way in this laboratory.

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. Melting points were determined on a Yanagimoto 1493 micro-melting-point apparatus. NMR spectra were obtained on a JEOL GSX-270 and JEOL GSX-400. Chemical shifts are given in ppm using TMS or H$_3$PO$_4$ as a standard.

3.2. Preparation of *trans*-Pd(CH$_2$C≡CPh/CPh=C=CH$_2$)(Cl)(PPh$_3$)$_2$ (**3**/**4**)

To a suspension of 2.82 g (2.44 mmol) of Pd(PPh$_3$)$_4$ in 120 ml of THF was added 523.8 mg (3.48 mmol) of PhC≡CCH$_2$Cl at room temperature (r.t.) and the mixture changed to a yellow solution within 10 min. After 40 min, addition of pentane to the solution and filtration yielded yellow solids (1.17 g, 62%). M.p. (dec.) 136–140°C; ^{1}H-NMR (C$_6$D$_6$) δ 1.89 (brs, 2H), 3.78 (brs, 2H); ^{31}P-NMR (C$_6$D$_6$) δ 24.45 (s), 27.79 (brs); Anal. Calc. for C$_{45}$H$_{37}$ClP$_2$Pd: C, 69.15; H, 4.77. Found: C, 69.05; H, 5.01%.

3.3. Preparation of *trans*-Pt(CH=C=CH$_2$)(Cl)(PPh$_3$)$_2$

The procedure was similar to that for **1** reported before [3b]. Yield 13%; m.p. (dec.) 205–210°C; ^{1}H-NMR (C$_6$D$_6$) δ 3.20 (dt, $J_{PH} = 3.5$ Hz, $J_{HH} = 6.5$ Hz, $J_{PtH} = 56.7$ Hz, 2H), 5.31 (tt, $J_{PH} = 4.3$ Hz, $J_{HH} = 6.5$ Hz, $J_{PtH} = 117.5$ Hz, 1H); ^{31}P-NMR (C$_6$D$_6$) δ 23.91 (s, $J_{PtP} = 3035$ Hz); Anal. Calc. for C$_{39}$H$_{33}$ClP$_2$Pt: C, 58.98; H, 4.19. Found: C, 58.75; H, 4.33%.

3.4. Preparation of *trans*-Pd(CH=C=CH$_2$)(Cl)(PPh$_3$)$_2$

The procedure was similar to that for **3**/**4** (at −15°C, in CH$_2$Cl$_2$). Yeld 80%; m.p. (dec.) 147–152°C; ^{1}H-NMR (C$_6$D$_6$) δ 3.48 (dt, $J_{PH} = 2.4$ Hz, $J_{HH} = 6.2$ Hz, 2H), 5.01 (tt, $J_{PH} = 6.2$ Hz, $J_{HH} = 6.2$ Hz, 1H); ^{31}P-NMR (C$_6$D$_6$) δ 24.45 (s); Anal. Calc. for C$_{39}$H$_{33}$ClP$_2$Pd: C, 66.40; H, 4.71. Found: C, 66.11; H, 4.82%.

3.5. Kinetic measurements of isomerizations

A solution of 9.3 mg of **1** (0.0107 mmol) and 0.6 mg of Pd(PPh$_3$)$_4$ (0.000519 mmol) in 0.9 ml of degassed dry C$_6$D$_6$ was heated at 40°C. The isomerization was monitored by ^{1}H-NMR spectroscopy measured at 25°C. Plots of ln $95/(p - 5)$ versus time gave straight lines (p: molar percent of the propargyl isomer), from whose slope $k_1 + k_{-1}$ can be obtained.

3.6. Reaction of *trans*-Pd(CH$_2$C≡CPh/CPh=C=CH$_2$)-(Cl)(PPh$_3$)$_2$ (**3**/**4**) with Pt(C$_2$H$_4$)(PPh$_3$)$_2$

A total of 8.7 mg (0.0111 mmol) of **3**/**4** and 9.3 mg (0.0124 mmol) of Pt(C$_2$H$_4$)(PPh$_3$)$_2$ in an NMR tube were dissolved in 0.9 ml of degassed dry C$_6$D$_6$. The NMR tube was sealed under vacuum, and left at r.t. The reaction was followed by ^{1}H-NMR. Compound **1** was obtained after 1.5 h (83%) accompanied with **5** (17%).

3.7. Reaction of trans-Pd($CH_2C{\equiv}CPh$/$CPh{=}C{=}CH_2$)-(Cl)(PPh_3)$_2$ (**3**/**4**) with Pt(PPh_3)$_4$

A total of 8.8 mg (0.013 mmol) of **3**/**4** and 15.3 mg (0.0123 mmol) of Pt(PPh_3)$_4$ in an NMR tube were dissolved in 0.7 ml of degassed dry C_6D_6. The NMR tube was sealed under vacuum, and left at r.t. The reaction was followed by ^{1}H-NMR. Compound **1** was obtained after 5 h (97%) accompanied with **5** (3%).

3.8. Reaction of trans-Pd ($CH{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ with Pt(C_2H_4)(PPh_3)$_2$

A total of 8.0 mg (0.0113 mmol) of *trans*-Pd($CH{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ and 9.5 mg (0.0127 mmol) of Pt(C_2H_4)(PPh_3)$_2$ in an NMR tube were dissolved under an atmosphere of argon in 0.6 ml of dry C_6D_6. The reaction was followed by ^{1}H-NMR. *trans*-Pd($CH{=}C{=}CH_2$)(Cl)(PPh_3)$_2$ was obtained after 10 min (84%).

3.9. Reaction of trans-Pt($CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ (**1**) with Pd(PPh_3)$_4$

A total of 8.7 mg (0.0100 mmol) of **1** and 24.3 mg (0.0210 mmol) of Pd(PPh_3)$_4$ in an NMR tube were dissolved in 0.8 ml of degassed dry C_6D_6 and an appropriate amount of trioxane was added as internal standard. The NMR tube was sealed under vacuum, and heated at 70°C in an oil bath. The reaction was followed by ^{1}H-NMR. Compound **5** was obtained after 1 h (9%). In a similar reaction in toluene-d_8 Pt(PPh_3)$_3$ (^{31}P-NMR: δ 50.3 in toluene-d_8) was observed at -80°C.

3.10. Reaction of trans-Pt($CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ (**1**) with Pd_2(dba)$_3$ and PPh_3

A total of 8.7 mg (0.0100 mmol) of **1**, 11.0 mg (0.0106 mmol) of Pd_2(dba)$_3$ and 8.2 mg (0.0313 mmol) of PPh_3 in an NMR tube were dissolved in 0.8 ml of degassed dry C_6D_6 and an appropriate amount of trioxane was added as internal standard. The NMR tube was sealed under vacuum, and heated at 70°C in an oil bath. The reaction was followed by ^{1}H- and ^{31}P-NMR. Compound **5** was obtained after 1 h (33%) accompanied with Pt(dba)(PPh_3)$_2$ (50%).

Acknowledgements

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