Redox Transmetalation Reaction Involving η^3-Allyl Group Transfer from Palladium(II) to Platinum(0)

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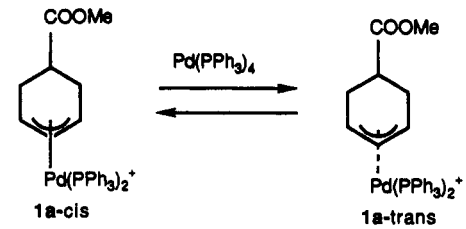
Summary: Reaction of (η^3-allyl)palladium(II) complexes with $Pt(PPh_3)_2L_n$ ($L = C_2H_4$, $n = 1$; $L = PPh_3$, $n = 2$) resulted in redox transmetalation involving η^3-allyl group transfer from Pd(II) to Pt(0), giving rise to (η^3-allyl)-platinum(II) and palladium(0) complexes. This type of reaction proceeded with greater ease when cationic (η^3-allyl)palladium(II) complexes were used than when the neutral (η^3-allyl)palladium(II) counterparts were used. Stereochemical examination of the reaction employing (trans- and cis-5-(methoxycarbonyl)-(1–3)-η^3-cyclohexenyl)palladium(II) analogues indicated the occurrence of the attack of the Pt(0) complex at the η^3-allyl ligand from the side opposite of the palladium atom.

Transmetalation of organic ligands is one of the most fundamental organometallic reactions.[1] Most transmetalation reactions which are encountered in the synthetically important organic transformations take place without the change of formal oxidation states of the metals concerned. There is increasing interest also in another class of transmetalation, namely a redox transmetalation which accompanies the change of oxidation state of both incoming and outgoing metals, typical examples including conversion from RM^{III}/M'^{I} to M^{I}/RM'^{III} (M = M' = Co, Rh)[2] and RPd^{IV}/Pt^{II} to Pd^{II}/RPt^{IV}.[3]

The redox transmetalation involving (η^3-allyl)palladium-(II) complexes has especially unique synthetic bearings. For example, transfer of the allyl ligand from Pd(II) to Sn(II),[4] Zn(0),[5] or Sm(II)[6] to form allylic derivatives of Sn(IV), Zn(II), or Sm(III) has been suggested, without proof, to be a key step in palladium-catalyzed allylation of electrophiles such as carbonyl compounds or organotin cations with allylic alcohols and carboxylates.

In another example, a direct attack of a Pd(0) nucleophile at the Pd(II)-bound allyl group resulting in Pd(0)–Pd(II) transmetalation[7] has been claimed to be responsible for a partial or complete loss of enantiomeric identity with respect to the η^3-allyl plane during Pd-catalyzed allylic substitution reactions.[8] A closely related stereochemical scrambling of (η^3-allyl)palladium(II) complexes induced by addition of Pd(0) species (eq 1) was first reported from



(1)

this group,[9] and a more detailed kinetic analysis of a similar system has been described recently.[10] Although these stereochemical results may most probably be explained in terms of Pd(0)–Pd(II) transmetalation, there remain a few alternative pathways responsible for the observed stereochemical scrambling.[11] We wish to report here our finding that the related external attack of Pt(0) complexes at the η^3-allyl ligand bound to palladium(II) indeed leads to displacement of Pd(0) species with a concomitant formation of (η^3-allyl)platinum(II) complexes.

Results and Discussion

Treatment of cationic (η^3-allyl)palladium(II) complexes (**1b,c**)[12] with $Pt(C_2H_4)(PPh_3)_2$ in $CDCl_3$ at room temperature resulted in the formation of good yields of the corresponding (η^3-allyl)platinum(II) complexes (**2b,c**) within 10 minutes (eq 2; $L = C_2H_4$, $n = 1$). A possible palladium product $Pd(C_2H_4)(PPh_3)_2$ was not detected by ^1H NMR measurements, but formation of free ethylene and metallic palladium was observed. The more definitive evidence for the liberation of a palladium(0) complex in the analogous reaction was obtained by confirming $Pd(PPh_3)_4$ by ^{31}P NMR measurement of the reaction mixture from **1c** and $Pt(PPh_3)_4$ (eq 2; $L = PPh_3$, $n = 2$). The

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(4) (a) Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577–2586 and references therein. (b) Masuyama, Y.; Hayakawa, A.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1102–1103.

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(6) (a) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1987**, *28*, 215–216. (b) *Ibid.* **1986**, *27*, 1195–1196. (c) *Ibid.* **1986**, *27*, 601–602.

(7) (a) A similar nucleophilic attack of Pd(0) at the benzylic carbon was once proposed to explain racemization of chiral benzylpalladium (II) complexes[7b] but denied later in a closely related work where the stereochemical scrambling could be due to a one-electron transfer leading to the formation of a caged radical pair.[7c] (b) Lau, K. S. Y.; Wong, P. K.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5832–5840. (c) Becker, Y.; Stille, J. K. *Ibid.* **1978**, *100*, 838–844.

(8) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*, 1st ed.; University Science Books: Mill Valley, CA, 1980; p 692. (b) Takahashi, T.; Jinbo, Y.; Kitamura, K.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5921–5924. (c) MacKenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046–2054.

(9) Kurosawa, H.; Ogoshi, S.; Chatani, N.; Kawasaki, Y.; Murai, S. *Chem. Lett.* **1990**, 1745–1748.

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(11) The kinetic and/or stereochemical evidence suggested[2,3] that the redox transmetalations for the Co(I)–Co(III), Rh(I)–Rh(III), and Pt(II)–Pd(IV) systems all proceed via the S_N2 pathway. An alternative path for the Pd(0)–Pd(II) allyl transfer would be an initial one-electron transfer[7] from Pd(0) to the (η^3-allyl)palladium(II) cation, which generates a Pd(I) cation and a (η^3-allyl)palladium(I) species, the latter of which would be very prone to undergo stereochemical scrambling possibly via an allylic radical intermediate. Then a back-electron-transfer between the two Pd(I) species would restore the starting complexes with net stereochemical scrambling.

(12) It was found that the nature of the counteranion in complexes **1a–c** has no effect on the course of the reaction with Pt(0) complexes.

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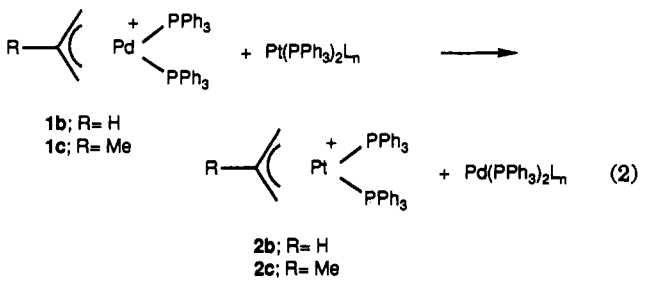


proceeding of the allyl transfer in this case was considerably slower than in the reaction of $Pt(C_2H_4)(PPh_3)_2$, with ca. 50% conversion after 0.5 h.

The neutral complex $Pd(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$ also reacted with $Pt(C_2H_4)(PPh_3)_2$ under similar conditions to give a moderate yield of $Pt(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$. However, this reaction was much slower than the reaction of **1c**, with only ca. 40% yield after 12 h at 25 °C. Notably, the reversed allyl transfer from Pt(II) to Pd(0) did not occur at all when a mixture of **2b** and $Pd(PPh_3)_4$ in $CDCl_3$ was left to stand at room temperature for 2 days.

Attempts were made to assess the stereochemical course of the present redox transmetalation by the use of two stereoisomers **1a**-cis and **1a**-trans.[13] However, each reaction of **1a** having a different isomer composition (cis/trans = 70/30, 47/53, 7/93)[14] at 25 °C always gave the corresponding (η^3-cyclohexenyl)platinum(II) complexes (**2a**) with a constant isomer ratio (**2a**-cis/**2a**-trans = 29/71). This result may well be explained in terms of the initial stereochemical equilibration of the palladium analog **1a**, followed by the cyclohexenyl group transfer with inversion of configuration from Pd(II) to Pt(0) having different reaction rates according to the configuration of **1a** (Scheme I).

The occurrence of the initial stereochemical equilibration of **1a** was confirmed when the reaction of **1a**-trans and $Pt(C_2H_4)(PPh_3)_2$ was monitored by ^1H NMR spectroscopy at −20 °C. Thus, when the reactants were mixed in $CDCl_3$ at ca. −20 °C and the solution was left to stand at this temperature for ca. 10 min, the isomer ratio of **1a** changed from the initial value of cis/trans = 7/93 to 47/53 (equilibrium ratio; see below) even though the reaction proceeded by only ca. 25% conversion. It was found that **1a** is stereochemically stable in the absence of a Pd(0) species, but the isomerization was completed immediately upon addition of $Pd(PPh_3)_4$ (0.1 equiv) at 25 °C or within 20 min upon addition of $Pd(PPh_3)_4$ (0.5 equiv) at −15 °C.[10] Therefore, the observed equilibration of **1a** at the early stage of the redox transmetalation must have been triggered by a small amount of a very active species, $Pd(C_2H_4)(PPh_3)_2$, which could have been formed at the very beginning of the transmetalation.

The above equilibrium isomer ratio for **1a** (47/53) remained unchanged as the redox transmetalation at −20 °C proceeded further. The isomer ratio for the platinum product **2a** also remained constant (29/71) throughout the reaction. Notably, this ratio (obtained from the transmetalation reaction at both +25 and −20 °C) was different from the equilibrium ratio for **2a** (42/58), which was

Scheme I

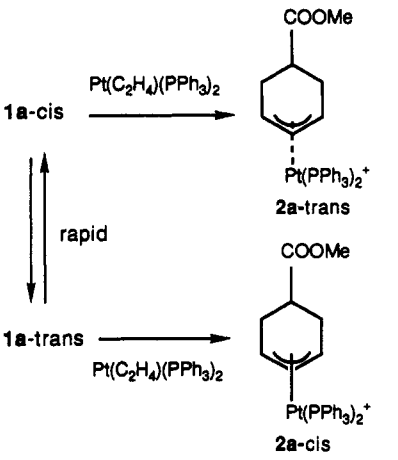
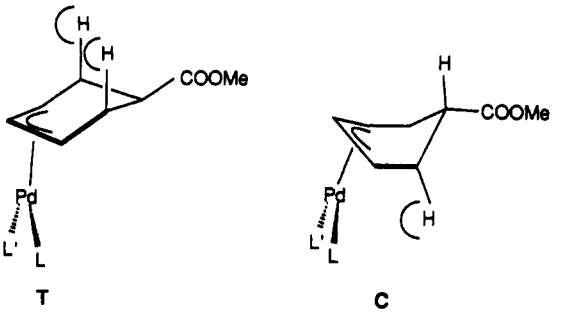


Chart I



determined by allowing the mixture of **2a** and $Pt(C_2H_4)(PPh_3)_2$ to stand for much longer periods (see Experimental Section). In other words the equilibration of **2a** is much slower under the transmetalation conditions, and thus the isomer ratio (29/71) of **2a** attained in the reaction would have contained a kinetic contribution.

We assume that the attack of Pt(0) at the allyl group takes place from the side opposite of Pd(II) with its ease greater for **1a**-cis than for **1a**-trans, resulting in the formation of a larger amount of **2a**-trans than **2a**-cis from approximately equal amounts of **1a**-trans and **1a**-cis. The same stereochemical course assumed for both Pd(II)–Pd(0) and Pt(II)–Pt(0) allyl group transfer can nicely explain the above mentioned isomerization of **1a** and **2a** catalyzed by Pd(0) and Pt(0) species, respectively. Inversion of configuration at the cobalt-bound alkyl group was also observed in the alkyl group transfer from Co(III) to Co(I).[2a]

The origin of the difference in the rate of the nucleophilic attack of Pt(0) at **1a**-trans and **1a**-cis would be steric judging from the molecular structure determinations[13,15] of the trans and the cis isomers of $[Pd\{\eta^3\text{-}\overline{CHCHCHCH_2\text{-}CH(COOMe)CH_2}\}Cl]_2$ and *trans*-$Pd\{\eta^3\text{-}\overline{CHCHCHCH_2\text{-}CH(COOMe)CH_2}\}Cl(PPh_3)$. That is, in the trans isomer having a pseudochair conformation the two axial hydrogens at C-4 and C-6 are located in positions so as to hinder the external approach of the nucleophile at the allylic end carbon (see Chart I; L = L′ = PPh_3). The cis isomer having a pseudoboat conformation may also involve a hindrance to the nucleophile by the hydrogen at C-5 but perhaps to a lesser degree than in the case of the trans isomer.

(13) Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.; Murai, S.; Ikeda, I. *J. Am. Chem. Soc.* **1992**, *114*, 8417–8424.

(14) Attempts to isolate an isomerically pure sample of **1a**-cis starting from pure *cis*-$[Pd\{\eta^3\text{-}\overline{CHCHCHCH_2CH(COOMe)CH_2}\}Cl]_2$ always led to isolation of the cationic complex contaminated by **1a**-trans in varying amounts.

(15) Grennberg, H.; Langer, V.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1190–1192.

The conformational difference between the *cis*- and *trans*-η^3-cyclohexenyl complexes shown in Chart I can also explain the difference in reactivity with respect to the reductive elimination of the similar η^3-cyclohexenyl complexes of palladium. We have found that the cis isomer *cis*-[Pd{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}Cl]$_2$ is much more reluctant to undergo the reaction with phenyl(tributyl)tin/maleic anhydride[16] to give the coupling product (*cis*-1-phenyl-5-(methoxycarbonyl)-2-cyclohexene) than its trans counterpart which gives rise to the other isomer (*trans*-1-phenyl-5-(methoxycarbonyl)-2-cyclohexene). It has been proved[17] that the phenyl anion initially attacks at the palladium atom in η^3-allyl complexes, followed by the reductive elimination of allylbenzenes. It is possible that in the present case the axial hydrogen atoms at C-4 and C-6 in conformation **C** exert considerably severe steric hindrance with regard to the ligand-exchange process (from L = Cl to L = Ph; Chart I). No such steric effect would be expected in the ligand exchange involving **T**.

It is also possible that the approach of the phenyl ligand to the allylic terminal carbon (C-1) in reductive elimination of **C** (L = Ph, L′ = maleic anhydride)[16] is retarded by the hydrogen atom at C-6. We have demonstrated before[16b,18] that the reductive elimination of (η^3-allyl)(aryl)palladium(II) complexes proceeds via the concerted C–C bond formation with the allyl ligand remaining coordinated in η^3 fashion. Finally, it should be pointed out that the analogous isomer-dependent rate difference in a related internal transfer of the OAc ligand to the 5-(carbomethoxy)cyclohexenyl ligand bound to palladium (the trans isomer being more reactive than the cis isomer) has been explained[15] in terms of the strain difference existent in the η^1-allylic intermediates rather than the η^3-allylic intermediates proposed above.

Experimental Section

All the reactions employing zerovalent platinum and palladium complexes were carried out under argon with standard vacuum line techniques. ^{1}H and ^{31}P NMR spectra were obtained on a JEOL GSX-400 spectrometer. The cationic η^3-allylic complexes, [M(η^3-allyl)(PPh$_3$)$_2$]BF$_4$ (M = Pd, allyl = CH$_2$CHCH$_2$ (**1b**), CH$_2$CMeCH$_2$ (**1c**); M = Pt, allyl = CH$_2$CHCH$_2$ (**2b**), CH$_2$CMeCH$_2$ (**2c**)) were prepared by the reported methods.[19] Preparation of [Pd{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}(PPh$_3$)$_2$]PF$_6$ (**1a**) was also described previously.[13] The platinum analog, *cis*-[Pt{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}(PPh$_3$)$_2$]PF$_6$ (**2a**-cis) was similarly prepared from *cis*-Pt{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}Cl,[13] PPh$_3$, and NH$_4$PF$_6$, mp 170 °C dec. Anal. Calcd for C$_{44}$H$_{41}$O$_2$F$_6$P$_3$Pt: C, 52.65; H, 4.12. Found: C, 53.04; H, 4.65. ^{1}H NMR (CDCl$_3$): δ 1.05–1.12 (m, 2H), 1.90 (tt, J = 5.5, 11.2 Hz, 1H), 1.9–1.97 (br, 2H), 3.59 (s, 3H), 4.77 (t, J = 6.0 Hz, 2H), 6.12 (t, J = 6.0, J_{Pt} = 64 Hz, 1H). The trans analog **2a**-trans contaminated by 20% of **2a**-cis was prepared from a trans/cis mixture (80/20) of Pt{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}Cl.[13] ^{1}H NMR (CDCl$_3$): δ 1.20 (br d, J = 16 Hz, 2H), 1.97–2.03 (br, 2H), 2.71 (tt, J = 6.2, 9.4 Hz, 1H), 3.60 (s, 3H), 4.63 (br, 2H), 5.89 (t, J = 6, J_{Pt} = 63 Hz, 1H).

Reaction of 1 with Platinum(0) Complexes. To a CDCl$_3$ solution (0.4 mL) of **1** (0.03 mmol) in an NMR tube capped with a septum rubber was added a CDCl$_3$ solution (0.1 mL) of Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (0.03 mmol) with a hypodermic syringe. The color of the solution changed from pale-yellow to brownish orange. ^{1}H NMR spectra were taken within 10 min to show near completion of the redox transmetalation. Gradual deposition of palladium metal took place. The reactions between **1c** and Pt(PPh$_3$)$_4$ and that between [Pd(η^3-CH$_2$CMeCH$_2$)Cl(PPh$_3$) and Pt(C$_2$H$_4$)(PPh$_3$)$_2$ were carried out similarly.

Isomerization of 2a. To a CDCl$_3$ solution (0.4 mL) of **2a** (cis/trans = 80/20) (0.01 mmol) in an NMR tube was added a CDCl$_3$ solution (0.05 mL) of Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (0.004 mmol) with a syringe. The progress of the isomerization was monitored by ^{1}H NMR spectra; the isomer ratio became 67/33 after 3 h and ca. 50/50 after 2 days at 25 °C. As the isomerization appeared to have slowed down at this stage, another portion of Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (0.004 mmol) was added, and the solution was kept at 25 °C for 1 week. The isomer ratio (42/58) at this stage no longer changed upon addition of further amounts of Pt(C$_2$H$_4$)(PPh$_3$)$_2$.

Reaction of Pd{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}Cl with Phenyl(tributyl)tin. To a CDCl$_3$ solution (0.5 mL) of *trans*- and *cis*-Pd{η^3-CHCHCHCH$_2$CH(COOMe)CH$_2$}Cl (6.0 mg, 0.0213 mmol each) and maleic anhydride (12.5 mg, 0.128 mmol) was added phenyl(tributyl)tin (7.9 mg, 0.0213 mmol) with a syringe. After 24 h, 57% of **1a**-trans and 27% of **1a**-cis were consumed and the corresponding phenylated products (*trans*- and *cis*-1-phenyl-5-(methoxycarbonyl)-2-cyclohexane) were formed, as confirmed by ^{1}H NMR spectra.[13]

Acknowledgment. We thank Professor Shinji Murai of our department for his interests and stimulating discussions. Thanks are due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of NMR facilities. Partial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan is also acknowledged.

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