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Allyl Group Transfer between M(II) and M(0) Centers (M= Pd, Pt) Proceeding through *Anti* Nucleophilic Attack at η^3-Allyl Ligand

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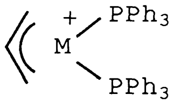
Reactions of $[Pd(\eta^3\text{-allyl})(PPh_3)_2]^+$ (allyl= CH_2CHCH_2, CH_2CMeCH_2, $\overline{CHCHCHCH_2CH(COOMe)CH_2}$ (**1c**)) with $Pt(C_2H_4)(PPh_3)_2$ in $CDCl_3$ readily afforded the corresponding η^3-allylplatinum(II) cations in high yields. *Cis-trans* isomerization of **1c** or its platinum analogue was catalyzed by Pd(0) or Pt(0) complexes via *anti* attack of M(0) species at the allyl ligand.

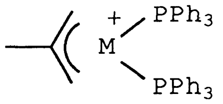
Transmetallation of organic ligands which accompanies the change of formal oxidation state of both incoming and outgoing metals, e.g. conversion from RM(III)/M'(I) to RM'(III)/M(I) (M= M'= Co, Rh)[1a,b] and from RPd(IV)/Pt(II) to RPt(IV)/Pd(II),[1c] has received increasing attention in recent years. We describe here new transfer of η^3-allyl ligands between M(II) and M(0) centers (M= Pd, Pt) proceeding through *anti* nucleophilic attack at η^3-allyl ligands, which appears of special relevance to a possible origin of stereochemical scrambling in some η^3-allylpalladium mediated catalytic transformations.[2-5]

Cationic η^3-allylpalladium(II) complexes (**1a-c**)[6,7] reacted with $Pt(C_2H_4)(PPh_3)_2$ (**2**) (1.5 equiv.) in $CDCl_3$ at 25 °C within 10 min to afford high yields (>80%) of the corresponding η^3-allylplatinum(II) cations (**3a-c**) (Eq. 1) (confirmed by comparison of ^1H NMR resonances with those of authentic samples[8]). We could not characterize a plausible palladium

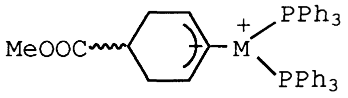
$$\underset{\mathbf{1}}{[Pd(\eta^3\text{-allyl})(PPh_3)_2]BF_4} + \underset{\mathbf{2}}{Pt(C_2H_4)(PPh_3)_2} \longrightarrow \underset{\mathbf{3}}{[Pt(\eta^3\text{-allyl})(PPh_3)_2]BF_4} + Pd(C_2H_4)(PPh_3)_2 \quad (1)$$



1a M= Pd
3a M= Pt



1b M= Pd
3b M= Pt

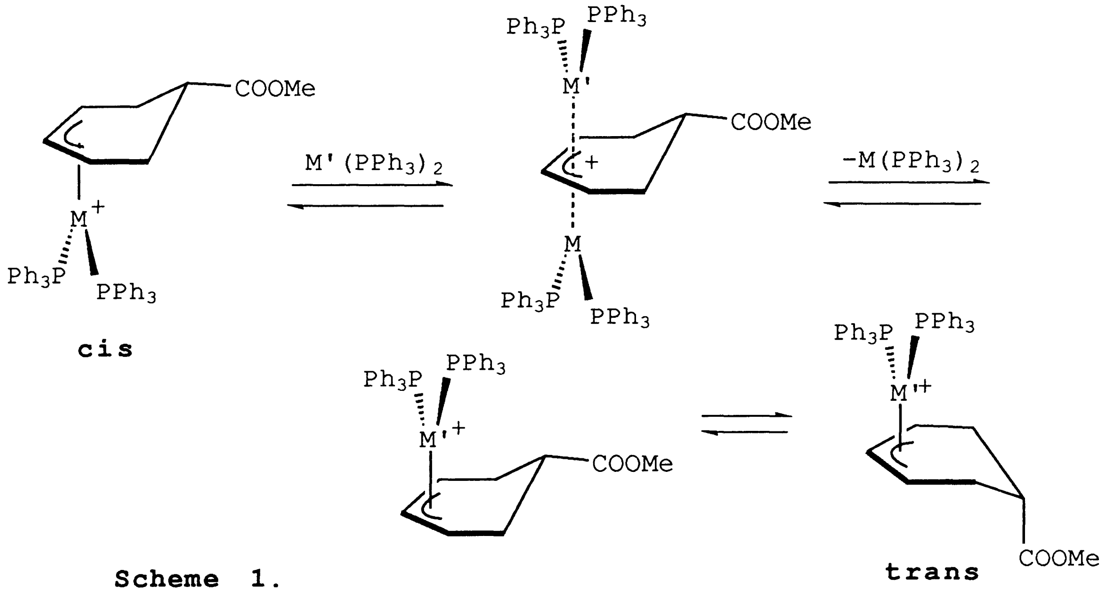


1c M= Pd
3c M= Pt

product $Pd(C_2H_4)(PPh_3)_2$ except for some metallic palladium and free ethylene, which might have been generated from this thermally labile complex under the reaction conditions. The analogous reaction of **1b** with $Pt(PPh_3)_4$ also gave **3b** and $Pd(PPh_3)_4$, though with a considerably slower rate. The reverse reaction, i.e. that of **3b** with $Pd(PPh_3)_4$, did not take place at all. The neutral complex $Pd(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$ similarly reacted with **2** to afford a moderate yield of $Pt(\eta^3\text{-}CH_2CMeCH_2)Cl(PPh_3)$, but again the rate of this reaction was much slower (ca. 40% yield after 12 h at 25 °C).

We were unable to directly determine the stereochemical course of the allyl transfer from **1c** to **3c**, since each reaction of **1c** having a different isomer ratio (*cis/trans*= 70/30, 47/53, 7/93) always gave the higher amount of **3c**-*trans* than **3c**-*cis* (*cis/trans*= 29/71, 30/70, 27/73). On the other hand, we can suggest a ready occurrence of *anti* nucleophilic attack of M(0) species at the η^3-allyl ligand in an analogous allyl transfer between Pd(II) and Pd(0) or Pt(II) and Pt(0) centers (Scheme 1; M= M'= Pd or Pt)[9] on the basis of the observation of M(0)-catalyzed *cis-trans* isomerization of **1c** or **3c**, as detailed below.

We found that treatment of **1c** (*cis/trans*= 70/30, 7/93) with 0.1 equiv. of $Pd(PPh_3)_4$ in $CDCl_3$ at 25 °C resulted in immediate equilibration of the two isomers (*cis/trans*= 46/54), whereas the configurational stability of **1c** was much higher in the absence of Pd(0) species (ca. 25% isomerization from **1c**-*trans* to **1c**-*cis* for 3 days at 25 °C). Addition of **2** to otherwise config-



Scheme 1.

urationally stable **3c**-*cis* also caused gradual isomerization giving rise to an equilibrium mixture of **3c** (*cis*/*trans*= 42/58). Importantly, the latter process was not sufficiently fast to affect the isomer ratio of **3c** obtained in Eq. 1. Neither did the Pd(0) species cause the rapid isomerization of **3c**. From these results, we suggest an origin of the isomer ratio for **3c** obtained in Eq. 1 to be occurrence of the rapid pre-equilibration of **1c**-*cis* and **1c**-*trans* mediated by Pd(0) species which is generated even at the very early stage of the reaction,10) followed by the *anti* attack of Pt(0) at the allyl group of **1c**-*cis* in preference to that of **1c**-*trans* owing to the less steric hindrance in the former,9) affording the higher amount of **3c**-*trans*.

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2) *Anti* attack of Pd(0) nucleophiles at η^3-allylpalladium(II) intermediates has been postulated, without any direct proof, in accounting for the loss of stereospecificity in Pd-catalyzed allylic alkylation[3] and azidation.[4] A similar nucleophilic attack of Pd(0) at the benzylic carbon was assumed originally to explain racemization of chiral benzylpalladium(II) complexes,[5a] but denied later in a closely related racemization process.[5b]

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6) B. Akermark, B. Krakenberger, S. Hansson, and A. Vitagliano, *Organometallics*, **6**, 620 (1987).

7) **1a** and **1c** were prepared in a manner similar to that[6] for **1b** starting from $[\text{PdCl}(\eta^3\text{-CH}_2\text{CHCH}_2)]_2$ and *trans* and *cis* isomers of $\{\text{PdCl}[\eta^3\text{-}\overline{\text{CHCHCHCH}_2\text{CH(COOMe)CH}_2}]\}_2$.[8a]

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9) ^{1}H NMR splitting patterns for the proton α to COOMe[8a] suggest that this proton is located in a pseudo-axial position in **1c**-*cis* and **3c**-*cis*, and in a pseudo-equatorial one in **1c**-*trans* and **3c**-*trans*.

10) In agreement with this proposal, the isomer ratio was found to remain constant for both **1c** (*cis/trans*= 47/53) and **3c** (*cis/trans*= 21/79) at any stage of the slower reaction of **1c**-trans with **2** carried out at -20 °C.

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