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New transformations of unsaturated hydrocarbon ligands coordinated with mono- and dinuclear palladium units

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Abstract: Some insights into mechanistic features of M-C bond formation (oxidative addition) and bond cleavage (reductive elimination) about allyl-palladium complexes are presented based on new transformations of allylic as well as propargylic ligands bound to Pd and Pt. 1) The oxidative addition is proposed to proceed through initial π-complex formation between allylic electrophiles and M(0) atom, which is followed by intramolecular η^3-allyl-M bond formation with either inversion or retention of configuration at an allylic sp^3-carbon depending on the nature of ligands and solvents. 2) The reductive elimination of allyl(organo)palladium complexes is suggested to proceed via cis C–C coupling between η^3-allyl and η^1-bound organic ligands. 3) A Pd(0) nucleophile is shown to exhibit dual selectivity with regard to the site of its attack on allylpalladium complexes depending on the nature of their ligands, leading to either redox transmetallation with net inversion of configuration at the allylic sp^3-carbon, or μ-allyl Pd-Pd complex formation with retention of stereochemistry. Some novel bonding and reactivity trends in those Pd-Pd bonded complexes which contain μ-allyl, μ-propargyl and μ-diene ligands are also presented.

INTRODUCTION

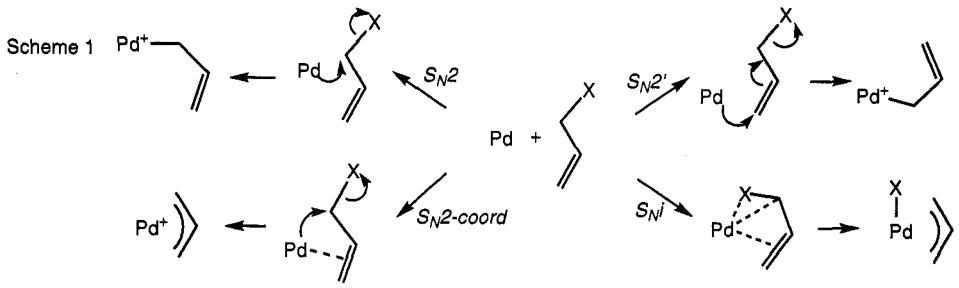
Mechanistic aspects of transformations involving allyl-palladium complexes are of great significance from a synthetic chemical point of view. Among the central issues relevant to many useful catalytic cycles is the way of generating allyl-palladium bonds (oxidative addition) and their cleavage (nucleophilic substitution or reductive elimination). Some useful informations on these matters have been provided by overall reaction profiles, especially stereochemical outcome of both catalytic and stoichiometric transformations (ref. 1). However, there still remain a number of mechanistic pictures to be precisely drawn. Our efforts have been made to gain deep insights into some steps involved in catalytic cycles in which allyl-palladium species are generated or consumed. We summarize here some representative results obtained in studies conducted along this line. In the course of these studies occasional consultations with the results which were obtained by the use of propargyl complexes of both Pd and Pt greatly helped us to gain the more detailed insight into the mechanistic allyl-palladium chemistry. Moreover, extension of these studies led to exploration of new chemistry of dinuclear Pd(I) organometallic complexes, which is another subject of this review.

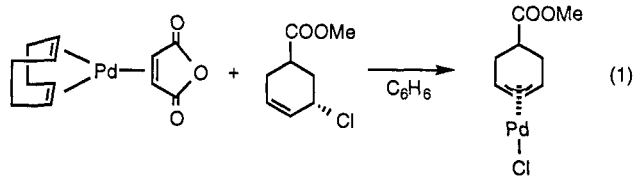
OXIDATIVE ADDITION

The possible reaction course of oxidative addition of allylic electrophiles with Pd(0) complexes may be outlined as shown in Scheme 1. The dominant stereochemical outcome, i.e. inversion at an allylic sp^3-carbon (ref. 1, 2), is consistent with either of S_N2, S_N2-*coord* and S_N2' paths. On the other hand, the unusual stereochemistry observed in reactions of an allylic chloride with Pd(0) complexes containing electron-withdrawing olefinic ligands carried out in non-polar solvents such as benzene (eq. 1) is suggested

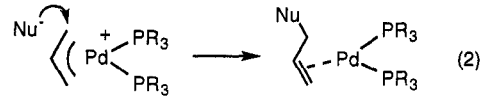
to proceed via initial coordination of the C=C bond of the substrate to Pd, followed by frontside attack of the Pd nucleophile at the C-Cl bond (S_Ni path) (ref. 3). This mode of C-Cl bond cleavage is thought to be greatly assisted by Pd-Cl interaction. The pre-coordination of the C=C bond has been supported by the effect of the methyl substituents attached to the C=C bond to retard the oxidative addition rate.

Scheme 1

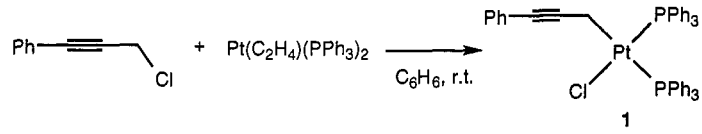


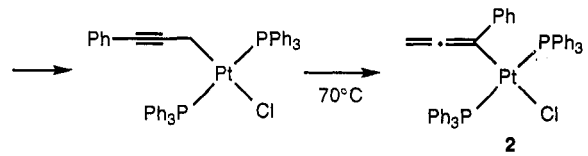


The nucleophilic attack at η^3-allylpalladium proceeding via inversion of configuration at the allyl carbon generates C=C bonded Pd(0) complex as the initial product (eq. 2) (ref. 4). In view of this widespread reaction course and a microscopic reversibility principle, most of the oxidative additions of allylic electrophiles may be deduced to involve, as the initial step, the C=C bond coordination to Pd. This is followed by intramolecular S_N2 displacement of the leaving group, affording η^3-allyl products, as is represented by *S_N2-coord* path of Scheme 1. Evidence for this sequence has not been provided experimentally, but examination of the reaction course between propargylic halides and a Pt(0) complex (ref. 5) lends strong support to such concept.



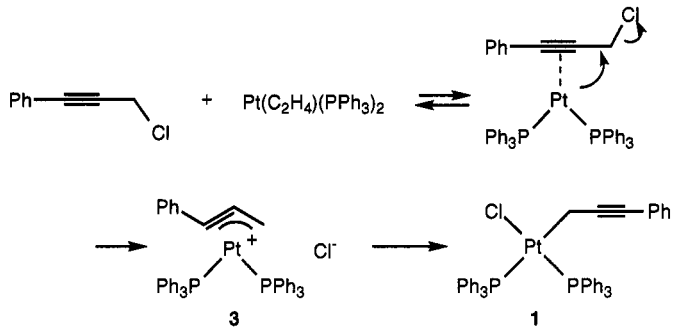
Scheme 2



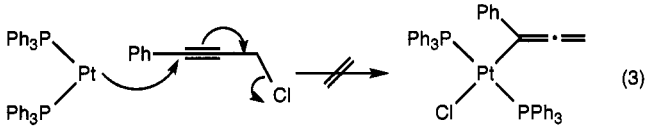


Reaction of phenylpropargyl chloride with $Pt(C_2H_4)(PPh_3)_2$ gives rise to **1** (Scheme 2) (ref. 6). **1** is a kinetic isomer; it isomerized to the trans isomer, trans-$Pt(CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ when left to stand in solution with PPh_3 at room temperature, and further to the allenyl complex **2** when heated. If Pt(0) attacked directly at the propargylic carbon in the oxidative addition (S_N2), the cis phosphine arrangement would not have been attained in view of the fact that the reaction of $Pt(C_2H_4)(PPh_3)_2$ with CH_3I gave the trans isomer, trans-$Pt(CH_3)(I)(PPh_3)_2$. We suggest a reaction sequence (Scheme 3) where a C≡C bonded intermediate undergoes intramolecular nucleophilic substitution to give cationic η^3-propargyl product **3**

Scheme 3



initially. This ion-pair may collapse to **1**; we separately confirmed formation of **1** by the reaction of [Pt(η^3-CH_2CCPh)$(PPh_3)_2$]BF_4 with [$^nBu_4N$]Cl. The failure to produce the more stable allenyl complex **2** at the initial stage of the oxidative addition rules out an S_N2' path (eq. 3). The oxidative addition sequence in Scheme 3 may be applicable to the reaction of analogous allylic electrophiles.

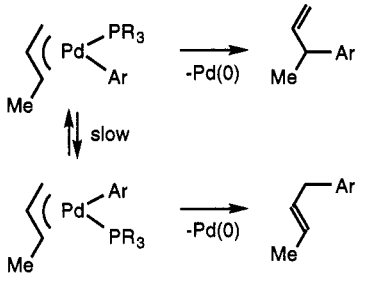


(3)

REDUCTIVE ELIMINATION

Synthetically important allyl-Pd bond cleavage reactions include nucleophilic attack at the allylic carbon with concomitant Pd(0) formation (eq. 2), and reductive eliminatioin of allyl(organo)palladium complexes. Stereochemical examination (ref. 7) and theoretical insight (ref. 4) of the former transformation have been published. With regard to the latter reaction, some η^3-allyl(aryl)palladium complexes were prepared and subjected to mechanistic examination of their thermolysis behaviors shown in Scheme 4 (ref. 8). Particularly informative was the observation that each of two geometrical isomers of Pd(η^3-$CH_2CHCHMe$)(Ar)[$P(OC_6H_4Cl\text{-}2)_3$] (Ar= $C_6H_3Cl_2$-2,5) underwent C-C coupling to give the corresponding allylbenzene derivative specifically. Furthermore, addition of excess free $P(OC_6H_4Cl\text{-}2)_3$

Scheme 4

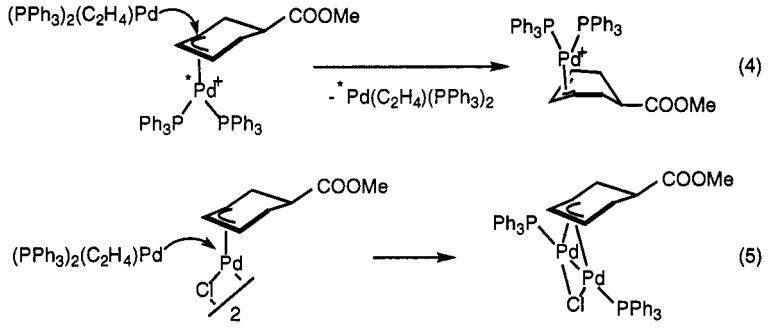


Ar= $C_6H_3Cl_2$-2, 5, R= OC_6H_4Cl-2

showed little influence on the rate of the C-C coupling in each isomer, suggesting insignificant contribution, if at all, of η^1-allyl species Pd(η^1-$CH_2CH{=}CHMe$)(Ar)[$P(OC_6H_4Cl\text{-}2)_3]_2$ to the reductive elimination. These results provided the first evidence for occurrence of the coupling between two mutually cis carbon ligands one of which is the η^3-allyl terminal carbon. The other facts of great significance with regard to the reductive elimination include the remarkably accelerating effect of the more withdrawing ligand L in Pd(η^3-allyl)(Ar)(L) on the C-C coupling (the reactivity order: L= maleic anhydride >> $P(OPh)_3$ > PPh_3 > $AsPh_3$) (ref. 9).

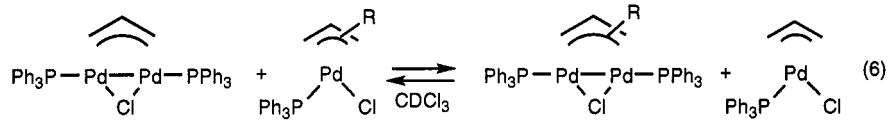
NUCLEOPHILIC ATTACK OF Pd(0) COMPLEX

The site of the nucleophilic attack at η^3-allylpalladium complexes (allyl carbon or Pd) is generally determined by the nature of the nucleophile (ref. 1, 7). We found that the attacking site can also be determined by the coordination environment about Pd when Pd(0) species is used as a nucleophile (ref. 10, 11). Thus, $Pd(C_2H_4)(PPh_3)_2$ reacted with $[Pd(\eta^3\text{-allyl})(PPh_3)_2]^+$ to result in transfer of the allyl group from one Pd to another (redox transmetallation) with inversion of configuration at the allylic carbon (eq. 4), while $Pd(C_2H_4)(PPh_3)_2$ and $[Pd(\eta^3\text{-allyl})(Cl)]_2$ gave a Pd-Pd bonded μ-allyl complex with retention of configuration (eq. 5). The former step has practical significance because the stereochemical identity of a η^3-allylpalladium intermediate in Pd(0)-catalyzed stereoselective transformations can be lost if too much amount of Pd(0) complex is used as a catalyst precursor (ref. 12).

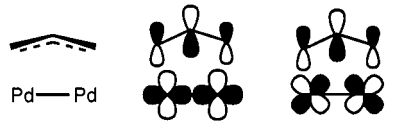


Pd-Pd COMPLEXES

Ready formation of μ-allyl Pd-Pd complexes (ref. 13) shown in eq. 5 prompted us to synthesize a series of dipalladium complexes containing μ-allyl ligands with different electronic properties (ref. 11). The equilibrium trend of eq. 6 revealed higher stability of the Pd-Pd complex of the μ-allyl ligand containing the more electron-withdrawing substituent. Moreover, structural determinations of several Pd-Pd μ-allyl complexes exhibited a unique structural trend not found in mononuclear η^3-allyl complexes of Pd(II); that is, in the dipalladium complexes the dihedral angle between the metal coordination plane and the allyl plane is smaller than 90° (the allyl center carbon leans toward the Pd-Pd region), while this value generally amounts to ca. 110° in the mononuclear complexes. The above stability and structural features have been nicely explained by invoking the greater degree of back-bonding interaction from the $d\sigma$-$d\sigma$ and $d\pi$-$d\pi$ orbitals of the $[Pd_2(\mu\text{-}X)(PR_3)_2]^+$ fragment to the allyl π^* orbital (Scheme 5), compared to that in the mononuclear η^3-allyl complexes, which is supported by *ab initio* MO calculations (ref. 11, 14).



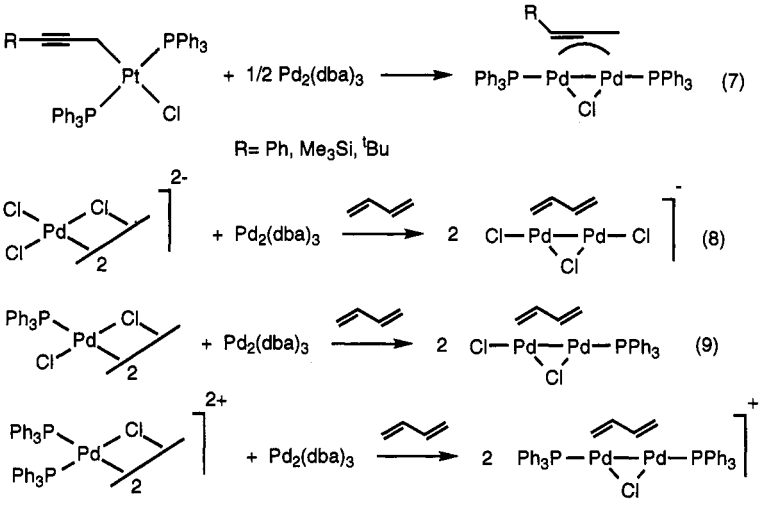
Scheme 5



The unique bonding scheme involved in the dipalladium μ-allyl complexes stimulated our interest to explore other organometallic complexes of the Pd(I)-Pd(I) fragment. Combination of Pd(0) and organometallic Pd(II) complexes enabled us to obtain new Pd-Pd complexes containing μ-propargyl (ref. 15) and μ-diene (ref. 16) ligands, as shown in eq. 7-10. Of particular note in eq. 8-10 is a unique role played by 1, 3-diene in generating the Pd-Pd bond; no interaction took place between $Pd_2(dba)_3$ and Pd(II)-halide complexes unless the diene has been added.

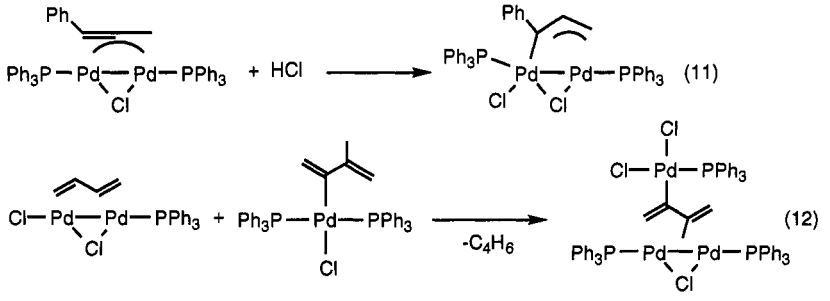
X-Ray structural studies of μ-propargyl and μ-diene Pd-Pd complexes revealed existence of the Pd-Pd bond with the normal length for a Pd(I)-Pd(I) interaction. The μ-propargyl ligand is almost linear, and is

parallel with the Pd-Pd vector, which is different from the more distorted μ-propargyl framework in dinuclear complexes of middle transition elements (e.g. Ru, Fe; ref. 17). The μ-diene ligands are



disordered in all the structures determined for anionic, neutral and cationic complexes. However, they must take an s-trans geometry judging from the C(terminal)-C(terminal) separations.

The μ-propargyl complex reacted with HCl, an electrophile, to give μ-vinylcarbene complex (eq. 11), in contrast to the generally high reactivity of mononuclear η^3-propargylpalladium and platinum complexes to nucleophiles (ref. 5, 18). The μ-diene complex underwent facile exchange of the coordinated diene with free diene, which can be applied to the synthesis of a novel tripalladium complex (eq. 12) (ref. 19).



CONCLUSION

There has been gained better understanding of precise mechanistic features about some key steps involved in Pd-catalyzed transformations of allylic substrates. This is attributed, in part, to new results obtained in the related stoichiometric transformations using propargylic substrates, insted of allylic substrates. Dual stereochemical course in the reaction of allylpalladiums with Pd(0) complex led to exploration of new chemistry of organopalladium complexes of the Pd(I)-Pd(I) fragment which exhibited structural and reactivity aspects considerably different from those in the mononuclear Pd(II) analogs. Further developments in this new field are expected.

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