

# From mononuclear to multinuclear complexes of palladium containing unsaturated hydrocarbon ligands

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## Abstract

This review summarizes the author's contributions to the field of chemistry of group 10 metal complexes containing unsaturated hydrocarbon ligands, with a brief introduction showing how his research subject has shifted from mononuclear type to multinuclear type complexes. New structure and reactivity trends in the multipalladium complexes with bridging allyl and allenyl/propargyl ligands, as well as bridging conjugated polyene molecules are discussed in terms of some unique bonding features of these complexes. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Palladium complex; Multinuclear complex; Unsaturated hydrocarbon ligands

## 1. Introduction

Transition metal  $\pi$  complexes with unsaturated hydrocarbon ligands still continue to play a central role in studies of both fundamental and applied organometallic chemistry at ca. 50 years after the publication of some revolutionary bonding concepts on these complexes. In particular, the report of Dewar in 1951 [1] proposing the synergic binding forces for the metal–olefin bond, and those of Wilkinson and coworkers [2] and Fischer and Pfab [3] in 1952 establishing the  $\pi$  sandwich structure for bis(cyclopentadienyl)iron were extremely influential on the progress of  $\pi$  complex chemistry in the later years. The chemistry of transition metal  $\pi$  complexes grew very rapidly during 1950s and 1960s, with the latter coinciding with the period when Journal of Organometallic Chemistry was launched and expanded.

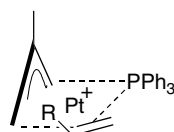
It was my postdoctoral experience at University of Western Ontario, Canada under Professor H. C. Clark

(1970–1972) that called my attention to the field of transition metal  $\pi$  complexes; before this I worked in the field of typical element organometallic chemistry in the PhD study. My first contribution to organotransition metal chemistry was concerned with the observation of greatly accelerated ethylene insertion reaction into the Pt–H bond through the four-coordinate, cationic intermediate, *trans*-[PtH(CH<sub>2</sub>=CH<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> [4]; by way of contrast the neutral hydride, *trans*-PtHCl(PR<sub>3</sub>)<sub>2</sub> had been recognized rather unreactive with regard to ethylene insertion (e.g., 95 °C, 80 atm ethylene for R = Et [5]), while the insertion via the four-coordinate cationic intermediate occurred at room temperature and 1 atm. Even now extremely facile insertion via this type of cationic  $\pi$  olefin complex intermediate forms a key basis on which highly efficient catalytic systems for olefin transformations such as ethylene polymerization, ethylene/CO copolymerization and Heck reaction are constructed [6].

After coming back to Osaka in 1973, I started the new project dealing with  $\pi$  olefin and  $\pi$ -allyl complexes. In some occasions, we dealt with the olefin and allyl ligands separately to gain significant new findings in the

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1 R= H, Ph

Scheme 1.

respective field, while in others we happened to combine two types of ligands in a single complex to enjoy very fruitful results. The latter examples include: (a) the first observation of the simple monoolefin ligand lying parallel to the coordination plane of the square-planar  $d^8$  system in  $[\text{Pt}(\eta^3\text{-allyl})(\text{olefin})(\text{PPh}_3)]^+$  (**1**) (Scheme 1) [7] and (b) the remarkable accelerating effect of the  $\pi$  olefin ligand on the C–C coupling between allyl and aryl groups in  $\text{Pd}(\eta^3\text{-allyl})(\text{Ar})(\text{olefin})$  (Scheme 2) [8].

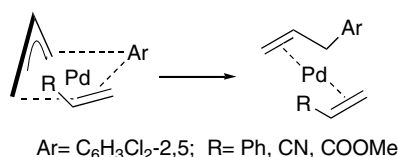
Some comments on the uniqueness of Schemes 1 and 2 seem to be appropriate. The in-plane orientation of the coordinated olefin has been thought indispensable for the migratory olefin insertion through four-coordinate intermediate such as  $[\text{M}(\text{olefin})(\text{R})\text{L}_2]^+$  [6,9], but no well-characterizable example demonstrating occurrence of such geometry had been reported prior to our finding [10]. It is evident that considerably wide space has to be provided for the in-plane coordination of olefin to be realized. In ordinary square-planar systems,  $\text{M}(\text{olefin})\text{L}_3$  (e.g.,  $\text{L}_3$  may be a combination of  $\text{NR}_3$ ,  $\text{PR}_3$  and/or halogen), such wide space could be given only by the deformation of ca.  $90^\circ$  L–M–L angle to a narrower one which costs considerable energy loss. Apparently the much smaller steric requirement of the  $\pi$ -allyl ligand (C–M–C bite angle being ca.  $70^\circ$ ) may have con-

tributed to the accommodation of the in-plane oriented olefin ligand in **1** without much destabilization. The rapid C–C coupling in Scheme 2 was not the first example of the olefin enhanced reductive elimination; addition of electron-withdrawing olefins accelerated the reductive elimination of dialkylnickels via five-coordinated intermediate,  $\text{NiR}_2(\text{bipy})(\text{olefin})$  [11]. Very remarkable in the  $\pi$ -allyl system was the new proposal that the allyl ligand remains  $\pi$ -coordinated during the C–C coupling.

Continuation of the  $\pi$ -allylpalladium chemistry made us encounter quite exciting new chemistry of multinuclear palladium complexes with unsaturated hydrocarbon ligands having novel structure and bonding aspects, the details of which will be described later. There has been wide interest in multinuclear organo-transition metal complexes as a surface activation model in heterogeneous catalysis or as an efficient catalyst or catalyst precursor in homogeneous systems. However, much less knowledge has been accumulated on the multinuclear organopalladium complexes, especially those with hydrocarbon ligands, than that on the middle transition metal cluster complexes. We thought that a much smaller number of known examples in the former case partly stems from the paucity of good starting materials to construct organopalladium clusters. Therefore in our new project, we initially made a special effort to obtain new starting materials. In the next two sections, I will make brief descriptions about how we started and developed the chemistry of multinuclear palladium  $\pi$  complexes.

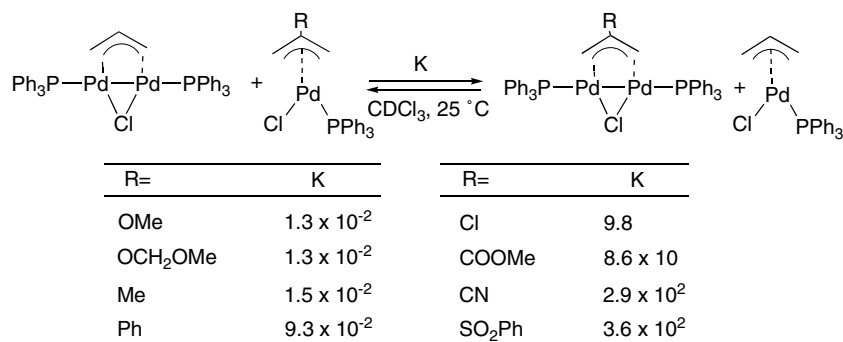
## 2. $\mu$ -Allyl, $\mu$ -propargyl and $\mu$ -diene dipalladium complexes

Our initial project in organopalladium cluster chemistry was concerned with a new equilibrium involving dinuclear  $\mu$ -allylpalladium(I) complexes (Scheme 3) [12]. Prior to this work some precedents of the similar type of dinuclear complexes [13,14] as well as the related  $\mu$ -cyclopentadienyl [14] and  $\mu$ -benzene [15] dinuclear analogs existed (Scheme 4). However, little had been

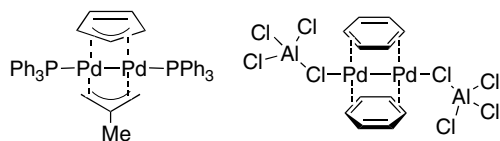


Ar=  $\text{C}_6\text{H}_3\text{Cl}_2\text{-2,5}$ ; R= Ph, CN, COOMe

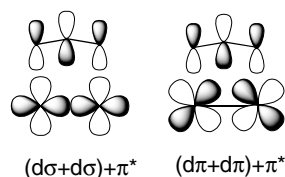
Scheme 2.



Scheme 3.



Scheme 4.



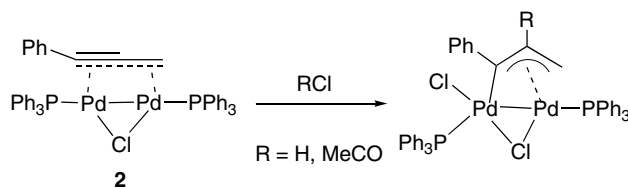
Scheme 6.

known about the bonding and reactivity aspects of these complexes which are unique to the dinuclear system as compared to those of the mononuclear counterparts. During our continued effort to elucidate new reaction patterns of  $\pi$ -allylpalladium complexes relevant to mechanisms of catalytic transformations [16], we encountered the nice equilibrium system (Scheme 3) for the purpose of evaluating the electronic effect of the substituents in the allyl ligand on the relative stability of the dinuclear and mononuclear series. Scheme 3 involves a rare transfer of allyl groups between metal atoms in the different oxidation states (redox transmetalation), where the discovery of Scheme 3 was the result of extension of our earlier finding that the  $\pi$ -allyl group is transferred from Pd(II) to Pd(0) with inversion of configuration at the  $sp^3$  allyl carbon (Scheme 5) [17,18].

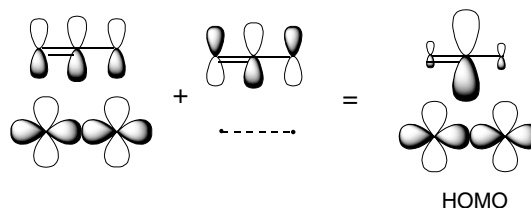
The equilibrium data for Scheme 3 indicate that the allyl ligand having the more electron-withdrawing substituent is bound to the Pd–Pd unit more strongly, while the more electron-donating allyl group prefers to coordinate to the mononuclear Pd unit. It was suggested by ab initio MO calculations that the stability trends observed in Scheme 3 are attributable to the greater degree of contribution of back-donating interaction between filled d orbitals ( $d\sigma$ – $d\sigma$  and  $d\pi$ – $d\pi$  MO of the Pd–Pd fragment) and an empty allyl  $\pi^*$  orbital in the dinuclear system (Scheme 6) than that between filled d orbital and allyl  $\pi^*$  orbital in the mononuclear system. The above MO analysis suggests a greater degree of accumulation of electron density on the allyl ligand in the dinuclear system than in the mononuclear system. Indeed, natural bond orbital (NBO) population analysis is consistent with this notion; the allyl ligand is negatively charged in dinuclear complex  $\text{Pd}_2(\mu\text{-C}_3\text{H}_5)(\mu\text{-Cl})(\text{PPh}_3)_2$  (–0.25) while it is positively charged in  $\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)$  (0.05).

We sought for reactions reflecting the newly proposed electronic aspect in the dinuclear  $\mu$ -allyl complexes, but we failed to find any satisfactory example. However, the

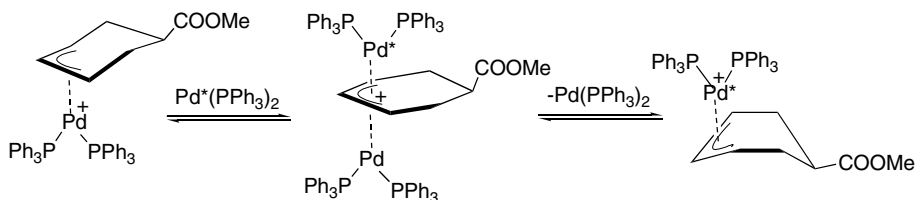
isoelectronic  $\mu$ -allenyl/propargyl Pd–Pd complex (**2** in Scheme 7) exhibited a new reactivity trend closely related with the unique bonding scheme in the dinuclear system [19]. The structure of the  $\mu$ -allenyl/propargyl Pd–Pd complex **2** is characterized by the linear C–C–C unit lying parallel with the Pd–Pd bond, with the five atoms (two Pd and three C of the ligand) forming a rectangle. This structure is particularly well suited for back-bonding interaction from Pd–Pd  $d\sigma$ – $d\sigma$  orbital to the bridging ligand  $\pi^*$  orbital. The back-bonding as a result of mixing interaction of ligand  $\pi^*$  with  $d\sigma$ – $d\sigma/\pi$  combination leads to development of a big lobe of HOMO at the backside of the propargyl center carbon (Scheme 8). Then it was understandable that dinuclear allenyl/propargyl palladium complexes underwent the addition of electrophiles at the center carbon of the bridging ligand to yield new dinuclear palladium complexes containing bridging vinylcarbene ligands (Scheme 7). This reaction



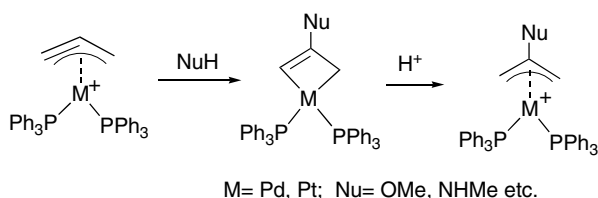
Scheme 7.



Scheme 8.



Scheme 5.



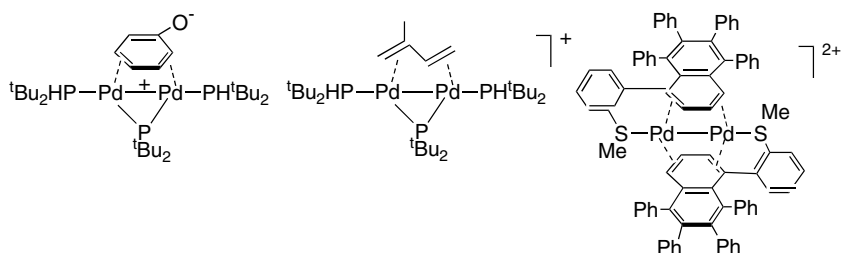
Scheme 9.

pattern should be contrasted with the opposite reactivity trend of mononuclear  $\pi$ -allyl/propargylpalladium(II) complexes which are susceptible to the attack of nucleophiles, particularly at the central carbon (Scheme 9) [20].

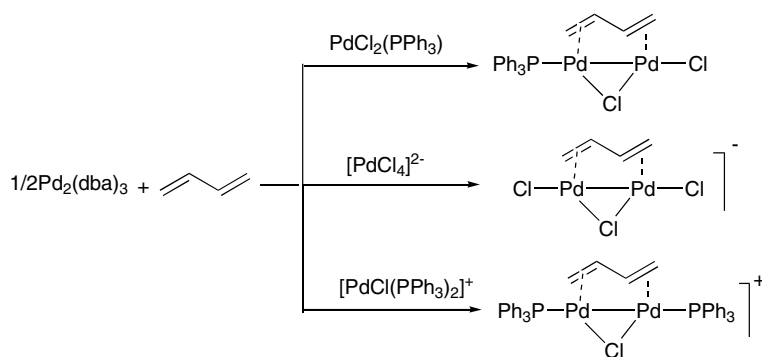
1,3-Diene has a combination of HOMO and LUMO which are isolobal with those of allyl and allenyl/propargyl anions. Therefore, we expected that the diene is perturbed by the interaction with the Pd–Pd unit in a manner similar to the allyl and allenyl/propargyl ligands. However, only a limited number of diene Pd–Pd complexes had been isolated previously, e.g., those shown in Scheme 10 [15,21]. We made efforts to gain a series of  $\mu$ -butadiene Pd–Pd complexes by the reaction

of Pd(II) complex with Pd(0) complex in the presence of the diene (Scheme 11) [22]. Remarkably, no Pd–Pd bond was formed from the reactants used in Scheme 11 unless butadiene is added. Non-conjugated diene (e.g., norbornadiene, 1,4-pentadiene) was found useless for forming Pd–Pd bond. The Pd–Pd lengths in the isolated complexes (2.57–2.71 Å) did not differ much from those in the  $\mu$ -allyl and  $\mu$ -allenyl/propargyl Pd–Pd complexes already described.

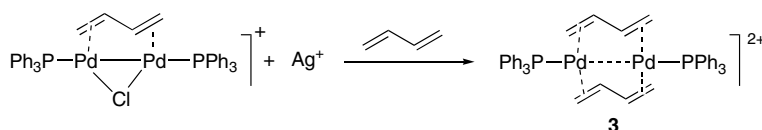
If the bridging halide in the dinuclear diene complex  $[\text{Pd}_2(\text{C}_4\text{H}_6)(\text{Cl})(\text{PPh}_3)_2]^+$  was replaced by another diene bridge on treatment with  $\text{Ag}^+$  in the presence of diene, the sandwich-type bis(butadiene) Pd–Pd complex **3** was obtained (Scheme 12) [23]. The structure determination showed that the Pd–Pd distance (3.19 Å) in **3** is unusually long for a Pd(I)–Pd(I) contact. This value for the known Pd(I)–Pd(I) complexes spans from 2.50 to 2.83 Å. MO calculations on a model complex  $[\text{Pd}_2(\text{C}_4\text{H}_6)_2(\text{PH}_3)_2]^{2+}$  suggested contributions of two key interactions to the overall bonding (Scheme 13). One is a donating interaction from the ligand  $\pi$  MO to the overall bonding (Scheme 13). One is a donating interaction from the ligand  $\pi$  MO to the  $[\text{d}\sigma\text{-d}\sigma]^*$  antibonding orbital of Pd–Pd, and the



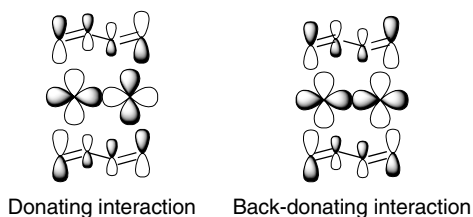
Scheme 10.



Scheme 11.



Scheme 12.

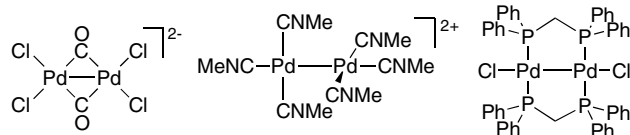


Scheme 13.

other a back-donating interaction from the  $d\sigma$ - $d\sigma$  bonding orbital of Pd–Pd to the ligand  $\pi^*$  MO. Owing to the latter interaction destabilization of the  $d\sigma$ - $d\sigma$  MO, which would otherwise become appreciable during elongation of the Pd–Pd separation, could be avoided, and the bonding energy would remain almost constant up to the observed long Pd–Pd separation. Perhaps steric repulsion between  $\text{PPh}_3$  and the diene terminal would have caused the Pd–Pd elongation. It may well be that the same kind of multicentered interaction between metal–metal and organic  $p\pi$  conjugation network is also involved in polyene–polymetal composites having unique shapes, as will be detailed in Section 4.

### 3. Synthesis of Pd(I)–Pd(I) complexes with labile ligands

As described in Section 1, we strongly felt the necessity of getting a Pd cluster complex which acts as a good starting material to construct a variety of organopalladium clusters. Some inorganic Pd cluster complexes supported by carbonyl, isocyanide or phosphine ligands had been known, as exemplified by Scheme 14 [24]. How-

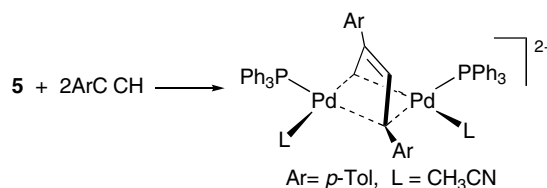


Scheme 14.

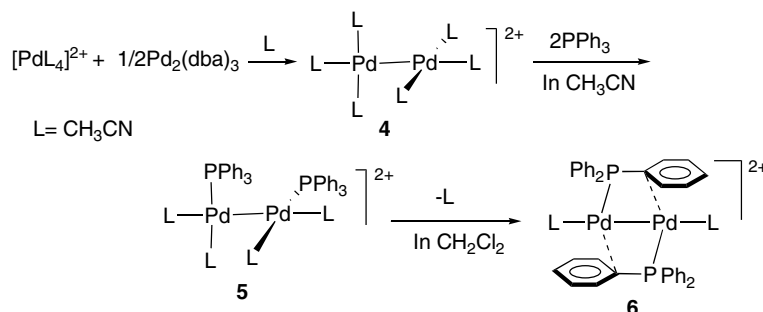
ever, these proved to be not so efficient starting materials for constructing a wide range of organopalladium clusters. Perhaps the supporter ligands in these are held to metals too tightly to allow coordination of unsaturated organic ligands which are, in nature, of the weakly coordinating ability.

In mononuclear Pd(II) chemistry, a cationic complex,  $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$  had been known to be a versatile reagent for making complexes or catalyzing reactions of olefins and acetylenes, thanks to the facile replacement of acetonitrile ligands by the unsaturated molecules [25]. This knowledge prompted us to try to synthesize Pd–Pd complex possessing acetonitrile ligands as many as possible. We succeeded in making such complex **4** and related ones **5** and **6**, as outlined in Scheme 15 [26]. Thus, treatment of  $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$  with  $\text{Pd}_2(\text{dba})_3$  gave **4**, which reacted with two equivalents of  $\text{PPh}_3$  to give **5**. Compound **5** lost two equivalents of acetonitrile in dichloromethane to give **6**, which is among rare examples of polynuclear metal complexes containing bridging phosphine ligands [21d,27]. The Pd–carbon(ipso) interaction in **6** appears very weak, as judged by rapid exchange between bridging and unbridging P-bound phenyl groups on the NMR timescale.

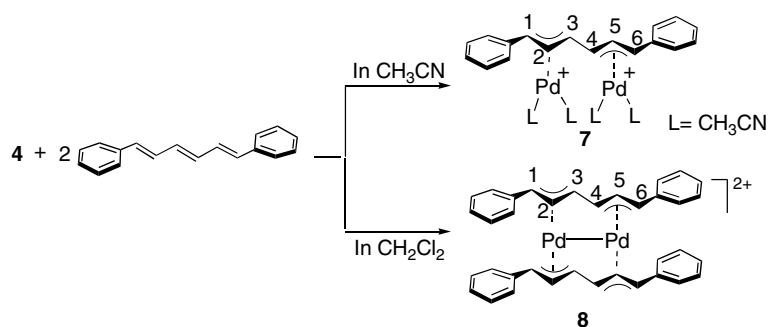
The complexes **4–6** showed nice reactivities toward some unsaturated hydrocarbon compounds, greatly contributing to the progress of organopalladium cluster chemistry. For example, the reaction pattern of alkynes with **4** and **5** [26b,28] turned out to be different from those with the known Pd(I)–Pd(I) complex  $\text{Pd}_2\text{Cl}_2(\text{dppm})_2$  (dppm = bis(diphenylphosphino)methane) [29]. In the latter reaction, only one equivalent of alkyne attacked the Pd–Pd bond to give a so-called



Scheme 16.



Scheme 15.



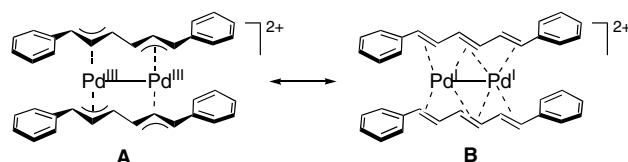
Scheme 17.

A-frame complex having a PdCR = CRPd framework, which appeared to be reluctant to accept attack of further molecule(s) of alkynes. In contrast, **5** reacted with two equivalents of alkynes to give  $\mu$ -butenediylidene Pd–Pd complex as summarized in Scheme 16, probably through an intermediary 1:1 adduct between Pd–Pd and alkyne. Furthermore, the reaction of **4** with EC≡CE (E = COOMe) resulted in stepwise growth of alkyne insertion products to give complexes containing Pd(EC=CE)<sub>n</sub>Pd framework ( $n = 1$  to 3). The greater reactivity of Pd–Pd/alkyne 1:1 adduct from **4** and **5** with further alkyne molecule than that from Pd<sub>2</sub>Cl<sub>2</sub>(dppm)<sub>2</sub> would be attributed to the presence of labile acetonitrile ligands in the former system. When pursuing further reactions of **4–6** with unsaturated hydrocarbons, namely conjugated polyenes, we faced a breakthrough point.

#### 4. Polyene–polypalladium sandwich complexes

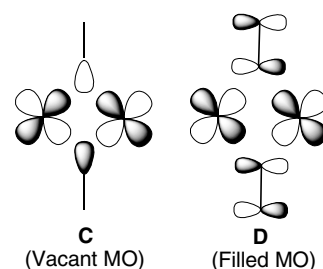
The substitutionary labile Pd–Pd complex **5** reacted with 1,3-butadiene to give the sandwich complex **3** which can be regarded as a halfway stage to the Pd–Pd bond cleavage as a result of  $[2\sigma + 4\pi]$  addition. Analogous reactions of **4** with the diene seemed to result in Pd–Pd bond cleavage [30], but no details are clear yet about the products. The adduct **7** obtained from **4** and 1,6-diphenylhexatriene in acetonitrile was more revealing. The X-ray structure determination unambiguously demonstrated cleavage of the Pd–Pd bond (Scheme 17) [31].

In contrast to the complex **7**, the structure elucidation of the adduct **8** from **4** and diphenylhexatriene in dichloromethane was a great surprise to us. The complex **8** is composed of two triene ligands of the  $\eta^3:\eta^3$ -bridging type and the Pd–Pd fragment without any capping ligand. One extreme formalism of **8** involves the presence of two bis( $\eta^3$ -allyl)palladium cations in Pd(III) state with a Pd–Pd single bond maintained (Scheme 18, A). However, a recent MP2-NBO calculation on a model  $[\text{Pd}_2(\text{C}_6\text{H}_8)_2]^{2+}$  suggests no electron occupation about the Pd–Pd region [32]. The Pd–Pd length in **8** (2.9156



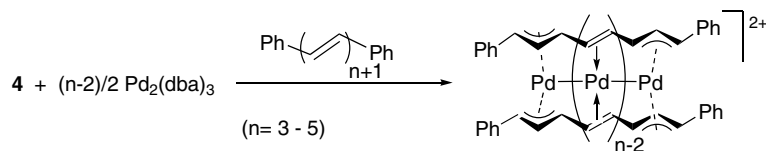
Scheme 18.

Å) [31] is somewhat longer than those in the known Pd–Pd  $\sigma$  bonded complexes (2.8–2.5 Å), although the X-ray determined metal–metal separation cannot always reflect the extent to which the direct metal–metal electronic interaction takes place [33]. An alternative formulation of **8** could involve a Pd(I)–Pd(I) unit which is coordinated by two triene ligands, each acting as a  $\eta^2:(\mu-\eta^2):\eta^2$  donor (Scheme 18, B). The central  $\mu$ -C=C part in this formalism may play a role similar to that of the  $\mu$ -CO ligands in  $[\text{Cl}_2\text{Pd}(\mu\text{-CO})_2\text{PdCl}_2]^{2-}$  [33]. For this carbonyl bridge complex having normal Pd–Pd separation (2.70 Å) [24b], the MO calculation suggested that considerable electron density flows from  $d\pi$ - $d\pi$  bonding orbital to  $(d\pi-d\pi)^*$  antibonding orbital of Pd–Pd unit by means of extensive electron delocalization over  $\pi^*$  orbitals of  $\mu$ -CO ligands (Scheme 19). The MO C in Scheme 19 is made by antibonding combination of the ligand lone pair and Pd–Pd  $d\pi$ - $d\pi$  orbitals, both being filled before interaction. However, C is not filled since the MO D made of the ligand  $\pi^*$  and Pd–Pd  $(d\pi-d\pi)^*$ , with both components being vacant, lies below C, and thus it is D that becomes occupied. These circumstances contribute to the disappearance

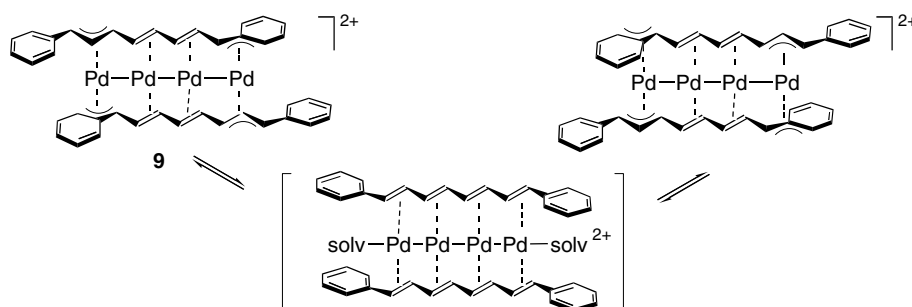


Scheme 19.





Scheme 20.



Scheme 21.

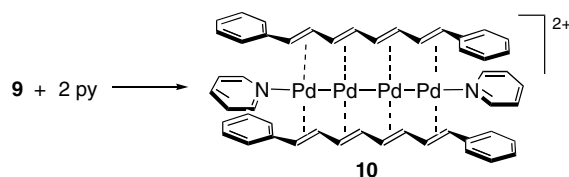
of the through-space Pd–Pd interaction in  $[\text{Cl}_2\text{Pd}(\mu\text{-CO})_2\text{PdCl}_2]^{2-}$ . The MO analysis of  $[\text{Pd}_2(\text{C}_6\text{H}_8)_2]^{2+}$  also suggested occurrence of orbital interactions similar to Scheme 19, which may be responsible for the lack of NBO occupation about Pd–Pd region in the model sandwich.

We now recognized that the way the triene ligand is perturbed by coordination to two Pd atoms is considerably different between the half-sandwich (**7**) and sandwich (**8**) systems. Such difference may be manifested in trends of the C–C bond length (Å); for **7**, C1–C2 = 1.395, C2–C3 = 1.411, C3–C4 = 1.474, while for **8** C1–C2 = 1.376, C2–C3 = 1.424, C3–C4 = 1.396. Thus, the longer C3–C4 length in **7** can be attributed to the diallyl dianionic formulation of the triene group in **7**. It should also be noted that addition of free triene to **7** led to conversion to the sandwich complex **8**.

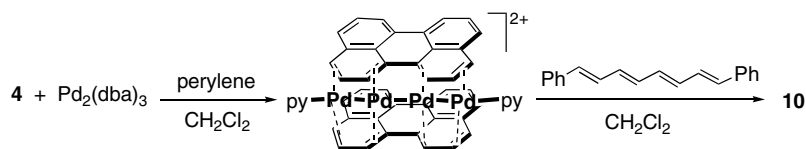
The reaction of **4** with the longer chain  $\alpha,\omega$ -diphenylpolyene (e.g., diphenylpentaene) gave a mixture of unidentified products. These are tentatively assigned as isomers of polyene Pd–Pd sandwich complexes in which some C=C bonds remain uncoordinated. We imagined that such uncoordinated C=C bonds could bind Pd(0) or Pd(II) atoms if these are supplied to the system by the use of an appropriate source. After several trials, we were able to construct a linear  $\text{Pd}_n$  skeleton which is sandwiched by two linear polyene ligands having  $(n + 1)$  C=C bonds by reacting 1 equiv of **4** and  $(n - 2)$  equiv of  $\text{Pd}(\text{dba})_{3/2}$  in the presence of the polyene (Scheme 20) [30,34]. The X-ray structure determination revealed that the  $\text{Pd}_n$  framework forms a linear rod with normal Pd–Pd lengths. The polyene ligand coordinates to the  $\text{Pd}_n$  chain in the  $\eta^3:\eta^2:\dots:\eta^2:\eta^3$  fashion.

Besides the standard type complexes expressed in Scheme 20, we obtained another type of complexes in which the number of C=C bonds of the polyene is one unit less and one C=C bond of the phenyl ring participates in coordination to the  $\text{Pd}_n$  rod, as shown in **9** (Scheme 21) [34]. In solution, there occurs the rapid sliding motion of the polyene ligand along the  $\text{Pd}_4$  rod (Scheme 21), as is evidenced by  $^1\text{H}$  NMR showing only the averaged four vinyl proton signals, even down to  $-90^\circ\text{C}$ . If the motion is not rapid enough on the NMR timescale eight vinyl signals should have been observed. An intermediate of this motion is proposed in which tetraene coordinates to  $\text{Pd}_4$  chain in a  $\eta^2:\eta^2:\eta^2:\eta^2$  fashion. Occurrence of this new coordination mode has been realized in the pyridine adduct **10** obtained in Scheme 22.

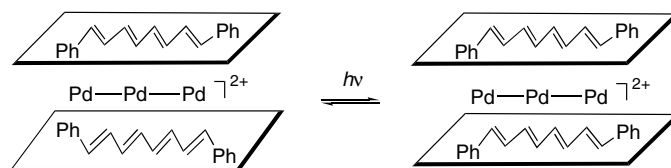
It seems of further interest that the similar way of binding of the  $\text{Pd}_4$  chain with the consecutive four C=C units existed in the newly isolated sandwich complex composed of  $\text{Pd}_4$  and a polycyclic aromatic compound, namely perylene (Scheme 23) [35]. Remarkably, eight carbons on an only one edge side of perylene are involved in the coordination to the metals, with each six-membered ring coordinating to two Pd atoms as in the  $\mu$ -benzene Pd–Pd complex previously



Scheme 22.



Scheme 23.



Scheme 24.

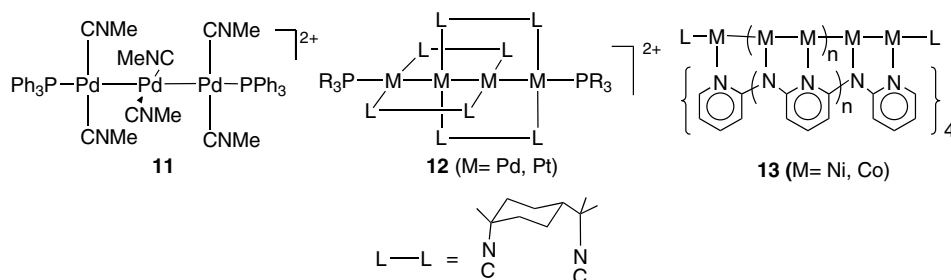
reported [15]. Moreover, two perylene planes are located in an eclipsed position to each other, leaving void space between two planes at the other side with respect to the Pd<sub>4</sub> chain. The coordination of perylene to the metals is not so tight that addition of diphenyltetraene resulted in complete displacement of perylene by the tetraene to give **10** (Scheme 23).

Besides the slide motion in Scheme 21 and ligand exchange in Scheme 23, the unsaturated hydrocarbon ligands which are  $\pi$ -coordinated to the polypalladium assembly exhibited another interesting dynamic property. This is concerned with a clean photo-induced face inversion of the diphenyltetraene ligands on the Pd<sub>3</sub> rod (Scheme 24) [36]. The irradiation also accelerated intermolecular exchange of trienes which is very sluggish under dark. It should be noted that no decomposition of the sandwich complex was apparent in the course of Scheme 24. It may well be that the irradiation causes no liberation of free tetraene molecule. Otherwise a naked [Pd<sub>3</sub>]<sup>2+</sup> or half-naked [(tetraene)Pd<sub>3</sub>]<sup>2+</sup> should have been generated and recombined with tetraene without decomposition, but this is apparently a difficult situation. At the moment, we assume that the irradiation would weaken the consecutive  $\pi$ -coordination bonds between Pd<sub>3</sub> and tetraene all at once, making the partic-

ular tetraene ready for inversion of the coordination face or exchange with outer tetraene.

## 5. Conclusion

The chemistry of palladium cluster complexes containing unsaturated hydrocarbon ligands described above has developed from mechanistic studies of mononuclear organopalladium complexes not straightforwardly, but rather accidentally. Whatever the starting point of our new chemistry may be, the type of complexes synthesized has no precedents and their coordination behavior is quite unique. Synthesis of linear polymetal chains and examination of their physical properties are receiving increasing interest from a viewpoint of material science. Most of the examples so far studied are a class of complexes which involve rather rigid metal–ligand frameworks such as **11–13** shown in Scheme 25 [37–40]. On the other hand, the organopolypalladium chain complexes obtained in our group can be characterized by some remarkable dynamic properties about the metal–ligand interaction which appear unique to the organometallic system. These characteristics will lead to new developments in related fields including heterogeneous catalysis and material science.



Scheme 25.



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