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Organopalladium complexes containing palladium–palladium bonds

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Contents

Abstract

This review covers recent achievements in the field of organopalladium chemistry involving Pd–Pd bonds. Several new aspects are reported with regard to the role of Pd–Pd bonds in catalysis, especially new binding modes and transformations of unsaturated hydrocarbons on a Pd–Pd bond. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Metal–metal bond; Metal complexes

1. Introduction

Remarkable catalytic activities of metal surfaces, metal colloids, or small metal particles have attracted wide attention from early days (the end of 19th century). Group-10 metals (Ni, Pd, Pt) have played a central role in this area owing to their high activity [1]. As heterogeneous systems involving Group-10 metals have been making progress, homogeneous catalytic systems have also developed remarkably in the field of synthetic organic chemistry [2]. Now, the Group-10 metal catalyses are indispensable for organic synthesis. Among the Group-10 metals, palladium frequently shows a unique and desirable activity. For example, palladium has a different preferred electron configuration (d^{10}) than platinum (s^1d^9), providing organopalladium(II) complexes with a greater thermodynamic advantage for reductive elimination than organoplatinum(II) complexes [3,4]. In addition, the greater ligand field splitting in palladium(II) complexes than nickel(II) complexes causes a higher barrier to five-coordinated intermediate formation in the reaction of the former relative to the latter.

It is of utmost importance to understand what occurs at a palladium site during both heterogeneous and homogeneous catalytic reactions. In the homogeneous system, examination of some elaborately designed stoichiometric reactions led to generation or even isolation of organopalladium intermediates, which can

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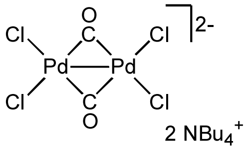
be involved in catalytic cycles. Most of these are of the mononuclear type. On the other hand, relatively less knowledge has been obtained about the role in catalysis of organopalladium complexes containing Pd–Pd bonds, while there are continuing efforts towards development of new kinds of reactivities at such multiple palladium sites in an attempt to explore new or more desirable organic transformations. Furthermore, the manipulation of Pd–Pd bonds in medium to large size clusters is also in progress towards creation of promising materials such as nano-structured palladium particles. In this review, we summarize the recent work to elucidate the structures, coordination behavior, reactivities, and functions of organopalladium complexes containing Pd–Pd bonds. The field is currently developing, but most of the previous work dealt with dinuclear Pd–Pd complexes. In this section, some historically important works about the earlier preparations of dinuclear Pd–Pd complexes are surveyed.

The first preparation of dipalladium(I) complexes was carried out by the reaction of $PdCl_4^{2-}$ with CO in aqueous acid in 1942 [5]. Goggin and Mink assigned the structure of the dianionic product **1** from the IR spectra in 1974 [6]. The crystal structure of the dianionic complex was finally determined in 1981 [7].



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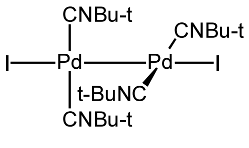
The first example of a structurally defined dipalladium(I) complex having unsaturated hydrocarbon ligands, bis-benzene dipalladium(I) complexes **2**, was prepared by Allegra et al. in 1965 [8,9]. These complexes were obtained simply by the reaction of $PdCl_2$ with $AlCl_3$ in refluxing benzene. Since then, a number of hydrocarbon bridged dipalladium complexes have been prepared. Particularly noticeable are the early preparations of the μ-η^3-allyl dipalladium(I) complex **3** (Yamazaki et al., 1972) [10] and the Cp-allyl sandwich dipalladium(I) complex **4** (Werner et al., 1975) [11].

The isocyanide dipalladium(I) complex $[Pd_2(t\text{-}BuNC)_4(I)_2]$ (**5**) prepared by Otsuka et al. [12] and the dppm dipalladium(I) complex $[Pd_2(dppm)_2(Br)_2]$ (**6**) prepared by Colton et al. [13] were the first to show unique reactivities associated with a Pd–Pd single bond. Particularly noticeable is the discovery of the insertion reaction into a Pd–Pd bond by Balch and coworkers [14].



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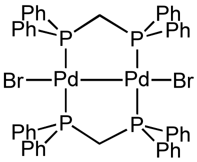

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Interestingly, most of the earlier preparations were attained by serendipitious, rather than planned reactions. Nevertheless, these early achievements stimulated subsequent research.

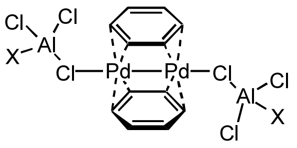
There are several excellent reviews including those by Werner [15], Maitlis et al. [16], and Moiseev et al. [17–19]. This review will focus on the recent attainments in this field, particularly those of interest from the viewpoint of organometallic chemistry, while the remarkable achievements also appeared in inorganic chemistry, catalysis, or material science, which deal with multiple palladium atoms. Furthermore, this review does not attempt to cover comprehensively the title area.

2. Discussion

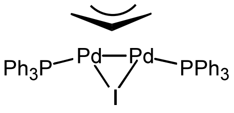
2.1. Classification of Pd–Pd complexes

2.1.1. Dinuclear Pd–Pd complexes

For dinuclear palladium complexes, various combinations of valences (Pd(0), Pd(I), Pd(II), Pd(III), and Pd(IV)) are possible. A simple consideration of the electronic configuration indicates that the Pd(I)–Pd(I) and Pd(III)–Pd(III) combinations have a Pd–Pd σ-bond. A number of Pd(I)–Pd(I) complexes have been isolated and characterized, while only one example is known of a Pd(III)–Pd(III) complex with a well-defined structure, as will be described later. Theoretical studies



2 X = Cl
X = $AlCl_4$



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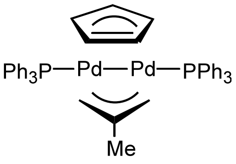

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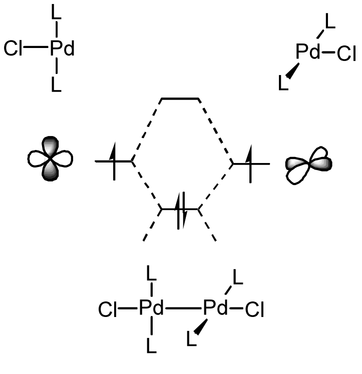
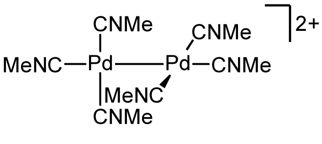


Scheme 1.

on a series of dinuclear palladium complexes were recently reviewed by Dedieu [20].

There are two extreme geometries for dinuclear Pd(I)–Pd(I) complexes; namely 'corner-sharing' and 'edge-sharing' geometries. Three homoleptic dipalladium complexes **7** (Pd–Pd 2.5310(9) Å), **8** (Pd–Pd 2.598(1) Å) and **9** are shown as the typical examples of 'corner-sharing' geometry [21–24].



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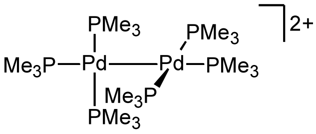

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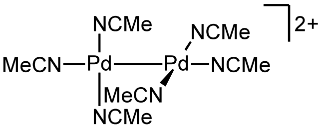

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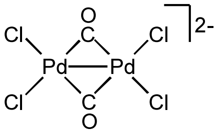
Extended Hückel calculations on the corner-sharing complex $[Pd_2(CH_3NC)_4Cl_2]$ showed that this type has a dσ–dσ bonding as depicted in Scheme 1 [25]. This leads to a low barrier rotation about the Pd–Pd bond when the complex has neither bridging nor bulky ligands.

The carbonyl-bridged complex **1** (Pd–Pd 2.697(3) Å) [6] and the dimer of $[Pd_2(\mu\text{-}CO)_2(OAc)_2]$ (**10**) (Pd–Pd 2.663(1) Å) [26] are typical examples of 'edge-sharing' geometry. Furthermore, some isocyanide complexes such as **11** (Pd–Pd 2.757(4) Å) are known [27,28].

The electronic structures of such edge-sharing complexes are quite different from those of the corner-sharing complexes. Hartree-Fock calculations on $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ showed that an MO involving contribution of a Pd–Pd antibonding interaction **12** is occupied (Scheme 2) [29]. This makes the nature of the Pd–Pd bond not simple. Indeed, no effective electron population was found in the region between two Pd atoms. Thus, a Pd–Pd interaction through the ligands was proposed instead of a Pd–Pd interaction through space.

The electronic structure is thus very different between the corner- and edge-sharing complexes. However, a thorough structural survey of isocyanide dipalladium complexes showed that both are possible depending on subtle changes of the electronic or steric factors of the other ligands [30]. The geometries not represented by the above two extremes are also known. One example includes single atom bridged dipalladium complexes such as **13** (Pd–Pd 2.628(2) Å) [31,32] and **14** (Pd–Pd 2.571(2) Å) [33]. In these complexes, the Pd–Pd bond consists of mainly dσ–dσ overlap as suggested by an MO calculation [34]. Some dipalladium complexes containing semi-bridging CO or isocyanide ligands are also known such as **15** (Pd–Pd 2.6521(3) Å) [35], and **16** (Pd–Pd 2.599(2) Å) [30]).

Some dipalladium complexes containing non-bridging cyclopentadienyl ligands such as **17** (Pd–Pd 2.673(1) Å) [27] or **18** (Pd–Pd 2.639(1) Å) [36,37] are known, in which the total electron counts are 34e, in constrast to the above-mentioned 30e dipalladium(I) complexes.



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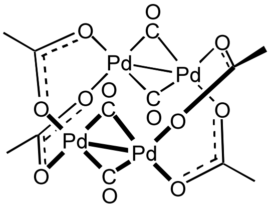

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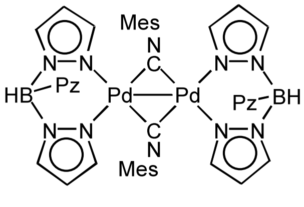

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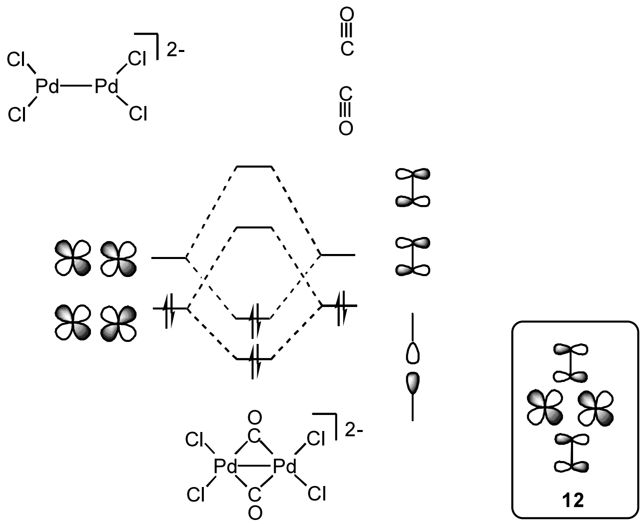

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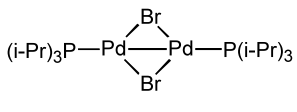

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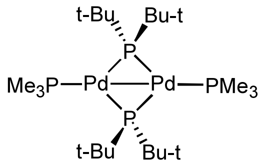

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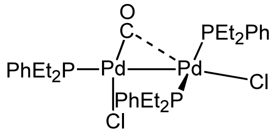

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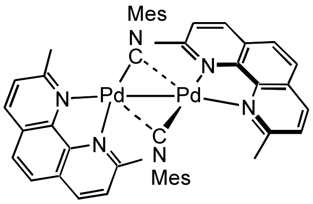

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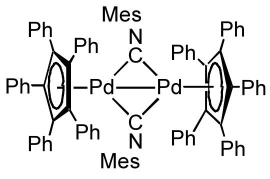

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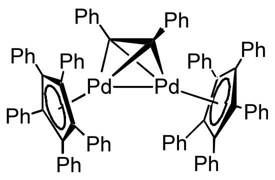

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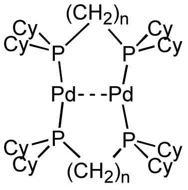
Some d^{10}–d^{10} $Pd(0)_2$ complexes with a short Pd–Pd separation such as **19** (for $n = 2$, Pd–Pd 2.7611(5) Å; for $n = 1$, Pd–Pd 2.8582(6) Å) have been structurally characterized [38]. A related complex $[Pd_2(dppm)_3]$ contains a somewhat longer Pd–Pd separation (Pd–Pd 2.9959(2) Å) where two parallel PdP_3 planes are bridged by three dppm ligands [39]. A d^{10}–d^{10} Pd(0)–Pd(0) interaction is expected to have no Pd–Pd σ-bond. However, there is still some bonding interaction [40] which is called a 'closed-shell interaction' [41]. Some examples of d^8–d^8 Pd(II)–Pd(II) interactions, although weak due to a pseudo-closed-shell type, are also known [42].



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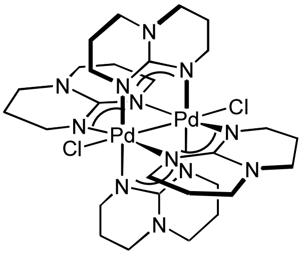
Finally, the very unstable dipalladium(III) complex **20** is known [43]. Interestingly, the Pd–Pd bond (2.391(2) Å) in **20** is the shortest among all of the known dinuclear palladium complexes.



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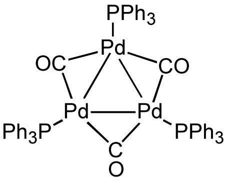
2.1.2. Trinuclear and higher nuclear complexes containing Pd–Pd bonds

A number of higher nuclear palladium carbonyl clusters have been prepared and structurally characterized [44]. In particular, the recent preparation of nanosized Pd_{38} [45], Pd_{59} [46], Pd_{145} [47], Pd_{561} [48], and Pd_{1415}, Pd_{2057} clusters [49] is remarkable. Furthermore, numerous heteronuclear Pd clusters have been prepared. Although such work is very interesting and important, particularly in the field of inorganic chemistry, catalysis and material science, this review does not cover them since only limited organometallic chemistry is presently known of these.

Nevertheless, some examples of small Pd clusters are illustrated here. The *triangulo*-Pd_3 complexes were reviewed by Puddephatt [50] and Mingos and coworker [51]. Some examples of Pd_3 and Pd_4 complexes are shown (**21**–**25**) [35,52–55].

The linear tripalladium cluster **26** was first prepared in 1978 [56], and the longer clusters such as **27** [57] and **28** [58] were prepared recently.



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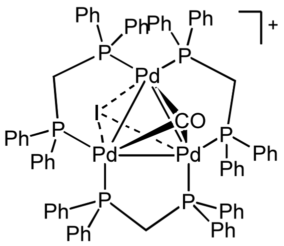

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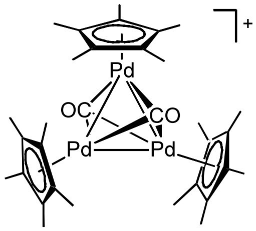

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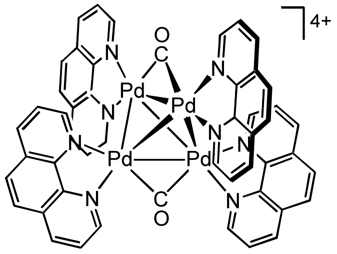

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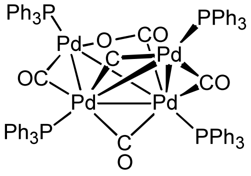

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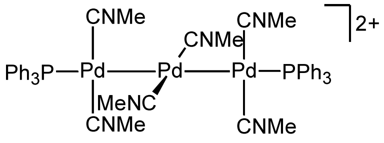

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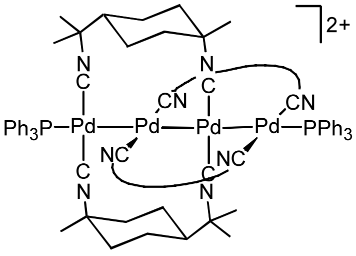

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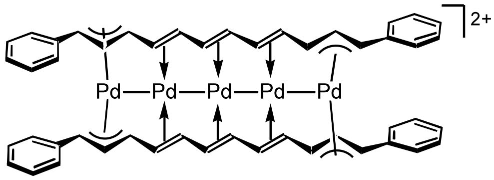

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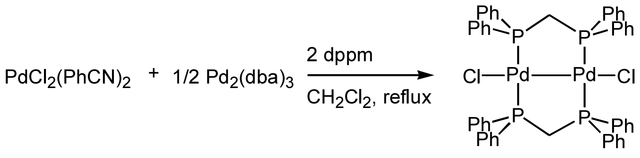
2.2. Coordination behavior and reactivity at dinuclear Pd–Pd sites

2.2.1. Dinuclear Pd–Pd sites with rigid bridging suppports

Rigid bridging ligands are very useful to stabilize a dinuclear Pd–Pd bonded framework as well as to bring two Pd atoms close to each other even when these Pd atoms interact only weakly. The dppm bridged complex [$Pd_2(dppm)_2Cl_2$] (**29**) [13,59,60], one of the most versatile dipalladium(I) complexes, was synthesized from the reaction of $Pd(PhCN)_2Cl_2$ with $1/2Pd_2(dba)_3$ in the presence of dppm [61]. Although a number of dipalladium complexes analogous to **29** have been prepared, here the reactivity of **29** and its derivatives is addressed to illustrate the reactivity of a dinuclear Pd–Pd site supported by rigid bridging ligands. Indeed, the complex **29** is particularly useful for investigating the coordination behavior of various substrates at a Pd–Pd site.



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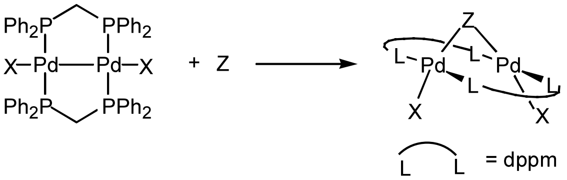
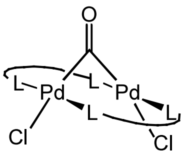
A typical reaction pattern is the insertion of small molecules into the Pd–Pd bond as described in Eq. (1). Such reactions yielded so-called ‘A-frame’ complexes as the main products, which were first designated by

Kubiak and Eisenberg [62]. In these A-frame complexes, the Pd–Pd distances are longer (ca. 3.5 Å) than those in the starting dipalladium complexes (ca. 2.7 Å).



(1)

Several carbenoids such as CO or RNC insert into the Pd–Pd bond to form μ-CO or μ-RNC dipalladium complexes, respectively (**30**, **31**) [14,61]. A diazonium cation also inserts into the Pd–Pd bond to give the cationic A-frame complex **32** [63]. In addition, $NOBF_4$ gives the cationic μ-NO complex **33** [64].



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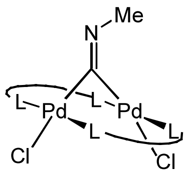

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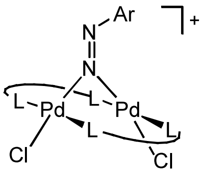

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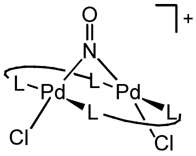

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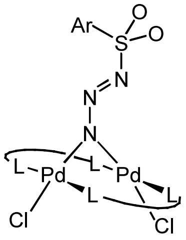
The reaction of **29** with azide afforded a mixture of the μ-azide complex **34** and the μ-nitrene complex **35** [64–68].



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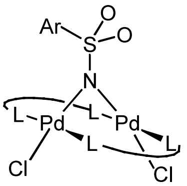

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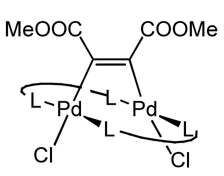
Sulfur dioxide also inserts into the Pd–Pd bond of **29** to afford the μ-SO_2 complex **36** [69,70]. The reaction with elemental sulfur (S_8) gives the μ-S dipalladium complex **37**, which is also formed by the reaction of **29** with propylene sulfide or H_2S with liberation of propylene or H_2 [70–72], respectively. Oxidation of the μ-S dipalladium complex with appropriate oxidants gives μ-SO dipalladium complex **38** [73].

With regard to the reactions of **29** with unsaturated hydrocarbons, only those with alkynes are known. The presence of electron withdrawing substituents in the alkyne facilitates the reaction to give the μ-η^1:η^1-alkyne complex **39** [74,75], while phenylacetylene requires the assistance of catalytic amounts of acid in order for analogous insertion to take place [76,77]. The reaction with alkynylsulfide in the presence of Lewis acid gives the μ-vinylidene dipalladium complex **40** [78].



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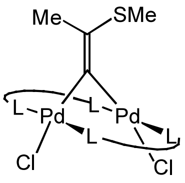

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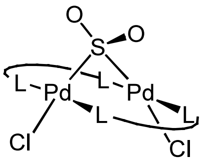
The reactivity of hydride, alkyl or aryl derivatives of **29** has been investigated in order to understand the proximity effect of two Pd atoms on C–H and C–C reductive eliminations. The reaction of **29** with Me_3Al afforded the very unstable monomethyl dipalladium(I) complex **41** [79,80]. This complex **41** is protonated by



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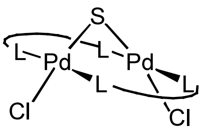

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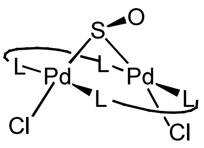

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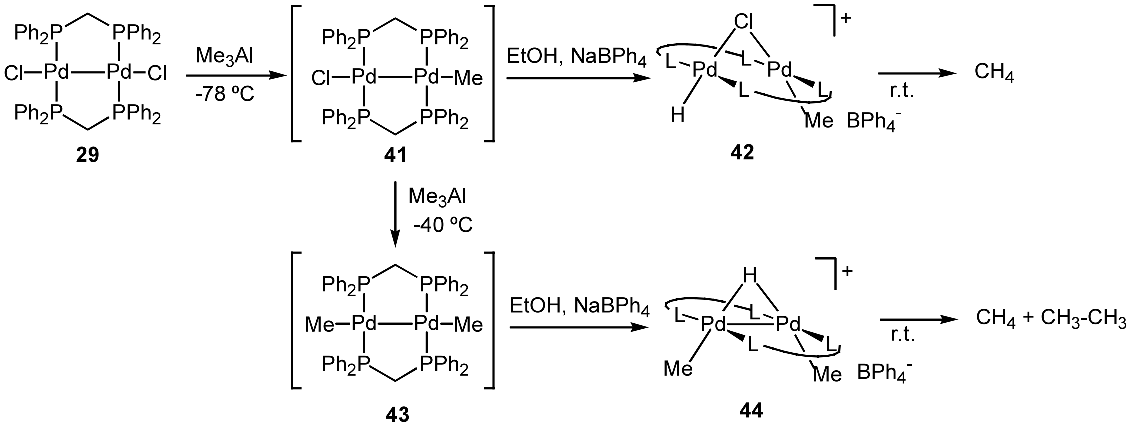
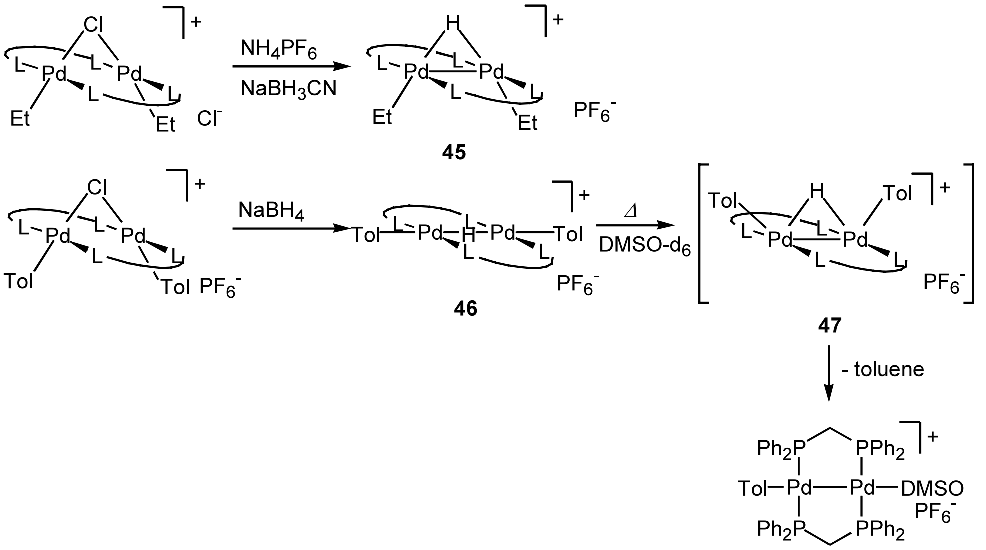
alcohol to give the hydride-methyl dipalladium complex **42**, which can easily release methane by reductive elimination. The reaction of the monomethyl complex **41** with additional Me_3Al generates the dimethyl complex **43**, which can also be protonated by alcohol to produce the dimethyl hydride dipalladium complex **44**. This complex liberates methane and ethane by thermal degradation. These reductive elimination reactions proceed intramolecularly. The A-frame complexes containing alkyl, aryl, or acyl moieties have also been prepared by other methods [81–84].

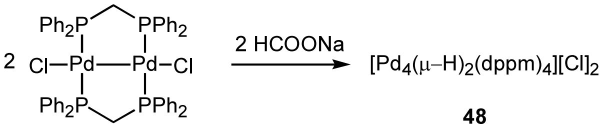
The geometry of μ-hydride complexes is variable; the diethyl-μ-hydride complex **45** exhibits the A-frame structure (C–Pd–Pd = 158.5°, Pd–Pd = 2.933(7) Å), while the di-*p*-tolyl-μ-hydride complex **46** shows linear Tol–Pd–Pd–Tol geometry (C–Pd–Pd = 178.4°) [85,86]. It was proposed only on the basis of the X-ray crystal structure that the hydride lies on the axis of the two Pd atoms (Pd–Pd = 3.0758(4) Å). Since A-frame complexes such as μ-hydride complexes usually show fluxional behavior accompanying the A-frame inversion [81,87,88], it was considered that the μ-hydride moves





more freely than the other ligands such as the *p*-tolyl moiety. Thus, the W-shape transient **47** was proposed as an intermediate of Ar–H reductive elimination from diaryl-μ-hydride complexes.

Reaction of **29** with HCOONa was found to give a tetranuclear palladium di-μ-hydride complex **48** [89–91]. A square Pd_4 geometry having two μ-hydride ligands was proposed without an X-ray crystal structure determination.



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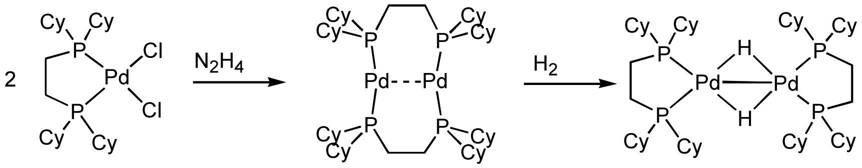
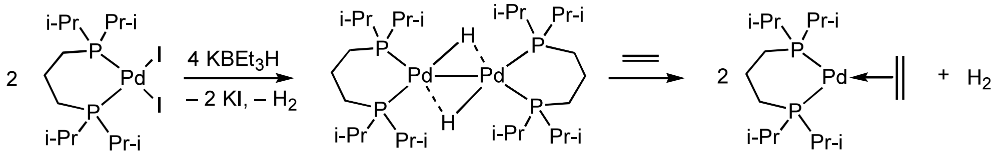
29

The above mentioned examples are concerned with the Pd(I)–Pd(I) complexes having a Pd–Pd σ-bond. Some interesting studies were also made on d^{10}–d^{10} dinuclear palladium complexes. A diphosphine ligand was devised to stabilize the 'closed-shell' d^{10}–d^{10} interaction effectively to make the complexes isolable. For example, the complex **19** was prepared by the reduction of the corresponding Pd(II) dichloride [38,39].



19 **49**



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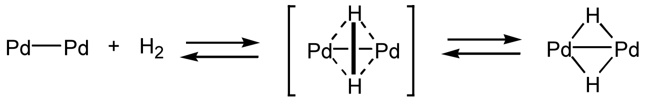
Dihydrogen reacted with the $Pd(0)_2$ complex **19** to afford a di-μ-hydride dipalladium(I) complex **49**. This process is related to dihydrogen activation on metallic palladium. Indeed, some theoretical studies suggested the importance of the cooperative function of multiple palladium atoms [92–95]. Dihydrogen was predicted to be more effectively activated by dinuclear Pd(0) rather than mononuclear Pd(0) [93,94]. A DFT calculation suggested that dihydrogen favorably approaches the bridging position of a naked Pd–Pd center in such a way as to keep the H–H axis perpendicular with the Pd–Pd axis (**50**).



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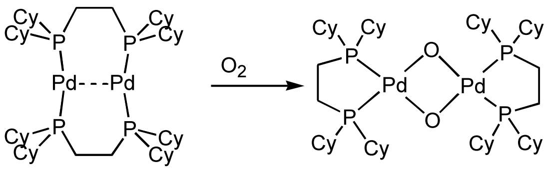
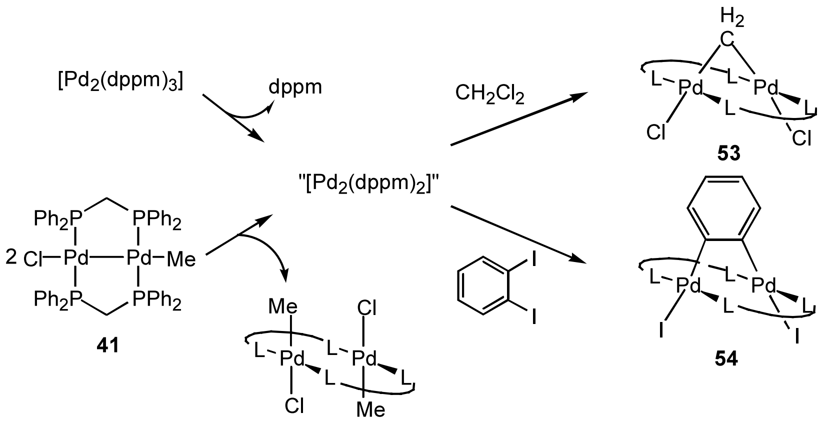
The di-μ-hydride dipalladium(I) complexes were prepared by the reaction of palladium(II) halide with $KBEt_3H$ [96,97]. The X-ray crystal analysis of the di-μ-hydride complex **51** showed that the hydride ligands coordinate to the Pd–Pd center (Pd–Pd 2.8245(8) Å) in an unsymmetrical bridging manner (shorter Pd–H 1.67(5) Å, longer Pd–H 2.13(4) Å) [97]. The reaction of such a di-μ-hydride dipalladium(I) complex with olefins or alkynes resulted in only reductive elimination of dihydrogen.

The $Pd(0)_2$ complex **19** also reacted with O_2 to afford the di-μ-oxo dipalladium complex **52** [38].



19 **52**

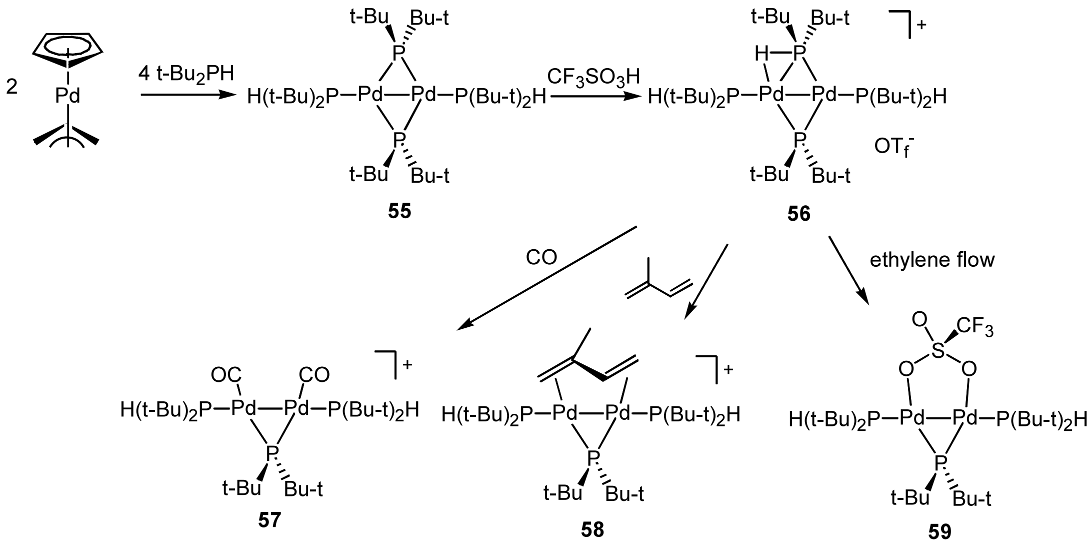
The d^{10}–d^{10} dipalladium complex '$[Pd_2(dppm)_2]$', which was expected to be generated from the degradation of $[Pd_2(dppm)_3]$ or, more effectively, from the degradation of $[Pd_2(dppm)_2MeCl]$, was active toward double oxidative addition [77,80,81]. For example, CH_2Cl_2 oxidatively added to $[Pd_2(dppm)_2]$ generated in situ to afford the μ-carbene A-frame complex **53**. The reaction with 1,2-diiodobenzene afforded the μ-benzyne A-frame complex **54**.



2.2.2. Dinuclear Pd–Pd sites with substitutionally labile supports

In Section 2.2.1, the reactivity of dinuclear Pd–Pd sites having rigid bridging supports is reviewed. Such dipalladium sites are susceptible to approach of a substrate in an associative manner with the Pd–Pd core remaining still rigidly supported by the bridging ligands. This section reviews somewhat different reaction behavior of dinuclear Pd–Pd sites bearing substitutionally labile supports.

Phosphide bridged complexes have been found to exhibit unique coordination properties and reactivities. The bis-μ-phosphide complex **55** (Pd–Pd 2.594(1) Å) can be prepared by the reaction of CpPd(η^3-allyl) with secondary phosphine. Interestingly, protonation of the bis-phosphide complex **55** afforded the μ-sec-phosphine bridged complex **56** (Pd–Pd 2.611(1) Å) [98,99], of which the μ-sec-phoshine ligand can be easily replaced by other substrates such as CO (**57** (Pd–Pd 2.682(1) Å)), 1,3-diene (**58** (Pd–Pd 2.751(2) Å)), triflate (**59** (Pd–Pd 2.648(2) Å)), or various phosphines [100–102]. Thus,

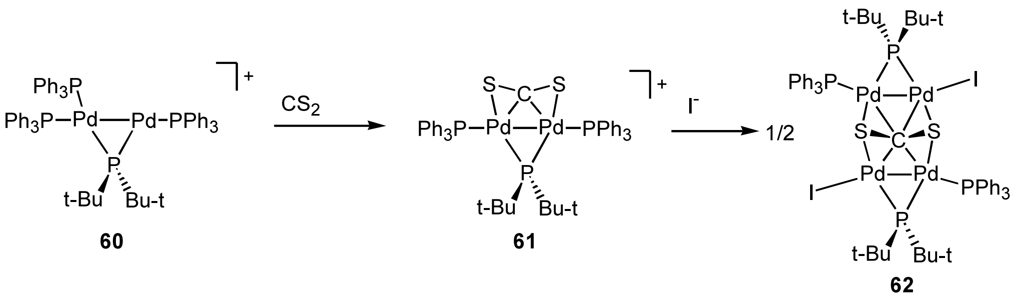


one of the bridging coordination sites at a Pd–Pd bonded center was opened while the other retained the μ-phosphide ligand.

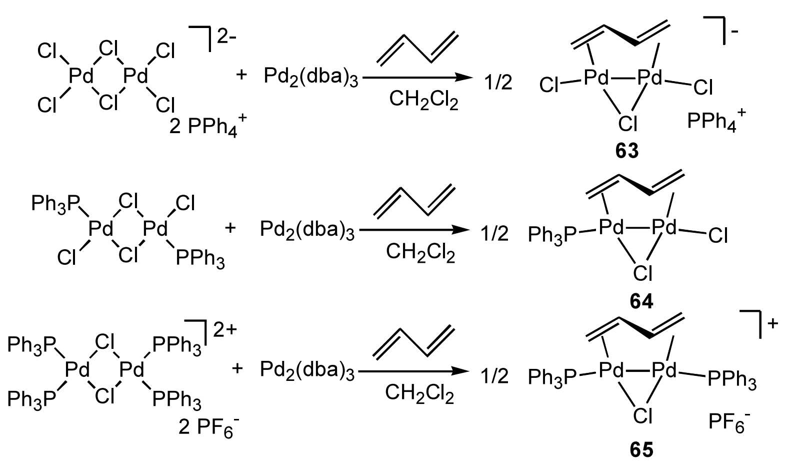
It is notable that the mono-triphenylphosphine complex **60**, a coordinatively unsaturated 28e complex, can be prepared from **56** and excess PPh_3 [103,104]. This complex reacted, for example, with CS_2 to afford the μ-CS_2 dipalladium complex **61** (Pd–Pd 2.7077(7) Å) [103]. The addition of iodide led to the formation of tetranuclear palladium complex **62** having μ-CS_2 ligands exhibiting a new coordination mode [105].

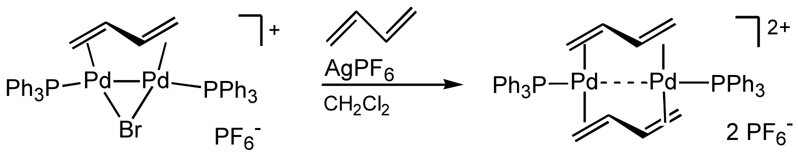
While some organic bridging ligands such as allyl and cyclopentadienyl groups (**3**, **4**) acted as a good supporting ligand for dinuclear Pd–Pd cores, 1,3-dienes can act as either substitutionally inert or labile ligands, depending on the reaction types, as illustrated below. Good starting materials for the examination of such dual character of μ-dienes are a series of μ-1,3-diene dipalladium complexes **63** (Pd–Pd 2.5776(2) Å), **64**, and **65**, which were easily obtained through redox condensation of Pd(II) and Pd(0) complexes in the presence of 1,3-diene [106]. Treatment of each Pd(II) complex with $Pd_2(dba)_3$ in the absence of the diene was found not to lead to effective Pd–Pd bond formation.

The μ-bromide ligand of the cationic dipalladium complex analogous to **65** can be replaced by 1,3-butadiene in the presence of silver salts to give the 1,3-butadiene sandwich complex **66** [107]. Interestingly, the Pd–Pd distance in **66** is unusually long (3.1852(6) Å). Theoretical calculations supported the retention of a Pd–Pd interaction at such long Pd–Pd distances. The strong donating (**67**) and back-donating (**68**) interactions between 1,3-diene ligands and the $[Pd–Pd]^{2+}$ moiety lead to elongation of the Pd–Pd bond. In particular, the back-bonding MO, which is the combination of diene π* and Pd_2 dσ–dσ (**68**), does not undergo appreciable destabilization, even when the Pd–Pd separation becomes longer up to the experimental value.



One of the 1,3-butadiene ligands in the bis-1,3-butadiene dipalladium complex can be readily exchanged by various substrates. For example, the reaction of the bis-1,3-butadiene dipalladium complex with phenylacetylene afforded the μ-alkynyl dipalladium





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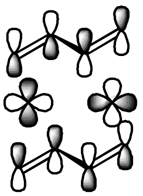

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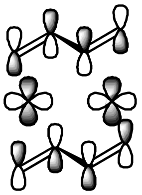

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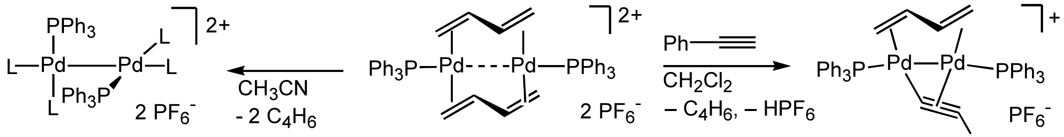
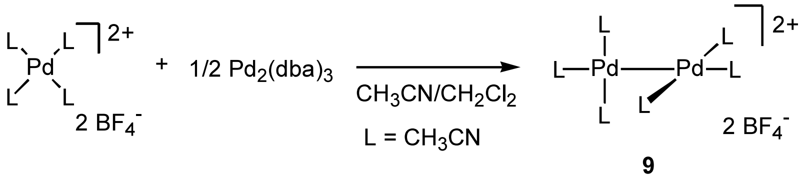
complex **69** [108]. The fluxional behavior of the μ-alkynyl moiety attached to the Pd–Pd bond was suggested by the temperature-dependent NMR spectra. Dissolution of **69** in CH_3CN resulted in the elimination of both 1,3-diene ligands leading to the acetonitrile dipalladium(I) complex **70**.

The complexes **9** and **70** are among a series of recently prepared dipalladium complexes [24,107,108] without rigid bridging ligands, which are still isolable without special techniques. Thus, the solvated dipalladium complex $[Pd_2(CH_3CN)_6]^{2+}$ (**9**) can be easily isolated by the reaction of $[Pd(CH_3CN)_4]^{2+}$ with $1/2Pd_2(dba)_3$ [24]. Acetonitrile is suitable as the non-bridging and substitutionally labile ligand. Acetonitrile is well-known in a mononuclear palladium center to be substitutionally labile enough to be replaced by various olefins [109].



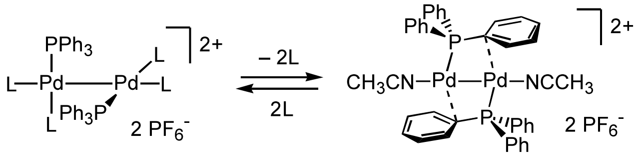
70 **66** **69**

In the bis-triphenylphosphine dipalladium complex **70**, the PPh_3 ligands are positioned cis to the Pd–Pd part. Furthermore, the Pd–Pd distance (2.4878(7) Å) in **70** is the shortest known Pd(I)–Pd(I) distance, and indicates the weak trans-influence of the CH_3CN ligand. Surprisingly, the bis-triphenylphosphine dipalladium complex **70** released its two acetonitrile ligands reversibly to afford the triphenylphosphine bridged dipalladium complex **71** [108]. The X-ray crystal structure of **71** (Pd–Pd 2.5833(7) Å) showed a unique coordination mode of the μ-PPh_3 ligand, which may involve both agostic donation of the P–C bond and η^1-phenyl coordination (Pd–C_{ipso} 2.336(4) Å). Rapid exchange between the coordinated and uncoordinated phenyl groups occurred on the NMR time scale, indicating rather weak interaction between Pd and η^1-phenyl



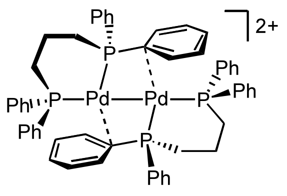
9

ligand. Thus, it was proved that triphenylphosphine, one of the most popularly used ligands in organometallic chemistry, can act as a labile bridging ligand.



70 **71**

Bridge or semi-bridge coordination of triarylphosphine or trialkylphosphine over a metal–metal bond was found only very recently [110]. Other interesting PR_3-bridged dipalladium complexes **72** (Pd–Pd 2.701(3) Å), **73** (Pd–Pd 2.7879(19) Å) are also known [111,112].



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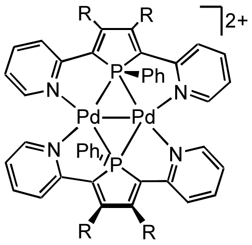

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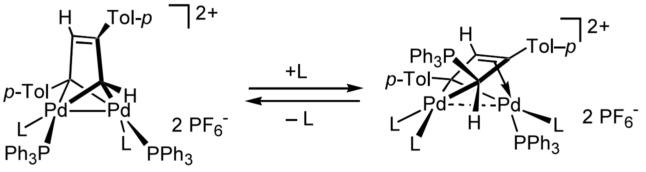
The PPh_3-bridged dipalladium complex **71** reacted with terminal arylalkynes to afford the μ-butenediylidene dipalladium complex **74** through head-to-tail alkyne dimerization (Pd–Pd 2.798(1) Å) [108]. The reaction proceeded too fast for detection of an intermediate such as a mono-alkyne adduct like **39**. The different reactivity of **71** from that of the bis-1,3-butadiene complex **66** on treatment with PhC≡CH should be noted. Moreover, the formation of **74** demonstrates, for the first time, that an unsaturated hydrocarbon undergoes a C–C bond forming reaction on a Pd–Pd bond. Another example using a μ-propargyl system will be shown in Section 2.2.3. The μ-butenediylidene moiey bound on the dipalladium core in **74** is electrophilic, and one of the PPh_3 ligands reversibly migrates to the terminal carbon of μ-butenediylidene moiety to give **75** (Pd–Pd 2.811(4) Å).



74 **75**

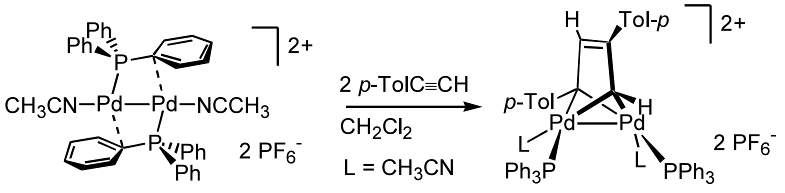
The reaction of the homoleptic acetonitrile dipalladium complex **9** with 1,6-diphenyl-1,3,5-hexatriene afforded the unique sandwich dipalladium complex **76** [113]. A Pd–Pd bonding interaction is indicated by the Pd–Pd distance (2.9156(6) Å). The oxidation state of the palladium atoms is obscure; the palladium atom may either be in +3 state with the μ-η^3:η^3-coordination mode of the triene, or in the +1 state with the μ-η^2:η^2:η^2-coordination mode. A very accurate calculation is needed for a precise estimation of the electronic structure. Interestingly, one of the triene ligands was liberated reversibly in acetonitrile with the other triene ligand remaining coordinated. The half-sandwich complex **77** thus formed no longer has the Pd–Pd bond.

The stereoisomer of **77**, namely the antifacial half-sandwich complex **78**, was also converted to the sandwich complex **76** by treatment with all-*trans*-1,6-diphenyl-1,3,5-triene. Interestingly in this case, *trans*,-*cis*,*trans*-triene was eliminated. This strongly suggests that during this reaction, a Pd–Pd bond is required for conversion of the η^3:η^3- to η^2:η^2-triene ligand, the latter being ready for ligand exchange. After this, the sandwich complex is formed. Thus, it was proved that the Pd–Pd bond formation or breaking is important in dinuclear sandwich–half sandwich interconversion.

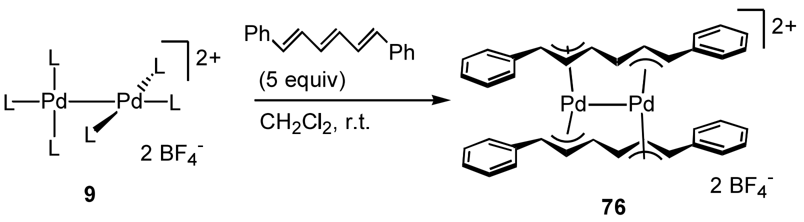
The results described so far in this section suggest that the coordination system involving a dipalladium core and an sp^2-carbon framework has unique and remarkable properties. Extension of this system to multipalladium–polyene complexes will be discussed later.

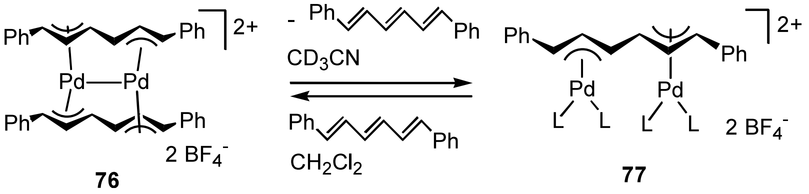
2.2.3. Organodipalladium complexes derived from R–Pd(II) and Pd(0)

One of the most popular methods to prepare organodipalladium complexes is the reaction between organopalladium(II) and palladium(0) as discussed in an



71 **74**

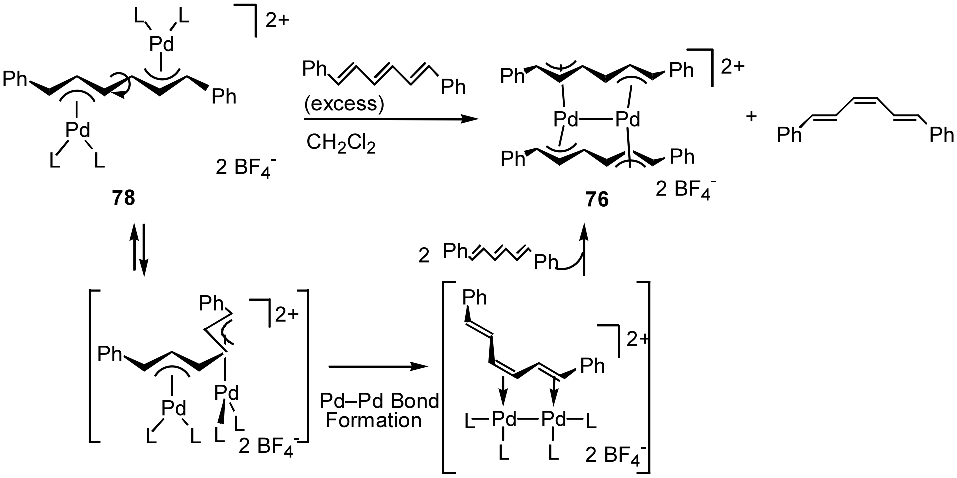


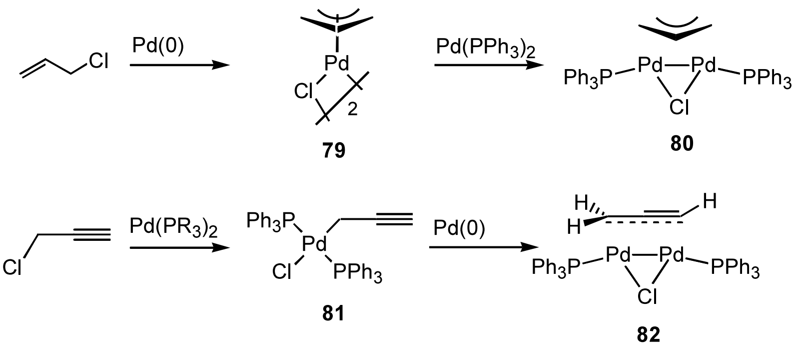


excellent review by Werner [15]. Such processes are very interesting since they are possibly involved in Pd(0)-catalyzed organic transformation. Thus oxidative addition of an organic halide to Pd(0) yields an organopalladium(II) complex which has a chance to react with another Pd(0) in the system. For example, oxidative addition of allyl halide to Pd(0) forms a η^3-allyl palladium(II) complex **79**, which further reacts with $Pd(PPh_3)_2$ to yield a μ-η^3-allyl dipalladium(I) complex **80** (Pd–Pd 2.623(1) Å) under very mild conditions [114–118]. Propargyl halides also give a corresponding dipalladium complex **82** via the formation of η^1-propargyl palladium(II) complex **81** [119,120]. Interestingly, the propargyl moiety is coordinated over the Pd–Pd bond (Pd–Pd 2.642(2) Å) in a propargyl/allenyl resonance manner with the linear C–C–C skeleton lying parallel to the Pd–Pd vector. The ratio of Pd(0)/phosphine determined the final distribution of the mono- and dinuclear complexes when propargyl halide was used in an equimolar amount; $[Pd(0)]/[PPh_3] = 1/2$ yielded a mononuclear complex of type **81**, while $[Pd(0)]/[PPh_3] = 1/1$ provided the dinuclear complex **82**. If excess propargyl halide is used with $[Pd(0)]/[PPh_3] = 1/1$, another product, $Pd(X)(\eta^3\text{-propargyl})(PPh_3)$, is obtained [121].

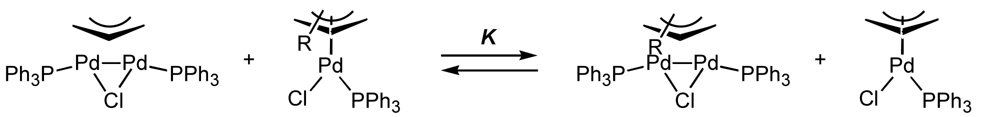
Recent attempts to compare systematically the bonding nature of allyl or propargyl moiety between a di- and a mononuclear palladium framework led to some important observations on structure and reactivity. In the initial investigation [122], η^3-allyl mono- and dinuclear palladium complexes were chosen. An equilibrium constant *K* shown in Eq. (2) (see table) obviously indicated that allyl groups having electron-withdrawing substituents favor binding to the dinuclear center rather than the mononuclear center.

This observation is reasonably explained by the electronic effect; there is a stronger back-bonding interaction in the dinuclear complexes compared to





79 **80** **81** **82**



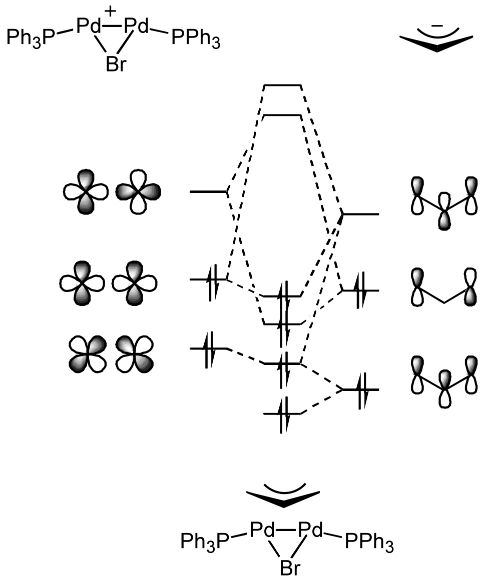
R	K
2-OCH_2Ph	9.2×10^{-3}
2-Me	1.5×10^{-2}
2-Cl	9.8
2-CN	1.4×10^{2}
2-COOMe	2.5×10^{2}
2-SO_2Ph	3.6×10^{2}

in $CDCl_3$, 25 °C

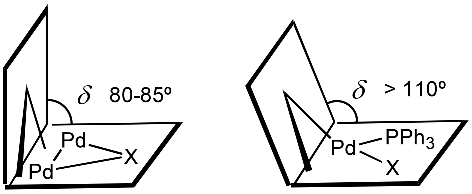
(2)

that in the mononuclear complexes. This explanation is supported by theoretical calculations [122,123]. Thus the electronic structure of the dinuclear complex (Scheme 3) is characterized by strong back-bonding interactions between the occupied dσ–dσ orbital of the Pd_2 fragment and the empty π* orbital of the allyl fragment. The occupied dπ–dπ orbital of Pd_2 fragment is also involved in back-bonding interaction to some extent owing to increase of the dπ–dπ energy level through an anti-bonding interaction with the filled p-orbital of the μ-Br ligand.

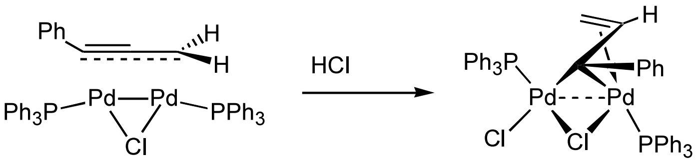
The strong back-donating interaction in dipalladium complexes also causes a remarkable change of the allyl coordination geometry compared to that in mononuclear complexes [122,123]. Thus, the dihedral angles between the coordination and the allyl planes in the dinuclear complexes were found to be much smaller (80–84°) than those in the mononuclear complexes (> 110°) (Scheme 4). As shown in the MO scheme for the dinuclear μ-allyl system above, the back-bonding interaction in the dipalladium complex involving overlap between the central carbon p-orbital and the dσ–dσ and dπ–dπ orbitals of Pd_2 becomes more favorable as the dihedral angle becomes smaller. On the other hand, the mononuclear η^3-allyl coordination is dominated by the donating interaction between the Pd dπ and the allyl nπ orbitals lacking a contribution of the central carbon p-orbital.



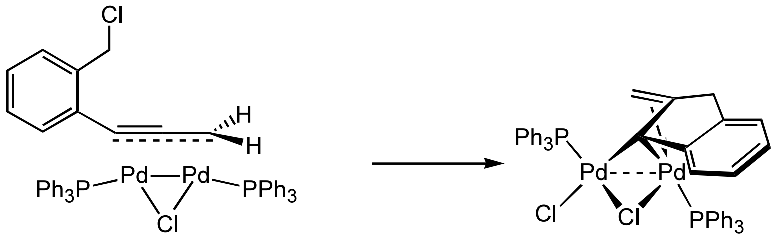
Scheme 3.



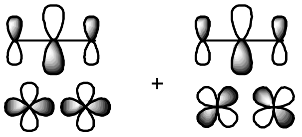
Scheme 4.



83 **84**



85 **86**



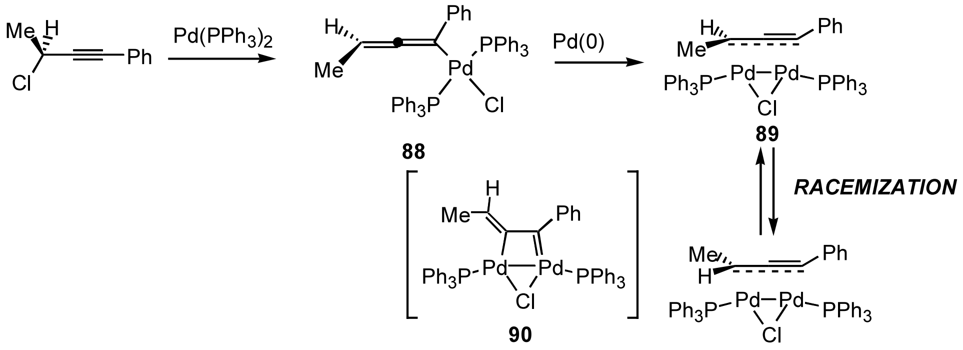
87

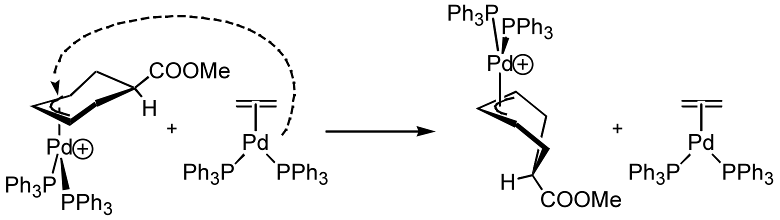
Strong back-bonding in dipalladium complexes also causes a dramatic change in the reactivity of the propargyl moiety. The μ-η^3-propargyl/allenyl moiety bound on a Pd–Pd bond of **83** accepts the attack of electrophiles such as H^+, Ac^+, etc. at the central carbon to afford μ-vinylcarbene dipalladium complexes such as **84** (Pd–Pd 2.868(1) Å) [119,120]. Intramolecular cyclization also proceeds in a same manner to afford **86** [120]. This reactivity in dinuclear complexes is in sharp contrast to that in mononuclear complexes; i.e. the η^3-propargyl/allenyl moiety bound on a mononuclear palladium center is known to accept nucleophiles at the central carbon [124–126]. Theoretical calculations indicate that the electrophilic addition to the propargyl/allenyl central carbon is led by the HOMO bearing a large lobe at the propargyl/allenyl central carbon (**87**), which is induced by mixing of the propargyl π and π* orbitals so as to enhance back-bonding. The μ-vinylcarbene dipalladium complex **84** and its analogue underwent C–C bond forming reactions with acetylene and organotin reagents [127].

Another new role of dinuclear propargyl/allenyl systems in organic chemistry is emerging. As described earlier in this section, the reaction of organopalladium(II) and palladium(0) that forms organodipalladium(I) complexes may be involved in catalytic systems employing organic halide and Pd(0). Interestingly, the formation of the dinuclear complex was found to lead to the configurational lability of mononuclear allenylpalladium(II) complexes [128]. The configurational stability of allenylpalladium(II) complex **88** was found quite high in the absence of Pd(0) species. After Pd(0) is generated or added, it reacts with the allenylpalladium(II) complex immediately to give the dinuclear complex **89**, which is supposed to be configurationally labile owing to a valence isomerization involving an achiral μ-vinyl intermediate **90**. The μ-allenyl/propargyl complex **89** can become a mediator for the racemization of **88**, since there is a fast allenyl exchange equilibrium between mono- and dinuclear complexes as observed in the allyl exchange system (vide supra). Detailed kinetic experiments showed that loss of optical activity of the allenyl moiety of **88** mediated by **89** takes place at the dinuclear site.

It should be noted that Pd(0) species also enhance the configurational lability of the η^3-allylpalladium(II) system, through the attack of Pd(0) at the allyl carbon, but not through Pd–Pd bond formation under certain conditions (Eq. (3)) [129–131]. The latter event was found to occur with retention of the configuration of the allyl fragment (Eq. (4)) [122].

The μ-cyclopentadienyl dipalladium complex **91** (Pd–Pd 2.609(1) Å) was prepared by the reactions of CpPd(II) complexes with Pd(0) [132,133]. Interestingly, the cyclopentadienyl moiety changed its coordination mode from η^5 for mononuclear Pd center to η^3 for the dinuclear Pd–Pd center. Thus, the $[Pd_2L_2(\mu\text{-}X)]$ fragment strongly favors a 4e-donating bridging ligand. This was supported by several theoretical calculations [34,105,122,123,134,135].

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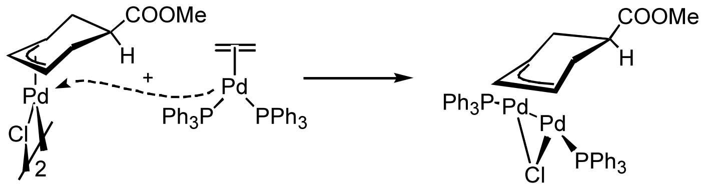
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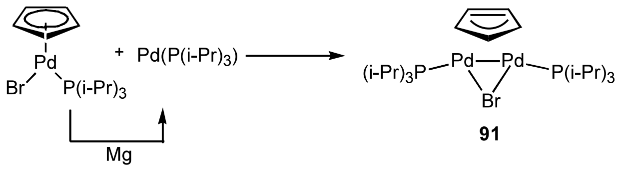

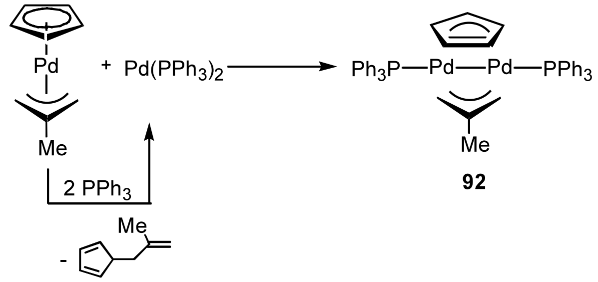

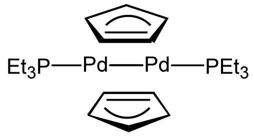
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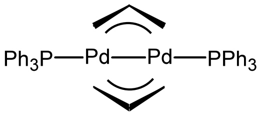
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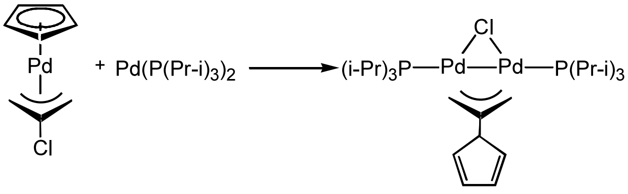
The dipalladium(I) complexes containing two unsaturated hydrocarbon ligands (sandwich type) were prepared from the corresponding dialkylpalladium(II) complexes. The complex **92** (Pd–Pd 2.679 Å) is generated by the reaction of CpPd(allyl) and phosphine, which is frequently used to generate the catalytically active Pd(0) species [11,136–138]. The sandwich dipalladium(I) complexes [(μ-Cp)$_2$Pd$_2$(PEt$_3$)$_2$] (**93**) (Pd–Pd 2.673(1) Å) and [(μ-allyl)$_2$Pd$_2$(PPh$_3$)$_2$] (**94**) (Pd–Pd 2.720 Å) can also be prepared in the same fashion [139–146].

A unique reaction occurred when the 2-chloroallylpalladium complex was used. The 2-cyclopentadienylallyldipalladium complex **95** was obtained probably via the allene elimination and migratory insertion steps [137].



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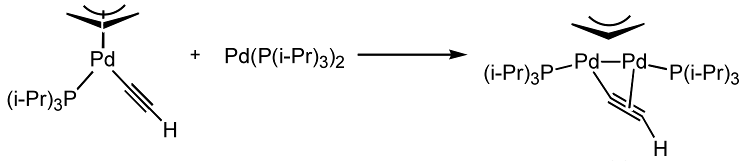
The allyl–alkynyl palladium complex also reacts with Pd(0) to afford the μ-allyl–μ-alkynyl dipalladium complex **96** (Pd–Pd 2.6597(4) Å) [147].



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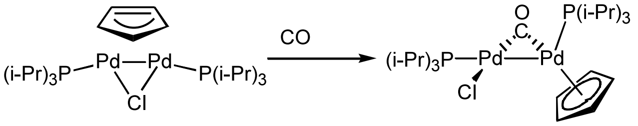
It is noteworthy that the chloro derivative of μ-Cp dipalladium complex **91** reacts with several 2e-donor ligands such as CO to afford the adduct **97** (Pd–Pd 2.675(1) Å) in which the Cp ligand is coordinated to a single Pd metal [148].



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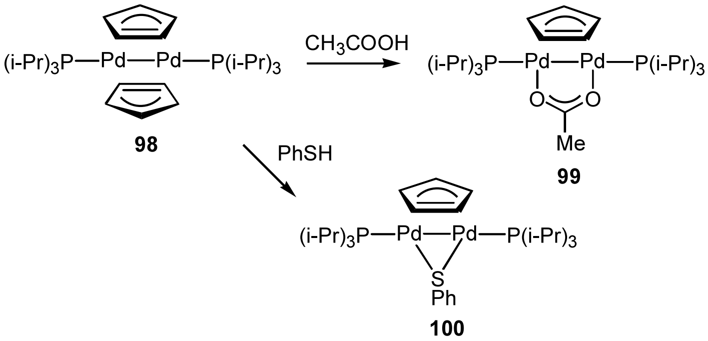
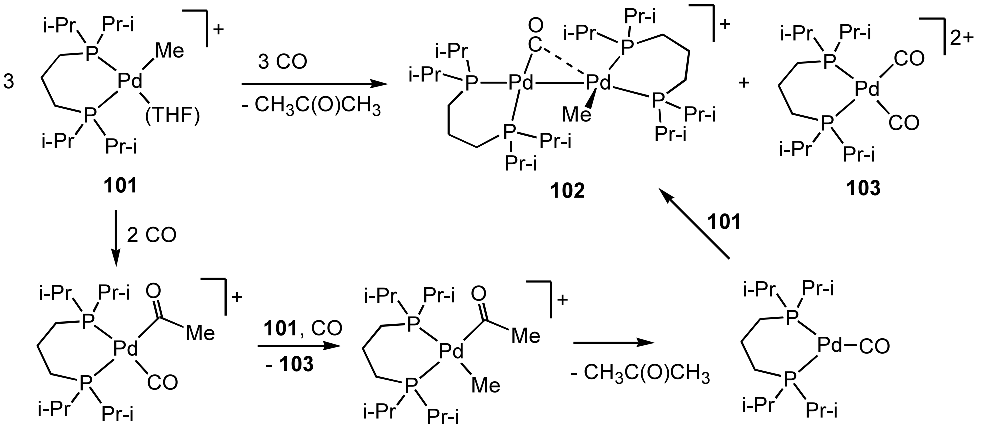
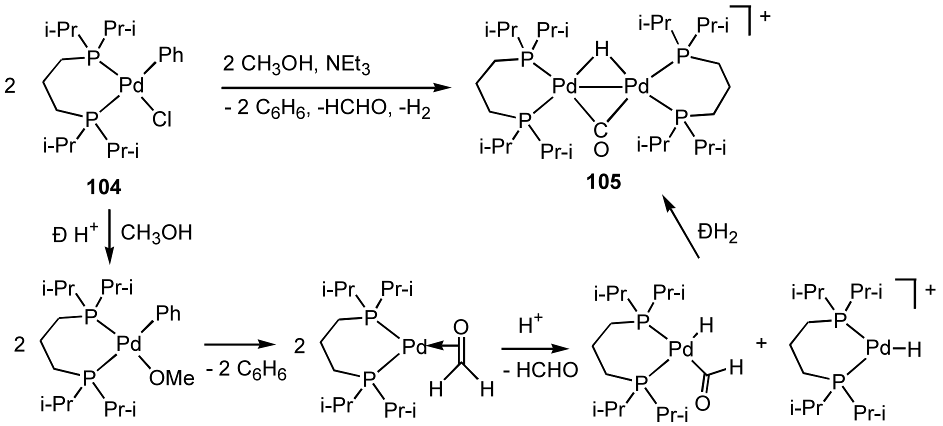
Several substitution reactions of the bridging ligands occur with the Pd–Pd bonded framework remaining intact [149]. Thus, reaction of the bis-μ-Cp dipalladium complex **98** with CH_3COOH afforded the μ-acetate dipalladium complex **99**, and the reaction with PhSH afforded the μ-thiolate dipalladium complex **100**. Interestingly, the μ-Cp ligand was selectively replaced in the reaction of μ-Cp–μ-allyldipalladium complexes. However, in such monoalkyl or dialkyl dipalladium systems, Pd–Pd bond cleavage occurred upon thermal decomposition or treatment with electrophiles such as HCl, MeI, etc. [138,149].

The cationic methylpalladium(II) complex **101**, which became a catalyst for olefin–CO alternating polymerization, reacted with CO to afford the methyldipalladium(I) complex **102** (Pd–Pd 2.6886(8) Å) containing a semi-bridging CO ligand [150]. In this case, Pd(0) was







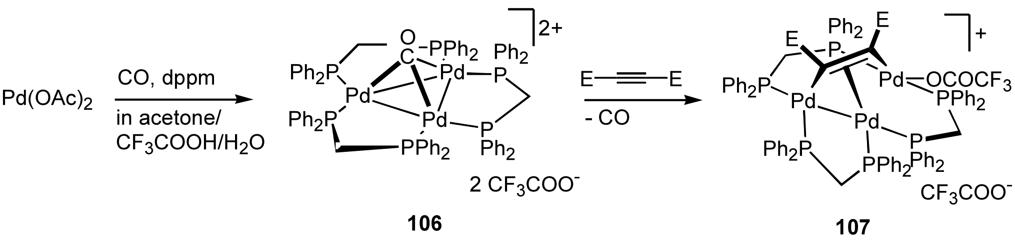
formed by the reductive elimination of acetone from the acetyl methyl palladium(II) complex.

The phenylpalladium(II) complex **104** was reduced by methanol to afford the μ-hydrido dipalladium(I) complex **105** (Pd–Pd 2.767(4) Å) [151].

2.3. Tri- and higher nuclear palladium complexes

Research concerning the reactivity of tri- and higher nuclear palladium complexes with unsaturated hydrocarbons remains very limited as well as their synthesis from mononuclear Pd complexes. In this review, only six unique examples are discussed.

Among the *triangulo*-Pd_3 clusters, the reactivity of the complex **106** has been studied extensively owing to its coordinative unsaturation (42e) [50]. The complex **106** was obtained by the reaction of $Pd(OAc)_2$ with CO and dppm in aqueous acid [152]. One reaction involving an unsaturated hydrocarbon was reported: the cluster **106** was found to react with dimethyl acetylenedicarboxylate (DMAD) to afford the DMAD adduct **107** with release of the CO ligand [153].



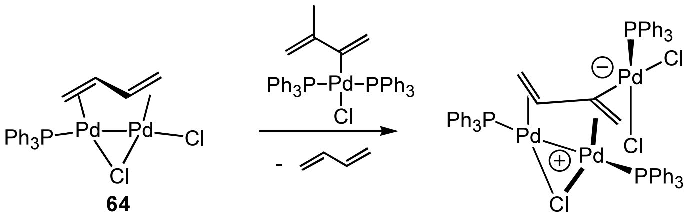
The exchange of the μ-1,3-butadiene ligand in the dipalladium(I) complex **64** with the 3-methyl-1,3-butadienylpalladium complex afforded a zwitterionic tripalladium cluster **108** [154]. It should be mentioned that zwitterionic forms are also favored in other dipalladium complexes (π-dienolate complex **109** [155], and π-phenolate complex **110** [156]).

A unique reaction proceeded between a triarylcyclopropenium bromide and Pd(0) to give a tripalladium cluster **111**, which contained two μ-C_3Ar_3 units derived by cleavage of one of the C–C bonds of the original cyclopropenium ion [157].

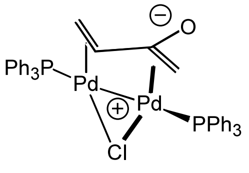
A unique triple oxidative addition of chloroform to Pd(0) afforded the μ-carbyne tetrapalladium complex **112** [158].

The tetrakis-triphenylphosphine Pd_3 complex **114** was obtained by reduction of the hydroxopalladium(II) complex **113**. In the complex **114**, two PPh_3 ligands bridge the linear Pd–Pd–Pd core in a μ-η^1:η^2:η^2 mode [159].

Finally, the chemistry of the one-dimensionally expanded organometallic sandwich chains should be mentioned. These were prepared by assembling palladium atoms between two α,ω-diphenylpolyene molecules [58]. The resulting structure is unique: three chains (two polyene chains and one Pd–Pd chain) are hybridized through sequential π-coordination. The following scheme shows an example employing 1,8-diphenyl-



64 **108**



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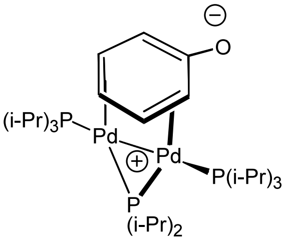

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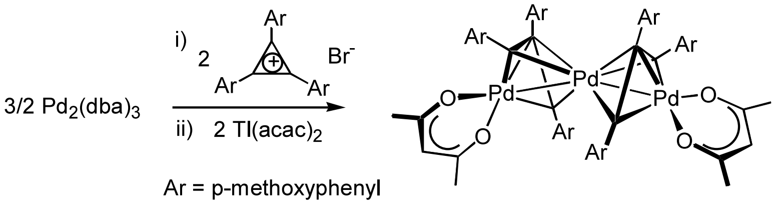

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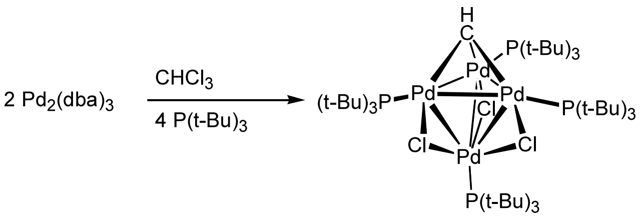

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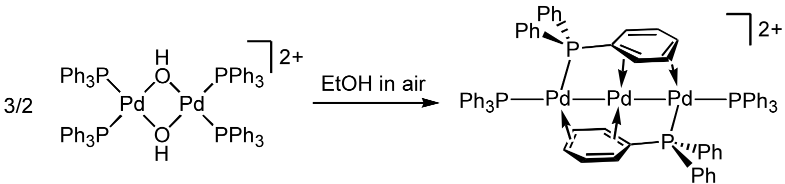
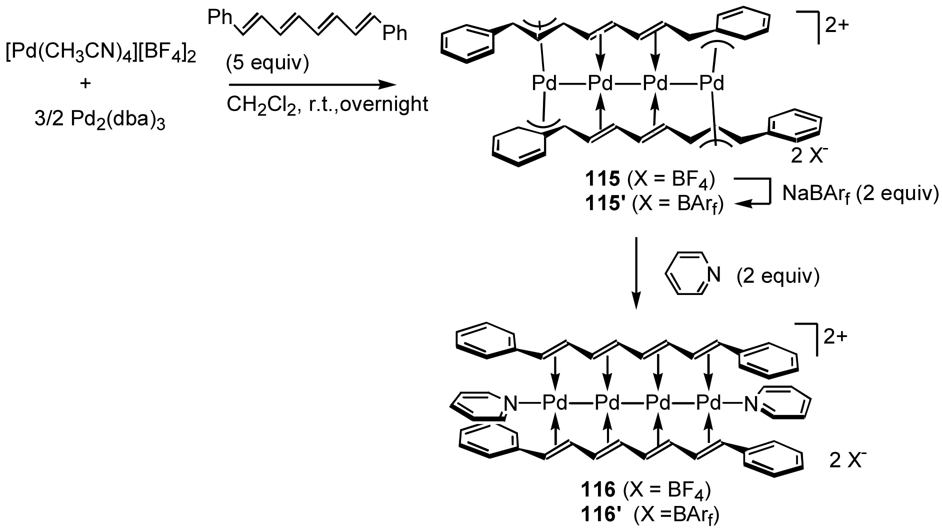
1,3,5,7-tetraene. Two coordination modes (μ-η^3:η^2:η^2:η^3-mode in **115** and μ-η^2:η^2:η^2:η^2-mode in **116**) were observed. Each has the one-dimensionally expandable form with the all-*trans* polyene framework. From a viewpoint of the unique physical and chemical properties of a palladium on carbon-surface such as graphite, the reactivity of these complexes is very interesting, and is currently under extensive investigation in our group.

3. Conclusion and perspectives

The study of organopalladium complexes containing Pd–Pd bonds is now proceeding at an accelerated rate. In this connection, a number of significant efforts have been made to date toward understanding stoichiometric reactions on the Pd–Pd bonds. An important key to such progress is the preparation of new, versatile, and highly reactive palladium complexes containing Pd–Pd bonds suitable for study of their organometallic reactions. However, at this time, few catalytic systems have been well-characterized which involve organopalladium complexes containing Pd–Pd bonds, even though some publications suggest the effectiveness of such complexes [17,18,160], particularly in the field reviewed by Moiseev and Vargaftik [17,18]. In the future, closer interplay between fundamental organometallic and catalytic chemistry involving multipalladium complexes is antici-



113 **114**



pated to lead to the discovery of new reactions in synthetic organic chemistry. Furthermore, it is expected that new and useful functional materials can be constructed from organometallic structures containing Pd–Pd bonds [161].

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