Accounts

Structure-Reactivity Relationship in Allyl and 2-Propynyl Complexes of Group 10 Metals Relevant to Homogeneous Catalysis

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Recent developments in the understanding of some fundamental reactions undergone by group 10 metal allyl and propargyl (2-propynyl) complexes are described. Emphasis was placed on the bonding-reactivity relationship of these complexes which are relevant as key intermediate models in transition metal catalyzed transformations of allylic and propargylic substrates as well as related transformations involving unsaturated hydrocarbons. The specific complexes surveyed include group 10 metal complexes of allyl and propargyl ligands bound to the metal both in η^1- and η^3-fashions. Specific reactions to be discussed include oxidative addition, nucleophilic and electrophilic attack at the allyl or propargyl ligands, and reductive elimination of the allyl ligands.

Increasing attention has been paid to metal mediated organic synthesis and homogeneously catalyzed reactions. For the development of highly elaborate and selective reactions in these fields, it seems of utmost importance to gain deep insight into the transformations of key metallic intermediates. Allylic complexes of transition metals are perhaps among the most important intermediates as well as starting materials for the above purposes.[1] The range of metals capable of forming the bond with the allyl group is wide, and thus the nature of carbon-metal bonding, in terms of both polarity and hapticity (η^1- and η^3-allyl), can vary from compound to compound. Moreover, the coordination environment also affects the polarity and hapticity of the allyl–metal bond in a significant manner. Because of these characteristics, it does not seem to be an easy task to find a correlation between structure/bonding aspects and reactivity patterns which is applicable to a wide range of allylmetal complexes. Even for allyl complexes of group 10 metals[2,3] of which the role in catalysis is receiving ever increasing attention since the pioneering studies by a few groups more than three decades ago,[4] it is only very recently that acceptable concepts on the bonding-reactivity correlation began to emerge.

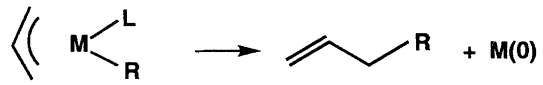
The chemistry of metal complexes containing propargyl (2-propynyl) ligands, electronically analogous to the allyl ligands, is also receiving increasing attention in recent years from both synthetic[5] and coordination[6] chemical points of view. We took additional interest in these complexes with a somewhat different expectation; that is, they might sometimes exhibit reactivity patterns which are potentially identical to those of the allylmetal complexes, but are sufficiently more precise to allow us to deduce otherwise unclear mechanistic pathways of the latter complexes.

In this account we describe the recent growth in our understanding of some fundamental transformations which are undergone by group 10 metal allyl and propargyl complexes. Emphasis will be placed on our own efforts to elucidate the bonding-reactivity relationship, primarily comprising isolation of key intermediate models and examination of their reaction profiles.

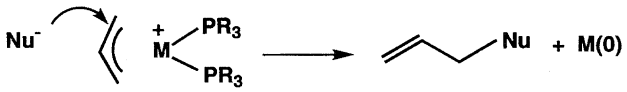
η^3-Allylmetal Mediated Catalytic Reactions

Before discussing the chemistry of isolable allylmetal complexes, we initially illustrate some specific examples of catalyses in which the reaction course is affected by the nature of metal and ligand in group 10 metal allyl complex intermediates. The first example is concerned with unique roles of metals in affecting efficiency and selectivity of some specific key steps involved in the catalytic cycle. For example, in cyclooligomerization of 1,3-dienes,[2,7] which is believed to proceed through reductive elimination of allyl and alkyl ligands on a metal center (e.g. Eq. 1), nickel catalysts are generally more effective than palladium catalysts, which in turn are far better catalysts than platinum catalysts. By contrast, catalytic efficiency in allylic substitution by means of soft nucleophiles (e.g. stabilized carbanions) proceeding through their external attack at the metal-bound allyl carbon (Eq. 2) shows a different metal dependency. Thus, this catalysis is more often carried out with palladium catalysts than with nickel catalysts.[2,3a,3d,8] Moreover, even platinum catalysts are also capable of catalyzing this transformation with

considerable ease.[9)]



(1)

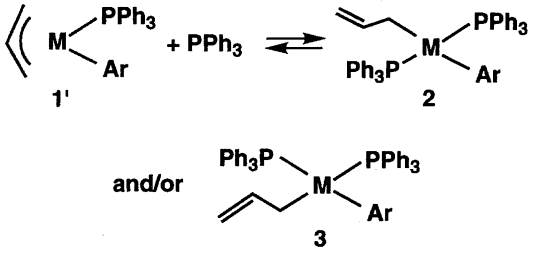


(2)

Another example of the critical metal effect is concerned with coupling of unsymmetrical allylic electrophiles with organometallic reagents, in which the reductive elimination similar to Eq. 1 plays a key role; nickel catalysts cause the C–C bond coupling at the more substituted allyl end with greater efficiency than the palladium catalysts, if chelate diphosphine complexes are used as a catalyst precursor.[10)] Moreover, the use of nickel catalysts with monodentate phosphines is not so efficient. This exemplifies the ligand effect as well, where the nature of the metal-bound ligand affects the course of the catalytic reactions in a critical way. An interesting ligand dependency of the product distribution in nickel-catalyzed diene oligomerization is a well-known example,[2)] although its origin is not yet fully understood. Of particular note is the finding that, in diene oligomerization and allylic cross coupling, palladium catalysts bearing ligand(s) other than phosphines exhibit unique activity and selectivity[7,11)] which cannot be attained by ordinary phosphine–palladium catalysts;[12)] see, e.g. clean allyl-allyl cross coupling to give 1,5-dienes[7)] and cross coupling between allylic chlorides and organometallics with net retention of configuration (Scheme 1).[11a)] Olefinic ligands, in particular, play a vital role in these reactions. Shedding more light on the origins of the metal and ligand effects mentioned above will be very rewarding.

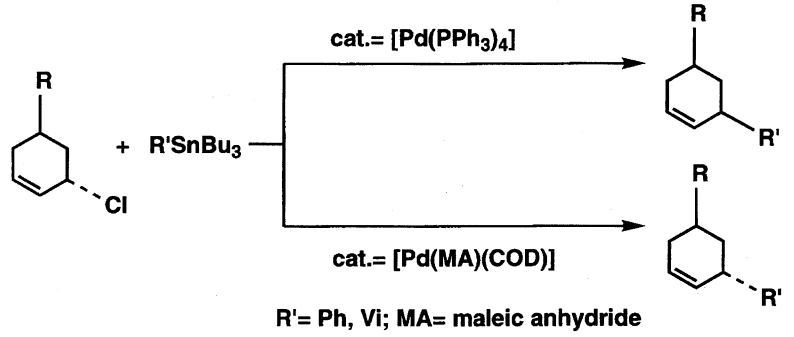
Bonding and Reactivity of η^3-Allyl and η^1-Allyl Complexes

Relative Stability of η^3-Allyl and η^1-Allylmetals. The interconversion between η^3- and η^1-bound forms of allylmetal complexes is one of the key issues in controlling selectivity of allylmetal-mediated synthetic reaction.[13)] In metal-catalyzed asymmetric allyl coupling, for example, the identity of the diastereo- and enantioface of the η^3-allyl ligand is lost during this interconversion.[13a,13b)] Ligand-induced η^3- to η^1-allyl conversion has long been a subject of extensive NMR spectroscopic studies primarily dealing with η^3-allylpalladium complexes containing readily ionizable ligands such as Cl and OAc.[13c)] Replacement of these ligands with organic groups (e.g. **1** or **1′** in Eq. 3) has a net effect of not only modeling key intermediates in catalysis but simplifying a dynamic system by elimination of additional pathways other than η^3–η^1-allyl interconversion, e.g. ionic dissociation and/or bridge bond formation of Cl and OAc ligands.[14)] We found[15)] that the ease of η^3- to η^1-allyl conversion, as expressed by the equilibrium constant of Eq. 3, decreases in the order: M = Pt > Pd > Ni. For example, in contrast to ready isolation of η^1-allylplatinum species **2** (M=Pt, Ar=C_6F_5, C_6HCl_4-2,3,5,6), PPh_3 ligand was not basic enough to convert **1′** where M = Pd and Ni to any stable η^1-allyl form which can be characterized by ^{1}H NMR spectroscopy. What was actually observed for M=Pd was rapid *syn–anti* allyl proton exchange on the NMR time scale via the *transient formation* of η^1-allyl species **2** and **3** (M = Pd, Ar = C_6H_5, C_6F_5, C_6HCl_4-2,3,5,6, $C_6H_3Cl_2$-2,5). For M = Ni, not even NMR evidence was obtained for a transient conversion into such η^1-allyl species.

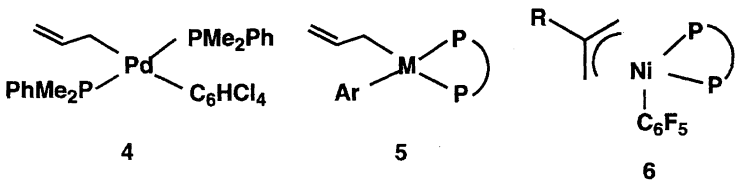


(3)

More basic phosphines such as PMe_2Ph, $Ph_2PCH_2CH_2PPh_2$ (dppe), and (*Z*)-$Ph_2PCH{=}CHPPh_2$ (dppen) stabilized the η^1-allylpalladium complexes **4** and **5** (M=Pd, Ar=C_6F_5, C_6HCl_4-2,3,5,6, $C_6H_3Cl_2$-2,5),[15b,15c,15d)] but similar attempts to obtain the η^1-allylnickel analogues failed (Scheme 2).[15e,15f)] Instead of the η^1-allyl form, the 18-electron η^3-allylnickel complex **6** was the ground state structure of a species generated when one molar amount of dppen was added to a solution of [Ni(η^3-CH_2CRCH_2)(C_6F_5)(PPh_3)] (R = H, Me). The variable temperature ^{1}H NMR spectra of **6** suggested transient formation of 16-electron η^1-allyl



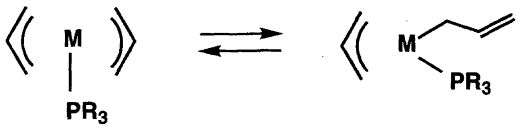
Scheme 1.



4 5 6

Scheme 2.

species **5** (M = Ni, Ar = C_6F_5). Others also noted that the tendency of Ni to form 18-electron η^3-allyl species was much stronger than that of Pd in the equilibrium mixture of complexes which were generated by adding PR_3 to bis(η^3-allyl)metal complexes (Eq. 4).[16]



(4)

The different tendencies of platinum and palladium η^3-allyl complexes to be converted to the η^1-allyl form also manifested themselves in the different stability trends of η^3-propargyl[17] (see later) and η^3-oxatrimethylenemethane complexes[18] of these metals. In the latter case, the spectroscopic and X-ray structure evidence indicated[18a,18b] that the ground state structure of the palladium complexes coordinated with the oxatrimethylenemethane ligand contains a greater contribution of the canonical form **7** and a smaller contribution of **8** than does the structure of the corresponding platinum complexes (Scheme 3). Moreover, in agreement with such differences in the bonding nature, protonation of **7** to form η^3-(2-hydroxyallyl)metal complex occurs more readily with the palladium analog than the platinum analog.

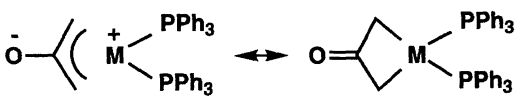
Origin of the Different Stability of η^3-Allyl and η^1-Allylmetals. Among group 10 metals, Ni was shown to have the strongest tendency to take the 18-electron η^3-allyl geometry, as far as steric congestion will allow. This is in agreement with the general trend that Ni(II) complexes are much more prone to take five-coordinated 18-electron structures than Pd(II) and Pt(II) complexes.[19] The covalent radii of Pd and Pt are about the same,[20] and thus the different tendency of these two metals to form η^1-allyl forms (Pt>Pd) would be electronic in origin, as explained below.

We suggest that the electronic configuration of the metal atom in η^3-allylmetal(II) complexes is intrinsically different from that in η^1-allylmeta(II) complexes and lies closer to that in the zerovalent complexes than the latter does; i.e. in terms of the GVB description developed by Goddard,[21] η^3-allyl complexes require the metal atom to have the electronic configuration with more d^{10} (configuration in M(0) complex) and less d^9s^1 (configuration in M(II) complex) character than do η^1-allyl complexes. As the ground state of Pd atom is d^{10} and that of Pt is d^9s^1, the observed weaker tendency of Pd complexes than of Pt complexes to take the η^1-allyl linkage is understandable. The electronic structure of the metal atom in the η^3-allyl form proposed above can also nicely explain the uniquely facile nucleophilic attack at the platinum-bound η^3-allyl ligand (see below).

Direct Nucleophilic Attack at η^3-Allyl Ligand. Especially unique in reactions of η^3-allylmetal complexes is the attack of certain nucleophiles (e.g. β-dicarbonyl anions, amines, etc.) at the η^3-allyl carbon from the side opposite to the metal atom (Eq. 2).[22] An analogous nucleophilic attack at the η^1-bound alkyl carbon with inversion of configuration is known to occur,[23] but its occurrence is limited (e.g. when assisted by increase of the formal oxidation state of the metal). An S_N2' attack at a η^1-allylmetal intermediate has been proposed,[24a] but later studies cast doubt about this possibility.[24b,24c] In fact, on the contrary, the η^1-allylmetal linkage is very much susceptible to the attack of *electrophiles*, as discussed later.

The MO calculations on Eq. 2 suggested[25] that the site of the nucleophilic attack is not charge-controlled, since the allylic terminal carbon bears a greater electron density than the central carbon. Rather, the reaction is frontier orbital-controlled through good overlap between a lone pair orbital of Nu^- and an LUMO (see **9**) of the complex bearing π-acidic ligands (PR_3) (Scheme 4). The nucleophile can attack the center carbon of the η^3-allyl ligands under different conditions.[26] For example, introduction of σ-donor ligands, e.g. amines, instead of phosphines, directs the site of the nucleophilic attack to the center carbon of the η^3-allyl ligand bound to Pd by increasing the LUMO coefficient at this carbon.[26a] Notice, also, a related finding[26b,26c] that the attack at the central carbon in allyl complexes of other metals (e.g. those of Ir^{III}) is a kinetic path and that at the terminal carbon is a thermodynamic path.

Of particular relevance to the nature of η^3-allyl–metal bonding proposed above is the ease with which a C–C bond formation via the external attack of $CH(COMe)_2^-$ ion at the η^3-allylplatinum cation proceeds (only less than 10^3 times as slow as that the at the η^3-allylpalladium cation).[9d] This is a remarkably small reactivity difference for a formal reduction



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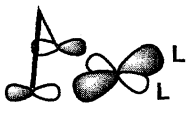
Scheme 3.



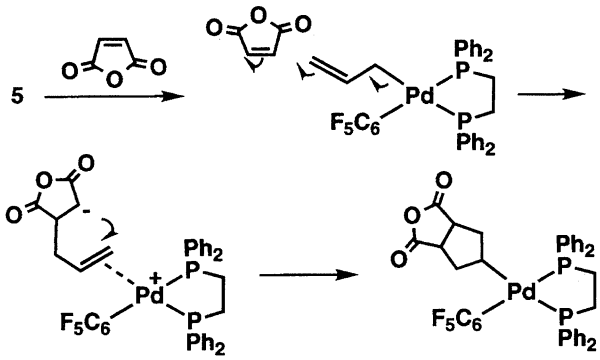
9

Scheme 4.

of Pd(II) and Pt(II), as compared in particular to the rate difference in the reductive elimination of dialkylpalladium and platinum complexes (Eq. 5), which was predicted to amount to a factor of 10^{22} (assuming comparable $\Delta S^{\ddagger}$ terms for the calculated difference of $\Delta H^{\ddagger}=30$ kcal mol^{-1}).[21] The principal origin of this big difference between the two metals in the activation barrier to Eq. 5 is the large difference in reaction exothermicity (Pd≫Pt), which in turn originates from the different character of the metal atom configuration in dialkylmetals (d^9s^1) and zerovalent metal complexes (d^{10}), and from the different ground state configuration of the two metals (see above).[21] On the other hand, as the Pt atom in η^3-allyl complexes has more d^{10} character than dialkylplatinums, the energy cost paid by Pt atom during the proceeding of the nucleophilic attack would be less than that required during the proceeding of Eq. 5. Furthermore, energy released upon the reduction of Pd(II) would be smaller in the reaction of η^3-allylpalladiums than in that of dialkylpalladiums. Thus, we suggest that the large difference of the reaction exothermicity in the reductive elimination of dialkylpalladium and -platinum (Eq. 5) would diminish considerably in the direct nucleophilic attack at the η^3-allyl ligand shown in Eq. 2; this was indeed the case.

(5)

Electrophilic Attack on η^3- and η^1-Allyl Ligands. In contrast to the electrophilic nature of the η^3-allyl ligand, the η^1-allyl ligand is nucleophilic. It seems that the η^1-allyl carbons bear considerable negative charge. This trend may become particularly important in comparing reactivity patterns of η^1- and η^3-allyl carbons; as shown in Scheme 5, we found that the complex **5** simultaneously containing η^1-allyl and aryl ligands reacted with some electrophiles with exclusive cleavage of the η^1-allyl–metal bond, whereas similar competition between C_6F_5 and the η^3-allyl ligand in complex **1′** (M = Pd, Ar = C_6F_5) afforded C_6F_5E almost exclusively.[15b] The η^1-allylpalladiums also react with electron-deficient olefins to give [3+2] cycloadducts (Scheme 6).[3b,15b] See also Ref. 27 for possible implication of nucleophilic η^1-allylpalladiums in application to organic syntheses in which insertion of C=O or C=N bond into the Pd–allyl bond is assumed. However, the precise mechanism of insertion of carbon monoxide[27d] into the Pd–allyl bond has not yet been elucidated. The role of η^1-allylpalladium intermediates in olefin insertion into the Pd–allyl bond has also been discussed.[28]

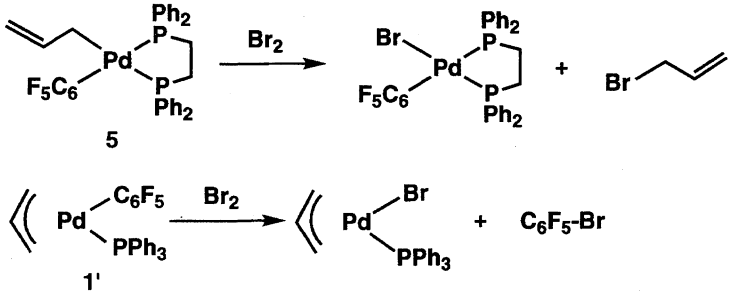


Scheme 6.

Reductive Elimination of η^3-Allyl and η^1-Allylmetals. We have examined the ease of reductive elimination of allyl(organo)metal complexes (Eq. 1) as a function of added ligand and the nature of metal.[15e,15f,29] Representative results are shown in Table 1. The following features are of particular relevance to the origin of the metal effect in catalysis and the relative ease of reductive elimination of η^3- and η^1-allylmetal species.

(1) The rate of the spontaneous reductive elimination of the η^3-allylpalladium and nickel complexes **1** (M = Ni, Pd; R = $C_6H_3Cl_2$, C_6F_5; L = PPh_3, $P(OPh)_3$) was not affected by the addition of excess PPh_3 or $P(OPh)_3$. This may rule out the participation, into the rate-determining step of the C–C bond formation, of η^1-allyl species **3**, the Pd analogue of which existed as a transient species in the dynamic NMR phenomena. The requirement for the two coupling groups to be located cis to each other was evidenced by regiospecific coupling of well-characterizable regioisomers **10** and **11** to give **12** and **13** respectively (Scheme 7).[29b,29c]

(2) The ratio of the first-order rate constant for the reductive elimination of **1** (M=Ni, R=$C_6H_3Cl_2$, L=PPh_3) at 0 °C in toluene (0.077 h^{-1}) vs. that of **1** (M=Pd, R=$C_6H_3Cl_2$, L=PPh_3) (0.0029 h^{-1}; extrapolated by using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) amounted to 26. This comparison, the first in the organonickel and organopalladium reactivity for the reductive elimination where the complex composition and reaction pathway are identical, is in good accord with the theoretical prediction[30] that dialkylnickels give a lower activation barrier to the reductive elimination than dialkylpalladiums. The

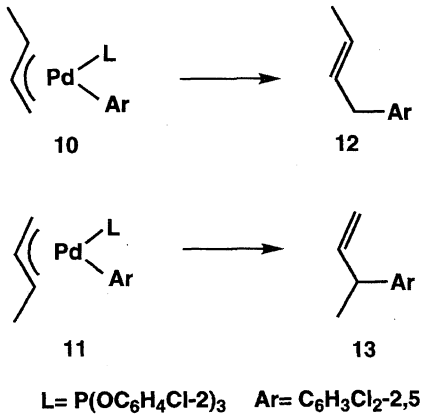


Scheme 5.

Table 1. First-Order Rate Constants for Reductive Elimination of [M(η^3-CH_2CHCH_2)-(R)(L)] in Toluene

Complex			Addend	Concn	Temp	Rate const.
M	R	L		mol dm^{-3}	°C	h^{-1}
Pd[a]	$C_6H_3Cl_2$-2,5	PPh_3	PPh_3	0.057	30	0.212
				0.120	30	0.211
				0.200	30	0.201
				0.200	40	0.693
			dppe	0.200	40	0.056
		$P(OPh)_3$	$P(OPh)_3$	0.130	30	1.03
				0.260	30	0.998
		$AsPh_3$	$AsPh_3$	0.200	30	0.438
Ni[a]	$C_6H_3Cl_2$-2,5	PPh_3	None	—	0	0.069
			PPh_3	0.02	0	0.071
				0.10	0	0.084
Ni[b]	C_6F_5	PPh_3	None	—	116	1.21
			PPh_3	0.50	116	1.46
			dppe	0.20	10	0.767

a) Initial concentration, 0.020 mol dm^{-3}. b) Initial concentration, 0.10 mol dm^{-3}.



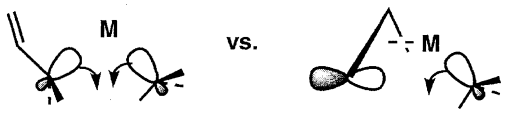
Scheme 7.

corresponding platinum analogue **1** (M=Pt, R=$C_6H_3Cl_2$, L=PPh_3) did not undergo the reductive elimination at all under the similar conditions.[9d] Thus, the ease of Eq. 1 decreases in the order: M=Ni>Pd≫Pt.

(3) Addition of chelate diphosphines to Ni complex **1** (M=Ni, R=$C_6H_3Cl_2$, L=PPh_3) remarkably *enhanced* the reductive elimination, whereas that to Pd analogue **1** (M=Pd, R=$C_6H_3Cl_2$, L=PPh_3) *retarded* the reaction. As already pointed out, the primary species formed on addition of dppe to **1** is **6** (M = Ni) or **5** (M = Pd). We confirmed[15e,15f] that the 18-electron η^3-allylnickel [Ni(η^3-CH_2CRCH_2)(C_6F_5)-(dppe)] is by far more labile (ca. 10^8 times) than the 16-electron η^3-allyl counterpart [Ni(η^3-CH_2CRCH_2)(C_6F_5)(PPh_3)] (R=H, Me) with respect to the reductive elimination. On the other hand, the η^1-allylpalladiums **5** (M=Pd) were less reactive than **1** (M=Pd). Moreover, the transient η^1-allyl isomer **5** (M=Ni, Ar=C_6F_5) was deduced to be much less reactive than **6** on the basis of the finding that the methylnickel complex [Ni(CH_3)(C_6F_5)(dppen)] underwent the reductive elimination much less easily than **6**.[15e] In deducing this argument, we assumed that the methyl complex has the reactivity comparable to or even higher than the η^1-allyl complex, since thermolysis of some Pt(IV), Pd(IV), and Au(III) complexes which simultaneously contain the methyl and the η^1-allyl ligands afforded coupling products from the methyl in amounts comparable to or higher than those from the η^1-allyl.[31,32]

We tentatively propose here possible origins of easier reductive elimination of the η^3-allyl than of the η^1-allyl ligand. As shown in Scheme 8, left, the η^1-bound allyl carbon may use primarily an sp^3-hybridized orbital for the bond with the metal, which then necessarily has to change its direction toward the C–C bond to be eliminated during the reductive elimination. This kind of pivotal movement of the sp^3-hybridized alkyl ligand was shown to produce a considerable activation barrier to the reductive elimination.[21] On the other hand, the η^3-bound allyl carbon would use an orbital with a less sp^3 and more p character for the bond with the metal. This orbital may certainly be oriented to the direction of the C–C bond to be newly formed in the reductive elimination more preferably than in the η^1-allyl case (Scheme 8, right), contributing to a decrease of the activation barrier.

The more recent MO analysis with the higher level calculations suggested, however, a rather low barrier process of the reductive elimination of [Pd(η^3-C_3H_5)(H)(PH_3)] via the η^1-allyl intermediate [Pd(η^1-C_3H_5)(H)(PH_3)], or [Pd-(η^1-C_3H_5)(H)(PH_3)$_2$] if there is additional PH_3 present.[33] The choice of the reaction course in the actual catalytic cycle might be affected by a delicate balance of electronic and

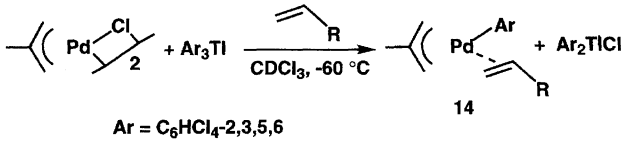


Scheme 8.

steric factors of allylic and η^1-organic groups to be coupled as well as of PR_3 ligands.

Roles of Olefinic Ligand in Allylic Cross Coupling

Reductive Elimination of η^3-Allyl Complexes Promoted by Olefin Coordination. Kinetic studies on spontaneous reductive elimination of η^3-allylpalladium complexes **1** (M=Pd) (see Table 1) indicated that the rate of Eq. 1 increases as the π-accepting ability of L becomes larger ($L=AsPh_3 < PPh_3 < P(OPh)_3$).[29a] This result, together with the remarkable accelerating effect of olefins on some catalytic allylic cross coupling discussed earlier, led us to examine how reactive these complexes are if L is replaced, by any means, by a much more π-acidic ligand, i.e. an olefin. Thus, we found that addition of olefins having electron-withdrawing substituents to **1** (M = Pd, L = $AsPh_3$) greatly accelerated the reductive elimination.[29a,34] A quite similar accelerating effect of adding olefins was found in the reductive elimination of a nickel complex, [Ni(η^3-CH_2CMeCH_2)(C_6F_5)(PPh_3)],[15e] as well as of allyl(methyl)metal complexes, [M(η^3-CH_2CHCH_2)(CH_3)(PPh_3)] (M = Pd, Pt).[35] Although we could not detect an olefin-coordinated intermediate spectrally during these reductive elimination reactions, an analysis of the detailed kinetic results in the case of the palladium complexes led us to suggest the composition of the intermediate having high reactivity,[29a] i.e. **1** (M = Pd, L = olefin). In order to confirm this kinetic implication, we separately generated η^3-allyl(olefin)palladium complexes **14** and examined their stability and reactivity profiles. Generation and NMR characterization of **14** were accomplished according to Eq. 6 at −60 °C.[29a] Raising the temperature of the solution containing **14** resulted in a clean reductive elimination to allow kinetic examination. The kinetic data in Table 2 showing the higher reactivity of the complex having the more electron-withdrawing olefin ligand are particularly noteworthy.



(6)

Table 2. First-Order Rate Constants for Reductive Elimination of **14** in Toluene

Olefin	Temp / °C	Rate const. / h^{-1}
$CH_2=CHC_6H_5$	10	0.281
$CH_2=CHC_6H_4OMe$-4	10	0.136
$CH_2=CHC_6H_4Me$-4	10	0.221
$CH_2=CHC_6H_4Cl$-4	10	1.01
$CH_2=CHC_6H_4NO_2$-4	10	2.44
	−10	0.175
Z-MeOOCCH=CHCOOMe	−45	2.71[a]
$CH_2=CHCOOMe$	−10	1.23
$CH_2=CHCN$	−10	2.56

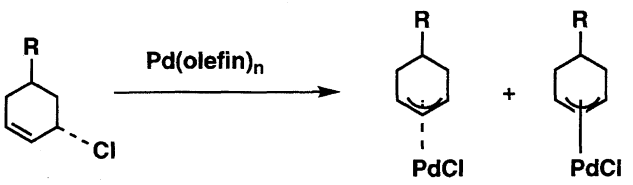
a) In $CDCl_3$.

The extended Hückel MO calculations on the interaction between a fragment, [Pd(η^3-CH_2CHCH_2)(CH_3)], and an olefin ligand revealed that the metal to olefin π back bond interaction stabilizes the η^3-allyl(olefin)metal moiety both in the ground state and, in particular, in the transition state of the reductive elimination step, if the olefin C=C axis lies within the coordination plane.[29a] Coordination of the C=C bond in the plane, a rather unfamiliar situation in four-coordinated olefin complexes of Pd(II) and Pt(II),[36] was actually demonstrated by both X-ray structure determinations and solution NMR studies of some relevant η^3-allyl(olefin)palladium and -platinum complexes.[37,38]

As the C–C bond formation between methyl and η^3-CH_2CHCH_2 ligands proceeds, the in-plane dπ orbital of the [Pd(η^3-CH_2CHCH_2)(CH_3)] fragment rises sharply primarily due to accumulation of the electron density on Pd. Importantly, it is this accumulation of the electron density that is primarily responsible for the activation barrier to the reductive elimination.[30] It is thus apparent that the energy of the transition state of the reductive elimination (Eq. 1) is lowered considerably by changing L from PR_3 to olefin which is capable of π interacting with the dπ orbital better than PR_3, resulting in effective electron flow from Pd to the olefin.[39]

Olefin Effect on Stereochemistry of η^3-Allylmetal Formation. In the cross coupling shown in Scheme 1, the nature of the olefin ligand plays a role of not only affecting the reaction rate but controlling the stereochemical outcome.[11a] Thus, when an electron-withdrawing olefin (e.g. maleic anhydride) was added as a co-catalyst to a catalyst precursor [Pd(η^3-CH_2CHCH_2)(Cl)]$_2$, the reaction afforded the coupling product with net retention of configuration (>90% selectivity) in benzene, CH_2Cl_2, or THF, while the product with net inversion (>95% selectivity) was obtained with a combination of [Pd(η^3-CH_2CHCH_2)(Cl)]$_2$/cyclooctadiene or /styrene. The choice of the solvent is also important; the inversion product dominated (>95%) in the reaction carried out in MeCN even when the catalyst precursor, [Pd(η^3-CH_2CHCH_2)(Cl)]$_2$/maleic anhydride was used.

We separately confirmed[11a] that the above stereochemical result is attributable to a novel dependency of the stereochemistry in oxidative addition of allylic chlorides with Pd(0) complexes upon ligands and solvents. As shown in Table 3, the oxidative addition (Eq. 7) in CH_2Cl_2 with a Pd(0) complex containing electron-donating olefin, e.g. norbornene (NBE), afforded predominantly anti addition product, while a complex containing electron-withdrawing olefins, e.g. maleic anhydride and fumaronitrile, which is either isolable or can be generated in situ from Pd(NBE)$_3$ and the olefin, underwent the unusual syn oxidative addition.



(7)

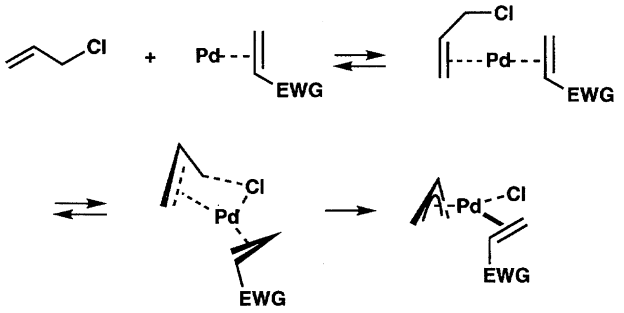
Table 3. Stereochemistry of Oxidative Addition of 5-(Methoxycarbonyl)-2-cyclohexenyl Chloride to Pd(0) Complexes[a)]

Complex	Solvent	Addend	mol amt./Pd	%syn	%anti
$[Pd_2(dba)_3]$	Benzene			100	0
	CH_2Cl_2			94	6
	THF			95	5
	Acetone			75	25
	DMF			29	71
	MeCN			5	95
	DMSO			3	97
[Pd(COD)(MA)]	Benzene			100	0
	CH_2Cl_2			91	9
		Styrene	10	62	38
		COD	10	58	42
		NBE	10	58	42
	MeCN			4	96
$[Pd(NBE)_2(MA)]$	CH_2Cl_2			92	8
		NBE	10	34	66
$[Pd(NBE)_3]$	CH_2Cl_2			7	93
		AN	5	20	80
		DMFUM	5	87	13
		FMN	5	93	7

a) Abbreviation: dba, dibenzylideneacetone. COD, 1,5-cyclooctadiene. MA, maleic anhydride. NBE, norbornene, AN, acrylonitrile. DMFUM, dimethyl fumarate. FMN, fumaronitrile.

Even with the electron-withdrawing olefin complexes, the reaction proceeded in the usual anti fashion if the solvent is changed to MeCN, DMF, or DMSO.

These results, together with the reactivity patterns in the oxidative addition of Pd(0) complexes with some methyl-substituted allyl chlorides (RR′C=CR″CHR‴Cl; R, R′, R″, R‴=H and/or Me), led us to propose a course of the novel syn addition as proceeding through an initial coordination of the C=C bond of the substrate, followed by the Cl–Pd interaction (Scheme 9). In the case of the reactions with the electron-donating olefin complexes or with the electron-withdrawing olefin complexes carried out in polar solvents, the metal atom coordinated with the allylic C=C bond would attack the Cl-bearing carbon from the side opposite to the Cl-atom. This process, which we call S_N2-coord path, may be the most common path in the oxidative addition of allylic



Scheme 9.

electropliles with Pd(0) and Pt(0) complexes, and we will discuss its feasibility in more detail in the later section.

It seems also interesting to note the decisive role of the electron-withdrawing olefin ligands in both the syn oxidative addition of allylic acetates to Pd(0) complexes[40,41)] and the syn reductive elimination of η^3-allyl(acetato)palladium complexes.[42)]

Comparison of Reactivity Patterns between η^3-Allylic and η^1-Organic Ligands

It seems appropriate here to compare some reactivity patterns of η^3-allylmetal complexes with those of organic ligands η^1-bound to the group 10 metals.

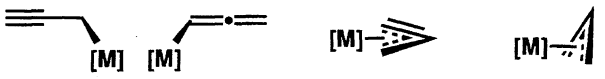
Spontaneous Reductive Elimination. The effect of adding free phosphine on the rate of the reductive elimination of diorganometals of group 10 elements appears to be diverse. A dissociative role of PR_3 in enhancing the reductive elimination of $[PdMe_2(PR_3)_2]$,[43)] which was reported at a relatively early stage of the investigations in this field, now is not warranted to be a prototype example. The later studies on the reaction of the more reactive complexes, such as $[PdMe(R')(PR_3)_2]$ (R′= aryl, vinyl),[44)] $[PtH(R)(PPh_3)_2]$,[45)] and $[Pd(\eta^3\text{-allyl})(Ar)(PR_3)]$,[29)] indicated that the PR_3 ligand remains coordinated during the reductive elimination.

Coordination of an additional PR_3 ligand to a 16-electron moiety $[MR'_2(PR_3)_2]$ forming an 18-electron intermediate $[MR'_2(PR_3)_3]$ has been found to accelerate the reaction of nickel[46)] and platinum[47)] complexes. Now the similar effect, coupled with the greater ease of the reductive elimination of the η^3-allyl than the η^1-allyl group, may have contributed to the unusually facile reductive elimination of the 18-electron, η^3-allylnickel complexes, $[Ni(\eta^3\text{-allyl})(Ar)(diphos)]$.[15e,15f)]

Olefin-Promoted Reductive Elimination. A dramatic acceleration of the reductive elimination of η^3-allyl(aryl)-palladiums via the 16-electron olefin complex intermediate **14** shows a sharp contrast with the failure of olefins to accelerate the reaction of $[PdR'_2(PR_3)_2]$[48)] as well as with the acceleration of the reaction of $[NiR_2L_2]$ (L = PR_3, bipy) not through the 16-electron but 18-electron olefin complex intermediate.[49)] The olefins were also shown to accelerate the reaction of $PdR_2(bipy)$,[50)] but the question of what is the actual intermediate responsible for this acceleration remains unresolved.

Propargyl/Allenyl Complexes of Palladium and Platinum

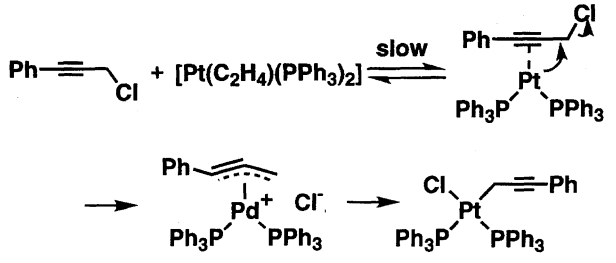
As mentioned in the general introduction, electronically propargyl/allenyl (1,2-propadienyl) complexes are analogs of the allyl complexes. However, η^1-form is much more common than η^3-form in propargyl/allenyl complexes, while η^3-form is the case in allyl complexes. The first platinum[51)] and palladium[52)] η^1-propargyl/allenyl complexes were reported in 1969 and 1983, respectively, but it is only very recently that η^3-propargylplatinum (1993)[53)] and palladium (1995)[17)] complexes were first prepared and characterized. No nickel analog has been reported yet. The structures of these complexes are depicted in Scheme 10. The dihedral an-



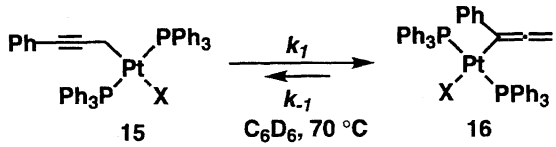
Scheme 10.

gle between the coordination plane and the plane on which are metal and three carbons is nearly 90° in η^1-propargyl η^1-allenyl complexes of palladium and platinum[54,55] In η^3-propargyl complexes, all three carbons of η^3-propargyl moiety and the metal coordination plane are almost coplanar,[17,56b] which is completely different from the case of the corresponding η^1-propargyl/allenyl complexes and η^3-allyl complexes. The η^3-propargyl complexes react with nucleophiles at the central carbon exclusively,[53,56] giving a metallacyclobutene initially, which is also in contrast to the common site of the attack at the η^3-allyl complexes (see before). Several reaction paths for the palladium-catalyzed reactions of propargyl electrophiles have been proposed by primarily invoking η^1-propargyl/allenyl intermediates,[5] but they should be reconsidered more carefully in view of the recent progress in η^3-propargy chemistry outlined above.

Oxidative Addition of Propargyl Electrophile to Pt(0) Complexes. The reaction of 3-phenyl-2-propynyl chloride with $[Pt(C_2H_4)(PPh_3)_2]$ gives *cis*-$[Pt(PhC{\equiv}CCH_2)(Cl)(PPh_3)_2]$ exclusively. This is a kinetic isomer; it isomerized[56b] to the trans isomer *trans*-$[Pt(PhC{\equiv}CCH_2)(Cl)(PPh_3)_2]$ (**15a**) when left to stand in solution with PPh_3 at room temperature,[57] and further to the allenyl complex *trans*-$[Pt(CPh{=}C{=}CH_2)(Cl)(PPh_3)_2]$ (**16a**) when heated (Eq. 8; see below). If Pt(0) attacked directly at the propargylic carbon (S_N2 path), the cis phosphine arrangement would not have been attained, in view of the fact that the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with CH_3I gave a trans isomer, *trans*-$[Pt(CH_3)(I)(PPh_3)_2]$. We suggest the reaction sequence outlined in Scheme 11, where a C≡C bond coordinated intermediate undergoes intramolecular nucleophilic substitution to give cationic η^3-propargyl product initially. This ion-pair may collapse to *cis*-$[Pt(PhC{\equiv}CCH_2)(Cl)(PPh_3)_2]$; we separately confirmed formation of this isomer by the reaction of $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]BF_4$ with $[^nBu_4N]Cl$. Significantly, the rate of the above oxidative addition is almost the same as that of π ligand exchange between $[Pt(C_2H_4)(PPh_3)_2]$ and $PhC{\equiv}CCH_2OAc$. The failure to obtain the more stable allenyl complex **16a** at the initial stage of the oxidative addition rules out an S_N2' path (Eq. 9). The oxidative addition sequence in Scheme 11 may be applicable to the reaction of analogous allylic electrophiles.



Scheme 11.



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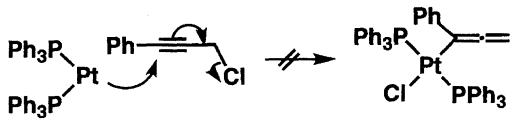

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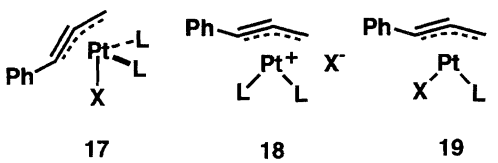
Mutual Isomerization between η^1-Propargyl and Allenyl Complexes. It has generally been believed that in catalytic reactions η^1-allenyl and η^1-propargyl complexes can interconvert into each other.[5] Surprisingly, however, direct demonstration of the interconversion employing isolable complexes has so far been very limited; the data showed that only η^1-propargyl complexes isomerized into η^1-allenyl complexes irreversibly.[58] Recently, two reversible interconversions between η^1-allenyl and η^1-propargyl complexes of Pt(II) were examined by our group; one is spontaneous isomerization via five-coordinate η^3-allenyl/propargyl intermediate, and the other is M(0)-catalyzed isomerization.

Spontaneous Isomerization.[59] The complex **15a** underwent slow isomerization at 70 °C to give an equilibrium mixture of **15a** and **16a** (**15a**/**16a** = 5/95, $k_1 = 1.6\times10^{-6}$ s^{-1}) (Eq. 8). No induction period was observed and the isomerization rate was first order in concentration of **15a** for more than 2 half-lives. Isomerically pure **16a** also could be isolated for the first time by recrystallization from the mixture of **15a** and **16a**. We then confirmed that isomerization of **16a** also occurred to give the equilibrium mixture. This is the first observation of isomerization of η^1-allenyl complex to η^1-propargyl complex.

The spontaneous isomerization reaction is assumed to occur through η^3-propargyl intermediate, such as 18-electron complex (**17**) and 16-electron complex, either ionic (**18**) or neutral (**19**) (Scheme 12). Addition of 40 mol% of PPh_3 did not affect the isomerization rate, which indicates that the intermediate **19** is unlikely. Significantly, bromide and iodide analogues **15b** and **15c** underwent the spontaneous isomerization in C_6D_6 at 70 °C faster than **15a** (Br: $k_1 = 2.4\times10^{-6}$ s^{-1}, I: $k_1 = 4.9\times10^{-6}$ s^{-1}). The order of the rate constant k_1 (I>Br>Cl) is consistent with the order of π-bonding ability of the halide ligand in which the five-coordinate intermediate might be more stabilized, but not consistent with the order of the leaving group ability in which the formation of the ionic intermediate might be more facilitated.



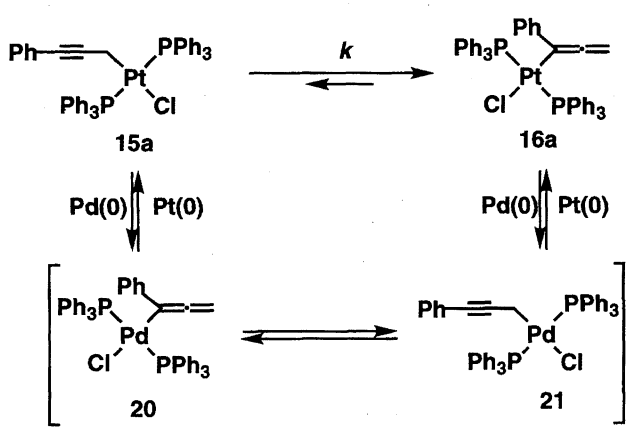
Scheme 12.

Even an organo(propargyl)platinum analogue (**15d**, X=C≡CPh), which can not form cationic η^3-propargyl intermediate, underwent extremely rapid isomerization in C_6D_6 at 70 °C for 1 h ($k_1=2.3\times10^{-4}$ s^{-1}). These results clearly support the five-coordinate 18-electron η^3-propargyl intermediate, rather than the ionic η^3-intermediate.

M(0)-Catalyzed Isomerization. In the course of our study on spontaneous reversible isomerization of **15a** to **16a**, we found the modest acceleration of the isomerization of **15a** on addition of 10 mol% of [Pt(PPh$_3$)$_4$] ($k_{cat}=1.6\times10^{-5}$ s^{-1} at 70 °C).[60] Remarkably the catalytic efficiency of [Pd(PPh$_3$)$_4$] was much larger.[57] The degree of the acceleration was estimated to amount to ca. 10^4; compare $k_{cat}=2.8\times10^{-4}$ s^{-1} in the presence of 5 mol% (5.7×10^{-4} M, 1 M = 1 mol dm^{-3}) of [Pd(PPh$_3$)$_4$] with $k_{uncat}=6\times10^{-8}$ s^{-1}, both at 40 °C in C_6D_6. We propose Scheme 13 for the Pd(0)-catalyzed isomerization of **15a** proceeding through three steps: 1) redox transmetalation between **15a** and Pd(0) to give allenylpalladium(II), *trans*-[Pd(CPh=C=CH$_2$)(Cl)(PPh$_3$)$_2$] **20**; 2) interconversion between **20** and propargylpalladium(II), *trans*-[Pd(CH$_2$C≡CPh)(Cl)(PPh$_3$)$_2$] **21**; and 3) redox transmetalation between **21** and Pt(0) to give **16a**.

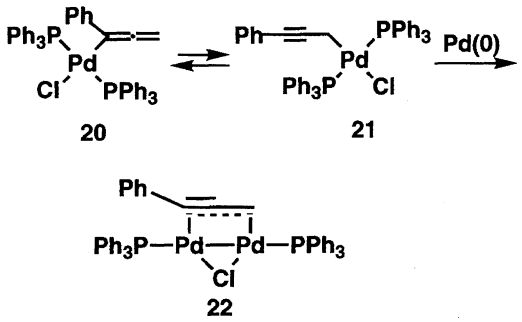
Among these three steps, the second[52] and the third[21] ones can be expected to occur with a sufficiently low activation energy. We actually confirmed rapid transfer of propargyl/allenyl ligands from Pd(II) to Pt(0); a mixture of **20** and **21** (**20**/**21**=25/75) was treated with [Pt(PPh$_3$)$_4$] or [Pt(C$_2$H$_4$)(PPh$_3$)$_2$], giving rise to **15a**/**16a** (5/95) in 97 or 83% yield, respectively, within 5 h at room temperature in C_6D_6.

The remaining problem is the feasibility of the first step of Scheme 13, i.e. Pt(II)–Pd(0) transmetalation, which appears to possess a thermodynamic disadvantage.[21] For example, cationic η^3-allylplatinum(II) complex, [Pt(η^3-C$_3$H$_5$)(PPh$_3$)$_2$]BF$_4$ did not react at all with [Pd(PPh$_3$)$_4$].[61] However, when heated in C_6D_6 with 2 molar amounts of Pd(PPh$_3$)$_4$ at 70 °C in 2 h, **15a** transferred 9% of its organic ligand to palladium to give **22**, which is prepared separately from a mixture of **20** and **21** with Pd(0) (Eq. 10).[62] The formation of **22** leads us to propose transient generation, at least, of propargyl/allenylpalladium(II) intermediates such as



Scheme 13.

20 and **21** from **15a** and Pd(0).

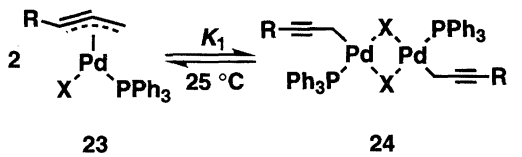


(10)

In all of the redox transmetalations involving η^1-propargyl or η^1-allenyl ligand described above, the first step would be the π-complexation of the C≡C or C=C bond with M(0), followed by the release of M′(0) which had originally formed the η^1-M′–C bond. The redox transmetalation is expected to be more commonly encountered during zerovalent metal catalyzed transformations of not only propargyl and allenyl[63] but allyl[61,64] substrates where its facility might have a crucial influence on the regiochemistry and stereochemistry of the catalytic reactions.

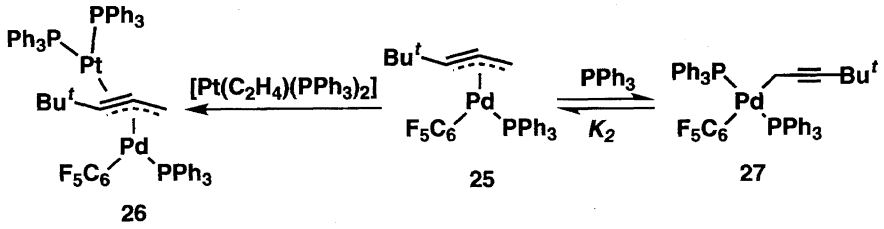
η^3-Propargylpalladium Complexes. As described above, cationic η^3-propargylplatinum complexes are very susceptible to the nucleophilic attack at the central carbon,[53,56] whereas the corresponding palladium analogs are more resistant to this reaction.[17] This parallels the greater stability of the η^3-allyl–palladium bond than the η^3-allyl–platinum bond, as discussed before. In addition, we confirmed much more facile formation of cationic η^3-propargylpalladium complexes [Pd(η^3-RCCCH$_2$)(PPh$_3$)$_2$]BPh$_4$ than of the platinum analogs when [M(η^1-CH$_2$C≡CR)(Cl)(PPh$_3$)$_2$] were treated with NaBPh$_4$.[17]

Neutral η^3-propargylpalladium complexes have been isolated very recently.[55] Thus, the reaction of propargyl chlorides with [Pd$_2$(dba)$_3$·CHCl$_3$] and PPh$_3$ (Pd/PPh$_3$ = 1/1) in CH$_2$Cl$_2$ at room temperature afforded new complexes [Pd(RCCCH$_2$)(Cl)(PPh$_3$)] (R=^{t}Bu, (CH$_3$)$_3$Si, ^{t}Bu(CH$_3$)$_2$Si, ^{i}Pr$_3$Si). These complexes exist as a mixture of the η^3-propargyl monomer (**23**) and the halide-bridged η^1-propargyl dimer (**24**) in solution (Eq. 11). Treatment of **23** (R=^{t}Bu)with C$_6$F$_5$Li gave [Pd(^{t}BuCCCH$_2$)(C$_6$F$_5$)(PPh$_3$)] (**25**), which exists in the monomeric η^3-propargyl structure both in the solid state and in a solution. The geometry of η^3-propargyl ligand in **25** is similar to that of [Pd(η^3-PhCCCH$_2$)(PPh$_3$)$_2$]BF$_4$.[17]



(11)

The equilibrium constants between η^3- and η^1-propargyl isomers show that the η^3-propargyl form is favored by the less bulky substituent R and more polar solvent. Although **25** did not react with MeOH and Et$_2$NH which add to the C≡C bond of cationic η^3-propargyl complexes of Pd and Pt to



Scheme 14.

give complexes of 2-alkoxy or 2-amino-substituted η^3-allyl ligands,[56] it did react with a Pt(0) nucleophile in a formally analogous manner to give a new complex **26** (Scheme 14), of which the X-ray crystallographic analysis revealed a remarkable structure containing μ-η^2 : η^3-^{t}BuCCCH$_2$ ligand. The addition of one equivalent PPh_3 to **25** in $CDCl_3$ generated a mixture of both η^3- and η^1-propargyl complexes ($k_2 = 25$ M^{-1}). This is in sharp contrast to the inertness of the corresponding η^3-allylpalladium complex to be converted to the corresponding η^1-allyl complex with additional PPh_3, as discussed before. Thus, it is apparent that the propargyl/allenyl ligand finds it more difficult to form the η^3-bonding structure than the allyl ligand does.

Conclusion

Some transformations of η^3-allyl complexes of group 10 metals which have been known and applied to synthesis for a few decades, e.g. external nucleophilic attack and reductive elimination, now have been given new mechanistic insights through detailed organometallic and coordination chemical studies. Based on the results from such basic directions, there have been developed other new reactivity patterns such as nucleophilic attack at the center carbon of the allyl ligand and electrophilic attack at this ligand and, at the same time, new synthetic applications thereof. Propargyl or allenyl complexes of group 10 metals also begin to show some structural and reactivity aspects not only complementary to the allyl chemistry but unique and novel by themselves. The topics introduced in this article will lead to future development in more elaborate coordination and synthetic chemistry dealing with the allyl and propargyl metal complexes.

We wish to thank all of the co-authors whose names appear in the cited references for their skillful cooperation and valuable discussions. Partial support of our work through Grants-in-aid for Scientific Research from the Ministry of Education, Science, Sports and Culture is also acknowledged.

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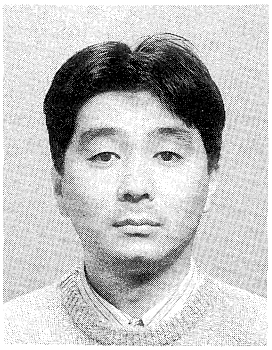

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