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**Review**

# Molecular basis of catalytic reactions involving $\eta^3$-allyl complexes of group 10 metals as key intermediates

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**Abstract**

The correlation between structure and bonding, and the reactivity patterns of $\eta^3$-allylmetal complexes is discussed. Emphasis was laid on the reactions which have a strong bearing on homogeneous catalysis involving group 10 metal complexes. The reactions surveyed here include; the generation and cleavage (nucleophilic substitution, and reductive elimination) of $\eta^3$-allyl complexes, dynamic equilibria, and electrophilic substitution of $\eta^1$-allyl complexes.

## 1. Introduction

Soon after the first unique structural feature was recognised in $\eta^3$-allyl–metal bonding [1], $\eta^3$-allyl complexes of certain metals have been found to play a key role in certain metal-mediated organic transformations, as exemplified by nucleophilic attack at $\eta^3$-allylpalladiums [2] and nickel-catalyzed diene oligomerization and polymerization [3]. Up to 1980 there has been a remarkable broadening of both structural [4] and organic synthetic aspects [5] of the $\eta^3$-allylmetal chemistry.

Currently it is of utmost importance in synthetic organic chemistry to design a catalytic system with high activity and selectivity and for this aim a deep understanding, on a molecular level, of the correlation between bonding and reactivity of true active species in catalysis is required. In this article we overview the current awareness of such correlation in regard to the $\eta^3$-allylmetal complexes. We have concentrated on the complexes of group 10 metals, and no attempt to give a comprehensive account was made. Even though an $\eta^3$-allylmetal framework is sometimes known to be retained during the whole process of catalysis [6,7], the reaction in which the $\eta^3$-allylmetal structure is generated at early stages and converted to organic products at later stages is predominant. The generation, dynamic equilibria and cleavage of the $\eta^3$-allyl–metal bonding are discussed in that order.

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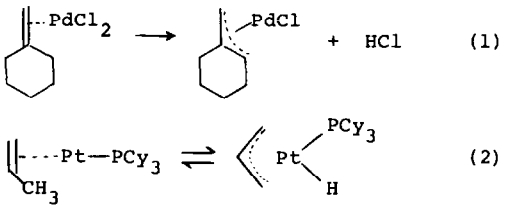
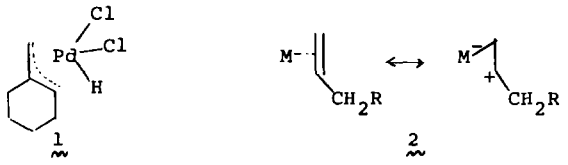
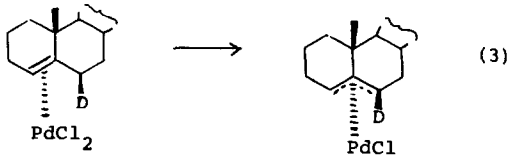


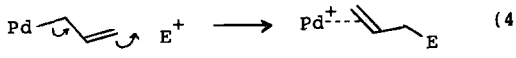

## 2. Appearance of $\eta^3$-allylmetal structure in catalysis

There are routes to $\eta^3$-allylmetal complexes which appear to be very unique, when compared to common routes to alkylmetal complexes, owing to the coordination of the C=C part of the allyl ligand prior to the metal–carbon bond forming step. One of these is $\eta^2$-olefin-to-$\eta^3$-allyl conversion by abstraction or extrusion of an allylic hydrogen, as illustrated in eqs. 1 [8] and 2 [9]. A reaction similar to eq. 2 is a key in the catalytic isomerization of olefins.

The electronic requirement of the metal for C–H bond activition appears to be different in eqs. 1 and 2, and analysis of the kinetic isotope effects in eq. 1 excluded possible intermediacy of **1** [8]. In eq. 1 the mode of action of metal atom towards olefin appears to be electrophilic, while in eq. 2 it may be nucleophilic. Thus, on complexation of olefins to electron-deficient metal moieties, especially those having a cationic metal center, the allylic hydrogen becomes very susceptible to internal or external attack of bases such as metal-bound $Cl^-$ or solvents (see **2**). Thermodynamic and NMR spectral studies of olefin complexes of $Pd^{II}$ and $Pt^{II}$ unambiguously confirmed the electrophilic activation of the type **2** [7,10]. The $Cl^-$-assisted *syn*-elimination of proton has received stereochemical scrutiny (eq. 3) [11].

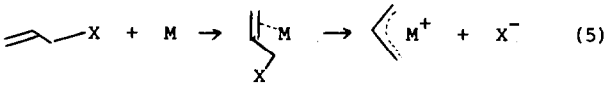



It is possible that the structure of the product in eq. 1 is $\eta^1$-bound immediately after proton abstraction, although unambiguous evidence to support this is not available. In this respect it is noteworthy, in view of the microscopic reversibility principle, that protonolysis of allylpalladium complexes takes place in the $\eta^1$-allyl form (1,3-transposition, see eq. 4, E = H) much more readily than in the $\eta^3$-allyl form [12] (see section 3B).



Equation 2 is regarded as the reverse of reductive elimination of $\eta^3$-allyl complexes, in which the allylic ligand group is $\eta^3$-bound (in the early stages) and $\eta^2$-bound (in the later stages) to the metal, as discussed later. Thus, eq. 2 may give the $\eta^3$-allyl species initially.

Another important route to the $\eta^3$-allyl complexes involving the prior C=C-bond coordination is one in which electronegative heteroatom substituents (X) are extruded (eq. 5). This process evidently plays a crucial role as the first step of the catalytic nucleophilic substitution of allylic electrophiles (eq. 6) [5]. Stereochemistry at the carbon which undergoes C–X bond cleavage in eq. 5 has been shown to be inversion for X = OAc and M = Pd(dppe) [13]. Application of the microscopic reversibility principle to the better understood, reverse step of eq. 5 (discussed later) makes the olefinic intermediate of eq. 5 highly likely. In the case of X = SR and M = Pd, introduction of substituents specifically at the olefinic terminal caused marked retardation of eq. 5 [14]. Although an $S_N2'$ mechanism was proposed for this particular case, it was not clear whether this mechanism implied prior C=C-bond coordination and the formation of an $\eta^1$-allyl species as an initial product.

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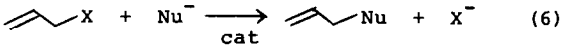
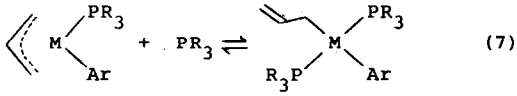



(6)

## 3. Generation and reaction of $\eta^1$-allylmetal complex

*A. Dynamic equilibrium in $\eta^3$–$\eta^1$-allyl interconversion*

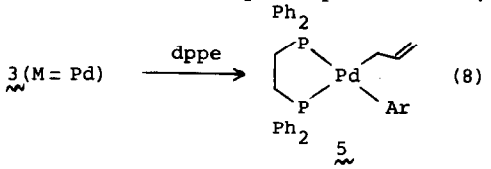
The interconversion between $\eta^3$- and $\eta^1$-bound forms of allylmetal complexes [4] is of particular relevance to asymmetric synthesis, since the identity of the diastereo- or enantioface of the $\eta^3$-allyl ligand is lost during such interconversion [15]. Extensive work has been done on the ligand-induced $\eta^3$–$\eta^1$ equilibrium of $\eta^3$-allylpalladium complexes containing anionic heteroatom ligand groups [4]. The presence of an ionizable ligand somewhat complicates equilibrium systems and makes characterization of the rather unstable $\eta^1$-allyl forms especially difficult, however such a problem does not arise in the metal moiety containing allyl and $\eta^1$-organic ligands together. Moreover, this system may serve as a good model for an intermediate in metal-catalyzed allylic alkylation and cyclooligomerization of dienes.



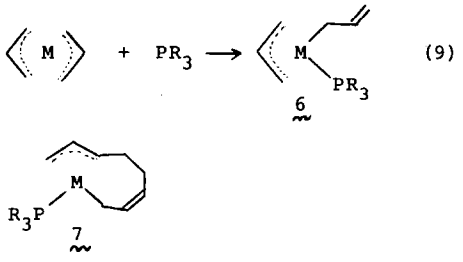

3 4 (7)

The ease of $\eta^1$-allyl formation (eq. 7; R = Ph) was found to decrease in the order M = Pt > Pd > Ni [16]. For M = Pt the equilibrium lies far to the right to give a stable isolable $\eta^1$-allyl species. For M = Pd and Ni, $PPh_3$ ligand was not basic enough for the $\eta^1$-allyl form to be detected, even by $^1H$ NMR spectroscopy. What was actually observed for M = Pd was rapid *syn–anti* allyl proton exchange via the transient formation of $\eta^1$-allyl species, whereas for M = Ni such an exchange was not observed on the NMR time scale. More basic phosphines such as $PMe_2Ph$ and

dppe stabilize the $\eta^1$-allylpalladium complexes (e.g. **4**, M = Pd, $PR_3 = PMe_2Ph$ and **5**), but similar attempts to produce the $\eta^1$-allylnickel analogs failed. In relation to




the catalytic cyclooligomerization of dienes, some interesting models containing both $\eta^3$- and $\eta^1$-allyl ligands simultaneously (**6**, **7**; M = Ni, Pd) were synthesized and their chemistry was investigated in some detail [17]. Complex **6** exhibited dynamic NMR spectral aspects due to $\eta^3$–$\eta^1$ interconversion. Again the $\eta^3$-allylnickel analogs are the most robust in forming the $\eta^1$-allyl form.

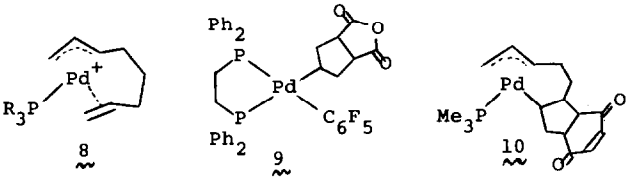



*B. Electrophilic substitution of $\eta^1$-allylmetal complexes*

$\eta^3$-Allylpalladium complexes are widely recognized as key intermediates in catalysis by virtue of the high reactivity toward nucleophiles [5]. More generally, however, $\eta^1$-allylmetal complexes are attacked by electrophiles with great ease [18]. Isolation of structurally rigid $\eta^1$-allylpalladium complexes **5** and **7** enabled detailed examination of the chemistry of the $\eta^1$-allylpalladium complexes.

The reaction of **5** with HCl, $Br_2$ and *N*-bromosuccinimide (Br-Suc) is characterized by facile attack of the electrophile at the olefinic terminal (eq. 4; E = H, Br) [12]. Among the $\eta^1$-allyl and Ar (= $C_6F_5$) ligands in **5**, the former reacted almost exclusively, whereas similar competition between $C_6F_5$ and the $\eta^3$-allyl ligands in **3** afforded $C_6F_5E$ almost exclusively.

Complex **7** also reacted with some substrates containing acidic hydrogen such as alcohol and $\beta$-dicarbonyl compounds to form **8**, with $H^+$ most probably attacking at the carbon $\gamma$ to Pd of the $\eta^1$-allyl part [17,b,c,f]. Attack of a very electron-deficient olefin (e.g. maleic anhydride) at the C=C part of $\eta^1$-allyl to afford formal [2 + 3] cycloadducts (**9**, **10**) [12,17d] is also reminiscent of the analogous reactions of $\eta^1$-allyl complexes of other metals (e.g. Fe) [18].

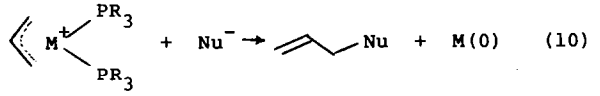


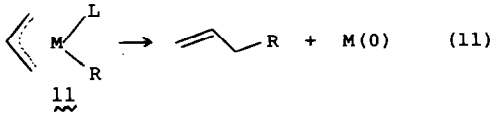

The higher reactivity of the $\eta^1$- compared with the $\eta^3$-allylpalladiums to electrophiles is not surprising, since there is a decrease in the number of electrons to be

supplied from the allyl group to Pd ($4 \rightarrow 2$) upon the $\eta^3 \rightarrow \eta^1$ allyl conversion. Moreover, this conversion usually requires coordination by very basic donors, which help to enhance the electron density on Pd and hence the allyl ligand. An extension of this idea would be that nucleophilic attack at the $\eta^1$-allyl ligand, if any, is much less favorable than that at the $\eta^3$-allyl ligand.

## 4. $\eta^3$-Allyl–metal bond cleavage

The electrophilic substitution of the $\eta^1$-allyl–metal bond as described in 3B is not widely utilized in catalysis. One example to be commented on would be catalytic diene telomerization (Scheme 1) [17b,f] in which the $\eta^1$-allyl–palladium bond is cleaved by compounds bearing an acidic hydrogen. On the other hand, the nucleophilic substitution (eq. 10) and the reductive elimination (eq. 11) of the $\eta^3$-allyl complexes find much more extensive application in catalysis.

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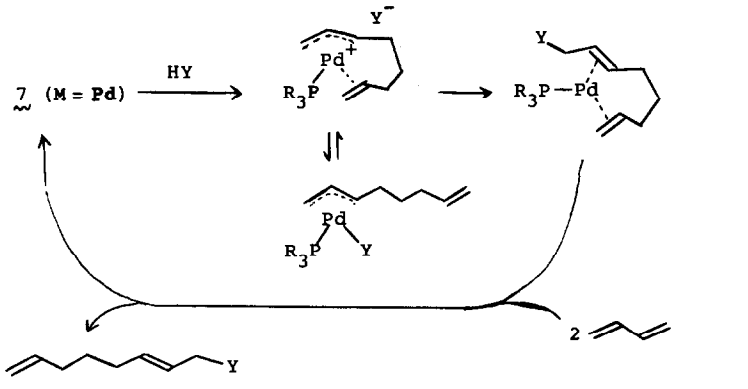
An example of the nucleophilic substitution is involved in Scheme 1. Very important examples of the reductive elimination step are found in the catalytic cross-coupling of active organometallics such as those of Mg, Zn, Zr, B, or Sn with allylic halides, alcohols or carboxylates [19], and in catalytic cyclooligomerization of dienes [20]. Complexes 7, among others, were suggested to exist as intermediates in the latter catalysis.

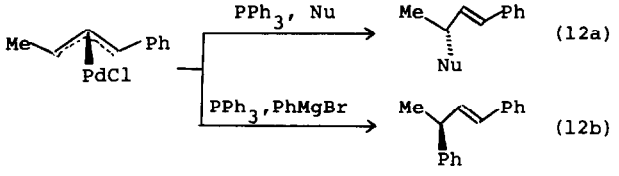



(Y = $CH(COOEt)_2$, $NR_2$, OR, OCOR etc.)

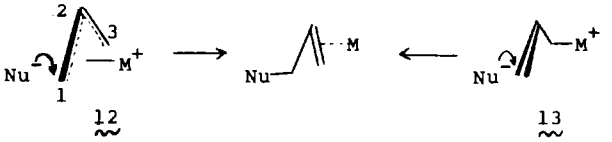
Scheme 1

*A. Nucleophilic substitution*

Reductive degradation of the $\eta^3$-allylmetal complexes (eq. 10) is a nucleophilic substitution because the stereochemistry at the carbon undergoing C–Nu bond formation is again inversion * for most of nucleophiles examined (typically $CH(COOEt)_2^-$, $Me_2NH$) (see eq. 12a) [21] with the significant exception of alkyl, vinyl and aryl carbanions. In spite of its frequent appearance in the reaction sequence of catalytic transformations, especially in the presence of palladium catalysts, precise depiction of this step in terms of the electronic structure remains somewhat vague.




Perhaps two extreme ways of depicting the reaction course would be **12** starting as a symmetrical allyl–metal framework and **13** starting as an $\eta^1$-allylmetal structure. The semi-empirical molecular orbital calculation for **12** was carried out [23] on



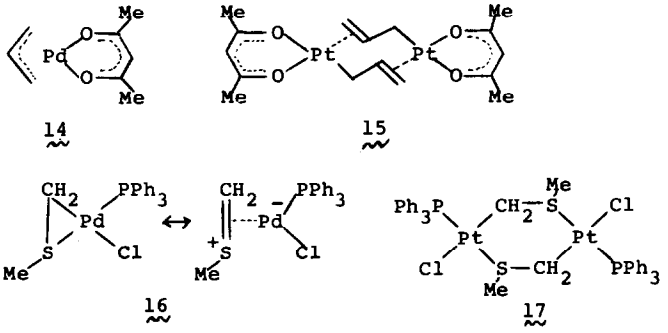

12 13

a model system where the Pd–allyl configuration was kept unchanged from the original symmetrical structure during the progressive approach of $Nu^-$ ($OH^-$) to C(1) with Pd behind the allyl plane. The calculation confirmed that the C(1)–Nu bond becomes stronger and the metal-coordinated C(2)–C(3) part becomes increasingly more like a double-bond as the C(1)–Nu distance shortens.

Interestingly, this work, and the related extended Hückel molecular orbital analysis [24] suggested that the site of nucleophilic attack is not charge-controlled but frontier-orbital controlled; the calculated charge density gave no indication of the carbocation character of the $\eta^3$-bound allylic terminus. Although these calculations did not take into account the effect of the deformation of the originally symmetrical Pd–allyl framework, such deformation might play a role in lowering reaction barriers, cf. that of the metal–olefin linkage during nucleophilic attack at the metal-bound olefinic carbon [25].

As suggested in 3B, the extreme case of the deformation, namely attack at the $\eta^1$-allyl structure, **13**, does not appear to play a very significant role. A previous report [26] describing the contrast between a supposedly $S_N2'$ attack of amines at the more substituted allylic terminus in neutral $\eta^1$-crotyl(chloro)palladium species and an attack of amines at the less-substituted allylic terminus in a cationic $\eta^3$-crotyl counterpart was later claimed [27] to require more detailed experiments

* Certain nucleophiles (e.g. $OAc^-$, $Me_2NH$) attack the allyl carbon with retention under certain specific conditions [22].



14 15



16 17

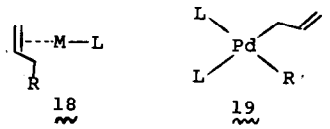
including a test of possible isomerization of the initial amination products. In any case, at present the prediction and control of the regioselectivity of the reaction shown in eq. 10 is not an easy task.

It is of interest to note the considerable ease with which $\eta^3$-allylplatinum complexes undergo reaction 10 (Nu = $CH(COMe)_2$, CH(COMe)(COOMe), $CMe_2NO_2$) [28]. Generally, reductive C–C coupling of $Pt^{II}$ complexes such as the reductive elimination of dialkylplatinum has much higher energy barriers (by > 30 kcal/mol) than those of the corresponding $Pd^{II}$ complexes [29]. According to Goddard and co-workers [29], the reduction of $Pd^{II}$ alkyls is more exothermic, and thus has a lower energy barrier, than that of $Pt^{II}$, since this reduction is accompanied by a change in the electron configuration of the metal from $s^1d^9$ to $d^{10}$ and since the ground states of Pd and Pt are $d^{10}$ and $s^1d^9$, respectively. If we assume that the electron configuration of the metal in the $\eta^3$-allyl complex has less $s^1d^9$ and more $d^{10}$ character than the alkyl complex, then we would expect the difference in exothermicity for the reduction of the $\eta^3$-allyl complexes of Pd and Pt to become smaller. This change in electronic structure of the $\eta^3$-allyl–metal bond framework, together with non-requirement of M–C bond formation for the attacking nucleophile, enable the $\eta^3$-allylplatinums to undergo eq. 10 with such ease.

The less $s^1d^1$ and the more more $d^{10}$ character of the $\eta^3$-allyl complex compared with the alkyl complex may also account for the greater ease of conversion from $\eta^3$- to $\eta^1$-allyl for Pt than for Pd (e.g. see eq. 7; see also **14** and **15**) [16,30]. A similar argument has also been applied to account for the difference in structure of $M(CH_2SMe)$ derivatives where M = Pd and Pt, namely **16** and **17** [31].

*B. Reductive elimination*

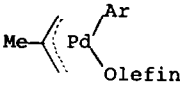
The stereochemical evidence of eq. 11 has been obtained by the use of the chiral $\eta^3$-allylpalladium complex (eq. 12b) [21]. The reaction course for eq. 11 has been followed by the use of isolated complexes **11** (R = aryl, alkyl for M = Ni, Pd; R = H for M = Ni, Pt) [9,32,33]. The most likely structure of the initial product is **18**. Kinetics of eq. 11 for M = Pd and R = $C_6H_3Cl_2$-2,5 was examined in some detail [33c–e] to reveal the following features which apparently are unique to $\eta^3$-allyl chemistry.



18 19

(1) The $\eta^1$-allyl form (**19**) does not participate in the C–C bond-formation step when L ($PPh_3$, $AsPh_3$) is added in excess, nor does the ligand L of **11** leave the coordination site during the C–C coupling step. This is contrary to the reductive elimination of dimethylpalladium analogs, which requires prior ligand dissociation [34]. The ligand plays a more direct role in affecting the barrier to the C–C coupling through its electronic effect; as the $\pi$-electron accepting ability of L becomes larger (e.g. $AsPh_3 < PPh_3 < P(OPh)_3$), the barrier becomes lower.

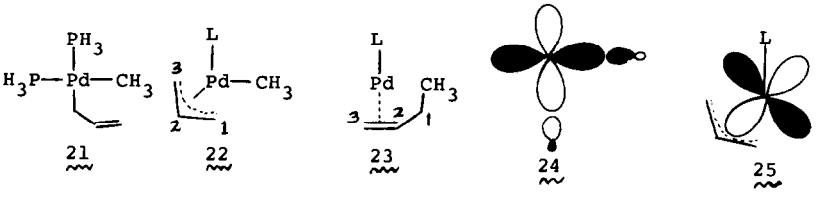
(2) Addition of olefinic ligands (e.g. $CH_2$=CHCN, maleic anhydride) to **11** (M = Pd, L = $PPh_3$, $AsPh_3$) greatly accelerates eq. 11, and kinetic studies suggest that this acceleration is due to the formation of an intermediate olefin complex **11** (M = Pd, L = olefin) which, in view of the above argument, is expected to undergo eq. 11 very rapidly. This notion was confirmed in separate experiments, where **20** was prepared and their rates of reductive elimination were compared with that of the $AsPh_3$ analog ($k$(olefin)/$k$($AsPh_3$) > $10^5$) as well as within themselves (Hammett $\rho = 1.42$ where olefin = *para*-substituted styrenes). The unique accelerating effect of the olefinic additives was actually utilized in some highly selective organic syntheses which proceed via $\eta^3$-allylpalladium intermediates [19d,35].




**20** (Ar = $C_6HCl_4$-2,3,5,6)

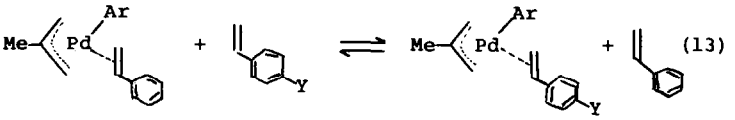
The extended Hückel MO calculations on these reactions using models **21** and **22** (L = $PH_3$) confirmed [36] that the barrier to converting **22** (L = $PH_3$) to **23** is indeed considerably lower than the reductive elimination of **21**. Behind this difference lies the contrasting behavior of one particular MO (**24**) along the C–C bond-forming step; in the reaction of **21** the level of **24** rises steeply thereby increasing the energy of the transition state, while in the reaction of **22** this orbital does not rise as high as that for **21**. The latter result may be ascribed to $\pi$ back-bond interaction between **24** and $\pi^*$ of the C(2)=C(3) part where double-bond character increases while Me–C(1) bond formation proceeds.

The reductive elimination of *cis*-$PdMe_2(PR_3)_2$ proceeded via a T-shaped intermediate, *cis*-$PdMe_2(PR_3)$, and MO calculations indicated that the barrier to be overcome from this intermediate to the next, is considerably lower than that of the direct path involving four-coordinated species [34]. On the other hand, the calculations showed that the barrier to the reductive elimination of **22** (L = $PH_3$) is even lower than that to be overcome from a T-shaped intermediate *cis*-Pd(Me)($\eta^1$-$CH_2CH$=$CH_2$)($PH_3$).



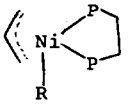

In the $\eta^3$-allylmetal species, another in-plane *d* orbital **25** is considerably higher in energy, particularly in the transition state of the reductive elimination. Conse-

quently, effective $\pi$ back-bond interaction is expected between **25** and the $\pi$-acceptor ligands, and in particular, in-plane coordinated olefins e.g. **22** (L = $CH_2$=$CH_2$), lower the energy level of **25**. In this respect the X-ray structural confirmation of the in-plane coordinated olefinic ligand in Pt($\eta^3$-$CH_2CMeCH_2$)(olefin)L (L = $C_6F_5$, olefin = styrene; L = $PPh_3^+$, olefin = $CH_2$=$CH_2$, styrene, Z-MeCH=CHMe) [37] is noteworthy. The $\pi$ back-bond interaction might be even more prominent in the transition state of the reductive elimination of **11** (L = olefin), thus lowering the reaction barrier. Compare the Hammett $\rho$ (1.42) for the rate constants of the reaction of **20** described above with $\rho$ (−0.25) for the equilibrium constants of eq. 13.




Finally, we note the relative ease of eq. 11 among M = Pt < Pd < Ni (Ar = $C_6H_3Cl_2$-2,5, L = $PPh_3$) [33e]. The Pt analog gave practically no coupling product even at 80 °C, while the rate constant for M = Pd and Ni was found to be $2.9 \times 10^{-3}$ $h^{-1}$ and $5.8 \times 10^{-2}$ $h^{-1}$, respectively, in toluene at 0 °C. This is the first case in which it is possible to directly compare the relative rates of the Pd and Ni complexes.

Very unique to the Ni complex is the fact that adding dppe to **11** (M = Ni) greatly accelerated the coupling reaction, while the same treatment of the Pd analog **11** resulted in retardation of the coupling [33e]. The reason for the latter observation is obvious because the addition of dppe gave rise to very stable $\eta^1$-allyl complex **5** (Ar = $C_6H_3Cl_2$-2,5) which was separately found to undergo the reductive elimination more slowly than **11** (M = Pd). Although we could not detect any intermediate species from the reaction of **11** (M = Ni) and dppe even at lower temperatures, it may well be that a five-coordinated complex **26** formed initially undergoes the C–C coupling step very rapidly, as was indeed the case in the reaction of dialkylnickel complexes [38]. Intermediates of type **26** have previously been postulated in nickel-catalyzed asymmetric allylic alkylation [15b,39].

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