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Recent developments in the chemistry of olefin complexes of palladium and platinum: some novel findings as well as elaborate extensions *

Hideo Kurosawa and Isao Ikeda
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

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Abstract

Recent developments in the chemistry of olefin complexes of palladium and platinum are described. Emphasis is placed on the molecular basis on which unique, hitherto unknown stability trends and C=C bond coordination geometry in certain complexes can be understood. Examples of these complexes include olefin complexes of Pd^{II} and Pt^{II}, having the 18-electron configuration or the η^3-allyl group as an ancillary ligand, which show stability trends not so strongly affected by the electronic factor of the olefinic substituents. Moreover, the C=C axis of the olefin ligand coordinated to the η^3-allylmetal moiety tends to lie within the coordination plane. A brief survey on some basic reactivity patterns exhibited by the olefin complexes of palladium and platinum is also given.

Introduction

Olefin complexes of platinum are among the most extensively investigated transition metal complexes of unsaturated organic ligands. In spite of their old history, they still continue to attract much attention because they are closely related to models as intermediates in modern organic synthesis mediated by complexes of not only platinum but other metals, especially palladium, and because they offer, for their own sake, a great theoretical and physico-chemical stimulus. Remarkable advancements in modern instrumental and computer technologies have provided better opportunities to shed renewed light into the old structure and bonding aspects of these complexes, which might have misleadingly constituted a few important sections of organometallic and inorganic textbooks used world-wide. In this review we describe some new developments in the chemistry of olefin complexes of palladium and platinum, primarily from the

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Correspondence to: Dr. H. Kurosawa, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan.

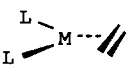
* Dedicated to Professor Akio Yamamoto for his outstanding contributions to organometallic chemistry for many years.

viewpoints of their structure, bonding and reactivities. We have made no effort to give a comprehensive account, but have concentrated on our own and closely related works.

Stability, structure and bonding

Brief historical survey

Until a decade ago, olefinic complexes of palladium and platinum were classified into two major types according to the structure type which also reflected the metal oxidation state [1]; one class of complexes contain a trigonal-planar structure having a zero-valent metal center (**1**), and the other a square-planar structure with a metal atom in the +2 oxidation state (**2**). The former was further characterized by the geometry of the C=C axis lying in the coordination plane (in-plane geometry), and the latter by that of the C=C axis lying perpendicular to the coordination plane (upright geometry). The rational electronic origin of the in-plane geometry for **1** was presented [2]. That is, there is a considerably larger π back bond interaction between the occupied metal $d\pi$ orbital and the empty olefin π^* orbital in the in-plane than in the upright geometry. Furthermore, this π interaction has amply been demonstrated to be a major factor in influencing the stability of type **1** complexes; more electron-withdrawing olefins give greater complexation ability [3].



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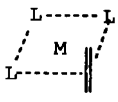

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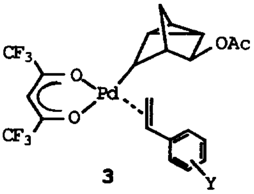

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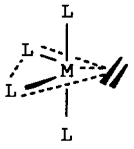

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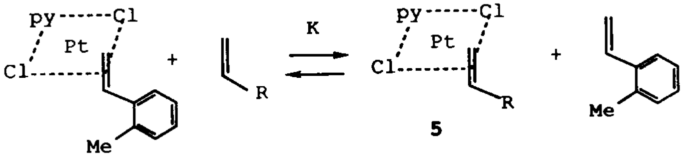
On the contrary, the upright olefin geometry observed in all of the type **2** complexes was attributed, from molecular orbital calculations [2], to a steric factor, rather than an electronic one, i.e. the π back bond interaction is comparable in this and in the in-plane geometry. However, there was controversy to what extent the π back bond interaction plays a role in determining the metal–olefin bond strength in **2**. Thus, relative stability studies on a series of closely related olefin-Pt^{II} complexes [4] and the IR studies on a similar series of complexes [5] suggested considerable importance of the π interaction in enhancing the Pt–olefin bond strength for a more electron-withdrawing olefin ligand, as observed in the class **1** complexes. Moreover, calorimetric studies on metal–olefin bond cleavage suggested [6] that the π interaction plays a considerable role in olefin-Pt^{II} complexes but a lesser role in olefin-Pd^{II} complexes. In contrast, studies based on ^{13}C NMR spectroscopy [7] and X-ray structure determination [8] led to a proposal that in olefin-Pt^{II} complexes, such π back bonding makes a rather minor contribution to the overall stability. The stability trend in a series of olefin-Pd^{II} complexes (**3**) was also consistent with the last notion [9]. No definitive solution had been given to this problem about a decade ago.

About the same time, Hartley emphasized [10] the existence of the second type of olefin complexes of Pt^{II} which have a trigonal bipyramidal structure with the

C=C axis lying in the trigonal plane (4). Even though increasing interest in this class of complexes was then slowly emerging, it took still a few more years before the general properties of this class of complexes, especially stability aspects, were uncovered.

Stability of Zeise's salt and its analogues

As described above, two opposing views were proposed concerning the stability trend of the most typical olefin-Pt^{II} complexes, Zeise's salt and its analogues (5). We were able to present a direct proof to solve this problem [11]; we determined the equilibrium constants of a competitive olefin coordination shown in eq. 1 by the use of the ^{1}H NMR technique. This method was far superior to the previous stability study [4] based on UV spectroscopy dealing with very dilute complex solutions in that it could avoid the occurrence of unwanted, additional solution equilibria (*e.g.* hydrolysis of Pt–Cl bond), which tend to be encountered more often in dilute solutions, and that their occurrence, if any, could easily be checked.



(1)

The NMR measurements were carried out for the equilibrium solution below 0°C in order to obtain two separate methyl proton resonances of the free and coordinated *o*-methylstyrene ligands; raising the temperature broadened these proton signals owing to a rapid exchange between the two forms. The results are shown in Table 1. Among others, a linear dependency of the equilibrium constant for the substituted styrene complexes on the Hammett constants (see Fig. 1) was particularly noteworthy. Thus, this figure unambiguously demonstrated, for the first time, the very electrophilic nature of the platinum atom in complexes of the type 5 toward the coordinated olefin.

It is also notable in Table 1 that methyl acrylate, which the previous IR study suggested made a stronger bond with platinum than other less electron-withdraw-

Table 1

Equilibrium constants (K) for eq. 1 [a]

Olefin	K
CH_2=CHMe	30
Z-MeCH=CHMe	5.6
E-MeCH=CHMe	2.9
CH_2=CHC_6H_4Y-*p*	
Y = NMe_2	7.0
OMe	1.4
Me	0.56
H	0.32
Cl	0.25
NO_2	0.052
CH_2=CHC_6H_4Cl-*o*	0.23
CH_2=CHCOOMe	0.001 [b]

[a] In $CDCl_3$ at −15°C. [b] At −30°C.

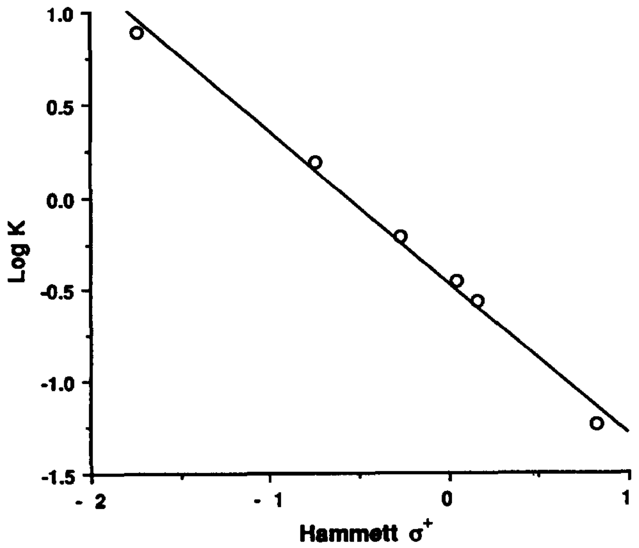


Fig. 1. Hammett plot for eq. 1 ($R = C_6H_4Y$-*p*) in $CDCl_3$ at −15°C ($\rho^+ = -0.82$, $r = 0.996$).

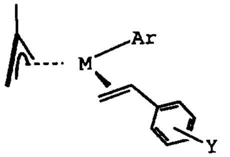
ing olefins (e.g. styrene, propene) [5], gave a much less stable complex than the others. It was now evident that the olefin-to-metal σ donation plays a much more important role than the π back bond in determining the solution stability of the type **5** complexes. Many Pd^{II}- and Pt^{II}-mediated transformations of olefins, described later, are also best interpreted in terms of the electrophilic activation of the C=C part by the metal center.

Metal center showing olefin affinity in between electrophilic and nucleophilic character

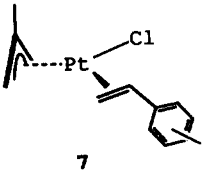
We next searched for those olefin complexes of platinum and palladium that show stability trends in between strongly nucleophilic (type **1**) and strongly electrophilic (type **2**) character of the metal center with respect to the olefin coordination. To this end, at least two approaches were conceivable in principle. The first was to reduce the electron density on the metal in the type **1** complexes and the second to increase the density in the type **2** complexes, both by the proper modification of the ancillary ligand groups. We also thought that the third possibility would have lain in a deeper examination of the stability of the type **4** complexes, since the unique stereoelectronic effect inherent in this class of complexes causes better π back donation from metal to olefin lying in the trigonal plane for a reason almost similar to that given to explain the in-plane coordination of the olefin in type **1** complexes [2,10]. Examples of the second and the third approaches above are described in the following.

16-Electron, organoplatinum(II) and -palladium(II) complexes. The existence of metal-bound organic ligand(s) is expected to increase the electron density on the metal atom. Among several olefin complexes bearing organometallic fragments we have examined, η^3-allyl(aryl)(olefin)platinum(II) and -palladium(II) complexes **6** indeed showed unusually small substituent dependency of the stability [12,13]. The slopes in the Hammett plot for the equilibrium constants of eq. 2 ($L_nM = M(\eta^3$-

$C_4H_7)(Ar))$ ($\rho = -0.38$ for **6a**, -0.25 for **6b**) clearly indicate that the metal atom in **6** is only slightly electrophilic toward the coordinated olefin.



6a M= Pt, Ar= C_6F_5
6b M= Pd, Ar= C_6HCl_4-2,3,5,6



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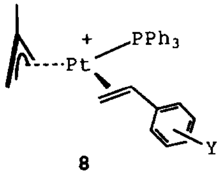

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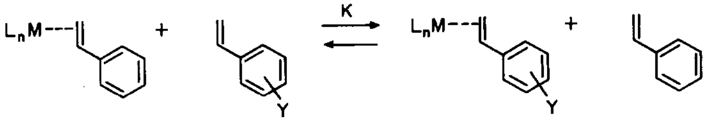
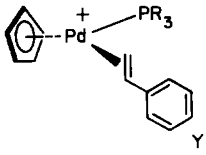


(2)

As expected, the analogous Hammett experiments employing related η^3-allyl complexes involving Cl (**7**) and PPh_3 (**8**) ligands, instead of the carbon ligands, showed more electrophilic nature of the platinum atom (Hammett $\rho = -0.73$ for **7**, -1.32 for **8**) [14,15]. The electronic origin of these results are discussed later.

18-Electron Pd^{II} and Pt^{II} complexes. The relative enthalpy of the Pd–olefin bond formation in complexes of the type **9** in solution was determined by variable temperature equilibrium studies of eq. 2 ($L_nM = Pd(\eta^5\text{-}C_5H_5)(PR_3)^+$) [16]. The results are quite remarkable in that the $\Delta H°$ values for the *p*-methoxystyrene complexes are almost the same as those for the corresponding non-substituted styrene analogues (within 1 kJ/mol which is an experimental error), although $-\Delta G°$ values for the former were some 2–3 kJ/mol larger than those for the latter. These contrast well with the result of the analogous experiments [9] employing the typical electrophilic complexes **3** where $-\Delta H°$ for *p*-methoxystyrene complex is 5.2 kJ/mol larger than that for unsubstituted styrene complex.



9 R = Ph, n-Bu

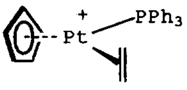
Table 2

Selected bond lengths (Å) in $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2{=}CHC_6H_4Y\text{-}p)]X$

Bond	Complex		
	Y = OMe, X = BF_4	Y = H, X = PF_6	Y = Cl, X = BF_4
Pd–C_α(olefin)	2.264(5)	2.255(5)	2.235(6)
Pd–C_β(olefin)	2.182(5)	2.182(5)	2.187(6)
Pd–C(Cp)(av)	2.310	2.288	2.316
Pd–Cp(center)	1.983	1.964	1.988
Pd–P	2.286(1)	2.288(1)	2.292(1)

Another important result with respect to the unique nature of the Pd–olefin bond in **9** comes from X-ray structure determinations. Thus, the Pd–C(olefin) bond lengths in **9** (Table 2) are almost substituent independent, or rather decrease with increasing electron-withdrawing ability of the substituent, in marked contrast to the trend observed in the typical electrophilic olefin complexes of the type **5** (longer Pt–C bond length in the more withdrawing olefin complex) [8]. From these results it is apparent that the palladium atom in **9** is much less electrophilic toward the olefin than in the 16-electron complexes **2**. Behind this notion will be an increased π back bond interaction in the 18-electron, ML_4(olefin) complexes **4** to which **9** formally belongs.

In related studies it was found [17] that in the 18-electron complex **10** the olefin rotation barrier is higher than in the 16-electron complex **11**. Moreover, *J*(Pt–C(ethylene)) of **10** (223 Hz) was much larger than that of **11** (82 Hz) while *J*(Pt–P) values are almost comparable between **10** (4343 Hz) and **11** (3818 Hz). These results suggest the stronger Pt–olefin bond in **10**, presumably owing to the better π back bonding, than in **11**. We confirmed that the difference in these properties of **10** and **11** is primarily due to the electronic origin, but not the steric one, by a comparison of MO calculations [18a] on an 18-electron complex model **12** and a hypothetical 16-electron complex model **13**. In **13**, two hydrogens were added to the C_5H_5 group perpendicular to the ring without changing the planar arrangement of the C_5H_5 group so that the C5 ring of **13** exerts the same steric effect as in **12**, but binds to platinum in a η^3-fashion. In particular, the calculation showed that the olefin rotation barrier is approximately 8 kcal/mol higher in **12** than in **13**.



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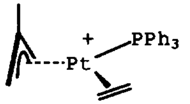

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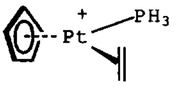

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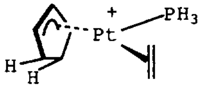

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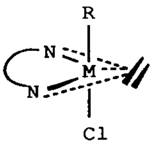
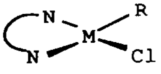
A similar unique nature of the metal–olefin bond in 18-electron complexes of type **4** has been presented in more recent works by some groups dealing with more typical 5-coordinated complexes **14** [19–21]. Thus, quantitative stability studies on a series of these olefin complexes showed greater bond strength for the electron-withdrawing olefins, although no attempt was made to rigorously separate the electronic and steric effects of the olefinic substituents. At any rate, these results were somewhat reminiscent of the behaviour of the type **1** complexes. All of the complexes of type **14** determined by X-ray structure analysis contained the C=C bond lying in or almost within the trigonal plane. One of the driving forces for the addition of olefin to the 4-coordinated complexes **15** to form **14** was suggested to be relief of specific steric constraints existing in the parent 4-coordinate complexes upon olefin coordination.



14 M= Pd, Pt
R= Cl, Me



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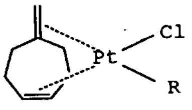
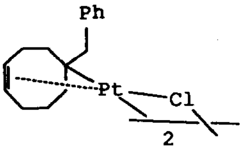
In-plane olefin coordination geometry in M^{II}-olefin complexes

As already pointed out, until about a decade ago all of the crystallographically determined structures of 4-coordinate 16-electron olefin complexes of $\mathrm{Pt^{II}}$ and $\mathrm{Pd^{II}}$ contained the upright C=C geometry. The in-plane C=C geometry in this class of complexes was thought to play a role during olefin insertion into M–R (R = H, alkyl) bonds proceeding through 16-electron intermediates, as well as in rotation of the coordinated olefin about the M–olefin bond. Thus, isolation of and a detailed look into the 16-electron in-plane olefin complexes had been awaited.

Exo-methylenecycloalkene complexes. The first isolable in-plane complex **16** was reported in 1980 [22] where chelate coordination of two C=C bonds in the diolefin molecule compelled the exocyclic one to lie in the coordination plane. This result developed into a series of analogous complexes simultaneously containing Pt–R bonds which are potentially good models for the olefin insertion reaction (*e.g.* **17**) [23]. The insertion product **18** was indeed formed from a methylenecyclooctene analogue of **16** and a phenyltin compound. Unfortunately, however, no direct detection of a putative precursor **19** was made.



16 R= Cl
17 R= Ph



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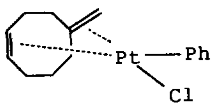

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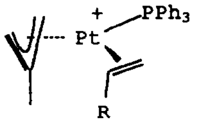
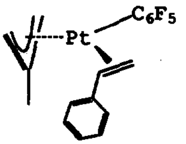
In structure **16**, the in-plane olefin–Pt bond was subject to greater steric hindrance with the *cis* Cl ligand and thus more elongated than the upright olefin–Pt bond. The former bond was also kinetically more labile. The in-plane coordination of the *exo*-methylene group was also shown to play a role in stabilizing an 18-electron tris(olefin)(dichloro)platinum(II) complex containing ethylene and bis(*exo*-methylene)bicyclic ligands [24].

η^3-Allyl(olefin)metal complexes. Another unique class of 16-electron, in-plane olefin complexes discovered and developed during the last decade are those of $\mathrm{Pt^{II}}$ and $\mathrm{Pd^{II}}$ containing the η^3-allyl group as the ancillary ligand. Those complexes where structure determination demonstrated the in-plane olefin geometry are listed in **20–23** [13,18,25,26]. The molecular structures for some of these are shown in Fig. 2. The most important factor which contributed to the realization of the in-plane coordination in these complexes is evidently the relatively small bite angle of the "bidentate" η^3-allyl ligand, providing enough room for the sterically more demanding in-plane olefin ligand.



20 R= H, Ph



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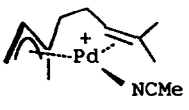

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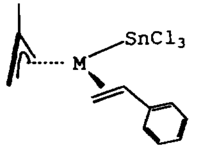


23 M= Pt, Pd

Some of these were further demonstrated to retain a similar structure also in solution, primarily from NMR analysis and a stability trend unique to the in-plane complexes [13,18]. In particular, diagnostic NMR features include interligand

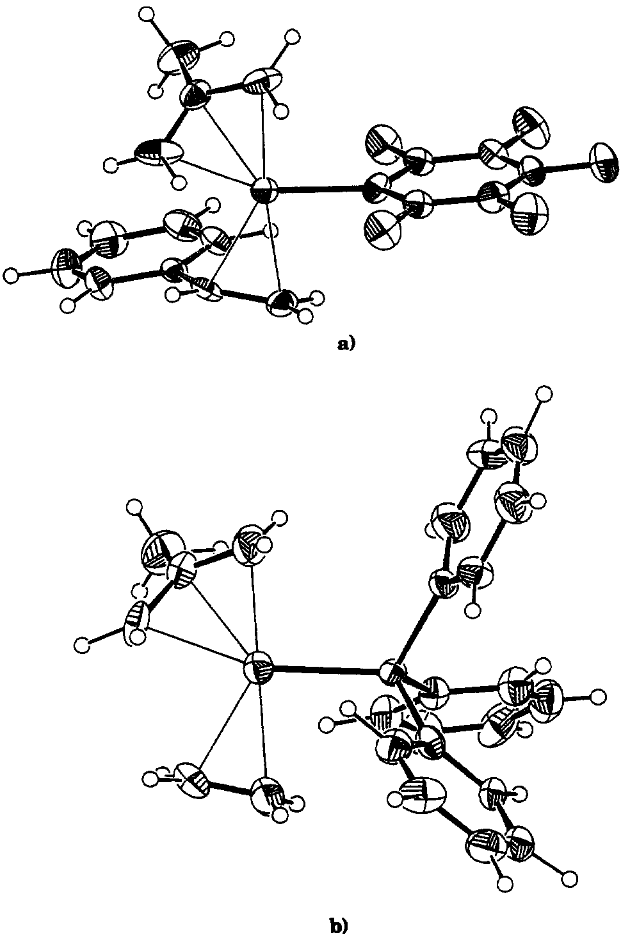
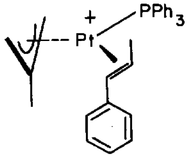


Fig. 2. Molecular structures of $Pt(\eta^3\text{-}CH_2CMeCH_2)(C_6F_5)(CH_2{=}CHPh)$ (a) and $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CH_2{=}CH_2)]PF_6$ (b; PF_6 omitted for clarity).

proton–proton NOE relations, appearance of interligand $^1H-^{31}P$ spin–spin coupling in those complexes that contained a phosphorus ligand, and diamagnetic shielding effects of the P–Ph group of PPh_3 on the nearby proton resonances, all suggesting the proximity of PPh_3 or one allylic terminal to only those protons which are attached to one olefinic carbon end. The stability diagnostics includes considerable decrease of the stability of the *ortho*-substituted styrene complexes relative to unsubstituted and *para*-substituted styrene counterparts in the complexes of the types **20** and **21**, while no such specific decrease of the *ortho*-substituted analogues was found in the series of complexes which contained the normal upright C=C geometry such as **5** (see Table 1). The reason for the former trend is readily traced to steric constraints in the in-plane geometry about the *ortho* substituent which lies at a position on the elongated line of the olefinic C=C axis.

The above results suggest the existence of an electronic origin, small or large, which enforces the in-plane C=C coordination in complexes **20**–**23**. The electronic requirement of the in-plane coordination in the cationic complexes would not be very large in view of the observed wide variation of olefin coordination geometry depending on the steric constraints about the olefinic ligands in **20** [18a]. Thus, as the steric crowding about the olefin in **20** becomes larger, the C=C bond declines more from the in-plane position (declining angle = 6° for $CH_2{=}CH_2 < 11°$ for $CH_2{=}CHPh < 25°$ for $CH_2{=}CHC_6H_4Cl\text{-}o < 46°$ for *E*-MeCH=CHPh < 67° for *E*-MeCH=CHMe). The smaller declining angle of the *E*-β-methylstyrene complex than the *E*-2-butene complex is due to an increase of steric interaction of the phenyl substituent with PPh_3 upon declining further (see **24**).



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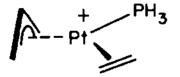

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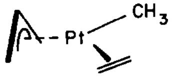

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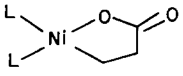
The extended Hückel MO calculation on model **25** also suggested [18a] that the metal–olefin π interaction energy is not so large and the level of the metal $d\pi$ orbital of the fragment $[Pt(\eta^3\text{-}CH_2CHCH_2)(PH_3)]^+$ appropriate for π interaction with the in-plane olefin π^* orbital is only slightly higher in energy than that for π interaction with the upright olefin π^* orbital. On going from the cationic model **25** to a neutral model **26**, the in-plane $d\pi$ orbital of the metal fragment is raised to a greater degree than the upright $d\pi$ orbital [27]. This suggests that the π interaction energy in the neutral complex with the in-plane olefin geometry is more appreciable than in the cationic complex, in agreement with the experimental results mentioned before. Moreover, the electronic force for the in-plane geometry would be larger in the former than the latter. At the moment, however, the last notion has not yet been verified experimentally.

Reactions of olefin complexes of Pd and Pt

General basic patterns of reactions exhibited by olefin complexes of palladium and platinum had been almost fully discovered by 1980 [1]. In the following we briefly summarize these patterns including some recent examples.

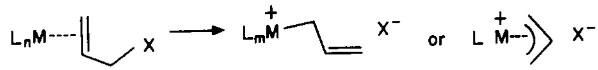
Reactions of olefin complexes of Pd^0 and Pt^0

Because of considerable electron flow from metal to olefins, the olefinic ligand coordinated to zero-valent metals can in principle get activated to the attack of electrophiles. However, electrophiles can also attack directly at the metal center to result in displacement of the olefin ligand, and to date authentic examples of electrophilic attack at the metal-bound olefin ligand have rarely been reported as far as the group 10 metal complexes are concerned. Cocyclization of olefin and CO_2 at the nickel center to give nickela(oxa)cyclopentanone derivatives **27** could be an example of such activation of the coördinated olefins [28]. Formation of analogous five-membered metallacycles from olefins and/or acetylenes with M^0 moieties (eq. 3) has been known for many years [1]. However, this step might not proceed via an ionic pathway, but a concerted one [29]. Elaborated applications of this step in synthetic organic chemistry continue to be the subject of active investigations [30].



27

(3)



(4)

Oxidative addition of vinylic and allylic electrophiles such as triflates and halides with zero-valent metal complexes is usually believed to proceed via an initial coordination of the C=C bond to the metal center (*e.g.* eq. 4) [31]. Apparently such coordination induces enhanced electron density on the olefin, thereby accelerating the departure of the leaving group in the form of a univalent anion.

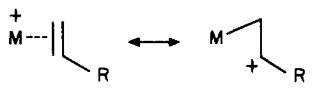
Reactions of olefin complexes of Pd^{II} and Pt^{II}

Some olefin transformations based on the coordinative activation with electrophilic Pd(II) and Pt(II) centers have been known. Perhaps the most popular and the oldest examples include attack of certain nucleophiles (*e.g.* H_2O, ROH, RNH_2) at the metal-coordinated olefin from the side opposite to the metal (eq. 5) [1], a process particularly important in the Wacker reaction. The attack completes the formation of β-substituted alkylmetal complexes. The process occurs mostly in 16-electron, 4-coordinated olefin complexes, but reactions with 18-electron olefin complexes are also known [32]. A recent MO analysis suggested the importance of the inductive effect of the cationic metal center upon the increased susceptibility of the olefin (see **28**) [33]. This effect may play a role comparable to, or in certain cases more significant than the slippage deformation of the olefin coordination geometry which had been proposed in the earlier MO study [34].

(5)

The effective positive charge induced on the olefinic carbon as in **28** may also cause the occurrence of other important olefin transformations than the reaction of eq. 5, *e.g.* double bond migration [14,35], oligomerization and polymerization [35], allylmetal formation [14,36]. Palladium(II) catalyzed Cope rearrangements are also initiated by a similar activation (eq. 6) [37].

An olefin transformation unique to those complexes which are intermediate in the nature of the olefin–metal bond between those of nucleophilic M^0 and electrophilic M^{II} complexes has been almost undeveloped. However, it seems worthwhile to add the significant role in accelerating η^3-allyl-aryl reductive elimination (eq. 7) played by the olefin ligand which is coordinated with a 16-electron metal center with in-plane geometry and whose electronic factor little affects the metal–olefin bond strength (see above). As the η^3-allyl-aryl coupling in **29** proceeds, the higher the level of the in-plane, occupied $d\pi$ orbital is raised, thus



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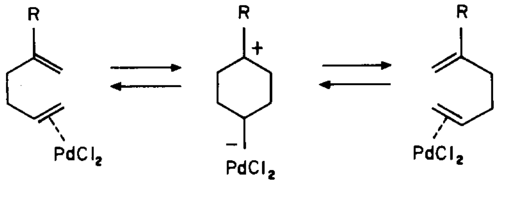
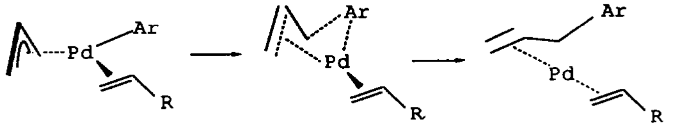


(6)

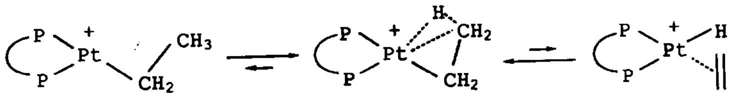
being primarily responsible for the activation barrier. This type of origin of the activation barrier is much the same as that presented in reductive elimination of *cis*-$Pd(CH_3)_2(PH_3)_n$ ($n = 1, 2$) [38]. Now the in-plane olefin ligand can lower that particular $d\pi$ orbital, through the π back bonding, and thus contribute to the lowering of the transition state energy of the coupling [12].



(7)

29

Another important class of olefin transformation in M(II) complexes is olefin insertion into M–H and M–R bonds. A theoretical calculation on ethylene insertion into the Pt–H bond suggested a more facile pathway in the 16-electron intermediate *cis*-$[PtH(C_2H_4)(PR_3)_2]^+$, rather than in the 18-electron intermediate $PtH(Cl)(C_2H_4)(PR_3)_2$ [39]. Recent studies have substantiated this notion in a very intriguing manner [40], *i.e.* remarkable stabilization of the transition state of the insertion step was realized in 16-electron complexes. The proper choice of the chelating diphosphine ligand in the system led to the occurrence of an agostic structure (**30**) in the ground state. Variable temperature NMR studies also demonstrated the occurrence of very rapid conversion from **30** to both Pt–C_2H_5 (**31**) and $PtH(C_2H_4)$ species (**32**). Rotation of ethylene about the Pt–ethylene bond in **32** was also quite rapid.



31 **30** **32**

(8)

Concluding remark

Future developments in more sophisticated and more selective transformations of olefinic substrates will be made by taking into account the basic structure and bonding concepts that have been clarified. A particular key to this goal would be the proper choice of both the metal center and ancillary ligand groups capable of modifying electronic and steric environments at the reaction center in a critical way.

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