ELSEVIER

Journal of Organometallic Chemistry 500 (1995) 337–348

Journal of Organometallic Chemistry

Invited review

Comparison of the reactivities of neutral and cationic transition metal alkyls and hydrides

Akio Yamamoto

Department of Applied Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo, 169, Japan

Received 22 February 1995

Abstract

Comparisons of the reactivities of neutral and cationic alkyl- and aryl-palladium and platinum complexes revealed that the creation of a vacant site adjacent to the alkyl or aryl ligand bound to the palladium center causes marked enhancement in the reactivities of these Group 10 metal alkyls and aryls toward β-hydrogen elimination, and olefin or CO insertion. The implications of the results on the fundamental processes of the transition metal alkyls and aryls with the mechanisms of palladium-catalyzed organic synthesis such as arylation of olefins and carbonylation of aryl halides are discussed. Comparisons of the reactivities of the neutral and cationic ruthenium hydrides also indicated enhancement in reactivity of the neutral hydride complex by its conversion to a cationic complex.

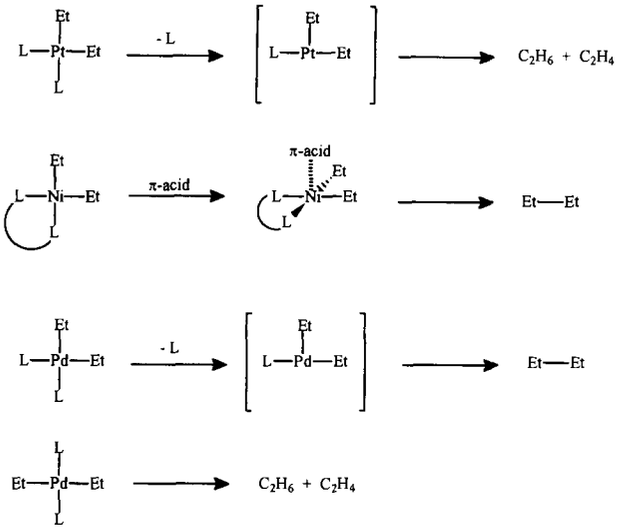
Keywords: Platinum; Palladium; Hydrides; Insertion reactions; Catalysis; Cationic complexes

1. Introduction

The chemistry of transition metal alkyls has developed remarkably in the past 30 years. When I first began work in the field, the known examples of the isolated transition metal alkyls were quite limited [1,2]. A possible reason suggested for the scarcity of transition metal alkyls was that β-hydrogen elimination provides a route for the further decomposition. (Eq. (1)).

It was thus considered that blocking of the β-hydrogen elimination pathway by using alkyls without β-hydrogens or alkyls not amenable to the β-hydrogen elimination on steric grounds might allow isolation of stable transition metal alkyls and some stable transition metal alkyls without the β-hydrogens were, in fact, isolated and shown to be thermally stable. The role of supporting ligands such as tertiary phosphines and amines was considered to to block access to the site for interaction of β-hydrogen with the metal center [3]. However, transition metal alkyls can decompose through mechanisms other than β-elimination, such as reductive elimination and α-hydrogen elimination. For the dialkyls of the late transition metals in particular, reductive elimination provides an important mode of decomposition, involving with concomitant C–C bond formation that finds many applications in organic synthesis. As I discussed in an earlier "centenary" issue of this journal [1], even for simple metal dialkyls of Group 10 elements, the thermolysis pathway varies with the nature of the metal, the alkyl, and the supporting ligands. Typical thermolysis routes are summarized in Scheme 1. It can be seen that the decomposition routes vary considerably. Platinum alkyls with β-hydrogens break down in most cases by the β-hydrogen elimination route following ligand dissociation from the square planar complex to give a T-shaped intermediate [4,5]. Nickel alkyls containing a bipyridine ligand undergo reductive elimination in the presence of a π-acid such as maleic anhydride through a penta-coordinate intermediate, the reductive elimination being accelerated by the acid [6]. Palladium dialkyls exhibit intermediate behavior, both the reductive elimination and β-hydrogen elimination being observed for palladium diethyls, depending upon whether the configuration of the complex *cis* or *trans*, and can take place with or without ligand dissociation [7,8]. In contrast to the attention given to the Group 10 metal dialkyls, studies of the thermolysis pathways for the corresponding metal monoalkyls have been very limited [9] except in the case of platinum. In our studies of the reactions of Group 10 metal alkoxides and thiolates we prepared some ethylmetal alkoxide- and thiolate complexes having trimethylphosphine ligands [10]; we found that palladium monoalkyls having β-hydrogens could be stabilized by the presence of

SSDI 0022-328X(95)00521-8



Scheme 1. Thermolysis pathways of dialkyls of Group 10 metals.

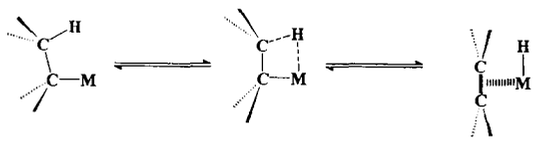
basic and compact ligands that dissociate less readily than the other less basic and more bulky tertiary phosphine ligands.

2. Chemistry of neutral and cationic monoorganopalladium complexes

2.1. Monoethylpalladium complexes

Our success in isolating stable monoethylpalladium complexes containing trimethylphosphine ligands together with electronegative ligands such as halides and carboxylates provides us with the opportunity to examine the thermolysis behavior of these simple monoethylpalladium complexes [11]. A series of monoethylpalladium complexes coordinated with various electronegative ligands, namely *trans*-[PdEt(X)(PMe_3)$_2$] (**1**), where X = OPh, O_2CCH_3, O_2CCH_2Cl, O_2CCHCl_2, O_2CCCl_3, $O_2CCH_2CH{=}CH_2$, SPh, $SCOCH_3$, Cl, Br or I, were prepared by protonolysis of *trans*-$PdEt_2(PMe_3)_2$ (**2**) with HX (Eq. (2)) or by metathesis of the monoethylpalladium acetate complex (**1a**) (Eq. (3)).

The monoethylpalladium complexes with PMe_3 ligands are moderately stable thermally but are readily thermolyzed on warming the solutions. The ethylpalladium acetate complex **1a** generates ethylene, acetic acid and palladium black on thermolysis in dichloromethane (Eq. (4)).

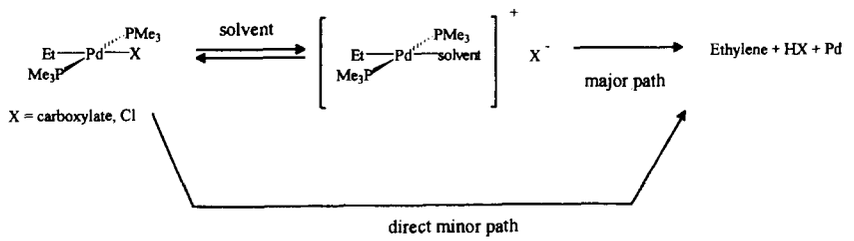

(1)

A kinetic study involving monitoring of the disappearance of the ethylpalladium-complex by NMR spectroscopy and the release of ethylene by gas chromatography showed that the disappearance of the ethylpalladium-complex is first order with respect to the concentration of the complex and that the thermolysis is hindered by addition acetate anion to the system. The results are in agreement with the mechanism shown in Scheme 2.

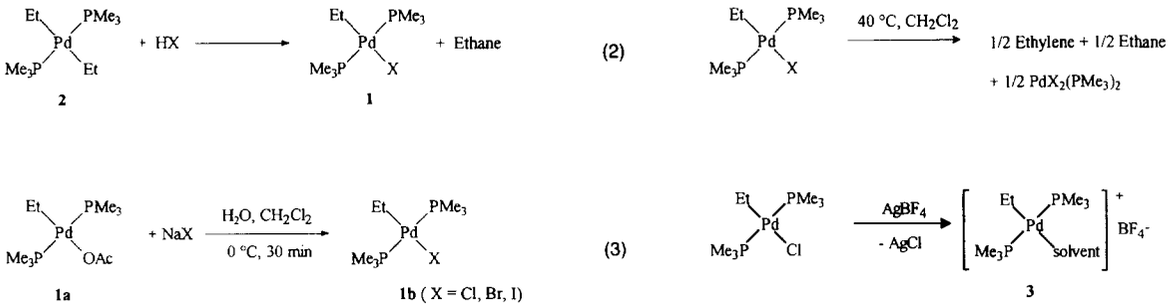
The thermolysis scheme comprises two routes. One is a minor direct route, and the other a major indirect route involving the generation of a cationic ethylpalladium intermediate by dissociation of the acetate ligand. The β-hydrogen elimination takes place cleanly from the ethylpalladium complex to liberate ethylene, without any dissociation of the PMe_3 ligand. Use of the nondissociating PMe_3 ligand made this and subsequent studies straightforward. The hydridopalladium acetate produced by the β-hydrogen elimination process may release acetic acid by reductive elimination.

When the protic acid HX produced in the thermolysis is more strongly acidic than acetic acid, subsequent attack of the HX (X = chloroacetates, thiolate, thioacetate, and halides) or of the $HPd(X)L_2$ on the remaining ethylpalladium complex takes place to generate ethane after the loss of ethylene (Eq. (5)). Thus a 1 : 1 mixture of ethylene and ethane is produced in a single β-hydrogen elimination process.

An inhibiting effect of added X^- anion on thermolysis of the ethylpalladium complexes was observed with all these complexes. The results point to a dissociative process leading to intermediate formation of the solvent-coordinated cationic ethylpalladium complex. In the light of the negative entropy values observed by formation of the cationic complex the process shown in



Scheme 2.



Scheme 3 is proposed, involving solvent assistance to the departure of the X ligand from the palladium center to generate the solvent-coordinated ionic species (Scheme 3).

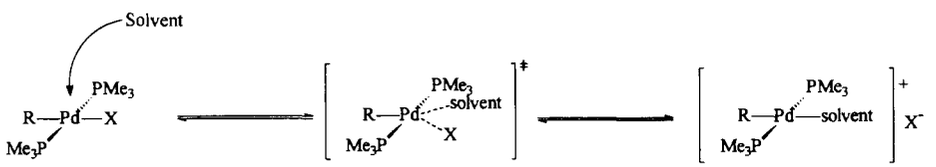
At the beginning of the study we did not predict the involvement of a dissociative process in the β-hydrogen elimination, but in hindsight its occurrence should not have been too surprising. In fact Romeo and coworkers had reported a halide dissociative process for *cis–trans* isomerization [12], and quite recently dissociation of the halide ligand in the β-hydrogen elimination process from the corresponding ethylplatinum halide complexes bearing triethylphosphine ligands was reported [13].

The recognition of the involvement of the cationic ethylpalladium complex in the thermolysis of the neutral ethyl palladium complexes, *trans*-$PdEt(X)(PMe_3)_2$, prompted us to prepare the cationic ethylpalladium complex by removing the halide ligand from *trans*-$PdEt(X)(PMe_3)_2$ (**1b**) with a silver salt. Removal of the bromide ligand from *trans*-$PdBr(Et)(PMe_3)_2$ did indeed give the thermally unstable complex *trans*-$[PdEt(solvent)(PMe_3)_2]BF_4$ (**3**), retention of the *trans* configuration being confirmed by NMR spectroscopy [14] (Eq. (6)).

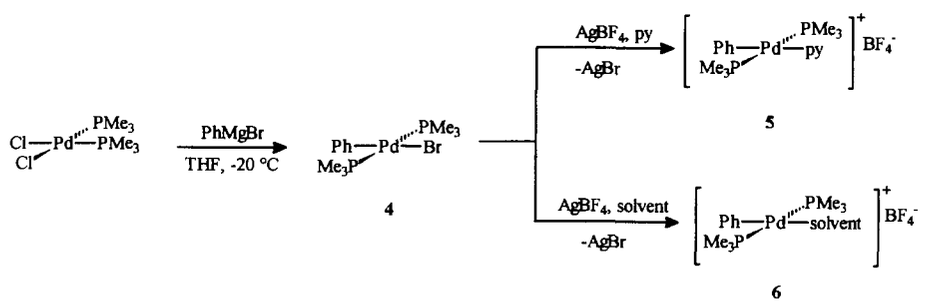
The cationic ethylpalladium complex **3** decomposes even at $-30°C$ in CD_2Cl_2 solution to release ethylene.

2.2. Behavior of monophenylpalladium complexes relevant to Heck olefin arylation reactions

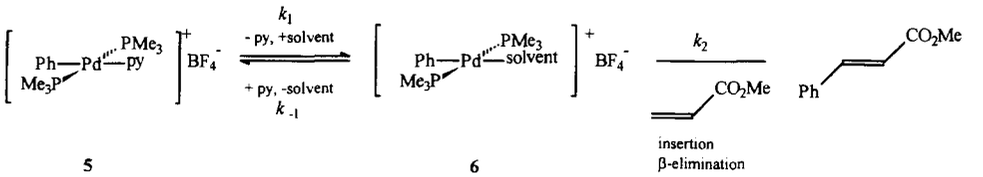
Prompted by the finding that the neutral monoethylpalladium complexes form by dissociation of the electronegative ligand, ionic monoethylpalladium complexes that are much more reactive than the corresponding parent, neutral palladium complexes, we began a comparison of the reactivities of the neutral and ionic monophenylpalladium complexes [15]. The palladium-catalyzed Heck-type arylation of olefins with aryl halides is considered to involve the following elementary processes: (a) oxidative addition of an aryl halide to a Pd(0) complex to give an arylpalladium halide species; (b) insertion of the olefin into the aryl–palladium bond



Scheme 3.



Scheme 4.



Scheme 5.

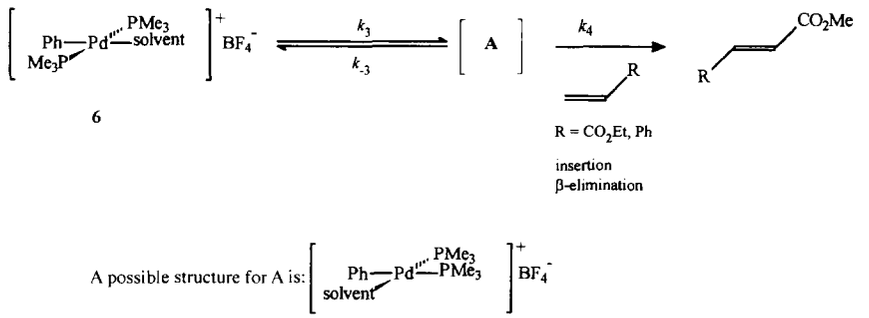
to give an alkylpalladium species; (c) β-hydrogen elimination from the alkylpalladium species to yield a hydridopalladium halide species; and (d) removal of the hydrogen halide by a base to regenerate the Pd(0) species that carries the catalytic cycle. However, the detailed mechanisms of the β-hydrogen elimination and the subsequent processes have not been clarified. Recently, addition of silver salts to the olefin arylation systems was found to enhance the rate and selectivity of the catalyzed process [16]. It has also been noted that the use of aryl and alkenyl triflates in combination with a Pd(0) catalyst facilitates the Heck reaction [17] [18]. These observations suggest the involvement of cationic organopalladium complexes in the catalytic cycle of the Heck reactions. We thus prepared neutral and cationic phenylpalladium complexes **4**–**6** by the routes shown in Scheme 4 and compared their reactivities toward olefins.

Removal of the bromide ligand from the neutral *trans*-phenylpalladium bromide complex **4** bearing two trimethylphosphine ligands by use of one equivalent of $AgBF_4$ in the presence and absence of pyridine yielded the pyridine- and solvent-coordinated cationic phenylpalladium complexes, **5** and **6**, respectively. The reactions of these neutral and cationic phenylpalladium complexes with olefins such as styrene, 1-hexene, methyl acrylate and methylvinylketone, cleanly gave the corresponding phenylated olefins. The reactions were of first order with respect to the phenylpalladium complex. The reactivity toward methyl acrylate decreases in the order **6** > **5** > **4**, indicating that the cationic phenylpalladium complex is more reactive than the neutral one and that the pyridine-coordinated complex **5** is less reactive than the complex **6** bearing a more weakly coordinating solvent such as acetone or dichloromethane. A kinetic study of the reaction with methyl acrylate showed that addition of pyridine strongly inhibits the reaction with the olefin. The result can be accommodated by the mechanism shown in Scheme 5.

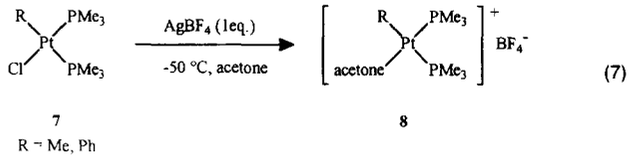
In the reaction of the cationic pyridine-coordinated phenylpalladium complex **5** with methyl acrylate, the dissociation of the coordinated pyridine from **5** to give the solvent-coordinated complex **6** is rate determining. This step is followed by interaction of **6** with the olefin, insertion of the olefin into the phenylpalladium bond in **6** and the subsequent β-hydrogen abstraction to produce methyl cinnamate. We also carried out a kinetic study of the reaction of the independently prepared cationic, solvent-coordinated phenylpalladium complex **6** with methyl acrylate, and the results can be explained in terms of the mechanism shown in Scheme 6.

The results can be accounted for by applying the steady state approximation to an intermediate complex **A** that is formed from **6** and then reacts with the olefin to give the phenylated olefin. It is reasonable to assume that the intermediate **A** is a cationic, *cis*-phenylpalladium complex that has a vacant site adjacent to the phenyl ligand to accommodate the incoming olefin. In the subsequent step the olefin is inserted into the phenyl–palladium bond in a concerted manner and subsequent β-hydrogen elimination releases methyl cinnamate.

In the case of organopalladium complexes containing monotertiary phosphine ligands we have not been able to detect a *cis*-organopalladium complex having the vacant site next to the organic ligand. In contrast, for neutral organoplatinum complexes such *cis* forms are commonplace. However, no cationic organoplatinum complexes with monodentate tertiary phosphines that



Scheme 6.

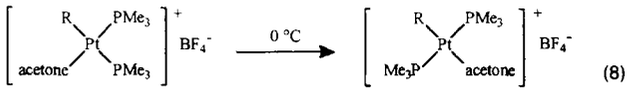


(7)

7
R = Me, Ph

8

have *cis* configuration have been reported to our knowledge, despite the abundance of the corresponding complexes with *trans* configurations [19]. We found that removal of the chloride ligand from the *cis*-monoorganoplatinum chloride **7**, bearing two trimethylphosphine ligands, with $AgBF_4$ at $-50°C$ in acetone gave the cationic acetone-coordinated *cis*-methyl and phenylplatinum complexes **8** (Eq. (7)) [20]. When the acetone solution of the *cis*-methylplatinum complex **8** was warmed from -50 to 0°C the *cis* complex readily isomerized to the *trans* form **9** (Eq. (8)):



(8)

8 9

Although the isomerization of the organoplatinum complex proceeds from the *cis* to the thermodynamically more stable *trans* form, it is not unreasonable to assume a reverse isomerization, from the stable *trans* form to the less stable and reactive *cis* form, for the corresponding organopalladium complex, to give a transient species **A** that can accommodate the olefin at the position *cis* to the phenyl ligand as in Scheme 6.

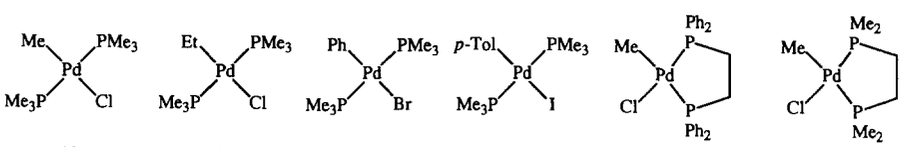
These results indicate that creation of a vacant site adjacent to the alkyl or aryl ligand is important to facilitate further reactions such as β-hydrogen elimination or olefin insertion into the phenyl–palladium bond. The vacant site can be generated by self-dissociation of the electronegative ligand or by removal of a halide ligand by a silver ion [21].

2.3. CO and isocyanide insertion into Pd–alkyl or Pd–aryl bond in neutral and cationic monoorganopalladium complexes

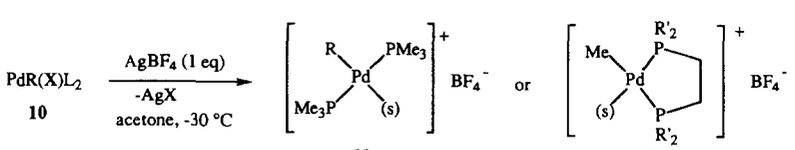
After finding that the marked rate enhancement in the β-hydrogen abstraction and olefin insertion processes involving monoorganopalladium complexes is due to generation of a cationic organopalladium complex from the neutral one, we decided to find out whether the insertion of CO into a carbon–palladium bond is also promoted by creation of a cationic complex [14]. A range of monoorganopalladium halide complexes (**10a–10f**) were prepared, along with their cationic counterparts (**11**) and (**12**) obtained by removal of the halide ligands from the neutral monoorganopalladium halide complexes by $AgBF_4$ (Scheme 7).

All the neutral and cationic organopalladium complexes reacted readily with carbon monoxide at 1 atm. pressure in acetone at low temperatures to give the corresponding acetylpalladium complexes **13** and **14**, as identified by NMR spectroscopy (Scheme 8).

No decarbonylation of the acetylpalladium complexes was observed at $-30°C$. Coordination of the CO ligand trans to the acetyl ligand in **14** was confirmed by an use of ^{13}CO [22]. Both reactions of the neutral and the cationic complexes toward CO were of pseudo-first order. The rate constant for CO insertion into the cationic methylpalladium complex **11** was found to be higher by a factor of 10^2 than that for reaction of the neutral methylpalladium complex **10a** to form **13**. The rate of CO insertion into the methylpalladium complexes **12a** and **12b** bearing the chelating ditertiary phosphines



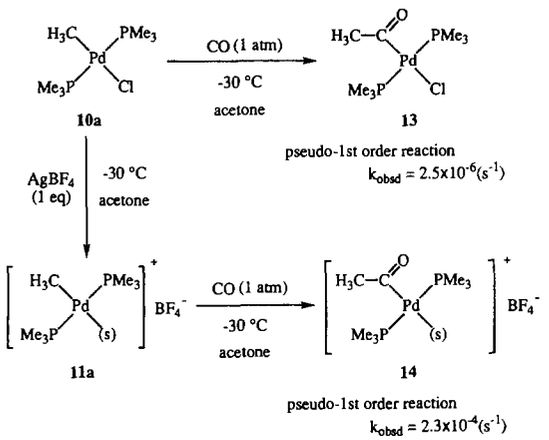
10a **10b** **10c** **10d** **10e** (PdMe(Cl)(dppe)) **10f** (PdMe(Cl)(dmpe))



10 **11** **12**

R = Me **11a**, Et **11b**, Ph **11c**, *p*-Tol **11d** R' = Ph **12a**, Me **12b**

Scheme 7.

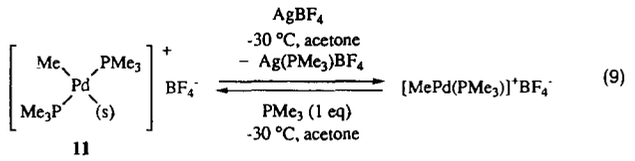


Scheme 8.

dppe and dmpe, was more than three times as fast than that into the *trans* methylpalladium complex bearing PMe_3 ligands (**11**).

The rate of CO insertion into the cationic *trans*-methylpalladium complex (**11**) depended on the solvent used. The rate fall with increase in the coordinating ability of the solvent in the order $CH_3CN < Me_2CO < CH_2Cl_2$, suggesting that stronger coordination of the solvent molecule retards the CO insertion.

Benzyl isocyanide or tert-butyl isocyanide, an analog of CO, coordinates with the cationic *trans*-methylpalladium complex **11** bearing two PMe_3 ligands to give benzyl isocyanide-coordinated complexes **15** when **11** is treated with one equivalent of the isocyanide. Treatment of **15** with a further equivalent of the isocyanide in acetone at room temperature gives the isocyanide-coordinated cationic complex **16** in which are molecules of the isocyanide has been inserted into the methyl–palladium bond of **15**. Insertion of CO into the isocyanide-coordinated methylpalladium complex **15**



(9)

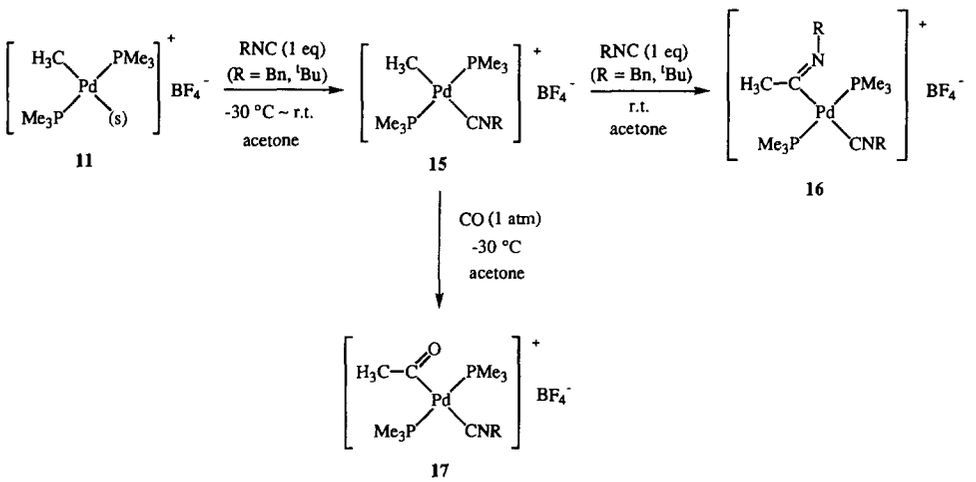
also takes place at −30°C, to give the isocyanide-coordinated acetylpalladium complex **17** (Scheme 9).

These results seemed to indicate that the cationic organopalladium complexes were generally more reactive than the neutral ones. However, a detailed study of the reactivities of the *trans*-methylpalladium complexes bearing two PMe_3 ligands revealed that the benzyl isocyanide-coordinated methylpalladium cation **15** was less reactive than the neutral methylpalladium chloride complex **10a** toward CO insertion. The result seems to indicate that the ability of a ligand coordinated to the metal center to block the incoming substrate such as CO is more important than whether the methylpalladium complex is neutral or cationic.

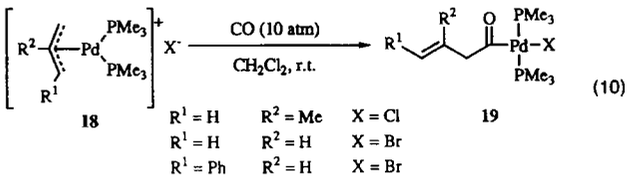
The above-mentioned comparisons were made using tertiary phosphine ligands such as trimethylphosphine or chelating phospines that show less tendency to dissociate from palladium in solution. When the PMe_3 ligands were replaced by less coordinating PPh_2Me ligands, the reactivity towards CO insertion was increased.

Although the halide ligand in monoorganopalladium halide complexes can be cleanly removed with an equivalent of $AgBF_4$ to afford the cationic *trans*-methylpalladium complex **11**, a further PMe_3 ligand can be removed from **11** by treating it with an excess of $AgBF_4$ (Eq. (9)) [23].

The rate of CO insertion into the methyl-Pd bond in **11a** was increased by a factor of 4 upon removal of one of the PMe_3 ligands in **10a** by use of an excess of the



Scheme 9.



(10)

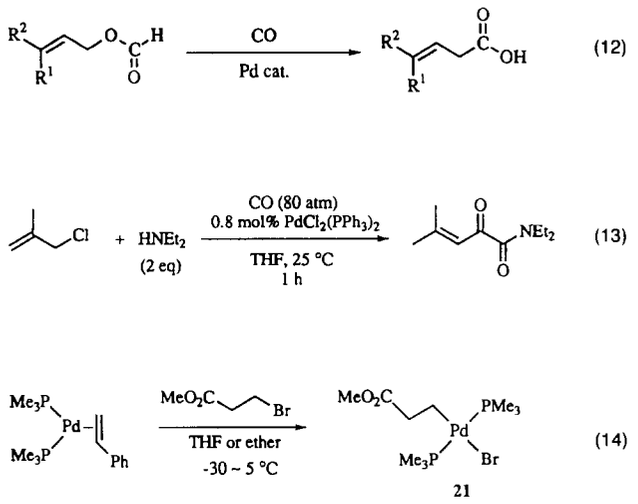
silver salt. The result suggests that the availability of the coordination site *cis* to the methyl ligand is important for occurrence of the insertion reaction of the methylpalladium complex.

2.4. Olefin insertion into an acyl–Pd bond

In contrast to the extensive studies of CO insertion into the alkyl–palladium bond and olefin insertion into the phenyl–palladium bond, there are few examples of olefin insertion into the acyl–Pd bond. The process is important for understanding the mechanism of the olefin and CO copolymerization [24] as well as for expanding the scope of processes involving the CO and the olefins in association with palladium catalysts. In keeping with results reported by Sen [25], Elsevier [26] and Brookhart [27] and their coworkers, we found that creation of a cationic acylpalladium species enhanced the reactivity of the acylpalladium complex toward olefin insertion and the penultimate carbonyl group is bound to the cationic palladium center to be stabilized after the olefin insertion [28].

2.5. CO insertion into the allyl–Pd bond

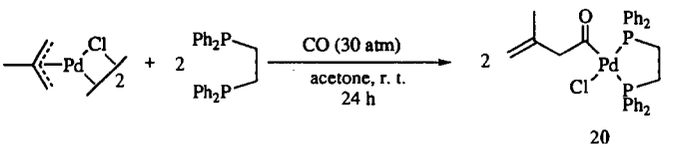
For development of catalytic systems involving transition metal complexes for incorporating CO into various organic compounds it is desirable to have available various elementary processes involving CO insertion into transition metal–carbon bonds. As noted above, CO insertions into the alkyl–Pd and aryl–Pd are established processes. In contrast, there have been only limited reports of CO insertions into allyl–palladium bonds. We previously reported that the CO insertion can take place under appropriate conditions depending on the nature of the allylic moiety and on the number and nature of the tertiary phosphine ligands attached to palladium, (Eq. (10)) [29]. The square planar cationic π-allylpalladium complex **18** bearing two PMe_3 ligands and a halide anion undergoes CO insertion at room



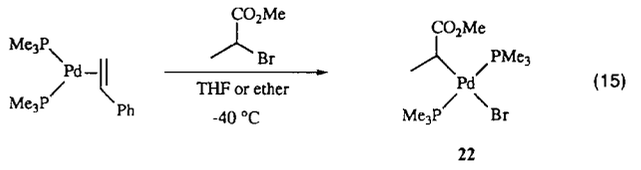
temperature to give the alkenoylpalladium complex **19**. In our experience, use of strongly coordinating ligands such as PMe_3 is favorable for CO insertion. Use of the more weakly coordinating ligand $PMePh_2$ does not lead to complete CO insertion even under pressure, and the resulting acylpalladium complex readily undergoes decarbonylation at room temperature to be regenerate the π-allylpalladium complex **18**. Use of the chelating ligand dppe also favors the CO insertion (Eq. (11)). Addition of dppe to the chloride-bridged 2-methylallylpalladium(II) complex followed by treatment with CO at room temperature in acetone gives the CO-inserted alkenoylpalladium complex **20** in a good yield [30]. The alkenoyl complex **20** is also susceptible to decarbonylation when the chloride ligand is removed by treatment with silver ion.

Among the halide ligands, those that dissociate less readily seem to be more suitable for permitting CO insertion into the Pd–allyl bond. This may be related to the reluctance of the halide ligand to dissociate from the palladium center to create a vacant site for the reverse decarbonylation from the alkenoylcomplex as we discussed for the monoorganopalladium halide complexes in Section 2.3. Indeed, if the halide ligand is removed by treatment of the alkenoylpalladium halide complex **19** with a silver ion the decarbonylation of the alkenoyl complex **19** to regenerate **18** takes place immediately.

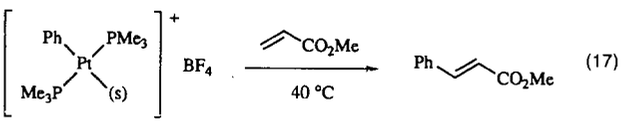
Knowing the feasibility of CO insertion into the allyl–Pd bond we have been able to develop two novel carbonylation processes [31]. One involves the conver-



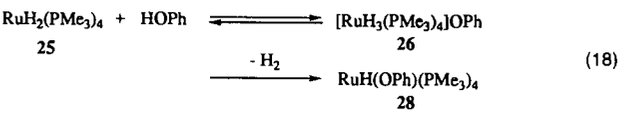
(11)



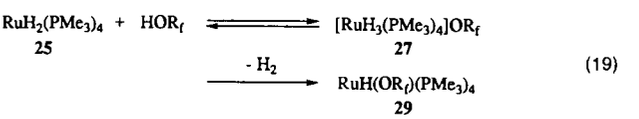
(15)



(17)



(18)



(19)

sion of allylic formates into β,γ-unsaturated acids (Eq. (12)) and the other involves double carbonylation of allylic chlorides with CO and secondary amine to give a β,γ-unsaturated α-ketoamide (Eq. (13)).

Mechanistically, both processes proceed by the CO insertion into intermediate allylpalladium complexes to give alkenoylpalladium complexes. In the process involving the allylic formates, oxidative addition of allylic formates gives allylpalladium formate complexes. The following CO insertion and the subsequent reductive elimination of the alkenoyl and the formate ligands releases the mixed acid anhydrides, which are further decarbonylated to give the β,γ-unsaturated carboxylic acids. In the latter process the catalytic cycle consists of: (a) oxidative addition of the allylic chlorides to form an allyl-palladium chloride; (b) CO insertion into the allyl–Pd bond to give an alkenonylpalladium chloride complex; (c) dissociation of the chloride ligand to give a cationic alkenoylpalladium species with a site for the CO coordination; (d) nucleophilic attack of the amine on the CO ligand coordinated to the cationic palladium center to give the carbamoyl ligand; and (e) reductive elimination of the alkenoyl and carbamoyl ligands to liberate α-keto amide. Generation of a vacant site for coordination of CO to the electrophilic cationic palladium center seems to be crucial for occurrence of the double carbonylation [32].

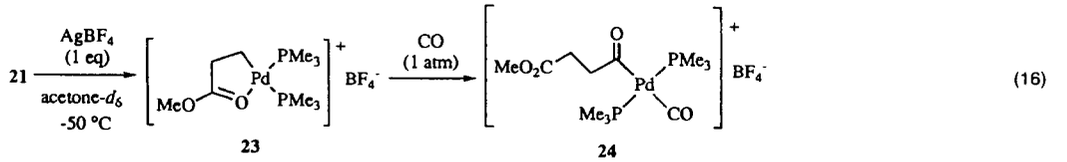
These results indicate that generation of a coordination site for a particular reaction plays an important role in determining the course of the reaction. Unstable monoorganopalladium complexes can be stabilized by blocking the site for a decomposition pathway such as β-hydrogen elimination, whereas creation of a site for coordination of an unsaturated substrate such as olefin, CO, and alkyl isocyanide facilitates the substrate coordination and the subsequent insertion reactions.

2.6. Synthesis and properties of other functionalized alkylpalladium complexes

Blocking the site for β-hydrogen elimination by using the basic and compact PMe_3 ligands enabled preparation of other alkylpalladium complexes with β-hydrogens [33]. Thus treatment of $Pd(PMe_3)_2$(styrene), which is coordinatively unsaturated and very reactive towards oxidative addition, with methyl α- and β-bromopropionates yielded linear and branched methoxycarbonyl-substituted ethylpalladium bromide complexes **21** and **22** (Eqs. (14) and (15)).

Removal of the bromide ligand from **21** by treatment with $AgBF_4$ gives a cationic β-methoxycarbonylethylpalladium complex **23**, in which the carbonyl group is bound to the palladium center [34,35]. The cationic alkylpalladium complex **23** is much more reactive towards CO insertion than the neutral bromide complex **22**, and affords the acylpalladium complex **24** even at low temperatures [33].

In contrast to phenylpalladium complexes, which undergo olefin insertion and the succeeding β-hydrogen elimination to liberate the phenylated olefins [15], the corresponding phenylplatinum complexes are only weakly reactive towards olefins. Neutral phenylplatinum halide compexes with PMe_3 ligands do not react



23 24

(16)

with methyl acrylate or methylvinylketone, and only after removal of the halide ligand to give the cationic phenylplatinum complex and with use of higher temperatures, does reaction occur with these olefins, as shown in Eq. (17).

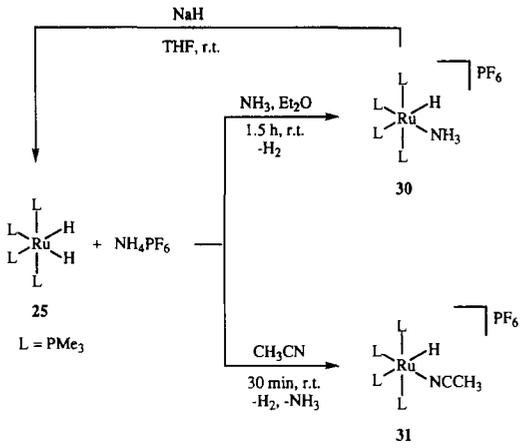
3. Comparison of neutral and cationic hydridoruthenium complexes

Recognition of the enhancement of the reactivity of alkyltransition metal complexes by generating cationic complexes from neutral ones prompted us to find out whether similar enhancement in reactivity would be observed on conversion of a neutral transition metal hydride into a cationic species. In an earlier program (prior to my move from Tokyo Institute of Technology to Waseda University), concerned with the synthesis and properties of hydridoruthenium alkoxide and aryloxide type compexes [36,37] we observed indications of participation of intermediate cationic hydridoruthenium complexes following treatment of the neutral $RuH_2(PR_3)_4$ with acidic alcohols and phenols, as depicted in Eqs. (18) and (19):

The reactions of phenol and hexafluoropropan-2-ol (R_fOH) with $RuH_2(PMe_3)_4$, **25**, were shown to involve initial formation of cationic species $[RuH_3(PMe_3)_4]OPh$ (**26**) and $[RuH_3(PMe_3)_4]OR_f$ (**27**) and subsequent loss of H_2 to give the monohydridoruthenium phenoxide of alkoxide complexes *cis*-$[RuH(OPh)(PMe_3)_4]$, **28**, and *cis*-$[RuH(OR_f)(PMe_3)_4]$, **29**. We also observed that the phenoxide and the fluoroalkoxide ligands tend to dissociate in solution to give a cationic hydridoruthenium complex.

After my move to Waseda University I was able to set up a small group to continue my study on the properties of alkyl- and hydrido-transition metal complexes. When post-doctoral fellow, Dr. Thomas Rappert, arrived from Professor H. Werner's group in Germany, we decided to see whether a reactivity enhancement similar to that we had observed with the organopalladium complexes would be found also for ruthenium complexes. Again, in the case of a ruthenium hydride complex used of the trimethylphosphine ligand allowed us to obtain clear-cut results [38].

Treatment of *cis*-$RuH_2(PMe_3)_4$ in ether with NH_4PF_6 or NH_4BPh_4 at room temperature under NH_3 gave almost quantitatively the ammonia-coordinated cationic hydridoruthenium complex *cis*-$[RuH(NH_3)(PMe_3)_4]X$ ($X = PF_6$ or BPh_4) (**30** in Scheme 10). When the reaction was carried out in acetonitrile, the acetonitrile-coordinated cationic hydridoruthenium complex *cis*-$[RuH(NCCH_3)(PMe_3)_4]X$, **31**, was obtained. The NH_3 ligand in **30** can be readily displaced by acetonitrile to give **31**, and treatment of **30** with hydride-donating reagents such as NaH regenerates the starting neutral *cis*-dihydride complex **25** (Scheme 10).

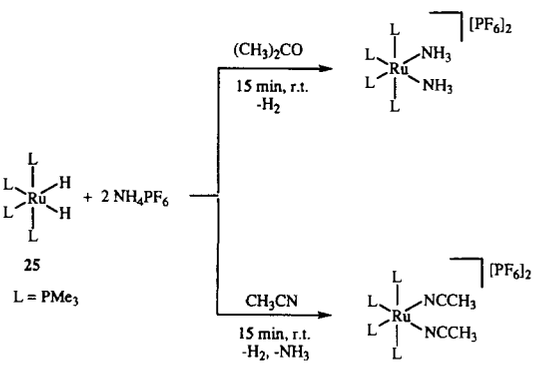


Scheme 10.

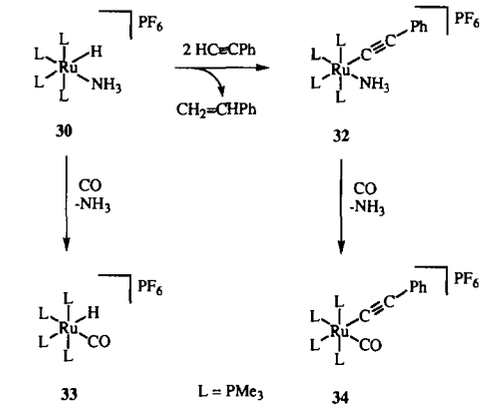
The monohydride complex **30** can also be converted by $NaBH_4$ into the neutral dihydride complex **25** through the intermediate hydride-bridged complex $RuH(\eta^2\text{-}BH_4)(PMe_3)_3$, which reacts further with added PMe_3 to give **25**.

On treatment of the neutral dihydride complex **25** with two equivalent of NH_4PF_6 in acetone or acetonitrile the two hydrido ligands in the neutral complex are protonated to give the dicationic complexes *cis*-$[Ru(NH_3)_2(PMe_3)_4](PF_6)_2$ and *cis*-$[Ru(NCCH_3)_2(PMe_3)_4](PF_6)_2$ (Scheme 11).

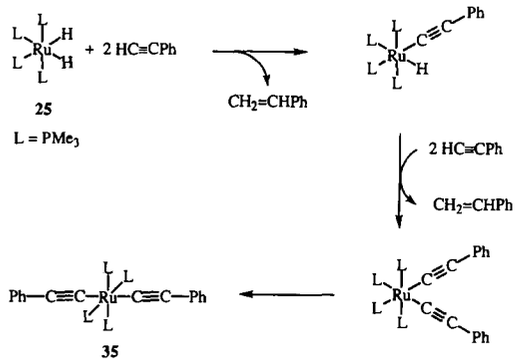
The ammonia-coordinated cationic monohydrido complex **30** does not undergo exchange with ethylene and PhC≡CPh but reacts readily with phenylacetylene in acetone at room temperature to give the the cationic alkynylruthenium complex *cis*-$[Ru(C{\equiv}CPh)(NH_3)(PMe_3)_4]PF_4$, **32**, along with styrene. The reaction probably proceeds by insertion of the phenylacetylene into the Ru–H bond in **30** to give a styrylruthenium complex, which reacts with a further equivalent of phenylacetylene to give the alkynyl complex **32**. The ammonia ligand coordinated to ruthenium in **30** and **32** can be readily displaced by CO to give the CO-coordinated complexes **33** and **34** (Scheme 12). No CO insertion



Scheme 11.



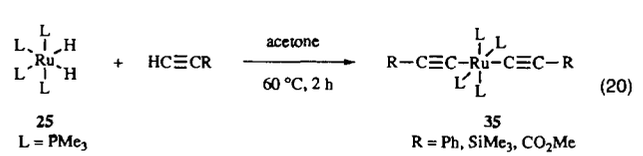
Scheme 12.



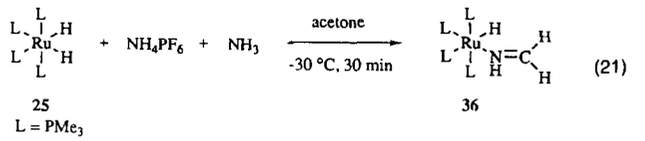
Scheme 13.

into the ruthenium–alkynyl bond was observed even on heating **32** under 50 atm of CO at 60°C.

In contrast to the ready reaction of the cationic hydridoruthenium complex **30** with phenylacetylene, the reactivity of the neutral dihydride complex **25** toward phenylacetylene was very much lower, and heating was necessary to initiate the reaction with alkynes. The reaction of **25** with phenylacetylene to give the bisalkynyl complex, *trans*-[Ru(C≡CPh)$_2$(PMe$_3$)$_4$], **35**, Eq. (20), was shown to proceed as shown in Scheme 13.The cationic monohydridoruthenium complexes **30** and **32** showed catalytic activity in the dimerization of phenylacetylene to give the enyne (*Z*)-1,4-diphenylbeten-3-yne at room temperature or above. The catalytic activity in the alkyne dimerization was lower in the presence of CO and ammonia, suggesting that generation of a vacant site for coordination of the substrate is required for the catalysis. In contrast, the neutral dihydridoruthenium complex **25** reacted with phenylacetylene only at elevated temperatures to give the catalytically inactive *trans*-dialkynyl complex **35**. A mechanism that accounts for the dimerization of phenylacetylene in the presence of the cationic hydridoruthenium complex **30** or **32** has been suggested [38].



(20)

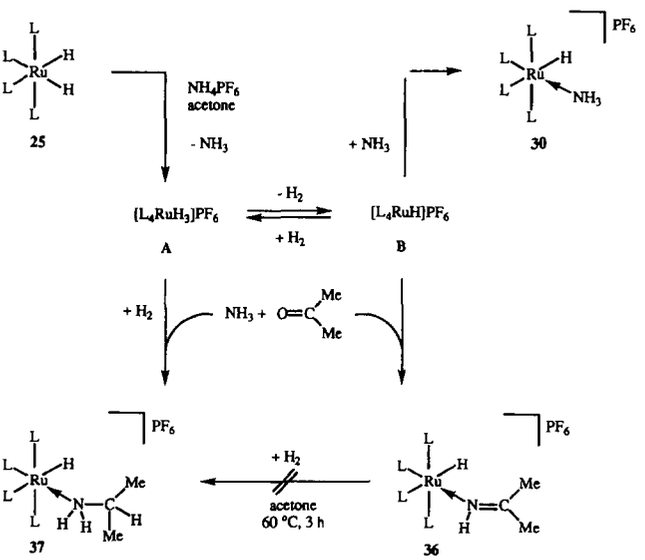


(21)

An increase in the reactivity of the hydridotransition metal complexes by conversion from a neutral into a cationic complex was observed for formation of the imine-coordinated complex **36** in the reaction of the neutral dihydride complex **25** under an atmosphere of ammonia in acetone at −30°C, Eq. (21):

When a solution of the neutral dihydride complex **25** was treated with NH_4PF_6 in acetone at −60°C under H_2, hydrogenation of the imine was observed and an amine-coordinated complex *cis*-[RuH(H_2NCHMe$_2$)(PMe$_3$)$_4$]PF_6, **37**, was obtained in a good yield [39]. Similarly, the reaction of **25** with NH_4PF_6 and benzophenone at −60 to −10°C yielded *cis*-[RuH(NH≡CPh$_2$)(PMe$_3$)$_4$]PF_6. Possible reaction pathways leading to the imine- and amine-coordinated, cationic hydridoruthenium complexes are shown in Scheme 14.

In view of our earlier observation of formation of cationic [RuH$_3$L$_4$]X type complexes in the reactions of **25** with protic reagents, generation of the cationic complex **A** in Scheme 14 seems probable. The complex may lose H_2 readily to provide a site for coordination of NH_3 to yield **30**. Acetone will also coordinate to the coordinatively unsaturated cationic complex, and the



Scheme 14. (L = PMe$_3$).

reactivity of the coordinated acetone towards ammonia may be raised to allow the formation of imine-coordinated complex. When a reactive $[RuH_3L_4]$-type complex, in which η^2-H_2 coordination may be involved, reacts with the coordinated imine hydrogenation of the imine to amine takes place. Once formed, the imine-coordinated complex **36** is inactive towards hydrogenation to give the amine-coordinated complex **37**. The synthesis and characterization of the imine- and amine-coordinated complexes may be relevant to the mechanism of reductive amination of ketones [40] [41] and of other ruthenium-promoted processes.

4. Concluding remarks

Comparison of the reactivities of the neutral and cationic monoorganopalladium complexes revealed the much higher reactivities of the latter towards β-hydrogen abstraction, and insertion of olefin, CO or isocyanide into Pd–C bonds. Even in aprotic solvents the electronegative ligands were found to dissociate to provide a site for further reactions. The most important consequence of the formation of the cationic organopalladium and ruthenium complexes is the creation of a vacant site at which reaction can occur. Generation of a cationic species is also thought to assist coordination of a nucleophilic substrate and to facilitate the ensuing reactions. The present study complements that of the mechanisms of reactions in Kaminsky–Brintzinger type polymerization of olefins initiated by Group 4 transition metal alkyls. Recent results on the mechanism of olefin polymerization support the view that creation of a cationic site suitable for olefin coordination and the succeeding insertion reactions enhances the activity of these Group 4 transition metal alkyls in the polymerization [42].

Acknowledgment

In this account I have summarized the results of work on basic aspects of the properties of the transition metal alkyls and hydrides carried out at Waseda University since my compulsory retirement from the Tokyo Institute of Technology. After the induction period required to set up a new team at the new place without the help of my former capable coworkers with whom I enjoyed working at T. I. T., I am very grateful that I have now been able to produce some publishable work from Waseda University by my small team of good, hard working, enthusiastic students. I am obliged for help to my colleague Professor Isao Shimizu at Waseda University, who was extremely helpful to me in setting up my research activity at Waseda. I am very grateful to Nippon Zeon Co. who kindly funded a Chair at Waseda University that allows me to continue my research. The work described here was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture.

References and notes

[1] A. Yamamoto, *J. Organomet. Chem., 300* (1986) 347.
[2] F.A. Cotton, *Chem. Rev., 55* (1955) 551.
[3] (a) W. Mowat, A. Shortland, N.J. Hill, M. Yagupsky and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1972) 533; (b) G. Wilkinson, *Science, 185* (1974) 109; (c) J.P. Davidson, M.F. Lappert and R. Pearce, *Chem. Rev., 76* (1976) 219.
[4] (a) G.M. Whitesides, *Pure and Appl. Chem., 53* (1981) 287, and references therein.
[5] (a) S. Komiya, T. Yamamoto, and A. Yamamoto, *Chem. Lett.*, (1978) 1273; (b) S. Komiya, Y. Morimoto, A. Yamamoto and T. Yamamoto, *Organometallics, 1* (1982) 1528.
[6] (a) T. Yamamoto, A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc., 93* (1971) 3350, 3360; (b) K. Tatsumi, A. Nakamura, S. Komiya, A. Yamamoto, and T. Yamamoto, *J. Am. Chem. Soc., 106* (1984) 8181.
[7] A. Yamamoto, T. Yamamoto, S. Komiya and F. Ozawa, *Pure Appl. Chem., 56* (1984) 1621, and references therein.
[8] (a) A. Gillie and J.K. Stille, *J. Am. Chem. Soc., 102* (1980) 4933; (b) M. Loar and J.K. Stille, *ibid., 103* (1981) 4174; (c) A. Moravsky and J.K. Stille, *ibid., 103* (1981) 4182.
[9] (a) L. Zhang and K. Zetterberg, *Organometallics 10* (1991) 3806; (b) R. Arnek and K. Zetterberg, *Organometallics 6* (1987) 1230; (c) D.L. Reger, D.G. Graza and J.C. Baxter, *Organometallics, 9* (1990) 873; (d) D.L. Reger, D.G. Graza and D.L. Graza, *Organometallics, 12* (1993) 554.
[10] (a) K. Osakada, Y. Ozawa and A. Yamamoto, *J. Chem. Soc., Dalton Trans.*, (1991) 759; (b) Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc., 112* (1990) 1096; (c) K. Osakada, Y. Ozawa and A. Yamamoto, *Bull. Chem. Soc. Jpn., 64* (1991) 2002.
[11] F. Kawataka, Y. Kayaki, I. Shimizu and A. Yamamoto, *Organometallics, 13* (1994) 3517.
[12] R. Romeo, *Comments Inorg. Chem., 11* (1990) 21, and references therein.
[13] R. Romeo, G. Alibrandi and L.M. Scolaro, *Inorg. Chem., 32* (1993) 4688.
[14] Y. Kayaki, F. Kawataka, I. Shimizu and A. Yamamoto, *Chem. Lett.* (1994) 2171.
[15] F. Kawataka, I. Shimizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn., 68* (1995) 654.
[16] (a) K. Karabelas and A. Hallberg, *Tetrahedron Lett., 26* (1985) 3131; (b) K. Karabelas, C. Westerlund and A. Hallberg, *J. Org. Chem., 50* (1985) 3896; (c) K. Karabelas and A. Hallberg, *J. Org. Chem., 51* (1986) 5286; (d) M.M. Abelman, T. Oh and L.E. Overman, *J. Org. Chem., 52* (1987) 4130; (e) M.M. Abelman and L.E. Overman, *J. Am. Chem. Soc., 110* (1988) 2328, and other more recent examples.
[17] W. Scott and J.E. McMurray, *Acc. Chem. Res.*, (1988) 47, and references therein.
[18] F. Ozawa, A. Kubo, and T. Hayashi, *J. Am. Chem. Soc., 113* (1991) 1417.
[19] For example, H.C. Clark and I.D. Ruddick, *Inorg. Chem., 9* (1970) 1226.
[20] Y. Kayaki, H. Tsukamoto, I. Shimizu and A. Yamamoto, unpublished results.
[21] Creation of a vacant site adjacent to the phenyl ligand in phenylpalladium halide complexes to accommodate incoming norbornene or norbornadiene by dissociation of the halide ligand

or triphenylphosphine ligand to allow the olefin insertion has been demonstrated; (a) C.S. Li, D.C. Jou and C.H. Cheng, *Organometallics, 12* (1993) 3945; (b) H. Portnoy, Y. Ben-David, I. Russo and D. Milstein, *Organometallics, 13* (1994) 3465.

[22] CO coordination to cationic acetyl-palladium and -platinum complexes with a chelating ligand was also reported recently by Tóth et al.: (a) I. Tóth and C.J. Elsevier, *J. Am. Chem. Soc., 115* (1993) 10388; (b) I. Tőth, T. Kégl, C.J. Elsevier and L. Lollar, *Inorg. Chem., 33* (1994) 5708.

[23] Y. Kayaki, I. Shimizu and A. Yamamoto, unpublished results.

[24] A. Sen, *Acc. Chem. Res. 26* (1993), and references therein.

[25] J.S. Brumbaugh, R.R. Whittle, M.A. Parvez and A. Sen, *Organometallics, 9* (1990) 1735; W.M. Vetter and A. Sen, *J. Organomet. Chem., 378* (1989) 485.

[26] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen and C.F. Roobeek, *J. Organomet. Chem., 430* (1992) 357.

[27] M. Broodhart, F.C. Rix, J.M. DeSimone and J.C. Barborak, *J. Am. Chem. Soc., 114* (1992) 5894.

[28] F. Ozawa, T. Hayashi, H. Koide and A. Yamamoto, *J. Chem. Soc., Chem. Commun.,* (1991) 1469.

[29] F. Ozawa, T.I. Son, K. Osakada and A. Yamamoto, *J. Chem. Soc. Chem. Commun.,* (1989) 1067.

[30] T. Terashima, I. Shimizu and A. Yamamoto, unpublished results.

[31] A. Yamamoto, *Bull. Chem. Soc. Jpn., 68* (1995) 433. Presented in part at the 67th Ann. Meet. Chem. Soc. Jpn., April 1, 1994, Tokyo, and at the 41st Symp. on Organometallic Chemistry, Osaka, Japan, October 1994, Abstract B113.

[32] A. Yamamoto, F. Ozawa, K. Osakada, L. Huang, T.I. Son, N. Kawasaki and M.K. Doh, *Pure Appl. Chem., 63* (1991) 687, and references therein.

[33] Y. Kayaki, I. Shimizu and A. Yamamoto, unpublished results.

[34] Insertion of methyl acrylate into the Ru–methyl bond in a cationic methylruthenium complex and stabilization of the resulting alkyl complexes by chelation through the methoxycarbonyl coordination to the metal center has been reported; E. Hauptman, M. Brookhart, P.J. Fagan and J.C. Calabrese, *Organometallics, 13* (1994) 774.

[35] Inhibition of the β-hydrogen elimination process by coordination of a hetero atom is known, see Ref. [4a].

[36] Y. Hayashi, S. Komiya, T. Yamamoto and A. Yamamoto, *Chem. Lett.,* (1984) 1363.

[37] K. Osakada, K. Ohshiro and A. Yamamoto, *Organometallics, 10* (1991).

[38] T. Rappert and A. Yamamoto, *Organometallics, 13* (1994) 4984.

[39] T. Rappert and A. Yamamoto, *Chem. Lett.,* (1994) 2211.

[40] For example, see G.Z. Wang and J.E. Bäckvall, *J. Chem. Soc., Chem. Commun.,* (1992) 980.

[41] For example, T. Kondo, S. Kotachi, S. Ogino and Y. Watanabe, *Chem. Lett.,* (1993) 1317 and references therein.

[42] (a) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem., 18* (1980) 99; (b) R.F. Jordan, *Adv. Organomet. Chem., 32* (1991) 325; (c) P.C. Möhring and N.J. Covil, *J. Organomet. Chem., 479* (1994) 1; (d) T.J. Marks, *Acc. Chem. Res., 25* (1992) 57.