

CHEMISTRY OF SQUARE PLANAR ORGANOMETALLIC COMPLEXES OF THE NICKEL GROUP RELEVANT TO CATALYSIS

Akio Yamamoto, Takakazu Yamamoto, Sanshiro Komiya, and
Fumiyuki Ozawa

Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, Nagatsuta, Yokohama, 227, Japan

Abstract - Square planar dialkyl complexes of nickel, palladium and platinum exhibit intriguing difference in their reactivities. Thermolysis pathways of these dialkyls vary depending on the metal, ligands, alkyl groups, geometry as well as the presence or absence of added ligand. Kinetic studies on the thermolysis and trans-cis isomerizations of PdR_2L_2 (L = tertiary phosphine) complexes showed involvement of 3-, 4-, and 5-coordinate intermediates. Effects of constraint of these geometries on the reaction pathways to induce reductive elimination or β -hydrogen elimination are discussed. Reactions of these dialkyl complexes with carbon monoxide give different products depending on the metal, geometry and the alkyl groups. Reaction courses of PdR_2L_2 type complexes with carbon monoxide can be accounted for consistently by assuming the alkyl migration to the coordinated CO ligand. Based on the information obtained in the basic studies novel catalytic systems promoted by palladium complexes converting organic halides, CO and amines into α -keto amides have been developed.

INTRODUCTION

Comparison of the chemistry of organonickel, -palladium, and -platinum complexes reveals intriguing difference in their reactivities (Ref. 1). In contrast to alkylplatinum compounds which have been known as stable complexes since the first preparation as old as 1907 (Ref. 2) the first thermally stable alkylpalladium compound having supporting ligands was prepared only half a century later (Ref. 3) followed by preparation of alkylnickel complexes (Ref. 4).

Why can some transition metal alkyls exist as stable compounds while others cannot? What are determinant factors controlling the stability and reactivities of transition metal alkyls? These are fundamental problems in organotransition metal chemistry. However, as most fundamental problems are difficult to answer, these problems concerning the stability and reactivities of transition metal alkyls still largely remain to be solved. A key to these problems may be obtained by kinetic studies of thermolysis and other reactions of isolated transition metal alkyls.

THERMOLYSIS PATHWAYS

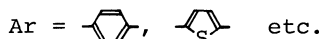
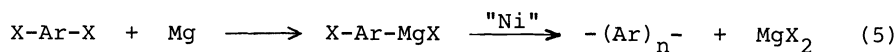
Dialkyl compounds of Ni(II), Pd(II) and Pt(II) having supporting ligands such as tertiary phosphines and bipyridine form square planar complexes. These compounds can be prepared by treating divalent metal halides or acetylacetonates with alkylating agents such as alkyllithium, -magnesium and -aluminum compounds in the presence of the ligands. The isolated and well-characterized alkyls are summarized in Table 1. While chelating ligands such as bipyridine and ditertiary phosphines restrict the configurations of these square planar complexes to cis, monodentate tertiary phosphines give rise to the possibility of forming cis and trans geometrical isomers. The cis geometry is strongly preferred by dialkylplatinum complexes having

monodentate tertiary phosphine ligands, whereas only trans isomers are known for the nickel analogue and both cis and trans isomers have been prepared for palladium analogues. The geometry preference is considered to be associated with the balance in enthalpy and entropy factors.

TABLE 1. Configurations of isolated Ni(II), Pd(II), and Pt(II) dialkyls

Ni	Pd	Pt

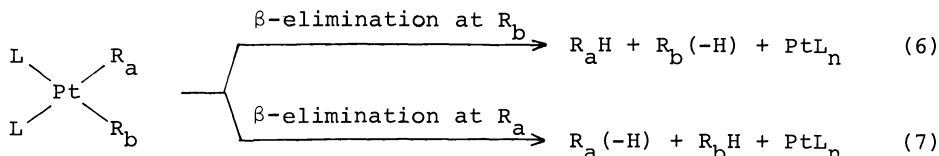
Application of the similar concept to dihalogenated arenes has led to the development of a novel polycondensation method to form polyarene (Ref. 8).



The polyarenes can be converted into electron-conducting polymers on doping with iodine and other electron donating agents.

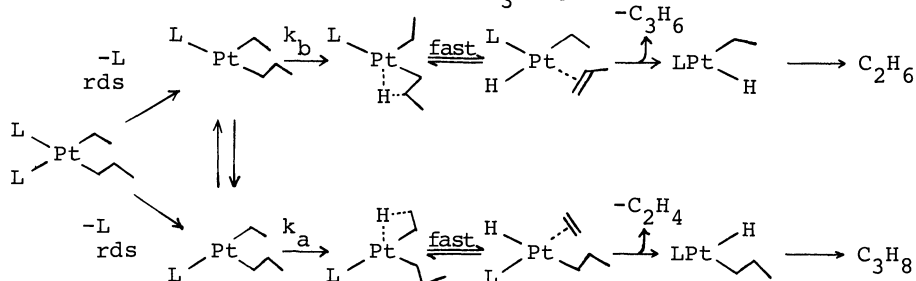
Palladium complexes also catalyze the C-C coupling reaction (Ref. 9) whereas the platinum analogues are inactive.

The reason for inactivity of platinum complexes may be associated with the stability of dialkyl- and alkylarylplatinum complexes and their propensity to decompose by β -elimination pathways. Detailed studies on thermolysis of symmetrical and unsymmetrical dialkylplatinum complexes having two tertiary phosphine ligands $cis\text{-Pt}(R_a)(R_b)L_2$ ($R_a, R_b = \text{Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, n-pentyl, C}_2\text{H}_5\text{Ph, C}_2\text{H}_5\text{C}_6\text{H}_4\text{-p-OMe}$; $L_2 = (PPh_3)_2, (PPhMe_2)_2, Ph_2PCH_2CH_2PPh_2$) revealed that the thermolysis proceeds in the absence of the added tertiary phosphine via a dissociative mechanism (Ref. 10). The thermolysis products are only those obtained by disproportionation of the two alkyl groups via β -hydrogen elimination.



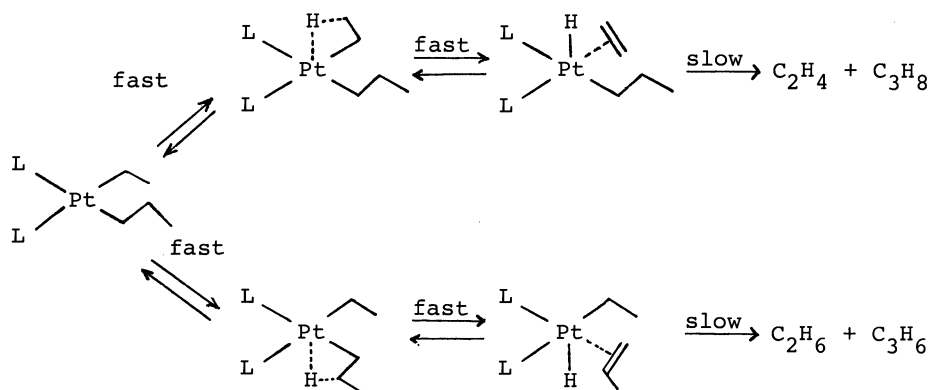
The ratios of $R_aH/R_b(-H)$ and $R_b(-H)/R_bH$ generated in thermolysis of $cis\text{-Pt}R_aR_b(PPh_3)_2$ in the absence of added PPh_3 were found to be identical with the ratio of numbers of β -hydrogens in the two alkyl groups. The results suggest that the thermolysis proceeds through a dissociative path involving the rate-determining step of the ligand dissociation to give an unstable three-coordinate T-shaped intermediate in agreement with the conclusion of Whitesides (Ref. 11). Based on the results of the thermolysis product analysis, kinetic studies and isotopic studies using $cis\text{-Pt}(\text{CH}_2\text{CD}_3)(n\text{-C}_3\text{H}_7)(PPh_3)_2$, the following dissociative mechanism has been proposed for thermolysis of $cis\text{-PtEt}(n\text{-Pr})(PPh_3)_2$.

Scheme I A thermolysis mechanism of $cis\text{-PtEt}(n\text{-Pr})(PPh_3)_2$ in the absence of added PPh_3 ligand

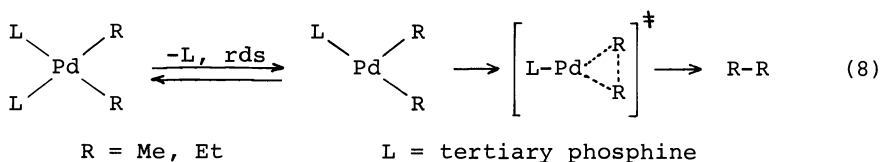


Thermolysis in the presence of a large excess of added ligand takes place much more slowly at higher temperatures compared with the thermolysis performed in the absence of added L. A deuterium labeling experiment shows that H-D exchange along the ethyl group takes place prior to the rate-determining step. The following non-dissociative path involving a five-coordinate intermediate explains the experimental facts.

Scheme II A thermolysis mechanism of *cis*-PtEt(*n*-Pr)(PPh₃)₂ in the presence of excess of PPh₃ ligand

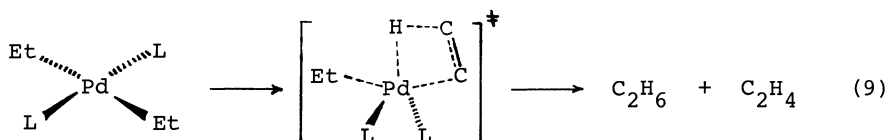


Thermolysis of dialkylpalladium complexes takes different routes depending on the configuration. In contrast to the behavior of *cis*-PtR₂L₂, reductive elimination takes place in thermolysis of *cis*-PdR₂L₂ through a dissociative pathway (Refs. 12, 13).

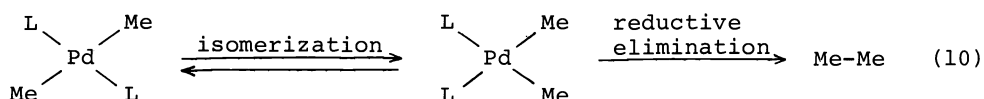


Thermolysis of *cis*-Pd(CH₂CD₃)₂(PMe₂Ph)₂ in the absence of added ligand cleanly liberated CD₃CH₂-CH₂CD₃. Thermolysis of a mixture of *cis*-Pd(CH₃)₂(PMePh₂)₂ and *cis*-Pd(CD₃)₂(PMePh₂)₂ in ca. 1 : 1 molar ratio released predominantly CD₃CD₃ and CH₃CH₃. These results indicate that the thermolysis of *cis*-PdR₂L₂ proceeds via unimolecular process. Addition of free ligand to the system containing *cis*-PdMe₂L₂ effectively blocks the reductive elimination pathway and forces the complex to be thermolyzed by a route involving liberation of methane. Kinetic studies in thermolysis of *cis*-PdMe₂L₂ is in agreement with the dissociative mechanism involving the rate-determining formation of the three-coordinate T-shaped intermediate (eq. 8).

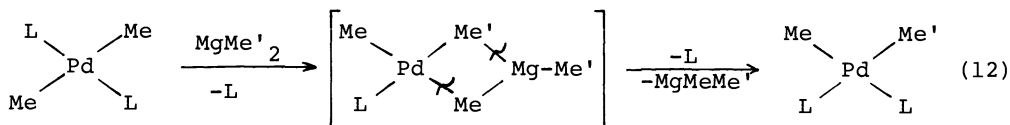
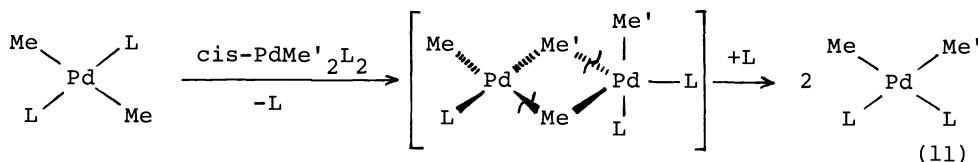
On the other hand, *trans*-PdEt₂L₂ (L = PMe₂Ph, PET₃, PET₂Ph, PMePh₂, PEtPh₂) is thermolyzed mainly via non-dissociative pathway liberating ethane and ethylene in a 1 : 1 ratio. Thermolysis of *trans*-[Pd(CH₂CD₃)₂(PMePh₂)₂] cleanly liberated CH₂=CD₂ and CH₂DCD₃. On the basis of a small kinetic isotope effect observed in thermolysis of the deuterated ethyl complex, *trans*-Pd(CH₂CD₃)₂(PMePh₂)₂ and a large influence of steric bulkiness of the tertiary phosphine ligands on enhancement of the thermolysis rate, a thermolysis mechanism proceeding through a distorted trigonal bipyramidal configuration has been proposed (Ref. 14).



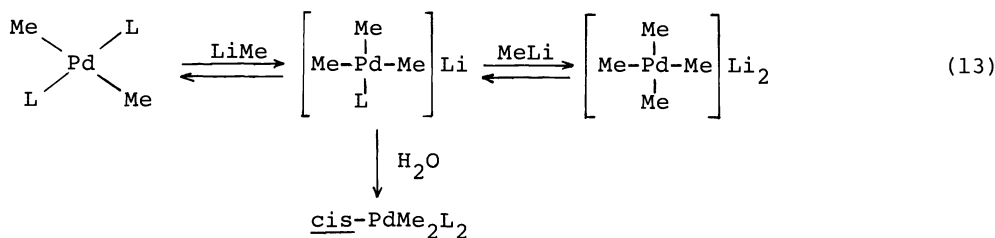
In thermolysis of *trans*-PdMe₂L₂, a *trans* - *cis* isomerization first takes place followed by reductive elimination of ethane.



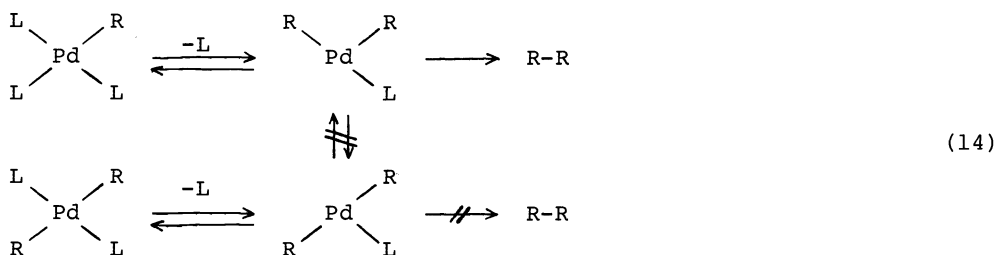
The isomerization is accelerated by addition of $\text{cis-PdMe}_2\text{L}_2$ (Ref. 13) and MgMe_2 or MgMeBr (Ref. 15). On the basis of studies using CD_3 -labelled complexes involvement of bimolecular mechanisms proceeding through methyl-bridged intermediates as shown below has been proposed.



Trans-cis isomerization is promoted also by addition of alkyllithium. In this case, however, involvement of alkylpalladate complexes was indicated on the basis of NMR study (Ref. 16).

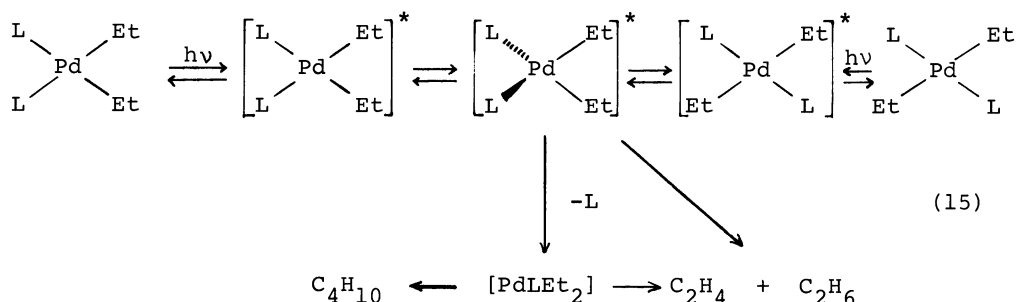


In these trans-cis isomerizations and reductive elimination from $\text{cis-PdR}_2\text{L}_2$ kinetic studies indicated the involvement of T-shaped three-coordinate intermediates and presence of a potential barrier for direct polytopal rearrangement between the T-shaped $\text{cis-PdR}_2\text{L}$ and $\text{trans-PdR}_2\text{L}$.

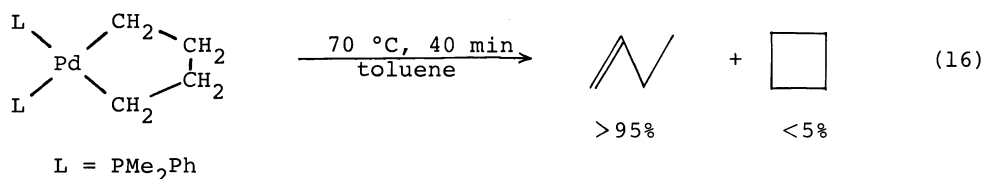


A theoretical support for the behavior of the putative planar three-coordinate T-shaped species has been given by calculations based on extended HMO (Ref. 17).

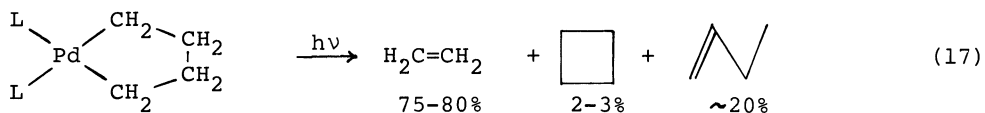
These reactions are all considered to proceed under constraint of planar geometry for Pd(II) complexes. On the other hand irradiation of light promotes the cis-trans isomerization as well as the decomposition of PdEt_2L_2 to liberate ethylene, ethane, and butane in a 2 : 2 : 1 ratio. The result was accounted for by assuming a tetrahedral PET_2L_2 as the common intermediate (Ref. 18a).



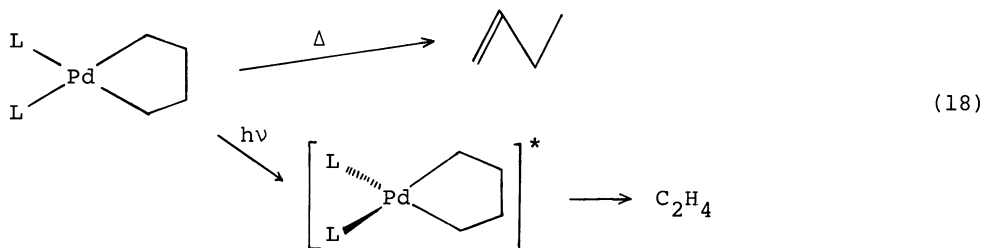
In relation to the photolysis of palladium dialkyls photolysis of palladacyclopentane was examined and compared with thermolysis behavior of the palladacycle. Thermolysis of bis(dimethylphenylphosphine)palladacyclopentane, prepared from $\text{PdCl}_2(\text{PMe}_2\text{Ph})_2$ and 1,4-dilithiobutane, was carried out in toluene at 70 °C. 2-Butene was liberated as the major thermolysis product accompanied by a minor amount of cyclobutane (eq. 16). No ethylene, butane, or 1-butene was detected.



The decomposition course is dramatically altered on photolysis. Ethylene is formed as the predominant photolysis product with minor amounts of 1-butene and cyclobutane (eq. 17).



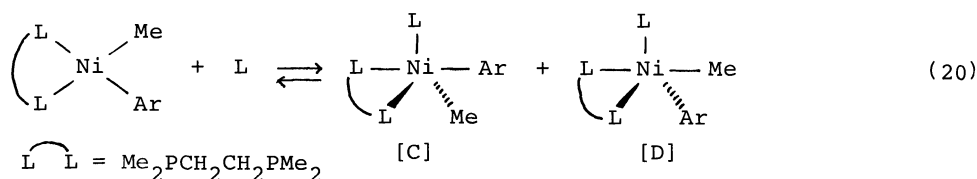
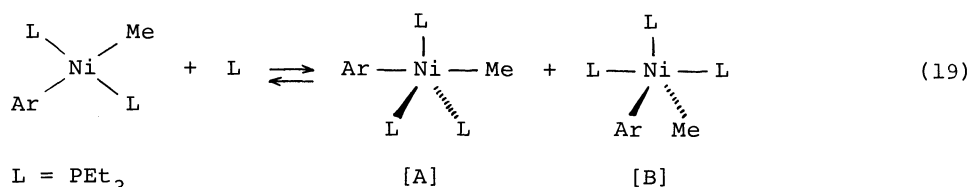
These results are consistent with assumption of the photoactivated tetrahedral intermediate.



The assumption of the tetrahedral intermediate in photolysis is supported by MO calculations by Hoffmann and his coworkers (Ref. 18b). According to their results, the process producing ethylene from a metallacyclopentane is thermally disallowed and photochemically allowed. These results suggest that constraint of planar geometry of Pd(II) complexes in their thermal reactions is lifted in photochemical processes.

The behavior of dialkynickel and alkylarylnickel complexes having tertiary phosphine ligands differs from that of the platinum and palladium analogues. A nickel complex having methyl and aryl groups is regarded as a model for the key intermediate species involved in cross-coupling reactions between alkyl-

magnesium compounds and aryl halides promoted by nickel catalysts as represented by eq (4). Kochi prepared *trans*-NiMePh(PET₃)₂ and found the inhibition effect of PET₃ on the thermolysis (Ref. 19). However, its *trans* geometry is not suitable for direct reductive elimination of the methyl and phenyl groups. As a model compound more closely related to the intermediate involved in the cross-coupling reaction a series of *cis*-NiMeAr(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) has been prepared by the ligand exchange reaction of *trans*-NiMeAr(PET₃)₂ with dmpe. The complex having the methyl and aryl groups at the adjacent positions was found to be much less stable than *trans*-NiMePh(PET₃)₂ (Ref. 20). Furthermore marked enhancement in the thermolysis rate by addition of trialkylphosphines has been observed. Sterically more demanding triphenylphosphine ligand showed little promotion effect for thermolysis. These results suggest that five-coordinate species are involved in the thermolysis of NiMe(Ar)L₂ and their geometries are of pivotal importance in determining the course of thermolysis. Since NiMe₂(PR₃)₃ is known to take a *trans* trigonal bipyramidal configuration in solution (Ref. 21), it is reasonable to assume that addition of trialkylphosphine to NiMe(Ar)(PET₃)₂ and NiMe(Ar)(dmpe), respectively, would give the following five-coordinate species.

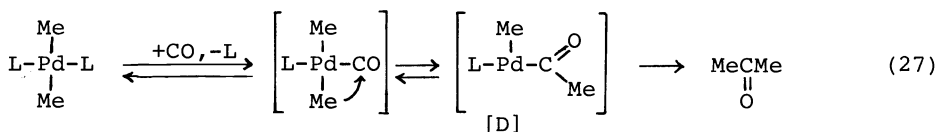
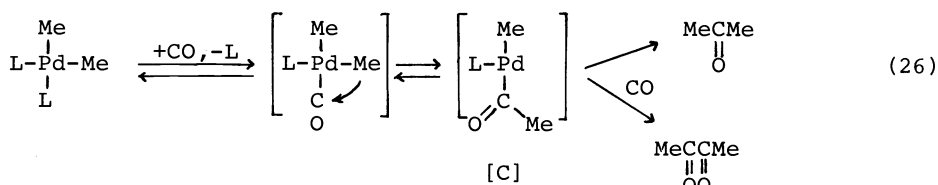


Obviously species [A] is not suitable for direct reductive elimination of Me-Ar because of the *trans* geometry of the methyl and the aryl groups in its trigonal bipyramidal configuration. A theoretical MO investigation on reductive elimination of Me-Ar from the five-coordinate intermediates [A]-[D] has revealed that reductive elimination from [C] and [D] having the methyl and aryl groups in apical and equatorial sites is symmetry-allowed, whereas the reductive elimination from [B] having both the methyl and aryl groups in equatorial sites is symmetry-forbidden (Ref. 22). Furthermore, the detailed MO calculations indicated that interconversion among species [A] to [D] via Berry pseudo-rotation pathways is energetically not favorable compared to reductive elimination from [C] or [D] in agreement with experimental results.

The results of these thermolysis experiments indicate diversified features in behavior of square planar complexes of nickel, palladium and platinum congeners having two alkyl or aryl groups. Despite the diversified features, several important conclusions relevant to catalytic C-C bond formation emerge from studies of reductive eliminations of the nickel triad.

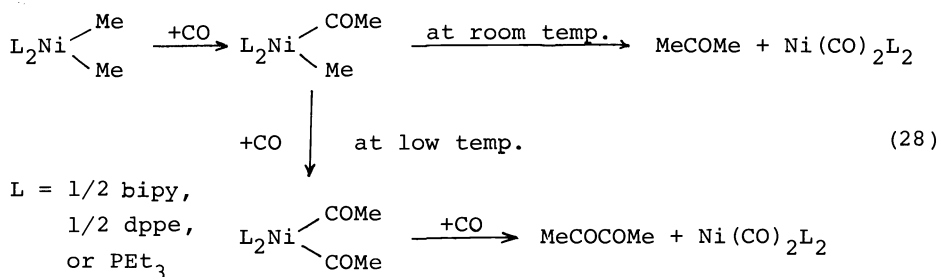
(a) For reductive elimination to proceed organic groups to be eliminated should be brought into adjacent coordination sites in four- or five-coordinate species. This is an obvious requirement but sometimes overlooked in discussions of stabilities and reaction courses of organotransition metal complexes. A corollary of this requirement is that rearrangement of the geometry such as *trans*-*cis* or square planar-tetrahedral isomerization should precede the reductive elimination.

(b) Constraint of the square planar geometry is stronger for platinum and palladium complexes than for nickel analogues which have greater inclination to form the five-coordinate or tetrahedral intermediates. These differences in the behavior of diorgano complexes of Ni(II), Pd(II) and Pt(II) influence strongly the activity and selectivity of catalytic reactions promoted by

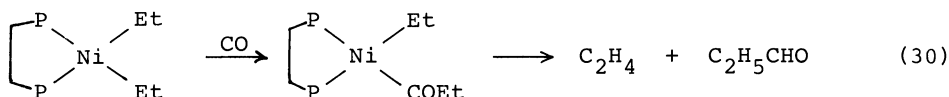


Thus all the reaction products in eqs. (21)-(23) can be accounted for consistently by assuming stereochemical retention in replacement of the tertiary phosphine ligand by CO, alkyl migration to the coordinated CO and stereochemical constraint of the T-shaped geometry on the reaction pathways.

Behavior of dialkylnickel complexes somewhat differs from that of the corresponding palladium analogues. For dialkylnickel complexes distribution of reaction products with carbon monoxide appears to be related with stabilities of the nickel-alkyl bonds (Refs. 25, 26). The dimethylnickel complexes, *trans*-NiMe₂(PET₃)₂, NiMe₂(bipy), and NiMe₂(dppe) all give acetone quantitatively on treatment with atmospheric pressure of CO at room temperature, whereas at lower temperatures 2,3-butanedione is formed, the yield increasing with relative stability of the dimethylnickel complex employed for the reaction. The reactions most probably proceed by CO insertion into the Ni-Me bond to give an acetyl-methylnickel species. If this species is unstable and readily undergoes the reductive elimination, acetone is formed. At lower temperature the acetyl-methyl intermediate may further react with CO to give a bis(acetyl)nickel species which on reductive elimination would liberate the diketone.

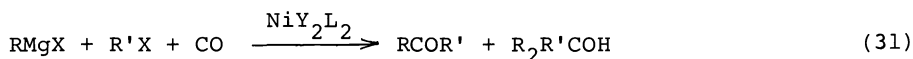


Support for the intermediacy of the acetylnickel species was obtained by confirming formation of MeCOEt on treatment of the reaction system with C₂H₅Br. Reaction products of CO with diethylnickel complexes differ depending on the ligand. A bipyridine-coordinated diethyl complex, NiEt₂(bipy) produces diethylketone, whereas the dppe-coordinated complex NiEt₂(dppe) affords propionaldehyde and ethylene.



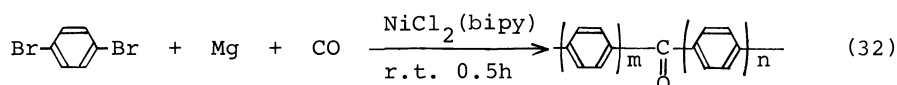
The difference in the reactivities between $\text{NiEt}_2(\text{bipy})$ and $\text{NiEt}_2(\text{dppe})$ toward CO may be related to the difference in the thermolysis behavior of these diethyl complexes. As mentioned earlier $\text{NiEt}_2(\text{bipy})$ liberates butane on thermolysis, whereas $\text{NiEt}_2(\text{dppe})$ gives ethylene and ethane in a 1 : 1 ratio.

The ease of formation of ketones by the reactions of dialkylnickel complexes with CO at room temperature prompted us to develop a new synthetic method of ketones and tertiary alcohols from Grignard reagent RMgX , alkyl (or aryl) halide $\text{R}'\text{X}$ and CO by using nickel complexes as catalysts (Refs. 26, 27).



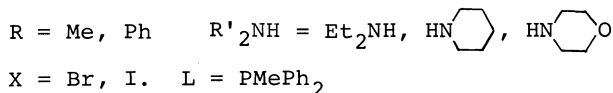
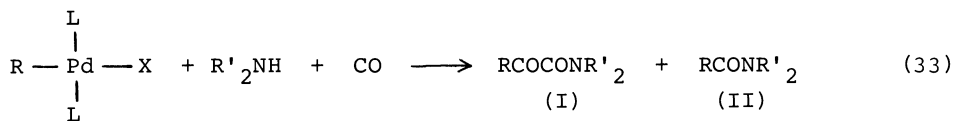
Y = halide or alkyl group

The process was further applied to production of polymers containing carbonyl groups in the polymer chain (Ref. 27).



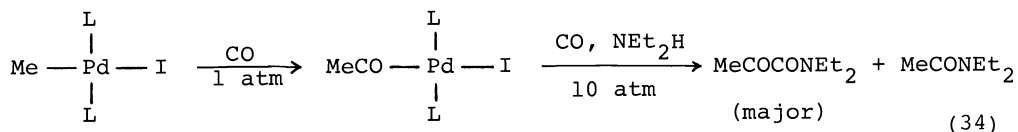
DOUBLE CARBONYLATION REACTIONS

In the process of establishing the mechanisms of reactions of dialkylpalladium complexes with CO addition of amines to the alkylpalladium complexes reacting with carbon monoxide was found to give α -keto amides in addition to amides. Further extension of the finding to examination of the reactions of alkyl- and arylpalladium halide complexes having tertiary phosphine ligands revealed that α -keto amides were produced in the following systems (Ref. 28).

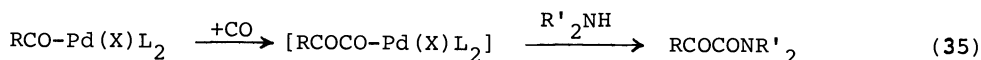


In these reactions quaternary ammonium salts $\text{R}'_2\text{NH}_2\text{X}$ and some tetraalkyl oxamides are produced as byproducts.

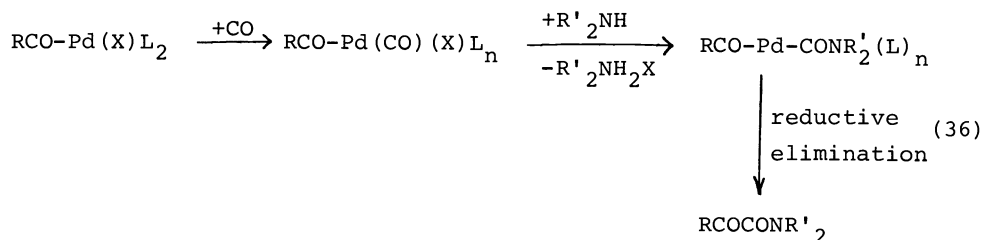
Clearly the reaction to give the α -keto amides proceeds through CO insertion into the Pd-R bond. The reaction of *trans*-PdMe(I)(PMePh₂)₂ with Et₂NH and 1 atm of CO in toluene at room temperature afforded MeCOCONEt₂ and MeCONEt₂ in a 8 : 2 ratio in the combined yield of 50% and *trans*-Pd(COMe)I(PMePh₂)₂ was recovered from the reaction system. Further reaction of the isolated acetyl palladium complex with Et₂NH and 10 atm of CO gave MeCOCONEt₂ and MeCONEt₂ in a 9 : 1 ratio in 98% yields.



For the process to give the α -keto amides two pathways are conceivable. One is consecutive CO insertion into the Pd-C bond to give a RCOCO-Pd(X)L_2 species which may be trapped by amines to liberate the α -keto amides.²

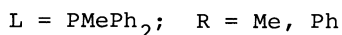
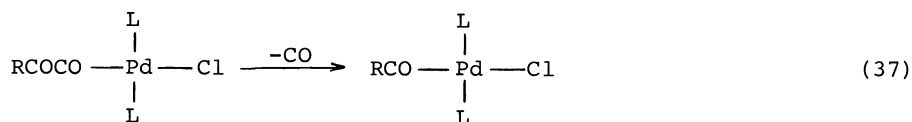


The other route is attack of the coordinated CO ligand by amine to give a carbamoylpalladium species which liberates α -keto amide on reductive elimination (Ref. 28).

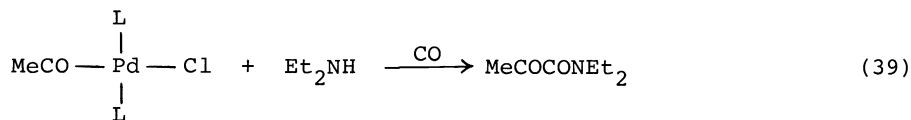
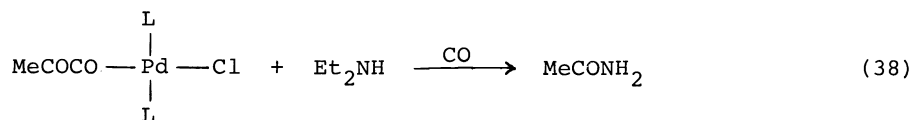


Although the consecutive CO insertion mechanism is thermodynamically unfavorable, formation of α -keto amides may be still possible, if the RCOCO-Pd entity is highly reactive toward amine. For examining the feasibility of the consecutive CO insertion mechanism $\text{trans-Pd(COCOR)ClL}_2$ (R = Me, Ph; L = PMePh₂) were prepared and their reactivities with Et₂NH were examined (Ref. 29).

The methyl- and phenylglyoxypalladium complexes were found to be readily decarbonylated to the corresponding acylpalladium complexes obeying the first-order kinetics in concentrations of the palladium complexes.



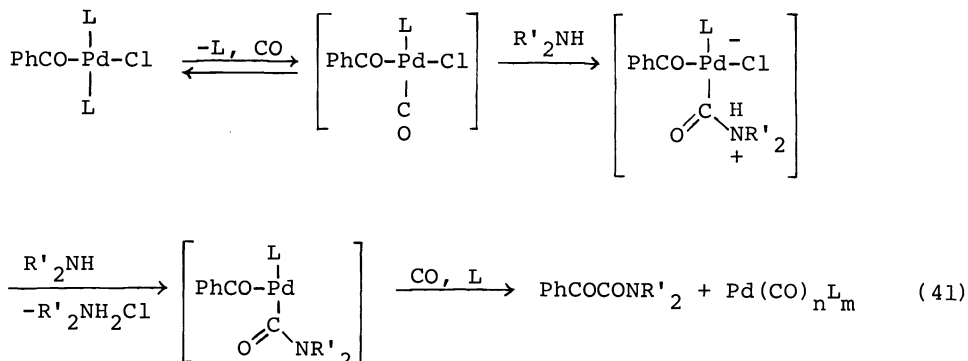
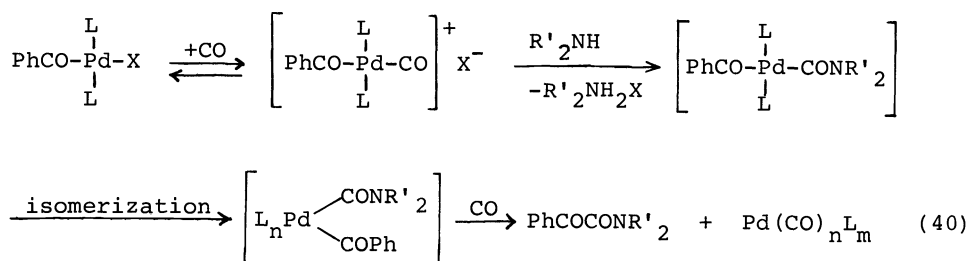
Interestingly, treatment of the pyruvoylpalladium complex with Et₂NH predominantly gave acetamide, whereas similar treatment of acetyl palladium complex with CO and Et₂NH generated pyruvamide as the major product.



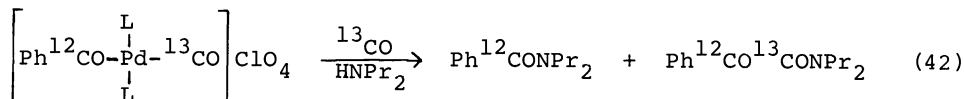
These results are against the consecutive CO insertion mechanism. On the other hand, several lines of experimental evidence support the mechanism involving formation of planar acyl-carbamoyl intermediates in the double carbonylation reaction (Ref. 30).

In the reactions of $\text{trans-Pd(COR)X(PMePh}_2)_2$ (R = Ph, X = Cl, Br, and I; R = Me, X = Cl) with CO and amides, benzoylpalladium complexes having bromide and iodide ligands gave better yields of α -keto amides in solvents of higher polarities, whereas the reaction of benzoyl(chloro)palladium complex afforded higher yields of α -keto amide in less polar solvents. From these studies involvement of two types of reaction intermediates was suggested. One involves an ionic benzoyl(carbonyl)palladium intermediate $[\text{PhCOPd(CO)L}_2]^+ \text{X}^-$ attacked by amine to give aroyl-carbamoyl species, which reductively

eliminates α -keto amide (eq. 40), while the other proceeds through a neutral acyl-carbonyl intermediate [Pd(COR)(CO)XL] (eq. 41).



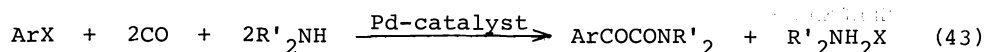
Evidence to support the involvement of the ionic species has been obtained from experiments using $\text{trans-[Pd(COPh)(CO)(PMePh}_2)_2]^+ \text{ClO}_4^-$ with amine. The reactions of the ionic perchlorate complex with CO and amine under ambient conditions proceeded smoothly to give α -keto amides at high selectivities. The reaction of $\text{trans-[Pd}^{12}\text{COPh}^{13}\text{CO}(\text{PMePh}_2)_2]\text{ClO}_4$ with $n\text{-Pr}_2\text{NH}$ under 1 atm of ^{13}CO at room temperature produced $\text{Ph}^{12}\text{CONPr}_2$ (free of $\text{Ph}^{13}\text{CONPr}_2$ over natural abundance) and $\text{Ph}^{12}\text{CO}^{13}\text{CONPr}_2$ which contained 90% of ^{13}CO as labeled.



The result confirms that the CO entity in the $\text{-CONR}'_2$ group of α -keto amide is derived from carbon monoxide and the α -keto carbonyl group in the α -keto amide originates from the benzoyl group without involvement of any decarbonylation and its reverse CO insertion processes.

CATALYTIC DOUBLE CARBONYLATION

On the basis of stoichiometric reactions of organopalladium complexes described above, a novel catalytic process for converting aryl (and alkenyl) halides to α -keto amides has been developed (Ref. 31)



The catalytic process is comprised of the following elementary steps: (a) oxidative addition of aryl halide to a Pd(0) species to give an arylpalladium halide complex, (b) CO insertion into the aryl-palladium bond to give an arylpalladium species, (c) further CO coordination, (d) attack of amine on

the coordinated CO ligand to give a carbamoyl species, and (e) reductive elimination of the aryl-carbamoyl groups to liberate α -keto amide and regenerate a Pd(0) species which further undergoes the oxidative addition to carry the catalytic process. The main catalytic process to give α -keto amide may be represented by Fig. 1.

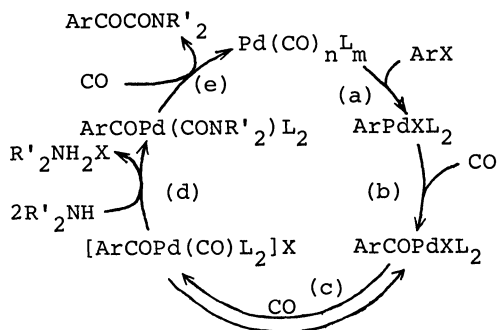
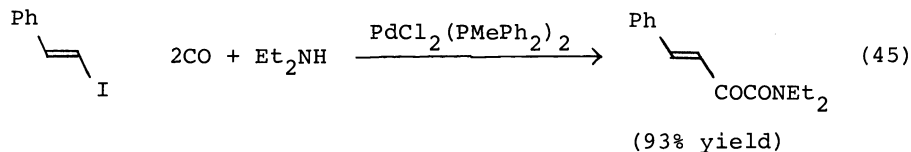
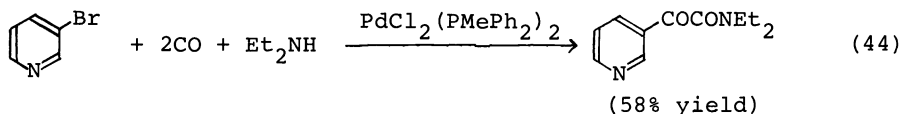


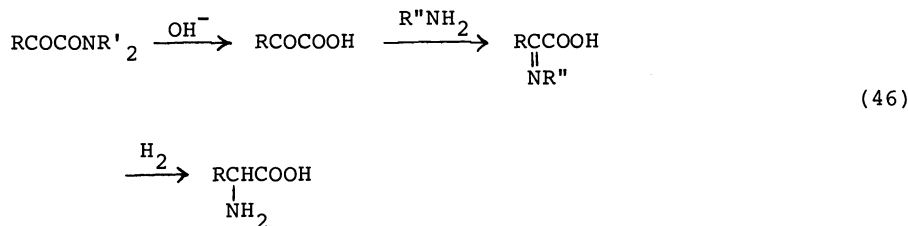
Fig. 1 Proposed mechanism of double carbonylation of aryl halide in the presence of secondary amine.

For the catalytic formation of amides produced as by-products aryl(carbamoyl)-palladium species seems to be involved (Ref. 32).

The catalytic double carbonylation reaction can be applied not only to aryl halides but also to alkenyl halides and halides of heterocyclic compounds. Representative examples are shown below.



The most promising application of the double carbonylation process is the synthesis of α -amino acids.



Synthesis of α -amino acids from α -keto acids is a well established process but the development of this route has been hindered by lack of a suitable general preparative method for preparation of α -keto acids. Since the catalytic double carbonylation process can be applied to a wide range of organic halides, it may be utilized as one of the general synthetic methods to α -amino acids.

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