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TRANSITION METAL ALKYLS, A PERSONAL PERSPECTIVE

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To young organometallic chemists these days transition metal alkyls are commonplace but this was not so in the nineteen fifties when I started work on transition metal complexes as a graduate student.

Table 1 shows a part of the Periodic Table indicating transition metal elements for which metal alkyl compounds * were known in 1955, as reviewed by Cotton [1]. It will be seen that the number of transition metal elements for which the presence of metal–carbon σ bond had been unequivocally established at that time was extremely limited. Platinum alkyls had been known since 1907 but they were regarded as an exception. In addition some chromium alkyls were known, and a titanium phenyl complex was first isolated in 1952.

For the majority of transition metal elements the existence of metal-alkyls remained in doubt, as shown in Table 1, which appeared in the review. A theory was even proposed to account for the 'intrinsic' instability of transition metal alkyls on the basis of Mulliken's magic formula [2]. Fortunately the instability of transition metal alkyls has proved not to be 'intrinsic', and there are now a number of isolated, stable transition metal alkyls for most transition metal elements. Reports of isolation of transition metal alkyls increased sharply after recognition that some auxiliary ligands such as cyclopentadienyl, CO, or tertiary phosphines help to stabilize transition metal alkyls. But two questions regarding stability of transition metal elements remained in my mind, viz. why can some transition metal alkyls exist as stable compounds while others cannot, and what is the role of the supporting ligands? These are fundamental questions in organometallic chemistry, and like many other fundamental questions, these questions remain unanswered. There are now some explanations of the effects involved, but these are not complete. The answers to my questions forms the thread of the present account.

The first research project suggested to me by my supervisor, Professor Shu Kambara, in 1954 was the preparation of a polymer containing titanium correspond-

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* For convenience in this review the term transition metal alkyl includes transition metal aryls and alkenyls.

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TABLE 1

TRANSITION METAL ALKYLS KNOWN IN 1955

3	4	5	6	7	8	9	10	11
Sc	○ Ti	V	○ Cr	▨ Mn	Fe	Co	Ni	Cu
Y	Zr	▨ Nb	▨ Mo	Tc	Ru	Rh	Pd	Ag
La	Hf	▨ Ta	▨ W	▨ Re	Os	Ir	○ Pt	Au
Ac								

○ One or more well established compounds.

▨ Some positive results requiring confirmation. Others: positive results very inconclusive or non existent.

ing to a silicone, a very stable polymer containing alkyl–silicon bonds and siloxane linkages. His suggestion was based on the naive assumption that since titanium and silicon both belong to the same group in the short Periodic Table they might have similar properties. But, of course, in the long Periodic Table they are situated far apart and a titanium–alkyl bond is too unstable to allow preparation of organopolytitanoxane type polymers. Consequently I prepared some titanium compounds containing chelating groups resistant to hydrolysis along with readily hydrolyzable alkoxy groups, so that on hydrolysis the monomers could be condensed into polytitanoxane type polymers. The work did not lead to any useful polymers with satisfactory physical properties, but I did learn the fun of synthesizing new transition metal complexes [3].

It was in this period that the discovery of the Ziegler process for converting ethylene into polyethylene under very mild conditions was announced [4]. The catalyst mixture contained a titanium compound with which I was involved! The excellence of the new catalyst systems composed of titanium chlorides and alkylaluminum compounds stimulated many Japanese laboratories oriented towards polymer chemistry to initiate studies of the mechanisms of the catalyst production and polymer formation. However, the complexity of the mixed catalyst systems has hindered clarification of the nature of the actual active center and of the mechanism of olefin polymerization. The real nature of the catalyst system has long remained unclarified and is still controversial. Although I was not involved in the study of the mechanisms of the catalyst formation and stereospecific polymerization of propylene, I retained my interest in these problems throughout the late fifties and early sixties.

From 1960 to 1962 I worked in the U.S. with Professor Melvin Calvin as a post doctoral fellow in Berkeley, on a Fulbright fellowship. From there I went on to Mülheim in Germany on an Alexander von Humboldt fellowship to work in the famous Max Planck Institut für Kohlenforschung under the directorship of Professor Karl Ziegler *. I was very fortunate that I was able to work there with Dr. G.

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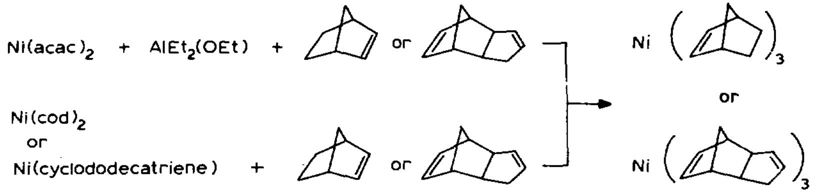
* Both Professor Calvin and Prof. Ziegler received Nobel Prizes. An American friend of mine remarked, "You should come to me next".

Wilke, then Privat Dozent and a group leader in Ziegler's institute and now the Director after Ziegler's retirement. Through the elegant studies of his group he had demonstrated unequivocally that monometallic transition metal complexes could be isolated after reactions of transition metal compounds with organoaluminum compounds, and that these aluminum-free low valent transition metal complexes act as catalysts for butadiene oligomerization and polymerization [5]. His group further showed that reactivities of these transition metal catalysts can be controlled by addition of other ligands such as tertiary phosphines.

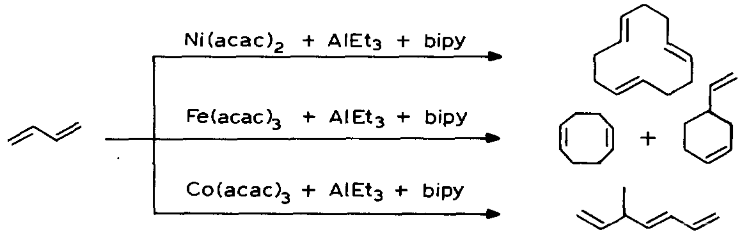
My work with Wilke in Mülheim was concerned with synthesis of tris(olefin) nickel(0) complexes by reduction of nickel acetylacetonate with diethylaluminum monoethoxide in the presence of strained olefins such as dicyclopentadiene and norbornene or by exchange reactions between Ni^0 complexes such as bis(cyclooctadiene)nickel and cyclododecatriene-nickel and such olefins.



(1)

These were the first zerovalent metal complexes involving coordination of three olefin molecules. The results were never published although the structure of tris(norbornene)nickel was established later by X-ray analysis [6]), but the experience I gained in Mülheim in handling and characterizing air-sensitive compounds was invaluable in helping me to establish myself in my academic career afterwards.

When I returned to Japan to resume my post as a research assistant at the Tokyo Institute of Technology with Professor Sakuji Ikeda I worked on my own for some time on my old topic of organic titanium complexes, since with the very limited resources available to me I avoided the field in which Wilke's powerful group was active. However, an event occurred which affected the rest of my research activity; I was asked to talk at a conference on studies I had carried out in Calvin's and Wilke's groups, and after my talk Dr. Yasuzo Uchida, who also was a research assistant of Tokyo University, approached me and suggested that we work jointly. He saw that I had gained much experience in handling and isolating air-sensitive transition metal complexes, and thought that collaboration with me might help his group to isolate an active species from their catalytic systems of nickel, iron and cobalt acetylacetonates mixed with alkylaluminum compounds in the presence of auxiliary ligands such as 2,2′-bipyridine and tertiary phosphines. They had found that the mixed catalyst systems convert butadiene into linear and cyclic dimers and trimers, such as 3-methylhepta-1,4,6-triene, cycloocta-1,5-diene and cyclododeca-1,5,9-triene [7].



(2)

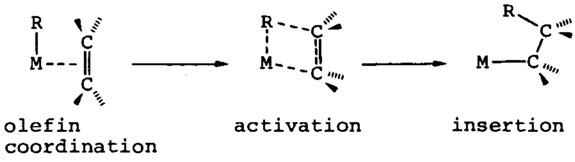
The Tokyo University group sent to me Taro Saito, then a graduate student and now a professor at Osaka University. We started to work together to see if we could get any isolable transition metal complexes from treatment of nickel, iron, or cobalt acetylacetonates with diethylaluminum monoethoxide in the presence of 2,2′-bipyridine or triphenylphosphine. In almost the first experiments using bipyridine as the ligand with nickel and iron acetylacetonates we obtained very dark green and blue crystalline complexes of nickel and iron. We thought initially that we might have obtained Ni^0 and Fe^0 complexes containing bipyridine ligands, since it appeared unlikely at the time that an ethyltransition metal complex could be so stable thermally. The nickel complex decomposed at ca. 110°C and the iron complex at somewhat lower temperature and analysis of the gases produced on thermolysis surprised us. We obtained butane from the nickel complex and ethylene and ethane from the iron complex. Because an NMR spectrometer was not readily available for us at that time it took some time to convince ourselves that what we obtained were ethyl complexes and not complexes containing coordinated ethylene. In retrospect it was not a bad thing that we had to carry out this somewhat tedious characterization by chemical means following our normal practice, because the studies of thermolysis and acidolysis often led to important new observations, as described below.

We were lucky in our choice of bipyridine as the auxiliary ligand in our study, and by its use we were able to isolate thermally stable ethyl complexes of nickel [8,9], iron [10], and cobalt [11].

$$\begin{aligned} &\mathrm{Ni(acac)_2 + AlEt_2(OEt) + bipy \rightarrow NiEt_2(bipy)} \\ &\mathrm{Fe(acac)_3 + AlEt_2(OEt) + bipy \rightarrow FeEt_2(bipy)_2} \\ &\mathrm{Co(acac)_3 + AlEt_2(OEt) + bipy \rightarrow CoEt(bipy)_2} \end{aligned} \tag{3}$$

These isolated monometallic alkyl complexes were found to show the same catalytic activities for butadiene oligomerization as the mixed systems [8–11].

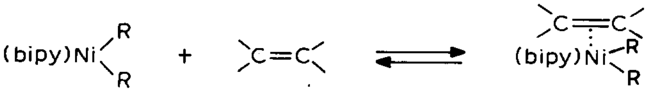
It was shortly before these observations that Cossee made a simple but attractive proposal about the nature of active site in Ziegler catalysts and the mechanism of olefin polymerization [14]. On the basis of earlier experimental observations on the Ziegler catalyst systems he made the simple assumption that the main role of aluminum alkyls in Ziegler catalysts is to alkylate titanium halides to give titanium alkyls. He further suggested that coordination of olefin to the titanium alkyl leads to activation of the titanium–alkyl bond, with concomitant activation of the coordinated olefin itself. The coordinated olefin is then 'inserted' into the Ti–R bond through a four-centered transition state to give a new alkyl, the process constituting the initiation step in the olefin polymerization [14].



SCHEME 1

Cossee further proposed together with Arlman that in stereospecific propylene polymerization the mode of coordination is influenced by the surface structure of solid $TiCl_3$ so that only a controlled coordination of propylene to titanium is allowed to give isotactic polypropylene [14b,c].

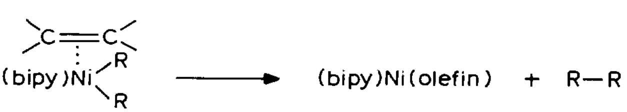
Our nickel and iron alkyls seemed to be good model complexes to examine the feasibility of the Cossee's proposal for activation of metal alkyls by olefin coordination. Thus we examined the reactions of various olefins with the nickel and iron alkyls. The bipyridine-coordinated planar dialkyls NiR_2(bipy) (R = Me, Et, i-Pr, and n-Bu) are 16-electron complexes and coordinatively unsaturated. Interaction of olefins with NiR_2(bipy) leads to the olefin-coordinated complexes, which are isolable at low temperature with olefins such as acrylonitrile and acrylaldehyde [15].



(1) (2)

(4)

By coordination of the electronegative olefins the Ni–R bonds are markedly activated and reductive elimination readily occurs [16].



(2) (3)

(5)

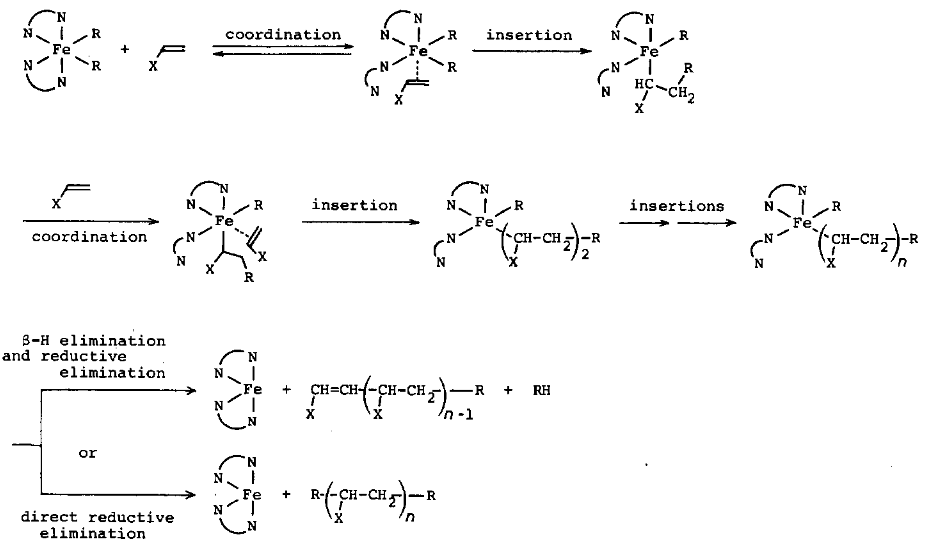
Coordination of electronegative olefins causes enhanced back donation from nickel to the olefin, as reflected in the change of the electronic spectra [16,17] and NMR spectra [18]. On coordination of electronegative olefins the charge transfer bands arising from electronic excitation of Ni *d* orbitals to 2,2′-bipyridine π^* orbital show a marked blue shift, indicating a fall in the nickel *d* orbital energy level. At the same time the ^1H chemical shift of the CH_2 groups in the ethyl groups moves downfield because of electron withdrawal from the nickel atom resulting from coordination of the electronegative olefin acting as a π acid. The electron withdrawal helps to depolarize the $Ni^{\delta+}$–$R^{\delta-}$ bond and so to induce a concerted fission of the Ni–R bonds to give the reductive elimination products (R–R) and olefin-coordinated zerovalent nickel bipyridine complexes.

The olefin-coordinated Ni^0 complexes release the coordinated olefins in solution, and stability constants for the olefin-coordinated complexes were determined [17].

$$\text{(bipy)Ni(olefin)} \overset{\text{solv.}}{\rightleftharpoons} \text{(bipy)Ni(solv)} + \text{olefin} \qquad (6)$$

It was confirmed that the more electronegative the olefin the stronger is the π bond formed. Furthermore the stronger the π bond, the more the nickel–alkyl bonds are activated [16,17].

Progress of this line of research was very much accelerated when Takakazu Yamamoto joined the group as a graduate student, since he was good at synthesis and spectroscopic and kinetic studies. We carried out further studies of the reactions of bipyridine-coordinated iron and cobalt alkyls with olefins, since these alkyls show catalytic activities for polymerization of some vinyl monomers [19–28]. The mechanism of polymerization of vinyl monomers by FeR_2(bipy) [29] was accounted for in



SCHEME 2

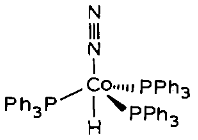
terms of a sequence of elementary processes involving (i) partial dissociation of one of the bipyridine ligands, (ii) coordination of the vinyl monomer to the central iron atom through π bonding, (iii) insertion of the coordinated vinyl monomer, as in Scheme 1, into one of the Fe–R bonds (initiation step), (iv) successive coordination and insertion of vinyl monomers into the Fe–C bond formed by the insertion of the first monomer into the Fe–R bond (growth reaction), and (v) termination involving β-hydrogen elimination or reductive elimination.

On the whole the mechanisms of polymerization of vinyl monomers by transition metal alkyls and hydrides, the properties of which were studied later [21,30,31], seemed to fit the general pattern represented in Scheme 2, and we turned our attention to other topics.

Our involvement with the chemistry of transition metal hydrides also had an unexpected start. Just after we had confirmed that nickel, iron and cobalt alkyls can exist as stable complexes, and Taro Saito had returned to the University of Tokyo after gaining sufficient experience in handling air-sensitive compounds, Uchida and I agreed to divide the projects, so that my group would examine the reaction system involving $Co(acac)_3$, organoaluminum compounds and tertiary phosphine, and his group the corresponding system containing $Fe(acac)_3$. Our choice of the cobalt system led to a surprising result. An undergraduate Shoji Kitazume was trying to find out whether an isolable cobalt alkyl was formed in the system of $Co(acac)_3$, $AlEt_2(OEt)$ and triphenylphosphine. We were using the general Schlenk tube techniques I had learned in Mülheim but with one difference, namely that we employed nitrogen instead of the argon which was always used in Mülheim. Argon contains less oxygen and water and because of its greater density is more effective as a blanket excluding air, but we could not afford to use it all the time because of its high price, and thus Kitazume worked with a nitrogen line. He obtained a crystalline orange powder from the system and measured the infrared spectrum of the sample. It showed an intense sharp absorption at 2088 cm^{-1}. It occurred to me that we must have obtained a cobalt hydride complex by β-hydrogen elimination from the assumed cobalt ethyl intermediate, and I asked Kitazume to thermolyze the complex in vacuum and collect the gas which did not condense at liquid nitrogen temperature by use of a Toepler pump, which had fortunately been installed for another purpose in Ikeda's group. The gas sample collected was handed to a mass spectrometer operator. When we examined the mass spectrum, we found a strong peak at *m/e* 28 and my first reaction was "Kitazume must have goofed somewhere in the gas collection and let air in into the vacuum line." However, the second inspection revealed that the peak of mass number 32 was as small as the background, which ruled the possibility of inadvertent admission of air. The peak 28 must come from dinitrogen, and since no nitrogen was present in the reagents used, it must have come from the nitrogen used as the blanket gas! This conclusion at first appeared unlikely, because molecular nitrogen was generally believed to be very unreactive. However, elemental analysis carried out in our laboratory confirmed that the sample did contain nitrogen.

Shortly before this finding the report by Vol'pin and Shur that ammonia was formed by hydrolysis of Ziegler type catalyst systems containing transition metal salts and alkyl compounds of Main Group elements under nitrogen caught my attention (through a translation from the Russian to Japanese) [32]. Soon afterwards Allen and Senoff had reported the first preparation of a dinitrogen-ruthenium complex by treatment of $RuCl_3$ with hydrazine [33]. Thus I was not totally unprepared to accept the idea that molecular nitrogen could be reduced under mild conditions by action of a low valent transition metal, but it still seemed somewhat unlikely that we had come across the first complex which could bind dinitrogen by picking it up from the atmosphere used to protect the air-sensitive compound. This was in February of 1966, and Kitazume had to present his results as undergraduate student before the faculty members as requirement for graduation, and the content of this presentation was hurriedly changed from that involved in his rehearsal in order to include the surprising discovery.

We waited about a year to publish the result [34]. For one thing we wanted to see if the complex might catalyse the conversion of N_2 and H_2 into ammonia; this seemed to be wishful thinking and, as I expected, the result was negative. For another thing the formulation of the complex was undetermined. From elemental analysis of C, H, N, and Co it was clear that the complex contained three PPh_3 ligands and one N_2 per cobalt, but $Co(N_2)(PPh_3)_3$ does not satisfy the eighteen electron rule. Evidence for a cobalt–hydride bond was not accessible with the equipment we had at the time. The amount of H_2 generated on thermolysis was negligible and a search for the Co–H band in the infrared spectrum by shifting the strong $\nu(N_2)$ band to lower frequency by labelling the dinitrogen with ^{15}N was unsuccessful. Finally I sent in the paper with the formulation of $Co(N_2)(PPh_3)_3$, persuading myself that if such an unlikely thing as fixation of N_2 under ambient conditions could take place then departure from the eighteen electron rule might also be possible. Later a British friend of mine confided to me that he had reviewed our communication and advised the editor to reject it on the grounds that the complex did not conform to the eighteen electron rule, although he accepted that the chemical characterization appeared sound. However, it was not rejected, and appeared in Chemical Communications [34a]. Two weeks after the publication of our paper Sacco reported that $CoH(N_2)(PPh_3)_3$ could be prepared from $CoH_3(PPh_3)_3$ by reaction with N_2 [35a]. Uchida, who was informed by us of the isolation of the Co–N_2 complex, started work along similar lines, and he reported that his group had prepared a mixture of $Co(N_2)(PPh_3)_3$ and $CoH(N_2)(PPh_3)_3$ by treatment of $Co(acac)_3$ and PPh_3 with triisobutylaluminum under N_2 [35b]. Eventually an X-ray crystallographic analysis by Ibers established that the sample prepared by Uchida's method had a trigonal bipyramidal structure for $CoH(N_2)(PPh_3)_3$, with the N_2 ligand bonded linearly to cobalt *trans* to the Co–H bond, as shown below [36].



Later I was told that a group of workers in Shell had prepared the same complex and was about to publish their results when they were thwarted by our report. I also heard that our compound was nicknamed the "Pearl Harbor complex" *. Such a name does not sound very pleasant to us Japanese, but the surprise and chagrin of those who had obtained the same complex but failed to publish the result was understandable, because we ourselves were surprised by the discovery. Anyhow this was an extremely exciting period for us, and I feel myself lucky that I experienced this period of turmoil.

Once a seemingly unlikely thing is observed and established, similar findings follow and are accepted without much surprise. Using a similar synthetic procedure to that which gave $CoH(N_2)(PPh_3)_3$, we prepared $RuH_2(PPh_3)_4$ and confirmed that it gave $RuH_2(N_2)(PPh_3)_3$ on treatment with N_2 gas [37,58]. Dinitrogen complexes are now known for most transition metals [38].

We failed to observe any reactions of the coordinated dinitrogen ligand with protic reagents [39,40] and turned our attention again to the chemistry of transition metal alkyls and hydrides. Table 2 summarises the transition metal alkyls, aryls, and hydrides we isolated. Most of the transition metal alkyls in the Table were prepared by treating transition metal acetylacetonates with $AlR_2(OEt)$ in the presence of appropriate stabilizing ligands. This method was convenient since the transition metal alkyls and hydrides formed precipitate out from the homogeneous systems and simple recrystallization usually suffices to purify the isolated complexes. On the other hand work-up after syntheses using Grignard reagents or lithium alkyls in combination with transition metal halides often requires purification processes involving water, which hinders isolation of water-sensitive or thermally unstable transition metal alkyls. When trialkylaluminums are employed the preparative conditions are somewhat more restricted, since trialkylaluminums, being stronger Lewis acids than dialkylaluminum monoethoxides, sometimes destabilize the isolated transition metal alkyls [41]. Another complicating factor when using trialkylaluminums is reverse alkyl migration from transition metal alkyls to trialkylaluminum, to give ionic complexes containing tetraalkylaluminate anions [12,13,42].

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* Admiral Yamamoto who attacked Pearl Harbor is not related to me. Yamamoto is quite a common name in Japan. Takakazu Yamamoto is also not a relative.

TABLE 2

PREPARATION OF TRANSITION METAL ALKYLS, ARYLS, AND HYDRIDES USING ORGANOALUMINUM COMPOUNDS [a]

Cr	Mn	Fe	Co	Ni	Cu
$CrRCl_2(THF)$	$MnPh_2PCy_3$	$FeR_2(bipy)$	$CoEt(bipy)_2$	$NiR_2(bipy)$	$CuMe$
$R = Me, Et, Pr^n, Bu^i$		$R = Me, Et, Pr^n$		$R = Me, Et, Pr^n, Bu^n$	$CuR(PR'_3)_n$
$CrRCl_2(base)_n$	$MnHI(thf)_{1.5}$		$[CoR_2(bipy)_2][AlR_4]$		$R = Me, Et, Pr^n, Bu^i$
$CrPh(acac)_2$		$FeMe_2(PPh_3)_3$	$R = Me, Et$	$NiR_2(PR'_3)_2$	$PR'_3 = PPh_3, PPh_2Me, PPhMe_2$
		$FeMe_2(dppe)_2$	$CoMe(PPh_3)_3$	$R = Me, Et$	PEt_3, PBu_3, PCy_3
			$CoMe(dppe)_2$	$PR'_3 = PEt_3, PBu_3$, 1/2dppe	$(CuR)_2(dppe)_3$
		$FeEt(acac)(PPh_3)_3$			$CuR(bipy)$
		$FeMe(acac)_2(PPhMe_2)$	$CoR_2(acac)(PR'_3)_2$	$NiR(acac)(PR'_3)_n$	
		$FeH_2(dppe)_2$	$R = Me, Et, Pr^n, Bu^i$	$R = Me, Et, Ph$	
			$PR'_3 = PPhMe_2, PPh_2Me$	$PR'_3 = PPh_3, PPh_2Et, PCy_3$	
			PEt_3, PBu_3, PCy_3		
			$CoMe_3(PR_3)_3$		
			$CoH(N_2)(PPh_3)_3$		
Mo		Ru	Rh	Pd	Pt
$MoH_2(dppe)_2$		$RuH_2(PPh_3)_4$	$RhH(PPh_3)_4$	PdR_2L_2	$PtR_2(PPh_3)_2$
$MoH(acac)(dppe)_2$				$R = Me, Et, Pr^n$	
				$L = PEt_3, PPh_2Me, PPhMe_2$	
				1/2dppe	

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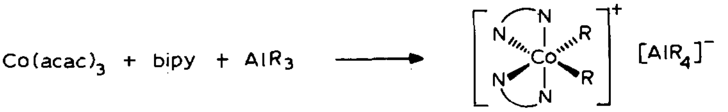
[a] For abbreviation and references, see text.



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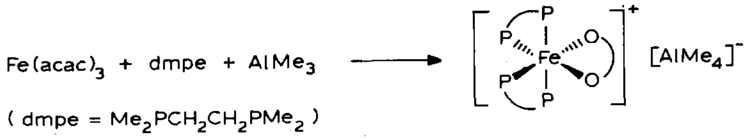


(8)

Dialkylaluminum monoethoxides and trialkylaluminums, being weaker alkylating agents than Grignard reagents or lithium alkyls, give various intermediate alkylation products of transition metals containing acetylacetonato or halide ligands such as $CrRCl_2(thf)_3$ [43], $CrPh(acac)_2$ [44], $FeEt(acac)(PPh_3)_3$ [45], $FeMe(acac)_2(PPhMe_2)$ [46], *cis*-$CoR_2(acac)(PR'_3)_2$ [47–49], and $NiR(acac)PR'_3$ [50–54]. Further alkylation of the intermediate alkyl complexes leads to peralkyl complexes. For this purpose use of stronger alkylating reagents such as lithium alkyls often gives better results [55].

In some cases transition metal alkyls having β-hydrogens in the alkyl groups undergo β-hydrogen elimination, with liberation of olefins and generation of transition metal hydrides. The hydride complexes, $RuH_2(PPh_3)_4$ [37], $FeH_2(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [46,56,57], $RhH(PPh_3)_4$ [37,58], $MoH(acac)(dppe)_2$ [59], and MnH(I)(thf) (thf = coordinated tetrahydrofuran) [60] were prepared by this route. Some of the hydrides were later found to be more conveniently prepared by treating transition metal halides with sodium borohydride [61]. Methyl and phenyl complexes without abstractable β-hydrogens are generally more stable than ethyl and higher homologs: examples of such complexes are $FeMe_2(PPh_3)_3$ [45], $FeMe_2(dppe)_2$ [46,56], $CoMe(PPh_3)_3$ [34b,45b], $CoMe(dppe)_2$ [62], $MnPh_2PCy_3$ (PCy_3 = tricyclohexylphosphine) [63], $NiPh(acac)(PR_3)_n$ [$(PR_3)_n = PPh_3$, PCy_3, $(PEt_3)_2$] [64], $CrPh(acac)(PEt_3)_2$ [65], and NiPh(Cl)(bipy) [66,67].

Treatment of dialkylnickel complexes with protic acids gives a variety of monoalkylnickel complexes [68,69].

$$NiR_2L_2 + HY \rightarrow NiR(Y)L_n + RH \qquad (9)$$

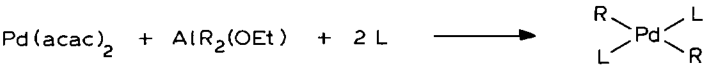
(L_2 = bipy, $(PEt_3)_2$; R = Me, Et; Y = OPh, OC_6H_4-*p*-CN, SPh, O_2CEt, acac, Cl, O_2CPh, $N(COR)_2$)

In general the monoalkyl complexes are thermally more stable than dialkyl complexes. This is partly due to the absence of available concerted decomposition routes such as reductive elimination.

From the beginning of our studies on chemistry of transition metal alkyls we used bipyridine and various tertiaryl phosphines just because they worked well for the preparation of transition metal alkyls. However, we do not yet completely understand why some stabilizing ligands are suitable for a particular type of complexes yet fail to work for a different type. Bipyridine, which serves as a quite effective stabilizing ligand for nickel, cobalt and iron, was found to be quite unsuitable for stabilizing copper alkyls, whereas use of tertiary phosphines gave remarkably stable copper alkyls. For example, ligand-free $CuCH_3$ decomposes explosively at room temperature, the explosion being particularly violent in the presence of a small amount of air. Bipyridine-coordinated copper alkyls CuR(bipy) (R = Me, Et, n-Pr) also decompose quite readily [70]. On the other hand tertiary phosphine-coordinated copper alkyls, $CuRL_n$ (R = Me, Et, n-Pr, iso-Bu, $L_n = (PPh_3)_3$, $(PPh_3)_2$, $(PPh_2Me)_3$, $PPhMe_2$, PEt_3, PBu_3), and $(RCu)_2(dppe)_3$ are thermally quite stable, and can be handled without danger [70–73].

A proposal to account for the instability of transition metal alkyls was made at that time by Wilkinson, who stressed the importance of low energy decomposition pathways, particularly the β-elimination process, and attributed the effect of stabilizing ligands mainly to blocking of the site required for the β-elimination process. Although the proposal was useful in leading to thermally stable "elimination-stabilized alkyls" such as trimethylsilylmethyl complexes, it failed to account for the thermal stability of $NiEt_2(bipy)$, which is thermally quite stable despite the fact that it contains β-hydrogens and has vacant sites available above and below the molecular plane for β-hydrogen abstraction [16,17]. It decomposes through a reductive elimination process which is accelerated by π-acids. Thus it is clear that one has to consider also other decomposition processes than β-hydrogen elimination in accounting for the kinetic stability of transition metal alkyls.

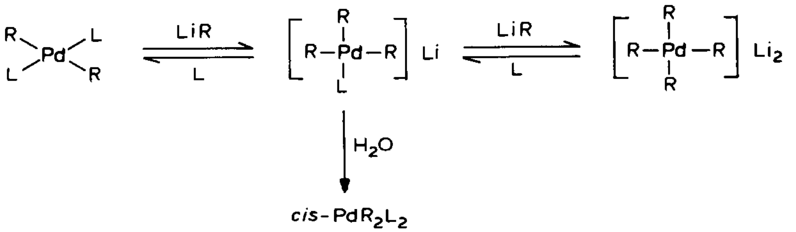
It was fortunate for us that we could prepare series of tertiary phosphine-coordinated *trans*- and *cis*-dialkylpalladium complexes [75–77]. *Trans*-PdR_2L_2 complexes were prepared by the usual method of treating palladium acetylacetonate with dialkylaluminum monoethoxide in the presence of tertiary phosphine ligands, whereas *cis*-PdR_2L_2 type complexes were synthesized by the reaction of $PdCl_2L_2$ with lithium alkyls [77,78].



(10)

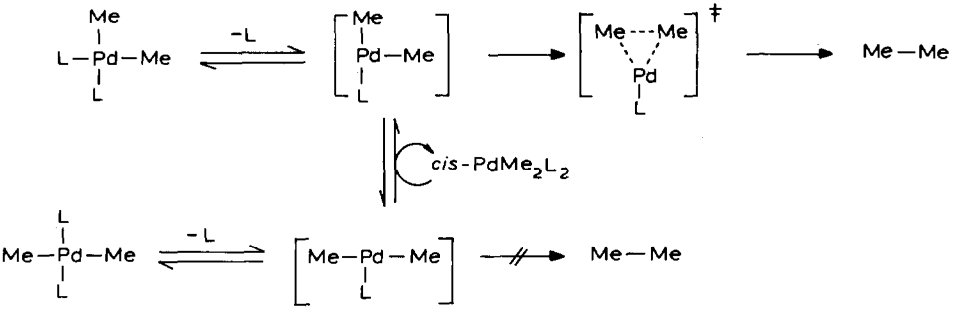
(11)

It puzzled us for some time why we should get *trans* or *cis* isomers depending on the method of preparation. We later found that the *trans* isomers can be isomerized by treatment with lithium alkyls followed by hydrolysis. The search for the reason for this revealed that treatment of PdR_2L_2 with LiR gives trialkyl- and tetraalkylpalladate complexes [79], and hydrolysis of the trialkylpalladium affords the *cis*-isomer.



(12)

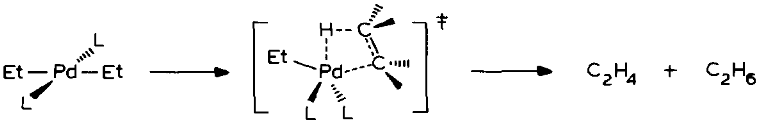
Studies of thermolytic behavior of the *trans*- and *cis*-$PdEt_2L_2$ complexes, carried out principally by Fumiyuki Ozawa, indicated that they decompose through quite different pathways. Particularly intriguing was the fact that thermolysis of *cis*-$PdEt_2L_2$ to liberate butane was hindered by addition of L [77], whereas inhibition effect of L on thermolysis of *trans*-$PdEt_2L_2$, which releases ethylene and ethane in a



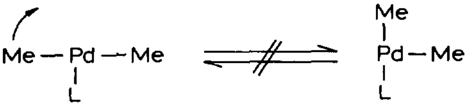
SCHEME 3

1/1 ratio, was small. It was further demonstrated that *trans*-$PdMe_2L_2$ is first isomerized to *cis*-$PdMe_2L_2$ in an autocatalytic process promoted by *cis*-$PdMe_2L_2$ before reductive elimination of Me–Me, and that the *trans–cis* isomerization as well as the reductive elimination are hindered by addition of L. These results suggested involvement of 3-coordinate T-shaped intermediates from which reductive elimination proceeds through a Y-shaped PdR_2-L-type intermediate (Scheme 3).

On the other hand thermolysis of *trans*-$PdEt_2L_2$ was accounted for in terms of a process involving a distorted trigonal bipyramidal configuration [76].

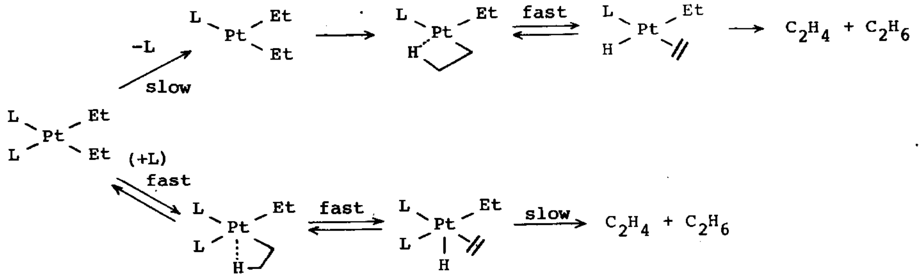


From experiments alone we could not explain why the ligand dissociation is necessary for the reductive elimination and why the isomerization from a three-coordinate "*trans*"-PdR_2L to another three coordinate complex "*cis*"-PdR_2L cannot take place without the help of another *cis*-PdR_2L_2, despite the fact that the process appears to involve just a simple swinging motion of one ligand to its adjacent coordination site.



(14)

Having noted the theoretical studies of Roald Hoffmann, who successfully accounted for the β-hydrogen elimination of square-planar transition metal alkyls [81] and the *cis–trans* isomerization and reductive elimination of trialkylgold complexes [82], I wrote to him asking if he could explain the behavior of the dialkylpalladium complexes on a theoretical basis. Just about the same time when he received my letter John K. Stille visited Cornell and gave a seminar on his work on the similar behavior of $PdMe_2L_2$ type complexes [83]. Stimulated by these independent observations relevant to C–C bond formation, Kazuyuki Tatsumi who was then working as a postdoctoral fellow in Hoffmann's group started on MO calculations and provided results which account reasonably for most of the experimental observations. The paper was published in Bull. Chem. Soc. Jpn. with both John Stille and myself as co-authors [84]. I hesitated first to include my name in a theoretical



SCHEME 4

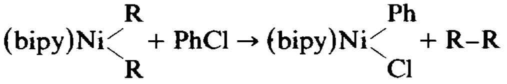
paper to which my contribution was only to stimulate the theoreticians but was persuaded by Roald who pointed out importance of stimulation to start a theoretical study. In retrospect I am glad I wrote the letter and aroused the interest of the theoreticians to work on the reductive elimination process; I would not have done it if Hoffmann's papers had been too difficult to follow for an experimentalist such as myself. Later when I visited Cornell (on my way to Toronto to attend the International Conference on Organometallic Chemistry) in the summer of 1981 and gave a seminar in the chemistry department, I told the audience that M. Calvin and K. Ziegler with whom I had worked before were both awarded Nobel Prizes and then made the confident prophecy that my visit to Cornell might bring another Nobel Prize to the University. The prophesy was fulfilled, to my great satisfaction, in the same year.

In contrast to the behavior of *cis*-$PdEt_2L_2$ which liberates butane via a dissociative process, quite similar complexes of platinum *cis*-PtR_2L_2 having alkyl groups with β-hydrogen atoms are thermolyzed via β-elimination processes involving dissociation of a coordinated tertiary phosphine ligand, whereas in the presence of an added tertiary phosphine ligand a process involving five-coordinate transition state operates [85,86]. The question of why palladium and platinum dialkyls of similar structures behave so differently requires further studies by theoretical chemists.

The results on the behavior of palladium and platinum alkyls indicate that the thermal processes for decomposition of these alkyls in the ground state are under the constraint of square-planar geometry. The constraint is released in photochemical reactions of palladium dialkyls, and the behavior of palladium alkyls can be accounted for by assuming a tetrahedral transition state [87].

In contrast to that from palladium and platinum dialkyls, reductive elimination from nickel dialkyls can proceed through a five-coordinate intermediate involving an associative proces [16,17,80,88]. Here again an MO approach [89] was useful in accounting for the reductive elimination behavior of nickel dialkyls.

Reductive elimination of nickel dialkyls is also promoted by interaction with aryl halides, which oxidatively add to nickel to give nickel aryl halide complexes [66,67].



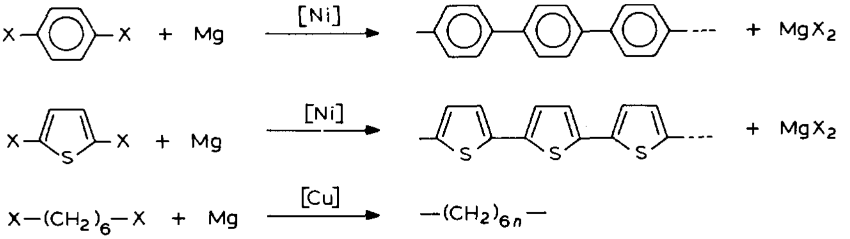
$$(\text{bipy})\text{Ni}\begin{matrix}\text{R}\\ \text{R}\end{matrix} + \text{PhCl} \rightarrow (\text{bipy})\text{Ni}\begin{matrix}\text{Ph}\\ \text{Cl}\end{matrix} + \text{R–R} \tag{15}$$

When we first observed this process in 1970 we failed to see the possibility of applying it to organic synthesis. Kumada's group [90] and also Corriu and Masse

[91] developed a new synthetic method for cross coupling of alkylmagnesium halides with aryl halides catalyzed by nickel and later by palladium complexes.

$$\mathrm{RMgX} + \mathrm{ArX} \xrightarrow{\text{catalyst}} \mathrm{R{-}Ar} + \mathrm{MgX_2} \tag{16}$$

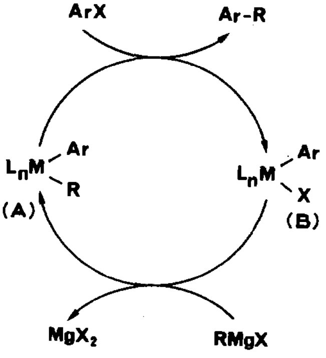
I realized only later the value of developing the fundamental process to bring about C–C bond formation using a transition metal complex. In our group Takakazu Yamamoto, who had a background in polymer chemistry, saw the possibility of applying the process to difunctional aromatics and developed a novel polycondensation process [92]. The dehalogenative polycondensation process is generally applicable in bringing about C–C coupling reactions to give polyaromatics or polyalkanes.



(17)

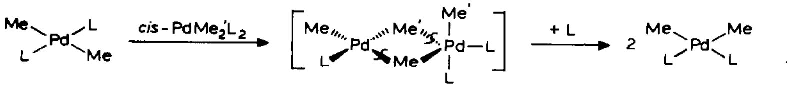
The polyarenes thus produced are thermally quite stable, and on doping with iodine they are converted into electricity-conducting polymers having a conductivity as high as 10 S cm^{-1}. Because of Takakazu's inventiveness we are now developing primary and secondary electric batteries utilizing these new materials [93].

The basic principles of the cross coupling reactions can be represented by Scheme 5. Although Scheme 5 represents the basic picture for the processes involved in the catalytic cycle, the representation is somewhat oversimplified. The scheme does not specify the configuration of the assumed intermediates (**A**) having the alkyl and aryl groups, and neglects the interactions of **A** with **B** and with Grignard reagents. For reductive elimination from a square-planar palladium complex to occur the alkyl and aryl groups must be brought into mutually *cis* positions. Isomerization of the *trans*-$\mathrm{PdMe_2L_2}$ complexes to their *cis* isomers was shown to be accelerated by addition of *cis*-$\mathrm{PdMe_2L_2}$ complexes [77] or alkylmagnesium compounds [94]. On the



SCHEME 5

basis of studies using CD_3-labelled complexes the following isomerization mechanism involving intermolecular process through methyl-bridged intermediates was proposed.



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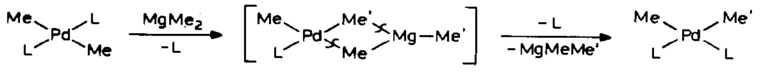


(19)

The situation is different for nickel systems. Evidence has been presented for involvement of five-coordinate intermediates in reductive elimination of R–R from NiR_2L_2 in an associative pathway [88], and theoretical calculations have provided support for the assumption of reductive elimination of alkyl groups at apical and equatorial sites [89].

Just as the behavior of organo-nickel, -palladium, and -platinum complexes toward thermolysis varies, the reactions of such complexes toward carbon monoxide also show considerable differences. Following our studies on reactions of CO with dimethyl- and diethyl-nickel complexes [95,96] we examined its reactions with *cis*-PdR_2L_2 and *trans*-PdR_2L_2 type. The results were strikingly different [97]. The products from *trans*-PdR_2L_2 were ketones regardless of the nature of the alkyl groups, whereas the *cis*-$PdEt_2L_2$ gave a 1/1 ratio of ethylene and propionaldehyde, and *cis*-$PdMe_2L_2$ gave acetone and MeCOCOMe.

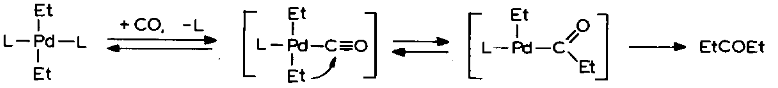
$$trans\text{-}PdR_2L_2 + CO \rightarrow RCOR \tag{20}$$

R = Me, Et, Pr, and Bu, L = tertiary phosphine

$$cis\text{-}PdEt_2L_2 + CO \rightarrow EtCHO + C_2H_4 \tag{21}$$

$$cis\text{-}PdMe_2L_2 + CO \rightarrow MeCOMe + MeCOCOMe \tag{22}$$

These results can be most satisfactorily accounted for by assuming the constraint of square-planar geometry and migration of the alkyl groups to the coordinated CO ligand. For example, the reactions of *trans*- and *cis*-$PdEt_2L_2$ with CO proceed as follows.



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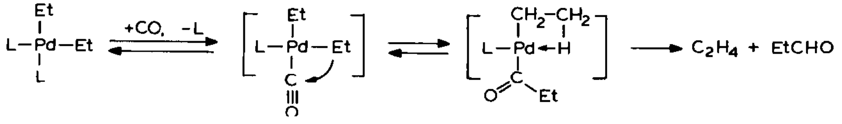
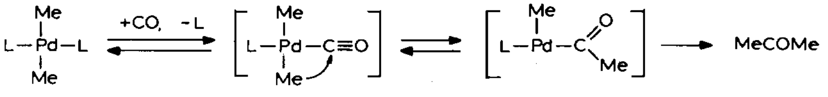


(24)

The same assumption can be adopted to explain the exclusive formation of acetone from *trans*-$PdMe_2L_2$ and the production of diketone along with acetone from *cis*-$PdMe_2L_2$.



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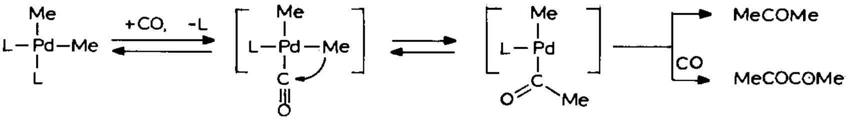
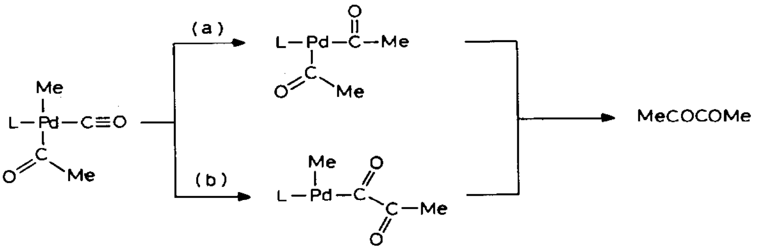


(26)

In the reaction of *trans*-$PdMe_2L_2$ with CO the intermediate acetyl-methyl species formed by methyl group migration to the coordinated CO ligand has T-shaped "*cis*" geometry suitable for direct reductive elimination of acetone (eq. 25) [98]. On the other hand the corresponding acetyl-methyl intermediate formed from *cis*-$PdMe_2L_2$ by methyl migration has a T-shaped "*trans*" geometry which is unsuitable for direct reductive elimination of acetone. The T-shaped *trans*-intermediate may react further with CO (eq. 26).

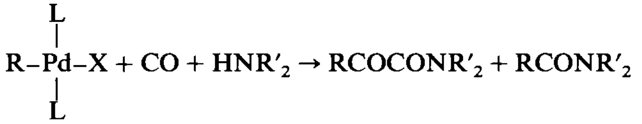
A question we faced at that time was whether the coordinated CO ligand is inserted into the remaining Pd–Me bond to give a bis-acetyl species (route (a) in eq. 27) or into the PdCOMe group to afford a methyl-pyruvoyl species (route (b)).



(27)

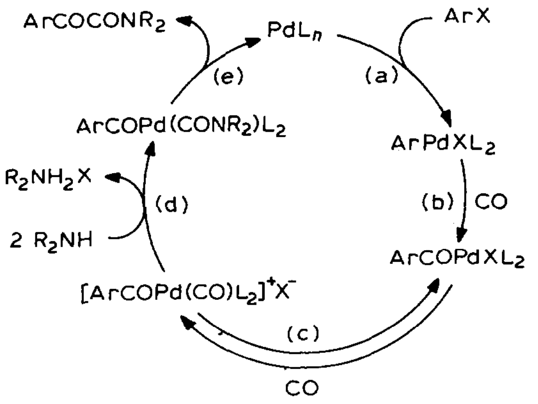
The double insertion process to give the pyruvoyl group was considered to be thermodynamically unfavorable, but it could not be excluded if the ensuing reductive elimination was a rapid process. In examining this problem we reasoned that addition of a secondary amine would trap the acetyl or pyruvoyl group to afford amide or α-keto amide. The reaction of *cis*-$PdMe_2L_2$ with CO in the presence of diethylamine gave methane and $MeCOCONEt_2$ in addition to $MeCONEt_2$, whereas similar reactions using *trans*-$PdMe_2L_2$ yielded only acetone. These results at first seemed to be compatible with the consecutive CO insertion mechanism but later studies disfavored it.

We further investigated the reactions of CO with monoalkyl- or aryl-palladium halides in the presence of secondary amines, and found that α-keto amides can be obtained as major products [99].



$$R\text{-}\underset{\displaystyle L}{\overset{\displaystyle L}{Pd}}\text{-}X + CO + HNR'_2 \rightarrow RCOCONR'_2 + RCONR'_2 \qquad (28)$$

Since oxidative addition of aryl halides to give arylpalladium halides is well known, extension of the newly found reaction (eq. 28) to devise a catalytic cycle to produce α-keto amides from aryl halides, CO and secondary amines seemed an obvious possibility. The very first experiment confirmed our expectation [100]. Unknown to



SCHEME 6

us Takana and Kobayashi, with a different stimulus, also observed this catalytic process independently at about the same time [101].

Our subsequent detailed study confirmed the reaction route represented in Scheme 6 [102–104].

The catalytic cycle comprises (a) oxidative addition of aryl halide to Pd^0 species, (b) CO insertion into the Pd–Ar bond, (c) coordination of CO to give an ionic aroylpalladium complex, (d) attack of the amine on the coordinated CO ligand to afford an aroylcarbamoylpalladium complex, and (e) reductive elimination of the carbamoyl and aroyl groups to liberate α-keto amide with regeneration of the Pd^0 species. Support for the mechanism was obtained by separate examination of all the steps, except the final reductive elimination step, using model organopalladium complexes. A similar conclusion was also reached by Sen and Chen [105].

Although the range of suitable reaction conditions for bringing about the double carbonylation is more limited than in the process using secondary amines, use of alcohol in combination with tertiary amines also gives the double carbonylation product [106].

$$\mathrm{ArI + ROH + CO + NEt_3 \xrightarrow{[Pd]} ArCOCOOR} \tag{29}$$

Before that process was observed a different type of double carbonylation utilizing benzyl chloride had been described [107], and it has attracted considerable attention because the phenylpyruvic acid formed can be used as a source for phenylalanine, which is used in the production of the new sweetener Asparteme. Although our process is not applicable to benzyl halide because of its reactivity with secondary amines, it seems to have wider applications; thus various α-amino acids, α-hydroxy acids, quinoline and indole derivatives [108] can be derived from the α-keto amides or esters. It was exciting that an attempt to clarify the mechanism of the CO insertion reaction led unexpectedly to a new process of possible practical utility.

Epilogue

Throughout this account I have shown how my interest in fundamental reactions of transition metal alkyls often led to unexpected findings. Throughout these studies

I have thoroughly enjoyed working in the developing field of organometallic chemistry. This would not have been possible without the help of my early supervisors, and the later assistance of my coworkers. I would like to express my sincere gratitude to all those who helped me and stimulated me, and whose names are included in the references.

Because of the space limitation this account has been confined to simple metal alkyls. Other important lines of research of my group involving C–O, C–H, and C–chalcogen bond cleavage and formation have not been considered, and I wish also to thank the coworkers who actively participated in those studies. Although their names could not be included in the references, they also contributed to the development of the work described through mutual stimulation and through their enthusiasm for organometallic chemistry.

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