Carbon–Carbon Bond Formation through Organometallic Elimination Reactions†

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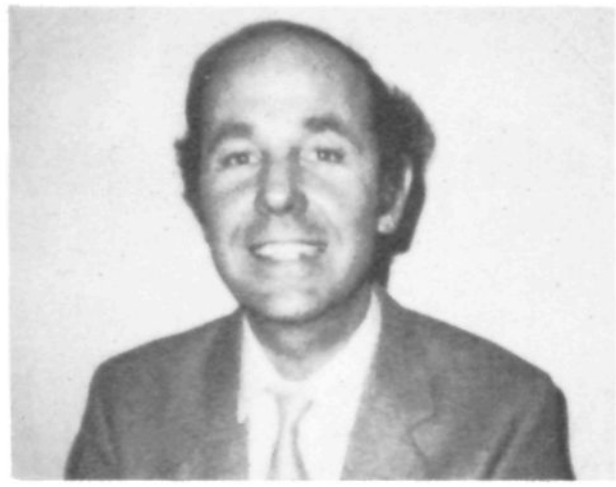

John Brown received his degrees from Manchester University (Ph.D. research with Prof. A. J. Birch) and went on to do post-doctoral work at Columbia University (with Prof. Ronald Breslow), the Australian National University, and Bristol University between 1963 and 1966. He was a lecturer at Warwick University before moving to his present posts in the Dyson Perrins Laboratory and Wadham College in 1974. Current interests include asymmetric synthesis, mechanism in organometallic catalysis, and chemistry in organized media.

Neil Cooley was born in Berkhamsted, near London, in 1961. He graduated in chemistry at Exeter University, where he also obtained a Ph.D. degree under the direction of Prof. E. W. Abel. After spending a year studying chromium-centered, organometallic radicals with Prof. M. C. Baird at Queens University, Kingston, he returned to the U.K. to take up a postdoctoral position with Dr. Brown. He is currently investigating mechanistic aspects of cross-coupling reactions.

I. Introduction

Organometallic reactions leading to the formation of a new carbon–carbon bond have secured an important place in synthetic organic chemistry. Two classes may be distinguished at the outset. In the first of these, the metal acts as a template which mediates the attack of an external reagent on a ligand without that reagent becoming bonded within the coordination sphere. Prominent examples include catalytic allylic alkylation, usually requiring palladium complexes,[1] and the reaction of electrophiles with iron acylate anions.[2] These respectively demonstrate enhanced reactivity and stereoselectivity through the involvement of organometallic complexes. In the second category, the new bond is formed between ligated species, and a further subdivision is needed. The key step may be cis-ligand migration, for which the most familiar example is alkyl migration to coordinated CO in catalytic hydroformylation. The product acyl remains coordinated and is only released in a subsequent reductive step.[3] Alternatively, the carbon–carbon bond is formed by coupling of adjacent carbon–metal bonds, concomitant with elimination of the organic fragment.[4] These different possibilities are illustrated in Figure 1.

This review emphasizes the elimination route to C–C bond formation and appraises the current state of mechanistic understanding. As will be seen, the distinction between migration and elimination reactions is not completely clear-cut, and the scope is sufficiently broad to take cognizance of this. Synthetic aspects will be incorporated only when there is a contribution to mechanism. Since there have been general reviews on elimination covering the literature to 1984,[5] recent work is strongly underscored. The discussion is subdivided according to the nature of the organic groups involved in coupling, and features of common interest or general importance are discussed separately.

II. Coupling of Saturated Alkyl Groups

In any survey of organometallic chemistry, the variation in stability among complexes with cis-related alkyl groups is particularly striking. It depends very much on the metal but also on the oxidation and coordination states. The ligand trans to M–C has a profound effect on thermal lability, with strong electron donors (al-

† The following acronyms for common ligands are used in the text: bpy = 2,2′-bipyridyl, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppf = 1,1′-bis(diphenylphosphino)ferrocene, (*R*,*R*)-DIOP = 2,2-dimethyl-4,5-bis-((diphenylphosphino)methyl)-1,3-dioxolane, and (*S*,*S*)-CHIRAPHOS = (2*S*,3*S*)-bis(diphenylphosphino)butane.

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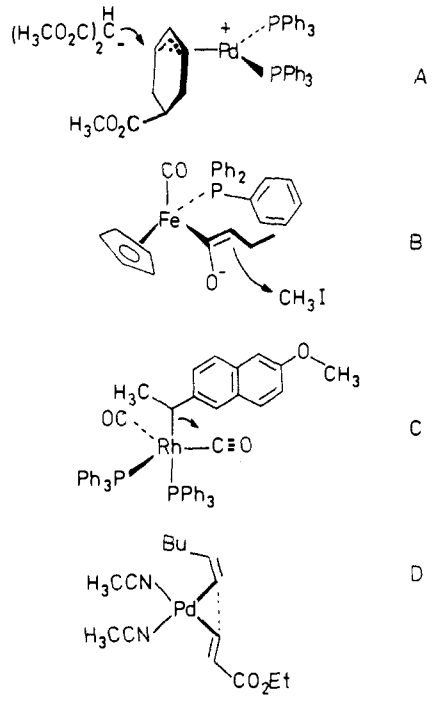


Figure 1. C–C bond formation in organometallic complexes through (A) catalytic allylic alkylation, (B) iron acyl complexes, (C) alkyl transfer in hydroformylation, and (D) alkyl coupling.

kylphosphines, bipyridyl) exerting a pronounced stabilization relative to arylphosphines. The extremes of behavior are represented by trialkylcopper(III) species, important in organocuprate chemistry but never observed because of the facility of alkane elimination,[6] and by the thermally stable dimethyl complexes of the heavier platinum group metals. For example, *cis*-$Me_2Os(CO)_4$ decomposes only on very protracted heating at 163 °C, and methane rather than ethane is the main product in consequence of homolytic M–C fission.[7] Comparable observations have been made with *cis*-$Me_2Pt(PR_3)_2$ both early on and in recent extensive work with adamantylphosphine complexes.[8]

Much of the incentive for understanding elimination reactions of this type stems from their relevance to catalytic cross-coupling. Consequently palladium and nickel complexes have been most thoroughly studied, often in comparison with platinum analogues. A careful X-ray structural analysis of *cis*-$(Ph_2PMe)_2MMe_2$ (M = Pd or Pt) fails to reveal any significant differences that could account for the pronounced contrast in thermal lability[9] but ab initio calculations offer substantial insight.[10] In two significant papers that carry comprehensive background material, Low and Goddard analyze these differences. They find that the metal in $M(CH_3)_2$ and $(PH_3)_2M(CH_3)_2$ is in s^1d^9 configuration and forms covalent M–C bonds through its sd hybrid orbitals. For the phosphine-free species, ethane formation is exothermic at palladium but endothermic at platinum. In both cases elimination from the phosphine complexes is exothermic. The metal configuration changes from s^1d^9 to d^{10} on traversing the energy surface for ethane elimination, and this is *much* more favorable for Pd than for Pt. Figure 2 demonstrates the main features of their calculations. With current computational power the theoretician must employ PH_3 complexes to limit the number of degrees of freedom in the calculations. Hence subtleties such as the difference between al-

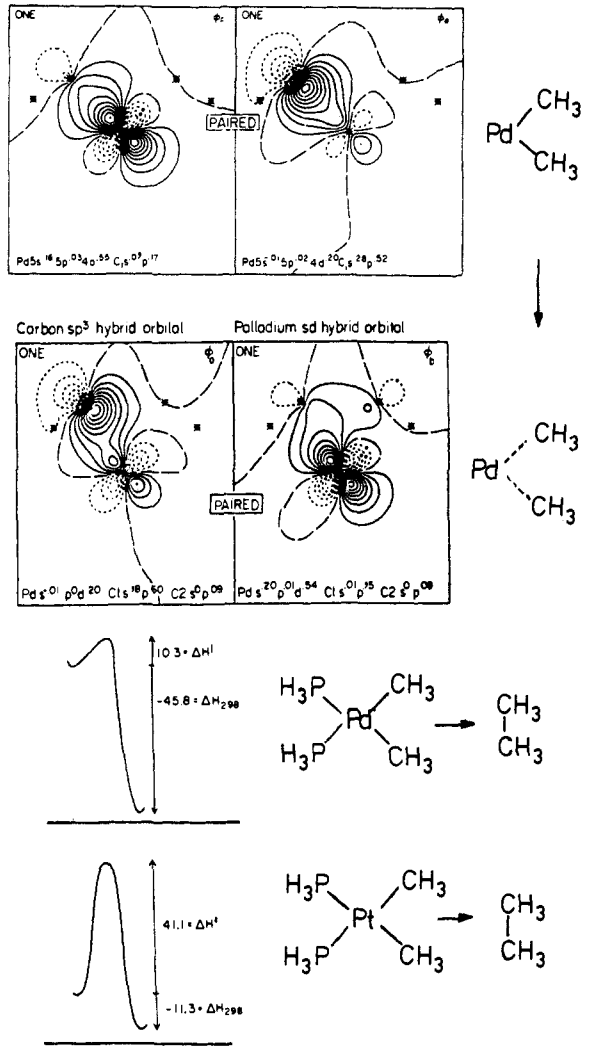


Figure 2. Comparison between ethane elimination from $PdMe_2$ and $PtMe_2$ species through MO calculations.[10]

kylphosphine and arylphosphine complexes cannot be probed.

Yamamoto, Stille, and their respective co-workers[11] have provided much of the experimental basis for alkane elimination mechanisms and for clarifying the consequences of added ligands. For *cis*-dialkylbis(phosphine)palladium complexes, C–C coupling is the predominant, or even exclusive, pathway whereas the corresponding trans isomers undergo some β-elimination in competition, producing equimolar amounts of alkane and alkene. Reaction of *cis*-$(MePh_2P)_2PdMe_2$ is strongly inhibited by added $MePh_2P$ and other phosphines, and good kinetic data were obtained. This showed an inverse dependence on phosphine concentration, consistent with prior phosphine dissociation before thermolysis, so that the three-coordinate intermediate is much more prone to elimination than its four-coordinate precursor (Figure 3). The corresponding trans isomer undergoes autocatalytic decomposition as it isomerizes to the cis isomer by a bimolecular mechanism involving mutual exchange of alkyl groups. Excess phosphine diverts reaction of the cis isomer L_2PdEt_2 toward β-elimination, which may then become the major reaction pathway when chelating bis(phosphine) complexes are concerned. In anticipation of work to be discussed later, these reactions are carried out in the presence of dimethyl maleate, which

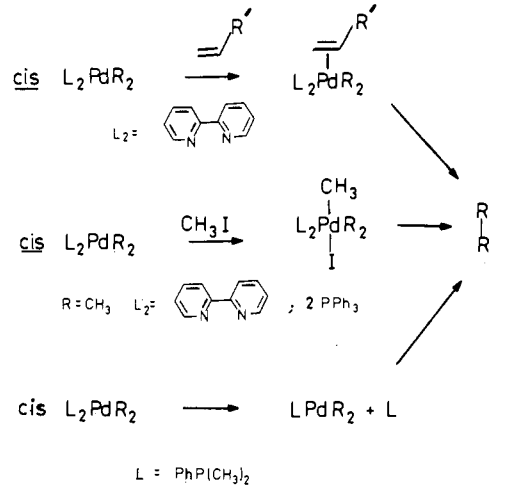
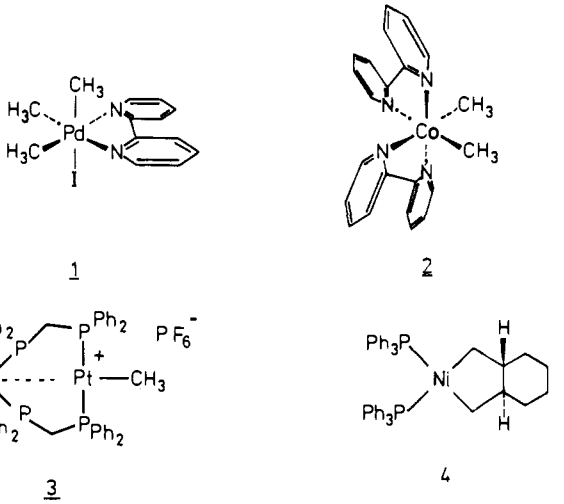


Figure 3. Pathways for *n*-alkane elimination from various L_nPdR_2 complexes.



is kinetically innocent in this particular case (but see the bpy complexes of ref 13) and operates solely to trap the L_2Pd fragment formed. The dissociative mechanism of C–C elimination and also reaction from the four-coordinate state have been probed by extended-Hückel calculations.[12] These indicate that the symmetrical trigonal LMR_2 is destabilized and undergoes Jahn–Teller distortion to a T- or Y-shaped species. The T-shaped cis isomer is very prone to eliminate alkane.

Whereas earlier work from the Yokohama group had shown that butane was formed on thermolysis of $(bpy)NiEt_2$ by a straightforward mechanism, Sustmann and Lau have shown that the corresponding Pd complex thermolyzes by β-elimination with rate inhibition by added [bpy]. In the presence of a substantial excess of methyl acrylate (10–1833-fold), C–C coupling becomes the dominant pathway, and the reaction is then first order in both complex and olefin. The result is rationalized[13] by postulating an 18e complex (Figure 3), which fragments exclusively to *n*-butane. To underscore this, the rate of reaction was shown to be strongly dependent on the olefin. With added tetracyanoethylene, it was too fast to measure at −50 °C, while the weaker acceptor methyl acrylate afforded slow butane elimination at room temperature. These and other examples indicate that three- or five-coordinate intermediates are often required for efficient C–C elimination from precursor square-planar four-coordinate complexes.

Alkyl-coupling reactions involving higher valencies of the nickel triad have been studied in some detail; it is known that platinum(IV) complexes are much more labile than their platinum(II) analogues.[5] The effect of added electrophiles on the thermolysis of dimethylnickel complexes has been studied. With alkyl and aryl halides, this normally promotes C–C elimination, and the observation of some cross-coupled products among the hydrocarbons formed indicates that oxidative addition is the initial step.[14] With CS_2, the *cis*-$(dppp)NiMe_2$ complex gives ethane cleanly whereas *trans*-$(PEt_3)_2NiMe_2$ forms a stable 1:1 adduct. Further support for the oxidative addition pathway is provided by the isolation of adduct **1** by reaction of MeI with $(bpy)PdMe_2$;[15a] this decomposes with formation of ethane in $(CD_3)_2CO$ solution at 10 °C. The analogous cationic tris(pyrazolyl)methane derivative is stable at ambient temperature.[15b] For related cobalt complexes, the thermal decomposition in the presence of added alkyl halides is dominated by homolytic cleavage.[16a] Thus in **2** the geminate alkyl radical/cobalt cation radical pair so formed may react by alkyl coupling or bromine atom transfer from added halide; the new radical leads on to further coupling products. The homocoupling of benzyl bromide is promoted by a paramagnetic tetrahedral iron complex $(Me_2NCH_2CH_2NMe_2)Fe(CH_2Ph)_2$ formed in situ from diamagnetic $[CpFe(COD)][Li(Me_2NCH_2CH_2NMe_2)]$.[16b]

Little work has been done on photochemical eliminations leading to carbon–carbon bond formation. The potential of this area is nicely demonstrated by the clean formation of ethane when complex **3** is photolyzed in $(CH_3)_2CO$ or other polar solvents.[17] The methyl groups are readily interchanged between the two platinum nuclei so that 1,1-elimination cannot be conclusively demonstrated.

Thermolysis of metallacycloalkanes rarely proceeds directly to the corresponding cycloalkane by C–C coupling. The most elegant example remains due to Grubbs and Miyashita,[18] who observed the catalytic dimerization of ethylene to cyclobutane by $(PPh_3)_2Ni$ complexes via a metallacyclopentane. Miyashita and co-workers[19] have now demonstrated the formation of 1,2-disubstituted cyclobutanes on photolysis of olefins in the presence of $(PPh_3)_2Ni(C_2H_4)$ and presume the involvement of nickelacyclopentanes. The products from metallobicyclic species (e.g., **4**) arise with α,ω-diolefins. Substituted cyclopropanes have been observed in the photolysis of titanacyclobutanes,[20a] and in their reaction with iodine via a two-step electrophilic cleavage reaction,[20b] in the treatment of some platinacyclobutanes with DMSO,[21] and in the thermolysis of 1,2-dicobaltacyclopentanes.[22] Thermolysis of 3,3-dimethylnickela- and -palladacyclobutanes gives varying amounts of 1,1-dimethylcyclopropane.[23] For the $(PPh_3)_2Ni$ complex addition of excess PPh_3 diminishes the yield and the major products are ethylene and isobutene (from metathesis). It is tempting to invoke metallacyclobutanes in asymmetric cyclopropane synthesis from chiral iron carbene cations and olefins but the authors prefer otherwise.[24]

Not all C–C bond-forming reactions between adjacent alkyl groups arise from direct coupling. Thorn has demonstrated that the formation of ethyl methyl ether from rhodium complex **5** (Figure 4) arises by 1,2-methyl

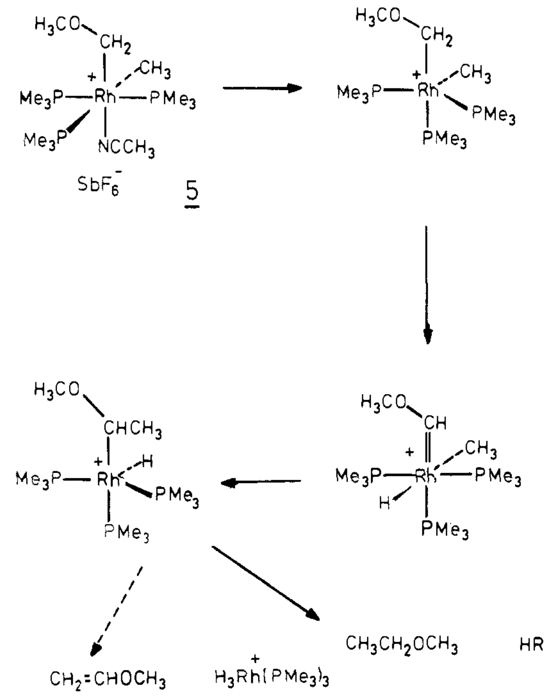


Figure 4. C–C bond formation via migration to a coordinated carbene.

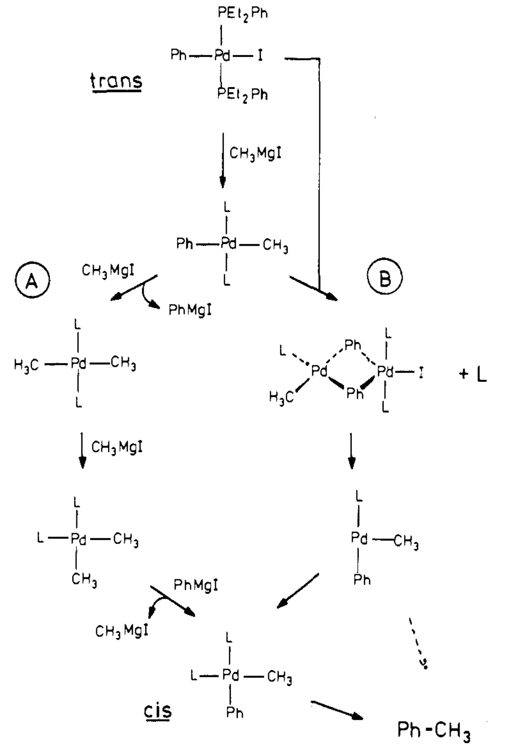


Figure 5. Reaction pathway for toluene elimination from $(Et_2PhP)_2Pd(Me)Ph$, generated from MeMgBr and *trans*-$(Et_2PhP)_2Pd(I)Ph$ in situ.

migration to a coordinated carbene.[25] The facility of this process is underscored by observations in osmium or ruthenium[26] and platinum[27] chemistry.

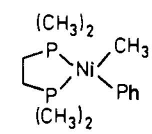
This section concludes with a brief consideration of catalysis—necessarily brief since it has generally been considered that simple alkyl halides cannot be employed in cross-coupling reactions because of competing β-elimination. Castle and Widdowson have now shown[28] that high yields may be obtained by using preactivated $(dppf)PdCl_2$ and alkyl iodides with organomagnesium bromides in refluxing tetrahydrofuran. Cross-coupling of α-stanno ketones and α-bromo ketones is successful with ruthenium or palladium complex catalysts.[29] Negishi and co-workers have demonstrated that ethane formation from in situ generated $(PPh_3)_2PdMe_2$ occurs at ambient temperature in tetrahydrofuran. This affords a synthetically convenient method for cross-coupling catalyst activation, and trapping of the resulting "$(PPh_3)_2Pd$" species by PPh_3 or maleic anhydride was demonstrated. As expected, the corresponding $(PEt_3)_2PdMe_2$ complex proved much more stable,[30] in accord with lower lability for square-planar alkyls possessing trans ligands with higher σ-basicity.

III. Cross-Coupling of Saturated and Unsaturated Groups

The topic is closely related to common areas of catalytic C–C bond formation, which has influenced the design of mechanistic experiments. In such reactions the electrophile is normally the unsaturated entity (to avoid the complications arising from β-elimination). The alternative approach occasionally works, as in the $(dppp)NiCl_2$-catalyzed reaction of arylmagnesium halides with α-bromopropionates en route to aryl propionates.[31] Palladium complexes are much inferior to nickel in related reactions.[32]

Studies on isolated and characterized species provide some useful insights, and organogold complexes fit this category well despite their lack of catalytic activity. Thermolysis of phosphine complexes **6a** always gives

6a 6b



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the methylarene cleanly, rather than ethane. A conventional kinetic approach establishes that phosphine dissociation occurs first, as in trialkylgold phosphine complexes[5] so that the reaction is favored by bulkier ligands.[33] The same selectivity trends are observed in related complexes **6b**, where R now represents a range of vinylic and aromatic groups. This is not universally true, for the species R = PhC≡C–, 2-pyridylmethyl, or benzyl give ethane as the predominant fragmentation product.[33]

Studies on viable catalytic systems are particularly valuable, and Yamamoto's recent work on intermediates in the cross-coupling of methylmagnesium bromide and iodobenzene falls into that category.[34] With *trans*-$(Et_2PhP)_2Pd(Ph)I$ as catalyst, several organopalladium species are observable under turnover conditions by ^{31}P NMR, including all possible dimethyl and methylphenyl complexes (Figure 5). Their interconversion is promoted by transmetalation with Grignard reagent(s), but only the *cis*-PhMePd complex undergoes ready elimination, with clean formation of toluene. Unlike the corresponding *cis*-Me_2Pd complex the elim-

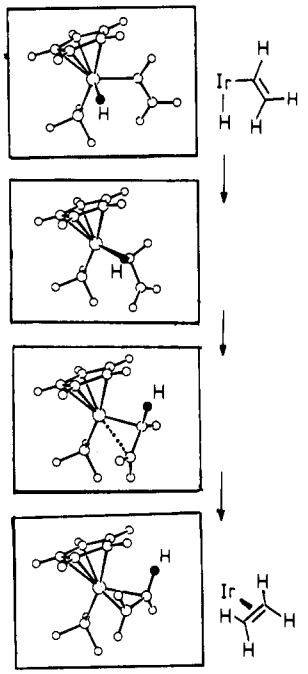


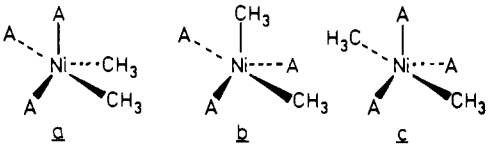
Figure 6. Extended-Hückel calculations on the interconversion pathway between $CpIr(C_2H_3)H$ and $CpIr(C_2H_4)$.

ination occurs *without* prior phosphine dissociation and is unaffected by excess PhI. The difference may reside in weak π-coordination to the developing vacant coordination site in PhMe elimination although the precise pathway is undetermined. The corresponding *trans*-PhMePd complex is thermally stable in the absence of autocatalytic Pd(0) species or of MeMgI, which promotes cis–trans isomerization.

Perhaps the trajectory calculated by Hoffmann and co-workers for $CpIr(C_2H_3)H \rightarrow CpIr(C_2H_4)$ interconversion[35] provides the closest analogy. There the sequence of events is distortion of vinyl geometry followed by H migration to the α-carbon and then rotation of the organic fragment (Figure 6). All of this should be relevant to Me–Ph coupling reactions, and indeed to any elimination involving an sp^2 carbon–metal bond.

These palladium reactions occur by a mechanistically simple C–C coupling from the 4-coordinate *cis*-16e state. Although formally similar in structure, the nickel complex **7** possesses two features that might be expected to discourage thermolysis—the ligand is a rigid chelate and a strong σ-donor. It was found that added phosphines greatly accelerated the decomposition, with clean formation of methylarene.[36a] This requires a thermolabile 5-coordinate intermediate, so Tatsumi and co-workers carried out extended-Hückel calculations on species of the R_2NiL_3 type, which may exist in trigonal-bipyramidal geometry.[36b] The study provides an explanation of why *trans*-R_2NiL_2 species do not undergo thermolysis by an associative mechanism. There are three stereoisomers pertaining to the 5-coordinate state, **8a–c**. Only in the case of **8a** is the C–C coupling reaction symmetry allowed; this is the isomer directly accessible from the *cis*-R_2NiL_2 species by ligand association.

Aryl–alkyl elimination may occur from the palladium(IV) state in appropriate cases. Acetanilide reacts with $Pd(OAc)_2$ to form the expected orthopalladation product, which adds MeI to give a putative palladium(IV) intermediate en route to *o*-methylacetanilide.[37]



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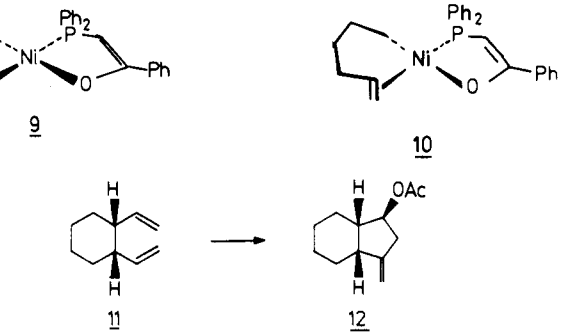
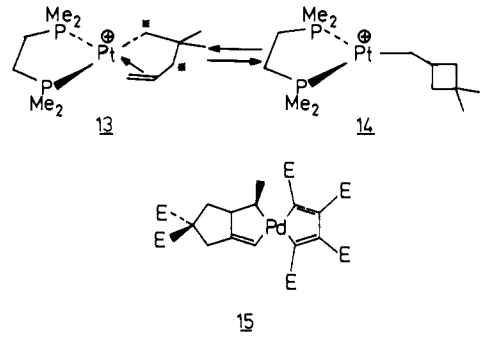
With *o*-iodoacetanilides carrying a pendant enamine group, a catalytic intramolecular Heck reaction occurs on treating the reactant with $Pd(OAc)_2$, PPh_3, K_2CO_3, and NEt_4Cl in acetonitrile.[38] The Heck reaction and related steps that occur in the catalytic dimerization of terminal olefins[39] involve cis migration of a carbon ligand to a coordinated double bond rather than C–C elimination. Accordingly, the energy surface for $MePd(C_2H_4) \rightarrow PdC_3H_7$ has been found to be favorable.[40] Reasons for preference of this pathway may be apparent on consideration of specific examples. Cyclization of α,ω-dienes using catalysts of type **9** introduced by Keim and co-workers occurs through the η^1,η^2-metallacycle **10**, in the case of hexa-1,5-diene. Migration of Ni–CH_2 to the bound olefin followed by Ni–H elimination leads to methylenecyclopentane.[41] Oxidative cyclization of hexadienes catalyzed by $Pd(OAc)_2$/benzophenone (e.g., **11** → **12**) involves related intermediates.[42] Support for this pathway is provided by the characterized platinum cation **13**, which undergoes a skeletal rearrangement interconverting the starred atoms (CD_2 labeled) via **14**.[43] Similar η^1,η^2 intermediates are required to explain the palladium complex catalyzed cyclization of 1,6-enynes. In some cases the η^1,η^2-metallacyclopentene may be intercepted by a cycloaddition reaction; the product is then formed by an authentic C–C elimination reaction from **15**.[44]



9 **10**

11 **12**



13 **14**

15

A. Asymmetric Cross-Coupling Chemistry

Chiral secondary Grignard reagents are always racemic, even when prepared from optically active halides, because reaction proceeds via trapping of radicals at the magnesium surface.[45] Racemization or epimerization of secondary carbon–magnesium bonds occurs at a

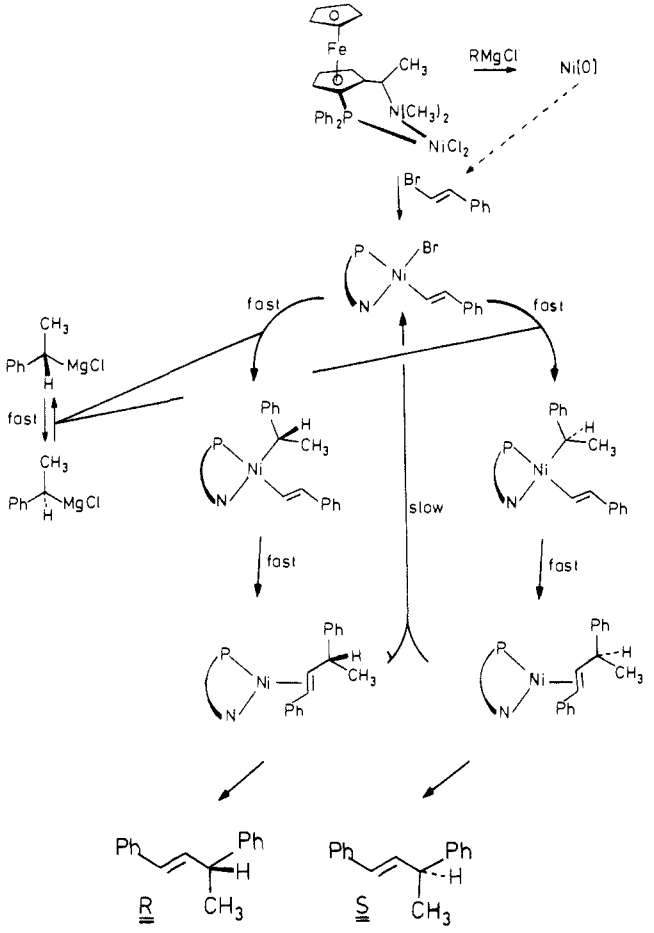
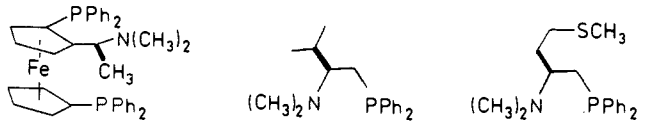


Figure 7. Possible pathway for asymmetric cross-coupling through a racemic secondary Grignard reagent.

moderate rate at ambient temperature.[46] If it is fast on the time scale of catalytic turnover, then one enantiomer of a secondary racemic Grignard reagent may participate in asymmetric cross-coupling preferentially while the other inverts before reaction. The organometallic addition stage defines the overall enantioselectivity provided that the C–C bond-forming elimination step is fast and MR_2 intermediates do not accumulate during the catalytic cycle, as indicated in Figure 7. The electrophile is normally a vinylic halide, and Grignard (or organozinc) reagents derived from silyl- or phenyl-stabilized carbanions are employed as the nucleophilic component, perhaps to ensure rapid racemization under catalytic conditions. The best catalysts are phosphines or bis(phosphines) carrying a potentially chelating tertiary amine or sulfide group (e.g., **16**–**18**).



16 **17** **18**

Remarkably little is yet known about the mechanism of this rather fundamental asymmetric reaction. In the present context it is unlikely that the C–C bond-forming step is a significant source of stereochemical variation, since the configuration at carbon is determined in the previous stage. It is presumed, although unproven, that the elimination occurs with complete retention of configuration.

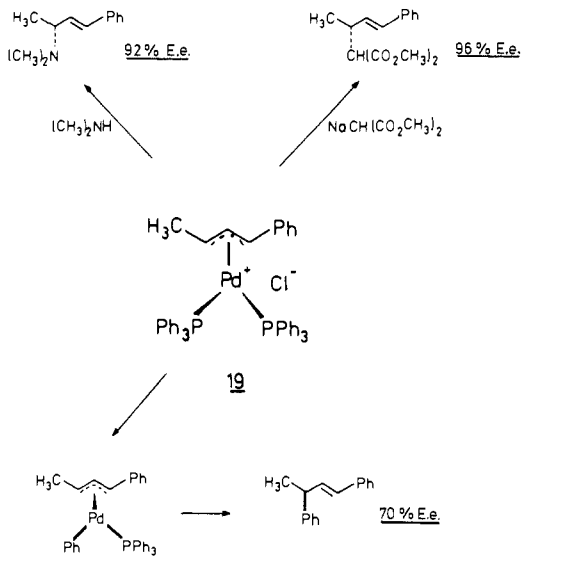
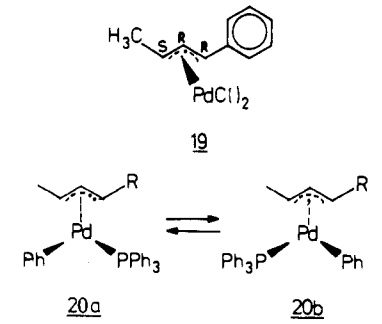


Figure 8. Stereochemical course of nucleophilic addition to a palladium allyl of defined absolute configuration.

Much of the impetus for asymmetric cross-coupling has come from the research group of Hayashi and Kumada in Kyoto, with contributions from Consiglio and Kellogg—pertinent recent references are recorded.[47]

IV. Couplings Involving Allylmetal Complexes

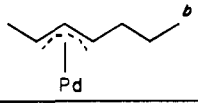
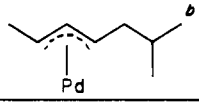
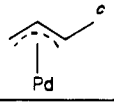
In Trosts' early work on catalytic allylic alkylation it was established that the "soft" nucleophiles employed attacked anti to the allylpalladium bond.[1,48] Negishi and co-workers demonstrated a complete reversal of stereochemistry in catalytic reactions with nucleophiles derived from "hard" carbanions—in this context PhZnCl is hard and $NaCH(CO_2Me)_2$ is soft—by employing a ring-substituted cyclohexenyl acetate.[48] This indicates that the reaction involves attack of the hard nucleophile at palladium, followed by coupling of the new Pd-bound entity with the allyl group. This result was reinforced in an elegant manner, depending on the availability of an optically active allylpalladium chloride dimer of defined absolute configuration (Figure 8).[49] Reaction of the allyl **19**, prepared in situ from the



19 **20a** **20b**

chloro-bridged dimer, with $NaCH(CO_2Me)_2$ or $HNMe_2$ and analysis of the major regioisomer showed essentially complete inversion at C1. With allylmagnesium chloride or phenylmagnesium bromide, the same preference for attack at the –CHMe terminus was observed but now the product is formed with retention of configuration. In these cases there is slight stereochemical leakage, indicating either that some exometallic attack is competitive or that some racemization of the allyl by two sequential η^3,η^1 tautomerisms occurs on the time

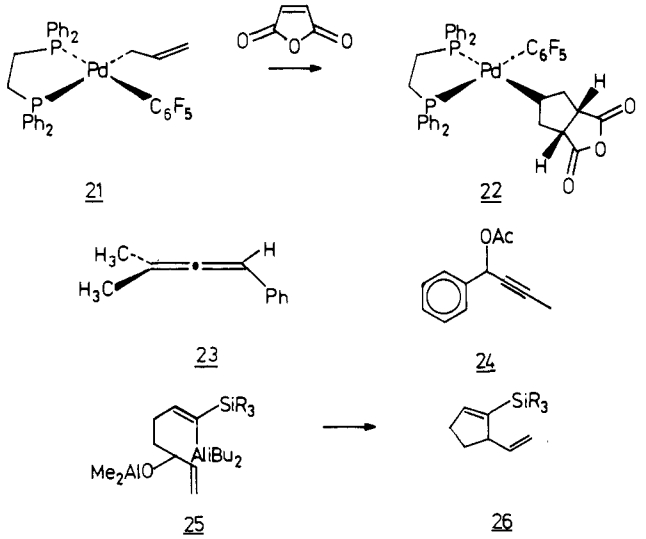
TABLE I. Regioselectivity in Catalytic Allylic Alkylation with Different Nucleophiles[a]

nucleophile	 Pd[b]	 Pd[b]	 Pd[c]
$O(C_2H_4)_2NH$	94:6	99:1	
$NaCH(CO_2Me)_2$	77:23	93:7	
PhZnCl	1:99	1:99	96:4[d] 12:88[e]

[a] Percent substitution at the less substituted terminus is specified first. [b] $Pd(PPh_3)_4$ [c] $(dppf)MCl_2$ [d] M = Pd [e] M = Ni.

scale of coupling. The catalytic reaction of PhZnCl with cyclohex-2-enyl acetate[50] must occur via a symmetrical η^3-allyl on the basis of chirality and isotopic labeling tests. Using $NiCl_2$, but not $PdCl_2$ complexes of (*S*,*S*)-CHIRAPHOS, it is possible to catalyze reactions of arylmagnesium compounds with but-2-enyl or pent-3-enyl acetate in up to 89% ee.[51] In the former case the reaction is not very regioselective, but optical yields are high. Since pent-3-en-2-yl acetate is chiral and was used as a racemate, the lower ee may be a consequence of kinetic resolution, with the slow-reacting enantiomer leading to lowered efficiency.[52]

Regiochemical control in these catalyzed allylpalladium reactions is of considerable synthetic interest and has been investigated systematically by Keinan and Sahai.[53] They find that the reaction regiochemistry depends on the nature of the nucleophile, with selected data recorded in Table I. Soft reagents attack at the less hindered end (via the exometallic route) and considerable selectivity is observed even in discrimination between Me and *n*-Pr. But phenyl transfer from PhZnCl (via the endometallic route) shows the opposite selectivity to an extremely high degree. In the latter case, the key intermediate is a monophosphine complex **20**, which may exist as two regioisomers **20a** and **20b**. It is not clear whether these interconvert rapidly prior to C–C coupling or whether the selectivity is set during nucleophilic addition of PhZnCl. A chelate bis(phosphine) analogue of **20**, albeit with a highly electron-withdrawing aryl group, exists entirely in the η^1-allyl form **21** and exhibits no tendency to undergo C–C



coupling and elimination.[54] With maleic anhydride (vide infra) reaction occurs to give the stable cycloadduct **22**. Nickel and palladium complexes exhibit contrasting regioselectivity in catalytic allylic alkylation with $PhMgBr$[55] (cf. Table I); with nickel, the phenyl group migrates preferentially to the more substituted carbon.

With hard nucleophiles, propargylic acetates are as responsive as allylic acetates toward palladium-catalyzed alkylation.[56] The product is invariably an allene derived by a formal S_N2' pathway, and (η^1-allenyl)palladium complexes have been proposed as intermediates; **23** would then be formed in the reaction between PhZnCl and $HC{\equiv}C{-}CXMe_2$ catalyzed by $Pd(PPh_3)_4$.[57] Acetate **24** reacts by an allylpalladium route with $NaCH(CO_2Me)_2$ but exclusively by an allenylpalladium pathway with an RZnCl species and also with Et_3Al.[56] The $Pd(PPh_3)_4$-catalyzed cyclization of vinylalanes **25**, produced by *i*-Bu_2AlH addition to the corresponding silylacetylene, is promoted by $ZnCl_2$ and leads exclusively to the corresponding cyclopentane **26**.[58]

Under conditions where the (η^3-allyl)palladium intermediate is prepared stoichiometrically, it may prove to be moderately stable. Kurosawa and co-workers[59] first observed that decomposition of the phenylpalladium complex **27a** (Figure 9) gives products other than 3-phenylbutene in $CDCl_3$ at −20 °C. In the presence of an excess of methallyl chloride, allylic exchange occurs, and rapid elimination to give the C–C coupled product occurs at −50 °C. This reaction is inhibited by addition of 1 mol % of PPh_3. Their initial interpretation was that palladium(IV) intermediates formed by oxidative addition to **27a** were responsible for both allyl exchange and elimination. This proved to be incorrect. Schwartz and co-workers had shown that electrophilic olefins promoted elimination of a 1,4-diene from allylpalladium alkenyl complexes[60] and subsequently made an extensive study of allylic coupling at palladium. They found that the elimination of a 1,5-diene from the bis(η^3-allyl)palladium precursor is strongly assisted by maleic anhydride via coordination; coupling was also induced by Ir^{IV} or Cu^{II} oxidation but without regioselectivity.[61]

A reinvestigation by Kurosawa and co-workers provides the mechanism outlined in Figure 9, quantitative work being carried out on the $AsPh_3$ adduct. The rate equation was derived by applying the steady-state approximation to intermediate **28**. The reaction rate was strongly dependent on the nature of the addend, with fastest elimination observed for the most electrophilic olefins.[62] In the absence of added olefin, the rate constant for alkene coupling and elimination is independent of added phosphine over a wide concentration range. Reactivity is not very dependent on the nature of the ligand with $P(OPh)_3$ and $AsPh_3$, the fastest and slowest respectively 20-fold different.[63] In the full paper arising from this work, attention was also directed to the nature of the aryl group, with the order of C–C coupling rates being Ph > 2,5-dichlorophenyl >

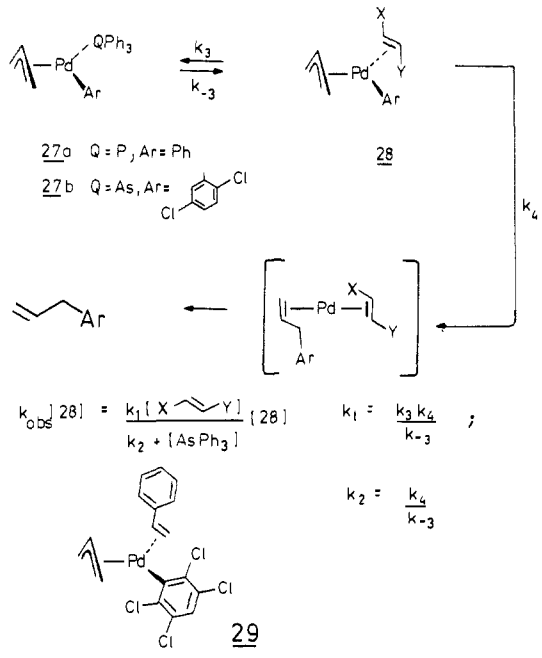
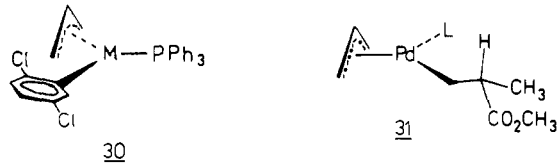


Figure 9. Mechanism for assisted elimination from (η^3-allyl)-arylpalladium complexes.

2,3,5,6-tetrachlorophenyl. This led to the successful identification of electrophilic olefin complexes of type **29** at −40 °C so that C–C coupling could be directly observed in situ at low temperatures.[64] An orbital energy diagram for the C–C bond-forming step in (η^3-C_3H_5)Pd(PH_3)CH_3 was constructed by the extended-Hückel method and compared with that for (η^3-C_3H_5)Pd(C_2H_4)CH_3.[64a] The value of these calculations is qualified by direct experimental comparison.[64b] When the complex (η^3-C_3H_5)Pd(PPh_3)CH_3 was thermolyzed in solution or in the solid state, only 3% of but-1-ene forms and ethane is the major product. It arises from PPh_3 dissociation, leading to formation of the dimer [(η^3-C_3H_5)PdCH_3]$_2$, which is methyl-bridged and loses ethane readily. When excess PPh_3 is added, but-1-ene becomes the major thermolysis product, and with added maleic anhydride it predominates.

Kurosawa and co-workers have compared the thermolysis of Ni and Pd aryl allyl complexes. For the PPh_3 species **30**, the Ni complex undergoes elimination over

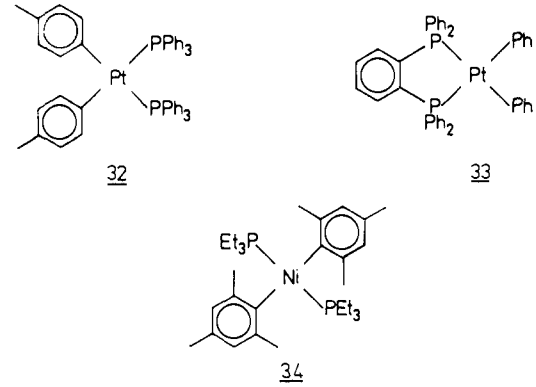


20 times more rapidly at 0 °C. Addition of chelating biphosphines to **30**–Pd gave 16e-chelate complexes with an η^1-allyl group, of *greater* thermal stability. In the case of **30**–Ni, displacement of PPh_3 by chelating phosphines gave an 18-electron η^3-allyl complex which was reactive to elimination even below −20 °C.[65] This marked difference between Ni and Pd chemistry affords an explanation for Hiyama's asymmetric allyl coupling, which is only effective with diphosphine Ni complexes.[51] In considering possible reaction pathways for catalytic alkyl–allyl cross-coupling (and other TM-catalyzed reactions) rational generation of possible reaction intermediates provides a useful approach—this and the interlinking schemes may be provided in the systematic computer program TAMREAC.[66]

Ligand-induced C–C bond formation between η^1- and η^3-allyls forms the basis of the very extensive nickel-catalyzed chemistry of dienes largely developed at the Max Planck Institute, Mulheim. The C_8 η^1,η^3 intermediate formed by dimerization of butadiene on a transition-metal template may be intercepted by reaction with olefins (e.g., (trimethylsilyl)ethylene),[67] affording the opportunity for analysis of ligand control. Oxidative dimerization of methyl methacrylate ($PdCl_2(PhCN)_2$; excess $AgBF_4$; benzophenone) gives mainly the linear product that would arise via intermediacy of **31**, and deuterium labeling of the substrate is consistent with this analysis.[68]

V. Couplings Involving Vinyl and Aryl Groups

The C–C coupling of two aryl groups in *cis*-diarylbis(phosphine)platinum complexes is well established. In contrast with the inertness of alkylplatinum complexes discussed earlier, **32** cleanly eliminates 4,4′-di-



methylbiphenyl with a half-life of 4 h at 80 °C. There is a *slight* rate acceleration observed in the presence of a substantial excess of PPh_3. The corresponding dppe complex is quite stable over 12 days at 60 °C in the presence or absence of excess phosphine.[69] At higher temperatures, following the reaction of **32** by differential thermal analysis, further biaryls are formed following the "primary process", but derived from PPh_3. Chelate complexes such as **33** undergo efficient photoelimination of biaryl on irradiation at 313 nm. The mechanism is not known but could involve initial electron transfer from Pt to solvent since the bis(phosphine)$PtCl_2$ complex can be isolated at the end of the reaction, implying an oxidation process.[70] In the electrochemically induced decomposition of *trans*-diaryl Ni complexes **34** on oxidation at a platinum anode, 100% of the aryl-coupled product is obtained. Oxidation with Br_2 also promotes biaryl formation, but in lower yield.[71] In a similar vein, mixed biaryls may be synthesized from two distinct aryl halides by electrooxidation in the presence of (bpy)-$NiBr_2$.[72] The method is not very efficient but is suggested to occur by a bimolecular mechanism that invokes the comproportionation of ArNiX and Ar′NiX′. Homocoupling of aryl chlorides may be effected with a Ni(0) phosphine complex formed in situ in Me_2NCOMe; electron-withdrawing groups in the aryl ring promote reactions.[73]

With thermal, electrochemical, and photochemical pathways for biaryl formation apparently accessible in different circumstances, it was of interest to examine the mechanism of thermolysis of a palladium biaryl relevant to cross-coupling. Yamamoto and co-workers have synthesized both the *trans*-diaryl complex **35** and

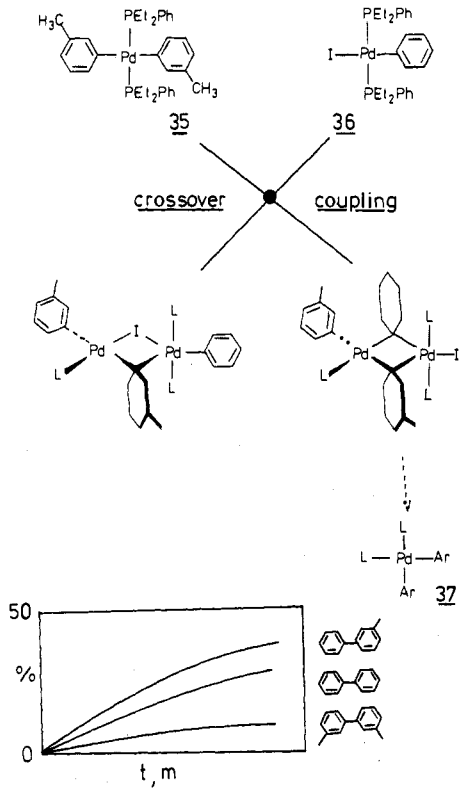
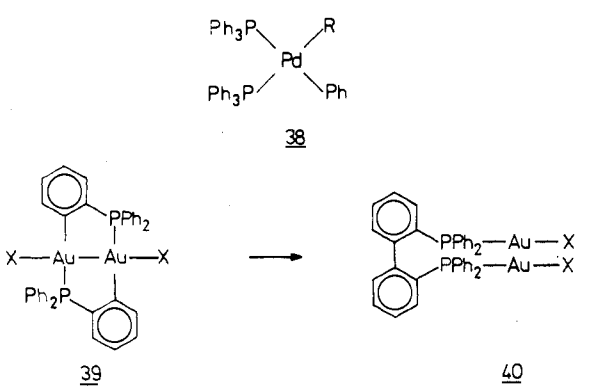


Figure 10. Crossover pathways in biaryl formation from arylpalladium phosphine complexes.

the *trans*-iodoaryl Pd complex **36** (Figure 10). There are hidden complexities to biaryl formation.[74] In the presence of *m*-tolyl iodide, which traps Pd after elimination, the initial rate is unaffected but acceleration occurs as reaction proceeds. The initial rate may be enhanced by having the trapping product **36** present at the outset. Starting with a mixture of **35** and **36** with different aryl groups (Ph vs *m*-tolyl), complete crossover was observed in the biaryl product, and mixed species were apparent in the ^{31}P NMR spectrum of the sample. These results were explained according to the mechanism of Figure 10. A Pd dimer with bridging aryl and iodo groups accounts for crossover. In the same vein, cis–trans isomerization of complex **35** can be promoted, giving **37**, which leads on to biaryl formation. Reaction of complex **35** (Ar = *m*-tolyl) with MeI yielded *m*-xylene rather than the biaryl, and mechanisms similar to those outlined in Figure 10 can be used to explain this result.[75] Carrying out the reaction with CD_3I leads to the predicted degree of deuterium incorporation in *m*-xylene as reaction proceeds. Further, the reaction of isolated cis complex **38** (R = Me), which is itself thermally



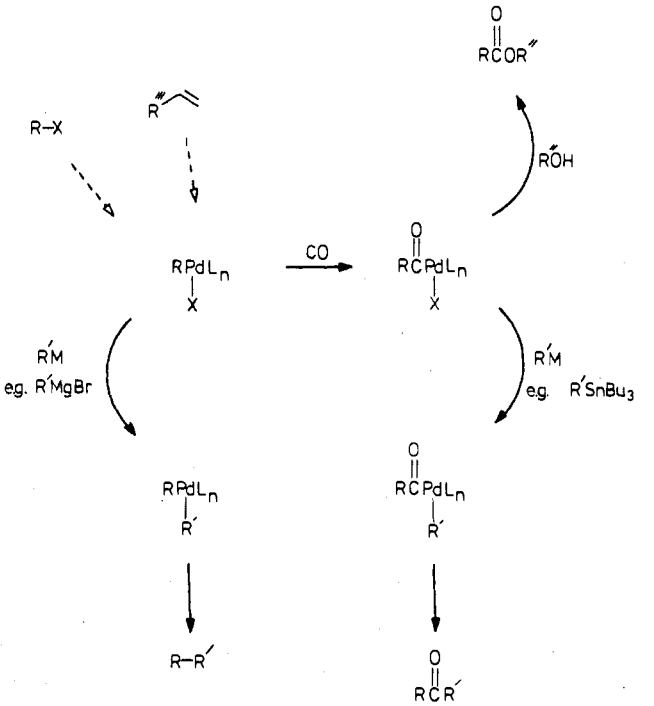


Figure 11. Palladium acyl chemistry: generation and trapping.

unstable toward C–C coupling at ambient temperature, with CD_3I gave only PhMe, undeuteriated. None of these reactions demand the intervention of Pd(IV) intermediates, and Yamamoto's alternative is quite consistent with all the experimental observations.

We complete this section by noting the continuing importance of linking unsaturated centers through cross-coupling reactions,[76] including the formation of five-membered rings[77] and arenes. The stepwise condensation of acetylenes on a cobalt template with final elimination of an arene has been well reviewed.[78] Aryl–aryl coupling at gold leads to the rearrangement of **39** → **40**.[79] Finally, the formal reverse of biaryl elimination occurs on treating biphenylene with Ni(PEt$_3$)$_4$, giving **41**. This is itself unstable with respect to a novel thermal dimer and may be intercepted by CO or PhC≡CPh, giving formal cycloaddition products.[80]

VI. Coupling Reactions Involving One Acyl Group

In catalytic cross-coupling reactions at palladium, addition of the electrophilic component is normally rate determining, with rapid displacement of halide ion from the RPdX intermediate, especially when the nucleophilic partner is a Grignard or organozinc reagent. Under a CO atmosphere, coordination and cis-ligand migration might be expected to lead to the corresponding acyl RCOPdX, familiar in many carbalkoxylation reactions at palladium in protic solvents, where an acid or ester is the ultimate product.[81] If attack of the organometallic nucleophile is sufficiently slow, then the formal CO insertion competes successfully with X substitution by R^1M, so that $RCOPdR^1$ is formed preferentially (Figure 11). This has been demonstrated with organoboron[82] and more particularly organotin[83] nucleophiles.

Many new syntheses of carbonyl compounds with unsaturated side chains have come from Stille's group exploiting the relatively weak nucleophilicity of tin

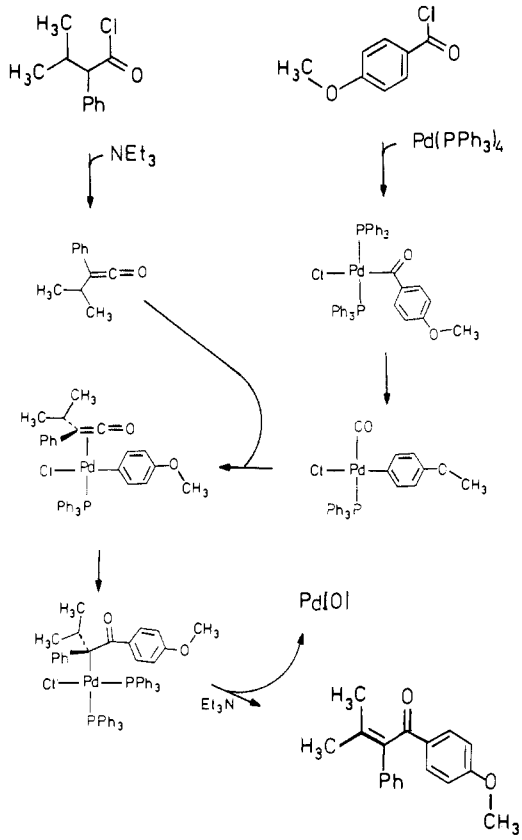


Figure 12. Aromatic ketone formation via cross-reaction of aliphatic and aromatic acyl chlorides at palladium.

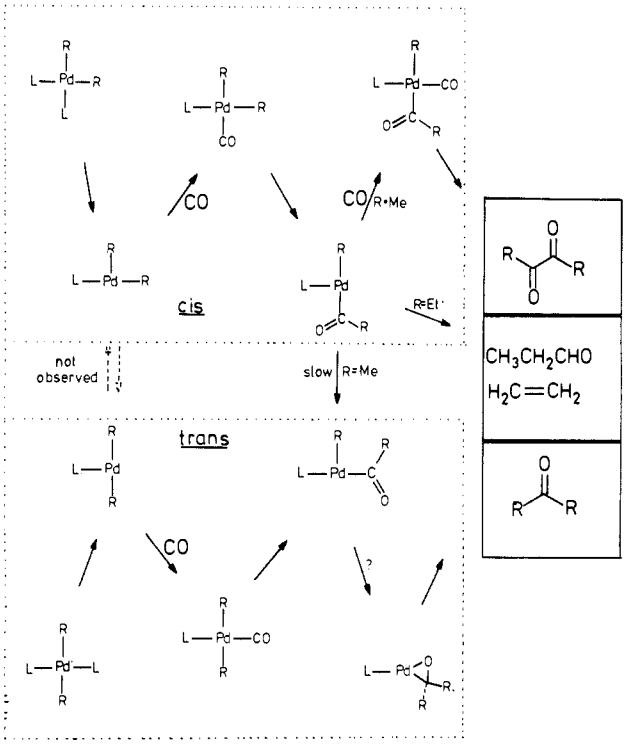
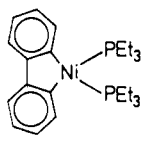


Figure 13. Different reaction pathways for *cis*- and *trans*-L_2PdMe_2 and L_2PdEt_2 with carbon monoxide.

alkyl, allyl, aryl, alkynyl, and vinyl compounds.[84a] Alternatively, the palladium acyl may be prepared directly from an acid chloride.[84b] In either case, the ketonic product is most probably formed by C–C coupling between coordinated RCO and R^1 groups rather than by direct attack of the nucleophile at the metal–acyl group. Because successful ketone synthesis requires that R migration to CO is faster than nucleophilic attack of R^1M, it is often necessary to perform reactions under positive CO pressure, say 3–20 atm. The palladium acyl may be intercepted by malonate and cyanoacetate anions to give α,α'-disubstituted β-keto esters.[85] Soft nucleophiles of this type are generally not very effective in cross-coupling, and it is not completely clear whether direct nucleophilic attack at the acyl group can prevail over the RCOPdR′ route in this case. A novel catalytic entry into this reactive intermediate involves the cross-reaction of α,α-disubstituted acid chlorides with aromatic acid chlorides, employing $Pd(PPh_3)_4$.[86] Intermediacy of a ketene and selective decarbonylation of the aromatic carbonyl group as delineated in Figure 12 represent the key reaction stages.

The increasing importance of catalytic C–C bond-forming reactions between acyl and alkyl moieties makes an understanding of the fundamental coupling step important. In this area the classic experiments were carried out by Yamamoto and co-workers and are worth describing briefly.[87] For the trans complexes of Figure 13, replacement of one phosphine by CO is followed by cis migration of an alkyl group. The resulting three-coordinate intermediate loses the ketone directly; it may be that the carbonyl oxygen remains transiently bound to palladium, as drawn. The *cis*-dimethyl Pd complex likewise undergoes replacement of one phosphine by CO and stereospecific methyl migration to give a semirigid three-coordinate intermediate. This either isomerizes and then eliminates acetone or alternatively intercepts a further CO molecule, giving rise to 2,3-butanedione via cis elimination of two acetyl groups (but see radical routes to biacetyl from **44** under CO). An ab initio MO study on alkyl migration to Pd-CO shows that the main atomic movement is translation of the alkyl-group[88] giving support to the stereochemistry assumed by Yamamoto and co-workers.

There are several examples of dialkylmetal carbonyl complexes that fragment with formation of the corresponding ketone. For the (pentamethylcyclopentadienyl)rhodium complex **42**, treatment with CO



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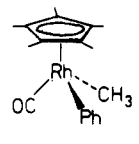

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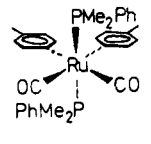

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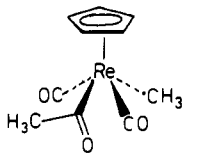


44

in CH_3CN at 20 °C produced acetophenone and the rhodium dicarbonyl quantitatively.[89] Similarly, the ruthenium complex **43** decomposes in $CDCl_3$ by an intramolecular mechanism to form the diaryl ketone.[90] The rhenium acyl **44** thermolyzes at 100 °C to give acetone, but on photolysis under 20 atm of CO biacetyl is formed. In this case it is due to homolytic cleavage

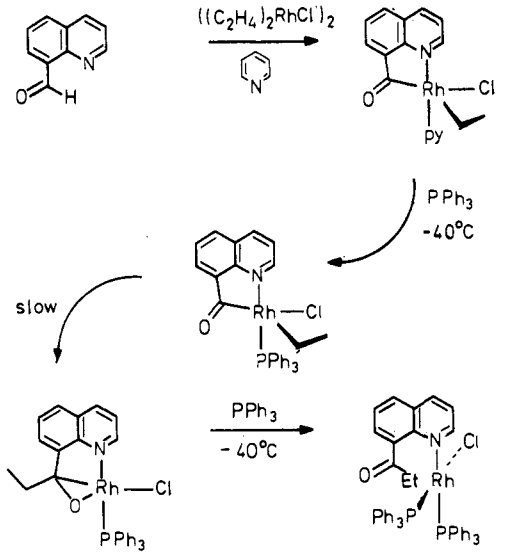
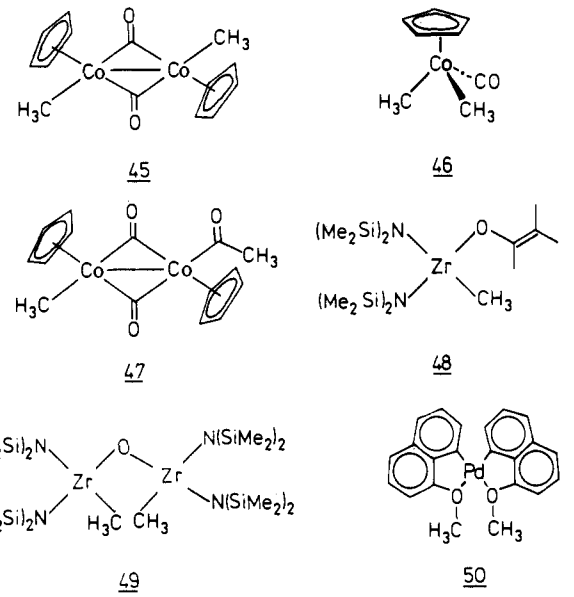


Figure 14. C–C bond formation and cleavage in rhodium-promoted chemistry of 8-substituted quinolines.

giving acetyl radicals that can be scavenged by $BrCCl_3$.[91] The dinuclear cobalt alkyl **45** also decomposes to form



acetone around ambient temperature, and mechanistic studies reveal two pathways, one dominant under CO. In thf solution, the appearance of a new band at 2001 cm^{-1} is associated with formation of **46**, which is the immediate precursor of acetone. Under CO in the same solvent, both *E* and *Z* isomers of the dinuclear complex **47** are formed. They decompose rapidly to give acetone without conversion into **46**, and therefore by a distinct pathway.[92] This raises an interesting mechanistic question. Assuming that the elimination process takes place at a single metal center, either acetyl or methyl must migrate between cobalt atoms while maintaining the integrity of the binuclear species.

Oxophilic complexes of the early transition metals can exhibit more extreme behavior. Treatment of $[(Me_3Si)_2N]_2ZrMe_2$ with CO leads to oxido complexes **48** and **49**. The former presumably arises by deoxygenation of coordinated acetone and then template-driven condensation with an acyl fragment.[93] Palladium metallocycle **50** is highly reactive toward various ad-

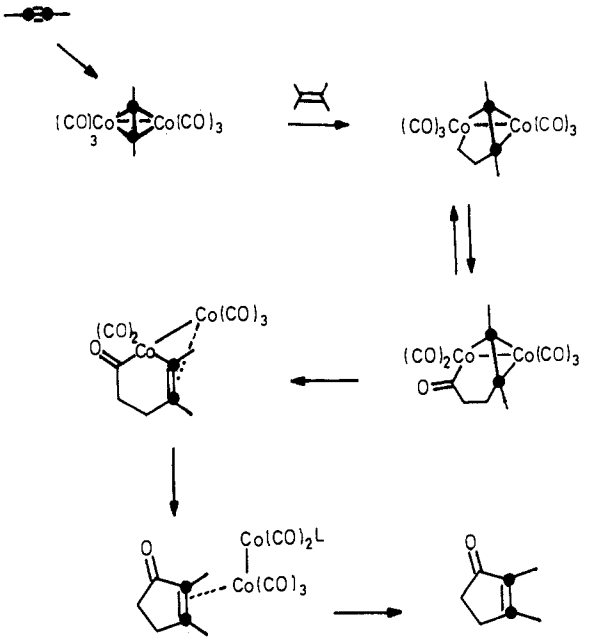


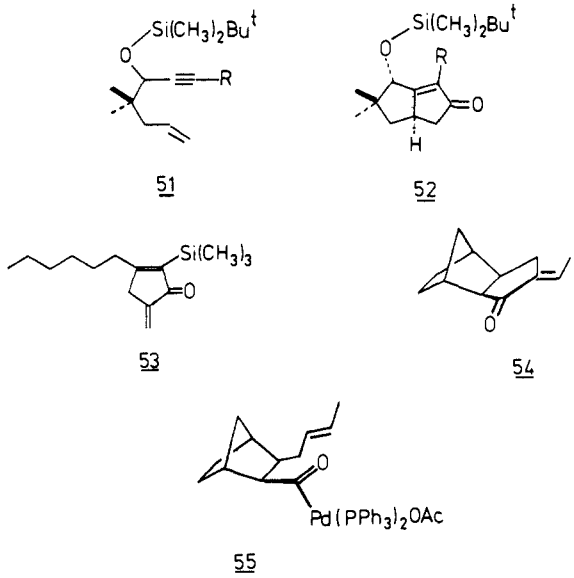
Figure 15. Possible mechanism for the Pauson–Khand enone cyclization.

dends but forms the symmetrical aromatic ketone on treatment with CO.[94] In one case favored by chelation, the alkyl migration reaction from rhodium to acyl is reversible, depending on other ligands present. These studies of Suggs and co-workers[95] have identified an η^2-acyl group formed as the immediate product of alkyl migration. This is readily displaced by PPh_3 at –40 °C (Figure 14). The structure of the corresponding benzylacyl complex has been confirmed by X-ray analysis. Acylation of α,β-unsaturated ketones may be achieved via their $Fe(CO)_3$ complexes. Reaction proceeds through nucleophilic attack of RLi or RMgBr at Fe–CO and C–C coupling between acyl fragment RCO and the β-carbon of the double bond.[96]

Intramolecular elimination of acyl and alkyl residues linked to a common backbone affords a method for the synthesis of cyclic ketones. This forms a basis for the $Co_2(CO)_8$-catalyzed cyclization procedure of Pauson and Khand[97] involving an acetylene and olefin under CO, which has found favor in recent synthetic work, particularly as intramolecular variants. For example, Magnus and co-workers have carried out a total synthesis of *dl*-coriolin. Treatment of **51** with $Co_2(CO)_8$ at 110 °C gave the cyclopentenone **52**. When R = $SiMe_3$, the reaction was 96% stereoselective but this dropped to 75% when R = Me. A possible mechanism for the Pauson procedure is outlined in Figure 15.

The general principle of enyne cyclization under CO to yield cyclopentenones has also been realized in zirconium chemistry,[98a] through carbometalation procedures—compound **53** is a typical product. Nickel-catalyzed enyne cyclizations with isonitriles provide a further variant.[98b] The range of this reaction type is also demonstrated by palladium catalysis;[99] treatment of norbornene with but-2-enyl bromide and $MeCO_2K/Pd(PPh_3)_4$ in catalytic amount leads to compound **54**, the product of intramolecular acylmetalation of **55**.

An alternative approach to five-membered rings involves interception of the intermediate in catalyzed decarbonylation of γ,δ-unsaturated aldehydes.[100]



Treatment of the α,α-disubstituted species in Figure 16 with ((*S,S*)-CHIRAPHOS)$_2$Rh$^+$Cl$^-$ in catalytic quantity at 150 °C leads to the cyclopentanone, and rhodacyclohexanone **56** is presumed to be the immediate precursor. The product is optically active, 70% *S* at low conversion; at long reaction times the recovered starting material is of high optical purity by kinetic resolution. These ring syntheses are interesting because metallacycles tend to be fairly inert, and it appears that the presence of an acyl group adjacent to the metal enhances the tendency for C–C coupling in a number of cases. There is a need for systematic studies on appropriate model complexes such as bis(phosphine)(η^1-acylpalladio)cyclohexanes.

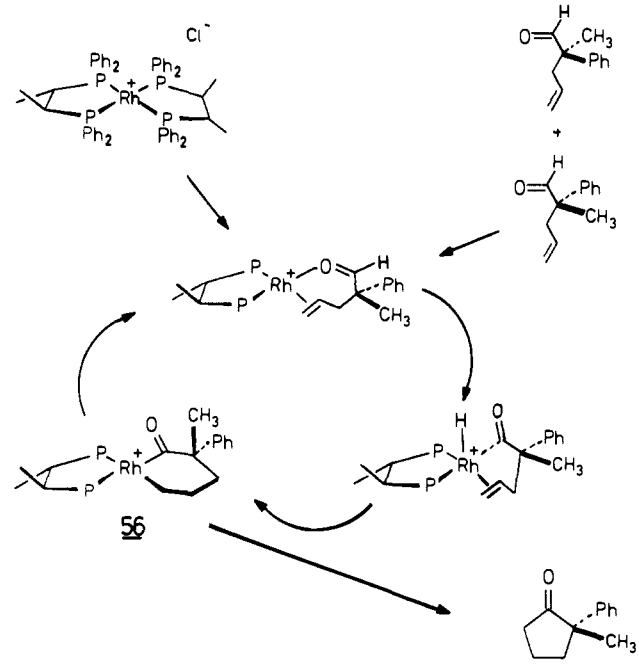


Figure 16. Formation of optically active cyclopentanones from γ,δ-unsaturated aldehydes under rhodium catalysis.

A. Alkyl Migration to Coordinated Nitrile

Hydrocyanation of olefins, acetylenes, and dienes is a useful synthetic reaction, for which Ni(0) complexes have proved to be most effective. Overall cis addition of DCN to cyclohexa-1,3-diene was proved by defining the relative stereochemistry of D and CN in the products.[101] For asymmetric hydrocyanation of olefins catalyzed by (DIOP)$_2$Pt, two intermediates in the process were tentatively identified as the HPtCN adduct and the HPt(alkyl) adduct from norbornene.[102] Recent studies have also been concerned with the regiochemistry of Ni- or Pd-catalyzed addition of HCN to olefins and acetylenes.[103]

The most important mechanistic contributions have come from the DuPont group.[104] Most recently, the hydrocyanation of C_2H_4 catalyzed by [P(*o*-tolyl)$_3$]$_2$Ni(C_2H_4) has been studied in detail. The rate equation is accurately given by

$$dP/dt = k_{obsd}[\mathbf{57}][L]$$

$$L = [P(o\text{-tolyl})_3]_2$$

On the basis of kinetic work and also direct examination of the catalytic system by ^{31}P and ^{13}C NMR, which permits the observation (but not full stereochemical identification) of the three stereoisomers of complex **57**, the C–C coupling step is thought to occur via the five-coordinate 18e intermediate **58** present at low concentration. This provides common ground with other elimination reactions at Ni which apparently require 18e, five-coordinate intermediates as discussed earlier.[105] The mechanism of alkyl cyanide elimination may be distinct from alkane elimination and resemble more a cis migration, followed by dissociation. The detailed pathway is delineated in Figure 17.

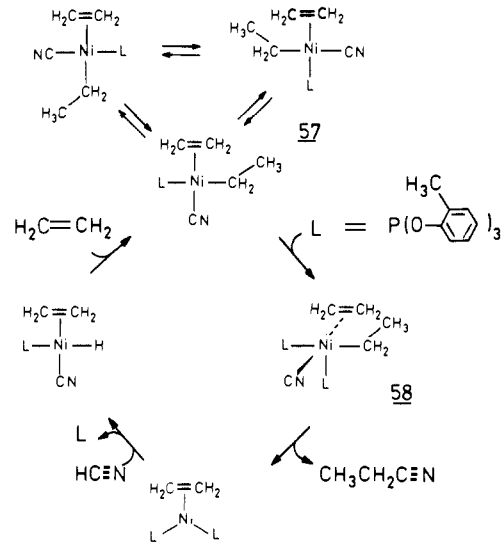


Figure 17. A mechanism for the Ni-catalyzed addition of HCN to ethylene, involving 5-coordinate intermediates.

VII. Acyl–Acyl Coupling and Related Reactions

Scattered reports exist of the coupling of adjacent C≡O groups, or ligands related to C≡O, although systematic mechanistic information is lacking.[106] Hoffmann and co-workers have carried out extended-Hückel calculations on the process,[107] using W(CO)$_2$H$_5^-$ as a model complex.

There has been a substantial effort to understand catalytic double carbonylation, the reaction whereby an aryl halide is converted into an α-keto ester on a α-keto amide. The basic reaction was codiscovered in 1982 by the research groups of Tanaka[108] and Yamamoto,[109]

TABLE II. Contrasting Behavior of Ketoacyl and Diketoacyl Palladium Complexes toward CO/$HNEt_2$ in CH_2Cl_2

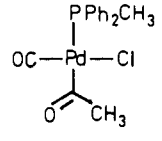
reactant	product	
	$MeCOCONEt_2$	$MeCONEt_2$
$MeCOCOPd(PMePh)_2Cl$[a]	3	89
$MeCOPd(PMePh_2)_2Cl$[b]	56	0

[a] 0–1 atm of CO. [b] 10 atm of CO.

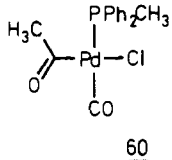
although examples of double carbonylations had appeared previously.[110] The scope of this reaction is fairly broad, for aqueous conditions give rise to α-keto acids,[111] and β-amino alcohols may be converted into cyclic morpholine-2,3-diones under palladium catalysis.[112]

Yamamoto and co-workers have carried out an extensive series of experiments to probe the mechanism of double carbonylation.[113] In particular they were concerned to discover whether the product arose from decomposition of $ArCOCOPdNR_2$ or from $ArCOPdCONR_2$ and were able to answer the question unequivolcally. Under 10 atm of CO, preformed methyl- and arylpalladium complexes *trans*-$RPdXL_2$ gave high yields of the respective α-keto amide in the presence of excess secondary amine, together with some amide $RCONR^1_2$. The reaction works best when L = PMe_2Ph. Benzoylpalladium complexes also give α-keto amides with high selectivity in CH_2Cl_2 under similar conditions. Evidence against the intermediacy of α-ketoacyl palladium complexes was obtained when the authentic complexes were prepared by displacement of styrene with the appropriate ketoacyl chloride. The results of carbonylation experiments are fairly remarkable, for the ketoacyl palladium chloride gives only amide under conditions similar to those where the acyl palladium chloride gives only α-keto amide (Table II).

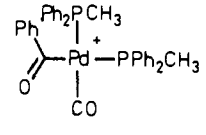
These observations were explained in terms of ready decarbonylation of the diketoacyl complex via intermediate **59**, following phosphine loss. This intermediate



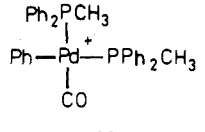
59



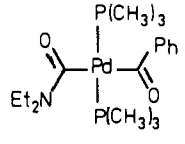
60



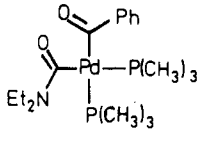
61



62



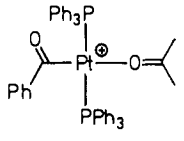
63



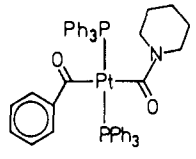
64

is the stereoisomer of **60**, derived from the acylpalladium complex, which is more reactive toward nucleophilic attack by secondary amine. The species proposed here are neutral PdCl complexes, but Yamamoto and co-workers later prefer to consider *cationic* Pd intermediates for catalytic double carbonylation and also for the competing monocarbonylation. The critical factor in competition between these two pathways is whether **61** or **62** is the electrophile toward the secondary amine. ^{13}CO labeling establishes that the first carbonylation is irreversible, since $PhCOPdIL_2$ gave only $PhCOCONEt_2$ with CO and Et_2NH. The cationic nature of late intermediates in catalytic double carbonylation is supported by the observation of **61** (ν = 2137 cm^{-1}) in CH_2Cl_2 containing 10% MeOH under 20 atm of CO, starting with the corresponding benzoylpalladium iodide complex. It was then discovered that the *trans*-diacyl complex **63** is stable in solution, but eliminates α-keto amide when treated with $Me_2NH_2BF_4$. This reaction looks like acid-catalyzed $HNEt_2$ loss, cis–trans isomerization, nucleophilic attack by $HNEt_2$ giving **64**, and then the C–C coupling step. On this basis, only *cis*-diacylpalladium complexes can participate in the elimination step.

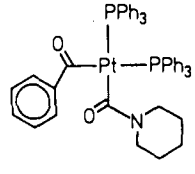
For the corresponding platinum case, where much information on stable ketoacyls has been obtained,[114,115] further stereochemical insights may be derived. Treatment of the cationic acetone complex **65** with CO



65



66



67

and then piperidine gives **66** but the *reverse* order gives the cis isomer **67**—formed by cis-ligand migration of piperidyl to PtCO rather than direct nucleophilic attack. The reversibility of these reactions affords a path for rapid cis–trans interconversion under catalytic conditions.

α-Keto esters may be formed in a related reaction, when the secondary amine is replaced by a tertiary amine in alcoholic media.[116] The selectivity of double over single carbonylation is less clear-cut; it is enhanced by bulky phosphines in relation to the cone angle of the ligand, and secondary alcohols are preferred. Overall, the same mechanism is likely, with C–C coupling of RCO and CO_2R groups at mutually cis positions on palladium.

VIII. Overview

Figure 18 delineates the various mechanisms which have been postulated for C–C bond-forming elimination reactions from nickel triad complexes. The most commonly observed is the simplest in a formal sense involving direct formation of RR^1 from *cis*-RR^1ML_2 without ligand dissociation or association. When at least one of these partners is unsaturated, i.e., vinyl, aryl, allyl, benzyl, or acyl, the elimination reaction can take place in two stages, so that the initially formed coupling product remains weakly bonded to the metal. It may then dissociate or alternatively remain in place

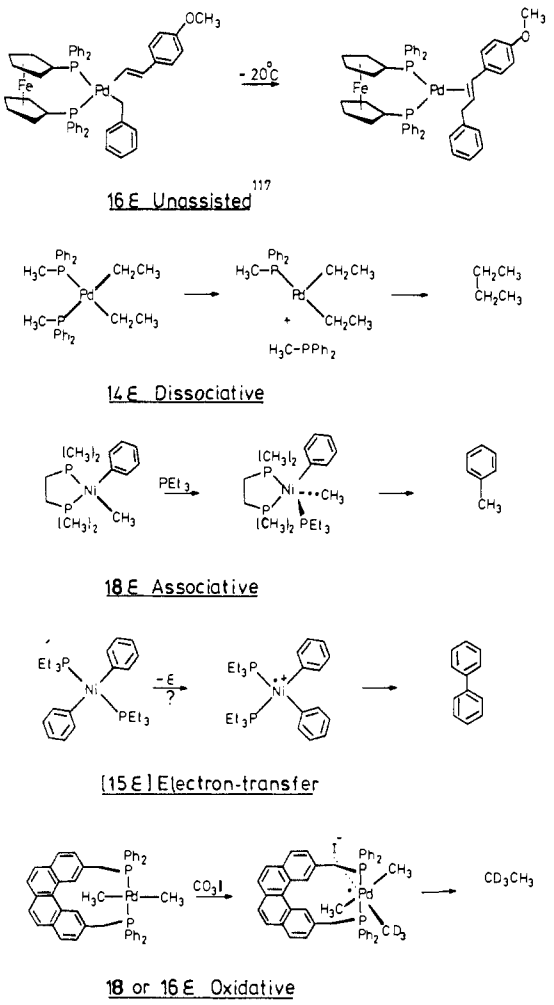


Figure 18. Summary of pathways for C–C bond-forming elimination reactions.

until displaced in a subsequent step. This means that the C–C coupling is an unsymmetrical process with the breaking of one R–M bond much ahead of the second. In an extreme case the transition-state region will resemble a cis-ligand migration of R to the unsaturated carbon center, particularly when this is M–COR or M–allyl.

This direct elimination is likely to be the commonest in reactions of catalytic importance, particularly cross-coupling, where most examples require at least one unsaturated R group. It raises the question of why it is not universally observed. The cis elimination of two adjacent saturated alkyl groups tends to be more difficult and is rarely observed in Pd or Pt chemistry. The reaction energy surface is less favorable here because M–C bond energy is completely lost. Two alternative pathways can then supersede simple elimination. For palladium complexes, ligand dissociation from *cis*-R_2ML_2 gives a 14e *cis*-R_2ML complex, from which alkane elimination is a highly favorable process. This is the pathway adopted by saturated palladium alkyls and also by mixed acyls $RPd(COR^1)L$ formed under CO. Whether this is the only route to ketones or whether it is a consequence of the availability of the 14e intermediate sui generis remains to be seen. The second alternative is more frequently adapted by Ni complexes when elimination from the 16e state is unfavorable. This involves ligand association and alkane elimination from the five-coordinate conformation corresponding to compound **8a**. Its adaption in nickel-catalyzed hydrocyanation of olefins, where the square-planar species are inert to elimination, makes it especially interesting.

Other pathways are rarer and tend to have been less systematically investigated. Oxidation of square-planar complexes by one-electron transfer increases their lability toward C–C elimination. Examples of this reaction mode are commonest in nickel chemistry, possibly due to the greater accessibility of the Ni(III) oxidation state. Furthermore, oxidative addition to square-planar 16e complexes, most commonly of alkyl or acyl halides, increases their lability toward C–C coupling and elimination. This process increases the formal oxidation state of the metal from II to IV; formation of platinum(IV) species in this way provides the only mild route for alkane elimination from platinum. In catalytic cross-coupling, the possibility exists for formation of palladium(IV) (or nickel(IV)) intermediates prior to the final fragmentation step. They have been postulated from time to time as an important mechanistic component of the reaction. This looks to be unlikely in cases where the *cis*-dialkylmetal complex is readily accessible and at least one of the components is an aryl, vinyl, or allyl group.

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