

NEW ASPECTS OF ORGANIC SYNTHESSES CATALYZED BY GROUP VIII METAL COMPLEXES

G. P. Chiusoli

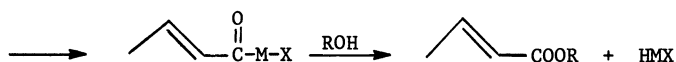
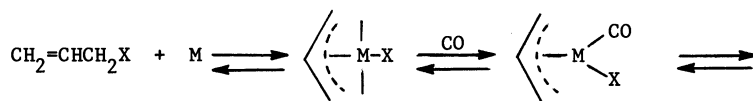
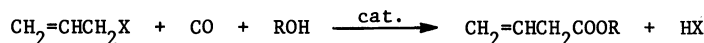
Istituto di Chimica Organica dell'Università, Via D'Azeglio 85, 43100 Parma, Italy

Abstract — Recent developments of C-C bond formation reactions catalyzed by group VIII complexes are reported and the effect of changing metal (from nickel to palladium, rhodium, and cobalt) is discussed. The reactions are carbomethoxylation of unsaturated substrates, carboxylation of dienes, allylation of double bonds, and arylation of activated olefins. Predictions based on metal and ligand properties are useful only as a broad guide, but generally fail to anticipate which of many competitive processes will occur on passing from a metal to another one, particularly in the case of difficult elimination of the metal from the organic substrate. Experimental work has put in evidence the role played by many factors in directing organometallic processes with Ni, Pd, Rh, and Co complexes towards the formation of organic structures.

INTRODUCTION

Each step of an organometallic process is influenced in different ways by the metal itself and by its environment. Although in principle it is possible to predict single effects, their combination in a single step and the combination of different steps in a sequential process generally cause unpredictable consequences. It seems useful to report here some experimental observations which show the effect of transferring certain reactions from a metal to another one and how to manage to push a reaction towards the desired objective. I have restricted the field to the four group VIII metals that so far have exhibited the highest catalytic activity in organic synthesis in general: nickel, palladium, rhodium, and cobalt. I have chosen examples from four categories of C-C bond forming reactions: carbonylation, carboxylation, C-alkylation, and C-acylation.

To introduce the subject I'll begin with well-known examples of substitutive carbonylation of allylic halides or esters in alcohols, where the reductive elimination step of the metal-bonded acyl group is generally favourable and the main problem usually lies in the metal complex ability to undergo oxidative addition of the allylic compound and subsequent carbon monoxide insertion.



X = Cl, Br, I, OAc, etc.;

M = Ni⁰, Pd⁰; if anionic complexes (Rh⁻¹, Co⁻¹) are used X reacts with counter-ions; non-reactive ligands are omitted.

TABLE 1. Reactions of allylic compounds with carbon monoxide in alcohols

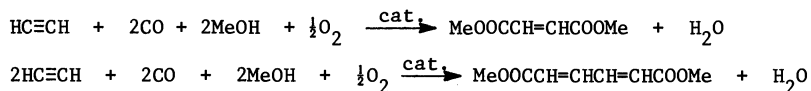
Starting complex	Conditions	References
Ni(CO) ₄	20°, 1-2 atm.	(1)
(π -C ₃ H ₅ PdCl) ₂	90°, 85 atm.	(2)
NaCo(CO) ₄	35°, 1 atm.	(3)
RhCl ₃	125-150°, 140 atm.	(4)

As shown in Table 1, the reaction is quite favourable with nickel, but it requires more drastic conditions with palladium. Tertiary phosphines increase the rate if used in amount not higher than 0.5 mol per mol of palladium complex (2). This could be expected on the ground of the higher ionization potential of palladium in respect to nickel, which renders oxidative addition of allyl compounds more difficult for palladium than for nickel. An excess of phosphines over 0.5 mol, however, causes a negative effect, probably owing to competition with the substrate for coordination sites. Cobalt carbonyl anion undergoes a facile oxidative addition, but the insertion step is not so favourable. A rapid reductive elimination step is required to shift the insertion equilibrium to right and alkoxides have been proved to be useful to this end (3). Rhodium appears to be not effective under mild conditions, probably because of the strength of the Rh-CO bond. Higher temperatures and pressures have to be used. Although there is a lack of thermodynamic data concerning C-metal bonds, some series are available (5) and enable us to roughly predict general trends.

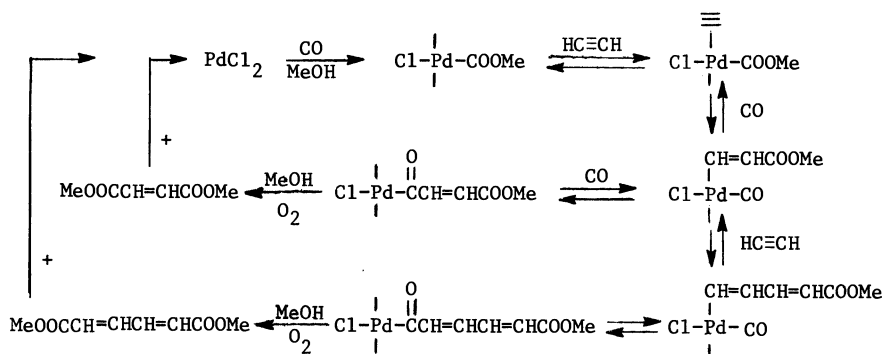
We have seen that the carbonylation reaction of allylic compounds in alcohols occurs with complexes of all the four metals. This circumstance is not easy to reproduce for other reactions. The situation becomes much more intriguing when, in addition to the problems just mentioned, a difficult elimination step has to be achieved and we shall see that this is the case in the following examples.

OXIDATIVE CARBONYLATION

Oxidative carbonylation is a quite general reaction, which can be applied to the synthesis of many interesting products, including oxalic and succinic acids (6). For this reaction to occur an activation of the unsaturated substrate toward nucleophilic attack is required. Furthermore the carboxoalkyl group must easily be formed by attack of alkoxy groups on carbon monoxide. Thus the metal that is able to accept more negative charge is the best to this purpose and palladium actually appears to be the best one. But there is another problem to solve in order to achieve a viable process: hydrogen must be transferred to a suitable acceptor. In the case of acetylene as the substrate (7), many years ago we used oxygen in mixture with carbon monoxide to obtain a catalytic reaction (8) with turn-over of the order of 50 mol of dimethyl maleate and dimethyl muconate per mol of PdCl₂-thiourea complex, as shown in the following equations:

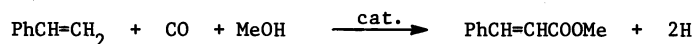


The following stepwise mechanism seems probable (non-reactive ligands are omitted):



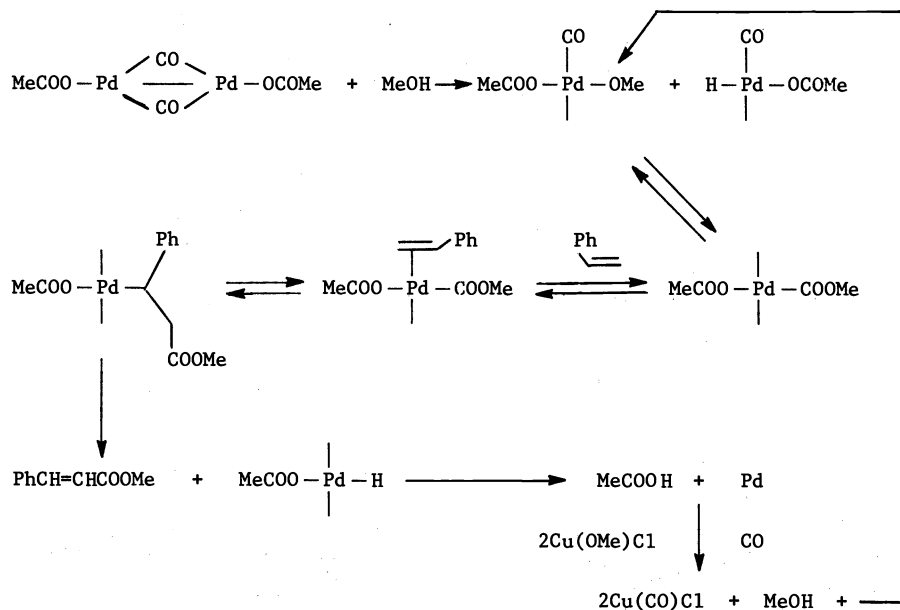
Other potential candidates for this reaction were nickel and cobalt carbonyl complexes, but they did not resist oxidation. In the absence of oxygen, hydrogen can hydrogenate the unsaturated substrates present in the reaction mixture. It is not clear, however, whether the oxidative carbonylation mechanism is operative in these cases, although bicarboxylic esters from acetylene and carbon monoxide have been obtained (9).

We also tried to obtain methyl cinnamate from styrene according to the following equation:

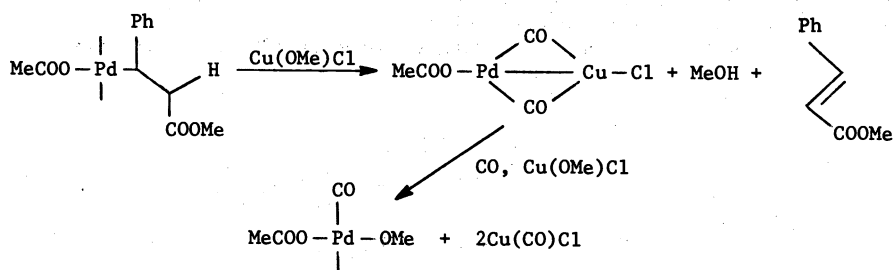


The PdCl₂-thiourea system was not effective in this case and oxygen caused undesired reactions. Thus other oxidative systems had to be used. Palladium acetate in methanol could serve as an efficient catalyst, provided that a large excess (>100 : 1 mol) of an oxidant was used, like copper(II) chloride-sodium acetate, together with an additional amount of a salt, like MgCl₂, able to prevent palladium black separation. Another condition had to be met, however, to obtain methyl cinnamate: carbon monoxide concentration in the reaction mixture had to be kept sufficiently low, for example by dilution with inert gases. In this way at ca. 30° and at atmospheric pressure a catalytic process was achieved, leading to methyl cinnamate with ca. 80% selectivity (ca. 5% dimethyl phenylsuccinate and 15% methyl 3-methoxy-3-phenylpropionate). Turn-over numbers higher than 100 (10), a figure thousand times higher than that reported in literature (11), could be reached. The success of this reaction depends on a delicate balance of factors. Competition between carbon monoxide addition and H-abstraction by methoxy or acetato groups in the last stage determines whether dimethyl phenylsuccinate or methyl cinnamate are formed. Cu(OMe)Cl is probably the species active as oxidant, but if it is used in excess the formation of phenylsuccinate is favoured.

The mechanism of this reaction appears quite complex. We recently observed that the palladium acetate-carbon monoxide cluster reported by Moiseev et al. (12) can be caused to react with styrene if the latter is used as solvent and methanol is added drop by drop (addition of methanol was found to decompose the cluster with formation of dimethyl carbonate (12)). If Cu(OMe)Cl is used as oxidant, 4-5 mol of methyl cinnamate per mol of palladium complex are obtained. Although these conditions are necessarily different from those of the reaction in methanol mentioned above, the result obtained suggests the following sequence of steps (non-reactive ligands are omitted):



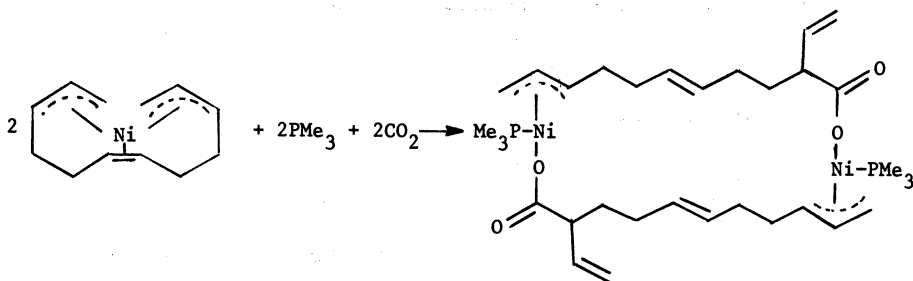
A dimeric unit of Moiseev's cluster should be opened by methanol as indicated. This type of oxidative addition across a metal-metal bond has recently been observed in the case of isopropyl alcohol attack on a Tu-Tu bond (13). Insertion of carbon monoxide to give a carbomethoxy complex and of styrene to give an α -phenyl- β -carbomethoxyethyl complex follows. At this point reductive elimination leads to the cinnamic ester and to palladium(0), which is reoxidized by the copper salt (14). It is possible, however, that another way is operative if copper methoxy chloride intervenes at an earlier stage, giving rise to a carbon monoxide-stabilized dimeric structure, analogous to the starting one (containing only palladium) and susceptible to be attacked by Cu(OMe)Cl or by methanol:



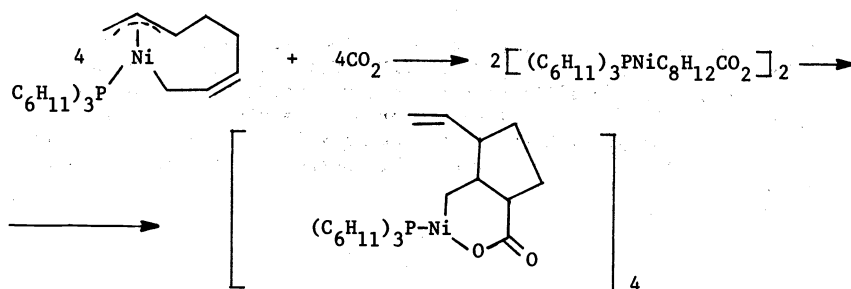
Further work is necessary, however, to get a clearer insight into the mechanism of the palladium acetate reaction in methanol. As I said before, palladium occupies a special position among the other metals because it combines the ability to form the carbomethoxy group easily with that to activate olefins and to stabilize hydrides. Rhodium does not appear suitable, at least at low temperature, probably owing to the stability of its carbonyl.

CARBOXYLATION WITH CARBON DIOXIDE

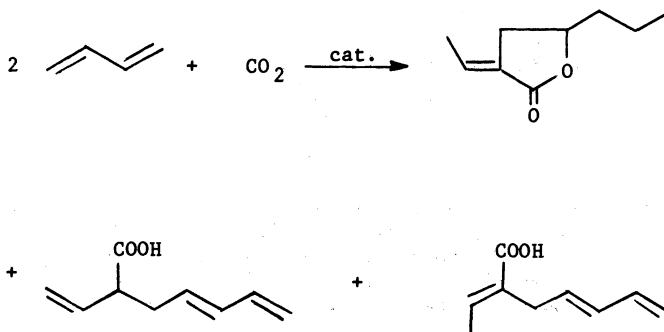
Although carbon dioxide had been used by us for many carboxylation processes, involving stoichiometric amounts of alkali metal complexes like the Zn Reformatski reagent and alkali phenoxides (15), the reaction with transition metal complexes was studied only recently. I'll report here only the carboxylation of butadiene. Analogously to what observed in carboxylation of alkali ion pairs (15) the reaction with transition metal complexes seems to require a metal-coordinated carbanionic species. To obtain a catalytic reaction, however, the metal carboxylate formed by carbon dioxide insertion should be able to undergo an easy reductive elimination. Nickel(0) easily reacts with dienes, giving rise to allylic complexes which insert carbon dioxide, but the resulting nickel carboxylate cannot be easily reduced and stoichiometric reactions occur, as shown by Wilke and coworkers (16):



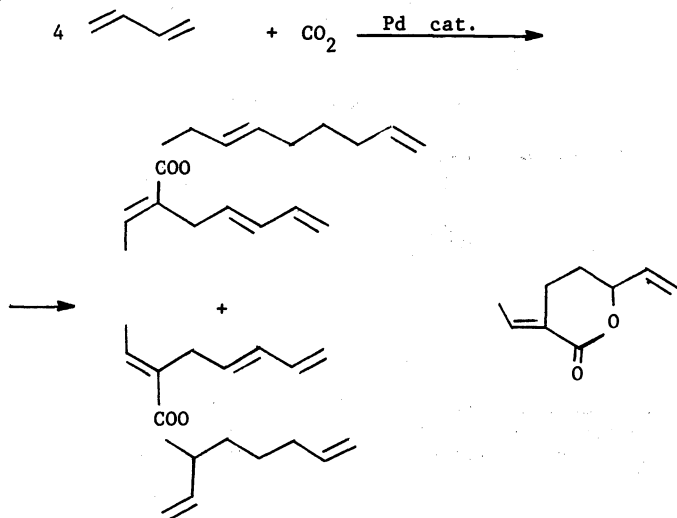
In keeping with the difficulty of reducing these nickel carboxylates, the carboxylate dimer obtained from 2 molecules of butadiene prefers to rearrange to a tetrameric lactone if heated in solution, rather than to give rise to the reductive elimination process which is needed for a catalytic cycle (16):



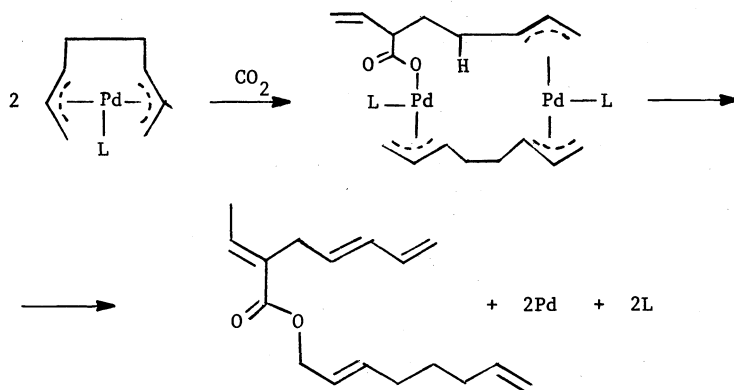
Although the achievement of a catalytic process with a nickel catalyst in the presence of suitable ligands is not excluded, the metal that appears more appropriate for a catalytic reaction is palladium because of its propensity to reductive elimination. Japanese workers recently reported the palladium catalyzed carboxylation of butadiene to acids and lactones (17). A palladium(0) complex with chelating phosphines was used at 120° under CO₂ pressure:



The type of products formed varies remarkably on passing to milder conditions in the presence of non-chelating tertiary phosphines. Two Italian groups have independently observed that if one starts either from palladium(0) complexes with tertiary phosphines or from palladium acetate plus tertiary phosphines, a catalytic reaction is obtained (18), leading to the following products (esters of the corresponding 3,5-cis acids are also formed):



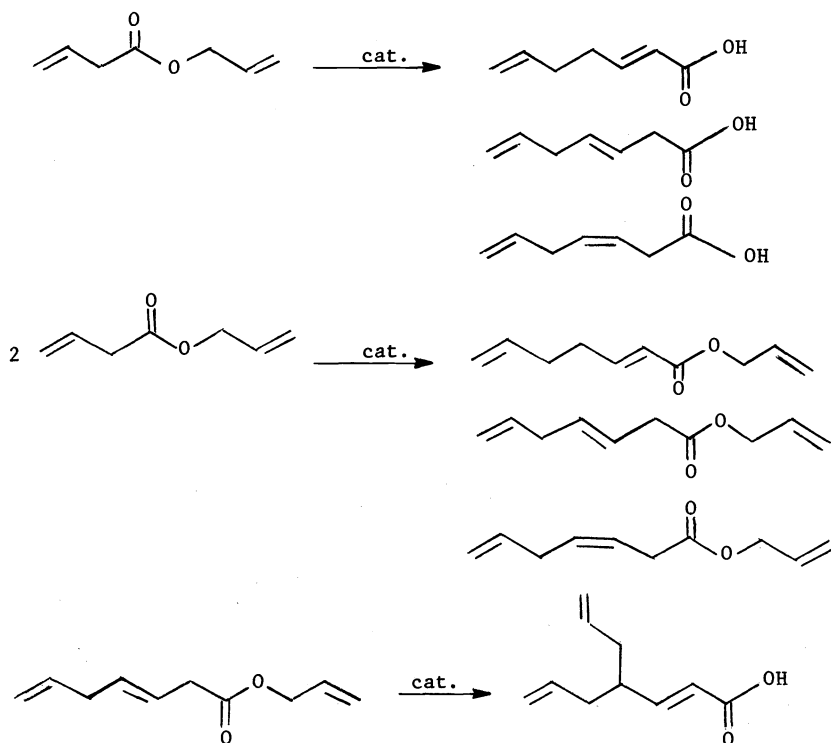
The reaction proceeds via allylic complexes of palladium, analogously to what observed by Wilke for nickel, as recently shown by Santi (19). Since no free acid is formed in the early stage of the reaction it is possible that the esters, which are the predominant products, are formed directly by reaction of the palladium carboxylate with an allylic ligand derived from a butadiene dimer. By analogy with the nickel complex isolated by Wilke it is possible that this process takes place in a dimeric structure, as shown in the following Scheme (L = ligand):



It is interesting to note in this context that the lactone reported above is formed only in minor amounts, unless an excess of phosphine is added, as found by Musco (18). As far as rhodium complexes are concerned, it seems that the tendency to form carbonyls by deoxygenation of carbon dioxide is predominant (19). Data on cobalt are lacking, but in view of its position in the periodic table it is not likely to give catalytic reactions under mild conditions.

C-ALKYLATION

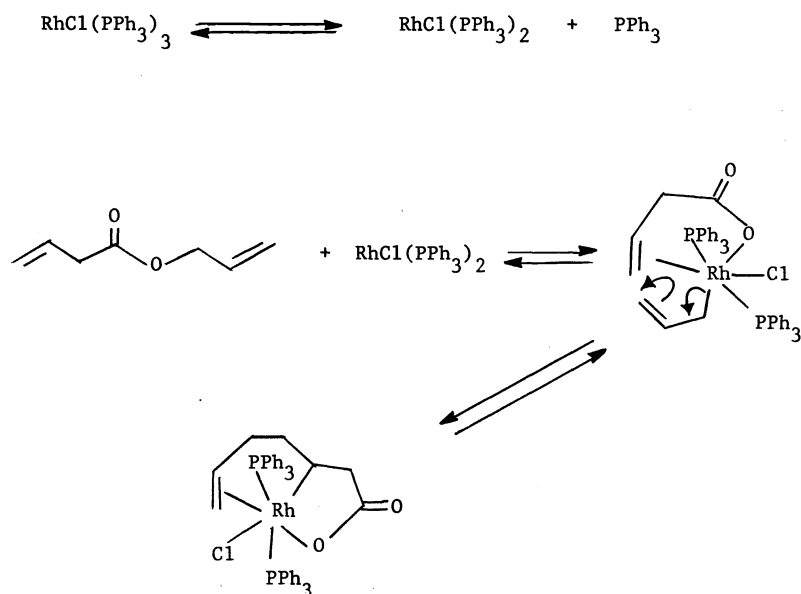
An example of C-alkylation is offered by the rearrangement of allylic 3-butenates (20), consisting of the allylic migration from oxygen to the terminal carbon of the double bond. In the case of allyl 3-butenate the equations are the following:



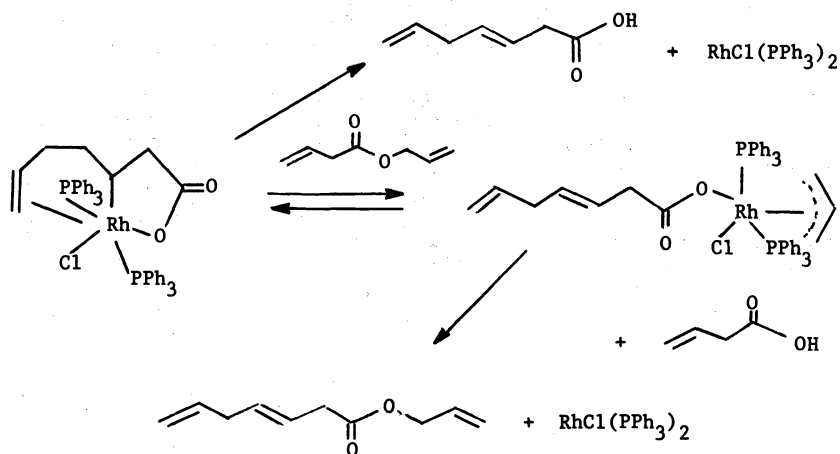
This reaction is quite simple from the preparative point of view and has been studied initially for nickel(0) complexes with trialkyl phosphites and later extended to rhodium(I) com-

plexes with tertiary phosphines. Alkyl C-O fission of allylic esters on nickel(0) is a well known feature (21) but two further steps occur in a surprisingly easy way: migration of the allylic group on the 3-double bond of the butenoic chain and hydrogen elimination. The reaction requires the presence of trialkyl phosphite ligands probably because the last reductive elimination step is favoured in this way. Yields of 2,6 and 3,6-heptadienoic acids and esters as high as 90% and turn-over numbers of ca. 200 have been obtained from allyl 3-butenate, working in tetrahydrofuran at 75° with tetrakis (triisopropyl phosphite)nickel as catalyst.

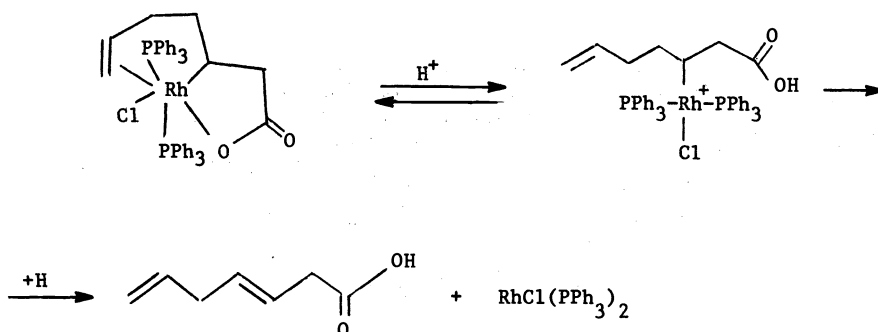
The need for facilitating the first oxidative addition process shows up with rhodium complexes. The latter give very slow reactions with phosphites as ligands, but give good reaction rates and yields if tertiary phosphines are used. Yields reach 90% and turn-over numbers are higher than 250 using allyl 3-butenate and chlorotris(triphenylphosphine)rhodium in acetonitrile at 80°. 3,6-Heptadienoic acid and its allyl ester are obtained selectively. The similarity of behaviour between nickel(0) phosphite complexes and rhodium(I) phosphine complexes is striking in view of the different properties of the two metals in different oxidation states, but clearly a compensation takes place: the slower reductive elimination and insertion processes counterbalance the easier oxidative addition in the case of nickel and the faster reductive elimination and insertion processes counterbalance the slower oxidative addition in the case of rhodium. The detailed mechanism of this reaction is quite complex. I have briefly reported on our studies on this subject in recent occasions and shall limit myself to a short summary of the main features of the rhodium reactions and to some additional aspects not reported previously. Once coordinative unsaturation is obtained in the complex by phosphine dissociation in solution, oxidative addition of allyl 3-butenate takes place, then insertion follows:



At this point we note different types of reductive elimination. In fact in the initial stages of the reaction we do not find free heptadienoic acid to a significant extent, but its allyl ester. The amount of the latter increases to a maximum, then it gradually gives rise to heptadienoic acid. The amount of this acid increases steadily from the beginning to the end of the reaction. We do not note an easy transesterification reaction using heptadienoic acid and allyl acetate in the presence of the same rhodium complex, thus we believe that two different reductive elimination processes are at work, the former and slower consisting of hydrogen transfer from the carbon to the oxygen of the same molecule, the latter and faster consisting of hydrogen transfer to the carboxylic oxygen of a second molecule of allyl butenoate, according to the equation shown below. This behaviour has a certain similarity with that observed in the case of butadiene carboxylation with carbon dioxide, where carboxylate addition to the allylic system of a butadiene dimer was noted.



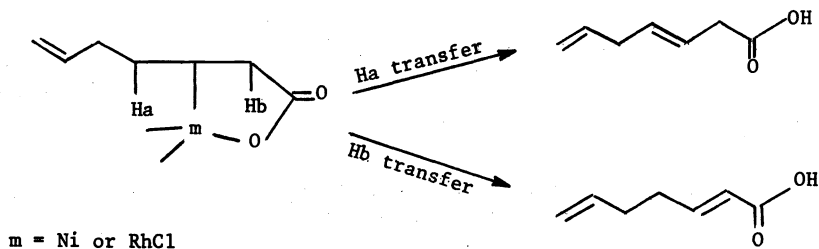
In the present case a third mechanism has also been detected: reductive elimination to free acid is favoured by organic acids. An excess of 3-butenoic acid increases the rate of formation of heptadienoic acid and the overall rate. The amount of allyl ester formed in the early stages of the reaction is remarkably curtailed. Probably butenoic acid exerts at least two actions: the first is general acid catalysis to open the metallacycle formed after insertion:



Acid catalysis of ring opening of metallacycles has been noted for metallacycles formed from two molecules of butadiene and nickel or palladium (22).

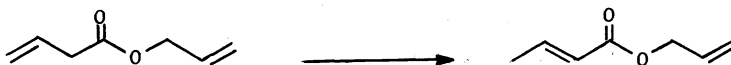
The second action that butenoic acid should exert is a mass action on the first equilibrium shown above, leading to the allylrhodium heptadienoate complex, whose formation would be reduced. Kinetic measurements show that reaction is first order in allyl 3-butenate. The observed rate constant varies linearly with rhodium and 3-butenic acid concentration, respectively, but in both cases it tends to become independent of the respective concentration when the latter is high (23).

We have seen that different types of elimination determine different types of products (ester and free acid). There also are two different ways for H-elimination to give free acids:



The first is the only way for rhodium, whereas both ways are operative in the case of nickel. The stereochemistry is trans for the 2-unsaturated acid and trans + cis for the 3-unsaturated one. In the case of rhodium in tetrahydrofuran, however, the trans product predominates. There are many other aspects of the rhodium and nickel-catalyzed rearrangement reactions, but what I want to stress now is the different behaviour of transition metals towards the same substrate.

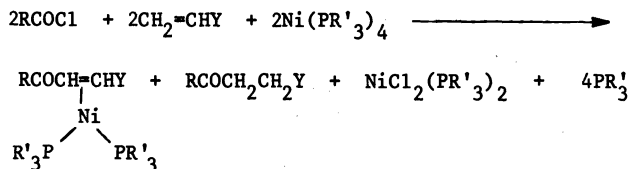
It could have been easy to forecast that also the other two metals considered, palladium and cobalt, would have been able to cause the same type of catalysis as nickel and rhodium, yet in both cases another reaction prevails (23) consisting of the isomerization of allyl 3-butenolate. This is not due to difficulties in the oxidative addition step to palladium(0), although the latter undergoes oxidative addition with more difficulty than nickel(0): addition of triphenylphosphine to palladium causes allyl acetate to add quite easily under mild conditions. There is, however, another property of palladium that shows up in competition with the ability to give oxidative addition. This is its tendency to stabilize hydrides, formed by hydrogen abstraction from an active methylene group. This process is the favoured one under the reaction conditions and isomerization results:



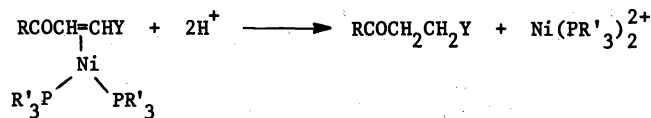
Cobalt, as tris(triphenylphosphine)cobalt chloride, also gives isomerization instead of rearrangement. In this case what hinders the rearrangement reaction in respect to isomerization possibly is related with the unfavourable tetrahedral stereochemistry and the instability of trivalent cobalt (24). Thus the first stage of the process, involving allylic C-O fission may be less favourable for cobalt(I) than for rhodium(I). Another possible explanation is that for rhodium insertion as well as reductive elimination are faster processes than for cobalt and the competitive isomerization reaction is left behind.

C-ACYLATION

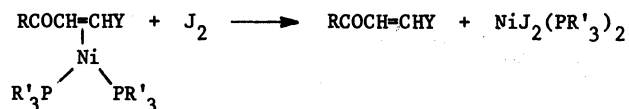
Migration of metal-coordinated acyl groups to activated olefins offers another example of C-C bond formation. The reaction requires hydrogen abstraction to give a catalytic process, whereas hydrogen uptake gives a stoichiometric process. Both these processes take place in the reaction of nickel(0) complexes with acyl chlorides and activated olefins according to the following equation (25, 26) where R, R' are aryl groups and Y electron-withdrawing substituents:



This stoichiometric reaction can also be caused to give only the hydrogenated product if the reaction mixture is treated with acids at the end of the reaction. The complex is destroyed in the following way:

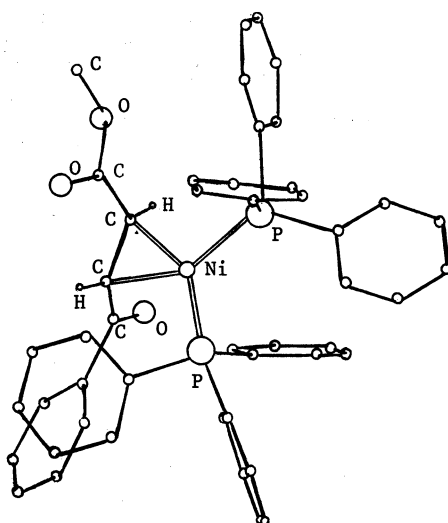


If, however, the reaction mixture is treated at the end with iodine in methanol, both the saturated and the unsaturated compounds are obtained, the latter being displaced from the complex as follows:

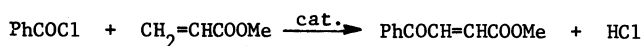


The first intermediate appears to be $\text{RCO-Ni}(\text{PPh}_3)_2\text{Cl}$. The best conditions were found when this complex was used in an excess of $\text{CH}_2=\text{CHY}$ at 0° . A 75% yield of $\text{RCOCH}_2\text{CH}_2\text{Y} + \text{RCOCH}=\text{CHY}$ was

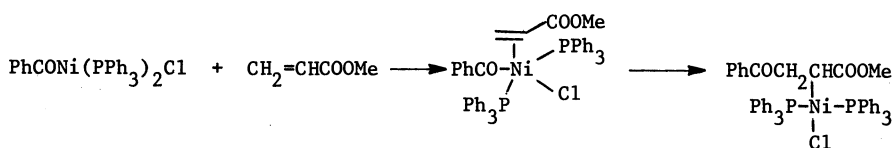
obtained for R = Ph and Y = COOMe. The structure of the (methyl benzoylacrylate) bis(triphenylphosphine)nickel complex, isolated by extraction with toluene and precipitation with n-hexane, has been determined recently (26):



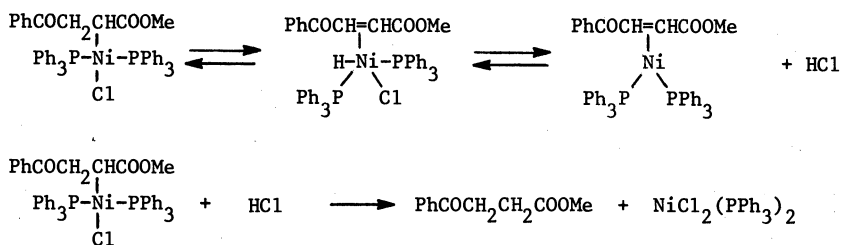
It is interesting to note that the simple catalytic reaction:



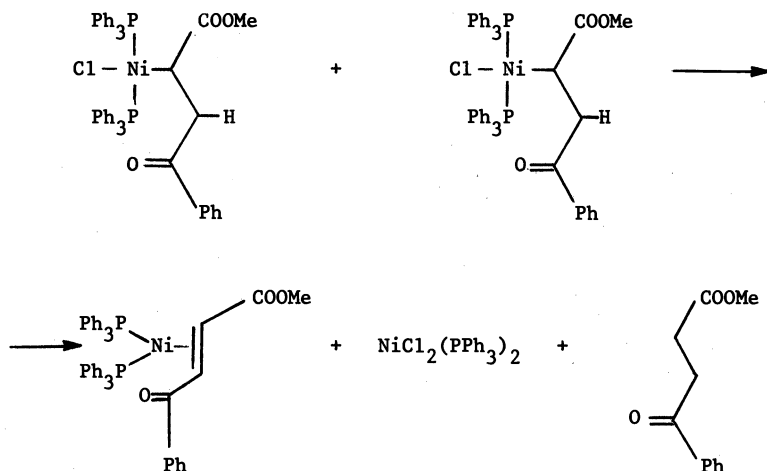
occurs only in part under the conditions tested (0° to room or slightly higher temperature) and what formally is a disproportionation process takes place in parallel. We believe that this is to be attributed to the high proton affinity of the nickel-bonded ligand, resulting from the double bond insertion:



This ligand successfully competes with chloride (or $\text{Ni}(\text{PPh}_3)_2\text{Cl}$) for the proton:

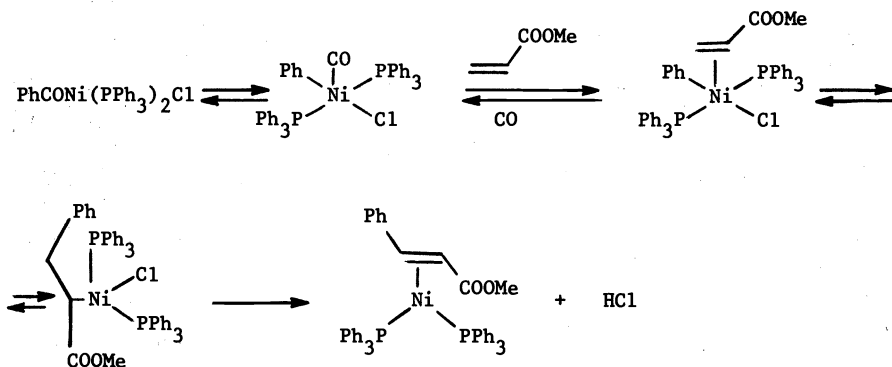


An experiment with toluynickelbis(triphenylphosphine) chloride and methyl benzoylacrylate in methyl acrylate, followed by treatment with I_2 , did not give hydrogenation of benzoylacrylate, but only gave toluylacrylate and toluylpropionate. On the contrary, when (methyl toluylpropionate)bis(triphenylphosphine)nickel and methyl benzoylacrylate were treated with half a molecule of an acid, both toluylpropionate and benzoylpropionate were found. This means that only the σ bond formed by acrylate insertion into the acylnickel bond is attacked during the final step. This behaviour, however, is also consistent with a direct disproportionation process between two molecules of the insertion intermediate, possibly via a dimeric complex:



Competition for hydrogen by tertiary amines leads to a slight catalytic activity. Thus when the nickel complex was used in an excess of 20 mol of benzoyl chloride and of triethylamine, 1.1 mol of methyl benzoylacrylate, 0.35 mol of methyl benzoylpropionate and 0.25 mol of methyl 3-phenylpropionate were formed per mol of complex (27).

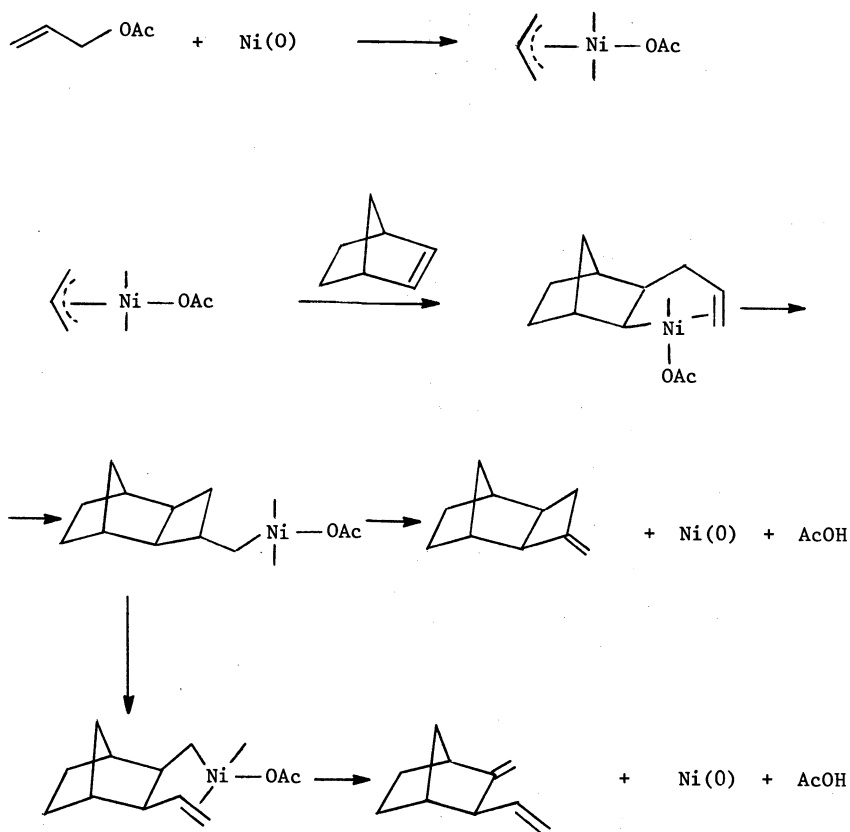
Another compound, which is found as by-product in the reaction with benzoyl chloride and methyl acrylate is methyl cinnamate. It derives from a preliminary decarbonylation reaction, followed by migration of the resulting phenyl group on methyl acrylate and hydrogen elimination:



We have seen that nickel reacts according to rather complex patterns. Let me now show to you what happens when we pass to the other metals. It could be anticipated that palladium would withdraw more charge from the olefin and also from the benzoyl group, which perhaps would not be able to carry out a nucleophilic attack on acrylate. On the other hand the palladium ability to stabilize hydrides and the lower basicity of the palladium-bonded carbon resulting from acrylate insertion should favour hydrogen elimination, thus leading to a catalytic process. The experimental results are the following: starting from the complex of benzoylpalladium chloride with triphenylphosphine and adding triethylamine, a stoichiometric reaction occurs in high yield, leading to methyl benzoylacrylate and methyl cinnamate. The latter forms in increasing amounts depending on the temperature ($70-85^\circ$) until it becomes the predominant product. It is worthwhile to note that under the same conditions chlorobenzene is not reactive

plex fragment (31), which in our case contains acetate and triisopropyl phosphite as ligands. Since the *anti* elimination process is much more slower than the *syn* elimination (32) the reaction proceeds further to reach a more favourable arrangement for reductive elimination. The double bond of the allyl group being available for a four-membered ring closure, which would place nickel on an exocyclic carbon, this way is followed by the system to achieve an easier reductive elimination. Another way becomes competitive at this point, however, consisting of the ring opening of the four-membered cycle to form a new complex, which easily gives rise to a vinyl group by reductive elimination. The series of steps occurring on the metal complex is shown in the sequence reported below (non reactive ligands are omitted). Two main products result (ca. 90% of the total), the one containing the cyclobutane ring prevailing at room temperature (4 to 3 ratio). 70 Mol of these products per mol of complex are obtained.

It can be concluded that the ability to undergo H-elimination is of paramount importance to many organometallic processes. From the synthetic point of view it will be possible to take advantage of a difficult elimination step to cause a multistep process to proceed further with insertion of new molecules and groups until a favourable arrangement for reductive elimination is reached.



Conclusion. We have seen that in all the cases described above general trends in reactivity can be broadly predicted for each metal, but many competitive reactions may occur. Quite slight differences in bond energies or stabilization energies of the complexes involved can cause one of these reactions to prevail. In particular the final elimination step can determine the formation of different products on passing from a metal to another one. Thus constructing an experimental reactivity map of VIII group metal complexes with organic substrates appears to be useful, also to appreciate the effect of caused by small variations

in many factors, which often are neglected or not appropriately evaluated in predicting the behaviour of a catalytic system.

Acknowledgement — I wish to thank my colleagues and coworkers, whose names appear in the references, for their enthusiastic work, which has made this report possible. I also wish to thank the Italian National Research Council for financial support.

REFERENCES

1. G.P. Chiusoli, Gazz. Chim. Ital. **89**, 1332 (1959).
2. D. Medema, R. van Helden and C. F. Kohll, In. Chim. Acta **3**, 255 (1969).
3. R. F. Heck and D. S. Breslow, J. Am. Chem. Soc. **85**, 2779 (1963).
4. J. L. Brewbaker (Ethyl Co.), USP 3367961 (1968).
5. A. J. O'Connor, Topics in Current Chemistry **71**, 71 (1977).
6. D. M. Fenton and K. L. Olivier, Chem. Tech., 220 (1972) and references therein.
D. M. Fenton and P. J. Steinwand, J. Org. Chem. **39**, 701 (1974).
D. E. James and J. K. Stille, J. Am. Chem. Soc. **98**, 1810 (1976) and references therein.
R. F. Heck, J. Am. Chem. Soc. **91**, 6707 (1969).
F. Rivetti and U. Romano, J. Organometal. Chem. **154**, 323 (1978).
7. J. Tsuji, J. Am. Chem. Soc. **86**, 2095 (1964).
8. G. P. Chiusoli, G. Venturello and S. Merzoni, Chem. & Ind. (London), 977 (1968).
9. P. Pino and G. Braca in Organic Syntheses via Metal Carbonyls, I. Wender and P. Pino Eds, Wiley, New York 1977, p. 419 and references therein.
10. G. Cometti and G. P. Chiusoli (Montedison), Ital. Pat. Appl. 22645/78.
11. R. F. Heck, J. Am. Chem. Soc. **94**, 2712 (1972).
12. I. I. Moiseev, T. A. Stromnova, M. N. Vargaftig, G. J. Mazo, L. G. Kuz'mina and Y. T. Struchkov, J. Chem. Soc. Chem. Commun., 27 (1978).
13. M. Akiyama, D. Little, M. Chisholm, D. Haitko, F. A. Cotton and M. W. Extine, J. Am. Chem. Soc. **101**, 2506 (1979).
14. G. Agnès, G. Bimbi, F. Guerrieri and G. Rucci (Montedison), Ital. Pat. Appl. 22169/76.
15. G. P. Chiusoli and G. Bottaccio, Chem. & Ind. (London), 1457 (1966).
G. Bottaccio and G. P. Chiusoli, Chem. Commun., 618 (1966); id. Z. Naturforsch. **23b**, 561 (1968); id. ibid. **23b**, 1016 (1968).
G. Bottaccio, G. P. Chiusoli and M. Felicioli, Gazz. Chim. Ital. **103**, 105 (1973); id. ibid. **106**, 831 (1976).
G. Bottaccio, M. Marchi and G. P. Chiusoli, Gazz. Chim. Ital. **107**, 499 (1977).
16. P. W. Jolly, S. Stobbe, G. Wilke, R. Goddard, C. Krüger, J. C. Sekutowski and Yi-Hung Tsay, Agew. Chem. Int. Ed. Engl. **17**, 124 (1978).
17. Y. Sasaki, Y. Inoue and H. Hashimoto, J. Chem. Soc. Chem. Commun., 605 (1976).
Y. Inoue, Y. Sasaki and H. Hashimoto, Bull. Chem. Soc. Japan **51**, 2375 (1978).
18. A. Musco, G. Santi and G. P. Chiusoli (Montedison), Ital. Pat. Appl. 27277/77.
A. Musco, C. Perego and V. Tartari, In. Chim. Acta **28**, L147 (1978).
19. G. Santi, private communication.
20. G. P. Chiusoli, G. Salerno and F. Dallatomasina, J. Chem. Soc. Chem. Commun., 793 (1977).
M. Catellani, G. P. Chiusoli and G. Salerno, Proc. 1^o Int. Symp. on Rhodium in Homogeneous Catalysis, Veszprém (Hungary) 1978.
21. N. L. Bauld, Tetrahedron Lett., 589 (1962).
22. S. Takahashi, H. Yamasaki and N. Hagihara, Bull. Chem. Soc. Japan **41**, 254 (1968).
P. Heimbach, Angew. Chem. Int. Ed. Engl. **7**, 882 (1968).
23. G. P. Chiusoli, G. Salerno and R. De Fanti, unpublished results.
24. M. Aresta, N. Rossi and A. Sacco, In. Chim. Acta **3**, 227 (1969).
25. G. P. Chiusoli, M. Costa and G. Pecchini, Transition Met. Chem. **2**, 270 (1977).
26. G. D. Andreotti, G. Bocelli, P. Sgarabotto, G. P. Chiusoli, M. Costa and A. Biavati, Transition Met. Chem., in press.
27. A. Biavati, G. P. Chiusoli, M. Costa and G. Terenghi, to be published.
28. K. Ohno and J. Tsuji, J. Am. Chem. Soc. **90**, 99 (1968).
J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. A, 1711 (1966).
K. S. Y. Lau, Y. Becker, F. Huang, N. Baenziger and J. K. Stille, J. Am. Chem. Soc. **99**, 5664 (1977) and references therein.
29. R. F. Heck, J. Am. Chem. Soc. **85**, 3383 (1963).
30. M. Catellani, E. Dradi, G. P. Chiusoli and G. Salerno, J. Organometal. Chem., in press.
31. M. C. Gallazzi, T. L. Hanlon, G. Vitulli and L. Porri, J. Organometal. Chem. **33**, C45 (1971).
32. J. Sicher, Angew. Chem. Int. Ed. Engl. **11**, 200 (1972).