

ORGANO TRANSITION METAL COMPOUNDS AS INTERMEDIATES IN HOMOGENEOUS CATALYTIC REACTIONS

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Abstract - Metallocycles occur in many cases as intermediates in processes which are catalyzed by transition metal complexes in the homogeneous phase. Frequently, it proved possible to isolate metallocycle complexes from catalytic experiments in crystalline form and to determine their structures by NMR-spectroscopy as well as x-ray analysis. 3,4,5,7,9,11,12,13,14-membered metallocycles have been shown to be important in catalytic reactions involving alkynes, alkenes and 1,3-dienes. Isolated binuclear metallocycles suggest pathways for catalytic reactions involving two metal atoms.

INTRODUCTION

The making and breaking of C-C-bonds is of central importance in organic chemistry. Frequently, these reactions proceed only in the presence of an organometallic catalyst whereby those containing transition metals are of particular importance. Familiar examples are the Ziegler polymerization, the metathesis reaction as well as acetylene and olefin cyclooligomerization. In order to understand the mechanism of these reactions it is advantageous to isolate and determine the structure of intermediates involved and this has indeed been carried out for many reactions. It has been repeatedly observed that organometallic compounds occupy key positions in these mechanisms and it is my objective in this lecture to draw your attention to the significance of metallocycle compounds and to give a general survey of their formation.

Right at the beginning of the development of transition metal catalyzed oligomerization reactions we come across a scientist dreaming that he is being attacked by a black sheep in the form of a cyclooctatetraene (COT) molecule.



Fig. 1 Walter Reppe and the black sheep, cyclooctatetraene

The scientist was Walter Reppe and the reaction the catalytic synthesis of COT from acetylene (1). With this dream he, apparently, became the "father" of metallocyclic chemistry as can be seen from the reaction mechanism which he proposed for the cyclotetramerization reaction.

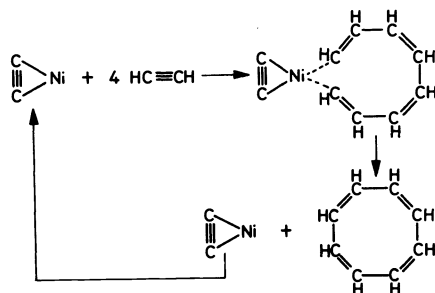


Fig. 2 Reppe's proposed mechanism for the catalytic cyclo octatetraene formation

It is interesting to read his account (1) which I have freely translated:

"It is, of course, possible in analogy to the modern view of the constitution of nickel tetracarbonyl to assume that four acetylene molecules are co-ordinated to a nickel-atom or -ion and coupled together."

and further

"We assume here that a hypothetical biradical is formed from four acetylene molecules which interacts with the 3d-level of the nickel atom through the terminal radical electrons."

This is indeed a remarkable description for 1948.

Reppe was not only the first to speculate about a metallocycle as an intermediate in the cyclooctatetraene synthesis but he was also the first to synthesize a metallocycle by reacting $\text{H}_2\text{Fe}(\text{CO})_4$ and butyne-(2). The product is a crystalline compound having the composition $\text{Fe}_2\text{C}_{12}\text{H}_4\text{O}_8$ (2).

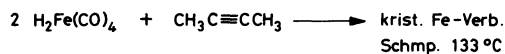
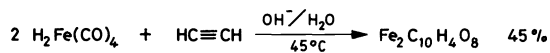


Fig. 3 Synthesis of the first metallocycle

and the structure was elucidated by A.A. Hock and O.S. Mills (3) in 1958 by x-ray analysis

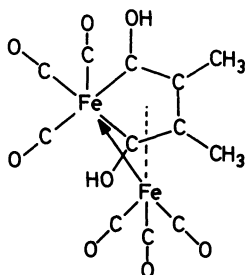


Fig. 4 X-ray structure of Reppe's iron-cyclopentadiene

After this introduction I would like to continue my description of the metallo-cycles by discussing them in the order of increasing size. The smallest metallocycle, a metallocyclopropene, was discussed for the first time by J. Chatt *et al.* (4) in 1957 as one possible structure for a platinum acetylene complex,

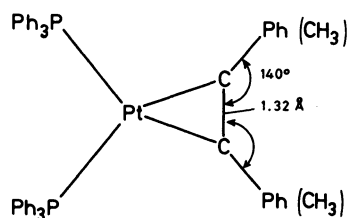


Fig. 5 Platinum acetylene complex, a 'metallocyclopropene'

and was shown to correspond to that formulation by x-ray analysis in 1967 (5). The formulation of this complex as a metallocyclopropene seems to be justified because the phenyl groups are bonded to the coordinated C-C-bond at an angle of about 140° and the length of the central bond approaches that of a C=C-bond.

The first metallocyclobutane was obtained by Tipper (6) from cyclopropane and PtCl_2 in 1955 but characterized as a cyclopropane complex. In 1960 Chatt *et al.* (7) were able to show by NMR that instead a metallocyclobutane is present and this structure was finally confirmed by x-ray analysis (8).

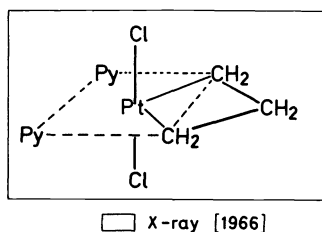


Fig. 6 Structure of the first metallocyclobutane

The metallocyclobutanes have attracted considerable attention in recent years with the proposal by H  risson and Chauvin (9) in 1970 of a monocarbene mechanism for the olefin metathesis reaction

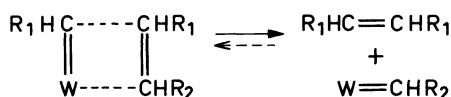


Fig. 7 Metathesis monocarbene mechanism by H  risson and Chauvin

and Lappert *et al.* (10) proposed a metallocyclobutane intermediate in the metathesis of electron rich olefins.

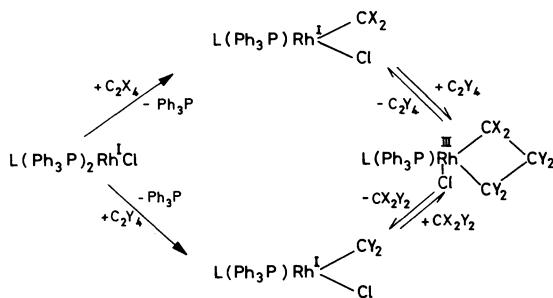


Fig. 8 Metallocyclobutane mechanism by Lappert *et al.*

This mechanism is now widely accepted to be the most likely one.

In 1961 Stone *et al.* (11) isolated a product from a reaction of $\text{Fe}(\text{CO})_5$ and tetrafluoroethylene which has been identified as a metallocyclopentane derivative. In the context of catalytic reactions the proposal by Halpern *et al.* (12) of a metallocyclopentane intermediate in the catalytic rearrangement of cubane by rhodium-(I) is of particular interest since a C-C-cleavage is involved. They were able to trap this intermediate as a CO-insertion Rh-(III) complex in the form of a metallocyclohexane derivative.

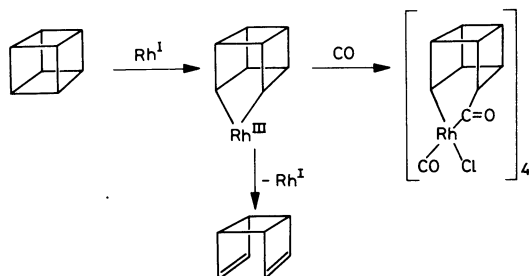


Fig. 9 Formation of a metallocyclopentane by oxidative addition of a C-C-bond

The first definite proof for the existence of metallocyclopentanes was obtained from the x-ray analysis of the product of the reaction of bicycloheptadiene with an iridium complex (13).

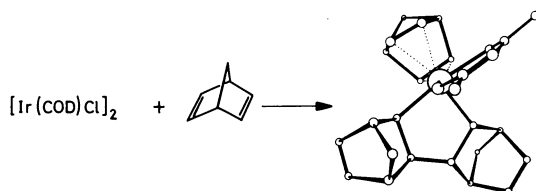


Fig. 10 x-ray structure of a metallocyclopentane

These metallocyclopentanes are the intermediates in the metal catalyzed 2+2-additions of olefins with formation of cyclobutanes. In this case the metal bonded C-atoms couple together, a process which is general for all cyclooligomerizations. As a model for these C-C-bond formation processes we have studied the decomposition of $\text{dipy} \cdot \text{Ni}(\text{CH}_3)_2$ (14) under the influence of Lewis-acids (15). The first step is the removal of the dipy-ligand from the nickel by complexation.

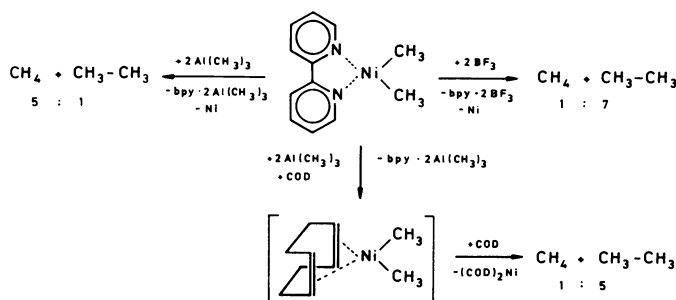


Fig. 11 Decomposition of $\text{dipy} \cdot \text{Ni}(\text{CH}_3)_2$ by Lewis-acids

The CH_3 -groups couple together to give mainly ethane in the cases where the Lewis-acid does not contain H-atoms or if the Ni-atom is complexed by cyclooctadiene-(1,5) (COD). In other cases larger amounts of methane are formed. In the case of $\text{Al}(\text{CH}_3)_3$ as Lewis-acid it could be shown that the CH_3 -groups formed by the decomposition of $\text{Ni}(\text{CH}_3)_2$ abstract H-atoms exclusively from the $\text{Al}(\text{CH}_3)_3$. Yamamoto *et al.* (16) have studied in great detail the C-C-coupling process which takes place if $\text{dipy} \cdot \text{NiEt}_2$ is treated with electron withdrawing olefins. They have been able to show that under these conditions the olefin attacks the fifth coordination site on the Ni-atom weakening the Ni-C-bonds and causing the coupling. In our experiments no radical formation could be detected, therefore, we suggest the intermediate formation of a three centre electron deficient bond leading finally to the new C-C-bond.

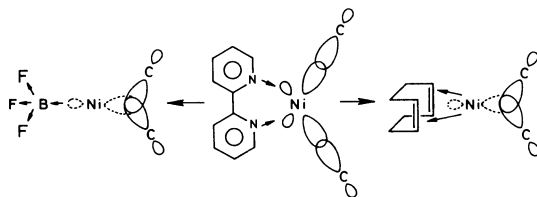


Fig. 12 Three centre electron deficient bonds formed before final C-C-coupling

P. Binger *et al.* (17) have studied extensively the catalytic cyclooligomerization of strained small ring olefins such as *exo*-methylenecyclopropane or dimethylcyclopropene and they were able to isolate a number of model complexes, the structures of which were determined by x-ray analysis (17e).

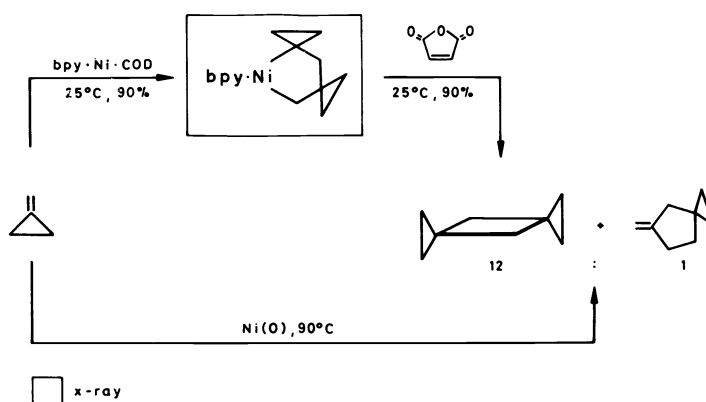


Fig. 13 Catalytic cyclooligomerization of *exo*-methylenecyclopropane

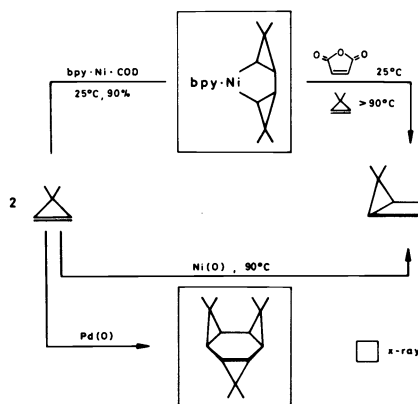


Fig. 14 Catalytic cyclooligomerization of di-methylcyclopropene

The formation of the derivative of a tris-homobenzene should occur through a metallocycloheptane intermediate. However, this has not yet been isolated from the catalytic reaction, but a model compound containing rhodium has been obtained (18a) and analyzed by x-ray crystallography (18b).

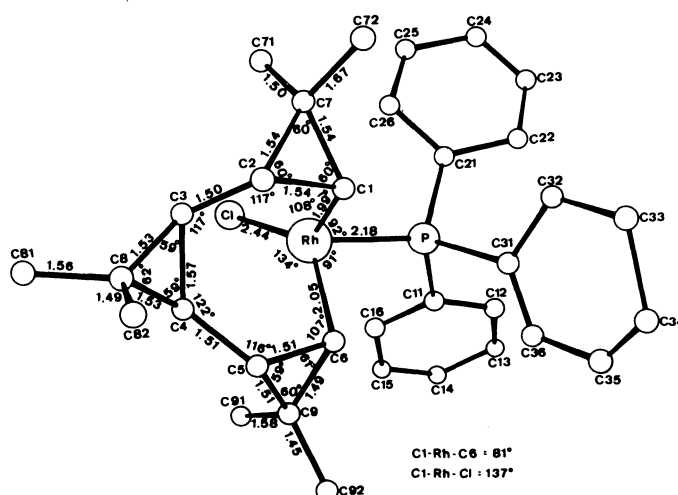


Fig. 15 X-ray structure of a rhodiocycloheptane

Even larger metalloring systems are important intermediates in the cyclooligomerizations of 1,3-diolefins. If butadiene is cyclodimerized on L-Ni-catalysts the formation of 1,2-divinylcyclobutane, 4-vinylcyclohexene-(3) and cyclooctadiene-(1,5) involves intermediates containing 5, 7 or 9-membered metallocycles (19) which exist in an equilibrium with different π -allyl forms. We assume that the final C-C-coupling process proceeds in general through bis- σ -allyl intermediates.

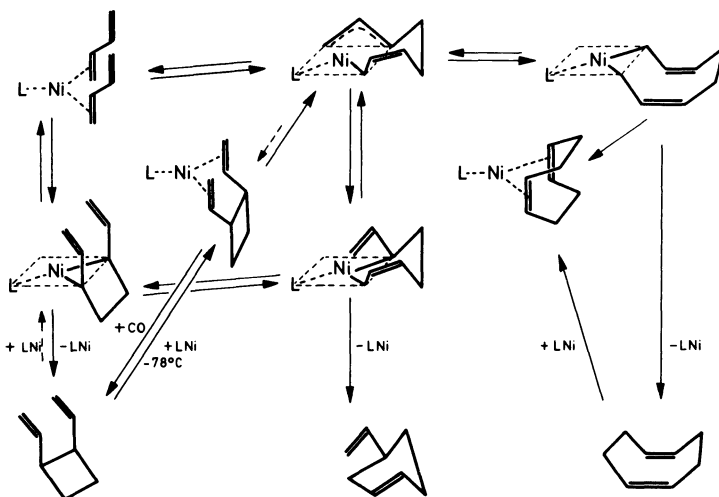


Fig. 16 Catalytic cyclodimerization of butadiene

Isolated and well characterized intermediates have been obtained from different 1,3-diolefins (20). It is interesting that the C_8 -chains bonded to nickel are in equilibrium with the corresponding diolefins, that is, under the influence of the metal atom C-C-bonds are not only easily formed but also cleaved.

The 9-membered ring system which is believed to be the final intermediate of the cyclooctadiene synthesis can also be detected by NMR in a zirconium complex which has been isolated from a catalytic reaction starting from cyclooctatetraenezirconium-diallyl and butadiene. Displacement of diallyl causes a complex with a C_8 -chain to be formed (21). The 1H -NMR-spectra of this complex are temperature dependent and show the equilibration of the endo- and exo-protons (marked $\bullet$ and —) at 0°C although they can be distinguished at -60°C. The equilibration must occur by rotation through a 9-membered bis- σ -allyl system.

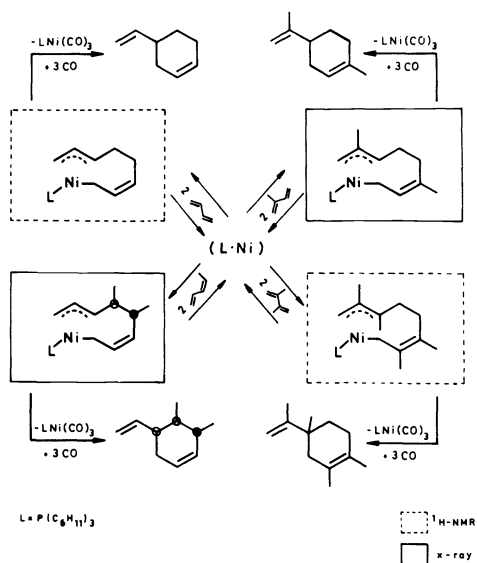


Fig. 17 Intermediates in catalytic cyclodimerizations of 1,3-diolefins

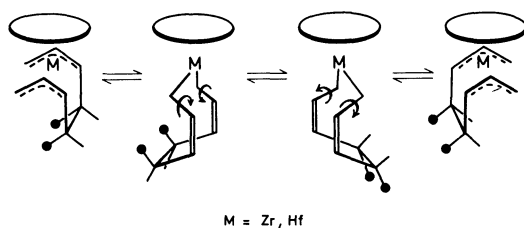


Fig. 18 Dynamization of $COTZrC_8H_{12}$ through a metallocyclo-nonadiene

The cyclo-cooligomerization of 1,3-diolefins and acetylenes leads to the formation of 10-membered ring systems (22). In one case we achieved the isolation of a precursor which was characterized by NMR to be a π -allyl- σ -vinyl- C_{10} -nickel system (23).

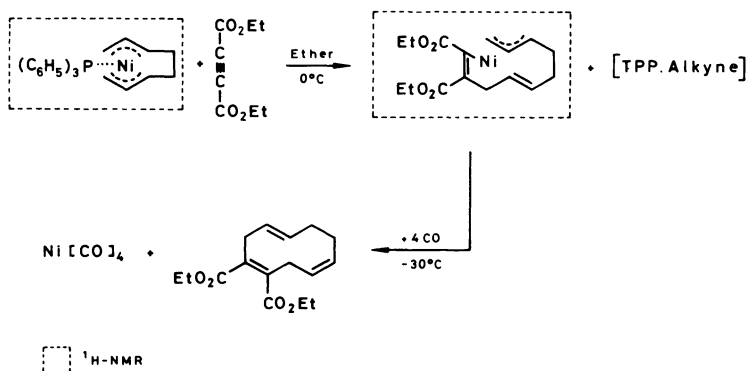


Fig. 19 Cyclo-cooligomerization of butadiene and an acetylene, isolation of an intermediate

The dynamization gives rise to the intermediate formation of an 11-membered metallocycle from which the cyclodecatriene derivative is displaced. Already in 1961 we described the prototype of these complexes originating from the reaction of "naked" nickel (19b) and butadiene, a $C_{12}H_{18} \cdot Ni$ (24). Recently, we have been able to refine the structure by 270 MHz 1H -NMR and ^{13}C -NMR and have been able to show that two different isomers exist (25a). The π -allyl groups are anti-substituted and cis to each other (25b) while the trans-

double bond is coordinated to the nickel parallel to the planes of the allyl-groups (Fig. 20).

This intermediate rearranges under the influence of excess butadiene probably to give the bis- σ -allyl metallocycle with 13 ring members from which all-trans-cyclododecatriene is formed by C-C-coupling. Similar processes occur if the complex is treated with t-butylisonitril or CO (26). Insertion occurs and a 14- or 12-membered metallocycle is formed as the immediate precursor of the final products - derivatives of cyclotridecatrienone and vinylcycloundecadienone, respectively.

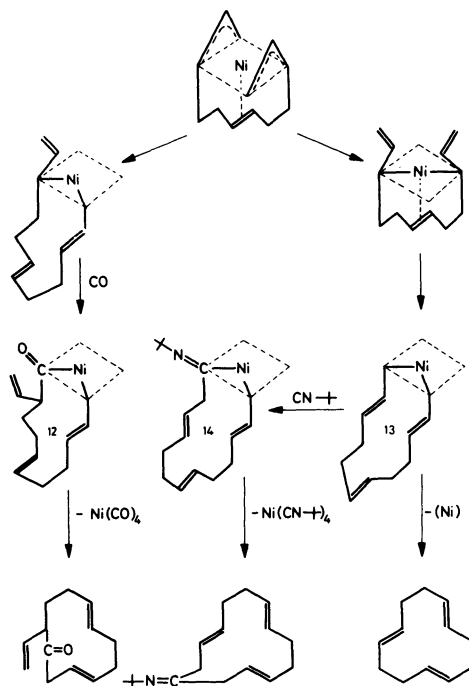


Fig. 20 Intermediate formation of 12, 13, and 14-membered metallocycles

Up to this point I have discussed only mononuclear intermediates in catalytic cyclization reactions. There is no doubt that binuclear complexes having catalytic activity should be of interest. However, concrete results are still very limited. As far as I know the first example was described by C. Hoogzand and W. Hübel as well as O.S. Mills and G. Robinson (27) in 1964 from the reactions of cobalt octacarbonyl with 3 alkyne molecules and characterized by x-ray analysis which showed that the terminal C-atoms of a C_6 -chain formed from acetylene and t-butylacetylene are each bonded to both cobalt atoms. Furthermore, the six C-atoms of the chain form two π -allyl groups complexed to the cobalt atoms. From this complex they obtained for the first time a 1,2-di-t-butylbenzene.

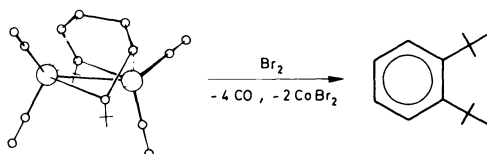


Fig. 21 X-ray structure of an intermediate in the formation of 1,2-di-t-butylbenzene

Recently, we have obtained some results in this context which appear to be of more general significance. In the course of a detailed study of cyclooctatetraene-chromium complexes (28) the reaction of chromocene and the disodium salt of cyclooctatetraene was investigated and a crystalline complex having the composition $(\text{CpCr})_2\text{C}_8\text{H}_8$ was isolated. The x-ray analysis (29a) showed that this complex does not contain an eight-membered ring complexing both Cr-atoms as in $(\text{COT})_3\text{Cr}_2$ (29b) but a C_8 -chain which is bonded in very similar manner to that shown in the above mentioned Co-complex. One $\text{C}=\text{C}$ -bond of cyclooctatetraene is cleaved and each of the terminal C-atoms are bonded to both Cr-atoms while in addition two π -allyl groups are formed by the six internal C-atoms. Remarkably, the ^1H - and ^{13}C -NMR-spectra show that the open chain structure of the molecule which is observed in the crystal can only be detected in solution at very low temperatures (-78°). At higher temperatures a dynamization takes place - particularly detected by the ^{13}C -signal of the terminal C-atoms - probably, through rapid C-C-bond making and breaking processes.

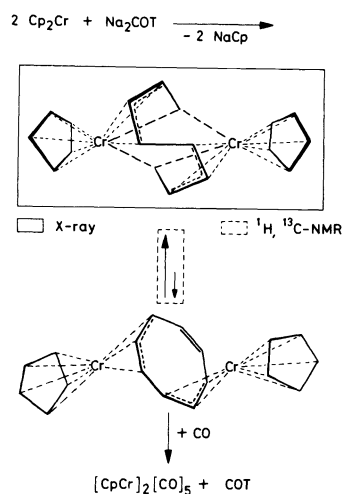


Fig. 22 X-ray structure of $(\text{CpCr})_2\text{C}_8\text{H}_8$ and it's dynamization in solution

The form with the closed ring corresponds to the x-ray structure of $(\text{COT})_3\text{Ti}_2$ (28a, 28c).

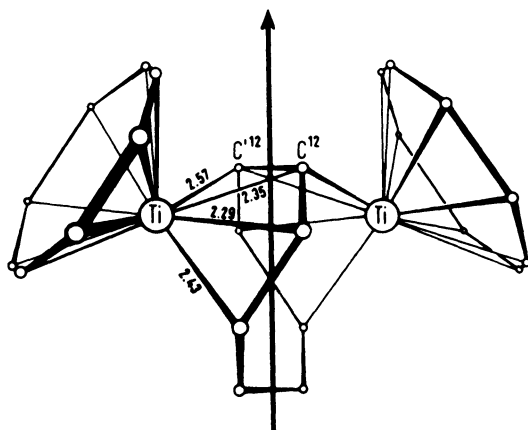


Fig. 23 X-ray structure of $(\text{COT})_3\text{Ti}_2$

This observation could account for the phenomenon of a formal dichotomy which we described earlier (30) when we observed the stoichiometric formation of cyclopentadienyl rings from acetylenes.

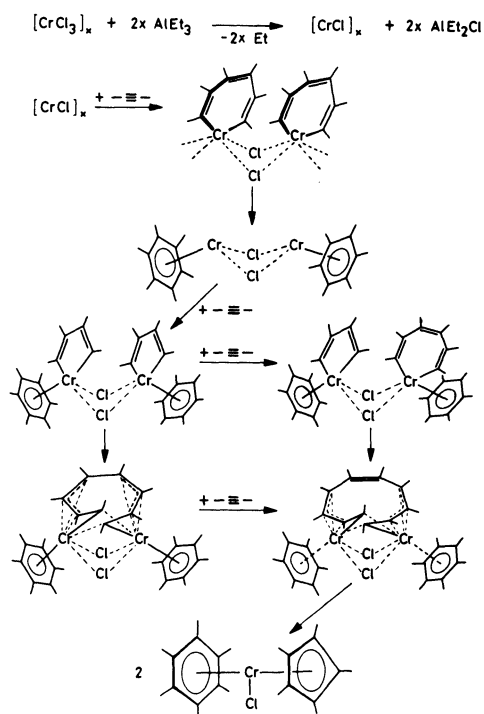


Fig. 24 Formation of hexamethylbenzene-chromium-(I)-penta-methylcyclopentadienyl by dichotomy of butyne-(2)

The reduction of crystalline CrCl_3 by AlEt_3 apparently leads to the formation of a chromium-(I)-chloride at least on the surface.

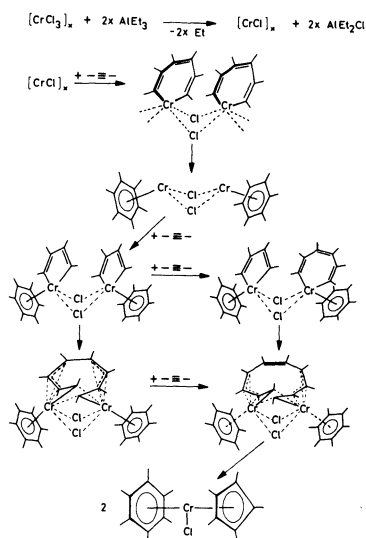


Fig. 25 Proposal of a mechanism for the formation of the five- and six-membered rings

Intermediate formation of metallocycloheptatrienes with formally chromium-(III) would account for the hexasubstituted benzenes which are finally coordinated to chromium-(I) again. In course of a similar sequence a C_{10} -chain from five acetylenes can be built up between two Cr-atoms. Splitting of the chain at the central bond and cyclization would give rise to the formation of two coordinated cyclopentadienyl rings. This mechanism seems to be very plausible. In the same context I would like to mention a result by H. Hoberg *et al.* (31). J. Fisch *et al.* (32) have synthesized a ligand stabilized nickelocyclopentadiene from a dilithiobutadiene and NiX_2 .

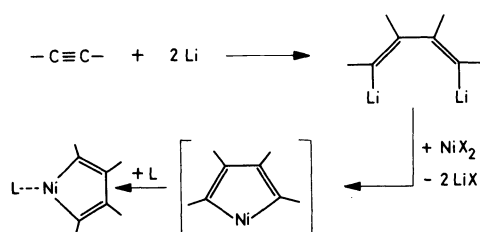


Fig. 26 Synthesis of a nickelocyclopentadiene

If this reaction is carried out in absence of stabilizing ligands a number of different compounds is obtained (31). One of these has a remarkable structure as shown by the x-ray analysis. Nevertheless, the formation of this complex can be explained in the light of the foregoing discussion.

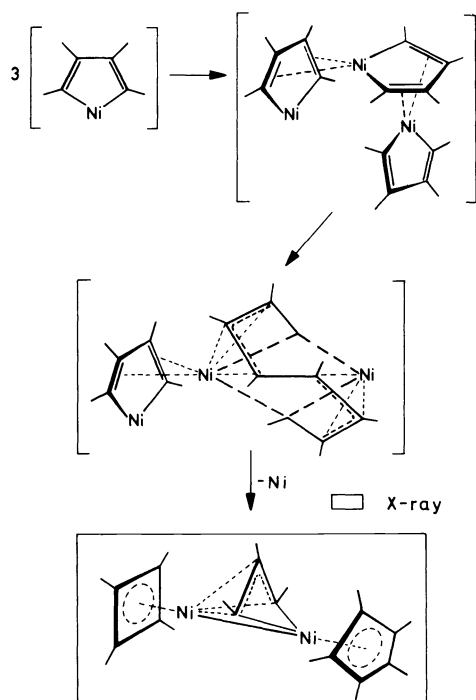


Fig. 27 Proposal of a mechanism for the cleavage of a C_8 -chain under formation of a π -allyl and a cyclopentadienyl group

Let us assume that the initially formed nickelocyclopentadiene polymerizes by coordination. In the next step an eight-membered chain results from a C-C-linking of two cyclopentadienes and the terminal C-atoms are bound in an analogous manner as determined for $(\text{CpCr})_2\text{C}_8\text{H}_8$. In this case no cyclooctatetraene is formed but C-C-cleavage occurs with formation of a π -allyl and a cyclopentadienyl group. In addition one Ni-atom is eliminated with simultaneous formation and coordination of cyclobutadiene to give the triple-decker sandwich with three different ligands.

Finally, I would like to return briefly to the beginning of my lecture and speculate on the relevance of these last mentioned results to the mechanism of Reppe's cyclooctatetraene synthesis. In 1960 we reported the synthesis of a $(\text{COT}\cdot\text{Ni})_2$ (33) which seemed to us at the time to be a polymeric species. Only recently^x has it been possible to determine the structure by x-ray analysis (34) and it is actually a sandwich consisting of two Ni-atoms and two COT-molecules. This complex which is of very limited solubility is able to catalyze the cyclotetramerization of acetylene to cyclooctatetraene and I would like to suggest the following mechanism:

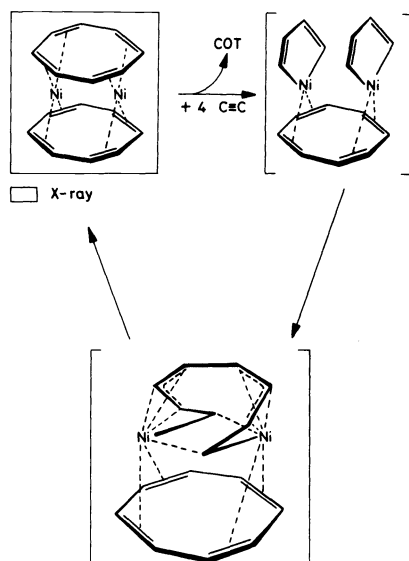


Fig. 28 Proposal of a mechanism for Reppe's COT-synthesis

Four acetylene molecules displace one COT generating two nickelocyclopentadienes which couple together forming a C_8 -chain between both Ni-atoms. Again analogous to $(\text{CpCr})_2\text{C}_8\text{H}_8$ a final C-C-coupling regenerates $(\text{COT})_2\text{Ni}_2$. If this mechanism should be correct the COT itself would have an important function in that it is able to complex both nickel atoms in nearly bonding distance to each other.

Summarizing I would like to point out again the importance of metallocycles as intermediates in catalytic cyclization reactions. The smallest metallocycles, the metallocyclobutanes, apparently are involved in the olefin metathesis while the largest metallocycles are formed as intermediates in the cyclization of 1,3-diolefins. In many cases the catalytic processes are accompanied by a change in the formal oxidation state of the central metal atom - in the sense of a redox system (19b, 35): the formation of a metallocycle from a metal atom and an unsaturated species corresponds to an oxidative addition and the final C-C-coupling process to a reductive elimination. The interactions of two or more metal atoms as catalytically active centres in the homogeneous phase seems to be of fundamental importance and it is to be anticipated that intensive studies will be undertaken in this direction in the future.

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