Some Advances in the Organometallic Chemistry of Nickel

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INTRODUCTION

After the discovery of nickel carbonyl [Ni(CO)₄] by Mond *et al.* (1) in 1890 nearly 50 years elapsed before the extraordinary catalytic activity of the carbonyl began to be recognized. In the period 1939–1940 Reppe (2) discovered the now famous carbonylation and cyclization reactions of acetylenes and olefins which are catalyzed by nickel carbonyl or by complexes derived therefrom. This, and his other work involving acetylene and olefin chemistry initiated further studies, in both industrial and academic laboratories. All this work played an essential part in the many recent developments in the chemistry of π complexes of transition metals. At first for nickel preparative success in the synthesis of π complexes was largely confined to cyclopentadienyls. In fact it appeared as if this transition metal did not have a pronounced tendency to form π complexes with unsaturated hydrocarbons at all. Very recently, however, the nickel atom "gave in" to the combined efforts of several research groups, and some interesting and reactive π complexes have now become known.

It is the purpose of this review to describe developments in the catalytic chemistry of nickel carbonyl, as well as the new π complexes of nickel. Related topics, such as the cyclopentadienyls, cyclobutadienyls, cyanyls, acetylides, or alkyls of nickel will not be discussed unless they are directly related to the above subject matter. Carbonylation reactions will be described first. Apart from the historical aspect, these provide several introductory examples for the various topics reviewed in the later sections.

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CATALYTIC REACTIONS WITH NICKEL CARBONYL

A. Carbonylation of Alkynes

1. Reaction Conditions and Scope

In an attempt to prepare acetylenic aldehydes from acetylene, carbon monoxide, and water in the presence of nickel carbonyl and acids Reppe and co-workers (2, 3) observed formation of acrylic acid. The reaction was soon extended to substituted acetylenes and was found to be general (2, 3, 4). The term "carbonylation" was suggested for describing this group of reactions and we will use it here, although it is not generally accepted in the literature. The reaction can be performed either stoichiometrically (nickel carbonyl is the source of carbon monoxide and is used in stoichiometric quantities) or catalytically (nickel carbonyl, present in catalytic amounts, is continuously regenerated under carbon monoxide pressure). If the carbonylation is conducted in the presence of alcohols, mercaptans, amines, or organic acids, their esters, thioesters, amides, or anhydrides, are obtained respectively. The reaction was originally represented by Eq. (1)

$$4C_2H_2 + 4H_2O + Ni(CO)_4 + 2HCl \rightarrow CH_2 = CH - COOH + NiCl_2 + H_2$$
(1)

More recent work (5), however, indicates that the actual stoichiometry is more complicated. The synthesis is preferably performed in the presence of aqueous hydrochloric, acetic, or phosphoric acids, at temperatures between 50-80°C. If anhydrous acids are used, extensive hydrogenation of the acrylic acid to propionic acid is observed (2, 3). This is attributed to hydrogenation by the hydrogen formed during reaction. Of all the metal carbonyls only cobalt carbonyl can replace nickel. Iron carbonyls do not react when used alone, but a partial conversion occurs if iron pentacarbonyl is mixed with nickel carbonyl. In the catalytic process an equimolecular mixture of acetylene and carbon monoxide is treated under pressure at 120-150°C with either nickel carbonyl or nickel, in the presence of water and an acid. Good results are also obtained using a mixture of metallic nickel and nickel iodide. Particularly well-suited, because of its ready convertibility into nickel carbonyl, is the complex $NiBr_2 \cdot 2P(C_6H_5)_3 \cdot 2C_4H_9Br$ (3). The carbonylation of substituted acetylenes yields unsaturated carboxylic acids. Successful carbonylations have been performed with phenylacetylene, vinylacetylene, phenylmethylacetylene, tolane (diphenyl acetylene), propargyl alcohol, butyne-1-ol-3, butyne-2-diol-1,4 and many other alkynes.

It is interesting to note that a naturally occurring antibiotic, methylenebutyrolactone (II) has been synthesized by carbonylating the acetylenic carbinol (I) (6):

$$\begin{array}{ccc} HO \cdot CH_2 CH_2 C_2 H \rightarrow CH_2 \cdot CH_2 \cdot C=CH_2 \\ & & I \\ O & & CO \\ (I) & (II) \end{array}$$

2. Mechanism

It was assumed (2, 3) as a working hypothesis, that the initial products of the carbonylation of acetylenes were cyclopropenones which, under the reaction conditions, undergo ring opening. This suggestion is invalidated by the fact that cyclopropenones are never detected among the reaction products. More recently it has been shown that diphenylcyclopropenone reacts with nickel carbonyl only after the three-membered ring ketone has been decomposed into carbon monoxide and diphenylacetylene (7). The carbonylation reaction generally requires an induction period, the length of which varies with the acetylenic reactant, the acid, and the temperature (5). The nature of the solvent is unimportant, but water is an essential reaction participant (5). In fact it appears as if free acrylic acids are formed in all cases and that the presence of, for example, an alcohol causes ester formation in a second step. In the absence of water side reactions occur, and only small amounts of unsaturated acids are isolated. Jones et al. (5) have also concluded that the acid molecules rather than protons participate in the main reaction.

A particular acetylene can afford various products depending on the conditions. Diphenylacetylene in the presence of water, acetic acid, and alcohol, affords 38% trans-PhCH: C(Ph)COOH and 10% of its ethyl ester (5). Tolane can also be carbonylated in alkaline solutions (8) where a complex carbonylate, possibly Ni₃(CO)₈²⁻, is the source of carbon monoxide. Under these conditions tetraphenylbutadiene is isolated in addition to trans-PhCH=C(Ph)COOH. The carbonylation of diphenyl-acetylene in dioxane in the presence of absolute alcohol and concentrated hydrochloric acid affords 1,2,3,4-tetraphenyl-2-cyclopentene-1-one (9). Finally, in inert solvents diphenylacetylene reacts with nickel carbonyl, forming both tetraphenylcyclopentadienone and a π complex, bis(tetraphenylcyclopentadienone)-nickel (10) (see Section VI). Since cyclopenta-dienones are often formed by treating alkynes with metal carbonyls other than nickel carbonyl the carbonylation reaction with this carbonyl must be closely related. The only difference apparently arises from the presence of

water and the acid, these constituents affecting the nature of the end products by reacting with an intermediate nickel carbonyl-alkyne complex. The nature of this intermediate is still unknown and the mode of interaction with the acid molecule not yet understood.

It has been suggested (11) that during the induction period a carbonium ion is formed from the proton of the acid and the acetylene molecule, which then reacts with nickel carbonyl. However, it is rather unlikely that this should be so. Acetic acid, even under the conditions of the carbonylation reaction, definitely is not polar enough to protonate alkynes. Very recently (12) it has been suggested that during the induction period a halonickel dicarbonyl hydride is formed, according to Eq. (2)

$$Ni(CO)_4 + HX \rightarrow HNi(CO)_2X + 2CO$$
 (2)

Nickel carbonyl, however, does not react with acids to form such complexes. Nevertheless, it is possible that a reaction similar to (2) could occur with an intermediate alkyne-nickel carbonyl complex, giving rise to the formation of an alkenylnickel dicarbonyl halide, RCH—CH—Ni(CO)₂X, which could then yield the unsaturated acid according to Eq. (3a) or (3b) (12). This reaction formally would resemble the carbonylation of allyl halides, discussed in Section II, C. Divinyl ketones may be formed as by-products of carbonylation (13), and the stereochemistry of addition to the acetylenic linkage is reported to be exclusively *cis* (13).



B. Carbonylation of Olefins

1. Reaction Conditions and Scope

Carbonylation of olefins (14) requires temperatures of $160-300^{\circ}$ C, and can be performed stoichiometrically as well as catalytically. For the latter process total pressure of 150 to 300 atm of carbon monoxide and the olefin are required. The general reaction may be represented by Eq. (4)



Although the reaction is frequently performed in the presence of small amounts of mineral acids these are not a necessary reaction participant and the water may be replaced by alcohols, mercaptans, ammonia, amines, and organic acids. With acetylenes and alcohols the esters are formed at a distinctly slower rate than the free acids, and temperatures of $120-220^{\circ}$ C are required. Nevertheless, yields of ester with olefins having four to eighteen carbon atoms are reported to be 90%. Various by-products are produced, e.g. carbonic acids, aldehydes, ethers, and other olefins. With ethylene small amounts of polyethylene and some higher carboxylic acids are also formed (14).

A large number of olefins have been successfully carbonylated, among them ethylene, propylene, butylene, octene, dialkylethylenes, cyclohexene, cyclooctatetraene, and styrene. Nickel carbonyl can be replaced by mixtures of $Co_2(CO)_8$ with CoI_2 , Ni Cl_2 with Ni, or Ni with CuI. Also nickel propionate, iron pentacarbonyl, and nickel on silica may be used. Apparently, no mechanistic study of this reaction has been performed or published so far.

Alcohols and linear or cyclic aliphatic ethers can be carbonylated to monoor dicarboxylic acids using Ni(CO)₄ in the presence of a "co-catalyst," e.g., CuI or NiI₂ (15). Reaction probably proceeds via olefinic intermediates formed by dehydration of the alcohol or ether. Thus, 1-octanol and 2-octanol both yield the same acid, 2-methyloctanoic (15a).

C. Carbonylation of Allylic Compounds

Reactions of nickel carbonyl with allylic halides have been studied by Chiusoli (16). At 100° and 50 atm of carbon monoxide in the presence of

water, alcohol, and acid, an allylic chloride reacts according to Eq. (5) (16)

$$RCH = CH - CH_2Cl + CO + R'OH \xrightarrow{Ni(CO)_4} RCH = CH - CH_2COOR' + HCl \quad (5)$$

At ordinary pressure only small amounts of acid are isolated; instead, dimerization of the allyl groups occurs (16, 17) (Eq. 6)

$$2RCH = CH - CH_2Cl + Ni(CO)_4 \rightarrow (RCH = CH - CH_2)_2 + NiCl_2 + 4CO$$
(6)

It has been proposed (16) that carbonylation proceeds according to Eqs. (7), (8), and (9)

$$RCH=CH-CH_{2}Cl+Ni(CO)_{4} \xrightarrow{-CO} RCH=CH-CH_{2}-Ni(CO)_{3}+Cl^{-} (7)$$

$$RCH = CH - CH_2 - Ni(CO)_3^+ Cl^- \xrightarrow{+ CO} RCH = CH - CH_2CO - Ni(CO)_3^+ Cl^- (8)$$

$$RCH \longrightarrow CH_2CO \longrightarrow Ni(CO)_3 + Cl^- \xrightarrow{+CO, +ROH} RCH \longrightarrow CH_2COOR + Ni(CO)_4 + HCl \quad (9)$$

Carbonylation of allylic halides in the presence of an acetylene occurs with insertion of one acetylene molecule, according to Eq. (10) (16)

 $RCH = CH - CH_2X + CH = CH + CO + R'OH \xrightarrow{Ni(CO)_4} RCH = CH_2 - CH = CH - COOR' + HC1$ (10)

Phenol is obtained as a by-product and is probably formed in a cyclic transition state (VIII), Eq. (11)



In this connection it is worth noting that phenol is also formed in 97% yield by heating hexadienoic acid (CH₂=CH--CH₂--CH=-CH--COOH)

with zinc chloride and acetic anhydride (18). Interestingly, carbonylation with propargyl chloride occurs without acetylene insertion (16)

$$HC = C - CH_2Cl + CO + H_2O \xrightarrow{Ni(CO)_4} CH_2 = C = CH - COOH + HCl + (12)$$
$$CH_2 = C(COOH) - CH_2 - COOH$$

It has recently been suggested (19) that π -allylnickel complexes are intermediates in reactions involving allylic halides. Although π -allylnickel chloride-triphenylphosphine (IX) is formed from allyl chloride and Ni(CO)₃P(C₆H₅)₃ without yielding a carbonylation product (20), the dimeric π -allylnickel chloride (X) [prepared (13) by heating allyl chloride with nickel carbonyl in benzene solution] reacts rapidly with carbon monoxide to form butenoylnickel dicarbonyl chloride (XI) (Eq. 13). Moreover, this complex is converted by additional carbon monoxide into butenoyl chloride and nickel carbonyl (13), Eq. (14)



 $CH_2 = CH - CH_2CO - Ni(CO)_2X + 2CO \rightarrow CH_2 = CH - CH_2COX + Ni(CO)_4 \quad (14)$

Furthermore, a mixture of acetylene and carbon monoxide reacts with π -allylnickelbromide dimer at 0° C in ether solution to give nickel carbonyl and probably hexadienoyl bromide (13). These experiments indicate that the carbon monoxide must be coordinated to the metal in order to react with the allylic system. Such a mechanism of initial coordination probably also applies to the acetylenes.

D. Miscellaneous Carbonylation Reactions

Under rather vigorous conditions aryl halides may be carbonylated in the presence of nickel carbonyl, water, or alcohol and acid, thereby yielding aryl carboxylic acids or esters, respectively (21-23).

Nickel carbonyl is also an effective dehalogenation agent. Apart from allyl halides (see above) gem-dihalides, e.g. dichlorodiphenylmethane, react with the carbonyl to form tetrasubstituted ethylenes (24). It is to be expected that carbonylation reactions would also occur in this case if the reaction were conducted under CO pressure.

Diazoalkanes are decomposed by nickel carbonyl yielding nitrogen and reaction products indicative of the presence of carbenes as intermediates (25). Although carbenes usually show little tendency to combine with carbon monoxide, formation of ketenes was detected by decomposing the diazoalkanes in the presence of excess nickel carbonyl. This carbonylation of carbenes undoubtedly occurs via nickel-carbene complexes (25)

Diazonium salts also readily react with nickel carbonyl, yielding mainly carboxylic acids and ketones in the presence of water and hydrochloric acid (26, 27). Iron pentacarbonyl and dicobalt octacarbonyl with diazonium salts behave similarly, but the hexacarbonyls of chromium and molybdenum are virtually ineffective. This reaction may be considered as a transition metal-catalyzed carbonylation of aryl radicals, and is closely related to the Meerwein reaction (26).

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SUBSTITUTION REACTIONS WITH NICKEL CARBONYL

The substitution of CO in metal carbonyls by olefinic and acetylenic compounds is one of the chief methods for preparing π complexes of transition metals. Unfortunately this procedure fails almost completely when applied to nickel carbonyl, and this may be one of the reasons why until recently no π complexes of nickel with olefinic or acetylenic ligands were known. The reasons for this behavior of nickel carbonyl will become clearer, if both its electronic structure and the mechanism of the ligand exchange reactions are considered.

A. General Remarks on the Electronic Structure of Nickel Carbonyl

The Ni—C bonds in nickel carbonyl are tetrahedral and of comparable strength to those in metal alkyls (28). To stabilize the coordinative Ni—C

bonds, dative π bonding is required to remove excessive negative charge from the nickel atom. If there were no π bonding at all, the coordinative σ - and π -bonding interactions would produce five antibonding MO's mainly localized at the nickel atom which would be occupied by the ten available nickel (3d/4s) electrons (29). Consequently only a small net bonding energy could result. However, two of the 3d orbitals (mainly the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals) may overlap appreciably with the antibonding π^* orbitals of the carbon monoxide molecules and this will reduce the antibonding character of the two 3d orbitals (29). In view of a comparatively large energy difference between the 3d and the $\pi^*_{C=0}$ orbitals, dative π bonding, although necessary, will not be very effective. It will become larger if the effective Coulomb term of the central metal is lowered, e.g., by giving it a negative electronic charge, but this in turn weakens the coordinative σ and π bonds. Edgell *et al.* (30) demonstrated the change in bond character in the isoelectronic series $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$. The CO-stretching infrared frequencies decrease considerably in going from Ni(CO)₄ to Fe(CO)₄²⁻, indicating a significant increase of dative π bonding in the given order. Thermochemical data (31) suggest that among the carbonyls of chromium, iron, and nickel, the Ni-C bonds are the weakest; approximate bond energies being 55, 58, and 46 kcal respectively, assuming valence states of d^6 , d^8 , and d^{10} for the central atoms (32, 32a).

B. Mechanism of Ligand Exchange Reactions

Ligand exchange reactions with labeled carbon monoxide performed by Basolo and Wojcicki (32) show that the carbonyls $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ exchange CO groups only slowly, whereas Ni(CO)₄ and Co₂(CO)₈ exchange rapidly. The kinetic lability of nickel carbonyl can in part be attributed to the thermodynamic weakness of the Ni—C bonds. The essential point, however, is that the exchange rate is independent of carbon monoxide concentration which supports a dissociative mechanism.

$$Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$$
 (16)

The Arrhenius activation energy for this rate-determining dissociation is 13 kcal/mole (in toluene solution). This value agrees well with the activation energy of the thermal and photochemical decomposition of nickel carbonyl in which the above dissociation (Eq. 16) is also rate determining (33, 34, 35).

The estimated average bond energy for the Ni—C bond lies in the range of 42–77 kcal and thus is much larger than the energy necessary to remove the first CO molecule. This suggests considerable π -bond stabilization of the resulting "fragment" Ni(CO)₃ (32).

It follows from Kimball's group-theoretical considerations (36) that it is only possible to form two strong π bonds from the central atom A to the ligands B in a tetrahedral molecule AB₄, whereas a triangular planar molecule could be stabilized by three strong π bonds. In the sp^2 Ni(CO)₃ fragment two of these π orbitals are filled and can effectively overlap with the antibonding ligand orbitals. It was therefore concluded (32) that the driving force for the dissociative exchange mechanism may be the stabilization effect of π bonding in the transition state. Ligand exchange reactions with various phosphines were performed by Meriwether and Fiene (37) and allow similar conclusions. Evidently dissociative exchange mechanisms are general for tetrahedral complexes of zero-valent nickel. It was found that if the entering ligand L is predominantly σ bonding, the remaining Ni—C bonds in the carbonyl complex will be more strongly stabilized by π bonding. Similar effects have also been demonstrated by measurements of the stretching force constants of the CO and Ni-C bonds in homologous series of complexes Ni(CO)_{4-x} L_x , where L is a phosphine (38).

As a consequence of enhanced π -bond stabilization of the remaining Ni—C bonds, the exchange rate for carbon monoxide and additional phosphines decreases as x in Ni(CO)_{4-x}L_x increases (37, 32). This explains why it is frequently observed that not all CO groups can be substituted by phosphines. A total replacement should only be possible if the ligands have comparable σ - and π -bonding abilities with carbon monoxide (e.g., the halides of phosphorus or some isonitriles). The first steps of the ligand exchange may be represented by Eqs. (16–19):

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$$
 (16)

$$Ni(CO)_3 + L \rightleftharpoons Ni(CO)_3L$$
 (17)

$$Ni(CO)_{3}L \rightleftharpoons Ni(CO)_{2}L + CO$$
 (18)

$$Ni(CO)_2L + L \rightleftharpoons Ni(CO)_2L_2 \tag{19}$$

If π -bond stabilization is accepted as being the driving force for CO replacement, then one would predict that *simple* olefins should not react with nickel carbonyl to yield stable substitution products. Successful exchange reactions are expected, however, if the olefinic ligands are strongly π bonding. A number of such ligands has been found and their reactions with nickel carbonyl will be discussed in the following sections.

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REACTIONS OF NICKEL CARBONYL WITH OLEFINIC COMPOUNDS YIELDING ISOLABLE COMPLEXES

A. Reaction with Cyclopentadiene and Other Olefins

Chelating olefins such as cycloocta-1,5-diene, cyclooctatetraene, or dicyclopentadiene have not yielded isolable complexes by direct reaction with nickel carbonyl, probably for reasons outlined in Section III, B. From this it should not be concluded that such complexes are incapable of existence. Using reactions in which nickel carbonyl is not the reactant it has been possible to prepare not only complexes of cyclooctadiene and cyclooctatetraene, but also of simple monoolefins (Section IX).

Norbornadiene when heated with nickel carbonyl also does not afford a complex, but is dimerized and carbonylated (Section VIII, C). Cyclopentadiene when refluxed with nickel carbonyl yields red, crystalline (m.p. 41–42°C), volatile, and air-sensitive, π -cyclopentenylcyclopentadienylnickel (XIII) (39, 40, 41). This complex may also be obtained from nickelocene by reducing it with sodium amalgam in absolute ethanol (40). The mechanism of its formation from nickel carbonyl is unknown. One might speculate that it is formed via the intermediate (XII)



A methyl-substituted compound (XIII) is obtained similarly from nickel carbonyl and methylcyclopentadiene (41a). Analogous to (XIII) is π -allyl-cyclopentadienylnickel, which was prepared from π -allylnickel (II) bromide and sodium cyclopentadienide (41b).

B. Reactions with Vinyl Compounds [Bis(acrylonitrile)-nickel and Derivatives]

1. Bis(acrylonitrile)-nickel

It was observed by the author in 1958 that if nickel carbonyl is refluxed with acrylonitrile in an inert atmosphere all four molecules of carbon monoxide are replaced by two molecules of acrylonitrile and red, crystalline bis(acrylonitrile)-nickel is formed (42). The compound is insoluble in all noncoordinating solvents, as well as being nonvolatile and pyrophoric. It decomposes irreversibly at about 105° into nickel and monomeric acrylonitrile. Spectral evidence unambiguously shows that the nickel atom must be coordinated to the olefinic double bond, and the nitrile groups interact with the metal atom little if at all. For the molecular unit a structure (XIV) was proposed which is also in accord with a more detailed infrared analysis (43). The complex is undoubtedly associated in the solid state, as follows from its physical properties. It is relatively inert to molecular hydrogen. Rhodium-supported hydrogenation catalysts are required to hydrogenate the coordinated acrylonitrile at normal pressure (44). It is possible that the complex has a chain structure with multicenter or metal-metal bonds (or both) between the individual molecules (XV), but it is difficult to assess the detailed nature of such intermolecular interactions without an accurate structural determination. Unfortunately, it is very difficult to grow single



crystals, so that a very interesting structural problem still awaits final solution.

Well-defined 1:1 and 1:2 adducts with triphenylphosphine are formed with ease (42, 45, 46). The yellow 1:1 adduct is more stable than bis(acrylonitrile)-nickel itself (dec. p. 185° C) and represents one of the first examples of a nickel complex with the coordination number three. The 2:1 adduct is monomeric in benzene and has a dipole moment of 6 Debye units (46). Unstable bis(pyridine) adducts were also isolated, but were found to decompose at room temperature, depositing metallic nickel (46).

Owing to the presence of the strongly electronegative CN group, acrylonitrile possesses a low-lying unoccupied molecular orbital which may effectively overlap with a 3d orbital of the nickel atom. The question of why acrylonitrile coordinates through the double bond rather than through the



FIG. 1. MO coefficients of the highest bonding (Ψ_2) and the lowest antibonding (Ψ_3) MO's in acrylonitrile. For the parameters used, see ref. (47).

nitrile group may be answered by employing MO theory (47). The MO coefficients of the two most strongly interacting acrylonitrile orbitals (which are the highest occupied and the lowest unoccupied MO's) are particularly large at the olefinic carbon atoms. Consequently, the positions of highest σ -donating and π -accepting strength are localized at the olefinic carbon atoms, which therefore will be the favored coordination sites for the nickel atom (Fig. 1).

Calculations for a monomeric structural unit show that dative π bonding is greatest if the nickel atom interacts symmetrically with the double bond (47). The reason why all four CO molecules are lost by simply refluxing nickel carbonyl with acrylonitrile is a consequence of the significant π bonding ability of this ligand. The replacement of two CO groups by two acrylonitrile molecules would lead to a Ni(CO)₂(CH₂=CHCN)₂, in which the π bonds would be mainly localized between the nickel atom and the CH₂=CHCN molecules, and this would provide insufficient stabilization for the CO groups. For precisely the same reason a complex of composition Ni(H₂C=CHCN)₄ is incapable of existence. The formation of stable mono and bis adducts with phosphines, on the other hand, is to be expected as the latter are mainly σ bonding (37). It was recently found that bis(acrylo-nitrile)-nickel is not formed if the reaction is performed under moderate carbon monoxide pressure. Evidently carbon monoxide may effectively compete with the acrylonitrile during the substitution process.

The complex (XIV) is diamagnetic. Previously reported small paramagnetic moments have now been recognized as being due to impurities (traces of finely divided metallic nickel) (47).

2. Structural Analogs

Complexes analogous to bis(acrylonitrile)-nickel were obtained with cinnamonitrile, fumaronitrile, acrolein, and maleic anhydride. Bis(cinnamonitrile)-nickel is dark violet in color and is somewhat less stable than the acrylonitrile complex (42, 46), whereas bis(fumaronitrile)-nickel appears to be more stable. Both complexes dissolve in bases such as pyridine, forming nonconducting, air-sensitive solutions (46). Bis(acrolein)-nickel is obtained in a manner similar to the acrylonitrile compound and forms deeply violet crystals which decompose at about 90-95°C into nickel and monomeric acrolein (42, 46). In the infrared spectrum (43) the C=C stretch is shifted only slightly as compared with liquid acrolein (1616 cm⁻¹ in liquid acrolein, 1605 cm^{-1} in the complex), and there is only a small change in the C-H out-of-plane vibration. The carbonyl frequency decreases from 1675 to 1518 cm⁻¹ upon complex formation. This indicates that the carbonyl group must be very strongly polarized, suggesting strong electron back-donation. It is, however, not known whether the oxygen atoms participate directly in the bonding or not. Bis(acrolein)-nickel also forms adducts with triphenyl phosphine. Its relationship to bis(acrylonitrile)-nickel may be elegantly demonstrated by treating it with acrylonitrile. Even at room temperature acrolein molecules are replaced, and bis(acrylonitrile)-nickel is formed (46). Maleic anhydride forms a complex which resembles bis(fumaronitrile)nickel in its reactivity, but the compound has not yet been extensively studied (49, 50).

3. Complexes Formed from 1,1-Dicyano- and 1,1,2-Tricyanoethylenes

The unsubstituted 1,1-dicyano- and 1,1,2-tricyanoethylenes are extremely reactive and polymerize when heated with nickel carbonyl. Phenylsubstituted derivatives of these nitriles, however, react with nickel carbonyl to form complexes. In contrast with acrylonitrile and fumaronitrile, only 1:1 species are formed. This has been attributed to the high electron affinity of these ligands. From spectral data and because of the chemical properties polymeric structures (XVI) were proposed (51). Tetracyanoethylene also reacts with nickel carbonyl but only saltlike ill-defined products were isolated, in which nickel is present in the +2 oxidation state (51, 52).



The compounds derived from 1,1-dicyanoethylene, and especially phenyltricyanoethylene, must still be regarded as covalent π complexes although they represent rare examples of compounds practically at the verge of oxidation. Thus in the solid state nickel-phenyltricyanoethylene exhibits ESR signals, indicating that a fraction of the valence electrons of nickel already occupy a low-lying ligand orbital. The complex also is paramagnetic with $\mu = 2.11$ B.M. (51). Both complexes dissolve in various bases, e.g., pyridine or piperidine, forming Ni(II) ions and ligand dianions (XVII); strong ESR signals appear close to the g factor of 2 in such solutions. With tri-n-butylphosphine 2:1 adducts (XVIII) are formed. These are diamagnetic and monomeric in benzene. Their infrared spectra establish that they are π complexes in which the nickel atom interacts with the olefinic double bond (51).

REACTIONS OF NICKEL CARBONYL WITH QUINONES

A. General Remarks

The fact that quinones may form π complexes with transition metals was first recognized by Sternberg *et al.* (53), who found that butyne reacts with iron pentacarbonyl in sunlight to afford duroquinone-iron tricarbonyl (XIX). These authors also reported that manganese pentacarbonyl hydride yields durohydroquinone under similar conditions whereas nickel carbonyl did not react (53a). However, more recent work has established that duroquinone and some other substituted quinones are capable of forming Ni(O) complexes, most of which are surprisingly stable.



B. Bis(duroquinone)-nickel

Most quinones, instead of forming π complexes, react with nickel carbonyl yielding salt like materials. With *p*-benzoquinone, for instance, a nearly black, insoluble, hydroscopic and paramagnetic ($\mu_{eff} = 3.3$ B.M.) material of composition Ni(quinone)₂ was obtained which is best formulated as Ni²⁺(quinone)₂²⁻ and considered as a metallic quinhydrone type of compound (54). However, duroquinone behaves exceptionally. In a smooth reaction all four molecules of carbon monoxide are evolved and red, crystalline, diamagnetic bis(duroquinone)-nickel (XX) (54) is obtained. This complex is stable in air and begins to decompose without melting at 205° C. It is nearly insoluble in all solvents except dichloromethane, in which it is monomeric. In the infrared spectrum, the quinone C==O stretching frequency appears at 1577 cm⁻¹ (in free duroquinone it is 1629 cm^{-1}), which again suggests extensive electron back-donation to the ligand from nickel. When heated *in vacuo*, it releases one molecule of duroquinone at about 160° C and yields a violet, pyrophoric residue of approximate composition Ni(duroquinone) (55). This material is insoluble in all common solvents, and is rapidly decomposed by dilute acids to Ni(II) ion and durohydroquinone. Extraction with warm dichloromethane yields bis(duroquinone)-nickel and a nickel-containing residue. From the similarity of its infrared spectrum with that of bis(duroquinone)-nickel, an associated structure (XXI) appears most probable



Since the donor strength of duroquinone is rather small, the capacity of the nickel atom in stabilizing *two* duroquinone molecules by dative π bonding is probably limited. The situation is similar to that in the nickel complexes of the 1,1-dicyano- and 1,1,2-tricyanoethylenes which also form only 1:1 complexes (Section IV, B, 3). During thermal decomposition of (XX) monomeric, coordinately unsaturated "Ni(duroquinone)" is formed. This species is evidently very reactive and rapidly associates to (XXI). It may be trapped in the monomeric state if generated in the presence of electron donors such as cyclic dienes and some phosphines. Under these conditions new complexes of composition olefin-Ni(0)-duroquinone and (phosphine)₂-Ni(0)-duroquinone are formed (55, 56, 57).

C. Complexes of Nickel with Duroquinone and Cyclic Olefins

It was found that if bis(duroquinone)-nickel is thermally decomposed in the presence of cyclooctatetraene, cyclooctatetraene-duroquinone-nickel, (XXII), is obtained (56). A more convenient synthesis was found shortly thereafter in a one-step reaction of duroquinone with nickel carbonyl in the presence of the polyolefin. Using the same procedure, analogous complexes with various other olefins were made, the properties of which are listed in Table I. Only olefins containing at least two roughly parallel double bonds are suitable as ligands and it follows from the NMR spectra of the complexes that they must have highly symmetrical structures, e.g., (XXIII, XXIV, and XXV) (55, 56). An X-ray structural determination of cycloocta-1,5diene-duroquinone-nickel has been performed by Glick and Dabl (56a). The space group is P(2/n) with four molecules per unit cell, a = 14.26,

TABLE I

Complex	Dec. p. (°C)	IR C=O (cm ⁻¹)	Dipole moment (Debye)	Color
Bis(duroquinone)-Ni(0)	205	1577	b	Brick red
Cyclooctatetraene-duroquinone-Ni(0)	165	1553	3.47	Brown-red
Cyclooctatriene-duroquinone-Ni(0)	151-152	1553	3.77	Brown-red
Cycloocta-1,5-diene-duroquinone-Ni(0)	205	1553	4.30	Dark red
Bicyclo(2.2.1)heptadiene-duroquinone-Ni(0)	130	1546	4.07	Brown-red
endo-Dicyclopentadiene-duroquinone-Ni(0)	137	1553	4.23	Brown
Cyclooctatrienone-duroquinone-Ni(0)	123-125	1565	ь	Dark red

PROPERTIES OF DUROQUINONE COMPLEXES OF NICKEL^a

^a References (55, 56, 58).

^b Dipole moment could not be determined due to insufficient solubility.

b = 7.95, and c = 14.17 Å. The nickel is symmetrically bonded to the double bond centers of both the cyclooctadiene and the duroquinone molecules. The arrangement of the four double bonds is such that a tetrahedrally coordinated nickel results. Similar structures may be anticipated for the remaining complexes of the type olefin-duroquinone-nickel.

All complexes of this kind are quite polar and water soluble. The permanent dipole moments are caused by the fact that the olefinic ligands are predominantly donors and only weak acceptors so that the duroquinone molecule interacts with filled 3d orbitals of nickel even more strongly than in the case of bis(duroquinone)-nickel. Consequently, the quinone C==O groups are more polarized than in the parent compound bis(duroquinone)-nickel (see Table I). The particularly high stability and polarity of the



cycloocta-1,5-diene complex is undoubtedly due to the favourable steric arrangement of the coordinating double bonds. Cyclooctatetraene, on the other hand, is a weaker donor as the distance between the adjacent double bonds is probably somewhat greater than in cycloocta-1,5-diene. It is instructive to compare the complex of cycloocta-1,3,5-triene with that of cyclooctatrienone. In spite of the nonplanarity of the latter ligand, the presence of the electronegative CO group would be expected to increase slightly the acceptor strength of the olefinic double bonds with respect to cyclooctatriene. This in turn would weaken the dative π bonds from the nickel atom to the duroquinone molecule. The relative positions of the

duroquinone C=O stretching frequencies in both (XXVI) and (XXVII) support this idea.



During thermal decomposition of the complexes in vacuo the olefinic component is released first and the nickel-quinone (1:1) complex (XXI) is again formed. The olefinic ligands can also be replaced by others, but the exchange reaction will only occur under relatively mild conditions (heating to 80–100° C in the presence of the displacing olefin) if a more stable complex is to be obtained. To convert a stable complex, e.g., cycloocta-1,5-dieneduroquinone-nickel, into a relatively labile one, e.g., bicycloheptadieneduroquinone-nickel(0), temperatures of more than 120° C are required and yields are poor. From such experiments a stability sequence for the complexes was obtained which parallels the dipole moments (56) (Table I). All complexes are converted into nickel carbonyl at 100 atm of CO and at 60° C, but are recovered unchanged at lower temperatures (59). When an attempt (56) was made to convert bis(duroquinone)-nickel into bis(acrylonitrile)nickel by treating (XX) with acrylonitrile it was found that this ligand rapidly decomposes the duroquinone complex with simultaneous formation of nickel-containing polyacrylonitrile. It has been suggested that this polymerization is initiated by the monomeric Ni(duroquinone) (56).

All the duroquinone-nickel complexes are diamagnetic. Attempts to prepare similar compounds with o-quinones have failed. It is also impossible to prepare bis(trimethylquinone)-nickel. Instead, the Ni(II) salt of trimethylquinone is isolated (58). Evidently a slight increase in the electron affinity of the quinone π system is sufficient to induce oxidation of nickel.

D. Complexes of Nickel with Duroquinone and Phosphines

The reaction of nickel carbonyl with duroquinone in the presence of an excess of triphenylphosphine produces the insoluble Ni(duroquinone). The same reaction in the presence of tri-*n*-butylphosphine, however, yields red, crystalline air-sensitive bis(tributylphosphine)-duroquinone-nickel (XXVIII), Eq. (20), (57).



E. Complexes with Other Quinones

When *p*-benzoquinone or toluquinone are treated with nickel carbonyl in the presence of cycloocta-1,5-diene only Ni(II)-hydroquinone or quinhydrone salts, respectively, are formed. When the somewhat less strongly oxidizing 2,5- or 2,6-dimethyl quinones are treated with nickel carbonyl under the same conditions cycloocta-1,5-diene-dimethylquinone-Ni(0) complexes are obtained. These substances resemble their duroquinone

TABLE II

C=0	STRETCHING	Frequencies	AND	DECOMPOSITION	Points	OF	Cycloocta-1,5-diene-
		NICKEL	Сом	PLEXES OF SOME	QUINON	ESa	

	CO stretching fro	2	
Quinone	In the free quinone	In the complex	Dec. p. (°C)
Duroquinone	1629	1553	205
Trimethylquinone	1650	1574	118-120
2,5-Dimethylquinone	1664	1580	150
2,6-Dimethylquinone	1654	1570	109–110
d, l - α -Tocopherylquinone	1647	1533	100

^a References (58, 59).

analog. 2,3-Dimethylquinone, however, oxidizes the nickel atom. The analogous trimethylquinone-nickel complex of cycloocta-1,5-diene has been prepared and has a dipole moment of 4.78D in benzene solution (58). All these complexes are readily soluble in water, but are somewhat less stable than the corresponding duroquinone complexes. Aqueous solutions are yellow-red and nonconducting. The C=O infrared stretching frequencies and decomposition points are listed in Table II.

It is worth mentioning that the first transition metal complex of a natural product was obtained by treating tocopherylquinone (vitamin-E-quinone) with nickel carbonyl in the presence of cycloocta-1,5-diene. A study of its physiological properties promises to be interesting (59).

F. Electronic Structure, Spectra, and Magnetism of Quinone Complexes of Nickel

1. Bis(duroquinone)-nickel

Molecular Orbital Theory has been applied (60) to complexes of the type duroquinone-Fe(CO)₃ and has also been used for bis(duroquinone)-nickel (61). The calculation was performed for the two possible symmetries, D_{2h}



(XXIX) and D_{2d} (XXX), respectively. From the magnitude of the calculated overlap integrals it follows that dative π bonding must be quite strong. Adopting the energetical sequence of the quinone MO's

$$1b_{1u} < 1b_{2g} < 2b_{1u} < b_{3g} < 2b_{2g} < 1a_u < 3b_{1u} < 3b_{2g}$$

$$(62)$$

it is concluded that for energetical reasons the interactions $2b_{1u}-4s/4p_z$, $b_{3g}-3d_{yz}/4p_y$, and $2b_{2g}-3d_{xz}/4p_x$ will be the most important. The first two correspond to the coordinative σ and π bonds and the last to the dative π bond. As the $2b_{2g}$ orbital is at low energy significant charge transfer from the nickel atom to the quinone molecule is to be expected. Depending on the electron affinity of the quinone, this may become so strong that the nickel atom is oxidized and only saltlike products are formed. The presence of the four CH₃ groups in duroquinone, however, lowers the electron affinity of the quinone π system to such an extent that a π complex may exist. For the twenty-six available electrons twelve bonding or relatively low energy nonbonding MO's may be used. Two electrons must be placed in an antibonding orbital, localized mainly on the nickel atom. This is expected to lower the stability of the complex and lead to a longer metal–, ring distance. Similar results are obtained for D_{2d} symmetry of the complex, in which four electrons would have to occupy an antibonding doubly degenerate metal orbital. For both (XXIX) and (XXX), however, the same total orbital stabilization results. Simple MO theory thus does not allow any predictions as to which of the two structures will be assumed.

2. Olefin-Quinone-Nickel Complexes

Complexes of this type have been treated assuming C_{2v} symmetry for the molecule, e.g., cycloocta-1,5-diene-duroquinone-nickel (61). It is possible to place twenty of the twenty-two electrons into ten bonding or virtually nonbonding orbitals. However, again two electrons must occupy an antibonding level. Owing to the absence of similar low-lying orbitals in the olefinic ligands, dative π bonding will be largely restricted between the metal and the quinone, causing an unsymmetrical charge distribution in these complexes.

3. Electronic Spectra

Spectra of some of the complexes are given in Fig. 2. The three characteristic absorptions in the spectra of quinones have been assigned to $n \rightarrow 2b_{2g}$ $b_{3g} \rightarrow 2b_{2g}$, and $2b_{1u} \rightarrow 2b_{2g}$ -transitions, respectively (62). It follows from the calculated orbital energies in the complexes (61) that the $b_{3g} \rightarrow 2b_{2g}$ - transition should be shifted to higher energies upon complex formation, whereas the remaining quinone transitions would remain almost unaffected. This indeed has been found to be the case. Experimental term-level schemes are given in Fig. 3. In addition to the quinone transitions, a new band is observed which was assigned to a charge transfer transition from the highest filled nickel orbital to the lowest unoccupied MO in the complexes. A duroquinone complex of cobalt, duroquinone-cyclopentadienylcobalt was recently prepared and found to have a very similar term-level scheme (64). Transitions involving the olefinic components in complexes of the type olefin-duroquinone-nickel have not been observed. They are expected to occur at shorter wavelengths and may be partly covered by the intense quinone $\log \varepsilon_{mol}$



FIG. 2. Electronic spectra of some duroquinone-Ni(0) complexes, recorded in methanol solution (63). $\times - \times - \times$ Bis(duroquinone)-nickel; $\triangle - \triangle - \triangle -$ cyclooctadiene-duroquinone-nickel; $- \bigcirc - \bigcirc - \bigcirc -$ norbornadiene-duroquinone-nickel.



FIG. 3. Experimental term-level schemes for duroquinone, bis(duroquinone)-nickel, and cyclooctatetraene-duroquinone-nickel (61).

transitions. In cyclooctatrienone-duroquinone-nickel, however, such transitions have been observed, as this cyclic ligand absorbs at longer wavelengths than unsubstituted cycloolefins.

Application of the quantum mechanical selection rules to the transitions

in bis(duroquinone)-nickel revealed that for D_{2d} symmetry of the complex all transitions are allowed, whereas for D_{2h} the transition corresponding to $b_{3g} \rightarrow 2b_{2g}$ in the isolated quinone molecule should remain symmetry forbidden. As the intensity of this transition is found to be comparatively low, it has been concluded that bis(duroquinone)-nickel has D_{2h} symmetry. In the olefin-duroquinone-nickel complexes all quinone transitions are allowed and appear with high intensity. This symmetry assignment may be incorrect in view of the observed structure of cycloocta-1,5-diene, duroquinone-nickel (see Section V, C), and symmetry D_{2d} , with a tetrahedral nickel atom, now appears more probable.

4. Magnetic Properties

According to the MO treatment, all duroquinone complexes should have a singlet ground state and should be diamagnetic. This has been confirmed by experiment. However, the cycloocta-1,5-diene complexes of Ni with 2,5- or 2,6-dimethylquinone are paramagnetic in the solid state with moments of 1.5 and 2.75 B.M., respectively (64). If it is assumed that the total wave function for these complexes already contains ionic contributions, as indicated by (XXXI), it is probable that intramolecular oxidation takes place, causing the observed magnetic moments.



VI

REACTION BETWEEN NICKEL CARBONYL AND ACETYLENES WHICH YIELD COMPLEXES

Reactions between nickel carbonyl and acetylenes which afford isolable complexes are rare. Diphenylacetylene is exceptional in that it yields nearly black, diamagnetic, unreactive bis(tetracyclone)-nickel (11). This complex may also be prepared directly from tetracyclone and nickel carbonyl. In its infrared spectrum the C=O stretch appears at 1597 cm⁻¹ (in free tetracyclone it is 1715 cm⁻¹). This significant decrease in frequency shows that electron back-donation must be stronger than in the tricarbonyliron complexes of tetracyclone, in which the same band appears at 1642 cm⁻¹.



VII

POLYMERIZATION OF ALKYNES BY PHOSPHINE-NICKEL CARBONYLS

In 1940 Reppe and Schweckendieck discovered that phosphine-substituted nickel carbonyl complexes could catalyze the cyclization of acetylenes (2, 65). This work has recently been extended by several groups of workers. An excellent review summarizing this topic has been written by Hübel and Hoogzand (66), and this article is warmly recommended to the reader. To avoid duplication we will only summarize briefly the present state of this field.

A. Reaction Conditions and Scope

In order to initiate the polymerization reaction, catalyst pretreatment is necessary. Various methods have been suggested, e.g. warming the solution to $100-110^{\circ}$ C in the presence of acetylenes, or agitating the reaction mixture by stirring (2, 67). The main reaction during the catalyst development is the evolution of carbon monoxide. Evidently a labile nickel-phosphineacetylene complex is formed. With this pretreated catalyst the trimerization of acetylene proceeds readily at temperatures of $60-70^{\circ}$ C and 15 atm of acetylene, yielding benzene and styrene in about 88% and 12% yield respectively (2, 65). A large number of monosubstituted but only a few disubstituted acetylenes may be cyclized similarly.

A detailed study of such reactions has been made by Meriwether *et al.* (67-70). The ability of monosubstituted acetylenes to form benzene derivatives depends on the substituent, and decreases from methyl to *n*-pentyl, indicating a steric effect. Linear oligomers are often formed as by-products. Monosubstituted alkynes carrying bulky groups, e.g. cyclohexylacetylene, yield only a linear dimer, whereas *t*-butylacetylene fails to react at all. The influence of the substituents is of course not only a steric one. Thus the yields of desired aromatic decrease in the sequence R = -COOR, -OR, COR, $-CH_2OH$, $-CH = CH_2$, -Ph, -Me, and *n*-pentyl. This sequence is difficult to interpret, although it would appear that the presence of polar groups generally facilitates trimerization. However, cyanoacetylene reportedly does not trimerize (67).

Less reactive 1-alkynes yield linear oligomers more readily than benzene derivatives. The chain lengths of the products varied from two to seven. Usually mixtures of several isomers are obtained, e.g.,

$$RC \equiv C - C(R) = CH - CH = CHR,$$

$$RC \equiv C - CH = C(R) - CH = CH - R,$$

$$RC \equiv C - [C(R) = CH - C(R) = CH -]_n - CH = CHR, \text{ or}$$

$$RC \equiv C - [C(R) = CH - CR = CH -]_n - CR = CH_2.$$

Insertion of the alkyne molecules appears to be exclusively *cis*. Most disubstituted acetylenes were found to be unreactive (e.g. 2-butyne, 3-hexyne, tolane, 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 1,4-dichloro-2-butyne, 2-butyne-1,4-dioldiacetate, diethyl-acetylene dicarboxylate, and phenylpropiolic acid). Butyne-1,4-diol is exceptional in forming high yields of hexamethylolbenzene (67, 71). Disubstituted conjugated diacetylenes also failed to react, but terminal unconjugated diacetylenes with the complex Ni(CO)₂ · 2P(C₆H₅)₃ yielded both high and low molecular weight polymers and aromatic ring structures (69)



Co-trimerization of the unreactive disubstituted acetylenes with acetylene proved possible in some cases. For instance, acetylene with 2-butyne produced benzene, o-xylene (72), tetramethylbenzene (67), and styrene (72, 67). Acetylene and divinylacetylene yielded mainly o-divinylbenzene (73, 74). The co-trimerization of acetylene with vinylacetylene yielded styrene (75). This reaction probably also accounts for formation of styrene during cyclotrimerization of acetylene, because small amounts of vinylacetylene are usually present or are formed from acetylene under the reaction conditions.

B. Mechanism of Formation of Linear Polymers

When deuterated 1-heptyne was polymerized it reacted at a considerably slower rate than the undeuterated species (70). Meriwether *et al.* conclude from this important effect that cleavage of a carbon-hydrogen bond determines the rate and that only one hydrogen transfer is involved in the formation of product. They assume intermediate σ -bonded species containing Ni—H and Ni—C bonds (XXXIII), (XXXIV), and (XXXV), (Fig. 4).

There is evidence for the intermediate formation of nickel hydrideacetylides in the polymerizations. Addition of $Ni(CO)_2 \cdot 2P(C_6H_5)_3$ to a mixture of 1-heptyne-1-*d* and 1-pentyne leads to a rapid deuterium exchange after an induction period (70). Rate-determining steps for this transition metal-assisted deuterium-hydrogen exchange are considered to be the termination and the catalyst recovery processes which involve the transfer of a hydrogen atom and the cleavage and formation of a new Ni—C bond. The suggested mechanism for linear oligomerization of alkynes thus reflects current mechanistic ideas on Ziegler-Natta polymerization reactions (70). However, some doubt must be cast on the assumed structure of some of the intermediate complexes.

Reactions between alkynes and phosphine-nickel carbonyl complexes show a remarkable insensitivity toward the solvent and may be performed



FIG. 4. Assumed mechanism of formation of linear oligomers by treating mono-substituted alkynes with Reppe catalysts (70).

in methanol, ethanol, cyclohexane, benzene, dimethylformamide, or acetonitrile without any essential difference in rate. It is difficult to see why this should be so, if the intermediate complexes are indeed square planar complexes of Ni(II) as has been suggested (70). It is interesting to note that the complexes Ni(CO)₃PR₃ and Ni(CO)₂·2PR₃ hardly differ from each other in their catalytic efficiency and that chelating phosphines as substituents in the nickel carbonyl complexes have no inhibiting effects (70).

C. Mechanism of the Aromatization Reaction

Meriwether *et al.* (70) also proposed a mechanism for the aromatization reaction, shown in Fig. 5. According to these workers formation of benzene derivatives would necessitate migration of hydrogen atoms. Since some disubstituted alkynes may also be cyclotrimerized with phosphine-nickel carbonyl catalysts, this mechanism is less probable.



FIG. 5. Proposed mechanism of formation of benzene derivatives (70).

VIII

CATALYTIC REACTIONS OF BIS(ACRYLONITRILE)-NICKEL AND DERIVATIVES

A. General Remarks on Transition Metal-Catalyzed Reactions of Alkynes

Reactions between alkynes and transition metal compounds yield a surprising variety of products (76, 77), indicating nonspecific mechanisms of formation. At least for the reaction of alkynes with metal carbonyls any simple polar mechanism must be excluded, in view of the insensitivity of the reactions to the degree of polarity of the solvents. A radical mechanism would perhaps be better suited for a general description but this has so far been rejected, since inhibition of the reactions with *t*-butylphenol or hydroquinone proved unsuccessful (78). Likewise, iron carbonyls react with diphenylacetylene, using ethyl acrylate, vinyl methyl ketone or vinyl acetate as the solvent, without polymerization of the vinyl compounds (79). These experiments, however, do not fully eliminate the possibility of a radical mechanism.

We have recently found (79a) that during polymerization of both monoand disubstituted acetylenes with a large variety of catalysts [e.g., phosphine substituted nickel carbonyls, nickelous cyanide, bis(acrylonitrile)-nickel, nickel acetylacetonate, bis(salicylaldehyde)-nickel, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$ or $PdCl_2.2C_6H_5CN$] *electron resonance signals* with g factors of about 2.0028 are detected if the viscosity of the reaction medium is kept high. Nevertheless, it is difficult to assess the mechanistic significance of the observation and a more detailed study of this effect is necessary. At any rate the fact that radicals are produced in transition metal-catalyzed alkyne polymerizations indicates the dramatic activation of the acetylenic carbon atoms in such reactions.

Acetylenes are *a priori* electron-donating ligands with only weak acceptor properties and their π complexes should be relatively labile. The initial step of at least some of the reactions could be a conversion of the complexed acetylene in its ground state to a biradical with sp^2 hybridized carbon atoms. This "activated" acetylene complex may then stabilize itself in many ways, depending largely on the type of the additional coordinated ligands in the transition state.

Longuet-Higgins and Orgel (80) predicted that two π -bonded acetylene molecules should combine to form a cyclobutadiene complex, a proposal which was brilliantly confirmed (81). The formation of four-membered rings, however, occurs only relatively rarely, and many different ways in which π -complexed acetylenes react have become known.

Two limiting cases may be distinguished: In certain simple cases, particularly if cyclic reaction products are formed it is possible to assume that the new C—C bonds are closed simultaneously. Such reactions could be properly described as " π -complex multicenter processes" (79). The linear polymerization of alkynes in which the new C—C bonds cannot be formed simultaneously may be considered the other extreme possibility, but it must also be expected that there are intermediate cases between these two types of reaction. In view of the generally nonspecific action of the catalysts any generalizations must be treated with caution. The reactions of alkynes and of norbornadiene with bis(acrylonitrile)-nickel and related complexes, however, appear to be simple enough to allow some mechanistic conclusions.

B. Reactions with Alkynes

Bis(acrylonitrile)-nickel is coordinately unsaturated and may be expected to add two acetylene molecules, forming intermediate 2:1 adducts of composition Ni(CH₂=CHCN)₂ · (alkyne)₂. The coordinated ligands (Fig. 6) could condense, in a fashion which will not be further specified, to form a benzonitrile derivative and a "fragment," Ni(CH₂=CHCN). The latter might add three more alkyne molecules to form a complex Ni(CH₂=CHCN)(alkyne)₃, which could produce a benzene derivative. These possibilities have been verified by treating bis(acrylonitrile)-nickel with diphenylacetylene, thereby affording 1,2,3,4-tetraphenylbenzonitrile and hexaphenylbenzene (79). Bis(acrolein)-nickel behaves similarly, producing tetraphenylbenzaldehyde. With acetylene, heptatrienenitrile (XXXVIII), benzene, and cyclooctatetraene are obtained in approximately



FIG. 6. Schematic representation of the reaction between bis(acrylonitrile)-nickel and diphenylacetylene (79).

stoichiometric yields (Fig. 7). The reaction of acetylene with bis(acrylonitrile)-nickel is not catalytic. During reaction, the π -bonded acrylonitrile molecules are displaced by acetylene molecules. The final intermediate complex would have the composition Ni(C₂H₂)₄ and could decompose into nickel and cyclooctatetraene. The nickel atom evidently cannot be resolvated by acetylene and the reaction comes to an end.

The reactions of bis(acrylonitrile)-nickel with acetylene do become catalytic if performed in the presence of triphenylphosphine (79). Under these conditions benzene is formed in excellent yields, using only small amounts of catalyst. Benzene formation has been accounted for by the scheme shown in Fig. 8 (79). Similar schemes to explain the formation of benzene derivatives have been used by other authors, especially Zeiss (77).



FIG. 7. Some reactions of bis(acrylonitrile)-nickel.

Triphenylphosphine stabilizes the nickel atom by forming a complex. As it blocks at least one of the coordination positions on the nickel atom, only three acetylene molecules may add to it, thus making the formation of cyclooctatetraene impossible (79). Complexes of nickel with 1,1-dicyanoand 1,1,2-tricyanoethylene behave similarly, yielding approximately stoichiometric quantities of benzene and cyclooctatetraene C_8H_8 , but affording exclusively benzene in the presence of triphenylphosphine (51, 82). The original catalysts for Reppe's (2, 83) cyclooctatetraene synthesis were all



FIG. 8. Suggested mechanism of benzene formation.

Ni(II) complexes. They are indeed much more effective and their function is different (84, 85).

Treatment of propiolic esters with catalysts of the type Ni(PX₃)₄ affords small amounts of tetrasubstituted cyclooctatetraenes in addition to benzene derivatives. This is the only other reported instance of cyclotetramerization of an alkyne using a Ni(0) catalyst (86). The synthesis of heptatrienenitrile was discovered in 1952 by Cairns *et al.* (87). These authors treated acetylene with acrylonitrile in the presence of phosphine-substituted nickel carbonyls. Under these conditions the reaction requires an induction period during which bis(acrylonitrile)-nickel and/or its phosphine adducts are formed. Bis(acrylonitrile)-nickel in the presence of triphenylphosphine is now known to be immediately reactive under similar conditions (42). Formation of (XL) must involve a hydrogen shift, and may proceed according to Eq. (22) Acrylonitrile can be replaced by acrylic esters in these processes (86). It is difficult to explain why these reactions afford only linear condensation products and not aromatic or cycloolefinic compounds. Bis(acrylonitrile)nickel also reacts with 2-butyne (78) and hexafluorobutyne (88), forming the corresponding benzene derivative and linear oligomers and polymers, respectively. Since phosphine-modified nickel carbonyls usually fail to



trimerize disubstituted acetylenes (see Section VIII), these results clearly show that the catalytic activity of the nickel atom strongly depends on the nature of the additional ligands attached to it.

C. Reactions with Olefins

Bis(acrylonitrile)-nickel catalyzes the dimerization of butadiene to cycloocta-1,5-diene in the presence of phosphites (89). Catalytic condensations of butadiene, however, will be discussed in Section IX. Of particular interest are reactions of bis(acrylonitrile)-nickel with norbornadiene. This highly strained diene is known to react with iron carbonyls forming complex (XLI) (90, 91), as well as the cyclic ketones (XLII), (XLIII), and (XLIV) (90). With nickel carbonyl under carbonylation conditions, bicyclo(2.2.1)-heptenecarboxylic ester (XLV) and the ketone (XLVI) are isolated (90). In inert solvents dimerization to the products (XLVII-L) occurs (90, 92, 93).

Bis(acrylonitrile)-nickel dimerizes norbornadiene at about 60° to (XLVII) and (XLVIII). In addition small amounts of the nitrile (LI) (see Fig. 9) may also be isolated, suggesting that the coordinated acrylonitrile reacted with the norbornadiene as well. The complexes of 1,1-dicyano- and 1,1,2-



tricyanoethylene are somewhat less active than bis(acrylonitrile)-nickel but afford larger yields of the dimer (XLVIII) and, in addition, the dimer (XLVIX) (94). This suggests that the structure of the catalytically active fragments (in this case, the complexes themselves), affects the nature of the

reaction products (94). Bis(fumaronitrile)-nickel is practically incapable of promoting the dimerization of norbornadiene. At 120° C only traces of dimers are obtained (94). This is undoubtedly because of its higher stability. In the presence of acrylonitrile, no dimers are produced and the nitrile



FIG. 9. Reaction of bis(acrylonitrile)-nickel with norbornadiene (94).

(LI), 6-cyanotetracyclo(3.2 1.1.0)nonane, is isolated in 95% yield [with bis(acrylonitrile)-nickel as catalyst]. This is the first case of a transition metal-catalyzed transannular addition. It may be formulated according to Fig. 9 and provides a good example of a π -complex multicenter process.

IX

CATALYTIC CYCLIZATION OF DIENES WITH NEW π COMPLEXES OF NICKEL

A. Bis(cycloocta-1,5-diene)-nickel

The thermal polymerization of butadiene yields, according to Ziegler *et al.*, a mixture of vinylcyclohexene with at most 15% of cyclooctadiene (95, 96). In 1954 Reed (97) discovered the catalytic cyclodimerization of butadiene to cycloocta-1,5-diene with Reppe catalysts, with a 30-40% conversion at 120–130° C. Wilke *et al.* recently synthesized a very efficient class of catalyst. If nickel-acetylacetonate is treated with metal alkyls (especially aluminum alkyls) in the presence of electron-donating compounds (mainly cycloolefins), new π complexes of nickel are obtained which catalyze the cyclo-oligomerization of butadiene (98, 99). Using cycloocta-1,5-diene as the olefinic component, the well-crystallized, faintly yellow bis(cyclooctadiene)-nickel, (LII), is obtained. This is the first π complex formed by nickel with a simple olefinic ligand. Spectral evidence shows that both cyclooctadiene molecules are symmetrically coordinated to the nickel atom. From a comparison of the infrared with the Raman spectrum it has been concluded that the molecule lacks a center of symmetry, suggesting that the nickel atom is in the sp^3 state of hybridization (100).



Since cyclooctadiene has no suitable low-lying unoccupied orbitals some of the 3d electrons of nickel are expected to have a relatively high antibonding character. It is therefore not surprising that the nickel complex is extremely reactive, air-sensitive, and very unstable in solutions even in the absence of oxygen. Carbon monoxide at room temperature completely displaces the cyclooctadiene molecules and yields nickel carbonyl (99). Acrylonitrile reacts with (LII) under similarly mild conditions, forming bis(acrylonitrile)-nickel (101), while duroquinone, well below room temperature, affords cyclooctadiene-duroquinone-nickel (101). These reactions uniquely demonstrate the close interrelationship between all complexes of zero-valent nickel.

B. Complexes of the Type (Phosphine)₂Ni(Olefin)

Reduction of nickel acetylacetonate in the presence of phosphines and olefins produces complexes of zero-valent nickel with the coordination number three. The ligands in (LIII) may be replaced by others under mild



conditions. Complexes of ethylene styrene, methylstyrene, stilbene, tolane, 2-butyne, and triethylphosphine as ligands have reportedly been prepared but have not yet been described in detail (99).

C. Cyclododecatriene-nickel and Complexes of Cyclooctatetraene

Perhaps the most important complex of this series is cyclododecatrienenickel, readily obtainable by reducing nickel-acetylacetonate with aluminum alkyls in the presence of cyclododecatriene. This complex (LIV) forms blood-red needles, is sublimable in vacuo, and is monomeric in the vapor phase (99). It is coordinately unsaturated and, being only a sixteen-electron complex, it not surprisingly reacts with carbon monoxide at -80° C, forming a monocarbonyl which is colorless and decomposes at 20°C into cyclododecatriene, nickel, and nickel carbonyl. More stable adducts are produced with phosphines which, due to their stronger σ -bonding character, will increase the electronic density on the nickel atom and thus favor π bonding to the olefinic ligand. It is still unknown whether the nickel atom is in a triangular environment or not. Although sp²-hybridized nickel would be more strongly π bonding it is possible that the available cavity in the cyclododecatriene molecule may be too small to allow a completely planar arrangement. Cyclododecatriene-nickel easily undergoes ligand replacement reactions. With cycloocta-1,5-diene it yields bis(cyclooctadiene)nickel. With cyclooctatetraene at -40° C a relatively unstable complex considered to be bis(cyclooctatetraene)-nickel is formed. This substance decomposes at 20°C into nearly black, sparingly soluble, and probably polymeric cyclooctatetraene-nickel (LV) (99). Complex (LV) may also be obtained by treating bis(cyclooctadiene)-nickel with cyclooctatetraene. It reacts with hydrogen yielding metallic nickel and cyclooctane, and with carbon monoxide to produce nickel carbonyl and cyclooctatetraene. Cyclododecatriene-nickel reacts instantly with hydrogen due to its coordinative unsaturation, whereas bis(cyclooctadiene)-nickel requires an induction period. Hydrogenation of the latter appears to take place only in the presence of small amounts of free nickel (99).



Complex (LIV) is extremely air-sensitive but is unaffected by deoxygenated water. This suggests that it is a π complex rather than a compound with Ni—C σ bonds (99).



D. Mechanism of the Formation of Cyclododecatriene

Butadiene reacts with cyclododecatriene-nickel or bis(cyclooctadiene)nickel at 20° C, replacing the olefinic ligands and forming a new molecule of cyclododecatriene (99). In this reaction "atomic" nickel must be the catalyst, as it is in some reactions of bis(acrylonitrile)-nickel. Most of the catalytically formed cyclododecatriene has the *trans-trans-cis* configuration, but, small amounts of the *trans-cis-cis* isomer have also been detected. When the reaction between (LIV) and butadiene was carried out at -40° C. Wilke *et al.* were able to isolate an intermediate (LVI) the nature of which was of great importance in elucidating reaction mechanism. Complex (LVI) is actually a bis(π -allyl)-nickel type of compound involving a twelve-carbonatom chain, formed by condensation of three molecules of butadiene. Allyl



groups at the ends of the chain are bonded to the nickel atom. Upon heating, (LVI) decomposes into nickel and cyclododecatriene, but on hydrogenation *n*-dodecane is obtained (Eq. 23).

The conversion of the C_{12} chain in (LVI) to cyclododecatriene can also be achieved by treating (LVI) with electron donors such as carbon monoxide, phosphines, or even butadiene. With phosphines under mild conditions the ring closure to cyclododecatriene takes place without decomposition of the complex and cyclododecatriene-nickel-phosphine adducts are isolated (99). With carbon monoxide at -60° C (LVI) affords a vinylcycloundecadienone (LVII) (99).

E. Bis(π -allyl)-nickel

The presence of a bis(π -allyl) system in (LVI) suggested the existence of a bis(π -allyl)-nickel. Previously Fischer and Bürger had prepared a dimeric π -allylnickel bromide (102) (see Section IV, A). Wilke and Hermann obtained the desired compound by treating ethereal allylmagnesium bromide with anhydrous nickel(II) bromide (99, 103). Bis(π -allyl)-nickel (LVIII) is volatile in ether and crystallizes below 1°C into long yellow



needles. Although pyrophoric, its solutions in ether are not affected by deoxygenated water, in accord with its nonclassical π -complex structure. The structure of bis(methallyl)-nickel has been determined by Dietrich and Uttech (103a). The crystals are monoclinic with a = 6.07, b = 13.5, and c = 5.86 Å. The space group is $C_{2h}^5 - P(2_1/c)$ with two molecules per unit cell. The nickel atom is situated in a center of symmetry and a two-dimensional projection indicates an "anti-sandwich" structure. With molecular hydrogen, propane and nickel are formed, and with phosphines the two allyl radicals combine to form diallyl (Eq. 24).

The insertion of carbon monoxide has not yet been achieved. Bis(π -allyl)nickel reacts with butadiene to form cyclododecatriene. The allylic groups may also be displaced by cycloocta-1,5-diene or cyclooctatetraene. Wilke regards (LVIII) as formally a complex of Ni(II), assuming that during the catalysis there is a constant and reversible change in the formal oxidation state of the nickel atom (99). This postulate, however, may lead to unnecessary complications. It must be stressed that the frequently exercised assignment of formal oxidation numbers to metal atoms in predominantly covalent metal-organic complexes should not be treated too seriously. $Bis(\pi$ -allyl)-nickel is best regarded as a Ni(0) complex, as follows from its physical properties (volatility, etc.) than as a Ni(II) derivative. All that distinguishes it, for instance, from bis(cyclooctadiene)-nickel, is that its ligands are radicals rather than normal olefins. The driving force for the electronic and the molecular rearrangements which occur during the various catalytic processes is the tendency of the complex system to achieve greater orbital stabilization.

F. Catalytic Formation of Cycloocta-1,5-diene

No cyclododecatriene is obtained if reaction of butadiene with nickelolefin complexes is conducted in the presence of donors, e.g. triphenylphosphine (99). It was mentioned previously (Section VIII, B) that triphenylphosphine stabilizes the catalytically active atomic nickel. Coordination with the electron pair of the donor in this case also has an inhibiting effect, and only cycloocta-1,5-diene is formed. In practice, the complex Ni \cdot 4P(C₆H₅)₃ is used, which can be made by treating bis(π -allyl)nickel with triphenylphosphine (99, 103) (Eq. 24). This complex easily releases triphenylphosphine. In the presence of butadiene evidently three molecules are displaced by two of the diene. The activity and lifetime of the catalyst are exceptional. It is possible to convert 800-900 gm of butadiene to cyclooctadiene of 95% purity, at 80°C and atmospheric pressure, per hour and gram of nickel in the catalyst. By analogy with the mechanism of cyclododecatriene formation it was assumed that the initial complex should contain two butadiene molecules which would at first combine to give an open-chain C_8 -bis(allyl) system (LIX). This intermediate was isolated by using a suitable phosphine as an additional donor. Complex (LIX), when hydrogenated at low temperature, yields over 80% of n-octane. Ring closure is achieved by warming it up to 20° C and displacing the cyclooctadiene with a donor molecule, e.g., triphenylphosphine. The total π -electron energy of two butadiene molecules is $E = 2(4\alpha + 2(5)^{1/2}\beta)$. The value for the energy of two butadienes in the allylic biradical form $CH_2 \xrightarrow{\cdots} CH \xrightarrow{\cdots} CH \xrightarrow{-} CH \xrightarrow{-} CH_2$ would be $E = 2(4\alpha + 2(2)^{1/2}\beta)$, using simple Hückel theory. The energy difference between the two pairs of molecules



is 3,287 β and could be offset by forming a new C—C bond and allowing the terminal allyl systems to interact with the nickel orbitals. Although vinylcyclohexene (LXI) is the major product of the noncatalytic thermal dimerization, it may also be formed catalytically. If (LIX) at -80° C is treated with carbon monoxide, one π -allyl group is displaced in part by the free electron pair of the carbon monoxide molecule (LX). Further reaction with carbon monoxide then produces vinylcyclohexene in 80% yield (99).

Butadiene may also be co-cyclized with ethylene, forming cyclodeca-1,5diene (LXII). With 2-butyne, 1,2-dimethylcyclodeca-1,4,8-triene (LXIV)



is obtained. Both products when heated undergo Cope rearrangements to (LXIII) and (LXV), respectively (99).

CYCLOPOLYMERIZATION OF ALLENE

Benson and Lindsey (104) were able to cyclopolymerize allene using phosphine-nickel carbonyl complexes as catalysts. They obtained a mixture of 1,2,4- and 1,3,5-trimethylenecyclohexane, and a remarkably stable tetramer, 1,3,5,7-tetramethylenecyclooctane, (LXVI).



Compound (LXVI) is particularly interesting as it undergoes a 1,7 addition with tetracyanoethylene. This transannular addition is possible since the opposite pairs of double bonds in (LXVI) parallel each other at a distance of only about 2.7 Å, which must lead to appreciable π -orbital interaction (105). In the presence of acetylene, with Ni(CO)₂·2P(OC₆H₅)₃ as the catalyst, a co-cyclopolymerization of allene to 3,5- and 3,6-dimethylenecyclohexene (LXVII) and (LXVIII), respectively, is possible (106). With nickel acetylacetonate as catalyst, (LXVII) and 3,5,7-trimethylenecyclooctene (LXVIII) are produced in 45% and 5% yield respectively. (106). This reaction makes *exo*-methylene cyclic compounds which are unsaturated easily accessible. The chemistry of (LXVII) has been studied in some detail (107).

References

- 1. L. Mond, F. Langer, and R. Quincke, J. Chem. Soc. 57, 749 (1890).
- 2. W. Reppe, "Neue Entwicklungen auf dem Gebiete der Chemie des Acetylens und des Kohlenoxyds," Springer, Heidelberg, 1949.
- 3. W. Reppe, A. Magin, and C. Schuster, Ann. Chem. 582, 1 (1953).
- 4. E. R. H. Jones, T. Y. Shen, and M. C. Whiting, J. Chem. Soc. 48, 763 (1951).
- 5. E. R. H. Jones, T. Y. Shen, and M. C. Whiting, J. Chem. Soc. p. 766 (1951).
- 6. E. R. H. Jones, T. Y. Shen, and M. C. Whiting, J. Chem. Soc. p. 230 (1950).
- 7. C. W. Bird and J. Hudec, Chem. Ind. (London) p. 570 (1959).
- 8. H. W. Sternberg, R. Markby, and I. Wender, J. Am. Chem. Soc. 82, 3638 (1960).
- 9. G. P. Mueller and F. L. MacArtor, J. Am. Chem. Soc. 76, 4621 (1954).
- 10. E. Weiss and W. Hübel, J. Inorg. Nucl. Chem. 9, 204 (1959).

- M. Almasi, L. Szabo, S. Farkas, F. Kasco, O. Vegh, and I. Muresan, Acad. Rep. Populare Romîne, Studii Cercetari Chim. 8, 509 (1960); Chem. Abstr. 55, 19427f (1961).
- 12. R. F. Heck, J. Am. Chem. Soc. 85, 2013 (1963).
- 13. M. C. Whiting, Proc. Chem. Soc. p. 50 (1958).
- 14. W. Reppe, H. Kröper, H. J. Pistor, and H. Schlenck, Ann. Chem. 582, 38 (1953).
- W. Reppe, H. Kröper, N. von Kutepow, H. J. Pistor, and O. Weissbarth, Ann. Chem. 582, 72 (1953).
- 15a. H. Adkins and R. W. Rosenthal, J. Am. Chem. Soc. 72, 4550 (1950).
- 16. G. P. Chiusoli, Angew. Chem. 72, 74 (1960).
- 17. I. D. Webb and G. T. Borcherdt, J. Am. Chem. Soc. 73, 2654 (1951).
- 18. G. P. Chiusoli and G. Agnès, Z. Naturforsch. 17b, 852 (1962).
- 19. E. O. Fischer and G. Bürger, Z. Naturforsch. 17b, 484 (1962).
- 20. R. F. Heck, J. C. W. Chien, and D. S. Breslow, Chem. Ind. (London) p. 467 (1960).
- 21. W. H. Groombridge, British Patent 621,520 (1949); Chem. Abstr. 43, 6650f (1949).
- W. W. Pritchard and G. E. Tabet, U.S. Patent 2,565,462 (1951); Chem. Abstr. 46, 2578a (1952).
- 23. G. E. Tabet, U.S. Patent 2,565,463 (1951); Chem. Abstr. 46, 2578a (1952).
- 24. C. E. Coffey, J. Am. Chem. Soc. 83, 1623 (1961).
- 25. C. Rüchardt and G. N. Schrauzer, Chem. Ber. 93, 1840 (1960).
- 26. G. N. Schrauzer, Chem. Ber. 94, 1891 (1961).
- 27. J. C. Clark and R. C. Cookson, J. Chem. Soc. p. 686 (1962).
- 28. J. W. Cable and R. K. Sheline, Chem. Rev. 56, 1 (1956).
- J. W. Richardson, in "Organometallic Chemistry" (H. Zeiss, ed.), p. 1. Reinhold, New York, 1960.
- W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, J. Am. Chem. Soc. 82, 1254 (1960).
- 31. F. A. Cotton, A. K. Fischer, and G. Wilkinson, J. Am. Chem. Soc. 81, 800 (1959).
- 32. F. Basolo and A. Wojcicki, J. Am. Chem. Soc. 83, 520 (1961).
- 32a. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," p. 63. Wiley, New York, 1958.
- 33. A. P. Garratt and H. W. Thompson, J. Chem. Soc. p. 1822 (1934).
- 34. A. P. Garratt and H. W. Thompson, J. Chem. Soc. p. 524 (1934).
- 35. A. P. Garratt and H. W. Thompson, J. Chem. Soc. p. 1817 (1934).
- 36. G. E. Kimball, J. Chem. Phys. 8, 188 (1940).
- 37. L. S. Meriwether and M. L. Fiene, J. Am. Chem. Soc. 81, 4200 (1959).
- M. Bigorgne, in "Advances in the Chemistry of the Coordination Compounds: Proceedings of the 6th International Conference on Coordination Chemistry, Detroit, Michigan, 1961" (S. Kirschner, ed.), p. 199. Macmillan, New York, 1961.
- E. O. Fischer and H. Werner, Chem. Ber. 92, 1423 (1959); Tetrahedron Letters p. 17 (1961).
- 40. M. Dubeck and A. H. Filbey, J. Am. Chem. Soc. 83, 1257 (1961).
- 41. D. Jones, G. W. Parshall, L. Pratt, and G. Wilkinson, Tetrahedron Letters p. 48 (1961).
- 41a. E. O. Fischer and H. Werner, Chem. Ber. 95, 695 (1962).
- 41b. E. O. Fischer and G. Bürger, Chem. Ber. 94, 2409 (1961).
- 42. G. N. Schrauzer, J. Am. Chem. Soc. 81, 5310 (1959).
- 43. H. P. Fritz and G. N. Schrauzer, Chem. Ber. 94, 650 (1961).
- 44. Unpublished work of the author with K. C. Dewhirst, 1962.
- 45. G. N. Schrauzer, J. Am. Chem. Soc. 82, 1008 (1960).

- 46. G. N. Schrauzer, Chem. Ber. 94, 642 (1961).
- 47. D. A. Brown and G. N. Schrauzer, Z. Physik. Chem. (Frankfurt) [N.F.] 36, 1 (1963).
- 48. Unpublished work of the author with H. Heinrich, 1963.
- 49. E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta* 46, 288 (1963).
- 50. Unpublished work of the author with P. Glockner, 1962.
- 51. G. N. Schrauzer, S. Eichler, and D. A. Brown, Chem. Ber. 95, 2755 (1962).
- 52. G. N. Schrauzer and S. Eichler, Chem. Ind. (London) p. 1270 (1961).
- 53. H. W. Sternberg, R. Markby, and I. Wender, J. Am. Chem. Soc. 80, 1009 (1958).
- 53a. R. Markby, H. W. Sternberg, and I. Wender, Chem. Ind. (London) p. 1381 (1959).
- 54. G. N. Schrauzer and H. Thyret, J. Am. Chem. Soc. 82, 6420 (1960).
- 55. G. N. Schrauzer and H. Thyret, Z. Naturforsch. 17b, 73 (1962).
- 56. G. N. Schrauzer and H. Thyret, Z. Naturforsch. 16b, 353 (1961).
- 56a. M. D. Glick and L. F. Dahl, Abstr. of papers, 147th Meeting, Am. Chem. Soc., 1964 p. 16L.
- 57. Unpublished work of the author with H. Thyret, 1962.
- 58. G. N. Schrauzer and H. Thyret, Chem. Ber. 96, 1755 (1963).
- 59. G. N. Schrauzer and H. Thyret, Angew. Chem. 74, 488 (1962).
- 60. D. A. Brown, J. Inorg. Nucl. Chem. 10, 49 (1959).
- 61. G. N. Schrauzer and H. Thyret, Theoret. Chim. Acta 1, 172 (1963).
- 62. L. E. Orgel, Trans. Faraday Soc. 52, 1172 (1956).
- 63. H. Thyret, Doctoral Thesis, University of Munich, Munich, 1962.
- 64. G. N. Schrauzer and H. Thyret, Angew. Chem. 75, 641 (1963).
- 65. W. Reppe and W. J. Schweckendieck, Ann. Chem. 560, 104 (1948).
- 66. W. Hübel and C. Hoogzand *in* "Organic Syntheses via Metal Carbonyls" (I. Wender and P. Pino, edrs.). J. Wiley and Sons, New York. To be published.
- L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.* 26, 5155 (1961).
- 68. L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, J. Org. Chem. 26, 5163 (1961).
- 69. E. C. Colthup and L. S. Meriwether, J. Org. Chem. 26, 5169 (1961).
- L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.* 27, 3930 (1962).
- 71. R. F. Kleinschmidt, U.S. Patent 2,542,417 (1951); Chem. Abstr. 45, 7594 (1951).
- 72. J. C. Sauer and T. L. Cairns, J. Am. Chem. Soc. 79, 2659 (1957).
- 73. A. C. Cope and C. T. Hardy, U.S. Patent 2,950,334 (1960); Chem. Abstr. 55, 1527b (1961).
- 74. F. W. Hoover, O. W. Webster, and C. T. Hardy, J. Org. Chem. 26, 2234 (1961).
- 75. K. Yamamoto and M. Oku, Japanese Patent 5360 (1952); Chem. Abstr. 47, 11217f (1953).
- For a recent review see e.g., R. G. Guy and B. L. Shaw, Advan. Inorg. Chem. Radiochem. 4, 77 (1962).
- See the reviews by H. Zeiss, G. E. Coates, and F. Glockling, and J. Chatt, P. L. Pauson and L. M. Venanzi, *in* "Organometallic Chemistry," A.C.S. Monograph No. 147 (H. Zeiss, ed.). Reinhold, New York, 1960.
- 78. W. Hübel and C. Hoogzand, Chem. Ber. 93, 103 (1960).
- 79. G. N. Schrauzer, Chem. Ber. 94, 1403 (1961).
- 79a.G. N. Schrauzer and G. Kiessling, unpublished experiments, 1963.
- 80. H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc. p. 1969 (1956).

- For a recent review on Complexes of Cyclobutadienes see E. O. Fischer and H. Werner, in "Metall-π-Komplexe mit di- und oligoolefinischen Liganden" pp. 18-25. Verlag Chemie, Weinheim/Bergstr., 1963.
- 82. Unpublished experiments of the author with S. Eichler, 1962.
- 83. W. Reppe, O. Schlichting, K. Klager, and T. Toepel, Ann. Chem. 560, 1 (1948).
- 84. G. N. Schrauzer and S. Eichler, Chem. Ber. 95, 550 (1962).
- G. N. Schrauzer, Angew. Chem. 76, 28 (1964): Angew. Chem. Internat. Ed. 3, 185, (1964).
- 86. J. R. Leto and M. F. Leto, J. Am. Chem. Soc. 83, 2944 (1961).
- T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb, and J. C. Sauer, *J. Am. Chem. Soc.* 74, 5636 (1952).
- 88. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, J. Chem. Soc. p. 3488 (1962).
- 89. N. V. Kutepow, H. Seibt, and F. Meier, German Patent B59,415 (1960).
- 90. C. W. Bird, R. C. Cookson, and J. Hudec, Chem. Ind. (London) p. 20 (1960).
- 91. R. Pettit, J. Am. Chem. Soc. 81, 1266 (1959).
- C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters* 11, 373 (1961).
- 93. D. M. Lemal and K. S. Shim, Tetrahedron Letters 11, 368 (1961).
- 94. G. N. Schrauzer and S. Eichler, Chem. Ber. 95, 2764 (1962).
- 95. K. Ziegler and H. Wilms, Ann. Chem. 567, 1 (1960).
- K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn, and J. Schneider, Ann. Chem. 589, 122 (1954).
- 97. H. W. B. Reed, J. Chem. Soc. p. 1931 (1954).
- 98. G. Wilke, Angew. Chem. 72, 581 (1960).
- 99. G. Wilke et al. Angew. Chem. 75, 10 (1963). Angew. Chem. Internat. Ed. 2. 105 (1963).
- 100. Unpublished work, in cooperation with G. Wilke, 1962.
- 101. Unpublished work, with H. Thyret, 1962.
- 102. E. O. Fischer and G. Bürger, Z. Naturforsch. 16b, 77 (1961).
- 103. G. Wilke and B. Bogdanovic, Angew. Chem. 73, 756 (1961).
- 103a. H. Dietrich and R. Uttech, Naturwissenschaften 50, 613 (1963).
- 104. R. E. Benson and R. V. Lindsey, Jr., J. Am. Chem. Soc. 81, 4247 (1959).
- 105. J. K. Williams and R. E. Benson, J. Am. Chem. Soc. 84, 1257 (1962).
- 106. R. E. Benson and R. V. Lindsey, Jr., J. Am. Chem. Soc. 81, 4250 (1959).
- 107. R. E. Benson, R. V. Lindsey, Jr., and B. C. Anderson, J. Am. Chem. Soc. 81, 4253 (1959).