Coordination Chemistry Reviews, 33 (1980) 3—53
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

SYNTHESIS WITH ELECTRON-RICH NICKEL TRIAD COMPLEXES

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(Received 20 August 1979)

CONTENTS

ABBREVIATIONS

cod = cyclo-octadiene (1,3)
cdt = e,e,e-1,5,9-cyclododeca-triene
dba = dibenzylideneacetone
msa = maleic anhydride
dch = duroquinone
solv = solvent
thf = tetrahydrofuran
si-H = succinimide
pi-H = phthalimide
sa-H = saccharin
ar = aryl
alk = alkyl
dmf = dimethylformamide

dma = dimethylacetylenedicarboxylate
nb = norbornene
nbd = norbornadiene

A. INTRODUCTION

Reactions with electron-rich complexes essentially aim at the preparation of new, preferably organometallic coordination compounds and the simplification of stoichiometric or catalytic synthesis of organic compounds. In both cases one falls back upon a certain sequence of reactions (Fig. 1). An electron-rich M^0L_n complex at first reacts with the XY substrate under partial or even complete substitution of L. Charge transfer to the substrate occurs at the same time because of the electron excess available in the $L_{n-m}M^0$ moiety. Its degree depends on the substrate in the case of a given $L_{n-m}M^0$ moiety. In type (cod)Ni(subst. *p*-quinone), for example, Schrauzer and Thyret [1] found a relationship between the redox potential of the substituted *p*-quinone and the magnetic moment, the magnitude of which in this case is an expression of the charge transfer.

In many cases, II is not the final but intermediate product and reacts further by oxidative addition (II → VII) [2,3]. Oxidative additions are partial steps of some catalytic cycles (Section D).

The metal-induced coupling (II → III) offers another possibility of modifying II [4] (when using 'naked' metals [5] as starting product II, *p* can also be greater than 2). The metallacycle III may be the aim of synthesis; in numerous cases, however, splitting of the organic part of the metallacycle follows.

This reductive elimination can be implemented in different ways. (i) The displacement of the organic fragment takes place by a ligand L'. An electron-rich complex IV which is not identical to the starting product II of the metal-induced coupling, is produced. At the same time a dimer of the substrate XY is formed. We call such a process 'metal induced stoichiometric synthesis'. (ii) The displacement takes place by the substrate XY itself. Apart from X_2Y_2, II is reformed as the starting product of the metal-induced coupling. Thereby, a catalytic synthesis of X_2Y_2 becomes possible [6]. (iii) The displacing substrate combines completely (III → V) or as a fragment (III → VI) with the organic part of metallacycle III. The step III → V is principally a link in a catalytic cycle, 'M^0L_{n-m}' does not occur as a free species [6]. III → VI (cf. [7]), however, results in a stable metallic end product and thus permits only a stoichiometric synthesis of X_2Y_2S'.

It is the purpose of this paper to review those typical synthetic reactions of nickel triad complexes which are summarized in Fig. 1 (Sections C, D, E). We shall start with a brief consideration of bond properties (Section B) to get a better insight into the role of the central atoms and of the different types of ligands on the course of these reactions.

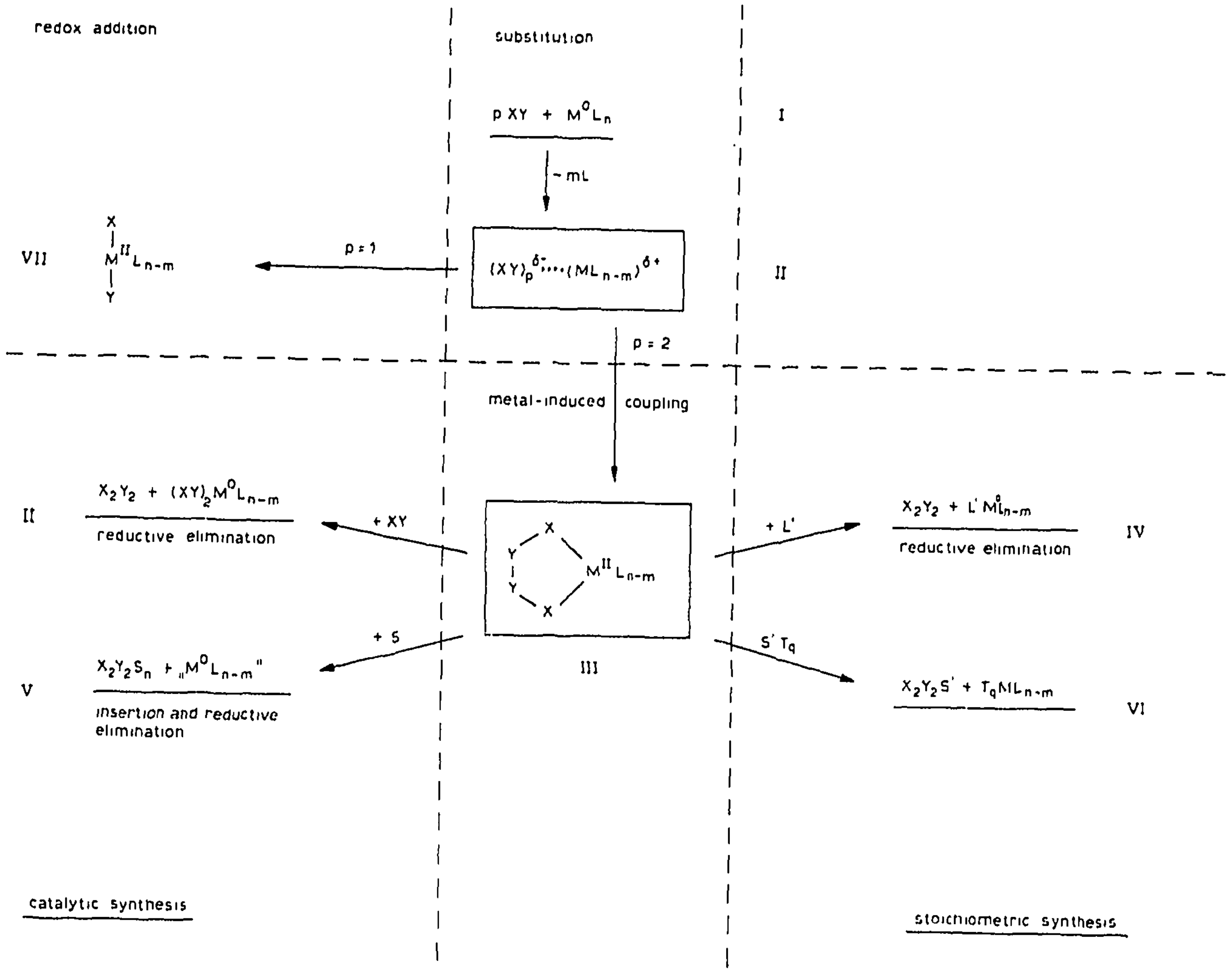


Fig. 1. Reactions of electron-rich complexes.

B. CHEMICAL BONDING IN ELECTRON-RICH COMPLEXES OF THE NICKEL TRIAD

The relative stability of both the zero-valent complexes I, II, IV, V and of the divalent compounds III and VII is determined by the different ability of the central atoms and ligands to form σ- and π-bonds. Considering only the zero-valent complexes of the nickel triad and the central atoms, the electron affinities EA ($d^{10}s^1 \rightarrow d^{10}$), the ionization potentials IP($d^{10} \rightarrow d^9$) and the differences EA — IP may serve for an estimate of the σ-bond strength, the π-bond strength and the overall bond strength respectively [8] (Table 1). The following sequence results

σ-bond	$Ni^0 \approx Pd^0 < Pt^0$
π-bond	$Ni^0 > Pd^0 \approx Pt^0$
bond strength	$Ni^0 > Pt^0 > Pd^0$

Impressive evidence of this is the situation concerning the pure metal carbonyls where the π-bond share is dominant. $Ni(CO)_4$ is a stable compound; binary carbonyls of palladium(0) [9,10] and platinum(0) [9,11], however, could only be detected under extreme conditions (reaction of carbon monoxide with metal vapours at low temperatures).

With the complexes of the divalent central atoms (nickel(II), palladium(II) and platinum(II)) with soft ligands (olefins, phosphines, carbyl anions), the π-bond decreases in importance compared to the σ-bond. In the case of nickel(II) olefin complexes, Akermark et al. [12] proved this by means of a MO-LCAO-SCF calculation. Thus, the bond strength sequence, Pt > Pd > Ni, observed for square planar (diamagnetic) complexes $M^{II}L_4$ can be attributed to a correspondingly improved ability to σ-bond [13].

Nickel(0) complexes without exception have more negative half-wave potentials than platinum(0) complexes [14]. Therefore, they are more easily oxidized by organic substrates than the latter. But compounds with platinum(II) carbon σ-bonds formed by these or other reactions, because of the above-mentioned bond strength sequence, are more stable against reductive eliminations under the influence of π-acceptor ligands or of unsaturated organic compounds (Section E(ii)). When applied to synthesis, this means that both platinum(0) and nickel(0) complexes are capable of a variety of oxidative

TABLE 1

Ionisation potentials (IP) and electron affinities (EA) of atoms of the nickel triad

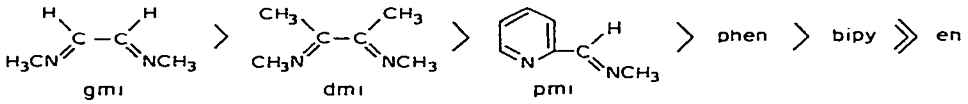
	IP(eV) $d^{10} \rightarrow d^9$	EA(eV) $d^{10}s^1 \rightarrow d^{10}$	EA—IP(eV)
Ni	5.81	1.2	—4.6
Pd	8.33	1.3	—7.0
Pt	8.20	2.4	—5.8

additions (II → VII) and metal-induced couplings (II → III). In the case of nickel, consecutive reactions follow frequently (III → II, III → IV, III → V), whereas they are exceptional in the case of platinum. Thus, nickel(0) complexes can be used for numerous stoichiometric and catalytic syntheses of organic compounds. Platinum(II) complexes with carbyl ligands are often suitable models for intermediate products of such syntheses.

Considering the ligands now, they are acting as partners of the central atoms nickel(0), palladium(0) and platinum(0) both as n-donors and π-acceptors. Both functions differ in intensity.

In the sixties, the 'π-acceptor series' were mainly deduced from i.r. spectroscopic data [15,16]. On the basis of the observation that steric factors play an important role in substitution reactions of phosphine complexes, their usefulness was called into question [17]. The more empirical 'electron donor—acceptor properties' for assessing the ligands in electron-rich complexes were used instead [18,19]. But there are a number of recent experimental and theoretical results which represent a useful basis for estimating the relative π-acceptor and sometimes even the n-donor strength. Reinhold et al. [20] used a NDDO method to calculate the LUMO energy and the 'quasi-lone-pair' density of N∩N chelate ligands and derived the following sequence.

π-acceptor strength



n-donor strength

en >> phen, dmi > gmi > bipy > pmi

The different sequences of the individual species in the two series is important for further discussion. dmi is stronger than bipy both as a π-acceptor and n-donor!

Photo-electron spectra of type $(OC)_5M(PR_3)$ (M = Cr, Mo, W) complexes provided a possibility to determine the relative π-acceptor and n-donor strength of phosphorus ligands [21].

π-acceptor strength

$PEt_3 \sim PMe_3 < P(NMe_2)_3 < P(OEt)_3 \sim P(OMe)_3 < PF_3$

n-donor strength

$PEt_3 \sim PMe_3 > P(OEt)_3 \sim P(OMe)_3 > P(NMe_2)_3 > PF_3$

It is noteworthy that the π-acceptor series is in agreement with that formerly deduced from i.r. data [16], even with regard to the statement that tertiary alkyl phosphines are acting as weak π-donors if they enter into π-interactions at all. Thus, the tertiary alkyl phosphines must be assigned to the n-donors for a qualitative discussion of substitution reactions (Section C).

The sequence of olefins, msa ~ tr-CH(CN)=CH(CN) > CH_2=CHCN > CH_2=CHPh > CH_2=CH_2 > tr-PhCH=CHPh > C_4H_9CH=CH_2 > $(CH_3)_2C$=$C(CH_3)_2$, found by Tolman [22] by the thermodynamic investigation of reaction (1) can be considered as a π-acceptor series because there is an extreme tendency of π-back-donation in nickel(0) complexes. Therefore ΔH of reaction (1) in close approximation reflects the nickel—olefin π-bond energies (more exactly the differences in π-bond energies between the moiety $[(o\text{-Me—}C_6H_4O)_3P)]_2Ni$ and RCH=CHR′ or CH_2=CH_2).

$$[(o\text{-Me—}C_6H_4O)_3P]_2Ni(C_2H_4) + \text{olefin} \rightleftharpoons [(o\text{-Me—}C_6H_4O)_3P]_2Ni(\text{olefin}) + C_2H_4 \qquad (1)$$

Ittel [23] judges the donor—acceptor properties of more than 100 substituted olefins on the basis of the position of ν^1_{NC} and ν^2_{NC} in $(Bu^tNC)_2Ni$(olefin) complexes. He includes hetero-olefins in his considerations and concludes that the increase of the π-acceptor properties is in parallel with the electronegativity of the hetero-atoms.

$$RR'C{=}CRR' < RR'C{=}NR'' < RR'C{=}O < R{-}N{=}N{-}R' < R{-}N{=}O < O{=}O$$

Summarizing, we can state that well-founded details as to the sequence of the π-acceptor strengths, and in some cases also of the n-donor strengths, are available for series of structurally related ligands, but little reliable data exist on the relations between these series. (i) PF_3 is a similar but somewhat weaker π-acceptor than CO [21] (but cf. [24,25]). (ii) In $(H_3P)_2Ni(C_2H_4)$, PH_3 is a n-donor, C_2H_4 a π-acceptor [12]. (PH_3 may serve as a model for alkyl phosphines.) (iii) msa, CS, CS_2 and tetracyanethene are stronger π-acceptors than CO [25]. (iv) bipy and phen are generally considered as weaker π-acceptors than CO or PF_3. We are not aware of relations to phosphines and olefins which are based on reliable molecular parameters. ESCA investigations of nickel(0) complexes showed, however, that the n-donor function prevails in the case of bipy [26].

In this situation the establishment of a complete π-acceptor or n-donor series of the ligands does not seem possible, but a distinction between ligands with dominating acceptor nature (A) and those with dominating donor nature (D) can be made in binary complexes. The following examples will demonstrate this (ligands enclosed in full lines are donors, those enclosed in dotted lines are acceptors).

$\boxed{D}-m^0-\dbox{A}$

$\boxed{(Ph_3P)_2}-Pt-\dbox{(C_2H_4)}$ $\qquad$ $\boxed{(Ph_3P)_2}-Ni-\dbox{$(CO)_2$}$

$\boxed{(bipy)}-Ni-\dbox{$[P(OPh)_3]_2$}$ $\qquad$ $\boxed{(bipy)}-Ni-\dbox{(cod)}$

$\boxed{(bipy)}-Pd-\dbox{(dba)}$ $\qquad$ $\boxed{(cod)}-Ni-\dbox{(msa)}$

The variable functionality of the ligand cod becomes evident on (bipy)Ni(cod) and (cod)Ni(msa). But cod is not a unique case (cf. Section C).

C. SUBSTITUTION REACTIONS

The most simple substrates for substitution reactions are binary metal(0) complexes with olefin or phosphine ligands: $M(PR_3)_n$ ($n = 3,4$: R = aryl or alkyl); $M(cod)_2$ [27—29]; Ni(cdt) [30]; $Pd_2(dba)_3$ [31]; $M(C_2H_4)_3$ [32—34]; $Ni(Ph{-}CH{=}CH_2)_3$ [35]; M = Ni, Pd, Pt.

Complete series which should permit the study of the specific influence of the central atom on the reactivity are available in the case of $M(PR_3)_n$, $M(cod)_2$ and $M(C_2H_4)_3$. But to date only a few investigations of the ligand exchange of this type, concerning mechanism [36,37] and thermodynamics [22,38] have been carried out, mainly for experimental reasons. Comprehensive knowledge, however, is available on substitution reactions of binary and ternary nickel(0) complexes. Therefore, they will be dealt with at the beginning and relations to palladium(0) and platinum(0) complexes will be worked out later.

It has been known for a long time that the combination of n-donor and π-acceptor ligands acts as a stabilizing factor in nickel(0) compounds [39]. Therefore, binary complexes of π-acceptor ligands (n-donor ligands) in general react quite smoothly with n-donors (π-acceptors) under partial substitution (2)—(4). But when the π-acceptor power of the ligand and the reagent differ only slightly, an equilibrium will build up between the substrate and its substitution products. This, for example, applies to $Ni(CO)_4$ and $Ni(CO)_{4-x}(PCl_3)_x$ in a closed system [17]. Complete conversion (5) only becomes possible if the carbon monoxide can escape from the equilibrium.

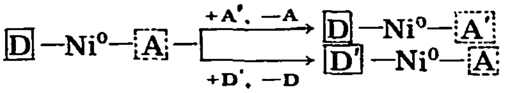
$Ni(CO)_4 + bipy \rightarrow (bipy)Ni(CO)_2 + 2\,CO$ [40] (2)

$Ni(cod)_2 + bipy \rightarrow (bipy)Ni(cod) + cod$ [41] (3)

$Ni(PEt_3)_3 + C_2H_4 \rightarrow (C_2H_4)Ni(PEt_3)_2 + PEt_3$ [42] (4)

$$Ni(CO)_4 + 4\,PCl_3 \rightarrow Ni(PCl_3)_4 + 4\,CO \tag{5}$$

Among other things, the reaction behaviour of the partial substitution products (bipy)Ni(cod) and $(Et_3P)_2Ni(C_2H_4)$ depends considerably on the electronic situation and on the nature of the attacking agent and, to a certain extent, also on the solvent. The experimental material can be classified according to the following rule. In electron-rich mixed-ligand complexes of the nickel triad, the π-acceptors (A′) substitute the π-acceptor ligands (A) and the n-donors (D′) the n-donor ligands (D). A prerequisite is that the reagent is a stronger π-acceptor (n-donor) than the ligand.



This rule can be understood by means of a very simple MO scheme (Fig. 2)

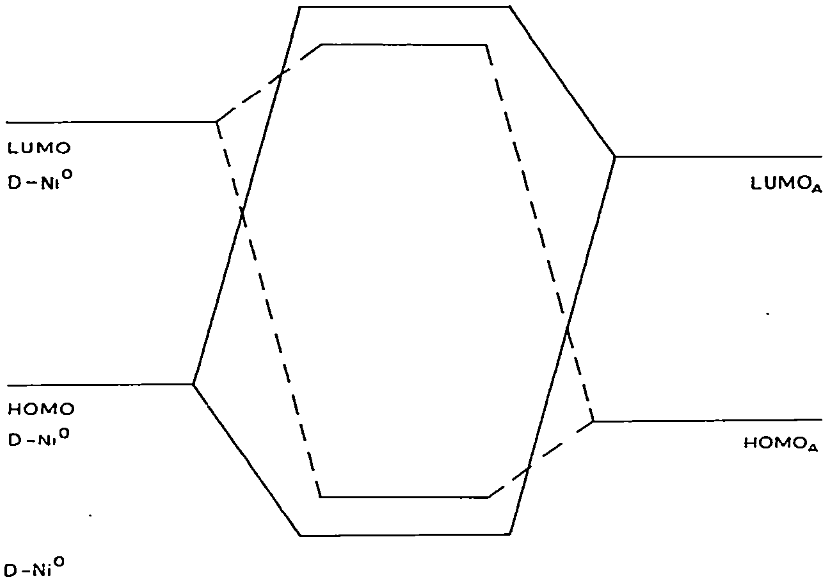


Fig. 2. Simplified MO-scheme of the n-donor and π-acceptor interaction of the ligand A (π-acceptor property dominant) with the moiety D-Ni^0.

[22]. According to this, it can be assumed to a first approximation that the following interactions determine the stability of the species D—Ni^0—A.

(a) $\mathrm{HOMO}_{\mathrm{D-Ni^0}}$—$\mathrm{LUMO'_{A}}$ (π-interaction)

(b) $\mathrm{LUMO}_{\mathrm{D-Ni^0}}$—$\mathrm{HOMO}_{\mathrm{A}}$ (σ-interaction)

The $\mathrm{LUMO}_{\mathrm{A'}}$ of a stronger π-acceptor A′ energetically lies below $\mathrm{LUMO}_{\mathrm{A}}$. That is why the interaction (a) increases in the transition from D—Ni^0—A to D—Ni^0—A′. In general, $\mathrm{HOMO}_{\mathrm{A'}}$ will also be energy-poorer than $\mathrm{HOMO}_{\mathrm{A}}$, and certainly the interaction (b) will decrease in D—Ni^0—A′. But owing to the high energy of $\mathrm{LUMO}_{\mathrm{D-Ni^0}}$ substitution of A by A′ is connected with a release of energy and therefore it should proceed voluntarily when no extraordinary entropy effects occur (Tolman [22] found $\Delta S \sim 0$ in three substitution reactions of nickel(0) complexes).

A stronger donor ligand D′ will lift the HOMO of the complex moiety (now $\mathrm{HOMO}_{\mathrm{D'-Ni^0}}$). Thus, assuming no change of A, the dominating interaction (a) will be amplified and a substitution of D by D′ can be expected under the mentioned prerequisites.

The indicated rule does not consider the chelate and steric effects. The latter are of major importance for the substitution of phosphorus ligands [17]. It is particularly in this case that deviations must be expected.

Moreover, the rule is based on the assumption that the π-acceptor strength

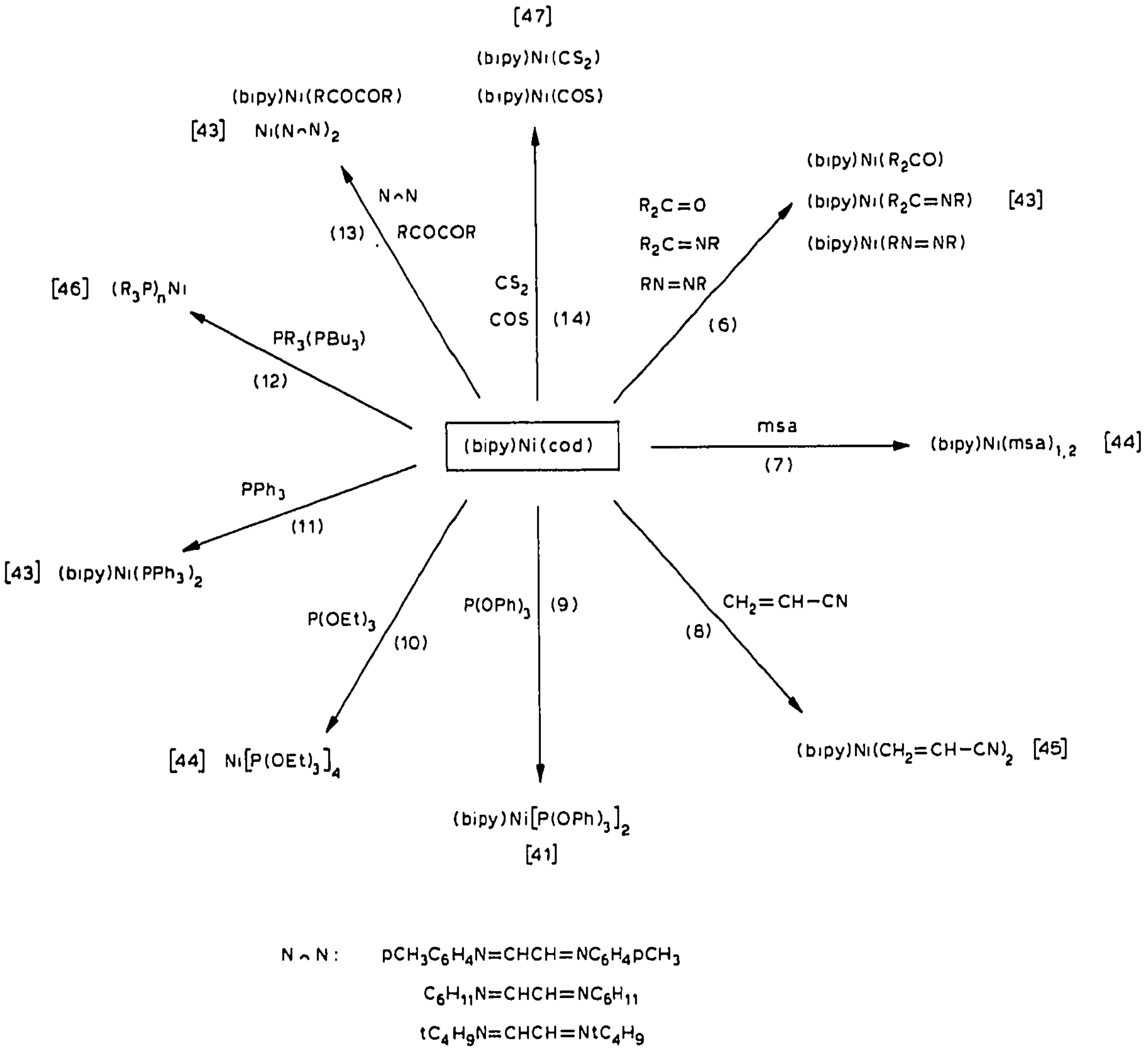


Fig. 3. Substitution reactions of (bipy)Ni(cod).

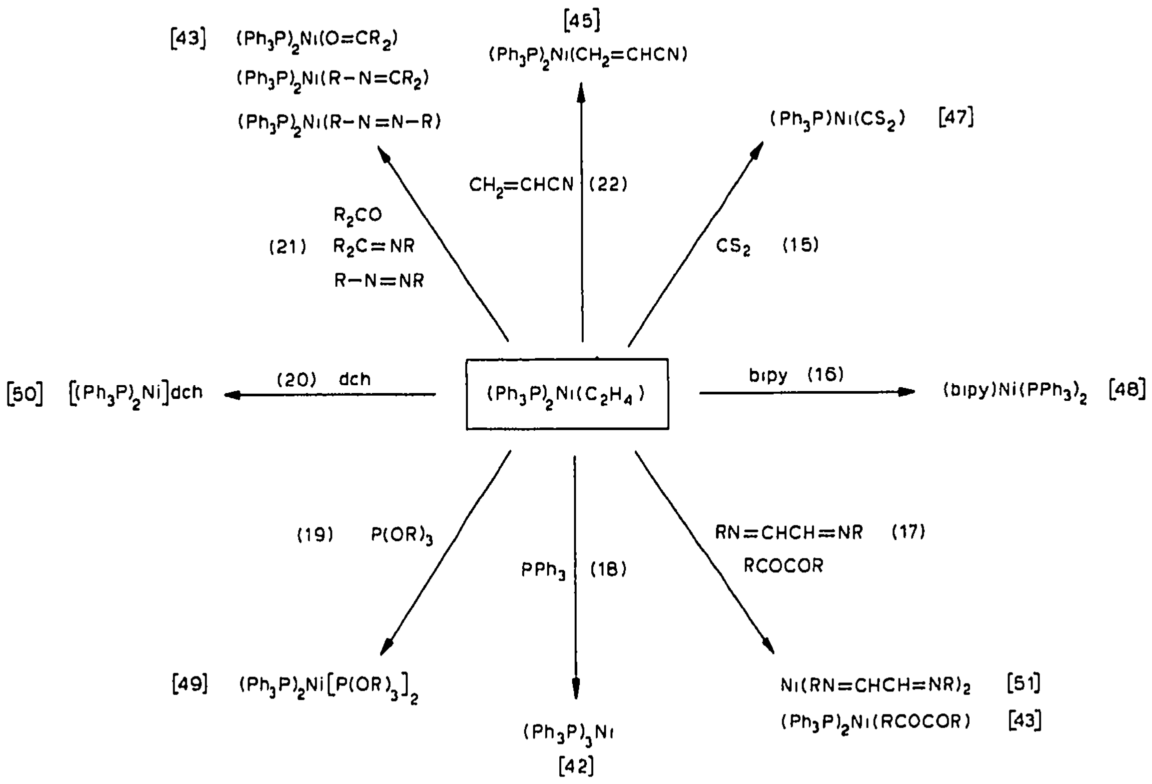


Fig. 4. Substitution reactions of $(Ph_3P)_2Ni(C_2H_4)$.

of a ligand as well as the balance of π-acceptor and n-donor strength do not vary much and are thus independent of the other ligands (D, etc.) adhering to the metal. According to our experience this is not true for triphenylphosphine.

The π-acceptor ability of compounds of trivalent phosphorus [21] (cf. Section B) depends on the electronegativity of that atom of the substituents which is directly bound to phosphorus. The carbon atom of an aryl substituent is more electronegative than that of an alkyl substituent. Therefore, aryl phosphines should be arranged between PMe_3 and $P(NMe_2)_3$, i.e. at a position where π-acceptor and π-donor abilities approximately counterbalance. Of course, a particularly high influence of the central atom and of the remaining ligands on the real donor/acceptor properties must be expected in a case like this.

Some substitution reactions of mixed-ligand complexes of nickel(0) are represented in Figs. 3 and 4 as well as in eqns. (38) to (42). Let us consider Fig. 3 first. Correlating the donor/acceptor properties of bipy, cod and of the reagents according to Section B, the above mentioned rule easily explains reactions (6)—(9) and (14). But the others deserve further discussion. Bidentate π-acceptor ligands such as 1,2-diketones RCOCOR and 1,4-diazabutadienes N—N substitute the π-acceptor cod. While the final product is already reached with (bipy)Ni(RCOCOR), in the reaction with the N—N ligands it becomes obvious that these are stronger n-donors and π-acceptors than bipy. Therefore substitution of bipy also takes place and the stable binary compounds $Ni(N—N)_2$ (13) form at the end. (bipy)Ni(cod) does not react with bipy. In accordance with the rule cod in (bipy)Ni(cod) is not substituted by bipy. But remember that $Ni(bipy)_2$ can be prepared from $Ni(\eta^5\text{-}C_5H_5)_2$ and bipy.

The delicate influence of the substituents on the π-acceptor and n-donor strength becomes evident within the ligand series $PR_3(PBu_3)$, PPh_3, $P(OEt)_3$, $P(OPh)_3$. Aliphatic or aryl—aliphatic phosphines as n-donors (cf. Section B) obviously substitute the n-donor bipy first. But the mixed-ligand complexes to be expected $(R_3'P)_2Ni(cod)$ are weakly stable to excess phosphines (cf. Fig. 4) and hence the binary complexes $Ni(PR_3)_n$ ($n = 3,4$) (12) result as final products.

The π-acceptor behaviour is dominant in the case of $P(OPh)_3$ (9). Libbey and Bancroft [54] on the other hand pointed out the good n-donor and π-acceptor properties of alkyl phosphites (alkoxo groups are less electron withdrawing than phenoxo groups and hence diminish less the basicity of the phosphorus). A certain relationship between alkyl phosphites and N—N-chelate ligands is indicated and reveals itself in the analogy of reactions (10) and (13). Steric factors must not be neglected in the interpretation of the differences between the reactions of (bipy)Ni(cod) with $P(OEt)_3$ and $P(OPh)_3$. The formation of $Ni[(POEt)_3]_4$ is more favoured than that of $Ni[P(OPh)_3]_4$ due to the smaller cone angle of $P(OEt)_3$ [17].

As mentioned above, a strong influence of the central atom and the

TABLE 2

Equilibrium constants for the reactions $(R_3P)_3M + C_2H_4 \rightleftharpoons (R_3P)_2M^0(C_2H_4) + PR_3$ in benzene at 25°C [38,42]

R_3P	Ni	Pd	Pt
Ph_3P	300	0.013	0.122
Et_3P	30 000	0.47	120

remaining ligands on the donor/acceptor properties can be expected for triphenylphosphine. That is why the interaction of at least three components (bipy/cod/PPh_3) must be considered in order to assess the reaction of (bipy) Ni(cod) with PPh_3 (11). With cod and PPh_3, potential ligands with n-donor and π-acceptor properties are exposed to the dominating n-donor bipy. In the present case, the dipy/PPh_3 combination is preferred and thus the PPh_3 substitutes the cod.

Reaction (6) proceeds only in a limited number of cases. The half-wave potential of the heteroolefin as an expression of the energy of the E_π^* orbital should be more positive than −2000 mV. Therefore, benzophenone reacts, but acetone does not [43].

The substitution reactions of $(Ph_3P)_2Ni(C_2H_4)$ (Fig. 4) do not provide new findings as compared to (dipy)Ni(cod). (15), (17), (19)–(22) follow the general rule, whereas in the case of (16) the triple interaction dipy/PPh_3/C_2H_4 again determines the final product. Equilibrium constants have been determined for (18) (Table 2). They indicate a moderately stronger bond of ethene to the moiety $(Ph_3P)_2Ni$ as compared to PPh_3. The exchange of PPh_3 by the n-(π-) donor PEt_3 increases the π-donor strength of the moiety $(R_3P)_2Ni$ and thus induces a stronger π-interaction of that moiety with ethene (cf. Section B). Therefore the bond of ethene is stronger in $(Et_3P)_2Ni(C_2H_4)$ than in $(Ph_3P)_2Ni(C_2H_4)$ (Table 2).

On the other hand, the relative weakness of the bond between a moiety of the type $(R_3P)_2Ni$ (R = alkyl) and a n-donor ligand can be gathered from the data of Table 2. It becomes clear why the reaction (23) does not proceed [41].

$$(Cy_3P)_2Ni(C_2H_4) + \text{dipy} \rightleftharpoons (Cy_3P)_2Ni(\text{dipy}) + C_2H_4 \qquad (23)$$

Therefore, (dipy)$Ni(PPh_3)_2$ remained the sole compound of type (dipy)Ni-$(PR_3)_2$ that could be isolated.

Figure 5 gives a survey of the substitution reactions of $Ni(cod)_2$ as the most important compound for access to the chemistry of nickel(0). This once more supports the rules on the reaction directions of binary nickel(0) complexes made at the beginning of this section. The displacement of a cod ligand can take place by n-donors [(25), (27)–(29)] and by strong π-accep-

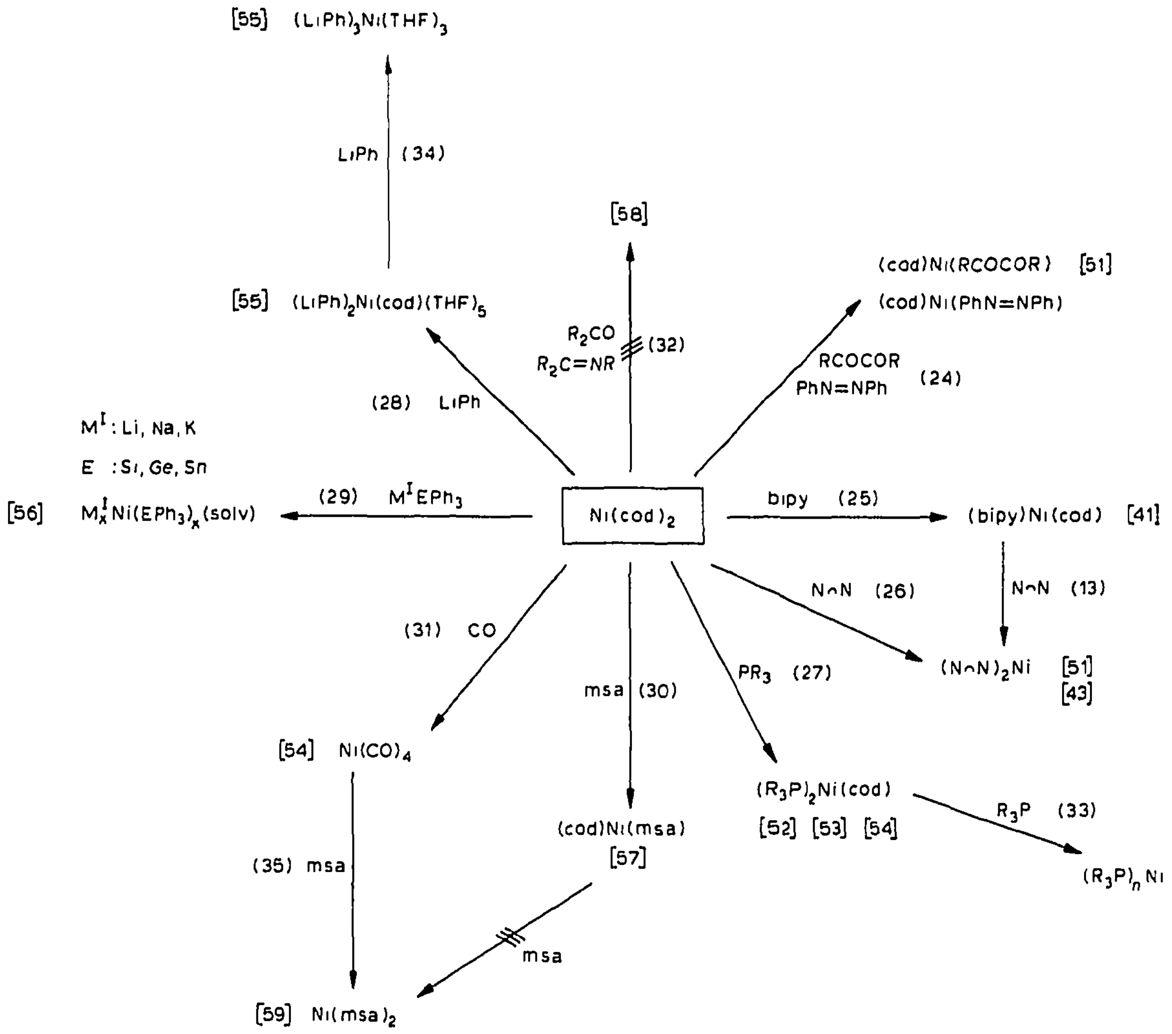


Fig. 5. Substitution reactions of Ni(cod)$_2$.

tors [(24), (30), (31): but cf. (32)]. In (cod)Ni(RCOCOR) and (cod)Ni(msa) the n-donor function of cod is then revealed and there is no further reaction with RCOCOR or msa. It is interesting that msa in $Ni(CO)_4$ completely substitutes the carbon monoxide (CO is a ligand with always dominating π-acceptor properties (35)).

Equilibrium investigations [22] show that the bonding strength of cod and C_2H_4 to moieties of the type $(R_3P)_2Ni$ is comparable. Because ethene, as stressed above, enters into an only moderately stronger bond with such moieties than phosphine, the equilibrium (36) establishes in solution.

$$(R_3P)_2Ni(cod) \underset{-cod}{\overset{+R_3P}{\rightleftarrows}} (R_3P)_3Ni \overset{+R_3P}{\rightleftarrows} (R_3P)_4Ni \qquad (36)$$

The position of equilibrium depends on the temperature and the solubility determines which complex compound crystallizes [52]. This explains why $Ni(cod)_2$ with nBu_2PPh forms $Ni(nBu_2Ph)_4$ in ether but with nPr_2PPh in hexane, $(nPr_2PPh)_2Ni(cod)$ is formed [53].

The anions EPh_3^- (E = Si, Ge, Sn) are related to the tertiary phosphines as far as their electronic structure is concerned. Thus, the analogy in the reactions (27/33) and (29) becomes clear. In bimetallic compounds solv/M^I/Ni^0-interactions are possible and these interactions may be a moment of stabilization for the whole species. This becomes quite clear for $(LiPh)_3Ni(THF)_3$, the remarkable final product of the reaction between $Ni(cod)_2$ and lithium phenyl (28/34).

$Ni(CO)_4 + 2\ msa \rightarrow Ni(msa)_2 + 4\ CO$ [59] (37)

$(bipy)Ni(PPh_3)_2 \overset{CS_2}{\rightarrow} (bipy)Ni(CS_2)$ [60] (38)

$(bipy)Ni(CO)_2 + 2\ PPh_3 \rightarrow (Ph_3P)_2Ni(CO)_2 + bipy$ [49] (39)

$(Ph_3P)_2Ni(CO)_2 + CS_2 \rightarrow (Ph_3P)Ni(CS_2) + 2\ CO + PPh_3$ [61] (40)

$(Ph_3P)_2Ni(C_2H_4) + PhNO \rightarrow (Ph_3P)_2Ni(PhNO) + C_2H_4$ [62] (41)

$Ni(PPh_3)_4 + [Me_2N{=}CH_2]Cl \rightarrow (Ph_3P)Ni^0(CH_2{=}NMe_2)Cl$ [63] (42)

$Ni(N{-}N)_2 + 4\ P(OPh)_3 \rightarrow Ni[P(OPh)_3]_4 + 2\ N{-}N$ [51] (43)

Reactions (38)—(41) show the validity of the above derived substitution rule on other ternary complexes. (42) is of interest because of the introduction of the unusual π-acceptor $CH_2{=}N^+Me_2$ and of the bonding of halogen on nickel(0). (37) and (43) supplement the knowledge of the displacement of π-acceptors among one another.

When we are going to establish relations between the substitution reactions on nickel(0) and its more heavy homologues palladium(0) and platinum(0), we should recall the following qualitative sequence of the bond between a complex moiety m^0 and a single ligand (Section B).

D—m^0: $Pt^0 > Pd^0 \sim Ni^0$ (D e.g. alkyl phosphine and even aryl phosphine, with some limitation)

m^0—A: $Ni^0 > Pd^0 \sim Pt^0$ (A e.g. CO, PF_3)

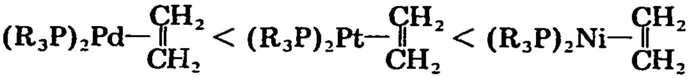
Most of the π-acceptor ligands, e.g. olefins, are also acting as n-donors. The last mentioned function particularly becomes effective when platinum(0) is the coordination partner.

m^0—(A/D): $Ni^0 > Pt^0 > Pd^0$

Therefore, the bonding strength for a third phosphine ligand in the case of moieties of the type $(R_3P)_2M^0$ increases in the series

$$(R_3P)_2Ni{-}PR_3 \sim (R_3P)_2Pd{-}PR_3 < (R_3P)_2Pt{-}PR_3$$

The bonding strength for ethene, however, increases according to



$$(R_3P)_2Pd{-}\overset{CH_2}{\underset{CH_2}{\|}} < (R_3P)_2Pt{-}\overset{CH_2}{\underset{CH_2}{\|}} < (R_3P)_2Ni{-}\overset{CH_2}{\underset{CH_2}{\|}}$$

Both series are important for establishing the equilibrium (44).

$$(R_3P)_3M^0 + C_2H_4 \rightleftharpoons (R_3P)_2M^0(C_2H_4) + PR_3 \qquad (44)$$

They explain the sequence of the equilibrium constants in Table 2 by their partly opposed oriented tendency.

A smaller π-donor strength must be assigned to complex moieties of the type $(C_2H_4)_2M^0$ as compared to those of the type $(R_3P)_2M^0$. Therefore the σ-interaction plays a more important role for the bonding of a third olefin ligand. This explains the somewhat higher stability of $Pt(C_2H_4)_3$ compared to $Ni(C_2H_4)_3$ [34]. Perhaps the particular nature of the σ-interaction is the cause of the smooth course of reaction (46) as it is not found for the corresponding nickel(0) compounds.

Figure 6 gives a survey of simple substitution reactions of $Pt(cod)_2$ and $Pt(C_2H_4)_3$. The formation of oligonuclear complexes $Pt_3(Bu^tNC)_6$ and $(cod)_2Pt_2[(CF_3)_2CO]$ characterized by structural analysis will be pointed out. Of course the latter is not the only product of the reaction of $Pt(cod)_2$ with $(CF_3)_2CO$, metal-induced couplings [67] take place besides.

Comparing Figs. 5 and 6, basic differences in the reactive behaviour of analogous nickel(0) and platinum(0) complexes to simple n-donors or π-acceptors cannot be recognized. But this is not always the case, particularly if a strong electron acceptor is offered as a reagent. In a case like this, complete electron transfer to the reagent is possible in the reaction with nickel(0) complexes (due to the high energy of their HOMO they are strong reducing reagents!). In platinum(0) or palladium(0) complexes, msa easily substitutes ethene (54), but $(Ph_3P)_2Ni(C_2H_4)$ as the analogous nickel(0) complex does

$$(Ph_3P)_2M(C_2H_4) + msa \rightarrow (Ph_3P)_2M(msa) + C_2H_4 \qquad (54)$$

not react in a simple way. Clearer relations were observed in the reaction of $(Cy_3P)_2Ni(C_2H_4)$ with msa. A paramagnetic nickel complex ($\mu_{eff.} = 2.92$ B.M.) with the unexpected molecular formula "$(Cy_3P)_2Ni(msa)_2$" could be isolated there.

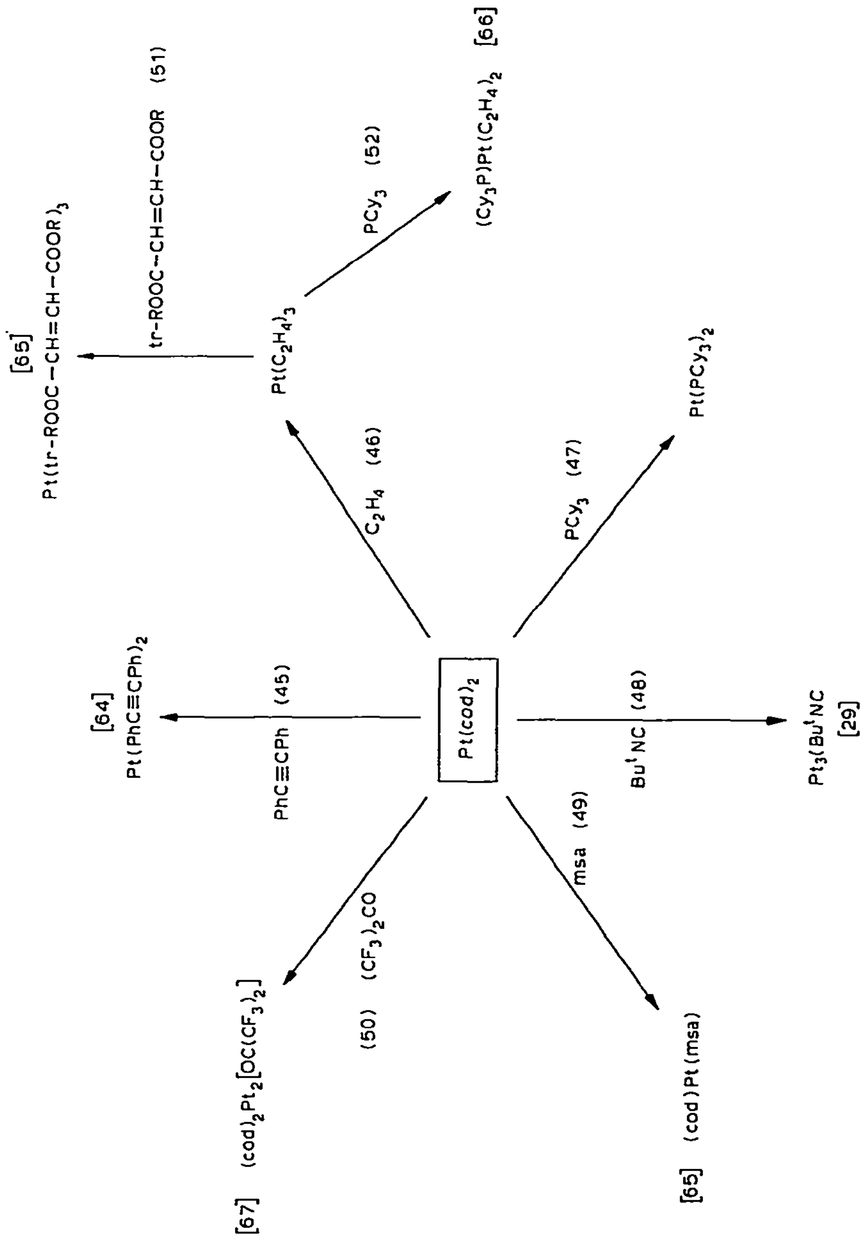
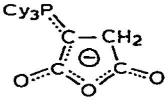


Fig. 6. Substitution reactions of $Pt(cod)_2$.

The structure is not yet known, but the radical anions VII could be



VII

detected by ESR-spectroscopy [68]. Nucleophilic additions of phosphines on msa have been known for a long time [69,70]. They do not take place in the coordination sphere of platinum(0) and palladium(0), evidently because the central atom reduces the nucleophilic behaviour of phosphine and the electrophilic behaviour of msa. This is no longer the case in a nickel(0) complex analogous to $(Ph_3P)_2Pt(msa)$ which is probably formed in the first step of reaction. The ligands react with one another with simultaneous uptake of an electron.

N-sulfinyl aniline is another reagent acting as a substituent or as an oxidant depending on the substrate offered. In phosphine-containing complexes of platinum and nickel, normal substitution takes place (PhNSO coordinates by the N=S group [74]). The reaction product with (bipy)Ni(cod),

$$(Ph_3P)_2M(C_2H_4) + PhNSO \rightarrow (Ph_3P)_2M(PhNSO) + C_2H_4 \qquad [71,72] \qquad (54)$$

M = Pt, Ni

$$(bipy)\,Ni(cod) + x PhNSO \rightarrow (bipy)Ni(PhNSO)_x + cod \qquad [73] \qquad (55)$$

$$1.4 < x < 1.6$$

however, does not contain unchanged PhNSO as a ligand. x varies within certain limits from preparation to preparation so that reliable characterization is difficult. But paramagnetism ($\mu_{eff.} = 3.08$ B.M.) shows clearly that a redox process took place here, too.

The reactions (54) and (55) show the strong influence of the ligands on nickel(0) on the run of redox reactions. This is particularly expressed in the redox additions which will be dealt with in Section D.

D. OXIDATIVE ADDITIONS

Oxidative additions may cover bonds between atoms of the same kind [H—H, O—O, C—C, P—P, Pb—Pb (56)—(60)]. In most cases, however, polar bonds encountered in organic halides (D(i)), tertiary phosphines (D(iii), silanes (61) and manifold Brönsted acids (D(ii)) are involved.

$$2(Cy_3P)Pt(C_2H_4)_2 \rightarrow (Cy_3P)HPtH_2Pt(H)(PCy_3) + 4C_2H_4 \qquad [75] \qquad (56)$$

$$(Ph_3P)_2Ni(C_2H_4) \xrightarrow[-Ph_3PO]{Bu^tOOBu^t} Ni(OBu^t)_2 \qquad [76] \qquad (57)$$

$$Ni(PR_3)_4 + NCCN \rightleftharpoons (R_3P)_3Ni(CN)_2 + PR_3 \qquad [77] \qquad (58)$$

$$2\,Ni(CO)_4 + Ph_2PPPh_2 \rightarrow (OC)_2Ni(PPh_2)_2Ni(CO)_2 + 4CO \qquad [78] \qquad (59)$$

$Pd(PPh_3)_4 + Ph_3PbPbPh_3 \rightarrow (Ph_3P)_2Pd(PbPh_3)_2 + 2PPh_3$ [79] (60)

$2(Cy_3P)Pt(C_2H_4)_2 + 2HSiEt_3 \rightarrow (Cy_3P)(Et_3Si)PtH_2\ Pt(SiEt_3)(PCy_3)$ [75] (61)

The most detailed knowledge is available on the oxidative additions of organic halides. For this reason we shall treat these reactions first and discuss questions such as the influence of the solvent and coordinative saturation of the central atom on the course of reaction. Catalytic processes including at least one oxidative addition as a partial step are discussed along with the corresponding organic substrates in Section D(ii).

As per definition, oxidative additions are connected with the splitting of a single bond. Reactions in the course of which double bonds are split in consequence of the reduction of a reagent by electron-rich complexes of the nickel triad are also known and will be dealt with in a separate section (D(iv)).

(i) Organic halides

The following will be mentioned before the discussion of the oxidative addition of organic halides to zero-valent complexes of the nickel triad. (i) Nickel(0) complexes are stronger reducing reagents than the corresponding platinum(0) and palladium(0) compounds [14]. (ii) Recently, some binuclear complexes of platinum(I) and palladium(I) were described [80—82], but monomeric examples are very rare [83]. Monomeric nickel(I) compounds, however, are easily accessible [84—86]. Phosphine containing nickel(0) complexes are oxidized by nickel(II) or cobalt(II) compounds (62) or by stoichiometric amounts of halogen yielding the corresponding nickel(I) complexes [87—89].

$Ni(PPh_3)_4 + (Ph_3P)_2CoCl_2 \longrightarrow (Ph_3P)_3NiCl + (Ph_3P)_3CoCl$ (62)

These factors cause certain differences in the redox addition of organic halides. The behaviour of the platinum(0) and palladium(0) complexes seems to be more simple. Despite numerous investigations [3,91—95] a consistent explanation cannot be given at the present stage.

Kramer and Osborn [93] postulate that the course of reaction depends on the structure of the reacted aliphatic halides (Fig. 7). Nucleophilic substitution according to a S_N2-mechanism represents one way (63). Leaving out the inversion at the α-carbon atom, this way leads to the same final product as (64/65) (formation of a radical pair which collapses subsequently). There is a third possibility for the formation of $R—Pt^{II}—X$, viz. through a radical chain (66/67). Considering only the variation of the oxidation stage, (63) involves a two-electron step, whereas (64/65) and (66/67) involve a series of one-electron steps.

There is another possibility for reaction of the unstable species $X—Pt^{I}$. It can interact with highly reactive halides, above all alkyl iodides due to the relative weakness of the C—I bond, yielding dihalogeno platinum(II) complexes directly (68). The organic radicals R resulting from (68) or (69) can be

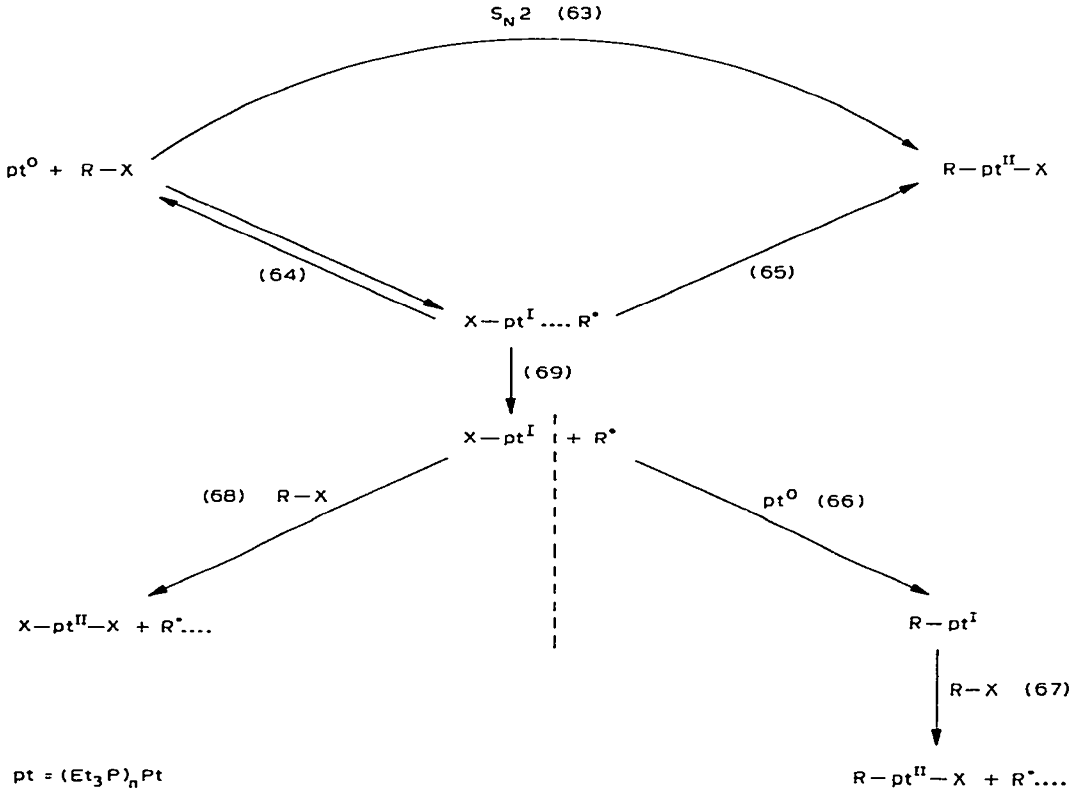
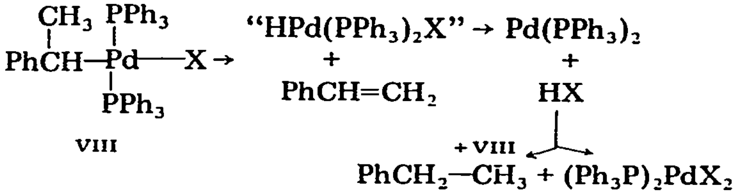


Fig. 7. Mechanisms of the redox addition of alkylhalides to platinum(0) complexes [93].

consumed by a disproportionation—combination reaction or even by interaction with solvent [95]. Therefore, the formation of the dihalogeno complex X—Pt^{II}—X is obviously preferred in the case of reactions in thf. H—Pt^{II}—X as a secondary product of the redox addition of alkyl halides is also noteworthy.

Kramer and Osborn [93] discuss path (63) for benzyl chloride as a substrate easily accessible to S_N2 reactions in general. Benzyl bromide is believed to react both according to (63) and (64/68) on account of the stronger favouring of radical mechanisms in the case of bromalkanes. For isopropylbromide they prefer the chain mechanism (66/67) (inhibition by adding duroquinone). In the case of isopropyliodide, (68) (observation of CIDNP) and (66/67) are said to compete with subsequent formation of the secondary product H—Pt^{II}—I.

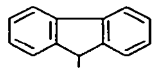
Lappert and Lednor [91] detected alkyl radicals in the reaction mixtures of $Pt(PPh_3)_3$ and alkyl halides by spin trapping with Bu^tNO and therefore they believe that the non-chain mechanism (64/65) is preferred. Lau and Stille [94] found other results in their investigations on the oxidative addition of aliphatic halides to $Pd(PPh_3)_4$. In at least two cases (benzyl-*α*-*d*-chloride and α-phenetyl bromide) they found inversion at the α-C-atom and did not observe CIDNP in the reaction with benzyl bromide [96]. Finally, they detected a reaction with $\mathrm{Bu^tNO}$ under formation of $\mathrm{Bu^tN(Ph)O}$ for $\mathrm{(Ph_3P)_2Pd(CH_2Ph)Cl}$ in contrast to the corresponding platinum compound [91]. From this they concluded that the oxidative addition of aliphatic halides takes place via a S_N2-mechanism at the central atom palladium(0) (63) and that radicals or their secondary products result by decomposition of the primary products $\mathrm{R{-}Pd^{II}{-}X}$, e.g. by β-hydrogen elimination (70) or reductive elimination (71).



$$\underset{\mathrm{VIII}}{\mathrm{PhCH(CH_3){-}Pd(PPh_3)_2{-}X}} \rightarrow \text{“}\mathrm{HPd(PPh_3)_2X}\text{”} + \mathrm{PhCH{=}CH_2} \rightarrow \mathrm{Pd(PPh_3)_2} + \mathrm{HX};\quad \mathrm{HX} \xrightarrow{+\,\mathrm{VIII}} \mathrm{PhCH_2{-}CH_3} + \mathrm{(Ph_3P)_2PdX_2} \qquad (70)$$

$$2\ \mathrm{R{-}Pd(PPh_3)_2Br} \rightarrow \mathrm{R{-}R} + \mathrm{Pd(PPh_3)_2} + \mathrm{(Ph_3P)_2PdBr_2} \qquad (71)$$

R =



Only differences in the reactive behaviour of $\mathrm{Pt(PEt_3)_3}$, $\mathrm{Pt(PPh_3)_3}$ and $\mathrm{Pd(PPh_3)_4}$ towards aliphatic halides can be concluded from these results. In the case of platinum compounds, the radical mechanisms (chain or non-chain) seem to be dominating, whereas the nucleophilic substitution seems to be dominating in the case of the palladium compound. At the present state of knowledge this statement must not be considered as final. In the following it must still be proved how the reactivity of electron rich complexes of the nickel triad is essentially determined by the ligands. All reactions indicated in Fig. 7 are possible. But in each special case the path of the reaction depends on the nature of the central atom and its ligands, on the substrate and the reaction conditions (solvent, temperature).

Although the degree of unsaturation of the central atom has been taken into account in the investigations of the oxidative addition to platinum(0) or palladium(0) complexes, definitive hints on qualitative differences in the course of reaction that can be attributed primarily to the number of potentially free coordination sites in the complex are scarcely available. In the case of nickel(0) complexes the relations are somewhat different. Substitution-unstable complexes like (bipy)Ni(cod) (Fig. 3) or $\mathrm{(Ph_3P)_2Ni(C_2H_4)}$ (Fig. 4) where the olefin can easily be replaced by other substrates are known here. Ascribing principal importance to the tendency of low valent nickel to be surrounded by four tightly bound donor atoms (an assumption which is supported by comprehensive experimental material), we can say that (bipy)Ni(cod) and $\mathrm{(Ph_3P)_2Ni(C_2H_4)}$ have two potentially free coordination sites.

It is true that substitutions of $\mathrm{(bipy)Ni(PPh_3)_2}$ and $\mathrm{Ni(PPh_3)_4}$ are possible with strongly π-acidic ligands such as $\mathrm{CS_2}$ (38). But normally they have only one free coordination site resulting from a dissociation in solution (72,73).

$(bipy)Ni(PPh_3)_2 \rightarrow (bipy)Ni(PPh_3) + PPh_3$ (72)

$Ni(PPh_3)_4 \rightarrow Ni(PPh_3)_3 + PPh_3$ (73)

Starting from these considerations we can understand the following reactive behaviour of mixed ligand nickel(0) complexes: (bipy)Ni(cod) and $(Ph_3P)_2Ni(C_2H_4)$ representing the nickel(0) complexes with two potentially free coordination positions can bond both fragments of an alkyl halide as required by normal oxidative addition (74—76).

$(Ph_3)_2Ni(C_2H_4) + PhCH_2Cl \xrightarrow{-20^\circ C} (Ph_3P)_2Ni(CH_2Ph)Cl + C_2H_4$ [97] (74)

$(bipy)Ni(cod) + PhCH_2Cl \rightarrow (bipy)Ni(CH_2Ph)Cl + cod$ [98] (75)

$(Cy_3P)_2Ni(C_2H_4) + RX \rightarrow (Cy_3P)_2Ni(R)X + C_2H_4$ [99] (76)

$RX = CH_3I, C_2H_5Br$

Assumptions on the course of reaction are possible. (74) yields pure $(Ph_3P)_2Ni(CH_2Ph)Cl$ at —20° C and a product contaminated by $(Ph_3P)_2NiCl$ is obtained at room temperature. There is no sufficient reason by assuming that a radical pair of the type $X—Ni^I \cdots R$ (cf. Fig. 7) will collapse completely yielding $(Ph_3P)_2Ni(CH_2Ph)Cl$ at —20°C, but dissociate to a larger extent at room temperature and then continue to react with $PhCH_2Cl$ yielding $(Ph_3P)_2NiCl_2$ in analogy with (68). More probably $(Ph_3P)_2Ni(C_2H_4)$ reacts with $PhCH_2Cl$ under nucleophilic substitution (63). When the temperature increases, a radical mechanism (64) becomes effective. Apart from (68), (77) must also be noted as a secondary reaction [97]. When using $PhCH_2Br$, the reaction sequence (64/69/77) already plays a role at —20°C, only a mixture

$2(Ph_3P)_2NiCl + PhCH_2Cl \rightarrow (Ph_3P)_2NiCl_2 + (Ph_3P)_2Ni(CH_2Ph)Cl$ (77)

of $(Ph_3P)_2Ni(CH_2Ph)Br$ and $(Ph_3P)_2NiBr_2$ is obtained. Hence, similar differences in the reactivity towards benzyl halides as in the case of $Pt(PEt_3)_3$ are observed for $(Ph_3P)_2Ni(C_2H_4)$ [93].

$(bipy)Ni(PPh_3)_2$ and $Ni(PPh_3)_4$ representing the nickel(0) complexes with only one potential free coordination site add only one of the fragments of alkyl halides during the starting phase, viz. the halogen (78,79). The alkyl radical as the second fragment is subject to secondary reactions already discussed in connection with redox additions to platinum(0) complexes.

$(bipy)Ni(PPh_3)_2 + R'Br \rightarrow (bipy)Ni(PPh_3)Br + PPh_3 + R'$ [60] (78)

$(Ph_3P)_4Ni + EtBr \rightarrow Ni(PPh_3)_3Br + Et\cdot + PPh_3$ [100] (79)

$R'Br = Bu^tBr, PhCH_2Br$

The complexes of this second group preferably react in a one-electron step. Nevertheless it happens that both fragments of an alkyl halide are bound to these compounds. One example is the reaction of $(bipy)Ni(PPh_3)_2$ with methyl iodide yielding (bipy)Ni(PPh_3)I and (bipy)Ni(CH_3)$_2$ [88]. The following mechanism is discussed.

$$\text{(bipy)Ni(PPh}_3\text{)}_2 \rightleftharpoons \text{(bipy)Ni(PPh}_3\text{)} + \text{PPh}_3 \qquad (72)$$

$$\underset{\text{IX}}{\text{(bipy)Ni(PPh}_3\text{)}\cdots\text{CH}_3\text{—I}\cdots\text{(Ph}_3\text{P)Ni(bipy)}}$$

$$\longrightarrow \text{“[(bipy)Ni(PPh}_3\text{)(CH}_3\text{)]}_2\text{”} + \text{(bipy)Ni(PPh}_3\text{)I} \qquad (80)$$

$$\underset{\text{X}}{\text{“[(bipy)Ni(PPh}_3\text{)(CH}_3\text{)]}_2\text{”}} \rightarrow \text{(bipy)Ni(PPh}_3\text{)}_2 + \text{(bipy)Ni(CH}_3\text{)}_2 \qquad (81)$$

The fact that only (bipy)Ni(PPh_3)I is obtained in the reaction with bulky alkyl iodides supports the assumption that IX is the activated complex. A direct proof of the probable methyl-bridged compound X has failed so far. The difficulties encountered in a detailed study of the reaction, i.e. the high sensitivity of all products to air and humidity, should be pointed out.

A redox addition comparable to (81/82) is known for cobalt(0) (82).

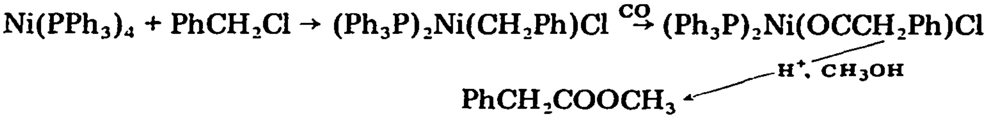
$$2\ \text{Co}^0[\text{P(CH}_3)_3]_4 + \text{CH}_3\text{Br} \rightarrow [(\text{CH}_3)_3\text{P}]_4\text{Co}^\text{I}\text{CH}_3 + [(\text{CH}_3)_3\text{P}]_3\text{Co}^\text{I}\text{Br} + \text{P(CH}_3)_3 \qquad [101] \quad (82)$$

Several papers discuss two-electron mechanisms with subsequent splitting of the organic residue from the nickel(II) complex (R_3P)$_3$Ni(R)X formed for oxidative addition of alkyl halides to nickel(0) complexes of the second group (Ni(PPh_3)$_4$ [83], Ni($HPPh_2$)$_4$ [102]). There are no arguments against the direct formation of (Ph_3P)$_3$NiX by one-electron transfer (cf. 79) or of ($HPPh_2$)$_3$NiX$_2$ through (83/84; cf. 64/68).

$$\text{Ni(HPPh}_2)_3 + \text{RX} \rightarrow \text{Ni(HPPh}_2)_3\text{X} + \text{R}\cdot \qquad (83)$$

$$\text{Ni(HPPh}_2)_3\text{X} + \text{RX} \rightarrow \text{Ni(HPPh}_2)_3\text{X}_2 + \text{R}\cdot \qquad (84)$$

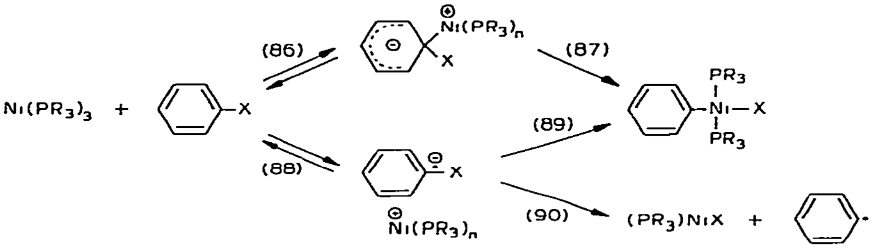
The fact that a phenylacetic acid ester (60% yield) results from the reaction of Ni(PPh_3)$_4$ with benzyl chloride and subsequent carbonylation and esterification calls for a comment [103]. It is explained from the reaction sequence (85). Nickel-containing intermediates were not isolated; the authors do not report on an intermediate dark violet colouration of the solution as would be expected in the formation of (Ph_3P)$_2$Ni(CH_2Ph)Cl [97]. It may be possible that, in analogy with (80), a nickel(I) compound results first and yields the phenylacetic acid methyl ester with CO and methanol. In contrast to the reaction of Pd(PPh_3)$_4$ with benzyl-*α*-*d*-chloride [94], the ester is obtained as racemate with Ni(PPh_3)$_4$. Therefore, differences in the mechanism are strongly suggested.



$$\text{Ni(PPh}_3)_4 + \text{PhCH}_2\text{Cl} \rightarrow (\text{Ph}_3\text{P})_2\text{Ni(CH}_2\text{Ph)Cl} \xrightarrow{\text{CO}} (\text{Ph}_3\text{P})_2\text{Ni(OCCH}_2\text{Ph)Cl} \xrightarrow{\text{H}^+,\ \text{CH}_3\text{OH}} \text{PhCH}_2\text{COOCH}_3 \qquad (85)$$

Nickel(II)-aryl complexes are more stable than nickel(II)-alkyl complexes, presumably on account of the higher electronegativity of the coordinated

C-atom. That is why they can be prepared in high yield by oxidative addition in boiling benzene [104]. Aryl halides having electron-withdrawing substituents react according to an aromatic nucleophilic substitution mechanism (86/87). A radical process initiated by an electron transfer to the aromatic system (88/89) [105,106] seems to be dominant for sterically-hindered and not activated aryl halides.



XI

The reaction scheme for aryl halides does not principally differ from that for alkyl halides (Fig. 7), but aryl halides are less active without exception. This is why dihalogeno complexes $(R_3P)_2NiX_2$ are not formed, leaving out C_6Cl_6 [106]. Due to the higher stability of the radical anions $Ar{-}X^{\cdot-}$, an appropriate lifetime can be expected for the pair of radical ions XI, and within this lifetime the kinetically unstable "cation" $Ni(PR_3)_3^{\cdot+}$ ($3d^9$-configuration) should be able to add or to split off phosphine ligands. Therefore, as far as the composition of the final products is concerned, no essential differences between reactions of $Ni(Par_3)_n$, $Ni(Palk_3)_n$ or $(R_3P)_2Ni(olefin)$ (n = 3, 4) are to be expected in this case. They become obvious when considering the reaction rate and product distribution in the same solvent (benzene or toluene). (i) The oxidative addition of chlorobenzene to $Ni(PEt_3)_3$ takes place immediately at room temperature, whereas hours are necessary with $Ni(PPh_3)_3$ [107]. (ii) Benzonitrile adds to $Ni(PEt_3)_3$ but not to $Ni(PPh_3)_3$ [107]. (iii) In reactions with $Ni(PPh_3)_3$ the radical process (88/89) plays a larger role than for $Ni(PEt_3)_3$ [106]. (iv) $Ni(PEt_3)_3$ is more active than $(Et_3P)_2Ni(cod)$ [106]. It is interesting in this connection that $Ni(cod)_2$ does not react with aryl halides in toluene or thf [108].

The "electron pressure" of nickel(0) should be decisive for the course of reaction, no matter whether the oxidative addition of aryl halides is initiated by a nucleophilic attack or by an electron transfer. The anodic half-wave potentials (Ni(0) → Ni(I)) determined by polarography may serve as reference for that electron pressure. Table 3 shows a clear sequence of these values and thus a decrease in reactivity is expected in the following direction:
$Ni(P\,alk_3)_3 > Ni(P\,ar_3)_3 > (P\,alk_3)_2Ni(olefin) > (P\,ar_3)_2Ni(olefin) > Ni(cod)_2$.

The results mentioned above for the oxidative addition of aryl-halides to nickel(0) complexes are in conformity with this "order of reactivity" and this encourages us to consider the palladium(0) and platinum(0) complexes in a similar way. Data obtained under the same conditions as the anodic half-

TABLE 3

Anodic half-wave potentials (V) of nickel(0) complexes [109]

(bipy)Ni(cod)	−0.55	$(Cy_3P)_2Ni(C_2H_4)$ [b]	−0.20
$(bipy)Ni(PPh_3)_2$ [a]	~−0.5	$(Ph_3P)_2Ni(C_2H_4)$	+0.16
$Ni(PPh_3)_4$ [a]	−0.33	$Ni(cod)_2$	+0.30

Conditions: Room temperature in thf; Hg-dropping electrode, calomel electrode as a reference, $c_{complex} \sim 1 \cdot 10^{-3}$ m, $c_{(NH_4)PF_6} = 1 \cdot 10^{-1}$ m.

[a] In dilute solutions dissociation to $(bipy)Ni(PPh_3)$ or $Ni(PPh_3)_3$.

[b] Because of its extreme air sensitivity a complex $Ni(Palk_3)_3$ was not investigated. But comparing $(Cy_3P)_2Ni(C_2H_4)$ and $(Ph_3P)_2Ni(C_2H_4)$ for $Ni(P\,alk_3)_4$ a more negative value than for $Ni(PPh_3)_4$ is to be expected.

wave potentials in Table 3 are not available. A smaller reactivity can be expected because the platinum(0) and palladium(0) complexes are weaker reducing agents without exception than the analogous nickel compounds (Section B). The following experimental results support this assumption [107]. (i) Within the complexes $Pt(PEt_3)_4$, $Pd(PEt_3)_4$ and $Ni(PEt_3)_4$ only the latter reacts with benzonitrile. (ii) $Ni(PEt_3)_4$ immediately reacts with fluorhalogen benzenes at room temperature, but $Pd(PEt_3)_4$ and $Pt(PEt_3)_4$ react only when boiled in toluene for several hours (91).

$$M(PEt_3)_4 + XC_6H_4F \rightarrow tr\text{-}(Et_3P)_2M(C_6H_4F)X + 2PEt_3 \qquad (91)$$

As mentioned above $Ni(cod)_2$ does not react with aryl halides in toluene. C—C coupling (92) takes place in dmf as a polar solvent. (92) is probably initiated by an oxidative addition (94). For interpreting these further steps, the

$$Ni(cod)_2 + 2\,ar\text{—}X \xrightarrow[dmf]{25°\text{—}40°C} NiX_2 + ar\text{—}ar + 2cod \qquad (92)$$

following observations are important. $(Ph_3P)_2Ni(Ph)Cl$ splits off diphenyl in toluene (80°C) [109]. Investigations of the corresponding complexes of substituted triphenylphosphines revealed that the coupled phenyl residues originate at least partially from tertiary phosphine. Nickel(I) complexes formed by phenyl elimination from $(Ph_3P)_2Ni(Ph)Cl$ are discussed as intermediates. But nickel(I) compounds are unstable in polar solvents and disproportionate [110]. Therefore in dmf a nickel(I) complex as an intermediate and an elimination according to

$$2(Ph_3P)_2Ni(Ph)Cl \rightarrow Ph\text{—}Ph + 2(Ph_3P)_2NiCl\cdots$$

are improbable. As a consequence only $(Ph_3P)_2Ni(Ph)_2$ is of interest as substrate for reductive elimination of diaryls. Actually, 99% of diphenyl to be expected according to (93) is found in the decomposition of $(Ph_3P)_2Ni(Ph)Cl$

$$\begin{array}{l} 2(Ph_3P)_2Ni(Ph)Cl \xrightarrow[dmf]{45°C} (Ph_3P)_2NiPh_2 + (Ph_3P)_2NiCl_2 \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad Ph\text{—}Ph + (Ph_3P)_2Ni\cdots \end{array} \qquad (93)$$

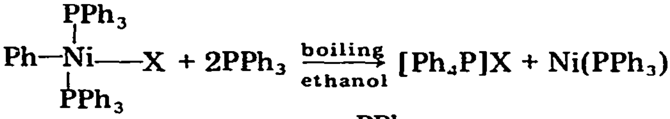
in dmf (45°C) [111]. This clarifies the special role of dmf as a reaction medium in the diaryl synthesis (92) and a reaction course according to (94—96) becomes very probable.

$$\mathrm{Ni(cod)_2 + ar{-}X \rightarrow (cod)_{\mathit{n}}Ni(ar)X + (2-\mathit{n})\,cod} \qquad (94)$$

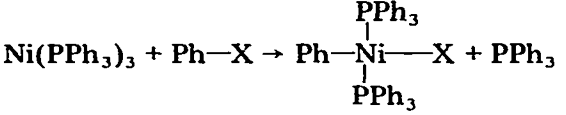
$$\mathrm{2(cod)_{\mathit{n}}Ni(ar)X \rightarrow (cod)_{\mathit{n}}Ni\,ar_2 + NiX_2 + \mathit{n}\,cod} \qquad (95)$$

$$\mathrm{(cod)_{\mathit{n}}Ni\,ar_2 + ar{-}X \rightarrow (cod)Ni(ar)X + ar{-}ar} \qquad (96)$$

The decomposition of $(Ph_3P)_2Ni(Ph)Cl$ proceeds in a different way when excess PPh_3 is added [112]. Now the main product is a quaternary phosphonium salt. The aryl residue attacks a phosphine molecule in a nucleophilic way (97); nickel(II) is reduced at the same time to nickel(0). The reaction can be carried out catalytically since $Ni(PPh_3)_3$ adds aryl halides (98).

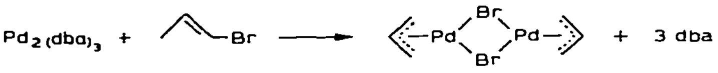


$$\mathrm{Ph{-}\overset{PPh_3}{\underset{PPh_3}{Ni}}{-}X + 2PPh_3 \xrightarrow[\text{ethanol}]{\text{boiling}} [Ph_4P]X + Ni(PPh_3)_3} \qquad (97)$$

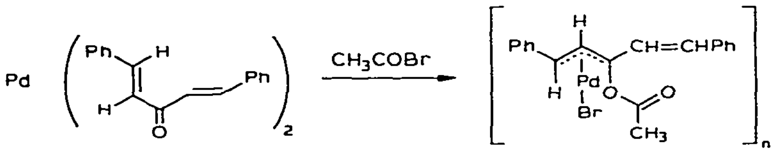


$$\mathrm{Ni(PPh_3)_3 + Ph{-}X \rightarrow Ph{-}\overset{PPh_3}{\underset{PPh_3}{Ni}}{-}X + PPh_3} \qquad (98)$$

In all the reactions discussed so far, the fragments of the organic halogen compound were added only to the central atom. But reactions during the course of which one of the fragments is bound to the ligand are also known. $Pd_2(dba)_3$ forms the normal redox addition product with allyl bromide (99), but the acyl group of acetyl bromide is added to the ligand in the case of the related complex $Pd(dba)_2$, namely to carbonyl oxygen as the most electronegative constituent (100). The central β,β'-dienone changes to the substituted allyl cation.



[113] (99)



[114] (100)

(ii) Brönsted acids

Brönsted acids of different strengths (101,102) are suitable for oxidative additions. It must be noted that, in contrast to the general tendency, the proton can also be added to four-coordinate nickel(0) complexes (103). Thus, the formation of five-coordinate nickel(II) complexes becomes possible in the course of oxidative additions (104). In the following, only the reactions with weakly acidic compounds (N—H and C—H acids) will be discussed because they are particularly suited for representing the synthetic potential of the oxidative addition.

$$(Cy_3P)_2Ni + HBr \rightarrow (Cy_3P)_2Ni(H)Br \qquad [99] \quad (101)$$

$$(Cy_3P)_2Ni + PhOH \rightarrow (Cy_3P)_2Ni(H)(OPh) \qquad [99] \quad (102)$$

$$Ni[P(OEt)_3]_4 + H_2SO_4 \rightarrow HNi[P(OEt)_3]_4^+ + HSO_4^- \qquad [90] \quad (103)$$

C—H acidic compounds, whose reactivities towards electron-rich complexes of the nickel triad have been investigated, are indicated in Table 4. Detailed data on the reactions of hydrogen cyanide and malonic acid ester are available.

Hydrogen cyanide is added both by $Ni(PR_3)_4$ [115] and $Pt(PPh_3)_4$ [116] (104, 105). The tendency mentioned above of nickel to extend the coordination sphere to 5 in the addition of hydrogenous species causes differences in the stoichiometry of the final products; platinum(II) complexes are square-planar, nickel(II) complexes are trigonal-bipyramidal. There are two pathways of formation for the complexes XII.

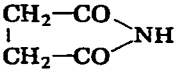
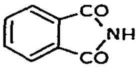
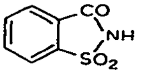
$$\underset{n\,=\,3,\,4}{Ni(PR_3)_n} + HCN \xrightarrow[\text{or methanol}]{\text{toluene}} \underset{\text{XII}}{HNi(PR_3)_3(CN)} + (n-3)PR_3 \qquad (104)$$

$$Pt(PPh_3)_3 + HCN \xrightarrow{\text{benzene}} HPt(PPh_3)_2(CN) + PPh_3 \qquad (105)$$

The non-ionic (106/107) pathway dominates in the case of compounds which easily split off a phosphorus ligand (L = tertiary phosphine), whereas

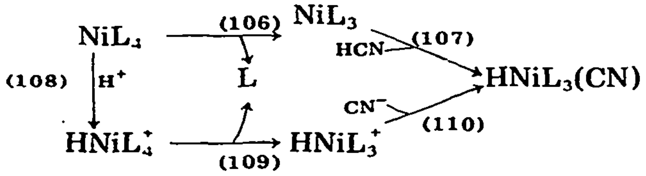
TABLE 4

C—H acidic and N—H acidic compounds and their reaction products with electron-rich complexes of the nickel triad

	pk_a(20°C)		Products	
$CH_3CH(NO_2)CH_3$	7.7	[117]	*cis*-$pt(NO_2)_2$	[120]
CH_3NO_2	10.2	[117]	$pt(C{\equiv}N{-}O)_2$	[120]
HCN	9.2		$(R_3P)_3Ni(H)CN$	[115]
$CH_2(COOEt)_2$	13.3	[117]	$(dipy)Ni[CH(COOEt)_2]_2$	[118]
CH_3CH_2CHO	13—14 [a]		$Et{-}CH{=}C(CH_3){-}CHO$	[119]
 (si—H)	10.5	[121]	pt(H)(si), $pd(si)_2$	[121]
 (pi—H)	8.3	[121]	pt(H)(si)	[121]
 (sa—H)	11.7	[121]	pt(H)(sa)	[121]

[a] Estimated (pk_a of acetaldehyde 12.9 and +*I*-effect of the methyl group).

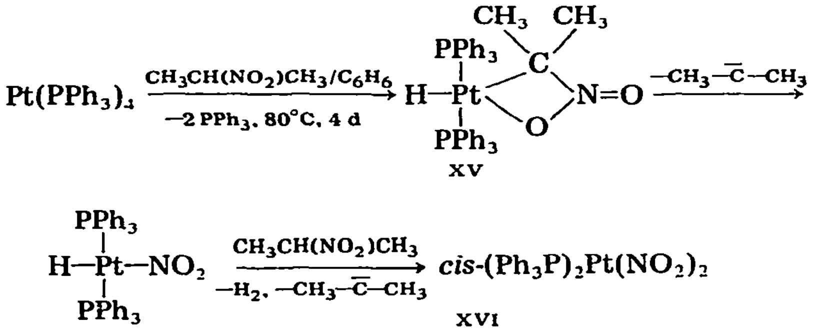
the ionic pathway (108—110) (solvent methanol) is important when slowly dissociating NiL_4 species are used, e.g. $Ni[P(OEt_3)]_4$.



A preliminary communication [118] reports that $Pt(PPh_3)_4$ yields the substitution product $(Ph_3P)_2Pt$ [EtOOC—CH=C(OH)(OEt)] with malonic ester in boiling benzene with coordination through the C=C-bond of the enol form. Clear dependence of the reactivity towards this ester on the set of the ligands is observed in the case of nickel(0) complexes [181]: $(Ph_3P)_2Ni(C_2H_4)$ and $Ni(cod)_2$ do not react in thf at room temperature and decomposition on precipiting metal occurs at increased temperature. With (bipy)Ni(cod), however, an octahedral complex of nickel(II) (XIII) where the anion of malonic acid ester is bound as a chelate ligand is formed (Fig. 8). In the first step it is likely that an oxidative addition of the acidic C—H group (111) takes place and then a simple acid—base reaction with hydrogen evolution follows (112). Here again the interrelationship between the redox potential and the reactivity of nickel(0) complexes already outlined in Section D(i) becomes apparent.

It is assumed that the catalytic effect of (bipy)Ni(cod) in the aldol condensation (Fig. 8) is also due to the oxidative addition of a C—H acidic methylene group (113). Insertion of a carbonyl group (114) and dehydration between the two C-containing ligands in the *cis* position (115) should follow. α-Methyl-β-ethyl-acrolein is obtained when propionaldehyde is used as a substrate. A nickel(0) complex of this aldehyde (XIV) can be isolated from the reaction mixture. This complex acts as a catalyst for aldol condensation at the same time (116) [181].

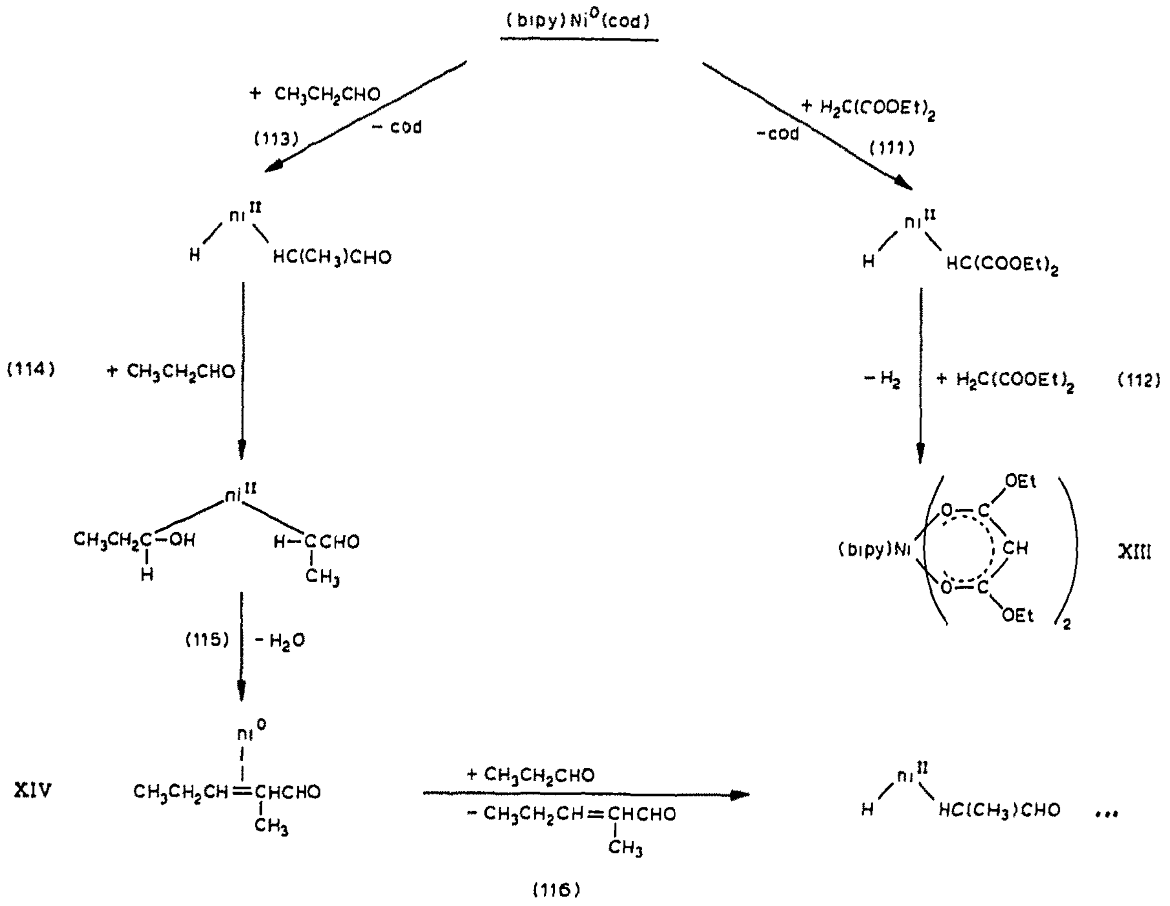
Secondary products of oxidative additions are also obtained in the reactions of aliphatic nitro compounds with $Pt(PPh_3)_4$. 2-Nitro propane as the strongest C—H acidic compound (117) is most active; transition to a polar protic solvent is required in the case of nitromethane to start the reaction.



XV

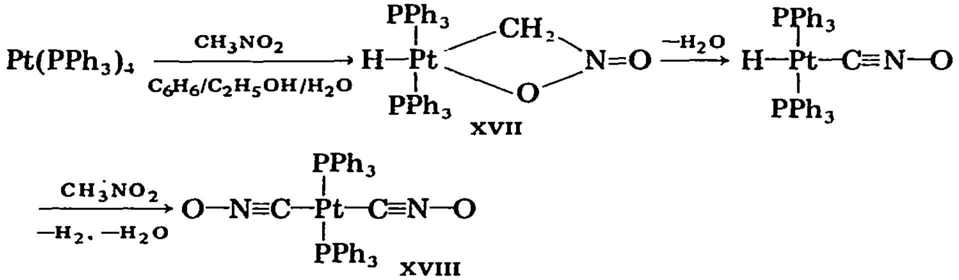
XVI

(117)



ni = Ni(bipy)

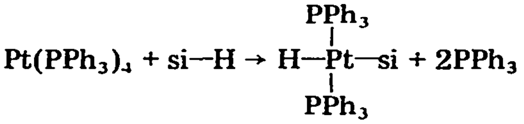
Fig. 8. Reactions of (bipy)Ni(cod) with malonic ester and propionic aldehyde.



XVII XVIII (118)

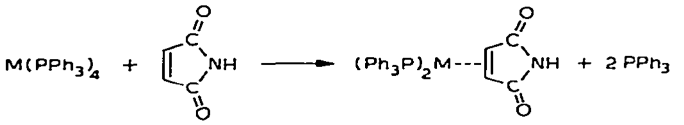
The primary products are unstable. XVII is stabilized by dehydration. Since this is not possible in the case of XV, dimethylcarbene is eliminated. A *cis*-dinitro compound (XVI) or a fulminate (XVIII) are finally formed via a simple acid—base reaction and a second elimination.

Cyclic acid imides also add to $Pt(PPh_3)_4$ (119) as expected on the basis of the pK_a values (Table 4). While the hydride $HPt(PPh_3)_2(si)$ (si is the anion of succinimide) in the reaction medium is stable, the corresponding palladium compound could not be isolated. On the contrary, it continues to react in a



$$Pt(PPh_3)_4 + si{-}H \rightarrow H{-}\overset{PPh_3}{\underset{PPh_3}{Pt}}{-}si + 2PPh_3 \qquad [121] \quad (119)$$

$$Pd(PPh_3)_4 + 2si{-}H \rightarrow (Ph_3P)_2Pd(si)_2 + H_2 + 2PPh_3 \qquad [121] \quad (120)$$



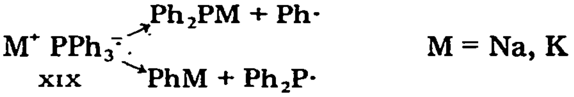
[121] (121)

simple acid—base reaction yielding the diimide $(Ph_3P)_2Pd(si)_2$. In Pauling's scale, platinum is more electronegative than palladium. Comparing $HPt(PPh_3)_2(si)$ and $HPd(PPh_3)_2(si)$, hydrogen is more negatively polarized in the case of the latter. Therefore, a reaction with the positively polarized hydrogen of si—H is more likely for $HPd(PPh_3)_2(si)$ than for $HPt(PPh_3)_2(si)$.

It is interesting that maleic acid imide behaves like a polar olefin towards $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$ and substitutes phosphine ligands (121).

(iii) Tertiary phosphines

Among the tertiary phosphines the triarylphosphines are only ones reduced at the dropping mercury electrode in a reversible one-electron step (PPh_3: $E_{1/2} = -2.670$ V in dmf [122]). The anion radical $PPh_3^{\overline{\cdot}}$ is also formed in the reaction of phosphine with alkali metals in thf at low temperatures and can be identified by ESR-spectroscopy. The following initial steps for the decomposition are discussed [123].



$$M^+\,PPh_3^{-\cdot} \;(\text{XIX}) \rightarrow Ph_2PM + Ph\cdot \qquad M = Na, K \qquad (122)$$

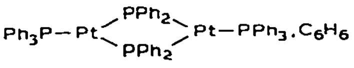
$$M^+\,PPh_3^{-\cdot} \;(\text{XIX}) \rightarrow PhM + Ph_2P\cdot \qquad (123)$$

XIX is suggestive of the radical ion pair XI and decomposition according to (122) is suggestive of (90). (89) was indicated for XI as a further secondary reaction yielding an oxidative addition product of RX to $Ni(PPh_3)_3$. XIX cannot react in this way, but an ion pair $M'(PR_3)_n^+\ PPh_3^-$ ($M' = Ni, Pd, Pt$) can. Consequently, there are possibilities for oxidative addition of PPh_3 to electron-rich complexes of the nickel triad as already found in several variants for $Os_3(CO)_8$ [124].

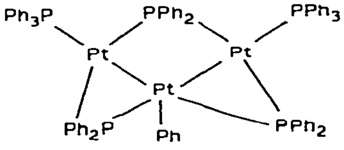
The binary compounds $M'(PPh_3)_{3 or 4}$ are stable by all means. But according to the results reported in Section D(i), redox addition of triphenylphosphine is conceivable when a complex of a still more negative redox potential than $Ni(PPh_3)_4$ (cf. Table 3) or one which is coordinatively strongly unsaturated is offered as reactant. These expectations are proved experimentally. (i) $Ni(PEt_3)_3$ reacts with PPh_3 in a multi-stage process (124). $(PEt_3)_2Ni(PPh_3)Ph$ is considered as the essential intermediate product [125].

$$2(PEt_3)_3Ni(PPh_3) \xrightarrow[\text{hexane}]{125°C} (Et_3P)_2Ni(PPh_2)_2Ni(PEt_3) + 3PEt_3 + Ph{-}Ph \qquad (124)$$

(ii) $(Ph_3P)_2Pt(C_2H_4)$ splits off ethane when heated over a longer period. The coordinatively unsaturated species $Pt(PPh_3)_2$ results. In a vague process this species reacts partly by internal oxidative addition and partly by splitting off phenyl radicals yielding oligonuclear complexes XX and XXI [126]. Already in 1962 Herrmann described a nickel compound completely analogous to XX [127]. He obtained it in the thermal decomposition of $(Ph_3P)_2Ni(C_2H_4)$ under milder conditions than for $(Ph_3P)_2Pt(C_2H_4)$, as expected.

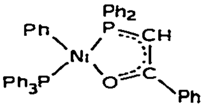


XX



XXI

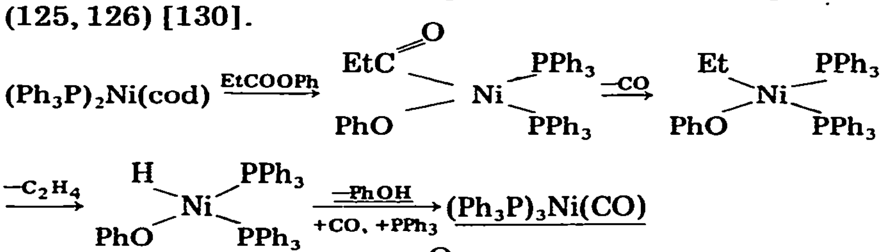
The splitting of Ph—P bonds was also observed in the reaction of $(Ph_3P)_2Ni(C_2H_4)$ with $LiSiPh_3$ [128] or $(Ph_3P)_2Ni(cod)$ with $Ph_3P{=}CH{-}CO{-}Ph$ [129]. A nickel(II) compound which oligomerizes ethene to linear α-olefins without further additions is formed with XXII in the latter case.

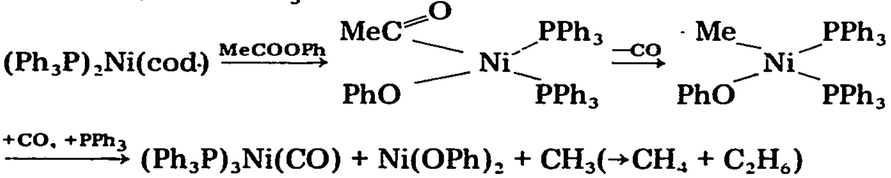


XXII

(iv) Compounds having a C—O bond

In general, compounds with C—O bonds do not add to electron-rich complexes of nickel(0). In contrast to bromobenzene, $CH_3C_6H_4SO_3C_6H_5$ does not react with $Ni(cod)_2$ in dimethylsulfoxide [108] and (bipy)Ni(cod) does not react with benzoic acid ester [43]. Phenoxo and alkenoxo compounds as well as carboxylic acid anhydrides and epoxides are exceptions. $(R_3P)_2Ni(cod)$ or (bipy)Ni(cod) split the CO—OPh bond of phenylcarboxylates and the final products (underlined) can be explained by the following reaction sequences (125, 126) [130].

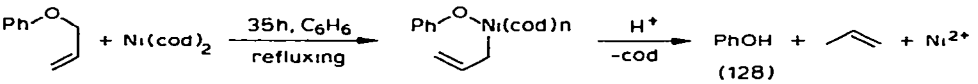

(125)


(126)

The individual steps (decarbonylation, β-hydrogen elimination, reductive elimination) are well known from other syntheses.

Alkene acetates preferably react through splitting of the COO—R bond (127), evidently because π-allyl complexes can be formed thereby [130]. Allyl phenolate behaves similarly. Due to the fact that the reaction (128) in

$$2\,Ni(cod)_2 + 2\,MeCOOCH{-}CH{=}CH_2 \xrightarrow[Et_2O]{10\ ^\circ C} Ni(\pi\text{-}C_3H_5)_2 + Ni(MeCOO)_2$$
(127)

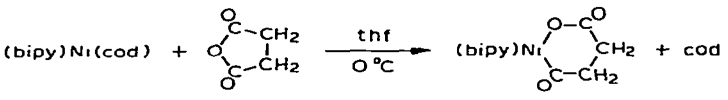

(128)

thf proceeds much more rapidly than in benzene and that $Ni(PEt_3)_3$ or (bipy)Ni(cod) react more easily than $Ni(cod)_2$, an electron transfer (cf. e.g. (88) and Table 3) as the initiating step is very likely [131].

Acetic acid anhydride adds to $Ni(PMe_3)_4$ on decarbonylation of the acetyl group (129). When keeping the temperature low during the reaction of (bipy)Ni(cod) with succinic acid anhydride, a six-membered metallacycle

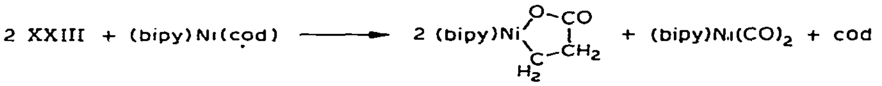
$$2Ni(PMe_3)_4 + (MeCO)_2O \rightarrow (PMe_3)_2Ni(Me)(OOCMe) + (PMe_3)_3Ni(CO) + 3PMe_3$$
$$\downarrow -PMe_3$$
$$\tfrac{1}{2}[(PMe_3)Ni(Me)(OOCMe)]_2$$
[132] (129)

results first (130). On heating, decarbonylation also takes place here, the carbon monoxide is bound by surplus (bipy)Ni(cod) (131). Phthalic anhydride reacts similarly.



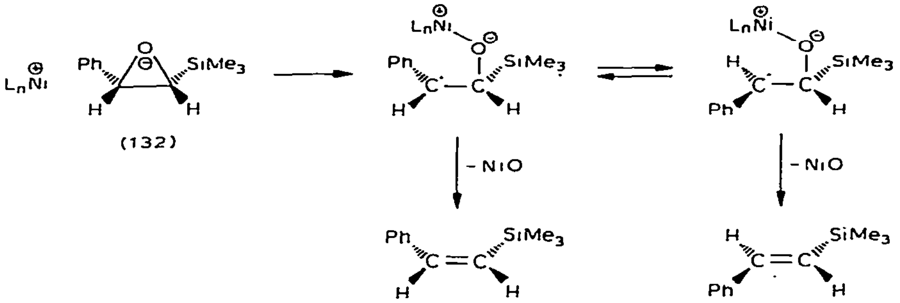
XXIII

[133] (130)



[133] (131)

Epoxides with electron-withdrawing substituents are deoxygenated by nickel(0) complexes [131]. Of course only (bipy)Ni(cod) and $Ni(PEt_3)_4$ are suited for this, and not $Ni(PPh_3)_4$ and $Ni(cod)_2$. Thus, a one-electron transfer again seems to be the starting step. Since approximately equal amounts of *e*- and *z*-olefin are formed irrespective of the structure of the starting product (*e* or *z*), stepwise separation of oxygen is probable (132).

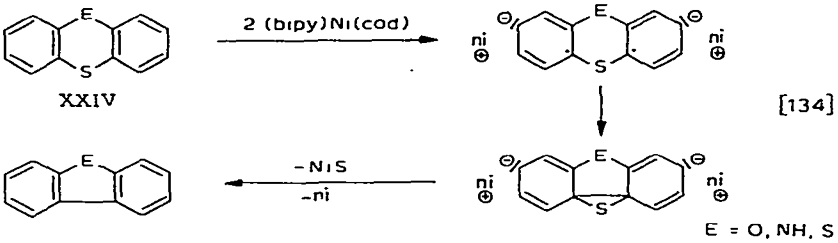


(132)

(v) *Reactions of compounds having a double bond*

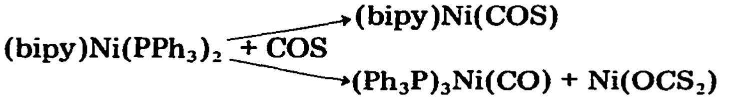
Strongly reducing nickel(0) complexes, e.g. (bipy)Ni(cod) and (bipy)Ni$(PPh_3)_2$, can not only transfer an electron to compounds of the R—X type, but to differently structured substrates as well [cf. Section C(55)]. Energy-rich radical anions which among other things may react on bond splitting are formed in most cases. The discussion of corresponding reactions in Section D is thus justified.

Heterocycles of the XXIV type are desulfurized by (bipy)Ni(cod) (not by $Ni(cod)_2$). As two mols of the nickel(0) complex per mol of substrate are necessary, a dianion which then eliminates sulfide is obviously formed first (133).



[134] (133)

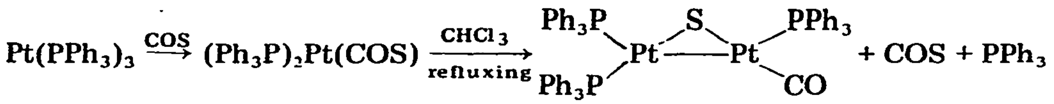
(bipy)Ni(PPh_3)$_2$ with COS yields a mixed metal carbonyl, Ni(OCS_2) and, in a secondary reaction, (bipy)Ni(OCS) (134). Taking the carbon disulphide the redox behaviour of which is far better known than that of COS [135] for comparison, the following course of reaction seems to be possible. The radical anion $COS^{\cdot-}$ results by electron transfer and then disproportionates to CO and OCS_2^{2-}. The redox process takes place in the coordination sphere of nickel, free CO and OCS_2^{2-} do not occur.



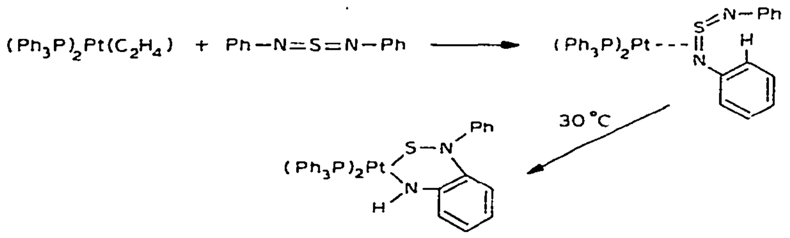
$$(\mathrm{bipy})\mathrm{Ni}(\mathrm{PPh_3})_2 + \mathrm{COS} \begin{array}{l} \nearrow (\mathrm{bipy})\mathrm{Ni}(\mathrm{COS}) \\ \searrow (\mathrm{Ph_3P})_3\mathrm{Ni}(\mathrm{CO}) + \mathrm{Ni}(\mathrm{OCS_2}) \end{array} \qquad (134)$$

$$2\ \mathrm{Ni} + 2\ \mathrm{COS} \rightarrow (2\ \mathrm{Ni}^{+}, 2\ \mathrm{COS}^{\cdot-}) \rightarrow \mathrm{Ni}^{0}(\mathrm{CO}) + \mathrm{Ni}^{\mathrm{II}}(\mathrm{OCS_2})$$

During the reaction of (bipy)Ni(PPh_3)$_2$ with COS a bond that originally was of a double-bond nature is split. While the liberated sulfur is bound here by a second molecule of the electronically changed reagent under formation of OCS_2^{2-}, another case is known where both fragments of COS are bound to the central atom (135). Recently the splitting of a N=S bond during a reaction with (Ph_3P)$_2$Pt(C_2H_4) has been reported (136).



[136] (135)



[74,137] (136)

E. METAL-INDUCED COUPLING OF UNSATURATED COMPOUNDS

Metal-induced coupling is typical of many transition metal compounds, in particular those of the nickel triad, and can be described formally as follows. Two π-bonding systems coordinated at the central atom and involving both carbon and hetero atoms are interlinked upon formation of a σ-bond. At the same time, two σ-bonds to the central atom are established. The latter supplies two electrons to the freshly resulting ligand system; consequently it is oxidised. The electron balance for metal(0) complexes therefore looks like eqn. (137). When the product of the metal-induced coupling contains a C=C

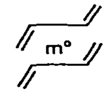
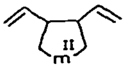
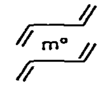
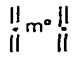
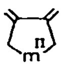
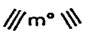
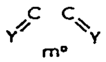
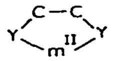
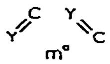
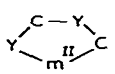
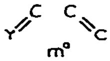
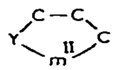
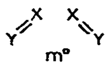
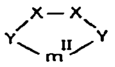
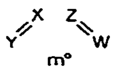
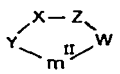
$$2\pi + 2\pi + \mathrm{M}(0) \rightarrow \mathrm{M}(\mathrm{II}) + 6\sigma \qquad (137)$$

double bond in β-position to the central atom, conjugation of this bond with the electron pair of the M^{II}—C bond is possible. The resulting allyl system then formally establishes two π-bonds to the central atom (140).

For the electron-rich complexes of the nickel triad we only know metal-induced couplings yielding simple metallacycles, except for (163). But we believe that metal-induced coupling and cyclization are not necessarily

TABLE 5

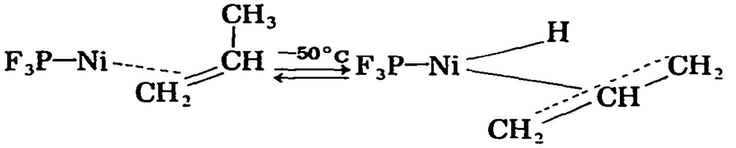
Metal-induced coupling of unsaturated compounds

	Initial products	Balance of the shared electrons	Final product	Number of new σ- and (partially delocalised) π-electrons. Type of metallacycle
(138)		$2\pi + 2\pi + 2e_m$		6σ C_4M
(139)		$2\pi + 2\pi + 2e_m$ (π-bonds conjugated)		6σ C_4M
(140)		$4\pi + 4\pi + 2e_m$		$2\sigma + 8\pi$ C_8M
(141)		$2\pi + 2\pi + 2e_m$ (π-bonds cumulated)		6σ C_4M
(142)		$4\pi + 4\pi + 2e_m$		$6\sigma + 4\pi$ C_4M
(143)		$2\pi + 2\pi + 2e_m$ (2 hetero-π-bonds, head-to-head)		6σ YCCYM
(144)		$2\pi + 2\pi + 2e_m$ (2 hetero-π-bonds, head-to-tail)		6σ YCYCM
(145)		$2\pi + 2\pi + 2e_m$ (1 hetero-π-bond)		6σ YCCCM
(146)		$2\pi + 2\pi + 2e_m$ (2 dihetero-π-bonds)		6σ YXXYM
(147)		$2\pi + 2\pi + 2e_m$ (2 dihetero-π-bonds)		6σ YXZWM

connected. The search for oligonuclear complexes as a product of metal-induced coupling therefore deserves special attention in the future.

Table 5 indicates linkage possibilities supported by at least one reaction example from the nickel triad. The formation of isomers which frequently occurs when substituted unsaturated compounds (e.g. isoprene) are used is not considered. As far as we know, the direct 1 : 1 coupling of 1,3-dienes with monoolefins has not yet been realized and therefore it was not included in Table 5. The insertion of $>C=N$ species into C_8Ni rings (cf. (140)) and thus the formation of ten-membered metallacycles or their secondary products are quite possible [138].

The metal-induced coupling to the metallacycles is not the only way for the conversion of π-systems at a low-valent central atom. Carbene formation or direct ring closure at the central atom as "forbidden-to-allowed" catalysis (for a critical discussion of this type of reaction see ref. 182) are other possibilities; moreover, metalliferous species with two reactive centres (148) which enter into secondary reactions may result by C—H or C—X addition of olefins. But the formation of metallacycles has been observed for the electron-rich complexes of the nickel triad so frequently that it can be concluded that the majority of conversion reactions of olefins catalyzed by them is initiated by metal-induced couplings. Despite numerous experiments, data on the relevant activation energies, on the thermodynamic stability of the formed metallacycles and on the activation energies of secondary reactions (reductive elimination or insertion), are not available yet.

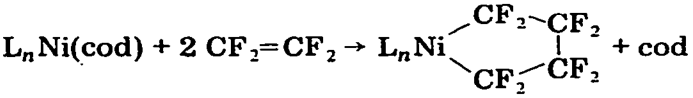


[139] (148)

(i) Monoolefins (reaction type (138))

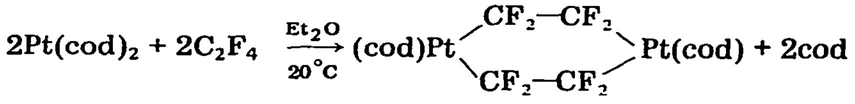
Recently, the coupling of two ethene molecules on a binuclear titanium species was reported [140]. Although the compounds $(R_3P)M(C_2H_4)_2$ and $M(C_2H_4)_3$ are known (cf. Section C), nothing is known of an analogous reaction in the coordination sphere of electron-rich complexes of the nickel triad. Things change in the transition to perfluorated compounds and other activated olefins such as 3,3-dimethylcyclopropene and methylenecyclopropane (strained-ring olefins).

Tetrafluorethene easily reacts with nickel(0) complexes yielding five-membered metallacycles (149). The ligands L can be varied widely (Et_3P, Ph_3P,



[141] (149)

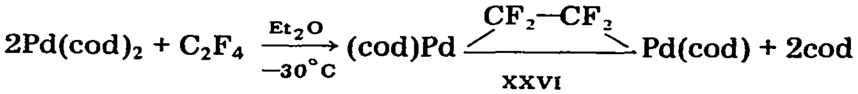
cod, bipy), being indicative of the fact that (149) does not require a precise balance of electrons at the central atom. Interestingly hexafluoropropene does not react with nickel(0) complexes by metal-induced coupling but by substitution. It is not only the change of reagent but also the change of the central atom that can lead the reaction in another direction. $Pt(PPh_3)_4$ with tetrafluoroethene forms the substitution product $(Ph_3P)_2Pt(C_2F_4)$ [142], but $Pt(cod)_2$ or $Pd(cod)_2$ forms four- or six-membered dimetallarings (XXV, XXVI) (150,151). Although the central atom is also oxidized in these extra-



$$2Pt(cod)_2 + 2C_2F_4 \xrightarrow[20^\circ C]{Et_2O} (cod)Pt\overset{CF_2-CF_2}{\underset{CF_2-CF_2}{\langle\quad\rangle}}Pt(cod) + 2cod$$

XXV

[143] (150)



$$2Pd(cod)_2 + C_2F_4 \xrightarrow[-30^\circ C]{Et_2O} (cod)Pd\overset{CF_2-CF_2}{\langle\quad\rangle}Pd(cod) + 2cod$$

XXVI

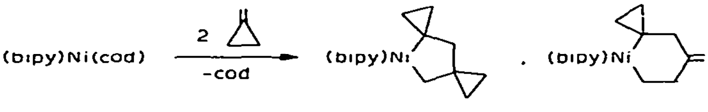
[143] (151)

ordinary reactions, the metal-induced coupling does not occur in contrast to (149).

Coupling of "strained-ring" olefins on nickel(0) proceeds according to eqns. (152) or (153). The resulting metallacycles eliminate the organic frag-

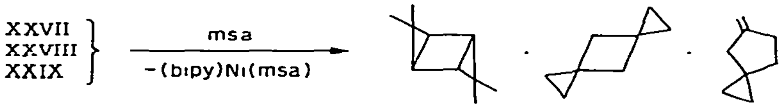
XXVII

[145] (152)



XXVIII XXIX

[144] (153)

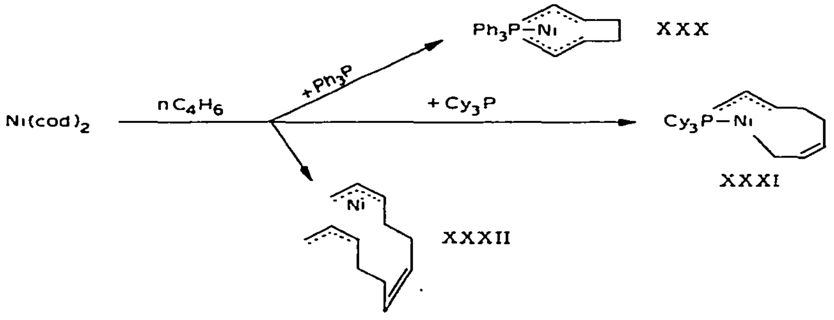


[144] (154)

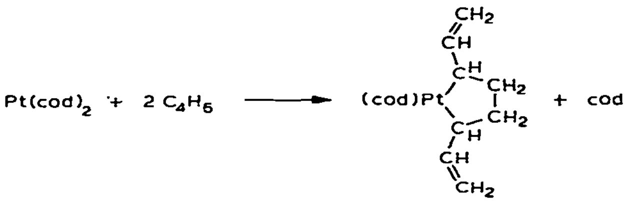
ment under the influence of strong π-acids (154) or thermally and strained carbocycles very difficult to reach by other reactions are formed. (152) and (154) are model reactions for two partial steps of catalytic dimerization of 3,3-dimethylcyclopropene which is possible with nickel(0)-phosphine systems [147]. It is interesting that a palladium(0)-phosphine catalyst yields cyclotrimers instead of cyclodimers [146]. An explanation of this is not yet available.

(ii) 1,3-dienes (reaction types (139) and (140))

Wilke et al. and Heimbach et al. investigated nickel(0)-induced couplings of 1,3-dienes and their secondary reactions systematically and used them for a variety of catalytic syntheses. Reflections on the mechanism have already been presented comprehensively [148,150] and there is no need for repetition. The reactions of platinum(0) complexes with 1,3-dienes were recently explored, above all by the studies of Stone et al. Therefore, it is interesting to compare the behaviour of nickel(0) and platinum(0) towards these reagents. To this end, recall the following findings from the chemistry of nickel(0). (i) Despite intensive research it was not possible to isolate a complex of two non-linked butadiene ligands on nickel(0). The attempt to get $Ni(C_4H_6)_2$ by the reaction of butadiene and metal vapour also failed. Larger amounts of $Ni(\pi\text{-}C_4H_7)_2$ resulted instead [149]. (ii) The oxidative coupling of two diene ligands is a very fast reaction [150]. (iii) Crystalline preparation of the products of oxidative coupling was possible in some cases. Their structure is highly influenced by additional neutral ligands. Cy_3P as a marked n-donor favours a σ-allyl-π-allyl-(XXXI), Ph_3P as a ligand with n-donor and π-acceptor properties (cf. Section C) favours a bis(π-allyl) structure (XXX). In the absence of additional ligands, another butadiene molecule is inserted into the nine-membered metallacycles in a rapid secondary step and a cyclododecatriene-diyl-nickel(II) in bis(π-allyl) form (XXXII) results. Stoichiometric reactions prove that cod or vinyl cyclohexene result mainly from XXX and XXXI, and cdt results from XXXII. The essential steps of the catalytic butadiene oligomerization can individually be simulated.



It is known that platinum(II) forms complexes where one olefin preferably acts as n-donor (cf. Zeise's-salt) and that platinum(II)-C-bonds are quite stable (cf. Section B). These are the essential reasons for the formation of different final products in the reaction of $Ni(cod)_2$ or $Pt(cod)_2$ with butadiene. A saturated five-membered ring (155) results with $Pt(cod)_2$ under the conditions which lead to complex XXXII with a twelve-membered ligand in the case of $Ni(cod)_2$. One cod ligand adheres to the central atom; but it can be displaced by Me_3P or Bu^tNC.



XXXIII

[151] (155)

XXXIV

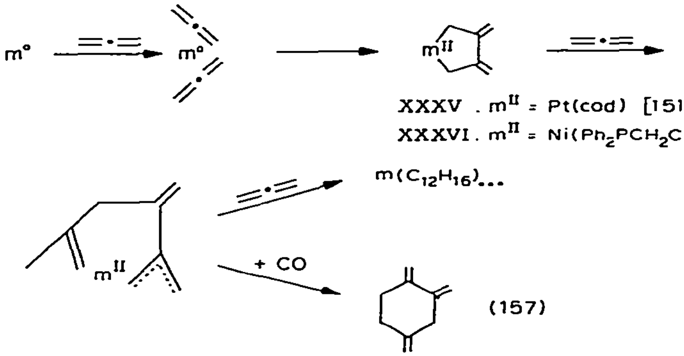
[151] (156)

On the other hand, detailed consideration of the reaction (156) and the behaviour of XXXIV towards Me$_3$P shows that the metal-induced coupling, as the most critical reaction step, proceeds on nickel(0) and palladium(0) alike.

Both XXXIII and XXXIV are stable towards an excess of butadiene. Therefore, they do not act as oligomerization catalysts like the corresponding nickel compounds.

(iii) Cumulenes (reaction type (141))

Allene with its cumulated π-bonds yields a number of oligomerization products at nickel(0) catalysts [152]. The first step of the catalytic cycles, the coordination of two allene ligands, could not be carried out stoichiometrically. The situation is similar to butadiene. The next step, the metal-induced coupling, is fast. Metal(II)-organocompounds, as the result of a metal-induced coupling of allene to platinum(0) and nickel(0), have only recently been isolated. Pt(cod)$_2$ with allene supplies the stable five-membered metallacycle XXXV. On Ni(cod)$_2$, however, the same substrate passes the coordination, oxidative coupling, insertion and reductive elimination steps in rapid sequence (157). It is possible to isolate intermediates by adding blocking ligands, e.g. chelate phosphines (XXXVI) and Cy$_3$P (XXXVII). XXXVII is subject to reductive elimination under the effect of carbon monoxide and with 1,2,4-trimethylenecyclohexane one of the isocyclic compounds from the catalytic process results.



XXXV . m^{II} = Pt(cod) [151]

XXXVI . m^{II} = Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$) [153]

(157)

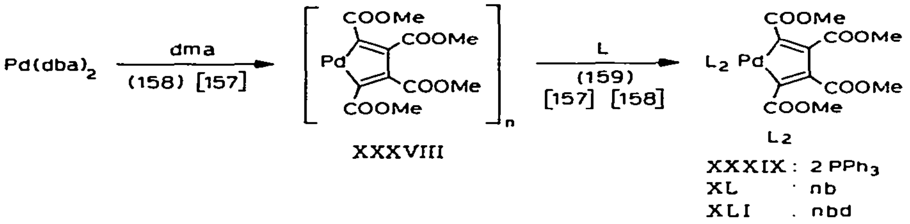
XXXVII . m^{II} = Ni(PCy$_3$)

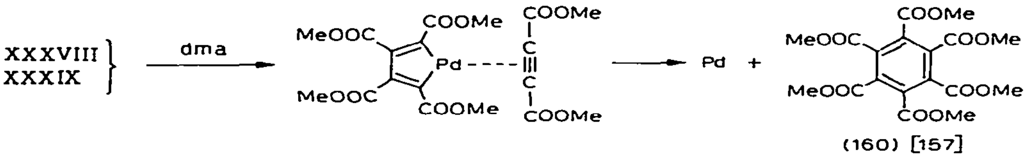
[154]

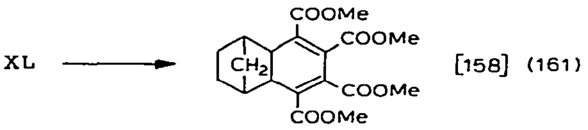
(iv) Alkynes (reaction type (142))

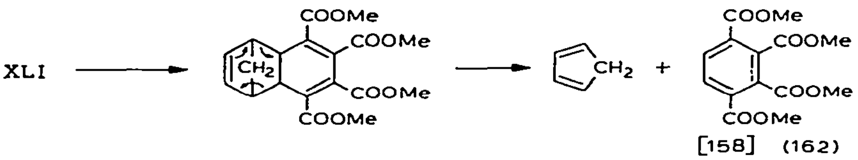
Many transition metal complexes catalyse the cyclomerization of alkynes and several possibilities are discussed for the catalytic cycle [155,156]. In one case, the first step in the metal-induced coupling is to form the five-membered metallacycle [157]. Complexes of this structure have been prepared for some transition metals, but in the nickel triad palladium is preferred.

Dimethylacetylenedicarboxylate (dma) reacts with $Pd(dba)_2$ yielding an oligonuclear complex XXXVIII where the central atoms are probably interlinked via ester groups (158). XXXVIII is split into mononuclear compounds by neutral ligands (159). Whereas XXXVIII and XXXIX with further dma yield mellitic acid ester (160), XL yields a cyclic cotrimer by reductive elimination with insertion (161). XLI is the starting point of an unusual reaction. It is very likely that here, too, a cyclic cotrimer results first but immediately splits off cyclopentadiene in a "cycloreversion" (162). (160)—(162) can be run catalytically. Cyclotrimerization of dma is also possible with $Pt(dba)_2$. The ring closure (158) is slower, but reductive elimination with insertion (160) is faster [157].



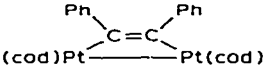






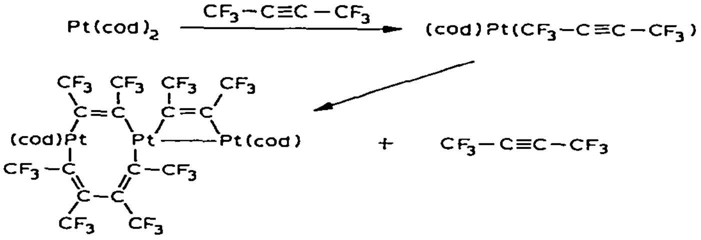
$Ni(cod)_2$ and, with a quite different result, $Pt(cod)_2$ were used as reactants for diphenylacetylene. Hexaphenylbenzene is formed at $Ni(cod)_2$ in a catalytic reaction [159]. (cod)Ni(PhC≡CPh)Ni(cod) (XLII) could be isolated as an intermediate where the alkyne "side-on" acts as a bridging ligand [160]. Reactions in analogy with (158) and (160) should model the most important partial steps of the catalytic cycles. The isolation of a cyclic compound corresponding to XXXVIII failed, but 1,2,3,4-tetraphenylbutadiene (1,3) as the associated hydrolysis product could be isolated.

Surplus diphenylacetylene completely substitutes the cod of $Pt(cod)_2$ [64]. But when this reagent is used in deficiency, a complex XLIII, corresponding to the compound XLII stoichiometrically but not structurally, is obtained [161]. The type of linkage of the two central atoms of XLIII resembles the reaction product of $Pd(cod)_2$ with tetrafluoroethene (XXVI).



XLIII

As expected, a catalytic reaction of diphenylacetylene was not observed at the platinum(0) species. The reaction of $Pt(cod)_2$ with hexafluorobutyne proceeds in a different way. Apart from the simple substitution product, a trinuclear complex is formed (163). In this complex, a C_4 species which resulted from metal-induced coupling in addition to the C_2 species is interlinking two central atoms. There are no reliable statements on the structure of the reaction products of $Ni(cod)_2$ with hexafluorobutyne to which the formulas $(cod)Ni[C_6(CF_3)_6]$ and $(cod)_2Ni_2[C_6(CF_3)_6]$ are assigned [103,104].



[162] (163)

(v) Hetero-π compounds (reaction types (143—147))

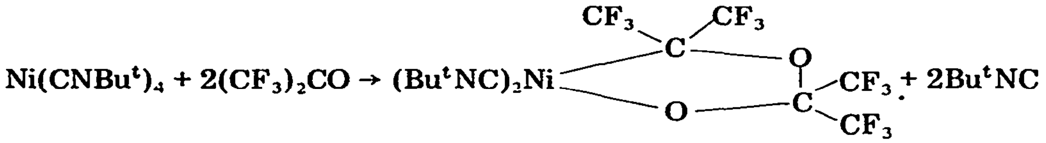
Stable mixed ligand nickel(0) complexes of non-activated carbonyl compounds have already been mentioned in Section C. In some cases, e.g. $(bipy)Ni(PhCHO)_2$ [165], even two carbonyl ligands can be coordinated by a central atom. But metal-induced coupling does only occur in the case of strongly π-acidic compounds like hexafluoroacetone.

Some nickel(0) complexes react with this substrate only under substitution (164—166). In other cases (167), the reaction proceeds to a five-membered metallacycle. $(CF_3)_2C{=}NH$ and $(CF_3)_2C{=}NCH_3$ behave quite similarly [168, 169].

$(Ph_3P)_2Ni(C_2H_4) + (CF_3)_2CO \rightarrow (Ph_3P)_2Ni[(CF_3)_2CO] + C_2H_4$ [166] (164)

$Ni(cod)_2 + (CF_3)_2CO \rightarrow (cod)Ni[(CF_3)_2CO] + cod$ [167] (165)

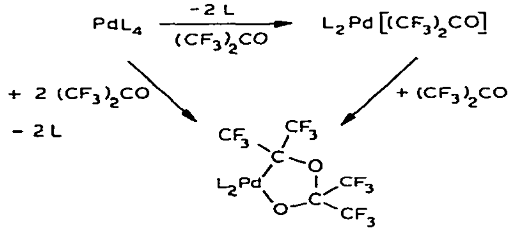
$Ni(CNPh)_4 + (CF_3)_2CO \rightarrow (PhNC)_2Ni[(CF_3)_2CO] + 2PhNC$ [168] (166)



[168] (167)

The reactions (164—167) show the controlling action of the neutral ligands available in the substitution products. The weaker π-acidic are these neutral ligands, the higher is the nucleophilic nature of the central atom and the more is the coupling with a second molecule of ketone favoured. This is in contrast to the missing influence of the neutral ligands on the metal-induced coupling of tetrafluoroethane (Section E(i)).

Palladium(0) complexes behave like nickel(0) complexes but the tendency to oxidative coupling seems to be stronger (168).

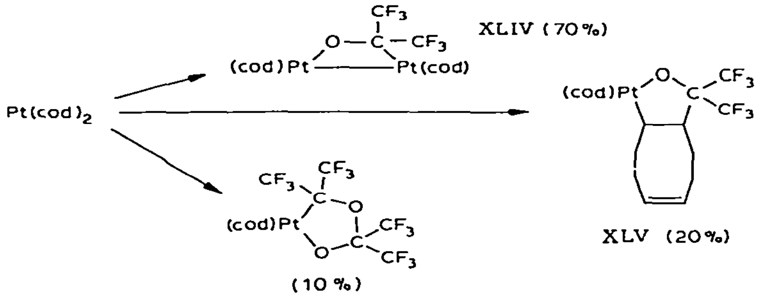


L · P(OPh)$_3$, PMePh$_2$
L$_2$. Ph$_2$PCH$_2$CH$_2$PPh$_2$

[170] (168)

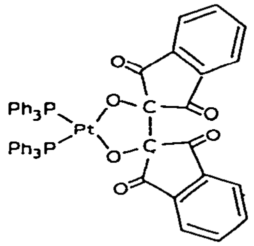
L . P(OMe)$_3$, P(OMe)$_2$Ph , PMePh$_2$
L$_2$: Ph$_2$PCH$_2$CH$_2$Ph$_2$

The reaction of Pt(cod)$_2$ with hexafluoroacetone in ether at room temperature yields three products (169). Among them XLIV as a binuclear complex with a CO bridge and XLV as one of the few compounds formed by metal-induced coupling of a hetero-2π-system with a non-activated homo-2π-system (reaction type (145)) are of particular interest.

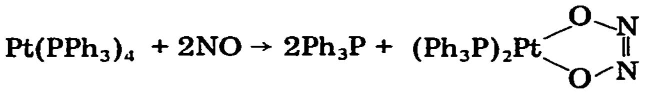


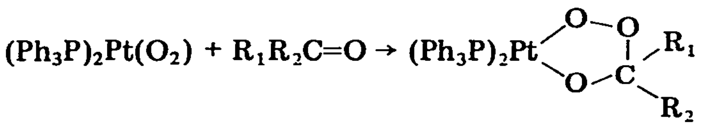
[67] (169)

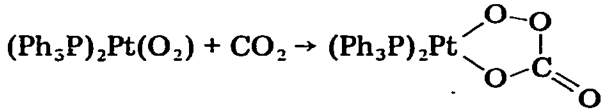
Head-to-tail linkage (144) took place exclusively in the case of all hitherto known metal-induced couplings of $(CF_3)_2CO$ and $(CF_3)_2CNH$. Now the question arose whether a head-to-head linkage of carbonyl compounds (143) is also possible. After the synthesis of XLVI from $Pt(PPh_3)_4$ and indan-1,2,3-trion [171] the answer is yes. But in this special case, the head-to-head linkage is preferably forced by steric factors.

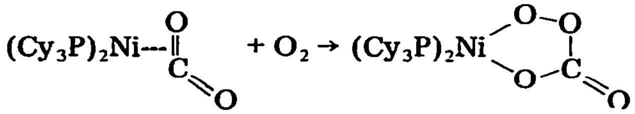

XLVI

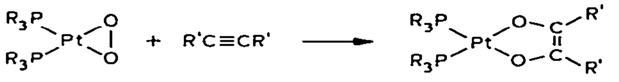
Examples of the reactions of types (146) and (147) where at least one dihetero-π-compound is involved are (170—173). In general, the possibility of metal-induced coupling with participation of dioxygen is more likely for platinum(0) and palladium(0) on account of the sufficient stability of type $L_2M(O_2)$ complexes. Equation (173), however, shows that such a reaction is also possible for nickel(0) when a suitable starting product is selected. Dioxygen complexes also react with activated alkynes (hexafluorobutyne, dimethylacetylenedicarboxylate, but not with diphenylacetylene) [176]. However, normal metal-induced coupling does not take place. Splitting of the O_2 ligand connected with the addition of the fragments to the alkyne yields a diolate species (174). ^{31}P-NMR measurements showed the appearance of two alkyne containing intermediates. The main one with the two phosphine ligands in a *cis*-position is thought to be formed by an attack of the alkyne to one of the oxygen atoms. For the second one the coordination number 5 with a trans-position of the phosphine ligands is discussed.


[172,173] (170)


[174] (171)


[174] (172)


[175] (173)

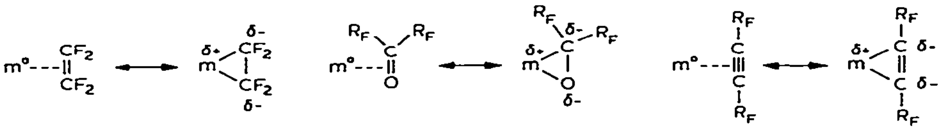


(174)

(vi) Metal-induced coupling of fluorinated unsaturated compounds

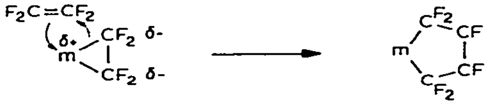
It becomes evident from Sections E (i), (iv) and (v) that fluorinated unsaturated compounds take a certain exceptional position in the mètal-induced coupling irrespective of the compound type. Catalytic reactions recede as compared to stoichiometric ones even for nickel(0) complexes; nickel and platinum-containing reaction products show remarkable structural differences in some cases.

To simplify the comparison, in the following section, reactions under UV radiation are excluded. A strong bending-back of the fluorine atoms from the C=C-plane and marked elongation of the C=C-bond are observed at the metal complexes of tetrafluoroethene (XVII) [177]. * For this reason, the contribution of form XLVII b is of considerable statistical importance.

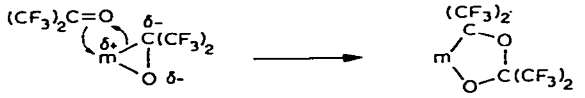


XLVIIa XLVIIb XLVIIIa XLVIIIb ILa ILb

The same should apply to perfluorinated carbonyl compounds (XLVIII) and alkynes (IL). When XLVIII or IL are coordinatively unsaturated, a substrate molecule to be added will act as n-donor in view of the positive charge at the metal. Thereby, the prerequisites for ring closure (176, 177) are pro-



[141] (176)



L

[168,170] (177)

vided in the activated complexes. This procedure is facilitated by the deformation mentioned above of the fluorine-containing ligands available in the 1,1-complexes. This deformation which is much greater than in coordinated

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* Tolman and Seidel [178] attribute the low rate of reaction (175) to the deformation of C_2F_4 which is connected with its coordination.

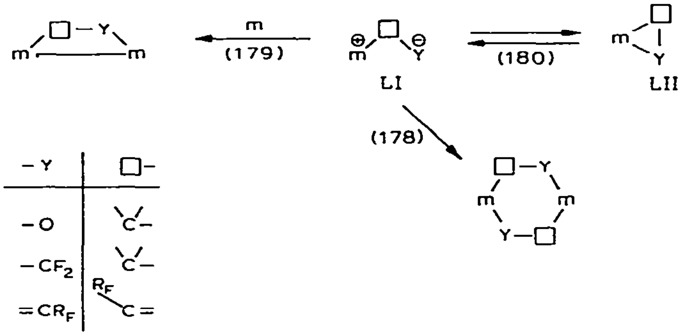
$$Ni[(oCH_3C_6H_4O)_3P]_3 + C_2F_4 \rightleftharpoons [(oCH_3C_6H_4O)_3P]_2Ni(C_2F_4) + P(OC_6H_4OCH_3)_3 \quad (175)$$

normal olefins [177] should favour the transition to the tetrahedral carbon of the metallacycles.

Charge separation as expressed in XLVII b should be strongest for nickel-(0) complexes when all other factors are constant. The ring closure according to (176) in the reaction of $(Ph_3P)_2Ni(C_2H_4)$ with C_2F_4 and the simple substitution in the case of $(Ph_3P)_2Pt(C_2H_4)$ (Section E(i)) can be understood on this basis. Such a differentiation in the reactivity is not observed in each case, however. $(CF_3)_2CO$ only forms the simple substitution product both with $(Ph_3P)_2Ni(C_2H_4)$ and $(Ph_3P)_2Pt(C_2H_4)$ [179].

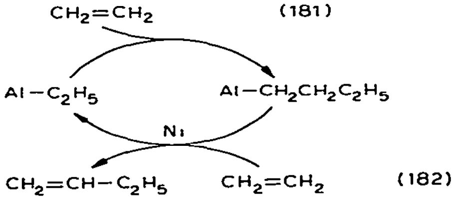
Once formed metallacycles of type L (M = Ni) with their Ni—O bond are stable. Reductive elimination of the organic residue, under the effect of a π-acidic ligand, is not possible. Thus, there is no possibility of a catalytic process.

But electron-rich complexes of the nickel triad cannot only react with unsaturated fluorine compounds in the sense of substitution or cyclization. In some cases, oligonuclear compounds where the inserted substrates have the function of bridging ligands are also formed. Stone et al. derive these complexes from 1,3-dipolar species with "skew-bonded" fluorine-containing ligands (LI). These reactive species either resulting from the action of π-acidic ligands (CO, olefins) on "normal" π-complexes (LII) [142] or also as primary products in the substitution of $Pt(cod)_2$ or $Pd(cod)_2$ [143], may stabilize by dimerization (178), reactions with another electron-rich complex (179), or by back-formation of LII (180). Species LI seem to play an essential role particularly in the platinum series. This can be understood because they contain a formal platinum(II)—C-σ-bond.



F. THE NICKEL EFFECT

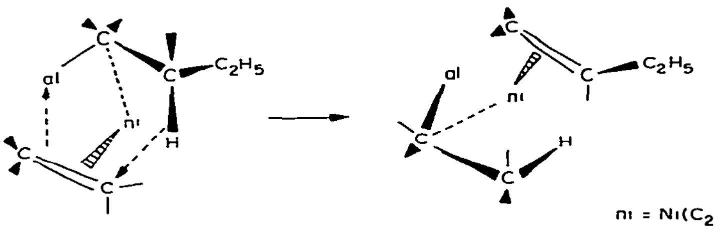
Except for substitutions, all previously described syntheses with electron-rich complexes involved a permanent or periodic change of the oxidation stage. But at the very beginning of the rapid development of organo-nickel chemistry there was a catalytic reaction in which the oxidation state of the transition metal does not obviously change: the dimerisation of ethene in the presence of $AlEt_3$ and minor amounts of "naked" nickel. The reaction (181) proceeds quite generally on trialkylaluminium compounds. Reaction (182)



(181)

(182)

which is not limited to $AlBu^n_3$ requires catalysis by the transition metal ("nickel effect"). Recent investigations carried out by Wilke and co-workers [180] showed that bimetallic species resulting from association of a nickel-(0)—olefin complex e.g. $Ni(C_2H_4)_3$ and an aluminium trialkyl via α-alkyl bridges represent the actual activated complexes.



(183)

ni = $Ni(C_2H_4)_2$
al = $AlBu^n_2$

In an arrangement like this, the C-atoms of a coordinated olefin, a β-H-atom of the butyl group and the Al-atom are so close to one another that rearrangement of the bonds in the sense of an electrocyclic reaction (183) seems to be possible. The moving force of the reaction is the formation of butene that is energetically favoured compared to ethene.

The migration of hydrogen atoms bound in alkyl groups is a phenomenon well known from heterogeneous catalysis. (183) once again demonstrates the relationship of electron-rich complexes and metals with regard to their catalytic effects. On the other hand, the nickel effect may be regarded as a request to enforce the studies of the catalytic behaviour of heteronuclear metal clusters.

G. CONCLUSION

Substitution reactions, oxidative additions and metal-induced coupling are the essential fundamentals of syntheses with electron-rich complexes of the nickel triad. It is a general rule, that binary complexes with π-acceptor ligands $M(A)_n$ react easily with n-donors D yielding comparably stable ternary compounds $(D)_xM(A)_y$. The following is valid for these $(D)_xM(A)_y$ complexes: a π-acceptor (n-donor) can substitute a π-acceptor (n-donor) when there is a sufficient difference in their π-acceptor (n-donor) strength. Knowledge of the sequence of the π-acceptor (n-donor) strength is available within the series of structurally related compounds, e.g. tertiary phosphines, N∩N ligands, olefins.

A reliable basis for a complete "π-acceptor (n-donor) series" does not exist. But it is possible to make a distinction between ligands of a dominating π-acceptor nature and those of a dominating n-donor nature in ternary complexes and to assess the behaviour towards a certain reagent on this basis.

Both homonuclear (H—H, O—O, C—C, Pb—Pb) and heteronuclear bonds [C—H, P—Ph, C—O, C—X (X = Cl, Br, I)] can be split by oxidative additions. Extensive studies of organohalogen compounds revealed that the final products ($R—M^{II}—X$, etc.) and the reaction mechanism (S_N2-, radical chain and non-chain radical mechanism) depend in a sensitive way on the central atom and its ligands as well as on the reagent and solvent. A clear dependence of the redox potential [Ni(O) → Ni(I)] is observed for nickel(0) complexes. Substitution-labile complexes like (bipy)Ni(cod) are suitable for S_N2-reactions, and 16-electron species e.g. (bipy)Ni(PPh_3) are suitable for non-chain radical reactions. Catalytic processes based on oxidative additions have recently been found.

Metallacycles result preferably from metal-induced coupling of unsaturated compounds on nickel(0) complexes. These metallacycles are unstable if there are only Ni—C bonds and easily undergo reductive elimination. Catalytic syntheses of numerous organic ring systems became possible on this basis.

In the case of platinum(0), metal-induced coupling frequently yields stable metallacycles having two Pt(II)—C-σ bonds. Bridging of two or more platinum atoms by reagents such as $(CF_3)_2CO$, C_2F_4, etc., to give oligonuclear complexes is also observed. 1,3-dipolar "skew-bonded" adducts of the unsaturated reagents to platinum(0) seem to play a role as reactive intermediates. Catalytic reactions where one step is the metal-induced coupling of the substrate at platinum(0) are rare.

Syntheses catalysed by electron-rich complexes of the nickel triad are normally dependent on periodic changes of the oxidation stage of the central atom. The nickel/aluminium-catalysed ethene dimerization (nickel effect) is an exception. A further search for similar reactions is requested.

Knowledge of the reaction mechanism is incomplete, above all in the case of metal-induced coupling. Improved kinetic and thermodynamic studies and new and more reliable physical methods for determining the structure of solved coordination compounds are needed.

Summing up we must state that the synthetic potential of electron-rich complexes of the nickel triad is known only in part and over and above the present knowledge is applied only to a small extent for preparative work. Further investigation of fundamentals and applications is useful and even requested.

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