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REACTIONS OF ZEROVALENT PLATINUM AND PALLADIUM COMPLEXES WITH ORGANOMETALLIC COMPOUNDS OF NON-TRANSITION METALS

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A. INTRODUCTION

The most typical feature of the reactivity of zerovalent complexes of nickel triad metals is the tendency to increase the formal oxidation state of the metal [1]. In the presence of an appropriate acceptor two electrons are transferred and the metal acquires a +2 oxidation state. Such reactions are known as oxidative addition; so far reactions with organic halides have attracted the most attention [1—5].

Oxidative addition to zerovalent transition metal complexes may proceed with increase not only of valency, but also of the coordination number of the central atom. However this is not mandatory, since some ligands can be eliminated during the reaction *.

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* For this type of reaction a special term "oxidative elimination" is sometimes used [5,6]. However, there seems to be no need to use different terms for analogous reactions of so similar complexes as ML_n when $n = 2$ or 3 depending on the nature of L. In the present survey only the term "oxidative addition" is used.

$$L_nM^0 + A{-}B \rightarrow L_nM^{II}(A)(B)$$

$$L_mM^0 + A{-}B \rightarrow L_nM^{II}(A)(B) + (m-n)L$$

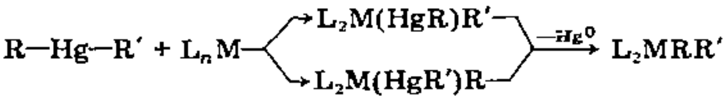
Novel aspects of this reaction involving certain organometallic compounds as electron-withdrawing substances, will be discussed here.

From the "point of view" of L_2M, whether it exists in a kinetically independent state, or is only a structural fragment, oxidative addition reactions may be interpreted as insertion. Insertion reactions are typical of species that are capable of forming two bonds, for instance olefins and carbenes. The similarity between complexes containing zerovalent platinum or palladium and carbenes was first noted in an important paper by Nefedov and Manakov [7]. Carbenoid features in the reactivity of L_2M^0 are revealed in insertion and cycloaddition reactions. The nature of L determines the character of the L_2M^0 species as a nucleophilic or electrophilic carbenoid. Extensively used ligands, triarylphosphines, and to a greater extent trialkylphosphines, are markedly electron-donating. The stronger the nucleophilicity of L_2M, the easier it participates in oxidative addition reactions. Zerovalent complexes with strong electron-withdrawing ligands, e.g. fluorophosphines L_4Pt ($L = PF_3$, CF_3PF_2, $(CF_3)_2PF$) do not react with HCl or alkyl halides [8], though one can imagine, in principle, similar reactions in which L_4Pt accepts electrons from an electron-donating substrate.

The first work specially devoted to the reaction of zerovalent platinum complexes with metal compounds was a small note by Layton et al. [9]. In 1967 they reported the use of $(Ph_3P)_4Pt$ for obtaining platinum—metal bonds (metal = gold, mercury, tin, copper and nickel). Only for two compounds $L_2Pt(Cl)HgCl$ and $L_2Pt(Cl)AuL$, elemental analysis data were provided and for several compounds the melting points provided. A full description of this work was never published.

B. REACTIONS WITH ORGANOMERCURIALS

Electron-donating properties of zerovalent complexes were compared with the known tendency of organomercurials to accept an electron. It was already known from polarographic studies that alkylmercury halides have higher electron affinity than the corresponding alkyl halides, at least for chlorides and bromides [10]. These considerations lead us to the conclusion that organomercurials should react with zerovalent platinum, palladium and nickel complexes. The first publication that reported on the capacity of RHgX and R_2Hg to react with triphenylphosphine complexes of Pt(0) and Pd(0) yielding organoplatinum and palladium compounds appeared in early 1974 [11]. Already the existence of intermediates with a transition metal—mercury σ-bond was suggested. In the following study [12] examples of preparation of a stable platinum—mercury compound and applications of zerovalent complexes with another ligand, dibenzylideneacetone, which became known [13,14] at that time, were reported. The general scheme of the reaction includes formation of bimetallic intermediates (generally speaking, of two isomers) which may eliminate mercury either under the given reaction conditions or in another way giving σ-organotransitionmetals.



$$R{-}Hg{-}R' + L_nM \begin{cases} \rightarrow L_2M(HgR)R' \\ \rightarrow L_2M(HgR')R \end{cases} \xrightarrow{-Hg^0} L_2MRR'$$

Further studies [15—27] were carried out in several directions: synthesis of bi- and oligometallic compounds, development of synthetic routes to various σ-organoplatinum and organopalladium compounds, study of the stereochemistry and mechanism of the reaction.

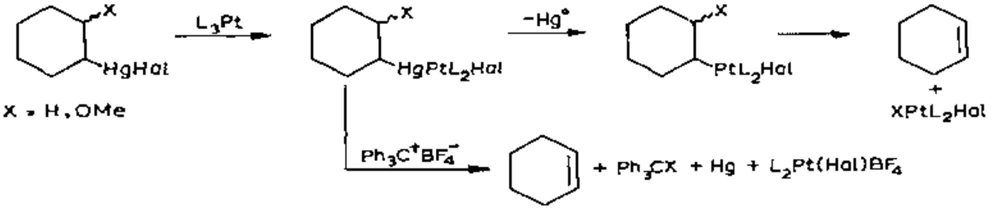
(a) Synthesis of σ-platinum and palladium organic derivatives via organomercurials

The reaction of organomercuric salts with tris(triphenylphosphine)platinum proceeds smoothly in hydrocarbon (benzene or toluene) or ether solvents, the colouring of the zerovalent complex rapidly disappears and then mercury gradually precipitates. The rate of mercury elimination depends on the nature of the organomercurial; it is also enhanced by the presence of a donating solvent, for instance tetrahydrofuran.

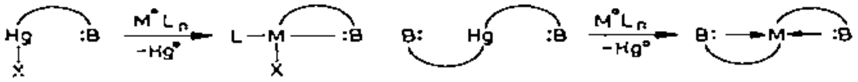
The applicability of the reaction to the synthesis of σ-organoplatinum compounds was extensively studied: the method provides an efficient route to aryl, vinyl, heteroaryl and alkyl derivatives. An important advantage of this method is that it allows the presence of active functional groups in the organic radical; for σ-organopalladiums see refs. 11, 17, 18, 35.

$(RCOCH_2)_2Hg + L_3Pt \rightarrow (RCOCH_2)_2PtL_2 + Hg$

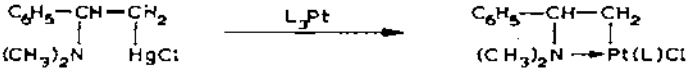
Such functionally substituted compounds cannot be obtained by the Chatt—Shaw method [28] using active organolithium and magnesium compounds. It should be noted that up to very recently all attempts to synthesize secondary alkyl derivatives of platinum both by the Chatt—Shaw method [28] and through oxidative addition [29] failed, with very few exceptions [18,30,31]. The usual product is a platinum hydride $HPtL_2Hal$. Using the organomercury route we obtained in high yields several cycloalkyl platinum derivatives, where the metal is attached to the secondary carbon atom [22]. Such compounds readily undergo elimination to form a cycloolefin and the corresponding platinum complex $XPtL_2Hal$. Fragmentation proceeds rapidly in the presence of other agents, such as triphenylmethyl cation Ph_3C^+.



If the organomercurial contains a donating atom in the appropriate position which is capable of chelation, the reaction gives a metallocycle according to the following scheme.

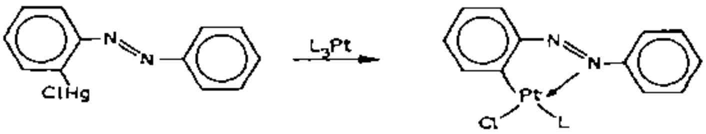


A five-membered cycle is the optimum size of the chelated ring *, although other cycles are known in organometallic chemistry. Thus, we prepared a compound from the product of styrene aminomercuration containing a four-membered metallocycle [36].

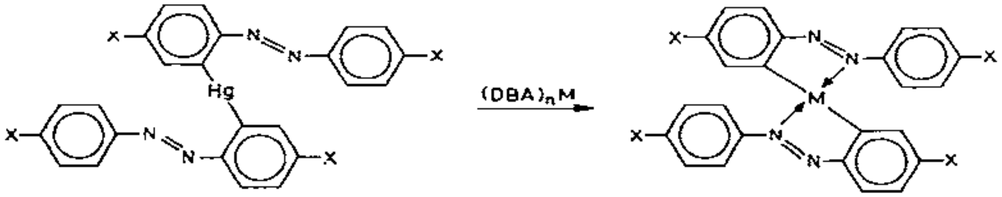


$$\begin{array}{ll} C_6H_5-CH-CH_2 & \\ \quad (CH_3)_2N \quad HgCl & \end{array} \xrightarrow{L_3Pt} \begin{array}{l} C_6H_5-CH-CH_2 \\ (CH_3)_2N \rightarrow Pt(L)Cl \end{array}$$

Five-membered cycles are easily obtained with tris(triphenylphosphine)-platinum [18].



The preparative method may be conveniently modified by using dibenzylideneacetone complexes, $(DBA)_nPt$ and $(DBA)_nPd$, where n is 2 or 1.5. These complexes, especially the palladium one, are readily obtained, are stable and easy to work with, also DBA as a ligand is retained at the metal only in the zero oxidation state. Therefore $(DBA)_nM$ was introduced as a synthetic equivalent (synthone) of the active transition metal atom. In the presence of a donor group in the organomercurial which is capable of closing the chelate metallocycle the reaction looks like the displacement of mercury with platinum or palladium [17]. Bis-chelate metallocycles were prepared in such a manner; synthesis of these compounds by other routes is very difficult and proceeds with low yields [32].



Dimeric organometal halides may be obtained from organomercurials and then cleaved with any ligand, whereas removal of tertiary phosphine, which is always present when starting from $(R_3P)_nM$, is very difficult and not always

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* See, for instance: J. Dehand and M. Pfeffer, Coord. Chem. Rev., 18 (1976) 327; or A.J. Cheney, B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc. A, (1971) 3833.

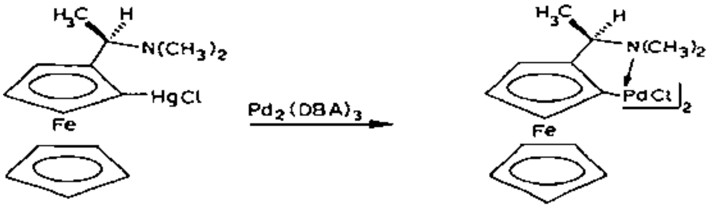
possible. This synthetic technique was applied as well to oxidative addition of alkyl halides leading to metallochelates [18].

Using zerovalent complexes with loosely bounded dibenzylideneacetone ligand, it is possible to introduce some new ligands directly into the reaction mixture. This was shown for the phenanthroline complex of arylpalladium chloride which was obtained in a high yield.

$$CH_3C_6H_4HgCl + Pd(DBA)_2 + phen \rightarrow CH_3C_6H_4Pd(phen)Cl + Hg + DBA$$

Presumably, mixed zerovalent complexes with different ligands are formed in situ [33].

In general, the described synthesis of palladium and platinum chelate metallocycles is complementary to the cyclometallation reaction which is not always smooth and straightforward. This organomercuric route was used, for instance when it was required to obtain a pure diastereomer of 2-chloropalladio-1-(1-dimethylaminoethyl)-ferrocene; cyclopalladiation renders a mixture of both diastereomers differing in the absolute configuration of the chiral plane.



Some σ-organoplatinum compounds prepared by this organomercurial route are listed in Table 1.

In principle, the use of zerovalent complexes with olefins that are easily removed by such ligands as DBA, or with simple olefins, such as ethylene, makes it possible to prepare organometallic derivatives without additional ligands. Such an attempt was made with the reaction $C_6F_5HgBr + Pd(DBA)_2$ [16]. However, although indirect data in favour of formation of C_6F_5PdBr in solution were obtained, we were unable to isolate this compound. It was later prepared by the direct reaction of palladium atoms with C_6F_5Br in the gaseous phase and was found to be rather stable [34].

(b) Synthesis of compounds with a transition metal—mercury σ-bond and of oligometallic chains

The reaction may frequently be carried out so as to obtain intermediate platinum—mercury compounds. The stability of the intermetallic bond is higher, the higher the electron-withdrawing capacity of radicals in the organomercurial. Thus, compounds with perfluoro groups [16] are especially stable, they cannot be even thermally demercurated.

$$(CF_3)_2Hg + (Ph_3P)_3Pt \rightarrow (CF_3Hg)Pt(PPh_3)_2CF_3$$

Steric hindrance in the vicinity of the metal—metal bond also increases the

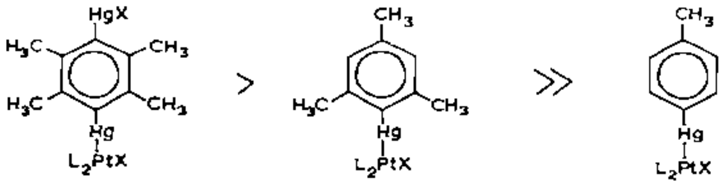
TABLE 1

σ-Organoplatinum derivatives prepared via the organomercurial route according to the equation: R—Hg—R′ + $L_3Pt \rightarrow$ R—PtL_2—R′ + Hg

R	R′	L	Yield (%)[a]	Ref.
p-$CH_3C_6H_4$	Br	Ph_3P	84	11
(p-$CH_3OC_6H_4)_2C{=}CH$	Cl	Ph_3P	66	11
$CH_3OOC{-}CH_2$	Cl	Ph_3P	72	12
C_6H_5	C_6H_5	Ph_3P	45	12
$C_5H_5FeC_5H_4$	Cl	Ph_3P	50	11
i-$BuOCOCH_2$	i-$BuOCOCH_2$	Ph_3P	47	12
CH_3	I	Ph_3P	58	12
CF_3COO	CF_3COO	Ph_3P	71	12
$CH_2{=}CH{-}CH_2$	Cl	Ph_3P	70	12
3-CH_3(5-$CH_3C_6H_3N{=}N)C_6H_3$	Cl	DBA	88	17
$C_6H_5{-}CH(NMe_2){-}HC_2$	Cl	Ph_3P	90	36
p-$CH_3C_6H_4$	Br	Cy_3P[b]	70	[c]
C_6H_{11} (cyclo)	Br	Ph_3P	86	22
2-$CH_3OC_6H_{10}$	Br	Ph_3P	73	22
C_5H_9(cyclo)	Br	Ph_3P	72	22
2-$CH_3OC_5H_8$	Br	Ph_3P	52	22
2-norbornyl	Br	Ph_3P	76	22
2-CH_3O—norbornyl	Br	Ph_3P	76	22
$(OC)_3MnC_5H_4$	Cl	Ph_3P	84	23
$(OC)_3ReC_5H_4$	Cl	Ph_3P	85	23
$COOCH_3$	Cl	Ph_3P	87	[c]
$COOCH_3$	$COOCH_3$	Ph_3P	92	[c]
$(OC)_2(Ph_3P)MnC_5H_4$	Cl	Ph_3P	81	[c]
$(OC)_2(Ph_3P)ReC_5H_4$	Cl	Ph_3P	72	[c]
I-$C_{10}H_7$	Br	Ph_3P	88	[c]
2,5-$(CH_3O)_2C_6H_3$	Br	Ph_3P	64	[c]
$C_6H_5{-}CH{-}COOC_{10}H_{19}$	Br	Ph_3P	74	[c]

[a] For pure product. [b] Cy = cyclo-C_6H_{11}. [c] This work.

stability of such bimetallic derivatives. This follows, for instance from the stability order in the aryl series [16].



Using organomercurials of the cycloalkyl series, platinum—mercury compounds may be obtained by carrying out the reaction in toluene at low temperatures (—20 + 0°).

Trialkylphosphines which are better donors than triarylphosphines seem to reduce the stability of bimetallic derivatives, whereas bidentate ligands (diphos) definitely exhibit a substantial stabilising effect.

Compounds with a mercury—platinum bond undergo with CF_3COOH a characteristic reaction of acidolysis with demercuration which may serve as a qualitative indicator of the presence of a Hg—Pt or Hg—Pd bond.

$$RHg{-}PtL_2{-}R' + CF_3COOH \rightarrow RH + Hg + CF_3COO{-}PtL_2R'$$

The stable mercury platinum compound prepared from bis(trifluoromethyl)-mercury was studied by the method of X-ray structural analysis [26]. The most important feature in its structure is the *cis*-configuration of the square planar arrangement around the platinum atom. Introduction of a large number of perfluorinated groups appreciably increases the stability of electron-rich metal—metal σ-bonds. This was used for the synthesis of chains consisting of 4 atoms of various metals from bis(trispentafluorophenylgermyl)mercury and bis(trispentafluorostannyl)mercury [20,21].

L_2Pt is inserted in one of the mercury—group IV metal bonds forming very stable compounds which can be demercurated only by heating in CF_3COOH or by photolysis.

$$(C_6F_5)_3Ge{-}M{-}Ge(C_6F_5)_3 + L_3Pt \rightarrow \mathit{cis}\text{-}(C_6F_5)_3Ge{-}M{-}L_2Pt{-}Ge(C_6F_5)_3$$

$M = Cd, Zn, Hg$

We were unable to achieve double insertion; nevertheless a stable product of L_2Pd insertion into a germyl derivative was obtained. This is the first instance of formation of a stable palladium—mercury bond. A mixed compound also reacts with tris(triphenylphosphine)platinum, the insertion presumably occurring in the Ge—Hg bond.

$$(C_6F_5)_3Ge{-}Hg{-}C_2H_5 + L_3Pt \rightarrow (C_6F_5)_3Ge{-}PtL_2{-}Hg{-}C_2H_5$$

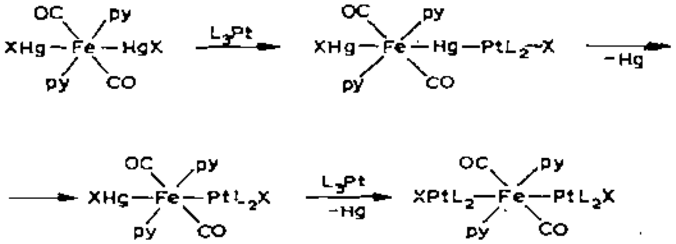
Moreover, we were able to carry out a similar insertion of L_2Pt into isostructural compounds of cadmium and zinc [20,21]. The cadmium compound is very similar to the mercury ones, while the zinc derivative is much less stable and is sensitive to moisture and oxygen. X-ray analysis of one of these compounds showed the *cis*-arrangement of two triphenylphosphine ligands in the coordination square of platinum.

A similar reaction has been described for tris(triphenylphosphine)palladium and bis(triphenylgermyl)cadmium in toluene: an insertion product was obtained in 75% yield, although the substrate did not contain strong electron-acceptor groups [37]. Replacement of phenyl groups with ethyl groups leads to complete decomposition.

$$(Ph_3Ge)_2Cd + (Ph_3P)_3Pd \rightarrow Ph_3Ge{-}(Ph_3P)_2Pd{-}Cd{-}GePd_3$$

Another example of a 4-atom oligometallic chain prepared by this reaction was obtained in the iron carbonyl series [27].

The bimetallic fragment —$(Ph_3P)_2Pt$—Hg—, considered as a whole, exhibits



very strong electron-donating properties, as was established while studying IR-frequencies of carbonyls in substituted cyclopentadienylmanganese tricarbonyl and its rhenium analogue. The ν(CO) shift to lower frequencies, under the influence of this substituent, is the largest among the substituents studied and even exceeds the shift caused by an amine group.

C. ORGANOMETALLIC DERIVATIVES OF GROUP IV ELEMENTS

This group of the periodic table begins with carbon and is followed by silicon which only partially exhibits metallic properties. Consequently, oxidative addition of organic halides, known for $(Ph_3P)_4Pt$ from 1959 [38], formally should be considered relevant to the topic of this review. Therefore, a priori it seems evident that the M—Hal bond, where M is a group IV metal, should react with zerovalent complexes of the platinum triad.

The relative reactivity of M—C and M—H bonds is less clear. Several studies which deal with the behaviour of compounds containing bonds between metals of groups II and IV were discussed in the previous section [21,30]. Here we shall consider the behaviour of organohalides and tetraorganoderivatives of group IV elements.

Layton et al. [9] were the first to isolate the product of reaction between $(Ph_3P)_4Pt$ and Ph_3SnCl. They assigned the structure of Ph_3Sn—PtL_2Cl to it, i.e. postulated insertion of L_2Pt into the Sn—Cl bond. According to this suggestion the kinetics of this reaction in benzene were later studied using $(Ph_3P)_4Pt$ and $(Ph_3P)_2Pt(C_2H_4)$ [39]; the reaction products were not isolated, nor characterized in this work. Cardin et al. [40] attempted to react zerovalent platinum complexes with trimethylstannane and trimethylchlorostannane. They established that reactions proceed, but failed to identify the products. Clark and Itoh [41] described a product of $(Ph_2PMe)_4Pt$ reaction with Me_3SnCl in benzene at 80° and assigned to it the structure *trans*-$L_2Pt(SnMe_3)Cl \cdot C_6H_6$; attempts to obtain an organoplatinum compound by reacting $(diphos)_2Pt$ with Me_3SnCl failed. Akhtar and Clark [42] noted that the ethylene complex, $(Ph_3P)_2Pt(C_2H_4)$, is a more convenient reagent, as compared with $(Ph_3P)_3Pt$, since ethylene is removed and the product is obtained in a relatively pure state. The most convincing reaction occurred with hexamethyldistannane. The ether—benzene solution instantly turns red and yellow crystals precipitate 10 min thereafter. The appearance of a quickly disappearing deep colour, as frequently in the case of organomercurials (vide supra), probably indicates the initial formation of a charge transfer complex rather than a polynuclear Pt(0) cluster. A *trans*-configuration was assigned solely on the basis of one (Pt—P) band at 470 cm^{-1} in the IR-spectrum. This assignment does not seem now adequately substantiated. Thus, in that work for the first time insertion of a platinum carbenoid into a metal—metal bond was established.

$(Ph_3P)_2Pt(C_2H_4) + Me_3Sn{-}SnMe_3 \rightarrow L_2Pt(SnMe_3)_2$

In a recent study of reactions of triorganotinhalides and Pt(0) complexes Eaborn et al. [43] critically examined and repeated all previous work in this field and studied in detail the structure of products by ^{1}H and ^{31}P NMR spectroscopy. They came to the conclusion that the insertion of the platinum carbenoid in all cases occurs at the Sn—C bond and that the product has a *cis*-configuration.

$R_3SnX + L_3Pt \rightarrow$ *cis*-$RPtL_2(SnR_2X)$

For triphenyltin derivatives even introduction of iodine (Ph_3SnI) does not change the direction of the reaction. The reaction of tetraphenyltin with bis-(triphenylphosphine)ethyleneplatinum at 50° after an hour renders a product of *cis*-insertion in 65% yield.

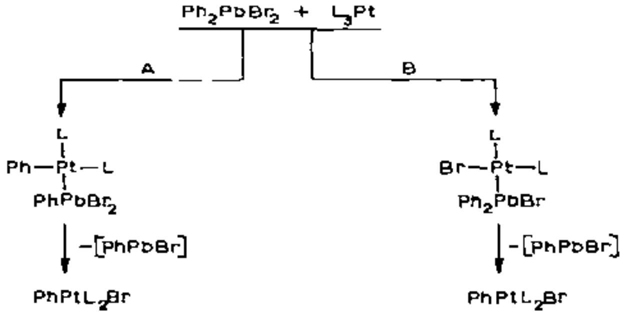
$Ph_4Sn + (Ph_3P)_2Pt(C_2H_4) \rightarrow$ *cis*-$PhPt(PPh_3)_2SnPh_3$

Tetramethyltin does not react with this complex, but with $(Et_3P)_4Pt$ in boiling benzene it forms *cis*-$MePtL_2SnMe_3$ according to $^{31}P\{^1H\}$ spectra; the latter compound, however, was not isolated. Formation of bimetallic products with *cis*-configuration of the planar platinum square indicates a common type of the transition state and reaction mechanism.

The reaction of $(Ph_3P)_4Pt$ with several Me_3SnR derivatives, where R is an electron-withdrawing radical ($-CH{=}CH_2$, $-CF{=}CF_2$, $-C{=}CC_6H_5$ was described by Lappert and coworkers [44,45].

In view of the results obtained by Eaborn et al. [43] determination of the geometrical configuration of the products must await further study. Reaction of $(Ph_3P)_4Ni$ with triphenylchlorostannane does not lead to formation of σ-organonickel compounds [46].

As for organolead compounds, only the reaction of diphenyldibromolead with tris(triphenylphosphine)platinum leading to the selective formation of phenylbis(triphenylphosphine)platinum or bromide in a high yield has been reported [12]. This reaction may proceed by two routes.



Route A seems more probable since for route B one would expect formation of L_2PtBr_2. The last step, elimination of R_2Pb (or R_2Sn) from bimetallic compounds was observed by Baird [47] for such compounds as shown below.

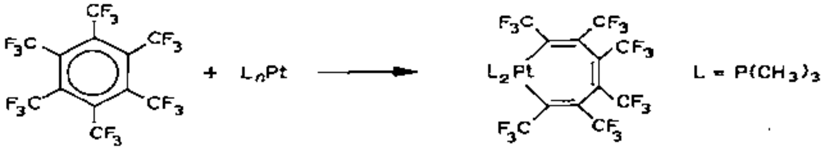
$Ph_3Pb—PtL_2—Cl \xrightarrow{\Delta} Ph—PtL_2—Cl + [Ph_2Pb]$

As for germanium compounds, $(Ph_3P)_2Pt(C_2H_4)$ and $(Et_3P)_4Pt$ do not react with $PhGeMe_3$, while in the case of Ph_3GeBr and Me_3GeBr small quantities of Pt(II) bromide complexes were found [43]. The previous authors proposed a rather sophisticated argument in favour of L_2Pt insertion into the Ge—C bond, which however should be less active than the Ge—Hal bond.

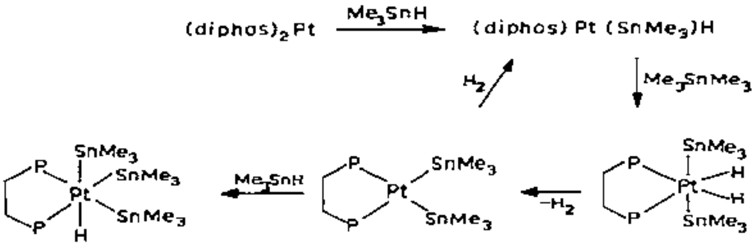
Formation of platinum(II) organic products from Pt(0) complexes and R_nSiHal_{4-n} has not be mentioned in the literature. The Si—C bond is very similar to the C—C bond, so one should expect that insertion of L_2Pt is possible only in exceptional cases, for instance in a strained 4-membered cycle of silacyclobutanes, or in the presence of appropriate substitutents. The possibility of such reactions is supported to a certain extent by the known insertion of bis(triphenylphosphine)platinum in the C—C bond of diphenylcyclopropenone [48], of 1,1,2,2-tetracyanocyclopropane [49] and of 1,1,2,2-tetracyanocyclobutane [50].

The zerovalent platinum complexes with tert-butylisonitrile undergo insertion into the C—C bond of a benzene ring with the breaking of the aromatic system [51].

A similar reaction proceeds with (*trans*-stilbene)$Pt(PR_3)_2$ where R = CH_3, but not C_2H_5, when the aromatic system is retained.



In the triorganohydrides of group IV metals the metal—hydrogen bond shows variable reactivity. According to Clemmit and Glockling [52] Me_3SiH and Me_3GeH do not react with $(diphos)_2Pt^0$, whereas Me_3SnH undergoes oxidative addition even to Pt(II) hydride and an octahedral hydrido Pt(IV) complex may be isolated from the reaction as a final product.



The same Pt(0) complex reacts at 60° with Me_3SnCl and Me_3SiCl yielding only

L_2PtCl_2 + Me_6M_2 which indirectly indicates a homolytic reaction path in these conditions.

The reaction of a related complex of bis(diphenylphosphino)methane, with trimethylstannane does not proceed to a Pt(IV)-containing product, but terminates at the platinum(II) product [53].

$(diphos)_2Pt + 2\ Me_3SnH \rightarrow (diphos)Pt(SnMe_3)_2$

Trimethylstannane, according to Akhtar and Clark [42], reacts with $(Ph_3P)_4Pt$ or $(Ph_3P)_2Pt(C_2H_4)$ to form a product corresponding to $(Ph_3P)_2Pt(SnMe_3)_2$ (elemental analysis only). The hydride, which presumably should be formed initially, was not isolated in this reaction in agreement with ref. 53. However, according to IR spectra it is formed during hydrogenolysis.

$L_2Pt(SnMe_3)_2 + H_2 \rightarrow HPtL_2SnMe_3 + HSnMe_3$

The oxidative addition of hydrido-silanes has been studied more extensively. In 1968 Chatt et al. [54] while boiling Pt(0) complexes with triphenylphosphine or 1,2-diphenylphosphineethane (diphos) in an excess of silanes obtained hydrido complexes of Pt(II) or bis-silyl derivatives, depending on the nature of R.

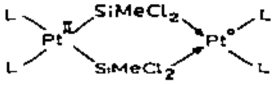
$R'R_2SiH + L_4Pt \rightarrow L_2Pt(SiR_2R')_2$; R=R'=Cl; R=Ph, R'=H

$R_3SiH + L_4Pt \rightarrow L_2Pt(SiR_3)H$; $R=XC_6H_4$, X=F, CF_3

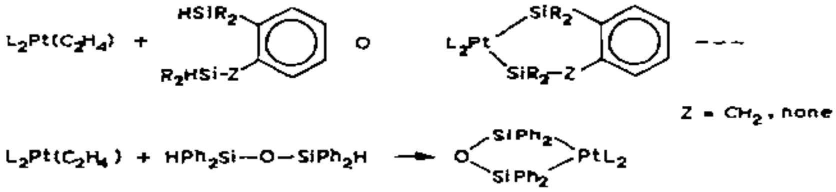
Triphenylsilane did not react. Later, other studies devoted to oxidative addition of hydridosilanes appeared, especially in connection with catalytic hydrosilation of olefins [55—59]. Yamamoto et al. [55] prepared a bis-silyl derivative from methyldichlorosilane and $(C_2H_4)Pt(PPh_3)_2$, while in the presence of an olefin (hexene-1) they obtained a hydride.

$(C_2H_4)Pt(PPh_3)_2 + CH_3SiCl_2H \rightarrow (PPh_3)Pt(H)SiCl_2CH_3$

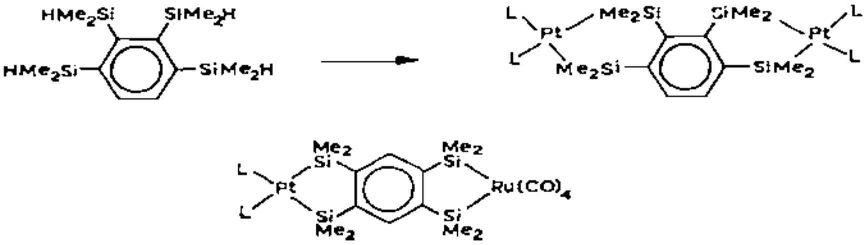
Complexes $Pt(PPh_2Me)_4$ and $(Ph_3P)_2Pt(RC{\equiv}CR)$ react similarly and those with several silanes were studied [56]. At the same time Fink and Wegner [57] studied the behaviour of $MeSiHCl_2$ towards $(Ph_3P)_4Pt$ and $(C_2H_4)Pt(PPh_3)_2$ and observed formation of three products under different conditions. In addition to the hydride and bis-silyl derivative, to which the *cis*-configuration was assigned, a substance that does not exhibit ν(Pt—H) in the IR spectrum was obtained when the reaction was carried out without a solvent. Elemental analysis corresponds to $(L_2PtSiCl_2Me)_n$ and the authors assigned to this product a structure containing both Pt(0) and Pt(II) atom and bridged silyl groups.



Eaborn et al. [58] studied the possibility of preparing platinumdisilaheterocycles from compounds with two hydridosilane groups. They used ethylenebis(triphenylphosphine)platinum as a zerovalent reagent. At room temperature six-, five- and four-membered cycles are easily formed.

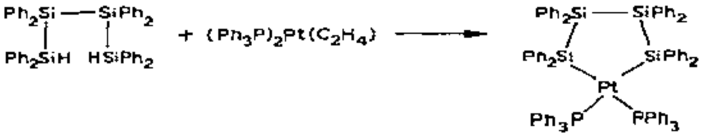


However bis-hydrido-silanes, $HSiMe_2(CH_2)_4SiMe_2H$ and *o*-1,2-$(HSiMe_2CH_2)C_6H_4$, which should yield 7-membered cycles, gave only acyclic hydrides $L_2Pt(H)SiR_2R'$ of *cis*-configuration. In a similar study, Fink [59] investigated tetrasilanes. Bis(silyl)chelates are rapidly and quantitatively obtained at room temperature when using $(C_2H_4)Pt(PPh_3)_2$. Replacement of PPh_3 with Ph_2PCH_2—CH_2PPh_2 was carried out and a mixed complex with two different metals was obtained stage-by-stage.



A similar route was used to close a purely non-carbon cycle.

The reaction of octaphenyltetrasilane-1,1-dihydride with bis(triphenylphosphine)ethyleneplatinum in benzene occurs instantly at 35° with evolution of ethylene and hydrogen [60]. Lemanski and Schram were able to obtain in a low yield an interesting five-membered heterocycle, composed of four silicon and one platinum atoms.



The difference in the reactivity of Pt(0) complexes which contain different phosphines as ligands is revealed here: on replacement of the ligands with methyldiphenylphosphine, a cyclic product was not obtained.

In an extensive study of the interaction of various classes of organosilicon compounds with Ni(0) complexes [61], only $HSiCl_3$ was found to give two products with a Ni—Si bond. In one of these products a hydride hydrogen band ν(Ni—H) was observed in the IR spectrum.

$(Ph_3P)_4Ni + HSiCl_3 \rightarrow [(Ph_3P)_2NiSiCl_2]_2$

$(diphos)_2Ni + HSiCl_3 \rightarrow (diphos)Ni(H)SiCl_3$

From various R_nSiCl_{4-n} only chloride complexes $(L_2NiCl)_n$ were obtained; products prepared from R_nSiH_{4-n} were not sufficiently characterized.

D. OTHER ORGANOMETALLIC COMPOUNDS

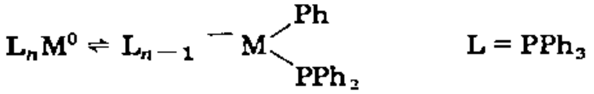
Data concerning derivatives of other metals are very scarce. In the brief communication by Layton et al. [9] already mentioned preparation of a gold–platinum compound was reported.

$(Ph_3P)AuX + (Ph_3P)_4Pt \rightarrow (Ph_3P)Au{-}Pt(PPh_3)_2X,\quad X = Cl, Br$

Reactions with L_2PtCl_2, L_2NiT_2 and LCuCl ($L = Ph_3P$) are also mentioned; as claimed by the authors they also lead to products with platinum–metal bonds.

Dimeric trimethylaluminum reacts yielding a poorly characterized complex of an approximate stoichiometry $L_2Pt \cdot [Al(CH_3)_3]_2$, which presumably is unstable and decomposes producing a paramagnetic species [62].

Reversible oxidative addition of triphenylphosphine to zerovalent complexes of Ni(0) and Pt(0) has even been observed [63]; this shows the complexity of equilibria that may exist in solution.



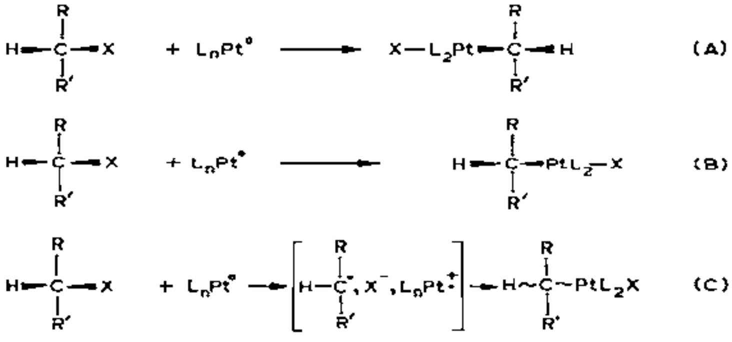
$$L_nM^0 \rightleftharpoons L_{n-1}{}^{-}M\begin{smallmatrix}\diagup Ph \\ \diagdown PPh_2\end{smallmatrix} \qquad L = PPh_3$$

Organolithium compounds lead to formation of anionic complexes [64].

$L_2Ni(C_2H_4) + LiR \rightarrow [L_2NiR]^{-}Li^{+}$; $R = Ph, Ph_3Si$

E. SOME MECHANISTIC CONSIDERATIONS

Species L_2Pt and L_2Pd possess the properties of nucleophilic carbenoids. In principle, there are three possible mechanisms for the interaction with metal–element bonds, as well as for oxidative addition of organic halides: S_N2 nucleo-

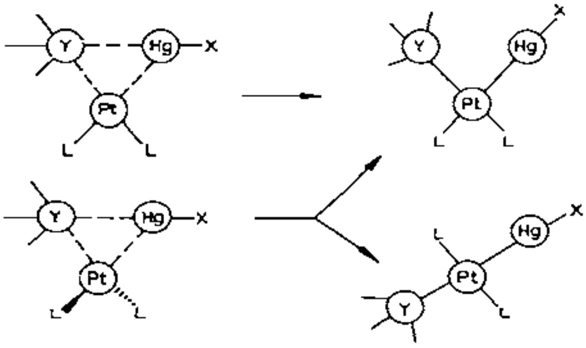


$X = L_kM$

philic substitution at metal or carbon atoms with subsequent recombination of the ionic pair (A), direct insertion into the metal—element bond (B) and one-electron transfer with subsequent recombination of the radical pair (C) [15].

The nucleophilic mechanism seems improbable, at least for the carbon—metal bonds. One can also hardly expect stereospecificity for this mechanism, whereas the available data indicate that the bimetallic products invariably have a *cis*-configuration around the square-coordination plane of platinum.

For insertion, generally speaking, two types of transition states are possible starting from zerovalent L_3Pt complexes: with the coordination number of platinum either equal to 4 or 5, depending on whether the L_3Pt species reacts directly or after preliminary dissociation of one of the ligands $PtL_3 \rightleftharpoons PtL_2 + L$. The readiness with which bis-ligand zerovalent complexes react supports the latter assumption. In this case, two possibilities remain: a tetrahedral or planar-square transition state. The routes by which *cis* and *trans* final products may be obtained from both transition states are shown below. The route from the square-planar transition state to the *cis*-product seems the most probable. However elucidation of the nature of the transition state requires further study.



Y = Hal, C, M

As a rather close analogy one should mention the insertion of electrophilic carbene $:CCl_2$ into the carbon—mercury bond in dialkylmercury which proceeds with complete retention of configuration [65,66].

$$R{-}Hg{-}R + :CCl_2 \rightarrow R{-}CCl_2{-}Hg{-}R$$

F. RELATED REACTIONS

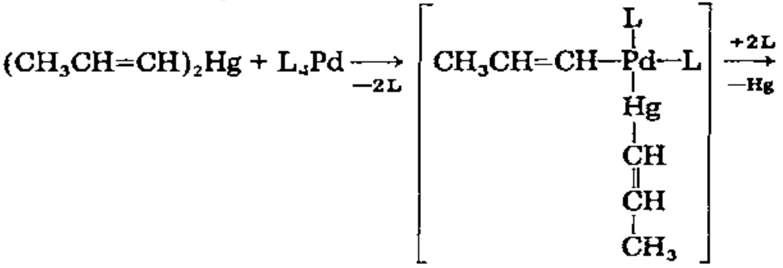
(a) Some reactions of organoelement compounds catalysed by zerovalent complexes of platinum or palladium

Catalytic properties of zerovalent complexes of platinum metals in relation to many organic reactions are well known and are extensively used. Many reactions of organic halides are catalysed by Ni(0) and Pd(0) complexes and for certain reactions it has been established that oxidative addition is the most important step.

Under conditions of such reactions zerovalent complexes are regenerated by reductive elimination

$$L_2M^{II}X_2 \xrightarrow{L} L_4M^0$$

Several examples have been described where zerovalent palladium complexes catalyse reactions of organometallic compounds. The mechanisms described in this review seem probable for these reactions. Consider the preparation of 1,4-dimethylbutadiene from di(propenyl)mercury in the presence of $(Ph_3P)_4Pd$ reported by Vedejs and Weeks [67]. For this reaction we have earlier proposed the following mechanism based on insertion of L_2Pd into the mercury—carbon bond.



$$(CH_3CH{=}CH)_2Hg + L_4Pd \xrightarrow[-2L]{} \left[CH_3CH{=}CH{-}\underset{\underset{\underset{\underset{CH_3}{|}}{CH}}{\|}}{\overset{L}{\overset{|}{Pd}}}\ldots \right] \xrightarrow[-Hg]{+2L}$$

$$\left[CH_3CH{=}CH{-}\overset{\overset{L}{|}}{\underset{\underset{Hg}{|}}{Pd}}{-}L \right], \quad Hg{-}CH{=}CH{-}CH_3$$

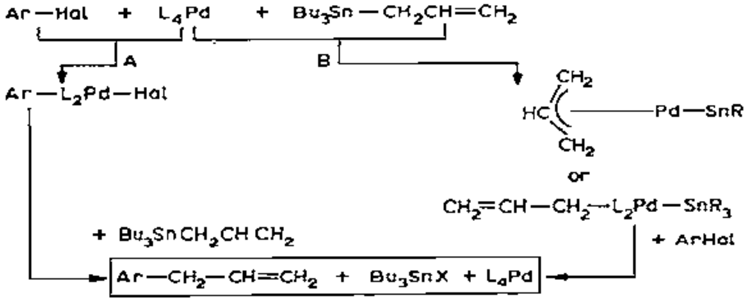
$$CH_3CH{=}CH{-}CH{=}CH{-}CH_3 + L_4Pd$$

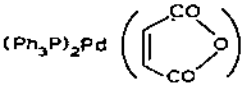
The instability of Pd—Hg compounds containing usual ligands leads to demercuration, which possibly may proceed simultaneously with coupling without formation of R_2PdL_2 intermediate. Insertion of the palladium carbenoid presumably affords a *cis*-product (vide supra) and the geometry of the complex is favourable for formation of a coupling product.

Japanese workers [68] have reported similar catalysis of allylation of aryl halides with tributylallyltin.

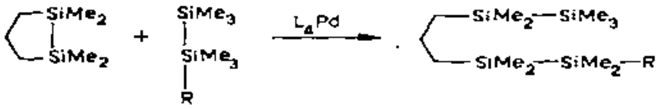
$$Ar{-}Hal + Bu_3Sn{-}CH_2{-}CH{=}CH_2 \xrightarrow[100°]{L_4Pd} Ar{-}CH_2{-}CH{=}CH_2$$

They proposed a mechanism based on oxidative addition of ArHal to L_4Pd (route A in Scheme), but the alternative mechanism of L_2Pd insertion at the allyl—tin bond is also quite possible (route B). No convincing evidence in favour of one of these mechanisms is yet available.

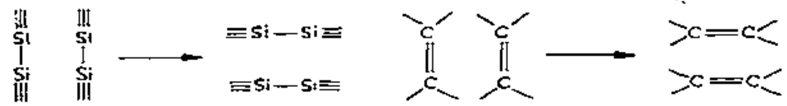


Complexes of zerovalent palladium $(Ph_3P)_4Pd$ and 

catalyse metathesis of disilanes along the Si—Si bond at 80° in boiling benzene, whereas in the absence of the catalyst, the reaction requires 200° [69].



The general scheme of metathesis of disilanes is quite similar to the metathesis of olefins, however, according to Sakurai et al. [69];



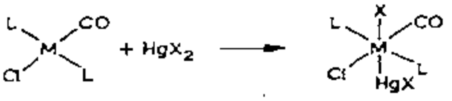
conversion of disilanes occurs with specific radicals R = —CH=CH$_2$, —C≡CH and the key step of the process involves rupture of the Si—Si bond with formation of a π-silaalyl—palladium complex.

Data on catalysis of hydrosilylation reactions by platinum metal compounds and on the role of zerovalent complexes are discussed in a recent review [70].

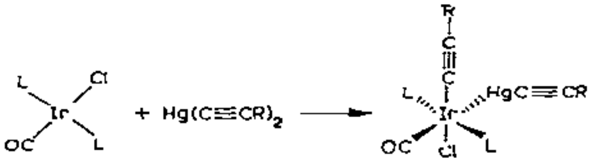
(b) Similar reactions of low-valent complexes of transition metals

The close analogy between zerovalent complexes of the nickel triad and the univalent complexes of the cobalt triad is well known. The same trend of reaching the most stable electronic configuration of the metal atom leads to predominant transition to valency 3. Reactions of oxidative addition are just as typical of rhodium and iridium as of palladium and platinum [2].

Reactions of low-valent rhodium and iridium complexes with mercury compounds have been reported in several studies. Only two reports however deal with organometallic derivatives of mercury [71,72]. The best studied compounds are the complex Ir(Ph$_3$P)$_2$CO(Cl) and its rhodium analogue, to which the addition of mercury halides has been established some time ago [73]. Later it was confirmed [74,75] that the product contains a mercury—transition metal bond. The reaction may be represented as follows.



In 1967 Collman and Kang [71] found that mercuric salts of monosubstituted acetylenes are instantaneously added to bis(triphenylphosphine)iridium(I)carbonyl chloride in CH$_2$Cl$_2$; the structure corresponding to *cis*-insertion was assigned to the product on the basis of IR spectral data.



Recently Baird and Surridge [72], while studying conversions of alkyl—mercury compounds in the presence of tris(triphenylphosphine)rhodium chloride, isolated an intermediate product the elemental composition of which corresponds to $(Ph_3P)_2RhCl(Ph)(HgOAc)$. The authors tentatively proposed that the insertion occurs into the mercury—aryl bond and not into the mercury—acetate bond.

In our preliminary experiments methylmercury iodide released mercury several hours after treating it with $(Ph_3P)_3RhCl$ in benzene, but we were unable to identify the metal derivative of Rh(III). 2-Dimethylaminomethyl-1-chloromercuriferrocene in the course of normal reaction leads to metallic mercury and a chelate rhodium metallocycle, which however has not yet been obtained in pure state.

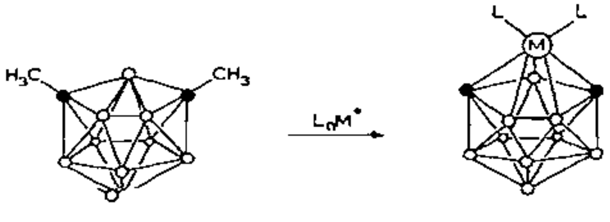
Due to the fact that transition metals frequently have several stable valent states, more distant analogies to the reactions discussed are possible. The interaction of vanadocene with organomercuric salts, the only identified products of which are vanadocene salts [76] may possibly be such an example.

$Cp_2V + RHgX \rightarrow Cp_2V^+X^- + Hg + ?$

All group IV elements in oxidation state +2 possess carbenoid properties. Inorganic derivatives of bivalent tin are well known, and the reaction established by Nesmeyanov and Kocheshkov in 1930 [77,78], which quite possibly proceeds through a bimetallic intermediate, is obviously relevant to our discussion.

$R_2Hg + SnHal_2 \rightarrow [R{-}Hg{-}SnHal_2{-}R] \rightarrow R_2SnHal_2 + Hg$

Organic derivatives of group IV bivalent metals of type $(R_3Z{-}CH_2)_2M$, where Z = C, Si; R = alkyl; M = Ge, Sn, Pb have been recently obtained by Lappert and coworkers [79]. The reactivity of these compounds in relation to various substrates should be considered as oxidative addition. The similar reaction of *closo*-carborane $Me_2C_2B_9H_9$ with zerovalent complexes $Pt(PEt_3)_3$, $Pt(PMe_2Ph)_3$, $Pd(ButNC)_2$, $Ni(COD)_2$ proceeding in toluene at ambient or lower temperatures should be mentioned. Spencer et al. [80] proposed a method for the synthesis of metallocarboranes containing a transition metal atom based on this peculiar insertion into a boron and carbon polyhedral system.



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REFERENCES

1 L. Malatesta and S. Cenini, Zerovalent Complexes of Metals, Academic Press, London, 1974.
2 J.P. Collman and W.P. Roper, Adv. Organometal. Chem., 7 (1968) 53.
3 J. Halpern, Accounts Chem. Res., 3 (1970) 386.
4 R. Ugo, Coord. Chem. Rev., 3 (1968) 319.
5 J. Lewis and S.B. Wild, J. Chem. Soc. A, (1966) 69.
6 F.G.A. Stone, Pure Appl. Chem., 30 (1972) 551.
7 O.M. Nefedov and M.N. Manakov, Angew. Chem., 78 (1966) 1039.
8 J.F. Nixon and M.D. Sexton, J. Chem. Soc. A, (1970) 321.
9 A.J. Layton, R.S. Nyholm, G.A. Pneumaticakis and M.L. Tobe, Chem. Ind., (1967) 465.
10 K.P. Butin, N.A. Belokoneva, A.A. Zenkin, I.P. Beletskaya and O.A. Reutov, Dokl. Akad. Nauk SSSR, 211 (1973) 878.
11 V.I. Sokolov, V.V. Bashilov, L.M. Anishchenko and O.A. Reutov, J. Organometal. Chem., 71 (1974) C41.
12 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 97 (1975) 299.
13 Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, J. Chem. Soc. D, (1970) 1065.
14 K. Moseley and P.M. Maitlis, J. Chem. Soc. D, (1971) 1604.
15 V.I. Sokolov, Abstr. Int. Conf. Organometal. Chem., VIIIth, Venice, SA5 (1975).
16 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 111 (1976) C13.
17 V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, J. Organometal. Chem., 93 (1975) C11.
18 L.L. Troitskaya, A.I. Grandberg, V.I. Sokolov and O.A. Reutov, Dokl. Akad. Nauk. SSSR, 228 (1976) 367.
19 V.V. Bashilov, V.I. Sokolov and O.A. Reutov, Dokl. Akad. Nauk SSSR, 228 (1976) 603.
20 V.I. Sokolov, V.V. Bashilov, O.A. Reutov, M.N. Bochkarev, L.P. Maiorova and G.A. Rasuvaev, J. Organometal. Chem., 112 (1976) C47.
21 M.N. Bochkarev, G.A. Razuvaev, L.P. Maiorova, N.P. Makarenko, V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 131 (1977) 399.
22 V.I. Sokolov, G.Z. Suleimanov, V.V. Bashilov, T.K. Kurbanov, I.A. Amiraslanov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1894.
23 V.V. Bashilov, O.A. Reutov, V.I. Sokolov, G.Z. Suleimanov and I.A. Amiraslanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2147.
24 L.L. Troitskaya, V.I. Sokolov and O.A. Reutov, J. Organometal. Chem., 133 (1977) C28.
25 L.L. Troitskaya, V.I. Sokolov and O.A. Reutov, Dokl. Akad. Nauk SSSR, 236 (1977) 371.
26 L.G. Kuzmina, Yu.T. Struchkov, V.V. Bashilov, V.I. Sokolov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 621.
27 V.I. Sokolov and G.Z. Suleimanov, Inorg. Chim. Acta, 25 (1977) L149.
28 J. Chatt and B.L. Shaw, J. Chem. Soc., (1960) 4020.
29 R.G. Pearson, W. Louw and J. Rajaram, Inorg. Chim. Acta, 9 (1974) 251.
30 J.A. Labinger, A.V. Kramer and J.A. Osborne, J. Am. Chem. Soc., 95 (1973) 7908.
31 V.I. Sokolov, Inorg. Chim. Acta, 18 (1976) L9.
32 M.M. Bagga, W.T. Flannigan, C.R. Knox and P.L. Pauson, J. Chem. Soc. C, (1969) 1534.
33 W.J. Cherwinski, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1974) 1405.

34 K.J. Klabunde and J.Y.F. Law, J. Am. Chem. Soc., 96 (1974) 7674.
35 G. Oehme, K. Ch. Röber and H. Pracejus, J. Organometal. Chem., 105 (1976) 127.
36 V.I. Sokolov and V.V. Bashilov, Zh. Org. Khim., 14 (1978) 1114.
37 V.T. Bychkov, S.N. Titova and I.V. Lomakova, Zh. Obshch. Khim., 46 (1976) 2629.
38 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 705.
39 J.P. Birk, J. Halpern and A.L. Pickard, Inorg. Chem., 7 (1968) 2672.
40 D.J. Cardin, S.A. Keppie and M.F. Lappert, J. Chem. Soc. A, (1970) 2594.
41 H.C. Clark and K. Itoh, Inorg. Chem., 10 (1971) 1707.
42 M. Akhtar and H.C. Clark, J. Organometal. Chem., 22 (1970) 233.
43 C. Eaborn, A. Pidcock and B.R. Steele, J. Chem. Soc., Dalton Trans., (1976) 767.
44 C.J. Cardin, D.J. Cardin, M.F. Lappert and K.W. Muir, J. Organometal. Chem., 60 (1973) C70.
45 B. Cetinkaya, M.F. Lappert, J. McMeeking and D.E. Palmer, J. Chem. Soc., Dalton Trans., (1973) 1202.
46 P.E. Garrou and G.F. Hartwell, J. Chem. Soc. Chem. Commun., (1972) 881; (1973) 100.
47 M.C. Baird, J. Inorg. Nucl. Chem., 29 (1967) 367.
48 W. Wong, S.J. Singer, W.D. Pitts, S.F. Watkins and W.H. Baddley, J. Chem. Soc. Chem. Commun., (1972) 672.
49 M. Lenarda, R. Ros, M. Graziani and U. Belluco, J. Organometal. Chem., 65 (1974) 407.
50 D.J. Yarrow, J.A. Ibers, M. Lenarda and M. Graziani, J. Organometal. Chem., 70 (1974) 133.
51 J. Browning, M. Green, A. Laguna, L.E. Smart, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1975) 723.
52 A.F. Clemmit and F. Glockling, J. Chem. Soc. A, (1971) 1164.
53 F. Glockling and R.J.I. Pollock, J. Chem. Soc., Dalton Trans., (1975) 497.
54 J. Chatt, C. Eaborn and P.N. Kapoor, J. Organometal. Chem., 13 (1968) P21.
55 K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 28 (1971) C37.
56 C. Eaborn, B. Ratcliff and A. Pidcock, J. Organometal. Chem., 65 (1974) 181.
57 W. Fink and A. Wegner, Helv. Chim. Acta, 54 (1971) 2186.
58 C. Eaborn, T.N. Metham and A. Pidcock, J. Organometal. Chem., 54 (1973) C3.
59 W. Fink, Helv. Chim. Acta, 59 (1976) 606.
60 M.F. Lemanski and E.P. Schram, Inorg. Chem., 15 (1976) 1489.
61 M.E. Lappert and G. Speier, J. Organometal. Chem., 80 (1974) 329.
62 T.R. Durkin and E.P. Schram, Inorg. Chem., 11 (1972) 1054.
63 D.R. Fahey and J.E. Mahan, J. Am. Chem. Soc., 98 (1976) 4499.
64 E. Uhlig and B. Hipler, Z. Chem., 17 (1977) 272.
65 J.A. Landgrebe and R.D. Mathis, J. Am. Chem. Soc., 86 (1964) 524; 88 (1966) 3545.
66 J.A. Landgrebe and D.E. Thurman, J. Am. Chem. Soc., 90 (1968) 6256; 91 (1969) 1759.
67 E. Vedejs, and P.D. Weeks, Tetrahedron Lett., (1974) 3207.
68 M. Kosugi, K. Sasazawa, Y. Shiuzi and T. Migita, Chem. Lett., (1977) 301.
69 H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Organometal. Chem., 131 (1977) 147.
70 J.F. Harrod and A.J. Chalk, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, vol. 2, Wiley, 1977.
71 J.P. Collman and J.W. Kang, J. Am. Chem. Soc., 89 (1967) 844.
72 W.C. Baird and J.H. Surridge, J. Org. Chem., 40 (1975) 1364.
73 R.S. Nyholm and K. Vrieze, J. Chem. Soc., (1965) 5337.
74 G.M. Intille and M.J. Braithwaite, J. Chem. Soc., Dalton Trans., (1972) 645.
75 P.D. Brotherton, C.L. Raston, A.H. White and S.B. Wild, J. Chem. Soc., Dalton Trans., (1976) 1799.
76 G.A. Razuvaev, E.N. Gladyshev, V.N. Latyaeva, E.V. Krasilnikova, A.N. Lineva and Yu.N. Novotorov, Dokl. Akad. Nauk SSSR, 231 (1976) 1138.
77 A.N. Nesmeyanov, and K.A. Kocheshkov, Ber., 63 (1930) 2496.
78 L.G. Makarova, in E. Becker and M. Tsutsui (Eds.), vol. 1, Wiley, 1970.
79 J.D. Cotton, P.J. Davidson and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1976) 2275.
80 J.L. Spencer, M. Green and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1972) 1178.