THE REACTIONS OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS WITH MOLECULAR NITROGEN AND CARBON DIOXIDE

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ABSTRACT

A development of organometallic chemistry has revealed wide possibilities for activating various unsaturated and saturated molecules for numerous novel reactions. Many nitrogen fixating systems based on the low-valent transition metal derivatives and reducing agents have been discovered. Depending on the reaction conditions, complexed nitrogen reduction occurs to form either hydrazine derivatives or ammonia. An investigation of the nitrogen fixating systems involving Lewis acids. to regenerate the catalyst, has led to catalytic nitrogen fixation. Nitrogen activated by complex formation with transition metal compounds is capable of insertion reactions into metal–carbon bonds to form organic amines. In this connection the possibility arises of forming amines from the reaction of nitrogen with hydrocarbons in the presence of transition metal compounds. Transition metal nitrogen compounds seem to be intermediates in the 'reverse' reactions as well, i.e. decompositions of nitrogen-compounds with nitrogen evolution (Sandmeyer reaction, hydrazine oxidation. etc).

Unlike nitrogen, carbon dioxide is rather reactive and undergoes insertion reactions into non-transition metal–carbon bonds. Carbon dioxide also appeared to be capable of direct or indirect complex formation with low-valent transition metal compounds (Ru, Rh, Pt, etc.). Investigation of the stability of such complexes permits novel synthetic and catalytic reactions to be found. Thus the formation of Me—H bonds (e.g. in the formic acid decomposition with CO_2 evolution) can be utilized for catalytic reduction of olefins and other unsaturated compounds by means of formic acid. When the intermediate carbon dioxide complexes with Me—C bonds (carboxylates) are formed. the competitive reaction occurs, i.e. olefin insertion into Me—H or Me—C bonds with elimination of the respective carboxylic acid. Another interesting reaction. insertion of CO_2 into Me—H or Me—C bonds, can follow either 'normal' (formation of a carbon–carbon bond) or 'reverse' (formation of the metallo-acid ester) pathways.

A development of organometallic chemistry has provided unusual possibilities for activating various unsaturated and saturated molecules and introducing them into the various reactions.

The present lecture deals with the problem of activation by transition

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metal compounds of the two rather simple molecules, molecular nitrogen (N_2) and carbon dioxide (CO_2). A common feature of these so different substances is, perhaps, their exclusive biological significance. The main source of terrestrial nitrogen is the atmospheric molecular nitrogen, which, through biological fixation or the industrial ammonia synthesis, provides almost the only source of nitrogen-containing compounds. On the other hand, carbon dioxide is practically the only source of carbon for all living matter. Photosynthesis and biological nitrogen fixation are the two processes which provide the life on Earth.

The main part of terrestrial carbon is in the form of carbon dioxide and the carbonates. It is possible that carbon dioxide and the natural carbonates will replace petroleum and coal as the main sources for the industrial organic synthesis of the future.

The exceptional chemical inertness of nitrogen is well known. It is the most inert of the unsaturated compounds with multiple bonds. This property of the nitrogen molecule is due to not only the high ionization potential, low affinity, and high dissociation energy but also the unusually high strength of the third bond (if one may say so) with respect to the second

Table 1.

$$N \equiv N$$
Dissociation energy 225 kcal mol^{-1}
Ionisation potential 367 kcal mol^{-1}
Electron affinity $\quad -84$ kcal mol^{-1}

Bond energies, kcal mol^{-1}

C—C 80 $\}\Delta = 65$	C—N 73 $\}\Delta = 74$	N—N 37 $\}\Delta = 63$
C=C 145 $\}\Delta = 53$	C=N 147 $\}\Delta = 63$	N=N 100 $\}\Delta = 125$
C≡C 198	C≡N 210	N≡N 225

and first bonds (*Table 1*). Thus until recently, all methods of nitrogen fixation, including the known Haber process, employed high temperatures and energies for activating the nitrogen molecule.

Approximately ten years ago, Shur and myself began to attempt nitrogen fixation by means of organometallic compounds. Our work was based on the hypothesis that complex formation between nitrogen and the transition metal compounds via formation of both the donor-acceptor and dative bonds may be an effective means of activating the nitrogen molecule. We did not attempt to isolate the nitrogen complexes (this was soon achieved by Allen and Senoff in Canada) but instead we searched for possible reaction products of activated nitrogen—ammonia, hydrazine, amines and other substances. At first, the numerous experiments either failed or afforded poorly reproducible results.
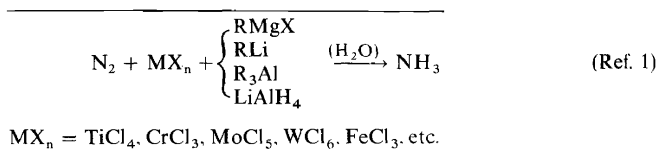
It should be noted that the study of nitrogen fixation requires that the results be rigorously checked, with necessary nitrogen labelling, since most reagents contain the admixtures of nitrates, nitrites and ammonium salts.

After a rather long time we at last found the conditions in which nitrogen reacting at room temperature with transition metal compounds gives a noticeable quantity of ammonia, after the action of water. We checked these results, manipulating with labelled ^{15}N until we were convinced that

molecular nitrogen itself was an actual source of the combined nitrogen. Thus in 1964 we decided to publish our first communication[1]. We reported that nitrogen readily reacts at room temperature with the low-valent organometallics of titanium, chromium, molybdenum, tungsten (see *Table 2*). These low-valent compounds were obtained from the reactions of

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Table 2.

$$N_2 + MX_n + \begin{cases} RMgX \\ RLi \\ R_3Al \\ LiAlH_4 \end{cases} \xrightarrow{(H_2O)} NH_3 \qquad \text{(Ref. 1)}$$

$MX_n = TiCl_4, CrCl_3, MoCl_5, WCl_6, FeCl_3,$ etc.

</div>

organomagnesium, lithium or aluminium compounds with transition metal salts. The action of water led to ammonia.

Further investigations into the reactions of nitrogen with transition metal compounds, carried out both in the Soviet Union and in many other countries, have confirmed these first results and showed that nitrogen may readily react and be reduced in the presence of many organometallic and inorganic transition metal compounds. The results are summarized in *Table 3*.
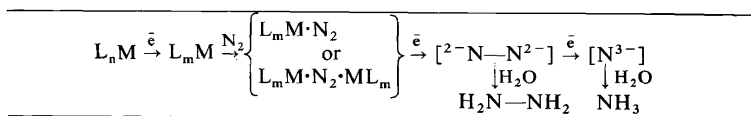
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Table 3. Nitrogen fixating systems

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Transition metals	Ligands	Reducing agents
Ti, Zr	Halides	Li, Na, K, Rb, Cs
V	Alkoxides	Mg, Ca, Al, La, Ce
Cr, Mo, W	Acetylacetonate	$LiAlH_4$, H_2
Mn	Phosphines	RLi, RMgX, R_3Al
Fe, Co	π-Cyclopentadienyl	Ti^{II}, Ti^{III}, V^{II}
	σ-Alkyls	Li, Na, K-naphthalides
	σ-Aryls	Li, Na, K-diphenylides
		Electric current

The metals of Groups IV, V and VI, titanium, vanadium, chromium and molybdenum are the most reactive. Different ligands may be bound with the metals—halides, alkoxides, acetylacetonates, cyclopentadienyls, aryls, alkyls and others. Ligand character determines essentially the activity of the compound towards its reaction with nitrogen, the nature of metal being decisive, however. It should be noted that the compounds of transition metals of high oxidation states do not react with nitrogen. Reduction to the lower oxidation states is always necessary for the reaction to occur. For this purpose a variety of reducing agents listed in the table can be used— alkali and alkali–earth metals, metallic aluminium or magnesium, organo-metallic compounds of lithium, magnesium, aluminium, the low-valent transition metal compounds, aromatic anion-radicals, electric current, etc.

The process of nitrogen fixation follows the general scheme presented in *Table 4*. Firstly, the transition metal compound is reduced to the low-valent

Table 4.

$$L_nM \xrightarrow{\bar{e}} L_mM \xrightarrow{N_2} \left\{ \begin{array}{c} L_mM \cdot N_2 \\ or \\ L_mM \cdot N_2 \cdot ML_m \end{array} \right\} \xrightarrow{\bar{e}} [^{2-}N\!-\!N^{2-}] \xrightarrow{\bar{e}} [N^{3-}]$$
$$\downarrow H_2O \qquad \downarrow H_2O$$
$$H_2N\!-\!NH_2 \qquad NH_3$$

state. Then it reacts with nitrogen to form the complexes. Such complexes are known after the pioneering work of Allen and Senoff[2] who were the first to isolate nitrogen complexes of ruthenium.

Table 4a

$RuCl_3 + N_2H_4 \rightarrow [Ru(NH_3)_5N_2]Cl_2$	(Ref. 2)
$RuCl_3 \cdot nH_2O + Zn/Hg + N_2 \xrightarrow{THF} RuCl_2(N_2)(H_2O)_2 \cdot THF$	(Ref. 3)
$Co(acac)_3 + R_3Al + PPh_3 + N_2 \rightarrow (Ph_3P)_3CoH(N_2)$	(Ref. 4)

$M\!-\!N\!\equiv\!N$	Ti	(Cr)	(Mn)	Fe	Co	Ni
$M\!-\!N\!\equiv\!N\!-\!M$		Mo			Ru	Rh	Pd
$N\!\equiv\!N\!-\!M\!-\!N\!\equiv\!N$		W	Re	Os	Ir

Shilov and his collaborators[3] and Yamomoto et al.[4] and then many other workers have shown the possibility of preparing stable complexes directly from molecular nitrogen. Nowadays nitrogen complexes (or dinitrogen according to the new nomenclature) are known for a great number of transition metals (Table 4a). Those for which the structure has been determined are linear. Both mono- and binuclear complexes and those with two nitrogen ligands have been synthesized. The complexes of rhenium and the Group VIII metals are most stable and have been studied in detail. However, until recently, the numerous attempts to reduce the nitrogen in these stable complexes were unsuccessful. In view of this it may be interesting to note that in the stable complexes such as Yamamoto's cobalt complex, nitrogen could be reduced in the presence of compounds of other transition metals[5]. This affords considerable amounts of ammonia (Table 5). The role of the second

Table 5. Reduction of $(Ph_3P)_3CoH(N_2)$ (yield of NH_3 in mol %)[5]

Reducing agent M'X$_n$	TiCl$_4$	MoCl$_5$	FeCl$_2$	CoCl$_2$
PhLi	17	—	3	2
$C_{10}H_8^-Na^+$	25	4	3	2
$Li + C_{10}H_8^-Li^+$	73	25	7	14
$Mg + MgI_2$	21	—	—	3

$$L_mM\!-\!N\!\equiv\!N + M'X_n \rightarrow L_mM\!-\!N\!\equiv\!N\!-\!M'X_n \xrightarrow[2)\,H_2O]{1)\,\bar{e}} NH_3$$

transition metal may be the formation of binuclear complexes in which nitrogen reduction takes place. However, the mechanism of such reduction requires special investigation.

Let us again discuss the general scheme of nitrogen fixation. The first steps of the process involve formation of the nitrogen complexes. Then the electron transfer to the complexed nitrogen takes place with rupture of the

first two N—N bonds and formation of hydrazine derivatives. The hydrazine can be isolated if the reaction is carried out under sufficiently mild conditions. More drastic conditions or the presence of more active reducing agents cleave the last N—N bond to give the ammonia derivatives.

It should be noted that until recently all the known nitrogen fixating systems were not catalytic. Stoicheiometric reaction of a transition metal compound with nitrogen was observed. As a result no more than one nitrogen molecule per one atom of transition metal was reduced in spite of a great excess of reducing agent. In our opinion the two main factors responsible for the absence of catalysis are (i) in some cases the instability of a low-valent transition metal compound active towards nitrogen and (ii) the high stability of the transition metal–nitrogen nitride bond in the product of nitrogen fixation. Therefore, in order to realize a catalytic fixation of nitrogen it is necessary to introduce the appropriate ligands for stabilizing the low-valent metal compound and then to add a reagent, such as a Lewis or protic acid, which cleaves the metal–nitrogen bond in the reaction product and regenerates the catalyst. On the basis of this hypothesis we started to search for catalytic systems.

The first nitrogen fixating catalytic system was discovered at our laboratory three years ago[6]. It consisted of the reducing agent, metallic aluminium and the Lewis acid, aluminium bromide. Compounds of titanium were used as catalysts. In the absence of titanium compounds nitrogen is not reduced by aluminium or by a mixture of aluminium and aluminium bromide. However, even in the presence of one-tenth per cent of titanium tetrachloride, nitrogen is rapidly reduced to give lithium nitrides, which produce ammonia and a small amount of hydrazine after hydrolysis. The yield of ammonia attains to several hundred mole per mole of the catalyst.

As can be seen from *Table 6*, on the basis of these principles, other catalytic

Table 6. The catalytic nitrogen fixation

| Transition metal compound	Reducing agent	'Acid'	Yield of $NH_3(N_2H_4)$ in moles per mole of transition metal compound	
$TiCl_4$	Al	$AlBr_3$	290	
$TiCl_4$	$LiAlH_4$	$AlBr_3$	125	
$C_6H_6 \cdot TiCl_2 \cdot 2AlCl_3$	Al	$AlBr_3$	113	(Ref. 6)
$Ti(OBu)_4$	$H_2 + i-Bu_3Al$	$AlBr_3$	11	
$Ti(OPr-i)_4$	electric current + naphthalene	$Al(OPr-i)_3$	6	(Ref. 7)
$Ti(OPr-i)_4$	Na-naphthalide	$Al(OPr-i)_3$	5	
$MoOCl_3$ Na_2MoO_4	$TlCl_3 + NaOH$	H_2O	100	(Ref. 8)

nitrogen fixating systems employing different titanium compounds as catalysts were also prepared. Reducing agents used were aluminium, lithium aluminium hydride and organoaluminium compounds. It is interesting that in some cases hydrogen may also be a participant in the catalytic reduction of nitrogen. In the catalytic systems studied by van Tamelen and

Seeley[7] titanium compounds were also used as the catalysts; the Lewis acid was aluminium isopropylate and the reducing agent was sodium naphthalide or electric current.

Interesting nitrogen fixating systems which are active in water have recently been found by Shilov and collaborators[8]. In this case the reducing agent was titanium trichloride and the catalysts were the compounds of molybdenum or vanadium. Water acts as the acid to give hydrazine as the main reaction product.

In all the above reactions nitrogen was reduced into ammonia or hydrazine. The ability of nitrogen to enter into a reaction with transition metal compounds, however, opens up the possibility of synthesizing nitrogen-containing compounds directly from molecular nitrogen. An analogy can be drawn with the reactions of carbon monoxide, olefins and acetylenes which are capable of inserting into transition metal–carbon bonds (*Table 7*). One
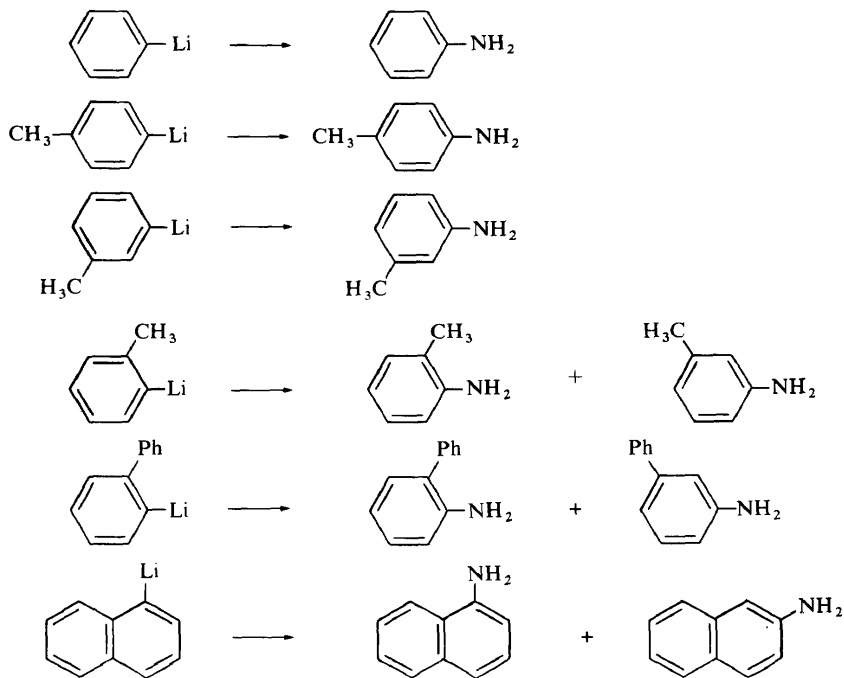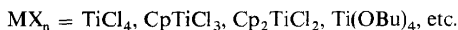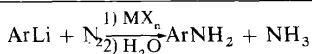
Table 7.
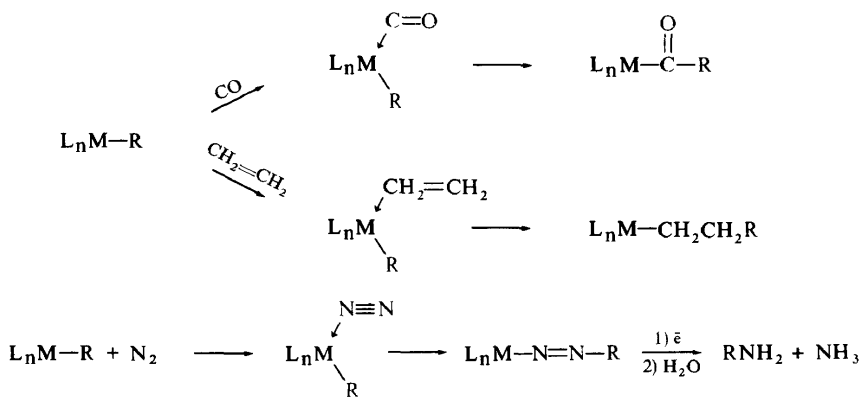
might expect that nitrogen activated by complex formation would undergo such insertion reactions to give amines after subsequent reduction and hydrolysis. Indeed, we found that organotitanium compounds containing titanium–aryl bonds react with molecular nitrogen to give amines[9]. The aromatic organolithium compounds react with nitrogen even at room temperature in the presence of halides of titanium and other transition metals. Hydrolysis of the reaction mixtures gives amines as the final products.

As can be seen from *Table 8*, the reaction of nitrogen, with phenyllithium gives aniline; with tolyllithium, the respective toluidines, and with naphthyllithium, the naphthylamines. These reactions occur only in the presence of compounds of the transition metals titanium, chromium, molybdenum, tungsten, and vanadium. The main reaction products are amines. The amino groups are in the aromatic ring positions which were previously occupied by the metal in the starting organometallic compounds. *Meta*-tolyllithium affords *meta*-toluidine and *para*-tolyllithium affords *para*-toluidine. Sterically hindered organometallic compounds with *ortho-*

Table 8.

$$ArLi + N_2 \xrightarrow[\text{2) H}_2\text{O}]{\text{1) MX}_n} ArNH_2 + NH_3$$

$MX_n = TiCl_4, CpTiCl_3, Cp_2TiCl_2, Ti(OBu)_4$, etc.

(Ref. 9)

substituents are an exception. Thus *ortho*-tolyllithium rearranges predominantly to the *meta*-isomer. The analogous rearrangements were detected with *ortho*-diphenyllithium and α-naphthyllithium.

In our opinion, the study of the reaction of nitrogen with individual organometallic compounds of transition metals should be of interest. On commencing our systematic investigations in this field we found that diphenyltitanocene reacts with nitrogen on heating (*Table 9*). Subsequent hydrolysis led to ammonia and aniline. It is natural to assume that the aniline formation is a result of nitrogen insertion into the titanium–carbon bond.

In the above reactions the amines resulted from nitrogen and organometallic compounds. However, a replacement of hydrogen (but not the metal) by nitrogen seems to be rather attractive. Such a reaction should occur in two steps: the rupture of the carbon–hydrogen bond by means of the transition metal compounds and a nitrogen insertion into the carbon–metal bond (*Table 10*).
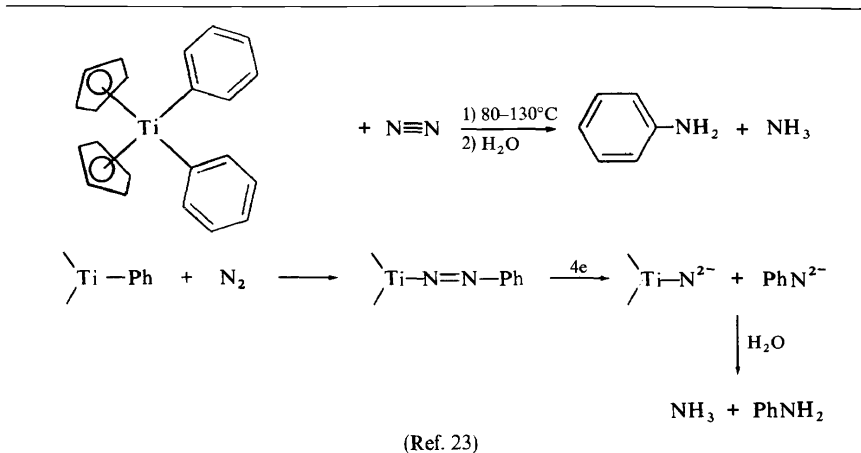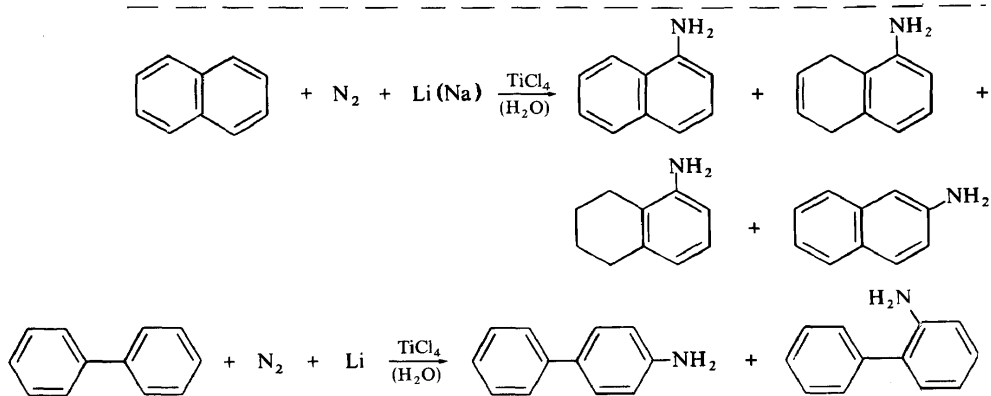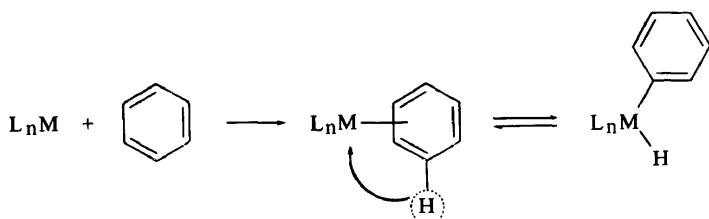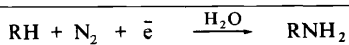
Table 9.

(Ref. 23)

Table 10.

$$RH + N_2 + \bar{e} \xrightarrow{H_2O} RNH_2$$

(Ref. 11)

To examine the possibility of realizing such processes we used the known reactions of aromatic hydrocarbons with transition metal compounds which, in some cases, lead to the σ-aryl derivatives via σ–π-rearrangements. It is known that similar systems, with participation of the aromatic anion-radicals and the compounds of titanium, readily react with nitrogen[10]. A combination of these two reactions should result in a synthesis of amines from aromatic hydrocarbons and nitrogen. We found that naphthalene reacts with nitrogen, in the presence of metallic lithium (or sodium) and titanium compounds, to give α-naphthylamine and 5,6,7,8-tetrahydro-α-naphthylamine as the main products[11]. Under the same conditions diphenyl gives *ortho-* and *para-*aminodiphenyls (*Table 10*).

The formation of amines in the reactions of molecular nitrogen with transition metal compounds leads one to examine the role of transition metals in the reverse reactions, i.e. cleavage of the organic nitrogen-containing compounds with nitrogen evolution, such as Sandmeyer's reaction, oxidation of hydrazine, etc. Thus for example, it is known that arylhydrazines are easily oxidized by transition metal salts, for example by $FeCl_3$, with nitrogen evolution. It may be assumed that this reaction proceeds in the metal coordination sphere via unstable phenyldiimide and nitrogen complexes (*Table 11*) which further decompose with nitrogen evolution. Recently the

Table 11.

$$2FeCl_3 + PhNHNH_2 \rightarrow 2FeCl_2 + N_2 + 2HCl + PhH$$

$$L_nM + ArNHNH_2 \rightarrow L_nM{\cdot}H_2NNHAr \xrightarrow{-2[H]} L_nM{\cdot}HN{=}NAr \xrightarrow{ArH}$$

$$\rightarrow L_nM{\cdot}N_2 \rightarrow L_nM + N_2$$

$$CuCl_2 + PhNHNH_2 \xrightarrow[20°C]{H_2O} (CuCl)_4{\cdot}PhN{=}NH \qquad \text{(Ref. 12)}$$

$$[Ru(NH_3)_5Cl]Cl_2 + RNHNH_2 \xrightarrow[20°C]{H_2O} [(NH_3)_5Ru{-}N{\equiv}N]Cl_2$$

$$+ [(NH_3)_5Ru{-}N{\equiv}N{-}Ru(NH_3)_5]Cl_4 + RH \qquad \text{(Ref. 24)}$$

$$R = Ph, \beta\text{-}C_{10}H_7 \text{ and } PhCH_2.$$
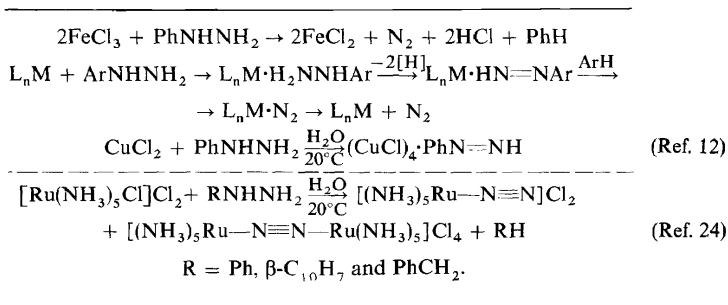
intermediate phenyldiimide complex was isolated in the reaction with copper compounds[12]. We aimed to 'trap' the intermediate nitrogen complexes in this oxidation reaction and for this purpose used the known stability of the ruthenium nitrogen complexes. Actually, the reaction of phenylhydrazine with trivalent ruthenium results in oxidation of phenylhydrazine and reduction of the ruthenium salt giving a high yield of mononuclear nitrogen complex[24]. The organic reaction products contain benzene, phenol and diphenyl. This reaction is similar to that of Allen and Senoff: oxidation of hydrazine with ruthenium trichloride to the same nitrogen complexes. Thus this reaction is the first example of nitrogen complex formation through the cleavage of the carbon–nitrogen bond.

Another organic reaction which could lead to the nitrogen complexes is the known Sandmeyer reaction (*Table 12*)—a decomposition of diazonium

Table 12.

$$Ar\overset{+}{N}\equiv NCl^- + CuCl \longrightarrow ArN\equiv N\text{---}CuCl_2 \longrightarrow$$

$$\longrightarrow \begin{bmatrix} Cl & Ar \\ & \diagdown \diagup \\ & Cu \\ & \diagup \diagdown \\ Cl & N\equiv N \end{bmatrix} \longrightarrow ArCl + N_2 + CuCl$$
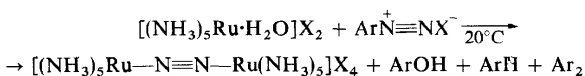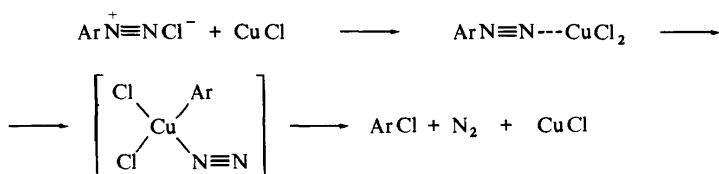
$$[(NH_3)_5Ru\cdot H_2O]X_2 + Ar\overset{+}{N}\equiv NX^- \xrightarrow{20°C}$$
$$\rightarrow [(NH_3)_5Ru\text{---}N\equiv N\text{---}Ru(NH_3)_5]X_4 + ArOH + ArH + Ar_2$$
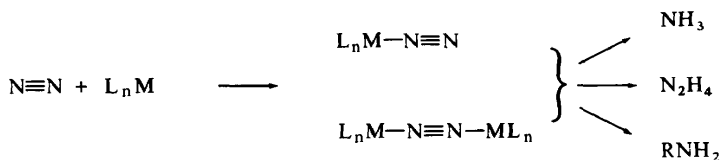$$Ar = Ph.\ p\text{--}MeOC_6H_4\ etc.$$

(Ref. 25)

salts in the presence of salts of copper and other metals. It is natural to assume that this reaction also proceeds via intermediate formation of the transition metal nitrogen complexes. However, the numerous attempts to isolate or show the presence of nitrogen complexes in these reactions were unsuccessful. In this case again a use of transition metal compounds which are able to form stable nitrogen complexes enables one to stop the reaction at the intermediate step. For example, in a decay of phenyldiazonium or other aryldiazoniums in the presence of ruthenium compounds we revealed the stable nitrogen complexes. The organic products of this reaction are typical for decomposition of aryldiazoniums.

These examples show that varying the transition metal compounds and the reaction conditions enable one to carry out the reaction in both forward and reverse directions: in the case of organotitanium compounds (and organometallic compounds of neighbouring metals in the Periodic Table), the nitrogen ligand can be inserted into the metal–carbon bond to produce the organonitrogen compounds, while with ruthenium (and other metals of Group VIII) decomposition of arylhydrazine and diazonium salts leads to nitrogen complexes.

In concluding this part of the lecture dealing with the reactions of molecular nitrogen with transition metal compounds I would like to point out once again the variety of nitrogen reactions known at the present time (*Table 13*).

Table 13.

$$N\equiv N + L_nM \longrightarrow \begin{matrix} L_nM\text{---}N\equiv N \\ \\ L_nM\text{---}N\equiv N\text{---}ML_n \end{matrix} \left. \begin{matrix} \\ \\ \\ \end{matrix} \right\} \begin{matrix} \nearrow NH_3 \\ \longrightarrow N_2H_4 \\ \searrow RNH_2 \end{matrix}$$

These reactions may give the stable nitrogen complexes or activate the

nitrogen molecule for subsequent reactions affording ammonia, hydrazine or amines.

Let us now consider the reaction of transition metal compounds with carbon dioxide. Unlike nitrogen, carbon dioxide is a rather active compound. Its reactions with organic compounds of lithium, magnesium and other non-transition metals have been studied in detail. All these reactions occur through insertion of carbon dioxide into the metal–carbon bond: the metal is bonded to the oxygen. The reactions of CO_2 with non-transition metal hydrides proceed analogously. However, until recently the reactions of carbon dioxide with transition metal compounds had not been investigated.

The first problem that we naturally considered was the possibility of the formation of complexes in carbon dioxide reactions. We found that complexes of CO_2 are sometimes produced very easily simply by bubbling carbon dioxide into a solution of the transition metal compound[13]. Such complexes of rhodium, ruthenium and platinum were isolated in their individual forms (Table 14). Recently, Simon, Speier and Marko[14] have

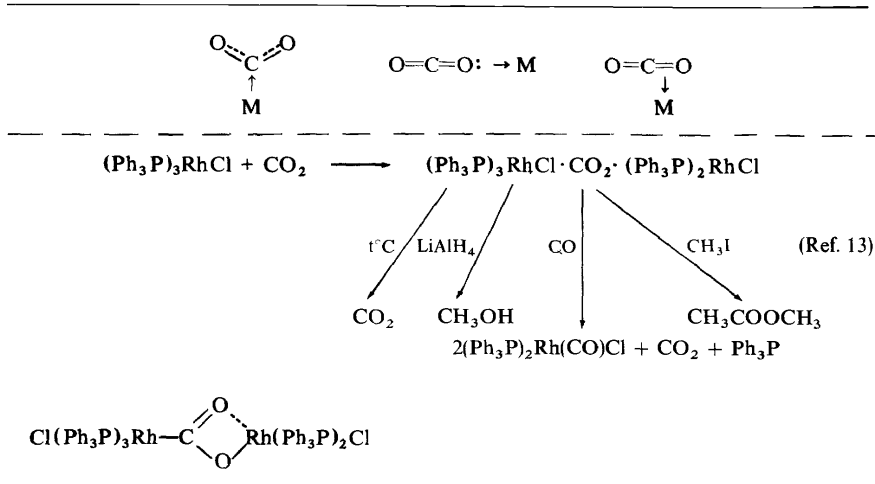Table 14. Carbon dioxide complexes.

Direct methods	
$2(Ph_3P)_3RhCl + CO_2 \rightarrow (Ph_3P)_5Rh_2 \cdot CO_2$	
$(Ph_3P)_4RuH_2 + CO_2 \rightarrow (Ph_3P)_3(MeO)RuH \cdot CO_2$	(Ref. 13)
$(Ph_3P)_3Pt + CO_2 \rightarrow [(Ph_3P)_2Pt \cdot CO_2]_n$	
$(Ph_3P)_3Co \cdot N_2 + CO_2 \rightarrow (Ph_3P)_3Co \cdot CO_2$	(Ref. 14)
Indirect methods	
$(Ph_3P)_4Rh_2(CO)_4 + O_2 \rightarrow (Ph_3P)_3(CO)_2Rh_2 \cdot CO_2$	(Ref. 15)
$(Ph_3P)_2Pt(OOCH)_2 + (Ph_3P)_4Pt \rightarrow [(Ph_3P)_2Pt \cdot CO_2]_n$	

Kolomnikov, Tshebotarjeva, Lobejeva and Vol'pin (1970).

reported a direct synthesis of the carbon dioxide–cobalt complex. Similar complexes can be obtained by an indirect synthesis. Iwashita and Hayata[15] have synthesized rhodium complexes of carbon dioxide by oxidation of the carbonyl ligand. We have prepared the platinum complex by two methods. Clearly carbon dioxide does react with transition metal compounds and replaces such ligands as triphenylphosphine, hydride hydrogen and nitrogen from the metal coordination sphere.

As can be seen from Table 15 the bond between carbon dioxide and the metal in these complexes may be formed either through the carbon atom by electron donation from the metal to a carbon orbital with formation of organometallic compounds of the metal-carboxylic acid type, or through the oxygen atom with transfer of the oxygen p-electron to the vacant orbitals of the metal, or finally by way of a π-complex formation via the C=O double bond. At present there are no x-ray or other physical or chemical data which could favour any of these or other structures. However, some information might be obtained from a study of the chemical properties of the complexes.

Table 15.

$$O{\small\cdot\cdot\cdot}C{\small\cdot\cdot}O \atop \uparrow \atop M \qquad O{=}C{=}O{:} \rightarrow M \qquad {O{=}C{=}O \atop \downarrow \atop M}$$

$(Ph_3P)_3RhCl + CO_2 \longrightarrow (Ph_3P)_3RhCl \cdot CO_2 \cdot (Ph_3P)_2RhCl$

$t^{\circ}C$ LiAlH$_4$ CO   CH$_3$I   (Ref. 13)

$CO_2 \qquad CH_3OH \qquad\qquad\qquad CH_3COOCH_3$

$2(Ph_3P)_2Rh(CO)Cl + CO_2 + Ph_3P$

$$Cl(Ph_3P)_3Rh{-}C{\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup\!\!\diagdown}}}Rh(Ph_3P)_2Cl$$

Let us discuss, for example, the properties of the rhodium complex (see *Table 15*). It was prepared by bubbling carbon dioxide into a solution of (triphenylphosphine)rhodium chloride and contains one molecule of CO_2 per two rhodium atoms. The presence of a CO_2 ligand in the molecule can be confirmed, by CO_2 evolution on heating, by the reduction with lithium aluminium hydride to give methanol, and, finally, by a quantitative CO_2 replacement under the action of carbon monoxide to afford bis(triphenyl-phosphine)rhodium carbonyl chloride. In order to reveal the presence of a metal–carbon bond the alkylation reaction was used. In the presence of a metal–oxygen bond alkylation should produce alkyl carbonates. If the CO_2 fragment is bonded to the metal via the carbon atom then alkylation might be expected to afford an alkyl carboxylic acid derivative. It was found that the action of methyl iodide on the rhodium complex leads to methyl acetate. These data give evidence in favour of a structure with the Rh—COORh fragment (shown in *Table 15*): the action of methyl iodide replaces the rhodium by a methyl group to give methyl acetate.

The respective ruthenium complex was prepared by the action of carbon dioxide on ruthenium hydride or the ruthenium nitrogen complex (*Table 16*). Both reactions lead to the same compound which contains a CO_2 molecule. The presence of a hydride hydrogen in the complex is confirmed by the reaction with carbon tetrachloride which gives chloroform and by the reaction with benzoyl chloride which leads to benzaldehyde. Carbon dioxide is evolved from the complex on heating or under the action of acids: it can be replaced by carbon monoxide or may transfer to platinum by reaction with the platinum oxocomplex to yield the known platinum carbonate. The structure of this complex is now under x-ray investigation.

Finally, the platinum CO_2 complex was prepared by two methods—by direct reaction of tris(triphenylphosphine)platinum with carbon dioxide, and by dehydrogenation of the platinum formate complex using tetrakis(tri-phenylphosphosphine)platinum (*Table 17*). The complexes obtained by

Table 16.

$(Ph_3P)_4RuH_2 + CO_2 \rightarrow (Ph_3P)_3\ RuH(CO_2) \leftarrow (Ph_3P)_3Ru(N_2)H_2 + CO_2$
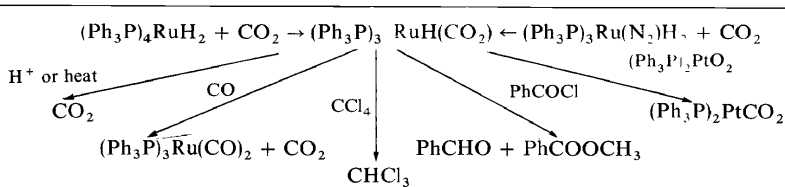
Kolomnikov, Lobejeva and Vol'pin (1971).

both the direct and indirect methods are of the same composition but differ in their spectra and chemical properties. The compounds prepared by the indirect method evolve CO_2 on heating and give methyl acetate in the reaction with methyl iodide. The chemical and physical data suggest the polymeric structure shown in *Table 17* with a metal–COO–metal fragment (analogous to the CO_2 complex of Rh).

Table 17.

$(Ph_3P)_3Pt + CO_2 \longrightarrow [(Ph_3P)_2Pt \cdot CO_2]_n$

$(Ph_3P)_2Pt(OOCH)_2 + (Ph_3P)_4Pt \longrightarrow [(Ph_3P)_2Pt \cdot CO_2]_n$

$L = Ph_3P$
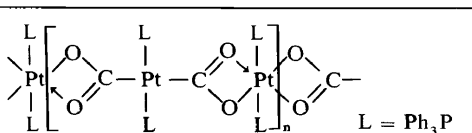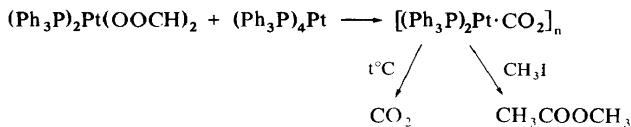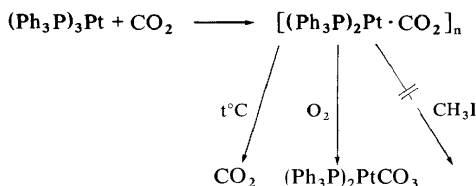
Kolomnikov, Tshebotarjeva, Lobejeva and Vol'pin (1971).

The data on the ways of formation and the properties of carbon dioxide complexes allow a search for new synthetic and catalytic reactions to be made. For example, I have mentioned that the formate of bis(triphenyl-phosphine)platinum easily converts to the carbon dioxide complex with hydride ion elimination. It may be assumed that from this viewpoint the known decomposition of formic acid to hydrogen and carbon dioxide, catalysed by transition metal compounds, may also proceed through

intermediate hydride–carbon dioxide complexes (*Table 18*). Formation of such complexes can be employed, first of all, for a catalytic reduction of olefins with formic acid. Thus, we have found that many olefins (first of all 1-alkenes) are reduced in high yield by formic acid in the presence of compounds of ruthenium, rhodium, iridium, platinum and other metals.

Table 18.

$$M + HCOOH \longrightarrow M\begin{matrix} COOH \\ H \end{matrix} \longrightarrow MH_2 \longrightarrow \overset{\bullet}{MH_2} + CO_2 \longrightarrow M + H_2 + CO_2$$

$$M{-}OCHO$$

$$MH_2 + RCH{=}CH_2 \longrightarrow M + RCH_2CH_3$$
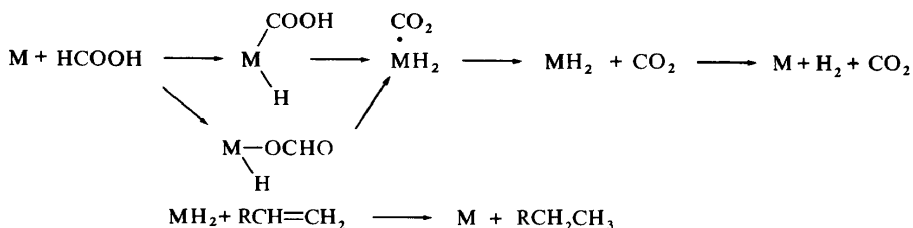
Catalytic reduction of olefins by formic acid:

$$RCH{=}CH_2 + HCOOH \xrightarrow{MX_n} RCH_2CH_3 + CO_2$$

$$MX_n = (Ph_3P)_3RuH(CO)Cl; (Ph_3P)_4RuCl_2, (Ph_3P)Rh(CO)_2Cl;$$

$$(Ph_3P_3)RhCl, (Ph_3P)_2Ir(CO)Br, cis\text{-}(Et_3P)_2PtCl_2 \text{ etc.}$$

(Ref. 26)
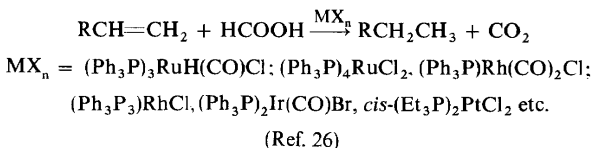
On the other hand, if a decomposition of formic acid involves an intermediate CO_2 complex of carboxylate type (e.g. with the metal–carbon bond), then in this case one would expect an occurrence of the other reaction, i.e. olefin insertion into the metal–carbon bond with subsequent elimination of the carboxylic acid (*Table 19*). Such a process should result in the addition of the formic acid fragments, H and COOH, to the olefin giving rise to a saturated carboxylic acid with the number of carbon atoms greater by one with respect to the olefin. Actually, we found (see *Table 19*) that in the presence of some transition metal compounds this reaction did take place. The olefins, 1-alkene and cyclohexene, were converted into the respective carboxylic acids in the reaction with formic acid.

An alternative direction of investigation in this field, which could be of interest, is the insertion of CO_2 itself into the metal–hydrogen and metal–carbon bonds. It is quite probable that these processes may also occur through intermediate formation of the CO_2 complexes. Such insertion reactions may follow two pathways with the formation of either the formate or the carboxylate (*Table 20*). Indeed, both processes are possible. The reaction of CO_2 with the hydride nitrogen cobalt complex and subsequent methylation yield both of the possible products: methyl formate—the product of 'normal' insertion (found by Yamamoto et al.[16] and Misono et al.[17]) and acetic acid (along with methyl acetate)—the product of 'reverse' insertion.

The insertion of CO_2 into the metal–hydrogen bond may serve as a basis for the homogeneous catalytic reduction of carbon dioxide with hydrogen

Table 19.

$$M + HCOOH \rightleftharpoons M\diagup\diagdown^{COOH}_{H} \rightleftharpoons MH_2 \xrightarrow{\overset{CO_2}{\cdot}} M + H_2 + CO_2$$

$$M\diagup\diagdown^{COOH}_{H} + RCH{=}CH_2 \longrightarrow M\diagup\diagdown^{COOH}_{CH_2CH_2R} \longrightarrow M + RCH_2CH_2COOH$$
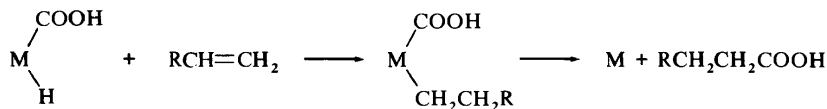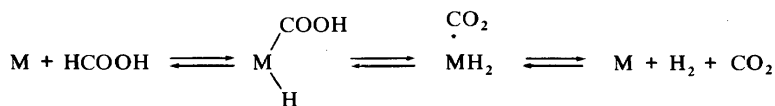
Formic acid, catalytic addition to olefins:

$$\diagup\!\!=\!\!\diagdown \quad + \quad H{-}COOH \xrightarrow{MX_n} \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown_{H \quad COOH}$$

$C_4H_9CH{=}CH_2$	$C_4H_9CH_2CH_2COOH$
$C_5H_{11}CH{=}CH_2$	$C_5H_{11}CH_2CH_2COOH$

cyclohexene $\longrightarrow$ cyclohexyl—COOH

(Ref. 27)

Table 20.

$$O{=}\overset{\delta^+}{C}{=}\overset{\delta^-}{O} + \overset{\delta^+}{M}{-}\overset{\delta^-}{H} \rightarrow M{-}O{-}\underset{\underset{O}{\|}}{C}{-}H$$

$$O{=}\overset{\delta^+}{C}{=}\overset{\delta^-}{O} + \overset{\delta^-}{M}{-}\overset{\delta^+}{H} \rightarrow M{-}\underset{\underset{O}{\|}}{C}{-}OH$$

$$(Ph_3P)_3Co(N_2)H + CO_2 \rightarrow [\geqslant Co{-}O{-}\overset{\overset{O}{\|}}{C}H] \xrightarrow{CH_3I} HCOOCH_3 \quad \text{(Refs. 16. 17)}$$

$$(Ph_3P)_3Co(N_2)H + CO_2 \rightarrow [\geqslant Co{-}COOH] \xrightarrow{CH_3I} CH_3COOH + CH_3COOCH_3$$

Stepovska. Kolomnikov and Vol'pin (1971).
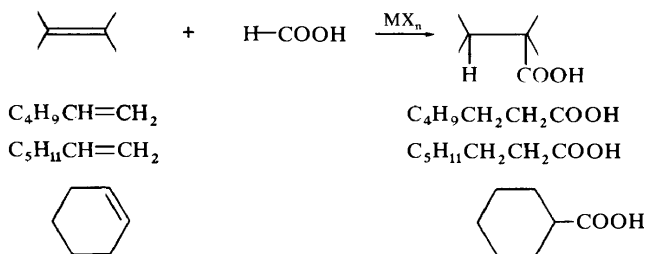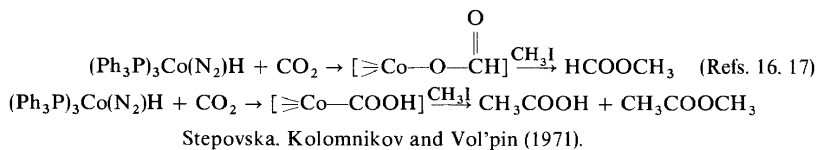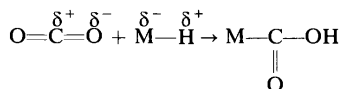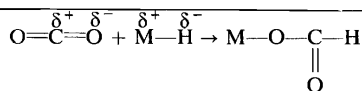
(*Table 21*). Depending upon the medium formamides[18] or formates[19] are observed. The probable pathway of the process is shown in *Table 21*. It involves a CO_2 insertion into the metal–hydrogen bond and a removal of the formate fragment with methanol followed by reduction and regeneration of the catalyst.

Table 21.

$$CO_2 + H_2 + R_2NH \xrightarrow{L_nM} HCONR_2 + H_2O \qquad \text{(Ref. 18)}$$

$$L_nM = (Ph_3P)_3RhCl, (Ph_3P)_2Ir(CO)Cl, (Ph_3P)_2PtCO_3, \text{ etc.}$$

$$CO_2 + H_2 + CH_3OH \xrightarrow[(BF_3)]{L_nM} HCOOCH_3 + H_2O \qquad \text{(Ref. 19)}$$

$$L_nM = (Ph_3P)_4RuCl_2, (Ph_3P)_3IrH_5, (Ph_3P)_3RhCl, \text{ etc.}$$

$$L_4RuCl_2 + H_2 \rightarrow L_4Ru(Cl)H \xrightarrow{CO_2} L_4Ru(Cl)\!-\!OC\!\!\underset{H}{\overset{\displaystyle O}{<}}\!\!\xrightarrow{CH_3OH} L_4Ru(Cl)OH + HCOOCH_3$$

$$L_4Ru(Cl)OH + H_2 \rightarrow L_4Ru(Cl)H + H_2O$$

The reaction of CO_2 with σ-alkyl or aryl transition metal compounds (*Table 22*) may also follow both 'normal' insertion with carbon–carbon

Table 22.

$$\underset{\text{O}}{\overset{\displaystyle O}{M\!-\!\underset{\|}{C}\!-\!OR}} \leftarrow M\!-\!R + CO_2 \rightarrow M\!-\!O\!-\!\overset{\displaystyle O}{\underset{\|}{C}}\!-\!R$$

$$(C_5H_5)_2Ti(CH_3)_2 + 2CO_2 \longrightarrow (C_5H_5)_2Ti(O\!-\!\overset{\displaystyle O}{\underset{\|}{C}}CH_3)_2$$

$$(Ph_3P)_2(CO)Co\!-\!C_2H_5 + CO_2 \underset{\diagdown}{\overset{\diagup}{}}$$

$$(Ph_3P)_2Co\!\!\left(\!O\!-\!\overset{\displaystyle O}{\underset{\|}{C}}C_2H_5\!\right)_2$$

$$(Ph_3P)(CO_3)_xCo\!-\!C\!\!\underset{OC_2H_5}{\overset{\diagup O}{\diagdown}}$$
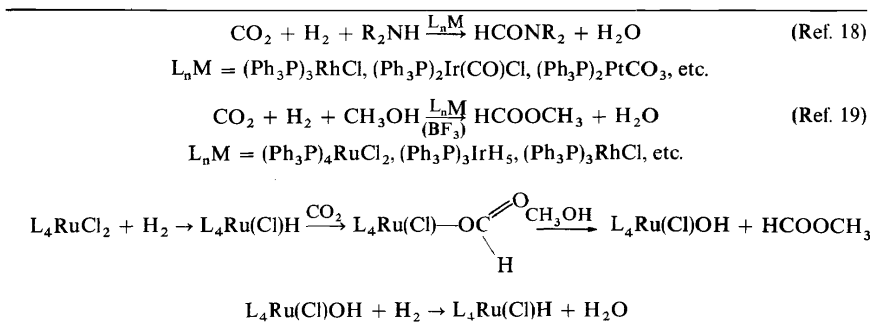
$$H^+\diagup \qquad \diagdown CH_3I$$

$$HCOOC_2H_5 \qquad CH_3COOC_2H_5$$

Stepovska, Lobejeva, Kolomnikov and Vol'pin (1971).
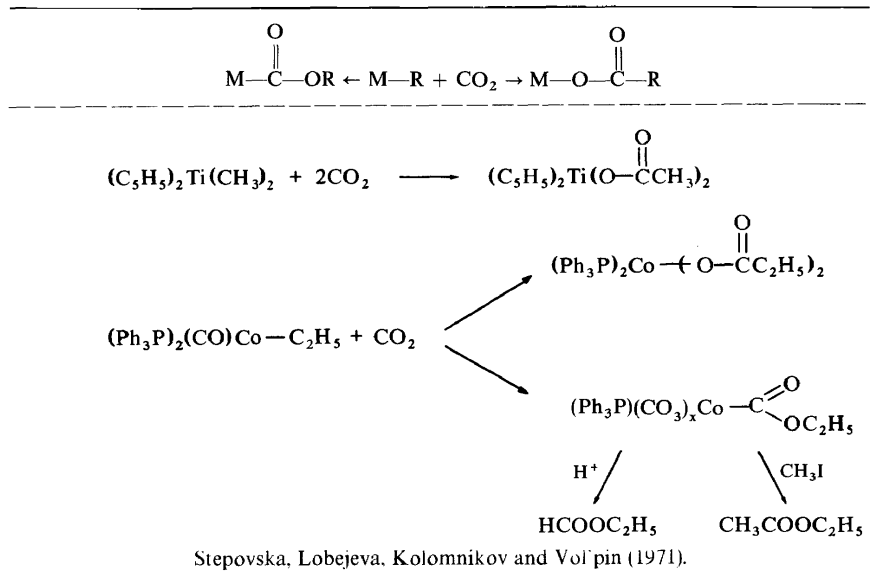
bond formation and 'reverse' insertion with formation of the ester of the metalloacid. Thus, the reaction of dimethyltitanocene with carbon dioxide results in the formation of titanocene diacetate, the product of 'normal' insertion. The reaction of carbon dioxide with the cobalt–ethyl bond follows both of the insertion pathways to give cobalt propionate and ethyl-cobalt carboxylate.

Schrauzer and Sibert[20] observed that methylcobaloxime reacted with

CO_2 with transfer of the methyl group and formation (although in low yield) of acetic acid, the product of 'normal' organometallic reaction. Such processes, i.e. the transfer of alkyl groups from cobaloximes and other planar cobalt complexes—the models of cobalamine (vitamin B_{12})—may be of importance for understanding some biological processes. However, the attempts to transfer alkyl groups from cobalt to organic substances up to now have been of little success. We found recently that transition metal compounds, primarily those of palladium, facilitate this transfer of alkyl and aryl groups from organocobaloximes and cobaloximes to olefins, with substitution of olefinic hydrogen by alkyl or aryl. As shown in *Table 23*,

Table 23.
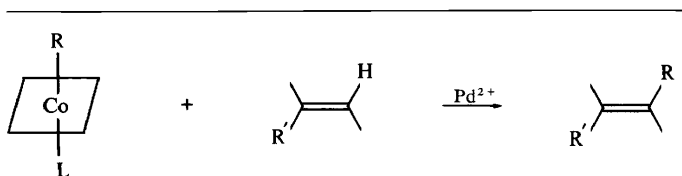
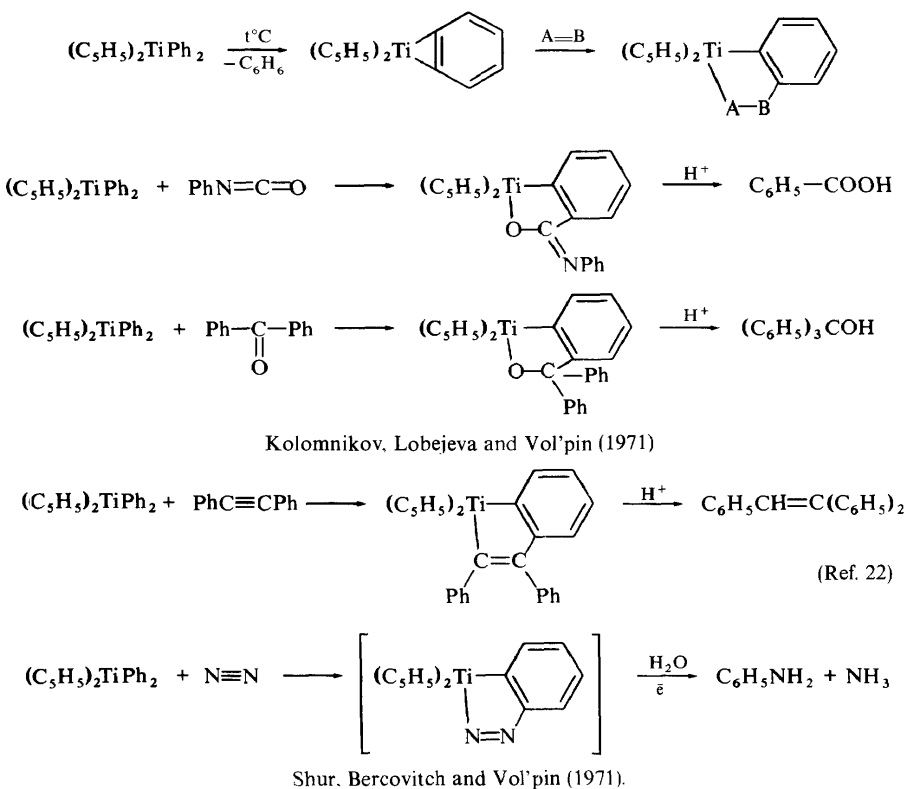Methylcobalamine, $RCo(DH)_2 \cdot L$, $RCo(salen) \cdot L$;
$L = Py, H_2O, PPh_3$

R	Olefin	Product
Methyl	Styrene	Propenylbenzene
	Hex-1-ene	Hept-2-ene
	Oct-1-ene	Non-2-ene
	Vinyl acetate	Propenyl acetate
	Methyl acrylate	Methyl crotonate
	Cyclohexene	1-Methylcyclohexene
Benzyl	Ethylene	Propenylbenzene
Phenyl	Styrene	*Trans*-stilbene

(Ref. 28)

various olefins may enter this reaction. In the case of α-alkenes the substitution proceeds at the terminal olefinic carbon. This reaction probably involves intermediate formation of the organopalladium compounds which then react with olefins by virtue of the known Heck reaction. In fact the stable organopalladium compound, allylpalladium chloride, was isolated in the reaction with allylcobaloxime.

Let us again discuss the insertion reactions of CO_2 into metal–carbon bonds. We observed an unusual insertion of CO_2 in the reaction of carbon dioxide with diphenyltitanocene (*Table 24*). Heating this compound in a stream of CO_2 leads to a stable substance which, according to its chemical properties and i.r., n.m.r. and mass spectroscopic data, has the metallocyclic structure with CO_2 bonded at the *ortho*-position of the phenyl ring. This compound reacts with hydrochloric acid to give benzoic acid and titanocene dichloride, and methylation affords methyl *ortho*-toluic acid. An x-ray study made by Struchkov and Aleksandrov confirmed the validity of this unexpected structure and enabled the geometry of this molecule to be

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Table 24.

(Ref. 29)

established. The molecule contains two cyclopentadienyl ligands with Ti—C bond distances which are practically equivalent and agree well with those found in other titanocene derivatives. The five-membered metallo-cycle containing the phenylene ring is strictly planar. It should be mentioned that the Ti—C(Ph) σ-bond in this case is significantly shorter (2.20 Å) than the Ti—C bond length in the starting diphenyltitanocene (2.32 Å).

In our opinion the formation of such a product in the reaction of diphenyl-titanocene with CO_2 can be explained in terms of an insertion of CO_2 into the Ti—C bond of the phenylene titanium complex. It has been shown recently by Dvorak *et al*[21] that the latter is an intermediate in the thermal decomposition of diphenyltitanocene.

In addition to CO_2, other molecules, A=B, with multiple bonds undergo such reactions resulting in the formation of metallocyclic compounds. *Table 25* lists the reactions of diphenyltitanocene with phenylisocyanate and benzophenone. These reactions give well-crystallized products whose structures (see *Table 25*) were confirmed by i.r., mass spectroscopy and chemical reaction.

Japanese workers[29] have also detected a cyclic product in the decomposition of diphenyltitanocene in the presence of diphenylacetylene. The formation of this product can be explained by a reaction of the phenylene complex with diphenylacetylene.

Extending this analogy it can be assumed that the reaction of diphenyl-titanocene with molecular nitrogen, mentioned in the first part of this lecture, proceeds in the same manner via a nitrogen-containing, five-membered

Table 25.

Kolomnikov, Lobejeva and Vol'pin (1971)

(Ref. 22)

Shur, Bercovitch and Vol'pin (1971).

cyclic intermediate which after reduction and hydrolysis gives aniline and ammonia.

In my lecture I wanted to point out the possibilities of using organometallic chemistry to solve such problems as the chemical fixation of nitrogen and carbon dioxide. I hope that the reactions of nitrogen and carbon dioxide will play the same important role in future organometallic chemistry as they do in living nature.

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