REACTIONS OF CARBON DIOXIDE WITH TRANSITION METAL COMPOUNDS†

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ABSTRACT

Activation via coordination is one of the most powerful and universal ways of inducing inert molecules to react. This lecture deals with the problem of carbon dioxide activation by means of transition metal compounds. The complexes formed from CO_2 in reactions with low-valent rhodium, platinum and ruthenium compounds were investigated. The CO_2 insertions into transition metal–hydrogen and –carbon bonds are discussed: they may lead not only to the 'normal' insertion products but also to metallo-acids and their esters—the products of 'reverse' pathways. The reduction of CO_2 and decomposition of formic acid open the way to some homogeneous catalytic processes.

Formation of the transition metal complex is one of the most powerful and universal ways of activating inert molecules. Coordination results in a change of reactivity of the ligands and creates favourable steric conditions for ligand interaction. This activation via coordination enables one to carry out numerous catalytic reactions under the influence of transition metal compounds.

Exceptional possibilities provided by coordination chemistry suggest catalytic processes which earlier have been only typical of living organisms.

We are not dealing with the problem of biological mechanisms, but rather with the creation of analogous purely chemical processes which effectively produce the same results as in the appropriate biochemical systems.

The two important biological processes, photosynthesis and nitrogen fixation, have long attracted the attention of chemists. We may hope that coordination chemistry, with its large number of ways for activating inert molecules, may now make a major contribution to the realization of such processes *in vitro*.

In recent years reactions of molecular nitrogen with transition metal compounds have been extensively studied. Eight years ago it was found that nitrogen may be reduced under mild conditions by the action of different transition metal compounds[1]. Seven years ago Allen and Senoff in their outstanding work obtained the first complex of molecular nitrogen—the

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† The authors of this article were unavoidably absent from the conference

dinitrogen ruthenium complex[2]. Since then a great variety of reactions of molecular nitrogen with transition metal compounds have been observed in many countries. On the one hand it was shown that nitrogen may produce complexes with compounds of different transition metals: Fe, Co, Ni, Ru, Pd, Os, Ir, Mn, Re, Mo, W and Ti. On the other hand nitrogen may be reduced in the presence of transition metal compounds affording ammonia or hydrazine after hydrolysis. These reactions may proceed at room temperature and normal pressure, and even in aqueous solution. In some cases they may occur catalytically. Nitrogen may also be introduced to the reactions with organometallic or organic compounds with formation of the nitrogen-containing organics. At the present time the chemical systems cannot compete with nitrogenase in the effectiveness of nitrogen fixation. We can hope that intensive work in this field may lead chemists to catalytic systems with comparable activity and stability.

Novel possibilities towards creating chemical processes similar to photosynthesis are disclosed by coordination chemistry. It is well known that photosynthesis is the process which includes a synthesis of organic substances from carbon dioxide and water under action of visible light.

$$CO_2 + H_2 \xrightarrow{h\nu} (CH_2O)_n + O_2$$

In spite of all the complexity of this remarkable biochemical process, schematically it may be regarded as involving two separate steps. At the first photochemical step water decomposes to oxygen and to a source of electrons—the reduced compounds, conventionally designated as the 'active hydrogen' or 'electron'.

$$2H_2O + h\nu \rightarrow 4[H] + O_2$$

or

$$2H_2O + h\nu \rightarrow 4e + O_2 + 4H^+$$

The second step—carbon dioxide fixation itself—does not need light. The CO_2 reduction and all subsequent enzymic reactions, in the cycle of carbon transformation and building the molecules of organic compounds, are the dark chemical processes promoted by the electrons produced at the first step.

$$CO_2 + 4e + 4H^+ \rightarrow (CH_2O)_n + H_2O$$

It should be noted that transition metal compounds of the enzymes and coenzymes are essential contributors to the biological fixation of CO_2. One may hope that use of transition metal coordination compounds may be helpful in realizing the purely chemical processes of reducing carbon dioxide, and its transformation to organic compounds.

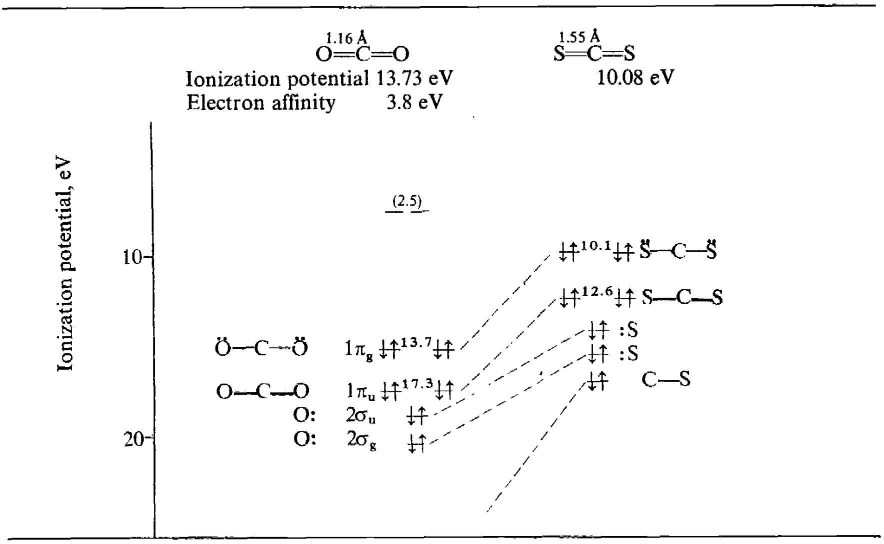
Another aspect which draws the attention of chemists towards carbon dioxide reactions is the fact that the main part of terrestrial carbon is in the form of carbon dioxide and carbonates. Actually whilst the reserves of all combustible minerals, coal, oil, etc., are estimated at about 10^{13} tons of carbon, the carbon dioxide in the atmosphere and hydrosphere contains

10^{14} tons of carbon, and carbonates contain about 10^{16} tons of carbon. Thus carbon dioxide and carbonates are the main, the cheapest and most readily available carbon sources. It is possible to suppose that carbon dioxide and the natural carbonates will replace petroleum and coal as the main sources for industrial organic synthesis of the future.

In our lecture we wanted to outline two main aspects of carbon dioxide reactions with transition metal compounds: a possibility of CO_2 complex formation and the reactions of this ligand leading to the new catalytic processes.

Carbon dioxide is a linear molecule with equivalent oxygen–carbon distances of 1.16 Å. Comparison of the energy level diagram of carbon dioxide with the isoelectronic carbon disulphide molecule shows that the highest occupied π_g and π_u orbitals of CO_2 are essentially below the corresponding species in the CS_2 molecule (*Table 1*)[3,4]. In this view the first ionization potential of CO_2 (13.7 eV) is considerably greater than that of CS_2 (10.1 eV). Thus CO_2 is the weaker donor of electrons with respect to CS_2.

Table 1.

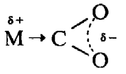


On the other hand carbon dioxide is specified by the lower energy of vacant orbital and therefore by the high electron affinity (about 3.8 eV). Thus one may expect that CO_2 in its reactions should be a comparatively poor donor and good electron acceptor. It should also be expected that upon excitation of the CO_2 molecule to the lowest excited state, or upon electron attraction, its configuration would change from a linear to non-linear one.

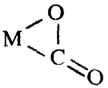
Carbon dioxide displays several alternate modes of coordination with transition metal compounds—via oxygen by donation of the oxygen lone p-electron pair to the vacant orbital of the metal (I), by electron donation from metal to the carbon orbital with formation of the metallo-acid derivative (II), or finally by way of π-complex formation via C=O double bond (III).

$M \leftarrow :O{=}C{=}O$

(I)



(II)



(III)

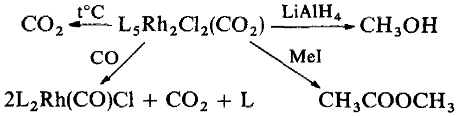
A priori on the basis of properties of the molecular orbitals of CO_2 one may expect the formation of complexes of the first type as less probable (such complexes of CO_2 may occur only for compounds with high oxidation states —strong Lewis acids). Formation of complexes of the second and third types is most favourable for transition metal compounds of the lower oxidation states.

Although the complexes of isoelectronic CS_2 have been investigated in detail (mainly by Wilkinson's school in England), study of carbon dioxide reactions with transition metal compounds started only several years ago. At first we surprisingly found that carbon dioxide may produce stable complexes replacing such ligands as triphenylphosphine. Bubbling CO_2 at room temperature into a benzene solution of tris(triphenylphosphine)rhodium chloride gives a red precipitate of the complex containing one CO_2 molecule per two rhodium atoms[5]. Its i.r. spectrum shows a characteristic band at 1630 cm^{-1}.

$$2(PPh_3)_3RhCl + CO_2 \rightarrow (PPh_3)_5Rh_2Cl_2(CO_2) + PPh_3$$

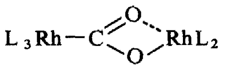
Chemical reactions of this complex manifest that it is neither a carbonate nor a formate compound but contains a coordinated CO_2 molecule. Thus carbon dioxide is evolved from the complex on heating. Upon introducing ^{18}O-labelled carbon dioxide in the reactions the newly labelled $C^{18}O_2$ is produced on heating.

CO_2 is displaced by carbon monoxide from the complex giving the known bis(triphenylphosphine)rhodium carbonyl chloride. Under the action of lithium aluminium hydride the coordinated CO_2 molecule reduces to methanol.



$L = PPh_3$

In order to reveal the presence of a metal–carbon bond the alkylation reaction was used. It was found that the reaction of the complex with methyl iodide leads to methyl acetate. All these data give evidence for the following probable structure of the complex.



This compound differs considerably in the infrared spectrum and other properties from the rhodium–CO_2 complex obtained by Ivashita and

Hayata indirectly by oxidation of the carbonyl ligand of triphenylphosphine-carbonyl rhodium complex[6]. These differences may be due to the types of CO_2 coordination in these two compounds.

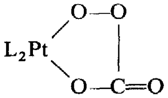
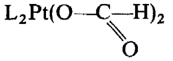
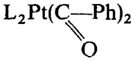
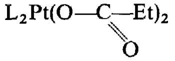
We then succeeded in preparing a platinum carbon dioxide complex by replacing the triphenylphosphine ligand from tris(triphenylphosphine)-platinum with carefully purified CO_2 under pressure and heating[7]. The reaction led to a compound containing one CO_2 molecule and two triphenylphosphine ligands per platinum atom.

$$(PPh_3)_3Pt + CO_2 \rightarrow (PPh_3)_2Pt \cdot CO_2 + PPh_3$$

The i.r. spectrum of the new complex shows three strong bands at 1640, 1370 and 1320 cm^{-1}. CO_2 is evolved on heating or acidification of the complex. Carbon dioxide may also be replaced by action of carbon disulphide to give $(PPh_3)_2Pt \cdot CS_2$ (described by Wilkinson *et al.*[8]). The oxidation of the complex by oxygen or $(PPh_3)_2PtO_2$ affords bis(triphenylphosphine)platinum carbonate. Unlike the behaviour of the rhodium complex, treatment of the platinum carbon dioxide complex with methyl iodide does not provide the CO_2 alkylation products.

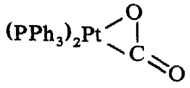
The character of CO_2 coordination in the platinum complex can also be judged from the x-ray photoelectron spectra investigated by Nefedov. As can be seen from *Table 2* the complex investigated has the 4f-electron energies of platinum different from those of the carbonate and formate complexes and close to that of the compounds with a platinum–acyl carbon bond.

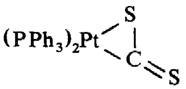
Table 2.

Energies of Pt $4f_{7/2}$-electrons (eV)			
L_2PtCO_3	73.4	$L_2Pt \cdot CO_2$	73.2
	73.4	$L_2Pt \cdot PhNCS$	73.1
 $L_2Pt(O-\underset{\substack{\| \\ O}}{C}-H)_2$	73.4	 $L_2Pt(\underset{\substack{\| \\ O}}{C}-Ph)_2$	73.1
 $L_2Pt(O-\underset{\substack{\| \\ O}}{C}-Et)_2$	73.3	$L_2Pt \cdot CS_2$	73.0
L_2PtO_2	73.3	$L_2Pt(COOEt)_2$	73.0

Energies of C 1s-electrons (eV)
CO_2 292.1, $L_2Pt \cdot CO_2$ 291.8, —COOH 289.5, CO_3^{2-} 285.7

Still more convincing data were obtained by x-ray photoelectron spectroscopic measurement of the energy of the carbon 1s-electrons. In the coordinated CO_2 molecule of the platinum complex a maximum is observed with an energy of 291.8 eV, close to that in free carbon dioxide (292.1 eV), at the same time for carbonates it is 285.7 eV and for the COOH group 289.5 eV. The data obtained indicate that the structure of this CO_2 complex is comparable to that of the platinum CS_2 complex prepared by Wilkinson *et al.*





Carbon dioxide may also give complexes by replacing not only phosphinic ligands but the dinitrogen ligand as well.

At the previous I.C.C.C. congress Simon, Speier and Marko reported that the action of CO_2 on $(PPh_3)_3Co(N_2)$ afforded a cobalt CO_2 complex which was unstable in air[9].

$$(PPh_3)_3Co \cdot N_2 + CO_2 \rightarrow (PPh_3)_3Co \cdot CO_2 + N_2$$

Quite recently the binuclear nickel complex was obtained by replacement of nitrogen with carbon dioxide[10].

$$[P(C_6H_{11})_3]_4Ni_2 \cdot N_2 + CO_2 \rightarrow [P(C_6H_{11})_3]_4Ni_2 \cdot CO_2 + N_2$$

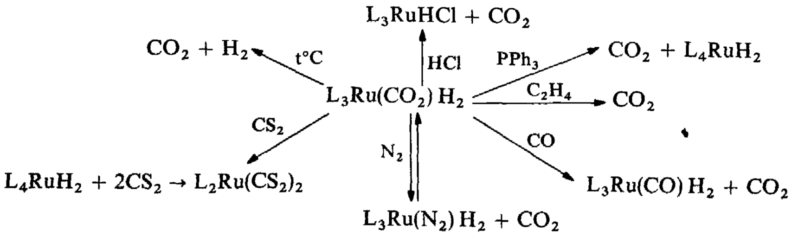
Our CO_2 reaction with the ruthenium dinitrogen complex ($L = PPh_3$) occurs analogously, via replacement of dinitrogen ligand[11].

$$L_3Ru(N_2)H_2 + CO_2 \rightarrow L_3Ru(CO_2)H_2 + N_2$$

The same compound is produced upon replacement of a triphenylphosphine ligand from the corresponding hydride.

$$L_4RuH_2 + CO_2 \xrightarrow{20°C} L_3Ru(CO_2)H_2 + L$$

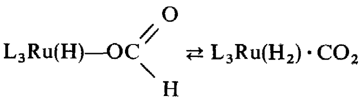
The properties of the compound obtained agree with the presence of CO_2 ligand. For example, CO_2 is evolved on heating or under the action of acids, and can be replaced in benzene solution by other ligands such as carbon monoxide and carbon disulphide, triphenylphosphine, ethylene and even nitrogen. It can be transferred to platinum by reaction with the platinum oxo-complex $(PPh_3)_2PtO_2$. The presence of a hydride hydrogen is confirmed by the reaction with carbon tetrachloride which gives chloroform and by that with benzoyl chloride leading to benzaldehyde.



However, some other properties of this compound suggest the presence of a formate fragment. Although the action of methyl iodide does not lead to methyl formate (a characteristic of formate complexes), under long treatment of the solid compound with alkali, sodium formate is produced. I.r. spectra of the complex and its deuterated analogue prepared from CO_2 and L_3RuD_4

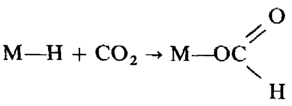
also indicate the presence of C—H (respectively C—D) of a formate fragment in the solid state.

Probably in this case interconversion of the formate and CO_2 complex easily occurs and this is responsible for the properties of this compound.



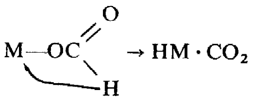
$$L_3Ru(H){-}OC(=O)H \rightleftarrows L_3Ru(H_2) \cdot CO_2$$

Thus here we are dealing firstly with CO_2 insertion to the metal–hydrogen bond



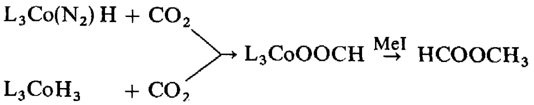
$$M{-}H + CO_2 \rightarrow M{-}OC(=O)H$$

and secondly with fission of the C—H bond of the formate via hydride hydrogen elimination.



$$M{-}OC(=O)H \rightarrow HM \cdot CO_2$$

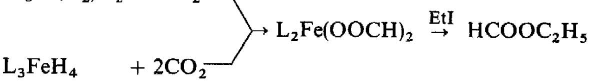
The first CO_2 insertion giving formates was observed by Misono *et al.*[12] and Yamamoto *et al.*[13] for the reaction of CO_2 with cobalt dinitrogen hydride complexes ($L = PPh_3$).



$$L_3Co(N_2)H + CO_2 \rightarrow L_3CoOOCH \xrightarrow{MeI} HCOOCH_3$$

$$L_3CoH_3 + CO_2 \rightarrow L_3CoOOCH$$

Recently Italian authors have carried out a similar reaction for the corresponding iron compounds ($L = PEtPh_2$)[14].



$$L_3Fe(N_2)H_2 + 2CO_2 \rightarrow L_2Fe(OOCH)_2 \xrightarrow{EtI} HCOOC_2H_5$$

$$L_3FeH_4 + 2CO_2 \rightarrow L_2Fe(OOCH)_2$$

We observed a reaction of the same type for hydride complexes of osmium, iridium and platinum[16].

Such carbon dioxide insertion reactions into the transition metal–hydrogen bond disclose possibilities for developing different catalytic processes and first of all, homogeneous hydrogenation of carbon dioxide in the presence of complex catalysts.

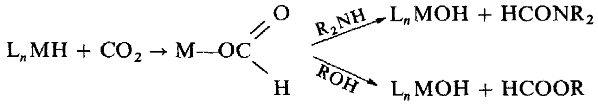
The reaction, $CO_2 + H_2 \rightarrow HCOOH$, at ordinary temperatures and pressures is thermodynamically disadvantageous. In order to shift this process to the right, one should bind the formate fragment, for example, by its transformation to amide or ester. Actually, phosphine complexes of the Group VIII metals are catalysts for reduction of CO_2 with hydrogen, in the presence of secondary amines, to dialkyl formamides[15]:

$$CO_2 + H_2 + R_2NH \xrightarrow{\text{cat.}} HCONR_2 + H_2O$$

and in the presence of alcohols with formation of alkylformates[16].

$$CO_2 + H_2 + ROH \xrightarrow{\text{cat.}} HCOOR + H_2O$$

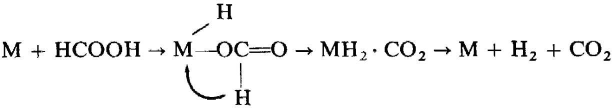
One mechanism assumed for these reactions involves an insertion of CO_2 along the metal–hydrogen bond and a removal of the formate fragment with amine or alcohol, followed by reduction and regeneration of the catalyst.



$$L_nMH + CO_2 \rightarrow M\!-\!OC\begin{matrix}\nearrow O\\ \searrow H\end{matrix} \begin{matrix}\xrightarrow{R_2NH} L_nMOH + HCONR_2\\ \xrightarrow{ROH} L_nMOH + HCOOR\end{matrix}$$

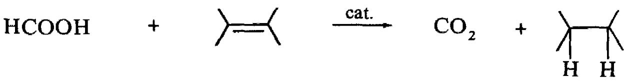
$$L_nMOH + H_2 \rightarrow L_nMH + H_2O$$

Another way towards creating the catalytic processes is to use the reverse reaction of formic acid decay in the presence of transition metal complexes. The data suggest that this reaction occurs through C—H fission, transfer of the hydride hydrogen to the metal, and intermediate formation of the carbon dioxide–hydride complex.

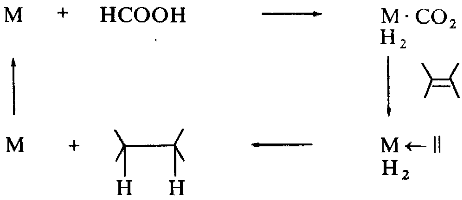


$$M + HCOOH \rightarrow \overset{H}{M}\!-\!\underset{H}{OC}{=}O \rightarrow MH_2 \cdot CO_2 \rightarrow M + H_2 + CO_2$$

The assumed intermediate formation of the hydride complex was employed by us for developing the catalytic process of hydrogen transfer from formic acid and formates to olefins[17].



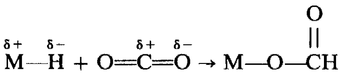
Thus, in the presence of catalytic quantities of $(PPh_3)_3Ru(H)Cl$ in dimethylformamide, formic acid even at room temperature rapidly and selectively reduces 1-alkenes to alkanes, but does not react with 2-alkenes. This catalyst decomposes formic acid to H_2 and CO_2, but it should be noted that under the same conditions molecular hydrogen does not hydrogenate olefins. This fact, as well as the kinetic data, lead to the following mechanism for this process.



A large number of other ruthenium, rhodium, iridium and platinum complexes are also effective catalysts for olefin reduction by formic acid and formates.

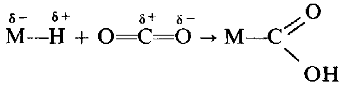
Up to this point we have discussed CO_2 insertion into the metal–hydrogen bond to give a formate fragment and a decomposition of this fragment to CO_2 and metal hydride. This reaction course, however, is not the only one. Depending upon the polarity of the metal–hydrogen bond, a reverse insertion giving a metallo-carboxylic acid fragment is possible.

Normal



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

Abnormal



$$\overset{\delta-}{M}-\overset{\delta+}{H} + O{=}\overset{\delta+}{C}{=}\overset{\delta-}{O} \rightarrow M-C\begin{matrix}{\nearrow}O \\ {\searrow}OH\end{matrix}$$

Actually, in the reaction of the hydride dinitrogen cobalt complex with carbon dioxide the metallo-carboxylic acid fragment forms along the formate: treatment with methyl iodide provides considerable quantities of acetic acid and its methyl ester[18].

$$(PPh_3)_3Co(N_2)H + CO_2 \rightarrow L_nCo{-}COOH \xrightarrow{MeI} CH_3COOH$$

Analogous formation of the metallo-carboxylic acid was also observed in the cleavage of the C—H bond in formic acid[19]. Along with catalysis of formic acid decay the reactions of formic acid with the low-valent transition metal complexes afford three types of products.

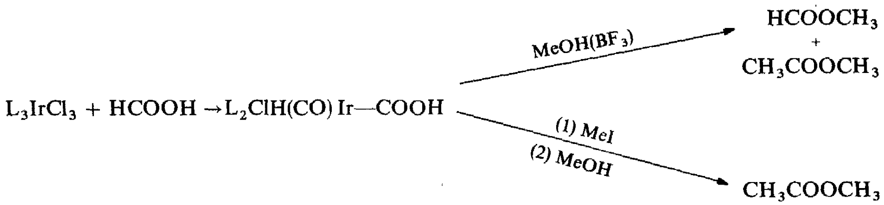
In reactions of phosphinic complexes of palladium, platinum, ruthenium and osmium we obtained formates, e.g.

$$(PPh_3)_4Pt + 2HCOOH \rightarrow (PPh_3)_2Pt(OOCH)_2$$
$$(PPh_3)_4Pd + 2HCOOH \rightarrow (PPh_3)_2Pd(OOCH)_2$$

In other cases, for example, with some ruthenium complexes, formic acid is easily decarbonylated.

$$(PPh_3)_3RuCl_2 + HCOOH \rightarrow (PPh_3)_2Ru(CO)_2Cl_2$$

However, in reactions of formic acid with the iridium complexes, $(Et_2PhP)_3IrCl_3$ and $(Me_2PhP)_3IrCl_3$, metallo-carboxylic acids were formed (study of their structure is under way)[19].



$$\mathrm{L_3IrCl_3 + HCOOH \rightarrow L_2ClH(CO)Ir{-}COOH}\begin{cases}\xrightarrow{\mathrm{MeOH(BF_3)}} \mathrm{HCOOCH_3 + CH_3COOCH_3}\\ \xrightarrow[\mathrm{(2)\ MeOH}]{\mathrm{(1)\ MeI}} \mathrm{CH_3COOCH_3}\end{cases}$$

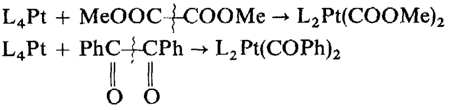
The metallo-carboxylic acid fragment was identified on the basis of i.r. spectra; its presence was also confirmed chemically. Treatment of this compound with boron trifluoride in methanol solution leads to methyl formate and methyl acetate, while the action of methyl iodide gives methyl acetate (after esterification with methanol).

Analogous fission of the C—H bond producing the metal–carbon bond was also observed in reactions of formic acid esters[20].

$$\mathrm{M + H \nmid COOR \rightarrow M{-}COOR\ or\ M(H){-}COOR}$$

Formation of metallo-carboxylic acid esters in reactions with ethyl formate was observed for such complexes as $(PPh_3)_3RuCl_2$, $(PPh_3)_3Ru(H)Cl$, $(PPh_3)_4Pd$, etc.

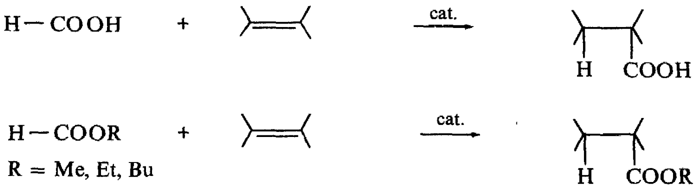
Finally we observed the formation of analogous fragments with metal–carbon bonds in the rather interesting reaction of C—C bond cleavage under the action of low-valent complexes ($L = PPh_3$)[21].



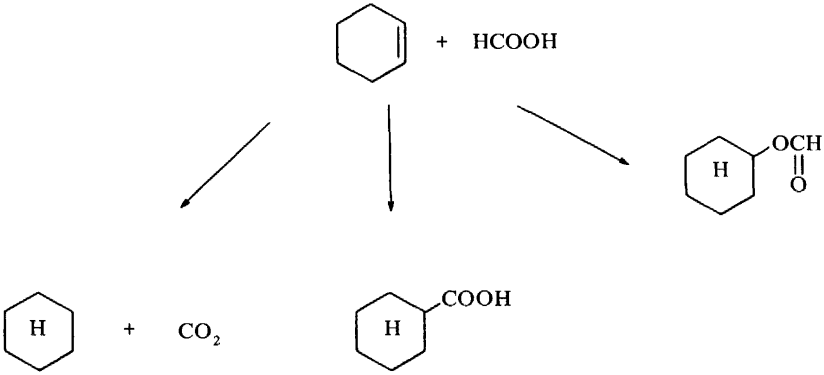
$$\mathrm{L_4Pt + MeOOC \nmid COOMe \rightarrow L_2Pt(COOMe)_2}$$
$$\mathrm{L_4Pt + Ph\underset{\underset{O}{\|}}{C} \nmid \underset{\underset{O}{\|}}{C}Ph \rightarrow L_2Pt(COPh)_2}$$

Similarly we observed the C—C bond cleavage in dimethyl oxalate in reactions with L_3IrCl_3, L_3IrHCl_2, L_3RuCl_2 and other compounds.

The reactions of C—H bond cleavage in formic acid and formates, leading to metallo-carboxylic acids and esters, can also be employed in developing new catalytic processes in which this carboxylate group is transferred to an olefin. It is shown that formic acid and alkyl formates may add to olefins to give carboxylic acids[22, 23].



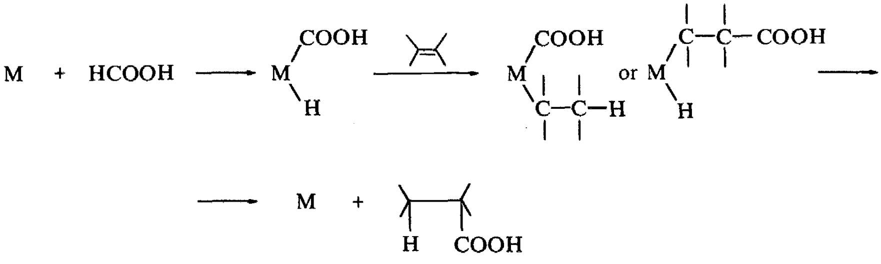
The yields of alkyl carboxylic acids generated do not exceed 10 per cent. This is probably due to the fact that simultaneously there occur several competitive reactions. Thus the reaction of formic acid with cyclohexene involves hydrogenation of cyclohexene, addition of formic acid with O—H bond cleavage and formation of cyclohexyl formate, and finally C—H bond fission and formation of cyclohexane carboxylic acid.



Reaction of cyclohexene with alkyl formate gives ethyl cyclohexane carboxylate along with cyclohexene dimer and other products. In spite of this fact, however, this formate addition to olefins is really catalytic and the yield of cyclohexane carboxylic acid and its esters attains 50 mole per mole of the catalyst (*Table* 3). Obviously this reaction may be regarded as C—H bond cleavage by transition metal with subsequent olefin insertion into the metal–hydrogen or metal–carbon bond.

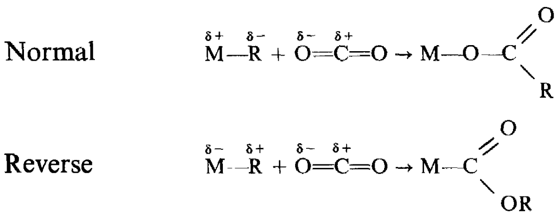
Table 3. Reaction of cyclohexene with formic acid (100°C) or ethyl formate (140–180°C)

Catalyst ($L = PPh_3$)	Yield of $C_6H_{11}COOH$		Yield of $C_6H_{11}COOEt$	
	%	moles per mole of catalyst	%	moles per mole of catalyst
L_3RhCl	7	39	2.3	5.3
$(Ph_2PH)_3RhCl$	7.3	42	2.7	6.0
$L_2Rh(CO)Cl$			0.3	0.8
$LRh(CO)_2Cl$			1.5	3.3
L_3IrH_3			0.1	0.2
$L_2Ir(CO)Cl$	8.7	32	0.6	1.2
$L_3Os(CO)HCl$			0.3	0.6
H_2PtCl_6	7	18	0	0

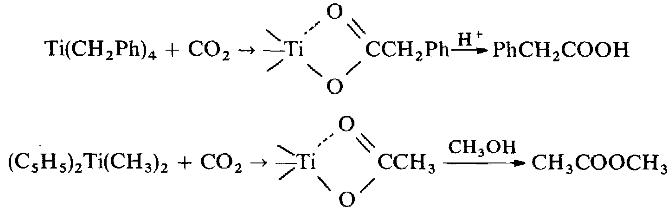


This may be confirmed by the fact that an authentic metallo-carboxylic acid ester prepared from the rhodium complex indeed reacts under analogous conditions with cyclohexene, producing cyclohexane carboxylic ester.

Interesting possibilities are also provided in the study of reactions of carbon dioxide not only with the metal–hydrogen bond but also with the metal–carbon bond. In this case the reaction may follow both the 'normal' path for the organometallic compounds, giving alkyl carboxylic acid, and the 'reverse' path with formation of metallo-acid ester.

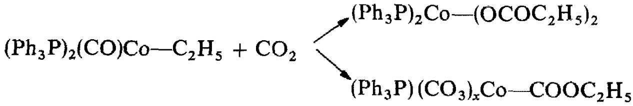


Examples of 'normal' reactions with a carbanion transfer to the CO_2 carbon were envisaged for some titanium and zirconium compounds[24,25].



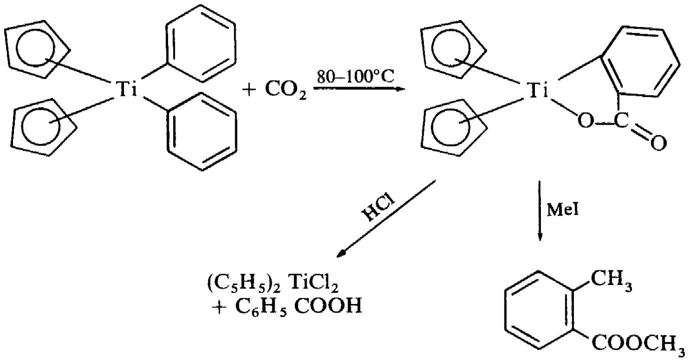
Schrauzer and Sibert have observed interesting methyl group transfer to CO_2 from methylcobaloxime in the presence of thiols[26].

An example of the 'reverse' reaction was observed by us upon CO_2 insertion into the cobalt–alkyl bond in the cobalt phosphine complexes[18].

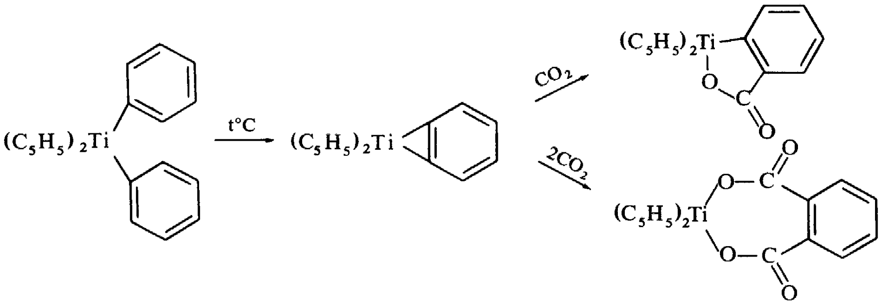


Two products were formed. The first was the product of 'normal' insertion, which under the action of methyl iodide affords methyl propionate. The second, the 'reverse' insertion product, gives ethyl acetate under similar treatment.

The result was rather unexpected when we studied CO_2 insertion into the titanium–phenyl bond in diphenyltitanocene[27]. The reaction of carbon dioxide with diphenyltitanocene at 80°C and atmospheric pressure leads to a stable complex in which CO_2 is inserted to give the five-membered cycle.

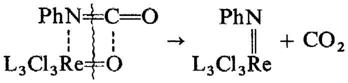


The structure of this compound was confirmed by different chemical reactions, mass spectra, n.m.r. and i.r. spectra and finally by x-ray analysis. Formation of such an unexpected product can be explained in terms of the hypothesis, proposed by Dvorak, O'Brien and Santo[33], that diphenyltitanocene decomposes via an intermediate formation of phenylene complex. Besides an insertion product involving one CO_2 molecule we also isolated the *ortho*-phthalic acid derivative—insertion product of two CO_2 molecules.



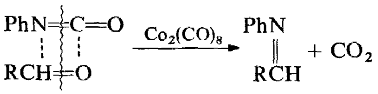
We now come to reactions of carbon dioxide which lead to still more complex organic molecules. In this view we would like shortly to outline the reverse reaction—CO_2 elimination from different compounds under the action of transition metal complexes. These reactions may occur via CO_2 complex intermediacy and receive wide application. It would be sufficient to indicate a catalytic role of transition metal compounds in decarboxylation of carboxylic acids, oxy- and ketoacids. This can be considered as a reaction reverse to CO_2 insertion into the metal–carbon bond. However, most interesting are reactions in which CO_2 is produced upon fragmentation of two different molecules. Several recent examples can be cited here.

Thus rhenium oxo-complexes react with phenylisocyanate with CO_2 evolution and formation of rhenium imido-complexes[28] prepared previously by Chatt and Rowe[29].



This reaction may be regarded as some dismutation—an exchange of O and NPh moieties with CO_2 elimination.

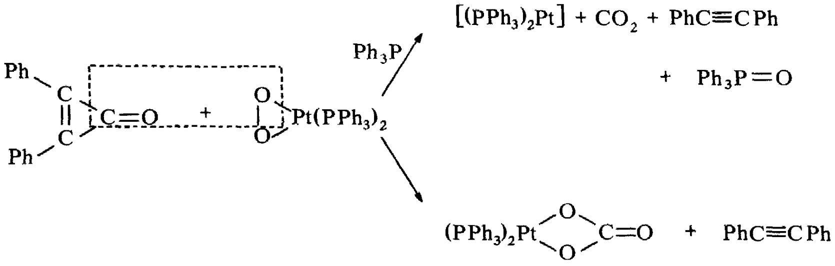
Very recently Drapier, Hubert and Teyssie described an interesting catalytic process of aldehyde transformation to phenylimides with CO_2 evolution[30].



$$PhN{=}C{=}O + RCH{=}O \xrightarrow{Co_2(CO)_8} PhN{=}CHR + CO_2$$

Here the catalysts are transition metal carbonyls, dicobalt octacarbonyl being the best.

Analogously one may consider the reaction of the platinum oxo-complex with diphenylcyclopropenone[31].



The reaction proceeds at room temperature with elimination of CO_2 and diphenylacetylene. With an excess of triphenylphosphine, formation of triphenylphosphinoxide and CO_2 is observed while in the absence of triphenylphosphine the platinum carbonate complex is generated.

So far we have discussed reactions of combination and formation of carbon dioxide under abiogenic conditions, i.e. in organic solvents, mostly at elevated temperatures, leading to products which are not natural.

We have also investigated other processes, e.g. CO_2 reactions with transition metal compounds in aqueous solution. We found that at room temperature and atmospheric pressure carbon dioxide reacts with different low-valent transition metal compounds giving organic substances: glycolic acid, malic acid, etc[32].

The formation of glycolic acid can be illustrated by the following scheme of reductive dimerization of carbon dioxide.

$$\begin{aligned}&2CO_2 + 2V^{2+} \rightarrow [2V^{3+}\text{—}COO^- \xleftarrow{H^+} 2V^{3+}\text{—}COOH \rightleftarrows\\ &\rightleftarrows 2V^{3+} + 2\dot{C}OOH] \rightarrow HOOC\text{—}COOH\\ &HOOC\text{—}COOH + 2V^{2+} \rightarrow HOCH_2COOH + 2V^{3+} + H_2O\end{aligned}$$

We hope that a combination of such carbon dioxide reactions with an electron source—electric current, photocells or reducing agents—may lead in the future to catalytic processes which could serve as specific functional models of photosynthesis.

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