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The Interaction of Carbon Dioxide with Transition Metal Complexes

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The reactions of transition metal compounds involving the formation of CO_2 complexes, reactions with insertion of CO_2 in transition metal-hydrogen and transition metal-carbon bonds, and homogeneous catalytic processes in which carbon dioxide behaves as a reactant or a modifying ligand are considered. A special section is devoted to reversible reactions accompanied by elimination of carbon dioxide under the influence of transition metal compounds.
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I. INTRODUCTION

During the last five years there has been a considerable growth of interest in the reactions of carbon dioxide with transition metal compounds, primarily owing to the considerable advances made recently in the field of metal complex catalysis and in the first place in the activation of inert molecules (hydrogen, nitrogen, etc.) which leads to the expectation that catalytic processes involving carbon dioxide will also be carried out successfully. On the other hand, the CO_2 molecule may participate in catalytic processes also as a ligand capable of modifying the activity, selectivity, and specificity of catalysts. Evidently these two problems are most closely related to the synthesis and investigation of the transition metal complexes of carbon dioxide.

One may also note that the study of reactions involving systems based on transition metals is of considerable interest in view of the role that carbon dioxide plays in nature. Thus one may expect interesting results also when processes of this kind are simulated.

It has been believed for a long time that carbon dioxide reacts with transition metal compounds only in a "trivial" manner with formation of carbonates. However, recently many reactions have been discovered in which CO_2 behaves as a ligand or reacts to form new metal-C, C-H, or C-C bonds. This review is devoted to these new aspects of the carbon dioxide reactions.

II. PRINCIPAL PHYSICAL PROPERTIES AND STRUCTURE OF CARBON DIOXIDE

The carbon dioxide molecule is a linear triatomic molecule in which the carbon atom forms two equivalent bonds with oxygen atoms (of the σ and π types). According to spectroscopic data, the C=O bond length in the CO_2 molecule is 1.1615 Å,[1] which agrees with data obtained by electron diffraction[2].

There are fairly considerable discrepancies between calculated estimates of the heteropolarities of carbon dioxide: 75%[3,4], 10%[5,6], and virtually zero[7]. There are experimental literature data showing that the molecule has a permanent dipole moment (0.06×10^{-18} e.s.u.)[8], but, according to a later investigation[9], $\mu = 0$.

In the ground $^1\Sigma_g^+$ state ($D_{\infty h}$ symmetry group) sixteen electrons of the carbonyl molecule are distributed among the orbitals in the following manner: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2 \cdot (2\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$, where the least strongly bound π_g electrons are those of the lone electron pairs of the oxygen atom. Fig. 1 presents the energy level diagram for the CO_2 molecule; the energies of the atomic levels were taken from Siegbahn[10] and the experimental data (or, if these were lacking, calculated data) were taken from the review of Rabalais et al.[11] (Table 1). The data in Table 1 demonstrate a fairly good agreement between theory and experiment.

Table 1. Comparison of experimental and calculated lowest ionisation potentials (eV) of CO_2, CS_2, COS, allene, and keten.

Molecule	Experimental data (Refs.1,12-17)	MWH method (Ref.11)	Extended Hückel method (Ref.18)	CNDO method (Ref.19)	Hartree-Fock method (Ref.19)
O=C=O	13.78	14.05	17.20	14.55	14.84
	17.32	14.93	17.51	14.55	19.45
	18.08	17.68	18.14	16.83	2 .23
	19.40	18.06	19.56	21.01	21.77
O=C=S	11.20	12.55	13.14	12.26	—
	15.08	13.67	14.67	13.84	—
	16.04	15.90	17.76	15.36	—
	17.96	16.50	18.40	19.32	—
S=C=S	10.09	11.33	12.24	11.33	—
	12.69	12.61	13.48	12.59	—
	14.47	14.44	14.18	13.28	—
	16.19	15.32	15.72	18.23	—
$H_2C=C=CH_2$	10.19	11.66	—	—	—
$H_2C=C=O$	9.60	11.49	—	—	—

Comparison of the energy level diagrams for the CO_2 molecule and the isoelectronic CS_2 and COS molecules (Fig. 2) shows that the highest occupied orbitals of the CO_2 molecule (π_g and π_u) lie appreciably below the corresponding CS_2 and COS orbitals[15].

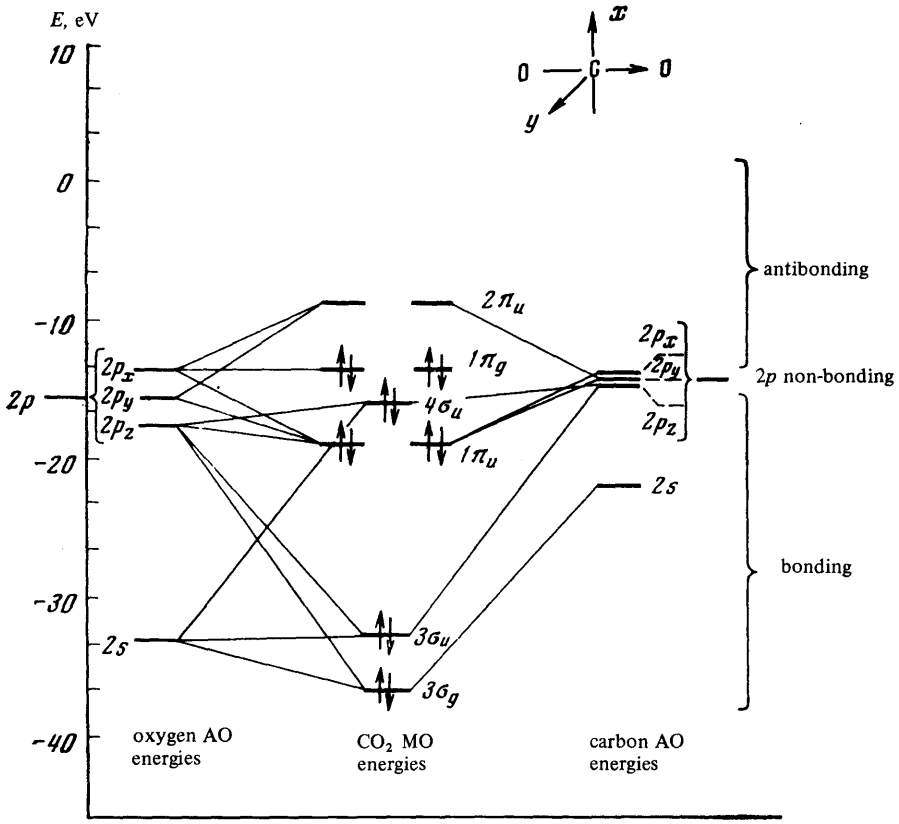


Figure 1. Molecular orbital diagram for the CO_2 molecule.

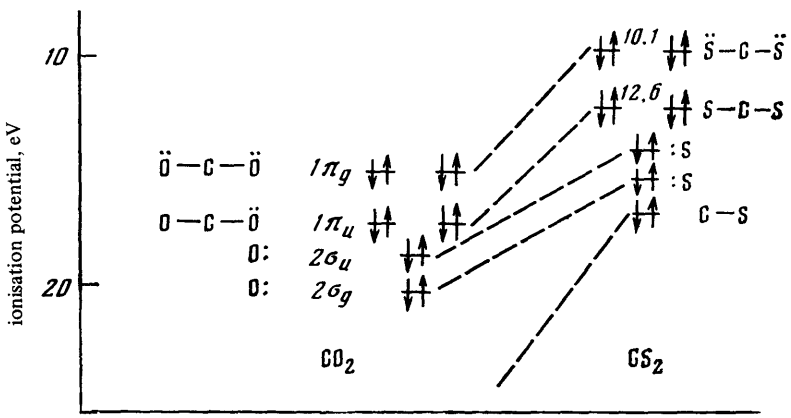


Figure 2. Electronic energy level diagram for CO_2 and CS_2 molecules according to photoelectron spectroscopic data.

Accordingly the ionisation potential of carbon dioxide (13.7 eV) is much higher than those of CS_2 (10.1 eV) and COS (11.2 eV). Thus the CO_2 molecule is a weaker electron donor than CS_2 or COS.

On the other hand, carbon dioxide has a low-lying $2\pi_u$ antibonding orbital, the position of which determines the electron affinity of the molecule [2.9 eV (Johnson and Albrecht[20]) or according to other (calculated) data ~ 3.8 eV (Buchel'nikova[21])]. These results appear to be rather too high. According to Berdnikov's calculated data[22], the electron affinity of CO_2 is ~ 0.5 eV, which agrees fairly well with experimental data[23,24].

The CO_2^+ species has been discussed[25-31] as a 15-electron species retaining its linearity in both the ground and excited states. The removal of one electron from the $1\pi_g$ orbital lengthens the C–O bond from 1.1615 Å ($^1\Sigma_g^+$) to

1.177 Å ($^2\pi_g$) or 1.229 Å ($^2\pi_u$) [30] (Table 2). However, there are data showing that the anomalies in the infrared spectrum of CO_2^+ may be due to the bending of the excited molecule, the angle (168° ± 3°) corresponding to the distance $r(CO)$ = 1.1830 ± 0.0004 Å.[32] The formation of the CO_2^{2+} ion has been observed by Newton and Sciamanna[33].

Table 2.

Molecule	Electronic state	Energy, eV	Bond length, Å	ν_1(symm.)	ν_2	ν_3(asymm.)
CO_2^+	$^2\Pi_u$	18.08	1.229	1131	560	1895
CO_2^+	$^2\Pi_g$	13.78	1.177	1280	632	2305
CO_2	$^1\Sigma_g^+$	0	1.163	1361	673	2379

The CO_2^- radical-ion, i.e. a species with a 17-electron configuration, has been obtained[34], in contrast to the extremely unstable CO_2^+ state, in a free form in a matrix on irradiation of sodium formate with high-energy γ-rays. Calculation of the valence angle by Coulson's method yielded 134°. According to the results of other workers[35, 36], the angle is 127 ± 8°. It is of interest that the O–C–O angle in sodium formate is 121.7° according to X-ray diffraction data[37].

It is noteworthy that Mulliken[4,38] and Walsh[39] predicted theoretically the possibility of the bending of the molecule on transition from the 16-electron linear configuration to the 17-electron configuration (i.e. from the $D\infty h$ symmetry group to the C_{2v} symmetry group) (see also the review of Rabalais et al.[11]).

According to ESR data, the free electron in CO_2^- is localised at the carbon atom[20,36]. When the carbon atom is replaced by the ^{13}C isotope, the infrared band corresponding to the asymmetric vibrations of the carboxy-group shifts from 1671 cm^{-1} to 1626 cm^{-1} [36] (see also other data[20,40]).

The formation of the CO_2^- radical-ion has been postulated in a number of chemical and physicochemical studies: in the decomposition of oxalates in the presence of transition metals[41–43,44,45], in the electrochemical reduction of the CO_2 molecule[44,45], in electron transfer from a metallic surface on irradiation[46], in the reduction of carbon dioxide by amides[47] and alkali metal and alkaline earth metal amalgams[48–51], and in other reactions[52–56].

The most important physical properties of carbon dioxide are presented below:

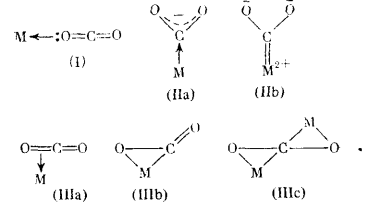
M.p. (5 atm)	−56.7°C
B.p. (sublimation at 1 atm)	−78.515°C
Density (at 0° and 1 atm)	1.9768 g $litre^{-1}$
Critical temperature	+31.3°C
Critical pressure	75.2 atm
Pressure corresponding to transition to liquid state (20°C)	58.46 atm
Heat of fusion (at 56.6°C)	2.24 kcal $mole^{-1}$
Standard free energy of formation	ΔF° = 94.260 kcal $mole^{-1}$
Standard entropy of formation	ΔS° = 51.011 cal $mole^{-1}$ K^{-1}
Standard heat of formation	ΔH°_{298} = −94.08 kcal $mole^{-1}$
Temperature dependence of molar heat capacity (in the range 0–1400°C)	$C_p = 0.00326t + 0.00000079t^2 + 8.84$

III. TRANSITION METAL COMPLEXES OF CARBON DIOXIDE

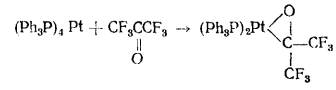
General consideration of the electron-donating and electron-accepting properties of carbon dioxide shows that there are several possibilities for the formation of complexes by CO_2 with transition metals. Complexes of the donor–acceptor type may be formed as a result of the transfer of the lone electron pair of the oxygen atom ($1\pi_g$ electrons) to the corresponding orbital of the metal atom (type I). In this case the transition metal plays the role of a Lewis acid. Interaction of this type is hindered by the comparatively high positive charge on the metal atom, the presence of low-lying vacant orbitals in the metal, and the presence of a free coordination site in the complex.

Another possibility may obtain as a result of the dative interaction involving the transfer of two electrons from the metal atom to the antibonding $2\pi_u$ orbital of carbon dioxide. In this case the CO_2 molecule is exhibiting electrophilic properties and a state of type IIa obtains. The transfer of two electrons from the metal atom to the antibonding orbitals of CO_2 may lead in the limiting case to the formation of a type IIb carbenoid complex. Clearly a low positive charge on the metal atom and the presence of electron-donating ligand in the complex will favour the formation of complexes of this type.

Finally the $1\pi_u$ orbital of the CO_2 molecule may interact with the corresponding vacant orbital of the metal with simultaneous transfer of the metal σ electrons to the vacant orbital of the CO_2 molecule which leads to the formation of a π-complex of type IIIa (or to the formation of a three-membered ring of type IIIb in the limiting case). Since the CO_2 molecule has two double bonds, an interesting possibility may arise when two metallic centres form a complex of type IIIb with a single carbon dioxide molecule:



It is remarkable that, when acetaldehyde acts on the ruthenium complex $(Ph_3P)_3RuCl_2$, a corresponding compound is formed in which the acyl group is coordinated to the metal atom by a π-type bond according to the authors[58]. When phosphine complexes of transition metals are acted upon by perfluoroacetone, adducts are also formed in which the carbonyl group is coordinated to the metal via both carbon and oxygen atoms, for example[59]:

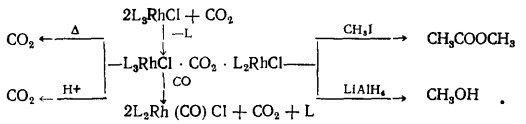


The above structures naturally do not exhaust the entire wide variety of the possible types of complexes, particularly polynuclear complexes (complexes of this kind involve a combination of different types of complex formation reactions).

Since carbon dioxide is a less effective electron donor and a more effective electron acceptor than the isoelectronic CS_2 molecule, presumably complexes of type I are less typical for CO_2 and structures of type II and III are more typical (see the relevant reviews[60–64]. A fairly

large number of CS_2 complexes are known[65,66], but the number of complexes with carbon dioxide which have been described is small.

The formation of complexes with carbon dioxide was observed for the first time for rhodium compounds[67]. Rhodium complexes of CO_2 are at present the most thoroughly investigated and we shall therefore begin our consideration of the available complexes by discussing the rhodium compounds. When carbon dioxide was allowed to interact with the complex L_3RhCl (where L = Ph_3P), a fairly stable adduct was obtained whose composition is $L_5Rh_2Cl_2.CO_2$ according to its chemical properties, the results of elemental analysis[67] and its infrared spectrum has an absorption band in the region of 1630 cm^{-1}. Chemical reactions also confirm the presence of coordinated carbon dioxide in the complex:



Carbon dioxide is evolved when the complex is acidified and pyrolysed. The formation of labelled carbon dioxide was demonstrated mass-spectrometrically in the thermal decomposition of the adduct formed in a $C^{18}O_2$ atmosphere[67]. Carbon dioxide is readily displaced from the complex by carbon monoxide.

It is interesting to note that the rhodium complex of carbon dioxide $L_5Rh_2(CO)_2(CO_2).C_6H_6$, obtained by an indirect procedure[68] (by oxidising the carbonyl group attached to the metal with oxygen), also has an asymmetric dinuclear structure according to molecular weight measurements. An interesting property of this complex is its ability to exchange the oxygen in a coordinated CO_2 molecule for dissolved molecular oxygen.

When the complex $[(Ph_3P)_2Rh(CO)]_2$ reacted with gaseous carbon dioxide at atmospheric pressure at room temperature in benzene, an asymmetric complex $(Ph_3P)_3Rh_2(CO)_2.(CO_2)_2.C_6H_6$ was again obtained[69,70]:

$$2\,[(Ph_3P)\,Rh\,(CO)_2] \xrightarrow{2Ph_3P} 2\,[(Ph_3P)_2Rh\,(CO)] \xrightarrow[-Ph_3P]{2CO_2} \rightarrow (Ph_3P)_3Rh_2\,(CO)_2\,(CO_2)_2 \cdot C_6H_6$$

This complex is fairly stable and hardly loses carbon dioxide on exposure to air for several days. Carbon dioxide is evolved completely on pyrolysis and on treatment with acids or carbon monoxide. In the latter case the product is the complex $[(Ph_3P)Rh(CO)_2]_2$, i.e. the reaction is reversible also at atmospheric pressure:

$$2\,[(Ph_3P)Rh\,(CO)_2] \underset{2CO(-2CO_2;\ 2Ph_3P)}{\overset{+2Ph_3P,\ 2CO_2(-2CO)}{\rightleftharpoons}} (Ph_3P)_3Rh_2\,(CO)_2\,(CO_2)_2$$

When the carbon dioxide is acted upon by oxygen, the familiar complex $(Ph_3P)_3Rh_2(CO)_2.CO_2$ is formed[68].

The infrared spectrum of the rhodium complex $(Ph_3P)_3.Rh_2(CO)_2(CO_2)_2$ contains, apart from the triphenylphosphine bands, two intense absorption bands in the region of 1600 cm^{-1} [ν(OCO)(asymm).] and 1355 cm^{-1} [ν(OCO)(symm.)] as well as a moderately intense band at 825 cm^{-1} [δ(OCO)]. When CO_2 in this complex is partly replaced by $^{13}CO_2$, the bands are split (Fig. 3). It is striking that the difference $\Delta = \nu$(OCO)(assym.) − ν(OCO)(symm.) amounts to 245 cm^{-1} for this complex, while Δ = 130 cm^{-1} for the complex $L_3Rh_2(CO)_2.CO_2$ [ν(OCO)(asymm.) = 1498 cm^{-1}, ν(OCO)(symm.) = 1368, and δ(OCO) = 813 cm^{-1}]. This shows that in the rhodium complex with two CO_2 molecules there is an incomplete charge transfer from the metal atom to carbon dioxide, unlike the complex $L_3Rh_2(CO)_2.CO_2$ (cf. these data with those quoted by Peri[71]). The carbon dioxide in the $L_2Rh_2(CO)_2(CO_2)_2$ molecule is therefore retained less strongly, which is confirmed by chemical reactions. When olefins or oxygen are allowed to react with the complex $L_3Rh_2(CO)_2(CO_2)_2$, one carbon dioxide molecule is readily displaced with formation of the complex $L_3Rh_2(CO)_2.CO_2$.

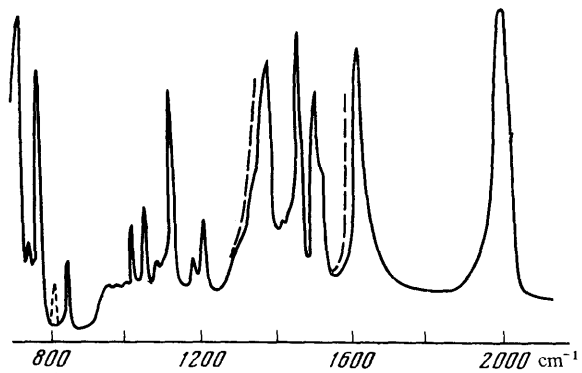
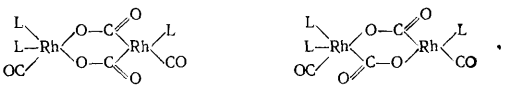


Figure 3. Infrared spectrum of the rhodium–carbon dioxide complex $(Ph_3P)_3Rh_2(CO)_2(CO_2)_2$ (the spectrum of the complex with $^{13}CO_2$ is indicated by dashed lines).

The complex $L_3Rh_2(CO)_2(CO_2)_2.C_6H_6$ is in all probability dinuclear, the two rhodium atoms being linked via two bent carbon dioxide molecules:



The appearance of three absorption bands in the spectrum of the coordinated carbon dioxide molecule instead of the two bands (2350 and 667 cm^{-1}) bands characteristic of the linear molecule (see Table 3) is associated with the bending of the CO_2 molecule on coordination.

Table 3. Vibration frequencies of the CO_2 molecule (cm^{-1}).

Molecule	State	ν_1	ν_2	ν_3	References
$^{12}CO_2$	gaseous	1343	667	2349	72
	solid (−190°C)	—	660	2344	73, 74
	aqueous solution	—	—	2342	75, 76
$^{13}CO_2$	gaseous	—	(649)	2284	75, 76
	solid (−190°C)	—	637	2280	73, 74
$^{14}CO_2$	gaseous	—	632	2226	75, 76

There are at present no X-ray diffraction data for carbon dioxide complexes of transition metals, but it is well known that the formation of complexes by carbon disulphide or allenes, which have linear molecules in the ground state, leads to the formation of compounds in which

these molecules are bent. Thus it has been established by X-ray diffraction that the carbon disulphide molecule in the complexes $(Ph_3P)_2Pt.CS_2$ [77,78] and $(Ph_2P)_2Pd.CS_2$ [79] is bent (Fig. 4).

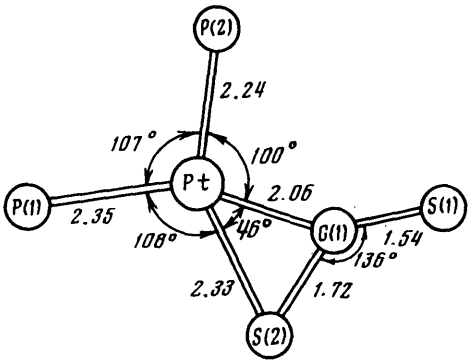
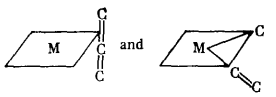


Figure 4. The structure of the platinum–carbon disulphide complex.

On the other hand, there are literature data showing that complexes of two types may be obtained with allene:



Thus in platinum, iron, and rhodium complexes [80–82] tetramethylallene is joined to the metal atom by a π-type linkage, while in the platinum complex $Pt(C_3H_4)(PPh_3)_2$ allene has a bent configuration [83].

Apart from the absorption bands of physically adsorbed CO_2, the infrared spectra of chemisorbed carbon dioxide [71,84–99] contain other bands which the authors believe [71,84–93] correspond to CO_2^- vibrations, the bands associated with the antisymmetric vibrations of the carboxy-group being located in the range 1570–1630 cm^{-1}, depending on the nature of the adsorbent, and those due to the symmetrical vibrations lying in the range 1320–1380 cm^{-1}.

The complexes $L_3Rh_2(CO)_2(CO_2).C_6H_6$ (2.83 μ_B) and $L_3Rh_2(CO)_2(CO_2)_2.C_6H_6$ (3.87 μ_B) proved to be paramagnetic [100] and their magnetic moments at room temperature (calculated per rhodium atom) are close to the spin-only value for two and three unpaired electrons respectively. It was shown in the same study that the anomalous paramagnetism of these complexes cannot be interpreted vigorously in terms of a model of the antiferromagnetic pair exchange in magnetically dilute dinuclear molecules.

The dimeric complex $(L_3RhH)_2.CO_2$, which Komiza and Yamomoto [101] obtained by passing carbon dioxide for a long time through a solution of the rhodium hydride $(Ph_3P)_4RhH$ in toluene, as well as the complex $L_5Rh_2Cl_2.CO_2$ [67] proved to be diamagnetic. The intense absorption band at 1460 cm^{-1} in the infrared spectrum of the resulting complex was attributed by the authors to the antisymmetric stretching vibrations of the OCO group, while the 1300 cm^{-1} band in the Raman spectrum was attributed to the symmetrical stretching vibrations of the same group. Carbon dioxide is evolved quantitatively from the complex on pyrolysis (at temperatures up to 200° C) and on acidification with sulphuric acid. On treatment with methyl iodide, carbon dioxide and methane are evolved.

The preparation of the complex $(Ph_3P)_3Co.CO_2$ in the form of a yellow compound inactive in air on treatment of $(Ph_3P)_3Co.N_2$ with carbon dioxide has been described [102]. When it is subjected to thermal decomposition or treated with sulphuric acid, the complex evolves CO_2. Its infrared spectrum has an absorption band in the region of 1890 cm^{-1}. The attempt [103] to obtain the analogous complex by treating the ethylene complex of cobalt $(Ph_2P)_3Co.(C_2H_4)$ with carbon dioxide at atmospheric or elevated pressure was unsuccessful.

The synthesis of the dinuclear nickel complex of carbon dioxide $\{[(C_6H_{11})_3P]_2Ni\}_2.CO_2$ by treating the corresponding nitrogenyl nickel complex with carbon dioxide has also been described [104]. The authors suggest that the metal atoms in this compound are coordinated via double bonds to the CO_2 molecule, which retains a linear structure:



An attempt has been made to obtain a platinum complex of carbon dioxide [105–107]. However, it was found that, when the complexes $(Ph_3P)_4Pt$ and $(Ph_3P)_3Pt$ react with CO_2 at an ordinary temperature and pressures up to 40 atm in the presence of traces of oxygen, carbonate complexes are formed (for further details, see below), while carefully purified carbon dioxide does not form stable products with platinum under these conditions, but the complex $(Ph_3P)_2Pt.CO_3$ is formed readily [108,109]. When the complex $(Ph_3P)_3Pt$ was treated with carefully purified carbon dioxide under pressure (40 atm) and a temperature in excess of 100° C, it was possible to obtain [61] a small yield of the compound $(Ph_3P)_2Pt.CO_2$, the infrared spectrum of which contains three intense absorption bands at 1640, 1370, and 1320 cm^{-1}. When the complex is pyrolysed, carbon dioxide is evolved.

Table 4. The energies of the $4f_{7/2}$ electrons of platinum (L = Ph_3P).

Compound	*E*, eV	Compound	*E*, eV
L_2PtCO_3	73.4	$L_2PtPhNCS$	73.1
L_2PtOCO_3	73.4	$L_2Pt(COPh)_2$	73.1
$L_2Pt(OOCH)_2$	73.4	L_2PtCS_2	73.0
$L_2Pt(OOCCH_3)_2$	73.7	$L_2Pt(COOMe)_2$	73.0
$L_2Pt(OOCEt)_2$	73.3	$L_2PtC_2H_4$	73.4
$L_2PtO_2\cdot(CH_3)_2CO$	73.3	$L_2Pt(PhC{\equiv}CPh)$	72.1
$L_2Pt\cdot O_2$	73.3	L_4Pt	71.7
L_2PtCO_2	73.2	Pt	71.3

A study of a series of platinum complexes with different types of ligand coordination (coordination to oxygen and carbon and coordination of the π-ligand type) by X-ray electron spectroscopy showed that the ability of the ligand to withdraw electrons from the metal atom decreases in the sequence (Table 4) [61]:

$$O_2 > CO_2 > CS_2 \sim PhNCS > COR > C_2H_4 > RC{\equiv}CR$$

The increase of the energy of the $4f_{7/2}$ electrons in the platinum complex of carbon dioxide relative to L_2PtCS_2 can be accounted for by the greater electronegativity of oxygen compared with sulphur.

Complexes of carbon dioxide and Group I metals (copper and silver) have also been obtained recently. When the complex $(Ph_3P)_2CuCH_3.CO_2$ is acted upon by carbon dioxide, the product is $(Ph_3P)_2CuOOCCH_3.CO_2$.[110] This complex is diamagnetic and evolves carbon dioxide on pyrolysis (above 200°C) and when treated with concentrated sulphuric acid. After the loss of carbon dioxide, the frequencies corresponding to the vibrations of the carboxylate group remain in the infrared spectrum, while the bands at 2620 (weak), 1600 (very strong), 1302 (very strong), 821 (moderately strong), and 648 (very weak) cm^{-1} disappear. On this basis, the authors[110] attribute the latter bands to the vibrations of coordinated carbon dioxide.

An interesting adduct was obtained when carbon dioxide was passed through a solution of copper complexes of ephedrine and its derivatives[111]. The authors investigated the ultraviolet spectra (λ = 250–260 nm) of these chelates in methanol solution and the visible spectra in benzene (Table 5). The study of the ultraviolet spectra showed that 1 : 1 adducts with carbon dioxide are formed in these solutions.

Table 5. Absorption spectra of copper(II) chelates in the visible region in benzene at 20°C.

Ligand in Cu^{II} chelate	λ^*_{max}, μm	ϵ^*, litre mole^{-1} cm^{-1}	λ^{**}_{max}, μm	ϵ^{**}, litre mole^{-1} cm^{-1}
(–)-Ephedrine	514	155	700	74
ψ-Ephedrine	500	121	700	82
N-Ethylnorephedrine	518	98	690	48
N-n-Butylnorephedrine	525	60***	660	41***

* $[Cu^{2+}]$ = 0.005 M.
** In the presence of CO_2.
*** Approximate value, because the chelate cannot be prepared in a crystalline form.

The thermodynamic functions for the complex-formation reaction between carbon dioxide and the complex Cu(ephedrine)$_2$ were determined[112] by gas–liquid chromatography (GLC): $\Delta G_{308} = -2.29 \pm 0.07$ kcal mole^{-1}, $\Delta H_{298-323} = 4.2 \pm 0.3$ kcal mole^{-1}; $\Delta S_{308} = -6.4 \pm 1.2$ kcal mole^{-1} K^{-1}.

It is of interest that silver compounds also readily form stable complexes with carbon dioxide under mild conditions. Thus, when carbon dioxide is passed through a saturated solution of PhAg–$AgNO_3$ in ethanol at 0°C, a precipitate having the composition $C_7H_5O_2Ag_2$ is deposited[113]; its thermal decomposition results in the evolution of carbon dioxide. The infrared spectrum of this compound contains intense absorption bands in the region of 1496, 1326, and 828 cm^{-1} and moderately intense bands at 325, 290, and 280 cm^{-1}. The authors[113] concluded that a polymeric silver compound containing carbon dioxide is formed in this instance: $(C_6H_5AgCO_2Ag)_n$. An analogous complex was synthesised also from the corresponding *para*-substituted phenyl derivatives of silver.

Thus it is evident that a fairly large group of transition metals is capable of forming complexes with carbon dioxide. There is no doubt that the study of the complex formation reactions between carbon dioxide and transition metals constitutes an important branch of the chemistry of carbon dioxide and that the number of studies in this important field will increase in the immediate future and the problem of the structure of these compounds will be elucidated.

The problem of the isolation of fairly stable complexes with carbon dioxide was discussed above. However, in many cases the immediate formation of unstable CO_2 complexes in the course of various reactions has been postulated. There are literature data indicating the possibility of the formation of CO_2 complexes by the rupture of C–H bonds in transition metal formate complexes. On refluxing in benzene or on pyrolysis, the platinum formate complex $(Ph_3P)_2Pt(OOCH)_2$ decomposes into carbon monoxide and hydrogen[113]. On the other hand, when the solution contains the complex $(Ph_3P)_4Pt$, in which a C–H bond can be readily ruptured, the platinum formate complex decomposes with evolution of carbon dioxide[114], which has been attributed to the intermediate formation of a complex with CO_2, readily losing carbon dioxide via the mechanism

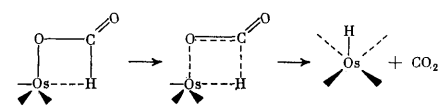
$$\rangle PtOOCH + Pt \rightarrow PtOOCPt{-}H \rightarrow CO_2 + \left\{\rangle Pt{-}PtH\right\} .$$

The intermediate formation of an unstable complex with carbon dioxide as a result of the intramolecular dissociation of the C–H bond in the formate group in all probability occurs in the reactions of ruthenium formate complexes[61,115]:

$$(Ph_3P)_3Ru(H)OOCH \rightleftarrows (Ph_3P)_3Ru(CO_2)H_2 .$$

The formation of the ruthenium complex of carbon dioxide in one of the stages has been postulated for the reduction of unsaturated hydrocarbons with formic acid in the presence of the complex $(Ph_3P)_3Ru(H)Cl$ [116] and also for the decomposition of HCOOH in the presence of iridium complexes[117].

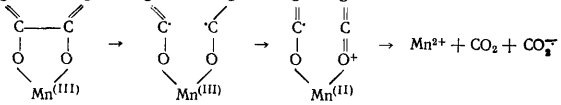
A complex with carbon dioxide is probably formed on thermal decomposition of osmium formate[118]:



When the cobalt formate complex $[Co^{III}(NH_3)_5OOCH]^{2+}$ is oxidised with manganese salts[119], the intermediate radical is fairly stable and reacts with another manganese species via the mechanism

$$[Co^{(III)}(NH_3)_5OOCH]^{2+} \xrightarrow{[MnO_4]^-;\ H^+} [Co(NH_3)_5OCO\cdot]^{2+} + HMnO_4$$
$$\downarrow$$
$$[Co^{III}(NH_3)_5OH_2]^{3+} + CO_2 + [MnO_4]^- .$$

According to the results of other workers[120–123], the decomposition of oxalate in the presence of manganese salts also proceeds via the intermediate formation of a manganese complex of carbon dioxide:



$$CO_2^- + Cl^\cdot \rightarrow CO_2 + Cl^- .$$

(See also other investigations[124–127].)

In all probability analogous unstable complexes with carbon dioxide are formed in the decomposition of oxalic acid catalysed by copper[128,129], silver[130], mercury[131], and uranium[132] salts.

The intermediate formation of a cobalt complex of carbon dioxide was postulated[133] in a study of the mechanism of the oxidation of the $[Co^I(CN)_2(PEt_3)_2(CO)]^-$ complex with

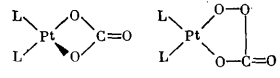
hexacyanoferrate(II) ions $Fe(CN)_6^{3-}$. Kinetic data confirm the occurrence of the equilibrium

$$[Co^{(I)}(CN)_2(PEt_3)_2(CO)]^- + 2Fe(CN)_6^{3-} + H_2O \rightarrow$$
$$\rightarrow \left[(NC)_5Fe^{(II)}CNCo^{(III)}(CN)_2(PEt_3)_2\left(C\begin{matrix}O\\OH\end{matrix}\right)\right]^{4-} + Fe(CN)_6^{4-} + H^+ +$$
$$+ (NC)_5Fe^{(II)}CNCo^{(III)}(CN)_2(PEt_3)_2(CO_2)^{5-}$$

in solution. The authors[133] suggest that this mechanism operates also in the oxidation of carbon monoxide with oxygen catalysed by aquocobalamines[134-138].

IV. TRANSITION METAL CARBONATE COMPLEXES

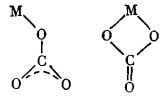
It is noteworthy that the widespread occurrence of the formation of transition metal carbonate complexes and their ability to evolve CO_2 on acidification of pyrolysis greatly hinder the identification of transition metal complexes of carbon dioxide or altogether prevent the formation of such complexes. As stated above, platinum and palladium complexes of the type $(Ph_3P)_4M$ (M = Pt or Pd) readily form carbonate complexes[105-109]. The possibility of the formation of a platinum carbonate complex on treatment of complexes of the type $(Ph_3P)_4Pt$ with carbon dioxide in the presence of traces of oxygen greatly depends on the nature of the coordinated ligand. Thus the carbonate complex is formed comparatively readily in the presence of the triphenylphosphine ligand, in the presence of the $(p\text{-tolyl})_3P$ ligand the yield of the corresponding complex is low, and in the presence of the $(p\text{-chlorophenyl})_3P$ ligand the complex is not formed at all. Carbonate complexes are formed when the complex $(Ph_3P)_2PtO_2$ reacts with carbon dioxide:



A platinum carbonate complex can be readily obtained when the complex *cis*-$(Ph_3P)_2PtCl_2$ is treated with Ag_2CO_3,[105] or when carbon monoxide is oxidised with oxygen coordinated to platinum[107]. Wilkinson and coworkers[107] made the following frequency assignments (cm^{-1}) in the infrared spectra of the compounds obtained:

Compound	ν(CO)	ν(C–O)(asymm.)	ν(C–O)(symm.)	ν_{III}(symm.)	ν(O–O)	ν(M–O)	ν(M–P)
L_2PtCO_3	1685 (s)	1185	980	815	—	363	409
L_2PtOCO_3	1678 (s)	1243	978	836	780	305	429

One may note that in general carbonates can behave as a monodentate [as in compounds (IV)] or bidentate [as in compounds (V)] ligand[139]:



(IV) (V)

Nakamoto and coworkers[139] made a careful study of the infrared spectra of cobalt carbonate complexes and found that the C–O stretching vibrations in the monodentate carbonates give rise to absorption in the ranges 1360–1380 and 1450–1500 cm^{-1}, while the corresponding vibrations in the bidentate carbonates give rise to bands in the ranges 1260–1290 and 1590–1640 cm^{-1}, i.e. on the basis of infrared spectra it is virtually impossible to distinguish a transition metal complex of CO_2 from the carbonate complex. The structures of the carbonate and bicarbonate complexes have been discussed extensively[71,84-92] in connection with the study of the infrared spectra of chemisorbed carbon dioxide on metal oxides.

Like the ionic compound $CaCO_3$, where all the C–O bonds are equivalent, the platinum complex $(Ph_3P)_2PtCO_3$ has the structure[140] of a distorted square, also with equal C–O bond lengths.

The structure of the platinum peroxocarbonate complex[141] is probably analogous to that of the adduct $(Ph_3P)_2.PtO_2.$acetone. The oxygen in this complex is extremely reactive and readily oxidises triphenylphosphine with formation of a carbonate complex:

$$(Ph_3P)_2PtOCO_3 \xrightarrow{Ph_3P} (Ph_3P)_2PtCO_3 + Ph_3PO \quad .$$

There are also data demonstrating the ready formation of carbonate complexes when cobalt[103] and ruthenium[62] complexes react with carbon dioxide in the presence of traces of oxygen. In his attempt to obtain a molybdenum complex of carbon dioxide, Chatt synthesised a carbonate complex[142]. Carbonate complexes are readily formed also when an attempt is made to obtain a transition metal complex of carbon dioxide by an indirect method involving the oxidation of the carbon monoxide coordinated to the metal with molecular oxygen. An osmium carbonate complex has been obtained[143] by oxidising carbon monoxide with molecular oxygen:

$$(Ph_3P)_2OsCl(CO)NO \xrightarrow{O_2} (Ph_3P)_2OsCl(CO_3)NO \quad .$$

In discussing the mechanism of the formation of CO_2 when carbon monoxide and rhodium are oxidised with molecular oxygen, the authors[144] assume the formation of the unstable octahedral carbonate complex $[Rh^{III}(CO_3)(CO).Cl_3]^{2-}$, which readily gives off CO_2 in an acid medium.

The oxygen in a transition metal carbonate complex can be fairly reactive. Thus, when carbon monoxide was passed through a solution of the platinum carbonate complex $(Ph_3P)_2PtCO_3$, it was almost quantitatively oxidised[145] to CO_2, i.e. the reaction proceeded in accordance with the equation

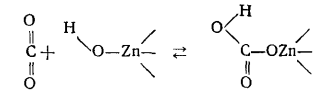
$$(Ph_3P)_2PtCO_3 + CO \rightarrow (Ph_3P)_2Pt + 2CO_2$$

Platinum carbonate complexes are used nowadays as catalysts for the synthesis of dimethylformamide from CO_2, H_2, and R_2NH and in the dimerisation of buta-1,3-diene to cyclo-octa-1,3,7-triene (see Sections V and VII respectively).

Ruthenium and rhodium bicarbonate complexes have been obtained recently[146,147] when the corresponding hydroxo-complexes were treated with carbon dioxide:

$$(Ph_3P)_2Rh(CO)OH + CO_2 \rightarrow (Ph_3P)_2Rh(CO)OCO_2H \quad ;$$
$$(Ph_3P)_4RuOH + CO_2 \rightarrow (Ph_3P)_4RuOCO_2H \quad .$$

These complexes are of some interest from the standpoint of the simulation of the action of a zinc-containing enzyme (carbonic anhydrase), which catalyses the reaction between carbon dioxide and water:



This type of analogy was drawn[148] in a study of the reaction of hydroxo-complexes of zinc with carbon dioxide. According to Riepe and Wang[149,150], in nature this process takes place in a hydrophobic cavity. There are data[151] showing that copper complexes also fulfill this function in nature.

V. INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL–HYDROGEN BOND

Depending on the polarity of the transition metal–hydrogen bond, carbon dioxide can be inserted in the latter either with formation of formate complexes (normal insertion) or of metal-carboxylic acids (anomalous insertion):

$$O{=}C^{\delta+}{=}O^{\delta-} + M^{\delta+} - H^{\delta-} \rightarrow M{-}OOCH \quad ;$$
$$O{=}C^{\delta+}{=}O^{\delta-} + M^{\delta-} - H^{\delta+} \rightarrow M{-}COOH \quad .$$

The first reaction can serve as the basis of the catalytic reduction of CO_2 by molecular hydrogen with formation of formic acid derivatives, methanol, and other products. On the other hand, the reaction involving the formation of a metal-carboxylic acid can be of interest both for the synthesis of complexes of a new type and for the study of their properties, on the one hand, and for catalytic reactions involving the transfer of the carboxy-group to olefins and acetylenes, on the other.

It is noteworthy that, when CO_2 is inserted in a transition metal–hydrogen bond with formation of both a formate complex and a metal-carboxylic acid, the complex hydride may form a complex with a CO_2 molecule in the first stage, this being followed by insertion in the M–H bond. Thus, in a study of the kinetics of the analogous insertion of carbon disulphide in the transition metal–hydrogen bond in the complex $(Et_3P)_2Pt(H)Cl$, the authors [152] showed that the complex $(Et_3P)_2Pt(H)Cl.CS_2$ is formed in the first stage.

The insertion of carbon dioxide in a transition metal–hydrogen bond was observed for the first time [153] in relation to the cobalt complex $(Ph_3P)_3Co(N_2)H$. When CO_2 is passed through a solution of the complex, it is inserted in the Co–H bond with formation of the cobalt formate complex $(Ph_3P)_xCoOOCH$ as well as the complex $[(Ph_3P)_3.Co(CO)]_2$ resulting from the decarbonylation of the formate complex. The presence of the formate group was confirmed by the formation of methyl formate when the complex was treated with methyl iodide. The authors [153] noted the presence in the infrared spectrum of two broad absorption bands (at 1585 and 1370 cm^{-1}) corresponding to the asymmetrical and symmetrical vibrations of the COO^- groups.

A study of the reaction of carbon dioxide with the complexes $(Ph_3P)_3CoH_3$ and $(Ph_3P)_3Co(N_2)H$ established [154,155] the formation of a formate complex having infrared absorption bands at 1620 and 1300 cm^{-1}. In the presence of a deficiency of phosphine in solution, a mixture of a formate complex of unknown composition $(Ph_3P)_xCo(OOCH)$ and the decarbonylation product $(Ph_3P)_3Co(CO)H$ is formed. When the formate complex is acted upon by concentrated H_2SO_4, one mole of carbon monoxide and half a mole of H_2 are evolved per mole of the complex, while thermal decomposition results in the evolution mainly of carbon dioxide, hydrogen, and a small amount of carbon monoxide.

Special mention must be made of the reaction of sulphuric acid with transition metal formate complexes, which is a kind of test distinguishing metal formate complexes from carbon dioxide complexes (their infrared spectra are extremely similar) [155]. When formate complexes react with concentrated sulphuric acid, carbon monoxide is evolved, while carbon dioxide complexes evolve CO_2 under these conditions. When a cobalt formate complex is treated with dry HCl, formic acid is formed. The formation of a cobalt formate complex was confirmed in the above studies [154,155] also by synthesis on treating the corresponding hydride complex with formic acid.

When carbon dioxide was allowed to interact with the iron complexes $(Et_2PhP)_2FeH_4$ and $(Et_2PhP)_2Fe(N_2)H_2$, the iron formate complex $L_2Fe(OOCH)_2$ was obtained [156]. On treatment with ethyl bromide, the latter gives rise to the formate ester and on treatment with concentrated H_2SO_4 it decomposes, evolving CO:

$$L_2Fe(OOCH)_2 + 4C_2H_5Br \rightarrow FeBr_2 + 2HCOOC_2H_5 + 2LC_2H_5Br \quad ;$$
$$L_2Fe(OOCH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O + 2CO + 2L \quad .$$

When carbon dioxide interacts with titanocene, a titanium formate complex is formed [157], in agreement with data [158] indicating the existence of the Ti–H bond in titanocene.

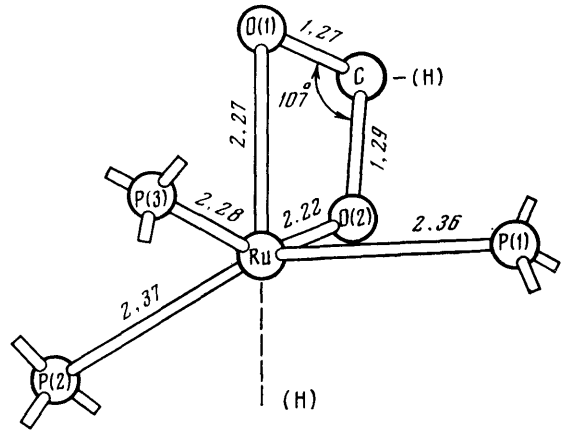
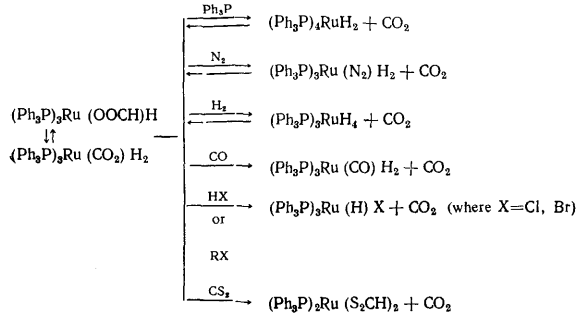


Figure 5. The structure of the ruthenium formate complex $(Ph_3P)_3Ru(H)OOCH$.

A ruthenium formate complex is formed [159,160] when carbon monoxide interacts with the complexes $(Ph_3P)_4.RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$, and $(Ph_3P)_3RuH_4$. A compound having the composition $(Ph_3P)_3Ru(OOCH)H$ was obtained, its infrared spectrum containing, together with the absorption band due to the triphenylphosphine ligand and the band corresponding to the vibrations of the Ru–H bond (at 2010 cm^{-1}), also the following distinct bands: at 1565 (s.), 1420 (m.), 1370 (m.), 1355 (m.), 1340 (m.), 800 (s.), and 690 (v.s.) cm^{-1}. These bands are very close to those in the spectrum of the rhodium complex of CO_2 [67] and, on the other hand, virtually coincide with the frequencies of the ruthenium formate complex [161]. A detailed study of the infrared spectrum of the complex obtained by Kolomnikov and coworkers [159,160] showed that in the solid state it is a ruthenium formate complex. Thus, when carbon dioxide acts upon the deuterated complex $(Ph_3P)_3RuD_4$, the product is the complex $(Ph_3P)_3Ru(OOCD)D$, in the spectrum of which there are no 2910 (m.) and 2820 (m.) bands corresponding to the ν(C–H) vibrations and a band appears at 2150 cm^{-1} [the ν(C–D) band]. There is a corresponding disappearance of the ν(Ru–H) = 2010 cm^{-1} band and its replacement by the ν(Ru–D) = 1450 cm^{-1} band. The 1370 and 1355 cm^{-1} bands, which might be assigned to the deformation vibrations of the C–H bonds, are also missing from the infrared spectrum of the deuterated product. The residual bands are due to the vibrations of the OCO group.

X-Ray diffraction data[159,162] also confirm that in the crystalline state the compound obtained is a ruthenium formate complex in which hydride hydrogen is in the *trans*-position relative to the formate group (Fig. 5), i.e. the complex has a structure analogous to that of the known complex $(Ph_3P)_3Ru(H)OAc$.[163] However, when the formate complex was treated with methanol containing BF_3 and also with methyl iodide, the corresponding alkyl formates were not detected. It was found that the reactions of this complex[101,115,159,160], accompanied by the elimination of CO_2 under mild conditions, are unusual for the transition metal formate complexes described previously (see the mechanism below).

Carbon dioxide may be displaced from the ethylene complex or transferred to platinum when the complex interacts with $(Ph_3P)_2PtO_2$, forming the known carbonate $(Ph_3P)_2PtCO_3$.[61] It is specially noteworthy that the reactions of the ruthenium formate complex with triphenylphosphine, molecular nitrogen, and hydrogen are reversible (at atmospheric pressure and room temperature).



When the ruthenium formate complex reacts with carbon disulphide, the product is, as already mentioned, a dithioformate complex, which has the *cis*-structure according to X-ray diffraction data[164]. It has been shown[159] that on heating the formate complex $(Ph_3P)_3$. .$Ru(OOCH)H$ is converted into the carbonylruthenium hydride complex $(Ph_3P)_3Ru(CO)H_2$, i.e. the formate fragment is decarbonylated. An analogous reaction involving the formation of a carbonyl derivative from a formate complex had been observed previously[155] for cobalt compounds. It has been shown quite recently[165] that under mild conditions CO_2 can serve as a source of CO for the synthesis of transition metal carbonyl complexes in the presence of reducing agents. Thus the complex $(Ph_3P)_3$. .$RhCl$ interacts with CO_2 in the presence of the hydride $(EtO)_3SiH$ to form the complex $(Ph_3P)_2Rh(CO)Cl$ (in a quantitative yield)[165]. A carbonyl complex is formed in the presence of other silanes or aluminium hydrides. When the ruthenium complex $(Ph_3P)_3RuCl_2$ is introduced into the reaction, the product is the carbonyl complex $(Ph_3P)_3Ru(CO)Cl_2$. Presumably the silane aids to the transition metal complex in the first stage via an oxidative addition mechanism with formation of a transition metal–hydrogen bond and then CO_2 is inserted in this bond, forming a formate group, the decarbonylation of which leads to the formation of transition metal carbonyl complexes.

The formation of a formate fragment after the insertion of CO_2 in a cobalt–hydrogen bond in the complex was pointed out by Haynes et al.[166] On treatment with carbon dioxide, certain osmium, platinum, and iridium hydride complexes give rise to fairly unstable formate complexes which cannot be isolated in a pure state; however, their formation can be confirmed by treating the reaction product with methyl iodide and by isolating the formate ester[167].

The insertion of CO_2 in a transition metal–hydrogen bond can be used for the catalytic reduction of carbon dioxide. However, the process $CO_2 + H_2 \rightleftharpoons HCOOH$ is thermodynamically unfavourable under mild conditions. In order to displace the above equilibrium to the right, it is necessary to bind the formate fragment formed as a result of the reaction (for example, into a formamide or a formate ester) by adding the corresponding amine or alcohol to the reaction mixture.

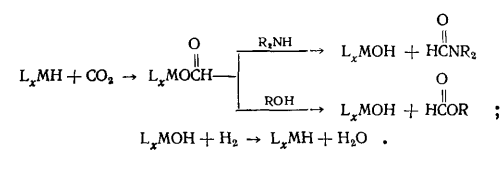
Thus it has been observed[166] that a whole series of transition metal complexes catalyse the formation of dimethylformamide in the reduction of carbon dioxide by molecular hydrogen in the presence of dimethylamine (Table 6). Other secondary amines, such as dipropylamine, pyrrolidine, and piperidine, also form rapidly the corresponding formamides. It proved impossible to extend the application of this reaction as far as the formation of *NN*-dimethylthioformamide by using carbon disulphide or carbon sulphide oxide in the presence of homogeneous hydrogenation catalysts.

Table 6. The reduction of CO_2 to dimethylformamide by molecular hydrogen in the presence of dimethylamine[166].

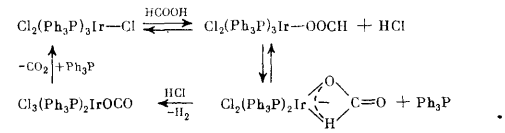
Catalyst	Catalyst concn., M	Me_2NH concn., M	Temp. *t*, °C	Yield, moles per mole of catalyst
$(diphos)_2CoH$	1.08	138	100	5
$(diphos)_2CoH$	0.05	131	125	1000
$(Ph_3P)_3RhCl$	0.3	122	100	43
$(Ph_3P)_3RhCl$	0.02	138	125	170
$(Ph_3P)_2Rh(CO)Cl$	0.38	144	100	1
$(Ph_3P)_2Ir(CO)Cl$	0.35	133	100	28
$(Ph_3P)_2Ir(CO)Cl$	0.2	138	125	1200
$(Ph_3P)_2PdCO_3$	0.79	159	100	120
$(Ph_3P)_2PtCO_3$	0.70	155	125	104
$(Ph_3P)_3Pt$	0.56	155	125	19
$(Ph_3P)_3RuCl_2$	0.39	132	125	8
$(Ph_3P)_3CuCl$	0.63	133	100	8

Formate esters have been obtained under similar conditions[167,168] using $CH_3OH–BF_3$ or $C_2H_5OH–BF_3$ mixtures as esterifying agents. Iridium and ruthenium complexes proved to be the most active catalysts. Although the formation of formaldehyde and methyl alcohol from carbon dioxide and hydrogen is thermodynamically favourable, these products were not detected in the reactions investigated[168]. Ruthenium complexes may catalyse the formation of formate esters also in the absence of BF_3. In a series of ruthenium complexes, the ruthenium(III) compound $(Ph_3P)_3RuCl_3$ proved to be the most active[65].

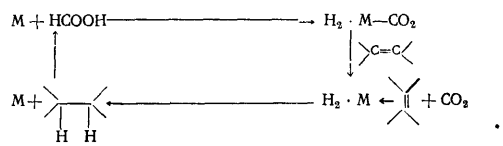
Formamides and formate esters are partly formed by the following mechanism in the reduction of carbon dioxide by molecular hydrogen in the presence of complex catalysts[167,168]:



The insertion of CO_2 in a transition metal–hydrogen bond and the reduction of carbon dioxide by molecular hydrogen in the presence of transition metal complexes are closely related to the reverse reaction—the decomposition of formic acid with evolution of carbon dioxide; this reaction is catalysed by various transition metal complexes [117,169–185]. It apparently proceeds via a stage involving the rupture of the C–H bond in the transition metal formate complex with transfer of hydrogen to the metal and the subsequent formation of a hydride complex with CO_2 as an intermediate. Thus it has been shown [117] that formic acid decomposes in the presence of an iridium catalyst via the following mechanism:



The suggested intermediate formation of a hydride complex when transition metal complexes (homogeneous hydrogenation catalysts) are acted upon by formic acid has been used for the catalytic transfer of hydrogen from formic acid to various organic substrates [184–193] (for further details, see Kolomnikov et al. [194]) via the mechanism



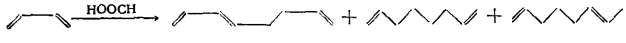
In the presence of catalytic amounts of $(Ph_3P)_3Ru(H)Cl$ in dimethylformamide formic acid reduces alk-1-enes rapidly and selectively to alkanes but does not reduce di- and tri-substituted alkenes (Table 7). It is noteworthy that under these conditions molecular hydrogen does not reduce olefins in the presence of the complex $(Ph_3P)_3$. .Ru(H)Cl, i.e. the reduction of olefins by formic acid proceeds via intramolecular hydrogen transfer [192].

Table 7. The reduction of olefins by formic acid in the presence of $(Ph_3P)_3Ru(H)Cl$ in dimethylformamide (25°C, 3 h, HCOOH : olefin = 1 : 1).

Compound	Reduction product	Yield, %
Oct-1-ene	n-Octane	100
Oct-4-ene	n-Octane	0
Hept-1-ene	n-Heptane	100
Hex-1-ene	n-Hexane	100
Methylcyclohexane	Methylcyclohexane	0
α-Methylstyrene	Cumene	0

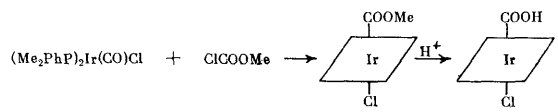
Many other complexes of rhodium [L_3RhX, $L_2Rh(CO)X$, $L_3Rh(CO)H$, etc., where L = Ph_3P and X = Cl, Br, or I], iridium [$L_2Ir(CO)X$, $L_3Ir(CO)H$, L_3IrH_2Cl, etc.], ruthenium [L_3RuCl_2, L_4RuH_2, $L_3Ru(H)OAc$, and $L_3Ru(CO)(H)X$], platinum, and palladium, are also effective catalysts of the reduction of unsaturated compounds [186–191].

The hydrogenation [193] with formic acid of octatriene, formed in the course of the dimerisation of buta-1,3-diene by phosphine complexes of platinum and palladium of the type L_2MCl_2, has been observed:

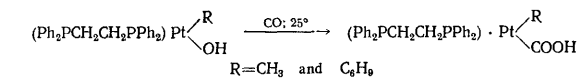


Consequently the formation of formic acid from CO_2 and molecular hydrogen as well as the decomposition of formic acid catalysed by transition metal complexes proceed via the formation of formate complexes. Together with the synthesis of such compounds by subjecting transition metal hydride complexes to the action of CO_2 (see above), the formation of formates on reaction between formic acid and ruthenium and osmium [118,195–197], platinum [114], rhodium [198], and iridium [199] has been described. An unusual formate complex has been obtained for niobium [200,201]. According to X-ray diffraction data, the complex $\{[\pi\text{-CpNbOOCH(OH)}]_3O\}H$ contains oxohydroxo-groups apart from bridging bidentate formate groups. According to the authors [201], these groups are formed as a result of the decarbonylation of formic acid.

It may be supposed that transition metal complexes can interact with formic acid not only to form formate complexes but also with the initial rupture of the C–H bond and the formation of metal-carboxylic acids. Such cleavage of the C–H bond has been observed [202] in the reaction of formic acid with complexes of the type L_3IrCl_3 (where L = Me_2PhP, Et_2PhP, or Ph_3P), a complex with the Ir–COOH fragment being formed [ν(CO) = 1660, 1635, and 1610 cm^{-1} depending on the nature of the phosphine]. The properties of the complex proved similar to those of the iridium–carboxylic acid obtained previously by an indirect method [203] [ν(CO) = 1663 and ν(OH) = 3313 cm^{-1}].

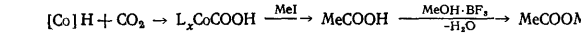


A metal-carboxylic acid was obtained recently also from a platinum complex [204]:



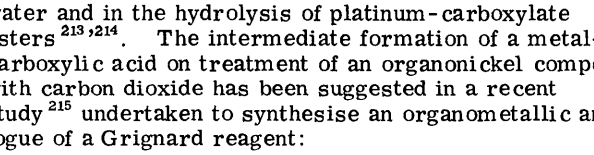
These compounds are stable in air in the solid state as well as in solution in methylene chloride or chloroform.

A metal-carboxylic acid is apparently formed also in the "anomalous" insertion of the CO_2 molecule in a Co–H bond when carbon dioxide interacts with the complex $[Ph_3P]_3Co(N_2)H$ in benzene solution. Methyl acetate is formed on treatment of the benzene solution with methyl iodide and then with a methanol solution of BF_3, as for iridium-carboxylic acids [103]:



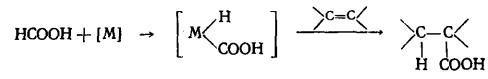
The formation of metal-carboxylic acids as intermediates has been suggested [205,206] in the oxidation of CO in the presence of mercury and silver salts.

The formation of cobalt-carboxylic acids [134–138], rhodium-carboxylic acids [207–210], and palladium-carboxylic acids [211,212] has been described. The formation of platinum-carboxylic acids has been suggested in the interaction of cationic carbonylphosphineplatinum complexes with water and in the hydrolysis of platinum-carboxylate esters [213,214]. The intermediate formation of a metal-carboxylic acid on treatment of an organonickel compound with carbon dioxide has been suggested in a recent study [215] undertaken to synthesise an organometallic analogue of a Grignard reagent:



A study of the reaction of carbon dioxide with NaCo.(Salen)$_2$ (where Salen is *NN'*-bis-salicylethylenediamine) showed[216] that the formation of the sodium salt of cobalt-carboxylic acid is reversible. The absorption bands of the coordinated carbon dioxide in this compound are in the region of 1680, 1278, and 1213 cm^{-1}.

Presumably the formation of metal-carboxylic acids is an intermediate stage in the catalytic transfer of the COOH group from formic acid to unsaturated compounds via transition metal complexes:



This reaction, involving the addition of formic acid to unsaturated compounds, leads to the formation of higher carboxylic acids[61,217] (Table 8).

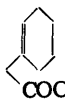
It is of interest that a platinum complex of the type (diphos)Pt  has been obtained recently[204]. Evidently this compound simulates to some extent the intermediate in the addition of the carboxylate group to an unsaturated compound.

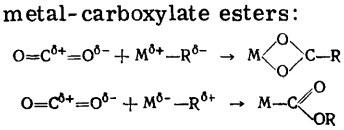
Table 8. The addition of formic acid to cyclohexene in the presence of metal complexes (100° C, 8 h, HCOOH : olefin = 1 : 1).

Catalyst	Solvent	Conversion, %	Yield of cyclohexanecarboxylic acid, moles per mole of catalyst
$(Ph_3P)_3RhCl$	—	7.0	39.0
$(Ph_2PH)_3RhCl$	—	7.3	42.0
$(Ph_3P)_2Ir(CO)Cl$	—	8.7	32.0
$RuCl_3$	DMF	2.1	3.0
H_2PtCl_6	Ethanol	7.0	18.0

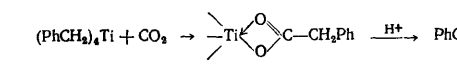
VI. INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL–CARBON BOND

The insertion of CO_2 in an M–C bond is well known and has been used successfully in the chemistry of non-transition metals[62]. However, reports of the insertion of gaseous CO_2 in a transition metal–carbon bond have appeared only very recently. Furthermore, such reactions are of great interest because they lead to the possibility of introducing CO_2 into catalytic and synthetic processes.

As in the reaction where CO_2 is inserted in a transition metal–hydrogen bond (see the previous Section), when it is inserted in a transition metal–carbon bond, two pathways may obtain—the "normal" pathway with formation of carboxylate complexes and the "anomalous" pathway with formation of metal-carboxylate esters:

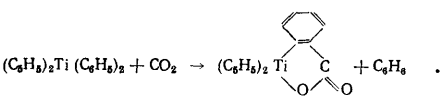


The normal insertion of CO_2 in transition metal–carbon σ bonds has been described for titanium, zirconium, zinc, cobalt, rhodium, and copper compounds. Thus it has been shown[218] that carbon dioxide is inserted in a titanium (zirconium)–carbon bond with formation of the corresponding acids after acidification. Organometallic compounds absorb up to two moles of CO_2 per mole of the complex and the reaction involving zirconium compounds proceeds at a rate higher by two orders of magnitude than for titanium compounds owing to the greater polarity of the zirconium–carbon bond. The authors[218] did not isolate the organometallic derivative from the reaction mixture but after hydrolysis yielded phenylacetic acid and triphenylcarbinol in equimolar amounts. The formation of phenylacetic acid is consistent with the mechanism of the "normal" insertion of CO_2 in a transition metal–carbon σ bond:



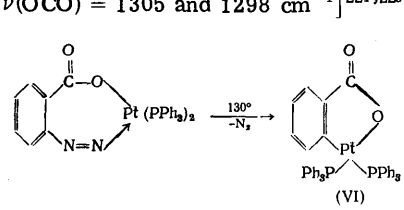
The insertion of CO_2 in a methyl–titanium σ bond has been observed[157] also in the reaction of dimethyltitanocene with CO_2 to form the $-TiOOCCH_3$ fragment. The infrared spectrum of the reaction products is identical with that of the known titanocene diacetate[219–221]. The presence of the acetate group has also been confirmed by the fact that, when the reaction product is esterified with methanol, methyl acetate is formed.

A fairly unexpected result was obtained in a study of the insertion of CO_2 in a titanium–carbon σ bond in diphenyltitanocene. At 80° C (this constitutes the condition for the thermal decomposition of diphenyltitanocene) and atmospheric pressure the reaction leads to the formation of a stable compound containing a five-membered ring incorporating a titanium atom, two *o*-carbon atoms of the benzene ring, and a CO_2 molecule[157,222,223]:



The compound obtained is diamagnetic. Its infrared spectrum contains a series of distinct bands together with the absorption bands of the phenyl and cyclopentadienyl groups: at 1660 (v.s.), 1620 (s.), 1280 (v.s.), 1130 (s.), and 880 (s.) cm^{-1}. A very intense band at 1660 cm^{-1} apparently corresponds to the ν(OCO) vibration. The frequency of this vibration is intermediate between the corresponding values for the ionised and unionised carboxy-groups. It is also of interest that in the region of the infrared spectrum characterising substitution of the benzene ring there are two bands: at 690 (m.) and 735 (s.) cm^{-1}; the region is as a rule uncharacteristic of 1,2-disubstitution.

It is noteworthy that an analogous infrared spectrum has been observed for a cyclic platinum complex obtained by the reaction of azocarboxylic acid followed by the elimination of nitrogen on heating [ν(OCO) = 1646 and 1620 cm^{-1}; ν(OCO) = 1305 and 1298 cm^{-1}][224,225]:



(VI)

On the other hand, the infrared spectrum of a cyclic organotitanium compound differs from that of $Cp_2Ti(OOCPh)_2$ (Cp = C_5H_5) [ν(OCO)(asymm.) = 1610 cm^{-1}; ν(OCO)

(symm.) = 1410 cm^{-1}][226] or the paramagnetic complex $Cp_2Ti(OOCPh)$[227].

Behaviour unusual for *o*-substitution has been observed in the Raman spectrum of compound (**VI**). Whereas the Raman spectrum of dicyclopentadienyldiphenyltitanium, recorded for comparison, has the usual monosubstitution lines at 620, 994 (v.s.), and 1006 (w.) cm^{-1}, the spectrum of compound (**VI**) has no 620 cm^{-1} line, but there are two new lines: at 1011 (s.) and 1027 (w.) cm^{-1}. Similar spectroscopic behaviour has been observed for certain *o*-substituted benzenes, but the above intensity ratios are unusual for *o*-substitution.

X-Ray diffraction data[222,223] have shown that the Ti–C σ bond in this compound is appreciably shorter (2.20 Å) than in dicyclopentadienyldiphenyltitanium (2.27 Å) (Fig. 6). This finding is fully consistent both with the thermal stability of the bond (the substance does not decompose on heating to 190°C, in contrast to Cp_2TiPh_2) and with the chemical stability of the compound, in contrast to the titanium benzoate complexes with the usual coordination, which were mentioned above.

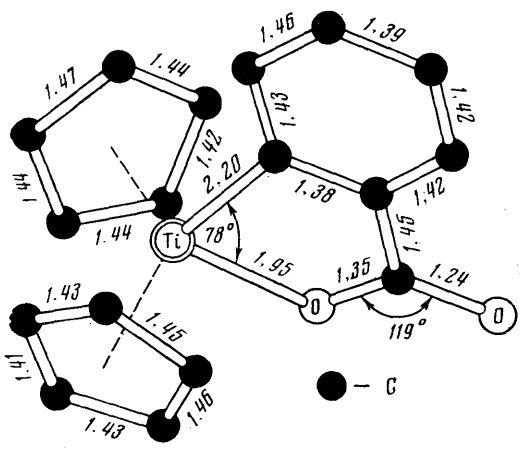
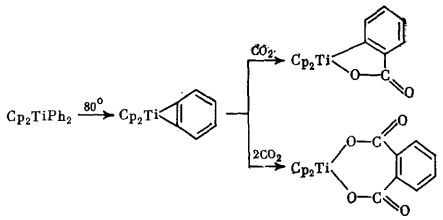
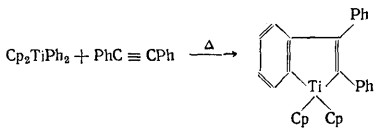


Figure 6. The structure of the complex $Cp_2TiOOCC_6H_4$.

All the data obtained are consistent with the hypothesis[228] that the decomposition of diphenyltitanocene proceeds via the intermediate formation of a titanium–dehydrobenzene complex:



It is of interest that, when diphenyltitanocene interacts with tolane under the thermal decomposition conditions, a cyclic compound is also formed[229]:



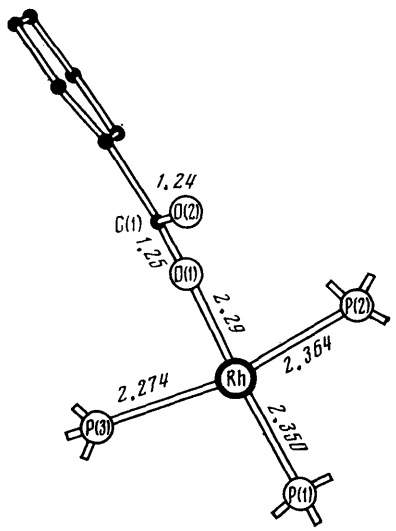
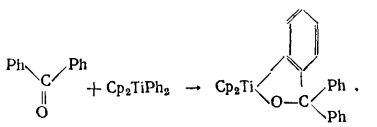


Figure 7. The structure of the rhodium benzoate complex $(Ph_3P)_3RhOOCC_6H_5$.

Other chemical reactions also agree with the proposed structure of the cyclic compound. Thus, on treatment with methanol containing BF_3 (at 100°C), methyl benzoate is formed, while treatment of the compound with methyliodide leads to the formation of a mixture of ethyl esters of benzoic and *o*-toluic acids. When the organotitanium complex is heated for a long time with hydrochloric acid, the products are benzoic acid and titanocene dichloride. It is noteworthy that the reaction of CO_2 with diphenyltitanocene takes place partly with insertion of a second carbon dioxide molecule in a titanium–carbon σ bond and the formation of a phthalate complex.

Ketones and isocyanates (analogues of CO_2) are similarly inserted in a carbon–titanium bond[230]. For example, when benzophenone reacts with diphenyltitanocene, a cyclic compound is formed:



Its hydrolysis leads to the formation of triphenylmethanol.

Carbon dioxide is readily inserted in a copper–carbon σ bond in the complex $(Ph_3P)_2CuCH_3$ with formation of the carboxylate complex $(Ph_3P)_2Cu(OOCCH_3)CO_2$ (see also Section IV) in tetrahydrofuran (THF) at −40° C and atmospheric pressure [110]. The NMR spectrum of the product (in pyridine) has a signal corresponding to the methyl of the acetate group (τ = 7.37 p.p.m.) but no signal due to the methyl group of the initial complex (τ = 10.3 p.p.m.). When the complex is treated with hydrochloric acid, acetic acid is produced:

$$CH_3COOCu(PPh_3)_2 \xrightarrow{3HCl} CH_3COOH + CuCl + PPh_3 \cdot HCl \ .$$

On the other hand, treatment with alkyl iodides results in the formation of the corresponding esters [110]:

$$CH_3COOCu(PPh_3)_2 \begin{cases} \xrightarrow{CH_3I} CH_3COOCH_3 \\ \xrightarrow{C_2H_5I} CH_3COOC_2H_5 \end{cases} .$$

The same complex may be obtained when a methyl complex of mercury is treated with acetic acid:

$$(Ph_3P)_2CuCH_3 + CH_3COOH \rightarrow CH_3COOCu(PPh_3)_2 + CH_4 \ .$$

The similarity of the infrared spectrum of the copper carboxylate complex with the spectrum of sodium acetate is evidence, according to the authors [110], for the ionic nature of the bond in the complex. The following assignment of the bands in the spectrum of the copper carboxylate complex $(Ph_3P)_2Cu(OOCCH_3)CO_2$ has been made (in terms of wavenumbers, cm^{-1}): ν(C–H) (asymm.) = 2980 (w.); ν(C–H)(symm.) = 2920 (w.); ν(OCO) (asymm.) = 1640 (s.); ν(OCO) (symm.) = 1393 (s.); $\nu(CH_3)$(rocking) = 1020 (w.); ν(C–C) = 925 (w.); ν(OCO) (symm.def.) = 622 (w.); bands corresponding to coordinated carbon dioxide: 2620 (w.); 1600 (v.s.); 1302 (v.s.); 821 (m.); 648 (w.).

When the unstable complex $[(PPh_3)_2Co(CO)C_2H_5]$, formed when acrolein interacts with the complex $(Ph_3P)_3Co(N_2)H$, was treated with CO_2, the product [103,231] was the carboxylate complex $(PPh_3)_2Co(OOCC_2H_5)_2$, which readily loses triphenylphosphine when an attempt is made to recrystallise it and is converted into cobalt propionate $Co(OOCC_2H_5)_2 \cdot 3H_2O$.

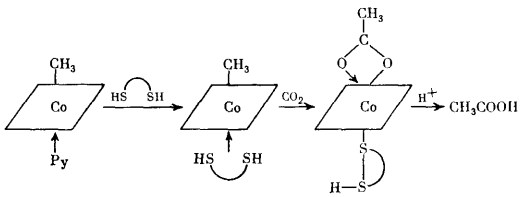
Carbon dioxide is readily inserted also in a rhodium–carbon σ bond in low-valence rhodium complexes of the type $(Ph_3P)_3RhR$, where R = CH_3 or C_6H_5, which results in the formation of carboxylate complexes of the type $(Ph_3P)_3RhOOCPh$. [232,233] When these complexes are treated with inorganic acids, the products are acids, whereas on treatment with BF_3-containing methanol the methyl esters of the corresponding acids are formed. Similar complexes may be obtained also when the complexes $(Ph_3P)_3 \cdot RhOR$ or $(Ph_3P)_3RhOH$ are treated with stoichiometric amounts of acid in the presence of an excess of triphenylphosphine. The infrared spectrum of the benzoate complex contains bands characteristic of transition metal carboxylate complexes: ν(OCO) (asymm.) = 1608 (s.) and 1570 (s.) cm^{-1} as well as ν(OCO) (symm.) = 1360 (v.s.) cm^{-1}. According to X-ray diffraction data [231,233], the rhodium atom in the benzoate complex (Fig. 7) is coordinated to three Ph_3P ligands and the benzoate ligand via a monodentate linkage, which is very rarely encountered in transition metal carboxylate complexes. The coordination of rhodium is close to the square planar form slightly distorted owing to steric interactions between the bulky triphenylphosphine ligands.

On the other hand, many compounds containing stable transition metal–carbon σ bonds do not interact with CO_2. Thus benzylchromium $PhCH_2Cr$ is stable in a CO_2 atmosphere [234]: the attempts [62] to insert carbon dioxide in a cobalt–carbon σ bond in compounds of the type $RCo(CN)_5^{3-}$, where R = $PhCH_2$, Me, etc., were unsuccessful. However, the introduction of certain ligands into the reaction mixture favours such insertion in many instances. Thus it has been found [148] that organic nitrogen-containing bases catalyse the insertion of CO_2 in a zinc–carbon bond. The increase of the reactivity of diethylzinc in the complexes with *NNNN'*-tetramethylenediamine, bipyridyl, and *N*-methylimidazole has been explained [148] by the increased nucleophilicity of the ethyl–zinc bond:

$$Et{-}Zn{-}Et \cdot L + CO_2 \rightarrow EtCOOZnEt \cdot L \ ,$$

where L is an organic nitrogen-containing base.

It has been shown [235] that in the case of methylcobaloxime, in which the cobalt–carbon bond is exceptionally stable, the presence of thiols, which promote the polarisation of the transition metal–carbon bond, makes possible the insertion of CO_2 in a cobalt–carbon bond with formation of the carboxylate fragment:



Thus the interaction of CO_2 with complexes containing a transition metal–carbon σ bond is evidently one of the pathways to the formation of transition metal carboxylate complexes. The space available in the present review precludes a detailed consideration of the properties of these compounds and we shall therefore confine ourselves merely to literature references to the employment of carboxylates in catalysis [236–248] and the preparation of the carboxylate complexes of copper [249,250], vanadium [251–254], tungsten, molybdenum [255,256], rhenium [257], iron [256,258], cobalt [259], and uranium [260], as well as a wide variety of platinum group metal complexes [261–290].

As stated at the beginning of this section, CO_2 can be apparently inserted in a transition metal–carbon bond not only with formation of carboxylate complexes but also "anomalously" with formation of metal-carboxylic acid esters, i.e. compounds containing the M–COOR fragment. Presumably factors such as a low positive charge on the metal combined with the electron-donating nature of the ligands promote this type of anomalous insertion of carbon dioxide.

Indeed the interaction of cobalt complexes containing the ethyl–cobalt σ bond with CO_2 leads to the formation of the ethyl ester of the metal–carboxylic acid as well as the cobalt carboxylate complex (see above) [103,231]. The properties of the complex $(Ph_3P)Co(CO_3)_nCOOEt$ (n = 0.5–1.0) obtained under these conditions are analogous to the properties of the familiar transition metal complexes containing the M–COOR group.

On treatment with hydrochloric acid, carbon dioxide is evolved with formation of the complex L_2CoCl_2 and ethyl formate. When the complex is treated with methyl iodide, ethyl acetate is formed in high yield, while esterification of the compound with MeOH–BF_3, for example, gives rise to a mixture of methyl and ethyl formates and acetates [231]. Analogous results were obtained when the known platinum,

cobalt, iridium, and rhodium complexes containing the M–COOR fragment are treated with an esterifying agent of the type $ROH-BF_3$ (R = CH_3 or C_2H_5). On the other hand, the interaction of carboxylate complexes of the type MOOCR with the $R'OH-BF_3$ mixture leads to the formation of RCOOR′ esters only, while complexes containing the M–COOR group yield a mixture of HCOOR and R′COOR.[65]

The cobalt complex containing the Co–COOEt group, obtained in solution when the complex $(Ph_3P)_3Co(N_2)H$ is treated with methyl chlorocarbonate, is readily decarbonylated with formation of a cobalt complex containing the CO and OEt ligands. This is the reverse of the reaction involving the formation of complexes containing the M–COOR fragment when metal carbonyls are treated with alcohols:

$$M{-}CO + OR^- \rightleftarrows M\begin{matrix}\diagup OR\\ \diagdown CO\end{matrix} \rightleftarrows MCOOR .$$

A fairly large number of transition metal complexes which are esters of metal–carboxylic acids are already known (see, for example, Angelici's review[291]).

Reactions involving the rupture of a carbon–hydrogen bond in formic derivatives can be of interest for the addition of formamides or formate esters to unsaturated compounds:

$$HCOOR + \rangle C{=}C\langle \xrightarrow{M} \begin{matrix}H\\ |\\ C\\ |\end{matrix}\!\!-\!\!\begin{matrix}|\\ C\\ |\end{matrix}\!\!-COOR .$$

Table 9. The addition of ethyl formate in the presence of transition metal complexes (8 h, HCOOEt : olefin = 1 : 1).

Catalyst	Temp., °C	Initial olefin	Reaction product	Yield, moles per mole of catalyst
$(Ph_3P)_3RhCl$	140	Cyclohexene	Ethyl cyclohexane-carboxylate	5.3
$(Ph_3PH)_3RhCl$	180	ditto	Ditto	6.0
$(Ph_3P)_2Rh(CO)Cl$	180	»	»	0.8
$(Ph_3P)_2Ir(CO)Cl$	180	»	»	1.2
$(Ph_3P)Rh(CO)_2Cl$	180	»	»	3.3
$(Ph_3P)_3IrH_3$	180	»	»	0.2
$(Ph_3P)_3Os(CO)(H)Cl$	180	»	»	0.6
$(Ph_3P)_2Rh(CO)Cl$	180	$H_2C{=}CH_2$	CH_3CH_2COOEt	0
$(Ph_3P)_2Rh(CO)Cl$	180	$CH_3CH{=}CH_2$	$CH_3CH_2CH_2COOEt$	3.0
$(Ph_3P)_2Rh(CO)Cl$	180	$(CH_3)_2C{=}CH_2$	$(CH_3)_2CHCH_2COOEt$	0
$(Ph_3P)_2Rh(CO)Cl$	180	Hex-1-ene	Ethyl oenanthate	7.0

Such a reaction has been achieved[61] in the presence of various transition metal complexes (Table 9). The yield of the reaction product depends on the nature of the olefin, temperature, reaction time, and the olefin : formate ester ratio. In certain cases the dimerisation of olefins was observed as a side reaction. Rhodium compounds proved to be the most active, while platinum complexes were found to be inactive, probably mainly due to the high stability of the platinum–carbon bond. Presumably the addition of formate esters to olefins proceeds via a stage involving the rupture of a C–H bond in the esters and the formation of esters of metal–carboxylic acids as intermediates:

$$M + HCOOR \rightarrow M\begin{matrix}\diagup COOR\\ \diagdown H\end{matrix} \xrightarrow{\begin{matrix}|\\ C{=}C\\ |\end{matrix}} M\begin{matrix}\diagup COOR\\ \diagdown \begin{matrix}|\\ C\\ |\end{matrix}\!\!-\!\!\begin{matrix}|\\ C\\ |\end{matrix}\!\!-H\end{matrix} \rightarrow M + H\!\!\begin{matrix}|\\ C\\ |\end{matrix}\!\!-\!\!\begin{matrix}|\\ C\\ |\end{matrix}\!\!-COOR .$$

It is noteworthy that the reaction of cyclohexene with the complex $(Ph_3P)Rh(CO)_2Cl_2COOEt$ led to the formation of ethyl cyclohexenecarboxylate.

In the synthesis of vinyl ethers from acetylene, alcohols, and carbon monoxide in the presence of palladium salts[292,293] the Pd–COOR fragment is formed in solution when the Pd–OR bond is acted upon by CO with subsequent transfer of the COOR group to acetylene.

It is evident from the foregoing how large is the set of reactions associated with the problem of the insertion of carbon dioxide in a transition metal–carbon bond known at the present time. For example, the insertion of CS_2,[65,66,294,295] or SO_2[296] in a metal–carbon bond, which is extremely common in the chemistry of organic derivatives of transition metals, may be included among reactions of this type.

VII. CATALYTIC PROCESSES WITH PARTICIPATION OF CARBON DIOXIDE

The catalytic reactions with participation of CO_2 can be divided into two main groups. The first group includes processes in which CO_2 is the starting material for the synthesis of various organic compounds, while the second group includes reactions in which CO_2 behaves as a ligand which modifies the catalyst. Processes involving the synthesis of formic acid derivatives (esters and amides) when CO_2 is reduced by molecular hydrogen to formate esters and formamides, which were discussed in Section IV, may be assigned to the first group of reactions.

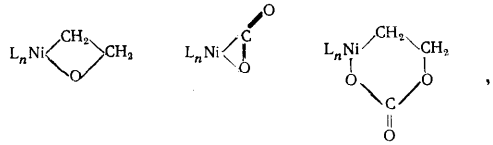
Particular consideration should be given to reactions involving the reduction of CO_2 by molecular hydrogen in the presence of the graphite–$PdCl_2$–sodium heterogeneous catalyst[297]. Together with C_1-C_4 hydrocarbons, dimethyl ether is formed in high yield under mild conditions. The yield of the ether increases greatly in the presence of methanol or formamaldehyde and also when the catalyst is subjected to preliminary treatment with carbon monoxide. The formation of dimethyl ether has also been observed in the hydrogenolysis of methyl formate, which may be formed, according to the authors[297], as an intermediate in the reduction of CO_2.

A number of workers[298–302] showed that certain organometallic compounds may catalyse the formation of polycarbonates from CO_2 and high-molecular-weight epoxides via the mechanism

$$n\left(\begin{matrix}R\\ |\\ HC-CH\\ \diagdown\ \diagup\\ O\end{matrix}\right) + n\,CO_2 \xrightarrow{Et_2Zn/water} \left(\begin{matrix}R\\ |\\ CH_2-CH-O-C-O\\ \qquad\qquad\ \ \|\\ \qquad\qquad\ \ O\end{matrix}\right)_n - \ldots$$

Optically active polymers have been obtained by this procedure[349].

It has been shown recently[303] that the carboxylation of epoxides is catalysed by zerovalent nickel complexes. The author[303] points out the possible existence in the system of compounds of the following type:



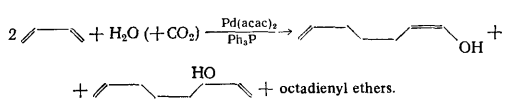
Despite the fact that the study of the modifying effect of CO_2 on organometallic catalysts based on a transition metal is only just beginning, it is already seen that this

field is fairly promising from the standpoint of the synthesis of selective and specific catalysts. In this connection one should note that the use of CO_2 as the cocatalyst for the modification of the catalytic system is fairly common in the chemistry of organometallic compounds based on transition metals[62].

The influence of CO_2 on the catalytic properties of nickel, platinum, and palladium catalysts in the dimerisation of butadiene has been reported[304]. Whereas in the absence of a catalyst butadiene dimerises slowly to 4-vinyl-1-cyclohexene and CO_2 has no effect on this process, in the presence of the phosphine complex of platinum $(Ph_3P)_4Pt$ in an atmosphere of argon the yield of 4-vinyl-1-cyclohexene increases to 90–97%; a small amount of octa-1,3,7-triene is formed as a side product. When argon is replaced by CO_2, only *trans*-octa-1,3,7-triene is formed in the reaction. Similar results were obtained in the presence of the complexes $(Ph_3P)_4Pd$, $(Ph_3P)_4Ni$, and $[(PhO)_3P]_4Ni$. The authors[304] do not discuss the mechanism of the action of carbon dioxide but suggest that unstable CO_2 complexes are formed during the reaction. The attempts to isolate such complexes were unsuccessful.

It may also be that the catalysts are involved in this reaction as carbonate complexes (see Section IV). At any rate, according to the results of the same workers[305], octa-1,3,7-triene is formed from butadiene in the presence of a platinum carbonate complex.

It has been observed[306] that CO_2 has a significant influence on the formation of octadienols from butadiene and water in the presence of palladium catalysts. The interaction of butadiene and water in the presence of the $Pd(acac)_2$–triphenylphosphine system (acac = acetylacetonate) in argon leads to the formation of octatriene as the main reaction product. However, in the presence of carbon dioxide octadienols are the main reaction products and the yield of octatriene is insignificant. It is noteworthy that small amounts of carbon dioxide are sufficient for the formation of octadienols:



It is seen from the present review that the chemistry of carbon dioxide in systems involving transition metals is being as it were reborn. The data for the formation of complexes of carbon dioxide with transition metal compounds and the studies on the insertion of carbon dioxide in metal–hydrogen and metal–carbon bonds, considered in this review, demonstrate the extensive scope of the applications of these reactions in various chemical processes. Particular mention should be made of the reactions in which carbon dioxide is involved in catalytic processes, on the one hand, as the starting material for the synthesis of various organic compounds and, on the other, as a ligand modifying known catalysts.

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