INTERACTION OF SMALL MOLECULES WITH METAL CENTERS: THE ROLE OF MODELING STUDIES

Carlo Floriani

Istituto di Chimica Generale, Università di Pisa, Via Risorgimento 35, 56100 PISA, Italy.

Dedicated to the late Paolo Chini (February 2, 1980)

Abstract - Bifunctional (acidic-basic) *vs* monofunctional (basic or acidic) activation of small molecules is the 'leit-motiv' of the present report. The genesis of the $M(CH_2O)$ and the $M(\mu-CH_2O)M$ fragments either from the reaction of formaldehyde with metal complexes (M) or from the CO insertion into metal-hydrogen bonds is described. Synthesis, structure determination and reactivity of three model complexes, namely $cp_2V(CO)(CHO)$, $cp_2V(\eta^2-CH_2O)$ and $[(cp_2ZrCl)_2(\mu-CH_2O)]$ ($cp = \eta^5-C_5H_5$) are described. "Bifunctional" activation of the CH_2O unit is the factor controlling its possible transformation into C_2 units. The key role of formaldehyde and of the $M(CH_2O)$ unit in syngas chemistry is exemplified. The significant difference between the fixation of carbon dioxide by monofunctional complexes and the fixation by bifunctional complexes is stressed. Simulation of carbon dioxide by related molecules disclosed general pathways leading to C-C bond formation.

INTRODUCTION

A recognised role played by coordination chemistry is that of providing stable compounds bonding small molecules, or species postulated as intermediates in their transformations, thus permitting a precise definition of their chemistry when bonded to a transition metal. Such modeling studies will allow a better understanding of the role played by the metal which has the task of driving the reactivity of the species bonded to it, selecting chemical pathways and making their transformations easier. Such an ensemble of metal influences on the substrate are called 'activation'. The discoveries of the 'activation' of molecular hydrogen and oxygen by coordination compounds in solution mark the beginning of homogeneous catalysis. Homogeneous catalysis using soluble compounds with low molecular complexity suffers from the intrinsic limitation of coordination compounds, and that is the fact that provide only a single reactive site for interacting with a given substrate. This limitation stems from the observations in heterogeneous systems or in enzymes where certain transformations such as reduction of dinitrogen to ammonia or the methanation of carbon monoxide are believed to require the cooperative interaction of two or more metal centers having the same characteristics (polymetallic activation) or different chemical properties (polyfunctional activation). Soluble metal clusters are offering possibilities for transformations of organic substrates as yet unobserved on single metal centers *via* a polynuclear activation. Bifunctional activation is an objective difficult to pursue in coordination chemistry, because metal complexes have either an acidic or a basic center, and not both simultaneously in the same structure. Therefore, in coordination chemistry, activation by model compounds means activation by high valent metals (acidic metals) or activation by low valent metals (basic metals). The aim of this paper is to describe some aspects of the chemistry of formaldehyde, formaldehyde derived species, carbon dioxide, and carbon dioxide analogues modified by the action of bifunctional systems.

METAL-FORMALDEHYDE CHEMISTRY

The interest in metal-formaldehyde chemistry stems from the following considerations:
i) formaldehyde is among the most probable products of a stoichiometric hydrogenation of CO;
ii) formaldehyde can serve as a raw material for selective syntheses of C_2 molecules, i.e., ethylene glycol;
iii) formaldehyde represents an excellent entry into syngas chemistry, where the $M(CH_2O)$ fragment seems to play a key role in metal-assisted carbon monoxide hydrogenation.

The genesis and the chemistry of the metal-bonded CH_2O is the purpose of the present study. Several schemes proposed for the synthesis gas conversion deal with the formation and the transformations of the CH_2O unit (Ref. 1). Its chemistry arises from a few metal-promoted transformations on the CH_2O unit, they include the carbon-oxygen and the carbon-hydrogen bond scission, and the carbon-carbon bond formation. This can be viewed as the consequence of the fact that $M(CH_2O)$ unit represents different interrelated chemical species, namely oxymethylene, hydrido-formyl, and hydroxycarbene bonded either to a mononuclear or to a dinuclear active site (Scheme I):
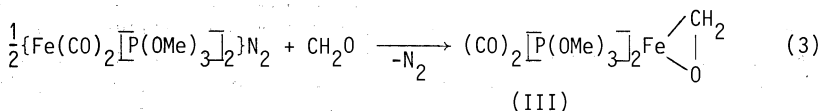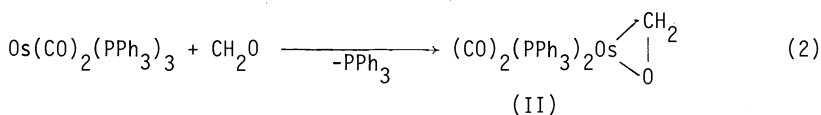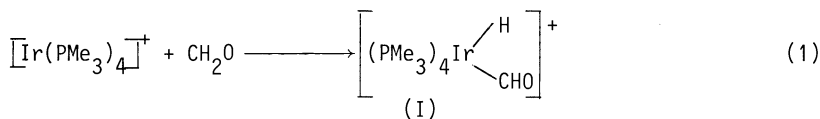

Scheme (I)

Oxymethylene   Hydrido-Formyl   Hydroxycarbene
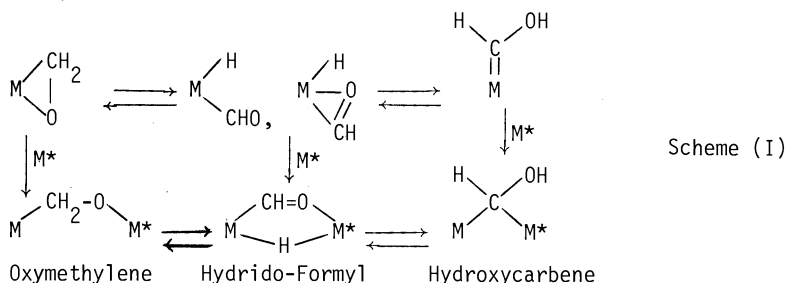
Hypothetical syntheses for the $M(CH_2O)$ unit are sketched in Scheme (II):

Scheme (II)
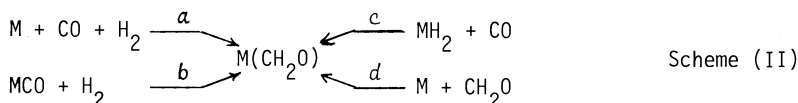
All of them are significant with regard to the genesis of $M(CH_2O)$ unit in catalytic processes, while the synthesis of a reasonably stable $M(CH_2O)$ complex to be used in a modeling study is restricted to reactions c and d. Reaction c is strictly limited to early transition metal-hydrido complexes, while the reaction of a metal complex with formaldehyde remains the most versatile approach to the $M(CH_2O)$ unit.

Genesis and reactivity of formaldehydo ligand.
The reaction of a transition metal complex with formaldehyde, though promising, was reported in a few cases. Reactions (1-3) (Refs 2-4) describe the most interesting results so far reported from the reaction of formaldehyde with transition metal complexes:

$$[Ir(PMe_3)_4]^+ + CH_2O \longrightarrow \left[(PMe_3)_4Ir\begin{smallmatrix}H\\CHO\end{smallmatrix}\right]^+ \qquad (1)$$

(I)

$$Os(CO)_2(PPh_3)_3 + CH_2O \xrightarrow{-PPh_3} (CO)_2(PPh_3)_2Os\begin{smallmatrix}CH_2\\|\\O\end{smallmatrix} \qquad (2)$$

(II)

$$\tfrac{1}{2}\{Fe(CO)_2[P(OMe)_3]_2\}N_2 + CH_2O \xrightarrow{-N_2} (CO)_2[P(OMe)_3]_2Fe\begin{smallmatrix}CH_2\\|\\O\end{smallmatrix} \qquad (3)$$
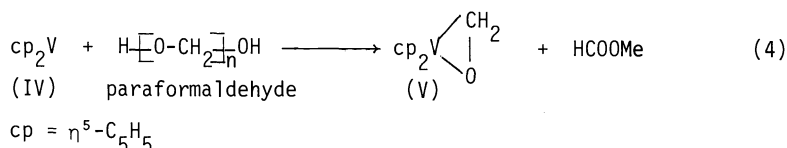
(III)

The oxidative addition of the C-H bond of formaldehyde to an Ir(I) complex led to the first stable cationic hydrido-formyl derivative, whose chemistry was recently described in great detail (Ref. 2). Complexes (II) and (III) contain an intact formaldehyde molecule η^2-C,O

bonded to a transition metal, as confirmed by the corresponding X-ray analysis. The CH_2O unit in complex (II) undergoes thermal transformation to the corresponding hydrido-formyl complex, while in both complexes acidic agents convert the η^2-C,O metal bonded formaldehydo group into a metal-carbon σ bonded oxymethylene ligand. Such a transformation is relevant to transformations of formaldehyde occurring with carbon monoxide.

The choice of vanadocene, cp_2V, (IV) $\left[cp = \eta^5\text{-}C_5H_5\right]$, to be used as a model compound in formaldehyde chemistry was mainly dictated by two characteristics of such a compound;
i) vanadocene is a carbene-like metal adding to a large number of organic functional groups (Refs 5-8);
ii) alkyl-vanadocene derivatives undergo insertion reactions of carbon monoxide in a well defined sequence (Ref. 9).
Vanadocene was found to react with paraformaldehyde under very mild conditions to form the monomeric complex (V) as deep-green crystals (Ref. 10):

$$cp_2V \;+\; H\!\!\left[\!O\text{-}CH_2\right]_{\!n}\!\!OH \longrightarrow cp_2V\!\!\underset{O}{\overset{CH_2}{\big<\big|}} \;+\; HCOOMe \qquad\qquad (4)$$

(IV)　　paraformaldehyde　　　(V)

$$cp = \eta^5\text{-}C_5H_5$$

Complex (V) was formed from reaction (4) along with a significant amounts of HCOOMe. Moreover complex (V) added to a toluene suspension of paraformaldehyde promoted the formation of HCOOMe. Before discussing the chemistry of the vanadocene-anchored formaldehydo group, it would be interesting to compare the C-O bond distances and stretching vibrations in the three formaldehydo complexes structurally identified so far (Figure 1):
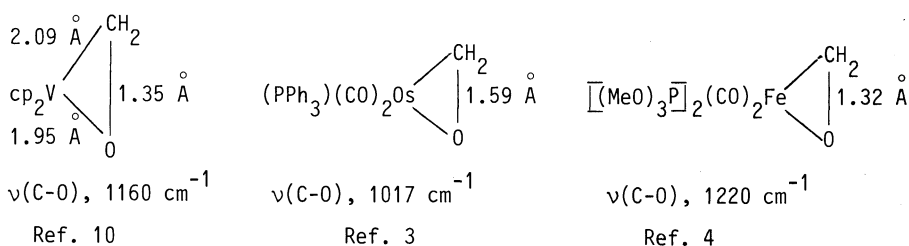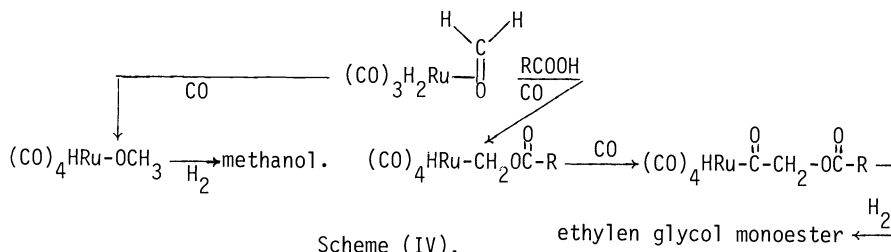

$$2.09\,\overset{\circ}{A}\,/CH_2$$
$$cp_2V\overset{1.35\,\overset{\circ}{A}}{\underset{O}{\big<\big|}}$$
$$1.95\,\overset{\circ}{A}$$

$$\nu(\text{C-O}),\ 1160\ cm^{-1}$$

Ref. 10

$$(PPh_3)(CO)_2Os\overset{CH_2}{\underset{O}{\big<\big|}}\,1.59\,\overset{\circ}{A}$$

$$\nu(\text{C-O}),\ 1017\ cm^{-1}$$

Ref. 3

$$\left[(MeO)_3\overline{P}\right]_2(CO)_2Fe\overset{CH_2}{\underset{O}{\big<\big|}}\,1.32\,\overset{\circ}{A}$$

$$\nu(\text{C-O}),\ 1220\ cm^{-1}$$

Ref. 4

Figure 1.

Carbon monoxide displaced CH_2O ligand from complex (V) forming HCOOMe and $cp_2V(CO)$ which itself is able to perform the paraformaldehyde $\rightarrow$ HCOOMe transformation (Refs 10, 11). The formaldehyde disproportionation to HCOOMe promoted by vanadocene derived species [Scheme(III)] was viewed as the main consequence of a possible equilibrium between the formaldehydo complex and the corresponding hydrido formyl complex (Ref. 10).
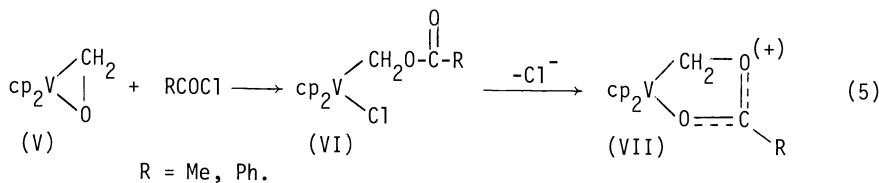

$A \equiv$ paraformaldehyde
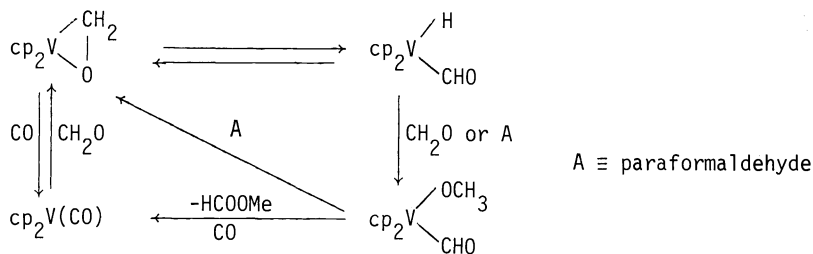
Scheme (III)

The vanadocene-promoted disproportionation of formaldehyde would suggest that the formation of HCOOMe from syngas could be the consequence of a preliminary metal-promoted formation of formaldehyde. The results outlined above suggest that the action of a C_1 molecule, namely formaldehyde or carbon monoxide, on a formaldehydo complex generates again a C_1 molecule. The result can be different if the reaction is carried out into the presence of an acidic substance. An interesting suggestion stems from the scheme proposed for CO hydrogenation to methanol and ethylene glycol promoted by ruthenium carbonyl (Ref. 12) [Scheme (IV)]:

$$
\begin{array}{c}
\xrightarrow{\quad CO \quad} \quad (CO)_3H_2Ru\!-\!\overset{\overset{\displaystyle H\;\;H}{\diagdown\,C\,\diagup}}{\underset{O}{\|}} \xrightarrow[CO]{RCOOH}
\end{array}
$$

$$
(CO)_4HRu\!-\!OCH_3 \xrightarrow[H_2]{} methanol. \quad (CO)_4HRu\!-\!CH_2O\overset{O}{\overset{\|}{C}}\!-\!R \xrightarrow{CO} (CO)_4HRu\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_2\!-\!O\overset{O}{\overset{\|}{C}}\!-\!R \rceil
$$

$$
\text{ethylen glycol monoester} \xleftarrow{\;H_2\;}
$$

<div align="center">Scheme (IV).</div>

In the presence of an acid, formaldehydo ligand is proposed to convert into an acyloxymethylene group inserting CO and forming a C_2 unit (Ref. 12). The acid-promoted transformation of formaldehydo group into an oxymethylene ligand was achieved for complex (V) by different Lewis acids, namely $TiCl_4$, $[cp_2TiCl]_2$, BF_3, H^+, etc. Reaction (5) illustrates such a general transformation.

$$
cp_2V\!\!\overset{\displaystyle\diagup CH_2}{\underset{\diagdown O}{|}} + RCOCl \longrightarrow cp_2V\!\!\overset{\displaystyle\diagup CH_2O\!-\!\overset{O}{\overset{\|}{C}}\!-\!R}{\diagdown Cl} \xrightarrow{-Cl^-} cp_2V\!\!\overset{\displaystyle\diagup CH_2\!-\!O}{\underset{\diagdown O\,=\!=\!=C}{}}\!\!\overset{(+)}{\underset{\diagdown R}{}} \qquad (5)
$$

<div align="center">(V)   (VI)   (VII)</div>
<div align="center">R = Me, Ph.</div>

Acyl halides attack the oxygen in complex (V) forming acyloxymethylene complexes, (VI). In the presence of an ionizing agent, the acyloxymethylene ligand chelates the metal forming metallacycles (VII). The structure of acyloxymethylene complexes (VI) $[\nu(C\text{-}O) = 1690\ cm^{-1}$, R = Ph; $\nu(C\text{-}O) = 1710\ cm^{-1}$, R = Me] and (VII) $[\nu(C\text{-}O) = 1600\ cm^{-1}$, R = Ph; $\nu(C\text{-}O) = 1630\ cm^{-1}$ R = Me] was clarified in detail. The X-ray structure of complex (VII)(R = Ph) is reported in Figure 2 along with the most relevant bond distances and angles:
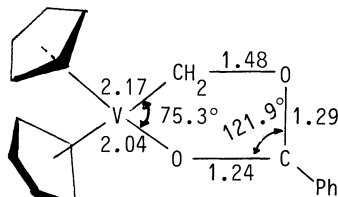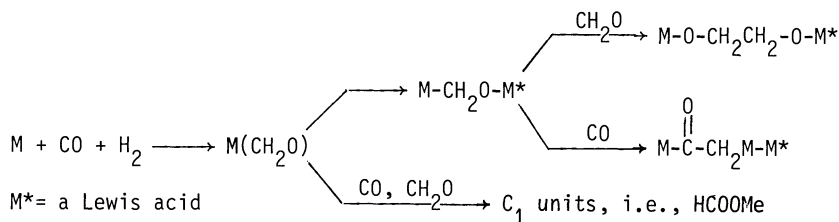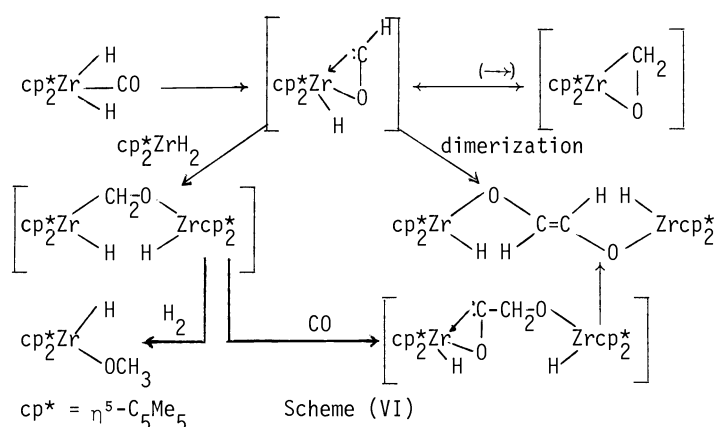
<div align="center">

CH₂ —1.48— O structure with V, 2.17, 2.04, 75.3°, 121.9°, 1.29, 1.24, C, Ph

</div>

<div align="center">Figure 2.</div>

Vanadium-carbon σ bond distance in complexes (VII) is significantly longer than in complex (V) $[2.092(8)\ \overset{o}{A}]$, as expected for a genuine V-C σ bond when we pass from a formaldehydo to an oxymethylene ligand. The two C-O bond distances are very close, showing an electronic delocalization over the CO_2 unit in agreement with a rather low CO stretching frequency. The formaldehydo group, when transformed into oxymethylene group (Refs 3,4,10,11), undergoes an insertion reaction related to that shown in Scheme (V) for producing C_2 units. These results confirm that, provided one has a system which forms formaldehyde from synthesis gas, the factor controlling the formation of C_2 units is the presence of a Lewis acid $[$Scheme (V)$]$:

$$
M + CO + H_2 \longrightarrow M(CH_2O)
\begin{cases}
\longrightarrow M\text{-}CH_2O\text{-}M^*
\begin{cases}
\xrightarrow{CH_2O} M\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}M^* \\
\xrightarrow{CO} M\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_2M\text{-}M^*
\end{cases} \\
\xrightarrow{CO,\ CH_2O} C_1 \text{ units, i.e., HCOOMe}
\end{cases}
$$

<div align="center">M* = a Lewis acid</div>

<div align="center">Scheme (V)</div>

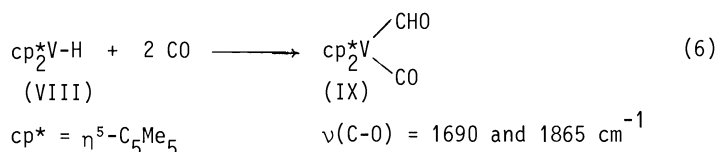### μ-Oxymethylene ligand: synthesis and reactivity.

All chemists interested in CO activation are familiar with the Bercaw modeling studies on stoichiometric reduction of carbon monoxide achieved using zirconium-hydrido species (Ref.13) $[$Scheme (VI)$]$:
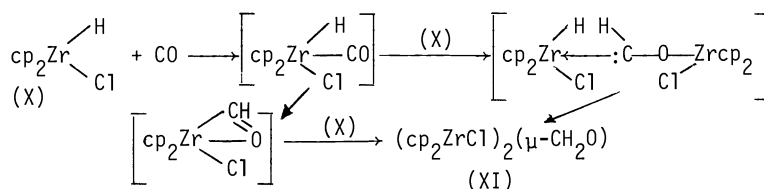
$$cp_2^*Zr\diagdown^H_{CO} \longrightarrow \left[cp_2^*Zr\cdots \overset{:C-H}{\underset{O}{|}}\diagdown_H\right] \longleftrightarrow_{(\longrightarrow)} \left[cp_2^*Zr\diagdown^{CH_2}_O\right]$$

$$cp_2^*ZrH_2 \qquad\qquad dimerization$$

$$\left[cp_2^*Zr\overset{CH_2O}{\underset{H}{\diagup}}\diagdown\overset{}{\underset{H}{Zrcp_2^*}}\right] \qquad cp_2^*Zr\overset{O}{\underset{H\ H}{\diagup\diagdown}}C=C\overset{H\ H}{\underset{O}{\diagup\diagdown}}Zrcp_2^*$$

$$cp_2^*Zr\diagdown^H_{OCH_3} \xleftarrow{H_2} \xrightarrow{CO} \left[cp_2^*Zr\overset{:C-CH_2O}{\underset{H}{\diagup}}\overset{}{\underset{H}{\diagdown}}Zrcp_2^*\right]$$

$$cp^* = \eta^5\text{-}C_5Me_5 \qquad Scheme\ (VI)$$

The scheme proposed for such a complex transformation is based mainly on the genesis and reactivity of two key intermediates:
i) a metal hydrido formyl or metal-formaldehyde unit;
ii) an oxymethylene ligand bridging two zirconium atoms.
Attempts to generate formyls from CO insertion into metal-hydrogen bonds have a long story, but only recently have there been any successes. They are: the insertion of CO into a Rh-H bond in [Rh(OEP)H] gave a structurally identified formyl group [Rh(OEP)(CHO)] (Ref. 14), while the very high oxophilicity of Th and the bulkiness of the substituent R seem to be the reasons for the stabilization of a η^2-C,O bonded formyl group in [$(C_5Me_5)_2$Th(OR)(η^2-CHO)] (Ref. 15). A related result was obtained by reacting decamethylvanadocene hydride $(C_5Me_5)_2$V-H (Ref. 16) with carbon monoxide:

$$cp_2^*V\text{-}H + 2\ CO \longrightarrow cp_2^*V\overset{CHO}{\underset{CO}{\diagup}} \qquad (6)$$

$$(VIII) \qquad\qquad (IX)$$

$$cp^* = \eta^5\text{-}C_5Me_5 \qquad \nu(C\text{-}O) = 1690\ and\ 1865\ cm^{-1}$$

Complex (IX) can be isolated as stable crystals. Pentamethylcyclopentadienyl ligand on vanadium stabilized a sterically protected V-H unit because of the small ionic radius of vanadium (III). Therefore the reaction with carbon monoxide led to a formyl which did not react with a further molecule of (VIII), as usually occurs for analogous zirconium species in Scheme (VI). In the present case the reaction is further semplified by the fact that there is only one potential migrating ligand on the metal. Despite the fact that CO insertion into a metal-hydrogen bond is thermodinamically forbidden, CO insertion into a V-H bond is favoured by the simultaneous coordination of CO to vanadium(III) [reaction (6)]. The carbonylation of a sterically non protected hydrido-zirconium complex, cp_2Zr(H)(Cl), (X), led to the isolation of a dinuclear zirconium complex containing a bridging oxymethylene ligand (Refs 17,18). A plausible pathway leading to this result is proposed in scheme (VII), in agreement with some of the Bercaw observations (Ref. 13).

$$cp_2Zr\diagdown^H_{Cl} + CO \longrightarrow \left[cp_2Zr\diagdown^H_{Cl}CO\right] \xrightarrow{(X)} \left[cp_2Zr\overset{H\ H}{\underset{Cl}{\diagup}}:C\text{-}O\overset{}{\underset{Cl}{\diagdown}}Zrcp_2\right]$$

$$(X)$$

$$\left[cp_2Zr\overset{CH}{\underset{Cl}{\diagup\diagdown}}O\right] \xrightarrow{(X)} (cp_2ZrCl)_2(\mu\text{-}CH_2O)$$

$$(XI)$$

$$Scheme\ (VII)$$

The intermediancy of a bridging oxymethylene ligand in a carbon monoxide reduction by metal hydrides was considered the most critical step in such a kind of reaction [(Refs 13,15) and Scheme (VI)]. The reactivity of the M(μ-CH$_2$O)M unit towards carbon monoxide would explain the generation of C$_2$ units (Refs 13,15). The structure of (XI), which was only recently clarified, is an important starting point for understanding the genesis and the transformation of the oxymethylene unit (Ref. 18). Figure 3 shows a semplified view of complex (XI) with the most relevant bond distances.
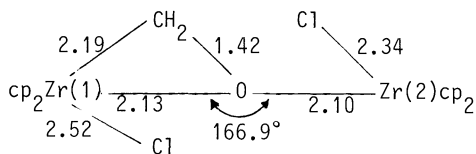
Figure 3.

The oxymethylene unit is η^2-C,O bonded to zirconium(1) while the oxygen is shared between the two zirconium atoms at very close distance and the three atoms Zr(1), O, Zr(2) are nearly co-linear. The C-O bond distance (1.42 Å) and C-O stretching vibration (1015 cm^{-1}) are those expected for a η^2-C,O bonded formaldehydo group. Complex (XI) resembles a formaldehydo complex activated by the Lewis acid cp_2ZrCl_2. In such a hypothetical form, complex (XI) reacts with carbon monoxide losing cp_2ZrCl_2 and forming (XII) as a crystalline solid in a sequence like that shown in Scheme (VIII).
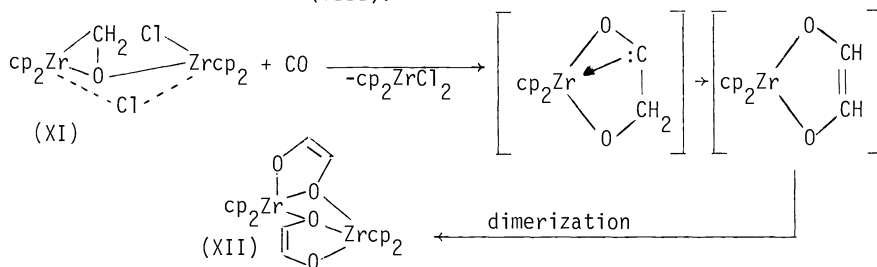
Scheme (VIII)

Bridging oxymethylene unit was only postulated as intermediate, while this is the first report on its structure determination and reactivity with carbon monoxide.
The results outlined above concerning the $M(CH_2O)$ unit, formed either from formaldehyde or from the reaction of carbon monoxide with metal hydrides, confirm the important role of such a unit as possible intermediate leading to a C_2 unit, provided a Lewis acid is present.
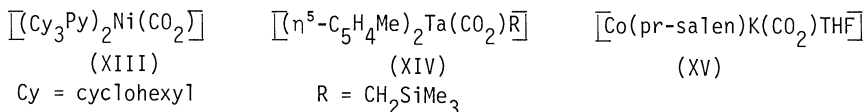

CARBON DIOXIDE ACTIVATION

A better knowledge of the transition metal-carbon dioxide chemistry is the first requisite for improving the possibilities to use carbon dioxide as a source of chemical carbon (Ref.19). For this purpose two main objectives must be pursued, they are:
i) how to fix carbon dioxide on a metal center forming a reactive metal-carbon σ bond;
ii) how to promote a C-C bond formation either between CO_2 molecules or incorporating CO_2 in an organic substrate.
An inspection of the most common reactions of CO_2 with transition metal complexes gives a few suggestions on how to devise strategies for CO_2 activation (Ref. 19). We must admit that any metal-promoted carbon dioxide transformation requires a detailed understanding of the preliminary metal-carbon dioxide interaction, namely of the carbon dioxide fixation.

Fixation of carbon dioxide.
Fixation of carbon dioxide in its intact form on a metal center is a very rare process. This is indirectly proved by the fact that only three CO_2 complexes have been so far structurally identified, they are (XIII)(Ref. 20), (XIV)(Ref.21), (XV)(Refs 22,23):

$[(Cy_3Py)_2Ni(CO_2)]$ $[(\eta^5-C_5H_4Me)_2Ta(CO_2)\overline{R}]$ $[Co(pr-salen)K(CO_2)TH\overline{F}]$
          (XIII)   (XIV)   (XV)
     Cy = cyclohexyl   R = CH_2SiMe_3

The most distinguishing feature of the three complexes stems from the fact that CO_2 interact with a single reactive site in (XIII) and (XIV) (monofunctional complexes), while in complex (XV) carbon dioxide is anchored to a bimetallic unit (bifunctional complex). The nature of CO_2 itself, which is an oxygen rich electrophilic molecule, and its usual reactivity justify the following approaches in a modeling study focused on carbon dioxide fixation, they are:
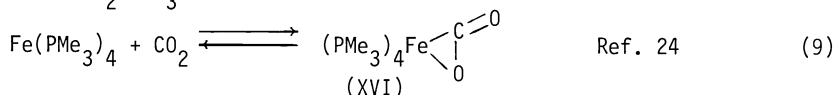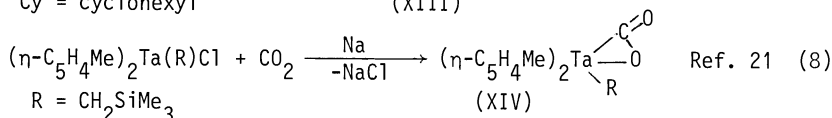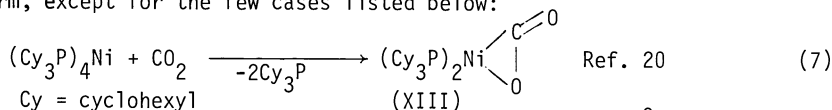i) the utilization of 'monofunctional' complexes containing in their structure an oxophilic metal in a low oxidation state;

ii) the utilization of 'bifunctional' complexes containing in their structure as reactive
    sites a transition metal in a low oxidation state (basic state) along with a Lewis acid
   (acidic site).
A brief account of the results and the limits obtained applying both strategies is sketched
below.

Reaction of carbon dioxide with 'monofunctional complexes'.
Utilization of potentially coordinative unsaturated complexes in reaction with unsaturated
substrates is a general rule in organometallic chemistry. Such metals add to the unsaturated
unit in a fashion which is reminiscent of carbenoid organic species. In spite of the success
with a large variety of unsaturated substrates, they fail in fixing carbon dioxide in its
intact form, except for the few cases listed below:

$$(Cy_3P)_4Ni + CO_2 \xrightarrow{-2Cy_3P} (Cy_3P)_2Ni\diagdown\!\!\overset{\displaystyle C\diagup O}{\underset{\displaystyle O}{|}} \qquad Ref.\ 20 \qquad (7)$$

Cy = cyclohexyl   (XIII)

$$(\eta\text{-}C_5H_4Me)_2Ta(R)Cl + CO_2 \xrightarrow[-NaCl]{Na} (\eta\text{-}C_5H_4Me)_2Ta\overset{\displaystyle C\diagup O}{\underset{\displaystyle R}{\diagdown\!\!-O}} \qquad Ref.\ 21 \quad (8)$$

R = CH_2SiMe_3   (XIV)

$$Fe(PMe_3)_4 + CO_2 \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} (PMe_3)_4Fe\diagdown\!\!\overset{\displaystyle C\diagup O}{\underset{\displaystyle O}{|}} \qquad Ref.\ 24 \qquad (9)$$

                        (XVI)

These results seem to allow a generalization for the preliminary interaction between a mono-
functional complex and carbon dioxide. It can be viewed as resulting from the addition of a
carbene-like metal to the C-O multiple bond. By this process the metal established two strong
metal-carbon and metal-oxygen bonds with carbon dioxide. Such an interaction prevents proba-
bly a true activation of carbon dioxide for further transformations, depending mainly on the
oxophilicity of the metal involved. The general objective in CO_2-transition metal chemistry,
namely to form reactive metal-carbon σ bonds, is only partially achieved by the fixing sys-
tems outlined above. Moreover very few studies have been reported on the reactivity of metal-
bonded CO_2 in complexes (XIII), (XIV), and (XVI). This lack of information makes difficult
the correlation of the CO_2-metal interaction described in reactions (7-9) with much more
complex metal-promoted transformations of carbon dioxide. Many coordination compounds form
CO_2-complexes in a preliminary step, which is followed by the so-called disproportionation
or deoxygenation of CO_2, shown in reactions (10) and (11) (Ref. 25):
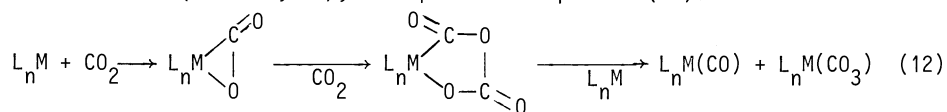
$$L_nM + 2\ CO_2 \longrightarrow L_nM(CO_3) + CO \qquad (10)$$

$$L_nM + CO_2 \longrightarrow L_nMO + CO \qquad (11)$$
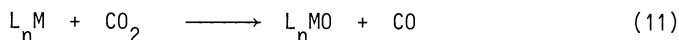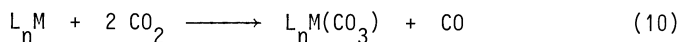
In both cases CO_2 is reduced to carbon monoxide by an electron-rich metal. Information on how
such complex transformations can occur or on how it may be possible to devise a control on
them can be derived from the chemistry of carbon dioxide 'analogues' when reacting with the
same kind of complexes. Carbon dioxide analogues are organic molecules, like isocyanates,
ketenes, carbodiimides and so on, having functional groups which maintain one of the preemi-
nent characteristics of CO_2, namely the cumulene structure and/or the electrophilic proper-
ties of the C=O group. The utilization of CO_2 related molecules allows the simulation of:
i) bonding modes of carbon dioxide to a single reactive site (Ref. 26);
ii) reactivity of the metal-bonded CO_2 molecule (Ref. 26);
iii) various steps leading to the disproportionation and deoxygenation of CO_2. Disproportio-
     nation of CO_2 seems to be the consequence of a metal-assisted head-to-tail dimerization
     of carbon dioxide (Refs 25, 27), as depicted in equation (12):

$$L_nM + CO_2 \longrightarrow L_nM\diagdown\!\!\overset{\displaystyle C\diagup O}{\underset{\displaystyle O}{|}} \xrightarrow{CO_2} L_nM\overset{\displaystyle O\diagdown\!\! C-O}{\underset{\displaystyle O-C\diagdown\!\! O}{|}} \xrightarrow{L_nM} L_nM(CO) + L_nM(CO_3) \quad (12)$$
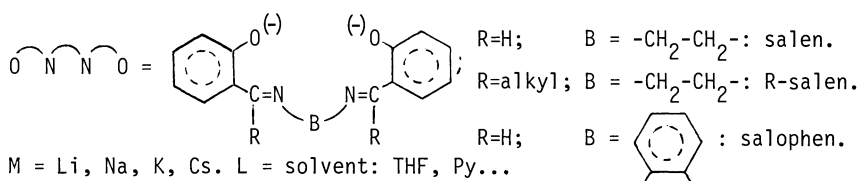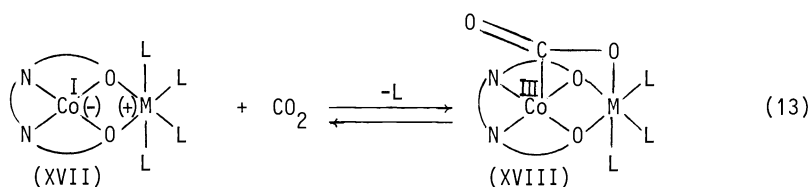
Transformations of CO_2 promoted by monofunctional complexes seem to be the consequence of a
preliminary addition of the carbenoid metal to the C-O multiple bond of carbon dioxide,
involving a two electron transfer.

Bifunctional complexes.
A careful examination of carbon dioxide reactivity engaged in very simple reactions, like the
hydration and the carboxylation of sodium phenoxide, shows that CO_2 seems to require the
simultaneous presence of acidic and basic sites for its activation (Ref. 28). Such a sugges-
tion, while very attractive, is very difficult to pursue in coordination chemistry, since a
large part of coordination compounds possess only one reactive site, either acidic or basic.
Such a combination of reactive sites is, however, typical of heterogeneous catalysts or of
enzymes, whose special activity is ascribed to this peculiar feature.

Our approach to complexes containing two different reactive sites is illustrated by the re-
duction of N,N'ethylenebis(salicylideneaminato)cobalt(II)-type complexes using alkali metals
(Ref. 29). Cobalt(II) is reduced to highly nucleophilic cobalt(I), while the alkali cation
remains complexed by the oxygen atoms of the same ligand. THF solutions of complexes (XVII)
are non-conducting, confirming the tight association between the alkali cation and Co(salen)-
type unit, and the X-ray structure showed the close proximity of the two reactive centers in
the solid state. Such complexes have been found active in fixing carbon dioxide in a rever-
sible way (Refs 22, 23). Fixation depicted in reaction (13) is viewed as resulting from the
nucleophilic attack by the cobalt(I) on the electrophilic carbon of CO_2, followed by the
interaction of the oxygen atoms with the Lewis acid (M^+):

$$\text{(XVII)} + CO_2 \; \underset{-L}{\rightleftharpoons} \; \text{(XVIII)} \tag{13}$$

M = Li, Na, K, Cs. L = solvent: THF, Py...

R=H;   B = $-CH_2-CH_2-$: salen.
R=alkyl;   B = $-CH_2-CH_2-$: R-salen.
R=H;   B = (phenyl) : salophen.

The anchoring mode of CO_2 to the bifunctional unit is well documented by the X-ray analysis
carried out on $[Co(pr-salen)(CO_2)K(THF)]$, (XV)(Refs 22, 23). The factors affecting both the
occurrence of reaction (13) and the status of coordinated CO_2 are: i) the bifunctional nature
of the complexes; ii) the tetradentate ligand, affecting the Co(I)-Co(III) reversible change;
iii) the reaction solvent, which can be competitive with the carbon dioxide oxygens in bin-
ding the alkali cation; iv) the nature of the alkali cation, making more or less strong the
M-O interaction. A further result emphasizes the fundamental role of the bifunctionality in
complexes (XVII): the same complexes resulted to be inactive in fixing carbon dioxide, when
the alkali cation is in a rigid coordination cage provided by a crown ether (Ref. 23). The
solid state structure of such a complex showed that all the coordination sites around the
alkali cation are filled by the oxygen atoms from the salen ligand and from the crown ether,
so that there is no coordination site available for the oxygen atoms from carbon dioxide
(Ref. 23).

The utilization of bifunctional complexes seems to provide the appropriate compounds promo-
ting the formation of a reactive metal-carbon σ bond from CO_2. Any study on the reactivity
of coordinated CO_2 in complexes like (XV) is prevented, however, by their reversibility,
since two different kinds of complexes are present in solution.

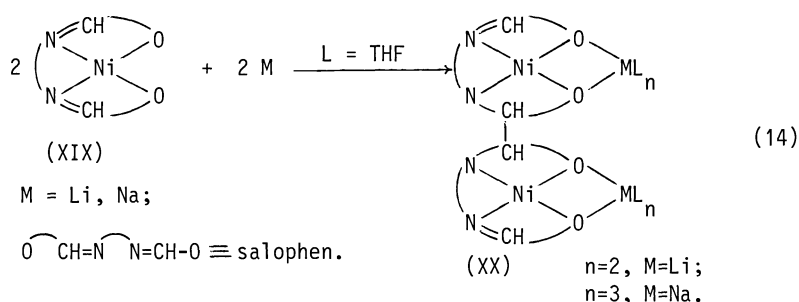Carbon-Carbon bond formation from carbon dioxide and carbon dioxide analogues.
Carbon dioxide can be engaged in different classes of reactions, by which a metal center
controls the carbon-carbon bond formation. They include:
i) reductive coupling of carbon dioxide;
ii) insertion of carbon dioxide in a metal-carbon σ bond;
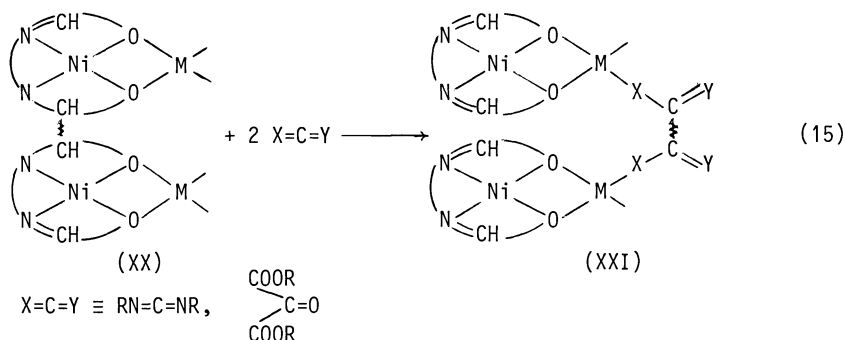iii) incorporation of carbon dioxide in an organic substrate.
The present report will deal with some new aspects of the reductive coupling reaction, the
other topics being covered by the reports of other laboratories (Ref. 19).

Reductive coupling.
Reductive coupling of carbon-carbon multiple bond promoted by metals is as much common as the reductive coupling of functional groups is rare. Various metal complexes promote the head-to-tail dimerization of a functional group (see carbon dioxide disproportionation)(Refs 27,30, 31,32). This result seems to be the consequence of a preliminary two electron transfer from the metal to the original functional group. Provided one has complex able to transfer only one electron to the substrate in a preliminary step, the metal-promoted process becomes the reductive coupling (Refs 31,32). The proposed pathway is variously supported by the utiliza-tion of mono- and bi-functional complexes undergoing one electron oxidations in reaction with carbon dioxide analogues (Refs 31,32). In case of bifunctional complexes, however, the assis-tance of the polydentate ligand, in terms of providing reactive sites, seems to play an inte-resting role (Ref. 32). Therefore the degree of electron transfer of the system towards carbon dioxide means a significantly different kind of activation for CO_2. This attractive hypothesis prompted us to search for a bifunctional complex which can act as one electron donor with carbon dioxide itself. To this purpose we reacted N,N'o-phenylenebis(salicylidene-aminato)nickel(II), Ni(salophen), with alkali metals:

$$2 \ (XIX) \ + \ 2 \ M \ \xrightarrow{L \ = \ THF} \ (XX) \tag{14}$$

(XIX)

M = Li, Na;

O⌒CH=N⌒ ⌒N=CH-O ≡ salophen.

(XX)   n=2, M=Li;
         n=3, M=Na.

In spite of the expected nickel(I) complex, reaction (14) promoted the reductive coupling of two imino groups, so that two Ni(salophen) complexes are joined by a C-C bond and the final complexes (XX) are nickel(II) derivatives (Refs. 33,34). The X-ray analysis confirmed the proposed structure for complexes (XX), the most relevant structural feature being the rather long C-C bond joining two metallic units [1.64(4) Å, M = Li; 1.58(2) Å, M = Na]. Complexes (XX) are diamagnetic both in solution and in the solid state, so that any equilibrium between the plausible free radical like species, formed in a preliminary step, and the dimeric form (XX) can be ruled out (Refs 33,34). Complexes (XX) are unexpectedly reactive, despite being Ni(II) derivatives, towards electron acceptor molecules. They act as two electron donors with a variety of reagents, cleaving the C-C bond and reforming the original Ni(salophen). In all their reactions, the electron reservoir of complexes (XX) appears to be neither the metal nor the salophen ligand, but rather the C-C bond. Because of their bifunctional nature and of their electron availability, complexes (XX) are possible candidates for the reduction of CO_2 and CO_2-like molecules. A preliminary result in this field is shown in equation (15):

$$(XX) \ + \ 2 \ X=C=Y \ \longrightarrow \ (XXI) \tag{15}$$

(XX)   (XXI)

$X=C=Y \equiv RN=C=NR,$ COOR
                            $>C=O$
                            COOR

Reaction (15) shows an intersting phenomenon: formation of a C-C bond between CO_2-like mole-cules occurs with the simultaneous cleavage of a C-C bond on the polydentate ligand, thus nickel(II) is able to promote electron transfer *via* cleavage and formation of C-C bonds. (Ref. 34).

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