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METAL-CARBON AND CARBON-CARBON BOND FORMATION FROM SMALL MOLECULES AND ONE CARBON FUNCTIONAL GROUPS.

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Abstract - Metal promoted elementary transformations on C_1 molecules (CO_2, CH_2O, CO), including their reversible fixation, are described. Utilization of monofunctional vs bifunctional (acid-base) complexes represents the main point in the strategy for the activation of a C_1 molecule, the primary objective being the formation of a reactive metal-carbon bond. Simulation of CO_2 by related molecules discloses general pathways leading to a C-C bond formation from one carbon functional groups. Transformations of a η^2-C,O metal-bonded formaldehyde generated metal-bonded species supposed to be key intermediates in carbon monoxide reduction and in C_2 units synthesis. A comparison is sketched on some extreme models [early transition metals vs copper(I)] to be used in carbon monoxide activation processes.

INTRODUCTION

Organometallic chemistry is variously pervaded with problems related to the activation of C_1 molecules, namely carbon dioxide, carbon monoxide and formaldehyde. Their utilization as a carbon source for the synthesis or functionalization of organic molecules represents the aim of a large part of inorganic chemistry. This goal, which can be achieved by a variety of processes,requires the utilization of transition metals for modifying the usual reactivity of these molecules. The so-called metal promoted 'activation' of C_1 molecules must have as a primary objective the formation of a:

i) metal-carbon σ bond.
   In a few cases this result is achieved by the simple fixation of the molecule to the metal in its intact form.
ii). carbon-carbon bond.
   The synthesis of a C_2 unit may represent the most attractive modelling study in this area.

The three C_1 molecules have different requests in terms of a metal center to be used; since we are dealing with an extraordinary large number of metals bonding CO, while only two carbon dioxide-(Refs 1-4) and two formaldehyde-(Refs 5&6) complexes have been identified so far. The general strategies we developed in this area and which have been variously applied according to the nature of the C_1 molecule forsee the utilization of:

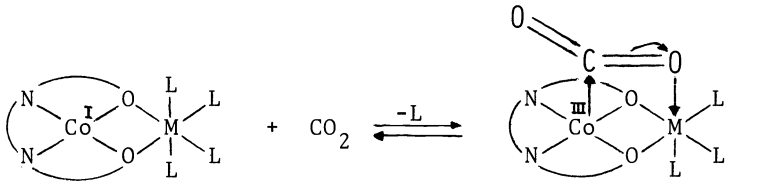
i) 'monofunctional' complexes, containing only one reactive metal center in a rather rich coordination sphere and with a very limited number of metal orbitals available for molecular activation processes.
ii) 'bifunctional' complexes, containing in their structure a transition metal in a low oxidation state (basic center) along with an acidic center. These complexes can simulate the bifunctional units working both in heterogeneous and enzymatic catalysis.

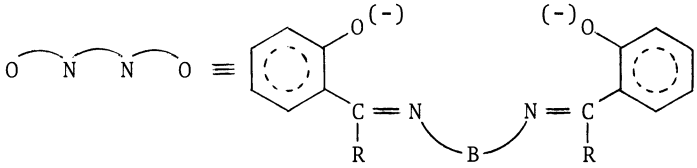
iii) structural and electronic 'analogues' of C_1 molecules. Since CO_2 very often entails rather complicated processes in reactions with transition metals, it can be simulated by analogous organic functional groups.

CARBON DIOXIDE AND RELATED MOLECULES ACTIVATION

Bifunctional complexes fixing carbon dioxide

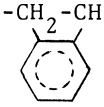
Fixation of carbon dioxide in its intact form to a transition metal is a very rare result, achieved by a unique class of compounds having the 'basic' structure sketched for complexes (1):





M = Li, Na, K, Cs R = H; B = $-CH_2-CH_2-$: salen

L = solvent: THF, Py... R = Alkyl; B = $-CH_2-CH_2-$: R-salen

R = H; B =  : sal-o-phen

They contain, in the same structure, a d^8-square planar nucleophilic Cobalt(I) and an acidic center (alkali cation) (Ref. 7). Reaction with carbon dioxide is a reversible process occurring under mild conditions. The bifunctional (acid-base) nature of the starting material (1), as well as the anchoring mode of carbon dioxide to the bifunctional unit in the final complex (2) are well documented (Refs 3 & 4). Fixation of carbon dioxide depicted in reaction (1) is viewed as resulting from the nucleophilic attack by the Cobalt(I) on the electrophilic carbon of carbon dioxide, followed by the interaction of the oxygens of carbon dioxide with the Lewis acid (Ref. 4). The factors affecting both the occurrence of reaction (1) and the 'status' of the fixed carbon dioxide are: i) the 'bifunctional' nature of complexes (1); ii) the tetradentate ligand; iii) the reaction solvent; iv) the alkali cation and the transition metal.

Our attention was mainly focused on the bifunctional nature of complexes (1), as the factor playing the most important role. It was found, in fact, that highly nucleophilic Cobalt(I) not occurring in the ion-pair form does not react either with carbon dioxide or with carbon dioxide-related molecules (Ref. 8). A further experiment emphasizes the fundamental role of the alkali cation. When alkali cation is encapsulated in a rigid coordination cage, complexes (1) are inactive in fixing carbon dioxide. Reaction (2) exemplifies such a result:

$$\underset{(3)}{2\left[Co(salen)Na(CO_2)\right]} + \left\{C_{20}H_{36}O_6\right\} \xrightarrow{-2\ CO_2} \underset{(4)}{\left\{\left[Co(salen)Na\right]_2(C_{20}H_{36}O_6)\right\}} \quad (2)$$

$C_{20}H_{36}O_6$ ≡ dicyclohexano-18-crown-6

Complex (3) loses carbon dioxide by the reaction with dicyclohexano-18-crown-6 and in the final complex sodium cation is surrounded by five oxygens from the 'salen' unit and from the crown ether. The solid state structure of (4) (Fig.1)

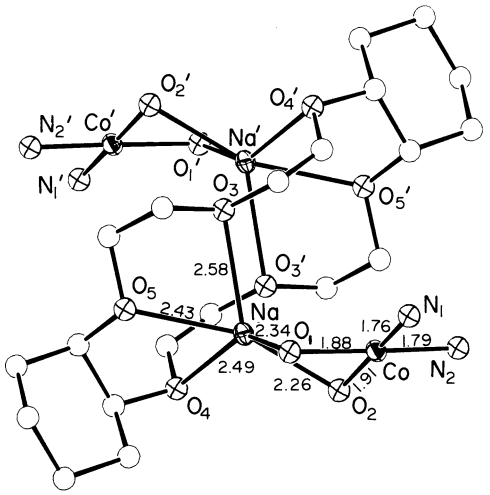


Fig. 1. X-ray structure of complex (4)

shows the presence of the intact bifunctional unit without coordination sites available on the alkali cation for binding the oxygens of carbon dioxide (Ref. 4). All the other factors cited above affect reaction (1) and the status of bonded carbon dioxide slightly less, as an indirect consequence of their influence on the Cobalt(I)-Cobalt(III) redox potential.

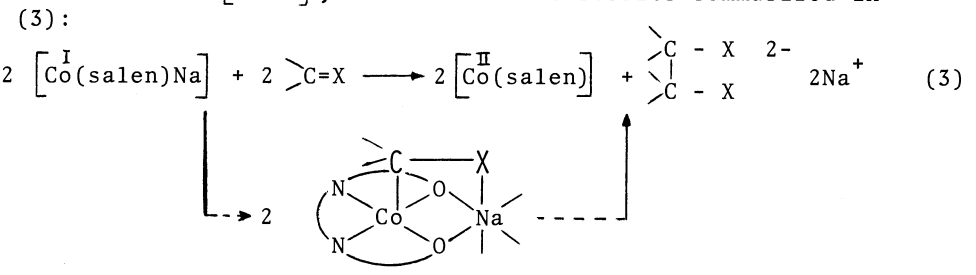
Bifunctional complexes promoting C-C bond formation from carbon dioxide related molecules

The utilization of carbon dioxide analogues in reaction with model complexes allows:

i) to simulate the fundamental steps involved in the most elementary metal-promoted carbon dioxide transformations, like the so-called disproportionation;

ii) to devise a special strategy for avoiding undesired transformations and for realizing transformations of carbon dioxide like those leading to a C-C bond formation.

Replacing carbon dioxide in reaction (1) by molecules which maintain one of its preeminent characters, that is, the [>C=O] activated functional group or the cumulene structure [X=C=Y], we observed the results summarized in reaction (3):



The carbon dioxide analogue [>C=X: Me-C(=O)-COOMe; EtOOC-C(=O)-COOEt; R-N=C=N-R] is reductively coupled to form a C-C single bond, while Cobalt(I) is oxidized to Cobalt(II) (Ref. 9). Reaction (3) shows a plausible pathway leading to the dimerization of a functional group: the fixation of the >C=X group on the bifunctional unit is followed by the homolytic splitting of the Co-C σ bond giving a carbon radical dimerizing to the final organic part. Reaction between [Co(salen)Na] and diphenylketene (DPK) suggests, however, that the

C-C bond formation might be a ligand-assisted process rather than a metal-assisted one (Ref. 9). The addition of two DPK molecules occurs to an imino functional group of the salen, which acts as a coupling agent. The constant feature observed in all reactions between Cobalt(I) and carbon dioxide-like molecules is the oxidation of the metal center by one electron, while fixation of carbon dioxide by the same metal occurs with the Cobalt(I) being oxidized to Cobalt(III).

Concluding, it seems that C-C bond formation might be a possible process, provided there is a complex able to transfer only one electron to carbon dioxide. This attractive hypothesis suggested us to synthesize $[Ni(salen)Na(THF)_3]$ (Ref. 10), a bifunctional complex which can act only as one electron donor system even with carbon dioxide itself.

Carbon dioxide and related molecules activated by monofunctional complexes

The utilization of 'oxophilic' metals like titanium and vanadium in low oxidation state in carbon dioxide chemistry, was mainly suggested by the nature of carbon dioxide, which is an oxygen-rich electrophilic molecule. $Cp_2Ti(CO)_2$ and Cp_2V promote $[Cp = \eta^5\text{-}C_5H_5]$ the so-called disproportionation of carbon dioxide

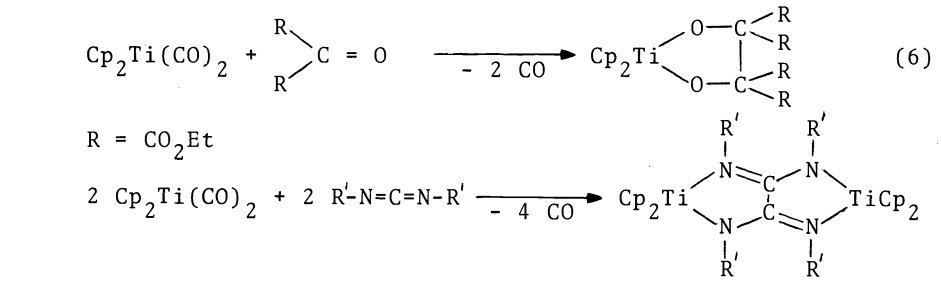
$$2\ CO_2 + 2\ e^- \longrightarrow CO_3^{--} + CO$$

by the following reactions

$$4\ Cp_2Ti(CO)_2 + 4\ {}^{13}CO_2 \xrightarrow[-8\ CO]{} [(Cp_2Ti)_4({}^{13}CO_3)_2] + 2\ {}^{13}CO \quad (4)\ (\text{Ref.}11)$$

$$Cp_2V + 2\ CO_2 \longrightarrow [Cp_2V(CO_3)] + [Cp_2V(CO)] \quad (5)\ (\text{Ref. } 12)$$

The pathway leading to this result was clarified replacing CO_2 with diphenylketene (Ref. 13). These reactions suggested that the disproportionation of carbon dioxide very probably involves, as a key step, the head-to-tail dimerization of carbon dioxide itself. Reducing the electron acceptor properties of the carbon dioxide-like molecule, we observed a head-to-head dimerization of the functional group (Ref. 14):



(6)

(7)

The occurrence of reactions (6) and (7), leading to a C-C bond formation has been viewed as being controlled by a preliminary step in which only one electron is transferred from the metal to the functional group:

$$L_nM^o + \rangle C{=}X \longrightarrow [L_nM^I\text{-}X\text{-}\dot{C}\rangle]$$

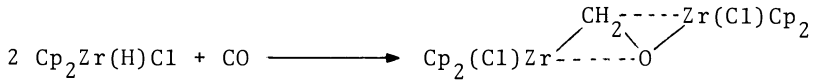
Once again the C-C bond formation from a $\rangle C{=}X$ functional group seems to require a metallic center able to transfer only one electron to the substrate.

FORMALDEHYDE ACTIVATION

A recognized role for organometallic chemistry is that of providing stable models for species postulated as intermediates thus permitting a precise definition of their chemistry when bonded to a transition metal. The most plausible products of a stoichiometric hydrogenation of carbon monoxide include formaldehyde (Ref. 15). Moreover, many plausible schemes have been proposed as

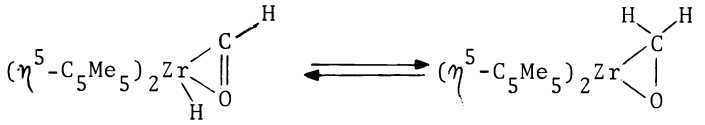
involving a close relationship between formyl, formaldehyde, hydroxymethyl and carbene.

A few years ago we observed that carbon monoxide can be reduced to a $[CH_2O]$ species bridging two zirconium atoms (Ref. 16):



(8)

the chemistry of which only slightly resembles that of a metal bonded formaldehyde, but more so that of an oxomethyl group. On the other hand, carbon monoxide undergoes a remarkable series of transformations by $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$ (Ref. 17) for which J.E. Bercaw and coworkers suggest a reaction scheme where the possibility of an equilibrium between a formyl zirconium hydride species and a formaldehyde zirconium species is shown, although there are no data that define this rearrangement clearly



We synthesized, very recently, a formaldehyde complex which is quite close to the intermediate proposed by J.E. Bercaw (Ref. 6). The chemistry of such a complex might give a significant contribution towards the understanding of the reduction of carbon monoxide by early transition metals. By a direct reaction of vanadocene with paraformaldehyde we isolated a monomeric formaldehyde complex containing $[CH_2O]$ acting as a η^2-C,O dihapto ligand in $[Cp_2V(CH_2O)]$, (5), which has been structurally characterized. The most relevant bond distance is the C-O length [1.35 Å] which is surprisingly shorter than the corresponding bond [C-O = 1.59 Å] found in the only formaldehyde complex reported so far, $[Os(CO)_2(PPh_3)_2(\eta^5\text{-}CH_2O)]$ (Ref. 5). The vanadium bonded formaldehyde undergoes a number of transformations to some species postulated as occurring in reduction of carbon monoxide. Reaction with carbon monoxide on complex (5) gives $[Cp_2V(CO)]$ and methyl formate by a process which is strictly related to the disproportionation of the formyl group observed in $[CpRe(CHO)(CO)(NO)]$, (Ref. 18), and involving the same kind of hydrido transfer from one $\eta^2\text{-}CH_2O$ to another one. Electrophiles attack the oxygen atom in complex (5) giving alkyl-vanadium(IV) derivatives, $[Cp_2V\text{-}CH_2OR]^+$, which undergo reaction with carbon monoxide (Ref. 6). Reaction with different sources of protons on (5) gave, probably, hydroxymethyl groups, whose carbonylation has been invoked as the process leading to the synthesis of C_2 units starting from carbon monoxide and hydrogen (Ref. 19).

CARBON MONOXIDE ACTIVATION: EARLY TRANSITION METALS AND COPPER(I) COMPLEXES AS EXTREME MODELS IN CARBON MONOXIDE CHEMISTRY

A useful comparison can be drawn between Copper(I) and early transition metals as extreme models to be used in carbon monoxide chemistry. The big difference in 'oxophilicity' and the different behaviour in reaction with H_2 give complementary information for devising new strategies and interpretative schemes in carbon monoxide chemistry. Recently our attention has been focused on the synthesis of some relatively stable Cu(I)-CO complexes to be used as models in carbon monoxide chemistry. They include:

i) mononuclear and dinuclear complexes containing terminal electrophilic carbon monoxide (Ref. 20):

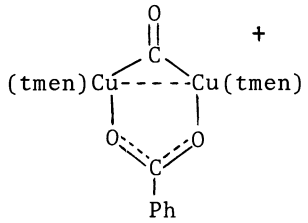
$[L_nCu(CO)]^+$ — L_n = diethylenetriamine, ethylenediamine, histamine,...

$[L'_n(CO)Cu\text{-}X\text{-}Cu(CO)L'_n]^+$ — L'_n = N,N,N',N'-tetramethylethylenediamine

X = Cl, Br, I

ν_{CO} = 2060 - 2117 cm^{-1}

ii) dinuclear complexes containing bridging carbon monoxide (Ref. 21), exemplified by complex (6)



tmen = N,N,N',N'-tetramethylethylenediamine

ν_{CO} = 1927 cm^{-1}

(6)

The bridging bonding mode of carbon monoxide in Copper(I) complexes gives insights both on the occurrence of dicopper units in natural systems and on the rôle played by Copper(I) in carbon monoxide reduction. The metal-induced change on the reactivity of bonded carbon monoxide is largely dominated in Copper(I) chemistry by its kinetic lability and its easy reaction with hydrogen, while in the case of complexes like $Cp_2Ti(CO)_2$, $Cp_2V(CO)_2^+$ and $Cp_2V(CO)$ the metal-oxygen bond energy is, probably, the driving force of carbon monoxide transformations.

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REFERENCES

1. M. Aresta and C.F. Nobile, J. Chem. Soc. Dalton Trans., 708 (1977).
2. C. Floriani and G. Fachinetti, J. Chem. Soc. Chem. Commun., 615 (1974).
3. G. Fachinetti, C. Floriani and P.F. Zanazzi, J. Am. Chem. Soc., 100, 7405, (1978).
4. S. Gambarotta, F. Arena, C. Floriani and P.F. Zanazzi, submitted.
5. K.L. Brown, G.R. Clark, C.E.L. Headford, K. Marsden and W.R. Roper, J. Am. Chem. Soc., 101, 503 (1979).
6. S. Gambarotta and C. Floriani, to be submitted.
7. G. Fachinetti, C. Floriani, P.F. Zanazzi and A.R. Zanzari, Inorg. Chem., 18, 3469 (1979).
8. H. Eckert and A. Schier, Angew. Chem. Int. Ed., 18, 794 (1979).
9. S. Gambarotta, F. Arena, C. Floriani and A. Gaetani-Manfredotti, submitted.
10. S. Gambarotta, C.Floriani and P.F. Zanazzi, submitted.
11. G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 101, 1767 (1979).
12. M. Pasquali and C. Floriani, unpublished results.
13. G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa and C. Guastini, Inorg. Chem., 17, 2995 (1978); S. Gambarotta, M.Pasquali, C. Floriani, A. Chiesi-Villa and C. Guastini, Inorg. Chem., 20, 1173 (1981).
14. M. Pasquali, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 101, 4740 (1979); Inorg. Chem., 20, 349 (1981).
15. E.L. Muetterties and J. Stein, Chem. Rev., 79,479 (1979).
16. G. Fachinetti, C. Floriani, A. Roselli and S. Pucci, J. Chem. Soc. Chem. Commun., 269 (1978).
17. P.T. Wolczanski and J.E. Bercaw, Acc. Chem. Res., 13, 121 (1980).
18. C.P. Casey, M.A. Andrews and D.R. McAlister, J. Am. Chem. Soc., 101, 3371, (1979); C.P. Casey, S.M. Neumann, M.A. Andrews and D.R. McAlister, Pure Applied Chem., 52, 625 (1980).
19. B.D. Dombek, J. Am. Chem. Soc., 101, 6466 (1979).
20. M. Pasquali, C. Floriani and al., Inorg. Chem., 17, 1684 (1978); idem, 19 1191 (1980); idem, 19, 2525 (1980); J. Chem. Soc. Chem. Commun., 197 and 937 (1979).
21. M. Pasquali, C. Floriani, A. Gaetani-Manfredotti and C. Guastini, J. Am. Chem. Soc., 103, 185 (1981).