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Carbon dioxide coordination chemistry: metal complexes and surface-bound species. What relationships?

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Abstract

Syntheses, studies of bonding and structures of carbon dioxide complexes have been well-developed in recent years as has the synthesis and characterization of metal formate complexes because of their perceived relationships to intermediates in the catalytic activation of carbon dioxide. Vibrational spectroscopy, usually infrared spectroscopy, has played a key role in the development of this chemistry. Surface scientists studying the reactions of CO_2 and its reduction by hydrogen are now able to use powerful techniques for acquiring vibrational data in the infrared region which help to identify surface-bound species. As more results emerge from these groups, it is apparent that there are many similarities in the spectral properties and reactions of the coordination compounds of CO_2 and their surface-bound analogs.

Keywords: Carbon dioxide; Metal complexes; Surface reactions; Vibrational spectra

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1. Introduction and scope

The possibility of using CO_2 as the starting material for the synthesis of fine chemicals provides an attractive alternative to compounds presently derived from petroleum [1] and efforts to convert CO_2 to useful chemicals will inevitably center on transition metal catalysts [2]. Furthermore, efforts to enhance the yield of hydrogen in water gas shift reactions also focus on carbon dioxide interactions with transition metal catalysts [3]. For all these reasons, a broader understanding of the coordination chemistry of CO_2 is being sought by investigators around the world. Transition metal–carbon dioxide complexes may provide both structural and functional models for surface-bound intermediates in catalytic conversion processes. Also, studies of the stoichiometric reactions of CO_2 with active metal complexes can provide useful synthetic routes to a variety of organic compounds and have formed the basis for some new catalytic procedures [4]. In addition to the activities of organometallic and coordination chemists, surface scientists have also been trying to find effective metal catalysts for the activation and reduction of CO_2. Several reviews of these activities have appeared recently [5,6]. The present article is intended to provide a brief overview of certain activities being pursued and will focus on the CO_2–metal complexes and their reactions from coordination chemistry that appear to be closely related to the surface chemistry of carbon dioxide.

2. Carbon dioxide–organometallic complexes

Particularly in the past decade, many CO_2–metal complexes have been identified. Although initially thought to be a poor ligand [7], carbon dioxide has demonstrated a variety of coordination modes in its metal complexes. The sections below profile the synthesis, characterization by X-ray crystallography and IR spectroscopy and some characteristic reactions of the compounds with emphasis on the complexes where CO_2 is bound to one or two metal centers.

2.1. Synthesis

The synthetic procedures for a few types of carbon dioxide complexes are described below; the structural types are illustrated in Fig. 1 (see discussion in Section 2.2). Discussion is further limited to those compounds which can be isolated or at least studied by IR and NMR spectral techniques to confirm a metal-bound CO_2 ligand.

Complexes of the η^1- and η^2-types are prepared by direct reaction of a metal complex with carbon dioxide. Thus metal centers which have a coordination vacancy (or an easily displaced ligand) and are nucleophilic because of high electron density on the metal center, due to charge or the presence of electron donating ligands, can bind the weakly electrophilic CO_2 molecule through carbon. The η^1-CO_2 complexes are not robust; their isolation usually requires glove box or Schlenk techniques, low temperatures and strict exclusion of oxygen and water. Examples of compounds which have been prepared by direct reaction with CO_2 are shown in Table 1.

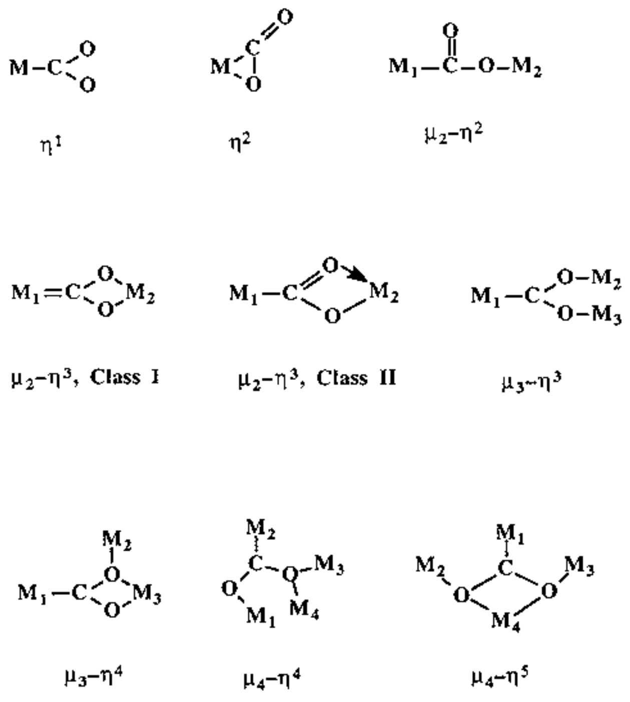


Fig. 1. Structural types of metal–CO_2 complexes.

Table 1
Examples of η^1 and η^2 CO_2 complexes prepared by direct carbonation

Compound	Precursors	Reference
	η^1-Complexes	
$Ir(diars)_2(Cl)(CO_2)$(**1**)	$Ir(diars)_2(Cl)$	[7]
$Ir(dmpe)_2(Cl)(CO_2)$(**2**)	$Ir(dmpe)_2(Cl)$	[7]
$Rh(diars)_2(Cl)(CO_2)$(**3**)	$Rh(diars)_2(Cl)$	[8]
	η^2-Complexes	
$Ni(PCy_3)_2(CO_2)$(**4**)	$Ni(PCy_3)_3$ or $[Ni(PCy_3)_3]_2N_2$	[9]
$Fe(PMe_3)_4(CO_2)$(**5**)	$Fe(PMe_3)_4$	[10]
$Fe(depe)_2(CO_2)$(**6**)	$Fe(depe)_2(N_2)$	[11]
$Pd(PMePh_2)_2(CO_2)$(**7**)	$Pd(PMePh_2)_2$ $(CH_2{=}CHCO_2Me)$	[12]
$Cp'_2Nb(CO_2)(CH_2SiMe_3)$(**8**)	$Cp'_2Nb(Cl)$ (CH_2SiMe_3)	[13]
$Cp_2Mo(CO_2)$(**9**)	$Cp_2Mo(PhC{\equiv}CPh)$	[14]
$Cp_2Ti(PMe_3)(CO_2)$(**10**)	$Cp_2Ti(PMe_3)_2$	[15]
Trans-$Mo(PMe_3)_3(CNR)(CO_2)_2$(**11**–**15**) R = Me, *i*-Pr, *t*-Bu, Cy, CH_2Ph	*Trans*-$Mo(PMe_3)_4$ $(CO_2)_2$, RNC	[15]

With the η^1 complexes reported by Herskovitz [7,8], it was necessary to pressurize the system with CO_2 in order to form iridium and rhodium complexes (**1**–**3**); ligand displacement does not occur in forming these compounds. The η^2 complex $Ni(CO_2)(PCy_3)_2$ (**4**) studied by Aresta and Nobile [9] was made by reaction of $Ni(PCy_3)_3$ or $[Ni(PCy_3)_3]N_2$, in toluene, with CO_2 at atmospheric pressure and was obtained as the toluene solvate (**4**).

Synthesis of an η^2-CO_2 complex (**5**) was reported also by Karsch [10] from reaction of $Fe(PMe_3)_4$ with CO_2 in pentane; a second product, $Fe(PMe_3)_3(CO)(CO_3)$ was also obtained. Properties of the complex $Fe(CO_2)(depe)_2$ (**6**), fully characterized recently by Komiya et al. [11], lend support to the formulation of the first compound by Karsch. Compound **6** was prepared by CO_2 displacement of nitrogen from the corresponding dinitrogen complex; other ligand displacement reactions have been used also [12–16]. Both direct CO_2 addition and other synthetic strategies have been developed for compounds with bridging CO_2 ligands; see Refs. [5a,b] for additional discussions.

Mascetti and Tranquille [17] prepared adducts of CO_2 by low-temperature matrix isolation techniques; the oxophilic metals Ti, Cr and V were observed to be oxidized, then coordinated to CO_2 in η^2 −C,O fashion. Complexes of Fe and Co were formulated with η^1-C bonding, but the adducts with Ni could not be identified precisely. Recently, matrix isolation studies by Galan et al. [18] have been reported for the interaction of Ni atoms with CO_2 under several conditions; the η^2-C,O mode was the preferred form here when CO_2 matrices were used. Also, the coordination of CO_2 was promoted by using N_2 together with CO_2 in the matrix; these studies, coupled with studies of isotopically labeled species and DFT studies suggest that $Ni(N_2)(CO_2)$ and $Ni(N_2)_2(CO_2)$ are formed.

2.2. Bonding and structural types

Several theoretical treatments of the bonding of a carbon dioxide molecule to a single metal center have appeared. The calculations have focused on four basic modes of CO_2 coordination: (a) η^1-C; (b) η^2-C, O (side-on); (c) η^1-O (end-on) and (d) η^2-O,O. A review of the results of calculations on the organometallic complexes (modes a and b) appeared in 1992 [19]; therefore, only a summary of these results and will be provided.

As a heterocumulene, CO_2 has two sets of π molecular orbitals which are orthogonal. For η^1 and η^2 bonding involving carbon and a metal, these are in two sets: (a) the π, $n\pi$, and π^* molecular orbitals which lie in the plane of the metal and CO_2 (parallel) and (b) an equivalent set which is in a plane perpendicular to the first set (perpendicular). The 'parallel' molecular orbitals are most important in bonding to transition metals. In qualitative terms, for the η^1-C mode there is a strong charge transfer interaction between a d_{z^2} metal orbital and the π^* orbital of CO_2. In contrast, the η^2 mode has been compared to olefin–metal binding. This model shows σ-bonding involving the π orbital of CO_2 and an empty d_{z^2} metal orbital together with π-bonding involving a filled d_{xz} metal orbital and the empty π^* orbital of CO_2. Although previous calculations on the interaction of Ti with CO_2 had indicated that end-on or η^2-O,O modes were preferred (see Section 3.3), recent calculations [20] suggest that an intermediate triplet state side-on complex may cause the C–O bond cleavage which was experimentally observed [17].

Since reviews of the structural characteristics of metal-CO_2 complexes have appeared recently [5], only a few of each representative type will be described here. The only complex of the η^1-C type to be structurally characterized is the rhodium complex (**3**) reported by Herskovitz et al. [8] X-ray structural analysis showed a Rh–C(1) bond distance of 2.05(2) Å and C–O bond distances of 1.20(2) and 1.25(2) Å; the O–C–O angle was 126(2)°.

The first compound of the η^2-type to be structurally characterized (and the first CO_2 complex to be so characterized), **4**, was reported by Aresta and Nobile [9] and involved an almost planar coordination environment about the nickel atom with two bulky phosphine ligands in addition to the CO_2. The carbon dioxide ligand has one short C–O bond (1.17 Å) and one longer one of 1.22 Å. The compound also showed a very large O–C–O angle of 133°. Later, Dohring et al. [21] were able to characterize structurally the solvent-free complex. The iron complex, $Fe(CO_2)(depe)_2$ (**6**), characterized by Komiya et al. [11] has trigonal bipyramidal geometry about the iron atom with the CO_2 ligand in the equatorial plane. It is unique among η^2-CO_2 complexes with two relatively long C–O bonds, 1.25(3) and 1.28(2) Å, and a relatively small O–C–O angle of 124(2)°.

The CO_2-bridged bimetallic complexes involve coordination of the carboxyl carbon to one metal and bonding of one or both carboxyl oxygens to a second metal center. The first compounds of the μ_2-η^2 type were reported by Collins et al. [22] The O-alkylated derivative of one was characterized by X-ray analysis, supporting the formulation of the precursor as a metallacycle. More recently, Bergman et al. [23] have structurally characterized a related metallacyclic complex with CO_2 bridged between iridium and zirconium.

Carbon dioxide complexes of cobalt have been studied by Creutz et al. [24]; the structure of a polymeric complex, $[Co^{III}(en)_2(CO_2)(ClO_4) \cdot H_2O]_n$, with CO_2 bridged in μ_2-η^2 fashion between cobalt atoms, was reported. At about the same time, Gibson et al. [25] reported the iron–rhenium compound, $CpFe(CO)(PPh_3)(CO_2)Re(CO)_4(PPh_3)$, which has the CO_2 ligand bound through carbon to the iron atom and through one oxygen to the rhenium atom. This complex also showed one short carboxyl C–O bond (1.226(3) Å) and one longer bond (1.298(3) Å) and had an O–C–O angle of 121.9(3)°.

There are two distinct types of compounds having the carboxylate carbon bound to one metal center and both oxygens bound to a second metal. The distinguishing feature for Class I and Class II compounds is the unequal nature of the $O–M_2$ bond lengths in Class II compounds (see discussion in Ref. [5b]). Additionally, the O–C–O bond angles of Class II compounds are usually larger than those in Class I. Most of the compounds in Class I have the CO_2 ligand bridged between two transition metals and are characterized by nearly equal C–O bond lengths as well as nearly equal $O–M_2$ bond lengths and a small O–C–O bond angle (in the range 106–114° in the compounds characterized to date). The compounds in Class II which have been structurally characterized, so far, are ones in which the two carboxylate oxygens are bound, unequally, to a tin atom.

The first CO_2-bridged compound of the μ_3-η^3 type to be structurally characterized was an osmium cluster anion [26]. Later, Guy and Sheldrick reported [27] the complete structural analysis of the compound. A tetranuclear rhenium complex was reported by Beck et al. [28] which showed two bridging CO_2 ligands, each bound in μ_3-η^3 fashion. Caulton et al. [29] reported the characterization of a rhodium/osmium complex which has the carboxylate carbon bound to the osmium center and each oxygen bound to different rhodium centers. Cutler et al. have characterized recently additional bis-CO_2 complexes which exhibit this type of bonding [30].

Although described previously [31] as an η^1-CO_2 complex with the molecular formula *cis*-$[Ru(bpy)_2(CO)(CO_2)] \cdot 3H_2O$, each unit is dimeric, held together with the aid of hydrogen bonding involving six water molecules [5b]. The bonding is μ_4-η^4 with hydrogen bonds assuming three of the coordination sites. Few examples exist of the other two structurally characterized types involving fully chelated CO_2 molecules [5]. Compounds of these types have not yet been implicated in catalytic processes.

2.3. Infrared spectral characteristics

All transition metal complexes which have been structurally characterized possess bent CO_2 ligands with the internal O–C–O angle varying from 101 to 136° [5]. The vibrational bands for coordinated CO_2 do not resemble those of the linear molecule [ν_{asym} 2349, ν_{sym} 1388 or 1285 (one of these is due to Fermi resonance; both are IR inactive) and δ 667 cm^{-1}] [32], but can be expected to be more closely related to metal-bound $\cdot CO_2^-$ or, possibly, to the radical anion itself. IR spectral bands for the free radical anion have been calculated [33] as 1677, 1405 and 607 cm^{-1}; the first two are stretching vibrations and the last is an O–C–O bending vibration.

With the isolated transition metal–CO_2 complexes, only the C–O stretching vibrations will be identified for each complex. The compounds are separated by type; data from representatives of each type are shown in Table 2. The higher frequency band is assigned to ν_{asym} and the lower one is assigned to ν_{sym} in each case. Few examples of the η^1-type are available, but these have ν_{asym} near 1600 cm^{-1} and ν_{sym} near 1200 cm^{-1}, including $Fe(CO_2)$ generated by matrix isolation techniques [17]. The η^2 complexes exhibit much higher ν_{asym} positions and the ν_{sym} band position is lower. With the μ_2–η^2 complexes it is apparent from Table 2 that $\Delta\nu$ is large for these compounds; differences in the range 300–400 cm^{-1} are typical for the acyclic compounds and can be much larger for those compounds with metallacyclic rings. The magnitude of $\Delta\nu$ and the band positions are sufficient to distinguish these from other types of CO_2-bridged bimetallic complexes. The ν_{asym}

Table 2
IR ν_{OCO} bands (cm^{-1}) for several types of CO_2 complexes

Compound	Type	ν_{asym}	ν_{sym}	Reference
$Rh(diars)_2(Cl)(CO_2)$	η^1	1610	1210	[8]
$Ni(PCy_3)_2(CO_2)$	η^2	1740	1140, 1094	[9]
$[Pt(PEt_3)_2(Ph)]_2(CO_2)$	μ_2-η^2	1495	1290, 1190	[30]
$[Co(en)_2(CO_2)](ClO_4)\cdot H_2O$		1512	–	[24]
$CpRe(NO)(PPh_3)(CO_2)GePh_3$		1545	1048	[34]
$CpFe(CO)(PPh_3)(CO_2)Re(CO)_4(PPh_3)$		1505	1135	[25]
$Cp^*Re(CO)(NO)(CO_2)W(CO)_3Cp$		1541	1100	[35]
$CpFe(CO)_2(CO_2)SnPh_3$		1499	1159	[36]
cis,cis-$Ru(bpy)_2(CO)(CO_2)$		1507	1176	[37]
–$Ru(bpy)_2(CO)^{+2}2PF_6^-$				
$[(PPh_3)_2(Cl)$(*t*-Bupy)Ir		1593	1022	[22]
–$(\mu$-$O)(\mu$-$CO_2)Os(O)_2$(*t*-Bupy)$_2]^+ClO_4^-$				
$Cp^*Ir(\mu$-*t*-$BuN)(\mu$-$CO_2)ZrCp_2$		1569	1015	[23]
$Ru_2(\mu$-$CO_2)(CO)_4[(\mu$-$OPr)_2PNEtP(OPr)_2]_2$		1710	–	[38]
$Cp^*Re(CO)(NO)(CO_2)Re(CO)_3(PPh_3)$	μ_2-η^3, Class I	1437	1282	[39]
$CpFe(CO)(PPh_3)(CO_2)Re(CO)_3[P(OEt)_3]$		1435	1252	[40]
$CpRu(CO)_2(CO_2)Zr(Cl)Cp_2$		1348	1290	[41]
$Cp^*Re(CO)(NO)(CO_2)Zr(Cl)Cp_2$		1348	1288	[42]
$Cp^*Re(CO)(NO)(CO_2)Mo(CO)_2Cp$		1319	1285	[35]
$Cp^*Re(CO)(NO)(CO_2)W(CO)_2Cp$		1321	1287	[35]
$CpRe(NO)(PPh_3)(CO_2)SnPh_3$	μ_2-η^3, Class II	1395	1188	[34]
$Cp^*Fe(CO)_2(CO_2)SnPh_3$		1450	1152	[36]
$Cp^*Re(CO)(NO)(CO_2)SnPh_3$		1429	1188 or 1175	[39]
$[Cp^*Re(CO)(NO)(CO_2)]_2SnMe_2$		1469	1186	[43]

band position for the symmetrical μ_2-η^3-bound complexes varies with the coordination geometry at the metal center which anchors the two carboxyl oxygens [5]. Also, the spectral characteristics of the two classes of μ_2-η^3 compounds are distinct. There are not enough examples of the other types of compounds at this time to identify these types by IR data alone.

2.4. Characteristic reactions

2.4.1. Decarboxylation

As indicated above, the η^1 and η^2 complexes and some of the anion complexes bind CO_2 reversibly. With metallocarboxylate anion complexes, the stability is directly related to that of the corresponding metal anion; if the anion is known, dissociative loss of CO_2 from the metallocarboxylate can be expected [44]. In contrast, salts of the metal anion, $CpFe(CO)(PPh_3)^-$, cannot be made, but salts of $CpFe(CO)(PPh_3)(CO_2)^-$ can be isolated [45]. The nature of the alkali metal exerted some control over the reversibility of CO_2 binding with cobalt(-salen)$(CO_2)^-M^+$($M = Li$, Na, K) [46]; the sodium and potassium salts lost CO_2 under vacuum, but the lithium salt did not. Also, solutions of the sodium salt lost CO_2 upon addition of dicyclohexano-18-crown-6.

The η^1 complexes reported by Herskovitz [8] lost CO_2 readily; the only adducts which could be formed were those in which a low-valent metal was further enriched in electron density by good σ-donor/poor π-acceptor ligands. The stability of η^2-coordinated compounds toward CO_2 loss appears to parallel the stability of ethylene-metal complexes [47]. Thus, strong electron-donor groups on the metal are required for thermal stability, probably to enhance the back-bonding to the CO_2 ligand.

Among the compounds having a CO_2 ligand bound between two metal centers, the ones which appear to lose CO_2 most readily are the μ_2-η^2 and μ_2-η^3 complexes in which the (one or both) carboxylate oxygen is bound to a main group atom such as tin. These systems have been studied by Senn et al. [34], Cutler [48] and Gibson et al. [36] and their coworkers. Where both metals are transition metals, several of the μ_2-η^2 types have been converted to μ_2-η^3 types via thermal dissociation of other ligands; both types are relatively stable toward decarboxylation [5].

2.4.2. Oxygen transfer

Metallocarboxylate anions, in particular, are very effective oxide transfer agents [51]. Reaction of $Li_2W(CO)_5(CO_2)$ with additional CO_2 results in formation of $W(CO)_6$ and Li_2CO_3, a reaction described as reductive disproportionation. Spectral evidence and labeling studies showed the oxide transfer to be a facile process. Lee and Cooper [51b] also showed that this dianion would transfer oxide to $CpFe(CO)_3^+BF_4^-$; labeling studies showed that oxygen, but not carbon, of the CO_2 ligand was incorporated into the iron product $[CpFe(CO)_2]_2$. Intramolecular oxide transfer from coordinated CO_2 to coordinated CO in the iron complex $CpFe(CO)_2(CO_2)^-Li^+$ has also been demonstrated.

Geoffroy et al. [49] reported that label scrambling occurred in the preparation of μ_2-η^3 CO_2-bridged complexes from $Cp_2W{=}^{17}O$ and $Cp^*Re(CO)_2(NO)^+BF_4^-$ or $Cp^*Fe(CO)_3^+BF_4^-$. The results of label-scrambling experiments led this group to propose intermediate metalloanhydride-like species. Recently, Cutler et al. [39] have presented evidence of oxygen transfer from carboxylate to CO within the μ_2-η^2 CO_2-bridged complex $Cp^*Fe(CO)_2(^{13}CO_2)SnMe_3$.

2.4.3. Reactions with electrophiles

Harlow et al. [50] alkylated the iridium complex $Ir(dmpe)_2(Cl)(CO_2)$ (**2**)with Me_5FSO_3 and structurally characterized the product, a methyl ester. Some other systems add electrophiles, but others show that either O–M or C–O cleavage reactions can be dominant [5]. The reactions of metallocarboxylate anions with electrophiles show interesting variations. The lithium salt of $W(CO)_5(CO_2)^{-2}$ gave only $W(CO)_6$ from reactions with a variety of electrophiles, including Me_3SiOTf [51]. This behavior contrasts with that of $CpFe(CO)(PPh_3)CO_2^-\ K^+$ and $Cp^*Fe(CO)(PPh_3)CO_2^-\ K^+$ which provide the corresponding esters in reactions with CH_3I and $Et_3O^+BF_4^-$ as the result of O–M bond cleavage [45b].

Tsai et al. and Fu et al. [52a,b], respectively, studied the reactions of $Cp_2Mo(CO_2)$ and $Cp'_2Nb(CO_2)CH_2SiMe_3$ with electrophiles. Both O–M and C–O bond breaking reactions can occur, but it has not been possible to determine which occurs first or even which carboxylate oxygen reacts first.

There are few reports of the reactions of electrophiles with compounds having bridging CO_2 ligands. The μ_3-η^3 CO_2-bridged complex studied by Lundquist et al. [29a,b] binds $ZnBr_2$ at the carboxylate oxygens and forms a stable adduct. Gibson et al. [25] reported that cleavage of the μ_2-η^2 complex $CpFe(CO)(PPh_3)(CO_2)Re(CO)_4(PPh_3)$ by Me_3SiOTf afforded the iron cation and $(Me_3SiO)Re(CO)_4(PPh_3)$ as a result of C–O bond cleavage.

2.5. Comparisons with surface-bound species

One of the few physical methods which coordination chemists and surface scientists have in common is vibrational spectroscopy; however, the specific methods being used differ. Coordination chemists usually employ FTIR now, and may use diffuse reflectance techniques, but surface scientists employ IRAS (infrared reflection absorption spectroscopy) and HREELS (high resolution electron energy loss spectroscopy) to probe the nature of surface-bound intermediates.

Recently, surface-bound and negatively charged ($CO_2{}^{\delta-}$) species have been identified on several transition metals as summarized in Table 3. This chemisorbed species is formed only when the surface is atomically rough or when it contains high defect density; generally, these species have been formulated as ions with both oxygens bound to the surface [6b]. However, the band positions from vibrational spectra are closely related to those seen for isolated and spectroscopically observed η^1 complexes, as can be seen from the discussions above and Table 2; therefore, the bonding of $CO_2^{\delta-}$ to the surface may be through carbon instead. The incidence of these ions has been shown to be enhanced by alkali metal promoters as is activation

Table 3
Vibrational frequencies of $CO_2^{\delta -}$ adducts on transition metal surfaces (in cm^{-1}) [6b]

Metal	ν_{asym}	ν_{sym}	δ
Ni (110)	1620	1130	750
Re (0001)	1650–1600	1230	650
Pd (110)	–	1200	770
Mo (110)	–	1155	855
Fe(100)	1634	1232	–

by C–O bond cleavage [6]. However, under these conditions, the position of the vibrational bands of the surface-bound $CO_2^{\delta -}$ species usually differ from those generated in the absence of an alkali metal. The band assigned to ν_{sym} is typically about 100 cm^{-1} higher when alkali metal is present; furthermore, all band positions are closely similar those of $LiCO_2$ and $CsCO_2$ (both with C_{2v} symmetry and coordination of both oxygens to the alkali metal; see Table 4 and discussion below in Section 3.2). For example, Solymosi and Klivényi [53] reported bands at 1620, 1360 and 820 cm^{-1} for $CO_2^{\delta -}$ on potassium-promoted rhodium(111) surfaces; the same investigators showed that the $CO_2^{\delta -}$ could be enhanced by UV irradiation of the same system. Complicating the assignments further is the fact that the bands for oxalate are in the same general region (e.g., 1716, 1342 and 806 cm^{-1}) [54]; however, the highest band (ν_{asym}) for oxalate is well above the highest band in the other species. An exception to the effect of alkali metal appears to be the species formed on potassium pre-dosed silver [55], which shows bands at 1600,

Table 4
IR bands for alkali metal-CO_2 adducts formed in Ar matrices (cm^{-1}) [57]

Adduct (symmetry)	Assignment	Band position
$LiCO_2$ (C_{2v})	ν_{asym}	1569.9, 1568.6
	ν_{sym}	1329.9
	δ	798.7
$LiCO_2$ (C_s)	ν_{asym}	1755.7, 1750.9
	ν_{sym}	1221.4, 1208.7
	δ	739.5
Li_2CO_2 (C_s)	ν_{asym}	1447.9
	ν_{sym}	984.2
$CsCO_2$ (C_{2v})	ν_{asym}	1595.3
	ν_{sym}	1352.8
Cs_2CO_2 (C_{2v})	ν_{asym}	1341.0
	ν_{sym}	1174.0
	δ	744.5
Cs_2CO_2 (C_s)	ν_{asym}	1334.8
	ν_{sym}	1017.6

1260 and 760 cm^{-1} and thus bears closer resemblance to $CO_2^{\delta -}$ species formed in the absence of any alkali metal.

Very recently, Wovchko and Yates [56] reported results of the UV photolysis of $Rh(^{13}C^{18}O)_2$ which was supported on Al_2O_3 in the presence of $^{12}C^{16}O_2$; strong evidence was obtained for photochemical activation of CO_2 in an unpromoted surface reaction. Although CO_2 adducts could not be directly observed by FTIR, results of the labeling studies suggested intermediate η^1-C and η^2-bound (C,O) complexes. The two major products were $Rh(^{12}C^{16}O)(^{13}C^{18}O)$ and $Rh(^{13}C^{16}O)(^{13}C^{18}O)$. Two dissociative paths were suggested: (a) direct dissociation of a C–O bond in rhodium-bound CO_2 and (b) O-atom exchange between coordinated CO_2 and CO, via a metalloanhydride, followed by C–O dissociation in the new CO_2 ligand. The further observation that no oxidized rhodium complexes were produced suggested that the intermediate was η^1-C bound to rhodium.

3. Reactions of CO_2 with metal complexes resulting in M–O bonds

3.1. Introduction

In addition to the complexes bearing CO_2 ligands bound through carbon to the metal centers, there are numerous reactions of CO_2 with metals or metal complexes that result in new M–O bonds. Many of the latter arise from insertion reactions of CO_2 with active metal compounds, but others are generated by direct reactions between metal atoms and CO_2. Compounds having CO_2 bound to a metal center through oxygen only have not yet been structurally characterized, but isotopic labeling studies, accompanied by normal coordinate analyses, support their existence.

3.2. Interaction of CO_2 with metal atoms at low temperatures

Kafafi et al. [57a] studied the reactions of Li atoms with CO_2 in Ar matrices and obtained IR spectral data for two species. Normal coordinate analyses were performed using the two geometries calculated previously; the stretching and bending frequencies which were observed and calculated for the two isomers were in good agreement as shown in Table 4. At high concentration of the alkali metal, an additional species was observed: Li_2CO_2. Labeling studies indicated that the two oxygens in this species were inequivalent; the IR bands for it are also shown in Table 4. Kafafi et al. [57b] later studied the reactions of Na, K and Cs with CO_2 in argon, nitrogen and neat matrices. The $M^+CO_2^-$ species found for all three metals was the one with C_{2v} symmetry. At high metal concentrations, only K and Cs formed M_2CO_2 species; in both cases, two geometric forms were observed. One isomer had C_{2v} symmetry but the other one had C_s symmetry; the IR bands are shown in Table 4.

Mascetti and Tranquille [17] studied the interaction of a series of metal atoms with CO_2 in neat matrices at 15 K by FTIR. The metals used were titanium, chromium, vanadium, iron, cobalt, nickel and copper; all formed complexes in which the CO_2 ligand was highly bent. As indicated above (Section 2.1), the oxophilic metals (Ti, Cr, V) were observed to be oxidized, then coordinated to CO_2 in η^2-C,O fashion. The ν_{OCO} bands in these compounds were found at 1750–1690 cm^{-1} and 1180–1090 cm^{-1}. For the copper adduct, ν_{OCO} bands were observed at 1716 and 1215; it was thought to have the end-on η^1-O coordination with a bent CO_2 ligand.

Recently, Souter and Andrews [58] have studied the interaction of CO_2 with Cr atoms generated by laser ablation. Although C–O bond cleavage is predominant, suggesting an intermediate η^2-CO_2 complex, there is also spectral evidence for an η^1-O-bound CO_2 complex.

Quere et al. [59] deposited Al and CO_2 together in argon matrices. The adduct formed was found to reversibly interconvert between two geometric isomers. The low-temperature form had C_s symmetry with inequivalence of the two C–O bonds; at higher temperatures, the chelated form (with C_{2v} symmetry) was preferred. Normal coordinate analysis was performed after data was obtained from isotopically labeled species; the isomer with C_s symmetry showed the ν_{OCO} bands at 1780 and 1146.5 cm^{-1} while the one with C_{2v} symmetry showed bands at 1443.5 (corrected) and 1265.5 cm^{-1}.

3.3. Bonding and calculated vibrational characteristics

Theoretical studies have been done with various metal centers to determine what circumstances might lead to stabilization of η^1-O (end-on) or η^2-O,O carbon dioxide coordination. SCF calculations [60] have shown that complexes having linear CO_2 ligands are appreciably destabilized relative to the other forms. However, if the CO_2 is allowed to bend, as shown [61] with CAS-SCF calculations for $Ni(NH_3)_2(CO_2)$, then the η^1-O form was found to be only slightly above the η^2-C,O form in energy. For $Cu(CO_2)$, the end-on and side-on coordination modes were predicted to be nearly degenerate in energy [62]. For more oxophilic metals, the η^2-O,O mode can be stabilized; thus for $Cr(CO_2)$ [63] and $Ti(CO_2)$ [64], the end-on and η^2-O,O modes were shown to be the lowest energy forms with the end-on form being most stable for chromium. Recent experimental and theoretical work by Souter and Andrews [58] supports this conclusion for chromium.

Using ab initio treatments that included electron correlation and methods based on the density functional approach, Sodupe et al. [65] studied the bonding of CO_2 to the early transition metal scandium and found that the η^2-C,O mode and the η^2-O,O mode are nearly degenerate in energy by these calculations. Vibrational modes for the CO_2 ligand in these models were calculated also. The SCF method gave band positions of 1968, 1020 and 779 cm^{-1} for the η^2-C,O mode and the DFT method gave 1754, 832 and 615 cm^{-1} for the vibrational bands. For the η^2-O,O mode the SCF method gave 1256, 1174 and 902 for the CO_2 vibrational bands while the DFT method gave 983, 927 and 745 cm^{-1} for these bands.

Because of the importance of defining the characteristics of CO_2 adsorbed on metal surfaces (see Section 2.5), Salahub et al. [66] performed a DFT study of the interaction of CO_2 with a single palladium atom. With this system also, the η^2-coordination mode was found to be lowest in energy. IR spectral bands for the CO_2 ligand were calculated as 2018, 1212 and 689 cm^{-1} for the asymmetric, symmetric and bending vibrational modes in this model.

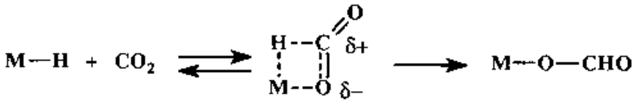
3.4. Insertion reactions

3.4.1. Introduction

Reactions with CO_2 which result in the breaking of M–X (X = H, O, C, N, Si, P or M) bonds and in the formation of products of the general type M–O–C(O)X are usually described as insertion reactions. Although the opposite type of insertion, to yield M–C(O)OX products, might appear to be possible, consideration of the characteristics of the M–X complexes that are known to be active toward the insertion of CO_2 quickly leads to the conclusion that only one type of insertion is likely. All compounds which insert CO_2 have electron-rich M–X bonds, resulting in high electron density at X; thus, the product always has a new M–O bond and a new C–X bond. These reactions may, or may not, involve coordination of CO_2 to the metal center prior to the bond reorganizations which occur; most probably involve concerted processes in which bonds involving existing ligands are broken and new bonds to CO_2 are formed at the same time. The two types of insertion reactions which currently have the most importance involve M–H and M–O bonds and examples of these in coordination chemistry and in surface science are readily available; discussion will be limited to reactions involving M–H bonds only since these result in CO_2 reduction.

3.4.2. Insertion of CO_2 into metal–H bonds

Insertion of CO_2 into metal–H bonds results in metal formate complexes, M–OCHO; the alternative type of insertion, leading to a metallocarboxylic acid (M–COOH), has so far not been demonstrated. Furthermore, there are no examples of the interconversion of these two types of complexes. The first product of M–H insertion will have an η^1-O coordinated formate as shown in Scheme 1; O,O′-type bidentate complexes may be formed from these and may be chelating or bridging. Very recently, complexes containing a single formate oxygen, bridged between two metal centers were characterized by X-ray analysis and IR spectroscopy. Table 5 shows examples of structurally characterized complexes of each type and the characteristic ν_{OCO} stretching frequencies for each compound [67–77]. The frequency difference, $\Delta\nu$, between the two bands is largest for the compounds with a single bridging formate oxygen atom and smallest for the bidentate O,O′-



Scheme 1.

Table 5
Carboxylate stretching frequencies of formate complexes

Compound	Structure assignment	Bonding	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu$	Reference
$Cp_2Ti(OCHO)_2$	X-ray	η^1	1644	1290 (1273)	354 (371)	[67]
trans-$(PCy_3)_2Pt(H)(OCHO)$	X-ray	η^1	1620	1310	310	[68]
$CpFe(CO)_2(OCHO)$	X-ray	η^1	1620	1293	327	[69]
trans-Ru(dmpe)(OCHO)(H)[a]	X-ray	η^1	1603	1329	274	[70]
$(PPh_3)_2Cu(OCHO)$	X-ray	η^2	1585	1350	235	[71]
mer-$Ru(H)(PPh_3)_3(OCHO)$	X-ray	η^2	1553	1310	243	[72]
trans-$Ru(CO)(PPh_3)_2(HC{=}CHPh)(OCHO)$	X-ray	η^2	1555	1358	197	[73]
$Mo(H)(PMe_3)_4(OCHO)$	X-ray	η^2	1570	1360	210	[74]
$[CpTi(OCHO)]_2(C_{10}H_8)$	X-ray	μ_2-η^1	1664	1205	459	[75]
$[Pd(PPh_3)(Me)(OCHO)]_2$	X-ray	μ_2-η^2	1595	1349	246	[76]
$[Rh(cod)(OCHO)]_2$[b]	X-ray	μ_2-η^2	1590	1354	236	[77]

[a] dmpe = bis(1,2-dimethylphosphino)ethane.

[b] dmpe = cod = 1, 5-cyclooctadiene.

type complexes. The M–H insertion reactions have received much attention because they are thought to play an integral part in catalytic hydrogenation processes leading to formic acid and other formates [78]. The reactions have been thought to involve transition states similar to ones proposed for olefin insertion. Recent theoretical work, however, suggests [79] that there may be only weak M–O interaction in the transition state leading to formate and that stable CO_2 complexes may not be essential precursors to the formate products.

3.5. Comparisons with surface reactions of CO_2 which yield formate

Catalytic reductions of CO_2 by H_2 on metal surfaces may yield formic acid [78], but there is also interest in directing the conversion further, to methanol [80]. Zirconia has emerged as an effective support material since it enhances the activitiy of copper in this conversion [80b]. Surface-bound formates are proposed intermediates in these processes, first as monodentate then bridging two zirconium centers before becoming *gem*-diolate (methylenebisoxy) species after further reduction. Since CO_2 insertion into a variety of copper hydrides is well known [71], copper formates probably should be considered as intermediates in the catalytic processes; in this case, the subsequent bridged formate would probably involve both Cu and Zr centers as a result of the oxophilicity of zirconium.

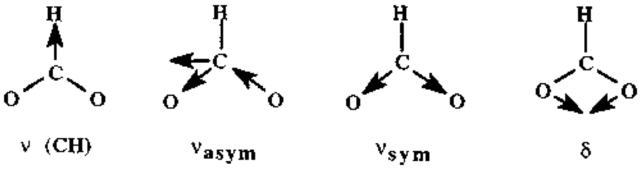
Examples of surface-bound monodentate and bidentate types of formate are shown in Table 6 [81–86]; in most cases, there is close similarity between the vibrational spectra of coordination compounds which exhibit η^1 bonding of the formate group and surface-bound species of the same type. Notable exceptions are the species identified recently as 'monodentate' on molybdenum surfaces by Xu and Goodman [85]; the very large $\Delta\nu$ between the two stretching frequencies for the

Table 6
Vibrational bands of surface-bound formate

Surface	ν(CH)	ν_{asym}(OCO)	ν_{sym}(OCO)	δ(OCO)	Reference
Bidentate or bridge-bonded					
Pt(111)	2950		1340	790	[81]
O/Pt(111)	2920		1330	780	[82]
Ni(110)	2940		1370	790	[83]
Cu(110)	2910, 2840	–	1330	760	[84]
Cu(100)[a]	2910, 2840	1640	1360	790	[84]
Mo(110)	2945		1360	775	[85]
O/Mo(110)	2950		1270	755	[85]
Ru(001)	2939		1361	784	[86]
Monodentate					
O/Pt(111)	2920	1620	1290	780	[82]
Mo(110)	2935	1745	1010	–	[85]
O/Mo(110)	2940	1720	1025–1070	–	[85]

[a] May be monodentate.

Table 7
Vibrational assignments of surface-bound formates [86]



Fundamental vibrations	Crystalline $HCOO^-K^+$	Symmetric representations			
		C_{2v}	$C_s(1)$	$C_s(2)$	C_1
ν (CH)	2803	A_1	A′	A′	A
ν_{asym} (OCO)	1585	B_1	A″	A′	A
δ (CH)	1383	B_1	A″	A′	A
ν_{sym}(OCO)	1351	A_1	A′	A′	A
π (CH)	1069	B_2	A′	A″	A
δ (OCO)	772	A_1	A′	A′	A

formates do not have any parallel with the coordination compounds of this type and suggest unusual binding of the formates to the Mo surfaces, possibly analogous to the μ_2-η^1 type of bridged complexes (see Table 5).

Identification of surface-bound bidentate (η^2 or bridging) formate is complicated by the fact that the ν_{asym} band may be absent; surface dipole selection rules [84] dictate that only certain types of these formates will have the necessary characteristics for this mode to be active. Vibrational bands for various formate types and their symmetry representations are shown in Table 7; the surface orientations and point groups for each are shown in Fig. 2. Only those which belong to the totally symmetric representations A_1, A′ and A are expected to show ν_{asym} bands; these will be present for $C_s(2)$ and C_1 types of orientations only.

Xu and Goodman [85] have recently reported the observation of $CO_2^{\delta-}$ as a product from decomposition of formic acid on O/Mo(110) surfaces; a possible-mechanism for the conversion of formate to $CO_2^{\delta-}$ is shown in Fig. 3. Although the species was formulated, in the usual way, as bidentate through the oxygens, the vibrational bands which were identified (1155 and 855 cm^{-1}) correspond closely to the ν_{asym} and δ bands observed for η^1-C bound CO_2 complexes isolated [8] and observed [17] previously, thus coordination of this species to the surface through carbon only appears to be a possibility. Also, since the ν_{sym} band position is near to the values observed for μ_2-η^2 bridged compounds (see Table 2), this type of binding should be considered also.

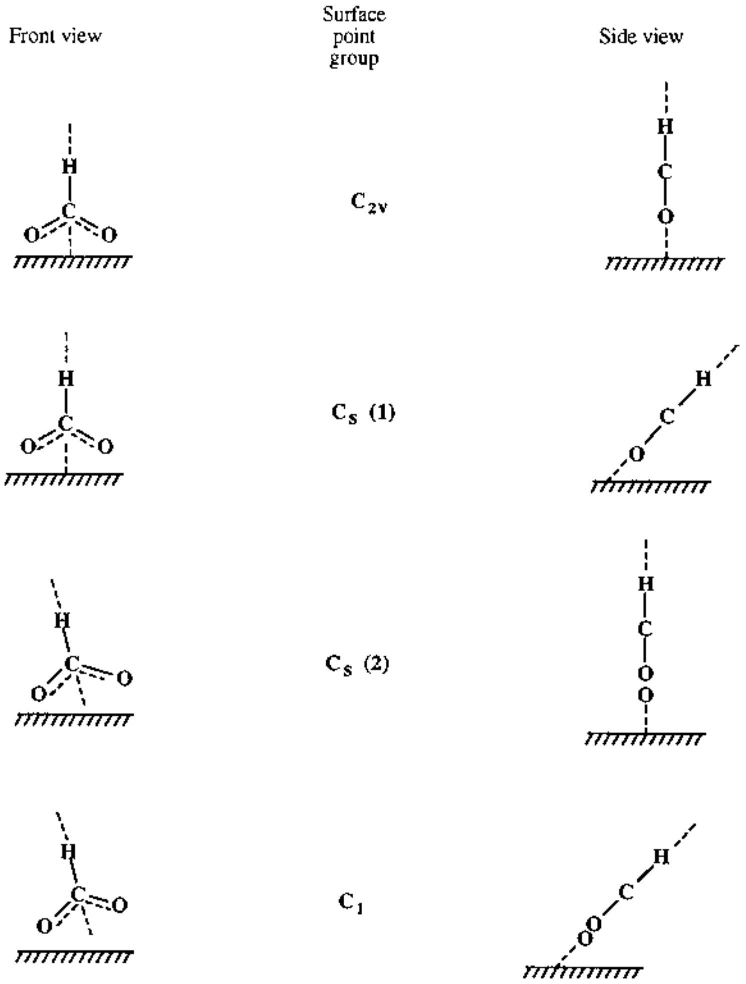


Fig. 2. Surface orientations for bidentate formate.

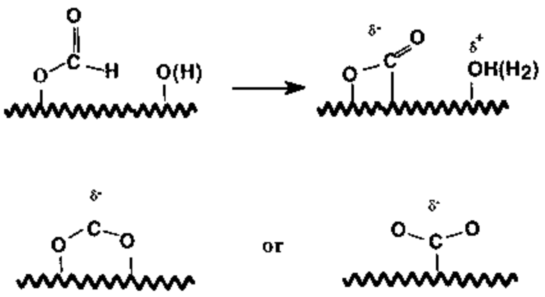


Fig. 3. Conversion of surface formate to $CO_2^{\delta-}$.

4. Conclusions

The binding of CO_2 to metals, in whatever way, results in a bent carbon dioxide ligand; theoretical results and experimental results are in agreement in this regard and observations on surface-bound species agree as well. Carbon-bound coordinated CO_2 is susceptible to electrophilic cleavage and this may occur at either a C–O bond or an O–M bond; highly oxophilic metal centers may facilitate the reactions. Oxygen transfer reactions are characteristic of coordinated CO_2 and include intramolecular transfer, via a metalloanhydride, to coordinated CO; such reactions have now been implicated on metal surfaces also.

Carbon dioxide insertion into M–H bonds has been demonstrated for coordination compounds and results in metal formate complexes only (not metallocarboxylic acids); such reactions are also implicated in reactions involving CO_2 and H_2 on metal surfaces. A variety of coordination modes for the formate ligands have been identified in isolated complexes and on metal surfaces. Bidentate and bridging formates have been well-characterized and are believed to be involved in homogeneous reductions of CO_2 to formic acid and in surface reactions leading to the conversion of CO_2/H_2 mixtures to methanol.

The various techniques for obtaining vibrational spectral data now available allow the results from different disciplines to be compared. As additional research is done in all of these areas, it becomes apparent that there are very close ties among the isolated compounds and those spectroscopically observed and their surface-bound analogs.

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