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Reactivities of carbonyl sulfide (COS), carbon disulfide (CS_2) and carbon dioxide (CO_2) with transition metal complexes

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Contents

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Abstract

Carbonyl sulfide, carbon disulfide and carbon dioxide interact with transition metal complexes to form complexes with a number of transition metals and undergo a variety of chemical transformations including insertion, dimerization, disproportionation, coupling and catalytic reactions. The coordination chemistry of these closely related molecules is very diverse. The metal–(η^2-CS_2) complexes are much more stable than the metal–(η^2-COS) and metal–(η^2-CO_2) complexes. Elimination of sulfur from the metal–(η^2-COS) complexes is more facile. Carbon dioxide undergoes coupling reactions with unsaturated organic compounds on transition metal centers to produce metallocycles. The reduction of carbon dioxide catalyzed by transition metal complexes, using different methods, is discussed.

Keywords: Reactivity; COS; CS_2; CO_2; Transition metal complexes

Abbreviations

alcn	$HNCHCHCHO^-$
bipy	2,2′-bipyridyl
n-Bu	*n*-butyl
t-Bu	tert-butyl
COD	cyclooctadiene
cp	cyclopentadienyl
Cy	cyclohexyl
dbu	diazabicyclo[5,4,0]undec-7-ene
diars	*o*-phenylenebisdimethylarsine
DMF	*N*,*N*′-dimethylformamide
dmpm	1,2-bis(dimethylphosphino)methane
dpam	1,2-bis(diphenylarsino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
EDTA	ethylenediaminetetraacetate
EHMO	extended Hückel molecular orbital

en	ethylenediamine
Et	ethyl
HOMO	highest occupied molecular orbital
L	ligand
M	metal atom
Me	methyl
MeCN	acetonitrile
mes	2,4,6-$Me_3C_6H_2$
NBD	norbornadiene
np_3	tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$
pc	phthalocyanine
ph	phenyl
phen	1,10-phenanthroline
n-Pr	*n*-propyl
i-Pr	iso-propyl
py	pyridine
R	alkyl or aryl group
salen	bis(salicyldehydeethylenediimine
sp	2-$CH_2{=}CHC_6H_4PPh_2$
terpy	terpyridine
THF	tetrahydrofuran
TMED	*N,N,N',N*-tetramethylethylenediamine
TPP	meso-tetraphenylporphyrin
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane

1. Introduction

The interaction of heterocumulene molecules such as carbonyl sulfide (COS), carbon disulfide (CS_2) and carbon dioxide (CO_2), which are a potential source of C_1 chemistry, with transition metal complexes has been extensively studied in the past decade and has been shown to give rise to complexes with a number of transition metals and to produce a variety of chemical transformations including insertion, dimerization and disproportionation reactions. Since the first report by Baird and Wilkinson of the reaction of COS, which is structurally similar to CS_2 and CO_2, with a transition metal complex, this subject has received relatively little attention.

The important physical properties of the linear triatomic molecules COS, CS_2 and CO_2 are presented in Table 1 [1–24]. The values of ionization potential [2,11–18] and electron affinity [19–22] show that CS_2 is a relatively better σ-donor and a better π-acceptor than COS and CO_2. The bond dissociation energy of the COS molecule indicates that it can function as a good carbonylating agent in the presence of a suitable thiophilic agent. The carbon binding energy C_{1s} has been observed to shift 2.1 eV between COS and CS_2 and 2.3 eV between CO_2 and COS [25]. The shifts are due to the lower electronegativity of sulfur compared with oxygen.

Table 1
Selected properties of COS, CS_2 and CO_2

	COS	CS_2	CO_2	Reference
Point group	$C_{\infty v}$	$D_{\infty h}$	$D_{\infty v}$	[1]
Ground state	$^1\Sigma^+$	$^1\Sigma_g^+$	$^1\Sigma_g^+$	[2]
Boiling point (°C)	−50.2	46.3	−78.5	
LUMO	2π	$2\pi_u$	$2\pi_u$	[3]
HOMO	1π	$1\pi_g$	$1\pi_g$	[2]
Bond length (Å)	1.16 (C−O) 1.56 (C−S)	1.56 (C−S)	1.16 (C−O)	[4–9]
Bond energy (eV)	3.12 (OC−S) 6.81 (O−CS)	4.463	5.453	[4,10]
Ionization potential (eV)	11.2	10.09	13.78	[2,11–18]
Electron affinity (eV)	0.46	1.0	−0.6	[19–22]
IR data (cm^{-1})	2062 859 521	1535 396	2396 677	[23,24]

The coordination chemistry of these closely related molecules is very diverse. The metal–(η^2-CS_2) complexes are much more stable than the metal–(η^2-COS) complexes. Sulfur abstraction from a metal–(η^2-CS_2) complex is not a general procedure for the preparation of metal thiocarbonyl complex. In contrast, elimination of sulfur from metal–(η^2-COS) complexes is more facile. Carbonyl sulfide chemistry has proven to be interesting with potential applications to carbonylation reactions. The weakening of the C=S bond of COS on coordination to a metal, due to $d\pi$–π^* back donation, is apparently sufficient to promote elimination of sulfur. The stronger C=S bond of CS_2 is less susceptible to metal-promoted cleavage, but in the presence of a suitable sulfur acceptor can facilitate sulfur elimination.

Although CS_2 is structurally very similar to CO_2, its behavior towards metal centers is different. CS_2 is a very reactive molecule, while CO_2 is not.

A number of review articles, dealing with various aspects of the chemistry of COS [26,27], CS_2 [27–32] and CO_2 [33–53] have been written. Because of new developments, it is necessary to review recent research involving reactivities of COS, CS_2 and CO_2 with transition metal complexes. Carbon dioxide can be converted into useful organic compounds by coupling with an organic substrate using homogeneous transition metal catalysts [45–48,50,54–79]. These catalytic reactions of CO_2 with the organic substrate are not examined here. This article covers the chemistry of COS and CS_2 from 1982 to 1992, and the chemistry of CO_2 from 1983 to 1992.

2. Coordination chemistry of carbonyl sulfide

2.1. Transition metal–carbonyl sulfide bonding and energetics

General consideration of the electron donating and electron accepting properties of carbonyl sulfide shows three possible bonding modes with transition metals [26].

2.1.1. End-on coordination ($M-\eta^1$-OCS)

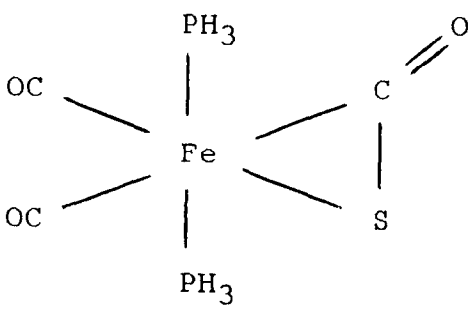
In this type of bonding, the transition metal behaves as a Lewis acid, accepting a lone pair of electrons from the 1π (HOMO) orbital of the COS into the corresponding metal vacant orbital.

2.1.2. Side-on coordination ($M-\eta^2$-COS)

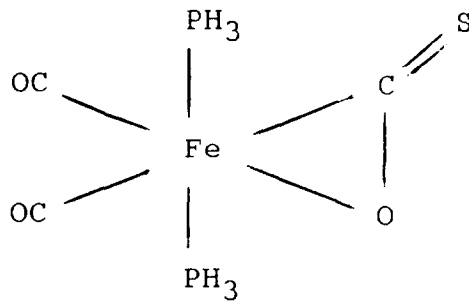
In this bonding mode, the main bonding orbital is the overlap between the metal-dπ and the COS-π^* orbitals. Thus, the main interaction is π-back donation from the metal atom to the COS ligand. Some contribution to the interaction between metal atom and COS arises from the COS ligand to metal σ-donation. Such complexes contain a three-membered ring.

In order to understand the nature and energetics of the interaction between metal and COS, ab initio molecular orbital calculations have been performed on the model systems $[Fe(CO)_2(PH_3)_2(\eta^2\text{-COS})]$ with two possible side-on coordination modes (**I**) and (**II**) [80].

Bonding energy and Mulliken population analysis of the systems (**I**) and (**II**) are presented in Table 2. Results of the theoretical calculations suggest that COS prefers the η^2-C,S coordination to the η^2-C,O coordination, in agreement with the experimental evidence that no η^2-C,O coordinated COS complex has so far been obtained.



(**I**)



(**II**)

Table 2
Binding energy and Mulliken population analysis of the systems (**I**) and (**II**) [80]

	System (**I**)	System (**II**)
Binding energy (kcal mol^{-1})	−35.8	−30.9
Atomic populations		
Fe s	6.40	6.39
Fe p	12.83	12.71
Fe d	7.17	7.18
COS	30.56	30.70
Net charges		
Fe	−0.40	−0.28
COS	−0.56	−0.70

The strength of the $d\pi(M)$–$\pi^*(COS)$ interaction increases as the overlap between $d\pi(M)$ and $\pi^*(COS)$ orbitals increases. The COS distortion on coordination lowers the $\pi^*(COS)$ orbital energy, reduces the gap between $d\pi(M)$ and $\pi^*(COS)$ and hence increases π-back donation. The π^* orbital energy of the distorted COS ligand is -0.0137 au for η^2-C,S coordination and -0.0099 au for η^2-C,O coordination, indicating stronger π-back donation in the η^2-C,S coordination mode. Mulliken population analysis reveals that the σ-donor and π-acceptor abilities of the η^2-C,S coordination mode are greater than those of the η^2-C,O coordination mode.

2.1.3. Bridging carbonyl sulfide complexes

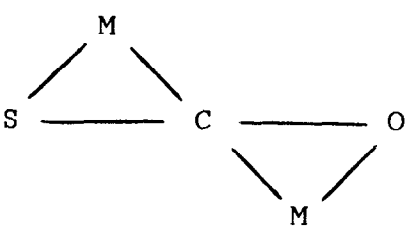
In addition to the end-on coordination and side-on coordination modes, COS can function as a bridge between two metal atoms (**III**) and (**IV**).

2.2. Preparation and structure

Relatively few transition metal COS complexes have been reported in the literature. These complexes have been prepared using the free ligand which is readily available as a starting material. The most accessible technique for identifying metal–COS complexes is IR spectroscopy. The frequency range for the carbonyl stretching vibration in COS complexes is 1630–1765 cm^{-1} and the position of the in-ring ν(CMS) vibration, for (M$-\eta^2$-COS) complexes lies in the regions 630–660 cm^{-1} and 800–860 cm^{-1} [26].

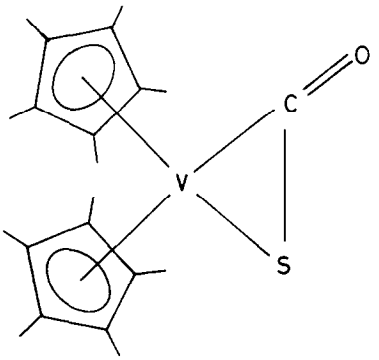
Titanium COS complex, $[H_4Ti(COS)]$, is prepared by the reaction of COS with a titanium hydride complex [81]. Reaction of carbonyl sulfide with the cyclooctadiene complex [Ni(COD)(bipy)] results in the formation of the COS complex [Ni(η^2-COS)(bipy)]. Attempts to prepare [Ni(η^2-COS)$(PR_3)_2$] (R ≡ Ph or Cy) were unsuccessful [82]. The thermally labile COS complex $[(C_5Me_5)_2V(\eta^2\text{-COS})]$ (**V**) is prepared by the reaction of $[(C_5Me_5)_2V]$ with COS [83]. Preparation of COS complexes of Ti, Ni, Pd and Pt have been reported [81,84]. Irradiation of $[Ni(S_2C_2O_2)(dppe)]$ in acetonitrile yields the carbonyl complex $[Ni(CO)_2(dppe)]$ and COS complex [Ni(η^2-COS)(dppe)] [85].

Reaction of $[ReH(PMe_3)_5]$ with COS affords a white crystalline complex (**VI**) whose ^1H NMR spectrum shows a singlet at δ 1.42, indicating a similar environment for the PMe_3 ligands, and a quintet at δ -3.10 due to Re—H. The IR spectrum



(III)

(IV)



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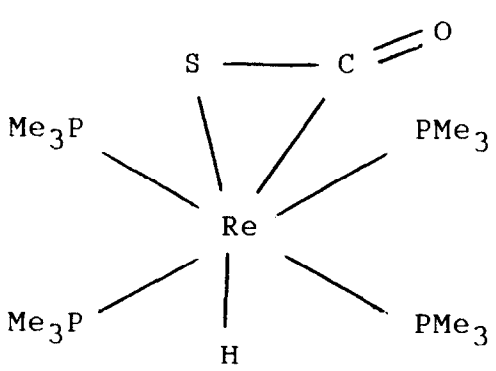
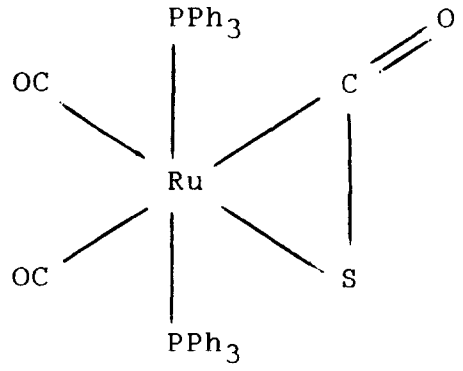


(VI)



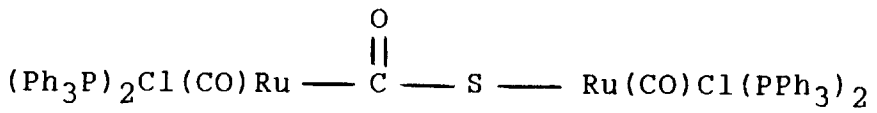
(VII)

exhibits bands at 1935 cm^{-1} due to ν(Re—H) and at 1791 cm^{-1} due to ν(C=O) of the η^2-COS ligand [86].

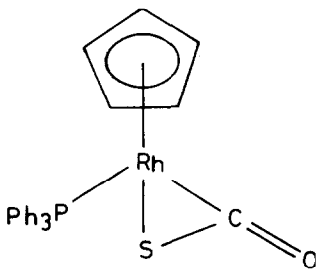
Exposing a toluene solution of $[Ru(CO)_2(PPh_3)_3]$ to 1 atm COS for 5 min yields a cream white microcrystalline complex $[Ru(CO)_2(COS)(PPh_3)_2]$ (**VII**). It is stable in the solid state under a nitrogen atmosphere and decomposes readily in solution to afford $[Ru(CO)_3(PPh_3)_2]$ and $SPPh_3$. The IR spectrum of (**VII**) exhibits absorption bands at 1701, 1678 cm^{-1} due to ν(CO) and at 638 cm^{-1} due to ν(RuCS) which are characteristic of η^2-COS through the C=S bond. The presence of a singlet in the ^{31}P NMR spectrum of (**VII**) at 36.32(s) and two carbonyl stretching frequencies at 2012 and 1951 cm^{-1} due to terminal carbonyl ligands support the structure (**VII**) for the zerovalent ruthenium COS complex [87].

COS reacts with $[Ru(CO)Cl(CH_3COO)(PPh_3)_2]$ to give a bridged COS complex (**VIII**) whose IR spectrum shows a broad band at 850 cm^{-1} due to the COS ligand [88]. Ruthenocene reacts with COS to afford the COS complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}COS)]$ [89].

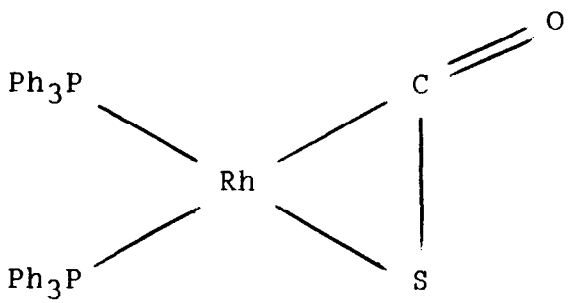
Reaction of COS with $[(\eta^2\text{-}C_5H_5)Rh(PPh_3)_2]$ gives the COS complexes (**IX**) and (**X**). The IR spectrum of (**IX**) shows absorption bands at 1720 cm^{-1} and 630 cm^{-1}



(VIII)



(IX)

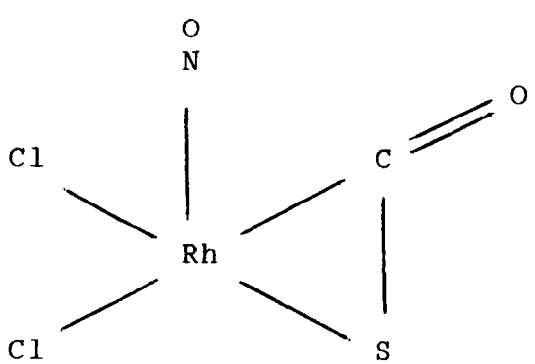


(X)

due to the coordinated COS group. In the ^1H NMR spectrum, the cylopentadienyl resonance is a doublet of doublets ($\delta = 6.00$ ppm) with $J_{P-H} = 1.60$ Hz and $J_{Rh-H} = 0.66$ Hz. The electronic spectrum exhibits λ_{max} (ε_{max}) at 806 (77), 417 (3195) 283 nm (14080 $M^{-1}\,cm^{-1}$). The IR spectrum of (**X**) exhibits bands at 1750 cm^{-1} and 635 cm^{-1} due to the coordinated COS group. The proton NMR spectrum shows a multiplet, with the chemical shift of the most intense line at δ 7.51 ppm due to the phenyl protons [90].

Reaction of COS with $Rh(NO)Cl_3$ in ethanol affords the red complex (**XI**) which shows IR spectral bands at 1615 cm^{-1} due to ν(NO) and at 1700 cm^{-1} due to ν(CO) of the coordinated COS.

Reactions of COS with iridium complexes $[Ir(CO)Cl(PR_3)_2]$ ($PR_3 \equiv PMe_2Ph$,

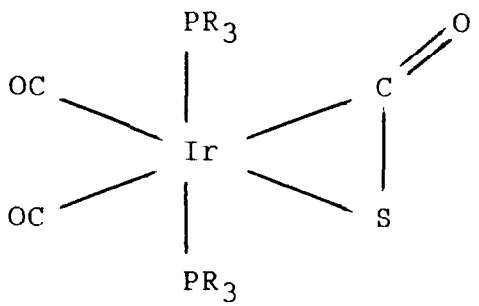


(XI)

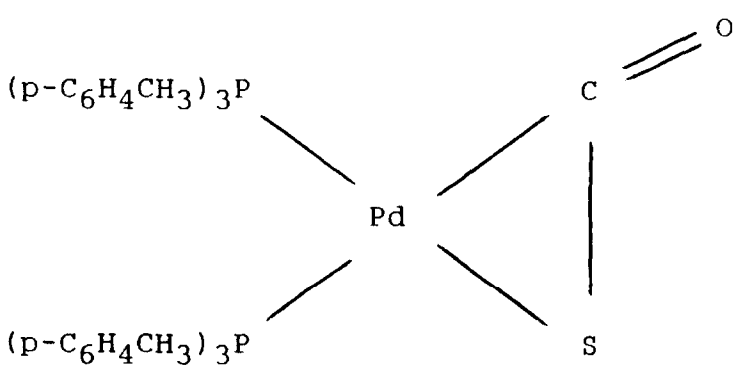
PMe_3, PPh_3) have been investigated [91]. The COS complexes (**XII**) and (**XIII**) form at low temperatures, below −78 °C. Attempts to prepare $[Ir(CO)Cl(COS)(PPh_3)_2]$ were unsuccessful. The complexes (**XII**) and (**XIII**), which decompose on warming to give COS, have IR spectra with absorption bands at 2036 cm^{-1} due to ν(CO), at 1748, 662 cm^{-1} due to COS ligand for the complex (**XII**), and at 2017 cm^{-1} due to ν(CO), at 1730, 660 cm^{-1} due to COS ligand and at 241 cm^{-1} due to ν(Ir—Cl) for the complex (**XIII**). ^{31}P NMR spectra exhibit a singlet at δ −27.8(s) for (**XII**) and at δ −32.1(s) for (**XIII**). These spectral data are consistent with structures (**XII**) and (**XIII**).

A very unstable complex $[Pd(COS)(PPh_3)_2]$ can be prepared from the reaction of COS and $Pd(PPh_3)_3$ or $Pd(PPh_3)_4$. The reaction of $Pd[P(p\text{-}C_6H_4CH_3)_3]_3$ with COS affords a relatively more stable complex (**XIV**) which exhibits IR spectral bands at 1739 and 630 cm^{-1} attributable to the bidentate COS ligand. ^{31}P NMR spectrum of (**XIV**) consists of an AB spin pattern (δ 22.2, 27.5) consistent with (**XIV**) [92].

Reaction of COS with Cu(TPP) in toluene gives a pinkish-brown complex



(XII), $PR_3 = PMe_2Ph$
(XIII), $PR_3 = PMe_3$



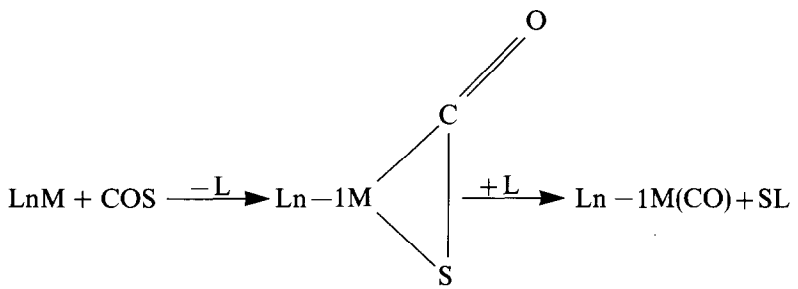
(XIV)

[Cu(TPP)(COS)] whose IR spectrum shows a band at 1712 cm^{-1} due to the coordinated COS ligand [93].

2.3. Reactions of carbonyl sulfide complexes

2.3.1. Carbonylation reaction

The coordination chemistry of COS is dominated by reactions that involve cleavage of the C—S bond and form carbonyl complexes. A plausible explanation for the carbonylation reactions is the initial formation of η^2-COS complex followed by sulfur elimination:



The carbonylation reactions, in which sulfur is eliminated by the phosphine ligand, are shown in the following equations.

$$[Fe(CO)_2(PPh_3)_3] + COS \rightarrow [Fe(CO)_3(PPh_3)_2] + SPPh_3 \quad [87]$$

$$[Ru(CO)_2(PPh_3)_3] + COS \rightarrow [Ru(CO)_3(PPh_3)_2] + SPPh_3 \quad [87]$$

$$2[Ru(MeCN)_2Cl_2(PPh_3)_2] + 2COS \rightarrow [Ru(CO)Cl(PPh_3)]_2(\mu\text{-}Cl)_2 + 2SPPh_3 \quad [88]$$

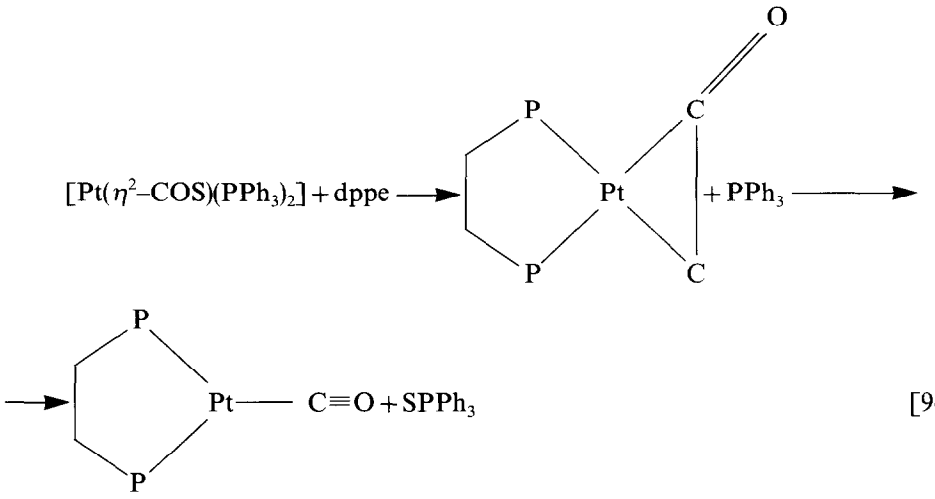
$$2[Ru(MeCN)_2Cl_2(PPh_3)_2] + 2COS + 2PPh_3 \rightarrow [Ru(CO)Cl(PPh_3)_2]_2(\mu\text{-}Cl)_2 + 2SPPh_3 \quad [88]$$

$$[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}COS)(PPh_3)] + PPh_3 \rightarrow [(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_3)] + SPPh_3 \quad [90]$$

$$[Rh(NO)(PPh_3)_3] + COS \rightarrow [Rh(CO)(NO)(PPh_3)_2] + SPPh_3 \quad [90]$$

$$[RhCl(AsPh_3)_3] + COS \rightarrow [Rh(CO)Cl(AsPh_3)_2] + SAsPh_3 \quad [90]$$

$$[Ni(CO)(PPh_3)_3] + COS \rightarrow [Ni(CO)_2(PPh_3)_2] + SPPh_3$$



[94]

The carbonylation reactions, in which the fate of the sulfur has not been determined, are presented in the following equations.

$$[Fe(TPP)] + COS \rightarrow [Fe(CO)(TPP)] + \ldots \quad [93]$$

$$[(np_3)CoH] + COS + NaBPh_4 \rightarrow [(np_3)Co(CO)][BPh_4] + \ldots \quad [95]$$

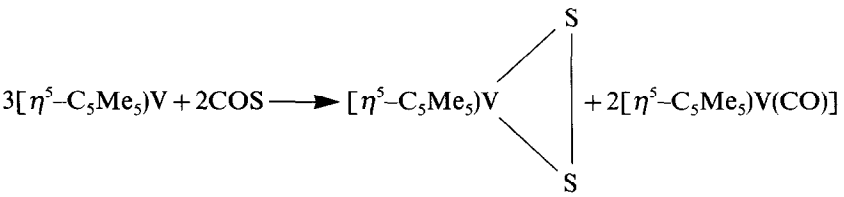
$$[Ni(bipy)(PPh_3)_2] + 2COS \rightarrow [Ni(CO)_2(PPh_3)_2] + \ldots \quad [82]$$

$$[(triphos)_2Ni] + COS \rightarrow [(triphos)Ni(CO)] + \ldots \quad [96]$$

$$[(np_3)_2Ni] + COS \rightarrow [(np_3)Ni(CO)] + \ldots \quad [97]$$

$$[Pt(COS)(PPh_3)_2] + PPh_3 \rightarrow [Pt(CO)(PPh_3)_3] + \ldots \quad [92]$$

Some carbonylation reactions have also been reported in which sulfur remains in the complex either as a bridged ligand or associated with other ligands.



[83]

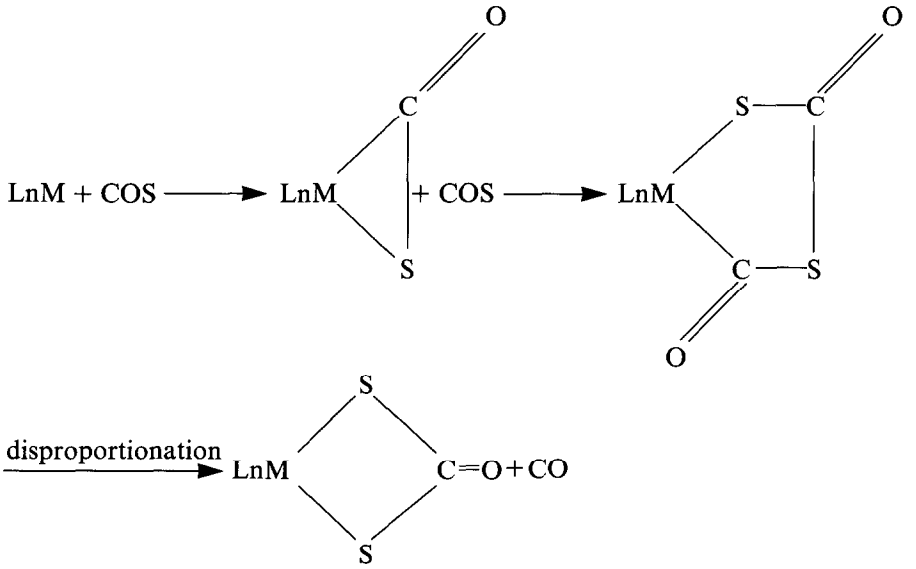
$$[RhH(PPh_3)_4] + COS \rightarrow [Rh(CO)(SH)(PPh_3)_2] + \ldots \quad [98]$$

2.3.2. Reductive disproportionation reaction: dithiocarbonate complexes

Carbonyl sulfide affords a convenient route to metal dithiocarbonate complexes. In the formation of dithiocarbonate from COS, the COS undergoes a metal-promoted

two-electron reductive disproportionation reaction. Dithiocarbonates could arise from an electrophilic attack on the endocyclic sulfur atom by another COS molecule, followed by elimination of CO [92]:

$$2COS + 2e^- \rightarrow S_2CO^{2-} + CO$$



Metal complexes with dithiocarbonate ligands show absorption bands in their IR spectra at 1680–1965, 1595–1615 and 830–865 cm^{-1} which are characteristics of a bidentate dithiocarbonate ligand [99,100]. Spectra data of the dithiocarbonate complexes are presented in Table 3 [101–104].

Reaction of COS with $[Fe(CO)_2(PPh_3)_3]$ in a liquid-nitrogen-cooled pressure reactor and with $[Ru(CO)_2(PPh_3)_3]$ in toluene solution result in the formation of dithiocarbonate complexes (**XV**) and (**XVI**). The IR and ^{31}P NMR spectra are consistent with the proposed structure with the presence of *cis*-carbonyl and *trans*-phosphine ligands.

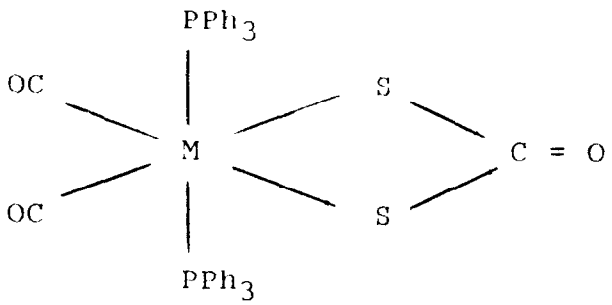
The complexes $[Pd(S_2CO)(PR_3)_2]$ ($PR_3 \equiv PMePh_2$, PMe_2Ph, $PiPr_3$) are prepared from the reaction of excess COS with $[Pd(PR_3)_4]$. The complex $[Pd(S_2CO)(PMe_3)_2]$ is obtained by the displacement of phosphine ligand from $[Pd(S_2CO)(PR_3)_2]$ with PMe_3. The X-ray crystal structure of $[Pd(S_2CO)(PMe_2Ph)_2]$ shows approximate square planar coordination of the palladium with planar dithiocarbonate ligand (**XVII**) [101].

Platinum carbonyl sulfide complex $[Pt(\eta^2\text{-}COS)(PPh_3)_2]$ reacts with PMe_3 or PMe_2Ph to afford dithiocarbonato-platinum(II) complexes $[Pt(S_2CO)(PR_3)_2]$. Complex $[Pt(S_2CO)(PPh_3)_2]$ is obtained by the reaction of excess COS with $[Pt(PPh_3)_4]$, $[Pt(\eta^2\text{-}COS)(PPh_3)_2]$ or $[Pt_2S(CO)(PPh_3)_3]$ [92].

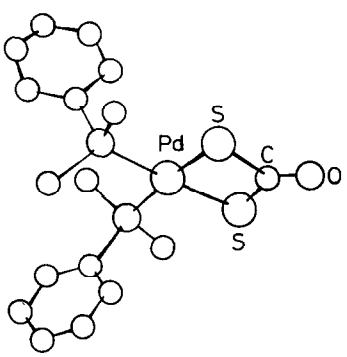
Reactions of COS with *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M ≡ Mo or W) in diethylether give dithiocarbonate complexes $[M(CO)_2(S_2CO)(PMe_3)_3]$ (M ≡ Mo (**XVIII**); W)

Table 3
Spectral data for dithiocarbonate complexes

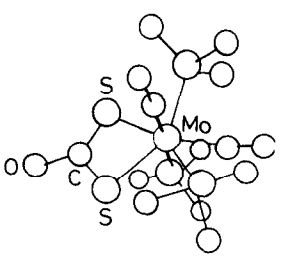
Complex	IR frequencies (cm^{-1})		^{31}P NMR, δ (ppm)	Reference
	ν(CO)	ν(CS)		
$[Mo(CO)_2(S_2CO)(PMe_3)_3]$	1690, 1570	—	16.9 −18.0	[104]
$[Fe(CO)_2(S_2CO)(PPh_3)_2]$	1688, 1611	838	51.1(s)	[87]
$[Ru(CO)_2(S_2CO)(PPh_3)_2]$	1688, 1609	832	30.83(s)	[87]
$[Pd(S_2CO)(PMePh_2)_2]$	1680, 1605	835	8.86(s)	[101]
$[Pd(S_2CO)(PMe_2Ph)_2]$	1680, 1610	835	−7.23(s)	[101]
$[Pd(S_2CO)(Pi\text{-}Pr_3)_2]$	1695, 1605	855		[101]
$[Pd(S_2CO)(PMe_3)_2]$	1690, 1595	860	−16.71(s)	[101]
$[Pd(S_2CO)\{P(p\text{-}C_6H_4Me)_3\}_2]$	1680, 1610	832	27.6(s)	[92]
$[Pt(S_2CO)(PMe_2Ph)_2]$	1680, 1615	835–850	−30.92(s)	[101]
$[Pt(S_2CO)(PMe_3)_2]$	1695, 1605	855–865	−20.42(s)	[101]
$[Pt(S_2CO)(PPh_3)_2]$	1688, 1615	835	16.6(s)	[92]



(XV), M = Fe; **(XVI)**, M = Ru



(XVII)



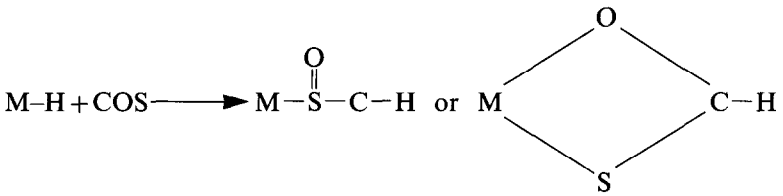
(XVIII)

[102–105]. The complex (**XVIII**) has also been prepared by the reaction of COS with bis(nitrogen) complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ or with bis(carbon dioxide) complex. The structure of (**XVIII**) has been determined by X-ray diffraction analysis and shows a pentagonal bipyramid coordination about the molybdenum with the axial positions occupied by one carbonyl and one PMe_3 ligand. Important bond distances and bond angles of dithiocarbonate complexes are given in Table 4.

2.3.3. Insertion reaction of carbonyl sulfide into M—X bonds

The insertion reactions of COS into metal–hydride, metal–carbon, metal–nitrogen and metal–oxygen bonds have been discussed by Pandey and Nigam [26]. In this article, recent developments in the insertion of COS into transition metal–hydride bonds is discussed.

Carbonyl sulfide insertion into a metal–hydride bond gives rise to monothioformate complexes:



The IR spectra of monothioformate complexes prove to be valuable in distinguishing between monodentate and bidentate bonding. The IR spectra of complexes containing a bidentate thioformate ligand show additional bands in the region 1340–1500 cm^{-1} which are assigned to $\nu(CO \cdots M)$ (Table 5). The ^1H NMR chemical shifts for monodentate thioformate ligand occur at a lower field than the bidentate thioformate ligand. The ^{13}C NMR spectra of monothioformate complexes exhibit a signal in the region δ 180–202 ppm.

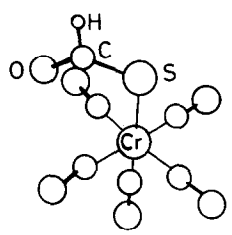
Darensbourg and Rockicki reported the formation of monothioformate complexes $[A][Cr(CO)_5(OSCH)]$ ($A \equiv [Ph_2P{=}N{=}PPh_2]$ or Et_4N) by the exchange of COS for carbon dioxide in $[A][Cr(CO)_5(O_2CH)]$ or by the direct reaction of COS with $[Cr(CO)_5H]^-$ [106,107]. The monothioformate ligand is coordinated to the chromium in the monodentate manner (**XIX**). Bianchini and co-workers have reported the insertion of COS into Cu—H bonds in the reactions of COS with copper(I) tetrahydroborates [108–110]. COS reacts with the η^2-BH_4 complexes

Table 4
Important bond distances (Å) and bond angles (deg) of dithiocarbonate complexes

Complex	M—S (Å)	S—C (Å)	C—O (Å)	S—M—S (deg)	S—C—S (deg)	Reference
$[Mo(CO)_2(S_2CO)(PMe_3)_3]$	2.577(7) 2.533(7)	1.83(3) 1.68(3)	1.236(12)	69.0(2)	111.0(5)	[104]
$[Pd(S_2CO)(PMe_2Ph)_2]$	2.318(3)	1.736(9)	1.23(2)	75.4(1)	109.5(5)	[101]

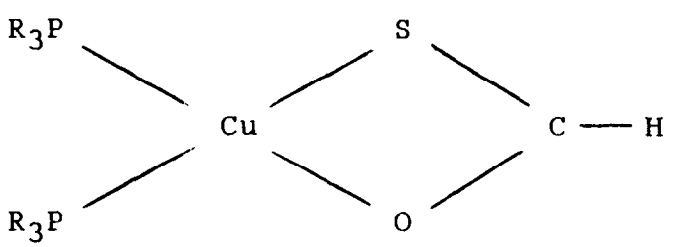
Table 5
Spectroscopic data for monolithioformate complexes

Complex	IR frequencies (cm^{-1})				^1H NMR, δ (ppm)	^{13}C NMR, δ (ppm)	Reference
	ν(CO)	ν(CO···M)	ν(CS)	ν(CH)			
$[Cr(CO)_5(\eta^1\text{-OCH})]^-$						198.8	[106]
$[(PPh_3)_2Cu(\eta^2\text{-SOCH})]$	1632	1340	800	2800	10.12		[110]
	1580			2770			
$[(PCy_3)_2Cu(\eta^2\text{-SOCH})]$	1630	1350	805	2800	10.76		[110]
	1580			2760			
[(triphos)Cu(η^1-SOCH)]	1625		805	2755	12.44	201.3	[110]
	1570			2660			
$[(np_3)Cu(\eta^1\text{-SOCH})]$	1635			2760			[141]
	1570						
$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-SOCH})(PPh_3)_2]$	1670					181.8	[111]
	1630						[112]
$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-SOCH})(AsPh_3)_2]$	1660					181.64	[111]
$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-SOCH})(SbPh_3)_2]$	1658					179.9	[111]

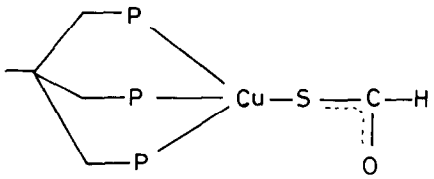


(XIX)

$[Cu(\eta^2\text{-}BH_4)(PR_3)_2]$ ($R \equiv Ph$, Cy) to afford the η^2-S,O-bonded monothioformates (**XX, XXI**) whereas the reaction of COS with the η^1-BH_4 complexes [(triphos)Cu(η^2-BH_4)] and $[(np_3)Cu(\eta^2\text{-}BH_4)]$ results in the formation of the η^1-S-bonded monothioformate (**XXII**) and (**XXIII**).



(XX), R = Ph; **(XXI)**, R = Cy



(XXII)

The IR spectra of (**XX**) and (**XXI**) exhibit absorption bands due to a monothioformate ligand bonding through sulfur in a bidentate manner. The IR spectra of (**XXII**) and (**XXIII**) are consistent with a monodentate thioformate ligand.

Carbonyl sulfide reacts with ruthenium hydride complexes $[(\eta^5\text{-}C_5H_5)RuHL_2]$ ($L \equiv PPh_3$, $AsPh_3$, $SbPh_3$) in methanol to give microcrystalline complexes (**XXIV**) [111,112].

2.3.4. Formation of sulfide complexes

The reactions of COS with metal complexes also results in the formation of sulfide complexes [26]. The trivalent uranium metallocene $[(C_5H_4Me)_3U]\cdot THF$ reacts with COS to form $[(C_5H_4Me)_3U]_2(\mu\text{-}S)$ [113].

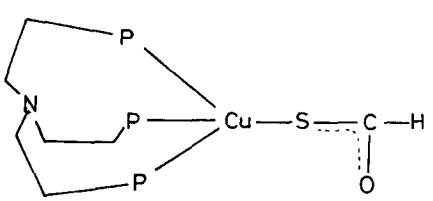
3. Coordination chemistry of carbon disulfide

3.1. Transition metal–carbon disulfide bonding and energetics

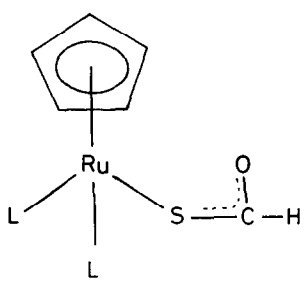
The coordination of CS_2 ligand to a transition metal (M) gives a wide variety of complexes which, apart from η^1-S end-on coordination, all involve bonding to carbon.

3.1.1. η^1-end-on coordination

In this type of bonding, CS_2 is bound to the transition metal through a sulfur atom with no change in the oxidation state of the metal. The CS_2 ligand behaves as a Lewis base, donating a lone pair of electrons from the $^1\pi_g$ (HOMO) orbital to the corresponding metal vacant orbital [29,114–118].



(XXIII)



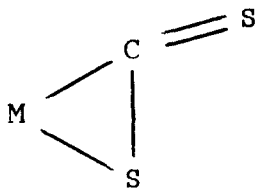
(XXIV)

3.1.2. η^2-side-on coordination

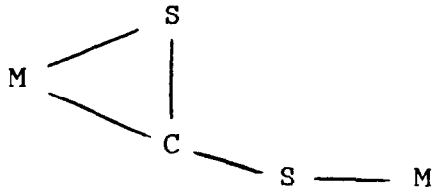
The main interaction in η^2-side-on coordination (**XXV**) is the π-back donation from the metal atom to the CS_2 ligand. Theoretical studies have led to a better understanding of the factors governing the bonding in CS_2 complexes [80,119–122]. The importance of the nature of the frontier molecular orbital has been emphasized. The best situation for the occurrence of the η^2-side-on coordination mode is the presence of a metal-dπ orbital as HOMO and an empty dσ orbital, pointing to the CS_2 ligand in the transition metal fragments. In the M-(η^2-CS_2) complex, the HOMO is a combination of metal dπ and CS_2 $1b_2$ and $2a_1$ orbitals. The theoretical calculations show that the carbon atom exerts a trans-influence stronger than that exerted by the sulfur atom [80]. Mulliken population analysis shows negative charges on the uncoordinated sulfur atom which confirms its nucleophilic character.

3.1.3. Bridging carbon disulfide complexes

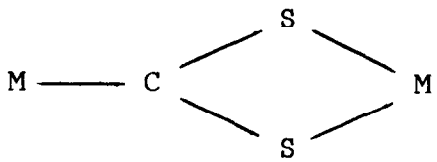
Carbon disulfide can also function as a bridge between two metal atoms and three metal atoms.



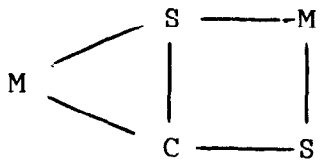
(XXV)



(XXVI)



(XXVII)



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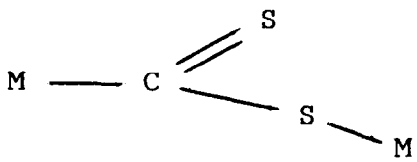
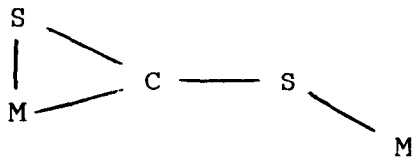


(XXIX)



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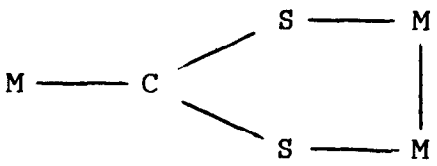
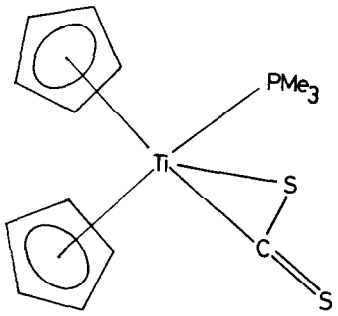


(XXXI)



(XXXII)

3.2. Preparation and structure

3.2.1. Mononuclear metal–carbon disulfide complexes

Transition metal CS_2 complexes are prepared by the reaction of CS_2 with transition metal complexes. The CS_2 ligand in M-η^2-CS_2 and M-η^1-CS_2 coordination modes acts as a better π-acceptor and a poor σ-donor. As a result, the net electron density shifts from metal (dπ orbital) to CS_2 (π^* orbital). This is expected to lead to a reduction in the C—S bond order of the CS_2 compared with the free CS_2. In fact, the (CS) stretching frequency of a variety of π-bonded CS_2 complexes is appreciably lower than that of free CS_2 (Table 6).

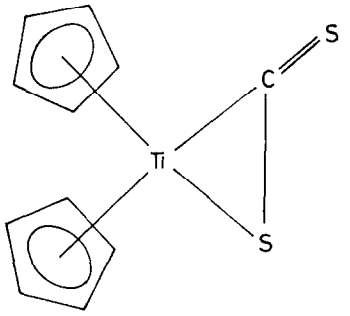
The titanium–CS_2 complex $[(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}CS_2)(PMe_3)]$ (**XXXII**) is prepared by the reaction of $[(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)_2]$ with CS_2 in pentane at 0 °C [123]. The reaction of $[(\eta^5\text{-}C_5H_5)_2Ti(\eta^3\text{-allyl})]$ with CS_2 yields $[(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}CS_2)]$ (**XXXIII**) [124]. Complex $[(\eta^6\text{-}C_6Et_6)Cr(CO)_2(C_4H_8)]$, obtained by UV irradiation of $[(\eta^6\text{-}C_6Et_6)Cr(CO)_3]$ in the presence of cyclooctene, reacts with CS_2 to produce $[(\eta^6\text{-}C_6Et_6)Cr(CO)_2(\eta^2\text{-}CS_2)]$ [125]. The complexes $[A]_2[W(CO)_5(\eta^1\text{-}CS_2)]$ (A ≡ Li or Na) may be prepared in solution by the reaction of CS_2 with $[W(CO)_5]^-$ in THF at −78 °C [126].

$Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ reacts with CS_2 at low temperature to give the η^1-CS_2 complex (**XXXIV**) [127]. Reaction of CS_2 with $[M(CO)_2(PPh_3)_3]$ (M ≡ Fe, Ru) gives the η^2-CS_2 complexes (**XXXV**) [87].

Reaction of ruthenocene with CS_2 gives $[(\eta^5\text{-}C_5H_5)_2Ru(\eta^2\text{-}CS_2)]$ [89]. UV irradiation of a solution of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ in CH_2Cl_2—CS_2 yields $[(\eta^5\text{-}C_5H_5)RuCl(\eta^2\text{-}CS_2)(PPh_3)_2]$. Complex $[(\eta^5\text{-}C_5H_5)RuCl(P(CH_2CH_2CN)_3)_2]$, owing to the lower basicity of the phosphine, does not react with CS_2. Reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)(PPh_3)_2]^+$, obtained by refluxing an acetonitrile solution of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ in the presence of $HgCl_2$, with CS_2 results in the formation of $[(\eta^5\text{-}C_5H_5)Ru(CS_2)(PPh_3)_2](HgCl_3)$. Complex $[(\eta^5\text{-}C_5H_4Me)Ru(CS_2)(PPh_3)_2]$-$(BF_4)$ is obtained by the reaction of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and $AgBF_4$ in the presence of CS_2 [128]. CS_2 reacts with osmium nitrosyl complex $[Os(NO)Cl(PPh_3)_3]$ to give (**XXXVI**) [129].

Table 6
IR frequencies of mononuclear carbon disulfide complexes

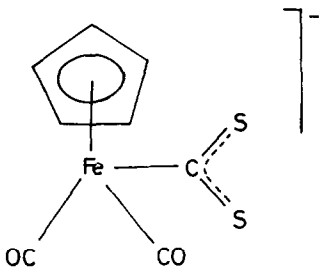
Complex	ν(CS) (cm^{-1})	ν(MCS) (cm^{-1})	Reference
$[(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}CS_2)(PMe_3)]$	1107		[123]
$[Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2]$	1142, 1155		[87]
$[Ru(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2]$	1126	650	[87]
$[(\eta^5\text{-}C_5H_5)_2Ru(\eta^2\text{-}CS_2)]$	1100		[89]
$[(\eta^5\text{-}C_5H_5)RuCl(\eta^2\text{-}CS_2)(PPh_3)_2]$	1173, 1000		[128]
$[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}CS_2)(PPh_3)_2][HgCl_3]$	1280	860	[128]
$[(\eta^5\text{-}C_5H_4Me)Ru(\eta^2\text{-}CS_2)(PPh_3)_2][BF_4]$	1280	860	[128]
$[Os(NO)Cl(\eta^2\text{-}CS_2)(PPh_3)_2]$	991		[129]
$[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}CS_2)\{P(OMe_3)\}]$	1165		[131]
$[(triphos)Ni(\eta^2\text{-}CS_2)]$	1145	630	[132]
$[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}CS_2)(PMe_3)]$	1159		[133]
$[(triphos)Rh(\eta^2\text{-}CS_2)]$	1160	640	[137]
$[(triphos)Rh(N_3)(\eta^2\text{-}CS_2)]$	1150	630	[137]
$[(triphos)IrCl(\eta^2\text{-}CS_2)]$	1140	650	[137]
$[Rh(NO)Cl_3(\eta^2\text{-}CS_2)]$	1140, 1000		[90]
$[Pd(\eta^2\text{-}CS_2)(PMePh_2)_2]$	1180		[140]
$[Pd(\eta^2\text{-}CS_2)(dppe)]$	1173		[140]
$[Pd(\eta^2\text{-}CS_2)(dpmb)]$	1173		[140]
$[Pt(\eta^2\text{-}CS_2)(dppe)]$	1158		[140,141]
	1141	650	[142]
$[Pt(\eta^2\text{-}CS_2)(dpmb)]$	1150		[140]
$[Pt(\eta^2\text{-}CS_2)(P\text{-}i\text{-}Pr_3)_2]$	1185		[140]



(XXXIII)

Complexes $[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}CS_2)L]$ (**XXXVII**) are obtained, in low yield along with other products, by the reactions of CS_2 with $[(\eta^5\text{-}C_5H_5)Co(CO)L)]$ ($L \equiv PEt_3$, P-*n*-Pr_3, P-*n*-Bu_3, PMe_2Ph, $PMePh_2$, PPh_3) [130]. $[(np_3)CoH]$ reacts with CS_2 to yield $[(np_3)Co(\eta^2\text{-}CS_2)]$ (**XXXVIII**) [13]. Kolb and Werner reported the formation of $[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}CS_2)\{P(OMe)_3\}]$ from the reaction of CS_2 with $[(\eta^5\text{-}C_5H_5)Co\{P(OMe)_3\}_2]$ [132].

Rhodium CS_2 complexes $[(\eta^5\text{-}C_5R_5)Rh(\eta^2\text{-}CS_2)(PMe)]$ ($R \equiv H$, Me) are formed when $[(\eta^5\text{-}C_5R_5)Rh(PMe_3)_2]$ reacts with CS_2 [133]. Bianchini and co-workers



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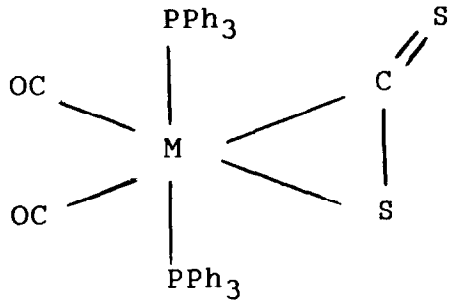
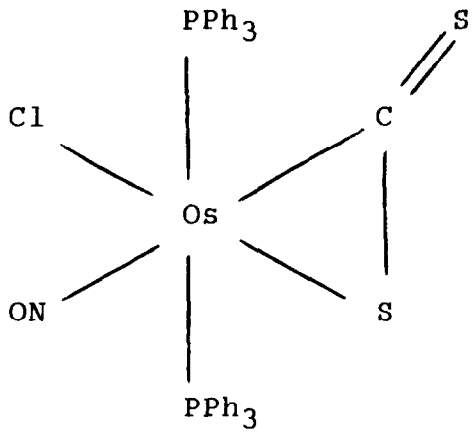
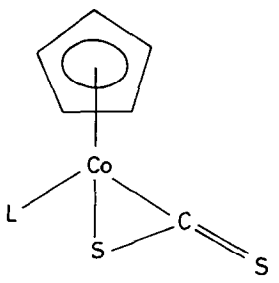


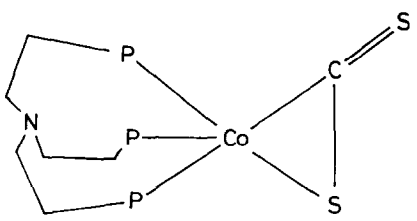
(XXXV)



(XXXVI)



(XXXVII)



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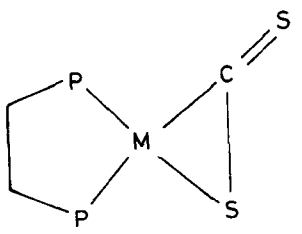


(XXXIX)

have synthesized CS_2 complexes of rhodium and iridium containing tridentate phosphine ligands [134–137]. Reaction of CS_2 with [(np_3)RhH] in the presence of $NaBPh_4$ yields [$(np_3)Rh(\eta^2\text{-}CS_2)](BPh_4)$. The molecular structure of [$(np_3)Rh(\eta^2\text{-}CS_2)][BPh_4]$ has been determined by X-ray diffraction analysis. [(triphos)$Rh(\eta^2\text{-}CS_2)\cdot C_6H_6$ is formed by the reaction of CS_2 with $[RhCl(C_2H_4)]_2$ in the presence of triphos. The reaction of $[RhN_3(COD)]_2$ with CS_2 in the presence of triphos results in the formation of [(triphos)$RnH_3(\eta^2\text{-}CS_2)$]. Complex

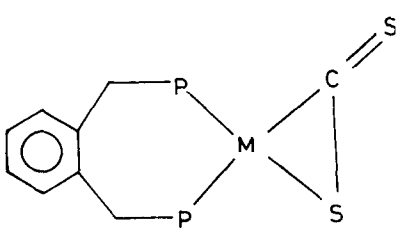
[(triphos)IrCl(η^2-CS_2)] can be obtained by the reaction of $[IrCl(COD)]_2$ with CS_2 in the presence of triphos. Carbon disulfide reacts with $[Rh(NO)Cl_3]$ in ethanol to produce $[Rh(NO)Cl_2(\eta^2\text{-}CS_2)]$ [90]. Iridium complexes $[Ir(COD)(\eta^2\text{-}CS_2)(PR_3)_2]$ (R ≡ Ph, Cy) can be obtained by the reaction of $[Ir(COD)(PR_3)_2]$ with CS_2 in dichloromethane [138].

The nickel complex $[(triphos)Ni(S_2CSMe)][BPh_4]$ reacts with $NaBH_4$ to afford the CS_2 complex $[(triphos)Ni(\eta^2\text{-}CS_2)]$ [96]. Hoffman and co-workers have reported a trimorpholinosphosphine nickel(0) complex of CS_2 [139]. Palladium CS_2 complexes $[Pd(\eta^2\text{-}CS_2)(PR_3)_2]$ ($PR_3 \equiv PMePh_2$, P-i-Pr_3) are prepared by the reaction of CS_2 with $[Pd(PMePh_2)_4]$ and $[Pd(P\text{-}i\text{-}Pr_3)_2]$ complexes. Complexes $[M(\eta^2\text{-}CS_2)(PR_3)_2]$ (M ≡ Pd, Pt) react with bidentate phosphine ligands (dppe, dpmb) to give the chelate complexes $[M(\eta^2\text{-}CS_2)(dppe)]$ (**XXXIX**) and $[M(\eta^2\text{-}CS_2)(dpmb)]$ (**XL**) [94,140,141]. Walker and co-workers have also reported the formation of $[Pt(\eta^2\text{-}CS_2)(dppe)]$ from the reaction of $[M(\eta^2\text{-}CS_2)(PPh_3)_2]$ [142,143]. Gregor has reported gas phase reactions of CS_2 with electron deficient carbonyl complexes $[Cr(CO)_3]^-$, $[CR(CO)_4]^-$, $[Mn(CO)_3]^-$, $[Mn(CO)_4]^-$, $[Fe(CO)_2]^-$, $[Fe(CO)_3]^-$, $[Ni(CO)_2]^-$ and $[Ni(CO)_3]^-$ affording CS_2 complexes [144].

3.2.2. *Bridging carbon disulfide complexes*

A number of transition metal complexes containing bridged CS_2 has been reported. The IR spectra of complexes with bridged CS_2 ligand show a (CS) absorption in the region 900–1050 cm^{-1}, substantially lower than the values (1100–1175 cm^{-1}) normally found for M-η^2—CS_2 complexes.

The complex anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ which is unstable at room temperature and has not been isolated as solid, reacts with a variety of Lewis acids. A number of bimetallic and trimetallic CS_2 complexes, containing one or two other $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $Cr(CO)_5$, $Mn(CO)_5$, $Re(CO)_5$ and $W(CO)_5$ functionalities on the sulfur centers, has been obtained from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ [145–150]. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ reacts with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ to afford (**XLI**). This bridged CS_2 complex $[(\eta^5\text{-}C_5H_5)(CO)_2FeC(S)SFe(CO)_2(\eta^5\text{-}C_5H_5)]$ (**XLI**) and the methylated complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS(SMe)]$ are useful precursors for the synthesis of bimetallic and trimetallic CS_2 bridged complexes. Bimetallic complexes $[(\eta^5\text{-}C_5H_5)(CO)_2FeC(SMe)SM'Ln]$ (**XLII**) (M'Ln ≡ $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $Cr(CO)_5$, $Mn(CO)_5$, $Re(CO)_5$ and $W(CO)_5$) have been prepared by the reaction of



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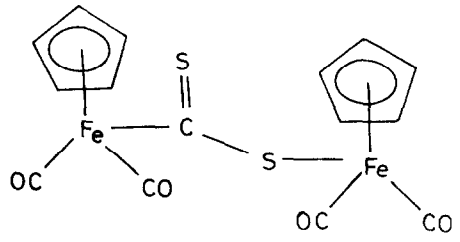

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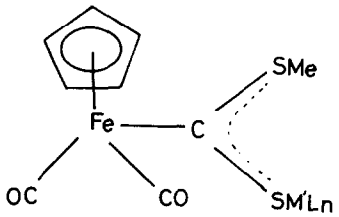
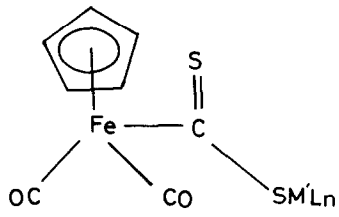


(XLII)

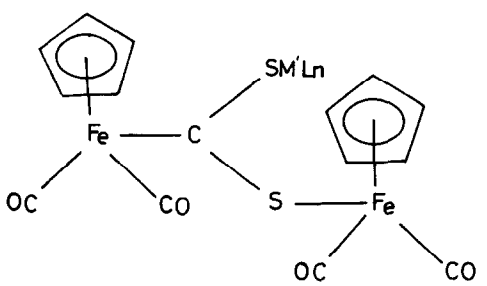


(XLIII)

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS(SMe)]$ with electrophiles. The synthesis and characterization of complexes of the types (**XLIII**) and (**XLIV**) ($M'Ln \equiv (\eta^5\text{-}C_5H_5)Fe(CO)_2$, $W(CO)_5$) have also been reported.

The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS(SMn(CO)_5)]$, spontaneously transforms on heating into (**XLV**). Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ with bis-acetonitrile complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(CH_3CN)_2)](PF_6)$ in THF produces (**XLVI**) ($X \equiv O$). The thiocarbonyl analog (**XLVI**) ($X \equiv S$) can be prepared from the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ with $[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)I]$ [150]. Busetto and co-workers [148] obtained (**XLVI**) ($X \equiv O$) by refluxing (**XLVII**) in dichloromethane. Photolysis of (**XLVII**) gives (**XLVI**) in 10%–17% yield [148,150].

Reaction of $[Ni(COD)_2]$ with CS_2 in the presence of PPh_3 yields complex (**XLVIII**) ($M \equiv Ni$, $R \equiv Ph$) [151]. Bimetallic complexes of platinum and palladium (**XLVIII**) containing monodentate phosphine ligands have been synthesized by Farrar and co-workers [152,153].



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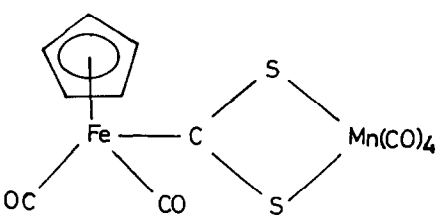

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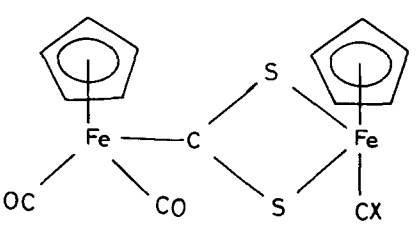

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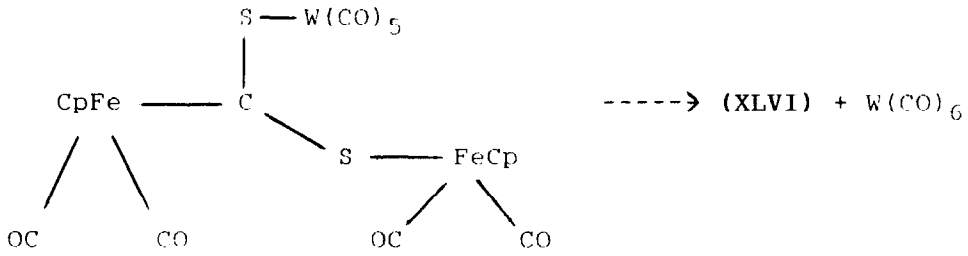

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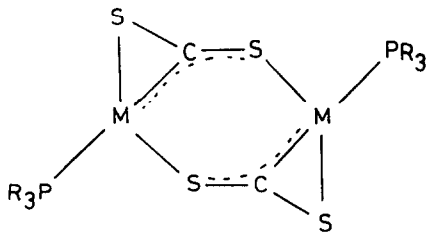

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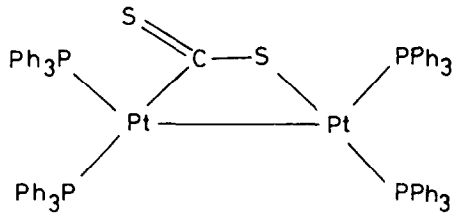


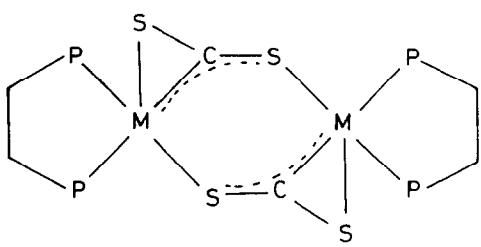
(XLIX)

The molybdenum complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(\mu_2,\eta^3\text{-}CS_2)]$ contains a bridging CS_2 ligand bonded to one Mo atom through the carbon and one of the sulfur atoms and to the other Mo atom through the second sulfur atom [154].

Reaction of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ results in the formation of (**XLIX**) [141,143].

The synthesis and characterization of bridged CS_2 complexes of platinum and palladium containing terminal or bridged diphosphine ligands have been a subject of interest. The complexes $[M(\eta^2\text{-}CS_2)(dppe)]$ (M ≡ Pd, Pt) slowly dimerize in solution to produce bridging CS_2 complexes $[(dppe)M(\mu\text{-}CS_2)M(dppe)]$ (**L**) [141].

Reaction of $[Pd_2Cl_2(dmpm)_2]$ with CS_2 results in the formation of a deep red–orange complex (**LI**) which may also be obtained by the reaction of $[Pd_2(\mu\text{-}CO)Cl_2(dmpm)_2]$ with CS_2 [155]. Complexes (**LII**) (R ≡ Ph, *p*-tolyl) are obtained by the reaction of $[Pt(C{\equiv}CR)_2(dppm)_2]$ with CS_2 in benzene [156].



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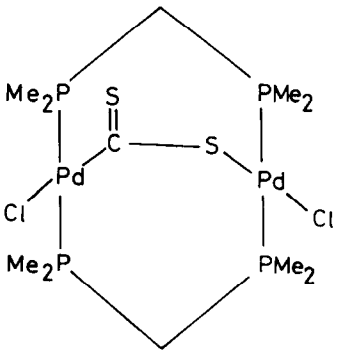

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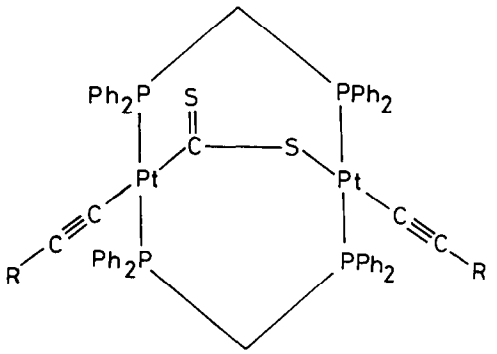


(LII)

Reaction of $[Pt_2Cl_2(dppm)_2]$ with CS_2 leads to the formation of complex (**LIII**) [157,158].

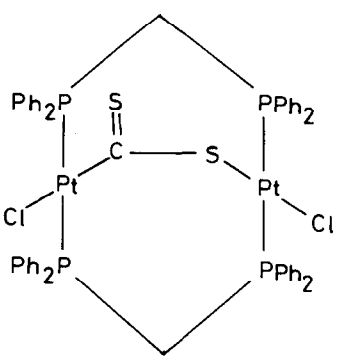
3.3. Reactions of carbon disulfide complexes

3.3.1. Thiocarbonylation reaction

One of the most important routes for the synthesis of thiocarbonyl complexes is by the reaction of CS_2 with transition metal complexes. There are various paths for preparation of the thiocarbonyl ligand via the CS_2 ligand.

(a) Coordination of CS_2 to a metal center is followed by methylation and the methylated moiety undergoes hydride attack producing a thiocarbonyl complex.

(b) Coordination of CS_2 to a metal center is followed by sulfur elimination. There are three routes for the abstraction of sulfur from CS_2 by PR_3 producing $S{=}PR_3$: (i) an isolated η^2-CS_2 complex is attacked by added phosphine ligand, (ii) coordinated phosphine ligand is displaced from a metal center and used as the abstracting moleule for the η^2-CS_2 ligand, and (iii) a $CS_2{-}PR_3$ mixture is used.



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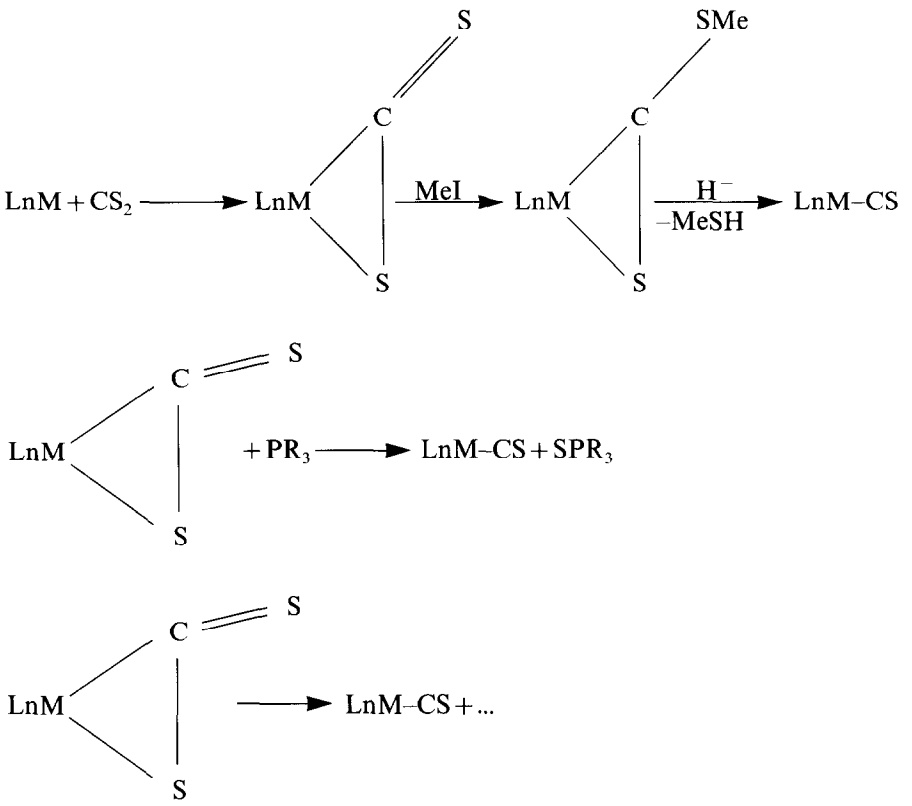


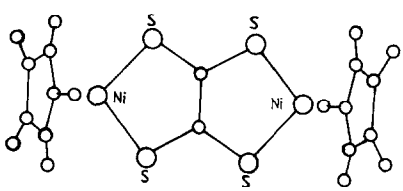
(c) Reductive cleavage of CS_2 ligand produces sulfido and thiocarbonyl ligands. Some examples of thiocarbonylation reaction are given in Table 7 [159–169]).

3.3.2. *Reductive dimerization of coordinated carbon disulfide*

3.3.2.1. Metal promoted head-to-head dimerization of carbon disulfide. Transition metal promoted reductive dimerization of two coordinated CS_2 molecules in the head-to-head coupling form the tetrathiooxalate ligand [135,165,170–174]. Maj and co-workers reported the first structurally characterized example of coordinated C_2S_4 (**LIV**) from the reaction of CS_2 with nickel pentamethylcyclopentadienyldicarbonyl $[(\eta^5\text{-}C_5Me_5)Ni(CO)_2]_2$ [171]. Reaction of CS_2 with the iron cluster carbonyl $[Fe_2(CO)_9]$ results in the formation of a tetranuclear complex $[(CO)_6Fe_2(C_2S_4)Fe_2(CO)_6]$ in low yield, along with other products [165]. In this complex the central μ-C_2S_4 unit links, end-on-fashion, two Fe_2 fragments (**LV**). Synthesis and structural studies of $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)\}_2(\mu\text{-}C_2S_4)]$ and $[\{(\eta^5\text{-}C_5Me_5)Co\}_2(\mu\text{-}C_2S_4)]$ have been reported [172]. Carbon–carbon bond formation by reductive head-to-head coupling of CS_2 is also activated by a titanium(II) complex. Reaction of $[(\eta^5\text{-}C_5H_5)Ti(CO)_2]$ with neat CS_2 under an inert atmosphere gives $[\{(\eta^5\text{-}C_5H_5)Ti\}_2(\mu\text{-}C_2S_4)]$ (**LVI**) [173]. Complex (**LVI**), unlike the

Table 7
Thiocarbonylation reactions of carbon disulfide

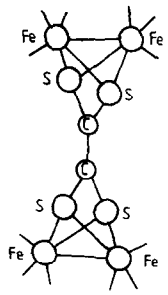
Precursor complex	Isolated product	Reference
$[(np_3)CoH] + MeI + NaBH_4$	$[(np_3)Co(CS)]^+$	[131,159]
$[(np_3)CoH] + NaBPh_4$	$[(np_3)Co(CS)]^+$	[131]
$[(\eta^5\text{-}C_5H_5)Co(CO)_2] + L$ ($L \equiv PEt_3$, P-*n*-Pr_3, P-*n*-Bu_3, PMe_2Ph, PPh_3, t-BuNC)	$[(\eta^5\text{-}C_5H_5)Co(CS)L] + \ldots$	[130]
$[Fe(CO)_2(PPh_3)_3] + MeI + NH_4PF_6 +$ P-*n*-Bu_6	$[Fe(CO)_2(CS)(PPh_3)_2]$	[160]
$[Fe(CO)_2(\eta^2\text{-}CS_2Me)L_2]^+ + Na/Hg$ ($L \equiv PMe_3$, PMe_2Ph, P-*n*-Bu_3)	$[Fe(CO)_2(CS)L_2]$	[161]
$[(\eta^6\text{-}C_6Et_6)Cr(CO)_2(C_8H_{14})] + PPh_3$	$[(\eta^6\text{-}C_6Et_6)Cr(CO)_2(CS)]$	[125]
$[W(CO)_3(\eta^2\text{-}CS_2)(L)] +$ P-*n*-Bu_3 ($L \equiv$ dmpe, dppe)	$[W(CO)_3(CS)(L)]$	[162]
$[RuCl_2(PPh_3)_3] + PPh_3$	$[Ru(CS)Cl_2(H_2O)(PPh_3)_2]$	[163]
$[RuCl_2(PPh_3)_3]$	$[\{Ru(CS)Cl_2(PPh_3)_2\}_2(\mu\text{-}Cl)_2]$	[164]
$[Fe_3(CO)_{12}]$	$[Fe_3(CO)_8(CS)(S_2)] + \ldots$	[165]
$[PtL_3]$ [$L \equiv$ t-BuN=P—N(SiMe$_3$)(t-Bu)]	$[\{PtL(CS)\}_2(\mu\text{-}S)_2]$	[166]
$[M(\eta^2\text{-}CS_2)(dppe)] + [Pt(PPh_3)_4]$	$[(dppe)M(\mu\text{-}S)Pt(CS)(PPh_3]$	[143]
[Ru(CO)(TPP)(EtOH)]	[Ru(CO)(CS)(TPP)]	[167]
$[Re_2X_4(\mu\text{-dppm})_2]$ ($X \equiv$ Cl, Br)	$[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2]$	[168]
$[Re_2Br_4(\mu\text{-dpam})_2]$	$[Re_2(\mu\text{-}S)(\mu\text{-Br})Br_3(CS)(\mu\text{-dpam})_2]$	[169]
$[RuH(MeCOO)(PPh_3)_3]$	$[\{Ru(CS)(MeCOO)(PPh_3)_2\}_2(\mu\text{-}S)]$	[88]
$[Ru(MeCN)_2Cl_2(PPh_3) + PPh_3$	$[\{Ru(CS)Cl(PPh_3)_2\}_2(\mu\text{-}Cl)2]$	[80]
$[RuH(CO)Cl(AsPh_3)_3]$	$[RuH(CO)(CS)(AsPh_3)_2] + \ldots$	[88]
$[Rh(NO)(PPh_3)_3]$	$[Rh(NO)(CS)(PPh_3)_3]$	[90]



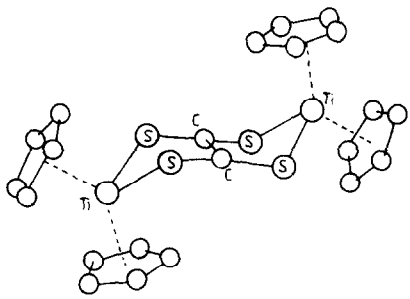
(LIV)

C_2O_4-bridged analog, is diamagnetic owing to much greater electron delocalization of the C_2S_4-bridged ligand. The bridging C_2S_4 unit is coordinated to two centrosymmetrically equivalent $(\eta^5\text{-}C_5H_5)Ti$ moieties.

Bianchini and co-workers reported an extensive experimental and theoretical study of C_2S_4-bridged bimetallic complexes of rhodium and iridium [135,174]. Complexes $[(triphos)M(\mu\text{-}C_2S_4)M(triphos)]X_2$ ($M \equiv Rh$, $X \equiv Cl^-$, BPh_4^-, BF_4^-, PF_6^-; $M \equiv Ir$, $X \equiv Cl^-$, BPh_4^-) have been prepared from $[(triphos)RhCl(\eta^2\text{-}CS_2)\cdot C_6H_6]$, $[(triphos)RhN_3(\eta^2\text{-}CS_2)]$ and $[(triphos)IrCl(\eta^2\text{-}CS_2)]$. The complex $[(triphos)Rh(\mu\text{-}C_2S_4)Rh(triphos)](BPh_4)_2$ can also be prepared by the reaction of CS_2 with

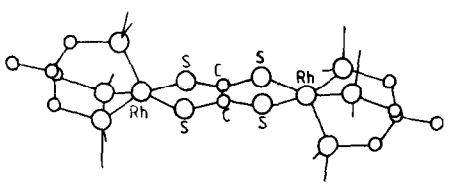


(LV)



(LVI)

[(triphos)Rh(COD)](BPh_4) or [(triphos)Rh(C_2H_4)$_2$](BPh_4). The neutral paramagnetic complex [(triphos)Rh(μ-C_2S_4)Rh(triphos)] is obtained by the reaction of [(triphos)RhCl(η^2CS_2)] with $NaBH_4$ or $LiHBEt_3$. The molecular structure of [(triphos)Rh(μ-C_2S_4)Rh(triphos)](BPh_4)$_2 \cdot CH_2Cl_2$ has been determined by X-ray diffraction analysis. The C_2S_4 unit is planar but the Rh(μ-C_2S_4)Rh unit is not completely planar, each Rh atom being 0.3 Å out of the C_2S_4 plane. The relative orientation of the bridge with respect to each terminal (triphos)Rh fragment is such that each metal is approximately square pyramidal (**LVII**). The C—C bond is shorter in these M(C_2S_4)M complexes compared with the free tetrathiooxalate dianion (the C—C bond is 1.461(19) Å) (Table 8).



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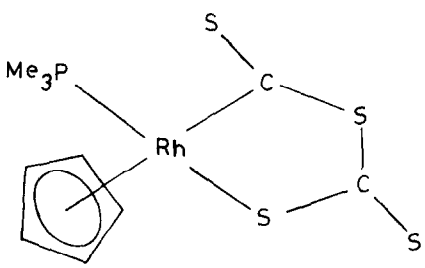


(LVIII)

Table 8
Selected bond distances (Å) of tetrathiooxalate complexes

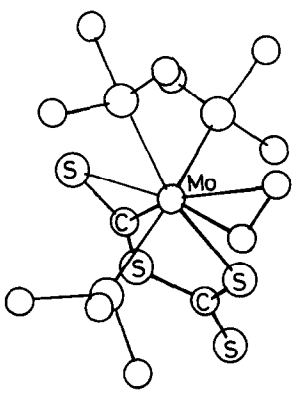
Complex	C—C (Å)	C—S (Å)	Reference
[(η^5-Me_5C_5)Ni(μ-C_2S_4)Ni(η^5-C_5Me_5)]	1.36(1)	1.718(2)	[171]
[$(CO)_6Fe_2$(μ-C_2S_4)$Fe_2(CO)_6$]	1.332	1.775	[165]
[(η^5-C_5H_5)$_2$Ti(μ-C_2S_4)Ti(η^5-C_5H_5)$_2$]	1.41	1.736	[173]
[(triphos)Rh(μ-C_2S_4)Rh(triphos)][BPh_4]	1.37(3)	1.76(2) 1.70(2)	[174]

3.3.2.2. Metal-promoted head-to-tail dimerization of carbon disulfide. The metal-promoted reductive dimerization of CS_2 in the head-to-tail coupling yields asymmetric heterometallocycles $M(\eta^2\text{-}C_2S_4)$ and $M(\eta^3\text{-}C_2S_4)$ [105,175–178]. The rhodium complex $[(\eta^5\text{-}C_5H_5)Rh(C_2S_4)(PMe_3)]$ has an $\eta^2\text{-}C_2S_4$ ligand with a five-membered RhSCSC heterometallocyclic ring (**LVIII**) [175]. *Trans*-$[M(C_2H_4)_2(PMe_3)_4]$ ($M \equiv Mo$, W) reacts with CS_2 in diethylether to afford black complexes. $[M(C_2S_4)(C_2H_4)_2(PMe_3)_3]$ [49,105,176]. The spectral studies (IR and NMR) are consistent with a head-to-tail reductive dimerization of CS_2 and formation of a heterometallocyclic unit M(SC(S)SC=S). Complexes $[Mo(C_2S_4)(C_2H_4)(PMe_3)_3]$ (**LIX**), $[Ni(C_2S_4PMe_3)(PMe_3)]$ (**LX**) [177], and $[Rh_2(C_2S_4)(CO)Cl_2(Ph_2PCH_2PPh_2)]$ (**LXI**) [178] have an $\eta^3\text{-}C_2S_4$ ligand with bonding through two sulfur atoms and one carbon atom.

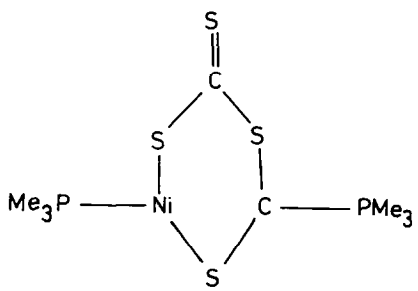
3.3.3. Insertion reaction of carbon disulfide

3.3.3.1. Insertion into the M—H bond. Insertion of CS_2 into an M—H bond results in the formation of dithioformato complexes.

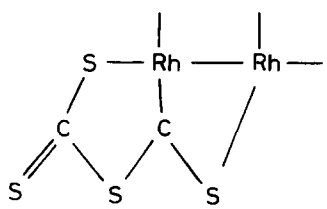
Carbon disulfide reacts with cobalt hydride complexes $[CoH_3(PPh_3)_2]$ and $[CoH\{P(OPh)_3\}_4]$ to give dithioformate complexes $[Co(S_2CH)(PPh_3)_2]$ and $[Co(S_2CH)\{P(OPh)_3\}_2]$ respectively by the insertion of CS_2 into the Co—H bond [112].



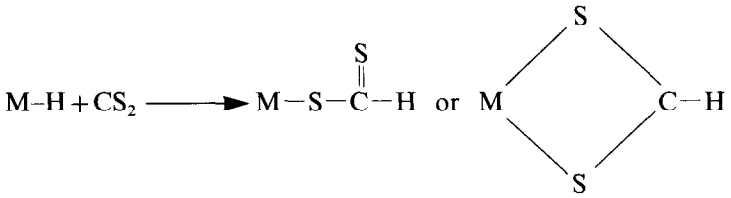
(LIX)



(LX)



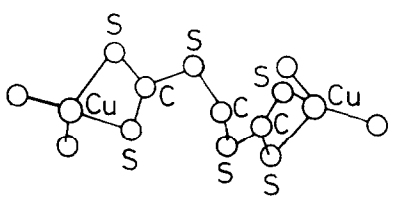
(LXI)



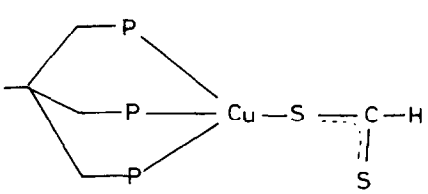
Bianchini and co-workers have reported insertion reactions of CS_2 into the copper–hydride bond [108,109,179–182]. The yellow complex $[(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2]$ (**LXII**) is obtained from the reaction of excess CS_2 with $[Cu(\eta^2\text{-}BH_4)(PPh_3)_2]$. In complex (**LXII**) two $(PPh_3)_2Cu$ units are held by a bridging $S_2CSCH_2SCS_2^{2-}$ ligand. On addition of n-heptane, a red complex $[Cu(\eta^2\text{-}S_2CH)(PPh_3)_2]$ is formed, which reacts with carbon disulfide to reproduce the yellow complex (**LXII**). The $\eta^1\text{-}BH_4$ complexes $[(triphos)Cu(\eta^1\text{-}BH_4)]$ and $[(np_3)Cu(\eta^1\text{-}BH_4)]$ react with CS_2 to give the dithioformato complexes $[(triphos)Cu(\eta^1\text{-}S_2CH)]$ (**LXIII**) and $[(np_3)Cu(\eta^1\text{-}S_2CH)]$ (**LXIV**) respectively [179].

The ruthenium dithioformate complex $[Ru(CO)Cl(S_2CH)(PPh_3)_2]$ is obtained from the reaction of CS_2 with $[RuH(CO)Cl(PPh_3)(4\text{-}vp)]$ (4-vp is 4-vinylpyridine) [183]. The IR absorption bands at 1235 cm^{-1} and 930 cm^{-1} are consistent with the presence of a bidentate dithioformate ligand (Table 9). Insertion of CS_2 into the Ru—H bond and the formation of dithioformate complexes $[(\eta^5\text{-}C_5H_5)Ru(S_2CH)L_2]$ ($L \equiv PPh_3$, $AsPh_3$, $SbPh_3$) have been reported [111].

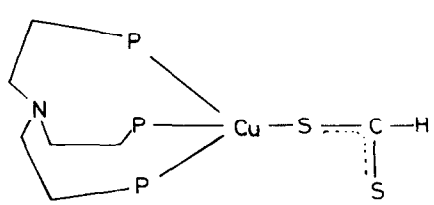
3.3.3.2. Insertion into the M—C bond. A number of insertion reactions of CS_2 into a metal–carbon bond have been studied [184–192]. Selected structural data of insertion products are summarized in Table 10. Campus and co-workers have



(LXII)



(LXIII)



(LXIV)

Table 9
IR and ^1H NMR spectral data for dithioformate complexes

Complex	IR frequencies (cm^{-1})			^1H NMR, δ (ppm)	Reference
	$\nu_{as}(CS_2)$	$\nu_s(CS_2)$	ν(HCS)		
$[Co(S_2CH)(PPh_3)_2]$	910	740	1230	—	[112]
$[Co(\eta^2\text{-}S_2CH)\{P(OPh)_3\}_2]$	950	—	1240	—	[112]
$[Cu(\eta^2\text{-}S_2CH)(PPh_3)_2]$	960	820	1235	11.27	[179]
$[(triphos)Cu(\eta^1\text{-}S_2CH)]$	1012	810	1245	—	[179]
$[(np_3)Cu(\eta^1\text{-}S_2CH)]$	985	—	1235	11.26	[179]
$[Ru(CO)Cl(\eta^2\text{-}S_2CH)(PPh_3)_2]$	930	—	1235	11.88	[183]
$[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}S_2CH)(PPh_3)(AsPh_3)]$	1020	—	—	11.6	[111]
$[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}S_2CH)(AsPh_3)_2]$	1020	—	—	11.6	[111]

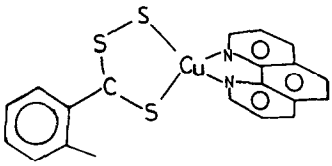
Table 10
Selected structural data of insertion products of carbon disulfide into the M—C bond

Complex	M—S (Å)	C—C (Å)	C—S (Å)	S—C—S (deg)	S—M—S (deg)	Reference
$[Cu_2(S_3C\text{-}o\text{-tolyl})(S_2C\text{-}o\text{-tolyl})$ (bipy)]	2.247(3) 2.201(2)	1.485(7)	1.680(4) 1.679(5)	128.2(3)	—	[186]
$[(C_5Me_5CS_2)Cu(PPh_3)_2]$	2.40(1) 2.381(9)	1.61(4)	1.68(3)	118(2)	75.2(3)	[187]
$[(C_5Me_5CS_2)Au(P\text{-}i\text{-}Pr_3)]$	2.317(3)	1.50	1.72(1) 1.65(1)	120.7(6)	—	[187]
[Ru(CO)Cl](S$_2$C—CH=CHR) $(PPh_3)_2]$	2.52(2) 2.35(2)	1.56	1.65(4) 1.83(5)	—	72.4(7)	[188]

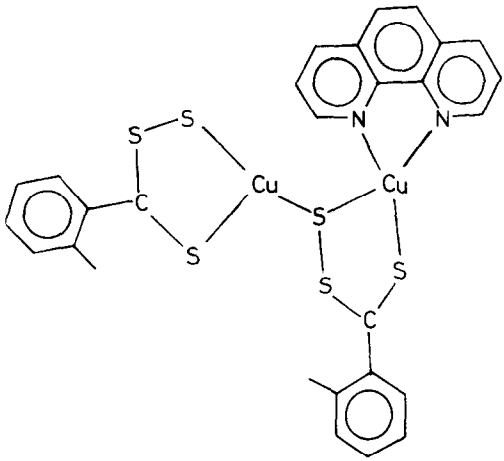
reported the insertion of CS_2 in copper–carbon bonds of arylcopper(I) [phenylcopper, *o*-tolylcopper and *p*-tolylcopper] complexes, in the presence of tertiary mono and bidentate phosphines [184–187] and in the presence of bidentate nitrogen-containing ligands such as 2,2′-bipyridine and 1,10-phenanthroline [188]. The structures of [Cu(S$_3$C-*o*-tolyl)(phen)] (**LXV**), [{Cu(S$_3$C-*o*-tolyl)}$_2$(phen)] (**LXVI**) and [Cu$_2$(S$_3$C-*o*-tolyl)(S$_2$C-*o*-tolyl)(bipy)] have been determined by X-ray diffraction analysis.

Otto and Werner reported the insertion of CS_2 into Cu—C, Ag—C and Au—C bonds. Reactions of CS_2 with $[(\eta^5\text{-}C_5Me_5)Cu(PR_3)]$ ($PR_3 \equiv PPh_3$, PMe_3, P-i-Pr$_3$) and with $[(\eta^5\text{-}C_5Me_5)Au(PR_3)]$ ($PR_3 \equiv PPh_3$, P-i-Pr$_3$) result in the formation of dithiocarboxylato complexes $[(C_5Me_5CS_2)Cu(PPh_3)_2]$ (**LXVII**), $[(C_5Me_5CS_2)Cu(PMe_3)_2]$, $[(C_5Me_5CS_2)Cu(P\text{-}i\text{-}Pr_3)]$, $[(C_5Me_5CS_2)Au(PPh_3)_2]$ and $[(C_5Me_5CS_2)Au(P\text{-}i\text{-}Pr_3)]$ (**LXVIII**) by insertion of CS_2 into the M—C_5Me_5 bond. Complex $[(C_5Me_5CS_2)Ag(PPh_3)_2]$ (**LXIX**) can be obtained from the reaction of excess CS_2 with $[AgCl(PPh_3)]_4$ and C_5Me_5Li [189].

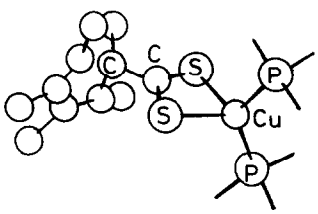
Insertion of CS_2 into an Ru—C bond has been observed in the reactions of CS_2 with $[Ru(CO)Cl(HC{\equiv}CHR)(PPh_3)_2]$ ($R \equiv$ Ph or t-Bu). The insertion products



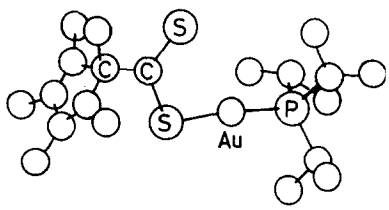
(LXV)



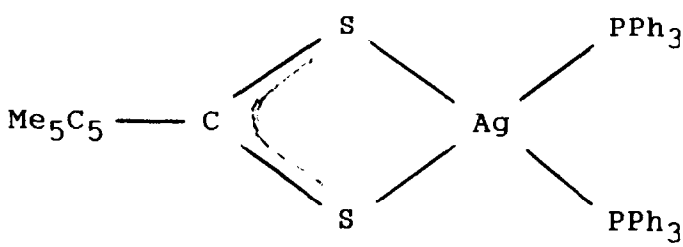
(LXVI)



(LXVII)



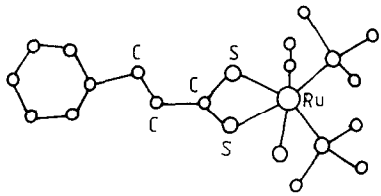
(LXVIII)



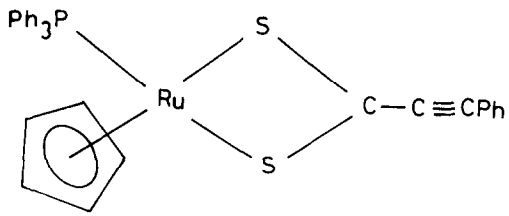
(LXIX)

$[Ru(CO)Cl(S_2C-CH=CHR)(PPh_3)_2]$ contain a bidentate alkenedithiocarboxylate ligand bonded through two sulfur atoms. The molecular structure of $[Ru(CO)Cl(S_2C-CH=CHR)(PPh_3)_2]$ (**LXX**) has been determined by X-ray crystallographic analysis [190]. Insertion of CS_2 into an Ru—C bond has also been observed in the reaction of CS_2 with $[(\eta^5\text{-}C_5H_5)Ru(C_2Ph)(PPh_3)_2]$ producing $[(\eta^5\text{-}C_5H_5)Ru(\eta^2\text{-}S_2CC{\equiv}CPh)(PPh_3)]$ (**LXXI**) [191].

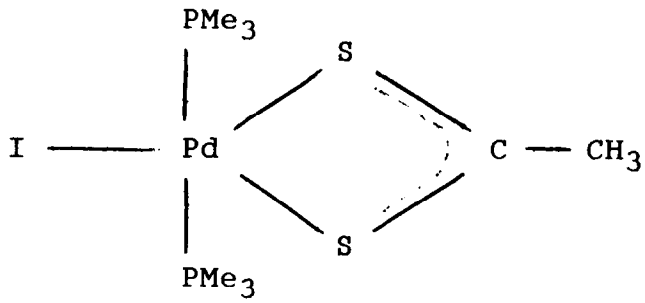
Reaction of CS_2 with $[PdI(CH_3)(PMe_3)_2]$ gives *trans*-$[PdI(S_2CCH_3)(PMe_3)_2]$ (**LXXII**) by insertion of CS_2 into the Pd—CH_3 bond [140].



(LXX)



(LXXI)



(LXXII)

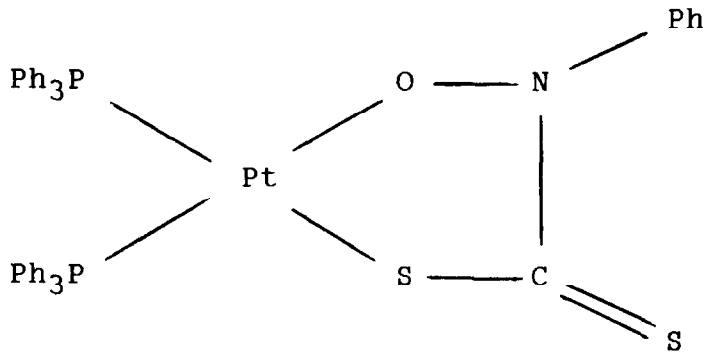
3.3.3.3. Insertion into the M—N bond. Insertion of CS_2 into an $M-NR_2$ bond produces dithiocarbamato complexes $[M(S_2CR_2)]$ [193,194].

Complex $[Pt(PhNO)(PPh_3)_2]$ reacts with CS_2 to give (**LXXIII**) by the insertion of CS_2 into the Pt—N bond [195,196].

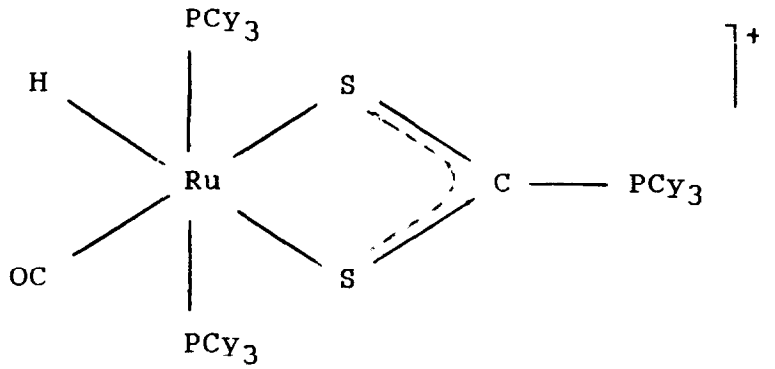
3.3.3.4. Insertion into the M—P bond. Insertion of CS_2 into an $M-PR_3$ bond produces phosphinodithiocarboxylate complexes $[M(S_2CPR_3)]$. Reaction of CS_2 with $[RuH(CO)Cl(PCy_3)_3]$ gives a phosphinodithiocarboxylate complex (**LXXIV**), by insertion of CS_2 into the $Ru-PCy_3$ bond [197].

Insertion of CS_2 into an $Rh-PPh_3$ bond was observed in the reaction of CS_2 with $[Rh_2(CO)_2(PPh_3)_4(\mu\text{-bipy})]$ and $[Rh(CO)L(PPh_3)_2]X$ ($L \equiv$ py, α-picoline; $X \equiv ClO_4$, NO_3). The insertion products are $[Rh_2(CO)_2(PPh_3)_2(S_2CPPh_3)_2(\mu\text{-bipy})]$ and $[Rh(CO)L(PPh_3)(S_2CPPh_3)]$ [198].

CS_2 inserts into the $Pd-PR_3$ bond in complexes $[Pd(PR_3)_4]$ ($PR_3 \equiv PMe_3$,



(LXXIII)



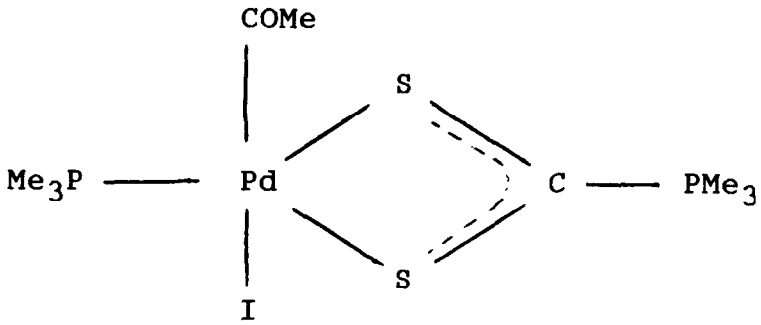
(LXXIV)

PMe_2Ph) to give binuclear complexes $[Pd(S_2CPR_3)(PR_3)]_2$. Complex $[Pd(S_2CPMe_3)(PMe_3)]_2$ can also be obtained from the reaction of $[Pd(\eta^2\text{-}CS_2)(PPh_3)_2]$ with PMe_3 [140]. Reactions of CS_2 with $[PdI(COCH_3)(PMe_3)_2]$ and $[PdR(PMe_3)_3](BPh_4)$ (R ≡ Me, COMe, Ph) give phosphinodithiocarboxylate complexes (**LXXV**) and (**LXXVI**) [140,199].

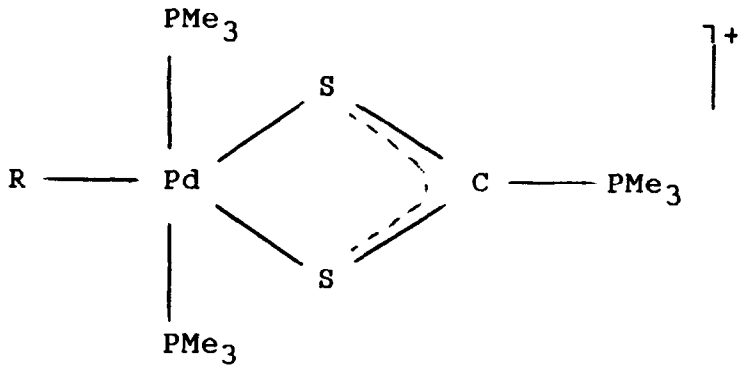
Carbon disulfide inserts into the Zr—P bond of $[(\eta^5\text{-}C_5H_5)_2ZrCl(P\{SiMe_3)_2\}]$ to give $[(\eta^5\text{-}C_5H_5)_2ZrCl\{\eta^2\text{-}S_2CP(SiMe_3)_2\}]$. The structure of the complex $[(\eta^5\text{-}C_5H_5)_2ZrCl(\eta^2\text{-}S_2CP(SiMe_3)_2\}]$ is pyramidal with average Zr—S distance of 2.686(8) Å and angle S—Zr—S of 63.4(2)° [200].

3.3.3.5. Insertion into the M—S bond. Insertion of CS_2 into M=S and $M(\eta^2\text{-}S_2)$ bonds gives trithiocarbonate and perthiocarbonate complexes:

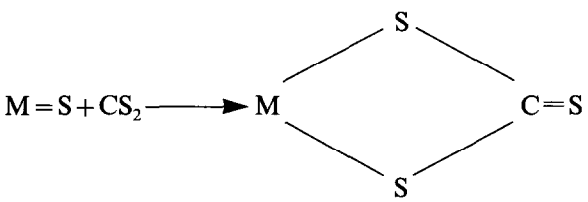
Reaction of CS_2 with sulfidomolybdenum complexes leads to the insertion of CS_2 into Mo=S and $Mo(\eta^2\text{-}S_2)$ bonds and to the formation of CS_3^{2-} and CS_4^{2-} complexes respectively [201,202]. The $Mo-\eta^2\text{-}CS_4$ units dissociate CS_2 with the formation of the $Mo-\eta^2\text{-}CS_4$ units while the $Mo-\eta^2\text{-}CS_3$ units do not dissociate. Reaction of CS_2 with $[Ph_4P]_2[(S)Mo(S_4)_2]$ in DMF results in the

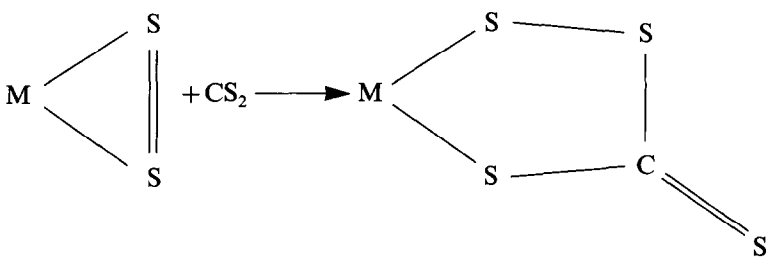

COMe
S
Me3P
Pd
C
PMe3
S
I

(LXXV)


PMe3
S
R
Pd
C
PMe3
S
PMe3
+

(LXXVI)


S
M=S+CS2
M
C=S
S

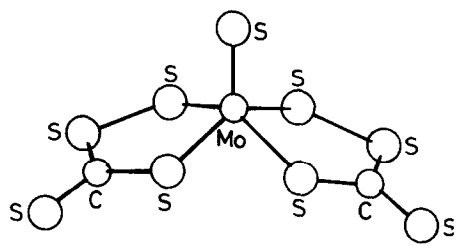

S
M
+CS2
M
S
S
S
C
S

formation of $[Ph_4P]_2[(S)Mo(CS_4)_2]$ (**LXXVII**). Complex $[Et_4N]_2[Mo_2(O)_2(\mu\text{-}S)(\eta^2\text{-}CS_4)(\eta^2\text{-}CS_3)]$ (**LXXVIII**) is obtained from the reaction of $[Et_4N]_2[(S)Mo(\mu\text{-}S)Mo(O)(S_4)]$. The synthesis and molecular structure of complex (**LXXIX**) has also been reported. The nickel complex $[Ph_4P]_2[Ni(CS_4)_2]$ can be obtained from the reaction of $[Ph_4P]_2[Ni(S_4)_2]$ [203].

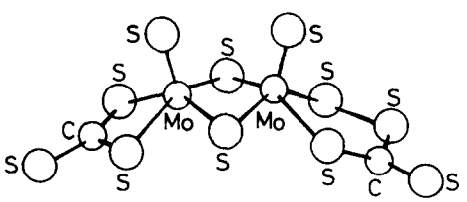
3.3.3.6. Insertion into the M—Cl bond. Insertion of CS_2 into an Au—Cl bond has been reported in the reaction of gold(III) chloride $[Au_2Cl_6]$ with CS_2. The insertion product $[AuCl_2(\eta^2\text{-}S_2CCl)]$ contains a chlorodithioformate ligand (**LXXX**). The structure was determined by X-ray crystallography. The molecule is planar with S—Au—S and S—C—S angles of 75.0(2)° and 114(1)° respectively [204].

3.3.4. Alkylation reaction of carbon disulfide

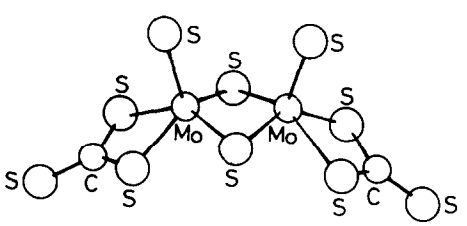
The negative charges on the sulfur atoms of CS_2 ligand in η^2-CS_2 and η^1-CS_2 coordination modes show its nucleophilic character and therefore it undergoes alkylation with a variety of electrophiles. Reaction of $[M\text{—}\eta^2\text{-}CS_2]$ and



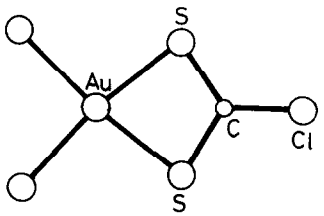
(LXXVII)



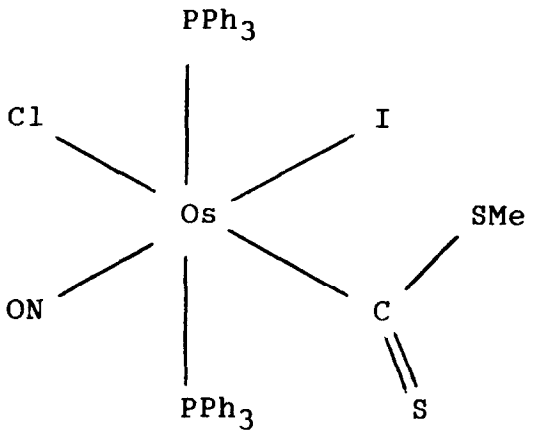
(LXXVIII)



(LXXIX)



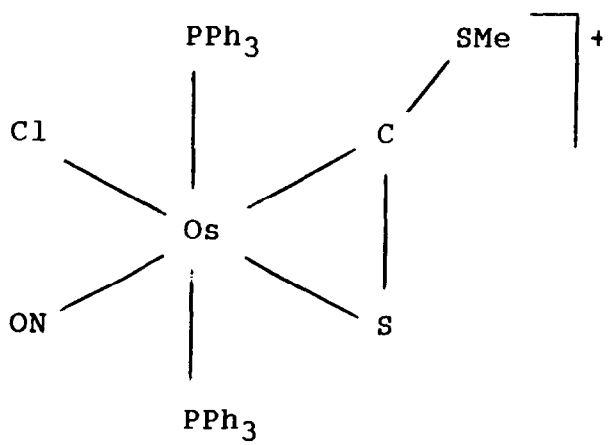
(LXXX)



(LXXXI)

[M−η^1-CS_2] complexes with methyl iodide results in the formation of [M−η^2-CS(SMe)], [M−η^1-CS(SMe)] and [M−η^1-C$(SMe)_2$] complexes. The CS stretching frequencies provide a useful diagnostic for determining the hapticity of the CS(SMe) ligand (ν(CS) ≈ 1000 cm^{-1} for η^1-CS(SMe) and ν(CS) ≈ 1100 cm^{-1} for η^2-CS(SMe) ligand).

[Os(NO)Cl$(CS_2)(PPh_3)_2$] reacts with methyl iodide in dichloromethane to afford the methylated complex (**LXXXI**). IR spectral studies (ν(CS), 991 cm^{-1}) reveal that the dithiomethoxycarbonyl ligand binds in a monodentate manner. In ethanol, [Os(NO)Cl$(CS_2)(PPh_3)_2$] yields a cationic complex (**LXXXII**) containing a bidentate CS_2Me ligand which may be isolated by addition of a non-coordinating anion (PF_6^- or ClO_4^-).



(LXXXII)

The complex (**LXXXII**) can also be prepared by the reaction of trifluoromethylsulfonate and NH_4PF_6 with $[Os(NO)Cl(CS_2)(PPh_3)_2]$ [129].

Complex $[Fe(CO)_2(\eta^2\text{-}CS(SMe)(PPh_3)_2](PF_6)$ is obtained by the reaction of MeI with $[Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2]$ in the presence of NH_4PF_6 [205]. A bimetallic complex (**LXXXIII**) is formed by treating $[Fe(CO)_2(\eta^2\text{-}CS(SMe)(PPh_3)_2](PF_6)$ with Na–Hg in THF.

The complex anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CS_2)]^-$ reacts with MeI or Me_3SiCl to afford dithiocarboxylate ester complexes (**LXXXIV**) (R ≡ Me or $SiMe_3$) [127,150] which on further methylation with $MeOSO_2CF_2$ afford the dithiocarbene complex (**LXXXV**) containing triflate or PF_6^- counter anions.

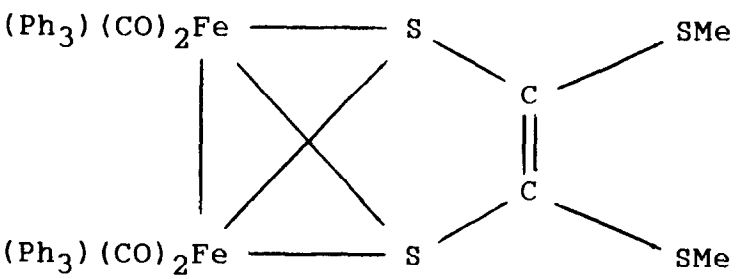
Platinum CS_2 complexes $[Pt(\eta^2\text{-}CS_2)L_2]$ (L ≡ PPh_3, 1/2 dppe) react with MeI to give $[PtI\{\eta^1\text{-}C(SMe)_2\}L_2]^+I^-$ (**LXXXVI**) [143].

3.3.5. Miscellaneous reactions

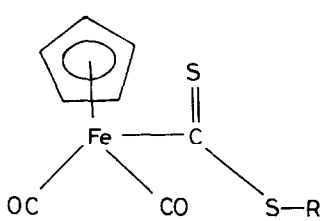
Carbon disulfide undergoes coupling reactions with ligands coordinated to a metal center. The thiocarbene complex $[Cr(CO)_5\{C(SEt)Ph\}]$ is isolated by successive treatment of CS_2 and $[Et_3O][BF_4]$ with the deprotonated aminocarbene complex $[Cr(CO)_5\{C(NH)Ph\}]^-$ [206].

No net incorporation of CS_2 occurs in the reaction of the secondary aminocarbene complex with CS_2 under the same conditions. The alkoxycarbene complex $[Cr(CO)_5\{C(OEt)Me\}]$ reacts with LiBu, CS_2 and $[Et_3O][BF_4]$ successively to produce (**LXXXVII**).

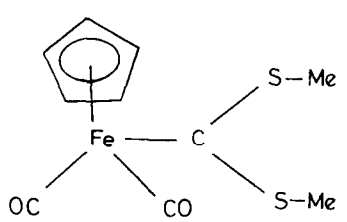
Reactions of deprotonated sulfur donor complexes of pentacarbonylchromium(0)



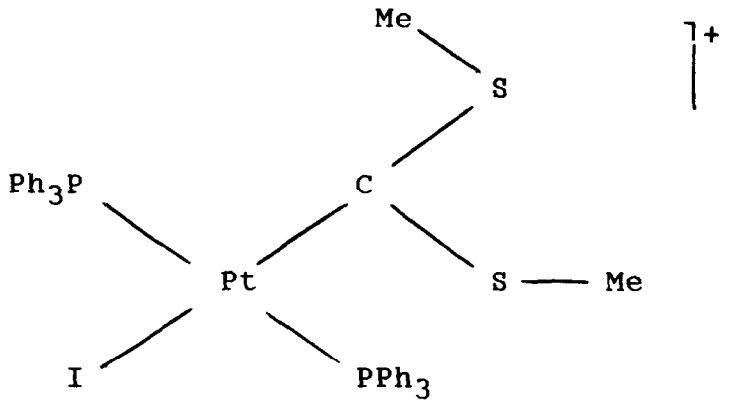
(LXXXIII)



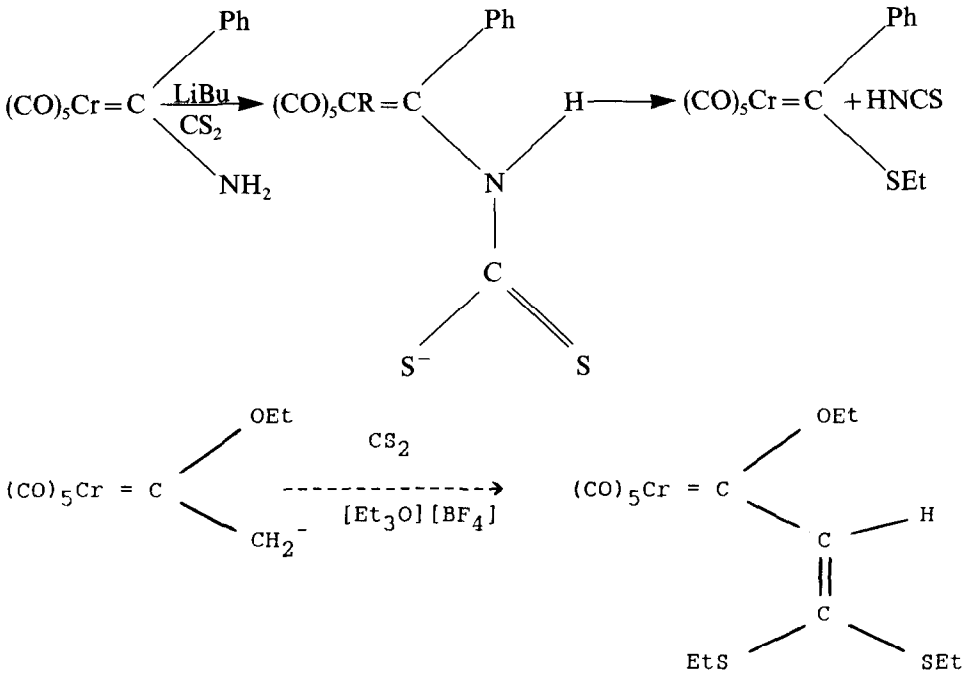
(LXXXIV)



(LXXXV)



(LXXXVI)



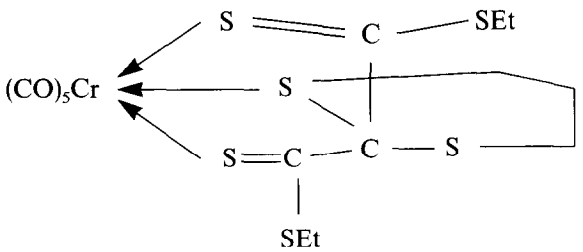
(LXXXVII)

with carbon disulfide have been reported by Raubenheimer and co-workers [207,208].

$$[(CO)_5Cr(SCHNMe_3)] \xrightarrow[[Et_3O][BF_4]]{LDA,\ CS_2} [(CO)_5Cr\{SC(SEt)_3\}]$$

$$[(CO)_5Cr\{SC(SEt)Me_3\}] \xrightarrow[[Et_3O][BF_4]]{LDA,\ CS_2} [(CO)_5Cr\{SC(Me)CHC(SEt)_2\}]$$

$[(CO)_5Cr\{S(CH_2)_3SCH\}]^- + CS_2 + [Et_3O][BF_4] \longrightarrow$



Reaction of CS_2 with complex $[(\eta^5\text{-}C_5H_5)Fe\{C(OMe)=CH_2]$ produces a thermolabile complex which reacts with MeI to give $[(\eta^5\text{-}C_5H_5)Fe\{C(OMe)=CH_2C(S)SMe\}(PMe_3)_2]I$ [209].

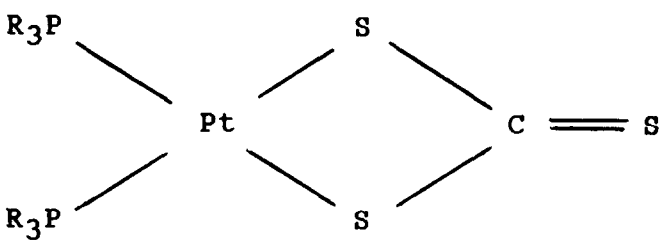
Reaction of $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ with PMe_3, PMe_2Ph and $PMePh_2$ results in the formation of trithiocarbonate complexes (**LXXXVIII**) [210].

Reduction of $[(triphos)Co(\mu\text{-}Cl)_2Co(triphos)]^{2+}$ in THF solution under nitrogen atmosphere with sodium amalgam produces a deep red–brown solution which reacts with CS_2 to afford [(triphos)Co(S_2CO)] (**LXXXIX**) [211]. Reaction of CS_2 with malonodinitrile in the presence of $[IrH(PMe_2Ph)_4]$ yields $[IrH_2(PMe_2Ph)_4]^+$-$[HS(SCC)(CH)_2]^-$ [212]. The coupling reaction of CS_2 in ruthenium complex $[(\eta^5\text{-}C_5H_5)RuH(sp)]$ (sp = 2-CH_2 = $CHC_6H_4PPh_2$) gives complex (**XC**) [213].

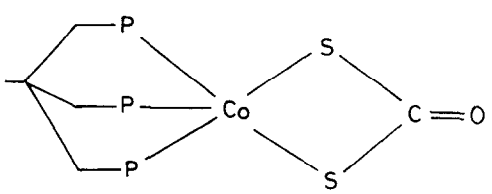
4. Coordination chemistry of carbon dioxide

4.1. Transition metal–carbon dioxide bonding and energetics

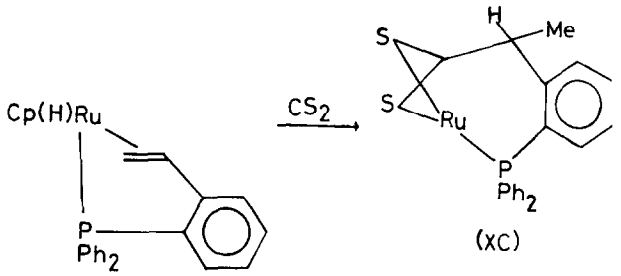
The coordination of CO_2 ligand to transition metal gives complexes of the following types: (a) η^1-end-on coordination (**XCI**), (b) η^1-C coordination (**XCII**),



(LXXXVIII)

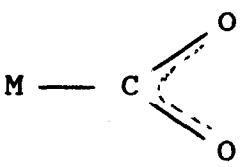


(LXXXIX)

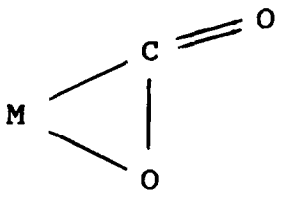


(XC)

(XCI)



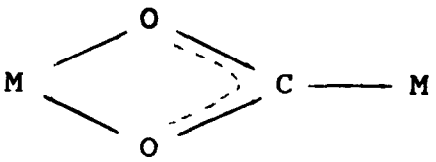
(XCII)



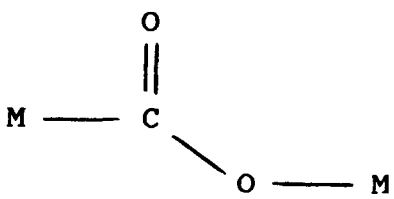
(XCIII)

(c) η^2-side-on coordination (**XCIII**), and (d) bridging CO_2 complexes (**XCIV–XCVI**).

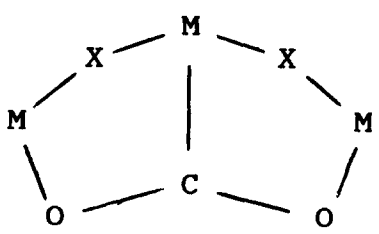
Molecular orbital studies of complexes containing a CO_2 ligand have led to a



(XCIV)



(XCV)



(XCVI)

better understanding of the nature of the coordinate bond, its electronic structure, conformational performance and reactivity. All three possible modes of coordination of the CO_2 molecule to a single metal atom, (a) η^1-O end-on mode (**XCI**), (b) η^1-C mode (**XCII**) and (c) η^2-side-on mode (**XCIII**), have been discussed in molecular orbital studies [80,119–122,214–230]. The gross atomic charges of the CO_2 complexes are presented in Table 11.

The end-on η^1-O coordination mode is preferred by the electrostatic interaction of the metal, having a considerable positive charge, with the negatively charged oxygen atom of the CO_2 ligand. No structural evidence for the end-on conformation has ever been observed, but it has been calculated theoretically for $[Cu(CO_2)(PH_3)_2]$ [119] and $[Cu(CO_2)]$ [221] and characterized spectroscopically for $[Cu(CO_2)]$ in a matrix [231].

Both the η^1-C coordination and η^2-side-on coordination modes need strong charge transfer interactions from the metal to the CO_2 ligand and weak four-electron destabilization interactions [120,219]. Mulliken population analysis shows negative charges on the coordinated CO_2 and positive charges on the metal in transition metal CO_2 complexes. These results suggest that the CO_2 ligand removes an electron from the central metal atom as a result of strong metal to ligand charge transfer interactions [80,119,219–221,223,226].

The η^1-C coordination requires charge transfer from metal dσ to the CO_2 π^* orbitals and the electrons accepted by the η^1-CO_2 ligand are distributed not only on the carbon atom but also on the oxygen atom. This coordination mode is most favored when the HOMO is mainly composed of a dσ (d_z^2) orbital and when the metal is in a low oxidation state as found in the Rh(I) complex $[RhCl(\eta^1\text{-}CO_2)(diars)_2]$ [166], the Co(I) complex $[Co(alcn)(\eta^1\text{-}CO_2)]^-$ [162], and Ni(I) complexes

Table 11
Binding energy and net charges on metal and carbon dioxide for metal carbon dioxide complexes

Metal system	Binding energy (kcal mol^{-1})	Charge		Reference
		Metal	CO_2	
η^1-end-on coordination				
$[CuCO_2]$	−11.7	+0.72	−0.72	[221]
$[Cu(CO_2)(PH_3)_2]^+$	−14.0	+0.85	+0.017	[119]
η^1-C coordination				
$[Co(alcn)_2(CO_2)]$	−6.2	+0.40	−0.72	[219]
$[RhCl(CO_2)(AsH_3)_4]$	−1.8	—	−0.53	[223]
$[NiF(NH_3)_4(CO_2)]$	−22.0	+0.687	−0.872	[226]
η^2-side-on coordination				
$[Mo(CO_2)_2(PH_3)_4]$	—	+1.31	−0.57	[220]
$[Mo(CO_2)_2(CNH)(PH_3)_3]$	—	+1.68	−0.42	[220]
$[Mo(C_2H_4)(CO_2)_2(PH_3)_3]$	—	+0.09	−0.51	[220]
$[Fe(CO)_2(CO_2)(PH_3)_2]$	−26.2	−0.38	−0.52	[80]
$[Fe(CO_2)(PH_3)_4]$	−63.4	−0.24	−0.73	[80]
$[Ni(CO_2)(PH_3)_2]$	−27.0	+0.569	−0.689	[119]

$[NiF(NH_3)_4(\eta^1\text{-}CO_2)]$ and $[Ni(NH_3)_5(\eta^1\text{-}CO_2)]^+$ [169]. Hoffman and co-workers, using the EHMO method, have proposed that for η^1-C coordination, two conditions must be fulfilled: a closed shell configuration of metal fragment and the presence of a free coordination site [120].

The η^2-side-on coordination requires charge transfer from metal $d\pi$ to CO_2 π^* orbitals. The best situation for η^2-side-on coordination is the presence of a metal $d\pi$ as HOMO and an empty $d\sigma$ orbital pointing to the CO_2 ligand. The CO_2 distortion on coordination lowers the π^* orbital energy of CO_2 and hence increases π-back donation.

Influence ligand on the $M-CO_2$ moiety

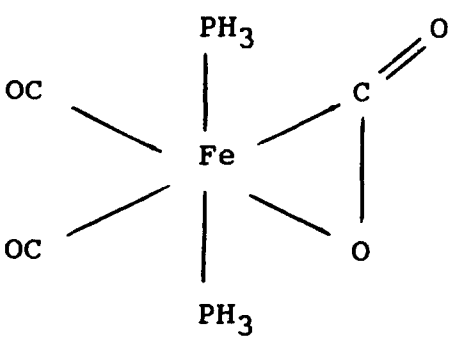
Substitution of a ligand by a more efficient π-acceptor ligand reduces the electron density on the central metal atom and hence decreases the metal to CO_2 π-back donation as well as the binding energy of $M-CO_2$. A comparison of bonding energies of (**XCVII**) and (**XCVIII**) shows that the substitution of phosphines by carbonyls involves a decrease in the CO_2 binding energy. A relatively smaller negative charge on CO_2 in (**XCVII**) is in agreement with decreased π-back donation. Similarly, for complexes (**XCIX**) and (**C**), on substitution of a phosphine ligand by an isocyanide ligand, which is a better π-acceptor than the phosphine ligand, the molybdenum net charge increases from 1.31 to 1.68 and the CO_2 net charge changes from -0.57 to -0.42.

4.2. Preparation and structure

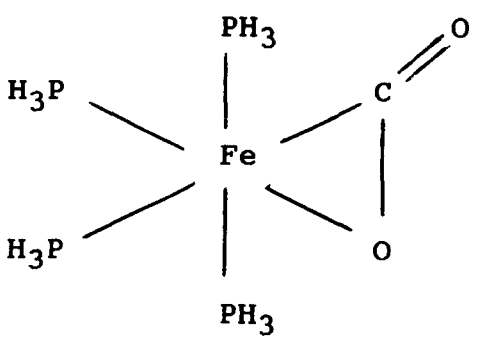
4.2.1. Mononuclear transition metal carbon dioxide complexes

Transition metal CO_2 complexes are prepared by (a) reaction of CO_2 with transition metal complexes and (b) oxidation of transition metal carbonyls.

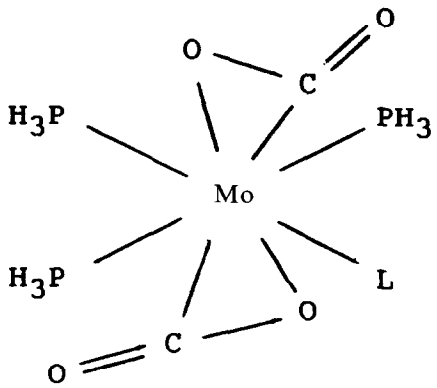
4.2.1.1. $M-\eta^1$-CO_2 complexes. The titanium complex $[(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)_2]$ reacts with CO_2 to give the yellow $[(\eta^5\text{-}C_5H_5)_2Ti(CO_2)(PMe_3)]$ [123,232]. The results of detailed IR spectral studies of $[(\eta^5\text{-}C_5H_5)_2Ti(CO_2)(PMe)]$ suggest η^1-CO_2 co-



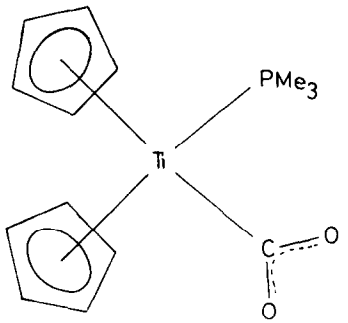
(XCVII)



(XCVIII)



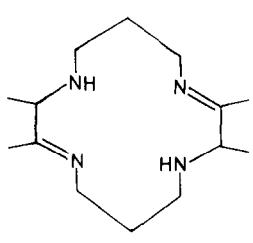
L = PH_3, **(XCIX)**; L = CNH, **(C)**



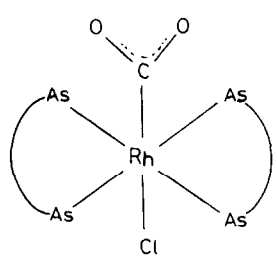
(CI)

ordination of CO_2 in the titanium complex (**CI**) [232]. The side-on coordination mode η^2-CO_2 was proposed by Rausch and co-workers [123]. Complex $Li_2[W(CO)_5(\eta^1\text{-}CO_2)]$ is prepared in THF solution at −78 °C by the reaction of CO_2 with $Li_2[W(CO)_5]$. An attempt to isolate a solid product was unsuccessful [126]. The IR and ^{13}C NMR spectral studies are consistent with the formulation as a W−η^1-CO_2 complex. The formation of complexes, containing η^1-CO_2 ligand with alkali metal counter anions, of the type $[A][(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CO_2)]$ ($A^+ \equiv Li^+$, Na^+, K^+) [233,234], $[A][(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^1\text{-}CO_2)]$ ($A^+ \equiv Li^+$, K^+) [235], $[A][(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}CO_2)]$ ($A^+ \equiv Li^+$, K^+) [236], $[A][(\eta^5\text{-}C_5H_5)Re(CO)(NO)(\eta^1\text{-}CO_2)]$ ($A^+ \equiv Na^+$, ET_3NH^+) [237], $[A][(\eta^5\text{-}C_5H_5)Re(CO)(N_2Ph)(\eta^1\text{-}CO_2)]$ ($A^+ \equiv Li^+$, Na^+) [238] has been observed.

Carbon dioxide complexes of Co(I) containing 14-membered tetraazamacrocycles (**CII**) have been prepared in acetonitrile solution by the addition of carbon dioxide to a solution of the Co(I) complexes, obtained by electrochemical reduction or sodium-amalgam reduction [239–241]. The solid perchlorate salt can be obtained from acetonitrile solution by rapid addition of THF [239]. $[Co([14]diene)(\eta^1\text{-}CO_2)][ClO_4]$ shows C−O stretching frequencies at 1653, 1304 and 1222 cm^{-1} which are similar to those reported for $[Co(n\text{-}pr\text{-}salen)(CO_2)(THF)]^-$ [242]. Electronic spectra, thermodynamic and reactivity studies carried out on the Co(I)−η^1-CO_2 complexes were reported [241]. The



(CII)



(CIII)

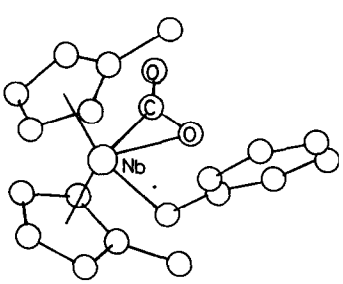
binding of CO_2 to CO(I) and Ni(I) tetraazamacrocyclic complexes has been determined using cyclic voltammetry or differential pulse polarography. The CO_2 binding constants showed a strong correlation with redox potential, solvent properties and ligand structure [243]. CO_2 binding by $[Co(L)]^+$ (L ≡ Me_6[14]4,11-diene) has been determined electrochemically. A K_{CO_2} value of $7 \times 10^4\ M^{-1}$ for CO_2 binding to $[Co(L)]^+$ has been obtained in 0.1 M tetrabutylammonium perchlorate in Me_2SO [244].

Herskovitz and co-workers reported the synthesis and X-ray crystal structure of $[RhCl(CO_2)(diars)_2]$ where CO_2 is η^1-CO_2 bonded and CO_2 and Cl ligands are mutually trans (**CIII**) [245,246]. The η^1-CO_2 coordination is stabilized by additional C—H ··· O interactions with the ligand.

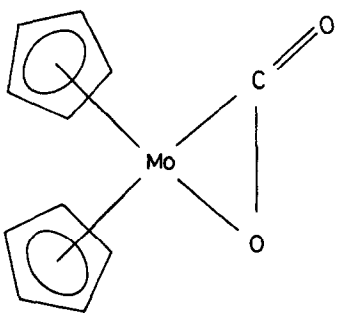
4.2.1.2. $M-\eta^2$-CO_2 complexes. The formation of transition metal CO_2 complexes as possible intermediates in the transition metal mediated oxidation of CO has been suggested [247–249]. The synthesis of CO_2 complexes from the reaction of transition metal carbonyls with molecular oxygen or air has been reported for the first time by Nicholas and co-workers [250]. Complexes $[(\eta^5\text{-}C_5Me_5)_2Nb(\eta^2\text{-}CO_2)(R)]$ (R ≡ Me, CH_2CMe_3, CH_2Ph, CH_2SiMe_3) are prepared by the addition of air or O_2 into a solution of $[(\eta^5\text{-}C_5Me_5)_2Nb(CO)(R)]$ in toluene. The molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Nb(\eta^2\text{-}CO_2)(CH_2Ph)]$ was determined by X-ray crystallography. The structure of (**CIV**) is same as that of $[(\eta^5\text{-}C_5H_4Me)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ (**CV**) [251] except for the longer Nb—CH_2R bond of (**CIV**) (2.337(4) Å vs. 2.282(11) Å for (**CV**)) (Table 12).

A molybdenum CO_2 complex $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ (**CVI**) is obtained from the reaction of $[(\eta^5\text{-}C_5H_5)_2Mo(PhC{\equiv}CPh)]$ [252]. Irradiation (more than 330 nm) of a THF solution of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ under 1 atm CO_2 at −10 °C for 3 h results in the formation of (**CVI**) along with a dimer $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Mo]_2$ [253]. Complex (**CVI**) can also be prepared in low yield when a THF solution of $[(\eta^5\text{-}C_5H_5)_2Mo(CO)]$ is exposed to O_2 at 0 °C [250].

The reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with CO_2 under pressure (4–5 atm) gives bis(carbon dioxide) complex *trans*-$[Mo(CO_2)_2(PMe_3)_4]$ (**CVII**) which reacts with various isocyanides to afford CO_2 complexes *trans,mer*-$[Mo(CO_2)(CNR)(PMe_3)_3]$ (R ≡ Me, i-Pr, t-Bu, Cy and CH_2Ph) [102–105]. Molecular structures of



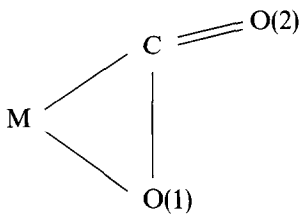
(CIV)

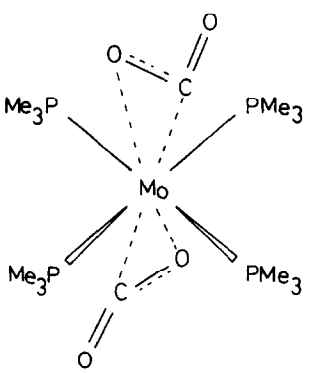


(CVI)

Table 12
X-ray structural data for mononuclear transition metal carbon dioxide complexes

Complex	M–C (Å)	M–O (1) (Å)	C–O (1) (Å)	C–O (2) (Å)	O (1)–C–O (2) (°)	Reference
K[Co(salen)(η^1-CO_2)]	1.99		1.22		132	[242]
[(η^5-$C_5H_4Me)_2Nb(\eta^2$-CO_2)-(CH_2SiMe_3)]	2.144(7)	2.172(4)	1.283(8)	1.216(8)	132.4(7)	[251]
[(η^5-$C_5H_5)_2Mo(\eta^2$-CO_2)]	2.112(11)	2.160(7)	1.288(14)	1.201(14)		[252]
[Mo(η^2-CO_2)(CN-i-Pr)($PMe_3)_3$]	2.10(1)	2.146(7)	1.26(2)	1.22(2)	133(1)	[104]
	2.11(1)	2.147(7)	1.26(1)	1.22(1)	134(1)	
[Mo(η^2-CO_2)(CN-CH_2Ph)-($PMe_3)_3$]	2.02(2)	2.14(1)	1.25(2)	1.28(3)	128(2)	[104]
	2.02(2)	2.16(1)	1.20(2)	1.28(3)	128(2)	
[Rh(η^1-CO_2)Cl($diars)_2$]	2.05(2)		1.25(2)		126(2)	[246]
			1.20(2)			

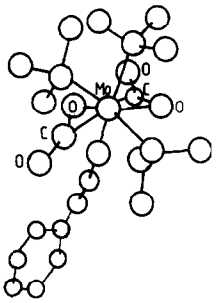




(CVII)

trans,mer-[Mo(CO_2)(CN-i-Pr)($PMe_3)_3$] (**CVIII**) and *trans,mer*-[Mo(CO_2)($CNCH_2$Ph)($PMe_3)_3$] (**CIX**) were determined by X-ray diffraction. The complexes (**CVIII**) and (**CIX**) are isostructural with the molybdenum atom bonded to two trans, staggered CO_2 molecules. The overall molecular geometry about molybdenum is approximately octahedral.

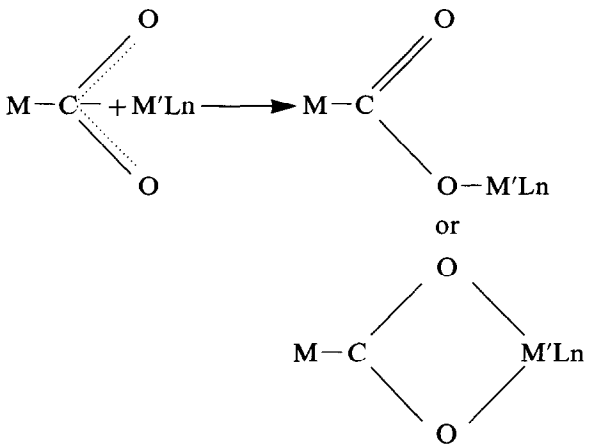
(CVIII)



(CIX)

4.2.2. Bimetallic and trimetallic carbon dioxide complexes

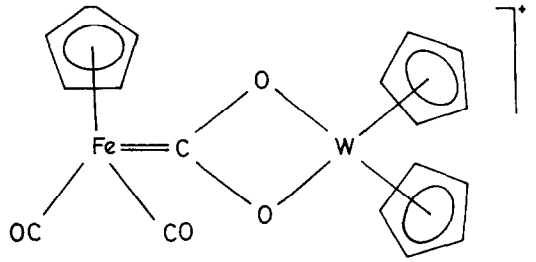
The $M-\eta^1\text{-}CO_2$ complexes react with metal complexes to afford bimetallic $\mu_2\text{-}(\eta^1\text{-}C;\ \eta^1\text{-}O)$ and $\mu_2\text{-}(\eta^1\text{-}C;\ \eta^2\text{-}O)$ CO_2 complexes.



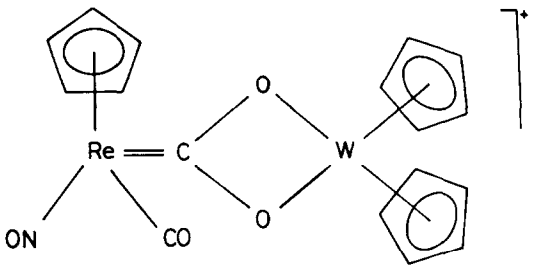
Geoffrey and co-workers reported the formation of bimetallic CO_2 complexes from the oxidation of transition metal carbonyl complexes with oxo complex [254]. The reaction of $[(\eta^5\text{-}C_5H_5)_2M'{=}O]$ ($M' \equiv Mo$, W) with carbonyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$, $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+$, $[(\eta^5\text{-}C_5H_4Me)Mn(NO)(CO)_2]^+$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+$ result in the formation of bimetallic CO_2 complexes. The structures of $Fe\{\mu_2\text{-}(\eta^1\text{-}C,\ \eta^2\text{-}O,O)W$ and $Re\{\mu_2\text{-}(\eta^1\text{-}C,\ \eta^2\text{-}O,O)W$ are shown as (**CX**) and (**CXI**) respectively. Reaction of $[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl]$ with $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CO_2H)]$ result in the formation of the yellow complex $[(\eta^5\text{-}C_5H_5)(NO)(CO)Re{-}C(O)O{-}ZrCl(\eta^5\text{-}C_5H_5)_2]$ (**CXII**) [255].

Reaction of metallocarboxylate $[(\eta^5\text{-}C_5H_5)M(CO)_2(CO_2)]^-Na^+$ ($M \equiv Fe$, Ru) with zircocene dichloride $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$ and titanocene dichloride $[(\eta^5\text{-}C_5H_5)_2TiCl_2]$ gives bridging CO_2 complexes $[(\eta^5\text{-}C_5H_5)(CO)_2MCO_2M'Cl\text{-}(\eta^5\text{-}C_5H_5)_2]$ (**CXIII**) ($M \equiv Fe$, Ru; $M' \equiv Zr$, Ti) [256].

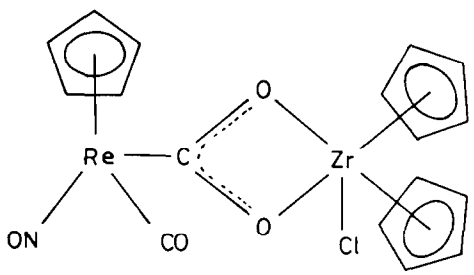
The nickel complex $[\{Cy_3P)_2Ni\}_2(\mu\text{-}CO_2)]$ is obtained by the splitting of the CO_2



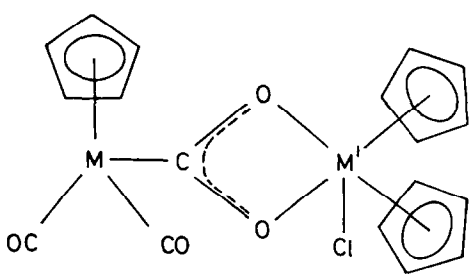
(CX)



(CXI)



(CXII)

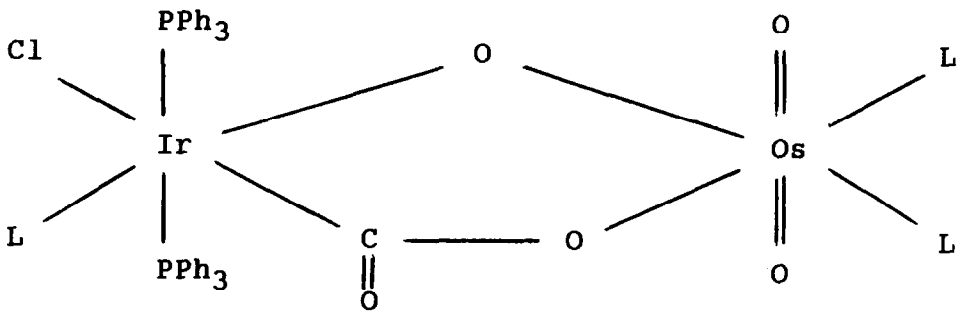


(CXIII)

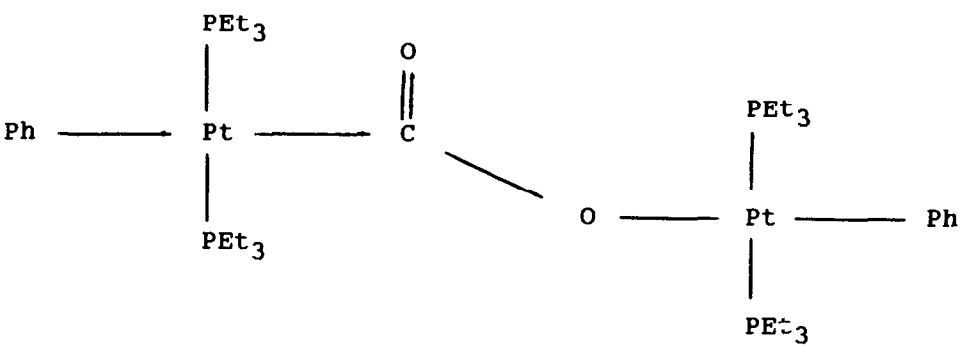
complex $[Ni(\eta^2\text{-}CO_2)(PCy_3)_2]$ [257]. The Vaska complex $[Ir(CO)Cl(PPh_3)_2]$ reacts with osmium tetra-oxide in 4-t-BuC_5H_4N (L) to give the μ_2-(η^1-C, η^1-O) bonded CO_2 complex (**CXIV**) [258].

A platinum carboxylic acid complex *trans*-$[Pt(CO_2H)(Ph)(PEt_3)_2]$, obtained from the reaction of CO_2 with *trans*-$(Pt(OH)(Ph)(PEt_3)_2]$, reacts with its precursor *trans*-$[Pt(OH)(Ph)(PEt_3)_2]$ to afford a bridging O_2 complex (**CXV**) which can also be obtained by the pyrolysis of *trans*-$[Pt(CO_2H)(Ph)(PEt_3)_2]$ [259]. The molecular structure of the complex $[Pt(CH_3)(dppp)]_2(\mu\text{-}CO_2)]$, prepared from $[Pt(OH)(CH_3)(dppp)]$ and $[Pt(CO_2H)(CH_3)(dppp)]$, has been determined by X-ray crystallography and shows the presence of a μ_2-(η^1-C, η^1-O) CO_2 ligand.

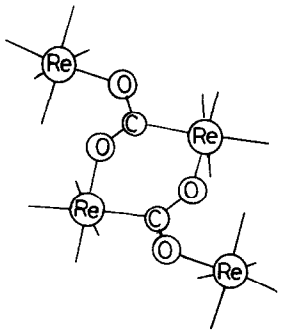
The synthesis and characterization of bridging CO_2 complexes involving three or more metal centers (μ_3-CO_2) have also been reported [260–266]. The complex $[Re(OH)(CO)_5]$ loses water at 20 °C in acetone to give the μ_3CO_2 complex (**CXVI**) [264]. The yellow complex $[(COD)_2Rh_2OsH_2(\mu_3\text{-}CO_2)(PMe_2Ph)_2]$ (**CXVII**) is obtained by the reaction of $[(COD)RhH_3Os(PMe_2Ph)_3]$ with CO_2 in THF [265,266].



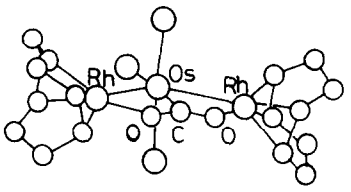
(CXIV)



(CXV)



(CXVI)



(CXVII)

4.3. Spectroscopic studies

Transition metal CO_2 complexes exhibit characteristic CO_2 vibrations in the regions 1650–1620 cm^{-1}, 1300–1100 cm^{-1}, 900–800 cm^{-1} and 600–400 cm^{-1} for the M—η^2-CO_2 coordination mode. The first two bands are assigned to ν_{as}(OCO) and ν_s(OCO) respectively. Comparison of the spectral data of the coordinated CO_2 ligand with the IR spectral data for free CO_2 [267] shows a decrease in ν_{as}(OCO) frequency on coordination to transition metal systems. A decrease in ν_{as}(OCO) on coordination to the metal and variation in ν(OCO) frequencies depend on the π-acceptor and σ-donor abilities of the CO_2 ligand. Mascetti and co-workers [231,232,268] have investigated the IR characterization of transition metal CO_2 complexes. The observations of isotropic shifts on the two ν_{as}(OCO) and ν_s(OCO) stretching modes and the splitting between the two CO stretching modes (ν_{as}(OCO)—ν_s(OCO)) give an indication of the CO_2 bonding mode in metal complexes. For the M—η^1-CO_2 coordination mode, the difference Δ (ν_{as}–ν_s) is approximately equal to 400 cm^{-1} while for the M—η^2-CO_2 coordination mode the difference Δ is above 500 cm^{-1} (Table 13).

The ^{13}C NMR spectrum of CO_2 exhibits absorption at δ 132 ppm. On coordination to transition metal systems, it shows downfield shifts (Table 14). The chemical shifts for the CO_2 carbon depend on (a) the extent of carbon hybridization, (b) charge delocalization and (c) the nature of the bond between the metal atom and CO_2. The higher chemical shifts δ of 260 ppm for [(η^5-C_5H_5)$(CO)_2$-Fe=CO_2W(η^5-C_5H_5)$_2$][PF_6] and δ 252 ppm for [(η^5-C_5Me_5)$(CO)_2$-Fe=CO_2W(η^5-C_5H_5)$_2$][BF_4] are in agreement with their formulation as dimetallated dioxocarbene ligands. ^1H NMR, ^{31}P NMR and electronic spectral studies have been reported for a number of transition metal CO_2 complexes.

4.4. Insertion reactions of carbon dioxide complexes

4.4.1. Insertion into the M—H bond

The insertion of CO_2 into the M—H bond leads to formato complexes (**CXVIII–CXIX**) or a l-metalated formic acid complex (**CXX**). Most of the insertion reactions result in the formation of formato complexes.

Table 13
Important IR frequencies (cm^{-1}) of transition metal carbon dioxide complexes

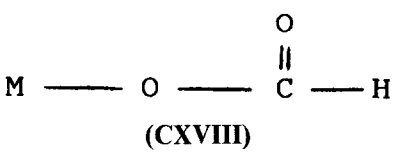
Complex	$\nu(CO_2)$ (cm^{-1})	Reference
$M-\eta^1$-CO_2 coordination		
$[(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}CO_2)(PMe_3)]$	1671, 1280, 1215	[232]
$Li_2[W(CO)_5(\eta^1\text{-}CO_2)]$	1450	[126]
$[Co([14]diene)(\eta^1\text{-}CO_2)][ClO_4]$	1653, 1304, 1222	[239]
$K[(Pr\text{-}salen)Co(\eta^1\text{-}CO_2)]$	1650, 1280, 1215	[242]
$[RhCl(\eta^1\text{-}CO_2)(diars)_2]$	1610, 1210	[245]
$M-\eta^2$-CO_2 coordination		
$[(\eta^5\text{-}C_5H_4Me)_2Nb(\eta^2\text{-}CO_2)(CH_2Ph)]$	1738	[250]
$[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$	1740	[252]
$[Mo(\eta^2\text{-}CO_2)(PMe_3)_4]$	1670, 1155, 1100	[104]
$[Mo(\eta^2\text{-}CO_2)(CNMe)(PMe_3)_3]$	1660, 1150, 1100	[104]
$[Mo(\eta^2\text{-}CO_2)(CN\text{-}i\text{-}Pr)(PMe_3)_3]$	1675, 1160, 1100	[104]
$[Mo(\eta^2\text{-}CO_2)(CN\text{-}t\text{-}Bu)(PMe_3)_3]$	1680, 1155, 1100	[104]
$[Mo(\eta^2\text{-}CO_2)(CNCy)(PMe_3)_3]$	1665, 1150, 1100	[104]
$[Mo(\eta^2\text{-}CO_2)(CNCH_2Ph)(PMe_3)_3]$	1670, 1150, 1100	[104]
$[Fe(\eta^2\text{-}CO_2)(PMe_3)_4]$	1623, 1106	[268]
Bridging carbon dioxide complexes		
$[(\eta^5\text{-}C_5H_5)(CO)(NO)Re(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	1348, 1288	[256]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	1363, 1264	[256]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO_2)TiCl(\eta^5\text{-}C_5H_5)_2]$	1379, 1273	[256]
$[(\eta^5\text{-}C_5H_5)(CO)_2Ru(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	1344, 1285	[256]
$[(\eta^5\text{-}C_5H_5)(CO)_2Ru(\mu\text{-}CO_2)TiCl(\eta^5\text{-}C_5H_5)_2]$	1349, 1284	[256]
$[(COD)_2Rh_2OsH_2(\mu\text{-}CO_2)(PMe_2Ph)_3]$	1365, 1260	[265]
$[(PPh_3)_2(L)ClIr(\mu\text{-}CO_2)(\mu\text{-}O)Os(O)_2(L)_2]$ ($L \equiv 4\text{-}t\text{-}BuC_5H_4N$)	1593, 1022	[258]
trans-$[Pt(Ph)(PEt_3)_2]_2(\mu\text{-}CO_2)$	1495, 1290, 1190	[259]

The titanium formato complex $[(\eta^5\text{-}C_5Me_5)_2Ti(O_2CH)]$, along with alkene, is formed in the reaction of $[(\eta^5\text{-}C_5Me_5)_2TiR]$ ($R \equiv Et$ or *n*-Pr) with CO_2 [269]. Lyons and co-workers reported the formation of a formato complex $[MoH(O_2CH)(PMe_2)_4]$ from the reaction of CO_2 with $[MoH_2(PMe_3)_5]$ by the insertion of CO_2 into the Mo—H bond. The pentagonal bipyramidal structure (**CXXI**) was determined for $[MoH(O_2CH)(PMe_3)_4]$ by X-ray diffraction [270]. The analogous formate complex $[MoH(O_2CH)(dppe)_2]$ (**CXXII**) is obtained by passing CO_2 into a irradiated yellow solution of $[MoH_4(dppe)_2]$ in benzene [271]. The ^1H NMR spectra of (**CXXI**) and (**CXXII**) show signals at δ −8.66 ppm and δ −6.47 ppm due to Mo—O_2CH proton respectively (Table 15). The complex $[Mo(O_2CH)(CO)_2(PEt_3)_2]$, obtained by the insertion of CO_2 into Mo—H bonds, contains both unidentate and bidentate formate ligands [272]. Reaction of CO_2 with $[WH_6(PMe_3)_3]$ results in the formation of complex $[WH_2(\eta^1\text{-}O_2CH)(\eta^2\text{-}O_2CH)(PMe_3)_3]$ containing both unidentate and bidentate formato ligands [273].

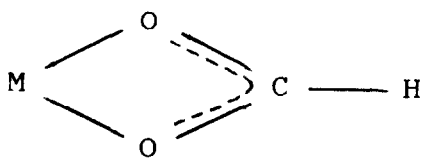
Carbon dioxide (at 50 atm) reacts with manganese dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}P{-}P)]$ (P—P ≡ dppm, tedp) to give hydridoformato complexes $[Mn_2(\mu\text{-}H)(O_2CH)(CO)_6(\mu\text{-}P{-}P)]$ (**CXXIII**) along with hydridohydroxy complexes

Table 14
^{13}C NMR spectral data of transition metal carbon dioxide complexes

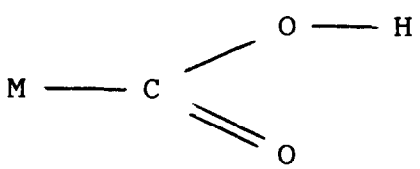
Complex	$\delta(CO_2)$ (ppm)	Solvent	Reference
O=C=O	132.0		
$[(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}CO_2)(PMe_3)]$	212.3(d)	$CDCl_3$	[123]
$[Mo(\eta^2\text{-}CO_2)(PMe_3)_4]$	206.1(q)	C_6D_6	[104]
$[Mo(\eta^2\text{-}CO_2)(CNMe)(PMe_3)_3]$	201.1(m)	C_6D_6	[104]
$[Mo(\eta^2\text{-}CO_2)(CN\text{-}i\text{-}Pr)(PMe_3)_3]$	201.4(m)	C_6D_6	[104]
$[Mo(\eta^2\text{-}CO_2)(CN\text{-}t\text{-}Bu)(PMe_3)_3]$	201.2(td)	C_6D_6	[104]
$[Mo(\eta^2\text{-}CO_2)(CNCy)(PMe_3)_3]$	201.4(td)	C_6D_6	[104]
$[Mo(\eta^2\text{-}CO_2)(CNCH_2Ph)(PMe_3)_3]$	201.1(m)	C_6D_6	[104]
$[(\eta^5\text{-}C_5H_5)(CO)(NO)Re(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	212.6	$CdCl_3$	[256]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO_2)W(\eta^5\text{-}C_5H_5)_2]^+$	260.0		[254]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	206.2	C_6D_6	[256]
$[(\eta^5\text{-}C_5Me_5)(CO)_2Ru(\mu\text{-}CO_2)W(\eta^5\text{-}C_5H_5)_2]^+$	252.0		[254]
$[(\eta^5\text{-}C_5H_5)(CO)_2Ru(\mu\text{-}CO_2)ZrCl(\eta^5\text{-}C_5H_5)_2]$	213.2	C_6D_6	[256]
$[(COD)_2Rh_2OsH_2(\mu\text{-}CO_2)(PMe_2Ph)_3]$	193.0(d)	C_6D_6	[265]
trans-$[Pt(Ph)(PEt_3)_2]_2(\mu\text{-}CO_2)$	201.0(m)	CD_2Cl_2	[259]



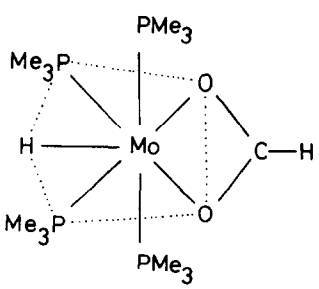
(CXVIII)



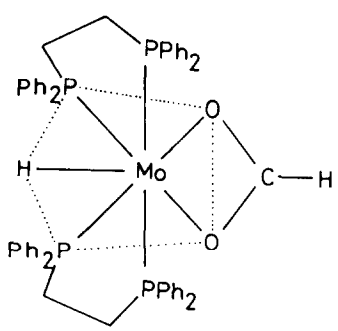
(CXIX)



(CXX)



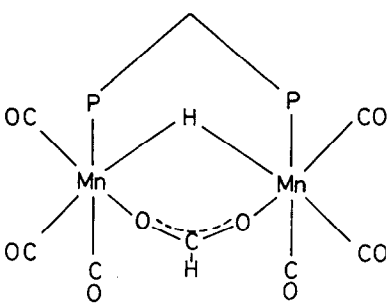
(CXXI)



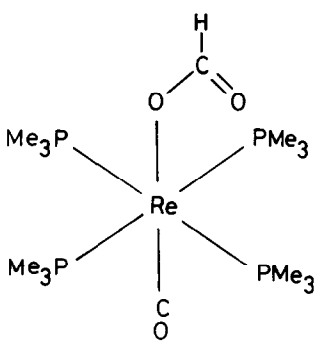
(CXXII)

Table 15
Spectral data of formate complexes

Complex	IR frequencies (cm^{-1})		^1H NMR (ppm), $\delta(O_2CH)$	Reference
	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$		
$[MoH(\eta^2\text{-}O_2CH)(dppe)_2]$	1550	1360	8.83	[271]
$[Mn_2(\mu\text{-}H)(O_2CH)(CO)_6(\mu\text{-}dppm)]$	1570	1440		[274]
$[Re(CO)(\eta'\text{-}O_2CH)(PMe_3)_4]$	1634	1318	8.66	[86]
$[Ru(NO)(O_2CH)(PPh_3)_2]$	1610	1390		[112]
$[(\eta^5\text{-}C_5H_5)Ru(O_2CH)(PPh_3)_2]$	1640	1360		[112]
$[NiH(O_2CH)(PCy_3)_2]$	1619	1310	8.90	[276]
$[Cu(\eta^2\text{-}O_2CH)(PPh_3)_2]$	1585	1350	8.55	[110]
$[Cu(\eta^1\text{-}O_2CH)(PPh_3)_3]$	1610	1340	9.00	[110]
$[Cu(\eta^1\text{-}O_2CH)(PMePh_2)_3]$	1620	1330	8.70	[110]
$[Cu(\eta^2\text{-}O_2CH)(PCy_3)_2]$	1600	1330	8.60	[110]
$[\{(PPh_3)_3Cu\}_2(\mu\text{-}O_2CH)][ClO_4]$	1585	1360	8.55	[110]
$[(triphos)Cu(\eta^1\text{-}O_2CH)]$	1620	1320	—	[110]
$[(np_3)Cu(\eta^1\text{-}O_2CH)]$	1610	1330	8.70	[110]
$[Cu(\eta^1\text{-}O_2CH)(PPh_3)_2(AsPh_3)]$	1610	1370		[112]
$[Cu(\eta^1\text{-}O_2CH)(PPh_3)_2(SbPh_3)]$	1605	1370		[112]



(CXXIII)



(CXXIV)

[274]. Rhenium hydrido complexes reacts with CO_2 to give $[Re(\eta^1\text{-}OC(O)H]$ complexes [86,275]. Reactions of $[ReH(PMe_3)_5]$ with CO_2 at 70 °C affords white crystals of *trans*-$[Re(CO)(O_2CH)(PMe_3)_4]$ (**CXXIV**) containing a monodentate formate ligand [86].

Reaction of CO_2 with $[RuH(NO)(PPh_3)_3]$ and $[(\eta^5\text{-}C_5H_5)RuH(PPh_3)_2]$ results in the formation of formato complexes $[Ru(NO)(O_2CH)(PPh_3)_2]$ and $[(\eta^5\text{-}C_5H_5)Ru(O_2CH)(PPh_3)_2]$ respectively [112]. The synthesis and molecular structure of the complex $[\{CoL\}_2(O_2CH)][ClO_4]_3$, containing LCo—C(OH)O—CoL moiety (L ≡ 5,7,7,12,14,14-hexamethyl-1,4,4,11-tetraazacyclotetradeca-4,11-diene) has been reported [239].

Carbon dioxide reacts with $[NiH(CH_3)(PCy_3)_2]$ in benzene at −50 °C to give the orange brown complex $[NiH(O_2CH)(PCy_3)_2]$ [276]. The platinum analog of

this complex *trans*-[PtH(O_2CH)(PCy_3)$_2$] has been characterized by X-ray crystallography [277]. Complex [Ni(Ph)(O_2CH)(PCy_3)$_2$] is obtained from the reaction of [NiH(Ph)(PCy_3)$_2$] with CO_2.

The formation of unidentate and bidentate formate ligands by the insertion of CO_2 into the Cu—H bond has been reported [108–110,112,278]. Reaction of CO_2 with [Cu(η^2-BH_4)(PPh_3)$_2$] gives different insertion products under different conditions. Complex [Cu(η^2-O_2CH)(PPh_3)$_2$] is formed when CO_2 is bubbled into a solution of [Cu(η^2-BH_4)(PPh_3)$_2$] for 24 h. Passing CO_2 into a solution of [Cu(η^2-BM_4)(PPh_3)$_2$] in the presence of one equivalent PPh_3 for 12 h gives complex [Cu(η^1-O_2CH)(PPh_3)$_3$]. In the presence of PPh_3 and NBu_4ClO_4, [Cu(η^2-BH_4)(PPh_3)$_2$] reacts with CO_2 to give [(Ph_3P)Cu(μ-O_2CH)Cu(PPh_3)$_3$] [ClO_4] (**CXXV**) [110].

The molecular structure of [Cu(η^2-O_2CH)(PPh_3)$_2$] has been determined by X-ray crystallography [110]. Reaction of CO_2 with [Cu(η^2-BH_4)(PCy_3)$_2$] results in the formation of [Cu(η^2-O_2CH)(PCy_3)$_2$]. The reaction of CO_2 with copper complexes [LCu(BH_4)] containing tridentate phosphine ligands L (L ≡ triphos, np_3, etp_3) and monodentate borohydrate (η^1-BH_4) ligand, give η^1-O_2CH bonded formato complexes [LCu(O_2CH)]. The coordination geometry about copper in [(triphos)Cu (η^1-O_2CH)] (**CXXVI**) is distorted tetrahedral with three phosphorus atoms of the triphos ligand and an oxygen atom of the formate group [110].

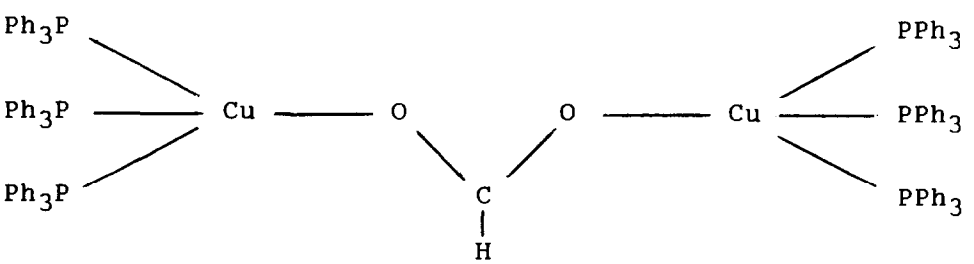
4.4.2. Insertion into the M—C bond

The normal insertion of CO_2 into metal–carbon bonds yields carboxylato complexes while the abnormal insertion gives l-metalated formate ester.

Insertion reactions of carbon dioxide into a metal–carbon bond are summarized in Table 16 [279–298]. Reaction of nickelacyclobutane with CO_2 at room temperature affords the nickel carboxylate complex (**CXXVII**) [299]. Insertion of CO_2 into a Pd—allyl bond has been investigated by Behr and co-workers [300]. The insertion products react with HCl to give organic compounds.

4.4.3. Insertion into the M—N bond

Only a few insertion reactions of CO_2 into the M—N bond have been reported [301–304]. The interaction of CO_2 with a secondary amine in the presence of a transition metal system results in the formation of carbamato complexes [303].



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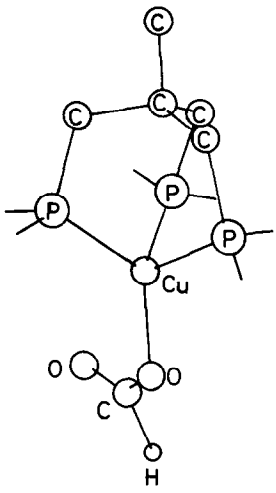

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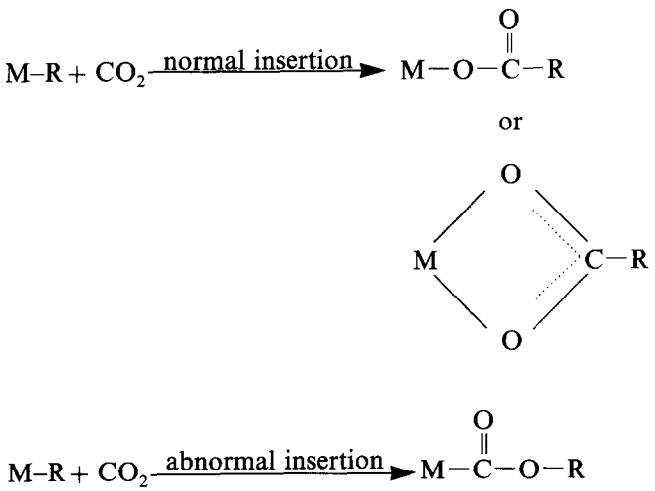


The reaction of CO_2 with $RZnNEt_2$ ($R \equiv Me$, Et) yields $[R_2Zn_4(O_2CNEt_2)_6]$ by the insertion of CO_2 into the Zn—N bond. The X-ray structure for $[Me_2Zn_4(O_2CNEt_2)_6]$ has been reported [304].

4.4.4. Insertion into the M—O bond

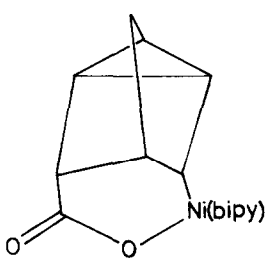
The insertion of CO_2 into an M—OR bond yields carbonate complexes.

$$M{-}OR + CO_2 \rightarrow MO_2COR$$

Carbon dioxide insertion into the W—OR bond of complexes $[Et_4N][W(CO)_5(OR)]$ ($R \equiv Ph$, C_6H_4Me-m) produces arylcarbonato complexes

Table 16
Insertion reaction of CO_2 into the M–C bond

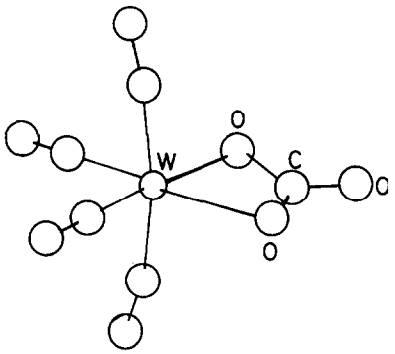
Precursor complex	Isolated product	Reference
$[(\eta^5\text{-}C_5H_5)_2TiMe_2]$	$[(\eta^5\text{-}C_5H_5)_2Ti(O_2CMe)Me]$	[279]
$[(\eta^5\text{-}C_5H_5)V(\eta^1\text{-}C_3H_5)]$	$[(\eta^5\text{-}C_5H_5)V(\eta^1\text{-}O_2CC_3H_5)]$	[280]
$[RM(CO)_5]^-$ ($M \equiv Cr, W$; $R \equiv Me, Et$)	$[(RCO_2)M(CO)_5]^-$	[281–286]
$[MeW(CO)_4L]^-$ ($L \equiv PMe_3, P(OMe)_3$)	$[(MeCO_2)W(CO)_4L]^-$	[281–286]
$[W(Me)(CO)_2(NO)L_2]$ ($L \equiv PPh_3, P(O\text{-}i\text{-}Pr)_3$)	$[W(\eta^2\text{-}O_2CMe)(CO)_2(NO)L]$	[287,288]
$[W(CO)_4(\eta^2\text{-}CH_2CH_2PPh_2)]^-$	$[W(CO)_4\{\eta^2\text{-}O_2C(O)CH_2CH_2PPh_2)\}]^-$	[289]
$[WH(Me_2PCH_2)(PMe_3)_4]$	$[W(\eta^1\text{-}Me_2PCH_2)(PMe_3)_3]_2(C_3H_2O_6)$	[290]
$[Mn(Ph)_2(PCy_3)_2]$	$[Mn(\eta^2\text{-}O_2CPh)_2(PCy_3)_2]$	[291]
$[Mn(CO)_4(\eta^2\text{-}CH_2CH_2PPh_2)]$	$[Mn(CO)_4\{\eta^2\text{-}O_2C(O)CH_2CH_2PPh_2)\}]$	[292]
[(TDP)Fe-Bu]	$[(TPP)Fe-OC(O)(CH_2)_3CH_3]$	[293]
$[Rh(Ph)(PPh_3)_3]$	$[Rh\{\eta^1\text{-}OC(O)Ph\}(PPh_3)_3]$	[286]
$[Rh(Ph)(PMe_3)_3]$	$[Rh(\eta^2\text{-}O_2CPh)(PMe_3)_2]$	[286]
$[Rh(Me)(PMe_3)_3]$	$[Rh(\eta^2\text{-}O_2CMe)(PMe_3)_2]$	[286]
$[Rh(Ar)(L)]$ ($Ar \equiv 4\text{-}MeC_6H_4$, $L \equiv t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2$)	$[Rh\{OC(O)Ar\}(L)] + \ldots$	[294]
$[Ni(Et)_2(bipy)]$	$[Ni(Et)(O_2CEt)(bipy)] + [Ni(O_2CEt)_2(bipy)]$	[295]
$[Ni(\eta^2\text{-}o\text{-}C_6H_4CH_2)(P\text{-}n\text{-}Bu_3)_2]$	$[Ni\{\eta^2\text{-}o\text{-}CH_2C_6H_4C(O)O\}(P\text{-}n\text{-}Bu_3)_2]$	[296]
$[Ni(\eta^2\text{-}CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2]$	$[Ni\{\eta^2\text{-}CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)O\}(PMe_3)_2]$	[297]
$[(phen)(PPh_3)Cu-CH(CN)_2]$	$[(Phen)(PPh_3)Cu-OC(O)CH(CN)_2]$	[298]
$[(phen)(PPh_3)Cu-CH(CN)(COOEt)]$	$[(Phen)(PPh_3)Cu-OC(O)CH(CN)(COOEt)]$	[298]



(CXXVII)

$[W(CO)_5\{OC(O)OR\}]^-$. A THF solution of arylcarbonato complexes reacts with water to give the carbonato complex $[Et_4N]_2[W(CO)_4(CO_3)]\cdot H_2O$ (**CXXVIII**) [305].

The formation of μ-carbonato-di-μ-hydroxybis(1,5-diamine-3-aza-pentane)cobalt (III) perchlorate from the interaction of CO_2 with $[(dien)Co(\mu\text{-}OH)_3Co(dien)]^{3+}$ has been proposed [306]. The dioxygen complex $[Rh(O_2)(S_2CNMe_2)(PPh_3)_2]$ reacts with CO_2 to afford peroxycarbonato complex $[Rh(CO_4)(S_2CNR_2)(PPh_3)_2]$ which reacts with PPh_3 to give the yellow carbonato complex $[Rh(CO_3)(S_2CNR_2)(PPh_3)_2]$ (**CXXIX**) [307]. Rection of CO_2 with $[(\eta^5\text{-}C_5Me_5)IrH(OEt)(PPh_3)]$



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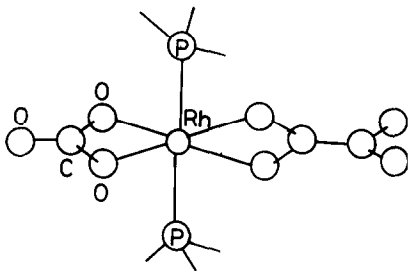
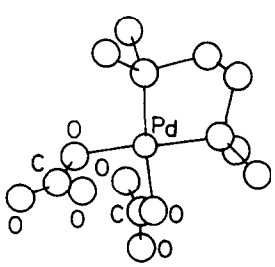


(CXXIX)

leads to insertion of CO_2 into the Ir—OEt bond and no insertion into the M—H bond is observed. The insertion product is $[(\eta^5\text{-}C_5Me_5)(PPh_3)(H)Ir{-}O{-}C(O){-}OEt]$ [308].

Insertion of CO_2 into a Pd—O bond has been observed in the reaction of CO_2 with hydroxy bridged palladium complexes. Reactions of $[Pd(\mu\text{-}OH)L_2][BF_4]_2$ ($L \equiv PPh_3$, $PMePh_2$, 1/2 dppe, 1/2 dcpe) with CO_2 result in the formation of bis(bicarbonato) complexes $[Pd\{OC(O)OH\}_2L_2]$. The structure of $[Pd\{OC(O)OH\}_2(dppe)]$ (**CXXX**) was determined by X-ray diffraction analysis. The geometry about the palladium atom is square planar [309]. Reaction of CO_2 with $[Pt(OH)(Ph)L_2]$ ($L \equiv P(CH_2Ph)_3$) affords a dimeric carbonato complex (**CXXXI**) [310].

The (μ-oxo)dichlorobis(1,10-phenonthroline)copper(II) reacts with CO_2 to afford the carbonate complex $[(phen)ClCu(\mu,\eta^3\text{-}CO_3)CuCl(phen)]$ [311]. The IR spectrum of this complex shows absorption bands at 1530, 1360, 820 and 750 cm^{-1} characteristic of the bridging tridentate carbonate ligand [312]. Photolysis of the μ-carbonato complex produces a μ-oxo complex by loss of CO_2. Alkyl carbonato complexes of Zn(II), (**CXXXII**) and (**CXXXIII**) are obtained by the reaction of CO_2 with zinc(II)-tetraazacycloalkane complexes in the presence of base (ROH) in alcohol [313,314].



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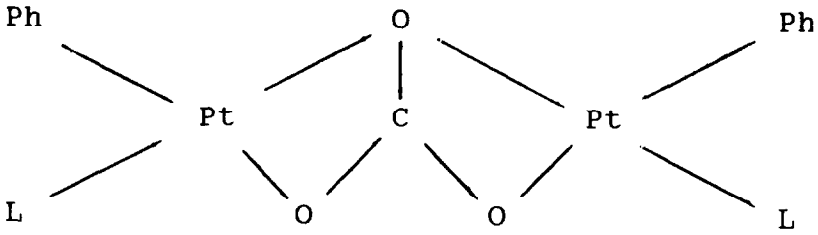
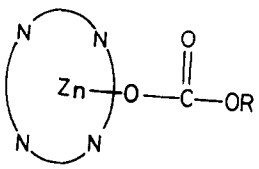


(CXXXI)



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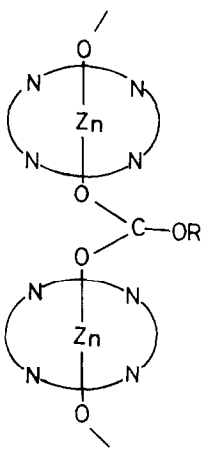
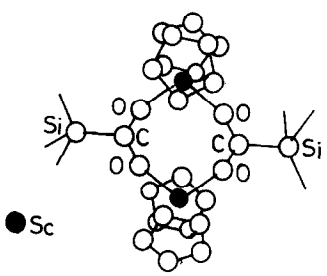


(CXXXIII)



(CXXXIV)

4.4.5. Insertion into the M—Si bond

Attempts to observe insertion of CO_2 into an M—Si bond were unsuccessful: complexes $[(\eta^5\text{-}C_5Me_5)TaCl_3(SiMe_3)]$, $[(\eta^5\text{-}C_5H_5)_2ZrCl(SiMe_3)]$ and $[W(CO)_5(SiMe_3)]$ do not react with CO_2 [315–317]. Reaction of excess CO_2 with zirconium-silyl complex $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ZrCl\{Si(SiMe_3)_3\}]$ gives an unidentified mixture of products [318].

Tilley and co-workers have successfully isolated the insertion product, for the first time, from the reaction of CO_2 with scandium-silyl complexes. $[(\eta^5\text{-}C_5H_5)_2Sc(SiR_3)(THF)]$ ($R_3 \equiv (SiMe_3)_3$, t-$BuPh_2$) react with CO_2 to afford

$[(\eta^5\text{-}C_5H_5)_2Sc(\mu\text{-}O_2CSiR_3)_2Sc(\eta^5\text{-}C_5H_5)_2]$ (**CXXXIV**). The structure of (**CXXXIV**) has been established by X-ray crystallography [319].

4.4.6. Insertion into the M—P bond

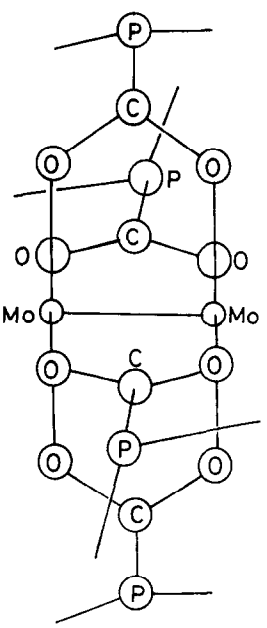
Carbon dioxide undergoes insertion into metal—PR_2 bonds to give phosphinocarboxylate O_2CPR_2 ligands [320–322].

Carbon dioxide reacts rapidly with phosphino-amido complexes $[M(NMe_2)_4(PR_2)_2]$ to afford complexes $[M_2(O_2CNMe_2)_2(NMe_2)_2(O_2CPR_2)_2]$ ($M \equiv Mo$, $R \equiv$ t-Bu (**CXXXV**); $M \equiv W$, $R \equiv$ t-Bu (**CXXXVI**), Cy). The ligands O_2CNMe_2 and O_2CPR_2 are bound to metal centers in an η^2 fashion. In benzene solution, complex (**CXXXV**) decomposes to give $Mo_2[O_2CP(t\text{-}Bu)_2]_4 \cdot 2C_6H_6$ (**CXXXVII**). The molecular structures of (**CXXXVI**) and (**CXXXVII**) have been determined by X-ray analysis [322].

The tungsten complex (**CXXXVI**), unlike its molybdenum analog, is inert with respect to decomposition in organic solvents. The coordination at each tungsten in complex (**CXXXVI**) is a distorted square planar WO_3 moiety. The W—W distance of 2.290(1) Å is consistent with other $d^3—d^3$ $(W \equiv W)^{6+}$ units [322].

4.4.7. Oxidative coupling of carbon dioxide with coordinated organic substrate

Carbon dioxide undergoes coupling reactions with unsaturated hydrocarbons (alkenes, alkynes, dienes, conjugated dienes and cumulenes), imines and aldehydes on the transition metal centers to produce metallocycles (**CXXXVIII–CXLIII**).



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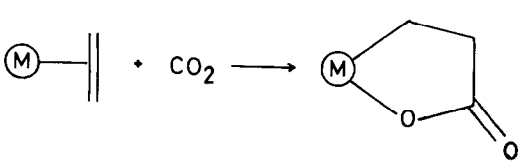
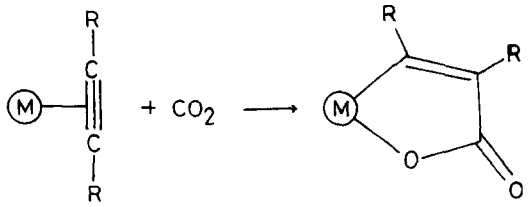
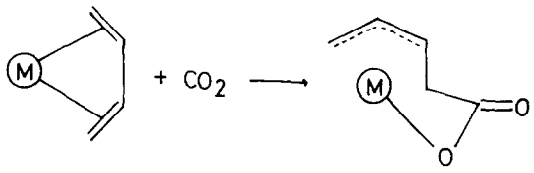


(CXXXVIII)



(CXXXIX)



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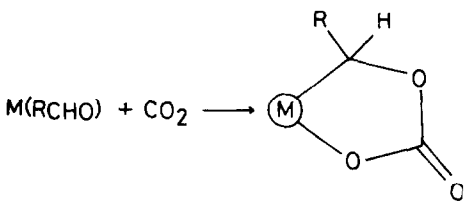
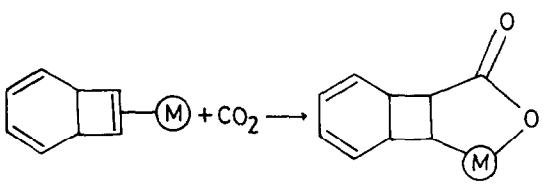
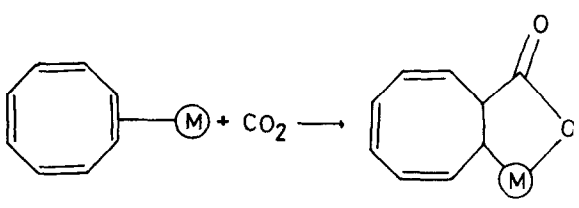


(CXLI)



(CXLII)



(CXLIII)

Two main requirements, which play an important role in the coupling reactions of CO_2 and unsaturated hydrocarbons, are (a) high electron density at the metal center and (b) the unsaturated coordination of the transition metal [323–345].

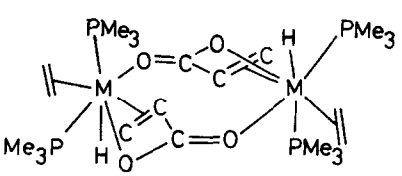
The reaction of CO_2 with $[(\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}C_2H_4)]$ in toluene at low temperature (−78 °C) gives complex $[(\eta^5\text{-}C_5Me_5)_2Ti\{\eta^2\text{-}CH_2CH_2C(O)O\}]$ [323]. In the reaction of CO_2 with allyltitanium complexes, the formation of complexes $[(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}O_2C_4H_7)]$ has been suggested [324]. The coupling reaction between alkynetitanium complex $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Ti(PhC{\equiv}CPh)]$ and CO_2 to produce a five-membered metallacyclic complex $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Ti\{\eta^2\text{-}PhC{\equiv}CPhC(O)O\}]$ has been reported by Demerseman and co-workers [325]. Complex $[(\eta^5\text{-}C_5H_5)_2Ti(HC{\equiv}CH)(PMe_3)]$ reacts with CO_2 to give $[(\eta^5\text{-}C_5H_5)_2Ti\{\eta^2\text{-}CH{=}CHC(O)O\}]$ and PMe_3 [326]. Zirconium complexes $[(\eta^5\text{-}C_5Me_5)_2Zr(\eta^2,\eta^2\text{-}C_2H_6)]$ and $[(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH{=}C(Me)CH_2)]$ react with CO_2 to give complexes $[(\eta^5\text{-}C_5Me_5)_2Zr\{\eta^3\text{-}C_3H_4CH_2C(O)O\}]$ and $[(\eta^5\text{-}C_5Me_5)_2Zr\{\eta^2\text{-}OC(O)CH_2CH{=}CMeCH_2C(O)O\}]$ [327].

The vanadium complex $[V\{\eta^2\text{-t-BuNC(mes)}_3\}]$ (mes ≡ 2,4,6-$Me_3C_6H_2$) reacts with CO_2 to give coupling product $[V\{\eta^2\text{-t-BuNC(mes)}\}\{\eta^2\text{-t-BuNC(mes)C(O)O}\}_2]$ by insertion of CO_2 in two V—C bonds [328]. Coupling of CO_2 to the activated benzene in chromium complex $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ yields an intermediate cyclohexanylcarboxylate complex $[Cr(\eta^5\text{-}C_6H_6CO)(CO)_3]^{2-}$ which is oxidized and silylated to form $[Cr(\eta^6\text{-}C_6H_5CO_2SiMe_3(CO)_3]$ [329]. Reaction of CO_2, at room temperature and normal pressure, with molybdenum and tungsten complexes *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M ≡ Mo, W) results in the formation of acrylato complexes $[M\{\mu\text{-}CH_2C{=}CHC(O)OH\}(C_2H_4)(PMe_3)_2]$ (**CXLIV**) [330].

Complex $[Mn(CO)_3\{\eta^3\text{-}C_3H_4CH_2C(O)O\}]^-$ can be obtained from the reaction of $[Mn(CO)_3(\eta^2,\eta^2\text{-}C_4H_6)]$ with CO_2 by the coupling of coordinated butadiene with CO_2 [331].

The coupling reaction of complex $[Fe(C_2H_4)_2(PEt_3)_2]$ with CO_2 yields $[Fe\{\eta^2\text{-}CH_2CH_2C(O)O\}(PEt_3)_3]$ [332]. The iron complex $[Fe(\eta^2,\eta^2\text{-}C_4H_6)(PMe_3)_3]$ reacts with CO_2 to give the allylcarboxylato complex $[Fe\{\eta^3\text{-}C_3H_4CH_2C(O)O\}(PMe_3)_3]$ [333].

Carbon dioxide reacts with *mer*-$[RhH(CH_2COMe)(PMe_3)_3Cl]$ to give



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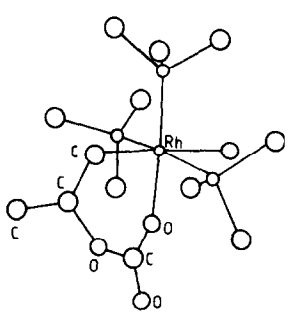


(CXLV)

$[Rh(CH_2CHMeOCO_2)(PMe_3)_3Cl]$ (**CXLV**) [334]. The formation of coupling product is reversible and the starting complex is regenerated by its dissolution in various solvents at 20 °C. Behr and co-workers have reported the coupling reaction between malonodinitrile and CO_2 on rhodium [335] and iridium [336] centers.

The coupling of CO_2 with alkynes [336–339], alkenes [340–345], conjugated dienes [346–353] or cumulenes [354] on nickel(0) centers, in the presence of chelating ligands such as 2,2′-bipyridyl TMED, 1,2-bis(dicyclohexylphosphino)ethane, diazabicyclo[5,4,0]undec-7-ene, have been reported. The coupling product $[(dbu)_2Ni\{\eta^2\text{-}CH_2CH_2C(O)O\}]$ (**CXLVI**), formed from ethylene and CO_2 at $Ni(COD)_2$ in the presence of dbu, has been isolated and structurally characterized by Hoberg and co-workers [345].

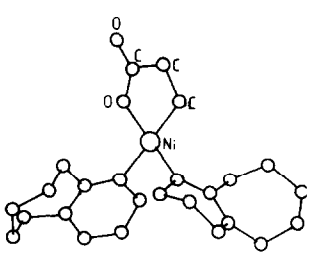
4.4.8. Reduction of carbon dioxide

Recently, there has been a considerable upsurge in the study of the reduction of CO_2 catalyzed by transmission metal complexes using different methods: (a) chemical reduction, (b) electrochemical reduction and (c) photochemical catalytic reduction. The reduction processes which have been observed are as follows: (a) reduction of CO_2 to formic acid or formate ion, (b) reductive disproportionation of CO_2 to CO and CO_3^{2-}, (c) reduction of CO_2 to oxalate, and (d) reduction of CO_2 to CO.

Transition metal complexes, which are powerful two-electron reductants, are promising substrates for reductive disproportionation of CO_2.

4.4.8.1. Chemical reduction. The binuclear oxalate complex $[\{(\eta^5\text{-}C_5H_5)Ti\}_2(\mu\text{-}C_2O_4)]$ is prepared via a reductive dimerization of CO_2 [355]. Reaction of CO_2 with $Na_2[(\eta^5\text{-}C_5H_5)V(CO)_3]$ results in reductive disproportionation of CO_2 and in the formation of $[(\eta^5\text{-}C_5H_5)V(CO)_4]$ and Na_2CO_3 [356]. Reactions of complex $[(\eta^5\text{-}C_5H_5)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ with several Lewis acids have been performed [357]. $[(\eta^5\text{-}C_5H_5)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ reacts with $ZnCl_2$ to form an unstable carbonyl complex $[(\eta^5\text{-}C_5H_5)_2Nb(CO)_2(CH_2SiMe_3)\cdot ZnCl_2]$ which decomposes with CO loss to produce $[(\eta^5\text{-}C_5H_5)_2Nb(CH_2SiMe_3)O\cdot ZnCl_2]_2$.

Reactions of CO_2 with $A_2[M(CO)_5]$ ($A \equiv K$, $M \equiv Cr$, Mo; $A \equiv Li$, Na, K, $M \equiv W$) give hexacarbonyls $[M(CO)_6]$ and alkali metal carbonates by the disproportionation of CO_2 to CO and CO_3^{2-}. Cooper and co-workers suggested that the reaction



(CXLVI)

involves discrete CO_2 adducts (**CXLVII**) and (**CXLVIII**) containing $M-\eta^1$-CO_2 [356].

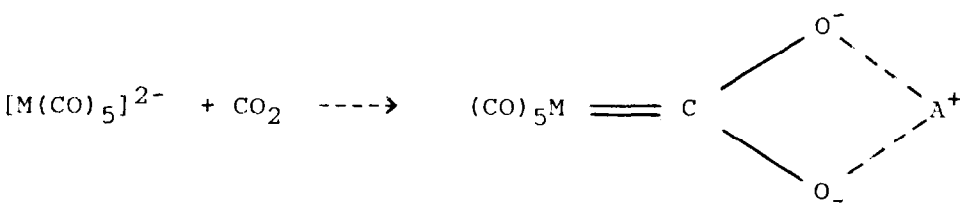
Nicholas and co-workers have reported the reactions of $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ with several electrophilic reagents and with transition metal hydrides which form carbonyl complexes via transfer of oxygen [358]. Reaction of $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ with R_3SiCl (or BCl_3 or HCl) gives $[(\eta^5\text{-}C_5H_5)_2Mo(CO)Cl]Cl$ and with $Me_3SiOSO_2CF_3$ in THF yields complex $[(\eta^5\text{-}C_5H_5)_2Mo(CO)(THF)(OSO_2CF_3)]$. RCOCl reacts with $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ to afford $[(\eta^5\text{-}C_5H_5)_2Mo(CO)(OC(O)R)]Cl$. Reactions of $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ with $[HCO(CO)_4]$ and $[H_2Fe(CO)_4]$ produce cationic carbonyl complexes [359].

$$[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)] + [HCO(CO)_4] \rightarrow [(\eta^5\text{-}C_5H_5)_2MoH(CO)]^+[CO(CO)_4]^- + HCO_3(CO)_9 + H_2O$$

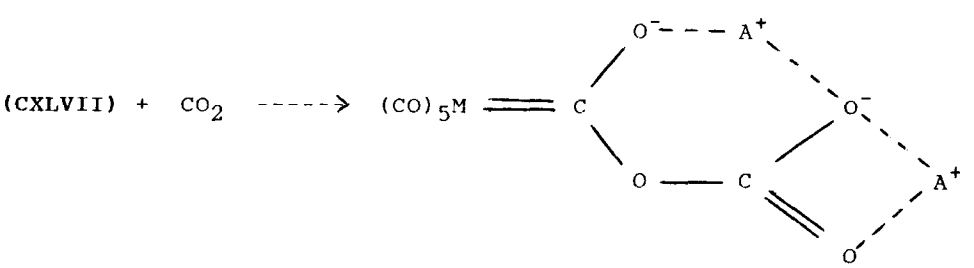
$$[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)] + [H_2Fe(CO)_4] \rightarrow [(\eta^5\text{-}C_5H_5)_2MoH(CO)][HFe_3(CO)_{11}] + H_2O$$

The complex $[(\eta^5\text{-}C_5H_5)_2MoH(CO)][CO(CO)_4]$ slowly converts to $[(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)CO(CO)_3)]$ (**CXLIX**) [359].

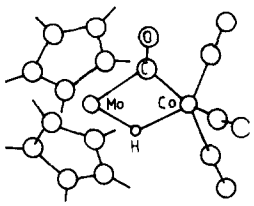
Reaction of CO_2 with *cis*-$[Mo(N_2)_2(PMe_3)_4]$ is very sensitive to the reaction conditions, in particular to the nature of the solvent used. If the reaction is performed in weakly coordinating solvents (Et_2O, THF, Me_2CO), the main products are either the red dimeric complex (**CL**) or the dark blue monomeric complex (**CLI**), obtained from the metal-induced reductive disproportionation of CO_2 to CO_3^{2-} and CO [360].



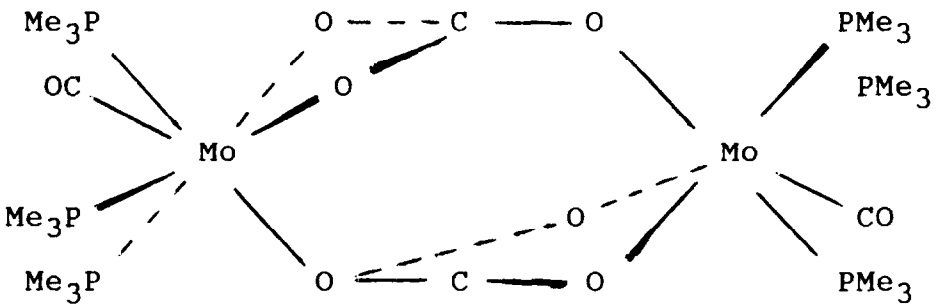
(CXLVII)



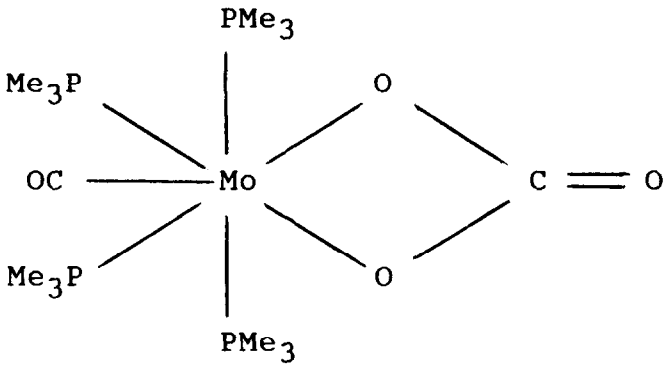
(CXLVIII)



(CXLIX)



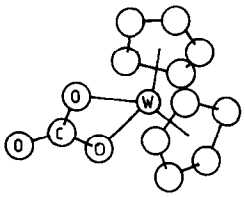
(CL)



(CLI)

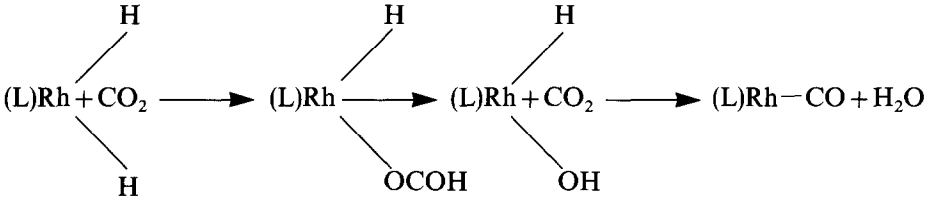
Carbon dioxide reacts with the tungsten complex $[WCl_2(PMePh_2)_2]$ to produce the carbonyl complex $[W(O)(CO)Cl_2(PMePh_2)_2]$ [361]. The carbonato complex $[(\eta^5\text{-}C_5H_5)_2W(\eta^2\text{-}CO_3)]$ (**CLII**) can be obtained from the reaction of $[(\eta^5\text{-}C_5H_5)_2WH(Ph)]$ with CO_2 in acetone in the presence of water [362].

Reactions of CO_2 with $Na_2[M'(CO)_4]$ ($M' \equiv$ Fe, Ru, Os) result in reductive disproportionation of CO_2 and in the formation of carbonyl metalates $[M'(CO)_5]$ and Na_2CO_3 [356]. The reductive hydrogenation of CO_2 has also been examined in the presence of cobalt complexes [238–240,363] and ruthenium clusters [364,365].



(CLII)

The reaction of CO_2 with transition metal hydroxides results in the formation of formate complexes [366–368]. The complex $[H_2Rh\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2(t\text{-}Bu)_2\}]$ reacts with CO_2 to produce a rhodium carbonyl complex by the reduction of CO_2 to CO and H_2O [369].



The iridium complex $[Ir_2(\mu\text{-}CNR)_2(CNR)_2(dmpm)_2]$ ($R \equiv 2,6,\text{-}Me_2C_6H_3$) reacts with CO_2 to give the CO_2 adduct $[Ir_2(\mu\text{-}CN(CO_2)R)_2(CNR)_2(dmpm)_2]$ which loses two equivalent of CO_2 on heating. In dichloromethane, the CO_2 adduct decomposes to give bridged carbonyl complex $[Ir_2(\mu\text{-}CO)(\mu\text{-}H)\{C(O)NHR\}_2(CNR)_2(dmpm)_2]$ by the reduction of CO_2 to CO [370]. Kubiak and co-workers have reported the mechanism of oxygen atom transfer from CO_2 to the methyl isocyanide ligand of a binuclear Ni(0) complex [371].

The reaction of RSH ($R \equiv H$, alkyl, benzyl, phenyl and substituted phenyl) with the CO_2 complex $[Ni(\eta^2\text{-}CO_2)(PCy_3)_2]$ leads to the formation of a nickel carbonyl complex.

$$3[Ni(\eta^2\text{-}CO_2)(PCy_3)_2] + 4RSH$$
$$\rightarrow [Ni(CO)_2(PCy_3)_2] + 2[Ni(SR)_2(PCy_3)_2] + CO_2 + 2H_2O$$

Reduction of CO_2 by $[NiCl(PCy_3)_2]$ and PhSH gives small amounts of the dicarbonyl complex $[Ni(CO)_2)(PCy_3)_2]$. All the Ni(II) complexes $[NiCl_2L_2]$ (L = monodentate phosphines, L_2 = bidentate phosphines) are inactive in the CO_2 reduction by thiols [372]. The formation of a nickel carbonate complex $[Ni_3(N,N\text{-}Me_2en)_6(CO_3)(H_2O)_4][ClO_4]_4$ arises from the reaction of CO_2 with the nickel(II) complex of *N,N*-dimethylethylenediamine, $[Ni(N,N\text{-}Me_2en)[ClO_4]_2$ in aqueous ethanol [373]. Reaction of CO_2 with $[Pt(C_2H_4)(PPh_3)_2]$ results in the formation of the carbonato complex $[Pt(\eta^2\text{-}O_2CO)(PPh_3)_2]$ and carbon monoxide [210].

Reductive hydrogenation of CO_2 gives formic acid in the presence of moisture or other proton source. The transition metal complex activates a water molecule with

the formation of a hydride complex which transforms the hydrogen to the CO_2 molecule coordinated to the metal. The hydrogenation of CO_2 to formic acid is catalyzed by complexes $[RuH_2(PPh_3)_4]$ [374], $[RuCl_3(EDTA)]$ [374] and $[Rh(NBD)(PMe_2Ph)_3][BF_4]$ [375]. The hydrogenation of CO_2 catalyzed by soluble metal catalysts with added alcohols [376,377], alkyl halides [378] or secondary amines [379] to give formate esters or formamides is enhanced by the formation of H_2O or HX.

The reaction of H_2 with $[Rh(NBD)(PMe_2Ph)_3][BF_4]$ gives rhodium dihydride complexes $[Rh(H)_2(PMe_2Ph)_3(S)]$ ($S \equiv H_2O$, THF) which are active catalysts for the hydrogenation of CO_2 to formic acid. The formation of the monodentate formate complex $[RhH(\eta^1\text{-}OC(O)H)(H_2O)(PMe_2Ph)_3]^+$ and bidentate formate complex $[RhH(\eta^2\text{-}O_2CH)(H_2O)(PMe_2Ph)_2]^+$ as unstable intermediate has been observed under catalytic conditions [375].

4.4.8.2. Electrocatalytic reaction. The electrocatalytic reaction of CO_2 in the presence of transition metal complexes has been extensively studied in the last decade [51]. The results are summarized in Table 17. In the electrocatalytic reactions, the coordination compound is either deposited onto the electrode surface or dissolved in the electrolyte. The formation of various reduction products depends mainly on the transition metal complex and solvent used.

Transition metal complexes which can reduce electrocatalytically CO_2 to various products are grouped into five categories: (a) transition metal tetraazamacrocyclic complexes [380–382], (b) phthalocyanine and porphyrin complexes [383–392], (c) metal clusters [393–395], (d) transition metal bipyridyl and polybipyridyl complexes [275,396–416], (e) phosphine complexes [417–420].

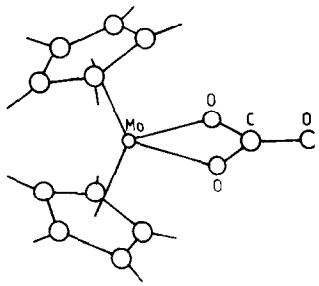
4.4.8.3. Photocatalytic reduction. A number of studies concerning photoreduction of CO_2 using transition metal complexes as photocatalyst have been reported [395–397,401–403,410,416,421–441]. This approach involves the photochemical generation of electron-rich transition metal species in homogeneous solution and these photogenerated species act as redox catalyst.

The oxo complex $[(\eta^5\text{-}C_5H_4Me)_2Nb(O)(CH_2SiMe_3)]$ can be isolated from the irradiated ($\lambda = 250$ nm) solution of $[(\eta^5\text{-}C_5H_4Me)_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)]$ in THF at $-20\,^{\circ}C$ [429]. Irradiation (at more than 330 nm) of a THF solution of $[(\eta^5\text{-}C_5H_5)_2MoH_2]$ at $-10\,^{\circ}C$ under 1 atm CO_2 for 30 h yields molybdenum carbonyl complex $[(\eta^5\text{-}C_5H_5)_2Mo(CO)]$ and carbonate complex (**CLIII**) [430]. The photolysis of $[Mo(\eta^2\text{-}CO_2)(PMe_3)_4]$ in toluene solution at $-20\,^{\circ}C$ results in oxygen transfer from CO_2 to phosphine and gives *cis*-$[Mo(CO)_2(PMe_3)_4]$ and $OPMe_3$ as the major products along with lesser amounts of *mer*- and *fac*-$[Mo(CO)_3(PMe_3)_3]$ and $[Mo(CO)(PMe_3)_5]$ [431]. The adducts $[W(CO)_5(PR_3)]^-$ ($R \equiv$ Ph, t-Bu), obtained by the reaction of phosphine ligands with photogenerated $[W(CO)_5]^-$, are powerful reducing agents. Irradiation of a CO_2 saturated solution containing $Na_2[W_2(CO)_{10}]$ and phosphine ligand gives formate, carbon monoxide, carbonate and bicarbonate [432].

The generation of CO by photoreduction of CO_2 to CO via visible light irradiation

Table 17
Electrocatalytic reduction of carbon dioxide

Catalyst	Solvent	Products	Reference
$[CoL_3]^{2+}$	$MeCN-H_2O$	CO, H_2	[380]
$[CoL_2]^{2+}$	$DMF-H_2O$	CO, H_2	[380]
(L ≡ 14 membered tetraazamacrocyclic ligands)			
$[Ni(cylam)]^{2+}$	H_2O	CO	[381,382]
(cyclam ≡ 1,4,8,11-tetraazacyclotetradecane)			
[Ti(pc)]	H_2O	CO	[390,391]
[Fe(pc)]	H_2O	CO	[390,391]
[Co(pc)]	H_2O	$HCOO^-$	[383,385]
	H_2O	CO, H_2	[384]
[Ni(pc)]	H_2O	$HCOO^-$	[383]
[Cu(pc)Cl]	H_2O	CO	[391]
[Co(TMPP)]	H_2O	CO, HCOOH	[387]
[Co(TPP)]	CH_2Cl_2	CO	[392]
[Pd(TPP)]	CH_2Cl_2	$C_2O_4^{2-}$	[386]
$[Fe_4S_4(SCH_2Ph)_4]^{2-}$	DMF	$HCOO^-$	[393]
$[Fe_4S_4(SXN-)_4]^{2-}$	DMF	$HCOO^-$	[395]
(X ≡ $-COCM_2-$, $-COC_6H_4CH_2-$)			
$[Re(CO)_3Cl(bipy)]$	DMF-H_2O	CO	[396–398]
$[Re(CO)_3Cl(vbipy)]$	MeCN	CO, CO_3^{2-}	[399,400]
(vbipy ≡ 4-vinyl-4′-methyl-2,2′-bipyridine)			
$[Re(CO)_3Cl(bipy\text{-}py)]$	MeCN	CO	[407]
(bipy-py ≡ 4[4″-{*N*-pyrrolyl)*n*-butyl-4′-methyl-2,2′-bipyridine)			
$[Fe(vtpy)_2]^{2+}$	MeCN	CO	[411]
(vtpy ≡ 4′-vinyl-2,2′:6′,2″-terpyridine)			
$[Ru(CO)_2(bipy)_2]^{2+}$	DMF	$HCOO^-$	[401–403]
cis-$[Ru(CH_2Ph)(CO)(bipy)_2]^+$	MeCN	CO	[400]
$[(\eta^6\text{-}C_6H_6)Ru(bipy)Cl]^+$	MeCN	CO, $HCOO^-$	[404]
$[Ru(terpy)(dppe)Cl]^+$	MeCN	CO, $HCOO^-$	[404]
cis-$[OsH(CO)(bipy)_2]^+$	MeCN	CO	[400]
	$MeCN-H_2O$	CO, $HCOO^-$	[400]
cis-$[Os(Me)(CO)(bipy)_2]^+$	MeCN	CO	[400]
cis-$[Os(Ph)(CO)(bipy)_2]^+$	MeCN	CO	[400]
$[Co(vtpy)_2]^{2+}$	MeCN	HCOOH	[411]
$[Rh(COD)(bipy)]^+$	MeCN	CO, $HCOO^-$	[404]
cis-$[Rh(bipy)_2(CF_3SO_3)_2]^+$	MeCN	CO, $HCOO^-$	[404,408]
cis-$[Ir(bipy)_2(CF_3SO_3)_2]^+$	MeCN	CO, $HCOO^-$	[404,408]
$[Ni(vtpy)_2]^{2+}$	MeCN	HCOOH	[411]
$[Ni(bipy)_3]^{2+}$	DMF	CO	[415]
[RhCl(dppe)]	MeCN	$HCOO^-$	[417]
$[Rh(CO)Cl(PPh_3)_2]$	DMF	CO	[419]
$[Ir(CO)Cl(PPh_3)_2]$	DMF	CO	[419]
$[Ni(MeCN)_4(PPh_3)_2]^{2+}$	DMF	CO	[415]
$[Ni_3(\mu\text{-}CNMe)(\mu_3\text{-}I)(dppm)_3]^+$	THF	CO, CO_3^{2-}	[420]
$[Pd(triphos)(PPh_3)]$	MeCN	CO, H_2	[418]
$[Pd(triphos)(PEt_3)]$	MeCN	CO, H_2	[418]
$[Pd(triphos)\{P(OMe)_3\}]$	MeCN	CO, H_2	[418]



(CLIII)

of solution containing $[Re(CO)_3X(bipy)]$ (X ≡ Cl, Br) and CO_2 in triethanolamine–dimethylformamide (TEOA–DMF) has been studied [396,398,433–435]. Similar irradiations, conducted in the presence of $[Co(bipy)]^{2+}$, lead to CO and H_2. The complex $[Re(CO)_3X(bipy)]$ absorbs visible light to yield the excited state $[Re(CO)_3X(bipy)^*]$ which may undergo either oxidative or reductive electron transfer quenching, depending on the redox potential of the quencher.

$$[Re(CO)_3X(bipy)] \xrightarrow{h\nu} [Re(CO)_3X(bipy)^*]$$

$$[Re(CO)_3X(bipy)^*] + TEOA \rightarrow [Re(CO)_3X(bipy)]^- + TEOA^{+*}$$

The $[Re(CO)_3X(bipy)]^-$ species should reduce CO_2 to CO [396,435]. The formation of CO depends on (a) the nature and concentration of the reducing agent, (b) the time of irradiation, and (c) the presence of additives (Table 18). Owing to labilization of the ligand species, the activity of the system decreases slowly. Addition of chloride or bromide anions to the corresponding $[Re(CO)_3X(bipy)]$ complex leads to an increase in stability, producing more CO [396].

Kitamura and Tazuke reported, for the first time, the photochemical reduction of

Table 18
Photochemical reduction of CO_2 to CO via visible light irradiation of solutions containing $[Re(CO)_3X(bipy)]$ and CO_2 in TEOA−DMF [396]

Complex	Additive	Irradiation time (h)	Volume of CO produced (ml)
$[Re(CO)_3Cl(bipy)]$	—	1	6.5
$[Re(CO)_3Cl(bipy)]$	—	2	9.7
$[Re(CO)_3Cl(bipy)]$	—	4	16.8
$[Re(CO)_3Cl(bipy)]$	NEt_4Cl	2	14.5
$[Re(CO)_3Cl(bipy)]$	NEt_4Cl	4	30.0
$[Re(CO)_3Br(bipy)]$	—	2	7.6
$[Re(CO)_3Br(bipy)]$	—	4	11.8
$[Re(CO)_3Br(bipy)]$	NEt_4Br	2	12.0
$[Re(CO)_3Br(bipy)]$	NEt_4Br	4	16.0

CO_2 and $HCOO^-$ by $[Ru(bipy)_3]^{2+}$ in the presence of methylviologen (MV^{2+}) in a TEOA–DMF mixture under irradiation of light ($\lambda > 320$ nm) [436]. Ziessel and co-workers have studied the photochemical reduction of CO_2 to formate by visible light irradiation ($\lambda > 400$ nm) of systems containing either the $[Ru(bipy)_3]^{2+}$ complex which yields the active catalytic species by photolabilization of a bipy ligand, or a mixture of $[Ru(L\text{-}L)_3]^{2+}$ (L-L ≡ 2,2′-bipyridyl or 1,10-phenanthroline) as photosensitizer and *cis*-$[Ru(CO)X(bipy)_2]^{n+}$ (X ≡ Cl, H, $n=1$ or X = CO, $n=2$) or *cis*-$[Ru(CO)_2Cl_2(bipy)]$ as homogeneous catalysts [437,438]. The solvent was either TEOA–DMF or TEOA–DMF–H_2O. Photocatalyst $[Ru(CO)_2(bipy)_2]^{2+}$ and photosensitizer $[Ru(bipy)_3]^{2+}$ (or $[Ru(phen)_3]^{2+}$) reduce CO_2 to afford HCO_2^- in the triethanolamine–DMF system under irradiation ($\lambda > 320$ nm) [439]. The complex *cis*-$[Ru(CO)_2(bipy)_2]^{2+}$ is reduced by 2 mol $[Ru(bipy)_3]^+$, a powerful monoelectronic reducing agent, to give a coordinatively unsaturated complex $[Ru(CO)(bipy)_2]$ [439]. The generation of active species $[Ru(CO)(bipy)_2]$ by double reduction $[Ru(CO)Cl(bipy)_2]^+$ and $[RuH(CO)(bipy)_2]^+$ has also been proposed by Lehn and Ziessel [438].

$$[Ru(CO)Cl(bipy)_2]^+ + 2[Ru(bipy)_3]^+ \rightarrow [Ru(CO)(bipy)_2] + 2[Ru(bipy)_3]^{2+}$$

$$[Ru(CO)Cl(bipy)_2]^+ + H^+ + 2[Ru(bipy)_3]^+ \rightarrow [Ru(CO)(bipy)_2] + 2[Ru(bipy)_3]^{2+} + H_2$$

The CO_2 reduction to formate might proceed through protonation of bound CO_2:

$$[Ru(CO)(bipy)_2] + CO_2 \rightarrow [Ru(CO)(CO_2)(bipy)_2] \xrightarrow{H^+} [Ru(CO)(HCOO)(bipy)_2]^+ \xrightarrow{Cl^-} [Ru(CO)Cl(bipy)_2]^+ + HCOO^-$$

The photochemical reduction of CO_2 to HCO_3^- was observed using a cobalt(II)-carbonic hydrase III [440]. Spreer and co-workers have reported photochemical reduction of CO_2 to CO and H_2 in water using $[Ru(bipy)_3]^{2+}$ as a photosensitizer, ascorbate buffer as electron donor and the $[Ni(cyclam)]^{2+}$ (cyclam ≡ 1,4,8,11-tetra-azacyclotetra-decane) as catalyst. $[Ni(cyclam)]^{2+}$ acts as a homogeneous catalyst for the photochemical reduction of CO_2 to CO, as well as for the reduction of H^+ to H_2 [441]. The possible reaction mechanism is shown as follows:

$$[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru(bipy)_3]^{2+*} \xrightarrow{HA^-} [Ru(bipy)_3]^+ + HA^*$$

$$[Ru(bipy)_3]^+ + [Ni(cyclam)]^{2+} \rightarrow [Ru(bipy)_3]^{2+} + [Ni(cyclam)]^+$$

$$[Ni(cyclam)]^+ + H^+ \rightarrow [NiH(cyclam)]^{2+} \xrightarrow{H^+} [Ni(cyclam)]^{3+} + H_2$$

$$[NiH(cyclam)]^{2+} + CO_2 \rightarrow [Ni\{OC(O)H\}(cyclam)]^{2+}$$

$$[Ni\{OC(O)H\}(cyclam)]^{2+} + H^+ \rightarrow [Ni(cyclam)]^{3+} + CO + H_2O$$

$$[Ni(cyclam)]^{3+} + HA^- \rightarrow [Ni(cyclam)]^{2+} + HA$$

Acknowledgments

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