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HOMOGENEOUS-CATALYTIC REACTIONS OF CARBON DIOXIDE WITH UNSATURATED SUBSTRATES, REVERSIBLE CO_2-CARRIERS AND TRANSCARBOXYLATION REACTIONS

DIRK WALTHER

Department of Chemistry, Friedrich-Schiller-University, 6900 Jena, (G.D.R.)

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CONTENTS

ABBREVIATIONS

ac	acetate
acac	acetylacetonate
bipy	2,2′-bipyridine
CDT	cyclododecatriene (1,5,9)
Cp	cyclopentadienyl
COD	cyclooctadiene (1,5)
COT	cyclooctatetraene (1,3,5,7)

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Cy	cyclohexyl
dad	1,4-diazadiene
dba	dibenzylideneacetone
dcpe	dicyclohexylphosphinoethane
DMF	dimethylformamide
diphos	diphenylphosphinoethane
Et	ethyl
L	ligand
L–L	bidendate chelate ligand
Me	methyl
Ph	phenyl
py	pyridine
TMED	tetramethylethylenediamine

A. THE PROBLEM OF CO_2 ACTIVATION AT TRANSITION METAL CENTRES

There are a number of scientific and practical reasons why carbon dioxide at the moment is and will increasingly become attractive as a C_1 synthetic unit in the immediate future. Of these reasons the following have the strongest influence on the current direction of research.

Carbon dioxide—the biggest carbon source on earth.

In view of the prospect of increasing scarcity of organic carbon carriers for the future, the following question is of interest even at the present time: which options are open to the chemist for changing CO_2 into organic compounds in an economically favourable way? In this field the development of catalytic methods is of maximum interest, especially as there is no raw material problem involved, neither from the aspect of quantity or from the distribution of sites.

Carbon dioxide—the basis of all biochemical organic synthesis processes.

Photosynthesis and other enzymatic methods for carboxylation represent the natural CO_2 activation processes which have been optimized in the course of billions of years of development and which proceed under mild conditions. The understanding of these reactions and their simulation in the laboratory may be helpful in answering the question of an "artificial photosynthesis" or in utilizing enzyme-analogous carboxylation reactions for chemical synthesis.

Carbon dioxide is nowadays obtained as a by-product in technical processes.

Access to carbon dioxide even in large quantities without significant technical effort, in relatively pure form, is easily possible because CO_2 occurs, for instance, in ethylene oxide production or in the industrial ammonia synthesis. Large amounts of CO_2 are also released in lime burning.

TABLE 1

Possibilities for homogeneous-catalytic reactions at transition metal centres

No.	Sources for energy	Cosubstrate	Products	Remarks	Ref.
1	$h\nu$	H_2O	CO, H_2	Artificial photosynthesis	[1–4] [15–19]
2	e	H_2O	HCOOH,CO $(HOOC)_2$	Electrocatal. conversion	[1,4] [20–28]
3a	H_2	H_2	CH_4,CH_3OH HCHO, CO+ H_2O	Hydrocondensation	[1–12] [29–35]
3b	H_2 + ROH	H_2 + ROH	HCOOR + H_2O		[1–14] [36–43]
4a	Oxiranes	Oxiranes	Cycl. carbonates		[1–12] [44–48]
4b	Oxiranes	Oxiranes	Polycarbonates		[1–12] [49–56]
5	Unsaturated substrates	Unsaturated substrates	Lactones, esters, acids	Co-oligomerization	
6	Metal–CO_2-carrier	C–H	C–COOH	Transcarboxylation	

Chemistry for catalytic activation of CO_2 is still underdeveloped.

This statement applies to both homogeneous-catalytic and heterogeneous-catalytic processes so that a promising field of research emerges here. The field is interesting both with respect to fundamental and applied research, not only for the manufacture of products on a large scale, but also for the synthesis of special chemicals having a high service value and offering applications in the field of aromatic and odoriferous substances as well as in the field of pharmaceuticals.

In view of the high thermodynamic stability of CO_2 and of the fact that the molecule is often kinetically inert, the problem of CO_2 activation is a permanent challenge to the art of the chemist to 'force' this substrate into selective reactions under mild conditions as far as possible. Overcoming the kinetic restrictions imposed by reactions at transition metal centres is still a young field of complex and metal–organic chemistry, the development of which was mainly initiated by Vol'pin [1,2].

Table 1 shows the principal possibilities for metal–complex catalyzed or induced activation reactions of CO_2 giving organic products.

An analysis of the present state of development shows that the variants indicated in Table 1 have to be assessed quite differently with regard to their practical suitability for the synthesis of organic products: All homogeneous-catalytic techniques where cheap, mass-products are produced (nos. 1–3, Table 1) are so far found to be inferior to the traditional ones for obtaining the final products described in Table 1. The essential causes of this are the relatively low conversion numbers and selectivities. It can be predicted that technical implementation of these reactions will remain unfulfilled in the near future. Particularly, "artificial photosynthesis" has not yet left the stage of exploratory fundamental research despite the highly successful work of, for instance, Lehn [15–17,19,25] and Tazuke [18]. The homogeneous-catalytic hydrogenation of CO_2 by means of transition metal complexes as catalysts is not competitive even though Sneeden [5,35,42], Darensbourg [40], Inoue [34,39,41], Kudo [31,38], and Vol'pin [1,2,37] have done pioneer work in gaining a mechanistic understanding of this conversion; conversion numbers of more than 1000 have already been found. Reaction 4a leads to cyclic carbonates (Table 1) which can be produced in technical processes with good yield even without the use of metal-complex catalysis. Experimental hints that nickel(0) complexes and other transition metal complexes can be used at relatively low temperatures are interesting [45,46].

Metal halides with high central atom oxidation numbers can be used as catalysts in combination with phosphine ligands at room temperature and normal pressure even if the reaction times are relatively long [44]. It is currently totally unclear whether metal-catalyzed processes will ever be able to replace the already established technical processes for the synthesis of cyclic carbonates. The synthesis of polycarbonates by means of metal-complex catalysts—organozinc compounds in combination with aluminium organyls (Table 1) are especially worth mentioning—has been reported in summary several times [49–55].

The following article deals with reactions 5 and 6 (Table 1) as well as with the basic and model reactions directly connected therewith. More recent developments of the past years have shown that reaction 5 in particular (Table 1) can be preparatively used technically for the synthesis of special chemicals. Then there follows an overview of reversible CO_2 carriers which are of interest mainly as model compounds for enzymatic carboxylation reactions and which may become preparatively significant for transcarboxylation reactions in due course. The last chapter discusses recent development concerning fundamental research on CO_2 activation at transition metal centres which allows deeper insight into the mechanistic aspects of the basic reactions or or serves to demonstrate novel reactions of CO_2 at transition metal centres.

B. CO-OLIGOMERIZATION REACTIONS OF CO_2 WITH 1,3-DIENES

The first homogeneous-catalytic co-oligomerization of CO_2 with an unsaturated substrate was observed by Inoue in 1976 [57,58], although the conversion numbers observed and selectivity of this reaction were extremely low.

Subsequent work focused first of all on "principal solutions" for the detection of new possibilities for C–C linkage between CO_2 and olefins or alkynes.

In the early eighties the situation was like this: There existed a number of homogeneous-catalytic methods in which complex compounds with noble metals as central atoms were especially used. The selectivity of the catalytic conversion was unsatisfactory in all cases (less than 60%); the conversion numbers were also low (5 to 50). Drastic reaction conditions (long reaction periods, high temperatures and a relatively high pressure) were the typical features of these conversions.

Work was then continued with just the aim of arriving at, or improving, the practical applicability of these reactions through purposeful design of the catalyst and by the systematic search for optimum reaction conditions as well as for increasing the synthesis potential of these reactions by experiments employing 3*d*-metals as central atoms and by the use of new substrates. Today many of these goals have already been achieved.

(i) Homogeneous-catalytic reactions

After the discovery of the first homogeneous-catalytic reaction of CO_2 proceeding with C–C linkage at a transition metal complex, this conversion

TABLE 2

Co-oligomerization of butadiene with carbon dioxide using palladium complexes as catalysts [a]

No.	Complex (mmol)	Ligand	Diene (mol)	t(°C)	Solvent time	Ref.
1	$Pd(diphos)_2$ (0.2)	–	0.14	120	Benzene (20 h)	[57,58]
2	$Pd(diphos)_2$ (0.2)	–	0.14	120	DMF(20 h)	[57,58]
3	methallyl-Pd(ac) (0.38)	diphos	0.31	70	Benzene (48 h)	[59–61]
4	methallyl Pd(ac) (0.38)	Et_3P	0.31	70	Benzene (48 h)	[59–61]
5	$Pd(acac)_2$ (0.16)	Cy_3P	0.25	90	Acetonitrile (15 h)	[62–64]
6	$Pd(acac)_2$ (0.16)	$(i\text{-}Prop)_3P$	0.25	90	Acetonitrile (15 h)	[62–64]

[a] For yields and selectivities see Table 3.

TABLE 3

Co-oligomerization of butadiene with carbon dioxide, selectivities and turnover numbers [a]

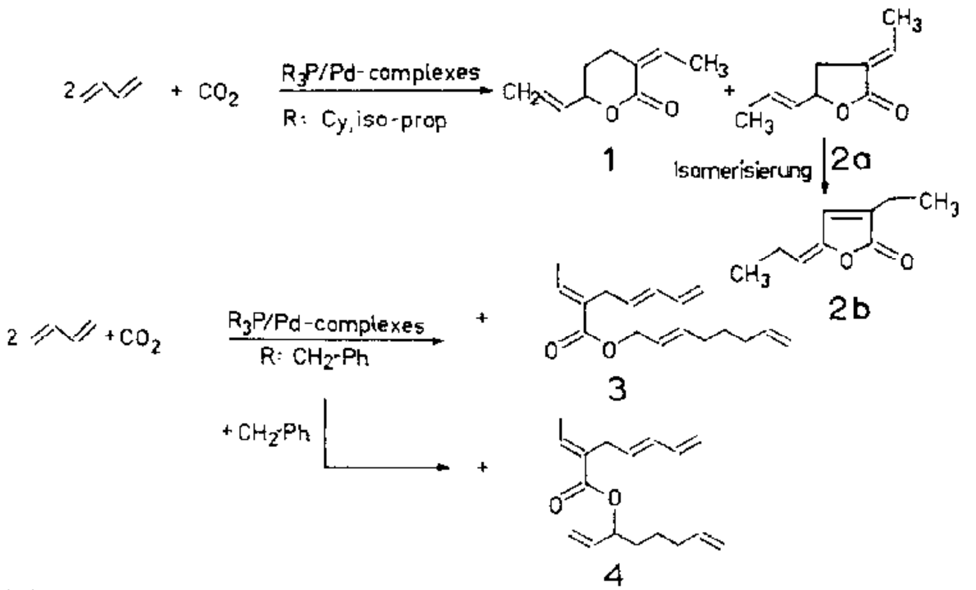
No.	Conversion % diene	Selectivity			Turnover number [b]	Ref.
		1	2	3+4		
1	90	—	0.4	—	2.5	[57,58]
2	90	—	4	—	1	[57,58]
3	90	5	—	39	300	[59–61]
4	90	64	—	23	500	[59–61]
5	44	96.2	0.2	3.4	670	[62–64]
6	44	96.2	0.7	3.1	670	[62–64]

[a] For reaction conditions see Table 2.
[b] The turnover numbers are calculated for the main product of the carboxylation.

was considered from various sides in order to improve considerably selectivities and yields which were low.

Tables 2 and 3 include systems used for that purpose. Scheme I shows the possible reaction products of the catalytic reaction. In particular the work of Keim and Behr [62–64] revealed that the δ-lactone **1** (scheme I) can be formed with very good selectivity (greater than 96%) if you work up to a maximum conversion of 50% diene (Tables 2 and 3).

Systematic investigation of the controlling influence of phosphine ligands on the selectivities and conversion numbers led to the result that basic



Scheme I.

phosphines with a large cone angle (according to Tolman [65]) are directing the reaction towards **1**. The best catalytic system for the synthesis of **1** at the present time is indicated in Table 3. The synthesis of **1** in preparative or even in technically relevant quantities has become relatively easy, particularly since the starting materials butadiene and CO_2, which are not converted can be recycled.

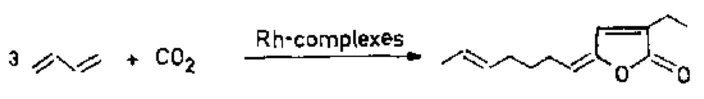
In view of the high reactivity of **1** and the close similarity to lactones of a similar type which occur in natural aromatic and flavouring substance (for instance jasmine lactone, 'whisky lactone' as well as lactones that can be isolated from hop, butter and animal fat), this catalytic conversion is highly interesting with regard to industrial applicability the more so since the production of **1** according to classical organic synthetic techniques would be more costly.

The γ-lactone **2** is also easily accessible by isomerization of **1** with palladium/phosphine catalyst combinations [63]. Musco [59,60] succeeded in guiding the catalytic co-oligomerization between butadiene and CO_2 in benzene with 45% selectivity to the unsaturated esters **3** and **4** (Scheme I) through the use of controlling ligands having a smaller cone angle (for example $PhMe_2P$ or $(Ph{-}CH_2)_3P$) at the palladium complex $[\eta^3$-2-methallyl-Pd(acetate)$]_2$; the acids on which these esters are based are generated with only 30% selectivity when the $Pd(PPh_3)_4$ catalyst system is used in combination with sodium acetate [67] or sodium phenolate [66].

Isoprene reacts with CO_2 only in very low yield to give lactone analogues [68]. However, it is possible to catalytically link isoprene, butadiene and CO_2 (1 : 1 : 1) or piperylene, butadiene and CO_2 to give mixtures of isomers containing lactones of type **1** at the same catalyst combinations of palladium(0) complex/basic phosphine in acetonitrile [64]. Butadiene can also be co-oligomerized with CO_2 with rhodium complexes.

The γ-lactone **5** (scheme II) is formed by linking three diene units with CO_2. So far, however, only low yields have been obtained (5% yield when 0.65 millimole $(acac)_2$rhodium(ethylene)$_2$ was used as a catalyst and 0.2 mole butadiene and 0.4 mole CO_2 at a temperature of 120 °C and a reaction time of 24 hours).

The relatively drastic reaction conditions and the poor selectivities as well as the low conversion numbers (maximum 15) are the reasons why any



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Scheme II.

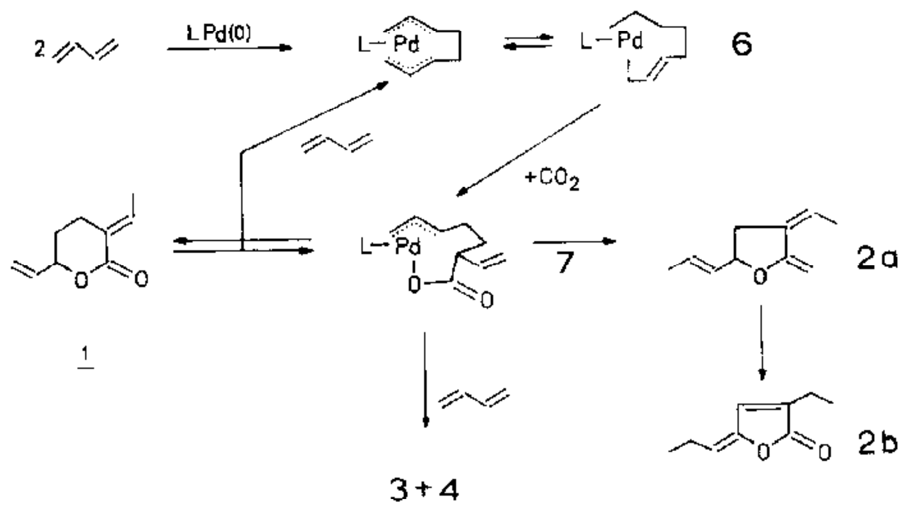
preparative applicability of this catalytic reaction cannot be thought of so far. Any attempt to convert 1,3-dienes with CO_2 by means of cheaper 3*d*-transition metal catalyst systems apparently failed hitherto. For instance, stoichiometric conversion with the formation of multinuclear complexes or mononuclear metalacycles were found with nickel(0) complexes.

(ii) Basic homogeneous-catalytic conversion reactions

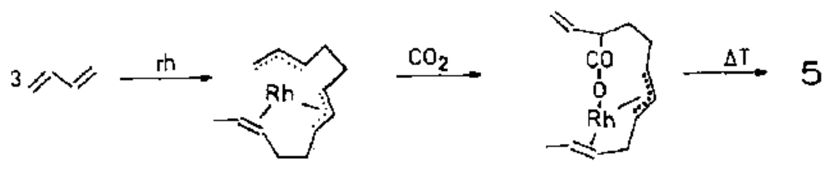
A plausible proposal for the co-oligomerization mechanism of butadiene with CO_2 at palladium complexes is based on the reaction steps shown in scheme III [61,63,64]: the oxidative coupling of two diene units with C–C linkage to give the C_8-chain which is bonded to the palladium (II) central atom at one end through a η^3-allyl group and at the other end through a η^1-allyl group takes place in the first step. This type of allyl palladium complexes was isolated by Jolly et al. [70].

Direct coupling of CO_2 with one diene at the palladium(0) central atom does not constitute a competitive reaction due to the rapid coupling of two dienes at this site. It is only after the subsequent step that CO_2 is inserted into the Pd–C σ-bond formed intermediately (scheme III). Therefore, the C_9 carboxylate formed represents the decisive intermediate product for the various organic products which can be formed in the course of the catalytic reaction.

Reductive elimination with H-shift yields the δ-lactone **1** in a relatively rapid reaction, whereas the thermodynamically more stable γ-lactone **2** is formed in a comparatively slow reaction. As the reaction **7** ⇄ **1** is reversible



Scheme III.



Scheme IV.

(scheme III), it becomes clear that γ-lactone **2** is formed by isomerization from **1** when high catalyst concentrations and long reaction times are used.

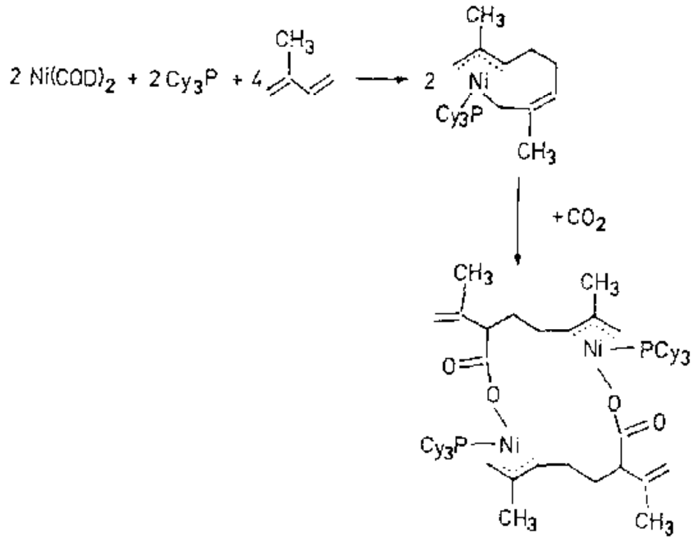
The formation of esters **3** and **4** is also a slow reaction taking place with excessive butadiene and **1**, the **7** intermediate product also being formed in this case.

The cyclo-oligomerization of three butadiene units and CO_2 to give the γ-lactone **5** can be explained with a similar mechanism [69] (scheme IV). First of all, a C_8 chain is formed from the conversion of two dienes and this continues to react in a relatively rapid reaction with another diene to give a bis-η^3-allyl-C_{12} chain. It is only after then that CO_2 is involved in the reaction. In this case too, the activation step of CO_2 is an insertion reaction. The subsequent reductive elimination supplies **5**. These reflections render comprehensible the fact that **1**–**4** are observed as by-products: the C_8 chain does not react selectively with butadiene but can react to a certain degree with CO_2 with insertion, that is to say the reaction sequence shown in scheme III takes place as a competitive conversion.

(iii) Stoichiometric activation reactions of CO_2 in the presence of 1,3-dienes

Ligand-free or phosphine-nickel(0) complexes with monodentate phosphines as controlling ligands react first of all in the 1,3-diene/CO_2 system with linkage of diene units without CO_2 interfering in the reaction. It is not until after the formation of bis-allyl C_8- or C_{12}-chains that CO_2 is inserted to give carboxylates which may partly be subject to rearrangement reactions which are not yet fully understood mechanistically. In this way the complex compound shown in scheme V is formed. **8** and **9** were structurally investigated by X-ray structure analysis [71]. The direct metalaring closure reaction between CO_2 and 1,3-dienes is possible, however, if nickel(0) complexes of the (L–L)Ni(diolefin) type are used (scheme VI). η^3-Allyl carboxylate complexes of the type **10** are formed, with **10h** being investigated by X-ray structure analysis. Table 4 deals with other representatives of this group of compounds.

η^3-Allyl carboxylates of type **10** are interesting synthons for further reactions with electrophiles or π-acidic neutral ligands. In this way unsaturated long-chain carboxyl acids [6,73] are formed by means of alkyl



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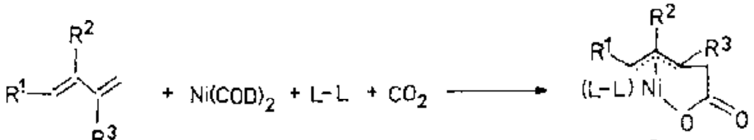
Scheme V.



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Scheme VI.

halides, R–X. Unsaturated dicarboxylic acids can be obtained with excess CO_2 [74]. Compound **10h** reacts with monodentate phosphines R_3P, exchanging the diamine with a phosphine ligand so that even phosphine-stabilized η^3-allyl carboxylates **10l** and **10m** can be obtained, in these according to an X-ray structure analysis, the same C_5O-chain exists as in **10h** (Table 4) [78]. Reactions of 1,3-dienes with CO_2 which proceed with 1 : 1 coupling and

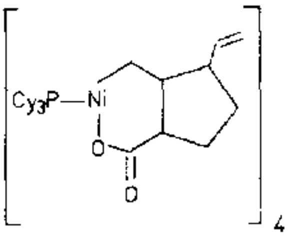

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TABLE 4

Metalacycles of type **10**, composition and IR spectra

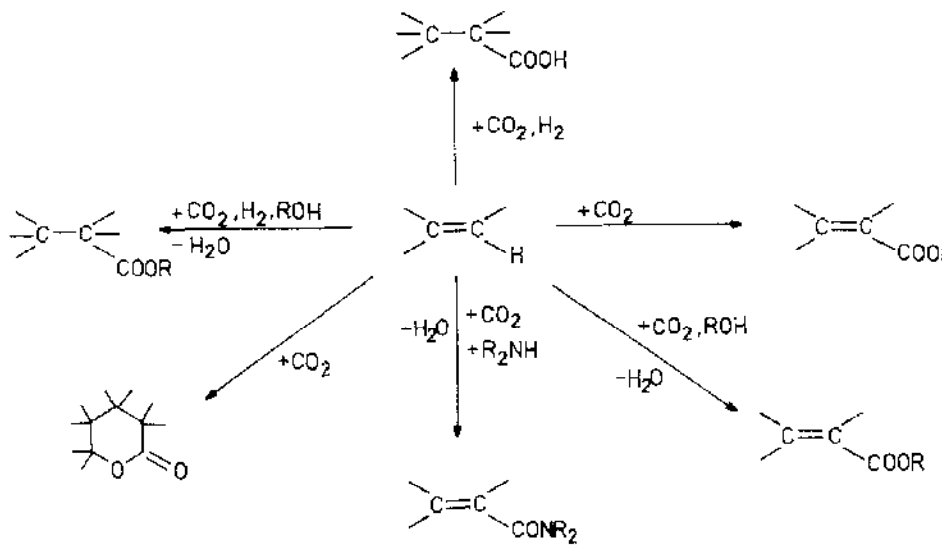
No.	Ligand	Diene	ν_{CO}	X-ray	Ref.
10a	bipy	Butadiene	1630	–	[72,73]
10b	TMED	Butadiene	1625	–	[74]
10c	dcpe	Butadiene	1608	–	[75]
10d	bipy	Isoprene	1624	–	[72,73]
10e	dcpe	Isoprene	1605		[75]
10f	bipy	2,3-dimethyl-butadiene		–	[76]
10g	bipy	1-methyl-butadiene	1605	–	[77]
10h	TMED	2,3-dimethyl-butadiene		+	[76]
10i	Ph_3P	2,3-dimethyl butadiene	1650	+	[78]
10k	Cy_3P	2,3-dimethyl-butadiene	1648	+	[78]

lead to compounds of type **10** can also be considered as model steps for metal-assisted or metal-catalyzed reactions for the formation of δ-lactones. But the formation of these lactones (formally the Diels–Alder product of dienes and CO_2 which, however, cannot be obtained through a Diels–Alder reaction) is only observed in the thermal reaction of **10h** to a low extent. The main products of the thermal reaction are the monomer diene and CO_2 [78] formed by reductive decoupling. Particularly strong π-acidic neutral ligands convert certain compounds of type **10** into doubly unsaturated carboxylic acids. This reaction to be classified formally as an insertion reaction of CO_2 into a C–H linkage will be dealt with in Section G.

C. CO-OLIGOMERIZATION REACTIONS OF CO_2 WITH ALKENES

(i) Homogeneous-catalytic codimerization of CO_2 with alkenes

So far relatively little is known of the homogeneous-catalytic conversions of CO_2 with monoolefines even though some technically attractive reactions are thermodynamically allowed (scheme VII). Under rather drastic conditions, with $(Ph_3P)_3RhCl$ as a catalyst, it is possible to convert ethylene in the presence of CO_2 and ethanol into a mixture of propionic acid and its ethyl esters. Table 5 includes detailed information about the reaction conditions and the selectivity of this catalytic reaction [79]. The conversion cannot be catalyzed heterogeneously by Rh or Pd catalyst metals. The mechanism of



Scheme VII.

this carboxylation reaction in which hydrogenation of the double bonds also takes place at the same time is not known. The alcohol is assumed to be the reducing agent.

The preparative value of this catalytic reaction so far is low. It has relatively poor selectivity compared to established techniques for the synthesis of saturated carboxylic acids, the more so since acceptable conversion numbers could be recorded only under extreme reaction conditions (up to 700 atmospheres of pressure). At low pressures propylene is catalytically converted in a solution of methanol and acetone in the presence of CO_2 into a isomer mixture of 2-methylpropionic acid ester and methyl butyrate. Both

TABLE 5

Catalytic reactions [a] of ethylene with carbon dioxide and ethanol to form propionic acid and the ethylester [b]

p (atm)	Mol ethylene	Conversion of ethylene (%)	Selectivity		Turnover number
			Acid (%)	Ester (%)	
150	ca. 0.5	36.4	23.4	53.6	ca. 250
350	ca. 0.7	44.7	40	45	ca. 500
600	ca. 1.0	80.8	30	19	ca. 750
700	ca. 1.4	91.6	42	12	ca. 1300

[a] Catalyst: $(Ph_3P)_3RhCl$; promotor: HBr; solvent: H_2O; t: 180 °C; time: 12 h.

[b] Ref. 79.

isomers are formed in approximately equal quantities. Under typical reaction conditions (215 °C, 45 atm., 20 h, reaction time, $(Ph_3P) RuCl_2$ being used as catalyst), some 28% of the propylene can be converted into carboxylic acid ester [80]. The low selectivities and conversion numbers of around 15 for each isomer are the reasons why hitherto there has been no application of this catalytic conversion. It is mechanistically interesting that the two C-atoms of the double bond are carboxylated in propylene at approximately the same speed under the reaction conditions chosen. So far it has not been possible to find catalytic reactions of monoolefins and CO_2 with formation of saturated δ-lactones or of acrylic acid (scheme VII) though partial steps on the way to a catalytic conversion are known.

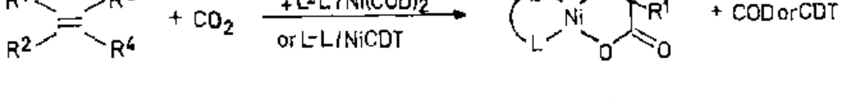
(ii) Stoichiometric reactions of CO_2 with alkenes at transition metal centres

The formation of acrylic acid from ethylene and CO_2 using molybdenum and tungsten complexes was reported recently. This reaction proceeds over two metal centres [81] and runs with formal insertion of CO_2 into a C–H bond and therefore it will be discussed in greater depth in Section G.

The stoichiometric metalaring closure reaction between olefins and CO_2 is interesting both as the initiating step of a conversion to give acrylic acid and as a possible first step of δ-lactone formation (scheme VII).

The 1:1 coupling can be conducted at nickel complexes with high effective electron density analogous to that described in the reaction of 1,3-dienes with CO_2 (Section B). Organometallic complexes of type **11** are formed at the complex moiety (L–L)Ni(0) (L–L: TMED, bipy, $Cy_2PCH_2CH_2PCy$) (scheme VIII). Table 6 presents representatives of these compounds which contain a Ni–C σ-bond.

The reaction product of dicyclopentadiene and CO_2 with the complex moiety (bipy)Ni(O) was studied by means of an X-ray structure analysis [84] as the only representative of this class of nickel heterocycles so far. Of the total of 24 possible metala heterocycles which can be formed from the two components by metalaring closure only two will be formed in the same ratio (Fig. 1). Compound **11 h** (Table 6) displays high stability which is surprising for organometallic compounds and it decomposes only at 230 °C with



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Scheme VIII.

TABLE 6

Metalacycles of type **11** from carbon dioxide and alkenes

No.	Alkene	Ligand	ν_{CO}	Selectivity	Ref.
11a	Ethylene	dcpe	1620	–	[82,83]
11b	Ethylene	bipy	1635	–	[82,83]
11c	Propene	dcpe	1630	Two regioisomers	[83]
11d	1-Hexene	dcpe	1630	Two regioisomers	[83]
11e	3-Hexene	dcpe	1630	–	[83]
11f	Norbornene	bipy	1625	Stereoselective (exo)	[83]
11g	Norbornene	dcpe	1630		[83]
11h	Dicyclopentadiene	bipy	1618	Stereoselective (exo, 2 regio-isomers)	[84]
11i	Norbornadiene	bipy	1633	Stereoselective	[85,86]
11k	COT	bipy	1630	–	[6,86]
11l	Bicyclooctatriene	bipy	1625	–	[86]

formation of CO_2 and dicyclopentadiene. Monosubstituted alkenes R–CH=CH_2 react with CO_2 to give regioisomers. Hoberg showed that the thermodynamically more stable product (with a Ni–CH_2 σ-bond) will only be formed when the reaction is heated for a longer period and when alkyl-substituted monoolefins are used, whereas only an isomer mixture will be formed at room temperature [83]. It was deduced that oxidative coupling can proceed reversibly as also observed with the coupling products of heteroolefins with CO_2 at the electron-rich nickel(0) complex moiety (Section G).

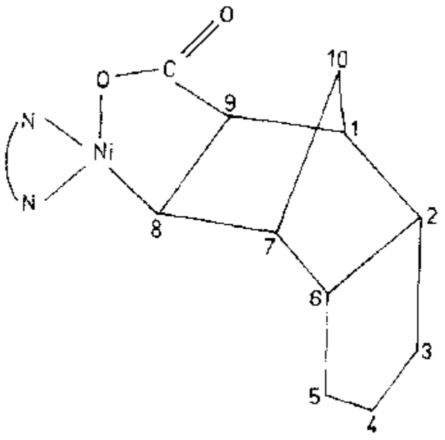
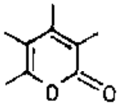


Fig. 1. Structure of the complex compound **11h**, product of the oxidative coupling between CO_2 and dicyclopentadiene at the complex moiety bipyNi(0) (N–N, bipy; Ni–C_8, 1.929(5) Å; Ni–O, 1.845 Å; C_4–C_5, 1.390(10) Å; C_3–C_4, 1.41(10) Å [84]).



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Recently it was shown that $(Me_5Cp)_2Ti(C_2H_4)$ can react with CO_2 under oxidative coupling to give a titanium heterocycle which is set up analogously to the compounds of type **11** [87].

D. CO-OLIGOMERIZATION OF CO_2 WITH ALKYNES AT METAL COMPLEXES

(i) Homogeneous-catalytic conversions to 2-pyrones

Inoue [88,89] described catalytic reactions of disubstituted alkynes (e.g. 3-hexyne and 4-octyne) as well as of monosubstituted alkyne 1-butyne at the chelate phosphine/Ni(0) catalyst complex. 2-Pyrones **14** are formed with relatively low conversion numbers in a reaction which is not very selective (Table 7).

The catalytic cyclo-oligomerization between 3-hexyne and CO_2 proceeds much more selectively when basic monodentate phosphines R_3P having a low steric demand are used as controlling ligands at the nickel(0) central atom and when acetonitrile is used as a solvent (Table 7) [90]. For instance

TABLE 7

Co-oligomerization of carbon dioxide with 3-hexyne using nickel(0) complexes as catalysts [a]

No.	Ligand	Solvent	Conversion (%)	Yield(%) 2-pyrone	Turnover number	Ref.
1	Diphos	Benzene	82	13	~1.2	[88,89]
2	$Ph_2P(CH_2)_4PPh_2$	Benzene	96	57	~6	[88,89]
3	Ph_3P	Benzene	99	~9	~1	[89,90]
4	Ph_3P	THF	20	~5	~0.6	[90]
5	Cy_3P	THF	99	12	6.6	[90]
6	Cy_3P	THF/AN	94	29	15	[90]
7	Ph_2EtP	THF/AN	94	75	39	[90]
8	Ph_2MeP	THF/AN	93	92	47	[90]
9	Et_3P	THF/AN	98	97	52	[90]

[a] Reaction conditions: 120 °C, 20 h, $L:Ni(COD)_2 = 2:1$. No. **1–3**: 3-Hexyne 8.8 mmol, turnover number (calculated): 22. No. **4–9**: 3-Hexyne 44.1–88.2 mmol, turnover number (calculated): 55. The yield of the 2-pyrone based on 3-hexyne charged. AN: acetonitrile, THF: tetrahydrofurane.

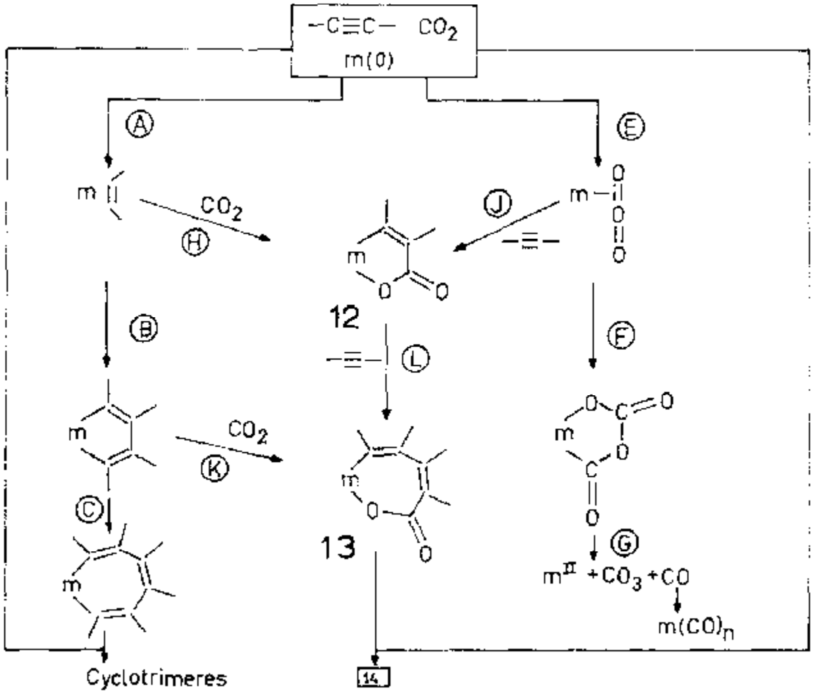
tetraethyl-2-pyrone can be obtained catalytically with high selectivity (96%) with 2 $Et_3P/Ni(COD)_2$/acetonitrile so that for the first time ever a co-oligomerization between CO_2 and an unsaturated substrate which proceeds catalytically and with a high selectivity could be implemented at a 3*d*-transition metal centre. This reaction can also be extended to other alkynes.

1-Propyne can also react at cationic rhodium(I)complexes to give 2-pyrone, but the yields of around 3% are extraordinarily low so that this reaction cannot be used preparatively [91]. So far the problem of selective co-oligomerization of monosubstituted alkynes with CO_2 has not yet been solved.

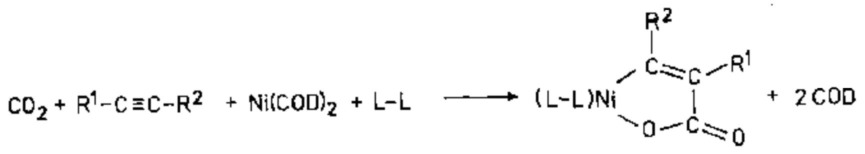
Acetylene also reacts partly with co-oligomerization with the catalyst system described above, yet the main product of the catalytic reaction is polyacetylene [90]. Cyclopentadienyl-titanium(II)-complexes, $(CpMe_5Cp)Ti$ (tolan) and $(Me_5Cp)_2Ti$(tolan), also react with carbon dioxide to give the oxidative coupling product [94,95].

(ii) Model reactions for the mechanism of 2-pyrone formation

Scheme IX shows the possible pathways for reactions of alkynes with CO_2 at a low oxidation state transition metal centre. A selective reaction to give



Scheme IX.



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$R^1 = R^2 = H$ L–L = $Cy_2P–CH_2–CH_2–PCy_2$ [93]

$R^1 = R^2 = CH_3$ + L–L = bipy [92]

$R^1 = R^2 = C_2H_5$ L–L = bipy [90]

Scheme X.

2-pyrone is ensured when the metalaring closure reaction between CO_2 and alkyne to give the metala heterocycle **12** can take place in the first step. Such a conversion proceeds easily at nickel(0) centres of high electron density according to stoichiometric investigations carried out with numerous unsaturated substrates (see ref. 6 and references therein). Basic monodentate phosphines satisfy this precondition especially well so that promotion of direct 1 : 1 coupling between CO_2 and the alkyne can be considered as the controlling effect of these ligands.

The reaction sequence A–B–C–D (scheme IX) is the selectivity-reducing conversion leading to the formation of cyclic alkyne trimers. In the presence of CO_2, benzene derivatives are formed to a lesser extent only, cyclopentadiene derivatives are formed instead [88–90]. The reaction steps E–F–G (scheme IX) lead to a reduction of activity of the catalytic system because the metal carbonate formed can no longer be regenerated to give the nickel(0) complex. Therefore, this "reductive disproportionation" should be inhibited as far as possible. Hoberg has shown under which conditions the "reductive disproportionation reactions" at nickel(0) proceed particularly easily [92]. Model compounds for the desired reaction path via the metala cycle **12** can be built up at the complex moiety (L–L)Ni(0) (L–L: TMED, bipy, $Cy_2PCH_2CH_2PCy_2$) [90,92,93,96] as shown in scheme X. The nickel heterocycle **12** reacts with the activated RCOO–C≡C–COOR alkyne, with insertion, to give the seven-membered ring chelate complex of type **13** (scheme IX) so that the partial step L of the catalytic cycle could also be modelled [93]. The structure of the compound was clarified by means of an X-ray structure analysis.

The catalytic co-oligomerization of alkenes with CO_2 is especially subject to solvent control, which can be attributed to the following three factors in the case of acetonitrile: as a polar solvent acetonitrile favours charge-con-

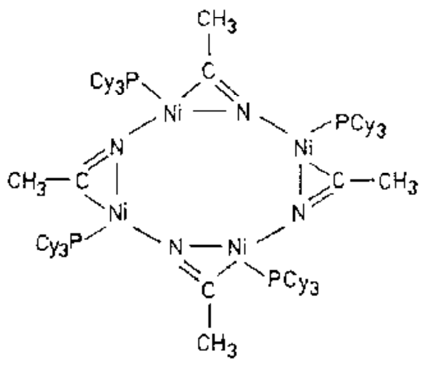

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Fig. 2. Structure of the complex compound $[(Cy_3P)Ni(NC-CH_3)]_4$ (compound **15**) (Ni–N, 1.9–1.94 Å: Ni–C, 1.85–1.87 Å: C≡N, 1.18–1.25 Å [90]).

trolled reactions such as the 1 : 1 coupling between CO_2 and unsaturated substrates; acetonitrile can also additionally activate CO_2 by forming an intermediate $CH_3-CN^+-COO^-$ compound; acetonitrile can also have direct control at the metal centre by an additional coordinative interaction with the central atom.

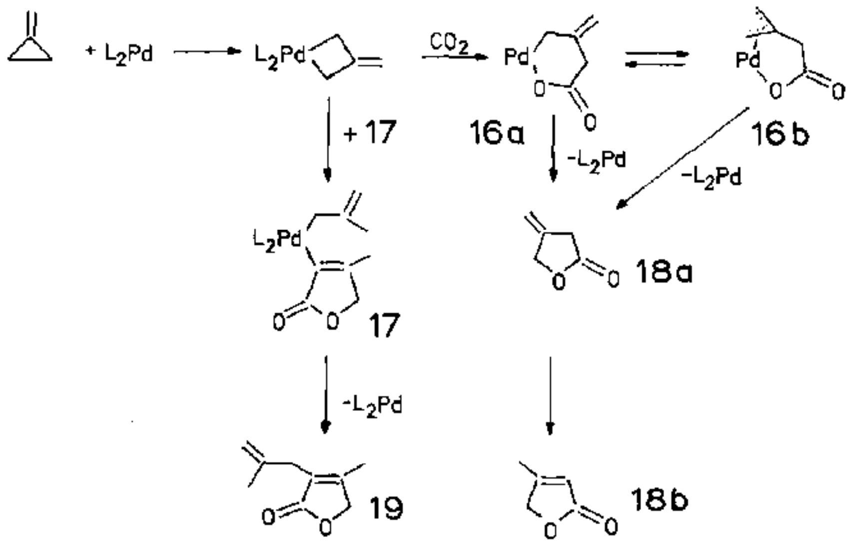
The actual existence of acetonitrile coordination at the nickel(0) centre can be demonstrated by isolating the tetranuclear complex **15** by reaction of $Ni(COD)_2$ with tricyclohexylphosphine in acetonitrile [90]. Figure 2 shows the structure of the nickel(0) complex in which acetonitrile is bonded like an alkyne to a metal centre, whereas the free electron pair at the nitrogen atom enters into an end-on bond with a second nickel central atom.

This reaction suggests that acetonitrile acts as a ligand even in the catalytic co-oligomerization of alkynes with CO_2. Possibly complexes of type **15** formed as intermediates, react with excess alkyne so that selective catalytic co-oligomerization takes place at the complex moiety $[(R_3P)(CH_3CN)Ni(0)]$ via metalaring closure of CO_2 and alkyne [90].

E. CO-OLIGOMERIZATION OF CO_2 WITH METHYLENECYCLOPROPANES

The first attempts at co-oligomerization of substituted methylenecyclopropanes with CO_2 at a $Pd(0)/R_3P$ catalyst system date back to the year 1979. Inoue showed that γ-lactones **18a** and **18b** can be formed, though only low selectivity was found at first (Table 8) [97] (scheme XI).

Experiments conducted at a later date demonstrated that other co-oligomerization products in which two and more cyclopropanes are linked with CO_2 to give lactones are also formed [98,99].



Scheme XI.

Recently, Binger succeeded in converting the unsubstituted methylenepropane with CO_2, in good yield (80% selectivity) and with relatively high conversion numbers to give 2(5*H*)-furanone **18** [98,99]. Table 8 shows that Ph_3P is particularly well suited as a controlling ligand. Higher oligomers are formed by further reaction of **18** with methylenecyclopropane, with, however, lower yields. Scheme XI indicates the understanding of the reaction

TABLE 8

The catalytic co-oligomerization of methylenecyclopropanes with carbon dioxide at palladium complexes as catalysts [a]

No.	Catalyst	Substrate	Conversion (%)	Selectivity γ-lactone (%)	Turnover number	Ref.
1	A	2,2-dimethylmethylenecyclopropane	97	73	~33	[97]
2	B	2,2-dimethylmethylenecyclopropane	93	48	~19	[97]
3	C	Methylenecyclopropane	ca. 100	45	168	[98,99]
4	C	Methylenecyclopropane	ca. 100	80	610	[98,99]

[a] Reaction conditions: **1–2**: 120 °C, 20 h, 0.3 mmol A or B, 17 mmol substrate; A, $Pd(dba)_2/PPh_3$(1:4); B, $Pd(diphos)_2$. **3**: 152 °C, 3.3 h; 0.47 mmol C, 172 mmol substrate. **4**: 165 °C, 2 h; 0.47 mmol C, 381 mmol substrate. C: (η^3-allyl)(η^5cp)Pd/PPh_3 (1:4).

sequence which exists at present but detailed investigation of the reaction mechanism has not been reported [98].

It is assumed that the conversion of the organic substrate with the palladium(0) complex is the initiating step; the ensuing metal–organic palladium(II) complexes **16a** and **16b** have already been described [100–102]. Insertion of CO_2 into the Pd–σ- or η^3-allyl bond (scheme XI) to give the carboxylate complex **17** happens after this oxidative addition. Then furanone **18** and palladium(0) will be obtained by reductive elimination. The formation of higher oligomers (for example **19**) can be explained by the further reaction of **18** with methylenecyclopropane.

Diphenylmethylenecyclopropane also reacts with CO_2 to give lactone when the catalytic system $Ph_3P/Pd(0)$ is used. However, the yields (18%) are still too low and so this conversion is not yet attractive preparatively [98]. The formation of 2(5*H*)-furanone derivatives from methylenecyclopropanes and CO_2 opens up independent access to these biochemically interesting substances.

Unsaturated lactones form part of numerous natural substance molecules and can also be used as pharmaceutical agents because of their antibiotic effect. They are also important as odorous and aromatic substances for the cosmetics and foodstuffs industries.

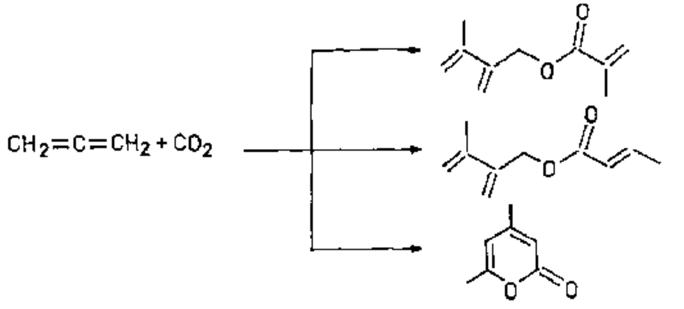
F. CO-OLIGOMERIZATION OF CO_2 WITH ALLENES

Jolly et al. reported on the catalytic reaction of allene with CO_2 in 1982. The catalyst systems were palladium complexes, the catalytic action of which can be controlled by way of basic chelate phosphines [103]. Further trials of the catalytic co-oligomerization of allenes with CO_2 using other catalyst systems have not been successful so far.

Even with the best catalytic systems known today, only low co-oligomer yields can be obtained so that the synthesis value of the conversion is low since the selectivity of the reaction is low. Scheme XII shows the isomers being formed during the conversion. Apart from 2 isomeric esters **20** and **21** the 2-pyrone **14** is also formed, the formation of which can be explained by isomerization of the allene to give 1-propyne and by the subsequent reaction of this substrate with CO_2 [103]. In addition, 6 oligomerization products of allene are formed which represent the main part of the conversion products.

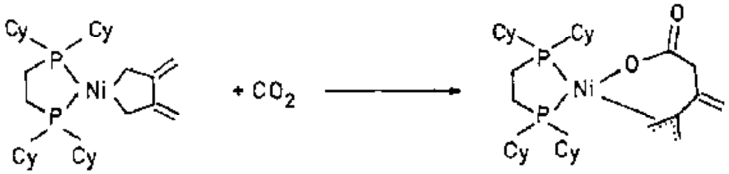
The stoichiometric conversion of allene and CO_2 (scheme XIII) can be considered as a model reaction for the CO_2 activation step [103]. Insertion of CO_2 into the Pd–C σ-bond can then take place after the dimerization of two allene units.

The direct metalaring closure reaction of allenes and CO_2 at electron-rich nickel(0) complexes which takes place in analogy with the conversion of



20 21 14

Scheme XII.



22 23

Scheme XIII.

olefins with CO_2 to give nickela five-membered ring heterocycles was reported recently. Investigation of the regioselectivity of this stoichiometric reaction has shown that a Ni–CH_2 bond is always formed when allenes of type $CH_2=C=CR^1R^2$ (R^1 : H or alkyl-, R^2 : alkyl) are used [104].

G. REVERSIBLE CO_2 CARRIERS AND CARBOXYLATION OF C–H BONDS

Investigation of the reversibility of CO_2 fixation is conducted for the following purposes: to obtain fundamental information about the relative bonding strength of CO_2 or carboxylate complexes as a function of the complex moiety and to support purposeful design of the catalysts; to find possibilities for transcarboxylation on organic substrates, especially with C–H bonds; to study models for CO_2 transfer to biological systems through CO_2 transferring enzymes.

The following basic reactions can be used for reversible CO_2 fixation:

$L_nM + CO_2 \rightleftarrows L_nM(CO_2)$ reversible coordination

$L_nM{-}X + CO_2 \rightleftarrows L_nM{-}OCO{-}X$ reversible insertion

$L_nM(A{=}B) + CO_2 \rightleftarrows L_nM{-}A{-}B{-}COO{-}$ reversible oxidative coupling (metala ring closure) *(i) Reversible CO_2 fixation through coordination*

Reversible coordination of CO_2 takes place at a number of Co, Ni, Rh and Ir complexes. A selection of these is given in Table 9. In none of the compounds, however, is the complex-fixed CO_2 active enough to be transferred to organic substrates. The complex **25**, which has been known for a long time, having side-on CO_2 coordination established by X-ray analysis, reacts at a slightly higher temperature with splitting of carbon dioxide. Intermediate products of the reaction in which the binuclear complex $(Cy_3P)_2Ni(CO)_2)Ni(PCy_3)_2$ is also formed, with olefin-analogous bonding of the bridge-forming CO_2 to give two nickel centres, were studied again recently [109]. Even in the Co complex **27** where CO_2 is bonded through a basic and an acid centre the complex-fixed CO_2 is evidently not yet sufficiently activated for transcarboxylation reactions [110–112].

(ii) Reversible insertion reactions of CO_2

Reversible insertion reactions in M–H-, M–C-, M–N- and M–O-bonds were observed in a relatively small number of compounds. Table 10 gives some new examples of these, other investigations in this field have been described [4,8,10,11].

In 1985 it was shown that zinc(II)-tetraazacycloalkane complexes bond CO_2 reversibly in the presence of bases in alcohol with formation of monoalkylcarbonatocomplexes [125]. The X-ray structure analysis of these derivatives was published [126] (Fig. 3).

Alkoxylanthanoid complexes, as well as trimethylsilylamide–lanthanoid compounds, can also bond CO_2 reversibly with insertion [127,128].

TABLE 9

Examples for the reversible coordination of CO_2 at transition metal complexes

Starting complex [a]	CO_2-carrier	Coordination	Ref.
$(Me_3P)_4Fe$	$(Me_3P)_4Fe(CO_2)$ **24**	–	[105]
$(Cy_3P)_2NiN_2$	$(Cy_3P)_2Ni(CO_2)$ **25**	Side on	[106,107] [109]
	$(Cy_3P)_2Ni_2(CO_2)$ **26**	Side on	[108,109]
Co(O–N–N–O)M^I	Co(O–N–N–O)$M^I(CO_2)$ (THF) **27**	Side on + M^I–O bonding	[110,112]
$(Ph_3P)_3RhCl$	$(Ph_3P)_3Rh(CO_2)$ **28**	Side on	[113]

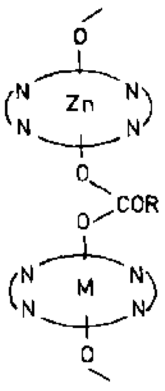
[a] O–N–N–O: Dianion of substituted salicylaldehyde-ethylendiimine ("salen"), M^I: alkali metal ions.

TABLE 10

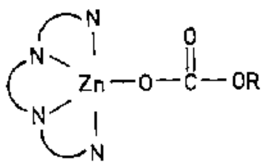
Examples for the reversible insertion of carbon dioxide into metal-element-bonds (M–E: E; H, R, OR, NR_2)

Starting complex	Insertion product	Compound no.	Ref.
trans-$H_2Pt(PCy_3)_2$	*trans*-$(H-Pt(O_2CH)(PCy_3)_2$	**29**	[114]
trans-$H_2Pt(PEt_3)_2$	*trans*-$(H-Pt(O_2CH)(PEt_3)_2$	**30**	[115]
$HM(CO)_5^-$ (Mo,W)	$HCOOM(CO)_5^-$	**31**	[116–118]
$(NC-CH_2)Cu(PBu_3)_n$	$(NC-CH_2COO)Cu(PBu_3)_n$	**32**	[119]
$(PhC{=}C)Cu(PBu_3)_n$	$(PhC{=}C-COO)Cu(PBu_3)_n$	**33**	[120]
$(MeO)_2Cu$/pyridine	$Cu(O_2COMe)_2$	**34**	[121]
$(HO)Cu(PR_3)_n$	$(HOCOO)Cu(PR_3)_n$	**35**	[122]
$Mo_2(OR)_6$	$Mo_2(OR)_4(O_2COR)_2$	**36**	[123,124]

Schiff-base–chelate complexes with Cu–O bonds likewise react with reversible insertion of CO_2 into the Cu–O bond [129] similar to the phosphine complex **35** (Table 10) in which CO_2 reacts with the Cu–OH bond [130]. The water-soluble complex **35** is able to transfer CO_2 to propylene oxide or cyclohexanone to form propylenecarbonate and the cyclohexanone-2-carboxylic acid (isolated as the methylester) [130]. Evidently the small number of examples of insertion reactions of CO_2 in M–C-bonds is due to the formation of stable metal carboxylates, the thermal decomposition of which happens at temperatures so high that the



A



B

Fig. 3. Reaction products between CO_2, ROH and zinc(1,4,8,11-tetraazacycloalkane)-complexes: A, Bis(μ-monomethylcarbonato)-tris-(1,4,8,12-tetraazacyclopentadecane)zinc(II) perchlorate; B, (μ-monomethylcarbonato)(1,4,8,11-tetraazacyclotetradecane)zinc(II)perchlorate. For principles of the structures see Kato and Ito [126].

resulting metal–organic M–R compounds are irreversibly decomposed by other reactions.

The following examples of reversible insertion reactions of CO_2 in M–C bonds are probably unique (Table 10):

$$(Bu_3P)_3Cu{-}R + CO_2 \rightleftarrows (Bu_3P)_3Cu{-}OCOR$$

(R: Ph–C≡C– and NC–CH_2–)

The resulting metal carboxylato complexes of Cu(I) are capable of reacting with certain organic substrates under CO_2 transfer. For example, the reaction of **32** with propylene oxide leads to the cyclic carbonate, cyclohexanone carboxylated in the 2-position being formed [119].

Reversible insertion of CO_2 into M–H bonds is essential for the homogeneous-catalytic hydrogenation reactions of CO_2 and plays a role also in the watergas shift reaction. A summarizing report of these investigations was compiled recently [8].

(iii) Reversible oxidative coupling reactions of CO_2 with hetero-olefins (reversible metalaring closure)

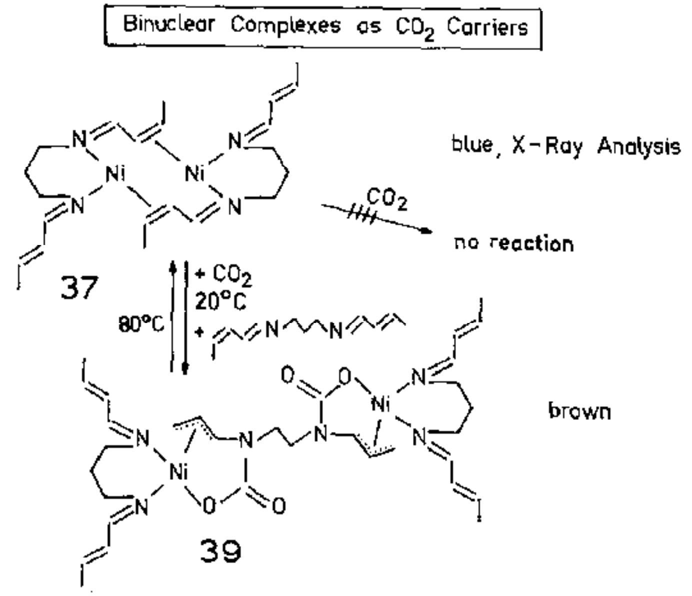
Reversible metalaring closure reactions with CO_2 and an unsaturated substrate have been observed at nickel(0) complexes with a high effective electron density, mainly when azomethines are used as substrates (Table 11). Scheme XIV illustrates the conversion of bis(cinnamaldehyde-*N*,*N*′-propylenediimine)dinickel(0)—a binuclear complex the structure of which is known [131]. Compound **37** (scheme XIV) does not react with CO_2. It is not until the addition of excess Schiff base that the conversion to give the binuclear complex **39** containing metalaheterocyclic rings with a *N*-

TABLE 11

Examples for the reversible oxidative coupling of CO_2 with unsaturated substrates at transition metal complexes (metalacycles as reversible CO_2-carriers)

Starting complex [a]	Metalacycle with CO_2	Ref.
bipyNi(PhCH=NPh)	bipyNi–O–CO–N(Ph)–CH(Ph)–	**41** [133,134]
(TMED)Ni(PhCH=NPh)	(TMED)Ni–O–CO–N(Ph)–CH(Ph)–	**40** [132]
bipyNi(PhCH=CHCH=N(Ph)	bipyNi–OCO–N(Ph)–CH=CH(Ph)–	**42** [134]
bipyNiL^1	**43**	[135]
$[L^1Ni]_2$ **37**	**39**	[135]
$[L^2Ni]_2$ **44**	**45**	[135]
$(Ph_3P)_2$Pt(ON–Ph)	$(Ph_3P)_2$Pt–OCO–N(Ph)–O–	**46** [136]

[a] L^1: Ph–CH=CH–CH=N–$(CH_2)_3$–N=CH–CH=CH–Ph. L^2: Ph–CH=CH–CH=N–$(CH_2)_2$–N=CH–CH=CH–Ph.



Scheme XIV.

carboxylate structure takes place. A typical model substance **40** was structurally determined by X-ray [132].

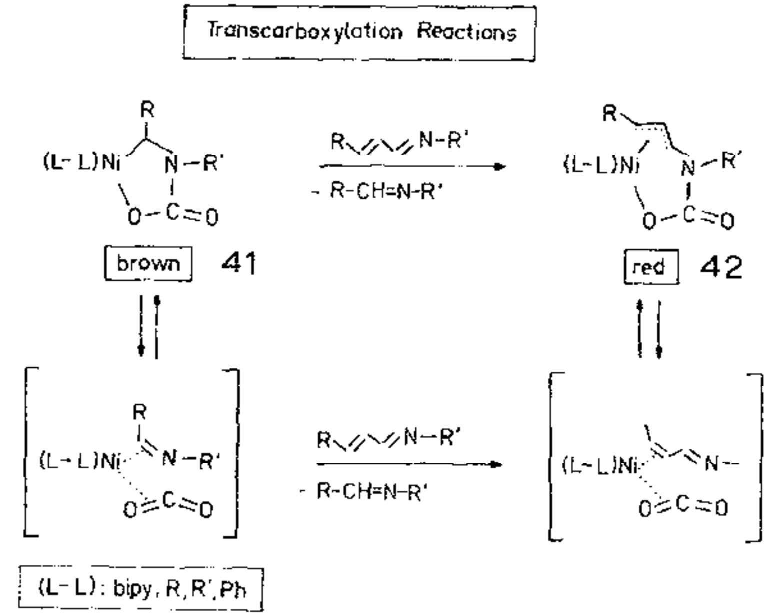
N-carboxylates are particularly interesting model compounds for biotin-containing enzymes which also bond CO_2 reversibly with formation of an *N*-carboxylate bond and can activate CO_2 for transcarboxylations.

Optical spectroscopy is an especially suitable indicator of CO_2 conversion for the reversible metalaring closure reaction (Table 11). CO_2 transfer reactions with the formation of new metalacyclic compounds can also be carried out when nickelaheterocycles with *N*-carboxylate structure are used, as shown in scheme XV [137].

The complex compound $(Ph_3P)_2Pt(ON-Ph)$, in which the nitroso group is coordinated side-on, can also react with CO_2 under reversible metalaring closure (Table 11).

Transcarboxylation reactions catalyzed by certain enzymes serve as an example for the CO_2 transfer of CO_2-fixing metal complexes. Scheme XVI demonstrates for example a biotin-dependent enzyme, whose function requires magnesium or manganese ions. The role of these metal atoms is unclear.

CO_2 transfer reactions using alkali alcoholate complexes have been used preparatively and technically for a long time ("Kolbe–Schmitt synthesis" and similar reactions); activated aromatics can be changed into aromatic carboxylic acids in this way [11].

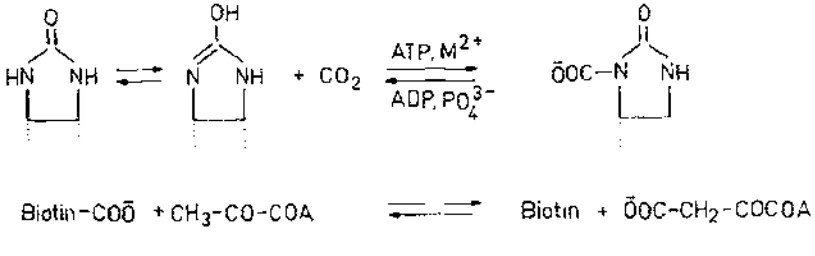


Scheme XV.

Recently the complex compound $(CH_3OCOO)_2Mg$, easily accessible from magnesium methylate and CO_2, was used as a CO_2 carrier for organic substrates with acidic C–H bonds [138–141].

Matsamura investigated new carboxylation reactions with C–H bonds using magnesium complexes of cyclic urea and thiourea, which are capable of fixing CO_2 by insertion into the Mg–N bond and of transferring it to ketones with formation of α-ketocarboxylic acids [142–145].

1,4-Diazadiene metal complexes with central atoms in formally low oxidation states are interesting biotin models [146]. Table 12 shows that only compounds with relatively polar M–N bonds react with CO_2. Of the CO_2-fixing systems only complexes with magnesium and manganese **48** and **49** (Table 12) are also capable of transferring CO_2 to compounds with active



Scheme XVI.

TABLE 12

Reaction of 1,4-diazadiene complexes with CO_2 with formation of *N*-carboxylates and the transcarboxylation reaction (insertion into the C–H Bond of $PhCOCH_3$ [a])

Starting complex [b]	No.	Reaction with CO_2 (A)	Reaction of the benzophenone (B)
Na_2(dad)	**47**	*N*-carboxylate	No reaction
Mg(dad)$(THF)_2$	**48**	*N*-carboxylate	Transcarboxylation
Mn(dad)$(solv)_2$	**49**	*N*-carboxylate	Transcarboxylation
Ni$(dad)_2$	**50**	No reaction	–
Fe$(dad)_2$	**51**	No reaction	–
Co$(dad)_2$	**52**	No reaction	–
Cp_2Ti(dad)	**53**	No reaction	–

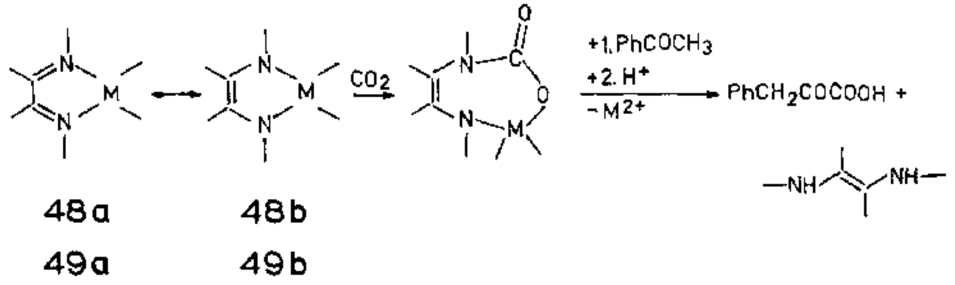
[a] Ref. 147. [b] dad, benzil-bis-*N*-phenylimine. Reaction conditions: A; THF, 20 °C. B; DMF, 90 °C.

C–H bonds—an interesting analogy to enzymatic transcarboxylation reactions. Schemes XVII and XVIII refer to the reaction sequence [146].

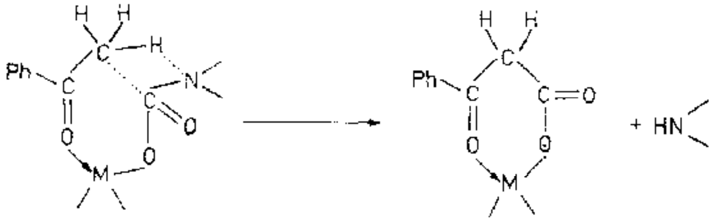
It is believed that strong participation of the "endiamide" structure in the totality of possible resonance structures which allow a smooth insertion reaction of CO_2 into the M–N bond is responsible for the fact that only Mg- and Mn-1,4-diazadiene complexes fix CO_2 and are capable of transfer. Coordinative fixation of acetophenone to the free coordination sites of the *N*-carboxylato complexes then allows activation of the C–H bond in the organic substrate with formation of benzoylacetate in the immediate coordination sphere of the central atom (scheme XVIII).

The $[Fe(OCO_2C_2H_5)(OC_2H_5)_2]$ compound can also transfer CO_2 to compounds with active C–H bonds although the yields of this CO_2 transfer reaction are relatively low [147].

New interesting possibilities could be achieved by transition metal catalyzed carboxylation of non-activated aromatics through palladium(0) complexes, described not long ago [148]. Table 13 shows that, under the reaction



Scheme XVII.



Scheme XVIII.

conditions studied hitherto, the conversion numbers are too low to be preparatively useful.

The formation of acrylic acid from ethylene and CO_2 was observed at molybdenum and tungsten complexes [149]. Evidently this reaction which occurs formally according to

$$CH_2{=}CH_2 + CO_2 \rightarrow CH_2{=}CH{-}COOH$$

is rendered possible through activation of both substrates at two metal centres. Figure **4** shows the structure of one of the reaction products formed (compound **54**). This conversion possibly models the initiating step for a catalytic acrylic acid synthesis which of course cannot yet be implemented. 1,3-Dienes can also react in the same way with CO_2 under C–H activation. In this case the C_5O chains at electron-rich nickel(0) centres (described in Section B) are first built up with oxidative coupling of the two substrates. These chains react either with maleic anhydride [77] or with a strongly acidic 1,4-diazadiene under reductive elimination of the organic system with H-shift (C–H → O–H) (scheme XIX). When benzil-bis-*N*-phenylimine is used as a diazadiene ligand, the bis-diazadienenickel(0) complex **50** can be isolated as

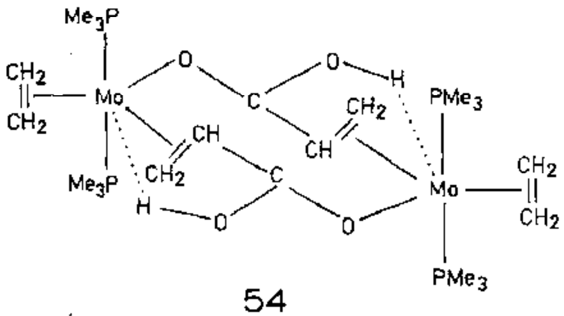
TABLE 13

Reaction of aromatic compounds with CO_2 at palladium complexes [a,b]

No.	Complex	Aromatic substrate	Carboxylic acid	Yield (%)
1	$Pd(ac)_2$	Anisole	Methoxybenzoic acid	13
2	$Pd(ac)_2$	Benzene	Benzoic acid	13
3	$Pd(NO_3)_2$	Benzene	Benzoic acid	66
4	$Pd(ac)_2$	Benzene	Benzoic acid	127
5	$Pd(ac)_2$	Anisole	Methoxybenzoic acid	128
6	$Pd(ac)_2$	Chlorobenzene	Chlorobenzoic acid	40

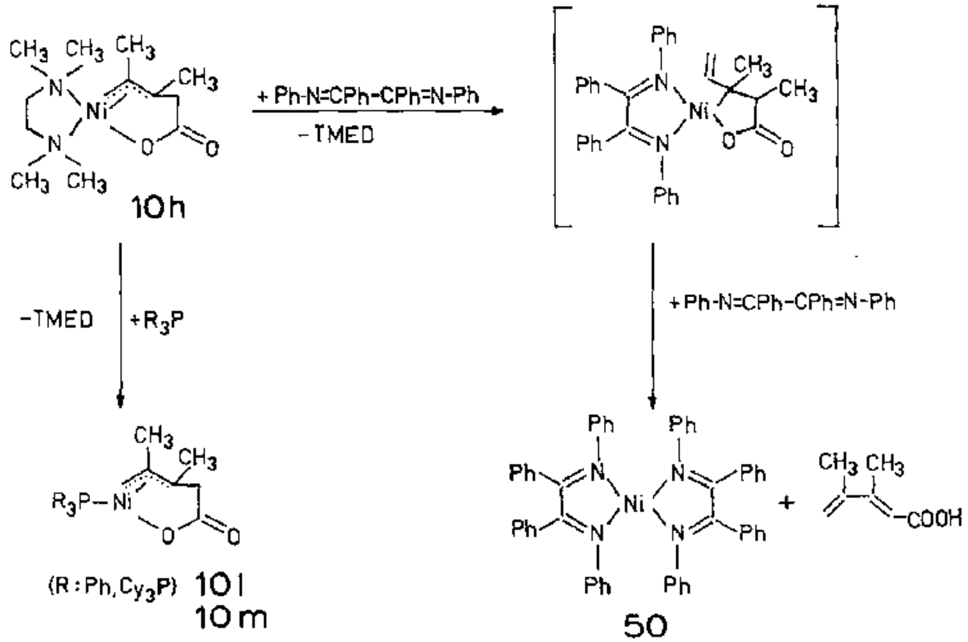
[a] Ref. 148.

[b] Reaction conditions: **1–3**; 150 °C, 20 h, 1 mmol Pd complex, 20 ml aromatic compound, 30 atm CO_2. **4–6**; 70 °C, 3 d, 1 mmol Pd complex, 16 ml aromatic compound, 1 atm CO_2, t-BuCOOH (8 mmol), 4 ml acetic acid. (Yield: 100% = 1 mmol.)



54

Fig. 4. Structure of the reaction product between CO_2 and $(C_2H_4)_2Mo(PMe_3)_4$ (compound 54) [149].



Scheme XIX.

the only metal-containing final product of the reaction [150]. Scheme XIX shows the probable reaction sequence of the carboxylation reaction of dimethylbutadiene formally according to

$$CH_2{=}C(Me){-}C(Me){=}CH_2 + CO_2 \rightarrow CH_2{=}C(Me){-}C(Me){=}CH{-}COOH$$

H. NEW RESULTS OF CO_2 ACTIVATION AT TRANSITION METAL COMPLEXES

(i) Mechanistic studies of CO_2 insertion

Comparative studies of carbonylation and carboxylation of organothorium complexes of the type $Cp_3Th{-}R$ (R: i-propyl-, sec-butyl-n-butyl-, methyl-, benzyl-) show that CO_2 insertion proceeds significantly slower than that of CO. A factor of 10^5 was found for the isopropyl compound and a factor of 50 for the methyl complex. These data reveal the much higher steric sensitivity of the carboxylation reaction and are in agreement with a concerted insertion mechanism [151].

In-depth studies of the mechanism of CO_2 insertion into W–C bonds of anionic alkyl or aryl-carbonyl compounds (Darensbourg) show that the reaction

$$[\textit{cis}\text{-R–W(CO)}_4\text{L}]^- + CO_2 \rightarrow \underset{\mathbf{55}}{[\textit{cis}\text{-R–COO–W(CO)}_4\text{L}]}$$

is of first order both with regard to the complex compound and CO_2. The relative rate increases relatively slightly in the sequence Ph (1) < Et (3,8) < Me (6), whereas the influence of ligands L is high

$$\underset{1}{CO} < \underset{57.8}{P(OMe)_3} < \underset{243}{PMe_3}$$

The insertion rate increases with increasing electron density at the central atom [152].

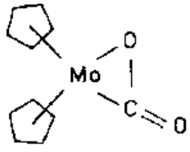
The activation parameters of the insertion reaction ($\Delta H^{\neq} = 42.7$ kJ mol^{-1}, $\Delta S^{\neq} = -181.2$ J mol^{-1} K^{-1}) suggest that there exists an ionic associative mechanism (I_A).

In accordance with this mechanism the insertion rate of CO_2 into analogous chromium complexes is six times less because the smaller central atom has a smaller tendency to increase its coordination number. Comparison with the rate of CO insertion into the same anionic tungsten complexes is interesting. In that case high influence of the R moiety and a low effect of the ligand can be observed.

Stereochemical investigation by means of ^1H NMR spectroscopy shows that the configuration is maintained upon insertion of CO_2 into *threo*-$[L(OC)_4W\text{–CHD–CHD–Ph}]^-$ (L: Co, PMe_3). This also applies to the carbonylation reaction with CO, suggesting a similar concerted mechanism [153].

(ii) Applications of the concept of bifunctional CO_2 activation

The importance of Floriani's fundamental studies of the bifunctional CO_2 activation through basic and acid metal centres (the prototype being the coordination of CO_2 at cobalt-salen complexes (Table 9)) was emphasized again recently. For instance Floriani showed that in a new CO_2 complex of molybdenocene $Cp_2Mo(CO_2)$ **56**, the structure of which is shown in Fig. 5, an interaction exists between the oxygen atom of CO_2 and one H atom of a



56

Fig. 5. Structure of the complex $Cp_2Mo(CO)_2$ **56**. Mo–O: 2.160(7) Å, Mo–C: 2.112(11) Å, C–O: 1.288(14) Å [154].

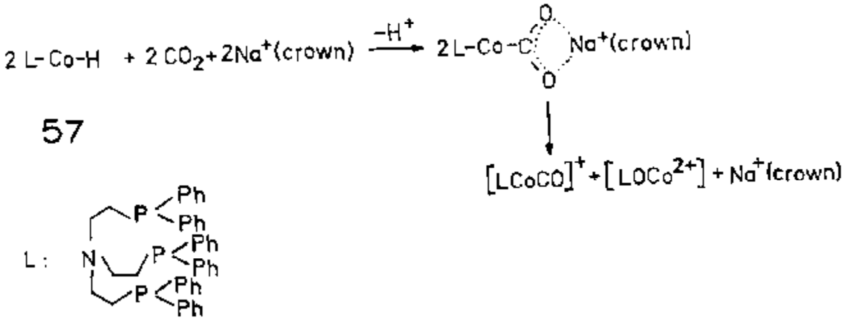
ligand ("acid interaction") in addition to bonding of CO_2 to the $Cp_2Mo(II)$ centre [154].

The complex compound is produced according to

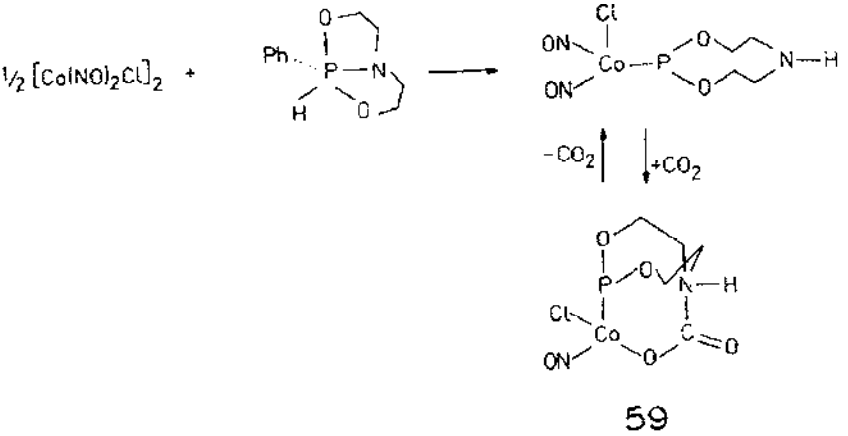
$$Cp_2Mo(tolane) + CO_2 \rightarrow \underset{\mathbf{56}}{Cp_2Mo(CO_2)} + tolane$$

and is worth mentioning because it also contains the robust, phosphine-free fragment Cp_2Mo which is believed to be susceptible to other interesting conversions. In complexes of type **57** (scheme XX) CO_2 is only activated if acid metal centres are additionally offered. "Reductive disproportionation", indicated in scheme XX, takes place after the addition of $NaBPh_4$/crown, whereas CO_2 cannot react with **57** alone [155].

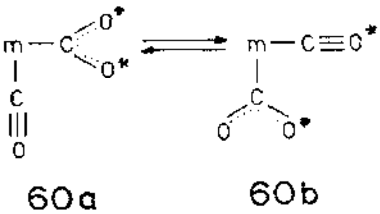
A bimolecular activation of CO_2 through basic and acid centres is also the basis of the reaction of Fp_2Mg with CO_2 (Fp: $CpFe(CO)_2$ fragment) which leads to carboxylate **58** (scheme XXIII). CO_2 is smoothly methylated with trifluoromethyl sulphonic acid [156]. Recently Aresta et al. described a bifunctional activation of CO_2 with formation of a carbamato complex **59** with Co as the central atom (scheme XXII). This complex can act as a reversible CO_2 carrier [157].



Scheme XX.



Scheme XXI.



Scheme XXII.

(iii) Various reactions

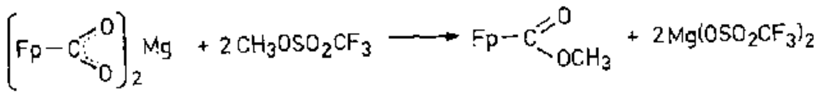
Oxygen transfer reactions of CO_2 at transition metal centres are important as initiating steps for reduction reactions of CO_2 by means of heterogeneous or homogeneous metal catalysts and as a potential synthetic way of transferring oxygen in the course of a catalytic reaction to an organic substrate. Last but not least, many inactivation reactions of homogeneous-catalytic systems are obviously attributable to oxygen transfer reactions of the following type

$$2CO_2 + M(0) \rightarrow M(II) + CO_3^{2-} + CO$$

("reductive disproportionation").

The reaction of the anionic complex $Li[FeCp(CO)_2(CO_2)]$ **60** shows how unstably oxygen can be bonded in coordinated CO_2. A rapid intramolecular O-transfer takes place even at −20 °C, as illustrated in scheme XXII [158].

A way to novel metallacycles is opened up by the reaction of the first anionic carbine complexes with CO_2 (scheme XXIV), described by Fischer, which leads to the structurally clarified binuclear chelate complex **62** [159].

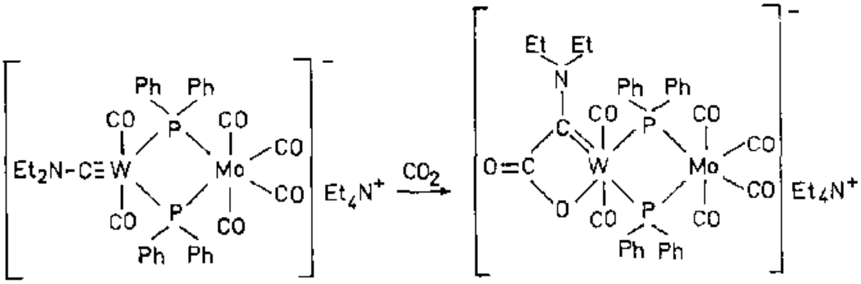


58 58

Scheme XXIII.

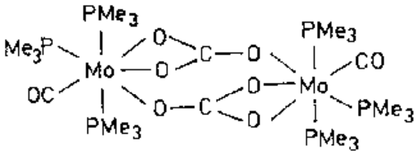
The reaction of *cis*-$[(Me_3P)_4Mo(N_2)]$ with carbon dioxide yields a number of interesting complex compounds [160]. Apart from products of "reductive disproportionation" such as the carbonato complexes (**63** and **64**) (Fig. 6) with a novel carbonate coordination (bidentate bridge-type ligand) the first stable bis-CO_2 complex of a transition metal was synthesized, *trans*-$(Me_3P)_4Mo(CO_2)_2$; the ^{31}P and ^{13}C NMR spectra prove the *trans*-structure of the compound [161]. In these complexes CO_2 is not displaced by ethylene or nitrogen. The compound $(Me_3P)_3$(i-propNC)$Mo(CO_2)_2$ **65** the structure of which was determined by X-ray analysis [162] could be produced by reaction with isopropyl isonitrile. Figure 7 shows that CO_2 is bonded like an olefin in the *trans* arrangement. The coordinated CO_2 units are oriented staggered, the short Mo–C and Mo–O bonds support the strong bonding to the central atom.

While the linkage of two CO_2 units at transition metal centres obviously leads only to head-to-tail linkage in the course of normal oxidative coupling (two-electron transfer) (the linkage $\overline{\text{M–O–CO–OCO-}}$ for instance was found in an Ir complex through X-ray structure analysis [163]), succeeding reactions often occur with "reductive disproportionation" to give CO and CO_3^{2-}. Recently it was found that head-to-head linkage to oxalate may

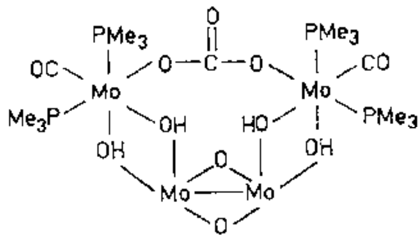


60 62

Scheme XXIV.



63



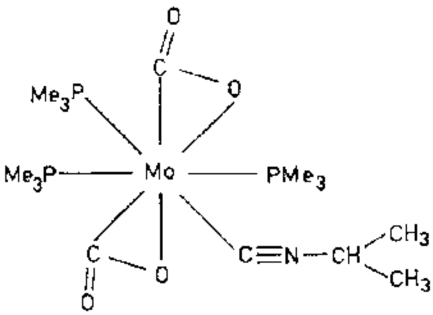
64

Fig. 6. Structure of the carboxylate complexes **63** and **64** [160].

happen at Ti(III) complexes when special parent compounds are used which force one-electron steps [164]

$$2Cp_2Ti–CH_2(CH_2)_2N(R)–(CH_2)_2–N(R)–(CH_2)_2CH_2–TiCp_2 + 6CO_2 \rightarrow$$
$$2Cp_2Ti(OOC–(CH_2)_3N(R)–(CH_2)_2N(R)(CH_2)_3COO)TiCp_2$$
$$+ Cp_2TiOOC–COOTiCp_2$$

Ab initio calculations for the complex compounds $(H_3P)_2Ni(0)$ and $(H_3P)_2Cu(I)$ show how important electrostatic and bonding effects may be for this type of CO_2 coordination. While the stable coordination form in the electron-rich nickel(0) compound is the olefin-like bond, the end-on bond (with oxygen as the donor atom) becomes the stable coordination form in



65

Fig. 7. Structures of the bis-CO_2-complex **65**, Mo–O: 2.160(7) Å, Mo–C: 2.105(10), Å [165].

the case of the Cu(I)complex on account of the overwhelming influence of electrostatic effects [165]. Hoffmann et al. conducted comparative studies of CS_2 and CO_2 coordination by means of EHT and they calculated the reaction modes which lead to the coordination of these substrates [166]. These calculations indicate clear results for CS_2. However those for CO_2 are ambiguous.

I. CONCLUSIONS

Carbon dioxide chemistry at transition metal centres has led towards attractive applications in the field of homogeneous-catalytic co-oligomerizations during the short period of its development. A thorough analysis of the present trends and of the rate of development justifies the following statements on future directions.

(i) Purposeful catalyst design will lead to a further increase in the selectivity and activity of homogeneous-catalytic co-oligomerization reactions and thus open up other fields of application for the synthesis of lactones, acids and esters.

(ii) Application of 3*d*-metals as the central atoms of new catalytic systems permits the range of potentially available catalysts to be expanded so that new synthesis products become possible.

(iii) Because simple substrates such as acetylene and ethylene hitherto were only seldom used in catalytic co-oligomerizations and as such the reactions were not attempted with highly sophisticated unsaturated substrates, it is clear that there exists a vast unexplored field which is attractive both fundamentally and for its application in synthesis.

(iv) It is likely that new reversible CO_2 carriers and transcarboxylation reactions will be investigated in the future, be it for the purpose of a better understanding of the biological reactions or for preparative considerations. A catalytic carboxylation of C–H compounds would be highly attractive in the eyes of a synthetic chemist—a problem hitherto unresolved.

(v) Today, the theory and especially a mechanistic understanding of the activation reactions of carbon dioxide at transition metal centres has not been sufficiently developed. It can be assumed that more attention will be devoted to this important aspect of fundamental research in the future and that new impetus will be given for catalytic and metal-centred CO_2 activation reactions.

REFERENCES

1 M.E. Vol'pin, Z. Chem., 12 (1972) 361.
2 M.E. Vol'pin and I. Kolomnikov, Organomet. React., 5 (1975) 313.

3 R. Ziessel, Nouv. J. Chem., 7 (1983) 613.
4 R. Eisenberg and D.E. Hendriksen, Adv. Catal., 28 (1979) 79.
5 R.P.A. Sneeden, Actual. Chim., (1979) 22.
6 D. Walther, E. Dinjus and J. Sieler, Z. Chem., 23 (1983) 237.
7 B. Denise and R.P.A. Sneeden, Chem. Tech., 12 (1982) 108.
8 D.I. Darensbourg and R.A. Kudraroski, Adv. Organomet. Chem., 22 (1983) 129.
9 A. Behr, Chem.-Ing. Tech., 57 (1985) 893.
10 D.A. Palme and R. van Eldik, Chem. Rev. 83 (1983) 651.
11 S. Inoue and N. Yamazaki, Eds, Organic and Bio-organic Chemistry of Carbon Dioxide, Kodansha, John Wiley, New York, 1982.
12 R.P.A. Sneeden in G. Wilkinson, F.G.A. Stone and E. Abel (Eds.) Comprehensive Organometal. Chem., Vol 8, Pergamon, New York, 1982, pp. 225.
13 A. Behr in W. Keim (Ed.), Catalysis in C_1 Chemistry. D. Reidel, Dordrecht, 1983, pp. 169–218.
14 A.L. Lapidus, Y.Y. Ping, Russ. Chem. Rev. (Engl. Transl.), 22 (1981) 50, 63
15 J. Hawecker, J.M. Lehn and R. Ziessel, J. Chem. Soc., Chem. Commun., (1983) 536.
16 J.-M. Lehn and R. Ziessel, Proc. Natl. Acad. Sci. U.S.A., 79 (1982) 701.
17 J. Hawecker, J.-M. Lehn and R. Ziessel, Nouv. J. Chem., 7 (1983) 271
18 N. Kitamura and S. Tazuke, Chem. Lett., (1983) 1109.
19 J. Hawecker, J.-M. Lehn and R. Ziessel J. Chem. Soc., Chem. Commun., (1985) 56.
20 S. Meshitsuka, M. Ichikawa and K. Tamaru, J. Chem. Soc., Chem. Commun., (1974) 158.
21 K. Hiratsuka, K. Takahashi, H. Sasaki and S. Tashima, Chem. Lett., (1977) 1137.
22 K. Takahashi, K. Hiratsuka, H. Sasaki and S. Toshima, Chem. Lett., (1979) 305.
23 B. Fischer and R. Eisenberg, J. Am. Chem. Soc., 102 (1980) 7361.
24 M. Tezuka, T. Yajima, A. Tsuchiya, Y. Uchida and M. Hidai, J. Am. Chem. Soc., 104 (1982) 6836.
25 J. Hawecker, J.-M. Lehn and R. Ziessel, J. Chem. Soc., Chem. Commun., (1984) 328.
26 T.R. O'Tod, L.D. Margerum, T.D. Westmoreland, W.I. Vining, R.W. Murray and T.I. Meyer, J. Chem. Soc., (1985) 1416.
27 J.Y. Becker, B. Vainas, R. Eker, L. Kaufman, J. Chem. Soc., (1985) 1471.
28 K. Ogura, I. Yoshida, J. Mol. Catal., 34 (1986) 67.
29 Jpn. Kokai Tokkyo Koho JP 81166 (1981) Teijn Ltd.
30 Jpn. Kokai Tokkyo Koho JP 81140948 (1981) Teijn Ltd.
31 K. Kudo, N. Sugita, Y. Takezaki, Nippon Kagaku Kaishi, (1977) 302.
32 Eur. Pat. Appl. EP 95321 (1983), British Petroleum Co.
33 Eur. Pat. Appl. EP 151510 (1984), British Petroleum Chemicals.
34 Y. Inoue, H. Izumida, Y. Sasaki, H. Hashimoto, Chem. Lett., (1976) 863.
35 B. Beguin, B. Denise and R.P.A. Sneeden, J. Organomet. Chem., 208 (1981) C18
36 P. Haynes, L.H. Slaugh and J.F. Kohnle, Tetrahedron Lett., (1970) 365.
37 J.S. Kolomnikov, T.S. Lobeeva, M.E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 2329.
38 K. Kudo, M. Phala, N. Sugita and Y. Takezaki, Chem. Lett., (1977) 1495.
39 H. Inoue, Y. Sasaki, H. Hashimoto and H. Izumida, J. Chem. Soc., Chem. Commun., (1975) 718.
40 R.J. Darensbourg and C. Ovalles, J. Am. Chem. Soc., 106 (1984) 3750.
41 Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, Chem. Lett., (1976) 863.
42 B. Denise and R.P.A. Sneeden, J. Organomet. Chem., 221 (1981) 111.
43 G.O. Evans and C.I. Newell, Inorg. Chim. Acta, 31 (1978) L 387.
44 M.R. Ratzenhofer and H. Kisch, Angew. Chem., 92 (1980) 303.

45 G.E. Backwall, O. Karlsohn and G.O. Ljungreen, Tetrahedron Lett. (1980) 4985.
46 R.I. de Pasquale, J. Chem. Soc., Chem. Commun., (1973) 157.
47 T. Tsuda, Y. Chujo and T. Saegusa, J. Chem. Soc., Chem. Commun., (1976) 415.
48 Jpn. Pat. 7226786 (1972) Mitsui Petrochemicals Industries.
49 E. Tsuchida and M. Kasai, Makromol. Chem., 181 (1980) 1613.
50 A. Rokicki and W. Kuran, Makromol. Chem., 180 (1979) 2153.
51 K. Soga, K. Hyakkoku and S. Ikeda, Makromol. Chem., 179 (1978) 2837.
52 K. Soga, K. Uenisha, S. Hosoda and S. Ikeda, Makromol. Chem., 178 (1977) 893.
53 S. Inoue, Chem. Tech., (1976) 588.
54 S. Inoue, H. Koinuma and T. Tsuruta, Makromol. Chem., 130 (1969) 210.
55 K. Soga, K. Hyakkoku and S. Ikeda, Makromol. Chem., 179 (1978) 2837.
56 W. Kuran, S. Pasynkiewicz and J. Skupinska, Makromol. Chem., 181 (1980) 1613.
57 Y. Inoue, Y. Itoh, H. Kazama and H. Hashimoto, Bull. Chem. Soc. Jpn., 53 (1980) 3329.
58 Y. Sasaki, Y. Inoue and H. Hashimoto, J. Chem. Soc., Chem. Commun., (1976) 605.
59 A. Musco, J. Mol. Catal., 1 (1975/76) 443.
60 A. Musco, C. Perego and V. Tartari, Inorg. Chim. Acta, 28 (1978) L 147.
61 A. Musco, J. Chem. Soc., Perkin Trans. I, (1980) 693.
62 A. Behr, K.-D. Juszak and W. Keim, Synthesis, (1983) 574.
63 A. Behr and K.-D. Juszak, J. Organomet. Chem., 255 (1983) 263.
64 A. Behr, R. He, K.-D. Juszak, C. Krüger and Y.-H. Tsay, Chem. Ber., 119 (1986) 991.
65 C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2953.
66 T. Itoh, Y. Kindaichi and Y. Takani, Nippon Kagaku Kaishi, 9 (1979) 1276.
67 Y. Inoue, R. Ohashi, M. Toyofuku and H. Hashimoto, Nippon Kagaku Kaishi, 3 (1985) 533; Chem. Abstr. 103 (1985) 215117.
68 Y. Inoue, S. Sekiya, Y. Sasaki and H. Hashimoto, Yuki Gosei Kagaku Kyokai Shi, 36 (1978) 328.
69 A. Behr and R. He, J. Organomet. Chem., 276 (1984) C 69.
70 A. Doehring, P.W. Jolly, R. Mynott, K.-P. Schick and G. Wilke, Z. Naturforsch., Teil B, 36 (1981) 1198.
71 P.W. Jolly, S. Stobbe, G. Wilke, R. Goddard, C. Krueger, Y.-H. Tsay and J.C. Sekutowski, Angew. Chem., 90 (1978) 144.
72 D. Walther and E. Dinjus, Z. Chem., 22 (1982) 228.
73 E. Dinjus, D. Walther and H. Schütz, Z. Chem., 23 (1983) 303.
74 H. Hoberg and B. Apotecher, J. Organomet. Chem., 270 (1984) C 15
75 H. Hoberg, D. Schaefer and B.W. Oster J. Organomet. Chem., 266 (1984) 313.
76 D. Walther, E. Dinjus, J. Sieler, N.N. Tanh, W. Schade and J. Leban, Z. Naturforsch., Teil B, 38 (1983) 835.
77 H. Hoberg and D. Schaefer, J. Organomet. Chem., 255 (1983) C 15.
78 D. Walther, E. Dinjus, H. Goerls, J. Sieler, O. Lindqvist and L. Andersen, J. Organomet. Chem., 286 (1985) 103.
79 A.L. Lapidus, S.D. Pirzhkov and A.A. Koryakin, Bull. Acad. Sci. USSR, Div. Chem. Sci., (1978) 2513.
80 S. Besecke and G. Schroeder, Ger. Offen. DE 2.948.888 (1981).
81 R. Alvarez, E. Carmona, D.J. Cole-Hamilton, A. Galindo, E. Gutie'rez-Puebla, A. Monge, M.L. Poveda and C. Ruiz, J. Am. Chem. Soc., 107 (1985) 5529.
82 H. Hoberg and D. Schaefer, J. Organomet. Chem., 251 (1983) C 51.
83 H. Hoberg, D. Schaefer, G. Burkhart and M.J. Romao, J. Organomet. Chem., 266 (1984) 203.
84 D. Walther, E. Dinjus, J. Sieler, L. Andersen and O. Lindqvist, J. Organomet. Chem., 276 (1984) 99.

85 E. Dinjus, D. Walther and H. Schuetz, Z. Chem., 23 (1983) 408.
86 A. Behr and G. Thelen, C_1-Mol. Chem., 2 (1984) 137.
87 A.S. Cohen and E.J. Bercaw, Organometallics, 4 (1985) 1006.
88 Y. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., (1978) 633.
89 Y. Inoue, Y. Itoh, H. Kazama and H. Hashimoto, Bull. Chem. Soc. Jpn., 53 (1980) 3329.
90 D. Walther, E. Dinjus and J. Sieler, J. Organomet. Chem. (in press).
91 P. Albano and M. Aresta, J. Organomet. Chem., 190 (1980) 243.
92 G. Burkhart and H. Hoberg, Angew. Chem., 94 (1982) 75; Angew. Chem. Int. Ed. Engl., 21 (1982) 76; Angew. Chem. Suppl., (1982) 147.
93 H. Hoberg and D. Schaefer, J. Organomet. Chem., 238 (1982) 383.
94 A.S. Cohen and E.J. Bercaw, Organometallics, 4 (1985) 1006.
95 B. Demerseman, R. Mahe and P. Dixneuf, J. Chem. Soc., Chem. Commun., (1984) 1394.
96 A.M. Bennett, T.W. Hambley and N.K. Nicholas, Organometallics, (1985) 1992.
97 Y. Inoue, T. Hibi, M. Sataka and H. Hashimoto J. Chem. Soc., Chem. Commun. (1979) 982.
98 P. Binger and H.-J. Weintz, Chem. Ber., 117 (1984) 654.
99 P. Binger and H.-J. Weintz, Ger. Offen. DE 3.403.793 (1984); Chem. Abstr., 103 (1985) 215149.
100 P. Binger and A. Germer, Chem. Ber., 114 (1981) 3325.
101 T.A. Albright, J. Organomet. Chem., 198 (1980) 159.
102 D.J. Gordon, R.F. Fenske, T.N. Nanninga and B.M. Trost, J. Am. Chem. Soc., 103 (1981) 5974.
103 A. Doehring and P.W. Jolly, Tetrahedron Lett., 21 (1980) 3021.
104 H. Hoberg and B.W. Oster, J. Organomet. Chem., 266 (1984) 321.
105 H.H. Kharsch, Chem. Ber., 110 (1977) 2213.
106 M. Aresta, C.F. Nobile, V.G. Albano, E. Forni and M. Marnasie, Chem. Commun. (1975) 636.
107 M. Aresta and C.F. Nobile, J. Chem. Soc., (1977) 708.
108 P.W. Jolly, K. Jonas, C. Krueger and Y.-H. Tsay, J. Organomet. Chem., 33 (1971) 109.
109 A. Doehring, P.W. Jolly, C. Krueger and M.J. Romao, Z. Naturforsch. Teil B, 40 (1985) 484.
110 C. Floriani and C. Fachinetti, J. Chem. Soc., Chem. Commun., (1974) 615.
111 G. Fachinetti, C. Floriani and P.F. Zanazzi, J. Am. Chem. Soc., 100 (1978) 7405.
112 G. Fachinetti, C. Floriani, P.F. Zanazzi and A.R. Zanzari, Inorg. Chem., 18 (1979) 3469.
113 M. Aresta and C.F. Nobile, Inorg. Chim. Acta, 24 (1977) L 49.
114 A. Immirzi and A. Musco, Inorg. Chim. Acta, 22 (1977) L 35.
115 R.S. Paonessa and W.C. Trogler, J. Am. Chem. Soc., 104 (1982) 3529.
116 D.J. Darensbourg, A. Rokiki and M.Y. Darensbourg, J. Am. Chem. Soc., 103 (1981) 3223.
117 D.J. Darensbourg and A. Rokiki, J. Am. Chem. Soc., 104 (1982) 349.
118 S.G. Slater, R. Lusk, B.F. Schumann and M.Y. Darensbourg, Organometallics. 1 (1982) 1662.
119 T. Tsuda, Y. Chujo and T. Saegusa, J. Am. Chem. Soc., 100 (1978) 630.
120 T. Tsuda, Y. Chujo and T. Saegusa, Chem. Commun., (1975) 963.
121 T. Tsuda and T. Saegusa, Inorg. Chem., 11 (1972) 2561.
122 T. Tsuda, H. Chujo and T. Saegusa, J. Am. Chem. Soc., 102 (1980) 431.
123 M.H. Chisholm, W.W. Rueckert, F.A. Cotton and C.A. Murillo, J. Am. Chem. Soc., 99 (1977) 1652.
124 M.H. Chisholm, F.A. Cotton, M.W. Extine and W.W. Rueckert, J. Am. Chem. Soc., 100

(1978) 1727.
125 M. Kato and T. Ito, Inorg. Chem., 24 (1985) 504.
126 M. Kato and T. Ito, Inorg. Chem., 24 (1985) 509.
127 M.N. Bochkarev, E.A. Fedorova, Yu.F. Radkov, G.S. Kalinina, S.Y. Khorshev and G.A. Razuvaev, Dokl. Akad. Nauk U.S.S.R., 279 (1984) 1386.
128 M.N. Bochkarev, E.A. Fedorova, Yu.F. Radkov, S.Ya. Khorshev, G.S. Galinina and G.N. Razuvaev, J. Organomet. Chem., 258 (1983) C 29.
129 Y. Inoue, S. Ohno and H. Hashimoto, Technol. Rep. Tohoku Univ., 41 (1983) 1; Chem. Abstr., 100 (1984) 28877y.
130 T. Tsuda, Y. Chujo and T. Saegusa, J. Chem. Soc., Chem. Commun. (1976) 415.
131 D. Walther, J. Kaiser and J. Sieler, Z. Anorg. Allg. Chem., 503 (1983) 115.
132 D. Walther, E. Dinjus, J. Sieler, J. Kaiser, O. Lindqvist and L. Anderson, J. Organomet. Chem., 240 (1982) 289.
133 D. Walther and E. Dinjus, Z. Chem., 21 (1981) 416.
134 D. Walther, E. Dinjus and V. Herzog, Z. Chem., 22 (1982) 303.
135 D. Walther and V. Herzog, Z. Chem., (1987) in press.
136 S. Cenini, F. Porta, M. Pizzotti and C. Srotti, J. Chem. Soc., Dalton Trans., (1985) 163.
137 D. Walther and V. Herzog, Z. Chem., in press.
138 M. Stiles and H.L. Finkbeiner J. Am. Chem. Soc., 81 (1959) 505.
139 M. Stiles, J. Am. Chem. Soc., 81 (1959) 2598.
140 S.W. Pelletier, R.C. Chappell, P.C. Parthasarathy and N. Lewin, J. Org. Chem., 31 (1966) 1147.
141 S.N. Balasubbrahmanyam and M. Balasubramanyan, Organic Synthesis Collect., 5 (1973) 439.
142 N. Matsamura, N. Asai and S. Yoneda, J. Chem. Soc., Chem. Commun., (1983) 1487.
143 N. Matsamura, Y. Sakaguchi, T. Ohba and H. Inoue, J. Chem. Soc. Chem., Commun., (1980) 326.
144 N. Matsamura, T. Ohba, Y. Sakaguchi and H. Inoue, Bull. Chem. Soc. Jpn., 55 (1982) 3949.
145 N. Matsamura, T. Ohba and S. Yoneda, Chem. Lett., (1983) 317.
146 D. Walther, Z. Chem., (1987) in press.
147 T. Ito and Y. Takami, Chem. Lett., (1974) 1035.
148 H. Sugimoto, I. Kawata, H. Taniguchi and Y. Fujiware, J. Organomet. Chem., 266 (1984) C 44.
149 R. Alvarez, E. Carmona, D.J. Cole-Hamilton, A. Galindo, E. Gutie'rez-Puebla, A. Monge, M.L. Poveda and C. Ruiz, J. Am. Chem. Soc., 107 (1985) 5529.
150 D. Walther, E. Dinjus, H. Goerls, J. Sieler, O. Lindqvist and L. Andersen, J. Organomet. Chem., 286 (1985) 103.
151 D. Sonnenberger, E.A. Mintz and T.J. Marks, J. Am. Chem. Soc., 106 (1984) 3484.
152 D.J. Darensbourg, R.K. Hanckel, C.G. Bauch, M. Pala, D. Simmons and J.N. White, J. Am. Chem. Soc., 107 (1985) 7463.
153 D.J. Darensbourg and G. Grotsch J. Am. Chem. Soc., 107 (1985) 7473.
154 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 107 (1985) 2985.
155 C. Bianchini and A. Meli, J. Am. Chem. Soc., 106 (1984) 2698.
156 T. Forschner, K. Menard and A. Cuttler, J. Chem. Soc., Chem. Commun., (1984) 121.
157 M. Aresta, D. Baffiret-Tkatchenko, M. Bonnet, R. Faure and H. Loiseleur, J. Am. Chem. Soc., 107 (1985) 2994.
158 G.R. Lee and N.J. Cooper, Organometallics, 4 (1983) 3365.

159 E.O. Fischer, A.C. Filipou, M.G. Alt and U. Thewalt, Angew. Chem., 97 (1985) 215.
160 E. Carmona, F. Gonzales, M.L. Poveda and J. Marin J. Am. Chem. Soc., 105 (1983) 3365.
161 R. Alvarez, E. Carmona, M.L. Poveda, R. Sanchez-Delgado, J. Am. Chem. Soc., 106 (1984) 2731.
162 R. Alvarez, E. Carmona, E. Gutierrez-Puebla, J.M. Marin, A. Monge and M.L. Poveda, J. Chem. Soc., Chem. Commun., (1984) 1326
163 T. Herskovitz and J.L. Guggenberger, J. Am. Chem. Soc., 98 (1976) 1615.
164 H.-O. Froelich and H. Schreer, Z. Chem., 23 (1983) 348.
165 S. Sasaki, K. Kitaura and K. Morokuma, Inorg. Chem., 21 (1982) 760.
166 C. Mealli, R. Hoffmann and S. Stockis, Inorg. Chem., 23 (1984) 56.