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Reactions of Carbon Dioxide with Carbon–Carbon Bond Formation Catalyzed by Transition-Metal Complexes

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Contents

1. Abbreviations

acac	acetylacetonato
bipy	2,2′-bipyridine
i-Bu	isobutyl
t-Bu	*tert*-butyl
n-Bu	*n*-butyl
cdt	1,5,9-cyclododecatriene
cod	cyclooctadiene
Cp	η^5-cyclopentadienyl
Cp′	η^5-pentamethylcyclopentadienyl
Cy	cyclohexyl
DMF	dimethylformamide
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
DMSO	dimethyl sulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
hfacac	1,1,1,5,5,5-hexafluoroacetylacetonato
Me	methyl
nbd	norbornadiene
OAc	acetate
Ph	phenyl
pip	piperidine
py	pyridine
PPN	bis(triphenylphosphine)nitrogen(1+)
i-Pr	isopropyl
n-Pr	*n*-propyl
THF	tetrahydrofuran
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine

2. Introduction

The fixation of carbon dioxide by green plants using solar energy is the most important chemical process running on Earth. The total amount of CO_2 in the atmosphere and in the oceans is estimated to represent 10^{14} tons of carbon while carbonates represent 10^{16} tons of carbon.[1,2] In photosynthesis, carbon dioxide is reduced by water into carbohydrates with sunlight as the energy source.[3a] Light-induced CO_2 fixation or reduction processes are actively studied in order to use CO_2 as a one-carbon precursor of organic chemicals.[4] Furthermore, carbon dioxide has been reduced to carbon monoxide, methanol, formate, oxalate, other organic acids, and methane with homogeneous, heterogeneous, or enzymatic catalysts.[4,5] In spite of the large amount of CO_2 available, only a few processes using carbon dioxide as a raw material have been developed in the synthetic chemical industry:[3c,6] synthesis of urea by reaction with ammonia and its numerous variants, e.g., the combined synthesis of urea and glycol from CO_2, NH_3, and ethylene oxide; synthesis of salicylic acid by the Kolbe–Schmidt reaction; synthesis of terephthalic acid by the Henkel process; preparation of monomeric or polymeric carbonates; adjustment of the $CO{:}H_2$ ratio in the steam cracking of methane; and methanol production involving addition of CO_2 to the CO/H_2 mixtures. One of the major problems associated with the use of CO_2 is that, together with water, it represents a thermodynamic end product of many chemical processes (e.g., combustion of hydrocarbons). Therefore, exploitation of carbon dioxide as a source of carbon necessitates an input of energy that should however be lowered by the judicious use of metal catalysts. In a number of cases, the presence of CO_2 was shown to assist or modify the course of the catalytic reaction. But since in these reactions CO_2 is not incorporated in the product(s) and only behaves as a cocatalyst, they will not be examined here.[1,3b,d] We shall be concerned here only with systems where both oxygen atoms of CO_2 are retained in the final product(s), avoiding therefore the use of oxygen sinks required when deoxygenation of CO_2 is envisaged. Thus, carbon dioxide can be converted into useful forms of organic compounds by coupling with an organic substrate, but in order to do so, carbon dioxide and/or the organic precursors have to be activated. These aspects will be examined in the following sections.

3. Stoichiometric Reactions with Carbon–Carbon Bond Formation

Carbon dioxide has a Lewis-acid carbon and weakly Lewis basic oxygen atoms; it is therefore not surprising that it can undergo various reactions in the coordination sphere of transition-metal compounds, such as insertion into M–X bonds (X = C, H, O, or N), condensation with

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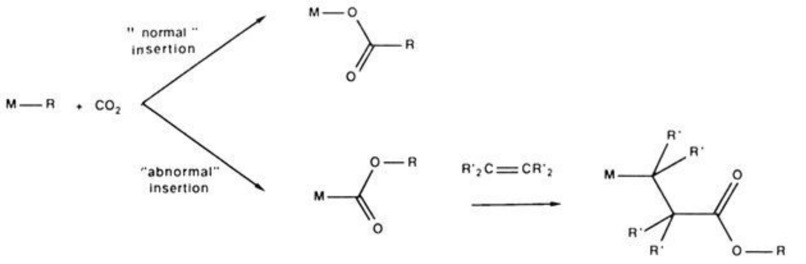
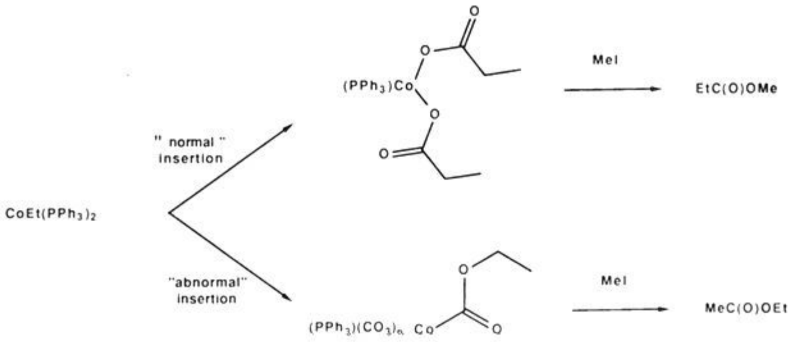
a precoordinated organic substrate, dimerization and/or reduction by the metal center. Some of these reactions have been reviewed recently.[7a-13]

Among these reactions, insertion of carbon dioxide into a metal–carbon bond is probably the most fascinating subject since it leads to carbon–carbon bond formation and potentially to further chain-lengthening processes. Thus, there are two possible pathways for this reaction, called the "normal" and the "abnormal" insertion (eq 1). There is only one example of the



(1)

so-called "abnormal" carbon dioxide insertion. Kolomnikov et al. described a reaction involving an ethylcobalt complex and carbon dioxide leading to ethyl metalloesters[7b,c] (entry 12, Table I). In this equivocal experiment, CO_2 was found to react via normal (eq 2) and abnormal (eq 3) insertion into the Co–C bond, although a different mechanism may account for the latter observation. After treatment with methyl iodide, methyl propionate and ethyl acetate were formed, respectively.



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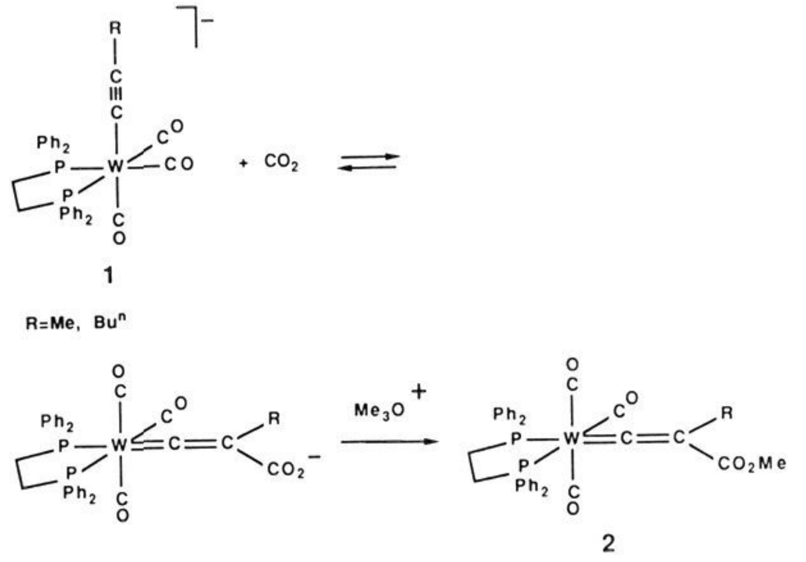
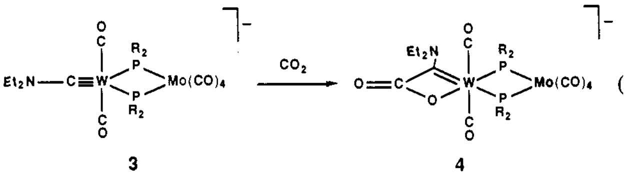
(3)

Two other unexpected reactions of carbon dioxide have been reported. The former is a rare example of C–C coupling (eq 4) where the tungsten acetylide anions **1** react with carbon dioxide with formation of the vinylidene products **2**, after methylation[14] (Table I, entry 48). The fact that C–C bond formation occurs at the β position can be understood in terms of transfer of the nucleophilicity of the C_2 fragment from C_α to C_β. Ion-pair formation at the β-carbon was suggested to act as kinetic mediator in this system, and significant counterion effects were observed in this reaction: in contrast to the Li^+ and Na^+ salts of **1**, the PPN^+ salt does not react with CO_2. Furthermore, when R = phenyl, even the lithium salt is unreactive toward CO_2.



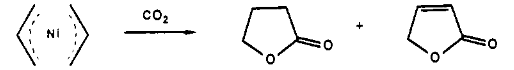
(4)

Another unusual reaction of CO_2 is that of the phosphido-bridged bimetallic anionic carbyne complex **3**, which adds 1 equiv of CO_2, affording the new oxatungstacyclobutanone complex **4**[15] (eq 5) (Table I, entry 49).



3 4 (5)

In all other cases, normal insertion takes place (see Table I). This reaction has been described for many complexes, particularly of nickel and palladium, which are known to be the most active CO_2–substrate coupling catalysts. Carbon dioxide insertion into allylic metal complexes can lead to several types of products, such as carboxylato species or lactones (eq 6–9), depending on the nature of the metal and of its ligands.



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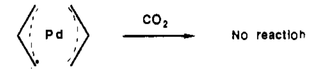

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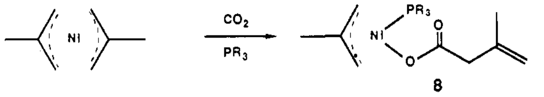

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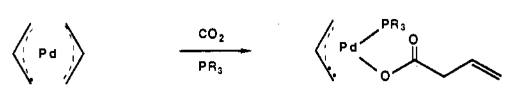

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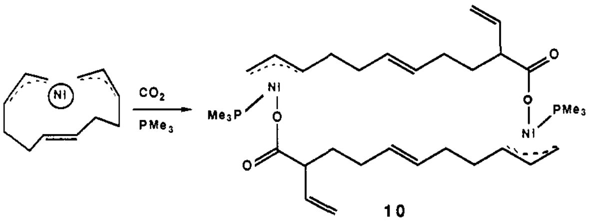

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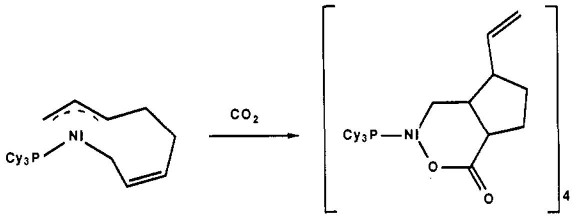

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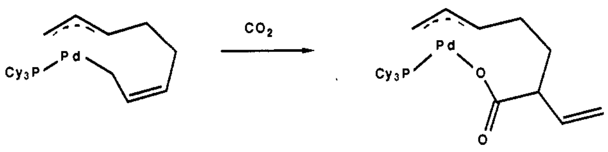
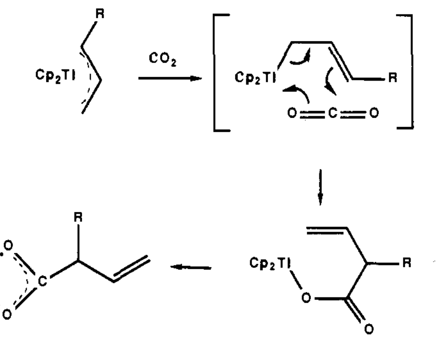
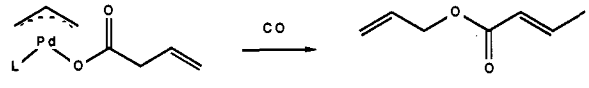


12 (12)

In the absence of tertiary phosphine ligands the bis(η^3-allyl)nickel complex **5** reacts with CO_2 to form the γ-butyrolactone **6** and the furanone **7** (eq 6).[50] Nickel or palladium carboxylato complexes may be isolated when a phosphine is present (eq 8–12). In the reaction of allyltitanium complexes with CO_2, Teuben et al. have suggested the following electrocyclic mechanism (Table I, entry 35):[47b]



The study of systems in which η^1- and η^3-allyl fragments are present allows to suggest that CO_2 inserts only into the metal–carbon σ-bond of the η^1-allyl ligand. The carboxylato ligand formed can be displaced by carbon monoxide in a reductive coupling reaction with the remaining allyl group, eliminating an ester (eq 13)[53] or a lactone (eq 14).[92a]



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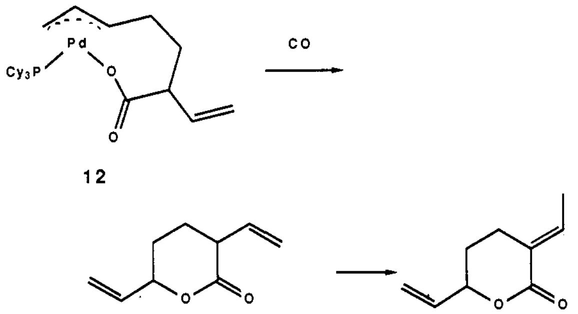
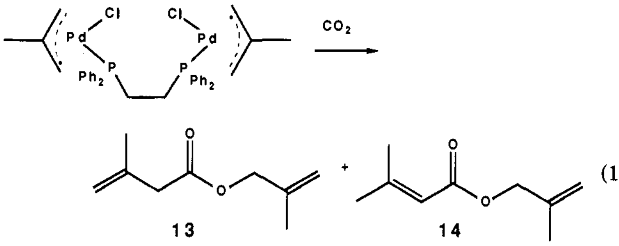


12 (14)

When bis(2-methylallyl)bis(diphenylphosphino)ethane)dipalladium complexes are reacted with CO_2, in acetonitrile at 80 °C, the esters **13** and **14** are formed in 30% and 15% yields, respectively (eq 15).[54] The (η^1-allyl)palladium complex **15** was proposed to be the intermediate in this reaction, consistent with the fact that the palladium carboxylate **16** is formed in 60% yield in the presence of an equimolar amount of dppe. Addition of (η^3-2-methylallyl)palladium chloride to **16** leads to the intermolecular formation of esters **13** and **14**. With (μ-1-3-η:6-8-η-octadienato)bis((1,1,1,5,5,5-hexafluoroacetylacetonato)palladium), **17**, another binuclear palladium complex, a 3,8-nonadienoic acid is isolated after acidification (eq 16).[55] In the former case both allyl groups participate in the CO_2 coupling re-



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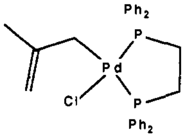

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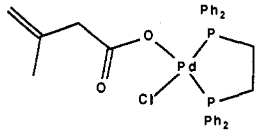

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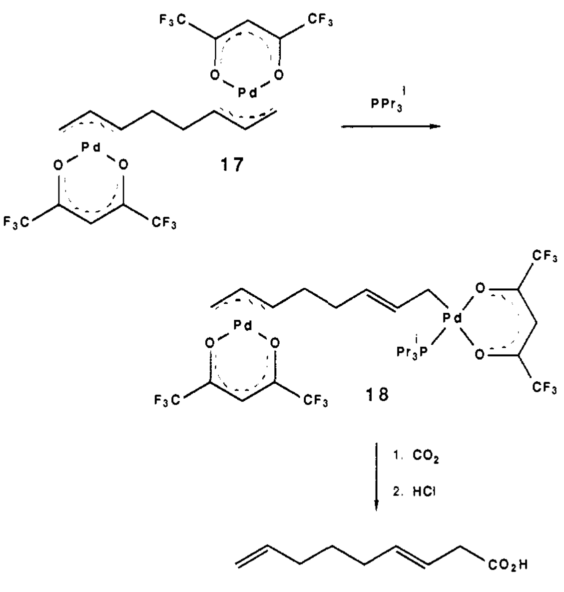
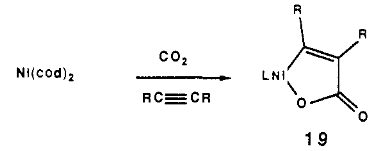


(16)

action whereas in the latter, only the allyl group coordinated to the palladium center bearing the phosphine ligand in **18** couples with CO_2. This can be related to the previous observations that CO_2 inserts only in a η^1-bonded allyl group.

Very interesting results have been published recently on the coupling reactions between alkynes (eq 17) (Table I, entry 50),[57] alkenes,[61] conjugated dienes[62–67a,b] or cumulenes,[68] and CO_2 on Ni(0) centers. No intermediate, such as a Ni–CO_2 complex, could be observed in the formation of the five-membered oxanickelacycles of type **19**. With alkenes, carbon–carbon bond formation was found to be sometimes reversible (eq 18).[61c]



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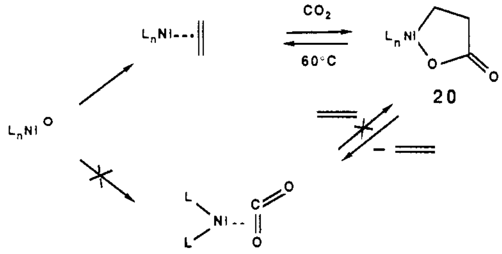

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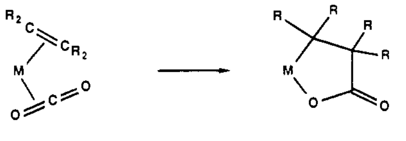
More generally, many metal-mediated reactions of CO_2 with unsaturated substrates may be rationalized in terms of electrocyclic transformations (eq 19, 20).[52]



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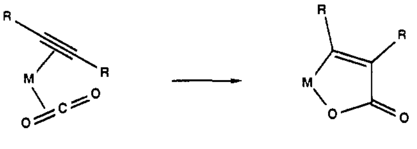
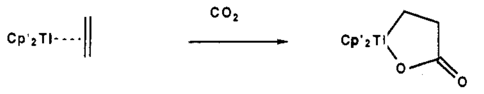


(20)

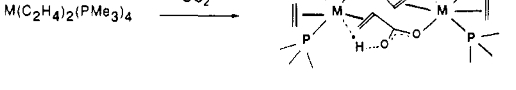
This may extend to coupling reactions of CO_2 with, e.g., aldehydes[65a,b] or imines,[65c] which lead to C–N or C–O bond formation, respectively (outside the scope of this review).

A complex of type **20** has been isolated recently for the first time and characterized by X-ray diffraction.[61f] In contrast to the titanium analogue **21** (eq 21) (Table I, entry 53a),[59a] **20** was found to react further with unsaturated substrates by insertion into the Ni–C σ-bond, yielding carboxylic acids. With nickel, these CO_2–substrate coupling reactions are stoichiometric, except with alkynes where they become catalytic.



(21)

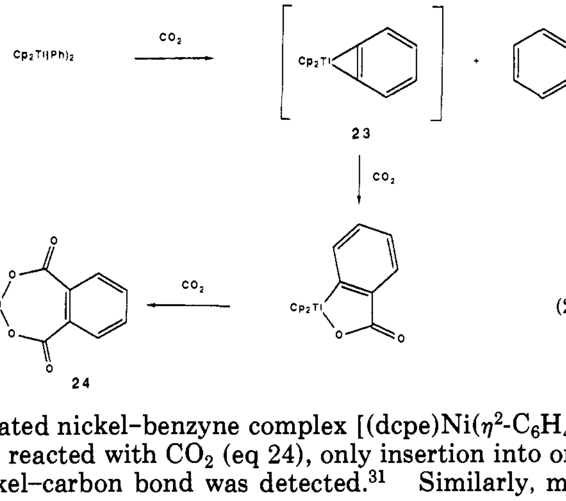
Ethylene complexes of tungsten and molybdenum have also been found to react with CO_2. The reaction of *trans*-$[M(C_2H_4)_2(PMe_3)_4]$ (M = Mo, W) with CO_2 yielded unexpected products (eq 22) (Table I, entry 54).[60a] An acrylic unit bridging the two metal atoms was generated, corresponding formally to a CO_2 insertion into one of the ethylene C–H bonds. The structure of the molybdenum complex has been established by X-ray and neutron diffraction, revealing a hydrido metal acrylate structure.[60]



22

(22)

In cases where two metal–carbon σ-bonds are present in the precursor complex, it is generally observed that carbon dioxide inserts, at best, only into one of these metal–carbon bonds. This applies to thermal or as found recently,[18b] to photochemical reactions. However, some complexes are able to insert two molecules of carbon dioxide per metal atom (eq 23). Formation of complex **24** was explained in terms of the hypothesis that diphenyltitanocene decomposes via the formation of a reactive benzyne complex.[2,20] However, when the isolated nickel-benzyne complex $[(dcpe)Ni(\eta^2\text{-}C_6H_4)]$ was reacted with CO_2 (eq 24), only insertion into one nickel–carbon bond was detected.[31] Similarly, mo-



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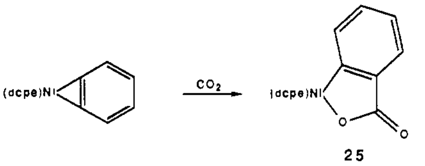

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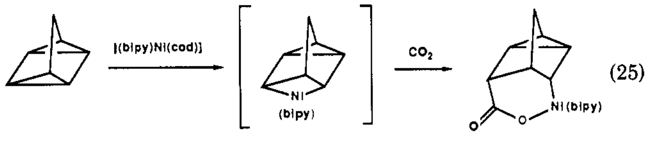
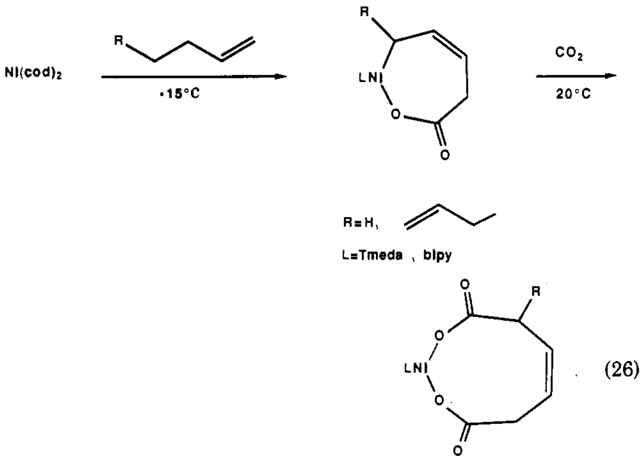
(24)

noinsertion of CO_2 occurred with the postulated intermediate of the reaction between quadricyclane and [(bipy)Ni(cod)], affording **26** (Table I, entry 70).[62]



26

When 1,3-dienes were reacted with CO_2 in the presence of [Ni(cod)$_2$] and N-donor ligands, two molecules of CO_2 were incorporated, affording α,ω-diacid derivatives (eq 26) (Table I, entry 63).[67a,b] Beside the above-mentioned titanium or nickel complexes, other examples of "bis CO_2 insertions", i.e., the coupling between two molecules of carbon dioxide with an organic substrate, have recently been reported for Zr(II) and Fe(0) olefin complexes (Table I, entries 53c, 55b–56).[59b,67c,d]



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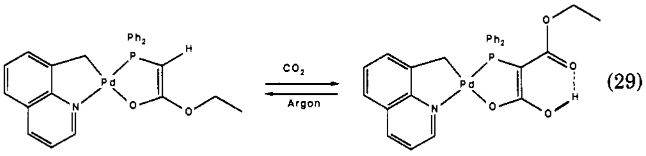
Carbon–carbon bond formation resulting from coupling of CO_2 with a coordinated ligand is generally an irreversible process. However, notable exceptions have been discovered (eq 18 (see above) and eq 27–29) (Table I, entries 26, 28, 68).[39a,40,71] In the latter three cases, the reversibility may be related to the electron-withdrawing properties of the substituent on the carboxylated C atom. When (ethyl (diphenylphosphino)acetato)palladium complexes, such as **30**, were reacted with carbon dioxide, under ambient conditions, carbon–carbon bond formation occurred, corresponding formally to CO_2 insertion into the PC–H bond of the complex (eq 29) (Table I, entry 68).[71] Bubbling argon through a THF solution of **31** causes immediate liberation of the coordinated CO_2 molecule and regeneration of **30**. This remains the only example, to our knowledge, where the reversible CO_2 insertion into a molecular complex has been fully characterized by X-ray diffraction as resulting from a C–C bond forming process.[71] This system has been used for the catalytic telomerization of CO_2 and butadiene[115] (see next section), while copper cyanoacetate has been successfully employed as a stoichiometric carboxylating agent of cyclohexanone.[40]

$$[Ir(depe)_2]Cl + CH_3CN + CO_2 \rightleftharpoons \underset{\mathbf{28}}{[Ir(H)(O_2CCH_2CN)(depe)_2]Cl} \qquad (27)$$

$$Cu(CH_2CN)L_n + CO_2 \rightleftharpoons \underset{\mathbf{29}}{Cu(O_2CCH_2CN)L_n} \quad (L = PBu^n_3) \qquad (28)$$



30 31

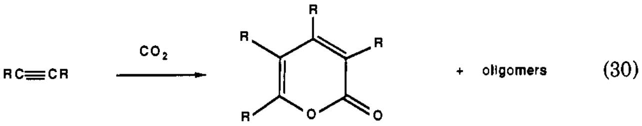
The products examined in this section result from stoichiometric CO_2-coupling reactions but are not necessarily involved in the catalytic reactions which will be examined in the next section. Thus, for example, a system analogous to **17** containing acac instead of hfacac, catalyzes the reaction of CO_2 with butadiene to yield lactones and esters but no linear dienic acid, in contrast to its stoichiometric counterpart (eq 18). On the other hand, stoichiometric reactions with palladium complexes never lead to the formation of lactones, whereas catalytic reactions do. Such palladium-catalyzed reactions may therefore proceed by a mechanism different from that of the stoichiometric reactions. However, the identification of elementary steps in these reactions may prove most useful for a better understanding of the catalytic ones.

4. Catalytic Reactions with Carbon–Carbon Bond Formation

At present, this highly desired class of reactions has only been described with unsaturated hydrocarbons. They all involve the formation of a new C–C bond between the organic substrate and CO_2 with retention of both oxygen atoms of CO_2 in the product. Alkynes, alkenes, dienes, strained cycles, and benzene react catalytically with CO_2 to afford pyrones, lactones, esters, and acids in the presence of ruthenium, rhodium, nickel, or palladium complexes (Table II).

4.1. Reactions with Alkynes

The reaction of alkynes with CO_2, catalyzed by Ni(cod)$_2$/Ph$_2$P(CH$_2$)$_n$PPh$_2$ systems (n = 2, 3, 4), was reported to yield pyrones and acetylenic oligomers.[73,74] The alkynes were reacted under 50-bar pressure of CO_2 in benzene at 120 °C for 20 h (eq 30). With hexynes the best yields were obtained when Ph$_2$P(CH$_2$)$_4$PPh$_2$ and an excess of PPh$_3$ were used.[73] The conversion of 4-octyne reached 98% whereas the yield of pyrone, based on 4-octyne charged, was 60%. More basic phosphines like Me$_2$P(CH$_2$)$_2$PMe$_2$ were scarcely effective for the formation of the pyrone ring.[74a] The steric bulk of the ligand is thought to play a significant role in this reaction and could influence the competition between the smaller molecule (CO_2) and the alkyne, leading to either pyrones or alkyne cyclotrimers. The pathways shown in Scheme I have been proposed.



Hoberg et al. have isolated a complex of type **32** (Table I, entry 50), considered to be a more likely intermediate than **33** in such Ni-catalyzed reactions. The latter is only involved in the trimerization of the alkyne.

TABLE I. Organometallic Reactions of CO_2 with C-C Bond Formation

entry	precursor complex	isolated product	ref
	Insertion into Metal–Alkyl or Metal–Aryl Bonds		
1	$RMgX$	RCO_2MgX	16
2	Cp_2TiR (R = Me, *n*-Bu)	$Cp_2Ti(O_2CR)$	17
3	$Ti(CH_2Ph)_4$	$(PhCH_2)_3Ti(O_2CCH_2Ph)$	19
4	Cp_2TiMe_2	$Cp_2Ti(O_2CMe)Me$	18
5	Cp_2TiPh_2	$Cp_2Ti[o\text{-}C_6H_4C(O)O]$ (**23**) + $Cp_2Ti[o\text{-}C_6H_4\{C(O)O\}_2]$ (**24**)	2, 20
6	$MeZrPh$	$MeCO_2ZrO_2CPh$	21
7	$VR_3(THF)_n$ (R = C_6F_5, CH_2SiMe_3)	$V(OCOR)_2$ + $V(OCOR)_3$	22
8	$[RM(CO)_5]^-$ (M = Cr, W; R = Me, Et, CHDCHDPh)	$[RCO_2M(CO)_5)]^-$	23, 24a
9a	$[MeW(CO)_4L]^-$ (L = PMe_3, $P(OMe)_3$)	$[MeCO_2W(CO)_4L]^-$	23b
9b	$WMe(CO)_2(NO)L_2$ (L = PPh_3, $P(O\text{-}i\text{-}Pr)_3$)	$W(\eta^2\text{-}O_2CMe)(CO)(NO)L$	24b,c
10	$Mn(CH_2Ph)_2$	$Mn(OCOCH_2Ph)_2$	25a
	MnR_2, R_3MnLi(or MgCl) (R = alkyl, alkenyl, alkynyl)	RCOOH	25b
	$MnPh_2(PCy_3)$	$PhCO_2Mn(PCy_3)$	25c
11	$FeMe_2(dppe)_2$	$Fe(O_2CMe)_2(CO_2)_m(py)_n$	26
12	$CoEt(CO)(PPh_3)_2$	$Co(CO_3)_n(COOEt)(PPh_3)$ + $Co(OCOEt)_2(PPh_3)_2$	7b,c
13	$RhArL_n$ (L = PMe_3, PPh_3, *n* = 3; L = dppe, *n* = 1; L = $t\text{-}BuP\{(CH_2)_3PPh_2\}_2$)	$Rh(O_2CAr)L_n$	27 28a 28b
14	$NiEt_2(bipy)$	$NiEt(O_2CEt)(bipy)$ + $Ni(O_2CEt)_2(bipy)$	29
15	$Ni(X^\frown O)Ph(PPh_3)$ + $MeOH/BF_3$ ($X^\frown O$ = $[Ph_2PCHC(O)Ph]^-$, $[Ph_2PNC(O)Ph]^-$, $[Ph_2AsCHC(O)Ph]^-$, $[MeC(O)CHC(O)Me]$)	$PhCO_2Me$	29b
	$Ni(X^\frown O)Ph(PPh_3)$ + $C_2H_4/MeOH/BF_3$ ($X^\frown O$ = as above)	$Ph(CH_2)_2CO_2Me$	
16	$Ni(o\text{-}C_6H_4CH_2)(P\text{-}n\text{-}Bu_3)_2$	$Ni[o\text{-}CH_2C_6H_4C(O)O](P\text{-}n\text{-}Bu_3)_2$	30a
	$Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$	$Ni\{CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)O\}(PMe_3)_2$	30b
17	$Ni(\eta^2\text{-}C_6H_4)(dcpe)$	$Ni[o\text{-}C_6H_4C(O)O](dcpe)$ (**25**)	31
18	RCu (R = alkyl, α- or β-ethylenic, or aryl group)	RCOOH	32
19	$RCuL_n$ (R = Me, Et, *n*-Pr, *i*-Bu; L = PPh_3, PCy_3, PPh_2Me, PBu_3, PEt_3)	RCO_2CuL_2	33
20	$RCu\cdot P\text{-}n\text{-}Bu_3$ (R = fluorenyl)	RCOOMe	34
21	$C_6F_5Cu(MgBrCl)$	$C_6F_5CO_2H$	35
22	$AgCF(CF_3)_2$, MeCN	$(CF_3)_2CFCO_2CH_2Ph$	36
23	$ZnEt_2$	$EtCO_2ZnEt$	37
24	$M(Cp')_2(Me)_2$ (M = Th, U)	$M(Cp')_2(O_2CMe)_2$ $M(Cp')_2(O_2CMe)(Me)$	120
	Insertion into Metal–CH_2CN Bonds		
25	$HFe(CH_2CN)(dmpe)_2$	$HFe(O_2CCH_2CN)(dmpe)_2$	38
26	$[IrL_4]Cl$ in CH_3CN (L = PMe_3, $^1/_2$depe)	$[HIr(O_2CCH_2CN)L_4]Cl$	39a
27	ML_nX + $CH_2(CN)_2$ (M = Ir, Rh; L = PMe_3 (*n* = 4), X = H; L = dmpe, depe (*n* = 2), X = Cl)	$[L_nMXH]^+[O_2CCH(CN)_2]^-$	39b,c
28	$Cu(CH_2CN)(P\text{-}n\text{-}Bu_3)_n$	$Cu(O_2CCH_2CN)(P\text{-}n\text{-}Bu_3)_n$	40
	Insertion into Metal–Carbon Bonds of Chelating Metalated Ligands		
29	$CpTi(o\text{-}C_6H_4CH_2NMe_2)_2$	$CpTi(o\text{-}C_6H_3CH_2NMe_2)\{m\text{-}C(O)O\}$	41, 42
30	$Cr(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$	$Cr\{OC(O)CH_2C_6H_4\text{-}o\text{-}NMe_2\}(CH_2C_6H_4\text{-}o\text{-}NMe_2)_2$	42
31	$[PPh_4][W(CO)_4(CH_2CH_2PPh_2)]$	$[PPh_4][W(CO)_4\{OC(O)CH_2CH_2PPh_2\}]$	43a
	$WH(PMe_3)_4(Me_2PCH_2)$	$[W(PMe_3)_3(\eta^1\text{-}Me_2PCH_2)]_2(C_3H_2O_6)$	43b
32	$Mn(CO)_4(CH_2CH_2PPh_2)$	$Mn(CO)_4\{OC(O)CH_2CH_2PPh_2\}$	44
33	$Fe(PMe_3)_4$	$HFe\{OC(O)CH_2PMe_2\}(PMe_3)_3$	45
34	$Ir(dmpe)_2Cl$	$[HIr(\{OC(O)CH_2\}MePC_2H_4PMe_2)(dmpe)]Cl$	46
	Insertion into Metal–Allyl Bonds		
35	$Cp_2Ti(\eta^3\text{-}C_4H_7)$	$Cp_2Ti(\eta^2\text{-}O_2CC_4H_7)$	47b
36	$Cp_2V(\eta^1\text{-}C_3H_5)$	$Cp_2V(\eta^1\text{-}O_2CC_3H_5)$	48
37	$Cr(\eta^3\text{-}C_3H_5)_3$	$(\eta^3\text{-}C_3H_5)Cr(O_2CC_3H_5)_2$ + $(\eta^3\text{-}C_3H_5)_2Cr(O_2CC_3H_5)$	49
38	$Ni(\eta^3\text{-}C_3H_5)_2$	$CH_2CH_2CH_2C(O)O$ (**6**) + $CH_2CH{=}CHC(O)O$ (**7**)	50
39	$Ni(\eta^3\text{-}2\text{-}MeC_3H_4)_2$	$(\eta^3\text{-}2\text{-}MeC_3H_4)Ni(\eta^1\text{-}O_2CC_4H_7)(PR_3)$ (**8**)	51
40	$Ni(\eta^2,\eta^3,\eta^3\text{-}C_{12}H_{18})$	$[Ni(\mu\text{-}\{\eta^3\text{-}C_{12}H_{18}C(O)O\})(PR_3)]_2$ (**10**) (R = Me, Cy)	51
41	$Ni(\eta^1,\eta^3\text{-}C_8H_{12})(PCy_3)$	$[\{Ni\{C_8H_{12}C(O)O\}(PCy_3)]_4$ (**11**)	51
42	$Pd(\eta^3\text{-}C_3H_5)_2$	$CH_2{=}CHCH_2COOH$	52
43	$Pd(\eta^3\text{-}C_4H_7)_2$	$CH_2{=}CH\text{-}CH(Me)COOH$	52
44	$Pd(\eta^1,\eta^3\text{-}C_3H_5)_2(PR_3)$ (R = Me, Cy)	$Pd(\eta^3\text{-}C_3H_5)(\eta^1\text{-}O_2CC_3H_5)(PR_3)$ (**9**)	53
	$Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PCy_3)$	$Pd[\eta^1,\eta^3\text{-}C_8H_{12}C(O)O](PCy_3)$ (**12**)	92
45	$[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2(dppe)$	$CH_2{=}C(Me)CH_2C(O)OCH_2C(Me){=}CH_2$ (**13**) + $Me_2C{=}CHC(O)OCH_2C(Me){=}CH_2$ (**14**)	54
46	$[Pd(hfacac)]_2(\eta^3,\eta^3\text{-}C_8H_{12})$ (**17**)	$CH_2{=}CH(CH_2)_3CH{=}CHCH_2COOH$	55

TABLE I (Continued)

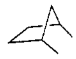
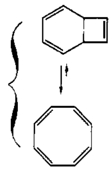
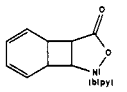
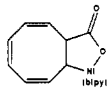
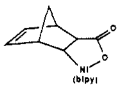
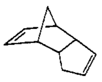
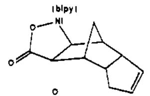
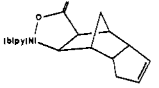
entry	precursor complex	isolated product	ref
	Reactions with Coordinated Alkynes and Related Ligands		
47	CpCp′Ti(PhC≡CPh)	CpCp′Ti{PhC=C(Ph)C(O)O}	56
	Cp$_2$Ti(Ph)$_2$	Cp$_2$Ti{*o*-C$_6$H$_4$C(O)O}, Cp$_2$Ti(*o*-C$_6$H$_4${C(O)O}$_2$) (**24**)	2, 20
48	Li[*fac*-(OC)$_3$(dppe)WC≡CR] (1)	*mer*-[(OC)$_3$(dppe)W{=C=C(R)CO$_2$Me}] (**2**)	14
49	[NEt$_4$][Et$_2$NC≡W(CO)$_2$(μ-PPh$_2$)$_2$Mo(CO)$_4$] (**3**)	[NEt$_4$][OC(O)(NEt$_2$)C=W(CO)$_2$(μ-PPh$_2$)$_2$Mo(CO)$_4$] (4)	15
50	"(L)Ni(0)" + MeC≡CMe (L = TMEDA, bipy)	(L)Ni[MeC=C(Me)C(O)O] (**32**)	57
51	Ni(η^2-C$_6$H$_4$)(dcpe)	Ni[*o*-C$_6$H$_4$C(O)O](dcpe) (**25**)	31
52	PhC≡CML$_n$ (M = Cu, Ag; L = P-*n*-Bu$_3$, *t*-BuNC)	PhC≡C-CO$_2$Me	35, 58
	Reactions with Coordinated Olefinic and Related Ligands		
53a	Cp′$_2$Ti(η^2-C$_2$H$_4$)	Cp′$_2$Ti[CH$_2$CH$_2$C(O)O] (**21**)	59a
53b	Cp′$_2$Zr(η^2,η^2-C$_4$H$_6$)	Cp′$_2$Zr{η^3-C$_3$H$_4$CH$_2$C(O)O}	59b
53c	Cp′$_2$Zr{CH$_2$CH=C(Me)CH$_2$}	Cp′$_2$Zr{OC(O)CH$_2$CH=C(Me)CH$_2$C(O)O}	59b
54	*trans*-M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ (M = Mo, W)	[M{μ-CH$_2$=CHC(O)OH}(C$_2$H$_4$)(PMe$_3$)$_2$]$_2$ (**22**)	60a
55a	[Mn(η^2,η^2-C$_4$H$_6$)(CO)$_3$]$^-$	[Mn{η^3-C$_3$H$_4$CH$_2$C(O)O}(CO)$_3$]$^-$	67f
55b	Fe(PEt$_3$)$_2$(C$_2$H$_4$)$_2$	MeO$_2$C(CH$_2$)$_2$CO$_2$Me, MeO$_2$CH(Me)CO$_2$Me	67d
56	Fe(η^2,η^2-C$_4$H$_6$)(PMe$_3$)$_3$ + CO$_2$, H$_3$O$^+$ + 2CO$_2$, H$_3$O$^+$ + CO$_2$, FeCl$_3$/H$_3$O$^+$	Fe[η^3-C$_3$H$_4$CH$_2$C(O)O}(PMe$_3$)$_3$ MeCH=CHCH$_2$CO$_2$H + H$_2$C=CH(CH$_2$)$_2$CO$_2$H (*E*)- + (*Z*)-(HO$_2$CCH$_2$CH=CHCH$_2$CO$_2$H) (*E*,*E*)-[HO$_2$CCH$_2$CH=CH(CH$_2$)$_2$CH=CHCH$_2$CO$_2$H]	67c
57	Fe[η^2,η^2-{H$_2$C=C(Me)C(Me)=CH$_2$}](PMe$_3$)$_3$ + CO$_2$, MeOH/HCl	H$_2$C=C(Me)CH(Me)CH$_2$CO$_2$Me + (*E*)-(Me)$_2$CHC(Me)=CHCO$_2$Me + (Me)$_2$C=C(Me)CH$_2$CO$_2$Me	67e
58	Fe(η^2,η^2-1,3-C$_5$H$_8$)(PMe$_3$)$_3$ + CO$_2$, MeOH/HCl	(*E*)-MeCH=CH(CH$_2$)$_2$CO$_2$Me + (*E*)-MeCH$_2$CH=CHCH$_2$CO$_2$Me + (*E*)-MeCH$_2$CH=C(Me)CO$_2$Me	67e
59	"(L)Ni(0)" + RCH=CHR′ (L = bipy, cdt, dcpe, Et$_2$NC$_2$H$_4$PCy$_2$; R = R′ = H; R = H, R′ = Me, *n*-Bu, Ph; R, R′ = 	(L)Ni[RCHCHR′C(O)O]	61
60	"(bipy)Ni(0)"		
	+ 	 + 	62
	+ 		62
	+ 	 	62, 63
61	"(L)Ni(0)" + H$_2$C=CRCR′=CHR″ (L = bipy, dcpe, R = R′ = R″ = H; L = TMEDA, PPh$_3$, R = R″ = H, R′ = Me; L = PCy$_3$, R = R′ = H, R″ = Me and R = R′ = Me, R″ = H)	(L)Ni[η^3-HR″C⋯CR′⋯CRCH$_2$C(O)O]	64
62	"(L)Ni(0)" + CHR=CR′CR″=CH$_2$ + R‴X (R, R′, R″ = H, alkyl, aryl; R‴ = alkyl, aryl, unsaturated group)	CHRR‴CR′=CR″CH$_2$COOH	66b
	+ CHR=CR′CR″=CHR‴	CHRCR′=CR″CHR‴C(O)O	66a
63	"LNi(0)" + CH$_2$=CRCH=CH$_2$ (L = TMEDA, bipy; R = H, (CH$_2$)$_2$CH=CH$_2$)	LNi[OC(O)CH(R)CH=CHCH$_2$C(O)O] (**27**)	67a,b
64	"(L)Ni(0)" + CH$_2$=C=CRR′ (L = bipy, dcpe; R = R′ = H; R = H, R′ = Me; R = R′ = Me)	Ni[CH$_2$C(=CRR′)C(O)O]	68
65	CuEt + RC≡CH [R = H, Me, *n*-Bu (in the presence of MgBr$_2$ or of donor ligands)]	Et(R)C=CH(COOH)	69
66	Ag[CH=C=C(Me)CH$_2$R]·2LiBr (R = *i*-Pr, *t*-Bu)	RCH$_2$C(Me)=C=CH(COOH)	70
67	Th(Cp′)$_2$Cl(η^2-C(O)CH$_2$-*t*-Bu)	Th(Cp′)$_2$(Cl){OC(CH$_2$-*t*-Bu)C(O)O}	120

TABLE I (Continued)

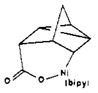
entry	precursor complex	isolated product	ref
	Insertion into Other Ligands		
68	$Pd(o\text{-}C_6H_4CH_2NMe_2)\{Ph_2PCH{=}C(O)OEt\}$ (**30**)	$Pd(o\text{-}C_6H_4CH_2NMe_2)[Ph_2PC\{{=}C(O)OH\}(CO_2Et)]$ (**31**)	71
	Reactions with Strained Cycles		
69	$RhCl(PMe_2Ph)_3$ + 	$CH_2CH_2CH_2C(O)O$	121
70	$Ni(cod)_2$ + bipy + 	 (26)	62
	Oxalate Formation from Two CO_2 Molecules		
71	$R_2Ti(CH_2)_3N(R')CH_2CH_2N(R')(CH_2)_3TiR_2$ (R = Cp, Cp′; R′ = aliphatic, cycloaliphatic, aromatic group)	$(R_2Ti)_2(C_2O_4)$	72

TABLE II. Catalytic Reactions of CO_2 Involving C–C Bond Formation

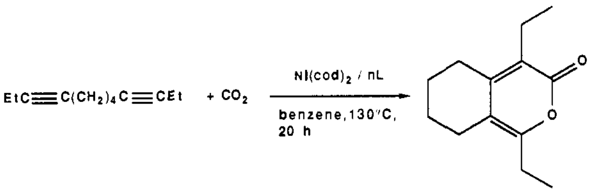
educts	metals	products
alkynes	Rh, Ni	pyrones
alkenes	Ru,[a] Rh	acids, esters
allenes	Pd	lactones, esters
dienes	Ru, Rh, Ni, Pd	lactones, acids, esters
cyclopropanes	Pd	lactones
aromatic compounds	Pd	acids

[a] See text.

Furthermore, **32** has been shown to react with one more alkyne molecule, affording complex **34**.[57b,c] Therefore, formation of the metallacyclopentadiene intermediate **33**, followed either by CO_2 insertion into the nickel–carbon bond (route A) or by its (4 + 2) cycloaddition with CO_2 in the sense of Diels–Alder reaction (route B), may be ruled out.

In general, nickel catalysts are active for various alkynes, but phenyl- or diphenylacetylene do not give any CO_2-containing product. The addition of catalytic amounts of water was studied.[73b,74a] Thus, 0.15 mmol of water/g-atom of nickel had a slight effect on the selectivity. One or more molar equivalents of water brought about the lowering of the catalytic activity, decreasing also the selectivity for the pyrone. This suggested that the increased selectivity for cyclotrimers was related to the presence of a nickel hydride complex.

Bicyclic α-pyrones of type **35** have been obtained recently by the nickel(0)-mediated cycloaddition of diynes with CO_2 (eq 31).[74b]

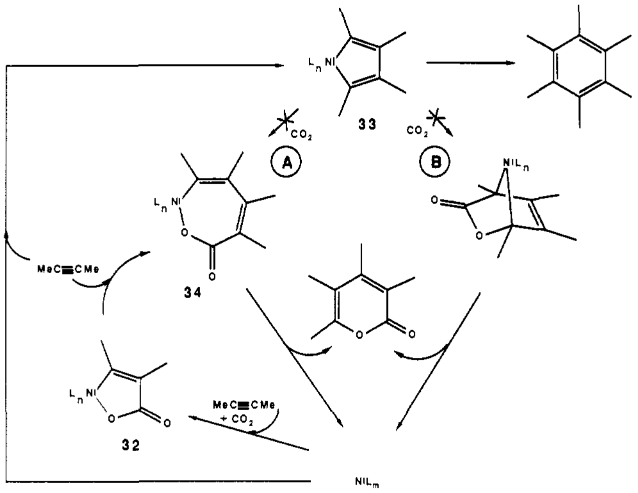


(31)

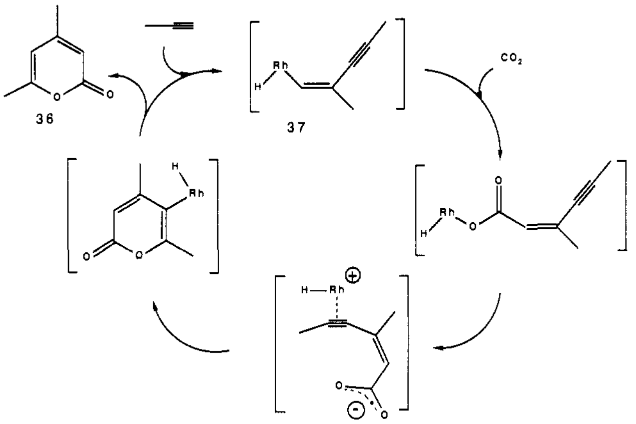
35

In contrast to nickel complexes, $[HCo(dppe)_2]$ afforded low yields of pyrone from 1-hexyne and CO_2[73a] and the rhodium complex $[Rh(dppe)_2(\eta\text{-}BPh_4)]$ yielded only 3% of 4,6-dimethyl-2-pyrone (**36**) obtained from propyne, the major products being cyclic trimers.[75] The formation of **36** was interpreted as a CO_2 insertion into the Rh–C σ-bond of the intermediate **37**. A possible catalytic cycle is shown in Scheme II. Cyclization would occur by nucleophilic attack of an oxygen atom at the coordinated alkyne, as in the proposed mechanism for lactone formation from alkynoic acids.[77] However, a route involving a rhodalactone analogous to **32** (Scheme I) should also be considered.

SCHEME I



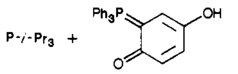
SCHEME II



4.2. Reactions with Alkenes

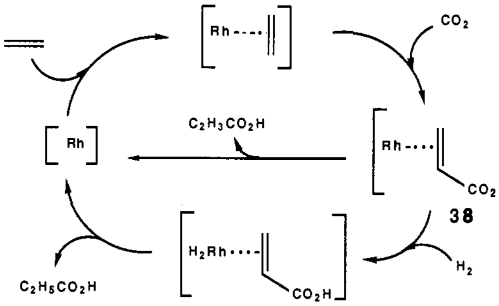
In contrast to alkene carbonylation reactions, only few carboxylation reactions of alkenes are known. Lapidus et al. reported the rhodium-catalyzed carboxylation of ethylene using Wilkinson's catalyst in the presence of a promoter (HCl, HBr, or HI) and distilled water as solvent.[76] When the reaction was carried out at a pressure of 700 atm and 180 °C, 38.4% of propionic acid, 24.3% of ethanol, and 11.2% of ethyl propionate were formed whereas the ethylene conversion reached 91.4% (CO_2 conversion 67.4%). When N_2 was intro-

TABLE III. Catalytic Systems for Butadiene–CO_2 Reactions

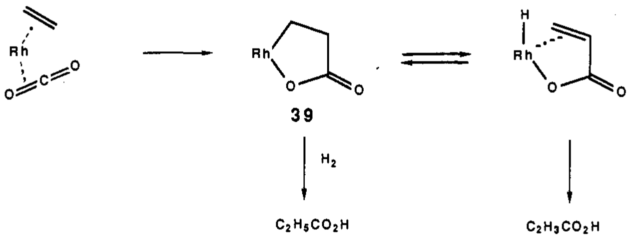
entry	catalyst	adducts	solvent	temp (°C) (time (h))	yields (%) (based on butadiene): lactones 43	lactones 42	lactones 44	esters 45, 46	butadiene dimers	acids 40, 41	acids 50	ref
1	$Ni(cod)_2$	P-*i*-Pr_3	CH_3CN	90 (15)	1.5			0.1				87
2	$Ni(cod)_2$	$P(OBu)_3$	CH_3CN	90 (15)				1.5				87
3	$Ni(cod)_2$ or Ni(cdt)	P(O-*i*-$Pr)_3$	DMF	60 (3)							7.1	88
4	$Pd(dppe)_2$		DMF	84 (20) then 120 (20)		12.3			60.5			80
5	$Pd(PPh_3)_4$	PhONa	DMF	80 (2)	0.47	0.12		0.47	11.3	30.5		82a
6	$[(\eta^3\text{-2-Me-}C_3H_4)Pd(OAc)]_2$	P-*i*-Pr_3	C_6H_6	70 (20)	27			19	25			83b
7	$[(\eta^3\text{-2-Me-}C_3H_4)Pd(OAc)]_2$	PMe_2Ph	C_6H_6	70 (20)				46	41			83b
8	$[Pd(PPh_3)_2$(*p*-benzoquinone)]	PPh_3, *N*-ethylpiperidine, hydroquinone, *p*-benzoquinone	CH_3CN	60 (18)	81			3.5	2.6			84
9	$[Pd(PPh_3)_2$(*p*-benzoquinone)]	PPh_3, *N*-ethylpiperidine, hydroquinone, *p*-benzoquinone	CH_3CN	60 (3)	51			1.7	2.8			84
10	$[Pd(PPh_3)_2$(*p*-benzoquinone)]	NEt_3, H_2O	CH_3CN	60 (18)	62.3			0.9	22			84
11	$Pd(acac)_2$	PPh_3	DMF	70 (20)		6				18.1		82b
12	$Pd(acac)_2$	PPh_3	DMF	120 (20)		3.7				14.7		82b
13	$Pd(acac)_2$	P-*i*-Pr_3	CH_3CN	90 (15)	40	0.3		1.3				85b
14	$Pd(acac)_2$	P-*n*-Bu_3	CH_3CN	90 (15)	3	0.1		14.5				85b
15	$Pd(dba)_2$	PPh_3, CH_3CO_2Na	DMF	60 (2)	50				2	2		86
16	$Pd(OAc)_2$	PPh_3	DMF	60 (2)	26				7			86
17	$Pd(acac)_2$	P-*i*-$Pr_3$$^+$  	CH_3CN	90 (15)	58.7		0.1	2.8				87
18	$[Pd(MeCN)_4][BF_4]_2$	PPh_3, NEt_3, hydroquinone, acetophenone	CH_3CN	90 (15)	35[a]							115
19	$RuH(OAc)(PPh_3)_3$	P-*i*-Pr_3	CH_3CN	90 (15)	6.4	0.4		0.1				87
20	$Rh(C_2H_4)_2(acac)$	PEt_3	CH_3CN	120 (24)		5–8[b]						87

[a] The total yield of products with the same molecular weight as **43** is 76% with a selectivity for **43** of 46%. A selectivity of 96% may be achieved by thermal isomerization. [b] Yield of lactone **51**.

SCHEME III



SCHEME IV



duced in the autoclave, no ethyl propionate was formed. Possible mechanisms and intermediates for the carboxylation reaction are shown in Schemes III and IV. The postulated intermediate **38** could result from a one to one coupling reaction of ethylene and carbon dioxide as observed in the recently isolated complex **22** (Table I, entry 54).[60] Hydrogenation of **38** would then lead to propionic acid. In Scheme IV, on the other hand, a metallalactone intermediate could be formed by an electrocyclic mechanism, analogous to that mentioned above in Section 3. It is appropriate to recall that an intermediate of type **39** has also been postulated with iron[67d] and isolated in the case of nickel (Table I, entry 59).[61d-f] However, there is no real proof that in the catalytic reaction the carboxyl group stems directly from CO_2 and it is furthermore well known that alcohols can act as sources of hydrogen and carbon monoxide.

It has been described in a Röhm GmbH patent[78] that propylene and CO_2 react at 230 °C in the presence of ruthenium catalysts, e.g., $[RuCl_2(PPh_3)_3]$, in methanol and acetone as solvents, yielding butyric methyl esters (20–30%) (eq 32). At the end of the reaction, form-

$$H_2C{=}CHCH_3 + CO_2 \rightarrow CH_3CH_2CH_2CO_2CH_3 + (CH_3)_2CHCO_2CH_3 \quad (32)$$

aldehyde and ethanol were detected as byproducts. This observation suggests that methanol is decomposed during the reaction and may act as the hydrogen source. On replacing CO_2 by N_2, the same yields and selectivities of esters were obtained.[79] Therefore, a carbonylation reaction rather than a carboxylation reaction might well be responsible for the products formed, CO_2 serving only to reach the required pressure.[6d,79] It must be emphasized that, at the present time, there is no definite proof of the *catalytic* C–C bond formation between monoolefins and CO_2.

4.3. Reactions with Conjugated Dienes

The catalytic coupling of butadiene and CO_2 has attracted a considerable interest, and the known systems are presented in Table III.

SCHEME V

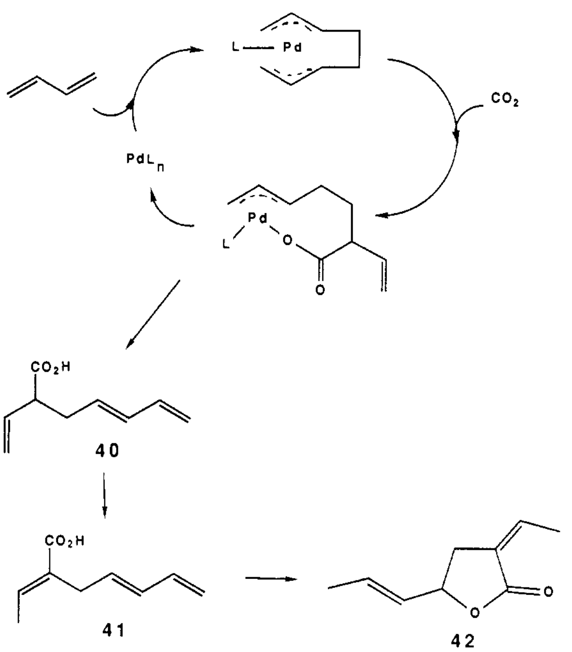


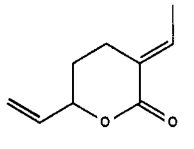
TABLE IV. Influence of the Phosphine Ligand on the Product Yields in Butadiene–CO_2 Cooligomerization Reactions (from Ref 83b)[a]

ligand	1,3,7-octatrienes	esters 45 + 46	lactone 43
PCy_3	14	14	28
P-*i*-Pr_3	25	19	27
P-*t*-Bu_2Ph	10	1	1
PEt_3	44	29	
PMe_2Ph	41	46	
$P(CH_2Ph)_3$	14	44	5
P(*o*-tolyl)$_3$	60	8	
$PMePh_2$	66	27	
PPh_3	11	17	3

[a] Experimental conditions: benzene (10 mL), 70 °C, 80–100 atm; catalyst [{(η-2-methylallyl)Pd(OAc)}] (0.38 mmol), ligand (2.28 mmol).

The catalytic incorporation of CO_2 into organic compounds was first reported by Inoue et al.[80,81] Butadiene and CO_2 were reacted in the presence of palladium(0)-phosphine complexes at 120 °C, producing a small amount of 2-ethylidenehept-5-en-4-olide (**42**) together with butadiene oligomers (Scheme V). They obtained the best yields of **42** (12.3%) when [$Pd(PPh_3)_4$] was used as catalyst in the presence of dppe, in DMF. When the reaction was carried out below 100 °C, the organic acids **40** and **41** were also obtained. The fact that both acids are easily converted into lactone **42** under the catalytic conditions suggests that they are the precursors of the lactone. The formation of these acids implies a hydrogen-transfer step, which presumably proceeds through the intermediacy of a palladium hydride species. Acid **40** isomerizes to **41**, which then is converted to **42** by intramolecular 1,4-addition.[80,81] Acid **41** can be obtained preferentially when the reaction is carried out in the presence of sodium phenoxide.[82a] A catalytic system consisting of $Pd(acac)_2/PPh_3$ in DMF at 70–120 °C was also found to convert butadiene and CO_2 into **41** and **42**.[82b]

Catalysts prepared in situ, e.g., from [{(η^3-2-methylallyl)Pd(OAc)}$_2$] and an appropriate phosphorus ligand, as well as palladium(0)–trialkylphosphine complexes, are also effective for coupling CO_2 and butadiene. Apart from **42**, the other coupling products **43**–**46** were identified by Musco.[83] The distribution of the reaction products was found to depend largely on the ligand bound to palladium (see Table IV). The δ-lactone **43** is the main product formed with the more basic phosphines [e.g., PCy_3, P*i*-Pr_3], whereas with less basic phosphines, e.g., PMe_2Ph, P-*t*-Bu_2Ph, $P(CH_2Ph)_3$, esters **45** and **46** are preferentially formed. When PCy_3 was used, catalytic quantities of water appeared necessary in order to obtain reproducible results. Esters **46** are isomerized to the corresponding **45** on heating, whereas **42** is the precursor of the fully conjugated lactone **44**. A selective synthesis of lactone **43** using palladium(0) complexes in the presence of tertiary amines, triphenylphosphine, and a quinone/hydroquinone mixture has been described.[84] The reaction was carried out in acetonitrile. Best yields of lactone **43** were obtained at 60 °C under 30 bar of CO_2, and after 18 h, the butadiene conversion was found to be 88% and the product selectivities were 92% for **43**, 4% for esters **45** and **46**, and 3% for octatrienes. The addition of catalytic amounts of water increased the reaction rate. A selective synthesis of the δ-lactone **43** or of the γ-lactone **44** can also be achieved in the presence of bis(acetylacetonato)palladium and a phosphine of high basicity and large cone angle (e.g., P-*i*-Pr_3, PCy_3).[85] Thus, the synthesis of lactone **43** is performed at low palladium concentration, e.g., at ratios butadiene/palladium of 1000:1, and **43** can be isolated in 39% yield by distillation (99% pure) whereas for the synthesis of **44**, butadiene/palladium ratios of 20:1 are required. Isomerization of **43** into **44** is quantitative when the latter system is used and **44** can be isolated in 90% yield (97% pure) from **43**. The study of the reaction conditions revealed that the optimum palladium/phosphine ratio was 1:3. Polar, aprotic solvents are necessary and acetonitrile proved the best: $CH_3CN > C_2H_5CN > PhCN > CH_3COCH_3 > THF$. The suitability of this solvent has been ascribed to the higher solubility of CO_2 in this medium, to its solvation effect and C–H acidity.



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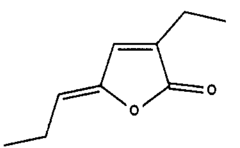

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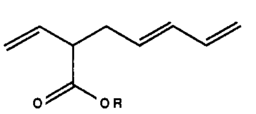

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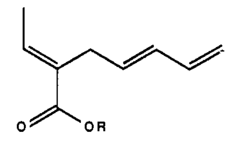

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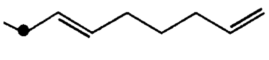
a, R =



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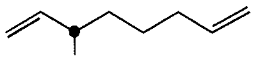
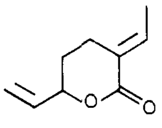


Further catalytic systems have been reported for this reaction, such as $Pd(dba)_2/PPh_3$ in DMF.[86] After 2 h of reaction at 60 °C, 14% of lactone **43** could be isolated. The yield increased up to 50% upon addition of sodium acetate. This observation suggested that the presence of the salt favors the reductive elimination step required in the reaction. The functional phosphines

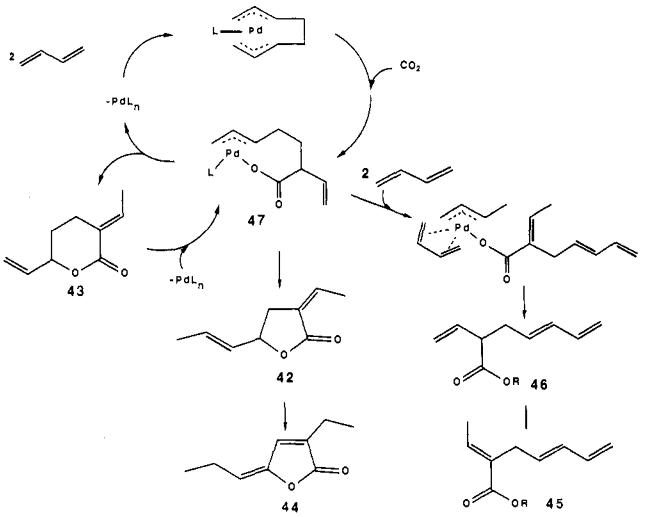
TABLE V. Efficient Catalysts for the Production of Lactone 43



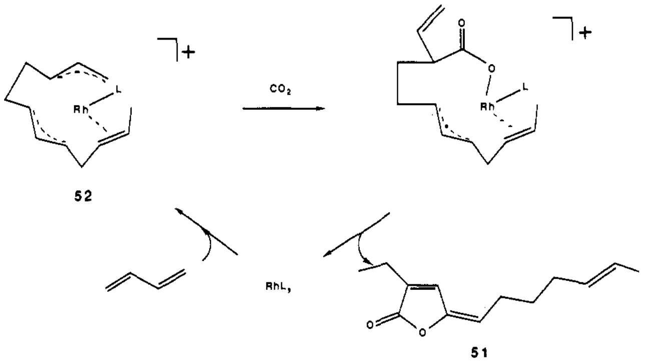
43

entry	catalyst	butadiene/Pd (mol/mol)	reactn time (h)	mol of lactone/ mol of Pd per h	ref
4	$Pd(dppe)_2$	676	40	2.1	80
6	$[\eta^3\text{-}2\text{-Me-}C_3H_4)Pd(OAc)]_2/P\text{-}i\text{-}Pr_3$	408	20	2.8	83b
8	$[Pd(PPh_3)_2(p\text{-benzoquinone})]/PPh_3/$ N-ethylpiperidine/hydroquinone/p-benzoquinone	1500	18	34.5	84
9	$[Pd(PPh_3)_2(p\text{-benzoquinone})]/PPh_3/$ N-ethylpiperidine/hydroquinone/p-benzoquinone	1500	3	130	84
10	$[Pd(PPh_3)_2(p\text{-benzoquinone})]/NEt_3/H_2O$	750	18	13	84
13	$Pd(acac)_2/P\text{-}i\text{-}Pr_3$	1625	15	21.7	85b
15	$Pd(dba)_2/PPh_3/CH_3CO_2Na$	240	2	30	86
16	$Pd(OAc)_2/PPh_3$	173	2	11	86
17	$Pd(acac)_2/P\text{-}i\text{-}Pr_3/P\text{-ylide}$	1563	15	30.6	87
18	$[Pd(MeCN)_4][BF_4]_2/PPh_3/NEt_3/hydroquinone/$ acetophenone	1625	15	20.4	115

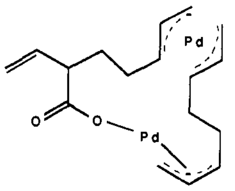
SCHEME VI



SCHEME VII



$Ph_2P(CH_2)_nCO_2H$ (n = 1–3), which might have combined the properties of phosphorus donors and of carboxylates, did not favor the reaction, and in these cases, the best yields of **43** (9%) were obtained for n = 3.[86] The following mechanism has been proposed to account for the formation of products **40–46** (Scheme VI).[85b] The catalytic precursor would generate in situ a Pd(0) species that reacts with butadiene to afford the bis(η^3-allyl) complex. Insertion of CO_2 into the palladium–carbon σ-bond occurs,[52] forming a carboxylate intermediate **47** that can evolve through three different routes (see Scheme VI). Evidence has become available that during the key step of the reaction, i.e., the CO_2 incorporation, binuclear palladium species of type **48** do not act as intermediates in the transformation.[55]



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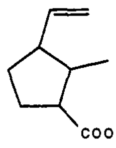

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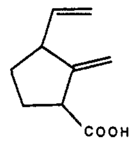

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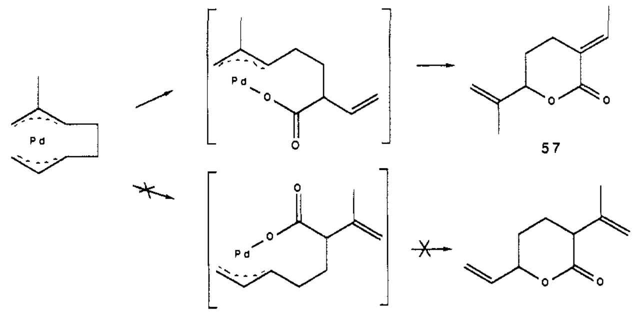
Lactone **43** takes part in an equilibrium with intermediate **47**, allowing formation of lactone **42**, which isomerizes to the thermodynamically more stable lactone **44**.[87,89] Note also that the Ni(0)-catalyzed synthesis of acids **49** and **50** has been achieved recently from butadiene and CO_2.[88] Recent work has shown that Pd/PPh_3-based systems obtained from cationic Pd(II) precursor complexes are efficient catalysts for the formation of lactone **43** (selectivity of 96%) (Table III, entry 18).[115]

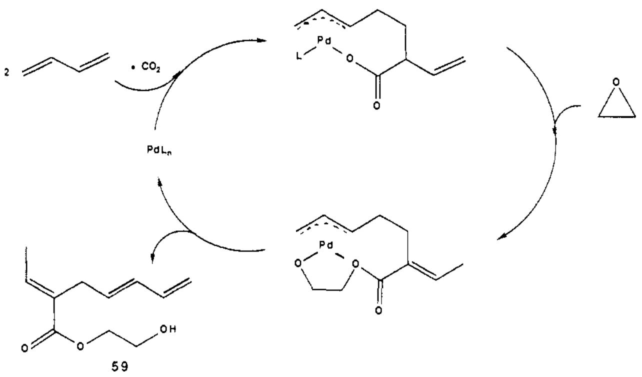
When rhodium(I) complexes such as $[Rh(C_2H_4)_2(acac)]$, $[Rh(nbd)(PPh_3)_2][BPh_4]$, $[Rh(cod)(PPh_3)_2][PF_6]$, or $[Rh(\eta^3\text{-allyl})_2(acac)]$ are used as catalysts, the new γ-lactone 2-ethyl-2,4,9-undecatrien-4-olide (**51**) is formed in 5% yield.[87,89] The pathway of Scheme VII was proposed. Condensation of three butadiene molecules on the rhodium center would lead to **52**. Related complexes are known for, e.g., nickel,[90] ruthenium,[91] and palladium.[92] CO_2 insertion into the rhodium–carbon σ-bond affords the corresponding carboxylato complex, which reductively eliminates lactone **51**. It is noteworthy that the telomerization reaction between CO_2 and butadiene is also catalyzed by nickel or ruthenium complexes, but the yields are low (1–6%).[87] A comparison of the catalytic systems known to efficiently convert butadiene and CO_2 into lactone **43** is presented in Table V.

Telomerization of isoprene with carbon dioxide has also been reported. The complex $[Pd(dppe)_2]$ was found to catalyze the dimerization of isoprene in the presence of CO_2 and incorporation of small amount of

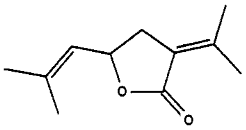
SCHEME VIII



SCHEME IX



the latter takes place (about 1%).[93] Five-membered ring lactones were identified:



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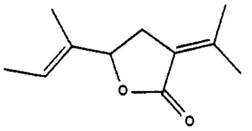

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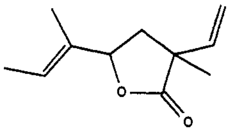

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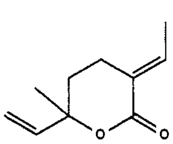
The coreaction of butadiene and isoprene with CO_2 has been investigated with various palladium catalysts.[87,89a,94] The new six-membered ring lactones 56 and 57 were formed. They could be obtained selectively



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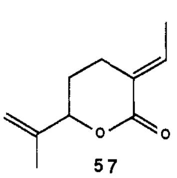

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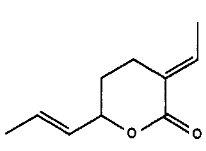

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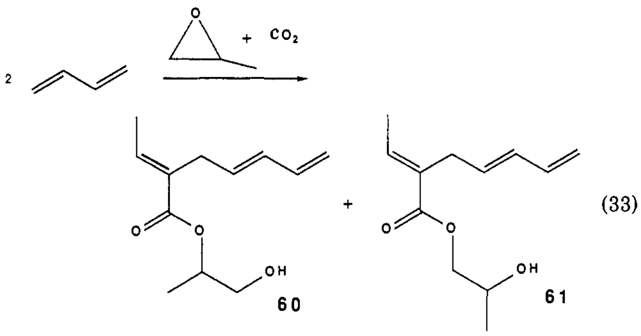
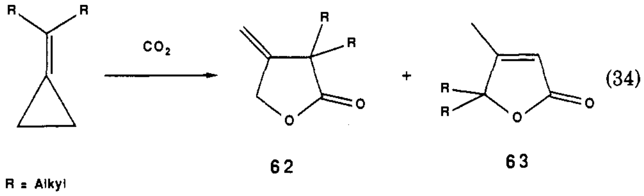
when isoprene/butadiene ratios higher than 7:1 were used. Reacting piperylene instead of isoprene afforded lactone 58. The structures of 56 and 57 show clearly that CO_2 incorporation occurs only into the η^3-allyl part originating from the butadiene unit (Scheme VIII). This fact may account for the observation that with these catalysts, isoprene or piperylene alone did not react with carbon dioxide.[87,89a]

Another coreaction of this type involving CO_2, butadiene, and ethylene oxide has been shown to occur in the presence of rhodium or palladium catalysts (Scheme IX).[95] With propylene oxide, esters 60 and 61 are formed in 22% yield using $Pd(acac)_2/P\text{-}i\text{-}Pr_3$/butadiene/$CO_2$/propylene oxide in a 1:3:200:300:200 ratio (eq 33).[95] The optimum yield of the glycol ester 59 is reached after a relatively long time (25 h), suggesting that it is not a primary product but is formed from lactone 43. This is furthermore supported by the fact that 43 reacts with propylene oxide under the same reaction conditions, to afford the same yields of esters 60 and 61. Presumably, the elimination of lactone 43 is competing with the insertion of the oxide into the metal–oxygen bond, which is consistent with the fact that 43 predominates at the early stage of the reaction.

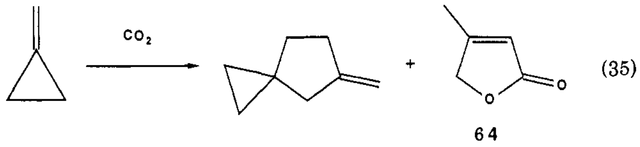


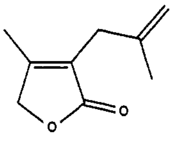
4.4. Reactions with Methylenecyclopropanes

Palladium(0) phosphine complexes catalyze the coupling of methylenecyclopropanes and carbon dioxide in benzene (40 atm of CO_2, 130 °C, 20 h) with opening of the three-membered ring to give the five-membered ring lactones 62 and 63 (eq 34).[96] The influence of the phosphine was studied. A less basic phosphine such as PPh_3 or the phosphite $P(OEt)_3$ tend to lead to 62 rather than to 63. Surprisingly, 2,2-dimethylmethylenecyclopropane and *cis*-2,3-dimethylmethylenecyclopropane did not react with CO_2 under similar conditions.



More recently, new efficient catalytic systems have been described for the reaction of methylenecyclopropane and CO_2, based on (η-allyl)(η-cyclopentadienyl)palladium complexes and PPh_3 at 165 °C in DMF (eq 35).[97] The yield of 64 reaches 80% after 2 h when the ratio Pd/PPh_3 is 1:4. The authors observed that Pd(0) species also catalyze the alkylation of the primary product 64 with methylenecyclopropane. Therefore, the formation of the cotrimers 65 and 66, the cotetramers 67–69, and the copentamers 70 and 71 cannot be avoided. The reaction course depends on several parameters, e.g., Pd/PPh_3 ratio, solvent, CO_2 pressure, and temperature. When the reaction was performed in DMSO, after 18 h at 140 °C (with a Pd/PPh_3 ratio of 1:2), a selectivity of 73.7% for 70 was





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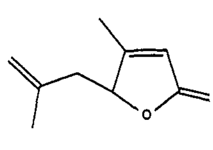

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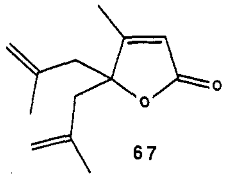

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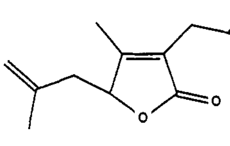

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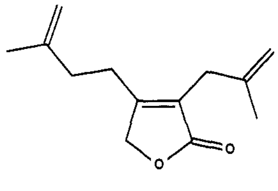

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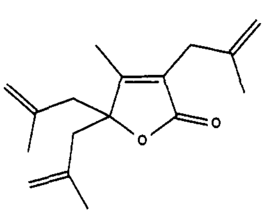

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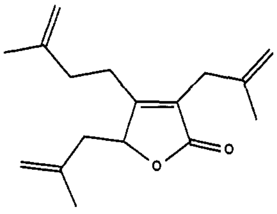
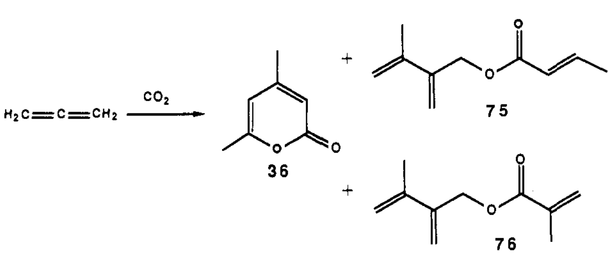


71

obtained. The reaction pathway shown in Scheme X was proposed. Methylenecyclopropane would react with palladium(0) species to form a palladacyclobutane **72**, in equilibrium with the suggested[96,97] trimethylenemethane complex **73**. CO_2 can insert into a palladium–carbon bond, affording carboxylic species, which would liberate lactone **74** by reductive elimination, the latter isomerizing into the thermodynamically more stable **64**. Intermediates **72** and **73** could also react with lactone **64**, which possesses three acidic protons. This reaction is similar to the well-known palladium-catalyzed alkylation of active methylene compounds.[98] By repeating cycle A on the primary lactone, one, two, or three times, the mixture of cooligomers **65**–**71** is produced.

4.5. Reactions with Allene

CO_2 reacts with allene in the presence of Pd(η^3-allyl)$_2$/dcpe[99a] or [Rh(dppe)(η-BPh$_4$)][99b] to give a mixture of lactone **36**, esters **75** and **76**, and oligomeric and polymeric materials. The reaction was carried out at 110 °C in toluene (eq 36). Lactone **36** is reminiscent of those formed in the cyclocooligomerization of CO_2 with alkynes and this suggested that the allene might be initially isomerized to propyne. However, an experiment involving propyne proved that esters **75** and **76** are not formed by this route. The mechanism of the reaction is not known, but it seems plausible that condensation of allene at the metal leads to the generation of metallacyclic systems that react further via insertion of CO_2 into the M–C bond. The formation of esters **75** and **76** implies a hydrogen-transfer step which presumably proceeds through the intermediacy of a palladium hydride species. Like in similar cases where the hydrogen comes from an external source, a strong solvent effect is observed. In contrast to toluene, methylene chloride favors the formation of homopolymers.[99b]



(36)

4.6. Reactions with Aromatic Compounds

In 1888, Friedel and Crafts reported the formation of benzoic acid from CO_2 and benzene in the presence of anhydrous aluminum chloride.[100] Recently, Fujiwara et al. reported the carboxylation of aromatic compounds with carbon dioxide, leading to the formation of aromatic acids via direct activation of an aromatic C–H bond by palladium(II) salts.[101] Anisole, thiophene, furan, and benzene were carboxylated with $Pd(NO_3)_2$ or $Pd(OAc)_2$ salts (30 atm of CO_2, 150 °C, 20 h), affording the corresponding acids. When benzene was treated with a mixture of $Pd(NO_3)_2$ and $Fe(NO_3)_3{\cdot}9H_2O$, 66% benzoic acid, 8% biphenyl, 417% nitrobenzene, and 60% picric acid (percent based on palladium salt) were formed. When *t*-BuOOH was used as a reoxidizing agent, the yield of benzoic acid increased up to 127%, suggesting that the reaction could be made catalytic with respect to palladium. However, the $Pd(OAc)_2$/*t*-BuOOH system itself, without added CO_2, has been found to result in high-yield carboxylation of benzene to benzoic acid. This latter observation suggests that CO_2 may not be the carboxylating agent in the previous reaction.

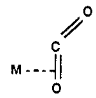
4.7. Electrochemical Reactions

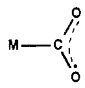
The search for transition-metal catalysts that mediate CO_2 reduction at lower potentials than ca. 2.2 V (vs saturated calomel electrode), the potential needed for the direct electrochemical reduction of CO_2,[102] has become an important research area.[103] Two reaction types are characterized by C–C bond coupling: oxalate formation and carboxylation of organic substrates. The homogeneous transition metal catalyzed electroreduction of CO_2 into oxalate has been claimed in only two cases: in the presence of some Ag(II) and Pd(II) metalloporphyrins[104] or of $[CpFe(CO)_2]^{\bullet-}$ which mediates the delivery of CO_2^-.[105a] Further examples are needed to understand the factors that govern the C–C bond formation and deviate the reaction course from the usual CO_2 reduction into a C_1 molecule (CO, HCOOH).

A currently expanding field is the electrocarboxylation of organic substrates by CO_2, catalyzed by transition metals. Thus organic halides may be converted into the corresponding carboxylates in the presence of nickel complexes.[106] Electrocarboxylation of ArCHMeCl can thus lead to 2-arylpropionic acids in ca. 70–80% faradic and chemical yields.[106c] Very efficient mono- and bis-carboxylation reactions of unsaturated substrates, e.g., styrene, butadiene, have recently been achieved with $[CpFe(CO)_2]_2$ as a catalyst precursor.[105b] Quantitative faradic and chemical yields have thus been attained in the carboxylation of styrene, the selectivity in hydrocinnamate $PhCH_2CH_2CO_2^-$ or phenylsuccinate $PhCH(CO_2^-)CH_2(CO_2^-)$ depending on the experimental conditions. The perspectives of transition metal mediated coupling reactions involving CO_2 are closely related to fundamental academic problems as well as to industrial applications, making this area of high current interest.

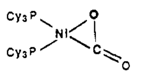
5. The Relevance of CO_2 Complexes

Coordination of CO_2 to transition metals has long been thought to be one of the initial steps in the catalytic conversion of CO_2. Therefore, investigations about "CO_2 complexes" have received considerable attention and they should continue as they increase our fundamental knowledge of this chemistry.[107] However, there is still a need for establishing that prior coordination of CO_2 to a transition metal is a prerequisite for a catalytic reaction with CO_2. The number of structurally unequivocally characterized complexes in which CO_2, used as a reagent, is interacting with the metal center(s), is very limited.


η^2 side-on coordination


η^1-C coordination


η^1 end-on coordination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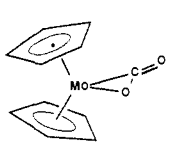
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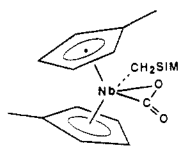
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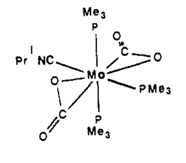
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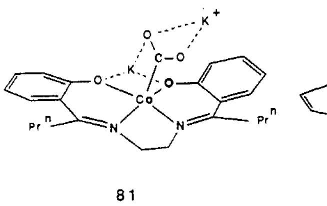
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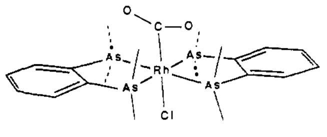
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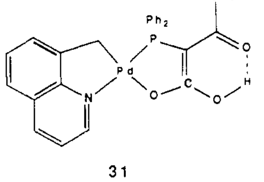
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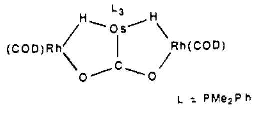
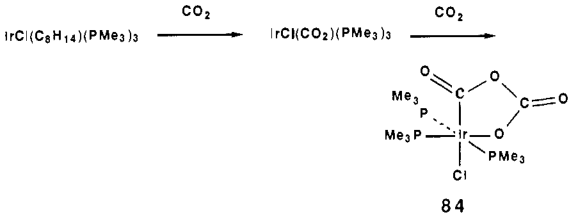


83

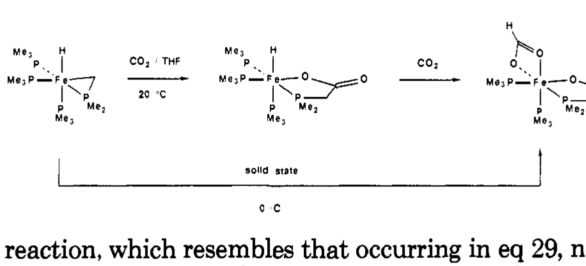
In the cases of **77**,[108] **78**,[109] **79**,[110] and **80**,[111] CO_2 is η^2-coordinated to the metal through the carbon atom and one of the oxygen atoms, whereas in complex **81**, CO_2 is μ, η^3-coordinated (C-bonded to cobalt and O-bonded to two different potassium ions).[112] Complex **82** was reported to have a η^1-coordinated CO_2 ligand (C-bonded to rhodium), although intra- and/or intermolecular C–H···O interactions could be involved.[113] Complex **83** is a unique example of CO_2 bound to three transition metals[114a] (osmium and rhenium complexes containing a bridging CO_2 fragment are not detailed here as they did not result from a direct reaction with carbon dioxide[114b–e]). The fact that these compounds were stable enough to permit isolation may account for the fact that they were unable to undergo further reactions. Therefore the question arises to know whether coordination of CO_2 correlates with chemical activation of CO_2. Note however that the stable CO_2-containing complex **31** has recently been shown to be a catalyst precursor in the synthesis of lactone **43** from butadiene and CO_2.[115] The reaction of $[IrCl(C_8H_{14})(PMe_3)_3]$ with CO_2 is thought to proceed in a stepwise manner by addition of the nucleophilic complex to CO_2, the resulting more basic oxygen atom binding to a second CO_2 molecule, via O–C bond formation (eq 37).[116] Complex **84** can be regarded as an intermediate of the metal-promoted conversion of CO_2 to carbonates and CO. The isolation of a transition-metal complex containing such a C_2O_4 unit is rather rare[72] while carbon–carbon bond formation is exceptional.



(37)

Recent theoretical studies have examined the coordination modes of CO_2 in its complexes.[107] They have led to a better understanding of the factors governing the bonding in CO_2 complexes. The importance of the nature of the frontier orbitals was emphasized. Thus, the best situation for the occurrence of the η^2 side-on mode is the presence of a dπ orbital as the HOMO and an empty dσ orbital pointing to the CO_2 ligand, as in **79** and **80**. The η^1-C mode is most favored when the HOMO is mainly composed of a dσ orbital and when the metal is in a low oxidation state, as found in the d^8 complexes **81**, **82**,[107h] or $Cp(CO)_2FeCO_2^-$.[107k,l] Although no complex with a η^1 end-on coordination of CO_2 has been isolated yet, this bonding mode could occur in the initial step of the formation of some CO_2 complexes and be easily converted to afford a side-on geometry. Conversely, calculations have suggested that weakening of the metal–carbon interaction involving a side-on coordinated CO_2 molecule can lead to the end-on conformer which facilitates nucleophilic attack at carbon.[107e] This could account, e.g., for the head-to-tail coupling of CO_2 shown in eq 37.

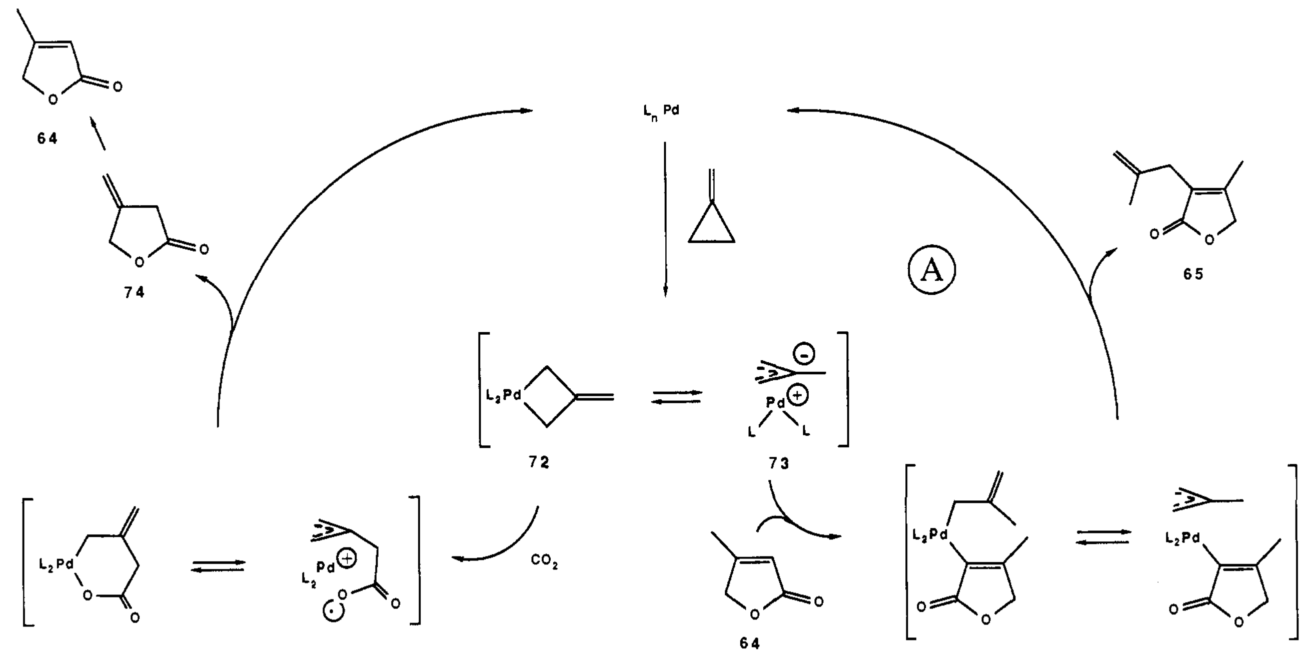
It is interesting to note that the addition of the first CO_2 molecule to $[Fe(PMe_3)_4]$ (entry 33, Table I) occurs with formation of a coordinated functional phosphine ligand (eq 38), which allows a second CO_2 insertion to occur into the Fe–H bond.[45] The first step in this reaction, which resembles that occurring in eq 29, nicely illustrates that a modification of the chemical reactivity of a complex can be induced by its reaction with CO_2. Such features might also occur in cases where the intermediate species is too unstable to be isolated.



(38)

Oxalate formation from carbon dioxide has been claimed in a German patent.[72] Titanium oxalate complexes $[(\eta\text{-}C_5Me_5)_2Ti]_2(C_2O_4)$ were prepared in 63% yield by reacting $[(\eta\text{-}C_5Me_5)_2Ti(CH_2)_3N(Bu)CH_2CH_2N(Bu)(CH_2)_3Ti(\eta\text{-}C_5Me_5)_2]$ with CO_2 in benzene. This is

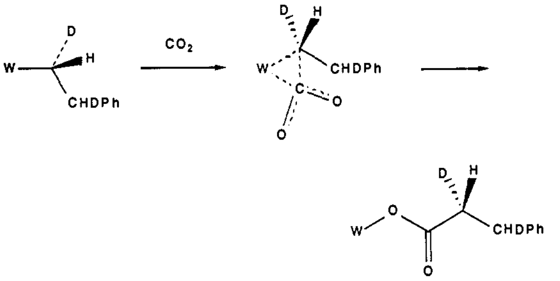
SCHEME X



a unique example of oxalate formation by reductive coupling of transition-metal-activated carbon dioxide. Such a reaction requires an electron transfer from the titanium center, affording a radical anion that is known to convert into an oxalate anion (eq 39). A related C–C

$$2CO_2 + 2e^- \rightarrow 2(CO_2^{\bullet -}) \rightarrow (C_2O_4)^{2-} \qquad (39)$$

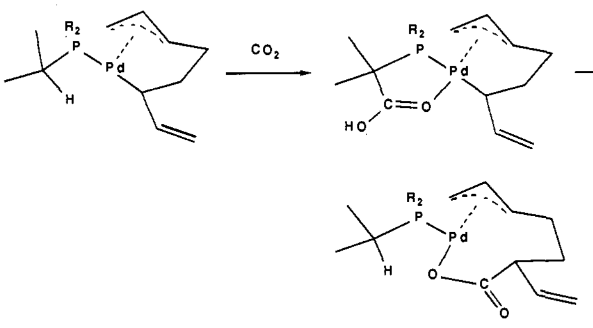
bond forming reaction has been observed between ketones on Cp_2TiR complexes.[17] The reaction of CO_2 with organic substrates may not require such a one-electron-transfer process but rather the activation of the organic substrate by the metal complex. CO_2 inserts readily in many M–C bonds. Elegant investigations about the mechanistic pathway of these reactions have been performed by Darensbourg et al.[24a] The reaction proceeds with retention of configuration at the originally metal-bound carbon atom, suggesting a concerted mechanism (eq 40), which is consistent with kinetic measurements. The participation of a free coordination site, where CO_2 may possibly be bound before the insertion process takes place, could be excluded. Therefore, coordination of CO_2 may not be required here to generate the new C–C bond. As a matter of fact, the CO_2 complexes isolated so far, with the exception of **31**,[115] have not been reported to display any significant catalytic activity in the coupling of CO_2 with organic substrates. Conversely, with the catalytically active systems, no CO_2 complex has been isolated yet. This may also simply reflect the situation of a conflicting balance between stability and reactivity.



(40)

6. Concluding Remarks

The highly desired carbon–carbon coupling between CO_2 and an organic substrate has been achieved stoichiometrically and catalytically. In the course of such studies, a number of interesting metallocarboxylate complexes have been prepared and characterized. Their further evolution with liberation of a CO_2-containing organic product relies on various conditions, e.g., the possibility of reductive elimination at the metal, which may be critically tuned by the ancillary ligands, a relatively easy metal–oxygen bond rupture, and/or the availability of external hydrogen sources. Among the latter, solvents are often decisive, they must also ensure a high solubility of CO_2 and not be too basic in order to maintain the electrophilic character of the C atom of CO_2. One of the major problems associated with the catalytic incorporation of carbon dioxide into organic substrates may well be that of the generation of M–C bonds via C–H or C–C bond cleavage of the organic substrate. It is also noteworthy that, if a ligand contains a C–H bond susceptible to insert CO_2, it may bring the "activated" CO_2 in proximity to the reactive site of the molecule where the C–C coupling will actually take place. On the basis of the results obtained with the reversible CO_2 carrier **31** shown in eq 29, it has been suggested recently that this might be a key step in the palladium-catalyzed telomerization of butadiene with CO_2, affording lactones (eq 41).[87] Although stoichiometric "bis CO_2 insertion" reactions have been reported,



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there is still no example of such a catalytic reaction, which would of course be of considerable interest. In the last few years, very promising results about aliphatic C–H bond activation have been published[117] and if insertion of CO_2 into the newly formed M–C bond were possible, direct functionalization of alkanes could result. Remember that formation of aliphatic acids from CO_2 and methane[118] or pentane[119] has been claimed and remains a thermodynamically conceivable possibility ($CH_4(g) + CO_2(g) \rightarrow CH_3COOH(l)$, $\Delta H° = -3.8$ kcal/mol!)

Acknowledgments. Our own research in this area was supported by the CNRS and SNPE in the GS CO_2 and by the Université Louis Pasteur de Strasbourg. We are grateful to Dr. Ballivet-Tkatchenko and Professors H. Hoberg and W. Keim for sharing results prior to publication and to Drs. J.-P. Collin and R. Ziessel for interesting discussions about the electrochemical reactions. We are grateful to the referees for constructive comments.

Registry No. CO_2, 124-38-9.

7. References

(1) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; Reidel: Dordrecht, 1983; p 169.

(2) Vol'pin, M. E.; Kolomnikov, I. S. *Pure Appl. Chem.* **1973**, *33*, 567.

(3) (a) Asada, K. In *Organic and Bioinorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha Ltd.: Tokyo, 1982; p 185. (b) Ito, T.; Yamamoto, A. In *Ibid.* p 79. (c) Haruki, E. In *Ibid.* p 5. (d) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Chem. Commun.* **1971**, 330.

(4) (a) Halmann, M. *Nature (London)* **1978**, *275*, 115. (b) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Ibid.* **1979**, *277*, 637. (c) Lehn, J. M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701. (d) Hawecker, J.; Lehn, J. M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (e) *Ibid.* **1985**, 56. (f) Bradley, M. G.; Tysak; T.; Graves, D. J.; Vlachopoulos, N. A. *Ibid.* **1983**, 349. (g) Sullivan, B. P.; Meyer, T. J. *Ibid.* **1984**, 1244. (h) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109. (i) Willner, I.; Mandler, D.; Riklin, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1022. (j) Maidan, R.; Willner, I. *J. Am. Chem. Soc.* **1986**, *108*, 8100. (k) *Carbon Dioxide as a Source of Carbon: Biochemical and Chemical Uses*; Aresta, M.; Forti, G., Eds.; Reidel: Dordrecht, NATO ASI Series C, Vol. 206, 1987. (l) Mandler, D.; Willner, I. *J. Am. Chem. Soc.* **1987**, *109*, 7884.

(5) (a) Ogura, K.; Yoshida, I. *J. Mol. Catal.* **1986**, *34*, 67. (b) Ogura, K.; Takamagari, K. *J. Chem. Soc., Dalton Trans.* **1986**, 1519. (c) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181. (d) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1987**, *109*, 3330 and references cited therein.

(6) (a) Sneeden, R. P. A. *Actual. Chim.* **1979**, 22. (b) Denise, B.; Sneeden, R. P. A. *CHEMTECH* **1982**, 108. (c) Sneeden, R. P. A. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 8, p 225. (d) Sneeden, R. P. A. *J. Mol. Catal.* **1982**, *17*, 349.

(7) (a) Vol'pin, M. E. *Pure Appl. Chem.* **1972**, *30*, 607. (b) Kolomnikov; I. S.; Stepovska, G.; Tyrlik, S.; Vol'pin, M. E. *Zh. Obshch. Khim.* **1972**, *42*, 1652. (c) *Ibid.* **1974**, *44*, 1743; *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 1710.

(8) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 334.

(9) Lapidus, A. L.; Ping, Y. Y. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 63.

(10) (a) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (b) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613.

(11) (a) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, 22, 129. (b) Darensbourg, D. J.; Ovalles, C. *CHEMTECH* **1985**, 636.

(12) Behr, A. *Angew. Chem., Int. Ed. Engl.* in press.

(13) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

(14) Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1985**, *4*, 2062.

(15) (a) Fischer, E. O.; Filippou, A. C.; Alt, H. G.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 203.

(16) See, for example: Ashby, E. *Q. Rev.* **1967**, *21*, 259.

(17) Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297.

(18) (a) Kolomnikov, I. S.; Lobeeva, T. S.; Vol'pin, M. E. *Zh. Obshch. Khim.* **1972**, *42*, 2232; *J. Gen. Chem. USSR (Engl. Transl.)* **1972**, *42*, 2229. (b) Johnston, R. F.; Cooper, J. C. *Organometallics* **1987**, *6*, 2448.

(19) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

(20) Kolomnikov, I. S.; Lobeeva, T. S.; Gorbachevskaya, V. V.; Aleksandrov, G. G.; Struchkov, Yu. T.; Vol'pin, M. E. *Chem. Commun.* **1971**, 972.

(21) Razuvaev, G. A.; Vyshinskaya, L. I.; Vasil'eva, G. A.; Malysheva, A. V.; Mar'in, V. P. *Inorg. Chim. Acta* **1980**, *44*, L285.

(22) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I.; Drobotenko, V. V. *J. Organomet. Chem.* **1981**, *208*, 169.

(23) (a) Darensbourg, D. J.; Kudaroski, R. *J. Am. Chem. Soc.* **1984**, *106*, 3672. (b) Darensbourg, D. J.; Kudaroski Hanckel, R.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. (c) Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 977.

(24) (a) Darensbourg, D. J.; Grötsch, G. *J. Am. Chem. Soc.* **1985**, *107*, 7473. (b) Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522. (c) Kundel, P.; Berke, H. *J. Organomet. Chem.* **1988**, *339*, 297.

(25) (a) Jacob, K.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1979**, *455*, 3. (b) Maruyama, K.; Ito, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 849. (c) Normant, J.-F.; Cahiez, G. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Verlag Salle/Sauerländer, 1983; p 173.

(26) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *118*, 65.

(27) (a) Kolomnikov, I. S.; Gusev, A. O.; Belopotapova, T. S.; Grigoryan, M. Kh.; Lysyak, T. V.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1974**, *69*, C10. (b) Darensbourg, D. J.; Grötsch, G.; Wiegreffe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827.

(28) (a) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069. (b) Dahlenburg, L.; Prengel, C. *J. Organomet. Chem.* **1986**, *308*, 63.

(29) (a) Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1978**, 615. (b) Behr, A.; Keim, W.; Thelen, G. *J. Organomet. Chem.* **1983**, *249*, C38.

(30) Neidlein, R.; Rufinska, A.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 641. (b) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 6424.

(31) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(32) Cahiez, G.; Normant, J. F.; Bernard, D. *J. Organomet. Chem.* **1975**, *94*, 463.

(33) (a) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1973**, *49*, C57. (b) Ikariya, T.; Yamamoto, A. *Ibid.* 1974, 72, 145. (c) Miyashita, A.; Yamamoto, A. *Ibid.* **1976**, *113*, 187. (d) Marsich, N.; Camus, A.; Nardin, G. *Ibid.* **1982**, *239*, 429.

(34) Tsuda, T.; Ueda, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 380.

(35) De Pasquale, R. J.; Tamborski, C. *J. Org. Chem.* **1969**, *34*, 1736.

(36) Dubot, G.; Mansuy, D.; Lecolier, S.; Normant, J. F. *J. Organomet. Chem.* **1972**, *42*, C105.

(37) Inoue, S.; Yokoo, Y. *J. Organomet. Chem.* **1972**, *39*, 11.

(38) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

(39) (a) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648. (b) Behr, A.; Herdtweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1262. (c) Behr, A.; Herdtweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *Organometallics* **1987**, *6*, 2307.

(40) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1978**, *100*, 630.

(41) Manzer, L. E.; Gearhart, R. C.; Guggenberger, L. J.; Whitney, J. F. *J. Chem. Soc., Chem. Commun.* **1976**, 942.

(42) (a) Manzer, L. E. *J. Organomet. Chem.* **1977**, *135*, C6. (b) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.

(43) (a) Darensbourg, D. J.; Kudaroski, R.; Delord, T. *Organometallics* **1985**, *4*, 1094. (b) Green, M. H.; Parkin, G.; O'Hare, D.; Wong, L.-L.; Derome, A. E. *J. Organomet. Chem.* **1986**, *317*, 61.

(44) Behr, A.; Kanne, U.; Thelen, G. *J. Organomet. Chem.* **1984**, *269*, C1.

(45) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2213.

(46) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 2391.

(47) (a) Sato, F.; Iijima, S.; Sato, M. *J. Chem. Soc., Chem. Commun.* 1981, 180. (b) Klei, E.; Teuben, J. H.; De Liefdemejer, H. J.; Kwak, E. J.; Bruins, A. P. *J. Organomet. Chem.* **1982**, *224*, 327.

(48) Nieman, J.; Teuben, J. H. *J. Organomet. Chem.* **1985**, *287*, 207.

(49) Kramarz, W.; Kurek, S.; Nowak, M.; Urban, M.; Wlodarczyk, A. *Pol. J. Chem.* **1982**, *56*, 1187.

(50) (a) Tsuda, T.; Chujo, Y.; Saegusa, T. *Synth. Commun.* **1979**, *9*, 427. (b) Saegusa, T.; Tsuda, T.; Nakajo, Y. Jpn. Kokai Tokkyo Koho 8015440, 1980; *Chem. Abstr.* **1980**, *93*, 204441z.

(51) Jolly, P. W.; Stobbe, S.; Wilke, G.; Goddard, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 124.

(52) Ito, T.; Kindaichi, V.; Takami, Y. *Chem. Ind.* **1980**, Jan. 19, 83.

(53) Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5.

(54) Santi, R.; Marchi, M. *J. Organomet. Chem.* **1979**, *182*, 117.

(55) Behr, A.; v. Ilsemann, G. *J. Organomet. Chem.* **1984**, *276*, C77.

(56) Demerseman, B.; Mahé, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394.

(57) (a) Burkhart, G.; Hoberg, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 76. (b) Hoberg, H.; Schaefer, D.; Burkhart, G. *J. Organomet. Chem.* **1982**, *228*, C21. (c) Hoberg, H.; Schaefer, D. *Ibid.* **1982**, *238*, 383.

(58) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1975**, 963.

(59) (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

(60) (a) Alvarez, R.; Carmona, E.; Cole-Hamilton, D. J.; Galindo, A.; Gutiérrez-Puebla, E. G.; Monge, A.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1985**, *107*, 5529. (b) Carmona, E. Concoord XVII, Carry le Rouet, 17–21 May 1987.

(61) (a) Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1982**, *236*, C28. (b) *Ibid.* **1983**, *251*, C51. (c) Hoberg, H.; Schaefer, D.; Burkhart, G.; Krüger, C.; Romao, M. J. *Ibid.* **1984**, *266*, 203. (d) Hoberg, H.; Peres, Y.; Milchereit, A. *Ibid.* **1986**, *307*, C41. (e) *Ibid.* **1986**, *307*, C38. (f) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771.

(62) Behr, A.; Thelen, G. *C_1 Mol. Chem.* **1984**, *1*, 137.

(63) Walther, D.; Dinjus, E.; Sieler, J.; Andersen, L.; Lindqvist, O. *J. Organomet. Chem.* **1984**, *276*, 99.

(64) (a) Walther, D.; Dinjus, E.; Sieler, J.; Thanh, N. N.; Schade, W.; Leban, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 835. (b) Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1983**, *255*, C15. (c) Hoberg, H.; Schaefer, D.; Oster, B. W. *Ibid.* **1984**, *266*, 313. (d) Walther, D.; Dinjus, E.; Görls, H.; Sieler, J.; Lindqvist, O.; Andersen, L. *Ibid.* **1985**, *286*, 103. (e) Schröder, W.; Pörschke, K. R. *Ibid.* **1987**, *322*, 385.

(65) (a) Dinjus, E.; Kaiser, J.; Sieler, J.; Walther, D. *Z. Anorg. Allg. Chem.* **1981**, *483*, 63. (b) Kaiser, J.; Sieler, J.; Braun, U.; Golic, L.; Dinjus, E.; Walther, D. *J. Organomet. Chem.* **1982**, *224*, 81. (c) Walther, D.; Dinjus, E.; Herzog, V. *Z. Chem.* **1984**, *24*, 260.

(66) (a) Dinjus, E.; Walther, D. Ger. (East) DD 222023, 1985; *Chem. Abstr.* **1985**, *103*, 195995d. (b) Dinjus, E.; Walther, D. Ger. (East) DD 218093, 1985; *Chem. Abstr.* **1986**, *104*, 50553u.

(67) (a) Hoberg, H.; Apotecher, B. *J. Organomet. Chem.* **1984**, *270*, C15. (b) Behr, A.; Kanne, U. *Ibid.* **1986**, *317*, C41. (c) Hoberg, H.; Jenni, K.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 810. (d) Hoberg, H.; Jenni, K.; Angermund, K.; Krüger, C. *Ibid.* **1987**, *26*, 153. (e) Hoberg, H.; Jenni, K. *J. Organomet. Chem.* **1987**, *322*, 193. (f) Brookhart, M.; Noh, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829.

(68) Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1984**, *266*, 321.

(69) (a) Normant, J. F.; Cahiez, G.; Chuit, C.; Villieras, J. *J. Organomet. Chem.* **1973**, *54*, C53. (b) *Ibid.* **1974**, *77*, 281.

(70) Westmijze, H.; Kleijn, H.; Bos, H. J. T.; Vermeer, P. *J. Organomet. Chem.* **1980**, *199*, 293.

(71) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(72) Froehlich, H. O.; Schreer, H. Ger. (East) DD 219488, 1985; *Chem. Abstr.* **1985**, *103*, 196262z.

(73) (a) Inoue, Y.; Itoh, Y.; Hashimoto, H. *Chem. Lett.* **1977**, 855. (b) *Ibid.* **1978**, 633.

(74) (a) Inoue, Y.; Itoh, Y.; Kazama, H.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329. (b) Tsuda, T.; Sumiya, R.; Saegusa, T. *Synth. Commun.* **1987**, *17*, 147. (c) Walther, D.; Schönberg, H.; Dinjus, E.; Sieler, J. *J. Organomet. Chem.* **1987**, *334*, 377.

(75) Albano, P.; Aresta, M. *J. Organomet. Chem.* **1980**, *190*, 243.

(76) Lapidus, A. L.; Pirozhkov, S. D.; Koryakin, A. A. *Bull. Acad. Sci. USSR., Div. Chem. Sci. (Engl. Transl.)* **1978**, 2513.

(77) Chan, D. M. T.; Marder, T. B.; Milstein, D.; Taylor, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 6385.

(78) Besecke, S.; Schröder, G. Ger. Offen. DE 2948888 A1, 1981; *Chem. Abstr.* **1981**, *95*, 97107m.

(79) Behr, A.; Kanne, U.; Keim, W. *J. Mol. Catal.* **1986**, *35*, 19.

(80) Sasaki, Y.; Inoue, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1976**, 605.

(81) Inoue, Y.; Sasaki, Y.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2375.

(82) (a) Ito, T.; Kindaichi, Y.; Takami, Y. *Nippon Kagaku Kaishi* **1979**, 1276. (b) Dzhemilev, U. M.; Kunakova, R. V.; Sidorova, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, *10*, 2273.

(83) (a) Musco, A.; Perego, C.; Tartiari, V. *Inorg. Chim. Acta* **1978**, *28*, L147. (b) Musco, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 693. (c) Musco, A.; Santi, R.; Chiusoli, G. P. Ger. Offen. DE 2838610 A1, 1979; *Chem. Abstr.* **1979**, *90*, 186403v (to Montedison S.p.A.).

(84) Daniels, J. A. E.P. 0050445, 1982; *Chem. Abstr.* **1982**, *97*, 127500w (to I.C.I.).

(85) (a) Behr, A.; Juszak, K.-D.; Keim, W. *Synthesis* **1983**, 574. (b) Behr, A.; Juszak, K.-D. *J. Organomet. Chem.* **1983**, *255*, 263. (c) Keim, W.; Behr, A.; Hergenrath, B.; Juszak, K.-D. Ger. Offen. DE 3317013, 1984; *Chem. Abstr.* **1985**, *102*, 78723g (to Hüls A. G.).

(86) Inoue, Y.; Ohashi, R.; Toyofuku, M.; Hashimoto, H. *Nippon Kagaku Kaishi* **1985**, 533.

(87) Behr, A.; He, R.; Juszak, K.-D.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1986**, *119*, 991.

(88) Hoberg, H.; Gross, S.; Milchereit, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 571.

(89) (a) Behr, A.; Juszak, K.-D.; He, R. *8th International Congress on Catalysis*, West Berlin, 2–6 July 1984, Proceedings, V-565. (b) Behr, A.; He, R. *J. Organomet. Chem.* **1984**, *276*, C69.

(90) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J.-C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425.

(91) Lydon, J. E.; Nicholson, J. K.; Shaw, B. L.; Truter, M. R. *Proc. Chem. Soc., London* **1964**, 421.

(92) (a) Jolly, P. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 283 and references cited therein. (b) Benn, R.; Jolly, P. W.; Mynott, R.; Schenker, G. *Organometallics* **1985**, *4*, 1136.

(93) Inoue, Y.; Sekiya, S.; Sasaki, Y.; Hashimoto, H. *Yuki Gosei Kagaku Kyokaishi* **1978**, *36*, 328.

(94) Behr, A. *Bull. Soc. Chim. Belg.* **1985**, *94*, 671.

(95) Behr, A.; Kanne, J. *J. Organomet. Chem.* **1986**, *309*, 215.

(96) Inoue, Y.; Hibi, T.; Satake, M.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1979**, 982.

(97) (a) Binger, P.; Weintz, H.-J. *Chem. Ber.* **1984**, *117*, 654. (b) Binger, P.; Weintz, H.-J. Ger. Offen. DE 3403793, 1985; *Chem. Abstr.* **1985**, *103*, 215149m.

(98) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

(99) (a) Döhring, A.; Jolly, P. W. *Tetrahedron Lett.* **1980**, *21*, 3021. (b) Aresta, M.; Quaranta, E.; Ciccarese, A. *C_1 Mol. Chem.* **1985**, *1*, 283.

(100) Friedel, C.; Crafts, J.-M. *Ann. Chim. (Paris)* **1888**, *6*, 441.

(101) Sugimoto, H.; Kawata, I.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1984**, *266*, C44.

(102) (a) Amatore, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021. (b) Amatore, C.; Nadjo, L.; Savéant, J.-M. *Nouv. J. Chim.* **1984**, *8*, 565 and references cited therein.

(103) See, for example: (a) Bolinger, C. M.; Sullivan, B. P.; Conrad, D.; Gilbert, J. A.; Story, N.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 796. (b) Slater, S.; Wagenknecht, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5367. (c) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 796. (d) Ulman, M.; Aurian-Blajeni, B.; Halmann, M. *CHEMTECH* **1984**, 235. (e) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. (f) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (g) Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, M. *Ibid.* **1982**, *104*, 6384. (h) Fischer, B.; Eisenberg, R. *Ibid.* **1980**, *102*, 7361. (i) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158 and references cited therein.

(104) Becker, J. Y.; Vainas, B.; Eger (Levin), R.; Kaufman (Orenstein), L. *J. Chem. Soc., Chem. Commun.* **1985**, 1471.

(105) (a) Tanji, J. Thèse de Doctorat, Université Paul Sabatier de Toulouse, 10 April 1987. (b) Tkatchenko, I.; Ballivet-Tkatchenko, D.; El Murr, N.; Tanji, J.; Payne, J. D. Fr. Pat. 2542764, 1985 (to SNPE).

(106) (a) Troupel, M.; Rollin, Y.; Perichon, J.; Fauvarque, J.-F. *Nouv. J. Chim.* **1981**, *5*, 621. (b) Fauvarque, J.-F.; Chevrot, C.; Jutand, A.; François, M.; Perichon, J. *J. Organomet. Chem.* **1984**, *264*, 273. (c) Fauvarque, J.-F.; Jutand, A.; Francois, M. *Nouv. J. Chim.* **1986**, *10*, 119.

(107) (a) Sakaki, S.; Kudou, N.; Ohyoshi, A. *Inorg. Chem.* **1977**, *16*, 202. (b) Demoulin, D.; Pullmann, A. *Theor. Chim. Acta* **1978**, *49*, 161. (c) Ozin, G. A.; Huber, H.; McIntosh, D. *Inorg. Chem.* **1978**, *17*, 1472. (d) Sakaki, S.; Kitaura, K.; Morokuma, K. *Ibid.* **1982**, *21*, 760. (e) Mealli, C.; Hoffmann, R.; Stockis, A. *Ibid.* **1984**, *23*, 56. (f) Sânchez Marcos, E.; Caballol, R.; Trinquier, G.; Barthelat, J.-C. *J. Chem. Soc., Dalton Trans.* **1987**, 2373. (g) Caballol, R.; Sânchez Marcos, E.; Barthelat, J.-C. *J. Phys. Chem.* **1987**, *91*, 1328. (h) Sakaki, S.; Dedieu, A. *Inorg. Chem.* **1987**, *26*, 3278. (i) Rosi, M.; Sgamellotti, A.; Tarantelli, F.; Floriani, C. *J. Organomet. Chem.* **1987**, *332*, 153. (j) Branchadell, V.; Dedieu, A. *Inorg. Chem.* **1987**, *26*, 3966. (k) Evans, G. O.; Walter, W. F.; Mills, D. R.; Streit, C.

A. *J. Organomet. Chem.* **1978**, *144*, C34. (l) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970.

(108) (a) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* **1975**, 636. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708. (c) Döhring, A.; Jolly, P. W.; Krüger, C.; Romao, M.-J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 484.

(109) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

(110) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

(111) (a) Alvarez, R.; Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1326. (b) Alvarez, R.; Carmona, E.; Marín, J. M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286.

(112) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(113) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914.

(114) (a) Lundquist, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1986**, *108*, 8309. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1358. (c) Beck, W.; Raab, K.; Nagel, U.; Steimann, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 526. (d) Tso, C. T.; Cuttler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069. (e) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2739.

(115) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.

(116) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615.

(117) (a) Haggin, J. *Chem. Eng. News.* **1983**, Feb 14, 9. (b) Ephritikhine, M. *Nouv. J. Chim.* **1986**, *10*, 9. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245 and references cited therein.

(118) Brit. Pat. 226248; U.S. Pat 1916061; U.S. Pat. 1704965.

(119) Hopf, H.; Zimmermann, T. *Helv. Chim. Acta* **1964**, *47*, 1293.

(120) Moloy, K. G.; Marks, T. J. *Inorg. Chim. Acta* **1985**, *110*, 127.

(121) Aresta, M.; Quaranta, E.; Ciccarese, A. *C_1 Mol. Chem.* **1985**, *1*, 267.