

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

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Contents

1. Abbreviations	747
2. Introduction	747
3. Stoichiometric Reactions with Carbon-Carbon Bond Formation	747
4. Catalytic Reactions with Carbon-Carbon Bond Formation	751
4.1. Reactions with Alkynes	751
4.2. Reactions with Alkenes	754
4.3. Reactions with Conjugated Dienes	755
4.4. Reactions with Methylene-cyclopropanes	758
4.5. Reactions with Allene	759
4.6. Reactions with Aromatic Compounds	759
4.7. Electrochemical Reactions	759
5. The Relevance of CO ₂ Complexes	760
6. Concluding Remarks	761
7. References	762

1. Abbreviations

acac	acetylacetonato
bipy	2,2'-bipyridine
<i>i</i> -Bu	isobutyl
<i>t</i> -Bu	<i>tert</i> -butyl
<i>n</i> -Bu	<i>n</i> -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>i</i> -Pr	isopropyl
<i>n</i> -Pr	<i>n</i> -propyl
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine

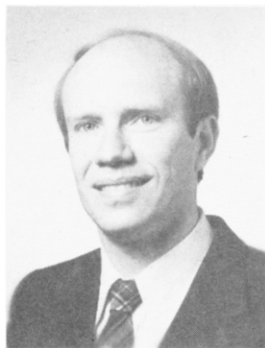
2. Introduction

The fixation of carbon dioxide by green plants using solar energy is the most important chemical process

running on Earth. The total amount of CO₂ in the atmosphere and in the oceans is estimated to represent 10¹⁴ tons of carbon while carbonates represent 10¹⁶ tons of carbon.^{1,2} In photosynthesis, carbon dioxide is reduced by water into carbohydrates with sunlight as the energy source.^{3a} Light-induced CO₂ fixation or reduction processes are actively studied in order to use CO₂ 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 CO₂ 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 CO₂, NH₃, 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:H₂ ratio in the steam cracking of methane; and methanol production involving addition of CO₂ to the CO/H₂ mixtures. One of the major problems associated with the use of CO₂ 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 CO₂ was shown to assist or modify the course of the catalytic reaction. But since in these reactions CO₂ 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 CO₂ are retained in the final product(s), avoiding therefore the use of oxygen sinks required when deoxygenation of CO₂ 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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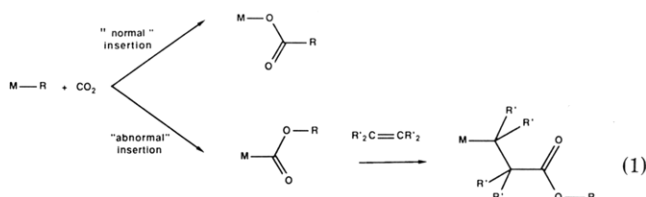


Dominique Nobel received his degree of Ingénieur-Chimiste from the Ecole Nationale Supérieure de Chimie de Strasbourg in 1983. During his Dr.-Ing. Thesis, which he obtained from the Université Louis Pasteur of Strasbourg in 1987, he has worked on the transition-metal chemistry of functional phosphines and the catalytic telomerization of butadiene with carbon dioxide.

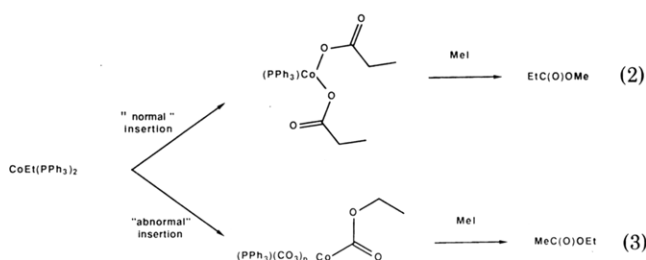
a precoordinated organic substrate, dimerization and/or reduction by the metal center. Some of these reactions have been reviewed recently.^{7a-13}

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

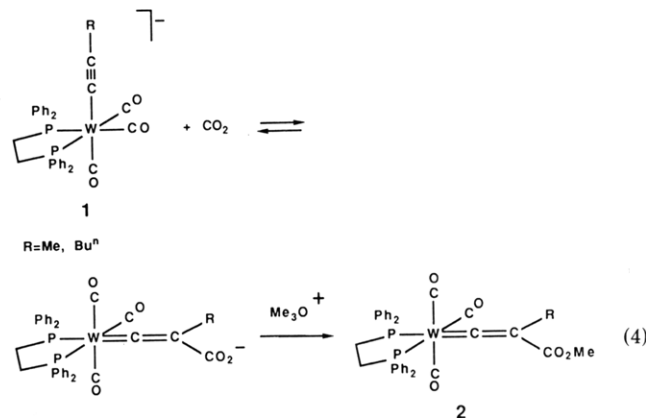
this reaction, called the "normal" and the "abnormal" insertion (eq 1). There is only one example of the



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, CO₂ 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.

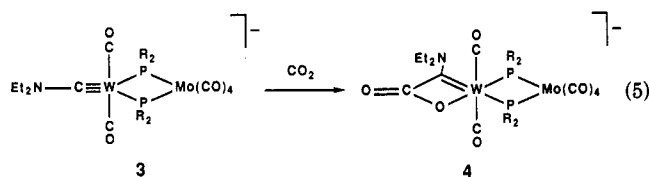


Two other unexpected reactions of carbon dioxide have been reported. The former is a rare example of C-C coupling (eq 4) where the tungsten acetylide anions **1** react with carbon dioxide with formation of the vinylidene products **2**, after methylation¹⁴ (Table I, entry 48). The fact that C-C bond formation occurs at the

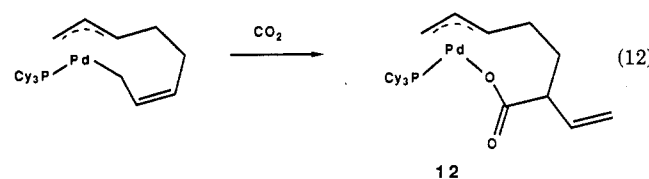
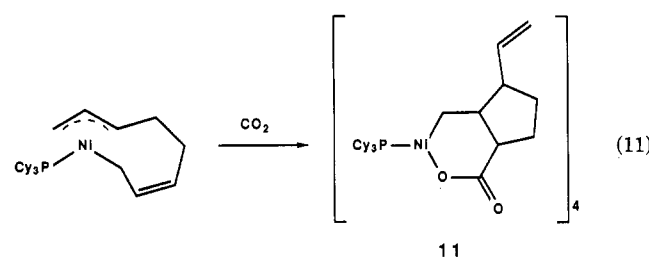
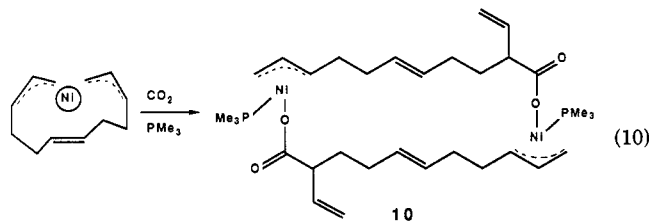
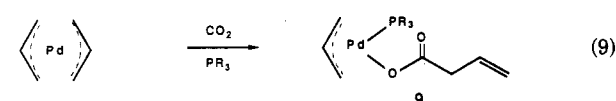
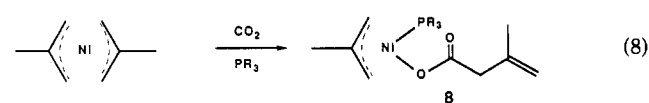
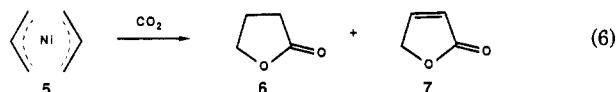


β position can be understood in terms of transfer of the nucleophilicity of the C₂ fragment from C _{α} to C _{β} . Ion-pair formation at the β -carbon was suggested to act as kinetic mediator in this system, and significant counterion effects were observed in this reaction: in contrast to the Li⁺ and Na⁺ salts of **1**, the PPN⁺ salt does not react with CO₂. Furthermore, when R = phenyl, even the lithium salt is unreactive toward CO₂.

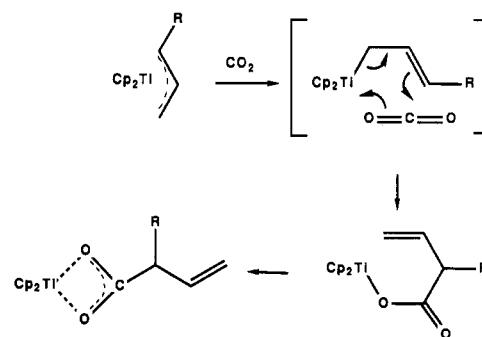
Another unusual reaction of CO₂ is that of the phosphido-bridged bimetallic anionic carbyne complex **3**, which adds 1 equiv of CO₂, affording the new oxatungstacyclobutanone complex **4**¹⁵ (eq 5) (Table I, entry 49).



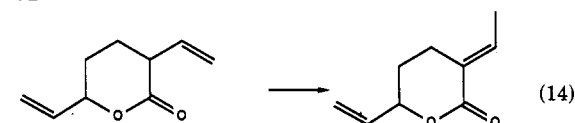
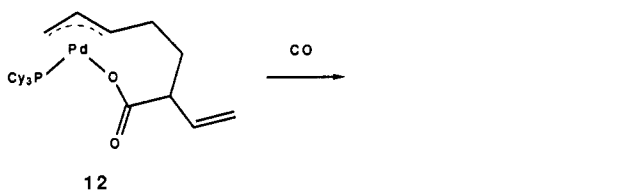
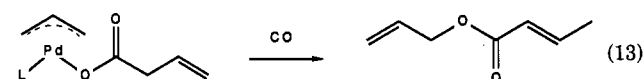
In all other cases, normal insertion takes place (see Table I). This reaction has been described for many complexes, particularly of nickel and palladium, which are known to be the most active CO₂-substrate coupling catalysts. Carbon dioxide insertion into allylic metal complexes can lead to several types of products, such as carboxylato species or lactones (eq 6–9), depending on the nature of the metal and of its ligands.



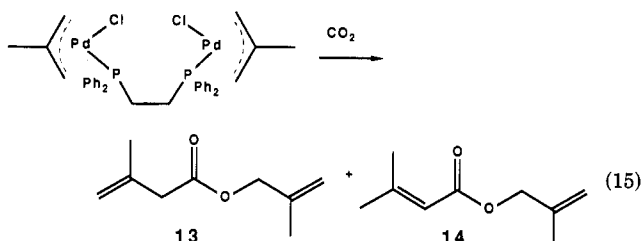
In the absence of tertiary phosphine ligands the bis(η³-allyl)nickel complex 5 reacts with CO₂ to form the γ-butyrolactone 6 and the furanone 7 (eq 6).⁵⁰ Nickel or palladium carboxylato complexes may be isolated when a phosphine is present (eq 8–12). In the reaction of allyltitanium complexes with CO₂, Teuben et al. have suggested the following electrocyclic mechanism (Table I, entry 35).^{47b}



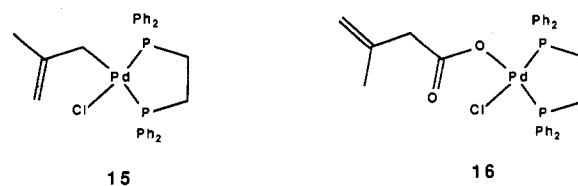
The study of systems in which η¹- and η³-allyl fragments are present allows to suggest that CO₂ inserts only into the metal-carbon σ-bond of the η¹-allyl ligand. The carboxylato ligand formed can be displaced by carbon monoxide in a reductive coupling reaction with the remaining allyl group, eliminating an ester (eq 13)⁵³ or a lactone (eq 14).^{92a}



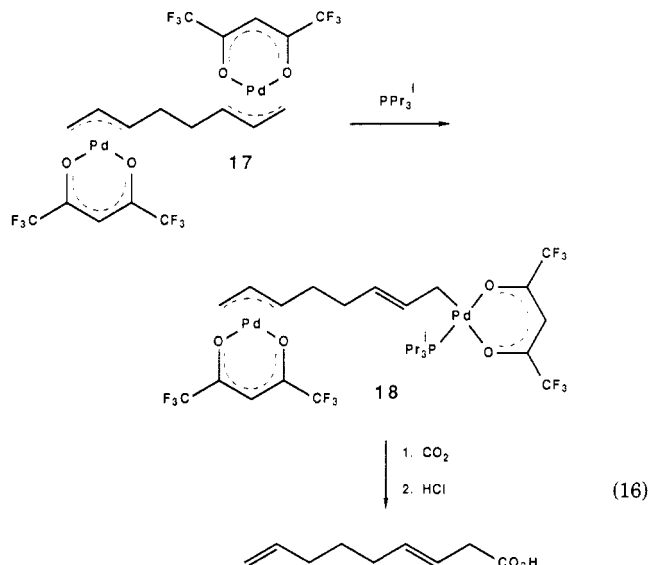
When bis(2-methylallyl)bis(diphenylphosphino)ethane)dipalladium complexes are reacted with CO₂, in acetonitrile at 80 °C, the esters 13 and 14 are formed in 30% and 15% yields, respectively (eq 15).⁵⁴ The



(η¹-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 (η³-2-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-

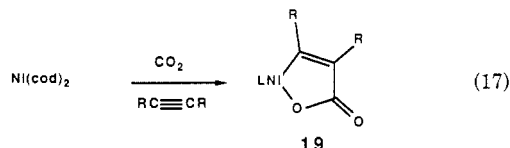


hexafluoroacetylacetonato)palladium), 17, another binuclear palladium complex, a 3,8-nonadienoic acid is isolated after acidification (eq 16).⁵⁵ In the former case both allyl groups participate in the CO₂ coupling re-

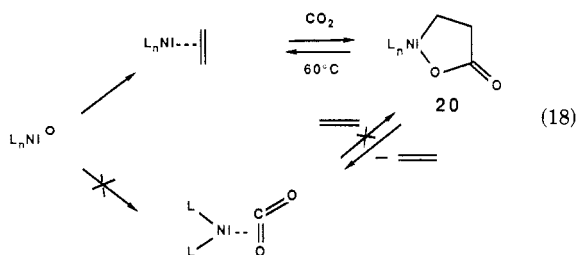


action whereas in the latter, only the allyl group coordinated to the palladium center bearing the phosphine ligand in 18 couples with CO_2 . This can be related to the previous observations that CO_2 inserts only in a η^1 -bonded allyl group.

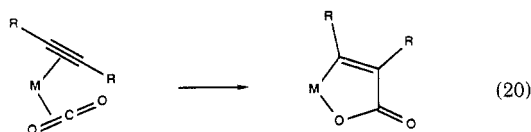
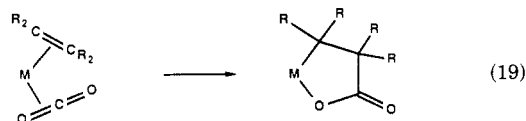
Very interesting results have been published recently on the coupling reactions between alkynes (eq 17) (Table I, entry 50),⁵⁷ alkenes,⁶¹ conjugated dienes^{62-67a,b} or cumulenes,⁶⁸ and CO_2 on Ni(0) centers. No inter-



mediate, 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}



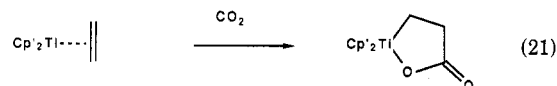
More generally, many metal-mediated reactions of CO_2 with unsaturated substrates may be rationalized in terms of electrocyclic transformations (eq 19, 20).⁵²



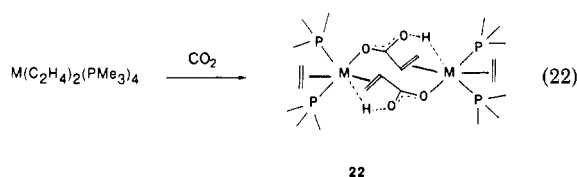
This may extend to coupling reactions of CO_2 with, e.g., aldehydes^{65a,b} or imines,^{65c} which lead to C-N or C-O

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.

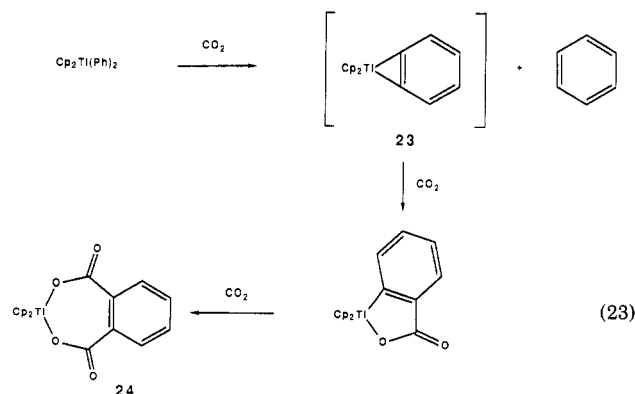


Ethylene complexes of tungsten and molybdenum have also been found to react with CO_2 . The reaction of *trans*- $[\text{M}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4]$ ($\text{M} = \text{Mo}, \text{W}$) with CO_2 yielded unexpected products (eq 22) (Table I, entry 54).^{60a} An acrylic unit bridging the two metal atoms

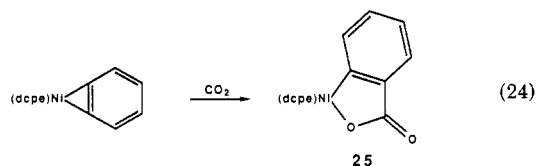


was generated, corresponding formally to a CO_2 insertion into one of the ethylene C-H bonds. The structure of the molybdenum complex has been established by X-ray and neutron diffraction, revealing a hydrido metal acrylate structure.⁶⁰

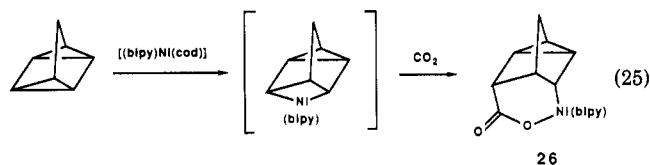
In cases where two metal-carbon σ -bonds are present in the precursor complex, it is generally observed that carbon dioxide inserts, at best, only into one of these metal-carbon bonds. This applies to thermal or as found recently,^{18b} to photochemical reactions. However, some complexes are able to 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



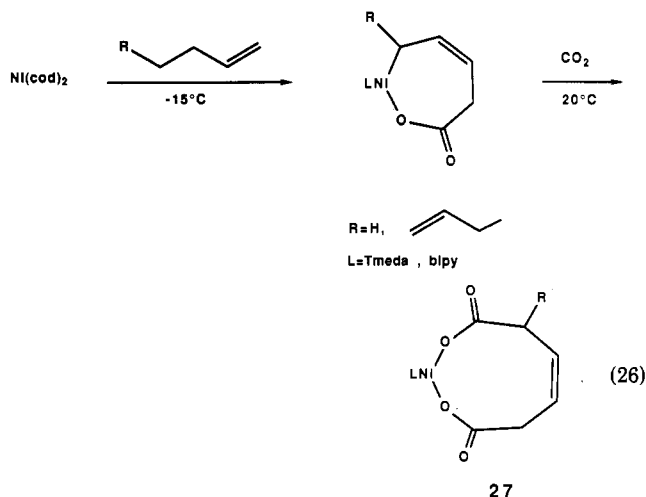
isolated nickel-benzyne complex $[(\text{dcpe})\text{Ni}(\eta^2\text{-C}_6\text{H}_4)]$ was reacted with CO_2 (eq 24), only insertion into one nickel-carbon bond was detected.³¹ Similarly, mo-



noininsertion of CO₂ occurred with the postulated intermediate of the reaction between quadricyclane and [(bipy)Ni(cod)], affording **26** (Table I, entry 70).⁶²

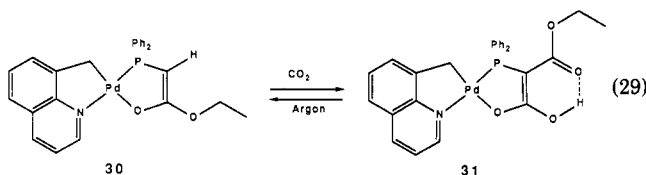
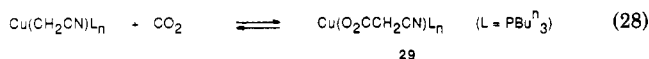
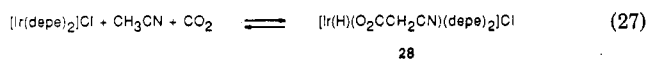


When 1,3-dienes were reacted with CO₂ in the presence of [Ni(cod)₂] and N-donor ligands, two molecules of CO₂ were incorporated, affording α,ω-diacid derivatives (eq 26) (Table I, entry 63).^{67a,b} Beside the above-mentioned



titanium or nickel complexes, other examples of “bis CO₂ 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}

Carbon-carbon bond formation resulting from coupling of CO₂ 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)pal-



ladium complexes, such as **30**, were reacted with carbon dioxide, under ambient conditions, carbon-carbon bond formation occurred, corresponding formally to CO₂ 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 CO₂ molecule and regeneration of **30**. This

remains the only example, to our knowledge, where the reversible CO₂ 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 CO₂ and butadiene¹¹⁵ (see next section), while copper cyanoacetate has been successfully employed as a stoichiometric carboxylating agent of cyclohexanone.⁴⁰

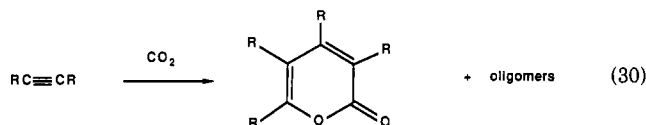
The products examined in this section result from stoichiometric CO₂-coupling reactions but are not necessarily involved in the catalytic reactions which will be examined in the next section. Thus, for example, a system analogous to **17** containing acac instead of hfacac, catalyzes the reaction of CO₂ 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 CO₂ with retention of both oxygen atoms of CO₂ in the product. Alkynes, alkenes, dienes, strained cycles, and benzene react catalytically with CO₂ 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 CO₂, catalyzed by Ni(cod)₂/Ph₂P(CH₂)_nPPh₂ systems (*n* = 2, 3, 4), was reported to yield pyrones and acetylenic oligomers.^{73,74} The alkynes were reacted under 50-bar pressure of CO₂ in benzene at 120 °C for 20 h (eq 30). With hexynes



the best yields were obtained when Ph₂P(CH₂)₄PPh₂ and an excess of PPh₃ 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 Me₂P(CH₂)₂PMe₂ 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 (CO₂) 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 CO₂ with C-C Bond Formation

entry	precursor complex	isolated product	ref
Insertion into Metal-Alkyl or Metal-Aryl Bonds			
1	RMgX	RCO ₂ MgX	16
2	Cp ₂ TiR (R = Me, <i>n</i> -Bu)	Cp ₂ Ti(O ₂ CR)	17
3	Ti(CH ₂ Ph) ₄	(PhCH ₂) ₃ Ti(O ₂ CCH ₂ Ph)	19
4	Cp ₂ TiMe ₂	Cp ₂ Ti(O ₂ CMe)Me	18
5	Cp ₂ TiPh ₂	Cp ₂ Ti[<u><i>o</i>-C₆H₄C(O)O</u>] (23) + Cp ₂ Ti[<u><i>o</i>-C₆H₄{C(O)O}</u>] ₂ (24)	2, 20
6	MeZrPh	MeCO ₂ ZrO ₂ CPh	21
7	VR ₃ (THF) _n (R = C ₆ F ₅ , CH ₂ SiMe ₃)	V(OCOR) ₂ + V(OCOR) ₃	22
8	[RM(CO) ₅] ⁻ (M = Cr, W; R = Me, Et, CHDCHDPh)	[RCO ₂ M(CO) ₅] ⁻	23, 24a
9a	[MeW(CO) ₄ L] ⁻ (L = PMe ₃ , P(OMe) ₃)	[MeCO ₂ W(CO) ₄ L] ⁻	23b
9b	WMe(CO) ₂ (NO)L ₂ (L = PPh ₃ , P(<i>o</i> - <i>i</i> -Pr) ₃)	W(η ² -O ₂ CMe)(CO)(NO)L	24b,c
10	Mn(CH ₂ Ph) ₂	Mn(OCOC ₂ H ₅) ₂	25a
	MnR ₂ , R ₃ MnLi(or MgCl) (R = alkyl, alkenyl, alkynyl)	RCOOH	25b
	MnPh ₂ (PCy ₃)	PhCO ₂ Mn(PCy ₃)	25c
11	FeMe ₂ (dppe) ₂	Fe(O ₂ CMe) ₂ (CO) ₂ (py) _n	26
12	CoEt(CO)(PPh ₃) ₂	Co(CO) ₃ (COOEt)(PPh ₃) + Co(OCOEt) ₂ (PPh ₃) ₂	7b,c
13	RhArL _n (L = PMe ₃ , PPh ₃ , <i>n</i> = 3; L = dppe, <i>n</i> = 1; L = <i>t</i> -BuP{(CH ₂) ₃ PPh ₂ } ₂)	Rh(O ₂ CAr)L _n	27 28a 28b
14	NiEt ₂ (bipy)	NiEt(O ₂ CET)(bipy) + Ni(O ₂ CET) ₂ (bipy)	29
15	Ni(X ⁻ O)Ph(PPh ₃) + MeOH/BF ₃ (X ⁻ O = [Ph ₂ PCHC(O)Ph] ⁻ , [Ph ₂ PNC(O)Ph] ⁻ , [Ph ₂ AsCHC(O)Ph] ⁻ , [MeC(O)CHC(O)Me])	PhCO ₂ Me	29b
	Ni(X ⁻ O)Ph(PPh ₃) + C ₂ H ₄ /MeOH/BF ₃ (X ⁻ O = as above)	Ph(CH ₂) ₂ CO ₂ Me	
16	Ni(<u><i>o</i>-C₆H₄CH₂</u>)(P- <i>n</i> -Bu ₃) ₂	Ni[<u><i>o</i>-C₆H₄C(O)O</u>](P- <i>n</i> -Bu ₃) ₂	30a
	Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)(PMe ₃) ₂	Ni[CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄ C(O)O](PMe ₃) ₂	30b
17	Ni(η ² -C ₆ H ₄)(dcpe)	Ni[<u><i>o</i>-C₆H₄C(O)O</u>](dcpe) (25)	31
18	RCu (R = alkyl, α- or β-ethylenic, or aryl group)	RCOOH	32
19	RCuL _n (R = Me, Et, <i>n</i> -Pr, <i>i</i> -Bu; L = PPh ₃ , PCy ₃ , PPh ₂ Me, PBu ₃ , PEt ₃)	RCO ₂ CuL ₂	33
20	RCu-P- <i>n</i> -Bu ₃ (R = fluorenyl)	RCOOMe	34
21	C ₆ F ₅ Cu(MgBrCl)	C ₆ F ₅ CO ₂ H	35
22	AgCF(CF ₃) ₂ , MeCN	(CF ₃) ₂ CFCO ₂ CH ₂ Ph	36
23	ZnEt ₂	EtCO ₂ ZnEt	37
24	M(Cp') ₂ (Me) ₂ (M = Th, U)	M(Cp') ₂ (O ₂ CMe) ₂ M(Cp') ₂ (O ₂ CMe)(Me)	120
Insertion into Metal-CH ₂ CN Bonds			
25	HFe(CH ₂ CN)(dmpe) ₂	HFe(O ₂ CCH ₂ CN)(dmpe) ₂	38
26	[IrL ₄]Cl in CH ₃ CN (L = PMe ₃ , 1/2 depe)	[HIr(O ₂ CCH ₂ CN)L ₄]Cl	39a
27	ML _n X + CH ₂ (CN) ₂ (M = Ir, Rh; L = PMe ₃ (<i>n</i> = 4), X = H; L = dmpe, depe (<i>n</i> = 2), X = Cl)	[L _n MXH] ⁺ [O ₂ CCH(CN) ₂] ⁻	39b,c
28	Cu(CH ₂ CN)(P- <i>n</i> -Bu ₃) _n	Cu(O ₂ CCH ₂ CN)(P- <i>n</i> -Bu ₃) _n	40
Insertion into Metal-Carbon Bonds of Chelating Metalated Ligands			
29	CpTi(<u><i>o</i>-C₆H₄CH₂NMe₂</u>) ₂	CpTi(<u><i>o</i>-C₆H₃CH₂NMe₂</u>){ <i>m</i> -C(O)O}	41, 42
30	Cr(CH ₂ C ₆ H ₄ - <i>o</i> -NMe ₂) ₃	Cr{OC(O)CH ₂ C ₆ H ₄ - <i>o</i> -NMe ₂ }(CH ₂ C ₆ H ₄ - <i>o</i> -NMe ₂) ₂	42
31	[PPh ₄][W(CO) ₄ (CH ₂ CH ₂ PPh ₂) ₂]	[PPh ₄][W(CO) ₄ {OC(O)CH ₂ CH ₂ PPh ₂ } ₂]	43a
	WH(PMe ₃) ₄ (Me ₂ PCH ₂) ₂	[W(PMe ₃) ₃ (η ¹ -Me ₂ PCH ₂) ₂](C ₃ H ₂ O ₆)	43b
32	Mn(CO) ₄ (CH ₂ CH ₂ PPh ₂)	Mn(CO) ₄ {OC(O)CH ₂ CH ₂ PPh ₂ }	44
33	Fe(PMe ₃) ₄	HFe{OC(O)CH ₂ PMe ₂ }(PMe ₃) ₃	45
34	Ir(dmpe) ₂ Cl	[HIr{OC(O)CH ₂ MePC ₂ H ₄ PMe ₂ }(dmpe)]Cl	46
Insertion into Metal-Allyl Bonds			
35	Cp ₂ Ti(η ³ -C ₄ H ₇)	Cp ₂ Ti(η ² -O ₂ CC ₄ H ₇)	47b
36	Cp ₂ V(η ¹ -C ₃ H ₅)	Cp ₂ V(η ¹ -O ₂ CC ₃ H ₅)	48
37	Cr(η ³ -C ₃ H ₅) ₃	(η ³ -C ₃ H ₅) ₂ Cr(O ₂ CC ₃ H ₅) ₂ + (η ³ -C ₃ H ₅) ₂ Cr(O ₂ CC ₃ H ₅)	49
38	Ni(η ³ -C ₃ H ₅) ₂	CH ₂ CH ₂ CH ₂ C(O)O (6) + CH ₂ CH=CHC(O)O (7)	50
39	Ni(η ³ -2-MeC ₃ H ₄) ₂	(η ² -2-MeC ₃ H ₄)Ni(η ¹ -O ₂ CC ₄ H ₇)(PR ₃) (8)	51
40	Ni(η ² ,η ³ -C ₁₂ H ₁₈)	[Ni(μ-η ³ -C ₁₂ H ₁₈ C(O)O)](PR ₃) ₂ (10) (R = Me, Cy)	51
41	Ni(η ¹ ,η ³ -C ₈ H ₁₂)(PCy ₃)	[Ni{C ₈ H ₁₂ C(O)O}(PCy ₃) ₄] (11)	51
42	Pd(η ³ -C ₃ H ₅) ₂	CH ₂ =CHCH ₂ COOH	52
43	Pd(η ³ -C ₄ H ₇) ₂	CH ₂ =CH-CH(Me)COOH	52
44	Pd(η ¹ ,η ³ -C ₃ H ₅) ₂ (PR ₃) (R = Me, Cy)	Pd(η ³ -C ₃ H ₅)(η ¹ -O ₂ CC ₃ H ₅)(PR ₃) (9)	53
	Pd(η ¹ ,η ³ -C ₈ H ₁₂)(PCy ₃)	Pd[η ¹ ,η ³ -C ₈ H ₁₂ C(O)O](PCy ₃) (12)	92
45	[PdCl(η ³ -2-MeC ₃ H ₄) ₂](dppe)	CH ₂ =C(Me)CH ₂ C(O)OCH ₂ C(Me)=CH ₂ (13) + Me ₂ C=CHC(O)OCH ₂ C(Me)=CH ₂ (14)	54
46	[Pd(hfacac)] ₂ (η ³ ,η ³ -C ₈ H ₁₂) (17)	CH ₂ =CH(CH ₂) ₃ CH=CHCH ₂ COOH	55

TABLE I (Continued)


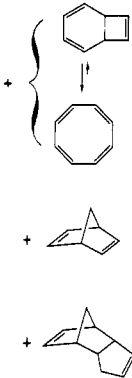
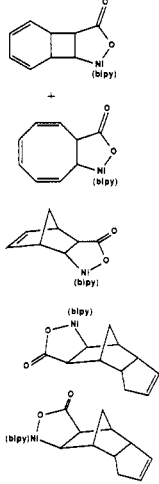
entry	precursor complex	isolated product	ref
Reactions with Coordinated Alkynes and Related Ligands			
47	CpCp'Ti(PhC≡CPh)	CpCp'Ti{PhC≡C(Ph)C(O)O}	56
	Cp ₂ Ti(Ph) ₂	Cp ₂ Ti{o-C ₆ H ₄ C(O)O}, Cp ₂ Ti(o-C ₆ H ₄ C(O)O) ₂ (24)	2, 20
48	Li[<i>fac</i> -(OC) ₃ (dppe)WC≡CR] (1)	<i>mer</i> -[(OC) ₃ (dppe)W{C=C(R)CO 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- <i>n</i> -Bu ₃ , <i>t</i> -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	<i>trans</i> -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 (<i>E</i>)- + (<i>Z</i>)-(HO ₂ CCH ₂ CH=CHCH ₂ CO ₂ H) (<i>E,E</i>)-[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 + (<i>E</i>)-(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 ₃ H ₅)(PMe ₃) ₃ + CO ₂ , MeOH/HCl	(<i>E</i>)-MeCH=CH(CH ₂) ₂ CO ₂ Me + (<i>E</i>)-MeCH ₂ CH=CHCH ₂ CO ₂ Me + (<i>E</i>)-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, <i>n</i> -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=CR'CR''=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=C-CR'CH 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) + CHR=CR'CR''=CHR'''	CHRR'''CR'=CR''CH ₂ COOH CHR'CR'=CR''CHR'''C(O)O	66b 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, <i>n</i> -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>i</i> -Pr, <i>t</i> -Bu)	RCH ₂ C(Me)=C=CH(COOH)	70
67	Th(Cp') ₂ Cl(η ² -C(O)CH ₂ - <i>t</i> -Bu)	Th(Cp') ₂ (Cl){OC(CH ₂ - <i>t</i> -Bu)C(O)O}	120

TABLE I (Continued)



entry	precursor complex	isolated product	ref
Insertion into Other Ligands			
68	$\text{Pd}(\text{o-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)[\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{OEt}]$ (30)	$\text{Pd}(\text{o-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)[\text{Ph}_2\text{PCH}=\text{C}(\text{O})\text{OH}](\text{CO}_2\text{Et})$ (31)	71
Reactions with Strained Cycles			
69	$\text{RhCl}(\text{PMe}_2\text{Ph})_3 + \triangle$	$\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}$	121
70	$\text{Ni}(\text{cod})_2 + \text{bipy} + $ 	 (26)	62
Oxalate Formation from Two CO ₂ Molecules			
71	$\text{R}_2\text{Ti}(\text{CH}_2)_3\text{N}(\text{R}')\text{CH}_2\text{CH}_2\text{N}(\text{R}')(\text{CH}_2)_3\text{TiR}_2$ (R = Cp, Cp'; R' = aliphatic, cycloaliphatic, aromatic group)	$(\text{R}_2\text{Ti})_2(\text{C}_2\text{O}_4)$	72

TABLE II. Catalytic Reactions of CO₂ Involving C-C Bond Formation

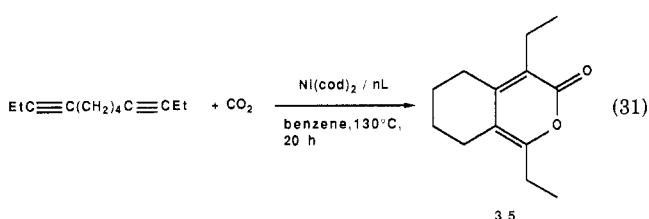
educts	metals	products
alkynes	Rh, Ni	pyrones
alkenes	Ru, ^a Rh	acids, esters
allenes	Pd	lactones, esters
dienes	Ru, Rh, Ni, Pd	lactones, acids, esters
cyclopropanes	Pd	lactones
aromatic compounds	Pd	acids

^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 CO₂ insertion into the nickel-carbon bond (route A) or by its (4 + 2) cycloaddition with CO₂ in the sense of Diels-Alder reaction (route B), may be ruled out.

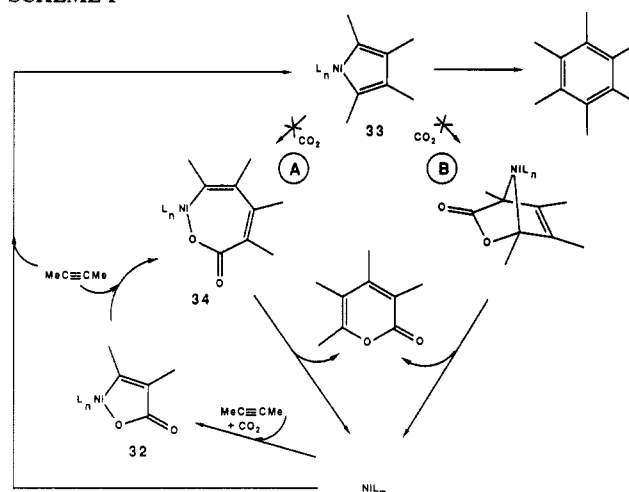
In general, nickel catalysts are active for various alkynes, but phenyl- or diphenylacetylene do not give any CO₂-containing product. The addition of catalytic amounts of water was studied.^{73b,74a} Thus, 0.15 mmol of water/g-atom of nickel had a slight effect on the selectivity. One or more molar equivalents 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 CO₂ (eq 31).^{74b}

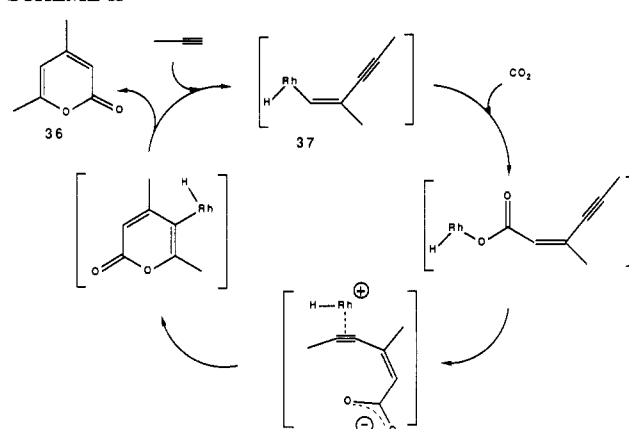


In contrast to nickel complexes, $[\text{HCo}(\text{dppe})_2]$ afforded low yields of pyrone from 1-hexyne and CO₂^{73a} and the rhodium complex $[\text{Rh}(\text{dppe})_2(\eta\text{-BPh}_4)]$ yielded only 3% of 4,6-dimethyl-2-pyrone (**36**) obtained from propyne, the major products being cyclic trimers.⁷⁵ The formation of **36** was interpreted as a CO₂ 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

SCHEME I



SCHEME II



However, a route involving a rhodalactone analogous to **32** (Scheme I) should also be considered.

4.2. Reactions with Alkenes

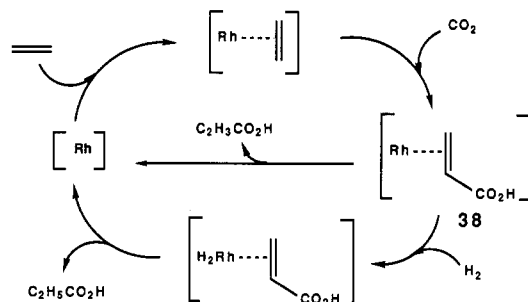
In contrast to alkene carbonylation reactions, only few carboxylation reactions of alkenes are known. Lapidus et al. reported the rhodium-catalyzed carboxylation of ethylene using Wilkinson's catalyst in the presence of a promoter (HCl, HBr, or HI) and distilled water as solvent.⁷⁶ When the reaction 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% (CO₂ conversion 67.4%). When N₂ was intro-

TABLE III. Catalytic Systems for Butadiene-CO₂ Reactions

entry	catalyst	adducts	solvent	temp (°C)	(time (h))	yields (%) (based on butadiene)					ref		
						lactones		esters	butadiene dimers	acids			
						43	42	44	45, 46		40, 41	50	
1	Ni(cod) ₂	P- <i>i</i> -Pr ₃	CH ₃ CN	90	(15)	1.5			0.1				87
2	Ni(cod) ₂	P(OBu) ₃	CH ₃ CN	90	(15)				1.5				87
3	Ni(cod) ₂ or Ni(cdt)	P(O- <i>i</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	[(η ³ -2-Me-C ₃ H ₄)Pd(OAc)] ₂	P- <i>i</i> -Pr ₃	C ₆ H ₆	70	(20)	27			19	25			83b
7	[(η ³ -2-Me-C ₃ H ₄)Pd(OAc)] ₂	PMe ₂ Ph	C ₆ H ₆	70	(20)				46	41			83b
8	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]	PPh ₃ , <i>N</i> -ethylpiperidine, hydroquinone, <i>p</i> -benzoquinone	CH ₃ CN	60	(18)	81			3.5	2.6			84
9	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]	PPh ₃ , <i>N</i> -ethylpiperidine, hydroquinone, <i>p</i> -benzoquinone	CH ₃ CN	60	(3)	51			1.7	2.8			84
10	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]	NEt ₃ , H ₂ O	CH ₃ CN	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>i</i> -Pr ₃	CH ₃ CN	90	(15)	40	0.3		1.3				85b
14	Pd(acac) ₂	P- <i>n</i> -Bu ₃	CH ₃ CN	90	(15)	3	0.1		14.5				85b
15	Pd(dba) ₂	PPh ₃ , CH ₃ CO ₂ Na	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>i</i> -Pr ₃ ⁺	CH ₃ CN	90	(15)	58.7		0.1	2.8				87
18	[Pd(MeCN) ₄][BF ₄] ₂	PPh ₃ , NEt ₃ , hydroquinone, acetophenone	CH ₃ CN	90	(15)	35 ^a							115
19	RuH(OAc)(PPh ₃) ₃	P- <i>i</i> -Pr ₃	CH ₃ CN	90	(15)	6.4	0.4		0.1				87
20	Rh(C ₂ H ₄) ₂ (acac)	PEt ₃	CH ₃ CN	120	(24)		5-8 ^b						87

^aThe 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. ^bYield of lactone 51.

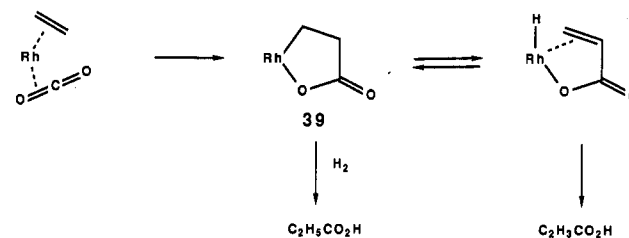
SCHEME III



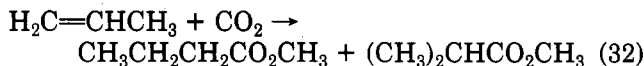
duced in the autoclave, no ethyl propionate was formed. Possible mechanisms and intermediates for the carboxylation reaction are shown in Schemes III and IV. The postulated intermediate 38 could result from a one to one coupling reaction of ethylene and carbon dioxide as observed in the recently isolated 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 CO₂ 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 patent⁷⁸ that propylene and CO₂ react at 230 °C in the presence of ruthenium catalysts, e.g., [RuCl₂(PPh₃)₃], in methanol

SCHEME IV



and acetone as solvents, yielding butyric methyl esters (20–30%) (eq 32). At the end of the reaction, form-



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 CO₂ by N₂, 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, CO₂ 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 CO₂.

4.3. Reactions with Conjugated Dienes

The catalytic coupling of butadiene and CO₂ has attracted a considerable interest, and the known systems are presented in Table III.

SCHEME V

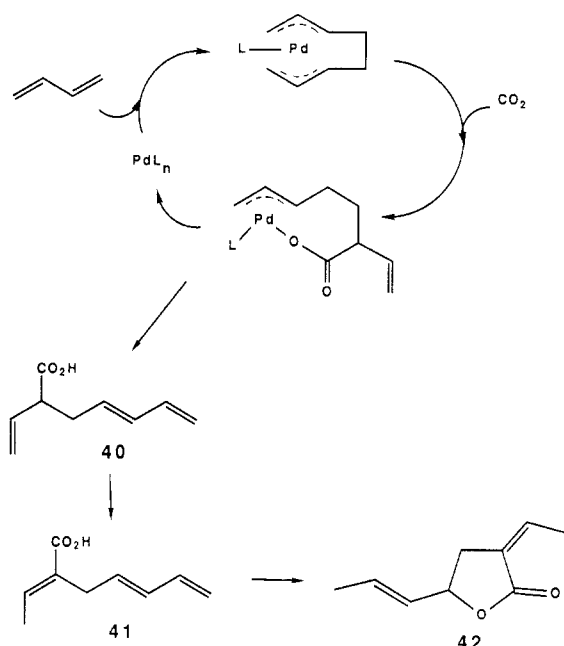


TABLE IV. Influence of the Phosphine Ligand on the Product Yields in Butadiene-CO₂ Cooligomerization Reactions (from Ref 83b)^a

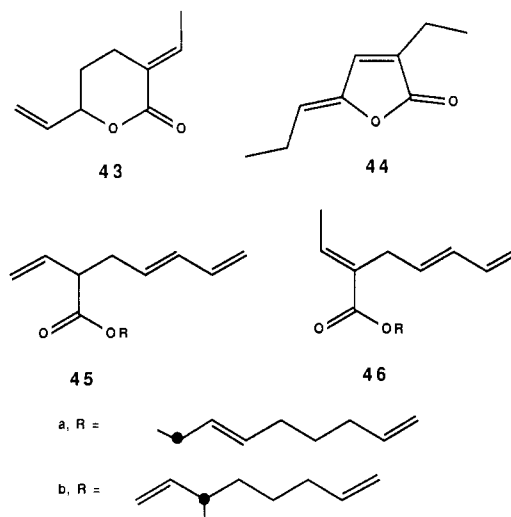
ligand	1,3,7-octatrienes	esters 45 + 46	lactone 43
PCy ₃	14	14	28
P- <i>i</i> -Pr ₃	25	19	27
P- <i>t</i> -Bu ₂ Ph	10	1	1
PEt ₃	44	29	
PMe ₂ Ph	41	46	
P(CH ₂ Ph) ₃	14	44	5
P(<i>o</i> -tolyl) ₃	60	8	
PMePh ₂	66	27	
PPh ₃	11	17	3

^a Experimental conditions: benzene (10 mL), 70 °C, 80–100 atm; catalyst [(η³-2-methylallyl)Pd(OAc)] (0.38 mmol), ligand (2.28 mmol).

The catalytic incorporation of CO₂ into organic compounds was first reported by Inoue et al.^{80,81} Butadiene and CO₂ 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(PPh₃)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/PPh₃ in DMF at 70–120 °C was also found to convert butadiene and CO₂ into 41 and 42.^{82b}

Catalysts prepared in situ, e.g., from [(η³-2-methylallyl)Pd(OAc)]₂ and an appropriate phosphorus ligand, as well as palladium(0)-trialkylphosphine complexes, are also effective for coupling CO₂ and butadiene.

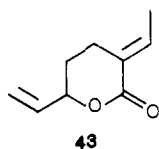
Apart from 42, the other coupling products 43–46 were identified by Musco.⁸³ The distribution of the reaction



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., PCy₃, P-*i*-Pr₃], whereas with less basic phosphines, e.g., PMe₂Ph, P-*t*-Bu₂Ph, P(CH₂Ph)₃, esters 45 and 46 are preferentially formed. When PCy₃ 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 CO₂, 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*-Pr₃, PCy₃).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: CH₃CN > C₂H₅CN > PhCN > CH₃COCH₃ > THF. The suitability of this solvent has been ascribed to the higher solubility of CO₂ in this medium, to its solvation effect and C–H acidity.

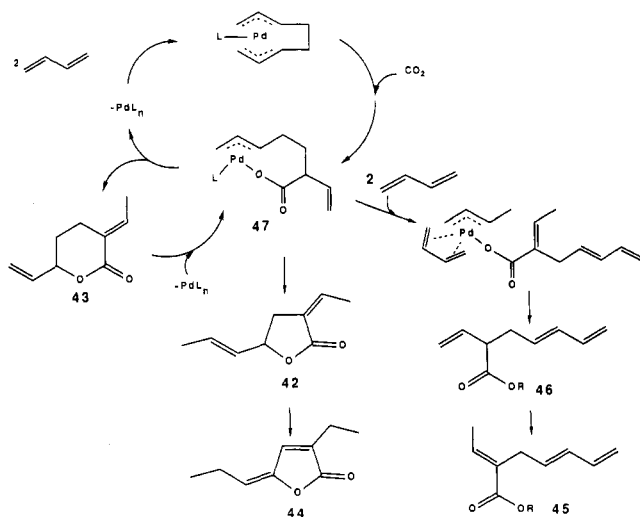
Further catalytic systems have been reported for this reaction, such as Pd(dba)₂/PPh₃ in DMF.⁸⁶ After 2 h of reaction at 60 °C, 14% of lactone 43 could be isolated. The yield increased up to 50% upon addition of sodium acetate. This observation suggested that the presence of the salt favors the reductive elimination step required in the reaction. The functional phosphines

TABLE V. Efficient Catalysts for the Production of Lactone 43

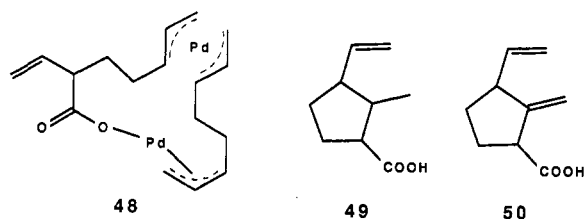


entry	catalyst	butadiene/Pd (mol/mol)	reactn time (h)	mol of lactone/ mol of Pd per h	ref
4	Pd(dppe) ₂	676	40	2.1	80
6	[η ³ -2-Me-C ₃ H ₄] ₂ Pd(OAc) ₂ /P- <i>i</i> -Pr ₃	408	20	2.8	83b
8	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]/PPh ₃ / <i>N</i> -ethylpiperidine/hydroquinone/ <i>p</i> -benzoquinone	1500	18	34.5	84
9	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]/PPh ₃ / <i>N</i> -ethylpiperidine/hydroquinone/ <i>p</i> -benzoquinone	1500	3	130	84
10	[Pd(PPh ₃) ₂ (<i>p</i> -benzoquinone)]/NEt ₃ /H ₂ O	750	18	13	84
13	Pd(acac) ₂ /P- <i>i</i> -Pr ₃	1625	15	21.7	85b
15	Pd(dba) ₂ /PPh ₃ /CH ₃ CO ₂ Na	240	2	30	86
16	Pd(OAc) ₂ /PPh ₃	173	2	11	86
17	Pd(acac) ₂ /P- <i>i</i> -Pr ₃ /P-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

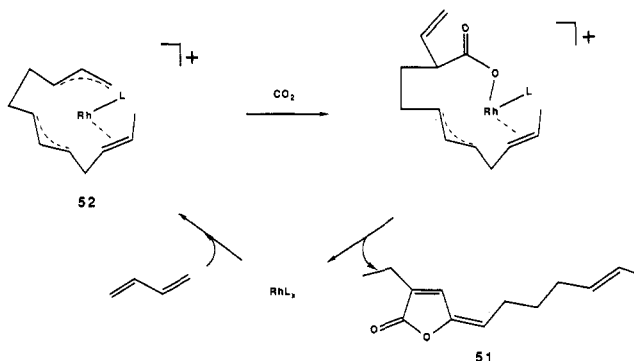


Ph₂P(CH₂)_{*n*}CO₂H (*n* = 1–3), which might have combined the properties of phosphorus donors and of carboxylates, did not favor the reaction, and in these cases, the best yields of 43 (9%) were obtained for *n* = 3.⁸⁶ The following mechanism has been proposed to account for the formation of products 40–46 (Scheme VI).^{85b} The catalytic precursor would generate in situ a Pd(0) species that reacts with butadiene to afford the bis(η³-allyl) complex. Insertion of CO₂ 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 CO₂ incorporation, binuclear palladium species of type 48 do not act as intermediates in the transformation.⁵⁵



Lactone 43 takes part in an equilibrium with interme-

SCHEME VII

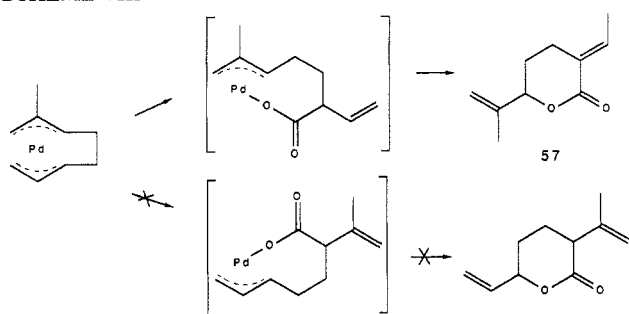


mediate 47, allowing formation of lactone 42, which isomerizes to the thermodynamically more stable lactone 44.^{87,89} Note also that the Ni(0)-catalyzed synthesis of acids 49 and 50 has been achieved recently from butadiene and CO₂.⁸⁸ Recent work has shown that Pd/PPh₃-based systems obtained from cationic Pd(II) precursor complexes are efficient catalysts for the formation of lactone 43 (selectivity of 96%) (Table III, entry 18).¹¹⁵

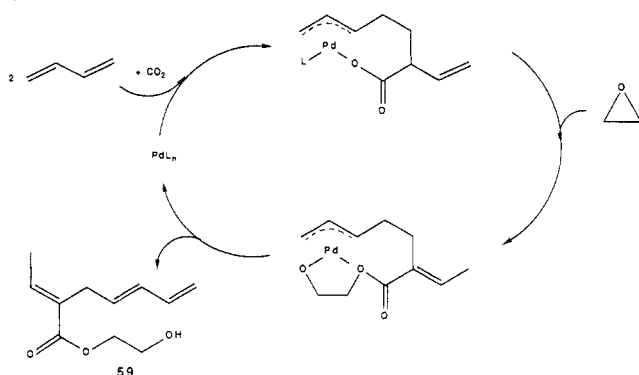
When rhodium(I) complexes such as [Rh(C₂H₄)₂(acac)], [Rh(nbd)(PPh₃)₂][BPh₄], [Rh(cod)(PPh₃)₂][PF₆], or [Rh(η³-allyl)₂(acac)] are used as catalysts, the new γ-lactone 2-ethyl-2,4,9-undecatrien-4-olide (51) is formed in 5% yield.^{87,89} The pathway of Scheme VII was proposed. Condensation of three butadiene molecules on the rhodium center would lead to 52. Related complexes are known for, e.g., nickel,⁹⁰ ruthenium,⁹¹ and palladium.⁹² CO₂ insertion into the rhodium–carbon σ-bond affords the corresponding carboxylate complex, which reductively eliminates lactone 51. It is noteworthy that the telomerization reaction between CO₂ 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 CO₂ 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 CO₂ and incorporation of small amount of

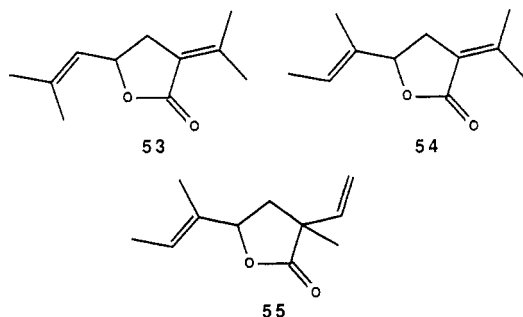
SCHEME VIII



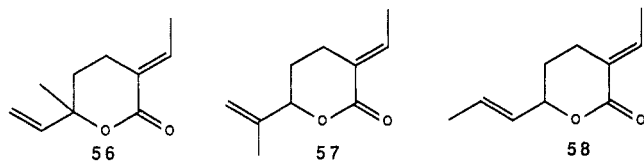
SCHEME IX



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



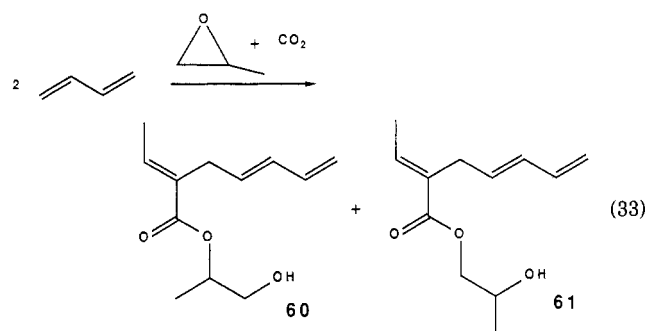
The coreaction of butadiene and isoprene with CO₂ has been investigated with various palladium catalysts.^{87,89a,94} The new six-membered ring lactones **56** and **57** were formed. They could be obtained selectively



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 CO₂ incorporation occurs only into the η³-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 CO₂, 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-*i*-Pr₃/

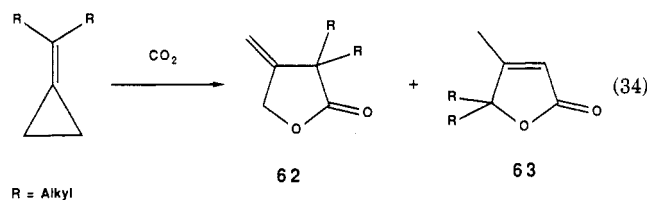
butadiene/CO₂/propylene oxide in a 1:3:200:300:200 ratio (eq 33).⁹⁵ The optimum yield of the glycol ester



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 Methylene cyclopropanes

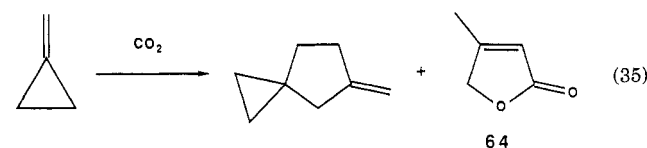
Palladium(0) phosphine complexes catalyze the coupling of methylenecyclopropanes and carbon dioxide in benzene (40 atm of CO₂, 130 °C, 20 h) with opening of the three-membered ring to give the five-membered ring lactones **62** and **63** (eq 34).⁹⁶ The influence of the



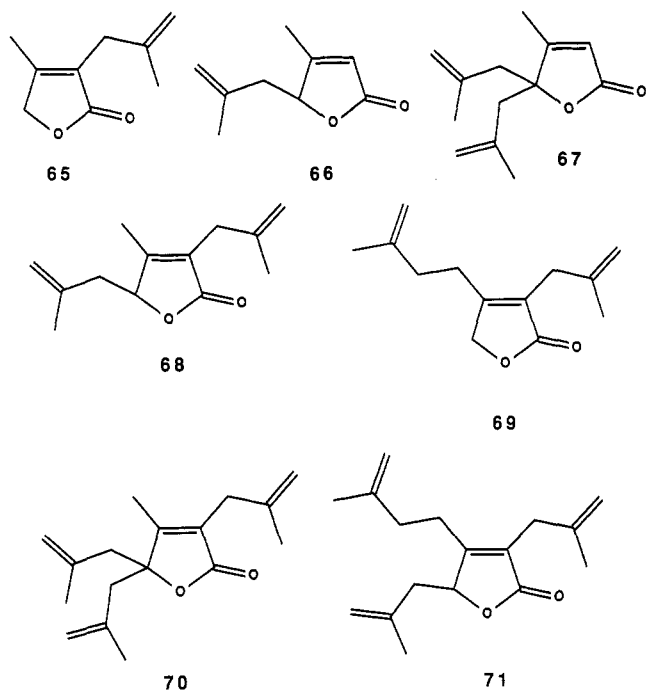
R = Alkyl

phosphine was studied. A less basic phosphine such as PPh₃ or the phosphite P(OEt)₃ tend to lead to **62** rather than to **63**. Surprisingly, 2,2-dimethylmethylene cyclopropane and *cis*-2,3-dimethylmethylene cyclopropane did not react with CO₂ under similar conditions.

More recently, new efficient catalytic systems have been described for the reaction of methylenecyclopropane and CO₂, based on (η-allyl)(η-cyclopentadienyl)palladium complexes and PPh₃ at 165 °C in DMF (eq 35).⁹⁷ The yield of **64** reaches 80% after



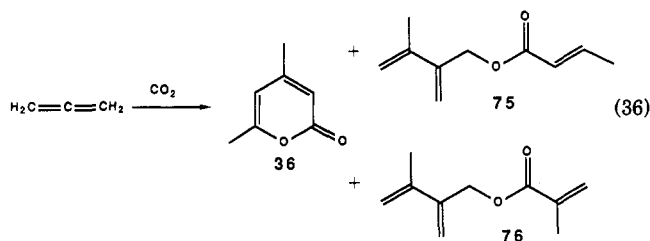
2 h when the ratio Pd/PPh₃ is 1:4. The authors observed that Pd(0) species also catalyze the alkylation of the primary product **64** with methylenecyclopropane. Therefore, the formation of the cotrimers **65** and **66**, the cotetramers **67**–**69**, and the copentamers **70** and **71** cannot be avoided. The reaction course depends on several parameters, e.g., Pd/PPh₃ ratio, solvent, CO₂ pressure, and temperature. When the reaction was performed in DMSO, after 18 h at 140 °C (with a Pd/PPh₃ ratio of 1:2), a selectivity of 73.7% for **70** was



obtained. The reaction pathway shown in Scheme X was proposed. Methylene-cyclopropane would react with palladium(0) species to form a palladacyclobutane **72**, in equilibrium with the suggested^{96,97} trimethylenemethane complex **73**. CO₂ 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 oligomers **65–71** is produced.

4.5. Reactions with Allene

CO₂ reacts with allene in the presence of Pd(η^3 -allyl)₂/dcpe^{99a} or [Rh(dppe)(η -BPh₄)]^{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 cyclooligomerization of CO₂ 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 CO₂ into the M–C bond. The formation of esters **75** and **76** implies a hydrogen-transfer step which presum-

ably 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}

4.6. Reactions with Aromatic Compounds

In 1888, Friedel and Crafts reported the formation of benzoic acid from CO₂ 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(NO₃)₂ or Pd(OAc)₂ salts (30 atm of CO₂, 150 °C, 20 h), affording the corresponding acids. When benzene was treated with a mixture of Pd(NO₃)₂ and Fe(NO₃)₃·9H₂O, 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 CO₂, has been found to result in high-yield carboxylation of benzene to benzoic acid. This latter observation suggests that CO₂ may not be the carboxylating agent in the previous reaction.

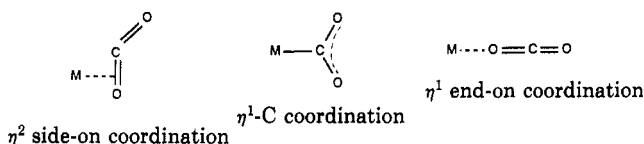
4.7. Electrochemical Reactions

The search for transition-metal catalysts that mediate CO₂ reduction at lower potentials than ca. 2.2 V (vs saturated calomel electrode), the potential needed for the direct electrochemical reduction of CO₂,¹⁰² 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 CO₂ into oxalate has been claimed in only two cases: in the presence of some Ag(II) and Pd(II) metalloporphyrins¹⁰⁴ or of [CpFe(CO)₂][–] which mediates the delivery of CO₂[–].^{105a} Further examples are needed to understand the factors that govern the C–C bond formation and deviate the reaction course from the usual CO₂ reduction into a C₁ molecule (CO, HCOOH).

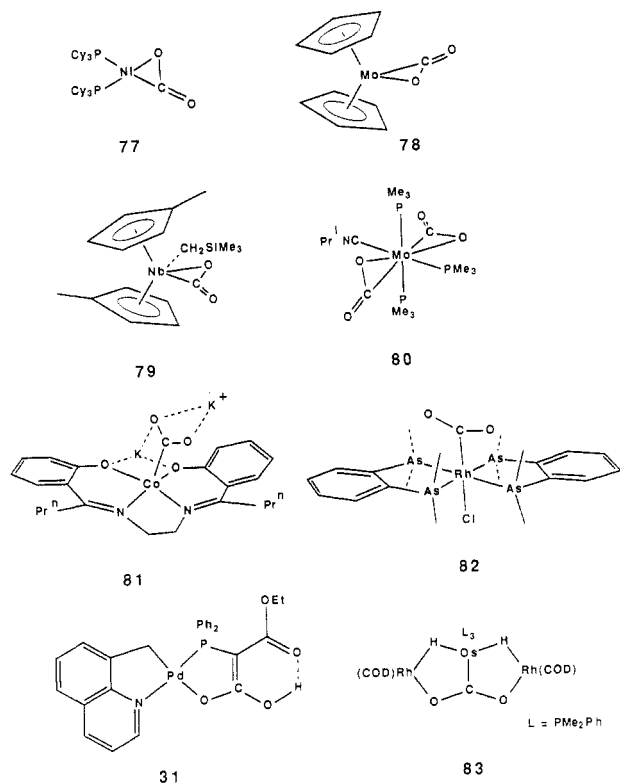
A currently expanding field is the electrocarboxylation of organic substrates by CO₂, catalyzed by transition metals. Thus organic halides may be converted into the corresponding carboxylates in the presence of nickel complexes.¹⁰⁶ Electrocarboxylation of ArCHMeCl can thus lead to 2-arylpropionic acids 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 PhCH₂CH₂CO₂[–] or phenylsuccinate PhCH(CO₂[–])CH₂(CO₂[–]) depending on the experimental conditions. The perspectives of transition metal mediated coupling reactions involving CO₂ are closely related to fundamental academic problems as well as to industrial applications, making this area of high current interest.

5. The Relevance of CO₂ Complexes

Coordination of CO₂ to transition metals has long been thought to be one of the initial steps in the catalytic conversion of CO₂. Therefore, investigations about "CO₂ 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 CO₂ to a transition metal is a prerequisite for a catalytic reaction with CO₂. The number of structur-

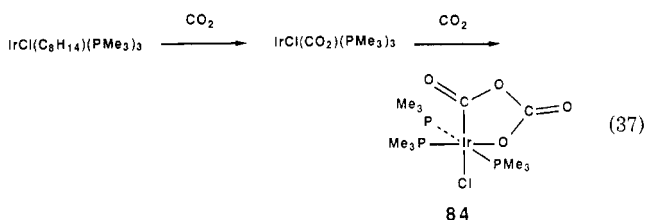


ally unequivocally characterized complexes in which CO₂, used as a reagent, is interacting with the metal center(s), is very limited.



In the cases of **77**,¹⁰⁸ **78**,¹⁰⁹ **79**,¹¹⁰ and **80**,¹¹¹ CO₂ is η^2 -coordinated to the metal through the carbon atom and one of the oxygen atoms, whereas in complex **81**, CO₂ 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 CO₂ 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 CO₂ bound to three transition metals^{114a} (osmium and rhenium complexes containing a bridging CO₂ 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 CO₂ correlates with chemical activation of CO₂. Note however that the stable CO₂-containing

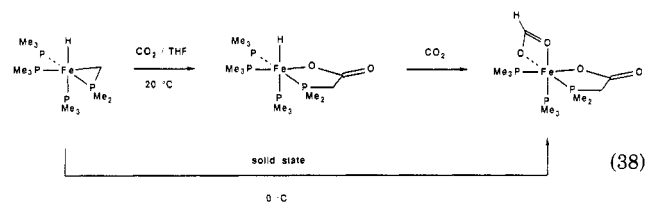
complex **31** has recently been shown to be a catalyst precursor in the synthesis of lactone **43** from butadiene and CO₂.¹¹⁵ The reaction of [IrCl(C₈H₁₄)(PMe₃)₃] with CO₂ is thought to proceed in a stepwise manner by addition of the nucleophilic complex to CO₂, the resulting more basic oxygen atom binding to a second CO₂ molecule, via O-C bond formation (eq 37).¹¹⁶ Complex



84 can be regarded as an intermediate of the metal-promoted conversion of CO₂ to carbonates and CO. The isolation of a transition-metal complex containing such a C₂O₄ unit is rather rare⁷² while carbon-carbon bond formation is exceptional.

Recent theoretical studies have examined the coordination modes of CO₂ in its complexes.¹⁰⁷ They have led to a better understanding of the factors governing the bonding in CO₂ 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 $d\pi$ orbital as the HOMO and an empty $d\sigma$ orbital pointing to the CO₂ ligand, as in **79** and **80**. The η^1 -C mode is most favored when the HOMO is mainly composed of a $d\sigma$ orbital and when the metal is in a low oxidation state, as found in the d^8 complexes **81**, **82**,^{107h} or Cp(CO)₂FeCO₂.^{107k,l} Although no complex with a η^1 end-on coordination of CO₂ has been isolated yet, this bonding mode could occur in the initial step of the formation of some CO₂ 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 CO₂ 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 CO₂ shown in eq 37.

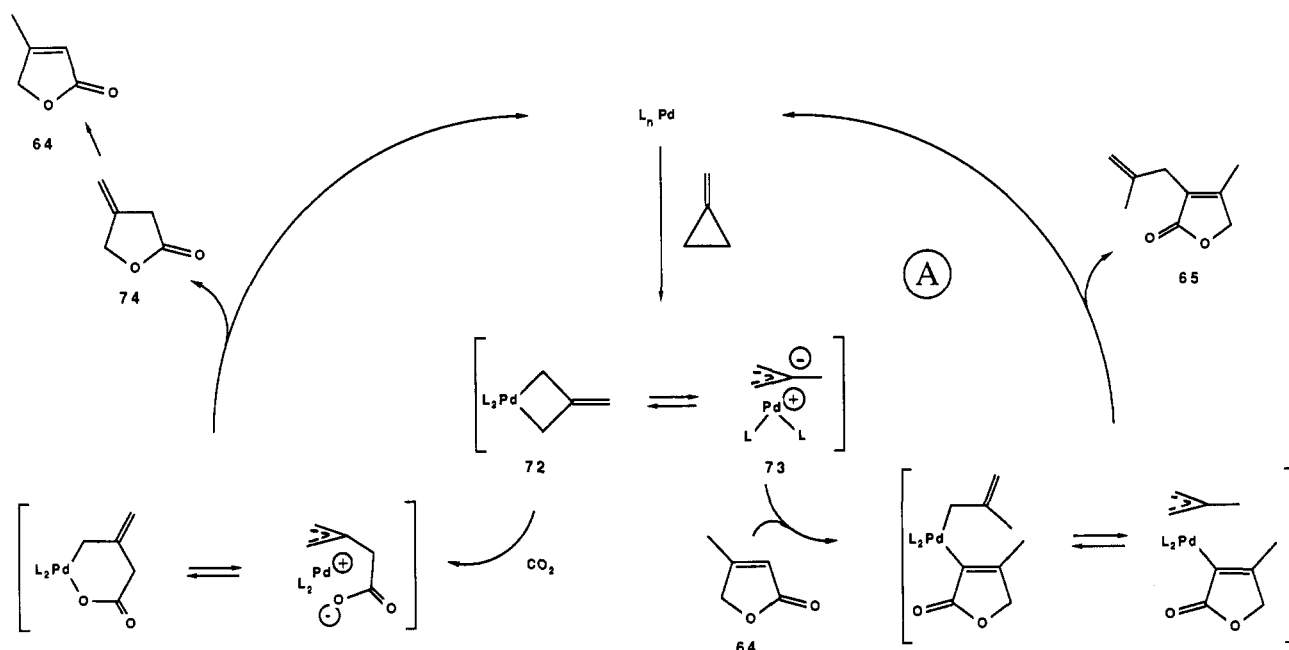
It is interesting to note that the addition of the first CO₂ molecule to [Fe(PMe₃)₄] (entry 33, Table I) occurs with formation of a coordinated functional phosphine ligand (eq 38), which allows a second CO₂ insertion to occur into the Fe-H bond.⁴⁵ The first step in this



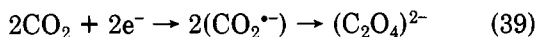
reaction, which resembles that occurring in eq 29, nicely illustrates that a modification of the chemical reactivity of a complex can be induced by its reaction with CO₂. Such features might also occur in cases where the intermediate species is too unstable to be isolated.

Oxalate formation from carbon dioxide has been claimed in a German patent.⁷² Titanium oxalate complexes [(η -C₅Me₅)₂Ti]₂(C₂O₄) were prepared in 63% yield by reacting [(η -C₅Me₅)₂Ti(CH₂)₃N(Bu)CH₂CH₂N(Bu)(CH₂)₃Ti(η -C₅Me₅)₂] with CO₂ in benzene. This is

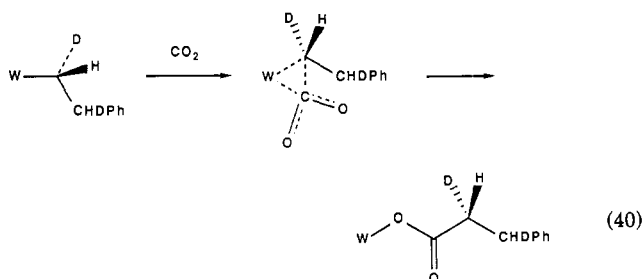
SCHEME X



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



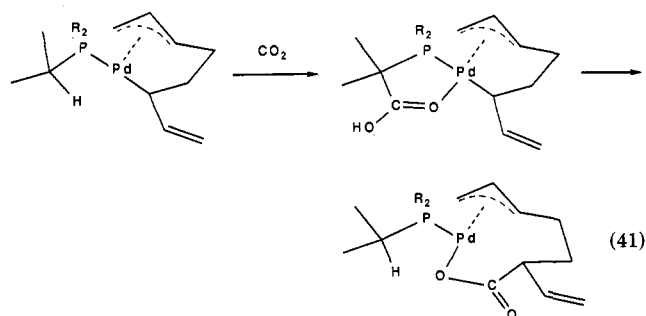
bond forming reaction has been observed between ketones on Cp₂TiR complexes.¹⁷ The reaction of CO₂ with organic substrates may not require such a one-electron-transfer process but rather the activation of the organic substrate by the metal complex. CO₂ inserts readily in many M–C bonds. Elegant investigations 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 coordina-



tion site, where CO₂ may possibly be bound before the insertion process takes place, could be excluded. Therefore, coordination of CO₂ may not be required here to generate the new C–C bond. As a matter of fact, the CO₂ complexes isolated so far, with the exception of 31,¹¹⁵ have not been reported to display any significant catalytic activity in the coupling of CO₂ with organic substrates. Conversely, with the catalytically active systems, no CO₂ complex has been isolated yet. This may also simply reflect the situation of a conflicting balance between stability and reactivity.

6. Concluding Remarks

The highly desired carbon–carbon coupling between CO₂ 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 CO₂-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 CO₂ and not be too basic in order to maintain the electrophilic character of the C atom of CO₂. 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 CO₂, it may bring the “activated” CO₂ 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 CO₂ 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 CO₂, affording lactones (eq 41).⁸⁷ Although stoichio-



metric “bis CO₂ insertion” reactions have been reported,

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 published¹¹⁷ and if insertion of CO₂ into the newly formed M-C bond were possible, direct functionalization of alkanes could result. Remember that formation of aliphatic acids from CO₂ and methane¹¹⁸ or pentane¹¹⁹ has been claimed and remains a thermodynamically conceivable possibility (CH₄(g) + CO₂(g) → CH₃COOH(l), ΔH° = -3.8 kcal/mol!)

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Registry No. CO₂, 124-38-9.

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