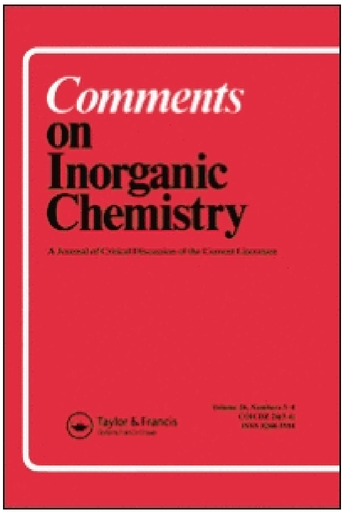

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The Organometallic Chemistry of Carbon Suboxide

Gastone Paiaro[a]; Luciano Pandolfo[a]
[a] Dipartimento di Chimica Inorganic, Metallorganica ed Analitica, Universita' di Padova, Padova, Italy

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The Organometallic Chemistry of Carbon Suboxide

GASTONE PAIARO and LUCIANO PANDOLFO
Dipartimento di Chimica Inorganica,
Metallorganica ed Analitica,
Universita' di Padova,
Via Marzolo, 1,
35134 Padova, Italy

Carbon suboxide, C_3O_2, reacts with a great variety of organometallic compounds. With organo-silicon and aluminium compounds it reacts with the C=O moiety, giving sililation and carboalumination reactions. Insertion reactions of C=C are performed with compounds having M–H, M–OR, M–NR_2, M–PR_2 bonds (M ≠ Si, Al), giving mono-metal derivatives (ketenyl) or di-metal derivatives of acil groups (amides, esthers, phospides). The coordination of C=O or C=C to transition metal complexes, the formation of allenic compounds and the decarbonylation reactions allow the synthesis of a series of particular metal derivatives (ketenyl, ketenylidene and carbonyl complexes) which, in some cases, present a peculiar reactivity.

Key Words: *carbon suboxide, organometallic derivatives, complexes, ketenyl compounds, ketenyl reactivity*

INTRODUCTION

Propadien-1,3-dione, C_3O_2, **1**, also referred to as carbon suboxide or di-oxoallene or di-oxopropadiene or bis-ketene, is formally the anhydride of the malonic acid. After its discovery in 1906 by O.

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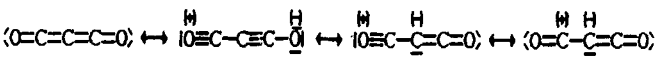
Diels,[1] it has been widely investigated by organic chemists on account of its high reactivity in a large number of reactions with nucleophilic and electrophilic reagents to obtain heterocyclic compounds of large interest. The characteristic organic chemistry of **1** is now well defined and excellent reviews on various aspects of its reactivity are available.[2] The polymers which can arise from **1**, also known as "carbon red," have been the subject of numerous studies[3] as well.

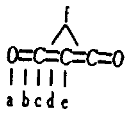
In contrast, only a few reactions of **1** with Grignard and organolithium reagents have been described in the early organometallic literature, and the organometallic chemistry of **1** is only now beginning to be seriously developed. However, reviews dealing with interactions between organometallics compounds and **1** do not exist and from this the present review arises.

The structure of **1** can be represented by resonant limit forms such as those shown in Scheme 1, pointing out an unusually high negative charge located on the central carbon atom as calculated and determined by ESCA, CNDO, *ab initio* methods.[4] This is a matter of basic consequence for understanding the reactivity of **1**: in fact electrophiles tend to add to the central (β) carbon atom, which presents a more negative charge than the terminal oxygen atoms, whereas nucleophiles add to the α carbon atoms. A careful inspection of the formula of **1** shows a great variety of reactivity centers (see Scheme 2): (a) nucleophilic oxygen, (b) double bond, (c) electrophilic carbon atom, (d) olefinic activated bond, (e) nucleophilic carbon atom, (f) two cumulated olefinic bonds (allenic



1

SCHEME 1



SCHEME 2

moiety), on which a relevant number of different types of reactions can take place.*

Moreover, **1** can be decarbonylated to give metalcarbonyls and ketenylidene,[5] the reactive fragment "C_2O".

The following exposition will be made according to the reaction ways of **1**, that is: (1) insertion reactions of the C=O bond; (2) insertion reactions of the C=C bond; (3) coordination reactions of C=C and C=O bonds; (4) formation of allenic complexes; (5) decarbonylation reactions; (6) reaction with coordinated ligands; (7) reaction of coordinated C_3O_2.

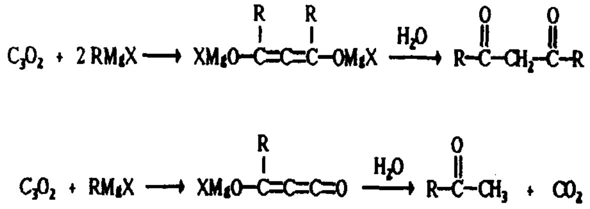
Coverage of the literature is throughout 1990.

1. INSERTION REACTIONS OF THE C=O BOND

The presence of two negative sites in the molecule of **1** (the oxygen atom and the central carbon atom) gives rise to the question: Where does the attack of an electrophile take place?

When the electrophile is the proton, derivatives of the malonic acid are formed, i.e., the attack occurs at the β carbon atom. Some uncertainty can be whether an unstable enole is first formed, which then isomerizes into the carbonylic form. However, the carbon atom is actually the most negative site,[4b] so that the attack goes in the expected direction, and it is controlled by the insertion of the C=C bond.

Nevertheless, cases are reported in which the reaction occurs at the C=O bond. Organomagnesium and organolithium compounds



$$C_3O_2 + 2\,RMgX \longrightarrow XMgO{-}\overset{\overset{R}{|}}{C}{=}C{=}\overset{\overset{R}{|}}{C}{-}OMgX \xrightarrow{H_2O} R{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}R$$

$$C_3O_2 + RMgX \longrightarrow XMgO{-}\overset{\overset{R}{|}}{C}{=}C{=}C{=}O \xrightarrow{H_2O} R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + CO_2$$

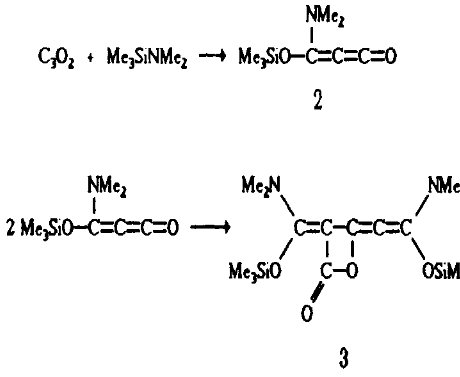
REACTION 1

---

*Note that in the more simple molecule of CO_2 there have been identified 24 different potential centers of coordination [A. Behr, Angew. Chem. Int. Ed. Engl. 27, 661 (1988)].

react with **1**, yielding β-diketones[6] and methylketones[7] (Reaction 1); the attack of the metal has been referred to take place at the oxygen atom.[8]

Dimethyl(trimethylsilyl)amine reacts with **1** via a 1,2 addition to the carbonyl bond, yielding a compound, **2**, bearing the silylaminale group (Reaction 2).[9] Dimerization of **2** occurs in head-to-tail fashion, giving **3**, which, by hydrolysis, decomposes, yielding CO_2, $(Me_3Si)_2O$, **4** and the dimethylamide of α-ketoglutaric acid, **5** (Reaction 3).

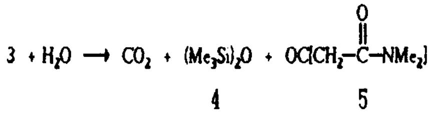


$$C_3O_2 + Me_3SiNMe_2 \rightarrow Me_3SiO-\overset{NMe_2}{\overset{|}{C}}=C=C=O$$

2

3

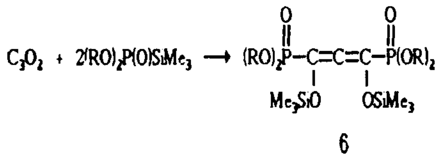
REACTION 2



$$3 + H_2O \rightarrow CO_2 + (Me_3Si)_2O + OC[CH_2-\overset{O}{\overset{\|}{C}}-NMe_2]_2$$

4 5

REACTION 3



$$C_3O_2 + 2(RO)_2P(O)SiMe_3 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}-\underset{Me_3SiO}{\underset{|}{C}}=C=\underset{OSiMe_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{P}}(OR)_2$$

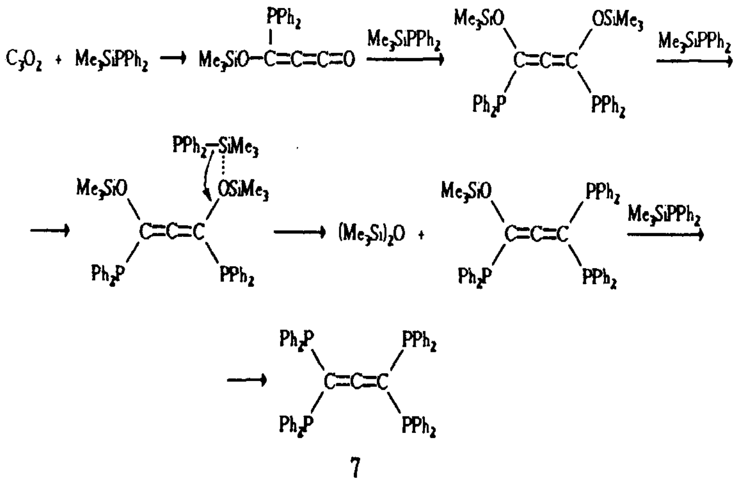
6

REACTION 4

Compounds containing Si–P bonds react with the CO groups of **1** as well. In the reaction between **1** and $Me_3SiPO(EtO)_2$ (Reaction 4), in which the phosphonallenic derivative **6** is formed, silicon adds to the oxygen atom and phosphorus to the carbon atom of the C═O groups.[10]

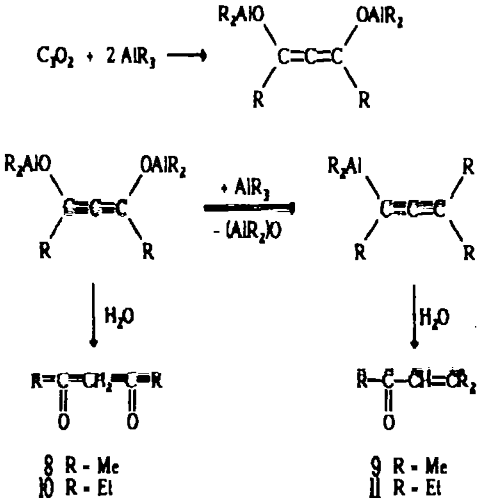
The products obtained from the reaction of **1** with Me_3SiPPh_2 depend on the molar ratios between the reagents.[11] Any step of the reaction, from the first product formed by mono-insertion of C═O to the final product, the "tetraphosphino allene derivative," **7**, was studied. As shown in Scheme 3 it is the excess of Me_3SiPPh_2 that leads to deoxygenation of **1**, elimination of $(Me_3Si)_2O$ and formation of **7**.

The reaction of organoaluminium compounds with **1** gives alkylated products through previous coordination of AlR_3 to the oxygen atoms, followed by the carboalumination reaction.[12] Also in this case the molar ratio of the reagents is the determining factor of the course of the reaction. For low values of $AlMe_3/C_3O_2$ the main product after hydrolysis is acetylacetone, **8**, whereas, with higher values of $AlMe_3/C_3O_2$, (~5), the excess of $AlMe_3$ leads to the formation of $(Me_2Al)_2O$ and, after hydrolysis of the residual product, of mesityl oxide, **9**, as primary product.



7

SCHEME 3



SCHEME 4

With $AlEt_3$ the course of the reaction is still the same and the products are 3,5-heptanedione, **10** (for low ratio Al/C_3O_2), and 5-ethyl-4-hepten-3-one, **11**, as major product (for high ratio Al/C_3O_2). Scheme 4 summarizes the course of the reactions.

Note that this reaction does not lead to a fully alkylated product, i.e., to 2,4-dimethyl-2,3-pentadiene or 3,5-diethyl-3,4-heptadiene, at least under the reported experimental conditions.

The reported reactions of **1** with organometallic derivatives of Li, Mg, Al and Si show that with highly electropositive (Li, Mg) or oxophilic (Al, Si) atoms the insertion into M–X bonds occurs with C=O groups instead of with the C=C groups of **1**.

Other metal-alkyl derivatives, such as $ZnEt_2$, are reported to react with **1**, initiating its polymerization.[12]

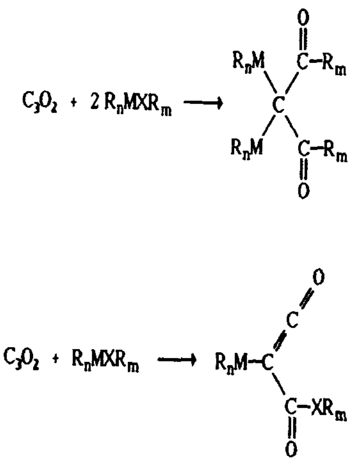
2. INSERTION REACTIONS OF THE C=C BOND

The C=C bonds of **1** can be considered as activated olefinic bonds in which α and β carbon atoms show opposite polarity. C_β is a highly negative site on which a number of polar reagents react with their positive end.

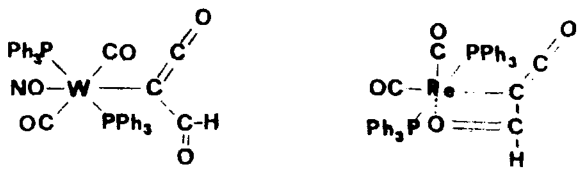
The reactions of organometallic compounds of the tipe R_nMXR_m (excluding the previously considered silicon derivatives) lead to the formation of di-substituted derivatives of malonic acid and, sometimes, to monosubstituted products, that is, ketenyl complexes (Scheme 5).

2a. Insertion Reactions of C═C into M–H Bond

The first example of insertion of **1** into M–H bonds was reported by Hillhouse,[13] with W and Re complexes, obtaining the η^1-ketenyl metal derivatives **12** and **13** (Fig. 1).



SCHEME 5



12 **13**

FIGURE 1 Structure of $(CO)_2(NO)(PPh_3)_2W[C(CHO)CO]$ (**12**) and $(CO)_2(PPh_3)_2$ Re[C(CHO)CO] (**13**).

A systematic study of the reactions between hydrides and **1** have been recently reported by Pandolfo and Paiaro.[14]

Ionic hydrides of groups 1 and 2 usually do not react with **1**. Sometimes (for example with $LiAlH_4$) polymers of **1** are obtained by anionic polymerization.[14]

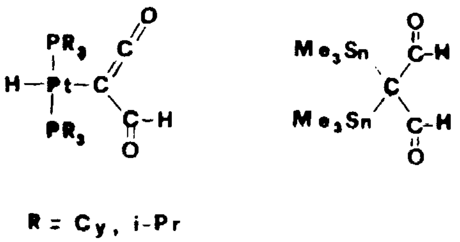
With other transition metal hydrides the reactions with **1** always require the following conditions: (a) the possibility of coordination of **1** to the metal, (b) a suitable energy of the M–H bond and (c) hydride transfer.

The bond energy can be roughly related to the M–H stretching frequency, and only compounds which present $\nu_{(M-H)}$ lower than 1900 cm^{-1} appear to react, which means that the M–H bond is, in these cases, weak enough to allow the hydrogen transfer. As an example *trans*-$(PR_3)_2Pt(H)_2$ ($\nu_{(Pt-H)} = 1710-1820\ cm^{-1}$) reacts with **1**, whereas *trans*-$(PR_3)_2Pt(H)Cl$ ($\nu_{(Pt-H)} = 2170-2370\ cm^{-1}$) does not.[14] Also note that R_3SnH, which reacts with **1**, presents $\nu_{(Sn-H)} = 1830\ cm^{-1}$.

These reactions lead to mono- and di-inserted derivatives. Dihydrido platinum complexes lead to formyl-ketenyl compounds, **14** (mono-insertion), whereas with "borderline hydrides," like R_3SnH, only the di-inserted products, **15**, are obtained (Fig. 2).

The molecular structure of **14** (Fig. 3) has been recently reported.[15]

The ligand "HC_3O_2" lies in a plane which is normal to the coordination plane of Pt. The molecular geometry of the ligand



14 **15**

FIGURE 2 Structure of *trans*-$H(PR_3)_2Pt[C(CHO)CO]$ (**14**) and $(Me_3Sn)_2C(CHO)_2$ (**15**).

14

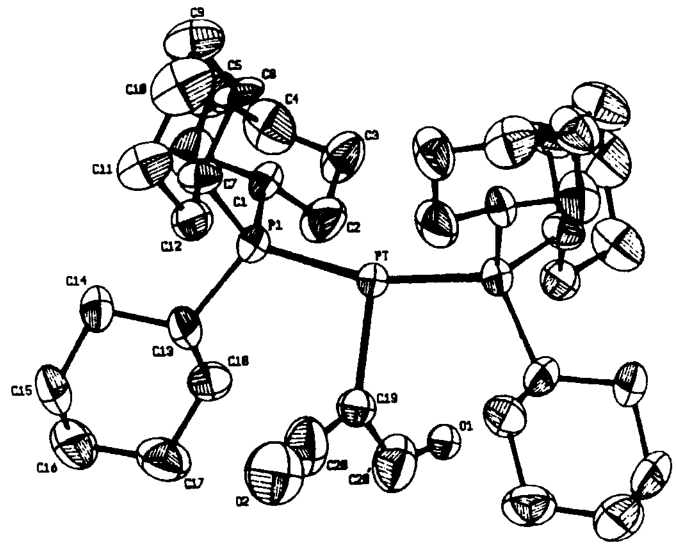


FIGURE 3 Molecular structure of *trans*-$H(PCy_3)_2Pt[C(CHO)CO]$ (**14**) reprinted with permission from Ref. 15.

can be interpreted, assuming for it a considerable amount of a dipolar form such as $=C=\overset{\delta+}{C}=\overset{\delta-}{O}$. This suggestion accounts for chemical data showing more marked nucleophilic character of O(2) and electrophilic character of C(20) with respect to **1** and other η^1-ketenyl metal complexes (for the reactivity of **14** see Section 7).

The rhodium hydride $H(CO)Rh(PPh_3)_3$ reacts with **1** in a quite complicated way,[14] yielding, through decarbonylation of **1** and intramolecular fission of P–C bonds, a rhodium cluster $Rh_3(\mu\text{-}PPh_2)_3(PPh_3)_3(CO)_3$, **15**, containing $Rh{-}PPh_2{-}Rh$ bridges; it is similar to the product obtained by thermal decomposition of rhodium hydride.[16]

2b. Insertion Reactions of C=C into M–OR, M–NR_2, M–PR_2 Bonds

Carbon suboxide inserts into M–OR, M–NR_2 and M–PR_2 bonds as illustrated in Scheme 5, giving mono- or di-inserted products.

Pandolfo and Paiaro reported the insertion of **1** into M–OR.[17] Alkyl germanium, tin, lead and mercury methoxides react with **1** to give gem-bimetallic derivatives, **16** (Fig. 4). The products are viscous oils or low-melting solids, all thermically unstable. The metal–carbon bonds easily hydrolyze giving dimethyl ester of malonic acid and the corresponding alkyl-metal oxides or hydroxides.

The analogous methoxy compounds of silicon, aluminium and boron do not react with **1** owing to the great stability of these compounds and the consequent difficulty of breaking the metal–oxygen bond. On the contrary EtZnOMe presents a highly ionic character and allows the anionic polymerization of **1**, as NaOMe[3d], LiOMe and $Ti(OR)_4$.[18]

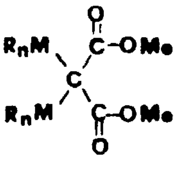
The insertion of **1** into L_nMNR_2 has been recently described.[19,20] Me_3GeNMe_2 and Me_3SnNMe_2 react with **1** giving the di-inserted products $(Me_3M)_2C(CONMe_2)_2$, **17**, whose molecular structures are shown in Fig. 5.

The molecular geometry around Ge and Sn appears to be strictly tetrahedral; no interactions exist between the metals and O or N atoms of the amidic groups.

It is unlikely to obtain and purify the corresponding mono-inserted (ketenyl) products, $[(Me_3M)(CONMe_2)C{=}C{=}O]$, **18**, being decomposable oils. On the other hand, the di-inserted product is preferred to the mono-inserted even though an excess of C_3O_2 is used.

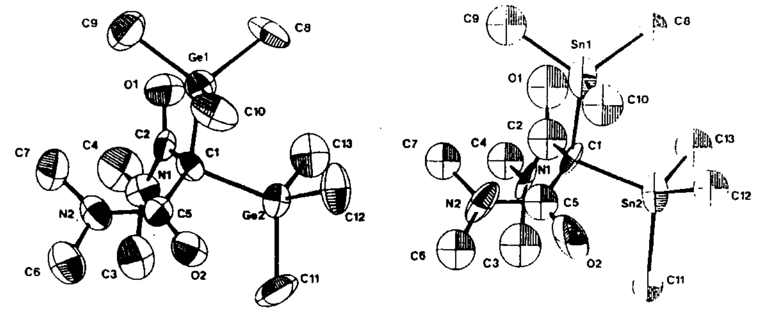
The amides of boron and mercury do not react with **1**, whereas titanium and zinc amides produce polymerization of **1**.[21]

Insertion reactions of **1** into Ge and Sn phosphides, phospines and chlorophosphines have been reported in the literature.[11] Ge and Sn phosphides react with **1** giving insertion of C=C bonds, in



16

FIGURE 4 Structure of $(R_nM)_2C(COOMe)_2$ (16).



17a **17b**

FIGURE 5 Molecular structure of $(Me_3Ge)_2C(CONMe_2)_2$ (**17a**) and $(Me_3Sn)_2C(CONMe_2)_2$ (**17b**) reprinted with permission from Ref. 20.

contrast to what happens with Si phosphide (see Section 1). With Me_3SnPPh_2 only the di-inserted derivative $(Me_3Sn)_2C(COPPh_2)_2$, **19**, is formed, which is surprisingly stable. It neither undergoes hydrolysis, nor reacts with atmospheric oxygen. Probably a favourable electronic interaction between the electron-donor phosphorous and the acceptor Me_3Sn groups takes place. Moreover **19** is able to act as a bidentate ligand toward transition metal ions.[22]

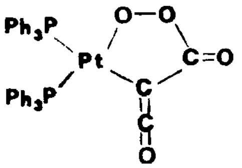
The reaction with Me_3GePPh_2 gives only the mono-inserted product, $[(Me_3Ge)(COPPh_2)C{=}C{=}O]$, **20**, which shows the $\nu_{(C=C=O)}$ stretching frequency at 2080 cm^{-1}, even when the reaction is performed with an excess of Ge compound. No explanation of this fact has been proposed (see also the reaction of platinum di-hydrides with **1** in Section 2a).

Whereas tri-aryl phosphines do not react with **1** and tri-alkyl phosphines cause its polymerization, secondary phosphines (PR_2H, R=Ph, Cy) allow the formation of di-phosphides $R_2P{-}C(O){-}CH_2{-}C(O){-}PR_2$, **21**, with high yields and clean reactions.

The chlorophosphines, PR_2Cl, in which the chlorine atom is the negative center, react with **1** giving, owing to their nature, the chloro-derivative $(PR_2)_2C(COCl)_2$, **22**.

2c. Insertion Reactions of C=C into M-O-O-Bond

The platinum di-oxygen complex $(PPh_3)_2PtO_2$ reacts with **1**.[23] In this reaction carbon suboxide behaves as an activated olefin versus



23

FIGURE 6 Structure of $(PPh_3)Pt{-}O{-}O{-}C(O){-}C{=}C{=}O$ (**23**).

the di-oxygen compound and inserts into a M–O bond giving the stable five-membered di-oxametallacyclic adduct **23** (Fig. 6).

23 presents significant IR signals at 2087 ($\nu_{(C=C=O)}$) and 1632 ($\nu_{(C=O)}$) cm^{-1}. The reactivity of **23** and the molecular structures of some derivatives are reported in Section 7.

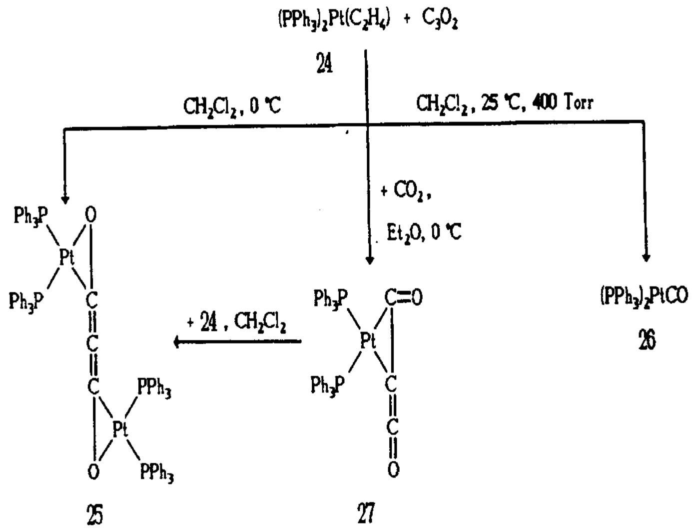
It is pointed out that the reaction between $(PPh_3)_2PtO_2$ and C_3O_2 has been previously reported incorrectly.[24,25]

3. REACTIONS OF COORDINATION TO C=O AND C=C BONDS

The reactions of the complex $(PPh_3)_2Pt(C_2H_4)$, **24**, with **1** have been described by Pandolfo, Morandini and Paiaro[2] and are reported in Scheme 6. The compound **25**, in which η^2-(C,O) coordination is present, is obtained in CH_2Cl_2 at 0°C.

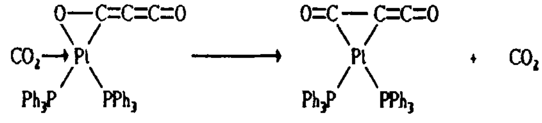
If the reaction is performed at 25°C and 400 mm Hg, the final product $(PPh_3)_3PtCO$, **26**, is obtained. Under these conditions the starting platinum complex loses ethylene[27] and the 14-electron species $(PPh_3)_2Pt$ can undergo decarbonylation of **1**. It is quite probable that unstable ketenylidene species, as $Pt_2C{=}C{=}O$, are formed, likewise with the analogous Rh complex (see Section 5).

In diethyl ether at 0°C, **1** coordinates to Pt η^2-(C,C), giving **27**, only in the presence of CO_2. The amount of CO_2 required can change within a wide range (10 to 100%) and no CO_2 is observed in the final product. When **27** reacts with **24**, it undergoes isomerization and subsequent η^2-(C,O) coordination with the formation of **25**. This last compound is also obtained in diethyl ether in the absence of CO_2.



SCHEME 6

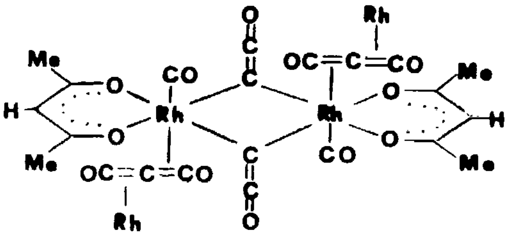
The influence of CO_2 in this reaction has been a matter of deep inquiry. The authors suppose that CO_2 is weakly coordinated to the metal, giving rise to a species containing both CO_2 and C_3O_2. Therefore, as CO_2 is an electrophilic species, the metal becomes more positive, making the isomerization reaction η^2-(C,O) → η^2-(C,C) possible (Scheme 7).



SCHEME 7

4. FORMATION OF ALLENIC COMPLEXES

The allenic moiety of **1** (C=C=C) is able to coordinate two Rh atoms, giving a polymeric structure, **28** (Fig. 7), in which a ketenylidenic bridge is also present.[28] Hydrolysis of **28** with diluted acids leads to the formation of acetic acid, malonic acid and Hacac in the ratio 2:1:2.



28

FIGURE 7 Structure of $[(\mathrm{Acac})\mathrm{Rh(CO)}(\mu\text{-C{=}C{=}O})(\mathrm{C_3O_2})_{1/2}]_n$ (**28**).

5. DECARBONYLATION REACTIONS

Several reactions have been reported in which **1** undergoes a decarbonylation process, mainly through the action of VIII group metals. In general the reaction leads to the formation of the metal carbonyl and the fragment :C=C=O which can react in various ways with different substrates yielding metal-ketenylidene complexes, tri-alkyl (or aryl) phosphoranylidene ketenes (R_3PCCO) and polymers of C_2O; the initiation of the polymerization of **1** is also possible.

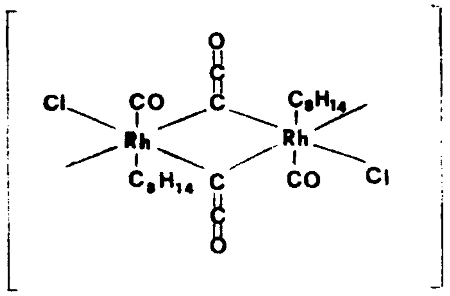
The first example of decarbonylation reaction of **1** has been reported by Paiaro and Pandolfo,[29,30] using $(PPh_3)_2RhCl$. The 16-electron Rh complex reacts with **1** giving high yields of *trans*-$(PPh_3)_2Rh(CO)Cl$. The IR spectroscopy shows, in the course of the reaction, signals attributable to the formation of unstable intermediates containing coordinated CO and C_2O.

The binuclear complex $[(C_8H_{14})_2RhCl]_2$ reacts with **1**, forming a polymeric product, **29**, having the structure shown in Fig. 8, in which Rh(III) is present.[29]

A similar compound is obtained in the first step of the reaction of **1** with $acacRh(C_2H_4)_2$. The compounds $[(COD)RhCl]_2$, $CpRh(C_2H_4)_2$ and $CpRh(CO)_2$ do not react with **1**.[28]

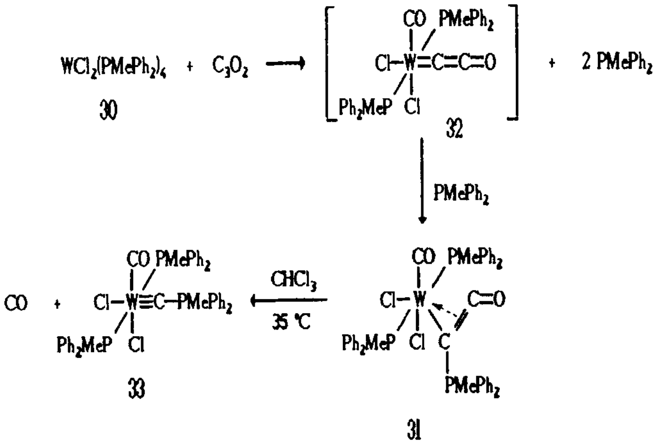
These results suggest that the reaction proceeds via electrophilic attack of a tri-coordinated rhodium atom (obtained by dissociation of starting complexes) on the C_β of **1**.

The reaction between $CpMn(CO)_2 \cdot THF$ and **1** gives $CpMn(CO)_3$, together with a dark brown solid recognized as a polymer of C_2O.[28]



29

FIGURE 8 Structure of $[(C_8H_{14})(Cl)Rh(CO)(\mu\text{-}C{=}C{=}O)]_n$ (**29**).

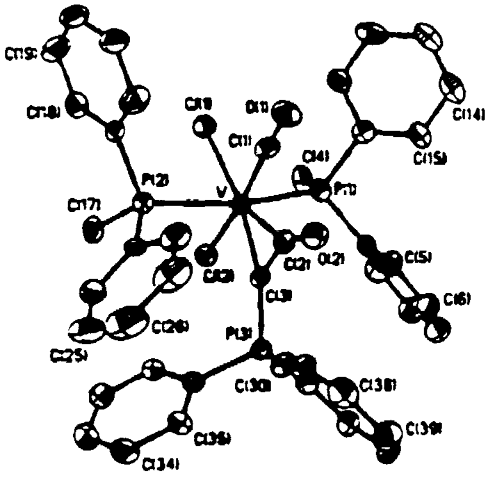


SCHEME 8

The 14-electron species $Ni(PCy_3)_2$ reacts with **1** yielding $Ni(PCy_3)_2(CO)_2$[28] whose structure has been described.[31]

Also $Fe_2(CO)_9$,[32] $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$[33] are able to decarbonylate **1**, forming the corresponding carbonyls $Fe(CO)_5$, $Pt(PPh_3)_3(CO)$ and $Pd(PPh_3)_3(CO)$.

According to List, Hillhouse and Rheingold,[34] **1** can undergo a double decarbonylation by action of $WCl_2(PMePh_2)_4$, **30**. The basic steps of such reaction are reported in Scheme 8. Here, as an intermediate step, the formation of the carbonylketenylidene deriv-



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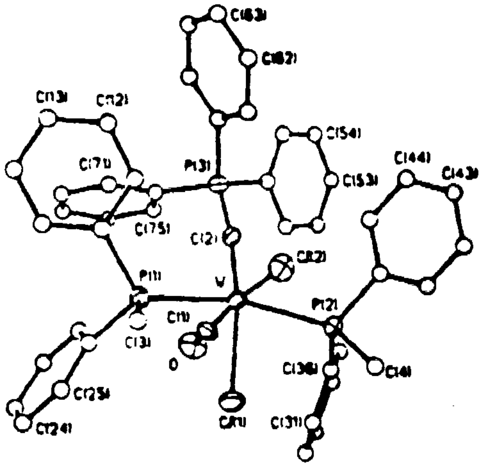


33a

FIGURE 9 Molecular structure of $(Cl)_2(CO)(PMePPh_2)_2W[C,C'{:}\eta^2\text{-}C(O)CPMePh_2]$ (**31**) and $(Cl)_2(CO)(PMePh_2)W(\equiv CPPh_3)$ (**33a**) reprinted with permission from Ref. 20.

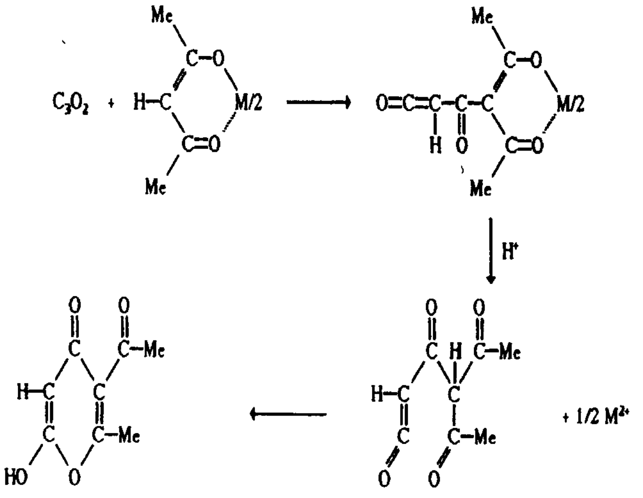
ative **32** has been supposed; it is subsequently trapped by $PMePh_2$ to give **31**.

In $CHCl_3$ at 35°C, **31** changes into **33**, with evolution of one mole of CO. The molecular structures of **31** and of a triphenylphosphine analogue of **33**, **33a** (Fig. 9), have been described.

6. REACTIONS WITH COORDINATED LIGANDS

Pandolfo and Paiaro reported the reaction between **1** and acetylacetone catalized by acetylacetonate metal complexes (Zn, Cu, Co, Ni).[35]

In this case there is no direct interaction of **1** with the metal and the so-obtained final product is 5-acetyl-2-hydroxy-6-methyl-4-pyrone, **34**. The proposed reaction mechanism provides, as a first step, the insertion of **1** into the C–H methine group of coordinated acetylacetone, followed by the protonation, from Hacac, of the central carbon atom of the chelate ring which detaches off the metal and cyclizes to form **34** (Scheme 9). Acac⁻ coordinates to the metal, re-forming the starting acetylacetonate complex.



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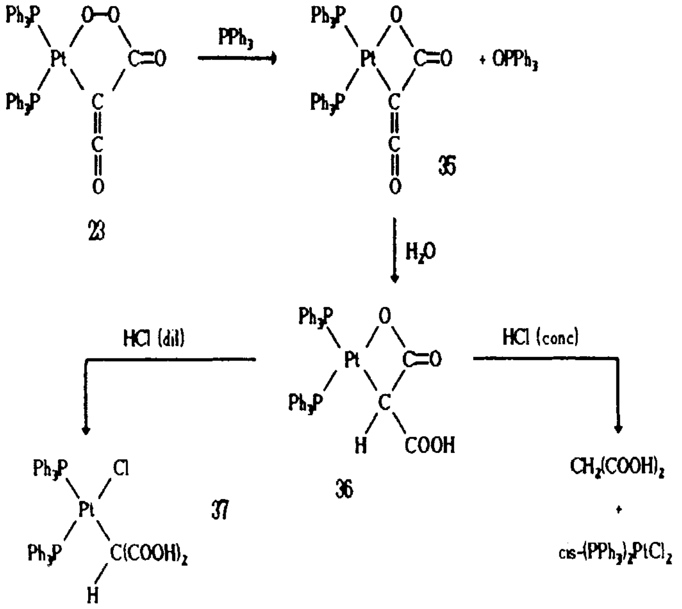
SCHEME 9

7. REACTIONS OF COORDINATED C_3O_2

Mono-insertion reactions of C_3O_2 lead to ketenyl, ketenylidene and methylenketene complexes. These complexes can, in turn, be used as substrates in addition reactions on the reactive ends of **1** bonded or coordinated to the metal.

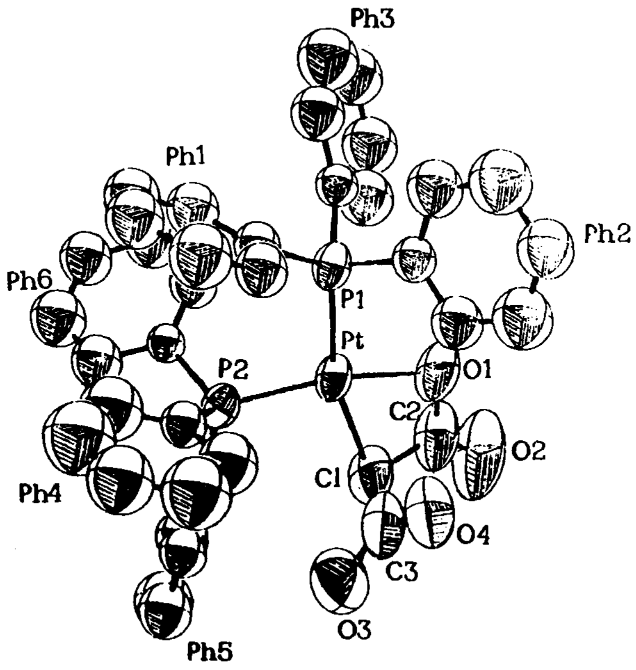
Some reactions of the di-oxaplatinum compound **23** (see Section 2c) have been described[36] and are reported in Scheme 10.



SCHEME 10

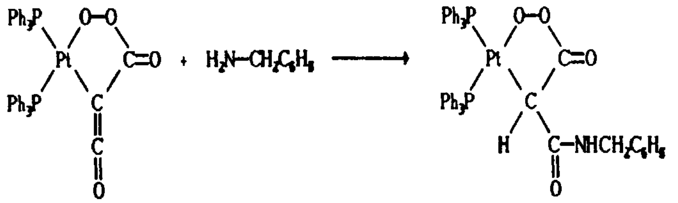
PPh_3 deoxidizes **23**, forming phosphine oxide and **35**; water can react with the ketene moiety of **35** giving the compound **36**. If **36** is treated with diluted HCl, the compound **37** is formed, whereas concentrated HCl produces a complete decomposition. The molecular structure of **36** is shown in Fig. 10.

23 reacts with benzylamine which adds to the ketene moiety, giving the amidic derivative **38** (Reaction 5). The molecular structure of **38** (Fig. 11) has been described.[23]



36

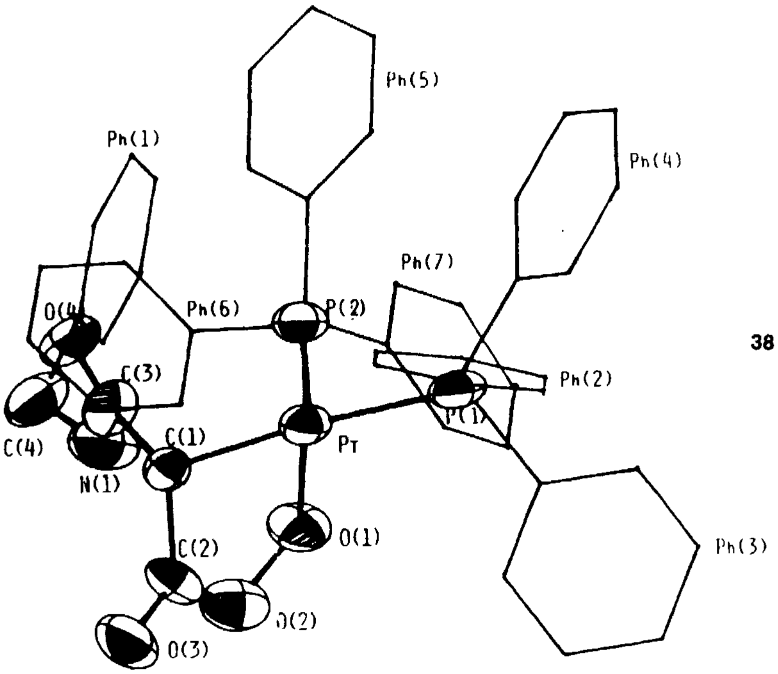
FIGURE 10 Molecular structure of $(PPh_3)_2Pt{-}O{-}C(O)CHCOOH$ (**36**) reprinted with permission from Ref. 36.



38

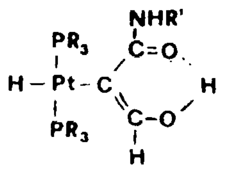
REACTION 5

Some reactions of the complexes **25** and **27** have been reported.[26] The complex **25**, in which **1** is η^2-(C,O) coordinated to Pt, reacts with O_2, forming phosphine oxide, and with NaOH aq., forming sodium malonate. Compound **27** (η^2-(C,C) coordination) reacts with iodine, producing C_3O_2, and RNH_2 or ROH change it into the amide or the esther derivative, respectively.



38

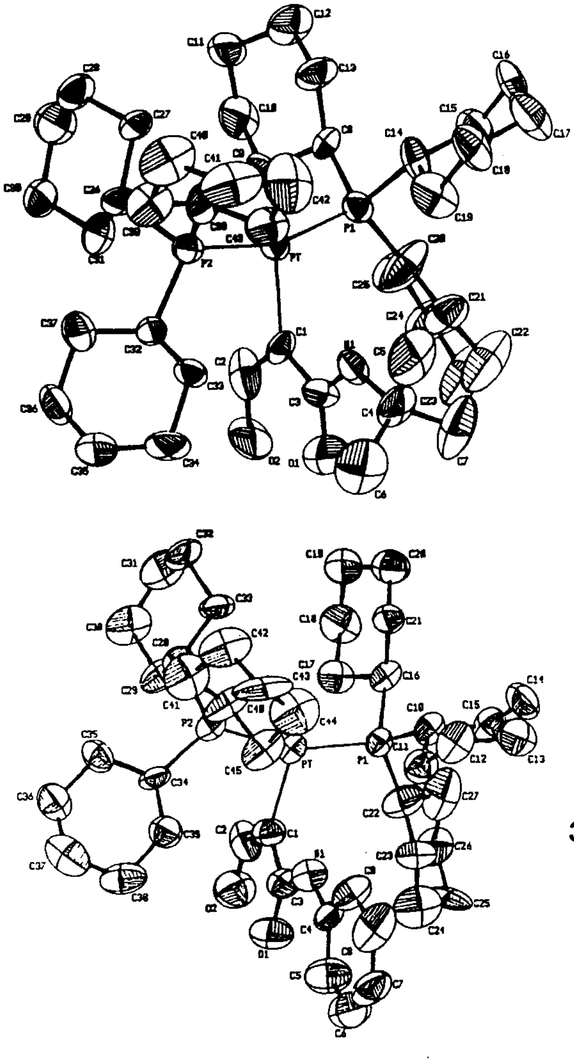
FIGURE 11 Molecular structure of (PPh$_3$)$_2$Pt–O–O–C(O)CHCONHCH$_2$Ph (38) reprinted with permission from Ref. 23.



39

FIGURE 12 Structure of *trans*-H(PR$_3$)$_2$Pt[C(=CHOH)(CONHR)] (39).

Alifatic or aromatic amines react with the ketene moiety of **14**, giving the amidic derivative **39**[37] whose structural formula can be written as in Fig. 12. The molecular structures of such complexes have been reported[37,38] and are shown in Fig. 13. The ligand lies in a plane normal to the coordination plane of Pt, as found in all cases of trigonal carbon atoms bonded to Pt.[39] ^{1}H NMR and IR



39a

39b

FIGURE 13 Molecular structure of *trans*-H(PCy$_3$)$_2$Pt[C(=CHOH)(CONH*t*-Bu)] (**39a**) and of *trans*-H(PCy$_3$)$_2$Pt[C(=CHOH)(CONHPh)] (**39b**) reprinted with permission of Refs. 38 and 37.

spectra indicate the total absence of the aldehydic group: the starting formyl group is completely changed in the enolic form, so that a vinyl alcohol is present.

CONCLUSIONS

This review has attempted to present an exhaustive summary of the reaction of carbon suboxide with organometallic complexes. This area has not been much investigated so far; nevertheless, the data here reported show the enormous potentiality of C_3O_2 to give a wide variety of reactions.

As a matter of fact it is possible to take advantage of the ability of C_3O_2 to react through the C═O or C═C double bonds and avail of the different nucleophilic character of the central carbon atom and of the oxygen atoms, in order to discriminate reagents having different oxophilicity.

Insertion of C═O or C═C, coordination to transition metal compounds, and decarbonylation reactions allow the synthesis of unusual metal derivatives.

The reaction of C_3O_2 with coordinated ligands can be usefully used to synthetize a variety of organic compounds otherwise not easily accessible.

The formation of metal-ketenyl or -ketenylidene compounds offers the possibility of investigating the interesting field of ketene chemistry, opening access to the synthesis of a large series of unusual organic molecules. Moreover the metal-bonded ketenyl group can be a center of stereospecific or enantioselective reactions.

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