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The organometallic chemistry of $Ph_3P{=}C{=}C{=}O$. A route to metal-substituted ketenes

Roberta Bertani [a], Maurizio Casarin [b], Luciano Pandolfo [c],*

[a] *Dipartimento di Processi Chimici di Ingegneria, Università di Padova, Via Marzolo, 1, I-35131 Padova, Italy*
[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan, 4, I-35131 Padova, Italy*
[c] *Dipartimento di Chimica, Università della Basilicata, Via N. Sauro, 85, I-85100 Potenza, Italy*

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Abstract

Ketenylidenetriphenylphosphorane, $Ph_3P{=}C{=}C{=}O$ (**1**), presents, at a first glance, the characteristics of both ylides and ketenes, but its behavior is that typical of ylides, undergoing electrophilic attacks on the ylidic carbon that transform **1** into a 'true' ketene having PPh_3 as one substituent. Here we review the synthesis, the chemical–physical properties as well as the reactivity of these compounds, with a particular emphasis on the interaction with transition metal complexes. With this compound it has always been observed that the ylidic carbon of **1** binds to coordinatively unsaturated metals, which act as electrophiles, forming η^1-ketenyl derivatives that can also be viewed as stabilized metal-substituted ketenes. Perspectives for the synthesis of other metal-substituted ketenes and developments on their study are also presented.

Keywords: Ketenylidenetriphenylphosphorane; Ph_3PCCO; Ylides; Ketenes; Metal-substituted ketenes; η^1-Ketenyl complexes

1. Introduction

Phosphorus ylides were obtained for the first time at the end of the 19th century by Mikhaelis and Gimborn [1], but were initially incorrectly formulated. In the years 1919–1921, Staudinger et al. [2,3] synthesized and characterized $Ph_3P{=}CH_2$ observing, at the same time, the occurrence of the reaction later named by Wittig, even though they did not recognize its importance at that time. It was only after the Second World War that Wittig and Geissler [4] studied and described the reaction of triphenylphosphonium methylide with benzophenone to give Ph_3PO and diphenylethene (Reaction 1) and realized its synthetic possibilities.

$$[Ph_3PCH_3]Br \xrightarrow{LiPh} Ph_3P{=}CH_2 \xrightarrow{Ph_2C{=}O} Ph_2C{=}CH_2 + Ph_3PO \qquad (1)$$

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* Corresponding author. Tel.: +39-0971-202210; fax: +39-0971-202223

E-mail address: pandolfo@unibas.it (L. Pandolfo).

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The widespread applications of this reaction, which represents an easy way to obtain substituted olefins with high selectivity, led, *inter alia*, to the industrial synthesis of vitamin A and Georg Wittig was awarded the Nobel Prize for his discovery [5]. The chemistry of phosphorus ylides has undergone continuous development and numerous books and reviews dealing with these compounds and their chemistry have been published [6].

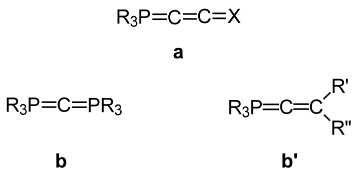


Chart 1.

An interesting class of phosphorus ylides is that in which cumulated double bonds are present, i.e. phosphacumulene (**a**), and phosphallene (**b** and **b′**), ylides (Chart 1). The organic reactivity of these ylides has been reviewed in 1977, by Bestmann [7] and has been also summarized in some books [6c,6d].

Here we will review the most recent studies on one of these cumulene ylides, ketenylidenetriphenylphosphorane, $Ph_3P{=}C{=}C{=}O$ (**1**), with particular emphasis on its reactivity towards metal complexes. The literature coverage is until March 2002. Throughout this work we will adopt for **1** the most commonly used name *ketenylidenetriphenylphosphorane*, even though it would be more correct to use *triphenylphosphonium ketenide* or *ketene ylide*. Furthermore, for the sake of simplicity, we will use mainly the *ylene* canonic structure instead of the *ylide* one (Chart 2). The ylene structure will also be used to represent other phosphorus ylides.

2. Syntheses of $Ph_3P{=}C{=}C{=}O$

Ketenylidenetriphenylphosphorane was first synthesized in 1966. In that year its synthesis [8] and X-ray crystal structure determination [9] were almost contemporaneously reported [10]. The synthesis was accomplished through the reaction of hexaphenylcarbodiphosphorane with CO_2, to give a zwitterionic compound that yielded Ph_3PO and **1**, through thermolysis (Scheme 1).

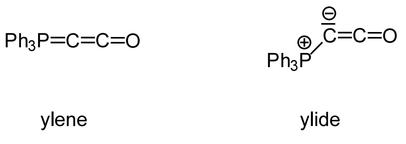
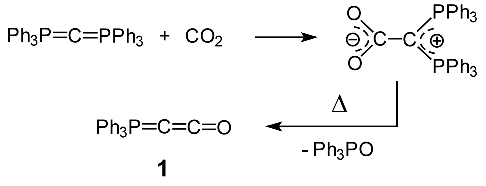


Chart 2.



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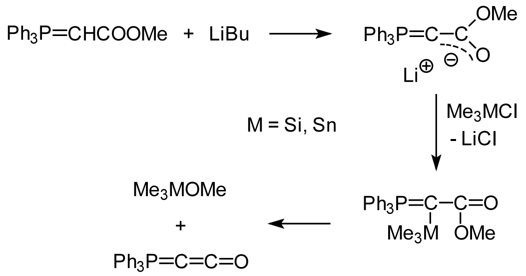
Scheme 1.



Scheme 2.

$Ph_3P{=}C{=}C{=}O$ was later obtained from the reaction of carbomethoxyphosphorus ylide with LiBu, followed by treatment with Me_3MCl (M = Si, Sn), according to Scheme 2 [11].

It is likely that this scheme, proposed on the basis of obtaining **1** and Me_3MOMe, does not correspond to reality, as the presence of Me_3MCl is not required to obtain **1**. As a matter of fact, the direct reaction of $Ph_3P{=}CHCOOR$ with bases was used by Bestmann et al. for the synthesis of **1**. The treatment of $Ph_3P{=}CHCOOEt$ with LiBu led to the formation of **1** with an overall yield of about 55% [12], through elimination of EtOH, according to Reaction 2.

$$\begin{aligned}&Ph_3P{=}CHCOOEt + LiBu\\&\quad \rightarrow BuH + LiOEt + Ph_3P{=}C{=}C{=}O \qquad (2)\end{aligned}$$

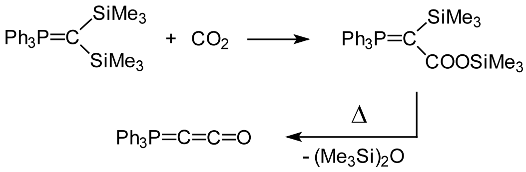
A higher yield (about 80%) was obtained from the reaction of $Ph_3P{=}CHCOOMe$ with bistrimethylsilyl sodium amide [13] (Reaction 3).

$$\begin{aligned}&Ph_3P{=}CHCOOMe + NaN(SiMe_3)_2\\&\quad \rightarrow NaOMe + HN(SiMe_3)_2 + Ph_3P{=}C{=}C{=}O \qquad (3)\end{aligned}$$

This synthetic method was further improved and extended to the synthesis of the sulfur analog of **1**, $Ph_3P{=}C{=}C{=}S$ [14]. More recently, the synthesis of **1** was achieved using $NaNH_2$ as base [15] (Reaction 4).

$$\begin{aligned}&Ph_3P{=}CHCOOMe + NaNH_2\\&\quad \rightarrow NaOMe + NH_3 + Ph_3P{=}C{=}C{=}O \qquad (4)\end{aligned}$$

Compound **1** can also be obtained in a completely different way, through the thermal decomposition of $Ph_3P{=}C(SiMe_3)(COOSiMe_3)$, which is formed by the treatment of $Ph_3P{=}C(SiMe_3)_2$ with CO_2, according to Scheme 3 [16].



Scheme 3.

3. Chemical–physical characteristics of $Ph_3P{=}C{=}C{=}O$

$Ph_3P{=}C{=}C{=}O$ is a white solid which melts with decomposition at 172–173 °C, soluble in most organic solvents. In the solid-state it is stable if stored under dry nitrogen. In chlorinated solvents it undergoes slow decomposition, most likely due to the presence of acid (protic) species.

The IR spectrum of **1** is characterized by an intense signal at 2110 cm^{-1}, typical for a C=C=O group [17]. The UV–vis spectrum in dichloromethane shows no characteristic features, as transitions concerning the C=C=O moiety are masked by the intense absorbance due to the phenyl groups [18].

The $^{31}P\{^{1}H\}$-NMR spectrum of **1** consists of one singlet at a chemical shift that is solvent-dependent: values of 2.6 ppm in C_6D_6 [8], 5.37 ppm in $CDCl_3$ [14] and 5.45 ppm in CD_2Cl_2 [19] have been reported. The ^{13}C-NMR spectrum of **1** has been also obtained [19] but the chemical shifts pertaining to the C=C=O fragment have been corrected in a more recent study (−9.69 ($^{1}J_{CP} = 194.2$ Hz) and 147.74 ppm ($^{2}J_{CP} = 44.4$ Hz) for the ylidic and carbonylic carbon, respectively) [20], in which the solid-state CP/MAS spectra $^{31}P\{^{1}H\}$- and $^{13}C\{^{1}H\}$-NMR have also been reported (^{31}P 4.5, ^{13}C −7.9 ($^{1}J_{CP} = 220$ Hz) and 143.3 ppm). The relatively high $^{1}J_{CP}$ value [6] indicates a large dipole moment, with a higher level of phosphorus shielding than in non-cumulenic phosphorus ylides, denoting the relative importance of the *ylide* canonic form, as confirmed also by the X-ray crystal structure of **1** [9]. The ^{13}C-NMR signal of the ylidic carbon is only slightly high-field shifted with respect to simple phosphorus ylides.

The mass spectrum of **1** obtained in EI ionization conditions [21] shows a 'normal' fragmentation pattern. Signals are present at m/z 302 $[M]^{+\bullet}$, 301 $[M-H]^{+\bullet}$ (which is larger than the molecular ion), 274 $[M-CO]^{+\bullet}$, 225 $[M-Ph]^{+\bullet}$, and 262 $[Ph_3P]^{+\bullet}$. Further signals at m/z 278 $[Ph_3PO]^{+\bullet}$, 201 $[Ph_2PO]^{+\bullet}$, 185 $[Ph_2P]^{+\bullet}$, and 183 $[(C_6H_4)_2P]^{+\bullet}$ are attributable to secondary decomposition processes. The mass spectrum obtained in FAB ionization conditions is more or less analogous [22]. As expected, due to the 'softer' ionization conditions employed, the signal at m/z 302 $[M]^{+\bullet}$ is the larger one in this case. An ms/ms experiment on these abundant ions showed the presence of three fragments directly related to the structure of **1**, i.e. signals at m/z 274 $[M-CO]^{+\bullet}$ and 262 $[PPh_3]^{+\bullet}$ arising from the loss of C_2O, and 183 due to a typical rearrangement of the PPh_3 moiety [23]. Other collisionally-generated species at m/z 194 and 166 indicate an extensive rearrangement of $[Ph_3PCCO]^{+\bullet}$ leading to the formation of diphenylketene molecular ion and its fragmentation product $[Ph_2C]^{+\bullet}$, respectively.

The X-ray crystal structure determination of **1** [9] shows that the P–C–C–O skeleton is not linear, with a P–C–C– angle of 145.5°, thus indicating the relative importance of the *ylide* canonic form (Chart 2), even though the $P-C_{(ylidic)}$ distance (1.648 Å), which is markedly shorter than the $P-C_{(phenyl)}$ distances (ca. 1.80 Å), could be indicative of an, at least partial, double bond character. The CCO fragment is almost linear (175.6°) and the C=C bond length (1.210 Å) is shorter than a normal double carbon–carbon bond and is comparable to the bond length of the acetylene triple bond (1.205 Å). The C=O bond distance, 1.185 Å, is in the range of organic carbonyls.

To the best of our knowledge, only two contributions dealing with the theoretical analysis of the electronic structure of $Ph_3P{=}C{=}C{=}O$ have been reported so far [24,25]. One of these [24] describes ab initio molecular orbital calculations performed on the model compound $H_3P{=}C{=}C{=}O$, even though this study was mainly devoted to finding an explanation for the different P–C–C angles experimentally observed along the series $Ph_3P{=}C{=}C{=}X$ (X = O, S, NPh, $(OEt)_2$). The second study [25] involved numerical experiments within the density functional theory, which were carried out on **1** as well as on $H_3P{=}C{=}C{=}O$. The whole structure of $H_3P{=}C{=}C{=}O$ was optimized, while in **1** the optimization procedure was limited to the C=C=O fragment. Relevant results are reported in Table 1 where experimental structural parameters [9] are also included for comparison. The agreement between theory and experiment is evident.

Hirshfeld atomic charges for the P–C–C–O skeleton of **1** and $H_3P{=}C{=}C{=}O$ (in parentheses) were calculated and are reported in Chart 3 [25].

Table 1
Relevant calculated (**1** and $H_3P{=}C{=}C{=}O$) and experimental (**1**) structural parameters

	$Ph_3P{=}C_1{=}C_2{=}O$	$H_3P{=}C_1{=}C_2{=}O$	Crystal data [9]
$P-C_1$ (Å)	1.657	1.648	1.648
C_1-C_2 (Å)	1.273	1.281	1.210
C_2-O (Å)	1.183	1.178	1.185
$P-C_1-C_2$ (°)	142.4	134.6	145.5

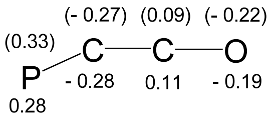


Chart 3.

4. Reactivity of $Ph_3P{=}C{=}C{=}O$

4.1. Reactions with organic compounds

Even though $Ph_3P{=}C{=}C{=}O$ looks like a ketene, its reactivity is quite different. The valence manifold of **1** is characterized by the presence of two orthogonal π electron systems, each of them constituted by three MOs. π orbitals lying in the same plane of the P–C–C–O skeleton are labeled as $\pi_{\|}$ while those perpendicular to the same plane are indicated as $\pi_{\perp}$. Four of the six π orbitals are occupied by the eight π electrons of C and O atoms (two electrons from each C atom and four electrons from the O atom).

This is an important difference from the electronic structure of ketenes, where the $\pi_{\perp}$ and $\pi_{\|}$ levels are not equivalently occupied; the former accommodates four electrons while the latter only two. This produces a dipolar character in the C–C bond of ketenes (Chart 4), which is responsible for their typical reactivity, such as dimerization, cycloaddition, etc.

As indicated by Bestmann [7] and then confirmed by theoretical calculations [24,25], this dipolar character is absent in **1** (Chart 5) and reactions typical of ketenes, such as dimerization, do not occur [26].

Instead, the charge density distribution of **1** (Chart 3) is responsible for the course of reactions with generic compounds El–Nu, leading to nucleophilic substitution on El–Nu, with formation of phosphonium salts, according to Scheme 4.

This reaction transforms **1** into a phosphonium cation, a 'true' ketene that can undergo the reactions typical of ketenes. This kind of organic reactivity has been studied and reviewed by Bestmann [7] and we will thus limit ourselves to a brief description of the most recent observations.

The intermediate phosphonium salt formed by the reaction between **1** and El–Nu (Scheme 4) can undergo different fates, depending on the nucleophilic strength of Nu^-. If this is strong enough, attack of the carbonyl carbon occurs, yielding a carbonyl stabilized ylide, as in the case of the reaction of **1** with MeOH which gives carbomethoxymethylene triphenylphosphorane [8] (Reaction 5).

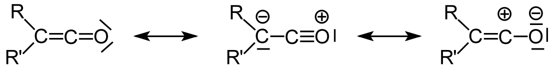


Chart 4.

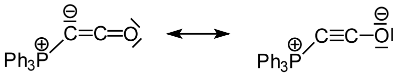
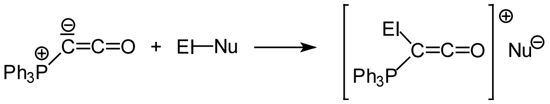
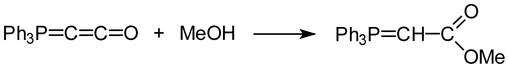


Chart 5.

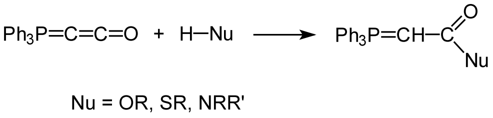


Scheme 4.



$$Ph_3P{=}C{=}C{=}O + MeOH \longrightarrow Ph_3P{=}CH{-}C({=}O)OMe \qquad (5)$$

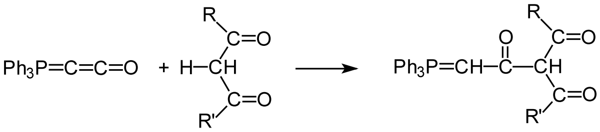
Numerous reactions of **1** with protic nucleophiles (alcohols, thiols and amines) proceed in this way, yielding carbonyl stabilized ylides, including some which would otherwise be difficult to synthesize [7,27] (Reaction 6).



$$Ph_3P{=}C{=}C{=}O + H{-}Nu \longrightarrow Ph_3P{=}CH{-}C({=}O)Nu \qquad (6)$$

Nu = OR, SR, NRR'

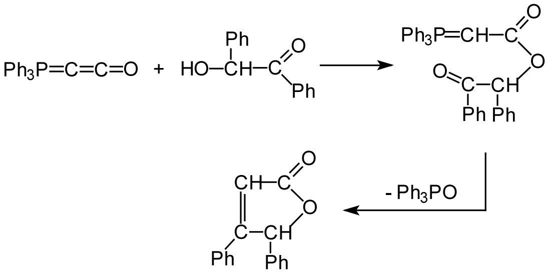
Some compounds containing acidic C–H bonds (i.e. 1,3-dicarbonyl derivatives) can also add to **1** in an analogous way, yielding novel ylides (Reaction 7) that can exist in different tautomeric forms [7,28].



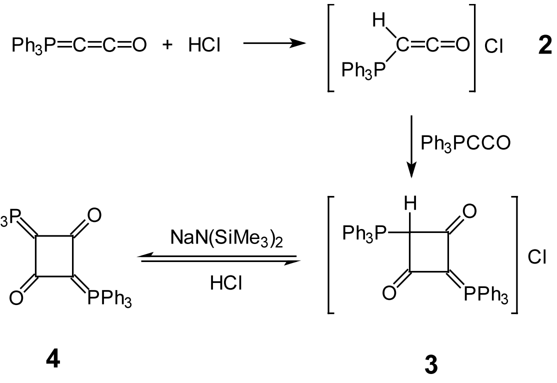
(7)

Reactions between **1** and acid compounds H–Y in which Y is a group potentially able to give intramolecular cyclization with the ylide moiety after addition to the carbonyl carbon, led to the formation of heterocyclic derivatives, mainly through Wittig Ph_3PO elimination [7,29]. An example is illustrated in Scheme 5.

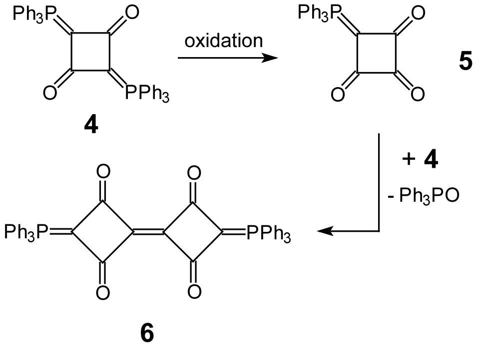
A large number of heterocycles have been prepared through this reaction, including some pharmaceutically interesting compounds. The reader specifically interested in these topics may refer to Ref. [30].



Scheme 5.

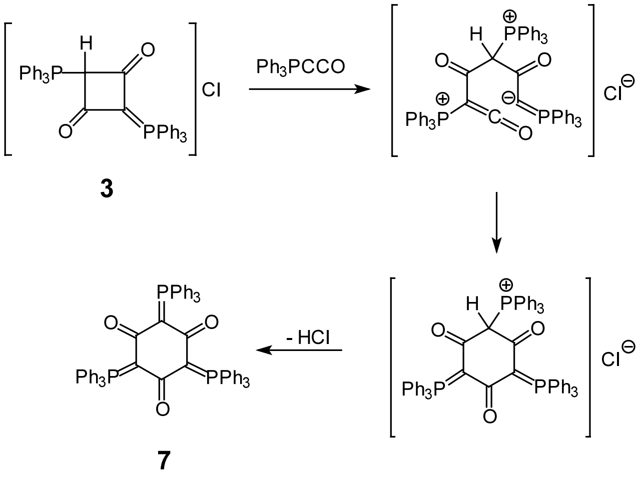


Scheme 6.

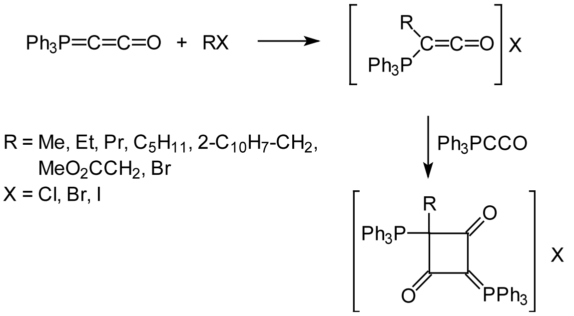


Scheme 7.

The characteristic of **1** whereby it becomes a ‘true’ ketene by attack of an electrophile on the ylidic carbon, has been exploited by Bestmann et al. to obtain some novel compounds. If the counterion Nu^- (Scheme 4) is not very strong, the ‘ketene’ cation can undergo different attacks by other, stronger, nucleophiles. As an example, treatment of **1** with HCl led to the formation of the phosphonium salt (**2**), which was not isolated (Scheme 6). The direct dimerization of this cationic ketene was not observed; instead, compound **2** reacted with one further molecule of **1** giving a cyclobutanedione phosphonium salt **3** that transformed into the stable cyclic dimer of $Ph_3P{=}C{=}C{=}O$ (**4**), on treatment with base [31].



Scheme 8.



Scheme 9.

Oxidation of **4** yields the cyclobutanetrione derivative **5**, the central CO group of which is very reactive, and undergoes a Wittig olefination with another molecule of **4**, to give compound **6** according to Scheme 7 [31,32].

Moreover, by refluxing the dimeric salt **3** in dichloromethane with an excess of **1**, the cyclic trimeric species **7** was obtained in 30% yield, according to a reaction scheme in which the excess of **1** acts as deprotonating agent [33] (Scheme 8).

The reaction of **1** with HCl has been extended to generic R–X compounds according to Scheme 9 [7,21,34], and the reactivity of the cyclobutanedione phosphonium salts thus obtained has also been reported [34].

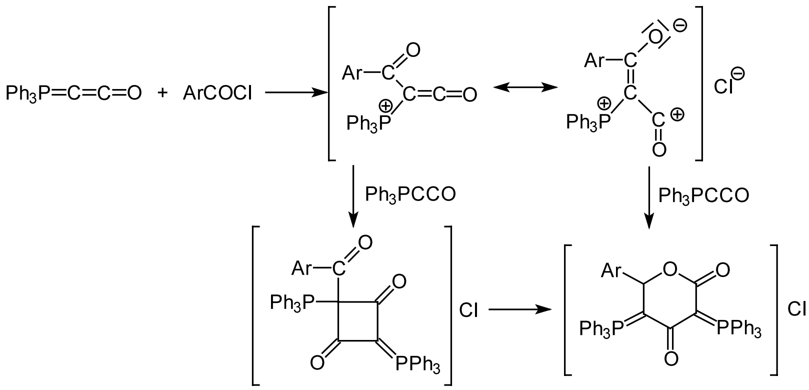
Compound **1** has been also reacted, in a similar way, with acyl chlorides, to give pyrone derivatives **8**, as indicated in Scheme 10 [35].

Due to its electronic structure, $Ph_3P{=}C{=}C{=}O$ is also expected to undergo cycloaddition reactions at C=C or P=C bonds. The first cycloaddition reactions were observed with aldehydes and ketones [21], yielding cyclobutanedione ylides, through the probable formation of a reactive methyleneketene intermediate that rapidly reacts with another molecule of **1**, according to Scheme 11.

An analogous mechanism has been proposed for the reactions of quinones and other aromatic ketones and thiones with **1** in 1:2 molar ratio, yielding cyclobutanedione derivatives [36]. One example [36d] is sketched in Scheme 12.

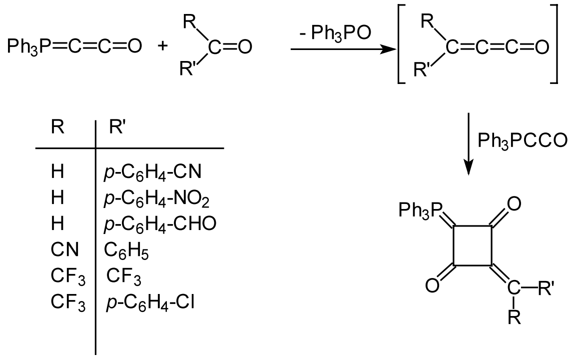
Evidence for this mechanism has been provided by the reactions, in 1:1 molar ratio, of **1** with substances containing cumulated double bonds, both ketene itself and diphenylketene, yielding cyclobutanedione derivatives [21] (Scheme 13).

An analogous unstable intermediate is likely to be formed in the reaction between **1** and CS_2, which is used to synthesize the sulfur analog of **1** [21] (Scheme 14).



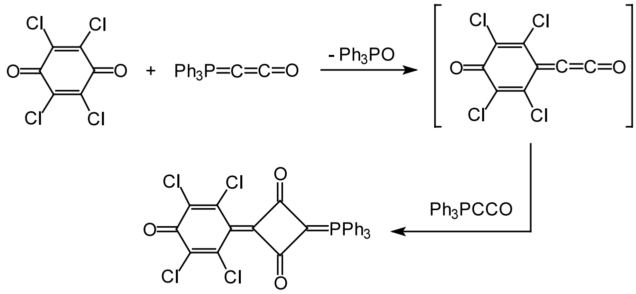
9 **8**

Scheme 10.

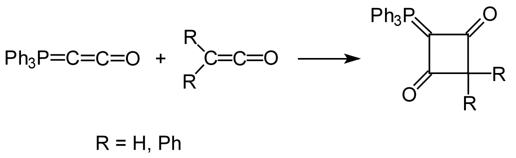


R	R'
H	*p*-C_6H_4-CN
H	*p*-C_6H_4-NO_2
H	*p*-C_6H_4-CHO
CN	C_6H_5
CF_3	CF_3
CF_3	*p*-C_6H_4-Cl

Scheme 11.



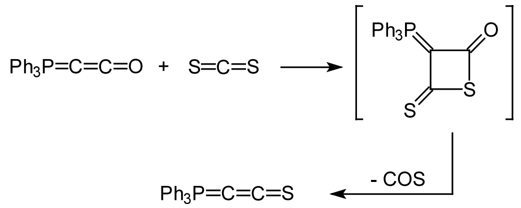
Scheme 12.



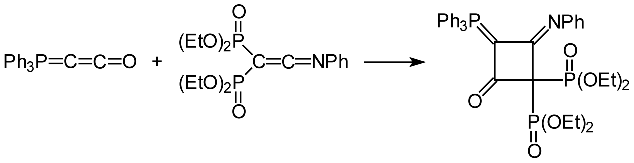
Scheme 13.

Recently, the reaction occurring between **1** and a ketenimine has been reported, once again forming a cyclobutane derivative according to Scheme 15 [37].

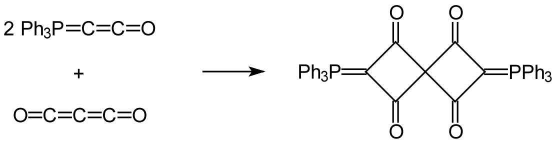
A particularly interesting case of a double [2+2] cycloaddition reaction was observed between ketenylidenetriphenylphosphorane and the simplest stable bisketene, carbon suboxide, C_3O_2 [38]. Two moles of **1** were treated with 1 mol of C_3O_2, yielding the bis(ylidic)spirobiscyclobutanedione (**10**) (Reaction 8).



Scheme 14.



Scheme 15.

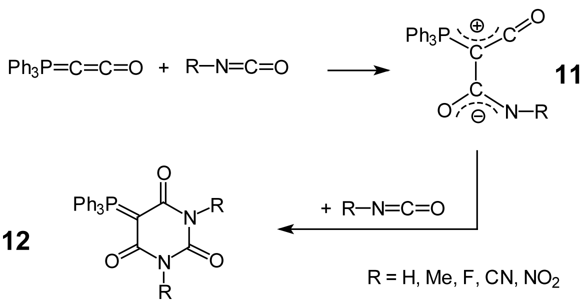


(8)

10

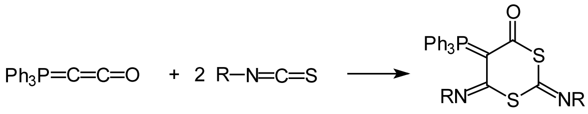
Isocyanates have been reacted with **1** in 2:1 molar ratio to give pyrimidine derivatives [21]. In the proposed mechanism one molecule of R–N=C=O reacts with $Ph_3P=C=C=O$ giving the zwitterionic intermediate **11** that yields the pyperidinic ylides **12** on reaction with another molecule of R–N=C=O, according to Scheme 16 [21,7].

The reaction of **1** with isothiocyanates [7] proceeds in an analogous manner but, due to the greater nucleophilicity of sulfur as compared to nitrogen, the six



Scheme 16.

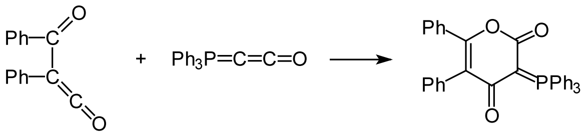
member dithio cyclic ylides **13** are obtained (Reaction 9).



13

(9)

$Ph_3P{=}C{=}C{=}O$ has been reacted with the indicated acyl ketene yielding the pyrone derivative **14** through a [4+2] cycloaddition according to Reaction 10 [39].



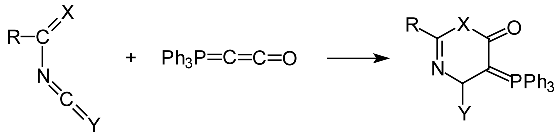
14

(10)

An analogous behavior was observed in the reaction with compounds isoelectronic (and isostructural) with acyl ketenes, $R{-}C({=}X){-}N{=}C{=}Y$, resulting in the formation of cyclic derivatives **15** [39] (Scheme 17).

Also α,β-unsaturated carbonyl compounds undergo [4+2] cycloaddition reactions with **1** producing pyrone derivatives **16** as shown in Scheme 18 [40,41].

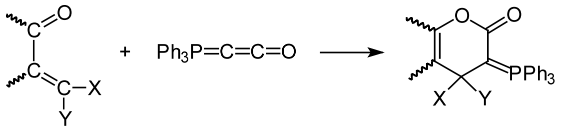
The reactions of **1** with vinyl isocyanates and vinyl isothiocyanates [42] proceed in a similar way (Scheme 19).



15

X	S	O	NPh
Y	S	S	S
R	NCy_2	Me, *p*-C_6H_4-Me	Ph

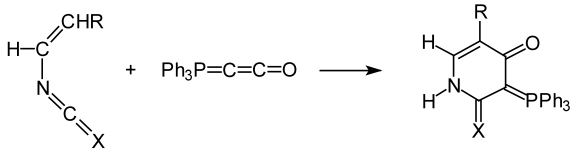
Scheme 17.



16

X	H	CN
Y	COOMe	CN

Scheme 18.



17

X	O	S	S
R	H	H	Ph

Scheme 19.

4.2. Reactions with metal systems

The charge distribution on **1** (Chart 3) indicates that the ylidic carbon is a strong nucleophile, able to attack an electrophilic metal center, analogously to what happens with other phosphorus ylides. Thus, it is rather strange that, among the huge number of known metal–ylide complexes [43], reports on the reactivity of $Ph_3P{=}C{=}C{=}O$ with metal systems are relatively scarce.

In this regard, the reactivity of phosphallene ylides, $R_3P{=}C{=}PPh_3$ (R = Me, Ph) with metal complexes has been tackled only in a few pioneering works of Kaska [44], Raymond [45] and Schmidbaur [46] and, more recently, the same argument has been addressed by Zybill [47], Sundermeyier [48] and Petz [49]. In these papers it is emphasized that the first step of the reaction of $R_3P{=}C{=}PPh_3$ with metal complexes is always the attack of the ylidic central carbon atom to the electrophilic metal center, sometimes followed by further

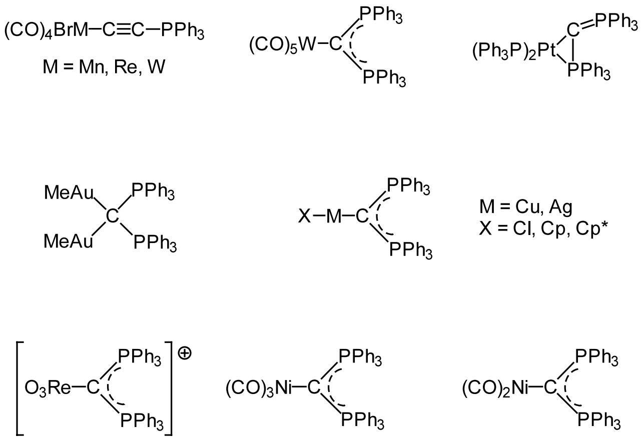


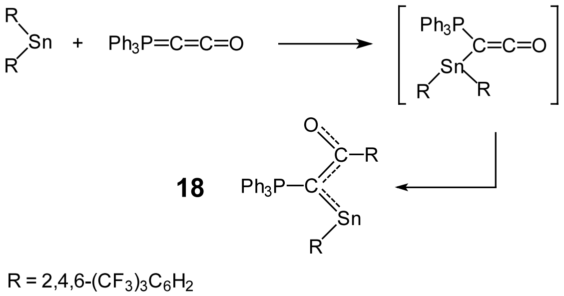
Chart 6.

reactions. Particularly, Wittig-type Ph_3PO eliminations, involving metal-coordinated CO have been reported [44,45]. Some products of these reactions are sketched in Chart 6.

In any case, for $Ph_3P{=}C{=}C{=}O$ the largest number of contributions concern the interactions of **1** with transition metal complexes, and only a few papers report reactions with main group metal compounds.

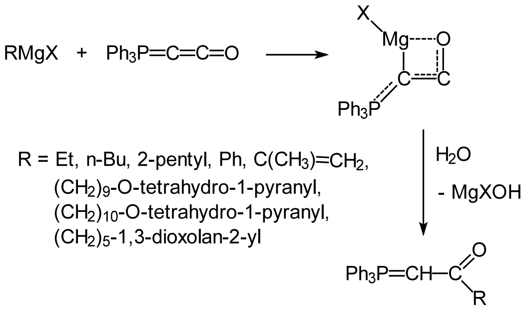
4.2.1. Main group metal systems

Excluding the reactions with Grignard reagents (vide infra) there is only one example of the reactivity of $Ph_3P{=}C{=}C{=}O$ with a main group metal compound reported in the literature. More specifically, the reaction of **1** with stannediyl gives rise to an unstable adduct formed through the coordination of the ylidic carbon to the metal (Scheme 20). This intermediate compound, on standing at 25 °C for 6 h, transforms into compound **18**, the X-ray crystal structure of which has been also reported [50].



Scheme 20.

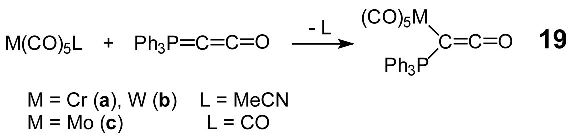
Grignard reagents have been reacted with $Ph_3P{=}C{=}C{=}O$ to produce carbonyl stabilized ylides through the hydrolysis of an intermediate adduct, as proposed by Bestmann et al. [51] (Scheme 21), who used this reaction as a key step in the synthesis of some insect pheromones [52].



Scheme 21.

4.2.2. Transition metal systems

All the reactions of ketenylidenetriphenylphosphorane with transition metals complexes that have been reported exhibit coordination of the ylidic carbon to the metal, with a behavior analogous to that observed when **1** reacts with an electrophilic organic group [7,21,34]. These reactions lead to η^1-ketenyl derivatives [53] that are often stable enough to be isolated and completely characterized. This type of coordination has also been postulated in the case of the reaction of R_2Sn with **1**, even though the possible η^1-ketenyl intermediate was not isolated as it rearranged to give **18**.

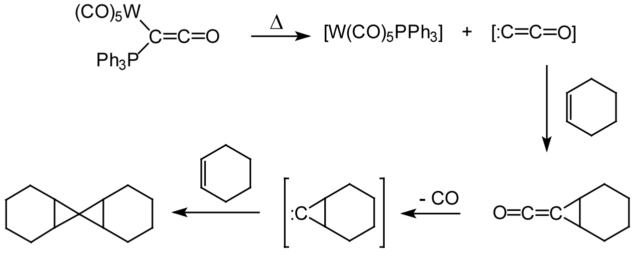


Scheme 22.

The first studies on the reactivity of $Ph_3P{=}C{=}C{=}O$ with transition metal complexes concerned some Group 6 metal carbonyl compounds, $[M(CO)_5L]$, that underwent substitution of L to give η^1-ketenyl compounds of the type $[M(CO)_5\{\eta^1\text{-}C(PPh_3)CO\}]$ (**19**) [54,55] (Scheme 22).

Complexes **19** were obtained in low yields (20–30%) by reacting $[M(CO)_5L]$ either in refluxing ethyl ether (**a**, **b**) or in refluxing benzene (**c**), in an inert atmosphere. They were characterized through molecular weight determinations and elemental analyses and show a typical sharp IR band at 2083 (**19a**, **b**) or 2084 cm^{-1} (**19c**), characteristic of the CCO group η^1-coordinated to a metal center through the ylidic carbon atom [53]. The η^1-ketenyl complexes thus obtained are stable at room temperature in the solid-state if stored in an inert atmosphere, but decompose quickly in solution, especially in chlorinated solvents. Moreover, coordinated $Ph_3P{=}C{=}C{=}O$ is easily displaced by coordinating solvents such as THF or DMFA, clear evidence of the weakness of the M–C bond. Such behavior has been attributed to the fact that coordinated $Ph_3P{=}C{=}C{=}O$ is a relatively good σ-donor, but a rather weak π-acceptor, as confirmed also by the carbonyl stretching vibrations of $M(CO)_5$ groups of **19**, which are shifted to lower energy values with respect to $M(CO)_6$ [54].

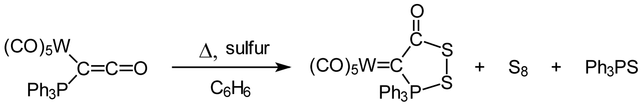
Compounds **19** decompose on heating. As represented in Scheme 23 for compound **19b**, the metal-assisted detachment of PPh_3 produces the reactive C_2O carbene



Scheme 23.

that is trapped by cyclohexene. The ketene thus obtained loses CO to yield a cyclopropane carbene that reacts with an excess of cyclohexene to give 7,7′-spirobinorcarane, as revealed by ^{1}H-NMR, IR and mass spectra [54–56].

Compound **19b** also reacts in another strange fashion. On refluxing in benzene in the presence of a large excess of sulfur, the formation of S_8 and Ph_3PS was observed, besides the isolation, in 10% yield, of a red–orange solid that was formulated as the carbene complex **20**, according to Reaction 11, reported with no further details [55,56].



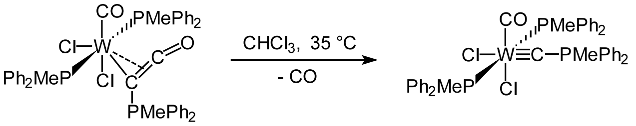
20

(11)

The structure of compound **20** was inferred on the basis of elemental analysis, molecular weight determination and the analysis of its EI mass spectrum, in which signals possibly related to the fragmentation of **20** were observed. The IR spectrum of **20** showed signals due to coordinated carbonyls, as well as bands at 1618, 631 and 472 cm^{-1} that were attributed to ν(C=O), ν(CS), and ν(SS), respectively [55,56].

A W(II) complex has also been reacted with **1**, in the course of a study on the reactivity of $[WCl_2(PMePh_2)_4]$ with carbon suboxide, C_3O_2 [57]. In this work the formation of the complex **21** was reported (Scheme 24), which can also be visualized as being the product resulting from the η^2-(*C*,*C′*) coordination to the metal of ketenylidenemethyldiphenylphosphorane, $Ph_2MeP=C=C=O$.

Compound **21** was completely characterized, including an X-ray crystal structure determination. Its mild thermolysis ($CHCl_3$, 35 °C, 48 h) yielded the phosphino carbine complex **22** according to Reaction 12. This reaction is the reverse of the CO insertion into a metal carbyne, the most common way to synthesize ketenyl derivatives [53].

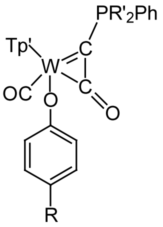


22

(12)

A compound analogous to **22** was directly synthesized by the treatment of a suspension of $[WCl_2(PMePh_2)_4]$ in toluene with **1** (1:1 ratio) at 35 °C over 8 h. The reaction gave $[WCl_2(CO)(PMePh_2)_2(\equiv C{-}PPh_3)]$ (**23**), whose structure was also determined through an X-ray analysis. Most likely, this reaction proceeds through coordination of **1** to the metal, followed by thermal decomposition, thus generating CO that is then intercepted by the metal to give **23** [57].

Very recently, a series of compounds in which **1** (and the parent molecule $PhMe_2P=C=C=O$) is η^2-*C*,*C′* bonded to W(II) complexes (Chart 7) have been reported, and some X-ray crystal structures determined [58].

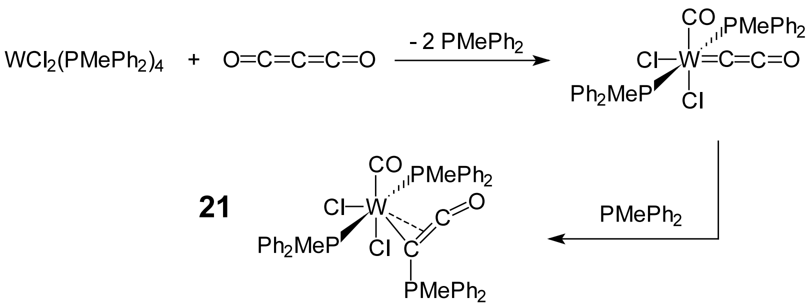


Tp' = hydridotris(3,5-dimethylpyrazolyl)borate
R = NO_2, CN, Cl
R' = Me, Ph

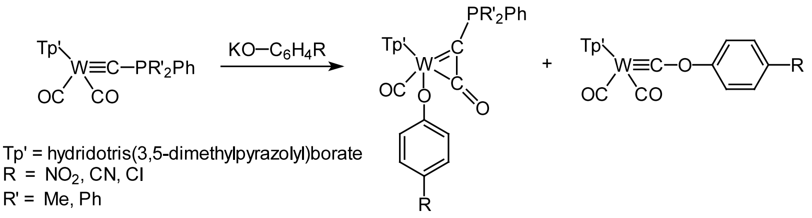
Chart 7.

The syntheses of these η^2-ketenyl derivatives have been achieved through the intramolecular migration of a CO to a carbyne ligand induced by a strong nucleophile (Scheme 25), i.e. through the quite complicated route usually adopted to get metal ketenyl derivatives [53].

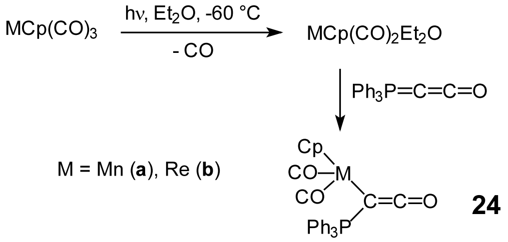
Reactions between $Ph_3P=C=C=O$ and Mn(I), Re(I) and Fe(0) complexes have also been reported [59]. $[MCp(CO)_3]$ (M = Mn, Re) loses CO by photolysis in ethyl ether and subsequent reaction with **1** produces η^1-ketenyl complexes **24** (Scheme 26) that present IR and ^{31}P-NMR signals characteristic of η^1-coordination of **1** through the ylidic carbon (Table 2). In the ^{13}C-NMR



Scheme 24.



Scheme 25.



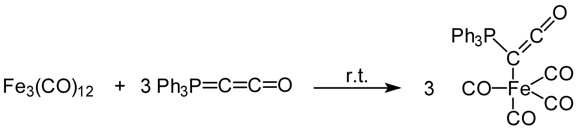
Scheme 26.

Table 2
IR and ^{31}P-NMR data for compounds **24**

	IR ν(CCO) (cm^{-1})	^{31}P{^{1}H}-NMR (ppm)
24a	2053	24.8
24b	2055	21.2

spectrum of **24a** no signal attributable to the ketenyl CO was detected and a doublet observed at 132.8 ppm ($^1J_{CP} = 12.5$ Hz) was attributed to the ylidic carbon, even if this signal is quite low-field shifted with respect to other η^1-ketenyl complexes [53] and the coupling constant seems too small.

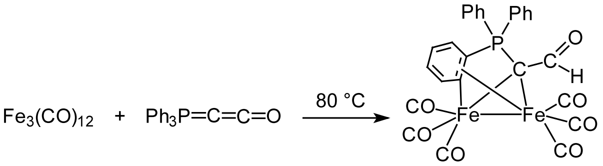
The reaction of $Fe_3(CO)_{12}$ with **1** (molar ratio 1:3) in toluene at room temperature produced a pale red compound in 30% yield (Reaction 13) [59] to which the η^1-ketenyl structure **25** was assigned, even if the IR, ^{31}P- and ^{13}C-NMR data pertaining to coordinated Ph_3PCCO are not in good agreement with those reported for analogous compounds. In fact, the ^{31}P{^{1}H}-NMR signal (38.1 ppm) is low-field shifted with respect to the normally observed range (21–28 ppm) and a medium intensity IR signal at 2032 cm^{-1} was attributed to the C=C=O stretching, whereas this group normally shows a sharp, intense band. Moreover, in the ^{13}C-NMR spectrum were observed, besides signals due to the phenyl carbons and a single signal at 214.23 ppm, assigned to coordinated carbonyls, two other resonances. A doublet at 132.3 ppm (no coupling constant reported) was assigned to the ylidic carbon (analogously to **24a**) and a signal at 67.95 was attributed to the CO of the C=C=O moiety. In this case the value is very high-field shifted with respect to other η^1-ketenyl derivatives [53].



25

(13)

When the reaction between **1** and $Fe_3(CO)_{12}$ was performed in a 1:1 molar ratio at 80 °C, a bimetallic compound **26** was isolated in 25% yield (Reaction 14).

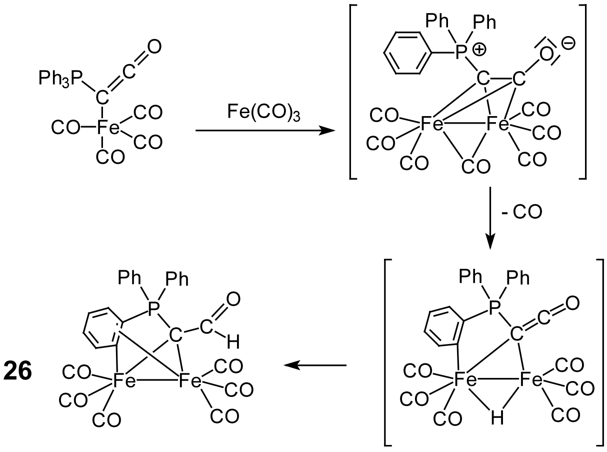


26

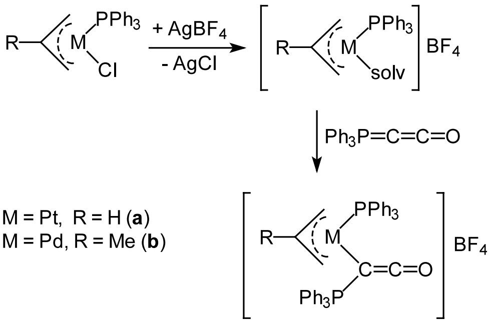
(14)

Compound **26** was characterized by elemental analysis, IR and ^{1}H-NMR spectra, and its structure has also been confirmed by an X-ray crystal structure determination. It was proposed to derive from the interaction of [Fe(CO)$_4${η^1-C(PPh$_3$)CO}] with $Fe(CO)_3$ generated by the decomposition of $Fe_3(CO)_{12}$, according to Scheme 27 [59].

Recently, the study of the organometallic reactivity of $Ph_3P{=}C{=}C{=}O$ has been extended to Pt(II) and Pd(II) systems. The reaction of **1** with coordinatively unsaturated 14e Pt(II) and Pd(II) species [60] yields stable (at

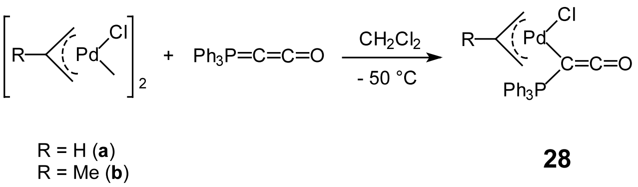


Scheme 27.



27

Scheme 28.



28

Scheme 29.

least in the cases of Pt complexes) 16e square-planar η^1-ketenyl compounds through coordination of the ylidic carbon to the metal.

Both cationic and neutral Pt(II) and Pd(II) complexes have been prepared. Among these, cationic η^1-ketenyl derivatives of the type $[M(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)\{\eta^1\text{-}C(PPh_3)CO\}PPh_3]BF_4$ (**27**) (M = Pt, R = H (**a**); M = Pd, R = Me (**b**)) have been synthesized, according to Scheme 28 [19]. The reactions were performed in THF at room temperature for the Pt complex **27a**, and −30 °C for the less stable Pd complex **27b**.

Ketenylidenetriphenylphosphorane is also able to cleave chlorine bridged Pd η^3-allyl complexes, yielding neutral η^3-allyl,η^1-ketenyl compounds **28** [19] (Scheme 29).

Compounds **27b** and **28a**, **b** are relatively unstable, their syntheses were possible only at low temperatures and they were characterized only by elemental analysis, IR, ^{1}H- and $^{31}P\{^1H\}$-NMR spectra at low temperature, whereas for the more stable compound **27a**, a ^{13}C-NMR determination has been also reported. Significant spectroscopic data for **27** and **28** are presented in Table 3.

An X-ray crystal structure determination [19] of compound **27a** shows that the geometry about Pt is slightly distorted square-planar. Relevant bond distances (Å) and angles (°) are reported in Table 4, with the corresponding values for **1** [9].

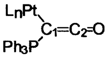
The most evident feature that can be observed in the structure of **27a** is the partial loss of the ylidic character of **1** on coordination, as shown by the elongation of $P-C_1$ distance. The $P-C_1-C_2$ angle is also indicative of sp^2 hybridization of C_1, thus revealing that the C=C=O moiety assumes a ketene character upon metal coordination. This important aspect will be discussed later.

Other η^1-ketenyls have been synthesized in a similar way. The neutral Pt derivative **29**, homologous to **28a**, was obtained by refluxing a THF suspension of the tetrameric allyl compound $[\{Pt(C_3H_5)Cl\}_4]$ with **1** (Reaction 15) [61], and another neutral η^1-ketenyl complex **30**, was obtained by treating dimeric $[\{PtCl_2(PPh_3)\}_2]$ with $Ph_3P{=}C{=}C{=}O$, according to Re-

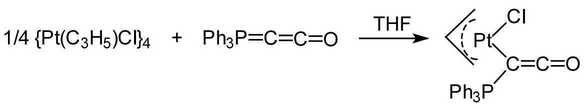
Table 3
IR, ^{13}C- and ^{31}P-NMR data for compounds **27** and **28**

	IR (Nujol) ν(CCO) (cm^{-1})	$^{31}P\{^1H\}$-NMR chemical shift (ppm), J (Hz)		^{13}C-NMR chemical shift (ppm), J (Hz)	
27a	2073	24.58 P_{Pt} $^3J_{PP}$ 6.0 $^1J_{PPt}$ 4070	24.31 P_C $^2J_{PPt}$ 101	156.73 CO $^2J_{CP}$ 18.9	9.62 *C*CO $^1J_{CP}$ 59.0
27b	2070	22.56	20.05		
28a	2072	28.16			
28b	2075	24.39			

Table 4
Relevant structural parameters of **27a** and **1**

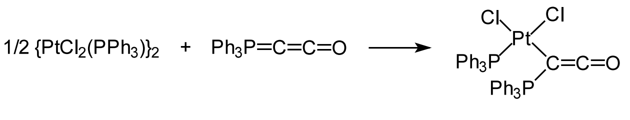
	P-C$_1$	C$_1$-C$_2$	C$_2$-O	Pt-C$_1$	C$_1$-C$_2$-O	P-C$_1$-C$_2$	Pt-C$_1$-C$_2$
27a	1.75	1.280	1.160	2.120	175	118	118
1	1.648	1.210	1.185		175.6	145.5	

action 16 [61].



29

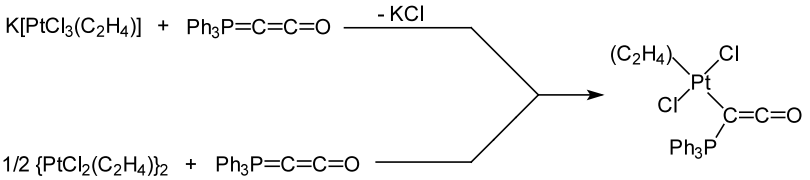
(15)



30

(16)

Reaction of Zeise's salt with ketenylidenetriphenylphosphorane produced the neutral *trans*-η^1-ketenyl derivative **31** that has also been obtained by breaking the chlorine bridges of $[\{PtCl_2(C_2H_4)\}_2]$, as indicated in Scheme 30 [25].



31

Scheme 30.

Other unstable cationic Pt(II) compounds **32** and **33** (Chart 8) have been obtained and characterized by IR and, in the case of **33**, also by ^{31}P-NMR at −50 °C [62].

In contrast, the cationic compounds **34a** and **34b** are stable and were easily prepared and isolated, according to Scheme 31 [63].

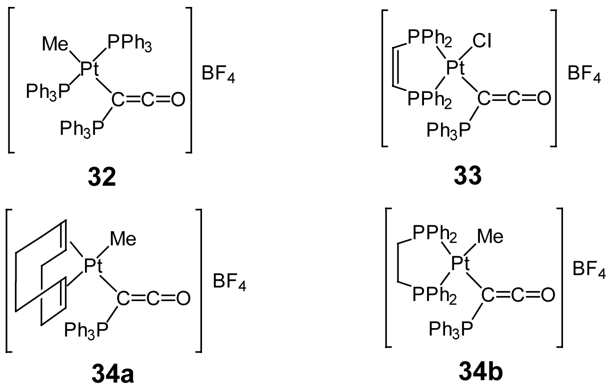
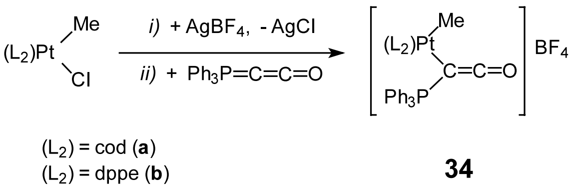


Chart 8.

The more salient spectroscopic data characterizing compounds **29**–**34** are reported in Table 5.



34

Scheme 31.

It was also possible to coordinate two molecules of **1** to the same Pt atom. As illustrated in Scheme 32, treatment of **29** with **1** at −50 °C, yields the bis-η^1-ketenyl derivative *cis*-$[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)\text{-}CO\}_2]BF_4$ (**35**), which is stable in solution only at low temperature. Its structure was inferred on the basis of the stoichiometry and IR, ^{1}H- and ^{31}P-NMR spectra at −50 °C. Particularly, IR spectrum shows only one signal at 2075 cm^{-1}, the ^{1}H-NMR spectrum presents a set of signals indicating a symmetrical arrangement of the allyl group around Pt and the ^{31}P-NMR spectrum contains only one singlet at 23.74 ppm [61].

The stable *trans*-bis-η^1-ketenyl derivative, *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$ (**36**), was obtained according to the reactions depicted in Scheme 33 [25].

Compound **36** was completely characterized by IR and multinuclear NMR spectroscopy in solution. Recently, the solid-state CP/MAS ^{13}C- and ^{31}P-NMR data of **36** (as well as those of **31** and **1**) have also been published [20]. The most important spectroscopic features of compounds **35** and **36** are reported in Table 6.

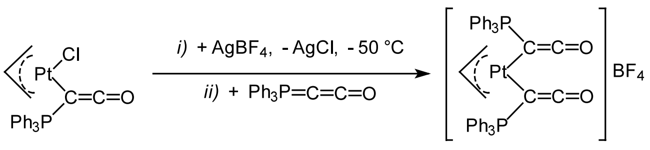
An X-ray crystal structure determination indicates that compound **36** has a centrosymmetrical geometry, with almost perfect square-planar coordination around Pt [25]. The most important geometrical parameters are reported in Table 7, where bond distances are in Å and angles in °.

The partial loss of the ylidic character of coordinated **1** is also observed in this case, analogously to what found for **27a**, such that coordinated $Ph_3P{=}C{=}C{=}O$ is better represented as a phosphonium cation. As a matter of fact the $P\text{–}C_1$ bond length is 1.76 Å, elongated with respect to free **1** (1.648 Å) [9] and very close to those of a $P\text{–}C_{(phenyl)}$ single bond lengths (1.79–1.80 Å). The $C_1\text{–}C_2$ and $C_2\text{–}O$ bond lengths (1.26 and 1.16 Å, respectively) are substantially analogous to those of **27a** [19]. The $C{=}C{=}O$ skeleton is linear and the bonding geometry around C_1 is almost trigonal, indicating sp^2 hybridization.

Table 5
IR, ^{13}C- and ^{31}P-NMR data for compounds **29**–**34**

	IR (Nujol) ν(CCO) (cm^{-1})	^{31}P{^{1}H}-NMR chemical shift (ppm), J (Hz)			^{13}C-NMR chemical shift (ppm), J (Hz)		
29	2069		22.83		164.60 CO		−0.65 *C*CO
			$^2J_{PPt}$ 93.7		$^2J_{CP}$ 21.6		$^1J_{CP}$ 48.4
30	2072	14.61 P_{Pt}		25.15 P_C	160.62 CO		10.48 *C*CO
			$^3J_{PP}$ 12.2		$^2J_{CP}$ 19.8		$^1J_{CP}$ 56.1
		$^2J_{PPt}$ 64.7		$^1J_{PPt}$ 3370	$^3J_{CP}$ 3.3		
					$^2J_{CPt}$ 2.91		$^1J_{CPt}$ 713
31	2078		26.14		190.1 CO		−0.7 *C*CO
			$^2J_{PPt}$ 96.6			80.3 C_2H_4	
						$^1J_{CPt}$ 133.8	
32 [a]	2065						
33 [b]	2079	52.98 P_{Pt}	63.45 P_{Pt}	27.79 P_C			
		$^1J_{PPt}$ 3515	$^1J_{PPt}$ 3013	$^2J_{PPt}$ 133			
34a	2088		26.05				
			$2J_{PPt}$ 91.9				
34b	2071	47.13 P'_{Pt}	49.05 P''_{Pt}	25.20 P_C			
		$^3J_{PP}$ 9.3	$^3J_{PP}$ 4.2	$^3J_{P'P}$ 9.3			
				$^3J_{P''P}$ 4.2			
		$^1J_{PPt}$ 3526	$^1J_{PPt}$ 1691	$^2J_{PPt}$ 67.5			

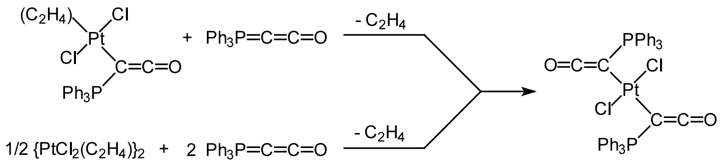
[a] Compound **32** decomposes immediately in solution.
[b] ^{31}P-NMR spectrum was measured at −50 °C.



35

Scheme 32.

Compounds **27a** and **36** present geometrical parameters that allow them to be considered as mono- and bis-ketenes that bear, as substituents, a PPh$_3$ molecule and a metal center. In particular, the very long Pt–C$_1$ bonds of **27a** and **36**, 2.120 and 2.171 Å, respectively, are indicative of a pure σ Pt–C bond, with no contribution arising from back-donation, as previously postulated by Berke and Lindner [54] for [M(CO)$_5${η^1-C(PPh$_3$)CO}]



36

Scheme 33.

Table 6
IR, ^{1}H-, ^{13}C- and ^{31}P-NMR data for compounds **35** and **36**

	IR $\nu_{(CCO)}$ (cm^{-1})	^{1}H-NMR, chemical shift (ppm), J (Hz)			^{31}P{^{1}H}-NMR, chemical shift (ppm), J (Hz)	^{13}C{^{1}H}-NMR, chemical shift (ppm)	
35	2075	1.53 H_{anti}	2.84 H_{syn}	4.31 H_{meso}	23.74		
		$^3J_{HH}$ 17.5	$^3J_{HH}$ 6.4		$^2J_{PPt}$ 93.7		
		$^2J_{HPt}$ 62.8	$^2J_{HPt}$ 18.3	$^2J_{HPt}$ 70.9			
36	2062				21.98	191.4 CO	1.4 *C*CO
					$^2J_{PPt}$ 99.2		

Table 7
Most relevant geometrical parameters for compound **36**

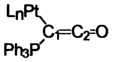
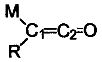
	P-C_1	C_1-C_2	C_2-O	Pt-C_1	C_1-C_2-O	P-C_1-C_2	Pt-C_1-C_2
36	1.76	1.26	1.16	2.171	179.6	114.3	123.3

Table 8
Most relevant geometrical parameters for structurally established η^1-ketenyls and μ_2-ketenylidene derivatives compared to those of some organic ketenes

	R-C_1	M-C_1	MC_1C_2	RC_1C_2	C_1-C_2	C_2-O	C_1C_2O	Ref.
27a$^{(a)}$	1.75	2.120	118	118	1.280	1.160	175	[19]
36$^{(a)}$	1.76	2.171	123.3	114.3	1.26	1.16	179.6	[25]
37$^{(b)}$		2.27			1.31	1.16		[65]
38$^{(b)}$	1.467	2.17	107.3	122.9	1.301	1.173	179.5	[66]
39$^{(c)}$	1.50$^{(*)}$	2.08	124		1.32$^{(*)}$	1.16$^{(*)}$	169	[67]
40$^{(d)}$	2.122	2.138	126	120.1	1.31	1.24	179.0	[68]
H_2CCO $^{(e)}$	1.08	1.08	119.01	119.01	1.3165	1.1614	180.0	[69]
H(Me)CCO$^{(f)}$	1.083	1.518	122.6	113.7	1.306	1.171	180.5	[70]
Me_2CCO $^{(g)}$	1.514	1.514	120.6	120.6	1.300	1.171	180.0	[71]

$^{(a)}$ R = Ph_3P, M = Pt; $^{(b)}$ R = p-C_6H_4-Me, M = W; $^{(c)}$ R = CHO, M = Pt;
$^{(d)}$ R = M = Zr; $^{(e)}$ R = M = H; $^{(f)}$ R = H, M = Me; $^{(g)}$ R = M = Me
$^{(*)}$ assumed or calculated values; see Ref. [67]

(M = Cr, W, Mo). Thus, Pt and PPh_3 are bonded to C_1 through σ bonds and the C=C=O moiety presents the geometric characteristics of ketenes, which are linear and the C=C and C=O bond distances comparable with those of organic ketenes [64]. Similar geometrical parameters have also been observed for the other three crystallographically established η^1-ketenyl derivatives, $[WCp\{\eta^1\text{-}C(p\text{-}C_6H_4\text{-}Me)CO\}(CO)(PMe_3)_2]$ (**37**) [65], $[WCp\{\eta^1\text{-}C(p\text{-}C_6H_4\text{-}Me)CO\}(CO)(\eta^2\text{-}Me\text{-}C{\equiv}C\text{-}NEt_2)]$ (**38**) [66], $[PtH\{\eta^1\text{-}C(CHO)CO\}(PCy_3)_2]$ (**39**) [67] and for the μ_2-ketenylidene compound $[Zr_3Cp_2(\mu_2\text{-}CCO)(\mu_3\text{-}O)(O_2CN\textit{i}Pr_2)_6]$ (**40**) [68]. The most relevant geometrical parameters of compounds **27a**, **36**–**40** and the corresponding data for some organic ketenes are compared in Table 8. Bond distances are in Å and angles in °.

Theoretical calculations performed on compound **36** [25] have confirmed its ketene character. As a matter of fact, the Pt–ligand bonding scheme is dominated by a ligand-to-metal σ donation without any metal-to-ligand π back-donation, in agreement with the rather large experimental Pt–C(1) bond length. Moreover, calcu-

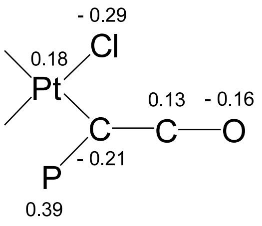


Chart 9.

lated Hirshfeld atomic charges (Chart 9) indicate that the negative charge σ-donated by the ylidic carbon to the metal is easily shared through inductive effects involving the electron-withdrawing Cl ligands. Charges on the C=C=O moieties are quite normal for a ketene group.

As far as steric factors are concerned, it is well known that they are of paramount importance in determining the stability of ketenes and bisketenes [64], and these seem to be particularly important for compounds **35** and **36**. The IR and NMR spectra of compound **35** (*cis*), indicate the presence of a molecular symmetry plane. Two distinct isomers are compatible with this symmetry, one with the *meso* allyl carbon atom on the same side as the C=C=O moieties (UP) and the other with this carbon on the opposite side (DOWN), as illustrated in Fig. 1. Preliminary theoretical results pertaining to the two isomers indicate that the UP geometry is only slightly more stable than the DOWN one, as a consequence of the lower steric repulsion energy which overcomes contributions due to orbital interactions, which are more favorable for the DOWN isomer [72].

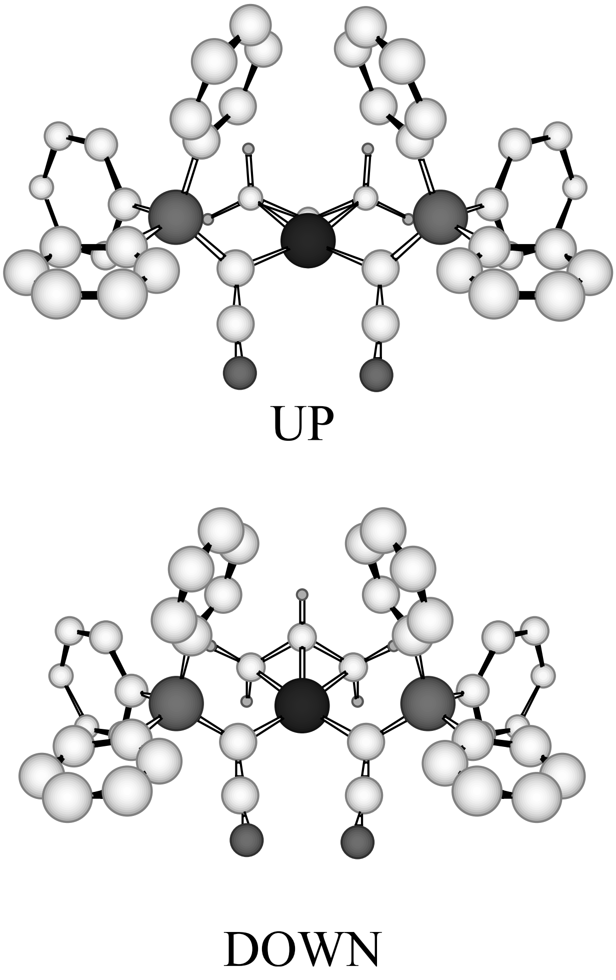
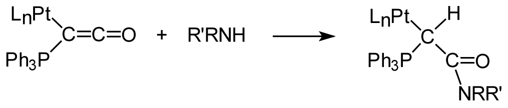


Fig. 1. The two possible isomers for compound **35**.

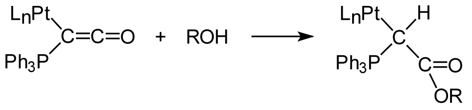
Steric factors are also important in determining the geometry of compound **36** (*trans*). In this case, both theoretical results and X-ray data indicate that the energy minimum corresponds to the largest possible contact distances between: (i) the C=C=O fragments of the Ph_3PCCO moieties; (ii) the Pt atom and the phenyl groups of PPh_3; (iii) the C=C=O groups and the chlorine atoms [25].

Structural and electronic observations, indicating that mono- and bis-η^1-ketenyl derivatives **27a** and **36**, respectively, can be considered as metal-substituted ketenes, have been confirmed by studies on the reactivity of $[L_nPt\{\eta^1\text{-C}(PPh_3)CO\}_n]$ ($n = 1, 2$). Some reactions of Pt(II) η^1-ketenyl derivatives with protic nucleophiles have been performed, observing addition reactions to C=C analogously to that observed for $[WCp\{\eta^1\text{-C}(p\text{-}C_6H_4\text{–}Me)CO\}(CO)_2(PMe_3)]$ [73]. Mono-η^1-ketenyl compounds **27a** [19], **29** [61], **31** [25] and **34a**, **b** [63] have been reacted with protic amines, RR′NH, yielding the corresponding amides, according to Scheme 34.

The course of the reaction above-indicated depends largely on the nucleophilicity of Nu–H, but also on the ketene, and this dependence is particularly evident in the reactions with alcohols to obtain esters (Scheme 35).



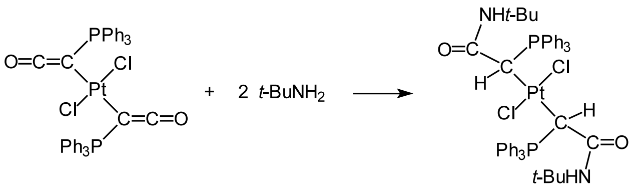
Scheme 34.



Scheme 35.

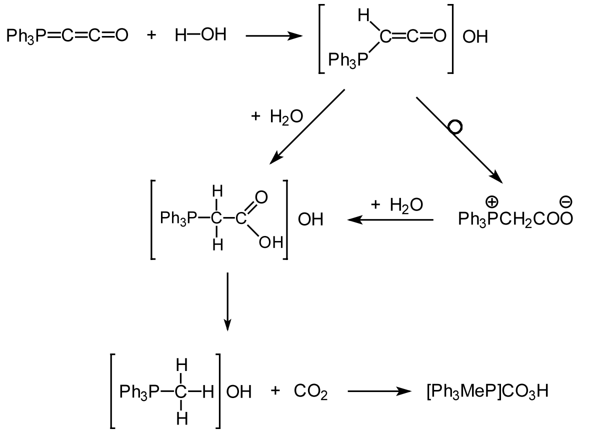
Compounds **29** and **34a** react completely with MeOH, whereas the long times required for the reactions with *i*-PrOH and *t*-BuOH enhance the occurrence of parasitic reactions [19,63]. The formation of side products, as well as long reaction times, was also observed for the reaction of **31** with MeOH or EtOH [25], whereas **34b** did not react with MeOH even after very long reaction times [63]. Compound **34b** was particularly unreactive with respect to protic nucleophiles. On treatment with Me_2NH, only about 50% of the corresponding amide were formed. It is to still be clarified if the differences in reactivity between **34a** and **34b** can be attributed to electronic or steric factors, but the latter ones are certainly important.

The bis-ketene **36** was reacted with *t*-$BuNH_2$, forming a diamide derivative, as illustrated in Reaction 17, whereas it did not react with alcohols or water [25].



(17)

Excluding **36**, all other Pt(II) substituted ketenes react, more or less rapidly, with water undergoing decomposition reactions with release of CO_2 [19,25,61]. Although the mechanism of these decomposition reactions is yet to be studied, it is almost certainly related to that of the recently reported hydrolysis reaction of free $Ph_3P=C=C=O$ with H_2O [74]. As a matter of fact, the reaction with an excess of H_2O (1:5 molar ratio) in THF, transforms **1** into $[Ph_3MeP]CO_3H$, according to a reaction pathway involving the decarboxylation of an unstable carboxylic species and formation of CO_2 (Scheme 36).



Scheme 36.

In the reactions of Pt(II) substituted ketenes with water, the appearance of free CO_2 that cannot be trapped by OH^- ions, is a further indication of the difference between free (ylide) and coordinated (ketene) $Ph_3P=C=C=O$ [75].

5. Conclusions and perspectives

The most important observation about the organic reactivity of **1** is trivial. In $Ph_3P=C=C=O$, analogously to other phosphorus ylides, the *ylide* dipolar form sketched in Chart 2 is extremely important. Thus, the carbanionic carbon presents a high Brønsted basicity and the first attack is always that of an electrophile to the ylidic carbon. This reaction, reported in Scheme 4, transforms **1** into a 'true' ketene, which is normally difficult to isolate and presents the typical ketene reactivity. In fact, the ketene thus formed reacts readily with any nucleophile leading to the formation of a great variety of organic compounds, very often through cyclization and/or Wittig Ph_3PO elimination reactions.

On the other hand, the strong donor character of the ylidic carbon drives also the reactivity of **1** towards coordinatively unsaturated (14 or 16e) transition metal complexes, and all reports indicate that the metal center acts as an 'isolated' electrophilic site. Also in this case, the attack to the ylidic carbon transforms **1** into a ketene, but the absence or the unreactivity of the nucleophilic center (for example an anion such as BF_4^-) enables the isolation of these unusual ketenes bearing the PPh_3 group and the metal center as substituents. These metal-substituted ketenes are normally solid, often stable and it is relatively easy to isolate and characterize them and investigate their physical and chemical properties.

Ketenes with metal substituents have been previously studied theoretically and predicted to be rather stable, thanks to the electropositivity of the metal [76]. Experimental observations, summarized here, confirm that hypothesis. Until now, by using **1**, stable ketenes having Cr(0), W(0 and II), Mo(0), Mn(I), Re(I) and Pt(II) complexes as the metal substituent have been isolated, whereas corresponding Sn(II) and Pd(II) compounds are relatively unstable. A stable neutral 1,3-bisketene, *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$, has also been isolated and completely characterized and an unstable cationic 1,3-bisketene, *cis*-$[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]BF_4$, has been observed and spectroscopically characterized at low temperature. The instability of this latter compound is likely mainly due to steric factors that are also important in the reactivity of all the other metal substituted ketenes towards protic nucleophiles such as alcohols and amines. Water causes decomposition with development of CO_2, but this reaction has not yet been intensively studied.

It is conceivable that the organometallic chemistry of **1** might be extended to complexes of other transition and main group metals and, most importantly, that the ketene stability and reactivity might be modulated to a large extent through the modification of the electronic and steric characteristics of the metal fragment, i.e. by changing the metal, its oxidation state and the ancillary ligands bonded to the metal.

In this regard, some points can be stressed. Firstly, as the reaction of **1** with metal systems consists of the nucleophilic attack of the ylidic carbon on the metal center, it is expected that it will be favored if the metal has a low charge density. Thus, higher oxidation states and cationic compounds are likely to be favored over lower oxidation states and neutral complexes. Moreover, ancillary electron-withdrawing ligands (both σ- and π-acceptors), able to discharge the metal, are expected to favor both the formation as well as the stability of these metal-substituted ketenes. Electron-donor substituents are expected either to have little influence or destabilize these compounds, due to the π-acceptor inertness of coordinated $Ph_3P{=}C{=}C{=}O$, that is unable to relieve an excess of negative charge on the metal [77]. Another important factor to be taken into account in the formation and stability of these compounds is the encumbrance of ancillary ligands bonded to the metal, in connection to the relative bulkiness of the Ph_3P moiety of **1**. On the other hand, once formed, the bulkiness of these groups can protect the C=C=O moiety against external attacks.

In conclusion, the reaction of **1** with metal systems is a valuable route to the attainment of stable ketenes, whose utility lies in the fact that they 'bottle' the reactive C=C=O fragment and facilitate its study and use in mild reactions allowing, for example, the formation of novel organometallic compounds if at least one C–metal bond is maintained. On the other hand, through breaking of the C–metal bond(s), in principle it is possible to obtain new organic products via processes that may be possible to be performed catalytically.

Some other fields remain almost completely unexplored. For example, it is conceivable that the great variety of coordination geometries, oxidation states and coordination numbers, typical of transition metals, will allow the coordination of more than one molecule of **1** thus leading to the formation of 1,3-bis-, tris-, and so on ketenes (see stable *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$ and unstable *cis*-$[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]BF_4$) having properties which are difficult to predict at the present time. Another field, which should certainly produce interesting developments, involves the study of the 'organometallic' reactivity of metal-substituted ketenes. Examples of this include the possible reactions of coordinated $Ph_3P{=}C{=}C{=}O$ with other coordinated ligands (which have never been reported) or the modification of coordinated $Ph_3P{=}C{=}C{=}O$. Only two examples of the latter kind of reactivity have been observed: the metal-assisted decarbonylation of coordinated $Ph_3P{=}C{=}C{=}O$ with breaking of the C=C double bond that results in formation of a metal carbyne $[L_nW(\equiv C{-}PPh_3)]$ [57] and the metal-assisted elimination of PPh_3 that produces an extremely reactive carbonylcarbene :C=C=O, that, in suitable conditions, can act as a source of 'monocarbon', through CO elimination [54–56]. It is conceivable that even these kinds of reactivity may be extended to other metal systems.

Finally, the observation that the reaction of **1** with RMgX also involves an interaction of Mg with the O atom should open the way for studies into the reactivity of **1** with oxophilic metals such as Al, Si, Ge, Sn or lanthanoids, a completely unexplored area.

We are confident that the organometallic chemistry of $Ph_3P{=}C{=}C{=}O$ will continue to have interesting developments in the next few years.

Acknowledgements

This report has been made possible through the efforts of a number of colleagues and students, whose names appear in the appropriate references. The revision of English language by Dr Deborah Tonei is gratefully acknowledged. We want to dedicate this paper to the memory of Professor Gastone Paiaro (1928–1998) who introduced us into the fascinating world of metal–ketenes interactions.

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