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Reactivity of keteylidenetriphenylphosphorane ($Ph_3PC{=}C{=}O$) with Pt(II) complexes. Evidences of formation of an up to now unknown bis-η^1-ketenyl derivative☆

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Abstract

Ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, **1**, has been used to synthesize some Pt(II) η^1-ketenyl derivatives, through reactions with dimeric and tetrameric chlorine-bridged compounds. Particularly it has been possible to isolate and characterize $[Pt(\eta^3\text{-}C_3H_5)Cl\{\eta^1\text{-}C(PPh_3)CO\}]$, **2**, and $[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}(PPh_3)]$, **3**. Moreover, the reaction of **2** with a further equivalent of **1**, in the presence of $AgBF_4$, lead to the formation of $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]$, **4**, the first bis-$\eta^1$-ketenyl derivative. Compound **4** is stable in solution only at low temperatures and its formation has been inferred unequivocally by IR, ^1H and ^{31}P-NMR measurements carried out at −50°C. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ketene; Ketenyl derivatives; Ketenylidentriphenylphosphorane; Bis-ketenyl derivatives; Ylides; Platinum

1. Introduction

Although ketenes are known from the beginning of the century [1] and their organic reactivity is well known and reviewed [2], their interactions with metal systems have been studied deeply only in the last 20 years [3], mainly due to the involvement of organometallic derivatives containing the ketene moiety in some important catalytic and stoichiometric reactions [3a, 4].

For the sake of clarity it is useful to distinguish between the three fundamental kinds of interactions in which a metal complex can be involved with a ketene moiety [3a], i.e.:

1. ketene derivatives, in which the ketene substituents are organic fragments;
2. ketenyl derivatives, in which one of the substituents is a metal center; and
3. ketenylidene derivatives, in which the substituents are only metals.

Some indicative examples are shown in Scheme 1.

The study of these compounds is not easy, due mainly to difficulties encountered in their synthesis. If metal ketene derivatives can be prepared, in principle and sometimes in practice, by the reaction of ketenes with suitable metal complexes, the syntheses of metal ketenyl and ketenylidene derivatives are normally rather complicated and, in any case, not generally applicable to different metal systems [3].

Ketenyl derivatives are particularly interesting but, to develop their study, it is necessary to find simplest routes to synthesize them. As a matter of fact they are obtained typically, in the case of early transition metal complexes, through complicated routes, as ligand-in-

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☆ Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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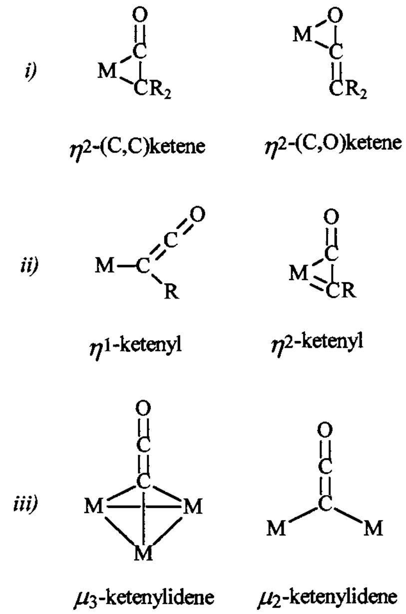
duced CO migration to a carbyne ligand [3a], a process which yields η^1- or η^2-ketenyl derivatives. Other ketenyl syntheses involve the use of the bis-ketene carbon suboxide (O=C=C=C=O), by coordination to Pt(0) and Ni(0) complexes [5] or by mono-insertion reactions in platinum–oxygen [6] or metal–hydride [7] bonds. Further, some years ago, the oxocumulenic ylide ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, **1**, [8] has been reported to displace weakly bonded or photochemically removable ligands from early or medium transition metal complexes, yielding peculiar η^1-ketenyl ylidic derivatives [9].

Recently, we have found that **1** reacts even with some Pt(II) and Pd(II) organometallic complexes giving ketenyl derivatives [10]. Particularly, we have reported the synthesis, characterization and the first X-ray crystal structure determination of a cationic platinum η^1-ketenyl complex, $[Pt(\eta^3\text{-}C_3H_5)\{(\eta^1\text{-}C(PPh_3)(CO)\}(PPh_3)]BF_4$, in which the C=C=O moiety bonded to platinum is also involved in an ylide grouping.

Continuing our studies on the reactivity of **1** [10,11] and particularly on its use as a synthon for ketenyl complexes, we here report some results obtained in the reactions of **1** with Pt(II) compounds. Through these reactions we have prepared new mono-η^1-ketenyl derivatives, whose reactivity has been examined, and it has been also possible to obtain spectroscopic (IR and multinuclear NMR) evidences of the formation of an up to now unreported bis-η^1-ketenyl complex, in which two C=C=O moieties are bonded to one Pt atom.



Scheme 1.

2. Experimental

All reactions and manipulations were carried out under an atmosphere of dry argon with standard Schlenk techniques. Solvents were dried by conventional methods and distilled under argon before use. $Ph_3PC{=}C{=}O$ [8c] $[\{Pt(C_3H_5)Cl\}_4]$ [12], and $[\{PtCl_2(PPh_3)\}_2]$ [13], were synthesized according to literature methods. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^1H, ^{31}P and ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

2.1. Syntheses

2.1.1. Synthesis of $[Pt(\eta^3\text{-}C_3H_5)Cl\{\eta^1\text{-}C(PPh_3)CO\}]$, **2** [14]

To a suspension of 0.473 g of $[\{Pt(C_3H_5)Cl\}_4]$ (0.435 mmol) in 30 ml of THF, 0.526 g of **1** (1.74 mmol) have been added. The mixture was refluxed under stirring for about 15 min, monitoring the decreasing of the IR signal of the free ylide (2105 cm^{-1}) and the appearance of the η^1-ketenyl signal at 2081 cm^{-1}. The solution was then concentrated under vacuum and a pale-yellow solid was obtained by adding 40 ml of Et_2O under vigorous stirring. The solid was filtered off, washed with Et_2O and dried under vacuum. Yield: 0.667 g, 67%.

2: M.p. 148–150°C (dec.). Elem. Anal.: Found: C 46.96; H 3.53. Calc. For $C_{23}H_{20}ClOPPt$.: C 48.13; H 3.51. IR (Nujol, cm^{-1}): ν_{CO} 2069, ν_{PtCl} 280. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 28°C) 22.83 (s, $^2J_{PPt}$ 93.7 Hz). ^1H-NMR($CDCl_3$, 28°C) H_c 4.18 (m, $^2J_{HPt}$ 76.4 Hz), H_1 3.92 (d br, $^3J_{HHc}$ 6.6 Hz, $^2J_{HPt}$ 22.2 Hz), H_4 2.40 (dd, $^3J_{HHc}$ 6.1 Hz, $^4J_{HP}$ 2.0 Hz $^2J_{HPt}$ 28.3 Hz), H_2 2.21 (d, $^3J_{HHc}$ 11.4 Hz, $^2J_{HPt}$ 58.7 Hz), H_3 1.13 (d, $^3J_{HHc}$ 10.7 Hz, $^2J_{HPt}$ 80.1 Hz), C_6H_5 7.86–7.48 (m). (The numbering of allylic hydrogen atoms is indicated in Reaction **1**).$^{13}C\{^1H\}$-NMR (CD_2Cl_2, 28°C): C–Pt −0.65 (d, $^1J_{CP}$ 48.4 Hz), CO 164.60 (d, $^2J_{CP}$ 21.6 Hz), C_{all} 41.67 (d, $^3J_{CP}$ 41.5 Hz, $^1J_{CPt}$ 266 Hz), C_{all} 89.97 (s, $^1J_{CPt}$ 99.8 Hz), C_{all} 95.16 (s, $^1J_{CPt}$ 78.6 Hz).

2.1.2. Synthesis of *cis*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}(PPh_3)]$, **3**

To a solution of $[\{PtCl_2(PPh_3)\}_2]$, (0.181 g, 0.17 mmol) in 15 ml of $(CH_3)_2CO$ were added 0.104 g, (0.34 mmol) of **1**. The mixture was stirred for 2 h at r.t., obtaining the formation of a yellow solid, **3**, which was filtered, washed with few ml of cold $(CH_3)_2CO$ and dried under vacuum. Yield: 0.112 g, 40%.

Mother liquors were taken to dryness under vacuum, yielding a solid whose IR and ^{31}P-NMR spectra indicated to be a mixture of compound **3** and other unidentified substance(s).

The course of the reaction was also monitored by ^{31}P-NMR spectroscopy in CD_2Cl_2 obtaining the indication of the exclusive formation of compound **3**.

3: M.p. 170–172°C (dec.). Elem. Anal.: Found: C 52.97; H 3.57. Calc. For $C_{38}H_{30}Cl_2OP_2Pt$: C 54.95; H 3.64. IR (Nujol, cm^{-1}): ν_{CO} 2072 ν_{PtCl} 330, 337. $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 28°C): P′ 25.15 (d, $^2J_{PPt}$ 64.7 Hz, $^3J_{PP}$ 12.2 Hz), P″ 14.61 (d, $^1J_{PPt}$ 3370 Hz, $^3J_{PP}$ 12.2 Hz). (The numbering of phosphorus atoms is indicated in Reaction 2.) ^{1}H-NMR (CD_2Cl_2, 28°C): C_6H_5 7.93–7.22 (m). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 28°C): C–Pt 10.48 (d, $^1J_{CP}$ 56.1 Hz, $^1J_{CPt}$ 713Hz), CO 160.62 (dd, $^2J_{CP}$ 19.8 Hz, $^3J_{CP}$ 3.3 Hz, $^2J_{CPt}$ 291 Hz).

2.1.3. Synthesis of $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]$, **4**

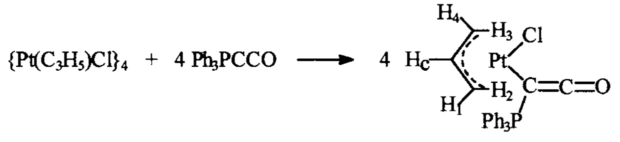
Compound **2** and an equimolecular amount of $AgBF_4$ were dissolved at − 50°C in $(CD_3)_2CO$, with formation of AgCl. The resulting solution was treated with an equimolecular amount of **1** and the course of the reaction was monitored by ^{1}H and ^{31}P-NMR at − 50°C and IR spectroscopy, obtaining convergent evidences of the formation of the *cis*-bis-η^1-ketenyl derivative **4** (see Discussion). As the temperature rises a large decomposition occurs, giving unidentified compounds.

2.1.4. Reactivity $[Pt(\eta^3\text{-}C_3H_5)Cl\{\eta^1\text{-}C(PPh_3)CO\}]$

The reactivity of compound **2** was tested with alcohols and amines, monitoring the reactions by multinuclear NMR spectroscopy. The results are reported in the Discussion section.

3. Results and discussion

The results obtained in the reactions of ketenylidenetriphenylphosphorane with Pt(II) complexes confirm that **1** can be an useful synthon to obtain η^1-ketenyl derivatives. Particularly, it is nucleophilic enough to break chlorine bonds in tetrameric $[\{Pt(C_3H_5)Cl\}_4]$ (Eq. (1)) and in dimeric $[\{PtCl_2(PPh_3)\}_2]$ (Eq. (2)) and adds to the metal center giving the η^1-ketenyl ylidic derivatives **2** and **3**, respectively.



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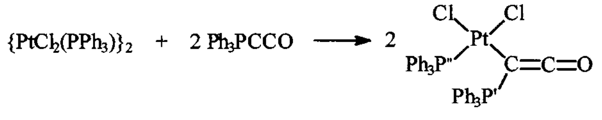
(1)



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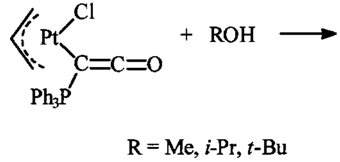
(2)

The spectroscopic features presented by compound **2** fall in the ranges of those reported for other η^1-ketenyl derivatives [3,10]. This fact could indicate that the η^1-ketenyl character of the C=C=O moiety bonded to Pt is not influenced largely by its involvement in an ylide grouping. If this is true compound **2** could present the typical η^1-ketenyl reactivity [3] and, to verify this hypothesis, we have tested the reactivity of **2** towards protic nucleophilic reagents as alcohols and amines, monitoring the course of the reactions by ^{1}H and ^{31}P-NMR spectroscopy.

The reactions of **2** with methanol, *iso*-propanol and *ter*-butanol show similar features, indicating in the attack of the alcohol to the ketenyl moiety, to form ester species, as the most important process (Eq. (3)). ^{1}H-NMR spectra show the formation of two diastereomeric species, due to the concomitant presence in **2** of the prochiral allyl group and the prochiral ylidic carbon atom bonded to Pt.



(3)

^{1}H-NMR data of the esters, collected in Table 1, are in agreement to ^{31}P-NMR data of the same compounds (Table 2) which show, in any case, signals due to the above mentioned diastereomeric species, in the range 23–28 ppm with Pt satellites ($^3J_{PPt}$ 80–120 Hz).

Particularly, in the reaction with methanol it has been observed the slow formation (5 days for the complete disappearance of **2**) of two diastereomeric ester derivatives in about 2:1 ratio.

Table 1
Selected ^{1}H-NMR signals of the products from reactions between **2** and alcohols [a]

Diastereomers [b]	C*H		CH$_3$	
	a	**b**	**a**	**b**
R				
Me	4.45(d) $^2J_{HP}$ 1.2 $^2J_{HPt}$ 89.7	4.54(bs) / $^2J_{HPt}$ 94.4	3.60(s)	3.53(s)
i-Pr	4.39(d) $^2J_{HP}$ 1.3 $^2J_{HPt}$ 90.5	4.47(bs) / $^2J_{HPt}$ 95.6	1.19(d) $^3J_{HH}$ 4.7	1.07(d) $^3J_{HH}$ 6.3
t-Bu	4.33(d) $^2J_{HP}$ 1.3 $^2J_{HPt}$ 92.0	4.42(bs) / $^2J_{HPt}$ 97.3	1.35(s)	1.30(s)

[a] Solvent $CDCl_3$, 28°C, δ in ppm, J in Hz.

[b] **a** indicates the most abundant diastereomer.

Table 2
^{31}P-NMR of the products obtained in the reactions between **2** and alcohols [a]

R	Diastereomers [b]	
	a	**b**
Me	23.36 $^2J_{PPt}$ 83.6	27.11 $^2J_{PPt}$ 116.8
i-Pr	23.01 $^2J_{PPt}$ 85.5	26.70 $^2J_{PPt}$ 118.9
t-Bu	23.11 $^2J_{PPt}$ 83.4	26.47 $^2J_{PPt}$ 115.9

[a] Solvent $CDCl_3$, 28°C, δ in ppm, J in Hz.

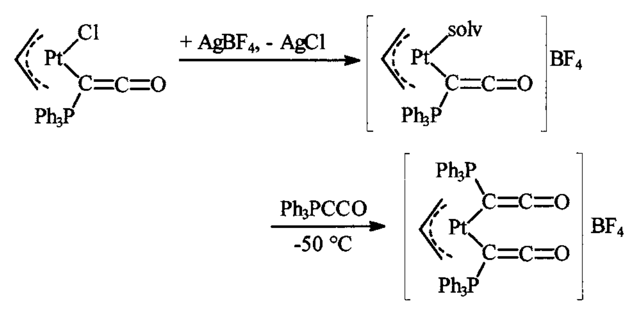
[b] **a** indicates the most abundant diastereomer.

As the steric encumbrance of R increases, the diastereomeric ratio between the ester species also increases but this results is obtained to reaction rate detriment. In fact, by using *iso*-propanol a diastereomeric ratio about 3:1 was obtained but the reaction needed 8 days to be completed. With *ter*-butanol the long time used in the experiment (15 days) lowered the overall yield, with formation of unwanted by-products. Particularly important resulted the formation of an uncoordinated protonated ylidic species (singlet at 22.97 ppm in the ^{31}P-NMR with no Pt satellites), and CO_2, inferred by the appearance in the IR spectrum of a signal at 2338 cm^{-1}, due likely to the reaction with traces of water and/or acidic species, always present in chlorinated solvents. This process has been observed previously [15], but in this case it assumed a particular relevance, due to the long reaction time.

More intriguing resulted the study of the reaction of **2** with amines. In fact, different results have been obtained with Ph_2NH with respect to more basic Et_2NH and *ter*-$BuNH_2$.

The aromatic amine reacted with **2** by adding to the ketenyl moiety analogously to what happens with alcohols, thus yielding two diastereomeric amidic species in 3:1 ratio, as indicated by ^{1}H and ^{31}P-NMR data (Table 3). With the more basic aliphatic amines the formation of the diastereomeric amidic species was observed only partly and other reactions assumed relevance. Particularly, the ^{1}H-NMR spectrum of the reaction with *ter*-$BuNH_2$ showed also signals which can be interpreted as a result of a nucleophilic attack of the amine to the coordinated allyl group and consequent coordination of a further amine to platinum. The reaction with Et_2NH leaded to an even more intricate mixture of products. ^{1}H-NMR spectrum evidenced the presence of free propene, indicating the elimination of the allylic group, and of several unidentified compounds. In the ^{31}P-NMR spectrum a singlet at 25.02 ppm flanked by Pt satellites ($^2J_{PPt}$ 77.6 Hz), can be tentatively attributable to the partial formation of an amidic ylidic derivative coordinated to Pt, likely Pt–$CH(PPh_3)CONEt_2$.

A peculiar reaction of **2** was observed when it was treated with one equivalent of **1** in the presence of $AgBF_4$. By ^{1}H and ^{31}P-NMR in $(CD_3)_2CO$ at −50°C it was possible to observe signals indicating the formation of the *cis*-bis-η^1-ketenyl derivative **4**, according to Eq. (4).



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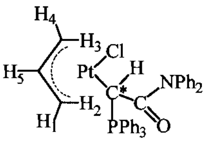
(4)

Table 3
^{1}H and ^{31}P-NMR of the reaction products from **2** and Ph_2NH[a]

	Diastereomers[b]	^{1}H						^{31}P
		H_1	H_2	H_3	H_4	H_c	C*H	
	**a**	3.60(m)	2.21(d) $^3J_{HH}$ 10.8	1.51(dd) $^3J_{HH}$ 10.3 $^2J_{HPt}$ 46.2 $^3J_{HPt}$ 51.6	1.72(ddd) $^3J_{HH}$ 5.6 $^4J_{HP}$ 2.4 $^3J_{HP}$ 2.1 $^2J_{HPt}$ 29.8	4.19(m) $^2J_{HH}$ 2.1	4.35(bs) $^2J_{HPt}$ 91.8	24.58 $^2J_{HPt}$ 100.1
	b	3.94(bd) $^3J_{HH}$ 5.8 $^2J_{HPt}$ 41.0	2.20(m)	0.23(dd) $^3J_{HH}$ 13.0 $^4J_{HP}$ 2.7 $^3J_{HPt}$ 83.8	2.38(ddd) $^3J_{HH}$ 7.7 $^2J_{HH}$ 1.8 $^3J_{HP}$ 1.8 $^2J_{HPt}$ 38.0	3.50(m)	4.62(d) $^2J_{HP}$ 1.1 $^2J_{HPt}$ 112.6	27.56 $^2J_{HPt}$ 129.7

[a] Solvent $CDCl_3$, 28°C, δ in ppm, J in Hz.

[b] **a** indicates the most abundant diastereomer.

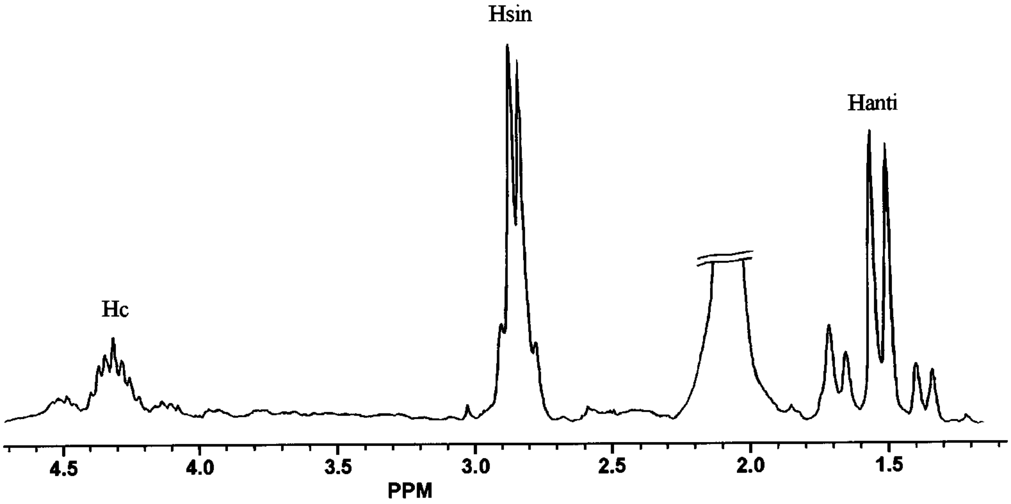


Fig. 1. ^{1}H-NMR spectrum at −50°C of compound **4**.

In fact, ^{1}H-NMR spectrum of the reaction mixture (Fig. 1) is characterized by a set of signals which indicate a symmetric arrangement of the allylic moiety around Pt. The symmetric multiplet at 4.31 ppm, flanked by Pt satellites, ($^2J_{HPt}$ 70.9 Hz) can be assigned unequivocally to H_c, whereas *anti* protons (H_a) are present as one doublet (with Pt satellites) at 1.53 ppm ($^3J_{HH}$ 17.5 Hz, $^2J_{HPt}$ 62.8 Hz) and *syn* protons (H_s) generate one doublet at 2.84 ppm ($^3J_{HH}$ 6.4 Hz, $^2J_{HPt}$ 18.3 Hz).

In agreement to these data, ^{31}P-NMR spectrum showed, immediately after the addition of **1** to the solvento species [[Pt(η^3-C_3H_5){η^1-C(PPh_3)CO}(solv)]-BF_4, only one singlet at 23.74 ppm ($^2J_{PPt}$ 91.9 Hz) thus indicating the presence of two phosphaketenylidene moieties symmetrically bonded to Pt.

Even the IR spectrum, showing only one η^1-ketenyl signal at 2075 cm^{-1}, supports the symmetrical *cis*-bis-η^1-ketenyl structure.

By increasing the temperature both ^{1}H and ^{31}P-NMR spectra changed, showing very complex patterns, according to an extended decomposition of compound **4**. In the IR spectrum the η^1-ketenyl signal disappeared with the concurrent formation of a signal due to free CO_2, at 2338 cm^{-1}. At the present we have not enough data to propose a reliable mechanism for this decomposition.

Finally, the results observed in the reaction between [{$PtCl_2(PPh_3)$}]$_2$ and **1** further confirm the ability of ketenylidenetriphenylphosphorane to act as a ketenyl source. The reaction led to the formation of an unique product, **3**, as inferred by IR and ^{31}P-NMR data (see Experimental). On the bases of the IR spectrum showing two signals at 330 and 337 cm^{-1} and of the value of the platinum–phosphorus coupling constant ($^1J_{PPt}$ 3370 Hz) [16], we suggest that this compound is the *cis*-dichloro η^1-ketenyl isomer, as sketched in Eq. (2). In Fig. 2 is reported the ^{31}P-NMR spectrum of compound **3**.

4. Conclusions

In this paper we have presented our last results in the study of the organometallic reactivity of ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$. To confirm our previous preliminary data [10] the oxocumulenic ylide reacts smoothly with Pt(II) complexes. Particularly, it breaks chlorine bonds in tetrameric [{Pt(C_3H_5)Cl}$_4$] and in dimeric [{$PtCl_2(PPh_3)$}$_2$] and adds to the coordinatively unsaturated resulting fragments, giving the η^1-ketenyl ylidic derivatives **2** and **3**, respectively, in which the C=C=O moiety bonded to Pt is also involved in an ylide grouping.

The spectroscopic data of compound **2** and **3**, quite similar to those reported for other η^1-ketenyl derivatives [3], are in agreement to what was observed preliminarily in the case of the cationic compound [Pt(η^3-C_3H_5){(η^1-C(PPh_3)(CO)}(PPh_3)]BF_4 [10], i.e. that the C=C=O moiety bonded to the metal maintains the η^1-ketenyl character even if it is yet involved in an ylidic grouping (the second ketene substituent is PPh_3). This assumption has been further confirmed by the study of the reactivity of **2** towards protic nucleophilic reagents (alcohols and amines) showing the formation of the corresponding esteric and amidic derivatives.

The most interesting result obtained in this study is, in our opinion, the indication that it is possible to obtain bis-η^1-ketenyl derivatives, never reported until now. As a matter of fact, the reaction of **2** with one further molecule of $Ph_3PC{=}C{=}O$, according to the indicated procedures, led to the formation of the unprece-

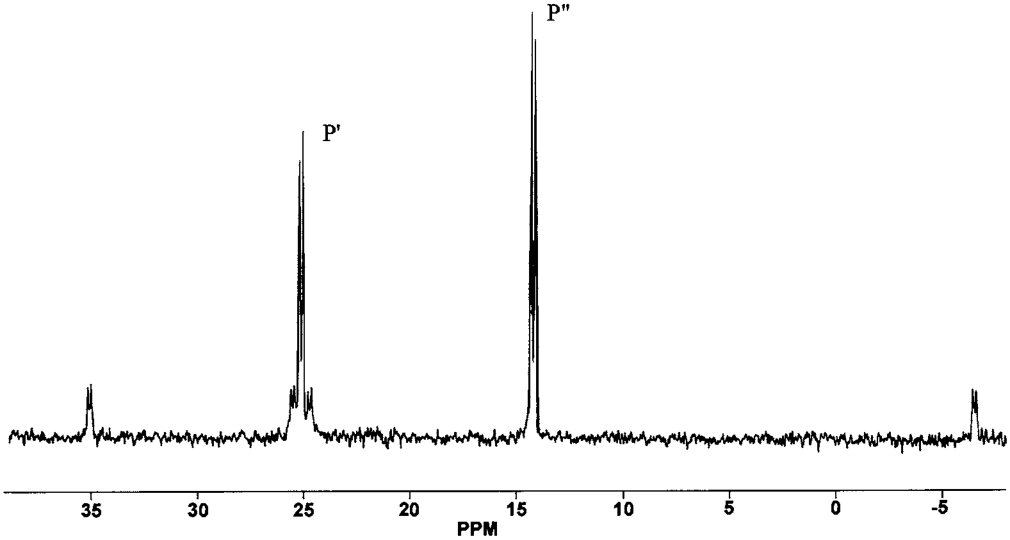


Fig. 2. $^{31}P\{^{1}H\}$-NMR spectrum of compound **3**.

dent *cis*-bis-η^1-ketenyl derivative **4** which is stable in solution only at low temperatures and has not yet isolated as pure material. Anyhow its synthetic procedure, IR, ^{1}H and ^{31}P-NMR data indicate that the hitherto unknown complex having two C=C=O moieties η^1-bonded to the same metal, has been obtained.

The instability of compound **4** as the temperature rises could be due to steric factors, being the two $Ph_3PC{=}C{=}O$ ligands in mutual *cis* position, quite cumbersome. The study of the stability (and possibly the reactivity) of this compound will be undertaken in our laboratories together the attempts to obtain other mono and bis-η^1-ketenyl derivatives.

References

[1] (a) H. Staudinger, Chem. Ber. 90 (1906) 689. (b) ibid, Die Ketene, Enke, Stuttgart, 1912.

[2] (a) S. Patai (Ed.), The Chemistry of Ketenes, Allenes, and Related Compounds, Wiley, NY, 1980. (b) T.T. Tidwell, Ketenes, Wiley, NY, 1995.

[3] (a) G.L. Geoffroy, S.L. Bassner, Adv. Organomet. Chem. 28 (1988) 1. (b) G. Paiaro, L. Pandolfo, Comments Inorg. Chem. 12 (1991) 213.

[4] (a) W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 117. (b) R.B. Anderson, The Fischer-Tropsch Synthesis, Academic Press, Orlando, FL, 1984, Chapter 5. (c) W. Keim, J. Organomet. Chem. 372 (1989) 15. (d) K.A. Belsky, M.F. Asaro, S.Y. Chen and A. Mayr, Organometallics, 11 (1992) 1926. (e) F. Calderazzo, U. Englert, A. Guarini, F. Marchetti, G. Pampaloni, A. Segre, G. Tripepi, Chem. Eur. J. 2 (1996) 412.

[5] (a) G. Paiaro, L. Pandolfo, Angew. Chem. Int. Ed. Engl. 20 (1980) 288. (b) L. Pandolfo, F. Morandini, G. Paiaro, Gazz. Chim. Ital. 115 (1985) 711. (c) A.K. List, M.R. Smith II, G.L. Hillhouse, Organometallics 10 (1991) 361.

[6] L. Pandolfo, G. Paiaro, G. Valle, P. Ganis, Gazz. Chim. Ital. 115 (1985) 59.

[7] (a) G.L. Hillhouse, J. Am. Chem. Soc. 107 (1985) 7772. (b) L. Pandolfo, G. Paiaro, Gazz. Chim. Ital. 120 (1990) 531. (c) P. Ganis, G. Paiaro, L. Pandolfo, G. Valle, Gazz. Chim. Ital. 120 (1990) 541.

[8] (a) C.N. Mattews, G.H Birum, Tetrahedron Lett. 46 (1966) 5707. (b) H.J. Bestmann, Angew. Chem. Int. Ed. Engl. 16 (1977) 349. (c) H.J. Bestmann, D. Sandmeier, Chem. Ber. 113 (1980) 274.

[9] (a) H. Berke, E. Lindner, Angew. Chem. Int. Ed. Engl. 12 (1973) 667. (b) H. Lindenberger, R. Birk, O. Orama, G. Huttner, H. Berke, Z. Naturforsch. 43b (1988) 749:

[10] L. Pandolfo, G. Paiaro, L.K. Dragani, C. Maccato, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle, Organometallics 15 (1996) 3250.

[11] L. Pandolfo, G. Facchin, R. Bertani, P. Ganis, G. Valle, Angew. Chem. Int. Ed. Engl. 35 (1996) 83.

[12] J. Lukas, Inorg. Synt. 15 (1974) 79.

[13] A.C. Smithies, P. Schmidt, M. Orchin, Inorg. Synt. 12 (1970) 240.

[14] Compound **2** was obtained previously (Ref. [10]) through a different synthetic procedure which gave, in very low yield, an impure compound for which partially incorrect NMR data were reported.

[15] G. Grandi, Dissertation Thesis, University of Padova, 1995/96.

[16] P.S. Pregosin, R.W. Kunz, NMR, Basic Principles and Progress, vol. 16, Springer Verlag, Germany, 1979.