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Synthesis, characterization and reactivity of platinum-substituted ketenes $[PtX\{\eta^1\text{-}C(PPh_3)CO\}L_2]BF_4$, (X = Me, Cl; L_2 = 1,5-cyclooctadiene, 1,2-bis(diphenylphosphino)ethane, *cis*-1,2-bis(diphenylphosphino)ethene). Steric and electronic effects of the ancillary ligands

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Dedicated to the memory of Professor Luigi M. Venanzi.

Abstract

Ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, **1**, has been used to synthesize platinum-substituted ketenes $[PtMe\{\eta^1\text{-}C(PPh_3)CO\}L_2]BF_4$, **2a**, **b** ($L_2$ = 1,5-cyclooctadiene, cod (**a**), 1,2-bis(diphenylphosphino)ethane, diphos (**b**)). Parent compound $[PtCl\{\eta^1\text{-}C(PPh_3)CO\}L_2]BF_4$, **3**, with L_2 = *cis*-1,2-bis(diphenylphosphino)ethene, diphoe, was also synthesized, which is stable only at low temperature. The stability of **2** and **3** and the reactivity of the C=C=O moiety have been examined and discussed in terms of the electronic and steric characteristics of the ancillary ligands, also taking into account the reactivity of the '$PtXL_2$' fragment with other carbonyl stabilized phosphorus ylides, $Ph_3PCHCOR$ (R = Me, Ph, OMe, OEt).

Keywords: Platinum complexes; Ketenes; Ylides; Ketenylidenetriphenylphosphorane; Metal substituted ketenes; η^1-ketenyls; Steric hindrance

1. Introduction

Ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, **1**, presents both ylide and ketene functionalities and, thanks to these characteristics, it has been employed in a large number of organic reactions which lead to several interesting compounds [1], whereas only few papers deal with its reactivity towards metal systems. After some early works [2] **1** has been recently employed in a series of reactions with coordinatively unsaturated Pt(II) complexes [3] yielding, through the bonding of the ylidic carbon to the metal, stable mono and bis-η^1-ketenyl derivatives (Chart 1)[1]. These compounds can be also referred as mono and bis-metal substituted ketenes in which one substituent is PPh_3 and the other one is the Pt complex [3c]. We are interested in the synthesis, characterization and study of the reactivity of this kind of compounds [3], with the aim, *inter alia*, to test the possibility to modulate the stability and reactivity of the metal substituted ketenes by modifying the characteristics of the metal fragment, i.e. by changing the metal, its oxidation state and the electronic and steric characteristics of the ancillary ligands bonded to the metal.

In the course of this research project we have obtained metal substituted ketenes $[PtX\{\eta^1\text{-}C(PPh_3)CO\}L_2]BF_4$, **2** and **3** (X = Me, L_2 = 1,5-cyclooctadiene, cod,

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[1] Some other Pd and Pt substituted mono and bisketenes resulted stable only at low temperature (see [3a,3b]).

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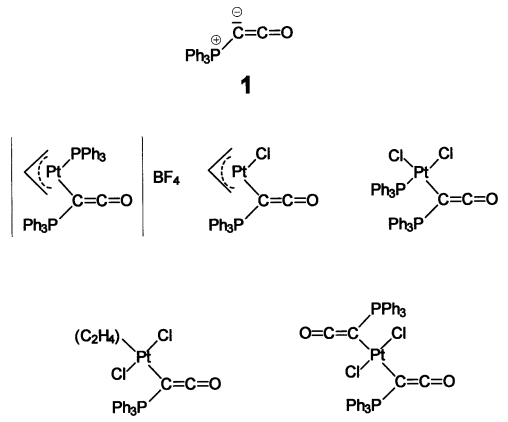
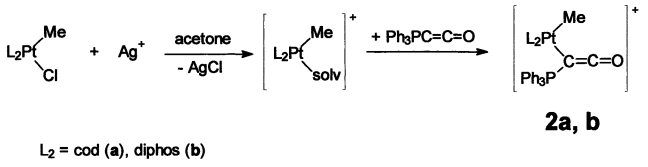


Chart 1.

2a, 1,2-bis(diphenylphosphino)ethane, diphos, **2b**), X = Cl, L_2 = *cis*-1,2-bis(diphenylphosphino)ethene, diphoe, **3**) and here we report data on their synthesis, stability and reactivity. Moreover, we also report the synthesis and characterization of [PtMe{η^1-CH(PPh_3)C(O)Me}(cod)]BF_4, **4a**, [PtMe{η^1-CH(PPh_3)C(O)Me}(diphos)]BF_4, **4b** and its O-coordinated isomer [PtMe{η^1-OCMeCHPPh_3}(diphos)]BF_4, **4b′**.

2. Results and discussion

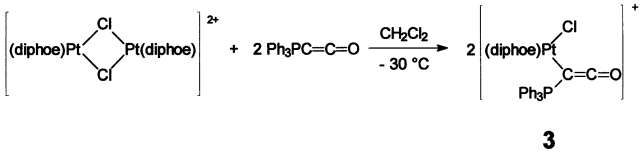
Compounds **2** were synthesized and isolated following a standard procedure involving the formation of a coordinative vacancy on Pt(II) followed by the addition of $Ph_3PC{=}C{=}O$, as sketched in Reaction 1, whereas for compound **3** it was adopted the procedure indicated in Reaction 2.



2a, b

L_2 = cod (a), diphos (b)

Reaction 1



3

Reaction 2

Both compounds **2a**, **b** are stable in the solid state, and they were isolated in almost quantitative yield and characterized spectroscopically. The only problem encountered was the obtaining of the $^{13}C\{^1H\}$ NMR spectra in solution. In fact, compounds **2**, dissolved in hexadeuteroacetone, decompose in the time with development of CO_2, likely due to interaction with adventitious water which is difficult to completely eliminate from the solvent. This behavior, which is currently under study, was previously observed with some other Pt(II) η^1-ketenyl derivatives obtained from **1** [3] and, likely, is related to the interaction of free $Ph_3PC{=}C{=}O$ with water [4]. On the other hand, decomposition processes were also observed in chlorinated solvent, analogously to what happens with other [L_nPt{η^1-C(PPh_3)CO}] derivatives [3]. Anyhow, it was possible to obtain, for compound **2a**, a solid-state CP/MAS $^{13}C\{^1H\}$ NMR determination that gave data completely in agreement with those of other [L_nPt{η^1-C(PPh_3)CO}$_n$] ($n = 1, 2$) derivatives, both in solution [3] and in the solid state [5]. A solid-state CP/MAS $^{31}P\{^1H\}$ NMR determination, carried out on the same compound **2a**, gave a chemical shift value in very good agreement with that found in solution. Compound **3**, instead, is unstable at room temperature and it was characterized by IR and $^{31}P\{^1H\}$ NMR spectra at -50 °C. The relevant spectroscopic data of compounds **2** and **3** are collected in Table 1.

The most evident feature observed in the IR spectra of all derivatives is the presence of a strong, sharp signal in the range 2071–2088 cm^{-1} corresponding to the C=C=O stretching of $Ph_3PC{=}C{=}O$ bonded to the metal through the ylidic carbon [3,6]. Also the ^{31}P NMR data pertaining to the $Ph_3PC{=}C{=}O$ moieties indicate the coordination of **1** through the ylidic carbon. As a matter of fact the chemical shifts (25–28 ppm) are in the range of other [L_nPt{η^1-C(PPh_3)CO}$_n$] ($n = 1, 2$) compounds [3] and the values of corresponding J_{PPt} (67–133 Hz) are typical for a through two bonds coupling [7]. As for the signals of coordinated diphosphines are concerned, the assignments can be made thanks to the ^{195}Pt coupling constants. Particularly, $^1J_{PPt}$ in the range 1500–2000 Hz is related to the phosphorus in *trans* position to the methyl (P″), whereas a value greater than 3000 Hz indicates P′, in *trans* position to coordinated **1**. Interestingly, in compound **3**, both the $^1J_{PPt}$ values are in the range 3000–3500 Hz, thus reflecting, for the ligand $Ph_3PC{=}C{=}O$ a *trans* influence similar to that of Cl [7]. Also ^{13}C NMR data pertaining to the C=C=O moiety of **2a** are in agreement with the corresponding data of ketenes having organic [8] or metal [3,5,6] substituents. Thus, even though we were unable to obtain crystals suitable for an X-ray determination, we are completely confident that compounds **2** and **3** are represented by the structures sketched in Chart 2.

Some reactivity tests, performed on compound **2a**, confirm its ketene characteristics. As a matter of fact, **2a** reacts in solution with protic nucleophiles (alcohols and amines), giving the corresponding esters and amides according to Reaction 3, with a behavior previously observed with other η^1-ketenyl derivatives [3a,3c,6].

The course of the reactions was monitored by NMR spectroscopy and reaction products were not isolated.

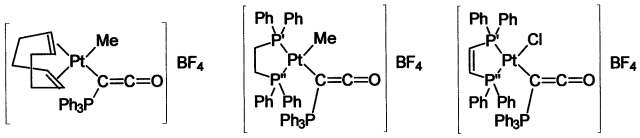
Table 1
Relevant IR and NMR data of compounds **2** and **3**

	IR	^{1}H NMR	^{31}P{^{1}H) NMR	^{13}C{^{1}H) NMR
2a	2088	0.73 s, $^2J_{HPt} = 70.8$, CH_3 2.28 m, 2.43 m, CH_2 4.95 m, 5.04 m, $^2J_{HPt} = 68.4$, CH	26.05 s, $^2J_{PPt} = 91.9$ 27.05 s, $^2J_{PPt} = 114$ [b]	−0.05 d, $^1J_{CP} = 95.7$, $^1J_{CPt} = 766$, *C*CO; 4.33 s, $^1J_{CPt} = 603$, CH_3 27.55, 31.90, 34.40, CH_2 100.67 s, 101.17 s, 104.38 s, 110.87 s, CH 161.03 s, CO
2b	2071	0.31 dd, $^3J_{HP} = 6.9$, $^3J_{HP} = 4.5$, $^2J_{HPt} = 58.9$, CH_3 2.42 m, CH_2	25.20 dd, $^3J_{PP} = 9.3$, $^3J_{PP} = 4.2$, $^2J_{PPt} = 67.5$, P_{yl} 47.13 d, $^3J_{PP} = 9.3$, $^1J_{PPt} = 3526$, P′ 49.05 d, $^3J_{PP} = 4.2$, $^1J_{PPt} = 1691$, P″	
3 [a]	2079		27.79 s, $^2J_{PPt} = 133$, P_{yl} 52.98 s, $^1J_{PPt} = 3515$, P′ 63.45 s, $^1J_{PPt} = 3013$, P″	

IR in Nujol (cm^{-1}). ^{1}H and ^{31}P{^{1}H) NMR in $CDCl_3$, ^{13}C{^{1}H) NMR in solid, (δ in ppm, J in Hz, 28 °C). ^{1}H and ^{13}C{^{1}H) NMR phenyls data are omitted.

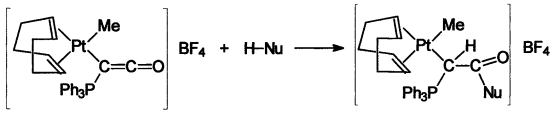
[a] ^{1}H and ^{31}P{^{1}H) NMR spectrum in CD_2Cl_2 at −50 °C.

[b] Solid state CP/MAS ^{31}P{^{1}H) NMR data.



2a **2b** **3**

Chart 2.



NuH = MeOH, $PhNH_2$, Me_2NH

Reaction 3

Most important NMR data of the amides and ester are collected in Table 2.

Compound **2b** presents a different behavior, *i.e.* the C=C=O moiety is almost completely unreactive towards the addition of protic nucleophyles. Particularly, the reaction with Et_2NH yielded only the substitution of coordinated $Ph_3PC{=}C{=}O$ with the amine, whereas the reactions with Me_2NH and $CyNH_2$, yielded mainly the substitution products accompanied by little quantities of the corresponding amides, as determined by ^{31}P{^{1}H} NMR spectra (Table 3). The reaction with the less basic $PhNH_2$ led, with long reaction times, to the formation of little quantities of the corresponding amide, accompanied by several unidentified products. MeOH and EtOH were completely unreactive even for long reaction times.

This loss of reactivity is quite strange for the C=C=O moiety and it was previously observed only in the case of bis-η^1-ketenyl derivative *trans*-[$PtCl_2\{\eta^1$-$C(PPh_3)$-$CO\}_2$], **A**, [3c] that reacts only with amines to give the bis-amidic derivatives and does not react with alcohols. This behavior was attributed to the insolubility of **A** in most organic solvents and to a particularly encumbered structure that protect the C=C=O moieties from external attacks [3c]. Steric factors are known to be of paramount importance in the stability and reactivity of ketenes [8] and are to be considered also in the evaluation of the different behaviors of **2a** and **2b**. In fact, even in the absence of X-ray crystal structure determinations for **2a** and **2b**, it is evident that the latter is much more encumbered than the former and it is

Table 2
Relevant NMR data on reactivity of **2a** with H–Nu

H–Nu	^{1}H NMR	^{31}P{^{1}H) NMR	Reaction time [a]
Me_2NH	0.46 s, $^2J_{HPt} = 71.5$, Pt–CH_3 2.94 s and 3.31 s, NMe_2	27.52 s, $^2J_{PPt} = 94.9$	30 min
MeOH	0.45 s, $^2J_{HPt} = 72.6$, Pt–CH_3 3.67 s, $^5J_{HPt} = 3.3$, OMe	27.70 s, $^2J_{PPt} = 70.1$	3 h
$PhNH_2$ [b]	0.53 s, $^2J_{HPt} = 72.5$, Pt–CH_3 8.85 s, NH	27.62 s, $^2J_{PPt} = 86.1$	10 days

Reactions performed in CD_2Cl_2 (δ in ppm, J in Hz, 28 °C). ^{1}H NMR data pertaining to phenyls and cod are omitted.

[a] Time required for complete disappearance of Nu–H.

[b] Little quantities of unidentified compounds were also observed.

Table 3
Relevant NMR data on reactivity of **2b** with H–Nu

		^{1}H NMR [a]	^{31}P{^{1}H) NMR
Et_2NH	Substitution product	0.47 dd, $^3J_{HP}=2.9$, $^3J_{HP}=6.6$, $^2J_{HPt}=53.1$, Pt–CH_3 3.15 m, N–CH_2–CH_3 1.18 m, N–CH_2–CH_3	37.75 s, $^1J_{PPt}=3662$, P′ 50.77 s, $^1J_{PPt}=1817$, P″
Me_2NH	Substitution product	0.49 dd, $^3J_{HP}=2.9$, $^3J_{HP}=6.7$, $^2J_{HPt}=54.1$, Pt–CH_3	38.71 s, $^1J_{PPt}=3596$, P′ 50.47 s, $^1J_{PPt}=1839$, P″
	Addition product	−0.02 dd, $^3J_{HP}=5.8$, $^3J_{HP}=6.8$, $^2J_{HPt}=58.9$, Pt–CH_3	29.84 dd, $^3J_{PP}=8.6$, $^3J_{PP}=2.3$, $^2J_{PPt}=69.7$, P_{yl} 45.98 d, $^3J_{PP}=8.6$, $^1J_{PPt}=2994$, P′ 45.56 d, $^3J_{PP}=2.3$, $^1J_{PPt}=1711$, P″
$CyNH_2$	Substitution product	0.48 dd, $^3J_{HP}=3.1$, $^3J_{HP}=6.8$, $^2J_{HPt}=54.8$, Pt–CH_3	39.59 s, $^1J_{PPt}=3753$, P′ 49.78 s, $^1J_{PPt}=1772$, P″
	Addition product	0.15 dd, $^3J_{HP}=5.6$, $^3J_{HP}=6.9$, $^2J_{HPt}=62.2$, Pt–CH_3	29.16 dd, $^3J_{PP}=6.2$, $^3J_{PP}=7.7$, $^2J_{PPt}=59.8$, P_{yl} 44.74 d, $^3J_{PP}=6.2$, $^1J_{PPt}=2935$, P′ 48.03 d, $^3J_{PP}=7.7$, $^1J_{PPt}=1670$, P″

Reactions in CD_2Cl_2 (δ in ppm, J in Hz, 28 °C).
[a] ^{1}H NMR data pertaining to diphos are omitted. Only well defined and assigned signals are reported.

possible that the phenyl groups of diphos contribute to 'protect' the C=C=O moiety from the attacks of not very strong nucleophiles, such as alcohols and also make difficult the attack of amines. Some evidences support this hypothesis. Firstly, a particularly overcrowded situation was previously observed in the crystal structure of the parent compound [PtMe{η^1-CH(PPh_3)COOEt}diphos]BF_4, **B**, which was synthesized through the direct interaction of [PtMe(Cl)diphos] with $Ph_3PCHCOOEt$ in the presence of $AgBF_4$ [9]. In the X-ray crystal structure of compound **B** it was possible to observe that the fragment CHCOOEt accommodates, with a full extended conformation, into a sort of 'molecular hollow' formed by the interactions between the phenyl groups. It is possible that the structure of **2b** presents analogous features, (the only 'chemical' difference is between CHCOOEt and CCO groups) and that also the C=C=O moiety accommodates into an analogous hollow that shields it from external attacks. Also different electronic effects of cod with respect to diphos should be taken into account. In this regard, it is worthwhile to remember that Ph_3PC=C=O binds to the metals through the nucleophilic ylidic carbon and acts as a σ-donor, without any contribution of back-donation [2a,3c]. For this reason it is possible that the good π-acceptor cod is able to relieve an excess of negative charge more effectively than diphos does. This would stabilize compound **2a** with respect to **2b**, but the reactivity of the ketene moieties are expected to be unaffected. At the most, cod would decrease, through the metal, the negative charge on the Pt-bonded carbon, thus making the ketene fragment of **2a** less reactive than in the case of **2b**, with a behavior opposite to that observed. Thus, it seems that steric factors, rather than electronic ones, drive the reactivity of these metal substituted ketenes.

Moreover, the fact that the structure of compound **2b** is particularly overcrowded is indirectly confirmed by the instability of compound **3** that, considering only the electronic effects, is expected to be more stable than **2b**. As a matter of fact, giving that the electronic effects of diphos and diphoe are very similar if not identical, the electron withdrawing Cl should stabilize **3** with respect to **2b**, in which the electron donating group Me is present. Since it is experimentally observed an opposite behavior it is possible to infer that the more restrictive steric demands due to the rigid planar diphoe, with respect to relatively deformable diphos are responsible for the instability of **3**. In other words, it is likely that in compound **2b** it has been reached a limit situation of stability (similarly to that observed in the overcrowded compound **B**), whereas in the case of compound **3** the rigid geometrical situation of the diphoe phenyl groups produces repulsive interactions with other ligands, and this fact makes compound **3** unstable and let to observe it only at low temperature.

Further support to these considerations has been provided by the results of the interactions of the 'PtMeL_2' fragments (L_2 = cod, diphos), with the carbonyl stabilized ylide $Ph_3PCHCOMe$. It is known that steric factors are of paramount importance to drive the coordination to Pt of carbonyl stabilized ylides. Ac-

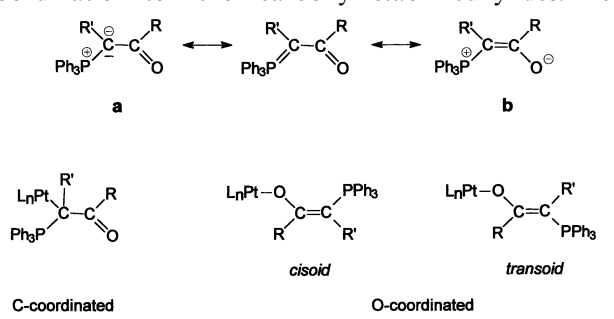
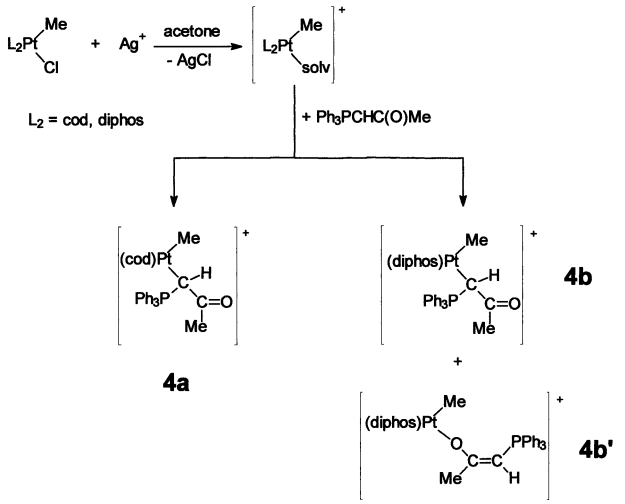


Chart 3.



Scheme 1.

cording to the limit structures **a** and **b** depicted in Chart 3, these ylides can use either the ylidic carbon or the carbonyl oxygen to bind to the metal, yielding C-coordinated or O-coordinated complexes, respectively, the latter in the *cisoid* or *transoid* form.

Particularly, it has been observed that, for R′ = H and R = Me, Ph, OMe, the relatively low sterically demanding 'PtCl(η^3-allyl)' allows fragment always the coordination through the ylidic carbon, whereas, in the cases of highly sterically demanding '*trans*-Pt(CF_3)-(PPh_3)$_2$', only the O-coordination is possible. In the case of 'PtClL_2' (L_2 = diphos, diphoe), presenting an intermediate degree of steric hindrance, the more sterically demanding C-coordination is obtained only with a strong nucleophilic ylide (R = OMe), whereas for the less nucleophilic ylides (R = Me, Ph) only the less sterically demanding O-coordination occurs [10].

The reaction of $Ph_3PCHCOMe$ with [PtMe(Cl)L_2] (L_2 = cod, diphos), carried out according to the same procedure used in the reactions with $Ph_3PC{=}C{=}O$, yielded solid stable compounds **4** that were isolated and characterized through IR and NMR spectroscopies. As indicated in Scheme 1, for L_2 = cod it was observed only the formation of the C-coordinated compound, **4a**, whereas for L_2 = diphos it was obtained a mixture of C-coordinated (**4b**) and O-coordinated (**4b′**) derivatives, with a prevalence of the latter. Recrystallization yielded **4b′** almost pure, while it was impossible to obtain pure **4b**. To the complex **4b′** it was assigned the *cisoid* form on the basis of the high value of $^2J_{HP}$ (22.9 Hz) for the methine proton and the observation of a $^4J_{HP}$ of 1.3 Hz for the C–CH_3 protons [11]. Relevant spectroscopic data pertaining compounds **4** are shown in Table 4 and complete data are reported in the Section 4.

These considerations together with the fact that the strong nucleophilic ylide $Ph_3PCHCOOEt$ adds to the 'PtMediphos' fragment exclusively through the ylidic carbon [9], confirm the particular overcrowded situation of **2b** (L_2 = diphos) with respect to **2a** (L_2 = cod), that is very likely responsible for the unreactivity of the former toward protic nucleophiles.

3. Conclusions

$Ph_3PC{=}C{=}O$ has further confirmed to be a valuable synthon to obtain, through clean and simple reactions, η^1-ketenyls that are, in effect, ketenes having as substituents the Ph_3P moiety and a metal complex fragment. As previously stated, it is conceivable that the ketene stability and reactivity may 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. As for the latter point is

Table 4
Relevant IR and NMR data of compounds **4**

	IR	^{1}H NMR	^{31}P{^{1}H} NMR	^{13}C{^{1}H} NMR
4a	1660	0.31 s, $^2J_{HPt}$ = 71.7, Pt–CH_3 2.41 d, $^4J_{HP}$ = 2.5, C–CH_3 5.56 d, $^2J_{HP}$ = 3.8, $^2J_{HPt}$ = 117.7, CH	27.80 s, $^2J_{PPt}$ = 63.1	7.79 s, $^1J_{CPt}$ = 654, Pt–CH_3 32.79 d, $^3J_{CP}$ = 10.7, C–CH_3 38.66 d, $^1J_{CP}$ = 44.9, $^1J_{CPt}$ = 634, CH 204.46 d, $^2J_{CP}$ = 7.1, $^2J_{CPt}$ = 44.6, CO
4b	1656	Pt–CH_3 not assigned 2.45 d, $^4J_{HP}$ = 2.3, C–CH_3 2.1–2.5 m, CH_2 4.96 d, $^2J_{HP}$ = 11.8, CH	27.33 dd, $^3J_{PP}$ = 8.9, $^3J_{PP}$ = 5.7, $^2J_{PPt}$ = 63.9, P_{yl} 42.74 d, $^3J_{PP}$ = 8.9, $^1J_{PPt}$ = 3153, P′ 48.70 d, $^3J_{PP}$ = 5.7, $^1J_{PPt}$ = 1687, P″	
4b′	1509	0.10 dd, $^3J_{HP}$ = 7.3, $^3J_{HP}$ = 2.4, $^2J_{HPt}$ = 51.6, Pt–CH_3 2.00 d, $^4J_{HP}$ = 1.3, C–CH_3 2.1–2.5 m, CH_2 4.23 dd, $^2J_{HP}$ = 22.9, $^5J_{HP}$ = 2.2, $^4J_{HPt}$ = 15.4, CH	13.61 s, P_{yl} 34.21 s, $^1J_{PPt}$ = 4246, P′ 48.66 s, $^1J_{PPt}$ = 1807, P″	8.50 dd, $^2J_{CP}$ = 90.8, $^2J_{CP}$ = 5.8, $^1J_{CPt}$ = 535, Pt–CH_3 30.60 d, $^3J_{CP}$ = 13.4, C–CH_3 25.14 dd, $^1J_{CP}$ = 34.8, $^2J_{CP}$ = 5.3, CH_2 30.85 dd, $^1J_{CP}$ = 43.2, $^2J_{CP}$ = 17.3, CH_2 65.24 dd, $^1J_{CP}$ = 105.4, $^4J_{CP}$ = 5.4, P–CH 190.76 s, CO

IR in KBr (cm^{-1}). NMR in $CDCl_3$ (δ in ppm, J in Hz, 28 °C). ^{1}H and ^{13}C{^{1}H) NMR data pertaining to phenyls and cod are omitted.

concerned, since it has been proposed [2a] and then calculated [3c] that **1** acts exclusively as a σ-donor, without back-donation, it is expected that the nucleophilic attack of the ylidic carbon is favored by the increase of the positive charge on the metal. For this reason electron-withdrawing ancillary ligands should favor the coordination and, likely, the stability of the resulting metal substituted ketene. The effects of steric parameters on the stability and reactivity are more difficult to be evaluated. In this work it has been observed that for the metal-fragment 'PtXL$_2$' (X = Cl, Me; L$_2$ = cod, diphos,diphoe) the addition of $Ph_3PC{=}C{=}O$ to Pt yields a stable and reactive ketene when L$_2$ is the low sterically demanding cod. A stable compound is also obtained with the more encumbered diphos, but the ketene moiety results almost completely unreactive, since it is in some way protected from the external attacks by the particular geometrical situation created by the phenyl groups of diphos and Ph_3P. Probably, this is a very unusual situation, since, with the more sterically demanding diphoe (and Cl instead Me), the platinum substituted ketene is unstable even if the electronic effects of the diphosphines are very similar and the difference between Me and Cl would, in the case, favor the latter. Very likely, the phenyl groups of Ph_3P interact with the phenyl groups of the rigid diphoe in some destabilizing way.

In conclusion, in this work it has been illustrated that it is possible to tune the steric factors of the ancillary ligands to modify the stability and reactivity of the metal substituted ketenes that can be obtained through the interaction of $Ph_3PC{=}C{=}O$ and coordinatively unsaturated metal systems. Further experimental and theoretical work can be done to deeply examine the influence of steric and electronic effects of other ligands on the stability and the reactivity of these Pt-substituted ketenes. Moreover, the study could be extended to other metals, with different oxidation states and coordination geometries, with the possibility to obtain poly-metal substituted ketenes, having stability and reactivity characteristics that are difficult to predict at the present time.

4. 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. [PtCl(Me)(cod)] [12], [PtCl(Me)(diphos)] [12], Ph_3PCCO [13], $Ph_3PCHCOMe$ [14] were synthesized according to reported methods. The dimer $[\{PtCl(diphoe)\}_2][BF_4]_2$ was obtained in about 95% yield by stirring a dichloromethane solution of $[PtCl_2(diphoe)]$ [15] with an equivalent amount of $AgBF_4$ (0.65 M in acetone) at room temperature (r.t.) for 30 min. Resulting AgCl was removed by filtration and $[\{PtCl(diphoe)\}_2][BF_4]_2$ was precipitated with ethyl ether, filtered and dried under vacuum.

IR spectra were taken on a Perkin–Elmer 983 spectrophotometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer and chemical shifts are reported in ppm (δ) relative to tetramethylsilane (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). The solid state CP/MAS $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of compound **2a** were obtained on a Bruker AC 200 spectrometer equipped for solid state analysis.

4.1. Synthesis of $[PtMe\{\eta^1\text{-}C(PPh_3)CO\}(cod)]BF_4$, 2a

A stirred solution of [PtCl(Me)(cod)] (0.141 g, 0.40 mmol) in 20 mL of acetone was treated at 0 °C with 0.62 mL of a 0.65 M acetone solution of $AgBF_4$. After 30 min AgCl was filtered off and the solution was cooled at −50 °C and reacted with 0.121 g (0.40 mmol) of $Ph_3PC{=}C{=}O$. After 10 min a white solid appeared and the reaction mixture was concentrated unde vacuum to about 5 mL and ethyl ether was added to complete the precipitation. The white solid was filtered and dried under vacuum. Yield 0.262 g, 93%.

2a: IR (Nujol, cm^{-1}) 2088, ν(CCO). ^1H NMR (δ, $CDCl_3$, 28 °C), 0.73 s, $^2J_{HPt} = 70.8$ Hz, CH_3, 2.28 m, CH_2, 2.43 m, CH_2, 4.95 m, CH, 5.04 m, $^2J_{HPt} = 68.4$ Hz, CH, 7.6–7.8 m, CH_{Ph}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 26.05 s, $^2J_{PPt} = 91.9$ Hz: CP/MAS $^{31}P\{^1H\}$ NMR (δ, 28 °C), 27.05, $^2J_{PPt} = 114$ Hz.; CP/MAS $^{13}C\{^1H\}$ NMR (δ, 28 °C), −0.05 d, $^1J_{CP} = 95.7$ Hz, $^1J_{CPt} = 766$ Hz, *C*CO, 4.33 s, $^1J_{CPt} = 603$ Hz, CH_3, 27.55, 31.90, 34.40, CH_2, 100.67 s, 101.17 s, 104.38 s, 110.87 s, CH, 120.93, 122,79, 125,50, 131.13, 132,77, Ph, 161.03 s, CO.

4.2. Synthesis of $[PtMe\{\eta^1\text{-}C(PPh_3)CO\}(diphos)]BF_4$, 2b

Complex **2b** was prepared as **2a**, obtaining a yield of 93%.

2b: IR (Nujol, cm^{-1}) 2071, ν(CCO). ^1H NMR (δ, $CDCl_3$, 28 °C), 0.31 dd, $^3J_{HP} = 6.9$ Hz, $^3J_{PH} = 4.5$ Hz, $^2J_{HPt} = 58.9$ Hz, CH_3, 2.42 m, CH_2, 7.2–7.8 m, CH_{Ph}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 25.20 dd, $^3J_{PP} = 9.3$ Hz, $^3J_{PP} = 4.2$ Hz, $^2J_{PPt} = 67.5$ Hz, P_{yl}, 47.13 d, $^3J_{PP} = 9.3$ Hz, $^1J_{PPt} = 3526$ Hz, P′, 49.05 d, $^3J_{PP} = 4.2$ Hz, $^1J_{PPt} = 1691$ Hz, P″.

4.3. Synthesis of $[PtCl\{\eta^1\text{-}C(PPh_3)CO\}(diphoe)]BF_4$ (3)

A chilled solutions (−40 °C) of 0.1 g of $[\{PtCl(diphoe)\}_2][BF_4]_2$, (0.07 mmol) in 10 mL of dichloromethane was added to a solution of 0.043 g (0.14 mmol) of Ph_3PCCO in 10 mL of dichloromethane at the same temperature. The resulting solution was stirred for

10 min and then taken to dryness under vacuum at −30 °C, obtaining a solid (**3**) that resulted unstable in solution at r.t.

3: IR (Nujol, cm^{-1}) 2079, ν(CCO). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, −50 °C), 27.79 s, $^2J_{PPt} = 133$ Hz, P_{yl}, 52.98 s, $^1J_{PPt} = 3515$ Hz, P′, 63.45 s, $^1J_{PPt} = 3013$ Hz, P″.

4.4. Synthesis of [PtMe{η¹-CH(PPh₃)-C(O)Me}(cod)]BF₄ (4a)

A stirred solution of [PtCl(Me)(cod)] (0.150 g, 0.424 mmol) in 20 mL of dichloromethane was treated at 0 °C with 0.65 mL of a 0.65 M acetone solution of $AgBF_4$. After 30 min AgCl was removed by filtration and the solution was reacted with 0.135 g (0.424 mmol) of $Ph_3PCHCOMe$. After 10 min the reaction mixture was concentrated under vacuum to about 5 ml and ethyl ether was added obtaining a white solid which was filtered and dried under vacuum. Yield 0.290 g, 94%.

4a: IR (KBr, cm^{-1}) 1660, ν(CO). ^1H NMR (δ, $CDCl_3$, 28 °C), 0.31 s, $^2J_{HPt} = 71.7$ Hz, Pt–CH_3, 2.41 d, $^4J_{HP} = 2.5$ Hz, C–CH_3, 5.56 d, $^2J_{HP} = 3.8$ Hz, $^2J_{HPt} = 117.7$ Hz, CH_{yl}, 1.97–2.51 m, CH_2, 4.23 m, 4.88 m, 4.99 m, 6.15 m, CH, 7.5–7.9 m, CH_{Ph}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 27.80 s, $^2J_{PPt} = 63.1$ Hz: $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$ 28 °C), 7.79 s, $^1J_{CPt} = 654$ Hz, Pt–CH_3, 32.79 d, $^3J_{CP} = 10.7$ Hz, C–CH_3, 38.66 d, $^1J_{CP} = 44.9$ Hz, $^1J_{CPt} = 634$ Hz, CH_{yl}, 29,03 $^2J_{CPt}$ = not detected, 29.82 s, $^2J_{CPt} = 12.9$ Hz, 31.17 s, $^2J_{CPt} = 12.9$ Hz, 32.09 s, $^2J_{CPt} = 15.1$ Hz, CH_2, 99.13 s, $^1J_{CPt} = 122.9$ Hz, 99.66 s, $^1J_{CPt} = 123.8$ Hz, 109.58 s, $^1J_{CPt} = 38{,}73$ Hz, 114.53 s, $^1J_{CPt} = 36.13$ Hz, CH_{cod}, 122.43 d, $^1J_{CP} = 85.3$ Hz, $^3J_{CPt} = 23.3$ Hz, C_{ipso}, 135.07, d, $^2J_{CP} = 10.2$ Hz, C_{orto}, 130.17, d, $^3J_{CP} = 12.5$ Hz, C_{meta}, 134.39 s, C_{para}, 204.46 d, $^2J_{CP} = 7.1$ Hz, $^2J_{CPt} = 44.6$ Hz, CO.

4.5. Synthesis of [PtMe{η¹-CH(PPh₃)C(O)Me}-(dphos)]BF₄ (4b) and [PtMe{η¹-OCMeCH(PPh₃)-(dphos)]BF₄ (4b′)

The reaction was performed as for **4a**, obtaining a sticky solid that was recrystallized from dichloromethane/ethyl ether yielding a whitish solid that was filtered and dried in vacuum, with an overall yield of 64%. IR and NMR experiments revealed the presence of both C-coordinated (**4b**) and O-coordinated (**4b′**) isomers in a 1:3 ratio. Repeated recrystallizations yielded the O-coordinated isomer almost pure, whereas it was impossible to isolate pure C-coordinated isomer.

4b: IR (KBr, cm^{-1}) 1656, ν(CO). ^1H NMR (δ, $CDCl_3$, 28 °C), 2.45 d, $^4J_{HP} = 2.3$ Hz, C–CH_3, 2.1–2.5 m, CH_2, 4.96 d, $^2J_{HP} = 11.8$ Hz, CH, 7.2–7.7 m, CH_{Ph}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 27.33 dd, $^3J_{PP} = 8.9$ Hz, $^3J_{PP} = 5.7$ Hz, $^2J_{PPt} = 63.9$ Hz, P_{yl}, 42.74 d, $^3J_{PP} = 8.9$ Hz, $^1J_{PPt} = 3153$ Hz, P′, 48.70 d, $^3J_{PP} = 5.7$ Hz, $^1J_{PPt} = 1687$ Hz, P″.

4b′: IR (KBr, cm^{-1}) 1509, ν(CO). ^1H NMR (δ, $CDCl_3$, 28 °C), 0.10 dd, $^3J_{HP} = 7.3$ Hz, $^3J_{HP} = 2.4$ Hz, $^2J_{HPt} = 51.6$ Hz, Pt–CH_3, 2.00 d, $^4J_{HP} = 1.3$ Hz, C–CH_3, 2.1–2.5 m, CH_2, 4.23 dd, $^2J_{HP} = 22.9$ Hz, $^5J_{HP} = 2.2$ Hz, $^4J_{HPt} = 15.4$ Hz, CH, 7.2–7.7 m, CH_{Ph}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 13.61 s, P_{yl}, 34.21 s, $^1J_{PPt} = 4246$ Hz, P′, 48.66 s, $^1J_{PPt} = 1807$ Hz, P″. $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 28 °C), 8.50 dd, $^2J_{CP} = 90.8$ Hz, $^2J_{CP} = 5.8$ Hz, $^1J_{CPt} = 535$ Hz, Pt–CH_3, 30.60 d, $^3J_{CP} = 13.4$ Hz, C–CH_3, 25.14 dd, $^1J_{CP} = 34.8$ Hz, $^2J_{CP} = 5.3$ Hz, CH_2, 30.85 dd, $^1J_{CP} = 43.2$ Hz, $^2J_{CP} = 17.3$ Hz, CH_2, 65.24 dd, $^1J_{CP} = 105.4$ Hz, $^4J_{CP} = 5.4$ Hz, Pt–CH, 124–135 m, C_{Ph}, 190.76 s, CO.

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