Organometallic Chemistry of $Ph_3PC{=}C{=}O$. Synthesis, Characterization, X-ray Structure Determination, and Density Functional Study of the First Stable Bis-η^1-ketenyl Complex, *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$

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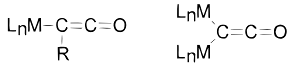
Mono- and bis-η^1-ketenyl Pt(II) complexes have been synthesized by reacting Zeise's salt or the related dimeric compound, $[\{PtCl_2(C_2H_4)\}_2]$, with the oxocumulenic ylide ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, **1**, in suitable ratios. In particular, the η^1-ketenyl derivative, *trans*-$[PtCl_2(C_2H_4)\{\eta^1\text{-}C(PPh_3)CO\}]$, **2**, has been isolated and characterized. The reaction of **2** with one more equivalent of **1** displaces the coordinated ethylene giving the first stable bis-η^1-ketenyl derivative, *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$, **6**. The X-ray crystal structure of **6** shows a trans centrosymmetric geometry around Pt, with the PCCO moiety and the metal lying in a plane that forms an angle of ~65° with the Pt(II) coordination plane. Density functional calculations indicate that steric effects play a leading role in determining such an arrangement. Data on the reactivity of **2** and **6** are also reported.

Introduction

At the beginning of this century Staudinger synthesized and characterized $Ph_2C{=}C{=}O$, the first reported ketene.[1] Since Staudinger's discovery, ketenes have been the subject of theoretical and experimental investigations, and comprehensive reports on these molecules have been published.[2] The electronic structure, the stability, and the reactivity of ketenes $(RR')C{=}C{=}O$ have been examined as a function of the steric and electronic characteristics of R and R′, usually organic fragments or silyl groups.[2c,3]

When the ketene moiety bears as substituent(s) one or two metal centers, in particular transition metals, the corresponding compounds are considered as metal complexes σ-coordinating a $C{=}C{=}O$ fragment and are, thereafter, named η^1-ketenyl (**a**) and μ_2-ketenylidene (**b**) complexes respectively (Chart 1).[4,5]

Chart 1



a **b**

Reports on η^1-ketenyl and μ_2-ketenylidene complexes are relatively scanty, likely due to difficulties encountered in the syntheses of these peculiar ketenes, with respect to those bearing organic and/or silyl substituents, for which a large variety of synthetic procedures are available.[6] To our knowledge, only one procedure has been so far reported for the synthesis of crystallographically established Zr(II) and Hf(II) μ_2-ketenylidene derivatives.[5,7] Moreover, general synthetic procedures for η^1-ketenyl derivatives are not yet available. In this regard, some Mo and W η^1-ketenyl derivatives have been synthesized by the Kreissl group through ligand-induced CO migration to a carbyne ligand,[8] while unstable compounds, which are at the same time η^1-ketenyl and η^2-(C,C) ketene derivatives, have been obtained by coordination of the bisketene carbon suboxide ($O{=}C{=}C{=}C{=}O$) to Pt(0) and Ni(0) complexes.[9]

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C_3O_2 also gives monoinsertion reactions into a Pt−oxygen bond[10] and some metal−hydride bonds as well,[11] yielding compounds where an η^1-ketenyl fragment and a carbonylic functionality are present. Furthermore, it was observed that the oxocumulenic ylide $Ph_3PC{=}C{=}O$, **1**,[12] is able to displace a weakly bonded ligand (CO or acetonitrile) from some low-valence complexes of early and medium transition metals, giving, by coordination through the ylidic carbon, η^1-ketenyl derivatives in which PPh_3 is the second ketene substituent.[13] Incidentally, η^1-ketenyl derivatives can be considered as a peculiar kind of ketenes, bearing two different substituents, an organic moiety and a metal center. This is supported by IR CO stretching values and ^{13}C NMR chemical shifts of the C=C=O moieties of η^1-ketenyl derivatives, falling in the same ranges reported for ketenes,[2,4] and this is particularly important in the case of η^1-ketenyls obtained through the use of $Ph_3PC{=}C{=}O$. As a matter of fact, although its structure is ketene-like, **1** is not a "true" ketene (for instance it does not dimerize), its π-electron system being different from that of ketenes.[12b] However, **1** assumes a ketene character by protonation or alkylation,[12b,14] i.e., by the attack of an electrophile, as it can be considered a metal center, to the ylidic carbon.

As a part of ongoing research dealing with the synthesis and characterization of metal−ketene derivatives, we are exploring the use of $Ph_3PC{=}C{=}O$ as a valuable synthon for η^1-ketenyl transition metal complexes where one of the C=C=O substituents is triphenylphosphine and the other one is a metal center. The electronic structure and the steric hindrance of the latter may be changed, in principle, to a large extent, thus influencing ketene stability and reactivity. Moreover, it also could be possible to address the reactivity of the bonded ketene fragment toward other ligands coordinated in suitable arrangements, and finally, taking advantage of the relatively high coordination number of transition metals, more than one C=C=O group could coordinate to the same metal center, obtaining 1,3-bis, tris, and so on, η^1-ketenyls.

Preliminary results indicated that **1** reacts with suitable Pt(II) and Pd(II) complexes yielding η^1-ketenyl derivatives.[15] Particularly, we obtained the first X-ray crystal structure determination of an η^1-ketenyl complex with a C=C=O moiety involved in an ylide grouping[15a] as well as IR and multinuclear NMR evidence of the existence, at low-temperature (−50 °C), of a *cis*-bis-η^1-ketenyl derivative (two C=C=O moieties bonded to the same Pt(II) center).[15b]

Here we report the synthesis of an η^1-ketenyl derivative, *trans*-$[PtCl_2(C_2H_4)\{\eta^1\text{-}C(PPh_3)CO\}]$, **2**, containing the C=C=O moiety and ethylene bonded to the same Pt atom, obtained by reacting Zeise's salt with $Ph_3PC{=}C{=}O$, and the study of its reactivity. The synthesis, the X-ray structure determination, and preliminary data on the reactivity of the first, stable, bis-η^1-ketenyl derivative, *trans*-$[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}_2]$, **6,** are also reported. Finally, the electronic structure of **6** has been investigated by means of density functional calculations.

Experimental Section

General Comments. All reactions and manipulations were carried out under an atmosphere of dry argon with standard Schlenk techniques. All solvents were dried by conventional methods and distilled under argon prior to use. $Ph_3PC{=}C{=}O$, **1**,[12c] Zeise's salt,[16] $[\{PtCl_2(C_2H_4)\}_2]$,[17] and $Ph_3PCHCOR$ (R = Me, Ph)[18] were synthesized according to literature methods. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra of compounds **2** and **6** were recorded at 298 K on a Bruker Avance-600 instrument equipped with a 5 mm TXI ^1H-1 reverse probe. Other ^1H and ^{31}P NMR spectra were recorded on a Bruker 200 AC instrument. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). The ^{13}C resonances were assigned through a 2D $^1H/^{13}C$ correlation via heteronuclear zero and double quantum coherence (HMQC) using a BIRD sequence with decoupling during acquisition.[19] Quadrature detection along F1 was achieved using the TPPI method.[20] Due to its low solubility (compound **6**) and occurrence of parasite reaction(s) in chlorinated solvents (compound **2**), it was impossible to observe any 1D detection of the ketenyl ^{13}C resonances, which instead were observed through a 2D $^1H/^{13}C$ correlation via heteronuclear zero and double quantum coherence optimized on long-range couplings with low-pass J-filter to suppress one-bond correlations (HMBC); no decoupling during acquisition was performed.[21] The electrospray ionization (ESI) mass spectrum of **6** was recorded on a LCQ (Finnigan MAT) instrument. The Microanalysis Laboratory of

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(7) (a) Compounds formulated as $M_2C{=}C{=}O$ (M = Ag, Cu, Au) and named "ketenides" have been reported (Blues, E. T.; Bryce-Smith, D.; Hirshìch, H.; Simons, M. J. *Chem. Commun.* **1970**, 699. Blues, E. T.; Bryce-Smith, D.; Kettlewell, B.; Roy, M. *J. Chem. Soc., Chem. Commun.* **1973**, 921. Blues, E. T.; Bryce-Smith, D.; Lawston, I. W.; Wall, G. D. *J. Chem. Soc., Chem Commun.* **1974**, 513), but poor crystallinity and low solubility hampered their complete characterization, as well as for Rh μ_2-ketenylidene compounds (Paiaro, G.; Pandolfo, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *20*, 289. Pandolfo, L.; Paiaro, G. *Gazz. Chim. Ital.* **1985**, *115*, 561). (b) In the literature (see ref 4) are even reported μ_3-ketenylidene derivatives, in which the C=C=O fragment interacts with three metal centers of some carbonylic clusters.

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the Inorganic Chemistry Department of the University of Padova provided elemental analyses.

Synthesis of *trans*-[PtCl$_2$(C$_2$H$_4$){η^1-C(PPh$_3$)CO}], 2. (a) To a solution of 0.980 g of K[PtCl$_3$(C$_2$H$_4$)]·H$_2$O (2.53 mmol) in 40 mL of THF was added 0.780 g of **1** (2.58 mmol). The course of the reaction was monitored by IR spectroscopy, observing the rapid disappearance of the free ligand signal and the formation of a sharp ketenyl peak at 2085 cm^{-1}. After 10 min the resulting suspension was quickly concentrated under vacuum and KCl filtered off. Addition of *n*-pentane to the solution produced the precipitation of a yellow solid, which was filtered, washed with ethyl ether, and dried under vacuum. Yield: 1.20 g (79%).

(b) The synthesis of **2** was also performed by using anhydrous [{PtCl$_2$(C$_2$H$_4$)}$_2$]. To a solution of 0.340 g of [{PtCl$_2$(C$_2$H$_4$)}$_2$] (0.58 mmol) in 50 mL of THF was added 0.350 g of **1** (1.16 mmol). The solution was stirred for 10 min and then concentrated under vacuum. Addition, under vigorous stirring, of *n*-pentane caused the precipitation of a yellow solid, which was filtered, washed with ethyl ether, and dried under vacuum. Yield: 0.650 g (94%).

2: mp 140−142 °C (dec). Anal. Found: C 44.18; H 3.15. Calcd for C$_{22}$H$_{19}$Cl$_2$OPPt: C 44.31; H 3.21. IR (Nujol, cm^{-1}): ν_{CO} 2078, (2085 in THF) ν_{PtCl} 303 and 330. ^{1}H NMR (CDCl$_3$): H$_{ortho}$ 7.83 (m), H$_{meta}$ 7.57 (m), H$_{para}$ 7.67 (m), C$_2$H$_4$ 4.64 (s) ($^2J_{HPt}$ 54.1 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$): 26.14 ($^2J_{PPt}$ 96.6 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): C$_{ortho}$ 134.0 ($^2J_{CP}$ 10.7 Hz), C$_{meta}$ 129.4 ($^3J_{CP}$ 13.4 Hz), C$_{para}$ 133.8 ($^4J_{CP}$ 3.2 Hz), C$_{ipso}$ 130.9 ($^1J_{CP}$ 12.9 Hz), C$_2$H$_4$ 80.3 (s) ($^1J_{CPt}$ 133.8 Hz), Pt−C 0.7, CO 190.1.

Synthesis of *trans*-[PtCl$_2${η^1-C(PPh$_3$)CO}$_2$], 6. (a) To a solution of 0.480 g of compound **2** (0.805 mmol) in 40 mL of THF was added 0.245 g of **1** (0.81 mmol). The solution was stirred for 24 h at room temperature (alternatively for 3 h at 50 °C), obtaining the formation of a light yellow solid, which was filtered off, washed with THF and ethyl ether, and dried under vacuum. Yield: 0.528 g (75%).

(b) To a solution of [{PtCl$_2$(C$_2$H$_4$)}$_2$] (0.160 g, 0.27 mmol) in 30 mL of THF was added 0.333 g of **1** (1.1 mmol). After 10 min a light yellow solid began to precipitate, and the suspension was stirred at room temperature for 24 h. The solid was filtered off, washed with THF and ethyl ether, and dried under vacuum. Yield: 0.285 g (59%).

6: mp 230−232 °C (dec). Anal. Found: C 54.53; H 3.38. Calcd for C$_{40}$H$_{30}$Cl$_2$O$_2$P$_2$Pt: C 55.18; H 3.47. IR (Nujol, cm^{-1}): ν_{CO} 2062, ν_{PtCl} 325. ^{1}H NMR (CDCl$_3$): H$_{ortho}$ 7.87 (m), H$_{meta}$ 7.51 (m), H$_{para}$ 7.64 (m). ^{31}P{^{1}H} NMR (CDCl$_3$): 21.98 ($^2J_{PPt}$ 99.2 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): C$_{ortho}$ 134.5 ($^2J_{CP}$ 11.6 Hz), C$_{meta}$ 125.1 ($^3J_{CP}$ 13.8 Hz), C$_{para}$ 133.2 ($^4J_{CP}$ 2.8 Hz), C$_{ipso}$ 130.7 ($^1J_{CP}$ 13.8 Hz), Pt−C 1.4, CO 191.4. ESI MS (saturated CH$_2$Cl$_2$ solution): *m/z* 870 [M]$^+$, 893 [M + Na]$^+$, 1741 [2M]$^+$, 1764 [2M + Na]$^+$.

The reactivity of compounds **2** and **6** was studied by monitoring the course of some reactions through IR and multinuclear NMR spectroscopies and will be discussed further on. Reaction products were not isolated or purified. ^{1}H NMR spectra of corresponding reaction mixtures are available as Supporting Information.

Table 1. Summary of the Crystal Data and Intensity Collection for Compound 6

formula	PtCl$_2$C$_{40}$H$_{30}$P$_2$O$_2$
M	870.62
space group	$P\bar{1}$
a/Å	10.004(2)
b/Å	9.973(2)
c/Å	9.395(2)
α/deg	90.6(1)
β/deg	112.9(1)
γ/deg	83.2(1)
V/Å^3	856.7
Z	2
cryst dimens/mm	0.20 × 0.25 × 0.25
D_C/gcm^{-3}	1.69
μ/cm^{-1}	41.83
T/K	298
radiation	graphite-monochromated Mo Kα (λ = 0.7107 Å)
take-off angle/deg	3
scan speed/deg min^{-1}	2.0 in the 2θ scan mode
2θ range/deg	$3.0 \leq 2\theta \leq 45$
obsd reflns [$F_o^2 \geq 3\sigma(F_o^2)$]	2747
R (on F_o)	0.067
R_w	0.070
GOF	1.0
highest map res./e Å^{-3}	0.80

Computational Details. Calculations have been performed by running the ADF package[22] based on the density functional (DF) theory and developed by Baerends and co-workers.[23] A triple-ζ Slater-type basis set with a single polarization function was used for all atoms. The inner cores of platinum (1s−5p), phosphorus and chlorine (1s−2p), and oxygen and carbon (1s) were treated by the frozen core approximation. Moreover, the binding energy (BE) was computed by employing the local density approximation (Vosko−Wilk−Nusair formula)[24] and including the quasi-relativistic scalar correction.[25] The BE has been then analyzed in terms of atomic orbitals by applying the Ziegler's generalized transition state method:[26]

$$\mathrm{BE} = -[\Delta E_{\mathrm{es}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{int}}] \qquad (1)$$

where ΔE_{es}, ΔE_{Pauli}, and ΔE_{int} represent contributions due to the pure electrostatic interaction, the Pauli repulsion (hereafter $\Delta E_{es} + \Delta E_{Pauli} = \Delta E_{sr}$, steric repulsion), and ΔE_{int}, the orbital interaction, respectively.

X-ray Crystal Structure Determination. X-ray-quality crystals of **6** were obtained by evaporation from a dilute CH$_2$Cl$_2$ solution. Single crystals were mounted on a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator. Standard centering and autoindexing procedures indicated a triclinic lattice. The space group $P\bar{1}$ was assigned and confirmed by well-behaved refinement processes. The orientation matrix and accurate unit cell dimensions were determined from angular settings of 25 high-angle reflections. The data were corrected for Lorentz and polarization effects; an empirical correction was also applied (Ψ scan). Crystallographic data are collected in Table 1. All the atoms, excluding the hydrogens, were located from successive Fourier maps (Pt is centered in 000). The hydrogen atoms were located at calculated positions and refined with fixed geometry with respect to the carrier atoms (C−H 1.08 Å). The non-hydrogen atoms were refined with anisotropic thermal parameters. Blocked-cascade least-squares refinements were used. They converged to the conventional R index reported in Table 1. Scattering factors for the atoms were taken from Cromer and Waber.[27,28] All the computations concerning the crystal structure determination were carried out on a Cyber 76 computer using the SHELX-76 program.[29]

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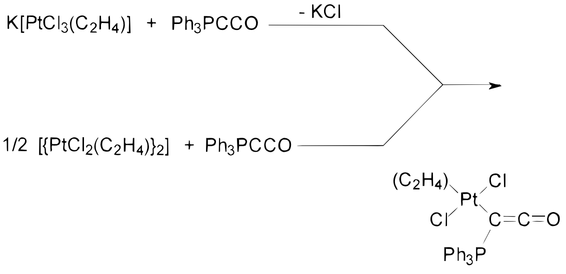
Results

Syntheses and Characterizations. By reacting Zeise's salt or $[\{PtCl_2(C_2H_4)\}_2]$ with 1 equiv of **1** (reaction I) the η^1-ketenyl derivative



(I)

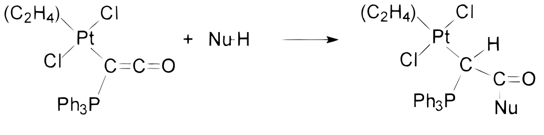
2

$[PtCl_2(C_2H_4)\{\eta^1\text{-}C(PPh_3)CO\}]$, **2**, has been isolated in good yields and characterized by elemental analysis, IR, and ^1H, ^{13}C, and ^{31}P NMR spectroscopies.

In the ^{31}P NMR spectrum of **2** only one singlet, flanked by ^{195}Pt satellites, is present. The chemical shift and the ^{195}Pt coupling constant are both in good agreement with the data previously reported for other η^1-ketenyl ylidic complexes $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)\{\eta^1\text{-}C(PPh_3)CO\}]BF_4$ (**A**)[15a] and $[Pt(\eta^3\text{-}C_3H_5)Cl\{\eta^1\text{-}C(PPh_3)CO\}]$ (**B**).[15b] Particularly, the value of the ^{195}Pt coupling constant (96.6 Hz) is consistent with a $^2J_{PPt}$.[30] The presence of coordinated ethylene is indicated by the singlets at 4.64 and 80.52 ppm in the ^1H and ^{13}C NMR spectra, respectively, both flanked by ^{195}Pt satellites. The $^2J_{HPt}$ and $^1J_{CPt}$ values (54.1 and 133.8 Hz, respectively) lie in the ranges found for *trans*-$[PtCl_2(C_2H_4)\{\eta^1\text{-}CH(PPh_3)COR\}]$ (R = Me, Ph, OMe).[31a] Since for this class of compounds $^2J_{HPt}$ and $^1J_{CPt}$ values are related to the trans influence of the ligand bonded to Pt in trans position to the olefin,[32] it can be inferred that $Ph_3PC{=}C{=}O$, σ bonded to Pt through the ylidic carbon, displays a trans influence quite similar to that of carbonyl-stabilized phosphonium ylides and greater than that of chlorine ($^2J_{HPt}$ 64 Hz and $^1J_{CPt}$ 195 Hz).[31] ^{13}C NMR signals at 0.7 and 190.1 ppm correspond to the η^1-coordinated ylidic and carbonylic carbon atoms, respectively. It was impossible to detect any ^{195}Pt satellites for both signals. Finally, the IR spectrum of **2** shows a sharp signal at 2078 cm^{-1}, typical for the CO stretching of η^1-ketenyl complexes,[4,15] and signals in the ν_{PtCl} region, consistent with a trans geometry.[33] These data converge to indicate for **2** the *trans*-η^1-ketenyl structure sketched in reaction I.

Compound **2** reacts with protic nucleophiles. If water is added to a THF solution of **2**, a complex reaction takes place, leading to the formation of CO_2, as evidenced by the appearance in the IR spectrum of a signal at 2338 cm^{-1}, whose intensity increases as the η^1-ketenyl signal decreases. The reaction of **2** with water has not been further investigated; nevertheless, it has to be pointed out that the synthesis of **2**, performed by using monohydrated Zeise's salt gave a lower yield with respect to that in which anhydrous $[\{PtCl_2(C_2H_4)\}_2]$ was used (see Experimental Section), likely due to water-promoted decomposition of the ketenyl derivative.

The reactivity of **2** with protic nucleophiles has been further tested with dimethylamine, methanol, and ethanol, observing the expected formation of amide and ester derivatives, as evidenced by IR as well as ^1H and ^{31}P NMR spectra of the reaction mixtures. Specifically, CH_2Cl_2 solutions of **2** were treated, separately, with equimolecular amounts of NMe_2H, MeOH, and EtOH, observing, in the corresponding IR spectra, the disappearance of the η^1-ketenyl signal and the formation of signals in the carbonylic region [ν_{CO} 1624, 1699, 1696 cm^{-1}, respectively]. Data obtained from ^1H and ^{31}P NMR spectra of the reaction mixtures in CD_2Cl_2 (Table 2) agree with IR data and are consistent with the formation of the carbonylic derivatives, **3a**−**c**, according to reaction II.

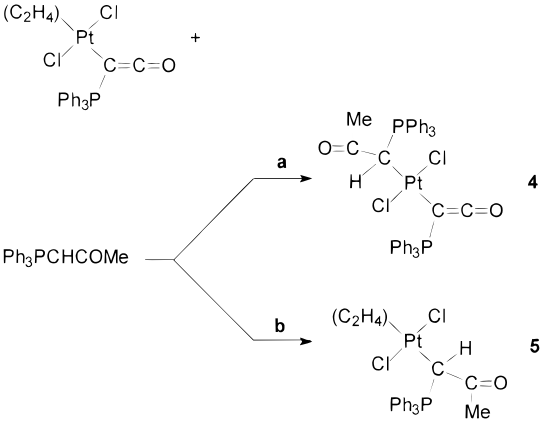


(II)

Nu = NMe_2 (**3a**), MeO (**3b**), EtO (**3c**)

Before going on, it has to be pointed out that the reaction of **2** with NMe_2H, carried out at −10 °C, produced the immediate formation of the amide derivative in more than 60% yield, together with some other products. In contrast to that, reactions of **2** with alcohols required, even at room temperature, longer times and some starting materials remained unchanged.

Compound **2** has been also reacted with carbonyl-stabilized ylides, observing the occurrence of two simultaneous processes. The ^1H NMR spectrum of the reaction mixture of **2** with an equimolecular amount of $Ph_3PCHCOMe$ indicated a partial release of ethylene, displaced by the stabilized ylide, according to route **a** in reaction III, with formation of the *trans*-bisylidic derivative **4**.



(III)

At the same time, ^1H and ^{31}P NMR spectra evidenced also the occurrence of a parallel reaction (route **b**),

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(30) Pregosin, P. S.; Kunz, R. W. In *NMR. Basic Principles and Progress*; Vol. 16, Springer-Verlag: Berlin, 1979.

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(32) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1976**, *16*, 191. (c) Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1977**, *21*, 25. (d) Pregosin, P. S.; Sze, S. N.; Salvadori, P.; Lazzaroni, R. *Helv. Chim. Acta* **1977**, *60*, 2514.

(33) Fracarollo, D.; Bertani, R.; Mozzon, M.; Belluco, U.; Michelin, R. A. *Inorg. Chim. Acta* **1992**, *201*, 15.

Table 2. ^1H and $^{31}P\{^1H\}$ NMR Data of $[PtCl_2(C_2H_4)\{\eta^1\text{-}CH(PPh_3)CONu\}]$ (Nu = NMe_2 (3a), OMe (3b), OEt (3c))[a]

	^1H				$^{31}P\{^1H\}$
	C_2H_4	CH_3	CH_2	CH	P
3a	4.61(s) $^2J_{HPt}$ 48.5	3.50(s)		5.51(d) $^2J_{HP}$ 8.6 $^2J_{HPt}$ 113.5	28.48(s) $^2J_{PPt}$ 79.3
3b	4.60(s) $^2J_{HPt}$ 49.9	3.60(s)		5.45(d) $^2J_{HP}$ 7.2 $^2J_{HPt}$ 113.5	27.24(s) $^2J_{PPt}$ 79.2
3c	4.59(s) $^2J_{HPt}$ 50.1	1.07(t) $^3J_{HH}$ 7.1	4.05(qd) $^3J_{HH}$ 7.1 $^5J_{HP}$ 2.9	5.42(d) $^2J_{HP}$ 7.1 $^2J_{HPt}$ 112.3	27.20(s) $^2J_{PPt}$ 75.9

[a] 28 °C, CD_2Cl_2, chemical shifts in ppm, J in Hz. Signals due to phenyl hydrogens are not reported.

Table 3. ^1H and $^{31}P\{^1H\}$ NMR Data of $[PtCl_2\{\eta^1\text{-}C(PPh_3)CO\}\{\eta^1\text{-}CH(PPh_3)COMe\}]$, 4, and $[PtCl_2(C_2H_4)\{\eta^1\text{-}CH(PPh_3)COMe\}]$, 5[a]

	^1H			$^{31}P\{^1H\}$	
	C_2H_4	CH_3	CH	PC=C	PCH
4		2.61(d) $^4J_{HP}$ 2.2	4.77(d) $^2J_{HP}$ 2.7 $^2J_{HPt}$ 14.1	25.92(s) $^2J_{PPt}$ 83.9	25.40(s) $^2J_{PPt}$ 139.8
5	4.70(s) $^2J_{HPt}$ 50.6	2.49(d) $^4J_{HP}$ 2.5	6.11(d) $^2J_{HP}$ 4.3 $^2J_{HPt}$ 113.9		27.83(s) $^2J_{PPt}$ 65.1

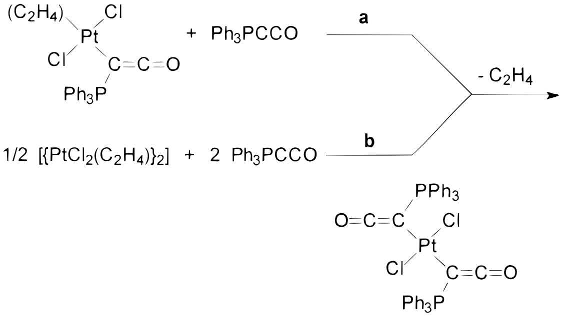
[a] 28 °C, $CDCl_3$, chemical shifts in ppm, J in Hz. Signals due to phenyl hydrogens are not reported.

where the coordinated heterocumulenic ylide **1** is displaced by $Ph_3PCHCOMe$, thus yielding the known Zeise's salt derivative, **5**.[31a] ^1H and ^{31}P NMR data of compounds **4** and **5** are reported in Table 3.

During the reaction of **2** with $Ph_3PCHCOMe$, decomposition reactions took place, evidencing, in the time, the formation of the Zeise's salt anion $[PtCl_3(C_2H_4)]^-$, with a behavior similar to that previously observed in the case of *trans*-$[PtCl_2(C_2H_4)\{(\eta^1\text{-}CH(PPh_3)COR\}]$.[31a]

Attempts to react **2** with a less nucleophilic ylide, such as $Ph_3PCHCOPh$, had the only result of drastically decreasing the reaction rates for both routes **a** and **b**, thus making more evident the above-mentioned decomposition reactions.

Particularly interesting was the result obtained by reacting compound **2** with one further equivalent of $Ph_3PC{=}C{=}O$. In THF solution, ethylene was completely displaced by **1**, thus obtaining complex **6** (reaction IV, route **a**). This compound, afterward obtained also by direct reaction of $[\{PtCl_2(C_2H_4)\}_2]$ with **1** (reaction IV, route **b**), is very scarcely soluble in most organic solvents, and it has been isolated, with good yields, by filtration.



(IV)

6

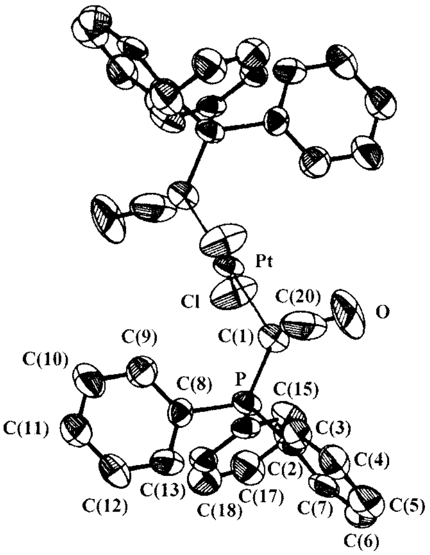


Figure 1. Molecular structure of **6** with atom labeling.

Compound **6** has been characterized by elemental analysis, IR, and ^1H, ^{31}P, and ^{13}C NMR spectroscopies and ESI mass spectrometry. Its low solubility prevented a molecular weight determination and did not allow any 1D detection of the ketenyl ^{13}C resonances, which instead were observed through a 2D $^1H-^{13}C$ correlation via heteronuclear zero and double quantum coherence (see Experimental Section). Once again, it was impossible to detect any ^{195}Pt satellites. The ESI mass spectrum showed the occurrence of signals at 870 and 893 m/z, corresponding to the molecular ($[M]^+$) and the $[M + Na]^+$ ions, respectively. Signals at 1741 ($[2M]^+$) and 1763 ($[2M + Na]^+$) are likely due to association phenomena, a feature often observed under ESI conditions.

The stoichiometry of the synthesis reaction with evolution of ethylene, ESI MS data, a single IR signal at 2062 cm^{-1} (ν_{CO}), a singlet in the ^{31}P NMR spectrum at 21.98 ppm ($^2J_{PPt} = 99.2$ Hz), and the signals at 1.4 and 191.4 ppm, in the ^{13}C NMR spectrum, corresponding to η^1-coordinated ylidic and carbonylic carbon atoms, respectively, strongly suggest for compound **6** the *trans*-bis-η^1-ketenyl structure sketched in reaction IV.

This structural hypothesis has been confirmed by an X-ray single-crystal structure determination. The molecular structure of compound **6** is shown in Figure 1, and selected molecular parameters are reported in Table 4.

Pt is located on an inversion center; thus the molecule is structurally centrosymmetrical; the coordination about Pt is almost exactly square-planar (C(1)−Pt−Cl = 91.2°, C(1)−Pt−Cl′ = 88.8°). The C=C=O grouping bonded to Pt is also involved in a potential ylide moiety, analogously to what is observed, for the first time, in the complex $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)\{\eta^1\text{-}C(PPh_3)CO\}]BF_4$ (**A**),[15a] whose most significant geometrical parameters are also reported for comparison (Table 4). In **6** the P−C(1) bond length (1.76(1) Å) is in the norm for an ylidic nature and exhibits a partial double-bond char-

Table 4. Selected Geometrical Parameters of Compounds 6 and A[15a] (in square brackets)

Bond Lengths (Å)		
Pt−Cl	2.300(6)	
Pt−C(1)	2.171(4)	[2.120(7)]
P−C(1)	1.76(1)	[1.75(1)]
P−C(2)	1.80(1)	[1.798(7)]
P−C(8)	1.79(1)	[1.786(9)]
P−C(14)	1.79(2)	[1.786(7)]
C(1)−C(20)	1.26(2)	[1.280(8)]
C(20)−O	1.16(2)	[1.160(8)]

Bond Angles (deg)		
C(1)−Pt−Cl	91.2(2)	
Pt−C(1)−P	121.7(2)	[124.0(7)]
Pt−C(1)−C(20)	123.3(2)	[118(1)]
C(1)−C(20)−O	179.6(9)	[175(1)]
P−C(1)−C(20)	114.3(2)	[118(1)]
C(1)−P−C(2)	106.5(2)	
C(1)−P−C(8)	119.3(5)	
C(1)−P−C(14)	108.0(4)	
C(1)−Pt−Cl′	88.8(2)	

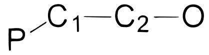
Torsion Angles (deg)			
Cl−Pt−C(1)−P	105	Cl−Pt−C(1)−C(20)	−66
Cl−C(1)−P−C(20)	−162	Pt−C(1)−P−C(8)	−42
Pt−C(1)−P−C(14)	80		

acter;[34] C(1)−C(20) (1.26(2) Å) and C(20)−O (1.16(2) Å) seem still to indicate both a partial triple-bond character. These values are in the range of those reported for several η^1-ketenyl derivatives[8h,11c,15a] and can be explained in terms of mesomeric effects,[4,15a] excluding any multiple character of the Pt−C(1) bond. Accordingly, the Pt−C(1) bond length (2.171(1) Å) is even longer than that observed in the case of **A** (2.120(7) Å, see Table 4). Furthermore, it is worth noting that for an angle P−C(1)−C(20) of 114.3° we would expect, as it has been previously described,[35] a longer C(1)−C(20) distance (in the range of 1.30−1.32 Å).[4,8h,35] The value of 1.26 Å found here seems to reveal, as in the case of **A**, a through-bond inductive effect of the metal center on the charge distribution in the ketenyl grouping.

The two ketenyl moieties of the molecule and the metal lie in a plane forming a dihedral angle of ~65° with the coordination plane of Pt. As a result, the C═C═O groups are almost oriented as far as possible from the chlorine atoms: they are also in eclipsed conformation with respect to one phenyl ring of the PPh_3 moiety, thus allowing the largest contact distances between Pt and the phenyl groups.

Electronic Structure and Reactivity of 6. To get further insight into the mechanism governing the attainment of the actual molecular geometry of compound **6**, the first stable, crystallographically established bis-η^1-ketenyl derivative, a series of numerical experiments, within the DF theory, have been carried out on it, as well as on the model complex *trans*-$[PtCl_2\{\eta^1\text{-}C(PH_3)CO\}_2]$, **6a**. It is in fact widely accepted that first-principle DF calculations can be used as a practical tool to get information about the molecular and electronic structure of complex molecules.[36] Incidentally, our calculations can take advantage of a complete set of structural data.

Table 5. Optimized Calculated Geometrical Parameters for $Ph_3PC{=}C{=}O$ (1) and $H_3PC{=}C{=}O$ (1a)[a]



	H_3PCCO (**1a**)	Ph_3PCCO (**1**)$_{calc}$	Ph_3PCCO (**1**)$_{exp}$
$P{-}C_1$	1.648	1.657	[1.648]
$C_1{-}C_2$	1.281	1.273	[1.210]
$C_2{-}O$	1.178	1.183	[1.185]
$P{-}C_1{-}C_2$	134.6	142.4	[145.5]

[a] Experimental values for **1**[39] in square brakets. Bond lengths and bond angles in Å and deg, respectively.

When dealing with molecular systems carrying bulky phenyl groups, they are usually theoretically modeled with H atoms in order to save computational time. Nevertheless, some of us recently demonstrated that this practice is not always successful.[37] For this reason, before tackling the study of **6**, we decided to carry out a series of preliminary total energy calculations on the actual ligand ($Ph_3PC{=}C{=}O$) as well as on the model compound $H_3PC{=}C{=}O$. The geometry optimization has been extended to the whole $H_3PC{=}C{=}O$, while it has been limited to the ketenyl moiety (C═C═O) in $Ph_3PC{=}C{=}O$.[38] Optimized bond lengths and bond angles are reported in Table 5.

At variance with theoretical results reported by Albright et al.,[40] but in agreement with X-ray data,[39] also included for comparison in Table 5, our calculations point out that the ylide inorganic skeleton (P−C−C−O) is not linear, the P−C−C bond angle being 142° and 135° in $Ph_3PC{=}C{=}O$ and $H_3PC{=}C{=}O$, respectively. As far as bond lengths are concerned, the agreement with literature crystallographic data[39] is also satisfactory.

In a hypothetical ylide with a linear P−C−C−O skeleton, the π atomic orbitals (AOs) localized on C and O atoms (six orbitals for a total of eight electrons) would originate three double degenerate π molecular orbitals (MOs): π_1, π_2, and π_3. π_1 is totally bonding (no node along the skeleton) and mainly localized on the O atom, π_2 is $C_1{-}C_2$ ($C_2{-}O$) bonding (antibonding) (one node along the skeleton) and highly concentrated on C_1, while π_3 is $C_1{-}C_2$ and $C_2{-}O$ antibonding (two nodes along the skeleton) with a strong participation of C_2 AOs. Among these three orbitals, π_1 and π_2 are occupied, while π_3 is empty.

Despite the nonlinearity of the inorganic skeleton, DF calculations point out that the two outermost occupied MOs of $Ph_3PC{=}C{=}O$ and $H_3PC{=}C{=}O$ are substantially degenerate, mainly localized on C_1 and accounting for a π interaction, $C_1{-}C_2$ ($C_2{-}O$) bonding (antibonding), parallel ($\pi_{2\parallel}$), and perpendicular ($\pi_{2\perp}$) to the P−C−C−O plane. Incidentally, the $\pi_{2\parallel}$ MO is the one responsible for the $Ph_3PC{=}C{=}O$ σ donor properties. Atomic charges of the inorganic skeleton, computed through the Hirshfeld scheme,[42] are reported in Figure 2 for the actual

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[34] Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993, and references therein.

[35] (a) Gil, J. M.; Howard, J. A. K.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1168. (b) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7360.

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[37] Bertoncello, R.; Bettinelli, M.; Casarin, M.; Maccato, C.; Pandolfo, L.; Vittadini, A. *Inorg. Chem.* **1997**, *36*, 4707.

[38] The bond angles and bond lengths involving phenyl moieties have been kept fixed to the experimental values[39] during the geometry optimization.

[39] Daly. J. J.; Wheatley, P. J. *J. Chem Soc. (A)* **1966**, 1703.

[40] Albright and co-workers[41] computed, by means of ab initio calculations, a P−C−C bond angle of 180° for $H_3PC{=}C{=}O$.

[41] Albright, T. A.; Hofmann, P.; Rossi, A. R. *Z. Naturforsch.* **1980**, *35b*, 343.

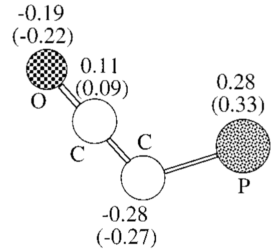

Figure 2. Hirshfeld atomic charges localized on the P−C−C−O skeleton of H_3PCCO and (in parentheses) Ph_3PCCO.

and model ligand. Minor differences are found in the two cases, confirming that the electronic properties of $Ph_3PC{=}C{=}O$ are reasonably mimicked by the model $H_3PC{=}C{=}O$.

Before entering into details of theoretical results pertaining to **6**, we wish to provide a qualitative description of the bonding scheme of the model complex **6a** mainly based on symmetry arguments and overlap considerations.

The Pt 5d orbitals can be divided into two sets according to the nature (σ or π) of their interactions with ligand-based MOs. In the adopted framework d_{xz}, d_{yz}, and d_{xy} AOs constitute the $5d_\pi$ set, while the d_{z^2} and $d_{x^2-y^2}$ orbitals belong to the σ one. The former is completely occupied, while the latter includes an empty AO, the $5d_{x^2-y^2}$ orbital.

In Figure 3 we have reported a sketch of the bonding combinations between the occupied $5d_\pi$ Pt orbitals and the symmetric combinations of Cl $3p_\pi$ and C_1 $\pi_{2\perp}$ levels for $\theta = 0°$ and 90° (θ is the angle between $\pi_{2\perp}$ and the Pt(II) coordination plane, i.e., $\theta = 0°$ corresponds to the C=C=O moiety perpendicular to the Pt(II) coordination plane, while $\theta = 90°$ is representative of the ketene fragments coplanar to the same plane).[43] Since both the metal-based and the ligand-based orbitals reported in Figure 3 are fulfilled, both bonding and antibonding combinations are completely occupied and the overall interaction is, as a whole, destabilizing.

Interestingly, the Pt 5d orbitals differently interact with the ligand-based MOs for different θ values. For $\theta = 0°$, the $5d_{xy}$ AO participates in a multicentered interaction, delocalized over the whole coordination plane; the $5d_{yz}$ AO can interact only with the symmetric combination of the Cl $3p_z$ AOs, while the $5d_{xz}$ behaves as a pure nonbonding orbital. For $\theta = 90°$, the interaction of the Pt $5d_{yz}$ with the Cl $3p_z$ AOs is unchanged, while the multicentered bonding in the coordination plane cannot take place any more. In detail, the $5d_{xy}$ and $5d_{xz}$ AOs limit their interaction to the gerade Cl $3p_x$ and C_1 $\pi_{2\perp}$ combination, respectively.

On qualitative grounds, the overlap between the Pt 5d AOs and the ligand-based MOs is substantially the same for $\theta = 0°$ and 90°. This does not hold when we consider the interligand repulsion. Actually, the multicentered, delocalized interaction taking place when $\theta = 0°$ has an overall destabilizing effect because, as already mentioned, it involves occupied orbitals. On this basis, it can be foreseen that, from a purely electronic point of view, the $\theta = 0°$ configuration should be less stable than the $\theta = 90°$ one.

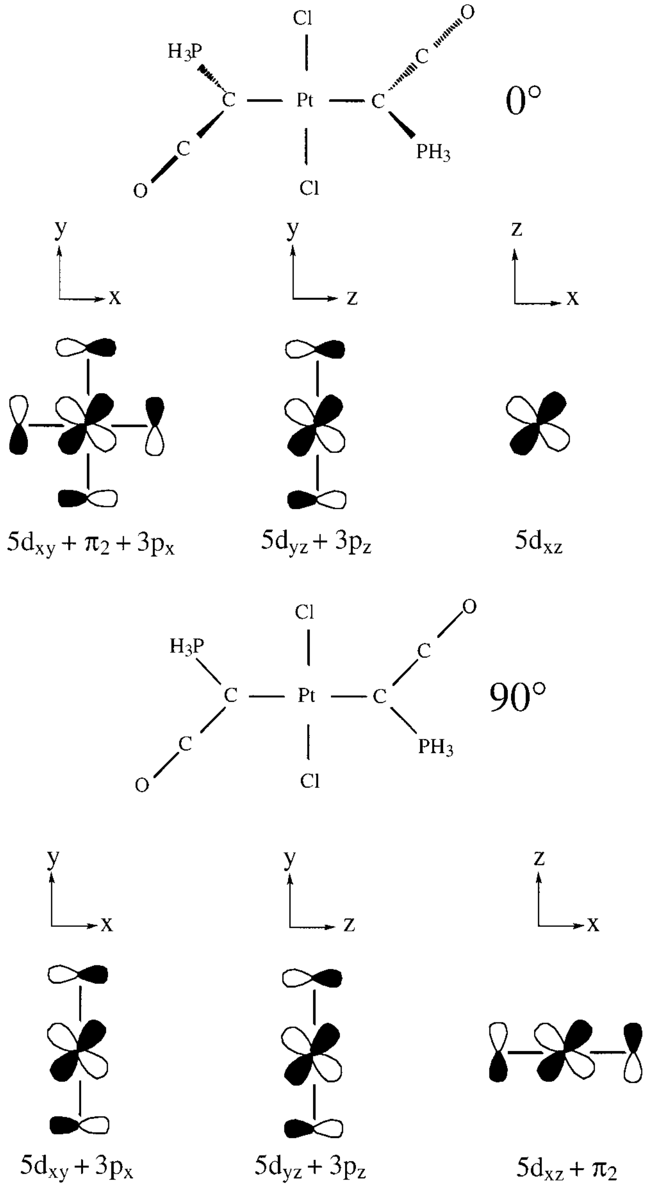

Figure 3. Qualitative representation of the bonding interactions between Pt 5d AOs and C_1 $\pi_{2\perp}$/Cl $3p_\pi$ orbitals for $\theta = 0°$ and 90° in **6a**.

In Figure 4 the values of BE, ΔE_{sr}, and ΔE_{int} (see eq 1 in the Experimental Section), pertaining to the model compound **6a**, as a function of θ ($0° \leq \theta \leq 90°$) are reported.[44]

According to the qualitative bonding scheme we have proposed, ΔE_{int} is a decreasing function of θ. In contrast to that, ΔE_{sr} shows the opposite behavior, despite the presence of the PH_3 moieties, which should minimize the ligand steric hindrance. The energy range spanned by ΔE_{sr} is close to that of ΔE_{int}, and the pattern of the BE curve has a minimum for $\theta = 70°$ and a maximum for $\theta = 30°$ (corresponding to an angle of 20° and 60°, respectively, between the Pt(II) coordination plane and the plane determined by the O−C−C−Pt−C−C−O skeleton). Furthermore, according to the qualitative bonding scheme, $BE(\theta = 0°) = BE(\theta = 90°)$.

These results stress the leading role played by steric effects in determining the molecular conforma-

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[42] (a) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 1703. (b) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

[43] The σ bonding between the Pt $5d_{x^2-y^2}$ and suitable linear combinations of Cl $3p_\sigma$ and π_1 levels is not displayed in the figure because it is negligibly affected by θ.

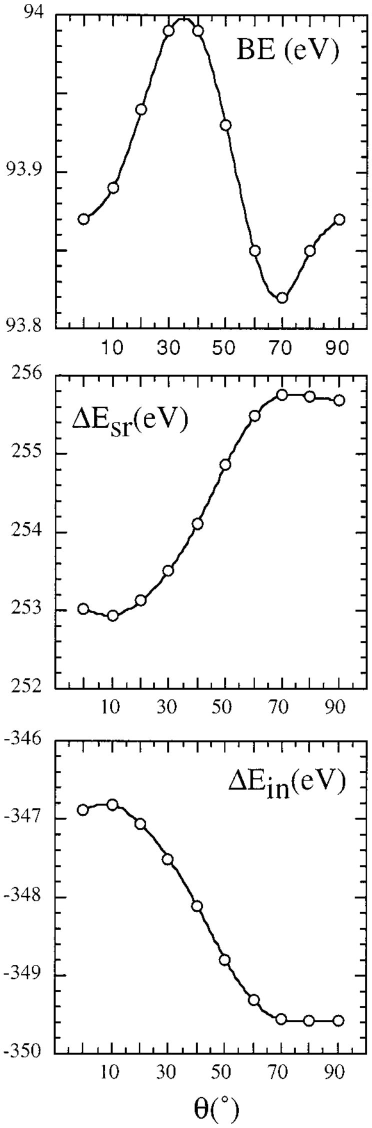


Figure 4. BE, ΔE_{sr}, and ΔE_{int} vs θ for **6a**.

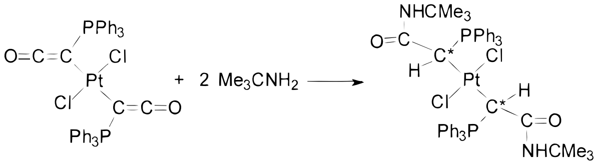
tion, and it sounds reasonable that their influence is much more important in determining the arrangement of **6**, where the bulkier phenyl groups are present.

Theoretical calculations for **6** have been run by idealizing its structure and assuming an angle of 90° rather than the experimental one of 65° between the Pt(II) coordination plane and the plane determined by the O−C−C−Pt−C−C−O skeleton. In this way the symmetry properties of **6** are described by the C_{2h} symmetry point group. In Figure 5 the gross partial density of states (hereafter GPDOS) of the Pt 5d AOs, together with those of C_1 and Cl atoms are reported. According to the well-established bonding scheme of Pt(II) square planar complexes,[45] the Pt 5d AO mainly contributing to the metal−ligand interaction is the $5d_{x^2-y^2}$ (see Figures 5 and 6), the only one having an empty antibonding component.

Among the remaining four 5d AOs, two of them (the d_{xz} and the d_{z^2}) have an atom-like character (see Figure 5), while the $5d_{xy}$ and the $5d_{yz}$ AOs strongly interact with symmetric combinations of Cl 3p and C_1 $\pi_{2\perp}$ orbitals. In Figure 7 (8) the $49a_g$ and $60a_g$ ($52a_g$ and $61a_g$) MOs are reported. The former pair accounts for the bonding and antibonding components of the multicentered, delocalized interaction above-described and involving the $5d_{xy}$ Pt AO, while the latter pair represents the bonding and antibonding partners of the interaction between the Pt $5d_{yz}$ and Cl $3p_z$ orbitals.

Hirshfeld atomic charges of **6** are reported in Figure 9. Their values are consistent with a bonding scheme dominated by a ligand-to-metal σ donation without any metal-to-ligand π back-donation and agree with the rather large Pt−C(1) bond length (see Table 4). Moreover, they 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. Finally, the calculated charge distribution on the C=C=O moieties is quite normal for a ketene grouping.[2b,c]

The reactivity of **6** with protic nucleophiles has been examined. In particular, we have treated the bis-η^1-ketenyl complex, suspended in CH_2Cl_2, with *t*-$BuNH_2$ (molar ratio 1:2), observing, through IR and ^1H and ^{31}P NMR spectroscopies, the formation of diastereomeric diamide species (reaction V).



(V)

In about 30 min the suspension changed to a clear yellow solution, and its IR spectrum showed the complete disappearance of the η^1-ketenyl signal and the formation of a broad amide CO signal at 1624 cm^{-1}. The solution was taken to dryness under vacuum, and the ^1H NMR spectrum in $CDCl_3$ of the obtained sticky solid showed (Figure 10) two doublets with ^{195}Pt satellites, at 4.83 ppm ($^2J_{HP}$ and $^2J_{HPt}$ are 9.3 and 133 Hz, respectively) and 4.75 ppm ($^2J_{HP}$ 9.4 Hz, $^2J_{HPt}$ masked), due to the CH of diastereomeric diamide species. These signals are in ca. 2:1 ratio, and the same integration ratio is presented by two singlets at 1.21 and 1.19 ppm ($C(CH_3)_3$) and two broad signals at 6.56 and 6.65 ppm, attributable to amide NH. The corresponding $^{31}P\{^1H\}$ NMR spectrum showed two singlets, once again in about 2:1 ratio, at 27.97 ppm ($^2J_{HPt}$ 67.5 Hz) and 28.49 ppm ($^2J_{HPt}$ 72.7 Hz), in a range formerly observed for *trans*-$[PtCl_2\{\eta^1\text{-}CH(PR_3)C(O)R'\}_2]$.[31a]

Analogously to compound **2**, we attempted to react **6** with alcohols and with water, but rather surprisingly, no reaction was observed even when THF suspensions of **6**, containing a 5-fold excess of water or MeOH, were refluxed for a week.

Discussion

As previously pointed out, η^1-ketenyl derivatives can be considered a particular kind of ketenes, bearing two different substituents, an organic fragment and a metal center. In this regard, it is worthwhile to note that

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(44) The geometry of **6a** for $\theta = 0°$ has been optimized. Calculations for $\theta > 0°$ have been carried out without any optimization by simply rotating the $H_3PC{=}C{=}O$ groups around the *x* axis.

(45) (a) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Hot-Saunders International Edition, Japan, 1985. (b) Cotton, F. A.; Wilkinson, G. *Advances in Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

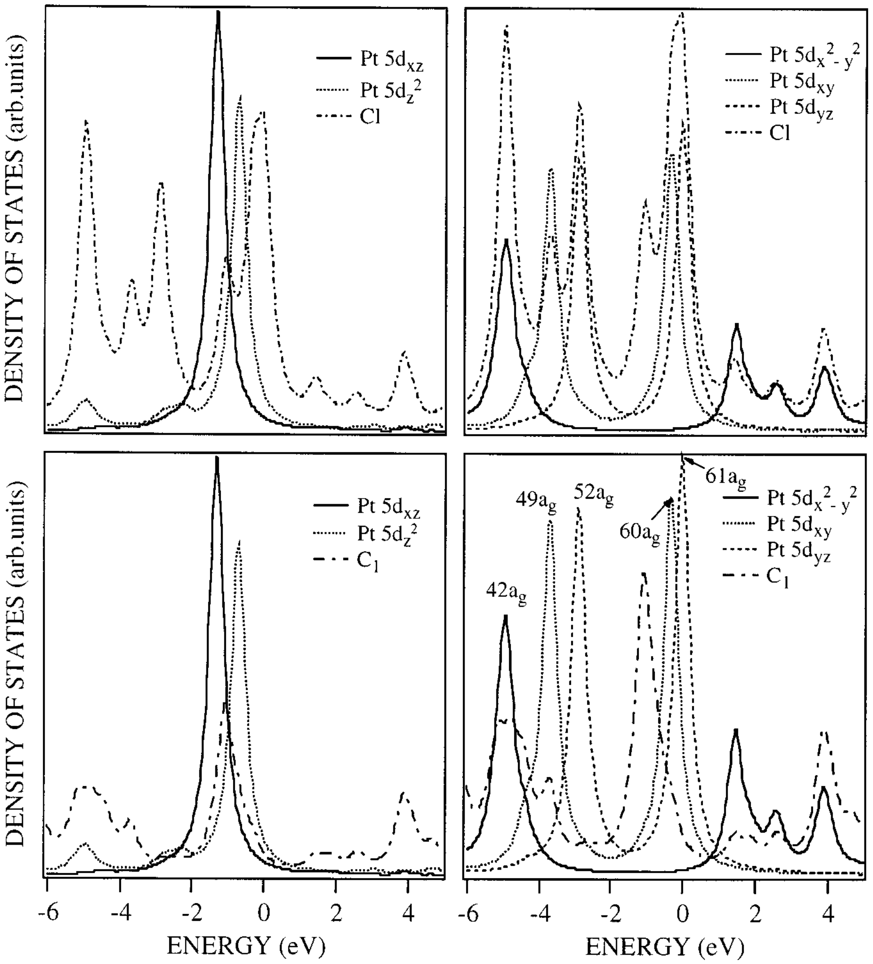
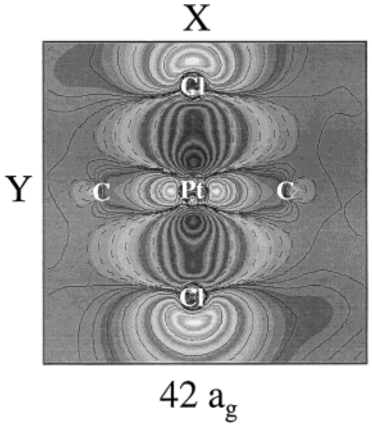


Figure 5. Partial density of states (PDOS) of Pt 5d, Cl, and C_1 in **6**. The zero corresponds to the HOMO energy.



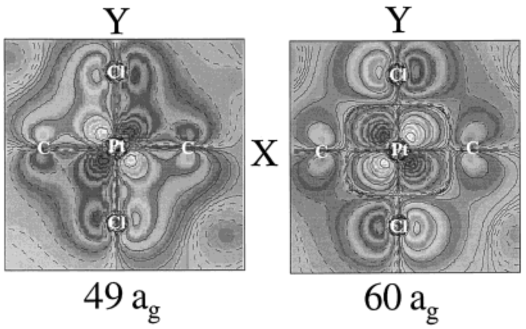


Figure 6. Contour plots of the $42a_g$ MO of **6**. Contour values are ±0.40, ±0.20, ±0, 10, ..., $Å^{1/2}/e^{3/2}$, with negative values in dashed lines.

Figure 7. Contour plots of the $49a_g$ and $60a_g$ MOs of **6**. Contour parameters are the same of Figure 6.

Bestmann and co-workers[12b,14] observed that, despite the presence of the ketene-like structure in the $C{=}C{=}O$ fragment, the π system and the reactivity of $Ph_3PC{=}C{=}O$ differ from those of ketenes. Instead, the oxocumulenic ylide is transformed into a highly reactive “true” ketene by attack of an electrophile, as H^+ or Me^+, to the nucleophilic ylidic C_1 atom. Exactly the same holds for η^1-ketenyl derivatives obtained by reacting $Ph_3PC{=}C{=}O$ with suitable metal systems. Accordingly, X-ray data available for η^1-ketenyl compounds derived from Ph_3PCCO (**A**[15a] and **6**) indicate that the $Pt-C_1$ distances (2.120 and 2.171 Å in **A** and **6**, respectively) are typical for single $Pt-C$ bonds with no multiple character, as already stressed by theoretical results pertaining to **6**. It is also of relevance to point out that experimental (**A**[15a] and **6**) and calculated (**6a**) $C{=}C$ and $C{=}O$ bond lengths as well as the $C{=}C{=}O$ electron charge distribution (**6**) are consistent with a ketene character.[2b,c] Incidentally, such a behavior seems to be insensitive to the formal charge localized on the electrophilic “metal” center (in **A** it is an ionic species, whereas it is neutral in **6**).

As a whole **6** is not only the first stable bis-η^1-ketenyl but also the first stable 1,3-bisketene structurally established. As far as this last point is concerned, it is noteworthy that **6** is one of the few 1,3-bisketenes quoted in the literature. As a matter of fact, after the synthesis of the first bisketene (the 1,1-bisketene carbon

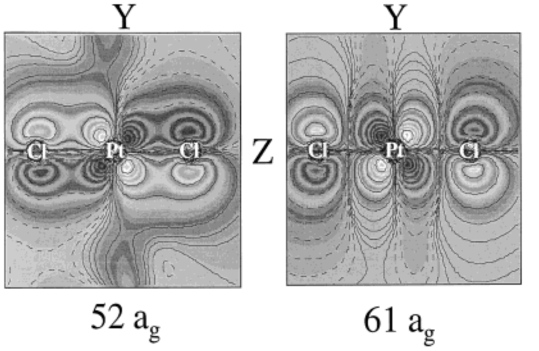


Figure 8. Contour plots of the 52a$_g$ and 61a$_g$ MOs of **6**. Contour parameters are the same as Figure 6.

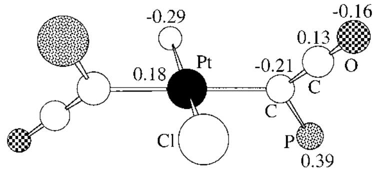


Figure 9. Hirshfeld atomic charges of **6**.

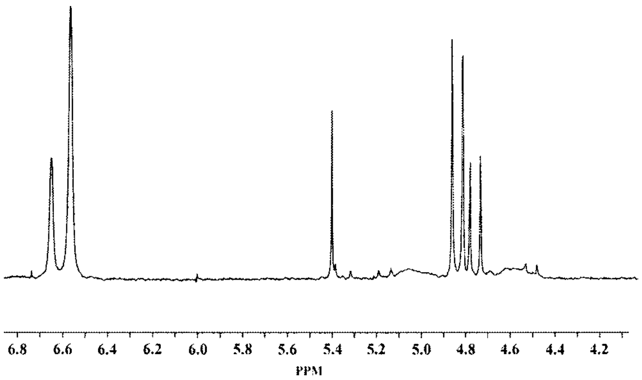
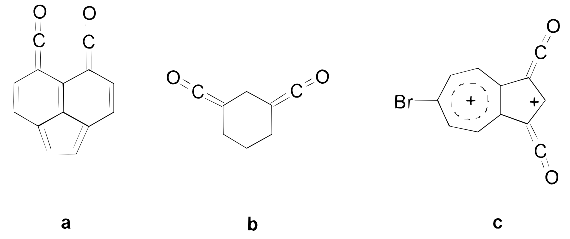


Figure 10. ^{1}H NMR spectrum of the diastereomeric diamides mixture resulting from the reaction of **6** with *t*-BuNH$_2$. Signals due to Me and Ph are not reported.

suboxide[46]), a large number of 1,2- and 1,4-bisketenes have been prepared[47] (mainly due to the stabilizing effect afforded by silyl substituents on these compounds),[3,48] while reports on 1,3-bisketenes are scanty. If we exclude the rather unstable 1,5-pentatetraendione, C_5O_2,[49] compounds **a** and **b** (Chart 2) postulated as reactive intermediates but never characterized,[50] and the dication **c**, whose existence has been claimed on the basis of the ^{1}H NMR spectrum of a reaction mixture,[51] only $Me_2Si(CH{=}C{=}O)_2$[52] has been recently synthesized and spectroscopically characterized.[53]

Steric factors are known to be of paramount importance in determining the stability of ketenes and bisketenes,[2c] and they seem to be particularly important even in the case of compound **6**, whose ketene moieties have sterically demanding substituents. Theoretical outcomes and X-ray data are in tune with this assumption and indicate that the coordination geometry of the two Ph_3PCCO moieties allows the largest possible contact distances between the C=C=O groups, as well as between Pt and the phenyl groups of PPh_3, and maintains the ketenyl groups as far as possible from the chlorine atoms.[54] Despite the lack of the molecular structure of $Me_2Si(CH{=}C{=}O)_2$, it is noteworthy that even for this compound a slightly distorted anti conformation has been calculated to be more stable than the syn one.[52] The different stabilities of **6** (stable even at relatively high temperature) and $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)\text{-}CO\}_2]BF_4$[15b] (it exists in solution only at low temperature) further support the above considerations.

Chart 2



As far as the reactivity of compounds **2** and **6** is concerned, we observed that the mono-η^1-ketenyl **2** reacts with protic nucleophiles (alcohols and amines) analogously to other known η^1-ketenyls,[4,15] yielding the expected amide or ester derivatives. At variance to that, compound **6** reacts, relatively slowly, only with the strong nucleophile *t*-BuNH$_2$, lacking the reactions with alcohols and water. Certainly, the insolubility of compound **6** contributes to its inertness, but it is very likely that even other factors are not to be disregarded.

Addition of water and amines is a prototypical reaction of ketenes, and these reactions have been deeply studied. Particularly neutral hydration[2c,55] and ammination[56] have been proved to occur with quite complex mechanisms, providing an initial nucleophilic attack to the carbonylic carbon atom. In neutral hydration it has been found that there is a significant effect of the structure on reactivity, crowded ketenes being quite unreactive, as indicated by the relative values of hydration rate constants (k_{H2O}) for $CH_2C{=}C{=}O$, $t\text{-}BuCH{=}C{=}O$, and $(t\text{-}Bu)_2C{=}C{=}O$, which are 1, 0.4, and 4×10^{-6}, respectively.[57]

Further, it is noteworthy that $Me_2Si(CH{=}C{=}O)_2$ is characterized by an unexpected high reactivity toward water, giving the relatively unstable acidic derivative $Me_2Si(CH_2COOH)_2$,[52] while the slightly more encum-

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(52) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1996**, *118*, 2768.

(53) Recently we succeeded in obtaining a *cis*-bis-η^1-ketenyl derivative, $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)CO\}_2]BF_4$ (ref 15b), which, although stable only at low temperature, is another example of a 1,3-bisketene.

(54) The trans geometry of **6** contributes to stabilize it because it is known that the interaction between two ketenyl groups in bisketenes is, as indicated by ab initio calculations, destabilizing (ref 3). In the 1,2-bisketene $(HC{=}C{=}O)_2$ the transoid form is 1.6 kcal/mol more stable than the cisoid form.

(55) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273.

(56) (a) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1998**, *120*, 3034. (b) Allen, A. D.; Tidwell, T. T. *J. Org. Chem.* **1999**, *64*, 266.

(57) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995; p 581.

bered 1,2-bisketene $(Me_3SiC{=}C{=}O)_2$ does not react with moist $CHCl_3$ without photolysis or acid catalysis.[58]

Even reactions of amines with ketenes, to give corresponding amides, are sensitive to steric factors, but ammination rates are largely greater than hydration rates (10^3 to 10^{13} times).[56b]

Without entering in the wide, and largely studied, field of addition reactions to ketenes,[2c] it is very likely that steric factors are important in the lack of reactivity of **6** toward water and alcohols, and only strong nucleophiles, as primary aliphatic amines, can add, in a reasonable time, to this particularly encumbered 1,3-bisketene.

Conclusions

In this paper we have reported the syntheses and the study of a mono-η^1-ketenyl derivative (compound **2**) containing an ethylene molecule coordinated to Pt and of the first stable and crystallographically established bis-η^1-ketenyl compound (compound **6**), both simply obtained from $Ph_3PC{=}C{=}O$. The electronic structure of **6** is typical of 1,3-bisketenes, and, from this point of view, it is the second isolated 1,3-bisketene and the first structurally established. The characteristics of these organometallic ketenes (and 1,3-bisketenes) are not easily predictable, but they appear to be very stable and, in some cases, poorly reactive.

As a whole, the present study is encouraging to further investigate the interaction of $Ph_3PC{=}C{=}O$ with other metal substrates for at least two reasons: (i) to synthesize more complex ketenes and bis- and trisketenes as well, whose reactivity can be modulated by changing the characteristics of the "metal" fragments, and (ii) to study the interaction of the $C{=}C{=}O$ moieties bonded to metals, from the small molecules' metal activation (or deactivation) point of view.

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Supporting Information Available: A listing of bond lengths and angles, the final values of all refined atomic coordinates, fractional atomic coordinates of H atoms, and anisotropic thermal parameters (U_{ij}) of **6** and ^1H NMR spectra of the reactions of **2** with NMe_2H, MeOH, EtOH, and $Ph_3PCHCOMe$, yielding **3a**−**c**, **4**, and **5**, are available free of charge via the Internet at http://pubs.acs.org.

OM990826D

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[58] Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847.