# A quasi-relativistic density functional study of structural and electronic properties of the bis-ketene $cis$-[Pt{$\eta^3$-C$_3$H$_5$}{$\eta^1$-C(PPh$_3$)CO}$_2$]$^+$

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## Abstract

Quasi-relativistic density functional calculations have been used to look into the molecular and electronic properties of $cis$-[Pt($\eta^3$-C$_3$H$_5$){$\eta^1$-C(PPh$_3$)(CO)}$_2$]BF$_4$. Numerical experiments have been run for both isomers compatible with IR and NMR outcomes. Binding energies and computed CCO stretching frequencies are very similar for both species, thus indicating their possible coexistence in solution. The comparison with homogeneous theoretical data pertaining to $cis$/$trans$-[Pt($\eta^3$-C$_3$H$_5$)$_2$] and $trans$-[PtCl$_2${$\eta^1$-C(PPh$_3$)(CO)}$_2$] provides a rationale of the [Pt($\eta^3$-C$_3$H$_5$){$\eta^1$-C(PPh$_3$)(CO)}$_2$]BF$_4$ low stability.
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*Keywords:* Density functional calculations; Ketenes; Pt complexes; Ketenylidenetriphenylphosporane

## 1. Introduction

Ketenes are known from the beginning of the last century [1] and their organic reactivity is well known and reported [2]. At variance to that, their interactions with metal systems have been thoroughly studied only in the last 20 years [3] allowing the discovery of a huge number of possible interactions between metal complexes and the C=C=O moiety, the most important being sketched in Chart 1 [3c].

In $\eta^1$-ketenyl and $\mu_x$-ketenylidene derivatives the C=C=O fragment maintains its identity, so that the corresponding compounds can be considered as ketenes where one or both substituents are metal(s). Theoretical studies performed by the Tidwell group predicted a high stability for this ketenes as a consequence of the electropositivity of the substituent(s) [4], and in fact this is the case for sylil-substituted ketenes and bis-ketenes [(R$_3$Si(H)C=C=O, (R$_3$Si)$_2$C=C=O, (R$_2$Si)(HC=C=O)$_2$] [5].

As a part of an on-going research project devoted to the study of the interaction of heterocumulenes with metal-systems, we have reacted Pd(II) and Pt(II) complexes with ketenylidenetriphenylphosphorane, Ph$_3$PC=C=O [6]. In these reactions the nucleophilic C$_\beta$ ylidic carbon atom binds to coordinatively unsaturated 14e species, leading to the formation of metal-substituted mono- and bis-$\eta^1$-ketenyl derivatives, also referred as metal-substituted mono- and bis-ketenes [6b]. Studies on ketenes having a PPh$_3$ fragment and a metal complex as substituents are in their infancy; nevertheless, it sounds reasonable that both their stability and reactivity might be tuned by varying the metal, its oxidation state and the ancillary ligands as well [7]. In this habit, bis-$\eta^1$-ketenyl $cis$-[Pt($\eta^3$-C$_3$H$_5$){$\eta^1$-C(PPh$_3$)CO}$_2$]BF$_4$ (**1**) [8] is particularly interesting because, at variance to $trans$-[PtCl$_2${$\eta^1$-C(PPh$_3$)CO}$_2$] (**2**), very stable, easily isolated, and completely characterised [9], it is highly unstable and the only way to get a qualitative information of its structure was through the analysis of IR, $^1$H- and $^{31}$P-NMR spectra recorded at low temperature ($-50$ °C).

First principle quantum mechanical calculations are by now considered a sort of new spectroscopy, being widely recognized that the chemical and structural information they provide is often more accessible and

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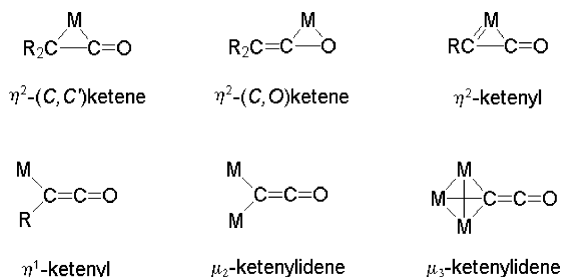
Chart 1.

likewise reliable than that provided by conventional spectroscopies [10]. In this regard, we recently employed quasi-relativistic density functional (QR-DF) calculations combined with spectroscopic measurements to investigate molecular systems relatively unstable or insoluble [9,11]. In this note we present the results of a series of non-local QR-DF numerical experiments carried out to look into the electronic and structural properties of $cis$-$[Pt(\eta^3$-$C_3H_5)\{\eta^1$-$C(PPh_3)CO\}_2]^+$, as well as to obtain information about the low stability of this species.

## 2. Computational details

Theoretical calculations have been performed by running the ADF package [12] based on DF theory and developed by Baerends and coworkers [13]. A triple-$\zeta$ Slater-type basis set was used for the central Pt atoms as well as for P, while a double-$\zeta$ basis set was adopted for H, C, and O atoms. In both cases a single polarization function was added. The inner cores of Pt (1s–4f), P (1s–2p), O and C (1s) were treated by the frozen core approximation. Non-local corrections to the LDA functional were self-consistently included by adopting the Becke [14a] and the Perdew [14b,c] functionals for the exchange and for the correlation parts, respectively. All the numerical experiments have been performed at a quasi-relativistic level [15], in the sense that the first-order scalar relativistic Pauli Hamiltonian is diagonalized in the space of the non-relativistic solutions, i.e. in the non-relativistic basis set. Finally, the metal-ligand binding energy BE) has been analyzed by means of the extended transition state (ETS) method [16], by considering, as interacting fragments, $[Pt(\eta^3$-$C_3H_5)]^+$ and $\{C(PPh_3)(CO)\}_2$. According to this scheme, the $[Pt(\eta^3$-$C_3H_5)$–$\{\eta^1$-$C(PPh_3)(CO)\}_2]^+$ BE may be written as:

$$BE = -(\Delta E_{es} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{prep})$$

Here, $\Delta E_{es}$, $\Delta E_{Pauli}$ and $\Delta E_{orb}$ represent contributions due to the pure electrostatic interaction, the Pauli repulsion (($\Delta E_{es} + \Delta E_{Pauli}$) is usually indicated as $\Delta E_{sr}$, the steric repulsion), and the orbital interaction, respectively. As far as the last term $\Delta E_{prep}$ is concerned, it provides information about the energy required to relax the structure of the free fragments to the geometry they assume in the actual complex. Finally, force constants and harmonic frequencies were calculated by numerical differentiation of energy gradients computed both at the equilibrium geometry and at slightly deviating geometries.

## 3. Results and discussion

Compound **1** may be obtained in acetone at $-50\,°C$, according to literature procedure [8]. Low-temperature spectroscopic measurements (IR, ^{1}H-, and ^{31}P-NMR) show: (i) a strong and rather large, IR signal centred at 2075 cm$^{-1}$; (ii) one ^{31}P-NMR singlet at 23.74 ppm (with [195]Pt satellites); (iii) three symmetric multiplets (with [195]Pt satellites) at 1.53, 2.84 and 4.31 ppm due to *anti*, *syn*, and *meso* $\eta^3$-$C_3H_5$ hydrogens respectively, in ^{1}H-NMR spectrum [8]. These data, implying the presence of a symmetry plane passing through the Pt atom and bisecting the $(\eta^3$-$C_3H_5)$ and $\{\eta^1$-$C(PPh_3)(CO)\}_2$ fragments, are consistent with two distinct geometries (*U* and *D* in Fig. 1) of the $[Pt(\eta^3$-$C_3H_5)\{\eta^1$-$C(PPh_3)(CO)\}_2]^+$ cation [17]. In this context, it is worth of note that: (i) discrepancies between theoretical MO ordering of occupied orbitals and gas-phase variable energy photoelectron spectra of $[Pt(\eta^3$-$C_3H_5)_2]$ (**3**) [11a]
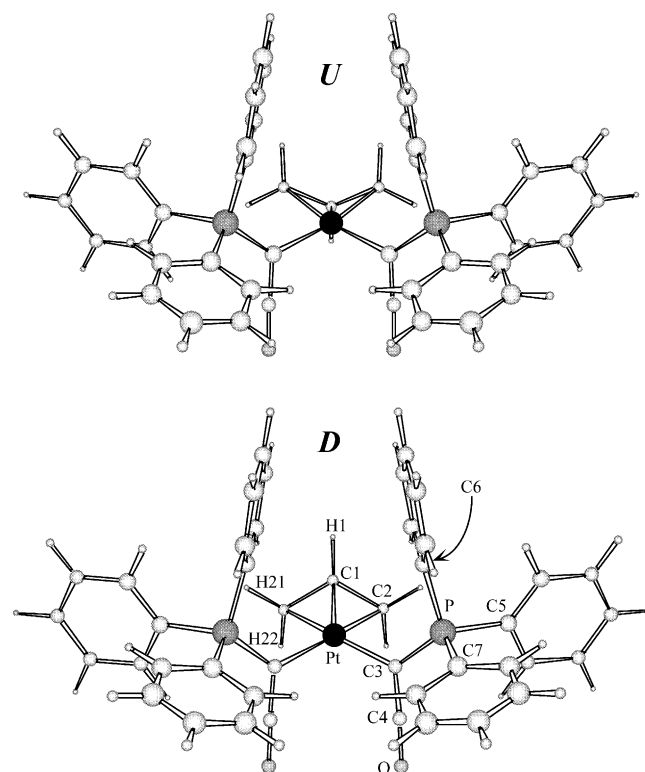


Fig. 1. Schematic representation of the *U* and *D* geometries of *cis*-$[Pt(\eta^3$-$C_3H_5)\{\eta^1$-$C(PPh_3)CO]^+$. Atom labelling is also included.

have been worked out by admitting that *cis* and *trans* isomers were present in the gas phase in a comparable amount (ΔBE between *cis* and *trans* conformers is 0.06 kcal mol$^{-1}$); (ii) we know from an experimental point of view that the allyl group of $[Pt(\eta^3-C_3H_5)\{(\eta^1-C(PPh_3)(CO)\}(PPh_3)]BF_4$ (**4**) [18] exhibits a structural disorder in its crystalline form deriving from the upward (u) and downward (d) orientation of the meso carbon atom with respect to the Pt coordination plane. On this basis, we decided to carry out a series of non-local QR-DF calculations to optimize the geometry of $[Pt(\eta^3-C_3H_5)\{\eta^1-C(PPh_3)(CO)\}_2]^+$ for both *U* and *D* arrangements (cartesian coordinates of all the atoms of the two isomers are provided as supplementary material) [19].

In Tables 1 and 2 structural/vibrational parameters of *U*/*D* conformers and different contributions to the $[Pt(\eta^3-C_3H_5)-\{C(PPh_3)(CO)\}_2]^+$ BE are reported, respectively. Moreover, the relationship of hydrogen

Table 2
$[Pt(\eta^3-C_3H_5)]^+$ –$[C(PPh_3)(CO)_2]$ BE (kcal mol$^{-1}$) decomposed by means of the Ziegler's ETS method

|  | *D* | *cis*-**3** |
|---|---|---|
| $\Delta E_{Pauli}$ | 233.62 | 259.23 |
| $\Delta E_{es}$ | −216.61 | −340.72 |
| $\Delta E_{orb}$ | −163.75 | −167.18 |
| $\Delta E_{prep}\{C_3H_5^-\}$ | – | 9.78 |
| $\Delta E_{prep}\{[C(PPh_3)CO]_2\}$ | 17.19 | – |
| BE | 129.55 | 238.89 |

Values computed for *cis*-$[Pt(\eta^3-C_3H_5)]^+$ –$(C_3H_5)^-$ are also reported for comparison. The ETS method has been applied only to *D*. $\Delta E_{prep}$ has been evaluated only for the $C_3H_5^-$ ion of *cis*-3 and the $\{C(PPh_3)CO\}_2$ moiety of *D*. The BE of the optimized $[Pt(\eta^3-C_3H_5)]^+$ fragment in *D* is 5.63 kcal mol$^{-1}$ more stable than the same optimized fragment in *cis*-3.

atoms to the carbon skeleton of $(\eta^3-C_3H_5)$ in *U* and *D* is displayed in Fig. 2 [20].

Table 1
Selected structural/vibrational parameters of *cis*-$[Pt(\eta^3-C_3H_5)\{\eta^1-C(PPh_3)CO]^+$ (*U* and *D*)

|  | **1** | | **2** [a] | **3** [b] | | **4** [c,d] | |
|---|---|---|---|---|---|---|---|
|  | *U* | *D* |  | *trans* | *cis* |  |  |
| *Bond lengths* | | | | | | | |
| Pt−C1 | 2.125 | 2.141 |  | 2.143 | 2.126 | 2.138 (**d**) | 2.256 (**u**) |
| Pt−C2 | 2.175 | 2.177 |  | 2.189 | 2.184 | 2.188 | |
| Pt−C2′ | 2.175 | 2.177 |  | 2.189 | 2.184 | 2.230 | |
| Pt−C3 | 2.121 | 2.117 | 2.171 | | | 2.120 | |
| C1−C2 | 1.426 | 1.423 |  | 1.423 | 1.426 | 1.354 (**d**) | 1.368 (**u**) |
| C1−C2′ | | | | | | 1.413 (**d**) | 1.400 (**u**) |
| C3−C4 | 1.317 | 1.316 | 1.26 | | | 1.280 | |
| C4−O | 1.176 | 1.176 | 1.16 | | | 1.160 | |
| C3−P | 1.748 | 1.748 | 1.76 | | | 1.75 | |
| P−C5 | 1.836 | 1.835 | 1.80 | | | 1.798 | |
| P−C6 | 1.826 | 1.826 | 1.79 | | | 1.786 | |
| P−C7 | 1.836 | 1.837 | 1.79 | | | 1.786 | |
| C1−H1 | 1.094 | 1.095 |  | 1.098 | 1.098 | | |
| C2−H21 | 1.091 | 1.092 |  | 1.093 | 1.093 | | |
| C2−H22 | 1.094 | 1.094 |  | 1.096 | 1.096 | | |
| *Bond angles* | | | | | | | |
| C2−C1−C2′ | 117.7 | 119.0 |  | 120.7 | 120.3 | 128.4 (**d/u**) | |
| C2−Pt−C2′ | 68.3 | 68.6 |  | 68.8 | 69.0 | 68.7 (**d/u**) | |
| C3−Pt−C3′ | 90.9 | 90.7 | | | | | |
| Pt−C3−P | 131.7 | 129.2 | 121.7 | | | 124.0 | |
| P−C3−C4 | 110.7 | 113.0 | 123.3 | | | 118.0 | |
| C3−C4−O | 176.0 | 175.8 | 179.6 | | | 175 | |
| ΔBE | 0.00 | 0.23 | | | | | |
| $v_{CCO}$ | 2112.6 | 2100.1 | | | | | |
| $\Delta v_{CCO}$ [e] | 50 | 63 | | | | | |

Bond lengths, bond angles, BE and $v$ are in Å, deg, kcal mol$^{-1}$ and cm$^{-1}$, respectively. Structural parameters for related compounds (**2**, **3** and **4**) are also included for comparison. During the optimization procedure, Ph rings have been frozen in a planar geometry; moreover, Ph C−C (C−C−C) and C−H (C−C−H) BLs (BAs) have been set to 1.395 (120.0) and 1.100 (120.0) Å (°), respectively.

[a] From. Ref. [9].
[b] From Ref. [11a].
[c] From Ref. 18.
[d] Compound **4** exhibits a structural disorder in its crystalline form deriving from down (d) or upward (u) orientation of the *meso* carbon atom with respect to the coordination plane of Pt; moreover, the allyl group is not symmetrically bound to the metal atom.
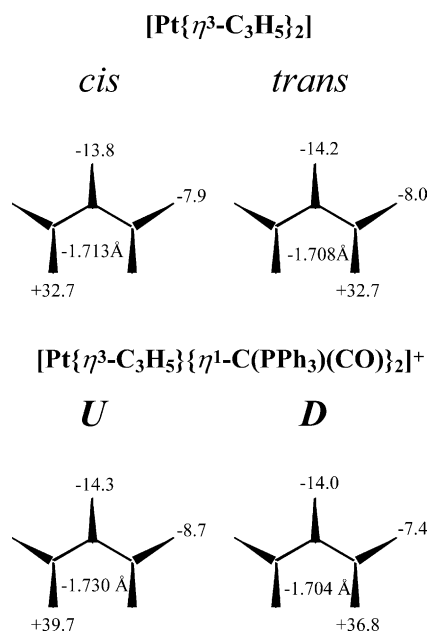[e] $\Delta v_{CCO}$ is the computed red shift of $v_{CCO}$ upon coordination.

**[Pt{$\eta^3$-C$_3$H$_5$}$_2$]**

*cis*        *trans*

-13.8          -14.2

-7.9          -8.0

-1.713Å        -1.708Å

+32.7         +32.7

**[Pt{$\eta^3$-C$_3$H$_5$}{$\eta^1$-C(PPh$_3$)(CO)}$_2$]$^+$**

*U*          *D*

-14.3          -14.0

-8.7          -7.4

-1.730 Å       -1.704 Å

+39.7         +36.8

Fig. 2. Optimized deviations (°) of the hydrogens out of the plane of the allyl carbon atoms for *cis*-[Pt($\eta^3$-C$_3$H$_5$){$\eta^1$-C(PPh$_3$)CO]$^+$ and *cis/trans*-[Pt($\eta^3$-C$_3$H$_5$)$_2$]. Values in Å represent the distance of Pt from this plane.

Data collected in Table 1 and Fig. 2 point out that: (i) bond lengths (BLs) and bond angles (BAs) of *U* and *D* are very similar; moreover, the $\Delta$BE between them is negligible ($\sim 0.2$ kcal mol$^{-1}$); (ii) the distance of Pt to the *meso* carbon atom C1 is significantly shorter than that to C2 and C2′; (iii) the anti hydrogen atoms H22 and H22′ appear to lie more than 35° out of the C1−C2–C2′ plane, away from the Pt atom, while H21, H1, and H21′ are bent toward Pt, the *meso* H1 atom being bent the most; (iv) structural parameters of the Pt{$\eta^1$-C(PPh$_3$)(CO)} and Pt($\eta^3$-C$_3$H$_5$) moieties in **1** are very similar to those experimentally determined in **2** and **4**, and theoretically computed for **3** [21]; (v) both the absolute value and the red shift of $\nu_{CCO}$ upon coordination agree well with experiment (2075 and 35 cm$^{-1}$) [8,21]. As far as this last point is concerned, it deserves to be mentioned that, both in *U* and *D*, $\nu_{CCO}$ corresponds to the in-phase combination of two C–C and C–O stretchings (see Fig. 3).

Overall, data included in Table 1 and Fig. 2 do not provide any explanation for the low stability of **1** [22]; however, the inspection of Table 2 allows us to gain insights into this issue. As a matter of fact, the analysis
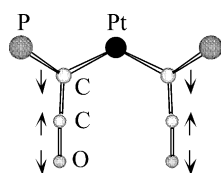
P      Pt

C

C

O

Fig. 3. Schematic representation of the vibrational mode corresponding to $\nu_{CCO}$ in *U* and *D*.

of different contributions concurring to the [Pt($\eta^3$-C$_3$H$_5$)−{C(PPh$_3$)(CO)}$_2$]$^+$/[Pt($\eta^3$-C$_3$H$_5$)−($\eta^3$-C$_3$H$_5$)] BEs testifies that, albeit $\Delta E_{Pauli}$, $\Delta E_{orb}$, and $\Delta E_{Prep}$ have quite similar values in *D* and *cis*-**3**, $\Delta E_{es}$ is definitely larger (in absolute value) in the latter than in the former. Such a fact, simply due to the interaction of the common [Pt($\eta^3$-C$_3$H$_5$)]$^+$ fragment with the allyl anion in **3** and with the neutral moiety {C(PPh$_3$)CO}$_2$ in **1**, has the final effect of making the BE of *cis*-**3** almost twice the one of [Pt($\eta^3$-C$_3$H$_5$)−{C(PPh$_3$)CO}$_2$]$^+$. Exactly the same arguments hold when taking into account the different stability of **1** and **2**. In both cases, the doubly charged fragment [Pt{C(PPh$_3$)CO}$_2$]$^{2+}$ is present (we already stressed that the $\Delta$BE between its *cis*- and *trans*- form is $\sim 3$ kcal mol$^{-1}$ [22]), but while in **1** it directly interacts with one single anion, in **2** it is directly bonded to two chloride anions.

## 4. Conclusions

In this contribution we have presented the results of a QR-DF study concerning the electronic and molecular structure of the unstable [Pt($\eta^3$-C$_3$H$_5$){$\eta^1$-C(PPh$_3$)(CO)}$_2$]$^+$ ion. Theoretical results point out that the two conformers compatible with IR and NMR spectra are substantially isoenergetic. Optimized geometrical parameters compare well with those of related systems; moreover, both the absolute values of $\nu_{CCO}$ and its red shift upon coordination are quantitatively reproduced. The comparison of QR-DF results with homogeneous data pertaining to *cis/trans*-[Pt($\eta^3$-C$_3$H$_5$)$_2$] and *trans*-[Pt{$\eta^1$-C(PPh$_3$)(CO)}$_2$Cl$_2$] allowed us to provide a rationale of the title compound low stability.

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[7] It is noteworthy that ancillary ligands able to relieve the effects of the $\mathbf{1} \rightarrow M$ $\sigma$ donation should play a stabilizing role on these compounds. Moreover, it has to be remarked that **1** acts towards metal systems as a pure $\sigma$ donor, with no $\sigma$ or $\pi$ acceptor properties. Details on these argument can be found in Ref. [6b] and references therein.

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[19] A thorough discussion of $Pt-\{\eta^1-C(PPh_3)(CO)\}$ and $Pt-(\eta^3-C_3H_5)$ bonding interactions can be found in Refs. [9] and [11a], respectively.

[20] The figure shows the degree of bending of C–H bonds out of the plane defined by C1, C2, and C2′, with a negative sign meaning a bend toward the Pt atom, which parenthetically lies $\sim 1.7$ Å from this plane.

[21] A further series of calculations has been run to evaluate the $\nu_{CCO}$ frequency in the free $\{C(PPh_3)(CO)\}$ ligand. The computed value (2163 cm$^{-1}$) compares very well with experiment (2110 cm$^{-1}$). Moreover, optimized geometrical parameters computed by freezing Ph rings in a planar geometry and fixing their C–C (C–C–C) and C–H (C–C–H) BLs (BAs) to 1.395 (120.0) and 1.100 (120.0) Å (°), respectively, perfectly reproduce data reported in Ref. [9] and obtained by limiting the otpimization procedure to the PCCO moiety.

[22] The steric repulsion of the two $\{C(PPh_3)(CO)\}$ ligand in the *cis*-conformation cannot be invoked because further calculations on *cis*- and *trans*-$[Pt\{C(PPh_3)(CO)\}_2]^{2+}$ fragments indicate the former more stable than the latter by $\sim 3$ kcal mol$^{-1}$. Incidentally, geometrical parameters adopted for the *trans*-$[Pt\{\eta^1-C(PPh_3)(CO)\}_2]^{2+}$ fragment are the same optimized for the *cis*-one.