Reaction of Ketenylidenetriphenylphosphorane ($Ph_3P{=}C{=}C{=}O$) with Platinum(II) and Palladium(II) Complexes. Synthesis, Characterization, and Molecular Structure of $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)(CO)\}(PPh_3)]BF_4$

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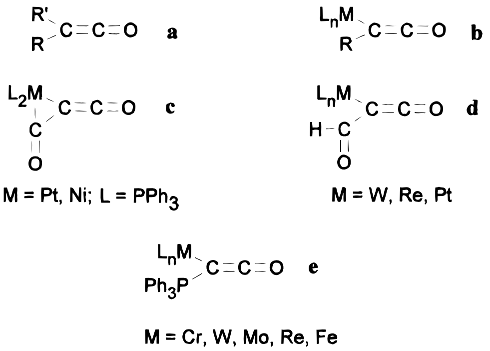
Summary: Ketenylidenetriphenylphosphorane, $Ph_3P{=}C{=}C{=}O$, reacts with Pt(II) and Pd(II) η^3-allyl complexes (allyl = C_3H_5, 2-MeC_3H_4) to give neutral or cationic mononuclear η^1-ketenyl derivatives $[M(\eta^3\text{-allyl})\{(\eta^1\text{-}C(PPh_3)(CO)\}L]^{m+}$ (L = Cl, m = 0; L = PPh_3, m = 1) that have been characterized by elemental analysis, IR, and multinuclear NMR. The X-ray molecular structure determination performed on a single crystal of the air-stable derivative $[Pt(\eta^3\text{-}C_3H_5)\{\eta^1\text{-}C(PPh_3)(CO)\}(PPh_3)]BF_4$ furnishes the first crystallographic evidence of an η^1-ketenyl derivative in which the ketene moiety is also involved in an ylide grouping.

Ketenes, **a** (Chart 1), are known from the beginning of the century,[1] and their organic chemistry is well-known and reviewed.[2] In the last years even the organometallic chemistry of ketenes has been more intensively studied,[3] since metal−ketene derivatives were reported to be involved in important catalytic and stoichiometric processes.[4] The first platinum−ketene derivative has been obtained by substitution of ethylene in $[Pt(PPh_3)_2(C_2H_4)]$ with diphenylketene,[5] and nowadays a large number of ketene and η^2-ketenyl derivatives are known.[3a] Despite their potentiality as useful synthetic reagents η^1-ketenyl derivatives, **b**, in which a metal center is one of the ketene substituents, are less studied. They are typically obtained by ligand-induced CO migration to a carbyne ligand.[6] Other syntheses involve the coordination of carbon suboxide, $O{=}C{=}C{=}C{=}O$, on Pt and Ni[7] with formation of η^1-ketenyl, η^2-(C,C)-ketene derivatives, **c**, or the insertion of carbon suboxide in transition metal−hydride bonds[8] giving η^1-ketenyl formyl derivatives, **d**. Peculiar η^1-ketenyl derivatives, in which the second substituent of the ketene moiety is $SiMe_3$, have been obtained by reaction of $Me_3P{=}CHSiMe_3$ with $[FeCp(CO)_2]I$ followed by rearrangements[9] and, more recently, by Wolff rearrangement of a Rh diazolkane complex.[10] Moreover it has been reported that ketenylidenetriphenylphosphorane, $Ph_3P{=}C{=}C{=}O$, **1**,[11] substitutes CO or MeCN from some early or medium transition metal complexes giving η^1-ketenyl derivatives, **e**.[12]

Chart 1



Continuing our interest in metal−ketene derivatives[3b,7a,b,8b,c] and in the reactivity of $Ph_3P{=}C{=}C{=}O$,[13] we started a systematic research on the use of **1** as a synthon for new ketenyl complexes of late transition metals. Actually the relevant negative charge on the β

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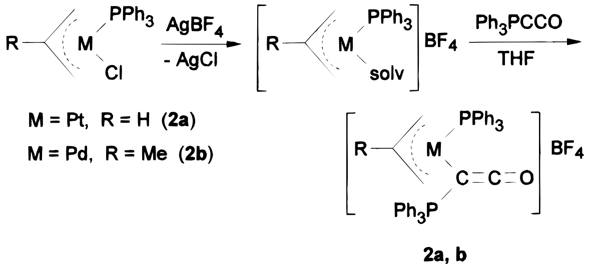
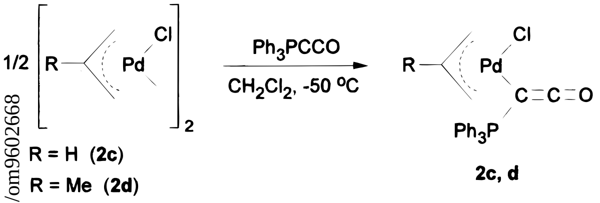
carbon atom of $Ph_3P{=}C{=}C{=}O$[14] makes possible, in principle, a nucleophilic attack of this carbon to an electron-deficient metal center.

Cationic η^1-ketenyl derivatives $[M(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)\{\eta^1\text{-}C(PPh_3)(CO)\}(PPh_3)]^+$ (M = Pt, R = H, **2a**;[15] M = Pd, R = Me, **2b**[16]) have been obtained by treating the corresponding *solvate* complexes[17] with 1 equiv of **1** at room temperature for **2a** and at −30 °C for **2b**, according to eq 1. Pd(II) η^3-allyl dimers $[Pd(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)Cl]_2$ (R = H, Me) have been reacted with **1** to give the neutral compounds $[Pd(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)\{\eta^1\text{-}C(PPh_3)(CO)\}Cl]$[18] (R = H, **2c**; R = Me, **2d**) (eq 2). The reaction of **1** with $[Pt(C_3H_5)Cl]_4$ gave $[Pt(\eta^3\text{-}C_3H_5)\{(\eta^1\text{-}C(PPh_3)(CO)\}Cl]$, **2e**,[19] in very low yield.



(1)



(2)

The IR spectra of compounds **2a**−**e** clearly indicate the presence of the η^1-ketenyl moiety,[3a] showing an intense absorption in the region 2060−2080 cm^{-1}. The ^1H NMR spectra point out the maintenance of the η^3-allylic moiety in the coordination sphere of the metal.[20] Besides the signals due to coordinated PPh_3 (**2a,b**) ^{31}P NMR spectra show signals at 22−25 ppm, a zone far from that of free $Ph_3P{=}C{=}C{=}O$,[21] attributable to the phosphonium group. The $^{13}C\{^1H\}$ NMR spectrum recorded for the most stable compound **2a** shows, together with the typical signals of the allyl moiety,[22] the carbonylic carbon as a doublet at 156.73 ppm ($^2J_{CP}$ = 18.9 Hz), in the range observed for other η^1-ketenyl derivatives.[3a,7c] A doublet at 9.26 ppm ($^1J_{CP}$ = 59.0 Hz), with ^{195}Pt satellites covered by instrumental noise, is assigned to the ylidic carbon; the high-field shift and the decrease of $^1J_{CP}$ with respect to free $Ph_3P{=}C{=}C{=}O$[21] are in agreement with the reduction of the charge density on the C−P bond by coordination to the metal.

For compound **2a** it was possible to obtain pale-yellow crystals, suitable for a X-ray structure determination,[23] by slow evaporation of a CH_2Cl_2/toluene solution. The structure of **2a** is shown in Figure 1 with the atom labeling (the counterion BF_4^- is omitted). The coordination about Pt is consistent with a slightly distorted square planar geometry assuming the allyl group as a bidentate ligand bonded to the metal through C(37) and C(39). The allyl group exhibits a structural disorder deriving from down- or upward orientation of the carbon atom C(38) with respect to the coordination plane of Pt.

Only a few structures of η^1-ketenyls have been reported,[8c,24,25] but this is a quite new example in which the C=C=O moiety is bonded to Pt and is involved also

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[14] Mulliken's charge density analysis (Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833) relative to density functional calculations carried out by using the DMOL method (Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. Delley, B. *J. Chem. Phys.* **1991**, *94*, 7245) on the model molecule H_3PCCO gives the following charge distribution on the $PC_\beta C_\alpha O$ moiety: P (0.436), C_β (−0.568), C_α (0.212), O (−0.282).

[15] **2a:** To a THF (40 mL) solution of $[Pt(\eta^3\text{-}C_3H_5)(Cl)(PPh_3)]$ (0.533 g, 1.00 mmol) was added a 0.24 M solution of $AgBF_4$ in acetone (1.05 mmol). AgCl was filtered off and the solution treated with **1** (0.302 g, 1.00 mmol) at room temperature. After 10 min a white solid started to precipitate. The mixture was stirred for 24 h, and the precipitate was filtered out and washed with THF. After drying, a white-yellow powder was obtained (0.540 g, 61%). Anal. Calcd for $C_{41}H_{35}OP_2PtBF_4$: C, 55.48, H, 3.97. Found: C, 54.73, H, 3.86. IR (Nujol, cm^{-1}): ν_{CO} 2073 (s). ^1H NMR (200 MHz, CD_2Cl_2, 25 °C, TMS ext.): 3.43, 2.38, 2.32 (3 m, 3H); 4.86 (m, $^3J_{HPt}$ = 61.2 Hz, H_c); 3.62 (ddd, $^3J_{HHc}$ = 7.1 Hz, $^4J_{HH}$ = 2.4 Hz, $^3J_{HP}$ = 2.4 Hz, $^2J_{HPt}$ = 13.5 Hz, 1H, H_{sin} trans to PPh_3). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, 25 °C, H_3PO_4 ext.): 24.58 (d, $^3J_{PP}$ = 6.0 Hz, $^1J_{PPt}$ = 4070 Hz); 24.31 (d, $^2J_{PPt}$ = 101.3 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2, 25 °C, TMS ext.): 57.58 (s, $^1J_{CPt}$ = 157.4 Hz, C_{all}); 62.83, (d, $^2J_{CP}$ = 33.4, $^1J_{CPt}$ = 74.5 Hz, C_{all}), 111.05, (s, $^1J_{CPt}$ = 37.3 Hz, C_c); 156.73(d, $^2J_{CP}$ = 18.9 Hz, CO), 9.62 (d, $^1J_{CP}$ = 59.0 Hz, C_β).

[16] **2b:** To a THF (40 mL) solution of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(Cl)(PPh_3)]$ (0.460 g, 1.00 mmol) was added a 0.23 M solution of $AgBF_4$ in acetone (1.05 mmol). AgCl was filtered off, and the solution, cooled at −30 °C, was treated with **1** (0.302 g, 1.00 mmol). After 1 h of stirring, the reaction mixture was taken to dryness at low temperature, obtaining a pale yellow solid that was washed with cold ethyl ether, filtered out, and dried under vacuum. Yield: 0.414 g (57%). Anal. Calcd for $C_{42}H_{37}OP_2PdBF_4$: C, 62.05, H, 4.60. Found: C, 61.03, H, 4.70. IR (Nujol, cm^{-1}): ν_{CO} 2070 (s). ^1H NMR (200 MHz, CD_2Cl_2, −50 °C, TMS ext.): 4.40, 3.62, 2.89, 2.82 (4 m, br, 4H); 1.70 (s, Me). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, −50 °C, H_3PO_4 ext.): 22.56 (s); 20.05 (s).

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[18] **2c:** To a −50 °C CH_2Cl_2 (5 mL) solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.060 g, 0.165 mmol) was added a cooled CH_2Cl_2 (5 mL) solution of **1** (0.100 g, 0.33 mmol). The solution was concentrated at −50 °C under vacuum to *ca.* 3 mL, and by adding 10 mL of cooled *n*-hexane, a green yellow solid precipitated, which decomposes rapidly at room temperature even in the solid state. IR (Nujol, cm^{-1}): ν_{CO} 2077 (s). ^1H NMR (200 MHz, CD_2Cl_2, −50 °C, TMS ext.): 3.90, 2.70, 2.10 (3 m, br, 4H); 4.70 (m, H_c). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, −50 °C, H_3PO_4 ext.): 22.16 (s). **2d**: The compound has been prepared similarly to **2c** starting from $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)Cl]_2$ (0.098 g, 0.25 mmol) and **1** (0.150 g, 0.5 mmol). The compound can be handled at room temperature in the solid state. Yield: 0.162 g (65%). Anal. Calcd for $C_{24}H_{22}ClOPPd$: C, 57.73, H, 4.45. Found: C, 56.55, H, 4.30. IR (Nujol, cm^{-1}): ν_{CO} 2075 (s), ν_{PdCl} 275 (m). ^1H NMR (200 MHz, CD_2Cl_2, −50 °C, TMS ext.): 3.90, 2.86, 2.24, 1.75 (4 m, br, 4H); 1.61 (s, Me). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, −50 °C, H_3PO_4 ext.): 24.39 (s).

[19] **2e**: A toluene suspension (15 mL) of $[Pt(C_3H_5)Cl]_4$ (0.090 g, 0.08 mmol) was treated with a toluene solution (10 mL) of **1** (0.100 g, 0.33 mmol), and the mixture was stirred for 3 h. The yellow solid was extracted with CH_2Cl_2, and from the resulting solution a yellow solid was obtained by addition of ethyl ether. The compound was filtered out, washed with ethyl ether, and dried under vacuum. Yield: 0.045 g, 24%. Anal. Calcd for $C_{23}H_{20}OPPt$: C, 48.13, H, 3.51. Found: C, 46.56, H, 3.45. IR (Nujol, cm^{-1}): ν_{CO} 2065 (s). ^1H NMR (200 MHz, CD_2Cl_2, −50 °C, TMS ext.): 3.79 (d, $^3J_{HHc}$ = 7.7 Hz, $^2J_{HPt}$ = 90.4 Hz, 1H); 1.04 (d, $^3J_{HH}$ = 11.0 Hz, $^2J_{HPt}$ = 77.9 Hz, 1H); 2.11 (d, $^3J_{HH}$ = 11.0 Hz, $^2J_{HPt}$ = 58.8 Hz, 2 H), 4.15 (m, H_c). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, −50 °C, H_3PO_4 ext.): 22.92 (s, $^2J_{PPt}$ = 216 Hz).

[20] Carturan, G.; Belluco, U.; Del Pra, A.; Zanotti, G. *Inorg. Chim. Acta* **1979**, *33*, 155.

[21] Ph_3PCCO: ^{31}P NMR (81 MHz, CD_2Cl_2, 25 °C, H_3PO_4 ext.) 5.45 (s); ^{13}C NMR (50 MHz, CD_2Cl_2, 25 °C, TMS ext.) 20.84 (d, $^1J_{CP}$ = 190.0 Hz, C_β), 145.57 (d, $^2J_{CP}$ = 44.1 Hz, C_α).

[22] Mann, B.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 208.

[23] Crystal structure analysis of **2a**: $C_{41}H_{35}OP_2PtBF_4$, M = 887.57; crystal dimensions 0.25 × 0.30 × 0.20 mm; Philips-PW 1100 computer-controlled four-circle diffractometer; graphite monochromator, 0.710 70 Å MoKα, 298 K; $\theta{-}2\theta$ scan method. The lattice constants were determined from 25 reflections: a = 10.907(1), b = 18.785(2), c = 9.086(1) Å; α = 100.2(1), β = 92.1(1), γ = 79.4(1)°; V = 1800.9(1) Å^3; space group $P\bar{1}$, Z = 2, ρ_{calcd} = 1.64 g cm^{-3}; $F(000)$ = 875.91; μ(Mo Kα) = 38.55 cm^{-1}; *hkl* range $-12 < h < 12$, $-22 < k < 21$, $0 < l < 10$. Of 6348 independent reflections 4161 were considered "observed" [$F_o \geq 3\sigma(F_o)$]; solution and refinement were obtained by standard Patterson methods and subsequent Fourier recycling (SHELX-76). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned geometrically and not refined. Final values are R (R_w) = 0.052 (0.062 with $w = 1/[\sigma^2(F_o) + 3 \times 10^{-3}F_o^2]$), 370 parameters, and maximum residual electron density 1.168 e/Å^3.

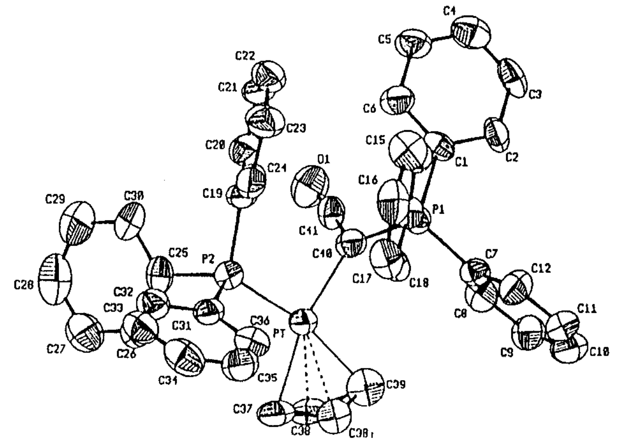
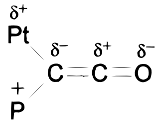


Figure 1. ORTEP view of the cation [Pt(η^3-C_3H_5){η^1-C(PPh_3)(CO)}(PPh_3)] (thermal ellipsoids at 30% probability level) with atom labeling. Dotted bonds refer to the disordered location of the allylic central carbon atom. Selected bond lengths (Å) and angles (deg) of relevant interest are reported: Pt−P(2) 2.278(1), Pt−C(40) 2.120(7), Pt−C(37) 2.188(2), Pt−C(38) 2.138(2), Pt−C(38′) 2.256(5), Pt−C(39) 2.230(2), P(1)−C(40) 1.75(1), P(1)−C(1) 1.798(7), P(1)−C(7) 1.786(9), P(1)−C(13) 1.796(7), C(40)−C(41) 1.280(8), C(41)−O 1.160(8); P(2)−Pt−C(40) 98.9(4), P(2)−Pt−C(37) 96.8(2), C(40)−Pt−C(39) 95.4(4), C(37)−Pt−C(39) 68.7(2), C(40)−C(41)−O 175(1), Pt−C(40)−C(41) 118(1), Pt−C(40)−P(1) 124.0(7), P(1)−C(40)−C(41) 118(1).

in a potential ylide grouping in the same molecule. Yet, the question arises whether this structure deals with an ylidic or a mere ketene nature of the complex cation.

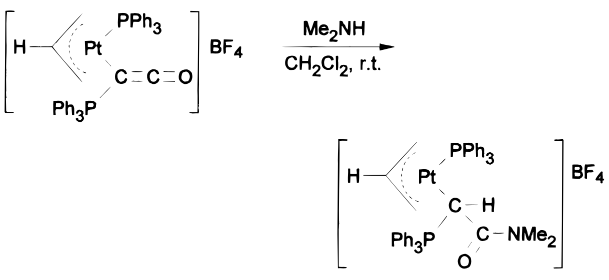
The bond length P(1)−C(40) (1.75(1) Å) is almost in the norm for an ylide and has been shown to indicate a substantial double-bond character[26] arising from the dipolar contribution of the form $P^{\delta+}-C^{\delta-}$; thereby the bond lengths C(40)−C(41), (1.280(8) Å) and C(41)−O (1.160(8) Å) seem to be influenced as to exhibit a partial triple-bond character. Actually these values are in the range of those reported in literature for some η^1-ketenyl complexes[8c,25] and other similar compounds[27] and have been tentatively explained in terms of mesomeric effects involving nonpolar, acylium, and dipolar forms.[3a] However, for an ylidic character, in terms of mesomeric effects, we would expect in the presence of the observed P−C(40)−C(41) bond angle (118(1)°) a longer distance C(40)−C(41);[27] in contrast, it is here even shorter than the values so far reported (1.31−1.33 Å).[3a,25,28]

On the other side, the geometrical parameters in the coordination sphere of Pt are almost in the norm, thus we believe that the Pt−C(40) bond electrons do not take part to any mesomeric state of the cation. In this case a somewhat measurable shortening of the bond Pt−C(40) was expected. Rather, the metal center seems to influence through inductive effects the charge distribution in the ketenyl grouping in cooperation with the ylide moiety, so provoking an increased polarization of the bond C(40)−C(41) and its shortening up to 1.28 Å. The bond angle C=C=O (175(1)°) is in agreement with this suggestion. Therefore the geometry of the ketenyl grouping can be more reasonably depicted with the dipolar form **A**; the coordination to the metal seems scarcely to change its geometry as compared with that of the free ylide $Ph_3P{=}C{=}C{=}O$.[29]



A

Preliminary assays on stability and reactivity of η^1-ketenyl compounds **2a**−**e** indicate that the Pt(II)- and Pd(II)-coordinated CCO moiety presents a reactivity that resembles that of ketenes. Compound **2a** is very stable in the solid and in solution and reacts with Me_2NH giving the amidic derivative **3** (eq 3) but is completely unreactive toward alcohols and water. Compound **3** is obtained as a mixture (*ca.* 1:1) of two diastereomeric forms, due to the contemporary presence of the coordinated prochiral allyl group and the asymmetric carbon atom Pt−CH(PPh_3)($CONMe_2$). Compound **2b** is much more reactive than **2a** and reacts even in the solid state with moisture undergoing further decomposition giving unidentified compound(s) through elimination of CO_2 well detected by IR. Other typical ketene reactions, i.e. cycloadditions, on **2a,b** and the reactivity of **2c,d,e** are at the present under study.



(3)

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The synthesis of compounds **2a**−**e** shows that the use of $Ph_3P{=}C{=}C{=}O$ furnishes a possible easy entry to new late transition metal ketenyl complexes. The extension of the reaction to different Pd, Pt, and Rh substrates offers a new platform for further developments.

Acknowledgment. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and by the Consiglio Nazionale delle Ricerche (CNR).

Supporting Information Available: Text giving the synthesis procedure and analytical and spectroscopic data for **3** and listings of final values of refined atomic coordinates and thermal parameters, calculated atomic coordinates of hydrogen atoms, anisotropic thermal parameters (U_{ij}), complete bond lengths and angles, and unit cell and complete crystal structure determination data for **2a** (7 pages). Ordering information is given on any current masthead page.

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