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A Cationic Unsaturated Platinum(II) Complex that Promotes the Tautomerization of Acetylene to Vinylidene

Laura Ortega-Moreno, Riccardo Peloso, Joaquín López-Serrano, Javier Iglesias-Sigüenza, Celia Maya and Ernesto Carmona*[a]

Dedication ((optional))

Abstract: Complex [PtMe$_2$(PMe$_2$Ar^{Dipp2})] (**1**) that contains a tethered terphenyl phosphine (Ar^{Dipp2} = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) reacts with [H(Et$_2$O)$_2$]BAr$_F$ (BAr$_F^-$ = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4^-$) to give the solvent complex [PtMe(S)(PMe$_2$Ar^{Dipp2})]$^+$ (**2·S**). Although the solvent molecule was easily displaced by a Lewis base (e.g. CO and C$_2$H$_4$) to afford the corresponding adducts, treatment of **2·S** with C$_2$H$_2$ yielded instead the allyl complex [Pt(η^3-C$_3$H$_5$)(PMe$_2$Ar^{Dipp2})]$^+$ (**6**) *via* the alkyne intermediate [PtMe(η^2-C$_2$H$_2$)(PMe$_2$Ar^{Dipp2})]$^+$ (**5**). Deuteration experiments with C$_2$D$_2$ and kinetic and theoretical investigations demonstrated that the conversion of **5** into **6** involved a Pt(II)-promoted HC≡CH to :C=CH$_2$ tautomerization in preference over acetylene migratory insertion into the Pt-Me bond.

Cationic organometallic complexes are valuable reagents that find numerous applications in catalysis.[1-3] Low-coordinate cationic methyl derivatives of Pt(II) are of particular importance, for they combine high metal electrophilicity with the accessible coordination sites and the intrinsic reactivity of the metal-carbon σ-bond.[4-6]

π-Acidic Pt(II) and Au(I) systems catalyze many electrophilic activations of alkenes and alkynes.[7] Carbene complexes, including metal-vinylidenes,[8-9] are often proposed as active intermediates, but in most instances there is no direct evidence for their involvement.[7a] Vinylidene complexes of transition metals have been widely investigated, the most convenient method to induce the alkyne-to-vinylidene rearrangement being the use of electron-rich metal fragments.[9a] By contrast, there is a scarcity of information about Pt and Au analogues,[10-12] which might be associated with the π-acid nature of compounds of these metals.[7]

Phosphines are one of the most important families of auxiliary ligands.[13] Following earlier work,[14] we describe herein the synthesis and structural characterization of the cationic, unsaturated complex [PtMe(S)(κ^2-P,C-PMe$_2$Ar^{Dipp2})]$^+$ (**2·S**), that features bidentate coordination of the bulky phosphine, PMe$_2$Ar^{Dipp2} (Dipp = 2,6-^{i}PrC$_6$H$_3$; Ar^{Dipp2} = 2,6-(2,6-

^{i}PrC$_6$H$_3$)$_2$C$_6$H$_3$).[15,16] Although complex **2·S** is not truly a low-coordinate species,[17] it exhibits a weakly-bonded molecule of solvent (S = H$_2$O, Et$_2$O, THF) and a labile Pt···C$_{arene}$ interaction. Therefore it could be viewed as a source of the two-ligand Pt fragment [PtMe(PMe$_2$Ar^{Dipp2})]$^+$, for which rich electrophilic reactivity can be foreseen. While no C—C bond formation was observed for C$_2$H$_4$ under ambient conditions, C$_2$H$_2$ yielded initially an unprecedented[18,19] [PtMe(η^2-C$_2$H$_2$)(PMe$_2$Ar^{Dipp2})]$^+$ complex (**5**), that experienced facile C—C coupling to afford the π-allyl complex [Pt(η^3-C$_3$H$_5$)(PMe$_2$Ar^{Dipp2})]$^+$ (**6**). The use of C$_2$D$_2$ provided unequivocal proof for a CH≡CH to :C=CH$_2$ tautomerism induced by the Pt(II) center, also supported by computational studies.

Protonation (CD$_2$Cl$_2$, −80 ºC) of complex **1** that features κ^2-P,C phosphine coordination[20] (see the Supporting Information) with [H(Et$_2$O)$_2$]BAr$_F$ (BAr$_F^-$ = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4^-$) did not permit observation of a transient σ-CH$_4$ complex.[2c] Liberation of CH$_4$ occurred instead with formation of complexes [PtMe(S)(PMe$_2$Ar^{Dipp2})]$^+$ (**2·S**) (Scheme 1) featuring rather large $^1J_{PPt}$ and $^3J_{PtH}$ (Pt—Me) couplings of about 4800 and 77 Hz, respectively. These complexes exhibited dynamic behavior at 25 ºC,[21] although below −10 ºC the molecular structure became rigid on the NMR time scale. The Dipp rings give rise below 25 ºC to two septets (2.38 and 2.28 ppm in C$_2$D$_2$Cl$_4$) and four doublets (between 1.52 and 1.06 ppm) for the ^{i}Pr substituents. At higher temperatures (Figure S12) the two rings become equivalent (above 110 ºC; ΔG‡ = 19 ± 2 kcal·mol^{-1} at the coalescence temperature of 100 ºC).
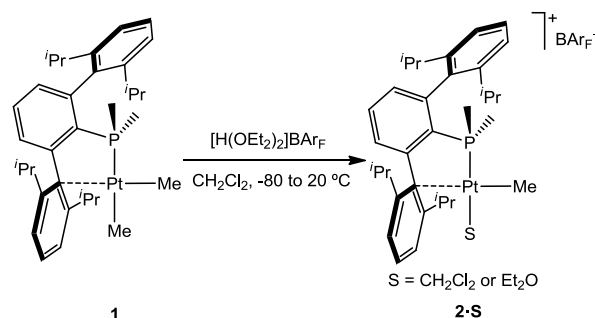

Scheme 1. Generation of complexes **2·S**.

Single crystals of **2·S** could only be obtained after prolonged cooling at −20 ºC of CH$_2$Cl$_2$/Et$_2$O solutions of the complex. Adventitious H$_2$O originated crystals of the aquo complex [PtMe(H$_2$O)(PMe$_2$Ar^{Dipp2})]BAr^F **2·H$_2$O** in preference to those of **2·Et$_2$O** or **2·CH$_2$Cl$_2$**. The H$_2$O ligand is *trans* to P (Figure 1) and forms a Pt—O bond with a normal[22] length of 2.143(4) Å. Other metric parameters have the expected values, though the Pt···C$_{arene}$ interaction (Pt1-C22 in Figure 1) of 2.348(5) Å is significantly longer than normal olefinic Pt(II)—C

[a]   Dr. L. Ortega-Moreno, Dr. R. Peloso, Dr. J. López-Serrano, Dr. C. Maya, Prof. Ernesto Carmona
        Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC). Avenida Américo Vespucio 49, 41092 Sevilla (Spain)
        E-mail: guzman@us.es

[b]   Dr. J. Iglesias-Sigüenza, Departamento de Química Orgánica, Universidad de Sevilla and Centro de Innovación en Química Avanzada (ORFEO-CINQA), C/Prof. García González 1, 41012 Sevilla, Spain.

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bonds (*ca.* 2.11-2.16 Å).[23-25] The X-ray data therefore support the notion that cations **2·S** could behave as a source of the electrophilic [PtMe(PMe₂Ar^{Dipp2})]⁺ fragment.
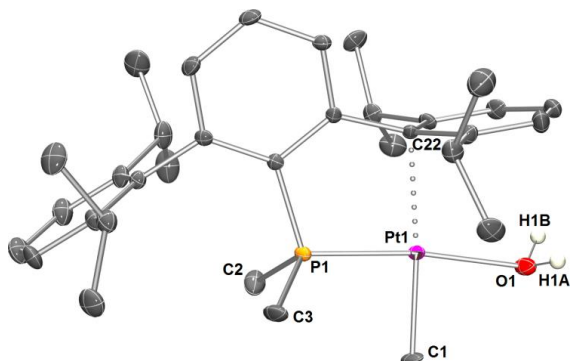
Figure 1. ORTEP view of the cation of complex **2·H₂O**; most hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 40% level probability. Selected bond distances (Å) and angles (º): Pt1-O1 2.143(4), Pt1-C1 2.034(6), Pt1-P1 2.170(1), Pt1-C22 2.348(5), O1-Pt1-C1 83.2(2), C1-Pt1-P1 89.6(2), P1-Pt1-C22 83.9(1), C22-Pt1-O1 103.1(2).

We sought empirical evidence for the electron density at the Pt(II) center of **2·S** by carrying out its reaction with CO. Treatment of **2·S** with CO (2 bar, 20 ºC) gave the carbonyl complex [PtMe(CO)(PMe₂Ar^{Dipp2})]⁺, (**3**), with a κ²-P,C tethered phosphine in a structure akin to **2·S**. Its carbonyl IR stretching frequency at 2127 cm⁻¹ is only somewhat smaller than the 2143 cm⁻¹ value of free CO. For comparison, cationic bis(diimine) complexes [PtMe(CO)(N^N)]⁺ [25] and recently reported [Pt(PCP)(CO)]⁺ derivatives[26] have $\tilde{v}$(CO) values of 2103-2116 cm⁻¹ and 2111-2145 cm⁻¹, respectively.

Complex **2·S** offered also the possibility of accommodating Pt—alkene or Pt—alkyne functions *cis* to the Pt—Me bond, thus amenable to experience insertion reactions.[24,27] These compounds are related to the catalyst resting state involved in the Pd- and Ni-catalyzed olefin polymerization[1a] and in the Pt-catalyzed dimerization of ethylene.[22,28-29]

Addition of C₂H₄ to CH₂Cl₂ solutions of complex **2·S** led to the adduct [PtMe(η²-C₂H₄)(PMe₂Ar^{Dipp2})]⁺ (**4**), exhibiting once again chelating κ²-P,C phosphine ligation. The Pt—C₂H₄ linkage undergoes fast C₂H₄ rotation at 20 ºC, with a barrier ΔG‡ = 11 ± 1 kcal·mol⁻¹ at the coalescence temperature of 25 ºC (Figure S13). It also experiences associative exchange with excess free C₂H₄ (EXSY NMR between 0 and 25 ºC, ΔG‡ = 16 ± 2 kcal·mol⁻¹). At room temperature, it gives rise to a broad ¹³C{¹H} NMR resonance at 102.2 ppm, thereby having an olefin coordination shift to lower frequencies, Δδ, of nearly −21 ppm. For comparison, in dicationic [Pt(PNP)(C₂H₄)]²⁺, Δδ = −45 ppm.[7c,30] This observation is indicative of a significantly decreased contribution of the π-back-donation in complex **4**,[31] in agreement with the high π-acidity of the Pt(II) center in **2·S**. Complex **4** is nonetheless stable at 20 ºC towards C₂H₄ migratory insertion into the Pt—Me bond, although under excess of C₂H₄ (2 bar) becomes a catalyst precursor for C₂H₄ dimerization[22,28-29] above 55 ºC (see the Supporting Information). Related diimine Pt catalysts required heating for 2 days at 100 ºC.[28]

When complex **2·S** was treated with C₂H₂ at room temperature (2 bar, CH₂Cl₂ solution) a clean reaction yielded the η³-allyl complex [Pt(η³-C₃H₅)(PMe₂Ar^{Dipp2})]⁺ (**6**), through the intermediacy of the π-C₂H₂ compound [PtMe(η²-C₂H₂)(PMe₂Ar^{Dipp2})]⁺ (**5**) (Scheme 2). Monitoring of the reaction

by variable temperature ¹H and ³¹P{¹H} NMR spectroscopy revealed that C₂H₂ coordination takes place even at −80 ºC, forming adduct **5** that features a ³¹P{¹H} resonance at 11.5 ppm, with a ¹J_{PPt} of 4282 Hz. This species contains Pt—Me (δ 0.60, ³J_{HP} = 3 Hz, ²J_{HPt} = 76 Hz) and Pt—η²-C₂H₂ linkages, the latter giving rise to a ¹H NMR doublet centered at 3.08 ppm (³J_{HP} = 4 Hz, ²J_{HPt} = 50 Hz) and to a ¹³C doublet resonance centered at 77.7 ppm, with ¹J_{CH}, ²J_{CH}, and ²J_{CP} couplings of 263, 44, and 12 Hz, respectively.
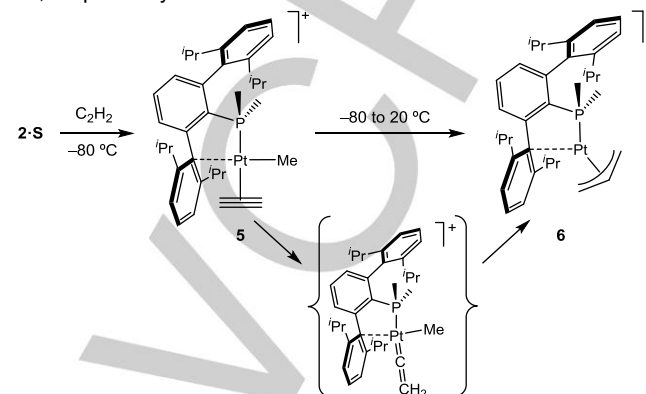

Scheme 2. Formation of the π-allyl complex **6** from **2·S** and C₂H₂ via η²-acetylene adduct **5**.

A second intermediate formed above −60 ºC and survived for a short time at room temperature before it converted into the η³-allyl complex **6** that was the only observable reaction end-product. Its NMR characterization was therefore attempted at −20 ºC. It contains an intact Pt—Me unit, as hinted by a ¹H NMR resonance at δ 0.43 ppm (²J_{HPt} = 74 Hz) and a corresponding ¹³C{¹H} signal at −6.6 ppm (²J_{CP} = 6 Hz). In addition, a ¹³C resonance was recorded at 221.2 ppm. Since in a recently reported cationic Pt(II) alkylidene a ¹³C signal at 209 ppm was assigned to the alkylidene carbon nucleus,[14a] it is tempting to ascribe the observed 221.2 ppm resonance to the Pt-bonded carbon of the Pt=*C*=CH₂ unit. The corresponding CH₂ resonance could not be assigned with confidence and therefore we defer a definite structural proposal for this intermediate until additional data become available. Noteworthy, for a recently reported Au(I) vinylidene, the key resonances of the α- and β-carbon of the vinylidene ligand could not be detected despite extended acquisition. ¹³C labeling was needed to identify two broad multiplets at 206 and 112 ppm for this vinylidene fragment.[10]

Unequivocal evidence for the participation of a Pt(II)-vinylidene in the formation of complex **6** was provided by isotopic labelling studies using C₂D₂. The newly formed allyl moiety of **6-d₂** contained two D atoms bound to a terminal allyl carbon atom. Furthermore, the use of C₂D₂ yielded a kinetic isotope effect k_H/k_D of 2.7 ± 0.3 suggesting that acetylene C—H bond cleavage was involved in the rate-determining step.

Computational studies at the DFT M06/6-31g(d,p)/SDD level were developed and two mechanistic routes were explored, namely, migratory insertion of the coordinated C₂H₂ molecule of **5** into the Pt—Me bond and a 1,2-hydrogen shift within the η²-bound alkyne. Δ$G^{\ddagger,DCM}$ values of 26.1 kcal·mol⁻¹ and 19.4 kcal·mol⁻¹ were respectively found (Figure 2).[32] The latter path led in its first elemental step to the vinylidene ligand of intermediate **A**, with energy only 6.5 kcal·mol⁻¹ above **5**. Fast CH₃ migration to the Pt=C bond (Δ$G^{\ddagger,DCM}$ = 5.9 kcal·mol⁻¹ from **A**) yields a second intermediate **B** that originates **6** after a facile, Pt-assisted H migration from CH₃ to the central Pt-bonded

carbon atom. The overall energy return $\Delta G^{0,DCM}$ is of 40.9 kcal·mol^{-1}. The calculations support therefore that the vinylidene route to the η^3-allyl complex **6** is preferred over the classical migratory insertion reactivity.
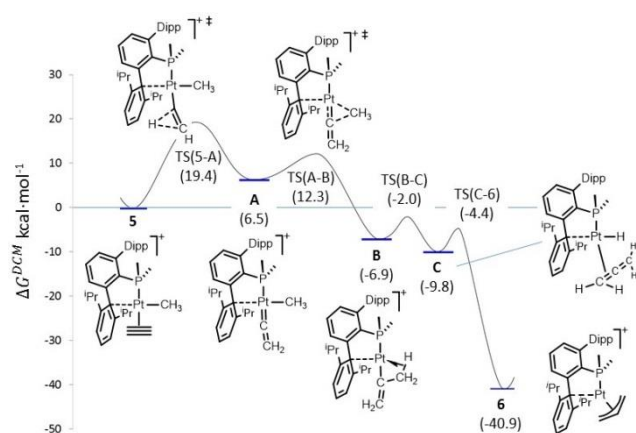
Figure 2. Free energy profile for the transformation of **5** to **6** via acetylene to vinylidene tautomerization.

The small energy difference computed for the tautomeric structures **5** and **A** (6.5 kcal·mol^{-1}) is rather intriguing. To gain further information, the donor-acceptor properties of the C_2H_2 and vinylidene ligands of **5** and **A** were analyzed by means of the Energy Decomposition Analysis (EDA; Table 1)[33] and Natural Orbital for Chemical Valence (NOCV) schemes.[34] For the sake of completeness, the Pt—C_2H_4 linkage of complex **4** was also investigated computationally. The results of this analysis confirm that the $C=CH_2$ ligand has the largest fragment interaction energy (ΔE_{int}: -72.2 vs. -32.5 (η^2-C_2H_4) and -31.6 (η^2-C_2H_2) kcal·mol^{-1}). The Pt(II)-vinylidene interaction has a strong electrostatic component (see Table 1 and the Supporting Information for further details)[7a,35] and it is largely responsible for the accessibility of the vinylidene isomer under mild conditions ($\Delta(\Delta E_{int})$ between η^2-HC≡CH and :$C=CH2$ coordination amounts 40.6 kcal·mol^{-1}).

Table 1. EDA analysis of the [Pt]-η^2-C_2H_4, [Pt]-η^2-C_2H_2 and [Pt]=$C=CH_2$ interactions in **4**, **5** and **B** optimized at the BP86/TZP level imposing Cs symmetry.

	[Pt]- η^2-C_2H_4	[Pt]- η^2-C_2H_2	[Pt]=$C=CH_2$
ΔE_{int} [a]	-32.5	-31.6	-72.2
ΔE_{Pauli}	148.0	153.2	267.3
ΔE_{elstat} [b]	-106.7 (59.1%)	-110.2 (59.6%)	-218.6 (64.4%)
ΔE_{orb} [b]	-73.8 (40.9%)	-74.6 (40.4%)	-120.9 (35.6%)
ΔE(A')[c]	-47.61 (64.6%)	-45.8 (61.3%)	-103.3 (85.4%)
ΔE(A'')[c]	-26.14 (34.4%)	-28.9 (38.7%)	-17.7 (14.6%)

[a] kcal·mol^{-1}; [b] Percentage of electrostatic/covalent contribution to the attractive interactions; [c] Percentage contribution to the orbital interactions.

In conclusion, this work proves that the electrophilic Pt(II) center of the cationic methyl-acetylene complex **5**, readily accessible from **2·S** and C_2H_2, induces a C—C bond forming reaction through an isomeric methyl-vinylidene structure in preference to classical migratory insertion reactivity.

[1] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169; b) D. S. McGuinness, *Chem. Rev.* **2011**, *111*, 2321; c) J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236.

[2] a) M. Joost, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2015**, *54*, 15022; b) J. J. Verendel, O. Pàmies, M. Diéguez, P. G. Andersson, *Chem. Rev.* **2014**, *114*, 2130; c) W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg, M. Brookhart, *Science* **2009**, *326*, 553.

[3] a) J. Carreras, M. Patil, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2012**, *134*, 16753; b) C. Hahn, M. Miranda, N. P. B. Chittineni, T. A. Pinion, R. Perez, *Organometallics* **2014**, *33*, 3040; c) R. Dorel, A. M. Echavarren, *Chem. Rev.* **2015**, *115*, 9028.

[4] a) R. Romeo, G. D'Amico, E. Sicilia, N. Russo, S. Rizzato, *J. Am. Chem. Soc.* **2007**, *129*, 5744; b) R. J. Puddephatt, *Coord. Chem. Rev.* **2001**, *219-221*, 157.

[5] a) L. Johansson, M. Tilset, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2000**, *122*, 10846; b) J. S. Owen, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2006**, *128*, 20056; c) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; d) U. Fekl, K. I. Goldberg, in *Advances in Inorg. Chem. , Vol. 54*, Academic Press, **2003**, p. 259.

[6] a) M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398; b) S. H. Crosby, G. J. Clarkson, J. P. Rourke, *Organometallics* **2011**, *30*, 3603; c) W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca, P. Rigo, *Angew. Chem. Int. Ed.* **2003**, *42*, 105; d) O. Rivada-Wheelaghan, M. Roselló-Merino, J. Díez, C. Maya, J. López-Serrano, S. Conejero, *Organometallics* **2014**, *33*, 5944; e) J. L. Spencer, G. S. Mhinzi, *J. Chem. Soc, Dalton Trans.* **1995**, 3819.

[7] a) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; b) A. R. Chianese, S. J. Lee, M. R. Gagné, *Angew. Chem. Int. Ed.* **2007**, *46*, 4042; c) C. Hahn, *Chem. Eur. J.* **2004**, *10*, 5888.

[8] a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197; b) C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 21763; c) C. Bianchini, M. Peruzzini, A. Vacca, F. Zanobini, *Organometallics* **1991**, *10*, 3697; d) F. De Angelis, S. Fantacci, A. Sgamellotti, *Coord. Chem. Rev.* **2006**, *250*, 1497; e) V. Cadierno, M. P. Gamasa, J. Gimeno, *Coord. Chem. Rev.* **2004**, *248*, 1627; f) Y. Wakatsuki, *J. Organomet. Chem.* **2004**, *689*, 4092.

[9] a) J. M. Lynam, *Chem. Eur. J.* **2010**, *16*, 8238; b) O. J. S. Pickup, I. Khazal, E. J. Smith, A. C. Whitwood, J. M. Lynam, K. Bolaky, T. C. King, B. W. Rawe, N. Fey, *Organometallics* **2014**, *33*, 1751; c) M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, M. A. Ortuño, G. Ujaque, A. Lledós, *Inorg. Chem.* **2013**, *52*, 8919; d) H. Werner, *Coord. Chem. Rev.* **2004**, *248*, 1693.

[10] R. J. Harris, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2015**, *54*, 6867.

[11] a) U. Belluco, R. Bertani, F. Meneghetti, R. A. Michelin, M. Mozzon, *J. Organomet. Chem.* **1999**, *583*, 131; b) U. Belluco, R. Bertani, R. A. Michelin, M. Mozzon, *J. Organomet. Chem.* **2000**, *600*, 37; c) U. Belluco, R. Bertani, R. A. Michelin, M. Mozzon, F. Benetollo, G. Bombieri, R. J. Angelici, *Inorg. Chim. Acta* **1995**, *240*, 567; d) M. Rashidi, R. J. Puddephatt, *J. Am. Chem. Soc.* **1986**, *108*, 7111.

[12] a) T. G. Appleton, M. H. Chisholm, H. C. Clark, K. Yasufuku, *J. Am. Chem. Soc.* **1974**, *96*, 6600; b) S. Carlisle, A. Matta, H. Valles, J. B. Bracken, M. Miranda, J. Yoo, C. Hahn, *Organometallics* **2011**, *30*, 6446; c) B. E. Cowie, D. J. H. Emslie, *Chem. Eur. J.* **2014**, *20*, 16899.

[13] a) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27; b) J. F. Hartwig, *Acc. Chem. Res.* **2008**, *41*, 1534; c) C. A. Fleckenstein, H. Plenio, *Chem. Soc. Rev.* **2010**, *39*, 694; d) M. Alcarazo, *Chem. Eur. J.* **2014**, *20*, 7868.

[14] a) J. Campos, R. Peloso, E. Carmona, *Angew. Chem. Int. Ed.* **2012**, *124*, 8380; b) J. Campos, L. Ortega-Moreno, S. Conejero, R. Peloso, J. López-Serrano, C. Maya, E. Carmona, *Chem. Eur. J.* **2015**, *21*, 8883.

[15] a) M. L. Scheuermann, K. A. Grice, M. J. Ruppel, M. Rosello-Merino, W. Kaminsky, K. I. Goldberg, *Dalton Transactions* **2014**, *43*, 12018; b) H. Grützmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 1814; c) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680; d) H. Werner, *Dalton Transactions* **2003**, 3829.

[16] a) L. Ortega-Moreno, R. Peloso, C. Maya, A. Suarez, E. Carmona, *Chem. Commun.* **2015**, *51*, 17008; b) L. Ortega-Moreno, M. Fernández-Espada, J. J. Moreno, C. Navarro-Gilabert, J. Campos, S. Conejero, J. López-Serrano, C. Maya, R. Peloso, E. Carmona, *Polyhedron* **2016**, *116,* 170.

[17] H. Braunschweig, P. Brenner, R. D. Dewhurst, J. O. C. Jimenez-Halla, T. Kupfer, D. Rais, K. Uttinger, *Angew. Chem. Int. Ed.* **2013**, *52*, 2981.

[18] R. G. Goel, R. C. Srivastava, *Can. J. Chem.* **1983**, *61*, 1352.

[19] a) M. Benedetti, V. Lamacchia, D. Antonucci, P. Papadia, C. Pacifico, G. Natile, F. P. Fanizzi, *Dalton Transactions* **2014**, *43*, 8826; b) F. P. Fanizzi, G. Natile, M. Lanfranchi, A. Tiripicchio, G. Pacchioni, *Inorg. Chim. Acta* **1998**, *275/276*, 500.

[20] A. Falceto, E. Carmona, S. Alvarez, *Organometallics* **2014**, *33*, 6660.

[21] M. D. Butts, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.* **1996**, *118*, 11831.

[22] J. J. Adams, N. Arulsamy, D. M. Roddick, *Organometallics* **2009**, *28*, 1148.

[23] M. Black, R. H. B. Mais, P. G. Owston, *Acta Cryst. B* **1969**, *25*, 1753.

[24] a) M. Fusto, F. Giordano, I. Orabona, F. Ruffo, A. Panunzi, *Organometallics* **1997**, *16*, 5981. b) M. Green, *J. Organomet. Chem.* **1986**, *300*, 93; c) M. Bottrill, M. Green, *J. Am. Chem. Soc.* **1977**, *99*, 5795.

[25] H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378.

[26] B. G. Anderson, J. L. Spencer, *Chem. Eur. J.* **2014**, *20*, 6421.

[27] P. Ganis, I. Orabona, F. Ruffo, A. Vitagliano, *Organometallics* **1998**, *17*, 2646.

[28] M. Shiotsuki, P. S. White, M. Brookhart, J. L. Templeton, *J. Am. Chem. Soc.* **2007**, *129*, 4058.

[29] a) S. White, B. L. Bennett, D. M. Roddick, *Organometallics* **1999**, *18*, 2536; b) S. Basu, N. Arulsamy, D. M. Roddick, *Organometallics* **2008**, *27*, 3659.

[30] C. Hahn, P. Morvillo, E. Herdtweck, A. Vitagliano, *Organometallics* **2002**, *21*, 1807.

[31] L. Cavallo, A. Macchioni, C. Zuccaccia, D. Zuccaccia, I. Orabona, F. Ruffo, *Organometallics* **2004**, *23*, 2137.

[32] The barrier for insertion of C_2H_4 in **4** is significantly higher at 33.6 kcal·mol^{-1} in agreement with the relative inertness of this complex.

[33] a) Morokuma, K. J. Chem. Phys. **1971**, *55*, 1236; b) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

[34] M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962.

[35] a) M. S. Nechaev, V. M. Rayon, G. Frenking, *J. Phys. Chem. A.*, **2004**, *108*, 3134; b) C. Massera, G. Frenking, *Organometallics* **2003**, *22*, 2758; c) S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.*, **1998**, *4*, 1428; d) G. Frenking, M. Solà, S. F. Vyboishchikov, *J. Organomet. Chem.*, **2005**, *690*, 6178.

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Layout 1:

COMMUNICATION

The cationic complex $[PtMe(S)(PMe_2Ar^{Dipp_2})]^+$ reacted with acetylene to yield the allyl complex $[Pt(\eta^3-C_3H_5)(PMe_2Ar^{Dipp_2})]^+$, formally the product of a classical migratory insertion reaction. Nevertheless, deuteration experiments with C_2D_2 and kinetic and theoretical investigations demonstrated that the transformation occurred *via* a Pt(II)-promoted $HC\equiv CH$ to $:C=CH_2$ tautomerization.

acetylene to vinylidene tautomerization at Pt(II)
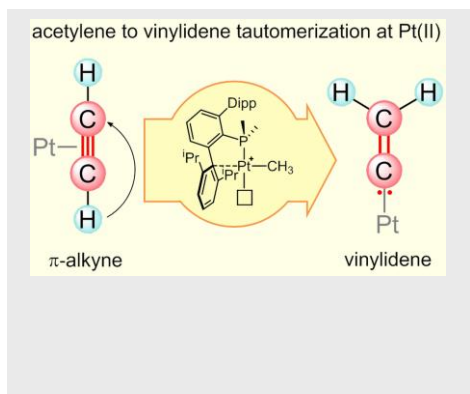
L. Ortega-Moreno, R. Peloso, J. López-Serrano, Javier Iglesias-Sigüenza, C. Maya and E. Carmona*

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A Cationic Unsaturated Platinum(II) Complex that Promotes the Tautomerization of Acetylene to Vinylidene