

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

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Dedication ((optional))

Abstract: Complex [PtMe₂(PMe₂Ar^{Dipp})₂] (1) that contains a tethered terphenyl phosphine (Ar^{Dipp} = 2,6-(2,6-ⁱPr₂C₆H₃)₂C₆H₃) reacts with [H(Et₂O)₂]BAR_F (BAR_F⁻ = B[3,5-(CF₃)₂C₆H₃]₄⁻) to give the solvent complex [PtMe(S)(PMe₂Ar^{Dipp})₂]⁺ (2-S). Although the solvent molecule was easily displaced by a Lewis base (e.g. CO and C₂H₄) to afford the corresponding adducts, treatment of 2-S with C₂H₂ yielded instead the allyl complex [Pt(η³-C₃H₅)(PMe₂Ar^{Dipp})₂]⁺ (6) via the alkyne intermediate [PtMe(η²-C₂H₂)(PMe₂Ar^{Dipp})₂]⁺ (5). Deuteration experiments with C₂D₂ and kinetic and theoretical investigations demonstrated that the conversion of 5 into 6 involved a Pt(II)-promoted HC≡CH to :C=CH₂ tautomerization in preference over acetylene migratory insertion into the Pt-Me bond.

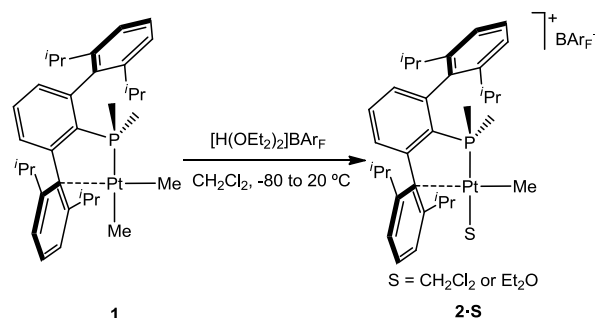
Cationic organometallic complexes are valuable reagents that find numerous applications in catalysis.^[1-3] Low-coordinate cationic methyl derivatives of Pt(II) are of particular importance, for they combine high metal electrophilicity with the accessible coordination sites and the intrinsic reactivity 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)(κ²-P,C-PMe₂Ar^{Dipp})₂]⁺ (2-S), that features bidentate coordination of the bulky phosphine, PMe₂Ar^{Dipp} (Dipp = 2,6-ⁱPrC₆H₃; Ar^{Dipp} = 2,6-(2,6-

ⁱPrC₆H₃)₂C₆H₃).^[15,16] Although complex 2-S is not truly a low-coordinate species,^[17] it exhibits a weakly-bonded molecule of solvent (S = H₂O, Et₂O, THF) and a labile Pt...C_{arene} interaction. Therefore it could be viewed as a source of the two-ligand Pt fragment [PtMe(PMe₂Ar^{Dipp})₂]⁺, for which rich electrophilic reactivity can be foreseen. While no C—C bond formation was observed for C₂H₄ under ambient conditions, C₂H₂ yielded initially an unprecedented^[18,19] [PtMe(η²-C₂H₂)(PMe₂Ar^{Dipp})₂]⁺ complex (5), that experienced facile C—C coupling to afford the π-allyl complex [Pt(η³-C₃H₅)(PMe₂Ar^{Dipp})₂]⁺ (6). The use of C₂D₂ provided unequivocal proof for a CH≡CH to :C=CH₂ tautomerism induced by the Pt(II) center, also supported by computational studies.

Protonation (CD₂Cl₂, -80 °C) of complex 1 that features κ²-P,C phosphine coordination^[20] (see the Supporting Information) with [H(Et₂O)₂]BAR_F (BAR_F⁻ = B[3,5-(CF₃)₂C₆H₃]₄⁻) did not permit observation of a transient σ-CH₄ complex.^[22] Liberation of CH₄ occurred instead with formation of complexes [PtMe(S)(PMe₂Ar^{Dipp})₂]⁺ (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 °C,^[21] although below -10 °C the molecular structure became rigid on the NMR time scale. The Dipp rings give rise below 25 °C to two septets (2.38 and 2.28 ppm in C₂D₂Cl₄) and four doublets (between 1.52 and 1.06 ppm) for the ⁱPr substituents. At higher temperatures (Figure S12) the two rings become equivalent (above 110 °C; ΔG[‡] = 19 ± 2 kcal·mol⁻¹ at the coalescence temperature of 100 °C).



Scheme 1. Generation of complexes 2-S.

Single crystals of 2-S could only be obtained after prolonged cooling at -20 °C of CH₂Cl₂/Et₂O solutions of the complex. Adventitious H₂O originated crystals of the aquo complex [PtMe(H₂O)(PMe₂Ar^{Dipp})₂]BAR_F 2-H₂O in preference to those of 2-Et₂O or 2-CH₂Cl₂. The H₂O 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

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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^{Dipp})₂]⁺ fragment.

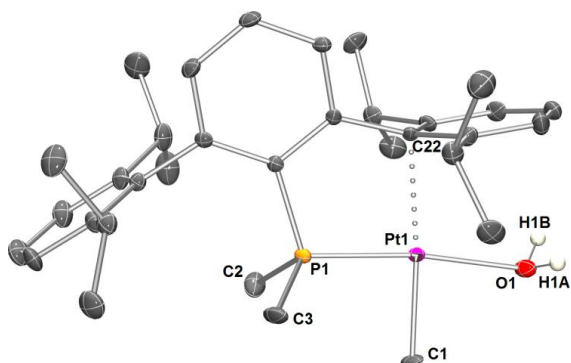


Figure 1. ORTEP view of the cation of complex **2·H₂O**; most hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 40% level probability. Selected bond distances (Å) and angles (°): Pt1–O1 2.143(4), Pt1–C1 2.034(6), Pt1–P1 2.170(1), Pt1–C22 2.348(5), O1–Pt1–C1 83.2(2), C1–Pt1–P1 89.6(2), P1–Pt1–C22 83.9(1), C22–Pt1–O1 103.1(2).

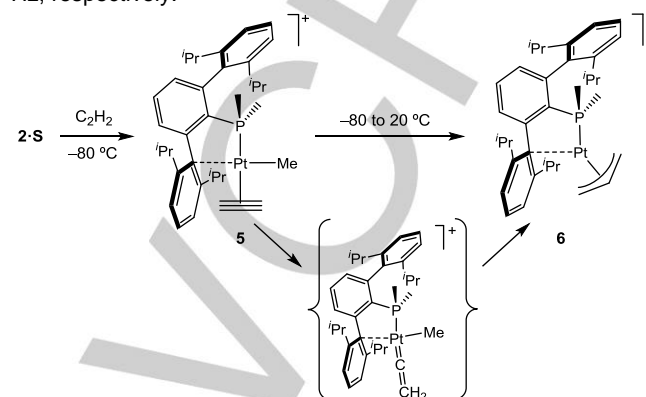
We sought empirical evidence for the electron density at the Pt(II) center of **2·S** by carrying out its reaction with CO. Treatment of **2·S** with CO (2 bar, 20 °C) gave the carbonyl complex [PtMe(CO)(PMe₂Ar^{Dipp})₂]⁺ (**3**), with a κ²-P,C tethered phosphine in a structure akin to **2·S**. Its carbonyl 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)(NⁱN^j)₂]⁺^[25] and recently reported [Pt(PCP)(CO)]⁺ derivatives^[26] have $\tilde{\nu}(\text{CO})$ 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^{Dipp})₂]⁺ (**4**), exhibiting once again chelating κ²-P,C phosphine ligation. The Pt–C₂H₄ linkage undergoes fast C₂H₄ rotation at 20 °C, with a barrier $\Delta G^\ddagger = 11 \pm 1$ kcal·mol⁻¹ at the coalescence temperature of 25 °C (Figure S13). It also experiences associative exchange with excess free C₂H₄ (EXSY NMR between 0 and 25 °C, $\Delta G^\ddagger = 16 \pm 2$ 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, $\Delta\delta$, of nearly –21 ppm. For comparison, in dicationic [Pt(PNP)(C₂H₄)₂]²⁺, $\Delta\delta = -45$ 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 °C 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 °C (see the Supporting Information). Related diimine Pt catalysts required heating for 2 days at 100 °C.^[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^{Dipp})₂]⁺ (**6**), through the intermediacy of the π-C₂H₂ compound [PtMe(η²-C₂H₂)(PMe₂Ar^{Dipp})₂]⁺ (**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 °C, forming adduct **5** that features a ³¹P{¹H} resonance at 11.5 ppm, with a ¹J_{Pt} of 4282 Hz. This species contains Pt–Me (δ 0.60, ³J_{HP} = 3 Hz, ²J_{HP} = 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_{HP} = 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 °C 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 °C. It contains an intact Pt–Me unit, as hinted by a ¹H NMR resonance at δ 0.43 ppm (²J_{HP} = 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. $\Delta G^{\ddagger, \text{DCM}}$ 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 ($\Delta G^{\ddagger, \text{DCM}} = 5.9$ 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.

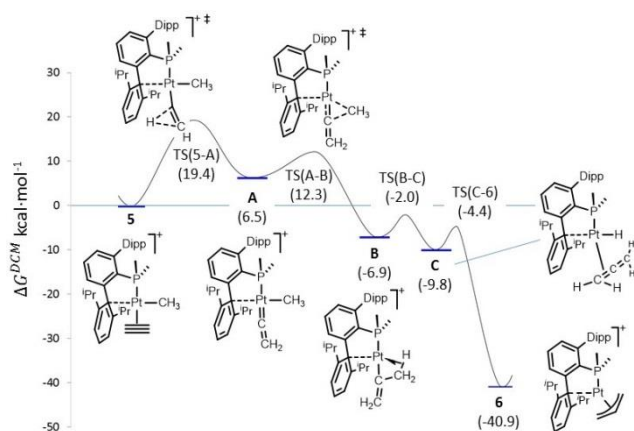


Figure 2. Free energy profile for the transformation of **5** to **6** via acetylene to vinylidene tautomerization.

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 C₂H₂ 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—C₂H₄ linkage of complex **4** was also investigated computationally. The results of this analysis confirm that the C=CH₂ ligand has the largest fragment interaction energy (ΔE_{int} : -72.2 vs. -32.5 (η^2 -C₂H₄) and -31.6 (η^2 -C₂H₂) 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 ($\Delta(\Delta E_{\text{int}})$ between η^2 -HC≡CH and :C=CH₂ coordination amounts 40.6 kcal·mol⁻¹).

Table 1. EDA analysis of the [Pt]- η^2 -C₂H₄, [Pt]- η^2 -C₂H₂ and [Pt]=C=CH₂ interactions in **4**, **5** and **B** optimized at the BP86/TZP level imposing Cs symmetry.

	[Pt]- η^2 -C ₂ H ₄	[Pt]- η^2 -C ₂ H 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%)
$\Delta E(A')$ ^[c]	-47.61 (64.6%)	-45.8 (61.3%)	-103.3 (85.4%)
$\Delta E(A'')$ ^[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 C₂H₂, induces a C—C bond forming reaction through an isomeric methyl-vinylidene structure in preference to classical migratory insertion reactivity.

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Keywords: phosphane ligands • π -acid complex • vinylidenes • platinum • DFT

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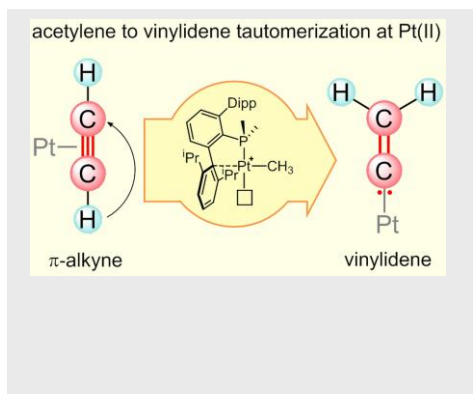
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Layout 1:

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The cationic complex $[\text{PtMe}(\text{S})(\text{PMe}_2\text{Ar}^{\text{Dipp}})]^+$ reacted with acetylene to yield the allyl complex $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)(\text{PMe}_2\text{Ar}^{\text{Dipp}})]^+$, 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 $\text{HC}\equiv\text{CH}$ to $:\text{C}=\text{CH}_2$ tautomerization.



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