COMMUNICATION

Electrophilic activation of alkynes promoted by a cationic alkylidene complex of Pt(II)

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Pt(II) alkylidene 1a has been reacted with terminal alkynes to afford ylide complexes 3a-d, resulting from electrophilic activation of the C≡C bond and its insertion into the platinacyclic fragment of 1a that contains the carbene functionality. DFT calculations indicate that the observed regioselectivity is determined by the nucleophilic attack of the alkyne to the alkylidene carbon.

Non-heteroatom stabilised alkylidene complexes of group 10 metals are in general elusive organometallic molecules, as witnessed by the small number of well-defined species of this class that have been reported to date.[1] The design of a suitable molecular scaffold that provides steric protection to the $M=CR_2$ fragment has been crucial for their stabilisation and, with the exception of Templeton's Pt(IV) methylidene complex supported by a tris(pirazolyl)borate ligand,[2] chelating P-donating ligands of high steric demand have proved effective for this purpose. Noticeably, the satisfactorily characterised non-heretoatom-substituted alkylidene complexes of Pt(II) and Pt(0) (Chart 1) bear di(isopropyl)-substituted phosphines as ancillary ligands, and were reported only recently by some of us in 2012,[3] and some years later by Iluc[4] and Piers.[5]

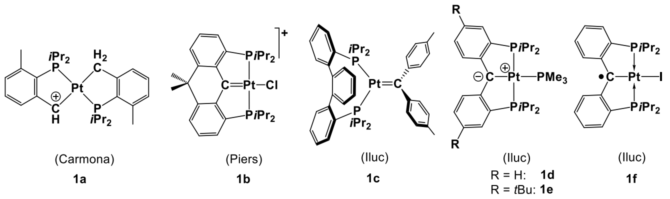

Chart 1 Known carbenes of Pt(II) and Pt(0) with no heteroatomic stabilization. Representation of the Pt—$C_{carbene}$ bond has been chosen in accord with the original reports or to emphasise the character of the carbon atom in terms of reactivity.

To date, the reactivity of the carbene complexes shown in Chart 1 remains mostly undisclosed. The behaviour of the cationic species **1a**[3,6] and **1b**[5] was assayed towards P-, N-, and C-donating neutral Lewis bases, dihydrogen, ethyldiazoacetate, and $PhICl_2$, the latter permitting the isolation of a Pt(IV) alkylidene from **1b** by formal oxidative addition of Cl_2. Complex **1c** was found to react with CH_3I and SiH_2Ph_2,[4a] whereas treatment of **1d** with I_2 afforded the paramagnetic alkylidene complex **1f**.[4b] To the best of our knowledge, there are no other studies on the reactivity of this class of compounds.

The previously reported experiments on the reactivity of complex **1a** confirmed its carbenic structure and its expected electrophilicity.[3,6] In view of the importance of electrophilic Pt(II) alkylidenes in catalytic organic transformations involving unsaturated hydrocarbons,[7] we decided to explore the reactivity of complex **1a** towards alkynes. In this contribution we describe, experimentally and theoretically, the stoichiometric activation of terminal alkynes promoted by the alkylidene complex **1a**, which results in the unprecedented formation of a cyclic allyl-phosphonium zwitterionic ligand in the coordination environment of the Pt(II) centre. We are not aware of earlier contributions on the reactivity of non-heteroatom-stabilised carbene complexes of platinum with unsaturated hydrocarbons.

The carbene complex **1a** was generated by stoichiometric addition of tritylium tetrafluoroborate or hexafluorophosphate to a dichloromethane solution of the bis(cyclometallated) complex **2** at low temperature (Scheme 1).[3] The reaction occurred with selective abstraction of a hydride anion from the Pt—CH_2 fragment, provoking a drastic colour change of the solution from pale yellow to dark green. After a few minutes, addition of 1 equivalent of a terminal alkyne RC≡CH (R = Ph, *t*Bu, *n*Bu) resulted in the gradual disappearance of the green colour to the final pale yellow. The $^{31}P\{^1H\}$ NMR spectrum of the crude revealed that a selective reaction had taken place with quantitative consumption of the alkylidene complex **1a**, responsible for a typical AB pattern centred at *ca.* 80 ppm ($^2J_{AB}$ = 351 Hz). Concomitant formation of a new product associated to two well-defined doublets at *ca.* 80 and 40 ppm with a J_{PP} of 14-15 Hz and ^{195}Pt-^{31}P couplings of *ca.* 3800 and 80-90 Hz, respectively, was also detected. The dramatic change in the

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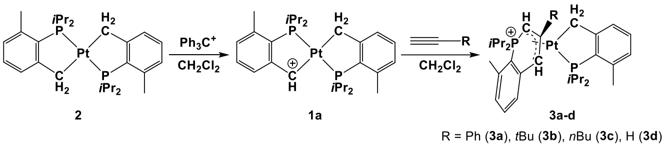
$^{31}P\{^1H\}$ NMR spectrum indicated that one of the P-donor atoms of **1a** was pulled out from the coordination sphere of the platinum centre with maintenance of certain proximity with both the metal centre and the Pt-bonded phosphorus nucleus, thus accounting for the observed scalar couplings. Evaporation of the volatiles and washing the solid residue with diethylether allowed the isolation of complexes **3a-c** with tetrafluoroborate or hexafluorophosphate counteranions as air stable colourless solid materials. Crystalline samples of complexes **3a-c** were analysed by X-ray diffraction methods, which permitted to ascertain their molecular structures as the cationic allyl-phosphonium complexes shown in Scheme 1.



Scheme 1 Synthesis of the cationic complexes **3a-d** by reaction of the alkylidene complex **1a** with terminal alkynes.

The reaction of **1a** with acetylene yielded **3d** as the main product, although the formation of unidentified species in considerable amounts did not permit its isolation as a pure solid material. Nevertheless, the presence of two doublets in the $^{31}P\{^1H\}$ NMR of the crude at 80.0 ($^3J_{PP}$ = 14 Hz, $^1J_{PPt}$ = 3855 Hz) and 34.0 ($^3J_{PP}$ = 14 Hz, $^2J_{PPt}$ = 80 Hz) ppm indicated unequivocally the formation of the expected insertion product, **3d**. Analogous reactions with some internal alkynes (3-hexyne, diphenylacethylene, diethyl acethylenedicarboxylate) were also attempted but no insertion products were detected, most probably for steric reasons. Besides, treatment of **1a** with the electron-rich alkyne 4-ethynylanisole, afforded a complex mixture of unidentified products, which was no further investigated.

Some relevant features of the ^1H- and $^{13}C\{^1H\}$ NMR spectra of complex **3a** will be discussed. Diagnostic resonances at 6.08 (C-C*H*-C) and 3.73 ppm (C-C*H*-P) due to the allylic methynes appear in the ^1H NMR spectrum of **3a** as an apparent triplet with $^4J_{HH} \approx {}^3J_{HP} \approx 2$ Hz and a doublet of doublet of doublets with satellites with $^4J_{HH}$ = 2.0 Hz, $^2J_{PH}$ = 8.0 Hz, $^3J_{PH}$ = 5.0 Hz, and $^2J_{PtH}$ = 18.4 Hz, respectively. The diasterotopic protons of the Pt-bonded methylene originate two well-defined doublets with ^{195}Pt satellites at 4.30 and 4.05 ppm ($^2J_{HH}$ = 16.3 Hz, $^2J_{PtH}$ = 102.8 and 93.5). The ^{13}C nuclei of the coordinated allyl group give rise to a singlet at 107.0 ppm (quaternary C-Ph), a doublet with satellites at 72.1 ppm (benzylic CH, $^1J_{CPt}$ = 24 Hz, $^2J_{CP}$ = 8 Hz) and a doublet of doublets at 27.7 ppm (CH-P, $^1J_{CP}$ = 64 Hz, $^2J_{CP}$ = 46 Hz).

The molecular structures of compounds **3a** and **3c** in the solid state, as representative examples of complexes **3**, are depicted in Fig. 1.

Both complexes possess a distorted square planar geometry with the platinacyclic fragment resulting from the metalation of the P*i*Pr$_2$Xyl almost unaltered with respect to the parent complex **2**.[6] Nevertheless, a slight contraction of the Pt—CH$_2$ bond distance in **3a** and **3c** compared to **2** is observed, as a consequence of the decreased *trans* influence of the η^3-allyl ligand. The plane defined by the three *sp*^{2} carbon atoms of the allyl group describes angles of *ca.* 70-80° with the coordination plane. The 6-membered ring generated by the insertion of the alkyne into the platinacycle is almost planar, with the central carbon atom of the allyl group lying at *ca.* 0.2 Å from the calculated middle plane.

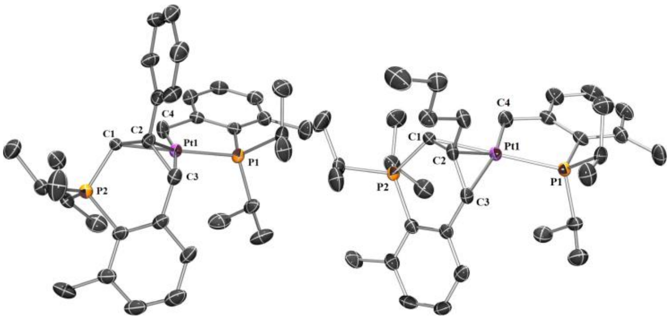
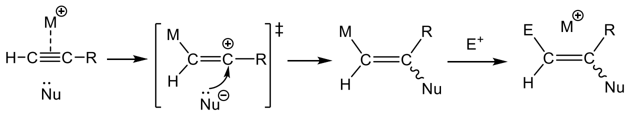


Fig. 1 Ortep views (50% thermal probability; H atoms omitted for clarity) of the molecular structure of one of the two independent cations in the asymmetric unit of complex **3a** (left) and the cationic complex **3c** (right). Selected bond distances (Å) and angles (°) for **3a**: Pt1-P1 2.250(1), Pt1-C1 2.172(5), Pt1-C2 2.158(5), Pt1-C3 2.301(5), Pt1-C4 2.061(6), C1-C2 1.446(8), C2-C3 1.390(8); C4-Pt1-P1 83.4(2), P1-Pt1-C3 109.3(1), C1-Pt1-C3 65.8(2), C1-Pt1-C4 101.6(2). For **3c**: Pt1-P1 2.248(1), Pt1-C1 2.186(4), Pt1-C2 2.137(4), Pt1-C3 2.314(4), Pt1-C4 2.075(5) C1-C2 1.443(5), C2-C3 1.400(5); C4-Pt1-P1 83.5(1), P1-Pt1-C3 108.3(1), C1-Pt1-C3 65.5(1), C1-Pt1-C4 103.3(2).

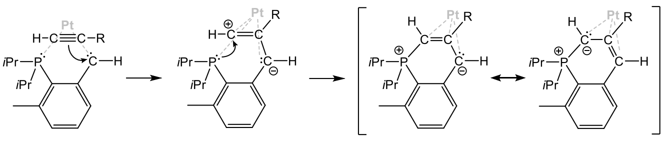
Complexes **3** result from the regioselective coupling of the terminal alkyne HC≡CR with the platinacyclic moiety of complex **1a** that contains the carbenic group. Such interaction creates a new six-membered cyclic structure and involves the formation of two new bonds, namely a P-*CH* bond leading to a phosphonium functionality, and a HC-*CR* bond between the alkylidene CH and the substituted carbon atom of the alkyne. The overall result of the process is the formation of a zwitterionic allyl ligand which binds the Pt(II) centre in a typical non-symmetric η^3-coordination mode.

Alkynes are electron-rich molecules which are prone to react with a variety of electrophiles, as dihalogens, hydrogen halides, boranes etc., following the Markovnikov rule. In such transformations, they exhibit a strong preference to generate the "more stable" carbocation as the key reaction intermediate and, eventually, the more substituted alkene as the reaction product. Text-book functionalization of alkynes catalysed by metal cations, *e.g.* the Hg(II) catalysed hydration, occurs as a consequence of the attack of a nucleophile onto the coordinated triple bond, passing through the formation of an incipient carbocation at the more substituted *sp*-carbon (Scheme 2).[8]



Scheme 2 General mechanism for the functionalization of alkynes catalyzed by metal cations. For M = Hg^{2+}, E-Nu = H-OH, it describes the mercury-catalyzed hydration of alkynes.

On the contrary, the process reported herein seemingly involves the nucleophilic attack at the terminal carbon atom of the alkyne (Scheme 3). The reason for this unexpected regioselectivity lies reasonably in the high steric demand of the phosphorus nucleophile and in the ability of the Pt(II) centre to stabilise the terminal carbocationic intermediate, which can be actually described as an alkylidene complex (*vide infra*).[1]



Scheme 3 Alleged mechanism for the coupling of terminal alkynes with the platinacyclic alkylidene fragment of **1a**.

We investigated the reaction of the cation **1a** with phenylacetylene by DFT methods, (SMD(dichloromethane)-ωB97XD/6-31g(d,p)/SDD level).[9] Several initial geometries were considered for the attack of the alkyne to the metal complex, with the calculations indicating a preference for direct interaction with the carbenic carbon, without explicit involvement of the metal. Insertion of the triple bond of the alkyne into the platinum—carbenic carbon bond has an overall barrier ($\Delta G^{\ddagger}$) of 15.0 kcal·mol^{-1} (Fig. 2), and occurs through a multistep process, in which initial intermolecular nucleophilic addition[10] of the alkyne affords a C—C bond between the alkyne's terminal ≡*C*H and the carbenic carbon to yield **A** (ΔG^{o} = + 3.4 kcal·mol^{-1}). This is at odds with the involvement of the internal RC≡ alkyne carbon implied in the alleged mechanism of Scheme 3. In view of the unexpected regioselectivity of the reaction, we also investigated the attack of the internal carbon of the alkyne to the carbenic carbon, but all attempts failed or resulted in rotamers of **A** (see below, and the SI for details). Natural Bonding Orbital[11] (NBO) analysis of **1a** and the transition state, **TS1**, for this transformation reveals NBO charges of +0.33 and -0.20 e^{-} for the Pt and the carbenic C atoms of **1a**, while other partial charges schemes offer inconsistent polarization pictures for this bond (Table S6).[12] Irrespective of the overall polarisation of the Pt—carbene bond the reactivity of the carbenes has been ascribed to the polarization of the σ and π components of the M=C bond, with Fisher-carbenes having a greater percentage of carbon character in the σ component and greater metal character in the π component.[13] In our case, the platinum character for the σ and π contributions in **1a** are 33.1% and 85.2% respectively,[14] which depicts a low degree of multiple bond character for the Pt=CH linkage and agrees with such formulation.[15]

Consistent with the above, the NBO analysis also indicates that the new C—C bond is the result of delocalization of π electron density of the alkyne's C≡C bond onto the vacant *p* orbital of the carbenic carbon (Fig. 3), and forms at the expense of the π-interaction between this carbon and the platinum, which involves the same *p* orbital. This is reflected in a reduction of the Wiberg bond order from 0.77 in the cation **1a** to 0.52 at **TS1** (*v*. 0.45 and 0.49 for the Pt—CH$_2$ bond).[16] A similar picture was obtained using a mechanistic analysis method based on the evolution of the centroids of localized orbitals (Boys-Foster) along the reaction coordinate (Fig. S2 and S3).[17]

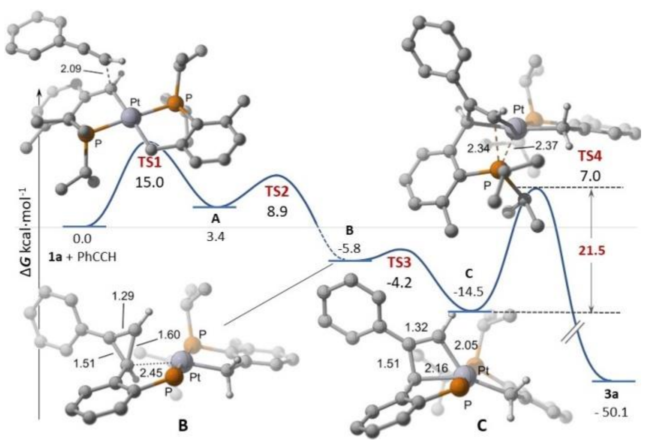


Fig. 2 Free energy profile in dichloromethane for the formation of **3a** from **1a**. Optimized geometries of relevant intermediates and transition states are also included (most H atoms omitted for clarity; distances are in Å).

While the formation of **A** is endergonic, it evolves through a low energy barrier, **TS2**, to intermediate **B** with an overall energy return from **1a** + phenylacetylene of 5.8 kcal·mol^{-1}. **B** features a significantly elongated Pt—C bond, from 1.97 Å in **1a** to 2.45 Å, as the result of back donation from the Pt—C carbenic σ bond to one π antibonding orbital of the alkyne moiety (see the SI). This situation is reminiscent of the activation of dihydrogen by **1a** reported by some of us,[6] in which H—H activation occurs at the Pt*C*H carbon, with concomitant cleavage of the Pt-carbon bond. However, while this H—H activation is related to the TM-catalysed C—H bond activation and C—C bond formation in reactions between alkanes and diazocompounds,[18] in the present case the dominant interactions involve the C≡C electron density. Thus, this situation is alike to that taking place in Rh-catalysed cyclopropenation of alkynes and related reactions such as alkene and enyne metathesis, and alkyne polymerization.[19]

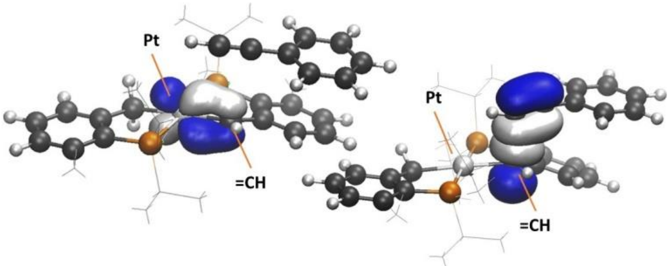


Fig. 3 NLMO for the Pt-carbene π interaction in the **1a·phenylacetylene** *adduct* (left), and NBOs for the donor-acceptor interaction between the π electron density of the alkyne and the vacant *p* orbital on the carbenic carbon at **TS1**.

Once formed, **B** yields **C** in an almost barrier-less step. **C** features a partially reformed Pt—CHPh bond ($d_{\text{Pt—C}}$ = 2.16 Å) and a new Pt—C bond with the former CH terminus of the alkyne. Although this intermediate could be considered as the end-product of the insertion of the C≡C into the metal-alkylidene bond, intramolecular nucleophilic attack of one of the phosphine functionalities to the =*C*HPt carbon has an affordable energy barrier of 21.5 kcal·mol^{-1} (**TS4**) and leads irreversibly to the formation of the η^3-allyl ligand of **3a** with an overall energy return (ΔG^0) from **1a** + phenylacetylene of 50.1 kcal·mol^{-1}. Finally, the formation of the regioisomer of **3a** resulting from initial attack of the substituted carbon of the alkyne, $\mathbf{3a_R}$ (Fig. S1), has an energy barrier of 19.5 kcal·mol^{-1} from the corresponding regioisomer of **C**. Even if only marginally, this barrier is lower than that leading to the observed regioisomer. In addition, the overall formation of $\mathbf{3a_R}$ is also very exergonic with $\Delta G^0 = 42.9$ kcal·mol^{-1}. Together with the failed attempts to model the initial nucleophilic attack of the ≡*C*Ph terminus of the alkyne to the metal cation, these results suggest that the regioselectivity of the formation of **3a** is probably imposed by steric interactions.

In summary, terminal alkynes have been selectively activated at the carbenic carbon of **1a** with subsequent anti-Markovnikov attack of a phosphorus nucleophile to the ≡CH terminus leading to unprecedented zwitterionic structures. DFT calculations disclose a mechanism with initial nucleophilic addition of the alkyne without direct involvement of the metal.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

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