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Reactivity of *cis*-{Pt^{II}(Ar)(alkyne)} Fragments (Ar = aryl): A Domino-Formation of Indenes

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Summary: The reactivity of cis-{Pt^{II}(Ar)(2-butyne)} fragments in cationic complexes is described. Coordination of the unsaturated ligand is observed at low temperature. Upon increasing at 298 K, a cascade of reactions affords a selective formation of indenes. Mechanistic implications of this domino-reaction are discussed.

Introduction

The reactivity of *cis*-{M^{II}(*HC*)(unsaturated ligand)} fragments (M = Ni, Pd, or Pt; *HC* = alkyl, aryl) attracts a remarkable interest in the field of metal-mediated synthesis.[1] A wide variety of products are obtainable, according to the nature of the ligands and the reaction conditions. Moreover, unprecedented mechanistic implications are often disclosed.

Previous systematic works[2–4] by our research team on cationic species of formula [Pt^{II}(*HC*)(unsaturated ligand)(N,N-chelate)]$^+$ (**1–3** in Figure 1; N,N-chelate = 1,10-phenanthroline or phen) demonstrated that, using alkenes as unsaturated ligands, the complexes are stable only if *HC* = alkyl (**1**).[5]

When *HC* = aryl it is not possible to isolate compounds **2**, but only to infer their formation in solution by NMR spectroscopy.[3] The fate of these species depends on the amount of olefin present in solution. With an excess of alkene the corresponding insertion products can be isolated. Otherwise, a fast rearrangement occurs, and formation of a Pt-2-alkylaryl moiety is observed. A detailed mechanistic study has also demonstrated that this result is an effect of the general behavior of "naked" metals, which can promote reactions which normally either do not occur or have different courses.[6]

The cis-coordination of alkynes in alkylplatinum(II) complexes of type **3** produced a different reactivity depending on the nature of the unsaturated ligand.[4] Notably, terminal alkynes gave rise to an unprecedented intramolecular rearrangement affording π-allyl derivatives. This kind of reaction was never observed in complexes showing a trans disposition of the alkyne and the alkyl group. Therefore, the cis geometry seems a necessary requisite for promoting this process.

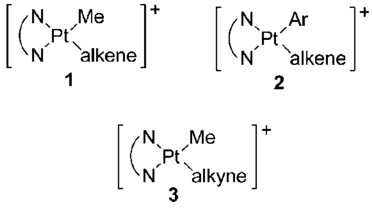


Figure 1. General formula of complexes of types **1–3**.

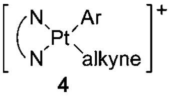
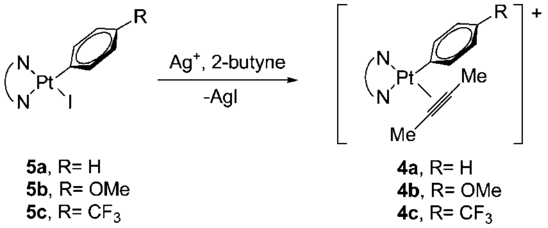


Figure 2. General formula of complexes of type **4**.

Scheme 1. Formation of Complexes of Type 4 Starting from Precursors 5



In this paper we report on the extension of this study to alkyne/aryl complexes of type **4** (Figure 2).

In line with our expectations, this investigation has disclosed unusual reactivity, which affords indenes through a cascade of transformations following the initial insertion product. A reasonable mechanism for this domino-reaction has also been proposed, which also can be a useful complement to the understanding of the analogous Pd-catalyzed process, recently described as a convenient access to substituted indenes.[7]

Results and Discussion

The study of the reactivity of type **4** complexes has been performed by adding stoichiometric 2-butyne to the cationic fragment {Pt(Ar)(phen)}$^+$, generated in situ through addition of silver tetrafluoroborate to the corresponding neutral precursors [Pt(Ar)I(phen)] (**5a**−**c**) (Scheme 1).

2-Butyne was used in all the experiments, and the electronic properties of the aryl groups were selected to rationalize their possible influence on the reactivity.

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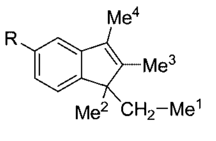


6a, R= H
6b, R= OMe
6c, R= CF$_3$

Figure 3. Formula of indenes **6a**–**c**.

Progress of the reactions was monitored through ^{1}H NMR spectroscopy in CD$_3$NO$_2$.

The initial coordination of the alkyne to the metal center (**4a** in Scheme 1) was observed when the addition of 2-butyne to **5a** was performed at 273 K. Evidence of this is the shift of the methyl resonance $\equiv$C–Me (δ 2.35 vs 1.85 of the free alkyne), which also presents coupling to ^{195}Pt ($^3J_{\text{Pt-H}} = 47$ Hz).

Upon increasing the temperature to 298 K, a sequence of reactions occurred, as shown by the ^{1}H NMR spectrum. The initial appearance of a quartet at δ 5.25 ($^2J_{\text{Pt-H}} = 46$ Hz) pointed to a =C*H*–Me group coordinated to the metal (δ_{Me} 1.60, doublet). Simultaneous growth of a not-^{195}Pt-coupled quartet at δ 5.76 revealed an analogous, though noncoordinating, =CH–Me moiety (δ_{Me} 1.52).

The NMR spectra became more complex upon aging, and several attempts to isolate the complexes were unfruitful. On these grounds, our attention was addressed to the identification of the organic fragment(s) bound to the metal through protolytic degradation. Therefore, gaseous HCl was added to the reaction mixture 30 min after mixing of the reagents. The NMR spectrum of the filtered solution disclosed the presence of an organic molecule, whose data were consistent with 1,2,3-trimethyl-1-ethylindene (**6a** in Figure 3).[8] This compound could be isolated from the reaction mixture as an oil.

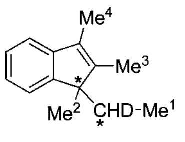
A distinctive feature of the ^{1}H NMR spectrum of **6a** is the Me^1 resonance that results in an apparent triplet at δ 0.25. The adjacent methylene hydrogen atoms are diasterotopic and resonate at δ 1.75 and 1.60 as multiplets.

The stoichiometric composition of **6a** reveals that two butyne molecules are linked to the same aromatic ring. In the hypothesis of a sequential butyne addition, this indicates that the initial product is more reactive than the starting aryl–alkyne complex **4a**. Therefore, a 1:2 Pt/2-butyne ratio was successfully used to improve the yield of the isolated product.

The rate increased when the reaction was carried out starting from **5b**. The recovered 1,2,3-trimethyl-1-ethyl-5-methoxyindene **6b** was identified through NOESY experiment. The unambiguous determination of the MeO position on the aromatic ring has been essential for the formulation of a reasonable mechanistic hypothesis (see below).

Also the reaction carried out on **5c** afforded the 5-substituted indene (**6c** in Figure 3), though in this case the reaction was slower than that for **5a**.

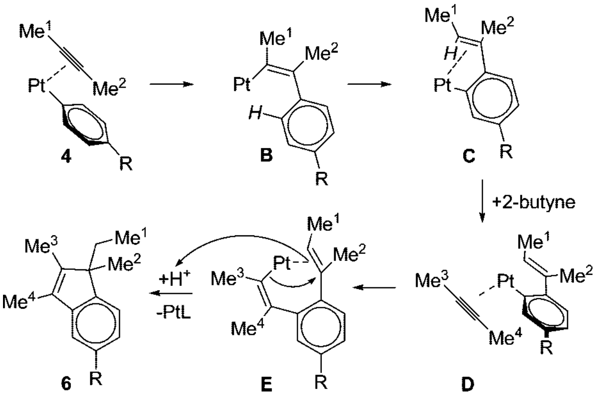
In analogy to that found for similar reactions involving olefin substrates,[3] this experimental observation suggests that an insertion step is involved in the mechanism. In fact, the trend of reactivity (MeO > H>CF$_3$) matches the inductive and resonance effects of the different substituents in the para position, which produce a significant variation of the carbanionic character of the migrating aryl group.



6a-D

Figure 4. Formula of **6a**-D.

Scheme 2. Mechanistic Hypothesis for the Formation of Indenes (6)



Aiming to gain insights on the mechanism of the reaction, further experiments were performed with suitably deuterated reagents. By using **5a**-C$_6$D$_5$ as the precursor, the spectrum of the initial mixture reaction lacked the =C*H*–Me signal, suggesting its deuteration. Accordingly, the corresponding methyl group resonated as a singlet. The spectrum of the isolated indene (**6a**-D in Figure 4) displayed the methyl resonance of the –CHDMe group as a doublet at δ 0.22. The multiplet at δ 1.60 was absent.

Protonolysis was also carried out with DCl in D$_2$O starting from **5a**. In this case, the spectrum of the product showed a complementary –CDHMe pattern: the methyl doublet was in fact shifted at δ 0.24, whereas the multiplet at δ 1.75 was now missing.

The ensemble of results suggest the mechanistic hypothesis reported in Scheme 2. Though many attempts to isolate the species shown in Scheme 2 were unfruitful, spectroscopic evidence allowed the reasonable hypothesis of their existence in solution:

(i) Initial coordination of 2-butyne occurs (**4**), as disclosed at low temperature for **4a** by the presence of a singlet at δ 2.35, coupled to ^{195} Pt.

(ii) The subsequent step is the migratory insertion of the alkyne into the Pt–aryl bond, followed by *H*–C$_{\text{aryl}}$ oxidative addition and *H*–C$_{\text{alkenyl}}$ reductive elimination (**B** and **C**). This fast sequence[9] is already known for the analogous olefin substrates **2**.[3]

Demonstration of its occurrence is the above-mentioned experiment carried out with the deuterated phenyl group. In this case a deuterium atom originally present in the ring is found in the coordinated alkene fragment =CD–Me of **C**.

(iii) This latter species cannot be stabilized through an effective coordination of the double bond to the metal. In fact, geometrical constraints would force an unusual coplanar arrangement of the double bond with respect to the coordination plane of the metal. This plausibly enhances reactivity of the

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(8) (a) Although literature related to indenes and their derivatives is widespread, **6a** has never been described before, to the best of our knowledge. Therefore, to confirm the structure of this novel species, an authentic sample was synthesized by adapting known procedures: Pittman, C. U.; Miller, W. G. *J. Am. Chem. Soc.* **1973**, 2947. (b) Miller, G.; Pittmann, C. U. *J. Org. Chem.* **1974**, *39*, 13. (c) Meurling, L. *Acta Chem. Scand., Ser. B* **1974**, *28*, 295.

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unsaturated bond toward substitution. Since alternative coordinating ligands are not present, a way to stabilize **C** must involve coordination of another 2-butyne molecule (**D**);

(iv) At this stage, a second migratory insertion reaction would afford **E**. In this case, a further rearrangement analogous to that experienced by the primary insertion product **B** seems to be prevented by steric hindrance. It is worth noting that the presence of an excess of olefin in analogous reactions also afforded a double insertion product;[3a]

(v) Evolution of **E** toward **6** is very fast if strong acids are added at this stage (e.g., HCl). Alternatively, this reaction slowly and spontaneously (though less selectively) takes place thanks to the traces of water, which are always present in the reaction mixture. The outcomes of the experiments with deuterated reagents (**5a**-C_6D_5 + HCl and **5a** + DCl) indicate that protonolysis and final cyclization are concerted. In fact, if the two processes occurred independently, two diastereomers (two enantiomeric couples) should form for deuterated **6a**, due to the presence of two stereogenic carbon atoms (labeled with an asterisk in Figure 4). The selective obtainment of either diastereomer in the two experiments indicates that the two configurations are correlated.

Further evidence of the mechanism proposed in Scheme 2 has been obtained by an alternative identification of the different organic fragments progressively bonded to the metal. To this aim, the reaction mixture was treated with $NaBH_4$ a few minutes after the mixing of the reagents, and the organic fragments were isolated in the usual conditions. The organic phase obtained from **5a** mainly contained equimolar amounts of **6a** and *Z*-Ph—C(Me)═CH—Me ((*Z*)-1-(but-2-en-2-yl)benzene), which derives from reduction of the monoinsertion products (**C** and/or **D** species of Scheme 2). This molecule has been identified by comparing its ^{1}H NMR spectrum with that reported in the literature.[10]

In the reaction mixture a second unsaturated species containing the ═CH—Me group is also present. Its spectrum is compatible with that of 1,2-bis[(*Z*)-1-(but-2-en-2-yl)]benzene, in other words, with the compound arising from the reductive cleavage of the double insertion product (**E** species of Scheme 2). Unluckily, a complete characterization of this molecule could not be performed since the amount in the mixture reaction is lower than 5%, and its characterization data are not present in the literature.

It should be noted that none of the above reactions takes place when cationic substrates with donor ligands adjacent to the aryl ring are taken as precursors, e.g., $[Pt(Ar)(MeCN)(phen)]^+$.

Conclusion

This work extends our previous study on *cis*-{Pt^{II}(*HC*)(unsaturated ligand)} fragments (*HC* = alkyl, aryl). A concerted process involving an aryl ring and two molecules of butyne has been disclosed, which affords indenes as unique organic products. The result confirms the strategic importance of cationic platinum(II) complexes in weakly coordinating environments for promoting unusual reactions, and gaining mechanistic implications.[7]

Experimental Section

General Comments. ^{1}H and ^{13}C NMR spectra were recorded with Varian XL-200, Varian Gemini-200, and Varian Gemini-500 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in δ (ppm) relative to the solvent ($CHCl_3$, δ 7.26; $^{13}CDCl_3$, δ 77.0; CHD_2NO_2, δ 4.33). The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; app. t, apparent triplet; m, multiplet. The coupling costants, when measurable, are reported in hertz. The neutral platinum(II) complexes [Pt(Ar)I(phen)] (**5a**−**c**) and [Pt(C_6D_5)I(phen)] (**5a**-C_6D_5) used as precursors were obtained according to described procedures.[3c] 1,2,3-Trimethylindene was prepared as described in the literature.[8a,b] 2-Butyne and organic reagents were commercially available (Sigma-Aldrich), and were used without further purification. Solvents were dried following standard procedures.

General Reaction Procedure. To a stirred suspension of the appropriate neutral [Pt(Ar)I(phen)] (**5a**−**c**) precursor (0.17 mmol) in CD_3NO_2 (1 mL) was added an equimolar amount of $AgBF_4$ dissolved in the same solvent (0.5 mL) at room temperature. Dissolution of the platinum complex and precipitation of silver iodide was observed. To the mixture reaction, quickly filtered through a thin layer of Celite to remove silver iodide, was added 2-butyne (0.018 g, 0.34 mmol). Progress of the reaction was monitored via NMR spectroscopy. Alternatively, the mixture were subjected to controlled decompositions (i) and (ii), 30 and 5 min after the mixing of the reagents, respectively.

(i) Protonolysis with Gaseous HCl. A portion of the reaction mixture was concentrated to small volume and diluted with $CDCl_3$. Gaseous HCl was added and the mixture was stirred for 10 min at room temperature. After filtration on Florisil, the resulting clear solution was evaporated under vacuum to afford **6a**−**c** as pale yellow oils. Yield: 92% (**6a**), 87% (**6b**), 95% (**6c**). Purification can be carried out through column chromatography (silica gel, hexane).

^{1}H NMR resonances ($CDCl_3$, δ): **6a**, 7.15–6.90 (m, 4H, Ph), 2.00 (s, 3H, Me^4), 1.78 (s, 3H, Me^3), 1.75 (m partially obscured, 1H, C*H*H), 1.60 (m, 1H, CH*H*), 1.15 (s, 3H, Me^2), 0.25 (app. t, 3H, $^3J_{H\text{-}H}$ = 7.5 Hz, Me^1); **6b**, 7.05 (d, 1H), 6.75 (s, 1H), 6.68 (d, 1H), 3.86 (s, 3H, OMe), 2.00 (s, 3H, Me^4), 1.79 (s, 3H, Me^3), 1.78 (m partially obscured, 1H, C*H*H), 1.65 (m, 1H, CH*H*), 1.15 (s, 3H, Me^2), 0.27 (app. t, 3H, $^3J_{H\text{-}H}$ = 8 Hz,Me^1); **6c**, 7.50 (d, 1H), 7.38 (s, 1H), 7.25 (d, 1H), 2.04 (s, 3H, Me^4), 1.82 (s, 3H, Me^3), 1.79 (m partially obscured, 1H, C*H*H), 1.71 (m, 1H, CH*H*), 1.17 (s, 3H, Me^2), 0.26 (app. t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, Me^1).

^{13}C NMR resonances ($CDCl_3$, δ): **6a**, 150.9, 146.0, 144.9, 130.7, 126.1, 123.8, 120.8, 117.8, 53.7, 30.0, 23.6, 10.1, 9.7, 8.3; **6b**, 158.9, 147.5, 146.4, 143.1, 130.5, 121.1, 108.7, 104.2, 55.4, 53.1, 30.1, 23.8, 10.1, 9.8, 8.4; **6c**, 150.0, 146.5, 130.2, 128.4, 125.0, 124.3, 122.2, 120.8, 54.1, 29.8, 23.3, 10.0, 9.8, 8.2.

(ii) Reduction with $NaBH_4$ (starting from 5a). A portion of the reaction mixture was concentrated to small volume and diluted with $CDCl_3$. To this solution was added $NaBH_4$ (10 equiv). The resulting reaction mixture, quickly blackened, was filtered on Florisil and examined by NMR spectroscopy. The NMR spectrum revealed the presence of **6a** and 1,2-bis[(*Z*)-1-(but-2-en-2-yl)]benzene, in a 1:1 ratio.[8]

Synthesis of 6a. The synthesis was adapted from a described procedure.[8] To a solution of 1,2,3-trimethylindene (0.182 g, 1.15 mmol) in dry diethyl ether (5 mL) was added a solution of butyllithium in pentane (4.6 mmol) at 273 K, under nitrogen. The resulting solution was stirred at room temperature for 30 min. Ethyl bromide (7.05 mmol) in dry diethyl ether (3 mL) was added with cooling to the mixture reaction. After standing at room temperature for 2 h, the solution was poured on to 20 mL of ice-cooled 2 M HCl. The organic phase was separated, washed with sat. aqueous NaCl, and dried over Na_2SO_4. Removing the solvent gave 0.112 g of product as a pale yellow oil (yield 53%).

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