Agostic Interactions

DOI: 10.1002/anie.201200070

Tuning N-Heterocyclic Carbenes in T-Shaped Pt^{II} Complexes for Intermolecular C–H Bond Activation of Arenes**

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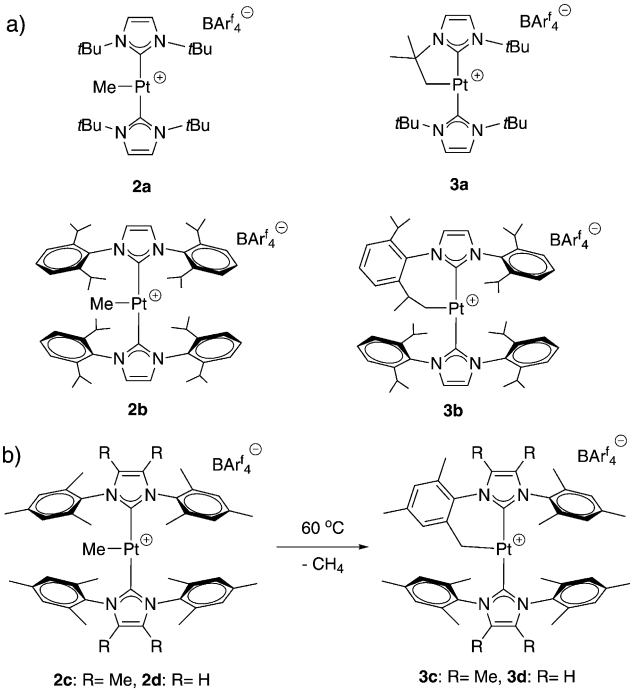
Dedicated to Professor Guy Bertrand on the occasion of his 60th birthday

C–H bond activation of hydrocarbons promoted by Pt^{II} complexes have been intensively studied since Shilov's first report on the catalytic conversion of methane into methanol and methyl chloride by $PtCl_4^{2-}$ salts.[1] Mechanistically, the first step of this process, prior to C–H bond cleavage of methane, is coordination of the hydrocarbon to the platinum center, and this might occur either associatively or with prior dissociation of a coordinated ligand. Although in most cases the C–H bond activation at Pt^{II} centers seems to take place by an associative mechanism,[1b] there are theoretical and experimental evidences in good agreement with a dissociative pathway that involves the formation of transient T-shaped 14-electron Pt^{II} species.[2] Some of these coordinatively unsaturated highly electrophilic species have been isolated and crystallographically characterized,[3] and a few of them undergo intramolecular C–H bond activation (cyclometalation) reactions. Nevertheless, we are not aware of intermolecular C–H bond cleavage of hydrocarbons induced by stable T-shaped Pt^{II} complexes. Recently, we have described the synthesis of this kind of highly electrophilic species stabilized by agostic interactions with N-heterocyclic carbene (NHC) ligands.[4] Herein, we report that alteration of the environment of the NHC ligands allows fine tuning of the steric and electronic properties of their platinum complexes, thereby enabling intermolecular C–H bond activation of some arenes.[5]

Previously,[4] we prepared the unsaturated, cationic Pt^{II} compounds $[PtMe(IPr)_2][BAr^f_4]$ (**2b**) and $[Pt(NHC')(NHC)][BAr^f_4]$, where NHC' represents the cyclometalated ligands I*t*Bu for compound **3a** and IPr for compound **3b** (Scheme 1a). The I*t*Bu species **2a** converts rapidly into **3a** and cannot be isolated. By following a similar synthetic method, namely reaction of $[PtMe_3I]_4$ with the corresponding NHC ligand and subsequent treatment with $NaBAr^f_4$, the analogous complexes **2c** and **3c** with the NHC ligand IMes* and complexes **2d** and **3d** with the NHC ligand IMes have been prepared and characterized (Scheme 1b).



Scheme 1. a) Structural representations of compounds **2b** and **3a–b**, described in ref. [4], and of compound **2a**, which cannot be isolated but converts rapidly into **3a**. b) Synthesis of the cyclometalated complexes **3c–d**.

The Lewis-acidic behavior of the cationic compounds **2b–c** and **3a–c** becomes evident in their reactions with aceto-

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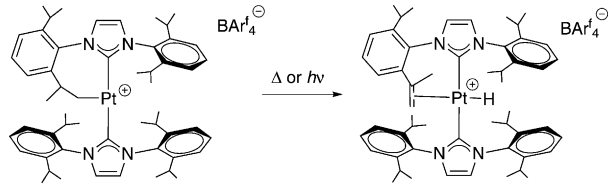
[**] Financial support from the Junta de Andalucía (project No. FQM-3151) and the Spanish Ministerio de Ciencia e Innovación (projects CTQ2011-23336, CTQ2010-17476 and CONSOLIDER-INGENIO 2010 CSD2007-00006, FEDER support) is acknowledged. O.R.-W. and M.A.O. thank the Spanish Ministerio de Ciencia e Innovación for a research grant. The authors thank Prof. Ernesto Carmona for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200070.

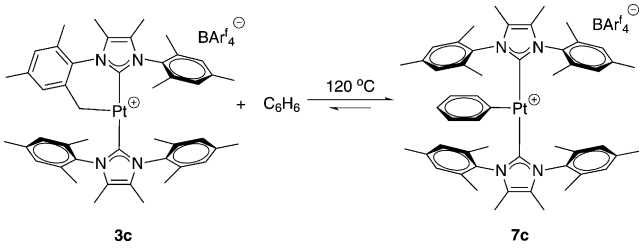
nitrile to generate the corresponding colorless adducts $[PtMe(NHC)_2(NCMe)][BAr^f_4]$ (NHC = IPr for **4b**; NHC = IMes* for **4c**) and $[Pt(NHC')(NHC)(NCMe)][BAr^f_4]$ (NHC = I*t*Bu for **5a**; NHC = IPr for **5b**; NHC = IMes* for **5c**, where NHC′ represents the cyclometalated NHC ligand).

Compounds **3a** and **3b** do not react with benzene after prolonged heating at 120 °C. Under these conditions, the I*t*Bu derivative **3a** remains unaltered, whereas the IPr analogue **3b** undergoes β-H elimination from one of the isopropyl substituents to afford the cationic complex **6** (Scheme 2).



Scheme 2. β-H elimination process for complex **3b**.

In contrast with this observation, ^{1}H NMR spectroscopy studies of the reaction of the IMes* complex **3c** and C_6H_6 (120 °C, four hours) reveal the formation of the phenyl derivative **7c** in approximately 4:1 ratio with respect to **3c** (Scheme 3). Prolonged heating at this temperature does not



Scheme 3. C–H bond activation of aromatic compounds leading to complex **7c.**

alter the ratio of these compounds. In fact, when a pure sample of **7c** (isolated by fractional crystallization; see the Supporting Information) is heated in C_6H_6 at 120 °C compounds **7c**/**3c** are obtained in a ratio of approximately 4:1. In turn, the use of heptane as the solvent allows full conversion back to **3c** and concomitant elimination of C_6H_6 (120 °C, one hour). Clearly compounds **3c** and **7c** exist in an equilibrium, which is characterized by thermodynamic parameters $\Delta H = 4$ kcal mol^{-1} and $\Delta S = 13$ cal mol^{-1} K^{-1} (measured in neat C_6H_6 for the equilibrium of **7c** with **3c**, that is, from right to left in Scheme 3, in the temperature range 100–140 °C).

For the analogous IMes compound **3d**, C–H activation is less favorable, and only 1–2 % of the corresponding phenyl derivative can be detected by ^{1}H NMR spectroscopy under similar conditions. Finally, it is worth mentioning that when the vacant (or accessible) coordination site of **3c** is blocked as in its NCMe adduct **5c**, benzene C–H activation and formation of **7c** is inhibited.

DFT calculations using PBE0 functional[6] were performed to study the benzene C–H bond activation with cyclometalated complexes **3a–d**. Gas-phase optimizations of complexes **3a** and **3b** show δ and ζ intramolecular, agostic interactions at the vacancy, respectively, as was found experimentally.[4] Conversely the geometry of the mesityl family of reactants, **3c** (Figure 1) and **3d**, corresponds with a pure T-shaped structure: no agostic interactions with NHC substituents are present.

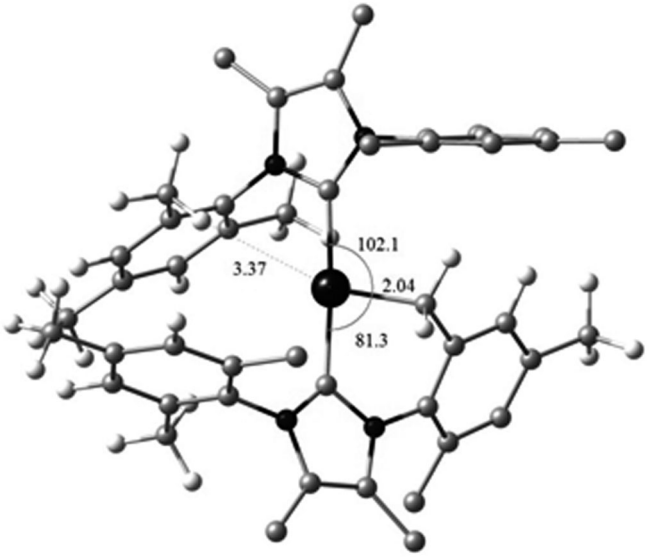


Figure 1. Gas-phase DFT-optimized structure of **3c**. Bond distances in Å and angles in degrees. Selected hydrogen atoms have been omitted for clarity. H white, C gray, N black, Pt large black sphere.

This structural difference can be explained by geometrical constraints of the NHC ligands (see the optimized geometries in Figure S2 in the Supporting Information). The second sp^3 carbon atom of isopropyl and *tert*-butyl groups provides flexibility to establish agostic interactions thereby filling the vacancy, whereas the planar carbon skeleton of mesityl groups avoids this kind of interaction. No agostic interactions are found in the products of benzene C–H bond activation **7a–d**.[7]

All C–H bond activation processes proceed through oxidative addition and reductive elimination mechanism via unstable Pt^{IV} intermediates **11a–d**, but the energy profiles are notably different depending on the NHC ligand (Figure 2).

For complexes containing I*t*Bu and IPr, **3a** and **3b**, the reaction has high energy barriers $\Delta E^{\ddagger}$ (more than 40 kcal mol^{-1}) and in addition is thermodynamically disfavored. On the other hand complexes containing IMes* and IMes ligands show feasible reaction barriers of approximately 30 kcal mol^{-1}. The barrier heights are closely related to the distortion energies $\Delta E^{\ddagger}_d$, that is, the energy required by the cyclometalated complexes to adopt the transition-state geometry. For transition states regarding **3a** and **3b** this energy is 20.1 and 20.6 kcal mol^{-1}, whereas for **3c** and **3d** the energy is 9.6 and 9.0 kcal mol^{-1}. Thus for IMes* and IMes complexes the

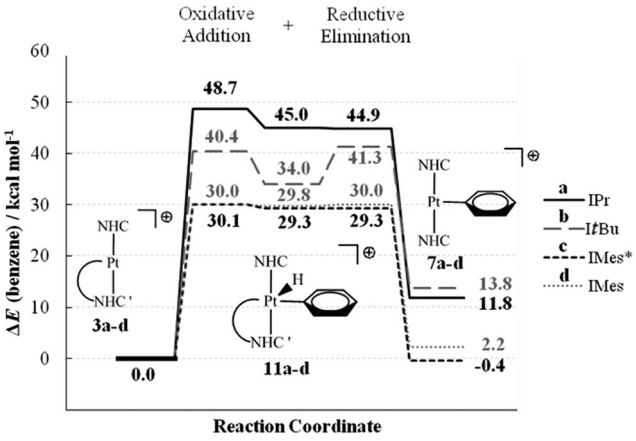
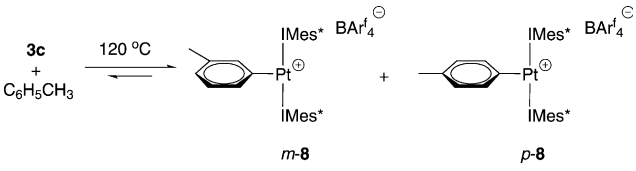


Figure 2. Energy profiles for the C–H bond activation of benzene with NHC-complexes **3a–d** (relative energies in benzene solvent in kcal mol^{-1}).

distortion energy is around 10 kcal mol^{-1} lower than for I*t*Bu and IPr complexes, and this difference is directly reflected on the energy barrier. Removal of the agostic interaction in complexes **3a** and **3b** by constrained optimizations accounts for about 2 kcal mol^{-1} (that is ca. 10%) of distortion energies. Owing to the branched nature of the ligand arms in complexes **3a** and **3b** the vacant position is still unreachable after removing this weak interaction, and a large ligand distortion is required to create a free space for the benzene molecule. The calculated buried volume[8] associated with each NHC ligand reflects this behavior, indicating the higher steric hindrance of I*t*Bu and IPr ligands (Table S1 in the Supporting Information). In agreement with experiments, the thermodynamic of the reaction suggests that the product **7c** should be found together with the reactant **3c**, whereas the product **7d** could be hardly detected. The different behavior of IMes* and IMes ligands regarding the product stabilization is an electronic effect that can be attributed to the slightly different basicities of both ligands (Scheme S1 and Table S2 in the Supporting Information).

To complete this study we have explored the reactivity of **3c** toward toluene[9] and some fluorinated aromatic hydrocarbons. As shown in Scheme 4, toluene experiences regioselective activation at the *meta* and *para* sites, to yield approximatly a 5:1 mixture of *m*-**8**/*p*-**8**. Similarly to C_6H_6, an equilibrium is established that appears to be insensitive to the nature of the aromatic hydrocarbon. As found also for the benzene reaction system, the heating of compounds **8** in heptane at 120 °C results in elimination of toluene and regeneration of the starting compound **3c**.

To throw light on the regioselectivity pattern of the toluene activation process, all possible products were calculated using **3c** as reactant (Scheme S2 in the Supporting Information). Only complexes *m*-**8** and *p*-**8** are slightly more stable than **3c**, in agreement with the ratio of products experimentally observed. The thermodynamic origin of the selectivity has been confirmed by calculating the energy reaction profiles of toluene activation in *meta* and *para* positions (Figure S8 in the Supporting Information).



Scheme 4. C–H bond activation of toluene.

Pentafluorobenzene, C_6F_5H, and 1,2,4,5-tetrafluorobenzene, $C_6F_4H_2$, experience under similar conditions chemoselective C–H (and not C–F[10]) activation, giving rise to related aryl complexes *trans*-$[Pt(C_6F_5)(IMes^*)_2][B(Ar^f)_4]$ (**9**) and *trans*-$[Pt(C_6HF_4)(IMes^*)_2][B(Ar^f)_4]$ (**10**), respectively. Once again, equilibria between **3c** and **9** or **10**, which are scarcely affected by the nature of the aryl group, are attained. Studies aimed at understanding this unexpected observation are presently under way. At this stage, it seems possible that steric hindrance exerted by the bulky IMes* groups may destabilize the fluorinated aryl complexes **9** and **10**, compared to phenyl species **7c**.

Crystals of the tetrafluorophenyl compound **10** that were suitable for X-ray studies have been obtained (Figure 3). Beyond any doubt, the most striking feature in the structure

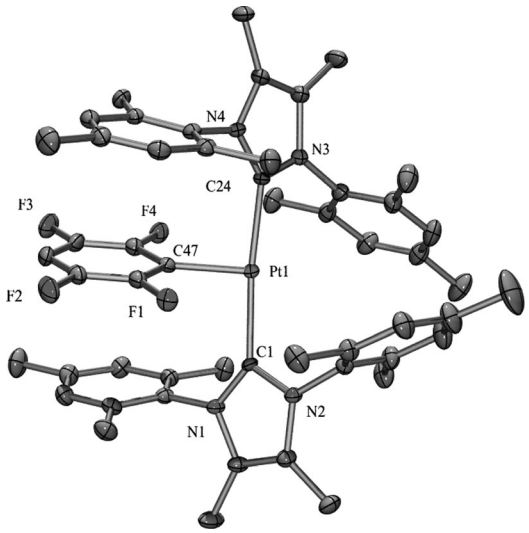


Figure 3. Molecular structure of **10** by X-ray crystallography. BAr^f_4 anion has been omitted for clarity. Thermal ellipsoids are set at 30% probability.

of **10** is the lack agostic or anagostic interactions[11] involving the methyl groups of the IMes* ligand. Indeed, the closest Pt···H-C contacts are of approximately 3.117 and 3.912 Å and lay out of the metal coordination plane. Therefore, complex **10** is strictly a T-shaped, 14-electron Pt^{II} complex with no additional stabilization other than steric. The isolation of these kind of platinum complexes is extremely rare, with only one report on Pt-boryl species.[3b,c]

In summary, the unsaturated 14-electron, T-shaped Pt^{II} complex $[Pt(IMes^{*\prime})(IMes^*)][BAr^f_4]$ activates the C–H bonds of aromatic hydrocarbons, including some fluoro derivatives, to provide the corresponding pure T-shaped Pt^{II} aryl species. The flexibility of the NHC ligand, the comparatively lower

steric hindrance and excellent electronic properties of the IMes* ligand, and to a lesser extent the lack of agostic interactions in its complex, are responsible for this reaction to occur.[12] These results highlight how subtle modifications of the NHC ligands in the coordination sphere of a metal complex can direct the reaction favoring a C–H bond activation reaction.

Received: January 4, 2012
Revised: February 8, 2012
Published online: March 8, 2012

Keywords: agostic interactions · carbene ligands · C–H activation · N-heterocyclic carbenes · platinum

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