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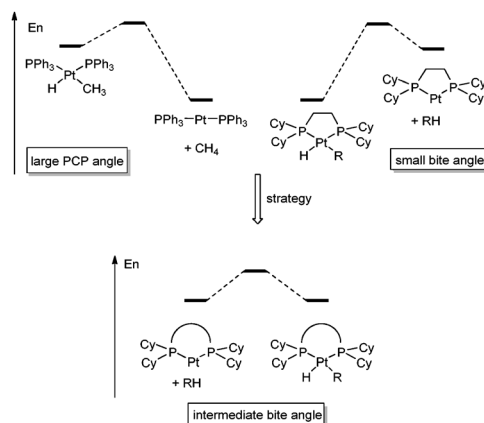
Room temperature reversible C–H activation mediated by a Pt(0) center, and stoichiometric biphenyl formation *via* solvent activation†Emmanuel Nicolas,^a Xavier-Frédéric le Goff,^a Stéphane Bouchonnet^b and Nicolas Mézailles^{*a}

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Room temperature reversible C–H activation mediated by a designed diphosphine platinum complex is presented. These findings are demonstrated through mechanistic studies involving kinetics, isotopic effects, and corroborated by DFT calculations. The coupling between two unactivated aromatic derivatives is also demonstrated.

C–H bond activation/functionalization is amongst the major challenges of chemistry nowadays, and in this field, the reaction of Pt centers with hydrocarbons has been extensively studied, following the discovery made by Shilov in the early 1970s.^{1,2} Most studies have been performed on Pt(II)/Pt(IV) systems, such as Periana's system, for the functionalization of methane in hot, concentrated sulphuric acid.^{3,4} In parallel, numerous mechanistic studies have been performed on these oxidized systems to probe the different elementary steps of the mechanisms of C–H bond activation and functionalization.^{5–12} On the other hand, Pt(0) fragments have been studied by very few groups, despite significant early findings. In particular, Halpern *et al.* described in 1978 the ability of the complex [(PPh₃)₂Pt(H)(CH₃)] to readily eliminate methane at low temperature (–25 °C), generating the transient 14 electron complex that could be trapped with triphenylphosphine to form the stable 16 electron Pt(0) complex.¹³ A few years later, Whitesides and Ibers described the thermolysis of the [(dcpe)Pt(H)(neopentyl)] complex (dcpe: bis-dicyclohexylphosphinoethane), leading to a high energy L₂Pt(0) fragment, capable of activating C–H bonds of alkanes (in low yield) or aromatics (quantitatively).^{9,14,15} These early findings showed that the energetic demand of the oxidative addition of C–H bonds is linked to the geometry of the 14 electron L₂Pt(0) fragment. In correlation, MO computations have predicted that a small bite angle, obtained with a bidentate ligand, can lead to an increased reactivity of the L₂Pt(0) fragment (Scheme 1). We reasoned that a careful choice of the bite angle of a diphosphine ligand should result in the stabilization



Scheme 1 Strategy of C–H activation.

of the L₂Pt(0), while keeping its ability to activate C–H bonds. Tuning the electronics and sterics of the ligand should then allow both complexes to be in equilibrium, opening ways for further transformations.

Firstly, we show here that the reduction of a stable Pt(II) precursor in toluene results in the formation of a Pt(0) fragment which inserts quantitatively C–H bonds of the solvent at room temperature. One of the key features of the designed system lies in the reversibility of the insertion at room temperature, proved by kinetic experiments. Secondly, the Pt(II) hydride complex was shown to further activate C–H bonds of the solvent leading to C–C bond formation from unactivated aromatic derivatives. Overall, the coupling of two molecules of the solvent to form the corresponding biphenyl derivative at mild temperatures is proved. DFT calculations rationalizing these findings are presented herein.

The low temperature (–35 °C) reduction of **1_I** in toluene or room temperature reduction of **1_{Cl}** with two equivalents of KC₈ resulted in the formation of graphite and KX salts, indicative of the efficient reduction of the Pt(II) complexes. The crude mixture, analyzed by ³¹P{¹H} NMR spectroscopy after 2 hours, did not present the signal (δ = 11.7 ppm, J_{Pt-P} = 3320 Hz for **1_I**, δ = 7.9 ppm, J_{Pt-P} = 3460 Hz for **1_{Cl}**) for the starting complex **1** and consisted instead of several platinum complexes featuring, for each species, two electronically different thus coupled phosphorus signals. It pointed to the formation of C–H inserted species (solvent and/or ligand insertions). This first experiment showed a fast

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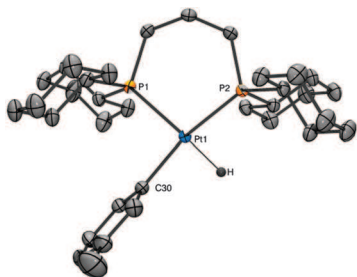
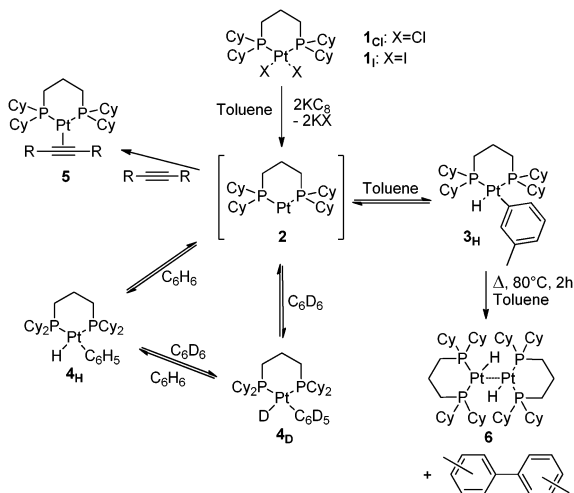


Fig. 1 X-Ray structure of complex **3_H**. Selected bonds and angles: Pt(1)–C(30) 2.063(3), Pt(1)–P(2) 2.2687(8), Pt(1)–P(1) 2.304(1), Pt(1)–H 1.56(3), C(30)–Pt(1)–P(1) 93.1(1), P(2)–Pt(1)–P(1) 98.16(3), C(30)–Pt(1)–H 84(1), P(2)–Pt(1)–H 84(1). The hydride has been refined using SHELX97.

reduction process followed by facile C–H insertions. Most interestingly, following the reaction in time, at room temperature, revealed that the kinetic mixture evolved to yield a single C–H inserted complex, within 2 days. This reaction allowed for a full NMR characterization of the thermodynamic product, **3_H**, after elimination of the graphite and the salts by filtration. Most importantly, this complex presents a signal for the hydride at -1.53 ppm in the ^1H NMR spectrum (dd, $J_{P_{trans}-H} = 179.3$ Hz, $J_{P_{cis}-H} = 21.2$ Hz, $J_{Pt-H} = 579$ Hz), and two coupled doublets at 18.8 ($J_{P-P} = 20$ Hz, $J_{Pt-P} = 1800$ Hz) and 31.4 ppm ($J_{P-P} = 20$ Hz, $J_{Pt-P} = 1785$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.



Scheme 2 Summary of reactions.

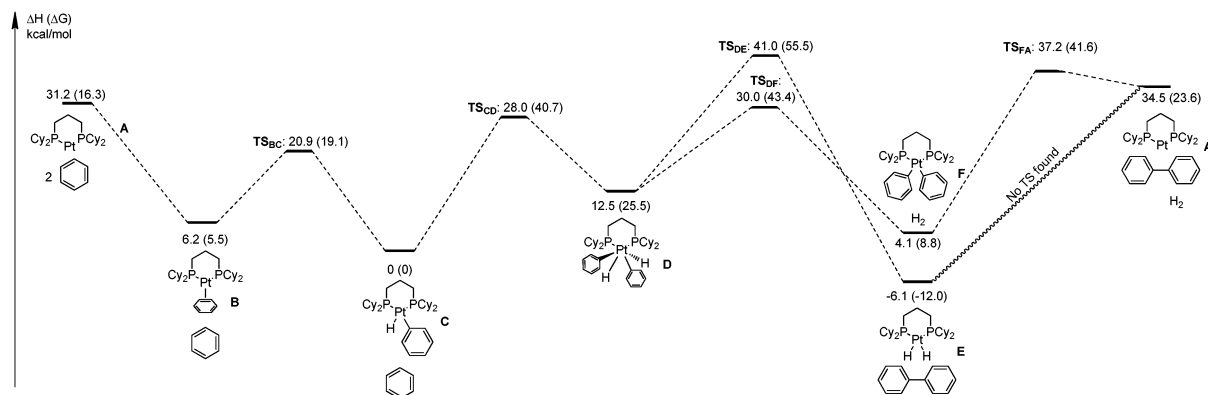
A similar reaction carried out in deuterated toluene leads to the analogous complex, by $^{31}\text{P}\{^1\text{H}\}$ NMR, for which no hydride signal could be observed, proving the C–H insertion into the solvent to form complex **3_D**. The final proof of the insertion in the solvent was given by X-ray crystal analysis, which showed the insertion at the *meta* position (Fig. 1).

Further evidence of the room temperature reversibility of the C–H insertion was obtained when complex **3_H** was dissolved in D_8 -toluene. The signal for the hydride decreased slowly to eventually disappear. The kinetics of the C–H insertion/elimination was then studied using complexes **4_H** and **4_D** obtained by the reduction of **1** in benzene and C_6D_6 respectively. The disappearance of the hydride signal from **4_H** dissolved in C_6D_6 , and the disappearance of the corresponding deuteride signal from **4_D** dissolved in C_6H_6 were followed (Scheme 2).

Since complexes **4_H** and **4_D** are not soluble in nonaromatic solvents, we could not measure a direct kinetic isotope effect. However, the study of the kinetics of the disappearance of **4_H** in C_6D_6 and **4_D** in C_6H_6 allowed us to measure the kinetic constants k_{-H} and k_{-D} of disappearance of complexes, thus confirming the first order kinetics, and the equilibrium of all Pt(II) species with the Pt(0) species at room temperature. Moreover, the study of the proportions of complexes at equilibrium in a C_6H_6 – C_6D_6 mixture allowed us to compute the full kinetic isotope effect (see ESI† for details of calculations), we thus observed an inverse kinetic isotope effect of 0.78, typical of exchange studies.¹⁶

Because of the facile reversible C–H insertion, the stable Pt hydride complex **3** was envisaged as a competent source of a 14 electron fragment. Accordingly, trapping of this fragment with several two electron donors was carried out providing the expected 16 electron complexes. The example of diphenylacetylene is given here, for which complete formation of complex **5** was observed within 5 minutes, and isolated in excellent 91% yield.

Quite unexpectedly, it was found that when a solution of complex **3** was kept at room temperature for several days, it evolved partly and colorless crystals deposited from the crude mixture. It was later found that this reaction could be performed within few hours at 80 °C (Scheme 3). This complex, **6**, was characterized by usual NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ spectrum was particularly informative, indeed, it presented one signal in solution for all P atoms, which were coupled with two Pt centers with 1J and 2J coupling constants pointing to the formation of a dimer ($^1J_{Pt-P} = 2510$ Hz, $^2J_{Pt-P} = 415$ Hz). Moreover, it is



Scheme 3 Energy profile of the reaction.

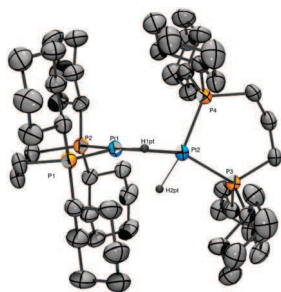


Fig. 2 ORTEP representation of complex **6**. Selected bonds and angles: Pt(1)–H(1PT) 1.48(4), Pt(2)–H(2PT) 1.59(4), P(1)–Pt(1)–P(2) 98.74(4), P(3)–Pt(2)–P(4) 99.17(4). Angle between planes (P1,Pt1,P2) and (P3,Pt2,P4): 85.02(4). Hydrides have been refined using SHELX97.

consistent with previous reports by L. Mole *et al.* who described the cationic analogues of similar dimers.¹⁷ The final proof of the structure of complex **6** was given by an X-ray analysis, an ORTEP of which is presented in Fig. 2. This unprecedented reactivity presented above prompted us to carry out a theoretical study within the frame of DFT, in the case of benzene. These calculations were performed with the Gaussian09 suite of programs, using the hybrid density functional ω -B97XD in order to describe more precisely long range interactions, as well as thermodynamics, and kinetic values. The Def2-TZVP basis set and its associated core potential were used for platinum, the 6-31G* basis set being used for all other atoms but for mobile hydrogen atoms which were described with the 6-311+G** basis set.¹⁸ The different energies of the intermediates as well as transition states were computed with the real system, the results are shown in Scheme 3.

We chose to focus the discussion on the ΔH rather than on the ΔG for two main reasons: first, it is well known that the entropic contribution is typically overestimated, and since the reactions involve multiple variations in the number of molecules, the overestimation is greatly increased. Secondly, the reaction is carried out in the solvent, the concentration of which is therefore very high and decreases its entropic contribution to the different steps.

This was confirmed thanks to the computation of the transition state energy of the dissociation of **4_H** through Eyring's method:¹⁹ we obtained, using the data of the previous kinetic study, a transition state energy of 22.2 kcal mol⁻¹, which fits well with the computed **TS_{BC}** (see ESI[†] for calculation details).

The calculations show that the hypothetically free 14 electron fragment **A** is higher in energy than both the solvent adduct **B** and the C–H inserted complex **C**. The reversibility of the insertion is readily explained by the energy of **TS_{BC}** which lies only 20.9 kcal mol⁻¹ higher than **C**, indicating a facile process at room temperature, and confirming our working hypothesis. Several possibilities for the formation of the coupling products were searched, involving either the intermediacy of Pt(IV) centers or *via* metathesis reactions in which only Pt(II) centers are involved. The process involving Pt(IV) was the lowest in energy. Thus Pt(IV) dihydride complex **D** was calculated only at 12.5 kcal mol⁻¹ (25.5 kcal mol⁻¹ in G) higher than **C**. The **TS_{CD}** was found at 28.0 kcal mol⁻¹ above **C**. The formation of the “Pt(H)₂Pt” complex was not searched because of the size of

the system. Rather, a path leading to a monomeric “Pt(H)₂” complex, **E**, which could then react with the Pt(0) complex **B** to form the observed dimer was searched from complex **D**. The reductive elimination from complex **D** does in fact lead to the formation of complex **E**, but the transition state connecting these two complexes, **TS_{DE}**, was calculated at 41.0 kcal mol⁻¹. On the other hand, the **TS_{DF}** leading to the elimination of H₂ and the formation of complex **F** was found at 30.0 kcal mol⁻¹, indicating a favored path. Reductive elimination leading to fragment **A** was found to require 33.1 kcal mol⁻¹ from **F** (**TS_{FA}** at 37.2 kcal mol⁻¹). Finally, the oxidative addition of H₂ leading to complex **E** was found to be barrierless. Overall, the calculations are in accord with the experimental facts, namely showing that inserted complex **C** is the preferred kinetic species of the reduction, and that an overall high activation energy of 37.2 kcal mol⁻¹ is required to eventually form the thermodynamic complex, the Pt(II) dimer *via* complex **E**.

In conclusion, we show here that using a strongly donating and flexible diphosphine ligand, featuring a propyl bridge between the P atoms, a reactive Pt(0) fragment can be generated, which does insert C–H bonds reversibly at room temperature. It was also shown, and corroborated by DFT calculations, that the Pt(II) complex can then further react with the solvent to yield biaryl derivatives at relatively low temperatures. The nature of the bidentate ligand therefore influences to a great extent the relative energies of complexes with formal oxidation states between 0 and 4. Pt(0), Pt(II) and even Pt(IV) species may be in equilibrium under readily accessible thermal conditions. Work is currently underway to further develop this coupling process between unactivated aromatic derivatives.

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