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ARTICLE TYPE

Room Temperature Reversible C–H Activation Mediated by a Pt(0) center, and Stoichiometric Biphenyl Formation via Solvent Activation

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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 ¹⁰ calculations. The coupling between two unactivated aromatic derivatives is also demonstrated.

C-H bond activation/functionalization is amongst the major challenges of nowadays chemistry, and in this field, the reaction of Pt centers with hydrocarbons have been extensively studied, ¹⁵ following the discovery made by Shilov in the early 70s.^{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 20 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 described in 1978 the ability of the complex $[(PPh_3)_2Pt(H)(CH_3)]$ to readily 25 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-

- ³⁰ dicyclohexylphosphinoethane), leading to a high energy $L_2Pt(0)$ fragment, capable of activating C–H bonds of alkanes (in low yield) or aromatics (quantitatively).^{14,9,15} 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 $L_2Pt(0)$
- 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 $L_2Pt(0)$ fragment (Scheme 1). We reasoned that careful choice of the bite angle of a diphosphine ligand should result in the stabilization of the $L_2Pt(0)$, while
- ⁴⁰ 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 ⁴⁵ which inserts quantitatively C–H bonds of the solvent at room temperature. One of the key points of the designed system lies



Scheme 1 Strategy of CH activation

in the reversibility of the insertion at room temperature, proved ⁵⁰ 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 derivative. Overall, the coupling of two molecules of the solvent to form the corresponding biphenyl derivative at mild temperatures is proved. ⁵⁵ DFT calculations rationalizing these findings are presented herein.

The low temperature (-35°C) reduction of $\mathbf{1}_{I}$ in toluene or room temperature reduction of $\mathbf{1}_{Cl}$ with two equivalents of KC₈ resulted in the formation of graphite and KX salts, indicative of the 60 efficient reduction of the Pt(II) complexes. The crude mixture, analyzed by ³¹P{¹H} NMR spectroscopy after 2 hours, did not present the signal ($\delta = 11.7$ ppm, $J_{Pt-P} = 3320$ Hz for $\mathbf{1}_{I}$, $\delta = 7.9$ ppm, $J_{Pt-P} = 3460$ Hz for $\mathbf{1}_{Cl}$ for the starting complex 1 and consisted instead in several platinum complexes featuring, for 65 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 reduction process followed by facile C-H insertions. Most interestingly, following the reaction in time, at 70 room temperature, revealed that the kinetic mixture evolved to vield a single C-H inserted complex, within 2 days. This reaction allowed for a full NMR characterization of the thermodynamic product, $\mathbf{3}_{H}$, after elimination of the graphite and the salts by filtration. Most importantly, this complex presents a signal for the

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Scheme 2 Summary of reactions

hydride at -1.53 ppm in the ¹H NMR spectrum (dd, $J_{Ptrans-H}$ = 179.3 Hz, J_{Pcis-H} = 21.2 Hz, J_{Pt-H} = 579 Hz), and two coupled ⁵ 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 ³¹P{¹H} NMR spectrum. The similar reaction carried out in deuterated toluene lead to the analogous complex, by ³¹P{¹H} NMR, but for which no hydride signal could be observed, proving the C–H insertion into the solvent to form complex **3**_D. Final proof of the insertion in the solvent was given by X-ray crystal analysis, which showed the insertion at the meta position (Figure 1).

Further evidence of the room temperature reversibility of the C– H insertion was obtained when complex 3_H was dissolved in D8-

¹⁵ toluene. The signal for the hydride decreased slowly to eventually disappear. The kinetics of the C–H insertion/elimination was then studied using complexes $4_{\rm H}$ and $4_{\rm D}$ obtained by the reduction of 1 in benzene and C₆D₆ respectively. The disappearance of the hydride signal form $4_{\rm H}$ dissolved in C₆D₆, and the disappearance ²⁰ of the corresponding deuteride signal form $4_{\rm D}$ dissolved in C₆H₆

were followed (Scheme 2). Since complexes 4_H and 4_D are not soluble in non aromatic solvents, we could not measure a direct kinetic isotope effect. However, the study of the kinetics of the disappearance of 4_H in

- 25 C₆D₆ and **4**_D in C₆H₆ allowed us to measure the kinetic constants k_H and k_D of disappearance of complexes, thus confirming the first order kinetic, 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 C₆H₆/C₆D₆ mixture
- ³⁰ allowed us to compute the full kinetic isotope effect (See supplementary information 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 ³⁵ hydride complex **3** was envisaged as a competent source of a 14 electron fragment. Accordingly, trapping of this fragment with several two electron donors were carried out providing the expected 16 electron complexes. The example of diphenylacetylene is given here, for which complete formation of ⁴⁰ complex **5** was observed within 5 minutes, and isolated in
- excellent 91% yield.

Quite unexpectedly, it was found that when a solution of complex



 $\begin{array}{l} \mbox{Fig. 1 X-Ray structure of complex $\mathbf{3}_{H}$. 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$ $1.56(3)$, $C(30)-Pt(1)-P(1) 93.1(1)$, $P(2)-Pt(1)-P(1) 93.1(3)$, $C(30)-Pt(1)-H$ $84(1)$, $P(2)-Pt(1)-H$ $84(1)$. The hydride has been refined using Shelx97. } \end{array}$



Fig. 2 ORTEP representation of complex 6 - Selected Bond 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.

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 ³¹P{¹H} 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 co coupling constants pointing to the formation of a dimer (¹ J_{PLP} = 2510 Hz ² J_{PLP} = 415 Hz). Moreover, it is consistent with previous reports by L. Mole who describes the cationic analogues of similar dimers.¹⁷ Final proof of the structure of complex **6** was given by an X-ray analysis, an ORTEP of which is presented in

- 65 Figure 2. This unprecedented reactivity presented above prompted us to carry a theoretical study within the frame of DFT, for 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 70 range interactions, as well as thermodynamics, and kinetics
- values. The Def2-TZVP basis set and its associated core potential was 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 ⁷⁵ 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 Δ H rather than on the Δ G for two main reasons: first, it is well known that the entropic contribution is typically overestimated, and since the reactions ⁸⁰ involve multiple variations in the number of molecules, the overestimation is greatly increased. Secondly, the reaction is carried out in the solvent, which concentration is therefore very high and decreases its entropic contribution to the different steps.



Scheme 3 Energy profile of the reaction

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This was confirmed thanks to the computation of the transition state energy of the dissociation of $4_{\rm H}$ through Eyring's method¹⁹: ⁵ we obtained, using the data of the previous kinetic study, a transition state energy of 22.2 kcal/mol, which fits well to the computed TS_{BC} (See ESI for calculation details).

The calculations show that the hypothetical free 14 electron fragment **A** is higher in energy than both the solvent adduct **B** and ¹⁰ 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 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 ¹⁵ searched, involving either the intermediacy of Pt(IV) centers or via metathesis reactions for 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 (25.5 kcal/mol in G) higher than **C**. The **TS**_{CD} was ²⁰ found at 28.0 kcal/mol 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
- ²⁵ 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. 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, indicating a favored
- ³⁰ path. Reductive elimination leading to fragment A was found to require 33.1 kcal/mol from F (TS_{FA} at 37.2 kcal/mol). Finally, the oxidative addition of H₂ to lead to complex E was found barrierless. Overall, the calculations are in accord with the experimental facts, namely showing that inserted complex C is
- ³⁵ the preferred kinetic species of the reduction, and that an overall high activation energy of 37.2 kcal/mol is required to eventually form the thermodynamic complex, the Pt(I) dimer via complex E. In conclusion, we show here that using a strongly donating and flexible diphosphine ligand, featuring a propyl bridge between
- ⁴⁰ the P atoms, a reactive Pt(0) fragment can be generated, which does insert C-H bonds reversibly at room temperature. It was also showed, 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 ⁴⁵ 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 50 between unactivated aromatic derivatives.

Notes and references

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 † Electronic Supplementary Information (ESI) available: Full experimental procedures, characterizations of products, CIF files for crystal structures, details of kinetic studies and geometry of optimized
60 structures are contained in the electronic supplementary information. See DOI: 10.1039/b000000x/

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A « (diphosphine)Pt(0) » fragment allows the room temperature reversible C–H activation as well as the coupling of two solvent molecules.