Platinum(II) mediated C^{sp3}-H activation of tetramethylthiourea[†]

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The C–H activation of the methyl group of tetramethylthiourea by cis-[PtL₂(NO₃)₂] (L = phosphine or N-heterocyclic carbene) has been investigated as a function of the ligand L. The presence of an electron-withdrawing group on the tertiary phosphine was found to promote the process. Moreover, when an excess of nitrate anion is present in the reaction mixture, the rate of C–H bond activation is retarded, suggesting the key role of an unsaturated tri-coordinate Pt^{II} species as intermediate.

Introduction

Since the groundbreaking report of Shilov and co-workers in 1969,¹ platinum(II)-mediated C–H activation is a topic of continued great interest.² Despite all efforts made, general, selective and efficient catalytic functionalization of C^{sp3}–H bond remains a challenge.³ Hence, an understanding of the factors affecting the reactivity of metal complexes towards C–H bond activation is of paramount importance. Notably, the electronic and steric properties of the ancillary ligands appear to be a key factor in achieving some control in this reaction.^{2a}

In our previous work, we reported that cis-[Pt(PPh₃)₂(NO₃)₂] is able to activate the sp³ C–H bond of tetramethylthiourea, tmtu, to afford complex 1 (Scheme 1).⁴

$$\frac{Ph_{3}P}{Ph_{3}P}Pt_{ONO_{2}}^{ONO_{2}} + -N \underset{I}{\overset{N}{\overset{N}{\longrightarrow}}} N \underset{I}{\overset{CH_{2}Cl_{2}}{r.t., 2h}} \frac{Ph_{3}P}{Ph_{3}P} \underbrace{Pt_{N}}_{Ph_{3}P} N \underset{N}{\overset{N}{\overset{N}{\longrightarrow}}} N \underset{N}{\overset{O}{\overset{O}{\longrightarrow}}} + HNO_{3}$$

Scheme 1 cyclometalation of tetramethylthiourea by cis-[Pt(PPh₃)₂-(NO₃)₂].

Proton abstraction is very likely to be driven by the nitrate anion, since nitric acid was detected at the end of the reaction. The cyclometalated product [Pt(PPh₃)₂(tmtu*)]NO₃ **1** is stable to air and moisture. More importantly, the Pt–C bond is not cleaved under the acidic reaction conditions.⁵ Encouraged by the stability of **1**, which implied the possibility of detection of the amount of product formed at different reaction stages, we decided to study the rate of the cyclometalation reaction as a function of the electronic properties of the ancillary ligand.

Results and discussion

A range of ancillary ligands were chosen for both their intrinsic steric and electronic characteristics. These ligands are shown in Fig. 1. A sample of possible phosphine ligands including a tertiary phosphine bearing an electron withdrawing group (P(4-F–Ph)₃ **4**), the unsubstituted PPh₃ **2**, a phosphine bearing a slightly electron-donating group (P(4-tol)₃ **3**) and the more electron donating dppp **5**, in which a phenyl group is substituted by an alkyl chain, were selected for use in this study. In addition, we included the N-heterocyclic carbene **6** (ICy),⁶ which is recognized to be even more σ -donating than alkyl phosphines.⁷ Of note, despite the great performance NHCs display as supporting ligands in several metal-catalyzed reactions,⁸ they are far less studied in platinum-mediated C–H activation.⁹



Fig. 1 Ligands (L) utilized in this study.

The tertiary phosphine-containing Pt^{II} complexes *cis*-[PtL₂ (NO₃)₂] were synthesized according to Scheme 2. Compounds **7a-d** were obtained in good yields from the reaction of *cis*-[PtL₂Cl₂] and an excess of AgNO₃ in refluxing DCM.¹⁰ The chloride precursors were synthesized according to the literature procedure (Scheme 2).¹¹

$$K_{2}PtCl_{4} \xrightarrow{2 L}{-2 KCl} \qquad L \xrightarrow{Pt}Cl \qquad AgNO_{3} \qquad L \xrightarrow{Pt}ONO_{2} \\ \hline Cl \qquad -2 AgCl \qquad L \xrightarrow{Pt}ONO_{2} \\ \hline L = PPh_{3} \qquad 7a \\ P(p-tol)_{3} \qquad 7b \\ P(4-F-tol)_{3} \qquad 7c \\ 1/2 \ dppp \qquad 7d \\ \hline \end{pmatrix}$$



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For the synthesis of the NHC-containing complex *cis*- $[Pt(ICy)_2(NO_3)_2]$ an alternative synthetic route was employed and is depicted in Scheme 3.



Scheme 3 Synthesis of cis-[Pt(ICy)₂(NO₃)₂] 9.

Addition of two equivalents of free ICy to *cis*-[Pt(dmso)₂Cl₂] in THF afforded *cis*-[Pt(ICy)₂Cl₂] in quantitative yield.¹² The new complex **8** was fully characterized by NMR spectroscopy and bulk purity was confirmed by elemental analysis. In order to unambiguously determine its structure, X-ray analysis was performed on a single crystal grown from CH₂Cl₂/pentane. Balland-stick representation of **8** with a selection of bond distances and angles are given in Fig. 2. Reaction of **8** with excess AgNO₃ in refluxing CH₂Cl₂ afforded the target complex **9**.¹⁰



 $\label{eq:Fig.2} \begin{array}{ll} \mbox{Ball-and-stick representation of 8 cis-[Pt(ICy)_2Cl_2]$. Selected bond distances (Å) and angles (°): Pt-C(1) 1.979(2), Pt-C(16) 1.991(2), Pt-Cl(1) 2.3657(6), Pt-Cl(8) 2.3701(6), C(1)-Pt-C(2) 94.66(9), Cl(1)-Pt-Cl(8) 89.70(2), N(1)-C(1)-N(2) 104.8(2). \end{array}$

The complexes were then reacted with an equimolar amount of tetramethylthiourea. From the complexes bearing tertiary phosphine **7a-d**, quantitative formation of the cyclometalated products **7*a-d** was obtained.¹¹ The activation of the methyl C–H bond and the formation of the Pt–C bond were confirmed by comparison of their NMR spectroscopic data with the previously fully characterized complex **1**.⁷ Of note is the appearance in the ¹H NMR spectra of a typical resonance around 3.50 ppm (triplet with satellites) for the CH₂–Pt protons and low *J* coupling constant for the phosphorus *trans* to CH₂ (*J* = 1800–2100 Hz) diagnostic of the

Table 1 ³¹ P NMR data	ta for	platinum	complexes
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L	CICI_02N0_PT_L		N-S-S Pt-L		N / S _⊕/ LPt_L		
P(4–F–Ph) ₃	$\delta^{\scriptscriptstyle 31} \mathrm{P} \ J_{\mathrm{Pt-P}} \ J_{\mathrm{P-P}}$	13.1 3666	1.8 4021	-1.0 3838 19.7	17.7 3284	15.6 2010 22.9	20.7 3483
P(4-tol) ₃	$\delta^{\scriptscriptstyle 31} \mathrm{P} \ J_{\mathrm{Pt-P}} \ J_{\mathrm{P-P}}$	13.2 3698	2.2 4028	0.2 3823 19.0	17.2 3293	15.1 2037 22.9	20.2 3406
PPh ₃	$\delta^{\scriptscriptstyle 31} \mathrm{P} \ J_{\mathrm{Pt-P}} \ J_{\mathrm{P-P}}$	14.9 3572	3.6 4010	1.7 3830 19.4	19 3257	17.1 2022 22.8	22.2 3462
dppp	$\delta^{\scriptscriptstyle 31} \mathrm{P} \ J_{\mathrm{Pt-P}} \ J_{\mathrm{P-P}}$	-5.0 3410	-13.4 3664	-13.3 3513 26.7	-1.6 2972	-5.4 1877 34.3	0.7 3189
			T				

^{*a*} CDCl₃ solution, δ values in ppm, *J* values in Hz.

formation of the cyclometalated product.¹¹ A summary of relevant NMR data is reported in Table 1.

Very interestingly when the reaction was performed with *cis*-[Pt(ICy)₂(NO₃)₂] no C–H bond activation was observed. In order to gain insight into the factors favoring this C–H activation, the formation of **1** was monitored by ³¹P NMR. The complex *cis*-[PtL₂(NO₃)₂] was dissolved in an NMR tube in CH₂Cl₂/CDCl₃ (1:1) and tmtu was then added. Spectra were recorded immediately after the addition of tmtu. Fig. 3 illustrates the formation of the cyclometalated product as a function of time. It is worth noting that, as previously reported for *cis*-[Pt(PPh₃)₂(NO₃)₂],⁴ substitution of one nitrate by tmtu proves rapid for all complexes, affording [PtL₂(NO₃)(tmtu)](NO₃) in a quantitative fashion in seconds.



Fig. 3 Formation of cyclometalated product with different ancillary ligands.

The data in Fig. 3 clearly shows that the reaction is faster for P(4–F–Ph)₃, the less electron rich tertiary phosphine. With dppp (diphenylphosphinopropane), the more electron donating phosphine, the reaction is considerably slower. A chelating ligand such as dppp might also play a role in stabilizing keys intermediates, thereby slowing the overall reaction. Despite this, it seems that the more σ -donor the ligand, the slower the cyclometalation of tmtu. The complete inhibition of C–H bond activation when ICy is used as a ligand follows this trend. NHCs are stronger σ donor ligand than tertiary alkyl phosphines.⁷ Surprisingly, complex **7b** bearing P(4–tol)₃ reacted faster then **7a** bearing PPh₃, although this difference is small when compared to the reactivity of complexes **7c**, **7d** and **9**. The reason for this inverted trend with respect to the Tolman electronic properties of the ligands¹³ is still unclear and is currently under investigation.

The role of the nitrate counter anion was then examined. Notably, when cis-[Pt(PPh₃)₂Cl₂] was used as a starting reagent, no cyclometalation occurred. On the other hand, addition of AgNO₃ salts to the reaction mixture effectively promoted C–H activation. This experiment suggests that formation of a coordinatively unsaturated Pt^{II} species, formed by abstraction of chlorides by Ag⁺, is key in leading to a Pt species capable of C–H activation.

In order to verify this hypothesis, we explored the influence of excess nitrate ligand on the reaction rate. Fig. 4 shows the reaction profiles obtained for the formation of $[Pt(P(4-tol)_3)_2(tmtu^*)]^+$ at different $[NO_3^-]$ concentrations. In these experiments, $(Et_4N)NO_3$ was employed as the nitrate anion source.



Fig. 4 Formation of cyclometalated product in the presence of different $[Pt]/[NO_3^-]$ ratio.

Clearly, the reaction rate decreases with an increasing NO_3^- concentration. These data suggest that dissociation of NO_3^- from $[PtL_2(S-tmtu)(NO_3)]^+$ and creation of a vacant coordination site likely facilitates C–H bond activation. To gain further evidence supporting our hypothesis, we performed the cyclometalation reaction in the presence of a coordinating ligand. We first tested triethylamine (Scheme 4). After 24 h stirring at room temperature, the reaction showed no evidence of cyclometalated product. Instead, we observed by ³¹P NMR the formation of $[Pt(PPh_3)_2(NEt_3)_2]^{2+}$



Scheme 4 Cyclometalation reaction in the presence of NEt₃.

 $(\delta = 8.7 \text{ ppm}, J = 3720 \text{ Hz})$. The identity of this compound was confirmed by independent synthesis from *cis*-[Pt(PPh₃)₂(NO₃)₂] and an excess of NEt₃. Only after refluxing the mixture for 5 h did we observe the formation of some cyclometalated product. However, another compound was present as the major product (5:1). Its ³¹P NMR spectrum displayed a doublet of doublets at $\delta = 6.7$ ppm (J = 3243 Hz) and $\delta = 17.1 \text{ ppm} (J = 3243 \text{ Hz})$. The chemical shift and the coupling constant of the upfield resonance are very similar to that of $[Pt(PPh_3)_2(NEt_3)_2]^{2+}$ ($\delta = 8.7$ ppm, J = 3720 Hz), while the downfield resonance had similar values to the resonance for P trans S in $[Pt(PPh_3)_2(S-tmtu)(NO_3)]^+$ ($\delta = 18.95$ ppm, J =3225 Hz). Thus, we attribute these resonances to $[Pt(PPh_3)_2(S$ tmtu)(NEt₃)]²⁺. Hence, NEt₃, being a less labile ligand than the nitrate anion, disfavors the formation of the vacant coordination site in the Pt sphere. A higher temperature is therefore required to promote its dissociation and drive the C-H bond activation.

As further support, an excess of triphenyl phosphine in the reaction mixture had the same rate decelerating effect. After 5 h refluxing in DCM, the cyclometalated product was present only in a small amount. With these data in hand, we propose the mechanism depicted in Scheme 5.



Scheme 5 Proposed mechanism for the formation of cyclometalated product.

Reaction of 9 with tmtu, a fast process,⁴ would lead to the cationic complex 10. Dissociation of one nitrate anion would lead to a tricoordinated dicationic species 11, both species very likely being in equilibrium. It has already been postulated that the formation of a vacant coordination site by dissociation of a labile ligand is a key step enabling C–H bond activation.¹⁴ Indeed, formation of unsaturated species such as 11, would allow an agostic interaction between the C–H bond and the platinum, leading to a σ complex such as 12,¹⁵ a critical intermediate for the C–H activation processes.^{2f} This dissociative mechanism is very likely to be also in play in the present case, as suggested by the decrease of reaction rate when excess coordinative ligand is present.

One of the mechanistic hypothesis for C–H bond activation addresses the uptake of the C–H bond by a tricoordinated T-shaped platinum species (like **11**) as the rate-determining step.¹⁶ Once the C–H bond is coordinated, its rupture is a fast process. Coordination of C–H bond would then be favored in Pt species with a high cationic character. Hence, less electron-donating ligands would stabilize the [PtL₂(tmtu)]²⁺ species to a lesser extent, promoting the formation of the agostic interaction.¹⁷ The trend observed in the present system for the cyclometalation rate as a function of L supports this hypothesis.

Conclusion

In summary, we showed that the activation of a C^{sp3} -H bond of tetramethylthiourea by *cis*-[PtL₂(NO₃)₂] is faster with a less electron-donating ligand L, while a strong σ -donor ligand such as a NHC can completely inhibit the reaction. This behavior supports the role of the cationic unsaturated species **11** as a key intermediate for the cyclometalation reaction. Moreover, increase of the reaction rate as a function of [NO₃⁻] suggests that C–H bond activation occurs through a dissociative mechanism.

Experimental

General considerations

The reaction was carried out in a MBraun glove box containing dry argon and less than 1 ppm of oxygen. Anhydrous solvent was either distilled from appropriate drying agents or purchased from Aldrich and degassed prior to use by purging with dry argon and kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were collected on 300 MHz and 400 MHz Bruker spectrometers. Elemental analyses were performed by Robertson Microlit Labs.

Synthesis of cis-[Pt(ICy)₂(Cl)₂] (8). In a 50 mL Schlenk flask, 215 mg (0.509 mmol) of cis-[Pt(dmso)₂(Cl)₂] was suspended in 20 mL of THF; a solution of 235 mg (1.02 mmol) of ICy in 10 mL of THF was added to the slurry which was then stirred overnight at room temperature. During this time, the *cis*-[Pt(dmso)₂(Cl)₂] gradually dissolved and a white precipitate formed. This solid was collected by filtration and washed with pentane. (322 mg, 87% yield). $\delta_{\rm H}$ (CDCl₃, 300 MHz) 6.93 (s, 4H, CH imidazole), 5.05 (m, 4H, CH cyclohexyl), 2.64 (d br, 4H, CH₂ cyclohexyl), 1.79 (m, 16H, CH₂ cyclohexyl), 1.55 (m, 12H, CH₂ cyclohexyl), 1.22 (m, 8H, CH₂ cyclohexyl). $\delta_{\rm C}$ (CDCl₃, 300 MHz) 145.79 (s, $J_{\rm Pt-C}$ = 1499 Hz, C carbene), 117.96 (s, $J_{\rm Pt-C}$ = 45.0 Hz, CH imidazole), 59.25 (s, $J_{Pt-C} = 36.7$ Hz, CH cyclohexyl), 35.91 (s, CH₂ cyclohexyl), 33.34 (s, CH₂ cyclohexyl), 25.59 (s, CH₂ cyclohexyl), 25.51 (s, CH₂ cyclohexyl), 25.39 (s, CH₂ cyclohexyl). δ_{Pt} (CD₂Cl₂, 400 MHz) 976.97 ppm. Anal. calcd for C₃₀H₅₀Cl₂N₄Pt (732.73): C, 49.18; H, 6.88; N, 7.65. Found: C, 49.07; H 6.64; N, 7.54.

X-ray data for 8. Crystals suitable for X-ray diffraction studies were grown from slow evaporation of a DCM/heptane solution. Formula: $C_{33}H_{51}Cl_{11}N_4Pt$, Fw: 1088.82, *T*/K: 100 (2); $\lambda/Å$: 0.71073; Cryst. Syst.: monoclinic; Space group: P2(1); *a*/Å: 9.6623(8); *b*/Å: 24.792(2); *c*/Å: 9.7344(8); $\alpha/^{\circ}$: 90.00; $\beta/^{\circ}$: 109.9250(10); $\gamma/^{\circ}$: 90.00; *V*/Å³: 2192.3(3); *Z* :2; D_c/g cm⁻³: 1.649; μ/mm^{-1} :3.900; F(000):1084; cryst. size/mm: 0.40 × 0.30 × 0.10; θ range/°: 5.38–36.83; No. of reflns collected: 16621; No. of ind. reflns /R_{int}: 16371/0.0228 No. of parameters: 442; GoF on F^2 :1.223; R₁, wR₂ (I > 2 σ (I)): 0.0211, 0.0528; R₁, wR₂ (all data): 0.0228, 0.0708; Flack parameter: 0.027(3).

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