Functionalization *vs.* β-elimination in alkane activation: a key role for 16-electron ML_5 intermediates

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Opinion

The structural preferences in the intermediate ML_5 d^6 alkyls are proposed to help determine the reactivity difference between Shilov systems, which convert R–H to R–X *via* reductive elimination, and alkane dehydrogenation catalysis, where R–H is converted to the alkene, *via* β-elimination of an R–M intermediate.

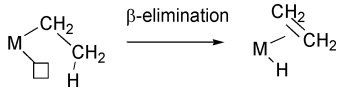
Alkane activation and functionalization is a topic of intense current interest.[1] In this paper, we compare the two main types of catalytic alkane functionalization reactions known for late transition metals—Shilov chemistry[2] [eqn. (1) and (2)] and alkane dehydrogenation [eqn. (3)].[3]

$$R\text{–}H + [PtCl_6]^{2-} \xrightarrow{[PtCl_4]^{2-}} R\text{–}Cl + H\text{–}Cl + [PtCl_4]^{2-} \quad (1)$$

$$R\text{–}H + [PtCl_6]^{2-} + H_2O \xrightarrow{[PtCl_4]^{2-}} R\text{–}OH + 2H\text{–}Cl + [PtCl_4]^{2-} \quad (2)$$

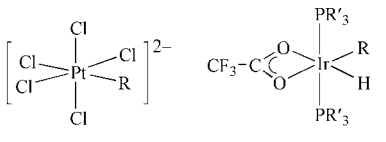
$$RCH_2CH_3 + tBuCH{=}CH_2 \xrightarrow{[IrH_2(tfa)(PR'_3)_2]} RCH{=}CH_2 + tBuCH_2CH_3 \quad (3)$$

Typical reactions of each type are shown. Both involve alkyl-metal intermediates, R–M, formed from an alkane R–H, yet paradoxically, the alkyls behave quite differently in the two cases. In Shilov chemistry, the R–M intermediate *selectively* undergoes an S_N2 attack by X^- {Cl^- [eqn. (1)] or OH^- from H_2O [eqn. (2)]} to give R–X as the final product ('reductive elimination'). In alkane dehydrogenation, the alkyl group β-eliminates to give alkene as the final product [eqn. (4)].



(4)

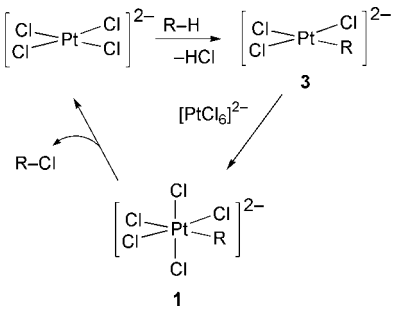
Structures **1** and **2** correspond to the alkyl Pt and Ir intermediates believed to be responsible for the Shilov[2a] and alkane dehydrogenation reactions,[3b] respectively, shown in Schemes 1 and 2. At first sight, they seem remarkably similar—both are d^6 octahedral species. Why does the Pt complex not undergo β-elimination to give alkene? This is not seen as a product, nor can the observed products be explained on the basis of a transient alkene intermediate. Conversely, why does **2** not give $R\text{–}OCOCF_3$?



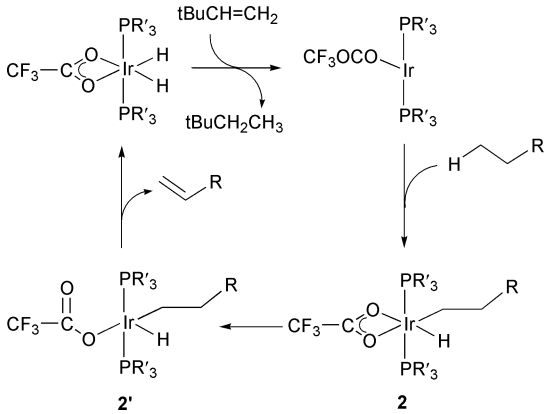
1 **2**

It is well known that a vacant site *cis* to the alkyl group is required for β-elimination.[4] This vacant site is denoted by the open box in eqn. (4). We propose that there is a both a kinetic and a thermodynamic reason why the Pt species, **1**, is unable to create a vacant site *cis* to the alkyl group. Kinetically, owing to the large difference in *trans* effects between R and Cl, R specifically labilizes a Cl^- ion *trans* to R. Thermodynamically, the 5-coordinate $[R\text{–}PtCl_4]^-$ intermediate, formed by Cl^- loss, has a very high tendency to maintain the high *trans* effect R ligand in an apical position. Although ML_5 d^6 species are thought to be fluxional, square pyramidal species with an apical Cl ligand are known to be inaccessible, lying at high energy.[5]

In contrast, in the Ir intermediate, **2**,[3b] there are two high *trans* effect ligands, R and H, in a *cis* arrangement; opposite them is a chelating trifluoroacetate (tfa). This structure is



Scheme 1 Schematic description of Shilov alkane chlorination.



Scheme 2 The proposed pathway for alkane dehydrogenation by $[IrH_2(tfa)(PR'_3)_2]$.

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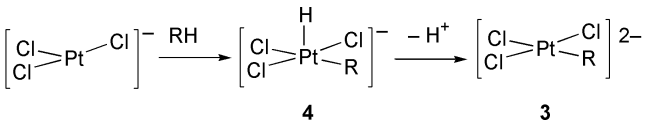
known to be appropriate because when Ph–H is used as substrate, β-elimination cannot take place and **2** (R = Ph) is isolated and directly observed. Since both ends of the tfa in **2** are *trans* to a high *trans* effect ligand, opening of the chelate ring at either side is easy and a vacant site can be readily formed *cis* to R. Consequently, β-elimination occurs even though a reductive elimination pathway to give R–$OCOCF_3$ is also in principle available.

The activation step, in which the alkane first reacts with Pt(II) to give the alkyl, constitutes a second point in the Pt mechanism where β-elimination might have occurred but did not. Unfortunately, this is also the step that is the least well understood. Mechanistic work[2,6] has identified two alternative pathways, at least one of which must be operative; it is also possible that both contribute.[2e] Unfortunately, this point is still not finally clarified.[2a]

The first is a σ-bond metathesis in which the alkane binds to a vacant site at Pt(II) and the bridging alkane proton is removed by a base to give the Pt(II)–R group directly. The Pt(II) alkyl so formed (**3**) cannot form a vacancy *cis* to R for the same reasons mentioned above. This pathway is not expected to give alkene.

The second possibility is that the alkane oxidatively adds to the Pt(II) to give a transient *cis*-Pt(IV)(H)(R) species, **4**. In view of our argument mentioned above, **4** should be capable of β-elimination, contrary to experiment. As Stahl, Labinger and Bercaw have noted[2a] this species, if formed, must be extremely reactive, losing H^+ very fast to give **3** *via* proton loss [eqn. (5)], favored because $[RPtCl_3]^{2-}$ is a good leaving group and a very weak base. The likely instability of the Pt(IV) alkene complex that would be formed also disfavors β-elimination.[2c]



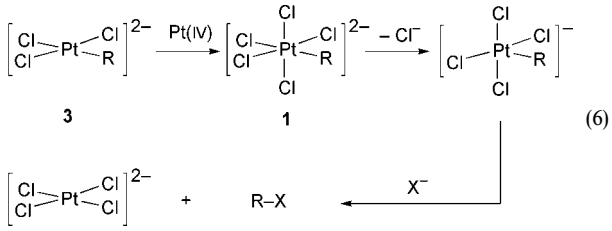
(5)

If this second activation pathway is indeed adopted, it follows that the difference between the Pt and Ir systems is not absolute but one of degree. The same type of *cis* alkyl hydride is formed as intermediate in both systems, **4** for Pt and **2′** for Ir. Although both **4** and **2′** potentially have the same reductive elimination and β-elimination pathways available, **4** gives essentially only reductive elimination, and **2′** gives essentially only β-elimination.

The reason, we believe, is the very different character of the metal fragments that constitute the leaving groups in reductive elimination from **4** *vs.* **2′**. In **4**, the *trans* effect of H should facilitate keeping H apical; R could also be apical but the two species should have an easy distortion[5] leading from one to the other. Species **4** has to lose a proton faster than it can undergo β-elimination, which is consistent with the idea that the stable square planar $[RPtCl_3]^{2-}$ fragment is an excellent leaving group.

If this is so, we have to ask why the corresponding Ir intermediate, **2′**, does not undergo rapid proton loss. This, we believe, may be because the analogous $[Ir(tfa)(PR'_3)_2R]^+$ fragment is a poor leaving group. Neither this species nor any stable analog has been synthesized or detected and, unlike Pt(II), Ir(I) species usually need π-acceptor ligands for stability. This point may be restated in terms of the relative stabilities of the oxidation states involved: Ir(III) > Ir(I) but Pt(II) > Pt(IV).

It now only remains to trace the fate of **3**.[2a] An oxidant, $[PtCl_6]^{2-}$, also present in the system, oxidizes **3** *via* electron transfer (not alkyl transfer) to give **1**, or possibly $[RPtCl_4]^-$ directly. Loss of Cl^- *trans* to the high *trans* effect R group in **1** sets the system up for S_N2 nucleophilic attack of Cl^- (or water) on the alkyl with loss of the excellent leaving group, $[PtCl_4]^{2-}$ [eqn. (6)]. This shows the close relationship between proton loss from **4** and loss of R^+ from **1**, both facilitated by the departure of a Pt(II) leaving group. Nucleophilic attack by X^- on R in eqn. (6) resembles base attack on H in eqn. (5) and whatever favors one can be expected to favor the other.



(6)

We therefore conclude that the balance between alkene and RX formation is sensitive to the circumstances. The role of the leaving group in the functionalization step is proposed to play a significant role in deciding the outcome.

Acknowledgements

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