An unexpected electronic preference for transfer of a β-hydrogen *trans* to a metal–hydride bond†

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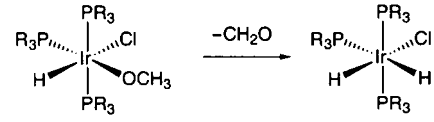
Density functional calculations (R = H) on the decomposition of *cis-mer*-$HIr(OCH_3)Cl(PR_3)_3$ to *cis-mer*-$(H)_2IrCl(PR_3)_3$ *via* a β-H transfer process are reported. The favoured computed pathway involves transfer of a β-H to a site *trans* to the Ir–H bond and is consistent with that deduced experimentally (R = Me, Et). Unexpectedly however, and in contrast to earlier calculations on analogous systems, this pathway is shown to be preferred on electronic grounds and not only on steric grounds as previously thought. The β-H transfer process involves rearrangement of a π-stabilised unsaturated alkoxide intermediate with the preferred pathway being favoured by reduced interactions between *trans* ligands in the resultant pseudo square-pyramidal transition state.

Understanding the factors that determine β-H transfer is fundamental to the control of the stability and reactivity of organometallic complexes. For metal alkyls, β-H transfer followed by alkene elimination leads to the formation of metal hydrides.[1] Analogous chemistry is proposed for late transition metal alkoxides, although the individual steps have rarely been observed directly.[2] The two kinetic studies of this process that have appeared show different behaviour. With $(dppe)Pt(OMe)_2$ β-H transfer is a facile, reversible process resulting in the formation of a 5-coordinate intermediate. Subsequent formaldehyde loss is rate-limiting.[3] In contrast, Blum and Milstein[4] in their study of the decomposition of *cis-mer*-$HIr(OCH_3)Cl(PR_3)_3$ to *cis-mer*-$(H)_2IrCl(PR_3)_3$ (R = Me, Et; **I** → **II** as in Scheme 1) demonstrated that the β-H transfer step was irreversible and was followed by facile aldehyde dissociation. The favoured pathway was shown to involve transfer of the β-H to a site *trans* to the original Ir–H bond with this route being thought to be preferred due to reduced steric hindrance in the transition state. However, we report here the results of a theoretical study that show, unexpectedly, that this pathway is also preferred on electronic grounds.

The two possible mechanisms proposed by Blum and Milstein for the decomposition of *cis-mer*-$HIr(OCH_3)Cl(PR_3)_3$ are shown in Fig. 1. Solvent-assisted chloride ion dissociation produces a π-stabilised 5-coordinate alkoxide species, **III**. Subsequent β-H transfer produces two possible formaldehyde complexes in which the hydrides are either *cis* ($\mathbf{IV_A}$, Pathway A) or ***trans*** ($\mathbf{IV_B}$, Pathway B). Along Pathway A, formaldehyde dissociation ($\mathbf{IV_A}$ → ***cis*-$\mathbf{H_2}$**) and re-co-ordination of chloride forms the *cis-mer*-product directly. Pathway B is still consistent with the observed product stereochemistry if ***trans*-$\mathbf{H_2}$**, formed upon formaldehyde dissociation from $\mathbf{IV_B}$, is assumed to isomerise rapidly to ***cis*-$\mathbf{H_2}$**. Blum and Milstein showed *via* labelling studies that, when R = Me, 94% of the reaction occurs *via* Pathway B, while when R = Et, Pathway B is in sole operation.



I **II**

Scheme 1

Blum and Milstein also considered the factors that favour these two alternative pathways. Evidence for an electronic preference for Pathway A was deduced from earlier calculations on the analogous β-H transfer reaction of $Ru(OCH_3)Cl(PH_3)_3$.[5] At the MP2//RHF level the transition state for β-H transfer was found to be 6.6 kcal mol^{-1} lower in energy when the β-H was transferred to a site *trans* to Cl, as compared to *trans* to PH_3 ($\mathbf{Ru_A}$ *cf.* $\mathbf{Ru_B}$ in Scheme 2). This preference was explained by the lower *trans* influence of the Cl

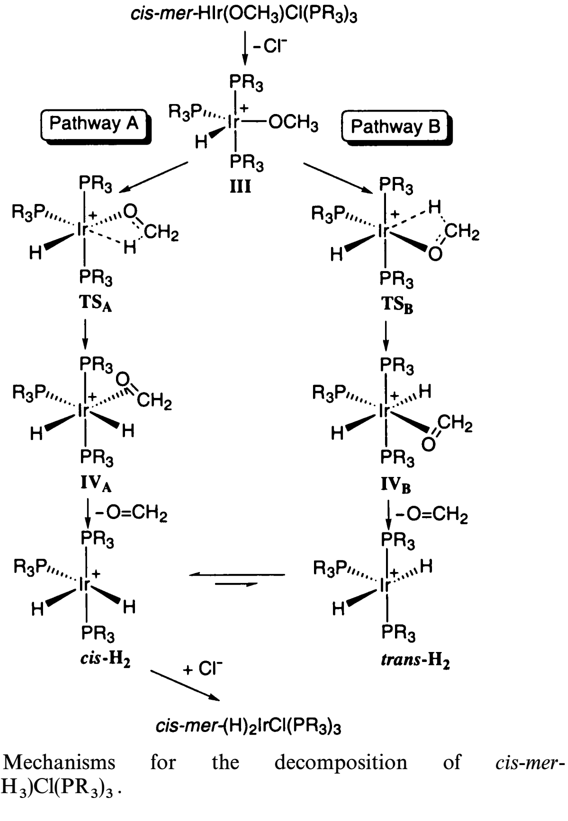


Fig. 1 Mechanisms for the decomposition of *cis-mer*-$HIr(OCH_3)Cl(PR_3)_3$.

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† Electronic supplementary information (ESI) available: computed Cartesian co-ordinates and energies of all molecules. See http://www.rsc.org/suppdata/nj/b0/b006546n/

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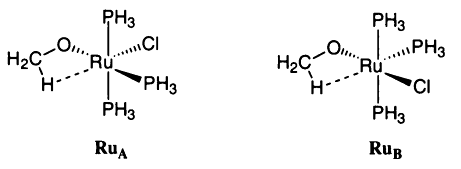


Scheme 2

ligand, which promotes a stronger, stabilising Ru···β-H interaction in the transition state.

As H has a higher *trans* influence than a PR$_3$ ligand, similar logic suggests that **TS$_A$** would be more accessible than **TS$_B$** in the Blum/Milstein system. The fact that Pathway B is actually observed experimentally has therefore been rationalised in terms of steric effects in the proposed pseudo square-pyramidal transition states (where the site destined to accept the transferring H atom is considered vacant). In **TS$_A$** two phosphines are in basal positions while the third occupies the sterically more encumbered axial position (*trans* to the vacant site). **TS$_B$** is sterically favoured as all three phosphines are in basal positions (*cis* to the vacant site). Therefore, even if there were an intrinsic electronic preference for Pathway A, the steric bulk of the PMe$_3$ ligands was considered sufficient to force almost all (94%) of the reaction to proceed *via* Pathway B. Use of the bulkier PEt$_3$ ligand increases the preference for Pathway B.

Initially, our interest in this system was to test whether calculations could reproduce the expected change in preferred pathway when different model systems were employed. Thus, according to the above analysis, calculations with PH$_3$ ligands should favour Pathway A (electronic factors dominant) but calculations with PMe$_3$ or PEt$_3$ ligands should favour Pathway B (steric factors dominant). To our surprise, calculations with PH$_3$ ligands already showed a preference for Pathway B, suggesting this pathway is also favoured on electronic grounds.

Results and discussion

Optimised geometries for stationary points along the alternative β-H transfer pathways are shown in Fig. 2. The computed structure of the common intermediate, **III**, exhibits a distorted trigonal-bipyramidal structure. This, along with the orientation of the methoxide ligand and the short Ir–O bond length (1.95 Å, compared to 2.06 Å computed for **I**) are all consistent with π-stabilisation in this species.[6] Along Pathway A a single transition state linking **III** to **IV$_A$** was located (**TS$_A$**, $E = +22.8$ kcal mol^{-1} *cf.* **III**). Compared to **III**, the alkoxide ligand in **TS$_A$** has rotated, the Ir–O bond has lengthened by 0.12 Å and there is evidence for some β-agostic interaction (Ir–O–C = 92.2°, Ir···H = 2.23 Å, C–H = 1.14 Å). Aldehyde dissociation (**IV$_A$** → ***cis*-H$_2$**) is calculated to be endothermic by 15.8 kcal mol^{-1}.

Along Pathway B a transition state arising from alkoxide rotation was also found (**TS$_{B1}$**, E = +7.1 kcal mol^{-1}). The geometry of this species suggests a weaker β-agostic interaction than that evident in **TS$_A$** (Ir–O–C = 102.0°, Ir···H = 2.57 Å, C–H = 1.12 Å), while the lengthening of the Ir–O bond is also not as pronounced (0.08 Å longer than in **III**). **TS$_{B1}$** connects to a β-agostic intermediate (**V**, $E = +5.8$ kcal mol^{-1}) from which a second transition state (**TS$_{B2}$**, $E = +12.6$ kcal mol^{-1}) corresponding to hydride transfer must be cleared to form **IV$_B$**. **IV$_B$** is 15.6 kcal mol^{-1} higher in energy than isomeric **IV$_A$** due to the unfavourable *trans* disposition of two hydride ligands in the former. Before the inclusion of zero point energies complex **IV$_B$** is calculated to be 0.7 kcal mol^{-1} more stable than **TS$_{B2}$**; however, incorporating this term reverses these energies with **TS$_{B2}$** becoming 0.2 kcal mol^{-1} more stable than **IV$_B$**. It is therefore not clear if a species corresponding to **IV$_B$** is a true minimum on the potential energy surface and whether the β-H transfer step and subsequent formaldehyde dissociation involves an intermediate of this type or is a concerted process. For the formaldehyde dissociation step from **IV$_B$** we were unable to locate a minimum corresponding to ***trans*-H$_2$**. This process therefore appears to lead directly to ***cis*-H$_2$** and is slightly endothermic (+0.3 kcal mol^{-1}).

Our computed reaction profiles for Pathways A and B are contrasted in Fig. 3. β-H transfer along Pathway A (**III** → **IV$_A$**) proceeds with an overall activation energy of +22.8 kcal mol^{-1} compared to +12.6 kcal mol^{-1} for

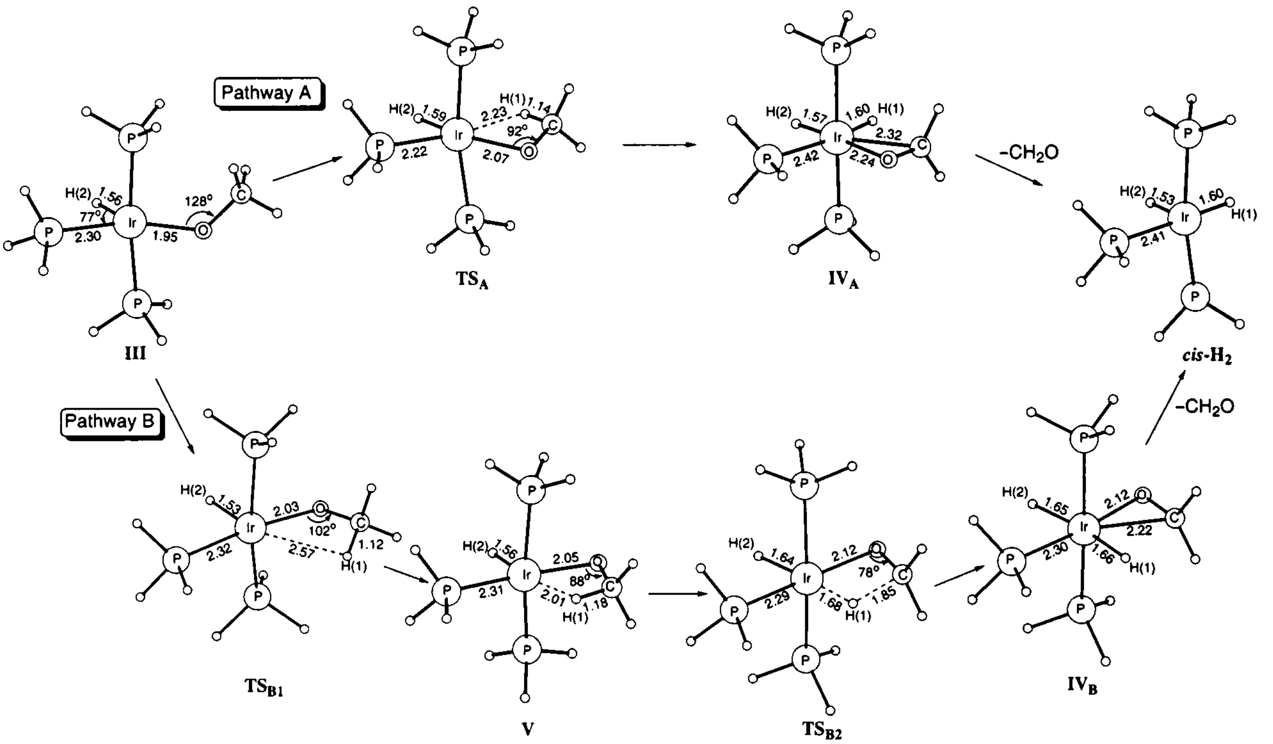


Fig. 2 Computed structures and selected optimised parameters (in Å and °) for stationary points along Pathways A and B.

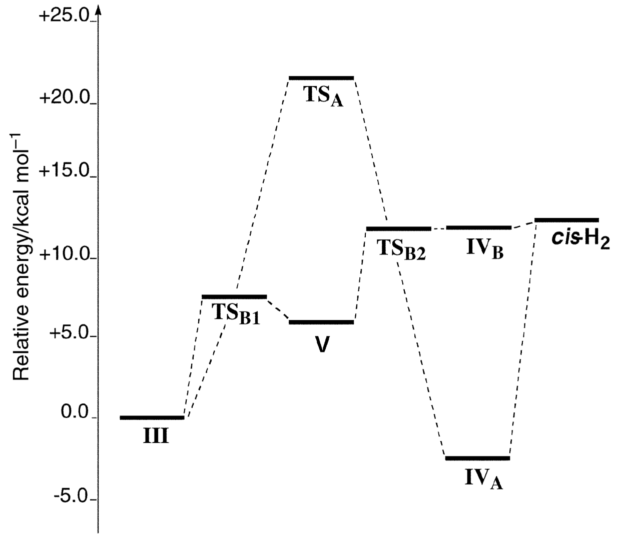
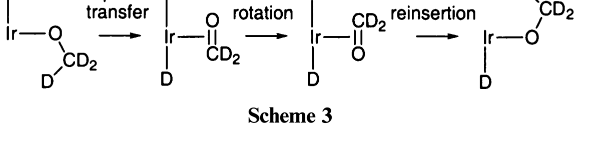


Fig. 3 Computed reaction profiles for Pathways A and B.

Pathway B (**III** → $\mathbf{IV_B}$). These results indicate that, in this case, β-H transfer is kinetically preferred when the β-H is transferred to a site *trans* to the stronger σ-donor ligand (H *vs.* PH_3). In addition, the use of PH_3 model ligands in our calculations suggests that Pathway B is intrinsically favoured on electronic grounds and not only on steric grounds as thought before.

This conclusion is clearly at odds with that reached previously from the study of β-H transfer in $Ru(OCH_3)Cl(PH_3)_3$. This species was calculated to have two alternative square-pyramidal minima in which the alkoxide ligand was *trans* either to PH_3 or Cl (see $\mathbf{Ru_A}$ and $\mathbf{Ru_B}$ in Scheme 2). The former was stabilised by the stronger β-H agostic interaction possible *trans* to the weaker *trans*-influence Cl ligand. The transition states for β-H transfer involved very little reorganisation of these minima other than an elongation of the cleaving C–H bond and in this case activation energies were determined by the strength of the developing Ru···β-H interaction. In the present study intermediate **III**, $[HIr(OCH_3)(PH_3)_3]^+$, differs significantly from the Ru complex in that, before β-H transfer can occur, the alkoxide ligand must first rotate to reach either $\mathbf{TS_A}$ or $\mathbf{TS_{B1}}$. This process is necessarily destabilising as it involves the loss of π-stabilisation in this species. The calculated structures of $\mathbf{TS_A}$ and $\mathbf{TS_{B1}}$ indicate a stronger Ir···β-H interaction in the former. This is consistent with the Ru study as in $\mathbf{TS_A}$ the β-H is *trans* to the weaker *trans*-influence ligand (PH_3 *cf.* H in $\mathbf{TS_{B1}}$). However, as $\mathbf{TS_{B1}}$ is about 16 kcal mol^{-1} more stable than $\mathbf{TS_A}$, the strength of this interaction cannot be the factor determining relative transition state energies. Instead, we suggest that *trans* interactions between the other ligands present in these pseudo square-pyramidal transition state structures are more important. In $\mathbf{TS_A}$ the hydride is *trans* to methoxide, itself a high *trans*-influence ligand, giving an arrangement that results in a destabilisation of this transition state and a high activation energy for β-H transfer along Pathway A. In contrast, $\mathbf{TS_{B1}}$ is much more accessible as it features the high *trans*-influence hydride ligand *trans* to what is essentially an empty site (or at least one containing only a very weak agostic interaction). As all subsequent points along Pathway B are significantly lower in energy than $\mathbf{TS_A}$, Pathway B will dominate, even in the absence of steric effects. Therefore, in contrast to the Ru systems above, relative activation energies in the Ir system are determined by the need of the π-stabilised intermediate **III** to reorganise *via* alkoxide rotation and the nature of the destabilising *trans* interactions that develop in the resultant pseudo square-pyramidal transition state structures.



Scheme 3

Although the unexpected electronic preference for Pathway B can be understood, some apparent inconsistencies between this computed pathway and known experimental data remain, however. We compute ***cis*-H_2** as the highest point along Pathway B and a minimal barrier for aldehyde reinsertion ($\mathbf{IV_B}$ → **V**). These results are more consistent with rate-limiting aldehyde dissociation preceded by reversible β-H transfer, while experimental data suggest an irreversible β-H transfer step that is followed by facile aldehyde loss. Experimental evidence for irreversible β-H transfer is based on the absence of any H/D scrambling in the formaldehyde products formed from the reactions of *cis-mer*-$HIr(OCD_3)Cl(PMe_3)_3$ and *cis-mer*-$DIr(OCH_3)Cl(PMe_3)_3$, which yield $[CD_2O]_x$ and $[CH_2O]_x$, respectively, as the sole organic products. However, for such scrambling to occur the formaldehyde ligand in $\mathbf{IV_B}$ must first rotate before reinserting into the original Ir–H (or Ir–D) bond (Scheme 3). We compute the transition state for this rotation to lie 13.9 kcal mol^{-1} higher than $\mathbf{IV_B}$ and therefore this process is much less favourable than formaldehyde dissociation, which occurs with a barrier of less than 1 kcal mol^{-1}.[7] In addition, the formaldehyde dissociation step would be expected to be favoured by entropy. Indeed when temperature (correction to 298.15 K) and entropy effects are incorporated into our results the free energy of this dissociation process becomes -11 kcal mol^{-1}. Similarly, the dissociation step along Pathway A ($\mathbf{IV_A}$ → ***cis*-H_2**) becomes more favourable but remains endothermic ($E = +3.9$ kcal mol^{-1}). The energetics of the other steps in our computed pathways are not significantly affected by these corrections.

Finally, our present calculations do not include any assessment of the effects of solvent or of the steric influence of the types of phosphine ligands used experimentally. As both pathways involve analogous cationic species solvation effects should be similar throughout and we do not expect the omission of solvation effects to introduce any bias in favour of one pathway or the other. As mentioned above, the inclusion of bulkier phosphines should increase any preference for Pathway B through reduced steric hindrance in $\mathbf{TS_B}$ compared to $\mathbf{TS_A}$. Calculations are underway on the *cis-mer*-$HIr(OCH_3)Cl(PMe_3)_3$ system to test this assertion. However, even in the absence of a treatment of steric effects our work has shown that the electronic factors controlling the precise pathway taken by a β-H transfer process are crucially dependent on the combination of ligands present.

In summary, in the decomposition of the *cis-mer*-$HIr(OCH_3)Cl(PR_3)_3$ species transfer of a β-H to a position *trans* to hydride is favoured kinetically on electronic grounds. This preference arises from the requirement for reorganisation of the π-stabilised alkoxide intermediate, coupled to the strong *trans* influence of the hydride ligand.

Computational details

Calculations used the GAUSSIAN 98 set of programs[8] and employed the B3 hybrid exchange potential of Becke[9] in conjunction with the PW91 correlation potential of Perdew and Wang.[10] Iridium was represented with the relativistic core potential (RECP) of the Stuttgart group with the associated (8s7p5d)/[6s5p3d] basis set augmented with an f polarisation function ($\alpha = 1.0$).[11] The phosphorus and chlorine atoms were also treated with Stuttgart RECPs and the associated basis sets[12] and included a d polarisation function.[13] H, C and O atoms were described with a 6-31G(d,p) basis set.[14,15] Geometry optimisation was performed without symmetry constraints and the nature of all stationary points was characterised by analytical frequency calculations. Energies include a correction for the zero point energy term. Further optimisations based on transition state structures, perturbed along the direction of the unique negative eigenvalue, were performed to ensure that they connected to the expected reactant and product minima.

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7 An alternative mechanism involving formaldehyde dissociation, rearrangement of ***trans*-H$_2$** to ***cis*-H$_2$**, reassociation of formaldehyde to give **IV$_B$** and reinsertion *via* **TS$_A$** can be ruled out on the basis of the very high calculated activation energy of this reinsertion step ($\sim$25 kcal mol^{-1}). Similarly, the fact that no minimum corresponding to ***trans*-H$_2$** could be located suggests that this species immediately rearranges to ***cis*-H$_2$** and that a mechanism involving formaldehyde dissociation from **IV$_B$** and reassociation to ***trans*-H$_2$** with effective formaldehyde rotation is unlikely.

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