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Generation and reactivity of sterically hindered iridium carbenes. Competitive α- *vs.* β-hydrogen elimination in iridium(III) alkyls†

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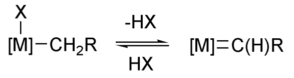
Some tris(pyrazolyl)borate complexes of iridium are able to cleave regioselectively the two α-CH bonds of ethers (cyclic and non-cyclic) and aliphatic amines, RCH_2X ($X = OR'$, NR_2'), with formation of Fischer-type carbene complexes, [Ir]=C(X)R. The last step of these rearrangements, namely an α-H elimination from an alkyl intermediate, [Ir]–CH(X)R, takes place even when β-H atoms are present. Migratory insertion reactions of hydride or alkyl ligands onto highly electrophilic iridium alkylidenes have also been investigated. It has been found that an *in situ* generated $[Ir]–C_2H_5^+$ species yields the corresponding $[Ir](H)(CHCH_3)^+$ derivative, that is, the α-H elimination product, at a rate faster than that of formation of the isomeric hydride ethene complex derived from β-H elimination.

Introduction

Despite their late development as compared to their main-group counterparts, transition metal alkyls and related organometallic species (*e.g.* metal aryls) lie at the heart of organometallic chemistry, as compounds that contain M–C σ bonds participate, directly or as reactive intermediates, in a plethora of synthetically useful stoichiometric and catalytic reactions.[1,2] Metal carbenes, a somewhat related family of compounds that possesses formally a metal–carbon double bond, M=C(R)(R′), have become in the last decades one of the most prominent class of transition metal organometallics.[3,4]

The metal–alkyl and –alkylidene functionalities are related by the generalized equilibrium[5] represented in eqn. (1)



$$\overset{X}{[M]-CH_2R} \underset{HX}{\overset{-HX}{\rightleftharpoons}} [M]=C(H)R \qquad (1)$$

For a given metal, several factors have been identified that may shift the equilibrium to the right. Pertinent in the context of this work are the use of a strongly basic alkyl (or related) leaving group (*viz.* X) and, above all, of a sterically congested metal environment.[5] The latter is often a critical factor in the generation of Schrock-type metal carbenes.[6] Not surprisingly, Schrock and co-workers have made extensive use of this approach to induce intramolecular "α-H abstraction" from an alkyl to an alkylidene complex.[6] An example in which α elimination is promoted by strongly coordinating PMe_3[7] is shown in eqn. (2). Following this line of reasoning, the neopentyl ligand was the optimal alkyl group of choice for this intramolecular H abstraction, as the CH_2SiMe_3 analogue does not produce as crowded an environment, by virtue of its longer C–Si bond, and

$$Ta(CH_2CMe_3)_3(=CHCMe_3) \xrightarrow[-CMe_4]{2\ PMe_3} Ta(CH_2CMe_3)(=CHCMe_3)_2(PMe_3)_2 \qquad (2)$$

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the benzyl, and specially the methyl groups, are not so sterically demanding.

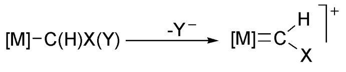
In contrast, sterically encumbered environments appear to disfavour β-H elimination, and complexes such as $Cr(CMe_3)_4$,[8] with numerous β hydrogen atoms, are stable despite the fact that tertiary alkyl ligands are much less stable than secondary and primary ones.[1a,9] In this respect, it is worth mentioning that when both α and β hydrogens are present in sterically hindered environments, α-H elimination may be faster than β elimination. For instance, in some particular Ta systems, α-H elimination can be 10^8 times faster than β-H elimination, although this is not a general observation.[10] Recently, it has been disclosed that in the highly congested molybdenum complex $Mo(C_5H_9)(NN_3)$, ($NN_3^{3-} = N(CH_2CH_2NSiMe_3)_3^{3-}$), β-H elimination to a Mo–cyclopentene-H is 6–7 orders of magnitude slower than α-H elimination to the related Mo–cyclopentylidene-H derivative.[11]

As it is generally assumed that an agostic CH_α or CH_β interaction precedes the corresponding H elimination,[12] it looks as if a very crowded environment could disfavour the β-agostic and favour the α-agostic intermediate. As a matter of fact, equilibria between CH_α and CH_β agostic interactions have been investigated recently in $Tp^{Me2}Nb$ species (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) and in other Ta–alkyl complexes.[13] For the $Tp^{Me2}Nb$ derivatives, the steric factors (imposed by the Tp^{Me2} ancillary ligand) favouring the α-CH interaction can override the electronic preference for the β-agostic structure.

Whereas as discussed above examples exist for α-H elimination being faster than β-H elimination in complexes of the early and mid transition elements, we are unaware of similar situations in compounds of the late transition elements. A preliminary investigation[14a] of alkene H/D exchange induced by $IrD_2(O_2CCF_3)(PAr_3)_2$ suggested competitive α- and β-H eliminations but this possibility was subsequently excluded.[14b] Nevertheless, carbene intermediates are invoked to explain multiple H/D exchange in methane and other hydrocarbons in the Shilov system.[14c] Work carried out in our laboratory over the last 10–12 years has led to a number of observations that evince that α-H elimination may indeed be competitive with β-H elimination. Here we make an account of this work, concentrating on two main aspects. Firstly, we will discuss double C–H bond activation reactions of ethers (cyclic and non-cyclic) and amines to give Fischer-type iridium carbenes, and subsequently we will analyse the migratory insertion chemistry of highly electrophilic, cationic iridium carbenes, that contain in addition a hydride or an alkyl ligand.

Fischer-type iridium carbenes by double α-CH bond activations of ethers and amines

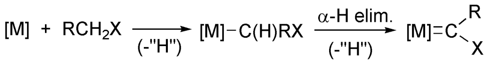
The generation of heteroatom-substituted carbene complexes by α-abstraction from a metal–alkyl compound [eqn. (3)] is a useful route to Fischer-type carbene.[4] Nevertheless, this methodology suffers from some limitations, for it requires access to the functionalised M–CHXY alkyl, plus the participation of an abstracting reagent (*e.g.* $[Ph_3C][PF_6]$).



$$[M]-C(H)X(Y) \xrightarrow{-Y^-} \left[[M]{=}C\genfrac{}{}{0pt}{}{H}{X}\right]^+ \qquad (3)$$

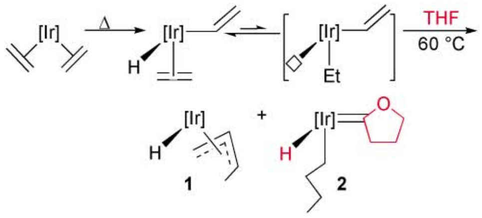
X = NR_2, OR, halogen
Y = H, OR, halogen

A potentially valuable alternative procedure is the regioselective activation of two α-CH bonds of an ether or amine functionality,[15–17] RCH_2X, where X stands for OR′ or NR_2' [eqn. (4)]. As applied to an aliphatic hydrocarbon (e.g. CH_4 to give $:CH_2 + H_2$) this transformation would be highly endothermic and it would face the opposing TΔS term of a bimolecular mechanism. However, for an ether or amine substrate, X coordination brings the C–H bond to be cleaved in close proximity to the metal, facilitating its subsequent attack. Moreover, the stabilization of the carbene ligand by metal coordination and by the α-heteroatom,[18,19] and the provision of a suitable "chemical sink" for the abstracted hydrogen atoms can make such a conversion thermodynamically allowed.



$$[M] + RCH_2X \xrightarrow[(\text{-"H"})]{} [M]-C(H)RX \xrightarrow[(\text{-"H"})]{\alpha\text{-H elim.}} [M]{=}C\genfrac{}{}{0pt}{}{R}{X} \qquad (4)$$

During studies aimed at the investigation of C–H bond activation and C–C bond forming reactions induced by Tp′Ir centres (Tp′ represents, in general, a hydrotris(pyrazolyl)borate ligand), we found that heating a tetrahydrofuran solution of the bis(ethene) Ir(I) derivative $Tp^{Me2}Ir(C_2H_4)_2$, provides a *ca.* 1 : 1 mixture of two complexes, namely the hydride allyl **1** and the hydride *n*-butyl carbene **2** (Scheme 1), the two compounds being formed through different competitive reaction pathways. It is pertinent to recall that when cyclohexane is used as the reaction solvent,[20] the hydride vinyl intermediate of Scheme 1 converts quantitatively into **1**, whereas in C_6H_6 only products resulting from C–H bond activation of benzene are observed.[15] Thus, it is clear that compound **2** results from a double α-CH bond activation of THF. Moreover, as revealed, in addition, by THF/C_6H_6 competition experiments, the cyclic ether is much less efficient than benzene in trapping the reactive $[Tp^{Me2}Ir(CH{=}CH_2)(C_2H_5)]$ intermediate that gives rise to all these C–C bond forming and C–H bond activation products.



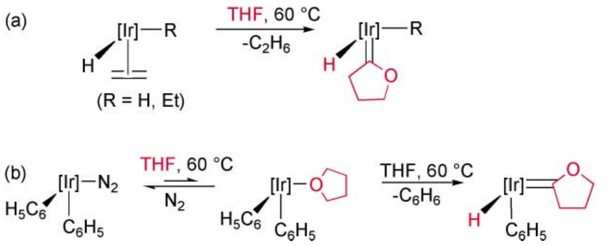
Scheme 1 Activation of THF by $Tp^{Me2}Ir(C_2H_4)_2$. Note: unless stated otherwise, [Ir] = $Tp^{Me2}Ir$ in all schemes and reactions.

Although some double α-CH bond abstractions from phosphines and amines were known at that time,[15a] the activation of THF that generates **2** was unprecedented. Simultaneous, albeit independent work from Werner *et al.* provided access to rhodium carbenes derived from the double metallation of a Me group of hemilabiles *i*-$Pr_2PCH_2CH_2OMe$ and *i*-$Pr_2PCH_2CH_2NMe_2$ ligands.[21] In subsequent years, similar double C–H bond activations have been reported.[18,19,22–25]

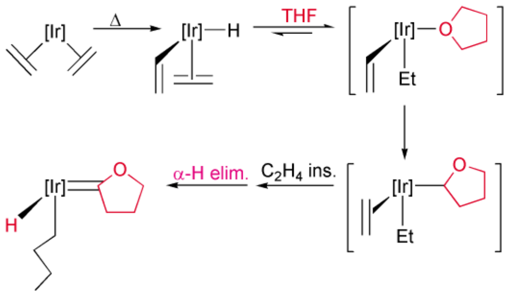
Diethyl ether, Et_2O, appears not to experience α-CH bond rupture under the conditions of Scheme 1. However, other cyclic ethers such as 2-MeTHF or dioxolane, provide products with structural features similar to those of **2**. Six-membered cyclic ethers are less prone than their C_4O counterparts to undergo this transformation, possibly due to steric hindrance associated with their coordination to iridium. Different $Tp^{Me2}Ir$ complexes that are able to generate *in situ* $[Tp^{Me2}Ir(R)(R')]$ intermediates (R, R′ = H, alkyl, aryl), with a vacant or readily accessible coordination site, are also capable of activating THF. Scheme 2 presents some examples studied by our group.[15b]

Mechanistic studies, including labelling with deuterium by means of d_8-THF, were in accord with the sequence of events depicted in Scheme 3.

Coordination of the ether to the metal, prior to C–H activation, is supported by the spectroscopic detection of the THF adduct represented in Scheme 2(b). Interestingly, the first of the cleaved H atoms couples to the vinyl carbon, while the second C–H bond rupture involves an α-H elimination (as shown by the use of d_8-THF). This occurs despite the existence of β hydrogen atoms, the reaction being most likely driven by the



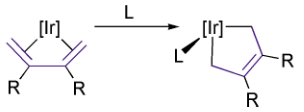
Scheme 2 C–H Bond activation of THF induced by different $Tp^{Me2}Ir$ centres.



Scheme 3 Proposed mechanism for the activation of THF by $Tp^{Me2}Ir(C_2H_4)_2$.

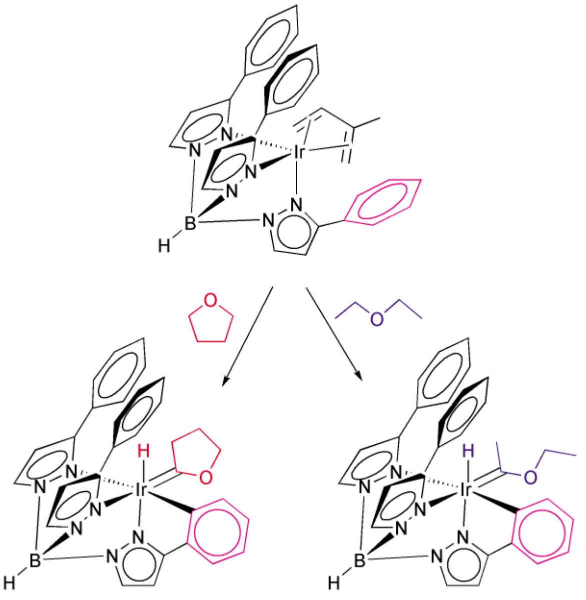
high thermodynamic stability of Fischer carbene complexes of this kind.

Generalisation of this chemistry to other ethers (cyclic or non-cyclic) and amine substrates was made possible, initially, by the use of the bulkier Tp^{Ph} ligand (Tp^{Ph} = hydrotris-(3-phenylpyrazolyl)borate). We had found previously[26] that Ir(I) diene compounds of composition $Tp^{Me2}Ir(\eta^4\text{-}H_2C{=}C(R)\text{-}C(R){=}CH_2)$ (R = H, Me), convert readily into the Ir(III) adducts $Tp^{Me2}Ir(\sigma^2\text{-}CH_2C(R){=}C(R)CH_2)L$, when reacted with a variety of Lewis bases [eqn. (5)].



(5)

Using $Tp^{Ph}Ir(\eta^4\text{-isoprene})$ (isoprene = 2-methyl-1,4-butadiene) as the precursor,[16] we were able to induce the activation of THF, to provide compound **3** in very high yields (Scheme 4). As can be seen, this is a more complex transformation than those previously described, for it involves the rupture of three C–H bonds. Two of these are the α-C–H bonds of the molecule of THF which is activated, and the third is an *ortho* hydrogen atom of a Tp^{Ph} phenyl substituent which undergoes cyclometallation.[16a] Deuteration experiments using d_8-THF reveal that one of the THF hydrogen atoms forms the Ir–H functionality. The other two cleaved H atoms add formally in a 1,4-fashion to the original η^4-diene and therefore this molecule acts as a sacrificial, hydrogen-atom acceptor, being evolved as 2-methyl-2-butene.



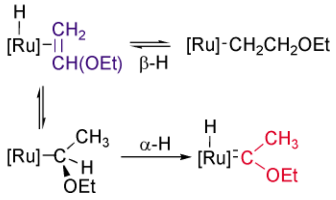
3

4

Scheme 4 Activation of THF and Et_2O by $Tp^{Ph}Ir(\eta^4\text{-isoprene})$.

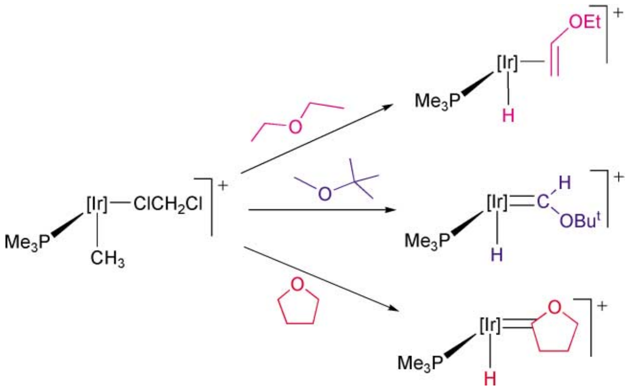
Anisole, C_6H_5OMe, and *N*,*N*-dimethylaniline, $C_6H_5NMe_2$, are also activated by this $Tp^{Ph}Ir$ system to give the corresponding carbenes.[16a] In all cases, the last reaction step is an α-H elimination, but whereas for the latter two molecules this is the only available reaction pathway once the first α-C–H bond has been broken, in the case of THF β-H elimination is once more possible (*vide supra*), but it is not observed. To ascertain whether the rigid, cyclic nature of the ether has any influence on this result, the activation of other more flexible ethers was investigated. Interestingly (Scheme 4) heating a solution of $Tp^{Ph}(\eta^4\text{-isoprene})$ in Et_2O gives the hydride ethoxycarbene complex **4** as the product of the double α-C–H bond activation. Compound **4** forms through a complex reaction pathway that requires, once more, metallation of one of the phenyl substituents of the Tp^{Ph} ancillary ligand.

C–H Bond activation of Et_2O is a rarely observed process, perhaps as a consequence of the low Lewis basicity of this molecule. A comparable activation, thereby leading to an ethoxycarbene complex, has been reported for platinum.[23] Ruthenium–(methyl ethoxy carbene) and related complexes, Ru=C(Me)OR, are also known and have been shown to result[24] from the isomerization of the vinyl ether by a Ru hydride (Scheme 5). In this system, the hydride carbene is thermodynamically more stable that either the hydride olefin or the alkyl isomers.



Scheme 5 The isomerization of vinyl ether to a coordinated carbene according to reference 24.

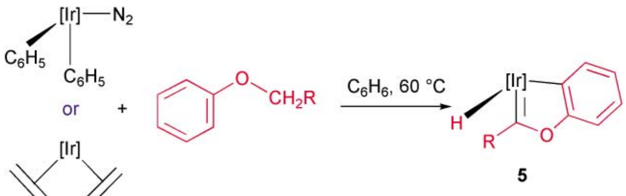
Nonetheless, it should be noted that the above observations cannot be generalised, since the cationic iridium complex $[(\eta^5\text{-}C_5Me_5)Ir(CH_3)(PMe_3)(ClCH_2Cl)]^+$ has been found to react with Et_2O, at room temperature, to give a vinyl ether complex (Scheme 6), with no indications of the isomeric methyl ethoxy carbene derivative being formed.[25] It seems that the last step of this reaction is a β-H elimination and moreover that the



Scheme 6 Activation of ethers by $[(\eta^5\text{-}C_5Me_5)Ir(CH_3)(PMe_3)(ClCH_2\text{-}Cl)]^+$ (see reference 25).

hydride–olefin product is thermodynamically more stable than its hydride carbene isomer. Methyl ethers give the expected hydride carbene products, and, even THF, despite the presence of β-H atoms, renders the corresponding hydride–carbene. The differences in the nature of the C–H bond activation products that result from the use of different metal precursors make, in our opinion, desirable additional studies on these systems.

The facility with which one of the phenyl substituents of the Tp^{Ph} ligand becomes metallated during the activation of ethers and amines, along with the observation already noted that benzene is much more efficient than THF in trapping reactive $Tp^{Me2}Ir(R)(R')$ intermediates, hinted that the double α-C–H bond activation could be extended to a number of ether and amine substrates, using *in situ* generated $[Tp^{Me2}Ir(C_6H_5)_2]$ intermediate,[15b] as the precursor. These assumptions were confirmed by the results summarized in Scheme 7.

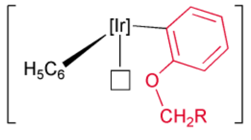


5

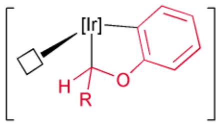
(R = H, Me)

Scheme 7 Activation of phenyl ethers by $Tp^{Me2}Ir(C_6H_5)_2$ fragments.

Reactions of either $Tp^{Me2}Ir(C_6H_5)_2(N_2)$ or $Tp^{Me2}Ir(C_2H_4)_2$, in C_6H_6, at 60 °C (under these conditions the bis(ethene) complex gives rise to the reactive intermediate $Tp^{Me2}Ir(C_6H_5)_2$) with the ethers $C_6H_5OCH_2R$ (R = H, Me) yield the expected iridium carbenes, in which the phenyl group of the molecule of the ether becomes also *ortho*-metallated.[17] Now three C–H bonds of the molecule of the ether are broken, two α-C–H bonds plus an aromatic *ortho* one. It is possible that *O*-coordination of the ether assists this transformation by bringing the α-C–H bonds to be cleaved into close proximity with the metal. Nevertheless, it is also plausible that the first C–H bond that is broken is the aromatic C–H bond (activation of the *ortho* C–H bond would also be facilitated by ether coordination) and that, eventually, in an intermediate alike **A**, *O*-coordination could help to generate the alkyl intermediate, **B**, and result in the activation of the first of the α-CH bonds. α-H elimination from **B** would yield the product. We highlight again the fact that, whereas in the case of anisole, **B** has only α-H atoms, for phenetol it has also H atoms in the β position. This does not change the course of the reaction. The product is, invariably, the hydride carbene that arises from α-H elimination. Whether α-H elimination is also kinetically preferred has yet to be ascertained, although it is our expectation that this matter will be clarified once the results of our on-going investigations become available.

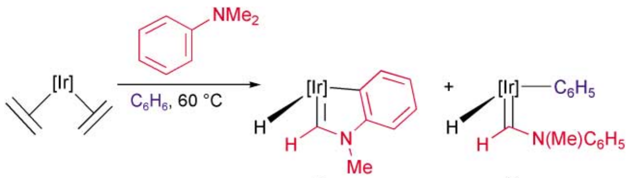


A



B

The analogous activation of *N*,*N*-dimethyl aniline gives also hydride carbene products, thereby demonstrating the wide applicability of this double α-C–H bond activation reactions induced by $Tp^{Me2}Ir(C_6H_5)_2$ fragments. Two products are obtained. They differ in the nature of the Ir–aryl functionality, which in one instance (**7**, Scheme 8) involves an intact phenyl group, whereas in the second product the amine phenyl substituent becomes *ortho*-metallated (**6**, Scheme 8).



6 **7**

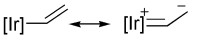
Scheme 8 Activation of $C_6H_5NMe_2$ by $Tp^{Me2}Ir(C_6H_5)_2$ fragments.

The ratio of these products remains constant with time, and an isolated sample of **6** does not convert into **7** when heated in C_6H_6. Moreover, heating **7** in the presence of the aniline does not yield **6**. Presumably, **6** and **7** are formed through different, competitive reaction pathways, the latter from the direct α-C–H activation of the amine, anchimerically assisted by N-coordination to iridium, and the former from initial aromatic *o*-CH activation, followed by formation of intermediates similar to **A** and **B** represented above.

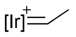
Migratory insertion reactions of cationic iridium carbenes

The heteroatom-substituted carbene complexes of iridium discussed in the preceding section contain hydride, hydrocarbyl and carbene ligands occupying adjacent coordination sites. This is an unusual situation. Some examples of either hydride carbene or alkyl carbene compounds are known, but in general their H and R ligands are prone to migrate onto the carbene carbon.[27–29] In our case, whereas under certain conditions H or R migration onto the carbene carbon atom may be observed, spontaneous rearrangement has not been detected so far. This may be due, at least in part, to low electrophilicity of the O- or N-substituted carbene carbon atom.

To gain access to this chemistry, we have generated highly reactive, cationic hydride– and alkyl–alkylidene species and studied their migrating properties. Protonation of neutral iridium(III)–alkenyl units is expected to occur at the β carbon atom (see structures **C** and **D**) with formation of a cationic alkylidene (**E**).

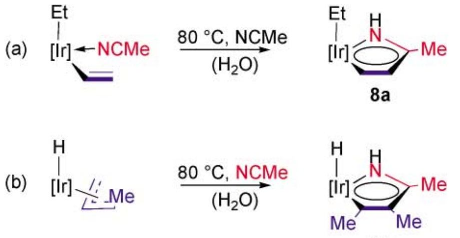


C **D**



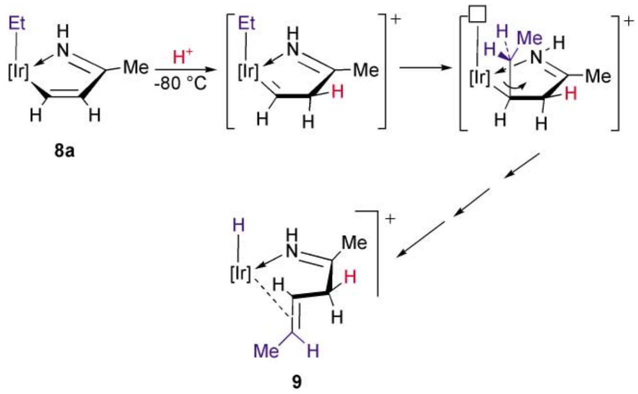
E

As iridapyrrole complexes of type **8** (Scheme 9) display considerable alkenyl character,[30] nucleophilic reactivity for their β ring carbon atom may be anticipated, and indeed a smooth reaction ensues (Scheme 10) when complex **8a** is treated with 1 equiv of $[H(OEt_2)_2][BAr'_4]$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$). A kinetic mixture of two isomeric *cis*- and *trans*-olefin products is initially formed, and it subsequently evolves with time to give exclusively the thermodynamically more stable *trans* isomer **9**.



Scheme 9 Examples of formation of iridapyrrole complexes.

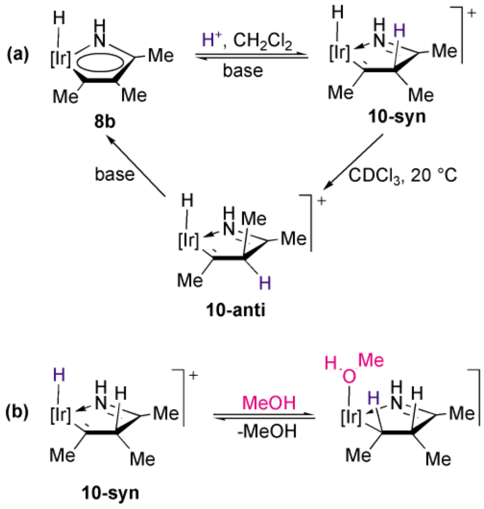
A mechanism in accord with the above arguments, that is, implying protonation at the β-ring carbon atom to generate the highly reactive ethyl–ethylidene intermediate of Scheme 10, is consistent with the overall reaction products.[30] As shown, the Ir–Et bond of this intermediate is aligned parallel to the pπ orbital of the carbene carbon, and moreover the alkyl product resulting from this migration can experience very facile β-H elimination. Interestingly, one of the diastereotopic H atoms



Scheme 10 Protonation of the iridapyrrole derivative **8a**.

has an important kinetic preference for β-elimination, perhaps due to hindered rotation around the C_{ring}–CH_2Me bond, in the presumably β-agostic intermediate.

Interesting results are also encountered during the protonation of the hydride iridapyrrole **8b** (Scheme 11(a)). Effecting the reaction in CH_2Cl_2 permits the isolation of a cationic *cis*-hydride alkylidene **10-*syn***. Formation of this species is quantitative by NMR, but in solution it rearranges irreversibly through an undisclosed mechanism, to **10-*syn***, possibly to avoid unfavourable contacts between the Me substituent of the ring $C_β$ atom and the Me groups of the ancillary Tp^{Me2} ligand. The protonation is reversible, the addition of a base to either of the isomers of **10** regenerates the starting iridapyrrole structure, **8b**.

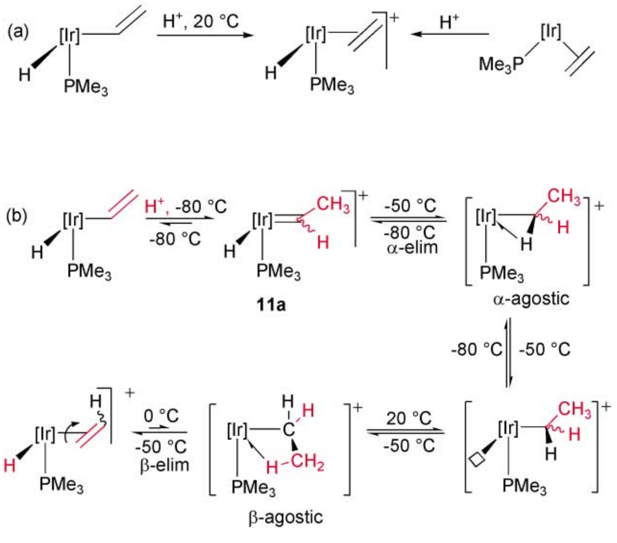


Scheme 11 (a) Protonation of iridapyrrole structures. (b) Reversible 1,2-H shift in **10-*syn***.

In accord with the high reactivity expected for a strongly electrophilic alkylidene ligand in a *cis* site with respect to a hydride functionality, the structural features of **10** can only be preserved in its solutions of weakly coordinating solvents (*e.g.* CH_2Cl_2 or $CHCl_3$). Methanol induces the 1,2-shift of the hydride atom from iridium to the carbene carbon, with formation of the migratory insertion product, stabilized as the methanol adduct (Scheme 11(b)). However, the low donicity of MeOH makes this rearrangement reversible, so that the simple evaporation of the solvent under vacuum restores the hydride alkylidene **10**. Although some examples are available,[11,18] Scheme 11(b) illustrates an uncommon, direct and reversible, α-H migration onto a well-defined electrophilic alkylidene carbon to generate an alkyl ligand.

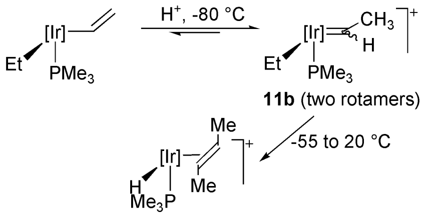
At first glance, the analysis of the migratory insertion chemistry experienced by complexes **8a** and **8b** upon protonation may be misleading for it could be taken as indicative of faster Et *vs*. H migration. As a matter of fact, both on theoretical arguments,[12b,31] and experimentally,[10,32] the opposite should be expected. Nevertheless, it is clear that neither of the above systems has provided quantitative data for the comparison to be made. Ethyl migration (Scheme 10) is too fast at −80 °C for its rate to be measured, whereas the 1,2-H shift, though not apparent because the resulting alkyl intermediate cannot rearrange further, may actually be much faster. Note that β-H elimination from this intermediate is not facile, as the ring β-H is too far from iridium to give rise to an accessible transition state, and moreover, following migration the Me substituent of the α-ring carbon atom would be placed on the side of the ring opposite to the generated coordination vacancy. Interestingly, the putative five-coordinate alkyl intermediate does not appear to undergo inversion readily. Hence, in the absence of a sufficiently strong Lewis base that could take over the hydride site, the 1,2-H migration is unproductive and its effects cannot be discerned. As noted, MeOH induces the rearrangement reversibly. Acetonitrile, a better donor toward cationic Ir(III) centres, yields the expected alkyl product.[30]

We have also investigated the migratory insertion chemistry of iridium alkylidenes resulting from protonation of the vinyl complexes $Tp^{Me2}Ir(CH{=}CH_2)(X)(PMe_3)$,[33] for X = H, C_2H_5. As summarized in Scheme 12, the room-temperature protonation of $Tp^{Me2}Ir(CH{=}CH_2)(H)(PMe_3)$ with $[H(OEt_2)_2][BAr'_4]$ gives a cationic hydride olefin compound, alternatively accessible from the direct reaction of $Tp^{Me2}Ir(C_2H_4)(PMe_3)$ with the acid. However, low-temperature ^1H NMR monitoring demonstrates the instantaneous formation of the cationic hydride ethylidene derivative **11a**, as a 1 : 1 mixture of two Ir–ethylidene rotamers, that undergo fast interconversion at −60 °C (rotation barrier 10.2 kcal mol^{-1}). At temperatures higher than −55 °C, they transform neatly into the hydride ethylene product without any other observable intermediates. The addition of D^+ to the *in situ* generated $Ir–CH{=}CD_2$ isotopomer reveals (^1H NMR monitoring) that **11a** converts into product by a 1,2-migration of the hydride onto the alkylidene carbon, and not by the alternative 1,2-hydrogen shift within the alkylidene ligand (*viz.* from the Me substituent to the metal-bound alkylidene carbon atom). $[Tp^{Me2}Ir(D)(C_2H_4)(PMe_3)]^+$ interchanges with $[Tp^{Me2}Ir(H)(C_2H_3D)(PMe_3)]^+$ at 0 °C ($\Delta G^{\neq}$ = 21.1 kcal mol^{-1}) while $[Tp^{Me2}Ir(H)(C_2H_4)(PMe_3)]^+$ reacts[34b] with NCMe in a bimolecular kinetic process (20 °C, $\Delta G^{\neq}$ ≈22 kal mol^{-1}) to give $[Tp^{Me2}Ir(C_2H_5)(PMe_3)(NCMe)]^+$, probably through the β-agostic intermediate.



Scheme 12 Protonation of an $Ir(CH{=}CH_2)$ unit and migratory insertion chemistry of the hydride alkylidene $[Ir]H(CHCH_3)(PMe_3)^+$.

The analogous low-temperature protonation of the related ethyl vinyl complex proceeds similarly (Scheme 13) to give the cationic compound **11b**, also as a mixture of two carbene

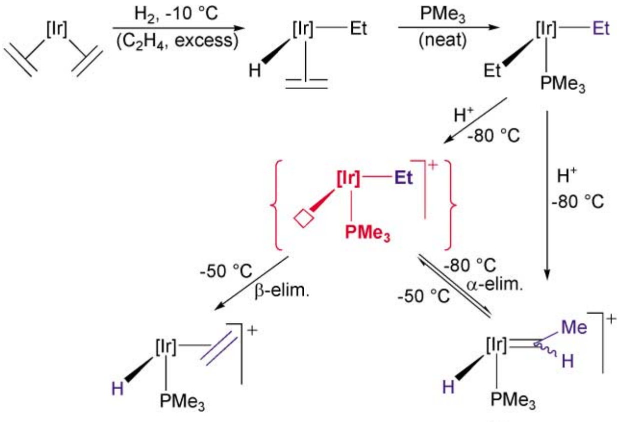


Scheme 13 Ethyl migration onto Ir=CHCH$_3$]$^+$.

rotamers ($\Delta G^{\neq}$ = 12.1 kcal mol^{-1}). Above −55 °C, a cationic hydride 2-butene compound forms, initially as a mixture of the *cis*- and *trans*-olefin isomers, which at room temperature converts into the themodynamically more stable *trans* isomer. As before, deuteration studies reveal that **11b** transforms into products by Et ligand migration onto the alkylidene carbon.

Most unexpectedly, measuring of the rate of disappearance of the alkylidenes **11a** and **11b** at −47 °C, leads to k_{obs} values of 2.0×10^{-4} and 2.5×10^{-4} s^{-1}, respectively ($\Delta G^{\neq}_{H} \approx \Delta G^{\neq}_{Et} \approx$ 16.7 kcal mol^{-1}, thereby $\Delta(\Delta G^{\neq})$ for H *vs.* Et approximately zero). As already mentioned, hydride migration is expected to be much faster than Et migration[12b,31] (this is largely due to differences in the spatial properties of the σ orbitals of the migrating H and Et groups). Indeed, hydride migration about ten orders of magnitude faster than methyl migration has been measured for the complexes (η^5-$C_5Me_5)_2Ta(CH_2)R$ (R = H, Me),[10] and similar, albeit somewhat smaller differences, have been encountered in the migration of H and Et groups to olefins.[32]

It seems, however, that our rate data do not provide a true comparison of the two elementary steps under investigation. Ethyl migration is most likely irreversible, whereas H migration appears to be reversible. A kinetic isotope effect, k_H/k_D, of *ca.* 2.5 has actually been found in the rearrangement of $[Tp^{Me2}Ir(CHCD_3)(H)(PMe_3)]^+$, and most importantly, treatment of the bis(ethyl) complex $Tp^{Me2}Ir(C_2H_5)_2(PMe_3)$[34a] with HBAr′$_4$ at −80 °C, while partially causing protonation of one of the Tp^{Me2} pyrazolyl rings (Scheme 14),[35] allows observation[34b] of the hydride ethylidene derivative **11a** (*ca.* 10–15% of the total conversion; this species is readily and unequivocally identifiable by its characteristic NMR parameters).

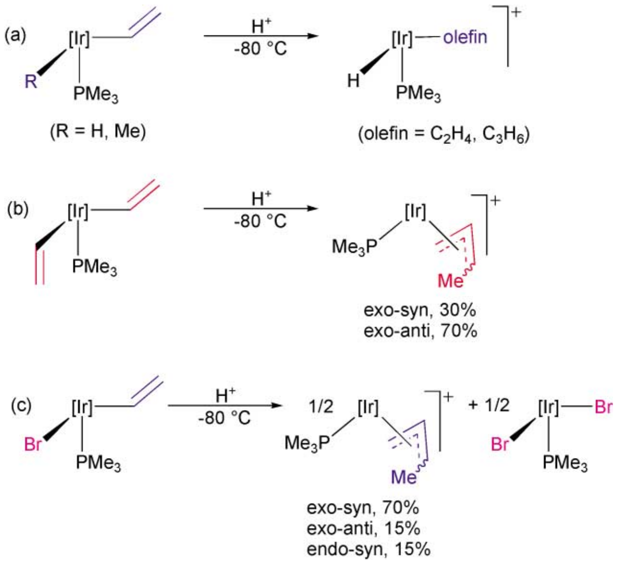


Scheme 14 Generation of **11a** by direct protonation of [Ir](C$_2$H$_5$)$_2$-(PMe$_3$).

Hence, only the product of the α-H elimination reaction from the purported $[Tp^{Me2}Ir(C_2H_5)(PMe_3)]^+$ five-coordinate ethyl intermediate (represented in red in Scheme 14) can be detected at these low temperatures. No indications about the formation under these conditions, of the hydride olefin complex $[Tp^{Me2}IrH(C_2H_4)(PMe_3)]^+$ can be found, but above −55 °C generation of this species takes place.

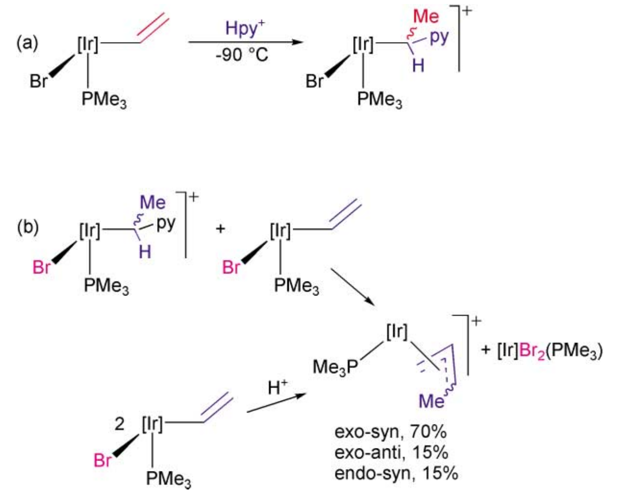
All these results demonstrate that in our system α-elimination of the Ir–ethyl intermediate is reversible. They also reveal that the product of the β-H elimination, that is in fact thermodynamically preferred over that of the α-H elimination, forms at a slower rate, perhaps as a consequence of restricted rotation around the Ir–ethyl bond caused by steric hindrance.[13a,36]

To complete these studies, we considered of interest to generate ethylidene derivatives of the (η^5-C_5Me_5)Ir fragment (from now on, Cp* will represent η^5-C_5Me_5). As shown in Scheme 15(a), the protonation of the vinyl complexes Cp*Ir(CH=CH$_2$)(R)(PMe$_3$) (R = H, CH$_3$)[37,34b] at −80 °C affords the corresponding hydride olefin complexes as the only detectable species.[34b] The analogous protonation of the bis(vinyl) and bromo(vinyl) compounds (Scheme 15(b) and 15(c), respectively) provides crotyl complexes[34b,38] (as different mixtures of stereoisomers) as a result of intra- (Scheme 15(b)) and intermolecular (Scheme 15(c)) coupling of two hydrocarbyl-derived fragments. For the latter reaction, the stoichiometry is different (2 : 1 molar ratio of Ir to acid) and besides, the complex Cp*IrBr$_2$(PMe$_3$) is also produced.



Scheme 15 Low-temperature protonation of Cp*Ir(CH=CH$_2$) complexes. [Ir] = (C$_5$Me$_5$)Ir.

Whilst the reactions of Scheme 15 provide only indirect evidence for the generation of a reactive Ir(CHCH$_3$)$^+$ unit, treatment of the bromo vinyl compound with [Hpy][BAr′$_4$] (Scheme 16) gives a pyridinium ylide, evidently as a result of nucleophilic attack by pyridine onto the highly electrophilic alkylidene carbon atom of such a unit. Two stereoisomers are formed which can be shown with the aid of EXSY experiments (60 °C, in the presence and in the absence of free py) to undergo



Scheme 16 Pyridinium ylide formation (a) and intermolecular C–C coupling between Ir(CH=CH$_2$) and Ir(=CHCH$_3$)]$^+$ units (b).

dissociative exchange. Accordingly, the ylide was used as the source of $Ir(CHCH_3)^+$ fragments and its mixing with $Cp^*Ir(CH{=}CH_2)Br(PMe_3)$ in equimolar amounts (Scheme 16(b)) provided a mixture of crotyl isomers identical with that resulting from the direct reaction of $Cp^*Ir(CH{=}CH_2)Br(PMe_3)$ with the acid (2 : 1 ratio).

The above results demonstrate that the $Cp^*Ir(CH{=}CH_2)$ fragment is also protonated at C_β, with formation of $[Cp^*Ir({=}CHCH_3)]^+$. However, in this Cp*Ir system the nucleophilic attack by a hydride or a hydrocarbyl ligand that would follow and the β-elimination of the resulting alkyls are so fast, that the ethylidene species cannot be detected by NMR. Even for $Cp^*Ir(CH{=}CH_2)Br(PMe_3)$ the intermolecular coupling is too fast to permit the detection of reaction intermediates. Whether α-H elimination is slower or faster than β-H elimination cannot be discerned. Nonetheless, it is evident that the rates of the migration step and of the ensuing β-H elimination are greater for Cp*Ir than for $Tp^{Me2}Ir$. As C_5Me_5 is a better electron donor[39] than Tp^{Me2}, the $Tp^{Me2}Ir$ alkylidenes are expected to be more electrophilic than the Cp*Ir alkylidenes, which apparently is contrary to our experimental observations. It seems, however, plausible that regardless of the nature of the ancillary ligand, the $Ir(CHMe)^+$ fragments investigated are highly electrophilic and that the reactivity differences between the two systems are not electronic in origin. The higher steric demands of the Tp^{Me2}, as compared with Cp*, would create very congested $Tp^{Me2}Ir$ environments. In addition, Tp^{Me2} enforces octahedral coordination at the metal, whereas Cp* is more flexible a ligand, so that coordination environments lower or higher than six become much less accessible for $Tp^{Me2}M$ centres than for Cp*M counterparts.[40,41] All these factors may seem to have a decisive role in the discrimination of the two systems.

In summary, we have demonstrated that sterically encumbered Tp′Ir(III) centres, that may be easily generated from readily available Tp′Ir(I) precursors, are able to induce the regioselective double C–H bond activation of a variety of ether and amine substrates. The products of these C–H bond activation reactions are Fischer-type carbenes, and in all the systems investigated, the last C–H bond cleavage is a α-H elimination that occurs even in the presence of β-hydrogens.

Despite the additional existence of adjacent hydride or hydrocarbyl (alkyl or aryl) functionalities, the carbene complexes do not rearrange spontaneously by migratory insertion chemistry. However, related albeit cationic, hydride carbene or alkyl carbene derivatives experience very fast migration of the H or R group onto the carbene carbon. For some specific systems, reversible α-H migration has been demonstrated, whereas in other cases the hydride carbene that results from the α-H elimination of an Ir(III)–alkyl may form faster than the hydride alkene complex derived from β-H elimination. Likewise, α-H elimination may also be more favourable, thermodynamically, than β-H elimination. The existing notion that the above observations were applicable only to complexes of the early transition elements[11] must therefore be amplified to encompass complexes of the late transition elements, notably of iridium.

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