# Electrophilic Cationic Ethylidene Complexes of Ir(III). Comparative α-Migratory Insertion Processes into Hydride and Ethyl Groups

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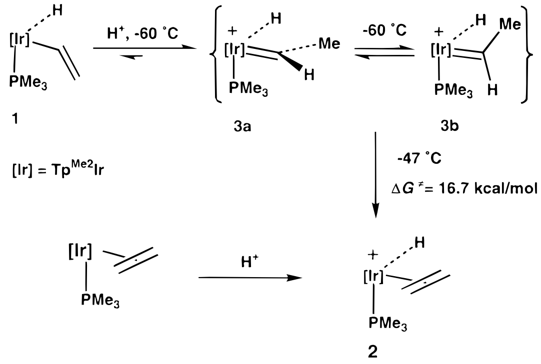
Transition metal carbenes M═CRR′ (R, R′ = H, alkyl, or aryl) are essential intermediates for many organic transformations and are playing an increasingly important role in modern organometallic chemistry.[1,2] Electrophilic alkylidene moieties can be generated by different routes.[1] A simple one, which appears to have higher synthetic potential than presently realized, is the protonation of electron-rich, late transition metal alkenyl complexes.[3] Such compounds are nucleophilic at $C_\beta$, implying that the carbenic resonance form $M^+{=}CHC^-H_2$ makes a significant contribution to the electronic ground state.

We have shown recently[4a,b] that $Ir^{III}$−alkenyl complexes that contain the ancillary hydrotris(pyrazolyl)borate ligands, Tp′,[5] undergo electrophilic attack at the β-carbon atom. Their protonation is therefore expected to produce cationic Ir(III) alkylidenes, a kind of functionality that for group 9 elements is only known in their lower oxidation states.[6] Here we demonstrate the utility of this approach which has given us access to unique electrophilic Ir(III) ethylidene−hydride and −ethyl complexes, $[Tp^{Me_2}Ir({=}CHMe)(R)(PMe_3)]^+$ ($Tp^{Me_2}$ = hydrotris(3,5-dimethylpyrazolyl)borate; R = H, $C_2H_5$). We describe the α-migratory insertion reactions of these species and compare the relative migratory aptitudes of hydride and alkyl ligands to Ir═C< in this fundamental transformation. Despite the importance of this class of rearrangements, and their proposed participation in the chain initiation and growth steps of the Fischer−Tropsch process,[7] these reactions remain largely unexplored.[8,9]

**Scheme 1**



The hydrido−vinyl precursor, $Tp^{Me_2}Ir(CH{=}CH_2)(H)(PMe_3)$ (**1**), is obtained readily from the thermal C−H activation[4b,c] of the corresponding Ir(I)−olefin adduct, $Tp^{Me_2}Ir(C_2H_4)(PMe_3)$.[4c] Protonation of **1**, in $CDCl_3$, with $[H(OEt_2)_2][BAr_4]$ (Ar = 3,5-$C_6H_3$-$(CF_3)_2$)[10] occurs rapidly at room temperature to give the cationic hydride−olefin species $[Tp^{Me_2}Ir(C_2H_4)(H)(PMe_3)][BAr_4]$ (**2**) in almost quantitative yield.[11] Compound **2** can also be obtained directly from $Tp^{Me_2}Ir(C_2H_4)(PMe_3)$ by addition of the acid. Not unexpectedly, NMR studies show that the rotation of the $C_2H_4$ ligand in **2** is fast even at low temperature (−60 °C).

The above results could be consistent with protonation of the vinyl group of **1** at $C_\alpha$.[3e−g] However, low-temperature $^1H$ NMR monitoring (−100 °C, $CD_2Cl_2$) of the reaction of **1** with $HBAr_4$ reveals the instantaneous formation of the cationic hydride−ethylidene complex $[Tp^{Me_2}Ir({=}CHMe)(H)(PMe_3)]^+$ (**3**). This clearly demonstrates that protonation takes place exclusively at the vinyl β-carbon (Scheme 1). Compound **3** exists as a thermodynamic 1:1 mixture of two isomers that undergo fast interconversion at −60 °C (likely by rotation around the Ir═C bond) ($\Delta G^\ddagger = 10.2$ kcal·mol$^{-1}$). At −90 °C the dynamic process is slow on the NMR time scale and distinct resonances are observed for the two isomers. Under these conditions they exhibit hydride signals at $\delta$ −16.02 (d, $^2J_{HP} = 24$ Hz, **3a**) and −16.04 (dd, $^2J_{HP} = 24$; $^3J_{HH} = 3$ Hz, **3b**) and C*H*Me ethylidene overlapping multiplets in the proximity of 20.10 ppm (q, $^3J_{HMe} = 6$ Hz, **3a** and m, $^3J_{HP} = 13$, $^3J_{HMe} = 6$, $^3J_{HH} = 3$ Hz, **3b**).[12] At higher temperatures (>−55 °C) solutions of **3** cleanly generate **2**, and no intermediates are detected by $^1H$ NMR spectroscopy.

Deuteration studies provide some additional mechanistic information. The addition of $CH_3CO_2H$ (a slight excess) to **1** at 20 °C in $CD_3OD$ produces **1**-$d_2$, [Ir]−CH═$CD_2$, i.e. selective deuterium incorporation at $C_\beta$ of the vinyl group,[3a] whereas the reaction of **1** with 1 equiv of $DBAr_4$ in a ca. 4:1 $CD_2Cl_2$:$CD_3OD$ solvent mixture instantaneously provides **2**-$d_n$ ($n \geq 2.5$), with the deuterium atoms scrambled between the hydride and ethylene

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[7] Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z. *J. Chem. Soc., Chem. Commun.* **1996**, 1 and references therein.

[8] For leading studies on comparative migration rates in early transition metal systems see: Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

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[10] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

[11] Selected spectroscopic data for **2**: $^1H$ NMR ($CD_2Cl_2$, 20 °C): $\delta$ −18.84 (d, 1H, $^2J_{HP} = 17.6$ Hz, Ir-*H*), 3.49 and 4.26 (m, 4H, AA′XX′ spin system upon $^{31}P$ decoupling, Ir−$C_2H_4$).

[12] $^{13}C$ NMR ($CD_2Cl_2$, −80 °C): $\delta$(Ir═C) 324.2 (br, $^2J_{CP} = 7$, $^1J_{CH} = 134$ Hz), and 324.4 (br, $^2J_{CP} = 8$, $^1J_{CH} = 122$ Hz). Specific structure assignments are based on 2D-NOESY and ROESY spectra and literature precedents: see ref 2b.

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sites.[13,14] NMR monitoring of this deuteration from −80 to 20 °C shows the initial formation of **3**-$d_{\geq 2.5}$, $[Ir]^+{=}CHCD_{\geq 2.5}H_{\leq 0.5}$ (1 h, −60 °C), with specific deuteration in the methyl group of the alkylidene ligand. At −40 °C, this species cleanly transforms into $[Tp^{Me_2}Ir(C_2H_2D_2)(D)(PMe_3)]^+$ (**2**-$d_3$), with a small amount of $[Tp^{Me_2}Ir(C_2H_2D_2)(H)(PMe_3)]^+$ being detected. Only at 0 °C the deuterium and hydrogen atoms of the olefin and hydride positions scramble,[13] with the Ir−H resonances[14] increasing accordingly ($k_{obs}(D{\rightarrow}H) = 6.8 \times 10^{-5}\ s^{-1}$, $\Delta G^{\ddagger} = 21.1$ kcal·mol$^{-1}$, this value being in good agreement with magnetization transfer measurements carried out with **2** at higher temperatures). The above results indicate (a) that the protonation of the vinyl group of **1** is reversible,[3a] at least in the presence of methanol, with the **1** ⇌ **3** equilibrium of Scheme 1 being faster than the formation of the final product **2**, (b) that **3** evolves by a 1,2 migration of the hydride onto the alkylidene carbon, to give an ethyl intermediate "$[Tp^{Me_2}Ir(C_2H_5)(PMe_3)]^+$", and not by a 1,2 hydrogen shift from the methyl ($C_\beta$) to $C_\alpha$,[1d] and last (c), as expected, **2** easily experiences reversible insertion of the olefin into the Ir−H bond at ambient temperature.

The low-temperature addition of $HBAr_4$ to the known[4a] ethyl derivative $Tp^{Me_2}Ir(CH{=}CH_2)(Et)(PMe_3)$ (**4**) yields the expected cationic ethyl−ethylidene species **5**, once again in the form of a thermodynamic mixture of two rotamers (1:1 ratio) that interconvert slower than **3** ($\Delta G^{\ddagger} = 12.1$ kcal·mol$^{-1}$) on the NMR time scale. Since the spectroscopic data,[15] in particular the $^3J_{HP}$ values of the alkylidene C*H*Me protons (0 and 13 Hz for **5a** and **5b**, respectively), are very similar to those found for **3** it is reasonable to assume that the **a** and **b** rotamers of these two species have the same spacial orientation. This reaction also proceeds further (−55 °C) to give the 2-butene complex $Tp^{Me_2}Ir(CHMe{=}CHMe)(H)(PMe_3)$ (**6**) as a mixture of isomers that subsequently evolves (−40 to 25 °C) into the thermodynamically more stable **6**-*trans* stereoisomer.[16] Moreover when $Tp^{Me_2}Ir(CH{=}CD_2)(C_2H_5)(PMe_3)$ (**4**-$d_2$) is reacted with $DBAr_4$, the $CD_3$ group of the alkylidene species is found intact in **6**-*trans* (no D incorporation into the vinylic positions). This clearly demonstrates that **6** evolves as the result of ethyl ligand migration onto the electrophilic alkylidene carbon in a manner analogous to the hydride shift during the generation of **2** from **3**.

At −47 °C, the rates of disappearance of the starting materials **3** and **5** can be conveniently measured by $^1H$ NMR spectroscopy in $CD_2Cl_2$. Both reactions obeyed first-order kinetics over at least 4 half-lives, and were characterized by $k_{obs}$ values of $2.0 \times 10^{-4}$ and $2.5 \times 10^{-4}\ s^{-1}$, respectively ($\Delta G_H^{\ddagger} \approx \Delta G_{Et}^{\ddagger} \approx 16.7$ kcal·mol$^{-1}$). Both on theoretical grounds[9c] and on the basis of previous studies,[8] the migratory insertion of =CH(Me) was expected to proceed much faster into the Ir−H bond of **3** than into the Ir−$C_2H_5$ bond of **5**.[17] This is also the case for reactions involving the migration of H and alkyl groups to olefins.[8a,18]

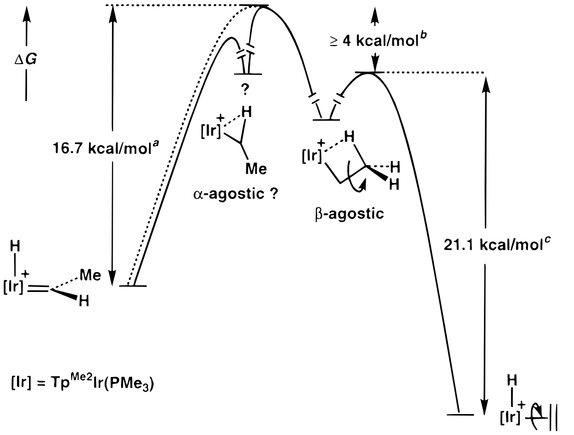

**Figure 1.** Data at −47,[a] 0,[b] and 25 °C,[c] respectively. To construct the diagram ΔG is assumed to be temperature independent.

It can be argued that these data may not allow a real comparison of the actual migration rates of the H and $C_2H_5$ ligands. As a matter of fact, the observation of a kinetic isotope effect, $k_H/k_D$, of ca. 2.5, in the rearrrangement of $[Tp^{Me_2}Ir({=}CHCD_3)(H)(PMe_3)]^+$ may well be taken as indicative of the reversibility of the α-H migratory insertion[19] (such an effect cannot be noted for **4**). Despite our efforts we have been unable, so far, to deuterate selectively the hydride position of complex **1** but, nevertheless, since the NMR resonance of the Ir=C*H*Me proton of the rotamers **3a** ⇌ **3b** remains sharp ($\omega_{half} \approx 1$ Hz, maximum broadening of 0.2 Hz) at the reaction temperature and assuming that the Et migration is irreversible, $(k_H/k_{Et})_{mig}$ must be at most of the order of $10^3$ (approximately $0.2\pi/2.5 \times 10^{-4}$). This value could be higher if the barriers associated with the inversion and the rotation of the $C_2H_5$ group around the Ir−$C_2H_5$ bond of the proposed ethyl intermediate are unusually high.[20] The two possible mechanistic interpretations, both implying the formation of a β-agostic intermediate[20] in the rate determining step, are depicted in Figure 1. To complete the energy diagram we measured the deuteration rate of **2** in pure $CD_3OD$ (25 °C, $k_{obs} \approx 1.5 \times 10^{-6}\ s^{-1}$, $\Delta G^{\ddagger} \approx 25.1$ kcal·mol$^{-1}$). This process is accelerated considerably by the presence of an acid or base catalyst.

In conclusion, highly reactive and strongly electrophilic alkylidene complexes of Ir(III) containing H and Et coligands can be generated by protonation of the corresponding neutral alkenyl complexes. Our findings clearly indicate that they evolve via migratory insertion processes with similar apparent rates and, therefore, that the difference in the migratory aptitudes of H and Et ligands in these complexes may be substantially less than in other systems (up to $10^{10}$ in Ta complexes[8]). Perhaps, the very reactive nature of the involved Ir=C bond makes a very poor discriminator of H vs Et. To our knowledge, this is the first example of such a comparative study in electrophilic alkylidene systems.

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[13] The equilibrium isotope effect for this system is best determined with **2**-$d_1$ ($K_{ef} = 2.4$, the deuterium preferring the olefinic positions). Crossover experiments show that the scrambling process is intramolecular under these conditions.

[14] Interestingly, the two expected stereoisomers of $[Tp^{Me_2}Ir(C_2H_3D)(H)(PMe_3)]^+$ exhibit Δδ of the Ir-*H* resonance of ca. +35 and −30 ppb when compared with the all-protio species. Remarkable deuteration effects upon $^1H$, $^{13}C$, and $^{31}P$ resonances in this and other Tp′Ir systems will be reported in due course. In this particular case, the effect, which is correlated with the degree of deuteration, allows for the analysis of complex deuterated mixtures.

[15] Selected spectroscopic data for **5a** and **5b**: $^1H$ NMR ($CD_2Cl_2$, −80 °C): δ 20.6 (q, $^3J_{HH} = 6.5$ Hz, Ir=C*H*Me, **5a**), 20.7 (dq, $^3J_{HH} = 6.5$, $^3J_{HP} = 13.5$ Hz, Ir=C*H*Me, **5b**).

[16] The assignment of the precise stereochemistry is based upon 2D-NOESY spectra and on the X-ray structure of $[Tp'Ir($*trans*-$CHMe{=}CHMe)(H)(CH_3CN)][BAr_4]$ (Tp′ = hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate) which is formed under the same sequence of events.

[17] This is largely due to differences in the spacial properties of the σ-orbitals of the respective migratory groups.

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[19] This would imply that the proposed ethyl intermediate experiences faster α-H than β-H elimination. This behaviour has been reported only scarcely in the literature. See ref 2a.

[20] We assume that complete rotation of the carbene poses no special problems. (a) Ward, T. R.; Schafer, O.; Danl, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207. (b) Casey, C. P.; Fagan, M. A.; Hallenbeck, S. L. *Organometallics* **1998**, *17*, 287. (c) Green, M. L. H.; Sella, A.; Wong, L.-L. *Organometallics* **1992**, *11*, 2650.