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Double α,α CH Bond Insertion into sp^3 CH_2 Moiety: Synthesis of a Fe Carbene bis-Hydride Dinitrogen Complex.

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Julien Petit,^{a§} Anthony Cavaillé,^{a§} Nathalie Saffon-Merceron,^b Marie Fustier-Boutignon^a and Nicolas Mézailles^{*a}

Reduction of high spin paramagnetic complex $[(\kappa^2-P, P'-PCH_2P^Cy)FeCl_2]$ **2 by two electrons under N_2 resulted in the formation of two isomeric low spin diamagnetic complexes **3trans** and **3cis** $[Fe(\kappa^3-P,C,P'-PCP^Cy)(H)_2(N_2)]$. Crystallization allowed isolation of complex **3d** $[Fe(\kappa^3-P,C,P'-PCP^Cy)(H)_2(\mu-N_2)]$, characterized by X-ray diffraction, Mössbauer and Raman spectroscopies. DFT calculations rationalized the facile double α,α CH bond insertion into a single sp^3 CH_2 moiety, as well as the fast exchange positions of the hydrides in the cis dihydride complex observed by NMR spectroscopy.**

Functionalization of alkanes has been extensively studied since the 1960s. Being poor Lewis bases, unactivated CH bonds are typically unreactive and strategies using transition metal complexes have been devised. Among them, seminal works by Bergman, Graham and Jones in the early 80s using late transition metal fragments, showed that oxidative addition of sp^3 CH bond can occur provided that a vacant coordination site could be generated but also that the metal center possesses high electron density.^{1,2,3} This allows the double electron flow to occur, i.e. donation of electron density from the CH bond to the metal, and back donation from the metal into the σ^* CH orbital. Early examples of insertion of $Fe^{(0)}$ into acidic CH bonds of α -carbonyl compounds and nitriles were reported in 1978,⁴ while insertion into alkanes was reported by Field in 1987.⁵ Indeed, they demonstrated that the $[Fe(dmpe)_2]$ complex generated by photolysis of the $[Fe(dmpe)_2(H)_2]$ precursor at $-100^\circ C$ inserted a terminal CH bond of pentane to form $[Fe(dmpe)_2(H)(C_5H_{11})]$.⁶ The presence of a β -hydrogen then led to the formation of 1-pentene and regeneration of the $[Fe(dmpe)_2(H)_2]$ complex. When the same reaction was carried out with CH_4 mixtures of *cis* and *trans* $[Fe(dmpe)_2(H)(CH_3)]$ were formed.⁷ The double α,α C-H bond insertion into a sp^3

CH_2 moiety at an Fe center is to date an unknown process. It would allow a straightforward access to Fe-carbene derivatives. Efforts have been made in that direction using substrates devoid of β -H as well as phosphine chelation prior to CH bond insertion, yet it stopped after a single insertion (scheme 1, middle).^{8,9} It demonstrates that the two CH activations are intrinsically different. Indeed, the first insertion occurs via an oxidative addition at the metal, resulting in a $Fe^{(II)}$ center. This metal center is not electron rich enough to allow a second oxidative addition, that would result in a high energy $Fe^{(IV)}$ complex.

Scheme 1 Selected example of oxidative addition of iron complexes into alkane C-H bonds, for comparison with present work.

The second CH activation would thus rely on a formal hydride transfer that would not change the oxidation state of the Fe

^a Laboratoire Hétérochimie Fondamentale et Appliquée, CNRS, and

^b Institut de Chimie de Toulouse ICT-FR2599, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France.

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§ : both authors contributed equally.

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center. Moreover, it requires a vacant coordination site to accept the hydride ligand.

Hill has recently shown that the overall double CH activation was possible using a proligrand $\text{PCH}_2\text{P}^{\text{R}}$ ($\text{PCH}_2\text{P}^{\text{R}} = \text{H}_2\text{C}(\text{NCH}_2\text{PR}_2)_2\text{C}_{10}\text{H}_6-1,8$; R = Ph or Cy) at electron rich Rh^{I} , Ir^{I} or Os^{III} centers,¹⁰ and at Ru^{III} only with the $\text{PCH}_2\text{P}^{\text{Cy}}$ ligand, yet it required H-X (X = H or Cl) elimination.¹¹ Notably, with less electron rich metal fragments of Ru^{III} , simple PNP coordination can be competitive with CH insertion and the outcome thus depends on the phosphine substituents.¹² We report here that the generation of a highly unsaturated electron rich Fe^{0} fragment does result in the desired double α,α C-H bond insertions into a sp^3 CH_2 moiety to form *cis* and *trans* Fe dihydride complexes (Scheme 1, bottom). Most importantly, the use of N_2 atmosphere is a requirement to stabilize the low valent highly reactive intermediate, and form the desired carbene dihydride complex. Notably, the first *trans* dihydride carbene complex of Fe featuring end-on bridging dinitrogen was isolated. DFT calculations were performed to rationalize our experimental findings.

The reaction between the $\text{PCH}_2\text{P}^{\text{Cy}}$ ligand **1** and $[\text{FeCl}_2(\text{THF})_{1.5}]$ at room temperature in THF resulted in a fast dissolution of the metal precursor accompanied by a bright yellow coloration of the solution attesting coordination (scheme 2). Analysis of the crude solution by $^{31}\text{P}\{^1\text{H}\}$ NMR shows the absence of any signal pointing the formation of a paramagnetic complex, **2**, which was isolated in 78% yield by crystallization at -30°C . ^1H NMR spectroscopy confirmed the paramagnetism of the complex, as signals are found between -10 ppm and 137 ppm (ESI). The magnetic moment was measured using Evans' method to $5.0 \mu\text{B}$,^{13,14} consistent with a quintet state high spin Fe^{II} center, confirmed by the analysis by Mössbauer spectroscopy with $\delta = 0,772 \text{ mm.s}^{-1}$, $\Delta E_{\text{Q}} = 2,714 \text{ mm.s}^{-1}$.

Scheme 2 Synthesis of complex **2**.

X-ray diffraction analysis of complex **2** revealed a distorted geometry at Fe (PFeP: $111.35(2)^\circ$ and ClFeCl: $123.30(3)^\circ$). Indeed, the calculated τ_4 geometry index of 0.89 is in between trigonal pyramidal ($\tau_4 = 0.85$) and tetrahedral ($\tau_4 = 1.0$).¹⁵ It also showed the bidentate coordination of the ligand via the two P centers in complex $[(\kappa^2\text{-}P,P'\text{-PCH}_2\text{PCy})\text{FeCl}_2]$ **2**. It is interesting to note that the tridentate PNP coordination of the ligand at Ru^{III} center is not observed here.¹¹ Indeed, the two N atoms are $3.65\text{\AA}$ and $4.21\text{\AA}$ away from the Fe center. Finally, no interaction is seen between the closest CH bond and the Fe center (FeH $3.35\text{\AA}$). The Fe-P bond distances at $2.4819(7)$ and $2.4717(7)\text{\AA}$ are usual for high spin Fe^{II} complex.

As expected, the Fe^{II} center is not electron rich enough to promote the CH bond insertion into the CH_2 moiety. Reduction to Fe^{I} and Fe^{0} was therefore attempted. Fürstner has shown that $[(\text{PP})\text{FeCl}_2]$ could be reduced by EtMgBr under ethylene to

the corresponding $[(\text{PP})\text{Fe}(\text{CH}_2\text{CH}_2)_2]$ in high yield,¹⁶ but the presence of ethylene was not desirable in our case. We therefore relied on one electron reducing agents.

Figure 1 structure of complex **2**. Fe1–P1 $2.472(1)$; Fe1–P2 $2.482(1)$; Fe1–Cl1 $2.257(1)$; Fe1–Cl2 $2.232(1)$; Cl2–Fe1–Cl1 $123.30(3)$; Cl2–Fe1–P1 $108.44(3)$; Cl1–Fe1–P1 $104.60(3)$; P1–Fe1–P2 $111.35(2)$; N1–C1–N2 $111.5(2)$.

In a first stage, one equivalent of KC_8 was added to a THF solution of complex **2** at -100°C under N_2 , and the mixture was warmed back to room temperature over 15h. Analysis of the crude mixture revealed decomposition as only the free PCH_2P ligand was observed (quantitatively vs comparison with an internal standard). More satisfyingly, the two electron reduction under the same conditions did result in the formation of Fe diamagnetic species, attested by the appearance of two singlets at 96.6 and 97.1 ppm in *ca* 5:2 proportions (**3trans** and **3cis** respectively), together with *ca* 10 % of free PCH_2P . Most importantly, the reaction has to be done under N_2 atmosphere. Indeed, when it was carried out under Ar, only decomposition was observed, attested by the signal of free ligand alone in the ^{31}P NMR spectrum. Moreover, we found out that the outcome of the reaction also depended on the volume of solvent, and thus on the amount of dissolved N_2 , available for the reaction. Isolation and characterization of the complexes **3trans** and **3cis** was rendered difficult by the fact that they are not stable under reduced pressure, likely because of N_2 elimination. Thus, initially, further characterization of the mixture of the two complexes was performed in the crude (THF). Two triplets in 5:2 ratio (identical to the ratio measured in the ^{31}P spectrum) were observed in the hydride region of the ^1H spectrum, at significantly different chemical shifts (-8.1 and -12.4 ppm respectively). A 2D $^{31}\text{P}\{^1\text{H}\}$ - ^1H spectrum confirmed that the two complexes are indeed hydride complexes. If a triplet was expected for the complex **3trans**, the apparent triplet for complex **3cis** suggested a dynamic process equilibrating the two hydrides at room temperature. A more concentrated experiment was carried out in *thf-d8* to perform a variable temperature experiment (see ESI). As mentioned above, the lower amount of N_2 in solution resulted in a less efficient reaction, as attested by an increased amount of free PCH_2P ligand, as well as two minor Fe species (ESI). The minor species at 94.7 ppm corresponds to the $[(\kappa^3\text{-}P,P',P'\text{-PCy})\text{Fe}(\text{H})_2]_2(\mu\text{-N}_2)$ **3d** (vide infra). Upon cooling down to -80°C , the signal at -8.1 ppm only broadened. On the other hand, the signal at -12.4 strongly decreased in intensity upon cooling,

and coalescence was observed at -40°C . Further cooling to -80°C did not allow observation of the slow exchange regime. Warming the solution back to room temperature showed the $\text{Fe}(\text{H})_2$ to $\text{Fe}(\text{H}_2)$ process to be reversible. This experiment demonstrated the fast hydride exchange process occurring at room temperature, resulting in an average signal for the two hydrides in cis position in complex **3cis**. The VT NMR behavior is due to reversible $\text{Fe}(\text{H}_2)$ and $\text{Fe}(\text{H})_2$ interconversion, and the static regime is not reached even at -80°C . This was subsequently corroborated by DFT calculations (vide infra). The IR solution spectrum of the crude mixture only reveals one band for the ν_{NN} stretching at 2092 cm^{-1} for a single terminal $\text{Fe}-\text{N}_2$ moiety.

Scheme 3 Synthesis of $\text{Fe}(\text{H})_2(\text{N}_2)(\text{carbene})$ complexes via double CH bond insertion.

Crystallization at -80°C of a crude mixture allowed for the isolation of the dimeric complex **3d** $[\text{Fe}(\kappa^3\text{-P,C,P'-PCPCy})(\text{H})_2(\mu\text{-N}_2)]$ in 44%. After crystallization, the supernatant still showed the presence of the two species by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR. The complex **3d** is poorly soluble. However, its $^{31}\text{P}\{^1\text{H}\}$ spectrum showed a signal at 94.7 ppm, and in the ^1H spectrum, the triplet for the hydride ligands was observed at -8.1 ppm (ESI). Finally, the CPMAS ^{13}C spectrum showed a signal at 244 ppm, in the expected range for the carbene ligand. The X-ray diffraction study demonstrated the end-on bridging N_2 moiety between the two Fe centers, as well as two hydrides in a very rare *trans* arrangement. The N-N bond distance at $1.125(3)\text{\AA}$ is only marginally elongated compared to free N_2 , attesting a negligible back donation from $\text{Fe}(\text{II})$. The Fe-H bonds are measured at $1.50\text{ \AA}$ average, which is classical (for Fe-H bond distances found in the CCDC base, see ESI).

The planar geometry at the carbon center finally confirmed the formation of the carbene ligand via the desired double CH bond insertion. The Fe-C bond distances at $1.877\text{\AA}$ and $1.869\text{\AA}$ are shorter than the $2.024\text{\AA}$ and $1.985\text{\AA}$ ($\text{Fe}(\text{O})(\text{CAAC})_2(\text{X})$), $1.922\text{\AA}$ ($\text{Fe}(\text{O})(\text{CAAC})_2$), and $1.92\text{\AA}$ ($[\text{Fe}(\text{I})(\text{CAAC})_2(\text{N}_2)]$) reported by Peters, as expected from the coordination to an $\text{Fe}(\text{III})$ center.¹⁷ As expected for a dimer with bridging N_2 , no ν_{NN} stretching band in IR was seen. On the other hand, an intense ν_{NN} stretch at 2084 cm^{-1} was observed in the RAMAN spectrum.

Finally, the complex **3d** was analyzed by Mössbauer spectroscopy, which clearly demonstrated the presence of a singlet state low spin $\text{Fe}(\text{II})$ center in an octahedral environment ($\delta = 0.0073(35)\text{ mm.s}^{-1}$, $\Delta E_{\text{Q}} = 1.5843(70)\text{ mm.s}^{-1}$).

Figure 2 structure of complex **3d**. Ellipsoids at 50% probability. H atoms of the backbone and solvent molecules omitted for clarity. Selected bond distances and angles. Distance ($\text{\AA}$) and angles ($^{\circ}$): Fe1-P1 2.151 (1) ; Fe1-P2 2.157(1) ; Fe2-P3 2.147(1) ; Fe2-P4 2.148(1) ; Fe1-H1 1.48(3) ; Fe1-H2 1.53(3) ; Fe2-H3 1.51(3) ; Fe2-H4 1.50(3) ; Fe1-C1 1.877(3) ; Fe2-C2 1.869(3) ; Fe1-N1 1.865(3) ; Fe2-N2 1.875(3) ; N1-N2 1.125(3).

Scheme 4 Mössbauer spectrum of complex **3d**.

The double CH bond insertion at Fe being unprecedented we became interested in the mechanism of the formation of complexes **3trans** and **3cis**. As mentioned above, N_2 is needed for the complex to be synthesized, as well as the two electron reduction from $\text{Fe}(\text{III})$. These prove the necessary coordination of N_2 at the reduced, unsaturated $\text{Fe}(\text{0})$ fragment, prior to CH bond insertions to reach a stable electronic configuration. As diamagnetic intermediates could not be observed on the way to complex **3**, DFT calculations were carried out to rationalize the experimental findings. Note that because the reaction occurs at low temperature, the activation energies for the two CH activations are necessarily low.

Lefevre has recently performed a benchmarking of DFT methods on several Fe complexes in diverse oxidation states and spin states, and concluded on the efficiency of OPBE functional, which we therefore used in our study.¹⁸ Dispersion (D3) and solvent (SMD, THF) effects were taken into account. First, calculations confirm that the coordination of one molecule of N_2 to the 12 electron fragment $[\text{Fe}(\kappa^2\text{-P,P'-$

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PCH₂P^{Cy})] (triplet, S=1) to form complex **A** [Fe(κ^2 -P,P'-PCH₂P^{Cy})(N₂)] (triplet S=1) is very favorable (-34.2 kcal/mol). In fact, two minima for complexes [Fe(κ^2 -P,P'-PCH₂P^{Cy})] were found within 5.0 kcal/mol (**A** and **B**, scheme 5). In both of them the geometry at the Fe center is trigonal planar, and they do differ by the orientation of the PCH₂P ligand with respect to the plane defined by P, P and N atoms. A transition state connecting these two complexes could not be located, in accordance with a very flat PES (a scan of the PES showed a maximum less than 1 kcal/mol higher than complex **B**). These complexes are therefore in rapid equilibrium in solution. Note that a stationary stable 14 electron-complex [Fe(κ^2 -P,P'-PCH₂P^{Cy})(N₂)] with singlet state could not be found.

Scheme 5 optimized geometries for complexes [Fe(κ^2 -P,P'-PCH₂P^{Cy})(N₂)] (S=1) **A** and **B**, showing the different orientations of the ligand.

The thermochemistry of the double insertion was computed. Both transformations leading to the *trans* and *cis* singlet complexes [Fe(κ^3 -P,C,P'-PCP^{Cy})(H)₂(N₂)] **C** and **E** were strongly exergonic (-27.7 and -26.8 kcal/mol from **A**). In this process, the bond breaking of two strong CH bonds is therefore more than compensated by the formation of two Fe-H and a strong Fe-C bonds. In accord with the micro-reversibility principle, the intermediates resulting from the first CH bond insertion were searched starting from the singlet dihydride complexes **C** and **E**. The singlet complex **D** was computed at -11.0 kcal/mol from **A** (15.8 kcal/mol higher than **E**). It is connected to **E** via a readily accessible transition state TS_{D-E} ($\Delta G^\ddagger$ = 4.3 kcal/mol). A similar alkyl-hydride singlet complex connected to **C** was not found as a stable intermediate. It was corroborated by the optimization of complex [Fe(κ^2 -P,P'-

PCH₂P^{Cy})] in the singlet state starting from the geometry of complex **A**. Indeed, a steep energy decrease concomitant with the two H migrations from the C to the Fe center, without noticeable transition state. A similar energy decrease was observed from the geometry of complex **B** upon optimization in the singlet state. In that case, complex **D** was obtained without going through a transition state. In conclusion, although we have not located the MECP (Minimum Energy Crossing Point) between the triplet and the singlet surfaces, which is clearly beyond the scope of the present article, we can be confident that they are early in the process leading to the double CH bond insertion. These calculations rationalize that even if *trans* and *cis* complexes **C** and **E** are very close in energy (-27.7 kcal/mol and -26.8 kcal/mol resp.) they are not in equilibrium because of the high reverse barrier (>32.2 kcal/mol). Note that a pathway involving N₂ decoordination-*cis*/*trans* isomerization-N₂ coordination was evaluated (see ESI) and required similar high energy barrier (*ca* 30 kcal/mol), inaccessible under experimental conditions.

Finally, a complex **F**, featuring an elongated H₂ ligand (H-H distance of 1.00 Å) was calculated 7.9 kcal/mol higher than the *cis* complex **E**, via a low energy transition state TS_{E-F} ($\Delta G^\ddagger$ = 9.9 kcal/mol). This low barrier is fully consistent with the fast hydrogen position exchange observed by NMR, even at low temperature.

These DFT calculations rationalize nicely our experimental findings, *ie* the irreversible formation of two isomeric di-hydride dinitrogen carbene complexes, one of these (*cis*) featuring two hydrides in rapid exchange at room temperature on the NMR time scale.

Conclusion

We have reported the first double CH bond insertion into a C sp³ moiety at Fe. It results in the formation of carbene-dihydride-dinitrogen Fe complexes. Notably, the *cis* and *trans* complexes appear to be close in energy, because of the similarly strong *trans* effect of H and carbene ligands. More importantly, the key to observe this reactivity lies in the generation of a highly unsaturated 14 electron fragment yet featuring an electron rich Fe⁰ center (d8).

Scheme 5 DFT calculations: double CH insertion to form *cis* and *trans* $[\text{Fe}(\kappa^3\text{-P,C,P'}\text{-PCP}^{\text{Cy}})(\text{H})_2(\text{N}_2)]$ complexes; Isomerism of the two H positions in the *cis* complex via $[\text{Fe}(\kappa^3\text{-P,C,P'}\text{-PCP}^{\text{Cy}})(\text{H}_2)(\text{N}_2)]$

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