Metal Hydrides

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Orbital-Like Motion of Hydride Ligands around Low-Coordinate Metal Centers**

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Dedicated to Professor Pablo Espinet on the occasion of his 65th birthday

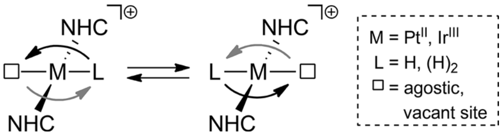
Abstract: *Hydrogen atoms in the coordination sphere of a transition metal are highly mobile ligands. Here, a new type of dynamic process involving hydrides has been characterized by computational means. This dynamic event consists of an orbital-like motion of hydride ligands around low-coordinate metal centers containing N-heterocyclic carbenes. The hydride movement around the carbene–metal–carbene axis is the lowest energy mode connecting energy equivalent isomers. This understanding provides crucial information for the interpretation of NMR spectra.*

Dynamic exchange in coordination compounds changes the stereochemistry at the metal center and is thus a process that may exert major influence on its reactivity and spectroscopic properties.[1] Investigating the occurrence of dynamic exchanges, and the associated time scales, is a key step in the characterization of a newly synthesized organometallic compound. Nuclear magnetic resonance (NMR) is the leading technique to investigate dynamic exchange in solution. Here we show that computational chemistry can conveniently be used to provide a reliable interpretation of spectroscopic NMR data.

Hydrides display great mobility in transition metal compounds, and a number of dynamic processes involving hydrides have been characterized.[2] As representative examples we may recall: 1) pairwise exchange involving a rotation of the H–M–H plane by 180° in dihydride complexes, 2) polytopal rearrangements permuting the hydrides in high-coordinate polyhydrides, and 3) H/H exchange between the hydride and a hydrogen atom from another ligand, particularly η^2-H_2 or agostic η^2-C−H bonds.[2]

Compounds featuring ligands of diverse mass and steric bulk are certainly attractive candidates to further our understanding of fluxional processes. In this regard, the combination of bulky ligands such as N-heterocyclic carbenes (NHCs),[3] small and mobile ligands such as hydrides, and vacant sites in the transition metal coordination sphere seems appealing. 14-electron Pt^{II} hydride complexes fulfill these requirements and are known to be stabilized by bulky phosphines,[4,5] but the versatile NHC ligands can also play such a role. These low-coordinate species are known to participate in a number of key organometallic processes and their structure could be stabilized by agostic interactions.[6]

Here we describe and characterize by computational methods[7] a dynamic process, not reported before, which involves hydride ligands in low-coordinate complexes with bulky NHC ligands. This process consists of an intramolecular motion of one or two hydride ligands around a transition metal center (Scheme 1). NMR data of several compounds are reinterpreted in the light of these results.



Scheme 1. Fluxional motion in NHC-based low-coordinate hydride complexes.

Recently, the low-coordinate T-shaped Pt^{II} complex $[Pt(H)(ItBu)_2]^+$ **1** (I*t*Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) has been characterized in dichloromethane solution.[8] This 14-electron complex features a formal vacant coordination site, but neither agostic interactions nor solvent coordination have been assigned on the basis of the NMR data. Even at low temperature (195 K), the ^1H and $^{13}C\{^1H\}$ NMR spectra for this compound exhibit a highly symmetric environment in which all the *t*Bu and =CH groups of the I*t*Bu ligand are equivalent. Furthermore, no significant changes were observed for the hydride resonance at different temperatures. On the contrary, the DFT-optimized structure (Figure 1a) clearly shows an agostic interaction between Pt and one CH of the *t*Bu group from the I*t*Bu ligand. The $Pt\cdots H_{ago}$ and $Pt\cdots C_{ago}$ lengths of 1.959 and 2.642 Å, respectively, are in the

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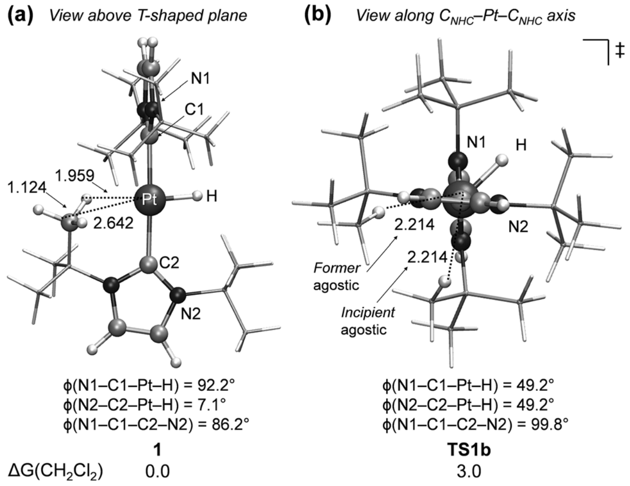
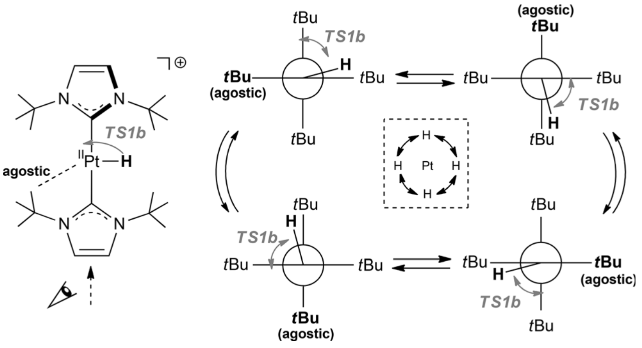


Figure 1. DFT-optimized geometries of a) complex **1** and b) transition state **TS1b**. Distances in Å and angles in degrees. Gibbs energies are given in $\mathrm{kcal\,mol^{-1}}$.



Scheme 2. Full motion process of the hydride ligand in $[\mathrm{Pt(H)(I}t\mathrm{Bu)_2}]^+$ **1**. Newman projections along the $\mathrm{C_{NHC}{-}Pt{-}C_{NHC}}$ axis.

typical range for agostic interactions.[9] Moreover, the $\mathrm{C_{ago}{-}H_{ago}}$ bond (1.124 Å) is significantly longer compared to the C−H bonds not involved in the agostic interaction (ca. 1.094 Å). These structural features were confirmed by optimizing **1** with other density functionals.[10] The possibility of solvent coordination was investigated including one explicit dichloromethane molecule in the calculation. Results indicate that solvent coordination at the vacant site is an unfavorable process (see the Supporting Information, SI).

The disparity between the computed structure and the experimental assignment may be the signature of a dynamic process, fast on the NMR time scale, which gives rise to the averaging of the NMR signals and precludes the detection of agostic contacts.[11] Thus, we investigated conformational changes that may result in exchanges of the *t*Bu groups. First, we considered the rotation of the NHC ligand about the $\mathrm{Pt{-}C_{NHC}}$ bonds.[12] Reaching the transition state **TS1a** for this rotation requires $13.5\,\mathrm{kcal\,mol^{-1}}$. Under the experimental conditions, a process with a barrier of ca. $9\,\mathrm{kcal\,mol^{-1}}$ would be frozen at 195 K.[13] In the search for less energy demanding conformational changes, we explored the movement of the hydride ligand.[14] The transition state **TS1b** corresponding to the rotation of the hydride ligand around the $\mathrm{C_{NHC}{-}Pt{-}C_{NHC}}$ axis was located only $3.0\,\mathrm{kcal\,mol^{-1}}$ above **1**. The geometry of **TS1b** is shown in Figure 1b. The vacant site is also moving along with the hydride. The former agostic interaction exchanges for a new one, in which both $\mathrm{Pt\cdots H_{ago}}$ distances are 2.214 Å in the transition state. **TS1b** displays orthogonal I*t*Bu ligands and the hydride forms dihedral angles of 49.2° with respect to the two imidazole planes. Transition states **TS1a** and **TS1b** were confirmed using other density functionals[10] and including continuum solvent conditions during optimizations (see SI).

The hydride ligand can repeat the motion corresponding to **TS1b** passing through degenerate structures in which C−H bonds from all *t*Bu groups eventually establish agostic interactions (Scheme 2). Methyl and *tert*-butyl rotation processes of the I*t*Bu wings, demanding 5.8 (**TS1c**) and $6.3\,\mathrm{kcal\,mol^{-1}}$ (**TS1d**), respectively, are necessary to obtain full equivalence of all hydrogens. Due to the orthogonal disposition of the NHC ligands in **1** (the dihedral angle between the NHC planes being 86.2°), the hydride may reside on any of four equivalent sites around Pt. Given the small Gibbs energy associated to the process ($3.0\,\mathrm{kcal\,mol^{-1}}$ via **TS1b**),[15] faster than any other rotation event, the hydride moves easily around the platinum center, precluding the observation of agostic interactions of **1** in solution. The hydride ligand and the transition metal center may be interpreted as a planetary system, with the hydride moving around the metal. Related planetary systems have been previously invoked for lithium cations.[16–18]

To further investigate the dynamic behavior of **1** under realistic solution environment, molecular dynamics simulations were performed using the hybrid quantum mechanics/molecular mechanics (QM/MM) approach. Complex **1** was treated at the DFT level and the bulk solvent (ca. 1000 dichloromethane molecules) at the MM level (see SI). An agostic interaction in **1** is maintained along the simulation (40 ps), exhibiting $\mathrm{Pt\cdots H_{ago}}$ and $\mathrm{Pt\cdots C_{ago}}$ distances of 2.0 ± 0.1 and 2.7 ± 0.1 Å, respectively.[19] At about 7 ps simulation, hydride translocation was observed to an equivalent coordination site characterized by a 90 degrees rotation around the $\mathrm{C_{NHC}{-}Pt{-}C_{NHC}}$ axis (Figure 2). An agostic interaction with another methyl group is briefly established, as the configuration is maintained for about 1 ps, eventually recovering the previous coordination geometry. Interestingly, the NHCs do not change their orientation during hydride migration. Thus, within a classical representation of nuclear motion, hydride rotation is not a continuous orbiting process, yet the barrier to

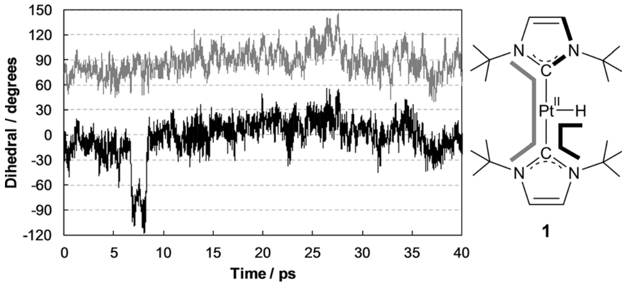


Figure 2. Evolution of the N-C-C-N (grey) and N-C-Pt-H (black) dihedral angles of **1** along the simulation time.

overcome is small enough for the process to take place even at low temperatures, and we may refer to it as an orbital-like movement.

As shown above, calculations support an agostic interaction stabilizing **1**. However, the agostic contact is not necessary for the dynamic process to take place. NMR spectra[8] and DFT calculations consistently predict no agostic interactions in the T-shaped complex $[Pt(H)(IMes^*)_2]^+$ **2** (IMes* = 1,3-bis(2,4,6-trimethylphenyl)imidazol-4,5-dimethyl-2-ylidene; Figure 3 a), yet an easy hydride movement also occurs via **TS2b** (Figure 3 b), which lays only 4.0 kcal mol^{-1} above the optimized structure.

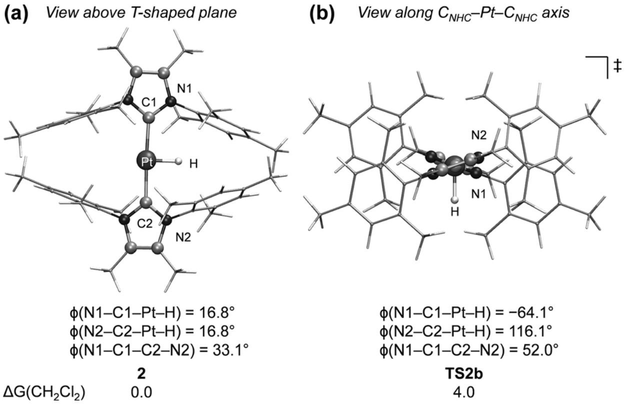
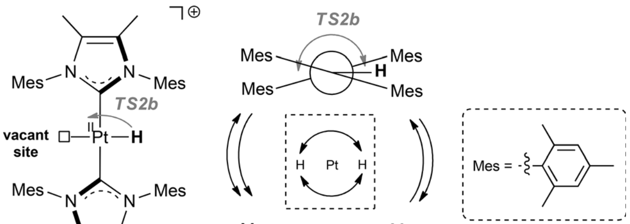


Figure 3. DFT-optimized geometries of a) complex **2** and b) transition state **TS2b**. Distances in Å and angles in degrees. Gibbs energies are given in kcal mol^{-1}.

In contrast to the I*t*Bu ligands, the imidazole planes of the IMes* ligands in **2** form a dihedral angle of 33.1° (52.0° in **TS2b**). Thus, the hydride ligand may reside on any of two equivalent minima (Scheme 3), easily exchanging between them.



Scheme 3. Full motion process of the hydride ligand in $[Pt(H)(IMes^*)_2]^+$ **2**. Newman projections along the C$_{NHC}$—Pt—C$_{NHC}$ axis.

This fluxional process is not exclusive of the Pt complexes **1** and **2**, but is likely operative in other low-coordinate species. For instance, Nolan and co-workers have reported the dihydride complex $[Ir(H)_2(ItBu)_2]^+$ **3**.[20] Two agostic interactions involving the *tert*-butyl groups were observed in the solid state. Interestingly, a dynamic exchange of the *t*Bu groups was detected by ^{1}H NMR spectroscopy, which was frozen out at low temperature. The Gibbs energy barrier at 215 K for such a process was estimated to be 10.0 kcal mol^{-1}.[20] We have performed DFT calculations on this system to account for the reported dynamics. In agreement with the X-ray data, the optimized structure of **3** exhibits two agostic interactions *trans* to the hydride ligands (Figure 4 a). The

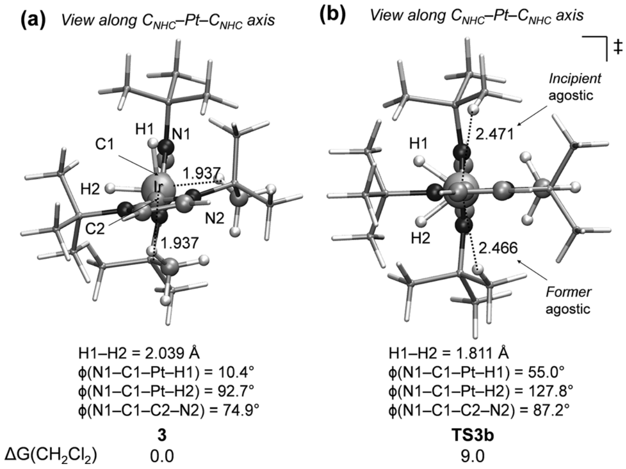
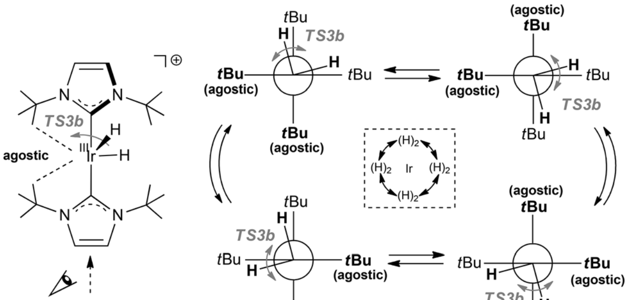


Figure 4. DFT-optimized geometries of a) complex **3** and b) transition state **TS3b**. Distances in Å and angles in degrees. Gibbs energies are given in kcal mol^{-1}.

transition state **TS3a** for the rotation of the I*t*Bu ligand along the Ir—C$_{NHC}$ bond is located at 18.0 kcal mol^{-1} above **3**. The motion of one hydrogen atom would form species **3H**, which features the hydride ligands *trans* to each other. This intermediate is found at 51.6 kcal mol^{-1}, thus its formation is ruled out. Instead, the two hydride ligands move more easily together (similarly to the so-called windshield wiper process[21]) via **TS3b** requiring 9.0 kcal mol^{-1} (Figure 4 b). The H⋯H distance in **TS3b** is 1.811 Å (shorter by 0.228 Å compared to **3**), more characteristic of a dihydride rather than a dihydrogen complex.[2d,22]

Consecutive dihydride migration events entail a full motion around Ir (Scheme 4). The calculated Gibbs energy barrier after thermal correction applied (215 K) is 9.3 kcal mol^{-1}, in excellent agreement with the experimental value of



Scheme 4. Full motion process of the hydride ligand in $[Ir(H)_2(ItBu)_2]^+$ **3**. Newman projections along the C$_{NHC}$—Pt—C$_{NHC}$ axis.

10 kcal mol^{-1}.[20] On the basis of these results we suggest that the events that are frozen at low temperature are not only I*t*Bu rotations (**TS3a**) but also hydride motions (**TS3b**).

This fluxional hydride movement may also operate in the dihydride complex $[Ir(H)_2(6\text{-}Mes)_2]^+$ **4** (6-Mes = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidine-2-ylidene) reported by Aldridge and co-workers, in which no agostic interactions were found.[23] According to our calculations, the motion of the two hydride ligands around Ir via **TS4b** requires 3.8 kcal mol^{-1} (in dichloromethane). So far, we have considered cationic complexes, but the neutral trihydride $[Ir(H)_3(6\text{-}Mes)_2]$ **5**[24] can also exhibit a dihydride migration through **TS5b** involving 4.1 kcal mol^{-1} (in toluene).

Although we have considered real systems hitherto, hypothetical Pd and Rh second-row derivatives of **1** and **3** were also computed, displaying lower barriers for the orbiting process than their third-row counterparts (see SI).

In conclusion, a novel fluxional process involving low-coordinate NHC–transition metal hydride complexes has been unveiled by computational means. The process consists in the motion of the small hydride(s) ligand(s) in an orbital-like path around the metal center, whereas the bulkier NHC ligands remain fixed. Importantly, the fluxional process allows a consistent interpretation of NMR spectra showing atom equivalence. It is indeed by the hydride movement (easy even at low temperatures), and not NHC ligand rotation, that averaging of the NMR signal takes place. The extension of this concept toward a broader set of organometallic species is currently under investigation.

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