Hydride Ligands Orbiting around Low-Coordinate Metal Centers**

Manuel A. Ortuño, Pietro Vidossich, Salvador Conejero* and Agustí Lledós*

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

Abstract: Hydrogen atoms in the coordination sphere of transition metal are highly mobile ligands. In this work, a new type of dynamic process involving hydrides has been characterized by computational means. This dynamic event consists in an orbiting motion of hydride ligands around low-coordinate metal centers containing N-heterocyclic carbenes. The ligand and the transition metal behave as a planetary system, with the hydride moving in orbit around the metal center. 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 a great mobility in transition metal compounds, and a number of dynamic processes involving hydrides have been characterized.^[2] As representative examples we may recall: (i) pairwise exchange involving a rotation of the H–M–H plane by 180° in dihydride complexes, (ii) polytopal rearrangements permuting the hydrides in high-coordinate polyhydrides, and (iii) H/H exchange

between the hydride and a hydrogen atom from another ligand, particularly $\eta^2\text{-H}_2$ or agostic $\eta^2\text{-C-H}$ 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 in the transition metal coordination sphere of bulky ligands as N-heterocyclic carbenes (NHCs),^[3] small and mobile ligands as hydrides and vacant sites seems appealing. 14-electron Pt^{II} hydride complexes can 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 may be stabilized by agostic interactions.^[6]

In this communication, we describe and characterize by computational methods^[7] a class of dynamic process, not reported before, which involves hydride ligands in low-coordinate complexes with bulky NHC ligands. This process consists of an intramolecular orbiting movement of one or two hydride ligands around a transition metal center (Scheme 1). NMR data of several compounds are reinterpreted on 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 $[\text{Pt}(\text{H})(\text{IrBu})_2]^+ \mathbf{1}$ ($\text{IrBu} = 1,3\text{-di-}i\text{-tert-butylimidazol-2-ylidene}$) has been characterized in solution.^[8] This 14-electron complex features a formal vacant coordination site, but no agostic interactions have been assigned on the basis of the NMR data. Even at low temperature (195 K), the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for this compound exhibit a highly symmetric environment in which all the $i\text{Bu}$ and $=\text{CH}$ groups of the IrBu 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 $i\text{Bu}$ group from the IrBu ligand. The $\text{Pt}\cdots\text{H}_{\text{ago}}$ and $\text{Pt}\cdots\text{C}_{\text{ago}}$ lengths of 1.959 and 2.642 Å, respectively, are in the typical range for agostic interactions.^[9] Moreover, the $\text{C}_{\text{ago}}\text{--H}_{\text{ago}}$ bond distance (1.124 Å) is significantly enlarged compared to the C–H bonds not involved in the agostic interaction (ca. 1.094 Å). These structural features were confirmed by optimizing $\mathbf{1}$ with other density functionals.^[10]

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]

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[**] Financial support from the Junta de Andalucía (project No. FQM-2126) and the Spanish Ministerio de Ciencia e Innovación (projects CTQ2011-23336, CTQ2013-45011 is acknowledged. M.A.O. thanks the Spanish Ministerio de Ciencia e Innovación for a research grant.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201xxxxx>.

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 Pt–C_{NHC} bonds.^[12] Reaching the transition state **TS1a** for this rotation requires 13.5 kcal mol^{−1}. Under the experimental conditions, a process with a barrier of ca. 9 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 C_{NHC}–Pt–C_{NHC} axis was located only 3.0 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, with both Pt···H_{ago} distances of 2.214 Å length at the transition state. **TS1b** displays orthogonal *Ir*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).

Figure 1. DFT-optimized geometries of (a) complex **1** and (b) transition state **TS1b**. Distances in Å and angles in degrees. Gibbs energies in kcal mol^{−1}.

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 *Ir*Bu wings, demanding 5.8 (**TS1c**) and 6.3 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 needs four movements to recover the initial structure. Given the small Gibbs energy associated to this process (3.0 kcal mol^{−1} via **TS1b**),^[15] faster than any other rotation event, the hydride formally moves freely around the platinum center in a kind of *orbiting* process, precluding the observation of agostic interactions of **1** in solution. The hydride ligand and the transition metal center behave as a *planetary system*, with the hydride moving in orbit around the metal center. Related planetary systems have been previously invoked for lithium cations.^{[16],[17],[18]}

Scheme 2. Full orbiting process of the hydride ligand in [Pt(H)(*Ir*Bu)₂]⁺ **1**. Newman projections along the C_{NHC}–Pt–C_{NHC} axis.

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. The agostic interaction in **1** is maintained along the simulation (25 ps), exhibiting Pt···H_{ago} and Pt···C_{ago} distances of 2.0 ± 0.1 and 2.7 ± 0.1 Å.^[19] Interestingly, the orbiting event happened once, showing that the hydride moves around Pt in the C_{NHC}–Pt–C_{NHC} axis whereas the NHCs remain static (see SI).

As shown above, calculations support an agostic interaction stabilizing **1**. However, the agostic contact is not necessary for the orbiting 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 2a), yet an easy hydride orbiting motion also occurs via **TS2b** (Figure 2b), which lays only 4.0 kcal mol^{−1} above the optimized structure.

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

In contrast to the *Ir*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 only needs two movements to complete a full orbiting process (Scheme 3).

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

The hydride orbiting 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 $[\text{Ir}(\text{H})_2(\text{IrBu})_2]^+$ **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 ^1H NMR spectroscopy, which was frozen out at low temperature. The Gibbs energy barrier at 215 K for such a process was estimated to be $10.0 \text{ kcal mol}^{-1}$.^[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 3a). The transition state **TS3a** for the rotation of the *Ir*Bu ligand along the $\text{Ir--C}_{\text{NHC}}$ bond is located at $18.0 \text{ kcal mol}^{-1}$ above **3**. Orbiting of one hydrogen atom would form the species **3H** with the hydride ligands *trans* to each other. This intermediate is found at $51.6 \text{ kcal mol}^{-1}$, 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 $9.0 \text{ kcal mol}^{-1}$ (Figure 3b).

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

Consecutive dihydride migration events entail a full orbiting motion (Scheme 4). The calculated Gibbs energy barrier after thermal correction applied (215 K) is $9.3 \text{ kcal mol}^{-1}$, in excellent

agreement with the experimental value of 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 *Ir*Bu rotations (**TS3a**) but also the orbiting process (**TS3b**).

Scheme 4. Full orbiting process of the hydride ligand in $[\text{Ir}(\text{H})_2(\text{IrBu})_2]^+$ **3**. Newman projections along the $\text{C}_{\text{NHC}}\text{--Ir--C}_{\text{NHC}}$ axis.

The orbiting process may also operate in the dihydride complex $[\text{Ir}(\text{H})_2(6\text{-Mes})_2]^+$ **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.^[22] According to our calculations, an orbiting motion of the two hydride ligands via **TS4b** requires $3.8 \text{ kcal mol}^{-1}$ (in dichloromethane). So far, we have considered cationic complexes, but the neutral trihydride $[\text{Ir}(\text{H})_3(6\text{-Mes})_2]$ **5**^[23] can also exhibit a dihydride migration through **TS5b** involving $4.1 \text{ kcal mol}^{-1}$ (in toluene).

Although we have considered real systems so far, 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 orbiting of the small hydride(s) ligand(s) around the metal center, while the bulkier NHC ligands remain fixed. Importantly, the orbiting 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 the *orbiting* concept toward a broader set of organometallic species is currently under investigation.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: agostic interactions • carbene ligands • fluxionality • hydrides • low-coordinate

- a) F. A. Cotton, *Acc. Chem. Res.* **1968**, *1*, 257–265; b) *Physical Organometallic Chemistry*, Vol. 4, *Fluxional Organometallic and Coordination Compounds* (Eds: M. Gielen, R. Willem, B. Wrackmeyer), John Wiley & Sons, Chichester, **2005**.
- a) D. G. Gusev, H. Berke, *Chem. Ver.* **1996**, *129*, 1143–1155; b) F. Maseras, A. Lledós, E. Clot, O. Eisenstein, *Chem. Rev.* **2000**, *100*, 601–636; c) G. S. McGrady, G. Guilera, *Chem. Soc. Rev.* **2003**, *32*, 383–392; d) D. M. Heinekey, A. Lledós, J. M. Lluch, *Chem. Soc. Rev.* **2004**, *33*, 175–182.
- a) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723–6753; b) H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841–861; c) T.

- Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094–7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; d) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478.
- [4] a) R. G. Goel, R. C. Srivastava, *Can. J. Chem.* **1983**, *61*, 1352–1359; b) W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca, P. Rigo, *Angew. Chem.* **2003**, *115*, 109–113; *Angew. Chem. Int. Ed.* **2003**, *42*, 105–108; c) J. Campos, R. Peloso, E. Carmona, *Angew. Chem.* **2012**, *124*, 8380–8383; *Angew. Chem. Int. Ed.* **2012**, *51*, 8255–8258.
- [5] For Rh(III) and Ir(III), see: a) M. J. Ingleson, S. K. Brayshaw, M. F. Mahon, G. D. Ruggiero, A. S. Weller, *Inorg. Chem.* **2005**, *44*, 3162–3171; b) A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1999**, *121*, 97–106.
- [6] M. A. Ortuño, S. Conejero, A. Lledós, *Beilstein J. Org. Chem.* **2013**, *9*, 1352–1382.
- [7] Optimized geometries in gas phase using the PBE0-D3 functional as implemented in Gaussian 09. Values were corrected with single-point calculations in dichloromethane using SMD. Gibbs energies in dichloromethane in kcal mol^{−1} at 298 K (see SI).
- [8] O. Rivada-Wheelaghan, M. Roselló-Merino, M. A. Ortuño, P. Vidossich, E. Gutiérrez-Puebla, A. Lledós, S. Conejero, *Inorg. Chem.* **2014**, *53*, 4257–4268.
- [9] M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6908–6914.
- [10] Other density functionals with different dispersion approaches have been used, namely M06 and APF-D.
- [11] O. Rivada-Wheelaghan, B. Donnadieu, C. Maya, S. Conejero, *Chem. Eur. J.* **2010**, *16*, 10323–10326.
- [12] a) C. P. Newman, R. J. Deeth, G. J. Clarkson, J. P. Rourke, *Organometallics* **2007**, *26*, 6225–6233; b) A. Kolmer, L. Kaltschnee, V. Schmidts, L. H. Peeck, H. Plenio, C. M. Thiele, *Magn. Reson. Chem.* **2013**, *51*, 695–700.
- [13] The Gibbs energy barrier was calculated using transition-state theory at 195 K. The value of k was estimated using the equation $k = \Delta v \cdot 2.22$ (500 MHz spectrometer), see P. J. Hore, *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1995. The chemical shift difference between agostic and non-agostic methyl groups was taken from the related cyclometalated species [Pt(ItBu')(ItBu)]⁺, see [11].
- [14] A high energy barrier has been found for a related process that exchanges a hydride between the top and bottom faces of a four-coordinate d⁶ pincer complex via a square-planar transition state, see M. Findlater, A. Cartwright-Sykes, P. S. White, C. K. Schauer, M. Brookhart, *J. Am. Chem. Soc.* **2011**, *133*, 12274–12284.
- [15] Note that nuclear quantum effects, not taken into account, would decrease the associated barrier.
- [16] a) M. Veith, M. Zimmer, S. Müller-Becker, *Angew. Chem.* **1993**, *105*, 1771–1773; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1731–1733; b) F. Maseras, A. Lledós, *J. Chem. Soc., Chem. Commun.* **1995**, 443–444.
- [17] J.-L. M. Abboud, I. Alkorta, J. Z. Dávalos, J.-F. Gal, M. Herreros, P.-C. Maria, O. Mó, M. T. Molina, R. Notario, M. Yáñez, *J. Am. Chem. Soc.* **2000**, *122*, 4451–4454.
- [18] a) A. Irigoras, J. M. Mercero, I. Silanes, J. M. Ugalde, *J. Am. Chem. Soc.* **2001**, *123*, 5040–5043; b) J. Rodríguez-Otero, E. M. Cabaleiro-Lago, A. Peña-Gallego, M. M. Montero-Campillo, *Tetrahedron* **2009**, *65*, 2368–2371.
- [19] M. A. Ortuño, P. Vidossich, G. Ujaque, S. Conejero, A. Lledós, *Dalton Trans.* **2013**, *42*, 12165–12172.
- [20] N. M. Scott, V. Pons, E. D. Stevens, D. M. Heinekey, S. P. Nolan, *Angew. Chem.* **2005**, *117*, 2568–2571; *Angew. Chem. Int. Ed.* **2005**, *44*, 2512–2515.
- [21] K. Abdur-Rashid, T. Fedorkiw, A. J. Lough, R. H. Morris, *Organometallics* **2004**, *23*, 86–94.
- [22] N. Phillips, J. Rowles, M. J. Kelly, I. Riddlestone, N. H. Rees, A. Dervisi, I. A. Fallis, S. Aldridge, *Organometallics* **2012**, *31*, 8075–8078.
- [23] N. Phillips, C. Y. Tang, R. Tirfoin, M. J. Kelly, A. L. Thompson, M. J. Gutmann, S. Aldridge, *Dalton Trans.* **2014**, DOI: 10.1039/c4dt01398k

Entry for the Table of Contents (Please choose one layout)

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_____ **Page – Page**

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