Reversible H_2 splitting between Ru(II) and a remote carbanion in a zwitterionic compound†

Elzbieta Stepowska, Huiling Jiang and Datong Song*

Received (in Berkeley, CA, USA) 21st September 2009, Accepted 25th November 2009
First published as an Advance Article on the web 11th December 2009
DOI: 10.1039/b919606d

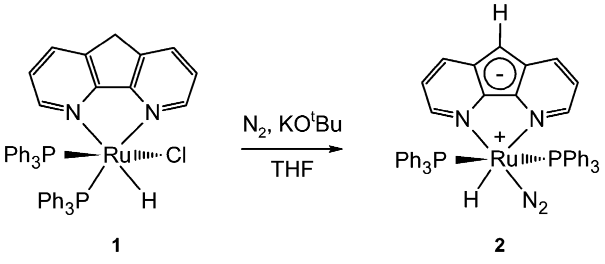
We report a reversible long-range splitting of H_2 between a Ru(II) center and a remote carbanion in a zwitterionic compound.

The formation and cleavage of dihydrogen have attracted much research effort in recent years because of their applications in hydrogenation and relevance to biological H_2 processing and the hydrogen economy.[1,2] Particularly, heterolytic splitting of dihydrogen is of vital importance in the hydrogenation of polar bonds[2,3] and the catalytic activity of hydrogenase.[4] The general scheme of heterolytic splitting of H_2 has been established: upon coordination to an electrophilic metal center, the H_2 molecule becomes more acidic and thus can release a mobile proton to an internal or external base, leaving a hydride on the metal center.[2,5] For example, in a key step of Noyori's catalytic system, H_2 is split into a hydride and a proton between the Ru(II) center and a highly basic amido ligand.[5] Variations of heterolytic H_2 splitting have been reported between various metal centers and adjacent nucleophilic heteroatoms (such as N, O, and S), facilitated by the close proximity between the metal center and the heteroatom.[6]

The recent advances by Stephan and others[7] demonstrated that heterolysis of H_2 can be achieved simply by unquenched Lewis acidity and basicity. Such frustrated Lewis pairs (FLPs) play a key role in polarizing H_2 and in turn, splitting it into H^+ and H^-.[7,8] What intrigued us most is Stephan's integrated phosphane–borane system in which the sterically encumbered phosphorus and boron centers in the same molecule are well spaced by a rigid C_6F_4 linker group.[9] This discovery prompted us to investigate a related scenario—zwitterionic metal complexes with unquenched basicity on negatively charged ligands and Lewis acidity on positively charged metal centers. Previously, we demonstrated the ability of the negatively charged 4,5-diazafluorenide (L^-) ligand to form zwitterionic Rh complexes, in which the Cp^- moiety of the L^- ligand remains uncoordinated and thus has unquenched basicity.[10] We envisioned that if the Lewis acidity of the metal center is sufficiently unquenched at the same time, the complex may have the capability of polarizing and heterolyzing H_2 molecules, resembling the integrated phosphane–borane system. The Rh(I) center in the complex $[RhL(PPh_3)_2]$, however, is too electron-rich to show the required Lewis acidity. As a result, when $[RhL(PPh_3)_2]$ was treated with H_2, only oxidative addition occurred to form the corresponding dihydride. Recently, we have extended our study to a more Lewis acidic Ru(II) system using the L^- ligand. This increased Lewis acidity in combination with the unquenched basicity of the L^- ligand indeed created a FLP situation. Herein, we report a reversible long-range heterolytic cleavage of H_2 between Ru(II) and a remote uncoordinated carbanion in a zwitterionic compound *cis,trans*-$[RuH(L)(N_2)(PPh_3)_2]$ (**2**).

Compound **2** can be prepared by reacting *cis,cis*-$[RuHCl(LH)(PPh_3)_2]$ (**1**) (where LH = 4,5-diazafluorene) with KO^tBu in a THF solution under a dinitrogen atmosphere (Scheme 1). Compound **2** is air- and moisture-sensitive both in the solid state and in solution. The ^1H NMR spectrum of compound **2** in C_6D_6 shows an unsymmetrical structure with two sets of signals for the two pyridine rings of the L^- ligand. The proton on the central ring of L^- resonates at 6.44 ppm indicating an increased aromatic character.[11] The Ru–*H* resonates at −12.23 ppm with a $^2J_{P-H}$ of 20 Hz. The proton decoupled ^{31}P NMR spectrum of **2** in C_6D_6 has only one singlet at 49.61 ppm. The N_2 stretching frequency appears at 2092 cm^{-1} in the IR spectrum, hinting that not much back-donation is involved.[12]

The solid-state structure of **2** (Fig. 1) confirmed by X-ray crystallography‡ is consistent with the solution NMR data. The Ru(II) center adopts a distorted octahedral geometry with two nitrogen donor atoms from L^-, two phosphorus donor atoms from two triphenylphosphine ligands that are *trans* to each other, a hydride and an end-on dinitrogen occupying the six coordination sites. The N–N bond length is 1.111(2) Å, slightly longer than that of a free N_2 (1.0975 Å), consistent with the IR data.[12] The Ru1–N2 bond (2.282(1) Å) is longer than the Ru1–N1 bond (2.114(1) Å) as a result of the strong *trans*-influence of the hydride. Similar to the previously reported zwitterionic Rh complexes of L^-, the Cp^- moiety of the chelating ligand is dangling and thus retains its unquenched basicity.[10] Although the Ru(II) center in **2** is



Scheme 1 Synthesis of compound **2**.

Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada. E-mail: dsong@chem.utoronto.ca; Fax: 1-416-978-7013; Tel: 1-416-978-7014

† Electronic supplementary information (ESI) available: Experimental and spectroscopic details of **2** and **3**. CCDC 743623 and 743624. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b919606d

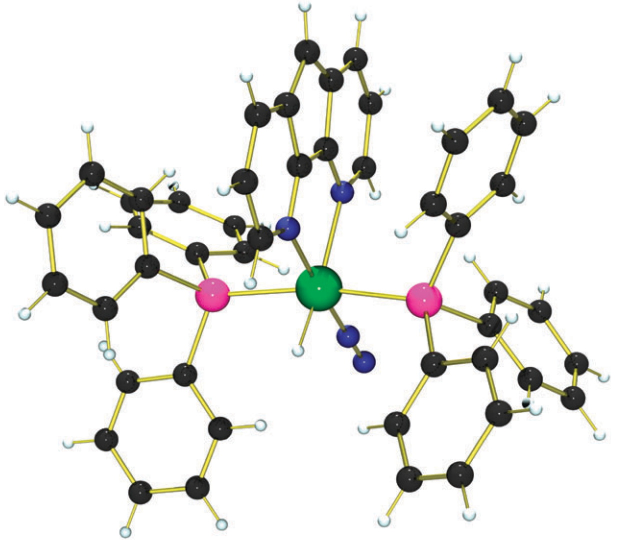


Fig. 1 POV-Ray drawing of **2**. Color key: C, black; P, pink; N, blue; H, white; Ru, green.

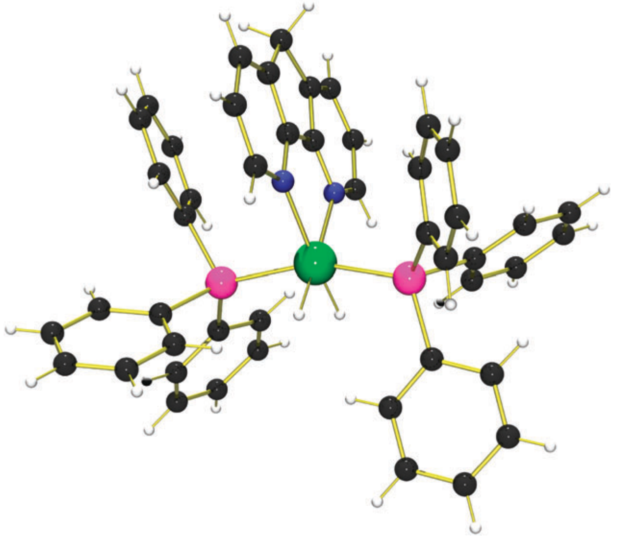
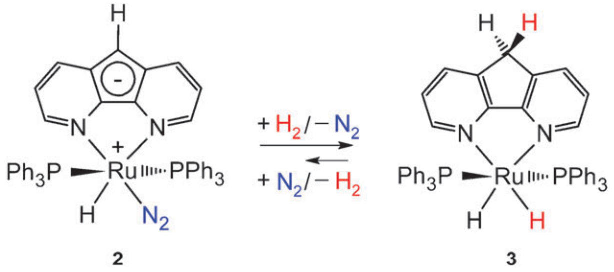


Fig. 2 POV-Ray drawing of **3**. Color key: C, black; P, pink; N, blue; H, white; Ru, green.

saturated with six ligands, the N_2 ligand is sufficiently labile, rendering the Ru(II) center Lewis acidic upon dissociation.

In solution (in C_6H_6 or THF), compound **2** reacts with 1 atm of H_2 at 60 °C to form *cis*,*cis*,*trans*-[Ru(H)$_2$(LH)(PPh$_3$)$_2$] (**3**) quantitatively within 1.5 h (Scheme 2, Fig. 2),‡ whereas the reaction is much slower at ambient temperature. The use of D_2 instead of H_2 results in deuterium incorporation to the 9-position of the LH ligand and Ru–*D* formation. Interestingly, the *ortho* positions of the phenyl groups of PPh$_3$ are deuterated in this process, indicating a concomitant reversible cyclometallation process. When the partially deuterated **3** is treated with 1 atm of H_2 at 60 °C in solution, protium can be incorporated to the 9-position of the LH ligand, the *ortho* position of the phenyl groups of PPh$_3$, and the Ru center, indicating the reversible nature of the hydrogen splitting and releasing process. When a solution of compound **3** (in benzene or THF) is heated at 60 °C in a sealed Schlenk bomb under a dinitrogen atmosphere for 12 h, compound **2** can be detected by NMR spectroscopy in 12% conversion. Prolonged heating does not change the conversion significantly, suggesting that the H_2 split and release equilibrium is lying on the split side.

The Milstein group has reported reversible H_2 splitting between the metal center and a non-adjacent carbon atom in (PNN)Ru and (PNP)Ru pincer compounds.[13a,b] The same group has also reported an intriguing H_2 splitting by the (PNP)IrPh (where PNP is 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine) system,[13c] where the carbon atom and the Ir center are ∼3.2 Å apart, resulting in to formation of a *trans*-dihydride rather than the expected *cis*-dihydride. Dyson and co-workers have reported H_2 splitting between the Ru(II) center and the carbon backbone of the β-diketiminate ligand in a Ru(II) arene β-diketiminate complex, in which the carbon atom and the Ru center are 3.4 Å apart.[14] More recently, Stradiotto and co-workers have reported a heterolysis of H_2 between a Ru(II) center and a carbon atom in a Cp*Ru(κ^3-*P*,*C*,*C*′) species,[15] in which the distance between the Ru center and the carbon atom is ∼4.2 Å. In contrast, the Ru center and C-9 of the L^- ligand are ∼5.0 Å apart in compound **2**.



Scheme 2 Reversible H_2 activation by compound **2**.

In the (PNP)Ir system, a unique mechanism involving deprotonation/protonation–aromatization/dearomatization has been supported by both experimental and DFT data;[16] in the Cp*Ru(κ^3-*P*,*C*,*C*′) case, a C–Ru bond is present, hinting the possibility of hydrogenolysis of the C–Ru bond followed by isomerization. A concerted mechanism has been suggested by DFT for the Ru(II) arene β-diketiminate case, whereas in compound **2** case, a concerted mechanism appears unlikely because of the large separation between the Ru center and the carbon atom, unless the proton transfer is assisted by a bridge of multiple solvent (*e.g.* H_2O) molecules.[16a] Although at first glance, H_2 splitting by compound **2** may also be the Noyori type, *via* a resonance structure with amido-Ru moiety, followed by isomerization, the D_2 experiment disfavors this mechanistic proposal.[17] Interestingly, even for Milstein's (PNP)Ir system, despite the presence of an amido nitrogen, DFT calculations suggested that the Noyori type of H_2 splitting followed by isomerization is unlikely.[16b] Mechanistic studies on the long-range H_2 splitting by **2** are currently underway and will be published in due course.

In summary, we have demonstrated a unique reversible heterolysis of dihydrogen between a Ru(II) center and a distant uncoordinated carbanion in the zwitterionic compound **2**. Although the mechanism of such heterolysis of H_2 is yet to be studied, the net result of this reaction represents an unusually long range heterolytic cleavage of H_2 between a metal center and a carbanion in the same molecule. The equilibrium favors hydrogen splitting. The mechanism of this reversible heterolytic H_2 splitting, the possibility to activate other small molecules with compound **2**, and the potential catalytic activity of **2** and **3** are being investigated in our laboratory.

This research was supported by grants to D. S. from Canadian Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, Ontario Ministry of Research and Innovation, the University of Toronto, Connaught Foundation. E. S. is grateful for a postgraduate scholarship from the OGS program of Ontario. We thank Professors Robert H. Morris and Douglas W. Stephan for helpful discussions.

Notes and references

‡ Selected crystallographic data, for **2**·C_6H_6: a = 18.4215(5), b = 9.9438(2), c = 25.1806(7) Å, β = 100.457(1)°, V = 4321.68(19) Å^3, Z = 4, space group $P2_1/n$, T = 150 K, unique data: 9914, (R_{int} = 0.0426), observed data ($I > 2\sigma(I)$): 8845, parameters: 545, R_1 = 0.0262, wR_2 = 0.0631; for **3**: a = 13.8338(4), b = 17.7363(6), c = 15.9357(3) Å, β = 105.997(2)°, V = 3758.57(18) Å^3, Z = 4, $P2_1/n$, T = 150 K, unique data: 8519 (R_{int} = 0.0438), observed data ($I > 2\sigma(I)$): 6283, parameters: 477, R_1 = 0.0396, wR_2 = 0.0920.

1 (*a*) J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza and Y. Nicolet, *Chem. Rev.*, 2007, **107**, 4273; (*b*) A. J. Esswein and D. G. Nocera, *Chem. Rev.*, 2007, **107**, 4022; (*c*) X. Cui and K. Burgess, *Chem. Rev.*, 2005, **105**, 3272.

2 G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152, and references therein.

3 M. Ito and T. Ikariya, *Chem. Commun.*, 2007, 5134.

4 A. L. De Lacey, V. M. Fernández, M. Rousset and R. Cammack, *Chem. Rev.*, 2007, **107**, 4304, and references therein.

5 (*a*) S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201; (*b*) T. Ikariya, K. Murata and R. Noyori, *Org. Biomol. Chem.*, 2006, **4**, 393; (*c*) G. J. Kubas, *Adv. Inorg. Chem.*, 2004, **56**, 127.

6 (*a*) M. Peruzzini and R. Poli, *Recent Advances in Hydride Chemistry*, Elsevier, Amsterdam, 2001; (*b*) R. C. Linck, R. J. Pafford and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2001, **123**, 8856; (*c*) A. Ienco, M. J. Calhorda, J. Reinhold, F. Reineri, C. Bianchini, M. Peruzzini, F. Vizza and C. Mealli, *J. Am. Chem. Soc.*, 2004, **126**, 11954; (*d*) Y. Ohki, Y. Takikawa, H. Sadohara, C. Kesenheimer, B. Engendahl, E. Kapatina and K. Tatsumi, *Chem.–Asian J.*, 2008, **3**, 1625; (*e*) P. Maire, T. Büttner, F. Breher, P. Le Floch and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2005, **44**, 6318; (*f*) Y. Shvo, D. Czarkie, Y. Rahamim and D. F. Chodosh, *J. Am. Chem. Soc.*, 1986, **108**, 7400; (*g*) C. P. Casey, J. B. Johnson, S. W. Singer and Q. Cui, *J. Am. Chem. Soc.*, 2005, **127**, 3100.

7 (*a*) D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535, and references therein; (*b*) A. L. Kenward and W. E. Piers, *Angew. Chem., Int. Ed.*, 2008, **47**, 38, and references therein.

8 (*a*) D. P. Huber, G. Kehr, K. Bergander, R. Fröhlich, G. Erker, S. Tanino, Y. Ohki and K. Tatsumi, *Organometallics*, 2008, **27**, 5279; (*b*) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7428.

9 G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124.

10 H. Jiang, E. Stepowska and D. Song, *Eur. J. Inorg. Chem.*, 2009, 2083.

11 H. Jiang and D. Song, *Organometallics*, 2008, **27**, 3587.

12 B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385.

13 (*a*) J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.*, 2005, **127**, 10840; (*b*) J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2006, **45**, 1113; (*c*) E. Ben-Ari, G. Leitus, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2006, **128**, 15390.

14 A. D. Phillips, G. Laurenczy, R. Scopelliti and P. J. Dyson, *Organometallics*, 2007, **26**, 1120.

15 M. A. Rankin, G. Schatte, R. McDonald and M. Stradiotto, *Organometallics*, 2008, **27**, 6286.

16 (*a*) M. A. Iron, E. Ben-Ari, R. Cohen and D. Milstein, *Dalton Trans.*, 2009, 9433; (*b*) G. Zeng, Y. Guo and S. Li, *Inorg. Chem.*, 2009, **48**, 10257.

17 If the H_2 splitting is Noyori type followed by isomerization through resonance structures, one would expect deuterium incorporation into the *meta*-position of the pyridine moiety during the D_2 splitting experiment to certain extent. However, this deuterium incorporation was not observed. For details, see ESI†.