Ruthenium trihydrides with *N*-heterocyclic carbene ligands: effects on quantum mechanical exchange coupling†

Aled L. Jones,[a] G. Sean McGrady,*[a] Peter Sirsch[a] and Jonathan W. Steed*[b]

Received (in Columbia, MO, USA) 8th September 2005, Accepted 17th October 2005
First published as an Advance Article on the web 4th November 2005
DOI: 10.1039/b512760b

Ruthenium trihydrides containing *N*-heterocyclic carbene ligands display large quantum mechanical exchange couplings in their ^{1}H NMR spectra: DFT calculations are used to explore this phenomenon and to compare them to their phosphine congeners.

The large, temperature-dependent coupling constants observed in the ^{1}H NMR spectra of certain polyhydride complexes of Nb, Mo, Ru, Ta, Os and Ir caused excitement in the 1990s, and the realisation that some were larger than that of molecular hydrogen itself (280.8 Hz)—in some cases greater than 10^4 Hz[1]—led to much speculation over their origin.[2] The effect has since been explained by *quantum mechanical exchange coupling* (QMEC), which is neatly represented by a double-well potential as shown in Fig. 1. Pairwise exchange of hydrogen nuclei occurs by tunnelling through the low barrier separating the two sides of the potential.[3–5] Whilst it is now clear that the phenomenon is quantum mechanical in origin, the dynamics of the process remain less defined. It was first proposed that an in-plane MH_3 bending vibration enabled the close approach of the hydride ligands,[3] until refinement by Limbach *et al.* invoked an out-of-plane rotational mechanism facilitated by an energetically low-lying $MH(\eta^2\text{-}H_2)$ state.[6] Clot *et al.* have since suggested that close contact of the two hydrides during a pseudorotational process is all that is necessary,[7] and the exchange is now generally considered to be mediated by a hybrid process involving aspects of each of these, with an out-of-plane bend preceding rotational tunnelling through the barrier.

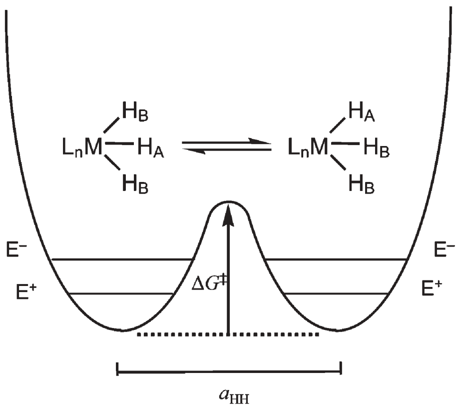

Fig. 1 Double-well potential for exchange in transition metal trihydrides displaying QMEC with the H···H separation represented by a_{HH}. Redrawn from ref. 4.

To date, all complexes displaying QMEC have contained one or both of cyclopentadienide or phosphine co-ligands. The dependence of QMEC on phosphine basicity has been firmly established, most notably in the series of complexes $[Cp^*RuH_3(PR_3)]$ and $[Cp^*IrH_3(PR_3)]^+$.[8–10] Strongly π-accepting phosphines assist QMEC by lowering the barrier to interconversion ($\Delta G^\ddagger$ in Fig. 1), ostensibly by stablilising a $MH(\eta^2\text{-}H_2)$ component, resulting in high values for J_{AB}; *e.g.* $[Cp^*RuH_3(PPy_3)]$ in Table 1. More basic phosphines such as P^iPr_3 result in much higher $\Delta G^\ddagger$ and lower J_{AB} values.[1,11]

The 1990s also saw advances in the synthesis and isolation of *N*-heterocyclic carbenes (NHCs),[12,13] and their exploitation as alternatives to phosphines in a variety of chemical and catalytic environments. The contrasting electronic nature of NHCs (strong σ-donors with insignificant π-backdonation) makes them an attractive substitute for phosphine ligands in polyhydride systems displaying QMEC, and may offer a valuable insight into the mechanism of the exchange as well as proving a sterner test for phosphine/NHC interchangability.[13] Such σ-only donors would be expected to destablise a $MH(\eta^2\text{-}H_2)$ state, resulting in an increased $\Delta G^\ddagger$ and highly diminished or even quenched QMEC. However, the H···H distance (a_{HH} in Fig. 1) in the MH_3 moiety is also important, as overlap of the H-atom wavefunctions (below *ca.* 1.65 Å) is necessary for QMEC.[4] Accordingly, we have prepared and studied the first NHC-containing trihydride complexes which exhibit QMEC; *viz.* $[Cp^*RuH_3(IMes)]$ **1**; Cp* = ($\eta^5\text{-}C_5Me_5$), and $[Cp''RuH_3(IMes)]$ **2**; Cp″ = ($\eta^5\text{-}C_5Me_4Et$), for which large temperature dependent J_{AB} coupling constants are observed.

Table 1 Exchange parameters determined by ^{1}H NMR spectroscopy for a series of $[(\eta^5\text{-}C_5R_5)RuH_3(L)]$ species displaying QMEC

Complex	$\Delta G^\ddagger$/kJ mol^{-1}	$J_{AB\ min}$/Hz	$J_{AB\ max}$/Hz
$[Cp^*RuH_3(PCy_3)]^a$	46	67 (185 K)	181 (237 K)
		62 (178 K)	94 (193 K)
$[Cp^*RuH_3(P^iPr_3)]^a$	46	64 (173 K)	131 (203 K)
$[Cp''RuH_3(IMes)]$ **2**^{b}	45	113 (173 K)	324 (213 K)
$[Cp^*RuH_3(IMes)]$ **1**^{b}	45	123 (173 K)	353 (213 K)
$[Cp^*RuH_3(PPh_3)]^c$	40	290 (190 K)	—
$[CpRuH_3(PPh_3)]^c$	40	900 (170 K)	—
$[Cp^*RuH_3(PPy_3)]$ **3**^{d}	34	950 (140 K)	3000 (180 K)

[a] Ref. 8 in d^8-THF and ref. 6 in d^8-toluene. [b] This paper in d^8-THF. [c] Ref. 13 in $CDFCl_2$. [d] Ref. 9 in d^8-THF.

---

[a] *Department of Chemistry, University of New Brunswick, Fredericton, N.B., Canada E3B 6E2. E-mail: smcgrady@unb.ca; Fax: +1 506 453 4981; Tel: +1 506 452 6340*
[b] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: jon.steed@dur.ac.uk; Fax: +44 (0)191384 4737; Tel: +44 (0)191 334 2085*

† Electronic supplementary information (ESI) available: Molecular representation and coordinates of optimised geometries for **1** and **3**. See DOI: 10.1039/b512760b

Addition of 2.1 equivalents of $LiBHEt_3$ at −75 °C to a THF solution of [Cp*RuCl(IMes)] (prepared by the literature method)[14] proceeds over 3 h with a colour change from blue to a red-brown. After work-up [Cp*RuH_3(IMes)] **1** is isolated from petroleum ether (60–80 °C) as an air-sensitive brown-red powder. Similar treatment of [Cp″RuCl(IMes)] results in [Cp″RuH_3(IMes)] **2**.‡

The single resonance observed for both **1** and **2** in the hydride region of the ^1H NMR spectrum at room temperature survives down to *ca.* 248 K, whereupon it decoalesces and a second-order AB_2 pattern emerges. As the temperature is lowered further, the four lines observed in each branch are seen to converge (two branches corresponding to both the H_A and H_B ligands), in a manner consistent with other trihydrides which display QMEC (Fig. 2). Computer simulation of these spectra with the gNMR programme results in surprisingly large values for J_{AB}—ranging from 123 Hz for **1** and 113 Hz for **2** at 173 K, to 324 and 353 Hz, respectively, at 223 K. From the coalescence temperature, $\Delta G^{\ddagger}$ for the classical thermal rearrangement is calculated to be 45 kJ mol^{-1} for both **1** and **2**. The small difference in J_{AB} for **1** and **2** reflects the more electron-rich nature of the Cp″ ligand with respect to Cp*, and is much less significant than the 610 Hz seen between Cp and the Cp* ligands (Table 1).[15] The J_{AB} for **1** and **2** lie surprisingly close to those of analogous RuH_3 complexes containing alkylphosphine ligands (Table 1), implying that the Ru–P π-backdonation is not a significant factor for trihydride systems incorporating such basic phosphines and that there is no significant difference between their ligand behaviour and that of the NHCs.

The magnitudes of J_{AB} are reflected in the chemical shift of the ruthenium-bound protons at room temperature. Suzuki *et al.*[8] noted that the shift was 'consistent with the electronic parameters of the PR_3 ligand according to Tolman' for the generic [Cp*RuH_3(PR_3)] complexes. The δ values of *ca.* −10 ppm seen for **1** and **2** appear at higher frequencies than for those trihydrides containing the PPh_3 (*ca.* −9.8 ppm) ligands but not as high as those containing PCy_3 and P^iPr_3 (*ca.* −11.0 ppm).

DFT calulations§ were carried out on **1** and [Cp*RuH_3(PPy_3)] **3**, the X-ray crystal structure of which is known,[9] in an attempt to determine whether the magnitude of J_{AB} arises from a short a_{HH} (a feature of their ground state geometry) or because of a small $\Delta G^{\ddagger}$ value (characteristic of the transition state). Both **1** and **3** are clearly trihydrides in the ground state, and the structural features of the RuH_3 moiety are very similar (Table 2, Fig. 3). The energies of the putative RuH(η^2-H_2) transition states of **1** and **3** were derived in a manner akin to those for the $[CpIrH_3(PH_3)]^+$ system by Jarid *et al.*, by scanning the potential energy surface and using as grid parameters the H_A-to-H_B distance (a_{HH}), along with the metal to the H_AH_B mid-point (a_{RuHx}) and the angle around this axis.[16] The method assumes that as the transition state is approached, the shortening of the H_A–H_B distance is accompanied by an increase in the Ru–H_x distance along with simultaneous 90° rotation around this axis (Fig. 3).

Table 2 Structural parameters (in Å) determined by DFT calculations for the ground state geometries of [Cp*RuH_3(IMes)] **1** and [Cp*RuH_3(PPy_3)] **3**

	[Cp*RuH_3(IMes)] **1**	[Cp*RuH_3(PPy_3)] **3**
Ru–H_A	1.587	1.588
Ru–H_B	1.586	1.600
	1.587	1.601
H_A–H_B	1.715	1.684
	1.718	1.683
Ru–Cp*	2.001	1.976
Ru–L	2.064	2.246

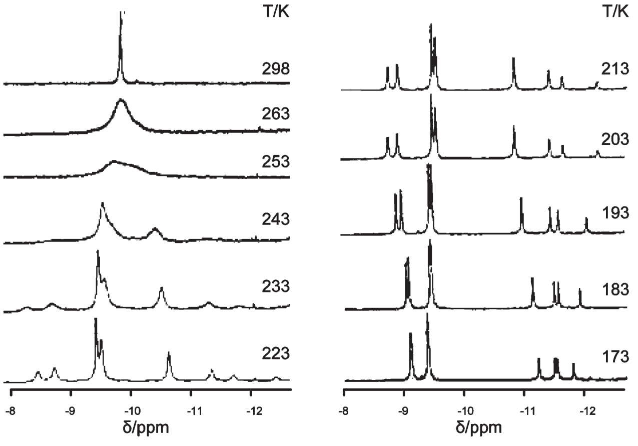

Fig. 2 ^1H NMR spectra for the hydride region of [Cp″RuH_3(IMes)] **2** between 173 and 298 K.

The height of the rotational energy barrier of **1** is calculated to be 74.1 kJ mol^{-1} above the ground state with a_{HH} and a_{RuHx} determined to be 0.86 and 1.65 Å, respectively. In contrast, the barrier height for **3** is 54.1 kJ mol^{-1} with values of 0.84 and 1.68 Å for a_{HH} and a_{RuHx}. These energetic values are in accordance with those obtained by Jarid *et al.*[16] in that they indicate a barrier 20 kJ mol^{-1} or more greater than that implied by $\Delta G^{\ddagger}$ as determined by NMR spectroscopy. Nevertheless, their relative magnitudes support the idea that increasing the basicity of the ligands at Ru destabilises the RuH(η^2-H_2) transition state, thereby increasing the barrier to interconversion and resulting in lower values of J_{AB}.

In conclusion, we have synthesised and studied [Cp*RuH_3(IMes)] **1** and [Cp″RuH_3(IMes)] **2**, the first trihydride complexes containing NHC ligands to display QMEC. The magnitude of QMEC for both **1** and **2** lies in the range for their phosphine analogues; unexpectedly high given the dominant σ-donor behaviour of IMes. DFT calculations reveal minimal difference in the equilibrium geometry of the NHC-containing **1** in comparison to its PPy_3 analogue **3**. The RuH(η^2-H_2) transition

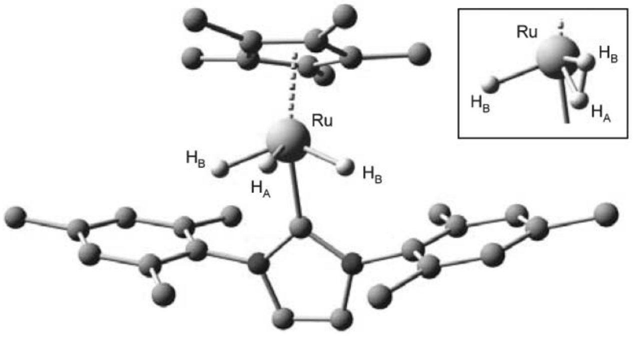

Fig. 3 Molecular representation of the ground state of **1** and its transition state (shown inset). All hydrogen atoms except those directly attached to the metal are omitted for clarity.

state for **1** lies some 20 kJ mol^{-1} higher than in **3**, a difference in good agreement with $\Delta G^{\ddagger}$ values from ^{1}H NMR experiments, which predict a higher barrier for the NHC complex. The enormous range of J_{AB} values spanned by trihydrides exhibiting QMEC provides a highly sensitive yardstick; our results indicate that the NHC ligands are indistinguishable from basic alkyl phosphines in these systems.

Support by NSERC and the Deutsche Forschungsgemeinschaft (Postdoctoral Fellowship to P.S.) is gratefully acknowledged.

Notes and references

‡ *Experimental*: **[Cp*RuH$_3$(IMes)] 1:** [Cp*RuCl(IMes)] (0.6 g, 1.0 mmol) was dissolved in THF (15 mL) and the mixture cooled to −75 °C. LiBHEt$_3$ (2.1 mL, 2.1 mmol) was then added and the mixture was stirred for 3 h as it was allowed to warm up to room temperature. The solution changed colour from blue to red during this time. Volatiles were removed under vacuum and extraction into pentane (15 mL) was followed by filtration. Isolation of a brown-red solid from pentane at −40 °C gave the product. Yield: 0.13 g, 0.24 mmol, 23%. ^{1}H NMR: (C$_4$D$_8$O) δ 6.77 (s, 4H, Mes-*H*); 6.60 (s, 2H, NC*H*); 2.31 (s, 12H, *o*-C*H*$_3$); 2.12 (s, 6H, *p*-C*H*$_3$); 1.30 (s, 15H, C$_5$*Me*$_5$); −9.80 (s, 3H, Ru-*H*). ^{13}C NMR: (C$_4$D$_8$O) δ 193.8 (N*C*N); 140.0, 137.3, 136.1, 128.8 (4 × Mes); 121.1 (N*C*H); 92.8 (*C*$_5$Me$_5$); 20.5, 18.5 (*o,p*-*C*H$_3$); 12.0 (C$_5$*Me*$_5$). Mass spec: 544.2 [M$^+$].

[Cp″RuH$_3$(IMes)] 2: [Cp″RuCl(IMes)] (0.20 g, 0.33 mmol) was dissolved in THF (15 mL) and the mixture cooled to −75 °C. LiBHEt$_3$ (0.7 mL, 0.7 mmol) was then added and the mixture was stirred for 3 h as it was allowed to warm up to room temperature. The solution changed colour from blue to red-brown during this time. Volatiles were removed under vacuum and extraction into pentane (15 mL) was followed by filtration. Removal of the extracting solvent revealed a dark brown oily substance. Prolonged pumping did not remove further solvent, and a ^{1}H NMR spectrum revealed the major product to be [Cp″RuH$_3$(IMes)]. ^{1}H NMR: (C$_4$D$_8$O) δ 6.98 (s, 4H, Mes-*H*); 6.79 (s, 2H, NC*H*), 2.33 (s, 12H, *o*-C*H*$_3$); 2.03 (s, 6H, *p*-C*H*$_3$); 1.98 (q, *J* = 8 Hz, 2H, C$_5$Me$_4$C*H*$_2$CH$_3$); 1.61 (s, 6H, C$_5$*Me*$_4$Et); 1.60 (s, 6H, C$_5$*Me*$_4$Et); 0.73 (t, *J* = 8 Hz, 3H, C$_5$Me$_4$CH$_2$C*H*$_3$); −9.96 (s, 3H, Ru–*H*). ^{13}C NMR: (C$_4$D$_8$O) δ 204.4 (N*C*N); 140.6, 137.9, 136.8, 129.4 (4 × Mes); 121.7 (N*C*H); 99.0, 94.6, 92.39 (*C*$_5$Me$_4$Et); 21.2, 19.2 (*o,p*-*C*H$_2$); 16.7 (C$_5$Me$_4$CH$_2$*C*H$_3$); 12.5, 12.4 (C$_5$*Me*$_4$Et). IR (Nujol): 1596, 1117, 852 cm^{-1}.

§ *Computational details*: All DFT calculations were performed with the Gaussian 03 set of programs[17] using the B3LYP functional.[18,19] Ruthenium was represented with the Hay–Wadt effective core potential and its associated double-ζ basis set.[20] A 6-31G(d)[21–23] basis set was used for carbon, nitrogen and phosphorus atoms, and a 6-31G(p) basis set for the hydrogen atoms directly attached to the metal.[21,22] The remaining hydrogen atoms were described with a 6-31G basis set.[21] All geometry optimisations were carried out without imposing any symmetry constraints and the reported structures were found to be true minima on the potential energy surface by calculating analytical or numerical frequencies.

1 S. Sabo-Etienne and B. Chaudret, *Chem. Rev.*, 1998, **98**, 2077.

2 A. Antinolo, B. Chaudret, G. Commenges, M. Fajardo, F. Jalon, R. H. Morris, A. Otero and C. T. Schweltzer, *J. Chem. Soc., Chem. Commun.*, 1988, 1210.

3 D. M. Heinekey, J. M. Millar, T. F. Koetzle, N. G. Payne and K. W. Zilm, *J. Am. Chem. Soc.*, 1990, **112**, 909.

4 K. W. Zilm, D. M. Heinekey, J. M. Millar, N. G. Payne, S. P. Neshyba, J. C. Duchamp and J. Szczyrba, *J. Am. Chem. Soc.*, 1990, **112**, 920.

5 F. Maseras, A. Lledós, E. Clot and O. Eisenstein, *Chem. Rev.*, 2000, **100**, 601.

6 H. H. Limbach, G. Scherer, M. Maurer and B. Chaudret, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1369.

7 E. Clot, C. Leforestier, O. Eisenstein and M. Pelissier, *J. Am. Chem. Soc.*, 1995, **117**, 1797.

8 H. Suzuki, D. H. Lee, N. Oshima and Y. Morooka, *Organometallics*, 1987, **6**, 1569.

9 T. Arliguie, C. Border, B. Chaudret, J. Devillers and R. Poilblanc, *Organometallics*, 1989, **8**, 1308.

10 D. M. Heinekey, A. S. Hinkle and J. D. Close, *J. Am. Chem. Soc.*, 1996, **118**, 5353.

11 S. Gründemann, H. H. Limbach, V. Rodriguez, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *Ber. Bunsen-Ges. Phys. Chem.*, 1998, **102**, 344.

12 D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.

13 N. M. Scott and S. P. Nolan, *Eur. J. Inorg. Chem.*, 2005, 1815.

14 J. K. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674.

15 D. M. Heinekey, N. G. Payne and C. D. Sofield, *Organometallics*, 1990, **9**, 2643.

16 A. Jarid, M. Moreno, A. Lledós, J. M. Lluch and J. Bertrán, *J. Am. Chem. Soc.*, 1995, **117**, 1069.

17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, J. C. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, B. Cioslowski, B. B. Stepanov, G. Liu, A. Liashenko, P. Piskorz, I. Komoromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, in *GAUSSIAN 03, (revision B.05)*, Gaussian Inc., Pittsburgh, PA, 2003.

18 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

19 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

20 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

21 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

22 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

23 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.