Intermolecular Re–H···H–N and Re–H···base hydrogen bonding estimated in solution by a UV-VIS spectroscopic method

Pascale Desmurs,† Konstantinos Kavallieratos,‡ Wenbin Yao and Robert H. Crabtree*

Chemistry Department, Yale University, PO Box 208107, New Haven CT, 06520-8107, USA

Received (in Montpellier, France) 23rd August 1999

Hydrogen bonding (Re–H···H–N) is estimated in solution between $ReH_5(PPh_3)_2L$ (L = pyridine, 4-picoline, 4-dimethylaminopyridine, and 4-carbomethoxypyridine), as hydrogen bond acceptor, and indole, as hydrogen bond donor. Re–H···base hydrogen bonding between $[Re(PPh_3)_2(MeCN)_4H][BF_4]_2$ as hydrogen bond donor and various amines as hydrogen bond acceptors is much weaker. The binding strengths are estimated by UV-VIS spectroscopy.

Metal hydrides can act either as hydrogen bond acceptors (weak bases)[1] or hydrogen bond donors (weak acids),[2–5] depending on the type of hydride involved. Cationic hydrides tend to act as hydrogen bond donors to give structures of the type $M–H^{\delta+}\cdots$base. Neutral hydrides on the other hand, can act as H-bond acceptors to give structures of the type $M-H^{\delta-}\cdots H^{\delta+}–X$ (X = O, N). This amphoteric behavior of metal hydrides in hydrogen bonding has led us to carry out the quantitative solution study reported here. If strong enough, such hydrogen bonding could be applied to altering rates and equilibria[6] of organometallic and catalytic reactions.

M–H···H–X (X = N, O) interactions are analogous to conventional hydrogen bonds except that the M–H σ electrons act as the hydrogen bond proton acceptor, the hydride being hydridic.[1] Intermolecular examples of M–H···H–X (X = O,N) hydrogen bonding have been characterized both structurally and spectroscopically.[1(d–f)] Some of us recently reported a neutron diffraction study of $[ReH_5(PPh_3)_3 \cdot \text{indole} \cdot C_6H_6]$ **1**,[1(d,e)] and an X-ray diffraction study of $[ReH_5(PPh_3)_2\text{-}(\text{imidazole}) \cdot 0.5\text{imidazole} \cdot 1.5C_6H_6]$ **2**,[1(e,f)] which characterize Re–H···H–N outer sphere coordination interactions in the solid state between a ReH bond and an aromatic NH.

M–H···X hydrogen bonds in which the metal hydride is protonic, have been found by our group[5] and by others.[2–4] $M–H\cdots OPPh_3$ hydrogen bonds have been previously detected for a variety of cationic iridium hydrides of the type $[IrH_2L_2(PPh_3)_2]^+$, and $[IrH(bzquin)L'(PPh_3)_2]^+$, for which IR studies give estimates of the H-bond free energies of 10 to 13 kJ mol^{-1}, the strongest being associated with those compounds having more electron-withdrawing ligands.[5]

Here we look at the solution behavior of the Re–H···H–N interaction by a UV-VIS spectroscopic study of various Re polyhydride hydrogen bond acceptors, $ReH_5(PPh_3)_2L$ (L = pyridine, **1**, 4-picoline, **2**, 4-dimethylaminopyridine, **3**, 4-carbomethoxypyridine, **4**), with the hydrogen bond donor, indole. We extend the method to a preliminary quantitative study of a hydrogen bond of the Re–H···base type that involves the protonic dicationic metal hydride *cis*-$[Re(PPh_3)_2(CH_3CN)_4H][BF_4]_2$ **5**, acting as a hydrogen bond donor with various hydrogen bond acceptors. Solution characterization, including estimation of the K_as, has not been carried out for this system previously, and only a few reports of solution characterization have appeared, mainly by FT-IR and NMR spin–lattice relaxation time studies.[7] ^{1}H-NMR spectroscopy was not suitable because the chemical shift changes, although observable, were not large enough to give reliable binding constants. From the shift in the indole ν(NH) in the FT-IR, only approximate values for the ΔG of interaction can be estimated from eqn. (1), as first suggested by Iogansen *et al.*[8] and used by Poliakoff *et al.*[9] for the case of $Cp^*Ir(CO)_2$ and perfluoroalcohols.

$$\Delta H = -1.28(\Delta\nu)^{1/2} \qquad (1)$$

The hydrogen bond enthalpies estimated from IR data using eqn. (1) and from theoretical studies are in the 17–25 kJ mol^{-1} range with H···H distances of 1.7–2.0 Å by X-ray and neutron diffraction for the cases studied.[1(a)]

Results and discussion

The effects of hydrogen bond formation on the UV-VIS spectra of organic compounds have been studied extensively in the past.[10] Charge transfer bands are particularly sensitive to intermolecular interactions.[11] Previous studies in our group demonstrated the effect of hydrogen bonding by various protic solvents on the high energy MLCT band of $ReH_5(PPh_3)_2py$.[12] We now find that intermolecular hydrogen bonding has a significant effect on the UV-VIS spectra of a number of hydrogen bond donors and acceptors and have examined UV-VIS spectroscopy as a method by which thermodynamic parameters can be obtained for outer sphere coordination involving hydrogen bonding in metal hydride complexes. UV-VIS spectroscopy is a powerful method for studying molecular association phenomena, particularly at low concentrations.[13]

Choice of systems for study

We hoped that the charge transfer (CT) bands of metal complexes would be particularly sensitive to outer sphere hydrogen bonding effects and so we looked for different types of hydridic and protonic metal hydride complexes having CT bands in the UV-VIS spectrum.

Compounds **1**–**4** are useful proton acceptor complexes because they have intense bands in their UV-VIS spectrum of which one ($\lambda = 437$ nm; $\varepsilon = 6.0 \times 10^3$ in toluene) has been assigned to a $M \rightarrow \pi^*$ MLCT.[14] This assignment has been

---

† Visiting scholar at Yale; present address: Laboratoire de Synthèse et Electrosynthèse Organométalliques. (CNRS UMR 5632), Université de Bourgogne, 6 Bd Gabriel, 21000 Dijon, France.

‡ Present address: Oak Ridge National Laboratory, Bldg. 4500S, MS-6119, PO Box 2008, Oak Ridge, TN 37831-6119, USA.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 1999

confirmed by the shift in band energy upon functionalizing the *para* position of the pyridine ring: incorporation of electron-withdrawing groups results in a red shift while electron-donating groups produce blue shifts.[14]

The hydridic character of the Re–H and the dodecahedral structure of this type of complex has been previously established.[6(c)] Moreover, it is easy to vary the ancillary pyridine group and look for any effect on the association constants and the strength of hydrogen bonding. As hydrogen bond donor we selected indole, since it has a strong UV band at 270 nm and its adduct with $\mathrm{ReH_5(PPh_3)_3}$ has been fully characterized. $\mathrm{ReH_5(PPh_3)_3}$ · indole shows an intermolecular N–H···H–M hydrogen bond with a *d*(H–H) of 1.73 Å by neutron diffraction.[2(d,e)] The aims of our UV-VIS study were to determine the K_as for the interaction in solution and the binding stoichiometry. $\mathrm{ReH_5(PPh_3)_2py}$ decomposes in $\mathrm{CH_2Cl_2}$ (1 h, 25 °C, at 2×10^{-4} M) so we used toluene, where a 10^{-4} M solution is stable during at least the 1.5 h required for the completion of our UV-titration experiments.

For a proton donor 'hydride', we selected the dicationic compound **5**, which can be readily prepared from $\mathrm{ReH_7(PPh_3)_2}$[15] and also shows an intense $M \rightarrow \pi^*$ MLCT band[16] in the UV-VIS spectrum, at 283 nm ($\varepsilon = 6.0 \times 10^3$ in $\mathrm{CH_2Cl_2}$). The hydrogen bond acceptors were pyridine, hexamethylenetetramine, 1-ethylpiperidine, tributylphosphine oxide and quinuclidine. In order to test the method, we also used triphenylphosphine oxide with indole, since the adduct is well known.[17] All the titrations for the **5**···base interaction were carried out in methylene chloride because **5** is stable in this solvent and therefore decomposition problems were not encountered.

UV-VIS spectroscopic studies

In order to determine the association constants for the interaction of the Re hydride acceptors with indole, we titrated a 10^{-5} M solution of indole in toluene with a 10^{-2} M toluene solution of $\mathrm{ReH_5(PPh_3)_2L}$ in the same concentration of indole, so that the total concentration of indole always remains fixed throughout the experiment. This gives data that can be analyzed in a straightforward fashion *via* a 1 : 1 binding isotherm[13] and non-linear regression analysis,[18] and also alleviates possible effects of competing equilibria involving self-association of indole.[19] The increase in the absorbance, *A*, of the 270 nm band of indole was monitored with increasing concentration of Re hydride and found to follow a saturation (binding curve) pattern (Fig. 1). As can be seen in Fig. 1, the indole absorbance increases almost seven-fold before reaching saturation, although its total concentration remains unchanged. The λ_{max} of the indole band, as well as the absorbance intensities and λ_{max} of the two $\mathrm{ReH_5(PPh_3)_2L}$ bands, were also monitored. Although the indole absorbance followed the binding curve model, the λ_{max} of the indole band remained unchanged throughout the experiment, suggesting that there is practically no competition effect in the equilibrium from indole self-association (a process that has been shown to affect the λ_{max}),[19] and that the total concentration of monomer indole had indeed remained approximately constant. This observation validates our experimental approach.

The absorbance of the $\mathrm{ReH_5(PPh_3)_2L}$ bands at 437 and 360 nm showed a linear dependence with total Re hydride concentration over the whole concentration range from 10^{-5} to 10^{-3} M, following the Lambert–Beer law (Fig. 2), suggesting that $\mathrm{ReH_5(PPh_3)_2L}$ and the $\mathrm{ReH_5(PPh_3)_2L}$···indole complex have identical or very similar extinction coefficients (ε).

Monitoring the λ_{max} of the $\mathrm{ReH_5(PPh_3)_2py}$ MLCT band showed a small linear λ_{max} shift with total $\mathrm{ReH_5(PPh_3)_2py}$ concentration up to the point where $[\mathrm{indole}]_t = [\mathrm{ReH_5(PPh_3)_2py}]_t$ (Fig. 3). Thereafter the λ_{max} remained unchanged during the rest of the experiment. This is indicative of a 1 : 1 indole–$\mathrm{ReH_5(PPh_3)_2py}$ complexation stoichiometry. Running the experiment in the opposite fashion, keeping $[\mathrm{ReH_5(PPh_3)_2L}]_t$ fixed and varying $[\mathrm{indole}]_t$, gave a linearly increasing shift of λ_{max} with $[\mathrm{indole}]_t$ for the MLCT band at 437 nm, but showing an initial curvature. However, this does not give any useful binding data because of the competing indole association. By keeping $[\mathrm{indole}]_t$ fixed, we avoid any significant effect from competing indole self-association, pro-

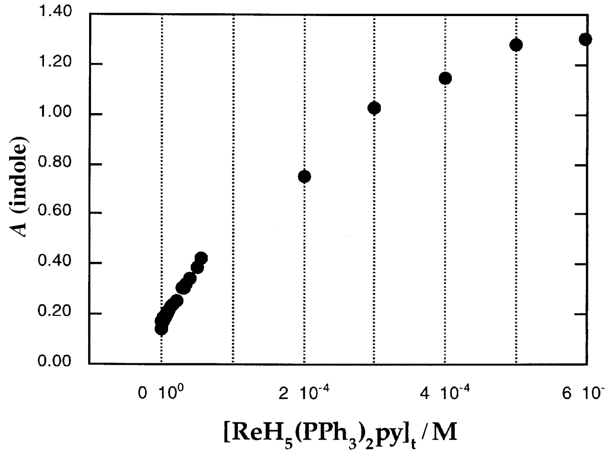

Fig. 1 Plot of A_{indole} *vs.* $[\mathrm{ReH_5(PPh_3)_2py}]_t$ concentration. The total concentration of indole remains unchanged throughout the experiment.

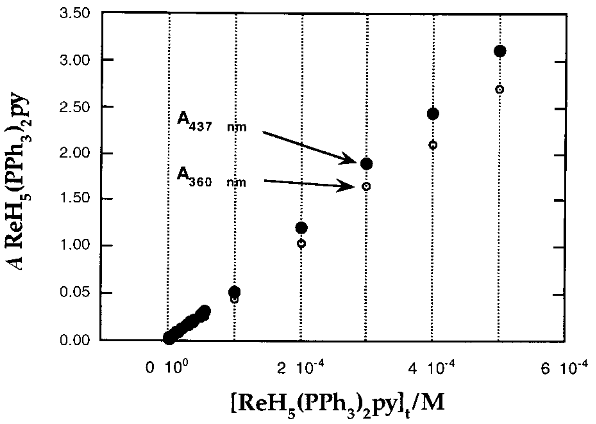

Fig. 2 Plot of the absorbance of $\mathrm{ReH_5(PPh_3)_2py}$ *vs.* its total concentration during the titration experiment, indicating Beer law behavior.

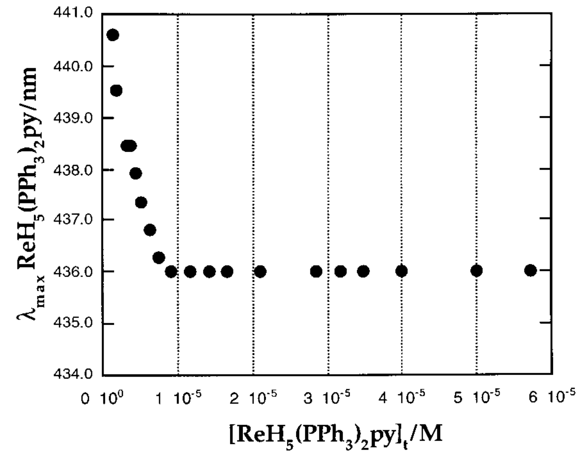

Fig. 3 Plot of λ_{max} for $\mathrm{ReH_5(PPh_3)_2py}$ *vs.* its total concentration $[\mathrm{ReH_5(PPh_3)_2py}]_t$. The total concentration of indole is fixed at 1×10^{-5} M. The inflection point at 1×10^{-5} M (mole ratio = 1 : 1) indicates 1 : 1 binding.

viding that $ReH_5(PPh_3)_2L$ does not self-associate. A control experiment proved that this was indeed the case for $ReH_5(PPh_3)_2py$ in toluene; only a small linear change in λ_{max} was seen and the expected linear Beer law behavior on the absorbances of the bands was observed.

Association constants were estimated at 25 °C from non-linear regression fitting of the A_{indole} *vs.* $[ReH_5(PPh_3)_2L]$ binding curves (Fig. 1) for complexes **1**–**4**. Eqn. (2) used for the fitting was directly obtained from the 1 : 1 binding isotherm.[18] A linear correction factor c was incorporated in order to account for the overlapping absorbance of $ReH_5(PPh_3)_2L$ in the indole region.

$$\begin{aligned} A_{obs} = A^{\circ}_{ind.} &+ \{([\text{indole}]_t + [ReH_5(PPh_3)_2L] \\ &+ 1/K - (([\text{indole}]_t \\ &+ [ReH_5(PPh_3)_2L] + 1/K)^2 \\ &- 4[ReH_5(PPh_3)_2L][\text{indole}]_t)^{1/2}\} \\ &\times \Delta A_{max}/(2[\text{indole}]_t) \\ &+ c[ReH_5(PPh_3)_2L] \end{aligned} \qquad (2)$$

The estimated association constants for the various Re hydride complexes, shown in Table 1, lead to two main conclusions.

First, the Re–H···H–X interaction between indole and the neutral $ReH_5(PPh_3)_2L$ complexes is significant in toluene. Although we did not carry out a variable temperature study in order to calculate the ΔS and ΔH of interaction, we find a reasonably good agreement between the values obtained for ΔG (Table 1) and the values obtained from theoretical calculations for ΔH for similar systems (20–30 kJ mol^{-1}),[1(a,d),20] especially considering that such interactions often have an unfavorable entropic term. The empirical Iogansen equation applied from thin film IR data for $ReH_5(PPh_3)_2py \cdot$indole (**1** · indole) and $ReH_5(PPh_3)_3 \cdot$indole gives values of − 18.3 and − 15.0 kJ mol^{-1} for the ΔH of interaction, respectively.[1(d,e),21] Second, the nature of the pyridine ligand has an effect on the hydrogen bond strength and the K_a. Unexpectedly, pyridines with electron-withdrawing groups give a stronger interaction with indole. It is possible that aromatic stacking and charge transfer interactions[22]—stronger between indole and pyridines with electron-withdrawing groups—might contribute to the overall interaction. Unfortunately, we have been unable to obtain any structural data to test this point. Examination of models indicate that the strongly bent structural preference found[1(a,b)] for the M–H···H–N interaction would certainly permit the indole to hydrogen bond to ReH and also pi-stack with the pyridine ligand.

To determine the number of indole molecules involved, we used a UV-VIS continuous variation method (Job plot). These experiments were carried out in a toluene solution ($c = 0$ to 10^{-4} M^{-1}) prepared from $[ReH_5(PPh_3)_2py]$ and indole solutions. The Job plots of $[ReH_5(PPh_3)_2py \cdot \text{indole}]$ *vs.* mole fraction gave us maxima for a mole fraction of (or near) 0.5, corresponding to a 1 : 1 binding stoichiometry (Fig. 4) as in the crystal.[1] For the complex of $ReH_5(PPh_3)_2py$ with indole, the mole fraction was defined as:

$$\text{mole fraction} = \frac{[ReH_5(PPh_3)_2\,py]_t}{[ReH_5(PPh_3)_2\,py]_t + [\text{indole}]_t} \qquad (3)$$

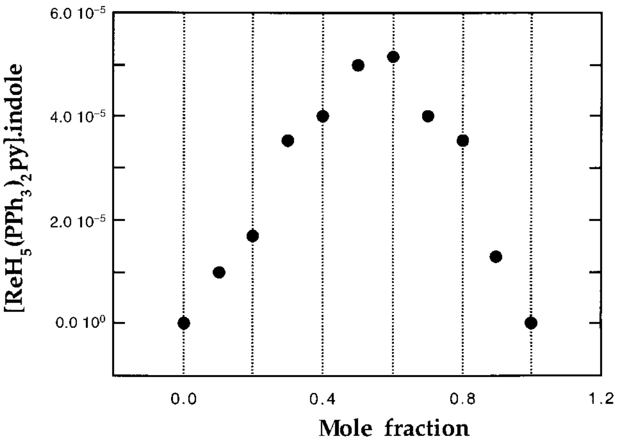

Fig. 4 Job plot for $ReH_5(PPh_3)_2py \cdot$indole, indicating 1 : 1 binding stoichiometry. Mole fraction is defined in eqn. (3).

Table 1 Interaction between indole and the neutral rhenium hydrides

$ReH_5(PPh_3)_2L$	K_a/M^{-1} [a]	$-\Delta G$/kJ mol^{-1}
$[ReH_5(PPh_3)_2(4\text{-}NMe_2\text{-}py)]$	700 ± 250	16
$[ReH_5(PPh_3)_2(4\text{-}Me\text{-}py)]$	780 ± 80	16
$[ReH_5(PPh_3)_2(py)]$	5000 ± 1300	21
$[ReH_5(PPh_3)_2(4\text{-}CO_2Me\text{-}py)]$	5500 ± 1000	21

[a] Reported errors were determined from the curve fitting.

The Job plots suggest the presence of one indole molecule in the outer sphere complex, possibly coordinated *via* two Re–H···H–N hydrogen bonds as indicated in the neutron study of $ReH_5(PPh_3)_3 \cdot$indole.[1(d,e)]

Re–H···base interactions

These interactions were also studied by a similar UV-VIS titration experiment monitoring the intensity of the Re complex absorbance and keeping its total concentration fixed (10^{-5} M) while adding a progressively larger amount of base (up to 0.1 M). For this experiment, it was necessary to avoid superimposed bands from the complex and the base so we avoided aromatic bases. With pyridine, for example, it was not possible to obtain reliable titration values because of overlapping, so we moved to aliphatic bases: hexamethyltetramine N-ethyl piperidine, quinuclidine and n-Bu_3PO.

The titration curves were very similar to those obtained for the hydridic hydride $ReH_5(PPh_3)_2py$–indole case. The absorbance of the Re complex band increased with the addition of base although the total Re concentration was kept fixed at 10^{-5} M. Plotting the absorbance of $[Re(PPh_3)_2(MeCN)_4H][BF_4]_2$ **5** *vs.* $[\text{base}]_t$ gave a binding curve, which was fitted using eqn. (4), a modification of eqn. (2) suitable for this experiment:

$$\begin{aligned} A_{obs} = A^{\circ}(\mathbf{5}) &+ \{[\mathbf{5}] + [\text{base}]_t + 1/K - (([\text{base}]_t \\ &+ [\mathbf{5}] + 1/K)^2 - 4[\text{base}]_t[\mathbf{5}])^{1/2}\} \\ &\times \Delta A_{max}/(2 \times [\mathbf{5}]) \end{aligned} \qquad (4)$$

The association constants for the $A\text{–}H^{\delta+}\cdots$base interaction for the different bases are given in Table 2. The values obtained show that the Re–H···base hydrogen bonding is much weaker, at least in this case, than the Re–H···H–N

Table 2 Interaction between $[Re(PPh_3)_2(MeCN)_4H][BF_4]_2$ **5** and various bases

Base	K/M^{-1} [a]	$-\Delta G$/kJ mol^{-1}
Hexamethylenetetramine	80.3 ± 15.6	11
1-Ethylpiperidine	1.23 ± 0.03	0.5
Tributylphosphine oxide	1.24 ± 0.11	0.5
Quinuclidine	1.79 ± 0.06	1.4

[a] Reported errors were determined from the curve fitting.

hydrogen bond. This is in agreement with previous IR studies from our group on cationic Ir metal hydrides.[5] Hexamethylenetetramine is the only base that gives relatively high association constants, perhaps due to its high basicity and low steric hindrance. No crystals for structural study could be isolated for any of the adducts of the cationic hydride with bases, perhaps because of the weak interaction.

Conclusion

We have used UV-VIS spectroscopy to characterize hydrogen bonding interactions in solution for Re hydride complexes related to the example for which neutron diffraction characterization of the indole adduct has been obtained.[1] For these Re–H···H–N systems we found association constants K_a that correspond to a significant interaction, and which are also dependent on the nature of the ancillary pyridine ligand. The values obtained are in good agreement with previous estimates and theoretical calculations. The binding stoichiometry was found to be 1 : 1 for the $ReH_5(PPh_3)_2(py)\cdots$indole case. For the Re–$H^{\delta+}\cdots$base hydrogen bond, much smaller association constants were obtained, indicating that this is a much weaker interaction and the structures involved are uncertain.

Experimental

All syntheses were carried out under an inert N_2 atmosphere using standard Schlenk techniques. The neutral and cationic Re hydrides were prepared according to the procedures[14] previously described. All starting materials were purchased from Aldrich Chemical Co. or Strem Chemicals and were used without further purification. All solvents used for UV measurements were either spectroscopic grade or freshly distilled immediately before used. UV-VIS absorption spectra were obtained on a Cary 3E spectrophotometer, with a thermostatted cell compartment. All the measurements were carried out in the solute concentration range 1×10^{-5}–0.5 M. NMR experiments were run on a GE Omega 300 spectrometer. IR experiments were carried out on a MIDAC 1200 FT-IR spectrometer.

UV-VIS titrations

In a typical experiment a stock solution of 10^{-3} M indole was prepared in toluene. Then 1.00 mL of this solution was diluted to 100 mL, resulting in a stock solution of indole with $c = 10^{-5}$ M (solution A). A solution of 10^{-2} M $ReH_5(PPh_3)_2py$ and 10^{-5} M indole (solution B) was prepared by weighing 40.3 mg of $ReH_5(PPh_3)_2py$ in a 5.00 mL volumetric flask and diluting with solution A. Solution A (1.500 mL) was put in a UV-VIS cell and subsequently titrated with increasing amounts of solution B using a microlitre syringe and the UV-VIS spectra were recorded. In most cases it was necessary to use solution B itself and solutions derived from it (always using solution A for dilutions) in order to obtain the end points of the titrations, individually.

Titration data analysis

Non-linear regression analysis was carried out on the saturation curves using the 1 : 1 binding model isotherm equation[18] *via* computer iteration,[23] using eqn. (2) and (4). This equation, obtained directly from the 1 : 1 binding isotherm,[13,18] requires a fixed $[\text{indole}]_t$ in order to provide accurate data fitting for K_a determination.

Continuous variation method (Job plot)[18]

To determine the number of indole molecules involved in outer sphere coordination of transition metal hydride complexes, we used a UV-VIS continuous variation method (Job plot). These experiments were carried out in a toluene solution ($C = 0$ to 10^{-4} M^{-1}) prepared from $(10 - x)$ mL of a 10^{-4} M $ReH_5(PPh_3)_2py$ solution and x mL of a 10^{-4} M indole solution with $0 < x < 10$. Plotting the concentration of $[ReH_5(PPh_3)_2py \cdot (\text{indole})_n]$ *vs.* the mole fractions of indole or total $[ReH_5(PPh_3)_2py]_t$ [as defined in eqn. (3)] gave us a bell-shaped curve with maximum around 0.5.

Acknowledgements

P.D. thanks the CNRS, and R.H.C. and K.K. thank the National Science Foundation for funding. We also thank Ben Patel for some preliminary results in this area.

References

1 (*a*) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold and T. F. Koetzle, *Acc. Chem. Res.*, 1996, **29**, 348. (*b*) J. C. Lee, Jr., E. Peris, A. L. Rheingold and R. H. Crabtree, *J. Am. Chem. Soc.*, 1994, **116**, 11014. (*c*) E. Peris, J. C. Lee, Jr., J. R. Rambo, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 3485. (*d*) J. Wessel, J. C. Lee, Jr., E. Peris, G. P. A. Yap, J. B. Fortin, J. S. Ricci, G. Sini, A. Albinati, T. F. Koetzle, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2507. (*e*) B. Patel, J. Wessel, W. Yao, J. C. Lee, Jr., E. Peris, G. P. A. Yap, J. B. Fortin, J. S. Ricci, G. Sini, A. Albinati, T. F. Koetzle, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *New J. Chem.*, 1997, **21**, 413. (*f*) B. P. Patel, W. Yao, G. P. A. Yap, A. L. Rheingold and R. H. Crabtree, *Chem. Commun.*, 1996, 991. (*g*) A. J. Lough, S. Park, R. Ramachandran and R. H. Morris, *J. Am. Chem. Soc.*, 1994, **116**, 8356. (*h*) R. Ramachandran and R. H. Morris, *J. Chem. Soc., Chem. Commun.*, 1994, 2201.

2 L. M. Epstein, E. S. Shubina, A. N. Krylov, A. Z. Kreindlin and M. I. Rybinskaia, *J. Organomet. Chem.*, 1993, **447**, 277.

3 (*a*) R. M. Bullock, J.-S. Song and D. J. Szalda, *Organometallics*, 1996, **15**, 2504. (*b*) S. A. Fairhurst, R. A. Henderson, D. L. Hughes, S. K. Ibrahim and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1995, 1569.

4 (*a*) D. Braga, F. Grepioni, E. Tedesco, K. Biradha and G. R. Desiraju, *Organometallics*, 1996, **15**, 2692. (*b*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.

5 E. Peris and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1995, 2179.

6 (*a*) W. Yao and R. H. Crabtree, *Inorg. Chem.*, 1996, **35**, 3007. (*b*) B. P. Patel, K. Kavallieratos and R. H. Crabtree, *J. Organomet.* J *Chem.*, 1997, **28**, 205. (*c*) R. Bosque, F. Maseras, O. Eisenstein, B. P. Patel, W. Yao and R. H. Crabtree, *Inorg. Chem.*, 1997, **24**, 5505.

7 (*a*) E. S. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann and H. Berke, *J. Am. Chem. Soc.*, 1996, **118**, 1105. (*b*) Y. Guari, J. A. Ayllon, S. Sabo-Etienne, B. Chaudret and B. Hessen, *Inorg. Chem.*, 1998, **37**, 640.

8 A. V. Iogansen, G. A. Kurkchi, V. M. Furman, V. P. Glazunov and S. E. Odinokov, *Zh. Prikl. Spektrosk.*, 1980, **33**, 460.

9 S. G. Kazarian, P. A. Hamley and M. Poliakoff, *Chem. Commun.*, 1996, 991.

10 (*a*) P. Haberfield, *J. Am. Chem. Soc.*, 1974, **96**, 6526. (*b*) P. R. Taylor, *J. Am. Chem. Soc.*, 1982, **104**, 5248. (*c*) S. E. DeBolt and P. A. Kollman, *J. Am. Chem. Soc.*, 1990, **112**, 7515. (*d*) M. Karelson and M. C. Zerner, *J. Am. Chem. Soc.*, 1990, **112**, 9405. (*e*) T. Fox and N. Roesch, *Chem. Phys. Lett.*, 1992, **191**, 33. (*f*) C. Lerf and P. Suppan, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 963.

11 (*a*) M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377. (*b*) M. J. Kamlet, R. R. Minesinger and W. H. Gilligan, *J. Am. Chem. Soc.*, 1972, **94**, 4744. (*c*) R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2887. (*d*) J. C. Curtis, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 224. (*e*) N. Kitamura, M. Sato, H.-B. Kim, R. Obata and S. Tazuke, *Inorg. Chem.*, 1988, **27**, 651.

12 B. P. Patel, P. Tan, B. J. Pistorio, W. Yao and R. H. Crabtree, *New J. Chem.*, 1997, **21**, 131.

13 (*a*) D. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4044. (*b*) D. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4050.

14 (*a*) J. C. Lee, Jr., W. Yao, R. H. Crabtree and H. Rüegger, *Inorg. Chem.*, 1996, **35**, 695. (*b*) R. H. Crabtree, G. G. Hlatky, C. A. Parnell, B. E. Segmuller and R. J. Uriarte, *Inorg. Chem.*, 1984, **23**, 354. (*c*) R. H. Crabtree, G. G. Hlatky and E. M. Holt, *Inorg. Chim. Acta*, 1987, **130**, 5.

15 J. D. Allison, G. A. Moehring and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 1986, 67.

16 (*a*) R. R. Ruminski and D. Lehmpuhl, *Inorg. Chim. Acta*, 1993, **204**, 45. (*b*) R. S. da Silva and E. Tfouni, *Inorg. Chem.*, 1992, **31**, 3313.

17 (*a*) M. H. Abraham, P. L. Grellier, D. V. Prior, R. W. Taft, J. J. Morris, P. J. Taylor, C. Laurence, M. Berthelot, R. M. Doherty, M. J. Kamlet, J. L. Abboud, K. Sraidi and G. Guihéneuf, *J. Am. Chem. Soc.* 1988, **110**, 8534. (*b*) P. Ruostesuo, U. Salminen and R. Liias, *Spectrochim. Acta*, *Part A*, 1987, **43**, 1135.

18 K. A. Connors, *Binding Constants*, John Wiley & Sons, New York, 1st edn., 1987.

19 (*a*) K. Kavallieratos, P. Desmurs and R. H. Crabtree, unpublished data. (b) E. H. Strickland, C. Billups and E. Kay, *Biochemistry*, 1972, **11**, 3657. (*c*) M. J. Tubergen and D. H. Levy, *J. Phys. Chem.*, 1991, **95**, 2175.

20 G. Sini, O. Eisenstein, W. Yao and R. H. Crabtree, *Inorg. Chim. Acta*, 1998, **280**, 26.

21 W. Yao, Ph. D. Thesis, Yale University, 1997.

22 (*a*) R. Foster, *Organic Charge Transfer Complexes*, Academic Press, New York, 1969. (*b*) V. Gutmann, *The Donor Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978. (*c*) U. M. Rabie, B. P. Patel, R. H. Crabtree and M. R. Mahmoud, *Inorg. Chem.*, 1997, **36**, 2236 and references cited therein.

23 KaleidaGraph, Version 3.0.2., Synergy Software (PCS Inc.), Reading, PA 19606. Developed by Abelbeck Software Inc.

Paper 9/06854F