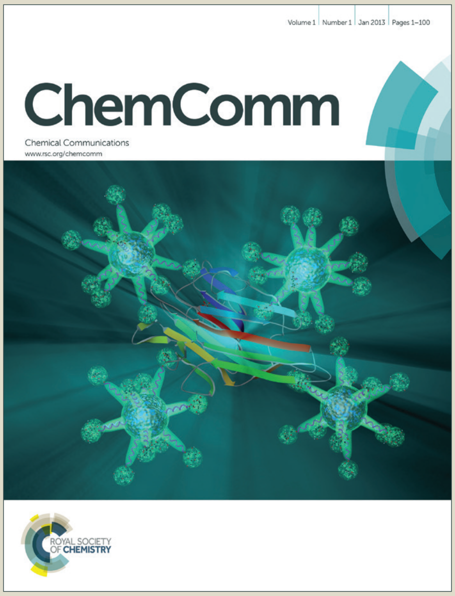
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

RSCPublishing

COMMUNICATION

Dehydrogenation of a Tertiary Amine-Borane by a Rhenium Complex

Cite this: DOI: 10.1039/x0xx00000x

Sohail Muhammad,[a] Salvador Moncho,[a] Edward N. Brothers,[a] Ashfaq A. Bengali*,[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Photolysis of $CpRe(CO)_3$ in the presence of H_3BNEt_3 yields the *trans*-$CpRe(CO)_2(H)_2$ complex. This preliminary finding presents a rare example of transition metal mediated dehydrogenation of a tertiary amine-borane and suggests that the abstracted hydrogens may be stored in the form of metal hydride complexes.

Amine-boranes ($H_3BNH_nR_{3-n}$; R=H, alkyl, aryl) are widely used as reducing and hydroboration reagents.[1] Due to their high volumetric and gravimetric hydrogen content, these molecules have been extensively explored as portable hydrogen source and storage materials.[2] In this context, B–H activation by transition metals is an area of active research as it provides an appealing method to release not only hydrogen from amine-boranes (dehydrogenation) but also obtain useful B-N polymeric materials at moderate temperatures and reasonable rates.[2e,2f,3]

Early work by Shimoi *et al.* demonstrated the binding of amine-boranes to electrophilic metal centers through an η^1 M-H-B interaction.[3e,4] Unlike the analogous weak M-H-C interactions with alkanes, these bonds were found to be surprisingly stable and several such complexes have been isolated and characterized.[5] Complexes of this type have been implicated in a variety of transition metal catalyzed dehydrocoupling reactions of amine-boranes. Pioneering studies by Manners,[6] Weller,[7] Alcaraz,[8] and Sabo-Etienne[9] have led to the identification of a number of catalytic systems for dehydrogenation of boranes. Several important intermediate species have been identified and isolated to assist in the determination of the dehydrocoupling mechanism. It is to be noted however that transition metal assisted dehydrogenation reactions, whether through hydrogen release or the formation of metal hydride complexes have been reported mostly in the case of primary or secondary amine-boranes. That is, the presence of hydrogen on the nitrogen atom appears to be important for this type of reactivity.

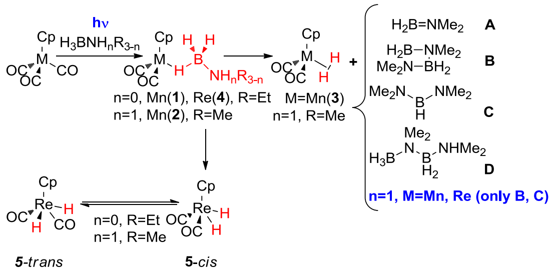


Figure 1. Photolysis of $CpM(CO)_3$ (M=Mn, Re) in the presence of amine-boranes $H_3BNH_nR_{3-n}$ (R=Me, Et).

Building on recent studies[3e,5d,6a,10] we were interested in using fast time resolved FTIR spectroscopy to identify intermediates in the photoinduced dehydrogenative coupling of amine-boranes by transition metal complexes. Previously, we determined the M-H-B binding enthalpy in the $BzCr(CO)_2(\eta^1\text{-}H_3BNEt_3)$ [Bz = $\eta^6\text{-}C_6H_6$] and $TpMn(CO)_2(\eta^1\text{-}H_3BNEt_3)$ [Tp = trispyrazolylborate] complexes which form upon photolysis of the parent tricarbonyls in the presence of H_3BNEt_3.[10a] As described in the present work, we were surprised to find that while photolysis of $CpMn(CO)_3$ in the presence of H_3BNEt_3 formed only $CpMn(CO)_2(\eta^1\text{-}H_3BNEt_3)$, the analogous reaction with $CpRe(CO)_3$ yielded facile generation of the rhenium dihydride complex at room temperature. To our knowledge, this study presents a rare example[7e] of the dehydrogenation of a tertiary amine-borane by a non-hydride containing transition metal complex. Herein we report preliminary findings of the reactions following photolysis of $CpMn(CO)_3$ and $CpRe(CO)_3$ in the presence H_3BNEt_3 and H_3BNHMe_2 (Figure 1).

Single shot photolysis of $CpMn(CO)_3$ with 355 nm light from a Nd:YAG laser in the presence of H_3BNEt_3 results in CO loss and yields the previously observed $CpMn(CO)_2(\eta^1\text{-}H_3BNEt_3)$ (**1**) complex absorbing at 1931 cm^{-1} and 1863 cm^{-1}.[4a,10d] Consistent with DFT calculations[11] which predict a 24.7 kcal/mol Mn-H-B bond dissociation enthalpy (BDE) (Table

S1), the IR signatures of this complex persist for several minutes at room temperature with no further reaction being observed (Table S2). Photolysis of $CpMn(CO)_3$ in the presence of the secondary amine-borane, H_3BNHMe_2, also results in the initial formation of the analogous Mn-H-B complex, $CpMn(CO)_2(\eta^1\text{-}H_3BNHMe_2)$ (**2**) absorbing at 1927 cm^{-1} and 1854 cm^{-1}.[10d] However, unlike **1**, it decays after a short induction period and a new dicarbonyl species with CO bands at 1985 cm^{-1} and 1924 cm^{-1} grows in at the same rate (Figure 2). Based on the identical CO band positions, this complex is assigned as the dihydrogen complex, $CpMn(CO)_2(\eta^2\text{-}H_2)$ (**3**) which has been observed before upon photolysis of $CpMn(CO)_3$ in the presence of H_2.[12] These spectroscopic results, along with visual observation of gas bubbles following photolysis of a methylcyclohexane solution of $CpMn(CO)_3$ with added H_3BNHMe_2 provide clear evidence of metal catalyzed dehydrogenation of an amine-borane.[10d] It is likely that the Mn center catalyzes H_2 production and residual $CpMn(CO)_2$ generated during the course of the reaction acts as an H_2 trap to yield **3**. By comparison with existing data,[10d] the boron containing products identified by ^{11}B NMR are shown in Figure 1. As mentioned earlier, these results are not surprising since several other instances are known where H_2 evolution is observed upon either thermal or photochemical activation of primary or secondary amine-boranes by organometallic complexes.[6a, 6d, 7g, 9b, 9c, 10d]

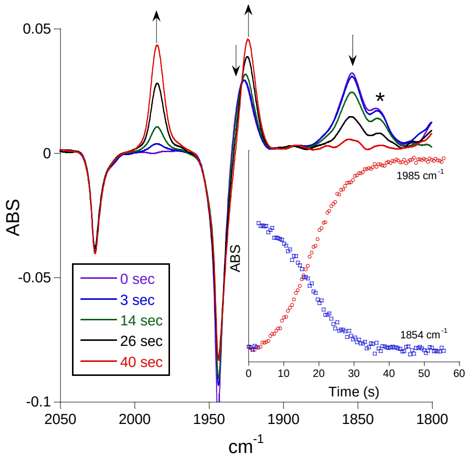


Figure 2. Difference FTIR spectra obtained upon photolysis of a methylcyclohexane solution of 0.6 mM $CpMn(CO)_3$ with 30 mM H_3BNHMe_2 at 293 K. The peak marked with an asterisk has not been assigned. Inset shows the temporal behaviour of species **2** and **3**.

Photolysis of a heptane solution of $CpRe(CO)_3$ with 266 nm light from a Nd:YAG laser in the presence of the tertiary amine-borane, H_3BNEt_3 initially results in the formation of the $CpRe(CO)_2$(heptane) complex.[13] This solvated species with CO stretching absorbances at 1949 cm^{-1} and 1884 cm^{-1} reacts with borane to form a dicarbonyl complex with CO bands at 1925 cm^{-1} and 1856 cm^{-1} (Figure S1). By comparison with the Mn system, this initial species is identified as the $CpRe(CO)_2(\eta^1\text{-}H_3BNEt_3)$ complex (**4**). DFT calculations (Figure S2) predict that the borane binds strongly to the Re center with a Re-H-B BDE of 36.1 kcal/mol, almost 10 kcal/mol stronger than for the analogous Mn complex (Table S1). In dramatic contrast to the Mn system however, this initially formed complex decays within 30 seconds at room temperature to generate an intermediate dicarbonyl species (**5**-*cis*) absorbing at 2008 and ≈ 1940 cm^{-1} which converts to a final dicarbonyl complex (**5**-*trans*) with CO bands at 2024 cm^{-1} and 1956 cm^{-1} (Figure 3 and Figure S3).[14]

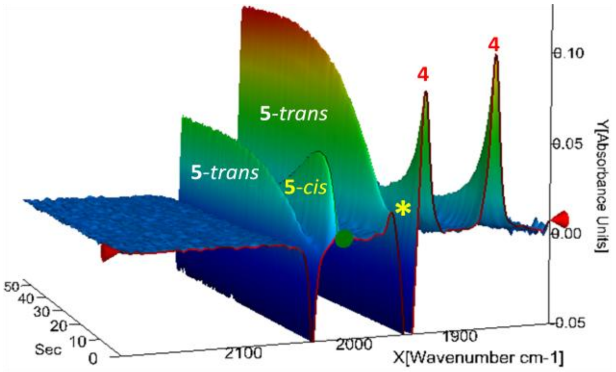
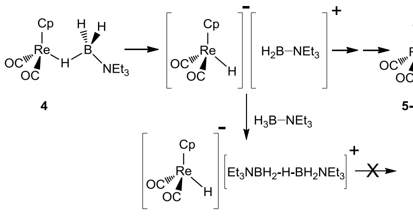


Figure 3. Spectral changes observed at 298 K upon 266 nm photolysis of a 5 mM solution of $CpRe(CO)_3$ in heptane with 40 mM H_3BNEt_3 added. Peak marked * is the second CO band of **5**-*cis* but is obscured by the parent $CpRe(CO)_3$ absorbance. The spectra are consistent with the chemical reaction: **4** → **5**-*cis* → **5**-*trans*.

By comparison with the position of the CO stretching bands of the previously characterized rhenium dihydride complexes (Table S2), intermediate **5**-*cis* is identified as *cis*-$CpRe(CO)_2(H)_2$ while the final complex **5**-*trans* as *trans*-$CpRe(CO)_2(H)_2$.[12,15] The presence of rhenium hydrides and the conversion of the *cis* to the *trans* isomer was also confirmed by NMR spectroscopy. The ^1H NMR spectrum in toluene-d_8 following photolysis of $CpRe(CO)_3$ in the presence of H_3BNEt_3 showed metal-hydride resonances at δ -8.28 and δ -9.50 for **5**-*cis* and **5**-*trans*, respectively.[15] The initial isomeric mixture yielded an equilibrium *cis*:*trans* distribution of 5:95 at 293 K (Figure S4). Previously, Casey *et al.*[15] have also reported a similar equilibrium distribution of the isomers and DFT calculations find that the *trans* isomer is favored over the *cis* form by only $\Delta G°_{298K} = 2.9$ kcal/mol (Figure S5).

Similar results were obtained with the boranes H_3BNMe_3 and H_3BPMe_3 and use of the $Cp^*Re(CO)_3$ [$Cp^* = \eta^5\text{-}C_5Me_5$] and ($\eta^5$-indenyl)$Re(CO)_3$ (indenyl = C_9H_7) complexes also yielded comparable spectroscopic features and rates. Taken together, these results indicate that photolytic dehydrogenation of H_3BNEt_3 is mediated by the rhenium center and it is reasonable to conclude that the borane is the hydrogen source for the formation of the rhenium hydride complexes. A key issue is whether H_2 gas is generated in the reaction mixture which then reacts with the Re complex to form the dihydride or whether the dihydride forms from a metal mediated mechanism that does not involve prior H_2 formation. We favor the latter scenario for the following reasons. There is strong precedence that a H on the nitrogen atom of the amine-borane is required for H_2 gas evolution in transition metal catalyzed dehydrogenations.[6a,6d,7g,9b,9c,10b,10d] Indeed, there is clear visual evidence for gas generation upon photolysis of $CpRe(CO)_3$ in the presence of H_3BNHMe_2 whereas no gas bubbles are observed with H_3BNEt_3. In both cases however, the rhenium dihydride species forms. Furthermore, with H_3BNHMe_2, the major boron containing species identified by ^{11}B NMR are identical to those observed in the case of the manganese system which clearly proceeds by H_2 gas evolution (Figure S6). By contrast, dehydrogenation of H_3BNEt_3 by $CpRe(CO)_3$ does not yield any boron complexes that could be identified by ^{11}B NMR spectroscopy.[16] This observation suggests that compared to the secondary amine-borane, the mechanism of borane activation is quite different in the case of H_3BNEt_3. It is therefore likely the metal dihydride is formed from H_3BNEt_3 by a metal mediated mechanism that does not involve H_2 gas generation. Finally, while H_2 gas was identified in the ^1H NMR spectrum of the solution after photolysis of $CpM(CO)_3$ (M = Mn and Re) with H_3BNHMe_2, it was not detected when the rhenium complex was photolyzed with H_3BNEt_3.[17]

Elucidation of the reaction mechanism presents a challenge. The decay of **4** exhibits biphasic exponential behavior with a fast component followed by a slower decay. This temporal behavior provides clear evidence that the reaction does not proceed by a first order mechanism. The reaction rate also appears to be inhibited by $[H_3BNEt_3]$. For example, increasing the concentration of amine-borane from 0.04 M to 0.14 M results in an almost four fold decrease in the decay rate constant of **4** (Figure S7). This observation may suggest that free H_3BNEt_3 stabilizes or removes a reactive intermediate in the reaction thereby slowing down the rate. Based upon the temperature dependence of the decay rates at 285 K and 298 K, we estimate an activation enthalpy of ≈ 20 kcal/mol for the formation of **5-*trans*** from **4**. Similar to the experimental activation enthalpy, DFT calculations predict an enthalpic barrier of 24 kcal/mol for the *cis* → *trans* isomerization (Figure S5) indicating that the mechanistic steps leading to the formation of the *cis* dihydride proceed with activation barriers less than 20-24 kcal/mol. Since DFT calculations predict that the Re-H-B BDE in **4** is 36.1 kcal/mol, the reaction mechanism does not involve the dissociation of the Re-H-B bond once it forms.



Scheme 1. Tentatively proposed early steps in the reaction

Several attempts were made to ascertain the complete mechanism of the reaction, yet they were unsuccessful since DFT calculations always yielded barrier heights greater than 20 kcal/mol for the elementary steps. However, with prior precedence supported by DFT modeling, early steps in the reaction may be tentatively proposed. Borane triethylamine in its reaction with electrophiles can act as a hydride donor.[18] Thus, after initial formation of **4**, the first step may be hydride abstraction from the borane to form $[CpRe(CO)_2H]^-$ and the borenium cation $[H_2B\text{-}NEt_3]^+$. Of the two ions, the Re species has been isolated and characterized whereas strong evidence exists for the intermediacy of the borenium species in a number of hydride transfer reactions.[18b,19] It has been further reported that $[H_2B\text{-}NEt_3]^+$ may be stabilized by free H_3BNEt_3 to form the hydro-bridged dimer $[Et_3NBH_2\text{-}H\text{-}BH_2NEt_3]^+$ which has been observed by NMR at 253 K in CD_2Cl_2 solution.[18a] This initial sequence of reactions (Scheme 1) is supported by DFT modeling which predicts that the ion pair $[CpRe(CO)_2H][H(BH_2NEt_3)_2]$ lies only 10.5 kcal/mol higher in enthalpy than **4** (Figure S8). The inverse dependence on $[H_3BNEt_3]$ may then be explained since dimerization would effectively trap the borenium cation and prevent further reaction. The steps leading to the transfer of a second hydrogen to the Re center to form **5-*cis*** remain unidentified and we are working towards determining the complete mechanism of the reaction.

The results described in this study suggest that transition metal promoted dehydrogenation of tertiary amine boranes is possible and that the abstracted hydrogens may be stored in the form of metal hydride complexes. Additionally, since metal hydrides have been used as synthons in several significant catalytic and stoichiometric reactions,[2g,20] the current findings demonstrate a method to generate metal hydrides without the use of H_2.

This publication was made possible by funding from the Qatar National Research Fund (member of Qatar Foundation). The experimental work was supported by NPRP award 6-1184-1-224 and the theoretical studies by NPRP award 09-143-1-022. The statements made herein are solely the responsibility of the authors.

Notes and references

[a] Department of Chemistry, Texas A&M University at Qatar, Doha, Qatar.

†Electronic Supplementary Information (ESI) available: Experimental and computational details, additional spectra, kinetic traces, calculated structures, energies, and CO band positions. See DOI: 10.1039/c000000x/

1. a) G. Bartoli, M. Bartolacci, A. Giuliani, E. Marcantoni and M. Massaccesi, *Eu. J. Org. Chem.*, 2005, **2005**, 2867-2879; b) O. T. Beachley and B. Washburn, *Inorg. Chem.*, 1975, **14**, 120-123; c) J. F. Hartwig, *Acc. Chem. Res.*, 2011, **45**, 864-873; d) F. Hartwig John, in *Activation and Functionalization of C-H Bonds*, ACS Symposium Series, **2004**, pp. 136-154; e) R. O. Hutchins, K. Learn, B. Nazer, D. Pytlewski and A. Pelter, *Org. Prep. Procedur. Int.*, 1984, **16**, 335-372; f) J. V. Kanth, *ChemInform*, 2003, **34**; g) C. F. Lane, *Chem. Rev.*, 1976, **76**, 773-799; h) L. Pasumansky, C. T. Goralski and B. Singaram, *Org. Proc. Res. Dev.*, 2006, **10**, 959-970; i) Z. A. Sergueeva, D. S. Sergueev and B. R. Shaw, *Nucleosides, nucleotides & nucleic acids*, 2000, **19**, 275-282; j) A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, *Chem. Rev.*, 2010, **110**, 4023-4078.
2. a) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 14034-14035; b) T. J. Clark, G. R. Whittell and I. Manners, *Inorg. Chem.*, 2007, **46**, 7522-7527; c) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048-12049; d) R. J.

Keaton, J. M. Blacquiere and R. T. Baker, *J. Am. Chem. Soc.*, 2007, **129**, 1844-1845; e) T. B. Marder, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 8116-8118; f) F. H. Stephens, V. Pons and R. Tom Baker, *Dalton Trans.*, 2007, **0**, 2613-2626; g) W. Grochala and P. P. Edwards, *Chem. Rev.*, 2004, **104**, 1283-1316; h) M. E. Bluhm, M. G. Bradley, R. Butterick, U. Kusari and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 7748-7749.

3. a) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey and J. C. Linehan, *Inorg. Chem.*, 2008, **47**, 8583-8585; b) J. Graetz, *Chem. Soc. Rev.*, 2009, **38**, 73-82; c) S. S. Mal, F. H. Stephens and R. T. Baker, *Chem. Commun.*, 2011, **47**, 2922-2924; d) A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson and M. Vasiliu, *Science*, 2011, **331**, 1426-1429; e) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa and H. Ogino, *J. Am. Chem. Soc.*, 2009, **131**, 14946-14957; f) G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152-4205.
4. a) T. Kakizawa, Y. Kawano and M. Shimoi, *Organometallics*, 2001, **20**, 3211-3213; b) Y. Kawano, M. Hashiva and M. Shimoi, *Organometallics*, 2006, **25**, 4420-4426; c) Y. Kawano, T. Yasue and M. Shimoi, *J. Am. Chem. Soc.*, 1999, **121**, 11744-11750.
5. a) B. Bera and B. R. Jagirdar, *Inorg. Chim. Acta.*, 2011, **372**, 200-205; b) B. Bera, Y. P. Patil, M. Nethaji and B. R. Jagirdar, *Dalton Trans.*, 2011, **40**, 10592-10597; c) R. Kumar and B. R. Jagirdar, *Inorg. Chem.*, 2012, **52**, 28-36; d) M. Shimoi, S.-i. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi and H. Ogino, *J. Am. Chem. Soc.*, 1999, **121**, 11704-11712.
6. a) J. R. Vance, A. Schäfer, A. P. M. Robertson, K. Lee, J. Turner, G. R. Whittell and I. Manners, *J. Am. Chem. Soc.*, 2014; b) E. M. Leitao, N. E. Stubbs, A. P. M. Robertson, H. Helten, R. J. Cox, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.*, 2012, **134**, 16805-16816; c) A. P. M. Robertson, E. M. Leitao and I. Manners, *J. Am. Chem. Soc.*, 2011, **133**, 19322-19325; d) M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 3831-3841.
7. a) H. C. Johnson, A. P. M. Robertson, A. B. Chaplin, L. J. Sewell, A. L. Thompson, M. F. Haddow, I. Manners and A. S. Weller, *J. Am. Chem. Soc.*, 2011, **133**, 11076-11079; b) T. M. Douglas, A. B. Chaplin and A. S. Weller, *J. Am. Chem. Soc.*, 2008, **130**, 14432-14433; c) T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2009, **131**, 15440-15456; d) L. J. Sewell, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.*, 2012, **134**, 3598-3610; e) A. B. Chaplin and A. S. Weller, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 581-584; f) R. Dallanegra, A. B. Chaplin and A. S. Weller, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 6875-6878; g) H. C. Johnson, C. L. McMullin, S. D. Pike, S. A. Macgregor and A. S. Weller, *Angew. Chem., Int. Ed. Engl.*, 2013, **52**, 9776-9780.
8. a) G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2007, **129**, 8704-8705; b) G. Bénac-Lestrille, U. Helmstedt, L. Vendier, G. Alcaraz, E. Clot and S. Sabo-Etienne, *Inorg. Chem.*, 2011, **50**, 11039-11045; c) Y. Gloaguen, G. Bénac-Lestrille, L. Vendier, U. Helmstedt, E. Clot, G. Alcaraz and S. Sabo-Etienne, *Organometallics*, 2013, **32**, 4868-4877.
9. a) G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 7170-7179; b) G. Alcaraz, L. Vendier, E. Clot and S. Sabo-Etienne, *Angew. Chem., Int. Ed. Engl.*, 2010, **49**, 918-920; c) C. J. Wallis, H. Dyer, L. Vendier, G. Alcaraz and S. Sabo-Etienne, *Angew. Chem., Int. Ed. Engl.*, 2012, **51**, 3646-3648.
10. a) M. Sohail, S. Moncho, E. N. Brothers, D. J. Darensbourg and A. A. Bengali, *Dalton Trans.*, 2013, **42**, 6720-6723; b) M. A. Esteruelas, I. Fernández, A. M. López, M. Mora and E. Oñate, *Organometallics*, 2014; c) M. A. Larsen and J. F. Hartwig, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja412563e; d) T. Kakizawa, Y. Kawano, K. Naganeyama and M. Shimoi, *Chemistry Letters*, 2011, **40**, 171-173.
11. Gaussian Development Version, Revision H.32, Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2009. Full GDV reference and computational details in Supporting Information
12. a) S. M. Howdle and M. Poliakoff, *Journal of the Chemical Society, Chemical Communications*, 1989, 1099-1101; b) J. Yang, B. R. N'Guessan, A. Dedieu, D. C. Grills, X.-Z. Sun and M. W. George, *Organometallics*, 2009, **28**, 3113-3122.
13. X.-Z. Sun, D. C. Grills, S. M. Nikiforov, M. Poliakoff and M. W. George, *J. Am. Chem. Soc.*, 1997, **119**, 7521-7525.
14. The second CO stretching absorbance of **5**-*cis* is obscured by overlap with the parent $CpRe(CO)_3$ complex.
15. C. P. Casey, R. S. Tanke, P. N. Hazin, C. R. Kemnitz and R. J. McMahon, *Inorg. Chem.*, 1992, **31**, 5474-5479.
16. This observation is unexpected and may be due to the formation of insoluble oligomeric material. Initial attempts to isolate the unidentified boron complexes were unsuccessful but efforts are ongoing.
17. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
18. a) T. S. De Vries and E. Vedejs, *Organometallics*, 2007, **26**, 3079-3081; b) T. S. De Vries, A. Prokofjevs and E. Vedejs, *Chem. Rev.*, 2012, **112**, 4246-4282.
19. a) G. K. Yang and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 6500-6501; b) A. Prokofjevs, J. W. Kampf, A. Solovyev, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2013, **135**, 15686-15689; c) M. Roselló-Merino, J. López-Serrano and S. Conejero, *J. Am. Chem. Soc.*, 2013, **135**, 10910-10913.
20. a) Y. Hu, L. Li, A. P. Shaw, J. R. Norton, W. Sattler and Y. Rong, *Organometallics*, 2012, **31**, 5058-5064; b) A. Z. Voskoboynikov, A. K. Shestakova and I. P. Beletskaya, *Organometallics*, 2001, **20**, 2794-2801; c) D. L. Cummings and G. J. Powers, *Industrial & Engineering Chemistry Process Design and Development*, 1974, **13**, 182-192; d) E. Y. Marrero-Alfonso, A. M. Beaird, T. A. Davis and M. A. Matthews, *Industrial & Engineering Chemistry Research*, 2009, **48**, 3703-3712; e) J. M. O'Connor and S. J. Friese, *Organometallics*, 2008, **27**, 4280-4281; f) A. G. Carr, D. M. Dawson, M. Thornton-Pett and M. Bochmann, *Organometallics*, 1999, **18**, 2933-2935; g) R. M. Bullock and J.-S. Song, *J. Am. Chem. Soc.*, 1994, **116**, 8602-8612; h) J. P. Collman, P. S. Wagenknecht and N. S. Lewis, *J. Am. Chem. Soc.*, 1992, **114**, 5665-5673; i) E. C. Ashby, A. B. Goel, R. N. DePriest and H. S. Prasad, *J. Am. Chem. Soc.*, 1981, **103**, 973-975; j) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231-281; k) M. A. Rankin and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 10021-10023; l) P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 5500-5503; m) Y. Zhang, B. S. Hanna, A. Dineen, P. G. Williard and W. H. Bernskoetter, *Organometallics*, 2013, **32**, 3969-3979.