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Dehydrogenation of amine–boranes catalyzed by a PC$_{sp3}$P pincer iridium complex

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Experimental details. All the manipulations were performed under an argon atmosphere. All solvents were dried over appropriate drying agent (Na/benzophenone for DME; CaH_2 for dichloromethane and C_6H_5F) and freshly distilled under an argon atmosphere prior to use. CD_2Cl_2 (Sigma Aldrich) was degassed by three freeze-pump-thaw cycles.

Complex **1** was synthesized as described.[S1,S2]

NMR investigations were carried out on Bruker AVANCE 600 NMR spectrometer supplied with a specially designed low temperature dual probe-head (SEI, 5 mm tube size). The IR spectra of solutions were measured on Nicolet 6700 FTIR spectrometer in CaF_2 cells using home modified cryostat Carl Zeiss Jena for variable temperature measurements.

Computational details. Calculations were performed with the Gaussian09[S3] package at the DFT/M06[S4] level without any ligand simplification. Effective core potentials (ECP) and its associated SDD basis set[S5-S8] supplemented with f-polarization functions (SDD(f))[S9] were applied to the Ir atom. The first coordination sphere of Ir (P, H, Cl and C1 atoms) as well as OH, BH and NH groups was described with 6-31++G(d,p) basis set,[S10–S13] while rest of atoms was described with a 6-31G basis set.[S10]

All the structures were fully optimized with this basis set without any symmetry restrictions. The nature of all of the stationary points on the potential energy surface was confirmed by vibrational analysis.[S14] No scaling factors were applied to the calculated frequencies.

Table S1 Catalytic activity (observed rate constants k_{obs} and maximum TOF) of complex **1** (1.20 mol%) in amine boranes ($c = 0.07$ mol dm^{-3}) dehydrogenation in DME.

	$Me_2NH{\cdot}BH_3$	$Bu^tNH_2{\cdot}BH_3$	$NH_3{\cdot}BH_3$
k_{obs}/s^{-1}	$1.8{\cdot}10^{-4}$	$1.3{\cdot}10^{-4}$	$2.6{\cdot}10^{-5}$
TOF/h^{-1}	36[a]	18[b]	15[c]

[a] 1 h, [b] 2 h, [c] 3 h

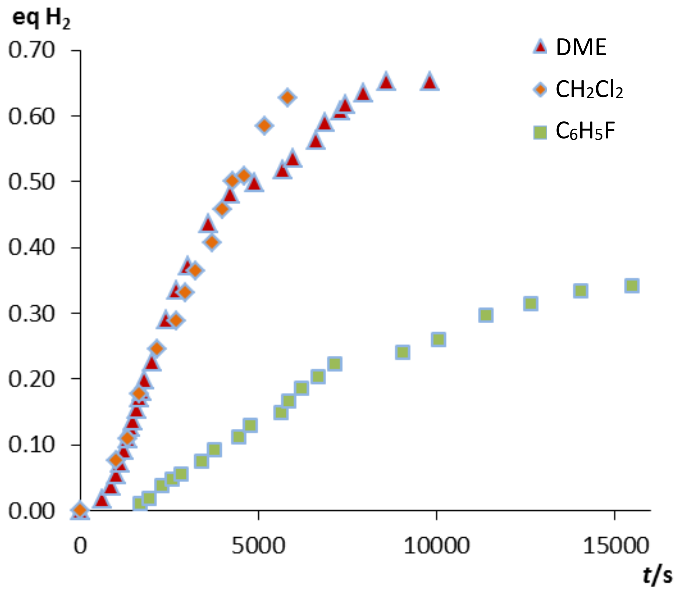


Figure S1 Kinetic curves of H_2 evolution from $Me_2NH\cdot BH_3$ (c = 0.07 mol dm^{-3}) in the presence of complex **1** (1.2 mol%) at 298 K in different solvents.

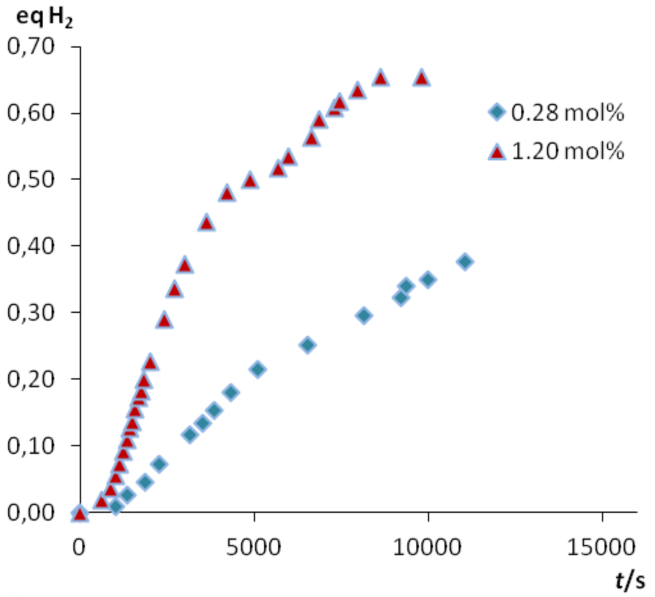
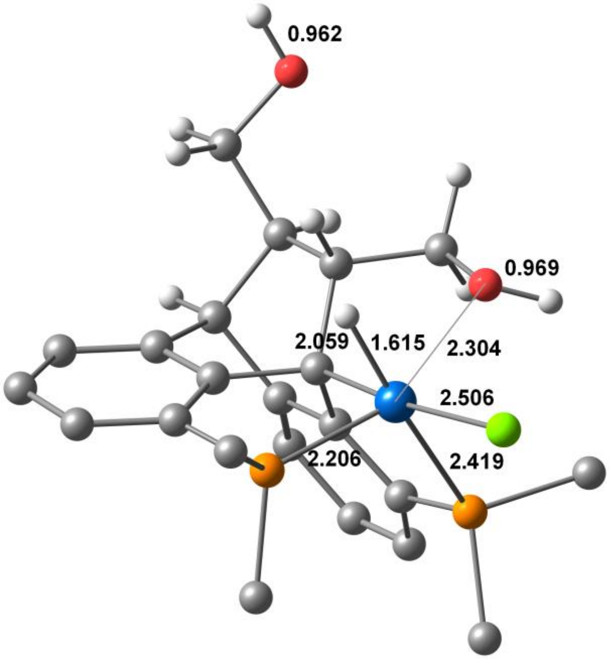
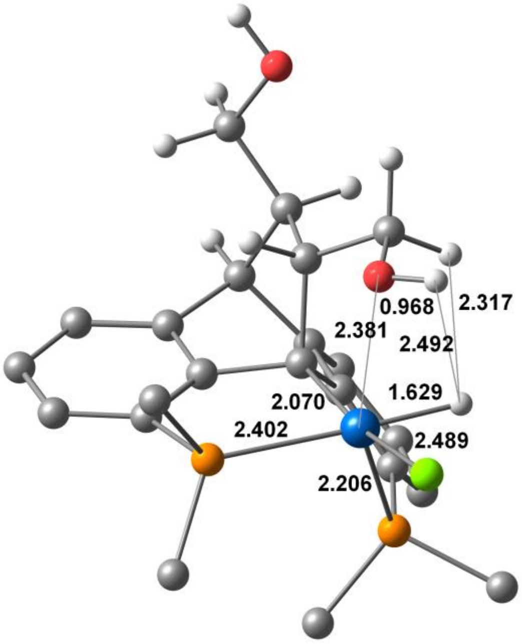


Figure S2 Kinetic curves of H_2 evolution from $Me_2NH\cdot BH_3$ (c = 0.07 mol dm^{-3}) in the presence of different amounts of complex **1** at 298 K in DME.

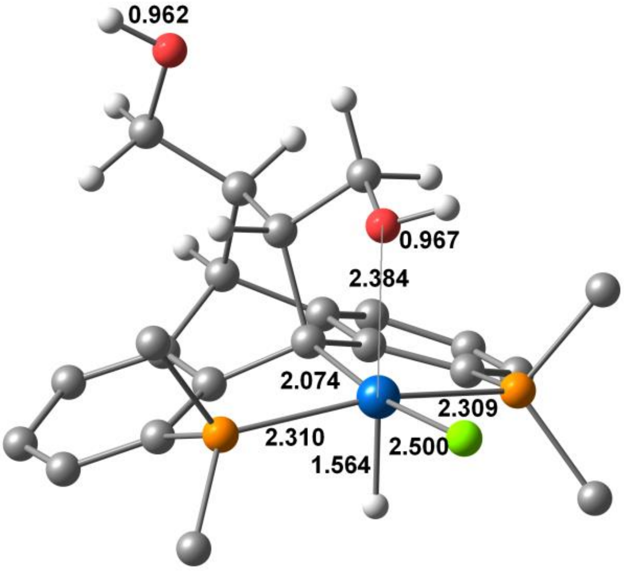




fac-**1-I**

fac-**1-II**

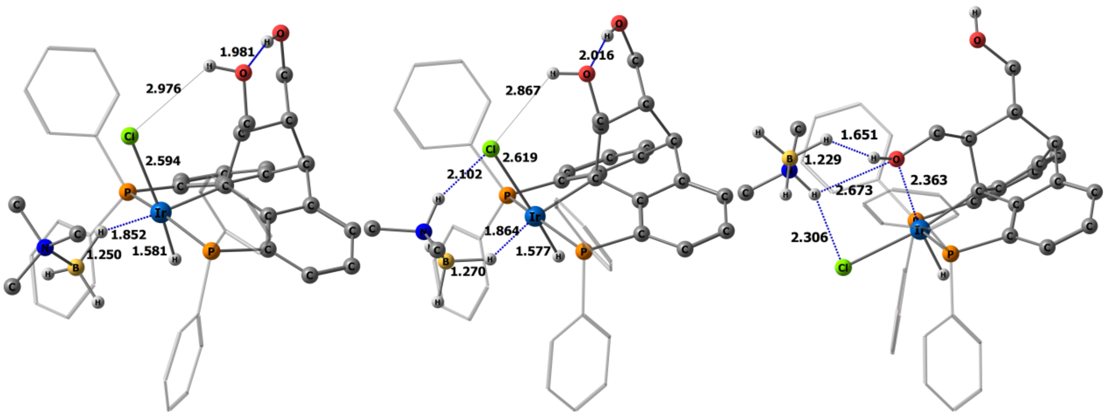
ΔE_{ZPE} = 0.0 8.4 kcal mol^{-1}



mer-**1**

ΔE_{ZPE} = –2.4 kcal mol^{-1}

Figure S3 DFT/M06-optimized structures of *fac*- (*fac*-**1-I** and *fac*-**1-II**) and *mer*-**1** isomers of complex **1**. Reproduced with permission from ref. 20**.**



ΔG_f^{298}= -4.0 ΔG_f^{298}= -11.7 ΔG_f^{298}= -6.6

Figure S4 DFT/M06-optimized structures of **1**·TMAB and **1**·DMAB complexes and their formation energies (in kcal mol^{-1}) from *mer*-**1** and amine borane.

Table S2 Computed formation energies (in kcal mol^{-1}) and selected stretching vibration frequencies (in cm^{-1}) for **1**·TMAB and **1**·DMAB complexes.

	1·TMAB	**1**·DMAB
ΔE	–18.6	–26.2
ΔH	–16.6	–24.4
ΔG	–4.0	–11.7
N(IrH)	2213	2241
N(BH$^{\text{br}}$)	2356	2210
N(BH$^{\text{term}}$)	2520	2487
N(BH$^{\text{term)}}$	2571	2580

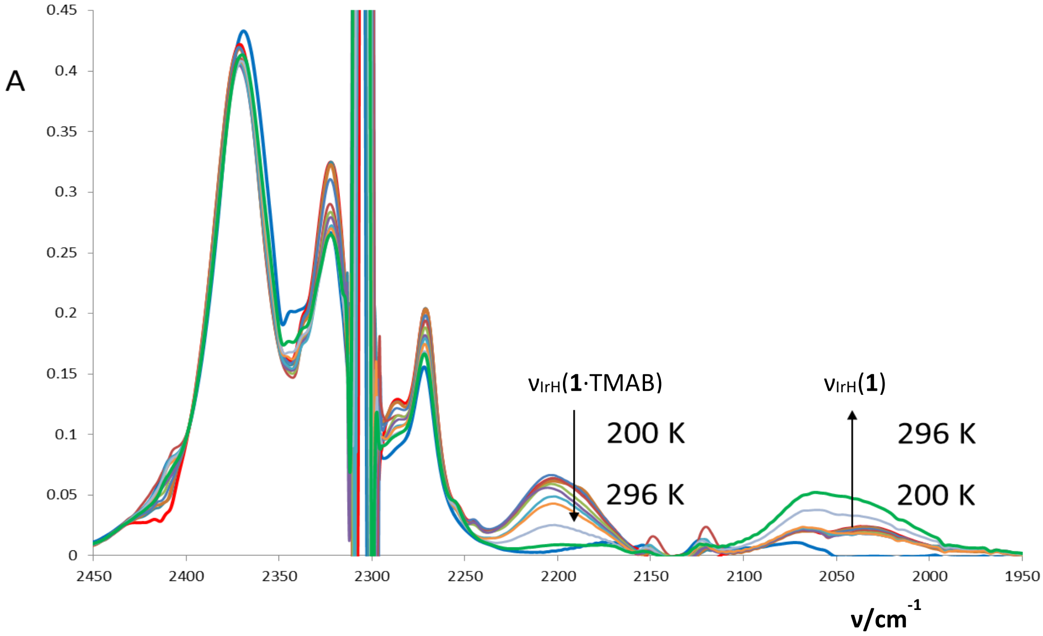


Figure S5 Variable temperature IR spectra of $Me_3N{\cdot}BH_3$ (blue line, *c* = 0.01 mol dm^{-3}) and its equimolar mixture with complex **1** in CH_2Cl_2, *l* = 0.01 cm.

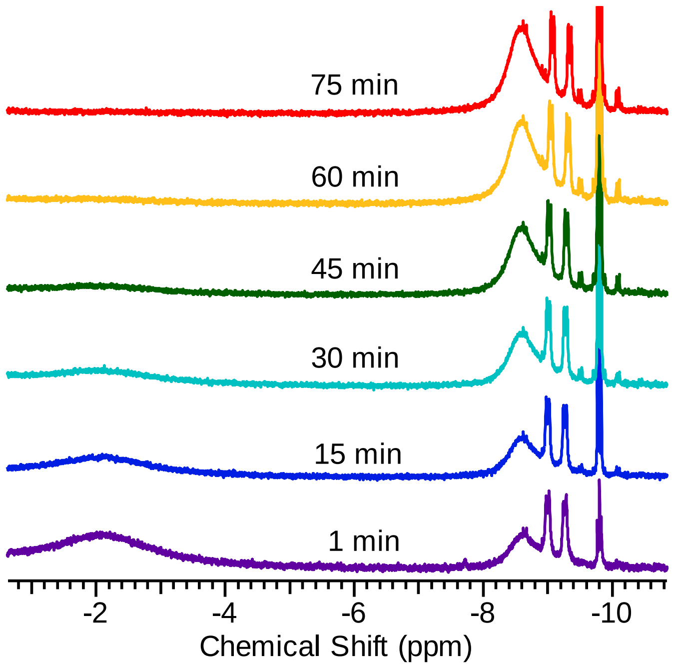


Figure S6 ^{1}H NMR monitoring of the DMAB dehydrogenation in the presence of 1 equiv of **1** in CD_2Cl_2 at 272.5 K.

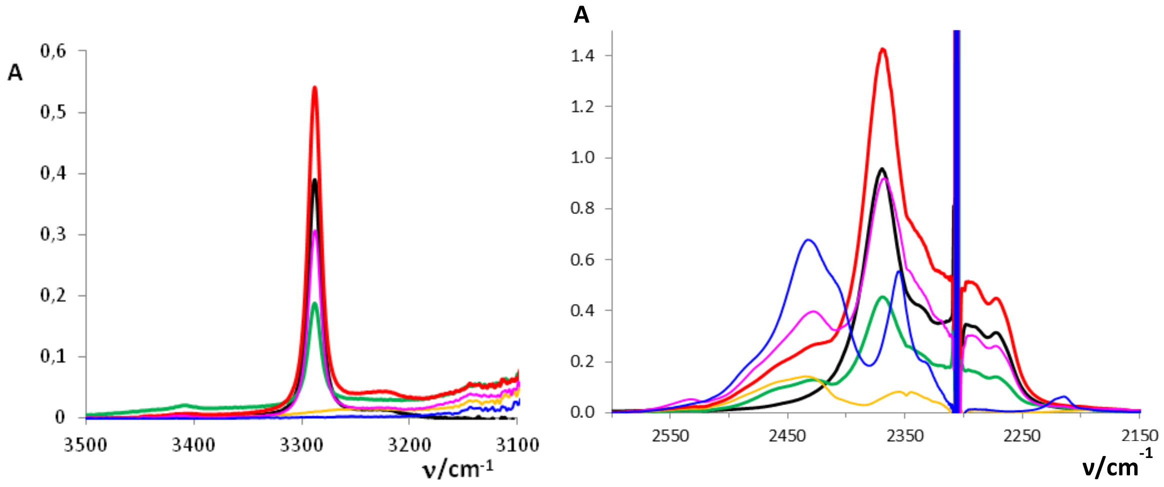


Figure S7 IR spectra in the ν(NH) (left) and ν(BH) (right) regions of DMAB (c = 0.06 mol dm^{-3}; black line), its mixture with complex **1** (c = 0.01 mol dm^{-3}) at DMAB:**1** ratio 3 to 1 (in 1 min after mixing – green, 2 h – orange) and after subsequent addition of 10 equiv. DMAB (1 min after mixing – red line, 2.5 h – purple; 10 h – blue), in CH_2Cl_2, l = 0.01 cm.

References

S1 S. Musa, I. Shaposhnikov, S. Cohen and D. Gelman, *Angew. Chem., Int. Ed.*, 2011, **50**, 3533.

S2 G. A. Silantyev, O. A. Filippov, S. Musa, D. Gelman, N. V. Belkova, K. Weisz, L. M. Epstein and E. S. Shubina, *Organometallics*, 2014, **33**, 5964.

S3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, revision B.01*, Gaussian, Wallingford, CT, 2010.

S4 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

S5 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123.

S6 U. Haussermann, M. Dolg, H. Stoll, H. Preuss, P. Schwerdtfeger and R. M. Pitzer, *Mol. Phys.*, 1993, **78**, 1211.

S7 W. Küchle, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1994, **100**, 7535.

S8 T. Leininger, A. Nicklass, H. Stoll, M. Dolg and P. Schwerdtfeger, *J. Chem. Phys.*, 1996, **105**, 1052.

S9 A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111.

S10 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

S11 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople and M. S. Gordon, *J. Chem. Phys.*, 1982, 77, 3654.

S12 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. von Ragué Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.

S13 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

S14 J. Fritsch and G. Zundel, *J. Phys. Chem.*, 1981, **85**, 556.