Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

DEHYDROGENATION OF A TERTIARY AMINE-BORANE BY A RHENIUM COMPLEX

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Experimental Details

IR studies

Time resolved IR spectra were obtained using a Bruker Vertex 80 FTIR equipped with step-scan and rapid-scan capabilities (2200-1800 cm^{-1}). Sample photolysis was conducted using the third or fourth harmonic [355 nm ($CpMn(CO)_3$) and 266nm ($CpRe(CO)_3$)] of a Nd:YAG laser (Quantel Brilliant B). To prevent multiple photolysis events, all spectra were obtained with a single shot of the laser. A temperature controlled 0.5 mm pathlength IR cell with CaF_2 windows (Harrick Scientific) was used to acquire the IR spectra. The temperature was monitored by a thermocouple located close to the photolysis solution and maintained by a water circulator to within ±0.1 ^{0}C. All spectra were obtained at 4 cm^{-1} resolution

Heptane solvent was of anhydrous grade (Aldrich) and 99% purity. NMR spectra of triethylphosphite (Sigma-Aldrich, >98%), dimethylamine borane (Sigma-Aldrich, 97%) and triethylamine borane (Sigma-Aldrich, >97%) were obtained prior to the kinetic runs to rule out the presence of contaminants such as $OP(OEt)_3$ and free amine. The complexes, $CpMn(CO)_3$ and $CpRe(CO)_3$ (Strem) were used as received. The photolysis solution contained ≈ 1-5 mM of the parent metal tricarbonyl. All kinetic experiments were conducted under at least a 10 fold excess of borane relative to the metal precursor. Kinetic parameters were obtained from least squares analysis of the data as implemented by the software program KaleidaGraph.

NMR studies

^{1}H and ^{11}B (128MHz) NMR spectra were recorded using a Bruker 400 MHz NMR spectrometer. The ^{1}H chemical shifts were reported with reference to toluene-d_8. ^{11}B NMR spectral signals are reported with respect to the unreacted borane used.

a) ^{1}H NMR: 50 mg of $CpRe(CO)_3$ and 25 µl H_3BNEt_3 were dissolved in 0.5ml of toluene-d_8 in a NMR tube fitted with a septum. The NMR tube was photolysed for 15 sec at 266 nm using a Nd:YAG laser at 293K. The reaction mixture was quickly frozen in liquid nitrogen and the NMR spectra were recorded at regular intervals as the solution warmed up to room temperature.

b) ^{11}B NMR: An NMR tube containing 0.5 mL toluene-d_8 solution with 50 mg of $CpRe(CO)_3$ and 25 mg of H_3BNHMe_2 was photolyzed for one hour at 260 nm using a Rayonet photoreactor. NMR spectra were acquired immediately afterwards.

Theoretical Details

All calculations were performed in the development version of the Gaussian suite of programs[1] using density functional theory. Geometries were optimized using the ωB97XD functional which includes different fractions of exact exchange in the long and short ranges, as well as a dispersion correction.[2] All atoms were described with the def2-TZVPP basis set which describes the core electrons of the heavy atom (Re) using an effective core potential.[3] The computed gas-phase geometries were confirmed to be ground state structures or transition states according to their number of imaginary frequencies. Solvent effects were included using the SMD continuum method,[4] with single-point calculations on the gas phase geometries. Energies reported in this paper are solvent enthalpies, obtained from the solvent energies and the gas phase enthalpy correction, *i.e.* $H^{solv}=E^{solv}+(H^{gas}-E^{gas})$. The enthalpies were computed at 298.15 K and 1 atm, and are expressed in kcal/mol. Figures of computed geometries included in this work were rendered using CYLview.[5]

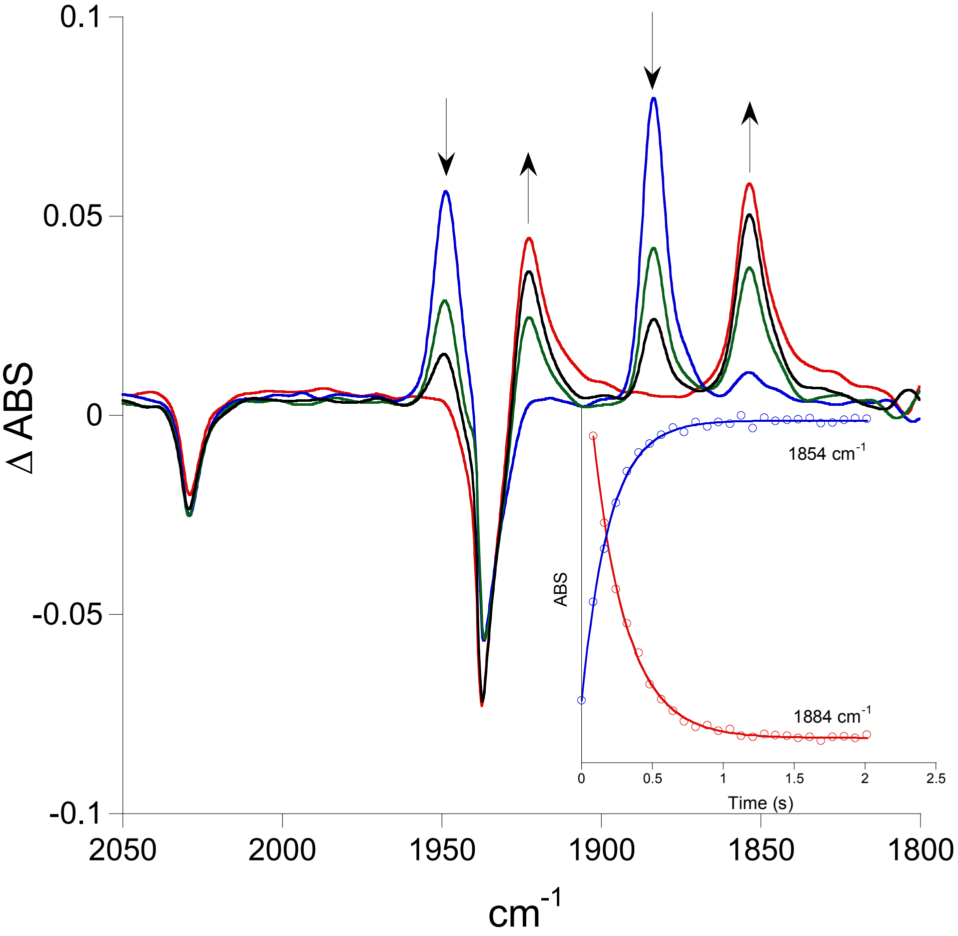

Figure S1: Spectral changes observed upon photolysis of a 5 mM heptane solution of $CpRe(CO)_3$ with 40 mM H_3BNEt_3 at 213 K.

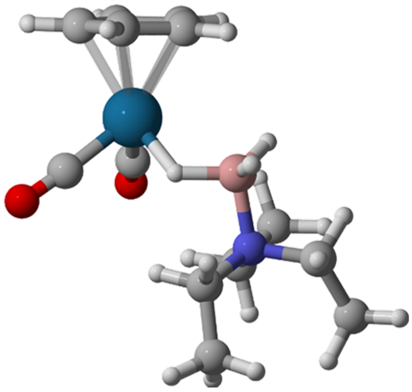

Figure S2: DFT optimized geometry of compound **4** with a calculated Re-H-B BDE of 36.1 kcal/mol. Some key geometric parameters: $\angle$Re-H-B = 119°, $R_{\text{Re-H}}$ = 1.773Å, $R_{\text{B-H (coord.)}}$ = 1.298 Å, and $R_{\text{B-H(uncoord.)}}$ = 1.212 Å (average).

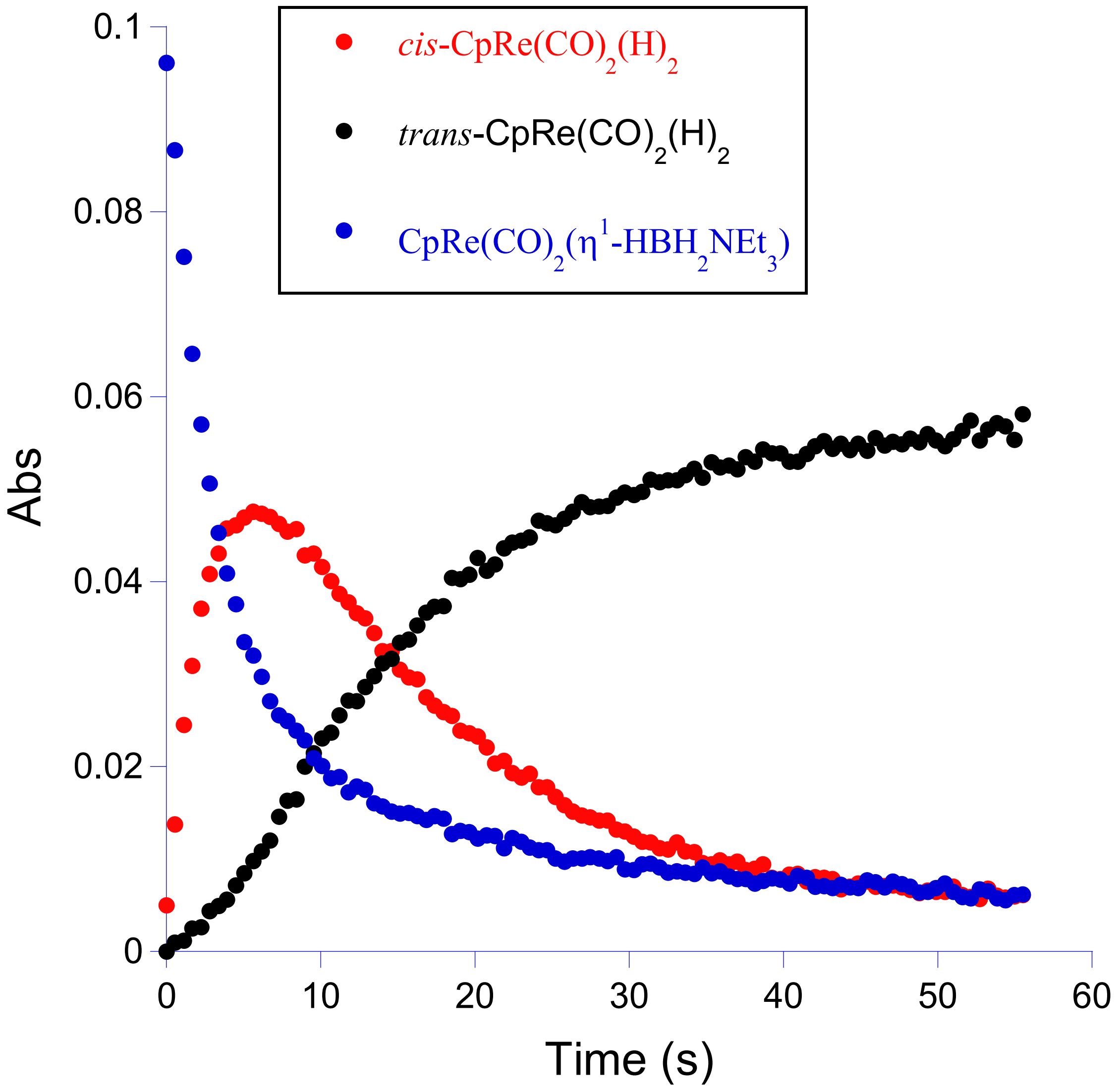

Figure S3: Temporal profile of the species formed upon photolysis of a 5 mM heptane solution of $CpRe(CO)_3$ with 40 mM H_3BNEt_3 added at 298 K.

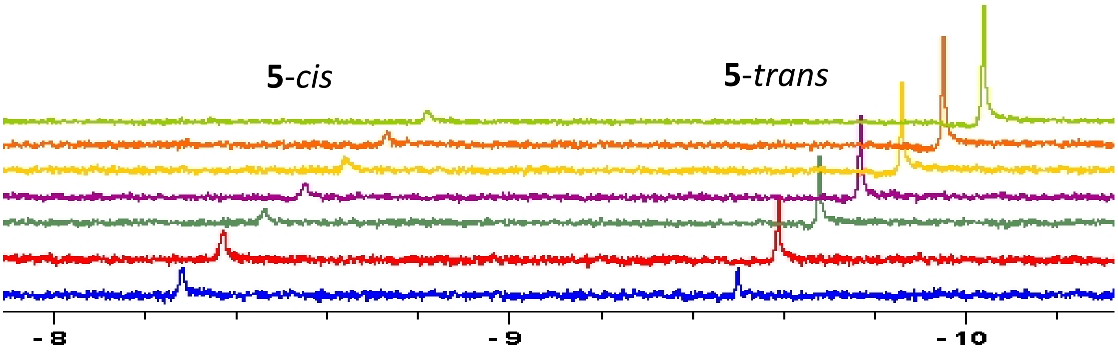

Figure S4: ^{1}H NMR spectra obtained after photolysis of a solution containing 50 mg $CpRe(CO)_3$ and 25 µL of H_3BNEt_3 in 0.5 mL of toluene-d_8 from 233 K to 293 K. The individual slices, representing qualitative information for the **5**-*cis* → **5**-*trans* conversion, were obtained as the solution was warming up.

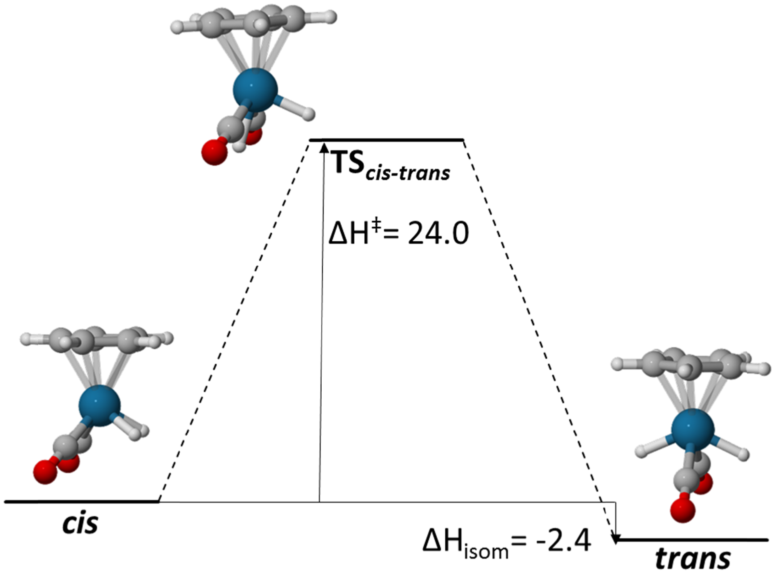

Figure S5: Calculated enthalpic profile for the conversion of **5**-*cis* to **5**-*trans*. All values in kcal/mol.

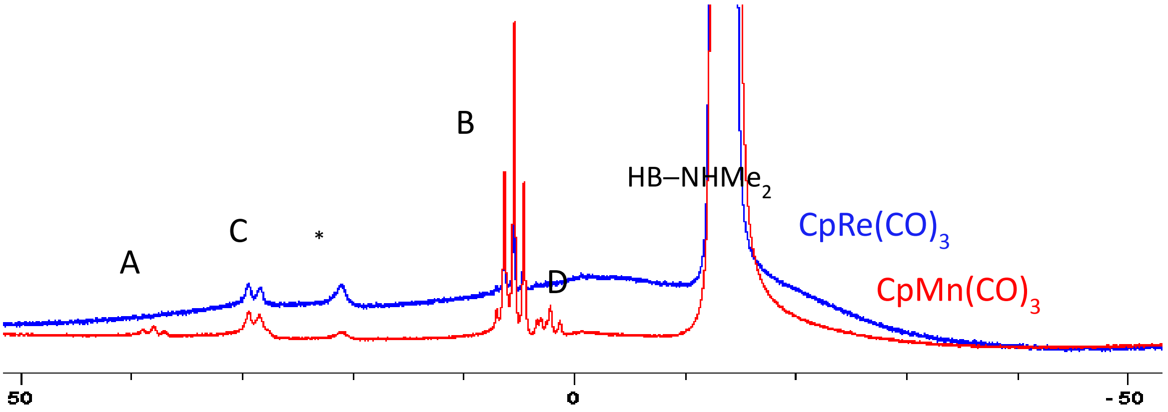

Figure S6: ^{11}B NMR spectra obtained after one hour of irradiation by a 260 nm UV lamp of 50 mg of CpRe(CO)$_3$ and 25 mg of H_3BNHMe_2 in 0.5 ml of toluene-*d*$_8$ at 293 K. Boron containing species include **A** (H_2B-NMe_2), **B** [(Me_2N-BH_2)$_2$], **C** [HB(NMe_2)$_2$] and **D** [Me_2NH-BH_2-NMe_2-BH_3]. All species were identified by comparison with the ^{11}B NMR chemical shifts reported in the literature. The peaks marked with an * is an unassigned borane species but may be due to complex **1** (Mn) and **4** (Re) (see reference 10d).

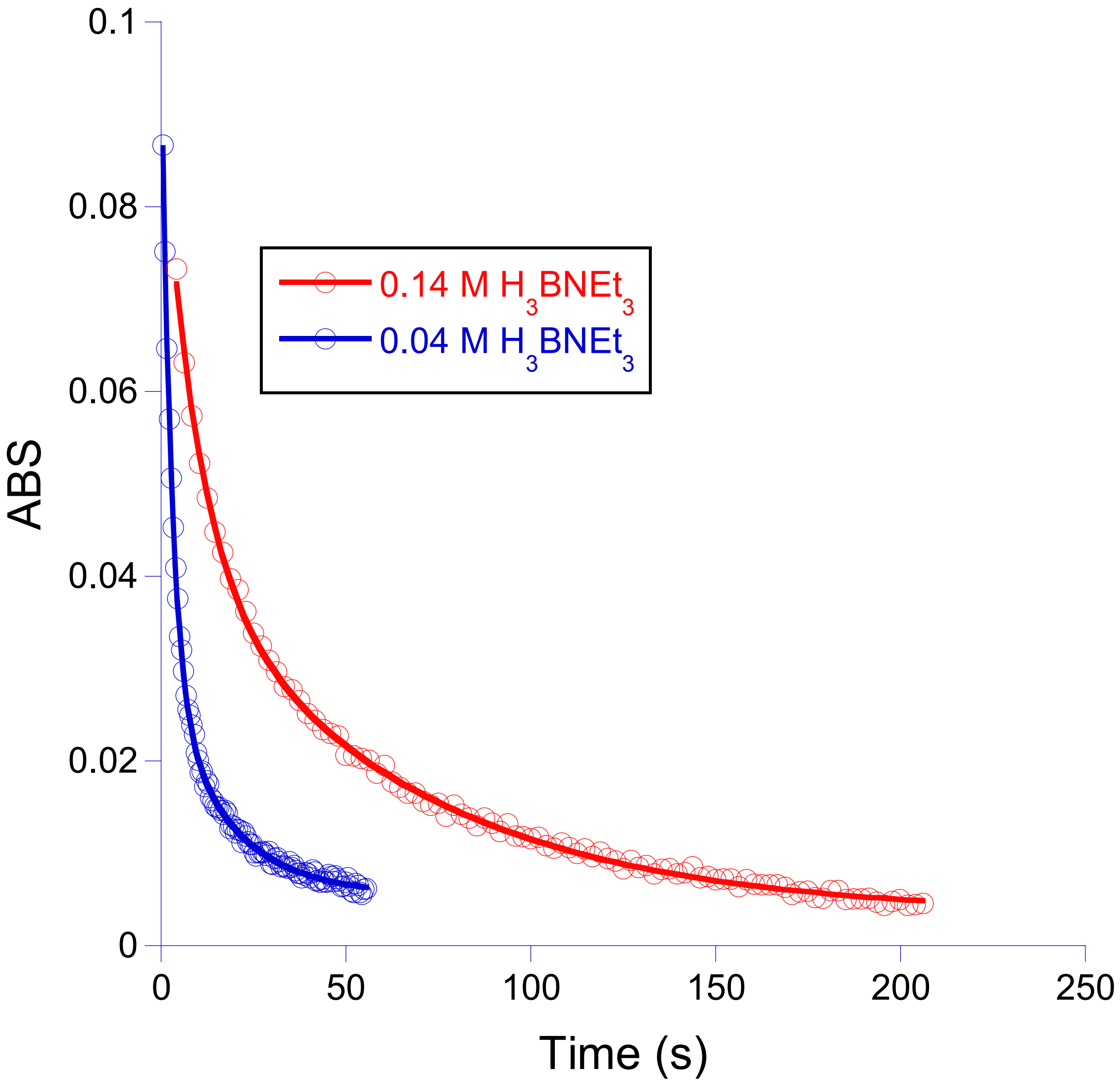

Figure S7: Plot showing the inverse dependence of the decay rate of **4** upon [H_3BNEt_3] at 298 K. Solid line represents a bi-exponential fit to the data.

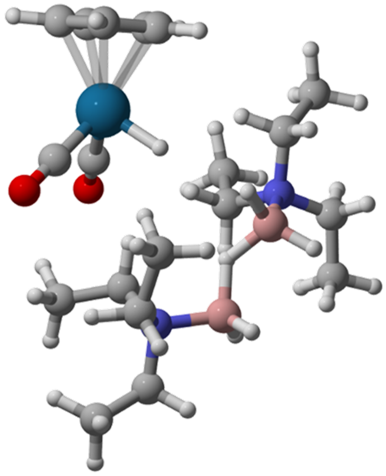

Figure S8: Calculated structure of the ion pair, $[CpRe(CO)_2H][H(BH_2NEt_3)_2]$ which lies 10.5 kcal/mol higher in enthalpy than **4** + H_3BNEt_3.

Table S1: DFT calculated parameters.

	H^{solv}	E^{solv}	E^{gas}	H^{gas}
BDE of $CpRe(CO)_2(\eta^1\text{-}H_3BNEt_3)$	36.1	38.0	43.6	41.7
$CpRe(CO)_2H_2$ *cis* → *trans* barrier	24.0	25.1	25.8	24.7
$CpRe(CO)_2H^- + H_2BNEt_3^+$ (isolated)	85.1	88.7	134.9	131.3
$CpRe(CO)_2H^- + H_2BNEt_3^+$ (ion pair)	38.0	39.1	41.7	39.4
$CpRe(CO)_2H^- + H(H_2BNEt_3)_2^+$ (isolated)	54.0	54.8	92.5	91.7
$CpRe(CO)_2H^- + H(H_2BNEt_3)_2^+$ (ion pair)	10.5	8.9	7.1	8.6
BDE of $CpMn(CO)_2(\eta^1\text{-}H_3BNEt_3)$	24.7	26.7	28.6	26.5

Table S2: CO stretching cm^{-1} for the complexes studied in the present work.

Complex	ν_{CO} (this study) (cm^{-1})^{a}	ν_{CO} (literature) (cm^{-1})	ν_{CO} (calculated) (cm^{-1})
1	1931, 1863	1927,1820[6]	2075, 2017
2	1927, 1854	-	
3	1985, 1924	1986, 1927[7]	2125, 2077
4	1925, 1856	-	2040, 1973
5-*cis*	2008, ~ 1940*	2010, 1934[7]	2123, 2052
5-*trans*	2024, 1956	2025, 1952[7]	2138, 2073

a) heptane solvent at 298 K, *peak obscured by parent tricarbonyl absorption

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