Photoinduced N_2 Loss as a Route to Long-Lived Organometallic Alkane Complexes: A Time-Resolved IR and NMR Study

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Supporting Information

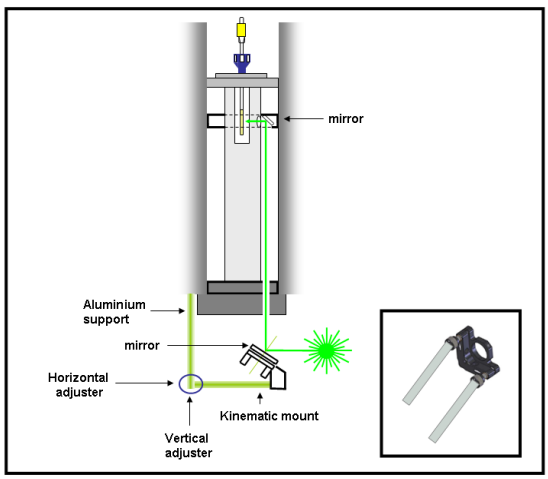

Fig. S1 Schematic of the in-situ laser based NMR photolysis set-up. The inset shows the kinematic mount for the mirror with adjustment rods

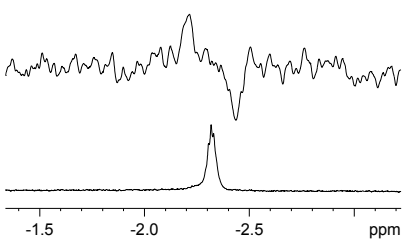

Fig. S2 Bottom: ^{1}H NMR spectrum of bound methylene protons of $CpRe(CO)_2$(cyclopentane); Top: same sample, ^{13}C edited showing $^1J_{C\text{-}H}$ = 114 (± 7) Hz, 1222 scans, processed with 8 Hz of line broadening.

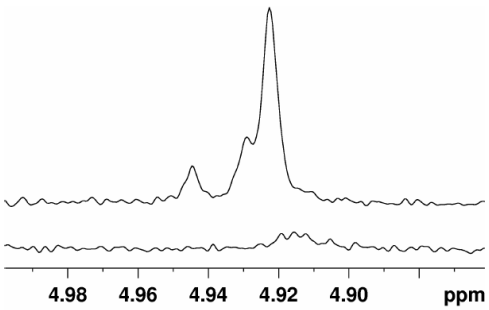

Fig. S3 - Expansion of ^{1}H NMR spectrum of $CpRe(CO)_2(N_2)$ in 2,2-dimethylbutane before (bottom) and after (top) photolysis using the fibre optic light source. New peaks after photolysis are due to the cyclopentadienyl resonances of three isomers of $CpRe(CO)_2$(2,2-dimethylbutane). Spectra processed with Gaussian resolution enhancement (LB = -1Hz; GB = 0.15; AQ = 2.18s)

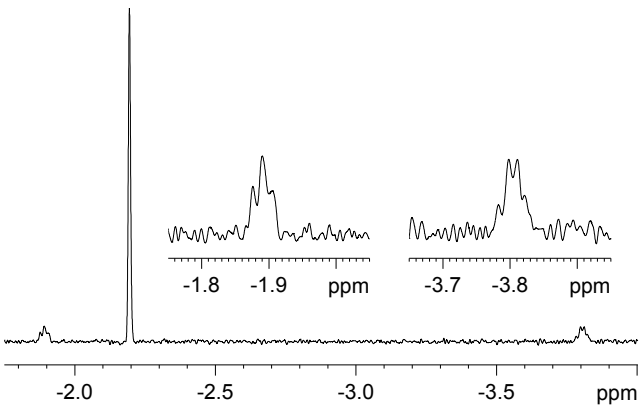

Fig. S4: 500 MHz ^{1}H NMR spectrum after UV lamp photolysis of $CpRe(CO)_2(N_2)$ in 95% 2,2-dimethylbutane/5% pentane-d_{12} at 170 K. 256 scans with resolution enhancement (LB = -3 Hz; GB = 0.1) Region shows bound alkane protons with expansions of multiplets inset.

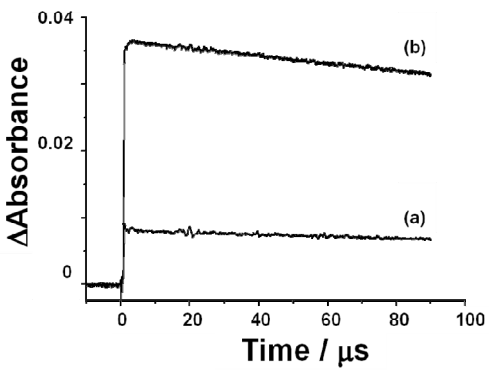

Fig. S5: TRIR traces monitoring the peak maximum of the organometallic alkane complex following 266 nm irradiation of (a) $CpRe(CO)_3$ and (b) $Cp^{\ddagger}Re(CO)_2(N_2)$ in cyclopentane. In both experiments, a very similar laser power and UV absorbance (at the excitation wavelength) was used.

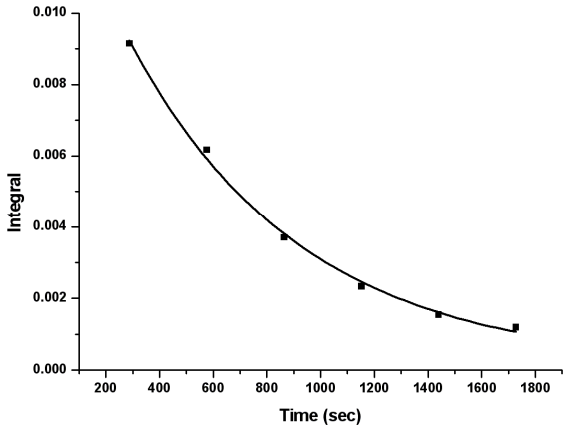

Fig. S6 Kinetics of decay of $Cp^{‡}Re(CO)_2(c\text{-}C_5H_{10})$ measured by NMR spectroscopy at 190 K. The integration of the resonance at δ = -2.44 was measured relative to that of benzene added as a calibrant in trace quantities.