

## Electronic Supporting Information for

# A systematic approach to the generation of long-lived metal alkane complexes: A combined IR and NMR study of **TpRe(CO)<sub>2</sub>(cyclopentane)**

Simon, B. Duckett,\*<sup>a</sup> Michael W. George,\*<sup>b</sup> Omar S. Jina,<sup>b</sup> Steven L. Matthews,<sup>a</sup> Robin  
N. Perutz,\*<sup>a</sup> Xue-Zhong Sun,<sup>b</sup> and Khuong Q. Vuong<sup>b</sup>

<sup>a</sup> *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*  
*Fax: +44 (0)1904 43 2516; Tel: +44 1904 432549 ; Email: [rnp1@york.ac.uk](mailto:rnp1@york.ac.uk);*  
*[sbd3@york.ac.uk](mailto:sbd3@york.ac.uk)*

<sup>b</sup> *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7*  
*2RD, UK. Fax: +44 115 9513563; Tel: +44 115 9513512; E-mail:*  
*[mike.george@nottingham.ac.uk](mailto:mike.george@nottingham.ac.uk)*

## Experimental:

**General.**  $\text{TpRe}(\text{CO})_3$  was synthesised according to literature procedure.<sup>1</sup> Cyclopentane (Sigma-Aldrich, *Reagent Plus*<sup>®</sup>) and was either distilled from  $\text{CaH}_2$  under argon (for IR spectroscopy) or vacuum distilled from Na/K benzophenone ketyl (for NMR spectroscopy). Argon (Pure Shield, BOC) and CO (CP grade, BOC) were used as supplied. The solubility of CO in cyclopentane<sup>2, 3</sup> was taken to be  $0.9 \times 10^{-2}$  M under 1 atm of CO at 298 K. For the TRIR experiments the concentrations of solutions used were *ca.*  $3 \times 10^{-4}$  M for the low temperature IR experiments the concentrations were *ca.*  $2 \times 10^{-4}$  M.

For NMR experiments, cyclopentane was stirred over conc.  $\text{H}_2\text{SO}_4$ . The cyclopentane was separated and stirred with fresh conc.  $\text{H}_2\text{SO}_4$  overnight. The cyclopentane was separated from  $\text{H}_2\text{SO}_4$  in a separating funnel and washed with  $3 \times 10$  mL water. It was then stirred over  $\text{MgSO}_4$  for one hour. After filtration it was stored over Na/K and small amount of benzophenone. It was transferred into NMR tubes by vacuum transfer on a high vacuum line.

**Synthesis of cyclo- $\text{C}_5\text{H}_9\text{D}$ .** To a boiling solution of 7.0 g magnesium turnings (292 mmol) in 400 mL of dry THF under argon was added dropwise 29.0 mL cyclopentylchloride (279 mmol) over 1 h. The solution turned a metallic grey colour as the turnings dissolved. Reflux was continued for 1 h, then left to cool to room temperature under argon. The solution was then cooled to  $0^\circ\text{C}$  and a solution of  $\text{D}_2\text{O}$  in THF (30 mL in 30 mL) was added dropwise with vigorous stirring. The solution became clear with the precipitation of white salts of magnesium. The solution was filtered through paper into a large flask followed by the addition of 800 mL of  $\text{H}_2\text{O}$ . The layers (cyclopentane: top, THF/water: bottom) are then separated in a separating funnel. The top layer was collected and washed further with  $5 \times 50$  mL  $\text{H}_2\text{O}$ . Analysis at this point revealed THF was still present and so further washings were conducted with  $10 \times 20$  mL  $\text{H}_2\text{O}$ . The crude product was then distilled at atmospheric pressure and the fraction distilling at  $46\text{-}49^\circ\text{C}$  was collected (9.89 g, 139 mmol, 50%).

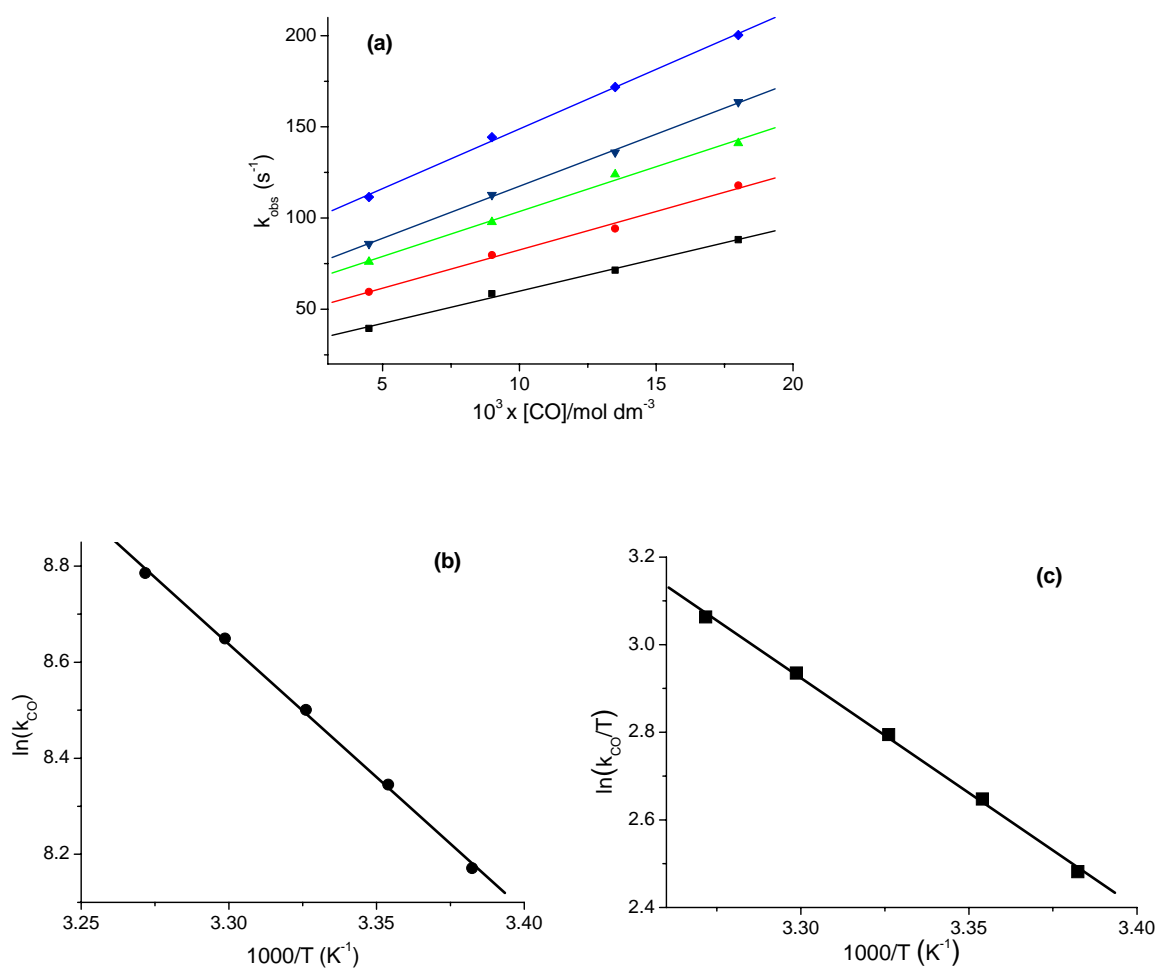
The distillate was then stirred over concentrated  $\text{H}_2\text{SO}_4$  overnight, washed with  $10 \times 10$  mL  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$ , filtered, and stored over NaK alloy under vacuum.



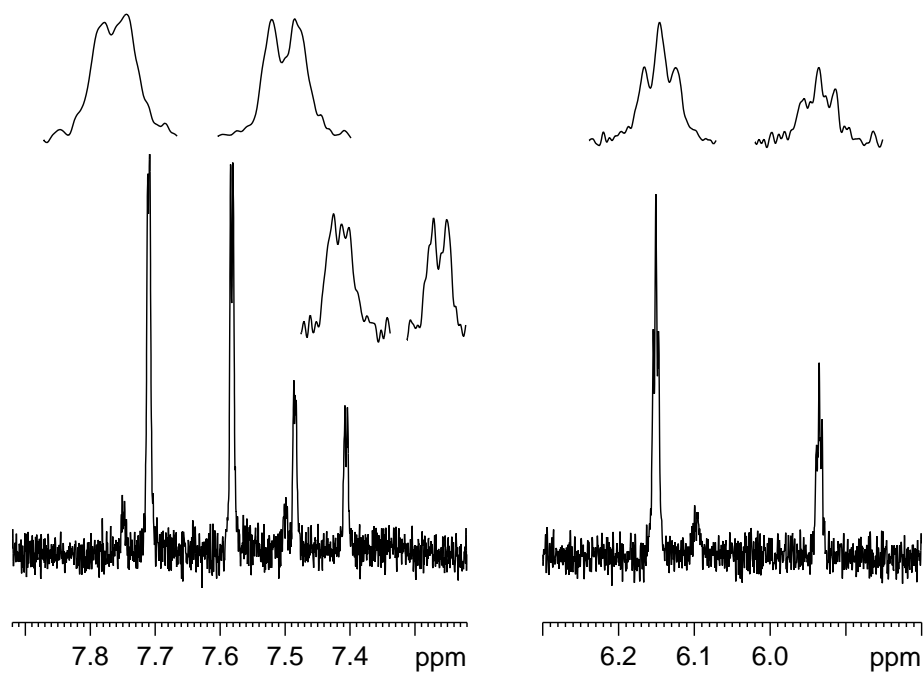
**NMR experiments using  $CpRe(CO)_3$  and  $C_5H_9D$  as solvent.** The solvent  $C_5H_9D$  has a  $^1H$  chemical shift of  $\delta$  1.49 in  $CDCl_3$ . The  $^{13}C\{^1H\}$  spectrum shows a three line pattern with resonances at  $\delta$  26.09, 25.98 and 25.71  $^2J_{HD} = 19.7$  Hz.

$CpRe(CO)_3$  (1 mg, 3  $\mu$ mol) was added to a Quartz NMR tube fitted with a J. Young Teflon stopcock and a graded glass seal. The tube was attached to a vacuum line ( $<1 \times 10^{-4}$  mbar) and evacuated for one hour.  $C_5H_9D$  was vacuum transferred into the tube at 77 K ( $\sim 0.3$  ml).

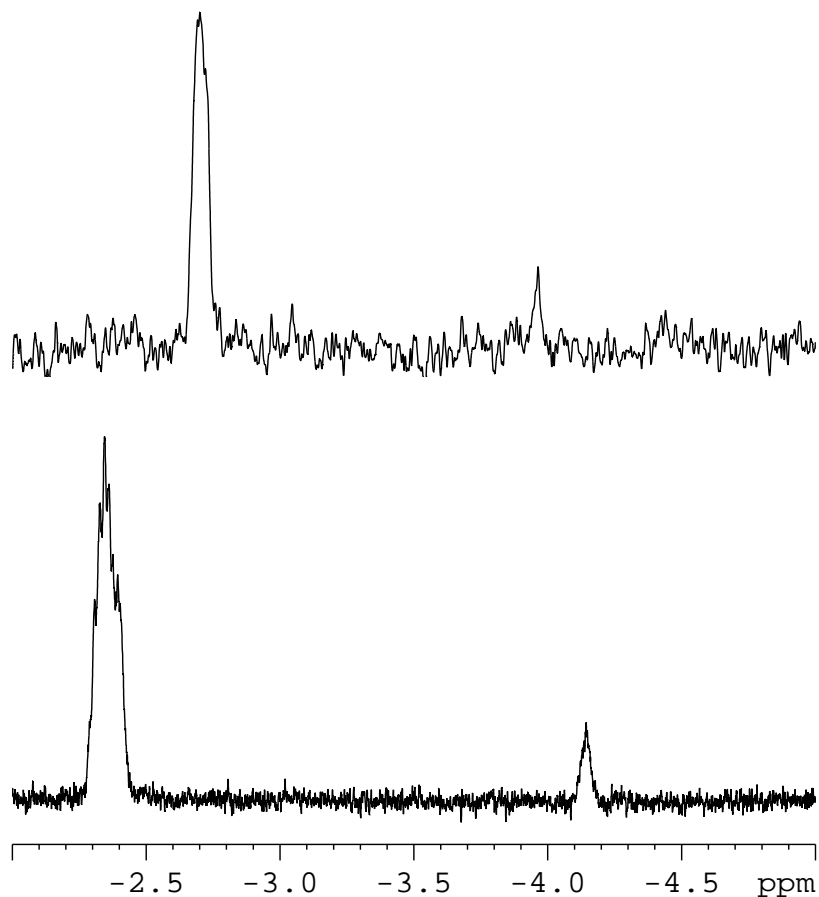
Photolysis of this sample within the NMR spectrometer at 266 nm while cooled to  $< 200$  K shows the expected resonance in the Cp region of the  $^1H$  NMR spectrum. In the hydride region new resonances are observed at  $\delta$   $-2.343$  (quartet,  $J_{HH} = 7.13$  Hz),  $-2.309$  (quintet,  $J_{HH} = 6.6$  Hz),  $-2.396$  (quartet,  $J_{HH} = 5.44$  Hz) and  $\delta$   $-4.153$  (quintet,  $J_{HH} = 6.10$  Hz, Fig. 3 of text). Modelling of the spin system around at  $\delta$   $-2.3$  suggests that it can be explained by intrinsic isotope shift as a perturbation from the  $C_5H_{10}$  spin system described by Ball et al. such that four isomers exists where the deuterium atom has been incorporated at a different position, and that exchange between these isomers is slow on the NMR time scale.



**Figure ESI 1:** (a) Plots of the pseudo first order rate constant ( $k_{obs}$ ) against the concentration of CO for the reaction  $TpRe(CO)_2(cyclo-C_5H_{10})$  with CO at various temperatures ( $\blacksquare$  22.5°C;  $\bullet$  25.0°C;  $\blacktriangle$  27.5°C;  $\blacktriangledown$  30.0°C;  $\blacklozenge$  32.5°C). These plots give the second order rate constant ( $k_{CO}$ ) for the reaction of  $TpRe(CO)_2(cC_5H_{10})$  with CO. The  $k_{CO}$  values at various temperatures can then be used to construct both Arrhenius (b) and Eyring (c) plots.



**Figure ESI 2.** Partial (Tp ligand resonances)  $^1\text{H}$  NMR spectrum (600 MHz, *cyclo*- $\text{C}_5\text{H}_{10}$ , 190 K)  $(\text{Tp})\text{Re}(\text{CO})_3$  after *in-situ* irradiation at 266 nm using Nd:YAG laser. Resolution enhanced using Gaussian function to reveal coupling.



**Figure ESI 3** Comparison of <sup>1</sup>H NMR spectra at 190 K of (Tp)Re(CO)<sub>2</sub>(C<sub>5</sub>H<sub>9</sub>D) (above) and CpRe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>9</sub>D) (Below)

## References

1 J. E. Joachim, C. Apostolidis, B. Kanellakopoulos, R. Maier, N. Marques, D. Meyer, J. Müller, A. P. de Matos, B. Nuber, J. Rebizant and M. L. Ziegler, *J. Organomet. Chem.*, 1993, **448**, 119.

2 To our knowledge, the solubility of CO in cyclopentane has not been determined. We have therefore used the value for the solubility of CO in cyclohexane. We have assumed that the solubility of CO in cyclopentane is unaffected over the small temperature range used in our studies to determine the activation parameters.

3 *IUPAC Solubility Data Series*, Pergamon Press, Oxford, 1990, Vol. 43.