

# The characterisation and reactivity of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{Xe})$ ( $\text{M} = \text{Nb}$ or $\text{Ta}$ ) in solution at room temperature

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Employing fast time-resolved infrared (TRIR) spectroscopy we have characterised  $\text{CpM}(\text{CO})_3(\text{Xe})$  ( $\text{M} = \text{Nb}$  or  $\text{Ta}$ ) at room temperature in supercritical Xe solution;  $\text{CpM}(\text{CO})_3(\text{Xe})$  were found to exhibit a similar reactivity with CO to the corresponding alkane complexes,  $\text{CpM}(\text{CO})_3(n\text{-heptane})$  and we report a trend in reactivity of the early transition metal Xe complexes.

Organometallic noble gas complexes have a long history. More than 20 years ago Perutz and Turner used matrix isolation to show that photolysis of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) in low temperature (12 K) matrices generated  $\text{M}(\text{CO})_5\text{L}$  ( $\text{L} = \text{Ar}, \text{Kr}, \text{Xe}$  or  $\text{CH}_4$ ).<sup>1</sup> Matrix isolation has subsequently been used to characterise a wide range of organometallic noble gas complexes.<sup>2–6</sup> Although matrix isolation is a powerful technique for the characterisation of unstable species at low temperature, it does not provide any kinetic information quantifying the reactivity of these species at room temperature.

Organometallic noble gas complexes have been observed in solution. Simpson *et al.* characterised  $\text{Cr}(\text{CO})_5(\text{Xe})$  in liquefied Xe (1Xe) at  $-98^\circ\text{C}$  using conventional FTIR spectroscopy following UV photolysis of  $\text{Cr}(\text{CO})_6$ .<sup>7</sup> Weiller extended this work, detecting  $\text{M}(\text{CO})_5\text{L}$  ( $\text{M} = \text{Cr}$  or  $\text{W}$ ;  $\text{L} = \text{Kr}$  or  $\text{Xe}$ ) in liquefied noble gas solution at low temperature using rapid-scan FTIR spectroscopy.<sup>8</sup> A similar approach was used to detect  $\text{Cp}^*\text{Rh}(\text{CO})\text{L}$  ( $\text{L} = \text{Kr}$  or  $\text{Xe}$ ).<sup>9–12</sup> Organometallic noble gas complexes have also been observed in the gas phase at room temperature<sup>13</sup> and theoretical studies have predicted Au–Xe bond dissociation energies (BDEs) up to  $127\text{ kJ mol}^{-1}$ .<sup>14</sup>

We have recently shown that organometallic noble gas complexes can be observed in fluid solution at room temperature following irradiation of transition metal carbonyls in supercritical fluids. Using fast TRIR spectroscopy we characterised  $\text{M}(\text{CO})_5\text{L}$  [ $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ;  $\text{L} = \text{Ar}$  ( $\text{W}$  only),  $\text{Kr}$  or  $\text{Xe}$ ]<sup>15</sup> and  $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2\text{L}$  [ $\text{M} = \text{Mn}$  or  $\text{Re}$ ;  $\text{R} = \text{H}, \text{Me}$  or  $\text{Et}$  ( $\text{Mn}$  only);  $\text{L} = \text{Kr}$  or  $\text{Xe}$ ].<sup>16,17</sup> The reactivity of these complexes increases in the order  $\text{Xe} < \text{Kr} < \text{Ar}$  and  $\text{Re} \approx \text{W} < \text{Mo} \approx \text{Cr} \approx \text{Mn}$ .

The comparison of reactivity between organometallic noble gas and alkane complexes is important. We reported  $\text{CpRe}(\text{CO})_2(n\text{-heptane})$  as being the longest lived alkane complex at room temperature<sup>16</sup> and this proved significant since Ball and Geftakis were subsequently able to characterise  $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$  at low temperature using NMR spectroscopy.<sup>18</sup>  $\text{CpRe}(\text{CO})_2(\text{Xe})$  was only twice as reactive towards CO in scXe compared to  $\text{CpRe}(\text{CO})_2(n\text{-heptane})$  in  $n\text{-heptane}$  solution.<sup>16</sup> Here, we investigate the photochemistry of the Group V complexes,  $\text{CpM}(\text{CO})_4$  ( $\text{M} = \text{Nb}$  or  $\text{Ta}$ ) in supercritical Xe at room temperature, and report a trend in reactivity for the early transition metal noble gas complexes.

Fig. 1(a) shows the TRIR spectrum† obtained 80 ns following 355 nm excitation of  $\text{CpNb}(\text{CO})_4$  in scXe (1940 psi,  $25^\circ\text{C}$ ) in the presence of CO (100 psi). The parent  $\nu(\text{CO})$  IR absorptions at  $2041$  and  $1936\text{ cm}^{-1}$  are bleached and new bands are produced at  $1986$  and  $1885\text{ cm}^{-1}$  which can be assigned to  $\text{CpNb}(\text{CO})_3(\text{Xe})$  by comparison with previous matrix isolation results<sup>19</sup> and the TRIR spectrum of the analogous  $n\text{-heptane}$

complex.<sup>20</sup> A similar experiment was performed with  $\text{CpTa}(\text{CO})_4$  dissolved in scXe (2070 psi,  $25^\circ\text{C}$ ) in the presence of CO (100 psi). The parent bands at  $2037$  and  $1929\text{ cm}^{-1}$  were bleached and new absorptions at  $1983$ ,  $1879(\text{sh})$  and  $1873\text{ cm}^{-1}$  were produced, which can be assigned to  $\text{CpTa}(\text{CO})_3(\text{Xe})$  [Fig. 1(b)]. In the presence of CO, the formation of  $\text{CpNb}(\text{CO})_3(\text{Xe})$  and  $\text{CpTa}(\text{CO})_3(\text{Xe})$  in scXe is completely reversible with no observable secondary photoproducts. This reversibility is demonstrated more clearly in Fig. 2, which shows the relevant TRIR kinetic decay traces. Fig. 2 also shows that the decay of  $\text{CpNb}(\text{CO})_3(\text{Xe})$  and  $\text{CpTa}(\text{CO})_3(\text{Xe})$  in scXe depends linearly on CO concentration and from these plots we estimate the second order rate constants for the reaction of  $\text{CpNb}(\text{CO})_3(\text{Xe})$  with CO [ $k_{\text{CO}} = 5.7 (\pm 0.6) \times 10^6\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ] and for  $\text{CpTa}(\text{CO})_3(\text{Xe})$  with CO [ $k_{\text{CO}} = 4.9 (\pm 0.5) \times 10^6\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ] in scXe.  $\text{CpNb}(\text{CO})_3(\text{Xe})$  and  $\text{CpTa}(\text{CO})_3(\text{Xe})$  have similar reactivities towards CO in scXe compared to the analogous alkane complexes,  $\text{CpNb}(\text{CO})_2(n\text{-heptane})$  and  $\text{CpTa}(\text{CO})_3(n\text{-heptane})$  in  $n\text{-heptane}$  solution (Table 1).

The reactivities of early transition metal noble gas and alkane complexes show several trends. Thus far we have found that for a given metal/ligand combination the reactivity of organometallic noble gas complexes towards CO is very similar ( $\approx \times 2\text{--}3$ ) to the reactivity of the corresponding alkane ( $n\text{-heptane}$ ) complex.<sup>15–17,21</sup> In our previous studies we have found that the alkane complexes decrease in reactivity on moving down the Periodic Table and on moving from Group V to Group VII. The results reported here further demonstrate the similarity of the reactivity of early transition metal organometallic xenon complexes to that of their corresponding alkane complexes (Table 1). Preliminary results‡ obtained with  $\text{CpV}(\text{CO})_4$

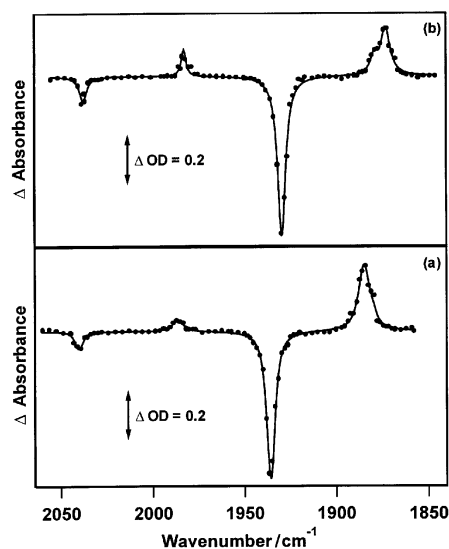
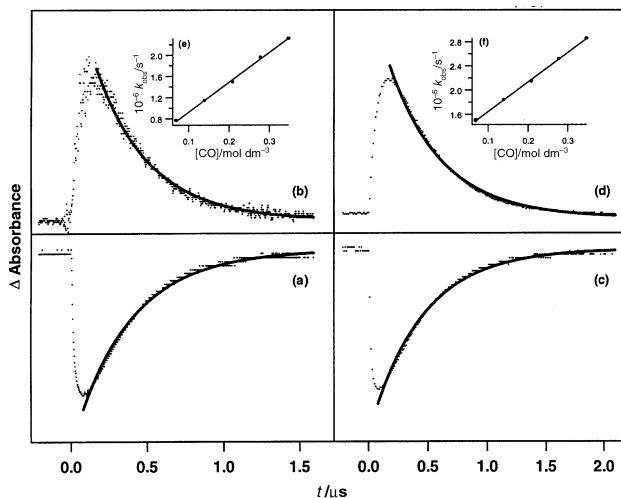


Fig. 1 (a) TRIR spectrum recorded 80 ns after 355 nm photolysis of  $\text{CpNb}(\text{CO})_4$  in scXe (1940 psi,  $25^\circ\text{C}$ ) in the presence of CO (100 psi). (b) TRIR spectrum recorded 150 ns after 355 nm photolysis of  $\text{CpTa}(\text{CO})_4$  in scXe (2070 psi,  $25^\circ\text{C}$ ) in the presence of CO (100 psi).



**Fig. 2** TRIR kinetic traces corresponding to (a) CpNb(CO)<sub>4</sub> (1936.4 cm<sup>-1</sup>), (b) CpNb(CO)<sub>3</sub>(Xe) (1883.9 cm<sup>-1</sup>), (c) CpTa(CO)<sub>4</sub> (1929.7 cm<sup>-1</sup>) and (d) CpTa(CO)<sub>3</sub>(Xe) (1875.3 cm<sup>-1</sup>) obtained from the experiments shown in Fig. 1. Plots of observed decay rates of (e) CpNb(CO)<sub>3</sub>(Xe) and (f) CpTa(CO)<sub>3</sub>(Xe) vs. CO concentration in scXe.

**Table 1** Second order rate constants,  $k_{\text{CO}}$  (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), for the reaction of early transition metal–xenon and *n*-heptane complexes with CO in scXe and *n*-heptane solution, respectively, at 298 K

| V   | VI                                     | VII                                      |
|---|--|--|
| CpV(CO) <sub>3</sub> (Xe)                 | Cr(CO) <sub>5</sub> (Xe) <sup>d</sup>  | CpMn(CO) <sub>2</sub> (Xe) <sup>f</sup>  |
| —   | 8.4 × 10 <sup>6</sup>                  | 1.6 × 10 <sup>6</sup>                    |
| CpV(CO) <sub>3</sub> (hep) <sup>a,b</sup> | Cr(CO) <sub>5</sub> (hep) <sup>e</sup> | CpMn(CO) <sub>2</sub> (hep) <sup>f</sup> |
| 1.3 × 10 <sup>8</sup>                     | 9.3 × 10 <sup>6</sup>                  | 8.1 × 10 <sup>5</sup>                    |
| CpNb(CO) <sub>3</sub> (Xe)                | Mo(CO) <sub>5</sub> (Xe) <sup>d</sup>  | —  |
| 5.7 × 10 <sup>6</sup>                     | 1.1 × 10 <sup>7</sup>                  | —  |
| CpNb(CO) <sub>3</sub> (hep) <sup>c</sup>  | Mo(CO) <sub>5</sub> (hep) <sup>e</sup> | —  |
| 4.5 × 10 <sup>6</sup>                     | 7.8 × 10 <sup>6</sup>                  | —  |
| CpTa(CO) <sub>3</sub> (Xe)                | W(CO) <sub>5</sub> (Xe) <sup>d</sup>   | CpRe(CO) <sub>2</sub> (Xe) <sup>g</sup>  |
| 4.9 × 10 <sup>6</sup>                     | 2.0 × 10 <sup>6</sup>                  | 4.8 × 10 <sup>3</sup>                    |
| CpTa(CO) <sub>3</sub> (hep) <sup>c</sup>  | W(CO) <sub>5</sub> (hep) <sup>e</sup>  | CpRe(CO) <sub>2</sub> (hep) <sup>g</sup> |
| 2.0 × 10 <sup>6</sup>                     | 1.8 × 10 <sup>6</sup>                  | 2.0 × 10 <sup>3</sup>                    |

<sup>a</sup> hep = *n*-heptane. <sup>b</sup> Ref. 20. <sup>c</sup> Ref. 23. <sup>d</sup> Ref. 15. <sup>e</sup> Ref. 24. <sup>f</sup> Ref. 17. <sup>g</sup> Ref. 16.

suggest that CpV(CO)<sub>3</sub>(Xe) also fits into this trend. The similarity between the reactivity of alkane and noble gas complexes towards CO is surprising since for a given metal/ligand system the BDE for a metal–xenon bond is expected to be significantly less than that of the corresponding metal–heptane bond. For example, the W–Xe BDE in W(CO)<sub>5</sub>(Xe) (34.3 kJ mol<sup>-1</sup>) determined from gas phase studies<sup>13</sup> is significantly less than the W–heptane BDE in W(CO)<sub>5</sub>(*n*-heptane) (62.8 kJ mol<sup>-1</sup>) estimated from photoacoustic calorimetry measurements.<sup>22</sup> Detailed kinetic studies on Group VII xenon and alkane complexes<sup>17,21</sup> suggested that the early transition metal xenon complexes react with CO in scXe by a different mechanism than the early transition metal *n*-heptane complexes in *n*-heptane.

In conclusion, there is a general decrease in reactivity of the early transition metal xenon complexes, similar to that observed for the analogous alkane complexes, upon moving down the Periodic Table and on moving from Group V to Group VII, resulting in CpRe(CO)<sub>2</sub>(Xe) being the least reactive transition metal xenon complex reported so far. It is therefore hoped that the similar reactivity of CpRe(CO)<sub>2</sub>(*n*-heptane) and CpRe(CO)<sub>2</sub>(Xe) will make the characterisation of an organometallic

xenon complex by low temperature NMR a realistic possibility. There is clearly still much to learn about organometallic alkane and noble gas complexes and it is likely that TRIR spectroscopy will prove increasingly useful for this purpose.

## Notes and references

† The TRIR experiments used a cw IR diode laser to monitor temporal changes in IR absorbance following 355 nm excitation by a Nd:YAG laser (Quanta-Ray GCR-12S, 7 ns pulse). IR spectra were built up on a ‘point-by-point’ basis by repeating this measurement at different IR frequencies. See: M. W. George and J. J. Turner, *Analyst*, 1994, **119**, 551 for further details.

‡ Initial TRIR kinetic decay studies on CpV(CO)<sub>3</sub>(Xe) in scXe show that CpV(CO)<sub>3</sub>(Xe) and CpV(CO)<sub>3</sub>(*n*-heptane) have a similar reactivity towards CO. However we have not been able to obtain, to our satisfaction, a linear behaviour of the rate of decay of CpV(CO)<sub>3</sub>(Xe) with respect to CO concentration in scXe.

- R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4791.
- M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1974, 2276.
- S. A. Fairhurst, J. R. Morton, R. N. Perutz and K. F. Preston, *Organometallics*, 1984, **3**, 1389.
- M. Brookhart, W. Chandler, R. J. Kessler, Y. Liu, N. J. Pienta, C. C. Santini, C. Hall, R. N. Perutz and J. A. Timney, *J. Am. Chem. Soc.*, 1992, **114**, 3802.
- R. J. Mawby, R. N. Perutz and M. K. Whittlesey, *Organometallics*, 1995, **14**, 3268.
- M. K. Whittlesey, R. N. Perutz, I. G. Virrels and M. W. George, *Organometallics*, 1997, **16**, 268.
- M. B. Simpson, M. Poliakoff, J. J. Turner, W. B. Maier II. and J. G. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1983, 1355.
- B. H. Weiller, *J. Am. Chem. Soc.*, 1992, **114**, 10910.
- B. H. Weiller, E. P. Wasserman, R. G. Bergman, C. B. Moore and G. C. Pimentel, *J. Am. Chem. Soc.*, 1989, **111**, 8288.
- R. H. Schultz, A. A. Bengali, M. J. Tauber, B. H. Weiller, E. P. Wasserman, K. R. Kyle, C. B. Moore and R. G. Bergman, *J. Am. Chem. Soc.*, 1994, **116**, 7369.
- A. A. Bengali, R. H. Schultz, C. B. Moore and R. G. Bergman, *J. Am. Chem. Soc.*, 1994, **116**, 9585.
- B. H. Weiller, E. P. Wasserman, C. B. Moore and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 4326.
- J. R. Wells and E. Weitz, *J. Am. Chem. Soc.*, 1992, **114**, 2783.
- D. Schröder, H. Schwarz, J. Hrusák and P. Pykkö, *Inorg. Chem.*, 1998, **37**, 624.
- X. Z. Sun, M. W. George, S. G. Kazarian, S. M. Nikiforov and M. Poliakoff, *J. Am. Chem. Soc.*, 1996, **118**, 10525.
- X. Z. Sun, D. C. Grills, S. M. Nikiforov, M. Poliakoff and M. W. George, *J. Am. Chem. Soc.*, 1997, **119**, 7521.
- D. C. Grills, X.-Z. Sun, G. I. Childs and M. W. George, *J. Phys. Chem. A*, 2000, **104**, 4300.
- S. Geftakis and G. E. Ball, *J. Am. Chem. Soc.*, 1998, **120**, 9953.
- T. E. Bitterwolf, S. Gallagher, J. T. Bays, B. Scallorn, A. L. Rheingold, I. A. Guzei, L. LiableSands and J. C. Linehan, *J. Organomet. Chem.*, 1998, **557**, 77.
- M. W. George, M. T. Haward, P. A. Hamley, C. Hughes, F. P. A. Johnson, V. K. Popov and M. Poliakoff, *J. Am. Chem. Soc.*, 1993, **115**, 2286.
- G. I. Childs, C. S. Colley, J. Dyer, D. C. Grills, X.-Z. Sun, J. Yang and M. W. George, *J. Chem. Soc., Dalton Trans.*, 2000, 1901.
- D. P. Burney and T. J. Burkey, *Abstr. Pap. Am. Chem. Soc.*, 1994, **207**, 19.
- The previously reported values of  $k_{\text{CO}}$  were slightly higher than these (see ref. 20). The earlier values were calculated by measuring  $k_{\text{obs}}$  at only one concentration of CO and using the relationship,  $k_{\text{obs}} = k_{\text{CO}}[\text{CO}] + k_{\text{Ar}}$  to obtain  $k_{\text{CO}}$ , where  $k_{\text{Ar}}$  is the observed rate constant in the absence of added CO. We have repeated the determination of these values by using a more accurate method in which  $k_{\text{obs}}$  is measured at a series of CO concentrations and  $k_{\text{CO}}$  is obtained from the slope of the resulting plot.
- C. J. Breheny, J. M. Kelly, C. Long, S. O’Keeffe, M. T. Pryce, G. Russell and M. M. Walsh, *Organometallics*, 1998, **17**, 3690.