

# High pressure NMR flow cell for the *in situ* study of homogeneous catalysis

Jonathan A. Iggo,\* Darren Shirley and Nicola C. Tong

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool,  
PO Box 147, Liverpool, UK L69 7ZD

Letter

A novel, convenient high pressure NMR flow cell for the *in situ* study of homogeneous catalysis capable of operating over the pressure range 1 to 200 bar and temperature range  $-40$  to  $175^{\circ}\text{C}$  is described; importantly, the inlet gas passes through the reaction solution ensuring good gas–solution mixing and maintaining the concentration of reacting gas in the solution thus preventing starvation of the reaction of gaseous reagents; the cell has been used to study the reaction of a rhodium–ruthenium bimetallic complex with CO.

The characterisation of the processes occurring in a homogeneously catalysed reaction can be of great importance both to the efficient operation of existing processes and to the development of new and/or improved processes. It has been recognised that in the *in situ* spectroscopic study of such reactions not only must the gas over-pressure be controlled but, crucially, the concentration of dissolved gases must be maintained. Thus, for example, the BP–Monsanto reaction will consume most of the dissolved CO in a sealed sample in a few minutes resulting in CO starvation leading to deactivation and decomposition of the catalyst.<sup>1</sup>

Several *in situ* high pressure NMR cells have been described and used to obtain valuable insight into organometallic chemistry under high gas pressure.<sup>2–8</sup> Of these, the “sapphire tube” or Roe cell has proved extremely popular since it is simple and convenient to use.<sup>3,9,10</sup> However, it suffers from small sample volumes and gas–solution mixing is only possible by physically shaking the tube containing a high pressure of gas, a process that must be repeated frequently during the experiment if the concentration of dissolved gas is to be maintained. The small gas head space can result in large pressure drops in a reacting system; thus gas starvation of the reaction is an important concern. The problem of gas–solution mixing has been addressed by the elegant designs of Jonas and Vander Velde<sup>4</sup> and of Merbach and co-workers<sup>5</sup> that use “flip-flop” stirrers essentially similar to that initially employed by Whyman and co-workers<sup>11</sup> to achieve mixing in high pressure IR cells, and by Rathke *et al.*<sup>6</sup> whose design circulates the reaction solution between a conventional autoclave and a high pressure NMR cell. Whilst these designs are effective solutions to the problem of gas–solution mixing, our experience is that high pressure NMR cells built inside metal pressure vessels require great skill in their design, maintenance and operation.<sup>2</sup> A simpler system that combines the ease of use of Roe’s sapphire tube with good gas–solution mixing and a large sample volume is shown in Fig. 1 and 2. This cell uses a sapphire tube supported between, and sealed using elastomer O-rings to, two titanium flanges. The maximum operating pressure of this arrangement is determined by the elastomer used, the tube internal diameter and the thickness of the sapphire tube walls; an i.d. of 1.06 cm and wall thickness of 0.081 cm gives a theoretical burst pressure in excess of 600 bar at  $25^{\circ}\text{C}$  and has been tested by us to 190 bar. Our design places the flow cell inside an outer aluminium sleeve (o.d. 7 cm length 42 cm), Fig. 2, protecting the sapphire tube from mechanical damage and allowing the use of relatively thin walled tubes thus maximising sample volume and hence

signal-to-noise ratio. The dimensions of the outer sleeve are close to those of a standard wide-bore Bruker NMR probe and allow our cell to be used inside a standard Bruker wide-bore shim set.

A notable feature of the design is that the inlet gas passes through the reaction solution providing a constant stream of gas bubbles through the solution ensuring both good mixing and maintaining the concentration of dissolved gases. Provided that a positive pressure is maintained at the base of the probe with respect to the gas head space, leakage of solvent down the feed lines is not problematic. Fig. 3 shows time lapse series of  $^1\text{H}$  NMR spectra comparing the dissolution of  $\text{H}_2$  in  $\text{CDCl}_3$ , containing 5%  $\text{CHCl}_3$  as an internal standard, for a sample placed directly inside the high pressure (HP) NMR cell, Fig. 3 (flow), and for a sample contained in an open topped sample tube placed inside the HPNMR cell, Fig. 3 (contained). In the flow experiment the pressurizing gas bubbles through the solvent whilst in the contained experiment gas dissolution relies solely on diffusion into the sample. Fig. 3 (flow) clearly shows dissolved  $\text{H}_2$   $\delta$  ca. 4.7 from the start of the flow experiment, the intensity of the resonance due to dissolved gas increasing in line with the increase in pressure.

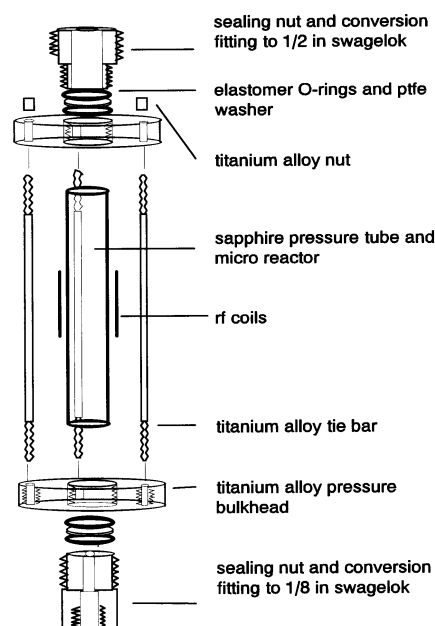


Fig. 1 Exploded view of the high pressure *in situ* NMR flow cell

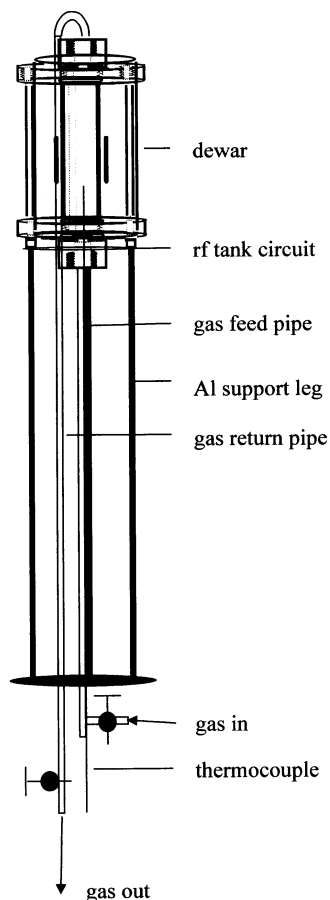


Fig. 2 Assembled view of the high pressure *in situ* NMR flow cell

In the contained sample, Fig. 3 (contained), however, almost no  $H_2$  has dissolved by the end of the pressurisation period. Even after standing 12 h at 90 bar the sample contains only half as much dissolved gas compared with the amount of gas immediately dissolved during pressurisation of the sample placed directly in the flow cell.

The inlet and outlet gas flow rates are controlled by Brooks mass flow controllers and are adjusted to ensure a constant pressure inside the cell and to minimise degradation of the resolution. Fig. 4 compares the resolution achieved in the  $^{31}P$  NMR spectrum of a sample of  $P(OMe)_3$  in toluene under 30 bar  $N_2$  pressure in the absence of gas flow and with a gas flow

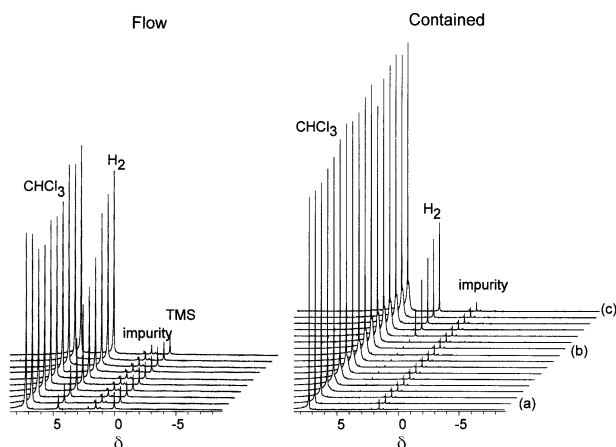


Fig. 3 Time lapse  $^1H$  NMR spectra of  $H_2$  dissolving in  $CDCl_3$ - $CHCl_3$  (95 : 5) during pressurisation of the HPNMR flow cell or contained in an open topped tube inside the flow cell; (a)–(b) during pressurisation at  $ca\ 1.5\ bar\ min^{-1}$  to 90 bar, then (b)–(c) every two hours at 90 bar

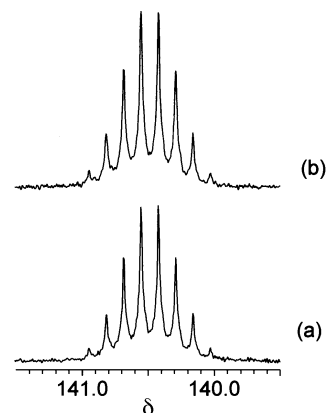


Fig. 4 The  $^{31}P$  NMR spectrum of a sample of  $P(OMe)_3$  in toluene under 30 bar  $N_2$  pressure, (a) in the absence of gas flow and (b) with a gas flow rate of  $10\ NI\ h^{-1}$

rate of  $10\ NI\ h^{-1}$  (where  $1\ NI = 1\ l\ at\ STP$ ) and shows minimal loss of resolution or signal-to-noise in the sample which has gas bubbling through it during acquisition of the free induction decay. Typical linewidths at half-height are  $<1\ Hz$  on  $^2H$ ,  $<2\ Hz$  on  $^{31}P$ ,  $<4\ Hz$  on  $^1H$ . The r.f. circuitry employs conventional tank circuits and the probe achieves  $90^\circ$  pulse lengths, resolution and sensitivities comparable with conventional, commercial broadband probes (using non-spinning samples).

One of us has previously reported a high pressure IR study of the reactions of a series of ruthenium–rhodium compounds  $[(C_5H_5)Ru(\mu-CO)_2(\mu-LL)RhX_2]$ ,  $\{LL = Ph_2PCH_2PPh_2, Me_2PCH_2PMe_2, \text{ or } PPh_2C(=CH_2)PPh_2, X = Cl \text{ or } I\}$  with  $CO$ .<sup>12</sup> These bimetallic complexes were found to fragment to mononuclear species  $[(C_5H_5)Ru(CO)_2(\eta^1-LL)]^+$  and  $[Rh(CO)_2X_2]^-$ . No intermediates were detected.

We have now investigated the reaction of  $[(C_5H_5)Ru(\mu-CO)_2(\mu-dcpm)RhCl_2]$ ,  $[dcpm = (C_6H_{11})_2PCH_2P(C_6H_{11})_2]$ , **1**, with  $CO$  using our *in situ* NMR probe and have found an

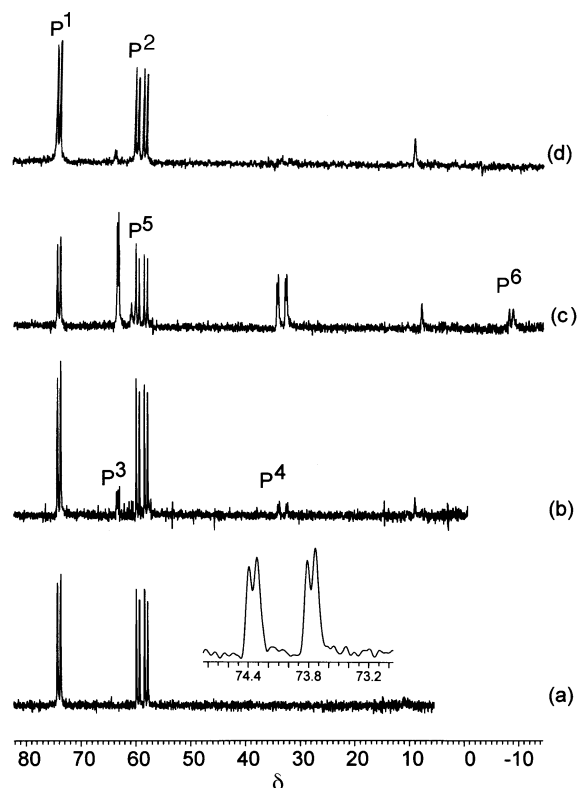
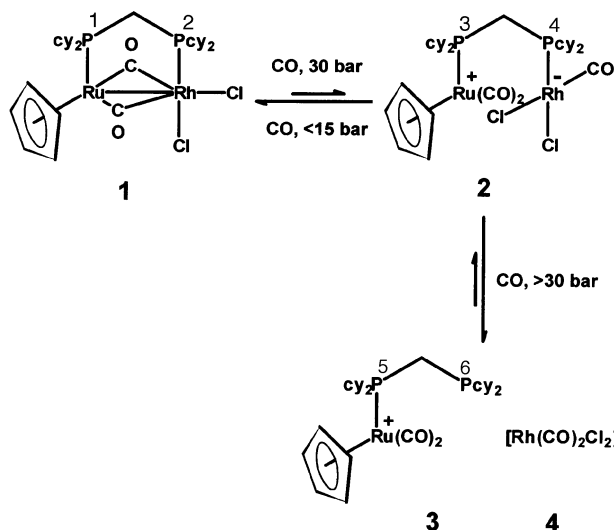


Fig. 5 *In situ*  $^{31}P$  NMR spectra of  $[(C_5H_5)Ru(\mu-CO)_2(\mu-dcpm)RhCl_2]$  **1** reacting with  $CO$ . (a) 1 atm  $N_2$ , (b) 30 atm  $CO$ , (c) 90 atm  $CO$ , (d) 15 atm  $CO$ . See Scheme 1 for assignments



**Scheme 1** Reaction of **1** with CO as revealed by *in situ* NMR spectroscopy. The position of equilibrium depends on the applied CO pressure; cy = C<sub>6</sub>H<sub>11</sub>

additional species to those reported previously<sup>12</sup> and that the species present in solution (as determined by *in situ*, high pressure NMR spectroscopy) depend on the applied gas pressure.

Fig. 5(a)–(d) shows the *in situ* <sup>31</sup>P NMR spectra of the reaction of **1** in toluene with CO.† The <sup>31</sup>P NMR spectrum of **1**, Fig. 5(a), shows two doublets of doublets, at δ 74.0 due to P<sup>1</sup> and at 59.3 due to P<sup>2</sup> (see Scheme 1 for the labelling scheme). Under 30 bar of CO new resonances attributable to the metal–metal bond-cleaved dinuclear species [ $\{(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2\}^+(\mu\text{-dcpm})\{\text{Rh}(\text{CO})\text{Cl}_2\}^-$ ] **2**, P<sup>3</sup> and P<sup>4</sup> are visible in addition to those of **1**, Fig. 5(b). The resolution achieved in these spectra allowed <sup>3</sup>J<sub>PRh</sub> = 6 Hz to be determined. On increasing the CO pressure to 90 bar cleavage of the dinuclear species to mononuclear species [ $(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\eta^1\text{-dcpm})$ ]<sup>+</sup> **3**, P<sup>5</sup> and P<sup>6</sup>, and  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$  **4** (the latter confirmed by *in situ* IR spectroscopy<sup>13</sup>) occurs, Fig. 5(c). The reaction is reversible, **3**

† <sup>31</sup>P NMR (80.3 MHz, CDCl<sub>3</sub>) spectroscopic data for the complexes: [ $(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-dcpm})\text{RhCl}_2$ ] **1**, δ 74.0 (dd, <sup>2</sup>J<sub>PP</sub> 47 Hz, <sup>3</sup>J<sub>RhP</sub> 6 Hz), δ 59.3 (dd, <sup>2</sup>J<sub>PP</sub> 47 Hz, <sup>1</sup>J<sub>RhP</sub> 121 Hz); [ $\{(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2\}^+(\mu\text{-dcpm})\{\text{Rh}(\text{CO})\text{Cl}_2\}^-$ ] **2**, δ 63.2 (dd, <sup>2</sup>J<sub>PP</sub> 22 Hz, <sup>3</sup>J<sub>RhP</sub> 6 Hz), δ 33.3 (dd, <sup>2</sup>J<sub>PP</sub> 22 Hz, <sup>1</sup>J<sub>RhP</sub> 123 Hz); [ $(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\eta^1\text{-dcpm})$ ]<sup>+</sup> **3**, δ 60.6 (d, <sup>2</sup>J<sub>PP</sub> 55 Hz), δ –8.7 (d, <sup>2</sup>J<sub>PP</sub> 55 Hz).

and **4** recombine essentially quantitatively to give **1** on reducing the CO pressure to 15 bar, Fig. 5(d), highlighting the importance of studying reactions *in situ*; an *ex situ* analysis would have indicated that no change had taken place. This reaction closely follows the scheme proposed by Bearman *et al.* on the basis of *in situ* IR measurements for the reaction of [ $(\text{C}_5\text{Me}_5)\text{Ru}(\mu\text{-CO})_2(\mu\text{-LL})\text{RhX}_2$ ] with CO although in those cases a metal–metal bond-cleaved dinuclear species analogous to **2** could not be identified.<sup>12</sup>

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