Carbon-13 N.M.R. Study of Rhodium Carbonyl Clusters under High Pressures of CO/H_2

By B. T. HEATON*
(*The Chemical Laboratory, The University of Kent, Canterbury* CT2 7NH)

and J. JONAS,* T. EGUCHI, and G. A. HOFFMAN
(*Department of Chemistry, School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois* 61801)

Summary High-pressure ^{13}C n.m.r. spectra (850 bar, CO:H_2 = 2·1:1) show that $[Rh_{12}(CO)_{30}]^{2-}$ is converted cleanly into $[Rh_5(CO)_{15}]^-$ and that interexchange of carbonyls with carbon monoxide under high pressure is slow on the n.m.r. time scale.

THE pentanuclear cluster, $[Rh_5(CO)_{15}]^-$, has recently been isolated from the low-pressure (*ca.* 10 bar) reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with carbon monoxide.[1] Because of the involvement of this cluster in the catalytic synthesis of ethylene glycol from synthesis gas,[1,2] it was of interest to monitor this reaction by ^{13}C n.m.r. spectroscopy at higher pressures of carbon monoxide and in the presence of hydrogen to see whether other species are formed. Only two other high-pressure ^{13}C n.m.r. measurements have been reported; one involves a high resolution study of $^{13}CH_4$ in a capillary tube[3] and the other a low resolution study of ^{13}CO.[4] This present paper is the first high resolution–high pressure ^{13}C n.m.r. experiment aimed at providing structural information on species produced in solution on gas pressurisation.

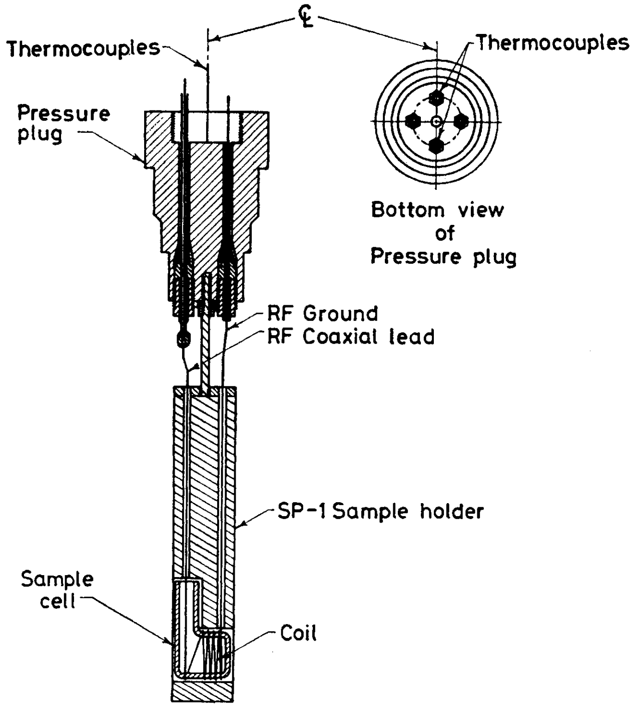

FIGURE 1. Assembly drawing for the high resolution–high pressure n.m.r. probe.

The n.m.r. probe is shown schematically in Figure 1 and is a modification of one previously used for hydrostatic pressurisation.[5] It consists of an open cell within a Helmholtz coil (4 turns of heavy armoured polythermaleze copper wire, 20 S.W.G.) which are both inside a 5 kbar titanium alloy pressure vessel (o.d. = 5·7 cm; i.d. = 1·4 cm); Macor was used to reduce the dead volume inside the pressure vessel to 6 ml. The probe allows the reaction to be monitored continuously with varying pressure and temperature† and incorporates a cell with sufficient volume (1 ml) to allow observation of ^{13}C n.m.r. spectra of transition metal carbonyl clusters.

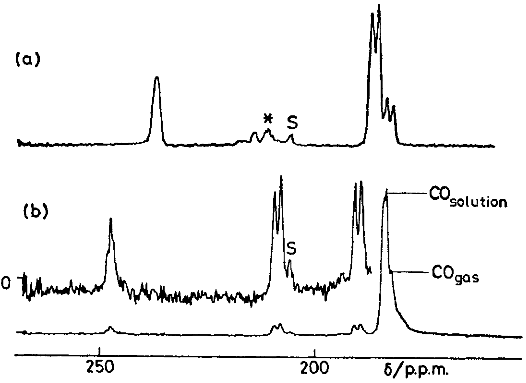

FIGURE 2. 45·2 MHz ^{13}C n.m.r. spectra in a high-pressure probe (a) $(NMe_3C_6H_4CH_2)_2[Rh_{12}(CO)_{30}]$ at −40 °C in $(CD_3)_2CO$, (b) after pressurising (850 bar) with CO/H_2 (2·1:1; 13·7% ^{13}CO) at −32·8 °C. S = solvent, * = impurity, $[Rh_6(CO)_{15}]^{2-}$.

The 45·2 MHz ^{13}C n.m.r. spectrum of $(NMe_3C_6H_4CH_2)_2$-$[Rh_{12}(CO)_{30}]$ in this high pressure cell, (Figure 2a), has good signal/noise ratio (50:1) and resolution (*ca.* 25 Hz)‡ and is similar to that obtained previously on a conventional high resolution spectrometer.[6] Upon pressurising with up to 575 bar of CO (13·7% ^{13}CO) at −52 °C, there is a progressive transformation of $[Rh_{12}(CO)_{30}]^{2-}$ into $[Rh_5(CO)_{15}]^-$ but, even after *ca.* 24 h under 77 bar of CO and 3 h under

---

† The pressure vessel can be used over the temperature ranges 213—298 and 298—523 °C, but the higher temperatures have not yet been studied with this probe design.

‡ At room temperature the resonance at 211·1 p.p.m. is clearly resolved into a triplet [^1J(Rh–CO) 38 Hz] but broadens on decreasing the temperature due to an increase in viscosity.

575 bar of CO, there is still evidence for unchanged $[Rh_{12}(CO)_{30}]^{2-}$; there is no change in the spectrum at this temperature on further pressurising with H_2 ($P_{total} = 850$ bar; $CO:H_2 = 2{\cdot}1:1$). Warming to room temperature, followed by cooling to −32·8 °C, results in complete formation of $[Rh_5(CO)_{15}]^-$ (Figure 2b); this spectrum is similar to that obtained previously, but, in addition to the resonance due to $CO_{solution}$ at 184·3 p.p.m., there is a resonance due to CO_{gas} at 182·0 p.p.m. At room temperature, the spectrum under 1000 bar of CO/H_2 (2·1 : 1) is similar to that obtained under 10 bar of CO and consists of a resonance at 247·5 p.p.m. due to the equatorial edge-bridging carbonyls and a broad resonance at *ca.* 200 p.p.m. due to the remaining carbonyls undergoing intramolecular exchange.

It is significant that, even under such high pressures of CO, exchange of carbonyls with CO is *not* fast on the n.m.r. time-scale at low temperatures. Thus, high-pressure n.m.r. studies offer the possibility of structural identification of intermediates formed under extreme conditions of industrial interest and further studies of potential catalytic systems are underway.

We thank the S.R.C., the National Science Foundation, and the Department of Energy for funds. We also thank Professor J. R. Shapley for laboratory facilities.

(*Received, 12th January* 1981; *Com.* 029.)

[1] A. Fumagalli, T. F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, **102**, 1740.
[2] J. Vidal and W. E. Walker, *Inorg. Chem.*, 1980, **19**, 896.
[3] N. J. Trappeniers and J. G. Oldenziel, *Physica* (*Utrecht*), 1976, **83**A, 173.
[4] E. Fukushima, A. A. V. Gibson, and T. A. Scott, *J. Chem. Phys.*, 1977, **66**, 4811.
[5] J. Jonas, D. L. Hasha, W. J. Lamb, G. A. Hoffman, and T. Eguchi, *J. Magn. Reson.*, in the press.
[6] B. T. Heaton, L. Strona, P. Chini, and S. Martinengo, *J. Organomet. Chem.*, 1980, **194**, C29.