Carbon-13 Nuclear Magnetic Resonance Studies of Rhodium Carbonyl Clusters on Pressurization with CO/H_2

By **Brian T. Heaton** * and **Luisella Strona**, Chemical Laboratory, The University of Kent, Canterbury CT2 7NH
Jiri Jonas,* Taro Eguchi, and **Greg A. Hoffman**, Department of Chemistry, School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.

Carbon-13 n.m.r. measurements on rhodium carbonyl clusters in solutions under high pressures of gaseous CO/H_2 are reported. Pressurization of solutions of $[Rh_{12}(CO)_{30}]^{2-}$ with CO (5 bar) shows that $[Rh_5(CO)_{15}]^-$ is formed quantitatively and that, below 298 K, further fragmentation does not occur on pressurization up to 1 kbar with CO/H_2. Variable-temperature measurements on $[Rh_5(CO)_{15}]^-$ show that the rate of inter-exchange of carbonyls with carbon monoxide at high pressure is slow on the n.m.r. time-scale and that, at room temperature, all the carbonyls, except the three bridging the Rh_3 equatorial plane, undergo intra-exchange. At high ^{13}C enrichments, the resonance due to the equatorial bridging carbonyls becomes complex due to an increasing abundance of isotopomers, $Rh_3(\mu\text{-}^{12}CO_{eq.})_{3-x}(\mu\text{-}^{13}CO_{eq.})_x$ (x = 0—3), with larger values of x for which $^2J(C_{eq.}\text{–}C_{eq})$ = 20 Hz. Despite claims to the contrary, the apex-connected, double-octahedral metallic skeleton in $[Rh_{12}(CO)_{30}]^{2-}$ remains intact up to 323 K under a nitrogen atmosphere. The high-resolution n.m.r. probe for measurements on solutions under 1 kbar pressures of CO and H_2 gases is described.

HOMOGENEOUS catalysts usually function at elevated pressures and temperatures.[1,2] Hitherto, high-pressure i.r. spectroscopy has been used to monitor these reactions but unambiguous structural identification of catalytic intermediates is often not possible from such studies. In order to overcome this problem, we are developing high-resolution multinuclear Fourier-transform n.m.r. probes for studying reactions in solution under high pressures of various gases.

Of particular interest in this area is the catalytic synthesis of ethylene glycol from CO/H_2 using rhodium carbonyls as catalyst;[3] this reaction is carried out at *ca.* 1 000 bar † CO/H_2 (1 : 1) and *ca.* 493 K. At low to ambient temperature, $[Rh_{12}(CO)_{30}]^{2-}$ fragments[4] under 5 bar of CO as shown in equation (1) (thf = tetrahydrofuran).

$$3\,[Rh_{12}(CO)_{30}]^{2-} \xrightarrow[\text{thf}]{\text{CO (5 bar)}} 6\,[Rh_5(CO)_{15}]^- + [Rh_6(CO)_{16}] \qquad (1)$$

High-pressure i.r. studies suggest that $[Rh_5(CO)_{15}]^-$ does not react further with higher pressures of CO/H_2 at $\leqslant$583 K[5] and a preliminary report on high-pressure ^{13}C n.m.r. measurements of this reaction at 850 bar of CO/H_2 shows that further fragmentation does not occur.[6] We now describe in detail the ^{13}C n.m.r. probe and associated equipment used for these high-pressure measurements together with the ^{13}C n.m.r. spectra of the above rhodium carbonyl clusters at variable temperatures and variable pressures of gas. This specific probe can presently only be used over the temperature range 213—298 K, because of hydrogen-embrittlement problems associated with the titanium alloy pressure vessel, but modifications to allow measurements at higher temperatures are in progress.

EXPERIMENTAL

Carbon-13 and $^{13}C\text{-}\{^{103}Rh\}$ n.m.r. spectra on solutions under $<$10 bar of gas were measured in thick-walled glass n.m.r. tubes on a conventional JEOL PS-100 spectrometer as described preciously.[7] For $\delta(^{103}Rh)$, 0 p.p.m. = 3.16 MHz at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 100 MHz. High-resolution ^{13}C n.m.r. spectra at high pressures of gas were measured on a spectrometer based on a wide-bore (12.7 cm), superconducting magnet made by Oxford Instruments Inc., operating at a proton frequency of 180 MHz.[8]

High-pressure N.M.R. Probe.—The high-pressure n.m.r. probe, as shown schematically in Figure 1, is a modification of the high-resolution, high-pressure n.m.r. probe described

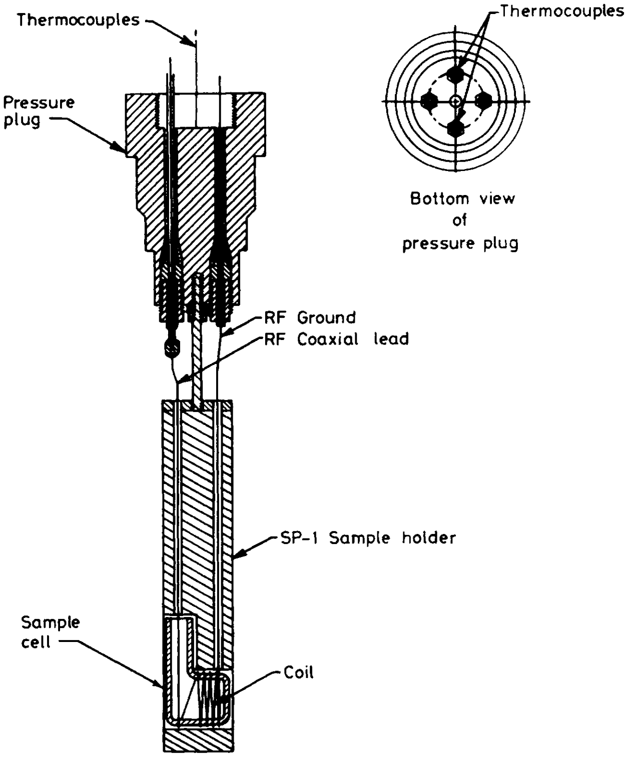


FIGURE 1 Assembly drawing for the high-resolution, high-pressure ^{13}C n.m.r. probe

---

† Throughout this paper: 1 bar = 10^5 Pa; 1 p.s.i. ≈ 6 895 Pa; 20 s.w.g. (standard wire gauge) = 3.6 × 10^{-2} in.

earlier. It consists of an open cell (1 cm^3 capacity) within a Helmholtz coil (four turns of heavy armoured polythermaleze copper wire, 20 s.w.g.). The high-pressure RF (radio frequency) feed-through is also shown in Figure 1. It consists of a coaxial transmission line (outside diameter 0.062 in, MgO dielectric material, Inconel sheath) on which an SS-316 cone is silver-soldered; the sealing cone is made of copper and we find this makes an extremely good seal for high pressures of gas and has a long lifetime.

Although we have found that it is much easier to achieve better resolution with a vertical sample cell using a saddle coil, a Helmholtz coil has been preferred since this has 3—4 times better signal-to-noise (S/N) and we chose to sacrifice some resolution for better S/N. Using this arrangement the resolution was *ca.* 25 Hz and S/N 50 : 1 for an acetone solution of $[NMe_3(CH_2Ph)]_2[Rh_{12}(CO)_{30}]$ (0.07 mol dm^{-3}; 80% ^{13}CO).

Pressure Vessel.—The n.m.r. probe is located inside a titanium 6AL-4V alloy (IMI-Titanium) pressure vessel (outside diameter 5.7 cm, inside diameter 1.4 cm) (Figure 2) which can be heated or cooled using thermostatting jackets. Since the high-pressure vessel was originally designed for n.m.r. experiments using liquids as the pressurizing medium,[9] its current design does not allow measurements at temperatures higher than 308 K under high pressure of H_2 because of severe hydrogen-embrittlement problems. In addition, the inner volume of the vessel had to be reduced by an insert machined out of Macor (Corning Glass Work, N.Y.) because of the different dimensions of the n.m.r. probe used in the present experiment.

Gas Pressurization.—The apparatus used for gas pressurization is shown schematically in Figure 3.[10] It has the advantage of having a relatively small dead volume so that small volumes of isotopically enriched gas can be pressurized. Using this apparatus, it was possible to pressurize 5 litres of ^{13}CO to 90 bar; further pressurization was carried out with unenriched carbon monoxide.

Preparation of Complexes.—$[NMe_3(CH_2Ph)]_2[Rh_{12}(CO)_{30}]$ was prepared as described previously [11] and $[Rh_5(CO)_{15}]^-$ was isolated as the bis(triphenylphosphine)iminium salt from the reaction of $[Rh_4(CO)_{12}]$ with $[N(PPh_3)_2][Rh(CO)_4]$ in thf solution under a carbon monoxide atmosphere [4] or in solution by pressurizing a thf solution of $[Rh_{12}(CO)_{30}]^{2-}$ with CO (5—10 bar) using standard vacuum-line techniques.

RESULTS AND DISCUSSION

The pentanuclear cluster $[Rh_5(CO)_{15}]^-$ can be obtained as described in equation (1) (above) or by reaction (2),

$$[Rh_4(CO)_{12}] + [Rh(CO)_4]^- \xrightarrow[\text{thf}]{\text{CO}} [Rh_5(CO)_{15}]^- + CO \quad (2)$$

but in thf solution, i.r. and ^{13}C n.m.r. spectra show the reversible equilibrium (3) occurs quantitatively.

$$6\,[Rh_5(CO)_{15}]^- \underset{\text{CO}}{\overset{N_2}{\rightleftharpoons}} 2\,[Rh_{12}(CO)_{30}]^{2-} + [Rh_6(CO)_{15}]^{2-} + 15\,CO \quad (3)$$

The crystal structure of $[Rh_5(CO)_{15}]^-$ is shown schematically in Figure 4(*a*). However, the low-temperature ^{13}C n.m.r. spectrum of $[Rh_5(CO)_{15}]^-$ (33.8% ^{13}CO) under CO (5 bar) [Figure 5(*c*)] indicates a more symmetrical structure which could be attributed to that shown in Figure 4(*b*) or to a fluxional process described previously.[4] The three sets of resonances of relative intensity 3 : 6 : 6 at 247.7, 207.9, and 190.6 p.p.m. are assigned to the equatorial bridging carbonyls, $CO_{eq.}$, the carbonyls which asymmetrically bridge the equatorial/apical edges, $CO_{ea.}$, and the apical carbonyls, $CO_{ap.}$, respectively; the ^{13}C-{^{103}Rh} n.m.r. spectra [Figure 5(*a*) and (*b*)] show decoupling of $Rh_{ap.}$ and $Rh_{eq.}$ respectively and completely support the above assignments. It should be noted that spectra similar to those shown in Figure 5 are obtained for $[Rh_5(CO)_{15}]^-$ (33.8% ^{13}CO) under a nitrogen atmosphere at 201 K. However, in this case there is a slow reaction, even at this low temperature, to give $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$ [equation (3)]; pressuriz-

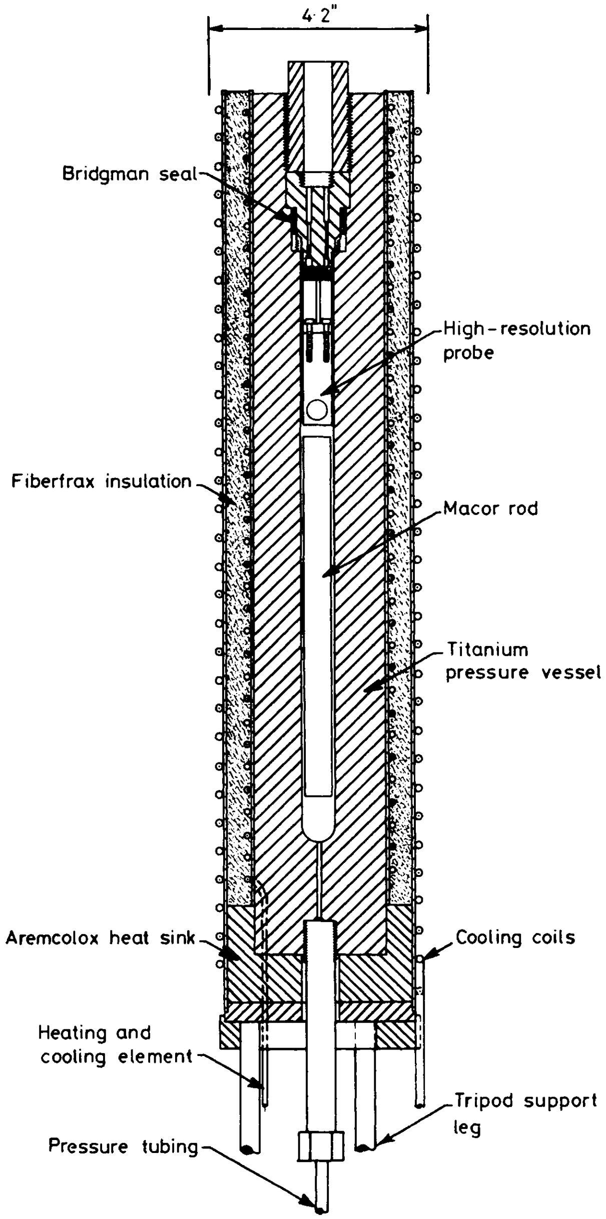


FIGURE 2 High pressure vessel for n.m.r. measurements

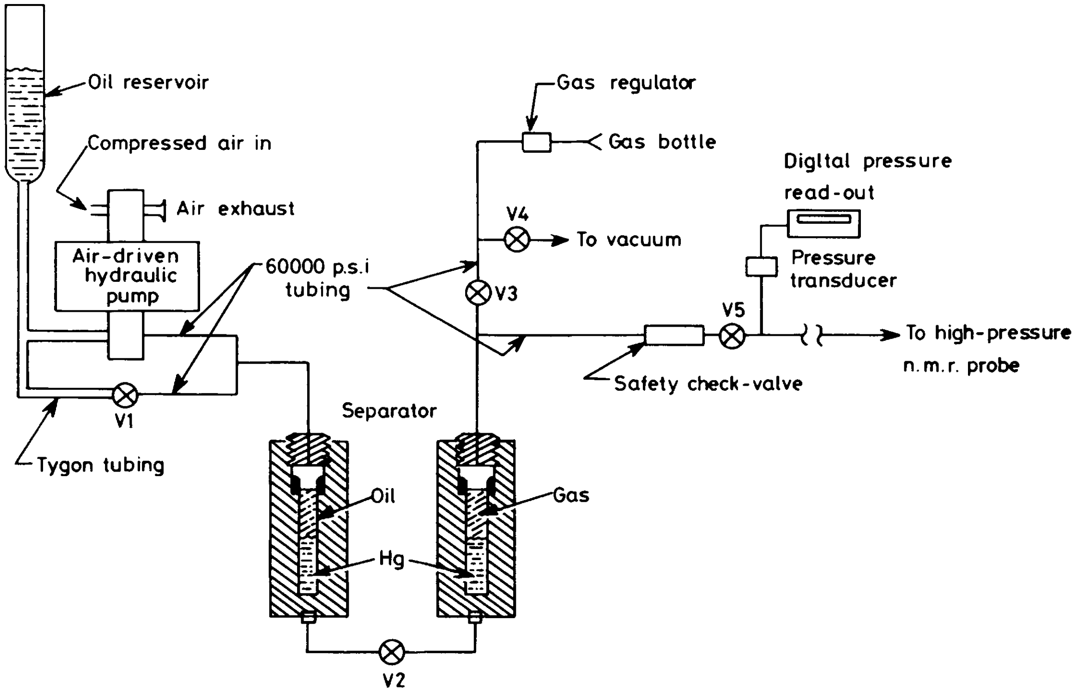
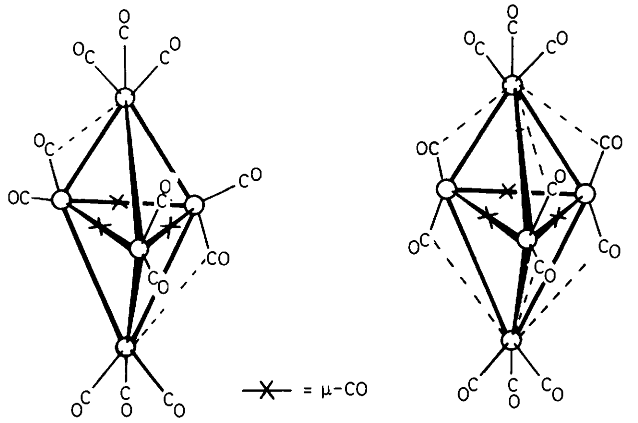


FIGURE 3 Schematic drawing of gas pressurization apparatus

ation of this solution with 33.8% ^{13}CO (5 bar) results in complete disappearance of these impurity peaks. However, pressurization with 90% ^{13}CO (5 bar) gives the spectra shown in Figure 6 which are essentially the same as those found in Figure 5 except for the resonance at 247.7 p.p.m. being more complex. Since this resonance becomes a singlet on decoupling $Rh_{eq.}$, Figure 6(*b*), the complexity must arise from second-order spectra resulting from $^2J(C_{eq.}-C_{eq.})$ between bridging carbonyls within the equatorial plane. Consideration of the isotopomers, $Rh_3(\mu\text{-}^{12}CO_{eq.})_{3-x}(\mu\text{-}^{13}CO_{eq.})_x$ (x = 0—3), and their relative abundances at 33.8% and 90% ^{13}CO allows the observed spectra to be simulated using the parameters $^1J(Rh-C_{eq.})$ 32.7, $^2J(Rh-C_{eq.})$ 0, $^2J(C_{eq.}-C_{eq.})$ 20, and $^1J(Rh-Rh)$ 0 Hz (Figure 7). The unusually large value of $^2J(C_{eq.}-C_{eq.})$ arises because the equatorial bridging carbonyls are in the equatorial plane and thus give rise to an angle $C_{eq.}RhC_{eq.}$ 161.6°; normally, CRhC $\leqslant$ 180° with $^2J(C-C)$ *ca.* 0. Warming the above solution to room temperature results in coalescence of the resonances associated with $CO_{ea.}$ and $CO_{ap.}$, with $CO_{eq.}$ remaining well resolved (Figure 8). A plausible mechanism for randomisation of $CO_{ea.}/CO_{ap.}$ could involve intermediates in which $Rh_{eq.}-Rh_{ap.}$ edges become doubly-bridged by $CO_{ea.}/CO_{ap.}$.



(*a*) (*b*)

FIGURE 4 Schematic representation of the structures of $[Rh_5(CO)_{15}]^-$ in (*a*) the solid state [4] and (*b*) solution

In order to investigate whether further cluster fragmentation of $[Rh_5(CO)_{15}]^-$ occurred on increasing the pressure of CO/H_2 to that used in the ethylene glycol synthesis, we developed the ^{13}C high-resolution, high-pressure n.m.r. probe described in the Experimental section.

Initial experiments with this high-pressure probe were carried out on an acetone solution of $[NMe_3(CH_2Ph)]_2[Rh_{12}(CO)_{30}]$ (0.17 g in 1 cm^3; 80% ^{13}CO) under N_2 (1 bar). Good quality spectra [Figure 9(*d*)] were obtained (100 transients) and, for comparison, Figure 9(*a*)—(*c*) shows the variable-temperature high-resolution spectra of $[Rh_{12}(CO)_{30}]^{2-}$ measured on a conventional spectrometer. It has recently been claimed, on the basis of ^{103}Rh n.m.r. data,[12] that the Rh–Rh bond joining the two octahedra in $[Rh_{12}(CO)_{30}]^{2-}$ undergoes facile cleavage at room temperature, thereby providing a route for randomisation of the otherwise inequivalent rhodium atoms. This is clearly incorrect since this Rh–Rh bond is doubly-bridged by carbonyls [13] which give rise to a triplet at 237.4 p.p.m. that is still sharp at 323 K; it is, however, interesting at this temperature that exchange between the face-bridging and terminal carbonyls occurs.

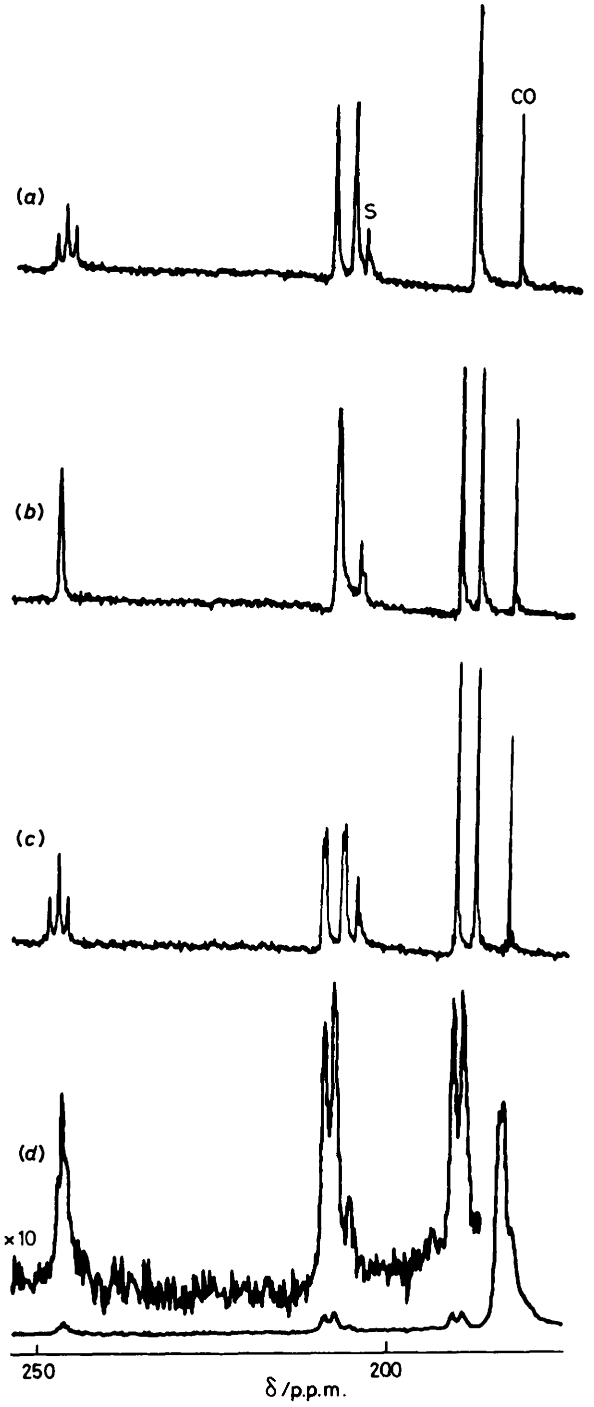


FIGURE 5 Carbon-13 n.m.r. spectra of $[Rh_5(CO)_{15}]^-$: (*a*)—(*c*) at 201 K (33.8% ^{13}CO) under CO (5 bar) with ^{103}Rh decoupling at (*a*) 3.157 093 MHz, $\delta(Rh_{ap.}) = -925.0$ p.p.m., (*b*) 3.159 531 MHz, $\delta(Rh_{eq.}) = -153.5$ p.p.m., (*c*) no decoupling, and (*d*) at 240.2 K (13.2% ^{13}CO) under 850 bar of CO/H_2 (2.1 : 1, 13.7% ^{13}CO). S = Carbonyl resonance of $[^2H_6]$acetone solvent

Upon pressurizing the above solution of $[Rh_{12}(CO)_{30}]^{2-}$ at 221 K with up to 575 bar of CO (13.7% ^{13}CO), ^{13}C n.m.r spectra show that there is a progressive transformation into $[Rh_5(CO)_{15}]^-$ according to equation (1). There is still evidence for unreacted $[Rh_{12}(CO)_{30}]^{2-}$ after *ca.* 24 h under 77 bar of CO and after 3 h under 575 bar of CO and there is no further change in the spectrum on further pressurizing with H_2 ($P_{total} = 850$ bar; $CO : H_2 = 2.1 : 1$) at this temperature. However, warming to room temperature followed by cooling to 240.2 K results in complete formation of $[Rh_5(CO)_{15}]^-$, Figure 5(*d*).

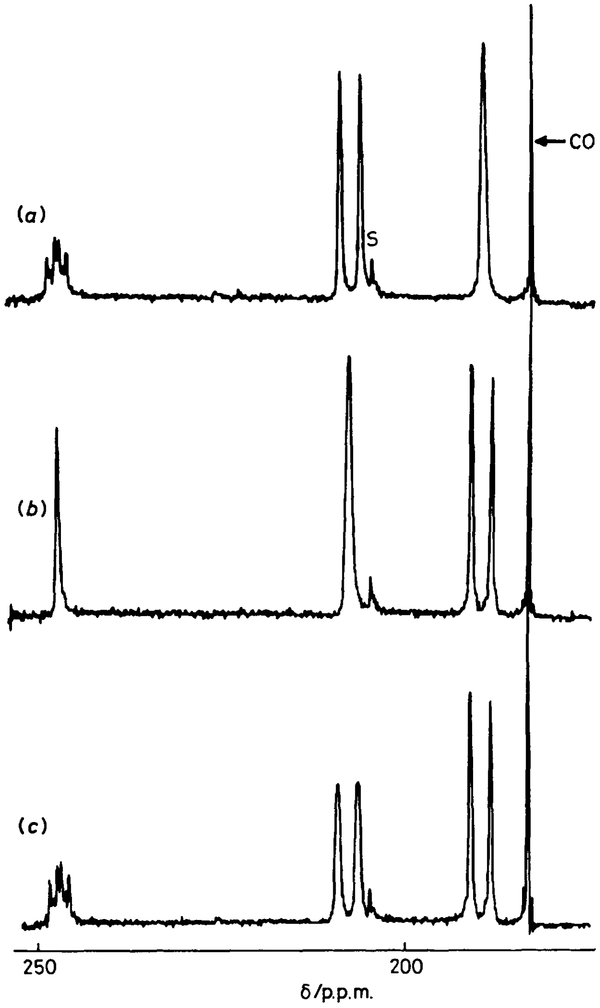


FIGURE 6 $^{13}C-\{^{103}Rh\}$ n.m.r. spectra of $[Rh_5(CO)_{15}]^-$ (90% ^{13}CO) at 201 K under 90% ^{13}CO (5 bar): decoupling of (*a*) $Rh_{ap.}$, (*b*) $Rh_{eq.}$, and (*c*) no decoupling. S = Carbonyl resonance of $[^2H_6]$acetone solvent

It should be noted that carbonyl inter-exchange with free CO is *not* fast on the n.m.r. time-scale under high pressure of CO. This suggests that high-pressure n.m.r. measurements have an extremely important future in elucidating reaction intermediates in industrial catalytic studies and recent work shows that our present instrumentation readily allows multinuclear (^1H, ^{31}P) n.m.r. measurements to be made.[14]

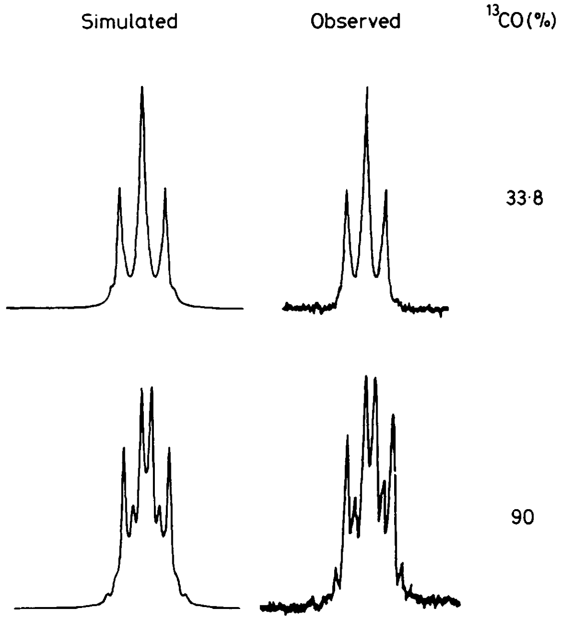


FIGURE 7 Observed and simulated CO$_{eq.}$ resonance in [Rh$_6$(CO)$_{15}$]$^-$ at 33.8 and 90% ^{13}CO using the parameters in the text

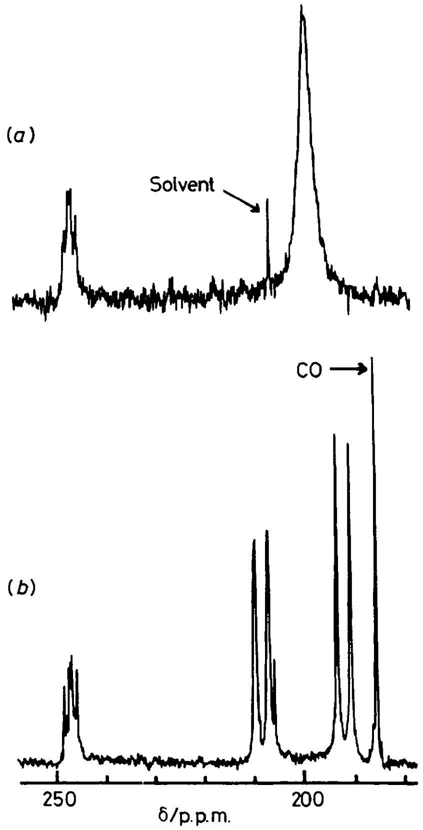


FIGURE 8 Variable-temperature ^{13}C n.m.r. spectra of [Rh$_6$(CO)$_{15}$]$^-$ (90% ^{13}CO) in [^{2}H$_6$]acetone under ^{13}CO (5 bar) at (a) 298 and (b) 203 K

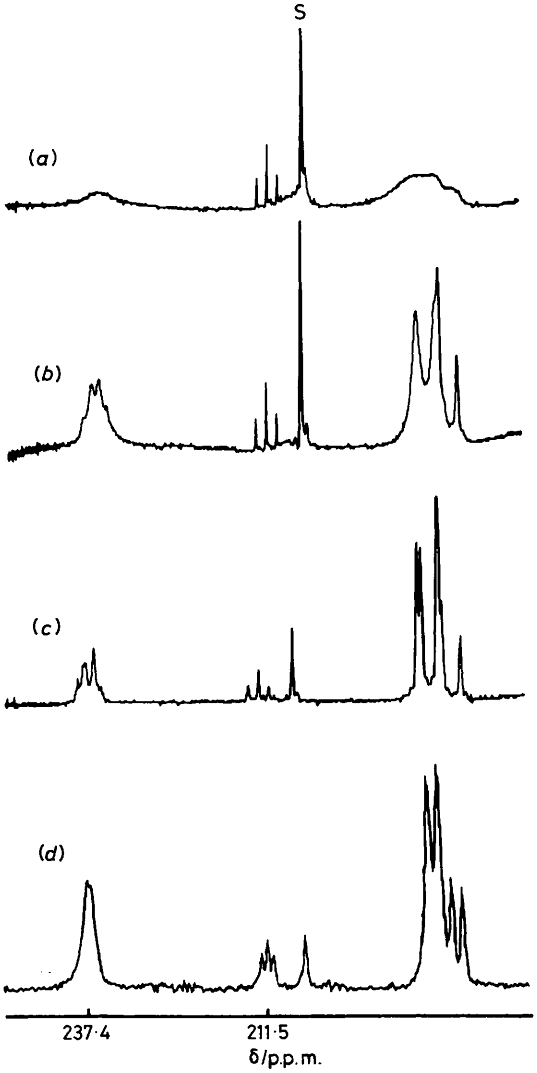


FIGURE 9 Carbon-13 n.m.r. spectra of [NMe$_3$(CH$_2$Ph)]$_2$[Rh$_{12}$(CO)$_{30}$] obtained under N$_2$ (1 bar) in a conventional high-resolution probe in thf-[^{2}H$_6$]acetone (9 : 1) at (a) 323, (b) 298, and (c) 193 K; (d) the high pressure probe in acetone solution at 298 K

We acknowledge financial support from S.E.R.C. including a research fellowship (to L. S.), The National Science Foundation, The Department of Energy, N.A.T.O. for travel grant (to B. T. H. and J. J.), and the Nuffield Foundation for the award of a Research Fellowship (to B. T. H.). We also thank Dr. S. Martinengo for experimental assistance and useful discussions and Professor J. R. Shapley for laboratory facilities.

[1/1918 *Received*, 14*th December*, 1981]

REFERENCES

[1] G. W. Parshall, 'The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes,' Wiley, New York, 1980.

[2] C. Masters, 'Homogeneous Transition-metal Catalysis—A Gentle Art,' Chapman and Hall, London, 1981.

[3] R. L. Pruett and W. E. Walker, U.S.P. 3 833 634/1974 and 3 957 857/1976.

[4] A. Fumagalli, F. T. Koetzle, F. Takusagawa, P. Chini, S.

Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, **102**, 1740.

[5] J. L. Vidal and W. E. Walker, *Inorg. Chem.*, 1980, **19**, 896.

[6] B. T. Heaton, J. Jonas, T. Eguchi, and G. A. Hoffman, *J. Chem. Soc., Chem. Commun.*, 1981, 331.

[7] C. Brown, B. T. Heaton, L. Longhetti, W. T. Povey, and D. O. Smith, *J. Organomet. Chem.*, 1980, **192**, 93.

[8] J. Jonas, D. L. Hasha, W. J. Lamb, G. A. Hoffman, and T. Eguchi, *J. Magn. Reson.*, 1981, **42**, 169, and refs. therein.

[9] J. Jonas, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 126.

[10] J. H. Campbell, Ph.D. Thesis, University of Illinois, 1975.

[11] P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 21.

[12] J. S. Vidal, *A.C.S. Symp. Ser.*, 1981, **155**, 61; O. A. Gansow, 181st A.C.S. Meeting, Atlanta, Georgia, 1981, paper ORGN 160; O. A. Gansow, *Chem. Eng. News*, 1981, 34.

[13] V. G. Albano and P. L. Bellon, *J. Organomet. Chem.*, 1969, **19**, 405.

[14] B. T. Heaton, J. Jonas, J. S. Ashcroft, and G. A. Hoffman, unpublished work.