Multinuclear Magnetic Resonance Studies on $[Rh_4(CO)_{12-x}L_x]$ $[L = P(OPh)_3, x = 1—4]$

Brian T. Heaton,* Luisella Strona, and Roberto Della Pergola
Chemical Laboratory, University of Kent, Canterbury CT2 7NH
Luigi Garlaschelli and Ugo Sartorelli
Università di Milano, Via G. Venezian 21, 20133 Milano, Italy
Ian H. Sadler
Chemistry Department, University of Edinburgh, Edinburgh EH9 3JJ

Direct ^{103}Rh n.m.r. studies on $[Rh_4(CO)_{12-x}L_x]$ $[L = P(OPh)_3, x = 1—4]$ at low temperatures support the solution structures previously proposed and, although the apical rhodium resonance always occurs at lowest frequency, there is little variation in $\delta(^{103}Rh)$ with increasing ligand substitution. Measurements of ^{13}C-{^{103}Rh} allow unambiguous assignment of the ^{13}C n.m.r. spectra when x = 1 and 3 and $\delta(^{13}CO_{ax})$ is always at lowest frequency with $^1J(^{103}Rh-^{13}CO_{ax}) \simeq {}^1J(^{103}Rh-^{13}CO_{ap}) < {}^1J(^{103}Rh-^{13}CO_{rad})$; this suggests a new assignment for the ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{12}]$.

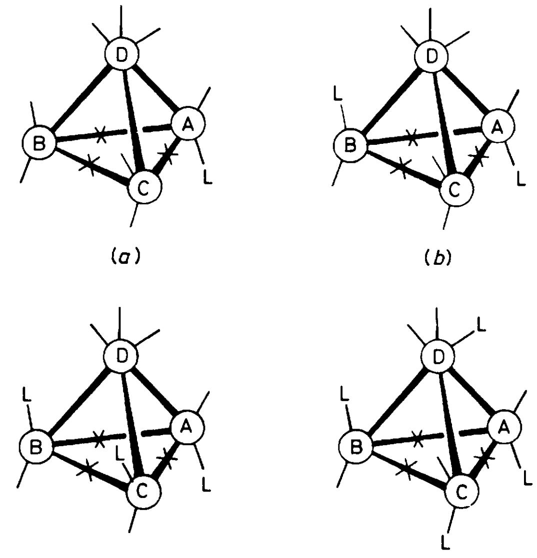
The stereochemistry of triphenyl phosphite (L) substituted derivatives of $[Rh_4(CO)_{12}]$ in solution has been investigated previously by ^{31}P n.m.r. for $[Rh_4(CO)_{12-x}L_x]$ (x = 1—3)[1] and by ^{13}C-{^{31}P,^{1}H} n.m.r. for $[Rh_4(CO)_8L_4]$.[2] Although ^{13}C n.m.r. measurements have been reported on $[Rh_4(CO)_{11}(PPh_2R)]$ (R = Ph or Me),[3] the terminal carbonyl resonances are difficult to assign because of coincidences and similar problems, together with a complex spin system and have so far prevented a complete analysis of the ^{31}P n.m.r. spectrum of $[Rh_4(CO)_8L_4]$ at low temperature.

We now report direct ^{103}Rh n.m.r. spectra of $[Rh_4(CO)_{12-x}L_x]$ (x = 1—4) at −54 °C, which provide an easy method of establishing the stereochemistries of these derivatives and substantiate the structures proposed earlier, together with ^{13}C-{^{103}Rh} n.m.r. measurements which allow a more detailed interpretation of their ^{13}C n.m.r. spectra.

Results and Discussion

Direct ^{103}Rh *N.M.R. Measurements.*—The previously proposed structures of $[Rh_4(CO)_{12-x}L_x]$ (x = 1—4) in solution at low temperatures are represented schematically in Figure 1 and are now substantiated by direct ^{103}Rh n.m.r. measurements (Figure 2), which are summarised in the Table.

When x = 1, the ligand is in an axial site (P_{ax}) and there are three rhodium resonances due to Rh_A, Rh_B/Rh_C, and Rh_D [Figure 1(*a*)] with Rh_A appearing as a doublet, $^1J(^{103}Rh-^{31}P_{ax})$ 203 Hz. Previous ^{31}P n.m.r. measurements showed that $^2J(^{103}Rh-^{31}P)$ is only significant between phosphites in radial sites (P_{rad}) and basal rhodium atoms (Rh_{bas}). This is clearly seen in the ^{103}Rh n.m.r. spectrum of $[Rh_4(CO)_{10}L_2]$ [Figure 2(*b*)] and allows an unambiguous assignment of all four inequivalent rhodium atoms (Table). For $[Rh_4(CO)_9\{P(OPh)_3\}_3]$, the apical rhodium resonance (Rh_D) is a singlet at lowest frequency and Rh_B/Rh_C together with the two radial phosphorus atoms give rise to an AA′XX′ spin system centred at −547 p.p.m., with Rh_A appearing as a doublet at −437 p.p.m., which shows a further small triplet splitting from $^2J(^{103}Rh_A-^{31}P_{rad})$. Because of the more complex spin system, the ^{103}Rh resonances in $[Rh_4(CO)_8\{P(OPh)_3\}_4]$ are clearly broader than those found for the other derivatives and this prevented us obtaining values for $^2J(^{103}Rh-^{31}P)$. Nevertheless, the spectrum is clearly consistent with the structure shown in Figure 1(*d*).



(*a*) (*b*)

(*c*) (*d*)

Figure 1. Schematic representation of the stereochemistry of $[Rh_4(CO)_{12-x}L_x]$ $[L = P(OPh)_3, x = 1—4]$; —×— = μ-CO

In view of the large range found for $\delta(^{103}Rh)$,[4] it was a little surprising that carbonyl replacement by triphenyl phosphite produced rather little variation in the rhodium resonance frequencies. However, it is worth noting that (*i*) $\delta(^{103}Rh_{bas}) > \delta(^{103}Rh_{ap})$ and phosphite substitution in the basal plane produces a low-frequency shift, which is greater for radial than axial substitution, and (*ii*) $^1J(^{103}Rh_{ap}-^{31}P_{ap}) \simeq {}^1J(^{103}Rh_{bas}-^{31}P_{ax}) < {}^1J(^{103}Rh-^{31}P_{rad})$ and these variations are paralleled by those observed for $^1J(^{103}Rh-^{13}CO)$ for the corresponding carbonyls.

^{13}C-{^{103}Rh} *N.M.R. Measurements.*—Using the frequencies obtained from the direct ^{103}Rh n.m.r. measurements and allowing for temperature effects, it has been possible to assign completely the ^{13}C n.m.r. spectra of $[Rh_4(CO)_{12-x}\{P(OPh)_3\}_x]$ (x = 1 and 3) by ^{13}C-{^{103}Rh} measurements; the assignment for the x = 4 derivative has already been pub-

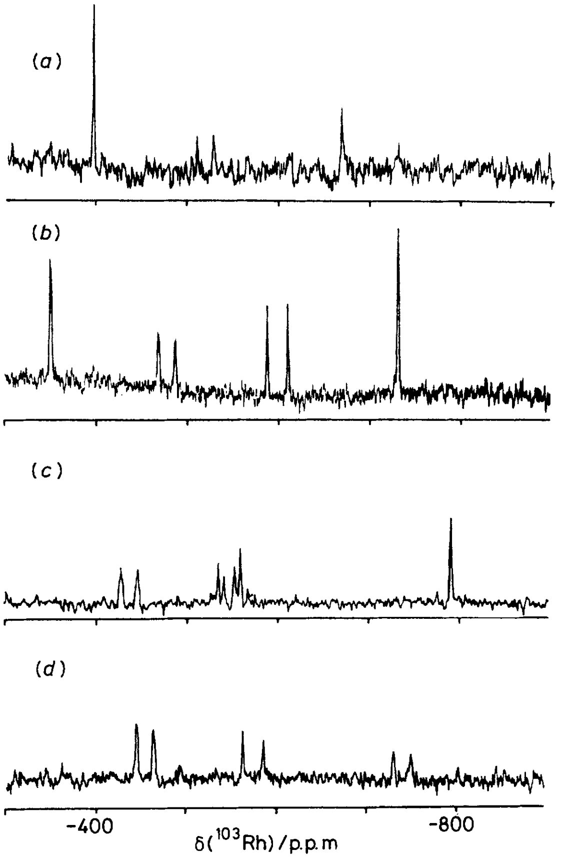


Figure 2. Direct ^{103}Rh n.m.r. spectra of [$Rh_4(CO)_{12-x}L_x$] in CD_2Cl_2 at −54 °C [L = $P(OPh)_3$, x = 1—4]; (*a*) x = 1, (*b*) x = 2, (*c*) x = 3, (*d*) x = 4

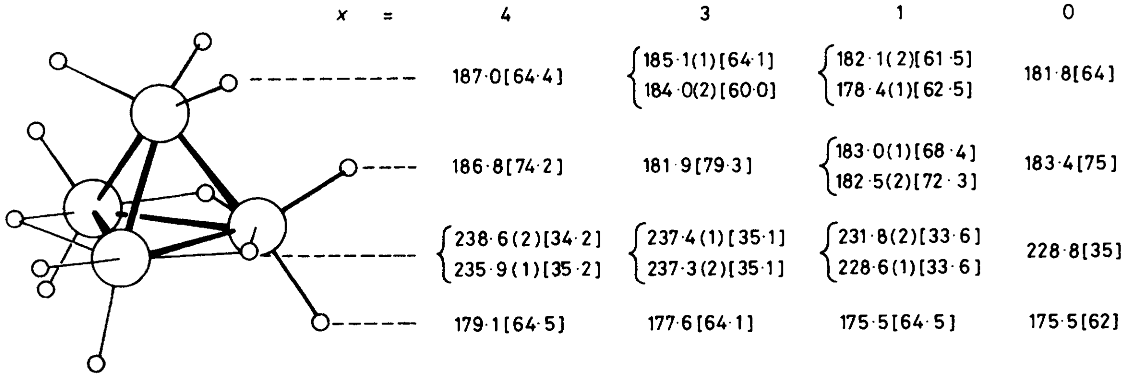
lished[2] but must now be slightly revised, *viz.*, the correct assignment of the two equally intense, almost coincident doublets due to the two equivalent apical carbonyls and two radial carbonyls is $\delta(^{13}CO_{ap})$ 187.0 p.p.m., $^1J(^{103}Rh_D-^{13}CO_{ap})$ 64.4 Hz and $\delta(^{13}C_{rad})$ 186.8 p.p.m.,[1] $J(^{103}Rh_{B,C}-^{13}CO_{rad})$ 74.2 Hz. Unfortunately, when $x = 2$ the ^{13}C spectrum is very complex and cannot be unambiguously assigned even with $^{13}C\text{-}\{^{103}Rh\}$ measurements.

The resulting data are summarised in Figure 3. It should be noted that (*i*) the mean carbonyl chemical shift moves progressively to lower field with increasing phosphite substitution [$\delta(^{13}CO)_{mean}$ 192.4,[3] 194.0, 200.2, and 205.0 for x = 0, 1, 3, and 4 respectively]; this is consistent with increased charge dissipation as was noted earlier for the isoelectronic clusters [$Rh_6(CO)_{16}$], [$Rh_6(CO)_{15}$]$^{2-}$, and [$Rh_6(CO)_{14}$]$^{4-}$,[5] (*ii*) that $\delta(^{13}CO_{ax}) < \delta(^{13}CO_{rad}) \simeq \delta(^{13}CO_{ap})$, which is similar to the variation in $\delta(^{31}P)$ for these derivatives,[1] and (*iii*) that $^1J(^{103}Rh-^{13}CO_{rad}) > {}^1J(^{103}Rh-^{13}CO_{ax}) \simeq {}^1J(^{103}Rh-^{13}CO_{ap})$. Because of points (*ii*) and (*iii*) it seems reasonable to reassign the terminal region of the ^{13}C n.m.r. spectrum of [$Rh_4(CO)_{12}$] (see Figure 3). Previous work[3] showed that the solid-state structure of [$Rh_4(CO)_{12}$][6] was retained in solution at low temperatures. The ^{13}C n.m.r. spectrum in the terminal carbonyl region consisted of two broad and one sharp, equally intense doublets due to the apical, radial, and axial carbonyls. The sharp doublet was suggested to be due to the apical carbonyls due to the lack of $^2J(^{13}C-^{13}C)$ which resulted in a sharper resonance. However, because the sharp doublet has the higher value of $^1J(^{103}Rh-^{13}CO)$ we prefer to assign it to the radial carbonyl and the low-frequency resonance would then be due to the axial carbonyl which has a value of $^1J(^{103}Rh-^{13}CO)$ similar to that now assigned to the apical carbonyls. The broadening must therefore principally arise from $^3J(^{13}C-^{13}C)$ which is now perhaps not too surprising since related *trans* couplings, $^3J(^{31}P-^{13}CO)$, have been shown to be more significant than two-bond couplings in Ir_4 derivatives.[7] Unfortunately because of the poor solubility of [$Rh_4(CO)_{12}$] at

Table. N.m.r. data (from direct ^{103}Rh n.m.r. spectra) on [$Rh_4(CO)_{12-x}L_x$] [L = $P(OPh)_3$, x = 1—4] in CD_2Cl_2 at −54 °C

	$\delta(^{103}Rh)$ [a]/p.p.m.				$^1J(^{103}Rh-^{31}P)$/Hz				$^2J(^{103}Rh-^{31}P_{rad})$/Hz		
x	Rh_A	Rh_B	Rh_C	Rh_D	Rh_A	Rh_B	Rh_C	Rh_D	Rh_A	Rh_B	Rh_C
1	−520	−397.5	−397.5	−668.5	203						
2	−478	−598	−351	−731	209	259			15		16
3	−437	−547	−547	−791.5	214	263 [b]	263 [b]		16	16 [b]	16 [b]
4	−455	−575	−455	−741	214	259	214	215			

[a] 11.376 MHz = 0 p.p.m. at such a magnetic field that the protons in the $SiMe_4$ resonate at exactly 360 MHz. [b] Data from ^{31}P n.m.r. From ^{103}Rh spectra: $|^1J(^{103}Rh-^{31}P) + {}^2J(^{103}Rh-^{31}P)|$ = 279 Hz and $^3J(P_{rad}-P_{rad})$ = 160 Hz.



x =	4	3	1	0
	187·0[64·4]	185·1(1)[64·1] 184·0(2)[60·0]	182·1(2)[61·5] 178·4(1)[62·5]	181·8[64]
	186·8[74·2]	181·9[79·3]	183·0(1)[68·4] 182·5(2)[72·3]	183·4[75]
	238·6(2)[34·2] 235·9(1)[35·2]	237·4(1)[35·1] 237·3(2)[35·1]	231·8(2)[33·6] 228·6(1)[33·6]	228·8[35]
	179·1[64·5]	177·6[64·1]	175·5[64·5]	175·5[62]

Figure 3. Carbon-13 n.m.r. assignments for [$Rh_4(CO)_{12-x}\{P(OPh)_3\}_x$] ($x$ = 1, 3, and 4) deduced by $^{13}C\text{-}\{^{103}Rh\}$ measurements, together with the suggested reassignment for [$Rh_4(CO)_{12}$]. Values indicate $\delta(^{13}CO)$ p.p.m. (relative intensity) [$^1J(^{103}Rh-^{13}CO)$] respectively.

low temperatures it has not been practical to carry out direct ^{103}Rh or ^{13}C-{^{103}Rh} measurements in order to support this reassignment.

CNDO (complete neglect of differential overlap) calculations [8] on $[Co_4(CO)_{12}]$ showed that the axial carbonyl carbon was most positive and thus involved in the least metal–carbonyl back-bonding. This is also consistent with the axial carbonyl ^{13}C resonance being at lowest frequency and with the patterns of substitution in $[M_4(CO)_{12}]$ (M = Co,[9] Rh,[1,2] or Ir [7]). The first ligand always occupies an axial site in $[M_4(CO)_{12}]$ and then it depends on steric effects as to whether the next ligand also goes into the electronically preferred but now sterically hindered axial site or into a radial site.

Experimental

The complex $[Rh_4(CO)_{12}]$ and the triphenyl phosphite substituted derivatives were prepared as described previously [1,2,10] and enriched with ^{13}CO (*ca.* 25—30%) by standard vacuum line techniques. The ^{103}Rh n.m.r. spectra were recorded in CD_2Cl_2 solution at −54 °C on a Bruker WH 360-MHz spectrometer as described previously [11] and ^{13}C-{^{103}Rh} measurements were made at −90 °C in CD_2Cl_2 on a JEOL PS-100 PFT spectrometer as described previously.[12]

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