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The reaction of mixtures of $[\text{Rh}_4(\text{CO})_{12}]$ and triphenylphosphite with carbon monoxide or syngas as studied by high-resolution, high-pressure NMR spectroscopy[†]

Gillian Overend, Jonathan A. Iggo,* Brian T. Heaton and Robin Whyman

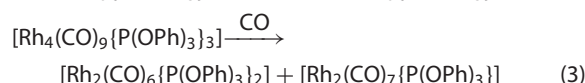
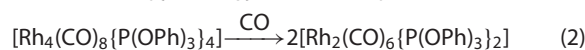
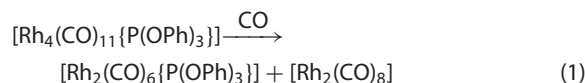
The fragmentation and redistribution reactions of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{OPh})_3\}_x]$ ($x = 1-4$) with carbon monoxide have been studied using high-resolution, high-pressure NMR spectroscopy. Under the conditions of efficient gas mixing in a high-pressure NMR bubble column, $[\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3]$ fragments to give mainly $[\text{Rh}_2(\text{CO})_6\{\text{P}(\text{OPh})_3\}_2]$; $[\text{Rh}_4(\text{CO})_{11}\{\text{P}(\text{OPh})_3\}]$ is also observed, implying redistribution of the phosphite ligand and/or recombination of the dimers to tetrameric clusters. Fragmentation of $[\text{Rh}_4(\text{CO})_{10}\{\text{P}(\text{OPh})_3\}_2]$ is found to be pressure-dependent giving predominantly $[\text{Rh}_2(\text{CO})_6\{\text{P}(\text{OPh})_3\}_2]$ at low CO pressure (1–40 bar), and increasing amounts of $[\text{Rh}_2(\text{CO})_7\{\text{P}(\text{OPh})_3\}]$ at higher (40–80 bar) pressure. Using Syngas ($\text{CO} : \text{H}_2$ (1 : 1)) instead of CO in the above fragmentations, homolytic addition of H_2 to the dimer $[\text{Rh}_2(\text{CO})_6\{\text{P}(\text{OPh})_3\}_2]$ to give $[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}]$ and $[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ is observed. The distribution of tetrameric species obtained is similar to that obtained under the same partial pressure of CO. On depressurisation/out-gassing of the sample, the original mixture of tetrameric clusters is obtained. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: NMR; ^1H ; ^{13}C ; ^{31}P ; high-pressure NMR spectroscopy; rhodium clusters; rhodium hydride; triphenylphosphite

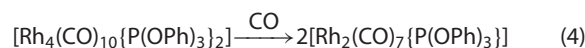
Introduction

Rhodium carbonyl clusters substituted with phosphites, phosphines, and arsines are well documented in the literature^[1–4] due to the role that ligand-substituted metal carbonyls can play as precursors for homogeneous hydroformylation catalysts. Thus, Rh/triphenylphosphite-substituted clusters^[5,6] are precursors to active alkene hydroformylation catalysts, and a number of NMR spectroscopic studies of these clusters have been undertaken.^[7–10] It has long been known that $[\text{M}_4(\text{CO})_{12}]$ -derived clusters will fragment into smaller species under high pressures of CO or Syngas,^[1,2] and that high-pressure *in situ* infrared (IR) and NMR spectroscopies are ideal for examining these reactive species. Thus, high-pressure IR spectroscopy has been used to examine the equilibria between $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Rh}_2(\text{CO})_8]$,^[2] $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{RhH}(\text{CO})_4]/[\text{RhD}(\text{CO})_4]$ ^[11–13] and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ and $[\text{CoRh}(\text{CO})_8]$ ^[14,15] when various substituents were present. We have previously studied the fragmentation and recombination of $[\text{Rh}_4(\text{CO})_{12-x}\text{L}_x]$ ($\text{L} = \text{P}(\text{OPh})_3$, $x = 1-4$) clusters under applied pressures up to 400 bar of CO and CO/H_2 (1 : 1) using both high-pressure IR and an unmixed high-pressure NMR spectroscopic cell.^[16] At 400 bar applied pressure of CO or Syngas, we found that cluster fragmentation into Rh dimers $[\text{Rh}_2(\text{CO})_{8-x}\text{L}_x]$ occurs and that tetrameric Rh clusters reformed on the release of pressure. The mono-tetra-substituted clusters behaved as expected. $[\text{Rh}_4(\text{CO})_{11}\{\text{P}(\text{OPh})_3\}]$ (Rh_4L_1) fragmented to give $[\text{Rh}_2(\text{CO})_7\{\text{P}(\text{OPh})_3\}]$ (Rh_2L_1) and, presumably, transiently, $[\text{Rh}_2(\text{CO})_8]$ (Rh_2L_0) or $[\text{Rh}_4(\text{CO})_{12}]$ (Rh_4L_0) (Eqn (1)). $[\text{Rh}_4(\text{CO})_8\{\text{P}(\text{OPh})_3\}_4]$ (Rh_4L_4) underwent complete conversion to $[\text{Rh}_2(\text{CO})_6\{\text{P}(\text{OPh})_3\}_2]$ (Rh_2L_2) (Eqn (2)). The fragmentation of $[\text{Rh}_4(\text{CO})_9\{\text{P}(\text{OPh})_3\}_3]$ (Rh_4L_3) was also studied and gave, predominantly, Rh_2L_2 (and redistribution/recombination products) rather

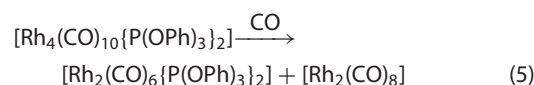
than the expected equimolar mixture of Rh_2L_2 and Rh_2L_1 (Eqn (3)). Rh_4L_1 was also observed in this reaction; however, free phosphite was not.



Homolytic cleavage



Heterolytic cleavage



For the disubstituted cluster $[\text{Rh}_4(\text{CO})_{10}\{\text{P}(\text{OPh})_3\}_2]$ (Rh_4L_2), there are two possible fragmentation pathways: (i) homolytic

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† Dedicated to Prof. Paul Pregosin on the occasion of his 65th birthday.

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cleavage in which the bond linking the two phosphite substituted rhodiums is cleaved (Eqn (4)) and (ii) heterolytic cleavage in which the bond between the two substituted rhodiums is retained (Eqn (5)).

Our earlier study^[16] observed a surprising concentration dependence for these last cleavage reactions. At low rhodium cluster concentration (5 mmol dm^{-3}), Rh_2L_1 was the major product observed, indicating that the homolytic pathway was dominant. However, at high cluster concentration (120 mmol dm^{-3}), Rh_2L_2 was the main species observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with only a small amount of Rh_2L_1 being formed, suggesting that heterolytic cleavage was dominant. Free phosphite was not observed and the amount of Rh_2L_1 decreased as the $[\text{CO}] : [\text{L}]$ ratio in solution increased, indicating that a simple ligand displacement reaction was not occurring. A further puzzling observation in our early study was that, on pressurisation with $\text{CO} : \text{H}_2$, (1:1), no hydride complexes were detected by high pressure NMR (HPNMR) spectroscopy, in contrast to other reports.^[17–23]

A limitation of our earlier design of HPNMR cell was that agitation of the sample, to ensure good gas dissolution, was not incorporated into the design for reasons of mechanical complexity.^[24,25] As a result, the rates of the cleavage reactions were determined by very slow gas diffusion across the interface into, or out of, solution reactions taking up to 48 h to reach equilibrium. In contrast, efficient gas mixing is achieved in the HPNMR bubble column allowing equilibrium to be rapidly established, albeit at the expense of a reduced maximum working pressure (*ca* 250 bar in the bubble column vs *ca* 1 kbar for the earlier design). In this paper, we re-examine these cluster fragmentation reactions using our HPNMR bubble column reactor to determine if the behaviour previously observed was a consequence of the slow dissolution of gas into the reacting solution.

Results and Discussion

Reaction of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$ ($x = 1–4$) with CO (1–80 bar)

Our earlier high-pressure IR spectroscopic study^[16] showed that fragmentation of $[\text{Rh}_4(\text{CO})_{10}\{\text{P}(\text{O}^i\text{Ph})_3\}_2]$ under 400 bar of CO gives the phosphite-substituted dimeric species Rh_2L_2 and Rh_2L_1 ; no IR spectroscopic absorptions attributable to unsubstituted species such as $[\text{Rh}_4(\text{CO})_{12}]$ (Rh_4L_0) or $[\text{Rh}_2(\text{CO})_8]$ (Rh_2L_0) were seen. To ensure that the ^{31}P NMR silent compounds Rh_4L_0 and Rh_2L_0 are absent from our experiments, we have used a slight excess of $\text{P}(\text{O}^i\text{Ph})_3$; i.e. a nominal $\text{P}(\text{O}^i\text{Ph})_3 : \text{Rh}_4$ cluster ratio of 2.1:1 was used. Addition of 2.1 equivalents of $\text{P}(\text{O}^i\text{Ph})_3$ to $[\text{Rh}_4(\text{CO})_{12}]$ (1 mmol dm^{-3}), in dry CDCl_3 , in the high-resolution, high-pressure NMR bubble column under 1 bar of CO, gave a mixture of tetranuclear clusters, consisting mainly of Rh_4L_2 and Rh_4L_3 .^[1,2,6] On pressurisation of the sample to 20, 40, and finally 80 bar, fragmentation to dinuclear species occurred, the degree of fragmentation ($\text{Rh}_2 : \text{Rh}_4$) being pressure-dependent. Figure 1 shows the evolution of the $^{31}\text{P}\{^1\text{H}\}$ HPNMR spectrum of the sample during pressurisation, and Table 1 presents the equilibrium speciation of the system at each pressure studied. In contrast to our previous report,^[16] in which an unmixed cell was used, equilibrium is rapidly established (<30 min) in the bubble column. Inspection of Fig. 1 and Table 1 reveals that the equilibrium concentration of Rh_4L_3 decreases sharply on

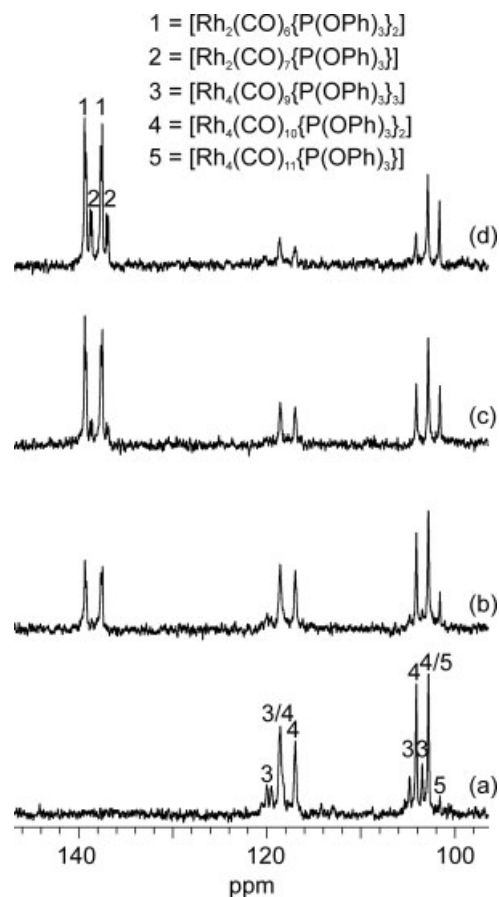


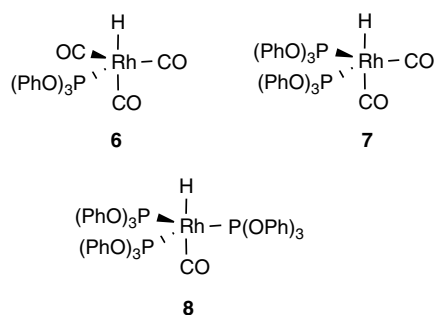
Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 233 K showing the fragmentation of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$ to $[\text{Rh}_2(\text{CO})_6\{\text{P}(\text{O}^i\text{Ph})_3\}_2]$ and $[\text{Rh}_2(\text{CO})_7\{\text{P}(\text{O}^i\text{Ph})_3\}]$ at increasing CO pressure where (a) is at 1 bar CO, (b) is at 20 bar CO, (c) is at 40 bar CO and (d) is at 80 bar CO.

pressurisation being *ca* 35% of its original value at 20 bar. At this pressure, there is a slight reduction in the amount of disubstituted cluster Rh_4L_2 present (*ca* 74% of its original value); however, the concentration of Rh_4L_2 does not significantly change until higher pressures, at which Rh_4L_3 is essentially completely fragmented to dimers, i.e. Rh_4L_3 fragments more readily than Rh_4L_2 . The major fragmentation product of both Rh_4L_3 and Rh_4L_2 is Rh_2L_2 ^[16] at all pressures, even though fragmentation of Rh_4L_3 would be expected to afford equal amounts of Rh_2L_2 and Rh_2L_1 ; contrast Eqn (3) with Fig. 1(b). The small amount of Rh_2L_1 that is formed and the increase in the amount of Rh_4L_1 present indicate that the reactions are under thermodynamic control, i.e. we are not observing the kinetic products of the fragmentation reaction. The terms 'homolytic' and 'heterolytic' cleavage are therefore intended in what follows to indicate this thermodynamic outcome of the cleavage reaction, and not the mechanism by which cleavage has occurred.

The amounts of both dimers, Rh_2L_1 and Rh_2L_2 , in the mixture increase as the pressure is raised from 20 to 40 bar (Fig. 1(b) and (c), Table 1) and the amount of Rh_4L_1 is expected to double (*vide infra*). Between 40 and 80 bar CO, much of the remaining Rh_4L_2 is fragmented; the ratio of Rh_2L_2 to Rh_2L_1 falls to 1.7:1, consistent with an increasing stability of the less substituted dimer Rh_2L_1 , versus the tetrameric clusters as the concentration of CO in solution increases. At 80 bar (Fig. 1(d)), Rh_4L_1 is the predominant cluster present, the species observed suggesting that the stability of Rh_4L_x with respect

Table 1. The equilibrium speciation of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{OPh})_3\}_x]$ and $[\text{Rh}_2(\text{CO})_{8-x}\{\text{P}(\text{OPh})_3\}_x]$ as percentages observed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at 233 K under CO

Rh concentration (mmol dm ⁻³)	P(OPh) ₃ : [Rh ₄ (CO) ₁₂] ^a	CO pressure (bar)	Rh ₄ L ₁ (%)	Rh ₄ L ₂ (%)	Rh ₄ L ₃ (%)	Rh ₄ L ₄ (%)	Rh ₂ L ₁ (%)	Rh ₂ L ₂ (%)	Rh ₂ L ₂ /Rh ₂ L ₁
1 ^b	2.2	1 ^d	7	69	22	3	0	0	–
		1 ^e	10	70	19	1.1	0	0	–
		20	12	51	8	0	5	24	5.1
		40	25	25	2	0	11	37	3.4
		80	26	11	2	0	23	39	1.7
5 ^b	2.3	1 ^d	2	61	36	1.1	0	0	–
		1 ^e	8	71	21	0.4	0	0	–
		20	11	53	8	1.5	2	25	13.3
		40	18	33	4	0	7	39	5.8
		80	25	14	2	0	22	37	1.7
5 ^c	2.0	1 ^d	13	74	13	0	0	0	–
		1 ^e	15	74	11	0	0	0	–
		20	23	54	4	0	2	17	8.5
		40	30	26	3	0	11	30	2.8
		80	32	13	1	0	25	29	1.2
10 ^c	2.1	1 ^d	4.6	74	20	2	0	0	–
		1 ^e	8	76	15	1	0	0	–
		20	12	58	10	0	0	19	–
		40	27	32	4	0	10	27	2.7
		80	28	17	3	0	15	38	2.5

^a Calculated by mass balance.^b Experiments carried out on the Bruker AVANCE-II 400 WB.^c Experiments carried out on the AMX-II 200 WB spectrometer.^d Spectra taken before fragmentation.^e Spectra taken after recombination.**Figure 2.** Schematic representation of the hydrides $[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}]$ **6**, $[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ **7** and $[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]$ **8**. The proposed major isomer is shown.

to fragmentation by CO increases as the substitution level of the cluster decreases. The observed low concentration of Rh_2L_1 and increasing concentration of Rh_4L_1 require further comment. Rh_4L_1 might be formed either by ligand displacement from Rh_4L_2 or by recombination of Rh_2L_1 with transient Rh_2L_0 , the latter being formed by the heterolytic cleavage of Rh_4L_2 . Rh_2L_0 would be expected to be extremely reactive towards $\text{P}(\text{OPh})_3$ for CO substitution and/or recombination to tetrameric clusters ($[\text{Rh}_6(\text{CO})_{15}\text{L}]$, $\delta^{31}\text{P} = 106.6$, $J(^{31}\text{P}, ^{103}\text{Rh}) = 240$ Hz, is not seen), i.e. Rh_2L_0 if formed should be an effective scavenger for Rh_2L_1 and $\text{P}(\text{OPh})_3$. The small amount of Rh_2L_1 seen might result from the substitution of CO by L to give Rh_2L_2 . Alternatively, recombination of this dimer to give Rh_4L_2

might occur; the amount of Rh_4L_3 decreases. It should be noted that at no stage in these reactions is free phosphite observed.

Fragmentation processes, similar to those described above, were observed in experiments conducted at higher initial $[\text{Rh}_4(\text{CO})_{12}]$ cluster concentrations of 5 and 10 mmol dm⁻³ (Table 1). Between 1 and 20 bar CO, Rh_4L_3 fragments to afford predominantly Rh_2L_2 as the phosphite-containing dimeric species. The amount of Rh_4L_2 present also decreases slightly, and again we suggest that this results from either heterolytic cleavage followed by recombination or ligand displacement since Rh_4L_1 is also formed. Between 20 and 40 bar of CO, Rh_4L_2 fragments to give Rh_2L_2 , i.e. heterolytic cleavage, although some homolytic cleavage is also evidenced by the increase in fraction of Rh_2L_1 present in the dimers. On increasing the pressure to 40, and then to 80 bar, Rh_4L_2 fragments and the proportion of Rh_2L_1 in the dimers increases markedly. Since it seems unlikely that the fragmentation mechanism should be pressure-dependent, we ascribe this effect to redistribution of $\text{P}(\text{OPh})_3$ between the dimers and clusters present until the thermodynamically favoured mixture of Rh_2L_x dimers is achieved, probably via a sequence of fragmentation and recombination reactions since free $\text{P}(\text{OPh})_3$ is not observed. On the basis of these results, the stabilities of the dimers, at $\text{P}(\text{OPh})_3: [\text{Rh}_4(\text{CO})_{12}] = 2.1: 1$, would appear to be $\text{Rh}_2\text{L}_2 > \text{Rh}_2\text{L}_1 \gg \text{Rh}_2\text{L}_0$, Rh_2L_3 , with tetrameric clusters being thermodynamically preferred to the less stable dimers.

No clear trends are evident in the $\text{Rh}_2\text{L}_2: \text{Rh}_2\text{L}_1$ ratios with respect to Rh cluster concentration that cannot be accounted

Table 2. NMR spectroscopic data for Rh/triphenylphosphite hydrides

Rh/triphenylphosphite hydride	$^1\text{H}^a$		^{31}P		^{13}C		Solvent	Reference
	δ (ppm)	$J(^1\text{H}, \text{X})$ (Hz)	δ (ppm)	$J(^{31}\text{P}, \text{X})$ (Hz)	δ (ppm)	$J(^{13}\text{C}, \text{X})$ (Hz)		
$[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_3]^b$	−10.8	br, d $^2J(^{31}\text{P}, ^1\text{H}) = 27$	151	d of d $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 225$ $^2J(^{31}\text{P}, ^1\text{H}) = 27$	190.3	d of d of d $^1J(^{13}\text{C}, ^{103}\text{Rh}) = 61$ $^2J(^{13}\text{C}, ^{31}\text{P}) = 20$ $^2J(^{13}\text{C}, ^1\text{H}) = 10$	CDCl_3	–
$[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]^b$	−11	br, t $^2J(^{31}\text{P}, ^1\text{H}) = 31$	148.6	d of broad m $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 230$	192.5	d of d of t $^1J(^{13}\text{C}, ^{103}\text{Rh}) = 61$ $^2J(^{13}\text{C}, ^{31}\text{P}) = 15$ $^2J(^{13}\text{C}, ^1\text{H}) = 13$	CDCl_3	–
$[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]^b$	−10.5	br, s $^2J(^{13}\text{C}, ^1\text{H}) = 34$	141.0	d $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 240$	196.9	d of q $^1J(^{13}\text{C}, ^{103}\text{Rh}) = 52$ $^2J(^{13}\text{C}, ^{31}\text{P}) = 14$	CDCl_3	–
$[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]^c$	−10.9	$^1J(^1\text{H}, ^{103}\text{Rh}) = 3$ $^2J(^{31}\text{P}, ^1\text{H}) = 3$	141.2	$^1J(^{31}\text{P}, ^{103}\text{Rh}) = 240$	–	–	CDCl_3	[17, 19]
$[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]^c$	−10.6	d of q $^1J(^1\text{H}, ^{103}\text{Rh}) = 7$ $^2J(^{31}\text{P}, ^1\text{H}) = 44$	130	d $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 233$	–	–	–	[17, 18, 20]
$[(\text{H})_2\text{Rh}\{\text{P}(\text{OPh})_3\}_4\text{BPh}_4]^c$	−9.5	d of m $^2J(^{31}\text{P}, ^1\text{H}_{\text{trans}}) = 230$	118.7	d of t $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 169$ $^2J(^{31}\text{P}, ^{31}\text{P}) = 48$	–	–	C_6D_6	[21, 22]
			110.5	d of t $^1J(^{31}\text{P}, ^{103}\text{Rh}) = 145$				

^a Only reporting the hydride chemical shift.^b Chemical shifts and coupling constants given at 233 K except ^{13}C NMR, which was at 292 K.^c Room temperature.

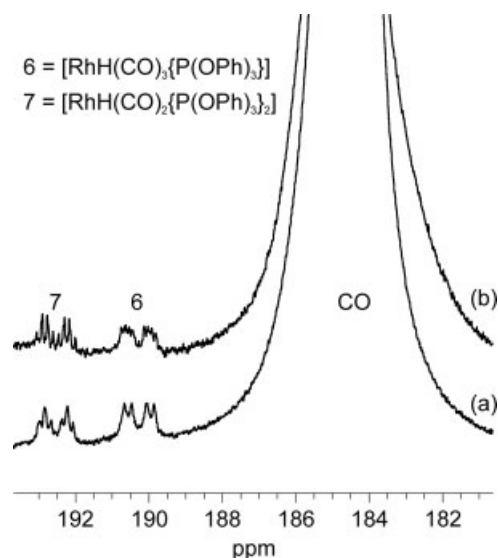


Figure 3. (a) $^{13}\text{C}\{^1\text{H}\}$ and (b) ^{13}C NMR spectra of $[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_3]$ **6** and $[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ **7** at room temperature and 40 bar $^{13}\text{CO} : \text{H}_2$ (3 : 1).

for by pressure dependence (Table 1). This suggests that, in our previous study, the concentration-dependent nature of the Rh_4L_2 fragmentation reaction was due to poor gas diffusion, the effect of which was not masked by the very high CO pressures used (400 bar).

Reaction of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{OPh})_3\}_x]$ ($x = 1-4$) with CO and H_2 (1 : 1, 75 bar)

A number of Rh/triphenylphosphite hydrides have been reported in the literature and characterised by NMR spectroscopy (Table 2); these include $[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]$,^[18,20] $[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]$ ^[17,19] and $[\text{Rh}(\text{H})_2\{\text{P}(\text{OPh})_3\}_4]\text{BPh}_4$,^[21,22] and $[\text{Rh}(\text{H})_2\{\text{P}(\text{OPh})_3\}_4]\text{ClO}_4$,^[23] the Raman and IR spectra of which have also been reported. Band-target entropy minimisation (BTEM) has also been used to detect the *in situ* high-pressure Fourier transform infrared (FTIR) spectra of $[\text{RhH}(\text{CO})_4]$ and $[\text{Rh}(\text{D})\text{CO}_4]$ under conditions similar to those used here, but in the absence of added phosphite.^[13] In the presence of a phosphite ligand, it is extremely unlikely that an observable concentration of an unsubstituted hydride, HRhL_0 , will be present. To the best of our knowledge, *in situ* high-pressure NMR spectroscopic data for $[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_3]$ and $[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ have not been published previously.

In our earlier report,^[16] the expected formation of hydride species on addition of H_2 to Rh_2L_x was not observed, even at total pressures up to 400 bar, in the unmixed HPNMR cell. We have, therefore, also re-examined this reaction in the HPNMR bubble column and found that, on pressurisation of a mixture of $[\text{Rh}_4(\text{CO})_{12}]$ (5 mmol.dm⁻³) and 2.1 equivalents of $\text{P}(\text{OPh})_3$ in CDCl_3 to 75 bar with CO : H_2 (1 : 1) at room temperature, the mono- and di-substituted hydrides $[\text{RhH}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_3]$ (RhHL_1) **6** and $[\text{RhH}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ (RhHL_2) **7** are formed [**6** and **7** in Fig. 2)]. The ratio of **6** : **7** at 233 K is 2 : 1. These hydrides have been characterised *in situ* by ^{31}P , $^{31}\text{P}\{^1\text{H}\}$ and ^1H HPNMR spectroscopy (Table 2) and in a high-pressure sapphire tube (40 bar CO : H_2 (3 : 1)) by ^{13}C and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Fig. 3 and Table 2).

There are several positional isomers possible in trigonal bipyramidal geometry for the 5-coordinate hydride complexes RhHL_1

and RhHL_2 , and the possibility of distortion towards a square-based pyramidal structure also exists. Buisman *et al.*^[26] have discussed the relationship between $^2J(^{31}\text{P}, ^1\text{H})$ and geometry for such complexes containing diphosphine, phosphite and diphosphite ligands. Small $^2J(^{31}\text{P}, ^1\text{H})$ values (<30 Hz) indicate a cis relationship between P and H, i.e. axial H and equatorial phosphorus-coordinated ligands with values of $^2J(^{31}\text{P}, ^1\text{H}) < 5$ Hz, indicating near perfect trigonal bipyramidal geometry.^[27] Conversely, large $^2J(^{31}\text{P}, ^1\text{H})$ values (>150 Hz) indicate a trans relationship between P and H, i.e. an axial-axial conformation. Intermediate $^2J(^{31}\text{P}, ^1\text{H})$ values indicate a time-averaged fluxional cis/trans relationship. From variable temperature NMR spectra of some Rh-diphosphite hydrides, Buisman *et al.*^[26] similarly concluded that large $^1J(^{31}\text{P}, ^{103}\text{Rh})$ couplings (up to 220 Hz) correspond to equatorially coordinated phosphorus, whereas axially bonded phosphites show somewhat smaller rhodium-phosphorus couplings ($^1J(^{31}\text{P}, ^{103}\text{Rh}) \sim 150-180$ Hz). Brown *et al.* report $^2J(^{13}\text{C}, ^1\text{H})$ coupling constants for Rh hydrides of 5-phenyl-5H-dibenzophosphole.^[28] The $^2J(^{13}\text{C}, ^1\text{H})$ coupling constant for axial CO is approximately 34 Hz, whereas the $^2J(^{13}\text{C}, ^1\text{H})$ for equatorial CO is 6 Hz, with intermediate coupling constants indicating rapid exchange between the two sites.

The ^1H HPNMR spectrum of RhHL_1 shows a broadened doublet at -10.8 ppm ($^2J(^{31}\text{P}, ^1\text{H}) = 27$ Hz) and $^1J(^1\text{H}, ^{103}\text{Rh})$ is not resolved. The ^{31}P NMR spectrum shows a doublet of doublets at 151 ppm ($^1J(^{31}\text{P}, ^{103}\text{Rh}) = 225$ Hz, $^2J(^{31}\text{P}, ^1\text{H}) = 27$ Hz). The ^{13}C NMR spectrum shows a doublet of doublet of doublets at 190.3 ppm ($^1J(^{13}\text{C}, ^{103}\text{Rh}) = 61$ Hz, $^2J(^{13}\text{C}, ^{31}\text{P}) = 20$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) = 10$ Hz). The ^1H NMR spectrum of RhHL_2 shows a broadened triplet at -11 ppm ($^2J(^{31}\text{P}, ^1\text{H}) = 31$ Hz); again $^1J(^1\text{H}, ^{103}\text{Rh})$ is not resolved. The ^{31}P NMR spectrum of RhHL_2 shows a doublet of broad multiplets at 148.6 ppm ($^1J(^{31}\text{P}, ^{103}\text{Rh}) = 225$ Hz), indicating that the two phosphorus atoms are in equivalent environments or rapidly exchanging on the NMR time scale. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is essentially unchanged between 233 and 292 K, indicating that any intramolecular fluxional process is slow on the timescale of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The ^{13}C NMR spectrum shows a doublet of doublet of triplets at 192.5 ppm ($^1J(^{13}\text{C}, ^{103}\text{Rh}) = 61$ Hz, $^2J(^{13}\text{C}, ^{31}\text{P}) = 15$ Hz, $^2J(^{13}\text{C}, ^1\text{H}) = 13$ Hz). The $^1J(^{31}\text{P}, ^{103}\text{Rh})$ values for both **6** and **7** are in the range expected for equatorially bound $\text{P}(\text{OPh})_3$. The $^2J(^{31}\text{P}, ^1\text{H})$ values for both hydrides are towards the upper limit for cis coordinating P and H, again indicating equatorially bound $\text{P}(\text{OPh})_3$ but possibly with either some exchange into the axial site occurring or a distorted trigonal bipyramidal geometry. The $^2J(^{13}\text{C}, ^1\text{H})$ values for **6** and **7** are in between the values expected for axial and equatorial CO, indicating that a rapid, fluxional process exchanges CO between the two types of sites. Consistent with such a process, $^2J(^{13}\text{C}, ^1\text{H})$ for **6** is smaller than **7** due to a 2 : 1 ratio of equatorial to axial CO in **6**, whereas the ratio in **7** is 1 : 1.

The speciation of Rh clusters under 75 and 80 bar CO : H_2 (1 : 1) (Table 3) is similar to that observed under 40 bar CO (Table 1), indicating that the presence of H_2 in solution has little effect on the speciation between the tetrameric clusters, and the mass balances indicate that unsubstituted compounds are absent. The sample is significantly depleted in the dimers, more so in Rh_2L_2 than in Rh_2L_1 , as required by mass balance. When the bubble column was depressurised, the hydrides and dimers recombined and a similar distribution of clusters reformed to that of the starting mixture.

In the presence of an excess of $\text{P}(\text{OPh})_3$ [$\text{Rh} : \text{P}(\text{OPh})_3$, 1 : 7, $[\text{Rh}] = 5$ mmol dm⁻³, 70 bar CO : H_2 (1 : 1)], the predominant

Table 3. The equilibrium speciation of $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$, $[\text{Rh}_2(\text{CO})_{8-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$ and $[\text{RhH}(\text{CO})_{4-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$ as percentages observed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at 233 K under CO and H_2 (1 : 1)

Rh concentration (mmol dm ⁻³)	CO pressure (bar)	Rh ₄ L ₁ (%)	Rh ₄ L ₂ (%)	Rh ₄ L ₃ (%)	Rh ₄ L ₄ (%)	Rh ₂ L ₁ (%)	Rh ₂ L ₂ (%)	RhHL ₁ (%)	RhHL ₂ (%)	Rh ₂ L ₂ /Rh ₂ L ₁	RhHL ₁ /RhHL ₂	P(OPh) ₃ : [Rh ₄ (CO) ₁₂] ^a
5 ^b	1 ^c	8	71	21	0.4	0	0	0	0	–	–	2.1
	1 ^d	6	72	20	3	0	0	0	0	–	–	2.2
	75	21	35	2	0	5	20	11	5	3.7	2.0	2.2
	75 ^e	19	36	3	0	4	21	12	5	4.6	2.1	2.3
5 ^f	1 ^c	15	74	11	0	0	0	0	0	–	–	2.0
	1 ^d	18	70	10	3	0	0	0	0	–	–	2.0
	40	19	43	7	0	4	6	12	9	1.6	1.4	2.2
	80	27	33	1	0	6	16	11	6	2.8	1.8	2.1

^a Calculated by mass balance.^b Experiments performed on a Bruker AVANCE-II 400 WB.^c Spectra taken before fragmentation.^d Spectra taken after recombination.^e Repeated using the same sample.^f Experiments performed on a AMX-II 200 WB spectrometer.

hydride observed was $[\text{RhH}(\text{CO})\{\text{P}(\text{O}^i\text{Ph})_3\}_3]$ (RhHL_3 and Fig. 2 **8**). The *in situ* $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopic data for **8** are presented in Table 2 and agree with literature values.^[19] $^1J(^{103}\text{Rh}, ^1\text{H})$ and $^2J(^{31}\text{P}, ^1\text{H})$ were not resolved in the ^1H HPNMR spectrum recorded in the bubble column; consequently, the hydride peak appeared as a broad singlet. When the reaction was repeated in a sapphire tube under ^{13}CO (at 38 bar, $^{13}\text{CO} : \text{H}_2$ 3 : 1), the hydride peak at -10.5 ppm in the ^1H NMR spectrum showed an additional doublet coupling assigned to $^2J(^{13}\text{C}, ^1\text{H})$ of 34 Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed a doublet of quartets at 196.9 ppm with $^1J(^{13}\text{C}, ^{103}\text{Rh})$ of 52 Hz and $^2J(^{13}\text{C}, ^{31}\text{P})$ of 14 Hz. The $^1J(^{31}\text{P}, ^{103}\text{Rh})$ and $^2J(^{13}\text{C}, ^1\text{H})$ values for this complex indicate that all $\text{P}(\text{O}^i\text{Ph})_3$ ligands are equatorial. When ^{13}CO was purged from the reaction mixture, replaced with 1 bar ^{12}CO and the sample repressurised with 5 bar H_2 , this coupling was lost, confirming the assignment and indicating that exchange of free and coordinated CO occurs readily.

Conclusions

The fragmentation and redistribution reactions of the tetrameric-phosphite-substituted rhodium clusters $[\text{Rh}_4(\text{CO})_{12-x}\{\text{P}(\text{O}^i\text{Ph})_3\}_x]$ ($x = 1-4$) under pressures up to 80 bar of CO and Syngas have been re-examined under conditions of efficient gas mixing and are found to be under thermodynamic control. ^1H , $^{31}\text{P}\{^1\text{H}\}$ and ^{13}C NMR data for the hydride species $[\text{RhH}(\text{CO})_3\{\text{P}(\text{O}^i\text{Ph})_3\}_3]$ (RhHL_1) **6** and $[\text{RhH}(\text{CO})_2\{\text{P}(\text{O}^i\text{Ph})_3\}_2]$ (RhHL_2) **7** are reported. On depressurisation/out-gassing of the samples, the original mixture of tetrameric clusters is obtained, confirming thermodynamic control of the cluster/dimer speciation of the system and offers an explanation for the absence of hydrides **6** and **7** in samples studied *ex situ*.^[17–21]

Equilibrium is more rapidly established with efficient gas mixing (<30 min) than in an unmixed cell when 24 h or more might be required.^[16] We have previously shown that gas delivery is an important factor governing the observed rate of homogeneously catalysed reactions in which one or more gases are a substrate.^[29,30] This work reveals that gas dissolution and out-gassing must also be considered in designing equilibrium reactions involving

dissolved gases and that very long equilibration times (of the order of days) can be avoided by the use of efficiently mixed cells.

Experimental

Chemicals were purchased from Sigma-Aldrich and Strem and were used as received except CDCl_3 , which was dried over activated molecular sieves. High-pressure NMR spectra were recorded on a Bruker AVANCE-II 400 WB or AMX-II 200 WB spectrometer, using home-built high-pressure bubble column NMR probes^[31] or on a DPX 400 MHz spectrometer using a high-pressure sapphire tube. All spectra were referenced to TMS following IUPAC guidelines.^[32,33] Solutions for the NMR spectroscopic measurements were prepared under CO using standard Schlenk techniques. Sample concentrations are given in the text.

Reaction of mixtures of $[\text{Rh}_4(\text{CO})_{12}]$ and triphenylphosphite with CO or Syngas in a HPNMR bubble column

Typically, a solution of $\text{P}(\text{O}^i\text{Ph})_3$ (19.2 μl , 0.074 mmol in CDCl_3 (3 ml)) was added dropwise, with stirring, over 1 h to a solution of $\text{Rh}_4(\text{CO})_{12}$ (26.2 mg, 0.035 mmol in CDCl_3 (4 ml)) to afford a 5 mmol dm⁻³ solution, which was transferred to the bubble column against a counter stream of CO. The probe was sealed, placed in the magnet, shimmed and pressurised with CO or $\text{CO} : \text{H}_2$ (1 : 1) mixture as appropriate (Tables 1 and 3). The sample was then held at this pressure, while CO or $\text{CO} : \text{H}_2$ was bubbled through the solution at 10 L_Nh⁻¹ (1 L_N = 1 l of gas at standard temperature and pressure (STP)) for 30 min at room temperature to allow equilibrium to be established. The sample was then cooled under pressure to 233 K, at that temperature the HPNMR spectra ($^{31}\text{P}\{^1\text{H}\}$ ^{31}P , ^1H) were recorded. Typically, 500–2000 transients (Time domain size (TD) = 8 k) were recorded, depending on the nucleus observed. The FIDs were zero filled to 32 k, and exponential multiplied, line broadening exponent (LB) = 5–15 (depending on the spectrometer), before Fourier transformation. Integrations are accurate to $\pm 5\%$.

Reaction of mixtures of $[\text{Rh}_4(\text{CO})_{12}]$ and triphenylphosphite with CO or Syngas in a HPNMR sapphire tube

Typically, $\text{P}(\text{OPh})_3$ (5.25 μl , 0.021 mmol) was added to a solution of $\text{Rh}_4(\text{CO})_{12}$ (7.5 mg, 0.01 mmol) in CDCl_3 (2 ml), which was transferred to a 10-mm sapphire tube under N_2 and pressurised up to 40 bar with ^{13}CO and H_2 (3:1). The sapphire tube was shaken well before being placed in the NMR magnet.

NB. Sapphire tubes are prone to sudden failure; adequate safety precautions must be taken while handling and using such tubes.

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