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FLUXIONAL BEHAVIOUR OF $Rh_4(CO)_8\{P(OPh)_3\}_4$: A ^{13}C-$\{^{31}P, {}^1H\}$ NMR STUDY

B.T. HEATON *, L. LONGHETTI,

Chemical Laboratory, University of Kent, Canterbury CT2 7NH (Great Britain)

L. GARLESCHELLI and U. SARTORELLI

Istituto di Chimica Generale ed Inorganica, Università di Milano, via G. Venezian 21, 20133 Milan (Italy)

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Summary

Variable temperature ^{13}C-$\{^{31}P, {}^1H\}$ NMR studies on $Rh_4(CO)_8\{P(OPh)_3\}_4$ show that the solid state structure is maintained in solution at low temperature; at higher temperatures carbonyl migration occurs around the metal polyhedron with the lowest energy migration occurring via a Cotton type mechanism which also involves a rocking motion about the unique rhodium in the basal plane. At +82° C, the fast exchange limiting ^{13}C-$\{^{31}P, {}^1H\}$ and ^{31}P spectra exhibit a quintet and doublet of quartets, respectively.

Introduction

Carbonyl clusters exhibit a variety of fluxional processes with carbonyl migrations being the most widely studied [1]. There is much interest in elucidating fluxional processes in tetranuclear carbonyl clusters, which have played a prominent part since the early proposal by Cotton for a $C_{3v} \leftrightarrow T_d$ mechanism [2]. Presently available evidence is consistent with this rearrangement occurring in $Rh_4(CO)_{12}$ [3], $Ir_4(CO)_{11}(PPh_2Me)$ [4] and $Ir_4(CO)_{11}(CNBu\text{-}t)$ [5] but not in $RhCo_3(CO)_{12}$ [6] and $Ir_4(CO)_{10}(diars)$ (diars = 1,2-bis(dimethylarsino)benzene) [7].

For these two apparent anomalies, different mechanisms have been suggested to account for their observed ^{13}C NMR [1,7,8]. We now present ^{13}C-$\{^{31}P, {}^1H\}$ NMR data for $Rh_4(CO)_8\{P(OPh)_3\}_4$ which necessitate an extension of the Cotton mechanism. The lowest energy rearrangement in this case involves a Cotton-like mechanism concomitant with a pseudo-rotation about the unique rhodium in in the basal plane.

Results and discussion

The solid state structure of $Rh_4(CO)_8\{P(OPh)_3\}_4$ has previously been determined [9] and the low temperature (—90° C) ^{13}C-$\{^{31}P, ^1H\}$ NMR spectrum (Fig. 1a) is entirely consistent with this geometry. The assignments, which are collected in Table 1, refer to Fig. 2a and, although the resonances are at lower field than in $Rh_4(CO)_{12}$, the trends in $\delta(^{13}C)$ are similar with the coupling constants remaining essentially unchanged [6]. It should be noted that although the doublets due to the carbonyls 3/3′ and 4/4′ are apparently coincident in THF solution, they are well-resolved in CH_2Cl_2 solution and this allows the assignment shown in Table 1. Moreover, well-resolved first order ^{13}C NMR spectra are only obtained with ^{31}P decoupling when working at relatively low levels of ^{13}C-enrichment (ca. 20%). At higher enrichment levels, the edge-bridging resonances become very complex due to the increased abundance of isotopomers containing two or three bridging ^{13}CO's which are strongly coupled when they are in the same plane as the Rh_3 triangle and give rise to complex second order spectra [10]. At —90° C, the ^{31}P-$\{^1H\}$ NMR of unenriched $Rh_4(CO)_8$-$\{P(OPh)_3\}_4$ is also complex due to second order effects.

On warming from —90 to —45° C all the carbonyl resonances broaden except the doublet due to 4/4′ (Fig. 1b). This doublet broadens on increasing the temperature further until at +82° C a sharp quintet, $\delta(^{13}C)$ 205.5 (calcd. 206.3) ppm, $J(^{103}Rh—^{13}C)$ 17.1 ± 2 Hz is observed due to the rapid scrambling of all the carbonyls over the $Rh_4\{P(OPh)_3\}_4$ skeleton (Fig. 1d); further splitting due to $J(^{31}P—^{13}C)$ is not resolved (Fig. 1e) in the ^{13}C-$\{^1H\}$ spectrum. At this temperature, the triphenylphosphite ligands also become equivalent as shown by the simple doublet of quintets, ($\delta(^{31}P)$ 110.6 ppm; $^1J(^{103}Rh—^{31}P)$ 221.2 and $^2J(^{103}Rh—^{31}P)$ 15.3 Hz), in the ^{31}P-$\{^1H\}$ NMR spectrum which gradually broadens as the temperature is decreased.

Rationalisation of the lowest energy carbonyl randomisation (Fig. 1b) involving all the carbonyls except 4/4′ (Fig. 2a) can be accommodated by the rearrangements shown in Fig. 2. This scheme incorporates the $C_{3v} \leftrightarrow T_d$ interconversion as well as a rocking motion on the unique rhodium atom (Rh_b). In this way the unique axial carbonyl (5 in Fig. 2a) can exchange with the edge-

TABLE 1

^{13}C NMR DATA AND ASSIGNMENTS FOR $Rh_4(CO)_8\{P(OPh)_3\}_4$

T (°C)	Solvent	$\delta(^{13}CO)$ (ppm) [J(Rh—CO) (Hz)] [a]				
		1/1′	2	3/3′	4/4′	5
—86	CD_2Cl_2	238.6 [34.2]	235.9 [35.2]	187.0 [64.4]	186.8 [74.2]	179.1 [64.5]
—90	C_4D_8O	240.0 [34.2]	236.9 [34.7]	188.3 [ca. 74]		180.4 [67.1]
+60	C_4D_8O			205.5		
+82	C_6D_8			205.5 [17.1]		

[a] The assignments refer to Fig. 2a.

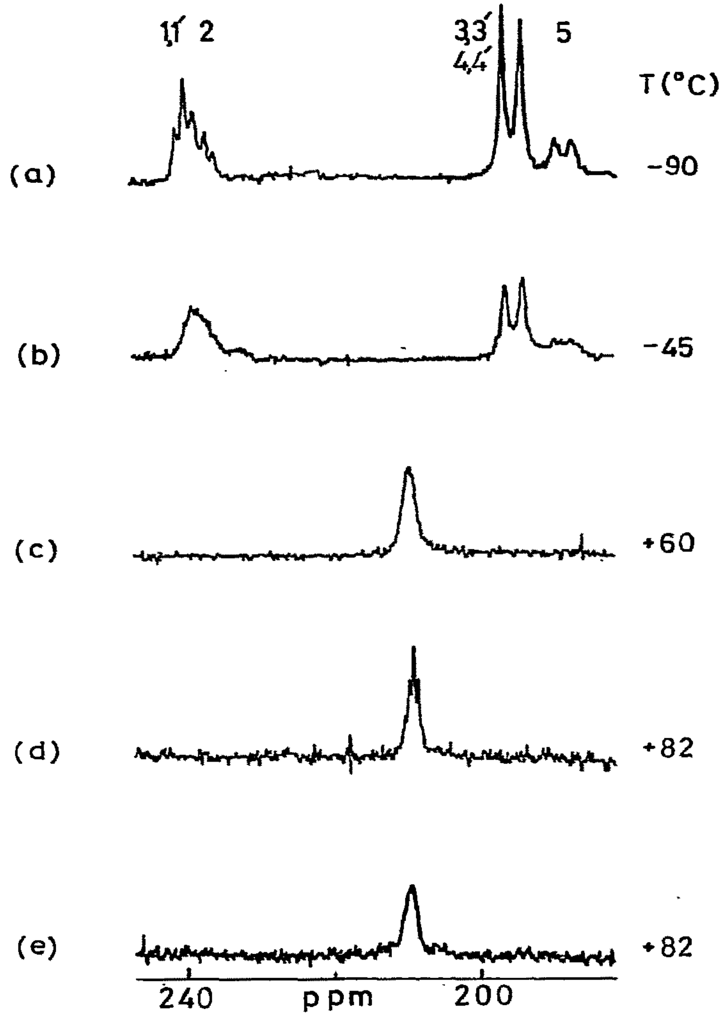

Fig. 1. Variable temperature NMR of $Rh_4(CO)_8\{P(OPh)_3\}_4$ (ca. 30% ^{13}CO). (a), (b), (c), ^{13}C-$\{^{31}P, ^{1}H\}$ NMR in tetrahydrofuran-d_8; (d), ^{13}C-$\{^{31}P, ^{1}H\}$ NMR in toluene-d_8; (e), ^{13}C-$\{^{1}H\}$ NMR in toluene-d_8.

bridging and radial carbonyls. This restricted rotation on Rh_b is probably dicated by the stereochemical distribution of the triphenylphosphites on the other rhodiums which are more rigidly locked. The rocking motion presumably develops into a complete localised rotation as the temperature increases and similar localised rotations on the other rhodium atoms is required in order to make all the triphenylphosphites equivalent and allow complete carbonyl randomisation. Although localised rotations have previously been suggested [7], the above example provides the first authentic example of such an effect and resembles the conflict between staggered versus eclipsed geometries found for $H_4Re_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, respectively, which have recently been discussed theoretically [11].

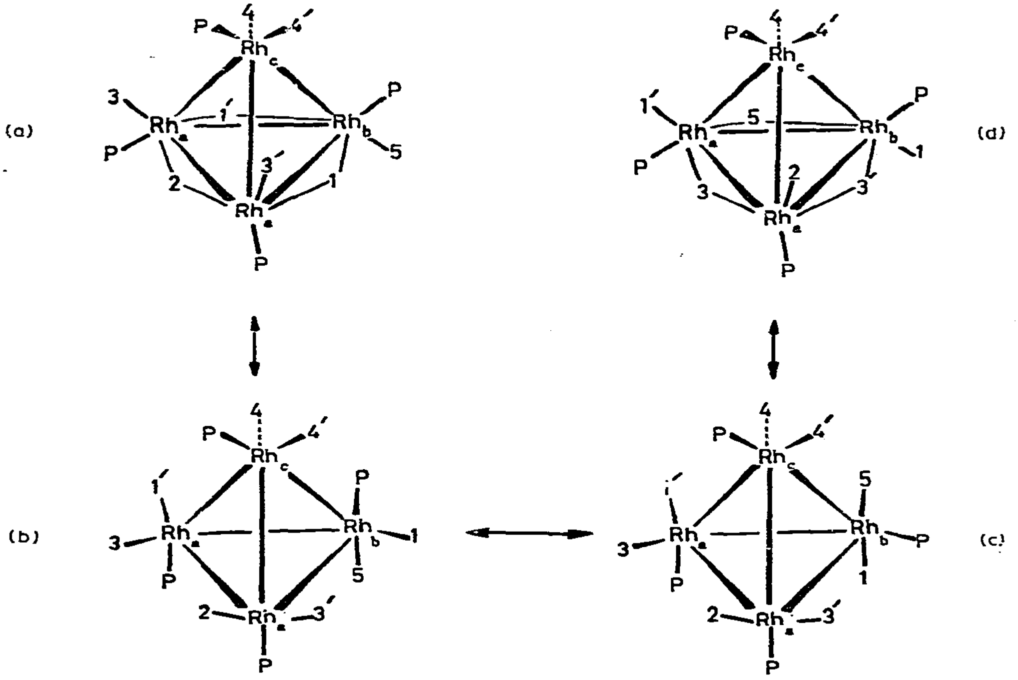

Fig. 2. Mechanism for lowest energy carbonyl scrambling in $Rh_4(CO)_8\{P(OPh)_3\}_4$.

Experimental

All NMR spectra were measured on a JEOL PS-100 PFT spectrometer operating at 25.15 MHz for ^{13}C and 40.48 MHz for ^{31}P. The ^{13}C NMR spectra were measured on solutions doped with $Cr(acac)_3$ as outlined earlier [12] and high power (10 watt) noise modulated irradiation at 40.484 and 100 MHz (both with band widths of 2.5 kHz) was used to obtain the $^{31}P/^{1}H$ decoupled ^{13}C spectra shown in Fig. 1.

^{13}CO enrichments were determined by high resolution mass spectrometry on the carbon monoxide resulting from thermal decomposition of $Rh_4(CO)_{12}$.

Preparation of $Rh_4(CO)_8\{P(OPh)_3\}_4$ (^{13}CO enriched)

To a solution of $Rh_4(CO)_{12}$ (0.72 g, 0.962 mmol), which had previously been enriched by direct ^{13}CO exchange, in dry, degassed toluene (75 ml) was added a solution of freshly distilled $P(OPh)_3$ (1.71 ml, 3.484 mmol) in toluene (75 ml). The solution was stirred at room temperature overnight under a nitrogen atmosphere and then concentrated under vacuum to 15—20 ml. Stratification with isopropanol (45 ml) produced crystals of the desired compound. Found: C, 51.7; H, 3.1; Rh, 21.2. $C_{80}H_{60}O_{20}P_4Rh_4$ calcd.: C, 51.2; H, 3.2; Rh, 21.9%.

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