# Internuclear Migration of a Bridging Phosphido Ligand

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Internuclear site exchange of a bridging diphenylphosphido ligand is rapid at room temperature for $[Rh_4(\mu\text{-}CO)_2(CO)_4(\mu\text{-}PPh_2)_4]$; a second higher temperature process allows one $PPh_2$ ligand to migrate between six sites about three Rh–Rh edges.

Phosphido ligands have attracted much attention as a means of stabilising metal–metal bonds in transition element dimers[1] and clusters.[2] The bridging phosphido group is generally considered to provide a non-fluxional frame supporting metal–metal bonds. However, we now report an exception to this assumption arising from a variable temperature n.m.r. study of $[Rh_4(\mu\text{-}CO)_2(CO)_4(\mu\text{-}PPh_2)_4]$, (**1**).[3,4]

At 210 K, the $\{^1H\}$-$^{31}P$ n.m.r. spectrum of complex (**1**) dissolved in toluene exhibits four resonances centred at δ 323.0, 263.0, 247.6, and 240.2 p.p.m.† consistent with the molecular structure in the crystal being maintained in solu-

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† Positive chemical shifts, δ, are downfield from external 85% $H_3PO_4$.

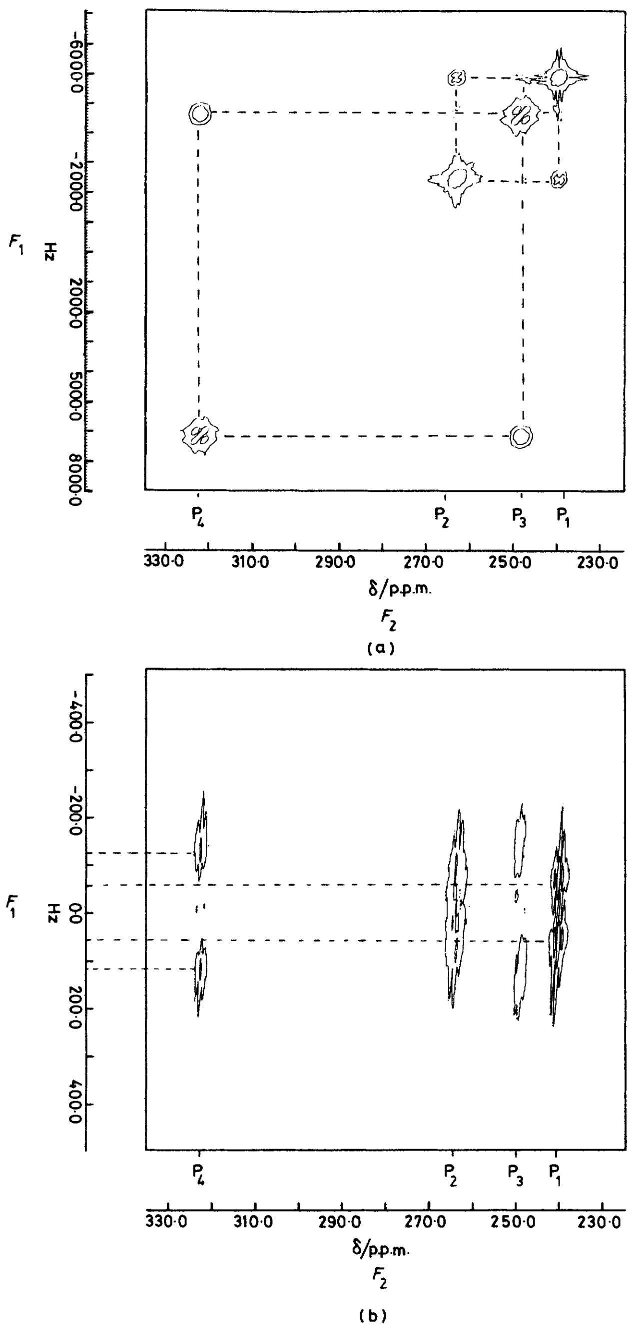

**Figure 1.** {$^1$H}-$^{31}$P-$^{31}$P 2-D N.m.r. (145.79 MHz) of [$Rh_4(CO)_6(\mu$-$PPh_2)_4$], (**1**) in toluene at 230 K. (a) COSY and (b) homonuclear *J*-resolved.

tion.[3,4] Broadening is evident at 190 K, perhaps because of restricted rotation of the phenyl rings. Assignment of this spectrum was complicated by the comparable values of $^1J(^{31}P$–$^{103}Rh)$ and $^2J(^{31}P$–$^{31}P)$ coupling constants, but was aided by two proton decoupled homonuclear $^{31}P$ 2-D n.m.r. spectra at 230 K. A COSY-90 spectrum [Figure 1(a)] indicated that the lowest field resonance was coupled only to the signal at δ 247.6 p.p.m. All of the three upfield resonances are mutually coupled, with the largest *J* value within this set being between the signals at δ 263.0 and 240.2 p.p.m. The $^{31}P$–$^{31}P$ and $^{31}P$–$^{103}Rh$ couplings were separated using a *J*-resolved 2-D spectrum [Figure 1(b)], projecting $J(^{31}P$–$^{31}P)$ values in the $F_1$ dimension. The largest $^2J(^{31}P$–$^{31}P)$ value (239 Hz) is expected to be due to the $P_3$–$P_4$ pair (Figure 2), which possess a transoid geometry in the crystal ($P_3$–$Rh_d$–$P_4$ 155°). Coupling between $P_1$ and $P_2$ is large (109 Hz), and these are also related by an obtuse bond angle ($P_1$–$Rh_b$–$P_2$ 124°). The assignment is presented in Figure 1. Since the lowest field resonance is coupled to only one other phosphorus, it is considered to be $P_4$; $P_3$ has a possibility of two bond couplings to all other phosphorus nuclei, and the resonance at δ 247.6 p.p.m. does show connectivity to the three other $^{31}P$ sites. $P_2$ and $P_1$ are differentiated on the basis of variable temperature behaviour. This assignment does not show a monotonic relation between chemical shift and M–P–M bond angle, as previously proposed.[5]

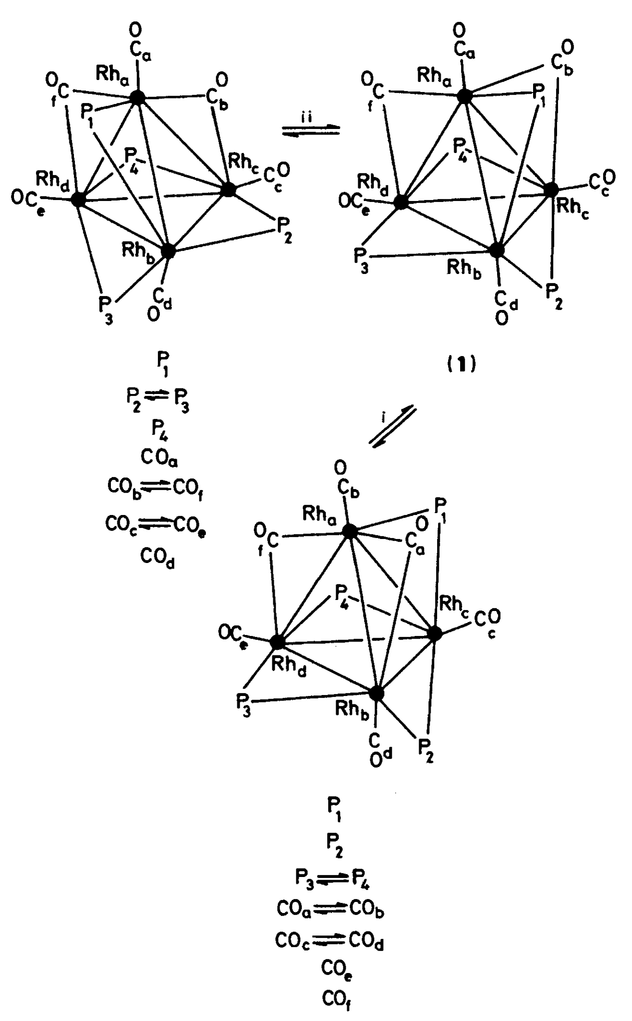

**Figure 2.** Atom sites in (**1**) and the low, i, and high, ii, temperature exchange processes.

At 230 K, selective exchange between $P_4$ and $P_3$ becomes evident, and this process gives rise to a broad, averaged resonance (δ 285 p.p.m.) at 323 K. However at that temperature, the resonance at δ 263.0 p.p.m. ($P_2$) also broadens, and at the highest temperature studied (377 K), the three low field resonances have formed a broad averaged signal at *ca.* δ 278 p.p.m. At that temperature, the resonance due to $P_1$ is a broadened doublet, showing retention of strong coupling to one $^{103}Rh$ nucleus.

The two exchange processes were only evident after studying the {$^1$H}-$^{13}$C n.m.r. spectra of complex (**1**) in the carbonyl region which, at 220 K, also accords with the expected solution structure.‡ At 255 K, four resonances broaden, with a bridging site at δ 222.59 and a terminal one at δ 194.03 remaining unaltered. At 295 K, it is evident that pairwise exchange between the bridging resonance at δ 216.21 and a terminal one near δ 192 had afforded one broad resonance and the two other terminal sites (δ 200.19 and one near δ 192) yielded a second averaged resonance. At that temperature also, the effects of the second exchange process become evident, causing the broadening of the two sites at δ 222.59 and 194.03.

These observations can be accounted for by the site exchange processes shown in Figure 2. The lower temperature process (labelled i) involves an oscillatory exchange of the terminal site $CO_a$, the bridging site $CO_b$, and the phosphido site $P_1$, generating an apparent plane of symmetry containing $P_2$, $CO_b$, $CO_f$, and $CO_e$. This makes $P_3$ equivalent with $P_4$ and $CO_c$ with $CO_d$. The high temperature process (labelled ii), is a twisting of the three phosphido ligands at $Rh_b$, equivalent to interchanging the disorder sites in the triclinic crystal habit of (**1**).[4] The combination of these two processes allows the phosphido group $P_1$ to migrate over the three Rh–Rh edges from $Rh_a$. Because of the asymmetry in complex (**1**), this requires six sites to be visited in the generation of an apparent three fold axis which renders $P_2$, $P_3$, and $P_4$ equivalent at 377 K.

It is clear that the assumption of rigid phosphido sites is not universally valid. Two viable intermediates for the low temperature process are either a terminal $PPh_2$ on $Rh_a$ or a face-bridging mode between $Rh_a$, $Rh_b$, and $Rh_c$. The low energy barrier to site exchange indicates possible mechanistic pathways for the labile disproportionation of several $PPh_2$ complexed systems.

A recent report included the observation of a terminal $PPh_2$ group in $[Fe_2(CO)_6(PPh_2)_2]^{2-}$ at low temperature prior to an irreversible isomerisation with the phosphido ligand adopting a bridging site.[6] In this work, we demonstrate that this type of transformation may be both reversible and rapid.

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‡ $\{^1H\}$-$^{13}C$ N.m.r. 90.5 MHz, toluene, 220 K: δ 222.59 (m, $CO_f$), 216.21 (m, $CO_b$), 200.19 [d, *J*(Rh–C) 74 Hz, $CO_c$ or $CO_d$], 194.03 [d, *J*(Rh–C) 90 Hz, $CO_e$], 192.07 [d, *J*(Rh–C) 78 Hz, $CO_a$, $CO_c$, or $CO_d$], and 192.01 [d, *J*(Rh–C) 92 Hz, $CO_a$, $CO_c$, or $CO_d$].