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Intramolecular dynamics of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ in solution

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A ^{103}Rh, ^{31}P and ^{13}C NMR study of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ in CD_2Cl_2 indicates that the strongly bonded, bridging, anionic ligand PPh_2^- takes part in the site exchange of the carbonyl ligands and is actually mobile about the metallic surface of this cluster compound.

Introduction

The overwhelming majority of studies on the fluxional behaviour of cluster compounds have dealt with the migration of carbon monoxide about the surface of the metallic skeleton.[1] It is now known that the energetics of CO migration in molecular clusters and on metal surfaces are of similar magnitudes.[2] Some ligands more strongly bonded to transition metals than CO are irreversibly chemisorbed on metal surfaces and considered as catalyst poisons. It would be interesting to see if such ligands are mobile or not on the surface of a molecular cluster at room temperature or lower. Non-CO ligands which have several coordination modes should lead to fluxionality or isomerisation of clusters, *i.e.* H^- has been found to participate in one of the fluxional processes of $[Ir_4(CO)_{11}(\mu\text{-}H)]^-$,[3] and quite a few other hydrido-clusters are fluxional.[4] The donor atom of the bidentate ligand $Ph_2PCH{=}CHPPh_2$ which can either be chelating or edge-bridging has been found to move between metal atoms in $[Ir_4(CO)_{10}(Ph_2PCH{=}CHPPh_2)]$.[5] More interestingly, the neutral phosphorus ligands were also been found to migrate intramolecularly from one metal to another in the heterometallic clusters $[Ir_2Rh_2(CO)_{11}PPh_3]$,[6] $[PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)]$[7a] and $[PtRu_5(CO)_{15}(P^tBu_3)(\mu_6\text{-}C)]$,[7b] but these examples are isomerisations and not fluxional processes. A fluxional process involving neutral ligands L (= $P(OMe)_3$, $P(OPh)_3$) was reported as a migration of L around the Pt_3 triangle in $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3L)]^{2+}$.[8]

The following question is addressed in the present study: Is a strongly bonded, bridging ligand actually mobile about the metallic surface of a fluxional molecular cluster?

The technique used to examine fluxional behaviour is NMR, the chosen metal and donor atom of the ligand should both have an isotope with nuclear spin one half. To be fluxional, the chosen cluster should have bridging and terminal CO ligands. The non-CO ligand should have only one coordination mode in the ground state structure of the molecular cluster and be inert with respect to substitution by CO. The rhodium(I) cluster $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$, whose structure is already know from two X-ray diffraction studies,[9,10] potentially satisfies these prerequisites and was chosen to see if the PPh_2^- ligand actually moves about the metal skeleton in the NMR time scale.

Results and discussion

Assignment of the ground state structure of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ in solution

$[Rh_4(CO)_4(\mu\text{-}CO)_2(\mu\text{-}PPh_2)_4]$ (**1**) is thermally stable in solution in dichloromethane up to the boiling point of the solvent. The PPh_2^- ligand is more strongly bonded to rhodium than CO in the sense that it is not displaced by stirring a solution of **1** overnight under ^{13}CO (1.2 atm) which only causes statistical isotopic substitution without decomposition to complexes with lower phosphorus contents. It has been reported to crystallise in two crystal systems, triclinic (with disorder)[9] and monoclinic.[10] The molecular scheme presented in Fig. 1 is restricted to the Rh_4 tetrahedron, the four P atoms and the six COs, and corresponds to the molecular structure of the enantiomer of **1** crystallising in the monoclinic system.[10] The numbering scheme is arbitrary, increasing numbers only corresponding to decreasing chemical shifts of NMR resonances.

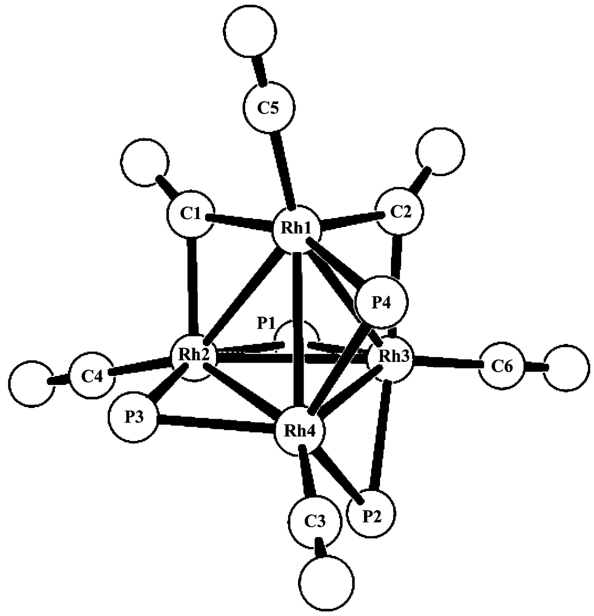

Fig. 1 Molecular structure of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ (phenyl groups omitted for clarity).

All NMR data show that the ground state structure of **1** in solution is similar to that found in the solid with two bridging and four terminal COs, and with four bridging PPh_2^- ligands. However, the numbered atoms must first be unambiguously located in the structure before looking at the dynamic properties. The starting point is the ^{103}Rh NMR spectrum of **1** in CD_2Cl_2 at 203 K (Fig. 2). The resonance at δ 3785.5 is a doublet (^1J(Rh1–P) = 107.9 Hz); Rh1 thus corresponds to the unique metal atom bonded to one P atom. The resonance at δ 2673 is an apparent quartet and thus corresponds to Rh4, the unique metal atom bonded to three P atoms. The resonances at δ 3556 and 3526 are apparent triplets due to Rh2 and Rh3 which

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Table 1 ^{31}P and ^{103}Rh NMR data of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$

Atom	δ	P1 *J*/Hz	P2 *J*/Hz	P3 *J*/Hz	P4 *J*/Hz
P1	324.7				
P2	265.1	4.5			
P3	246.0	236.5	46.0		
P4	236.8	−23.7	110.4	0.1	
Rh1	3785.5	13.2	−0.3	−5.4	107.9
Rh2	3556.0	103.6	−19.1	103.2	11.2
Rh3	3526.0	103.7	114.8	24.9	−5.0
Rh4	2673.0	7.8	−126.3	100.7	108.0

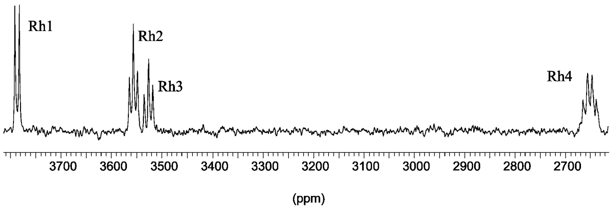

Fig. 2 ^{103}Rh NMR spectrum (CD_2Cl_2, 203 K) of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$.

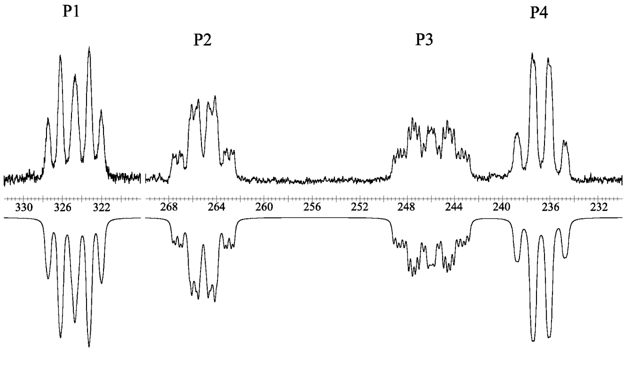

Fig. 3 ^{31}P NMR spectrum (CD_2Cl_2, 203 K) of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ (the inverted spectrum is calculated).

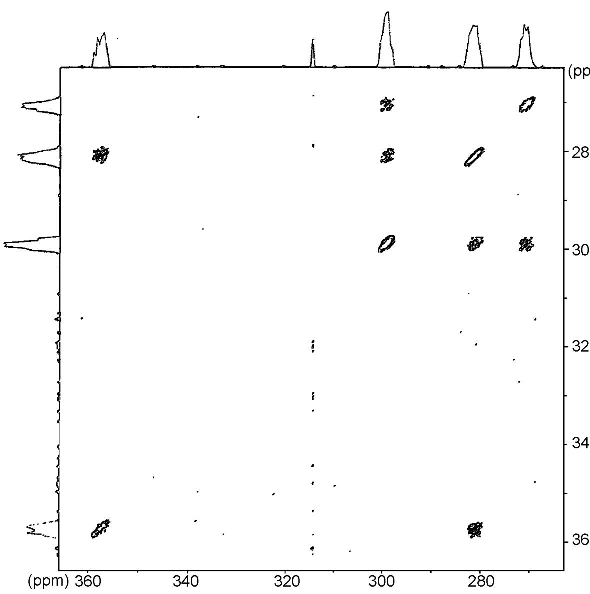

Fig. 4 ^{31}P COSY spectrum (CD_2Cl_2, 223 K) of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$.

cannot be distinguished, but selective irradiations at the ^{31}P frequencies will establish the Rh–P connectivities.

The ^{31}P NMR spectrum of **1** in CD_2Cl_2 at 203 K (Fig. 3) shows four resonances at δ 324.7 (dt, P1), 265.1 (m, P2), 246.0 (m, P3) and 236.8 (m, P4). Irradiation at the frequency of P1 does not modify the multiplicity of the resonances of Rh1 and Rh4, therefore P1 bridges the Rh2–Rh3 bond. Likewise, irradiation at the frequency of P2 (P3 respectively) does not affect the resonances of Rh1 and Rh2 (Rh1 and Rh3 respectively), therefore P2 bridges the Rh3–Rh4 bond and P3 bridges the Rh2–Rh4 bond. Lastly, irradiation at the frequency of P4 suppresses the coupling of the Rh1 resonance and leaves that of Rh4 as an apparent triplet, therefore P4 unambiguously bridges the Rh1–Rh4 bond. The resonance of P1 is a quintet caused by coupling with two Rh atoms and one P atom. The latter is identified as P3 by Rh decoupling and by a ^{31}P COSY spectrum (CD_2Cl_2, 223 K, Fig. 4) which shows that the largest coupling is between P1 and P3 (^2J(P1–P3) = 236.5 Hz). This starting value was then introduced in the simulation of ^{31}P resonances using the gNMR program.[11] The calculated coupling constants are reported in Table 1 and the simulated spectrum is the inverted one in Fig. 3. The position of P1 and P4 being unambiguously assigned, the location of P3 is deduced from the fact that the largest coupling constant (236.5 Hz) should involve a pair of P atoms which are more or less in the plane of a face of the tetrahedron. The structural data[10] show that the values of the P1–Rh2–Rh4–P3 and P1–Rh3–Rh4–P3 torsion angles are −169.4 and −15.7°, respectively, whereas all other values of P–Rh–Rh–P torsion angles are between 48 and 90° (*i.e.* 89.7° for P2–Rh4–Rh3–P1). P3 being positioned, the above mentioned observation that P3 must bridge the Rh2–Rh4 bond resolves unambiguously the assignment of the Rh and P atoms. The structural data[10] show that P4 is in the plane of the Rh1–Rh2–Rh4 face (the torsion angle Rh4–Rh2–Rh1–P4 has a value of 0.1°). This places P4 above the Rh1–Rh3–Rh4 face which has an edge bridged by a carbonyl ligand. The geometrical proximity between P4 and a bridging CO will be important for the discussion of the site exchanges.

The ^{13}C NMR spectrum of a ^{13}C enriched (*ca.* 30%) sample of **1** in CD_2Cl_2 at 203 K (Fig. 5) exhibits six resonances at δ 224.5 (m, *J*(C1–Rh1) 29.3; *J*(C1–Rh2) 37.8; *J*(C1–P4) 63 Hz), 219.5 (m, *J*(C2–Rh1) 30.8; *J*(C2–Rh3) 40.4; *J*(C2–P3) 56 Hz), 200.7 (d, *J*(C3–Rh4) 74 Hz), 194.4 (d, *J*(C4–Rh2) 94 Hz); 192.5 (d, *J*(C5–Rh1) 95 Hz), and 191.7 (d, *J*(C6–Rh3) 80 Hz). The two highest resonances are clearly due to bridging COs. The latter always resonate above 200 ppm with C–Rh coupling constants in the order of 30 Hz (*i.e.* at 228 ppm with ^1J(C–Rh) = 34.6 Hz for $Rh_4(CO)_{12}$).[12,13] The reported coupling constants for the two COs come from a simulation of the corresponding resonances using the gNMR program. The respective positioning of C1 and C2 results from the following experiment. A selective irradiation at the frequency of P2 leaves the resonance of C1 essentially unaffected, whereas that of C2 becomes an apparent triplet (due to coupling with two Rh nuclei) as shown in Fig. 5. It is known that geminal C–P couplings are small in Rh4 clusters with mono-, di- and triphosphines except when the two atoms are more or less in *trans* positions.[14] The structural data (and Fig. 1) show that C2 is more or less in *trans* position relative to P2 whereas C1 is not (the value of the C1–Rh2–Rh4–P2 torsion angle is −134.2°). It may also be noted that there is no correlation between highest C–Rh coupling constant and shortest C–Rh distance [*d*(C1–Rh1) 2.00 < *d*(C2–Rh1) 2.07 Å and *d*(C2–Rh3) 2.10 < *d*(C1–Rh2) 2.17 Å].[10] The resonance of C3 has the highest δ value and the smallest C–Rh coupling constant among the terminal COs. It thus corresponds to the carbonyl linked to Rh4, the metal atom having the greatest number of electronegative substituents. It is known that in $Rh_4(CO)_{12}$ (and in other Rh_4 clusters) the radial COs which are approximately coplanar with the bridging ones have a higher value (73.2 Hz) for the ^1J(C–Rh) coupling constant than axial carbonyls which are perpendicular to µ-COs (61.0 Hz).[12,13] We propose to assign the C4 and C5 resonances which have the highest C–Rh coupling constants to the terminal carbonyls linked to Rh2 and Rh1, since these are nearly coplanar with Rh2, Rh1 and C1 (the values of the C4–Rh2–Rh1–C5 and C1–Rh1–Rh4–Rh2 torsion angles are 8.7 and 12.9°, respectively). The positioning of C4 and C5 may as well be inverted, but we will see that the locations given in Fig. 1 are the only ones which

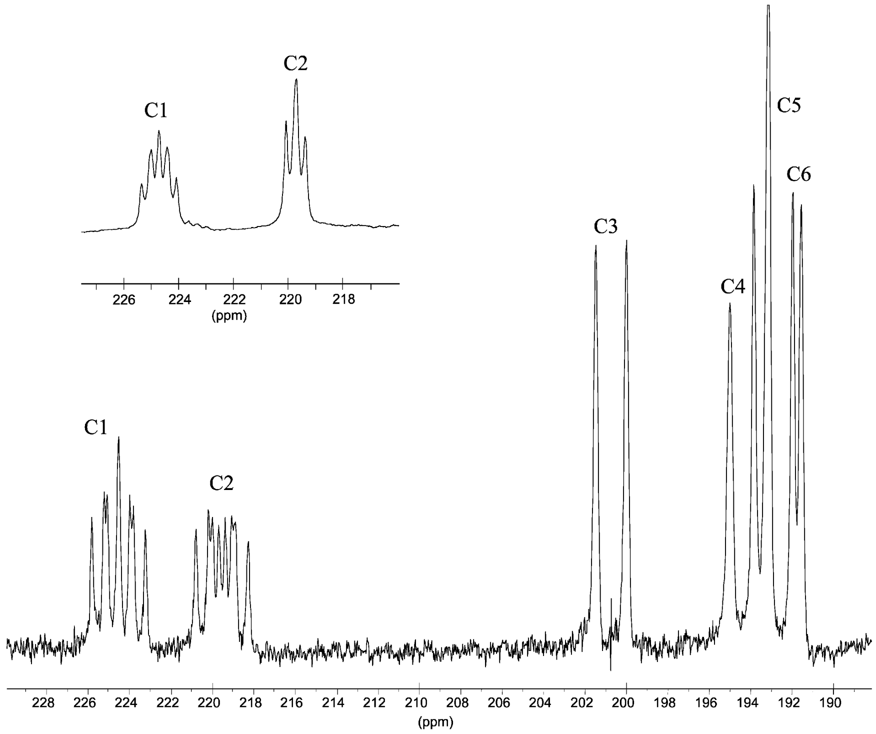

Fig. 5 ^{13}C NMR spectrum (CD$_2$Cl$_2$, 203 K) of [Rh$_4$(CO)$_6$(μ-PPh$_2$)$_4$]. The insert shows the effect of selective radiation at the frequency of P2 on the resonances of C1 and C2, see text.

are compatible with the dynamic connectivities. Finally, one should note that C2 is closer to P4 than C1, and that C5 and C2 are linked to a common Rh atom, whereas C4 is not.

Intramolecular dynamics of [Rh$_4$(CO)$_4$(μ-CO)$_4$(μ-PPh$_2$)$_4$]

A ^{31}P EXSY spectrum (CD$_2$Cl$_2$, 248 K, mixing time 150 ms) of **1** shows only one site exchange P1 ↔ P3, which is therefore mutual, following Muetterties' definition.[14] The ^{31}P NMR spectra at variable temperature (203 to 303 K, Fig. 6) were then simulated using a two-site exchange matrix with one rate constant k. A linear regression of $\ln(k/T) = \ln(k_B/h) - (\Delta G^{\#}/RT)$ *vs.* $1/T$ (see Experimental) gave values of 37.4 ± 1 kJ mol^{-1}and -49 ± 7 J K^{-1} mol^{-1} for $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively. A value of 49.7 ± 0.9 kJ mol^{-1} for $\Delta G^{\#}$(250 K) was obtained.

A ^{13}C EXSY spectrum (CD$_2$Cl$_2$, 240 K, mixing time 100 ms, Fig. 7) of **1** shows two site exchanges, each being mutual: C2 ↔ C5 and C3 ↔ C6. The ^{13}C NMR spectra at variable temperature (233 to 283 K, Fig. 8) were then simulated using a four-site exchange matrix with one rate constant k. Regression of the Eyring plot $\ln(k/T)$ *vs.* $1/T$ gave: $\Delta H^{\#} = 35.0 \pm 1$ kJ mol^{-1}, $\Delta S^{\#} = -64 \pm 8$ J K^{-1} mol^{-1}, and $\Delta G^{\#}$(250 K) = 51.0 ± 0.9 kJ mol^{-1}. Fitting all ^{31}P- and ^{13}C-NMR data with a single rate constant k gave a value of 51.3 ± 0.8 kJ mol^{-1} for ΔG(250 K). Taking into account the experimental errors, one may conclude that the site exchanges of the phosphorus ligands and of the carbonyls are part of the same fluxional process. Comparing the rate of carbonyl exchange in Rh$_4$(CO)$_{12}$ [k(263K) = 7040 ± 300 s^{-1}][13] with the rate of site exchange in **1** [k(263K) = 257 ± 10 s^{-1} (^{13}C) and 270 ± 10 s^{-1} (^{31}P)], one notes that the exchange process is about 30 times slower in **1** than in Rh$_4$(CO)$_{12}$ where the rate determining step is the debridging of carbonyls. This may indicate that debridging of a phosphido group, which is more strongly bonded to Rh than CO, is the rate determining step of the site exchange in **1**. However, this argument is not conclusive. Bridging COs being better π-acceptors than terminal COs, the former may be relatively more stabilised in the more electron-rich, ground-state structure of **1** than in that of Rh$_4$(CO)$_{12}$, and/or the presence of phenyl rings in **1** might sterically hinder the movement of the carbonyls.

The answer to the question raised in the introduction will come from the conjunction of the observed site exchanges. First, the exchange μ-C2 ↔ η-C5 being mutual and not the only one observed, debridging of C2 must occur by breaking the C2–Rh3 bond and bridging of C5 must take place on another edge than the Rh1–Rh3 bond. In addition, two phosphido groups are mutually exchanging. This leaves the following alternative: either P1 and/or P3 move or P1 and P3 do not move. If P1 moves, that is bridges the Rh1–Rh3 edge while μ-C2 becomes terminal on Rh1, C5 cannot bridge the Rh2–Rh3 edge. If μ-C2 became terminal on Rh3, C6 would have to exchange with C2 and this is not observed. If P3 moves and bridges the Rh2–Rh1 edge, an isomer of **1** is obtained of different energy which is excluded for a fluxional process. Therefore, P1 and P3 do not move. Since the observed exchanges imply a time averaged mirror plane through the Rh1–Rh2 edge and the mid-point of the Rh3–Rh4 edge, P4 must move to the Rh1–Rh3 edge and C5 to the Rh1–Rh4 edge, μ-C2 becoming terminal on Rh1. The comparison of the initial and final configurations shown in Fig. 9 indeed gives the observed dynamic connectivities: C1 ⟶ C1, C2 ⟶ C5, C3 ⟶ C6, C4 ⟶ C4, C5 ⟶ C2, C6 ⟶ C3, P1 ⟶ P3, P2 ⟶ P2, P3 ⟶ P1 and P4 ⟶ P4.

In conclusion, [Rh$_4$(CO)$_6$(μ-PPh$_2$)$_4$] is an example of a cluster where an anionic and strongly bonded ligand (compared to CO) effectively moves about the metallic surface during an intramolecular site exchange process.

If the cluster-metal surface analogy is accepted, a phosphido group which is considered as a carbonylation catalyst poison may effectively hop between metal atoms.

Finally, the mirror image of the enantiomer shown in Fig. 1 could as well be obtained by rocking P4 around the Rh1–Rh4 edge. This would push P3 to a position about coplanar to the Rh1–Rh2–Rh4 face and P2 coplanar to the Rh2–Rh3–Rh4 face, and lead to the exchanges P2 ↔ P3, μ-C1 ↔ μ-C2 and C4 ↔ C6 which are not observed. Therefore, rocking a bridging PPh$_2^-$ group around a metal tetrahedron edge is not a process of lowest activation energy. Since new NMR resonances start to broaden above 310 K, interconversion between these enantiomers may eventually occur at higher temperatures.

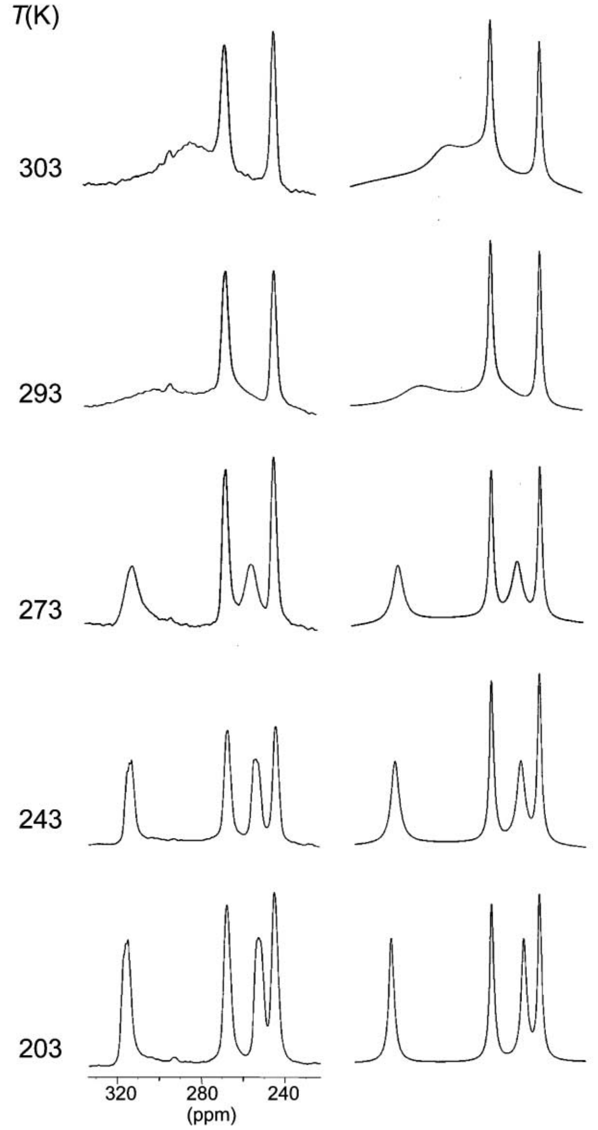

Fig. 6 Variable temperature ^{31}P NMR spectra of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ in CD_2Cl_2. Left: experimental, right: calculated.

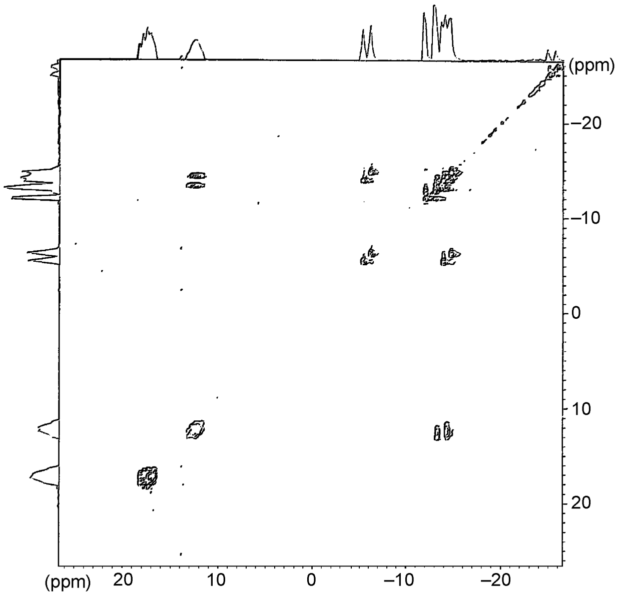

Fig. 7 ^{13}C EXSY spectrum (CD_2Cl_2, 240 K, mixing time 100 ms) of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$.

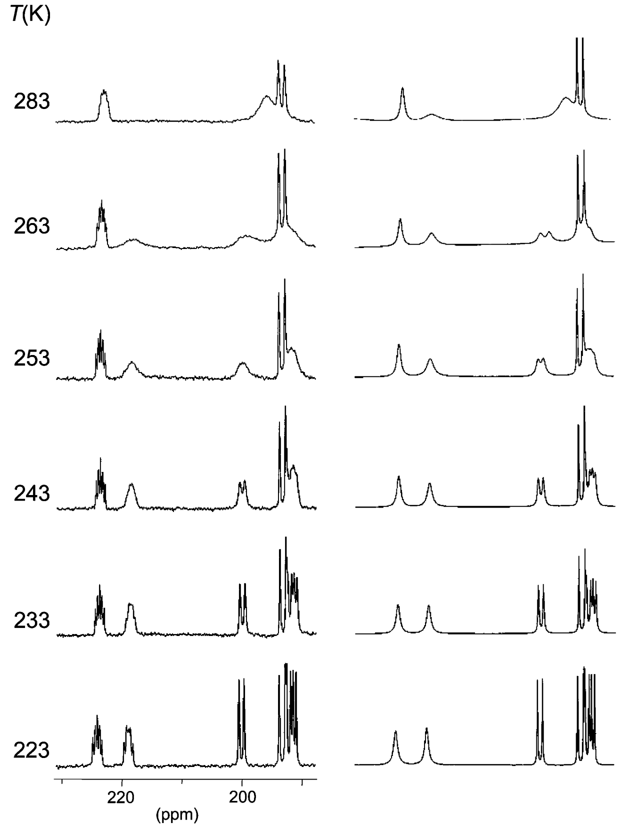

Fig. 8 Variable temperature ^{13}C NMR spectra of $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ in CD_2Cl_2. Left: experimental, right: calculated.

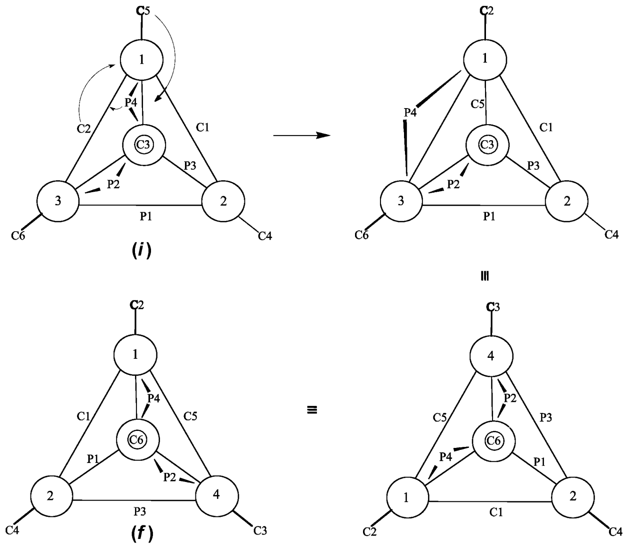

Fig. 9 Proposed site exchange of lowest activation energy in $[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ (*i*: initial configuration; *f*: final configuration, mirror image of *i*).

Experimental

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on Bruker AC 200 (^{1}H at 200.13 MHz, ^{31}P at 81.02 MHz and ^{13}C at 50.32 MHz), on Bruker WH 360 (^{13}C at 90.55 MHz) and on Bruker DRX 400 (^{31}P at 161.93 MHz, ^{13}C at 100.6 MHz) spectrometers. The chemical shifts (δ) are referred to Me_4Si (^{1}H and ^{13}C), to external 85% H_3PO_4 (^{31}P), and to the spectrometer frequency (^{103}Rh). The ^{13}C and ^{31}P spectra were ^{1}H decoupled, and the NMR data are given in the text.

$[Rh_4(CO)_6(\mu\text{-}PPh_2)_4]$ was prepared by one of the literature methods,[9] starting with $[Rh_2(CO)_4Cl_2]$,[15] $PHPh_2$ (Strem

Chemicals, > 99%) and Et_2NH (Fluka, < 98%). It was purified by thick layer chromatography on silica gel using CH_2Cl_2–heptane 1:2 as eluent. Black crystals of **1** obtained by cooling a solution in hexane to −10 °C gave satisfactory elemental analyses. Its IR spectra measured in cyclohexane and measured as a Nujol mull were very similar and corresponded to those given in ref. 9. Samples of **1** enriched in ^{13}C (*ca.* 30%) were obtained by stirring the compound in CH_2Cl_2 at 0 °C for 12 h under ^{13}CO (1.2 atm). Statistical isotopic substitution was confirmed by the presence of ^{13}C satellites of the ν(CO) IR bands (2014–1972 cm^{-1}) and of the μ-CO bands (1871 and 1851 cm^{-1}).

Kinetic data

Simulation of the variable temperature ^{13}C and ^{31}P NMR spectra of **1** gave the following values of the rate constant k in s^{-1} (temperature in K is given in parentheses). ^{13}C data: 21.4 (233), 77.0 (243), 185 (253), 257 (263), 730 (283). ^{31}P data: 143 (243), 935 (273), 4484 (293), 6169 (303).

Acknowledgements

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