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## <sup>13</sup>C and <sup>31</sup>P NMR studies on geometrical non-rigidity in heterobinuclear complexes [WM(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (M = Rh, Cu)

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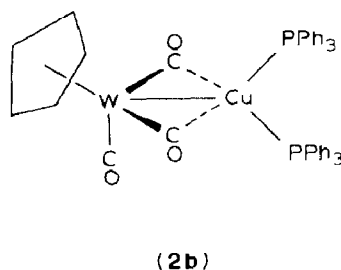
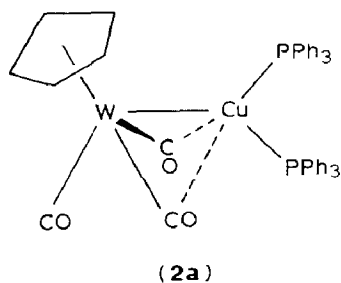
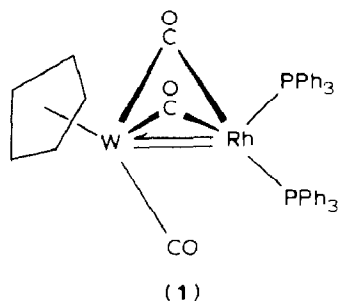
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### Abstract

<sup>13</sup>C NMR studies on [W<sub>2</sub>(CO)<sub>6</sub>Cp<sub>2</sub>] (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), including a 2D EXSY study, confirm that simple rotation about the W–W bond is responsible for the isomerisation in solution. Variable temperature <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of [WRh(μ-CO)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>Cp] establish that a pseudo-rotational process, with Δ*G*<sup>‡</sup> 27.9 ± 0.8 kJ mol<sup>-1</sup> at -108 ± 8°C, results in interchange of the inequivalent PPh<sub>3</sub> groups and all the CO ligands. The mechanism of this facile fluxional process is discussed in relation to that of [W<sub>2</sub>(CO)<sub>6</sub>Cp<sub>2</sub>], and an intermediate (or transition state) of the type [WRh(μ-CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cp] is proposed. Variable temperature <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of [WCu(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cp] in solvents of various polarities establish a related geometrical non-rigidity for this complex, but with Δ*G*<sup>‡</sup> ca. 39–41 kJ mol<sup>-1</sup>, in the range -57 to -69°C; this result, considered along with the very low electrical conductivity in acetone, suggests that an intramolecular mechanism also operates for this interchange.

The stoichiometrically related complexes [WM(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Cp] (M = Rh (**1**); Cu (**2**); Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) have been previously fully characterised in the solid state by X-ray diffraction [1,2]. Complex **1** contains two bridging CO ligands and may be considered to possess a formal double bond between W and Rh, as indicated in **1**, although EHMO calculations do not support the presence of an unusually strong direct metal–metal interaction [3]. Complex **2**, with two extra valence shell electrons, exists in two different structural forms in the solid state, **2a** and **2b**, containing only semi-bridging CO groups interacting weakly with Cu. Both structural forms of **2** have relatively long W–Cu bonds, consistent with a small Cu–W reduced orbital overlap population calculated by the EHMO method for [WCu(CO)<sub>3</sub>(PH<sub>3</sub>)<sub>2</sub>Cp] [3], and these Cu–W bonds will also possess significant polarity.



In both of the complexes **1** and **2** two types of non-equivalent CO and PPh<sub>3</sub> groups are present in the solid state, but, although  $\nu(\text{CO})$  bands in IR spectra do support similar molecular symmetry in solution, previous  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in solution at temperatures  $> -60^\circ\text{C}$  have shown all the  $^{13}\text{CO}$  and  $^{31}\text{PPh}_3$  ligands to be equivalent [1]. This is consistent with geometrical non-rigidity. It may be noted that paramagnetic  $[\text{W}\text{Ni}(\text{CO})_3(\text{PPh}_3)_2\text{Cp}]$ , which is structurally related to complex **2**, clearly retains the solid state structure in solution, since inequivalent PPh<sub>3</sub> groups are detected at ambient temperature by ESR spectroscopy [3].

Herein we present the results of variable temperature (VT) NMR and other studies of the fluxional processes for complexes **1** and **2**.

## Experimental

$[\text{W}_2(\text{CO})_6\text{Cp}_2]$ , enriched with  $^{13}\text{CO}$  (23%), was prepared by stirring the unlabelled complex [4] in dichloromethane solution with an excess of  $^{13}\text{CO}$  gas (99% enriched, Amersham International) in a vacuum system for 2 d. The content of  $^{13}\text{CO}$  in the purified product was established by mass spectrometry. The  $^{13}\text{CO}$ -enriched complexes  $[\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{Cp}]$  ( $\text{M} = \text{Rh}$  (**1**),  $\text{Cu}$  (**2**)) were prepared by published methods [1] from  $^{13}\text{CO}$ -labelled  $[\text{W}_2(\text{CO})_6\text{Cp}_2]$ .

VT NMR spectra were obtained with a Bruker WP 200 SY instrument at 81.0 MHz ( $^{31}\text{P}$ ) and 50.3 MHz ( $^{13}\text{C}$ ) and also with a Bruker WH 360 spectrometer at 90.56 MHz ( $^{13}\text{C}$ ). All samples for  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis, except in the case of 2D studies, contained  $0.05 \text{ mol dm}^{-3}$  tris(acetylacetonato)chromium(III). Chemical shifts are quoted as positive to high frequency of tetramethylsilane ( $^{13}\text{C}$ ) or of external 85% orthophosphoric acid ( $^{31}\text{P}$ ). Electrical conductivities were measured under nitrogen with solutions of concentrations  $10^{-2}$ – $10^{-4} \text{ mol dm}^{-3}$  in dried,

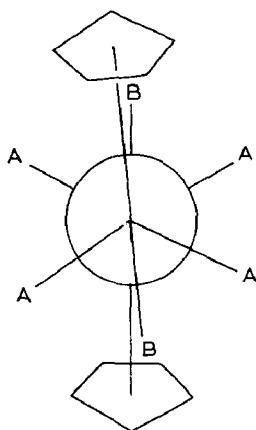
freshly distilled AR grade acetone at  $19 \pm 1^\circ\text{C}$ , using a Wain Kerr 4225 LCR meter operating at 1 KHz.

## Results and discussion

### $[\text{W}_2(\text{CO})_6\text{Cp}_2]$

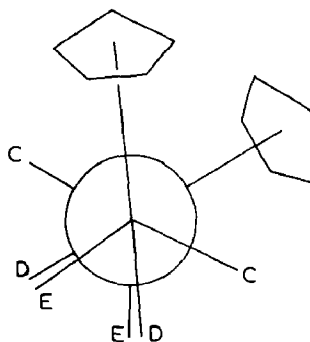
Previous investigations involving  $^1\text{H}$  NMR spectroscopic studies on the simple homodinuclear complex  $[\text{W}_2(\text{CO})_6\text{Cp}_2]$  (**3**) by Cotton and coworkers [5] have established the existence of two rotamers in solution. In polar organic solvents *anti* and *gauche* forms, **3a** and **3b**, exist. These undergo interconversion apparently by rotation about the unbridged W–W bond, although other pseudo-rotational mechanisms for this interchange have not been ruled out. In acetone solution this process has  $\Delta G^\ddagger = 67.7 \pm 2.0 \text{ kJ mol}^{-1}$  [5a]. Our  $^{13}\text{C}\{^1\text{H}\}$  studies on complex **3**, enriched with  $^{13}\text{CO}$  (23%), support this previous analysis: at  $-25^\circ\text{C}$  in acetone the *anti* rotamer shows two  $^{13}\text{CO}$  resonances at 214.4 ppm (rel. int. 2, *cis*-CO) and 222.3 ppm (rel. int. 1, *trans*-CO), whilst the *gauche* form shows three separate  $^{13}\text{CO}$  resonances (215.2, 216.2 and 223.1 ppm) with the ratio *anti/gauche*, ca. 1/0.8. Interchange between rotamers is revealed by the broadening of these resonances above  $25^\circ\text{C}$ ; complete coalescence of the resonances assigned to *cis*-CO ligands is not observed below  $60^\circ\text{C}$ , but coalescence of *trans*-CO resonances (222.3 *anti* and 223.1 *gauche*) occurs at ca.  $55^\circ\text{C}$ , giving  $\Delta G_c^\ddagger \sim 69 \text{ kJ mol}^{-1}$  [6,7].

Complex **3** has a rather low solubility in acetone and this makes detailed  $^{13}\text{C}$  NMR studies difficult. The solubilities in tetrahydrofuran (thf) or dichloromethane are higher, but in these less polar media the *anti*-rotamer predominates. A more suitable medium for NMR studies of the isomerisation process is a mixture of thf and dimethylsulphoxide (dmsO), which has a dielectric constant comparable to that



(**3a**)

*anti*- $[\text{W}_2(\text{CO})_6\text{Cp}_2]$   
(CO groups A and B)



(**3b**)

*gauche*- $[\text{W}_2(\text{CO})_6\text{Cp}_2]$   
(CO groups C, D and E)

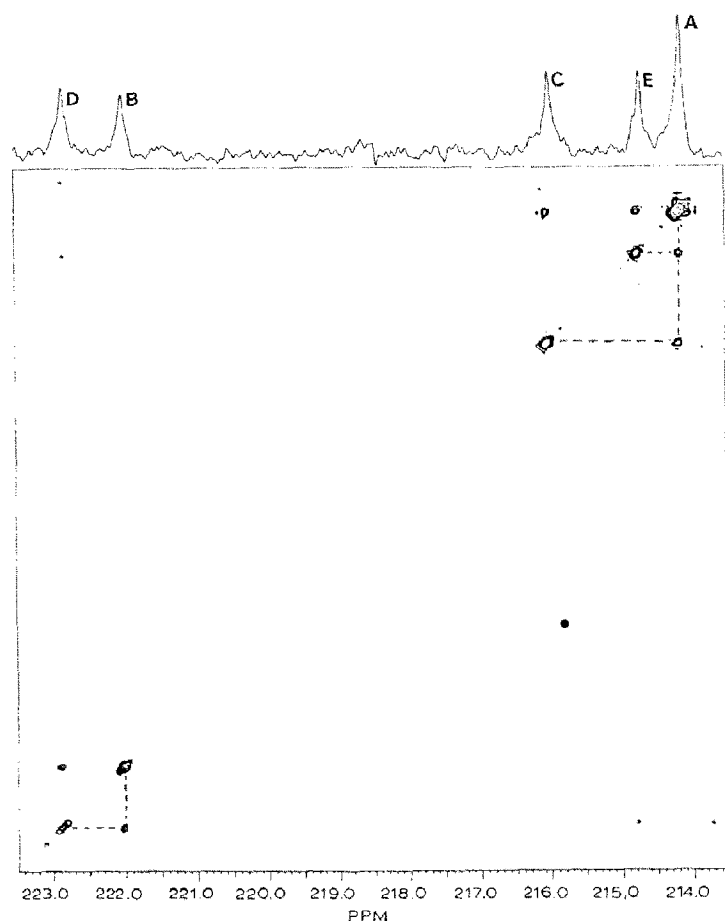


Fig. 1. 2D  $^{13}\text{C}$ O EXSY NMR spectrum of  $[\text{W}_2(\text{CO})_6\text{Cp}_2]$  (**3**) in  $\text{dmsO-}d_6/\text{thf}$  at  $20^\circ\text{C}$ . using a mixing time of 200 ms.

of acetone; in  $\text{thf}/\text{dmsO}$  (ca. 3/2) the ratio of *anti*/*gauche* isomers at  $20^\circ\text{C}$  is 45/55, see Fig. 1. A 2D  $^{13}\text{C}$ O EXSY (NOESY sequence) [8] NMR spectrum of complex **3** in  $\text{thf}/\text{dmsO-}d_6$ , with a mixing time of 200 ms at  $20^\circ\text{C}$ , clearly indicates (Fig. 1) that the exchange between rotamers occurs by a simple rotational process about the W–W bond and not by a pseudo-rotation via a more symmetrical intermediate (or transition state) which could cause random exchange of *cis*- and *trans*-CO ligands. Thus, it is found that a *trans*-CO (B) in the *anti*-rotamer **3a** exchanges solely with a *trans*-CO (D) in the *gauche* rotamer **3b**, whereas *cis*-CO ligands (A) in **3a** exchange only with ligands (C) and (E) in **3b**.

It is of interest that CO groups (C) and (E) in **3b** are distinguishable by the observation of a weak 2D NOESY NMR interaction between resonances of (D) and (E) groups, which is not evident for groups (D) and (C). This NOESY effect arises since (D) and (E) are spatially closer than (D) and (C).

$[\text{WRh}(\mu\text{-CO})_2(\text{CO})(\text{PPh}_3)_2\text{Cp}]$  (**1**)

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$  at temperatures down to  $-90^\circ\text{C}$  shows a single doublet  $\{^1J(\text{Rh-P})\ 171\ \text{Hz}\}$ , but this broadens at ca.

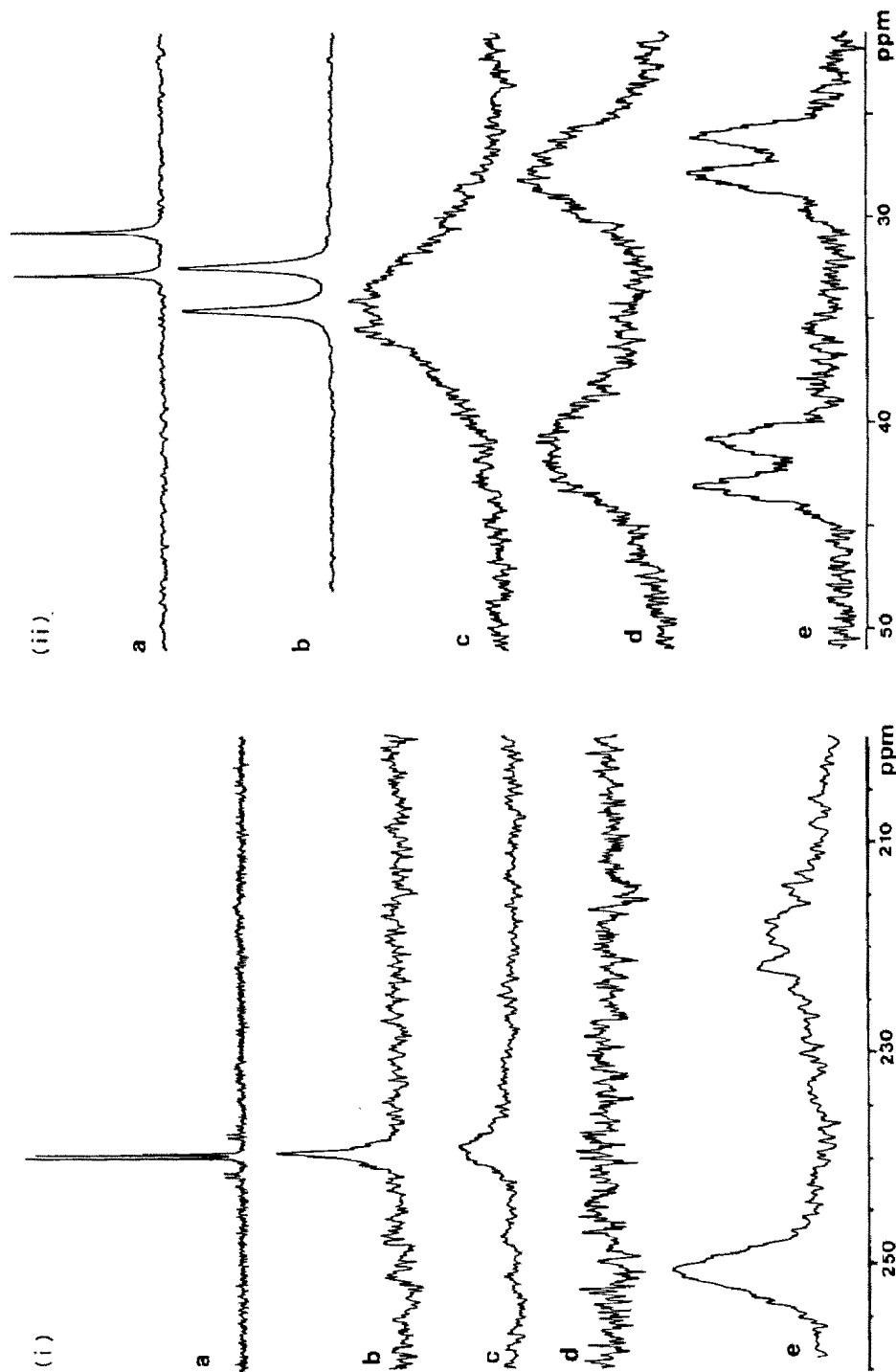


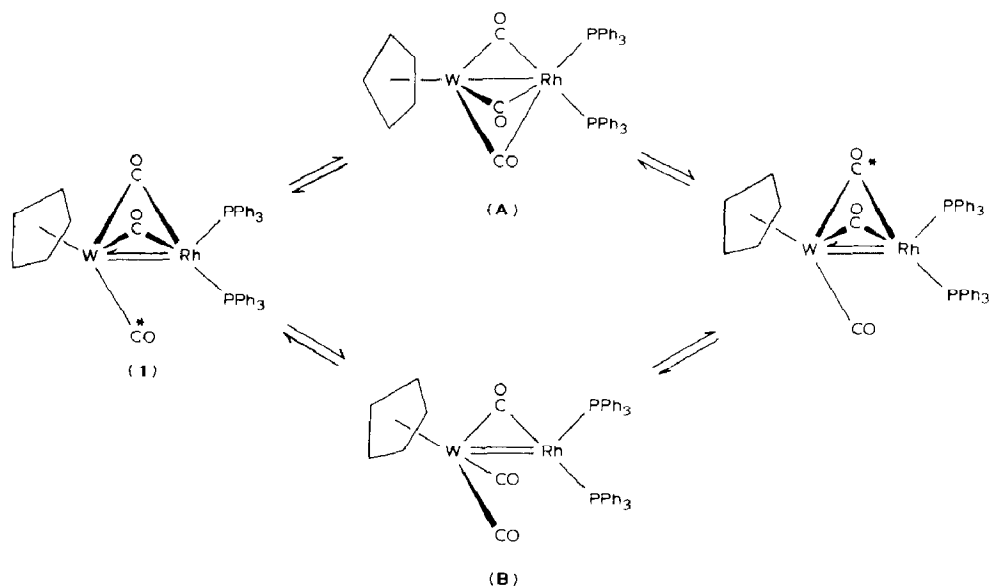
Fig. 2. NMR spectra of complex 1 in  $\text{CD}_2\text{Cl}_2/\text{CFC}_13$ : (i)  $^{13}\text{C}$  ( $^1\text{H}$ ); (a) 50.32 MHz, 22 °C; (b) 90.56 MHz, -75 °C; (c) 90.56 MHz, -90 °C; (d) 90.56 MHz, -106 °C; (e) 90.56 MHz, -120 °C; (ii)  $^{31}\text{P}$  ( $^1\text{H}$ ) at 81.0 MHz: (a) 20 °C; (b) -90 °C; (c) -110 °C; (d) -120 °C; (e) -128 °C.

$-100^{\circ}\text{C}$  and is resolved into two relatively broad doublets below  $-120^{\circ}\text{C}$  {42.1 ppm,  $^1J(\text{Rh}-\text{P}) \sim 190$  Hz; 27.0 ppm,  $^1J(\text{Rh}-\text{P}) \sim 140$  Hz} with any smaller mutual P-P coupling not observed. Coalescence of these resonances occurs at  $-113 \pm 3^{\circ}\text{C}$ , giving  $\Delta G_c^\ddagger = 27.8 \pm 0.6$  kJ mol $^{-1}$  (See Fig. 2).

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex **1** gives a single doublet for the  $^{13}\text{CO}$  groups at  $22^{\circ}\text{C}$  showing coupling to  $^{103}\text{Rh}$  (17.3 Hz), and also satellites due to  $^{183}\text{W}$  (14.4%) with  $J(\text{W}-\text{C})$  186 Hz. This clearly indicates that the binuclear complex is fluxional but retains its integrity in solution. At  $-90^{\circ}\text{C}$  the resonance broadens when monitored at 50.3 or 90.56 MHz. Resolution into two broad resonances at  $-250.6$  ppm (2  $\mu\text{-CO}$  groups) and  $-219.0$  ppm (1CO) occurs at  $-120^{\circ}\text{C}$ . The coalescence of this two site system [6] at  $-106 \pm 5^{\circ}\text{C}$  (90.56 MHz) gives  $\Delta G_c^\ddagger = 27.9 \pm 0.8$  kJ mol $^{-1}$  (Fig. 2).

The identical values, within experimental error, of  $\Delta G^\ddagger$  for both  $^{13}\text{CO}$  and  $^{31}\text{PPh}_3$  exchange are consistent with a single dynamic process causing simultaneous interchange of these ligands. The barrier is less than half that for rotation in the homonuclear complex **3**, in spite of the presence of the shorter, formally multiple, Rh-W bond in **1**. The barrier to rotation in **3** is primarily of steric origin, whereas the pseudo-rotational process of **1** involves the cleavage and formation of carbonyl bridges and probably involves a favourable electronic process. An associative process at the 16-electron Rh atom is most likely, via a tri-bridged (or, at least, tri-semibridged) intermediate or transition-state (cf. A in Scheme 1). A related mechanism has been proposed for the non-rigidity of the mixed carbonyl/thiocarbonyl complexes  $[\text{MnPt}(\mu\text{-CS})(\text{CO})_2(\text{PR}_3)_2\text{Cp}]$ , although the interchange between inequivalent CO ligands in these complexes was still fast on the NMR time-scale at the experimental low temperature limits [9].

An alternative mechanism for fluxionality of **1**, involving an intermediate (or transition state) with a mono-bridging CO ligand, i.e. a dissociative process at Rh (B



Scheme 1

in Scheme 1) appears to be less likely but cannot be definitively excluded. Such an intermediate bears some analogy to the structure [9] of  $[\text{MnPt}(\mu\text{-CS})(\text{CO})_2(\text{PMe-Ph}_2)_2\text{Cp}]$  in the solid state although this latter complex contains two more valence electrons than **1**.

$[\text{CuW}(\text{CO})_3(\text{PPh}_3)_2\text{Cp}]$  (**2**)

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **2** in  $\text{CD}_2\text{Cl}_2/\text{CFC}_l_3$  shows a sharp singlet with chemical shift of ca.  $-1$  ppm at temperatures above  $-60^\circ\text{C}$ , but this passes through a coalescence point at  $-65 \pm 3^\circ\text{C}$  to become a well resolved, P-P

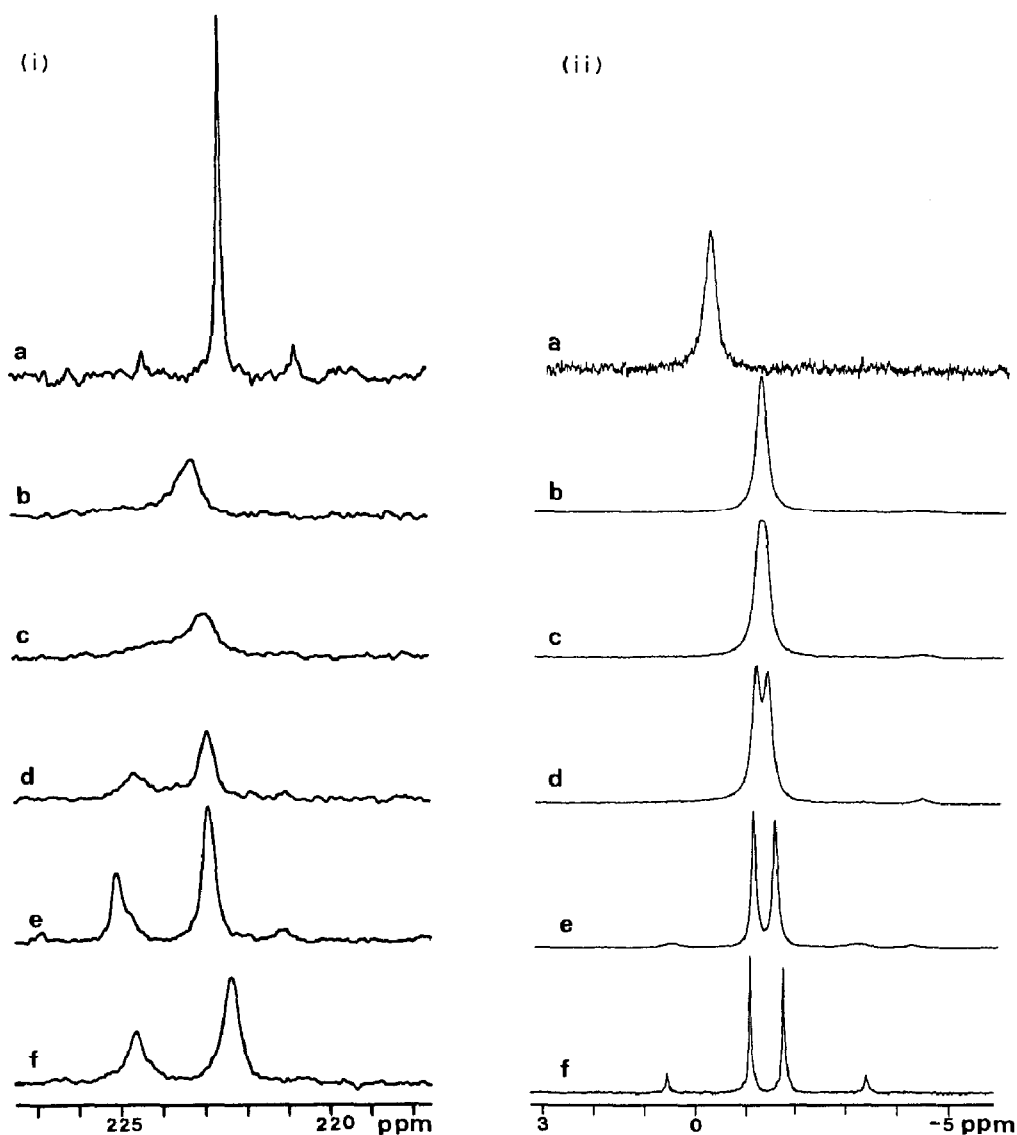


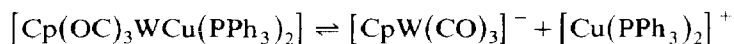
Fig. 3. NMR spectra of complex **2** in  $\text{CD}_2\text{Cl}_2/\text{CFC}_l_3$ ; (i)  $^{13}\text{CO}\{^1\text{H}\}$  at 50.32 MHz: (a)  $18^\circ\text{C}$ ; (b)  $-60^\circ\text{C}$ ; (c)  $-69^\circ\text{C}$ ; (d)  $-75^\circ\text{C}$ ; (e)  $-110^\circ\text{C}$ ; (f)  $-125^\circ\text{C}$ ; (ii)  $^{31}\text{P}\{^1\text{H}\}$  at 81.0 MHz: (a)  $23^\circ\text{C}$ ; (b)  $-60^\circ\text{C}$ ; (c)  $-65^\circ\text{C}$ ; (d)  $-70^\circ\text{C}$ ; (e)  $-80^\circ\text{C}$ ; (f)  $-100^\circ\text{C}$ .

spin coupled, AB signal at  $-100^\circ\text{C}$  ( $-0.62$  and  $-2.26$  ppm,  ${}^2J(\text{P-P})$  132.5 Hz), (see Fig. 3). At coalescence  $\Delta G_c^\ddagger = 38.8 \pm 0.6$  kJ mol $^{-1}$ , calculated [7] by use of the equation:  $k = \pi\{0.5[(\delta\nu)^2 + 6(J_{\text{AB}})^2]\}^{1/2}$ . In acetone- $d_6$ , related spectra are obtained with a coalescence at  $-57 \pm 2^\circ\text{C}$ , giving a slightly higher value for  $\Delta G_c^\ddagger$ ,  $40.3 \pm 0.5$  kJ mol $^{-1}$ .

The  ${}^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** at ambient temperature in  $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$  is a singlet with satellites from coupling to  ${}^{181}\text{W}$  ( $J(\text{W-C})$  183 Hz); this signal broadens around  $-60^\circ\text{C}$  and separates into two resonances of relative intensities 1/2 below  $-75^\circ\text{C}$ . These signals are well resolved at  $-110^\circ\text{C}$  (224.8 ppm,  $J(\text{W-C})$  189 Hz, *trans*-CO; 222.7 ppm,  $J(\text{W-C})$  175 Hz, 2 *cis*-CO). At coalescence,  $-68.5 \pm 5^\circ\text{C}$ ,  $\Delta G^\ddagger$  is  $40.1 \pm 1.0$  kJ mol $^{-1}$ . In  $d_6$ -acetone, related  ${}^{13}\text{C}\{^1\text{H}\}$  spectra give  $\Delta G_c^\ddagger = 41.0 \pm 0.5$  kJ mol $^{-1}$  at the coalescence temperature of  $-63 \pm 2^\circ\text{C}$ . (cf. Fig. 3).

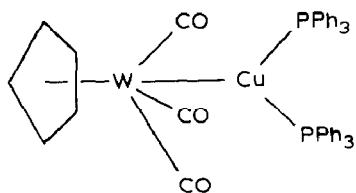
Within experimental error, the  $\Delta G^\ddagger$  values for  ${}^{13}\text{CO}$  and  ${}^{31}\text{PPh}_3$  exchanges are the same in either  $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$  or  $(\text{CD}_3)_2\text{CO}$ , suggesting that both ligands are interchanged by the same process. The values of  $\Delta G^\ddagger$  for exchange in the more polar solvent acetone are marginally higher, although the differences are virtually within experimental error: at least it is clear that the more polar solvent does not promote geometrical non-rigidity and this is contrary to expectation if a mechanism involving ionic intermediates were operating. Also, it should be noted the  $\Delta G^\ddagger$  for exchange in complex **2** is substantially higher than that for **1**.

The electrical conductivity of complex **2** in acetone has been measured over the concentration range  $10^2$ – $10^{-4}$  mol dm $^{-3}$  at  $19^\circ\text{C}$ : the values are low and linear extrapolation against  $c^{1/2}$  ( $c$  mol dm $^{-3}$ ) gives  $\Lambda_0 = 7 \pm 1^{-1}$  mol $^{-1}$  cm $^2$ , with a gradient  $\Lambda/c^{1/2}$  of  $< 10\%$  of the value expected for a typical 1/1 electrolyte in this solvent [10]. Under identical conditions  ${}^n\text{Bu}_4\text{NPF}_6$  gave  $\Lambda_0$  160  $\Omega^{-1}$  mol $^{-1}$  cm $^2$  and gradient  $\Lambda/c^{1/2} = 510$  (cf. value calculated by the limiting Onsager equation: 610) [10]. Thus, complex **2** is not appreciably ionised in acetone at  $19^\circ\text{C}$ , and any dissociation of the following type must be small.



Minor ionic dissociation nevertheless still could account for the interchange of CO and  $\text{PPh}_3$  ligands in **2**, but if this were a kinetically significant step, the rate in more polar solvents should be greater. Hence it is proposed that, even for this complex, a pseudo-rotational mechanism occurs within an intact binuclear system. The two structural isomers of **2** observed in the solid state may be readily interconverted by deformation of the Cu–W bond in the approximate mirror-plane. An extension of this deformation mode will generate the approximately trigonal-bipyramidal (3/3/1) intermediate **2c**, and this, combined with rotation about the W–Cu bond, will result in interchange of the CO and the  $\text{PPh}_3$  ligands. This mechanism is analogous to that proposed for *cis*–*trans* isomerisation of complexes  $[\text{CpMR}(\text{CO})_2\text{L}]$  [11]. The intermediate, possessing two more valence electrons than the W–Rh analogue from **1**, will have negligible bridge-bonding CO interactions with the Cu atom, and this, in combination with the barrier to forming of the intermediate by deformation, must account for the higher  $\Delta G^\ddagger$  value for fluxionality of complex **2** relative to **1**.





(2c)

## Acknowledgements

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