Upon the Existence of a Trihydrogen Ligand. Preparation and Spectroscopic Studies of the Adducts $(C_5Me_5)RuH_3P(cyclo-C_6H_{11})_3\cdot CuCl$ and $[\{(C_5Me_5)RuH_3P(cyclo-C_6H_{11})_3\}_2Cu]PF_6$

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$(C_5Me_5)RuH_3PCy_3$ **(1)** (Cy = cyclohexyl) reacts smoothly with $1/n[CuCl]_n$ in toluene and with 1 or 1/2 equivalent of $[Cu(MeCN)_4]PF_6$ in tetrahydrofuran (THF) to give $(C_5Me_5)RuH_3PCy_3CuCl$ **(2)** and $\{(C_5Me_5)RuH_3PCy_3)_2Cu\}PF_6$ **(3)** respectively, and the anomalous n.m.r. behaviour of **(1)** characterized in particular by the observation of AB_2 spectra showing large temperature dependent AB coupling constants is preserved in **(2)** whereas in **(3)** a disymmetry is observed in agreement with the presence of one hydride and one dihydrogen molecule; an interpretation is given and a model taking into acount these data is proposed for the structure of the 'trihydrogen' derivatives.

After the discovery of the existence of dihydrogen directly bonded to a metal without dissociation,[1] the question arose as to whether polyhydrogen structures could exist and be stabilized by co-ordination to a transition metal. Polyhydrogen ligands could be invoked to account for the fluxionality of complexes containing both hydride and dihydrogen ligands[2] and also for some H/D exchange reactions observed even in the solid state.[1,3] Theoretical calculations in particular by Burdett and co-workers have opened this possibility.[4]

We have recently reported that the 'trihydride' complexes $(C_5Me_5)RuH_3PR_3$,[5] also prepared by other groups,[6] exhibited an anomalous n.m.r. behaviour characterized by the observation of large temperature dependent AB_2 spectra for the hydrides.[7] We first proposed the existence of a 'non-classical'[†]

interaction between a hydride and co-ordinated dihydrogen to explain the phenomenon. Since then, the phenomenon has been observed in iridium and niobium derivatives, respectively by Heynekey *et al.*[8] and by us,[9] and the existence of the trihydrogen ligand proposed. However, since in each case the ground state is a classical trihydride (at least for Ru[6b] and Nb complexes[10]) and since spectroscopic methods alone do not seem to be entirely conclusive, we have looked for a chemical characterization of the phenomenon.

Caulton *et al.* reported some years ago the preparation of interesting polynuclear Ir–Cu and Re–Cu species through the reaction of polyhydride derivatives with $[Cu(MeCN)_4]BF_4$. We have shown later that $[CuCl]_n$ and $[Cu(MeCN)_4]BF_4$ reacted in a similar way with ruthenium hydrides.[12]

With the hope of being able to discriminate the hydride from dihydrogen in a hypothetical hydrido dihydrogen derivative, we have treated $((C_5Me_5)RuH_3PCy_3$ with $[CuCl]_n$ and $[Cu(MeCN)_4]PF_6$ and report our results here.

$(C_5Me_5)RuH_3PCy_3$ **(1)** (Cy = cyclohexyl) reacts smoothly

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[†] The term 'non-classical interaction' was used to account for the non-rotation of the dihydrogen ligand.
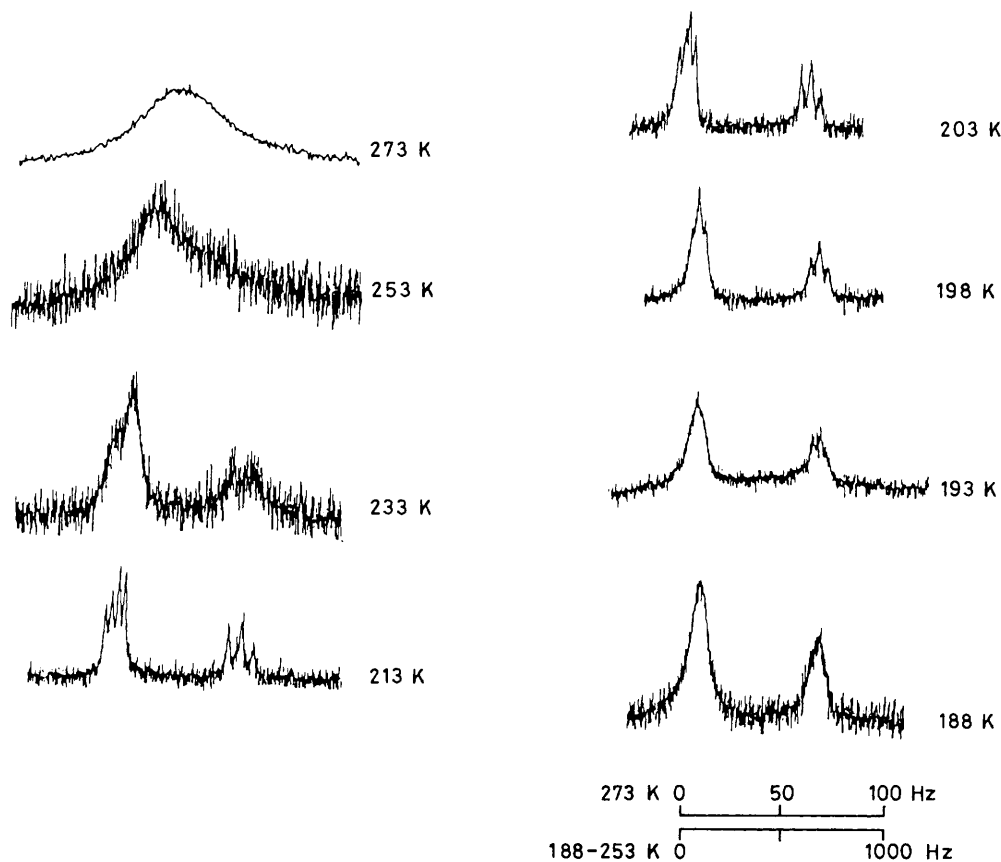
273 K 0   50   100 Hz

188—253 K 0   1000 Hz

Figure 1. Variation of the high field ^{1}H n.m.r. spectrum (250 MHz) of $(C_5Me_5)RuH_3PCy_3 \cdot CuCl$ (**2**) as a function of temperature.

with $1/n[CuCl]_n$ at room temperature (in toluene) to give the adduct $(C_5Me_5)RuH_3PCy_3 \cdot CuCl$ (**2**)‡ as a white, hydrocarbon-soluble, complex. The solid state i.r. spectrum shows a terminal hydride at 2010 cm^{-1} (m, sharp) and a broad peak for bridging hydrides centred at 1740 cm^{-1}. Only a doublet (J_{PH} 13 Hz) is observed on the high field ^{1}H n.m.r. spectrum at room temperature indicating the fluxionality of the 'hydrides'; however at lower temperatures an AB_2X type spectrum is observed as for (**1**) (see Figure 1). They are similarly characterized by J_{HBP} 0 Hz and a variation of $J_{HA}J_{HB}$ as a function of the temperature (from ~60 Hz for the first observed value to <5 Hz). The result implies the preservation of the 'non-classical' behaviour of the system. It is also interesting to note that the presence of copper freezes the system and in particular allows the observation of the low temperature limit. This demonstrates that the difference of behaviour observed between the ruthenium[7] and the niobium[9] complexes is only due to a difference of range of temperature. However it is surprising to find symmetrical spectra since whatever model is adopted (H_3^- or H^-/H_2) a disymmetry should result from copper co-ordination. We were thus led to try another Lewis acid.

The reaction of 1 or ½ an equivalent of $[Cu(MeCN)_4]PF_6$ with (**1**) leads to the same compound analysing for $[\{(C_5Me_5)RuH_3PCy_3\}_2Cu]PF_6$ (**3**).§ Complex (**3**) is very

similar to (**2**) (i.r., ^{1}H n.m.r. spectra at room temperature.§ However, at lower temperatures, at first splitting into two sets of broad peaks is observed as usual, but then an ABC X type spectrum appears and sharpens down to 173 K (see Figures 2, 3). It consists of a doublet of doublets at δ −11.92 (H_A, J_{HAHB} 6, J_{HAHC} 45 Hz), a doublet of doublets at δ −10.40 (H_B, J_{HAHB} 6, J_{HB-P} 15 Hz) and a doublet of doublets at δ −9.22 (H_C, J_{HAHC} 45, J_{HCP} 22 Hz). The important value of J_{HAHC} 45 Hz and the increase of this value as a function of temperature are in agreement with the presence of a direct H_A–H_C bond at least in an equilibrium as are the measures of the relaxation time T_1.§

The result demonstrates that the co-ordination of a Lewis acid like a copper salt does not modify the nature of the phenomenon observed in (**1**) but freezes it. In the solid state a classical hydrido bridged complex represented by structure (a) (Scheme 1) is present [see i.r. spectrum and J_{H-H} <5 Hz in (**2**)]. Then an equilibrium with a dihydrogen complex (b) is observed [process (II)]. The only difference between complexes (**2**) and (**3**) is the speed of the fluxional processes (I) and (III).¶ They are rapid at the n.m.r. time scale in (**2**) and slow

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‡ $(C_5Me_5)RuH_3(PCy_3) \cdot CuCl$: Found C: 54.2, H: 9.5%; Calc. C: 54.4, H: 8.25%, i.r. v Ru–H terminal 2010 cm^{-1}, bridging 1700–1780 (br.); ^{31}P n.m.r. (101.3 MHz, C_7D_8) δ 74.9 s; ^{1}H n.m.r. (250 MHz, C_7D_8) 298 K −10.37 (d, J_{PH} 13 Hz, 3H) 2.10 (s, 15H, C_5Me_5*) 1.4—2.2 (m, 33H, PCy_3). At lower temperature, see text and Figure 1.

§ (**3**) $[\{(C_5Me_5)RuH_3PCy_3\}_2Cu]$ PF_6: Found C: 53.95, H: 8.9; Calc. C: 53.9, H: 8.2%, i.r. v Ru–H: 2005 (m, sh), 1790 (m, br.), 1710 (m, br.) cm^{-1}. ^{1}H n.m.r. [250 MHz, $(CD_3)_2CO$], 295 K: δ −10.38 (d, J_{P-H} 14.5 Hz, 3H, hydride; T_1 at 173 K 140 ms, 203 K: 75 ms) 2.23 (s, 15H, C_5Me_5), 1.2—2.2 (m, 33H, PCy_3). At lower temperature, see text and Figures 2, 3.

¶ As pointed out by a referee, the cationic character of (**3**) could lead to the presence, at least in a tautomeric form, of a positive charge on ruthenium. This would stabilize the (η^2-H_2) ligand towards the H–H bond dissociation.
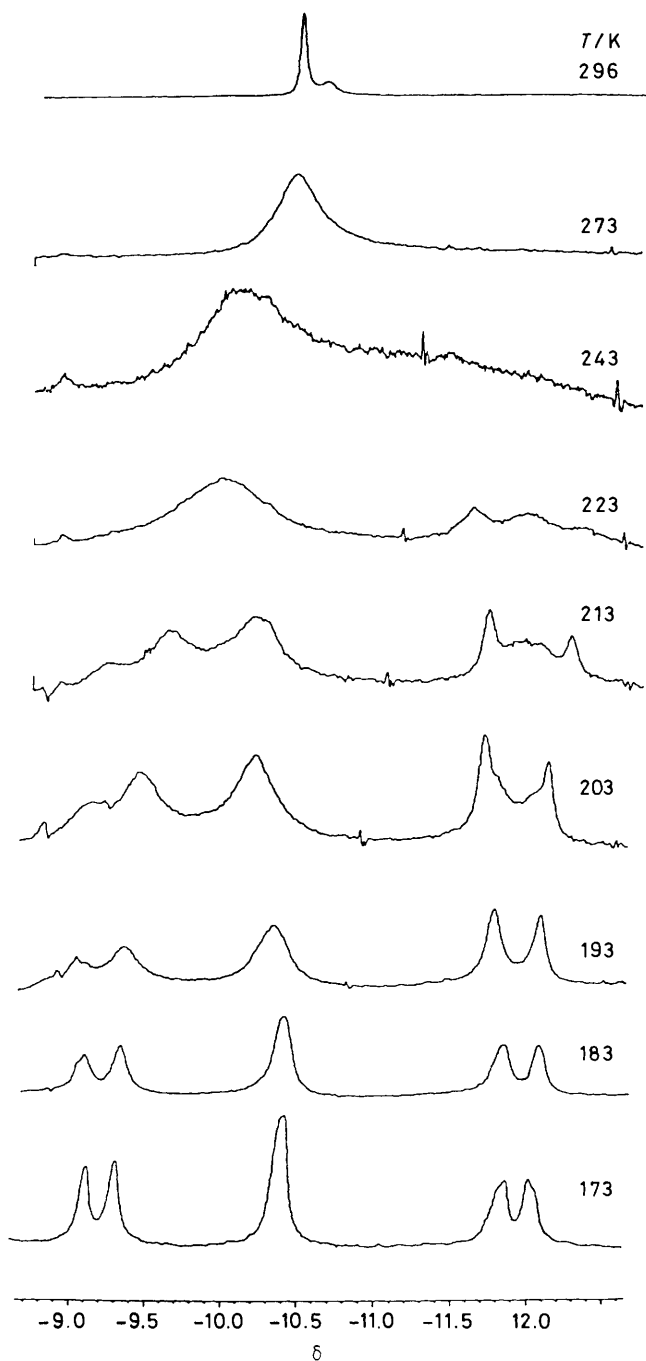
Figure 2. Variation of the high field $^1H\{^{31}P\}$ n.m.r. spectrum (250 MHz) of [{$(C_5Me_5)RuH_3PCy\}_2Cu$]PF_6 (**3**) as a function of temperature.

Figure 3. ^1H N.m.r. spectrum (250 MHz) of (**3**) at 173 K; (A) observed, (B) ^{31}P decoupled, (C) ^{31}P and H_B decoupled, (D) ^{31}P and H_A decoupled.

in (**3**). It is not clear whether a link remains between the copper and the central hydrogen atom in form (b). At higher temperatures the fluxionality of the 'hydrides' results from the rotation of H_2. All these processes were proposed for explaining the the non-classical behaviour of (**1**) but were not demonstrated.

Since the observation of AB_2 spectra results from a fluxional process in the presence of copper, we think that our first proposal for the structure of (**1**) of a hydrido dihydrogen derivative seems more likely than a static trihydrogen ligand.[7] However the observation of coupling constants above 140 Hz
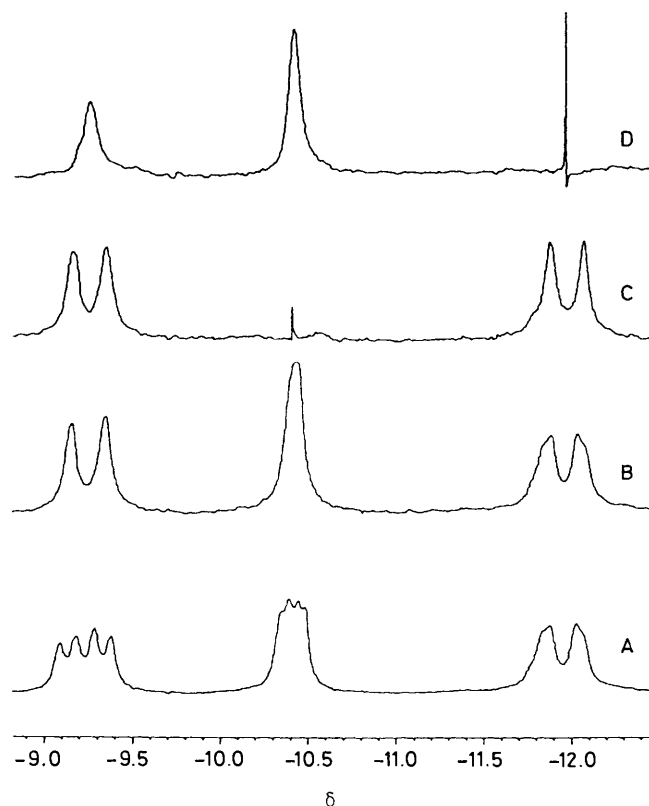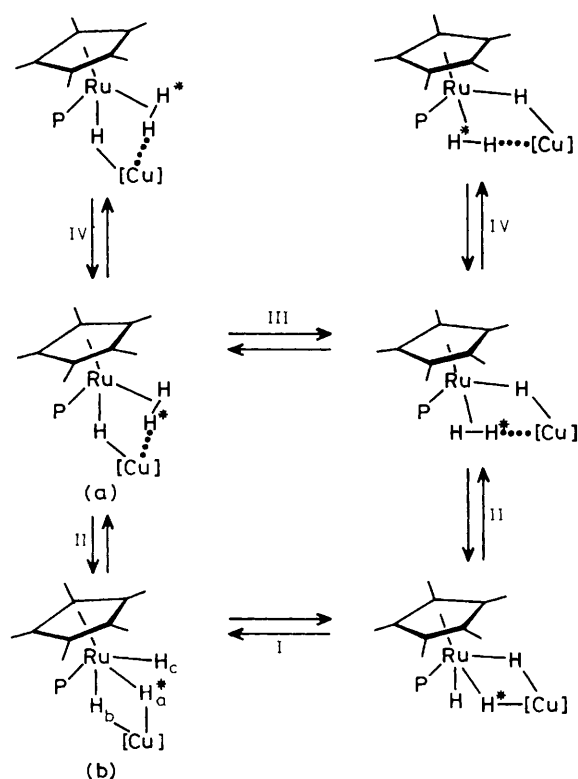

Scheme 1. Proposed structures and equilibria for explaining the spectroscopic properties of (**2**) and (**3**).

and of the non-rotation of H_2 implies that a normal hydrido dihydrogen derivatives cannot be involved. A link must be present between the hydride and dihydrogen (electrostatic, chemical bonding . . .) or (and ?) a very rapid H/H_2 exchange better described as a rapid jump of the central hydrogen atom from a hydride to the other (see Scheme 1). As already proposed this would be a vibrational state of H_3.[7] On the other hand, the presence of copper may be sufficient to break a weak H–H bond of a triangular polarized H_3^- ligand.

In conclusion, our results are more in favour of a dynamic system to explain the anomalous spectroscopic properties of a series of trihydride complexes, even if the interaction (or jump) of the hydride with dihydrogen is not yet understood. They do not rule out the presence of an open trihydrogen ligand but definitively rule out the presence of a triangular trihydrogen ligand even as part of the fluxional process.

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References

1 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120 and references therein.

2 R. H. Crabtree, M. Lavin, and L. Bonneviot, *J. Am. Chem.*, 1986, **108**, 4032; M. T. Bautista, K. A. Earl, P. A. Maltby, and R. H. Morris, *ibid.*, 1988, **110**, 4056.

3 F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1986, 506; 1987, 1675; R. K. Upmacis, M. Poliakoff, and J. J. Turner, *J. Am. Chem. Soc.*, 1986, **108**, 3645.

4 J. K. Burdettt and M. R. Pourian, *Organometallics*, 1987, **6**, 1684; J. K. Burdett, J. R. Phillips, M. R. Pourian, M. Poliakoff, J. J. Turner, and R. Upmacis, *Inorg. Chem.*, 1987, **26**, 3054.

5 T. Arliguie and B. Chaudret, *J. Chem. Soc., Chem. Commun.*, 1986, 985; T. Arliguie, C. Border, B. Chaudret, J. Devillers, and R. Poilblanc, *Organometallics*, in the press.

6 (a) R. Paciello and J. E. Bercaw, Abstr. 191st ACS Nat. Meeting New York, 1986, Inor 82; (b) H. Suzuki, D. H. Lee, N. Oshima, and Y. Moro-Oka, *Organometallics*, 1987, **6**, 1569.

7 T. Arliguie, B. Chaudret, J. Devillers, and R. Poilblanc, *Compte-Rendus Sc. Hebd. Acad. Sciences, Série II*, 1987, **305**, 1523.

8 D. M. Heinekey, N. G. Payne, and G. K. Schulte, *J. Am. Chem. Soc.*, 1988, **110**, 2303.

9 A. Antinolo, B. Chaudret, G. Commenges, M. Fajardo, F. Jalon, R. H. Morris, and C. T. Schweitzer, *J. Chem. Soc., Chem. Commun.*, 1988, 1210.

10 $(C_5H_5)_2NbH_3$ shows the same variation of J_{H-H} coupling constant but at higher temperature. Its neutron diffraction crystal structure has been established: R. D. Wilson, T. F. Koetzle, D. W. Hart, A. Kvick, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, 1977, **99**, 1775.

11 L. F. Rhodes, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 5137; 1984, **106**, 6874; 1985, **107**, 1759.

12 B. Delavaux, B. Chaudret, F. Dahan, and R. Poilblanc, *J. Organomet. Chem.*, 1986, **317**, 69. B. Delavaux, T. Arliguie, B. Chaudret, and R. Poilblanc, *Nouv. J. Chim.*, 1986, **10**, 619.