N.M.R. Studies of the Motion of the Hydride Proton in Solid $HRu_{10}C(CO)_{24}^-$

Philip J. Bailey and Melinda J. Duer*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

Cluster molecules, $HRu_{10}C(CO)_{24}^-$, are characterised by interstitial hydride ligands down to 250 K, but below that temperature, progressively more and more molecules acquire externally-bound hydrogens.

The two subjects of molecular motion in solids[1] and interstitial atoms in transition metal clusters[2] have received increasing attention in recent years. In particular, the nature and reactivity of interstitial atoms still remains a contentious issue. We have undertaken variable temperature ^1H n.m.r. and i.r. studies on static, powder samples of the transition metal cluster, $HRu_{10}C(CO)_{24}^-$ with the PPN^+ [$PPN^+ = (Ph_3P)_2N^+$] cation.

The metal core in $HRu_{10}C(CO)_{24}^-$ is a tetra-capped octahedron of Ru atoms, the overall geometry of the core being tetrahedral[3] (Figure 1). The carbide atom lies at the centre of the Ru_6 octahedron. Though not established by *X*-ray diffraction, the hydrogen atom was proposed to lie at a tetrahedral site inside a Ru 'cap'.[3]

The ^1H n.m.r. spectra shown in Figure 2 are characterised by: (i) at 300 K a single, relatively sharp resonance is observed at δ *ca.* +0.2; (ii) as the temperature decreases below 300 K the resonance at δ +0.2 broadens and features begin to appear around δ −24 with a shoulder at δ −35; (iii) at 140 K, a spectrum is acquired which has features centred at δ *ca.* −5 and −35. We interpret these spectra in terms of a changing hydrogen site, from one characterised by a high frequency at

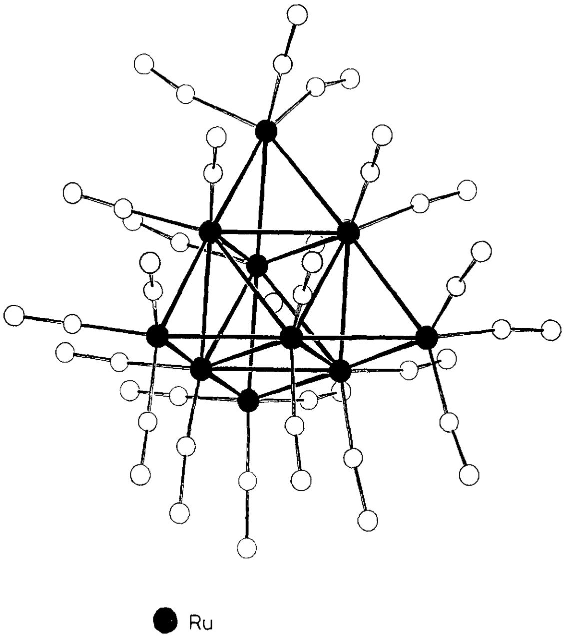

Figure 1. A schematic diagram of the metal core geometry in $HRu_{10}C(CO)_{24}^-$.

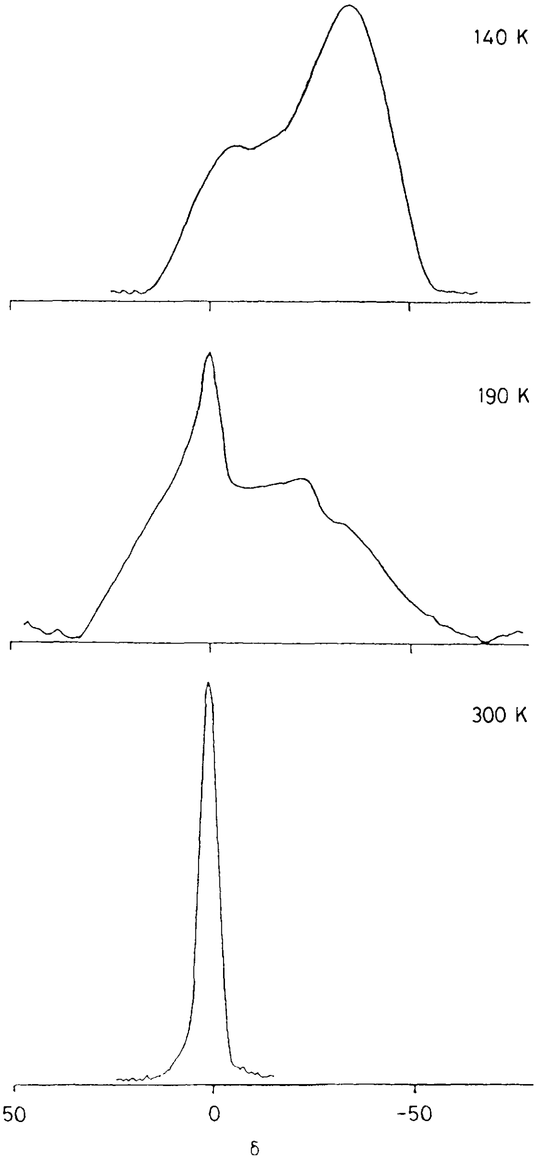

Figure 2. The static, powder ^{1}H n.m.r. spectra of $HRu_{10}C(CO)_{24}PPN$ at various temperatures. For all spectra, 5 μs pulses were used with 10 s delay time between pulses. Over 400 scans were acquired for the spectrum at 300 K whilst fewer were required at lower temperatures. (The spectra do not have the same intensity scales.)

high temperatures to one characterised by a low frequency at low temperatures.

Interstitial ^{1}H nuclei in transition metal clusters have previously been observed with low field resonances:[4,5] for example, the ^{1}H resonance occurs at δ +16.4 in $HRu_6(CO)_{18}^-$,[4] where the hydride is known to be at the centre of an octahedron of Ru atoms,[6] and at δ +23.2 in $HCo_6(CO)_{15}^-$.[5] By contrast, hydrogen atoms bonded terminally to transition metals, including those that are edge-bridging or face-capping on the exterior of transition metal clusters, resonate at much higher field.[7] This site-dependence of ^{1}H resonances will be discussed at length in a future paper. Meanwhile, we follow these precedents and assign the high temperature resonance in $HRu_{10}C(CO)_{24}^-$ at δ +0.2 to an interstitial hydrogen, and the upfield resonance at lower temperatures to an externally-bound hydrogen.

At temperatures above 250 K, the resonance assigned to an interstitial hydrogen at δ +0.2 is a single, sharp, symmetric line. Given that the ^{1}H n.m.r. spectra are of static, powder samples, this implies either that the interstitial hydrogen lies at a cubic symmetry site or that it is moving very rapidly over equivalent sites. We discard the former in view of the inexact crystallographic cubic symmetry but especially in view of the occupation of the only cubic site in the molecule by the interstitial carbide. We therefore propose that the hydride is hopping rapidly between the interstitial sites formed by the Ru caps† on the Ru_6 octahedron.

At temperatures below 250 K, a proton resonance assigned to an externally-bonded hydrogen begins to appear. Two features that define the n.m.r. of this second site are: (a) at 190 K a relatively sharp resonance is observed at δ −24, with a shoulder at δ −35 and (b) at 140 K a resonance profile is observed which is compatible with the powder spectrum of a hydrogen with effective axial symmetry and characterised by $\sigma_\perp \sim -35$ p.p.m., $\sigma_\parallel \sim -3$ p.p.m. and, therefore, $\bar{\sigma} \sim -24$ p.p.m.

Altogether, the 190 and 140 K spectra provide a consistent set of data if we suppose that at 190 K the externally bonded hydrogen is hopping over equivalent sites at a relatively high frequency (so causing a large intensity for the isotropic chemical shift of the hydrogen nucleus), whilst at 140 K the hopping frequency is much lower. Confidence in this proposal is increased by the similarity between the chemical shift (δ −24) of the sharp absorbance in the 190 K spectrum and that of the isotropic chemical shift (δ −24) of the nucleus in this site as estimated above from the 140 K spectrum.

---

† The X-ray crystal structure of $HRu_{10}C(CO)_{24}PPN$ shows all caps to be of similar size and geometry in contrast to the Os analogue, $HOs_{10}C(CO)_{24}^-$, where one cap (assumed to be that containing the hydrogen) is expanded relative to the others.[8] This is consistent with the hydrogen moving very rapidly over the interstitial 'cap' sites in the Ru compound.

The i.r. spectra of the $[Bu^t{}_4N]^+$ salt of $HRu_{10}C(CO)_{24}^-$ at 293 and 113 K for the region 600—800 cm^{-1} were recorded. The strong bands in this region of the spectrum may be assigned to the vibrational modes of the carbide atom.

For a hydride ligand in $HRu_{10}C(CO)_{24}^-$ located in one of the tetrahedral caps, the cluster has C_{3v} symmetry and the carbide ligand would display an A and a degenerate E vibration mode. Consistent with this, the observed spectrum at 293 K displays one band at 738 cm^{-1} and a more intense band at 720 cm^{-1}, which may be assigned to the A and E modes, respectively. At 113 K, however, the lower frequency band splits to give a distinct shoulder at 728 cm^{-1}. This band can be unequivocally assigned as a *new* band, and not simply a result of higher resolution achieved at low temperatures. This is consistent with a lowering of the cluster symmetry to C_{2v} or lower, where the degeneracy of the E mode is lifted.

In summary, therefore, both ^1H n.m.r. and i.r. spectra are consistent with the hydride ligand being expelled from the interior of the cluster with decreasing temperature, to reside on or above one of the uncapped triangular metal faces in a less symmetrical geometry.

We thank Drs. M. W. Anderson and J. Klinowski for their assistance with the n.m.r. experiments and Dr. M. Gerloch, Dr. B. F. G. Johnson, and Prof. Lord Lewis for helpful discussions. One of us (P. J. B.) thanks the S.E.R.C. and British Petroleum plc for financial support.

Received, 4th April 1989; Com. 9/01375J

References

1 M. Mehring, 'NMR Basic Principles and Progress,' eds P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag (Berlin), 1976, vol. 11.

2 M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203.

3 P. J. Bailey, G. Conole, B. F. G. Johnson, J. Lewis, M. McPartlin, and H. R. Powell, to be published.

4 C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 945.

5 D. W. Hart, R. G. Teller, C.-Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 80.

6 P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, W. J. H. Nelson, K. D. Rouse, J. Allibon, and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1980, 295.

7 A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 1964, 2747, 4583.

8 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 49.