

## Structural, bonding and mechanistic rearrangement information on transition metal carbonyl clusters from multinuclear magnetic resonance studies

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**Abstract** - The use of multinuclear magnetic resonance studies to obtain information on structures, bonding and mechanisms of ligand and/or metal rearrangements for carbonyl clusters in solution will be illustrated.

There has been a rapid increase in both the variety (different metal polyhedral geometries and different combinations of metals/interstitial elements) and size of transition metal clusters during the last 15 years with some of the highest nuclearity clusters now of the size (> 40 metal atoms) of small metallic crystallites (ca. 10 Å). This growth has been in part due to the developing preparative expertise of different research groups and also to the improvements in instrumentation, particularly X-ray diffraction and multinuclear magnetic resonance, which are necessary for their characterisation.

### STRUCTURAL CHARACTERISATION FROM MULTINUCLEAR MAGNETIC RESONANCE MEASUREMENTS

X-ray crystallography is extremely important in the structural characterisation of transition metal carbonyl clusters. Nevertheless, multinuclear magnetic resonance measurements in solution can also provide important structural information, particularly if the metal has a spin, e.g.  $^{103}\text{Rh}$ ,  $I = 1/2$ . Such measurements are especially useful:-

- (a) when suitable crystals cannot be obtained for X-ray analysis and/or the cluster only stable at low temperature, e.g.  $[\text{Ag}_n\{\text{Rh}_6(\text{CO})_{15}\text{C}\}_2]^{(4-n)-}$  ( $n=1$  and  $3$ ), (ref.1)  $[\text{Ag}_n\{\text{Rh}_6(\text{CO})_{15}\text{C}\}_3]^{(6-n)-}$  ( $n=2$  and  $4$ ), (ref.1)  $[\text{Ag}\{\text{Rh}_6(\text{CO})_{15}\text{C}\}_2]^{3-}$ , (Fig.1) (ref.1)  $[\text{HRh}_6(\text{CO})_{15}]^-$ , (Fig.2) (ref.2.)  $[\text{HRh}_6(\text{CO})_{15}\text{C}]^-$ , (Fig.2b) (ref.2),  $[\text{HRh}_6(\text{CO})_{15}\text{C}]^-$  (Fig.2c) (ref.3.)

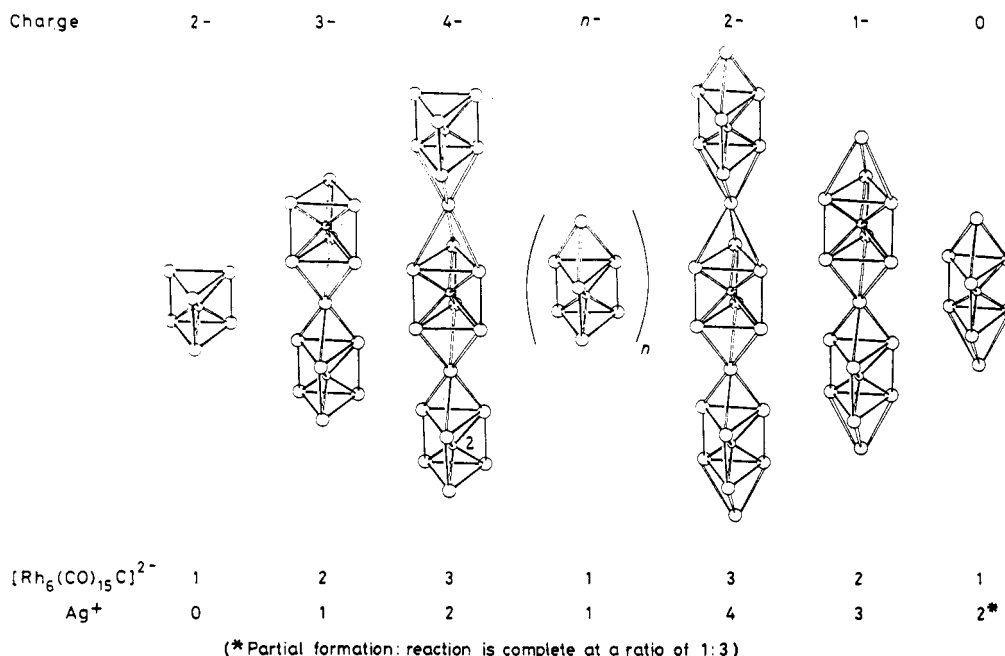


FIGURE 1.

Schematic representation of the adducts produced on successive addition of  $\text{Ag}[\text{BF}_4]$  to  $(\text{NMe}_2)_2[\text{Rh}_6(\text{CO})_{15}\text{C}]$  in acetone solution. (There is one terminal CO on each Rh atom and all edges of the trigonal prism are bridged by CO)

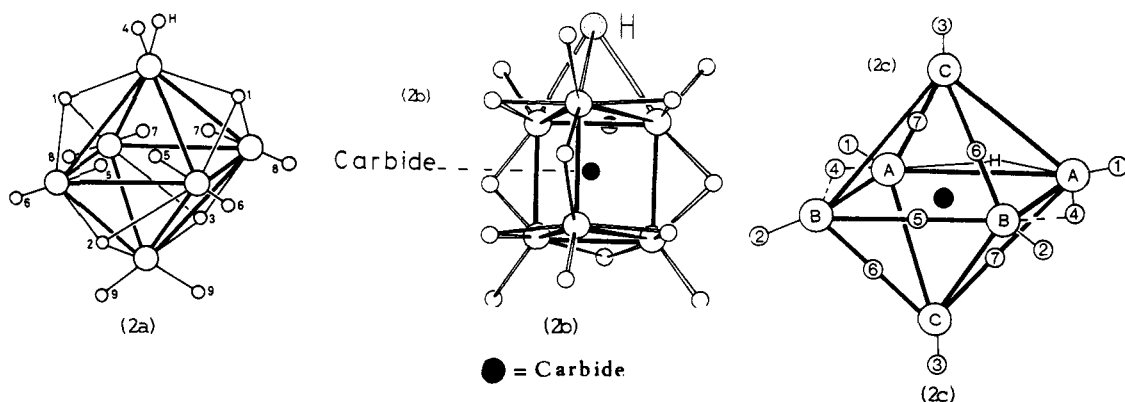


FIGURE 2

Schematic representation (large spheres = Rh, small spheres = CO) of the structures of:-  
 (a)  $[\text{HRh}_6(\text{CO})_{15}]^{2-}$ , (b)  $[\text{HRh}_6(\text{CO})_{15}\text{C}]^{2-}$ , (c)  $[\text{HRh}_6(\text{CO})_{13}\text{C}]^{2-}$

- (b) when the cluster contains similar metals in different sites but X-ray analysis cannot distinguish the different metals because they are so similar, e.g.  $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$  (Fig. 3) (ref. 4).
- (c) for H-location in hydrido-clusters e.g.  $[\text{HRh}_6(\text{CO})_{15}]^{2-}$  (Fig. 2a) (ref. 2)  $[\text{HRh}_6(\text{CO})_{15}\text{C}]^{2-}$  (Fig. 2b) (ref. 2)  $[\text{HRh}_6(\text{CO})_{13}\text{C}]^{2-}$  (Fig. 2c) (ref. 3)  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  (Fig. 3) (ref. 4)  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$  (Fig. 4) (ref. 5).

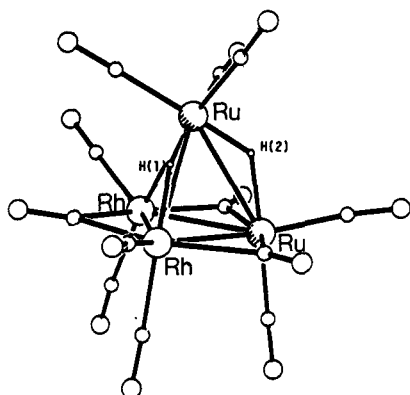


FIGURE 3

Schematic representation of the structure of  $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$

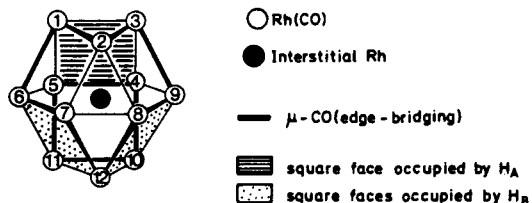


FIGURE 4

Schematic representation of the structure of  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$

There is a good correlation of Rh-CO bond length with  $^1\text{J}(^{103}\text{Rh}-^{13}\text{C})$ , especially within a single cluster (ref. 6). Whenever distortions have been found by X-ray crystallography in the solid state, n.m.r. measurements show that the same distortions are retained in solution, e.g.  $[\text{Rh}_9\text{E}(\text{CO})_{21}]^{2-}$  (E = P, As), (ref. 7)  $[\text{Rh}_{10}\text{E}(\text{CO})_{22}]^{2-}$  (E = P, As), (ref. 7)  $[\text{Rh}_{10}\text{S}(\text{CO})_{22}]^{2-}$  (ref. 8).

The above structural studies have concentrated upon multinuclear magnetic resonance measurements in solution under an ambient pressure of gas. However, we have recently developed a cell which enables multinuclear magnetic resonance measurements ( $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{59}\text{Co}$  etc.), with or without  $^1\text{H}$ -decoupling, to be carried out under high pressures of gas (< 500 atm) within the temperature range  $-80^\circ\text{C}$  to  $190^\circ\text{C}$ . (ref. 9,10). Excellent signal:noise is obtained under these conditions and  $^{13}\text{C}$  spectra with  $w_{1/2} = 2.5$  Hz can be obtained routinely. This cell is useful for gaining information about the mechanisms of homogeneous catalytic reactions *in situ* and the lecture will demonstrate how the rhodium catalysed hydroformylation of hex-1-ene has been studied in this way.

## EXCHANGE INFORMATION FROM MULTINUCLEAR MAGNETIC RESONANCE MEASUREMENTS

### Inter-exchange with CO

There are few examples of clusters, which are static on the n.m.r. time-scale, that undergo differential rates of exchange with free CO. One such cluster which exhibits this phenomenon is  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$  (Fig. 5). In this case, preferential exchange of the bridging CO's within a  $\text{Rh}_3$ -triangle occurs and this suggests that a dissociative mechanism is involved since the intra-triangular  $\text{Rh}_2\text{-CO}$  bond length 2.12 Å is significantly longer than the inter-triangular bond length 2.04 Å (ref. 11).

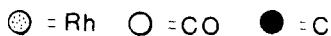
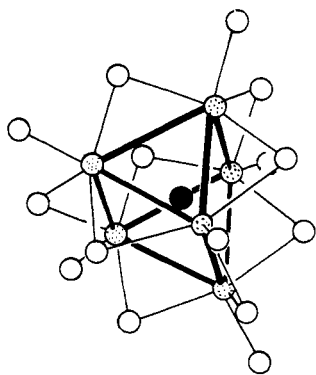


FIGURE 5  
Schematic representation of  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$

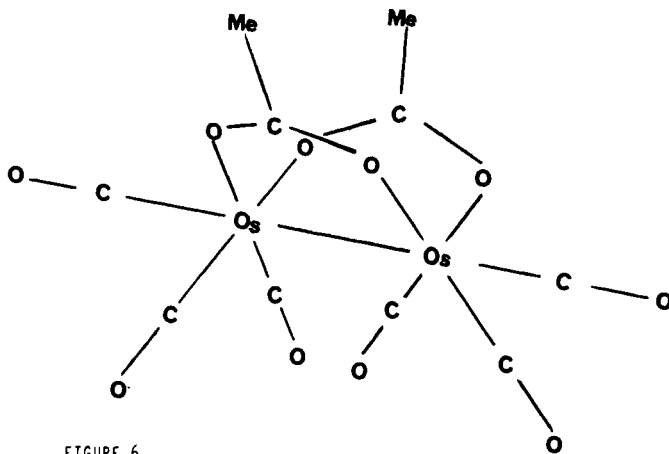


FIGURE 6  
Schematic representation of  $[\text{Os}_2(\mu\text{-MeCO})_2(\text{CO})_6]$

Recently,  $^{13}\text{C}$  n.m.r. has shown that  $[\text{Os}_2(\mu\text{-MeCO})_2(\text{CO})_6]$  (Fig. 6) undergoes exchange with free CO entirely at sites which are trans to the Os-Os bond (ref. 12) This is in-keeping with the preferential replacement of CO by other ligands, e.g.  $\text{PR}_3$ ,  $\text{P}(\text{OR})_3$ , in sites trans to formal M-M bonds (ref. 13) but, in these cases, it is not clear whether this is due to thermodynamic or kinetic effects.

### Intra-exchange of CO

Early n.m.r. measurements for obtaining information about CO rearrangement pathways relied heavily upon variable temperature measurements and observation of differential line-broadening/coalescence of different, unambiguously assigned resonances, e.g.  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  (ref. 14). It is now possible to obtain much more precise information about "what goes where" through the use of the DANTE pulse sequence (ref. 15), and we have used this method for a variety of clusters ranging from  $\text{Rh}_4$  to  $\text{Rh}_{17}$  (ref. 16). In all of our work, CO-exchange involves either localised rotation of inequivalent CO's about a particular metal atom or terminal-bridge CO-exchange which is particularly facile if such an exchange regenerates the original structure, e.g.  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_n]^{(5-n)-}$  (ref. 5), ( $n = 1, 2, 3, 4$ )  $[\text{Rh}_6(\text{CO})_{13}\text{C}]^{2-}$  (ref. 11). In fact, it was not possible to stop the CO-exchange (on the n.m.r. time-scale) around the  $\text{Rh}_4$ -equator in  $[\text{Rh}_6(\text{CO})_{13}\text{C}]^{2-}$  even at  $-80^\circ\text{C}$  in solution and the 7 CO's involved in exchange around this equator also show a large correlated vibrational motion in this same  $\text{Rh}_4$ -plane even in the solid state (ref. 17).

Although it has been claimed that solid state n.m.r. measurements on  $\text{Co}_4(\text{CO})_{12}$  in the solid state provides evidence for rotation of the metal tetrahedron within the carbonyl polyhedron, (ref. 18) we have no evidence for this mechanism being responsible for the CO-exchange in any cluster we have studied in solution and in many cases we have definite evidence against this occurring.

Among isostructural/isoelectronic clusters, the energies of activation for CO-migration appear to decrease with increasing negative charge (ref. 16) and this appears to be related to subtle changes in back-bonding of the metal to carbonyl ligands since we have shown that, of all the homometallic rhodium clusters so far studied, the bridging CO first to migrate has the fastest  $T_1$ .

### Intra-exchange of H

H-migration over the surface of a cluster has long been known and we have recently shown that this can occur concomitantly with CO-migration over the same surface (ref. 3). An increasing number of examples of clusters, (e.g.  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_n]^{(5-n)-}$  ( $n = 1, 2, 3, 4$ ) (ref. 5)  $[\text{Ni}_9\text{Pt}_3(\text{CO})_{21}\text{H}_{4-n}]^{n-}$  ( $n = 3, 2$ ) (ref. 19), are known where H migrates interstitially within the metallic framework. In the case of  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$ , the H's occupy pseudo-octahedral holes at low temperature and migrate with an activation energy similar to that found for the migration of hydrogen c.c.p. bulk metals (ref. 5). In the case of the  $\text{Rh}_{13}$ -hexagonal-close-packed cluster, this migration must involve octahedral-tetrahedral hole jumps.

### Intra-exchange of the metal polyhedron

$^{195}\text{Pt}$  n.m.r. was first used to show that the essentially eclipsed  $\text{Pt}_3$ -triangular stacks in  $[\{\text{Pt}_3(\text{CO})_6\}_n]^{2-}$  ( $n = 2, 3, 4$ ) rotate about the pseudo-3-fold axis in solution (ref. 20) Since then, other examples of metal polyhedral rearrangements have been found for clusters which contain a metal polyhedron containing a hetero-interstitial atom e.g.  $[\text{Rh}_6\text{E}(\text{CO})_{15}]^{2-}$  ( $\text{E} = \text{P, As}$ ) (ref. 7);  $[\text{Rh}_{10}\text{E}(\text{CO})_{22}]$  ( $\text{E} = \text{P, As, n} = 3$  (ref. 7);  $\text{E} = \text{S, n} = 2$  (ref. 8));  $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$  (ref. 7). So far, no examples have yet been discovered of homo-metallic close-packed metal polyhedra undergoing metal rearrangement.

### BONDING OF INTERSTITIAL ELEMENTS WITHIN METAL POLYHEDRA

A variety of main group elements, including C, Si, Ge, Sn, N, P, As, Sb, and S have been found to occupy interstitial sites within metal polyhedra in transition metal carbonyl clusters. All of these interstitial atoms can occupy sites which have a hole size smaller than the covalent radius of the interstitial atom. This suggests that the interstitial atom loses electron density and Mossbauer measurements on  $[\text{Ni}_{12}\text{Sn}(\text{CO})_{22}]^{2-}$  show that the  $^{119}\text{Sn}$  isomer shift is  $2.5 \text{ mm s}^{-1}$  (ref. 21), which is well within the range found for  $\text{Sn(II)}$ , and is in-keeping with a positively charged interstitial atom.

C occupies the largest variety of sites ranging from octahedral, e.g.  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$  to trigonal prismatic, e.g.  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$  to square antiprismatic as found in  $[\text{Ni}_{18}\text{C}(\text{CO})_{18}]^{2-}$ ,  $[\text{Ni}_9\text{C}(\text{CO})_{19}]^{2-}$ ,  $[\text{Ni}_{10}\text{C}(\text{CO})_{20}]^{2-}$  (ref. 22).  $T_1$  relaxation times (Table 1) on these interstitial carbides at various field strengths in solution show that the relaxation rate is dominated by the Chemical Shift Anisotropy mechanism (Table 2) (ref. 23) and this has been confirmed by measurements in solid state. By analogy with organic compounds, (ref. 24) the occurrence of  $sp$  or  $sp^2$  by hybridisations produces a large anisotropy which is absent in compounds with an  $sp^3$  carbon. The relaxation data for  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ , coupled with the symmetry of the cluster and previous vibrational studies, (ref. 25) suggest that the carbide is probably more correctly viewed as an  $sp$  carbon and this is in keeping with Huckel molecular orbital calculations (Fig. 7) (ref. 26). This result should be contrasted with the extremely long  $T_1$  and low Chemical Shift Anisotropy found for the carbide in  $[\text{Ni}_{10}\text{C}(\text{CO})_{18}]^{2-}$ . In this case, the data show that the shielding tensor is almost completely isotropic, which is similar to previous observations on halomethanes, (refs. 24, 27, 28) and thus suggests that the carbide atom in  $[\text{Ni}_{10}\text{C}(\text{CO})_{18}]^{2-}$  is tending towards  $sp^3$  hybridisation in agreement with Huckel molecular orbital calculations (Fig. 8) (ref. 26).

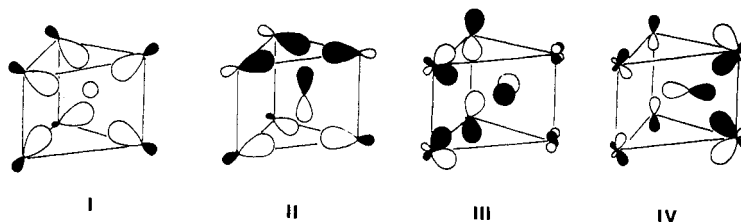


FIGURE 7  
Interacting Rh and C carbide atomic orbitals in  $[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$   
I and II are the most important

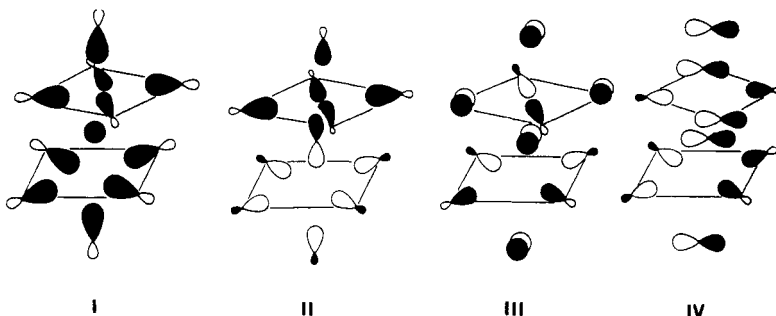


FIGURE 8  
Interacting Ni and C carbide atomic orbitals in  $[\text{Ni}_{10}\text{C}(\text{CO})_{18}]^{2-}$   
I, II, III and IV are all important

TABLE 1.  $T_1$ 's of interstitial carbides at ambient temperature.

Compound	$T_1$ at 4.7 T(sec.)	$T_1$ at 6.34 T(sec.)	$T_1$ at 9.4 T(sec.)
$[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$	4.31	/	1.15
$[\text{Rh}_6(\text{CO})_{13}\text{C}]^{2-}$	5.77	/	1.58
$[\text{Ni}_{10}(\text{CO})_{18}\text{C}]^{2-}$	325.0	216.1	/

TABLE 2. NMR data on interstitial carbides.

Compound	$\tau_c$ (sec.)	$\delta(^{13}\text{C carbide ppm})$	$\Delta\sigma$ (ppm)	$\sigma_{\parallel}$ (ppm)	$\sigma_{\perp}$ (ppm)
$[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$	$7.10 \cdot 10^{-11}$	+264	477	+54	-423
$[\text{Rh}_6(\text{CO})_{13}\text{C}]^{2-}$	$6.10 \cdot 10^{-11}$	+470	438	-178	-616
$[\text{Ni}_{10}(\text{CO})_{18}\text{C}]^{2-}$	$1.10 \cdot 10^{-10}$	+278	38	-253	-291

## REFERENCES

- B.T. Heaton, L. Strona, S. Martinengo, D. Strumolo, V.G. Albano and D. Braga, *J. Chem. Soc. Dalton Trans.*, 2175-2182 (1983).
- B.T. Heaton, L. Strona, S. Martinengo, D. Strumolo, R.J. Goodfellow and I.H. Sadler, *J. Chem. Soc. Dalton Trans.*, 1499-1502 (1982).
- S. Bordoni, B.T. Heaton, C. Seregni, L. Strona, R.J. Goodfellow, M.B. Hursthouse, M. Thornton-Pett and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, accepted for publication.
- J. Pursianen, T.A. Pakkanen, B.T. Heaton, C. Seregni and R.J. Goodfellow, *J. Chem. Soc. Dalton Trans.*, 681-686 (1986).
- C. Allevi, B.T. Heaton, C. Seregni, L. Strona, R.J. Goodfellow, P. Chini, and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, 1375-1381 (1986).
- B.T. Heaton, R. Della Pergola, L. Strona, D.O. Smith and A. Fumagalli, *J. Chem. Soc. Dalton Trans.*, 2553-2555 (1982).
- B.T. Heaton, L. Strona, R. Della Pergola, J.L. Vidal and R.C. Schoening, *J. Chem. Soc. Dalton Trans.*, 1941-1947 (1983).
- L. Garlaschelli, A. Fumagalli, S. Martinengo, B.T. Heaton, D.O. Smith and L. Strona, *J. Chem. Soc. Dalton Trans.*, 2265-2267 (1982).
- B.T. Heaton, J. Jonas, T. Eguchi, and G.A. Hoffman, *J. Chem. Soc. Chem. Commun.*, 331-332 (1981); B.T. Heaton, L. Strona, J. Jonas, T. Eguchi and G.A. Hoffman, *J. Chem. Soc. Dalton Trans.*, 1159-1164 (1982).
- T. Eguchi, M. Kishita and B.T. Heaton, *Chem. Express, Japan* 2, 659-662 (1987).
- B.T. Heaton, L. Strona and S. Martinengo, *J. Organometal. Chem.*, 215, 415-422 (1981).
- A.J. Deeming, N.P. Randle, M.B. Hursthouse and R.L. Short, *J. Chem. Soc. Dalton Trans.*, 2473-2477 (1987).
- B.T. Heaton, *Amer. Chem. Soc. Symp. Ser.*, 227-234 (1983).
- C. Brown, B.T. Heaton, L. Longhetti, D.O. Smith, P. Chini and S. Martinengo, *J. Organometal. Chem.*, 169, 309-314 (1979).
- G.A. Morris and R. Freeman, *J. Mag. Res.*, 29, 433-462 (1978).
- B.T. Heaton, E. Occhiello, C. Seregni and L. Strona, *J. Chem. Soc. Dalton Trans.*, submitted for publication.
- D. Braga and B.T. Heaton, *J. Chem. Soc. Chem. Commun.*, 608-610 (1987).
- B.E. Hanson and E.C. Lisic, *Inorg. Chem.*, 25, 715-716 (1986).
- A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, G. Piva, G. Piro, M. Sansoni and B.T. Heaton, *J. Organometal Chem.*, 301, C5-C8 (1986).
- C. Brown, B.T. Heaton, A.D.C. Towl, P. Chini, A. Fumagalli and G. Longoni, *J. Organometal. Chem.*, 181, 233-254 (1979).
- B.T. Heaton, P. Ingallina, G. Longoni and C. Johnson, unpublished results.
- A. Ceriotti, G. Longoni, M. Manassero, M. Perego and M. Sansoni, *Inorg. Chem.*, 24, 117-120 (1985).
- B.T. Heaton, E. Occhiello, G. Piro and L. Strona, unpublished results.
- B.P. Appleman and B.P. Dailey, *Adv. Magn. Res.*, 7, 231-320 (1974).
- J.A. Creighton, R. Della Pergola, B.T. Heaton, S. Martinengo, L. Strona and D.A. Willis, *J. Chem. Soc. Chem. Commun.*, 864-865 (1982).
- D. Evans, unpublished results.
- P.K. Bhattacharya and B.P. Dailey, *Mol. Phys.*, 26, 1379-1388 (1974).
- P.K. Bhattacharya and B.P. Dailey, *J. Magn. Res.*, 13, 317-327 (1974).