Hydride and Carbonyl Fluctionality in $[HM_{10}C(CO)_{24}]^-$ (M = Ru, Os)

Philip J. Bailey[a[1]], **Lutz H. Gade**[a[2]], **Brian F. G. Johnson**[b], **and Jack Lewis***[a]

University Chemical Laboratory[a],
Lensfield Road, Cambridge CB2 1EW, U.K.

Department of Chemistry, University of Edinburgh, Kings Buildings[b],
West Mains Road, Edinburgh EH9 3JJ, U.K.

Received April 29, 1992

Key Words: Synthesis gas adsorption, model systems / Hydrido ligand / Clusters / Ligand migration / Ruthenium complexes / Osmium complexes

The nature of the crystallographically isostructural hydrido-cluster anions $[HOs_{10}C(CO)_{24}]^-$ (**1**) and $[HRu_{10}C(CO)_{24}]^-$ (**2**) in solution has been probed by variable-temperature ^{13}C-NMR and two-dimensional $\{^1H\}^{13}C$-EXSY spectroscopy. The results of the study are interpreted in terms of both localised and global intramolecular exchange of the carbonyl and hydrido ligands which appear to occur by the same mechanisms in both clusters. The significance of the derived model for the understanding of the dynamic behaviour of more complicated systems such as $[H_4Os_{10}(CO)_{24}]^{2-}$ (**4**) is discussed. The latter is at present the best molecular model for the structural aspects of synthesis gas adsorption at high density on metal surfaces.

The chemisorption of H_2 and CO on metal surfaces is one of the most extensively studied areas of surface science[3,4]. The role that the adsorption of these molecules (e.g. in "synthesis gas") plays in various heterogeneous catalytic processes provides the underlying motivation for the research effort. Certain structural and dynamic aspects of the chemisorption of small molecules on extended metal surfaces may be modelled by the interaction of molecular fragments in discrete transition metal cluster molecules[5]. In the context of synthesis gas chemistry the study of structures, chemical reactivity and ligand dynamics of high-nuclearity hydrido carbonyl clusters has received particular attention.

We have previously reported the syntheses and structures of several decanuclear hydrido-carbonyl clusters of ruthenium and osmium which exhibit a cubic close-packed tetrahedron (i.e. tetracapped octahedron) of metal atoms surrounded by a shell of 24 carbonyl and 1 – 5 hydrido ligands (Figure 1): $[HOs_{10}C(CO)_{24}]^-$ (**1**)[6], $[HRu_{10}C(CO)_{24}]^-$ (**2**)[7], $H_2Os_{10}C(CO)_{24}$ (**3**)[6], $[H_4Os_{10}(CO)_{24}]^-$ (**4**)[8], and $[H_5Os_{10}(CO)_{24}]^-$ (**5**)[8].

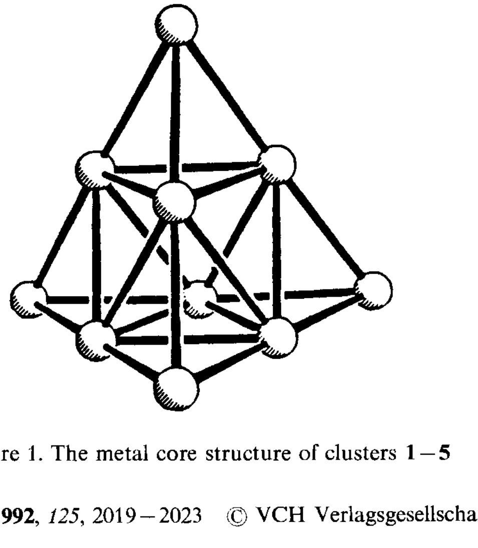

Figure 1. The metal core structure of clusters **1** – **5**

For the $[(Ph_3P)_2N]^+$ salt of **4**, in particular, a neutron diffraction study has established the surface location of the four hydrido atoms which are intimately embedded in the CO-ligand sphere[9]. Very short C···H contacts were interpreted as being indicative of an incipient interaction between the two types of ligands, a key step in Fischer-Tropsch related catalysis. The determination of the solid-state structure of **4** prompted a series of ^1H- and ^{13}C-NMR studies in order to obtain information about the behaviour of the system in solution. These established a high degree of mobility for the H ligand which is reflected in the NMR spectra at temperatures above 295 K. Unfortunately, the chemical exchange patterns observed on lowering the temperature were too complex to enable the proposition of a model for the dynamic processes occuring in the system. The situation is additionally complicated by the fact that, in spite of the results of the neutron structure analysis, a conceivable interstitial migration of the hydrido ligands in **4** cannot be fully ruled out.

In order to gain some insight into the migrational processes of a hydride ion in a tetrahedral "$M_{10}(CO)_{24}$"-type cluster, it was therefore decided to reinvestigate and extend the ^{13}C-NMR spectroscopic characterisation of the monohydrido cluster anions **1** and **2**. Both species are derived from the decametal carbido cluster dianions $[M_{10}C(CO)_{24}]^{2-}$ (M = Ru, Os) which may be quantitatively converted into the hydrido monoanions, $[HOs_{10}C(CO)_{24}]^-$ **1** and $[HRu_{10}C(CO)_{24}]^-$ **2**, by protonation with strong acids[6,7]. The occupation of the central octahedral cavity in the metal core structures of **1** and **2** by a carbido atom precludes a potential migration of the hydrogen atom between interstitial sites within the cluster core, as was for example found for $[H_3Rh_{13}(CO)_{25}]^{2-}$[10]. Thus, global hydride fluctionality is restricted to the surface of the metal framework. The information obtained from the investigation

0009 – 2940/92/0909 – 2019 \$ 3.50+.25/0

of **1** and **2** will be useful for the analysis of the dynamic processes in the more complicated tetrahydrido cluster **4**.

Results and Discussion

^{13}C-NMR spectra of **1** and **2** in the ^{13}CO chemical shift region recorded at 300 K and 200 K, respectively, are shown in Figure 2 (the carbide resonances are observed as singlets at considerably higher frequencies: δ = 409.0 and 374.5, respectively).

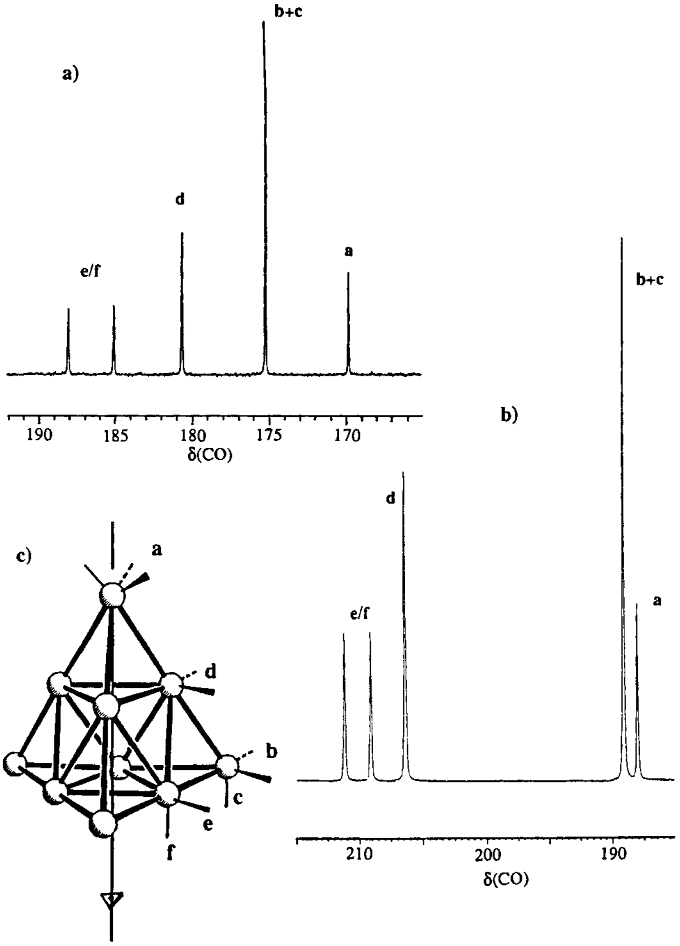

Figure 2. 100.62 MHz ^{13}C-NMR spectra of (a) $[HOs_{10}C(CO)_{24}]^-$ (**1**) at 300 K and (b) $[HRu_{10}C(CO)_{24}]^-$ (**2**) at 200 K in $C_2D_2Cl_4$; (c) labeling of the CO ligands for the assignment of the spectra

The spectra are entirely analogous and consist of five signals in the intensity ratio 1:1:2:3:1 which are split into a high-frequency set of three (1:1:2) and a low-frequency set of two (3:1) signals.

For these systems the spectra can be interpreted unambiguously in terms of a C_{3v} molecular symmetry on the timescale of the experiment, as is shown in Figure 2c, and by assuming rapid tripodal rotation of the apical $M(CO)_3$ units which is a fast process for both systems even at 170 K. An interesting observation on these spectra, and one which has been found to be equally applicable to other derivatives of $[M_{10}C(CO)_{24}]^{2-}$ (M = Ru, Os), is that the signals associated with the apical metal atoms (a, b, c) appear at a lower frequency as those on edge sites (d, e, f) (Table 1)[11]. The original interpretation of this effective C_{3v} symmetry[12] of **1** and **2** was that the hydride ion resided within a tetrahedral interstitial site; however, with the recent discovery of the surface location of all four hydrido ligands in **4**, along with the evidence for a similar situation obtained for the dihydrido species $[H_2Os_{10}C(CO)_{24}]$[6b], it is of interest to reinvestigate the system and reevaluate the data[9]. The similarity of the ^{1}H-NMR chemical shifts of the hydrides in **1**, **2**, and **4** (Table 1) does not support the proposal of significantly different chemical environments for the H nuclei in the three species. Indeed, there is at present no firm evidence for the existence of hydride ions located in tetrahedral interstitial sites in any known carbonyl cluster, and we are therefore obliged to consider the possibility that the H ligands in **1** and **2** are located on the surface of the metal core.

The only possible position in which a static surface-located hydride ion may confer C_{3v} symmetry on both species is in a symmetrical μ_3-coordination site above one of the exposed faces of the central octahedron (i.e. in the centre of one of the surfaces of the cluster core), as found in the solid state for two of the four hydrido atoms in **4**. However, such an interpretation of the ^{13}C-NMR spectra may be discounted in the case of **1** and, by implication, **2** with reference to the reported ^{1}H-NMR spectrum of **1**[13]. Associated with the hydride resonance at δ = -15.3 are two sets of ^{187}Os satellites ($I = 1/2$, 1.96% natural abundance) with an intensity ratio of ca. 1:3 and $^1J(^{187}Os,^1H)$ coupling constants of 26.6 and 15.9 Hz, respectively. Clearly, μ_3 coordination of the hydride as proposed above would lead only to one set of satellites since all three of the osmium atoms in this site are equivalent. We are therefore led to consider the location of the H ligand on the surface of one of the capping tetrahedra of the metal core, and in this situation the ^{187}Os-satellite pattern suggests the association of the hydride with three equivalent osmium atoms in additions to the apical one. This is consistent with the ^{13}C-NMR spectrum since

Table 1. ^{1}H- and ^{13}C-NMR data of **1** and **2** recorded in $C_2D_2Cl_4$

Compound	δ(^{13}C)						δ(^{1}H)
	a	b + c	d	e	f	carbide	Os-H
$[HOs_{10}C(CO)_{24}]^-$ (**1**) (300 K)	169.8	175.2	180.6	185.1	188.0	409.0	−15.3
$[HRu_{10}C(CO)_{24}]^-$ (**2**) (200 K)	188.1	189.9	206.7	209.5	211.3	374.5	−13.5

static location of the hydrido ligand on a face (μ_3) or edge (μ_2) of a tetrahedral cap would lead at best to C_s symmetry, whilst its equal association (on the NMR time scale) with the three osmium atoms at the base of a cap and with that at a vertex would clearly result in the required effective C_{3v} symmetry (Figure 3).

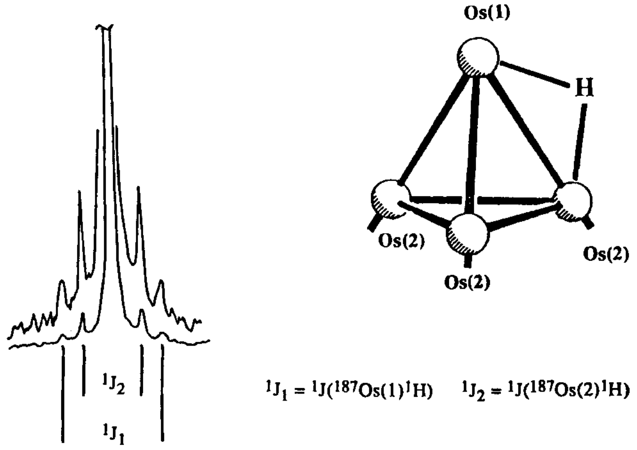

Figure 3. $^1J(^{187}Os,^1H)$ satellite pattern of the hydride resonance in the ^1H-NMR spectra of **1** (adapted from ref.[13]) and its reinterpretation in terms of a rapidly migrating external H ligand

Returning to the ^{187}Os-satellite pattern, the coupling constant of 15.9 Hz for the more intense satellites is unusually small for a static hydride in an osmium cluster (typical values are between 26 and 40 Hz, although the pubished data is by no means extensive)[13,14]. It is, however, comparable to the average $^1J(^{187}Os,^1H)$ found for rapidly exchanging systems such as $H_4Os_4(CO)_{12}$ [$^1J(^{187}Os,^1H)$ = 14.4 Hz at 298 K and 30.5 Hz at 168 K][13]. We must therefore consider a model in which the hydrido ligand is surface-located and rapidly "rotating" around the three equivalent edges and faces of one of the capping tetrahedra, a situation which generates the observed overall symmetry, and is in addition consistent with the ^1H-NMR data. The $^1J(^{187}Os,^1H)$ of 26.6 Hz is attributed to the coupling to the vertex osmium nucleus whilst the splitting of the set of satellites with threefold intensity corresponds to the average coupling to the three chemically equivalent osmium nuclei as depicted in Figure 3. Such a rotation of the hydride ion would not be surprising considering the above-mentioned observation that the apical $M(CO)_3$ units are undergoing rapid tripodal rotation with which the hydride motion may be concerted. This is therefore now our favoured model. The ^{13}C-NMR spectra of **1** and **2** shown in Figure 2 thus conceal some residual motion of both the hydrido and carbonyl ligands, and indeed, the spectra recorded above these temperatures reveal a development of these motions.

A series of ^{13}C-NMR spectra of **1** recorded in $C_2D_2Cl_4$ up to 416 K is shown in Figure 4a. The initial effect of increasing the temperature is the exchange broadening of all resonances in the spectrum followed by coalescence above 380 K. The appearance of the spectra suggests that the three signals at $180 < \delta < 190$ [those due to the edge-$M(CO)_2$ units] and the two signals at lower frequency [the $M(CO)_3$ carbonyls] internally coalesce, but that there is no visible exchange between the two sets of signals. This results in the emergence of two resonances at 416 K (δ = 173.6, 182.9), each due to the 12 CO ligands and indicative of a transformation of the effective point symmetry from C_{3v} to T_d.

In order to unambiguously establish the exchange network for the ^{13}CO resonances of **1**, a $\{^1H\}^{13}C$-EXSY spectrum was recorded at 340 K and is shown in Figure 4b. In

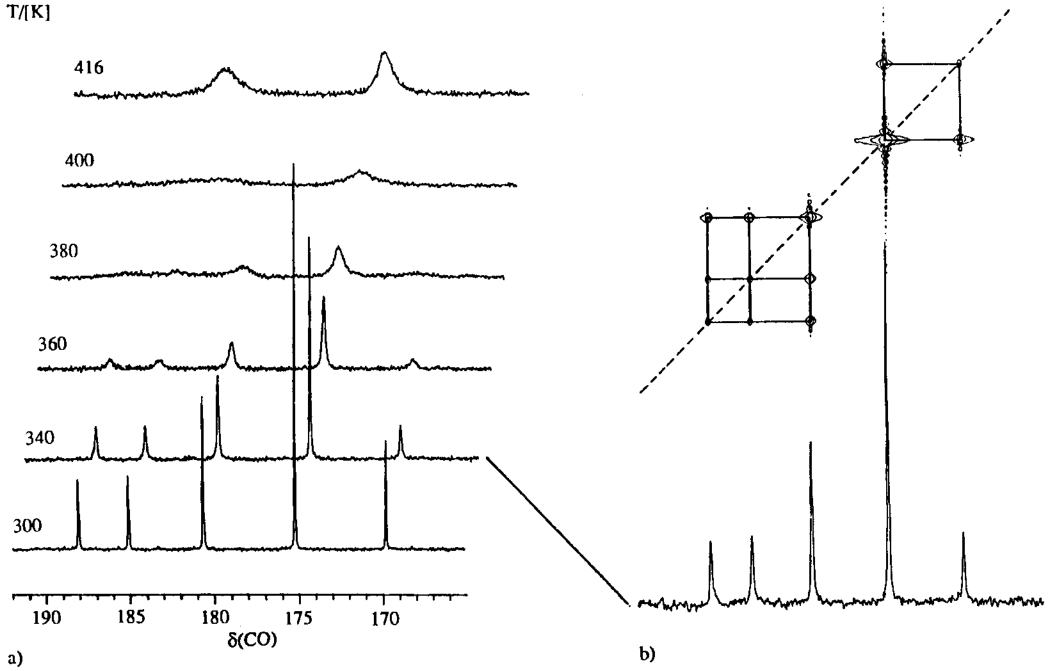

Figure 4. (a): A high-temperature ^{13}C-NMR series of **1** in $C_2D_2Cl_4$; (b): ^{13}C-EXSY spectrum of **1** recorded in $C_2D_2Cl_4$ at 340 K

the experiment the standard NOESY pulse sequence was used[15]:

$$\pi/2 - \tau - \pi/2 - t_{mix} - \pi/2 - \mathrm{FID}$$

The mixing time, t_{mix}, was set at 0.2 s and randomly varied within a range of ±0.04 s in order to suppress coherent J-cross peaks due to scalar coupling between the ^{13}C nuclei. This measure was taken, although earlier reports of similar experiments on clusters indicated that COSY-type peaks between CO ligands of relative *cis* orientation are not observed even at high levels of ^{13}C enrichment[16]. The incoherent cross-peak correlations in the spectrum may therefore be attributed to spins involved in chemical exchange. The pattern is consistent with the deductions made from the one-dimensional variable-temperature spectra in that only cross peaks attributable to exchange between the two apical $M(CO)_3$ sites or the three $M(CO)_2$-edge sites are observed but not between these two environments. In addition, both processes appear to be correlated. Since CO exchange between the vertex positions cannot occur without involving the edge sites, the only possible explanation is the exchange of the hydride ion between all possible positions on the cluster surface, and if this were a rapid process, the expected effective symmetry at high temperatures would be T_d, as is observed. In this way the migration of the hydride ion over the surface of the cluster core is indirectly probed by the observation of its effect on the effective point symmetry of the system. It should be pointed out that the observed behaviour of the hydride in **1** is closely related to that of Hg−Y-fragments (Y = Cl, Br, I, CF_3) attached to Os_{10} cores which we reported recently[17]. This is an example for the usefulness of the isolobal analogy in this area of chemistry[18].

A series of ^{13}C-NMR spectra of **2** recorded in $C_2D_2Cl_4$ between 250 K and 380 K are shown in Figure 5. Here, between 250 K and 335 K we observe spectral changes which are entirely analogous to the those found for **1**.

However, due to the larger frequency separation of the two sets of signals for this cluster, the exchange pattern more obviously only involves exchange within the two sets as shown conclusively for **1** by the EXSY spectrum. Thus, at 335 K we have a two-resonance indicating an effective T_d symmetry brought about by the global migration of the hydrido ligand. However, a further increase of the temperature does not result in a high-temperature limiting spectrum for this process, i.e. the development of two sharp signals. On the contrary, above 335 K the two signals again broaden indicating the emergence of chemical exchange between the two CO environments on the timescale of the experiment. At these elevated temperatures, therefore, the spectra are to be interpreted in terms of not only global exchange of the hydride but also of the carbonyl ligands. Beyond 380 K **2** is unstable and rapidly decomposes; however, it is resonable to assume that the spectra above this temperature would show coalescence of the two signals and the emergence of a single resonance for all 24 CO groups, as is found in the high-temperature limiting spectrum of the decanuclear parent cluster dianion, $[Ru_{10}C(CO)_{24}]^{2-}$[7].

In summary, the dynamic behaviour of the hydrido ligand in **1** and **2** can be rationalised by invoking two limiting regimes:

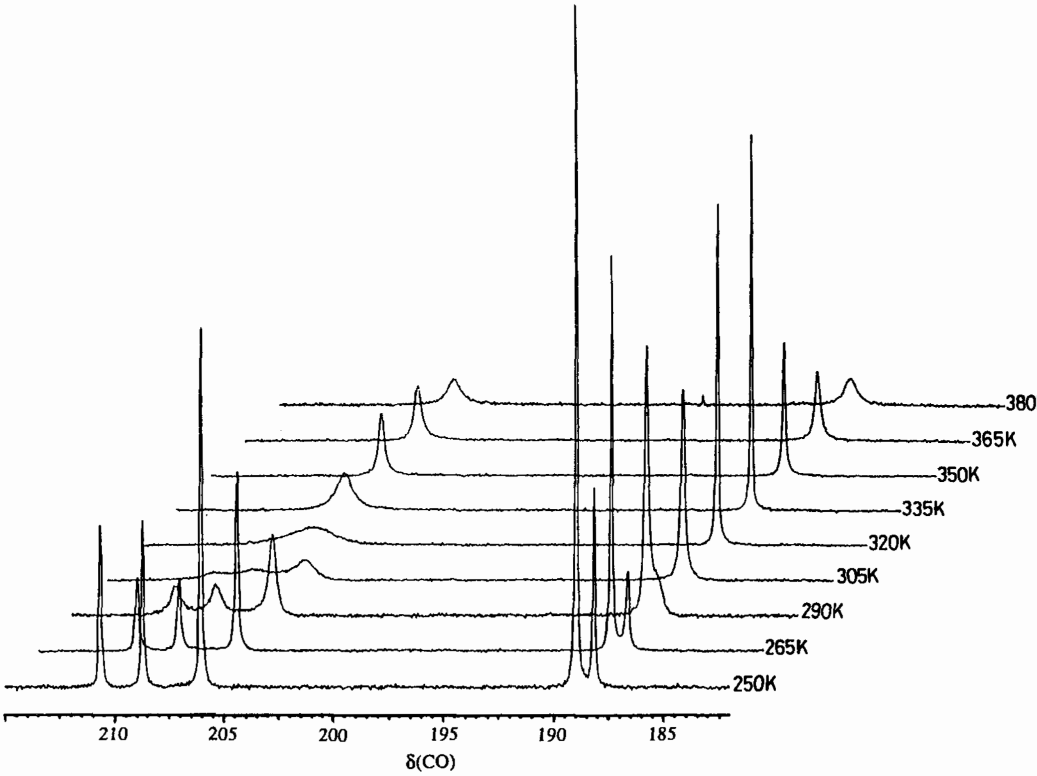

Figure 5. A series of high-temperature ^{13}C-NMR spectra of $[HRu_{10}C(CO)_{24}]^-$ (**2**) recorded in $C_2D_2Cl_4$

i) the rapid migration of the hydride around the symmetry-related edges and faces of a single capping tetrahedron of the M_{10} core (M = Ru, Os), possibly synchronous with the $M(CO)_3$ "rotation", conferring effective C_{3v} symmetry;

ii) the total fluctionality of the hydride over the surface of the metal core at elevated temperatures resulting in effective T_d symmetry;

whilst it is evident from the highest temperature spectra of **2** that the carbonyl ligands in these systems are also, albeit slowly, exchanging between the metal atoms of the cluster cores. In general, CO migration in Os-cluster cores is found to be a more highly activated process than in their ruthenium analogues. This is thought to be consequence of the energetically less favourable intermediate μ_2-CO coordination mode for the Os species which the carbonyl ligands must necessarily adopt in interatomic migrational processes in clusters.

Conclusion

The migration of the surface-bound hydrogen atoms in the decanuclear clusters **1** and **2** has been found to be a highly structured process and may be broken down to various elementary processes which determine the limiting dynamic regimes as reflected in the ^{13}C-NMR spectra. It may be assumed that a similar behaviour of the hydrido ligands in **4** is responsible for the spectral patterns observed in the ^1H- and ^{13}C-NMR spectra. The detailed investigation of the latter system is currently under way[19].

As far as the experimental method employed is concerned, we have found that for the probing of the hydride-ion mobility in symmetrical high-nuclearity carbonyl clusters the indirect monitoring of its effect on the CO shell as a whole by means of ^{13}C-NMR spectroscopy may be the method of choice. As the amount of accumulated data increases an even more specific interpretation of the spectroscopic results will be feasible.

P. J. B. thanks the *S. E. R. C.* and *British Petroleum Plc.* for financial support. L. H. G. acknowledges the award of scholarships by the *British Council*, the *Kurt Hahn Trust*, the *Studienstiftung des Deutschen Volkes*, and *ICI Plc.*.

Experimental

All the spectra displayed were recorded by using samples of 50% and 30% ^{13}C-enriched $[HOs_{10}C(CO)_{24}]^-$ (**1**) and $[HRu_{10}C(CO)_{24}]^-$ (**2**), respectively. Both compounds were synthesised from ^{13}C-enriched $M_3(CO)_{12}$ (M = Ru, Os)[6,7], the latter being obtained by literature procedures[20,21].

The ^{13}C-NMR spectra were recorded by using a Bruker AM400 spectrometer with an ASPECT 3000 computer and equipped with a B-VT-1000 variable-temperature unit. $C_2D_2Cl_4$ was used in all experiments and chromium(III) acetylacetonate was routinely added as a shiftless relaxation agent which enabled the reduction of the delay between consecutive pulses (i.e. the sum of the aquisition time AQ and the relaxation delay RD) to ca. 1.4. Typical aquisition parameters were as follows: number of pulses (NS): 200–1000; number of data points (SI): 64 K; sweep width (SW): 45000–48000 Hz; relaxation delay (RD): 0.7–0.8 s. The accumulated free-induction decay was treated with an exponential filter (LB = 1.0–1.5) before Fourier transformation.

The ^{13}C-EXSY spectrum (recorded at 340 K) was obtained with the Bruker automation programme NOESYX which produces homonuclear-correlated 2D spectra with power-gated ^1H decoupling. The pulse sequence is $D1 - 90^\circ - D0 - 90^\circ - D9 - 90^\circ$ – FID. The initial relaxation time was set at 1.1 s, $D0$ was initially 3×10^{-6} s, and $D9$ was the mixing time t_{mix} which was set at 0.2 s. The basic experiment was repeated for 128 values of $D0$, i.e. the $F1$ dimension of the data matrix contained 128 words, and was zero-filled to 256 W, while the $F2$ dimension contained 1024 data points. $D9$ ($= t_{mix}$) was randomly varied within the range of ±40 ms to suppress J-cross peaks. The number of scans per experiment was 32 which gave a total experiment time of ca. 2.5 h. The data were processed by using an unshifted sine-bell apodization in both dimensions, and the data matrix was not symmetrised.

---

[1] Present address: Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4, W-8046 Garching, F. R. G.

[2] Present address: Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, W-8700 Würzburg, F. R. G.

[3] See for example: L. Westerland, L. Jonsson, S. Anderson, *Surf. Sci.* **1988**, *199*, 109 and references cited therein.

[4] G. A. Somorjai, *J. Phys. Chem.* **1990**, *94*, 1013.

[5] [5a] P. Chini, *Inorg. Chim. Acta Rev.* **1968**, *2*, 3. – [5b] B. F. G. Johnson, J. Lewis, *Pure Appl. Chem.* **1975**, *44*, 43. – [5c] E. L. Muetterties, *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. – [5d] G. Ertl, *Gazz. Chim. Ital.* **1979**, *109*, 217. – [5e] E. L. Muetterties, *Angew. Chem.* **1978**, *90*, 545; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 545. – [5f] E. L. Muetterties, T. N. Rodin, E. Band, C. F. Brucker, W. R. Pretzer, *Chem. Rev.* **1979**, *79*, 91.

[6] [6a] P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.* **1982**, 49. – [6b] D. Braga, F. Grepioni, S. Righi, B. F. G. Johnson, P. Frediani, M. Bianchi, F. Piacenti, J. Lewis, *Organometallics* **1992**, *11*, 706.

[7] P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin, H. R. Powell, *J. Organomet. Chem.* **1989**, *377*, C17.

[8] D. Braga, J. Lewis, B. F. G. Johnson, M. McPartlin, W. J. H. Nelson, M. D. Vargas, *J. Chem. Soc., Chem. Commun.* **1983**, 241.

[9] A. Bashall, L. H. Gade, B. F. G. Johnson, J. Lewis, G. J. McIntyre, M. McPartlin, *Angew. Chem.* **1991**, *103*, 1186; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1164.

[10] S. Martinengo, B. T. Heaton, R. J. Goodfellow, P. Chini, *J. Chem. Soc., Chem. Commun.* **1977**, 39.

[11] P. J. Bailey, M. J. Duer, B. F. G. Johnson, J. Lewis, M. McPartlin, H. R. Powell, G. Conole, C. E. Anson, *J. Organomet. Chem.* **1990**, *383*, 441.

[12] The term *effective symmetry* is used instead of "observed symmetry on the NMR time scale". It emphasises the fact that the symmetry of a molecule is to be defined with respect to the timescale of the experiment with which it is determined.

[13] E. C. Constable, B. F. G. Johnson, J. Lewis, G. N. Pain, M. J. Taylor, *J. Chem. Soc., Chem. Commun.* **1982**, 754.

[14] J. S. Holmgren, J. R. Shapley, P. A. Belmonte, *J. Organomet. Chem.* **1985**, *284*, C5.

[15] R. R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford, **1987**, p. 490.

[16] G. E. Hawkes, L. Y. Lian, E. W. Randall, K. D. Sales, S. Aime, *J. Chem. Soc., Dalton Trans.* **1985**, 225.

[17] L. H. Gade, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1992**, 933.

[18] R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711.

[19] L. H. Gade, B. F. G. Johnson, J. Lewis, unpublished results.

[20] D. J. Darensbourg, R. L. Gray, M. Pala, *Organometallics* **1984**, *3*, 1928.

[21] L. R. Martin, F. W. B. Einstein, R. K. Pomeroy, *Organometallics* **1988**, *7*, 294. For a detailed description of the procedure, see also: L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, T. Kotch, A. J. Lees, *J. Am. Chem. Soc.* **1991**, *113*, 8698.

[188/82]

CAS Registry Numbers

1: 82533-00-4 / **2**: 126082-28-8