Inorganica Chimica Acta, 146 (1988) 151–152

^{13}C Solid State MAS NMR Spectra of $[M_3(CO)_{12}]$ Complexes (M = Ru and Os). Evidence for Motional Effects in $[Ru_3(CO)_{12}]$

SILVIO AIME, MAURO BOTTA, ROBERTO GOBETTO, DOMENICO OSELLA

Istituto di Chimica Generale ed Inorganica, Facoltà di Scienze MFN, Università di Torino, Via P. Giuria 7, 10125 Turin, Italy

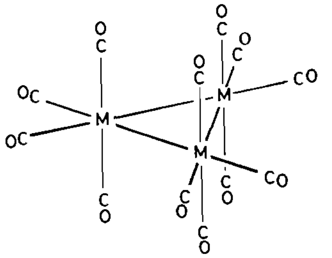
and LUCIANO MILONE

Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Torino, Via P. Giuria 9, 10125 Turin, Italy

(Received January 15, 1988)

Recently the availability of instruments operating in the MAS mode [1] has allowed the observation of high resolution ^{13}C solid state NMR spectra of a number of metal carbonyl complexes. Among them of particular interest is the $[Fe_3(CO)_{12}]$ case where the number and position of the observed resonances suggested that, at ambient temperature, a dynamic process is occurring [2]. In a later paper [3] it was shown that this motion (rotation of the Fe_3 triangle inside the icosahedral ligand polyhedron) can be 'frozen out' on lowering the temperature. In another VT study [4] it has been shown that rapid carbonyl scrambling on the NMR time scale is occurring in the high temperature ^{13}C spectra of solid $[Co_2(CO)_8]$.

In this communication we report the ^{13}C solid state MAS spectra of $[M_3(CO)_{12}]$ clusters (M = Ru and Os) recorded at 6.34 Tesla (observing frequency: 67.9 MHz).



$M_3(CO)_{12}$ (M = Ru, Os)

Both species crystallize without disorder, in marked contrast to $[Fe_3(CO)_{12}]$, showing D_{3h} symmetry slightly distorted due to packing effects [5, 6]. The ^{13}C NMR spectra in solution showed the two expected resonances (integrated intensity ratio 1:1) for the set of axial and equatorial carbonyls for $[Os_3(CO)_{12}]$ but a fast scrambling process, leading to a single resonance down to -120 °C, is occurring in $[Ru_3(CO)_{12}]$ [7].

The ^{13}C NMR spectrum of $[Os_3(CO)_{12}]$ (35% ^{13}CO enriched) recorded under MAS is reported in Fig. 1. The pattern observed in the isotropic region exhibits the expected separation between the axial and equatorial sets of carbonyls [7] but each set is now split into five and six resonances respectively. This multiplicity has to be related to structurally different positions occupied by carbonyls which are averaged out in solution by localized motions induced by the collisions with solvent molecules.

An accurate determination of the crystal structure in this molecule [6] shows that all the carbon atoms in the molecule represent crystallographic independent sites inside an idealized D_{3h} symmetry. The solid state ^{13}C MAS technique is a powerful tool for obtaining evidence of their differences. The range of about 5 ppm for each set of absorptions is rather large for such minor structural differences and appears very promising for the determination of small conformational changes in this class of molecules, especially when the measurement is carried out at high magnetic field. The difference between the average values of axial and equatorial COs (13.2 ppm) is similar to that found in solution (11.5 ppm) [7] suggesting then that the solvation process has a limited influence on the electronic and structural parameters determining the ^{13}C chemical shift of coordinated carbonyl ligands. Recently, Dybowsky and coworkers [8] reported the ^{13}C MAS spectrum of $[Os_3(CO)_{12}]$ recorded at 25.01 MHz with a spinning frequency of 2700 Hz. On comparing their spectrum with our one the advantage gained by working at a higher magnetic field on this class of molecules is clearly shown. Although in general we agree with their comments on site effects as responsible for the complex splitting observed in the ^{13}C spectrum of crystalline $[Os_3(CO)_{12}]$, we do not think that the dipolar interaction between ^{13}C

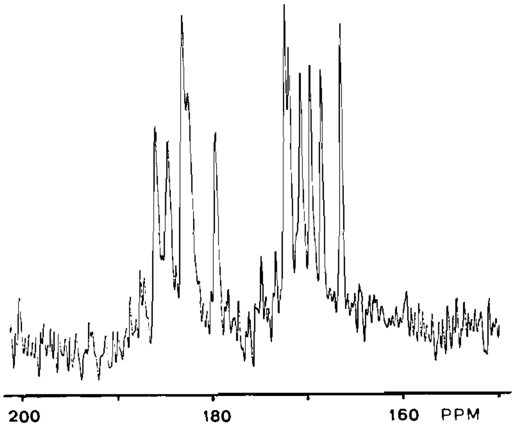


Fig. 1. Room temperature ^{13}C NMR spectrum of $[Os_3(CO)_{12}]$ (isotropic region).

0020-1693/88/$3.50

and ^{189}Os nuclei can result from satellites flanking the main resonances as they suggest.

The [$Ru_3(CO)_{12}$] case is even more interesting. The observation of two sets of resonances for axial and equatorial carbonyls indicates that the intramolecular exchange process occurring in solution is 'frozen out' at the solid state. However in this cluster the axial CO resonances (downfield pattern) are significantly broader than the equatorial ones (Fig. 2). Likely, this broadening arises from packing effects which result in a dispersion of ruthenium–carbon bond distances and angles [5]. As the temperature is increased to +45 °C, the observed narrowing of these resonances is taken as an evidence of the occurrence of local motion involving these carbonyls. The extent of the fluctuations should be very limited since a complete equilibration to a single resonance is not observed. The frequency of these motions is of the order of the linewidth (*i.e.* few tens of Hz) and this represents, to our knowledge, the first spectroscopic observation of such slow motional effects occurring in the solid state for this class of molecules [9].

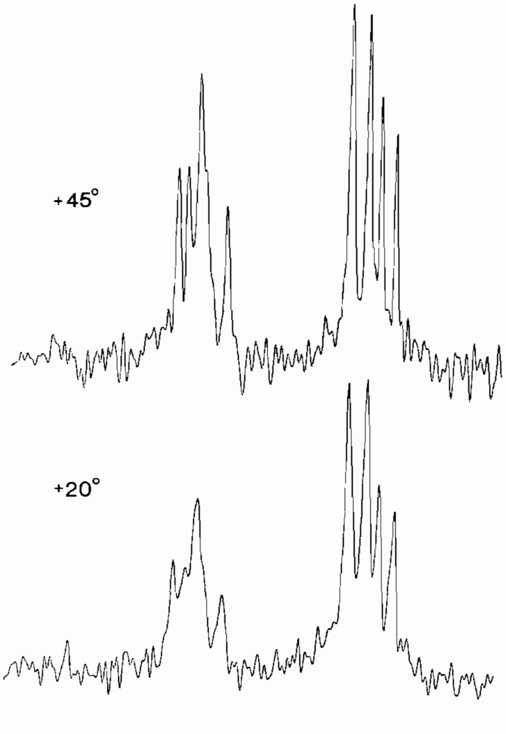


Fig. 2. Variable temperature ^{13}C NMR spectra of [$Ru_3(CO)_{12}$] (isotropic region).

From the better resolved spectrum of [$Os_3(CO)_{12}$] we have extracted the tensor shielding components by using the graphical method developed by Herzfeld and Berger [10]. The resulting Shift Anisotropy terms (average values of 366 and 352 ppm for axial and equatorial carbonyls respectively) are not much different from the average value reported by Gleeson and Vaughan ($\Delta\sigma = 347$ ppm) from the static powder spectrum [11], but our findings suggest significative departure from an axially symmetric pattern for both axial and equatorial carbonyls ($\sigma_{11} \neq \sigma_{22}$).

Finally, attempts to measure the ^{13}C spin-lattice relaxation time in these molecules in the solid state were frustrated by their exceedingly long values ($T_1 > 400$ s); however in [$Ru_3(CO)_{12}$] it has been qualitatively assessed by saturation recovery experiments that T_1 for axial COs is much longer than for equatorial ones. Since we have employed ^{13}C highly enriched samples (>40%) this means that spin-diffusion (which would lead to a unique T_1 value for all the carbon nuclei) is not occurring in these systems.

Acknowledgements

Financial support by the Ministry of Education is gratefully acknowledged. We also thank Johnson Matthey Ltd. for a loan of $RuCl_3$ and Mr P. A. Loveday (University of Cambridge) for high pressure syntheses of [$Ru_3(CO)_{12}$] and [$Os_3(CO)_{12}$].

References

1 C. A. Fyfe, in 'Solid State NMR for Chemists', C. F. C. Press, Ontario, 1983.
2 H. C. Dorn, B. E. Hanson and E. Motell, *Inorg. Chim. Acta, 74,* L71 (1981).
3 B. E. Hanson, E. C. Lisic, J. T. Petty and G. I. Iannacone, *Inorg. Chem., 25,* 4062 (1986).
4 B. E. Hanson, M. J. Sullivan and R. J. Davis, *J. Am. Chem. Soc., 106,* 251 (1984).
5 M. R. Churchill, F. J. Hollander and J. P. Hutchinson, *Inorg. Chem., 16,* 2655 (1977).
6 M. R. Churchill and B. G. DeBoer, *Inorg. Chem., 16,* 878 (1977).
7 S. Aime, O. Gambino, L. Milone, E. Sappa and E. Rosenberg, *Inorg. Chim. Acta, 15,* 53 (1975).
8 L. Hasselbring, H. Lamb, C. Dybowski, B. Gates and A. Rheingold, *Inorg. Chim. Acta, 127,* L49 (1987).
9 J. R. Lyerla, C. S. Yannoni and C. A. Fyfe, *Acc. Chem. Res., 15,* 208 (1982).
10 J. Herzfeld and A. E. Berger, *J. Chem. Phys., 73,* 6021 (1980).
11 J. W. Gleeson and R. W. Vaughan, *J. Chem. Phys., 78,* 5384 (1983).