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^{13}C NMR OF $H_2M_3(CO)_9S$ (M = Ru, Os) AND SOME RELATED COMPOUNDS

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Summary

Variable temperature ^{13}C NMR studies confirmed that the solid state geometries of $H_2M_3(CO)_9S$ and $H_3M_3(CO)_9CCH_3$ (M = Ru, Os) persist in solution. A number of CO scrambling processes have been considered.

Introduction

Although a considerable volume of evidence has been collected [1] supporting carbonyl exchange via some form of bridge opening-bridge closing mechanism in metal carbonyl complexes containing CO-bridges there is no definite requirement that this process must occur in complexes without bridging carbonyl groups. An equally valid mechanism for these compounds is one in which CO exchange occurs about an individual metal atom without CO transfer from one metal atom to another. This mechanism is supported by recent work [2-4] which has shown that "localized" carbonyl scrambling occurs in a variety of metal carbonyl compounds. We now further report investigation of complexes in which this process may be occurring.

While the cobalt alkylidene complexes, $Co_3(CO)_9C—R$, have been known for a number of years [5], only recently have the analogous Group VIII compounds $H_3M_3(CO)_9CCH_3$ (M = Ru, Os) been prepared [6,7]. ^{13}C NMR studies of a number of the cobalt complexes have shown that they undergo facile carbonyl exchange [8]. In contrast, the ruthenium compound $H_3Ru_3(CO)_9CCH_3$ was shown to be rigid at room temperature [6]. By utilising variable temperature ^{13}C NMR we have investigated the fluxional properties and structure in solution of this compound, $H_3Ru_3(CO)_9CCH_3$, and the osmium compound, and also some structurally related sulphur capped complexes $FeCo_2(CO)_9S$, $H_2Ru_3(CO)_9S$ and $H_2Os_3(CO)_9S$.

Experimental

$H_3Ru_3(CO)_9CCH_3$ [6], $H_3Os_3(CO)_9CCH_3$ [7], $FeCo_2(CO)_9S$ [9], $H_2Ru_3(CO)_9S$ [10] and $H_2Os_3(CO)_9S$ [11] were prepared by published methods. ^{13}CO (≈50%) was introduced by enriching the parent carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$; $FeCo_2(CO)_9S$ was enriched directly by stirring under an atmosphere of ^{13}CO. The ^{13}C variable temperature measurements were recorded on a Varian XL100-15 Fourier transform spectrometer at 25.196 MHz; the solutions contained 0.05 *M* $Cr(acac)_3$ as a shiftless relaxation agent.

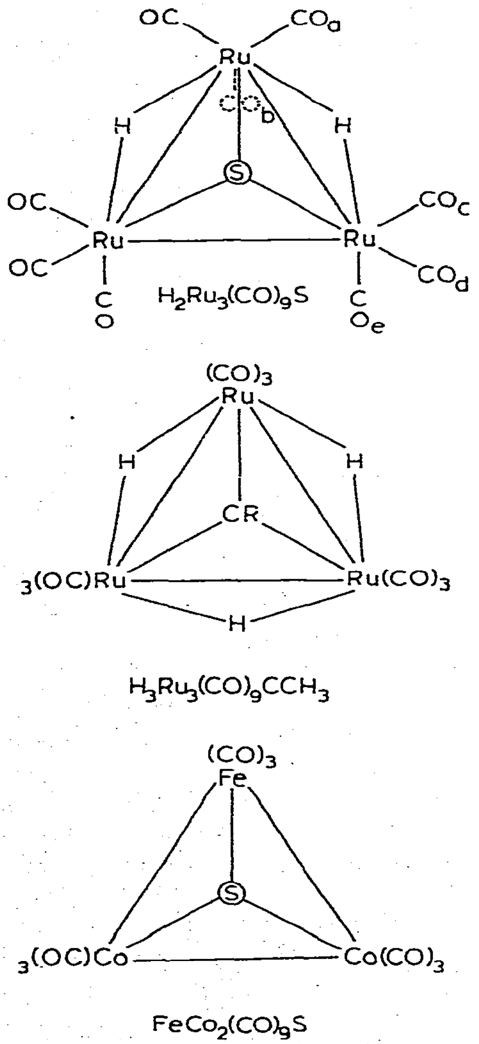

Fig. 1.

Results and discussion

X-ray crystallographic studies on $H_3Ru_3(CO)_9CCH_3$ [12], $FeCo_2(CO)_9S$ [13] and $H_2Ru_3(CO)_9S$ [14] have shown that the solid state structure of these compounds is based on a metal triangle symmetrically capped by the bridging ligand (C or S) with the hydrogen atoms forming bridges along the metal—metal edges (Fig. 1). Our results have shown that this structural form persists in solution. Chemical shifts of the slow exchange spectra are given in Table 1.

$H_2M_3(CO)_9S$ (M = Ru, Os)

The slow exchange spectrum of $H_2Ru_3(CO)_9S$ (Fig. 2) has five resonances in the carbonyl region in the ratio 2/2/1/2/2; entirely consistent with the structure and hydride configuration shown in Fig. 1. Two of these resonances displayed ^{13}C—^1H coupling; probably the carbonyls *trans* to the hydride ligands (a and d). On raising the temperature the signals broadened and coalesced (—60°C) and two lines were resolved [0°C; δ 193.9(1), δ 187.3(2)]. This behaviour can be accommodated by hydride exchange around the metal triangle or local carbonyl scrambling about each ruthenium atom. Further warming led to another coalescence (50°C) and finally the fast exchange limit, a single sharp line at δ 189.3, was reached at a temperature of 90°C. This could result from a combination of the previous two processes or by total carbonyl stretching about the metal framework involving some bridged intermediate. These results were paralleled for $H_2Os_3(CO)_9S$ except the barriers to rearrangement were higher — slow exchange limit at —20°C, first coalescence at 10°C — and the fast exchange limit was not reached; the two signals at δ 173.3(1) and δ 164.2(2) remaining separate although broadened at 100°C.

$FeCo_2(CO)_9S$

Owing to poor solubility the lowest temperature that could be reached for this compound was —80°C and the slow exchange limit was not reached. At this temperature two signals were obtained (δ 207.7, δ 196.2) in the ratio 1/2. On raising the temperature both signals broadened, the highfield one more so than the other. Coalescence occurred at about —20°C and at 35°C a very broad reso-

TABLE 1

SLOW EXCHANGE SPECTRA

Compound	T (°C)	Chemical shifts [a,b,c]				
$H_2Ru_3(CO)_9S$	—108	197.7(2)	193.3(2) d, J 8 Hz	187.9(1)	186.1(2)	181.8(2) d, J 13 Hz
$H_2Os_3(CO)_9S$	—20	176.1(2)	169.5(2) d, J 6 Hz	166.5(1)	165.1(2)	156.1(2)
$FeCO_2(CO)_9S$ [d]	—80	207.7(1)	196.2(2)			
$H_3Ru_3(CO)_9CCH_3$	—60→90	190.5(2) d, J 12 Hz	189.7(1)			
$H_3Os_3(CO)_9CCH_3$	—50→100	167.6(2) d, J 8 Hz	166.7(1)			

[a] Chemical shifts relative to TMS. [b] Relative intensity of each resonance in parentheses. [c] $J(^{13}C—^1H)$ immediately below the relevant chemical shift. [d] Not a slow exchange spectrum, but limit of solubility.

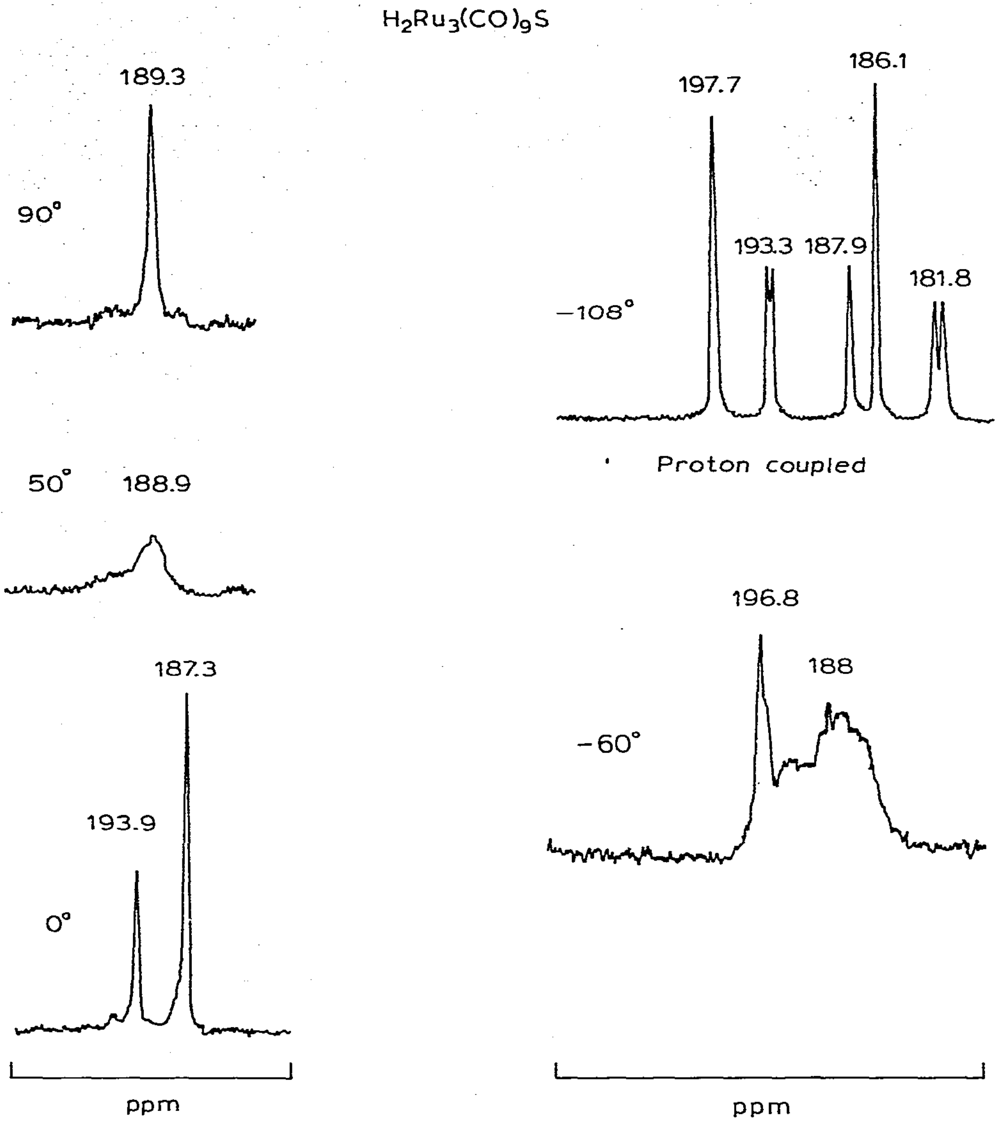

Fig. 2. The ^{13}C NMR spectra of $H_2Ru(CO)_9S$ in the CO region at various temperatures; shifts are relative to TMS.

nance (≈ δ 201) was obtained. There are two possible explanations for this behaviour: *(i)* local scrambling about individual atoms; *(ii)* coincident but independent exchange of axial and equatorial carbonyls.

(i) is favoured for several reasons. First, similar behaviour has been observed in an increasing number of other systems [2,3]. Second, it is difficult to envisage a mechanism which will alow axial exchange and equatorial exchange without leading to axial—equatorial exchange. Third, more rapid broadening of the resonance due to six carbonyls is an indication that they could be bonded to cobalt; quadrupole broadening by cobalt has been observed for a number of

other cobalt-containing compounds [1,5]. This phenomena also produces the broad line observed in the fast exchange limit; an exchange which must involve CO transfer between metal atoms.

$H_3M_3(CO)_9CCH_3$ ($M = Ru, Os$)

Previous work [6] has shown that the ruthenium compound has two resonances in the carbonyl region (consistent with the C_{3v} symmetry found for the solid state) at room temperature; these persist over the temperature range studied (—60→+90°C). Similarly, the carbonyls in the osmium analogue were non-fluxional over a similar temperature range (—50→+100°C) and were in the 2/1 intensity ratio expected for the C_{3v} symmetry predicted by other spectroscopic measurements [16] and by analogy with the ruthenium compound. The equatorial carbonyl resonances of both compounds exhibited doublets ($J \approx 10$ Hz) due to $^{13}C—^{1}H$ coupling. The simplicity of the coupling pattern implies that *cis* $^{1}H—^{13}C$ coupling was very small; similarly coupling to the axial carbonyls was not observed.

The expected trends for transition metal carbonyls in chemical shift (upfield shift on moving down a group) and energy barriers to fluxionality (increase down a group) are again confirmed by these studies. Furthermore, total carbonyl scrambling can apparently occur without involving transfer of carbonyls between metal atoms, while increasing the coordination number of the metal [e.g. $H_3M_3(CO)_9CCH_3$] appears to preclude carbonyl fluxionality by either process. Definitive proof of these premises must await the synthesis of a suitable compound containing a metal with nuclear spin.

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References

1 See e.g., B.F. Johnson, J. Lewis and T.W. Matheson, J. Chem. Soc., Chem. Commun., (1974) 441.
2 A. Forster, B.F.G. Johnson, J. Lewis, T.W. Matheson, B.H. Robinson and W.G. Jackson, J. Chem. Soc., Chem. Commun., (1974) 1042.
3 F.A. Cotton, D.L. Hunter and P. Lahuerta, Inorg. Chem., 14 (1975) 511.
4 J. Evans, B.F.G. Johnson, J. Lewis and T.W. Matheson, submitted for publication.
5 R.B. King, in S.J. Lippard (Ed.,) "Progress in Inorg. Chem.", Vol. 15, Wiley-Interscience, 1972, p. 361.
6 A.J. Canty, B.F.G. Johnson, J. Lewis and J.R. Norton, Chem. Commun., (1972) 1331.
7 A.J. Deeming and M. Underhill, J. Chem. Soc., Chem. Commun., (1973) 277.
8 See e.g. T.W. Matheson and B.H. Robinson, J. Organometal. Chem., 88 (1975) 367.
9 S.A. Khattab, L. Marko, G. Bor and B. Marko, J. Organometal. Chem., 1 (1964) 373.
10 A.J. Deeming, R. Ettorre, B.F.G. Johnson and J. Lewis, J. Chem. Soc. A, (1971) 1797.
11 A.J. Deeming and M. Underhill, J. Organometal. Chem., 42 (1972) C60.
12 G.M. Sheldrick and J.P. Yesinowski, J. Chem. Soc., Dalton Trans., in press.
13 D.L. Stevenson, C.H. Wei and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 6027.
14 R. Mason and V. Duckworth, personal communication.
15 J. Evans, B.F.G. Johnson, J. Lewis and T.W. Matheson, J. Amer. Chem. Soc., 97 (1975) 1275.
16 J.P. Yesinowski and D. Bailey, J. Organometal. Chem., 65 (1974) C27.