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Stereochemically Nonrigid Carbonyl Complexes of Group VIII B Metal Clusters

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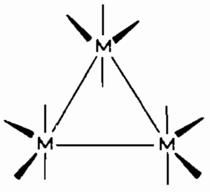
The variable temperature ^{13}C nmr of $M_3(CO)_{12}$ ($M = Fe$, Ru, Os) have been studied. $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ give one sharp resonance down to –100° C. $Os_3(CO)_{12}$ shows two resonances at room temperature which coalesce to a single resonance at +150° C. Possible mechanisms for carbonyl averaging are considered. The ^{13}C nmr of the acetylenic complexes $HM_3(CO)_9C_2C(CH_3)_3$ ($M = Ru$, Os) were examined and shown to be stereochemically nonrigid. Both the osmium and ruthenium compounds show axial equatorial exchange on the metal atom which is sigma bonded to one of the acetylenic carbons. Only the ruthenium compound shows exchange between metal atoms in the temperature range examined. The importance of bridging intermediates in this exchange process is discussed.

Introduction

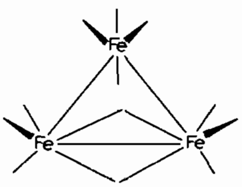
In the past few years new insight has been gained into the mechanisms of stereochemical nonrigidity in transition metal carbonyl complexes using ^{13}C-nmr. Investigations of the variable temperature ^{13}C nmr of complexes $Fe(CO)_4L$ (L = olefin[1,2] or phosphine[3]) and $(CO)_3FeL$[4,5] (L = diene or Bis-1,2-diphenyl phosphine ethane[6]) have shown that ligand (L) rotation and polytopic rearrangement of carbonyl groups can occur both independently or simultaneously in this class of compounds. In the case of dinuclear[7–10] and tetranuclear complexes[11–14] ^{1}H nmr and ^{13}C nmr have shown that exchange of carbonyl groups between metal atoms takes place by interchanging bridging with terminal carbonyl ligands or via bridged intermediates. However, besides accounts on $Fe_3(CO)_{12}$[15,16] there has been only one reported investigation of trinuclear carbonyl clusters[17]. We report here a new class of stereochemically nonrigid trinuclear carbonyl cluster complexes with acetylenic ligands which exhibit both polytopic rearrangement on a single metal atom and intramolecular exchange between metal atoms. We have also examined the variable temperature ^{13}C nmr of the parent trinuclear metal carbonyls $M_3(CO)_{12}$ ($M = Fe$, Ru, Os), two of them over a wider temperature range than has been previously reported[17].

Results and Discussion

The X-ray crystal structures of the trinuclear clusters $M_3(CO)_{12}$ have all been determined. The ruthenium and osmium compounds are isostructural, each metal atom having twelve terminal carbonyls in a slightly distorted octahedral environment (I)[18] (II)[19]. The iron compound (III) has two bridging carbonyls between two metals with three terminal carbonyls each while the third metal atom has four terminal carbonyls[20]. The ^{13}C nmr of (I) and (III) show one sharp resonance in the carbonyl region at 198.0 ppm and 210.1 ppm respectively down to –100° C[21]. Complete scrambling of all carbonyl groups could occur by simple axial equatorial exchange of carbonyls in the case of $Ru_3(CO)_{12}$ as has been shown for mononuclear complexes. In the case of iron this process requires prior opening of the carbonyl bridges. Alternatively scrambling could occur by exchange of carbonyl groups between metal atoms via bridged intermediates. The solid state structure of (III) might represent an intermediate in the exchange for $Ru_3(CO)_{12}$ and *vice versa*. In addition axial–equatorial interchange may precede formation of bridged intermediates since this mechanism requires severe distortion of the pseudo-octahedral environment on a metal atom with four terminal carbonyl ligands.



(I) (M-Ru) (II) (M-Os)



(III)

The variable temperature ^{13}C nmr of $Os_3(CO)_{12}$ (III) is very different from its iron and ruthenium analogs (see Figure 1). At +22° C two partially broadened resonances are observed at 183.9 ppm and 172.3 ppm (W 1/2 = 5Hz) in 1:1 integrated intensities. These resonances broaden, coalesce and sharpen to a single resonance at +156° C. The tendency to form

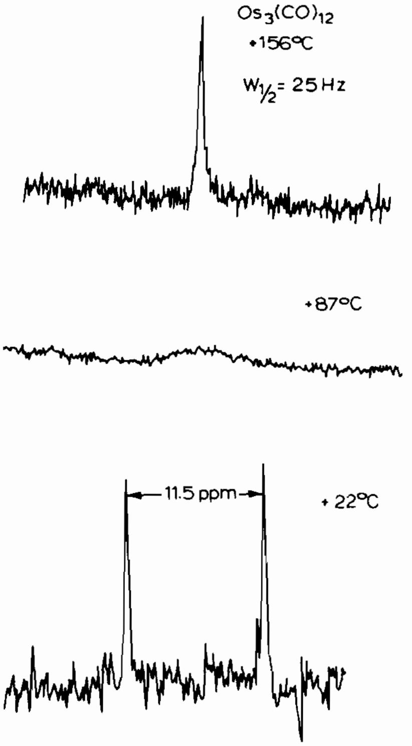
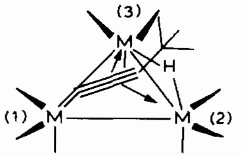


Figure 1. Variable temperature ^{13}C-nmr of $Os_3(CO)_{12}$ (II) in the carbonyl region in C_6D_6 and $C_6D_5CD_3$.

carbonyl bridges decreases as one goes down a given metal triad, due to increased metal–metal bond lengths and the smaller back donation (metal d – to CO π^*) requirements of second and third row transition metals[22]. Ruthenium and to a lesser degree, osmium do form carbonyl bridges in derivatives where strong donor ligands are substituted for carbon monoxide[22]. If we assume that the availability of bridged intermediates varies in the same way, the slower rate of averaging of axial and equatorial carbonyl groups in (II) could be due to the higher activation energies necessary to form these intermediates. However, it is possible that simple axial–equatorial exchange could also require higher activation energies in the osmium compound. There is no way to experimentally distinguish between these possibilities in the parent carbonyls.

We have investigated the variable temperature ^{13}C-nmr of two acetylenic complexes, $HM_3(CO)_9[C_2C(CH_3)_3]$ [M = Ru (IV), Os (V)][23].



(IV), (V)

Although it was not known at the start of our investigation whether (IV) and (V) would exhibit stereochemical nonrigidity, it is known that the barrier to axial–equatorial exchange increases with increasing electronegativity of the substituted ligand in mononuclear iron carbonyl complexes[1,2].

In compounds (IV) and (V) M(1) is σ-bound to an acetylenic carbon while M(2) and M(3) are π-bound, affording the opportunity to investigate the effect of two different bonding environments on carbonyl ligand exchange in the same complex. The low temperature limiting spectra of (IV)(–62° C) and (V)(–37° C) are shown in figures 2 and 3 respectively. Five resonances in integrated intensities of 1 : 2 : 2 : 2 : 2 are observed in each case [(IV) 196.5, 194.3, 190.1, 186.5, 185.6 ppm; (V) 183.3, 173.7, 171.8, 169.6, 162.8 ppm][24]. This pattern of resonances is consistent with the solid state structure of (IV) and confirms that (V) is isostructural with (IV)[25]. As the temperature is raised both (IV) and (V) show similar changes in their ^{13}C-nmr. The resonance assigned to the

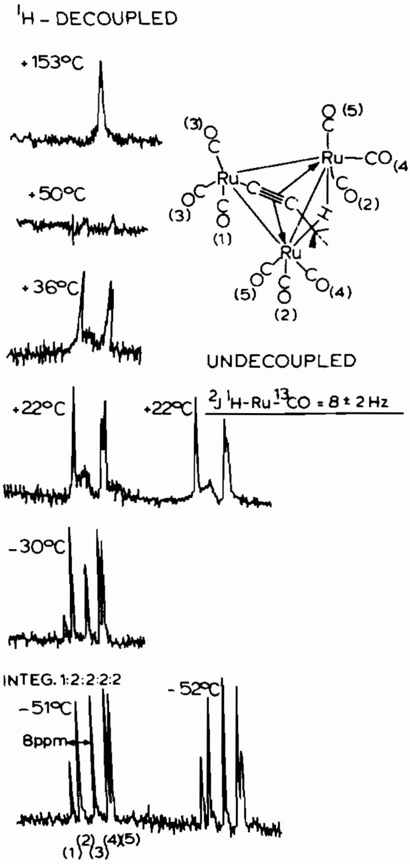


Figure 2. Variable temperature ^{13}C-nmr of $HRu_3(CO)_9[C_2C(CH_3)_3]$ (IV) in the carbonyl region in $CDCl_3$, C_6D_6 and $C_6D_5CD_3$.

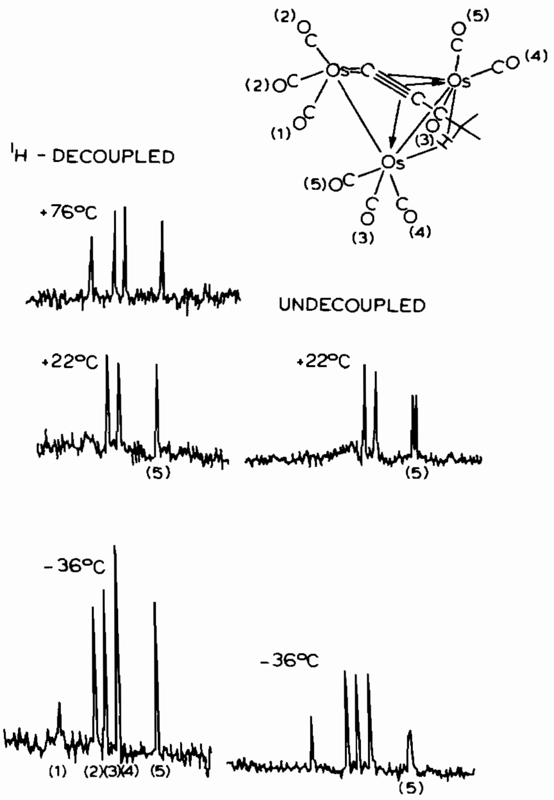


Figure 3. Variable temperature ^{13}C-nmr of HOs$_3$(CO)$_9$ [C$_2$C(CH$_3$)$_3$] (V) in the carbonyl region in CDCl$_3$, C$_6$D$_6$ and C$_6$D$_5$CD$_3$.

unique axial ligand (1) begins to average with resonance (3) at 190.1 ppm in (IV) and with resonance (2) at 173.7 ppm in (V). Above +22° C the spectra of (IV) and (V) differ markedly. In the ^{13}C-nmr of (V) resonances (1) and (2) average to a single resonance at 178.9 ppm (+76° C) of relative integrated intensity three. Resonances (3)–(5) in (V) remain unchanged until +173° C where slight broadening of all resonances is observed. In (IV), however, resonances (2), (4) and (5) begin to broaden at +35° C, before (1) and (3) average to a single sharp resonance. Broadening of all resonances continues followed by the appearance of a single average resonance at 189.9 ppm at +153° C. We interpret these results to mean that axial-equatorial exchange at M(1) in (IV) and (V) is taking place independently of exchange between metal atoms. The barrier to axial–equatorial exchange is lower at M(1) than at M(2) and M(3) since it is bound to a better charge donor (*i.e.* σ-bound to the acetylenic carbon). The static nature of the hydride ligand during this averaging process is indicated by the observation that the hydride is coupled only to resonance (5) ($^2J^1H$–M–^{13}CO = 4–6 Hz) in (IV) and (V) at low and intermediate temperature in both compounds. These results suggest that the acetylenic ligand is also static since its rotation on an axis perpendicular to the plane of the metal atom triangle would most probably be coupled with hydride exchange between metal atoms. We feel that the difference in the high temperature spectra of (IV) and (V) is best understood in terms of exchange of carbonyls between metal atoms via bridged intermediates. The bridged intermediates are of lower energy in (IV) than in (V) and leads to more facile exchange in the ruthenium complex.

We conclude from our results on (I)–(V) that ligand charge donor ability is of primary importance in determining the barrier to axial–equatorial exchange of carbonyl groups, as has been found for mononuclear complexes, and that this process can take place at a single metal in a cluster independently of exchange between metal atoms. Furthermore, it is likely that simultaneous axial–equatorial exchange at different metal atoms in a cluster is coupled to formation of bridged intermediates and subsequent exchange of carbonyls between different metal atoms. We are currenly extending these studies to other derivatives of (I)–(III) in the hope of shedding further light on the details of the exchange mechanisms in carbonyl metal clusters.

Experimental

Materials

Compounds I, II and III were prepared by known literature proceedures[26]. Compounds IV and V were prepared by the reaction of I and II with tertiary butylacetylene which is described in detail elsewhere[23]. Deuterated solvents were purchased from NMR Ltd. and were used directly after drying over molecular sieves. Samples of (I)–(V) were enriched 45–65% by stirring for five days at 40–90° C in the presence of < 1 atmosphere of 90% enriched ^{13}Co (Stohler Isotope Chemicals). Sample purity after enrichment was confirmed by mass spectroscopy. Solutions of (I)–(V) (0.05–0.2*M*) were sealed under vacuum in 10 mm tubes with the addition of 0.05*M* Cr(acac)$_3$ as an inert relaxation reagent and tetramethylsilane as an internal standard. ^{13}C-nmr spectra were recorded on a Jeol-PFT-100 operating at 25.1 MHz in the Fourier transformer mode. All chemical shifts are reported downfield positive with respect to internal TMS. Accumulations of 2000–10000 transients were performed at each temperature at a spectral width of 5.000 Hz. The temperature was monitored by a Jeol JNM-DBT-P-5-H100E temperature control unit with a thermocouple approximately 1 cm below the sample (outside of the RF and decoupling coils).

References

1 L. Kruczynzki, L.K.K. LiShing Man and J. Takats, *J. Am. Chem. Soc., 96,* 4006 (1974).

2 S.T. Wilson, N.J. Coville, J.R. Shapely and J.A. Osborn, *J. Am. Chem. Soc., 96,* 4038 (1974).

3 B.E. Mann, *Chem. Comm.,* 1173 (1971).

4 L. Kruczynski and J. Takats, *J. Am. Chem. Soc., 96,* 932 (1974).

5 C.G. Kreiter, S. Stuber and L. Wackerle, *J. Organometal. Chem., 66,* C49 (1974).

6 M. Akhtar, P.D. Ellis, A.G. MacDiarmid and J.D. Odom, *Inorg. Chem., 11,* 2917 (1972).

7 R.D. Adams and F.A. Cotton, *J. Am. Chem. Soc., 95,* 6589 (1973).

8 R.D. Adams, Michael Brice and F.A. Cotton, *J. Am. Chem. Soc., 95,* 6594 (1973)

9 R.M. Kirchner, T.J. Marks, J.S. Kristoff and J.A. Ibers, *J. Am. Chem. Soc., 95,* 6602 (1973).

10 D.C. Harris, E. Rosenberg and J.D. Roberts, *J. Chem. Soc. (Dalton),* 2398 (1974).

11 E. Rosenberg, L. Milone, S. Aime and E.W. Randall, *Chem. Comm.,* in the press.

12 B.F.G. Johnson, J. Lewis and T.W. Matheson, *J. Chem. Soc. Chem. Comm.,* 441 (1974).

13 J. Evans, B.F.G. Johnson, J. Lewis, J.B. Norton and F.A. Cotton, *J. Chem. Soc. Chem. Comm.,* 807 (1973).

14 P.E. Cattermole, K.G. Orrell and A.G. Osborne, *J. Chem. Soc. (Dalton),* 328 (1974).

15 O.A. Gansow, A.R. Burke and W.D. Vernon, *J. Am. Chem. Soc., 94,* 2550 (1972).

16 F.A. Cotton and D.L. Hunter, *Inorg. Chim. Acta, 11,* L9 (1974).

17 A. Forster, B.F.G. Johnson, J. Lewis, T.W. Matheson, B.H. Robinson and W.G. Jackson, *Chem. Comm.,* 1042 (1974).

18 R. Mason and A.I.B. Rae, *J. Chem. Soc. (A),* 778 (1968).

19 E.R. Corey and L.F. Dahl, *Inorg. Chem., 1,* 521 (1962).

20 a) C.H. Wei and L.F. Dahl, *J. Am. Chem. Soc., 91,* 1351 (1969). b) F.A. Cotton, J.M. Troup, *J. Am. Chem. Soc., 96,* 4155 (1974).

21 a) L.J. Todd and J.R. Wilkinson, *J. Organometal. Chem., 77,* 1 (1974). These authors have reported two resonances at 198 and 187 ppm for $Ru_3(CO)_{12}$. We have had the opportunity to examine this compound under a variety of conditions and in different solvents and find only one resonance at 198.0 ppm. The other resonance these authors report may be due to $H_4Ru_4(CO)_{12}$ (which we find to have a chemical shift of 187.7 ppm) or some other hydride. b) F.A. Cotton *et al.* have predicted[20] and verified[16] one sharp resonance for (III) down to −150° C.

22 P. Chini, *Inorg. Chim. Acta Rev., 2,* 31 (1968).

23 a) E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organometal. Chem., 39,* 169 (1972). b) O. Gambino and E. Sappa, *Atti Acc. Scienze Torino, 108,* 212 (1973–74).

24 We have measured the chemical shifts of the tertiary butyl ligand in (IV). The σ-bound acetylenic carbon $\delta C(1) = 164.2$ ppm; $\delta C(2) = 110.6$ ppm; $\delta C(CH_3)_3 = 34.6$, $\delta CH_3 = 32.5$. The ^{13}C-nmr of this ligand is invariant with temperature.

25 a) G. Gervasio and G. Ferraris, *Cryst. Struct. Comm., 3,* 447 (1973). b) The location of the hydride as shown here has been confirmed by neutron diffraction studies; G. Gervasio, M. Catti and S.A. Mason, unpublished results.

26 R.B. King, *"Progress in Inorganic Chemistry", 15,* 287 (1972).