Fluxional Behaviour of 1,1,2,2,2,2,3,3,3,3-Decacarbonyl-1-(η-cyclohexa-1,3-diene)-*triangulo*-triosmium

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Variable-temperature ^{13}C(carbonyl) and ^{1}H n.m.r. spectra of the title complex [$Os_3(C_6H_8)(CO)_{10}$] have been recorded. Four independent dynamic processes involving both organic-ligand and carbonyl-site exchange have been shown to occur and the limiting ^{13}CO n.m.r. spectrum leads to a determination of the molecular geometry of the complex.

ALTHOUGH the potential of ^{13}CO n.m.r. spectroscopy as a structural tool in metal-carbonyl cluster chemistry has become apparent,[1,2] relatively few examples of the applications of this technique to unsolved structural problems in organometallic cluster chemistry have appeared. The reaction of the *triangulo*-cluster [$Os_3(CO)_{10}H_2$] (1) with cyclohexa-1,3-diene yields the disubstituted triosmium carbonyl [$Os_3(C_6H_8)(CO)_{10}$],[3] the first reported reaction of (1) with a simple organic moiety found to occur without cleavage of a C–H bond followed by oxidative-addition of C–H to three metal atoms. Variable-temperature ^{13}CO and ^{1}H n.m.r. spectra of this complex have now been recorded; a number of dynamic processes have been shown to occur involving both organic-ligand and carbonyl-site exchange. The ^{13}CO limiting spectrum leads to an unambiguous determination of the molecular geometry of the complex.

RESULTS AND DISCUSSION

A low-temperature ^{13}CO limiting spectrum (−80 °C, proton decoupled) was obtained which displayed features corresponding to the static structure (Figure 1) in which the cyclohexadiene moiety occupies an axial and an equatorial co-ordination site on one osmium atom. Thus nine signals were observed of relative intensity 2 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 [Figure 2(*a*)] which, allowing for the accidental degeneracy of two single resonances, is compatible with the proposed structure. Other possible structures would have higher symmetry and require fewer than nine signals.

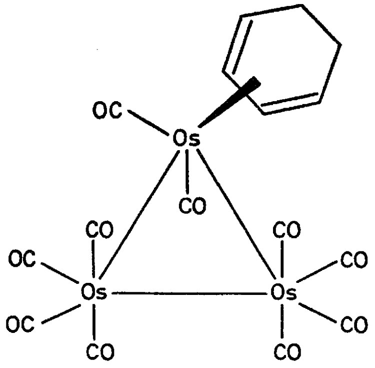

FIGURE 1 Probable structure of [$Os_3(C_6H_8)(CO)_{10}$]

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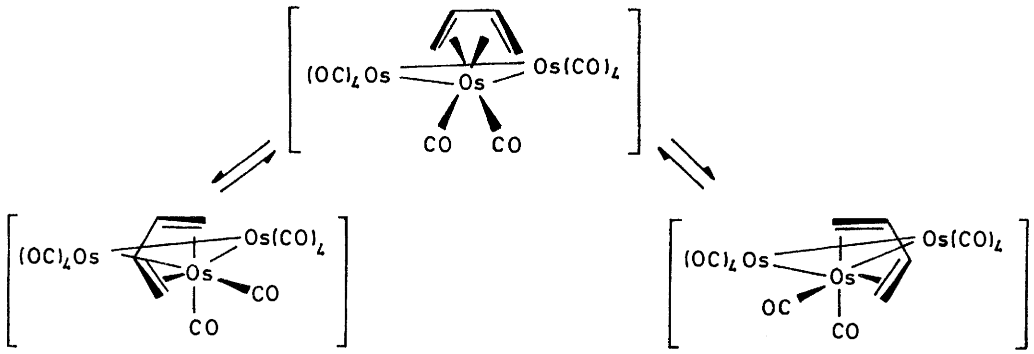
[1] F. A. Cotton and M. J. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4155.

[2] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1043.

[3] E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis, and M. McPartlin, *J.C.S. Chem. Comm.*, 1976, 254.



SCHEME 1 Proposed mechanism of exchange in the temperature range −80 to 40 °C

On increasing the temperature, adjacent peaks began to broaden, reaching coalescence at −60 °C. Further warming to −40 °C gave five signals of relative intensity 1 : 1 : 1 : 1 : 1 [Figure 2(*b*)]. This cannot be explained in terms of a carbonyl-exchange process but is consistent with a mechanism involving a rocking of the organic moiety above the plane of the osmium triangle about one axial and two equatorial co-ordination sites on one osmium atom (Scheme 1). This results in a mirror plane through the organic ligand and is supported by the ^1H n.m.r. data. Thus at a temperature corresponding to the activation energy calculated for the exchange process from the ^{13}CO n.m.r. data (10 kcal mol^{-1}) * the spectrum simplified from the low-temperature limit [Figure 3(*a*)] to one corresponding to the usual spectrum of co-ordinated cyclohexadiene [4] which has a plane of symmetry [Figure 3(*b*)].

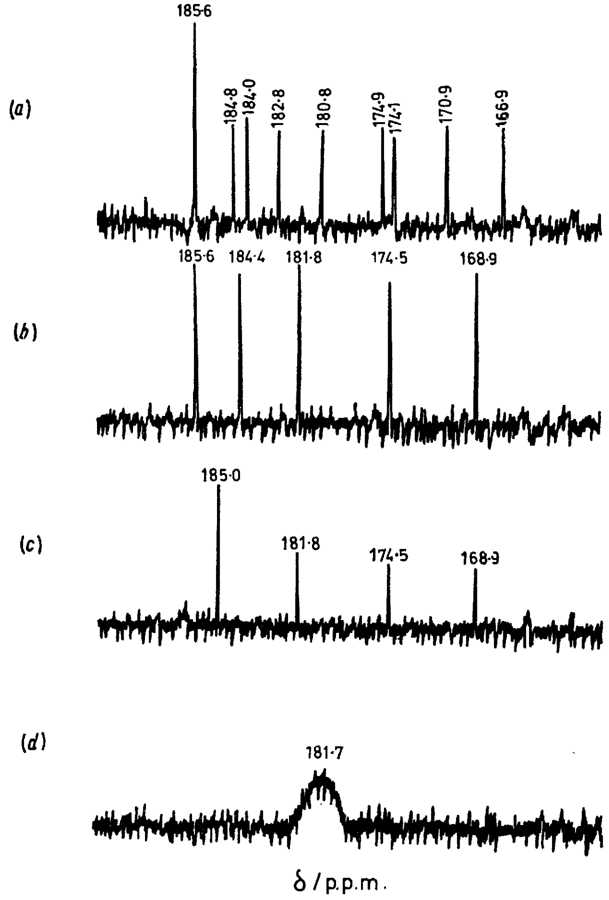


FIGURE 2 Variable-temperature ^{13}C n.m.r. spectra of [$Os_3(C_6H_8)(CO)_{10}$]: (a) −80 °C, (b) −40 °C, (c) 0 °C, and (d) 80 °C

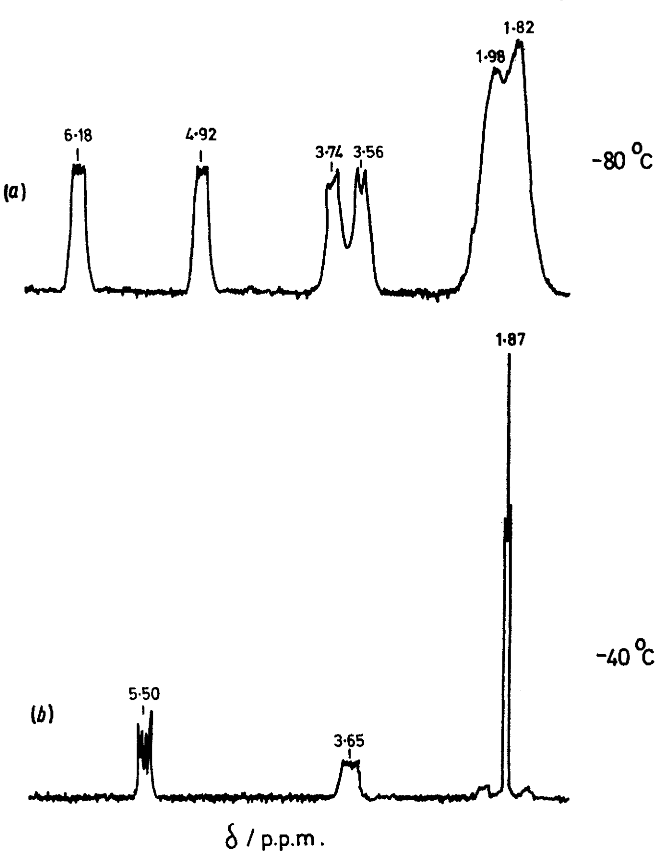


FIGURE 3 Variable-temperature ^1H n.m.r. spectra of [$Os_3(C_6H_8)(CO)_{10}$]

Increasing the temperature caused broadening of the two peaks at δ 185.6 and 184.4 p.p.m. reaching coalescence at −10 °C corresponding to an activation energy

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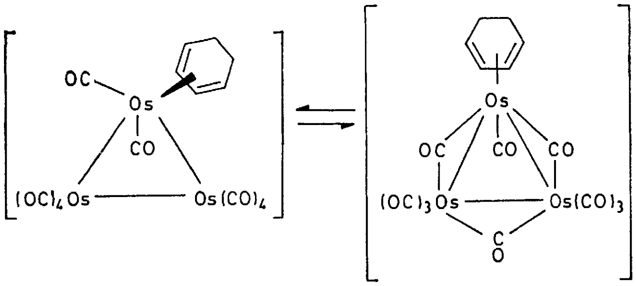
* Throughout this paper: 1 cal = 4.184 J.

[4] A. J. Birch, P. E. Cross, D. A. White, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

of 12 kcal mol^{-1}. At 0 °C the relative intensity of the signals in the spectrum was 2 : 1 : 1 : 1 [Figure 2(*c*)]. This is consistent with a mechanism involving scrambling of the co-ordinated ligand around one osmium atom and resulting in the generation of a second plane of symmetry perpendicular to that formed in the previous process.



SCHEME 2 Proposed mechanism of exchange in the temperature range 0—40 °C

Further warming caused broadening of the three peaks of equal intensity at δ 181.8, 174.5, and 168.9 p.p.m. reaching coalescence at 10 °C. This is best explained in terms of a mechanism involving carbonyl bridges formed by equatorial carbonyl groups exchanging around the metal triangle[2] (Scheme 2). The activation energy for this process cannot be calculated as just before the coalescence temperature was reached the remaining signal at δ 185.0 p.p.m. began to broaden and at 60 °C had completely coalesced. This indicates that complete scrambling of the carbonyls is occurring presumably *via* a simple twist mechanism about an individual metal atom coupled with carbonyl bridging.

Finally, the fast-exchange spectrum, consisting of just one signal, was not observed. Increasing the temperature to 80 °C resulted in the appearance of a broad resonance at δ 181.7 p.p.m. [Figure 2(*d*)]. However, the complex decomposed before a sharp singlet was obtained.

EXPERIMENTAL

The complex $[Os_3(C_6H_8)(CO)_{10}]$ was prepared by the published procedure.[3] Carbon-13 n.m.r. spectra were recorded on a Varian Associates XL 100 spectrometer operating in the Fourier-transform mode at 25.2 MHz. All the spectra were proton decoupled. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates CFT 20 spectrometer operating in the Fourier-transform mode at 80 MHz.

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