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EVIDENCE FOR A TRIGONAL TWIST MECHANISM INVOLVING A PHOSPHITE LIGAND OF $Os_3(CO)_7[P(OMe)_3]_5$

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Summary

The fluxional molecule $Os_3(CO)_7[P(OMe)_3]_5$ has been prepared from $Os_3(CO)_{12}$ and $P(OMe)_3$ by a combination of thermal and UV irradiation synthetic methods. An investigation by ^{31}P and ^{13}C NMR spectroscopy indicated that the mechanism of fluxionality in this compound probably involves the $P(OMe)_3$ ligand of the $Os(CO)_3[P(OMe)_3]$ unit moving from one equatorial site to the other via a trigonal twist mechanism.

Introduction

Stereochemical nonrigidity is a feature of metal carbonyl cluster compounds [1]. A variety of different mechanisms have been proposed for these nonrigid processes and the factors which favor a particular mechanism over another are, as yet, not clear. Also, the decision as to which mechanism is operative in a given case is usually critically dependent on the correct assignment of the carbonyl signals in the ^{13}C NMR spectrum and this is often a difficult task. Herein, we describe the fluxional molecule $Os_3(CO)_7[P(OMe)_3]_5$. The variable temperature ^{31}P and ^{13}C NMR spectra of this compound are readily interpreted and lead to the conclusion that a simple rearrangement of a phosphite ligand is involved in the nonrigid process. The study also shows that a phosphorus-donor ligand in a cluster can be nonrigid. It has been previously thought that such ligands were relatively non-mobile [2,3].

Experimental

The general procedure and instrumentation used in this study have been described previously [4]. Exceptions were that the infrared spectra were recorded on a Perkin–Elmer 983 instrument, and the $^{31}P\{^1H\}$ (at 161.96 MHz) and $^{13}C\{^1H\}$ (at 100.57 MHz) NMR spectra which were recorded on a Bruker WM400 spectrometer. The chromatography was performed on a Florisil column (11 × 3.5 cm) which had

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been deactivated by eluting with hexane/$P(OMe)_3$ (4/1 by volume) and then freed from excess $P(OMe)_3$ by washing with hexane.

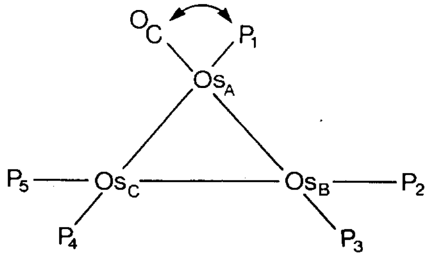
Preparation of $Os_3(CO)_7[P(OMe)_3]_5$

A Pyrex Carius tube with $Os_3(CO)_{12}$ (0.50 g, 0.55 mmol), $P(OMe)_3$ (4 ml, ≈ 34 mmol) and heptane (15 ml) was evacuated at −196°C and the solution degassed with three freeze-thaw cycles. The tube was heated at 140–145°C for 24 h. At this stage the solution contained $Os_3(CO)_8[P(OMe)_3]_4$, some $Os(CO)_3[P(OMe)_3]_2$, and other minor products. The tube was again evacuated at −196°C and the solution degassed with one freeze-thaw cycle. The tube was warmed so as to dissolve the precipitated solids and then subjected to ultraviolet irradiation (200 W source) for 8 h (the progress of the reaction was monitored by infrared spectroscopy). After the irradiation the orange solid, which had formed during the reaction, and the solution were transferred to a Schlenk flask. The solution was decanted and the solid washed with hexane (5 × 10 ml) and dried on the vacuum line. The crude product (0.36 g, 47%) contained some $Os_3(CO)_8[P(OMe)_3]_4$ (ν(CO) 2049vw, 1989m, 1969s, 1941msh, 1909wsh cm^{-1}; CH_2Cl_2 solution) and $Os_3(CO)_6[P(OMe)_3]_6$ (ν(CO) 2013vw, 1938sbr, 1881m cm^{-1}; CH_2Cl_2 solution). The crude product was dissolved in toluene (5 ml) and subjected to chromatography. Elution of the column with toluene/CH_2Cl_2 mixtures, or pure CH_2Cl_2, served to remove the tetrasubstituted cluster. Elution with CH_2Cl_2/$P(OMe)_3$ (6/1 by volume) gave the desired product (0.26 g, 34%). The compound may be recrystallized from toluene or toluene/hexane at −15°C as orange plates (m.p. 162.5–163°C). Found: C, 18.94; H, 3.28; P, 11.13; mol.wt. 1387.2 (most abundant peak of the parent ion in the mass spectrum); $C_{22}H_{45}O_{22}P_5Os_3$ calcd.: C, 19.05; H, 3.27; P, 11.17; mol.wt. 1388.0; (the observed and computer simulated patterns of the parent ion were also in excellent agreement); ν(CO) 2033w, 1952sbr, 1902w, 1889wsh cm^{-1} (CH_2Cl_2 solution). The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra of $Os_3(CO)_7[P(OMe)_3]_5$ are reported in the discussion.

Results and discussion

The pentasubstituted triosmium carbonyl cluster $Os_3(CO)_7[P(OMe)_3]_5$ has been synthesized from $Os_3(CO)_{12}$ and $P(OMe)_3$ by a combination of thermal and UV irradiation synthetic methods. It is an air-stable, orange crystalline solid. The compound represents the most highly phosphite-substituted derivative of $Os_3(CO)_{12}$ yet reported. (We have, however, synthesized and completely characterized $Os_3(CO)_6[P(OMe)_3]_6$ [5].)

Previous investigations have shown that phosphorus ligands invariably adopt equatorial positions in triruthenium and triosmium carbonyl clusters [3,6]. If this is



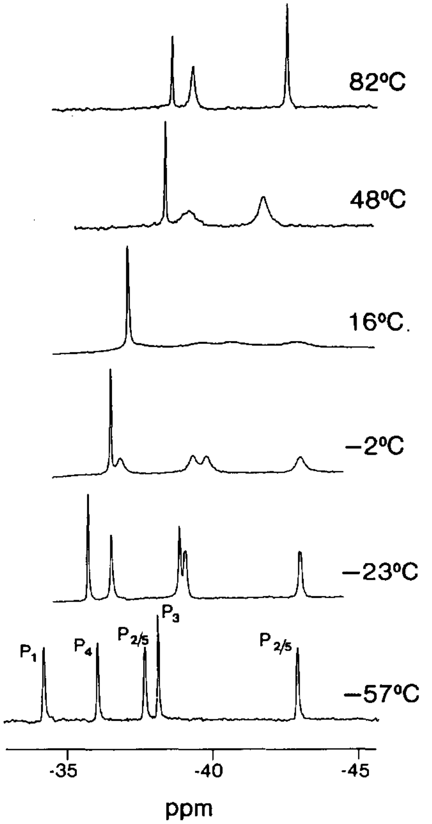


Fig. 1. Variable temperature $^{31}P\{^1H\}$ NMR spectra of $Os_3(CO)_7[P(OMe)_3]_5$ in toluene-d_8. Operating frequency is 161.96 MHz.

the case in $Os_3(CO)_7[P(OMe)_3]_5$ (**1**) then there is only one possibility for the structure of **1**, namely that shown (OMe and axial-CO groups omitted). The $^{31}P\{^1H\}$ NMR of 1 in toluene-d_8 at −57°C (Fig. 1) was consistent with this view: −34.2 (6.4), −36.0 (6.1), −37.6 (7.6), −38.0, −42.8 (7.3) ppm *. The figures in brackets are ^3J(P–P) in Hz; these couplings were consistently better resolved at 40.5 MHz operating frequency versus 162 MHz which suggested that broadening from chemical shift anisotropy [7] may occur at the higher field strength. On warming the solution of **1** two pairs of signals in the spectrum each collapsed to a singlet such that at above 80°C three singlets in the ratio of 1/2/2 were observed (Fig. 1). The process was entirely reversible. This behavior is, of course, indicative of fluxional character. The signal due to added $P(OMe)_3$ remained sharp during the collapse which showed the process did not involve phosphite dissociation.

It is reasonable to assume that the fluxional process does not involve an intermediate in which a phosphite ligand bridges two osmium atoms: to our knowledge there are no reports in the literature to suggest $P(OMe)_3$ can bridge two metal atoms even in a transitory intermediate. Given this information it is possible

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* The chemical shifts are quoted relative to internal $P(OMe)_3$, upfield negative. We find 1% $P(OMe)_3$ in toluene/toluene-d_8 (5/1) at 31°C occurs at 140.2 ppm relative to external 85% H_3PO_4.

to assign the singlet of intensity 1, in the high temperature spectrum, as due to P(1). Because of the *cis*-carbonyl ligand no exchange process can render it equivalent to any of the other phosphorus atoms. The ^{31}P NMR resonance of this atom exhibited phosphorus coupling at low temperature. This must, therefore, be *trans* three-bond coupling to P(4). (We have observed such three-bond couplings in other derivatives e.g., in one isomer of $Os_3(CO)_{10}[P(OMe)_3]_2$ [5].) From the size of the couplings it was thus possible to assign the peak due to P(4). The resonance which was a singlet in the low temperature spectrum was attributed to P(3) since there is no phosphorus atom in the *trans* three-bond position to this atom in **1**. It is not possible to distinguish between the remaining two resonances as arising from P(2) or P(5) but this is not essential to the argument concerning the mechanism of rearrangement. (Note, the coupling between these signals was equal, within experimental error, and different to the P(1)–P(4) coupling.) A detailed analysis of the ^{31}P NMR spectra, taking into account the marked temperature dependence of the chemical shifts of the peaks, revealed that the signal due to P(3) collapsed with that due to P(4) whereas the two signals assigned to P(2) and P(5) merged. This can be seen to be qualitatively the case from Fig. 1. Furthermore, the processes which brought about these equivalences had the same activation energy: P(3,4), $\Delta G^\star$ (6°C) 13.2 ± 0.3 kcal mol^{-1}; P(2/5) $\Delta G^\star$ (10°C) 13.4 ± 0.3 kcal mol^{-1} (data from spectra at 40.5 MHz operating frequency). That the activation barriers were the same suggests it was a single process which brought about the changes. The simplest rearrangement that

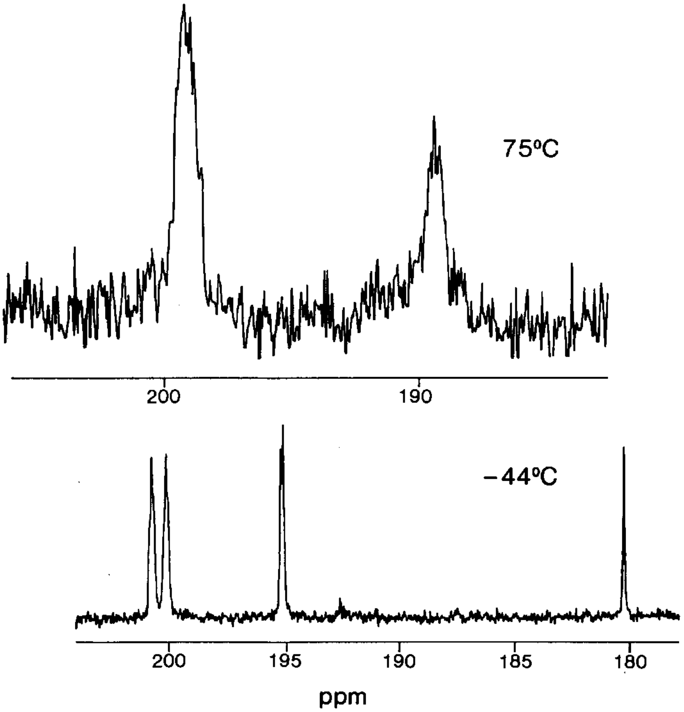
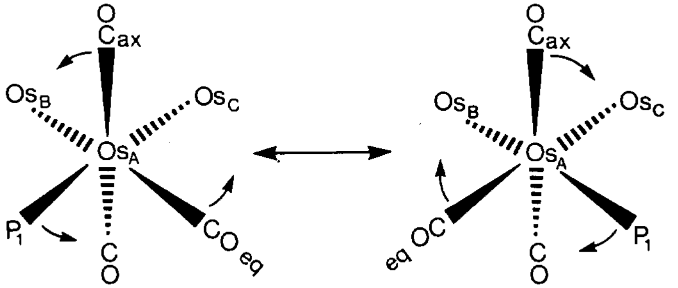


Fig. 2. Low and high temperature $^{13}C\{^1H\}$ NMR spectra of $Os_3(CO)_7[P(OMe)_3]_5$ in toluene-d_8. Operating frequencies: low temperature spectrum, 100.57 MHz; high temperature spectrum, 25.2 MHz.

accounts for the observations is movement of P(1) from one equatorial position to the other on osmium-A as is shown in the diagram for **1**.

The variable temperature $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO enriched sample of **1** (Fig. 2) was also consistent with this rearrangement. The low temperature spectrum (−44°C) gave two barely resolved triplets at 200.7 and 200.1 ppm, assigned to the axial carbonyls on osmium atoms B and C. There was also a doublet (195.1 ppm, *J*(P–C) 9.5 Hz) and a singlet (180.2 ppm) in the ratio of 2/1 assigned to the axial and equatorial CO ligands on Os(A), respectively. (Phosphorus coupling to axial but not equatorial carbonyls has been observed previously [3].) On warming the solution the triplets collapsed to a broad singlet as required from the proposed mechanism of rearrangement of **1**. However, the signals due to the carbonyls on Os(A) also merged to a singlet at the same rate as the other signals (allowing for the different chemical shift differences of the collapsing signals). This observation is consistent with a trigonal twist mechanism for the movement of P(1) from one equatorial position to the other since this simultaneously exchanges an axial and the equatorial carbonyl as shown.



Models show that if a bulky trimethylphosphite ligand occupies an axial position in a triangular Os_3 cluster there is a severe interaction of this ligand with the two axial carbonyls on the same side of the osmium plane. (This interaction has similarities to the well-known 1,3-diaxial interactions found in cyclohexane derivatives.) For this reason we believe the twist mechanism by which the exchange takes place in **1** is very specific in that the phosphite ligand never enters an axial site i.e., the fluxional process involves the simple movement of P(1) back and forth between the two equatorial sites by a twist mechanism, as shown. Although trigonal twist mechanisms have been implicated before in the nonrigidity of osmium clusters [8] we believe this study represents the case where the evidence for the process has been most clearly demonstrated.

Preliminary results for $Os_3(CO)_{12-x}[P(OMe)_3]_x$, with $x = 1$–4, have shown these molecules were also nonrigid in solution. Furthermore, the barriers to the rearrangement in each case did not appear to be dramatically different from that found for **1**. This suggests that similar rearrangements may take place in these less-substituted molecules. Other lower-energy processes may also occur. For example, the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of $Os_3(CO)_{11}[P(OMe)_3]$ in toluene-d_8 underwent changes at low temperature in a manner similar to that found for the PEt_3 analogue [3]. These changes were consistent with a fluxional process in which the phosphite remained rigid. A mechanism with bridging carbonyls has been proposed for this process in $Os_3(CO)_{11}(PEt_3)$ [3]. In both cases complete collapse of all signals occurred above room temperature which indicated nonrigidity of the phosphorus-donor ligand was taking place. (The synthesis and detailed analysis of the NMR spectra of the molecules $Os_3(CO)_{12-x}[P(OMe)_3]_x$ ($x = 1$–4, 6) will form the subject of a separate paper [5].)

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