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Journal of Organometallic Chemistry 584 (1999) 174–178

Journal of Organometallic Chemistry

Structural characterisation of the elusive isomer of $Os_3(CO)_{10}(PPh_3)_2$

Weng Kee Leong *, Yao Liu

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

Received 7 January 1999

Abstract

The X-ray crystal structure of the elusive isomer of $Os_3(CO)_{10}(PPh_3)_2$ in which the two phosphine ligands are *cis* and *trans* with respect to the phosphine-substituted Os–Os edge has been determined; the first direct confirmation for the existence of this isomer in $Os_3(CO)_{10}(PR_3)_2$ clusters. In contrast to the *trans*,*trans* isomer, the *cis*,*trans* isomer shows little twisting of the $Os(CO)_3(PPh_3)$ groupings with respect to the $Os(CO)_4$ unit. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Osmium; Phosphine; Clusters; Isomers

1. Introduction

Phosphine-substituted triosmium clusters are among the most studied derivatives of osmium carbonyl clusters. One interesting feature of these clusters is the almost-exclusive tendency for the phosphine ligands to occupy an equatorial site with respect to the triosmium plane [1]. In the particular case of the disubstituted derivatives, $Os_3(CO)_{10}(PR_3)_2$, there are in principle four different isomers possible which are depicted in Fig. 1.

Of these, some examples with structure **A** have been isolated, clusters with structure **D** have only been observed for diphosphine ligands, while clusters with structural types **B** and **C** frequently occur as mixtures in rapid equilibrium. Although many of the $Os_3(CO)_{10}(PR_3)_2$ clusters are known to contain structural types **B** and **C** in rapid equilibrium, all these clusters appear to crystallise out in the **B** form; this appears to be the case even when it has been demonstrated that the major isomer in solution is that with the structure **C** [2,3].

In the course of our investigations into the bromination reaction of $Os_3(CO)_{10}(PR_3)_2$ clusters [4], we have found that the cluster $Os_3(CO)_{10}(PPh_3)_2$ (**1**) can be crystallised out in both the **B** and **C** forms; the former gave red crystals (**1b**) while the latter yielded yellow crystals (**1c**) by rapid cooling of a concentrated solution in a CH_2Cl_2/hexane mixture.[1] Recrystallisation of **1c** invariably gives crystals of **1b**, indicating the more favourable thermodynamics for crystallisation of the latter.

The solid-state IR spectra in the carbonyl region of these two isomers show subtle differences (Fig. 2), but just as has been observed for $Os_3(CO)_{10}(PMe_2Ph)_2$ and $Os_3(CO)_{10}[P(OMe)_3]_2$, there is a rapid equilibrium between these two isomers in solution; at −80°C, the $^{31}P\{^1H\}$-NMR spectra of either crystalline form in CD_2Cl_2 showed two equally intense signals at −2.50 and −5.64 ppm, attributable to **1c**, and a lower intensity signal at −1.91 ppm attributed to **1b**. The major isomer in solution is thus **1c**, in an approximately 3.4:1 ratio with respect to **1b**, from integration of the ^{31}P-NMR signals. These signals coalesce completely at about 30°C; the isomerization mechanism in these systems has been fairly well studied, and involves restricted turnstile rotation at one of the phosphine-bearing osmiums [2,3].

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* Corresponding author. Fax: +65-7791691.
E-mail address: chmlwk@nus.edu.sg (W. Kee Leong)

[1] The crystal structure of **1b** has been reported earlier by Bruce et al. [1b]. We have chosen to make comparisons with our own study; such a comparison would be less likely to suffer from diffractometer-dependent systematic errors. As one of the two crystallographically distinct molecules was found to be disordered (ca. 3% for Os(5) and Os(6)), comparisons have been made with the ordered molecule only.

PII: S0022-328X(99)00133-3

The molecular structures of both **1b** and **1c** are shown in Fig. 3, and selected bond parameters are collected in Table 1. The X-ray crystal structure of **1c** reported here represents the first direct confirmation for structural type **C**. In **1c**, the Os(1)–Os(2) and Os(2)–Os(3) bond lengths are much longer (0.0194 and 0.0170 Å, respectively) than the Os(1)–Os(3) bond, consistent with the observation that a PR_3 ligand tends to lengthen the cis Os–Os bond [5,6]; the longer Os(1)–Os(2) bond may be the consequence of a combination of steric repulsions between CO(22) with P(1) and P(2), which is also reflected in the Os(1)–P(1) bond being longer than the Os(2)–P(2) bond by a 10σ difference (σ = e.s.d.), as compared with a 5σ difference for the two Os–P bond lengths in **1b**. It is also noteworthy that the Os(1)–Os(2) bond length in **1c** is the longest at 2.9204(3) Å; this is consistent with our earlier suggestion that in the bromination reaction of $Os_3(CO)_{10}(PPh_3)_2$, the isomer **1c** is the one that undergoes bromination and it involves cleavage of this bond [4]. The most significant structural difference between **1b** and **1c**, however, is the greater degree of twisting of the $Os(CO)_3(PPh_3)$ units with respect to the $Os(CO)_4$ unit in the former (Table 1).

In a recent exhaustive study on $Os_3(CO)_{11}(PR_3)$ clusters, Pomeroy et al. have found that the nature of the PR_3 ligand can have profound structural implications [6]. Essentially, their argument was that a better donor PR_3 ligand increases electron density at the Os atom of the $Os(CO)_3(PR_3)$ unit, leading to expansion of its filled 5d orbitals. This in turn causes an increase in repulsive interaction with filled 5d orbitals on the other Os atoms and hence a reduction in the bonding contribution of the edge-bridging MOs. Steric effects from the PR_3 ligand will then lead to lengthening of the *cis* Os–Os bond as well as a propensity towards greater twisting of the $Os(CO)_3(PR_3)$ group, i.e. the adoption of what Pomeroy et al. termed the *S* conformation, in order to alleviate the 5d orbitals repulsive interaction.

From the electronic viewpoint, **1b** and **1c** should have the same degree of expansion of the 5d orbitals at both the $Os(CO)_3(PPh_3)$ units. As measured by the C_{ax}–Os–Os–C_{ax} torsion angles (Table 1), there is much less twisting or distortion towards the *S* conformation in **1c**. This observation may be rationalised if we consider the steric interactions involving the PPh_3 ligands (Fig. 4). In **1b**, the steric effects of both PPh_3 ligands impinge on Os(3), while in **1c** this is not the case. It may thus be expected that **1b** will have a greater tendency to distort towards the *S* conformation in order to relieve the strain, while the steric effects are 'relayed' round the equatorial plane in **1c**; the latter is evident in the bond angles about the equatorial plane for Os(3), which show that the equatorial carbonyls (CO(32) and CO(34)) are bent away from Os(2) and towards Os(1).

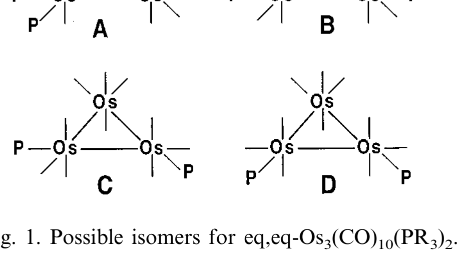

Fig. 1. Possible isomers for eq,eq-$Os_3(CO)_{10}(PR_3)_2$.

If our discussions above were correct, then it would appear that the relative orientation of ligands on clusters can have very significant effects on both the gross ligand sphere structure of the cluster as well as its chemistry. For instance, we may expect that an $Os_3(CO)_{10}(PR_3)_2$ cluster which exists in solution solely as the B form will undergo halogenation less favourably; this is currently under investigation.

2. Experimental

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Infrared spectra were recorded as KBr disks. ^{31}P-NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer and referenced to 85% aqueous H_3PO_4. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore.

Cluster **1** was prepared from the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with two equivalents of PPh_3. Crystallisation from hexane/dichloromethane solution gave a mixture of red crystals (**1b**) (Found: C, 39.86; H, 2.12. Calc. for $C_{46}H_{30}O_{10}Os_3P_2$: C, 40.17; H, 2.18) and yellow crystals (**1c**) (Found: C, 39.99; H, 2.14).

2.1. Crystal data for 1b

$C_{46}H_{30}O_{10}Os_3P_2$, M = 1375.24, monoclinic, space group $P2_1/n$, $a = 14.8216(2)$, $b = 34.4785(2)$, $c = 17.1059(3)$ Å, $\beta = 92.373(1)°$; $U = 8734.1(2)$ Å^3; $Z = 8$; $\rho_c = 2.092$ Mg m^{-3}; μ(Mo–K$_\alpha$) = 8.838 mm^{-1}, $T = 295$ K, 56 987 reflections collected, 21 737 unique reflections, final $R = 11.13\%$, $wR = 8.44\%$ for all data, 1106 parameters and three restraints.

2.2. Crystal data for 1c

$C_{46}H_{30}O_{10}Os_3P_2$, M = 1375.24, triclinic, space group $P\bar{1}$, $a = 12.5013(5)$, $b = 13.0248(5)$, $c = 14.2326(5)$ Å, $\alpha = 71.784(1)$, $\beta = 79.384(1)$, $\gamma = 89.220(1)°$; $U = 2161.23(14)$ Å^3; $Z = 2$; $\rho_c = 2.113$ Mg m^{-3}; μ(Mo–K$_\alpha$) = 8.929 mm^{-1}, $T = 295$ K, 18 290 reflections collected, 10 275 unique reflections, final $R = 4.11\%$, $wR = 7.58\%$ for all data and 550 parameters.

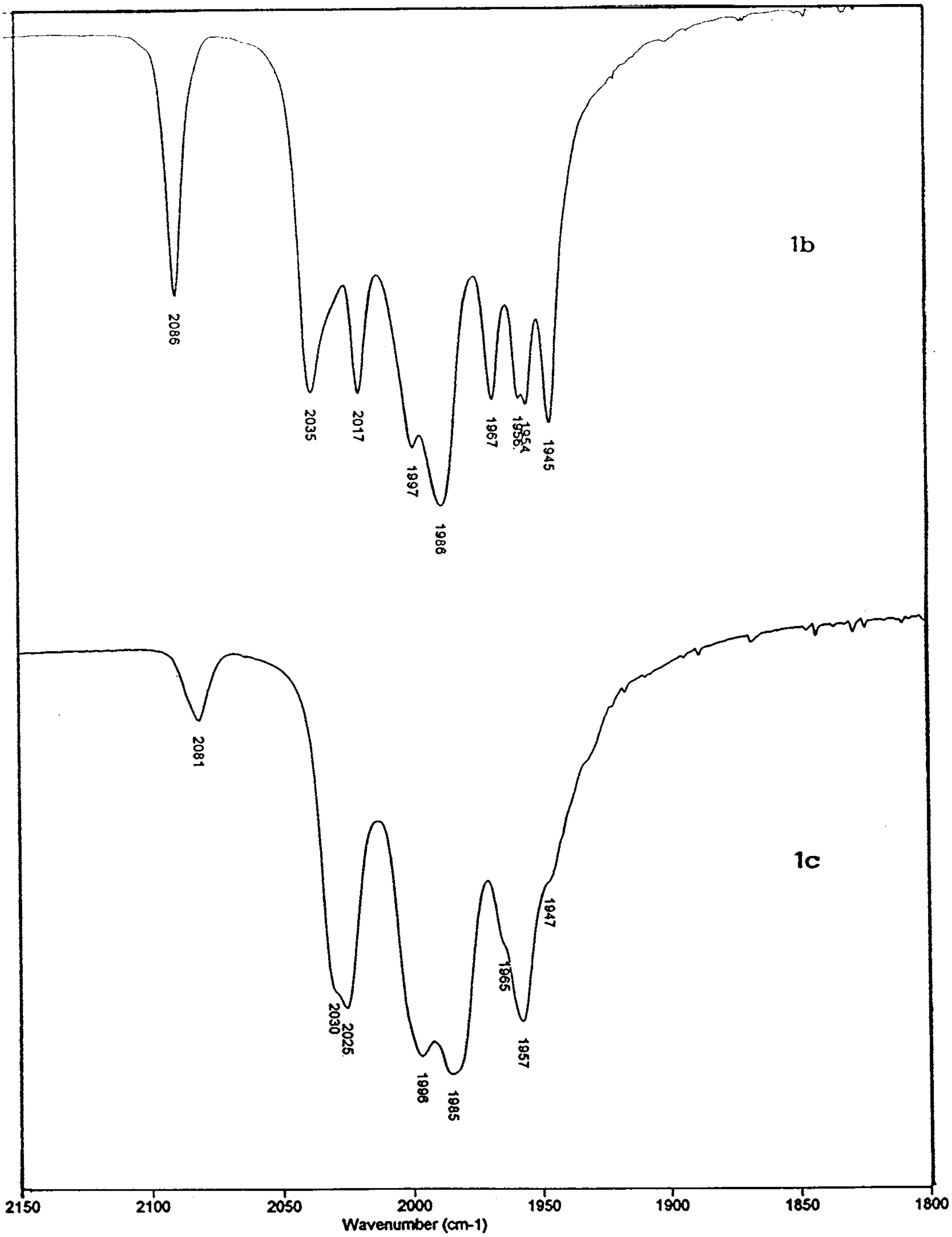

Fig. 2. Solid-state IR spectra (KBr disks, carbonyl region) for **1b** and **1c**.

2.3. Summary of structural determination

The crystals were sealed in glass capillaries. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo–K_{α} radiation at ambient temperature (298 K). Ten second exposures were used.

Data was corrected for Lorentz and polarisation effects with the SMART suite of programs [7], and for absorption effects with SADABS [8]. The final unit cell parameters were obtained by least squares on 8192 (**1b**) or 6272 (**1c**) strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs [9].

The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The terminal metal hydride was located by a low angle difference map and refined;

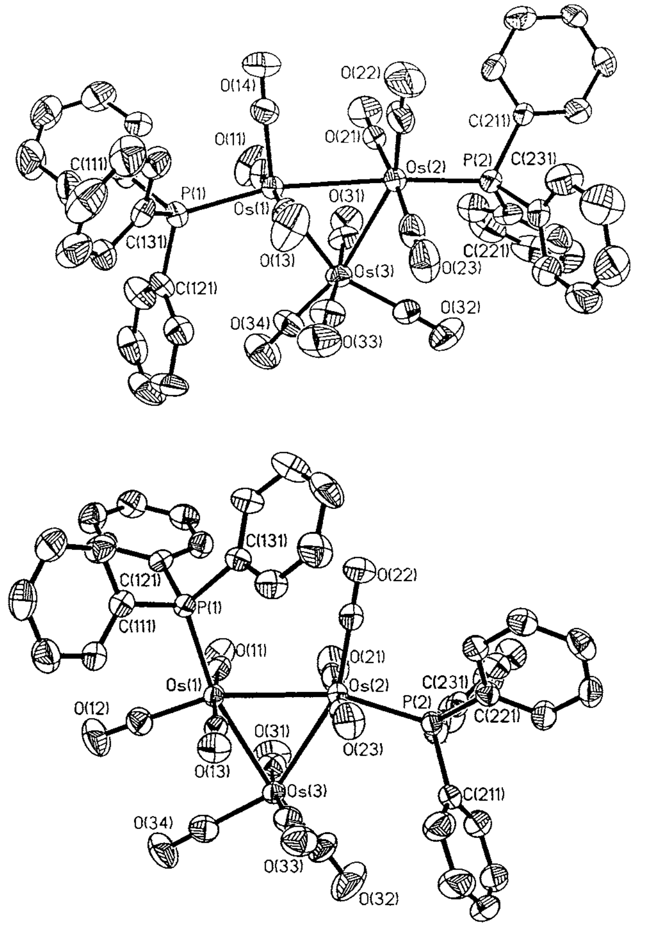

Fig. 3. ORTEP diagrams of **1b** and **1c** (50% probability thermal ellipsoids).

the phenyl hydrogens were placed in calculated positions. The final refinement was with an all non hydrogen atoms anisotropic model.

There were two independent molecules in the asymmetric unit for **1b**, one of which showed fairly large residuals near two Os atoms (Os(5) and Os(6)) which were modelled as disorder of the Os_3 triangle. The minor component of the disordered Os atoms were given the same anisotropic thermal parameters as those of the corresponding major components; the corresponding Os–Os bond distances were restrained to be the same, and the occupancies of major and minor components summed to unity.

Table 1
Selected bond lengths (Å) and torsion angles (°) for **1b** and **1c**

Bond parameter	1b	1c
Os(1)–Os(2)	2.9065(4)	2.9204(3)
Os(1)–Os(3)	2.9095(4)	2.9010(3)
Os(2)–Os(3)	2.8988(5)	2.9180(3)
Os(1)–P(1)	2.351(2)	2.3607(12)
Os(2)–P(2)	2.361(2)	2.3478(13)
C(11)–Os(1)–Os(2)–C(21)	24.8(4)	8.1 (3)
C(13)–Os(1)–Os(2)–C(23)	19.9(4)	10.5(2)
C(11)–Os(1)–Os(3)–C(31)	21.5(4)	4.7(3)
C(13)–Os(1)–Os(3)–C(33)	19.3(4)	8.7(3)
C(21)–Os(2)–Os(3)–C(31)	18.7(4)	3.1(3)
C(23)–Os(2)–Os(3)–C(33)	22.1(4)	10.0(3)

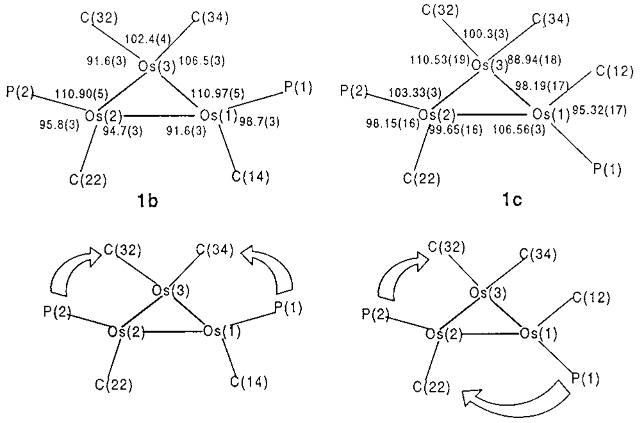

Fig. 4. Schematic view down the Os_3 planes showing selected bond angles (°) and steric interactions of the PPh_3 ligands, in **1b** and **1c**.

3. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 114318 and 114319. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: + 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National University of Singapore (Research Grant No. RP 960677) and one of us (Y.L.) thanks the University for a Research Scholarship.

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