

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Spectroscopic and X-Ray Crystallographic Studies of Pentameric Ethyl Cyclopolyphosphine Derivatives of Triosmium Carbonyl Clusters

How-Ghee Ang; Siau-Gek Ang; Qi Zhang

To cite this Article Ang, How-Ghee , Ang, Siau-Gek and Zhang, Qi(1996) 'Spectroscopic and X-Ray Crystallographic Studies of Pentameric Ethyl Cyclopolyphosphine Derivatives of Triosmium Carbonyl Clusters', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 109: 1, 145 – 148

To link to this Article: DOI: 10.1080/10426509608545111

URL: <http://dx.doi.org/10.1080/10426509608545111>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPIC AND X-RAY CRYSTALLOGRAPHIC STUDIES OF PENTAMERIC ETHYL CYCLOPOLYPHOSPHINE DERIVATIVES OF TRIOSMIUM CARBONYL CLUSTERS

HOW-GHEE ANG, SIAU-GEK ANG AND QI ZHANG

Department of Chemistry, National University of Singapore, Lower Kent
Ridge Road, Singapore 0511, Republic of Singapore

Abstract Reaction of pentaethylcyclophosphine, (EtP)₅, with triosmium cluster [Os₃(CO)₁₀(NCMe)₂] in dichloromethane at room temperature afforded [Os₃(CO)₁₀{1,2-(EtP)₅}] (1) with an unusual 1,2-chelation mode for the cyclophosphine. The same reactants at a higher temperature gave rise to [Os₃(CO)₁₀{1,3-(EtP)₅}] (2). Treatment of the same ligand with triosmium cluster [Os₃(CO)₁₁(NCMe)] yielded several new clusters [Os₃(CO)₁₁(EtP)₅] (3), [{Os₃(CO)₁₁}]₂{1,3-(EtP)₅} (4), [{Os₃(CO)₁₁}]₂{1,2-(EtP)₅} (5), [Os₃(CO)₁₀{1,2,3-(EtP)₅}Os₃(CO)₁₁] (6) and [Os₃(CO)₁₀{1,2,4-(EtP)₅}Os₃(CO)₁₁] (7).

Key words: cyclophosphine, cluster, osmium, phosphorus

INTRODUCTION

Studies on the reactions of homocyclic phosphines with a variety of metal carbonyls have shown that cyclophosphines can function as monodentate, bidentate, and tridentate ligands, respectively.¹ However, little attention has been paid recently to coordination chemistry with transition metal carbonyl clusters where cyclophosphines ligate intact or where phosphorus ring fission occurs to afford phosphido groups to stabilize formed clusters. We found that the reactions of the pentameric phosphine (PhP)₅ and the tetrameric phosphine (CF₃P)₄ with ruthenium or osmium carbonyl clusters gave rise to not only phosphido groups but also rare diphosphene fragments to build up several interesting cluster structures.^{2,3} On the other hand, we found that the reactions of (PhP)₅ with the activated triosmium or

triruthenium carbonyl clusters give several cluster derivatives where the phosphorus ring structure remains intact.⁴ Furthermore, the solution NMR data of these derivatives yielded a lot of useful information on the cyclophosphine structure in solution. As an in-depth extension of this investigation, we report here reactions of pentaethylcyclophosphine, (EtP)₅, with the activated triosmium carbonyl clusters [Os₃(CO)₁₀(NCMe)₂] and [Os₃(CO)₁₁(NCMe)].

RESULTS AND DISCUSSION

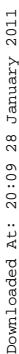
I Synthesis and Characterisation of 1 and 2 Reaction of (EtP)₅ with an equivalent amount of the activated triosmium cluster [Os₃(CO)₁₀(NCMe)₂] in dichloromethane at room temperature afforded a 1,2-substituted product **1** (yield 17%). The reaction carried out at 80°C yielded the 1,3-substituted product **2** (yield 7%). The ³¹P NMR spectrum of **1** shows an AA'BXX' pattern with two multiplets at δ 8.33 and 71.64 in the ratio of 3 : 2, respectively. The elemental analysis data was found to be consistent with the calculated values. The molecular structure of **1** was determined by a single-crystal X-ray diffraction study and is shown together with the atomic labelling scheme in Fig 1. The cyclophosphine, (EtP)₅, acts as a bidentate ligand, taking up equatorial sites of the osmium triangular plane and chelating across an Os-Os edge, through two P atoms in the 1,2-positions of the phosphorus ring. This is the first example in cyclophosphine chemistry where chelation occurs via the 1,2-positions in the cyclophosphorus ring. **1** possesses approximate m symmetry with the symmetry plane passing through Os(3), the mid-points of the Os(1)-Os(2) and P(1)-P(2) bonds, and P(4). It is also noteworthy that the P atoms bonded to Os atoms, P₁ and P₂, are in an almost fully eclipsed conformation. The ³¹P NMR spectrum of **2** shows a perfect first-order pattern. The COSY-45 ³¹P NMR spectrum of **2** (Fig. 2) shows that ¹J cross-peaks are seen at AD, AE, BC, BE and CD, while ²J cross-peaks are observed at AB, AC, BD and ED. The molecular structure of **2** was determined by a single-crystal X-ray diffraction study and is shown together with the atomic labelling scheme in Fig 3. In this case, (EtP)₅ acts as a bidentate ligand, chelating via two equatorial sites of the osmium triangular plane through two P atoms in the 1,3-positions of the phosphorus ring. However, unlike the phenylcyclophosphine system, the expected inversion isomer of **2**, was not found in this case.

II Synthesis and Characterisation of 3 - 7 The reaction of (EtP)₅ with a two-fold molar amount of the activated triosmium cluster [Os₃(CO)₁₁(NCMe)] in

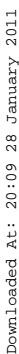
dichloromethane at room temperature overnight afforded $[\text{Os}_3(\text{CO})_{11}(\text{EtP})_5]$ **3** (yield 35%), $[\{\text{Os}_3(\text{CO})_{11}\}_2\{1,3-(\text{EtP})_5\}]$ **4** (yield 35%), $[\{\text{Os}_3(\text{CO})_{11}\}_2\{1,2-(\text{EtP})_5\}]$ **5** (yield 19%), and a mixture (yield 2%) of $[\text{Os}_3(\text{CO})_{10}\{1,2,3-(\text{EtP})_5\}\text{Os}_3(\text{CO})_{11}]$ **6** and $[\text{Os}_3(\text{CO})_{10}\{1,2,4-(\text{EtP})_5\}\text{Os}_3(\text{CO})_{11}]$ **7**. The elemental analysis data of **3**, **4** and **5** were found to be consistent with calculated values. The IR data in the carbonyl region of **3** is similar to that of $[\text{Os}_3(\text{CO})_{11}(\text{PhP})_5]$. In the carbonyl region, the IR data of **4** is similar to that of $[\{\text{Os}_3(\text{CO})_{11}\}_2\{1,3-(\text{PhP})_5\}]$. The IR data in the carbonyl region of **5** is quite similar to that of **4**. The correlation of P atoms in **3**, **4** and **5** has been established by two-dimensional COSY-45 ^{31}P NMR spectroscopy. Although the one dimensional ^{31}P NMR spectrum of **5** looks very similar to that of **4**, obvious differences between the two clusters were detected in their two-dimensional COSY-45 NMR spectra. The molecular structure of **4** has been established by X-ray crystallography and is shown in Fig. 4 together with the atomic labelling scheme. The cyclopolyphosphine links through phosphorus atoms in the 1,3-positions to equatorial sites in the two triosmium triangles. The average length (2.215 Å) of P-P bonds in **4** is quite similar to that of free cyclopolyphosphines, but shorter than that (2.241 Å) in $[\{\text{Os}_3(\text{CO})_{11}\}_2\{1,3-(\text{PhP})_5\}]$. The isomers, **6** and **7**, cannot be separated by TLC. Their ^{31}P NMR spectrum shows eight sets of signals containing ten phosphorus atoms in total. However, the ^{31}P NMR (COSY-45) spectrum shows that there are two five-membered rings, unconnected to each other. The electrospray ionization (ESI) mass spectrum of the mixture shows the molecular ion at m/z 2030 agreeing with $[\text{Os}_3(\text{CO})_{10}\{1,2,3-(\text{EtP})_5\}\text{Os}_3(\text{CO})_{11}]$ **6** or $[\text{Os}_3(\text{CO})_{10}\{1,2,4-(\text{EtP})_5\}\text{Os}_3(\text{CO})_{11}]$ **7**.

REFERENCE

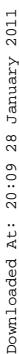
- 1 H. G. Ang, and B. O. West, *Aust. J. Chem.*, 1967, 20, 1133.
- 2 H. G. Ang, K. W. Ang, S. G. Ang and [W. L. Kwik], presented at the Symposium on the Fluorine Chemistry, Yokohoma, Japan, 1994.
- 3 H. G. Ang, L. L. Koh and Q. Zhang, *J. Chem. Soc. Dalton. Trans.*, accepted.
- 4 H. G. Ang, S. G. Ang, W. L. Kwik and Q. Zhang, *J. Organomet. Chem.*, 1994, 485, C6.



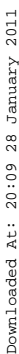
Downloaded At: 20:09 28 January 2011



Downloaded At: 20:09 28 January 2011



Downloaded At: 20:09 28 January 2011



Downloaded At: 20:09 28 January 2011