A Cluster Compound with an Unsupported, Dative Metal–Metal Bond: Structure and Unusual Nonrigidity of $(Me_3P)(OC)_4OsOs_3(CO)_{11}$

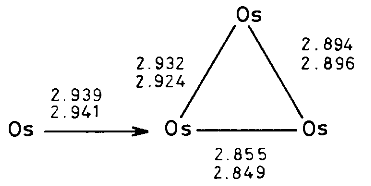
Frederick W. B. Einstein,* Lillian R. Martin, Roland K. Pomeroy,* and Paul Rushman

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

The cluster compound $(Me_3P)(OC)_4OsOs_3(CO)_{11}$, which contains an unbridged Os–Os donor-acceptor bond, exhibits stereochemical nonrigidity in solution that involves all the carbonyl ligands.

Recent work in this laboratory has established that unbridged donor–acceptor metal–metal bonds are stable structural entities.[1—3] Herein we describe the synthesis and structure of $(Me_3P)(OC)_4OsOs_3(CO)_{11}$, the first cluster compound with such a bond. Furthermore, the complex exhibits interesting stereochemical nonrigidity in solution that involves all the carbonyl ligands in the molecule.

Reaction of $Os_3(CO)_{11}(MeCN)$[4] with $Os(CO)_4(PMe_3)$[5] in hexane at 60 °C afforded $(Me_3P)(OC)_4OsOs_3(CO)_{11}$ (**1**) in excellent yield after 2 h. (The product precipitated from solution which prevented decomposition, see below.) The i.r. spectrum of (**1**) in CH_2Cl_2 exhibited only terminal carbonyl stretches: 2115vw, 2086m, 2068.5vw, 2047.5s, 2032.5s, 2005m(asym.), 1974w, 1960w, and 1914w(br.) cm^{-1}. The crystal structure of (**1**) was determined by *X*-ray crystallography† and the molecular structure for one of two independent molecules is shown in Figure 1. It reveals that the 18-electron complex $Os(CO)_4(PMe_3)$ acts as a ligand to the $Os_3(CO)_{11}$ fragment *via* an unbridged, osmium–osmium dative bond. Although dative metal–metal bonds have been proposed before in metal cluster compounds they have always been supported by other metal–metal bonds in the metal framework.[6] The Os–Os bond lengths (Å) within each of the two independent molecules of (**1**) are shown in structure (A). (The standard deviation in each length was 0.001 Å.) The donor–acceptor bond in each molecule is long compared to most Os–Os bonds which are usually within 0.03 Å of the Os–Os distance of 2.877 Å in the parent $Os_3(CO)_{12}$.[7] The shortening of the Os–Os bond *trans* to the dative metal–metal bond may be taken to indicate that $Os(CO)_4(PMe_3)$ is a weak donor ligand.[8]



(A)

Os–Os Bond lengths (Å) within each of the two independent molecules of $(Me_3P)(OC)_4OsOs_3(CO)_{11}$ (**1**).

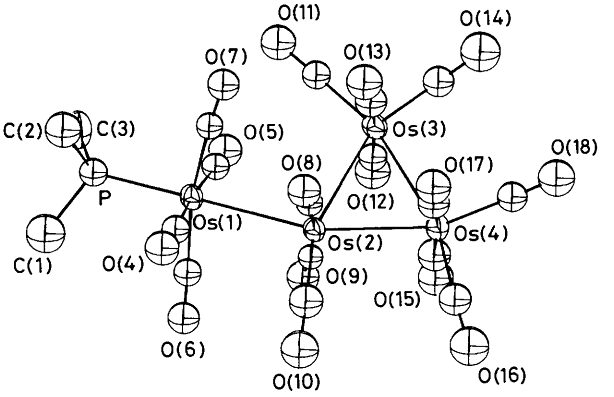


Figure 1. Molecular structure of molecule 2 of $(Me_3P)(OC)_4$-$OsOs_3(CO)_{11}$ (**1**).

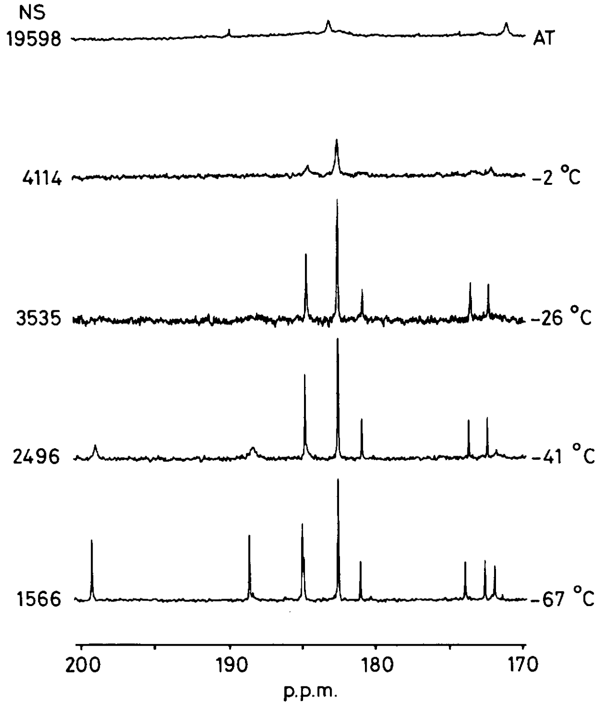


Figure 2. Variable temperature, 100.6 MHz ^{13}C n.m.r. spectra of (**1**) (^{13}CO-enriched: NS = number of scans). The three signals in the spectrum at ambient temperature (AT) are due to decomposition products of (**1**).

---

† *Crystal data for* (**1**): $C_{18}H_9Os_4O_{15}P$, $M = 1257$, triclinic, space group $P\bar{1}$, $a = 12.473(2)$, $b = 13.325(2)$, $c = 17.547(2)$ Å, $\alpha = 109.05(1)$, $\beta = 90.44(1)$, $\gamma = 94.60(1)°$, $Z = 4$, $D_c = 3.036$ g cm^{-3}. Data were collected on an Enraf–Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K_α radiation ($K_{\alpha1}$, $\lambda = 0.70930$, $K_{\alpha2}$ $\lambda = 0.71359$ Å) using ω—2θ scans ($\theta_{max.}$ of 22.5°), and were corrected for absorption. The osmium atoms were located by direct methods and the other non-hydrogen atoms by alternating Fourier difference maps with block-diagonal least-squares refinement. The final R value was 0.0367 for 5172 independent reflections [$I < 2.5\sigma(I)$] and 386 parameters. The Os, P, and C atoms on the phosphine ligand were anisotropic; other non-hydrogen atoms were isotropic. The hydrogen atoms were included in calculated positions with fixed isotropic temperature factors.

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample of (**1**) in CD_2Cl_2–CH_2Cl_2 at −67 °C was consistent with the solid-state structure: resonances at δ 198.4, 187.7, 184.0 (intensity 2, axial CO); 183.9, 180.1, 173.0, 171.6, 171.0 (intensity 1, equatorial CO); 181.6 [intensity 4, J_{PC} 4.0 Hz, Os(CO)$_4$(PMe$_3$)]. On warming the solution, sets of signals collapsed to the baseline at different rates such that at ambient temperature no resonances could be detected, except for very weak signals due to Os(CO)$_4$(PMe$_3$) and Os$_3$(CO)$_{12}$ resulting from partial decomposition (Figure 2). Apart from the decomposition, the collapse process was reversible. [Higher temperatures were not investigated because of extensive decomposition of (**1**) above room temperature.] The mode of collapse of the signals due to the Os$_3$(CO)$_{11}$ unit is typical of Os$_3$(CO)$_{11}$(L) [L = PEt$_3$,[9] P(OMe)$_3$[10]] derivatives. A mechanism which involves an intermediate with two carbonyls bridging the Os–Os bond *cis* to the ligand L was proposed to account for the observed changes in the spectrum of Os$_3$(CO)$_{11}$(PEt$_3$).[9] Of special interest was that the carbonyls on the Os(CO)$_4$(PMe$_3$) unit also underwent exchange with those of the cluster at ambient temperature. This exchange probably occurs *via* an intermediate with the donor–acceptor metal–metal bond also bridged by two carbonyls, in a manner previously proposed for (Me$_3$P)(OC)$_4$OsW(CO)$_5$ [2] and (η^5-C$_5$Me$_5$)(OC)$_2$IrW(CO)$_5$.[3] When (**1**) was prepared from Os$_3$(CO)$_{11}$(MeCN) and ^{13}CO-enriched Os(CO)$_4$(PMe$_3$), the ^{13}C n.m.r. spectrum revealed that the ^{13}C label was equally distributed over all the carbonyl sites within the molecule. This result is consistent with the bridge–terminal exchanges proposed for (**1**).

We thank the Natural Sciences and Engineering Research Council of Canada and the President's Research Fund (Simon Fraser University) for financial support.

Received, 29th October 1984; Com. 1528

References

1 F. W. B. Einstein, R. K. Pomeroy, P. Rushman, and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1983, 854.
2 F. W. B. Einstein, T. Jones, R. K. Pomeroy, and P. Rushman, *J. Am. Chem. Soc.*, 1984, **106**, 2707.
3 F. W. B. Einstein, R. K. Pomeroy, P. Rushman, and A. C. Willis, *Organometallics*, in the press.
4 B. E. Hanson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 1852.
5 L. R. Martin, F. W. B. Einstein, and R. K. Pomeroy, *Inorg. Chem.*, submitted for publication.
6 G. R. John, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1979, **181**, 143 and references therein.
7 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
8 R. D. Adams, I. T. Horvath, B. E. Segmüller, and L.-W. Yang, *Organometallics*, 1983, **2**, 144.
9 B. F. G. Johnson, J. Lewis, B. E. Reichert, and K. T. Schorpp, *J. Chem. Soc., Dalton Trans.*, 1976, 1403.
10 R. F. Alex and R. K. Pomeroy, unpublished results.