A Boroxine-supported Triosmium Oxymethylidyne Cluster System, $[(\mu\text{-H})_3(CO)_9Os_3CO]_3(B_3O_3)$: its Structure and its Conversion into Halogeno- and Phenyl-methylidyne Complexes

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From the hydroboration of the unsaturated cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ in the presence of tetrahydrofuran, a cluster system was prepared with boroxine (B_3O_3) supporting three triosmium units, which was shown to be a useful starting material in the synthesis of the triosmium methylidyne clusters, $(\mu\text{-H})_3(CO)_9Os_3(CCl)$, $(\mu\text{-H})_3(CO)_9Os_3(CBr)$, and $(\mu\text{-H})_3(CO)_9Os_3(CPh)$.

Hydroboration of $(\mu\text{-H})_2Os_3(CO)_{10}$ by tetrahydrofuran–borane $(THF\text{–}BH_3)$ in $THF\text{–}CH_2Cl_2$ produces $[(\mu\text{-H})_3(CO)_9Os_3(\equiv CO)]_3(B_3O_3)$ (**1**), a boroxine (B_3O_3) supported triosmium oxymethylidyne $(\mu\text{-H})_3(CO)_9Os_3(\equiv CO)$-cluster system (Figure 1) which has proved to provide a new and useful approach to the preparation of other triosmium methylidyne cluster derivatives: $(\mu\text{-H})_3(CO)_9Os_3(CCl)$ (**2**), $(\mu\text{-H})_3(CO)_9Os_3(CBr)$ (**3**), and $(\mu\text{-H})_3(CO)_9Os_3(CPh)$ (**4**).

The cluster (**1**) was obtained (reaction 1) as a pale yellow precipitate from a mixture of $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.114 mmol), $THF\text{–}BH_3$ (0.114 mmol), THF (1.13 mmol), and CH_2Cl_2 (5 ml) which was stirred at room temperature for 30 min.

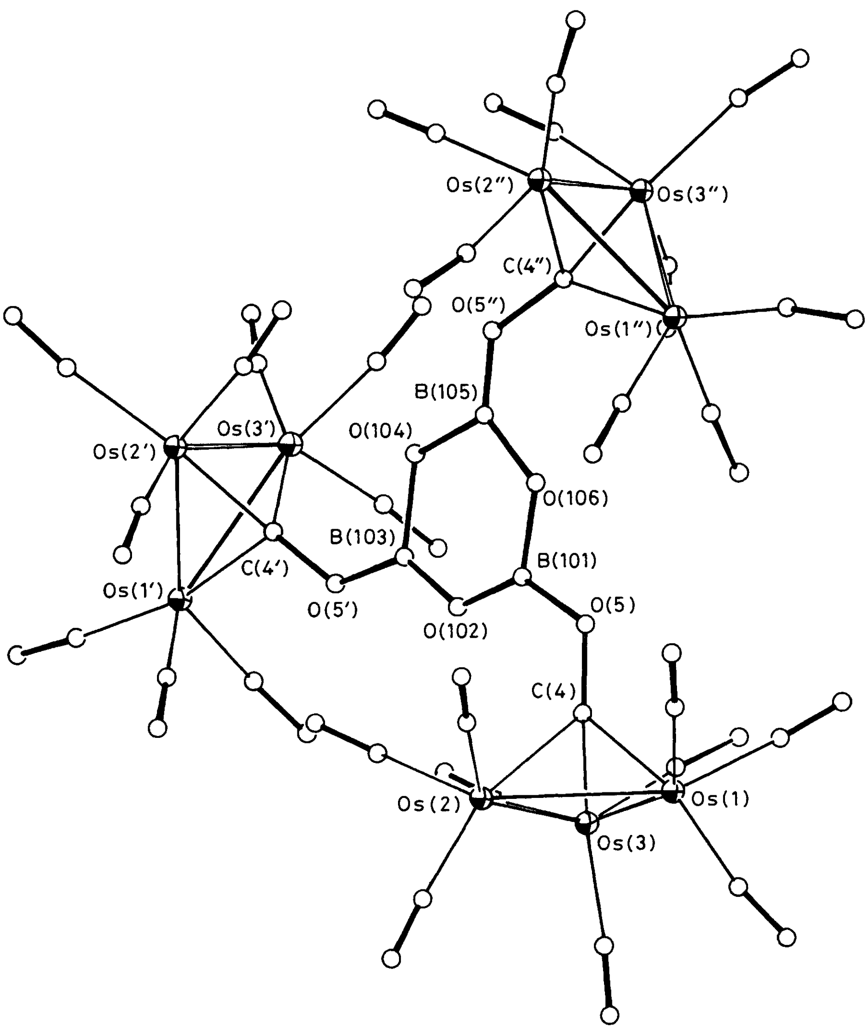
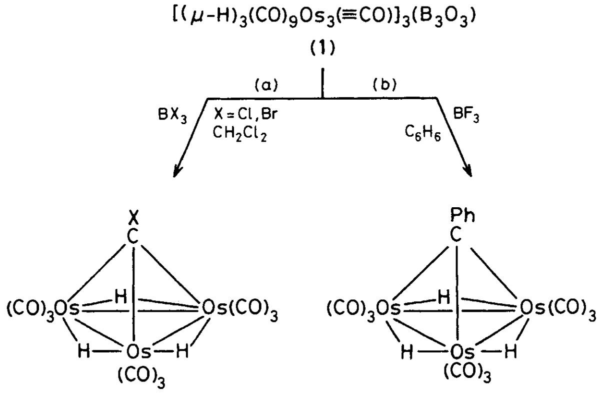


Figure 1. The molecular structure of (non-hydrogen atoms) $[(\mu\text{-H})_3(CO)_9Os_3CO]_3(B_3O_3)$. Bond lengths: Os–Os 2.892(3)—2.881(3); oxymethylidyne CO 1.42(5)—1.32(5). non-ring B–O 1.39(6)—1.25(6) Å; ∠ C–O–B 126.3(45)—121.3(39)°.



(**2**) X = Cl (**4**)
(**3**) X = Br

Scheme 1

$$(\mu\text{-H})_2Os_3(CO)_{10} + \text{THF–}BH_3 \longrightarrow \tfrac{1}{3}\underset{(\mathbf{1})}{[(\mu\text{-H})_3(CO)_9Os_3(CO)]_3(B_3O_3)} + C_4H_{10} \qquad (1)$$

On the other hand, when more dilute solutions of reactants were used: THF–BH_3 (0.18 mmol), $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.18 mmol), and hexane (12 ml), the carbonyl borylidyne, $(\mu\text{-H})_3(CO)_9Os_3BCO$, was the favoured product.[1] The formation of $[(\mu\text{-H})_3(CO)_9Os_3CO]_3(B_3O_3)$ is accounted for if one hydrogen from the BH_3 unit of THF–BH_3 adds to the unsaturated $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule while the two remaining B–H hydrogens from the BH_3 unit are transferred to the OC_4H_8 (THF) ring system to form C_4H_{10}, (identified by g.c.–mass spectrometry), as oxygen is abstracted from the ring by boron to form the B_3O_3 unit. The crystal structure of the cluster (**1**) has been determined.

Crystal data: $Os_9C_{30}O_{33}B_3H_9$, monoclinic, space group $P2_1/c$, a = 13.136(3), b = 24.932(12), c = 16.106(4) Å, β = 99.72(5)°, U = 5199 Å^3, D_c = 3.38 g cm^{-3} for M_r = 2641.6 and Z = 4. Diffraction data were collected at −150 °C on an automated Picker four-circle goniostat. The structure was solved by direct methods, Fourier, and least-squares refinement techniques. R_F = 0.072 and R_{wF} = 0.059 for 5646 reflections in the range $5° \leqslant 2\theta \leqslant 50°$ (Mo-K_α radiation).†

The molecular structure of (**1**) has approximate C_3 symmetry in the crystalline state. In the centre of the molecule

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

the B_3O_3 ring forms an approximatly regular hexagon while the three oxymethylidyne clusters which are bound to the B_3O_3 ring have near -C_{3v} symmetry. Hydrogen atoms were not located, but the ^{1}H n.m.r. spectrum of (**1**), consisting of a single signal at τ 28.5 in CD_2Cl_2, is consistent with the presence of bridging hydrogen. Os–Os distances (Figure 1) are appropriate for hydrogen-bridged osmium atoms.[2—6] Methylidyne CO distances (Figure 1) are consistent with the presence of a carbon–oxygen single bond.

The cluster (**1**) (*ca.* 0.2 mmol) reacts with BCl_3 and with BBr_3 (*ca.* 1 mmol) in CH_2Cl_2 (10 ml) at room temperature (Scheme 1) to give (**2**) and (**3**) as white crystalline solids in 44 and 60% yields respectively. (**3**) has been prepared previously *via* another synthetic route.[7] When the boron halide used in Scheme 1(a) was BF_3, a highly air- and moisture-sensitive, as yet uncharacterized, product was obtained; however, when benzene was substituted for CH_2Cl_2 [Scheme 1(b)], the phenyl substituted methylidyne complex (**4**) was obtained as a pale yellow crystalline solid in 45% yield.

Reactions which produce the halogenomethylidyne complexes are envisaged to occur through a scheme which involves co-ordination of BX_3 (X = halogen) to the oxygen of the carboxy group with subsequent transfer of halogen to the carbon atom and rupture of the carbon–oxygen bond.[7—9] Formation of the phenylmethylidyne complex is also believed to involve initial addition of BF_3 to the carboxy oxygen, but in this case heterolytic scission of the CO bond occurs to give a cluster carbonium ion which displaces a proton from benzene.[9,10]

The molecular formulae of (**2**), (**3**), and (**4**) were established from the $(^{192}Os)_3$ member of the parent ion isotopic multiplet obtained by positive-ion Fourier transform mass spectrometry with a Nicolet FT/MS 1000 spectrometer:[11] *m/z* 878, 922/924, and 920 for the chloro-, bromo-, and phenyl-derivatives. The appearance of isotopic clusters corresponding to the sequential loss of each of the nine carbonyl groups further confirmed the number of carbonyl groups present.

I.r. and ^{1}H n.m.r. spectra of (**2**), (**3**) and (**4**) were obtained. All the ^{1}H n.m.r. spectra revealed the presence of bridging hydrogen atoms and, in the case of (**4**), phenyl hydrogens were observed: (**2**): i.r. [ν(CO), CH_2Cl_2] 2004 m, 2038 s, 2070 w, and 2092 s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 25 °C) τ 28.9; (**3**): i.r. [ν(CO), cyclohexane] 1979 w, 2022 m, 2035 s, and 2095 s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 25°C) τ 28.9; (**4**): i.r. [ν(CO), cyclohexane] 1979 w, 2025 s,br., and 2087 s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 25 °C) τ 2.24 (2H, m), 2.78 (2H, m), 2.99 (1H, m), and 28.56 (3H, s).

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References

1 S. G. Shore, D. Y. Jan, L.-Y. Hsu, and W.-L. Hsu, *J. Am. Chem. Soc.*, 1983, **105**, 5923.
2 S. Bhaduri, B. F. G. Johnson, J. Lewis, P. R. Raithby, and D. J. Watson, *J. Chem. Soc., Chem. Commun.*, 1978, 343.
3 M. R. Churchill, C. Bueno, W.-L. Hsu, J. S. Plotkin, and S. G. Shore, *Inorg. Chem.*, 1982, **21**, 1958.
4 M. R. Churchill, C. Bueno, S. Kennedy, J. S. Bricker, J. S. Plotkin, and S. G. Shore, *Inorg. Chem.*, 1982, **21**, 627.
5 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1980, **19**, 306.
6 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1979, **18**, 161.
7 J. B. Keister and T. L. Horling, *Inorg. Chem.*, 1980, **19**, 2304.
8 M. F. Lappert, *J. Chem. Soc.*, 1958, 3256.
9 R. Dolby and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 1972, 2046.
10 D. Seyferth, J. E. Hallgren, and C. S. Eschbach, *J. Am. Chem. Soc.*, 1974, **96**, 1730.
11 L.-Y. Hsu, W.-L. Hsu, D.-Y. Jan, A. G. Marshall, and S. G. Shore, *Organometallics*, in the press.