

A Method of Making Os–SR₂ Bonds: Chemistry and Structure of Meridional [Os{S(CH₂Ph)₂}₃Br₃]

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The title complex is afforded by the reaction of diammonium hexabromoosmate(IV) with dibenzyl sulfoxide; its X-ray structure, spectra and potential utility as a starting material for synthesis are scrutinised.

There is a surprising paucity of authentic thioether-bonded osmium species.^{1,2} Only a single member of the potentially diverse [Os(SR₂)_mX_n] (R = alkyl, aryl; X = halogen; m + n = 6,5) family is currently known: [Os(SET₂)₃Cl₃] prepared from OsCl₄ generated by a high-temperature route.³ Solution reactions of SR₂ with OsX₆²⁻ failed to afford any SR₂ complex.⁴ Herein we report a method for making [Os(SR₂)₃Br₃] based on sulfoxides as *in situ* precursors to thioethers, the R = CH₂Ph case being illustrated.

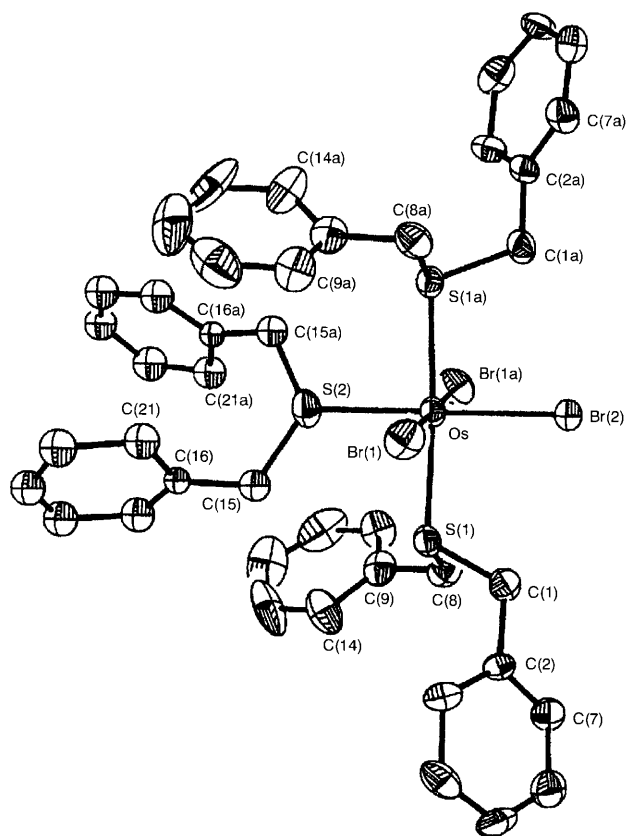
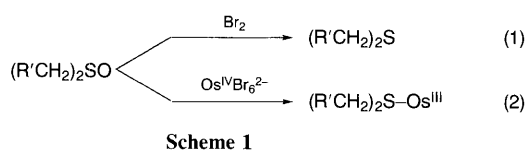


Fig. 1 ORTEP plot and labelling scheme for [Os{S(CH₂Ph)₂}₃Br₃] with all atoms represented by their 40% probability ellipsoids. Selected bond distances (Å) and angles (°): Os–Br(1) 2.495(2), Os–Br(2) 2.497(2), Os–S(1) 2.398(3), Os–S(2) 2.387(5), S(1)–C(1) 1.830(14), S(1)–C(8) 1.834(15), S(2)–C(15) 1.734(27), Br(1)–Os–Br(2) 90.3(1), Br(1)–Os–S(1) 82.9(1), Br(2)–Os–S(1) 91.8(1), Br(1)–Os–S(2) 89.7(1), Br(2)–Os–S(2) 180.0(1), S(1)–Os–S(2) 88.2(1), Br(1)–Os–Br(1a) 179.4(1), Br(2)–Os–Br(1a) 90.3(1), S(1)–Os–Br(1a) 97.1(1), S(2)–Os–Br(1a) 89.7(1), Br(1)–Os–S(1a) 97.1(1), Br(2)–Os–S(1a) 91.8(1), S(1)–Os–S(1a) 176.3(2), S(2)–Os–S(1a) 88.2(1), Br(1a)–Os–S(1a) 82.9(1).

A solution of (NH₄)₂OsBr₆ (0.14 mmol) and (PhCH₂)₂SO (0.43 mmol) in 30 ml 2-methoxyethanol was heated to reflux (≈ 80 min) affording a clear red solution which was evaporated to dryness under reduced pressure. Upon chromatographic purification of the residue on neutral silica gel with benzene as eluent, vermilion-coloured [Os{S(CH₂Ph)₂}₃Br₃] was obtained in >50% yield (based on metal).[†] The complex has one unpaired electron (μ_{eff} , 1.90 μ_{B}) and in frozen (77 K) dichloromethane–toluene solution its EPR spectrum is rhombic (*g* values: 2.776, 2.130, 1.541), consistent with C₂ symmetry (see below).

In devising the above synthesis, a lead was taken from the conversion of eqn. (1) (Scheme 1) in which the thioether is catalytically formed *via* facile α -bromination.⁵ We propose that OsBr₆²⁻ acts as an incipient halogen and the thioether formed remains bound to the reduced metal, eqn. (2) (Scheme 1). It is significant that the use of Me₂SO in place of (PhCH₂)₂SO affords [Os(SMe₂)₃Br₃] in 30% yield but Ph₂SO (no α -hydrogen) does not furnish any thioether complex. Further studies are in progress.

The X-ray[‡] structure of [Os{S(CH₂Ph)₂}₃Br₃] is shown in Fig. 1. The OsS₃Br₃ coordination sphere is meridional. The Br(2)–Os–S(2) axis is collinear with a crystallographic twofold axis and the point group symmetry of the molecule is C₂. The Br(1)–Os–Br(1a) axis is also linear but the S(1)–Os–S(1a) triad has a slightly bent configuration (176.3°). The S(1) atom lies closer to Br(1) than Br(1a), the S(1)–Os–Br(1) and S(1)–Os–Br(1a) angles being 82.9 and 97.0°, respectively. The S(2) and Br(2) atoms lie respectively on the Br₃ and S₃ planes, the metal atom being common to both; the dihedral angle between the planes is 97.1°. Both the planes are orthogonal to the third coordination plane incorporating S(1), S(1a), Br(1), Br(1a) and Os (mean deviation 0.03 Å). The Os–S(1) bond, 2.398(3) Å, is slightly longer than Os–S(2), 2.387(5) Å. The nonbonded S(1)⋯S(2) distance is 3.328(6) Å.

While M^{III}S₃X₃ has been a long-standing motif in platinum metal chemistry with physical data generally consistent with meridional configuration,^{1c,6} the present complex appears to be the first member for which complete structural characterisation has finally been achieved. This is also the first case of such characterisation of Os^{III}–thioether binding; in the few known osmium–thioether structures the metal has other oxidation states.^{1a,2a,b} The complex [Os(SET₂)₃Cl₃] was initially assigned³ facial geometry but, in view of the subsequent findings^{1c,6} on M^{III}S₃X₃ and especially the present work, a revision of geometry is imperative.

Complexes of type [Os(SR₂)₃X₃] can be potentially versatile starting materials for syntheses. Their virtual inaccessibility has been a major reason for the lack of growth of Os–SR₂ chemistry [contrast Os(PR₃)₃X₃ *vis-à-vis* Os–PR₃ chemistry].^{1b,7} Preliminary findings on [Os{S(CH₂Ph)₂}₃Br₃] reactivity are very encouraging. Chemical/electrochemical reduction is attended with partial bromide loss yielding Os^{II}–SR₂ species. On the other hand, oxidative bromine addition causes partial thioether loss, furnishing Os^{IV}–SR₂ complexes. Characterisation of these and other derived species is in progress.

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Footnotes

† Satisfactory elemental analysis was obtained. *Selected spectral data*: IR(KBr): no ν_{SO} is present. UV-VIS $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 385 (ϵ 2300 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 435(2670), 470(2500).

‡ *Crystal data* for $[\text{Os}(\text{S}(\text{CH}_2\text{Ph})_2)_3\text{Br}_3]$: $\text{C}_{42}\text{H}_{42}\text{Br}_3\text{OsS}_3$, $M = 1072.9$, orthorhombic, space group $P2_12_12_1$, $Z = 2$, $a = 17.792(6)$, $b = 9.261(2)$, $c = 12.290(3)$ Å, $V = 2024.8(9)$ Å³, $T = 295$ K, $D_c = 1.760$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 62.92$ cm^{-1} , crystal dimensions $0.3 \times 0.25 \times 0.36$ mm. Data were collected in the range $3.0 \leq 2\theta \leq 52^\circ$ by the ω -scan method on a Siemens R3m/V four-circle diffractometer. Out of 1989 unique reflections, 1376 with $I \geq 3.0\sigma(I)$ were used for structure solution (Patterson method). An empirical absorption correction was done on the basis of azimuthal scans.⁸ All non-hydrogen atoms except those of the S(2) benzyl group which displays twofold disorder around the C_2 axis were refined anisotropically. Hydrogen atoms were included at calculated positions ($U = 0.08$ Å²). The structure was refined to $R = 0.0365$ and $R_w = 0.0390$. The highest difference Fourier peak was 0.69 e Å⁻³. All calculations were done using the SHELXTL-PLUS program⁹ package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- (a) A. J. Blake and M. Schroder, *Adv. Inorg. Chem.*, 1990, **35**, 1; (b) W. P. Griffith, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, J. A. McCleverty and R. D. Gillard, Pergamon, Oxford, 1987, vol. 4, p. 519; (c) S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.
- (a) R. D. Adams, M. P. Pompeo, W. Wu and J. H. Yamamoto, *J. Am. Chem. Soc.*, 1993, **115**, 8207; (b) J. E. Fergusson, W. T. Robinson and R. K. Coll, *Inorg. Chim. Acta*, 1991, **181**, 37; (c) M. J. Root, B. P. Sullivan, T. J. Meyer and E. Deutsch, *Inorg. Chem.*, 1985, **24**, 2731; (d) S. K. Harbron and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1985, 205; (e) D. J. Gulliver, W. Levason, K. G. Smith, M. J. Selwood and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 1872; (f) E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 2185.
- B. E. Aires, J. E. Fergusson, D. T. Howarth and J. M. Miller, *J. Chem. Soc. A*, 1971, 1144.
- R. Ali, S. J. Higgins and W. Levason, *Inorg. Chim. Acta*, 1984, **84**, 65.
- T. Aida, N. Furukawa and S. Oae, *Tetrahedron Lett.*, 1973, 3853.
- E. A. Allen and W. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 613 and references therein; J. Chatt, G. J. Leigh and A. P. Storace, *J. Chem. Soc. A*, 1971, 1380; E. W. Abel, G. W. Farrow and K. G. Orell, *J. Chem. Soc., Dalton Trans.*, 1976, 1160.
- R. A. Cipriano, W. Levason, R. A. S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1990, 2609; J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, *J. Chem. Soc. A*, 1968, 2636.
- A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- G. M. Sheldrick, SHELXTL-PLUS, Structure Determination Software Program, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990. Computations were carried out on a Micro VAX II Computer.