

## A Closed Paramagnetic Electron-Precise Cluster<sup>1</sup>

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A pentametallic cluster is formed by addition of two [SnR<sub>2</sub>] [R = CH(SiMe<sub>3</sub>)<sub>2</sub>] groups to [Os<sub>3</sub>(CO)<sub>8</sub>(μ-H)(C<sub>6</sub>H<sub>4</sub>PhPCH<sub>2</sub>PPh<sub>2</sub>)], in a reaction reversing the *ortho*-hydrogen abstraction and giving the first closed electron-precise paramagnetic cluster.

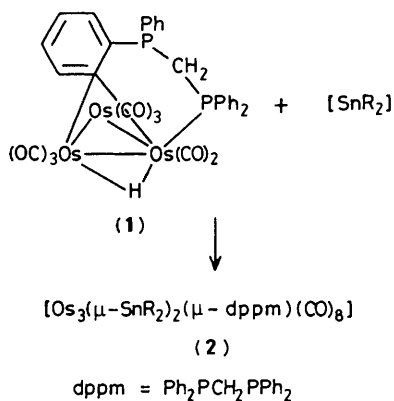
Paramagnetic carbonyl clusters are very unusual,<sup>2</sup> and hitherto no closed clusters were known to be both paramagnetic and electron precise. Our studies of heterometallic clusters containing the heavier members of Groups 14 and 8 have provided the first example (see Scheme 1).

Thus, heating the unsaturated tri-osmium cluster (1)<sup>3</sup> with excess of [SnR<sub>2</sub>] [R = CH(SiMe<sub>3</sub>)<sub>2</sub>] in refluxing hexane (6 h) gave the heterometallic cluster (2). The product was isolated as fragile amber platelets, which were not sensitive to air or moisture, but which reacted under inert atmosphere with either chlorinated or donor solvents.† The structure is shown in Figure 1.‡

Compound (1) is produced by an example of the well known *ortho*-hydrogen abstraction process, which is reversed in the process which produces (2). This sense of reaction has not

been demonstrated structurally to our knowledge in this area, although it has been postulated as a step in several catalytic cycles.<sup>4</sup>

Compound (2) was found to be paramagnetic,§ which can be viewed as being related to the presence of the diphosphine ligand. In other structures containing M<sub>3</sub>(μ-SnR<sub>2</sub>)<sub>2</sub> (M = Ru or Os)<sup>1</sup> all three metal atoms attain an eighteen electron configuration by CO bridging of the third M-M vector. In the present case, the diphosphine is sterically constrained to the equatorial plane, but naturally behaves as a bis(2-electron) donor, making a formal eighteen electron count for two of the osmium atoms improbable. Since the Os(1) ··· Os(2) separation is essentially non-bonding [3.048(2) Å], the obvious electron counts for Os(1), Os(2), and Os(3) are 18, 17, and 17,



Scheme 1

† Satisfactory elemental analysis was obtained for (2); m.p. 191–193 °C (decomp.); i.r. (KBr disc) 2050 m, 2010 vs, 1973 vs(b), 1952 vs, 1964s cm<sup>-1</sup>.

‡ Crystal data for (2): A single crystal of (2) with approximate dimensions 0.08 × 0.10 × 0.60 mm was grown from n-hexane at -20 °C. C<sub>61</sub>H<sub>98</sub>O<sub>8</sub>Os<sub>3</sub>P<sub>2</sub>Si<sub>8</sub>Sn<sub>2</sub>, M = 2054.05, triclinic, space group P1̄; a = 11.607(6), b = 17.316(12), c = 24.165(16) Å; α = 110.83(5), β = 91.94(5), γ = 92.48(5)°, U = 4529(5) Å<sup>3</sup>, Z = 2, D<sub>c</sub> = 1.506 g cm<sup>-3</sup>. 11 794 Unique diffractometric data in the range 0 ≤ 2θ ≤ 45° were collected on a Syntex P2<sub>1</sub> four circle diffractometer using ω-scans and Mo-K<sub>α</sub> radiation (λ = 0.71069 Å), of which 6362 with I > 3σ(I) were used in the refinement. After data reduction, the structure was solved (Patterson, SHELX 84) and refined using full-matrix least-squares. An absorption correction was applied using the program XABS (H. Hope and B. Moezzi, University of California, Davis). Anisotropic refinement was carried out on the Os, Sn, P, and Si atoms. All other atoms were refined isotropically. Hydrogens were not included in the refinement. Refinement converged at R = 0.070. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

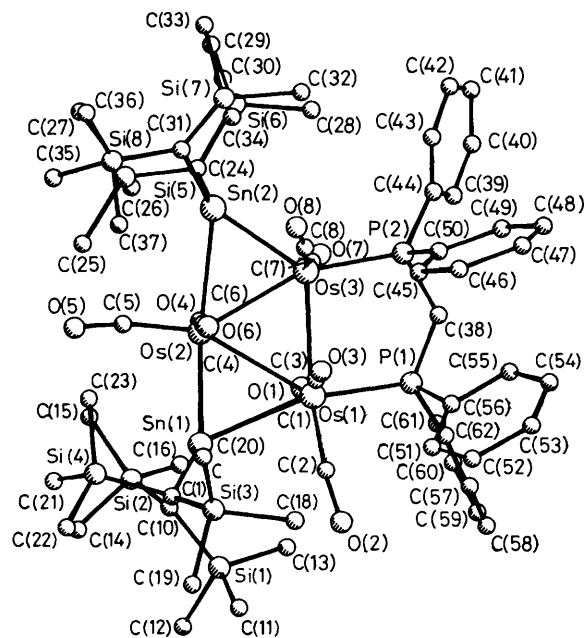


Figure 1. Computer generated thermal ellipsoid plot of (2) (45% probability level thermal ellipsoids, isotropic atoms given arbitrary fixed radius circles). Important bond distances and angles: Os(1)–Os(2) 3.048(2), Os(2)–Os(3) 2.854(2), Os(1)–Os(3) 2.909(2), Os(1)–Sn(1) 2.873(3), Os(1)–P(1) 2.356(8), Os(2)–Sn(1) 2.649(3), Os(2)–Sn(2) 2.866(3), Os(3)–Sn(2) 2.651(2), Os(3)–P(2) 2.297(8) Å; Os(3)–Os(1)–Os(2) 57.2(1), Os(1)–Os(2)–Os(3) 59.0(1), Os(1)–Os(3)–Os(2) 63.8(1), Os(1)–Sn(1)–Os(2) 66.8(1), Os(2)–Sn(2)–Os(3) 62.1(1), C(10)–Sn(1)–C(17) 99.5(12), C(24)–Sn(2)–C(31) 110.6(11)°.

§ Measured moment, 2.4 μ<sub>B</sub>, at 297 K by the Evans method: the n.m.r. spectra show severely broadened lines and the solid material gives a typical triplet e.s.r. signal.

respectively. The paramagnetism is presumably related to the pair of osmium atoms with a formally odd electron configuration (in harmony with the measured moment). In molecular orbital terms, this demands the additional constraint that the two HOMOs be approximately degenerate. It is interesting that theoretical considerations suggest that these conditions are most probable in planar clusters, such as (2).<sup>5</sup>

A feature of the structure of (2) is the Os(2)–Os(3) distance of 2.854(2) Å, shorter than the average (2.877 Å) found in Os<sub>3</sub>(CO)<sub>12</sub>, surprising since hitherto [SnR<sub>2</sub>] bridging groups have invariably been found to lengthen Os–Os vectors.<sup>1</sup> This, and the asymmetry of the tin bridging groups, are presumably associated with the electron poor Os(3) atom. Thus, Sn(2) forms a shorter bond with Os(3), and the effect is apparently relayed to Sn(1) which forms a shorter bond to Os(2). These bridges, then, may be likened to the semi-bridging CO ligands often associated with similarly electron poor metal atoms.<sup>6</sup>

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