

METAL CLUSTER EXPANSION BY ADDITION OF LOW VALENT GROUP 14 REAGENTS

III *. REACTION OF BIS[BIS(TRIMETHYLSILYL)METHYL]TIN WITH $M_3(CO)_{12}$ OR ITS DERIVATIVES ($M = Fe, Ru, \text{ or } Os$): THE CRYSTAL AND MOLECULAR STRUCTURES OF $M_3(\mu-SnR_2)_2(CO)_{10}$ ($R = CH(SiMe_3)_2$; $M = Ru \text{ or } Os$) **

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(Received October 20th, 1986)

Summary

The stannylene $[SnR_2]$ ($R = CH(SiMe_3)_2$) reacts in different ways with the three dodecacarbonyls of the iron triad: $[Fe_3(CO)_{12}]$ gives $[Fe_2(CO)_8(\mu-SnR_2)]$, $[Ru_3(CO)_{12}]$ gives the planar pentametallic cluster $[Ru_3(CO)_{10}(\mu-SnR_2)_2]$, for which a full structural analysis is reported, while $[Os_3(CO)_{12}]$ fails to react. Different products are also obtained from three nitrile derivatives: $[Fe_3(CO)_{11}(MeCN)]$ gives $[Fe_2(CO)_6(\mu-SnR_2)_2]$, which has a structure significantly different from that of known Fe_2Sn_2 clusters, $[Ru_3(CO)_{10}(MeCN)_2]$ gives the pentametallic cluster described above, while $[Os_3(CO)_{10}(MeCN)_2]$ gives the isostructural osmium analogue, which shows the unusual feature of a CO group bridging two osmium atoms.

Introduction

We reported recently [2] on the synthesis of osmium-tin clusters by treatment of the unsaturated $[Os_3H_2(CO)_{10}]$ with the low-valent tin reagent $[SnR_2]$ ($R =$

* For part II see ref. 1.

** Paper dedicated to Professor G.E. Coates on the occasion of his 70th birthday, with the grateful thanks of one of us (D.J.C.) for many stimulating hours' teaching and for first awakening his interest in organometallic chemistry.

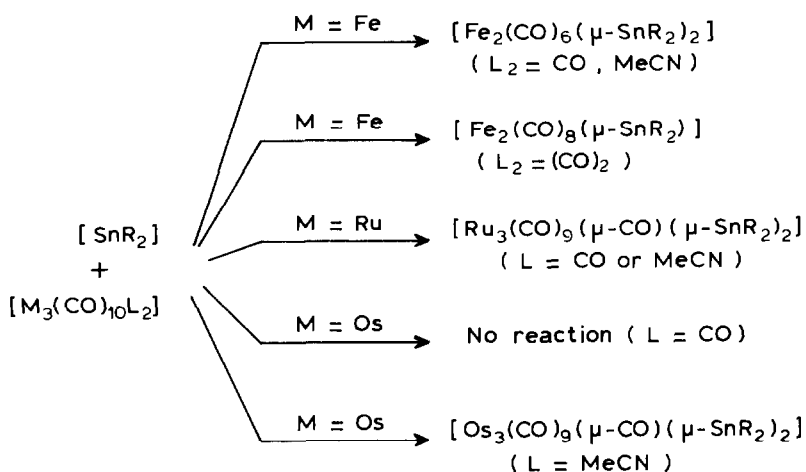
[CH(SiMe₃)₂] and on their reactivity [1]. We now report on the reactions of the saturated species [M₃(CO)₁₂] (and a derivative for osmium) with [SnR₂], which afford new heterometallic clusters, in high yield for M = Ru or Os, and illustrate the considerable potential of the route.

Results and discussion

The reactions, which are summarised in Scheme 1, occur under mild conditions and in high yield (e.g., at 40 °C in ca. 80% yield for the Ru compound).

That there is partial fragmentation with iron and not with either of the heavier metals is not unexpected in terms of the increasing metal-metal (and metal-CO) bond strengths on descending the group, and the greater lability of the ruthenium (compared with osmium) carbonyl is normal, though the isolation of a single product in high yield is unusual. In view of our earlier results with the unsaturated [Os₃(μ-H)₂(CO)₁₀], and the report that the (unknown) ruthenium analogue might be an intermediate in reactions of the dodecacarbonyl carried out under dihydrogen [3], we also examined the products for the ruthenium reaction under these conditions. The product was the same (no hydrido compounds were detected) although formed in slightly lower yield. This may be because traces of residual moisture inevitably present in the gas consumed some of the highly sensitive tin reagent, although it is noteworthy that the reaction is very temperature sensitive: the yield falls from 83 to 14% when the temperature is raised from 20 to 90 °C. The same product can be obtained in excellent yield (90%) from [Ru₃(CO)₁₀(MeCN)₂] (the method employed for the osmium analogue, see below) and the tin reagent at ambient temperature. In the osmium case, the dodecacarbonyl is unreactive to the tin reagent under all conditions investigated, but the bis(acetonitrile) derivative reacts readily at room temperature, affording the pentametallic cluster in excellent yield (~95%).

The new compounds were characterised by elemental analysis, mass spectrometry, IR and NMR spectroscopy, and the structures determined from single crystal



SCHEME 1

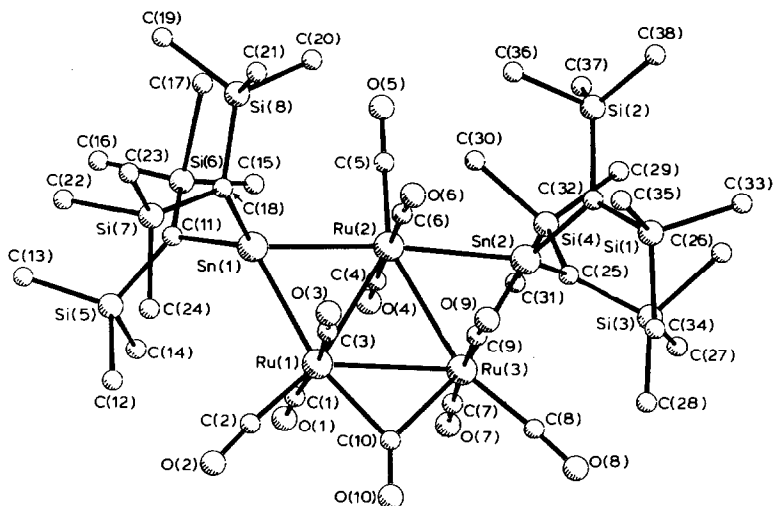


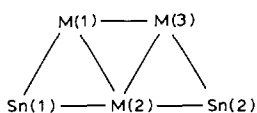
Fig. 1. A molecule of $[\text{Ru}_3(\text{CO})_{10}(\text{SnR}_2)_2]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$).

TABLE 1

CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR THE MOLECULES $[\text{M}_3(\text{CO})_{10}(\mu\text{-SnR}_2)_2]$ ($\text{M} = \text{Ru}$ or Os ; $\text{R} = \text{CH}(\text{SiMe}_3)_2$)

	M = Ru	M = Os
Diffractometer	CAD-4	CAD-3
a (Å)	16.311(4)	16.70
b (Å)	11.884(2)	22.35
c (Å)	18.610(4)	19.67
α (°)	105.62(2)	90
β (°)	66.18(2)	110
γ (°)	108.48(2)	90
V (Å ³)	3087.96	6486.68
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
Radiation	Graphite-mono- chromated Mo-K_α (λ 0.71069 Å)	Mo-K_α
$F(000)$	1799.95	3631.42
μ (Mo-K_α)	20.08	65.09
Absorption correction	empirical	none
"reflections" measured	11 437	8 992
θ -min, θ -max	1.5, 25.0	2.0, 22.0
No. unique	10 862	7 335
No. observed	6 620	1 485
Criterion	$ F > 3\sigma(F)$	$ F > 3\sigma(F)$
Final conventional R (%)	5.68%	6.98%
Crystal	orange needle	orange needle
Approx. dimensions (mm ³)	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.1

TABLE 2
METAL FRAMEWORK GEOMETRIES



	M = Ru	M = Os
<i>Bond lengths (Å)</i>		
M(1)–M(2)	2.963(2)	2.981(0)
M(1)–M(3)	2.881(2)	2.893(0)
M(2)–M(3)	2.950(2)	2.967(0)
Sn(1)–M(1)	2.737(2)	2.736(6)
Sn(1)–M(2)	2.734(2)	2.753(7)
Sn(2)–M(2)	2.733(2)	2.732(7)
Sn(2)–M(3)	2.737(2)	2.727(7)
<i>Bond angles (°)</i>		
M(1)–M(2)–M(3)	58.3(0)	58.2(0)
M(2)–M(1)–M(3)	60.6(0)	60.6(0)
M(1)–M(3)–M(2)	61.1(0)	61.1(0)
Sn(1)–M(1)–M(2)	57.2(0)	57.4(2)
M(1)–M(2)–Sn(1)	57.3(0)	56.8(1)
M(2)–M(3)–Sn(2)	57.3(0)	57.2(1)
M(3)–M(2)–Sn(2)	57.4(0)	57.0(1)
M(2)–Sn(2)–M(3)	65.3(0)	65.8(2)
M(1)–Sn(1)–M(2)	65.6(0)	65.8(2)

X-ray data. For the osmium and ruthenium compounds the structures reveal a planar array of the five metal atoms, the tin atoms bridging two sides of the M_3 triangle, with the third being bridged equatorially by a carbonyl group. The molecules are isostructural, and Fig. 1 shows the structure for the ruthenium complex.

The three bridges are symmetrical, a feature which is not always observed [5,6]. Carbon monoxide bridging of osmium atoms remains rather rare [7], particularly for clusters with more than three metal atoms. A further feature of these structures, is, as expected, the close similarity of the bond lengths and angles, (which is in marked contrast to the appreciable differences between the related platinum and palladium amide clusters $[M_3\{\mu\text{-Sn}\{N(\text{SiMe}_3)_2\}_2\}_3(\text{CO})_3]$ [8]). In both structures the M–M distances are considerably greater than those in the corresponding parent carbonyls, the effect being greater for a tin than for a carbonyl bridge (e.g., $\langle\text{Os–Os}\rangle$ 2.967, 2.981 (tin bridged); 2.893 Å (carbonyl bridged)). The substituents on the tin metals are oriented essentially perpendicular to the metal plane, and the proton NMR spectrum in both cases reveals that the methyl groups on Si are diastereotopic. Lists of atomic coordinates and of bond lengths and angles for the ruthenium compound are given in Tables 3 and 4 respectively, and the list of atomic coordinates for the osmium species in Table 5. A list of bond lengths and angles for the latter has been deposited with the Cambridge Crystallographic Data Centre.

The product from the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with $[\text{SnR}_2]$ reveals non-diastereotopic methyl groups on Si (^1H NMR), and is similar in colour, IR and ^1H NMR

(Continued on p. 211)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR $[\text{Ru}_3(\text{CO})_{10}(\text{SnR}_2)_2]$ (R = CH(SiMe₃)₂)

Ru(1)–Ru(2)	2.964(1)		
Ru(1)–Ru(3)	2.880(2)		
Ru(2)–Ru(1)–Ru(3)	60.62(4)	Ru(3)–Ru(1)	2.880(2)
Ru(1)–Sn(1)	2.739(2)	Ru(3)–Ru(2)	2.950(2)
Ru(2)–Ru(1)–Sn(1)	57.16(4)	Ru(1)–Ru(3)–Ru(2)	61.09(4)
Ru(3)–Ru(1)–Sn(1)	117.74(4)	Ru(3)–Sn(2)	2.739(1)
Ru(1)–C(1)	1.954(15)	Ru(1)–Ru(3)–Sn(2)	118.38(10)
Ru(2)–Ru(1)–C(1)	90.66(40)	Ru(2)–Ru(3)–Sn(2)	57.29(4)
Ru(3)–Ru(1)–C(1)	93.34(60)	Ru(3)–C(7)	1.924(13)
Sn(1)–Ru(1)–C(1)	89.45(50)	Ru(1)–Ru(3)–C(7)	93.17(50)
Ru(1)–C(2)	1.899(16)	Ru(2)–Ru(3)–C(7)	90.83(50)
Ru(2)–Ru(1)–C(2)	163.68(60)	Sn(2)–Ru(3)–C(7)	88.32(40)
Ru(3)–Ru(1)–C(2)	135.70(60)	Ru(3)–C(8)	1.879(19)
Sn(1)–Ru(1)–C(2)	106.54(60)	Ru(1)–Ru(3)–C(8)	139.10(50)
C(1)–Ru(1)–C(2)	88.18(60)	Ru(2)–Ru(3)–C(8)	159.74(50)
Ru(1)–C(3)	1.938(13)	Sn(2)–Ru(3)–C(8)	102.48(50)
Ru(2)–Ru(1)–C(3)	92.05(40)	C(7)–Ru(3)–C(8)	89.53(70)
Ru(3)–Ru(1)–C(3)	93.02(50)	Ru(3)–C(9)	1.966(14)
Sn(1)–Ru(1)–C(3)	87.17(40)	Ru(1)–Ru(3)–C(9)	89.77(60)
C(1)–Ru(1)–C(3)	173.63(80)	Ru(2)–Ru(3)–C(9)	89.66(50)
C(2)–Ru(1)–C(3)	87.60(60)	Sn(2)–Ru(3)–C(9)	89.34(40)
Ru(1)–C(10)	2.132(17)	C(7)–Ru(3)–C(9)	176.87(70)
Ru(2)–Ru(1)–C(10)	107.60(40)	C(8)–Ru(3)–C(9)	88.94(70)
Ru(3)–Ru(1)–C(10)	47.06(40)	Ru(3)–C(10)	2.115(13)
Sn(1)–Ru(1)–C(10)	164.75(40)	Ru(1)–Ru(3)–C(10)	47.55(50)
C(1)–Ru(1)–C(10)	90.39(70)	Ru(2)–Ru(3)–C(10)	108.57(50)
C(2)–Ru(1)–C(10)	88.70(70)	Sn(2)–Ru(3)–C(10)	165.71(50)
C(3)–Ru(1)–C(10)	94.28(60)	C(7)–Ru(3)–C(10)	90.01(70)
		C(8)–Ru(3)–C(10)	91.69(70)
		C(9)–Ru(3)–C(10)	92.77(50)
Ru(2)–Ru(1)	2.964(1)		
Ru(2)–Ru(3)	2.950(2)		
Ru(1)–Ru(2)–Ru(3)	58.29(4)	Sn(1)–Ru(1)	2.739(2)
Ru(2)–Sn(1)	2.735(2)	Sn(1)–Ru(2)	2.735(2)
Ru(1)–Ru(1)–Sn(1)	57.28(4)	Ru(1)–Sn(1)–Ru(2)	65.56(4)
Ru(3)–Ru(2)–Sn(1)	115.53(4)	Sn(1)–C(11)	2.173(31)
Ru(2)–Sn(2)	2.733(2)	Ru(1)–Sn(1)–C(11)	124.17(60)
Ru(1)–Ru(2)–Sn(2)	115.76(10)	Ru(2)–Sn(1)–C(11)	126.41(60)
Ru(3)–Ru(2)–Sn(2)	57.47(4)	Sn(1)–C(18)	2.220(19)
Sn(1)–Ru(2)–Sn(2)	172.57(4)	Ru(1)–Sn(1)–C(18)	115.60(60)
Ru(2)–C(4)	1.929(14)	Ru(2)–Sn(1)–C(18)	116.04(70)
Ru(1)–Ru(2)–C(4)	88.69(40)	C(11)–Sn(1)–C(18)	105.36(100)
Ru(3)–Ru(2)–C(4)	88.15(50)		
Sn(1)–Ru(2)–C(4)	92.44(50)	Sn(2)–Ru(2)	2.733(2)
Sn(2)–Ru(2)–C(4)	89.87(50)	Sn(2)–Ru(3)	2.739(1)
Ru(2)–C(5)	1.862(14)	Ru(2)–Sn(2)–Ru(3)	65.24(4)
Ru(1)–Ru(2)–C(5)	148.85(70)	Sn(2)–C(25)	2.211(15)
Ru(3)–Ru(2)–C(5)	152.74(70)	Ru(2)–Sn(2)–C(25)	119.66(60)
Sn(1)–Ru(2)–C(5)	91.72(70)	Ru(3)–Sn(2)–C(25)	113.35(40)
Sn(2)–Ru(2)–C(5)	95.35(70)	Sn(2)–C(32)	2.200(21)
C(4)–Ru(2)–C(5)	89.78(70)	Ru(2)–Sn(2)–C(32)	120.02(60)
Ru(2)–C(6)	1.922(15)	Ru(3)–Sn(2)–C(32)	121.18(40)
Ru(1)–Ru(2)–C(6)	89.58(40)	C(25)–Sn(2)–C(32)	110.72(80)
Ru(3)–Ru(2)–C(6)	89.42(50)		

continued

TABLE 3 (continued)

Sn(1)–Ru(2)–C(6)	88.12(60)	Si(1)–C(32)	1.845(22)
Sn(2)–Ru(2)–C(6)	89.27(60)	Si(1)–C(33)	1.881(33)
C(32)–Si(1)–C(33)	111.35(110)	C(11)–Si(6)–C(15)	121.16(160)
Si(1)–C(34)	1.917(17)	Si(6)–C(16)	1.831(43)
C(32)–Si(1)–C(34)	116.78(90)	C(11)–Si(6)–C(16)	114.82(130)
C(33)–Si(1)–C(34)	105.04(100)	C(15)–Si(6)–C(16)	120.03(160)
Si(1)–C(35)	1.899(22)		
C(32)–Si(1)–C(35)	108.89(130)	Si(7)–C(18)	1.799(20)
C(33)–Si(1)–C(35)	107.36(120)	Si(7)–C(22)	2.005(50)
C(340)–Si(1)–C(35)	106.96(100)	C(18)–Si(7)–C(22)	107.70(120)
		Si(7)–C(23)	1.801(35)
Si(2)–C(32)	1.840(15)	C(18)–Si(7)–C(23)	121.60(140)
Si(2)–C(36)	1.831(43)	C(22)–Si(7)–C(23)	97.42(200)
C(32)–S(12)–C(36)	111.20(120)	Si(7)–C(24)	1.879(19)
Si(2)–C(37)	1.767(34)	C(18)–Si(7)–C(24)	114.86(100)
C(32)–Si(2)–C(37)	110.66(120)	C(22)–Si(7)–C(24)	106.55(140)
C(36)–Si(2)–C(37)	106.93(190)	C(23)–Si(7)–C(24)	106.46(140)
Si(2)–C(38)	1.837(44)		
C(32)–Si(2)–C(38)	117.09(120)	Si(8)–C(18)	1.877(21)
C(36)–Si(2)–C(38)	102.82(180)	Si(8)–C(19)	1.772(31)
C(37)–Si(2)–C(38)	107.45(180)	C(18)–Si(8)–C(19)	116.84(140)
		Si(8)–C(20)	1.716(32)
Si(3)–C(25)	1.832(23)	C(18)–Si(8)–C(20)	120.39(120)
Si(3)–C(26)	1.983(33)	C(19)–Si(8)–C(20)	119.64(130)
C(25)–Si(3)–C(26)	108.61(140)	Si(8)–C(21)	2.196(65)
Si(3)–C(27)	1.876(20)	C(18)–Si(8)–C(21)	95.21(200)
C(25)–Si(3)–C(27)	114.36(110)	C(19)–Si(8)–C(21)	98.11(290)
C(26)–Si(3)–C(27)	104.27(110)	C(20)–Si(8)–C(21)	94.43(230)
Si(8)–C(28)	1.820(27)		
C(25)–Si(3)–C(28)	113.88(120)	O(1)–C(1)	1.101(18)
C(26)–Si(3)–C(28)	106.68(200)		
C(27)–Si(3)–C(28)	108.33(130)	O(2)–C(2)	1.134(19)
		O(3)–C(3)	1.124(16)
Si(4)–C(25)	1.889(18)		
Si(4)–C(29)	1.910(20)	O(4)–C(4)	1.140(17)
C(25)–Si(4)–C(29)	115.03(100)		
Si(4)–C(30)	1.869(26)	O(5)–C(5)	1.143(17)
C(25)–Si(4)–C(30)	116.13(90)		
C(29)–Si(4)–C(30)	104.52(100)	O(6)–C(6)	1.133(18)
Si(4)–C(31)	1.911(23)		
C(25)–Si(4)–C(31)	106.39(100)	O(7)–C(7)	1.145(17)
C(29)–Si(4)–C(31)	109.03(100)		
C(30)–Si(4)–C(31)	105.21(100)	O(8)–C(8)	1.137(24)
Si(5)–C(11)	1.856(26)	O(9)–C(9)	1.107(18)
Si(5)–C(12)	1.845(26)		
C(11)–Si(5)–C(12)	116.73(140)	O(10)–C(10)	1.161(16)
Si(5)–C(13)	1.818(44)		
C(11)–Si(5)–C(13)	113.01(130)	C(1)–Ru(1)	1.954(15)
C(12)–Si(5)–C(13)	107.20(140)	C(1)–O(1)	1.101(18)
Si(5)–C(14)	2.036(30)	Ru(1)–C(1)–O(1)	176.08(120)
C(11)–Si(5)–C(14)	111.11(130)		
C(12)–Si(5)–C(14)	101.65(120)		
C(13)–Si(5)–C(14)	106.07(170)		

TABLE 3 (continued)

		C(2)–Ru(1)	1.899(16)
		C(2)–O(2)	1.134(19)
Si(6)–C(11)	1.880(21)	Ru(1)–C(2)–O(2)	176.35(140)
Si(6)–C(15)	1.724(29)		
		C(3)–Ru(1)	1.938(13)
C(3)–O(3)	1.124(16)	C(18)–Si(8)	1.877(27)
Ru(1)–C(3)–O(3)	176.91(160)	Sn(1)–C(18)–Si(8)	120.49(90)
		Si(7)–C(18)–Si(8)	115.11(120)
C(4)–Ru(2)	1.929(14)		
C(4)–O(4)	1.140(17)	C(19)–Si(8)	1.772(31)
Ru(2)–C(4)–O(4)	177.56(110)		
		C(20)–Si(8)	1.716(32)
C(5)–Ru(2)	1.862(14)		
C(5)–O(5)	1.143(17)	C(21)–Si(8)	2.196(65)
Ru(2)–O(5)–O(5)	179.22(150)		
		C(22)–Si(7)	2.005(50)
C(6)–Ru(2)	1.922(15)		
C(6)–O(6)	1.133(18)	C(23)–Si(7)	1.801(35)
Ru(2)–C(6)–O(6)	179.17(130)		
		C(24)–Si(7)	1.879(19)
C(7)–Ru(3)	1.924(13)		
C(7)–O(7)	1.145(17)	C(25)–Sn(2)	2.211(15)
Ru(3)–C(7)–O(7)	177.87(130)	C(25)–Si(3)	1.832(23)
		Sn(2)–O(25)–Si(3)	116.73(10)
C(8)–Ru(3)	1.879(19)	C(25)–Si(4)	1.889(18)
C(8)–O(3)	1.137(24)	Sn(2)–C(25)–Si(4)	124.57(100)
Ru(3)–C(3)–O(8)	175.19(140)	Si(3)–C(25)–Si(4)	114.41(80)
		C(26)–Si(3)	1.983(33)
C(9)–Ru(3)	1.966(14)		
C(9)–O(9)	1.107(18)	C(27)–Si(3)	1.876(20)
Ru(3)–C(9)–O(9)	174.89(160)		
		C(28)–Si(3)	1.820(27)
C(10)–Ru(1)	2.132(17)		
C(10)–Ru(3)	2.115(13)	C(29)–Si(4)	1.910(20)
Ru(1)–C(10)–Ru(3)	85.39(50)		
C(10)–O(10)	1.161(16)	C(30)–Si(4)	1.869(26)
Ru(1)–C(10)–O(10)	137.91(140)		
Ru(3)–C(10)–O(10)	136.69(150)	C(31)–Si(4)	1.911(23)
C(11)–Sn(1)	2.173(31)	C(32)–Sn(2)	2.200(21)
C(11)–Si(5)	1.856(26)	C(32)–Si(1)	1.845(22)
Sn(1)–C(11)–Si(5)	121.68(100)	Sn(2)–C(32)–Si(1)	125.80(70)
C(11)–Si(6)	1.880(21)	C(32)–Si(2)	1.840(15)
Sn(1)–C(11)–Si(6)	120.23(14)	Sn(2)–C(32)–Si(2)	116.27(110)
Si(5)–C(11)–Si(6)	112.20(150)	Si(1)–C(32)–Si(2)	117.84(100)
C(12)–Si(5)	1.845(20)	C(33)–Si(1)	1.881(33)
C(13)–Si(5)	1.818(44)	C(34)–Si(1)	1.917(17)
C(14)–Si(5)	2.036(30)	C(35)–Si(1)	1.899(22)
C(15)–Si(6)	1.724(29)	C(36)–Si(2)	1.831(43)
C(16)–Si(6)	1.831(43)	C(37)–Si(2)	1.767(34)
C(18)–Sn(1)	2.220(19)	C(38)–Si(2)	1.837(44)
C(18)–Si(7)	1.799(20)		
Sn(1)–C(18)–Si(7)	119.98(100)		

TABLE 4

ATOMIC COORDINATES FOR $[\text{Ru}_3(\text{CO})_{10}(\text{SnR}_2)_2]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$)

Atom	x	y	z
Ru(1)	0.89084(10)	0.76754(10)	0.60042(10)
Ru(2)	0.72738(10)	0.82535(10)	0.73688(10)
Ru(3)	0.73520(10)	0.78444(10)	0.57094(10)
Sn(1)	0.88274(10)	0.81466(10)	0.75521(10)
Sn(2)	0.58635(10)	0.84030(10)	0.69878(10)
Si(1)	0.56989(40)	1.10123(40)	0.64657(30)
Si(2)	0.50790(40)	1.08232(50)	0.82782(30)
Si(3)	0.39266(30)	0.67603(50)	0.65292(30)
Si(4)	0.39425(30)	0.62241(40)	0.80791(30)
Si(5)	0.96308(40)	0.57466(60)	0.75885(40)
Si(6)	0.79473(40)	0.63547(80)	0.90478(40)
Si(7)	1.09354(40)	1.01213(60)	0.75317(30)
Si(8)	0.92195(50)	1.08921(70)	0.88665(40)
O(1)	0.81851(80)	0.49904(90)	0.60840(80)
O(2)	1.07521(70)	0.70875(110)	0.49604(70)
O(3)	0.98815(70)	1.03308(90)	0.59361(60)
O(4)	0.64232(80)	0.55571(90)	0.73998(70)
O(5)	0.62977(80)	0.87172(150)	0.91382(60)
O(6)	0.81222(80)	1.09232(90)	0.72751(70)
O(7)	0.64091(80)	0.51707(90)	0.57576(70)
O(8)	0.68525(100)	0.76768(110)	0.42855(60)
O(9)	0.81840(80)	1.05323(90)	0.56161(70)
O(10)	0.89541(80)	0.70768(110)	0.42667(60)
C(1)	0.84211(90)	0.59659(130)	0.60798(90)
C(2)	1.00767(110)	0.73363(130)	0.53663(90)
C(3)	0.95029(90)	0.93622(120)	0.59605(80)
C(4)	0.67538(90)	0.65525(130)	0.73723(80)
C(5)	0.66744(110)	0.85469(170)	0.84657(90)
C(6)	0.78055(100)	0.99351(130)	0.73160(90)
C(7)	0.67577(90)	0.61719(120)	0.57552(80)
C(8)	0.70011(110)	0.77335(130)	0.48425(80)
C(9)	0.78937(100)	0.95695(120)	0.56736(80)
C(10)	0.86077(90)	0.73753(120)	0.49449(80)
C(11)	0.89277(150)	0.68728(220)	0.81422(140)
C(12)	1.04080(160)	0.59354(250)	0.65615(160)
C(13)	1.03203(190)	0.56162(290)	0.81101(200)
C(14)	0.88159(260)	0.40758(260)	0.74135(190)
C(15)	0.68213(170)	0.59454(340)	0.90811(180)
C(16)	0.82694(180)	0.57735(340)	0.96884(170)
C(17)	0.79444(280)	0.84462(760)	0.98363(180)
C(18)	0.97007(130)	0.98948(190)	0.79079(130)
C(19)	0.97514(160)	1.12018(330)	0.95840(130)
C(20)	0.81262(180)	1.10883(250)	0.91577(150)
C(21)	0.98990(460)	1.25756(390)	0.83768(550)
C(22)	1.12598(200)	0.92874(410)	0.81495(180)
C(23)	1.16798(240)	1.15782(330)	0.76926(270)
C(24)	1.14443(120)	0.94821(240)	0.64524(120)
C(25)	0.46072(110)	0.69222(160)	0.71453(100)
C(26)	0.31993(200)	0.80032(250)	0.69909(230)
C(27)	0.30381(150)	0.53010(190)	0.65158(130)
C(28)	0.46195(190)	0.69721(400)	0.55049(150)
C(29)	0.27252(120)	0.64727(220)	0.86332(120)
C(30)	0.44889(130)	0.67051(280)	0.88574(130)

TABLE 4 (continued)

Atom	x	y	z
C(31)	0.38700(170)	0.45370(190)	0.77588(180)
C(32)	0.55204(150)	1.01457(150)	0.72251(90)
C(33)	0.46115(180)	1.14319(230)	0.66260(140)
C(34)	0.60908(130)	1.02429(170)	0.53773(100)
C(35)	0.66032(180)	1.24648(180)	0.65501(190)
C(36)	0.59762(240)	1.12943(330)	0.87237(180)
C(37)	0.41651(280)	0.97730(350)	0.88348(180)
C(38)	0.46800(280)	1.22014(310)	0.84970(160)

spectra, and m.p. to the product from $[\text{Fe}_2(\text{CO})_9]$ formulated as $[\text{Fe}_2(\text{CO})_8(\mu\text{-SnR}_2)]$ [4]. However, the compound obtained from the reaction of $[\text{Fe}_3(\text{CO})_{11}(\text{MeCN})]$ [6b] with the tin reagent is a second orange crystalline material with the composition $[\text{Fe}_2(\mu\text{-SnR}_2)_2(\text{CO})_6]$, whose structure, determined by a single crystal X-ray study is shown in Fig. 2. Full structural details will be reported elsewhere [9]. Whether the Fe_2Sn compound is formed by $[\text{SnR}_2]$ elimination from this molecule has not been established, but we have observed such eliminations at moderate temperatures from other clusters [6b].

We note here that the structure is markedly different from that of $[\text{Fe}_2(\mu\text{-SnMe}_2)_2(\text{CO})_8]$ [10], both in stoichiometry, and structure, as shown in Fig. 3(a) and (b). In the latter molecule (Fig. 3(a)), the SnMe_2 groups allow a closer approach of the tin atoms, and the irons acquire an 18-electron configuration from coordination by the carbonyls and bridging tin groups. In the present case, however, the bulky R substituents on tin presumably preclude such a close approach, allowing the

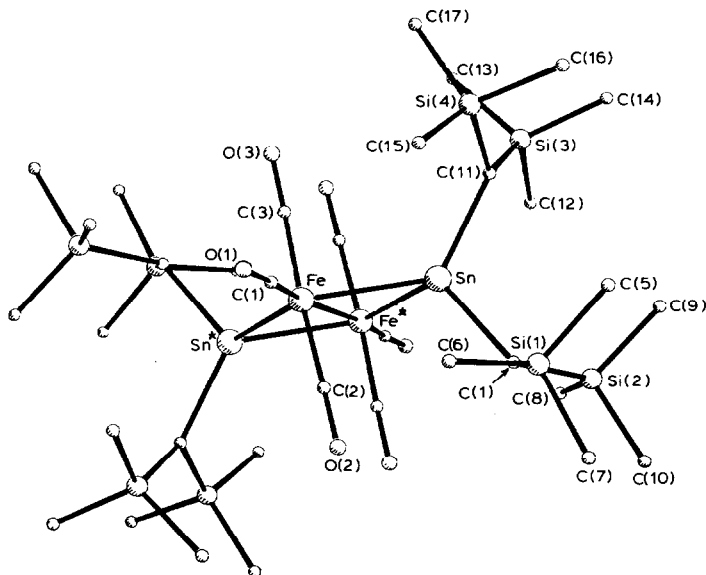


Fig. 2. A molecule of $[\text{Fe}_2(\text{CO})_6(\text{SnR}_2)_2]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$).

TABLE 5

ATOMIC COORDINATES FOR $[\text{Os}_3(\text{CO})_{10}(\text{SnR}_2)_2]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$)

Atom	x	y	z
Os(1)	0.0019(0)	0.1501(0)	0.4764(0)
Os(2)	-0.0973(0)	0.1785(0)	0.3213(0)
Os(3)	-0.1941(0)	0.1462(0)	0.4219(0)
Sn(1)	0.0880(8)	0.1839(5)	0.3831(6)
Sn(2)	-0.2806(7)	0.1753(5)	0.2821(5)
C(11)	0.1528(133)	0.2717(82)	0.3943(93)
Si(1)	0.1386(56)	0.3138(39)	0.3025(41)
C(12)	0.0223(56)	0.2981(39)	0.2389(41)
C(13)	0.2164(56)	0.3248(39)	0.2504(41)
C(14)	0.1369(56)	0.3828(39)	0.3550(41)
Si(2)	0.2359(49)	0.2978(29)	0.4793(36)
C(15)	0.2525(49)	0.2581(29)	0.5661(36)
C(16)	0.2055(49)	0.3772(29)	0.4877(36)
C(17)	0.3424(49)	0.2947(29)	0.4581(36)
C(18)	0.1880(112)	0.1430(77)	0.3618(83)
Si(3)	0.1479(57)	0.0840(38)	0.2586(42)
C(19)	0.0612(57)	0.1208(38)	0.1806(42)
C(20)	0.1117(57)	0.0061(38)	0.2679(42)
C(21)	0.2583(57)	0.0826(38)	0.2431(42)
Si(4)	0.2752(38)	0.0851(25)	0.4224(30)
C(22)	0.3108(38)	0.1142(25)	0.5166(30)
C(23)	0.3754(38)	0.0810(25)	0.3925(30)
C(24)	0.2256(38)	0.0091(25)	0.4191(30)
C(25)	-0.3535(146)	0.2587(88)	0.2682(103)
Si(5)	-0.3472(51)	0.3179(36)	0.1949(36)
C(26)	-0.4164(51)	0.3832(36)	0.2032(36)
C(27)	-0.4085(51)	0.2761(36)	0.1105(36)
C(28)	-0.2365(51)	0.3445(36)	0.1914(36)
Si(6)	-0.4541(51)	0.2277(32)	0.7883(38)
C(29)	-0.4328(51)	0.1528(32)	0.8320(38)
C(30)	-0.5369(51)	0.2205(32)	0.6949(38)
C(31)	-0.5008(51)	0.2786(32)	0.8416(38)
C(32)	-0.3692(188)	0.1229(115)	0.2096(142)
Si(7)	-0.3393(47)	0.1043(29)	0.1169(33)
C(33)	-0.2881(47)	0.1701(29)	0.0878(33)
C(34)	-0.4346(47)	0.0751(29)	0.0387(33)
C(35)	-0.2520(47)	0.0449(29)	0.1510(33)
Si(8)	-0.4255(59)	0.0533(36)	0.2235(40)
C(36)	-0.4526(59)	0.0617(36)	0.3079(40)
C(37)	-0.3378(59)	-0.0057(36)	0.2364(40)
C(38)	-0.5297(59)	0.0317(36)	0.1478(40)
O(1)	0.0033(65)	0.0168(43)	0.4328(48)
O(2)	0.1434(73)	0.1237(39)	0.6064(50)
O(3)	0.0049(100)	0.2840(65)	0.5170(71)
O(4)	-0.1095(104)	0.3120(80)	0.3643(80)
O(5)	-0.0970(62)	0.2240(41)	0.1761(48)
O(6)	-0.0838(68)	0.0499(47)	0.2809(51)
O(7)	-0.1584(68)	0.0126(44)	0.3907(47)
O(8)	-0.3357(118)	0.1175(72)	0.4891(90)
O(9)	-0.2289(98)	0.2821(68)	0.4528(71)
O(10)	-0.1116(67)	0.1085(44)	0.5281(51)
C(1)	0.0208(114)	0.0746(71)	0.4721(81)
C(2)	0.0685(124)	0.1373(62)	0.5473(90)

TABLE 5 (continued)

Atom	x	y	z
C(3)	0.0087(147)	0.2300(88)	0.5049(104)
C(4)	-0.1122(114)	0.2774(76)	0.3402(85)
C(5)	-0.0990(97)	0.1932(61)	0.2320(75)
C(6)	-0.0891(108)	0.0844(74)	0.2990(79)
C(7)	-0.1779(90)	0.0622(58)	0.4003(68)
C(8)	-0.2986(107)	0.1256(68)	0.4439(84)
C(9)	-0.2379(135)	0.2331(89)	0.4409(98)
C(10)	-0.1088(102)	0.1529(77)	0.4710(77)

iron-iron distance to shorten, and these atoms acquire an 18-electron configuration from a combination of carbonyl, bridging tin, and Fe-Fe interactions. Such indirect steric control of metal-metal bond formation is reminiscent of the different behaviour of $[\{\text{CpMo}(\text{CO})_3\}_2]$ when Cp = pentamethylcyclopentadienyl (ready elimination of CO and Mo≡Mo bond formation) from when Cp = cyclopentadienyl [11].

Experimental

All manipulations were carried out under pure, dry nitrogen or argon, using dried distilled solvents.

Preparation of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-SnR}_2)_2]$ from $[\text{Ru}_3(\text{CO})_{12}]$

Treatment of a solution of ruthenium dodecacarbonyl in n-octane with 2 moles of bis{bis(trimethylsilyl)methyl}tin in the same solvent (1.5 h) gave a red-orange solution. Concentration, filtration, extraction into hexane, and cooling of the extract to -20°C gave crystals of the product, which was recrystallised from hexane. Yield from reaction at 20°C , 83%; from reaction at 90°C , 14%. The cluster has m.p. $141\text{--}143^\circ\text{C}$ (dec.). Found: C, 31.82; H, 4.97; $\text{C}_{38}\text{H}_{76}\text{O}_{10}\text{Ru}_3\text{Si}_8\text{Sn}_2$ calc: C, 31.30; H, 5.25%. ^1H NMR (CDCl_3): δ (ppm): 1.247 (s,4H), 0.383 (s,36H), 0.355 (s,36H). IR (KBr disc, cm^{-1}): 2100s, 2066s, 2046vs, 2021vs, 2016vs, 2000s, 1984vs, 1856s.

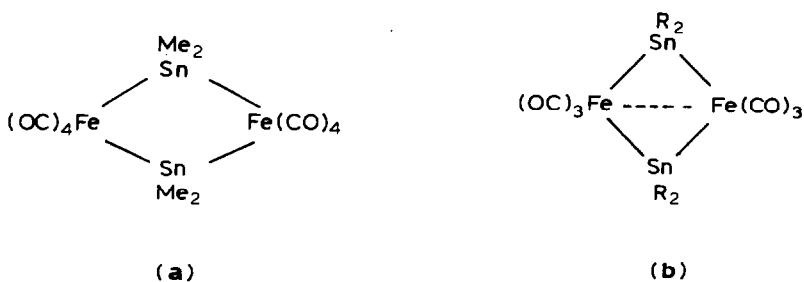


Fig. 3. Structures of (a) $\text{Fe}_2(\mu\text{-SnMe}_2)(\text{CO})_8$ and (b) $\text{Fe}_2(\mu\text{-SnR}_2)_2(\text{CO})_6$, showing respectively the short tin-tin and iron-iron vectors ($\text{R} = \text{CH}(\text{SiMe}_3)_2$).

Preparation of [Ru₃(CO)₁₀(μ-SnR₂)₂] from [Ru₃(CO)₁₀(MeCN)₂]

Addition of [SnR₂] (0.248 mmol) in toluene (50 cm³) at ambient temperature to the ruthenium reagent (0.124 mmol) in the same solvent (100 cm³) and stirring (1 h) followed by evaporation to dryness, extraction of the residue with hexane (2 × 50 cm³ aliquots), cooling of the extract to -23 °C and filtration gave the product (90%) as red-orange crystals: Found: C, 31.68; H, 5.36; C₃₈H₇₆O₁₀Ru₃Si₈Sn₂ calc: C, 31.30; H, 5.25%, identical to those obtained as above.

Preparation of [Os₃(CO)₁₀(μ-SnR₂)₂]

The procedure used in the previous experiment afforded the product in 98% yield, ¹H NMR (CDCl₃) δ (ppm): 1.40 (s,4H), 0.26 (s,36H), 0.29 (s,36H). IR (KBr disc, cm⁻¹): 2075m, 2025s, 2018s, 1995s,sh, 1985s,br, 1970s, 1962s, 1783s.

Preparation of [Fe₂(CO)₈(μ-SnR₂)₂]

To iron dodecacarbonyl (1 mmol) in hexane (200 cm³) a solution of [SnR₂] (1.1 mmol) in the same solvent (50 cm³) was added dropwise with stirring, at ambient temperature. After stirring under reflux (for 24 h), the brown-orange solution was pumped to dryness, and the residue extracted with hexane. The extract was chromatographed on silica (hexane eluent), and the major red-orange band collected. After removal of solvent under vacuum, the solid was recrystallised from ethyl acetate to give the orange crystalline product (28%), m.p. 133–135 °C (dec.). Found: C, 33.91; H, 4.92; C₂₂H₃₈Fe₂O₈Si₄Sn calc: C, 34.17; H, 4.95%. IR (KBr disc, cm⁻¹) 2086m, 2035s, 2019m, 2003sh, 1999s, 1987w.

Preparation of [Fe₂(CO)₆(μ-SnR₂)₂]

To a degassed solution of [Fe₃(CO)₁₁(MeCN)] (0.50 mmol) in toluene (100 cm³), a solution of [SnR₂] (0.50 mmol) in toluene (25 cm³) was added dropwise with stirring at -70 °C. The solution was allowed to reach 0 °C, and solvent removed under vacuum at that temperature. The residual orange-red solid was extracted into hexane (2 × 50 cm³), and the extract filtered, then stored at -27 °C. Orange red crystals were collected, m.p. > 150 °C (contrast material in the previous experiment) and characterised by X-ray analysis (see text).

Acknowledgements

We thank Cork Co. Council and the Kriebel Fund for maintenance awards (to J.M.P.), Prof. G.M. Sheldrick (University of Göttingen) for the use of his programmes SHELX 76 and SHELX 84, P.R. Raithby for generous use of diffractometer time for the iron structure, and Johnson-Matthey PLC for generous loans of osmium.

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