Notes

Synthesis and Structure of $[Os(CO)_4(SnPh_2)]_6$: A Compound with an Unprecedented 12-Membered Ring of Metal Atoms

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*Summary: The compound $[Os(CO)_4(SnPh_2)]_6$ (**1**) has been isolated as one product from the reaction of $Na_2[Os(CO)_4]$ and Ph_2SnCl_2 in THF. The X-ray structure of **1** reveals it possesses an approximately planar 12-membered ring of alternating tin and osmium atoms. Carbon-13 NMR spectroscopy indicates there is free rotation about the Os−Sn bonds in **1** in solution so as to render all the carbonyl ligands equivalent.*

Introduction

The structural motifs exhibited by molecules with group 8 metals and the heavier 14 elements are many and diverse.[1] Recent work from this laboratory has described the synthesis and structure of several Os−Ge and Os−Sn clusters with various skeletal geometries.[2,3] One of these, $Os_4(SnMe_2)_4(CO)_{14}$, was envisaged as the result of dimerization of $Os_2(SnMe_2)_2(CO)_7$, which in turn was the product of loss of CO from the precursor $[Os(CO)_4(SnMe_2)]_2$.[2] In order to prevent the dimerization, we sought to prepare derivatives of the type $[Os(CO)_4(SnR_2)]_2$, where R was a more bulky organic substituent than the methyl group. In our attempt to synthesize the phenyl compound from the reaction of $[Os(CO)_4]^{2-}$ and Ph_2SnCl_2, not only was the expected product obtained but also $[Os(CO)_4(SnPh_2)]_6$. Herein, we describe the latter product, the crystal structure of which shows it to contain an unprecedented ring of 12 metal atoms.

Results and Discussion

At least three Os-containing products are formed in the reaction of $[Os(CO)_4]^{2-}$ with Ph_2SnCl_2 in THF at or below room temperature. A ^{13}C NMR spectrum in the carbonyl region of the unseparated products of the reaction, which used ^{13}CO-enriched $[Os(CO)_4]^{2-}$, is shown in Figure 1. Two of the products, $[Os(CO)_4(SnPh_2)]_2$ (**2**) and $[Os(CO)_4(SnPh_2)]_6$ (**1**), have been isolated and characterized (eq 1). The identity of the

$$[Os(CO)_4]^{2-} + Ph_2SnCl_2 \xrightarrow{<25\ °C} \underset{\mathbf{2}}{[Os(CO)_4(SnPh_2)]_2} + \underset{\mathbf{1}}{[Os(CO)_4(SnPh_2)]_6} + \text{other product(s)} \quad (1)$$

other product(s) is unknown, but the similarity of its ^{13}C NMR spectrum to that of **1** suggests it is also a cyclic oligomer of $Os(CO)_4(SnPh_2)$ (see Figure 1). Compound **2** with a planar four-membered ring of metal atoms was the expected product. It has been found that reactions of $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) with R_2ECl_2 (E = Ge, Sn, Pb; R = Me, Bu^t) yield analogous derivatives with M_2E_2 units.[2−5] The spectroscopic properties of **2** are unremarkable.

Problems were encountered in the separation of the hexameric product **1** from the other products in the reaction; it was, however, found that **1** could be separated from **2** by size-exclusion chromatography. Although yields of **1** were estimated spectroscopically (Figure 1) to be about 10%, only small samples of pure **1** have thus far been isolated, by fractional crystallization from the unknown product(s). Several unsuccessful attempts were made to grow crystals of sufficient size to determine the structure of **1** on a conventional X-ray diffractometer. The structure of **1** was eventually determined on an extremely small, platelike crystal with an X-ray diffractometer equipped with a charge coupled device (CCD) area detector. The structure determination was carried out with the crystal at −100 °C to limit decomposition that was found to occur when crystals of **1** were exposed to X-rays at room temperature.

A view of the molecule, which has a crystallographic center of inversion, is shown in Figure 2. As can be seen from the figure, **1** has an approximately planar ring of 12 metal atoms, which, to our knowledge, is an unprec-

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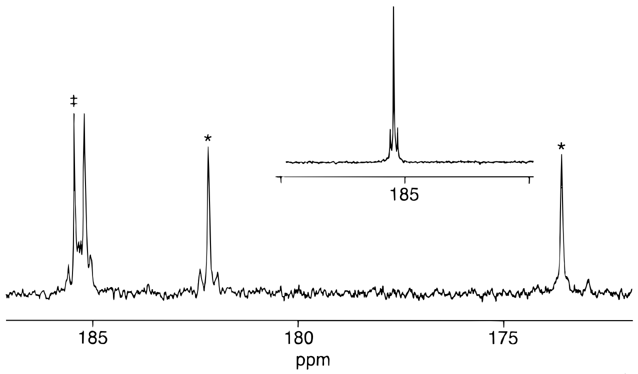

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of the products of the reaction given in eq 1. The signals marked with an asterisk are due to **2**, and the resonance to lowest field at δ 185.4 (marked ‡) is due to **1**. Inset: spectrum (0.6 scale) of pure **1**. The signal at δ 185.2 is due to an unidentified product.

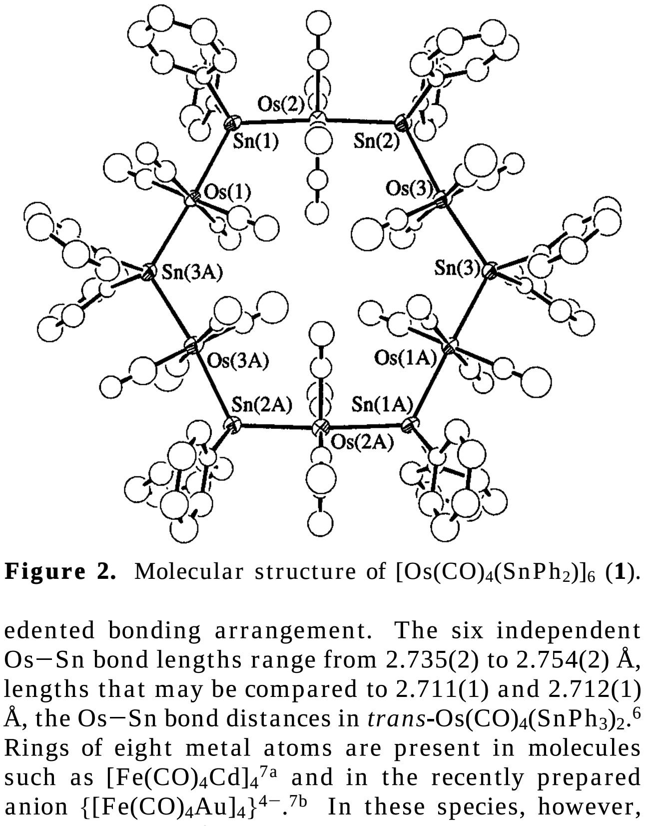

Figure 2. Molecular structure of $[Os(CO)_4(SnPh_2)]_6$ (**1**).

edented bonding arrangement. The six independent Os—Sn bond lengths range from 2.735(2) to 2.754(2) Å, lengths that may be compared to 2.711(1) and 2.712(1) Å, the Os—Sn bond distances in *trans*-$Os(CO)_4(SnPh_3)_2$.[6] Rings of eight metal atoms are present in molecules such as $[Fe(CO)_4Cd]_4$[7a] and in the recently prepared anion $\{[Fe(CO)_4Au]_4\}^{4-}$.[7b] In these species, however, the orientation of the metal atoms about an individual (six-coordinate) iron atom is *cis*, whereas the Sn—Os—Sn arrangement in **1** is *trans*.

The *trans* configuration of the $OsSn_2$ units in **1** and the corresponding *cis* configuration in **2** suggests that the formation of these products occurs via the *trans* and *cis* forms of $Os(CO)_4(SnPh_2Cl)_2$, respectively. It has been previously established for complexes of the type $M(CO)_4(ER_{3-x}Cl_x)_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn; R = organic group) that the trans isomer is favored for M = Os,[6,8,9] R = bulky group,[6,10] and $x = 3$ (i.e., for the electron-withdrawing ECl_3 ligands).[8,9,11] Furthermore, interconversion of the *cis* and *trans* forms of complexes such as $Os(CO)_4(SiMeCl_2)_2$ is sufficiently slow that the two isomers may be separated at room temperature.[8] The preponderance of the *cis* form combined with more rapid *cis*—*trans* isomerization in $Os(CO)_4(SnR_2Cl)_2$ may explain why only the dimeric derivatives were observed in the reaction of $[Os(CO)_4]^{2-}$ with the corresponding R_2SnCl_2 (R = Me, Bu^t).[2,4] Furthermore, we have found no evidence for the Ge, or Pb, analogue of **1** in the reaction of Ph_2GeCl_2, or Ph_2PbCl_2, with the osmium anion. It may be that the formation of the germanium derivative is prevented due to increased across-ring repulsions arising from the shorter Os—Ge bonds. From the view of **1** with space-filling atoms shown in Figure 3, it is apparent the oxygen atoms of the carbonyl ligands attached to adjacent osmium atoms make close approach to one another.

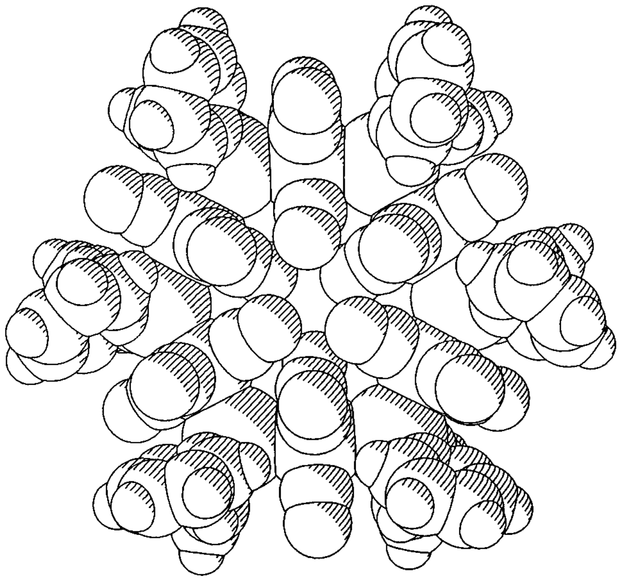

Figure 3. View of **1** with space-filling atoms.

Despite the close approach of the carbonyls of **1** in the solid state, the ^{13}C NMR spectrum of **1** (^{13}CO-enriched) in CD_2Cl_2/CH_2Cl_2 at ambient temperature showed just one sharp resonance (with tin couplings)[12] for the carbonyls (Figure 1); the resonance was only slightly broadened in the spectrum at −65 °C. This observation is consistent with rapid rotation about the Os—Sn bonds in **1** so as to render the inner and outer carbonyl ligands equivalent. (A similar low-energy barrier to rotation is observed for the P—Mo—P bonds in *trans*-$Mo(CO)_4[Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′].[14])

Complexes of the type *trans*-$M(CO)_4(L)_2$ exhibit just one strong CO stretch in the infrared spectrum even when the ligand L is asymmetric, as in *trans*-$Os(CO)_4(SiMeCl_2)_2$.[8] The IR spectrum of **1** in CH_2Cl_2, however, exhibits four CO stretches, two of which are intense. For D_{6h} symmetry two IR-active bands are expected for

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[12] The intensity and magnitude of the couplings are consistent with $^{117,119}Sn$—C couplings reported for related compounds.[9,13]

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Table 1. Crystal Data and Structure Refinement for $[Os(CO)_4(SnPh_2)]_6$

empirical formula	$C_{96}H_{60}O_{24}Os_6Sn_6$
fw	3450.78
temp	173(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$C2/c$
unit cell dimens	$a = 35.036(4)$ Å
	$b = 10.104(1)$ Å
	$c = 34.223(4)$ Å
	$\beta = 118.27\ (1)°$
V, Z	10 669(1) $Å^3$, 4
D(calcd)	2.148 Mg/m^3
abs coeff	8.554 mm^{-1}
F(000)	6336
cryst size	0.08 × 0.16 × 0.01 mm
θ range for data collcn	1.32−17.50°
index ranges	$-38 \leq h \leq +34$, $-11 \leq k \leq +10$, $-38 \leq l \leq +37$
no. of reflns collcd	10 621
no. of indpdt rflns	3384 ($R_{int} = 0.1070$)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3384/180/296
goodness of fit on F^2	1.121
final R indices ($I > 2\sigma(I)$)	R1 = 0.0653, wR2 = 0.1428
R indices (all data)	R1 = 0.0836, wR2 = 0.1526
extn coeff	0.000 001(7)
largest diff peak and hole	+1.123 and −1.272 e $Å^{-3}$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Os(1)−Sn(1)	2.751(2)	Os(1)−Sn(3)	2.741(2)
Os(2)−Sn(1)	2.753(3)	Os(2)−Sn(2)	2.738(3)
Os(3)−Sn(2)	2.754(2)	Os(3)−Sn(3)	2.735(2)
Os−C (range)	1.75(3)−2.01(4)	Sn−C (range)	2.11(2)−2.17(2)
Sn(1)−Os(1)−Sn(3)	175.9(1)	Os(3)−Sn(3)−Os(1)	118.2(1)
Sn(2)−Os(2)−Sn(1)	174.4(1)	C−Sn(1)−C	103(1)
Sn(3)−Os(3)−Sn(2)	173.5(1)	C−Sn(2)−C	104(1)
Os(1)−Sn(1)−Os(2)	119.1(1)	C−Sn(3)−C	105(1)
Os(2)−Sn(2)−Os(3)	118.4(1)		

the 12 inner and 12 outer carbonyl ligands. In other words, IR spectroscopy detects the different environments of the carbonyl ligands in **1** and exchange between the two sites is, as expected, slow on the IR time scale.

Besides the aesthetic appeal of **1**, with its approximate D_{6h} symmetry, the molecule is also intriguing from a chemical standpoint. We plan to investigate aspects of the chemistry of **1** such as its CO substitution by other ligands, its ability to act as a crown-like ligand, and the products formed in decarbonylation reactions.

Experimental Section

All reactions were carried out under nitrogen with use of standard Schlenk techniques. Other synthetic and spectroscopic techniques used in the preparation of **1** and **2** have recently been described.[2] Disodium tetracarbonylosmate(−II), $Na_2[Os(CO)_4]$, was prepared by the addition of $Os_3(CO)_{12}$ to Na in liquid ammonia.[6]

Preparation of $[Os(CO)_4(SnPh_2)]_2$ (2) and $[Os(CO)_4(SnPh_2)]_6$ (1). To $Na_2[Os(CO)_4]$ (prepared from 178 mg, ~0.19 mmol, of ^{13}CO-enriched $Os_3(CO)_{12}$, ca. 70% ^{13}C) at −50 °C was added Ph_2SnCl_2 (210 mg, 0.610 mmol), followed by THF (30 mL) prechilled to −78 °C. The reaction mixture was stirred, with the exclusion of light, and warmed to room temperature overnight. The solvent was removed on the vacuum line and the residue extracted with hexane (15 mL and 2 × 10 mL). The extracts were combined, concentrated, and stored at −25 °C to afford a small amount of pure **2**. The residue remaining after the hexane extraction was further extracted with CH_2Cl_2 (20 mL, 2 × 10 mL, and 5 mL). The CH_2Cl_2 extracts were combined, filtered through silica, and concentrated to ~15 mL. Hexane (10 mL) was carefully added so as to form two layers and the mixture stored at −25 °C, whereupon pale yellow needles of $[Os(CO)_4(SnPh_2)]_6$ (5 mg) were obtained that were pure by $^{13}C\{^1H\}$ NMR spectroscopy. The supernatant solution was evaporated to dryness to provide a pale yellow residue (126 mg), a $^{13}C\{^1H\}$ NMR spectrum of which in CD_2Cl_2/CH_2Cl_2 (1/4) showed it contained **1**, **2**, and a third, as yet unidentified, product (or products) in an approximate ratio of 1:2:1. In a separate experiment the supernatant solution, rather than being evaporated to dryness, was concentrated and stored at −25 °C to afford colorless crystals of $[Os(CO)_4(SnPh_2)]_2$ (**2**) that were pure by IR spectroscopy. Better separation of **1** and **2** was achieved on a size-exclusion column (BioBeads SX-8, 90 cm × 14 mm) with CH_2Cl_2 as the eluent: the pale yellow **1** eluted just ahead of the colorless **2**. Both **1** and **2** can be handled for short periods in air without apparent decomposition. (The elemental analyses and IR data are for samples not enriched in ^{13}CO.)

$[Os(CO)_4(SnPh_2)]_6$ (**1**): IR (CH_2Cl_2) ν(CO) 2105.5 w, 2030.5 vs, 2013.5 s 2002 m, sh cm^{-1} (obtained on a sample of hand-picked crystals shown by X-ray crystallography to be **1**); ^1H NMR (CD_2Cl_2) δ 7.47 m, 7.30 m; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2 1/4) δ 185.4 ($J_{SnC} = 30.2$ Hz), 136.4 (2C, Ph), 128.6 (2C, Ph), 128.5 (1C, Ph) (the signal due to the ipso carbon was not observed). Anal. Calcd for $C_{96}H_{60}O_{24}Os_6Sn_6$: C, 33.41; H, 1.75. Found: C, 33.56; H, 1.77.

$[Os(CO)_4(SnPh_2)]_2$ (**2**): IR (CH_2Cl_2) ν(CO) 2079.5 m, 2019.5 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.3 m; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1/4) δ 182.1 ($J_{SnC} = 39.6$ Hz, *ax*-CO), 173.5 ($J_{SnC} = 123.6$ Hz, *eq*-CO), 136.7 (2C, Ph), 128.8 (1C, Ph), 128.6 (2C, Ph). Anal. Calcd for $C_{32}H_{20}O_8Os_2Sn_2$: C, 33.41: H, 1.75. Found: C, 33.17: H, 1.76.

Structure Determination of 1. A small, pale yellow, platelike crystal of **1** was mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal-focus Mo-target X-ray tube ($\lambda = 0.710\ 73$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 173 K; the detector was placed at a distance of 6.015 cm from the crystal. A total of 1321 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s/frame. The total data collection time was 13.5 h. The frames were integrated with the Siemens SAINT software package with a narrow-frame algorithm. The integration of the data using a *C*-centered monoclinic unit cell yielded a total of 10 621 reflections to a maximum 2θ angle of 35°, of which 3384 were independent and 2779 were greater than $4\sigma(I)$. The final cell constants (Table 1) were based upon the *xyz* centroids of 1256 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were corrected for absorption using a face-indexed numerical method with transmission coefficients ranging from 0.368 to 0.916. The structure was solved and refined with the Siemens SHELXTL (version 5.0) software package,[15] using the space group $C2/c$ with $Z = 4$ for the formula $[Os(CO)_4SnPh_2]_6$. Each molecule possesses a crystallographic center of symmetry. Because of the small size of the specimen and its weak diffracting power, and the limited number of reflections available for use in refinement, the structure was refined with a model in which the Sn and Os atoms were refined anisotropically, the C and O atoms were refined isotropically, and the H atoms were placed in idealized positions. The final full-matrix refinement based on F^2 yielded R1 = 0.0653 and wR2 = 0.1526 and a goodness of fit of 1.121; the largest peak in the final difference map was 1.12 e Å^{-3}.

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Supporting Information Available: Listings of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for compound **1** (6 pages). Ordering information is given on any current masthead page.

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