

# The 1,3-Sn<sub>2</sub>O<sub>2</sub>-Heterocycle as a Ligand in Organometallic Compounds – Dimerization of the Inidene Species $[(\text{CO})_5\text{M}]_2\text{SnOR}]^-$ (M = Cr, W)<sup>☆</sup>

Peter Kircher, Gottfried Huttner\*, Katja Heinze, and Laszlo Zsolnai

Anorganisch-Chemisches Institut der Universität Heidelberg,  
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany  
Fax: (internat.) + 49(0)6221/545707

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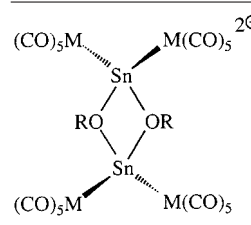
Dimerized inidene complexes  $[(\text{CO})_5\text{M} \cdots \text{Sn}(\text{OR}) \cdots \text{M}(\text{CO})_5]_2^{2-}$  (M = Cr, W; R = Et, *i*Pr), **1**, are obtained from  $[(\text{CO})_5\text{M}]_2\text{SnCl}_2]^{2-}$  by different routes. Dimerization occurs via alkoxy-donor tin-acceptor bonding by which a planar Sn<sub>2</sub>O<sub>2</sub> ring is formed. The Sn–M(CO)<sub>5</sub> bonds are made in a plane vertical to this ring such that, with the R–O groups being almost coplanar with the Sn<sub>2</sub>O<sub>2</sub> ring, the overall geometry of the compounds shows idealized D<sub>2h</sub> symmetry. – The <sup>119</sup>Sn-NMR resonances of **1** are found at rather low fields (M = Cr:  $\delta \approx 1400$ ; M = W:  $\delta \approx 1170$ ) indicating a low-lying tin-centered orbital in the LUMO range. Correspondingly EHT analyses show that the 3-center-4 $\pi$

system, which characterizes monomeric inidene species  $[\text{L}_n\text{M} \cdots \text{E}(\text{X}) \cdots \text{ML}_n]^n$ , is still prevalent in the dimeric species **1**. The low-lying  $\pi^*$ -type LUMOs of **1** are the rationale for the observed <sup>119</sup>Sn-NMR low-field shifts of **1**. The dimeric compounds **1** react with 2,4-pentanedione to form chelate compounds of the same type as those characteristically obtained from monomeric inidene complexes:  $[(\text{CO})_5\text{Cr}]_2\text{SnOEt}]_2^{2-}$  (**1a**) reacts to give  $[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{acac})]^-$  (**2**). The experimental results are verified by X-ray analyses in addition to the usual spectroscopic and analytical investigations.

Trigonal planar coordination around a tin center has so far only been achieved in a few types of compounds: stan-nylene complexes  $[(\text{CO})_5\text{M}]_2\text{SnR}_2$  (M = Cr, Mo, W)<sup>[1]</sup> which are isolobal analogues of olefins, the star-type compound  $[(\text{CO})_5\text{Cr}]_3\text{Sn}]^{2-}$ <sup>[2]</sup> which is isolobal to the carbonate anion,  $[(\text{L}_n\text{M})_2\text{Sn}=\text{ML}_n]$  ( $\text{L}_n\text{M} = \text{W}(\text{CO})_5$ ,  $\text{Cp}^R(\text{CO})_2\text{Mn}$ ;  $\text{Cp}^R = \text{Cp}, \text{Cp}', \text{Cp}^*$ )<sup>[3]</sup> which are analogues of the methylenecyclopropane system, and inidene compounds  $[\text{L}_n\text{M} \cdots \text{Sn}(\text{X}) \cdots \text{ML}_n]^-$  ( $\text{ML}_n = \text{MnCp}'(\text{CO})_2$ , R = Cl, Br, *St*Bu)<sup>[4]</sup> which are analogues of the allylic anion, represent the few types of compounds for which trigonal-planar coordination of tin is known. For the inidene series of compounds there is strong evidence that the species  $[\text{L}_n\text{M} \cdots \text{Sn}(\text{X}) \cdots \text{ML}_n]^-$  are only stable, as such, if the  $\text{L}_n\text{M}$  fragment is a potent d- $\pi$  donor such as  $[\text{Cp}^R(\text{CO})_2\text{Mn}]$ , while  $\text{L}_n\text{M}$  groups such as  $[(\text{CO})_5\text{M}]$  (M = Cr, Mo, W) with their reduced  $\pi$ -donor capabilities<sup>[5]</sup> will not sufficiently stabilize the allylic-type 3-center-4 $\pi$  system characteristic of these compounds.<sup>[6][7]</sup> Inidene compounds  $[(\text{CO})_5\text{M} \cdots \text{Sn}(\text{X}) \cdots \text{M}(\text{CO})_5]^-$  are obviously strongly Lewis-acidic at their unsaturated tin center, such that in any attempt to prepare them the base adducts,  $[(\text{CO})_5\text{M} - \text{Sn}(\text{X})(\text{B}) - \text{M}(\text{CO})_5]^-$ , appear to be inevitably formed. Quite a number of such base adducts have now been characterized,<sup>[8][9]</sup> while no unprotected compound  $[(\text{CO})_5\text{M} \cdots \text{Sn}(\text{X}) \cdots \text{M}(\text{CO})_5]^-$  has so far been obtained. In order to prepare such compounds it appears natural to try to compensate for the reduced d- $\pi$ -donor capabilities of the  $[(\text{CO})_5\text{M}]$  entities by introducing a p- $\pi$  donor as the substituent X at the tin center. As potentially  $\pi$ -donating substituents R–O or R–S entities are a straightforward choice. While an R–S substituent would be

preferable due to its soft sulfur donor, hitherto uncontrollable side reactions have precluded the successful synthesis of  $[(\text{CO})_5\text{M} \cdots \text{Sn}(\text{SR}) \cdots \text{M}(\text{CO})_5]^-$  compounds.<sup>[8b]</sup> With the R–O substituent, which is decidedly less soft when compared to the R–S entity, the working hypothesis met with partial success:  $[(\text{CO})_5\text{M} \cdots \text{Sn}(\text{OR}) \cdots \text{M}(\text{CO})_5]^-$  entities are in fact formed, albeit not as monomeric species but as dimers  $[(\text{CO})_5\text{M}]_2\text{Sn}(\mu_2\text{-OR})_2\text{Sn}\{\text{M}(\text{CO})_5\}_2]^{2-}$  (**1**) (Table 1). The Lewis acidity at the tin centers is still large enough to call for compensation by an oxygen “lone pair” of a second inidene species.

Table 1. Complexes of type **1**

|                                                                                      | no.                                          | M  | R           | cation                   |
|--------------------------------------------------------------------------------------|----------------------------------------------|----|-------------|--------------------------|
|  | $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$ | Cr | Et          | $[\text{nBu}_4\text{N}]$ |
|                                                                                      | $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  | Cr | Et          | $[\text{Ph}_4\text{P}]$  |
|                                                                                      | $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1b}$ | Cr | <i>i</i> Pr | $[\text{nBu}_4\text{N}]$ |
|                                                                                      | $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1c}$ | W  | Et          | $[\text{nBu}_4\text{N}]$ |
|                                                                                      | $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1d}$  | W  | Et          | $[\text{Ph}_4\text{P}]$  |
|                                                                                      |                                              |    |             |                          |

This type of dimerization is similar to that observed for  $[\text{Cp}(\text{CO})_2\text{Mn}]_2\text{BiCl}]$ .<sup>[7][10]</sup> The dimeric entities have a strong relation to the well-characterized main-group ring species  $[\text{R} - \text{Sn}(\mu_2\text{-OR})_2\text{Sn} - \text{R}]$ <sup>[11]</sup> as well as to the theoretically well-understood species  $[\text{Sn}_2\text{H}_4]$  and  $[\text{Sn}_2\text{H}_6]^{2+}$ .<sup>[12]</sup> They are also closely related to genuine inidene compounds.

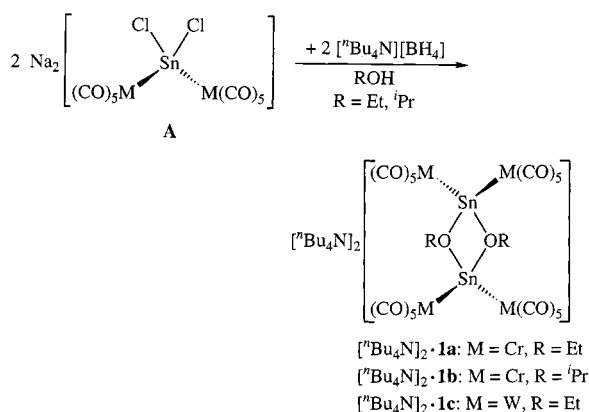
In this paper we describe the syntheses, structure, spectroscopy, and reactivity of type-**1** compounds, as well as the specific bonding situation pertaining to them.

## Results and Discussion

### Synthesis and Reactivity

When the dichlorostannate compounds **A**,  $[(\text{CO})_5\text{M}]_2\text{SnCl}_2^{2-}$  ( $\text{M} = \text{Cr}, \text{W}$ )<sup>[8]</sup>, are treated with  $[\text{nBu}_4\text{N}][\text{BH}_4]$  in an alcoholic solution the alkoxy-bridged dimers  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1}$  are obtained (Scheme 1) instead of the desired hydridotin species.

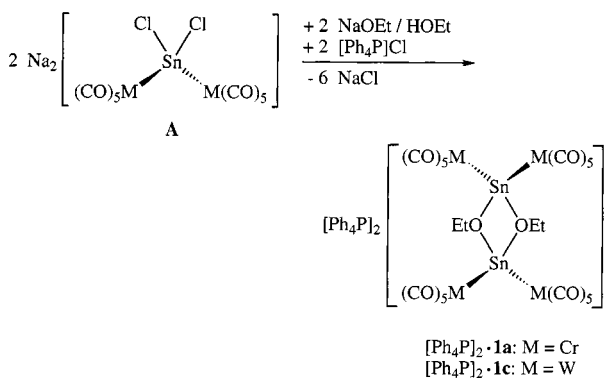
Scheme 1. Reaction of  $[(\text{CO})_5\text{M}]_2\text{SnCl}_2^{2-}$  ( $\text{M} = \text{Cr}, \text{W}$ ) (**A**) with  $[\text{nBu}_4\text{N}][\text{BH}_4]$  in alcoholic solution



The yellow compounds  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1}$  are obtained as microcrystalline solids, the constitution of which is documented by the usual spectroscopic and analytical techniques as well as by a series of X-ray analyses (Tables 3, 4, and 5). It is observed that under the reaction conditions described addition of  $[\text{nBu}_4\text{N}][\text{BH}_4]$  to the solutions of **A** is accompanied by a rapid evolution of gas. It might therefore be assumed that the primary product, and hence intermediate in the formation of  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1}$ , is a hydridotin species.

While this hypothesis can not be completely ruled out, it appears more probable that the hydridoborate is merely active as a base, deprotonating the alcohol which is used as the solvent; no hydridoborate is needed for the transformation of **A** into **1** if sodium ethoxide, NaOEt, is used as the reagent (Scheme 2).

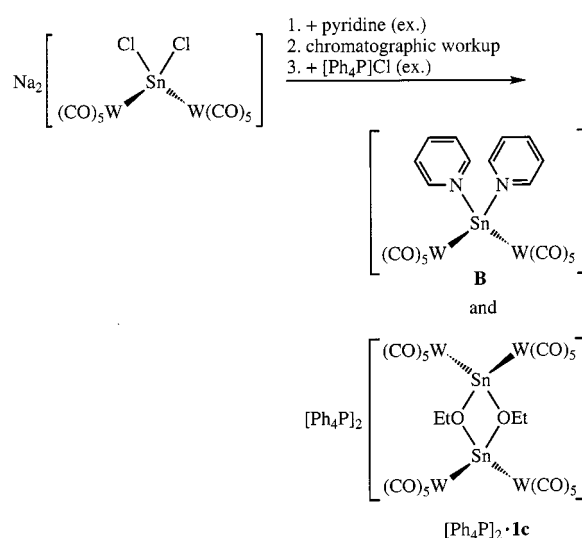
Scheme 2. Reaction of  $[(\text{CO})_5\text{M}]_2\text{SnCl}_2^{2-}$  ( $\text{M} = \text{Cr}, \text{W}$ ) (**A**) with NaOEt



Under these conditions the dimeric dianions are immediately formed (IR control), and the salts  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  are precipitated, by the addition of  $[\text{Ph}_4\text{P}]\text{Cl}$ , in the form of microcrystalline yellow powders. Since solutions of **A** in alcohols are stable as such, it is evident that basic conditions are necessary to induce the transformation of **A** into **1**.

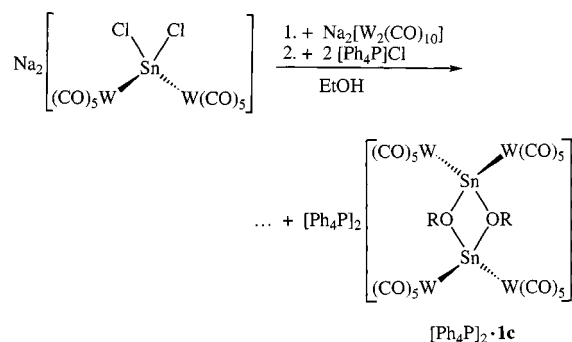
This fact is also inferred from the observation that treating THF solutions of  $\text{Na}_2[(\text{CO})_5\text{W}]_2\text{SnCl}_2$  with pyridine (py), which leads to the formation of the pyridine adduct **B**,  $[(\text{CO})_5\text{W}]_2\text{Sn}(\text{py})_2$  as the major product<sup>[9]</sup>, will also produce minor amounts of  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  when ethanol is used as the eluent during the chromatographic workup (Scheme 3). In this case pyridine obviously acts as the HCl scavenger.

Scheme 3. Reaction of  $\text{Na}_2[(\text{CO})_5\text{W}]_2\text{SnCl}_2$  with an excess of pyridine



Yet another way to produce  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  relies upon the basicity of the  $[\text{W}_2(\text{CO})_{10}]^{2-}$  anion (Scheme 4): when **A** is allowed to react with  $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$  in ethanol an immediate color change from yellow to dark red is observed.

Scheme 4. Reaction of  $\text{Na}_2[(\text{CO})_5\text{W}]_2\text{SnCl}_2$  with  $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$  in ethanol

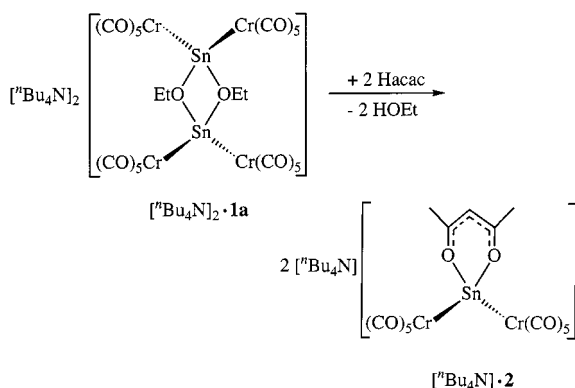


<sup>119</sup>Sn-NMR spectroscopy shows that a mixture of at least 5 species is formed, one of them being  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  which may be precipitated by addition of  $[\text{Ph}_4\text{P}]\text{Cl}$ .

As far as the reactivity of **1** is concerned the compounds behave similarly to dimerized indenyl species; it is a charac-

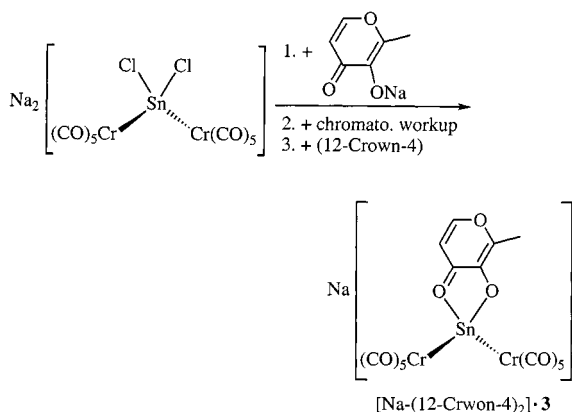
teristic of  $[L_nM \equiv E(X) \equiv ML_n]^n$  ( $E$  = group 15 element,  $n = 0$ ;  $E$  = group 14 element,  $n = -1$ ;  $X$  = leaving group: e.g. Cl, etc.) to undergo substitution and addition with monovalent chelate bases to form chelate derivatives.<sup>[13]</sup> Correspondingly,  $[nBu_4N]_2 \cdot \mathbf{1a}$  reacts with 2,4-pentanedione (Hacac) to give **2** as its  $[nBu_4N]$  salt (Scheme 5).

Scheme 5. Reaction of  $[nBu_4N]_2 \cdot \mathbf{1a}$  with 2,4-pentanedione



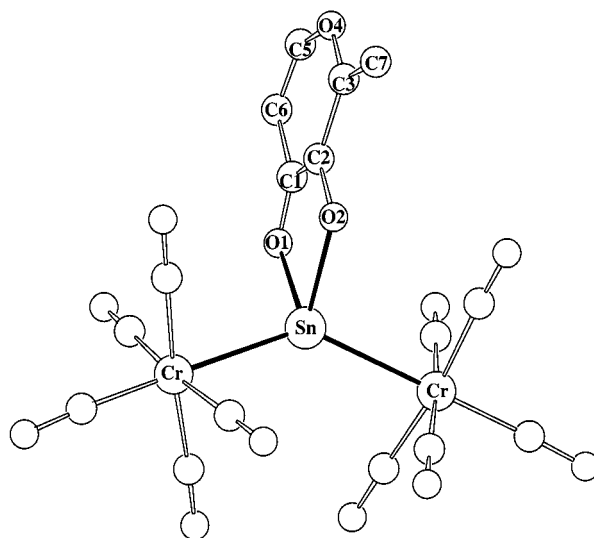
No external base is needed to promote this reaction. The reaction itself is monitored by NMR spectroscopy, either by observing the disappearance of the <sup>1</sup>H-NMR resonance of the diketo tautomer of 2,4-pentanedione in acetone solution or by observing the disappearance of the <sup>119</sup>Sn-NMR signal of  $[nBu_4N]_2 \cdot \mathbf{1a}$  ( $\delta = 1445$ ) and the appearance of the signal at  $\delta = 1205$  characterizing  $[nBu_4N] \cdot \mathbf{2}$  (Table 3). The spectroscopic data leave no doubt about the constitution of  $[nBu_4N] \cdot \mathbf{2}$ . Its solid-state structure could, however, not be analyzed since  $[nBu_4N] \cdot \mathbf{2}$  is (even after the chromatographic workup) an oil with no tendency to crystallize. Since the  $[Ph_4P]$  salt of **2** was also found to be an oil, the  $\gamma$ -pyronate analogue **3** of **2** was synthesized (Scheme 6) with the hope of obtaining a crystalline compound showing a bonding situation closely related to that in **2**. As an easy access to chelate compounds of this type the reaction of **A** with chelate bases had been described.<sup>[8b][9]</sup> Following this route **3** was prepared from  $Na_2[\{(CO)_5Cr\}_2SnCl_2]$  and the sodium salt of 3-hydroxy-2-methyl- $\gamma$ -pyrone (pyro) (Scheme 6).

Scheme 6. Reaction of  $Na_2[\{(CO)_5Cr\}_2SnCl_2]$  with the sodium salt of 3-hydroxy-2-methyl- $\gamma$ -pyrone



$[Na(12-Crown-4)]_2 \cdot \mathbf{3}$  was prepared as a crystalline salt. The structure of the anion of this salt, as obtained by X-ray analysis, is shown in Figure 1. The accuracy of the structure determination is rather low due to insufficient crystal quality and the notorious disorder of the 12-Crown-4 entities.

Figure 1. Molecular structure of the anion of  $[Na(12-Crown-4)]_2 \cdot \mathbf{3}^{[a]}$



<sup>[a]</sup> The numbering system chosen does not correspond to the one adopted in the data deposited.

Even though the overall geometry of the chelate compound is established beyond doubt (Table 2), comparison of the spectroscopic properties of  $[Na(12-Crown-4)]_2 \cdot \mathbf{3}$  with those observed for  $[nBu_4N] \cdot \mathbf{2}$  (Table 3) shows that the general structural and electronic features of both compounds are very similar.

Table 2. Selected bond lengths [pm], angles [°], and torsion angles [°] for the anion **3** of  $[Na(12-Crown-4)]_2 \cdot \mathbf{3}^{[a]}$

|                              |          |                                         |                   |
|------------------------------|----------|-----------------------------------------|-------------------|
| Cr–Sn                        | 262.6(2) | Cr–Sn–Cr                                | 137.17(6)         |
| Sn–O1                        | 262.8(2) | O–Sn–O                                  | 76.9(4)           |
| Sn–O2                        | 217.8(8) | Cr–Sn–O                                 | 107.8(2)          |
| O1–C1                        | 216.5(8) |                                         | 105.1(2)          |
| O2–C2                        | 120(1)   |                                         | 105.7(2)          |
| C1–C2                        | 151(1)   |                                         | 107.8(2)          |
| C2–C3                        | 129(2)   | Sn–O–C                                  | 102.6(6)/118(1)   |
| C3–O4                        | 146(2)   | Sn–Cr–C <sub>COax</sub>                 | 178.1(4)/178.8(4) |
| O4–C5                        | 130(1)   | Sn–Cr–C <sub>COeq</sub>                 | 85.7(3)–89.5(3)   |
| C5–C6                        | 146(2)   | C <sub>COax</sub> –Cr–C <sub>COeq</sub> | 90.7(5)–94.3(6)   |
| C6–C1                        | 123(2)   | C <sub>COeq</sub> –Cr–C <sub>COeq</sub> | 86.6(5)–92.2(5)   |
| C3–C7                        | 156(2)   | Cr–C–O                                  | 172.3(5)–176.2(5) |
| Cr–C <sub>COax</sub>         | 136(2)   |                                         | 176.1(9)–179.5(9) |
| Cr–C <sub>COeq</sub>         | 184(1)   |                                         |                   |
| torsion angle $\alpha^{[b]}$ |          | 11                                      |                   |

<sup>[a]</sup> Estimated standard deviations in units of the least significant figures given in each case are quoted in parentheses. – <sup>[b]</sup>  $\alpha$  is defined elsewhere in the text.

The integrity of the ligand is in both cases (**2** and **3**) supported by the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra (see Experimental Section). The symmetrical binding of the acac ligand of **2** (averaged over time at least) is also apparent from these spectra.

Table 3.  $\tilde{\nu}_{\text{CO}}$ -IR and  $^{119}\text{Sn}\{^1\text{H}\}$ -NMR-spectroscopic data for the compounds **1–3**

|                                                     | IR-in $\text{CH}_2\text{Cl}_2$<br>$\tilde{\nu}$ [ $\text{cm}^{-1}$ ] |          |           |          | $^{119}\text{Sn}\{^1\text{H}\}$<br>$\delta$ [ppm] |
|-----------------------------------------------------|----------------------------------------------------------------------|----------|-----------|----------|---------------------------------------------------|
| $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$        | 2032 (w)                                                             | 2007 (s) | 1917 (vs) | 1886 (s) | 1445 <sup>[a]</sup>                               |
| $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$         | 2033 (w)                                                             | 2007 (s) | 1918 (vs) | 1880 (s) | 1460 <sup>[b]</sup>                               |
| $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1b}^{[c]}$  | 2032 (w)                                                             | 2005 (s) | 1918 (vs) | 1884 (s) | 1379 <sup>[a]</sup>                               |
| $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1c}$        | 2045 (w)                                                             | 2026 (s) | 1925 (vs) | 1881 (s) | 1169 <sup>[b][d]</sup>                            |
| $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$         | 2044 (w)                                                             | 2025 (s) | 1923 (vs) | 1878 (s) | 1169 <sup>[b][e]</sup>                            |
| $[\text{nBu}_4\text{N}] \cdot \mathbf{2}^{[c]}$     | 2039 (w)                                                             | 2004 (s) | 1919 (vs) | 1891 (s) | 1205 <sup>[b]</sup>                               |
| $[\text{Na}(\text{12C4})_2] \cdot \mathbf{3}^{[c]}$ | 2037 (w)                                                             | 2001 (s) | 1917 (vs) | 1889 (s) | 1361 <sup>[b]</sup>                               |

<sup>[a]</sup> In  $\text{CD}_2\text{Cl}_2$ , 25 °C. – <sup>[b]</sup> In  $[\text{D}_6]\text{acetone}$ , 25 °C. – <sup>[c]</sup> In THF. – <sup>[d]</sup>  $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 540 \text{ Hz}$ ; intensity ratio of peaks 17:100:17. – <sup>[e]</sup>  $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 523 \text{ Hz}$ ; intensity ratio of peaks 15:100:17.

### Structure and Bonding

X-ray analyses have been performed for the salts of  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$ ,  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$ , and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$ . The analysis of  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$  was hampered by the instability of the crystal, even at 173 K. Data were finally collected at 200 K (Table 5). Even when applying a rather high scan speed only the range up to  $2\Theta = 28^\circ$  could be covered. The phosphonium salts  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  did not pose these problems

and data sets of good quality could be obtained up to  $2\Theta \approx 50^\circ$  for the two isotopic crystals (Table 5). The results of these three structure analyses are qualitatively similar for all three compounds (Table 4).

Only the structure of  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  is, therefore, shown in Figure 2. The structures of  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  have crystallographic inversion symmetry while the structure of  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$  has no crystallographic symmetry constraint (Table 4). The distances and angles, which by chemical reasoning should be equivalent in each case, are in fact very similar within each compound and, where appropriate, also for the whole class of compounds (Table 4).

Even the rotational position of the  $[(\text{CO})_5\text{M}]$  groups with respect to the Sn–M axes are almost identical in all three compounds; the angle  $\alpha$  given in Table 4 (see also Table 2) refers to the pseudo torsion angle  $\text{C}_{\text{COeq}}-\text{M}-\text{M}'-\text{C}_{\text{COeq}}'$  were M,  $\text{C}_{\text{COeq}}$  and M',  $\text{C}_{\text{COeq}}'$  belong to  $[(\text{CO})_5\text{M}]$  groups bonded to one and the same tin center.<sup>[8b][9]</sup>

A characteristic feature of all three compounds  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$ ,  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$ , and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$  is a planar four-membered  $\text{Sn}_2\text{O}_2$  ring (Table 4). Coordination of the  $[(\text{CO})_5\text{M}]$  groups occurs in a plane vertical to this cycle. The  $\alpha$ -carbon atoms of the  $(\mu_2\text{-OEt})$  groups do not gener-

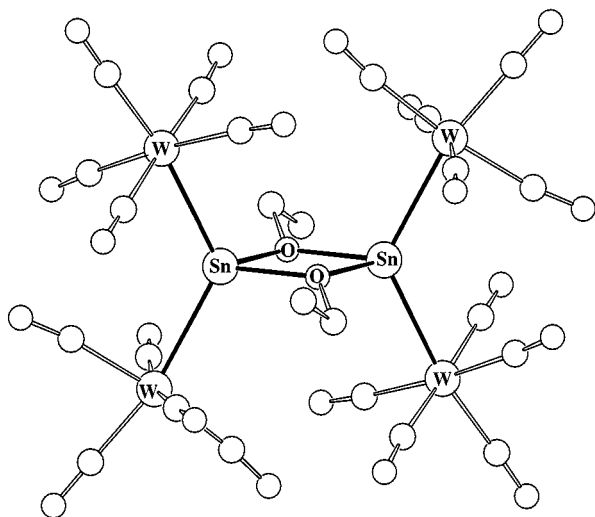
Table 4. Selected bond lengths [pm], angles  $^\circ$ , torsion angles  $^\circ$ , and deviations of individual atoms from the  $\text{Sn}_2\text{O}_2$  plane [pm] for the complex anions **1** in  $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$ ,  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$ , and  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}^{[a]}$ 

|                                          | $[\text{nBu}_4\text{N}]_2 \cdot \mathbf{1a}$<br>M = Cr | $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$<br>M = Cr | $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$<br>M = W |
|------------------------------------------|--------------------------------------------------------|-------------------------------------------------------|------------------------------------------------------|
| M–Sn                                     | 265.4(2)<br>262.5(3)<br>263.5(3)<br>264.7(2)           | 265.3(1)<br>265.4(1)<br>–<br>–                        | 278.8(1)<br>279.4(1)<br>–<br>–                       |
| Sn–O                                     | 216.6(9)<br>215(1)<br>214(1)<br>215.2(9)               | 216.1(3)<br>214.7(3)<br>–<br>–                        | 214(1)<br>215(1)<br>–<br>–                           |
| O–C $_{\alpha}$                          | 142(2)<br>140(2)                                       | 144.2(5)<br>–                                         | 142(2)<br>–                                          |
| C–C                                      | 145(2)<br>148(2)                                       | 151.0(7)<br>–                                         | 151(2)<br>–                                          |
| M–C $_{\text{COax}}$                     | 178(2)–181(2)                                          | 183.0(5)/185.4(5)                                     | 196(2)/198(2)                                        |
| M–C $_{\text{COeq}}$                     | 180(2)–189(2)                                          | 187.5(5)–190.6(5)                                     | 199(2)/208(2)                                        |
| M–Sn–M                                   | 125.22(8)<br>124.40(8)                                 | 124.52(2)<br>–                                        | 125.52(5)<br>–                                       |
| O–Sn–O                                   | 70.8(4)<br>71.2(4)                                     | 72.8(1)<br>–                                          | 73.5(4)<br>–                                         |
| Sn–O–Sn                                  | 108.8(4)<br>109.1(5)                                   | 107.2(1)<br>–                                         | 106.5(4)<br>–                                        |
| M–Sn–O                                   | 109.0(3)–117.4(3)                                      | 110.6(8)–113.4(8)                                     | 110.3(3)–113.7(3)                                    |
| Sn–O–C $_{\alpha}$                       | 121.5(9)–125.1(8)                                      | 122.0(3)/123.3(3)                                     | 121.6(9)/123.2(9)                                    |
| Sn–M–C $_{\text{COax}}$                  | 174.3(5)–178.3(5)                                      | 170.1(2)/171.9(2)                                     | 167.6(6)/170.5(6)                                    |
| Sn–M–C $_{\text{COeq}}$                  | 81.9(4)–93.4(4)                                        | 82.4(2)–100.7(1)                                      | 82.3(5)–100.4(5)                                     |
| C $_{\text{COax}}$ –M–C $_{\text{COeq}}$ | 87.5(6)–96.3(6)                                        | 82.2(2)–97.9(2)                                       | 81.3(7)–96.1(8)                                      |
| C $_{\text{COeq}}$ –M–C $_{\text{COeq}}$ | 84.6(6)–94.9(6)                                        | 86.3(2)–94.1(2)                                       | 87.4(7)–92.5(7)                                      |
| M–C–O                                    | 168.6(6)–178.1(6)                                      | 166.0(2)–177.7(2)                                     | 168.1(7)–177.9(8)                                    |
| O–C $_{\alpha}$ –C $_{\beta}$            | 175(1)–179(1)<br>115(1)/117(1)                         | 173.1(4)–177.5(5)<br>110.3(4)                         | 172(2)–179(2)<br>113(1)                              |
| $\alpha^{[b]}$                           | 43                                                     | 37                                                    | 39                                                   |
| C $_{\alpha}$ –O–Sn–O                    | 13.7–21.7                                              | 29.4/29.9                                             | 31.6/32.2                                            |
| deviation of Sn                          | –2/–2                                                  | 0/0                                                   | 0/0                                                  |
| deviation of O                           | 2/2                                                    | 0/0                                                   | 0/0                                                  |
| deviation of C $_{\alpha}$               | –26/–41                                                | $\pm 63$                                              | $\pm 60$                                             |

<sup>[a]</sup> Estimated standard deviations in units of the least significant figures given in each case are quoted in parentheses. – <sup>[b]</sup> Average values.

Table 5. Crystal structure data for [nBu<sub>4</sub>N]<sub>2</sub>·1a, [Ph<sub>4</sub>P]<sub>2</sub>·1a, [Ph<sub>4</sub>P]<sub>2</sub>·1c, and [Na-(12-Crown-4)]·3

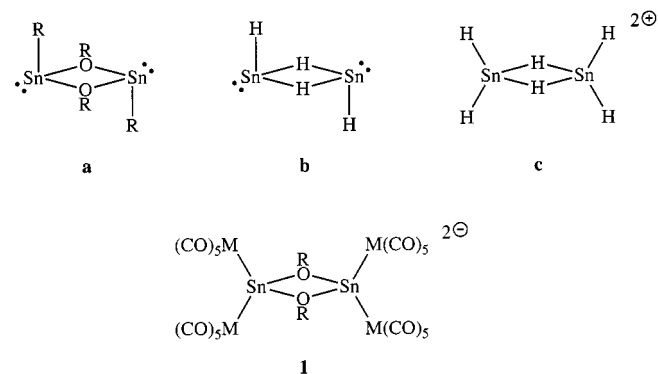
| compound                                                            | [nBu <sub>4</sub> N] <sub>2</sub> ·1a                                                          | [Ph <sub>4</sub> P] <sub>2</sub> ·1a                                                           | [Ph <sub>4</sub> P] <sub>2</sub> ·1c                                                          | [Na-(12-Crown-4)]·3                                                  |
|---------------------------------------------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
| formula                                                             | C <sub>56</sub> H <sub>43</sub> Cr <sub>4</sub> N <sub>2</sub> O <sub>22</sub> Sn <sub>2</sub> | C <sub>72</sub> H <sub>50</sub> Cr <sub>4</sub> O <sub>22</sub> P <sub>2</sub> Sn <sub>2</sub> | C <sub>72</sub> H <sub>50</sub> O <sub>22</sub> P <sub>2</sub> Sn <sub>2</sub> W <sub>4</sub> | C <sub>32</sub> H <sub>37</sub> Cr <sub>2</sub> NaO <sub>21</sub> Sn |
| molecular mass [g]                                                  | 1541.300                                                                                       | 1774.440                                                                                       | 2301.840                                                                                      | 1003.300                                                             |
| crystal dimensions [mm]                                             | 0.30 × 0.30 × 0.40                                                                             | 0.50 × 0.40 × 0.30                                                                             | 0.20 × 0.20 × 0.25                                                                            | 0.30 × 0.30 × 0.20                                                   |
| crystal system                                                      | triclinic                                                                                      | monoclinic                                                                                     | monoclinic                                                                                    | monoclinic                                                           |
| space group (No.)                                                   | P $\bar{1}$ (2)                                                                                | P2 <sub>1</sub> /c (14)                                                                        | P2 <sub>1</sub> /c (14)                                                                       | P2 <sub>1</sub> /c (14)                                              |
| a [pm]                                                              | 1145.8 (2)                                                                                     | 947.3 (1)                                                                                      | 965.4 (2)                                                                                     | 1061.6 (8)                                                           |
| b [pm]                                                              | 1361.7 (3)                                                                                     | 2447.3 (3)                                                                                     | 2473.0 (5)                                                                                    | 1934.8 (9)                                                           |
| c [pm]                                                              | 2262.3 (4)                                                                                     | 1594.2 (2)                                                                                     | 1588.5 (3)                                                                                    | 2005.6 (8)                                                           |
| α [°]                                                               | 85.45 (1)                                                                                      | 90.00 (0)                                                                                      | 90.00 (0)                                                                                     | 90.00 (0)                                                            |
| β [°]                                                               | 88.40 (1)                                                                                      | 99.66 (1)                                                                                      | 98.61 (1)                                                                                     | 86.90 (4)                                                            |
| γ [°]                                                               | 86.35 (2)                                                                                      | 90.00 (0)                                                                                      | 90.00 (0)                                                                                     | 90.00 (0)                                                            |
| cell volume [10 <sup>6</sup> pm <sup>3</sup> ]                      | 3511 (1)                                                                                       | 3643.5 (7)                                                                                     | 3750 (1)                                                                                      | 4113 (4)                                                             |
| molecular units / cell                                              | 2                                                                                              | 2                                                                                              | 2                                                                                             | 4                                                                    |
| density (calculated) [g cm <sup>-3</sup> ]                          | 1.458                                                                                          | 1.617                                                                                          | 2.039                                                                                         | 1.620                                                                |
| absorption coefficient [cm <sup>-1</sup> ]                          | 13.65                                                                                          | 13.69                                                                                          | 68.81                                                                                         | 12.12                                                                |
| temperature [K]                                                     | 200                                                                                            | 200                                                                                            | 200                                                                                           | 180                                                                  |
| no. rflns. for cell parameter refinement                            | 39                                                                                             | 36                                                                                             | 31                                                                                            | 25                                                                   |
| scan range                                                          | 4.5° ≤ 2θ ≤ 28.0°                                                                              | 4.2° ≤ 2θ ≤ 56.0°                                                                              | 4.2° ≤ 2θ ≤ 45.0°                                                                             | 3.8° ≤ 2θ ≤ 60.0°                                                    |
| scan speed [° min <sup>-1</sup> ]                                   | ω = 15                                                                                         | ω = 11                                                                                         | ω = 13                                                                                        | 8.0 ≤ ω ≤ 60.0                                                       |
| no. rflns. measured                                                 | 3120                                                                                           | 9306                                                                                           | 5175                                                                                          | 6787                                                                 |
| no. unique rflns.                                                   | 2666                                                                                           | 8796                                                                                           | 4696                                                                                          | 6467                                                                 |
| no. rflns. observed                                                 | 2443                                                                                           | 7441                                                                                           | 3245                                                                                          | 3918                                                                 |
| observation criterion                                               | 2 σ (I)                                                                                        | 2 σ (I)                                                                                        | 2 σ (I)                                                                                       | 2 σ (I)                                                              |
| no. parameters refined                                              | 476                                                                                            | 560                                                                                            | 401                                                                                           | 512                                                                  |
| residual electron density [· 10 <sup>-6</sup> e pm <sup>-3</sup> ]  | 0.38 / - 0.38                                                                                  | 1.27 / - 1.92                                                                                  | 1.26 / - 1.32                                                                                 | 1.36 / - 0.99                                                        |
| R <sub>I</sub> / R <sub>W</sub> [%] (refinement on F <sup>2</sup> ) | 4.2 / 11.1                                                                                     | 4.2 / 15.2                                                                                     | 5.6 / 14.0                                                                                    | 6.8 / 19.7                                                           |

Figure 2. Molecular structure of the anion of [Ph<sub>4</sub>P]<sub>2</sub>·1c

ally deviate too much from coplanarity with the heterocyclic plane (Table 4). The valence angles at the bridging oxygen atoms (Table 4) show that their coordination is more appropriately idealized as trigonal planar as compared to pseudo tetrahedral. Consequently, the torsion angles C<sub>α</sub>-O-Sn-O (Table 4) are small.<sup>[11]</sup> The idealized symmetry of the core of the compounds, including the metal atoms, the tin centers and the O-CH<sub>2</sub> fragments, is close to D<sub>2h</sub> (Figure 2).

As far as the bonding situation is concerned compounds 1 may be considered as composed of two [(CO)<sub>5</sub>M≡Sn(OR)≡M(CO)<sub>5</sub>]<sup>-</sup> species which, due to the electron deficiency at the tin centers in these indenene-type entities, dimerize by oxygen-donor-tin-acceptor bonding (Figure 2).

On the other hand, the planar Sn<sub>2</sub>(OR)<sub>2</sub> ring forming the central ligand entity in compounds 1 has a strong resemblance to the corresponding entities in [RSn(OR)]<sub>2</sub> (a in Figure 3). These species, which may be seen as dimerized stannylenes RSnOR, have been thoroughly analyzed by M. Veith and his group.<sup>[11]</sup>

Figure 3. Relationship between 1 and some Sn<sub>2</sub>(OR)<sub>2</sub>- and Sn<sub>2</sub>H<sub>2</sub>-heterocycles

This kind of view is well born out by theoretical reasoning which makes clear that the most stable dimerized form

of  $\text{H}_2\text{Sn}$  does correspond to the cyclic structure of **b**<sup>[12]</sup> which is mutatis mutandis the same as that for the well-characterized compounds **a** (Figure 3). Protonation of the "lone pairs" in **b** leads to the dication **c** (Figure 3) which, as will be discussed later, is a close relative to the anions **1**. A structure corresponding to **c** is established as a true minimum on the potential surface for the isoelectronic  $\text{C}_2\text{H}_6^{2+}$  cation and is a global minimum for  $\text{B}_2\text{H}_6$  which is also an isoelectronic analogue.<sup>[14]</sup> The relationship of **c** to the anions **1** is the following:

1. Bridging hydrogen atoms may be replaced by bridging R–O groups without much change being caused by the three additional p-valence orbitals at the oxygen atom, as is seen by comparing **a** and **b**. The major change in bonding is the replacement of the 3-center-2-electron Sn–H–Sn bridges by 3-center-4-electron Sn–(OR)–Sn bridges, both referring to  $\sigma$ -bonding. The disturbance by potential  $\pi$ -interactions between the relevant oxygen and tin p orbitals will only be slight, due to the misfit of these two types of p orbitals in size as well as in energy. So far to the similarity of the  $\text{Sn}_2\text{H}_2$  core in **b** and **c** and the  $\text{Sn}_2(\text{OR})_2$  core in **a** and **1**.

2. The analogy of **c** and **1** is immediately apparent by comparing the  $\sigma$ -bonding properties of H and  $[(\text{CO})_5\text{Cr}]^-$ . Both species have just one orbital filled with one electron in each case for this type of interaction. They are "isoelectronic" in the sense that a seventeen-electron organometallic species  $[(\text{CO})_5\text{Cr}]^-$  is an analogue of a seven electron main-group species [R] or of hydrogen [H] with all three of them being short by one electron with respect to the noble-gas electronic configuration.

Many of the ideas worked out for **a–c** may therefore be applied to **1** as well. With compounds **a** it is observed that the O–Sn–O angles are without exception considerably smaller than  $90^\circ$  with the Sn–O–Sn angles being correspondingly larger.<sup>[11]</sup> This type of angle distribution has been analyzed for **b** as the model compound.<sup>[12a]</sup> It has been rationalized in terms of the charge distribution within compounds of this type with both the bridging hydrogen atoms and the terminal hydrogen atoms being rather negatively charged.<sup>[12a]</sup> A merely electrostatic model built on these grounds will reproduce structures as well as energies. Similar reasoning will apply to **1**.

The approach of looking at **1** as an analogue of **c** by replacing the terminal hydrogen atoms in **c** by negatively charged "isoelectronic"  $[(\text{CO})_5\text{M}]^-$  groups in **1** does appear somewhat less arbitrary with the  $\nu(\text{CO})$ -IR data of **1** (Table 3) in mind: these  $\nu(\text{CO})$ -IR absorptions occur at wavelengths which are characteristic for negatively charged  $[(\text{CO})_5\text{M}]$  groups.<sup>[15]</sup> The R–O groups should bear  $\delta^-$  charges by simple electronegativity arguments.

When the bonding in **1** is rationalized in these terms, the structural properties of **1** are not astonishing. What is, however, astonishing at first glance is that the  $^{119}\text{Sn}$ -NMR shift of **1** is far more on the low-field side than is usually observed for tin in pseudo-tetrahedral four-coordination ( $\text{R}_2\text{SnCl}_2$ ).<sup>[16]</sup> From the observations made with indenyl-type compounds there is convincing evidence that the low-

field shifts observed for the central main-group elements in these compounds are intimately connected to the presence of a low-energy  $\pi^*$  orbital of these 3-center-4 $\pi$  systems.<sup>[17]</sup> The theory of NMR shifts predicts that the presence of such a low-lying main-group-centered orbital will strongly contribute to the paramagnetic (low-field) term of the shift observed for this element.<sup>[18]</sup> Since the symmetry of **1** would allow for such a low-lying orbital in **1** an EHT-MO analysis of **1** was performed as well. As a simplified model of **1**, following common practice, its "isoelectronic" analogue  $[(\text{H}_5\text{Cr})_2\text{Sn}(\mu_2\text{-OH})_2\text{Sn}\{\text{CrH}_5\}_2]^{2-}$  with R–O replaced by H–O and  $[(\text{CO})_5\text{Cr}]$  replaced by  $[\text{H}_5\text{Cr}]^{5-}$  was chosen.<sup>[19]</sup>

3-center-4 $\pi$  systems, only slightly disturbed by the interaction with oxygen p orbitals localized at the Cr–Sn–Cr entities, make up an essential part of the orbital pattern.

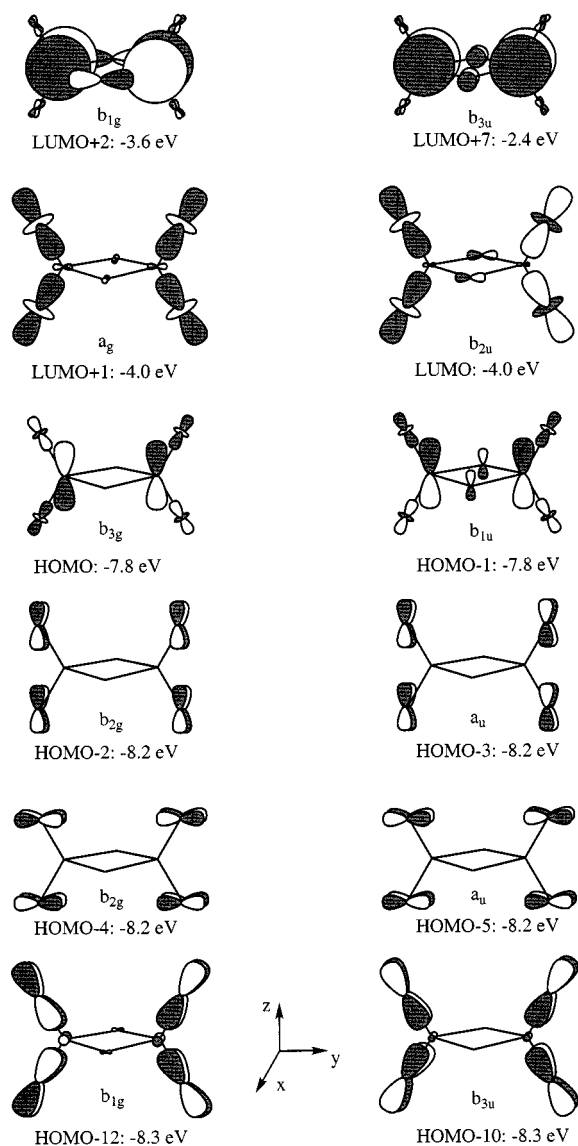
The totally bonding combinations of the 3-center-4 $\pi$ -parts are found at the HOMO-10 and HOMO-12 positions (Figure 4). Due to the  $D_{2h}$  symmetry of **1** and the model compound as well, orbitals must occur in pairs, one with *gerade* (*g*) symmetry and the other one with *ungerade* (*u*) symmetry with respect to the phases characterizing the contributions of the two  $\text{Cr}_2\text{Sn}$  parts (Figure 4). Due to a modulation by minor contributions from the oxygen valence orbitals these pairs may be at slightly different energies in those cases where this interaction is allowed by symmetry (Figure 4). The energy differences calculated for these pairs are smaller than 0.1 eV for the bonding orbitals (Figure 4) but are significant for some of the unoccupied ones (Figure 4).

The non-bonding orbital of each 3-center-4 $\pi$  constituent will have a zero coefficient for the tin  $p_x$  orbital and will be composed by an anti-phase combination of the d orbitals which might by symmetry maximally interact with the tin  $p_x$  orbital as individuals. The relevant orbitals are found at the positions HOMO-2 to HOMO-5 (Figure 4). Due to the coordinate system chosen the relevant d orbitals are a combination of  $d_{xy}$  and  $d_{xz}$ . These orbitals transform in groups as  $a_u$  and  $b_{2g}$ . A linear combination of the  $a_u$  pair as well as the  $b_{2g}$  pair are the representatives of the *u* and *g* combination of the terminal orbitals of the two 3-center-4 $\pi$  systems characterizing the compound.

The HOMOs of the compound correspond to *g* and *u* combinations of mainly Cr–Sn  $\sigma$ -bonding orbitals with a significant Sn- $p_z$  contribution (Figure 4). The LUMOs of the model compound are  $\sigma$ -anti-bonding with an almost negligible tin contribution (Figure 4).

The totally antibonding combinations of the 3-center-4 $\pi$  systems are found at the positions LUMO+2 and LUMO+7. These orbitals have large Sn- $p_x$  contributions and comparatively small contributions from the relevant d orbitals. They are modified by contributions of the oxygen p orbitals and are thus at different energies.

The essence of this analysis is the following: the 3-center-(M–E–M)-4 $\pi$  system, which is characteristic for indenyl compounds, is as well a characteristic ingredient to the bonding situation in **1**: non-bonding contributions of the relevant d orbitals make up MOs in the HOMO range. Anti-bonding combinations of the relevant metal d and

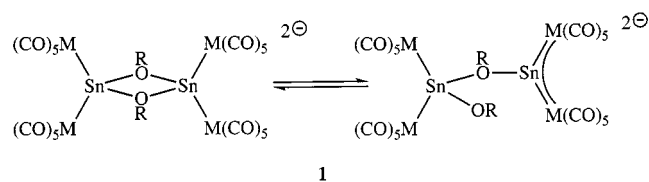
Figure 4. Characteristic orbitals of  $[\{L_5Cr\}_2Sn(\mu_2-OR)_2Sn\{CrL_5\}_2]^{2-}$  [a,b]

[a] The actual calculations were performed with  $[CrH_5]^{5-}$  templates instead of  $[L_5Cr]$ . The R–O groups were replaced by H–O entities. – [b] The bottom three pairs of orbitals refer to the bonding and non-bonding sets of the (Cr–Sn–Cr) 3-center-4 $\pi$ -systems. The top pair corresponds to the LUMOs of these systems. The  $\sigma$ -type HOMO pairs and LUMO pairs of the model compound are given as well.

main-group p orbitals are found in the LUMO range. This situation is typically the one giving rise to large low-field shifts<sup>[2][8b][9][17][20]</sup> in the NMR spectra of the bridging elements as is also observed for **1**.<sup>[21]</sup>

It has been argued that real indenyl-type compounds  $[(CO)_5M \equiv Sn(X) \equiv M(CO)_5]^-$  should have their  $^{119}Sn$ -NMR shifts close to  $\delta = 3000$ .<sup>[9]</sup> This argument was inferred in part from the observation that base adducts of these compounds  $[(CO)_5M-Sn(X)(B)-M(CO)_5]^n$  show strong temperature dependence of their  $^{119}Sn$ -NMR resonances. Equilibria of the type  $[(CO)_5M-Sn(X)(B)-M(CO)_5]^n \rightleftharpoons [(CO)_5M \equiv Sn(X) \equiv M(CO)_5]^- + B$  have been put forward as

Figure 5. Ring-opening/ring-closing equilibrium



an explanation.<sup>[9]</sup> Based on the same type of arguments the temperature dependence of the  $^{119}Sn$ -NMR resonance of  $[Ph_4P]_2 \cdot \mathbf{1c}$  may be interpreted in terms of a ring-opening/ring-closing equilibrium (Figure 5). Upon cooling from 298 K to 198 K the  $^{119}Sn$ -NMR signal of  $[Ph_4P]_2 \cdot \mathbf{1c}$  shifts to lower fields (from  $\delta = 1158$  to  $\delta = 1135$ ).

The shift difference observed for 10 K temperature difference is thus only 2 ppm in the case of  $[Ph_4P]_2 \cdot \mathbf{1c}$  while in other cases shifts of up to 20 ppm/10 K have been observed.<sup>[9]</sup>

Under the hypothesis that the temperature-induced shift is due to an equilibrium between three- and four-coordinated tin species the relatively small temperature dependence observed for  $[Ph_4P]_2 \cdot \mathbf{1c}$  indicates a high intrinsic stability of the four-membered  $Sn_2O_2$  heterocycle.

Financial support by the *Fond der Chemischen Industrie* is gratefully acknowledged. The work had formerly been supported by the *Deutsche Forschungsgemeinschaft* (SFB 247).

## Experimental Section

**General:** All manipulations were carried out under an argon atmosphere by means of standard Schlenk techniques at 25°C unless mentioned otherwise. All solvents were dried by standard methods and distilled under argon.  $[D_6]$ acetone and  $CD_2Cl_2$  used for the NMR-spectroscopic measurements were degassed by three successive “freeze-pump-thaw” cycles and dried over 4-Å molecular sieves. Silica gel (Kieselgel z. A., 0.06–0.2 mm, J. T. Baker Chemicals B. V.) used for chromatography and Kieselgur (Kieselgur, gereinigt, gegläht, Erg. B.6, Riedel-de Haen AG) used for filtration were degassed at 1 mbar at 180°C for 12 h and saturated with argon. – NMR: Bruker Avance DPX 200 at 200.13 MHz ( $^1H$ ), 50.323 MHz ( $^{13}C\{^1H\}$ ), 74.631 MHz ( $^{119}Sn\{^1H\}$ ), 81.015 MHz ( $^{31}P\{^1H\}$ ); chemical shifts ( $\delta$ ) in ppm with respect to  $[D_6]$ acetone ( $^1H$ :  $\delta = 2.04$ ,  $^{13}C$ :  $\delta = 29.8$ ) and  $CD_2Cl_2$  ( $^1H$ :  $\delta = 5.32$ ,  $^{13}C$ :  $\delta = 53.5$ ) as internal standards; chemical shifts ( $\delta$ ) in ppm with respect to  $SnMe_4$  ( $^{119}Sn$ :  $\delta = 0$ , at 25°C) and to 85%  $H_3PO_4$  ( $^{31}P$ :  $\delta = 0$ ) as external standard. – IR: Bruker FT-IR IFS-66;  $CaF_2$  cells. – UV/Vis/NIR: Perkin Elmer Lambda 19; cells (0.2 cm; Hellma 110 suprasil). – MS (FAB or EI): Finnigan MAT 8400; TEA (triethanolamine) matrix. – Elemental analyses: Microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. – Melting points: Gallenkamp MFB-595 010; values not corrected. – The dinuclear sodium salts of the composition  $Na_2[\{(CO)_5M\}_2SnCl_2]$  ( $M = Cr, W$ ) were prepared by salt metathesis from the corresponding stable phosphonium salts  $[Ph_4P]_2[\{(CO)_5M\}_2SnCl_2]$  as described<sup>[8b]</sup>. All other chemicals were commercially obtained and used without further purification.

$[nBu_4N]_2[\{(CO)_5Cr\}_2Sn(\mu_2-OEt)_2Sn\{Cr(CO)_5\}_2]$  ( $[nBu_4N]_2 \cdot \mathbf{1a}$ ):  $Na_2[\{(CO)_5Cr\}_2SnCl_2]$  (310 mg; 0.5 mmol) was dissolved in ethanol (50 ml). At 0°C solid  $[nBu_4N][BH_4]$  (257 mg; 1 mmol) was added in portions under spontaneous evolution of gas as well as precipitation of  $[nBu_4N]_2 \cdot \mathbf{1a}$  as a yellow microcrystalline powder.

The reaction mixture was stirred until no further evolution of gas was observed. The yellow solid of  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$  was separated from the reaction mixture by filtration, washed with ethanol ( $3 \times 10$  ml) and diethyl ether ( $2 \times 10$  ml) and dried in vacuo. Yield: 670 mg, 85%. For growing single crystals of  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$  the yellow powder was dissolved in dichloromethane (10 ml) and overlaid with ethanol (100 ml). Within 7 d yellow single crystals suitable for X-ray structure analysis were obtained. M.p. 65°C (dec.). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2032 \text{ cm}^{-1}$  (w), 2007 (s), 1917 (vs), 1886 (s). – UV/Vis (THF):  $\lambda$  (lg  $\epsilon$ ) = 430 nm (3.41). –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 4.30$  (q, 4 H,  $\text{OCH}_2$ ), 3.14 (m, 16 H, 1- $\text{H}_\text{N}$ ), 1.64 (m, 16 H, 2- $\text{H}_\text{N}$ ), 1.48 (m, 16 H, 3- $\text{H}_\text{N}$ ), 1.44 (t, 6 H,  $\text{OCH}_2\text{CH}_3$ ), 1.09 (t, 24 H, 4- $\text{H}_\text{N}$ ). –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 230.5$  (s,  $\text{C}_{\text{COax}}$ ), 222.9 (s,  $\text{C}_{\text{COeq}}$ ), 61.6 (s,  $\text{OCH}_2$ ), 59.2 (s,  $\text{C}_\text{N-1}$ ), 24.1 (s,  $\text{C}_\text{N-2}$ ), 20.0 (s,  $\text{C}_\text{N-3}$ ), 19.5 (s,  $\text{OCH}_2\text{CH}_3$ ), 13.6 (s,  $\text{C}_\text{N-4}$ ). –  $^{119}\text{Sn}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 1445$ . – MS (neg.-FAB, TEA);  $m/z$  (%): 547 (30)  $[(\text{CO})_5\text{Cr}\}_2\text{SnOEt}]^-$ .

$[n\text{Bu}_4\text{N}]_2[(\text{CO})_5\text{Cr}\}_2\text{Sn}(\mu_2\text{-}i\text{OPr})_2\text{Sn}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1b}$ ): In an analogous procedure to that for  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$ ,  $\text{Na}_2[(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$  (310 mg; 0.5 mmol) was dissolved in 2-propanol (50 ml) and treated with  $[n\text{Bu}_4\text{N}][\text{BH}_4]$  (257 mg; 1 mmol) at 0°C. The workup and crystal growth followed the methods described above. Even at 200 K, the obtained yellow single crystals of  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1b}$  were not stable enough to allow for the collection of high-quality X-ray diffraction data set. Yield: 280 mg, 35%. – M.p. 65°C (dec.). – IR (THF):  $\nu_{\text{CO}} = 2032 \text{ cm}^{-1}$  (w), 2005 (s), 1918 (vs), 1884 (s). –  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 5.00$  (sept, 2 H,  $\text{OCH}$ ), 3.16 (m, 16 H, 1- $\text{H}_\text{N}$ ), 1.66 (m, 16 H, 2- $\text{H}_\text{N}$ ), 1.51 (d+m, 12+16 H,  $\text{OCH}(\text{CH}_3)_2 + 3\text{-H}_\text{N}$ ), 1.09 (t, 24 H, 4- $\text{H}_\text{N}$ ). –  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 230.1$  (s,  $\text{C}_{\text{COax}}$ ), 223.2 (s,  $\text{C}_{\text{COeq}}$ ), 68.9 (s,  $\text{OCH}$ ), 59.1 (s,  $\text{C}_\text{N-1}$ ), 26.5 [s,  $\text{OCH}(\text{CH}_3)_2$ ], 24.0 (s,  $\text{C}_\text{N-2}$ ), 19.9 (s,  $\text{C}_\text{N-3}$ ), 13.6 (s,  $\text{C}_\text{N-4}$ ). –  $^{119}\text{Sn}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 1379$ .

$[n\text{Bu}_4\text{N}]_2[(\text{CO})_5\text{W}\}_2\text{Sn}(\mu_2\text{-OEt})_2\text{Sn}\{\text{W}(\text{CO})_5\}_2]$  ( $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1c}$ ): At 0°C  $\text{Na}_2[(\text{CO})_5\text{W}\}_2\text{SnCl}_2]$  (442 mg; 0.5 mmol) in ethanol (50 ml) was treated with  $[n\text{Bu}_4\text{N}][\text{BH}_4]$  (257 mg; 1 mmol) in an analogous procedure. The further workup and single-crystal growth followed the methods described for  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$ . Yield: 830 mg, 72%. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2045 \text{ cm}^{-1}$  (w), 2026 (s), 1925 (vs), 1881 (s). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 4.24$  (q, 4 H,  $\text{OCH}_2$ ), 3.45 (m, 16 H, 1- $\text{H}_\text{N}$ ), 1.85 (m, 16 H, 2- $\text{H}_\text{N}$ ), 1.49 (m, 16 H, 3- $\text{H}_\text{N}$ ), 1.44 (t, 6 H,  $\text{OCH}_2\text{CH}_3$ ), 1.02 (t, 24 H, 4- $\text{H}_\text{N}$ ). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 209.2$  (s,  $\text{C}_{\text{COax}}$ ), 204.7 (s,  $\text{C}_{\text{COeq}}$ ), 62.7 (s,  $\text{OCH}_2$ ), 59.4 (s,  $\text{C}_\text{N-1}$ ), 24.4 (s,  $\text{C}_\text{N-2}$ ), 20.4 (s,  $\text{C}_\text{N-3}$ ), 19.5 (s,  $\text{OCH}_2\text{CH}_3$ ), 13.9 (s,  $\text{C}_\text{N-4}$ ). –  $^{119}\text{Sn}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 1169$  ( $^1J_{\text{W,Sn}} = 540 \text{ Hz}$ ).

$[\text{Ph}_4\text{P}]_2[(\text{CO})_5\text{Cr}\}_2\text{Sn}(\mu_2\text{-OEt})_2\text{Sn}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$ ): A yellow solution of  $\text{Na}_2[(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$  (310 mg; 0.5 mmol) in ethanol (50 ml) was added to a solution of NaH (25 mg; 1 mmol) in ethanol (20 ml), with no color change observed. After stirring for 30 min, the yellow solution was filtered through Kieselgur (3 cm). By addition of solid  $[\text{Ph}_4\text{P}]\text{Cl}$  (375 mg; 1 mmol) in one portion the phosphonium salt  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  precipitated immediately as a yellow solid. After stirring for another 1 h, the yellow microcrystalline powder was separated from the mother liquor by filtration, washed with ethanol ( $3 \times 10$  ml) and diethyl ether ( $2 \times 10$  ml) and dried in vacuo. Yield: 660 mg, 75%. For growing single crystals of  $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1a}$  suitable for X-ray structure analysis the same procedure as described for  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$  was performed. M.p. 182°C (slow dec.). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2033 \text{ cm}^{-1}$  (w), 2007 (s), 1918 (vs), 1880 (s). – UV/Vis (THF):  $\lambda$  (lg  $\epsilon$ ) = 340 nm (4.32, sh), 392 (3.93, sh). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 8.02\text{--}7.87$  (m, 40 H, aromatic H), 4.35 (q, 4 H,  $\text{OCH}_2$ ), 1.45 (t, 6 H,  $\text{OCH}_2\text{CH}_3$ ). –  $^{13}\text{C}$

NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 230.6$  (s,  $\text{C}_{\text{COax}}$ ), 223.2 (s,  $\text{C}_{\text{COeq}}$ ), 136.4 (s,  $\text{C}_{\text{para}}$ ), 135.6 (d,  $^2J_{\text{P,C}} = 11 \text{ Hz}$ ,  $\text{C}_{\text{ortho}}$ ), 131.3 (d,  $^3J_{\text{P,C}} = 13 \text{ Hz}$ ,  $\text{C}_{\text{meta}}$ ), 118.9 (d,  $^1J_{\text{P,C}} = 90 \text{ Hz}$ ,  $\text{C}_{\text{ipso}}$ ), 61.9 ( $\text{OCH}_2$ ), 19.8 ( $\text{OCH}_2\text{CH}_3$ ). –  $^{119}\text{Sn}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 1460$ . –  $^{31}\text{P}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 24.3$  ( $^1J_{\text{C,P}} = 89 \text{ Hz}$ ). –  $\text{C}_{72}\text{H}_{50}\text{Cr}_4\text{O}_{22}\text{P}_2\text{Sn}_2$  (1774.4): calcd. C 48.74, H 2.96; found C 47.90, H 2.84.

$[\text{Ph}_4\text{P}]_2[(\text{CO})_5\text{W}\}_2\text{Sn}(\mu_2\text{-OEt})_2\text{Sn}\{\text{W}(\text{CO})_5\}_2]$  ( $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1c}$ ): In an analogous procedure  $\text{Na}_2[(\text{CO})_5\text{W}\}_2\text{SnCl}_2]$  (442 mg; 0.5 mmol) in ethanol (50 ml) was treated with a solution of NaH (25 mg; 1 mmol) in ethanol (20 ml). The workup and crystal growth followed the methods described above. Yield: 780 mg, 68%. – M.p. 203°C (dec.). – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2044 \text{ cm}^{-1}$  (w), 2025 (s), 1923 (vs), 1878 (s). – UV/Vis (THF):  $\lambda$  (lg  $\epsilon$ ) = 318 nm (4.21), 369 (3.86, sh), 417 (3.62). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 8.04\text{--}7.86$  (m, 40 H, aromatic H), 4.24 (q,  $J = 6.8 \text{ Hz}$ , 4 H,  $\text{OCH}_2$ ), 1.41 (t,  $J = 6.8 \text{ Hz}$ , 6 H,  $\text{OCH}_2\text{CH}_3$ ). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 209.1$  (s,  $\text{C}_{\text{COax}}$ ), 204.7 (s,  $\text{C}_{\text{COeq}}$ ), 136.4 (d,  $^4J_{\text{P,C}} = 3 \text{ Hz}$ ,  $\text{C}_{\text{para}}$ ), 135.7 (d,  $^2J_{\text{P,C}} = 11 \text{ Hz}$ ,  $\text{C}_{\text{ortho}}$ ), 131.5 (d,  $^3J_{\text{P,C}} = 13 \text{ Hz}$ ,  $\text{C}_{\text{meta}}$ ), 119.1 (d,  $^1J_{\text{P,C}} = 90 \text{ Hz}$ ,  $\text{C}_{\text{ipso}}$ ), 62.7 ( $\text{OCH}_2$ ), 19.5 ( $\text{OCH}_2\text{CH}_3$ ). –  $^{119}\text{Sn}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 1169$  ( $^1J_{\text{W,Sn}} = 523 \text{ Hz}$ ). –  $^{31}\text{P}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 24.3$ . –  $\text{C}_{72}\text{H}_{50}\text{O}_{22}\text{P}_2\text{Sn}_2\text{W}_4$  (2301.9): calcd. C 37.57, H 2.19; found C 37.18, H 2.60.

$[n\text{Bu}_4\text{N}][(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{acac})]$  ( $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{2}$ ): 2,4-Pentandione (50 mg; 0.5 mmol) was added in one portion to a solution of  $[n\text{Bu}_4\text{N}]_2[(\text{CO})_5\text{Cr}\}_2\text{Sn}(\mu_2\text{-OEt})_2\text{Sn}\{\text{Cr}(\text{CO})_5\}_2]$  ( $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{1a}$ ) (790 mg; 0.5 mmol) in THF (30 ml). The reaction mixture was stirred for 2 h, filtered through Kieselgur (3 cm) and dried. The oily yellow residue was dissolved in THF (3 ml) and chromatographed on silica gel (10 cm;  $\varnothing = 3 \text{ cm}$ ; diethyl ether). Elution with diethyl ether gave a yellow band which was found, by IR-spectroscopic comparison, to consist mainly of  $[\text{Cr}(\text{CO})_6]$ .<sup>[22]</sup> An orange band which contained  $[n\text{Bu}_4\text{N}]_2 \cdot \mathbf{2}$  was eluted with THF. This THF solution was dried in vacuo leaving a yellow orange oil which could not be crystallized. Yield: 350 mg; 42%. – IR (THF):  $\nu_{\text{CO}} = 2039$  (w), 2004 (s), 1919 (vs), 1891 (s)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 5.58$  (s, 1 H,  $\text{CH}$ ), 3.42 (m, 16 H, 1- $\text{H}_\text{N}$ ), 2.05 (s, 6 H,  $\text{CH}_3$ ), 1.82 (m, 16 H, 2- $\text{H}_\text{N}$ ), 1.47 (m, 16 H, 3- $\text{H}_\text{N}$ ), 1.04 (t, 24 H, 4- $\text{H}_\text{N}$ ). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 229.7$  (s,  $\text{C}_{\text{COax}}$ ), 222.7 (s,  $\text{C}_{\text{COeq}}$ ), 192.8 ( $\text{C}_{\text{C=O}}$ ), 101.4 ( $\text{C}_{\text{C=C}}$ ), 59.5 (s,  $\text{C}_\text{N-1}$ ), 27.7 ( $\text{C}_{\text{Me}}$ ), 24.4 (s,  $\text{C}_\text{N-2}$ ), 20.4 (s,  $\text{C}_\text{N-3}$ ), 13.9 (s,  $\text{C}_\text{N-4}$ ). –  $^{119}\text{Sn}$  NMR ( $[\text{D}_6]\text{acetone}$ , 25°C):  $\delta = 1205$ .

$[\text{Na}(12\text{-Crown-4})_2][(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{pyro})]$  ( $[\text{Na}(12\text{-Crown-4})_2] \cdot \mathbf{3}$ ): 3-Hydroxy-2-methyl- $\gamma$ -pyrone (63 mg; 0.5 mmol) was deprotonated with NaH (12 mg; 0.5 mmol) at  $-70^\circ\text{C}$  in THF (20 ml). The solution was allowed to warm up slowly to 25°C and was poured into a yellow solution of the disodium salt  $\text{Na}_2[(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$  (310 mg; 0.5 mmol) in THF (30 ml). The reaction mixture was stirred for 2 h, filtered through Kieselgur (3 cm) and dried. The oily orange residue was dissolved in diethyl ether (3 ml) and chromatographed on silica gel (15 cm;  $\varnothing = 3 \text{ cm}$ ; diethyl ether). Elution with diethyl ether gave a yellow band which contained  $[\text{Cr}(\text{CO})_6]$  and another unidentified product (by IR-spectroscopic comparison with  $[(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{oxinato})_2]$  (oxinato = 8-oxoquinolato)<sup>[8b]</sup> it appears probable that the product is  $[(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{pyro})_2]$ . An orange band which contains  $[\text{Na}(\text{THF})_x] \cdot \mathbf{3}$  could be eluted with THF. This THF fraction was concentrated to 5 ml and 12-Crown-4 (36 mg; 0.2 mmol) was added.

For growing single crystals of  $[\text{Na}(12\text{-Crown-4})_2] \cdot \mathbf{3}$  the following procedure was carried out: A concentrated THF solution (5 ml) of  $[\text{Na}(12\text{-Crown-4})_2] \cdot \mathbf{3}$  was shared out between three test-tubes ( $\varnothing =$

1 cm) which were brought into a Schlenk tube (250 ml). Diethyl ether (30 ml), within the tube, was allowed to diffuse through the gas phase into the THF solution (3 h). After this period of time the diethyl ether was replaced by petroleum ether (boiling range 40–60°C) (50 ml). Vapor diffusion of the petroleum ether (10 d) yielded yellow single crystals suitable for X-ray structure analysis. Crystalline yield: 110 mg; 11%. M.p. 166°C (dec.). – IR (THF):  $\nu_{\text{CO}} = 2037$  (w), 2001 (s), 1917 (vs), 1889 (s)  $\text{cm}^{-1}$ . – UV/Vis (THF):  $\lambda$  (lg  $\epsilon$ ) = 309 (4.45), 357 (3.98). – <sup>1</sup>H NMR for [Na(sol<sub>v</sub>)<sub>x</sub>]<sub>2</sub>·3 ([D<sub>6</sub>]acetone, 25°C):  $\delta$  = 8.04 (d, 1 H, H5), 6.73 (d, 1 H, H6), 2.44 (s, 3 H, H7) (numbers refer to Figure 1). – <sup>13</sup>C NMR for [Na(sol<sub>v</sub>)<sub>x</sub>]<sub>2</sub>·3 ([D<sub>6</sub>]acetone, 25°C):  $\delta$  = 229.8 (s, C<sub>COax</sub>), 222.6 (s, C<sub>COeq</sub>), 177.6 (C1), 156.0 (C5), 155.3 (C2), 153.7 (C3), 111.5 (C6), 15.3 (C7) (numbers as given in Figure 1). – <sup>119</sup>Sn NMR for [Na(sol<sub>v</sub>)<sub>x</sub>]<sub>2</sub>·3 ([D<sub>6</sub>]acetone, 25°C):  $\delta$  = 1361. – [Na(12-Crown-4)<sub>2</sub>]<sub>2</sub>·3, C<sub>32</sub>H<sub>37</sub>Cr<sub>2</sub>NaO<sub>21</sub>Sn (1003.3): calcd. C 38.31, H 3.72; found C 38.37, H 3.85.

**X-ray Structure Determinations:** The measurements for [nBu<sub>4</sub>N]<sub>2</sub>·1a, [Ph<sub>4</sub>P]<sub>2</sub>·1a, [Ph<sub>4</sub>P]<sub>2</sub>·1c, and [Na(12-Crown-4)<sub>2</sub>]<sub>2</sub>·3 were carried out with a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-K $\alpha$  radiation. The intensities of three check reflections (measured every 100 reflections) remained constant (except for [nBu<sub>4</sub>N]<sub>2</sub>·1a) throughout the data collection, thus indicating crystal and electronic stability. All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-86 program and refined with the SHELX93 program.<sup>[23]</sup> The program XPLOR<sup>[24]</sup> was used for graphical handling of the data. Absorption corrections ( $\psi$  scan,  $\Delta\psi = 10^\circ$ ) were applied to the data. The structures were refined in fully or partially anisotropic models by full-matrix least-squares calculations. Hydrogen atoms were introduced at calculated positions. Table 5 compiles the data for the structure determinations. Peculiarities about the structure of [Na(12-Crown-4)<sub>2</sub>]<sub>2</sub>·3 are the following: One of the crown ether molecules shows disorder and could only be refined isotropically.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408368 ([nBu<sub>4</sub>N]<sub>2</sub>·1a), -408369 ([Ph<sub>4</sub>P]<sub>2</sub>·1a), -408367 ([Ph<sub>4</sub>P]<sub>2</sub>·1c), -408370 ([Na(12-Crown-4)<sub>2</sub>]<sub>2</sub>·3).

\* Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

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trigonal-planar coordination around the oxygen atom (see ref.<sup>[11]</sup>). While Sn–O  $\pi$ -bonding might be a reason for this this  $\pi$  contribution is found to be small. In an EHT analysis the model as used above was compared with a model in which the hydrogen atoms of the H–O groups were deliberately set at positions 40° away from the  $x$  direction in the  $xz$  plane (Figure 4) in a mutually anti-sense. Only a minor change in the total energy was observed; the “in-plane” model being about 0.1 eV more stable than the “out-of-plane” model. Bonding and antibonding effects of this bending must therefore almost compensate each other within the set of occupied orbitals. An analogous model calculation was done for [HSnOH]<sub>2</sub> as a prototype of the species **a**. Here as well bending did not cause dramatic change in the total energy (the “in-plane” model is about 0.01

eV more stable). It appears therefore that the potential describing this bending motion is quite soft and that neither the coplanarity nor the distortion from coplanarity of the R–O-bonds has any specific and easy to interpret meaning. It is observed that the compounds [RGe( $\mu_2$ -SR)<sub>2</sub>GeR], isoelectronic to **a**, show distinctively pyramidal coordination around sulfur (see ref.<sup>[11]</sup>).

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