

# Molybdenum and Tungsten Tricarbonyl Complexes with the Tripodal Ligands [<sup>n</sup>BuSn(2-pyridyl)<sub>3</sub>] and [RSn(methylthiomethyl)<sub>3</sub>]

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The ligands [<sup>n</sup>BuSn(2-pyridyl)<sub>3</sub>] and [RSn(methylthiomethyl)<sub>3</sub>] (R = <sup>n</sup>Bu, Me) have been prepared in a one-pot, two-step procedure from the corresponding alkyltin trichloride and 2-pyridyl or methylthiomethyl carbanions. The reaction of these ligands with [M(CO)<sub>3</sub>(NCR)<sub>3</sub>] (M = Mo, W) afforded the tricarbonyl compounds [{<sup>n</sup>BuSn(2-pyridyl)<sub>3</sub>}M(CO)<sub>3</sub>] and [{RSn(methylthiomethyl)<sub>3</sub>}M(CO)<sub>3</sub>]. In addition to IR and NMR characterization, the structure of three of these new complexes was determined by single-crystal X-ray diffraction.

## Introduction

Since their invention by Trofimenko in the 1960s, tris(pyrazolyl) borate ligands (**A**) have become some of the most useful auxiliaries in coordination chemistry.<sup>1</sup> These ligands are conveniently prepared by reaction of pyrazoles with the tetrahydroborate anion. Complexes with tris(pyrazolyl)borates are now known with almost every metallic element, and their applications include stoichiometric organic transformations,<sup>2–12</sup> catalysis,<sup>13</sup> and modeling of enzymatic metal sites.<sup>14</sup>

In recent years, Riordan published the preparation of the related tris(alkylthiomethyl)borate ligands (**B**) (which, having sulfur as donor atoms, provide a softer metal environment) and of several metal derivatives.<sup>15</sup> The synthesis of these ligands is based on the reaction of lithium methylthioalkyls (generated in situ by metalation of methylalkylsulfides) with boron halides.

Tris(pyrazolyl)alkanes (**C**), the neutral, isoelectronic, and isosteric analogues of tris(pyrazolyl)borates, were reported by Trofimenko as early as 1970,<sup>16</sup> but their

coordination chemistry remains considerably less developed than that of tris(pyrazolyl)borates.<sup>17</sup> This is partly due to the lower yield and more tedious procedures involved in the synthesis of tris(pyrazolyl)alkanes, a consequence of the low reactivity of the C–Cl bonds in the precursors.<sup>16,17f,18</sup>

Recently, Rabinovich reported the preparation of neutral tris(alkylthiomethyl)silanes<sup>19</sup> (**D**) and tris(pyrazolyl)silanes<sup>20</sup> (**E**) and their tricarbonyl-group 6 metal derivatives. The change in the bridgehead atom from

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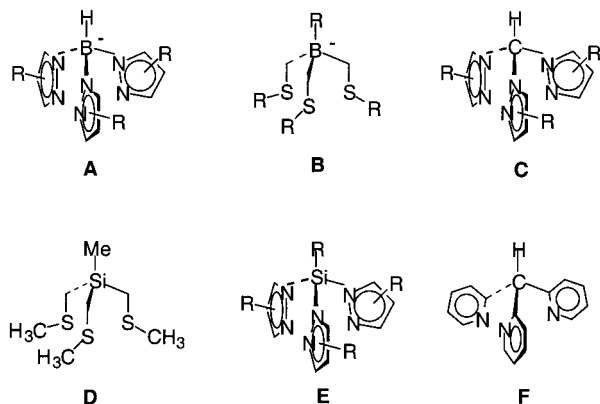
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**Figure 1.** Several tripodal ligands.

carbon to silicon provided a better synthetic procedure as a result of Si–Cl bonds being more reactive than C–Cl bonds.

Neutral tris(pyridyl)methane tripod ligands (**F**) received far less attention than tris(pyrazolyl)borates, despite pyridine being considered both a better  $\sigma$ -donor and a better  $\pi$ -acidic ligand than pyrazole.<sup>21</sup> Again, this may be due to the multistep, laborious procedures needed for the synthesis of the ligands.<sup>22</sup> The molybdenum and tungsten tricarbonyls [ $\{HC(py)_3\}M(CO)_3$ ] ( $py = 2$ -pyridyl) have been employed by Faller for the synthesis of highly electrophilic complexes.<sup>23</sup> Recently, Wright reported the isolation of the LiBr adduct of the new ligand  ${}^nBuSn(py)_3$  as the product of the reaction of  $Sn(C_5H_5)_2$  with 2-lithiopyridine (generated in situ from

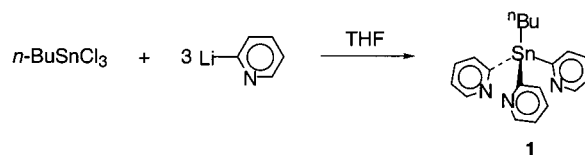
2-bromopyridine and  ${}^nBuLi$ ) and the byproduct  ${}^nBuBr$ .<sup>24</sup> We envisaged the free ligand  ${}^nBuSn(py)_3$  as an alternative to tris(pyridyl)alkanes if a rational, straightforward synthesis could be found.

Here we report the synthesis of  ${}^nBuSn(py)_3$  by reaction of  $n$ -butyltin trichloride and 2-lithiopyridine, the preparation of new  $RnSn(CH_2SCH_3)_3$  ligands by a similar route, and the synthesis and characterization of molybdenum and tungsten tricarbonyl complexes of both kinds of ligands.

## Results and Discussion

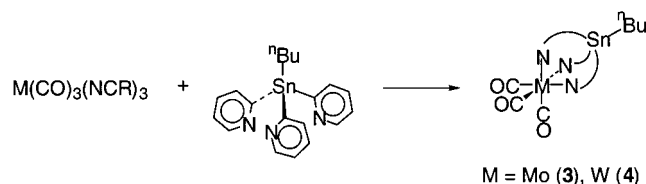
The reaction of  $n$ -butyltin trichloride with 3 equiv of 2-lithiopyridine (generated in situ from 2-bromopyridine and  ${}^nBuLi$ ) in THF afforded  ${}^nBuSn(py)_3$  (**1**) ( $py = 2$ -pyridyl) (see Scheme 1). Metathetical reactions between halotin(IV) compounds and organolithium reagents are well known and, in fact, are the main entry to organotin compounds. However, the fact that the reaction of 2-lithiopyridine and  ${}^nBuSnCl_3$  works well to give  ${}^nBuSn(py)_3$  could not be anticipated as a sure, trivial outcome. Thus, 2-lithiopyridine shows a great tendency to undergo carbon–carbon coupling to yield 2,2'-bipyridine. Oxidant reagents such as  $P(O)Cl_3$ , but also  $PCl_3$ , have been found to effect this coupling, limiting the use of the 2-lithiopyridine reagent.<sup>25</sup>

### Scheme 1



Once the lithium halides were removed by filtration, the crude ligand **1** was used directly for the synthesis of metal complexes. Thus, its reaction with an equimolar amount of molybdenum hexacarbonyl in refluxing THF afforded the complex [ $\{{}^nBuSn(py)_3\}Mo(CO)_3$ ] (**3**). Alternatively, **3** was obtained by reaction of **1** with the labile complex  $[Mo(CO)_3(NCMe)_3]$ .<sup>26</sup> In a similar manner, the complex [ $\{{}^nBuSn(py)_3\}W(CO)_3$ ] (**4**) was prepared by reaction of  $[W(CO)_3(NCet)_3]$ <sup>27</sup> and **1** (see Scheme 2). The

### Scheme 2



tricarbonyl complexes **3** and **4** were purified by filtration through alumina followed by crystallization. Although crude **1** can be used for the preparation of complexes as described above, the ligand could be purified by extraction into acidic aqueous phase, followed by neu-

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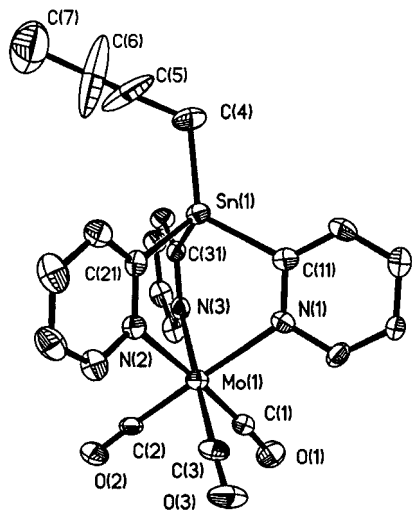
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**Figure 2.** Molecular structure and numbering scheme of **3** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

triazolization and extraction to organic phase (see Experimental Section). This shows that **1** is resistant toward hydrolysis, a property not shared by tris(pyrazolyl)borates.<sup>28</sup>

The complexes **3** and **4** are virtually insoluble in pentane and hexane and show moderate solubility in toluene, methylene chloride, and THF. This contrasts with the insolubility in  $\text{CH}_2\text{Cl}_2$  shown by  $[\{\text{HC}(\text{py})_3\}\text{Mo}(\text{CO})_3]^{23}$  and can be attributed to the presence of the  ${}^n\text{Bu}$  group. A sample of complex **3** could be refluxed in toluene for 6 h without change, showing that decomposition pathways are not facile.<sup>29</sup>

The IR spectra of complexes **3** and **4** in the carbonyl region showed two strong absorption bands, as expected for a facial arrangement of the three carbonyl ligands. The observed  $\nu_{\text{CO}}$  values for **3** are similar to those of the complex  $[\{\text{HC}(\text{py})_3\}\text{Mo}(\text{CO})_3]$ ,<sup>30</sup> showing that the donor-acceptor properties of the tris(pyridyl) ligands are little sensitive to the nature of the bridgehead atom. The  ${}^1\text{H}$  NMR data of **3** indicate the equivalence of the three 2-pyridyl groups, which further confirms the  $C_{3v}$  symmetry of the complex. The close similarity in the spectroscopic data of **3** and **4** indicates that both compounds are isostructural.

The structure of **3** was determined by single-crystal X-ray diffraction, and the results (see Figure 2) confirm the  $[\{\text{BuSn}(\text{py})_3\}\text{Mo}(\text{CO})_3]$  composition of the molecule. The coordination geometry around the molybdenum atom corresponds to a distorted octahedron, with the leaning of the  ${}^n\text{Bu}$  group ( $\text{C}(4)\text{--Sn--C}(11) = 123.4(5)^\circ$ ,  $\text{C}(4)\text{--Sn--C}(21) = 120.1(5)^\circ$ , and  $\text{C}(4)\text{--Sn--C}(31) = 105.7(4)^\circ$ ) surely due to packing forces, making the molecule somewhat asymmetric. The molybdenum-nitrogen distances are close to those found in tris(pyrazolyl)silane and tris(pyrazolyl)borate molybdenum

**Table 1.** Selected Bond Distances and Angles for Complex **3**

Bond Distances (Å)			
Mo(1)–C(1)	1.872(13)	Sn(1)–C(21)	2.144(10)
Mo(1)–C(2)	1.932(12)	Sn(1)–C(31)	2.157(11)
Mo(1)–C(3)	1.952(13)	Sn(1)–C(4)	2.124(11)
Mo(1)–N(1)	2.339(8)	C(1)–O(1)	1.206(13)
Mo(1)–N(2)	2.342(9)	C(2)–O(2)	1.173(12)
Mo(1)–N(3)	2.315(9)	C(3)–O(3)	1.151(12)
Sn(1)–C(11)	2.154(10)		
Bond Angles (deg)			
C(1)–Mo(1)–C(2)	85.4(5)	C(21)–Sn(1)–C(31)	103.2(4)
C(1)–Mo(1)–C(3)	83.0(5)	C(4)–Sn(1)–C(11)	123.4(5)
C(2)–Mo(1)–C(3)	88.1(5)	C(4)–Sn(1)–C(21)	120.1(5)
C(1)–Mo(1)–N(1)	92.6(4)	C(4)–Sn(1)–C(31)	105.7(4)
C(2)–Mo(1)–N(1)	177.9(4)	C(4)–C(5)–Sn(1)	114.6(12)
C(3)–Mo(1)–N(1)	92.0(4)	C(11)–N(1)–Mo(1)	127.9(7)
C(1)–Mo(1)–N(2)	173.4(4)	C(21)–N(2)–Mo(1)	127.0(7)
C(2)–Mo(1)–N(2)	94.3(4)	C(31)–N(3)–Mo(1)	117.0(9)
C(3)–Mo(1)–N(2)	90.3(4)	N(1)–C(11)–Sn(1)	113.4(7)
C(1)–Mo(1)–N(3)	94.9(4)	N(2)–C(21)–Sn(1)	115.5(7)
C(2)–Mo(1)–N(3)	91.3(4)	N(3)–C(31)–Sn(1)	116.0(7)
C(3)–Mo(1)–N(3)	177.9(4)	O(1)–C(1)–Mo(1)	177.4(10)
C(11)–Sn(1)–C(21)	98.7(4)	O(2)–C(2)–Mo(1)	176.7(11)
C(11)–Sn(1)–C(31)	103.0(4)	O(3)–C(3)–Mo(1)	176.0(11)

tricarbonyl complexes.<sup>20</sup> The metrical data of the tridentate ligand in **3** are similar to those found in tetrahedral complexes  $[\{\text{BuSn}(\text{py})_3\}\text{MBr}]$  ( $\text{M} = \text{Li}, \text{Cu}$ ),<sup>24</sup> but the magnitude of the standard deviations precludes detailed comparisons.

We wanted to extend the synthesis of tin-based tripodal ligands to include sulfur donors. By analogy with the synthetic schemes employed by Riordan<sup>15</sup> and Rabinovich,<sup>19</sup> we first considered the reaction of  ${}^n\text{BuSnCl}_3$  with 3 equiv of  $\text{LiCH}_2\text{SCH}_3$ . The preparation of  $\text{LiCH}_2\text{SCH}_3$  is usually carried out by metalation of dimethyl sulfide with the strongly basic  ${}^n\text{BuLi}$ /tetramethylethylenediamine reagent.<sup>31</sup> Due to the very low acidity of the sulfide, a 2 h refluxing period is sometimes used to complete the deprotonation. Rabinovich reported an additional 18 h refluxing time for the reaction of  $\text{LiCH}_2\text{SCH}_3$  with  $\text{MeSiCl}_3$ .<sup>19a</sup> We have investigated the metalation of dimethyl sulfide with alternative reagents and have found that the  ${}^n\text{BuLi}/\text{NaO}^t\text{Bu}$  "superbasic" reagent<sup>32</sup> led to an improved procedure. The metalation of  $\text{SMe}_2$  was conducted without an additional solvent to avoid competitive metalation reactions.<sup>33</sup> Thus, addition of  $\text{NaO}^t\text{Bu}$  and  ${}^n\text{BuLi}$  in a 1:1 ratio to  $\text{SMe}_2$  gave an equimolar solution of the deprotonated dimethyl sulfide. The reaction took place instantaneously, and the resulting solution was used for the reaction with  ${}^n\text{BuSnCl}_3$  (see Scheme 3). Despite repeated attempts, the new tris(methylthiomethyl)tin ligand obtained in this way could not be isolated in a pure state; therefore, the crude ligand was allowed to react with the complexes  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$  and  $[\text{W}(\text{CO})_3(\text{NCe}t)_3]$  (see Scheme 4), and the resulting tricarbonyl complexes

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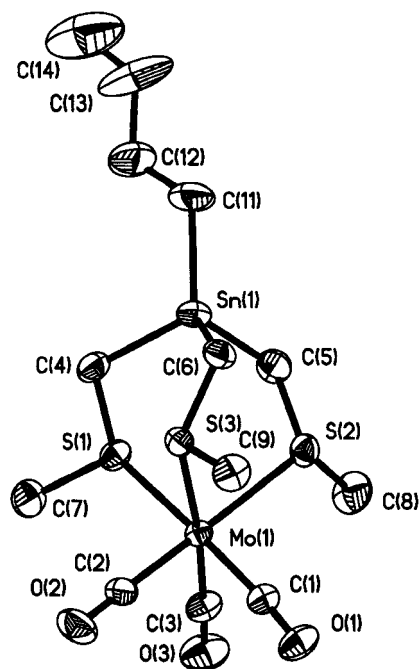
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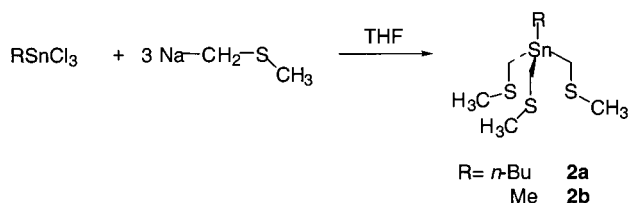
(30) The IR spectrum of  $[\text{HC}(\text{py})_3\text{Mo}(\text{CO})_3]$  is reported (ref 23) in KBr pellet as consisting of two  $\nu_{\text{CO}}$  bands at 1897 and 1769  $\text{cm}^{-1}$ . For complex **3**, the broad, lower-frequency, E-mode band (at 1779  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solution) splits into two bands in KBr, leaving a pattern of three bands at 1900, 1788, and 1739  $\text{cm}^{-1}$ , with an average of the two lower bands at 1763  $\text{cm}^{-1}$ .



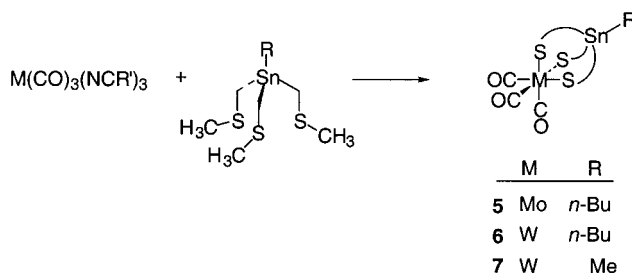
**Figure 3.** Molecular structure and numbering scheme of **5** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

[<sup>n</sup>BuSn(CH<sub>2</sub>SCH<sub>3</sub>)<sub>3</sub>]Mo(CO)<sub>3</sub> (**5**) and [<sup>n</sup>BuSn(CH<sub>2</sub>SCH<sub>3</sub>)<sub>3</sub>]W(CO)<sub>3</sub> (**6**) were purified by filtration through alumina. The methyltin derivative [MeSn(CH<sub>2</sub>SCH<sub>3</sub>)<sub>3</sub>]W(CO)<sub>3</sub> (**7**) was prepared by an identical route. The IR spectra of **5** and **6** show  $\nu_{\text{CO}}$  bands at wavenumbers significantly higher than **3** and **4**, showing thiolates to be weaker donors than pyridyls. Wavenumber values for **6** (1920 and 1803 cm<sup>-1</sup>) are lower than those of **5** (1928 and 1811 cm<sup>-1</sup>), a trend also found for complexes **3** and **4** that reflects the more electron-rich nature of

**Scheme 3**



**Scheme 4**

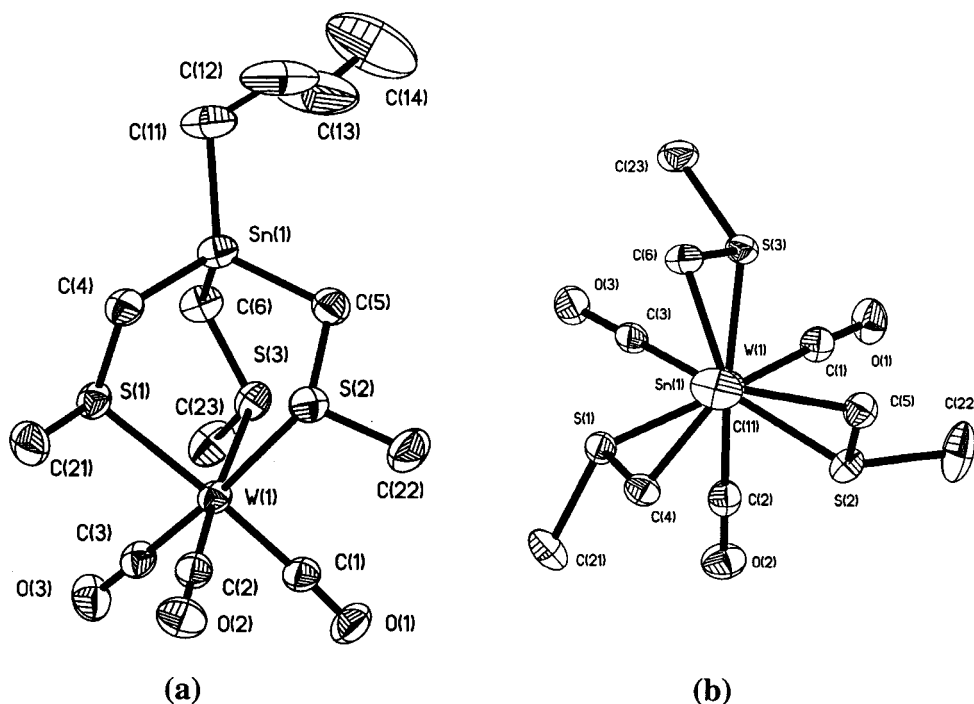


tungsten. The IR of **6** and **7** are indistinguishable; thus, the remote R group on tin has a negligible effect on the donor capabilities of the tripod ligand.

The structures of **5** and **6** were determined by X-ray diffraction, and the results are shown in Figures 3 and 4, and in Tables 2 and 3.

The molecules of **5** and **6** are isostructural and consist of the <sup>n</sup>BuSn(CH<sub>2</sub>SCH<sub>3</sub>)<sub>3</sub> ligand coordinated as face-capping tridentate to Mo(CO)<sub>3</sub> and W(CO)<sub>3</sub> moieties. As found in the structures of other complexes with tridentate thioethers,<sup>15,19</sup> the methylthiomethyl arms in complexes **5** and **6** show a propeller-like arrangement, being canted in the same direction with respect to the C<sub>3</sub> axis (see Figure 4b).

The IR  $\nu_{\text{CO}}$  values of compounds **5**–**7** are very close to those of Rabinovich's MeSi(CH<sub>2</sub>SCH<sub>3</sub>)<sub>3</sub> analogues.<sup>19a</sup>



**Figure 4.** (a) Molecular structure and numbering scheme of **6** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Perspective view of **6**.

Table 2. Bond Distances and Angles for Complex 5

Bond Distances (Å)							
Mo(1)–C(1)	1.935(5)	Sn(1)–C(11)	2.132(6)	S(2)–C(5)	1.791(5)	C(3)–O(3)	1.163(6)
Mo(1)–C(2)	1.938(6)	Sn(1)–C(6)	2.146(5)	S(2)–C(8)	1.814(6)	C(11)–C(12)	1.337(10)
Mo(1)–C(3)	1.943(5)	Sn(1)–C(5)	2.165(6)	S(3)–C(6)	1.785(5)	C(12)–C(13)	1.510(11)
Mo(1)–S(1)	2.580(1)	Sn(1)–C(4)	2.173(5)	S(3)–C(9)	1.804(5)	C(13)–C(14)	1.191(16)
Mo(1)–S(2)	2.599(1)	S(1)–C(4)	1.797(5)	C(1)–O(1)	1.168(6)		
Mo(1)–S(3)	2.592(1)	S(1)–C(7)	1.799(6)	C(2)–O(2)	1.153(6)		
Bond Angles (deg)							
C(1)–Mo(1)–C(2)	85.2(2)	C(1)–Mo(1)–S(2)	93.3(2)	C(5)–Sn(1)–C(4)	103.4(2)	O(1)–C(1)–Mo(1)	175.0(5)
C(1)–Mo(1)–C(3)	85.9(2)	C(2)–Mo(1)–S(2)	174.5(1)	C(4)–S(1)–C(7)	102.1(3)	O(2)–C(2)–Mo(1)	176.2(5)
C(2)–Mo(1)–C(3)	87.6(2)	C(3)–Mo(1)–S(2)	97.6(2)	C(4)–S(1)–Mo(1)	113.0(2)	O(3)–C(3)–Mo(1)	176.2(5)
C(1)–Mo(1)–S(1)	173.9(1)	S(1)–Mo(1)–S(2)	86.73(4)	C(7)–S(1)–Mo(1)	108.1(2)	S(1)–C(4)–Sn(1)	108.2(2)
C(2)–Mo(1)–S(1)	95.3(2)	S(3)–Mo(1)–S(2)	87.83(4)	C(5)–S(2)–C(8)	101.3(3)	S(2)–C(5)–Sn(1)	109.9(3)
C(3)–Mo(1)–S(1)	88.0(1)	C(11)–Sn(1)–C(6)	116.1(3)	C(5)–S(2)–Mo(1)	113.3(2)	S(3)–C(6)–Sn(1)	109.9(3)
C(1)–Mo(1)–S(3)	95.5(1)	C(11)–Sn(1)–C(5)	112.3(3)	C(8)–S(2)–Mo(1)	110.8(3)	C(12)–C(11)–Sn(1)	123.3(6)
C(2)–Mo(1)–S(3)	87.0(1)	C(6)–Sn(1)–C(5)	104.6(2)	C(6)–S(3)–C(9)	99.7(3)	C(11)–C(12)–C(13)	125.8(17)
C(3)–Mo(1)–S(3)	174.3(2)	C(11)–Sn(1)–C(4)	113.8(3)	C(6)–S(3)–Mo(1)	114.6(2)	C(14)–C(13)–C(12)	125.8(17)
S(1)–Mo(1)–S(3)	90.60(4)	C(6)–Sn(1)–C(4)	105.5(2)	C(9)–S(3)–Mo(1)	108.8(2)		

Table 3. Bond Distances and Angles for Complex 6

Bond Distances (Å)							
W(1)–C(3)	1.918(7)	Sn(1)–C(11)	2.126(8)	S(2)–C(5)	1.793(7)	C(3)–O(3)	1.189(8)
W(1)–C(2)	1.938(9)	Sn(1)–C(4)	2.144(7)	S(2)–C(22)	1.797(9)	C(11)–C(12)	1.45(2)
W(1)–C(1)	1.948(8)	Sn(1)–C(5)	2.154(7)	S(3)–C(6)	1.785(5)	C(12)–C(13)	1.30(2)
W(1)–S(1)	2.557(2)	Sn(1)–C(6)	2.180(6)	S(3)–C(6)	1.806(7)	C(13)–C(14)	1.41(2)
W(1)–S(2)	2.595(2)	S(1)–C(4)	1.784(7)	C(1)–O(1)	1.164(8)		
W(1)–S(3)	2.570(2)	S(1)–C(21)	1.797(8)	C(2)–O(2)	1.186(9)		
Bond Angles (deg)							
C(1)–W(1)–C(2)	85.9(3)	C(3)–W(1)–S(2)	175.9(2)	C(5)–Sn(1)–C(6)	103.0(3)	O(1)–C(1)–W(1)	175.6(7)
C(3)–W(1)–C(1)	89.4(3)	C(2)–W(1)–S(2)	91.8(2)	C(4)–S(1)–C(21)	100.9(4)	O(2)–C(2)–W(1)	176.9(6)
C(2)–W(1)–C(1)	84.9(3)	C(1)–W(1)–S(2)	94.7(2)	C(4)–S(1)–W(1)	113.8(2)	O(3)–C(3)–W(1)	179.5(7)
C(3)–W(1)–S(1)	87.15(19)	S(1)–W(1)–S(2)	88.81(6)	C(21)–S(1)–W(1)	110.6(3)	S(1)–C(4)–Sn(1)	108.8(3)
C(2)–W(1)–S(1)	94.9(2)	S(3)–W(1)–S(2)	85.75(6)	C(5)–S(2)–C(22)	101.8(4)	S(2)–C(5)–Sn(1)	108.8(3)
C(1)–W(1)–S(1)	176.5(2)	C(11)–Sn(1)–C(4)	111.2(3)	C(5)–S(2)–W(1)	115.3(2)	S(3)–C(6)–Sn(1)	108.3(3)
C(3)–W(1)–S(3)	93.7(2)	C(11)–Sn(1)–C(5)	117.2(4)	C(22)–S(2)–W(1)	108.9(3)	C(12)–C(11)–Sn(1)	116.1(9)
C(2)–W(1)–S(3)	175.9(2)	C(4)–Sn(1)–C(5)	104.4(3)	C(6)–S(3)–C(23)	100.9(3)	C(13)–C(12)–C(11)	124.8(17)
C(1)–W(1)–S(3)	92.0(2)	C(11)–Sn(1)–C(6)	114.7(3)	C(6)–S(3)–W(1)	114.1(2)	C(12)–C(13)–C(14)	132(2)
S(1)–W(1)–S(3)	88.37(6)	C(4)–Sn(1)–C(6)	105.1(3)	C(23)–S(3)–W(1)	1108.7(3)		

Thus, **5** shows bands at 1929 and 1817  $\text{cm}^{-1}$  in THF solution, in which solvent the bands of  $[\{\text{MeSi}(\text{CH}_2\text{SCH}_3)_3\}\text{Mo}(\text{CO})_3]$  occur at 1931 and 1819  $\text{cm}^{-1}$ . This indicates that there is a small difference in the donor–acceptor properties of the two thioether ligands. However, Mo–S distances in **5** (from 2.580(1) to 2.599(1) Å) are slightly shorter than those in  $[\{\text{MeSi}(\text{CH}_2\text{SCH}_3)_3\}\text{Mo}(\text{CO})_3]$  (from 2.620(1) to 2.625(1) Å), and interestingly, this structural difference correlates with the fact that the tin-based ligand is not as labile as the tris(methylthiomethyl)silane. Thus,  $[\{\text{MeSi}(\text{CH}_2\text{SCH}_3)_3\}\text{Mo}(\text{CO})_3]$  dissociates instantaneously when dissolved in acetonitrile to yield  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$  and the free thioether,<sup>19a</sup> whereas  $[\text{BuSn}(\text{CH}_2\text{SCH}_3)_3\text{Mo}(\text{CO})_3]$  remained unchanged in acetonitrile solution over a 2 day period at room temperature.

## Conclusions

Molybdenum and tungsten tricarbonyl derivatives of the tripodal ligands  ${}^n\text{BuSn}(\text{py})_3$  and  $\text{RSn}(\text{CH}_2\text{SCH}_3)_3$  have been prepared, and three of the new complexes have been structurally characterized. Expedient synthetic procedures have been devised. The new complexes show a stability that should allow studies of their reactivity and encourages the use of the new tripodal ligands toward other metal fragments.

## Experimental Section

**General Procedures.** All manipulations were carried out under nitrogen using standard Schlenk techniques or in a drybox. Solvents were distilled from freshly wired Na (hexanes and toluene), Na/benzophenone ( $\text{Et}_2\text{O}$  and THF), and  $\text{CaH}_2$  ( $\text{CH}_2\text{Cl}_2$ ) prior to use. Acetonitrile, propionitrile, and dimethyl sulfide were purchased as the highest purity available and were purged with nitrogen. Acetone- $d_6$ ,  $\text{CD}_2\text{Cl}_2$ , and  $\text{CDCl}_3$  were degassed by three freeze–pump–thaw cycles, dried over molecular sieves (MS4A), and stored in the dark in Young tubes. Elemental analyses were obtained using a Perkin-Elmer 240-B microanalyzer. The IR and NMR spectra were recorded on Perkin-Elmer FT 1720-X and Bruker AC-200 or AC-300 spectrometers, respectively. 2-Bromopyridine was dried and distilled prior to use.<sup>34</sup>  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ <sup>26</sup> and  $[\text{W}(\text{CO})_3(\text{NCEt})_3]$ <sup>27</sup> were prepared according to literature procedures. All other chemicals were used as received from commercial sources. Hydrogen/carbon atoms of the  ${}^n\text{Bu}$  group are referred to as  $\text{H}_1/\text{C}_1$  to  $\text{H}_4/\text{C}_4$  in the NMR data.

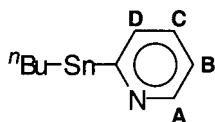
**Crystal Structure Determination for Compounds 3, 5, and 6.** A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized  $\text{Mo K}\alpha$  X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to  $2\theta = 48.6^\circ$ . Raw frame data were integrated with the SAINT<sup>35</sup> program. The structure was solved by direct methods with SHELXTL.<sup>36</sup> A semiempirical absorption correction was ap-

(34) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980; p 140.

(35) SAINT+.SAX area detector integration program, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

**Table 4.** Crystal Data and Refinement Details for Complexes **3**, **5**, and **6**

	<b>3</b>	<b>5</b>	<b>6</b>
formula	C <sub>22</sub> H <sub>21</sub> MoN <sub>3</sub> O <sub>3</sub> Sn	C <sub>13</sub> H <sub>24</sub> MoO <sub>3</sub> S <sub>3</sub> Sn	C <sub>13</sub> H <sub>24</sub> O <sub>3</sub> S <sub>3</sub> SnW
fw	590.05	539.13	627.04
cryst syst	rhombohedral	monoclinic	monoclinic
space group	<i>R</i> 3̄	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> , Å	36.287(8)	8.7421(4)	14.1071(10)
<i>b</i> , Å	36.287(8)	17.3956(9)	10.0682(7)
<i>c</i> , Å	9.125(3)	13.4689(7)	15.4943(12)
α, deg	90	90	90
β, deg	90	92.543(1)	113.797(1)
γ, deg	120	90	90
<i>V</i> , Å <sup>3</sup>	10406(5)	2046.25(18)	2013.6(3)
<i>Z</i>	18	4	4
<i>T</i> , K	293(2)	293(2)	299(2)
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	1.695	1.750	2.068
<i>F</i> (000)	5220	1064	1192
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst size, mm	0.03 × 0.05 × 0.1	0.12 × 0.14 × 0.21	0.14 × 0.16 × 0.17
μ, mm <sup>-1</sup>	1.649	2.144	7.264
scan range, deg	1.12 ≤ θ ≤ 23.37	1.91 ≤ θ ≤ 23.27	1.65 ≤ θ ≤ 23.30
abs corr	SADABS	SADABS	SADABS
no. of reflns measd	15 837	9156	9007
no. of ind reflns	3360	2944	2904
no. of data/restraints/params	3360/0/272	2944/0/195	2904/0/195
goodness-of-fit on <i>F</i> <sup>2</sup>	1.000	1.039	1.044
<i>R</i> <sub>1</sub> / <i>R</i> <sub>w</sub> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0471/0.1350	0.0297/0.0719	0.0268/0.0655
<i>R</i> <sub>1</sub> / <i>R</i> <sub>w</sub> 2 (all data)	0.0853/0.1571	0.0355/0.0755	0.0313/0.0688

**Figure 5.** Atom labeling schemes for the <sup>125</sup>BuSn(2-pyridyl)<sub>3</sub> ligand.

plied with the program SADABS.<sup>37</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL. Crystal and refinement data are presented in Table 4.

**Synthesis of [<sup>125</sup>BuSn(2-pyridyl)<sub>3</sub>] (1).** To a solution of 2-bromopyridine (95 μL, 1 mmol) in THF (20 mL) cooled to -78 °C was added <sup>125</sup>BuLi (625 μL, 1 mmol), and the mixture was stirred for 1 h. To the resulting orange solution was added <sup>125</sup>BuSnCl<sub>3</sub> (55 μL, 0.33 mmol) via microsyringe, and the mixture was allowed to reach room temperature, stirring for 2 h. The yellow solution obtained was evaporated in vacuo, and the residue was redissolved in diethyl ether (20 mL). Hydrochloric acid (6 N, 20 mL) was added, the two phases were thoroughly mixed, and the diethyl ether solution was separated from the aqueous layer. The resulting organic solution was washed with 6 N hydrochloric acid (3 × 10 mL). The combined aqueous solutions were stirred with decolorizing carbon for 1 h at room temperature. Then the solution was filtered, and a saturated potassium hydroxide solution was added until the pH was basic. Chloroform (50 mL) was added, the mixture was stirred to provide a good contact between the phases, and the aqueous layer was separated from the chloroform solution. The aqueous solution was washed with chloroform (2 × 20 mL), and the combined organic layers were dried over MgSO<sub>4</sub> overnight. After filtration and evaporation of the solvent, **1** was obtained as a white powder. Yield: 0.094 g, 69%. Anal. Calcd for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>Sn: C, 55.65; H, 5.16; N, 10.24. Found: C, 55.58; H, 5.27; N, 10.12. <sup>1</sup>H NMR(CDCl<sub>3</sub>): 8.80 [d(4.62), 3H, H<sub>A</sub>], 7.63

[m, 6H, H<sub>B</sub> and H<sub>D</sub>], 7.21 [m, 3H, H<sub>C</sub>], 1.74 [m, 2H, H<sub>I</sub>], 1.39 [m, 4H, H<sub>2</sub> and H<sub>3</sub>], 0.84 [t(7.18), 3H, H<sub>4</sub>].

**Synthesis of [<sup>125</sup>BuSn(methylthiomethyl)<sub>3</sub>] (2a).** To a suspension of NaO<sup>t</sup>Bu (1.2 mmol, 0.115 g) in 5 mL of SME<sub>2</sub> was added <sup>125</sup>BuLi (0.75 mL, 1.6 M solution in hexanes, 1.2 mmol), and the mixture was stirred for 15 min. The volatiles were removed in vacuo. A tiny amount of this white solid on the tip of a spatula was exposed to the air, causing a violent detonation. *Proper care is therefore advised.* A solution of <sup>125</sup>BuSnCl<sub>3</sub> (55 μL, 0.33 mmol) in THF (20 mL) cooled to -78 °C was transferred via cannula onto the solid. The mixture was allowed to reach room temperature and then kept stirring for 2 h. The solution was assumed to contain 0.3 mmol of **2a** and employed for subsequent syntheses.

**Synthesis of [MeSn(methylthiomethyl)<sub>3</sub>] (2b).** The procedure was similar to that described above for the preparation of **2a** starting from SME<sub>2</sub> (7 mL), NaO<sup>t</sup>Bu (0.67 mmol, 0.065 g), <sup>125</sup>BuLi (0.420 mL, 1.6 M solution in hexanes, 0.67 mmol), and MeSnCl<sub>3</sub> (0.050 g, 0.21 mmol).

**Synthesis of [{<sup>125</sup>BuSn(2-pyridyl)<sub>3</sub>}Mo(CO)<sub>3</sub>] (3). (a) From [Mo(CO)<sub>6</sub>].** A stirred suspension of [Mo(CO)<sub>6</sub>] (0.081 g, 0.31 mmol) and **1** (0.33 mmol) in THF (20 mL) was heated to reflux under nitrogen for 6 h, giving an orange solution. The solvent was evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through alumina (activation grade III). The volatiles were removed in vacuo, and the residue was washed with hexane (3 × 10 mL). Slow diffusion of Et<sub>2</sub>O into a solution of [{<sup>125</sup>BuSn(2-pyridyl)<sub>3</sub>}Mo(CO)<sub>3</sub>] in THF (5 mL) at room temperature produced orange crystals of **3**. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.110 g, 60%. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>MoN<sub>3</sub>O<sub>3</sub>Sn: C, 44.78; H, 3.58; N, 7.12. Found: C, 44.87; H, 3.69; N, 6.95. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1906 (vs), 1779 (s) cm<sup>-1</sup>. IR ν(CO) (KBr): 1900 (vs), 1788 (vs), 1739 (vs). IR ν(CO) (Nujol): 1900 (vs), 1790 (vs), 1740 (vs). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 9.41 [d(5.41), 3H, H<sub>A</sub>], 7.78 [m, 6H, H<sub>B</sub> and H<sub>D</sub>], 7.30 [m, 3H, H<sub>C</sub>], 2.38 [m, 4H, H<sub>I</sub> and H<sub>2</sub>], 1.70 [m, 2H, H<sub>3</sub>], 1.09 [t(7.25), 3H, H<sub>4</sub>].

**(b) From [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>].** A solution of **1** (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added onto a solution of [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>]<sup>26</sup> (0.98 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. Immediately the initially yellow solution turned orange. The mixture was stirred for 30 min and filtered through alumina (activation grade III). The workup was as described above. Yield: 0.325

(36) Sheldrick, G. M. *SHELXTL*, An integrated system for solving, refining, and displaying crystal structures from diffraction data, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

(37) Sheldrick, G. M. *SADABS*, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1997.

g, 56%. The product exhibits the same spectroscopic properties as the compound obtained in (a).

**Synthesis of [<sup>n</sup>BuSn(2-pyridyl)<sub>3</sub>W(CO)<sub>3</sub>] (4).** A solution of **1** (0.33 mmol) in 10 mL of THF was transferred onto a solution of [W(CO)<sub>3</sub>(NCET)<sub>3</sub>]<sup>27</sup> (0.134 g, 0.31 mmol) in THF (20 mL). The deep yellow solution obtained was stirred for 30 min. After evaporation to dryness in vacuo, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through diatomaceous earth, and the solution was concentrated by in vacuo evaporation to a volume of 5 mL. Addition of hexane (20 mL) caused the precipitation of **4** as a yellow microcrystalline solid, which was washed with hexane (3 × 10 mL) and dried under reduced pressure. Yield: 0.105 g, 50%. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>-SnW: C, 38.97; H, 3.12; N, 6.19. Found: C, 38.75; H, 2.97; N, 6.06. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1897 (vs), 1779 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.52 [d(4.22), 3H, H<sub>A</sub>], 7.63 [m, 6H, H<sub>B</sub> and H<sub>D</sub>], 7.15 [m, 3H, H<sub>C</sub>], 1.83 [m, 4H, H<sub>I</sub> and H<sub>J</sub>], 1.65 [m, 2H, H<sub>3</sub>], 1.09 [t(7.29), 3H, H<sub>4</sub>].

**Synthesis of [<sup>n</sup>BuSn(methylthiomethyl)<sub>3</sub>Mo(CO)<sub>3</sub>] (5).** To a solution of [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] (0.37 mmol) in THF (20 mL) freshly prepared was added a solution of **2a** (0.49 mmol) in THF. The color changed immediately to deep yellow. The resulting slurry was stirred for 15 min. The solvent was evaporated in vacuo, and the residue was extracted with CH<sub>2</sub>-Cl<sub>2</sub> and filtered through alumina (activation grade IV). Pure **5** was obtained by slow diffusion of hexane into a solution of **5** in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C. One of the resulting crystals was used for the X-ray determination. Yield: 0.114 g, 66%. Anal. Calcd for C<sub>13</sub>H<sub>24</sub>MoO<sub>3</sub>S<sub>3</sub>Sn: C, 28.96; H, 4.48. Found: C, 29.10; H, 4.52. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1928 (vs), 1811 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.65 [s, 9H, SCH<sub>3</sub>], 2.36 [s, <sup>2</sup>J<sub>Sn-H</sub> = 18.82 Hz, 6H, SnCH<sub>2</sub>S], 1.53 [m, 2H, H<sub>I</sub>], 1.30 [m, 4H, H<sub>2</sub> and H<sub>3</sub>], 0.89 [t(7.26), 3H, H<sub>4</sub>]. <sup>13</sup>C{<sup>1</sup>H}NMR (CD<sub>2</sub>Cl<sub>2</sub>): 223.01 [s, CO], 31.28 [s, SCH<sub>3</sub>], 28.73 [s, C(1)], 27.18 [s, C(2)], 13.82 [s, C(4)], 13.67 [s, <sup>1</sup>J<sub>119Sn-C</sub> = 281.25 Hz, <sup>1</sup>J<sub>117Sn-C</sub> = 269.30 Hz, SnCH<sub>2</sub>S].

**Synthesis of [<sup>n</sup>BuSn(methylthiomethyl)<sub>3</sub>W(CO)<sub>3</sub>] (6).** Compound **6** was prepared as described above for **5**, from a

solution of [W(CO)<sub>3</sub>(NCET)<sub>3</sub>] (0.23 mmol) and **2a** (0.27 mmol). Slow diffusion of hexane into a concentrated solution of **6** in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C afforded orange crystals, one of which was used for the X-ray analysis. Yield: 0.091 g, 63%. Anal. Calcd for C<sub>13</sub>H<sub>24</sub>O<sub>3</sub>S<sub>3</sub>SnW: C, 24.90; H, 3.85. Found: C, 25.05; H, 3.80. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1920 (vs), 1803 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.83 [s, 9H, SCH<sub>3</sub>], 2.48 [s, <sup>2</sup>J<sub>Sn-H</sub> = 37.62 Hz, 6H, SnCH<sub>2</sub>S], 1.59 [m, 2H, H<sub>I</sub>], 1.35 [m, 2H, H<sub>2</sub>], 1.29 [m, 2H, H<sub>3</sub>], 0.89 [t(7.29), 3H, H<sub>4</sub>]. <sup>13</sup>C{<sup>1</sup>H}NMR (CD<sub>2</sub>Cl<sub>2</sub>): 215.94 [s, CO], 32.99 [s, <sup>2</sup>J<sub>183W-C</sub> = 37.74 Hz, SCH<sub>3</sub>], 28.72 [s, C(1)], 27.19 [s, C(2)], 13.81 [s, C(4)], 13.65 [s, C(3)], 13.54 [s, <sup>1</sup>J<sub>119Sn-C</sub> = 311.36 Hz, <sup>1</sup>J<sub>117Sn-C</sub> = 298.16 Hz, SnCH<sub>2</sub>S].

**Synthesis of [MeSn(methylthiomethyl)<sub>3</sub>W(CO)<sub>3</sub>] (7).** The procedure was similar to that described above for the preparation of **5** starting from [W(CO)<sub>3</sub>(NCET)<sub>3</sub>] (0.070 g, 0.16 mmol) and **2b** (0.21 mmol). Yield: 0.052 g, 55%. Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O<sub>3</sub>S<sub>3</sub>SnW: C, 20.53; H, 3.10. Found: C, 20.61; H, 3.15. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 1920 (vs), 1803 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.83 [s, 9H, SCH<sub>3</sub>], 2.51 [s, <sup>2</sup>J<sub>Sn-H</sub> = 39.5 Hz, 6H, SnCH<sub>2</sub>S], 0.56 [s, <sup>2</sup>J<sub>119Sn-H</sub> = 63.67 Hz, <sup>2</sup>J<sub>117Sn-H</sub> = 61.57 Hz, 3H, SnCH<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H}NMR (CD<sub>2</sub>Cl<sub>2</sub>): 215 [s, CO], 32.95 [s, <sup>2</sup>J<sub>183W-C</sub> = 37.74 Hz, SCH<sub>3</sub>], 14.17 [s, <sup>1</sup>J<sub>119Sn-C</sub> = 311.36 Hz, <sup>1</sup>J<sub>117Sn-C</sub> = 298.16 Hz, SnCH<sub>2</sub>S], -7.64 [s, SnCH<sub>3</sub>].

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**Supporting Information Available:** Tables giving positional and thermal parameters and bond distances and bond angles for **3**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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