Inorg. Chem. **1990**, *29*, 4051–4055 **4051**

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Preparation and Properties of Tris(trimethylstannyl)silyl Complexes of Chromium, Molybdenum, and Tungsten. X-ray Structure of $[NEt_4][(CO)_5WSi(SnMe_3)_3]$

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Received December 18, 1989

Preparations of the silyl complexes $[NEt_4][(CO)_5MSi(SnMe_3)_3]$ (M = Cr, $[NEt_4]$[**1**]; M = Mo, $[NEt_4]$[**2**]; M = W, $[NEt_4]$[**3**]) from $[NEt_4][(CO)_5MCl]$ and $(THF)_3LiSi(SnMe_3)_3$ are reported. Additionally, syntheses of $Si(SnMe_3)_4$ and $(THF)_3LiSi(SnMe_3)_3$ are described. Attempts to cleave a Si–Sn bond in $[NEt_4]$[**3**] are discussed. Halogens I_2 and ICl react with $[NEt_4]$[**3**] to yield $[NEt_4][(CO)_5WI]$ and $ISi(SnMe_3)_3$ or $ClSi(SnMe_3)_3$, respectively. Two equivalents of HCl are necessary to effect complete conversion of $[NEt_4]$[**3**] to $[NEt_4][(CO)_5WCl]$ and $ClSi(SnMe_3)_3$. No Si–Sn bond cleavage in $[NEt_4]$[**3**] is observed with Li or Na metal, sodium naphthalenide, NaOMe, $LiBEt_3H$, or LiMe. The one-electron oxidants $[Cp_2Fe][FeCl_4]$ and AgOTf react with $[NEt_4]$[**3**] to give uncharacterized solids. The complex $[NEt_4]$[**3**] crystallizes in the monoclinic space group $P2_1/n$, with a = 13.958 (4) Å, b = 18.501 (4) Å, c = 14.035 (4) Å, β = 94.96 (2)°, V = 3611 (2) Å^3, and Z = 4. The W–Si bond is 2.652 (4) Å, slightly longer than the W–Si bond in the previously reported $[PPN][(CO)_5WSiMe_3]$ (2.614 (2) Å).

Introduction

There is long-standing interest in transition-metal silylene complexes due to their possible intermediacy in reactions between transition-metal centers and silicon compounds.[1] Such complexes have been elusive synthetic targets, but recently syntheses of base-stabilized silylene complexes have been reported.[2] A base-free analogue has not been isolated although there is evidence for existence of $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}SiPh_2]BPh_4$ in solution.[2b] The synthetic route that we have used for synthesis of the cationic species $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuSiPh_2(NCMe)]BPh_4$ involves abstraction of a group from a silyl ligand.[2a,b] Two approaches that might allow extension of this method to preparation of a base-free silylene complex are (1) incorporation of more electron-releasing substituents at silicon that would help stabilize an electron-deficient, three-coordinate silicon center and (2) removal of a group bound to silicon in a negatively charged silyl derivative, so that a neutral silylene complex results. A neutral silylene complex should be less electrophilic at silicon than a cationic silylene complex, although electron density at the metal center could play a more dominating role.

To investigate the approaches described above, we have designed a silyl ligand that contains electropositive (trimethylstannyl) substituents, $-Si(SnMe_3)_3$, and have introduced this group into anionic complexes of chromium, molybdenum, and tungsten. It was hoped that the anions $[(CO)_5MSi(SnMe_3)_3]^-$ ([**1**]$^-$, M = Cr; [**2**]$^-$, M = Mo; [**3**]$^-$, M = W) would possess relatively weak Si–Sn bonds that could be cleaved to produce neutral silylene complexes. These species were expected to possess relatively strong transition-metal–silicon bonds due to the low-valent transition-metal center and an overall negative charge.[1] In this paper, we report the synthesis and characterization of $Si(SnMe_3)_4$ and $(THF)_3LiSi(SnMe_3)_3$, and use of the latter species to prepare salts of [**1**]$^-$, [**2**]$^-$, and [**3**]$^-$. Attempts to bring about cleavage of the Si–Sn bonds in these complexes are also described.

Results and Discussion

Synthesis of $(THF)_3LiSi(SnMe_3)_3$. The silyl lithium $(THF)_3LiSi(SiMe_3)_3$ is well-established as a useful reagent for synthesis of a variety of transition-metal silyl complexes.[1,3] Its synthesis from $Si(SiMe_3)_4$ and methyllithium[4] suggested that an analogous reaction of $Si(SnMe_3)_4$ with methyllithium might provide a convenient route to $(THF)_3LiSi(SnMe_3)_3$. A first attempt to prepare $Si(SnMe_3)_4$ was based on the known synthesis of $Si(SiMe_3)_4$[5] and involved stirring Me_3SnCl and $SiCl_4$ with lithium metal in tetrahydrofuran. This procedure gave no isolable product. However, a moderate yield of $Si(SnMe_3)_4$ is obtained when a solution of $LiSnMe_3$ in tetrahydrofuran[6] is added to $SiCl_4$ (eq 1). $Si(SnMe_3)_4$ is a light-yellow, crystalline compound that

$$SiCl_4 + 4LiSnMe_3 \xrightarrow[-4LiCl]{THF} Si(SnMe_3)_4 \qquad (1)$$

unlike $Si(SiMe_3)_4$ is moderately air-sensitive. The stannyl derivative is less thermally stable in the solid state than $Si(SiMe_3)_4$ (mp 319–321 °C[5]), decomposing at 240 °C. The infrared spectrum of $Si(SnMe_3)_4$ exhibits bands assigned to the Si–Sn bonds at 491, 510, and 755 cm^{-1}. These may be compared to analogous Si–Si bands in $Si(SiMe_3)_4$ at 614, 679, and 830 cm^{-1}.[5]

The synthesis of $(THF)_3LiSi(SnMe_3)_3$ is analogous to that of $(THF)_3LiSi(SiMe_3)_3$ (eq 2). The compound is obtained in 81% yield as light-yellow crystals from pentane. Efforts to obtain pure

$$Si(SnMe_3)_4 + MeLi \xrightarrow[-SnMe_4]{THF} (THF)_3LiSi(SnMe_3)_3 \qquad (2)$$

analytical samples were consistently hampered by persistent impurities (5–10%) that do not impede subsequent reactions. A minor decomposition product is $Si(SnMe_3)_4$, which is observed only after repeated recrystallization attempts. As expected, the ^{29}Si NMR shift for $(THF)_3LiSi(SnMe_3)_3$, −122.0 ppm, is upfield from that of $Si(SnMe_3)_4$, −69.2 ppm. The $^1J_{SnSi}$ coupling constants for the two compounds are similar: 227 Hz for $Si(SnMe_3)_4$ and 239 Hz for $(THF)_3LiSi(SnMe_3)_3$. The ^{29}Si NMR shifts for $(THF)_3LiSi(SnMe_3)_3$ and $Si(SnMe_3)_4$ are downfield of shifts for the analogous $(THF)_3LiSi(SiMe_3)_3$ and $Si(SiMe_3)_4$ derivatives, which occur at −184.5 and −135.5 ppm respectively.[4] A previous report briefly describes the synthesis of $LiSi(SnMe_3)_3$ from $Si(SnMe_3)_4$ and methyllithium in diethyl ether.[7] In addition,

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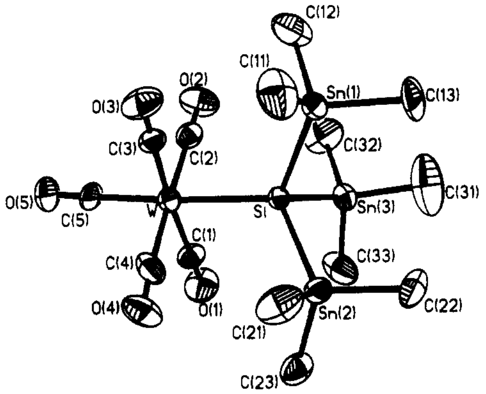

Figure 1. ORTEP view of the anion of $[NEt_4][(CO)_5WSi(SnMe_3)_3]$ with atom-labeling scheme.

Table I. Crystallographic Data for $[NEt_4][3]$

chem formula: $C_{22}H_{47}NO_5SiSn_3W$
fw = 973.63
$a = 13.958$ (4) Å
$b = 18.501$ (4) Å
$c = 14.035$ (4) Å
$\beta = 94.96$ (2)°
$V = 3611$ (2) Å
$Z = 4$

space group: $P2_1/n$ (No. 14)
$T = 23$ °C
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.79$ g cm^{-3}
$\mu = 53.6$ cm^{-1}
transm coeff = 0.590–1.000
$R_F = 4.44\%$
$R_{wF} = 5.20\%$

$Si(SnMe_3)_4$ and $HSi(SnMe_3)_3$ were isolated, among other products, from the complex reaction between $KSiH_3$ and Me_3SnCl.[8]

The lithium silyl $(THF)_3LiSi(SnMe_3)_3$ undergoes the expected reaction with HCl, giving LiCl and the silane $HSi(SnMe_3)_3$. The latter compound was isolated as an oil and characterized by ^1H NMR and infrared spectroscopy. Reaction of $HSi(SnMe_3)_3$ with carbon tetrachloride gives quantitative yields of $CHCl_3$ and $ClSi(SnMe_3)_3$.

Synthesis of $[NEt_4][(CO)_5MSi(SnMe_3)_3]$ Complexes. Reaction of the metal halides $[NEt_4][(CO)_5MCl]$ (M = Cr, Mo, W) with $(THF)_3LiSi(SnMe_3)_3$ in tetrahydrofuran gives good yields of the corresponding anionic silyl complexes as light-yellow to orange crystals from diethyl ether (eq 3). This procedure is analogous

$$[NEt_4][(CO)_5MCl] + (THF)_3LiSi(SnMe_3)_3 \xrightarrow[-3THF,\ -LiCl]{THF} [NEt_4][(CO)_5MSi(SnMe_3)_3] \quad (3)$$
$$[NEt_4][\mathbf{1}],\ M = Cr$$
$$[NEt_4][\mathbf{2}],\ M = Mo$$
$$[NEt_4][\mathbf{3}],\ M = W$$

to that of Graham[9] for the anions $[(CO)_5MSiR_3]^-$ ($R_3 = Ph_3$, $MePh_2$; M = Cr, Mo, W). These compounds were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, elemental analysis, and IR spectroscopy and, for $[NEt_4][3]$, by X-ray crystallography. Salts of $[1]^-$, $[2]^-$, and $[3]^-$ are very mildly air-sensitive, but show no sign of decomposition over extended periods under an inert atmosphere. Solutions of $[NEt_4][3]$ in acetonitrile-d_3 are stable for up to 1 month, but solutions in dichloromethane-d_2 exhibit marked decomposition within days. The ^{29}Si NMR chemical shifts for anions $[1]^-$–$[3]^-$ move progressively to higher field going from chromium to tungsten, which is the expected trend for complexes of this type.[1,10] The magnitude of the $^1J_{SiSn}$ coupling constant for $[3]^-$ (172 Hz) is greater than that observed for $[1]^-$ (158 Hz). Unfortunately, this coupling was not observed in the room-temperature ^{29}Si NMR spectrum of $[2]^-$. Note that these $^1J_{SiSn}$ coupling constants are significantly lower than those observed for $Me_3SnSiMe_3$ (580 Hz)[11] and $Si(SnMe_3)_4$ (227 Hz).

X-ray Structure of $[NEt_4][(CO)_5WSi(SnMe_3)_3]$. The structure and atom-labeling scheme for the anion $[3]^-$ are shown in Figure 1. Crystal and data collection parameters are listed in Table I.

Table II. Selected Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[NEt_4][3]$[a]

	x	y	z	U(eq)[b]
W	1321 (1)	7457 (1)	3203 (1)	49 (1)
Sn(1)	3703 (1)	7190 (1)	1351 (1)	60 (1)
Sn(2)	4408 (1)	7305 (1)	4198 (1)	58 (1)
Sn(3)	3205 (1)	5531 (1)	3079 (1)	60 (1)
Si	3046 (3)	6919 (2)	2964 (2)	40 (1)
O(1)	1207 (10)	6396 (8)	4929 (9)	118 (7)
O(2)	476 (10)	6300 (7)	1676 (9)	106 (6)
O(3)	1624 (10)	8498 (6)	1485 (8)	104 (6)
O(4)	2283 (10)	8588 (7)	4709 (9)	110 (6)
O(5)	−705 (10)	8107 (9)	3348 (9)	125 (7)
C(1)	1253 (11)	6768 (9)	4305 (11)	65 (6)
C(2)	779 (12)	6712 (9)	2226 (11)	64 (6)
C(3)	1524 (11)	8131 (9)	2118 (10)	61 (6)
C(4)	1935 (14)	8209 (9)	4148 (12)	78 (7)
C(5)	22 (11)	7852 (10)	3303 (11)	76 (7)
C(11)	3949 (16)	8296 (11)	1096 (15)	140 (12)
C(12)	2707 (14)	6821 (12)	234 (12)	127 (11)
C(13)	5056 (12)	6678 (13)	1103 (13)	138 (12)
C(21)	4718 (14)	8462 (9)	4126 (14)	115 (10)
C(22)	5726 (13)	6797 (12)	3997 (15)	131 (11)
C(23)	4066 (12)	7093 (10)	5629 (11)	91 (8)
C(31)	4465 (16)	5068 (10)	2737 (19)	174 (15)
C(32)	2095 (17)	4966 (10)	2168 (14)	141 (12)
C(33)	3047 (18)	5147 (9)	4473 (12)	134 (12)

[a] Positional parameters for the cation $[NEt_4^+]$ are given in the supplementary material. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[NEt_4][3]$

(a) Bond Distances			
W–Si	2.652 (4)	W–C(4)	2.06 (2)
Si–Sn(1)	2.564 (4)	W–C(5)	1.97 (2)
Si–Sn(2)	2.561 (4)	C(1)–O(1)	1.12 (2)
Si–Sn(3)	2.581 (4)	C(2)–O(2)	1.14 (2)
W–C(1)	2.01 (2)	C(3)–O(3)	1.14 (2)
W–C(2)	2.04 (2)	C(4)–O(4)	1.13 (2)
W–C(3)	2.01 (2)	C(5)–O(5)	1.12 (2)
(b) Bond Angles			
Si–W–C(1)	87.9 (5)	C(3)–W–C(5)	90.9 (7)
Si–W–C(2)	87.1 (5)	C(4)–W–C(5)	92.1 (7)
Si–W–C(3)	87.0 (4)	W–Si–Sn(1)	115.8 (1)
Si–W–C(4)	90.2 (5)	W–Si–Sn(2)	116.0 (1)
Si–W–C(5)	176.8 (4)	W–Si–Sn(3)	116.1 (1)
C(1)–W–C(2)	92.8 (6)	Sn(1)–Si–Sn(2)	103.9 (1)
C(1)–W–C(3)	174.6 (6)	Sn(1)–Si–Sn(3)	102.4 (1)
C(1)–W–C(4)	88.7 (6)	Sn(2)–Si–Sn(3)	100.4 (1)
C(1)–W–C(5)	94.3 (7)	W–C(1)–O(1)	178 (1)
C(2)–W–C(3)	88.7 (6)	W–C(2)–O(2)	180 (1)
C(2)–W–C(4)	176.9 (7)	W–C(3)–O(3)	178 (1)
C(2)–W–C(5)	90.5 (7)	W–C(4)–O(4)	176 (2)
C(3)–W–C(4)	89.5 (6)	W–C(5)–O(5)	177 (2)

Relevant geometrical parameters are collected in Tables II and III. The W–Si bond length in $[3]^-$ is 2.652 (4) Å, which is slightly longer than the corresponding distance in $[PPN][(CO)_5WSiMe_3]$, 2.614 (2) Å.[12] The Si–Sn distances of 2.564 (4), 2.561 (4), and 2.581 (4) Å agree with the other observed Si–Sn distances, such as those found in $Cp_2Zr[Si(SnMe_3)_3]Cl$ (average 2.569 (4) Å)[13] and $Ph_3SnSiPh_2SnPh_3$ (average 2.575 (5) Å).[14] The W–Si–Sn angles, which average to 116.0 (1)°, are somewhat greater than the Re–Si–Si angles (average 113.0 (5)°) in the closely related $(CO)_5ReSi(SiMe_3)_3$.[3a] In addition, the Sn–Si–Sn angles in $[3]^-$, 103.9 (1), 102.4 (1), and 100.4 (1)°, are more acute than analogous Si–Si–Si angles in $(CO)_5ReSi(SiMe_3)_3$, which average to 105.8 (6)°. The W–C distances for the four equatorial CO ligands range from 2.01 (2) to 2.06 (2) Å, while the W–C bond

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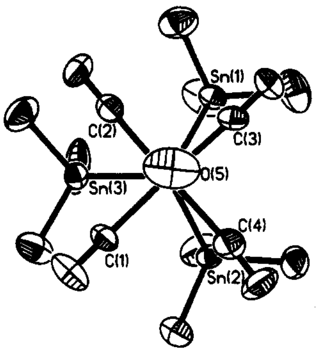

Figure 2. Newman projection down the W-Si bond of $[3]^-$.

to the axial CO ligand is only 1.97 (2) Å. This is possibly a reflection of greater π-back-bonding to the CO ligand that is trans to the silyl group. A similar effect is seen in $[PPN][(CO)_5WSiMe_3]$.[12] Three of the four equatorial CO's are bent toward the $Si(SnMe_3)_3$ ligand, resulting in C(1)-W-Si, C(2)-W-Si, and C(3)-W-Si angles of 87.9 (5), 87.1 (5), and 87.0 (4)°, respectively. This structural feature has been observed for many other carbonyl/silyl complexes.[3a,b,15] These angles are less acute than those observed for $[PPN][(CO)_5WSiMe_3]$, which average 82.1 (3)°.[12] As in $[PPN][(CO)_5WSiMe_3]$ and $(CO)_5ReSi(SiMe_3)_3$ there is one C(carbonyl)-M-Si angle in $[3]^-$ that is slightly greater than 90°, corresponding to a carbonyl ligand that is closest to a substituent on the silyl ligand. A view of $[3]^-$ down the W-Si bond is shown in Figure 2.

Reactions of $[NEt_4][(CO)_5WSi(SnMe_3)_3]$. Since $[NEt_4][3]$ is expected to possess the strongest metal-silicon bond, we chose to study it in search of clean Si-Sn bond cleavage reactions. Precedents for such reactions exist in the reported cleavage of the Si-Sn bond of $Me_3SiSnMe_3$ by HCl (to give Me_3SiCl and Me_3SnCl) and by ICl (to give Me_3SiCl and Me_3SnI).[16] Compound $[NEt_4][3]$ is stable to large excesses of both water and methanol in acetonitrile-d_3 over 24 h. Reaction of $[NEt_4][3]$ with 2 equiv of HCl (generated in methanol by addition of MeCOCl) gave $[NEt_4][(CO)_5WCl]$ and $ClSi(SnMe_3)_3$. If only 1 equiv of HCl is used $[NEt_4][(CO)_5WCl]$, $ClSi(SnMe_3)_3$, and unreacted $[NEt_4][3]$ are isolated. This reaction probably proceeds by initial cleavage of the W-Si bond to produce the silyl chloride and $[NEt_4][(CO)_5WH]$, which rapidly combines with a second equivalent of HCl to give H_2 and $[NEt_4][(CO)_5WCl]$.[17] Dropwise addition of a diethyl ether solution of ICl (1 equiv) to a cold (-78 °C) suspension of $[NEt_4][3]$ in diethyl ether resulted in formation of $[NEt_4][(CO)_5WI]$[18] and $ClSi(SnMe_3)_3$, as determined by infrared and NMR spectroscopy. Addition of I_2 (1 equiv) to $[NEt_4][3]$ in a similar manner resulted in isolation of $[NEt_4][(CO)_5WI]$ as the only tungsten-containing product (based on IR spectroscopy). The silicon-containing product is presumably $ISi(SnMe_3)_3$.

Further attempts at cleavage of a Si-Sn bond were based on known reactions of reductants or nucleophiles that cleave Si-Si bonds.[19] Stirring $[NEt_4][3]$ with a large excess of either Li or Na metal chips for 54 h in tetrahydrofuran gave no evidence of reaction. Compound $[NEt_4][3]$ was also stirred with sodium naphthalenide in tetrahydrofuran at -78 °C for 20 min, after which MeI (2 equiv) was added. On the basis of the ^1H NMR data, no reaction had taken place.

Sakurai has reported that reaction of Me_6Si_2 with NaOMe in hexamethylphosphoramide (HMPA) results in Si-Si bond cleavage to give $NaSiMe_3$ and $MeOSiMe_3$.[19b,c] An analogous attempt to cleave a Si-Sn bond of $[3]^-$ involved addition of an HMPA solution of $[NEt_4][3]$ to an HMPA solution of NaOMe, followed by addition of MeI. This appeared to result only in the isolation of a cation-exchanged product, and no evidence for the expected Si-Sn bond cleavage products was observed by NMR. Attempts to cleave a Si-Sn bond of $[3]^-$ with other nucleophiles gave similar results. Compound $[NEt_4][3]$ did not react with $LiBEt_3H$ in tetrahydrofuran over 48 h. The attempted reaction of $[NEt_4][3]$ with LiMe in tetrahydrofuran over 5.5 h gave similar results.

Other attempts at Si-Sn bond cleavage were based on the known stability of the $^\bullet SnMe_3$ radical[20] and the possibility that a one-electron oxidation might produce a silylene complex (eq 4).

$$[(CO)_5WSi(SnMe_3)_3]^- \xrightarrow[-e^-]{ox} [(CO)_5WSi(SnMe_3)_3] \xrightarrow{-{}^1/_2Me_3SnSnMe_3} (CO)_5W{=}Si(SnMe_3)_2 \quad (4)$$

Oxidation of $[NEt_4][3]$ with $[Cp_2Fe][FeCl_4]$ in diethyl ether gave Cp_2Fe and an unidentified mixture of tungsten-containing products. Infrared spectroscopy of these solids showed only absorptions that can be attributed to coordinated CO, and no absorptions that can be assigned to a $-Si(SnMe_3)_3$ ligand were observed. Therefore, oxidative cleavage of the W-Si bond of $[3]^-$ probably occurred. When AgOTf was used as an oxidant in benzene-d_6, Ag precipitated as a black solid, but no clean tungsten- or silicon-containing products could be isolated. There was no evidence for formation of Me_6Sn_2, on the basis of ^1H NMR spectroscopy.

In conclusion, $[NEt_4][3]$ readily reacts with electrophilic reagents such as acids, halogens, and oxidants, and the preferred site of reactivity is the W-Si bond. Nucleophiles and reducing reagents are unreactive toward $[NEt_4][3]$. The latter reagents should be more reactive toward a neutral or cationic complex with the $-Si(SnMe_3)_3$ ligand. We are currently investigating the ability of other transition-metal systems to incorporate the $-Si(SnMe_3)_3$ ligand and the possibility that a more successful route to a neutral silylene complex could involve abstraction of $SnMe_3^+$ from a cationic $[L_nMSi(SnMe_3)_3]^+$ complex.

Experimental Section

Manipulations were performed under an atmosphere of nitrogen or argon by using high-vacuum-line techniques, Schlenk techniques, or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Microanalytiches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. NMR spectra were recorded with a GE-QE 300 instrument at 300, 75.5, or 59.6 MHz (^1H, ^{13}C, and ^{29}Si, respectively) or on a Varian EM 390 instrument (90 MHz, ^1H). ^{29}Si NMR spectra were obtained by using INEPT,[21] with an optimized coupling constant $^3J_{SiH}$ = 3 Hz. Generally, ^{119}Sn-^{29}Si couplings were only observable after overnight acquisitions with 75-100 mg of sample in 0.5 mL of benzene-d_6 or acetonitrile-d_3. Hydrogen chloride (Matheson), trimethylstannyl chloride, methyllithium, and iodine monochloride (Aldrich) were used as received. Silicon tetrachloride and MeCOCl were distilled under argon prior to use. $M(CO)_6$ (M = Cr, Mo, W) and iodine were purified by sublimation. Tetraethylammonium chloride (Alfa) was dried by heating at 80 °C under vacuum overnight. The compounds $[NEt_4][(CO)_5MCl]$ (M = Cr, Mo, W) were prepared according to a published procedure.[18]

$Si(SnMe_3)_4$. A 1000-mL three-neck flask equipped with a 250-mL addition funnel was charged with 35.0 g (5.00 mol, 41 equiv) of Li wire

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(Na content ca. 2%), cut into approximately 2 mm-long pieces. To a cooled (0 °C, constant-temperature bath) suspension of the Li in 250 mL of tetrahydrofuran was added a solution of Me$_3$SnCl (100 g, 0.50 mol, 4.1 equiv) in tetrahydrofuran (150 mL) dropwise over 1 h. After the mixture was stirred for 3 h at 0 °C, the dark green supernatant was decanted away from the partially reacted Li wire and added to a second 1000-mL three-neck flask, which was equipped with a 125-mL addition funnel. A solution of 14.0 mL of SiCl$_4$ (0.12 mol, 1 equiv) in 100 mL of tetrahydrofuran was placed in the addition funnel and added dropwise over 1 h to the cooled (0 °C) solution of LiSnMe$_3$. The resulting dark brown, heterogeneous mixture was stirred at 0 °C for 12 h and then warmed to room temperature and stirred for an additional 36 h. After removal of all volatiles, the resulting dark brown residue was extracted three times with 150 mL of pentane. The combined, dark yellow extracts were concentrated and cooled (−40 °C). Light yellow crystals of Si(SnMe$_3$)$_4$ were collected by filtration. Subsequent crystallizations gave a total combined yield of 20 g (0.03 mol, 25%). Yellow to orange discoloration may occur due to slight impurities, which do not seem to adversly affect subsequent reactions. Further purification of isolated crystals is possible via sublimation (100 °C, 0.001 Torr). Mp: 240 °C dec. Anal. Calcd for C$_{12}$H$_{36}$SiSn$_4$: C, 21.1; H, 5.31. Found: C, 21.5; H, 5.27. ^{1}H NMR (300 MHz, 23 °C, benzene-d_6): δ 0.29 ($^2J_{\mathrm{SnH}}$ = 48.6 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, benzene-d_6): δ −6.80 ($^1J_{\mathrm{SnC}}$ = 253 Hz, 265 Hz, $^3J_{\mathrm{SnC}}$ = 9.8 Hz). ^{29}Si{^{1}H} NMR (59.6 MHz, 23 °C, benzene-d_6): δ −69.2 ($^1J_{\mathrm{SnSi}}$ = 227 Hz). IR (Nujol, CsI, cm^{-1}): 1187 w, 1180 w, 755 vs br, 510 s, 491 s, 363 w.

(THF)$_3$LiSi(SnMe$_3$)$_3$. Si(SnMe$_3$)$_4$ (11.13 g, 16.3 mmol) was placed in a 500-mL three-neck flask equipped with a 250-mL addition funnel. The solid was dissolved in tetrahydrofuran (200 mL) to give a dark yellow solution. Methyllithium (11.8 mL, 1.4 M solution in Et$_2$O) was syringed into the addition funnel and diluted with 50 mL of tetrahydrofuran. The MeLi solution was added dropwise over 0.5 h. The resulting red-brown solution was stirred for 22 h. Volatiles were removed in vacuo, and the resulting orange-brown residue was extracted with pentane (2 × 150 mL; 1 × 75 mL). Concentration and cooling to −40 °C gave an initial crop of yellow crystals, which was isolated by filtration and dried. Repeated concentration, cooling, and filtration gave a total of four crops of yellow crystals (9.74 g, 81.2%). The amount of coordinated tetrahydrofuran can vary from crop to crop, depending on the concentration of the starting solution and the drying time of the isolated crystals. ^{1}H NMR (300 MHz, 23 °C, benzene-d_6): δ 0.44 ($^2J_{\mathrm{SnH}}$ = 39.4 Hz, 27 H, SnCH_3), 1.47 (m, 12 H, OCH$_2$CH_2), 3.51 (m, 12 H, OCH_2). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, benzene-d_6): δ −3.74 ($^1J_{\mathrm{SnC}}$ = 162 Hz, $^3J_{\mathrm{SnC}}$ = 22.0 Hz, SnCH$_3$), 25.5 (OCH$_2$$CH_2$), 68.6 (O$CH_2$). ^{29}Si{^{1}H} NMR (59.6 MHz, 23 °C, benzene-d_6): δ −122.0 ($^1J_{\mathrm{SnSi}}$ = 239 Hz). IR (Nujol, CsI, cm^{-1}): 1266 m, 1046 vs, 916 m, 894 s, 747 vs br, 495 vs, 391 m, 382 m, 372 m.

HSi(SnMe$_3$)$_3$. (THF)$_3$LiSi(SnMe$_3$)$_3$ (1.210 g, 1.63 mmol) was placed in a 100-mL Schlenk flask, and addition of 40 mL of pentane produced a yellow suspension. A gas addition bulb of known volume was connected to the reaction flask. The stirred suspension of (THF)$_3$LiSi(SnMe$_3$)$_3$ was cooled to −196 °C, and the flask was evacuated. HCl gas (1 equiv) was introduced into the bulb and then condensed into the flask. After gradual warming of the reaction mixture to room temperature with stirring, volatiles were removed in vacuo. Extraction of the residue with 25 mL of pentane provided a yellow solution. Removal of all volatiles from this extract gave HSi(SnMe$_3$)$_3$ as a yellow oil (0.645 g, 76%). ^{1}H NMR (300 MHz, 23 °C, benzene-d_6): δ 0.28 ($^2J_{\mathrm{SnH}}$ = 48.9 Hz, 27 H, SnCH_3), 3.16 ($^2J_{\mathrm{SnH}}$ = 11.3 Hz, 1 H, SiH). IR (neat, CsI, cm^{-1}): 2977 s, 2910 s, 2072 m (Si–H), 1258 w, 1172 w, 1095 w, 1016 w, 760 vs, 600 s, 589 s, 511 s, 496 s, 350 w.

ClSi(SnMe$_3$)$_3$. In an NMR tube, HSi(SnMe$_3$)$_3$ (0.061 g, 0.12 mmol) was dissolved in benzene-d_6 (0.4 mL). Carbon tetrachloride (0.012 mL, 0.12 mmol) was added via syringe. After 6 h, NMR spectroscopy showed only signals for ClSi(SnMe$_3$)$_3$ and CHCl$_3$ (as determined by addition of an authentic sample). ^{1}H NMR (300 MHz, 23 °C, benzene-d_6): δ 0.28 ($^2J_{\mathrm{SnH}}$ = 49.8 Hz).

[NEt$_4$][(CO)$_5$CrSi(SnMe$_3$)$_3$] ([NEt$_4$][1]). [NEt$_4$][(CO)$_5$CrCl] (0.328 g, 0.917 mmol) and (THF)$_3$LiSi(SnMe$_3$)$_3$ (0.692 g, 0.918 mmol) were placed in an aluminum-foil-covered flask. Tetrahydrofuran (50 mL) was added, and the solution was stirred for 18 h. The volatiles were removed in vacuo, and the yellow residue was extracted with diethyl ether (2 × 25 mL). The combined extracts were concentrated to 5 mL, and the somewhat murky solution was cooled to −35 °C. Isolation of the resulting yellow crystals gave an initial crop of 0.27 g (0.256 mmol). Subsequent crystallizations gave a total yield of 0.339 g (0.403 mmol, 43.9%). Anal. Calcd for C$_{22}$H$_{47}$CrNO$_5$SiSn$_3$: C, 31.4; H, 5.63; N, 1.66. Found: C, 31.4; H, 5.65; N, 1.70. Mp: >115 °C dec. ^{1}H NMR (300 MHz, 23 °C, acetonitrile-d_3): δ 0.095 ($^2J_{\mathrm{SnH}}$ = 43.4 Hz, 27 H, SnCH_3), 1.20 (tt, J = 7.3, 2 Hz, 12 H, NCH$_2$CH_3), 3.15 (q, J = 7.3 Hz, 8 H, NCH_2). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, acetonitrile-d_3): δ −5.41 ($^1J_{\mathrm{SnC}}$ = 190 Hz, $^3J_{\mathrm{SnC}}$ = 18.3 Hz, SnC), 7.66 (NCH$_2$$CH_3$), 53.0 (N$CH_2$), 226.7 ($^3J_{\mathrm{SnC}}$ = 21.4 Hz, CrCO), 231.0 (CrCO). ^{29}Si{^{1}H} (59.6 MHz, 23 °C, acetonitrile-d_3): δ −26.2 ($^1J_{\mathrm{SnSi}}$ = 158 Hz). IR (CH$_3$CN, CsF, cm^{-1}): ν_{CO} 2019, 1898, 1871.

[NEt$_4$][(CO)$_5$MoSi(SnMe$_3$)$_3$] ([NEt$_4$][2]). The procedure was analogous to that for [NEt$_4$][**1**], starting with [NEt$_4$][(CO)$_5$MoCl] (0.365 g, 0.977 mmol) and (THF)$_3$LiSi(SnMe$_3$)$_3$ (0.709 g, 0.983 mmol). The total yield of orange-yellow crystals was 0.196 g (0.221 mmol, 23%). Anal. Calcd for C$_{22}$H$_{47}$MoNO$_5$SiSn$_3$: C, 29.8; H, 5.35; N, 1.58. Found: C, 29.8; H, 5.33; N, 1.63. Mp: 172–196 °C dec. ^{1}H NMR (300 MHz, 23 °C, acetonitrile-d_3): δ 0.071 ($^2J_{\mathrm{SnH}}$ = 42.7 Hz, 27 H, SnCH_3), 1.20 (tt, J = 7.3, 2 Hz, 12 H, NCH$_2$CH_3), 3.15 (q, J = 7.3 Hz, 8 H, NCH_2). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, acetonitrile-d_3): δ −5.24 ($^1J_{\mathrm{SnC}}$ = 190 Hz, SnC), 7.69 (NCH$_2$$CH_3$), 53.1 (N$CH_2$), 214.7 (MoCO), 217.4 (MoCO). ^{29}Si{^{1}H} NMR (59.6 MHz, 23 °C, acetonitrile-d_3): δ −59.9. IR (CsF solution cells, CH$_3$CN, cm^{-1}): ν_{CO} 2037, 1910, 1862.

[NEt$_4$][(CO)$_5$WSi(SnMe$_3$)$_3$] ([NEt$_4$][3]). The procedure was analogous to that of [NEt$_4$][**1**], starting with [NEt$_4$][W(CO)$_5$Cl] (4.12 g, 8.41 mmol) and (THF)$_3$LiSi(SnMe$_3$)$_3$ (6.22 g, 8.42 mmol). Several crops of yellow crystals were isolated in a combined yield of 5.79 g (5.95 mmol, 70.7%). Anal. Calcd for C$_{22}$H$_{47}$NO$_5$SiSn$_3$W: C, 27.1; H, 4.86; N, 1.44. Found: C, 27.2; H, 4.87; N, 1.45. Mp: >147 °C dec. ^{1}H NMR (300 MHz, 23 °C, dichloromethane-d_2): δ 0.097 ($^2J_{\mathrm{SnH}}$ = 42.8 Hz, 27 H, SnCH_3), 1.34 (tt, J = 7.3, 2 Hz, 12 H, NCH$_2$CH_3), 3.19 (q, J = 7.3 Hz, 8 H, NCH_2). ^{13}C{^{1}H} NMR (75.5 MHz, 23 °C, dichloromethane-d_2): δ −5.46 ($^1J_{\mathrm{SnC}}$ = 192 Hz, $^3J_{\mathrm{SnC}}$ = 17 Hz, SnC), 7.73 (NCH$_2$$CH_3$), 53.1 (N$CH_2$), 204.5 ($^3J_{\mathrm{SnC}}$ = 18 Hz, WCO), 207.6 (WCO). ^{29}Si{^{1}H} NMR (59.6 MHz, 23 °C, acetonitrile-d_3): δ −75.7 ($^1J_{\mathrm{SnSi}}$ = 172 Hz). IR (CH$_3$CN, CsF, cm^{-1}): ν_{CO} 2035, 1903, 1864.

Reaction of [NEt$_4$][3] with 2 equiv of HCl. [NEt$_4$][**3**] (0.525 g, 0.539 mmol) was placed in a 100-mL flask, dissolved in methanol (20 mL), and cooled to −78 °C. In a separate flask, HCl was formed by the addition of MeCOCl (0.08 mL, 1.12 mmol) to 20 mL of MeOH. This HCl/MeOH solution was then added to the solution of [NEt$_4$][**3**] via cannula. The reaction was allowed to slowly warm to room temperature, after which it was stirred for an additional 2 h. Volatiles from the dark yellow solution were removed, and the residue was extracted first with diethyl ether (30 mL) and then with dichloromethane (10 mL). No crystals were obtained from the diethyl ether extract, but analysis of this solution by ^{1}H NMR spectroscopy revealed the presence of only ClSi(SnMe$_3$)$_3$. After concentration and cooling (−40 °C), yellow crystals were obtained by filtration from the dichloromethane solution (0.099 g, 37%). IR spectroscopy identified these crystals as [NEt$_4$][(CO)$_5$WCl].[18]

Reaction of [NEt$_4$][3] with 1 equiv of HCl. This reaction was conducted as described for 2 equiv of HCl (see above) with [NEt$_4$][**3**] (0.441 g, 0.453 mmol), MeCOCl (0.035 mL, 0.492 mmol), and MeOH (25 mL). The diethyl ether extract contained [NEt$_4$][**3**] and ClSi(SnMe$_3$)$_3$, as determined by ^{1}H NMR spectroscopy. The dichloromethane extract gave 0.041 g of yellow crystals upon cooling to −35 °C. NMR and IR spectroscopies identified these crystals as a mixture of [NEt$_4$][**3**] and [NEt$_4$][(CO)$_5$WCl].

Reaction of [NEt$_4$][3] with I$_2$. A 100-mL flask equipped with a 125-mL addition funnel was charged with [NEt$_4$][**3**] (0.190 g, 0.195 mmol) and dichloromethane (20 mL), giving a pale yellow solution. A solution of iodine (0.052 g, 0.205 mmol) in 20 mL of dichloromethane was added to the solution of [NEt$_4$][**3**] dropwise over 30 min. After the mixture was stirred for 3 h, volatiles were removed in vacuo. Extraction of the yellow residue with dichloromethane, followed by concentration and cooling, gave two crops of [NEt$_4$][(CO)$_5$WI] (0.075 g, 67%), as determined by its IR spectrum.[18]

Reaction of [NEt$_4$][3] with ICl. A 100-mL flask equipped with a 125-mL addition funnel and containing a light yellow solution of [NEt$_4$][**3**] (0.712 g, 0.731 mmol) in diethyl ether (30 mL) was cooled to −78 °C. The addition funnel was charged with a 0.95 M solution of ICl in dichloromethane (0.77 mL, 0.732 mmol) and diethyl ether (30 mL). The entire apparatus was covered with Al foil to protect the light-sensitive ICl. The light orange solution of ICl was added dropwise to [NEt$_4$][**3**] over 20 min. No color change was observed. After 1.25 h at −78 °C, the reaction was gradually warmed to room temperature and stirred for an additional 0.75 h, resulting in a heterogeneous yellow mixture. The Al foil was removed, and the reaction was stirred for 1 h more. The volatiles were removed in vacuo, and the resulting yellow residue was first extracted with diethyl ether (2 × 25 mL). The remaining yellow residue was extracted with dichloromethane (25 mL). The volatiles from the diethyl ether extract were removed in vacuo, and ^{1}H NMR spectroscopy indicated the presence of ClSi(SnMe$_3$)$_3$. The dichloromethane extract was concentrated slightly and cooled to −35 °C. Two crops of yellow crystals were isolated via filtration. Infrared spectroscopy identified the crystals as [NEt$_4$][(CO)$_5$WI] (0.285 g, 67%).

Reaction of [NEt$_4$][3] with NaOMe. A 100-mL flask was charged with NaOMe (0.022 g, 0.407 mmol), which was then suspended in hexamethylphosphoramide (5 mL). A yellow-orange solution of [NEt$_4$][3] (0.400 g, 0.411 mmol) in hexamethylphosphoramide (5 mL) was generated in a separate flask and subsequently added to the NaOMe suspension via cannula. After being stirred for 1 h, the reaction had evolved into a homogeneous, dark orange solution. The reaction vessel was evacuated to remove any volatiles formed during the reaction. Addition of pentane (50 mL) to the remaining orange solution resulted in the formation of a white precipitate, probably NEt$_4$I or NaI. The light orange solution was filtered away from the precipitate, and the precipitate was washed with pentane (2 × 50 mL). Cooling the light yellow hexamethylphosphoramide/pentane solution to −35 °C yielded an orange oil. The colorless supernatant was decanted, and the oil was washed with pentane (2 × 25 mL). After excess pentane was removed by evacuation, the oil was dissolved in diethyl ether (5 mL). Cooling the resulting yellow solution to −78 °C afforded yellow crystals (0.110 g). Infrared and ^{1}H NMR spectroscopies showed peaks that are consistent with the stoichiometry $[Na(HMPA)_{4.5}][(CO)_5WSi(SnMe_3)_3]$.

X-ray Structure Determination of [NEt$_4$][3]. A pale yellow fragment of approximate dimensions 0.22 mm × 0.34 mm × 0.50 mm was cut from a much larger crystal and was mounted in a thin-walled glass capillary under N$_2$. Centering of 25 randomly selected reflections with $15° \leq 2\theta \leq 30°$ provided the unit cell dimensions. Axial photographs confirmed the lattice assignment as monoclinic. A summary of the data collection and refinement is provided in Table I. The data were corrected for a 9% decay in the intensities of three check reflections, Lorentz and polarization effects, and absorption. The space group was uniquely determined by systematic absences. Solution was achieved by direct methods, and the structure was refined by using full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated, idealized positions with fixed isotropic thermal parameters (d(C–H) = 0.96 Å, H thermal parameter approximately equal to 1.2 times the isotropic thermal parameter of the parent carbon atom).

Acknowledgment is made to the National Science Foundation for financial support, and to the DOD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–90).

Supplementary Material Available: Tables of crystal, data collection, and refinement parameters, complete atomic coordinates, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (6 pages); listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Formation and Chemical Reactions of Ruthenium Tricarbonyls Adsorbed on Metal Oxides. Use of Chemical Reactions as a Method of Surface Structure Determination

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Received January 30, 1990

The adsorption of $Ru(CO)_3Cl_2(THF)$ onto the surface of hydroxylated metal oxides yields one of two surface metal carbonyls depending on the metal oxide. Depending on the nature of the metal oxide, the surface species either retains or loses coordinated chloride. The surface species may be described as $[Ru(CO)_3Cl_2(HO–)]$ and $[Ru(CO)_3(HO–)(O–)_2]$, where HO– and O– represent surface hydroxyl and oxo groups, respectively. Although the exact nature of the ligands provided by the surface remains unknown in the adsorbed complexes, the ligands shown provide for the formation of a neutral carbonyl fragment when ruthenium remains in the +2 oxidation state. The former species is generated on silica and NaY zeolite, and the latter is generated upon adsorption on alumina and MgO. The proposed structures are consistent with the reactions of the surface species with bipyridine and tetracarbonylcobaltate(1−). The more strongly adsorbed species, $[Ru(CO)_3(HO–)(O–)_2]$, generated on alumina and MgO does not react with tetracarbonylcobaltate(1−), while the more weakly adsorbed species, $[Ru(CO)_3Cl_2(HO–)]$, on silica and NaY zeolite reacts to yield a bimetallic cluster.

Much of the interest in the chemistry of metal carbonyls with solid metal oxides stems from the observation that metal carbonyls offer alternative starting materials for the preparation of supported metal catalysts.[1] Metal carbonyls themselves, when supported on metal oxides, also have been shown to be catalytically active for a wide range of reactions.[2] Furthermore, heterogeneous catalysts derived from metal carbonyls give, in some cases, higher selectivity and activity than those prepared from metal salts.[3] Supported ruthenium carbonyls and the catalysts derived from them have been shown to be active for the catalytic reduction of CO,[4] the water gas shift reaction,[5] and the hydrogenation of olefins.[6]

One problem that plagues the study of adsorbed metal carbonyls is the determination of the composition and structure for the adsorbed species. It is important to determine the structure of the adsorbed carbonyls, since this may influence the catalytic activity of materials derived from the carbonyls. Structures for adsorbed carbonyls are typically deduced from spectroscopic data and by comparison of this data with known compounds that serve as models for the adsorbed carbonyls. Preferably a variety of spectroscopic techniques are applied to the supported carbonyl; a consistent set of results from several methods is most likely to give a reliable indication of the structure of the supported carbonyl.

The formation of ruthenium tricarbonyl on many metal oxides has been implicated in the surface chemistry of ruthenium carbonyls under a variety of conditions.[7-11] The starting material for the adsorbed carbonyls is typically $Ru_3(CO)_{12}$ although $[Ru(CO)_3Cl_2]_2$[8] and $Ru(CO)_3Cl_2THF$[11] have also been used.

Bell et al. have shown that $Ru_3(CO)_{12}$ readily sublimes onto untreated SiO$_2$ to yield initially physisorbed $Ru_3(CO)_{12}$.[7] The physisorbed cluster can then be fragmented under H$_2$ at 500 K to give mononuclear and dinuclear ruthenium carbonyls. Basset et al. have demonstrated that the oxo-bridged cluster $[HRu_3(CO)_{10}OSi–]$ can be formed on hydroxylated SiO$_2$.[8] Furthermore, they showed that the grafted cluster can be fragmented at high

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