Table I. Oxidative Addition of Allylic Halides to Ruthenium(II) Carbonyl Complexes[a]

entry	Ru(II) complex[b]	allylic halide	product	yield,[c] %
1	Cp′Ru(CO)$_2$Br (**1**)	allyl bromide	**5a**, R^1 = CH$_3$, R^2 = H, X = Br	96
2	Cp′Ru(CO)$_2$Cl (**2**)	allyl chloride	**5b**, R^1 = CH$_3$, R^2 = H, X = Cl	90
3	Cp′Ru(CO)$_2$Cl (**2**)	methallyl chloride	**5c**, R^1 = CH$_3$, R^2 = CH$_3$, X = Cl	94
4	Cp′Ru(CO)$_2$Br (**1**)	1-bromo-2-phenyl-1-propene	**5d**, R^1 = CH$_3$, R^2 = Ph, X = Br	96
5	CpRu(CO)$_2$Br (**3**)	allyl bromide	**5e**, R^1 = H, R^2 = H, X = Br	92
6	CpRu(CO)$_2$Cl (**4**)	allyl chloride	**5f**, R^1 = H, R^2 = H, X = Cl	92
7	CpRu(CO)$_2$Cl (**4**)	methallyl chloride	**5g**, R^1 = H, R^2 = CH$_3$, X = Cl	94
8	CpRu(CO)$_2$Br (**3**)	1-bromo-2-phenyl-1-propene	**5h**, R^1 = H, R^2 = Ph, X = Br	82

[a] All reactions were carried out in *n*-decane at 140 °C for 3-12 h. [b] Cp = η^5-C$_5$H$_5$; Cp′ = η^5-C$_5$(CH$_3$)$_5$. [c] The reactions were accompanied by the recovery of a small amount of the starting Ru(II) complex (~10%). The yields listed are those taking into account the recovery of starting complex and are not optimized. [d] **1** and **2** were prepared by the same procedure as **3** and **4**. [e] Haines, R. J.; du Preez, A. L.; *J. Chem. Soc., Dalton Trans.* **1972**, 944. [f] Blackmore, T.; Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2931.

Oxidative addition of some organic halides to Ru(0) complexes $Ru_3(CO)_{12}$[10] and RuCl(NO)(PPh$_3$)$_3$[11] have been reported. On the other hand, group 6 d^6 complexes, Mo(CO)$_6$,[12] W(CO)$_6$,[13] and their derivatives and bis(arene) complexes of Mo and W[14] are known to undergo oxidative addition of allylic halides to give the corresponding divalent η^3 complexes. The present work is the first example of the oxidative addition of organic halides to d^6 Ru(II) complexes, which are isoelectronic to Mo(0) complexes[12,14] to our knowledge.

Reaction of Ru(IV) complexes **5** with CO resulted in reductive elimination of the allylic halides from the metal center to give ruthenium(II) halogeno carbonyl complexes **1**–**4**. This result implies that reversal of the above described oxidative addition is easily induced by coordination of CO. Typically, a diglyme solution of **5h** was heated at 140 °C for 0.5 h under an atmosphere of CO to give the Ru(II) complex **3** and 1-bromo-2-phenyl-1-propene in 80 and 73% yields, respectively. In the absence of CO, **5h** was completely recovered under the same conditions. We recently found that a ruthenium(IV) methyl complex, Ru(CH$_3$)I(1–3,6,7,10–12-η-C$_{12}$H$_{18}$), underwent smooth reductive coupling of the methyl moiety with one of the π-allyl moieties under CO atmosphere.[15] It was proven that reduction of electron density on the metal center was crucial in reductive elimination of alkanes from dialkylnickel complexes.[16] It is reasonable that coordination of CO to the Ru(IV) metal center of **5h** reduces the electron density on the metal, facilitating the reductive elimination of allylic halides. Other Ru(IV) complexes **5a** and **5d** also underwent reductive elimination under conditions similar to those above to give **1** (70–80%) and the corresponding allylic halides (50–70% yields).

Attempted carbonylation of the coordinated allylic moiety was unsuccessful; heating a diglyme solution of **5h** at 120–140 °C under 30 atm of CO pressure results in no incorporation of CO into the allylic moiety but only simple reductive elimination of the allylic halides.[17]

High-valent organometallic complexes of late transition metals are of interest because they have comparable numbers of d electrons to those of early transition metals and would be expected to have properties that differ from those found for the more commonly encountered transition-metal complexes. Chemistry stemming from the Ru(IV) complexes described in this paper is under active study.

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Supplementary Material Available: Tables of ^{1}H NMR and analytical data for **5a–h** (2 pages). Ordering information is given on any current masthead page.

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Solvated Triorganotin Cations. Structure and Use as Catalysts for Diels–Alder Additions to Furan

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Summary: The title compounds, R$_3$SnL$_2$$^+X^-$, where L is acetonitrile and X is a non-coordinating anion (e.g. SbF$_6$$^-$), have been prepared and characterized. They are effective Lewis acid catalysts for the Diels–Alder addition of α,β-unsaturated nitriles to furan.

Uncharged group 3B derivatives (AlEtCl$_2$, BF$_3$, BPh$_3$, etc.) constitute a broadly useful class of Lewis acid cata-

Table I. Selected Bond Distances (Å) and Bond Angles (deg) for $Cy_3Sn(NCMe)_2(SbF_6)$

Bond Distances

Sn-N(1)	2.374 (3)	N(1)-C(1)	1.129 (4)
Sn-N(2)	2.472 (3)	N(2)-C(3)	1.128 (4)
Sn-C(11)	2.161 (3)	C(1)-C(2)	1.451 (5)
Sn-C(21)	2.159 (3)	C(3)-C(4)	1.461 (5)
Sn-C(31)	2.158 (3)		
Sb-F(av)	1.850 (3)	C-C(Cy-C_6,av)	1.519 (7)

Bond Angles

N(1)-Sn-N(2)	177.2 (1)	Sn-C(11)-C(12)	113.4 (3)
N(1)-Sn-C(11)	89.7 (1)	Sn-C(11)-C(16)	111.4 (2)
N(1)-Sn-C(21)	91.5 (1)	C(12)-C(11)-C(16)	111.2 (3)
N(1)-Sn-C(31)	94.1 (1)	Sn-C(21)-C(22)	114.7 (3)
N(2)-Sn-C(11)	87.6 (1)	Sn-C(21)-C(26)	110.7 (3)
N(2)-Sn-C(21)	89.4 (1)	C(22)-C(21)-C(26)	111.1 (3)
N(2)-Sn-C(31)	87.9 (1)		
C(11)-Sn-C(21)	122.3 (1)	Sn-C(31)-C(32)	114.6 (2)
C(11)-Sn-C(31)	120.5 (1)	Sn-C(31)-C(36)	111.7 (2)
C(21)-Sn-C(31)	116.9 (1)	C(32)-C(31)-C(36)	110.5 (3)
Sn-N(1)-C(1)	168.3 (3)		
Sn-N(2)-C(3)	173.2 (3)		
N(1)-C(1)-C(2)	178.1 (4)		
N(2)-C(3)-C(4)	179.5 (4)		

lysts. We felt that the isoelectronic group 4B cations might be effective Lewis acids since the positive charge of the metal should further enhance the electron deficiency of a coordinated substrate. In this regard, we wish to report that anhydrous triorganotin hexafluoroantimonates are easily prepared as their bis(acetonitrile) adducts and are fully ionic. We also report the first of several applications of these catalysts, the Diels–Alder addition of α,β-unsaturated nitriles to furan.

The literature contains several reports of unsolvated organotin compounds containing poorly coordinating anions (e.g., Me_3SnBF_4).[1] However, for our purposes the preparative procedures seemed unnecessarily complicated. Therefore, we developed a straightforward preparation of these salts as their acetonitrile solvates. Treatment of either a triorganotin bromide[2] or a triorganotin hydride[3] in acetonitrile with 1 equiv of silver hexafluoroantimonate proceeded according to eq 1 or eq 2, respectively.[4]

$$R_3SnBr + AgSbF_6 \xrightarrow{MeCN} \underset{1}{R_3Sn(NCMe)_2(SbF_6)} + AgBr \quad (1)$$

$$R_3SnH + AgSbF_6 \xrightarrow{MeCN} 1 + Ag + {}^1/_2H_2 \quad (2)$$

Analogous reactions with $AgBF_4$ and $AgClO_4$ proceeded similarly. In each case, filtration, evaporation of the solvent, and drying in vacuo afforded the desired tin compound. However, application of this procedure for all of the isomeric C_1 to C_4 alkyl groups and a variety of substituted aryl groups resulted in CHN analyses corresponding to nonintegral incorporation of acetonitrile (e.g., $R_3Sn(NCMe)_nX$, $1 < n < 2$), and we were unable to identify conditions to recrystallize most of these compounds. However, for three cases with bulky alkyl groups (R = *tert*-butyl, neopentyl, or cyclohexyl), the products could be recrystallized from ether/acetonitrile to afford the analytically pure bis(acetonitrile) adducts.[5]

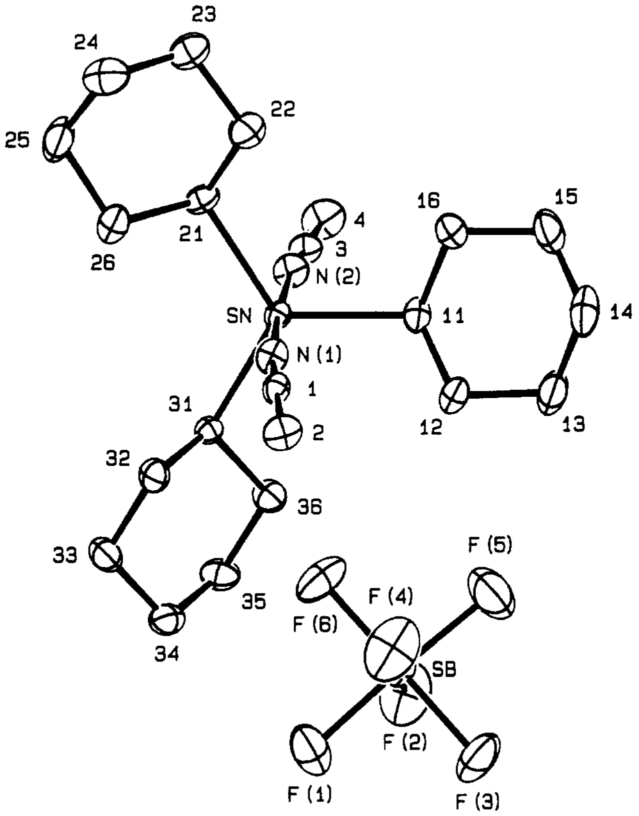

Figure 1. Structure of bis(acetonitrile)tricyclohexyltin hexafluoroantimonate showing the numbering scheme.

The fully ionic character of compounds 1 is shown by the X-ray crystal structure[6] for the case R = cyclohexyl. An ORTEP diagram is shown in Figure 1, and selected bond lengths and angles are in Table I. The coordination about the tin atom is trigonal bipyramidal with the two acetonitrile ligands in the axial sites. The acetonitrile ligands are loosely coordinated with tin as judged by the long Sn–N bonds which, interestingly, differ in length by 0.1

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(2) Use of the corresponding trialkyltin chlorides led to incomplete precipitation of silver chloride in solvent acetonitrile. This could be circumvented by carrying out the initial metathesis in nitromethane and subsequent ligand exchange.

(3) Oxidation of triorganotin hydrides by silver salts has been known for some time: Anderson, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 4913–4915.

(4) In a typical preparation tricyclohexyltin bromide (22.5 g, 50.2 mmol) in acetonitrile (375 mL) under dry N_2 was treated with silver hexafluoroantimonate (16.25 g, 47.3 mmol). After 0.5 h the mixture was concentrated to 100 mL and filtered to remove AgBr, and the remaining solvent was removed in vacuo. Washing the residue with 2 × 100 mL of hexane and drying provided **1**, R = cyclohexyl (30.3 g, 93%), of adequate purity for synthetic applications. Anal. Calcd for $C_{22}H_{39}F_6N_2SbSn$: C, 38.52; H, 5.73; N, 4.08. Found: C, 38.00; H, 5.74; N, 3.89.

(5) For instance, 1 g of **2**, R = cyclohexyl, was dissolved in 10 mL of ether and 0.4 mL of acetonitrile and cooled to −25 °C to afford, after drying, 0.7 g of crystalline **2**. Found: C, 38.40; H, 5.64; N, 3.99.

(6) Data were collected on a Syntex P3 diffractometer with the crystal cooled to −100 °C (graphite monochromator; Mo Kα radiation; λ = N 0.710 69 Å). The crystal chosen for study was a parallelpiped measuring 0.25 × 0.24 × 0.30 mm which was mounted in a quartz capillary. Axial photographs and systematic absences were consistent with the monoclinic space group $P2_1/n$. The unit-cell dimensions were refined from the Bragg angles of 48 reflections: a = 13.923 (3) Å, b = 16.501 (3) Å, c = 11.891 (3) Å, α = 93.85 (2)°. The cell volume, 2725.7 Å, yields a calculated density of 1.810 g cm^{-3} for $Z = 4$. Intensity data for 6896 reflections were collected by using the ω scan technique ($4° < \theta < 55°$; scan width of 1.2°; variable scan rate of 4.0–10.0° min^{-1}). The intensities of three standard reflections were monitored after every 200 reflections; only statistical fluctuations were noted. Empirical absorption correction factors ranging from 0.936 to 1.000 were applied. (The linear absorption coefficient is 19.91 cm^{-1}.) Solution of the structure by direct methods and refinement was carried out as described previously[7] and afforded a final R of 0.033. Hydrogen positions were calculated. The three largest peaks in the final difference Fourier map were in the range 0.81–1.00 e $Å^3$ and appear to be disordered residues of the cyclohexyl group containing C(21)–C(26).

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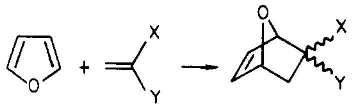
Å. The different conformations of the cyclohexyl groups probably play a role in determining the Sn-N distances (and the C-Sn-C angles as well). Some support for this notion is provided by a recently published structure of a hydrated tributyltin cation $Bu_3Sn(OH_2)_2^+$ in which more nearly identical Sn-O bond lengths of 2.295 (4) and 2.326 (5) Å were reported.[8]

Compounds 1 are effective promoters of Diels-Alder additions to furan (eq 3). The 7-oxabicyclo[2.2.1]heptene system 2 has found considerable utility in organic synthesis.[9-12] However, eq 3 has typically required either very high pressures[9] or extended reaction times of up to 2-3 months.[10] Recently copper[11] or zinc[12] Lewis acids were reported to increase the rate of these reactions, though from the standpoint of large scale synthesis, both of these systems have practical drawbacks.[13] Using 0.2 M 1, R = cyclohexyl at 40 °C, the addition of either acrylonitrile or 2-chloroacrylonitrile to furan could be effected in 70-75% yield in 24 h (40% excess of furan; no solvent). The products had identical physical and spectroscopic properties to those of the (uncatalyzed) thermal reaction.[14] Interestingly, varying the steric size of the alkyl ligands in 1 from cyclohexyl to methyl had no discernible effect on the ratio of isomeric products (endo/exo) obtained from eq 3. Diels-Alder addition of methyl acrylate to furan was also promoted by 1, but the reaction additionally produced ca. 5% of resinous side products.



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(3)

Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, and structure factor amplitudes (observed and calculated) (34 pages). Ordering information is given on any current masthead page.

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A New Anion Rearrangement Involving Silyl Migration to Oxygen

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Summary: The proton that is added to carbon during rearrangements of $(Me_3Si)_3CCH_2CH_2OH$ to $(Me_3Si)_2CHCH_2CH_2OSiMe_3$ has been shown, by deuterium labeling, to originate from the hydroxyl group of the parent carbinol and not the solvent. Examples of a related new intramolecular rearrangement that appears to involve oxyanion to silanion isomerization are described.

The metal-(Na/K etc.) and base-catalyzed conversions of α-silylcarbinols to alkoxysilanes (eq 1) that involve oxyanion to carbanion rearrangements (Brook rearrangement) have been thoroughly investigated.[1-3] More recently a related rearrangement has been shown to occur when β-hydroxy silanes are treated with strong base in protic medium.[4] Under these conditions the carbanion intermediate, instead of losing silanolate ion as in the well-known Peterson olefination reaction,[5] is protonated to give the related alkoxysilane (eq 2). (β-Hydroxyvinyl)silanes similarly rearrange to allyl silyl ethers by using sodium hydride in HMPA.[6]

$$R_3SiCR_2OH \xrightarrow{Na/K} R_3SiCR_2O^- \rightarrow R_3SiOC^-R_2 \rightarrow R_3SiOCHR_2 \quad (1)$$

$$R_3SiCR_2CR_2OH \xrightarrow{B} R_3SiCR_2CR_2O^- \rightarrow {}^-CR_2CR_2OSiR_3 \rightarrow HCR_2CR_2OSiR_3 \quad (2)$$

A related rearrangement of a γ-hydroxy silane has recently been described, where the proton that becomes attached to carbon was said to arise from the attack of the carbanion intermediate on THF, the only solvent found in which rearrangement occurred by using NaH or potassium *tert*-butoxide as isomerizing agents. In our view a more probable source of the hydrogen was unrearranged carbinol present in the reaction mixture, and this has now been confirmed by deuteration studies.

Thus, a 0.56-g sample of 3,3,3-tris(trimethylsilyl)-1-propanol,[7,8] 1, was exchanged twice with solutions of 0.5 mL of 99.7% D_2O in 5 mL of THF. On evaporation to dryness, mass spectrometric studies, using the ratio of the abundance of the $(M - Me)^+$ ions for deuterated (*m/e* 262) and protonated (*m/e* 261) species, showed that the carbinol was at least 80.1% deuterated (after taking account of the D, ^{13}C, and ^{29}Si natural abundance isotopes).[9] After rearrangement at about 5% concentration in dry THF using a small droplet of Na/K (<1-mm diameter) for 1 h at room temperature, workup by evaporation after removal of the largely unconsumed Na/K yielded the isomeric 3,3-bis(trimethylsilyl)-3-deuterio-1-(trimethylsiloxy)propane, 2, in quantitative yield, shown by mass spectrometry (after taking account of natural abundance isotopes) to be 92.2% deuterated. That the carbinol appears to be less deuterated than the derived silyl ether is accounted for by the

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[†] Visiting Research Fellow from the Technical University, Lodz, Poland.

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(8) The ^1H NMR, IR, and mass spectra of this compound were essentially the same as recorded in ref 7. In addition for 1: ^{29}Si NMR ($CDCl_3$) δ 2.95; ^{13}C NMR ($CDCl_3$) 2.68 (MeSi), 3.77 ($(Me_3Si)_3C$), 34.06 (CH_2), 62.99 (CH_2OH) ppm. For 2: ^{29}Si NMR (C_6D_6) δ 3.33 (MeSi), 15.7 ($OSiMe_3$). For $(Me_3Si)_2CHCH_2CH_2OH$ (from 2 by hydrolysis): ^{29}Si NMR (C_6D_6) δ 3.35; ^{13}C NMR ($CDCl_3$) -0.03 (Me), 9.28 (CH), 29.08 (CH_2), 64.76 (CH_2OH) ppm.

(9) Thus $(262/261)_{exptl} = M_D/M_H + M_{nat.\ isotopes}/M_H$.

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