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Reviews

Similarities and Contrasts between Silyl and Stannyl Derivatives of Ruthenium and Osmium

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Silyl and stannyl complexes of ruthenium and osmium bearing halogen substituents on the silicon and tin atoms undergo many interesting reactions. While there are formal similarities, there are also marked differences between these silyl and stannyl derivatives. This review first surveys the synthetic approaches we have developed to the silyl and stannyl complexes that involve oxidative addition of halogenated silanes coupled with reductive elimination for the preparation of the silyl complexes $L_nM(SiR_nX_{3-n})$ (M = Ru, Os) and reaction between L_nMH and the vinylstannane $R_3SnCH{=}CH_2$ to give first the triorganostannyl complexes $L_nM(SnR_3)$ (M = Ru, Os), which are then functionalized by redistribution reactions to give $L_nM(SnR_nX_{3-n})$ (M = Ru, Os). Among the unusual compounds derived from these halogenated silyl and stannyl complexes are derivatives with the following novel ligands: $Si(OH)_3$, $Sn(OH)_3$, silatranyl, stannatranyl, SnH_3, and $SnMe_2SnPh_3$. A contrast between the osmasilanol $L_nOs(SiMe_2OH)$ and the osmastannol $L_nOs(SnMe_2OH)$ is that the former deprotonates to a silanolate anion, $[L_nOs(SiMe_2O)]^-$, while the latter, when treated with base, ortho-stannylates a triphenylphosphine ligand. Another contrast is provided by the ease with which osmium trimethylstannyl complexes undergo α-methyl migration reactions.

I. Introduction

This review, which summarizes our research on ruthenium and osmium silyl and stannyl complexes over the past 16 years, begins with a short introductory section that highlights some of our earlier results involving the synthesis and study of coordinatively unsaturated organometallic derivatives of ruthenium and osmium. This early organometallic work emphasized the extraordinary opportunities afforded by coordinative unsaturation at the metal center, together with the presence of good leaving groups on a carbon donor atom, for the synthesis of unusual products. In an extension of this work, coordinatively unsaturated (as well as saturated) silyl and stannyl complexes of ruthenium and osmium that bear good leaving groups on the silicon or tin donor atoms have been synthesized. Studies have shown that these compounds are versatile precursors to complexes with novel silicon and tin ligands, and in addition, the results have allowed interesting comparisons to be made between the silyl and stannyl complexes.

A. Haloalkyl and Dihalocarbene Complexes. A valuable development in the organometallic chemistry of ruthenium and osmium was the discovery that five-coordinate, coordinatively unsaturated, σ-aryl derivatives, $MRCl(CO)(PPh_3)_2$ (M = Ru, Os; R = aryl), were easily accessible from reaction between $MHCl(CO)(PPh_3)_3$ and HgR_2.[1] In the solid state these colored compounds (red or orange) proved to have tetragonal-pyramidal geometry[2] and in solution readily take up a variety of small ligands to form colorless six-coordinate complexes. Examples of these five- and six-coordinate complexes are shown in Scheme 1. A divergence between the ruthenium and osmium complexes is that whereas the osmium complexes, e.g., **3**, take up CO to form the stable dicarbonyl complexes **4**, the ruthenium complexes, e.g., **1**, take up CO to give the six-coordinate complexes **2a**, which in solution are in dynamic equilibrium with the η^2-acyl complexes **2b**. The position of this equilibrium depends on steric[3] and electronic[4] factors associated with both the aryl group and the halide on the metal.

The coordinative unsaturation of complexes such as **3** opened pathways to exotic organometallics such as the stable and structurally characterized methylene complex **5** [5] (Scheme 2). A related observation is that the trichloromethyl complex **6** spontaneously rearranges to the dichlorocarbene complex **7**. This rearrangement is driven by a combination of coordinative unsaturation at osmium and the presence of a good leaving group on the metal-bound carbon atom. The dichlorocarbene complex **7**, in turn, opens the way to complexes bearing the complete set of chalcocarbonyl ligands, **8** [6] (Scheme 3), and the five-coordinate carbyne complex **9**[7] (Scheme 3). The key to the formation of **8** and **9** is the dichlorocarbene complex **7**, and dihalocarbene complexes in general undergo many other interesting reactions dependent upon the presence of good

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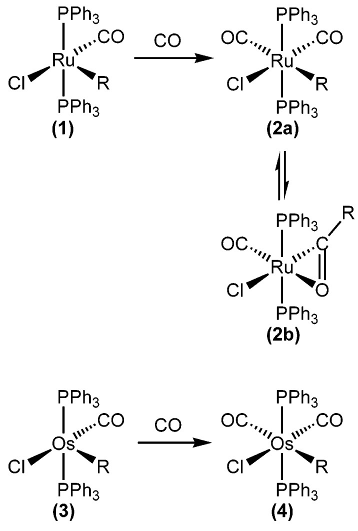
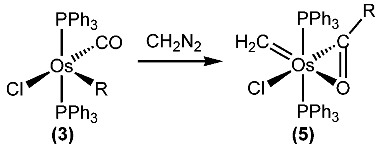
10.1021/om060526d CCC: $33.50

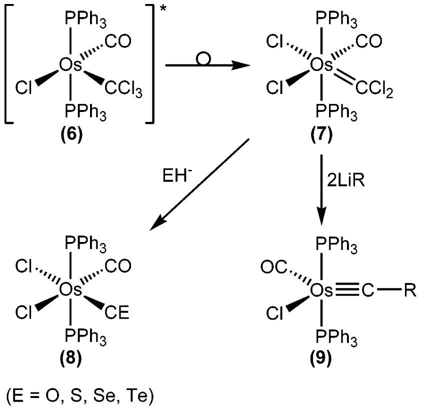
Scheme 1



Scheme 2

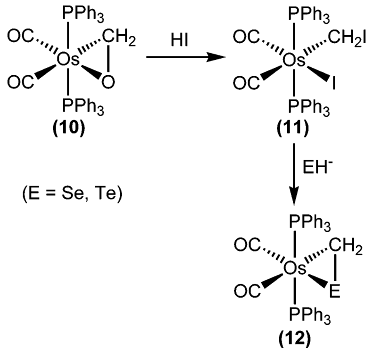


Scheme 3[a]



[a] The asterisk denotes the proposed intermediate from the reaction between $OsHCl(CO)(PPh_3)_3$ and $Hg(CCl_3)_2$.

Scheme 4



leaving groups on the carbene carbon atom.[8] Even coordinatively saturated haloalkyl complexes related to **6** (see complex **11** in Scheme 4) exhibit interesting nucleophilic substitution reactions at the metal-bound carbon.[9]

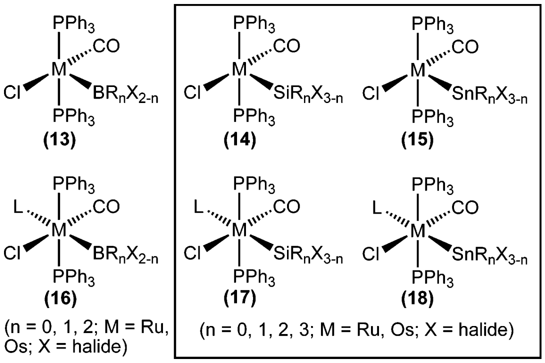


Figure 1.

B. From Compounds with M−C Bonds to Compounds with M−B, M−Si, and M−Sn Bonds (M = Ru, Os). Looking beyond organometallic chemistry to "inorganometallic" chemistry, the remarkable chemistry associated with halogenated alkyl ligands sketched above suggested to us that it would be worthwhile to explore analogous complexes with transition-metal−boron, −silicon, and −tin bonds. Therefore, we decided to synthesize both coordinatively unsaturated boryl, silyl, and stannyl complexes of ruthenium and osmium and their coordinatively saturated analogues, especially those which bear at least one good leaving group on the main-group element. Accordingly, the complexes **13**−**18** (Figure 1) became target molecules. This work began about 16 years ago, and the metal−boron results have been reviewed.[10,11] In this review article we summarize our results on the silyl and stannyl derivatives, focusing particularly on the similarities and contrasts between the two classes of compounds.

II. Methods for the Preparation of Transition-Metal Silyl Complexes

Most transition-metal silyl complexes have been made by either oxidative addition of a Si−element bond (most commonly Si−H) or through attack of transition-metal anions at an electrophilic silicon center (or less commonly the inverse reaction, attack of silicon anions at a transition-metal center).[12] Reactions with transition-metal anions are not appropriate for the preparation of compounds with halogen-substituted silyl ligands. Since chlorosilanes are readily available, the oxidative addition approach to the target molecules **14** with a halosilyl ligand (i.e., with $n = 0-2$; see Figure 1) is at first sight attractive. However, reactive zerovalent ruthenium and osmium complexes (e.g., $M(CO)_2(PPh_3)_3$) are usually incompatible with compounds containing Si−X (X = halogen) bonds, because of the difficulty of preventing the formation of trace amounts of HX, which bring about rapid protonation of zerovalent complexes. Simple oxidative addition reactions to these zerovalent complexes were therefore limited to organosilanes without Si−X bonds.

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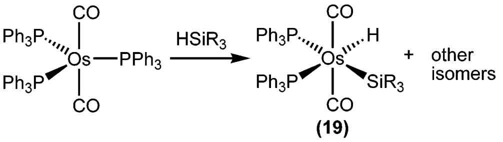
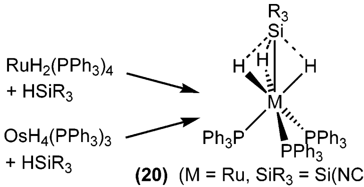
Scheme 5



(19)

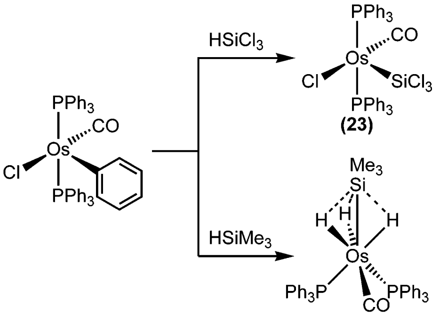
(SiR$_3$ = SiEt$_3$, SiMe$_3$, SiPh$_3$, SiHPh$_2$, Si(NC$_4$H$_4$)$_3$, Si(OCH$_2$CH$_2$)$_3$N)

Scheme 6



(20) (M = Ru, SiR$_3$ = Si(NC$_4$H$_4$)$_3$)
(21) (M = Os, SiR$_3$ = Si(NC$_4$H$_4$)$_3$)
(22) (M = Os, SiR$_3$ = Si(OC$_2$H$_4$)$_3$N)

Scheme 7



(23)

(24)

III. Synthesis of Six- and Seven-Coordinate Silyl Complexes via Oxidative Addition of Si−H Bonds to Reactive Complexes of Ruthenium and Osmium

A. Oxidative Addition to Os(CO)$_2$(PPh$_3$)$_3$. As illustrated in Scheme 5, the zerovalent osmium complex Os(CO)$_2$(PPh$_3$)$_3$ reacts with a range of organosilanes to give the octahedral silyl complexes **19**.[13−15] These products sometimes exist as a mixture of geometrical isomers, with the isomer depicted in **19** usually predominating and confirmed crystallographically for OsH(SiEt$_3$)(CO)$_2$(PPh$_3$)$_2$[13] and OsH[Si(NC$_4$H$_4$)$_3$](CO)$_2$(PPh$_3$)$_2$.[14] The fact that the osmium is coordinatively saturated in these complexes and especially that the silyl substituents do not include good leaving groups means that these complexes cannot readily be further modified and therefore do not offer a route to the target molecules **14**, **15**, **17**, and **18** (see Figure 1). The solution to this problem lay in using not a zerovalent complex of osmium but a five-coordinate phenyl derivative of osmium(II), OsPhCl(CO)(PPh$_3$)$_2$, as a substrate for oxidative addition reactions with silanes, as described below in section IV. Before we describe this approach, we summarize other interesting silyl derivatives of Ru(IV) and Os(IV) prepared from oxidative addition reactions.

B. Oxidative Addition to either RuH$_2$(PPh$_3$)$_4$ or OsH$_4$(PPh$_3$)$_3$. As shown in Scheme 6, the seven-coordinate silyl trihydride complexes Ru[Si(NC$_4$H$_4$)$_3$]H$_3$(PPh$_3$)$_3$ (**20**)[16] and Os(SiR$_3$)H$_3$(PPh$_3$)$_3$ (**21**, R = NC$_4$H$_4$;[16] **22**, SiR$_3$ = silatranyl[15]) are prepared through treatment of either RuH$_2$(PPh$_3$)$_4$ or OsH$_4$(PPh$_3$)$_3$ with the appropriate silane. Compounds of this general structural type are well-known for both iron (Fe(SiR$_3$)H$_3$L$_3$)[17] and ruthenium (Ru(SiR$_3$)H$_3$L$_3$).[18] However, there was neither good structural data with location of the hydride ligands nor extensive NMR data, particularly Si−H coupling constant measurements for this class of compounds, until the ruthenium and osmium complexes **20**−**22** were reported. The new information, together with ab initio calculations on the model compounds Os(SiR$_3$)H$_3$(PH$_3$)$_3$ (R = H, NH$_2$, NC$_4$H$_4$), allowed the recognition of a unique kind of bonding in **20**−**22**, in which the silicon atom interacts with all three equivalent hydrogen atoms. The hydride ligands are in bridging positions, as shown in Scheme 6, and three partial Si···H−Os three-center bonds are formed.[16] An alternative description of this bonding has been discussed.[19] Crystal structures have been determined for both **21** and **22**. The Os−Si bond in **21** is 2.293(3) Å, and the corresponding distance in **22** is 2.3442(8) Å. These are both short distances when they are compared with typical values for octahedral osmium complexes, and the value for **21** is almost as short as those found in the five-coordinate trihalosilyl complexes Os(SiF$_3$)Cl(CO)(PPh$_3$)$_2$ (2.254(2) Å) and Os(SiCl$_3$)Cl(CO)(PPh$_3$)$_2$ (2.273(6) Å) (see section IVB below). The marked difference between the Os−Si bond distances for **21** and **22** is a reflection of the powerful electron-withdrawing effect of the *N*-pyrrolyl substituents on silicon. This effect is also evident from the theoretical calculations.[16] In the crystal structure of **22** the hydrides are located and the measured Os−H distances are 1.52(3), 1.66(3), and 1.57(3) Å. The calculated distances between silicon and hydrogen are Si···H(1) = 2.06(4) Å, Si···H(2) = 2.00(4) Å, and Si···H(3) = 1.96(3) Å. These numbers are indicative of very weak Si···H interactions in complex **22**. Nevertheless, the measured Si−H coupling constants in **20** and **21** are 47.4 and 29.2 Hz, respectively. The three compounds **20**−**22** represent new examples of nonclassical interligand interactions between one silyl group and three hydride ligands.[19]

IV. Five-Coordinate Ruthenium and Osmium Silyl Complexes

A. Synthesis. As shown in Scheme 7, the reaction between the red, coordinatively unsaturated complex OsPhCl(CO)(PPh$_3$)$_2$, and excess trichlorosilane proceeds under mild conditions and in high yield to give the yellow complex Os(SiCl$_3$)Cl(CO)(PPh$_3$)$_2$ (**23**).[20] This reaction probably involves initial oxidative addition of the Si−H bond followed by favorable reductive elimination of benzene. Complex **23** is a member of the class of compounds represented by **14** in Figure 1 and is a versatile starting material because of the three reactive Si−Cl bonds, the coordinative unsaturation at the osmium center, and the lability of the Os−Cl bond. Moreover, the transformation of the five-coordinate phenyl complex to the corresponding five-coordinate silyl complex is equally effective with the ruthenium analogue RuPhCl(CO)(PPh$_3$)$_2$,[21] with silanes bearing either one

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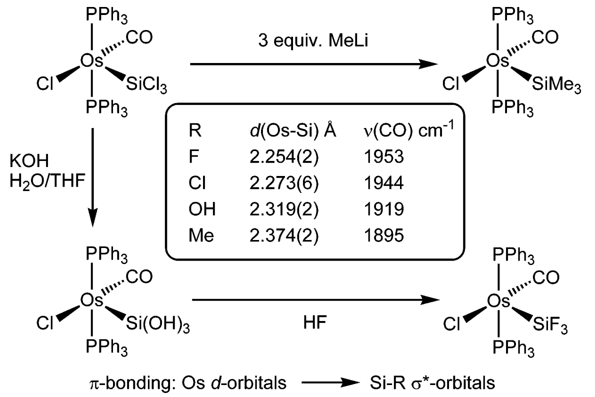


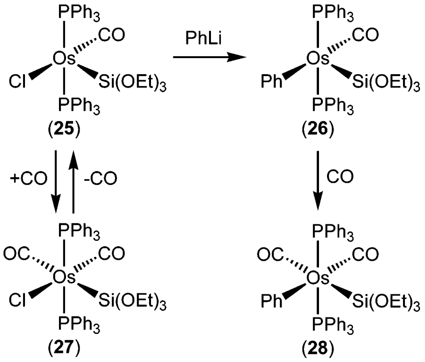
R	d(Os-Si) Å	ν(CO) cm^{-1}
F	2.254(2)	1953
Cl	2.273(6)	1944
OH	2.319(2)	1919
Me	2.374(2)	1895

Figure 2. Structural data for the five-coordinate osmium complexes $Os(SiR_3)Cl(CO)(PPh_3)_2$ (R = F, Cl, OH, Me). In addition to a strengthening of the Os−Si bond due to ionic contributions, calculations reveal the importance of increasing π-bonding in the order $SiMe_3 < Si(OH)_3 < SiCl_3 < SiF_3$.

or two chlorine substituents, viz., $H-SiR_2Cl$ and $H-SiRCl_2$, with silanes bearing other electronegative substituents such as $H-Si(NC_4H_4)_3$, $H-Si(OEt)_3$, and $H-Si(OC_2H_4)_3N$,[14,22−24] and even with trimethyl- and triethylsilane. However, in an atypical reaction, trimethylsilane with $OsPhCl(CO)(PPh_3)_2$ gives the osmium(IV) complex $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**24**) (see Scheme 7) rather than the expected $Os(SiMe_3)Cl(CO)(PPh_3)_2$.[25] The formation of this product must involve multiple oxidative addition and reductive elimination steps. Complex **24** is clearly related to the trihydride silyl complexes $MH_3(SiR_3)(PPh_3)_3$ (M = Ru, Os), which have been discussed in section IIIB, above.

B. Structure and Bonding. The tetragonal-pyramidal geometry of the five-coordinate silyl complexes represented by **14** in Figure 1 has been confirmed by numerous X-ray crystal structure determinations. In all of these structures the silyl ligand is located in the apical site. It is worth noting here that the related five-coordinate boryl complexes of ruthenium and osmium also adopt this structure with the boryl ligand apical, as do the five-coordinate stannyl derivatives to be discussed below.[26,27] Structural data for the set of five-coordinate osmium complexes $Os(SiR_3)Cl(CO)(PPh_3)_2$ (R = F, Cl, OH, Me) (see Figure 2) confirm other observations that the transition-metal−silicon distance becomes shorter as the electronegativity of the substituents on silicon becomes greater.[12] The measured distances are $Os-SiR_3$ = 2.254(2), 2.273(6), 2.319(2), and 2.374(2) Å for R = F, Cl, OH, Me, respectively.[20] These very short distances lie at the short end of the range of 75 observations for Os−Si distances recorded in the Cambridge Crystallographic Data Base, and indeed, the value of 2.254(2) Å remains the shortest Os−Si distance ever reported. A computational study of this same set of four isostructural compounds[20] shows that, in addition to the expected strengthening of the Os−Si σ bond as the ionic contributions increase, there is at least for the SiF_3 and $SiCl_3$ ligands a significant contribution to the bonding from an Os−Si π bond formed from overlap of appropriate osmium d orbitals with a suitable linear combination of either Si−F or Si−Cl σ* orbitals. In $Os(SiF_3)Cl(CO)(PPh_3)_2$ the SiF_3 ligand was estimated to have almost half the π-acceptor ability of the CO ligand in the same molecule. In a related observation, a photoelectron spectral study established that the $SiCl_3$ ligand in $CpFe(SiCl_3)(CO)_2$ is an effective π-acceptor ligand.[28] The ν(CO) values for $Os(SiR_3)Cl(CO)(PPh_3)_2$ (R = F, Cl, OH, Me) measured in the IR spectra and presented in Figure 2 are consistent with this picture of the bonding.

Scheme 8



C. Reactions at Osmium. The silyl ligand, once introduced into a five-coordinate ruthenium or osmium complex, can in some cases undergo an exchange process with a differently substituted silane; e.g., $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$ when treated with $HSiMe_2Cl$ affords $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ in good yield.

An illustration of the usefulness of the labile halide on osmium in the five-coordinate silyl complexes **14** (see Figure 1) is depicted in Scheme 8, where $Os[Si(OEt)_3]Cl(CO)(PPh_3)_2$ (**25**) (from $OsPhCl(CO)(PPh_3)_2$ and $HSi(OEt)_3$) undergoes a reaction with PhLi to replace the chloride and form an Os−phenyl bond in $Os[Si(OEt)_3]Ph(CO)(PPh_3)_2$ (**26**). Both **25** and **26** take up CO to form the six-coordinate complexes $Os[Si(OEt)_3]Cl(CO)_2(PPh_3)_2$ (**27**) and $Os[Si(OEt)_3]Ph(CO)_2(PPh_3)_2$ (**28**), respectively. Interestingly, the formation of **27** is reversible, and on heating in solution CO is lost and complex **25** is reformed. Most bis(triphenylphosphine) dicarbonyl complexes of osmium(II) resist loss of CO. We have observed one other osmium silyl complex to behave similarly, $Os[Si(NC_4H_4)_3]Cl(CO)_2(PPh_3)_2$, which loses CO in solution even at room temperature within minutes.[14] It is interesting that in complex **26**, where there are two ligands (phenyl and silyl), both of recognized strong σ bonding/trans influence character, it is the silyl ligand which dominates and which adopts the apical site of the tetragonal pyramid, as revealed by crystal structure determination. Complexes **26** and **28**, with adjacent silyl and aryl ligands, are models for the kind of metal complex intermediates postulated to facilitate silicon−carbon bond formation through reductive elimination in metal-catalyzed processes such as hydrosilation.[29] However, both **26** and **28** are remarkably robust compounds which resist thermal decomposition at elevated temperatures over long periods of time, and $PhSi(OEt)_3$ is not observed among the decomposition products that eventually form.[23] These observations are in marked contrast to the reactivity of the analogous boryl complex Os(Bcatecholate)(o-tolyl)$(CO)_2(PPh_3)_2$, which at room temperature readily undergoes reductive elimination to form o-tolylBcatecholate.[30,31]

D. Insertion Reactions into the Ru/Os−Si Bond. Another reflection of the low reactivity of the Os−Si bonds in both the

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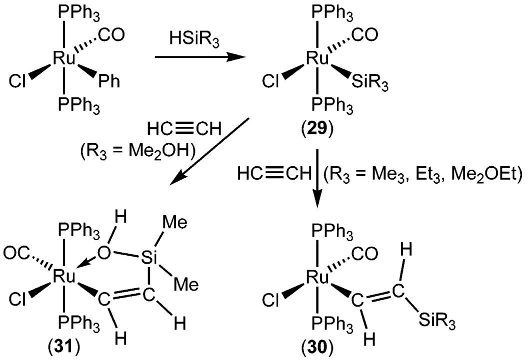
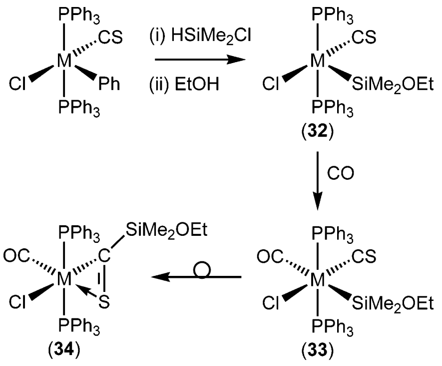
Scheme 9

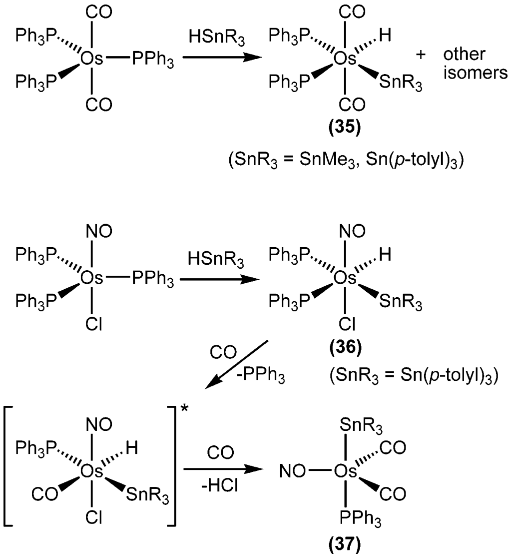


Scheme 10



(M = Ru, Os)

Scheme 11



five- and six-coordinate silyl complexes discussed above is that no insertion reactions with alkynes have been observed. However, the analogous ruthenium complexes readily undergo insertion reactions with ethyne, as shown in Scheme 9.[32] The orange, five-coordinate, silyl-substituted vinyl derivatives **30** (R_3 = Me_3, Et_3, Me_2OEt) are formed when the corresponding five-coordinate silyl complexes **29** are placed under ethyne at a pressure of 0.8 atm and at room temperature for several hours. In the special case when R_3 = Me_2OH, the isomer with cis geometry about the double bond is trapped by the OH group coordinating to the ruthenium to form the stable chelated complex **31**. The presence of this five-membered ring was confirmed by a crystal structure determination of a derivative of **31**. This chemistry parallels the ethyne insertion into the Ru−B bond in Ru(Bcatecholate)Cl(CO)(PPh_3)$_2$, where a related Ru−O donor bond from an oxygen of the catecholate group forms a similar five-membered ring.[33]

While the insertion reactions described above are limited to ruthenium, one insertion reaction which did proceed readily with an osmium complex involved insertion of a thiocarbonyl ligand into an Os−Si bond. This is depicted in Scheme 10, where the five-coordinate ruthenium and osmium thiocarbonyl complexes **32** take up CO to give the six-coordinate complexes **33**, which then immediately rearrange at room temperature to the red η^2-silathioacyl complexes **34**.[34] The structure of the ruthenium complex was confirmed by an X-ray crystal structure determination. A similar migration occurs with the corresponding silatranyl complex.[24] It is well-established that insertion reactions involving the thiocarbonyl ligand are much more facile than the corresponding carbonyl insertion reactions.[10,35]

Before discussing in detail the nucleophilic substitution reactions undergone by the halosilyl complexes introduced above, which are examples of target molecules **14** and **17** (Figure 1), we describe the preparation of the corresponding stannyl complexes **15** and **18**, in order that the reactions of the silyl and stannyl complexes can be discussed together, drawing attention to similarities and contrasts between them.

V. Methods for the Preparation of Transition-Metal Stannyl Complexes

The methods detailed above in section II for the synthesis of transition-metal silyl complexes are generally applicable also to the synthesis of transition-metal stannyl complexes.[36] Restrictions are that, once again, reactions with transition-metal anions are not appropriate for the preparation of compounds with halogen-substituted stannyl ligands and there are fewer available stable stannanes, particularly those bearing both hydrogen and halogen substituents. Nevertheless, the oxidative addition of simple organostannanes to low-oxidation-state complexes of the platinum-group metals has been widely used as a method of preparing compounds containing metal−tin bonds.[37]

VI. Synthesis of Six-Coordinate Stannyl Complexes via Oxidative Addition to Zerovalent Complexes of Ruthenium and Osmium

Stannanes can replace silanes in oxidative addition to the zerovalent osmium complexes Os(CO)$_2$(PPh_3)$_3$ and OsCl(NO)(PPh_3)$_3$, as shown in Scheme 11, to give the octahedral stannyl complexes **35**[38] and **36**.[39] Like the silyl complexes, these

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(30) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1110.

(31) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2000**, *19*, 4344.

(32) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793.

(33) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *Organometallics* **1997**, *16*, 5499.

(34) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, *11*, 3931.

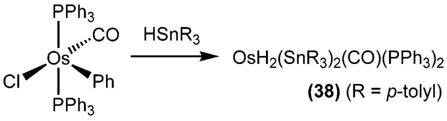
(35) (a) Collins, T. J.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1976**, 1044. (b) Roper, W. R.; Town, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781. (c) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *157*, C23.

(36) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

(37) Mackay, K. M.; Nicholson, B. K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, p 1043.

(38) Rickard, C. E. F.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *J. Organomet. Chem.* **2004**, *689*, 605.

Scheme 12



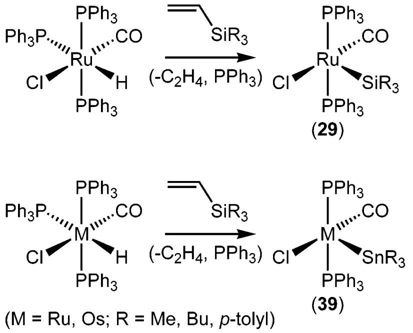
products sometimes exist as a mixture of geometrical isomers, with the isomer depicted in **35** usually predominating. It is worth noting that $OsH(SnMe_3)(CO)_2(PPh_3)_2$ exists as mixture of four isomers, each of which has been characterized by multinuclear NMR spectroscopy. However reaction between the isomeric mixture of $OsH(SnMe_3)(CO)_2(PPh_3)_2$ and SnI_4 results in replacement of two of the methyl groups on tin to form $OsH(SnMeI_2)(CO)_2(PPh_3)_2$, which remarkably exists as only one isomer, that with mutually trans triphenylphosphine ligands and mutually trans CO ligands. Further reaction with I_2 cleaves the Os−H bond to give $OsI(SnMeI_2)(CO)_2(PPh_3)_2$, which retains the same arrangement of CO and PPh_3 ligands, as revealed by an X-ray crystal structure determination. The nitrosyl complex **36** has only one detectable isomer, that with mutually cis triphenylphosphines and trans chloride and nitrosyl ligands (see Scheme 11). The reaction of **36** with CO brings about a formal reduction of the osmium and formation of the five-coordinate mono(triphenylphosphine) complex $Os[Sn(p\text{-tolyl})_3](CO)_2(NO)(PPh_3)$ (**37**). Once again, this preparative route involving oxidative addition to zerovalent complexes is not productive in leading to coordinatively unsaturated stannyl complexes and attention was therefore directed to other possible routes to the target molecule **15** in Figure 1.

VII. Five-Coordinate Ruthenium and Osmium Stannyl Complexes

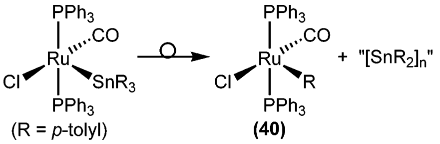
A. Synthesis. In attempting to extend the successful synthetic route for five-coordinate silyl complexes detailed in Schemes 7 and 9, a serious limitation is that suitable compounds with Sn−H bonds are restricted to stannanes of the formula R_3SnH, which have moderate stability and are readily available. Stannanes of the formula R_2SnHX are much less stable, decomposing at room temperature mainly to distannanes $R_2XSnSnXR_2$ and H_2 or the oligostannanes $(R_2Sn)_n$[40] and clearly would not withstand thermal reaction with $OsPhCl(CO)(PPh_3)_2$. Accordingly, the reaction was investigated with $HSnMe_3$.[13] Like the reaction between $HSiMe_3$ and $OsPhCl(CO)(PPh_3)_2$, which led to the osmium(IV) hydride $OsH_3(SiMe_3)(CO)(PPh_3)_2$, the reaction with $HSnMe_3$ also led to an osmium(IV) hydride. However, this was not "$OsH_3(SnMe_3)(CO)(PPh_3)_2$" but, rather, the dihydride $OsH_2(SnMe_3)_2(CO)(PPh_3)_2$ (**38**) (see Scheme 12). Complex **38** is a classical hydride of very high thermal stability, showing no tendency to undergo reductive elimination of either H_2 or $HSnMe_3$. Clearly, a quite different synthetic approach to coordinatively unsaturated stannyl complexes of the type illustrated by **15** in Figure 1 was needed.

A clue was provided by the observation of Wakatsuki et al.[41] that trimethylvinylsilane reacts with $RuHCl(CO)(PPh_3)_3$ (see Scheme 13) to give the five-coordinate trimethysilyl complex $Ru(SiMe_3)Cl(CO)(PPh_3)_2$.[21] This reaction probably proceeds via initial insertion of the vinyl double bond into the Ru−H bond and subsequent β elimination of the trimethylsilyl group with release of C_2H_4. There is precedent for reversible insertion of C_2H_4 into an $Fe-SiMe_3$ bond.[42] For this reaction strategy to be successful for the introduction of stannyl ligands to ruthenium and osmium, both vinyl insertion into M−H and subsequent β-stannyl elimination must be viable. The vinyl insertion seemed quite plausible for $RuHCl(CO)(PPh_3)_3$, but we were doubtful about this step for $OsHCl(CO)(PPh_3)_3$, in view of the strength of the Os−H bond and the relative inertness of $OsHCl(CO)(PPh_3)_3$ toward triphenylphosphine dissociation. Remarkably, as shown in Scheme 13, the reaction works well for both ruthenium and osmium to give the five-coordinate triorganostannyl derivatives **39**.[43] These compounds have the same geometry as the silyl analogues: i.e., a tetragonal pyramid with the stannyl ligand in the apical position. This was verified by a crystal structure determination of $Ru(SnMe_3)Cl(CO)(PPh_3)_2$.[43] While the ruthenium trimethylstannyl and tributylstannyl complexes have good solution stability, it is interesting that even at room temperature the ruthenium tri-*p*-tolylstannyl derivative undergoes a slow transformation to the σ-*p*-tolyl derivative **40** (see Scheme 14). This process most likely involves an α-elimination reaction with release of the stannylene fragment "SnR_2", but the nature of the organotin product was not determined. Further discussion of α-elimination reactions involving stannyl ligands will be presented in section VIIIF.

Scheme 13



Scheme 14



The five-coordinate trimethylstannyl derivative of osmium $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**41**) is a relatively unstable compound, and thermal reactions of this compound will be discussed below. However, introduction of a sixth ligand to form the coordinatively saturated derivatives $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**42**), $Os(SnMe_3)Cl(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**43**), and $Os(SnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**44**) proceeds smoothly, and these products have high stability (see Scheme 15).[44,45] The corresponding coordinatively saturated ruthenium complexes are also easily prepared.[44]

B. Functionalization of Stannyl Ligands. Having developed a successful and reasonably general route to these five- and six-coordinate triorganostannyl complexes, it remained only for us

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[39] Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1997**, *543*, 111.

[40] Davies, A. G. *Organotin Chemistry*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004.

[41] Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703.

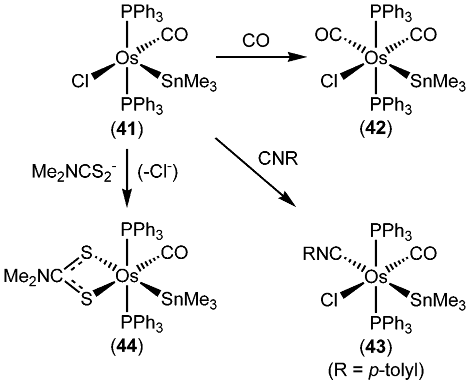
[42] Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

[43] Clark, G. R.; Flower, K. R.; Roper, W. R.; Wright, L. J. *Organometallics* **1993**, *12*, 259.

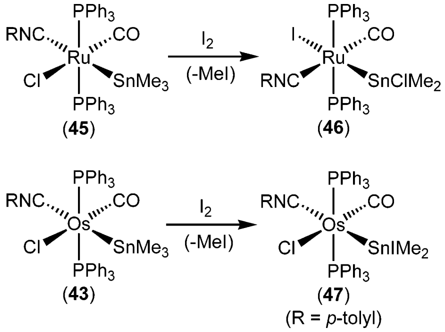
[44] Craig, P. R.; Flower, K. R.; Roper, W. R.; Wright, L. J. *Inorg. Chim. Acta* **1995**, *240*, 385.

[45] Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Woodman, T. J.; Wright, L. J. *Organometallics* **2000**, *19*, 1766.

Scheme 15



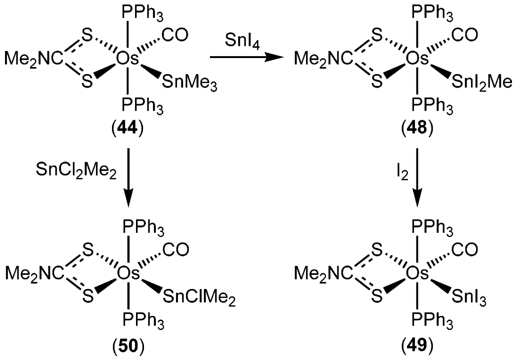
Scheme 16



to find ways to functionalize the tin center to reach the target molecules represented by **15** and **18** in Figure 1. Initial attempts were focused on selective iodine cleavage of Sn−C bonds, under mild conditions. This is successful in some cases. In Scheme 16 it can be seen that Os(SnMe$_3$)Cl(CO)(CN-*p*-tolyl)(PPh$_3$)$_2$ (**43**) is cleanly converted to Os(SnIMe$_2$)Cl(CO)(CN-*p*-tolyl)(PPh$_3$)$_2$ (**47**) through reaction with iodine and the stereochemistry at osmium is retained in this process.[46] However, not all iodine cleavages proceed in such a straightforward manner. When the ruthenium analogue of **43**, Ru(SnMe$_3$)Cl(CO)(CN-*p*-tolyl)-(PPh$_3$)$_2$ (**45**), is treated with iodine, one methyl group is cleaved from tin but the intriguing and unexpected product is Ru-(SnClMe$_2$)I(CO)(CN*p*-tolyl)(PPh$_3$)$_2$ (**46**), in which the CO and CN-*p*-tolyl ligands are now mutually trans, as are the iodide and stannyl ligands (see Scheme 16).[46] A possible rationale for this transformation is that the initial Sn−C bond cleavage produces a tin ligand with some “stannylene” character and rapid intramolecular migration of chloride from ruthenium generates the chlorodimethylstannyl ligand in the intermediate “[Ru-(SnClMe$_2$)(CO)(CN-*p*-tolyl)(PPh$_3$)$_2$]$^+$”. When iodide finally coordinates to ruthenium in this cation, it is directed to the site trans to this stannyl ligand, thus producing **46**.

Another unsatisfactory reaction with iodine is that attempted selective Sn−C bond cleavage in Os(SnMe$_3$)(κ^2-S$_2$CNMe$_2$)-(CO)(PPh$_3$)$_2$ (**41**) leads mainly to complete removal of the stannyl ligand from osmium.[45] Clearly, a more predictable and controllable process for replacing organic substituents on tin with halide substituents was required. The venerable Kocheshkov reaction is the answer.[47] This redistribution of alkyl and halogen groups on tin works extremely well for organotin compounds bearing a metal substituent, L$_n$M−SnR$_3$. It appears that the metal has an activating effect on this process, since these redistributions involving stannyl ligands occur under very mild conditions. An early recognition of this type of reaction is discussed by Kummer and Graham.[48] The efficiency of this approach is well-illustrated in Scheme 17, where it can be seen that Os(SnMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**44**, which with iodine loses the stannyl ligand) is cleanly transformed by reaction with excess SnI$_4$ into Os(SnI$_2$Me)(κ^2-S$_2$CNMe$_2$)(CO)-(PPh$_3$)$_2$ (**48**).[45] The last methyl group in **48** is cleanly removed through reaction with iodine without affecting the Os−Sn bond, to give Os(SnI$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**49**). In yet another high-yielding reaction, **44** when treated with SnCl$_2$Me$_2$ gives Os(SnClMe$_2$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**50**) (see Scheme 17).[49] The redistribution reaction is even effective between two stannyl complexes: e.g., Os(SnI$_2$Me)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ and Os-(SnMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ give Os(SnIMe$_2$)(κ^2-S$_2$-CNMe$_2$)(CO)(PPh$_3$)$_2$.[45] The halostannyl complexes **46**−**50**, prepared as described above, are all examples of the target molecule **18** (Figure 1), and all were suitable for the study of nucleophilic substitution reactions at the tin center.

Scheme 17



VIII. Special Silyl and Stannyl Ligands Derived from Ligand Reactions at Silicon and Tin, Respectively

A. Trihydroxysilyl (−Si(OH)$_3$) and Trihydroxystannyl (−Sn(OH)$_3$) Ligands. A characteristic property of both organosilicon halides[50] and organotin halides[40] is their ready hydrolysis, which is usually followed rapidly by condensation reactions to give complex oligomeric or polymeric materials. Several organosilanetriols with very bulky organo substituents have been characterized, but in the solid state even these compounds show extensive intermolecular hydrogen bonding.[51] However, organosilicon halides bearing a metal−ligand fragment as a substituent frequently show much reduced susceptibility toward hydrolysis, particularly when the metal fragment is very electron releasing toward the silicon atom.[52] This relative inertness of chlorosilyl ligands toward hydrolysis has led to the development of alternative synthetic approachs to metallasilanols, such as the reaction between dimethyldioxirane and a ligated Si−H function.[53] Nevertheless, as shown in Scheme 18,

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[46] Clark, G. R.; Flower, K. R.; Roper, W. R.; Wright, L. J. *Organometallics* **1993**, *12*, 3810.

[47] Kocheshkov, K. A. *Ber. Dtsch. Chem. Ges.* **1926**, *62*, 996.

[48] Kummer, R.; Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 1208.

[49] Lu, G.-L.; Möhlen, M. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Inorg. Chim. Acta* **2005**, *358*, 4145.

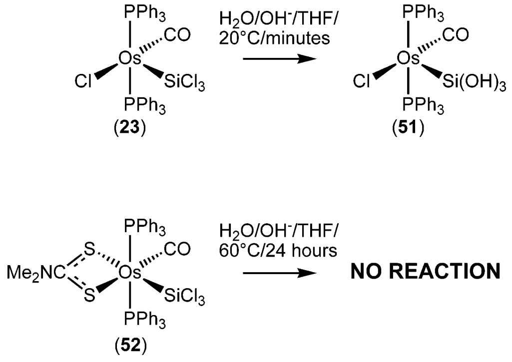
[50] Corey, J. Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 1.

[51] (a) Ishida, H.; Koenig, J. L.; Gardner, K. C. *J. Chem. Phys.* **1982**, *77*, 5748. (b) Al-Juaid, S. S.; Buttrus, N. H.; Damja, R. I.; Derouiche, Y.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1989**, *371*, 287.

[52] Malisch, W.; Schmitzer, S.; Kaupp, G.; Hindahl, K.; Käb, H.; Wachtler, U. In *Organosilicon Chemistry, From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1994; p 185.

[53] Möller, S.; Fey, O.; Malisch, W.; Seelbach, W. *J. Organomet. Chem.* **1996**, *507*, 239.

Scheme 18

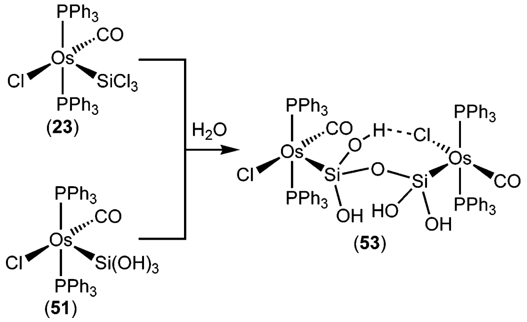


the coordinatively unsaturated trichlorosilyl complex $Os(SiCl_3)Cl(CO)(PPh_3)_2$ (**23**) is readily hydrolyzed to the corresponding trihydroxysilyl complex $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$ (**51**), which is a stable crystalline material showing no tendency to further self-condensation. Remarkably, a crystal structure of **51** reveals the absence of any intra- or intermolecular hydrogen bonding, the trihydroxysilyl ligand remaining as a completely discrete ligand.[54] The steric protection offered by the two triphenylphosphine ligands may contribute to the absence of hydrogen bonding, but other factors must also be important, since the structures of related complexes such as $Os[B(OH)_2]Cl(CO)(PPh_3)_2$, where steric factors are comparable, are dimeric with substantial hydrogen-bonding interactions.[55]

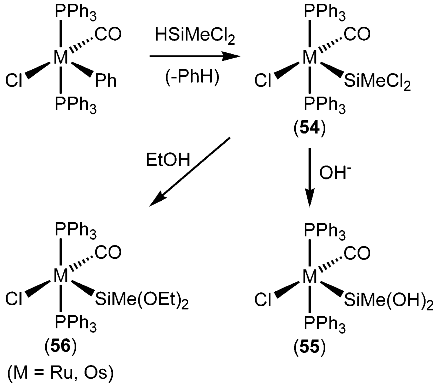
In striking contrast to the facile hydrolysis of $Os(SiCl_3)Cl(CO)(PPh_3)_2$, the coordinatively saturated trichlorosilyl complex $Os(SiCl_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**52**) is completely resistant to hydrolysis, even under very forcing conditions (see Scheme 18).[56] It is difficult to believe that the steric environment about the silicon differs significantly in these two compounds, and the dramatic difference in reactivity must be because a different mechanism of hydrolysis is available to the coordinatively unsaturated complex **23**. A plausible interpretation is that the facile hydrolysis of coordinatively unsaturated $Os(SiCl_3)Cl(CO)(PPh_3)_2$ occurs because the nucleophile, hydroxide, attacks at the osmium to form an anionic complex, $[Os(SiCl_3)Cl(OH)(CO)(PPh_3)_2]^-$, and the ensuing hydrolysis becomes intramolecular. Support for this anionic intermediate is that the closely related anion $[Os(SiCl_3)Cl_2(CO)(PPh_3)_2]^-$ has been characterized.[56] This same contrast in reactivity toward hydroxide is also shown by the two chlorodimethylsilyl complexes $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ and $Os(SiMe_2Cl)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$; the first of these two is readily hydrolyzed, but the six-coordinate complex is not.[57]

Although the simple hydrolysis of $Os(SiCl_3)Cl(CO)(PPh_3)_2$ (**23**) with excess hydroxide gives only $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$ (**51**), a condensation product is formed when $Os(SiCl_3)Cl(CO)(PPh_3)_2$ (**23**) is treated with $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$ (**51**) in the presence of water (see Scheme 19).[54] The product, complex **53**, has an unusual bridging $-Si(OH)_2OSi(OH)_2-$ ligand, and a crystal structure determination again reveals the absence of any intermolecular hydrogen bonding, but there is a weak intramolecular hydrogen bond to an osmium-bound chloride ligand, as depicted in Scheme 19.

Scheme 19



Scheme 20



Other five-coordinate chlorosilyl complexes such as $M(SiMeCl_2)Cl(CO)(PPh_3)_2$ (**54**; M = Ru, Os), as shown in Scheme 20, readily undergo similar hydrolysis reactions to the corresponding hydroxysilyl complexes $M[SiMe(OH)_2]Cl(CO)(PPh_3)_2$ (**55**; M = Ru, Os) and also related reactions with ethanol to give the ethoxysilyl complexes $M[SiMe(OEt)_2]Cl(CO)(PPh_3)_2$ (**56**; M = Ru, Os).[22] An interesting feature associated with $Os[SiMe(OEt)_2]Cl(CO)(PPh_3)_2$ is that there are structural data for this compound and for the corresponding CO adduct $Os[SiMe(OEt)_2]Cl(CO)_2(PPh_3)_2$. The Os−Si distance in the five-coordinate complex is 2.3196(11) Å, whereas with CO trans to the silyl ligand in the six-coordinate complex the Os−Si distance increases to 2.4901(8) Å. In conjunction with this lengthening of the Os−Si bond, the Os−CO distance for the carbonyl trans to the silyl ligand is 2.024(4) Å, whereas the Os−CO distance for the carbonyl trans to the chloride ligand is 1.887(3) Å. Clearly, the silyl and CO ligands, when located mutually trans, have a pronounced bond lengthening effect on each other.[22]

Further examples of nucleophilic attack at chlorosilyl ligands, involving both oxygen and nitrogen nucleophiles, are illustrated in Scheme 21. Here it can be seen that 2-hydroxypyridine, 2-aminopyridine, and acetate all give rise to mono(triphenylphosphine) complexes with tethered silyl ligands, each forming a five-membered chelate ring, in complexes **58**−**60**, respectively.[58]

While the trichlorosilyl ligand in the coordinatively saturated trichlorosilyl complex $Os(SiCl_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**52**) is spectacularly inert, as discussed above, the related coordinatively saturated triiodostannyl complex $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**49**) readily undergoes a hydrolysis reaction, at room temperature within minutes, with hydroxide ion (see Scheme 22).[45] This was the first trihydroxystannyl complex reported and, remarkably, shows no tendency to condense to more complex products. More recently a trihydroxystannyl

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[54] Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682.

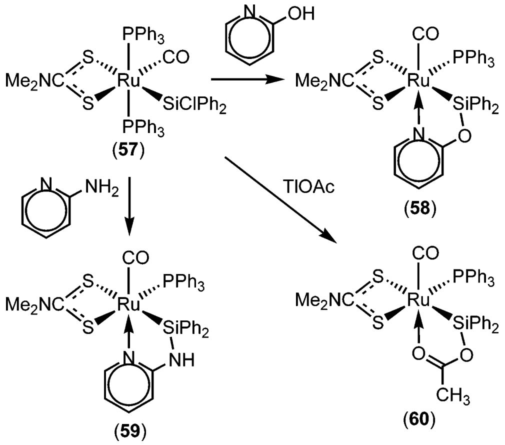
[55] Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2003**, *680*, 81.

[56] Kwok, W.-H.; Lu, G.-L.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2006**, *691*, 2593.

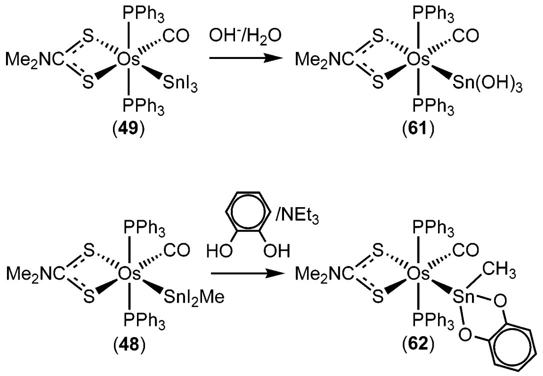
[57] Albrecht, M.; Kwok, W.-H.; Lu, G.-L.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Inorg. Chim. Acta* **2005**, *358*, 1407.

[58] Kwok, W.-H.; Lu, G.-L.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2004**, *689*, 2979.

Scheme 21



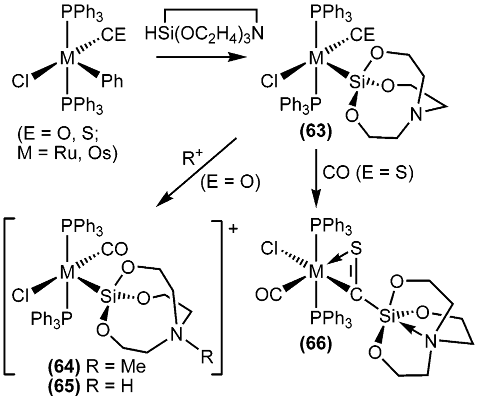
Scheme 22



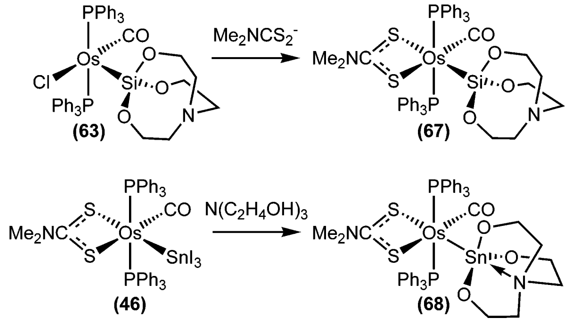
ligand has been recognized bridging a trinickel cluster.[59] Other halostannyl ligands in coordinatively saturated complexes readily undergo nucleophilic substitution reactions. For example, the SnI_2Me ligand in complex **48** reacts with catechol in the presence of base to form the elaborate stannyl ligand depicted in complex **62** (see Scheme 22). Other examples of facile nucleophilic substitution reactions, and of stannyl complexes that retain electrophilicity at the tin, where the silicon analogues do not, will be discussed in detail in subsequent sections.

B. Silatranyl and Stannatranyl Complexes. Silatranes, cyclic organosilicon ethers of tris(2-oxyalkylamine), are a special class of hypervalent silicon compounds with a cage structure characterized by a variable transannular N−Si bonding interaction. It is straightforward to incorporate a silatranyl ligand into an osmium complex utilizing the synthetic approach given in Scheme 7: i.e., reaction between $OsPhCl(CO)(PPh_3)_2$ and the silatrane $HSi(OC_2H_4)_3N$ (see Scheme 23).[24] The coordinatively unsaturated silatranyl complex **63** can be made with either carbonyl or thiocarbonyl as accompanying ligand. The structure of the complex bearing the carbonyl ligand reveals that the silatrane cage is opened to the extent that the distance between the nitrogen atom and the silicon atom is 3.000(7) Å, while the Os−Si distance remains essentially the same as the value for $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$. The silicon−nitrogen separation in silatranes is generally in the range 2.00−2.26 Å. The observed elongation in **63** results in the geometry about the nitrogen atom becoming planar. A consequence of this is that the nitrogen atom can be quaternized by reaction either with MeI or with triflic acid, reactions previously unobserved for silatranes. An even greater elongation of the silicon−nitrogen interatomic distance (3.242(3) Å) is observed in the osmium(IV) silatranyl complex $Os[Si(OC_2H_4)_3N]H_3(PPh_3)_3$ (see section IIIB), and this complex has also been protonated and methylated at nitrogen.[15]

Scheme 23



Scheme 24



A graphic illustration of the unique influence the metal has on the shape of the silatrane cage is that when the thiocarbonyl analogue of **63** is treated with CO, a migratory insertion reaction occurs to form the η^2-thioacyl complex **66** (replacing the Si−Os bond with a Si−C bond), and in this complex the characteristic architecture of the silatrane is reestablished with a Si−N distance of 2.086(6) Å (see Scheme 23).

The established reactivity of $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**46**) toward hydrolysis suggested that a direct route to the unknown stannatranyl complexes could be the reaction between **46** and triethanolamine. This approach works beautifully, as shown in Scheme 24, to give $Os[Sn(OC_2H_4)_3N](\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**68**).[60] Indeed, the reaction is also successful with nitrilotriacetic acid to give the first example of a metal-substituted stannatranone, $Os[Sn(OC\{O\}CH_2)_3N](\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$.[45] For a direct structural comparison of silatranyl and stannatranyl ligands in the same coordination environment, the silicon analogue of **68** was prepared by treating **63** with dimethyldithiocarbamate to produce the silatranyl complex $Os[Si(OC_2H_4)_3N](\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**67**) (see Scheme 24).

There is a telling contrast between the structures of the two cage ligands. Whereas the silatranyl ligand in **67** shows the expanded cage structure observed for the other silatranyl complexes (a silicon−nitrogen separation of 3.176(6) Å), the stannatranyl ligand in **68** has a Sn−N bond distance of 2.422(4) Å,[60] which is quite comparable to the distance found in non-metal-substituted stannatranes such as $MeSn(OC_2H_4)_3N$ (2.28(1) Å).[61] Clearly, attachment of the stannyl ligand to osmium does

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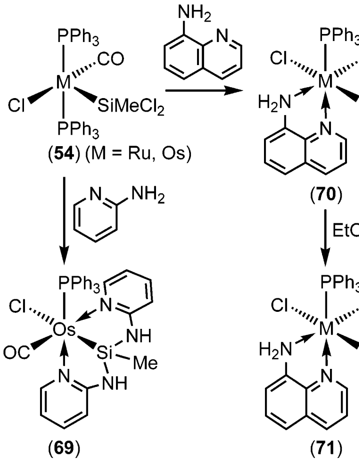
[59] Simón-Manso, E.; Kubiak, C. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 1125.

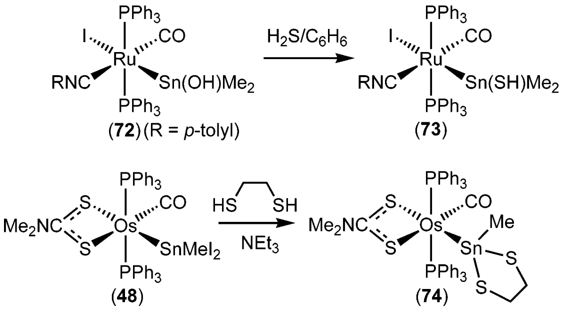
[60] Rickard, C. E. F.; Roper, W. R.; Woodman, T. J.; Wright, L. J. *Chem. Commun.* **1999**, 837.

[61] Swisher, R. G.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3692.

Scheme 25



Scheme 26

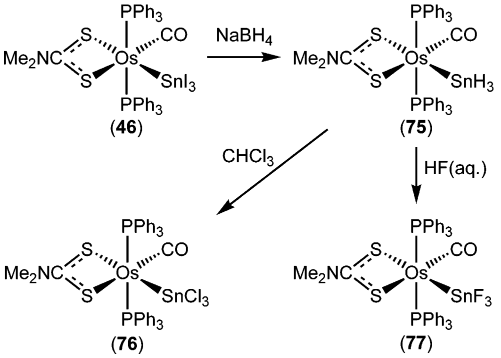


not significantly reduce the electrophilicity of the tin atom. This is very different from the situation with the corresponding silyl ligands and must be related to the greater ability of the tin atom to attain higher coordination numbers.

C. Unusual Silyl and Stannyl Ligands from Reactions with Nitrogen and Sulfur Nucleophiles. In Scheme 21 it has been shown that a monochlorosilyl ligand reacts with a nitrogen nucleophile in the form of 2-aminopyridine to form complex **59**, which has a tethered silyl ligand containing a Si−N bond. An extension of this reaction is depicted in Scheme 25, where the dichlorosilyl complex $Os(SiMeCl_2)Cl(CO)(PPh_3)_2$ (**54**) reacts with 2-aminopyridine to form complex **69**, which contains a novel tridentate κ^3N,N,Si-silyl ligand.[22] Complexes **59** and **69** both contain five-membered chelate rings associated with the tethering arms. When the coordinatively unsaturated complexes $M(SiMeCl_2)Cl(CO)(PPh_3)_2$ (**54**; M = Ru, Os) are treated with 8-aminoquinoline, the reaction follows a different course. The unusual products $M(SiMeCl_2)Cl(CO)(PPh_3)(\kappa^2N,N\text{-}NC_9H_6NH_2\text{-}8)$ (**70**; M = Ru, Os) have the 8-aminoquinoline bound as simple chelate ligands that utilize both the quinoline nitrogen and the NH_2 nitrogen as donor atoms with displacement of a triphenylphosphine ligand (see Scheme 25). Remarkably, a crystal structure determination reveals that the NH_2 function is coordinated adjacent to the unchanged $SiMeCl_2$ ligand. A condensation reaction between NH_2 and $SiMeCl_2$ would result in formation of a six-membered ring. This less favorable chelate ring size must be a factor contributing to the lack of reactivity of the adjacent NH_2 and $SiMeCl_2$ functions. The Si−Cl bonds do, however, show reactivity toward ethanol, and at room temperature in contact with ethanol complex **70** is rapidly converted to complex **71** (see Scheme 25).

In unusual reactions, depicted in Scheme 26, it is possible to use ligand reactions at a metal-bound stannyl ligand to form new stannyl ligands containing Sn−S bonds. The ruthenastannol $Ru[Sn(OH)Me_2]I(CO)(CNR)(PPh_3)_2$ (**72**), which is derived from $Ru(SnClMe_2)I(CO)(CNR)(PPh_3)_2$ (**46**; see Scheme 16) through reaction with aqueous KOH, when treated with H_2S forms the unprecedented thiohydroxystannyl complex $Ru[Sn(SH)Me_2]I(CO)(CNR)(PPh_3)_2$ (**73**).[46] This compound is quite stable and once again shows a reluctance to undergo a self-condensation reaction or disproportionation. Other molecules containing the Sn−S−H moiety are usually unstable and disproportionate to the ditin sulfides and H_2S,[40] unless very bulky substituents such as *tert*-butyl are present on the tin atom, as in $(Bu^t)_3SnSH$.[62]

Scheme 27



In a more straightforward reaction the methyldiiodostannyl complex $Os(SnMeI_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**48**) reacts with ethanedithiol in the presence of the base triethylamine to give the sulfur-substituted stannyl complex **74** (see Scheme 26).[45]

D. SnH_3 and Related Ligands from Reactions with Hydride Nucleophiles. It is well-established that complexes with halostannyl ligands such as $Cp(CO)_2FeSnR_2I$ can undergo nucleophilic substitution at tin with hydridic reagents such as $K[BHEt_3]$ to give a corresponding stannyl complex containing a Sn−H bond, $Cp(CO)_2FeSnR_2H$ ($R = CH(SiMe_3)_2$).[63] The demonstrated ease with which all three iodides can be displaced from $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**49**; see section VIIIA) suggested that this complex could be used in the synthesis of the SnH_3 complex $Os(SnH_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**75**). Stable examples of SnH_3 complexes were previously unknown. The reaction as drawn in Scheme 27, using $NaBH_4$, proceeds in high yield, and complex **75** has been isolated as a stable crystalline solid. Complex **75** was characterized by multinuclear NMR spectroscopy and by an X-ray crystal structure determination, which located the hydrogen atoms.[64] In the IR spectrum of **75** bands at 1763, 1750, and 1735 cm^{-1} are attributed to $\nu(SnH)$. These values are lower than in the simple organostannane $Si(CH_2CH_2SnH_3)_4$, where $\nu(SnH)$ is found at 1852 cm^{-1}.[65] A similar observation has been made for another transition-metal-substituted stannane, $Cp_2Hf(SnHMes_2)Cl$, where $\nu(SnH)$ is 1728 cm^{-1}, whereas the value for Mes_2SnH_2 is 1864 cm^{-1}.[66] In the ^1H NMR the SnH_3 protons are seen as a triplet at 2.86 ppm through coupling to two equivalent phosphorus atoms ($^3J_{PH}$ = 3.2 Hz) with Sn satellites ($^1J_{^{119}SnH} = 1348$, $^1J_{^{117}SnH} = 1288$ Hz). These one-bond Sn−H coupling constants are conspicuously lower than those observed in simple organostannanes,

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(62) Hänssgen, D.; Reuter, P.; Döllein, G. *J. Organomet. Chem.* **1986**, *317*, 159.

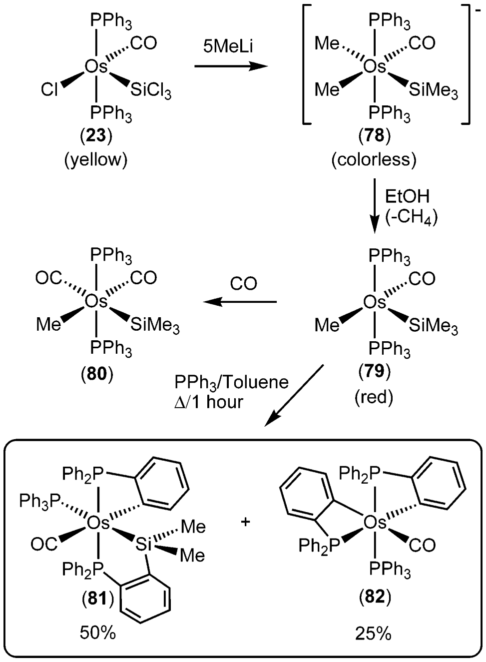
(63) Lappert, M. F.; McGeary, M. J.; Parish, R. V. *J. Organomet. Chem.* **1989**, *373*, 107.

(64) Möhlen, M. M.; Rickard, C. E. F.; Roper, W. R.; Whittell, G. R.; Wright, L. J., *Inorg. Chim. Acta*, in press.

(65) Schumann, H.; Wassermann, B. C.; Frackowiak, M.; Omotowa, B.; Schutte, S.; Velder, J.; Mühle, S. H.; Krause, W. *J. Organomet. Chem.* **2000**, *609*, 189.

(66) Neale, N. R.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *124*, 3802.

Scheme 28



R_nSnH_{4-n} ($n = 1-3$), which are typically 1900−1600 Hz.[65,67] Even lower values, 961 and 918 Hz, have been recorded for $Cp_2Hf(SnHMes_2)Cl$.[66] These reduced values have been attributed to the presence of the transition metal as a substituent on tin of very low effective electronegativity.[68] The Sn−H distances in **75** are Sn−H(1) = 1.79(5) Å, Sn−H(2) = 1.68(5) Å, and Sn−H(3) = 1.81(5) Å. The average of these values (1.76 Å) is long compared with the average for the Sn−H bonds in $Si(CH_2CH_2SnH_3)_4$, which is 1.60(7) Å [10].[65] This bond lengthening is consistent with the reduced ν(SnH) and J_{SnH} values in **75**.

As expected, the Sn−H bonds are quite reactive, and dissolution in chloroform converts **75** to the corresponding trichlorostannyl complex $Os(SnCl_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**76**), while reaction with HF gives the corresponding trifluorostannyl complex $Os(SnF_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**77**) (see Scheme 27). The Os−Sn distances in **76** and **77** are almost identical at 2.5969(5) and 2.5934(3) Å, respectively, and these are the shortest Os−Sn distances recorded in the Cambridge Crystallographic Data Base for six-coordinate osmium and four-coordinate tin. In closely related reactions with complexes containing appropriate mixed methyl/halostannyl ligands, $Os(SnH_2Me)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $Os(SnHMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ have also been isolated.[64]

E. Coordinatively Unsaturated $Os(SiMe_3)Me(CO)(PPh_3)_2$ from Reaction of $Os(SiCl_3)Cl(CO)(PPh_3)_2$ with MeLi and the Thermal Reactions of this Complex. At an earlier point in this review, section IVC, the complex $Os[Si(OEt)_3]Ph(CO)(PPh_3)_2$ (**26**) was described as the product of reaction between $Os[Si(OEt)_3]Cl(CO)(PPh_3)_2$ (**25**) and PhLi (see Scheme 8). Complex **26** proved to be remarkably resistant to reductive elimination of $PhSi(OEt)_3$, and to explore whether an analogous complex with the simpler trimethylsilyl ligand might behave differently, the complex $Os(SiMe_3)Me(CO)(PPh_3)_2$ (**79**) was prepared. As shown in Scheme 28, treatment of $Os(SiCl_3)Cl(CO)(PPh_3)_2$ (**23**) with an excess of methyllithium in an ether/toluene mixture led to the precipitation of the colorless lithium salt of the complex anion $[Os(SiMe_3)Me_2(CO)(PPh_3)_2]^-$ (**78**). When this salt is in contact with ethanol, methane is liberated and the red complex $Os(SiMe_3)Me(CO)(PPh_3)_2$ (**79**) is formed.[69] Addition of CO to complex **79** gives the more stable, saturated complex $Os(SiMe_3)Me(CO)_2(PPh_3)_2$ (**80**).

Before describing the thermal reactions of the trimethylsilyl methyl complex $Os(SiMe_3)(Me)(CO)(PPh_3)_2$ (**79**), it is relevant to consider the thermal reaction of the trimethylsilyl chloride complex $Os(SiMe_3)Cl(CO)(PPh_3)_2$. This latter compound is very stable, and it is only after heating in molten triphenylphosphine at 160 °C for 2 h that decomposition occurs, the major products being the ortho-metalated complex $Os(\kappa^2C,P\text{-}C_6H_4PPh_2)Cl(CO)(PPh_3)_2$[70] and $OsHCl(CO)(PPh_3)_3$, both products involving loss of the silyl ligand. In marked contrast to the stability of $Os(SiMe_3)Cl(CO)(PPh_3)_2$, the corresponding trimethylsilyl methyl complex $Os(SiMe_3)(Me)(CO)(PPh_3)_2$ (**79**) shows solution instability and, as depicted in Scheme 28, readily undergoes a thermal reaction (toluene reflux, 1 h) in the presence of triphenylphosphine, to give as the major product the ortho-silylated as well as ortho-metalated complex $Os(\kappa^2Si,P\text{-}SiMe_2C_6H_4PPh_2)(\kappa^2C,P\text{-}C_6H_4PPh_2)(CO)(PPh_3)$ (**81**). This unusual product, which retains the Os−Si bond, has also been observed from the thermal reaction of $OsHCl(CO)(PPh_3)_3$ and $Hg(SiMe_3)_2$.[21] The same ortho-silylated ligand, $\kappa^2Si,P\text{-}SiMe_2C_6H_4PPh_2$, has been described by others in the thermal reaction of a base-stabilized silylene triphenylphosphine complex of ruthenium(II).[71] This suggests the possibility that a dimethylsilylene intermediate is involved in the formation of complex **81**. Such an intermediate could arise from a migration of a methyl group from the trimethylsilyl ligand to osmium. There is precedent for this sort of process on osmium, in that a methyl group has been observed to migrate to osmium from a bound trimethylstannyl ligand (see section VIIIF below). However, the details of the mechanism are unknown and the reaction must be of some complexity, since an ortho-metalated triphenylphosphine ligand is also formed. An interesting aside is that when complex **81** reacts with tris(pyrrolyl)phosphine the product is $Os(\kappa^2Si,P\text{-}SiMe_2C_6H_4PPh_2)(\kappa^2C,P\text{-}C_6H_4PPh_2)(CO)[P(NC_4H_4)_3]$, where only the triphenylphosphine trans to silicon is replaced. The effect of introducing the very good π-accepting ligand tris(pyrrolyl)phosphine is to lengthen the Os−Si distance from 2.4716(13) Å in **81** to 2.5110(8) Å in $Os(\kappa^2Si,P\text{-}SiMe_2C_6H_4PPh_2)(\kappa^2C,P\text{-}C_6H_4PPh_2)(CO)[P(NC_4H_4)_3]$. This is the longest recorded Os−Si distance for an octahedral osmium silyl complex.[69]

A minor product from the thermal reaction of $Os(SiMe_3)(Me)(CO)(PPh_3)_2$ (**79**) in the presence of triphenylphosphine involves loss of the trimethylsilyl ligand and the methyl ligand, giving eventually $Os(\kappa^2C,P\text{-}C_6H_4PPh_2)_2(CO)(PPh_3)$ (**82**), which contains two ortho-metalated triphenylphosphine ligands (see Scheme 28).

F. α-Methyl Migration Reactions in Trimethystannyl Complexes and Thermal Reactions of the Coordinatively Unsaturated Trimethystannyl Complex $Os(SnMe_3)Cl(CO)(PPh_3)_2$. In section VIIA the facile transformation of the coordinatively unsaturated complex $Ru[Sn(p\text{-tolyl})_3]Cl(CO)(PPh_3)_2$ to $Ru(p\text{-tolyl})Cl(CO)(PPh_3)_2$ was described. This must involve as an initial step an α-*p*-tolyl migration reaction, and in this section we describe several other examples of this same process involving stannyl complexes of osmium. It can be noted that the zirconium and hafnium triphenylstannyl complexes

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[67] Maddox, M. L.; Flitcroft, N.; Kaesz, H. D. *J. Organomet. Chem.* **1965**, *4*, 50.

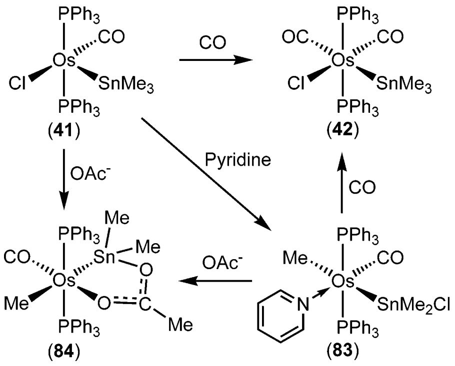
[68] Aylett, B. J. *J. Organomet. Chem., Libr.* **1980**, *9*, 327.

[69] Clark, G. R.; Lu, G.-L.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2005**, *690*, 3309.

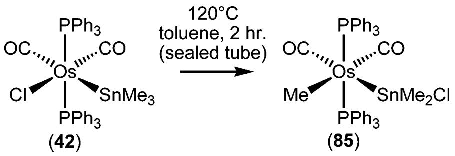
[70] Bennett, M. A.; Clark, A. M.; Contel, M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2000**, *601*, 299.

[71] Wada, H.; Tobita, H.; Ogino, H. *Organometallics* **1997**, *16*, 3870.

Scheme 29



Scheme 30



$CpCp^*M(SnPh_3)Cl$ (M = Zr, Hf) can be induced to form $CpCp^*M(Ph)Cl$[72,73] in reactions similar to that undergone by $Ru[Sn(p\text{-tolyl})_3]Cl(CO)(PPh_3)_2$, but under much more vigorous conditions.

It is shown in Scheme 29 that the five-coordinate trimethylstannyl complex $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**41**) undergoes the expected reaction with CO to form the six-coordinate complex $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**42**). However, quite unexpectedly the reaction of **41** with pyridine at room temperature leads to the rearranged pyridine adduct $Os(SnMe_2Cl)(Me)(CO)(pyridine)(PPh_3)_2$ (**83**), where a methyl group has migrated to osmium and a chloride has migrated from osmium to tin. Even more unexpectedly, when **83** is treated with CO at room temperature, these migrations are reversed and the trimethylstannyl complex $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**42**) is formed in good yield.[74] Methyl migration to osmium is also promoted by the addition of acetate to $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**41**) to form **84**, where acetate bridges the Os−Sn bond (see Scheme 29). The same product is also formed when **83** is treated with acetate. Both **83** and **84** have been structurally characterized.[74]

The coordinatively saturated complex $Os(SnMe_3)Cl(CO)_2(PPh_3)_2$ (**42**) is much more stable than **41**, but under forcing conditions it too undergoes a methyl migration from tin to osmium to form the dimethylchlorostannyl complex $Os(SnMe_2Cl)(Me)(CO)_2(PPh_3)_2$ (**85**), as depicted in Scheme 30.

These observations can be rationalized if the coordinatively unsaturated trimethylstannyl complex **41** is in equilibrium with the transient stannylene species **A** and **C**, depicted in Figure 3. Further support for the intermediacy of stannylene complexes is provided by the thermal reactions of $Os(SnMe_3)Cl(CO)(PPh_3)_2$ (**41**) shown in Scheme 31.

Heating complex **41** in solution, in the presence of triphenylphosphine, induces an ortho stannylation of one phenyl group of a triphenylphosphine ligand and an ortho metalation of another triphenylphosphine ligand, to produce the metallacyclic complexes $Os(\kappa^2Sn,P\text{-}SnMeClC_6H_4PPh_2)(\kappa^2C,P\text{-}C_6H_4PPh_2)(CO)(PPh_3)$ (**86**) and $Os(\kappa^2Sn,P\text{-}SnMe_2C_6H_4PPh_2)(\kappa^2C,P\text{-}C_6H_4PPh_2)(CO)(PPh_3)$ (**87**).[75] The formation of **86** can be understood by invoking the intermediacy of the transient stannylene complex **C** in Figure 3. Complex **87** is converted to complex **86** by a redistribution reaction with $SnMe_2Cl_2$. These complexes are analogues of the silicon-containing complex **81** in Scheme 28. In the formation of these compounds there are parallels with electrophilic carbene and silylene ligands attacking the ortho position of a phenyl ring in a PPh_3 ligand.[71,76]

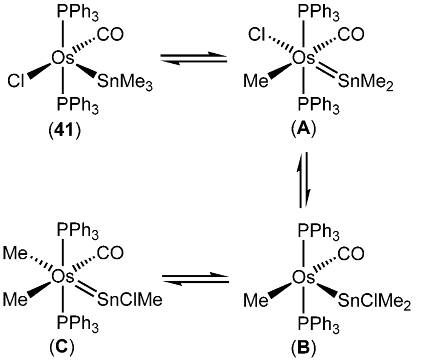
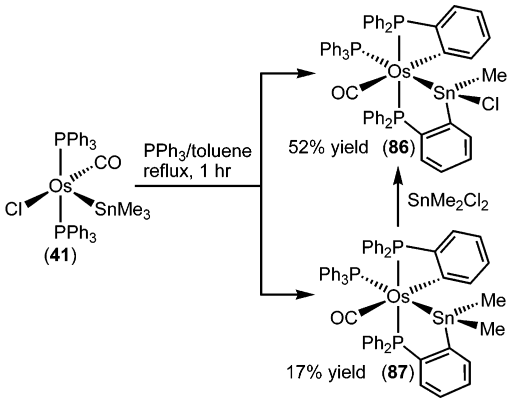


Figure 3.

Scheme 31



G. The Very Different Reactions of an Osmasilanol ($L_nOs{-}SiMe_2OH$) and an Osmastannol ($L_nOs{-}SnMe_2OH$) with Strong Base. Metallasilanols ($L_nM{-}SiR_2OH$)[52] are likely to be valuable synthetic intermediates, as are the nonmetalated analogues. Although these compounds are now well-established, the chemical reactivity associated with M−Si−OH linkages has been mostly unexplored. Significant reports include the conversion of metallasilanols to both dimetalladisiloxanes (through condensation)[54] and to metalladisiloxanes.[52] In one instance, the conversion of a metallasilanol to an isolated lithium metallasilanolate ($L_nM{-}SiR_2OLi$) has been reported, and this was shown to be a dimer in the solid state.[77]

The five- and six-coordinate (dimethylchlorosilyl)osmium(II) complexes $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ and $Os(SiMe_2Cl)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ provide the opportunity to access, through hydrolysis, the corresponding silanol complexes. The accompanying set of ligands in these compounds constitute rather inert groupings that allow focus on reactions at the Si centers. As shown in Scheme 32, the osmasilanol $Os(SiMe_2OH)Cl(CO)(PPh_3)_2$ (**88**), which is readily obtained by hydrolysis of $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$, is conveniently deprotonated by ^tBuLi to give the solid lithium silanolate complex $Os(SiMe_2$-

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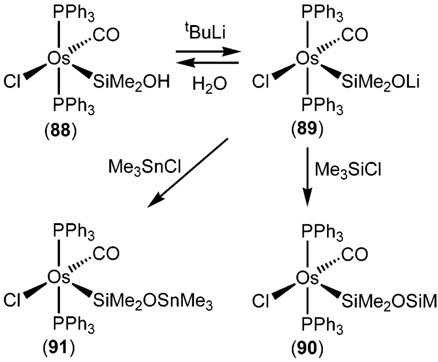
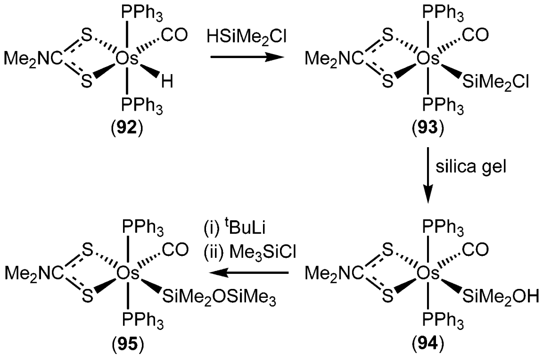
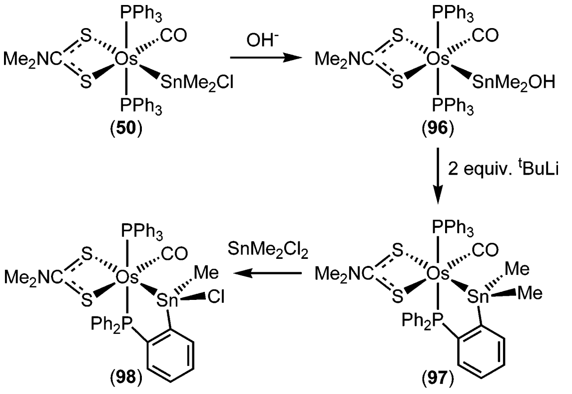
Scheme 32



Scheme 33



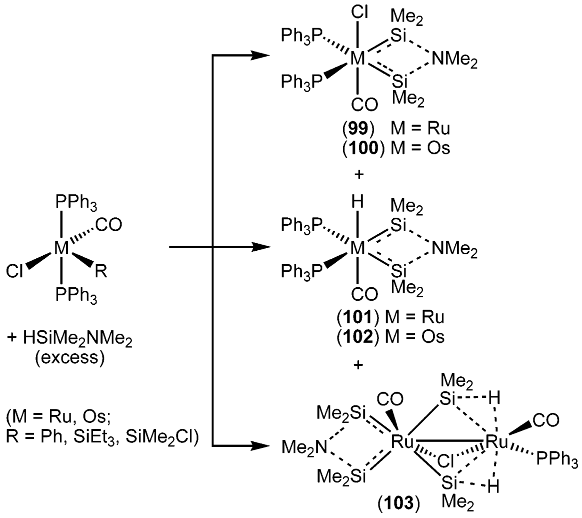
Scheme 34



OLi)Cl(CO)(PPh$_3$)$_2$ (**89**).[57] Complex **89** reacts with either Me$_3$SiCl or Me$_3$SnCl to give the corresponding osmadisiloxane Os(SiMe$_2$OSiMe$_3$)Cl(CO)(PPh$_3$)$_2$ (**90**) or osmastannasiloxane Os(SiMe$_2$OSnMe$_3$)Cl(CO)(PPh$_3$)$_2$ (**91**), respectively. As already mentioned in section VIIIA, the hydrolysis of the coordinatively saturated Os(SiMe$_2$Cl)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**93**) (see Scheme 33) is not effected by KOH but can be achieved by chromatography on silica gel. The resulting osmasilanol Os(SiMe$_2$OH)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**94**) is also deprotonated with ^{t}BuLi, and subsequent treatment with Me$_3$SiCl gives the expected osmadisiloxane Os(SiMe$_2$OSiMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**95**).[57]

The chemistry described above for the osmasilanols **88** and **94** is predictable and expected. However, the behavior of the corresponding osmastannol Os(SnMe$_2$OH)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**96**), prepared by the ready hydrolysis of Os(SnMe$_2$Cl)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**50**; see Scheme 34), is completely unexpected. Treatment of the osmastannol **96** with ^{t}BuLi does not produce an isolable osmastannolate but rather gives the structurally characterized cyclic complex Os(κ^2*Sn,P*-SnMe$_2$C$_6$H$_4$PPh$_2$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$) (**97**), in which the Sn−O bond has been ruptured and one of the phenyl rings of a triphenylphosphine ligand is "ortho-stannylated".[49] The yield of **97** is maximized (79%) when 2 equiv of ^{t}BuLi is used. Use of only 1 equiv of ^{t}BuLi leaves unreacted starting material and complex **97** is formed in reduced yield. No information is available on the mechanism of this reaction, but the observed product is compatible with the intermediacy of an electrophilic stannylene complex.

Scheme 35



The novel cyclic complex **97** is selectively functionalized at the tin atom by reaction with SnMe$_2$Cl$_2$, which exchanges one methyl group for chloride, giving Os(κ^2*Sn,P*-SnMeClC$_6$H$_4$PPh$_2$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$) (**98**) as a mixture of diastereomers. Complex **98** undergoes facile nucleophilic substitution reactions at the Sn−Cl bond, and reaction with hydroxide ion gives the osmastannol complex Os(κ^2*Sn,P*-SnMeOHC$_6$H$_4$PPh$_2$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$), while reaction with sodium borohydride gives the corresponding tin hydride complex Os(κ^2*Sn,P*-SnMeHC$_6$H$_4$PPh$_2$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$), as expected.[49]

H. The Special Case of a (Dimethylamino)dimethylsilyl Ligand Leading to Dimethylamino-Bridged Bis(silylene) Complexes. Despite the versatility of the preparative procedure shown in Scheme 7 for the synthesis of variously substituted silyl complexes of ruthenium and osmium, when the procedure was applied to the use of (dimethylamino)dimethylsilane, HSiMe$_2$NMe$_2$, the ensuing reaction followed a completely different course. As shown in Scheme 35, treatment of MRCl(CO)(PPh$_3$)$_2$ with an excess of HSiMe$_2$NMe$_2$ produces three compounds for M = Ru: the dimethylamino-bridged bis(dimethylsilylene) complexes **99** and **101**, together with the unusual diruthenium complex **103** (formed in low yield). For M = Os, only two compounds are formed: the dimethylamino-bridged bis(dimethylsilylene) complexes **100** and **102**.[78] The reaction proceeds for R = Ph, SiEt$_3$, SiMe$_2$Cl. However, yields were best for R = SiMe$_2$Cl, and since M(SiMe$_2$Cl)Cl(CO)(PPh$_3$)$_2$ (M = Ru, Os) can both be prepared directly in high yield from MHCl(CO)(PPh$_3$)$_3$ and HSiMe$_2$Cl, M(SiMe$_2$Cl)Cl(CO)(PPh$_3$)$_2$ were the starting materials of choice. It is likely that the first step in the reaction is an exchange of silyl ligand (see section IVC) to give M[SiMe$_2$(NMe$_2$)]Cl(CO)(PPh$_3$)$_2$, but

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(78) Choo, T. N.; Kwok, W.-H.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2002**, *645*, 235.

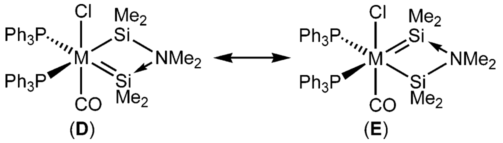


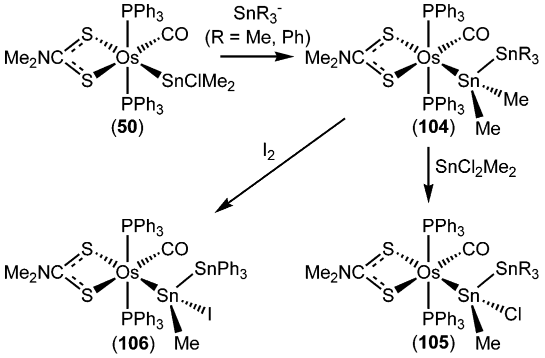
Figure 4.

the subsequent steps can only be speculated upon. Nevertheless, the dimethylamino-bridged bis(dimethylsilylene) complexes are formed in reasonable yield and preference for either the chloride products **99** and **100** or the hydride products **101** and **102** can be controlled by varying the experimental conditions. Structural data reveal that the RuSiNSi and OsSiNSi rings of the bis(silylene) ligand system are folded at the Si atoms and the Ru−Si and Os−Si distances are short, while Si−N distances are long. These structural data suggest some multiple-bond character in the metal−silicon bonds, and this is further supported by the downfield chemical shifts observed in the ^{29}Si NMR spectra of these compounds. Overall, the bonding in these compounds can be represented by the valence bond structures **D** and **E**, shown in Figure 4. Closely related bis(dimethylsilylene) complexes bridged with a methoxy function have been derived through rearrangement of intermediate disilanyl complexes of the type $L_nM{-}SiMe_2SiMe_2OMe$.[79]

The diruthenium complex **103** has a short Ru−Ru bond (2.7557(2) Å) that is bridged by chloride and two dimethylsilylene ligands. One ruthenium retains the dimethylamino-bridged bis(dimethylsilylene) ligand system and a CO, while the other has CO, PPh$_3$, and two hydride ligands. Structural evidence indicates that each of the bridging dimethylsilylene ligands is involved in a three-center bonding situation (RuSiH), as depicted in Scheme 35.

I. Osmium Complexes with Distannyl Ligands ($L_nOsSnMe_2$-SnR_3) from Reaction between $L_nOs(SnMe_2Cl)$ and SnR_3^-. Disilanyl complexes of the type $L_nM{-}SiR_2SiR_3$ are reasonably easily accessible from appropriately substituted disilanes by introducing the metal either as an anion or through an elimination reaction.[80] On the other hand, distannyl complexes of the type L_nM-$SnR_2{-}SnR_3$ are quite rare, with the best previously characterized example being CpCp*ClHf(SnPh$_2$SnHMes$_2$) (which was spectroscopically but not structurally characterized) from the complicated and unexpected reaction of CpCp*ClHf(SnHMes$_2$) with Ph$_2$SnH$_2$.[81] In view of the demonstrated reactivity of Sn−Cl bonds in chlorostannyl ligands bound to ruthenium and osmium (see section VIIIA−D,F,G) it seemed likely that reaction between LiSnR$_3$ and a halostannyl complex, $L_nM{-}SnR_2X$, could offer a general and direct route to the distannyl complexes $L_nM{-}SnR_2SnR_3$. Accordingly, the reactions shown in Scheme 36 were studied.[82] These reactions proceed cleanly in good yield to give the stable crystalline distannyl complexes Os(SnMe$_2$SnMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**104**; R = Me) and Os(SnMe$_2$SnPh$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**104**; R = Ph). The reaction is equally effective with Os(SnMe$_2$Cl)Cl(CO)$_2$(PPh$_3$)$_2$ as substrate, the reaction with KSnPh$_3$ giving the distannyl complex Os(SnMe$_2$SnPh$_3$)Cl(CO)$_2$(PPh$_3$)$_2$. The X-ray crystal structures of Os(SnMe$_2$SnPh$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ (**104**; R = Ph) and Os(SnMe$_2$SnPh$_3$)Cl(CO)$_2$(PPh$_3$)$_2$ have been determined. The Os−Sn distances are unremarkable, and the Sn(1)−Sn(2) distance in **104** is 2.8236(6) Å, while the corresponding distance in Os(SnMe$_2$SnPh$_3$)Cl(CO)$_2$(PPh$_3$)$_2$ is 2.8367(2) Å. These distances lie between those found in simple organopolystannanes, e.g., Ph$_6$Sn$_2$ (2.770(4) Å),[83] and the distance found in Br$_2$Sn$_2$[Mn(CO)$_5$]$_4$ (2.885(1) Å).[84]

Scheme 36



The complexes give beautifully resolved ^{119}Sn NMR spectra which allow direct measurement of both ^{119}Sn−^{119}Sn and ^{119}Sn−^{117}Sn one-bond Sn−Sn coupling constants. As an example, we discuss in detail the ^{119}Sn NMR spectrum of Os(SnMe$_2$SnMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$. In this compound both the α-Sn and β-Sn resonances, at −283.3 and −170.8 ppm, respectively, are observed as triplets through coupling to phosphorus. The two-bond coupling of the α-Sn is 88 Hz, and the three-bond coupling of the β-Sn is 9 Hz. Each of these triplets shows two sets of satellites arising through one-bond Sn−Sn coupling to the adjacent tin atom, when present as either the ^{117}Sn isotope or the ^{119}Sn isotope. The satellite signals are not symmetrically distributed about the central triplet signal, because the chemical shift of the ^{119}Sn resonance changes according to whether the adjacent isotope is ^{117}Sn or ^{119}Sn. The assignments of the appropriate pairs of satellite triplets, for determination of the coupling constants, are based upon the requirement that the ratio $J_{^{119}\mathrm{Sn}^{119}\mathrm{Sn}}/J_{^{119}\mathrm{Sn}^{117}\mathrm{Sn}}$ is the same as magnetogyric ratio for ^{119}Sn/^{117}Sn: that is, 1.0462.[40] The coupling constants so measured for the α-Sn in Os(SnMe$_2$SnMe$_3$)(κ^2-S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$ are $^1J_{^{117}\mathrm{Sn}^{119}\mathrm{Sn}} = 2333$ and $^1J_{^{119}\mathrm{Sn}^{119}\mathrm{Sn}} = 2442$ Hz and for the β-Sn are $^1J_{^{117}\mathrm{Sn}^{119}\mathrm{Sn}} = 2332$ and $^1J_{^{119}\mathrm{Sn}^{119}\mathrm{Sn}} = 2441$ Hz. These coupling constants are far less than that reported for Me$_3$SnSnMe$_3$ ($^1J_{^{119}\mathrm{Sn}^{119}\mathrm{Sn}} = 4404$ Hz).[40] Two other transition-metal distannyl complexes where the one-bond Sn−Sn coupling constants have been measured are CpCp*ClHfSnPh$_2$SnHMes$_2$, for which $^1J_{^{117/119}\mathrm{Sn}^{119}\mathrm{Sn}}$ is 185 Hz,[81] and Cp[P(OPh)$_3$]$_2$FeSn(SnMe$_3$)$_3$,[85] for which a value near zero was measured by a heteronuclear double-resonance experiment. It is clear that the presence of a transition metal and associated ligands as a substituent on a ditin fragment has the effect of reducing the one-bond Sn−Sn coupling constant.

An interesting feature of the reactivity of the osmium distannyl complexes is that it is possible to carry out selective functionalization at the osmium-bound tin atom (the α-Sn) while maintaining the integrity of the Sn−Sn bond (see Scheme 36). This can be achieved through a redistribution reaction either with SnMe$_2$Cl$_2$ or even with molecular iodine.[82] It should be

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noted that iodine cleaves a methyl group from the α-Sn more rapidly than it cleaves either the Sn−Sn bond or the Sn−phenyl bonds on the *β*-Sn. The activating effect of the L_nOs substituent on redistribution reactions at the osmium-bound tin atom has been remarked upon in section VIIB.

IX. Concluding Remarks

The five-coordinate silyl and stannyl derivatives of ruthenium(II) and osmium(II) all exhibit tetragonal-pyramidal geometry with the silicon or tin atoms at the apical position. The six-coordinate silyl and stannyl derivatives of ruthenium(II) and osmium(II) are all octahedral. However, apart from these structural similarities, in other aspects of the chemistry of these complexes marked differences emerge. These begin with synthesis, where the oxidative addition of silanes to $MPhCl(CO)(PPh_3)_2$ (M = Ru, Os) leads directly to coordinatively unsaturated silyl derivatives. This is not a viable route to the corresponding stannyl complexes, and these are prepared from vinylstannanes and $MHCl(CO)(PPh_3)_3$ (M = Ru,Os). The reactivities of halosilyl and halostannyl ligands are often quite different. For example, coordinatively unsaturated complexes containing the trichlosilyl ligand are easily hydrolyzed but coordinatively saturated complexes containing the trichlosilyl ligand are resistant to hydrolysis. In contrast, the corresponding coordinatively saturated trihalostannyl complexes are readily hydrolyzed. This reduced electrophilicity of the silicon atom when bound to an electron-rich saturated metal center is also reflected in very different structures for silatranyl and stannatranyl complexes. The high reactivity of Sn−halogen bonds in substituted stannyl complexes makes it possible to access unusual derivatives such as an SnH_3 complex and distannyl (SnR_2SnR_3) complexes. Another difference is that trimethylstannyl complexes of osmium often undergo reversible reactions in which a methyl group migrates from tin to osmium, whereas trimethylsilyl complexes of osmium do not.

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