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Journal of Organometallic Chemistry 691 (2006) 4065–4075
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Syntheses, reactions, and structures of osmium(II) distannyl complexes, $L_nOs–SnMe_2SnR_3$ (R = Me, Ph), from reaction between $L_nOs–SnClMe_2$ and either $LiSnMe_3$ or $KSnPh_3$

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Received 31 March 2006; received in revised form 2 June 2006; accepted 8 June 2006
Available online 15 June 2006

Abstract

Reaction between $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and either $LiSnMe_3$ or $KSnPh_3$ produces the distannyl complexes, $Os(SnMe_2SnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**1**) or $Os(SnMe_2SnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**3**), respectively. Similarly, reaction between $Os(SnClMe_2)Cl(CO)_2(PPh_3)_2$ (**6**) and $KSnPh_3$ produces the distannyl complex, $Os(SnMe_2SnPh_3)Cl(CO)_2(PPh_3)_2$ (**7**). In the ^{119}Sn NMR spectra of these stable osmium(II) distannyl complexes both the α-Sn and β-Sn atoms show well-resolved $^{119}Sn–^{119}Sn$ and $^{119}Sn–^{117}Sn$ coupling. Each of these three distannyl complexes can be selectively functionalised at the α-Sn atom by reaction with $SnCl_2Me_2$ giving $Os(SnClMeSnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**2**), $Os(SnClMeSnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**4**), and $Os(SnClMeSnPh_3)Cl(CO)_2(PPh_3)_2$ (**8**), respectively. Treatment of compounds **3** or **7** with iodine also cleaves one α-methyl group, selectively, to give $Os(SnIMeSnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**5**), or $Os(SnIMeSnPh_3)Cl(CO)_2(PPh_3)_2$ (**9**). Crystal structures for complexes **3** and **7** have been determined.

Keywords: Distannyl complex; Tin; Osmium; Selective α-Sn functionalisation; X-ray crystal structure

1. Introduction

Disilanyl complexes of type $L_nM–SiR_2–SiR_3$, when coordinatively unsaturated, have proved to be interesting precursors for silylene complexes through reversible migration of the β-silyl group to the metal [1,2]. Furthermore, in regioselective reactions the α-silicon in $Cp^*(CO)_2FeSiMe_2SiMe_3$ is bromodemethylated by reaction with BBr_3 to form $Cp^*(CO)_2FeSiBr_2SiMe_3$ [3], and the α-Si–H bonds in $Cp^*(CO)_2FeSiH_2SiH_3$ react selectively with either CCl_4 or with dimethyldioxirane to give either $Cp^*(CO)_2FeSiCl_2SiH_3$ [4] or $Cp^*(CO)_2FeSi(OH)_2SiH_3$ [5], respectively.

This interesting chemistry prompted us to examine corresponding distannyl complexes of type $L_nM–SnR_2–SnR_3$. Most disilanyl complexes of type $L_nM–SiR_2–SiR_3$ have been prepared beginning with a readily available and appropriately substituted disilane, and introducing the metal either as an anion or through an elimination reaction [1,2]. This approach for the corresponding distannyl complexes is less favourable because of the scarcity of suitably substituted distannanes. The very few reported distannyl complexes of type $L_nM–SnR_2–SnR_3$ include $(PPh_3)_2PhPtSnPh_2SnPh_3$ (which was neither spectroscopically nor

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doi:10.1016/j.jorganchem.2006.06.010

structurally characterised) from oxidative addition of a Sn–Ph bond in Sn_2Ph_6 to $Pt(C_2H_4)(PPh_3)_2$ [6] and $CpCp^*ClHfSnPh_2SnHMes_2$ (which was spectroscopically but not structurally characterised) from the complex reaction of $CpCp^*ClHfSnHMes_2$ with Ph_2SnH_2 [7]. Minor products also formed in this reaction include the tristannyl complex, $CpCp^*ClHfSnPh_2SnPh_2SnHPh_2$. Complexes involving the $Sn(SnMe_3)_3$ ligand, which result from reaction between $LiSn(SnMe_3)_3$ and the appropriate metal halide, include $Cp[P(OPh)_3]_2FeSn(SnMe_3)_3$ [8] and $Mo_2[Sn(SnMe_3)_3]_2(NMe_2)_2$ [9]. Other distannanes substituted with transition metal fragments include the complex, $H_2Sn_2[Mn(CO)_5]_4$, which results from the remarkable reaction between $HMn(CO)_5$ and Cp_2Sn [10], $Ph_2Sn_2[FeCp(CO)_2]_4$ produced by electrochemical reduction of $PhClSn[FeCp(CO)_2]_2$ [11] and $Ph_4Sn_2[Mn(CO)_5]_2$ [12]. This last complex results from the unexpected reaction between $Ph_2ClSnMn(CO)_5$ and C_6F_5Li. The authors proposed that the reaction proceeds through an initial lithium-halogen exchange to produce the tin anion, $Li[Ph_2SnMn(CO)_5]$, which then attacks $Ph_2ClSnMn(CO)_5$ to give the observed product. This observation suggested that reaction between $LiSnR_3$ and a halostannyl complex, $L_nM–SnR_2–X$, could offer a general route to distannyl complexes, $L_nM–SnR_2–SnR_3$.

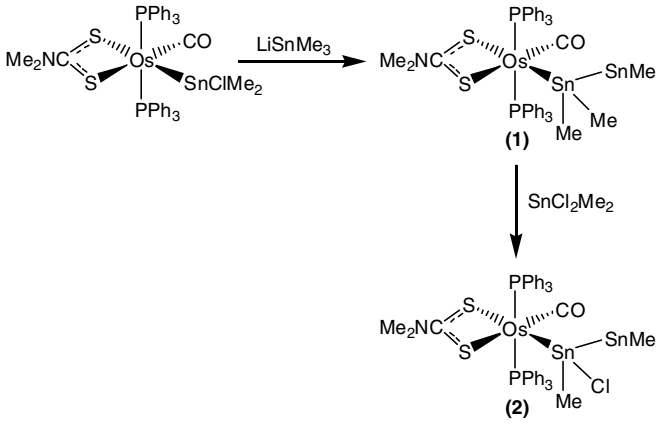
We had previously developed preparative routes to several halostannyl complexes of osmium which undergo facile substitution reactions to yield novel products, e.g., a stannatranyl complex from $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and triethanolamine [13], a hydroxystannyl complex, $Os(SnMe_2(OH))(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ from $Os(SnMe_2Cl)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with KOH [14], a trihydroxystannyl complex, $Os(Sn(OH)_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ from $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with KOH [15], and the simple SnH_3 complex, $Os(SnH_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ from $Os(SnI_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with $NaBH_4$ [16]. Accordingly, we selected two chlorodimethylstannyl complexes, $Os(SnMe_2Cl)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $Os(SnMe_2Cl)Cl(CO)_2(PPh_3)_2$, and examined the reactivity of these two compounds towards the tin anions $[SnMe_3]^-$ and $[SnPh_3]^-$ in the salts $LiSnMe_3$ and $KSnPh_3$.

In this paper we report: (i) the syntheses of the distannyl complexes $Os(SnMe_2SnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**1**), $Os(SnMe_2SnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**3**), and $Os(SnMe_2SnPh_3)Cl(CO)_2(PPh_3)_2$ (**7**) from reaction between $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $LiSnMe_3$, $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $KSnPh_3$, $OsSnClMe_2)Cl(CO)_2(PPh_3)_2$ (**6**) and $KSnPh_3$, respectively, (ii) ^{119}Sn NMR spectroscopic data for these stable osmium(II) distannyl complexes which reveal that both the α-Sn and β-Sn atoms show well-resolved $^{119}Sn–^{119}Sn$ and $^{119}Sn–^{117}Sn$ coupling, (iii) crystal structure determinations for distannyl complexes **3** and **7**, and (iv) selective functionalisation reactions at the α-tin atom in the distannyl complexes by reaction with either $SnMe_2Cl_2$ or I_2.

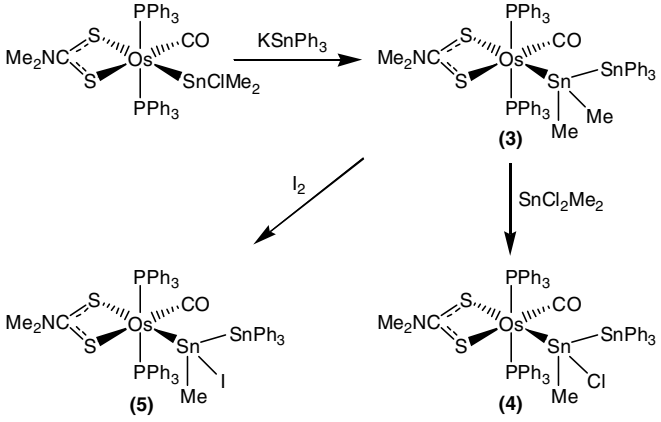
2. Results and discussion

2.1. The syntheses of the distannyl complexes, $Os(SnMe_2SnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (1), $Os(SnMe_2SnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (3), and $Os(SnMe_2SnPh_3)Cl(CO)_2(PPh_3)_2$ (7) from reaction between $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $LiSnMe_3$, $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $KSnPh_3$, $Os(SnClMe_2)Cl(CO)_2(PPh_3)_2$ (6) and $KSnPh_3$, respectively

As illustrated in Schemes 1–3, $LiSnMe_3$ and $KSnPh_3$ readily displaces chloride from the $SnClMe_2$ ligands in $Os(SnClMe_2)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ and $Os(SnClMe_2)Cl(CO)_2(PPh_3)_2$ (**6**) to form the distannyl complexes **1**, **3**, and **7** in good yields. All three complexes are colourless crystalline solids and show good solution stability. The IR spectra of **1** and **3** show ν(CO) bands at 1907 and 1895 cm^{-1}, respectively, and the dicarbonyl complex **7** shows two ν(CO) bands at 2017, 1958 cm^{-1} as expected for a *cis* arrangement of CO ligands. Full spectroscopic data for all the compounds appears in Section 4. The ^1H



Scheme 1. Synthesis and reactions of $Os(SnMe_2SnMe_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**1**).



Scheme 2. Synthesis and reactions of $Os(SnMe_2SnPh_3)(\kappa^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (**3**).