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Soluble Polyethylene- and Polystyrene-Bound Tin Halides as Catalysts for Reductions of Alkyl and Aryl Bromides and Iodides by Sodium Borohydride

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The synthesis, characterization, and use of soluble polyethylene- and polystyrene-bound tin chlorides as catalysts for the reduction of alkyl halides using a suspension of sodium borohydride in toluene and a crown ether as a phase-transfer catalyst are described. These tin-containing soluble macromolecules were synthesized by anionic oligomerization of ethylene or styrene followed by electrophilic substitution of the resulting "living" oligomer with various organic tin halides including tin tetrachloride, *n*-butyltin trichloride, di-*n*-butyltin dichloride, and diphenyltin dichloride. The resulting oligomer-bound tin reagents were characterized by ^1H and ^{119}Sn NMR spectroscopy, and the tin content of the oligomers was analyzed by ICP analysis. Typically the tin reagents were used as cocatalysts (ca. 10%) along with 10–20% of a crown ether as a phase-transfer catalyst in reductions of primary, secondary, and aryl halides using a suspension of sodium borohydride in hot toluene at 110 °C. Kinetic studies showed that the reaction rate was dependent on the concentration of the tin catalyst and that secondary halides reacted slightly faster than primary halides.

Organotin hydrides such as tributylstannane along with related tin compounds are indispensable as reducing agents in organic synthesis for reactions such as reduction of alkyl halides to hydrocarbons and as reagents in other free-radical chain reactions.[1,2] Such reductions produce various tin-containing byproducts including trialkyltin halides and hexabutylditin. As a result, these reductions along with other applications of these tin reagents are complicated by problems in eventual product purification. Specifically, separation of the eventual organic reduction product from these tin-containing byproducts has proven to be a serious limitation of these reagents. Here we describe soluble oligomeric organotin reagents that offer a means to circumvent this problem and that demonstrate that these soluble linear oligomers can be used as catalysts in radical chain processes.

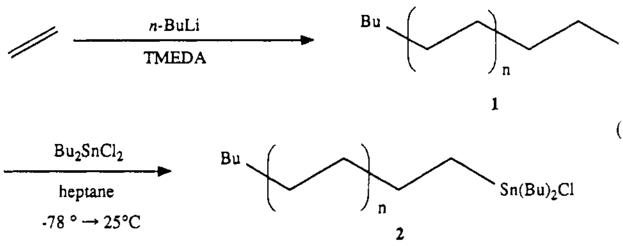
Several approaches have already been developed to minimize problems encountered in separation of trialkyltin halides or tin-containing byproducts from the products of reduction reactions. Corey and Suggs[3] have developed a catalytic procedure using 0.1–0.3 equiv of trialkyltin chloride, sodium borohydride, and ethanol at 25 °C to dehalogenate organic halides. Initiation of the radical chain reaction is accomplished photochemically. A similar procedure for reduction of alkyl halides using phase-transfer catalysis (PTC) with a suspension of excess sodium borohydride and a solution of 5–10% tri-*n*-butyltin chloride in nonpolar aprotic solvents has been reported by our group.[4] Phase-transfer catalysts used in this procedure were crown ethers such as benzo-15-crown-5 or a polyethylene-bound version of benzo-15-crown-5. As was true in the Corey and Suggs procedure, this procedure used catalytic amounts of tri-*n*-butyltin chloride. Thus, product purification was simplified.

The use of stoichiometric amounts of tin reagents attached to insoluble polymers is a conceptually different alternative developed by Crosby to minimize the effects of tin contamination.[5] This polymeric tin hydride's utility has been demonstrated by Still in the synthesis of a macrocyclic antibiotic.[6] Additional advantages of the DVB-cross-linked polystyrene-bound tin dihydride were its greater stability versus diphenyltin dihydride or di-*n*-butyltin dihydride and its facile recovery and regeneration. More recently, DVB-cross-linked polystyrene-bound tin monohydrides and monochlorides have been developed as effective reagents for alkyl halide reductions.[7,8]

We have combined the desirable features of the above approaches for recycling the tin reagent along with a means for facile separation and isolation of the reduced organic product from any tin byproducts and have developed a new procedure for tin hydride reductions of alkyl halides that uses a catalytic amount of a soluble oligomeric tin chloride. Specifically, we have attached several different tin halides to two linear oligomers, polyethylene and polystyrene, and have studied the use of these reagents for alkyl halide reductions. The results of these studies are described below.

Results and Discussion

Polyethylene-bound di-*n*-butyltin chloride was synthesized by anionic oligomerization of ethylene with *n*-butyllithium as an initiator followed by treatment of the resulting suspension of living polyethylene with di-*n*-butyltin dichloride at −78 °C (eq 1).[9] The product tin-containing ethylene oligomer was purified and separated from any insoluble inorganic products of these reactions by hot Soxhlet extraction with toluene. Lithiated linear polystyrene was prepared by anionic oligomerization of styrene



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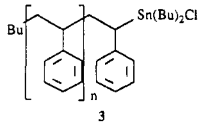
with butyllithium in THF at −78 °C.[10] The living oligomer so formed was then quenched by using a procedure analogous to that used for preparation of **2** to yield **3**. These two tin-containing oligomers along with oligomeric tin derivatives **4–7** prepared by using *n*-butyltin trichloride,



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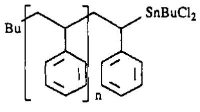

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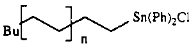

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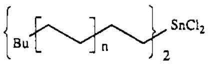

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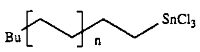

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diphenyltin dichloride, and tin tetrachloride, respectively, were characterized by ^{1}H and ^{119}Sn NMR spectroscopy (see Experimental Section). In the case of the functionalized polyethylene derivatives, this NMR characterization had to be carried out at 110 °C. The oligomer-bound tin compounds' NMR spectra were compared to the ^{119}Sn NMR of their lower molecular weight analogues.[11-13] The resulting ^{119}Sn NMR data chemical shifts were useful in identifying the reaction products. The loading was also estimated by integration of ^{119}Sn NMR peaks versus standards such as tetramethyltin and tetra-*n*-butyltin. Typically this qualitative analysis showed the loading to be in the range 0.1–0.4 mmol of tin/g of oligomer. However, digestion of the oligomer and analysis of the residue for tin by ICP analysis showed these values were minimal estimates of the loading and that the actual tin contents were on the order of 0.3–0.6 mmol of Sn/g of oligomer.

Use of these soluble oligomer bound tin reagents was unexceptional (eq 2). In a typical procedure involving a polyethylene-bound di-*n*-butyltin chloride reagent, toluene

$$CH_3(CH_2)_{10}CH_2Br \xrightarrow[\text{10–20\% benzo-15-crown-5, NaBH}_4\text{(excess), 110 °C}]{\text{polymer-bound tin catalyst}} CH_3(CH_2)_{10}CH_3 \quad (2)$$

(30 mL), 2 mmol of an alkyl bromide, 0.2 mmol of benzo-15-crown-5, a 6-fold excess of sodium borohydride (12 mmol), and 500 mg of oligomer-bound catalyst (0.2 mmol) were heated to reflux for 16–18 h. Cooling the reaction mixture to room temperature precipitated the polyethylene-bound tin catalyst, which was recovered by filtration. GC analysis of the filtrate using internal standards showed that the yield of alkane was >90%. No starting alkyl halide remained under these conditions. Lower amounts of tin catalyst could be used, but the reaction times exceeded 1 day.

The tin catalyst was typically reused by first washing it with isopropyl alcohol and then with acetone and air-drying. When this same sample of polyethylene-bound tin catalyst was used in a subsequent reaction to reduce a different alkyl halide, none of the first alkyl halide or its corresponding hydrocarbon reduction product was detected by GC, indicating that the polyethylene precipitate does not entrain low molecular weight hydrocarbon reductions products. This is in accord with earlier results from our laboratory that show that only polyethylene-like species are readily entrapped in polyethylene precipitates.[14,15]

Table I. Reduction of Alkyl and Aryl Bromides and Iodides with Polyethylene-Bound Di-*n*-butyltin Chloride, Benzo-15-crown-5, and Sodium Borohydride at 110 °C in Toluene[a]

substrate	product	yield, %	time, h
2-bromodecane	decane	92	17
2-bromododecane	dodecane	95	17
1-bromodecane	decane	100	18
1-bromododecane	dodecane	100	16
1,10-dibromodecane	decane	95	19
1-bromooctadecane	octadecane	92[b]	17
1-iodooctadecane	octadecane	100	16
1,2-dibromooctadecane	octadecane	94	18
iodobiphenyl	biphenyl	92	18
4-iodomethoxybenzene	methoxybenzene	88	16
bromonaphthalene	naphthalene	51	24
ethyl 11-bromoundecanoate	ethyl undecanoate	100	16
1-iodododecane	decane	98	16
4-bromo-*tert*-butylbenzene	*tert*-butylbenzene	78	28
octyl 2-bromopropanoate	octyl propoanate	97	16

[a] Reductions were carried out in refluxing toluene using 10% polyethylene-bound tin catalyst, 20% benzo-15-crown-5 catalyst, and a 6-fold excess of sodium borohydride. Product yields were measured by GC using internal standards. [b] This yield was an isolated yield of a 10-mmol scale reaction.

Table II. Kinetic Data for the Reduction of Primary and Secondary Alkyl Bromides with Polyethylene-Bound Tin Catalysts, Benzo-15-crown-5, and Sodium Borohydride at 110 °C in Toluene[a]

		10^3 *k*, s^{-1}	
polymer-bound tin catalyst	[tin], mmol/L	*n*-$C_{12}H_{25}Br$	$CH_3(CH_2)_8CHBrCH_3$
PE–Sn(Bu)$_2$Cl	11.25	3.13[b]	3.95[b]
PE–Sn(Bu)$_2$Cl	6.75		2.60[c]
PE–Sn(Bu)$_2$Cl	4.35		2.80[d]
PE–Sn(Bu)$_2$Cl[e]	7.5		0.13[b]
PE–Sn(Bu)$_2$Cl[f]	7.5		6.5[b]
PE–Sn(Ph)$_2$Cl	15.5	3.95[b]	
PE–Sn(Ph)$_2$Cl	11.37	3.85[g]	
PE–Sn(Ph)$_2$Cl	7.75		2.8[d]
(PE)$_2$SnCl$_2$ + PE–SnCl$_3$[h]	19.4	1.8	3.26
(PE)$_2$SnCl$_2$ + PE–SnCl$_3$[h]	9.7	0.93	1.06
PS–SnBu$_2$Cl	8.67	5.77	2.31
PS–SnBu$_2$Cl	4.33	5.77	3.0
PS–SnBu$_2$Cl	2.17	5.3	2.0
no tin catalyst		0.007	no reaction

[a] Reductions were carried out in refluxing toluene using 10% benzo-15-crown-5 as a cocatalyst and a 6-fold excess of sodium borohydride. Reactions were followed by measuring product alkanes by GC using internal standards. [b] The tin catalyst was recycled once. [c] The tin catalyst was recycled three times. [d] The tin catalyst was recycled four times. [e] This reaction was carried out under an oxygen atmosphere. [f] The reaction mixture included 10% AIBN. [g] The tin catalyst was recycled twice. [h] A 1:1 mixture of **6** and **7** (^{119}Sn NMR analysis) was used as the catalyst.

The reduction shown in eq 2 is applicable to a wide variety of primary alkyl and secondary alkyl and aryl bromides and iodides as shown by the data in Table I. High yields of reduced product were generally obtained. Alkyl chlorides were also reduced with these reagents. However, the reaction rates were substantially lower and complete reduction required longer periods of time than were required for the halides listed in Table I.

The rate of reduction of alkyl halides using these polyethylene-bound tin catalysts has been studied. The results are listed in Table II. Rate constants listed in this table were obtained from experiments that contained 10 or 20

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mol % benzo-15-crown-5 as a cocatalyst and a 6-fold excess of sodium borohydride. The effects on these rates of changing the amounts of either the crown cocatalyst or the reagent sodium borohydride were not studied. The concentrations of tin catalyst used are listed in the table. Several features of these results are noteworthy. First, secondary bromides are reduced slightly faster than primary alkyl bromides when the two halides are reduced in a competitive reaction. Second, recycling the tin catalyst has little or no effect on the catalysts' efficacy in subsequent reductions. The only problem we encountered in recycling the polyethylene-bound di-*n*-butyltin chloride catalyst was physical losses resulting from handling small amounts of catalyst. However, recycling catalysts derived from **4** or from a mixture of **6** and **7** was not as successful. Apparently thermal decomposition of the polyhydrides produced from these polychlorides occurred during the reaction, and recycling in these cases was accompanied by substantial (ca. 30–50%) losses in catalyst activity. Control experiments were also carried out with sodium borohydride and a crown ether alone. In these cases, no reaction of the secondary alkyl bromide occurred and slow rates of reduction of the primary alkyl bromide were observed. These latter reductions proceeded with a rate dependent on the amount of crown ether present. The example listed in Table II was with 4.2% crown ether catalyst and was representative of the reduction rate expected for sodium borohydride–benzo-15-crown-5 under conditions of the tin-catalyzed reductions. As shown by the data in the table, addition of AIBN did not substantially alter the reaction rate. However, when a reaction was run under an oxygen atmosphere, a significant rate reduction was noted.

Reductions using polystyrene-bound di-*n*-butyltin chloride were also studied. Again, high yields (>85%) of reduction products were obtained (36 h). The rate constants measured for reactions with this soluble oligomer-bound tin halide were similar to those obtained with the polyethylene-bound tin reagent. However, in this case the rate constants for the secondary bromide were slightly smaller than those for the primary bromide.

While we did not set out to explicitly determine the effect of changing the concentration of soluble oligomer-bound tin species on the reaction rate, the data listed in Table II show that reactions using different concentrations of tin catalyst have the same or nearly the same k_{obs}/["Sn"] values. This suggests that the reaction was first order in the tin catalyst.

A disadvantage of these procedures is that the required high temperature for dissolution of the oligomer (and for thermal initiation of the reaction) led to some undesirable side reactions. This limited the functional group compatibility of these procedures. For example, under our conditions alkenes react to yield hydrostannation products. Carboxylic acids were also reduced under these conditions as evidenced by the formation of 11-undecanol from 11-bromoundecanoic acid. However, carbonyl groups such as esters were stable under the reaction conditions.

Conclusion

The yield and rates of the reduction reactions using the soluble oligomer-bound tin catalysts were comparable to yields of typical tin hydride reductions. Use of these soluble polyethylene- and polystyrene-bound tin chlorides as reducing agents maintains the advantages typical of a polymeric reagent. The spent oligomeric tin catalysts were easily removed from solution and separated from the reaction products. These soluble oligomeric tin reagents were also reusable. In the case of oligomeric polyethylene-bound di-*n*-butyltin chloride, the tin catalyst was reusable with no loss in activity. Recycling of tin catalysts based on oligomeric polyethylene-bound tin di- and trichloride was possible but was accompanied by 30–50% loss of catalyst activity. All of these oligomeric tin catalysts are soluble and function chemically the same way as do their lower molecular weight counterparts. The principal disadvantages of these reagents as catalytic reducing agents are the need for excess sodium borohydride and hydrostannation and the other side reactions that occur.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 200E, XL200, or XL400 NMR spectrometer. ^{119}Sn NMR spectra were recorded on either a XL200 or XL400 NMR spectrometer. Low molecular weight products and starting materials were analyzed as $CDCl_3$ solutions with chemical shifts measured relative to TMS (^{1}H) or tetra-*n*-butyltin (^{119}Sn, $\delta = -13$). Polyethylene samples were analyzed at 110 °C in C_7D_8 with 1,1,2,2-tetrachloroethane or hexamethyldisiloxane as internal standards. An HP 5830A gas chromatograph with a 30-m dimethylsilicone fused silica column was used to analyze reactions. GC/MS were obtained on an HP 5790 GC connected to a Model 5970A mass selective detector. IR spectra were recorded on an IBM IR44 FTIR spectrometer either as KBr pellets (solid samples) or as neat liquids. Solvents were purified by distillation from sodium–benzophenone ketyl prior to use. Styrene for the oligomerization reaction was purified by washing with base and water, dried, treated with CaH_2, and finally distilled under vacuum. Ethyl 11-bromoundecanoate and octyl 2-bromopropanoate were prepared from their corresponding acids according to literature procedures.[16,17] All other reagents were used as received and not purified prior to use.

Diphenyl dichloride was prepared from triphenyltin chloride and a methylene chloride solution of HCl (0.07 M) according to a literature procedure.[18] The product of this protonation was isolated as a crude solid and characterized by NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 7.3–7.7; ^{119}Sn NMR ($CDCl_3$) δ −28.9.

Lithiated ethylene oligomer 1 was prepared according to a literature procedure.[9] A dry 500-mL Fisher-Porter pressure bottle equipped with a magnetic stirring bar was connected to a multiple-use (vacuum, nitrogen, and ethylene) pressure line through a pressure coupling. This bottle was then evacuated and purged with nitrogen three times. Dry heptane (250 mL), 6.2 mL of 1.6 N *n*-butyllithium in hexane, and 2 mL of *N,N,N',N'*-tetramethylethylenediamine were added successively by syringe. The bottle was pressurized with ethylene to 30 psig and the oligomerization was carried out at this pressure. The reaction was initially homogeneous, and slight warming of the pressure bottle was detectable. After about 30 min, a precipitate formed. Depending on the desired size of the final product, the oligomerization was continued for varying lengths of time. Typical times ranged from 36 to 48 h. This living oligomer was not itself characterized but rather was converted by electrophilic substitution reactions to the desired terminally functionalized ethylene oligomers described below.

Preparation of Tin-Containing Ethylene Oligomers. Tin was introduced onto the end of ethylene oligomers in several ways. First, **1** was quenched with excess di-*n*-butyltin dichloride by adding di-*n*-butyltin dichloride to a −78 °C suspension of **1** and then allowing the reaction mixture to warm to room temperature with stirring for 8 h. The product oligomer was isolated by filtration and purified by dissolution precipitation and then by hot extraction with toluene from any insoluble impurities. The product formed in this case was polyethylene-bound di-*n*-butyltin chloride. This trialkyltin chloride was not readily characterized by ^{1}H NMR spectroscopy because of the low electronegativity of tin and the consequent lack of differentiation in chemical shifts

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of signals in the product from signals due to polyethylene. However, ICP analysis for tin from an acid-digested sample showed that some tin had been introduced at a level of 0.45 mmol of $SnBu_2Cl$/g of oligomer. Similar procedures using diphenyltin dichloride and tin tetrachloride yielded oligomer **3** and a 1:1 mixture of oligomers **6** and **7**, respectively, which were analyzed and shown to have 0.62 mmol of $-SnPh_2Cl$/g of oligomer and 0.58 mmol of "Sn"/g of oligomer. Oligomer **3** was further characterized by ^1H NMR spectroscopy and shown to have a molecular weight of 1423 on the basis of integration of the $-CH_3$ signal versus 1,1,2,2-tetrachloroethane as an internal standard. ^{119}Sn NMR spectroscopy showed these oligomers to have the following tin signals: **2**, δ 137.2; **3**, δ −74.1; **6**, δ 139.2; **7**, δ 119.6.

Preparation of Polystyrene-Bound Di-*n*-butyltin Chloride (4). A 500-mL round-bottomed three-necked flask equipped with a 125-mL pressure-equalized addition funnel and a magnetic stirring bar was flame dried and purged with nitrogen three times. After the apparatus cooled, it was placed in an acetone–dry ice bath under a static nitrogen pressure. THF (100 mL) was added, and the mixture cooled to −78 °C. Then 2 mL of a 1.6 N *n*-butyllithium solution in hexane was added. The oligomerization was carried out by dropwise addition of 10.81 g (104 mmol) of styrene as a solution in 10 mL of THF. The product dark red solution was stirred for 1 h at −78 °C, and then di-*n*-butyltin dichloride was added as a THF solution. After the mixture was warmed to room temperature and stirred for 2 h, the solvent was removed at reduced pressure. Dissolution of the residue in chloroform and filtration removed some insoluble impurities. Removal of the solvent left 10 g of a crude tin-containing oligomer that was characterized by ^{119}Sn NMR ($CDCl_3$) δ 155. ICP analysis of this oligomer showed it to have 0.26 mmol of Sn/g of oligomer.

Preparation of polystyrene *n*-butyltin dichloride (5) was accomplished by a procedure analogous to that used for **4** with the only difference being the use of $BuSnCl_3$ as the stannylating agent. The product **4** so prepared had a ^{119}Sn NMR spectrum with a peaks at δ 70 and 76. The presence of more than one peak was presumably the result of the presence of more than one diastereomeric center in the polystyrene oligomer. GPC analysis showed this oligomer had a molecular weight of 1250, and ICP analysis showed that it contained 0.3 mmol of $-SnBuCl_2$/g of oligomer.

Digestion of Oligomer Samples. The procedure used was a modification of Shanina's.[19] To a 20-mL quartz crucible was added 0.2 g of the oligomer sample and 4 mL of concentrated H_2SO_4. The oligomer mixture was gently heated on a hot plate until the oligomer sample was completely decomposed. Then, 10 mL of concentrated HNO_3 was added dropwise to the decomposed oligomer sample, followed by further heating on the hot plate for an additional 24 h with occasional shaking. A brownish homogeneous solution was finally obtained after this acidic digestion. After this solution was cooled to 25 °C, it was diluted with distilled water in a 25-mL volumetric flask and analyzed for tin content by atomic absorption spectroscopy by the Agricultural Analytical Services Laboratory at Texas A&M University. Control analyses for tin using the same amount of reagents excluding the oligomer sample were also carried out.

Reduction of Alkyl Halides with Polyethylene-Bound Tin. Toluene (20 mL), 2 mmol of the organic halide, 0.2 mmol of benzo-15-crown-5, a 6-fold excess of sodium borohydride, and 500 mg of **2** were mixed together at 25 °C under a nitrogen or argon atmosphere to form a suspension. No reaction occured with this suspension at room temperature, but on heating to reflux (110 °C) a solution formed. After 16–18 h of reflux, GC analysis showed that no starting material remained. Cooling the reaction mixture at this point re-formed the suspension of a polyethylene-bound tin reagent, which was recovered by filtration. This recovered tin catalyst could be reused by washing it with 2-propanol and acetone and air drying it. Analysis of a concentrated sample of the filtrate by ICP showed that >99.9% of the starting tin reagent had been recovered from solution. Specifically, in the case of using 1.5 g of $PESnPh_2Cl$ in a synthetic reaction, the filtrate contained less than 9×10^{-3}% of the starting tin compound. Similarly, the filtrate from a reaction using 1.5 g of $PESnBu_2Cl$ as a catalyst contained less than 3×10^{-2}% of the starting tin reagent.

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Asymmetric Induction during the Reactions of Dienyl–Iron and Diene–Molybdenum Complexes with Chiral *N*-Acyloxazolidinone Enolates

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The addition of chiral *N*-acyloxazolidinone enolates to diene–molybdenum and dienyl–iron complexes gives enantiomeric excesses as high as 80%. The oxazolidinone derived from valinol adds preferentially to the *pro-S* terminus of the diene/dienyl complex while the oxazolidinone derived from norephedrine adds to the *pro-R* terminus. A rationalization of these experimental results is attempted based on Seebach's topological rules for the Michael addition of enamines to nitro olefins.

Introduction

The use of transition metal stabilized diene and dienyl complexes as intermediates for the synthesis of natural products has been of continuing interest in our research group.[1] We have demonstrated that the cyclohexadiene–$Mo(CO)_2Cp$ complex **1** can be converted to the 1,3-cis-disubstituted π-allyl complex **2** and thence to the acyclic molecule **3**, which corresponds to a right-hand subsection of macrolide antibiotics such as tylosin (**4**).[2] We have also shown that the cycloheptadiene–$Mo(CO)_2Cp$ complex **5** can be converted to lactone **7** via complex **6**.[3]

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