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Communication

Synthesis of a Lewis acid bearing cyclopentadienyl ligand and its tricarbonylmanganese(I) complex

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Abstract

The synthesis of a bimetallic compound comprising a Lewis acidic organochlorostannane and a transition metal carbonyl is reported. The target complex, $[(CO)_3Mn(\eta^5\text{-}C_5H_4(CH_2)_3SnMe_2Cl)]$, **2**, is prepared in four steps. The final step involves an exchange reaction between $[(CO)_3Mn(\eta^5\text{-}C_5H_4(CH_2)_3SnMe_3)]$, **1**, and $SnMe_2Cl_2$. Infrared spectroscopy demonstrates no interaction between the Lewis acid and lone pair on the carbonyl oxygen.

Keywords: Organostannanes; CO activation; Cyclopentadienyl ligands; Heterobimetallic complexes; Intramolecular Lewis acid base adduct

1. Introduction

The transition metal mediated reduction of small molecules has received much attention over the past several decades because of potential biological and industrial applications [1,2]. To date, many successful transition metal catalyzed electrocatalytic processes have been developed. One class of catalysis involves utilizing both a transition metal (TM) and a Lewis acid (LA) to bind the substrate (A = B)

TM–A = B–LA.

Lewis acid effects have been observed or suggested in the reductions of O_2 [3], N_2 [4], CO_2 [5], and CO [1,6]. One method of exploiting this bifunctional binding is the preorganization of a complex with both Lewis acid and transition metal binding sites in close proximity. Examples of such ligands include crown ethers bearing one or two pendant phosphines [6,7], as well as diporphyrin [3a] and porphyrin-crown [3b,8] ligands. Challenges encountered in utilizing such ligands involve synthetic difficulties in inserting two different metals into a ditopic ligand [3], and Lewis acid-transition metal distances that do not favor bifunctional binding [8]. Our goal is to devise a scheme whereby a Lewis acid is covalently tethered, via a variable length linkage, to a TM binding site. We have chosen chloroalkylstannanes as the Lewis acid moiety due to the versatility of organostannane chemistry [9] and because of the ability of tethered organochlorostannanes to act as Lewis acids as demonstrated by Kuivila et al. [10] with ketoorganochlorostannanes (Fig. 1).

The focus of this work is to tether an organostannane and chloroorganostannane to a $CpMn(CO)_3$ fragment to determine if any interaction occurs between the Lewis acid and the carbonyl group. A metal carbonyl has been chosen because interactions between Lewis acids and the carbonyl oxygen are well documented [1,11–13]. The synthetic strategy chosen is straightforward and widely variable and could be used to prepare a range of similar complexes.

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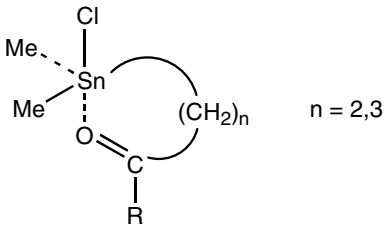


Fig. 1. Example of an intramolecular Lewis acid–base interaction [10].

2. Results and discussion

2.1. Syntheses

This approach involved the preparation of two model systems (i.e., **1**, and **2**, Fig. 2), followed by investigation of the C–O triple bonds of both compounds using IR spectroscopy. Synthesis of organotin compounds is the subject of a recent review [9], however, to our knowledge, the preparation of these novel bimetallic organostannanes has not been previously addressed. Herein, we report a simple and convenient route to two bimetallic complexes of this type. This method, which may in principle be extended to other variants, allows for rapid installation of key functional units in as little as three steps.

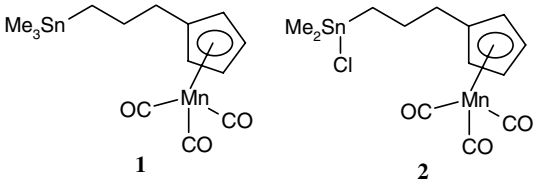
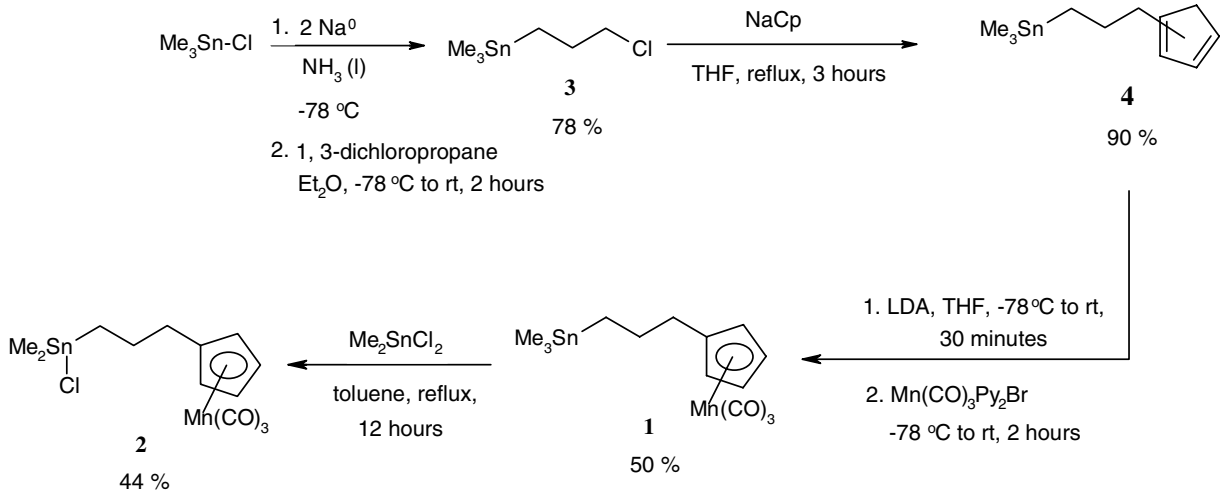


Fig. 2. Target complexes with Lewis acid moieties tethered to the $CpMn(CO)_3$ fragment.

The synthesis of **1** and **2** (Scheme 1) began with preparation of the functionalized alkylstannane, **3**, according to the literature procedure [14]. Alkylation of the cyclopentadienyl (Cp) ring with this tether was performed in a manner similar to a Cp alkylation published by Wang et al. [15] and afforded stannane **4**, as a mixture of regioisomers, in excellent yield after distillation (90%).

Metallation of the Cp ring was accomplished by deprotonation of the Cp ring using LDA, followed by addition of $Mn(CO)_3Py_2Br$, affording **1** in reasonable chemical yield (50%). Finally, an exchange reaction with dichlorodimethylstannane provided **2** in modest chemical yield (44%) using a procedure analogous to that published by Jurkschat et al. [16]. Compound **2** is somewhat unstable as a purified sample under ambient conditions, i.e., by ^1H NMR it shows substantial decomposition in several days. Compound **4** is also unstable and should be freshly prepared as it decomposes significantly over a period of two weeks at −5 °C.

Due to the aforementioned instability, we were unable to obtain satisfactory elemental analysis of **2**. However, **2** gave very clean ^1H and ^{13}C NMR spectra and was characterized by the singlet at 0.82 ppm in the proton NMR spectrum. This absorption displayed typical $^2J_{P\text{-}Sn}$ coupling, and integrated for six protons (two methyl groups). Both the chemical shift, slightly downfield of the analogous absorption in **1** (0.05 ppm), and the integration are consistent with the incorporation of the chlorine atom. The remainder of the spectrum was very similar to that of **1**. In addition, though we have been unable to observe the parent ion of **2** in the mass spectrum, the two dominant fragments in the MS occur at 395 (consistent with loss of Cl from Sn on the parent) and 346 (consistent with loss of three CO from the parent) and are thus consistent with the proposed structure. This fragmentation pattern is similar to that of **1**, where



Scheme 1. Preparation of substituted manganese tricarbonyl complexes **1**, and **2**.