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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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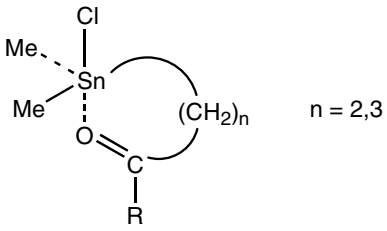


Fig. 1. Example of an intramolecular Lewis acid–base interaction [10].

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.

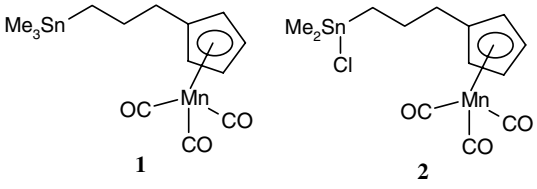
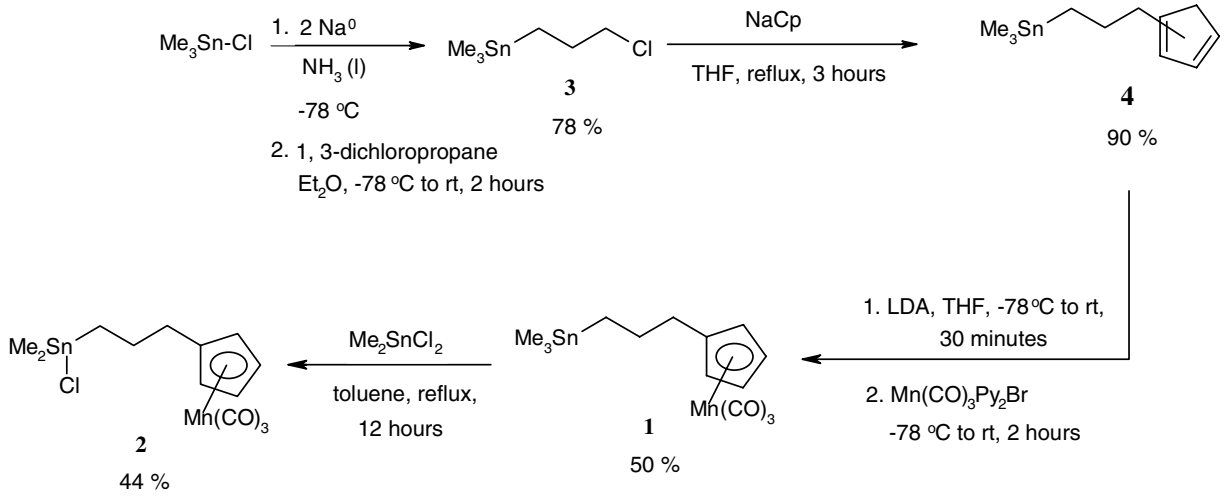


Fig. 2. Target complexes with Lewis acid moieties tethered to the $CpMn(CO)_3$ fragment.

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**.

the dominant fragments occur at 395 (consistent with loss of a methyl group from Sn on the parent) and 326 (consistent with loss of three CO from the parent). For **1**, the parent 410 is also observable but substantially lower in intensity than either dominant fragment. Parent and fragment peaks for both compounds exhibit typical isotopic distributions for Sn containing compounds.

2.2. Spectroscopic characterization

With both manganese complexes in hand, our attention turned to the IR spectra of the two complexes. A difference in frequency of the respective CO stretches would likely indicate differential interactions between the two very different Lewis acids and the carbonyl oxygens. A similar Lewis acid–base interaction has been observed for the aforementioned ketoorganochlorostannanes (Fig. 1) as demonstrated by an approximately 30 cm^{-1} shift of the CO stretching frequency to lower energy for the ketoorganochlorostannanes vs. the corresponding ketoorganostannanes [10]. However, for the case of **1** and **2**, prepared herein, the CO stretching frequencies overlapped almost exactly (1943 and 2024 cm^{-1} for **1** and 1944 and 2025 cm^{-1} for **2**). These values also agree well with the literature spectrum of (η^5-C_5H_4Et)$Mn(CO)_3$ [17] and thus there appears to be little, if any, interaction between the LA and the lone pair on the carbonyl oxygens.

2.3. Conclusions

Straightforward synthetic strategies have yielded the desired carbonyl complexes tethered to a Sn moiety with varying Lewis acidity. However, we have noted no evidence of interaction between the carbonyl oxygen and tethered Lewis acid. Though CPK models and simple molecular mechanics calculations (Spartan) demonstrated that a three carbon spacer should allow interaction between the Lewis acidic Sn moiety and the carbonyl oxygen without undue strain, our result does not preclude the possibility of interaction in analogous complexes with different separation between the LA and the TM. It is also likely that the Lewis acidity of the organochlorostannane is insufficient to bind to the CO ligand which is presumably less basic than the ketone oxygen in the Kuivila precedent [10,13].

3. Experimental

3.1. General remarks

Reactions and manipulations were carried out using standard Schlenk line techniques under an argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl and diisopropylamine from CaH_2 prior to use. $Mn(CO)_3Py_2Br$ was prepared from $Mn(CO)_5Br$ according to the literature procedure [18]. All other reagents were purchased from commercial sources and used without further purification. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. NMR spectra were recorded in $CDCl_3$ using either Varian VXR 300 (300 MHz) or INOVA 500 (500 MHz) spectrometers. IR spectra were recorded in hexanes using a Perkin–Elmer Spectrum BX FT-IR spectrometer. Mass spectra were obtained on a Varian Saturn 2100D GC/MS equipped with an electron impact ionization source and an ion-trap MS.

3.2. Reaction procedures

3.2.1. $C_5H_4(CH_2)_3SnMe_3$ (**4**)

In an inert atmosphere box, NaCp (0.486 g, 5.5 mmol) was weighed into a 25-mL round bottom flask. The flask was sealed, removed from the drybox, and freshly distilled THF (10 mL) was added by syringe. Stannane **3** (1.22 g, 5 mmol) was added by syringe and the reaction mixture was refluxed with stirring under Ar for 3 h. Afterwards, the mixture was diluted with Et_2O (40 mL), and washed with H_2O (20 mL). The layers were separated, and the organic layer was dried ($MgSO_4$), and concentrated in vacuo to afford a brown oil. This was distilled (80 °C, 30 mTorr) to give **4** as a clear, colorless oil which was present as a mixture of two regioisomers (1.23 g, 90%, R_f 0.7, pentane, silica gel). ^1H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.04 (s, 9H), 0.80–0.90 (m, 4H), 1.60–1.80 (m, 4H), 2.30–2.45 (m, 4H), 3.85–3.90 (m, 2H), 3.95–4.00 (m, 2H), 5.95–6.00 (m, 1H), 6.10–6.15 (m, 1H), 6.20–6.25 (m, 1H), 6.35–6.45 (m, 3H). Anal. Calc. for $C_{11}H_{19}Sn$: C, 48.94; H, 7.09. Found: C, 48.74; H, 7.41%.

3.2.2. $[(CO)_3Mn(\eta^5$-$C_5H_4(CH_2)_3SnMe_3)]$ (**1**)

Diisopropyl amine (202 mg, 2 mmol) was dissolved in freshly distilled THF (5 mL) under argon and cooled to 0 °C. To this was added *n*-BuLi (0.6 mL, 1.78 M, 1 mmol) and the mixture allowed to stir for 15 min. This solution (LDA) was added to a solution of **4** (135 mg, 0.5 mmol) in THF (5 mL) dropwise with stirring, at −78 °C. After complete addition, the reaction mixture was allowed to warm to 0 °C for 30 min, and then recooled to −78 °C. A solution of $Mn(CO)_3Py_2Br$ (170 mg, 0.5 mmol) in THF (5 mL) was added dropwise the resulting brown solution was allowed to slowly warm to room temperature over 2 h. Afterwards, Et_2O (40 mL) was added and the mixture washed with H_2O (20 mL). After separation of the layers, the organic layer was dried ($MgSO_4$) and concentrated in vacuo to give a brown oil. This was purified by chromatography on silica gel (R_f 0.45, pentane, 100%) to afford **1** as a light yellow oil (98 mg, 50%). IR (neat) 1909 (w), 1943 (vs), 2013 (w), 2024 (s), cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.05

(s, 9H), 0.78–0.85 (m, 2H), 1.60–1.72 (m, 2H), 2.23 (t, $J = 7$ Hz, 2H), 4.55–4.65 (m, 4H);); ^{13}C NMR −10.0, 10.3, 28.5, 33.1, 81.5, 82.5, 107.3, 225.0; GC–MS *m*/*z* (rel intensity) 410 (5, M^+), 395 (100), 326 (26), 223 (5), 204 (1); Anal. Calc. for $C_{14}H_{19}SnMnO_3$: C, 41.12; H, 4.68. Found: C, 41.31; H, 4.68%.

3.2.3. *[(CO)$_3$Mn(η^5-C$_5$H$_4$(CH$_2$)$_3$SnMe$_2$Cl)] (**2**)*

Compound **1** (50 mg, 0.125 mmol) was dissolved in toluene (5 mL) and solid dichlorodimethylstannane (100 mg, 0.45 mmol, 3.5 equiv.) was added. The reaction mixture was refluxed with stirring under Ar (g) for 12 h. Afterwards, the solvent was removed in vacuo, and the residue chromatographed on silica gel (R_f 0.5, Et_2O, 100%) to afford **2** as a light yellow oil (23 mg, 44%). IR (neat) 1909 (w), 1944 (vs), 2013 (w), 2025 (s), cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (s, 6H), 1.30 (t, $J = 10$ Hz, 2H), 1.86 (quint, $J = 10$ Hz, 2H), 2.30 (t, $J = 10$ Hz, 2H), 4.55–4.65 (m, 4H); ^{13}C NMR −1.90, 18.3, 28.3, 33.0, 82.0, 83.0, 109.0, 226.0; GC–MS, *m*/*z* (rel intensity) 395 (100), 346 (27), 225 (5), 196 (3).

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