

Syntheses and NMR Characterization of Tin Monohaptotetraphenylcyclopentadienyl and Group VB Transition Metal Pentahaptotetraphenylcyclopentadienyl Compounds

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Abstract

Two VB transition metal compounds, η^5 - $C_5H_5(C_6H_5)_4NbCl_4$ (**1**) and η^5 - $C_5H_5(C_6H_5)_4TaCl_4$ (**2**), and the trimethyltin monohapto compound $C_5H_5(C_6H_5)_4Sn(CH_3)_3$ (**3**) were synthesized and characterized by 1H and ^{13}C -NMR. The purple-brown niobium complex and the tantalum homologue were synthesized in 46% and 50% unoptimized yields, respectively, while the preparation of tin compound gave crude yield of 54%. Complexes **1** and **2** display identical 1H -NMR, $\delta_H(CD_2CN)$: 6.36 – 7.51 ppm (20H, *m*) and 4.68 ppm (1H, *s*) and similar ^{13}C -NMR, $\delta_C(CD_2)$: 144.9 ppm (*q*), 137.8 ppm (*q*) and 129.4 ppm (*m*). For compound **3** $\delta_C(CDCl_2)$: 6.87 – 7.35 ppm (20H, *m*), 5.02 ppm (1H, *s*, $J_{Sn-H} = 88$ Hz) and -0.19 ppm (1H, *s*, $J_{Sn-H} = 52$ Hz) and $\delta_C(CDCl_2)$: . The transmetalation of **3** with $NbCl_5$ led to **1**. The Lewis acid catalysis of the silylcyanation of butyraldehyde using **1** was monitored via 1H -NMR.

Experimental

The general pathway for the syntheses of all three compounds is displayed in Scheme 1; all were made using proper Schlenk and glovebox techniques. 1H and ^{13}C -NMRs were taken on either a 300 or a 400 MHz Bruker analyzer. Tin complex **3** (TMSnD) was prepared by adding diethyl ether to a 1:1 molar ratio of trimethyltin chloride and lithium tetraphenylcyclopentadienide. The resulting turbid yellow solution was stirred for 24 hrs and then gravity-filtered in order to remove the lithium chloride; the resultant solution was subsequently dried in vacuo to afford a yellow solid.

Complexes **1** and **2** were made by adding diethyl ether to an equimolar ratio of lithium tetraphenylcyclopentadienide and either $NbCl_5$ or $TaCl_5$ and letting the mixture stir for 4 hrs. The mixture was then filtered using a Schlenk filter and the product was dried in vacuo. The niobium complex was alternatively prepared by using the above procedure but methylene chloride instead of ether was used as the solvent as indicated in Scheme 2.

The transmetalation of **3** to give **1** was accomplished by performing a small-scale reaction in which a 1:1 molar ratio of TMSnD and $NbCl_5$ were dissolved in dry deuterated methylene chloride and stirred for 24 hours. A 1H -NMR of the resulting product was directly taken with no further work-ups.

The catalytic effects were studied by dissolving equimolar amounts of butyraldehyde and trimethylsilyl cyanide in CH_2Cl_2 . A couple of drops of CD_2Cl_2 were added to the solution in order to facilitate locking a 1H -NMR signal. A control and a study sample were prepared by placing equal volumes of the solution into 2 separate tubes. The control tube only contained the reaction solution while the study tube contained 1% molar mass equivalent to the starting materials of **1**. The progress of the reaction of both samples was monitored using 1H -NMR

Table 1. 1H -NMR Chemical Shifts

Compound	Chemical Shift (ppm)
η^5 - $C_5H_5(C_6H_5)_4NbCl_4$ (1)	6.36 – 7.51 (20H, <i>m</i>), 4.68 (1H, <i>s</i>)
η^5 - $C_5H_5(C_6H_5)_4TaCl_4$ (2)	6.36 – 7.51 (20H, <i>m</i>), 4.68 (1H, <i>s</i>)
$C_5H_5(C_6H_5)_4Sn(CH_3)_3$ (3)	6.87 – 7.35 (20H, <i>m</i>), 5.02 (1H, <i>s</i> , $J_{Sn-H} = 88$ Hz), -0.19 (1H, <i>s</i> , $J_{Sn-H} = 52$ Hz)

Table 2. Sn-H Coupling Constants

Compound	Coupling Constant (Hz)
η^5 - $C_5H_5(C_6H_5)_4Sn(CH_3)_3$ (3)	88 (1H, <i>s</i>), 52 (1H, <i>s</i>)

Table 3. ^{13}C -NMR Chemical Shifts

Compound	Chemical Shift (ppm)
η^5 - $C_5H_5(C_6H_5)_4NbCl_4$ (1)	144.9 (<i>q</i>), 137.8 (<i>q</i>), 129.4 (<i>m</i>)
η^5 - $C_5H_5(C_6H_5)_4TaCl_4$ (2)	144.9 (<i>q</i>), 137.8 (<i>q</i>), 129.4 (<i>m</i>)
$C_5H_5(C_6H_5)_4Sn(CH_3)_3$ (3)	130, 138, 145 (<i>m</i>)

Table 4. Sn-C Coupling Constant

Compound	Coupling Constant (Hz)
η^5 - $C_5H_5(C_6H_5)_4Sn(CH_3)_3$ (3)	~100 (130, 138, 145 ppm)

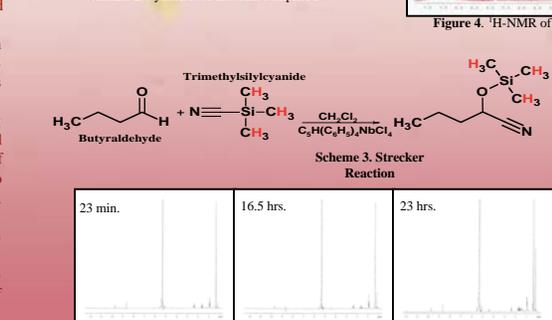
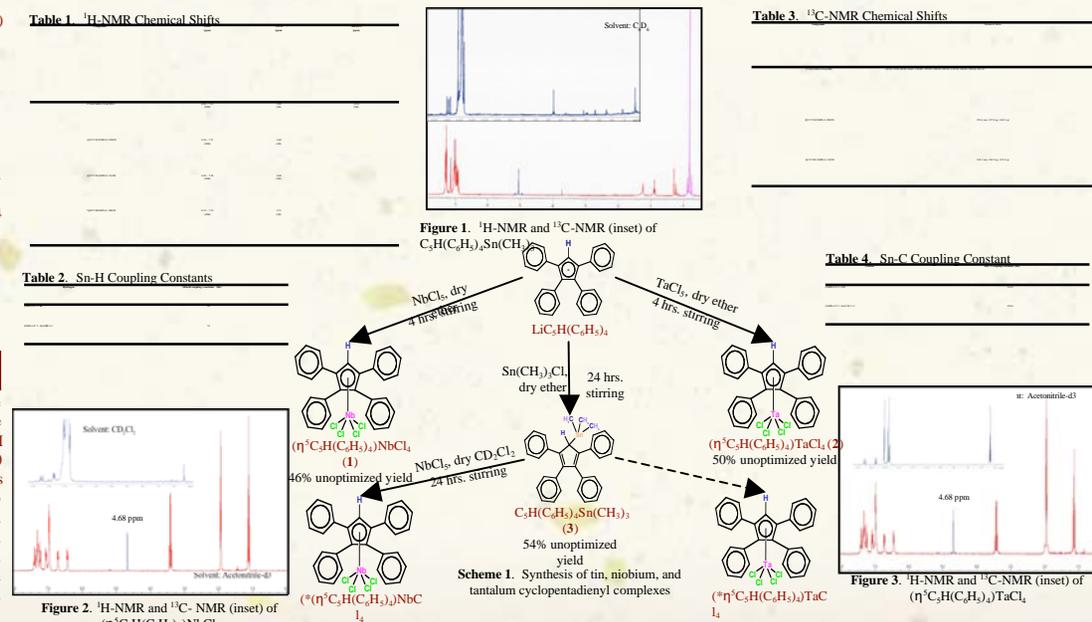
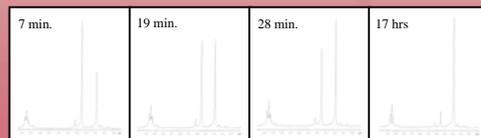
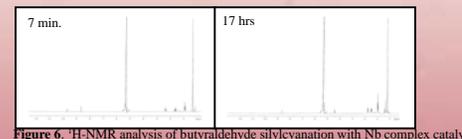
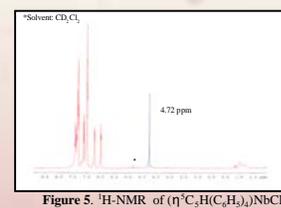
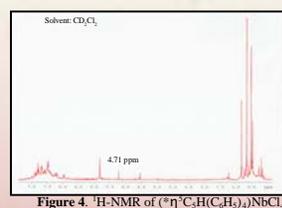
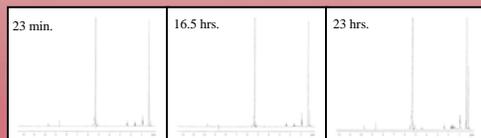


Figure 6. 1H -NMR analysis of butyraldehyde silylcyanation, control (expanded)



Results and Discussion

The original synthesis design for **1** and **2** was via the transmetalation of **3** with the corresponding chloride salt. Experimentation and failed attempts using this scheme led to the discovery that the reaction would proceed using just diene with either of the metal salts. What is essential to this step is the quality of the diene used. Once this was learned, we observed that the complexation reaction via the TMSnD intermediate does yield the niobium complex, leading to expectations that the tantalum complex can also be synthesized by this pathway. It is also both interesting and exciting that we are potentially able to synthesize both metal complexes and by two different methods. Figures 1, 2 and 3 display the NMR spectra of the mentioned compounds. As it can be seen in these figures the 1H and ^{13}C -NMR for the niobium and tantalum complexes is strikingly similar. They both display similar aromatic regions between 6.36 and 7.51 ppm and an identical singlet at 4.68 ppm for the proton NMR (δ_H, CH_2CN) while the ^{13}C spectra shows multiplets at about 130, 138 and 145 ppm (δ_C, CD_2Cl_2). The once elusive tin complex is characterized by the presence of two singlets and their satellites in both the 1H and the ^{13}C -NMR, (δ_H, C_6D_6): singlets at -0.19 and 5.05 ppm and (δ_C, CD_2Cl_2): singlets at -0.34 and 54.7 ppm. The use of different solvent for the synthesis of **1** led to a cleaner 1H -NMR, (δ_C, CD_2Cl_2) with the characteristic singlet at 4.72 ppm (Fig 5). Although the transmetalation reaction led to several products one of them seems to be the desired niobium product as can be seen in Figure 4. Tables 1 through 4 display all the NMR numerical data. The catalytic effects of **1** are clearly seen in Figures 6 through 8. The silylcyanation of butyraldehyde proceed at a faster rate with the catalyst then without it

Future Work

The next step is to successfully recrystallize the tin, niobium, and tantalum complexes in order to perform elemental analysis and to further elucidate the structure of our compounds. The synthesis of the tantalum complex using TMSnD will also be explored, and the synthesis of the niobium complex by this pathway will be optimized. The catalytic activities of the niobium as well as the tantalum complexes will be further investigated.

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