



MoCl₄(CH₃CN)₂-Catalyzed Hydrosilylation of Alkynes in the Presence of PTA

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Abstract A molybdenum(IV) complex, *trans*-MoCl₄(CH₃CN)₂ was used as a pre-catalyst in the presence of PTA (1,3,5-triaza-7-phosphaadamantane) in hydrosilylation of 1-heptyne and 1,6-heptadiyne using a tertiary hydrosilane, Ph₂MeSiH. The silylated products formed were characterized by Gas Chromatography (GC), Nuclear Magnetic Resonance (NMR) Spectroscopy, and Mass Spectrometry techniques. With a higher catalyst loading of 20 mol%, the hydrosilylated products were formed in a lower yield, but with a good regioselectivity. The hydrosilylation reaction formed the β -*trans* isomer as a major product and α -isomer as a minor product. This study is the first example of investigation of homogeneous hydrosilylation reaction using a Mo(IV)-CH₃CN complex as a pre-catalyst.

Keywords Hydrosilylation, Mo(IV) catalyst, Molybdenum-catalyzed, MoCl₄(CH₃CN)₂, MoCl₄(MeCN)₂ catalyst

Introduction

Catalytic hydrosilylation is the addition of a Si-H bond in a hydrosilane to an unsaturated substrate in the presence of a catalyst [1-2]. Hydrosilylation is the most common method of forming a Si-C bond. Catalytic hydrosilylation is used for the industrial production of organosilicon compounds which are widely used as polymers, adhesives, and coupling agents [3-4]. Platinum-catalyzed hydrosilylation reactions are well-known and have been known since 1965 [5].

Mo(0) complexes, carbonyl compounds of Mo, have been widely used as pre-catalysts in homogeneous catalysis [6]. These complexes can act as an electron donor and undergo displacement reactions with phosphines and phosphites and therefore, can be utilized in catalysis [7-8]. Commercially available and relatively inexpensive Mo(CO)₆ could be a good candidate, but it demands further studies for using it as an alternative of widely-used transition metal catalysts in hydrosilylation [9]. The catalytic carbonyl hydrosilylation by cationic [CpMo(CO)₂(IMes)]⁺ complex and its mechanism has recently been studied [10]. Recently, molybdenum bis(alkyl) complexes were examined for the catalytic activity in the hydrogenation of some arenes [11]. Hydrosilylation of carbonyl compounds catalyzed by imido-hydride complex of Mo(IV) has also been reported [12]. Previously, we had studied catalytic activity of Mo(0) and Mo(IV) complexes including MoCl₄(CH₃CN)₂, hereafter MoCl₄(MeCN)₂, in epoxidation reaction and it was found to be a good catalyst in terms of regioselectivity and yield of products [13]. MoCl₄(MeCN)₂ is easy to prepare, cost-effective, and can be stored in a glove box for weeks [14]. Because of high solubility in both water and organic solvents, resistance to oxidation, stability in air, moisture, and at room temperature condition, the tertiary phosphine 1,3,5-triaza-7-phosphaadamantane (PTA), has drawn a considerable attention in the area of organometallic chemistry [15-16]. Additionally, as evident from its Tolman cone angle, PTA ligand has a small steric size which makes it prominent candidate for its application in catalytic



organometallic and coordination chemistry [17-18]. Transition metal-PTA complexes have widely been used in catalytic hydrosilylation reactions [19] as well as in a number of other organometallic catalysis [13, 20-23]. Efficiency of some of the catalytic reactions involving the transition metal complexes as pre-catalysts have been found to be enhanced when the complex was mixed with PTA in a certain proportion [24].

Some labile ligands in the Mo-complex are replaced by PTA [25]. The CH_3CN group in $\text{MoCl}_4(\text{MeCN})_2$ is labile and therefore, it may form the reaction intermediate during the catalytic reactions [26]. The homogeneous catalytic activity of the Mo(0) complex, $\text{Mo}(\text{CO})_3\text{Mes}$ was studied in dehydrohalogenation reaction and the catalytic activity was suppressed by the phosphine ligand attached to the metal [27]. Therefore, it seems quite reasonable to anticipate that the opposing reaction such as addition of Si-H to an unsaturated substrate will be favored by the addition of a phosphine to $\text{MoCl}_4(\text{MeCN})_2$. Herein, we report the application of $\text{MoCl}_4(\text{MeCN})_2$ complex as a pre-catalyst for hydrosilylation of alkynes in the presence of PTA.

Materials and Methods

General Comments: Unless otherwise mentioned, the reactions were performed under inert atmosphere of nitrogen using dry glassware on a dual-manifold Schlenk line. The chemicals and solvents were purchased from Sigma-Aldrich Chemical Co. $\text{MoCl}_4(\text{MeCN})_2$ was prepared using the literature procedure [14]. The solvents were used after distillation followed by degassing using freeze-pump-thaw method, then, were stored into the glove box over activated 4Å molecular sieves for at least 24 hours. All other chemicals were stored in the glove box prior to use. NMR spectra were recorded on Bruker Ascend-400 MHz spectrometers at ambient temperature, which was 400 and 100 MHz, for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR respectively. Chemical shifts (δ) were reported relative to the residual deuterated solvent. Coupling constants (J) were reported in Hertz (Hz) and chemical shifts were reported in parts per million (ppm). Gas Chromatography (GC) analysis was carried out on Buck Scientific 310 educational GC with CCD detector. Mass spectrometric analysis was performed on Bruker Esquire 6000 LC-MS spectrometer.

Hydrosilylation of 1-heptyne using Ph_2MeSiH . A sample of 0.384 gm of $\text{MoCl}_4(\text{MeCN})_2$ (20 mol% based on silane) and 0.189 gm of PTA (20 mol% based on silane) were placed in a 100 ml three-necked round bottom flask fitted with a condenser and magnetic stirrer and stirred with 30 ml of toluene and 30 ml of methanol. Then, 0.631 gm (6.60 mmol) of 1-heptyne and 1.20 gm (6.00 mmol) of Ph_2MeSiH were injected into the flask through a syringe. The reaction mixture was refluxed under nitrogen for 12 hours with continuous stirring and monitored periodically by GC. The distillate was collected at 100°C and 1.5 torr pressure after the reaction mixture was distilled under reduced pressure. The product was purified by column chromatography containing silica gel using *n*-hexane and dichloromethane (1:1) as the eluents, then evaporated *in vacuo*. The silylated product was obtained as a colorless oily substance with 25% combined yield (0.220 g, based on silane) having β -*trans* to α isomers' ratio nearly 6:1. ^1H NMR (CDCl_3): δ 7.51-7.39 (m, 4H), 7.31-7.24 (m, 6H), 6.40 (dt, $J = 18.6$ Hz, 6.0 Hz, 1H), 6.10 (dt, $J = 18.4$ Hz, 1.4 Hz, 1H), 2.10 (m, 2H), 1.42-1.15 (m, 8H), 0.81 (m, 3H), 0.52 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 151.9, 137.2, 135.1, 134.9, 129.4, 128.0, 125.2, 37.0, 31.5, 28.5, 22.8, 14.2, -3.3. GC/MS (m/z , %): 294 (10, M^+), 279 (18), 223 (10), 197 (100), 183 (17), 160 (10), 121 (32), 105 (66).

Hydrosilylation of 1,6-heptadiyne using Ph_2MeSiH . A sample of 1.08 gm of $\text{MoCl}_4(\text{MeCN})_2$ (20 mol% based on silane) and 0.529 gm of PTA (20 mol% based on silane) were placed in a 100 ml three-necked round bottom flask fitted with a condenser and magnetic stirrer and stirred with 30 ml of toluene and 30 ml of methanol. Then, 0.774 gm (8.00 mmol) of 1,6-heptadiyne and 3.32 gm (16.8 mmol) of Ph_2MeSiH were injected into the flask through a syringe. The reaction mixture was refluxed under nitrogen for 14 hours with continuous stirring and monitored periodically by GC. The distillate was collected at 95°C and 1.2 torr pressure after the reaction mixture was distilled under reduced pressure. The product was purified by column chromatography containing silica gel using *n*-hexane and dichloromethane (1:1) as the eluents, then evaporated *in vacuo*. The silylated product was obtained as a colorless oily substance with 20% combined yield (1.64 gm) having β -*trans* to α isomers' ratio nearly 7:3. ^1H NMR (CDCl_3): δ 7.71-7.43 (m, 20H), 6.29 (dt, $J = 18.5$ Hz, 6.0 Hz, 2H), 6.06 (dt, $J = 18.5$ Hz, 1.2 Hz, 2H), 2.39-2.23 (m,



4H), 1.63-1.50 (m, 2H), 0.72 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 151.5, 137.1, 135.3, 135.1, 129.2, 128.0, 125.6, 37.0, -3.3. MS (EI^+): m/z (%) 491 [10, ($\text{M}+2\text{H}$) $^+$], 476 (18), 378 (49), 307 (100), 267 (34), 235 (25), 195 (10).

Results and Discussion

The reaction was started with the reaction of a tertiary silane, Ph_2MeSiH with the terminal alkyne, 1-heptyne, in a 1:1 molar ratio. The reaction solution was refluxed in the mixture of toluene and methanol in the presence of the pre-catalyst, $\text{MoCl}_4(\text{MeCN})_2$ and PTA as a co-catalyst. The reaction was started with a lower catalyst loading, however, no reaction occurred. Formation of product was observed as indicated by GC analysis carried out periodically when the catalyst loading of both catalysts was 20 mol% each with respect to the silane. Disappearance of the Si-H and appearance of vinylic proton resonances in the ^1H NMR spectrum also indicated the formation of the products. After 12 hours, only 15% of silane was converted into the products, as indicated by GC. Extended reaction time did not help the conversion and yield. The product was purified by silica gel column chromatography, then characterized by GC, ^1H NMR, and ^{13}C NMR.

Two large resonances for the alkenyl protons were observed as doublet of triplets in the non-first order ^1H NMR spectra at the chemical shifts of 6.40 ppm and 6.10 ppm showing the coupling of different protons; which correspond to the β -*trans* isomer (anti-Markovnikov product). Similarly, a pair of multiplets was shown in the relatively upfield region (5.52 ppm) corresponding to the α -isomer (Markovnikov product), which were minor peaks (Figure 1). As determined by ^1H NMR spectra, the ratio of these two isomers was found to be nearly 6:1.

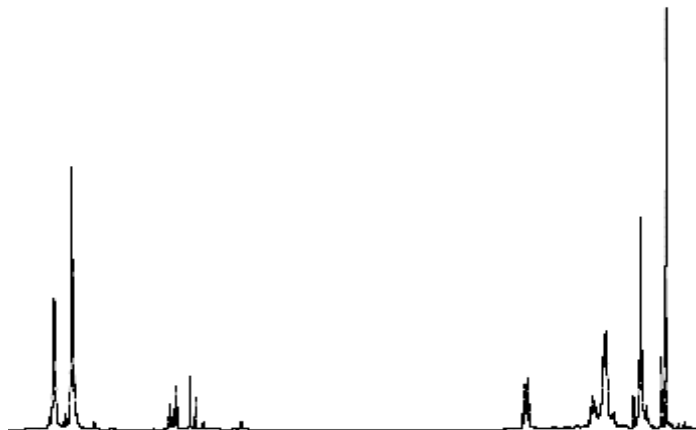
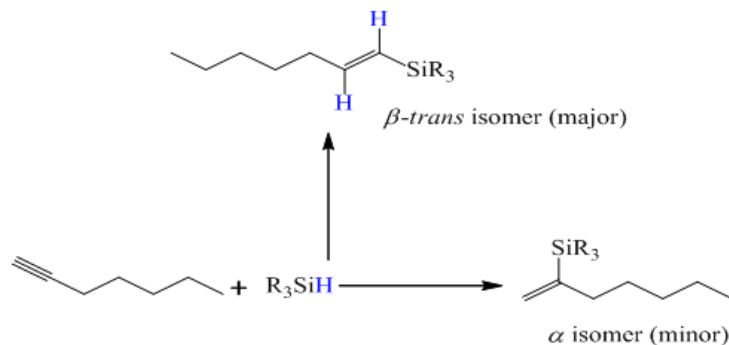


Figure 1: ^1H NMR for the reaction product of Ph_2MeSiH and 1-heptyne

The regioselectivity distribution was as expected since approach of the R_3Si moiety of the silane to the secondary carbon atom of the substrate does not appear to be an easy task because of steric hinderance in the silane (Scheme 1). From the mechanistic point of view, the β -*trans* isomer forms because of *cis* addition of the silane to the metal center in the catalytic cycle whereas the β -*cis* isomer forms due to *trans* addition [5].



Scheme 1: Hydrosilylation products of 1-heptyne [19]



Hydrosilylation of a dialkyne, 1,6-heptadiyne with Ph_2MeSiH in 1:2 molar ratio in the presence of 20 mol% of $\text{MoCl}_4(\text{MeCN})_2$ and 20 mol% of PTA led to the formation of a disilylated product and again, a mixture of β -*trans* isomer and α -isomer in 20% of combined yield and nearly 7:3 ratio after purification by silica gel containing column chromatography (Figure 2). About 25% of the silane was converted into the two disilylated addition products after 14 hours, as shown by GC. Extended reaction time did not assist to improve the yield and conversion significantly. As in the case of 1-heptyne's hydrosilylation, the ^1H NMR spectra exhibited a pair of doublets of triplets for the β -*trans* isomer and two sets of broad multiplets as the minor peaks in the relatively upfield region for the α -isomer. The proton-decoupled ^{13}C NMR as well as LC-MS spectral data were also found to be consistent with the formation of these disilylated products. Also, there was another hardly diagnosable peak observed in GC, which was barely identified in the NMR spectra. This could be most likely due to formation of traces of β -*cis* isomer.

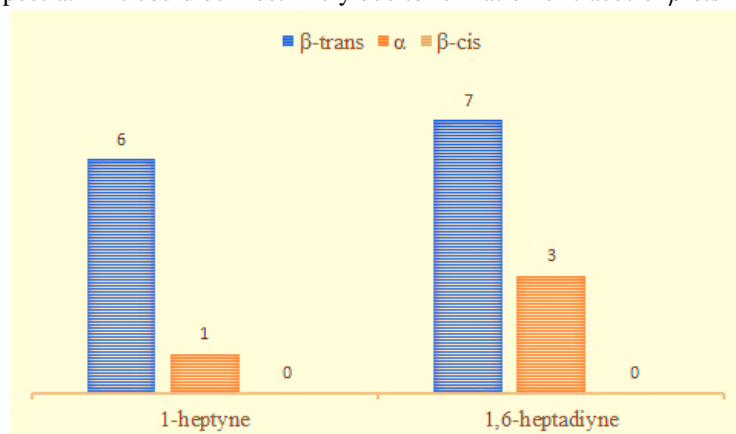


Figure 2: Regioselectivity of different isomers formed by hydrosilylation of alkynes with Ph_2MeSiH , catalyzed by the mixture of $\text{MoCl}_4(\text{MeCN})_2$ and PTA

This regioselectivity, conversion, catalytic turn over number, and yield was better for similar reactions with the terminal alkynes when the traditional catalysts were used [28-29]. The reactions were not possible when the reactions were carried out in the absence of PTA. Although the role of PTA was not clearly understood in these reactions, the enhanced catalytic activity of $\text{MoCl}_4(\text{MeCN})_2$ in the presence of PTA could most likely be due to the formation of a reactive intermediate, that is, an active catalytic species by replacing the labile MeCN ligand by PTA during the course of the reaction [30-31]. The reactivity did not improve when using combination of other solvents such as hexane/methanol or methylene chloride/methanol.

Conclusions

We have investigated the catalytic effect of $\text{MoCl}_4(\text{MeCN})_2$ in the presence of a tertiary phosphine, PTA in the hydrosilylation of 1-heptyne and 1,6-heptadiyne using Ph_2MeSiH . Although the conversion of alkynes and yield of the hydrosilylated product was not very impressive, the regioselectivity of the products was good. As expected, the major product was β -*trans* isomer and minor product was α -isomer. Future-plans focus on investigation of an efficient way for enhancement of the catalytic activity.

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