Synthesis of Tethered Chromium Carbene Complexes

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ABSTRACT

Hydroxycarbene complexes have been proposed as intermediates in industrial processes such as the Fischer-Tropsch process and hydroformylation. We are developing a general method for the synthesis of hydroxycarbenes utilizing tetramethylammonium ion precursors. Specifically we report here the reaction of a biphenyl lithium reagent with chromium hexacarbonyl to give a pentacarbonyl chromium Fischer carbene complex that was isolated as its air-stable tetramethylammonium salt. Prolonged heating led to the formation of the tetramethylammonium precursor of an aryl-tethered dicarbonyl Fischer carbene complex suitable for further functionalization to form tethered alkoxy- or hydroxycarbene derivatives.

INTRODUCTION

The Fischer-Tropsch process combines hydrogen gas and carbon monoxide over a metal or organometallic catalyst to form long chains of bonded carbon atoms, including materials such as gasoline and diesel fuel. Controlling exactly which molecules are formed as major products is one of the main problems in this process. Hydroxycarbenes are thought to be intermediates in the Fischer-Tropsch process. Hydroformylation is an industrial process, catalyzed by organometallic molecules, for converting alkenes in to more complex aldehydes. These aldehydes can then be used in the synthesis of larger, industrially useful molecules. A major problem associated with hydroformylation is the conversion of alkene starting materials into undesirable products through competing side reactions. Acyl hydrides are proposed intermediates in the hydroformylation process.

While most hydroxycarbenes and acyl hydrides that have been synthesized are stable for only short periods of time, a recent report on the synthesis of a hydroxycarbene complex has suggested that incorporation of an alkyl tether between the carbene carbon and another ligand in the complex can stabilize the structure allowing it to undergo slow transformation to its isomeric acyl hydride complex, which is also stabilized by the alkyl tether (Figure 1.)[1]

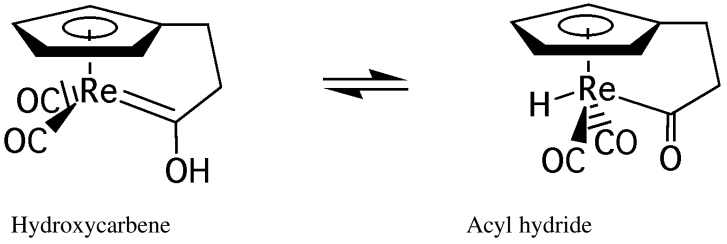

Figure 1: Equilibrium between rhenium hydroxycarbene complex and rhenium acyl hydride complex

This equilibrium is thought to exist due to strain in the hydroxycarbene, introduced by the tether, that can be relieved by rearrangement to the acyl hydride form. This equilibrium could account for some of the problems associated with the hydroformylation and Fischer-Tropsch processes. The overall goal of the current project was to develop a synthetic path for the creation of molecules exhibiting this equilibrium. If knowledge can be gained about how to control the equilibrium, it is hoped the principles can be applied to the hydroformylation and Fischer-Tropsch processes to improve efficiency and increase yield.

RESULTS AND DISCUSSION

Two synthetic pathways were investigated using chromium in place of rhenium since it is somewhat cheaper and was expected to be more air-stable. Pathway A (Figure 2) is the route through which the tethered rhenium molecules were made. This synthesis has progressed to the tosylate stage (structure 2) where it currently remains. NMR spectroscopy of the solid formed at this stage is inconclusive. Either the synthesis failed at this stage or some of the desired product was made but the purification techniques used were not sufficient to isolate the product for characterization through NMR spectroscopy. Extreme air-sensitivity of the molecules and intermediates formed, as well as side reactions that can occur if a –78 °C temperature is not strictly maintained during the addition of n-butyllithium may account for failure of this synthetic route. Further work for this synthesis includes the development of better purification techniques as well as better methods of temperature regulation.

The second pathway investigated for the synthesis of tethered hydroxycarbenes was developed from a pathway reported by Merlic for the synthesis of methoxycarbene **11**, which was repeated during this study to demonstrate the effectiveness of the overall method.[2] This synthesis was altered to create hydroxycarbenes by going through a tetramethylammonium

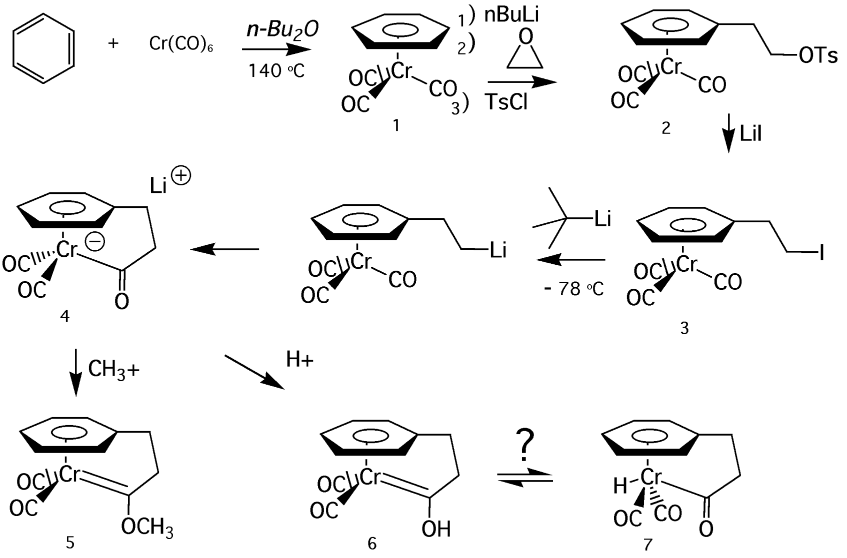

Figure 2: Pathway A for the synthesis of tethered hydroxycarbenes.

intermediate.[3] Pathway B has progressed as far as the untethered tetramethylammonium salt **12**. During reflux, the ring attachment and loss of carbonyls (CO) can be monitored via IR spectroscopy. As the ring attaches to the chromium, electron density is increased on the metal. Some of this added electron density is shifted onto the two remaining carbonyls resulting in lower frequency stretching, measured by IR spectroscopy. An IR spectrum indicating the formation of the desired tethered dicarbonyl carbene **13** from untethered pentacarbonyl carbene **12** would contain two stretching bands (characteristic of dicarbonyls) at lower frequency than the original carbonyl bands for **12**.

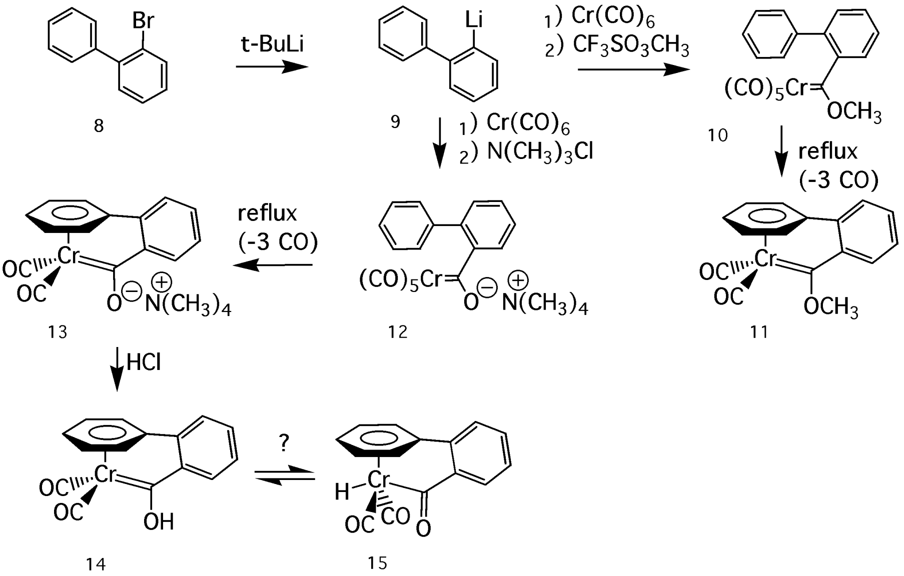

Figure 3: Pathway B for the synthesis of tethered hydroxycarbenes.

After refluxing **12** in THF for 24 h the IR spectrum showed the appearance of two carbonyl stretches at lower frequencies than the original carbonyl stretches, as expected, indicating the tethered product was forming. After 48 h of reflux, the lower frequency carbonyl stretches were absent and a precipitate had formed. These results indicate that either the precipitate is the desired tethered tetramethylammonium intermediate or, reflux was continued too long and any tethered product formed decomposed into starting materials. IR spectroscopy of the precipitate showed carbonyl stretches at the same frequency of those in untethered **12**. This indicates formation of tethered carbene **13** was unsuccessful. NMR spectroscopy of the precipitate was inconclusive due to low solubility. Future work for this pathway includes repetition with closer monitoring of reflux via IR spectroscopy.

CONCLUSIONS

Air sensitivity and time constraints were the major problems associated with this project. All work was done on a Schlenk line using air-sensitive techniques, but it is difficult at best to completely prevent all contamination and these molecules and intermediates are quick to decompose. With time constraints, it was sometimes difficult to characterize and use the molecules and intermediates before they had decomposed.

With further work and technique refinement to combat some of the problems associated with these syntheses, both Pathways A and B have the potential to successfully construct tethered hydroxycarbenes. Pathway B appears to be more promising as transient formation of the tethered intermediate was actually achieved. Pathway B also has the advantage of intermediates and products with greater air stability than Pathway A, and the aryl tether may allow for addition of electron donating or withdrawing groups to probe electronic effects in the hydroxycarbene-acyl hydride equilibrium.

EXPERIMENTAL

All reactions were carried out under nitrogen using standard schlenk line techniques. Diethyl ether and tetrahydrofuran were disilled from sodium bezophenone ketyl under nitrogen. All other reagents were used as received. Infrared spectra were recorded on a Midac PRS-102 Infrared Spectrometer.

[(1,1'-Biphenyl-2-yl)methoxymethylene]pentacarbonylchromium (10).

A 1.7 M pentane solution of *tert*-butyllithium (2 mL, 3.4mmol) was added to a solution of 2-bromobiphenyl (0.2956 g, 1.27 mmol) in ether (20 mL), and the milky solution was stirred for 1 h at –78 °C and then 0.5 h at 0 °C. The resulting yellow solution was transferred via syringe to a solution of chromium hexacarbonyl (0.3613 g, 1.64 mmol) in ether (20 mL) at room temperature. The yellow orange solution was stirred for 0.5 h after complete addition and then cooled to 0 °C. A saturated aqueous sodium bicarbonate solution was added (2 mL) to the dark orange-red solution turning the mixture pumpkin-orange and forming a precipitate. After rapid addition of methyl triflate (0.20 mL, 1.77 mmol) the reddish-brown mixture was stirred at room temperature for 0.5 h during which time the precipitate went into solution. The reaction was quenched with saturated aqueous sodium bicarbonate solution (10 mL) and saturated aqueous potassium carbonate solution (5 mL). The organic layer was separated and the solvents were removed under vacuum. Silica gel column chromatography (95:5 hexane:ethyl acetate) gave 10 as a broad red-orange band (0.355 g, 72 %.) IR (THF; CO only): 2063 (w), 1948 (vs) cm^{-1}.

{[(1',2',3',4',5',6'-η)-1,1'-Biphenyl-2-yl]methoxymethylene}-dicarbonyl-chromium (11)

A solution of 10 in THF was refluxed for 24 h. Solvent was removed under vacuum. Since this synthesis was performed only to prove competency in the method, purification was not performed and yield was not determined. IR (THF; CO only): 1911, 1850 cm^{-1}.

Tetramethylammonium salt (12)

A 1.7 M pentane solution of tert-butyllithium (5 mL, 8.5 mmol) was added to a solution of 2-bromobiphenyl (1.0344 g, 4.44 mmol) in ether (20 mL), and the milky solution was stirred for 1 h at –78 °C and 0.5 h at 0 °C. The resulting yellow solution was transferred via syringe to a solution of chromium hexacarbonyl (1.0863 g, 4.94 mmol) in ether (20 mL) at room temperature. The solution was stirred for 0.5 h after complete addition. Solvent was removed under vacuum leaving 5 mL behind to which water was added (15 mL). An aqueous tetramethylammonium chloride solution was added until yellow-orange precipitate ceased to form4. Methylene chloride (10 mL) was added to the solution dissolving the precipitate. The organic layer was drawn off and solvent removed under vacuum yielding 1.27 g (64%) of crude product. IR (THF; CO only): 2031 (sh), 2032 (sh), 1977 (vs), 1904 (vs), 1879 (sh) cm^{-1}.

Tethered tetramethylammonium salt (13)

A solution of complex (3) (1.27 g) was refluxed in THF (20 mL) for 48 h, a black precipitate began to form after 24 h. Solvent was removed under vacuum. IR (THF; after 24 h reflux; CO only): 1979 (vs), 1941 (s), 1907 (s), 1858 (m) cm^{-1}. IR (THF; after 48 h reflux; CO only): 1979 (vs), 1895 (vs) 1778 (m), 1725 (s) cm^{-1}. IR (KBr pellet; precipitate; CO only): 1964 (m), 1186 (m) cm^{-1}.

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