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The ring expansion of a dimethyl-substituted vinylcyclobutene derivative by metal complexes that can undergo an inner-sphere electron transfer

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Abstract

The ring expansion of a dimethyl-substituted vinylcyclobutene derivative to the corresponding dimethyl-substituted cyclohexadiene or aromatic compound was studied. It was found that metal complexes of Ni(I), Ti(III), Sm(II), and Fe(II), which can undergo an inner-sphere electron-transfer reaction, allow the rearrangement to occur at room temperature. Other oxidation states of these metals and complexes that can only undergo an outer-sphere electron-transfer process do not promote this ring expansion reaction. © 2000 Elsevier Science S.A. All rights reserved.

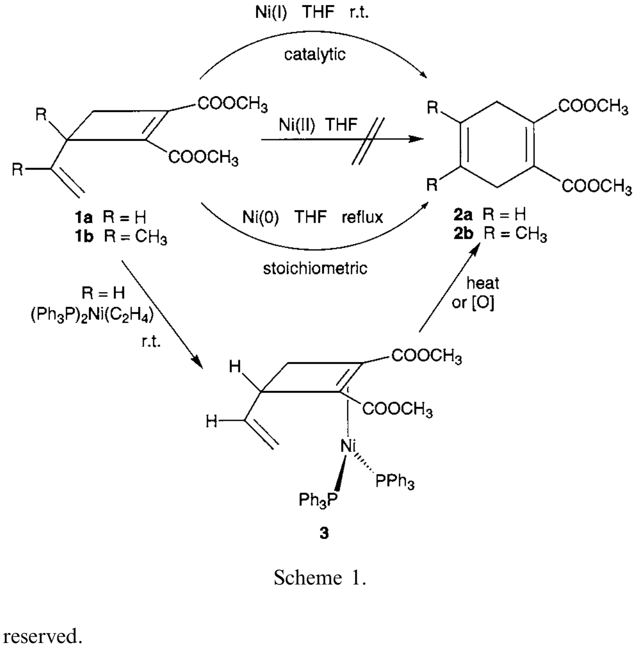
Keywords: Rearrangement reaction; Inner-sphere electron transfer; Ring expansion

1. Introduction

Over the past several years, we have studied the nickel-promoted ring expansion of vinylcyclobutene derivatives **1** to cyclohexadiene derivatives **2** [1–3]. Scheme 1 summarizes our results. (1) When compound **1** is treated with a Ni(II) complex, no reaction occurs and starting compound **1** can be re-isolated. (2) When compound **1** is treated with a stoichiometric amount of a Ni(0) complex, compound **2** is generated, but only at elevated temperatures (e.g. refluxing THF or benzene). (3) In contrast, when compound **1** is treated with a Ni(I) complex, the rearrangement reaction is catalytic in nickel and occurs at room temperature.

In the case in which R = H (compound **1a**) and the Ni(0) complex is $(Ph_3P)_2Ni(C_2H_4)$, complex **3** can be isolated when the reaction is performed at room temperature under an inert atmosphere. Complex **3** can be converted to compound **2a** either at elevated temperature by refluxing in THF, or at room temperature by reacting complex **3** with a mild oxidant such as air, $(Ph_3P)_2NiBr_2$, or Cp_2Fe^+. A strong oxidant such as I_2 converts complex **3** back to compound **1a** [2].

One possible explanation of why the Ni(I) reaction is catalytic and the Ni(0) reaction is not catalytic is that the Ni(0) complex decomposes under the higher-temperature conditions required for this reaction. Our evidence for this decomposition includes the fact that



Scheme 1.

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$$R_3P + NiCl_2 \longrightarrow (R_3P)_2NiCl_2 \xrightarrow{BuLi} (R_3P)_2Ni(C_4H_8)$$

Scheme 2.

unreacted nickel complex cannot be isolated from the reaction mixture, the formation of solids as the reaction progresses, and in some cases, the formation of a nickel mirror on the glassware. The decomposition of the metal complex leads to the question: is it really Ni(0) that is causing the rearrangement to occur at elevated temperatures, or is the Ni(0) generating small amounts of Ni(I) and it is Ni(I) that is catalyzing the reaction?

In this article, we shall show that Ni(0) simply is a source of Ni(I) and that Ni(I) causes the rearrangement reaction to occur. In addition, we shall show that other metal complexes that can be oxidized easily *by an inner sphere process* cause similar rearrangement reactions to occur.

2. Synthesis of starting materials

In our previous work, as mentioned in Scheme 1, we used the complex $(Ph_3P)_2Ni(C_2H_4)$. Unfortunately, the synthesis of this nickel complex is very time consuming. In addition, the complex is very air sensitive and cannot be stored for extended periods. For the research discussed in this manuscript, we have employed the analogous butene complex, $(Ph_3P)_2Ni(C_4H_8)$, which, as shown in Scheme 2, is much easier to synthesize [4] and duplicates all of the chemistry of the ethylene complex. This chemistry is not restricted to only triphenyl phosphine as a ligand, the butyl phosphine analog, $(Bu_3P)_2Ni(C_4H_8)$, can be synthesized in a similar manner and works well in all of our nickel chemistry.

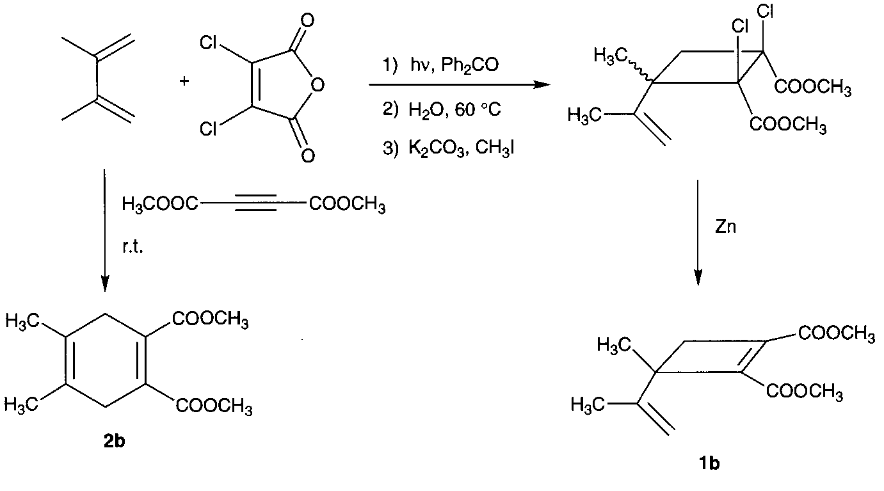
The titanium(III) complex Cp_2TiCl [$Cp = \eta^5\text{-}C_5H_5$] (which is green in solution) was prepared by a zinc reduction of the readily available titanium(IV) complex Cp_2TiCl_2 (which is red in solution) [5]. The titanium(II) complex Cp_2Ti was prepared by a butyllithium reduction of Cp_2TiCl_2 [6]. The complex $TiCl_3$ can be prepared by a zinc reduction of the titanium(IV) complex $TiCl_4$ [7], or is commercially available. The complexes SmI_2, $SmCl_3$, $FeCl_2$, $FeCl_3$, and Cp^*_2Fe [$Cp^* = \eta^5\text{-}C_5(CH_3)_5$] are all commercially available.

Organic compound **1b** ($R=CH_3$) was synthesized in a manner similar to that previously reported for compound **1a** [2], except 2,3-dimethylbutadiene was used in place of butadiene in the photoreaction (Scheme 3). Significant improvements in two of the steps have made the synthesis easier. Firstly, for the esterification step, we have found that simply adding a weak base and methyl iodide generates the ester in good yield [8]. More importantly, we have found that the dechlorination reaction can be accomplished by using zinc, rather than with the expensive nickel complex $(Ph_3P)_2Ni(C_2H_4)$. However, this process works only if the zinc is activated by removing the oxide coating with a sulfuric acid wash. After the acid wash, the zinc then must be rinsed with water to ensure that all the acid is removed, and then rinsed with dry THF to insure that all the moisture is removed.

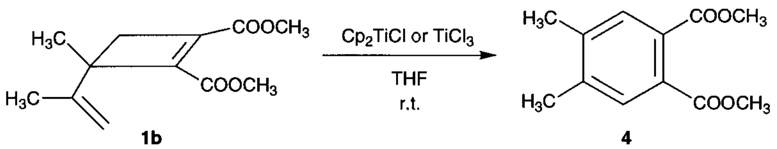
Also, as shown in Scheme 3, an authentic sample of compound **2b** was easily synthesized from a Diels–Alder reaction of 2,3-dimethylbutadiene and dimethyl acetylenedicarboxylate.

3. Ni(I) or Ni(0) as the active metal complex

To determine if Ni(0) is simply generating Ni(I), which in turn is causing the rearrangement to occur, we needed a method to quench immediately any Ni(I) that could be forming under the reaction conditions by reducing it back to Ni(0). If all the Ni(I) is reduced and



Scheme 3.



Scheme 4.

the rearrangement reaction still occurs, then both Ni(I) and Ni(0) are active metal complexes for this reaction. In contrast, if reducing all the Ni(I) to Ni(0) stops the rearrangement reaction, then the most straightforward explanation is that Ni(I) is the only oxidation state of the nickel which is active for this reaction.

Previously [2], we have shown that decamethyl ferrocene [Cp_2^*Fe, $Cp^* = \eta^5$-$C_5(CH_3)_5$] will reduce Ni(I) to Ni(0) but that decamethyl ferrocinium [$Cp_2^*Fe^+$] will not oxidize Ni(0) to Ni(I). A major concern was the relative rate of the reduction of Ni(I) in comparison to the rate of the rearrangement reaction. For this reaction to be successful, Cp_2^*Fe must reduce Ni(I) to Ni(0) faster than the Ni(I) catalyzes the rearrangement reaction. Given the approximate relative rates of these two reactions, which are based on the length of time each reaction must stir to obtain a good yield (less than an 1 h for the reduction reaction and overnight for the rearrangement reaction), we felt confident that the reaction rates were in our favor.

When compound **1b** and either the butyl or the phenyl bis(phosphine)nickel butene complex [$(R_3P)_2Ni(C_4H_8)$] were mixed in THF and heated to reflux overnight, compound **2b** was obtained. In contrast, when the same reaction was run with the addition of Cp_2^*Fe, for the same or even for a longer period of time, not even a trace of compound **2b** or any other product could be detected by gas chromatography. As a control experiment, the reaction of compound **1b** and Cp_2^*Fe was run under similar conditions and again not even a trace of compound **2b** or any other product could be detected.

Therefore, under reaction conditions such that all the Ni(I) is reduced to Ni(0), no rearrangement reaction occurs. Therefore, it was concluded that Ni(I) is causing the rearrangement of **1** to **2**. Simply put, Ni(0) is nothing more than a source of Ni(I). (For a subsequent section of this manuscript, it is important to note that Cp_2^*Fe does not cause a rearrangement reaction to occur.)

4. Titanium-promoted rearrangement

We next decided to try another odd-electron species, Ti(III), to see if it would cause a similar rearrangement of compound **1b**. Ti(III) was chosen because it is known to initiate other radical-type reactions [9]. When compound **1b** was treated at room temperature with either Cp_2TiCl or $TiCl_3$ as the Ti(III) complex, as shown in Scheme 4, aromatic compound **4** was obtained in about a 75% yield. (The remainder of the material is mainly unreacted starting material **1b**.) Control experiments show:

1. As with Ni(II), the Ti(IV) complex Cp_2TiCl_2 does not catalyze nor promote any reaction.
2. Zn, which is used to reduce Ti(IV) to Ti(III), and $ZnCl_2$, the by-product of the reduction reaction, were found to have no effect on compound **1b**.
3. The yield of compound **4** for the Cp_2TiCl reaction is approximately the same whether or not the Zn and $ZnCl_2$ are filtered off prior to the reaction of Cp_2TiCl with compound **1b**.
4. The Ti(II) complex Cp_2Ti was found to be too strong a reagent. When **1b** was subjected to Cp_2Ti, only intractable materials were observed.

To test whether compound **2b** could be an intermediate in this conversion, **2b** was put under the same Ti(III) reaction conditions and was found to aromatize faster than compound **1b** converts to compound **4**. Thus, Ti(III) causes chemistry similar to that observed with Ni(I) to occur; however, Ti(III) is not catalytic due to the net oxidation of the cyclohexadiene to the aromatic product.

5. Samarium-promoted rearrangement

Next, we decided to try SmI_2 and $SmCl_3$. In contrast to the nickel and titanium cases in which a complex with an odd number of electrons on the metal causes the rearrangement to occur, when compound **1b** was treated with the odd electron Sm(III) complex, no reaction was observed. However, when SmI_2 and **1b** reacted at room temperature, aromatic compound **4** was obtained in an even higher yield than with titanium. Thus, it seems that it is not whether the active metal has an even or an odd number of electrons that determines if it will cause the rearrangement reaction to occur, but if the metal has a readily available next higher oxidation state.

6. Iron-promoted rearrangement

To further investigate the 'next higher oxidation state theory', we needed another metal with a readily available pair of oxidation states in which the lower oxidation state has an even number of electrons on the metal. Although an obvious choice is Fe(II), as discussed above, Cp_2^*Fe, which is an Fe(II) complex, does not react with compound **1b**. However, due to the reactivity of the titanium and samarium halides, we decided to try the iron halides anyway.

As expected, when compound **1b** was treated with $FeCl_3$ at room temperature, no reaction occurred. When the $FeCl_3$ was treated with the activated zinc, to generate Fe(II), prior to the addition of compound **1b**, compound **2b** was formed in addition to small amounts of two cyclohexadiene double bond isomers. (The reaction of 1,4-cyclohexadiene **2b** with $FeCl_3$ and Zn generates the exact same mixture of these three cyclohexadiene isomers.) Thus, $FeCl_2$ will cause the rearrangement reaction to occur but not Cp_2^*Fe. This suggests that the electron transfer must be an inner-sphere process because the ferrocene derivatives are known to undergo only outer sphere processes [10].

7. Other evidence for an inner-sphere process and a proposed mechanism

There are a number of reported cases [11] in which electrochemical reduction of a metal complex causes an isomerization reaction to occur more easily. However, this is not one of them. Previously [2], we have shown that compound **1a** is very difficult to reduce and that when it is reduced electrochemically, only high molecular weight compounds are observed. Similarly, a potassium naphthalide reduction of compound **1b** only generates intractable materials. Combining these results with the decamethylferrocene result, we believe that an inner-sphere electron transfer process is necessary for the isomerization of **1** to **2**. Other metal complexes with readily available next higher oxidation states and which can undergo an inner-sphere process, e.g. Cu(I) and Cr(II), are under investigation.

8. Experimental

8.1. General procedure

All reactions were carried out with oven-dried (120°C) glassware, under an argon atmosphere. Photoreactions were carried out using a Rayonet photoreactor employing 350 nm bulbs and Pyrex reaction tubes. Solvents were purchased from Fisher Scientific and were freshly distilled from potassium metal. The complexes $(Ph_3P)_2Ni(C_4H_8)$, Cp_2TiCl, Cp_2Ti, and $TiCl_3$ were prepared by literature methods [4–7]. All other reagents were purchased from Aldrich, Fluka, or Strem and used without further purification.

All IR spectra were recorded on a Perkin–Elmer 1600 Series FTIR spectrophotometer using KBr or CaF_2 cells. All NMR spectra were recorded on a Bruker 250-MHz spectrometer and referenced to TMS at 0.00 ppm, deuterated chloroform was the solvent unless otherwise noted. Mass spectra were obtained on a Hewlett–Packard 6890 GC/MS instrument using a Supelco SPB-1 column and temperature programming.

*8.2. Spectral data for compound **1b***

^{1}H-NMR: δ 1.50 (s, 3 H), 1.73 (s, 3 H), 2.55 (dd, $J = 30$, $J = 14.9$ Hz, 2 H), 3.79 (s, 6 H), 4.78 (s, 1 H), 4.80 (s, 1 H); ^{13}C-NMR: δ 19.5, 21.9, 41.6, 50.1, 51.9, 110.8, 127.1, 127.2, 128.7, 188.3; IR (neat): 3021 (w), 2951 (s), 2870 (m), 1735 (vs), 1653 (m), 1431 (s), 1261 (s), 1214 (s) 1068 (s) cm^{-1}; MS (*m*/*z*): 224 (0.8%), 192 (32%), 177 (37%), 165 (20%), 133 (49%), 105 (100%), 91, (73%), 77 (44%), 65 (34%), 59 (68%).

*8.3. Spectral data for compound **2b***

^{1}H-NMR: δ 1.66 (s, 6 H), 2.88 (s, 4 H), 3.78 (s, 6 H); ^{13}C-NMR: δ 28.1, 52.6, 66.1, 121.2, 132.6, 171.0; IR (THF): 2895 (s), 1740 (vs), 1437 (s), 1260 (s), 1043 (s) cm^{-1}; MS (EI): 224 (1%), 192 (50%), 177 (80%), 106 (33%), 91 (30%), 77 (100%), 71 (44%), 59 (66%).

*8.4. Spectral data for compound **4***

^{1}H-NMR: δ 1.74 (s, 6 H), 3.71 (s, 6 H), 7.77 (s, 2 H); ^{13}C-NMR: δ 15.3, 50.1, 128.6, 130.2, 143.0, 167.1; IR (THF): 2993 (m), 1750 (vs), 1645 (s), 1455 (s), 1267 (s), 1070 (s) cm^{-1}; MS (EI): 222 (3%), 207 (10%), 190 (30%), 163 (90%), 105 (45%), 96 (29%), 75 (100%), 59 (60%).

8.5. Preparation of activated zinc

To zinc dust (4.0 g, 62 mmol) in a 50 ml Erlenmeyer flask with a stir bar was added 10% sulfuric acid (20 ml), and this mixture was stirred. When the zinc formed a sponge-like solid (after about 10 min), the sulfuric acid was decanted off. The remaining zinc was washed with water until the rinse water was no longer acidic. The moist zinc was washed several times with distilled THF to dry the zinc. The remaining THF was removed by a stream of Ar gas or in vacuo. The zinc is now activated, and should be stored as a solid in a glove box or made into a slurry using freshly distilled solvent.

*8.6. Synthesis of **1b***

To a thick-walled phototube was added dichloromaleic anhydride (1.87 g, 11.1 mmol) and benzophenone

(0.15 g, 0.82 mmol) under an inert atmosphere. To the phototube was added THF or acetonitrile (21 ml). The mixture was purged with argon for 10 min. To the purged solution was added 2,3-dimethyl-1,3-butadiene (2.0 ml). The phototube was then sealed, placed in a Rayonet reactor, and irradiated for 88 h. The volume of the reaction solution was then reduced in vacuo. Then 60°C water was added and the solution stirred for 10 min. The resulting mixture was made basic with 2N sodium hydroxide, then extracted with ether (4×25 ml). The aqueous portion was made acidic with 10% sulfuric acid, and extracted with ether (4×20 ml). The combined ether layers were dried with magnesium sulfate, filtered, and concentrated to yield the diacid (2.47 g, 9.25 mmol) in 83% yield from the anhydride.

In a round-bottomed flask, equipped with a stir bar, was added the newly formed diacid (2.47 g, 9.25 mmol). The diacid was dissolved in DMF (21 ml), and then reacted with potassium carbonate (5.31 g, 38.4 mmol). After stirring for 5 min, methyl iodide (10.0 ml, 177 mmol) was added. The combined mixture was stirred at room temperature for 30 h. The resulting mixture was added to water (50 ml). The bottom viscous layer was removed and saved as an organic layer. The remaining layer was extracted with ether (2×20 ml). The combined ether extracts were combined with the organic layer which was removed initially, and washed with brine (2×20 ml). The organic layer was dried with anhydrous potassium carbonate, filtered, and concentrated, yielding a diester (1.56 g, 5.29 mmol) in 57% yield.

Five ml of 1,4-dioxane was added to a 10 ml pear-shaped flask containing a magnetic spin bar. The dichloro diester (0.25 g, 0.85 mmol) was added by Pasteur pipet. The oil was stirred until it dissolved. Argon gas was bubbled through the solution for 2 min. The flask was then sealed with a rubber septum. Then, 0.50 ml (0.25 g, 3.8 mmol) of a zinc–hexane slurry was added to the flask through the rubber septum. The mixture was stirred for 5–6 h at r.t. The mixture was allowed to settle without stirring for at least 30 min. The liquid was removed from the flask via a syringe and placed in a argon filled 2 dram vial. The vial was spun down in a centrifuge for 2 min at high speed. The liquid was transferred to a 5 ml flask and the solvent was removed. The yield of compound **1b** was nearly quantitative (0.188 g, 0.84 mmol).

*8.7. Synthesis of authentic **2b***

Forty milliliters of freshly distilled THF was placed in an 100 ml Erlenmeyer flask with a magnetic stir bar. Dimethyl acetylenedicarboxylate (2.88 g, 20.3 mmol) was added and the mixture stirred until the acetylene dicarboxylate was dissolved. The mixture was added to a thick-walled phototube under an argon atmosphere. Then, 2,3-dimethylbutadiene (1.64 g, 19.5 mmol) was added to the tube. The tube was then sealed and the solution was allowed to react for 6 days at r.t. The contents of the tube were poured into a 100 ml flask, and the solvent and unreacted diene were removed in vacuo. Compound **2b** was isolated (4.02 g, 17.8 mmol, 88% yield).

*8.8. Nickel-promoted rearrangement of **1b** to **2b***

In a three-neck round-bottomed flask containing a stir bar was added bis(triphenylphosphine)nickel dichloride (0.66 g, 1.0 mmol) and THF (30 ml). The resulting slurry was cooled to ice-bath temperatures, and butyllithium (1.6 M, 1.25 ml, 2.00 mmol) was slowly added over the period of 1 min via a syringe. The resulting solution was stirred at 0°C for 15 min. Vinylcyclobutene (**1b**) (0.24 g, 1.1 mmol) was added to the newly formed nickel(0) complex. The resulting solution was allowed to reflux 19 h. GC–MS analysis of this solution showed the formation of compound **2b**.

Alternatively, in a three-neck round-bottomed flask containing a stir bar was added nickel dichloride ($NiCl_2$) (0.18 g, 1.4 mmol), THF (15 ml), and tri-*n*-butylphosphine (0.7 ml, 2.5 mmol). This mixture was allowed to stir at r.t. for 1.5 h (a slight modification of the literature procedure [4]). The solution then was cooled 0°C and butyllithium (1.6 M, 1.25 ml, 2.00 mmol) was added slowly over a period of 1 min via a syringe. The resulting solution was stirred at 0°C for 10 min. The nickel–butene complex was then added via cannula to compound **1b** (0.305 g, 1.36 mmol) and the mixture was refluxed. The reaction was monitored by GC.

For the reactions with added decamethylferrocene, the ferrocene (0.23 g, 7.0 mmol) and compound **1b** were mixed together prior to the addition of the nickel–butene complex. For these reactions, GC–MS analysis showed no formation of compound **2b** or any other new compound even when the solution was allowed to reflux 39 h.

*8.9. Reaction of titanium, samarium, iron, or potassium naphthalide with compounds **1b** and **2b***

Ten millilters of 1,4-dioxane was added to a 25 ml flask containing a magnetic stir bar. Either compound **1b** (0.25 g, 1.1 mmol) or compound **2b** (0.25 g, 1.1 mmol) was added and stirred under an argon atmosphere for 10 min to complete solution. The flask was then sealed with a rubber septum. Two milliliters of zinc suspension (0.2 g ml^{-1}, 0.4 g, 6 mmol) in hexane, as prepared above, was added by syringe to the flask. Biscyclopentadienyl titanium dichloride (Cp_2TiCl_2) (0.25 g, 1.0 mmol) dissolved in 2 ml of 1,4-dioxane was added by syringe in the same way as the zinc suspension. When commercially available $TiCl_3$, SmI_2, or $SmCl_3$, were used or when potassium naphthalide was used, the solution was removed from the stock bottle using cannula techniques to exclude air. The zinc addition was eliminated. When $FeCl_3$ was used, the zinc step was not included for the iron(III) reaction and was included for the iron(II) reaction. The mixture was allowed to react for 240 h at r.t. with constant stirring. Either samples were taken at 48 h intervals for GC–MS monitoring, or at the end of the reaction, the solution was worked-up by adding 20 ml of water and then extracting the water with ether. The ether extracts were combined, dried with Na_2SO_4, and the solvent was removed.

8.10. Amounts and yields for the above reactions

1b with $TiCl_3$ (1.0 M, 2.0 ml, 2.0 mmol), yield = 0.190 g, 0.86 mmol, 78%; **2b** with $TiCl_3$ (1.0 M, 2.0 ml, 2.0 mmol), yield = 0.179 g, 0.81 mmol, 74%; **1b** with Cp_2TiCl_2 (0.20 g, 0.80 mmol), yield = no reaction; **2b** with Cp_2TiCl_2 (0.20 g, 0.80 mmol), yield = no reaction; **1b** with SmI_2 (1.0 M, 1.0 ml, 1.0 mmol), yield = 0.193 g, 0.87 mmol, 79%; **2b** with SmI_2 (1.0 M, 1.0 ml, 1.0 mmol), yield = 0.189 g, 0.85 mmol, 77%; **1b** with $SmCl_3$ (0.2 g, 0.78), yield = no reaction; **2b** with $SmCl_3$ (0.2 g, 0.78), yield = no reaction; **1b** with $FeCl_3$ (0.20 g, 1.2 mmol), Zn (0.20 g, 3.1 mmol), yield = 0.133 g, 0.60 mmol, 55%; **2b** with $FeCl_3$ (0.20 g, 1.2 mmol), Zn (0.20 g, 3.1 mmol), yield = 0.25 g, 1.1 mmol, 100%; **1b** with $FeCl_3$ (0.20 g, 1.2 mmol), yield = no reaction; **2b** with $FeCl_3$ (0.20 g, 1.2 mmol), yield = no reaction; **1b** with $K^+C_{10}H_8^-$ (0.30 g, 1.8 mmol), yield = intractable solids.

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