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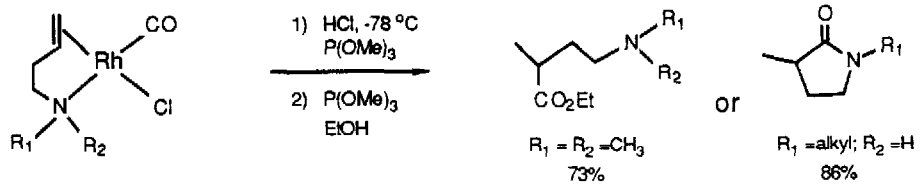
RHODIUM COMPLEXES OF TRISUBSTITUTED OLEFINS: *SYN* SELECTIVE DIRECTED HYDROCARBOXYLATION

Marie E. Krafft
Department of Chemistry
Florida State University, Tallahassee, Florida 32306-3006

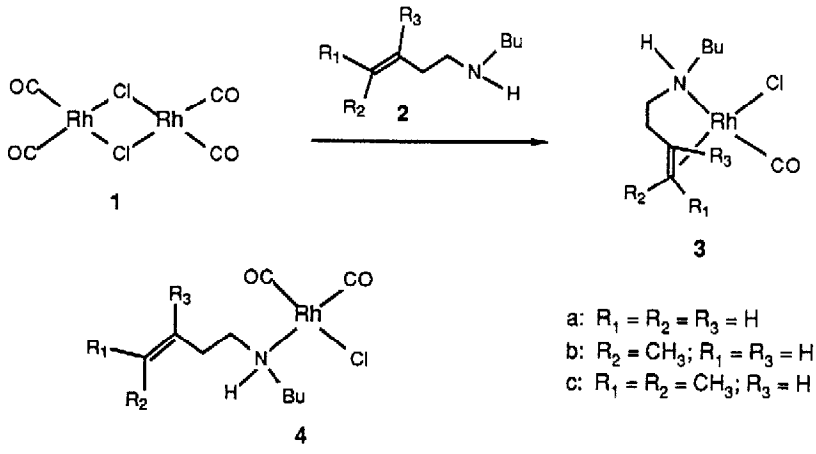
Summary: *Use of [di-μ-chloro(diethylene)(dicarbonyl)dirhodium(I)] allows for the formation of bidentate trisubstituted olefinic amine complexes which could not be prepared from the analogous tetracarbonyl complex. These trisubstituted olefin complexes allow for the verification of the syn selectivity in the directed hydrocarboxylation reaction.*

Recently we reported an amine directed, rhodium promoted, olefin hydrocarboxylation reaction (eq 1).[1,2] The reaction was highly regioselective, however, we were unable to demonstrate its stereoselectivity due to problems with the formation of the required Rh(I) complexes of appropriately trisubstituted olefins. We now report that Rh(I) complexes of trisubstituted olefinic amines can be prepared and that these new complexes allow us to demonstrate the *syn* selectivity of the directed hydrocarboxylation.



(1)

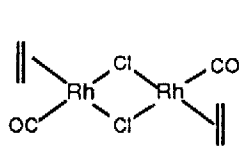
A series of bidentate rhodium(I) complexes, **3**, were prepared by the reaction of di-μ-chloro(tetracarbonyl)dirhodium(I)[3] (**1**) with a number of substituted olefinic secondary and tertiary amines in hexane/CH_2Cl_2 at ambient temperature or in refluxing $CHCl_3$ (eq 2). These complexes have been fully characterized and X-ray crystallographic analysis shows that the carbon monoxide ligand is *cis* to the olefin.[4] A plausible mechanistic rationale for the formation of **3** incorporates two steps. Cleavage of the Rh(I) chloro-bridged dimer by 3-butenyl butylamine (**2a**) should give a monomeric dicarbonyl complex **4a**. Primary or secondary monoamines are known to cleave the chloro bridge of **1** to give 4-coordinate amine complexes analogous to the dicarbonyl complex **4**.[5] Subsequent displacement of the carbon monoxide ligand by the alkene, probably via a 5-coordinate associative mechanism,[6] yields the bidentate Rh(I) complex **3**. This two step mechanism is supported by the isolation of complex **4b** from the reaction of **1** with *cis*-3-pentenyl butylamine (**2b**) in hexane at ambient temperature. Refluxing a $CHCl_3$ solution of **4b** for 24 h was required for the complete conversion of **4b** to **3b** in 95% yield.



(2)

The acyclic trisubstituted olefin **2c**, (R_1=R_2=CH_3; R_3=H), reacted with complex **1** to give **4c** in good yield, however, attempted conversion of the monodentate dicarbonyl complex **4c** to the bidentate ligand complex **3c** led only to decomposition of **4c** (Rh metal precipitated) with no evidence for the formation of any of the desired bidentate ligand complex. We reasoned that the poor kinetic lability of the carbon monoxide ligand was responsible for the low reactivity of **4c** (R_1=R_2=CH_3; R_3=H) toward carbon monoxide displacement by the more sterically hindered olefin, and, that replacement of one of the carbon monoxide ligands on **4** with a more labile ligand would allow for a more facile ligand exchange.

Accordingly, substitution of two of the CO ligands on complex **1** with ethylene, as described by Shaw,[7] gave rise to the dimeric complex [di-μ-chloro(diethylene)(dicarbonyl)dirhodium(I)] (**5**). Treatment of **5** with the trisubstituted olefinic amine **2c** (R_1=R_2=CH_3; R_3=H) in CH_2Cl_2 at ambient temperature for 10 minutes yielded the anticipated bidentate olefin complex **3c**. However, the Rh(I) bidentate complex **3c** was stable for only short periods of time in solution. This instability, apparently due to the decomplexation of the sterically hindered olefin, prevented any purification of the complex. Several other terminally disubstituted olefin Rh(I) complexes behaved in a similar fashion. These complexes were 90 - 95% pure as determined by ^{1}H NMR analysis and could be used without further purification in the hydrocarboxylation reaction.[1] The use of complex **5** also facilitated the preparation of other olefin complexes. Two complexes, **3b**[4] and **7**,[4] which were formed only after refluxing in $CHCl_3$ for up to 24 h when prepared starting with **1**, were formed in 87% and 92% yields respectively upon reaction of *cis* 3-pentenyl butylamine or 4-pentenyl butylamine with **5** at ambient temperature for 10 min. Unfortunately, reaction of complex **5** with 5-hexenyl butylamine did not give rise to the homolog of complex **7**. Rhodium (I) complex **6**, which we were unable to prepare by reaction with complex **1**, was formed in 77% yield upon reaction of the corresponding amine with **5** for 10 min at ambient temperature.



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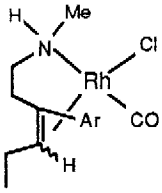

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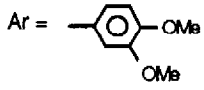

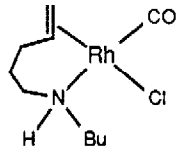

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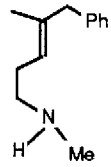
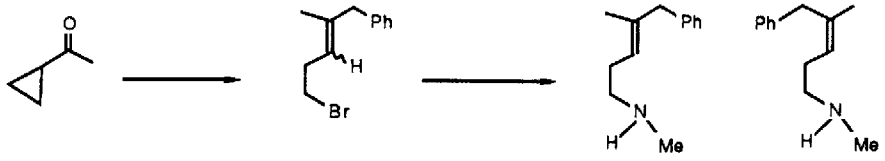


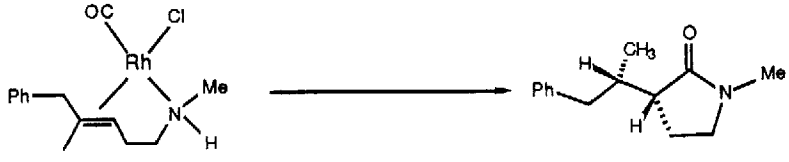
8E

To determine the stereochemical outcome of the directed hydrocarboxylation, we required a trisubstituted olefin with different groups at the terminus of the olefin. Olefin **8E** was chosen as a suitable candidate and was prepared by using the procedure of Julia,[8] as outlined in eq 3. Treatment of cyclopropyl methyl ketone with benzylmagnesium bromide (-78 °C, ether) followed by rearrangement of the resulting cyclopropyl carbinol with 48% HBr at 0 °C gave rise to an inseparable mixture of homoallylic bromides (E/Z : 5/1) in 85% yield. Subsequent reaction of the bromo olefins with an excess of methylamine (resealable tube, ether, 36h, ambient temp) yielded a mixture of olefinic amines (98% yield). Separation of the isomers was achieved by



E:Z 5:1 **8E** **8Z** (3)

recrystallization of the amine hydrochlorides (Ether, HCl; EtOAc). Treatment of complex **5** with amine **8E** gave the desired complex **9** which, not unexpectedly, was stable for only short periods of time in solution at ambient temperature. Spectral characterization of **9** followed by subjecting it to the previously described hydrocarboxylation conditions[1,9] provided lactam **10** in 49% yield. No other lactam isomers were observed in the ^{1}H NMR spectrum of the crude reaction mixture. Extensive NOE experiments with **10** verified the stereochemistry as shown, which clearly resulted from a *syn* addition across the double bond.[10]



9 **10**

Further investigations on the synthetic utility of the Rh(I) complexes are in progress and the results will be reported in due course.

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9. Typical experimental procedure: To a solution of 31 mg of Rh(I) complex **5** (0.154 mmol in 1.5 mL of CH_2Cl_2 at ambient temperature was added 29 mg of olefinic amine **8E** (0.154 mmol) in CH_2Cl_2. The resulting yellow solution was then allowed to stir for 10 min at ambient temperature. Removal of the solvent in vacuo gave rise to complex **9** as a waxy yellow solid which was used without further purification.

   Complex **9** was dissolved in 3 mL of anhydrous methylene chloride and cooled to -78 °C. Then, a cold, ethereal solution of anhydrous HCl (0.108 mL of a 7 M solution) was slowly added down the side of the flask. After stirring for 10 min at -78 °C, 0.118 mL of cold trimethyl phosphite in 0.4 mL of CH_2Cl_2 was added down the side of the flask (to prevent warming). Stirring was continued for another 8 h as the orange-yellow solution slowly warmed to ambient temperature. The solvent was removed in vacuo and the resulting orange oil (Rh (III) alkyl complex) was dissolved in 1 mL of MeOH and 1 mL of $CHCl_3$ and then 0.050 mL of $P(OMe)_3$ was added. After 24 h at room temperature, solvent removal and flash chromatography (100% EtOAc) yielded 16 mg (49%) of lactam **10** as a colorless oil. (It is important to remove the solvent and thus the excess HCl before conversion of the alkyl complex to the lactam otherwise, epimerization occurs and a mixture of lactam isomers is obtained.) Inspection of the ^1H NMR spectrum of the crude reaction mixture prior to chromatography revealed the presence of uncoordinated olefin, which presumably resulted from β–elimination and olefin decomplexation, as the other product. No other lactam isomers were present in the crude reaction mixture.

10. All new compounds gave satisfactory spectral data and were analyzed by combustion analysis or high resolution mass spectroscopy.

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