Communications

1,2-Rearrangements of β-Nitrogen-Substituted (Porphyrinato)rhodium(III) Ethyls

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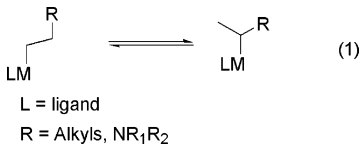
Summary: (Porphyrinato)rhodium(III) ethyls containing β-nitrogen substituents have been showed to undergo clean, thermal 1,2-rearrangements into the α-nitrogen-substituted rhodium ethyls. The rates and the equilibrium positions were found to be dependent on the electronic nature of the N substituents. Complexes ***1a*****−*****3a*** *were characterized by X-ray crystallography.*

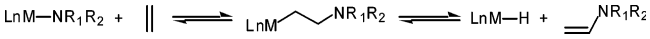
1,2-Rearrangements of alkylmetal complexes, in which the bonding position of the metal interchanges with an adjacent hydrogen atom, play crucial roles in bioinorganic chemistry[1−4] and organometallic chemistry[5−8] (eq 1). The rate of this isomerization and the equilibrium



constant are very important in determining the rates and regioselectivity in a variety of processes.

In bioinorganic chemistry, the mechanism of 1,2-rearrangements catalyzed by coenzyme B_{12} has been a subject of much interest.[3] Although radicals are commonly accepted to be formed during the enzymatic process, the nature of the rearrangement process still remains a subject of much discussion.[9] Alkyl 1,2-rearragnements bear potential relevance to the mechanistic studies of the coenzyme B_{12} dependent rearrangements. Metal complexes with macrocyclic ligands are widely used vitamin B_{12} coenzyme models. We have previously reported that (porphyrinato)phenylethyl-

Scheme 1. Reaction Pathway via 2-Aminoethyl Metal Complexes



rhodium(III) complexes undergo 1,2-rearrangement through a stepwise β-hydride elimination/metal hydride insertion pathway.[10] The rates approaching the equilibria and the equilibrium constants are often dependent on the nature of the alkyl substituents. Expanding the studies into metal alkyls containing a heteroatom such as nitrogen at the β-position will likely aid in further understanding 1,2-rearrangements which may bear potential relevance to B_{12} chemistry.

In basic organometallic chemistry, alkyl transition-metal complexes containing β-nitrogen substituents may (1) undergo relatively facile 1,2-rearrangements of the alkyl groups via β-hydride elimination or (2) form metal−olefin complexes via β-elimination of the amino group, depending on the alkyl ligands and reaction conditions (Scheme 1). 2-Aminoalkyl transition-metal complexes have been reported[11] and proposed to be intermediates in the catalytic amination of olefins. These intermediates usually undergo β-hydride elimination to yield enamines or imines.[12−14] On the other hand, β-amino elimination of amine to regenerate the cationic metal olefin complex has also been reported.[15] The propensity increases with increasing stability of the nitrogen-substituted group.[16,17] The effect of substituents at nitrogen of the β-aminoethyl ligands is not well-known in the partition between β-amino elimination or 1,2-rearrangement pathways via β-hydride elimination.

We have successfully synthesized four electronically different β-nitrogen-substituted[18] rhodium porphyrins

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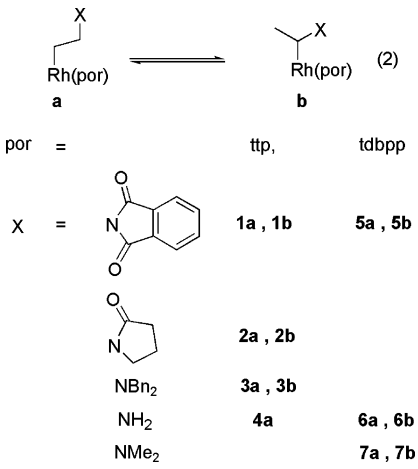
Table 1. Result of 1,2-Rearrangements of β-Nitrogen-Substituted (Porphyrinato)rhodium(III) Ethyls

complex	temp/°C	time[a]	$10^6 k_{obs}$ [b]/s^{-1}	isomeric ratio (2°/1°)	yield[c]/%
1a	120	31 days	2.9	8	86
1b	120	29 days	0.36	~7	88
2a	90	18 h	95.0	19	85
3a	80	11 h	100	~992	69
4	80	3 h		*d*	
5a	120	53 days	0.59	6	39
6a	80	45 h		4	31
7a	60	5 min		*e*	81

[a] Time to achieve equilibrium. [b] Estimated from the first-order rate fit. For blank entries, the rate was too fast to measure or there was extensive decomposition. [c] Total yield of two isomers. [d] Only Rh(ttp)CH_2CH_2(ttp)Rh was observed in 23% yield. [e] Only complex **7b** was observed.

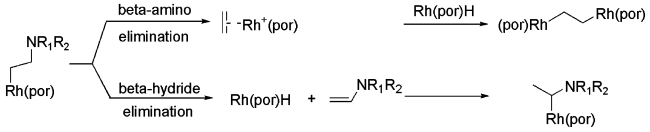
in order to examine their thermal behavior. β-N-substituted ethylrhodium complexes of Rh(ttp)CH_2CH_2X (ttp = 5,10,15,20-tetratolylporphyrinate; X = *N*-phthalimido (**1a**; 70%), *N*-pyrrolidonyl (**2a**; 50%), dibenzylamino (**3a**; 39%), amino (**4a**; 67%)) have been prepared by reduction of Rh(ttp)Cl with $NaBH_4$ followed by subsequent alkylation with the corresponding 2-N-substituted ethyl bromides or aziridine.[19] Rh(ttp)$CH_2CH_2NMe_2$ could not be prepared, as it is thermally unstable at room temperature. More stable β-N-substituted ethylrhodium complexes, Rh(tdbpp)CH_2CH_2X (tdbpp = 5,10,15,20-*meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate; X = *N*-phthalimido (**5a**; 65%), amino (**6a**; 65%), dimethylamino (**7a**; 68%)), were prepared by using more electron rich porphyrins.

Complexes **1a**−**3a** underwent smooth thermal 1,2-rearrangements in anaerobic benzene-d_6. The secondary complexes **1b**−**3b** were formed cleanly (eq 2). The



isomerization was found to be reversible (Table 1). The backward reaction starting from **1b** gave a similar equilibrated mixture of **1a** and **1b** upon heating at 120 °C for 29 days. Even the good leaving group *N*-phthalimido in **1a** did not undergo β-amido elimination in the presence of pyridine. Complex **4a** was thermally unstable and decomposed rapidly at 60 °C in 2 h, with the dirhodium complex Rh(ttp)CH_2CH_2(ttp)Rh (**8**) observed

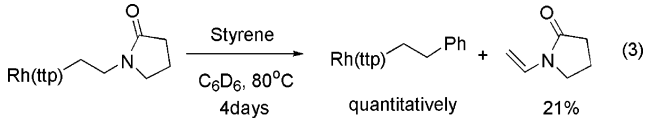
Scheme 2. Two Potential Reaction Pathways for Rh(por)$CH_2CH_2NR_1R_2$



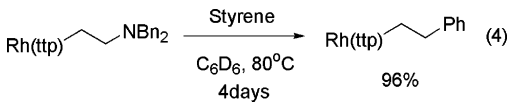
in 23% yield in 7 days. It is likely formed from hydrometalation of Rh(ttp)H, generated via β-hydride elimination of **4a**, with the Rh(ttp)−ethylene complex, produced also via parallel β-amine elimination of **4a** (Scheme 2).

Complex **5a**, with a more electron rich porphyrin, also underwent thermal 1,2-rearrangement at 120 °C in 53 days to give **5b**. The rate of thermal rearrangement of **5a** was 15 times slower than that of **1a**, which may be accounted for by the slight increase of Rh−C bond strength in **5a** with an electron-donating porphyrin.[20] The β-aminoethyl complex **6a** decomposed to give a small amount of the secondary isomer **6b**, and no Rh(tdbpp)CH_2CH_2(tdbpp)Rh was observed. The dimethylamino complex **7a** rearranged rapidly and completely to **7b** at 60 °C in 5 min.

The mechanism of the 1,2-rearrangements is consistent with a β-hydride elimination/metal hydride reinsertion pathway. A cis vacant coordination site is known to be necessary for β-hydride elimination to occur.[21] Complex **1a** remained stable at 120 °C for 1 month in the presence of added pyridine (1 equiv). The rearrangement was therefore inhibited by pyridine coordination.[10a] Existence of a free olefin intermediate was confirmed by exchange experiments with styrene. Heating the *N*-pyrrolidonyl ethyl complex **2a** in the presence of styrene (15 equiv) at 80 °C for 4 days in benzene-d_6 led to the slow formation of the exchange product Rh(ttp)CH_2CH_2Ph. The coproduct 1-vinyl-2-pyrrolidine was formed in 21% yield (eq 3). No secondary alkyl complex



was detected by ^1H NMR spectroscopy. Complex **3a** also yielded Rh(ttp)CH_2CH_2Ph in the presence of styrene. However, no dibenzylvinylamine was detected, presumably due to its extensive oligomerization (eq 4).[22]



Therefore, the rearrangement goes through a Rh hydride/olefin reinsertion pathway.

The complexes **1a**−**3a** were further characterized by single-crystal X-ray analyses. X-ray crystal data of complexes showed that the β-carbons on the pyrrole

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rings are displaced alternatively above and below the least-squares plane of the 24-atom porphyrin core[23] (see Figure 4 in the Supporting Information). The distortion of the macrocycle is a result of unfavorable steric interactions between the alkyl ligand and the porphyrin core. These nonplanar porphyrin structures may facilitate the β-hydride elimination through conformational change to allow cis coordination.

The rate of isomerization increased with a more electron-donating group at the nitrogen atom (Table 1). The rates of the 1,2-rearrangements followed the order (X) dimethylamino $\gg$ dibenzylamino $\gg$ *N*-pyrrolidonyl $>$ *N*-phthalimido. The reactivity trend is consistent with the β-hydride elimination pathway in forming a carbonium ion like intermediate which is stabilized by a more electron donating group.[21,24]

The isomeric ratios depend on the electronic effect at the nitrogen atom. The sterically more crowded secondary complexes were obtained as the major isomers. The positions of the isomeric ratios followed the order (X, secondary/primary) dimethylamino $\gg$ dibenzylamino $\gg$ *N*-pyrrolidonyl $>$ *N*-phthalimido. The relative stability of isomeric rhodium alkyls has been reported to depend on the polarity of the metal−carbon bond.[20,21] The strength of a metal−carbon bond is enhanced by the inductive electron-withdrawing N substituent at the α-carbon.[20] Notably, **3a** and **7a** completely isomerized to the secondary isomer, which may be further stabilized by the possible coordination of an amino group.

In summary, we have shown that a series of electronically different β-nitrogen-substituted rhodium porphyrins underwent clean thermal 1,2-rearrangements into the α-N-substituted isomer. The mechanism of the reaction is consistent with a β-hydride elimination/metal hydride insertion pathway.

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Supporting Information Available: Text, tables and figures giving experimental and spectroscopic details for new compounds and crystallographic data for complexes **1a**−**3a**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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