Novel 1,2-Rearrangement of Porphyrinatorhodium(III) Alkyls: Cis β-Hydride Elimination/Olefin Metal−Hydride Insertion Pathway

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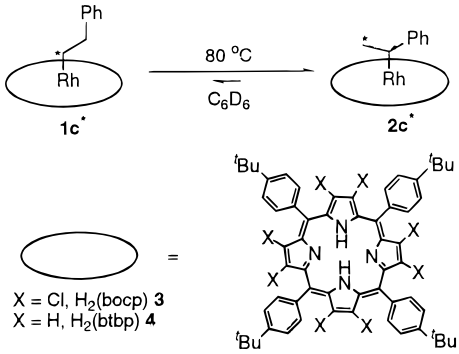
Alkyl 1,2-rearrangements of alkylmetal complexes (eq 1) play a crucial role in organometallic chemistry on both grounds of transition-metal catalysis and bioinorganic chemistry. It is a governing factor in determining the regioselectivity of the products formed in transition-metal promoted catalysis.[1−4] Furthermore, alkyl 1,2-rearrangement is important in bioinorganic chemistry due to its potential relevance to the coenzyme B_{12} dependent 1,2-rearrangements.[5−9]

(1)

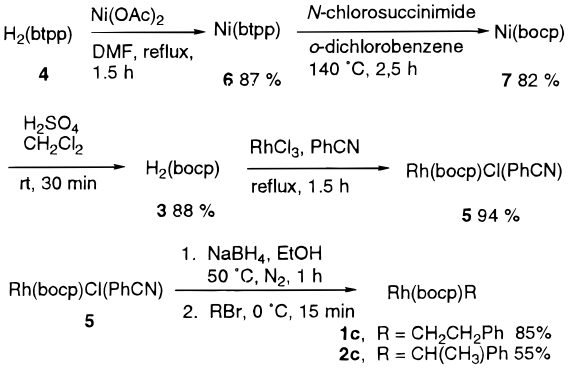
Alkyl 1,2-rearrangements have been reported,[10−12] and were proposed to undergo a stepwise β-hydride elimination and metal−hydride olefin reinsertion mechanism.[10b,11b,d] Alkyl 1,2-rearrangements in metal complexes with macrocyclic ligands were rare due to the unavailability of mutual cis coordination sites.[13] We now report that the Rh(bocp)CH_2CH_2Ph **1c**[14] (Scheme 1) undergoes reversible thermal 1,2-alkyl rearrangement via a stepwise cis β-hydride elimination/olefin Rh−H insertion pathway.[15]

The electron-deficient porphyrin ligand, H_2(bocp) **3**, was synthesized from H_2(btpp)[14] by octachlorination of H_2(btpp) **4** at the β positions in a procedure similar to that reported by Dolphin.[16] **3** was then metalated with $RhCl_3 \cdot xH_2O$ in refluxing PhCN to give Rh(bocp)Cl(PhCN) **5** in 94%. Complex **1c** was then obtained in 85% yield by the reductive alkylation of **5** with $NaBH_4$/$BrCH_2CH_2Ph$ (Scheme 2).[17]

Scheme 1. 1,2-Alkyl Rearrangement of Rh(bocp)(alkyl)



Scheme 2. Synthesis of Porphyrinatorhodium(III) Alkyls



The novel 1,2-alkyl rearrangment was observed upon heating a solution of **1c** in benzene-d_6 (25 mM) at 80 °C for 10 h to form Rh(bocp)$CH(CH_3)C_6H_5$ **2c** in 87%. The structure of **2c** was confirmed by independent synthesis. Monitoring the reaction at 80 ± 0.2 °C by ^{1}H NMR spectroscopy yielded a first-order dependency on [**1c**] with k_{obs} estimated to be $(1.4 \pm 0.1) \times 10^{-4}$ s^{-1}.

The isomerization was found to be reversible. **2c** gave an equilibrating mixture of **1c** and **2c** upon heating at 80 °C for 48 h. The equilibrium constant was estimated roughly to be 35 with the secondary alkyl complex being the major isomer, which corresponded to a free energy difference of about 10.5 kJ mol^{-1}. The driving force for the isomerization into the sterically more bulky secondary isomer probably resulted from the presence of the slightly electron-withdrawing phenyl group in stabilizing the secondary Rh−C bond through bond polarization.[10,18−20]

Thermolysis of the ^{13}C-labeled complex Rh(bocp)*$CH_2CH_2C_6H_5$ **1c*** [21] gave Rh(bocp)$CH(*CH_3)$Ph **2c*** with the ^{13}C-labeled atom migrated to the α-methyl group. Therefore, rhodium atom rather than phenyl group migrated in the isomerization (Scheme 1).

Cis coordination sites are apparently absent in complex **1c** and β-hydride elimination is therefore presumably hindered. It prompted us to investigate the possible radical involvement via

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Rh−C bond homolysis. **1c** [9.5 mM] was found to react much slower in the presence of $^{n}Bu_3SnH$ [95 mM] at 80 °C to give the apparent radical trapping adduct ethylbenzene in 14 d with 93% yield. This slower rate of trapping argued against the involvement of radical intermediate.

The Eyring plot[22] of the rearrangement of **1c** studied over the temperature range from 75 to 90 °C yields the $\Delta H^{\ddagger}_{obs}$ and $\Delta S^{\ddagger}_{obs}$ of the 1,2-rearrangement to be 53 ± 3 kJ mol^{-1} and −171 ± 9 J mol^{-1} K^{-1}, respectively. Compared with a typical rhodium−carbon bond dissociation energy of 187 kJ mol^{-1} as in Rh(oep)-CH(Bu)OH,[14,23] the small $\Delta H^{\ddagger}_{obs}$ measured precludes Rh−C homolysis being the rate-determining step. Furthermore, the extremely negative $\Delta H^{\ddagger}_{obs}$ supports a structurally organized transition state, contrary to homolytic fission of the Rh−C bond. On the basis of the measured activation parameters, a β-hydride elimination/Rh−hydride olefin insertion mechanism is proposed for the rearrangement.

The rates of the alkyl rearrangement were found to increase with electron-rich para-substituted phenylethyl moieties. The increased rate with electron-donating para-substituted phenylethyl ($k_{obs}/10^{-4}$s^{-1}: NO_2 **1a**, 0.10; Cl, **1b** 0.35; H, **1c**, 1.4; Me, **1d**, 1.8; OMe, **1e**, 3.7) supported the concept that a positive charge is developing at the benzylic carbon. Therefore, the benzylic hydrogen likely migrated as a hydride.

The rate of 1,2-rearrangement of **1c** also exhibited a kinetic isotope effect of 5.6 when the two benzylic hydrogen atoms were replaced by deuterium atoms. It established that the benzylic C−H bond cleavage occurred before or at the rate-determining step of the 1,2-rearrangement.

The intermediacy of olefin was established by exchange experiments.[10b] **1c** underwent slow alkyl exchanges with excess *p*-nitrostyrene to give Rh(bocp)$CH_2CH_2C_6H_4NO_2$ **1a**. No rearrangement product was observed probably due to slow rearrangement (observed half-life about 20 h) (eq 2).

$$\mathbf{1c} \xrightarrow[80\ ^{\circ}C,\ 8\ d]{p\text{-}NO_2C_6H_4CHCH_2} \underset{\mathbf{1a}\ 63\%}{Rh(bocp)CH_2CH_2C_6H_4NO_2} \qquad (2)$$

Independently synthesized Rh(bocp)H **8**[24] was found to react readily with styrene to give complex **1c** in 88% yield, which further confirmed the intermediacy of Rh−H and olefin in the 1,2-rearrangement.

The rate of alkyl rearrangement of **1c** was found to be retarded to one-eighth in the presence of added pyridine (5 equiv) as the sixth coordinating axial ligand. Coordination of pyridine to Rh was confirmed by ^{1}H NMR and UV−visible spectrophotometric titrations. Titration of **1c** in anaerobic benzene with pyridine between 15 and 35 °C confirmed a 1:1 complex of Rh−pyridine was formed with the $\Delta H°$ and $\Delta S°$ determined to be −63 ± 8 kJ mol^{-1} and −140 ± 30 J mol^{-1} K^{-1} respectively.[25] The Rh−pyridine binding constant (log *K*) at 80 °C was estimated to be 1.52. The retardation of alkyl rearrangement by axial ligand coordination may be attributed to the coordination saturation caused by ligand coordination which hindered β-hydride elimination.

A basic requirement for β-hydride elimination is the availability of vacant cis coordination sites, which is apparently lacking in the Rh(bocp)alkyl complexes. Nonetheless, β-hydride elimination reactions of organocobalamins,[27] organocobalt complexes with coplanar N_4 donor corrin ligands, and agostic interaction[28] in metalloporphryin have been reported. Furthermore, crystal structures of metalloporphyrin complexes, having two mutually cis coordinations on the same axial side, are known.[29] The above-mentioned mechanistic evidences support the stepwise β-hydride elimination/Rh−H olefin reinsertion as a plausible mechanism for the alkyl 1,2-rearrangement. It implied the possibility of axial cis coordination on organorhodium porphyrin complexes. This study may serve as a model for the possible metal involvement in vitamin B_{12} dependent 1,2-rearrangement.[5]

In summary, the novel reversible 1,2-alkyl rearrangement was observed with the Rh(bocp)CH_2CH_2Ph complex. Mechanistic studies have shown that the rearrangement proceeds through rhodium migration via a stepwise cis β-hydride elimination/Rh−H olefin insertion pathway. Further studies of this 1,2-rearrangements are in progress.

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Supporting Information Available: Experimental procedures and spectroscopic data for selected compounds (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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