DALTON
COMMUNICATION

Electronic effects in reversible 1,2-rearrangement of planar porphyrinato rhodium(III) alkyls

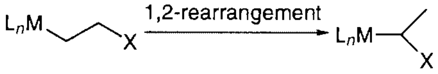
Kin Wah Mak, Feng Xue, Thomas C. W. Mak and Kin Shing Chan *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. E-mail: KSC@cuhk.edu.hk

Received 14th June 1999, Accepted 11th August 1999

Several β-substituted ethyl planar porphyrinato rhodium(III) complexes were found to undergo reversible alkyl 1,2-rearrangements at 120 °C with the reaction rates and the equilibrium positions depending on the electronic nature of the β-substituents, and Rh(ttp)CH_2CH_2Ph 1 and Rh(ttp)CH(CH_3)Ph 4 were characterized by single crystal X-ray crystallography.

1,2-Rearrangement of alkyl ligands in alkyl metal complexes, as typified in eqn. (1), involves an isomerization of the alkyl ligand



(1)

in which the bonding position of the metal formally interchanges with that of an adjacent hydrogen atom. It is a fundamentally important process in organometallic chemistry due to its potential relevance to the product regioselectivity in transition-metal promoted catalysis[1] and the coenzyme B_{12} dependent 1,2-rearrangements.[2]

Despite its importance, alkyl 1,2-rearrangements of alkyl metal complexes have only been infrequently reported and a stepwise β-hydride elimination/metal hydride olefin insertion mechanism has been proposed for the reported rearrangements.[3] Since the readiness of alkyl rearrangement depends on the availability of an accessible *cis*-coordination site, 1,2-rearrangement of alkyl metal complexes with coplanar macrocyclic ligands is rare.[4]

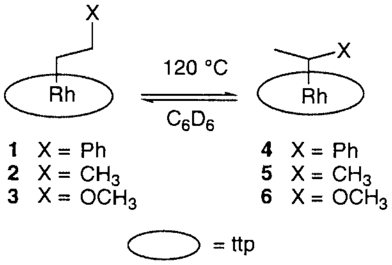
We have previously reported that a non-planar porphyrinato phenethylrhodium(III) complex underwent reversible thermal 1,2-rearrangement through a stepwise β-hydride elimination/olefin metal-hydride insertion pathway despite its apparent lack of a vacant *cis* coordination site.[5] Furthermore, this highly distorted rhodium porphryin may facilitate the accessibility of the *cis*-coordination site through conformational changes. We now report that the 1,2-rearrangements are feasible for planar rhodium porphyrin alkyl complexes and both the rates and equilibrium positions depend on the electronic effects of the substituents.

Several β-substituted ethylrhodium complexes Rh(ttp)-CH_2CH_2X (X = Ph **1**, CH_3 **2**, and OCH_3 **3**) were synthesized[6] and underwent 1,2-alkyl rearrangement at 120 °C in benzene-d_6 (Scheme 1). The reversibility of the rearrangement was established by the reversed rearrangement of the secondary complexes Rh(ttp)CH(CH_3)X (X = Ph **4**, CH_3 **5**). Similar tautomeric ratios were obtained as for those from the primary complexes.

Table 1 Tautomeric ratios of Rh–alkyl complexes at 120 °C

Rh–alkyl complex	Reaction time/h[a]	Secondary/primary ratio
Rh(ttp)$CH_2CH_2CH_3$	246	0.70
Rh(ttp)CH_2CH_2Ph	144	7.5
Rh(ttp)$CH_2CH_2OCH_3$	18	15

[a] Reaction time equilibrium secondary/primary ratio without significant Rh–alkyl decomposition.



Scheme 1 1,2-Rearrangement of porphyrinato rhodium alkyl complexes.

Complexes **1** and **4** were structurally characterized by X-ray crystallography (Fig. 1 and 2).† The coordination geometry of the rhodium atoms of both complexes were square pyramidal with the four porphyrinato nitrogen atoms occupying the basal sites and alkyl moieties residing at the axial sites. The Rh–N bond lengths in complexes **1** and **4** ranged from 2.006 to 2.040 Å and 2.006 to 2.029 Å respectively. The axial displacements of the rhodium atoms from the basal mean plane constituted by the four donor nitrogen atoms were determined to be 0.0333 and 0.0933 Å respectively for complexes **1** and **4**. The rhodium atoms were essentially located at the center of the N_4 mean planes without any significant out-of-plane displacement. As previous studies established that the 1,2-rearrangement was initiated by β-hydride elimination of the alkylrhodium(III) complexes,[5] these structural data supported the theory that β-hydride elimination was still feasible in planar rhodium porphyrin alkyl metal complexes lacking vacant *cis*-coordination sites.

Both the reaction rates and the equilibrium tautomeric ratios depend on the β-substituents X (Table 1). The rates of the 1,2-rearrangements ‡ were found to be much slower than that of the non-planar porphyrin.[5] The rates of the rearrangements followed the order (X) $OCH_3 \gg$ Ph > CH_3. The difference in rate is accounted for by the ease of β-hydride elimination; a carbocation-like intermediate is more stabilized by electron donating substituents X through resonance effects.[5]

In the rearrangements of the phenethyl and methoxyethyl rhodium complexes **1** and **3**, the corresponding secondary complexes **4** and **6** were obtained as the favored isomers despite their increased steric crowding. The positions of the equilibria followed the order (X, secondary/primary) OCH_3 > Ph $\gg CH_3$. The observed equilibrium positions are attributed to the electronic stabilization of the metal-bonded carbon atom by electron withdrawing substituents.[2,7] The electron withdrawing phenyl and methoxy substituents favor the secondary alkyl tautomers while the electron donating methyl substituent favors the sterically less bulky primary tautomer.

The mechanism of the reaction is likely to proceed *via* a β-hydride elimination with an olefin formed as the intermediate.[5] Rh(ttp)CH_2CH_2Ph **1** underwent exchange with *p*-nitrostyrene (4 equivalents) at 120 °C for 2 days to give the primary *p*-nitrophenylethyl rhodium porphyrin **7** in 52% together with the unexchanged **1** in 23% yield.

This journal is © The Royal Society of Chemistry 1999

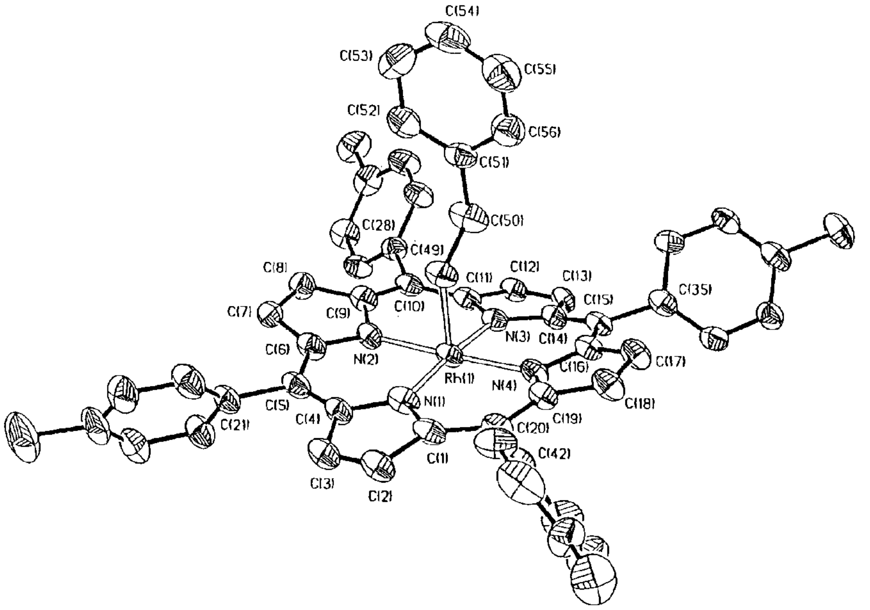


Fig. 1 ORTEP[9] view of Rh(ttp)CH_2CH_2Ph **1** showing the atom labeling. The thermal ellipsoids are drawn at a 35% probability level and hydrogen atoms have been omitted for clarity.

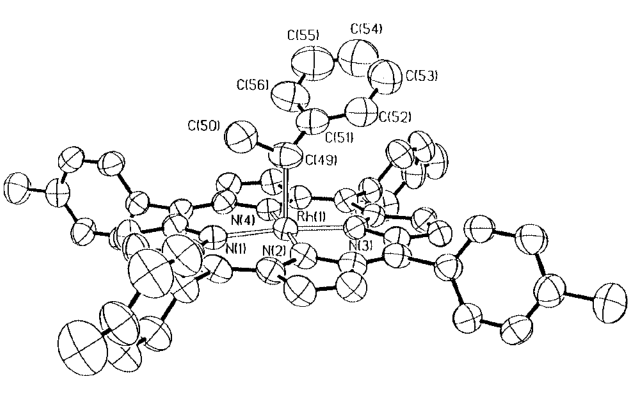


Fig. 2 ORTEP view of Rh(ttp)$CH(CH_3)Ph$ **4** showing the atom labeling. The thermal ellipsoids are drawn at a 35% probability level and hydrogen atoms have been omitted for clarity.

In summary, the 1,2-rearrangements of porphyrinato rhodium(III) alkyls were shown to be a general reaction with several β-substituted ethyl complexes. The reaction rates and equilibrium positions depended on the electronic nature of the β-substituents of the alkyl groups.

Acknowledgements

We thank Research Grants Council of Hong Kong (RGC Ref No: CU 96702) for financial support.

Notes and references

† Single crystals of complexes **1** and **4** suitable for X-ray crystallographic studies were grown by slow evaporation of solutions of the complexes in chloroform–ethanol. The selected crystals were mounted on top of glass fibers for data collection. The intensity data for complex **1** were collected in the variable *w*-scan mode on a Rigaku AFC7R four-circle diffractometer and the intensity data of **4** were collected on a Rigaku RAXIS IIc Imaging-plate system. The data were collected using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 294 K. The crystal structures were determined by the direct method and the final refinement was carried out by full-matrix least squares. Computations were performed with the Siemens SHELXTL-PLUS program (PC version).[8] CCDC reference number 186/1613.

Complex **1**: $C_{56}H_{45}N_4Rh{\cdot}(CH_3CH_2OH)_{0.25}{\cdot}(H_2O)_{1.5}$: red prism, 0.10 × 0.20 × 0.30 mm, $P\bar{1}$, $a = 13.286(3)$ Å, $b = 13.782(3)$ Å, $c = 14.740(3)$ Å, $\alpha = 95.93(3)°$, $\beta = 101.09(3)°$, $\gamma = 112.66(3)°$, $V = 2396.8(12)$ Å^3, $Z = 2$ and R(calc.) = 1.264 g cm^{-3}, 2Θ range = 4.0 to 50.0°, 8460 collected reflections, 8460 independent reflections, 5204 observed reflections with $|F_o| > 6.0\sigma(|F_o|)$, 604 parameters refined, refinement converged to $R_F = 7.22\%$, $wR = 10.18\%$. Rh–C = 2.026(6) Å.

Complex **4**: $C_{56}H_{45}N_4Rh{\cdot}(CHCl_3)_{0.5}$: red prism crystal, 0.12 × 0.15 × 0.22 mm, $P2_1/c$, $a = 13.796(3)$ Å, $b = 22.304(4)$ Å, $c = 15.777(3)$ Å, $\beta = 97.18(3)°$, $V = 4817(2)$ Å^3, $Z = 4$ and R(calc.) = 1.290 g cm^{-3}, 2Θ range = 3.0 to 55.0°, 13989 collected reflections, 8481 independent reflections, 5234 observed reflections with $|F_o| > 6.0\sigma(|F_o|)$, 653 parameters refined, absorption correction was made by the ABSCOR method, transmission factors 0.940 to 1.084, refinement converted to $R_F = 6.50\%$, $wR = 8.71\%$. Rh–C = 2.078(5) Å.

‡ 1,2-Rearrangement reaction of porphyrinato rhodium(III) alkyl complexes [Rh(por)R]. Rh(por)R, recrystallized from CH_3OH–CH_2Cl_2 (0.01 mmol) was dissolved in anhydrous benzene-d_6 (0.40 mL) in an NMR tube. Tetra(trimethylsilyl)silane (≈1.0 mg) was added as the internal standard for NMR integration. The solution was degassed for three freeze–thaw–pump cycles and the NMR tube was flame sealed under high vacuum. The solution was protected from light and heated in an oil bath. The progress of the reaction was monitored by ^{1}H NMR and the composition of the reaction mixture was determined by NMR integration with reference to tetra(trimethylsilyl)silane.

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd edn., University Science Books, Mill Valley, CA, 1987.
2 D. Dolphin, *B_{12}*, Wiley, New York, 1982; J. Halpern, *Science*, 1985, **227**, 869; R. G. Finke, in *Molecular Mechanisms of Bioorganic Processes*, eds. C. Bleasdale and B. T. Golding, The Royal Society of Chemistry, Cambridge, 1990.
3 D. L. Reger, D. G. Garza and L. Lebioda, *Organometallics*, 1992, **11**, 4285.
4 K. J. Del Rossi and B. B. Wayland, *J. Am. Chem. Soc.*, 1985, **107**, 7941.
5 K. W. Mak and K. S. Chan, *J. Am. Chem. Soc.*, 1998, **120**, 9686.
6 (*a*) ttp = 5,10,15,20-tetratolylporphyrinate; (*b*) Rh(ttp)alkyl complexes were prepared by reductive alkylation of the porphyrinato rhodium(III) chloride complex Rh(ttp)Cl(PhCN) **3** with $NaBH_4$/alkyl bromides; (*c*) H. Ogoshi, J. Setsune, T. Omura and Z. Yoshida, *J. Am. Chem. Soc.*, 1975, **97**, 6461.
7 L. Randaccio, S. Geremia, R. Dreos-Garlatti, G. Tauzher, F. Asaro and G. Pellizer, *Inorg. Chim. Acta*, 1992, **194**, 1.
8 G. M. Sheldrick, SHELXTL PLUS, Program package for structure solution and refinement, version 4.2, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
9 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Communication 9/04737I