Journal of Organometallic Chemistry, 185 (1980) 95—104

RING CLEAVAGE REACTIONS OF CYCLOPROPANE DERIVATIVES WITH OCTAETHYLPORPHYRINATORHODIUM(I) ANION

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(Received May 30th, 1979)

Summary

The monovalent octaethylporphyrinatorhodium(I) anion (I) shows very strong nucleophilic character. Ring cleavage of heterocyclopropanes, cyclopropanes substituted with an electron-withdrawing group and of highly strained molecules such as quadricyclane and bicyclobutane has been effected by nucleophilic attack of I. The PMR spectra of the resulting organorhodium(III) porphyrins indicate that inversion of configuration occurs at the reaction center.

Introduction

Facile nucleophilic reactions of vitamin B_{12s} and reduced Co^I species of the mimetic metal complexes have been noted: displacement of halide from organic halides; additions to acetylenes and electron-deficient olefins; ring opening reactions of heterocyclopropanes [1]. Nucleophilic reactivities of these low valent metal complexes have been shown by the nucleophilicity factor n_{CH_3I} which is defined by Pearson [2] as:

$$n_{CH_3I} = \log(K_Y/K_{CH_3OH})$$

where K_Y and K_{CH_3OH} are the second order rate constants for the reaction of CH_3I in methanol at 25°C with the nucleophile Y and with methanol, respectively. The factors for these metal complexes are 2—7 times larger than those of I^- or PhS^- [3]. As vitamin B_{12s} has been reported to cleave the C—O bond of tetrahydrofuran [4], other novel reactions due to this supernucleophilicity are expected to occur in these metal complexes.

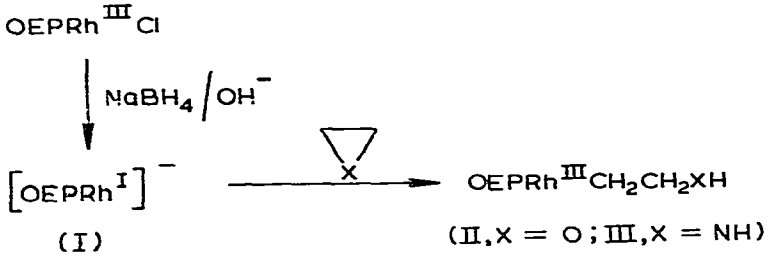
In this paper, we report the ring cleavage of cyclopropanes substituted with an electron-withdrawing group and of highly strained polycyclic compounds by the complex octaethylporphyrinatorhodium(I) ($[OEPRh^I]^-$, I). In order to ob-

tain an insight into the reaction behavior of the square planar Rh^I complex, their nucleophilic reactions with various cyclopropane derivatives have been examined.

Results and discussion

Reaction of $[OEPRh^I]^-$ (I) with ethylene oxide and ethylene imine

Octaethylporphyrinotorhodium(I) anion (I) was prepared by treatment of an ethanol solution of chlororhodium(III) octaethylporphyrin with $NaBH_4$ in a 0.5 *N* NaOH solution under argon [5]. The reaction mixture showed the characteristic visible spectrum of a rhodium(I) porphyrin at 384, 420 and 521 nm. Reactions of I with ethylene oxide and ethyleneimine took place rapidly at room temperature to afford β-hydroxy- and β-amino-ethylrhodium(III)-OEP complexes II and III, respectively, which were characterized by spectroscopic measurements. Metal—carbon bond formation resulted in these reactions as is commonly observed for vitamin B_{12s} and monovalent cobalt complexes of square planar macrocyclic systems [6], since O—O or C—N bond fission is favorable in these strained compounds. While C—O bond fission of tetrahydro-



furan has been claimed to occur with vitamin B_{12s} [4], the reaction of THF with complex I gave no ring cleavage products. This trend is seen in all the synthetic cobalt(I) complexes. It is unlikely that the C—O bond of THF is cleaved by vitamin B_{12s}. More elaborate experiments are required for the reaction of vitamin B_{12s} with THF.

Cleavage of cyclopropanes substituted with an electron-withdrawing group

Although the cyclopropane ring usually is cleaved by an acid-catalyzed process or by oxidative addition to a transition metal complex [7], nucleophilic attack of I on some cyclopropane derivatives caused the rupture of the C—C bond of the cyclopropanes under mild conditions. 4-Oxopentylrhodium(III)-OEP (IV) was readily formed in 77% yield when cyclopropyl methyl ketone was added to complex I. 3-Ethoxycarbonylpropylrhodium(III)-OEP (V) was also obtained in low yield using cyclopropane carboxylic acid ethyl ester as substrate. Neither treatment of cyclopropane nor phenylcyclopropane with complex I yielded the corresponding organorhodium(III)-OEP. These facts indicate that the nucleophilic ring opening of the C—C bond of cycloprane is facilitated by activation by an acyl or ester group.

The organorhodium(III)-OEP (VI) has been obtained from the reaction of I

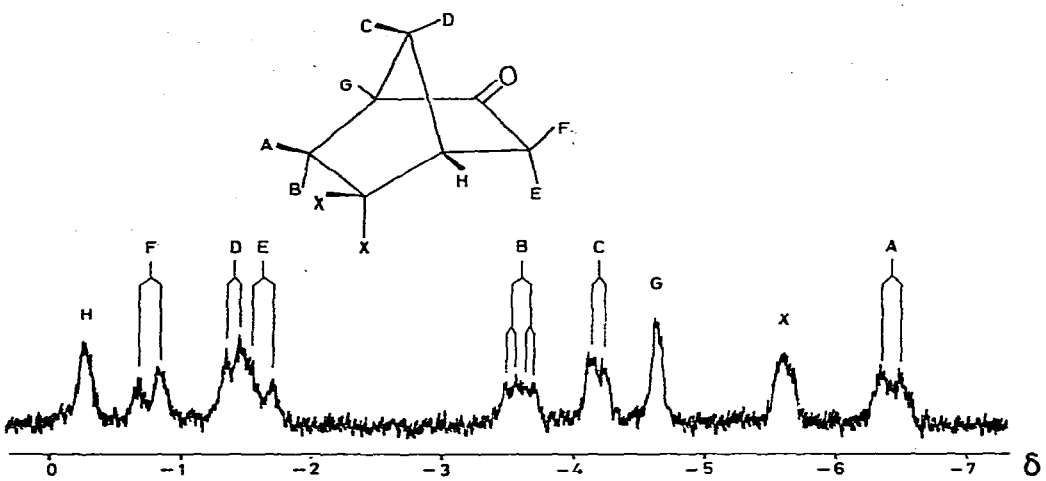
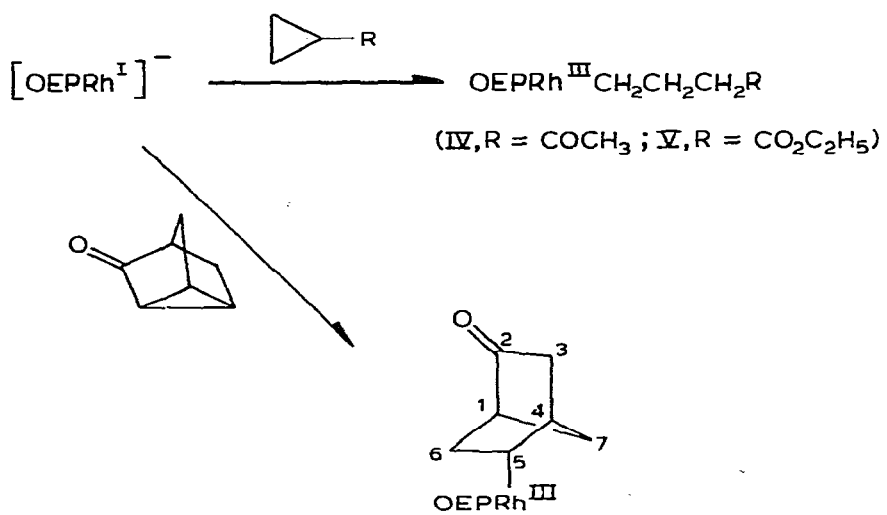


Fig. 1. PMR spectrum of axial organogroup of the complex VI.

with nortricyclanone (66%). The structure of complex VI was analyzed on the basis of the PMR spectrum as shown in Fig. 1.



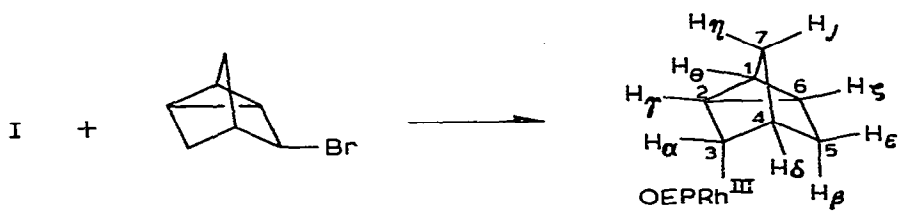
(VI)

In bicyclic systems such as norbornanone, the geminal coupling constant, J_{gem}, of the C(7)-bridge methylene protons (~10 Hz) is smaller than that of other CH_2 groups (~15 Hz). In particular, the value of J_{gem} of the CH_2 group adjacent to carbonyl is larger than 15 Hz [8]. The assignment of three pairs of doublets to three methylene protons at C(3), C(6), C(7) can be made on the basis of their coupling constants (18, 15 and 9 Hz, respectively). Signals due to protons at C(6) (appeared at δ −6.27 and −3.45 ppm) or C(7) (δ −4.03 and −1.30 ppm) appear at higher magnetic fields than those of the C(3)-methylene protons (δ −1.50 and −0.61 ppm) and the difference of the chemical shifts of

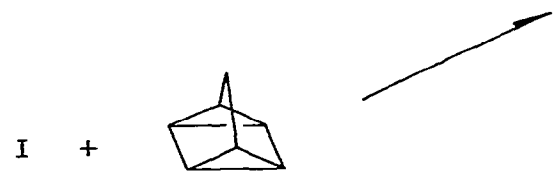
the two geminal protons at C(6) or C(7) is remarkable. This indicates that the C(6) and C(7) methylenes experience very strong shielding effect due to diamagnetic ring current of porphyrin. Therefore, the geometry of the axial ligand is qualitatively determined by means of both chemical shifts and coupling constants. It is concluded that the rhodium porphyrin is bonded to the *exo* position rather than *endo* position of C(5) in complex VI. The formation of the *exo*-form indicates that complex I attacks the C(5)-carbon from the back side of the C—C bond which is cleaved with inversion of configuration at the reaction center.

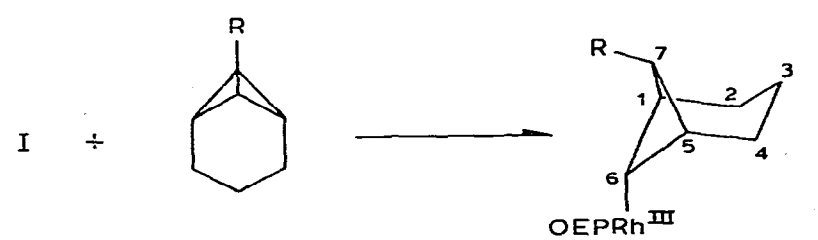
Reaction of I with highly strained compounds

Cyclopropanes involved in highly strained cyclic systems such as quadricyclane and bicyclobutane underwent ring opening by treatment with complex I to give organorhodium(III) porphyrin complexes. When complex I was treated with quadricyclane at 50° C for 8 h, nortricyclylrhodium(III)-OEP (VII) was formed by cleavage of one cyclopropane ring of quadricyclane without fission of the other cyclopropyl ring. In the PMR spectrum of complex VII, signals due to the axial organo ligand appeared at higher magnetic fields than those of TMS. A tentative assignment has been made on the basis of the splitting pattern. The anomalous chemical shifts result from the anisotropic effect of the diamagnetic ring current of the porphyrin. For example, three



(VII)





(VIII, R = H
IX, R = CO_2Me)

triplets (J_{gem} 5 Hz) are assigned to H_γ, H_ξ and H_θ, and two pairs of doublets (J_{gem} 10 Hz) are due to H_β, H_ϵ, H_η and H_ι (see ref. 9). The direction of attack of I toward quadricyclane is not determined due to the symmetric feature of the product (VII). The PMR spectrum of VII is identical with that of the complex prepared by the displacement reaction of I toward nortricyclyl bromide. This fact provides evidence to support the presence of the norticyclyl group in complex VII.

The fission of the central C(1)—C(7) bond of the bicyclobutane ring framework was observed in reactions of I with [4.1.0.$0^{2,7}$]-tricycloheptane and its 1-methoxycarbonyl derivative to give organorhodium(III)-OEP complexes VIII and IX, respectively. The latter complex was formed much more smoothly than the former due to the activation by the electron-withdrawing substituent (see Experimental). The formation of the Rh^{III}—C bond at the *endo* side of the C(6) bridge carbon to give *endo*-6-norpinylrhodium(III)-OEP (VIII) is shown by the clear doublet (J_{gem} 9 Hz) at δ −1.70 ppm. This signal can be interpreted solely by the *endo* proton (H_e) of the C(7) methylene bridge of VIII. This implies the absence of long range coupling with the C(6)-*endo* proton which would have a value of ca. 6 Hz in the 6-*exo*-norpinyl derivatives [10]. Additional coupling for H_a and H_e is due to nuclear spin (I = 1/2) of ^{103}Rh. The NMR spectra of complexes VIII and IX cannot be explained by alternative axial organic ligands such as norcarane and methylenecyclohexene derivatives.

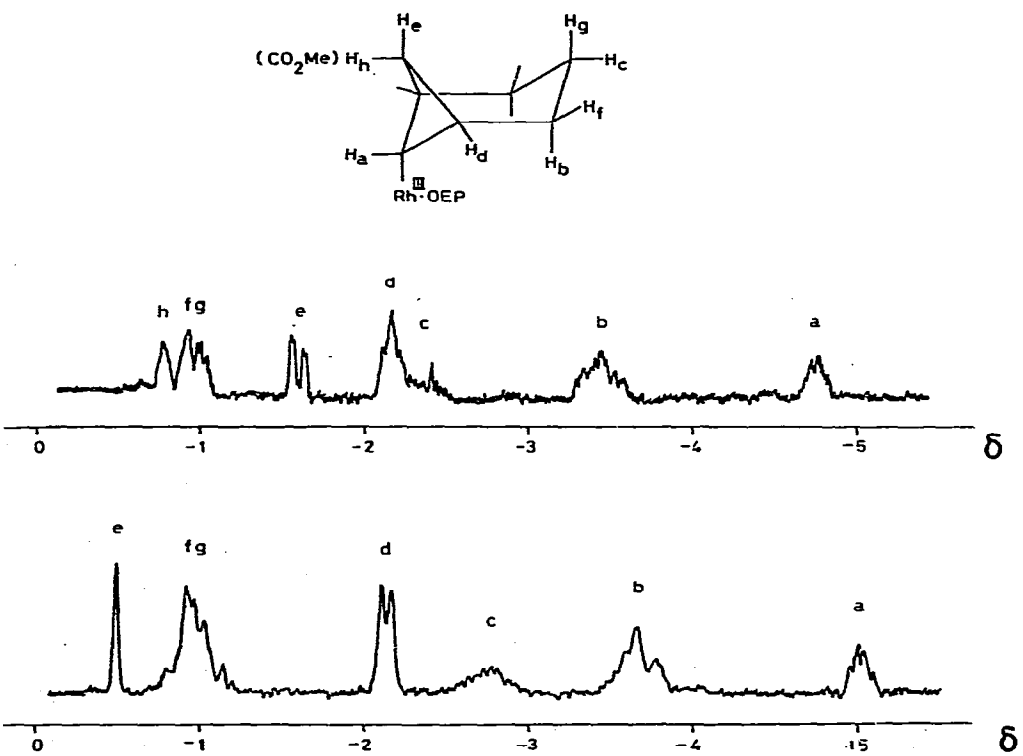
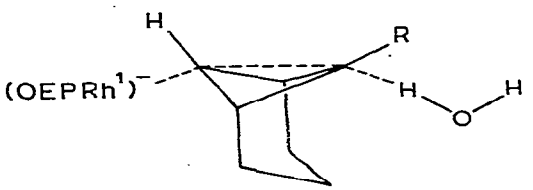


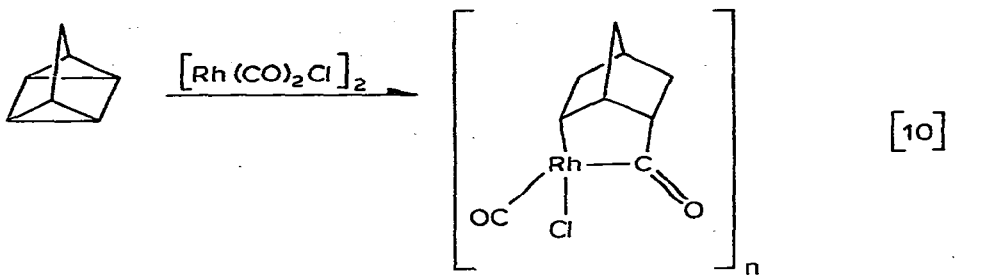
Fig. 2. PMR spectra of axial norpinyl group of the complex VIII (top) and IX (bottom).

Tentative assignment of the PMR spectrum of VIII has been made on the basis of the chemical shifts and decoupling experiments as shown in Fig. 2. The PMR spectrum of IX resembles that of VIII except for the signals due to H_e and H_h protons. The H_e proton of IX resonates at lower magnetic field than that of VIII without geminal coupling. The absorption due to H_a disappeared upon replacement of the ester group. While the 7-*exo* position shows relatively large coupling with H_d and H_b, the 7-*endo* position has not any coupling if both 7-*exo* and 6-*endo* positions are substituted. Therefore, the singlet at δ —0.55 ppm definitely indicates that the methoxycarbonyl group occupies the 7-*exo* position as shown in Fig. 2. The above result suggests that cleavage of the central C(1)—C(7) bond takes place concertedly as shown below:

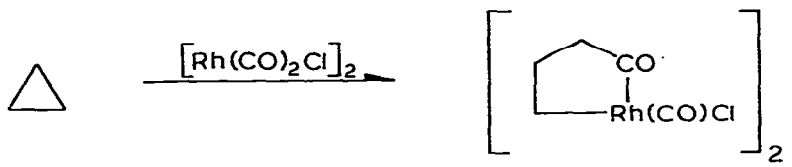


It has been reported that Rh^{I} or Pt^{II} ion inserts into a carbon—carbon σ-bent bond of cyclopropanes to give metallocycloalkane derivatives of Rh^{III} of Pt^{IV} [7]. Complexing of Rh^{I} or Pt^{II} with cyclopropane requires electron-donating substituents on the cyclopropane ring in contrast to the ring opening reaction catalyzed by [OEP-Rh^{I}]$^{-}$. Halpern has found that treatment of quadricyclane with [$Rh^{I}(CO)_2Cl]_2$ leads to breaking of only one carbon—carbon bond through an oxidative addition to Rh^{I} followed by the insertion of a carbonyl group into the initially formed Rh^{III}—C bond to give an acylrhodium adduct [11]. It is concluded that the rhodium(I)-catalyzed valence isomerization of quadricyclane to norbornadiene proceeds through the intermediate formation of this adduct complex. Isomerization of [4.1.0.0.^{2,7}]-tricycloheptane catalyzed by [$Rh^{I}(CO)_2Cl]_2$ yielded norcarane derivatives and methylenecyclohexene [12]. However, no norpinane derivatives were obtained. On the other hand, the C(1)—C(7) central bond of [4.1.0.0^{2,7}]tricycloheptane was cleaved by action of $HgCl_2$ [13].

Reductive C—C bond cleavage of conjugated cyclopropyl ketones and bicyclobutane derivatives takes place with lithium in liquid ammonia [14,15]. One electron transfer from [OEP-Rh^{I}]$^{-}$ to the substrate is an alternative mechanism, where OEP-Rh^{II} and an organic radical anion are generated. The stereochemistry of the products obtained from the reaction of I with nortricyclanone and [4.1.0.0^{2,7}]tricycloheptane seems to be rationalized by nucleophilic attack [OEPRh^{I}]$^{-}$ via the S_N2 reaction mechanism. In general, nucleophilic cleavage of the cyclopropane ring has hardly been observed. However, fission of a three-membered ring with I occurred smoothly under mild condition. The cyclopropanes activated by two geminal groups such as esters undergo ring opening with amines, mercaptans, enamins, cuprates and malonate anion [16]. The present ring opening proceeds through nucleophilic attack of monovalent Rh on mono-activated cyclopropane and cyclopropane in highly strained systems. In addition, the nucleophilic reaction derived from the filled d_{z^2} orbital is facilitated by the electron-donating character of the porphyrin ligand to the central metal ion.



[10]



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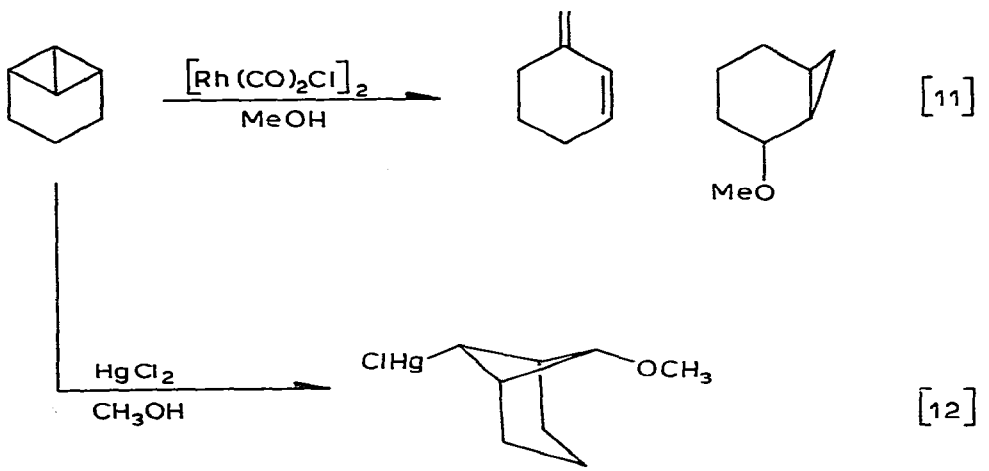

[11]

[12]

Experimental

Spectral measurement

Infrared spectra (4000 ~ 400 cm^{-1}) were recorded on a KBr disk with a Hitachi EPI-G31 grating spectrophotometer. ^1H NMR spectra were recorded with Varian HA-100 and HR-220 spectrometers using tetramethylsilane as internal reference in $CDCl_3$ solution. Visible spectra were measured in $CHCl_3$ with a Hitachi EPS-3T spectrophotometer.

Generation of $[OEPRh^I]^-$ (general procedure)

$OEPRh^{III}Cl$ was prepared according to ref. 5. $OEPRh^{III}Cl$ (100 mg) was dissolved in 30 ml of hot ethanol. $NaBH_4$ (20 mg) in an aqueous 0.5 *N* NaOH solution (2 ml) was added to the solution and the solution was stirred for 1 h at

50° C under argon atmosphere. The color of the reaction mixture turned from pink-red to brown-red to indicate the formation of $[PEPRh^{I}]^{-}$ (I). When tetrahydrofuran was used as solvent instead of ethanol, complex I was formed by addition of aqueous NaOH solution.

$OEPRh^{III}CH_2CH_2OH$ (II)

When ethylene oxide was introduced to an ethanol solution of I at 25° C, a red precipitate was formed immediately. The precipitate was collected by filtration, washed with water and then methanol. Recrystallization from CH_2Cl_2-CH_3OH gave $OEPRh^{III}CH_2CH_2OH$ in 72% yield: PMR: δ(ppm) 9.94 (s, 4H, =CH), 3.97 (q, 16H, CH_2CH_3), 1.87 (t, 24H, CH_2CH_3), 0.19 (broad s, 1H, OH), −2.73 (t, 2H, CH_2OH) and −5.62 (dd, 2H, Rh−CH_2, *J*(Rh−H) 3 Hz); IR: ν(O−H) 3550 cm^{-1}; IR-vis: λ_{max} (log ϵ) 399(5.11), 516(4.07) and 548 nm (4.33). Anal. Found: C, 67.02; H, 7.38; H, 8.14. $C_{38}H_{49}N_4ORh$ calcd.: C, 67.04; H, 7.26; N, 8.23%.

$OEPRh^{III}CH_2CH_2NH_3Cl \cdot \frac{1}{2}(H_2O)$ (III)

$[OEPRh^{I}]^{-}$ prepared in THF solution was treated with ethyleneimine (0.5 ml) and the reaction mixture was stirred for 3 h. The solution was evaporated to dryness under reduced pressure. The residue was dissiolved in chloroform and washed with 1 *N* HCl (3 × 20 ml) to remove the unreacted imine. The chloroform solution was dried over Na_2SO_4. Recrystallization from $CHCl_3$/petroleum ether afforded $OEPRh^{III}CH_2CH_2NH_3Cl$ (III) in 68% yield: PMR: δ (ppm) (C_5D_5N) 9.81 (s, 4H, =CH), ~6.10 (broad s, 2H, NH_2), 3.58 (q, 16H, CH_2CH_3), 1.43 (t, 24H, CH_2CH_3), −2.99 (t, 2H, CH_2NH_2) and −5.90 (t, 2H, Rh−CH_2): IR: ν(N−H) 3240 cm^{-1}; IR-vis: λ_{max} (log ϵ) 383(5.08), 932(5.10), 510(4.12) and 543 nm(4.62). Anal. Found: C, 62.93; H, 7.20; N, 9.44; Cl, 5.46. $C_{38}H_{52}N_5O_{0.5}ClRh$ calcd.: C, 62.93; H, 7.09; N, 9.66, Cl, 4.95%.

$OEPRh^{III}CH_2CH_2CH_2COCH_3 \cdot \frac{1}{2}(H_2O)$ (IV)

To I in ethanol was added 1 ml of cyclopropyl methyl ketone. A red precipitate formed immediately. $OEPRh^{III}CH_2CH_2CH_2COCH_3$ (IV) was obtained in 77% yield: PMR: δ (ppm) 9.92 (s, 4H, =CH), 3.96 (q, 16H, CH_2CH_3), 1.89 (t, 24H, CH_2CH_3), 0.53 (s, 3H, $COCH_3$), −1.05 (t, 2H, CH_2CO), −4.77 (m, 2H, Rh−CH_2CH_2) and −5.77 (dd, 2H, Rh−CH_2, *J*(Rh−H) 3 Hz); IR: ν(C=O) 1709 cm^{-1}; IR-vis: λ_{max} (log ϵ) 400(5.15), 516(4.10) and 548 nm (4.39). Anal. Found: C, 67.40, H, 7.38; N, 7.46. $C_{41}H_{54}O_{1.5}Rh$ calcd.: C, 67.47; H, 7.32; N, 7.68%.

$OEPRh^{III}CH_2CH_2CH_2CO_2C_2H_5$ (V)

Ethylcyclopropane carboxylate was added to I prepared in ethanol. The formation of a red precipitates was observed after 10 min. The mixture was stirred at 35° C for 1.5 h. Solvent was removed under reduced pressure. $CHCl_3$ was added and the solution was washed with water and dried over Na_2SO_4. The $CHCl_3$ solution was concentrated and chromatographed on silica gel (Merck, Kieselgel 60 PF_{254}). The top orange band was eluted with benzene and was collected and extracted with $CHCl_3$. $OEPRh^{III}CH_2CH_2CH_2CO_2C_2H_5$ (V) was afforded in 12% yield: PMR: δ (ppm) 9.97 (s, 4H, =CH), 4.02 (q, 16H, CH_2-

CH_3), 3.21 (q, 2H, O—CH_2CH_3), 1.88 (t, 24H, CH_2CH_3), 0.58 (t, 3H, OCH_2-CH_3), —1.06 (t, 2H, CH_2CO_2), —4.67 (m, 2H, Rh—CH_2CH_2) and —5.66 (dt, 2H, Rh—CH_2); IR: ν(C=O) 1732 cm^{-1}; IR-vis: λ_{max} (log ϵ) 385(5.04), 392(5.08), 510(4.08) and 543 nm (4.59). Anal. Found: C, 66.95; H, 7.49; N, 7.59. $C_{42}H_{55}$-N_4O_2Rh calcd.: C, 67.18; H, 7.38; N, 7.46%.

$OEPRh^{III}C_7H_9O$-exo (VI)

Nortricyclanone reacted readily with $[OEPRh^{I}]^-$ in ethanol to give product VI in 66% yield. PMR: δ (ppm) 9.92 (s, 4H, =CH), 3.98 (q, 16H, CH_2CH_3), 1.87 (t, 24H, CH_2CH_3), —0.10 (m, 1H, C(1)—H), —0.61 (dm, 1H, C(3)-*exo*-H, J_{gem} 18 Hz), —1.30 (dm, 1H, C(7)-*anti*-H, J_{gem} 10 Hz), —11.50 (dm, 1H, C(3)-*endo*-H), —3.45 (dm, 1H, C(6)-*endo*-H, J_{gem} 15 Hz), —4.03 (dm, 1H, C(7)-*syn*-H), —4.47 (m, 1H, C(4)-H), —5.43 (m, 1H, C(5)-H) and —6.27 (dm, 1H, C(6)-*exo*-H); IR: ν(C=O) 1740 cm^{-1}; IR-vis: λ_{max} (log ϵ) 386(5.18), 511(4.12) and 543 nm (4.63). Anal. Found: C, 69.28; H, 7.17; N, 7.54. $C_{43}H_{53}N_4ORh$ calcd.: C, 69.34; H, 7.17; N, 7.52%.

$OEPRh^{III}C_7H_9$ (VII)

Quadricyclane (1 ml) was added to the ethanol solution of I. The mixture was stirred for 10 h at 50° C. The red precipitate which formed was collected and washed with water to afford $OEPRh^{III}C_7H_9$ (VII) in 23%yield. Complex VII could be purified further by preparative TLC (silica gel) with n-hexane/benzene: PMR: δ (ppm) 9.97 (s, 4H, =CH), 4.01 (q, 16H, CH_2CH_3), 1.88 (t, 24H, CH_2CH_3), —1.24 (d, 1H, C(7)-H, J_{gem} 10 Hz), —1.25 (m, 1H, C(6)-H), —1.67 (d, 1H, C(7)-H), —1.78 (t, 1H, C^1-H, J_{vic} 5 Hz), —11.86 (d, 1H, C(5)-H, J_{gem} 10 Hz), —3.93 (m, 1H, C(4)-H), —4.76 (t, 1H, C(2)-H), —4.82 (d, 1H, C(5)-H) and —5.48 (m, 1H, C(3)-H); IR: ν(C—H) 3080 cm^{-1}; IR-vis: λ_{max} (log ϵ) 388(5.03), 511(4.02) and 544 nm (4.41). Anal. Found: C, 68.98; H, 7.34; N, 7.49. $C_{43}H_{53}$-N_4Rh calcd.: C, 69.15; H, 7.42; N, 7.50%.

$OEPRh^{III}C_7H_{11}$ (VIII)

[4.1.0.$0^{2,7}$]Tricycloheptane was added to I in ethanol solution. The mixture was stirred for 27 h at 50° C. The precipitate which formed was collected and washed with water to give $OEPRh^{III}C_7H_{11}$ (VIII) in 24% yield. Complex VIII was further purified by preparative TLC; PMR δ (ppm) 9.98 (s, 4H, =CH), 4.01 (q, 16H, CH_2CH_3), 1.87 (t, 24H, CH_2CH_3), —0.70 (m, 1H, C(7)-*exo*-H), ~—1.00 (m, 3H, C(5)-H, C(3)-H and C(4)-H), —1.70 (d, 1H, C(7)-*endo*-H, J_{gem} 7 Hz), —2.26 (m, 2H, C(1)-H and C(5)-H), —2.54 (m, 1H, C(3)-H), —3.54 (m, 2H, C(2)-H and C(4)-H) and —4.84 (m, 1H, C(6)-*exo*-H); IR-vis: λ_{max} (log ϵ) 387-(5.10), 395(5.16), 511(4.16) and 544 nm (4.60). Anal. Found: C, 69.01; H, 7.34; N, 7.40. $C_{43}H_{55}N_4Rh$ calcd.: C, 68.96; H, 7.67; N, 7.48%.

$OEPRh^{III}C_7H_{10}CO_2CH_3$ (IX)

Addition of 1-methoxycarbonyl [4.1.0.$0^{2,7}$]tricycloheptane [17] to I in ethanol solution caused immediate formation of red crystals at ambient temperature. Recrystallization from CH_2Cl_2/methanol gave $OEPRh^{III}C_7H_{10}CO_2CH_3$ (IX) in 85% yield; PMR: δ (ppm) 9.75 (s, 4H, =CH), 3.89 (q, 16H, CH_2CH_3), 2.71 (s, 3H, OCH_3), 1.80 (t, 24H, CH_2CH_3), —0.55 (s, 1H, C(7)-*endo*-H),

~—0.94 (m, 3H, C(2)-H, C(4)-H and C(3)-H), —2.15 (m, 2H, C(1)-H and C(5)-H), —2.79 (m, 1H, C(3)-H), —3.68 (m, 2H, C(2)-H and C(4)-H) and —5.03 (m, 1H, C(6)-*exo*-H); IR: ν(C=O) 1728 cm^{-1}; IR-vis: λ_{max} (log ϵ) 387(5.12), 393 [sh] (5.11), 512(4.11) and 544 nm (4.34). Anal. Found: C, 68.21; H, 7.14; N, 7.08. $C_{45}H_{57}N_4O_2Rh$ calcd.: C, 68.51; H, 7.28; N, 7.10%.

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