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REACTIONS OF RHODIUM(III) PORPHYRIN WITH VINYL ETHER AND ACETYLENES

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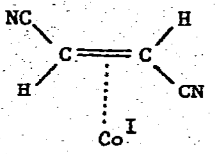
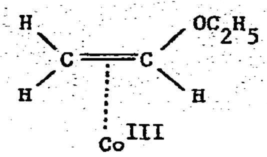
Summary

Chloro(aquo)rhodium(III) octaethylporphyrin, $OEPRh^{III}-Cl(H_2O)$ (I), reacted with ethyl vinyl ether to give 2,2-diethoxyethylrhodium(III)OEP (II) in the presence of ethanol and triethylamine. The complex (II) was readily hydrolyzed to afford (formylmethyl)rhodium(III)OEP (III). The hexa-coordinate complexes, $OEPRh^{III}-CH_2CHO(B)$ (B = pyridine (IV), triphenylphosphine (V)), were prepared and the spectral properties of these complexes (III-V) were compared. Complex (I) reacted with acetylenic compounds to give β-chlorovinylrhodium(III) porphyrins (VI and VII) and acylrhodium(III) porphyrins (VIII-X). The reactions of (I) with electron-rich olefin and acetylenes took place very rapidly, compared with those of tri-valent cobalt complexes. Metal-induced carbonium ions are proposed as plausible intermediates in these reactions.

Introduction

Synthetic methods for the formation of a cobalt-carbon bond in various cobalt complexes have been developed in view of the chemistry of coenzyme vitamin B_{12} [1]. Recently Dolphin reported the direct formation of $Co^{III}-C$ bonds by the reactions of alkyl vinyl ethers with vitamin B_{12a} or cobal(III)-oxime and suggested the intermediacy of an olefin π-complex of Co^{III} in these reactions [2]. Schrauzer has questioned this formulation and reexamined the reaction schemes of formylcobalamin [3], because transition metal π-complexes are considered to be unstable when a metal in a high oxidation state and an electron-rich olefin are coupled, while metal π-complexes of a low-valent metal with an electrondeficient olefin are stable [4]. Indeed, Schrauzer observed the formation of a π-complex consisting from a mono-valent cobaloxime and fumaronitrile in the solution [5].





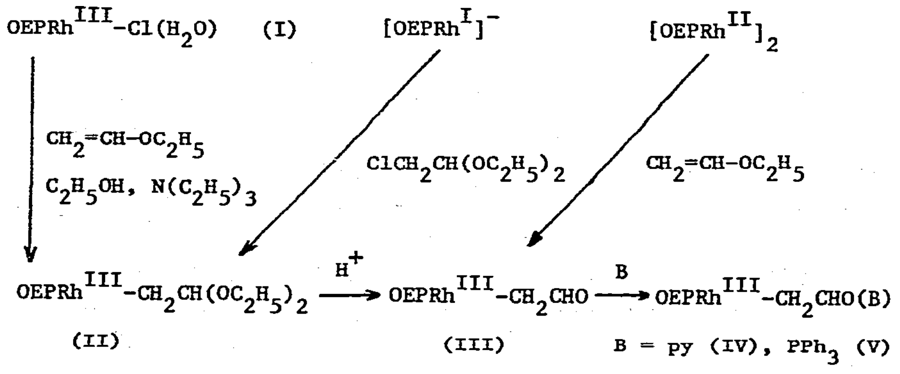
We have found that the reaction behavior of mono- and di-valent rhodium porphyrins is similar to that of cobalamin and cobaloxime and that organorhodium(III) porphyrins are more stable than those organocobalt(III) complexes [6]. It is expected that electrophilic reactions of Rh^{III} complex with an electron-rich olefin and acetylene lead to organorhodium(III) porphyrins *via* π-complex intermediates. In this paper, direct Rh^{III}–C bond formation by the reactions of Rh^{III} porphyrin with vinyl ethers and acetylenes are described.

Result and discussion

Reaction of $OEPRh^{III}$-$Cl(H_2O)$ with ethylvinylether

Organorhodium porphyrin complexes are generated through: the reaction of an anionic mono-valent rhodium porphyrin, $[OEPRh^{I}]^-$, as a supernucleophile [6a]; the reaction of a dimeric divalent rhodium porphyrin, $[OEPRh^{II}]_2$, with alkyl halides, olefins and acetylenes [6b]; the treatment of a trivalent rhodium porphyrin with organolithium reagents [6a]; the intramolecular oxidative alkylation of monovalent rhodium complexes of N-alkyloctaethylporphyrin [6c].

It has been reported that organocobalt complexes are generated when hydroxocobalamin or bromo(pyridine)cobaloxime is treated with a vinyl ether [2]. Whereas the above reaction required 2–3 days, the reaction of $OEPRh^{III}$-$Cl(H_2O)$ (I) with a vinyl ether complete within 30 min at ambient temperature. In the presence of ethanol and triethylamine, 2,2-diethoxyethyl-



Scheme 1. Formation of formylmethylrhodium(III)OEP

rhodium(III)OEP (II) was isolated. The presence of the acetal group was evidenced by the absorptions at 1127 and 1090 cm^{-1} in the ir spectrum of (II). The pmr signals due to methylene protons of the diethylacetal moiety appear at δ 1.09 and 0.79 as two doublets of quartets because the methylene protons are diastereotopic and therefore magnetically nonequivalent. The coupling pattern of these signals is explainable in terms of geminal coupling with each other and vicinal coupling with methyl group. Complex (II) was readily hydrolyzed to give (formylmethyl)rhodium(III)OEP (III). Absorptions due to the formyl group appear at 2710 and 1680 cm^{-1} in the ir spectrum of (III) and the formyl proton resonates at δ 2.90 (J_{CH-CH} = 5 Hz). Complex (II) was alternatively synthesized by the nucleophilic substitution reaction of [OEPRh^{I}]$^{-}$ with chloroacetal. Complex (III) also was prepared by the reaction of [OEPRh^{II}]$_2$ with ethyl vinyl ether. (See Scheme 1.). Thus, two organorhodium complexes (R·Rh(III)OEP, R = $CH_2CH(OC_2H_5)_2$ (II) and CH_2CHO(III)) were isolated as crystals in stable forms respectively. Less stable diethylacetalrhodium complex was completely converted to the (formylmethyl)rhodium complex on silica gel. Similar trend was found for the conversion of diethylacetal of (formylmethyl)cobalmin to the (formylmethyl)-cobalamin [3].

The reaction of OEPRh^{III}-Cl(H_2O) with ethyl vinyl ether seems to be facilitated by the formation of a similar cationic intermediate as shown in Figure 1. The present mechanism is identical with that proposed in alcoholysis of 2-acetoxyethyl(pyridine)cobaloxime [2c, 7]. In the intermediate stage, π-complex which possess a carbonium center at the β-carbon atom with respect to Rh atom are considered to be equilibrium with a σ-complex in which the rhodium atom is bonded equally to both carbon atoms.

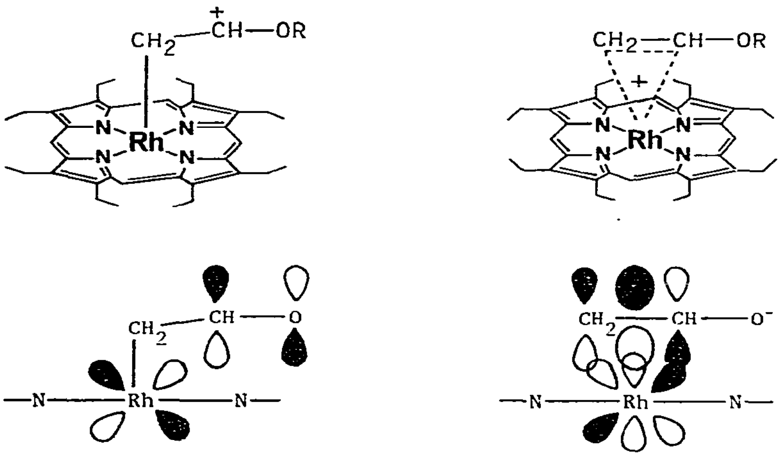


Figure 1. Cationic σ- and π-complex formed in the reaction of Rh^{III}OEP and vinylether (top). σ- And π-interaction of formylmethyl ligand with tri-valent Rh in the complex (III) (bottom).

The hexa-coordinate complexes, OEPRh^{III}-$CH_2CHO(B)$ (B = pyridine (IV), triphenylphosphine (V)) were prepared from (formylmethylrhodium(III)OEP (III) and the respective basic ligand. The spectral properties of these complexes (III-V) are summarized in Table 1. The ir spectra of the complexes (III-V) show much lower carbonyl stretching frequencies which suggests a considerable interaction between the metal and the β-carbon. The ν(C=O) absorption of the aldehyde group was observed at 1655 cm^{-1} both for the σ-bonded formylmethyl groups of $(C_5H_5)Fe^{II}(CO)_2$-CH_2CHO [8], and formylmethyl(pyridine)-cobaloxime [2c]. Deviation of ν(C=O) of these complexes from ordinary values of aldehyde ν(C=O) (1730 cm^{-1}) is attributed to the interaction of d_π orbitals of d^6 metal with the carbonyl π-system, rather than the inductive effect of the metal through σ-bonds. The overlap of filled d_π orbitals of Rh^{III} with the anti-bonding orbital (π^*) of the carbonyl decreases the carbonyl bond order. (See Figure 1.). The signals of methylene protons bonded to rhodium in the complex (III) appear at higher magnetic fields than TMS due to the diamagnetic ring current effect of porphyrin [6a]. Coordination of the sixth ligand causes the further up-field shifts of the -CH_2- signals. These chemical shifts depend on the strength of the σ-donation of the coordinating bases. A similar trans effect was found in the case of OEPRh^{III}-CH_3(B) [6a]. The carbonyl stretching frequencies of the formylmethyl group become lower as the trans effect increases, as is seen in Table 1. The decrease of ν(C=O) may be explained in terms of the polarization of the Rh-C bond due to the coordination of sixth ligand.

Reaction of OEPRh^{III}-Cl(H_2O) with acetylenic compounds

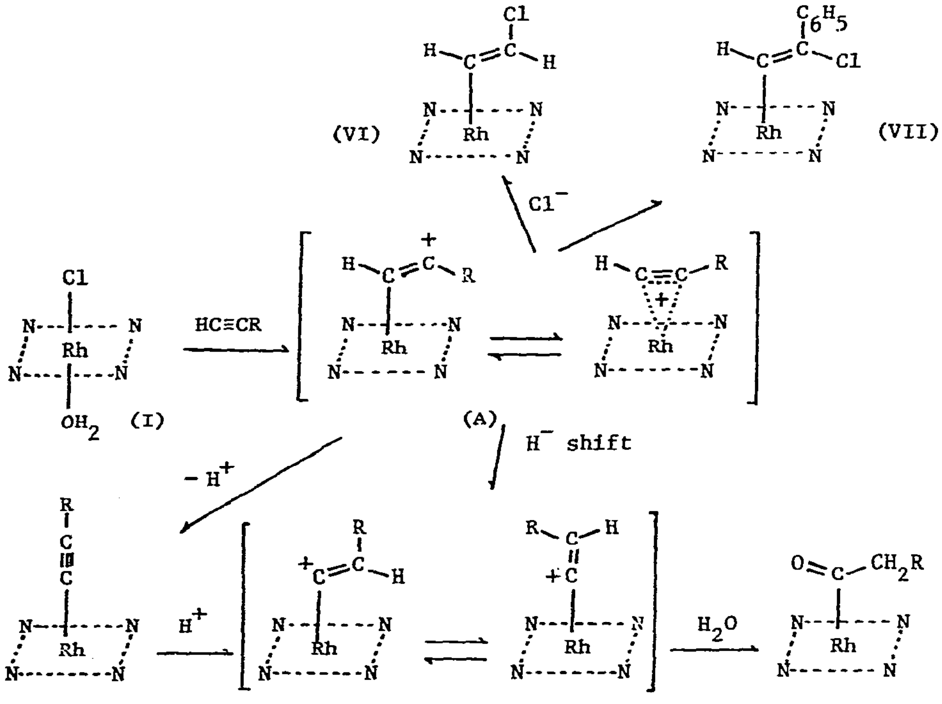
Reactions of the trivalent rhodium porphyrin with acetylenic compounds in benzene solution afforded organorhodium(III)OEP complexes (VI-X). Insertion of the triple bond into the Rh^{III}-Cl bond occurred to produce β-chlorovinylrhodium(III)OEP. Trans addition of the Rh^{III}-Cl bond to the acetylene

Table 1. Spectral data of OEPRh^{III}-$CH_2CHO(B)$

complex	ν(C=O) cm^{-1}	δ(Rh-$C\underline{H}_2$-)
OEPRh-CH_2CHO	1680 [a]	-5.55 [b]
OEPRh-CH_2CHO(py)	1671	-5.89
OEPRh-$CH_2CHO(PPh_3)$	1664	-6.12

a) measured in a KBr pellet. b) measured in $CDCl_3$ using TMS as an internal reference.

was confirmed by the vicinal coupling constant (12 Hz) and the chemical shifts of the olefinic protons in the pmr spectrum of (VI). That is, the chemical shift of the β-vinylic proton of (VI) (δ −1.79) is closer to that of the β-vinylic proton of cis (δ −2.07) rather than trans (δ 0.60) position relative to the rhodium atom of vinylrhodium(III)OEP [6a]. On the other hand, cis addition of the Rh^{III}-Cl bond to the phenyl acetylene was evidenced by the comparison of the chemical shifts of the phenyl protons of (VII) with those of cis and trans isomers of the β-styrylrhodium(III)OEP complex [6a]. Signals due to phenyl protons of cis-styrylrhodium(III)OEP appear at considerably different magnetic fields (δ 3.73(ortho), 6.49 (meta) and 6.87(para)) from those of trans isomer (δ 4.69(ortho) and 6.14(meta, para)) due to the different shielding effect of the porphyrin ring. Phenyl protons of (VII) resonate at δ 4.81(ortho) and 6.21(meta, para). Therefore, (VII) is considered to be the trans-styryl complex. Bond formation between the β-vinylic carbon and chlorine occurs so as to minimize the steric repulsion between the substituents of β-vinylic position and porphyrin ligand. This suggests that the reaction proceeds through a cationic intermediate (A) which is probably stabilized by a participation of the metal. (See Scheme 2). The complexes (VIII-X) possess



R = C_6H_5 (VIII)
n-C_4H_9 (IX)
$(CH_2)_3OH$ (X)

Scheme 2. Reactions of (I) with acetylenes a carbonyl group at the α-position but not at the β-position relative to rhodium atom. This formulation has been verified by the absence of splitting due to coupling with ^{103}Rh (I = 1/2) in the NMR signal of the methylene group that appears at the highest magnetic field. Formation of acylrhodium-(III)OEP complexes is probably due to hydration of the Rh^{III} acetylide by the axially coordinated water in the complex (I). Deprotonation from the cationic intermediate gives the Rh^{III} acetylide as a precursor. Indeed, the complexes, $OEPRh^{III}-C\equiv CR$ ($R = C_6H_5$, $n-C_4H_9$), have been isolated from the reaction of (I) with $HC\equiv CR$ in the presence of triethylamine. A similar reaction has been found in the square planar Co^{III} complex [10]. The complex (VIII) has been obtained by treatment of $OEPRh^{III}-C\equiv CC_6H_5$ with aqueous HCl. Protonation to the Rh^{III} acetylide appears to generate a cationic intermediate (B) which is subject to resonance stabilization due to carbene structure. Therefore, formation of a cationic center at the α-carbon atom is preferable to the regeneration of β-cationic complex (A). Recently the remarkable lability of an α-chlorovinylplatinum(II) complex was reported and cationic alkoxy-carbene complexes of Pt^{II} were isolated in the alcoholysis of the former complex [11]. Similar cationic carbene complexes of Rh^{III} or Ir^{III} are obtainable from the reactions of the metal complexes with acetylene [12]. The direct hydride migration from the cationic intermediate (A) to (B) can be an alternative route, while Rh^{III} porphyrin complex with alkoxy-carbene ligand could not be isolated even in the reaction of (I) with 3-butyne-1-ol under anhydrous conditions. Although detailed studies on cationic carbene complexes in model systems of coenzyme B_{12} have not yet been carried out , a cationic carbene complex was suggested to play an important role in the enzymatic reaction of coenzyme B_{12}-dependent enzymes [13].

It is noted that the reaction pathway is significantly changed by the substituent effect of acetylene. That is, the vinyl-type complex (VI) has been exclusively formed in the reactions of (I) with $HC\equiv CH$ (67 % yield), whereas the reactions of (I) with mono-alkyl acetylenes have afforded only acyl-type complexes (IX) (75 %) and (X) (45 %), respectively. The vinyl- and acyl-type complexes are thought to be derived from the cationic intermediates (A) and (B), respectively. Bulky substituents on the acetylene seem to enhance the transformation from (A) to (B) due to the relaxation of steric constraint between the substituent of acetylene and porphyrin ligand. In spite of considerable steric constraint in the reaction of (I) with phenylacetylene, delocalization of positive charge in the axial ligand stabilizes the cationic species (A) to give both vinyl- and acyl-type complex (VII) and (VIII) in the yields of 20 and 23 %, respectively.

Acetylene π-complexes of zero-valent palladium and platinum react oxidatively with electrophiles to give σ-alkenyl metal(II) complexes [14], whereas M^{II}-X bond adds to acetylenes *via* intermediate formation of an acetylene π-complex of metal(II) [15]. The reaction of (I) seems to be similar to the latter case. Nucleophilic attack of acetylide at Rh^{III} is not likely to take place under the present reaction conditions. Reactions of disubstituted acetylenes such as diphenylacetylene and 3-hexyne with complex (I) did not yield any organorhodium complexes due to steric repulsion between substrate and porphyrin ring. Formation of the cationic intermediate (A) is probably facilitated by the electron donation to the metal in a high valence state through σ-bond of the metal-carbon and inverse donation of electron density from d_{π}(metal) to a cationic center of the axial organo ligand.

Experimental

Infrared specra were recorded on a Hitachi EPI-G31 grating spectrophotometer as a KBr pellet. Pmr spectra were obtained on a JOEL JNM-PMX 60 and a Varian HA-100 spectrometer using Me_4Si as an internal reference. Visible spectra were measured on a Hitachi EPS-3T recording spectrophotometer. Thin layer chromatography was done on Kieselgel 60 F_{254} (Merck). Wakogel C-200 (Wako Junyaku) was used for column chromatography. Chloro(aquo)octaethylporphyrinatorhodium(III) was prepared according to the method of our previous report [6a]. The complexes (II) ∿ (X) did not show clear melting points and decomposed above 300°.

$OEPRh^{III}-CH_2CH(OC_2H_5)_2$ (II)

(A) $NaBH_4$ (10 mg) in 1 ml of 0.5N-NaOH aqueous solution was added to $OEPRh^{III}-Cl(H_2O)$ (I) (50 mg) dissolved in ethanol and the solution was stirred at 50°C under argon atmosphere to generate the $[OEPRh^{I}]^-$ anion. After the solution had cooled, the chloroacetal (0.5 ml) was added dropwise. The reaction mixture was allowed to stand overnight. Orange needles were separated by filteration, washed with water and dried over P_2O_5 to give $OEPRh^{III}-CH_2CH(OC_2H_5)_2$ (II) in 45 % yield.

(B) Triethylamine (0.1 ml), absolute ethanol (0.5 ml) and ethyl vinyl ether (1.0 ml) were successively added to $OEPRh^{III}-Cl(H_2O)$ (I) (80 mg) dissolved in dry CH_2Cl_2. The mixture was stirred for 30 min at ambient temperature. Then the solvent was removed under reduced pressure. The residue was recrystallized from methylene dichloride-ethanol to give orange crystals, $OEPRh^{III}-CH_2CH(OC_2H_5)_2$ (II) in 50 % yield: pmr $\delta(C_6D_6)$ 9.93 (s, 4H, $=C\underline{H}-$), 3.87(q, 16H, $-C\underline{H}_2CH_3$), 1.86(t, 24H, $-CH_2C\underline{H}_3$), 1.09 and 0.79(doublets of quartets, 4H, $-OC\underline{H}_2CH_3$), -0.10(t, 6H, $-OCH_2C\underline{H}_3$), -2.51 (t, 1H, $Rh-CH_2C\underline{H}$) and -5.31(dd, 2H, $Rh-C\underline{H}_2-$); ir 1127, 1090 cm^{-1} (C-O-C);

vis(C_6H_6) λ_{max}(logε) 387(5.12), 397(5.15), 513(4.19) and 544 nm(4.76). Anal. Calcd for $C_{42}H_{47}N_4O_2Rh$: C, 67.00; H, 7.63; N, 7.44. Found: C, 66.98; H, 7.66; N, 7.52.

OEPRh^{III}-CH$_2$CHO (III)

(A) When ethyl vinyl ether (0.4 ml) was added to the benzene solution (30 ml) of [OEPRh^{II}]$_2$ (60 mg) under an argon atmosphere, the color of the solution changed immediately from brown to dark red. The reaction mixture was then concentrated under reduced pressure. The residue was chromatographed on a silica gel column. The first orange band eluted with benzene afforded OEPRh^{III}-CH$_2$CHO (III) in 54 % yield.

(B) A chloroform solution of (II) was treated with silica gel or allowed to stand for 1 day. The solvent was evaporated under vacuum. The residue was recrystallized from n-hexane-CH$_2$Cl$_2$ to give an orange red powder, OEPRh^{III}CH$_2$CHO (III), in a quantitative yield: pmr δ(CDCl$_3$) 9.97(s, 4H, $=C\underline{H}-$), 3.99(q, 16H, $-C\underline{H}_2CH_3$), 2.90(t, 1H, $-C\underline{H}O$, J_{vic} = 5 Hz), 1.86(t, 24H, $-CH_2C\underline{H}_3$) and -5.55(dd, 2H, $Rh-C\underline{H}_2-$, J_{Rh-H} = 4 Hz); ir 2710, 1680 cm^{-1} (CHO); vis(CHCl$_3$) λ_{max}(logε) 386(5.29), 512(4.25) and 544 nm (4.65). Anal. Calcd for $C_{38}H_{47}ORh$: C, 67.24; H, 6.98; N, 8.26. Found: C, 66.94; H, 6.86; N, 8.32.

OEPRh^{III}-CH$_2$CHO(B) (B = py (IV), PRh$_3$ (V))

The complex (III) was recrystallized from CH$_2$Cl$_2$-n-hexane in the presence of a slight excess of pyridine or triphenylphosphine. The red crystals were washed with n-hexane to give hexa-coordinate complexes, (IV) and (V), in almost quantitative yield. Complex (IV) shows the following properties: pmr δ(CDCl$_3$) 10.06(s, 4H, $=C\underline{H}-$), 5.86(t, 1H, pyridine γ-$\underline{H}$), 4.99(t, 2H, pyridine β-$\underline{H}$), 4.09(q, 16H, $-C\underline{H}_2CH_3$), 3.09(t, 1H, $-CH_2C\underline{H}O$, J_{vic} = 5 Hz), 1.91(t, 24H, $-CH_2C\underline{H}_3$), 1.32(d, 2H, pyridine α-$\underline{H}$) and -5.89(dd, 2H, $Rh-C\underline{H}_2-$, J_{Rh-H} = 3 Hz); ir 2705, 1671 cm^{-1} (CHO); vis(CHCl$_3$) λ_{max}(logε) 352(4.51), 407(5.24), 522(4.27) and 552 nm(4.49). Anal. Calcd for $C_{43}H_{52}N_5ORh$: C, 68.15; H, 6.92; N, 9.24. Found: C, 67.78; H, 7.08; N, 9.14. Complex (V) shows the following properties: pmr δ(CDCl$_3$) 9.83(s, 4H, $=C\underline{H}-$), 6.78(t, 3H, phenyl para-$\underline{H}$), 6.41(t, 6H, phenyl meta-$\underline{H}$), 3.94(m, 22H, $-C\underline{H}_2CH_3$ and phenyl ortho-$\underline{H}$), 2.80(t, 1H, $-CH_2C\underline{H}O$, J_{vic} = 5 Hz), 1.90(t, 24H, $-CH_2C\underline{H}_3$) and -6.12(dd, 2H, $Rh-C\underline{H}_2-$, J_{Rh-H} = 3 Hz); ir 2710, 1664 cm^{-1} (CHO); vis(CHCl$_3$ λ_{max}(logε) 365(4.51), 419(4.94), 530(4.16) and 560 nm(4.18). Anal. Calcd for $C_{56}H_{62}N_4OPRh$: C, 71.47; H, 6.64; N, 5.95. Found: C, 70.69; H, 6.58; N, 5.91.

OEPRh^{III}-CH=CH-Cl (VI)

Acetylene gas washed with water and dried over sulfric acid was introduced into the benzene solution of (I) and the mixture was stirred for 2 hr at room temperature. An orange precipitate was formed. The solvent was removed and the residue was chromatographed on silica gel. The fraction eluted with benzene was collected and concentrated under reduced pressure. Recrystallization from CH_2Cl_2-n-hexane gave $OEPRh^{III}$-CH=CH-Cl (VI) in 67 % yield: pmr δ($CDCl_3$) 10.03(s, 4H, =C$\underline{H}$-), 4.01(q, 16H, -C$\underline{H}_2$CH_3), 1.88(t, 24H, -CH_2C$\underline{H}_3$), -1.48(dd, 1H, Rh-C$\underline{H}$=, J_{trans} = 12 Hz, J_{Rh-H} = 2 Hz) and -1.79(d, 1H, =C$\underline{H}$-Cl); vis($CHCl_3$) λ_{max}(logε) 395(5.23), 512(4.23) and 544 nm(4.74). Anal. Calcd for $C_{38}H_{46}N_4ClRh$: C, 65.47; H, 6.65; N, 8.04; Cl, 5.08. Found: C, 65.28; H, 6.51; N, 7.85; Cl, 5.36.

$OEPRh^{III}$-CH=C(C_6H_5)-Cl (VII) and $OEPRh^{III}$-$COCH_2C_6H_5$ (VIII)

Phenylacetylene was added to the benzene solution of (I). The solution was stirred for 30 min at room temperature. Two products were isolated by the column chromatography on silica gel. The first orange band eluted with benzene-n-hexane (1 : 2) afforded $OEPRh^{III}$-CH=C(C_6H_5)-Cl (VII) in 20 % yield: pmr τ($CDCl_3$) 10.06(s, 4H, =C$\underline{H}$-), 6.21(m, 3H, phenyl meta- and para-$\underline{H}$), 4.81(d, 2H, phenyl ortho-$\underline{H}$), 4.03(q, 16H, -C$\underline{H}_2$CH_3), 1.88(t, 24H, -CH_2C$\underline{H}_3$) and 1.34(d, 1H, Rh-C$\underline{H}$=, J_{Rh-H} = 2 Hz); vis(C_6H_6) λ_{max}(logε) 394(5.05), 513(4.06) and 546 nm(4.67). Anal. Calcd for $C_{44}H_{50}N_4ClRh$: C, 68.34; H, 6.52; N, 7.25; Cl, 4.58. Found: C, 67.61; H, 6.34; N, 7.09; Cl, 4.80. The second fraction eluted with benzene from the silica gel column afforded $OEPRh^{III}$-$COCH_2C_6H_5$ (VIII) in 23 % yield: pmr δ($CDCl_3$) 10.00(s, 4H, =C$\underline{H}$-), 6.28(m, 3H, phenyl meta- and para-$\underline{H}$), 4.30(d, 2H, phenyl ortho-$\underline{H}$), 4.01(q, 16H, -C$\underline{H}_2$CH_3), 1.99(t, 24H, -CH_2C$\underline{H}_3$) and -2.27 (s, 2H, Rh-CO-C$\underline{H}_2$-); ir 1725 cm^{-1} ν(C=O); vis(C_6H_6) λ_{max}(logε) 397(5.21), 512(4.15) and 544 nm (4.72). Anal. Calcd for $C_{44}H_{51}N_4ORh$: C, 70.01; H, 6.81; N, 7.42. Found: C, 70.11; H, 7.00; N, 7.49.

$OEPRh^{III}$-COC_5H_{11} (IX)

The complex (I) was allowed to react with an excess of 1-hexyne at room temperature for 1 hr. Purification of the crude product by the silica gel column with benzene afforded $OEPRh^{III}$-COC_5H_{11} in 75 % yield: pmr δ($CDCl_3$) 10.00(s, 4H, =C$\underline{H}$-), 3.97(q, 16H, -C$\underline{H}_2$CH_3), 1.86(t, 24H, -CH_2C$\underline{H}_3$), 0.04(t, 3H, -CO$(CH_2)_4$C$\underline{H}_3$), -0.12(m, 2H, -CO$(CH_2)_3$C$\underline{H}_2$-), -1.22(qui, 2H, -CO$(CH_2)_2$C$\underline{H}_2$-), -1.76(qui, 2H, -COCH_2C$\underline{H}_2$-) and -3.77(t, 2H, -COC$\underline{H}_2$-) ir 1710 cm^{-1} ν(C=O); vis(C_6H_6) λ_{max}(logε) 397(5.31), 513(4.20) and 545 nm (4.81). Anal. Calcd for $C_{42}H_{55}N_4ORh{\cdot}H_2O$: C, 67.00; H, 7.63; N, 7.44. Found: C, 67.08; H, 7.66; N, 7.87.

$OEPRh^{III}$*-CO*$(CH_2)_3$*OH (X)*

3-Butyne-1-ol (0.2 ml) was added to the benzene solution of (I) (70 mg) and the solution was stirred for 2 hr at ambient temperature. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel. The orange eluate with benzene was collected, concentrated and recrystallized from $CHCl_3$-n-hexane to afford 34 mg of red crystals, $OEPRh^{III}-CO(CH_2)_3OH$ (X), in 45 % yield: pmr $\delta(CDCl_3)$ 10.02(s, 4H, $=C\underline{H}-$), 4.02(q, 16H, $-C\underline{H}_2CH_3$), 1.90(t, 24H, $-CH_2C\underline{H}_3$), 1.28(s, 1H, -OH), 1.03(t, 2H, $-C\underline{H}_2OH$), -1.20(qui, 2H, $-C\underline{H}_2CH_2OH$) and -3.63(t, 2H, $Rh-C\underline{H}_2-$); ir 3580 cm^{-1} ν(OH) and 1714 cm^{-1} ν(C=O); vis($CHCl_3$) λ_{max}(logε) 394(5.25), 510(4.13) and 544 nm(4.70). Anal. Calcd for $C_{40}H_{51}N_4O_2Rh\cdot H_2O$: C, 64.85; H, 7.21; N, 7.56. Found: C, 64.11; H, 6.82; N, 7.50.

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