Reactions of C–H bonds in organic oxygenates with octaethylporphyrinato rhodium(II) and iridium(II) dimers

Kenneth J. Del Rossi, Xiao-Xiang Zhang, Bradford B. Wayland *

Department of Chemistry, University of Pennsylvania Philadelphia, PA 19104-6323, USA

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Abstract

Metalloporphyrin dimers, [(OEP)M]$_2$ (1a, M = Rh; 1b, M = Ir; OEP = octaethylporphyrin dianion), are observed to react with C–H bond units in aldehydes, ketones and benzyl alcohols. Aldehydes, R$_2$CHCHO, preferentially react at the alkyl group adjacent to the carbonyl position to yield β-formyl complexes, (OEP)M–CR$_2$CHO, even when reaction of the aldehydic C–H unit is thermodynamically favored. Reaction at the carbon–hydrogen bond adjacent to the carbonyl group is proposed to occur by addition of the metalloporphyrin to the enol isomer to produce an intermediate alkyl bridged complex, (OEP)M–CR$_2$CR'(OH)–M(OEP), which subsequently reacts by an effective β-O–H migration to form (OEP)M–CR$_2$C(O)R' and (OEP)M–H complexes. [(OEP)Rh]$_2$ (1a) also reacts with benzyl alcohols, C$_6$H$_5$CH(OH)R (R = H, CH$_3$, C(O)C$_6$H$_5$), to produce intermediate α-hydroxyalkyl derivatives, (OEP)Rh–CR(OH)C$_6$H$_5$, which subsequently dissociate to give organic carbonyl species, C$_6$H$_5$C(O)R, and (OEP)Rh–H.

Keywords: Rhodium; Iridium; C–H activation; Metalloporphyrins

1. Introduction

One of the focal issues of organometallic-catalysis studies is the development of new strategies and materials for hydrocarbon activation [1]. Addition of C–H bonds to metal species is one approach which offers potential for selective functionalization of hydrocarbons. Substantial advances have been made in hydrocarbon C–H bond reactions involving oxidative addition to single metal centers [2,3] (Eq. (1)), σ-bond metathesis of M–X units [4], and addition to M = X groups [5].

$$M + R-H \rightleftharpoons H-M-R \qquad (1)$$

Our studies have focused on one electron oxidative addition of the C–H unit with two metal centers to produce separate metal–hydride and metal–alkyl species, in accord with Eq. 2 [6]. Selective methane activation has been achieved by reactions of stable

$$M-M + R-H \rightleftharpoons M-R + M-H \qquad (2)$$
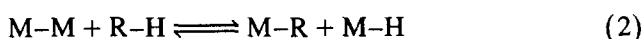
mono and bimetalloradical complexes of rhodium(II) porphyrins [6a–6d]. Oxidative addition to a M–M

bonded species (Eq. (2)) is more thermodynamically demanding than to stable metalloradicals or to a single metal center (Eq. (1)) because of the M–M bond energy. Thermodynamic studies for the (OEP)Rh system have provided estimates for the (OEP)Rh–H (62 kcal mol^{-1}), (OEP)Rh–CH$_3$ (58 kcal mol^{-1}) and (OEP)Rh–Rh(OEP) (16 kcal mol^{-1}) bond energies [7] which indicate that [(OEP)Rh]$_2$ (1a) should be thermodynamically capable of producing readily observable reactions with hydrocarbons that have C–H bond energies up to ~ 100 kcal mol^{-1}. We have previously reported selective reactions of the alkyl C–H bonds in alkylaromatics with both [(OEP)Rh]$_2$ and [(OEP)Ir]$_2$ [6e–6g]. This paper presents C–H bond reactivity studies of [(OEP)M]$_2$ (1a, M = Rh; 1b, M = Ir) with aldehydes and ketones and further extends the alkylaromatic reactions to benzylalcohols.

2. Results

2.1. Reactions of aldehydes with [(OEP)M]$_2$

2.1.1. Ethanal, propanal
[(OEP)M]$_2$ complexes (1a, M = Rh; 1b, M = Ir) react with ethanal and propanal at room temperature to

yield approximately equal quantities of β-formyl complexes (OEP)M-CHRCHO (7a, M = Rh, R = H; 7b, M = Ir, R = H; 8, M = Rh, R = CH₃) and α-hydroxyalkyl complexes (OEP)M-CH(OH)CH₂R (9a, M = Rh, R = H; 9b, M = Ir, R = H; 10, M = Rh, Rh = CH₃) (Eq. (3)). The ¹H NMR spectra for (OEP)Ir-CH₂CHO (7b) and (OEP)Ir-CH(OH)CH₃ (9b) display approximately

$$[(OEP)M]_2 + 2RCH_2CHO$$

$$\rightleftharpoons (OEP)M\text{-}CHRCHO$$
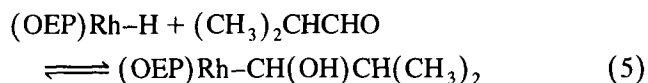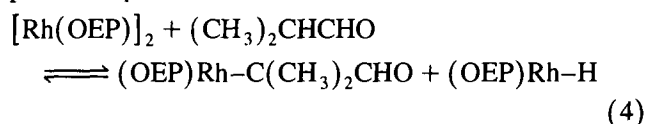
$$+ (OEP)M\text{-}CH(OH)CH_2R \qquad (3)$$
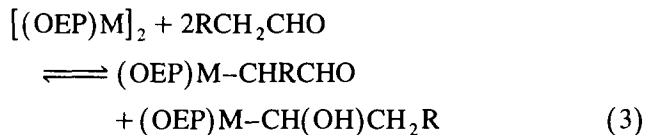
mately equal intensity methine peaks at $\delta = 10.07$ ppm and $\delta = 9.96$ ppm respectively (Fig. 1). The high field doublet at $\delta = -4.16$ ppm, and triplet at $\delta = 3.79$ ppm with $^3J_{HH} = 4.4$ Hz are the most characteristic resonances for the iridium β-formyl complex [6e,8]. The chemical shifts and splitting patterns observed for (OEP)Ir-CH(OH)CH₃ (9b) are comparable to those previously reported for the rhodium analog [9]. Infrared

spectra of 7a, 7b and 8 show carbonyl stretching bands at 1686 cm⁻¹, 1693 cm⁻¹ and 1659 cm⁻¹ respectively.

2.1.2. 2-Methylpropanal

Reaction of 2-methylpropanal with [(OEP)Rh]₂ (1a) at 296 K in the dark in C₆D₆ occurs exclusively at the α-C-H group which produces equal quantities of the β-formyl, (OEP)Rh-C(CH₃)₂CHO (11) and α-hydroxyalkyl, (OEP)Rh-CH(OH)CH(CH₃)₂ (12) complexes (Eqs. (4) and (5)).

$$[Rh(OEP)]_2 + (CH_3)_2CHCHO$$

$$\rightleftharpoons (OEP)Rh\text{-}C(CH_3)_2CHO + (OEP)Rh\text{-}H$$

$$\qquad (4)$$

$$(OEP)Rh\text{-}H + (CH_3)_2CHCHO$$

$$\rightleftharpoons (OEP)Rh\text{-}CH(OH)CH(CH_3)_2 \qquad (5)$$

Exposure of these solutions to ambient laboratory light or heating at 373 K results in conversion of the β-formyl to an acyl complex, (OEP)Rh-C(O)CH(CH₃)₂
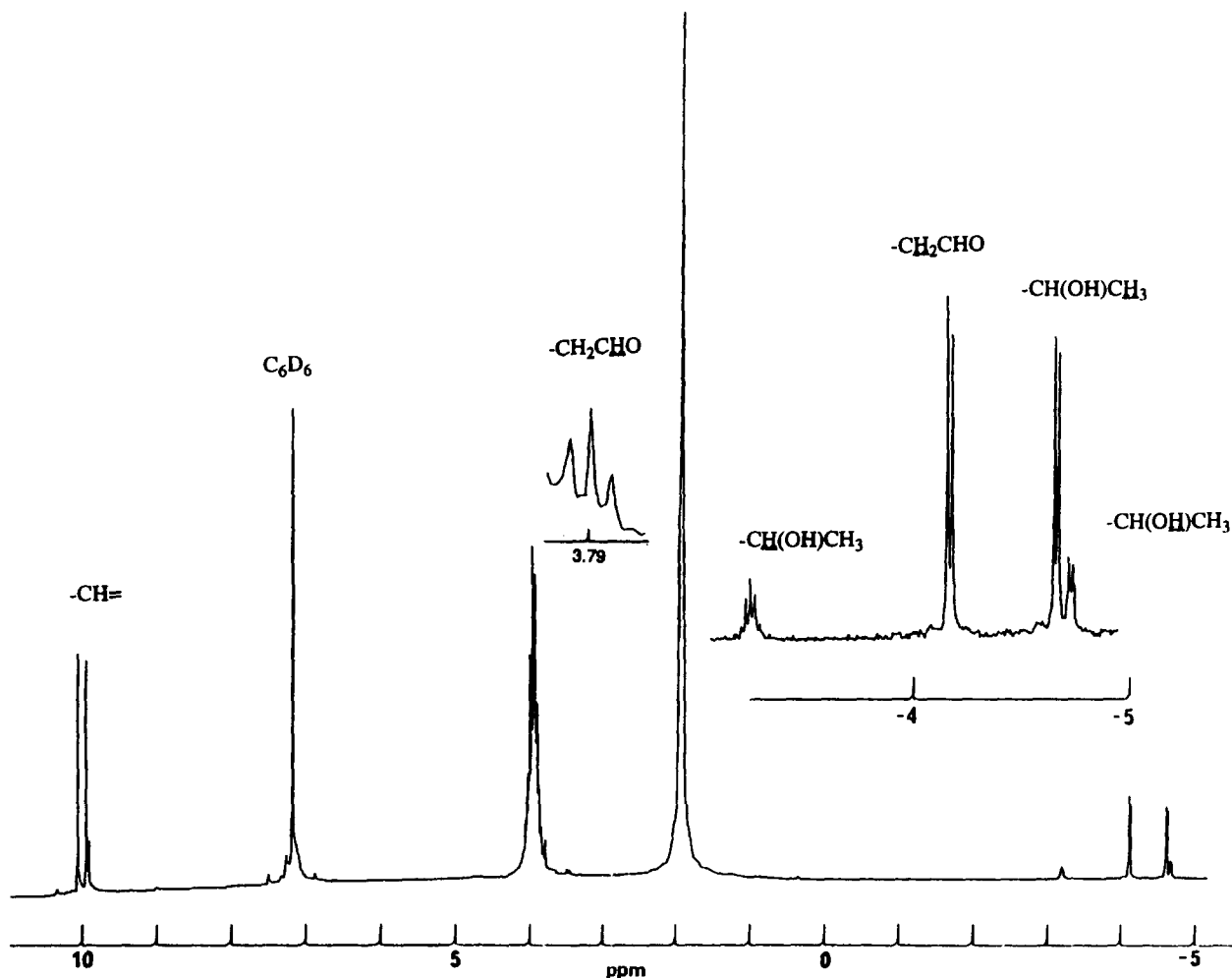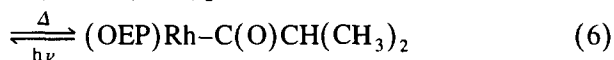

Fig. 1. Proton NMR spectrum for compound 7b, (OEP)Ir-CH₂CHO, and compound 9b, (OEP)Ir-CH(OH)CH₃, in C₆D₆. Inset: expanded high field region.

(13) (Eq. (6)). The acyl complex 13 is also produced when a solution of [(OEP)Rh]$_2$ (1a) in neat 2-methyl-

$$(OEP)Rh-C(CH_3)_2CHO$$

$$\xrightleftharpoons[h\nu]{\Delta} (OEP)Rh-C(O)CH(CH_3)_2 \qquad (6)$$

propanal is heated (373 K, 1 h). Compound 13 has a carbonyl stretching vibration at 1709 cm^{-1} and a parent ion at m/e 707 in the mass spectrum.

2.1.3. 2,2-Dimethylpropanal

Solutions of [(OEP)Rh]$_2$ in 2,2-dimethylpropanal failed to react at a finite rate under ambient conditions, but upon heating (373 K, 18 h) the aldehyde reacts to form an acyl complex, (OEP)Rh-C(O)C(CH$_3$)$_3$ (14), and 4 as the predominant products (Eq. (7)). The ^{1}H

$$[Rh(OEP)]_2 + (CH_3)_3CCHO$$

$$\longrightarrow (OEP)Rh-H + (OEP)Rh-C(O)C(CH_3)_3 \qquad (7)$$
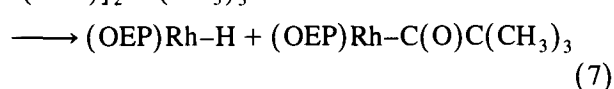
NMR spectrum for the acyl complex 14 shows a sharp singlet at $\delta = -2.51$ ppm corresponding to the t-butyl group. Complex 14 was also identified by the strong parent ion at m/e 721 in the mass spectrum and carbonyl stretching vibration at 1678 cm^{-1}. A minor

organometallic species (OEP)Rh-CH$_2$CH(CH$_3$)$_2$, (15), is also observed which was identified by ^{1}H NMR and a parent ion at m/e 693 in the mass spectrum.

2.2. Reactions of ketones with [(OEP)Rh]$_2$

2.2.1. Dimethyl and methylphenyl ketones

[(OEP)Rh]$_2$ (1a) reacts with ketones, CH$_3$C(O)R, (R = CH$_3$, C$_6$H$_5$) (393 K, 5 h) to produce β-carbonyl, (OEP)Rh-CH$_2$C(O)R (16, R = CH$_3$; 17, R = C$_6$H$_5$), and metal-hydride, (OEP)Rh-H (4) (Eq. (8)). ^{1}H NMR of compound 16 in C$_6$D$_6$ displays a high field doublet

$$[(OEP)Rh]_2 + CH_3C(O)R$$

$$\rightleftharpoons (OEP)Rh-CH_2C(O)R + (OEP)Rh-H \qquad (8)$$
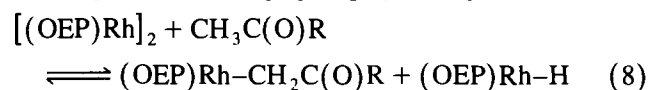
($\delta = -4.46$ ppm; $^2J_{Rh-CH2} = 4.0$ Hz) corresponding to the α-methylene group (Fig. 2). Complexes 16 and 17 were also identified by the mass spectra which have parent ion peaks at m/e 693 and m/e 755, respectively, and CO stretching vibrations centered at 1675 cm^{-1}.

2.3. Reactions of benzyl alcohols with [(OEP)Rh]$_2$

[(OEP)Rh]$_2$ reacts with neat benzyl alcohols (393 K, 5 h) to yield (OEP)Rh-H (4) and carbonyl species,
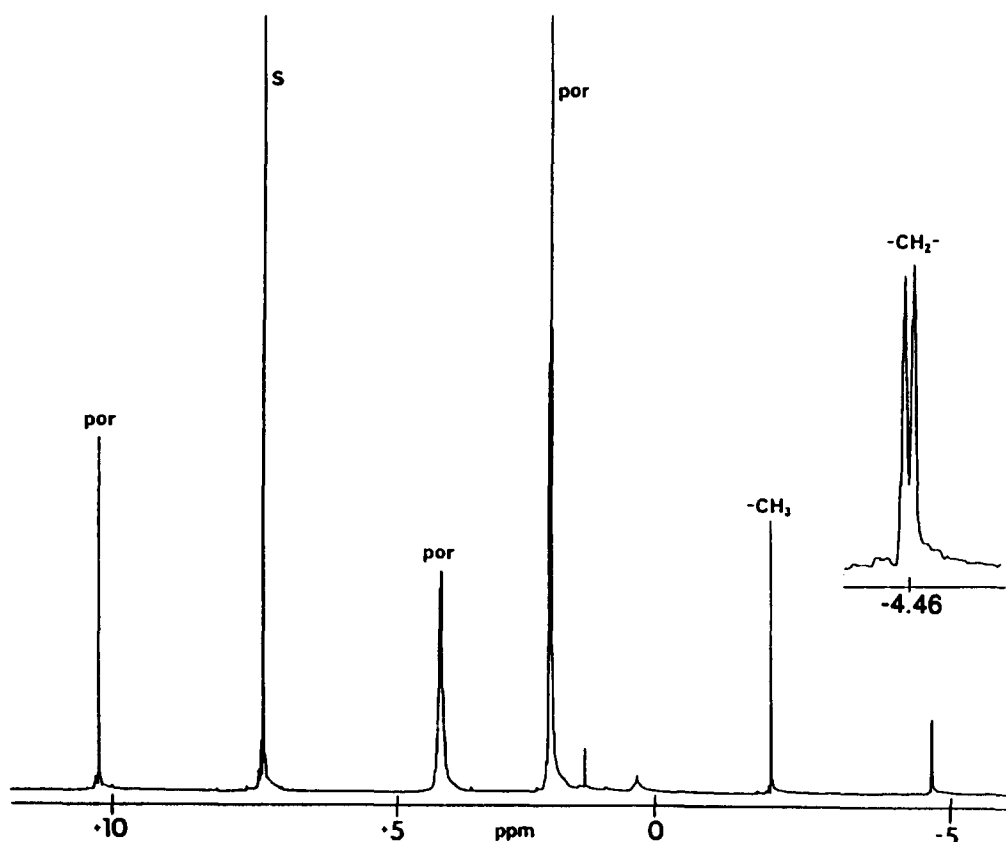
Fig. 2. Proton NMR spectrum for compound 16, (OEP)Rh-CH$_2$C(O)CH$_3$, in C$_6$D$_6$. Inset: expanded high field region.

$C_6H_5C(O)R$ (R = H, CH_3, $C(O)C_6H_5$) (Eq. (9)). Fig. 3 shows the ^1H NMR spectra for a sample of [(OEP)-

$$[(OEP)Rh]_2 + C_6H_5CH(OH)R$$

$$\rightleftharpoons 2(OEP)Rh-H + C_6H_5C(O)R \qquad (9)$$
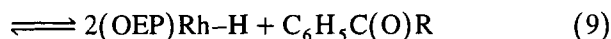
$Rh]_2$ with $C_6H_5CH_2OH$ before and after heating at 393 K for 5 h in the dark. Complete loss of the characteristic $[(OEP)Rh]_2$ resonance (δ_{CH} = 9.29 ppm) is accompanied by formation of (OEP)Rh–H ($\delta_{-CH=}$ = 10.14 ppm) and a stoichiometric amount of benzaldehyde (δ_{CHO} = 9.61 ppm).

When $[(OEP)Rh]_2$ was reacted with neat benzyl alcohol at lower temperature (363 K, 1 h) a transient α-hydroxyalkyl complex, $(OEP)Rh-CH(OH)C_6H_5$ (**18**),

was detected in the ^1H NMR (Fig. 4). Compound **18** subsequently reacts to form (OEP)Rh–H (**4**) and benzaldehyde fragments.

2.4. Reactions of ethyl vinyl ether with [(OEP)M]₂

Addition of excess ethyl vinyl ether, $CH_2 = CH(OEt)$, to a saturated benzene solution of $[(OEP)Rh]_2$ at 295 K results in the immediate formation of a red complex identified as (OEP)Rh–CH₂CH(OEt)–Rh(OEP) (**19a**) (Eq. (10)). The high field ^1H NMR spectra for ethoxy

$$[(OEP)M]_2 + CH_2 = CHX \rightleftharpoons (OEP)M-CH_2CH(X)-M(OEP) \qquad (10)$$

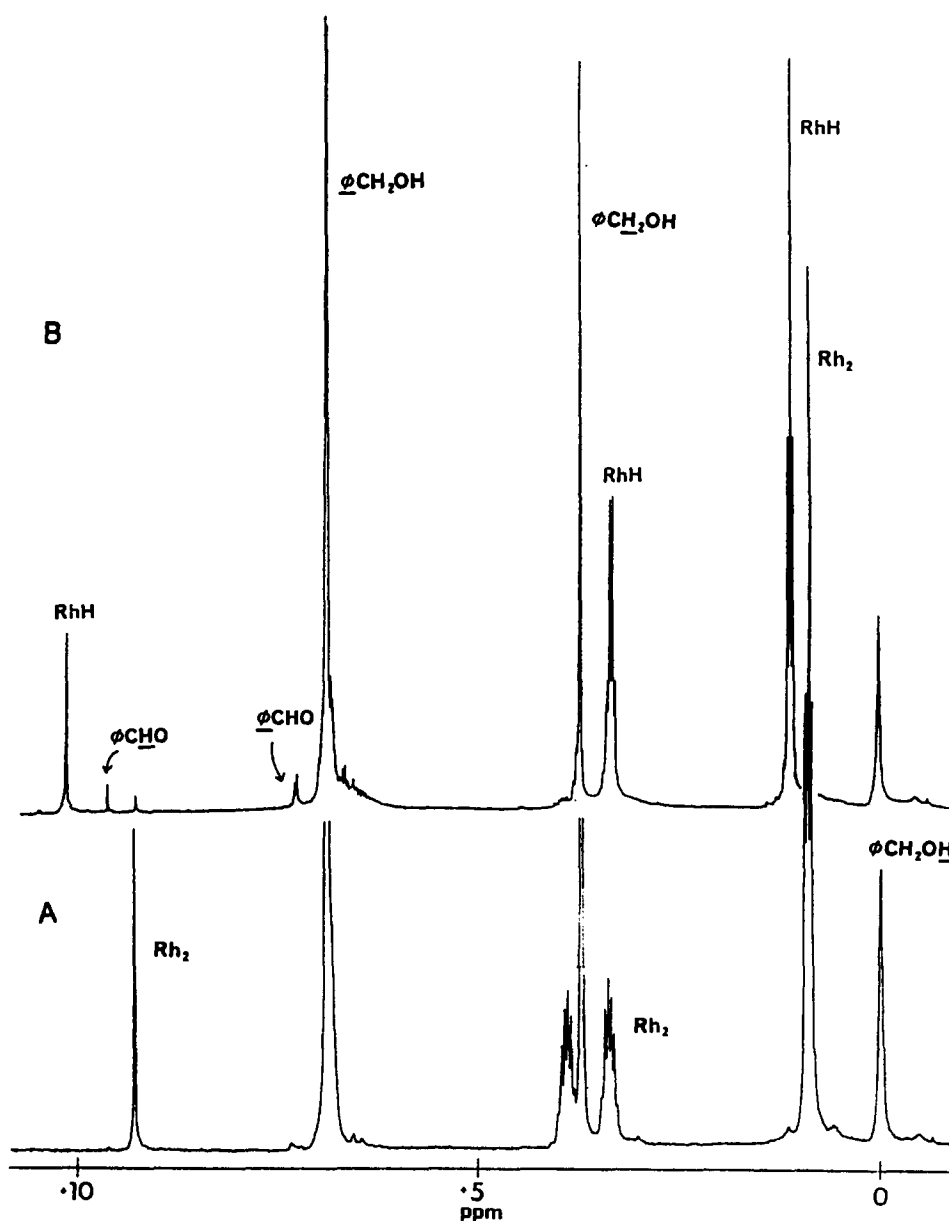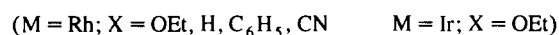(M = Rh; X = OEt, H, C_6H_5, CN   M = Ir; X = OEt)

Fig. 3. Proton NMR spectrum for the reaction of $[(OEP)Rh]_2$ with $C_6H_5CH_2OH$ in C_6D_6: (A) initial spectrum ($t = 0$), (B) after heating for 5 h at 393 K.

substituted (OEP)M–CH$_2$CH(X)–M(OEP) complexes (**19a**, M = Rh; **19b**, M = Ir) are shown in Fig. 5. Hydrogen atoms in the bridging alkyl groups show exceptional high field chemical shifts (−8 to −11 ppm) which are characteristic of hydrogens that are positioned between two aromatic porphyrin rings [7b,10].

3. Discussion

3.1. Reactions of aldehydes and ketones

Carbon–hydrogen bonds in aldehydes and ketones are partially activated relative to alkanes. The aldehydic C–H bond in ethanal, CH$_3$CHO ($D_{CH} \sim 86$ kcal mol^{-1}), is significantly weaker than the methyl C–H bonds ($D_{CH} = 100$ kcal mol^{-1}) which is comparable to the methyl C–H bonds in alkanes ($D_{CH} = 100$–105 kcal mol^{-1}) [11]. The weaker aldehydic C–H bond is ex-

pected to provide more favorable thermodynamic and kinetic factors for reactions that occur at this site compared with reactions at an alkyl C–H fragment. Several examples of ketone alkyl C–H bond reactions with transition metals are known [12], but aldehydes have invariably been reported to react at the weaker aldehydic C–H bond [13]. One of the most prominent examples of this type of reactivity is the metal promoted decarbonylation of aldehydes which occurs through oxidative addition of the aldehydic C–H unit [13a,13b].

In contrast with previously reported metal systems, [(OEP)M]$_2$ (**1a**, M = Rh; **1b**, M = Ir) complexes preferentially react with alkyl α-CH bonds in both aldehydes and ketones. The observed reactivity is unusual because the stronger alkyl C–H bonds ($D_{CH} = 92$–100 kcal mol^{-1}) react in preference to the weaker aldehydic C–H bonds ($D_{CH} = 72$–88 kcal mol^{-1}). Reaction of [(OEP)Rh]$_2$ (**1a**) with 2-methylpropanal, (CH$_3$)$_2$-CHCHO, initially occurs with the α-C–H bond to produce the β-formyl complex, (OEP)Rh–
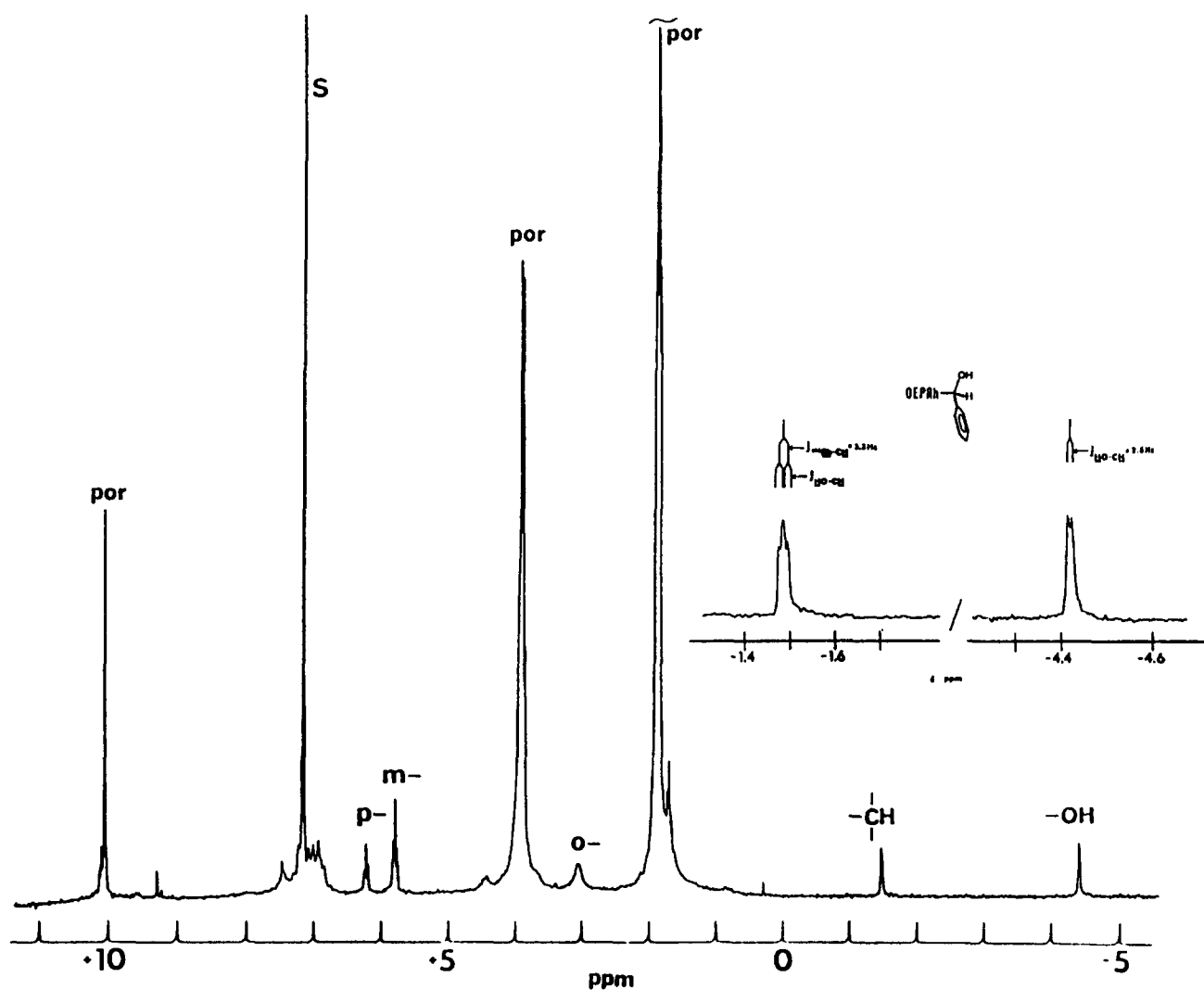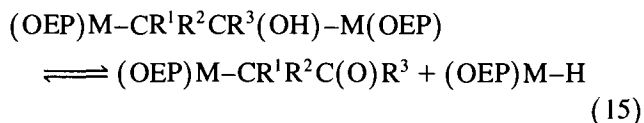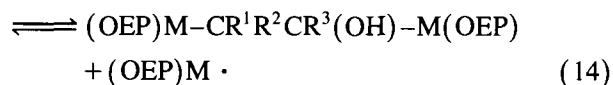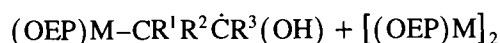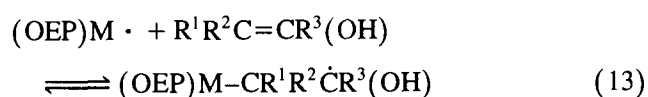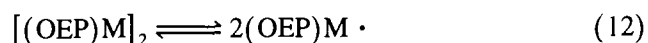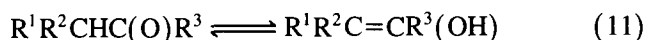

Fig. 4. Proton NMR spectrum for compound **18**, (OEP)Rh–CH(OH)C$_6$H$_5$, in C$_6$D$_6$. Inset: expanded high field region.

$C(CH_3)_2CHO$ (**11**), but both light and heat promote rearrangement to the acyl complex, (OEP)Rh–C(O)$CH(CH_3)_2$ (**13**), as the thermodynamic product. The presence of an α-CH group apparently provides a lower energy pathway for reaction even when reaction of the aldehydic C–H group produces the more thermodynamically stable acyl complex. A plausible explanation for this behavior is that [(OEP)M]$_2$ (**1a, 1b**) dimers initially react with the enol isomers of aldehydes and ketones. One of the characteristic reactions of [(OEP)M]$_2$ complexes (**1a**, M = Rh; **1b**, M = Ir) is addition with alkenes to form alkyl bridged complexes (Eq. (10)) [7b,10]. Halpern has demonstrated that a radical chain mechanism is operative in the reaction of styrene with [(OEP)Rh]$_2$ (**1a**) [10a], and an analogous reaction pathway could be operative in the reactions of α-CH bonds in aldehydes and ketones, as depicted in Eqs. (11–15).

$$R^1R^2CHC(O)R^3 \rightleftharpoons R^1R^2C=CR^3(OH) \quad (11)$$

$$[(OEP)M]_2 \rightleftharpoons 2(OEP)M \cdot \quad (12)$$

$$(OEP)M \cdot + R^1R^2C=CR^3(OH)$$
$$\rightleftharpoons (OEP)M-CR^1R^2\dot{C}R^3(OH) \quad (13)$$

$$(OEP)M-CR^1R^2\dot{C}R^3(OH) + [(OEP)M]_2$$

$$\rightleftharpoons (OEP)M-CR^1R^2CR^3(OH)-M(OEP)$$
$$+ (OEP)M \cdot \quad (14)$$

$$(OEP)M-CR^1R^2CR^3(OH)-M(OEP)$$
$$\rightleftharpoons (OEP)M-CR^1R^2C(O)R^3 + (OEP)M-H \quad (15)$$

Formation of the proposed vinyl alcohol intermediate (Eqs. (13) and (14)) has been modeled by observing the corresponding reactions of [(OEP)M]$_2$ (**1a**, M = Rh; **1b**, M = Ir) with ethyl vinyl ether (Eq. (10)). The proposed intermediate depicted in Eq. 14 contains a β-O–H unit which readily eliminates the metal hydride. Substitution of an alkoxy group in place of the hydroxy unit provides sufficient kinetic stability to observe the model intermediate.

Reaction of [(OEP)Rh]$_2$ with 2,2-dimethylpropanal, $(CH_3)_3CCHO$, requires both higher temperatures and longer reaction times than aldehydes and ketones that contain α-CH groups. The dominant organometallic product is the acyl complex, (OEP)Rh–C(O)C(CH$_3$)$_3$ (**14**) but a second organometallic species, (OEP)Rh–$CH_2CH(CH_3)_2$ (**15**), is also observed in low yield. Compound **15** most likely results from trapping of a tert-butyl radical by (OEP)Rh · , and subsequent rear-
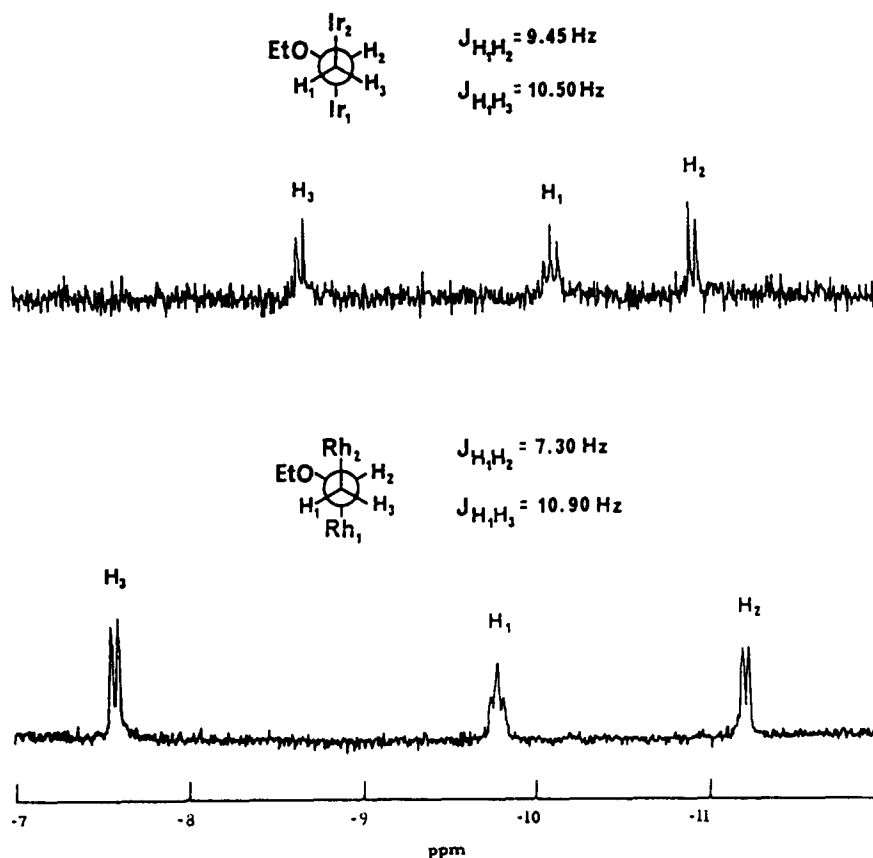

Fig. 5. High field proton NMR spectra for ethoxy substituted { μ-CH$_2$CH(X)}[(OEP)M]$_2$ complexes (**19a**, M = Rh; **19b**, M = Ir) in C_6D_6.

Table 1
Proton NMR data for (OEP)M–X complexes in C_6D_6

No.	M	X	–CH=	–CH$_2$	–CH$_3$	X
7a	Rh	CH$_2$CHO	s, 10.26	m, 3.97	t, 1.90	CHO, t, 3.44, J_{H-H} = 4.5; CH$_2$, dd, −5.11, J_{Rh-H} = 3.5
7b	Ir	CH$_2$CHO	s, 10.07	m, 3.93	t, 1.88	CHO, t, 3.79, J_{H-H} = 4.4; CH$_2$, d, −4.16
8	Rh	CH(CH$_3$)CHO	s, 10.25	m, 3.96	t, 1.90	CHO, d, 3.13, J_{H-H} = 2.0; Rh–CH, −4.32, m, J_{Rh-CH} = 3.7, J_{CH-CHO} = 2.0, J_{CH-CH_3} = 7.3; CH$_3$, dd, −4.78, $J_{Rh-C-CH_3}$ = 2.0
9a	Rh	CH(OH)CH$_3$	s, 10.17	m, 3.95	t, 1.90	Rh–CH, m, −2.33, J_{Rh-H} = 4.0, J_{CH-CH_3} = 5.9, J_{CH-OH} = 4.9; CH$_3$, d, −4.10; OH, d, −4.36
9b	Ir	CH(OH)CH$_3$	s, 9.93	m, 3.94	t, 1.87	Rh–CH, m, −3.25, J_{CH-CH_3} = 5.3; CH$_3$, d, −4.68; OH, d, −4.37
10	Rh	CH(OH)CH$_2$CH$_3$	s, 10.20	m, 3.93	t, 1.90	CH$_3$, t, −1.77, J_{H-H} = 7.3; Rh–CH, m, −2.40, J_{CH-OH} = 5.3, J_{Rh-H} = 3.7, J_{trans} = 11.0, J_{cis} = 3.0; CHaHb, m, −4.02; CHaHb, m, −4.39; OH, d, −4.48
11	Rh	C(CH$_3$)$_2$CHO	s, 10.29	m, 3.97	t, 1.89	CHO, s, 3.19; CH$_3$, d, −4.60, $J_{Rh-C-CH_3}$ = 2.0
12	Rh	CH(OH)CH(CH$_3$)$_2$	s, 10.19	m, 3.92	t, 1.91	CH$_3$, d, −1.65, J_{CH-CH_3} = 6.9; CH(OH), dd, −2.60, J_{Rh-CH} = 3.3, J_{CH-OH} = 4.65; CH$_3$, d, −2.63; OH, d, −4.27; CH(CH$_3$)$_2$, m, −4.62
13	Rh	C(O)CH(CH$_3$)$_2$	s, 10.31	m, 3.97	t, 1.89	CH$_3$, d, −2.32, J_{H-H} = 7.1; CH, m, −3.95
14	Rh	C(O)C(CH$_3$)$_3$	s, 10.30	m, 3.97	t, 1.88	CH$_3$, s, −2.51
15	Rh	CH$_2$CH(CH$_3$)$_2$	s, 10.22	m, 3.98	t, 1.91	CH$_3$, d, −2.39, J_{H-H} = 6.6; CH, m, −4.94; Rh–CH$_2$, dd, −5.18, J_{Rh-H} = 3.3, J_{H-H} = 5.3
16	Rh	CH$_2$C(O)CH$_3$	s, 10.27	m, 3.96	t, 1.91	CH$_3$, s, −2.07; Rh–CH$_2$, d, −4.46, J_{Rh-CH_2} = 3.95
17	Rh	CH$_2$C(O)C$_6$H$_5$	s, 10.12	m, 3.94	t, 1.91	p-phenyl, t, 6.61; m-phenyl, t, 6.39; o-phenyl, d, 4.54; Rh–CH$_2$, d, −4.47, J_{Rh-CH_2} = 3.5
18	Rh	CH(OH)C$_6$H$_5$	s, 10.04	q, 3.90	t, 1.88	p-phenyl, t, 6.21; m-phenyl, t, 5.78; o-phenyl, brs, 3.04; Rh–CH, dd, −1.49, J_{CH-CH} = 2.7, J_{Rh-CH} = 3.3; OH, d, −4.42
22	Rh	C(O)CH$_3$	s, 10.30	m, 3.98	t, 1.90	CH$_3$, s, −3.16
23	Rh	C(O)CH$_2$CH$_3$	s, 10.31	m, 3.99	t, 1.91	CH$_3$, t, −2.13, J_{H-H} = 7.2; CH$_2$, q, −3.33
24a	Rh	C(O)C$_6$H$_5$	s, 10.14	q, 3.94	t, 1.87	p-phenyl, t, 5.96; m-phenyl, t, 5.59; o-phenyl, d, 2.28
24b	Ir	C(O)C$_6$H$_5$	s, 10.00	m, 3.89	t, 1.85	p-phenyl, t, 6.00; m-phenyl, t, 5.62; o-phenyl, d, 2.41

Resonances are given in units of ppm and J values in Hz. brs, broad singlet.

rangement of the sterically hindered tert-butyl complex (Eqs. (16) and (17)). Dissociation of CO from · C(O)-

$$\cdot C(O)C(CH_3)_3 \rightleftharpoons CO + \cdot C(CH_3)_3 \qquad (16)$$

$$\cdot C(CH_3)_3 + (OEP)Rh \cdot$$

$$\rightleftharpoons [(OEP)Rh-C(CH_3)_3]$$
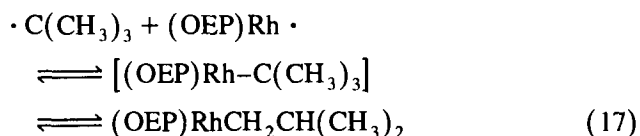
$$\rightleftharpoons (OEP)RhCH_2CH(CH_3)_2 \qquad (17)$$

$C(CH_3)_3$ is suggested as the source of t-butyl radicals (Eq. (16)). Organometallic species where (OEP)Rh is bonded to a tertiary carbon center are known to rearrange or eliminate alkenes [6f]. Isomerization of (OEP)-Rh–C(CH$_3$)$_2$C$_6$H$_5$ to (OEP)RhCH$_2$CH(CH$_3$)C$_6$H$_5$ at 380 K in benzene provides a precedent for this type of rearrangement [6f].

3.2. Reactions of benzyl alcohols

[(OEP)Rh]$_2$ (1a) dehydrogenates benzyl alcohols to give (OEP)Rh–H (4) and carbonyl species, C$_6$H$_5$C(O)R (R = H, CH$_3$ or C(O)C$_6$H$_5$). Direct observation of an intermediate α-hydroxyalkyl (OEP)Rh–CH(OH)C$_6$H$_5$ (18) in the reaction of [(OEP)Rh]$_2$ with neat benzyl alcohol indicates that the initial step is reaction of the benzylic C–H bond to form an α-hydroxyalkyl complex and (OEP)Rh–H (4) (Eq. (18)). Reactions of benzylic C–H bonds in alkylaromatics with [(OEP)M]$_2$

$$[(OEP)Rh]_2 + C_6H_5CH_2OH$$

$$\rightleftharpoons (OEP)Rh-CH(OH)C_6H_5 + (OEP)Rh-H \qquad (18)$$
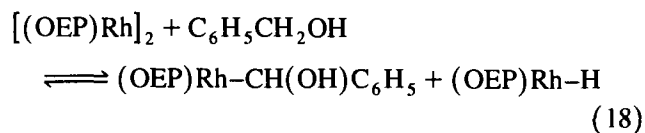
(1a, 1b) have been previously observed, and proposed to occur by a metallo radical, (OEP)Rh · , pathway [6e,6f]. Dehydrogenation of benzyl alcohol is completed by elimination of benzaldehyde from (OEP)Rh–CH(OH)C$_6$H$_5$ (18).

4. Summary

Octaethylporphyrin rhodium(II) and iridium(II) dimers undergo oxidative addition of carbon–hydrogen bonds in aldehydes, ketones and benzyl alcohols to yield mononuclear M–C and M–H species. [(OEP)M]$_2$ complexes (M = Rh, Ir) initially react with aldehydes at the α-carbon hydrogen bond whenever this type of site is available. Thermal rearrangement of (OEP)Rh–

$C(CH_3)_2CHO$ to $(OEP)Rh-C(O)CH(CH_3)_2$ demonstrates that reaction of the α-C–H unit is kinetically favored over reaction of the aldehydic C–H even when this pathway produces a less thermodynamically favorable product. Reaction of the α-carbon hydrogen bond is proposed to occur by addition of metalloporphyrin dimer to the enol isomer to form an unstable alkyl bridged complex, $(OEP)M-CH_2CR(OH)-M(OEP)$, which subsequently dissociates through β-O–H migration to yield $(OEP)M-H$ and a β-carbonyl organometallic derivative $(OEP)M-CH_2C(O)R$. $[(OEP)Rh]_2$ reacts with benzyl alcohols, $C_6H_5CH(OH)R$ (R = H, CH_3, $C(O)C_6H_5$), to produce intermediate α-hydroxyalkyl derivatives, $(OEP)Rh-CR(OH)C_6H_5$, which subsequently dissociate to give organic carbonyl species, $C_6H_5C(O)R$, and $(OEP)Rh-H$.
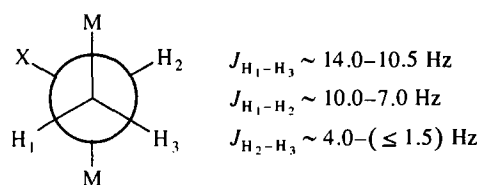
5. Experimental section

5.1. General methods

All manipulations were performed under nitrogen/argon or by vacuum line techniques. NMR data were recorded on a Bruker WH-250 spectrometer. Infrared spectra were obtained on KBr pellets with an IBM IR/97 spectrometer. Low resolution mass spectra were obtained on a VG Analytical 7070 mass spectrometer.

5.2. Materials

All reagents were purchased from Aldrich or Strem. $[Rh(CO)_2Cl]_2$ was sublimed prior to use. Deuterated solvents were distilled from sodium benzophenone ketyl. Chloroform was washed with 0.1 N H_2SO_4/H_2O followed by chromatography on grade 1 alumina for the removal of ethanol and water.

Table 3
Carbonyl stretching vibrational data for (OEP)M–X complexes

No.	M	X	$IR(KBr)\nu_{CO}$ (cm^{-1})
7a	Rh	CH_2CHO	1686
7b	Ir	CH_2CHO	1693
8	Rh	$CH(CH_3)CHO$	1659
13	Rh	$C(O)CH(CH_3)_2$	1709
14	Rh	$C(O)C(CH_3)_3$	1687
16	Rh	$CH_2C(O)CH_3$	1676
22	Rh	$C(O)CH_3$	1704
23	Rh	$C(O)CH_2CH_3$	1709
24a	Rh	$C(O)C_6H_5$	1684
24b	Ir	$C(O)C_6H_5$	1657

5.3. Synthesis of [(OEP)Rh]_2 (1a)

$[(OEP)Rh]_2$ complex (1a) was prepared and characterized as previously described [9,10b,14].

5.4. Synthesis of [(OEP)Ir]_2 (1b)

$[(OEP)Ir]_2$ complex (1a) was prepared and characterized as previously described [6e,14c].

5.5. Reactions of [(OEP)M]_2 (M = Rh, Ir) with organic oxygenates

Thermal reactions were carried out on solutions of $[(OEP)M]_2$ (1a, M = Rh; 1b, M = Ir) (1–2 mg) in neat reaction solvent or in solution of $[(OEP)M]_2$ (1a, 1b) and C_6D_6 with approximately 1%, by volume, reaction reagent. The samples were sealed under vacuum in NMR tubes and heated by immersion in a silicon oil bath encased in a black box to exclude light. NMR spectra for the reaction products from neat solutions were obtained in NMR tubes that were sealed after

Table 2
Proton NMR data for (OEP)M–CH₂CH(X)–M(OEP) complexes in C_6D_6

$J_{H_1-H_3} \sim 14.0–10.5$ Hz

$J_{H_1-H_2} \sim 10.0–7.0$ Hz

$J_{H_2-H_3} \sim 4.0–(\le 1.5)$ Hz

No.	M	X	–CH=	–CH₂	–CH₃	H₁	H₂	H₃	X
19a	Rh	OCH_2CH_3	brs, 9.32	om, 3.94, 3.76	t, 1.73	dd, −9.79	d, −11.21	d, −7.59	CH_3, t, −1.30, $J_{CH_2-CH_3} = 7.3$
19b	Ir	OCH_2CH_3	s, 9.20, 8.99	om, 3.92, 3.73	t, 1.72	dd, −10.11	d, −10.92	d, −8.65	CH_3, t, −1.14, $J_{CH_2-CH_3} = 6.6$
20	Rh	H	s, 8.97	m, 3.62	t, 1.62	s, −11.66			
21	Rh	C_6H_5	s, 9.29, 9.25	om, 4.06, 3.91	t, 1.90	m, −9.91	m, −11.34	m, −8.94	o, d, −0.74, 0.62 m, t, 5.05, 5.55 p, t, 6.31

Resonances are given in units of ppm and J values in Hz. brs, broad singlet; om, overlapping multiplets.

Table 4
Low resolution MS data for (OEP)M–X complexes

No.	M	X	Formula	Calcd. M^+	Found M^+
13	Rh	$C(O)CH(CH_3)_2$	$C_{40}H_{51}N_4ORh$	706.8	707
14	Rh	$C(O)C(CH_3)_3$	$C_{41}H_{53}N_4ORh$	720.7	721
15	Rh	$CH_2CH(CH_3)_2$	$C_{40}H_{53}N_4Rh$	692.8	693
16	Rh	$CH_2C(O)CH_3$	$C_{39}H_{49}N_4ORh$	692.7	693
17	Rh	$CH_2C(O)C_6H_5$	$C_{44}H_{51}N_4ORh$	754.8	755
22	Rh	$C(O)CH_3$	$C_{38}H_{47}N_4ORh$	678.7	679
23	Rh	$C(O)CH_2CH_3$	$C_{39}H_{49}N_4ORh$	692.8	693
24a	Rh	$C(O)C_6H_5$	$C_{43}H_{49}N_4ORh$	740.7	741
24b	Ir	$C(O)C_6H_5$	$C_{43}H_{49}N_4OIr$	830.11	830

removal of excess solvent and replacement with C_6D_6. The species in solution that resulted from reactions of $[(OEP)M]_2$ (**1a, 1b**) with organic oxygenates were identified by ^1H NMR (Tables 1 and 2) through comparison with the spectra for complexes which were directly synthesized from the $(OEP)Rh^1$ anion and alkyl bromides. In a typical reaction, $NaBH_4$ (0.25 mmol) in 1.0 N NaOH solution (2 ml) was added to an ethanol solution (40 ml) of $(OEP)Rh–I$ (0.05 mmol) under nitrogen. The mixture was stirred for 2 h at 40°C, and then cooled to room temperature. A slight excess of alkyl bromide was added and the mixture was stirred for an additional 3 h under nitrogen in the dark. The mixture was shaken in a separatory funnel with benzene (30 ml) and water (20 ml). The benzene layer was collected, washed with three portions of water (20 ml), and dried over anhydrous Na_2SO_4. The benzene solution was concentrated, and loaded on a silica gel column. The first eluate with benzene (red-orange color) contained the alkyl complex, $(OEP)Rh–R$, and was collected and dried under vacuum.

The volatile components in the reaction mixture were collected in a liquid nitrogen trap, and analyzed by low resolution mass spectrometry. The stable organometallic species were then separated by TLC for further analysis by IR spectroscopy and low resolution mass spectrometry (Tables 3 and 4).

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