ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 584 (1999) 235–239

Journal of Organo metallic Chemistry

# Synthesis and reactivity of the non-bridged metal–metal bonded rhodium octamethoxyporphyrin dimer

Maoqi Feng, K.S. Chan *

*Department of Chemistry, Chinese University of Hong Kong, Shatin, NT, Hong Kong*

Received in revised form 8 March 1999

**Abstract**

Electron-rich rhodium porphyrin alkyls (omp)RhR (R = Me, $^i$Pr, omp = 2,3,7,8,12,13,17,18-octamethoxyporphyrin dianion) were photolyzed to give the non-bridged metal–metal bonded complex $Rh_2(omp)_2$. Reaction of (omp)RhH with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) also yielded $Rh_2(omp)_2$ quantitatively. $Rh_2(omp)_2$ reacted with $CH_3I$ to produce (omp)RhMe and (omp)RhI, and with $Et_3SiH$ to give (omp)$RhSiEt_3$ and (omp)RhH in 42–52% yield, respectively. Addition of $Rh_2(omp)_2$ with styrene yielded phenylethyl-bridged complexes, (omp)$RhCH_2CH$(Ph)Rh(omp). $Rh_2(omp)_2$ reacted with triphenylphosphine to produce the cationic and anionic $Rh^{III}$ species of $[(omp)Rh]^+$ and $[(omp)Rh]^-$. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Rhodium; Hydride; TEMPO; Photolysis; Metal–metal bond; Porphyrin

## 1. Introduction

Non-bridged $d_7$–$d_7$ metal–metal bonded complexes have attracted considerable interest owing to their rich chemistry. Besides this unique structural aspect, the metal–metal bond undergoes facile dissociation to yield an extremely reactive metal centered radical. These monomers undergo halogen abstraction [1], C–H activation [2] and olefin insertion [3].

There are three literature methods for synthesizing rhodium metal–metal bonded complexes: (i) photolysis of metal alkyls [4]; (ii) aerobic oxidation of rhodium hydride [5]; and (iii) reaction of metal hydride with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) [6]. The first method usually requires a long reaction time, while the second method is difficult to handle because over-oxidation of the air-sensitive metal–metal bonded dimer is possible. The third method is the most convenient and efficient since TEMPO and the TEMPO reduction coproduct (TEMPOH) are easily removed by vacuum evaporation. $Rh_2(oep)_2$ and $Ir_2(oep)_2$ (oep = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion) have been synthesized using this method in over 90% yield [6].

Synthesis of the electron-rich rhodium octamethoxyporphyrin dimer provides further example to study the reactivity of electron-rich metal–metal bonded porphyrin dimer. In this paper we report the synthesis and chemistry of an electron-rich octamethoxyporphyrin (Fig. 1) non-bridged Rh–Rh bonded dimer.

## 2. Results and discussion

### 2.1. Synthesis of $Rh_2(omp)_2$

### 2.1.1. Photolysis of (omp)RhR (R = Me, $^i$Pr)

$H_2omp$ (omp = 2,3,7,8,12,13,17,18-octamethoxyporphyrin dianion) (see Fig. 1) was prepared according to the literature method [7]. $H_2omp$ and rhodium trichloride hydrate were refluxed in benzonitrile under nitrogen for 2 h to give 30% yield. The solubility of (omp)RhCl was very good in most organic solvents.

$$\text{(omp)RhCl} \xrightarrow[\text{2. CH}_3\text{I, N}_2\text{, 0°C, 1 h}]{\text{1. NaBH}_4\text{/NaOH, N}_2\text{, 50°C, 2 h}} \underset{48\%}{\text{(omp)RhMe}} \qquad (1)$$

Rhodium octamethoxyporphyrin methyl was prepared from the reductive alkylation of (omp)RhCl.

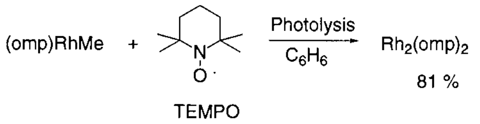
---

* Corresponding author. Fax: +852-26035057.

*E-mail address:* ksc@cuhk.hk (K.S. Chan)

PII: S0022-328X(99)00147-3

After the red solution of (omp)RhCl was reduced to the brown solution of $Rh^I$ and oxidative addition with $CH_3I$, (omp)RhMe was obtained in 48% yield (Eq. (1)) [8]. The synthesis of rhodium octamethoxyisopropyl was similar to that of (omp)RhMe.



(2)

Photolysis of (omp)RhMe in $C_6H_6$ in the presence of TEMPO yielded a new species with a methine peak of the *meso*-protons at $\delta$ 9.72 ppm shifted from 10.45 ppm and methoxy group of β-positions at $\delta$ 4.82 ppm shifted from 4.45 ppm in its proton NMR spectrum (Eq. (2)). These features are highly characteristic of metal–metal bonded dimers of rhodium porphyrin derivatives because of increasing shielding of the protons after dimer formation [9,10]. Besides, the singlet at $\delta$ 3.60 ppm was assigned to the methyl group of the coproduct of $TEMPOCH_3$ which was formed after photolysis, the value was the same as the literature data [11]. In the UV–vis spectrum the Soret band was red shifted from 385 to 397 nm after photolysis. $TEMPOCH_3$ and excess TEMPO were removed by vacuum evaporation.

The photolysis time of (omp)RhMe was much shorter when TEMPO was used, the reaction time was reduced to 32 h from more than 72 h when six equivalents of TEMPO was added.

The photolysis time of $(omp)Rh^iPr$ in the presence of TEMPO was shorter than that of (omp)RhMe and required only 20 h. The bond strength of Rh–isopropyl is probably lower than that of Rh–Me due to steric effects as well as the greater stability of the isopropyl radical compared to the methyl, and therefore the Rh–C bond was more easily cleaved [12].

A plausible mechanism for the synthesis of $Rh_2(omp)_2$ was shown in Scheme 1. The Rh–alkyl bond underwent photolytically initiated homolysis to yield $Rh^{II}$(omp) and the methyl radical. The methyl radical was trapped by TEMPO to yield 2,2,6,6-tetramethylpiperidine-1-methoxy. The $Rh^{II}$(omp) underwent dimerization to yield $Rh_2(omp)_2$.

### 2.1.2. Reaction of (omp)RhH with TEMPO

The compound (omp)RhH was synthesized by the method similar to the synthesis of (oep)RhH [5]. A suspension of (omp)RhCl in EtOH (aq.) (75%) solution was reduced to $Rh^I$(omp) and was protonated with HCl (2 M) to yield (omp)RhH as a red precipitate in 52% yield (Eq. (3)). When 95% EtOH was used as the solvent, (omp)RhH formed, remained in solution and only a little precipitate was produced thus lowering the yield. When 75% EtOH was used as the solvent, more precipitate formed and the yield was improved. The compound (omp)RhH exhibited a characteristic hydride resonance at −50.64 ppm as a doublet with $J_{Rh-H} = 43.2$ Hz which was similar to the −41.4 ppm and $J_{Rh-H} = 44$ Hz of (oep)RhH [13].

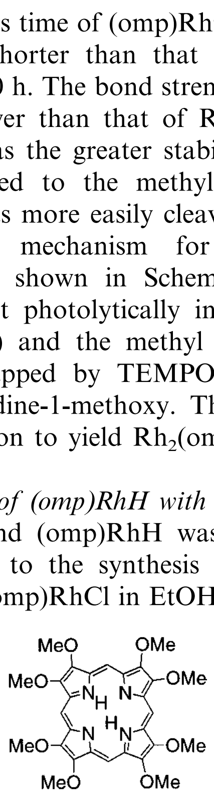
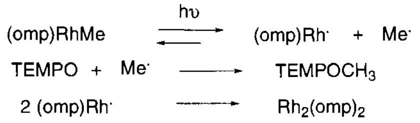


Fig. 1. Molecular structure of $H_2$omp.



Scheme 1.

$$(omp)RhCl \xrightarrow[\text{2. HCl, } N_2\text{, 0°C, 1 h}]{\text{1. NaBH}_4\text{, EtOH (75\%), } N_2\text{, 50°C, 2 h}} \underset{52\%}{(omp)RhH} \qquad (3)$$

The compound (omp)RhH reacted with $PhCH{=}CH_2$ to afford $(omp)RhCH_2CH_2Ph$ in 82% yield (Eq. (4)). The mechanism is a probable concerted [2 + 2] addition, or not purely via a carbon centered intermediate [14] as opposed to a radical mechanism since no other isomeric product was observed [1].

$$(omp)RhH + PhCH{=}CH_2 \xrightarrow[\text{r.t., 2 h}]{C_6D_6} \underset{82\%}{(omp)RhCH_2CH_2Ph} \qquad (4)$$

The compound (omp)RhH reacted with TEMPO to yield $Rh_2(omp)_2$ quantitatively in about 4 h at room temperature. The $^1H$-NMR of the dimer synthesized in this way was identical with that of the dimer synthesized from photolysis of (omp)RhR.

$$(omp)RhH + TEMPO \xrightarrow[\text{quantitatively}]{C_6D_6} Rh_2(omp)_2 \qquad (5)$$

### 2.2. Properties of $Rh_2(omp)_2$

$Rh_2(omp)_2$ underwent typical oxidative addition with organic substrates. Reaction of $Rh_2(omp)_2$ with $CH_3I$ afforded (oep)RhMe and (omp)RhI in 44 and 32% yield, respectively (Eq. (6)). When $Rh_2(omp)_2$ reacted with triethylsilane, $(omp)Rh(SiEt_3)$ and (omp)RhH were produced in 52 and 33% yield, respectively (Eq. (7)). Styrene underwent facile insertion reaction into the Rh–Rh bond of $Rh_2(omp)_2$ to give $(omp)RhCH_2$-CH(Ph)Rh(omp) in 85% yield (Eq. (8)). The chemical shifts of the *meso*-methine protons in the two porphyrin rings were 9.78 and 10.56 ppm and the diastereotopic methylene protons binding to Rh were split into two peaks.

When excess triphenylphosphine was added into $Rh_2(omp)_2$ in $C_6D_6$, the chemical shift of *meso*-methine protons had shifted from 9.76 to 9.78 and 10.56 ppm, and that of methoxy protons had shifted from 4.85 to 4.38 and 4.67 ppm. The shifts were due to the heterolytic cleavage of $Rh_2(omp)_2$ into $Rh(omp)^+$ and $Rh(omp)^-$ as observed similarly in the reaction of $Rh_2(oep)_2$ with pyridine [15]. This heterolytic cleavage of $Rh^{II}$ dimer into $Rh^I$ and $Rh^{III}$ monomers by $PPh_3$ may involve ligand-induced polarization of the Rh–Rh bond [16].

$$Rh_2(omp)_2 + CH_3I \xrightarrow[\text{r.t., 2 h}]{C_6D_6} \underset{44\%}{(omp)RhMe} + \underset{32\%}{(omp)RhI} \tag{6}$$

$$Rh_2(omp)_2 + Et_3SiH \xrightarrow[\text{r.t., 2 h}]{C_6D_6} \underset{52\%}{(omp)RhSiEt_3} + \underset{33\%}{(omp)RhH} \tag{7}$$

$$Rh_2(omp)_2 + PhCH{=}CH_2 \xrightarrow[\text{r.t., 2 h}]{C_6D_6} \underset{85\%}{(omp)RhCH_2CH(Ph)Rh(omp)} \tag{8}$$

$$Rh_2(omp)_2 + 2PPh_3 \xrightarrow[\text{r.t., 2 h}]{C_6D_6} (omp)Rh^+(PPh_3) + (omp)Rh^-(PPh_3) \tag{9}$$

## 3. Conclusions

An electron-rich metal–metal bonded porphyrin dimer $Rh_2(omp)_2$ has been synthesized by the reaction of (omp)RhH with TEMPO and photolysis of (omp)RhR (R = Me, $^i$Pr). The oxidative addition of $Rh_2(omp)_2$ with MeI, $Et_3SiH$, and styrene is typical of the chemistry of a metal–metal bonded dimer.

## 4. Experimental

All manipulations were performed under nitrogen by vacuum line techniques or in a Braun MB 150 M glovebox. $^1$H-NMR spectra were recorded on either a Bruker WM-250 (250 MHz), Bruker DPX-300 (300 MHz) or Bruker AMX-500 (500 MHz) spectrometer. Chemical shifts ($\delta$) were reported with reference to the residual $CHCl_3$ ($\delta$ 7.24 ppm) in $CDCl_3$ or $C_6H_6$ ($\delta$ 7.15 ppm) in $C_6D_6$, the coupling constant ($J$) was reported in Hz. Low-resolution mass spectra were recorded on a VG7070F mass spectrometer. High-resolution mass spectra were recorded on a Bruker APEX 47e FT-ICR mass spectrometer. IR spectra were obtained on a Perkin–Elmer 1600 FT-IR spectrophotometer. UV–vis spectra were recorded on a Hitachi U-3300 spectrophotometer. Yields were reported in either isolated yield or NMR yield using the residue solvent proton as the internal standard.

Unless otherwise noted, all materials were obtained from commerical suppliers and used without further purification unless otherwise specified. Rhodium trichloride ($RhCl_3{\cdot}3H_2O$) was obtained from Johnson Matthey. Benzene-$d_6$ was vacuum distilled from sodium.

### 4.1. Synthesis of octamethoxyporphyrin $H_2omp$

$H_2omp$ was prepared and characterized as Ref. [7].

### 4.2. Synthesis of rhodium$^{III}$ octamethoxyporphyrin (omp)RhCl

$H_2omp$ (60 mg, 0.11 mmol) and $RhCl_3{\cdot}3H_2O$ (43 mg, 0.16 mmol) were added into PhCN (10 ml) in a 50 ml flask and the suspension was heated to reflux for 2 h under $N_2$. Then PhCN was vacuum distilled off. The dark brown residue was separated by column chromatography using $CH_2Cl_2$ as the eluent to give (omp)RhCl as a purple red solid (22.5 mg, 30% yield). $R_f = 0.62$ ($CH_2Cl_2$); FAB MS (NBA) 686 [$M^+$]; $^1$H-NMR ($CDCl_3$, 250 MHz) $\delta$ 4.82 (s, 24H), 10.26 (s, 4H); UV–vis ($CH_2Cl_2$, nm, log $\varepsilon$) 392 (5.46), 518 (4.63), 553 (4.66); HRMS Calc. for $RhC_{28}H_{28}N_4O_8Cl$: 686.0665. Found: 686.0665.

### 4.3. Synthesis of octamethoxyporphyrinato methyl rhodium$^{III}$ (omp)RhMe

To a degassed solution of (omp)RhCl (24 mg, 0.035 mmol) in EtOH (10 ml) was added nitrogen-purged $NaBH_4$ (15 mg, 0.39 mmol) solution in NaOH (0.2 M, 1 ml) through a cannular, slowly. The red solution changed into brown quickly. The brown solution was stirred under nitrogen at 0°C for 1 h, then methyl iodide (0.1 ml, 0.16 mmol) was added and red precipitate was produced immediately. The reaction mixture was extracted with $CH_2Cl_2$ ($3 \times 20$ ml) and purified by column chromatography using a solvent mixture of $CH_2Cl_2$:hexane (1:2) as the eluent to give (omp)RhMe (11 mg, 48%). $R_f = 0.86$ ($CH_2Cl_2$). FAB MS (relative intensity, %) 666 ([$M^+$], 51), 651 (63), 620 (31), 591 (19), 561 (8), 413 (17), 391 (26); $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ 6.04 (d, 3H, $J = 2.7$ Hz), 4.45 (s, 24H), 10.45 (s, 4H); UV–vis ($CH_2Cl_2$, nm, log $\varepsilon$) 385 (4.94), 549 (4.50); HRMS Calc. for $RhC_{29}H_{31}N_4O_8$: 666.1191. Found: 666.1208.

### 4.4. Synthesis of octamethoxyporphyrinato isopropyl rhodium$^{III}$ (omp)Rh($^i$Pr)

The procedure was similar to the synthesis of Rhomp(Me). Yield 32%. $R_f = 0.82$ ($CH_2Cl_2$). FAB MS (NBA) 694 [$M^+$]; $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ $-4.35$ (d, 6H, $J = 4.4$ Hz), $-2.35$ (d, 1H, $J = 2.4$ Hz), 4.42 (s, 24H), 10.49 (s, 4H); UV–vis ($CH_2Cl_2$, nm) 384, 514, 548; HRMS Calc. for $RhC_{31}H_{35}N_4O_8$: 694.1504. Found: 694.1469.

### 4.5. Photolysis experiment

In a glovebox, (omp)RhMe (50 mg, 0.075 mmol) and TEMPO (70 mg, 0.45 mmol, six equivalents) in degassed benzene (10 ml) was loaded into a 50 ml flask fitted with a vacuum-line-adapted Teflon valve. The tube was closed, removed from the glovebox. Then it was irradiated using a mercury lamp. Progress of the photolysis was monitored by $^1$H-NMR by aliquots of about 0.4 ml of reaction mixture. These samples were transferred through a rubber septum of a NMR tube, the solvent was evaporated by vacuum and then benzene-$d_6$ (ca. 0.4 ml) was added. After the rhodium methyl was completely consumed, the reaction mixture was evaporated to dryness under vacuum. $Rh_2(omp)_2$ was obtained (39 mg, 81% yield). $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ 4.81 (s, 48H), 9.74 (s, 8H); UV–vis ($C_6H_6$, nm) 397, 519, 555.

### 4.6. Synthesis of rhodium$^{III}$ octamethoxyporphyrin hydride (omp)RhH

To a degassed solution of (omp)RhCl (24 mg, 0.035 mmol) in EtOH (75%, 10 ml) was added nitrogen-purged $NaBH_4$ (15 mg, 0.39 mmol) solution in NaOH (1 M, 1 ml) slowly through a cannular. The red solution changed brown quickly. The brown solution was stirred under nitrogen at 50°C for 2 h, cooled down to 0°C, and then HCl (2 M, 5.0 ml) was added. Red precipitate was produced immediately. After filtration under nitrogen with a cannular, the red solid was washed with degassed $H_2O$ (4.0 ml) and MeOH (1.0 ml), respectively. The red solid was then dried over vacuum (11.9 mg, 52% yield). $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ $-50.64$ (d, 1H, $J_{Rh-H} = 43.2$ Hz), 4.41 (s, 24H), 10.54 (s, 4H); UV–vis ($C_6H_6$, nm) 385, 542, 620.

### 4.7. Reaction of (omp)RhH with $PhCH{=}CH_2$

To a solution of (omp)RhH (4 mg, 6 μmol) in degassed $C_6H_6$ (1.0 ml) was added styrene (0.1 ml) with a microsyringe. The red solution changed into dark red. After 2 h, the mixture was evaporated to dryness under vacuum and the residue was separated by column chromatography using $CH_2Cl_2$ as the eluent to give $(omp)Rh(CH_2CH_2Ph)$ (3.8 mg, 82% yield). $R_f = 0.54$ ($CH_2Cl_2$); $^1$H-NMR (300 MHz, $C_6D_6$) $\delta$ $-5.62$ (dt, 2H, $J_{Rh-H} = 3.0$, $J_{H-H} = 7.5$ Hz, $RhCH_2$), $-3.95$ (t, 2H, $J = 8.1$ Hz, $RhCH_2CH_2$), 4.28 (d, 2H, $J = 6.9$ Hz, *ortho*-H), 4.73 (s, 24H, OMe), 6.15 (m, 2H, *meta*-H in $C_6H_5$), 6.29 (m, 1H, *para*-H), 9.89 (s, 4H, *meso*-H in omp); FAB MS (relative intensity, %) 756 ([M$^+$], 2), 651 ([M$^+$ $-CH_2CH_2Ph$], 13); UV–vis (benzene, nm) 384, 512, 548, 712.

### 4.8. Reaction of (omp)RhH with TEMPO

The compound (omp)RhH (5 mg, 8 μmol) was dissolved in $C_6D_6$ (0.7 ml) in an NMR tube, and then TEMPO (6 mg, 40 μmol) was added. The red solution changed into dark red. The reaction was monitored by $^1$H-NMR. After 4 h, $Rh_2(omp)_2$ formed quantitatively by NMR integration. $^1$H-NMR of $Rh_2(omp)_2$ was identical with that obtained from the photolysis experiment.

### 4.9. Reactions of $Rh_2(omp)_2$ with $Et_3SiH$

General procedure: in a glovebox, $Rh_2(omp)_2$ (4 mg, 6 μmol), $Et_3SiH$ (0.1 ml) and benzene-$d_6$ (0.5 ml) were loaded into a 5 mm diameter NMR tube fitted with a vacuum-line-adapted Teflon valve. The tube was closed and removed from the glovebox. It was degassed by the freeze-pump-thaw method (three cycles), and then the tube was sealed under vacuum. The reaction was monitored by $^1$H-NMR. After about 2 h, (omp)RhH (33% NMR yield) and $(omp)RhSiEt_3$ (52% NMR yield) were produced. Separation of the residue by column chromatography gave pure $(omp)RhSiEt_3$ using $CH_2Cl_2$ as eluent, while (omp)RhH was oxidized and remained in the column. $(omp)RhSiEt_3$: $R_f = 0.64$ ($CH_2Cl_2$); $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ $-3.23$ (q, 6H, $J = 7.8$ Hz), $-1.14$ (t, 9H, $J = 7.9$ Hz), 4.41 (s, 24H), 10.44 (s, 4H); FAB MS 765 [M$^+$ $-$ 1]; UV–vis (hexane, nm) 385, 512, 545, 617.

### 4.10. Reaction of $Rh_2(omp)_2$ with $CH_3I$

The procedure was the same as that in Section 4.9. (omp)RhMe (44% NMR yield) and (omp)RhI (32% NMR yield) were produced. Pure products were separated by column chromatography, at first $CH_2Cl_2$ was used as solvent to elute (omp)RhMe and then diethyl ether was used to elute (omp)RhI. (omp)RhI: $R_f = 0.18$ ($CH_2Cl_2$); $^1$H-NMR ($C_6D_6$, 300 MHz) $\delta$ 4.86 (s, 24H), 10.24 (s, 4H); FAB MS (NBA) 778 [M$^+$].

### 4.11. Reaction of $Rh_2(omp)_2$ with $PhCH{=}CH_2$

$Rh_2(omp)_2$ (4 mg, 6 μmol) was dissolved in benzene-$d_6$ (0.5 ml) in an NMR tube, $PhCH{=}CH_2$ (0.1 ml) was added with a microsyringe. The reaction was monitored by $^1$H-NMR. After 2 h, $(omp)RhCH_2CH(Ph)Rh(omp)$ was produced in 85% yield. $^1$H-NMR (300 MHz, $C_6D_6$) $\delta$ $-11.19$ (m, 1H), $-9.54$ (m, 1H), $-8.71$ (m, 1H, *CHH′CHPh*), $-0.30$ (d, 1H, $J_{H-H} = 7.5$ Hz, *ortho*-H), 0.93 (d, 1H, $J_{H-H} = 7.5$ Hz, *ortho′*-H), 4.49 (s, 24H, OMe), 4.80 (s, 24H, OMe), 5.05 (dd, 1H, $J = 2.4$, 9.0 Hz, *meta*-H), 5.60 (dd, 1H, $J = 2.4$, 9.0 Hz, *meta*-H′), 6.62 (dd, 1H, $J = 2.4$, 9.0 Hz, *para*-H), 9.78 (s, 4H, *meso*-H in OMP), 10.56 (s, 4H, *meso*-H in omp); UV–vis (benzene, nm) 386, 516, 549, 713.

### *4.12. Reaction of $Rh_2(omp)_2$ with $PPh_3$*

$Rh_2(omp)_2$ (4 mg, 6 μmol) was dissolved in benzene-$d_6$ (0.5 ml) in an NMR tube, $PPh_3$ (5.4 mg, 20 μmol) was added. The reaction was monitored by $^1$H-NMR. After 3 h, $(omp)Rh^+PPh_3$ and $(omp)Rh^-PPh_3$ was produced. $^1$H-NMR (300 MHz, $C_6D_6$) $\delta$ 4.38 (s, 24H, OMe in $(omp)Rh^-$), 4.67 (s, 24H, OMe in $(omp)Rh^+$), 7.08–7.35 (m, $PPh_3$), 9.61 (s, 4H, *meso*-H in $(omp)Rh^-$), 10.76 (s, 4H, *meso*-H in $(omp)Rh^+$).

## Acknowledgements

We thank the Croucher Foundation of Hong Kong for financial support.

## References

[1] R.S. Paonessa, N.C. Thomas, J. Halpern, J. Am. Chem. Soc. 107 (1985) 4333.

[2] B.B. Wayland, S. Ba, A.E. Sherry, J. Am. Chem. Soc. 113 (1990) 5305.

[3] B.B. Wayland, Y. Feng, S. Ba, Organometallics 8 (1989) 1438.

[4] M. Hoshino, K. Yasufuku, H. Seki, H. Yamazaki, J. Phys. Chem. 89 (1985) 3080.

[5] J. Setsune, Z. Yoshida, H. Ogoshi, J. Chem. Soc. Perkin Trans. I (1982) 983.

[6] K.S. Chan, Y.-B. Leung, Inorg. Chem. 33 (1994) 3187.

[7] (a) A. Merz, R. Schopp, E. Dotterl, Synthesis 7 (1995) 795. (b) A. Merz, R. Schropp, J. Lex, Angew. Chem. Int. Ed. Engl. 32 (1993) 291.

[8] H. Ogoshi, J. Setsune, T. Omura, Z. Yoshida, J. Am. Chem. Soc. 97 (1975) 6461.

[9] (a) B.B. Wayland, A.R. Newman, Inorg. Chem. 20 (1981) 3093. (b) B.B. Wayland, A.E. Sherry, V.L. Coffin, J. Chem. Soc. Chem. Commun. (1989) 662.

[10] (a) J.T. Chen, A. Sen, J. Am. Chem. Soc. 106 (1984) 1506. (b) A. Ozawa, T. Sugimoto, Y. Yuasa, M. Santra, T. Yamamoto, A. Yamamoto, Organometallics 3 (1984) 683.

[11] J.E. Anderson, D. Casarini, J.E.T. Corrie, L. Lunazzi, J. Chem. Soc. Perkin Trans. I (1993) 1299.

[12] J. Halpern, Acc. Chem. Res. 15 (1982) 238.

[13] M.D. Farnos, B.A. Woods, B.B. Wayland, J. Am. Chem. Soc. 108 (1986) 3659.

[14] D. AndersonJoe, R. Eisenberg, Organometallics 15 (1996) 1697.

[15] B.B. Wayland, K.J. Balkus Jr., M.D. Farnos, Organometallics 8 (1989) 950.

[16] J. Telser, R.S. Drago, Inorg. Chem. 25 (1986) 2989.