560 *Inorg. Chem.* **2001,** *40,* 560−563

# Unexpected Reactivity of Rh(TPP)I(CO) toward an Alkoxide in $CH_2Cl_2$: Synthesis and Crystal Structure of Rh(TPP)($CH_2Cl$)

**James P. Collman* and Roman Boulatov**

Department of Chemistry, Stanford University,
Stanford, California 94305

*Received July 21, 2000*

## Introduction

The high reactivity of many coordinatively unsaturated Rh(I) complexes opens a possibility that in a course of a synthetic transformation where such an intermediate forms the solvent can become an unintended substrate. Several (chloromethyl)-rhodium(III) compounds have been inadvertently obtained by carrying out ligand substitution reactions in $CH_2Cl_2$.[1] Similar species have been deliberately synthesized by reaction between Rh(I) complexes and $CH_2Cl_2$.[2,3] Halomethyl derivatives are thought to be involved in a number of catalytic cycles, which explains the current interest in synthesis and chemistry of such species. Chloroalkyl complexes are particularly interesting because activation of the relatively inert C−Cl bond is more challenging than that of the C−Br and C−I bonds.[4] These species can also be suitable precursors for Schrock type metallocarbenes[5a] and hydroxymethyl[5b] and methylene-bridged[5c] complexes, all of which are plausible intermediates in diverse catalytic reactions. For example, porphyrinatorhodium−carbene intermediates have been implicated in catalytic (including asymmetric) cyclopropanation of olefins and carbene insertion into O−H bonds.[6] More thorough mechanistic work in this area is, however, complicated by the lack of synthetic routes to Rh(por)−carbene complexes;[7] indeed, only a single example of such species has so far been prepared.[8]

Among the Rh(I) compounds that activate $CH_2Cl_2$, the neutral and cationic complexes react with dichloromethane to yield octahedral Rh(III) derivatives, with the $CH_2Cl$ and Cl fragments usually in a cis arrangement.[2] In contrast, anionic Rh(I) complexes of rigid, multidentate ligands produce five-coordinate square-pyramidal derivatives, wherein only the $CH_2Cl$ group enters the coordination sphere.[3] In all such transformations the metal undergoes a one-step, two-electron oxidation, so high-energy Rh(II) intermediates are avoided. A few reactions that were originally thought to involve one-electron processes were later explained by more conventional mechanisms. For example, formation of the trichloride $RhL_3Cl_3$ (L = phosphine) from $RhL_3Cl$ and $CH_2Cl_2$ was originally proposed[1b,c,9] to proceed by two consecutive chlorine atom abstraction steps via $Rh^{II}L_3Cl_2$. Later, the trichloride was shown[2b] to be formed by hydrolysis of the rhodium−chloromethyl complex in the presence of adventitious protic sources. Likewise, generation of Rh(por)($CH_2Cl$) complexes upon electrochemical reduction of $Rh^{III}(por)^+$ in dichloromethane was at first suggested[10] to occur via an $S_N2$ reaction between $Rh^{II}$(por) and $CH_2Cl_2$, yielding a Rh(IV) complex, which subsequently underwent reduction by solvent. A recent mechanism proposes[11] rapid disproportionation of the initially generated $Rh^{II}$(por) into $Rh^{III}(por)^+$ and the reactive nucleophile $Rh^{I}(por)^-$. Indeed, the only other examples of chloromethyl−metalloporphyrin complexes, Co(por)($CH_2Cl$),[12] have been synthesized by reaction between $Co^{I}(por)^-$ and $CH_2Cl_2$. Herein we report that Rh(TPP)($CH_2Cl$) is formed from Rh(TPP)I(CO) and excess alkoxide in dichloromethane under CO. The transformation likely proceeds via an $S_N2$ reaction between $Rh^{I}(TPP)^-$ and $CH_2Cl_2$, and no evidence suggesting one-electron processes has been observed.

## Results and Discussion

Whereas addition of sodium ethoxide to a solution of Rh(TPP)Cl(CO) in $CH_2Cl_2$ produces Rh(TPP)($CO_2Et$),[13] the iodide analogue yields exclusively the chloromethyl complex, Rh(TPP)($CH_2Cl$). The latter reaction requires an excess of both the base and CO and also proceeds with NaOMe but not with KOH or $KO^tBu$ as a base. Thus, addition of up to 35 equiv of

---

(1) (a) Nishiyama, H.; Horihata, M.; Hirai, T.; Wakamatsu, S.; Itoh, K. *Organometallics* **1991**, *10*, 2706−2708. (b) Ziessel, R.; Toupet, L.; Chardon-Noblat, S.; Deronzier, A.; Matt, D. *J. Chem. Soc., Dalton Trans.* **1997**, 3777−3784. (c) Kashiwabara, K.; Morikawa, A.; Suzuki, T.; Isobe, K.; Tatsumi, K. *J. Chem. Soc., Dalton Trans*. **1997**, 1075−1081.

(2) (a) Bradd, K. J.; Heaton, B. T.; Jacob, C.; Sampanthar, J. T.; Steiner, A. *J. Chem. Soc., Dalton Trans*. **1999**, 1109−1112. (b) Haarman, H. F.; Ernsting, J. M.; Kranenburg, M.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 887−900. (c) Nishiyama, H.; Hirai, T.; Itoh, K. *J. Organomet. Chem*. **1992**, *431*, 227−231. (d) Blake, A. J.; Halcrow, M. A.; Schroeder, M. *J. Chem. Soc., Chem. Commun.* **1991**, 253−256. (e) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun*. **1987**, 1543−1545. (f) For a review of the syntheses and reactivity of transition metal halomethyl complexes see the following. Friedrich, H. B.; Moss, J. R. *Adv. Organomet. Chem.* **1991**, *33*, 235−290.

(3) (a) Steinborn, D.; Rausch, M.; Bruhn, C. *J. Organomet. Chem*. **1998**, *561*, 191−197. (b) Randaccio, L.; Geremia, S.; Dreos-Garlatti, R.; Tauzher, G.; Asaro, F.; Pellizer, G. *Inorg. Chim. Acta* **1992**, *194*, 1−8. (c) Collman, J. P.; Murphy, D. W.; Dolcetti, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 2687.

(4) Huser, M.; Youinou, M.-T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1386−1388.

(5) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 879−881 and references therein. (b) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663−666 and references therein. (c) Ciriano, M. A.; Tena, M. A.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2123−2124. (d) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679−1680.

(6) (a) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544−1547. (b) Bartley, D. W.; Kodadek, T. *J. Am. Chem. Soc.* **1993**, *115*, 1656−1660. (c) Brown, K. C.; Kodadek, T. *J. Am. Chem. Soc.* **1992**, *114*, 8336−8338. (d) Gross, Z.; Galili, N.; Simkhovich, L. *Tetrahedron Lett.* **1999**, *40*, 1571−1574. (e) Hayashi, T.; Kato, T.; Kaneko, T.; Asai, T.; Ogoshi, H. *J. Organomet. Chem.* **1999**, *473*, 323−327. (f) Hayashi, T.; Kato, T.; Kaneko, T.; Asai, T.; Ogoshi, H. *J. Organomet. Chem*. **1994**, *473*, 323−327.

(7) por = any porphyrin dianion; TPP = *meso*-tetraphenylporphyrin dianion; OEP = octaethylporphyrin dianion.

(8) Boschi, T.; Licoccia, S.; Paolesse, R.; Tagliesta, P. *Organometallics* **1989**, *8*, 330−336.

(9) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511−518.

(10) Anderson, J. E.; Yao, C.-L.; Kadish, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 1106−1111.

(11) Lexa, D.; Grass, V.; Saveant, J.-M. *Organometallics* **1998**, *17*, 2673−2676.

(12) por = OEP: Ogoshi, H.; Watanabe, E.; Koketsu, N.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2529−2536. por = TPP: Kadish, K. M.; Lin, X. Q.; Han, B. C. *Inorg. Chem.* **1987**, *26*, 4161−4167. por = tetraxis(*p*-methoxyphenyl)porphyrin: Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1993**, *12*, 4871−4880. Co(TPP)-$CH_2Cl$ is also obtained upon treatment of Co(TPP)Cl with $CH_2N_2$: Callot, H. J.; Shaeffer, E. *J. Organomet. Chem.* **1978**, *145*, 91−99.

(13) Cohen, I. A.; Chow, B. C. *Inorg. Chem.* **1974**, *13*, 488−489.

10.1021/ic000820c CCC: $20.00

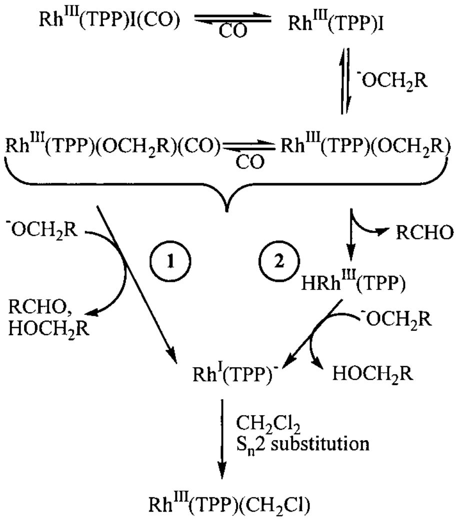

**Figure 1.** Proposed reaction sequence accounting for production of Rh(TPP)(CH$_2$Cl) in CH$_2$Cl$_2$ solutions of Rh(TPP)I in the presence of an alkoxide (R = H, CH$_3$) and CO. Two possible pathways for generation of the reactive nucleophile, Rh(TPP)$^-$, are (1) E$_2$ elimination and (2) $\beta$-hydride elimination/deprotonation. HRh(TPP) and Rh(TPP)$^-$ have not been observed experimentally in the reaction mixtures.

NaOMe (as a methanol solution) to a CH$_2$Cl$_2$ solution of Rh(TPP)I(CO) or Rh(TPP)I under N$_2$ generates a second species with the UV−vis spectrum identical to that of Rh(TPP)(OMe), prepared via an independent route (see Supporting Information). No further changes are observed over 2 days. However, if CO is introduced into the solution, Rh(TPP)(CH$_2$Cl) is rapidly formed. Likewise, no reaction occurs if less than 2 equiv of an alkoxide is added to a CH$_2$Cl$_2$ solution of Rh(TPP)I(CO) under a CO atmosphere.

One of the easiest synthetic routes to (por)Rh−alkyl derivatives is an S$_N$2 reaction between an alkyl halide[14] and Rh$^I$(por)$^-$. Rh(TPP)(CH$_2$Cl) is quite likely produced via a similar pathway (Figure 1). The most plausible source of Rh$^I$(TPP)$^-$ appears to be elimination of an aldehyde from the alkoxo complex Rh(TPP)(OCH$_2$R).[15] While the M−O(R) bond strengths are comparable to those of M−C(sp$^3$) for late transition metals,[16] the corresponding alkoxo complexes are much less stable[17] because of their susceptibility to M−O bond heterolysis or presumed $\beta$-H elimination.[18] Indeed, $\beta$-H elimination from Rh(TPP)(OCH$_2$R) would generate Rh(TPP)H, which is known to undergo facile deprotonation, yielding Rh(TPP)$^-$.[19] While porphyrin complexes of late transition metals lack adjacent open coordination sites, which are usually thought necessary for $\beta$-hydride elimination, several reactions of Rh(por) are believed to proceed via such a mechanism or its microscopic reverse.[20] Alternatively, alkoxide-assisted E$_2$ elimination would produce Rh(TPP)$^-$ directly.[21] Although such mechanism has not, to our knowledge, been invoked in decomposition of transition metal−alkoxo complexes, dehydrogenation of alcohols on Al-doped MgO surfaces is believed to proceed via a process similar to E$_2$ elimination.[22]

To test this hypothesis (Figure 1), we have examined reactions of Rh(TPP)(OMe). This species is prepared by addition of a slight excess of NaOMe to a CH$_2$Cl$_2$ solution of Rh(TPP)(PF$_6$) under anhydrous and anaerobic conditions followed by rapid removal of the solvent and extraction of the product into C$_6$H$_6$. Whereas the complex is stable in hydrocarbon solvents, it reacts slowly with CH$_2$Cl$_2$ under N$_2$ in the presence of excess NaOMe, yielding Rh(TPP)(CH$_2$Cl).[23] In contrast, Rh(TPP)(CH$_2$Cl) is not generated, within a week, upon addition of up to 100-fold excess of KO$^t$Bu to a Rh(TPP)(PF$_6$) solution in CH$_2$Cl$_2$, even though formation of the corresponding *tert*-butoxo complex is observed under such conditions.

Remarkably, the presence of CO dramatically accelerates decomposition of Rh(TPP)(OMe). This seems to favor an E$_2$ mechanism. CO should enhance the reactivity of (CO)Rh(TPP)(OMe) toward E$_2$ elimination by stabilizing the transition state via delocalization of the developing negative charge on the metalloporphyrin moiety from Rh onto CO. In contrast, such an adduct would be expected to be less reactive toward $\beta$-hydride elimination because coordination of the second axial ligand usually decreases displacement of Rh from the plane of the coordinating nitrogens, thus making the required vacant cis coordination site less accessible.[24] Within this mechanism, the stability of Rh(TPP)(OX) (X = H, $^t$Bu) toward CH$_2$Cl$_2$ is due to their inability to undergo reductive elimination. A slow

---

(14) Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121−1146.

(15) Benzene solutions of Rh(por)Cl(CO) (por = OEP, TPP) react with solid KOH under CO pressure, producing Rh(por)H and subsequently Rh(por)(CHO) (Wayland, B. B.; Duttaahmed, A.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1983** 142−143). We have examined whether Rh(TPP)H may be generated via such water-gas shift reaction (WSGR) in our system. While addition of methanolic solution of KOH (up to 100 equiv) to solutions of Rh(TPP)I in CH$_2$Cl$_2$ results in the spectral changes suggestive of formation of (OH)Rh(TPP), no further reactions have been observed for 24 h upon exposure to 1 atm of CO. This excludes WGSR as a source of Rh(TPP)H in our system.

(16) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188. (b) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456.

(17) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994; pp 57−59. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 60. (c) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley: New York, 1999; p 1241.

(18) Decomposition of only a limited number of transition metal−alkoxo complexes is mechanistically characterized. (a) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582−4594. (b) Hoffman, D. M.; Lappas, D.; Wierda, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 1531−1532. (c) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805−4813. (d) Sasson, Y.; Blum, J. *J. Chem. Soc., Chem. Commun.* **1974**, 309−310. Many other examples of decomposition of alkoxo complexes of transition metals are known: ref 18a (refs 5 and 6 therein). (e) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390−391.

(19) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042.

(20) WGSR: (a) Reference 15. (b) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302−303. Olefin insertion into Rh−H bond in Rh(OEP)H and related 1,2-alkyl shift of Rh(por) alkyls: (c) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333−4335. (d) Mak, K. W.; Chan, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 9686−9687. (e) Mak, K. W.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Dalton Trans.* **1999**, 3333−3334. Aldehyde insertion into the Rh−H bond of Rh(por)H species: (f) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545−1555. (g) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4042. Possibly decomposition of Rh(por)C(=O)R to Rh(por)R: (h) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans.* **1977**, 1395−1403.

(21) A possibility of E$_2$ elimination in our system was suggested by a referee.

(22) Di Cosimo, J. I.; Apesteguia, C. R.; Gines, M. J. L.; Iglesia, E. *J. Catal.* **2000**, *190*, 261−275.

(23) Other stable metalloporphyrin−methoxo complexes are known. Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015−3024.

(24) Coordination of an axial imidazole to alkylcobalamines was reported to *promote* $\beta$-hydride elimination despite the increase in the steric congestion around the metal. Cross, R. J. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; p 570. We are aware of only one study of the effect of axial ligation on the facility of a reaction that is presumed to proceed via $\beta$-hydride elimination at a Rh(por) moiety.[20d]

decomposition of Rh(TPP)(OMe) in the absence of CO may result from relatively poor leaving capabilities of $Rh(TPP)^-$. When such alkoxo intermediates are generated in the Rh(TPP)I/$Na(OCH_2R)$ (R = H, Me) mixtures, competition from $I^-$ for Rh results in only a very small concentration of Rh(TPP)($OCH_2R$), which, together with its relatively high stability in the absence of CO, makes the subsequent transformations too slow to be observed. Finally, since CO adducts of $Rh^{III}$(por) derivatives are unstable toward dissociation of CO in solution, excess CO is likely required to build up sufficient concentration of the more reactive six-coordinate intermediate (CO)Rh(TPP)($OCH_2R$) (R = H, Me).

Two other mechanisms yielding metallohydride via decomposition of a methoxo complex are conceivable:[18a] (a) homolysis of the Rh−O bond followed by hydrogen atom abstraction from the resulting methoxo radical $CH_3O^{\bullet}$ or methanol cosolvent by a $d^7$ $Rh^{II}$(TPP) complex;[25] (b) heterolysis of the Rh−O bond followed by hydride abstraction from $CH_3O^-$ by $Rh^{III}(TPP)^+$. While $Rh^{II}$(por) species are known to activate C−H bonds,[26] such an intermediate should generate, via chlorine atom abstraction from $CH_2Cl_2$, a Rh(TPP)Cl byproduct. Neither this complex nor possible products of its further transformations (such as Rh(TPP)($CO_2Et$)) were detected in the reaction mixtures, suggesting against the Rh−O bond homolysis as a major reaction pathway. Likewise, the hydride abstraction by $Rh(TPP)^+$ is not consistent with the stability of Rh(TPP)(OMe) in relatively polar $CH_2Cl_2$ in the absence of NaOMe.[27]

The different reactivities of the related complexes Rh(TPP)X(CO) (X = Cl, I)[13] are likely the result of a kinetic competition between ligand metathesis (and subsequent reactions) and nucleophilic attack on coordinated CO.[28] Compared to chloride, $I^-$ is both a better leaving group, which favors ligand substitution, and a more basic ligand, which decreases the electrophilicity of the trans-bound CO.[29] The irreversible formation of Rh(TPP)($CH_2Cl$) provides the overall driving force for the Rh-based reactivity, as opposed to the C-based reactivity of the chloro complex.

Whereas the $CH_2Cl$ moiety in a related complex, $Rh(dmgH)_2(PPh_3)(CH_2Cl)$ (dmgH = dimethylglyoxime), undergoes facile methanolysis yielding $Rh(dmgH)_2(PPh_3)(CH_2OMe)$,[3a] Rh(TPP)($CH_2Cl$) is stable toward alkoxides. Since methanolysis likely proceeds via an $S_N1$ mechanism, destabilization of the higher formal oxidation state of the metal in the carbenoid intermediate, $[(TPP)Rh^{IV}=CH_2]^+$ by electron-withdrawing TPP may account for the increased stability of Rh(TPP)($CH_2Cl$).

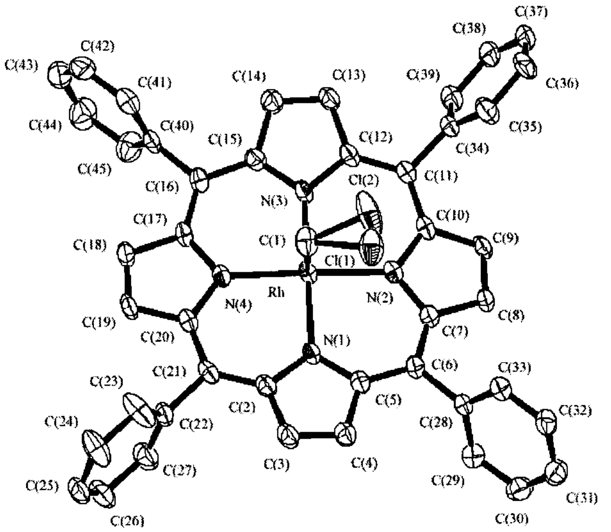

**Figure 2.** ORTEP view of Rh(TPP)($CH_2Cl$) (50% probability thermal ellipsoids) showing the numbering scheme and the disordering of the $CH_2Cl$ unit. Cl(1) and Cl(2) represent the Cl positions with occupancies of 68% and 32%.

**Table 1.** Crystallographic Data for Rh(TPP)($CH_2Cl$)

| | |
|---|---|
| empirical formula | $RhClN_4C_{45}H_{30}$ |
| fw | 765.12 |
| cryst size (mm) | 0.20 × 0.30 × 0.25 |
| $a$ (Å) | 12.1012(6) |
| $b$ (Å) | 12.6451(6) |
| $c$ (Å) | 12.8335(7) |
| α (deg) | 0.605(1) |
| $\beta$ (deg) | 88.848(1) |
| $\gamma$ (deg) | 65.654(1) |
| $V$ (Å$^3$) | 1672.0(1) |
| space group | $P\bar{1}$ (No. 2) |
| $Z$ | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.520 |
| $R$ (4341 reflns, $I > 3\sigma(I)$) | 0.040 |
| wR2 | 0.092 |
| goodness of fit indicator | 1.63 |

The solid-state structure of Rh(TPP)($CH_2Cl$) was studied crystallographically (Figure 2, Table 1). Its most conspicuous feature is an unusually large "saddle" distortion of the porphyrin (Figure 3) wherein the pyrrole rings are alternately displaced above and below the mean plane of the core. The maximum deviation of 0.484 Å for a porphyrin-core atom from the corresponding 24-atom least-squares plane is even larger than that in Ni(TPP) (0.46 Å)[30] and $Fe^{II}$(TPP) (0.40 Å)[31] complexes, which are often considered some of the most distorted simple metalloporphyrins. The origin of this distortion is not clear. Peripheral crowding, which is sometimes regarded as a cause of nonplanarity,[30] is not present in Rh(TPP)($CH_2Cl$). The nonbonding Cl2···N2 distance of 3.080 Å is shorter than the sum of the respective van der Waals radii (1.80 Å + 1.55 Å).[32] However, the value of the Rh−C−Cl angle is in the range normally observed for other chloromethylrhodium species. The closest Rh···Rh separation in the crystal lattice is 5.319 Å with a respective interporphyrin separation of 3.670 Å. These values

---

(25) Decomposition of alkoxo complexes via homolysis of the M−O(R) bond has been reported: Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829−2835.

(26) (a) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897−7898. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305−5311. (c) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941−7944.

(27) A referee suggested an alternative mechanism for generation of $Rh(TPP)^-$ in the Rh(TPP)I/NaOMe/$CH_2Cl_2$/CO system. The initially formed Rh(TPP)($CO_2CH_3$) undergoes an $S_N2$ substitution at the $CH_3$ group by $I^-$, generating the unstable Rh(TPP)($CO_2^-$) and, subsequently, $Rh(TPP)^-$ (+$CO_2$). Although this may constitute a parallel reaction, and such a possibility was not examined, the observed decomposition of Rh(TPP)(OMe) in $CH_2Cl_2$ in the presence of only NaOMe suggests that reductive aldehyde elimination is the simplest possible mechanism.

(28) Rh(TPP)($CO_2Et$) is also generated from $Rh_2(OEP)_2$ in the presence of CO and ethanol. Miller, R. G.; Kyle, J. A.; Coates, G. W.; Anderson, D. J.; Fanwick, P. E. *Organometallics* **1993**, *12*, 1161−1166. The reaction, however, proceeds via a radical pathway (Zhang, X.-X.; Parks, G. F.; Wayland, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 7938−7944) and is therefore mechanistically different from the transformation found in the present work.

(29) The CO stretch is at 2108 and 2100 $cm^{-1}$ in the chloride and the iodide complexes, respectively.

(30) Scheidt, W. R. In *The Porphyirn Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, pp 49−112.

(31) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676−2681.

(32) *Book of Data*, revised edition; Ellis, H., Ed.; Longman: Harlow, U.K., 1984; p 49.

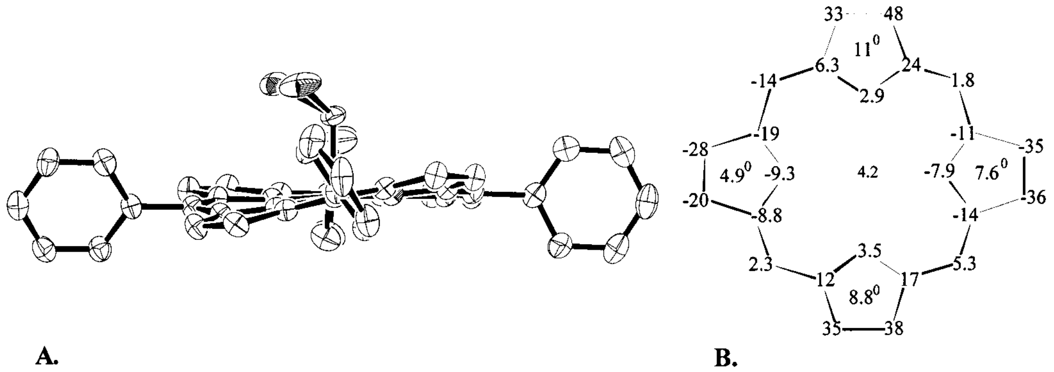

**Figure 3.** (A) Side view of Rh(TPP)($CH_2Cl$) showing the distortion of the porphyrin core (50% thermal ellipsoids). (B) Displacement (pm) of the atoms of the porphyrin core and Rh from the 24-atom least-squares plane (excluding Rh) and the absolute values of the angles between the 5-atom least-squares planes of the pyrrole rings and the 24-atom least-squares plane of the porphyrin core.

**Table 2.** Select Bond Distances (Å) and Angles (deg) for Rh(TPP)($CH_2Cl$) and Related Complexes

| | Rh(TPP)-($CH_2Cl$) | [Rh]−$CH_2Cl$ [a] range | Rh(por)−C [b] range |
|---|---|---|---|
| Rh−C | 2.010(4) | 2.050(7)−2.161(2) | 1.896(6)−2.078(5) |
| C−Cl[c] | 1.708(6) | 1.688(6)−1.803(8) | |
| Rh−$N_{av}$[d] | 2.020 | | 2.023−2.035 |
| Rh−$N_4$[e] | 0.018 | | 0.024−0.096 |
| Rh−C−Cl | 116.1 | 115.3(4)−120.0(3) | |

[a] In the complexes containing the Rh−$CH_2Cl$ moiety. [b] In the complexes containing the (por)Rh−C moiety. [c] Of the chloromethyl group. [d] Average of the four Rh−N bonds in the Rh(por) moiety. [e] Displacement of Rh atom from the least-squares plane of the four N atoms of the porphyrin core.

are similar to those found in phase A of Ni(OEP) (Ni···Ni separation of 7.62 Å and interporphyrin separation of 3.48 Å),[33] suggesting weak $\pi-\pi$ interactions in pairs of Rh(TPP)($CH_2Cl$) molecules.

The nonplanarity of the core is accompanied by shortening of the Rh−N bonds (Table 2), which is usual. On the other hand, Rh(TPP)($CH_2Cl$) manifests a remarkably small displacement of Rh from the plane of the coordinating nitrogens. Finally, although the Rh−C distance in Rh(TPP)($CH_2Cl$) is comparable to other organometallic Rh(por) derivatives, it is the shortest among the chloromethylrhodium complexes whose crystal structures have been reported (Table 2). Shortening of the Rh−C bond in porphyrin derivatives, compared to the non-porphyrin analogues, is normally observed.

**Acknowledgment.** We thank the NSF (Grant CHE-9612725) and Stanford Graduate Fellowship (R.B.) for financial support. Special thanks are extended to Adam Cole (Stanford) and Dr. F. Hollander (UC−Berkeley) for help with the crystallographic studies.

**Supporting Information Available:** Details of experimental procedures, crystallographic data in the CIF format, least-squares planes, and deviations therefrom. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000820C

---

(33) Brennan, T. D.; Scheidt, W. R.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919−3924.