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Aromatic and Benzylic C−H Bond Activation in the System Bis(dicarbonylrhodium(I))-porphyrinate−Hydrocarbon Solvent

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Introduction

Porphyrin complexes of both d^6 Rh^{III} and d^7 Rh^{II} are known to activate C−H bonds. Electrophilic aromatic metalation by Rh^{III}(OEP)$^+$[1] has been reported to show remarkable regioselectivity, yielding exclusively para-metalated arenes, Rh^{III}(OEP)(p-C$_6$H$_4$X) with ortho/para-directing substituents (X = CH$_3$, OCH$_3$, Cl). The meta isomers Rh^{III}(OEP)(m-C$_6$H$_4$X) have been observed in reactions with benzonitrile and methyl benzoate.[2] Ortho metalation does not proceed for steric reasons. Using Rh^{III}(OEP)$^+$, catalytic derivatization of arenes has been achieved. On the other hand, these species are not known to react with aliphatic C−H bonds. In contrast, monomeric metalloradical Rh^{II}−porphyrin complexes, Rh^{II}(por), readily react with methane and benzylic C−H bonds, as well as Si−H and Sn−H bonds, but are inert toward aromatic substrates.[3] Both the d^7 configuration of Rh^{II} and the steric restrictions of the porphyrin ligand prohibit the oxidative-insertion mechanism. The reaction is thought to proceed by concerted homolysis of the C−H bond by two Rh^{II}(por) centers via a linear termolecular transition state (TS). While the trigonal-bipyramidal geometry of the TS in the case of an aliphatic substrate ensures sufficient separation between the Rh^{II}(por) moieties, activation of non-sp^3 C−H bonds would require too close an approach of the two metalloporphyrins, destabilizing the corresponding TS. Such steric factors are believed to be responsible for the inertness of Rh^{II}(por) toward aromatic C−H bonds.

Finally, mononuclear d^8 Rh^I(por)$^-$ species are not reactive toward any type of C−H bonds. However, it has been known since 1967 that heating solutions of a bimetallic Rh^I porphyrin complex, (TPP)Rh$_2$(CO)$_4$, in benzene yields, as a side product, a phenylrhodium(III) derivative.[4] Details of this transformation have not been studied. From crystallographic studies Rh$_2$(CO)$_4$(OEP) is known to contain two equivalent square-planar Rh^I centers, residing on the opposite faces of the porphyrin and at a separation of 3.04 Å.[5] Each metal is coordinated to two CO molecules and two adjacent nitrogens of the macrocyle. Therefore, it is not surprising that Rh$_2$(CO)$_4$(por) species undergo relatively facile oxidative addition reactions with various alkyl and aryl iodides, carboxylic acid anhydrides, aldehydes, and methyl ketones.[6] However, insertion into a strong arene C−H bond is much more challenging, and only a limited number of Rh^I complexes capable of such chemistry have been discovered.[7] Such presumed reactivity of Rh$_2$(CO)$_4$(por) could conceivably be promoted by the synergetic effect of the two metal centers. We are particularly interested in the different reactivities of similar complexes containing one or several metal centers because such information could assist in designing better catalysts. In addition, since Rh$_2$(CO)$_4$(por) is a common starting material for most other Rh(por) derivatives, a direct reaction between a hydrocarbon and (por)Rh$_2$(CO)$_4$ can be an efficient synthetic route to some organometallic Rh^{III}(por) species. Such complexes have attracted attention in part because they are pertinent to the reactivity of cobalamine in vitamin B$_{12}$.[8]

Results and Discussion

Carefully purified samples of Rh$_2$(CO)$_4$(por) (por = OEP or TPP) fail to react with benzene or toluene after prolonged heating at reflux under rigorously anaerobic and anhydrous conditions. In the presence of at least 3 equiv of H$_2$O under N$_2$, Rh$_2$(CO)$_4$(TPP) reacts slowly with toluene at 80 °C yielding Rh(TPP)(CH$_2$Ph). Arene metalation of toluene or activation of benzene is not observed. The reactive species under these conditions is undoubtedly Rh^{II}(TPP). Thus, if a solution of Rh$_2$(CO)$_4$(TPP) in CD$_3$C$_6$D$_5$ containing three equiv of H$_2$O is heated in a sealed NMR tube at 80 °C for a few hours, two high-field ^{1}H NMR resonances corresponding to Rh-bound hydrides appear. The doublet at −40.23 ppm is that of the known species Rh(TPP)H.[9,11a] The position (−36.76 ppm) and the large value of the spin-coupling constant ($J_{^{103}\mathrm{Rh}-^{1}\mathrm{H}}$ = 42 Hz) of the second signal indicate a Rh(por)H unit, rather than a non-porphyrin Rh hydride,[10] while the slight deshielding of this signal relative to that in Rh(TPP)H suggests the presence of a ligand trans to the hydride, XRh(TPP)H.[11] The nature of X is presently unknown. A small amount of Rh$_2$(TPP)$_2$ is also observed. Continued heating leads to further decrease in the intensity of

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

(2) (a) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168−173. (b) Zhou, X.; Tse, M. K.; Wu, D.; Mak, T. C. W.; Chan, K. S. *J. Organomet. Chem*. **2000**, *598*, 80−86. (c) Zhou, X.; Li, Q.; Mak, T. C. W.; Chan, K. S. *Inorg. Chim. Acta* **1998**, *270*, 551−554.

(3) (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. (d) Mizutani, T.; Uesaka, T.; Ogoshi, H. *Organometallics* **1995**, *14*, 341−346.

(4) Fleischer, E. B.; Lavallee, D. *J. Am. Chem. Soc*. **1967**, *89*, 7132−7133.

(5) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z. *Acta Crystallogr*. **1975**, *B31*, 1−6.

(6) (a) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977** 1395−1403. (b) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977**, 36−44.

(7) (a) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995−1997. (b) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc*. **1999**, *121*, 3974−3983 and references therein. (c) McNamara, B. K.; Yeston, J. S.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1999**, *121*, 6437−6443. (d) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260−263. (e) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res*. **1995**, *28*, 154−162.

(8) For general references on chemistry and biomimetic studies of B$_{12}$, see: (a) *Chemistry and Biochemistry of B$_{12}$*; Banerjee, R., Ed.; Wiley: New York, 1999. (b) Murakami, Y.; Kikuchi, J.; Hisaeda, Y.; Hayashida, O. *Chem. Rev.* **1996**, *96*, 721−758. For related work on Rh porphyrins, see: (c) Wayland, B. B.; Van Voorhees, S. L.; Del Rossi, K. J. *J. Am. Chem. Soc*. **1987**, *109*, 6513−6515.

(9) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039−4024.

(10) Hydride resonances of Rh−H moieties in non-porphyrin complexes appear at ca. −10 to −30 ppm with $J(^{103}\mathrm{Rh}-^{1}\mathrm{H})$ values of 0−10 Hz: (a) Bergman, R. G. *J. Organomet. Chem*. **1990**, *400*, 273−282. (b) Sheridan, P. S. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; pp 920−925, 1017−1027.

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Table 1. Product Distribution and Yields of Organometallic Rh(por) Derivatives under Various Experimental Conditions[a]

solvent	reactn *T*, °C	reactn time, h	isolated organometallic species (molar ratio)	total isolated yield, %
		$Rh_2(CO)_4(TPP)$		
C_6H_6	80 (reflux)	12	Rh(TPP)Ph	80−90[b]
$C_6H_5CH_3$	80 or 110	12	$Rh(TPP)CH_2Ph$	75−90[b]
$C_6H_5OCH_3$	80	12	$Rh(TPP)CH_2OPh$	85
C_6H_5Cl	110	24	Rh(TPP)(*m*-C_6H_4Cl), Rh(TPP)(*p*-C_6H_4Cl) (2:1)	15
C_6H_5F	85 (reflux)	24	none	−
$C_6H_5CF_3$	102 (reflux)	24	none	−
C_6H_5CN	150	24	$Rh(TPP)CH_3$	5
$C_6H_5CH_3$[c]	80	12	Rh(TPP)(*m*-$C_6H_5CH_3$), Rh(TPP)(*p*-$C_6H_5CH_3$) (2:1)	65
$C_6H_6-C_6H_5CH_3$ (1:1)[c]	80	12	Rh(TPP)(*m*-$C_6H_5CH_3$), Rh(TPP)(*p*-$C_6H_5CH_3$), Rh(TPP)Ph (3:2:6)	65
		$Rh_2(CO)_4(OEP)$		
C_6H_6	80 (reflux)	12	Rh(OEP)Ph	15−30[b]
$C_6H_5CH_3$	80	12	Rh(OEP)(*m*-$C_6H_5CH_3$), Rh(OEP)(*p*-$C_6H_5CH_3$), Rh(OEP)(CH_2Ph), Rh(OEP)Ph, Rh(OEP)Me (4:2:3:0.5: 0.5)	20
		$Rh^{III}(OEP)(PF_6)$		
$C_6H_5CH_3$[d]	80	2	Rh(OEP)(*m*-$C_6H_5CH_3$), Rh(OEP)(*p*-$C_6H_5CH_3$) (1.6:1)	100 by NMR

[a] In the presence of traces of H_2O and O_2 unless noted otherwise. [b] Range of yields observed in three repeats. [c] Anhydrous solvent. [d] Anhydrous and anaerobic conditions.

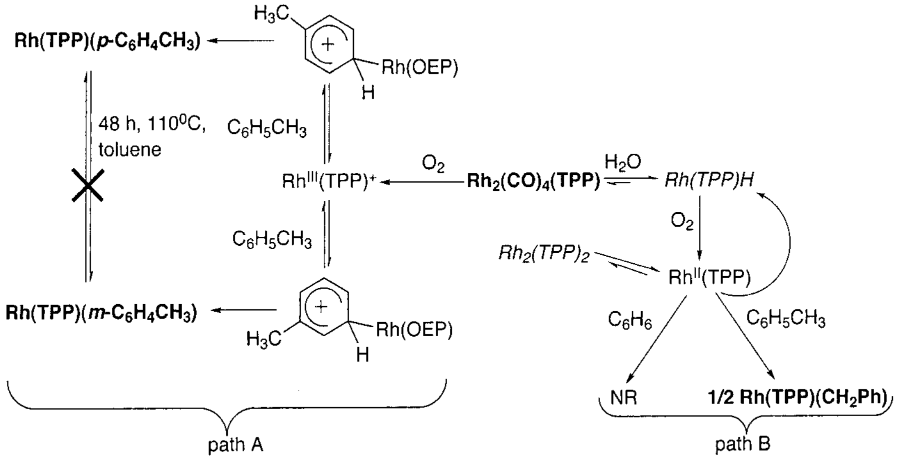

Figure 1. Proposed reaction sequence leading to activation of aromatic and benzylic C−H bonds in the system $Rh_2(CO)_4(TPP)$−aromatic hydrocarbon. The starting material and the final products are in bold; the intermediates in italics have been observed by ^1H NMR.

the ^1H NMR signals corresponding to $Rh_2(CO)_4(TPP)$ and appearance of those corresponding to $Rh(TPP)(CD_2C_6D_5)$. Formation of Rh(TPP)D is also evident. A similar reaction is observed with a sample of Rh(TPP)H in $CD_3C_6D_5/H_2O$ mixtures at 80−110 °C. The presence of H_2O is essential, as anhydrous Rh(TPP)H does not undergo homolysis of the Rh−H bond under these conditions and is therefore unreactive toward hydrocarbons.[11a] These data suggest that neither Rh^I nor Rh^{II} states are the active species in the *arene* metalation which is a side reaction in refluxing benzene solutions of $Rh_2(CO)_4(por)$. Such a transformation most likely proceeds by an S_EAr mechanism via an electrophilic $Rh^{III}(por)$ derivative, apparently arising from a relatively facile oxidation of the starting material, $Rh_2(CO)_4(por)$, by adventitious O_2.[12] Thus, heating at 80 °C under N_2 a solution of anhydrous $Rh_2(CO)_4(TPP)$ in anhydrous toluene, which was saturated with dry air and briefly degassed prior to dissolving $Rh_2(CO)_4(TPP)$, yielded a statistical mixture of meta- and para-metalated tolyls, Rh(TPP)(*m*-$C_6H_4CH_3$) and Rh(TPP)(*p*-$C_6H_4CH_3$). In a similar experiment using a 1:1 benzene−toluene solvent, a mixture of the tolyl and phenyl complexes, enriched in the former, was isolated (Table 1). In a control experiment, which was run under identical conditions, with the exception that water-saturated toluene was used as a solvent, $Rh(TPP)(CH_2Ph)$ was cleanly produced. These observations suggest that apparent activation of aromatic and benzylic C−H bonds in solutions of $Rh_2(CO)_4(por)$ in aromatic hydrocarbon solvents at elevated temperatures arises from $Rh^{II}(por)$ and $Rh^{III}(por)$ derivatives, rather than representing the intrinsic reactivity of $Rh_2(CO)_4(por)$.

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(11) Deshielding of the hydride in Rh(por)H upon coordination of an axial ligand has been observed before: (a) Collman, J. P.; Boulatov, R. *J. Am. Chem. Soc.* **2000**, *122*, 11812−11821. (b) Collman, J. P.; Ha, Y.; Guilard, R.; Lopez, M.-A. *Inorg. Chem.* **1993**, *32*, 1788−1794. (c) Wayland, B. B.; Balkus, K. J.; Farnos, M. D. *Organometallics* **1989**, *8*, 950−955. (d) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 6063−6069.

(12) (a) Grodowski, J.; Neta, P.; Hambright, P. *J. Phys. Chem.* **1995**, *99*, 6019−6023. (b) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3093−3097. (c) James, R. R.; Stynes, D. V. *J. Am. Chem. Soc.* **1972**, *94*, 6225−6226.

In order to test this hypothesis further we have examined the reactions of $Rh^{III}(OEP)(PF_6)$ and $Rh^{III}(TPP)(O_2)$ with toluene at elevated temperatures. Electrophilic metalation of arenes with $Rh^{III}(OEP)^+$ was reported to yield *p*-aryls irrespectively of the reaction temperature.[2a] However, we have found that, at 80 °C, $Rh^{III}(OEP)(PF_6)$ reacts with anhydrous toluene under N_2 yielding a mixture of *m*- and *p*-tolyls. The product distribution is comparable to that observed in the $Rh_2(CO)_4(TPP)$−anhydrous toluene system (Table 1). Oxidation of $Rh_2(CO)_4(TPP)$ with O_2 produces a relatively stable superoxido derivative, $Rh(TPP)(O_2)$, rather than the more reactive "naked" $Rh^{III}(por)^+$ electrophile. Nonetheless, heating a toluene solution of $Rh(TPP)(O_2)$ at reflux overnight produces a mixture of the *m*- and *p*-tolyl complexes. No reaction was observed with C_6H_5F.

A plausible set of reactions which accounts for production of Rh(por) alkyl complexes upon heating solutions of $Rh_2(CO)_4(por)$ in an aromatic hydrocarbon under various experimental conditions is shown in Figure 1. In the presence of traces of H_2O, Rh(TPP)H is produced,[13,14] which is converted to $Rh^{II}(TPP)$ either via the Rh−H bond homolysis or by reaction with adventitious O_2.[15] The monomeric $Rh^{II}(por)$ species reacts with substrates that possess activated CH_3 groups (toluene and anisole, vide infra), generating the observed organometallic products, $Rh(TPP)(CH_2Ph)$ and $Rh(TPP)(CH_2OPh)$, and Rh(TPP)H. During the course of the reaction, significant amounts of the intermediate, Rh(TPP)H, were detected by ^1H NMR. The active $Rh^{II}(TPP)$ is regenerated via a reaction of Rh(TPP)H with O_2 or the thermal homolysis of the Rh−H bond.[16] The former reaction also scavenges traces of O_2, suppressing further oxidation to electrophilic $Rh^{III}(TPP)$ species. In contrast, in a solvent that does not react with $Rh^{II}(TPP)$ (such as benzene), $Rh^{III}(TPP)$ species are more readily produced, ultimately resulting in arene activation. The same outcome is obtained in anhydrous toluene, probably because a sufficient concentration of Rh(TPP)H does not build up in the absence of H_2O. Generation of both $Rh(TPP)(m\text{-}C_6H_4CH_3)$ and $Rh(TPP)(p\text{-}C_6H_4CH_3)$ under the latter conditions apparently reflects the reversible formation of Wheland complexes,[17] since these isomers do not interconvert even after prolonged heating in toluene.

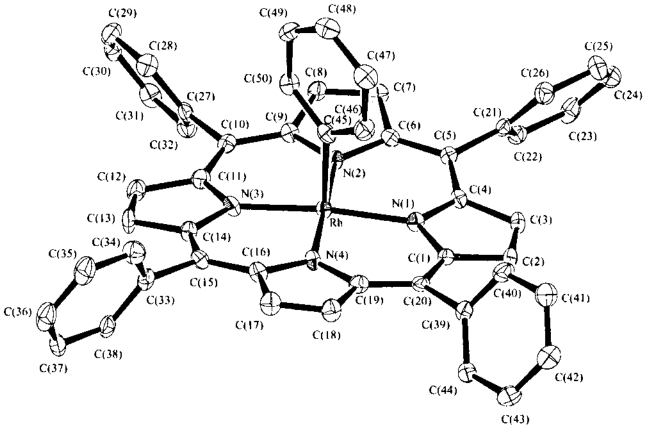

Figure 2. ORTEP drawing of Rh(TPP)Ph (50% probability thermal ellipsoids) showing the atom number scheme. Hydrogen atoms are omitted for clarity.

Table 2. Crystallographic Data for Rh(TPP)Ph

empirical formula	$C_{56}H_{47}N_4Rh$
fw	878.92
cryst dimens (mm)	0.26 × 0.17 × 0.10
lattice params	$a = 12.1483(3)$ Å
	$b = 12.5044(3)$ Å
	$c = 16.7334(4)$ Å
	$\alpha = 91.356(1)°$
	$\beta = 110.979(1)°$
	$\gamma = 114.425(1)°$
	$V = 2116.5(1)$ Å^3
space group	$P\bar{1}$ (No. 2)
Z value	2
D_{calc}	1.38 g/cm^3
R1 (wR2)[a]	0.086 (0.135)
GOF indicator	1.86

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

While the above data indicate that the long-known benzene activation observed in solutions of $Rh_2(CO)_4(por)$ does not reflect the intrinsic reactivity of the Rh^I species, such transformations can provide a suitable synthetic route to organometallic $Rh^{III}(por)$ derivatives. Since various degrees of decomposition have been observed during careful purification of $Rh_2(CO)_4(por)$ (por = OEP or TPP, see Experimental Section), the synthetic utility of this reaction was studied using crude samples. Likewise, to find the simplest synthetic protocols, we used solvents "as received" which were briefly degassed.[18] Finally, the experiments intended to probe *relative* reactivities of $Rh_2(CO)_4(por)$ toward different hydrocarbons were carried out under as uniform conditions as were experimentally achievable (see Experimental Section).

The aromatic C−H bond activation was observed in benzene solutions of $Rh_2(CO)_4(TPP)$, but metalation of both toluene and anisole proceeded exclusively at the methyl group (Table 1). Arenes bearing electron-withdrawing substituents yielded Rh-aryls either in poor yields (C_6H_5Cl) or not at all (C_6H_5F, $C_6H_5CF_3$, C_6H_5CN). Analogous reactions of $Rh_2(CO)_4(OEP)$ were qualitatively similar, but displayed poorer regioselectivity, yields, and reproducibility, compared with the TPP analogue. For example, toluene underwent activation of both aromatic and benzylic C−H bonds, as well as an apparent $C_{phenyl}-C_{methyl}$ bond cleavage (Table 1).[19−20] The different reactivity of $Rh_2(CO)_4(OEP)$ reflects both its higher susceptibility to oxidation, as a result of stronger σ-donor properties of the OEP ligand, and more facile homolysis of the (OEP)Rh−H bond. This leads to competition between the two reaction pathways (A and B, Figure 1) and observation of both aromatic and aliphatic metalation in the same reaction.

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(13) $Rh_2(CO)_4(TPP)$ was also reported to undergo a photoinduced intramolecular redox reaction producing $Rh^{II}(por)$ and metallic Rh.[14]

(14) (a) Yamamoto, S.; Hoshino, M.; Yasufuki, K.; Imamura, M. *Inorg. Chem.* **1984**, *23*, 195−198. (b) Hoshino, M.; Yasufuku, K. *Inorg. Chem.* **1985**, *24*, 4408−4410. (c) Hoshino, M.; Yasufuku, K.; Konishi, S.; Imamura, M. *Inorg. Chem.* **1984**, *23*, 1982−1984.

(15) This reaction has occasionally been used for preparative purposes of converting Rh(por)H into the corresponding dimer, $Rh_2(por)_2$: Reference 11b. Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869−3870.

(16) It has been reported that conversion of Rh(por)H into $Rh^{II}(por)$ is promoted by metallic Rh;[3b] in the reactions studied deposits of metallic Rh appear only at late stages of the transformation and this Rh-assisted decomposition of Rh(por)H is probably not a dominant pathway for $Rh^{II}(por)$ regeneration.

(17) Reversible formation of Wheland-type complexes has been proposed to account for generation of para/meta isomers in metalation of toluene with Pt(IV) species: (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. (b) Shul'pin, G. B.; Nizova, G. V.; Nikitaev, A. T. *J. Organomet. Chem.* **1984**, *276*, 115−153. The ratio of tolyl to phenyl derivatives observed for a reaction in a 1:1 benzene−toluene mixture was higher than expected from statistical arguments, which suggests either that the reaction is not completely under thermodynamic control or that the Wheland-type complex derived from benzene is thermodynamically less stable than the corresponding toluene derivative.

(18) Reactions in thoroughly degassed solvents were much slower and manifested poor yields.

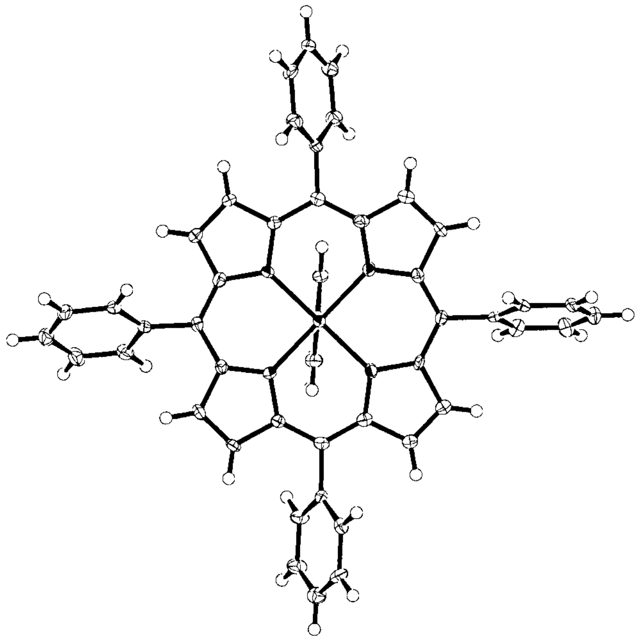

Figure 3. ORTEP view of Rh(TPP)Ph (50% probability thermal ellipsoids) along the Rh−C axis.

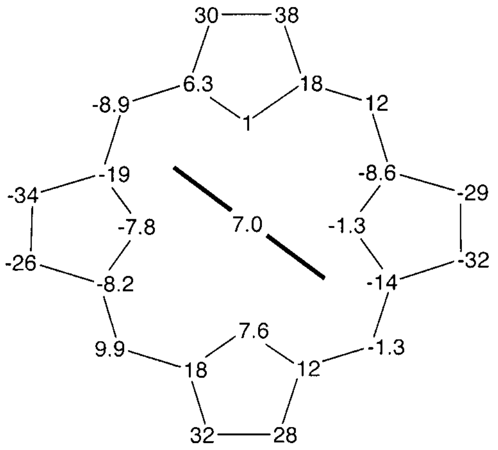

Figure 4. Displacement (in pm) of the atoms of the porphyrin core and Rh from the 24-atom least-squares plane. Positive values correspond to displacement toward the phenyl axial ligand. Relative orientation of the phenyl axial ligand is shown in bold lines.

Finally, Rh(TPP)Ph, generated in one such reaction was studied crystallographically (Figure 2, Table 2). The four N atoms of the TPP and a C atom of the phenyl group make up a slightly distorted square-pyramidal coordination around Rh. The Rh−C bond at 1.984(6) Å is within the range of values observed in other organometallic Rh(por) derivatives (1.896−2.078 Å). The axial phenyl group is almost perpendicular to the least-squares plane of the porphyrin core (the corresponding angle is 88.5°) and is oriented away from the N atoms (the N3−Rh−C45−C50 angle of 40.5°) (Figure 3). This relative orientation of aromatic axial ligands (such as phenyl or pyridine) and the M−N vectors decreases steric interactions between the ortho hydrogens and the porphyrin core.[21] A rather significant "saddle" distortion of the TPP core in Rh(TPP)Ph (Figure 4) is most likely caused by the same forces. As is often the case, this distortion is accompanied by shortening of the Rh−N bonds (average Rh−N distance of 2.024 Å). Interestingly, while the macrocycle undergoes a relatively large distortion, the displacement of Rh from the least-squares plane of the chelating nitrogens is only 0.03 Å.

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

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(19) Metal-assisted cleavage of C−C bonds both on metal surfaces[20a] and by metal complexes in solution[20b] is known. The latter, however, is limited to special substrates.[20b] The generation of Rh(OEP)Ph and Rh(OEP)Me in the $Rh_2(CO)_4(OEP)$−toluene system may provide an interesting lead in search for metal complexes capable of C−C bond activation in relatively unreactive substrates. However, at this time any conclusions regarding the mechanistic aspects of the observed C−C bond cleavage in the above system are precluded by the complexity of the $Rh_2(CO)_4(OEP)$−toluene reaction mixture. The possibility of heterogeneous C−C bond activation on metallic Rh[16] is less likely, since in such a case C−C bond cleavage should not be limited to the OEP derivatives. However, which of the three species—$(Rh^{I})_2(CO)_4(OEP)$, $Rh^{II}(OEP)$, or $Rh^{III}(OEP)X$, present in the reaction mixture in significant relative amounts—is responsible for the C−C bond activation is not obvious.

(20) (a) See, for example: Hagedorn, C. J.; Weiss, M. J.; Kim, T. W.; Weinberg, W. H. *J. Am. Chem. Soc.* **2001**, *123*, 929−940 and references therein. (b) For a comprehensive review, see: Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870−883.

(21) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 3, pp 49−112.