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Nonradical Trapping Pathway for Reactions of Nitroxides with Rhodium Porphyrin Alkyls Bearing *β*-Hydrogens and Subsequent Carbon−Carbon Bond Activation

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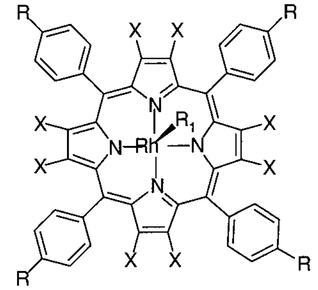
Summary: A novel nitroxide-induced hydrogen atom abstraction and β-elimination of rhodium porphyrin alkyls has been observed. Subsequent carbon−carbon bond activation of methyl-substituted nitroxides by the rhodium(II) porphyrin radical yielded rhodium porphyrin methyl complexes.

2,2,6,6-Tetramethylpiperidinoxy (TEMPO) and related nitroxide radicals have been extensively used as efficient radical traps in organic, bioorganic, and organometallic chemistry. The estimations of bond dissociation energies of metal−alkyl bonds by kinetic methods using nitroxides as radical traps have been successfully accomplished in vitamin B_{12} and related models,[1,2] cyclopentadienylmetal alkyl complexes,[3] and ruthenium porphyrin alkyl complexes.[4,5] These radicals, however, can behave as reagents rather than as innocuous traps in the reactions with organometallics. An interesting comment was made by James and Dolphin in the report on $Ru(oep)(CH_3)_2$ and $Ru(oep)(C_6H_5)_2$ reactivity (oep = octaethylporphyrin dianion): "the rate of decomposition of $Ru(oep)(CH_3)_2$ was found to be dependent on the concentration of TEMPO which also appears to react with $Ru(oep)CH_3$".[5] Nitroxides are well-known ligands for a variety of transition-metal complexes.[6,7] TEMPO has been reported to react with the porphyrin $Ru(oep)CH_3$ to yield Ru(oep)CO.[7] We have also reported recently that rhodium(II) porphyrin also reacts with nitroxides in a carbon−carbon bond activation (CCA) to yield methylrhodium porphyrin.[8] In the course of investigating the mechanism of 1,2-rearrangements of rhodium porphyrin alkyls,[9] we have observed that TEMPO did not act as an innocuous radical trap but reacted directly with rhodium porphyrin alkyls bearing *β*-hydrogens via a novel *β*-hydrogen abstraction/elimination process to generate rhodium porphyrin radicals, which then underwent aliphatic CCA with nitroxides.



R	X	Rh(por)
Me	H	Rh(ttp)
^tBu	H	Rh(btpp)
^tBu	Cl	Rh(bocp)

Figure 1. Structures of rhodium porphyrins.

The results of the thermal reactions of TEMPO and rhodium porphyrin alkyls are summarized in Table 1 (Figure 1, eq 1). $Rh(bocp)CH_3$ (**3a**) was formed unexpectedly from the thermolysis of **3** with TEMPO (5 equiv). $Rh(bocp)CH_2CH_2Ph$ was consumed within the first 1 h of the reaction without any $Rh(bocp)CH_3$ formed, as determined by TLC analysis. The rate of disappearance of **3** was therefore found to be much faster than that of 1,2-rearrangement into $Rh(bocp)CH(Ch_3)Ph$ (10 h at 80 °C).[9a] Then, after a total reaction time of 7 h, $Rh(bocp)CH_3$ was formed in 45% isolated yield. Increasing the amount of TEMPO to 15 equiv did not increase the rate of disappearance of **3** but accelerated the rate of the formation and the yield of product **3a (**90 min and 81%). Therefore, a stable rhodium

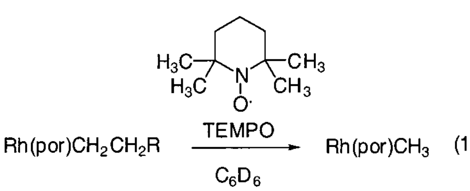


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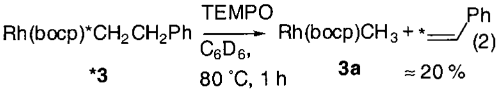
Table 1. Summary of Thermolysis of (Porphyrinato)rhodium Alkyls with TEMPO

complex	amt of TEMPO (equiv)	temp (°C)	time for disappearance of complex	total reacn time	Rh(por)CH_3; yield, %
Rh(ttp)CH_2CH_2Ph (**1**)	5	80	48 h	6 days	**1a**; 70[b]
Rh(bttp)CH_2CH_2Ph (**2**)	5	80	48 h	6 days	**2a**; 25[b]
Rh(bocp)CH_2CH_2Ph (**3**)	5	80	15 min	7 h	**3a**; 45[b]
Rh(bocp)CH_2CH_2Ph (**3**)	15	80	15 min	90 min	**3a**; 81[a]
Rh(bocp)$CH(CH_3)Ph$ (**4**)	5	120	3 days	3 days	**3a**; 70[b]
Rh(bocp)CH_2CH_2CN (**5**)	10	120	12 h	24 h	**3a**; 86[b]
Rh(ttp)CH_2CH_3 (**6**)	10	120	NA[c]	14 days[c]	**1a**; 10[d] (51[e])
Rh(ttp)$CH_2CH_2CH_3$ (**7**)	10	120	7 days	7 days	**1a**; 74[b]

[a] Isolated yield from column chromatography. [b] Estimated yields from ^1H NMR integration. [c] Only 19% of starting material converted. [d] Based on 100% of starting material. [e] Based on 19% starting material converted.

porphyrin intermediate likely formed. More electron rich porphyrin rhodium alkyls such as **1** and **2** reacted with excess TEMPO similarly. The reactivity appeared to decrease with the increasing strength of the β-C−H bond (**3** vs **5**, **1** vs **6** and **7**).

To elucidate the mechanism of the formation of Rh(por)CH_3 complexes, the ^{13}C-enriched phenylethyl rhodium complex ***3** was reacted with TEMPO (eq 2). The

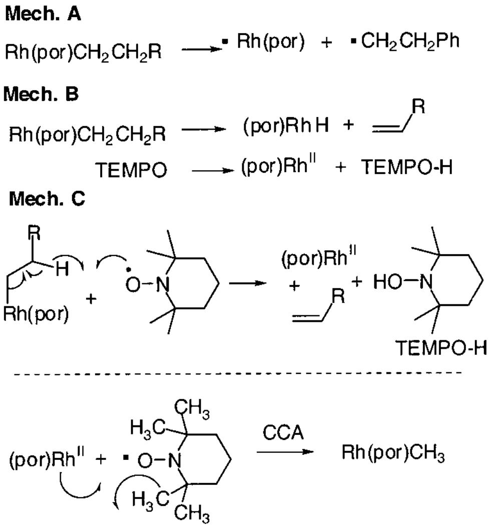


methyl ligand of **3a** formed from the reaction was found to be unenriched with ^{13}C and appeared as a broad singlet at −4.84 ppm in the ^1H NMR spectrum of the reaction mixture without any $^1J_{C-H}$ coupling observed. This ruled out the possibility that the methyl ligand came from the α-carbon of the phenylethyl ligand of **3**.

From the proton-coupled ^{13}C NMR spectrum of the reaction mixture of ***3** with TEMPO, two enhanced triplets at 73.7 and 113.8 ppm with $^1J_{C-H}$ values equal to 148 and 157 Hz, respectively, were observed. At least two products were therefore formed. The resonance at 113.8 ppm was assigned to the terminal sp^2 carbon of styrene and was quantified in 20% yield by ^1H NMR spectroscopy (cf. $\delta(C_6H_5CH{=}CH_2)$ 112.3 ppm, $^1J_{C-H}(CH_2{=}CH_2) = 156$ Hz in $CDCl_3$).[10a] However, the signal at 73.7 ppm could not be unambiguously assigned and is unlikely to be TEMPO-$^*CH_2CH_2Ph$.[10b] Therefore, the CH_2-CH_2Ph fragment remained intact and the Rh−C bond was cleaved in the reaction.

The reaction of of Rh(por)CH_2CH_2R with TEMPO to form Rh(por)CH_3 appears to involve a two-step process with the formation of a rhodium porphyrin radical intermediate. The activation of the reaction by the coordination of TEMPO to Rh(por)CH_2CH_2R is also possible. The first step likely involves the generation of the rhodium(II) porphyrin radicals, and the second step is possibly the CCA of TEMPO with Rh^{II}(por) radical to produce Rh(por)CH_3.[8] Three mechanistic possibilities exist for the generation of Rh(por) radicals (Scheme 1): (A) homolysis of a rhodium−alkyl bond, (B) β-hydride elimination of Rh(por)CH_2CH_2R to Rh(por)H−hydrogen abstraction with TEMPO,[11] and (C) β-hydrogen abstraction of Rh(por)CH_2CH_2R with TEMPO−Rh−C homolysis.

Scheme 1. Proposed Mechanism for the Formation of Rh(por)CH_3 from Rh(por)CH_2CH_2R



Mechanism A is disfavored on the basis of the unlikely homolysis of the rather strong Rh−C bond at 120 °C (BDE ≈ 60 kcal/mol)[12,13] as well as the absence of $PhCH_2CH_2$-TEMPO in the presence of an excess of the efficient spin trap TEMPO. Though mechanism B is apparently supported by the established intermediate of Rh(por)H, generated via β-hydride elimination in the 1,2-rearrangements of Rh(por)CH_2CH_2R,[9] the rates of disappearance of the starting materials were, however, much faster in the presence of TEMPO. In the absence of TEMPO, the 1,2-rearrangements of Rh(bocp)CH_2CH_2Ph and Rh(ttp)CH_2CH_2Ph took 10[9a] and 144 h,[9b] respectively. Therefore, Rh(por)CH_2CH_2Ph must react with TEMPO directly. Furthermore, Rh(bocp)CH_2CH_2CN did not undergo any significant 1,2-rearrangement after heating in benzene at 150 °C for 11 days. No Rh(bocp)H was formed, as no rearrangement was observed. However, it reacted with TEMPO at 120 °C within 2 days to give **3a**. Therefore, the presence of Rh(por)H is ruled out. Mechanism C remains the most probable. Abstraction of the fairly weak C−H bond α to Ph, CN, and Me groups in these rhodium complexes is energetically feasible at the reaction temperature of 80−120 °C, and the reaction rates increased as the C−H bond strengths decreased (BDE($PhCH_2$−H) = 88 kcal/mol,[13]

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BDE(Me(H)(CN)C−H) = 90 kcal/mol,[14] BDE(Me(Me)-CH_2−H) = 95 kcal/mol,[14] BDE(MeCH$_2$−H) = 98 kcal/mol,[14] BDE(TEMPO−H) = 70 kcal/mol[15]). The hydrogen abstraction step may likely be synchronous with the homolysis of the Rh−C bond to generate a Rh(por) radical.

In summary, we have identifed a nonradical trapping pathway for reactions of TEMPO nitroxide with rhodium porphyrin alkyls bearing β-hydrogens and subsequent carbon−carbon bond activation via rhodium porphyrin radicals. The innocuous nature of TEMPO as a radical trap in the determination of metal alkyls of organometallics, especially stronger ones, needs to be viewed cautiously.

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