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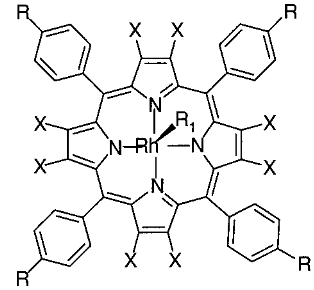
Summary: A novel nitroxide-induced hydrogen atom abstraction and β-elimination of rhodium porphyrin alkyls has been observed. Subsequent carbon−carbon bond activation of methyl-substituted nitroxides by the rhodium(II) porphyrin radical yielded rhodium porphyrin methyl complexes.

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)
^{t}Bu	H	Rh(btpp)
^{t}Bu	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

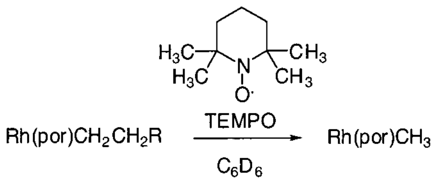


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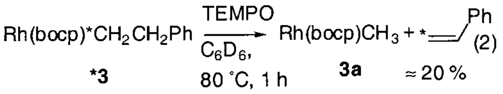
Table 1. Summary of Thermolysis of (Porphyrinato)rhodium Alkyls with TEMPO

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 ^{1}H 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**).

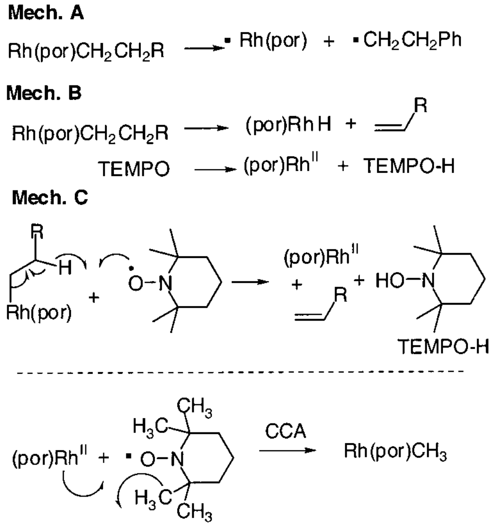
To elucidate the mechanism of the formation of Rh(por)CH_3 complexes, the ^{13}C-enriched phenylethyl rhodium complex ***3** was reacted with TEMPO (eq 2). The methyl ligand of **3a** formed from the reaction was found to be unenriched with ^{13}C and appeared as a broad singlet at −4.84 ppm in the ^{1}H 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 ^{1}H 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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