The Chemistry of Ru(OEP)(CH_3). A CH_3 to CO Transformation

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TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is commonly employed as a radical trap in the measurement of metal–carbon bond energies[1] within macrocyclic complexes in solution.[2-8] Finke has shown[2,3] that TEMPO is a more appropriate trap of alkyl radicals than *n*-BuSH, C_6H_5SH, $HMn(CO)_5$, and O_2 for macrocyclic complexes where redox reactions are possible. Collman,[4] James and Dolphin,[5] and we[6] have employed TEMPO to study bond homolysis of porphyrin complexes, while Finke,[2,3] Halpern,[7] and others[8] have studied related macrocyclic complexes. An interesting comment was made[5] by James and Dolphin in a preliminary report on Ru(OEP)(CH_3)$_2$ and Ru(OEP)(C_6H_5)$_2$ reactivity: "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)." The implication that TEMPO might not always be innocuous in such bond dissociation energy measurements is of great importance in the field of organometallic chemistry. We report herein that the reaction of TEMPO with Ru(OEP)(CH_3) ultimately leads to Ru(OEP)(CO). Isotopic labeling and IR spectroscopy verify that the CH_3 ligand is the source of the bound CO. *This is the first report of a CH_3 to CO transformation with a metal complex.*

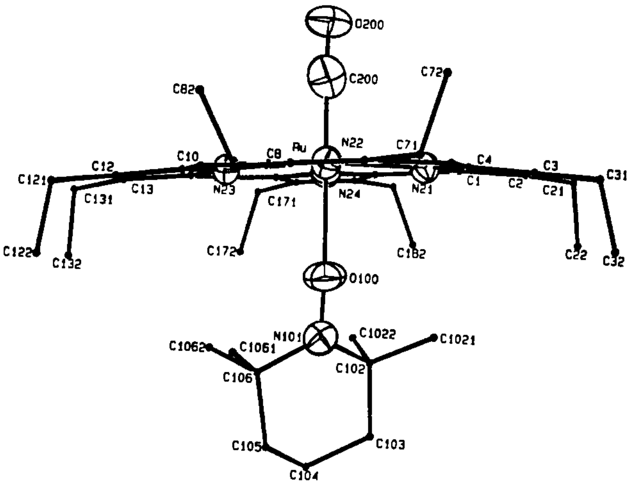

Figure 1. ORTEP representation of Ru(OEP)(CO)(TEMPO).

Addition of excess TEMPO ([TEMPO]$_0$/[Ru]$_0$ ≥ 5) to a C_6H_6 solution of Ru(OEP)(CH_3) leads to little immediate change in the ^1H NMR or UV–vis spectra.[9] However, after several hours both spectra indicate the conversion of the starting paramagnetic Ru^{III} complex to a diamagnetic Ru^{II} complex. After several days, the spectra change very little. X-ray crystallographic analysis[12] of the crystals obtained from slow evaporation of C_6H_6 reveals the presence of Ru(OEP)(CO)(TEMPO). The ORTEP representation of this structure is shown in Figure 1. The complex possesses the expected linear binding mode for the CO ligand (178.6°) with a Ru–C bond distance of 1.798 (5) Å and a C–O bond distance of 1.150 (5) Å. The UV–vis and ^1H NMR spectroscopic properties of this material are comparable to those of authentic[11b] Ru(OEP)(CO)(CH_3OH) and Ru(OEP)(CO)(THF) samples. The ^1H spectrum reveals slight broadening of the OEP peaks attributable to the presence of TEMPO in solution but reveals no evidence of TEMPO ligation with Ru(OEP)(CO) in solution. The Ru–O distance of 2.348 (3) Å is somewhat larger than those[11b] in Ru(TPP)(OEt)(HOEt) (2.019 (3) Å), Ru(TPP)(CO)(HOEt) (2.21 (2) Å), or (Ru(OEP)(HO))$_2$O (2.195 Å), suggesting weak ligation in the solid state.

The product of the reaction of Ru(OEP)($^{13}CH_3$) with excess TEMPO possesses a CO stretch in the IR spectrum at 1884 cm^{-1}, which is in excellent agreement with that calculated (1887 cm^{-1})

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(9) All manipulations were performed[10] at room temperature in a Vacuum Atmospheres inert-atmosphere box or on a Schlenk line using oven-dried glassware and dried and deoxygenated solvents. TEMPO (Aldrich Chemical Co.) was sublimed before use. $^{13}CH_3I$ (99.4 atom % ^{13}C, Aldrich Chemical Co.) was subjected to three freeze–pump–thaw cycles and stored over Cu. Ru(OEP)(CH_3)$_2$,[5,11a] Ru(OEP)($^{13}CH_3$)$_2$,[11a] and Ru(OEP)(CO)(THF)[11b] were prepared by literature methods. Ru(OEP)(CH_3) was prepared by reduction[10d] of Ru(OEP)(CH_3)$_2$ in C_6H_6 and subsequent aerial oxidation of the Ru(OEP)(CH_3)$^-$. Typically the product mixture contains 88–90% Ru(OEP)(CH_3), 6–7% unreacted Ru(OEP)(CH_3)$_2$, and 4–5% μ-oxo species[11b] (Ru(OEP)(X))$_2$O; the amounts of these minor components remain relatively constant during the transformation described in the text, so their participation is omitted from the discussion. Aerial oxidation, although responsible for the 4–5% μ-oxo species, is preferable to Ag^+ oxidation, since over-oxidation to Ru(OEP)(CH_3)$^+$ leads to an unknown species X and ultimately $Ru_2(OEP)_2^+$. UV–vis spectra were obtained on a Hewlett-Packard 8450 diode array spectrophotometer using 0.1-cm cells. ^1H NMR spectra were obtained on Varian 200-MHz or GE 300-MHz spectrometers. Samples were prepared with 2–4 mM porphyrin complex in C_6D_6 containing ca. 1 mM anthracene (Aldrich Gold Label) as an internal standard.

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(12) An orange crystal with approximate crystal dimensions of 0.3 × 0.17 × 0.11 mm was investigated on an Enraf-Nonius CAD4 diffractometer using previously described procedures.[10c] The structure was solved in the $P\bar{1}$ (No. 2) space group with $R(F_o m = 0.035$ and $R_w(F_o) = 0.042$. See supplementary material for complete crystallographic parameters.

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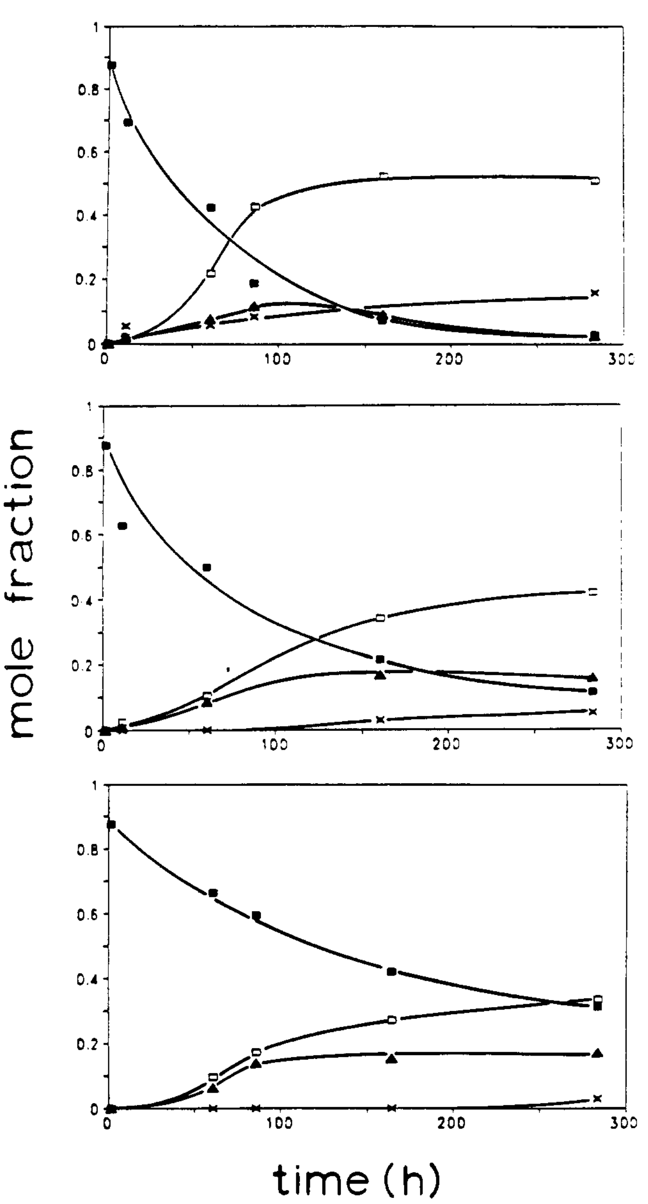

Figure 2. Composition vs time plots for transformation of Ru(OEP)(CH_3) (■) to Ru(OEP)(CO) (□), $Ru_2(OEP)_2$ (▲), and species X (×) for $[TEMPO]_0/[Ru]_0$ = 5 (top), 2.5 (middle), and 1 (bottom). Lines are drawn to aid visualization. Data were obtained from ^1H NMR spectra and are available in supplementary material. The solutions also contained trace amounts of $(Ru(OEP)(X))_2O$ and $Ru(OEP)(CH_3)_2$ whose levels (4% and 6–7%, respectively) remained relatively constant during the transformation; see footnote 9 for further comments.

from the reduced masses and the 1930-cm^{-1} stretch for Ru(OEP)(CO)(THF). *Clearly, the CO is derived from the axially-bound CH_3 of Ru(OEP)(CH_3):*

$$Ru(OEP)(^*CH_3) + \text{xs TEMPO} \xrightarrow[C_6H_6]{} Ru(OEP)(^*CO) \quad (1)$$

This CH_3 to CO transformation is unprecedented in the organometallic chemistry literature.

The composition vs time plots of the transformation with $[TEMPO]_0/[Ru]_0$ values of 1, 2.5, and 5 are shown in Figure 2. Note the steady decrease in [Ru(OEP)(CH_3)] and the corresponding increases in [Ru(OEP)(CO)], $[Ru_3(OEP)_2]$, and an unidentified[9] paramagnetic species (X). Note also the increased rate at higher molar ratio. At $[TEMPO]_0/[Ru]_0$ = 5, the transformation is 92% complete after 6 days yielding 59% Ru(OEP)(CO), 12.5% Ru_2OEP_2, and 9.6% X; at longer times X grows in at the expense of Ru_2OEP_2 (17.9% X and 2.7% Ru_2OEP_2 after 12 days). At the two lower molar ratios, the Ru_2OEP_2 formation is ca. 50–60% that of Ru(OEP)(CO) early in the reaction but again drops as X forms.

The isotope labeling experiment proves that CH_3 is the source of CO and the component distribution plots in Figure 2 provide visualization of the time course of the transformation, but neither provide insight into the general mechanism. Although we have no precedent for this transformation for comparison, we can provide several comments on the possible pathways from CH_3 to CO on the basis of the properties of Ru(Por) complexes and TEMPO reactivity: (i) TEMPO is known[13] to react rapidly with R$^\bullet$ and H$^\bullet$ species. Successive H$^\bullet$ abstraction and O atom transfer could convert a bound CH_3 to a bound CO. This would not necessarily be an efficient process, since the putative Ru(OEP)(CH_2) intermediate could decompose[5,10d,11a] to C_2H_4 and $^1/_2$ $Ru_2(OEP)_2$, thereby accounting for the observed $Ru_2(OEP)_2$. (ii) TEMPO could react with a putative Ru(OEP)(CH_2) species to form a Ru(OEP)(CH_2OX) species which reacts to form Ru(OEP)(CO). Casey has demonstrated[14] that $(C_5H_5)Re(NO)(CO)(CH_2OH)$ yields $(C_5H_5)Re(NO)(CO)_2^+$ and $(C_5H_5)Re(NO)(CO)(CH_3)$ upon acid-catalyzed disproportionation, so a (CH_2OX) → (CO) transformation is possible. (iii) TEMPO and Ru(OEP)(CH_3) could react to form (TEMPO)CH_3 and $^1/_2$ $Ru_2(OEP)_2$; decomposition of (TEMPO)CH_3 to CO (or a hydrogenated synthon like HCHO) would yield Ru(OEP)(CO) due to the affinity of Ru(OEP) complexes for CO. (This CO affinity is so great in fact that it prevents us from performing a CO–*CO scrambling experiment of reacting Ru(OEP)($^*CH_3$) + TEMPO in the presence of CO; CO rapidly decomposes Ru(OEP)(CH_3) to Ru(OEP)(CO).) This possibility highlights the necessity to state that the data do not rule out the CH_3 moiety from forming CO while separated from the Ru(OEP) center. This possibility is consistent with our data since $Ru_2(OEP)_2$ is noticeably present during the transformation. However, there is no published report of (TEMPO)R species decomposing to CO. If this is occurring, the participation of Ru(OEP) species is suggested.

Clearly more data are required to better define the reaction pathways responsible for this novel CH_3 to CO transformation. However, this transformation is another in the list[4–6,10,11,15] of interesting reactions that have been uncovered for Ru(Por) complexes. It also illustrates the caution necessary in employing spin traps like TEMPO[16] with organometallic complexes.

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Supplementary Material Available: Tables of reaction mixture compositions from ^1H NMR spectroscopy used to generate Figure 2 and crystallographic parameters for Ru(OEP)(CO)(TEMPO) (19 pages). Ordering information is given on any current masthead page.

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