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Radical Mechanism for the Decomposition of RuOEP(CH_2CH_3)$_2$. Determination of the Metal-Carbon Bond Dissociation Energy

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We recently reported the conversion of RuOEP(CH_2CH_3)$_2$ (**1**)[1] to the ethylidene complex RuOEP($CHCH_3$) (**2**).[2] The presumed lack of cis-coordination sites on one face of the metalloporphyrin seemed to limit mechanistic possibilities to those that involve loss of the α hydrogen directly without migration to the metal. Rearrangement of alkyl to alkylidene ligands in non-porphyrinic complexes has been observed to occur via deprotonation[3] and hydride abstraction[4] from the α-position of the ligand. In addition, Cooper has shown that reaction of (η^5-C_5H_5)$_2$W(CH_3)$_2$ with the trityl cation goes by electron transfer from the organometallic substrate. The resulting trityl radical then abstracts an α-hydrogen to give a methylidene complex which undergoes further reaction.[5] The known tendency for metal alkyls to undergo homolysis[6] suggested the possible involvement of alkyl radicals in the observed rearrangement. In this paper, we present the results of our studies on the conversion of **1** to **2** and demonstrate the radical nature of the mechanism. In the course of our kinetic studies, we have also determined the bond dissociation energy (BDE) of the ruthenium–carbon bond in **1**.

Upon standing at room temperature in benzene for a few hours, samples of **1** are converted to a 34:66 mixture of RuOEP($CHCH_3$) and a paramagnetic compound that we have assigned as RuOEP(CH_2CH_3) (**3**).[7,8] The product ratio does not change appreciably during the course of the reaction, indicating that the products are formed simultaneously and **3** does not lead to **2** on this time scale. Kinetic studies[9] show that the reaction is greater than first order in **1**. Addition of a large excess (>80 equiv) of TEMPO, a nitroxide known to trap alkyl radicals at nearly diffusion-controlled rates in the presence of organometallics,[10] resulted in first-order decomposition of **1** over 4 half-lives and an approximately sixfold increase in the rate. Control experiments demonstrated that in this regime of TEMPO concentrations, the reaction is zero order in TEMPO.[11] In the presence of excess TEMPO, formation of ethylidene species **2** is suppressed.

Scheme I

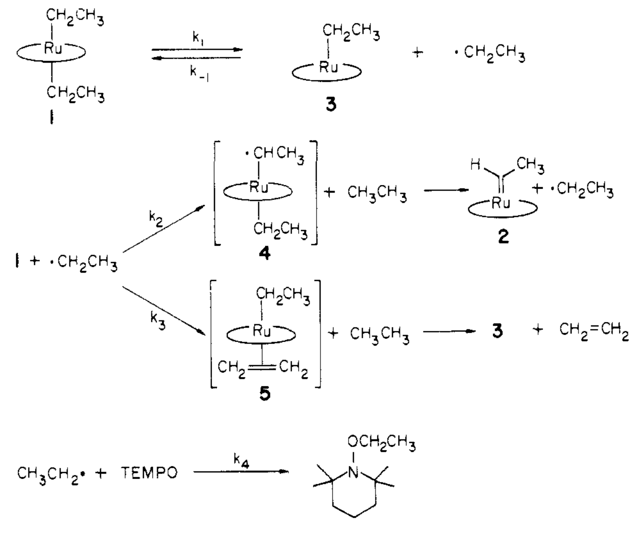

Table I. Rate Constants for the Decomposition of **1**[a]

T, °C	$k_{obsd} \times 10^4$, s^{-1} [b]	T, °C	$k_{obsd} \times 10^4$, s^{-1} [b]
12	0.243	25	1.68
15	0.487	30	3.32
20	0.867	35	6.48

[a] Rates determined at TEMPO concentrations of 0.162 M in C_6D_6. [b] All rate constants are ±15%.

The mechanism shown in Scheme I is consistent with these observations. The initial step is reversible homolysis of the ruthenium–carbon bond to give **3** plus an ethyl radical which then attacks the starting material by abstracting either an α- or a β-hydrogen (k_2 or k_3, respectively). The product ratio, which reflects the competition between these two processes, is close to the statistical value, indicating that there is little intrinsic preference for β over α abstraction. Loss of the α-hydrogen leads to the radical species **4** which would be expected to undergo homolysis much more easily than **1** due to the formation of a metal–carbon double bond in the ethylidene product **2**. β abstraction would give olefin complex **5**, which would be expected to lose ethylene rapidly due to the strong *trans* effect of alkyl ligands. Ethane and ethylene, both predicted by this mechanism, are indeed observed by GC.[12] The rate expression for this scheme (eq 1) rationalizes

$$\frac{-d[\mathbf{1}]}{dt} = k_1[\mathbf{1}]\left[1 + \frac{(k_2 + k_3)[\mathbf{1}] - k_{-1}[\mathbf{3}]}{k_{-1}[\mathbf{3}] + k_3[\mathbf{1}] + k_4[\text{TEMPO}]}\right] \quad (1)$$

both the kinetic behavior of the system in the absence of TEMPO and the effect of trapping ethyl radicals when it is present (k_4).

At sufficiently high concentrations of TEMPO, both recombination (k_{-1}) and attack of ethyl radical on **1** ($k_2 + k_3$) are no longer competitive. Homolysis is then the rate-determining step[13] and the rate expression simplifies to eq 2. We have measured

$$\frac{-d[\mathbf{1}]}{dt} = k_1[\mathbf{1}] = k_{obsd}[\mathbf{1}] \quad (2)$$

the temperature dependence of k_{obsd} over a 23 °C temperature range (Table I) in the presence of excess TEMPO. An Arrhenius plot of the data yields log $A = 14.1 \pm 0.2$ and $E_a = 24.3 \pm 0.5$ kcal/mol or $\Delta H^\ddagger_1 = 23.7 \pm 0.5$ kcal/mol. As the bond dissociation energy is equal to $\Delta H^\ddagger_1 - \Delta H^\ddagger_{-1}$, this sets an upper limit of 23.7 kcal/mol for the metal–carbon bond energy in RuOEP(CH_2CH_3)$_2$.

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(7) RuOEP(CH_2CH_3): MS (CI), *m/z* M^+ 663, $[M - CH_2CH_3]^+$ 634; ^{1}H NMR (C_6D_6) δ por$CH_2$$CH_3$ 11.9 (8 H), 5.4 (8 H); H_{meso} −0.75 (4 H); porCH_2CH_3 −1.8 (24 H) ppm. As in the Fe(III) porphyrin alkyls, the ethyl ligand is not expected to be observable by NMR due to extreme line broadening. Lexa, D.; Mispelter, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806–6812. Cocolios, P.; Lagrange, G.; Guilard, R. *J. Organomet. Chem.* **1983**, *253*, 65–79.

(8) Compound **3** has been synthesized independently from $[(RuOEP)_2]^{2+}(BF_4)_2$ and CH_3CH_2MgBr. Collman, J. P.; Prodolliet, J.; Leidner, C. R.; McElwee-White, L.; Rose, E., unpublished results.

(9) Kinetics were followed by 300-MHz ^{1}H NMR of C_6D_6 solutions. Samples were 0.0100 M in anthracene as an internal standard and ca. 0.0020 M in **1**. Due to the lability of **1**, its initial concentration was estimated in making up the sample and determined at the beginning of the run by integration vs. the anthracene standard. Data points were taken every 5 min over the course of 2 to 4 half-lives. When TEMPO was included, its concentration was 0.162 M.

(10) TEMPO is 2,2,6,6-tetramethylpiperidine-1-oxyl. Nigam, S.; Asmus, K.-D.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2324–2340. Hill, C. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 870–876.

(11) At 25 °C, the concentrations of TEMPO and k_{obsd} (s^{-1} ±15%) were as follows: 0.127 M, 1.82×10^{-4}; 0.162 M, 1.68×10^{-4}; 0.185 M, 1.75×10^{-4}.

(12) GC analyses were performed on a 10 ft × 1/8 in. Porapak Q column.

(13) For an elegant example of application of this approach to the determination of the Co–C bond energy in adenosylcobalamin and its analogues, see: Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3041–3043. Finke, R. G.; Smith, B. L.; Mayer, B. J.; Molinero, A. A. *Inorg. Chem.* **1983**, *22*, 3677–3679.

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Measurements of $\Delta H^{\ddagger}_{-1}$ for recombination of Ru(III) and alkyl radicals are not available, but the literature contains data on analogous Co(II) systems,[13,14] for which recombination occurs at nearly diffusion-controlled rates ($\Delta H^{\ddagger}_{-1}$ = ca. 2 kcal/mol). Assumption of a similar rate for the Ru(III) species **3** yields a bond dissociation energy of 21.7 ± 1.5 kcal/mol for **1**.

Thermochemical data are sparse for organometallic complexes[15] with the exception of the cobalt alkyls which have been of great interest due to metal–carbon bond homolysis in the vitamin B_{12} cofactor.[13,16] It is interesting to note that our value for the BDE in **1** lies within the 18–32 kcal/mol range found by Finke and Halpern for Co–C bond dissociation in cofactor B_{12} and its analogues.[13,14,16] However, the stability of **3** to further Ru–ethyl cleavage under our reaction conditions suggests that the BDE of **1** may be anomalously low, possibly due to the large trans effect of the second alkyl ligand.

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$[4_5]$(1,2,3,4,5)Ferrocenophane: Superferrocenophane

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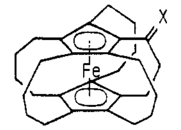
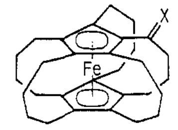
A large number of cage hydrocarbons have been synthesized in the last few decades.[1-5] These compounds do not have an atom or metal ion in the center of the molecule and their inner cavities are vacant. Some attempts have been made to entrap a metal ion or a small neutral molecule into the cavity of such cage hydrocarbons,[6,7] but the desired "core compounds" have not yet been reported.[8,9] Synthesis of intramolecularly pentabridged ferrocene, an analogue of superphane,[3] provides an example of this type of core compound. Much effort to synthesize such compounds[10] has been made by several groups.[11-14] However, compounds having four or five bridges have not been found until we recently synthesized some tetrabridged ferrocenophanes[15] and pentabridged $[4_4][3]$ferrocenophanes (**1**)[16] containing one trimethylene bridge. This paper describes the synthesis and characterization of symmetrical perbridged $[4_5]$ferrocenophane (**2b**),[17] the ultimate target compound.



1



2

a: X=O
b: X=H_2

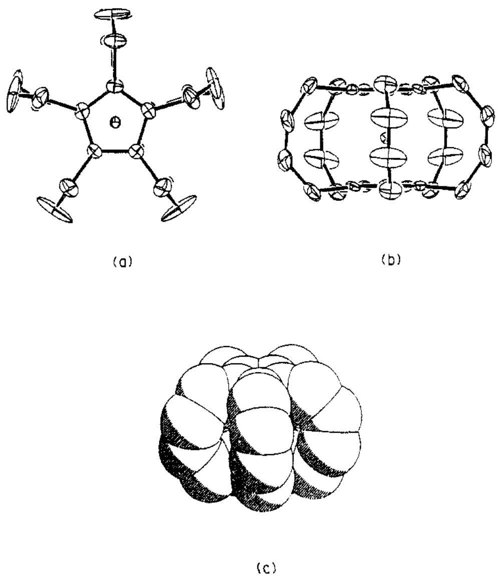


Figure 1. ORTEP drawings of **2b** projected on the Cp ring (a) and on the side of the molecule (b) and space-filling representation (c).

Insertion of a one-carbon unit into the oxotrimethylene bridge of the precursor ferrocenophane **1a**[16] was not successful by application of the reaction conditions which we had developed for the bridge enlargement of multibridged ferrocenophanes.[18] This

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