

Mass spectroscopy studies confirmed the molecular topology of the [2]- and [3]catenanes **13**, **11**, and **12**. For instance, as shown in Figure 3, the spectrum of **12** exhibits peaks at 2178 ($M + 2$), 1610 ($M - 566$, corresponding to the opening and loss of one 30-membered ring), 1088 (metastable ion of **12**; $m/2e$), and 1044 (molecular peak of the 54-membered ring, after loss of the two lateral cycles). No ion can be detected between these peaks, proving that **12** is indeed a [3]catenane.^{8,11}

In conclusion, copper(I)-templated synthesis allows preparation of dimetallic [3]catenanes, whose decomplexation affords the corresponding [3]catenanes.

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Registry No. **1**⁺, 88478-97-1; **2**, 31255-10-4; **3**, 31255-26-2; **4**·2BF₄, 97877-28-6; **5**·2BF₄, 97877-30-0; **6**, 97877-33-3; **7**, 89333-98-2; **8**, 90730-13-0; **9**·BF₄, 97877-32-2; **10**·BF₄, 97907-55-6; 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline, 88498-43-5.

Reactivity of Zero-Valent Metalloporphyrin Dianions toward Organic Electrophiles

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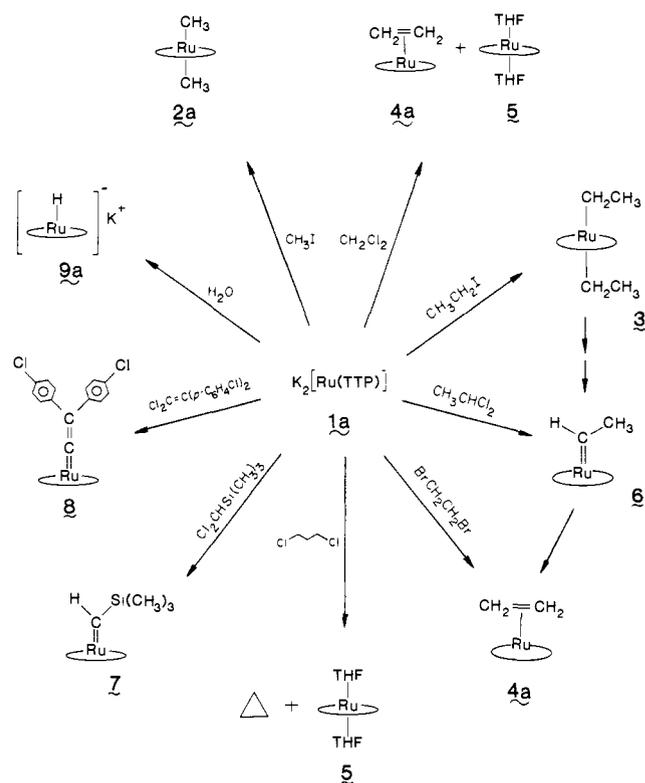
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The interface between metalloporphyrin coordination chemistry and organometallic chemistry has produced some novel species. We recently described the preparation of the ruthenium and osmium porphyrin dianions K₂[Ru(TTP)] (**1a**), K₂[Ru(OEP)] (**1b**) and K₂[Os(TTP)] (**1c**), by potassium metal reduction of the corresponding dimers [M(Por)]₂ in THF.^{1,2} We present here the reactions of these reduced species with electrophiles to produce a number of novel organometallic porphyrin complexes.

When a suspension of the dianion **1a** in THF is treated with an excess of methyl iodide the solid material dissolves instantly to yield an orange-brown solution. Addition of ethanol precipitates the alkyl complex Ru(TTP)(CH₃)₂ (**2a**).³ Trans coordination of the methyl groups is apparent from the ¹H NMR spectrum of **2a**. The related complexes Ru(OEP)(CH₃)₂ (**2b**) and Os(TTP)(CH₃)₂ (**2c**) are prepared in a similar fashion.⁴ The diethyl derivative, Ru(TTP)(CH₂CH₃)₂ (**3**), can be observed spectroscopically (¹H NMR) upon reaction of **1a** with ethyl iodide in THF,⁵ but further reaction ensues (vide infra).

The dianions **1a** and **1c** undergo a rapid reaction with the vicinal dihalide, 1,2-dibromoethane, to yield Ru(TTP)(CH₂=CH₂) (**4a**)¹ and Os(TTP)(CH₂=CH₂) (**4c**),⁶ respectively. We next inves-

Scheme I



igated the interactions of geminal dihalides with **1a** in the hope of preparing carbene complexes by the general reaction shown in eq 1.



However, the reaction of **1a** in THF with the simplest such dihalides, CH₂X₂ (X = Cl, I), is demonstrated by ¹H NMR spectroscopy to yield a mixture of two products, Ru(TTP)(CH₂=CH₂) (**4a**) and Ru(TTP)(THF)₂ (**5**). Upon treatment with CH₂Cl₂ **1b** and **1c** exhibit similar reactivity. The reaction of [Ru(TTP)]₂ with N₂CH₂ gave the same mixture of **4a** and **5**.¹ Although we have no direct evidence for the involvement of "Ru=CH₂" intermediates, the bimolecular coupling of M=CH₂ fragments to form M(CH₂=CH₂) and M(solvento) species is not unprecedented.⁷ In this case the steric bulk of the porphyrin ligand may impose some restraint on the mechanism of the coupling reaction.

Reaction of **1a** with 1,1-dichloroethane in THF leads to a mixture of Ru(TTP)(CHCH₃) (**6**) and the ethylene complex **4a**. The ethylidene complex (**6**) had previously been prepared cleanly by the reaction of [Ru(TTP)]₂ with N₂CHCH₃ in benzene.¹ Our suspicion that there is a pathway which leads from ethyl to ethylidene and finally to ethylene ligands in this system was confirmed by further observation of the ethyl complex **3**. Over the course of weeks in solution, **3** decomposes to a mixture of **6** and **4a** and finally to pure **4a** (Scheme I). Both free ethylene and ethane can be detected by GC during this process.⁸ It is worth noting that rearrangement of alkylidene to alkene ligands⁹ and both radical^{10a} and acid-catalyzed^{10b} processes for the formation

(7) (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811-5819. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577-6578.

(8) GC analyses were performed on a 10 ft × 1/8 in. Porapak Q column. (9) (a) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596-5598. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31-C36. (c) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157-6158. (d) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709-711.

(10) (a) Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435-440. (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958-4972.

of CHR=CH₂ from M(CHRCH₃) are preceded. The increase in coordination number required for a β-elimination step could be accommodated since **3**, **4a**, and **6** are all 16-electron species. Such reactions offer the intriguing possibility that cis coordination sites on one face of the metalloporphyrin may be involved.

(Dichloromethyl)trimethylsilane, Cl₂CHSi(CH₃)₃, proved to be a suitable precursor to a kinetically stable carbene complex since coupling reactions should be hindered by steric bulk. Treatment of **1a** with this reagent yields the (trimethylsilyl)carbene complex Ru(TTP)(CHSi(CH₃)₃) (**7**).¹¹ The reaction of **1a** with Cl₂C=C(*p*-C₆H₄Cl)₂ yields the vinylidene species Ru(TTP)-(C=C(*p*-C₆H₄Cl)₂) (**8**). The TPP congener of this complex had previously been prepared by Balch and co-workers by an alternate route.^{12,13}

A ruthenium porphyrin hydride complex **9a** results when **1a** is treated with excess water or with 2.2 equiv of benzoic acid in THF. ¹H NMR spectroscopy indicates that the two sides of the porphyrin plane are no longer equivalent. A singlet in the ¹H NMR at -57.04 ppm is indicative of a transition-metal hydride shifted to very high field by the porphyrin ring current effect.¹⁴ We formulate **9a** as the ruthenium(II) hydride anion [Ru-(TTP)H]⁻.¹⁵ On addition of further benzoic acid the bis-THF complex **5** is formed, possibly by a second protonation and rapid elimination of dihydrogen (identified by ¹H NMR) to yield the solvato complex. The β-pyrrolic resonance of **9a** is shifted upfield in the ¹H NMR spectrum so that it lies between the two sets of phenyl resonances, in contrast to the neutral Ru(II) species where it is downfield of both. A similar upfield shift of the β-pyrrolic protons occurs in the anionic monoethyl complex [Ru(TTP)-(CH₂CH₃)]⁻ (**10**) which has been observed by ¹H NMR.¹⁶ The analogous osmium hydride K[Os(TTP)H] (**9c**) is produced by the reaction of **1c** with water.¹⁷

Treatment of **1a** with 1,3-dichloropropane in THF leads cleanly to Ru(TTP)(THF)₂ (**5**) (identified by ¹H NMR) and cyclopropane (GC and ¹H NMR).^{8,18} As reductive elimination of cyclopropane from a metallacyclobutane intermediate is a likely mechanism,¹⁹ once again the possible involvement of cis coordination sites on one face of the metalloporphyrin must be considered.

The reactions of K₂[Ru(TTP)] in THF are summarized in Scheme I.

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(11) Ru(TTP)(CHSi(CH₃)₃): NMR (THF-*d*₈, 300 MHz) H_β 8.21 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.91 (m), 7.46 (m); PhCH₃ 2.62 (s); Si(CH₃)₃ -2.05 (s, 9 H); CH 19.44 (s, 1 H) ppm. MS (NDCl) *m/z* [M]⁺ 856; [M - Si(CH₃)₂]⁺, base peak 798; [M - CHSi(CH₃)₃]⁺ 770. UV-vis (THF) λ_{max} (log ε) 408 (5.24), 527 (4.15) nm.

(12) Chan, Y. W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888-1889.

(13) Ru(TTP)(C=C(*p*-C₆H₄Cl)₂) was identified by comparison with literature data for the TPP congener.¹² NMR (THF-*d*₈, 300 MHz) H_β 8.90 (s); H_α, H_γ, H_δ, H_ε, H_ζ 8.14 (d), 7.86 (d), 7.28 (d + d); PhCH₃ 2.38 (s); *p*-C₆H₄Cl 6.42 (d), 3.92 (d) ppm.

(14) (a) K[Ru(TTP)H]: NMR (THF-*d*₈, 300 MHz) H_β 7.60 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.78 (d), 7.74 (d), 7.35 (d + d); PhCH₃ 2.55 (s); RuH -57.04 (s) ppm. (b) Rh(OEP)H constitutes the only other example of a metalloporphyrin hydride complex. NMR (C₆D₆N) RhH -32.99 (d) ppm (*J*_{RhH} = 22.5 Hz). Setsune, J.-I.; Yoshida, Z.-I.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983-987.

(15) Although only 1 equiv of benzoic acid is required by the stoichiometry, neutralization of hydroxides arising from the potassium metal reduction step may account for the extra 1.2 equiv required for the reaction.

(16) K[Ru(TTP)(CH₂CH₃)]: NMR (THF-*d*₈, 300 MHz) H_β 7.50 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.79 (d + d), 7.33 (d); PhCH₃ 2.54 (s); CH₂CH₃ -2.77 (t); CH₃CH₂ -7.22 (q) [*J*(CH₂CH₃) = 7.5 Hz] ppm.

(17) K[Os(TTP)H]: NMR (THF-*d*₈, 300 MHz) H_β 7.28 (s); H_α, H_γ, H_δ, H_ε, H_ζ 7.66 (m), 7.35 (m); PhCH₃ 2.54 (s), OsH -66.06 ppm.

(18) GC analysis indicates traces of propene, comprising less than 2% of the volatile products, are also formed.

(19) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500-6501.

Mechanism of the Azulene to Naphthalene Rearrangement

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According to a recent review,¹ "no single mechanism yet proposed can adequately account" for the rearrangement of azulene (**1**) to naphthalene (**2**) (AN reaction). Here we report a theoretical study which has provided further insight into the solution of this long-standing mechanistic problem.

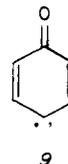
The calculations were carried out using MNDO² for closed-shell species and the spin-unrestricted³ version of MNDO (UMNDO) for biradical or open-shell ones, as implemented in the MOPAC package of computer programs.⁴ All geometries were fully optimized, transition states (TS) located, and stationary points characterized, by procedures included in MOPAC.

The intramolecular mechanisms that have been suggested are outlined in Schemes I⁵ and II.⁶ We first calculated the activation energy (*E*_a) for the mechanism outlined in Scheme II. The UMNDO *E*_a for the homolytic cleavage of **1** to **4** was 75.2 kcal/mol and the UMNDO *E*_a for the hydrogen shift from **4** to **5** was 49.8 kcal/mol. Since MNDO tends to give activation energies for hydrogen migrations that are too positive by about 20 kcal/mol,⁷ the (corrected) *E*_a for **1** to **5** is 104 kcal/mol (see Table I). This *E*_a is much larger than the activation energies we have calculated for other possible mechanisms (see below); hence this mechanism can be eliminated as a major contributor to the AN reaction. The heats of formation calculated for the various stable species and TSs are given in Table I.

In Scheme I, **3** undergoes ring cleavage to a vinylidene (**6**) which then rearranges either to **2** or to 1-phenylbuten-3-yne (**7**). Becker et al.⁵ have shown that independent generation of **6** does indeed lead to **1**, **2**, and **7** and that the pyrolysis of **7** does give **1** and **2**. We were, however, unable to locate a TS corresponding to the direct formation of **6** from **3** and the heat of formation (Δ*H*_f) calculated for **6** is very high. If **6** is an intermediate, it seems clear that it cannot be formed in this way.

Further study of the potential energy surface led to an alternative mechanism; see Scheme III.

The first step is the same as in the mechanism proposed by Becker et al., but the second step involves cleavage of just one bond in **3**, the product being a carbene (**8**) or a biradical (**9**). These are distinct orbital isomers, their wave functions differing in symmetry, because **9**, unlike **8**, contains an unpaired π-electron. This kind of isomerism seems to have been first pointed out by Dewar and Narayanaswami⁸ in the case of an analogous species (**10**) derived from benzene 1,4-diazooxide, the carbene being the more stable form. Here the biradical **9** seems to be the lower in



energy, even allowing for the known tendency of UMNDO to

- (1) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.
- (2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
- (3) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.
- (4) QCPE publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.
- (5) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 5110.
- (6) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875.
- (7) Dewar, M. J. S.; Zobeisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Brown, S. B.; Dewar, M. J. S.; Ford, G. P.; Nelson, D. J.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 7832.
- (8) Dewar, M. J. S.; Narayanaswami, K. *J. Am. Chem. Soc.* **1964**, *86*, 2422.