is planar as expected.[10] The carbenoid hydrogen atom, H(1), resonates at a characteristically low-field position, δ 11.8.[9] This ligand was formed evidently by a 1,1 diactivation of CH bonds in one of the methyl groups of the NMe$_3$ molecule.[11] The hydrogen atoms were transferred to the metal atoms and became the bridging hydride ligands.
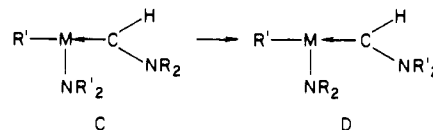
Compound **1** was tested for its ability to promote transalkylation in the archetypical reaction of NEt$_3$ with N-n-Pr$_3$ (eq 1; R = Et, R' = n-Pr). In a typical reaction 1.0 mL of N-n-Pr$_3$, 0.8 mL of NEt$_3$, 1.0 mL of MeOH, and 15.0 mg of **1** were heated to 143 ± 3 °C in a Pyrex-sealed tube for 16 h.[13] During this time the solution remained clear and there was no visible evidence of decomposition or precipitate formation. Upon opening the solution was analyzed by GC–mass spectrometry and was found to contain the four tertiary amines NEt$_3$, NEt$_2$-n-Pr, NEt-n-Pr$_2$, and N-n-Pr$_3$ in the relative amounts 21%, 25%, 26%, and 27%, in addition to the MeOH solvent. The liquid material was removed from the catalyst by vacuum distillation and the residue was separated by TLC on silica plates to yield only four bands. These were identified on the basis of IR and ^{1}H NMR spectroscopies as three alkyl derivatives of **1** plus **1**. In order of elution they were Os$_3$-(CO)$_8$[C(H)NRR'$_2$](μ-H)$_2$(μ_3-S), **2** (R = R' = n-Pr), **3** (R = Et, R' = n-Pr), and **4** (R = R' = Et) in the amounts, **2**, 3.4, **3** 2.8, and, **4**, 4.1 mg.[14] The fourth band was a trace amount (0.8 mg) of **1**.

It is well-known that nucleophiles will attack the electron-deficient carbon atom of coordinated-carbene ligands. In fact, the reaction of primary and secondary amines with heteronuclear carbene complexes has been the most efficient route for the synthesis of amino–carbene complexes.[15] A similar process could provide a rational explanation for the facile transalkylation reaction reported here with tertiary amines. Addition of the tertiary amine NR'$_3$ to the carbenoid carbon could yield a zwitterionic intermediate like A. The lone pair of electrons on the dialkylamino group NR$_2$ could then attack the alkyl group R' causing displacement and formation of the transalkylated intermediate B
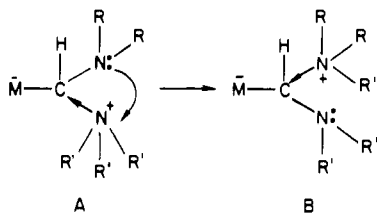
which could then decompose to yield a new carbene ligand and the transalkylated tertiary amine NR$_2$R'.

Alternatively, a metal-assisted cleavage of a carbon–nitrogen bond of the tertiary amine, such as that proposed by Laine,[16] could lead to an amido–alkyl metal intermediate, C. Interchange of the amido and carbene amino groups, D, followed by reductive elimination of the new tertiary amine would complete the transalkylation.

(11) The reaction of Os$_3$(CO)$_{12}$ with NMe$_3$ at 170 °C gives a low yield of the compound Os$_3$(CO)$_{10}$(μ-η^2-HC=NMe)(μ-H) which was apparently formed by a 1,1 diactivation of CH groups on one of the CH$_3$ groups.[12]
(12) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123.
(13) **Caution**: At this temperature the vapor pressures of MeOH and NEt$_3$ are high and the sealed tubes can explode.
(14) As expected the IR spectra of compounds **2–4** are very similar to that of **1**: for **2** ν(CO)(cm^{-1}), 2083.2 (m), 2046.2 (s), 2032.2 (m), 2002.5 (s), 1986.2 (m), 1970.1 (w), 1963.8 (m); for **3**, 2083.5 (m), 2046.4 (s), 2033.2 (m), 2002.7 (s), 1986.3 (m), 1970.9 (w), 1963.8 (m); for **4**, 2083.6 (m), 2046.4 (s), 2033,7 (m), 2002.7 (s), 1986.3 (m), 1971.6 (w), 1963.6 (m). ^{1}H NMR spectra were taken in CDCl$_3$ solvent: for **2** δ 11.15 (s, NCH), 3.50–3.95 (m, CH_2CH$_2$CH$_3$), 1.52–2.00 (m, CH$_2$CH_2CH$_3$), 0.80–1.24 (m, CH$_2$CH$_2$CH_3), –20.32 (s OsH), –21.14 (s, OsH); for **3** 11.24 (s, NCH), 11.14 (s, NCH), 3.42–4.10 (m, CH_2CH$_2$CH$_3$ and CH_2CH$_3$), 0.80–1.87 (m, CH$_2$CH_3 and CH$_2$CH_3), –20.35 (s, OsH), –21.14 (s, OsH); for **4** 11.23 (s, NCH), 4.02 (q, J_{HH} = 7 Hz CH_2CH$_3$, 3.69 (q, J_{HH} = 7Hz CH_2CH$_3$), 1.47 (t, J_{HH} = 7 Hz, CH$_2$CH_3), 1.31 (t, J_{HH} = 7 Hz, CH$_2$CH_3), –20.35 (br, OsH), 21.13 s, OsH).
(15) (a) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578. (b) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1118.
(16) Laine, R. M. *Catal. Rev.—Sci. Eng.* **1983**, *25*, 459.

Synthesis of Dicopper(I) [3]Catenates: Multiring Interlocked Coordinating Systems

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Molecules whose topology does not allow planar representation are fascinating.[1] Among them, [2]catenanes,[2,3] consisting of two interlocked rings, and a Möbius strip[4] have been prepared.

We have recently described a template synthesis of interlocked macrocyclic ligands, the catenands.[5,6] We now report that topologically more complex molecules,[7] specifically as [3]catenanes, can be made by taking advantage of the templating effect of copper(I) in 1,10-phenanthroline-based molecular systems. [3]Catenanes have previously been obtained by Schill et al.,[8] following a multistep directed synthesis. The principle of our strategy is represented in Figure 1.

If the linking fragment used in the cyclization step is too short to allow intramolecular ring formation, dimerization leads to a [3]catenane.

The synthesis actually performed is shown in Figure 2.

The starting complex **1**$^+$ is made according to our previously published procedure,[5] from the corresponding 30-membered ring **8**[9] (see Chart I), the diphenolic derivative of 1,10-phenanthroline[9] and Cu(CH$_3$CN)$_4$$^+$. Reacting **1**$^+$ and **2** or **3** in N,N'-dimethylformamide (DMF) under high-dilution conditions, in the presence of Cs$_2$CO$_3$ (excess), affords poor yields of the dinuclear [3]catenates **4**$^{2+}$ (6%) or **5**$^{2+}$ (2%). In the course of the reaction, relatively large amounts of monocyclic compounds are also formed. For instance, besides **4**$^{2+}$, the 48-membered ring **6** is obtained (11%); **7** and **8** are isolated in the workup of the reaction mixture leading to **5**$^{2+}$. Interestingly, small amounts of the mixed catenates

(1) Walba, D. M. In "Chemical Applications of Topology and Graph Theory"; King, R. B., Ed.; Elsevier: New York, 1983.
(2) Wasserman, E. *J. Am. Chem. Soc.* **1960**, *82*, 4433. Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789.
(3) Schill, G. "Catenanes, Rotaxanes and Knots"; Academic Press: New York, 1971; and references cited.
(4) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 3219.
(5) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983**, *46*, 5095.
(6) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.
(7) The topological complexity of closed curves can be scaled by their *linking number*, as defined by: Bauer, W. R.; Crick, F. H. C.; White, J. H. *Sci. Am.* **1980**, *243* (1), 100. For a [2]- and a [3]catenane, the linking numbers would be 1 and 2, respectively.
(8) Schill, G.; Zürcher, C. *Chem. Ber.* **1977**, *110*, 2046.
(9) Dietrich-Buchecker, C. O., Sauvage, J. P. *Tetrahedron Lett.* **1983**, *46*, 5091.

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Chart I

6

7 n = 1
8 n = 2

9⁺ n = 2
10⁺ n = 3

11 a = CH₂(CH₂ O CH₂)₂ CH₂ , b = CH₂(CH₂OCH₂)₄ CH₂

12 a = CH₂(CH₂OCH₂)₃CH₂ , b = CH₂(CH₂OCH₂)₄CH₂

13 a = CH₂(CH₂ OCH₂)₂CH₂
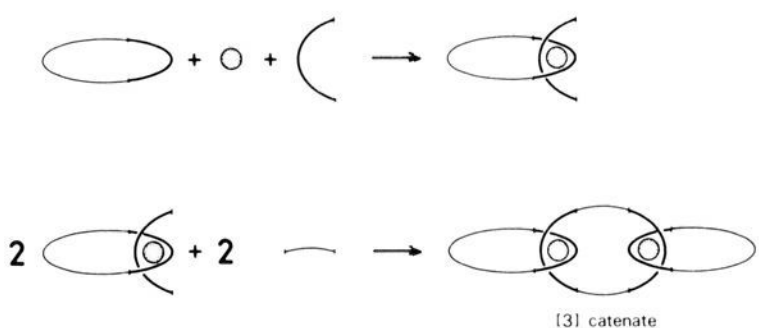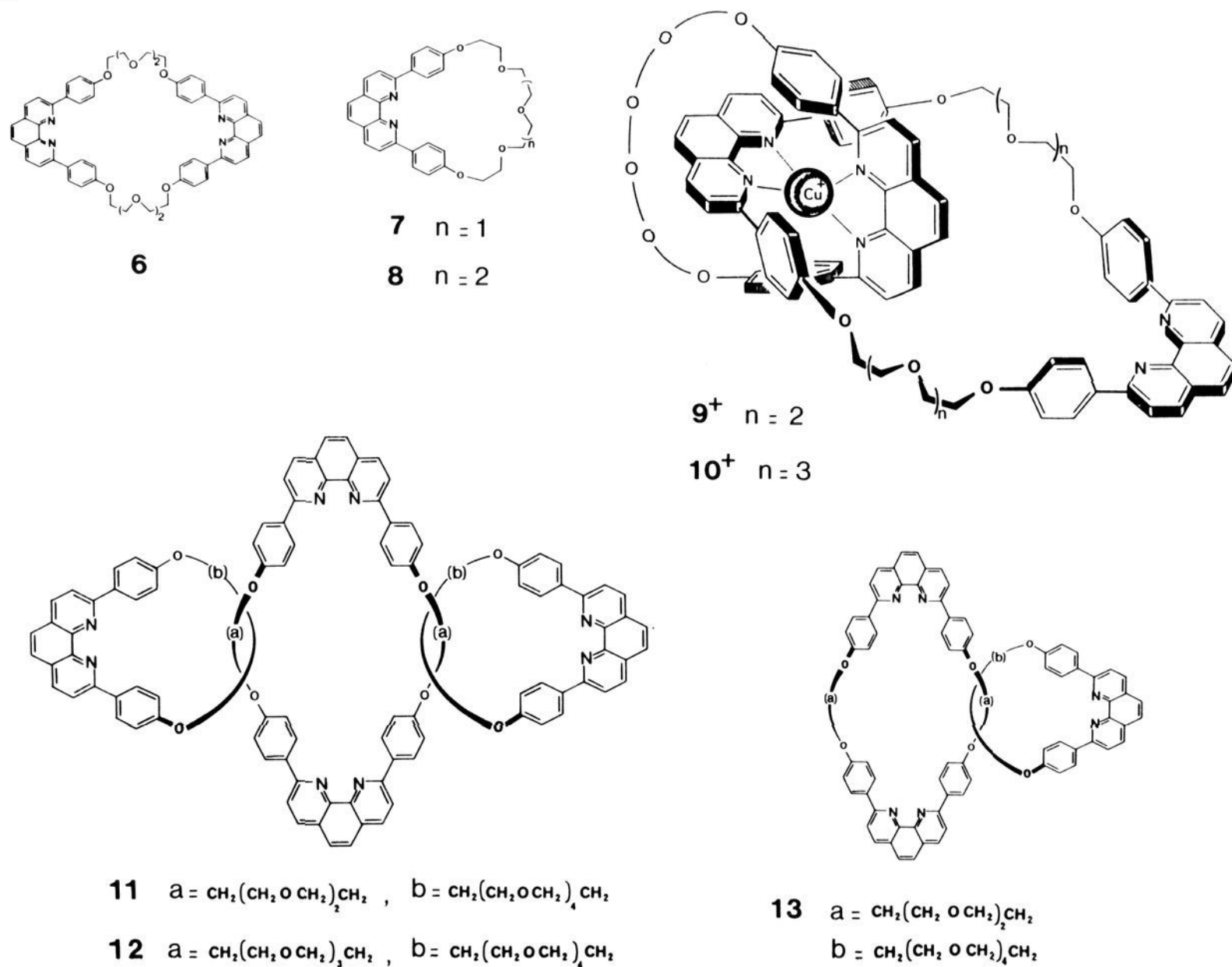   b = CH₂(CH₂ O CH₂)₄CH₂

[3] catenate

Figure 1. Templated synthesis of a [3]catenate. Principle: The transition metal disposes the two coordinating fragments (thick line) perpendicular to one another.
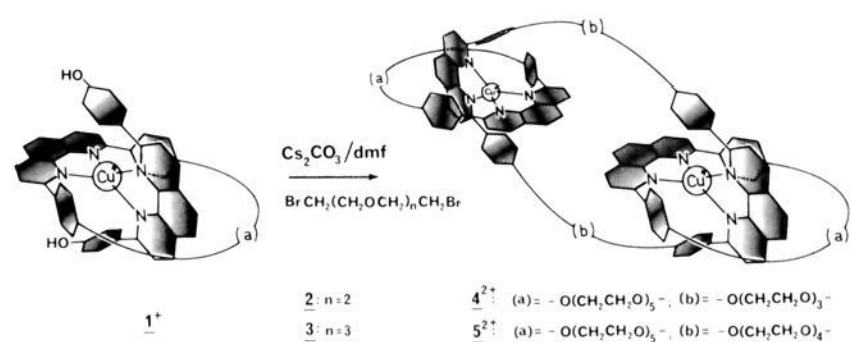

Figure 2.

9⁺ (5%) or **10⁺** (1.2%) were obtained in addition to **4²⁺** or **5²⁺**, respectively. These compounds might allow synthesis and study of heterodimetallic systems by complexation of an appropriate transition metal in the remaining free phenanthroline. Such molecular systems, as well as the presently reported dicopper [3]catenates might be of interest in long-range electron-transfer studies between redox sites located at fixed positions.[10] Deme-
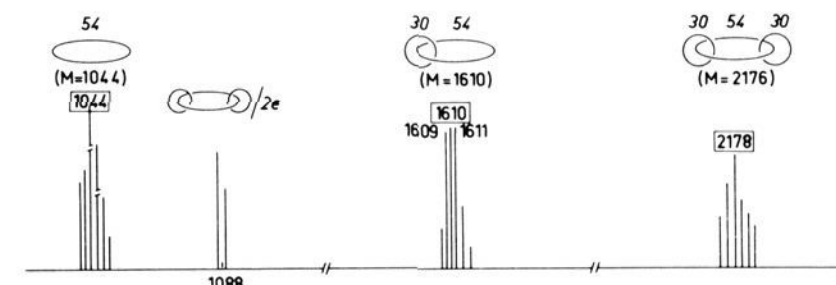

Figure 3. Mass spectrum of the [3]catenand **12**.

talation of **4²⁺** or **5²⁺** by KCN leads respectively to the [3]catenands **11** (15%) or **12** (82%).[11] The size of the central ring is important, both during the cyclization step and for demetalation. **4²⁺** contains a 48-membered central ring which is more easily formed than the 54-membered cycle of **5²⁺**, as reflected by their respective yields of preparation. On the other hand, since the latter [3]catenate is more flexible than **4²⁺**, it is more readily demetalated. The high rigidity of **4²⁺** is due to the relatively small size of the central ring which surrounds two copper atoms and two 1,10-phenanthroline subunits. Such a stretched arrangement prevents the three cycles from sliding freely one into the other, as required during the decomplexation process. Indeed, this reaction involves such strained intermediates that besides the free ligand **11**, large amounts of the fragmentation product **8** are found. Related to the specific properties of catenanes, it is noteworthy that **6** has a much higher melting point (mp 317–319 °C) than the [2]- or [3]catenands in which it constitutes a cyclic subunit: **13** (prepared in 65% yield by demetalation of **9⁺**) mp *139–140 °C* and **11** mp 245–246 °C.

(10) McGourty, J. L.; Blough, N. V.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 4470. Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145 and references cited.

(11) All the new compounds have been characterized by ¹H and ¹³C NMR spectroscopy; they have good elemental analysis (C, H, N). The cationic species **4²⁺**, **5²⁺**, and **9⁺** have been isolated as BF₄⁻ salts.

(12) For mass spectroscopy studies of [2]catenanes, see: Vetter, W.; Schill, G. *Tetrahedron* **1967**, *23*, 3079. Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351.

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]catenates, whose decomplexation affords the corresponding [3]catenands.

Reactivity of Zero-Valent Metalloporphyrin Dianions toward Organic Electrophiles

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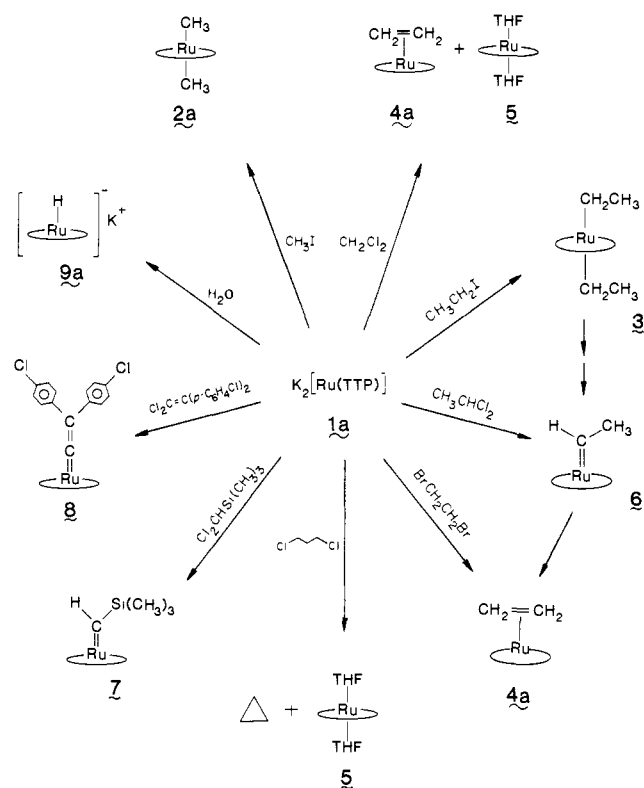*Stanford, California 94305*
Received May 17, 1985

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 K$_2$[Ru(TTP)] (**1a**), K$_2$[Ru(OEP)] (**1b**) and K$_2$[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)(CH$_3$)$_2$ (**2a**).[3] Trans coordination of the methyl groups is apparent from the ^{1}H NMR spectrum of **2a**. The related complexes Ru(OEP)(CH$_3$)$_2$ (**2b**) and Os(TTP)(CH$_3$)$_2$ (**2c**) are prepared in a similar fashion.[4] The diethyl derivative, Ru(TTP)(CH$_2$CH$_3$)$_2$ (**3**), can be observed spectroscopically (^{1}H 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)(CH$_2$=CH$_2$) (**4a**)[1] and Os(TTP)(CH$_2$=CH$_2$) (**4c**),[6] respectively. We next investigated the interactions of geminal dihalides with **1a** in the hope of preparing carbene complexes by the general reaction shown in eq 1.

$$\text{K}_2[\text{Ru(TTP)}] + \text{X}_2\text{CRR}' \rightarrow \text{Ru(TTP)}(=\text{CRR}') + 2\text{KX} \quad (1)$$
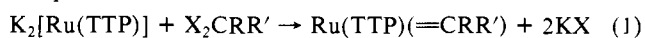
However, the reaction of **1a** in THF with the simplest such dihalides, CH$_2$X$_2$ (X = Cl, I), is demonstrated by ^{1}H NMR spectroscopy to yield a mixture of two products, Ru(TTP)-(CH$_2$=CH$_2$) (**4a**) and Ru(TTP)(THF)$_2$ (**5**). Upon treatment with CH$_2$Cl$_2$ **1b** and **1c** exhibit similar reactivity. The reaction of [Ru(TTP)]$_2$ with N$_2$CH$_2$ gave the same mixture of **4a** and **5**.[1] Although we have no direct evidence for the involvement of "Ru=CH$_2$" intermediates, the bimolecular coupling of M=CH$_2$ fragments to form M(CH$_2$=CH$_2$) and M(solvato) 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)(CHCH$_3$) (**6**) and the ethylene complex **4a**. The ethylidene complex (**6**) had previously been prepared cleanly by the reaction of [Ru(TTP)]$_2$ with N$_2$CHCH$_3$ 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 ligands[9] and both radical[10a] and acid-catalyzed[10b] processes for the formation

Scheme I

(1) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570–4571.

(2) Abbreviations: Por = porphyrinato dianion unspecified; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; TTP = 5,10,15,20-tetra-p-tolylporphyrinato dianion; THF = tetrahydrofuran.

(3) Ru(TTP)(CH$_3$)$_2$: NMR (THF-d_8, 300 MHz) H$_\beta$ 8.28 (s); H$_o$, H$_m$ 7.92 (d), 7.51 (d); PhCH$_3$ 2.63 (s); RuCH$_3$ −2.78 (s) ppm. Anal. Satisfactory C, H, N for C$_{50}$H$_{42}$N$_4$Ru. MS (EI) m/z [M]$^+$ 800, [M − CH$_3$]$^+$ 785, [M − (CH$_3$)$_2$]$^+$, base 770. UV-vis (THF) λ_{max} (log ϵ), 410 (5.10), 521 (3.95), 592 (3.57) nm.

(4) Ru(OEP)(CH$_3$)$_2$: NMR (THF-d_8, 300 MHz) H$_{meso}$ 9.67 (s); CH$_2$ 3.88 (q); CH$_3$ 1.84 (t); RuCH$_3$ −3.51 (s) ppm. Os(TTP)(CH$_3$)$_2$: NMR (THF-d_8, 300 MHz) H$_\beta$ 7.86 (s); H$_o$, H$_m$ 7.85 (d), 7.47 (d); PhCH$_3$ 2.60 (s); OsCH$_3$ −0.50 (s) ppm.

(5) Ru(TTP)(CH$_2$CH$_3$)$_2$: NMR (THF-d_8, 300 MHz) H$_\beta$ 8.25 (s); H$_o$, H$_m$ 7.92 (d), 7.50 (d); PhCH$_3$ 2.63 (s); RuCH_2CH$_3$ −1.97 (q); RuCH$_2$CH_3 −4.08 (t) ppm.

(6) Os(TPP)(CH$_2$=CH$_2$): NMR (THF-d_8, 300 MHz) H$_\beta$ 8.02 (s); H$_o$, H$_{o'}$, H$_m$, H$_{m'}$ 7.84 (d + d), 7.45 (d + d); PhCH$_3$ 2.60 (s); CH$_2$=CH$_2$ −3.40 (s) ppm.

(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.