Figure 3. Proposed mechanism for formation of the dimeric and dihydro species formed in the reaction of bis(η^5-cyclopentadienyl)titanium dicarbonyl with phthalazine.

The ring system C(2)–C(3)–C(4)–C(5)–C(6)–C(7) (shown in Figure 2) is clearly aromatic, with an average carbon–carbon bond length of 1.382 (9) Å. The N(1)–N(2) bond length of 1.338 (6) Å is less than that observed for the uncomplexed ligand.[8] The C(7)–C(8) carbon–carbon bond has a length of 1.525 (7) Å and is evidently a carbon–carbon single bond. Additional evidence that C(8) is sp³ hybridized includes the N(1)–C(8)–C(7) angle of 112.5 (5)° and the C(7)–C(8)–C(8)′ angle of 110.1°. Also, this carbon atom is raised out of the ligand plane by 0.066 Å.[9]

A proposed mechanism for dimerization is given in Figure 3. As in the other heteroaromatic systems we have described,[3,4] an electron is transferred from the electron-rich titanium atom onto the ligand, with the greatest electron density of the unpaired electron at C(8) (I). Fenske–Hall molecular orbital calculations[10] predict a high percent (23%) of carbon p_z character for C(8) in the highest partially occupied molecular orbital. This radical species (I) can subsequently interact with a second monomer to form the dimeric complex (II). Although no direct evidence was found for a bimolecular intermediate in the reaction of Cp₂Ti(CO)₂ and 3,4,7,8-tetramethyl-1,10-phenanthroline, which leads to the carbon–hydrogen bond dissociation, a similar bimolecular species was proposed.[4] Similar bimolecular intermediates are also suggested for the flavin one-electron-transfer process in biological systems.[11]

The radical species (I) can also react with the α-hydrogen atoms of the THF solvent or unreacted ligand to give complex III, which accounts for the mass spectral ion peak at 309 *m/e*. Dissociation of II and subsequent reaction with the solvent or unreacted ligand could also give III. Reaction of a similar type of radical species in deuterated THF showed the solvent to be the primary source of the hydrogen.[4]

EPR spectra of toluene/benzene (4:1) glasses of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium] at liquid-nitrogen temperatures showed a complicated triplet state spectrum. This complex has two titanium(III) ions. Using the relation[12]

$$R = (0.050 g_z^2/D_{dd})^{1/3}$$

where *R* is the titanium–titanium distance and D_{dd} is the dipolar zero-field splitting parameter, one calculates *R* = 6.8 Å. This relation assumes the *z* component of the **g** tensor is colinear with

the Ti–Ti vector, which is unlikely in this case. Nonetheless, the calculated value is close to the observed value of 6.14 Å from the crystal structure. It is also possible that the radical species I, formed upon dissociation of the dimer in the solution, could contribute to the complicated triplet-state spectrum.

The intramolecular electron-transfer-induced chemistry observed in this and earlier systems is important in understanding the mechanisms involved in the reduction of heteronuclear aromatics. This type of reduction is important in the radical chemistry associated with coal liquefaction (donor solvent and others) as well as in the hydrotreating and denitrification of crude oil. It now appears that a similar chemistry exists for related complexes of the later transition elements.[13] Additional studies are being conducted in order to further characterize the systems described here and to examine heterogeneous aromatic reduction by other metals.

Supplementary Material Available: Listings of atomic positional and thermal parameters (Tables II and III, respectively), interatomic bond distances (Table IV), bond angles (Table V), deviation from planarity of rings (Table VI), and observed and calculated structure factors (Table VII) (22 pages). Ordering information is given on any current masthead page.

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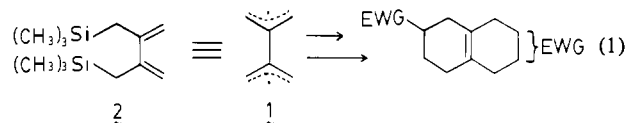
2,3-Bis[(trimethylsilyl)methyl]-1,3-butadiene. A Conjunctive Reagent for Tandem Diels–Alder Reactions

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Awareness of the power of the Diels–Alder reaction in organic synthesis stimulates the search for novel dienes and dienophiles. An intriguing possibility is the accessibility of an equivalent of bi-allyl, **1**[1] which would permit simultaneous formation of two

rings as shown in eq 1. Our interest in generating synthons for reactive intermediates and the limitations posed by the current methods for equivalents of **1**[2,3] induced us to consider the use of 2,3-bis[(trimethylsilyl)methyl]-1,3-butadiene (**2**) as such a synthon.

Diene **2** is available in 70–88% yields from (2-bromoallyl)-trimethylsilane[4–6] (eq 2, TMS = trimethylsilane) by oxidative

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Table I. Diels-Alder Reactions

entry	first dienophile	adduct[a,b]	yield,[c] %	second dienophile	adduct[i]	yield, %
1			63^d–100^e			59^j
2			R = H, 100 R = CH$_3$,^{f} 64			R = CH$_3$ 41^k
3			63^f			45^m
4			82			43
5			R = H,^{g} 53 R = CH$_3$,^{g} 52^h–65^f R = CO$_2$CH$_3$, 85			R = H, 66 R = CO$_2$CH$_3$, 82
6			76			60^l
7			47			

[a] Reactions normally performed in refluxing toluene in the presence of hydroquinone. In some cases, the reaction was performed in methylene chloride or benzene with 0.1–1.0 equiv of AlCl$_3$ at room temperature. [b] All new compounds have been fully characterized by spectral means and have satisfactory elemental composition by either high-resolution mass spectrometry and/or combustion analysis. [c] Isolated yield of pure product; product normally purified by flash chromatography. [d] Yield obtained by using a 1:1 ratio of diene and dienophile. [e] Yield obtained by using a 1.5:1 ratio of diene and dienophile. [f] Reaction performed in the presence of AlCl$_3$; see footnote a. [g] Reaction performed with excess dienophile in the absence of solvent. [h] Yield obtained in the thermal reaction. [i] Performed by adding the second dienophile to the reaction mixture for generation of the dimethylenecycloalkane. [j] A 5:1 stereoisomeric mixture. [k] A 9:1 stereoisomeric mixture. [l] A 2:1 stereoisomeric mixture. [m] Isomer ratio not determined.
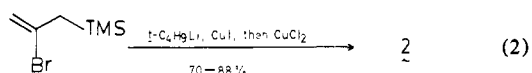
dimerization of its corresponding cuprate.[7] The diene [^{1}H NMR δ 4.92 (s, 2 H), 4.73 (s, 2 H), 1.75 (s, 4 H), 0.0 (s, 9 H)] is a colorless distillable liquid, bp 70–75 °C at 3 mmHg, which has been stored for 2 months in the freezer in the presence of hydroquinone with no detectable decomposition. Table I summarizes the range of dienophiles that has been examined. Thermal reactions were normally performed with 1.0–2.0 equiv of diene in refluxing toluene containing hydroquinone. Aluminum chloride may be used to catalyze these reactions without any apparent problems of desilylation (see entries 2, 3, and 5).

(4) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 0000.
(5) An alternative synthesis which proceeds in 63% overall yield involves the reaction of 2,3-dibromopropene with trichlorosilane [(C$_2$H$_5$)$_3$N, CuCl, ether] followed by methylmagnesium bromide. Coppola, B., unpublished work in these laboratories. Cf.: Nishiyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1981**, *22*, 5289.
(6) A typical preparation of 2 follows. To a solution of 2-bromo-3-(trimethylsilyl)propene (5.79 g, 30 mmol) in 50 mL of ether was added *tert*-butyllithium (2.2 M, 27.3 mL, 60 mmol) at –78 °C. The mixture was stirred at that temperature for 1 h and then at –23 °C for 1 h. Then the yellow mixture was cooled to –78 °C, and to it was added cuprous iodide (6.27 g, 33 mmol). After the solution was stirred at –78 °C for 1 h and at –23 °C for 30 min, cupric chloride (4.44 g, 33 mmol) was added and the mixture was stirred at –23 °C for 1 h and was allowed to stand at room temperature for 15 h. Saturated aqueous sodium carbonate (1 mL) was added, and the mixture was filtered through Celite. Concentration followed by bulb-to-bulb distillation gave the diene in yields ranging from 70% to 88%.

$$\text{(2)}$$

Conversion of the adducts to the dimethylenecyclohexane (eq 3) required oxidative bis-desilylation, a type of transformation

$$\text{(3)}$$
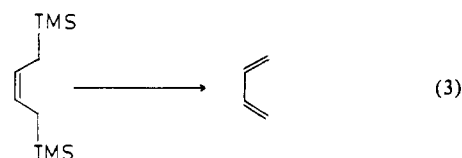
previously stated to fail.[8] In contrast to that report, we find that treatment of these adducts with 1.05 equiv of NBS in THF (0.05–0.1 M) at –100 °C (10 min) to –78 °C (1 h) in the presence of 5 equiv of propylene oxide produced the requisite dienes. The second dienophile is then added directly to this solution at –78 °C and the reaction allowed to warm to room temperature overnight to complete the cycloaddition.[9] Table I summarizes some

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(8) Carter, M. J.; Fleming, I. Percival, A. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2415.
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of the cases that have been examined. Esters, ketones, amides, and silyl ethers remain unaffected by this sequence. Most interesting, the dihydroaromatic adduct **3** (entry 4) participates in this sequence without complication. On the other hand, the oxidative desilylation failed for the naphthoquinone adduct **4** R = H unless aromatization was precluded by substitution such as in **4** R = CH₃ or by carbonyl reduction (vide infra). The stereochemistry of the second Diels–Alder reaction varies according to the size of the substituent from the first dienophiles. Thus, by comparison of entries 1 and 6, initiating the sequence with the bulkier dienophile followed by the less bulky dienophile leads to an advantageous increase in stereoselectivity. High stereoselectivity was observed in the case of **5** (eq 4), which derived from
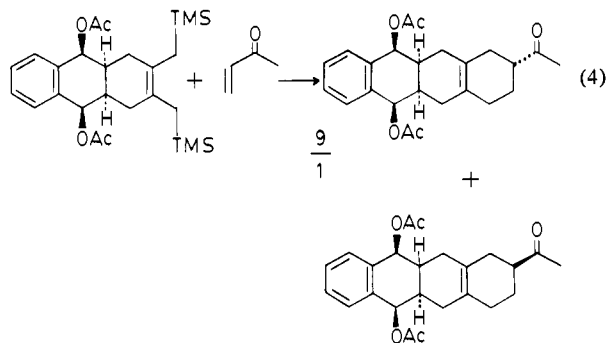
the naphthoquinone adduct **4** (table, entry 2) by reduction with DIBAL-H (PhCH₃, −78 °C) followed by acetylation (AcCl, DMAP, C₅H₅N). The question of remote regiochemical control in the second cycloaddition, at present, limits the type of one of the dienophiles to its being a symmetrically 1,2-disubstituted one. For example, cycloaddition of **6** R = CO₂CH₃ and methyl vinyl ketone (entry 5) produced adducts **7** R = CO₂CH₃ and **8** R = CO₂CH₃ in a 1.2:1 ratio.

Bicycloannulation derived from **2** offers a mild and rapid elaboration of multicyclic systems. For example, the simple availability of tetracene derivatives provides particular interest with respect to tetracycline antibiotics and antitumor agents. The fact that remote stereoselectivity can be excercised in this sequence enhances its utility.

Ruthenium-Containing Dinuclear Complexes of *meso*-Tetrakis(*o*-nicotinamidophenyl)porphyrin

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meso-α,α,α,α-Tetrakis(*o*-nicotinamidophenyl)porphyrin (**1**, nic₄H₂TPP) is a ligand capable of binding two metals in square-planar coordination sites oriented in parallel planes coaxial to one another (Figure 1). Metal complexes of **1** have been the subject of several reports that are of interest because of their potential utility as models for cytochrome *c* oxidase.[1–5]

The coordination chemistry of **1** has proven less straightforward than initially thought. A major problem is the propensity of **1** to form intermolecular coordination oligomers, especially with metals such as iron(II).[6] Additional complications arise because **1** can be thermally converted into the other possible atropisomers (i.e., isomers having the nicotinamide groups distributed on either side of the porphyrin plane).

Despite reports to the contrary[1–4] the insertion of substitution-labile metals such as Fe²⁺, Fe³⁺, and Cu²⁺ into **1** cannot be accomplished cleanly by using the techniques reported. For example, refluxing **1** in DMF or acetic acid (both standard methods[7,8] used to insert metals into **1**)[1–4] causes virtually instantaneous isomerization. The insertion of Cu²⁺ from refluxing DMF/CuCl₂ solution produces at least eight separable products. Subsequent treatment with cold dilute acid followed by base breaks up copper coordination to the pyridine and yields the expected statistical distribution of four isomers (~50% α,α,α,β, 25% α,α,β,β, 12% α,β,α,β, 12% α,α,α,α). These can be isolated, by using proper chromatographic conditions, and unambiguously characterized by comparison to pure atropisomers.

In contrast to substitution-labile metal ions, attempts to insert more substitution-inert metals such as Ni²⁺ do succeed under conditions identical with those used for the attempted Cu²⁺ insertion.[1,2]

Ruthenium, in either the 2+ or 3+ oxidation state, is even more substitution-inert than Ni²⁺. In reaction with **1**, Ru²⁺ is complexed by the pyridyl groups; however, it will not insert into the porphyrin under these conditions. This, therefore, provides a convenient route to the preparation of heterodinuclear species of **1**. Ruthenium is also especially interesting because of its rich redox chemistry. The treatment of **1** with hydrated RuCl₃ in refluxing DMF produces a mixture of products. Chromatography on silica gel with 1:10 acetone/benzene yields pure RuCl₂nic₄H₂TPP **2** (varying from ~5% to 30% depending on solvent purity, reflux time, etc.). Subsequently a second metal can be inserted into **2** to produce heterodinuclear complexes of the type RuCl₂nic₄MTPP (M = divalent or trivalent first-row transiton metals). It is worth noting that forcing conditions (refluxing DMF) can be used to insert the second metal into **2** without isomerization. Once coordinated, Ru(II) appears to lock the nicotinic acid "pickets" into place.

The 250-MHz NMR spectrum of **2** is consistent with the coordinated α,α,α,α-isomer structure. C, H, N, and Cl analyses

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