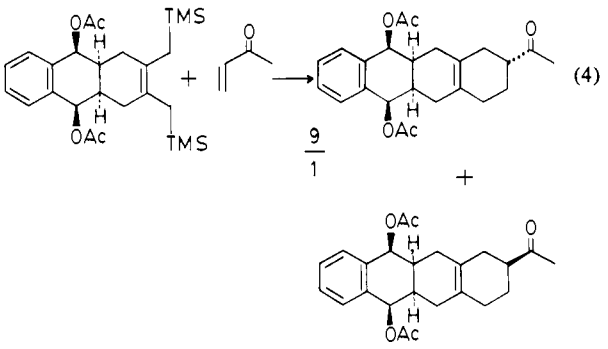
of the cases that have been examined. Esters, ketones, amides, and silyl ethers remain unaffected by this sequence. Most interesting, the dihydroaromatic adduct **3** (entry 4) participates in this sequence without complication. On the other hand, the oxidative desilylation failed for the naphthoquinone adduct **4** R = H unless aromatization was precluded by substitution such as in **4** R = CH_3 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



(4)

the naphthoquinone adduct **4** (table, entry 2) by reduction with DIBAL-H ($PhCH_3$, −78 °C) followed by acetylation (AcCl, DMAP, C_5H_5N). 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 = CO_2CH_3 and methyl vinyl ketone (entry 5) produced adducts **7** R = CO_2CH_3 and **8** R = CO_2CH_3 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.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

Registry No. 2, 82167-48-4; **3**, 82167-49-5; **4** (R = H), 82167-50-8; **4** (R = CH_3), 82167-51-9; **5**, 82167-52-0; **6** (R = H), 82167-53-1; **6** (R = CH_3), 82167-54-2; **6** (R = CO_2CH_3), 82167-55-3; **7** (R = H), 82167-56-4; **7** (R = CO_2CH_3), 82167-57-5; **8** (R = H), 82167-58-6; **8** (R = CO_2CH_3), 82167-59-7; 1-phenyl-1*H*-pyrrole-2,5-dione, 941-69-5; 1,4-naphthalenedione, 130-15-4; 2-methyl-1,4-naphthalenedione, 58-27-5; dimethyl (*Z*)-2-butenedioate, 624-48-6; dimethyl 2-butynedioate, 762-42-5; methyl 2-propenoate, 96-33-3; methyl 2-methyl-2-propenoate, 80-62-6; dimethyl methylenepropanedioate, 3377-21-7; 3-buten-2-one, 78-94-4; 2,5-cyclohexadiene-1,4-dione, 106-51-4; 2-henyl-5,6-di(trimethylsilylmethyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione, 82167-60-0; dimethyl (*cis*)-1,2-di(trimethylsilylmethyl)-4,5-cyclohexadienecarboxylate, 82167-61-1; 4-acetyl-1,2-di(trimethylsilylmethyl)cyclohexene, 82167-62-2; 2,4,6,7-tetra(trimethylsilylmethyl)-1,4,4a,5,8,8a-octahydroanthraquinone, 82167-63-3; 2-phenyl-6-acetyl-3a,4,5,6,7,8,9,9a-octahydro-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione, 82167-64-4; 2-phenyl-5a-methyl-6,12-oxa-3a,4,5,5a,6,11,12,13-decahydro-1*H*-anthra[2,3-*f*]isoindole-1,3(2*H*)dione, 82167-65-5; 2-phenyl-6,7-dicarbomethoxy-3a,4,5,8,9,9a-hexahydro-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione, 82167-66-6; (2α,5a,α,6β,11β,11aα)-2-acetyl-6,11-diacetoxy-1,2,3,4,5a,6,11,11a,12-decahydronaphthacene, 82167-67-7; (2α,5aβ,6α,11α,11aα)-2-acetyl-6,11-diacetoxy-1,2,3,4,5a,6,11,11a,12-decahydronaphthacene, 82167-68-8; (2-bromoallyl)trimethylsilane, 81790-10-5; 2-phenyl-6,7-dicarbomethoxy-3a,4,5,6,7,8,9,9a-octahydro-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione, 82167-69-9.

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

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meso-α,α,α,α-Tetrakis(*o*-nicotinamidophenyl)porphyrin (**1**, nic_4H_2TPP) 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 Fe^{2+}, Fe^{3+}, and Cu^{2+} 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 Cu^{2+} from refluxing DMF/$CuCl_2$ 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 Ni^{2+} do succeed under conditions identical with those used for the attempted Cu^{2+} insertion.[1,2]

Ruthenium, in either the 2+ or 3+ oxidation state, is even more substitution-inert than Ni^{2+}. In reaction with **1**, Ru^{2+} 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 $RuCl_3$ in refluxing DMF produces a mixture of products. Chromatography on silica gel with 1:10 acetone/benzene yields pure $RuCl_2nic_4H_2TPP$ **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 $RuCl_2nic_4MTPP$ (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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Table I

no.	compound	$E_{1/2}$, V vs. SCE[c] Ru(III)/(II)	M(II)/(I)[d]	M(III)/(II)[d]	other	λ, nm[e] (ε × 10⁻³)
1	nic_4H_2TPP				L(0/−1) −0.96, L(+1/0) 1.09 irr	
2	$RuCl_2nic_4H_2TPP$	+0.42			L(0/−1) −0.93	421 (230), 482 s (7), 516 (17), 548 (4.3), 590 (4.8), 646 (1.1)
3	$RuCl_2DENA_4$[a]	+0.46				
4	$RuCl_2nic_4MnClTPP$	+0.52	−1.08	−0.58		371 (23), 389 s (19), 421 s (14), 477 (35), 520 (2.5), 580 (3.2), 613 (2.4)
5	$RuCl_2nic_4FeClTPP$	+0.47	−0.97	−0.16 (irr)		417 (110), 500 (9.5), 574 (5.0), 672 (1.6)
6	$RuCl_2nic_4NiTPP$	+0.43	−1.08			408 (310), 526 (80), 556 s (4.7)
7	$RuCl_2nic_4CuTPP$	+0.47	−1.09			419 (220), 504 s (4.3), 542 (16), 582 s (2)
8	$RuCl_2nic_4ZnTPP$	+0.50	−1.12			426 (260), 511 s (3.8), 551 (21), 588 s (2.1)
9	$RuCl_2nic_4CoTPP$	+0.47	−0.88	+0.90		416 (290), 476 s (9.7), 520 (18), 589 s (2.4)
10	$Ru(ClO_4)_2nic_4CoTPP$	+0.50	−0.90	+0.79		
11	$Ru(ClO_4)_2nic_4CoTPP$ + excess TBA^+Cl^-	+0.46	−0.90	+0.46		
12	$RuCl_2nic_4CoTPP$ + excess 1-MeImz[b]	+0.45	−0.95	+0.29		

[a] DENA = *N,N*-diethylnicotinamide. [b] 1-MeImz = 1-methylimidazole. [c] Electrochemical measurements were all made in DMF with $TBA^+PF_6^-$ (0.10 M) supporting electrolyte on Pt. [d] The oxidation state designation of the porphyrin-bound metal is intended only as a formalism and does not necessarily imply any other significance. [e] Spectra were measured in CH_2Cl_2.

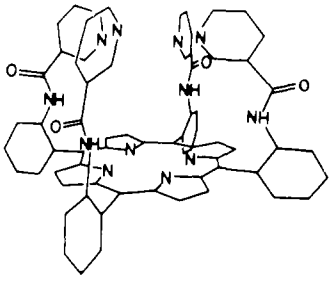

Figure 1. *meso*-α,α,α,α-Tetrakis(*o*-nicotinamidophenyl)porphyrin. Multiple bonds have been omitted for clarity.

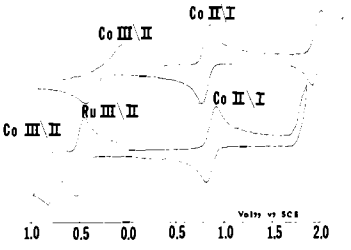

Figure 2. Top, cyclic voltammogram of CoTPP on platinum in DMF, 0.1 M $TBA^+PF_6^-$; bottom, $RuCl_2nic_4CoTPP$, same conditions.

performed on the cobalt derivative are each within 0.3% of calculated values.[9]

Table I contains spectral data for the series Mn^{3+} through Zn^{2+}. Comparison of these data with literature data for tetraphenylporphyrin (TPP) complexes[10,11] indicates that no major spectral differences exist. Relative to MTPP random red or blue shifts (≤10 nm) are observed for corresponding peaks. Some differences in relative ε values occur, but absolute ε values agree in each case to within a factor of 3 with the corresponding MTPP. The spectral comparisons between monomeric MTPP and the corresponding dinuclear compounds suggest nothing to indicate any significant metal–metal interaction.

In an effort to generate vacant coordination sites on the ruthenium, the cobalt complex of **2** was treated with $AgClO_4$ in benzene (>60 °C for 12 h). Both chlorides were quantitatively removed (2 equiv of AgCl produced). Conductivity measurements (DMF) on this cobalt complex, compound **2**, and $Ru(ClO_4)_2nic_4H_2TPP$ indicate that all three compounds are nonelectrolytes,[12] suggesting that the perchlorate ions are coordinated. Ru(III)/Ru(II) redox potentials for both forms of the cobalt complex differ by only 40 mV (enteries 9 and 10), which also suggest that the ClO_4^-'s are coordinated and not simply tightly ion paired.

Cyclic voltammetry (CV) data are also presented in Table I. For every complex there is a one-electron oxidation occurring between +0.52 and +0.42 V assigned to the Ru(III)/(II) couple (by virtue of analogy to the porphyrin free model (entry 3)[13] and its relative constancy within the series). Comparison of entries 4–8 with literature values for analogous TPP complexes[14,15] reveals that respective redox couples occur within a few hundred millivolts of each other. These results support the conclusion drawn from spectral data that the proximity (~5 Å) of two metal centers does not, in and of itself, constitute a major electronic perturbation on either metal center.

The redox chemistry of the cobalt complex (entry 9), however, is different from the other members of the series. Figure 2 compares the CV of CoTPP with that of $RuCl_2nic_4CoTPP$. Both the Co(II)/(I) and ring reduction potentials coincide fairly well. Also, the Ru(III)/(II) couple appears at the same potential as in the other compounds. The Co(III)/(II) couple, however, is ~600 mV more positive in the dinuclear complex than in CoTPP, and it is considerably more reversible (ΔE_p = 90 mV compared to ~400 mV for CoTPP).

The ability of the cobalt to bind ligands is also affected. The addition of large excesses (×100) of TBA^+Cl^- to DMF solutions of CoTPP causes virtually no change in the voltammogram. In contrast, the serial addition of only 1 equivalent of Cl^- to solutions of either $RuCl_2$- or $Ru(ClO_4)_2nic_4CoTPP$ causes the stepwise disappearance of the peak at +0.90 V and a simultaneous appearance of a peak at +0.46 V on the top of the Ru(III)/(II) couple (cf. Table I, entries 9 and 11). Differences are also observed with the addition of nitrogenous bases. The addition of 1 equiv of 1-methylimidazole to CoTPP in DMF causes the disappearance

(9) Anal. Calcd for $C_{68}H_{44}N_{12}O_4Cl_2CoRu$: C, 61.68; H, 3.33; N, 12.70; Cl, 5.36. Found: C, 61.61; H, 3.42; N, 12.42; Cl, 5.48.

(10) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315 (1951).

(11) L. Edwards, D. H. Dolphin, M. Gouterman, and A. D. Adler, *J. Mol. Spectrosc.*, **38**, 16 (1971).

(12) The conductivities of these solutions were the same as for the neat solvent (<4 × 10^{-6} mho) and less than 0.1 that of cobalticinium$^+PF_6^-$ at equivalent concentration (~8 × 10^{-5} M).

(13) This compound is presumably trans by analogy to the tetrakis-pyridine complex.

(14) D. G. Davis, in "The Porphyrins", D. H. Dolphin, Ed., Academic Press, New York, 1978, pp 127 ff.

(15) J. H. Fuhrhop, in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, pp 593 ff.

of the Co(III)/(II) reduction at +0.27 V and the simultaneous appearance of a new couple at +0.01 V. The addition of the same relative amount of 1-methylimidazole to $RuCl_2nic_4CoTPP$ causes the peak at +0.90 V to disappear and a new peak at +0.29 V to appear (i.e., a ~600-mV change compared to a ~300-mV change for CoTPP).

The addition of moderate excesses (×5) of either Cl^- or 1-methylimidazole to DMF solutions of $RuCl_2nic_4CoTPP$ produces no detectable changes in the visible spectra. This result indicates that there is no significant binding of either ligand in the Co^{2+} oxidation state. By assumption of a one-to-one stoichiometry, the binding constants for the Co^{3+} species calculated from potential shifts are $K_f = 2.8 \times 10^7$ for Cl^- and $K_f = 2.2 \times 10^{10}$ for 1-methylimidazole.

Given the spectral similarities between CoTPP and $RuCl_2nic_4CoTPP$ and the similarity of the Ru(II)/(III) potential to those of the other species in Table I, it is unlikely that the unusual coordination chemistry of the Co^{3+} species can be reasonably attributed to an electronic metal–metal interaction. We feel that the binding difference between the two cobalt complexes are instead primarily steric in nature. The Co in $RuCl_2nic_4CoTPP$ is confronted with a fixed "ligand", i.e., the $RuCl_2$ moiety, which sterically prevents other ligands from binding to one side of the porphyrin and enforces an otherwise unencountered (for CoTPP) "trans effect". Again, a large electronic interaction would be expected to effect the potential of the Ru(II)/(III) couple, which is not observed.

While no effects as large as those evident for the cobalt complex have been observed for other species in Table I, small differences in reduction potentials (relative to MTPP) are evident for Mn^{3+} and Fe^{3+}. Further study is underway to determine the extent of this phenomenon with respect to other complexes of **1**.

Acknowledgment. We thank the U.S. Department of Energy (DE-AC02-80ER10589) for support of the electrochemical and spectral studies and the National Institutes of Health (GM 26958 and 30306) for support of the coordination studies with substitution labile metal ions.

Registry No. 1, 68000-73-7; **2**, 82248-51-9; **3**, 82265-56-3; **4**, 82248-52-0; **5**, 82265-57-4; **6**, 82281-48-9; **7**, 82265-58-5; **8**, 82265-59-6; **9**, 82265-60-9; **10**, 82265-61-0.

Direct Chiral Synthesis of Boronic Acids and Esters of High Optical Purity via Asymmetric Hydroboration Displacement

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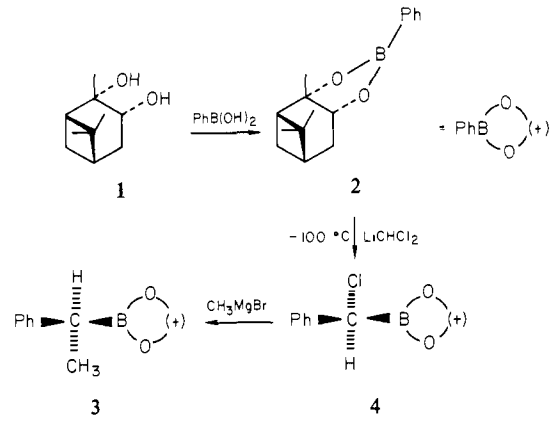
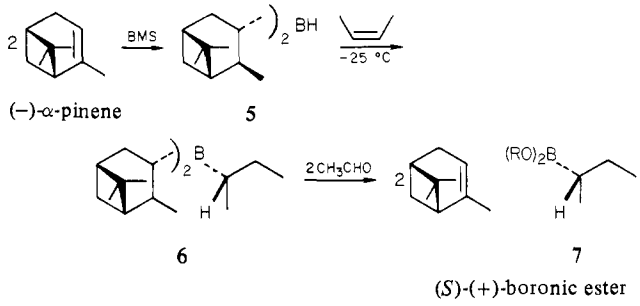
Chiral hydroboration of appropriate alkenes by diisopinocampheylborane (Ipc_2BH)[2] or isopinocampheylborane ($IpcBH_2$)[3] produces intermediates that readily eliminate α-pinene on treatment with acetaldehyde. This procedure makes readily available optically active boronic acids and esters of high optical purities.

Recently Matteson and Ray reported[4] an elegant directed chiral synthesis of boronic acids and esters based on (+)- and (−)-pinanediol. In a typical procedure they converted (+)-pinanediol (**1**) (Scheme I) to the phenylboronate (**2**). Treatment with (dichloromethyl)lithium at −100 °C, followed by methylmagnesium bromide at 20 °C gave (*S*)-1-phenylethaneboronate (**4**) of high optical purity, as estimated by oxidation to (*S*)-1-phenylethanol and its acetate (93.7% ee).

Scheme I



Scheme II



(*S*)-(+)-boronic ester

Alkylboronic esters, containing only one alkyl group attached to boron, are esthetically appealing intermediates for carbon–carbon bond-forming reactions.[5] These reactions are especially promising for chiral synthesis proceeding through boron intermediates. Accordingly, we undertook to see whether hydroboration might provide an alternative convenient route to these derivatives.

Both (+)- and (−)-diisopinocampheylborane (**5**) (Scheme II) with optical purities approaching 100% are now readily synthesized from commercially available α-pinene of lower optical purities (92–95% ee).[2b,c,6c] Hydroboration of *cis*-2-butene with Ipc_2BH gives organoborane **6** containing the chiral 2-butyl group with >98% ee.[2b,c]

Treatment of organoborane **6** with acetaldehyde[6] (25 °C) liberated α-pinene quantitatively and provided optically active diethyl 2-butylboronate (**7**, R = Et). This intermediate is readily separated from α-pinene by extraction with aqueous sodium hydroxide and converted by reesterification to (*S*)-(+)-dimethyl 2-butylboronate (**7**, R = Me, 71%): bp 38 °C (30 mmHg); $[\alpha]^{23}_D$ +9.1° (*c* 11.7, THF). Oxidation of the boronate with alkaline hydrogen peroxide gave (*S*)-(+)-2-butanol, $[\alpha]^{23}_D$ +13.1° (neat), suggesting an ee of ≥97%[7] for **7**.

Isopinocampheylborane (**8**) (Scheme III) of high optical purity is now also readily available from commercially available (92–95%

(1) Postdoctoral research associates on Grant 2R01 GM 10937-19 from the National Institutes of Health.

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(3) (a) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 5514. (b) Mandal, A. K.; Jadhav, P. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3543. (c) Brown, H. C.; Jadhav, P. K. *Ibid.* **1981**, *46*, 5047. (d) Brown, H. C.; Jadhav, P. K.; Mandal, A. K., submitted for publication.

(4) Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590.

(5) (a) Matteson, D. S.; Majumdar, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) Brown, H. C.; Imai, T., to be submitted for publication.

(6) Benzaldehyde has been used previously for such displacements. (a) Mikhailov, B. M.; Bubnov, Yu, N.; Kiselev, V. G. *J. Gen. Chem. USSR* **1966**, *36*, 65. (b) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1978**, *156*, 203. (c) Brown, H. C.; Jadhav, P. K.; Desai, M. C. submitted for publication. However, acetaldehyde is more reactive. Its greater volatility also offers advantages.

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