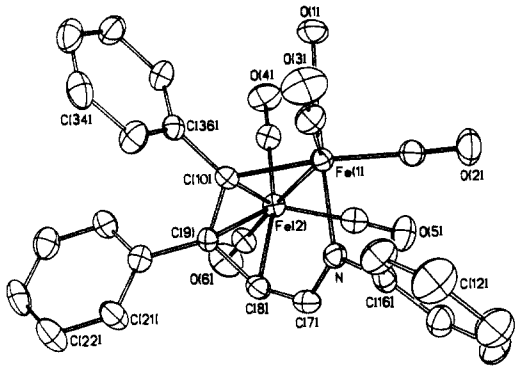
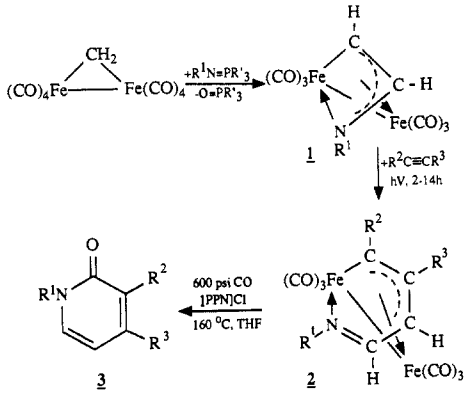


Figure 1. Molecular structure and labeling scheme for **2e** (40% thermal ellipsoids). Fe(1)-Fe(2), 2.632 (1) Å; Fe(1)-N, 2.028 (5) Å; Fe(1)-C(10), 2.028 (5) Å; Fe(2)-C(8), 2.102 (5) Å; Fe(2)-C(9), 2.085 (5) Å; Fe(2)-C(10), 2.111 (5) Å; N-C(7), 1.283 (7) Å; C(7)-C(8), 1.451 (8) Å; C(8)-C(9), 1.455 (8) Å; C(9)-C(10), 1.404 (7) Å.

Scheme I



Fe-carbon bond of **1** to give only the isomer with the substituted carbon adjacent to the iron center. For example, the ferrapyridine complex formed from reaction of **1** (R^1 = Ph) with PhC≡CH shows three ^{1}H NMR resonances for the ring hydrogens at δ 8.26 (d, J = 5.5 Hz), 5.6 (d, J = 6.1 Hz), and 3.34 (dd), with the coupling pattern implying adjacent hydrogen atoms.

As illustrated in Scheme I, free 2-pyridinones are readily released from the ferrapyridine complexes by heating THF solutions under 600 psi of CO in the presence of 1 equiv of [PPN]Cl or by refluxing acetonitrile solutions in air overnight. The 2-pyridinones **3a-g** shown in Table I were isolated in moderate to high yield by silica gel chromatography and were spectroscopically characterized.[8] Due to the regiospecificity of the alkyne insertion step, monosubstituted alkynes gave 2-pyridinones substituted only in the 3-position. As illustrated by the entries for **3h** and **3i** in Table I, the NBu^t pyridinones can be converted in high yield into NH pyridinones by refluxing in neat CF_3CO_2H followed by aqueous K_2CO_3 workup. The NH pyridinones constitute an important class of biologically active molecules, with **3i** being a patented antiinflammatory agent.[2d] Furthermore, NH pyridinones give potentially wide substituent variability at the nitrogen atom by employing known methods for alkyl, acyl, and aryl substitution at this position.[1b,2b,c] The use of HC≡CSiMe$_3$ to prepare **3g** is significant since the SiMe$_3$ functionality allows for further manipulation at the 3-position by known organic methods.[9]

(7) **2e**: $P2_1/n$, a = 10.797 (3) Å, b = 19.580 (4) Å, c = 12.454 (2) Å, β = 103.61 (2)°, V = 2559.1 (10) Å^3, Z = 4, R_F = 4.78%, R_{wF} = 4.80% for 1915 reflections ($F_o \geq 5\sigma(F_o)$).

(8) **3a**: Anal. C, H. MS (EI): m/z for M$^+$ 227.1310 (calcd), 227.1309 (found). ^{1}H NMR ($CDCl_3$): δ 7.39, 7.36 (m, 5 H, Ph), 7.33 (dd, 1 H, ^3J = 7.0 Hz, ^4J = 2.1 Hz, C*H*), 7.26 (dd, 1 H, ^3J = 6.7 Hz, ^4J = 1.9 Hz, C*H*), 6.18 (dd, 1 H, ^3J = 7.0, 6.7 Hz, C*H*), 1.38 (s, 9 H, Bu^t). IR (CH_2Cl_2): ν_{CO} = 1653 cm^{-1}.

(9) (a) Fleming, I. In *Comprehensive Organic Chemistry The Synthesis and Reactions of Organic Compounds*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 4, Part 13, p 539. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

Table I

compd	R^1	R^2	R^3	yield,[a] %	yield,[b] %
3a	Ph	Bu^t	H	87	57
3b	Bu^t	Bu^t	H	86	66
3c	Bu^t	Ph	H	79	57
3d	Bu^t	Ph	D	79	57
3e	Ph	Ph	Ph	34	16
3f	Bu^t	Et	Et	76	61
3g	Bu^t	SiMe$_3$	H	79	73
3h[c]	H	Bu^t	H	81	62
3i[c]	H	Ph	H	68	54

[a] Isolated yields based on conversion from **2**. [b] Isolated yields based on conversion from $Fe_2(\mu\text{-}CH_2)(CO)_8$. [c] **3h** and **3i** were synthesized by using the same methodology to produce **3b** and **3c** followed by a 48-h reflux in neat CF_3CO_2H.

The reactions of Scheme I offer a convenient synthesis of substituted 2-pyridinones from alkynes, phosphinimines, and the readily available $Fe_2(\mu\text{-}CH_2)(CO)_8$.[10] The method appears to have considerable substituent variability at the 1- and 3-positions, and the yields of the sequential reactions are high. If desired, the entire reaction can be conducted without isolation of any of the intermediates, giving the overall yields from $Fe_2(\mu\text{-}CH_2)(CO)_8$ shown in Table I. Finally, the starting complex $Fe_2(\mu\text{-}CH_2)(CO)_8$ and the intermediate metallacycles are not particularly air sensitive, and the reactions can be readily conducted under tank N_2. Its present limitation is that only mono-, di-, and trisubstituted pyridinones can be formed as the substituents in the 5- and 6-positions are restricted to hydrogen atoms.[4]

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work and the National Science Foundation for contributing funds toward purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters for **2e**, analytical data for **2a-c,e,f**, and spectroscopic data for **2a-f** and **3a-i** (4 pages). Ordering information is given on any current masthead page.

(10) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

Synthetic and Structural Studies of Sapphyrin, a 22-π-Electron Pentapyrrolic "Expanded Porphyrin"

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Sapphyrin, **1**, first discovered serendipitously by Woodward,[1] is one of the more intriguing products to emerge from initial studies directed toward the synthesis of vitamin B_{12}.[1-3] It is a 22-π-electron pentapyrrolic macrocycle that forms a dark blue solid (hence the name sapphyrin) which exhibits an intense Soret-like band at ca. 450 nm ($CHCl_3$) along with weaker Q-type transitions

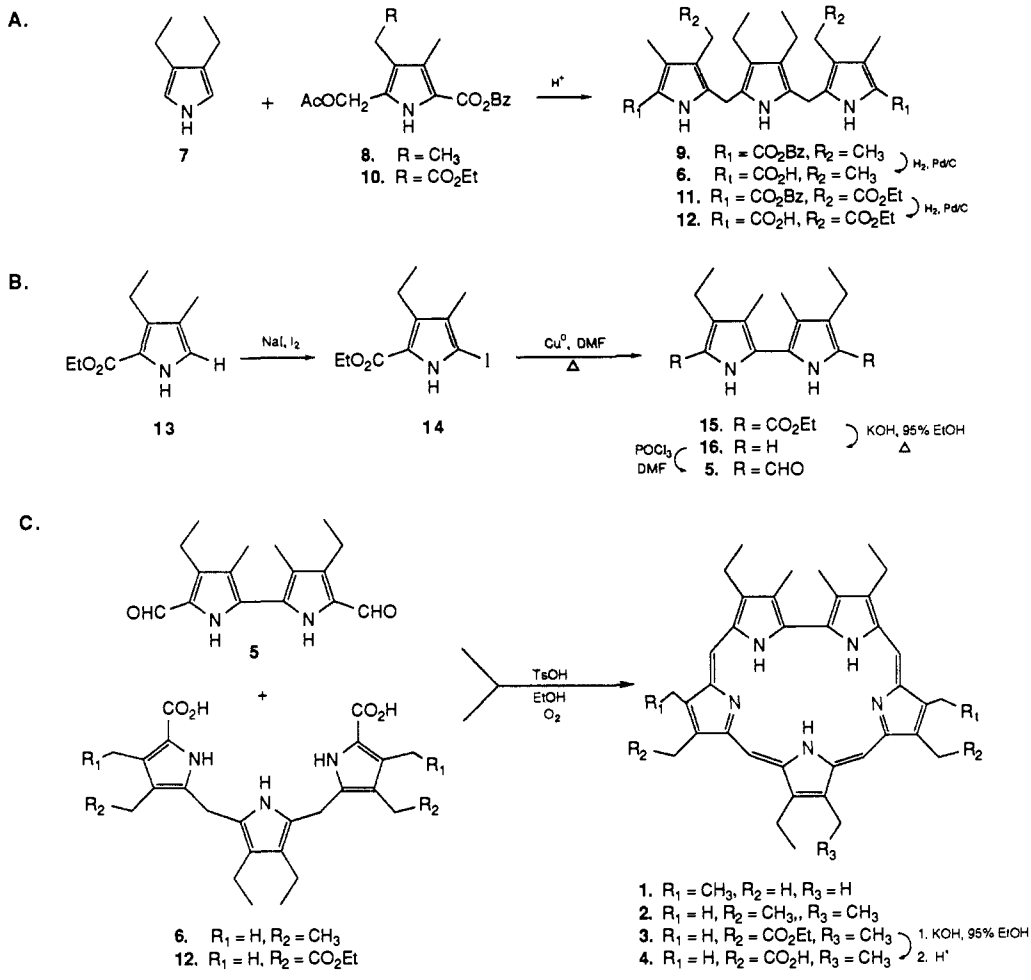
(1) (a) First reported by R. B. Woodward at the Aromaticity Conference, Sheffield, U.K., 1966 (see ref 1b). (b) Bauer, V. J.; Clive, D. R.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429-6436. To date only tetracoordinated metal complexes have been prepared from these potentially pentadentate ligand systems.

(2) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2111-2116.

(3) Grigg, R. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York; 1978, Vol. II, pp 327-391.

0002-7863/90/1512-2810$02.50/0

Scheme I



in the 620–690-nm region. These optical properties along with the presence of a large central cavity, which could possibly serve for metal binding, suggest that sapphyrin and its derivatives might find use in a variety of emerging biomedical applications, notably photodynamic therapy (PDT)[4] where long wavelength (≥680 nm) absorptions are desired,[5] and magnetic resonance imaging enhancement (MRI) where chelation of highly paramagnetic metal cations such as gadolinium(III) would be particularly worthwhile.[6] However, in spite of being known for over 20 years, almost no work has been devoted to the systematic study of this intriguing "expanded porphyrin",[3] in part, perhaps, because of the tedious nature of the syntheses involved. Quite recently, we found that sapphyrin acts as an efficient sensitizer for the in vitro photoeradication of both herpes simplex virus (HSV-1)[7] and cell-free human immunodeficiency virus (HIV-1)[8] and wish to report here an improved synthesis of C_2 symmetric sapphyrins, namely **2** and **4**, as well as the first crystallographic characterization of a sapphyrin.

The original sapphyrin syntheses[1b,2] involved MacDonald-type [3 + 2] condensations between a functionalized bipyrrole, analogous to **5**, and a dicarboxyl-substituted tripyrrane, similar to **6**, as shown in part C of Scheme I. Unfortunately, the syntheses of these precursors were long and tedious. Recently, however, we have developed a simple, three-step, high-yield synthesis of the dicarboxyl-substituted tripyrrane (**6**),[9] which involves as its key transformation the near-quantitative condensation between 3,4-diethylpyrrole (**7**)[10] and benzyl 5-(acetoxymethyl)-4-ethyl-3-methylpyrrole-2-carboxylate (**8**) (Scheme I, part A).[11] Therefore, for an improved synthesis of C_2 symmetric sapphyrins, an improved synthesis of the diformyl-substituted bipyrrole component is necessary. Originally, the requisite diformyl bipyrrole was prepared from the direct Ullman coupling of a 5-iodopyrrole-2-carboxylate and subsequent functionalization in analogy to part B of Scheme I.[1b,2] However, the difficulty inherent in synthesizing the starting iodo pyrroles led to the use of a less direct but overall higher yielding sequence involving Ullman coupling of a protected preformylated pyrrole.[1b] Recently, however, we have found that the Barton–Zard pyrrole synthesis[12] provides a facile means of preparing the α-free pyrrole **13** in >100 g lots.[13]

(4) For overviews of PDT, see: (a) Gomer, C. J. *Photochem. Photobiol.* **1987**, *46*, 561–562 (special issue on this topic). (b) Dahlman, A.; Wile, A. G.; Burns, R. G.; Mason, G. R.; Johnson, F. M.; Berns, M. W. *Cancer Res.* **1983**, *43*, 430–434. (c) Dougherty, T. J. In *Methods in Porphyrin Photosensitization*; Kessel, D., Ed.; Plenum Press: New York, 1985; pp 313–328. (d) Dougherty, T. J. *Photochem. Photobiol.* **1987**, *45*, 879–889. (e) Gomer, C. J. *Semin. Hematol.* **1989**, *26*, 27–34.

(5) For a specific discussion of the desirability of obtaining long-wavelength photosensitizers, see: Kreimer-Birnbaum, M. *Seminars in Hematology* **1989**, *26*, 157–173.

(6) For an introductory discussion of MRI contrast agents, see: Tweedle, M. F.; Brittain, H. G.; Eckelman, W. C.; et al. In *Magnetic Resonance Imaging*, 2nd ed.; Partain, C. L., et al.; Eds.; W. B. Saunders: Philadelphia; 1988, Vol. I, pp 793–809. For a comprehensive review of paramagnetic MRI contrast agents, see: Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901–927.

(7) Judy, M. L.; Matthews, J. L.; Newman, J. T.; Skiles, H.; Boriack, R.; Cyr, M.; Maiya, B. G.; Sessler, J. L. Submitted to *Photochem. Photobiol.*

(8) Sessler, J. L.; Cyr, M.; Maiya, B. G.; Judy, M. L.; Newman, J. T.; Skiles, H.; Boriack, R.; Matthews, J. L.; Chanh, T. C. *Proc. SPIE Int. Opt. Eng.* In press.

(9) (a) Sessler, J. L.; Murai, T.; Lynch, V.; Cyr, M. *J. Am. Chem. Soc.* **1988**, *110*, 5586–5588. (b) Sessler, J. L.; Murai, T.; Lynch, V. *Inorg. Chem.* **1989**, *28*, 1333–1341. (c) Sessler, J. L.; Murai, T.; Hemmi, G. *Inorg. Chem.* **1989**, *28*, 3390–3393.

(10) Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* In press.

(11) Sessler, J. L.; Lynch, V.; Johnson, M. R. *J. Org. Chem.* **1987**, *52*, 4394–4397.

(12) Barton, D. H. R.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1098–1100.

(13) Sessler, J. L.; Johnson, M. R.; Creager, S.; Fettinger, J.; Ibers, J. A. To be submitted to *J. Am. Chem. Soc.*

Given this advance, the original Woodward–Johnson bipyrrole synthesis is finally synthetically viable. Iodination of pyrrole **13** (to give **14**) followed by Ullman coupling in the presence of copper–bronze affords the bipyrrole **15** in roughly 50% overall yield. After saponification and decarboxylation (to give **16**), standard Vilsmeier formylation affords the key bipyrrolic intermediate **5** in 82% yield (based on **15**). Subsequent [3 + 2] condensation[1b,2] between **5** and **6** gives the decaalkyl sapphyrin **2** in 45% yield after chromatographic purification. When this same condensation is carried out with tripyrrane **12**, sapphyrin **3**, which may be saponified to produce the dicarboxyl-substituted sapphyrin **4**, is obtained in roughly 40% overall yield based on **5**.

The decaalkyl sapphyrin **2** produced by the present synthetic approach is analogous to the systems produced earlier[1,2] but differs in the arrangement of the alkyl substituents about the macrocyclic periphery. Nonetheless, it remains a 22-π-electron pentapyrrolic system and shows typical spectroscopic and reactivity features expected of a decaalkyl sapphyrin. For instance, the most stable form of this material is the diprotonated dicationic form, which as its dihydrochloride salt ($[\mathbf{2}\cdot(2H^+)]Cl_2$) in dilute $CHCl_3$ solution exhibits an intense Soret-like band at 456 nm ($\log \epsilon = 5.71$) and two weaker Q-type bands at 624 (4.07) and 676 (4.15) nm.[14] The ^{1}H NMR spectrum of this dicationic material displays well-resolved meso-like peaks at 11.66 and 11.70 ppm and internal pyrrole NH signals at −4.31, −4.64, and −4.97 ppm in a 2:1:2 ratio and is typical of a sapphyrin. Interestingly, however, we find that both the neutral and dicationic (diprotonated) forms exist as monomers at low concentration in nonpolar media, such as chloroform, but undergo extensive dimerization at higher concentrations or in solvents of higher polarity, such as MeOH or CH_3CN.[7,14]

X-ray quality single crystals of the diprotonated form of **2** were obtained by treating the free-base form in dichloromethane with aqueous HCl (to make the dihydrochloride salt), adding $AgPF_6$, and crystallizing by vapor diffusion with diethyl ether under nonanhydrous conditions. The material so obtained was assumed to be the bis-hexafluorophosphate salt of $\mathbf{2}\cdot(2H^+)$ and to be comparable to the dihydrochloride salt discussed above. However, the visible spectrum in chloroform showed features, including a blue-shifted Soret band, that were more characteristic of the dihydrochloride salt in methanol,[14] and the ^{1}H NMR spectrum revealed pyrrolic NH signals at −7.35 and −6.20 ppm in a 4:1 ratio that were shifted to considerably higher field than those observed for $[\mathbf{2}\cdot(2H^+)]Cl_2$. In addition, the X-ray structure determination[15] revealed only one PF_6 anion per sapphyrin cation. This cation displayed a central core in which there is a hydrogen atom attached to each of the five nitrogen atoms and a central peak (X) of electron density about that of a nitrogen atom. Since the five N–H···X bonds are nearly linear and about 2.7 Å in length, it is clear from simple stereochemical considerations[16] that X can correspond only to N, O, or F. The species X must be uninegative, and hence OH^- and F^- are possible. But the chemical sequence employed (involving an acidic wash) does not provide any obvious source of OH^-, and hence F^- is more likely.[17] Although not a proof, the structural data refine better with X as F rather than O. The resultant structure (Figure 1) shows N···F distances ranging from 2.697 (3) to 2.788 (3) Å, N–H distances ranging from 0.83 (3) to 0.92 (4) Å, and N–H···F angles ranging from 167 (2) to 177 (3)°. The five N atoms and the central F atom are essentially planar (average deviation, 0.03 Å), and no H atom deviates by more than 0.14 Å from this plane. Thus, from the X-ray results and the chemistry involved[17] the determined structure is best formulated as the mixed hexafluorophosphate fluoride salt of **2**, $[\mathbf{2}\cdot(2H^+)\cdot F^-][PF_6]$. Consistent with this interpretation is the observation of signals in the ^{19}F NMR spectrum ascribable to both PF_6^- (at $\delta = -73.9$) and F^- (at $\delta = -153.7$ and −153.8, in a ca. 1:4 ratio), and the finding that the dihydrofluoride salt of **2** ($[\mathbf{2}\cdot(2H^+)\cdot F^-]F$) (prepared independently) gives rise to essentially identical ^{1}H NMR, laser desorption MS, and optical spectra as did the crystallographically characterized material and shows bound fluoride anion signals at −153.4 and −153.5 ppm in the ^{19}F NMR spectrum.[18]

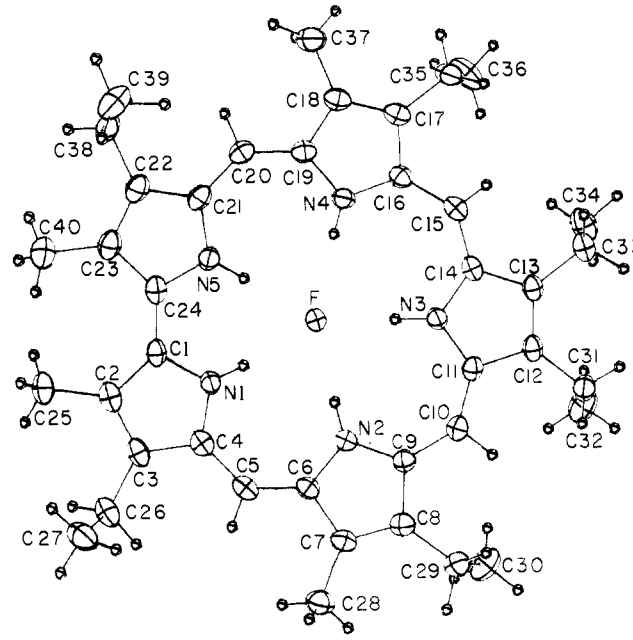


Figure 1. Molecular structure of the $[\mathbf{2}\cdot(2H^+)\cdot F^-]^+$ cation showing the atom-labeling scheme. Non-hydrogen atoms are drawn with 50% ellipsoids; H atoms are drawn artificially small. Details of the core geometry are in the text.

The binding of a species such as F^- centrally within the core of the 18-π-electron porphyrin system is not possible as the trans nitrogen distances (at about 4 Å[18]) are too short. The present 22-π-electron sapphyrin system has a core size of roughly 5.5 Å diameter and is nicely suited to the binding of a central moiety about the size of the F^- ion with appropriate strong hydrogen-bonding interactions. As such, the fully protonated sapphyrin **2** stands as a new example of a rapidly increasing class of anion receptors.[19,20] Preliminary experiments (in mixed CD_2Cl_2/

(14) Maiya, B. G.; Harriman, A.; Cyr, M.; Sessler, J. L. *J. Phys. Chem.* In press.

(15) $[\mathbf{2}\cdot(2H^+)\cdot F^-][PF_6]$; $C_{40}H_{51}F_7N_5P$; $C_{2h}^5 - P2_1/c$; $Z = 4$ in a cell of dimensions $a = 9.148$ (1) Å, $b = 26.880$ (2) Å, $c = 15.229$ (1) Å, $\beta = 92.87$ (1)° at 160 K. Data collection with filtered Cu Kα radiation on a CAD4 diffractometer to 75° in θ; 7867 unique observations, 5122 with $F^2 > 3\sigma(F^2)$. Final model involved anisotropic refinement of all non-hydrogen atoms and isotropic refinement of hydrogen atoms, 682 variables. $R(F^2) = 0.093$; $R(F)$ for $F^2 > 3\sigma(F^2) = 0.065$. The PF_6 group may be disordered as thermal parameters on the F atoms of that group are very high for a low-temperature data set.

(16) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968.

(17) According to the supplier (Alfa Products), the starting $AgPF_6$ contains up to 1/2% AgF as an impurity. Under the metathesis conditions (involving an excess of $AgPF_6$), this impurity could have served as the source of the observed, bound fluoride anion. Alternatively, it is possible that the $AgPF_6$ underwent hydrolysis (to give HF, AgOH, H_3PO_4, etc.) during the course of crystallization.

(18) C.f. Supplementary Material.

(19) Scheidt, W. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York; 1978; Vol. III, pp 463–511.

(20) For overviews of anion binding receptors, see: (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligands*; Cambridge University Press: Cambridge, 1989; Chapter 5. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112. (c) Potvin, P. G.; Lehn, J.-M. In *Synthesis of Macrocycles* (*Progress in Macrocyclic Chemistry, Vol. 3*); Izatt, R. M., Christensen, J. J., Eds., Wiley: New York, 1987; pp 167–239. (d) Vögtle, F.; Sieger, H.; Müller, W. M. *Top. Current Chem.* **1981**, *98*, 107–161. (e) Kimura, E. *Top. Current Chem.* **1981**, *128*, 113–141. (f) Schmidtchen, F. P. *Top. Current Chem.* **1986**, *132*, 101–133. (g) Schulthess, P.; Ammann, D.; Simon, W.; Caderas, C.; Stepānek, R.; Kräutler, B. *Helv. Chim. Acta* **1984**, *67*, 1026–1032. For examples of specific fluoride anion complexing agents, see: (h) Graf, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 6403–6405. (i) Suet, E.; Handel, H. *Tetrahedron Lett.* **1984**, *25*, 645–648. (j) Dietrich, B.; Guilhem, J.; Lehn, J.-M.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91–104. (k) Newcomb, M.; Blanda, M. T. *Tetrahedron Lett.* **1988**, *29*, 4261–4264. (l) Dietrich, B.; Lehn, J.-M.; Guilhem, J.; Pascard, C. *Tetrahedron Lett.* **1989**, *30*, 4125–4128.

CD_3OD) indicate that the bound fluoride anion is labile on the ^{19}F NMR time scale, undergoing rapid exchange with free fluoride anion in solution. Currently, we are studying this exchange process and exploring the extent to which the protonated sapphyrins may serve as binding agents for other small anions and neutral molecules.

Acknowledgment. This work was supported by Grant No. 1581 from the Texas Advanced Research Program to J.L.S. and by NIH Grant HL 13157 to J.A.I. J.L.S. also thanks the NSF for a Presidential Young Investigator Award (1986), the Alfred P. Sloan Foundation for a Research Fellowship (1989-1991), and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1988-1992). J.L.S. and M.J.C. are grateful to Prof. David Dolphin for making available unpublished details of his sapphyrin-directed synthetic studies, to Prof. David Laude for laser desorption mass spectrometric analyses of compounds [**2**·$(2H^+)$·F^-][PF_6] and [**2**·$(2H^+)$·F^-]F, and to Kaori Furuta for synthetic assistance.

Supplementary Material Available: Preparative details and characterization data for compounds **2**, **3**, **4**, **5**, **10**, **11**, **12**, **14**, **15**, and **16** and a table of positional parameters for [**2**·$(2H^+)$·F^-][PF_6] (9 pages). Ordering information is given on any current masthead page.

Novel Dependency of Stereochemistry upon Metal, Ligand, and Solvent in Oxidative Addition of Allylic Chloride to Pd(0) and Pt(0) Complexes

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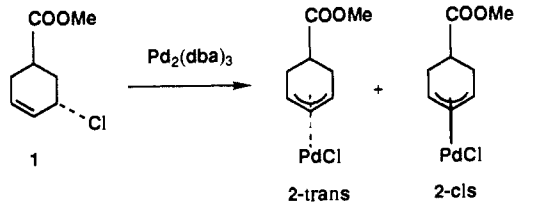
The reaction of allylic electrophiles with electron-rich metal complexes forming allylmetal intermediates is one of the most crucial steps in various metal-catalyzed organic transformations.[1] The stereochemistry of this reaction with regard to the relative disposition of the metal and the leaving groups is predominantly anti.[1a,2] The syn stereochemistry is limited to very few cases,[3,4] of which direct isolation of allylmetals has been achieved in only one example (a Mo complex and allylic acetate).[4] We describe here novel variation of the stereochemistry, ranging from almost pure anti to almost pure syn, in the synthesis of allylmetals from reactions of allylic chlorides with Pd(0) and Pt(0) nucleophiles depending on the nature of metal, ligands, and solvents. We also report a catalytic C-C coupling exhibiting a hitherto unknown stereochemical outcome based on the newly found syn stereochemistry of the stoichiometric process.

Table I. Reaction of **1** with $Pd_2(dba)_3$[a]

run	solvent	isomer ratio: **2**-trans/**2**-cis
1	benzene	100/0
2	dichloromethane	94/6
3	THF	95/5
4	acetone	75/25
5	DMF	29/71
6	acetonitrile	5/95
7	DMSO	3/97

[a] Reaction was run at room temperature for 5-10 h. Yields were almost quantitative in each case. Isomer ratio was determined by ^1H NMR.

Reactions of allylic chloride **1**[2b] with $Pd_2(dba)_3$[5] (dba = dibenzylideneacetone) at room temperature for several hours afforded good yields of a mixture of η^3-allyl complexes,[6] **2**-trans and **2**-cis, with the isomer ratio depending on the solvent used (eq 1 and Table I). In none of these reactions was trans to cis isomerization of **1** observed, nor did the interconversion between **2**-trans and **2**-cis occur under the reaction conditions. The structure of **2** could be assigned by converting these into **3** and **4**, of which both trans and cis configurations have been established before,[2b,e] via attack of phenyl anion[7a] (retention)[8] and dimethyl malonate anion[7b] (inversion).[8] Of particular interest is the almost exclusive formation of **2**-trans in the reaction carried out in benzene, CH_2Cl_2, and THF. To the best of our knowledge, this is the first example of the syn oxidative addition of allylic halides with metallic nucleophiles. Although the cis isomer of **1** did not react with $Pd_2(dba)_3$ under similar conditions so cleanly as to allow stereochemical examination, the results of catalytic reactions described later suggest that this isomer also undergoes dominant, albeit not exclusive, syn addition with Pd(0) olefin complexes in benzene. Contrary to these results, the anti addition dominated in acetonitrile and DMSO (Table I). It may well be that these solvents play a role in preventing Pd-Cl bond formation inherent in the syn addition[9] through coordination to Pd, and/or stabilizing the transition state of the anti addition in which charge separation would take place to a much greater extent than in the syn addition.



The anti addition dominated in the reaction of Pd(0) nucleophiles coordinated with much stronger donors. Thus, the anti

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(6) Satisfactory analytical results were obtained. **2**-trans: ^1H NMR ($CDCl_3$) δ 1.74 (ddd, J = 3.6, 7.5, 17.0 Hz, 2 H), 2.22 (ddd, J = 3.0, 6.4, 17.0, Hz, 2 H), 3.41 (tt, J = 6.4, 7.5 Hz, 1 H), 3.66 (s, 3 H), 5.08 (ddd, J = 3.0, 3.6, 6.5 Hz, 2 H), 5.49 (t, J = 6.5 Hz, 1 H). **2**-cis: ^1H NMR ($CDCl_3$) δ 2.00-2.06 (m, 3 H), 2.26 (br m, 2 H), 3.67 (s, 3 H), 5.21 (t, J = 6.3 Hz, 2 H), 5.55 (t, J = 6.3 Hz, 1 H).

(7) (a) One equivalent of $NaBPh_4$ and 4 equiv of maleic anhydride in CH_2Cl_2 at room temperature for 24 h (yield 95%, stereospecificity almost 100%). (b) Addition of 2 equiv of PPh_3 in CH_2Cl_2 at 0 °C, followed by 1.5 equiv of $NaCH(COOMe)_2$ in THF for 2 h (yield and specificity almost 100%).

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