Table I. Calculated and Observed Isotopic Frequencies (cm^{-1}) for the Strongest E Band

	$^{11}B^{12}C_2H_2$	$^{10}B^{12}C_2H_2$	$^{11}B^{12}C^{13}CH_2$	$^{11}B^{13}C_2H_2$	$^{10}B^{13}CH_2$	$^{11}B^{12}C_2D_2$	$^{10}B^{12}C_2D_2$
$\nu(B-C_2)_{obsd}$	1170.6	1197.4	1161.9	1147.3	1172.0	1169.4	1196.0
$\nu(B-C_2)_{calcd}$	1214.9	1242.8	1206.3	1190.8	1216.4	1211.0	1239.2
ν(scaled 0.964)	1171.2	1198.1	1162.8	1147.9	1172.6	1167.4	1194.6
Δ(obsd–scaled)	–0.6	–0.7	–0.9	–0.6	–0.6	2.0	1.4

Table II. Calculated (MPZ/DZP) Infrared Intensities (km/mol) and Frequencies (cm^{-1}) for $^{11}B^{12}C_2H_2$ (C_{2v} Symmetry)

symmetry	b_1	a_1	b_2	a_2	b_2	a_1	a_1	b_2	a_1
intensity	50	16	31	0	3	65	2	2	0.3
frequency	733.6	910.6	925.9	1010.0	1200.9	1214.9	1506.1	3289.4	3313.0

program.[16] The optimized structures for BC_2H_2, HBC_2, HBC_2H_2, and cyclopropene are given in Figure 2. Calculated vibrational frequencies and intensities are given in Table II for the 11-12-12-1-1 BC_2H_2 isotope. The strong calculated 1214.9-cm^{-1} band dominates the spectrum. Table I also lists the calculated harmonic isotopic fundamentals; multiplying by the average scale factor 0.964 gives calculated bands in agreement within a 1.0-cm^{-1} average for seven isotopic E band frequencies. (The fit for the five hydrogen isotopes with similar anharmonicities is ±0.3 cm^{-1}.) This excellent agreement between calculated and observed isotopic frequencies confirms the identification of BC_2H_2. The out-of-plane deformation calculated at 733.6 cm^{-1} is probably masked by the very strong C_2H_2 band at 720–750 cm^{-1}. Large basis set coupled cluster calculations[17] predict BC_2H_2 to be 74 kcal/mol more stable than B + C_2H_2.

On the other hand, the F bands are assigned to the cyclic HBC_2 species; the different 28.7-cm^{-1} boron-10, 16.5-cm^{-1} carbon-13, and 47.0-cm^{-1} deuterium isotopic shifts are matched (±1.7 cm^{-1}) by quantum chemical calculations for HBC_2.[17] Calculations for the similar borirene molecule HBC_2H_2 reveal still different isotopic shifts for the strong B–C_2 fundamental calculated at 1215.8 cm^{-1}:26.3-cm^{-1} boron-10, 22.3-cm^{-1} carbon-13, and 50.2-cm^{-1} deuterium shifts. Clearly, each molecule has a unique arrangement of atoms and unique normal vibrational modes, which can be characterized by *isotopic substitution at all atomic positions*. The important conclusion reached from this study is that agreement between scaled calculated and observed isotopic frequencies for *one vibrational fundamental with substitution at all atomic positions* constitutes a *fingerprint match* for identification of the molecule, which is demonstrated here for BC_2H_2.

It is clearly seen that the C=C bonds in BC_2H_2 and HBC_2H_2 are longer than in C_3H_4 (Figure 2). Likewise the B–C bonds are shorter than typical single bonds [1.558 Å in $B(C_2H_3)_3$].[13] Similar evidence has been offered to support delocalization of the two π electrons over the three-membered ring and aromatic character for the BC_2 ring in trimesitylborirene.[12] Furthermore, the BC_2 rings in BC_2H_2 and HBC_2H_2 are seen to be virtually identical. Thus, the σ radical site in BC_2H_2 has no effect on the delocalized π bonding in the BC_2 ring.

The photolysis of BC_2H_2 in the near ultraviolet range indicates a strong absorption band in this region, in agreement with trimesitylborirene.[13] The photolysis behavior also provides evidence for delocalized bonding as acetylene and ethylene absorb at shorter wavelengths.

The appearance of BC_2H_2 on diffusion and reaction of B atoms at 18 K in solid argon follows similar behavior for BO_2.[1] These exothermic reactions proceed without activation energy. The BC_2H_2 radical is the simplest borirene species yet observed and characterized. Further studies are in progress in this laboratory to prepare substituted borirene radicals.

Acknowledgment. The experimental work was supported by NSF Grant CHE 91-22556 and the theoretical work by the San Diego Supercomputer Center. J.M.L.M. is a Senior Research Assistant of the National Fund for Scientific Research Belgium (NFWO/FNRS) and acknowledges Fulbright/Hays and NATO travel grants.

(15) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92, Revision A*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(17) Andrews, L.; Hassanzadeh, P.; Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1993**, to be published.

Cyclopropanation Catalyzed by Osmium Porphyrin Complexes

Daniel A. Smith, David N. Reynolds,[1a] and L. Keith Woo*[,1b]

Ames Laboratory and the Department of Chemistry Iowa State University, Ames, Iowa 50011

Received November 19, 1992

Cyclopropanation of alkenes can be accomplished catalytically[2] or stoichiometrically.[3] Catalytic systems typically use a diazo reagent as the carbene source and a metal-containing mediator which forms a postulated metal carbene intermediate. Transfer of the carbene fragment from the metal to an alkene produces the cyclopropane product. Despite the wide variety of catalytic cyclopropanation systems, the putative carbene complex has never been isolated or observed in a catalytic system. This is somewhat surprising since the second category of cyclopropanation reactions involves the stoichiometric reaction of isolated carbene complexes with an alkene to form a cyclopropane. None of the isolated carbene complexes show catalytic cyclopropanation activity. Several years ago Callot demonstrated that rhodium porphyrins catalytically cyclopropanated a variety of alkenes in the presence of ethyl diazoacetate.[4] Kodadek and co-workers have expanded this work and have attempted to prepare synthetically useful enantioselective catalysts for the formation of cyclopropanes.[5] Their approach has been to use rhodium complexes with optically active porphyrins to induce chirality into the product. A similar approach was used for a variety of non-porphyrin copper catalysts.[6] Kodadek has shown that the carbon-bound diazonium complex $[(TTP)RhC(H)(CO_2Et)(N_2)]^+$ is an intermediate in the catalytic cyclopropanation of styrene with ethyl diazoacetate.[7,8] In addition,

(1) (a) Ames Laboratory summer student from Lawrence University, Appleton, WI. (b) 1990–1995 Presidential Young Investigator.

(2) (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (b) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348.

(3) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(4) (a) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 311. (b) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365.

(5) (a) O'Malley, S.; Kodadek, T. *Organometallics* **1992**, *11*, 2299. (b) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645. (c) Maxwell, J.; Kodadek, T. *Organometallics* **1991**, *10*, 4.

(6) (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. (b) Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430. (c) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553.

(7) Abbreviations: TTP = meso-tetra-*p*-tolylporphyrinato, Py = pyridine.

0002-7863/93/1515-2511$04.00/0

Table I. Catalytic Cyclopropanation Using Osmium Porphyrins

catalyst	substrate A	diazoreagent B	ratio [A]/[B]	olefin[a] yield	olefin[a] (z/e)	cyclopropane yield	cyclopropane a/s
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	2	11(2)	*b*	54(1)	9.0(1)
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	1	12(1)	*b*	65(3)	9.5(2)
(TTP)Os(CO)(py)	styrene	N_2CHCO_2Et	0.55	26(1)	*b*	44(1)	9.0(3)
$[Os(TTP)]_2$	styrene	N_2CHCO_2Et	1	trace	*b*	79(2)	10.2(1)
(TTP)Os=$CHCO_2Et$	styrene	N_2CHCO_2Et	1	trace	*b*	63(2)	8.9(6)
(TTP)Os(CO)(py)	PhCCH	N_2CHCO_2Et	0.5	41(1)	*b*	11(1)[c]	*d*
$[Os(TTP)]_2$	PhCCH	N_2CHCO_2Et	0.5	20(1)	*b*	46(2)[c,e]	*d*
(TTP)Os(CO)(py)	1-decene	N_2CHCO_2Et	1	31(1)	*b*	32(1)	4.3(1)
(TTP)Os(CO)(py)	α-CH_3 styrene	N_2CHCO_2Et	1	29(1)	*b*	39(1)	2.8(1)
(TTP)Os(CO)(py)	(*E*)-β-CH_3 styrene	N_2CHCO_2Et	1	43(2)	23	13(2)	*f*
(TTP)Os=$CHCO_2Et$	styrene	none				73(5)	11.5(4)

[a] Diethyl maleate/diethyl fumarate products. [b] (*Z*)-isomer is the only one detected. [c] Bicyclobutanes are the only cyclopropane products detected. No cyclopropene has been observed. [d] Only one isomer observed. [e] Ten-hour addition. [f] Ethyl-*trans*-2-phenyl-*cis*-3-methylcyclopropane-(*r*)-carboxylic acid ester was the only isomer.

kinetic studies suggest that the formation of a rhodium carbene complex is at least partially rate limiting.[8] However, this carbene complex has not been isolated or directly observed. We report herein the use of osmium porphyrins as stereoselective cyclopropanation catalysts using ethyl diazoacetate with a variety of alkenes. In addition, our studies show that an isolable carbene complex ((TTP)Os=$CHCO_2Et$) is capable of catalytically and stoichiometrically cyclopropanating styrene.

Slow addition of a toluene solution of ethyl diazoacetate (0.10 mL, 950 μmol) over 2 h to a vigourously stirred solution of $[(TTP)Os]_2$ (3.0 mg, 1.7 μmol) and styrene (0.11 mL, 960 μmol) at 22 °C results in the formation of ethyl-2-phenyl-1-cyclopropanecarboxylic acid ester (**1**) in 79(2)% yield as determined by GC. The anti/syn (a/s) isomer ratio is 10.2:1 (see Table I). Under similar conditions, the carbene complex (TTP)Os=$CHCO_2Et$ (**2**) catalytically cyclopropanates styrene and ethyl diazoacetate to produce cyclopropane **1** in 63(2)% yield with an a/s isomer ratio of 8.9(6). The oxygen- and water-stable complex (TTP)Os(CO)(Py) (**3**) also serves as a catalyst precursor. When a toluene solution of ethyl diazoacetate (0.10 mL, 950 μmol) was added to a vigorously stirred solution of **3** (2.8 mg, 2.8 μmol) and styrene (0.11 mL, 961 μmol), **1** was obtained in 65(3)% yield with a/s = 9.5(2).

In the isoelectronic Rh porphyrin systems, carbene complexes have been proposed as the active species. From previous work we have demonstrated that the reaction of $[(TTP)Os]_2$ and ethyl diazoacetate forms the osmium porphyrin carbene complex **2**.[9] Consequently, cyclopropanation reactions catalyzed by $[(TTP)Os]_2$ are likely to proceed through an osmium carbene complex. As a test for this hypothesis, (TTP)Os=$CHCO_2Et$ was treated with an excess of styrene. Cyclopropane **1** was formed stoichiometrically (73(5)%) and identified by proton NMR and GC analysis. The a/s isomer ratio of cyclopropane **1** produced in this reaction was a/s = 11.5(4). The similarity of the stoichiometric and catalytic stereoselectivities strongly supports a catalytic cycle in which an osmium carbene complex is initially formed and subsequently transfered to an alkene. In addition, a new porphyrin complex was observed by ^1H NMR[10] and formulated as a π-bound styrene complex ($(TTP)Os(C_6H_5CH{=}CH_2)_n$, n = 1 or 2). The observed styrene signals are broadened and shifted upfield, indicating that a fast exchange process is occurring between coordinated and unbound styrene. Upon decreasing the ratio of styrene to osmium porphyrin, the alkene signals broaden into the base line.

Olefins such as α-methylstyrene, *trans*-β-methylstyrene, and 1-decene were also cyclopropanated with ethyl diazoacetate when (TTP)Os(CO)(Py) was employed as the catalyst. However, in these cases, significantly lower yields (13–39%) were observed, Table I. The anti/syn ratios are also lower with 1-decene and α-methylstyrene. The assignment of the syn and anti isomers for the α-methylstyrene–derived cyclopropane product was confirmed by 500-MHz 2D-NOESY proton NMR. For the cyclopropanation reaction of *trans*-β-methylstyrene with ethyl diazoacetate, only the cyclopropane isomer with the ethyl ester group anti to the phenyl was detected.

A vast majority of cyclopropanation catalysts transform alkynes to cyclopropenes. However, only a few are able to doubly cyclopropanate alkynes to generate the biocyclobutanes.[11] In contrast, (TTP)Os(CO)(Py) and $[(TTP)Os]_2$ catalytically produce *exo,exo*-2,4-dicarbethoxy-1-phenylbicyclo[1.1.0]butane as the only product from phenylacetylene and ethyl diazoacetate. The exo,exo assignment was established by the singlet at 1.71 ppm in the ^1H NMR for the protons on carbons 2 and 4. The exo,endo isomer should exhibit a doublet for these protons.[11a]

Several significant aspects have evolved from the use of osmium *meso*-tetra-*p*-tolylporphyrin complexes as catalysts for the cyclpropanation of a variety of alkenes by ethyl diazoacetate. This system provides the highest anti/syn isomer ratio reported to date (a/s = 10) for the catalytic cyclopropanation of styrene by ethyl diazoacetate.[12] Unlike typical cyclopropanation catalysts which produce cyclopropenes from alkyne substrates, the osmium porphyrin catalysts generate bicyclobutanes from phenylacetylene. Moreover, we have isolated, on preparative scale, the first carbene complex, (TTP)Os=$CHCO_2Et$, that is catalytically active toward cyclopropanation. The fact that this carbene complex can stoichiometrically cyclopropanate styrene with the same stereoselectivity as in the catalytic process is further evidence for it as an important species in the catalytic cycle.

The neutral osmium complexes reported here are isoelectronic with the cationic rhodium porphyrin complexes observed by Kodadek. The positive charge on the rhodium complexes may be an important factor which activates the carbene ligand toward nucleophilic attack by the alkene and prevents isolation of the cationic carbene complex. However, the lack of a positive charge in the osmium system allows the isolation of the osmium carbene complexes. Nonetheless, the neutral osmium complexes appear to be highly efficient cyclopropanation catalysts. Other diazo

(8) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544.

(9) Woo, L. K.; Smith, D. A. *Organometallics* **1992**, *11*, 2344.

(10) ^1H NMR (C_6D_6): 8.63 (s, 8 H, β-H), 7.94 (d, 8 H, aryl), 7.27 (d, 8 H, aryl) 7.04 (br, α-H styrene), 6.13 (br, cis-β-H styrene), 4.62 (trans-β-H styrene), 2.40 (s, 12 H, CH_3).

(11) (a) Conde-Petiniot, N.; Hubert, A. J.; Noels, A. F.; Warin, R.; Teyssie, P. *Bull. Soc. Chim. Belg.* **1986**, *95*, 649. (b) Graziano, M. L.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 289. (c) Pomerantz, M.; Fink, R. *J. Labelled Compds. Radioph.* **1979**, *16*, 275. (d) Shimadate, T.; Hosomaya, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2971. (e) D'yakonov, I. A.; Komendantov, M. I.; Razin, V. V. *J. Gen. Chem. USSR* **1963**, *33*, 2360. (f) Leftin, J. H.; Gilv-Av, E.; Pines, A. *J. Chem. Soc., Chem. Commun.* **1968**, 396.

(12) For diazoacetates with bulky ester substituents, higher anti/syn ratios have been observed. See, for example: Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K.-L. *J. Am. Chem. Soc.* **1990**, *112*, 1906 and ref 6a.

reagents are being examined for use in the catalytic cyclopropanation of alkenes and alkynes. In addition, further mechanistic investigation is under way.

Acknowledgment. The authors thank The National Science Foundation (NSF-PYI Grant CHE-9057752) and the Exxon Education Foundation for the financial support of this work and Aesar/Johnson Mathey for donation of osmium chloride. D.N.R. was supported as a summer student by the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-ENG-82. We also thank Professor Thomas Kodadek for helpful suggestions and Ms. Kathlynn Brown for samples of several cyclopropanes used as GC standards.

Catalytic Conversion of Simple Haloporphyrins into Alkyl-, Aryl-, Pyridyl-, and Vinyl-Substituted Porphyrins

Stephen G. DiMagno, Victor S.-Y. Lin, and Michael J. Therien*

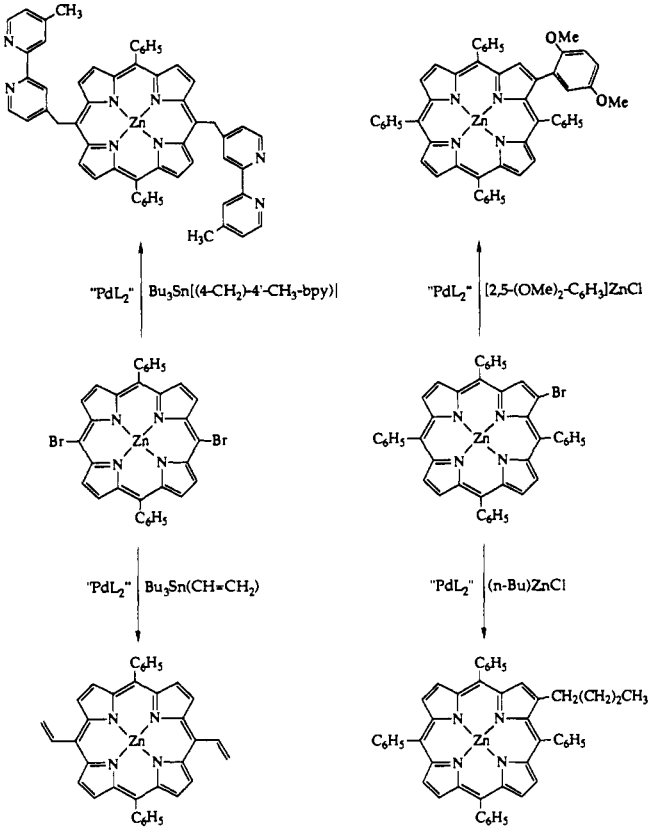
Department of Chemistry, University of Pennsylvania Philadelphia, Pennsylvania 19104-6323

Received September 16, 1992

Appending unusual organic moieties to the porphyrin periphery has often involved elaborate synthetic strategies and difficult separations of reactants from product(s).[1] For example, typical routes to porphyrins that possess one or more differing *meso* or β substituents have employed condensation of the appropriate aldehyde(s) with various monopyrroles,[2] substituted dipyrrylmethanes,[3] or prefabricated 1,19-dideoxybiladienes.[4] In addition to the considerable chromatography that is generally required, other limitations inherent in these approaches include (1) the sensitivity of the cyclization step in a porphyrin synthesis to the steric and electronic features of substituents at the methine and pyrrolic positions and (2) the potential incompatibility of one or more of the components in the syntheses to conditions common to all previous porphyrin preparations, namely, protic or Lewis acid catalysis[5] or high temperature.[6] We report herein a powerful new approach to both mixed meso-substituted porphyrins and unsymmetrical porphyrins; this methodology greatly simplifies the fabrication of such molecules and *dramatically* amplifies[7,8] the types of porphyrins which can now be synthesized.

Metal-mediated cross-coupling methodology, developed largely by Kumada,[9] Negishi,[10] Heck,[11] and Stille,[12] has become an important tool in modern organic chemistry to facilitate formation of carbon–carbon bonds between aryl or alkenyl halide substrates and a variety of alkyl, aryl, and vinyl organometallic reagents. We have recently discovered in our laboratory that this methodology is directly applicable to a wide variety of porphyrin synthetic schemes, provided the reducing power of the organometallic species used in the reaction is insufficient to participate in an outer sphere electron transfer reaction with the porphyrin.

Scheme I



In a typical reaction, (5,15-dibromo-10,20-diphenylporphinato)zinc (**1**)[13] or (2-bromotetraphenylporphinato)zinc (**2**)[14] and an excess of the desired organometallic reagent (RZnX or Bu_3SnR) were brought together in dry THF under nitrogen at 60 °C for 12–48 h in the presence of a catalytic amount of $Pd(PPh_3)_4$. Over the course of several hours, the initially nonfluorescent reaction mixture became increasingly more fluorescent, signaling the gradual transformation of the halogenated porphyrin complex to the alkyl-, vinyl-, aryl-, or pyridyl-substituted zinc porphyrin. For the organometallic reagents depicted in Scheme I, quantitative conversion of reactants to products took place within 48 h.[15]

It is interesting to note that the oxidative addition–transmetalation–reductive elimination reaction sequence occurs much more rapidly at the porphyrin pyrrolic carbon than the analogous re-

(1) *Porphyrins and Metalloporphyrins*; Smith, K. D., Ed.; Elsevier: New York, 1975.

(2) (a) Kim, J. B.; Adler, A. D.; Longo, F. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: London, 1978; Vol. I. (b) For a recent example of a porphyrin synthesized via this approach, see: O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L.; Wasielewski, M. R. *Science (Washington, D.C.)* **1992**, *257*, 63–65.

(3) (a) Paine, J. B. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: London, 1978; Vol. I. (b) For a recent example of a porphyrin synthesized via this approach, see: Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388–390.

(4) (a) Johnson, A. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: London, 1978; Vol. I. (b) For a recent example of a porphyrin synthesized via this approach, see: Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090–6092.

(5) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836.

(6) Adler, A. D.; Sklar, L.; Longo, F. R.; Finarelli, J. D.; Finarelli, M. G. *J. Heterocyclic Chem.* **1968**, *5*, 669–678.

(7) DiMagno, S. G.; Lin, V.S.-Y.; Therien, M. J. *J. Am. Chem. Soc.*, submitted.

(8) (a) DiMagno, S. G.; Lin, V.S.-Y.; Therien, M. J., manuscript in preparation. (b) Lin, V.S.-Y.; DiMagno, S. G.; Therien, M. J. Manuscript in preparation.

(9) (a) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fijioka, A.; Kodama, S.-I.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969. (b) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669–678.

(10) Negishi, E.-I.; Luo, F. T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117–122.

(11) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146–151.

(12) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508–524.

(13) Prepared in high yield (88%) from 5,15-diphenylporphyrin under conditions analogous to those employed by Longo for the halogenation of porphine. Nudy, L. R.; Hutchinson, H. G.; Schieber, C.; Longo, F. R. *Tetrahedron* **1984**, *40*, 2359–2363. The selective bromination of porphyrins at free meso positions can be carried out with a *wide variety* of substituents present.

(14) (a) Samuels, E.; Shuttleworth, R.; Stevens, T. S. *J. Chem. Soc. C* **1968**, 145–147. (b) Callot, H. J. *Bull. Soc. Chim. Fr.* **1974**, 1492. 2-Bromoporphyrin and 2-nitroporphyrin have been utilized previously for several direct substitution reactions. Direct substitution reactions involving porphyrin substrates are neither general nor efficient; see: (c) Callot, H. J. *Tetrahedron Lett.* **1973**, *50*, 4987–4990. (d) Crossley, M. J.; Harding, M. M.; Sternhall, S. *J. Am. Chem. Soc.* **1986**, *108*, 3608–3613.

(15) More recent work in our lab[7] has shown that Pd^0(dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] is a much more reactive catalyst for cross-coupling chemistry on porphyrin templates; reactions similar to those described in the text have been observed to go to completion within 1 h at room temperature with the Pd^0(dppf) catalyst. See: Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, *21*, 1871–1874.

0002-7863/93/1515-2513$04.00/0