change reaction with 2-naphthylsulfonyl azide[13] to afford **7b**, identical in all respects with the sample obtained by the direct route described above. Ring closure via carbenoid insertion of **7b**, according to the published procedure,[14] in the presence of $Rh_2(OAc)_4$ afforded the bicyclic keto ester (**8**) in good yield. This was found to be identical with a sample prepared by Shinkai et al.[15] which they had previously converted to thienamycin (**9**).[16]

The key features of this synthesis are brevity, inexpensive starting material, and virtually complete stereospecificity. In addition, this transformation formally interrelates the stereochemistry of these two important antibiotics. Thus, more than half a century after its discovery penicillin proves to be a practical source of another new highly potent antibiotic.

Acknowledgment. We thank Drs. F. P. DiNinno, I. Shinkai, M. Sletzinger, S. H. Pines, and Professors S. Danishefsky and J. Schwartz for stimulating discussions.

(13) Hazen, G. G.; Weinstock, L. M.; Connell, R.; Bollinger, F. W. *Synth. Commun.*, submitted for publication.
(14) Ratcliffe, R. W.; Saltzmann, T. N.; Christensen, G. B. *Tetrahedron Lett.* **1980**, 31.
(15) We thank Dr. Shinkai for the comparison sample of **8** and for the procedures of the last two steps. He informed us that this sample was prepared and converted to thienamycin by an identical procedure which they have reported for the corresponding *p*-nitrobenzyl esters.[16]
(16) Sletzinger, M.; Liu, T.; Reamer, R. A.; Shinkai, I. *Tetrahedron Lett.* **1980**, *21*, 4221.

Internal Reactions of Tetraalkylstannanes with Carbon-Centered Electrophiles

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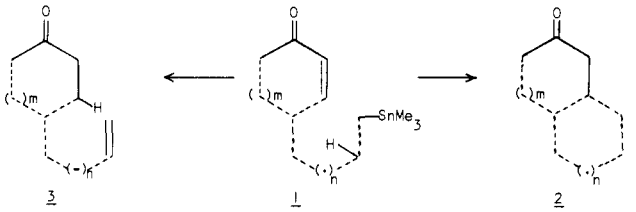
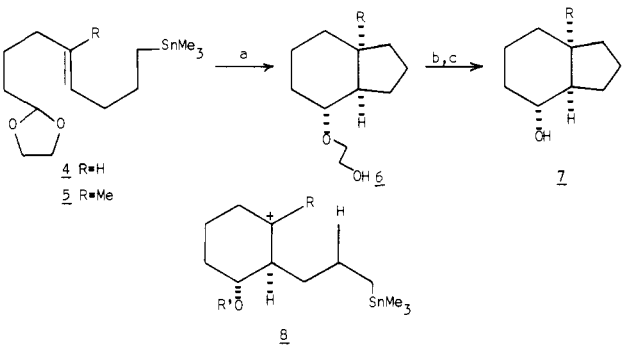
We recently uncovered a method for effecting intramolecular conjugate addition to α-enones of unactivated carbon nucleophiles which proceeds through the mediation of novel alkyltin(IV) chemistry (e.g., **1** → **2**).[1] This approach to carbocyclization represents the first general method for internal conjugate addition to α-enones of unactivated carbon nucleophiles,[2] a central reaction type in intermolecular carbon–carbon bond formation, and illustrates the use of the carbon–tin σ bond as a latent carbanionic nucleophile.[3] The method employs activation of the α-enone moiety with Lewis acids to engender a β-electrophilic site (e.g., an oxy-substituted allyl carbocation) which is sufficiently potent to react with a stereoproximate carbon–tin σ bond.



† Research Fellow of the Alfred P. Sloan Foundation (1981–1983).
(1) Macdonald, T. L.; Mahalingam, S. *J. Am. Chem. Soc.* **1980**, *102*, 2113.
(2) For an alternate approach to internal conjugate enone addition, see: Scheffold, R.; Dike, M.; Dike, S.; Herold, T.; Walder, L. *J. Am. Chem. Soc.* **1980**, *102*, 3642.
(3) For recent examples of the use of the carbon–tin bond to promote carbon–carbon bond formation, see: (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7108. (b) Naruta, Y. *Ibid.* **1980**, *102*, 3774. (c) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2591. (d) Godschaly, J.; Stille, J. K. *Ibid.* **1980**, *21*, 2599. (e) Nicolau, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704. (f) Luijten, J. G. A.; van der Kerk "The Bond to Carbon"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Part II, pp 91–191.

Scheme I[a]



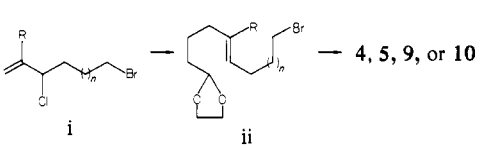
[a] Conditions: (a) $SnCl_4$ (5%), CH_2Cl_2, 0 °C (**4**, 83%; **5**, 58%), (b) $SOCl_2$ (1.5 equiv), LiBr (3.0 equiv), CH_3CN (R = H, 95%; R = Me, 98%); (c) Li (4.0 equiv), NH_3, THF (R = H, 72%; R = Me, 84%).

We have extended the basic strategy illustrated by this process to other carbon-centered electrophiles by establishing that carbocations engendered from a variety of precursors including allylic and tertiary alcohols, acetals, epoxides, olefinic cyclization, and iminium ions can be employed in the initiation of internal alkyltin(IV)-mediated reaction processes. The carbon–tin σ bond can react with these electrophiles via two distinct modes resulting either in the formation of a carbon–carbon bond via electrophilic cleavage of the carbon–tin bond (e.g., **1** → **2**) or in the transfer of a hydride β to the trimethylstannyl moiety via an internal redox process (e.g., **1** → **3**). We report here on the substrate and reaction condition parameters which direct the mode of tin(IV)-mediated reaction to either reaction type.

The balance between these two reaction processes is sensitive to the size of the ring being formed, the substitution pattern of the electrophilic site, and the catalyst employed to initiate the reaction. Carbon–carbon bond formation is the only reaction process that we have observed in the formation of five-membered rings via this tetraalkyltin-mediated cyclization strategy. Both di- and trisubstituted carbocations undergo cyclization reactions, and β-hydride transfer does not appear to be a competitive reaction mode. For example, olefinic acetals **4** and **5**[4] undergo smooth carbocyclization (Scheme I). In the pentannulation of substrates with identical stereoelectronic, enthalpic, and entropic requirements,[6] alkyl substitution at the electrophilic site for carbon–tin bond attack appears to retard carbon–carbon bond formation but not to alter the course of reaction (e.g., to β-hydride transfer).

The ring junction stereochemistry generated during the cyclization of olefinic acetals **4** and **5** is independent both of the olefin substituent (hydrogen, methyl) and of the olefin geometry (*E* or *Z*). Cyclization of (*E*)-acetals **4** and **5** produces exclusively the *cis*-hydrindane skeleton **6** (R = H, Me)[7] implying that tri-

(4) All new compounds were characterized by infrared, mass, ^1H NMR, and ^{13}C NMR spectroscopy and by combustion analysis. Spectral and analytical data appear as supplementary material. Acetals **4** (or **5**) and **9** (or **10**) were synthesized according to the scheme outlined below. Thus, a requisite bromochloroolefin *i* (R = H, Me; *n* = 1, 2) prepared by the method of Macdonald et al.[5] was treated with the heterocuprate derived from 3-(ethylenedioxy)-1-propylmagnesium bromide[5] to afford olefinic acetals *ii* (R = H, Me; *n* = 1, 2) after low pressure chromotographic isolation of the predominant *E* isomer (46–63%). Subsequent stannylation ($LiSnMe_3$, NH_3, THF, −33 °C) of acetal bromides ii gave the desired stannyl acetals **4** (or **5**) and **9** (or **10**) (85–95%). Allylic alcohol **14** was synthesized by methyllithium addition to 2-[4-(trimethylstannyl)butyl]-2-cyclohexen-1-one[1] (8.7%).



(5) Macdonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504.
(6) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

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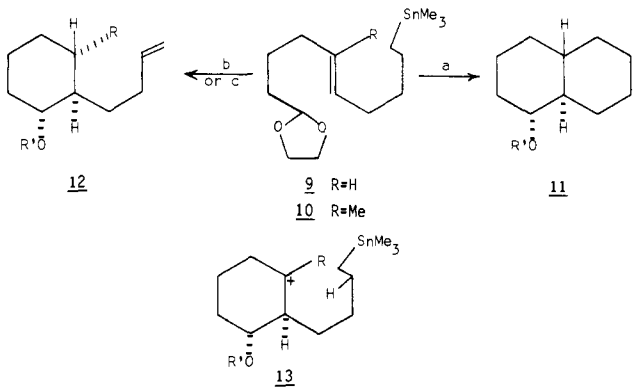
Scheme II[a]



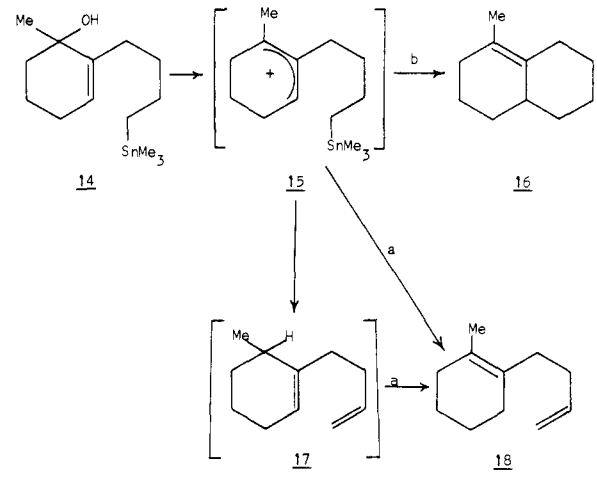
[a] Conditions: (a) 9, $SnCl_4$ (5%), CH_2Cl_2, 0 °C (85%); (b) 9 [to 12 (R = H)], $BF_3 \cdot ET_2O$ (5%), CH_2Cl_2, 20 °C (11 ≤ 4%/12 ≥ 90%); (c) 10 [to 12 (R = Me)], $TiCl_4$ (5%), CH_2Cl_2, 20 °C (93%).

methylstannyl termination of these olefinic cyclizations[9,10] proceeds via discrete intermediate carbocations (e.g., **8**). Ring closure of the intermediate carbocation (**8**) occurs kinetically and proceeds to the thermodynamically most stable ring junction as a function presumably of the diminished strain energy in the transition state for *cis*- vs. *trans*-hydrindane ring fusion.[8,11] In conjunction with such olefinic cyclizations, the carbon–tin σ bond is the first example of a C sp^3-hybridized "terminator" in contrast to the variety of C sp-hybridized (acetylenic) and C sp^2-hybridized (olefinic) terminators which Johnson and others have developed.[10d,e,f]

The preferential formation of carbon–carbon bonds during these and related pentannulation processes and the insensitivity of these reactions to the electrophilic catalyst employed (vide infra) suggests that a severe constraint exists for the internal transfer of hydride in a position β to the trimethylstannyl moiety through a five-membered transition state (e.g., **8**).[12] The precise nature of this constraint on β-hydride transfer via five-membered transition states is not clear at present and is the source of continuing investigations.

In contrast to the formation of five-membered rings, in the formation of six-membered rings via this alkyltin-mediated strategy, the balance between carbon–carbon formation and β-hydride transfer for a variety of carbon-centered electrophiles is sensitive both to the substitution pattern of the electrophilic site and to the Lewis acid catalyst employed to initiate the reaction. When titanium tetrachloride or stannic chloride is employed, secondary-carbocationic sites favor carbon–carbon bond formation and tertiary carbocations favor β-hydride transfer. Thus, upon

Scheme III[a]



[a] Conditions: (a) CF_3CO_2H (2%), CH_2Cl_2, 20 °C (95%); (b) $TiCl_4$ (2%), CH_2Cl_2, 20 °C (72%).

electrophilic activation with these agents, disubstituted olefinic acetal **9**[4] undergoes predominate carbon–carbon bond formation, leading exclusively to *trans*-decalin **11** (R' = CH_2CH_2OH),[8] whereas trisubstituted olefinic acetal **10**[4] reacts exclusively via β-hydride transfer proceeding to a trisubstituted cyclohexane, to which we tentatively assign structure **12** (R = Me, R' = CH_2CH_2OH)[8] (Scheme II). The formation of *trans*-dialkylcyclohexane **12** (R = Me) from trisubstituted olefinic acetal **10** is thought to occur by internal hydride transfer via a carbocationic transition state (resembling **13**) in which the β-hydride is transfered cis to the trimethylstannyl-containing side chain (e.g., a *cis*-decalin-like transition state). Although other factors are undoubtedly involved, when the electrophilic site is sterically encumbered, the β-hydride transfer process is promoted relative to C–C bond formation since hydride transfer is presumably less sterically demanding and is a viable alternative process in six-membered transition states. However, when either boron trifluoride or trifluoroacetic acid was employed to initiate the cyclization of disubstituted olefinic acetal **9**, β-hydride transfer generating **12** (R = H, R' = CH_2CH_2OH)[4] was the predominant mode of reaction (≥95%). These data demonstrate that the course of tetraalkyltin-mediated reaction for the intermediate *sec*-cyclohexyl cation **13** is dependent upon the electrophilic catalyst.

In order to probe the question of whether carbon–carbon bond formation or β-hydride transfer is the intrinsically preferred mode of reaction in these 4'-(trimethylstannyl)butyl-containing cyclohexyl cation systems (e.g., **13**), we examined cyclohexenol **14** (Scheme III).[4] The in situ generated allyl cation **15** derived from **14** has available for reaction both a secondary electrophilic site, which should favor carbon–carbon bond formation, and a tertiary electrophilic site, which should favor β-hydride transfer, and should possess related stereoelectronic, entropic, and enthalpic constraints[6] for either reaction mode. We have found the reactivity pattern in this system to be acutely sensitive to the electrophilic catalyst employed. When cyclohexenol **14** is treated with titanium tetrachloride in methylene chloride, carbon–carbon bond formation leading to $\Delta^{1,9}$-octalin **16** is the sole mode of reaction; when trifluoroacetic acid is the electrophilic catalyst in methylene chloride, β-hydride transfer is the exclusive reaction process providing the observed product cyclohexene **18**. We have been unable to establish whether cyclohexene **18** is derived directly from a hydride transfer process to a secondary allylic cation position (e.g., **15** → **18**) or alternatively via a sequence involving hydride transfer to the tertiary allylic site affording cyclohexene **17** followed by acid-catalyzed isomerization to the thermodynamically preferred tetrasubstituted olefin isomer **18** (e.g., **15** → **17** → **18**). The nature of the electrophilic catalyst presumably affects the extent of both the electron deficiency in the allyl cation via ion pairing and the interaction of the anionic counterion with the trimethylstannyl function as the cation proceeds to product. Our

(7) The products of these cyclizations (except **12** R = Me) have been correlated with authentic standards. In addition to the illustrated predominant product of the acetal initiated cyclizations obtained in the stated yields, 4–12% of the epimeric 2-ethoxy ether products were isolated (e.g., **6** β-OR; **11** β-OR). Hydrindanols **7** (R = H, Me) were correlated with the products of borohydride reduction of the *cis*-4-hydrindanones[8] and decalinol **11** (R^1 = H) with the products of borohydride reduction of *trans*-1-decalone (Aldrich Chemical Co.).

(8) (a) Cicero, B. L.; Weisbuch, F.; Dana, G. *J. Org. Chem.* **1981**, *46*, 914. See also: (b) Serebryakov, E. P.; Kuchceror, V. F. *Russ. Chem. Rev. (Engl. Transl.)* **1963**, *32*, 523. (c) Allinger, N. T.; Trubble, M. T. *Tetrahedron* **1972**, *28*, 1191.

(9) For recent reviews of olefinic cyclization, see: (a) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 72. (b) Johnson, W. S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9.

(10) See the following and references therein: (a) Johnson, W. S.; Bartlett, P. A.; Brauman, J. A.; Volkman, R. V. *J. Am. Chem. Soc.* **1973**, *95*, 7502. (b) Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *Ibid.* **1977**, *99*, 8341. (c) van Tamelen, E. E.; Taylor, E. G.; Leiden, T. M.; Kreft, A. F. *Ibid.* **1979**, *101*, 7423. (d) Schmid, R.; Huesman, P. L.; Johnson, W. S. *Ibid.* **1980**, *102*, 5122. (e) Johnson, W. S.; Daub, G. W.; Lyle, T. A.; Nina, M. *Ibid.* **1980**, *102*, 7800. (f) Johnson, W. S.; Yarnell, T. M.; Meyers, R. F.; Morton, R. D.; Boots, S. G. *J. Org. Chem.* **1980**, *49*, 1254.

(11) (a) For a related discussion, see: Crandall, J. K.; Magaha, H. S.; Widener, R. K.; Tharp, G. A. *Tetrahedron Lett.* **1980**, *21*, 4807. (b) Macdonald, T. L.; Mahalingan, S. *Ibid.* **1981**, *22*, 2077.

(12) The difficulty in hydride transfer via five-membered-ring transition states has been noted: (a) Verhoeven, J. W.; Pasman, P. *Tetrahedron* **1981**, *37*, 943. (b) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588. (c) Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev. Chem. Soc.* **1966**, *20*, 119.

tentative conclusion concerning the impact of electrophilic catalyst on the mode of reaction in these and related cyclohexane ring forming substrates is that electrophilic catalysts which effect considerable cationic charge development with limited counterion donation to the trimethylstannyl moiety promote β-hydride transfer (BF_3, CF_3CO_2H, $Me_3Si\text{-}OSO_2CF_3$), whereas those which effect cationic charge buildup concurrent with anionic ligand donation to the trimethyl stannyl unit promote carbon–carbon bond formation ($TiCl_4$, $SnCl_4$).

Our initial investigations of tin(IV)-mediated internal reaction processes have established that the tetraalkyltin moiety and carbon-centered electrophilic precursor are compatible until electrophilic activation and that an array of carbon-centered electrophiles and carbon–tin nucleophiles can be employed in these reactions, thereby providing variable product functionality. The studies outlined here have helped to define those substrate and reaction condition parameters which direct the mode of carbon–tin bond mediated reaction to carbon–carbon bond formation or β-hydride transfer. In addition, the finding of a Lewis acid dependence on the mode of reactivity in these cyclohexane ring forming substrates could have implications in other Lewis acid catalyzed reaction processes.

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Supplementary Material Available: Spectral and analytical data for new compounds (1 page). Ordering information is given on any current masthead page.

Synthesis and Structure of a "Dicuprophane", a Dicopper(I) Complex Derived from [*o*-(Diphenylphosphino)benzoyl]pinacolone

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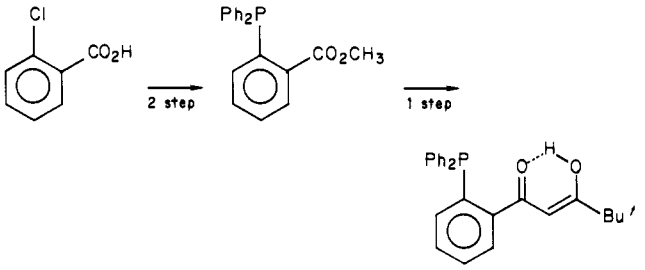
We wish to report the preparation of an unusual binucleating chelating agent and the synthesis and structure of its copper(I) complex which contains two cofacial three-coordinate $16e^-$ copper(I) moieties. The present results bear on the general challenge of the preparation of bimetallic coordination compounds containing metal ions in *reactive* oxidation states. Representative developments in this field include studies of bimetallic complexes of 2-(diphenylphosphino)pyridine,[1] bis(diphenylphosphino)methane,[2] and imine derivatives of 2,6-diformylcresol.[3]

With the goal of preparing an unsymmetrical uninegative compartmentalized chelating agent capable of binding two metal ions in low oxidation states, we synthesized the phosphine-substituted β-diketone ligand *o*-[(diphenylphosphino)benzoyl]pinacolone.[4] The target compound was efficiently constructed in three steps on a 0.06-mol scale by using inexpensive reagents (Scheme I). The product, which we call HacacP, exists in the enol form in $CDCl_3$ solution and was isolated as pale yellow, air-stable crystals which are readily soluble in polar organic solvents.

Scheme I



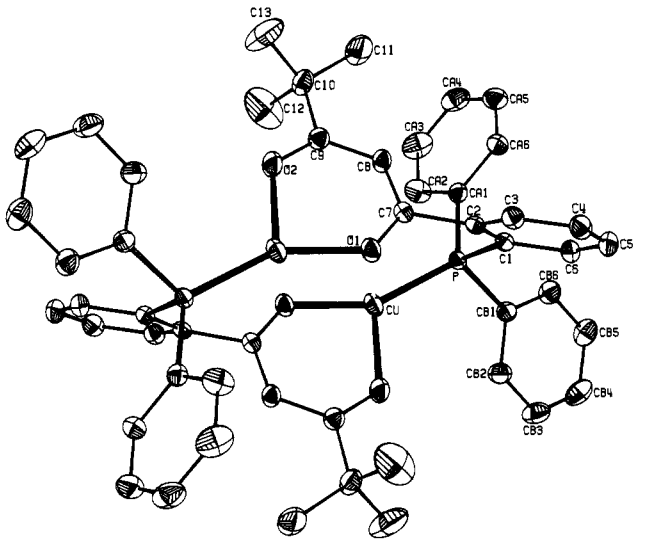


Figure 1. ORTEP plot of the nonhydrogen atoms of the $[Cu(acacP)]_2$ molecule with thermal ellipsoids set at the 50% probability level.

Treatment of HacacP with 1 equiv of $[Cu(MeCN)_4]ClO_4$ in acetonitrile in the presence of triethylamine quantitatively afforded yellow microcrystalline $[Cu(acacP)]_2$ (**1**) (eq 1) which was

$$2[Cu(MeCN)_4]ClO_4 + 2HacacP + 2Et_3N \rightarrow [Cu(acacP)]_2 + 8MeCN + 2Et_3NHClO_4 \quad (1)$$

characterized by combustion analysis, IR, ^1H and ^{31}P NMR, and field desorption mass spectrometry.[7] These measurements all indicated the expected stoichiometry and a symmetrical structure but provided no definitive information concerning the geometry about the metal ions. On the basis of extensive precedent of other structurally characterized dimetal(II) complexes derived from

(1) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 6654.

(2) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049. Kubiak, C. P.; Eisenberg, R. *Ibid.* **1977**, *99*, 6129. Cowie, M.; Mague, J. T.; Sanger, A. R. *Ibid.* **1978**, *100*, 3628. Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500 and references therein.

(3) Robson, R. *Aust. J. Chem.* **1970**, *23*, 2217. Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225. Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571. Gagné, R. R.; Kreb, R. P.; Dodge, J. A. *Ibid.* **1979**, *101*, 6917.

(4) *o*-(Diphenylphosphino)benzoic acid was prepared from *o*-chlorobenzoic acid and $NaPPh_2$.[5] Esterification of the acid with diazomethane gave the methyl ester $o\text{-}Ph_2PC_6H_4CO_2CH_3$ in 85% yield as colorless crystals from methanol, mp 96–97 °C; IR (mull) 1712 cm^{-1} (s); ^1H NMR (90 MHz, $CDCl_3$ solution) δ 7.6–6.9 (m, 14 H), 3.70 (s, 3 H); $^{31}P\{^1H\}$ NMR (40.5 MHz, $CDCl_3$ solution) 5.1 ppm upfield of 85% H_3PO_4. Anal. Calcd for $C_{20}H_{17}O_2P$: C, 75.00; H, 5.35; P, 9.67. Found: C, 75.00; H, 5.32; P, 9.70. Condensation of the methyl ester with $KCH_2COC(CH_3)_3$[6] in THF followed by acidification (HCl) and crystallization (methanol) gave a 65% yield of cream colored crystals, mp 118 °C; IR (mull) 1605 (s), 1580 (s) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$ solution) δ 14.8 (br s, 1 H), 6.8–7.7 (m, 14 H), 5.87 (s, 1 H), 1.09 (s, 9 H); $^{31}P\{^1H\}$ NMR (40.5 MHz, $CDCl_3$ solution) 8.98 ppm upfield of 85% H_3PO_4. Anal. Calcd for $C_{25}H_{25}O_2P$: C, 77.32; H, 6.44; P, 7.99. Found: C, 77.22; H, 6.56; P, 8.02.

(5) Issleib, K.; Zimmerman, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 197. Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.*, in press.

(6) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 1324.

(7) Anal. Calcd for $C_{50}H_{48}Cu_2O_4P_2$: C, 66.59; H, 5.33; Cu, 14.10; P, 6.88. Found: C, 66.64; H, 5.28; Cu, 14.10; P, 6.91. Spectral data: IR (mineral oil mull) 1571 (s), 1548 (s) cm^{-1}; ^1H NMR (90 MHz, CD_2Cl_2 solution) δ 7.4–6.7 (m, 14 H), 5.7 (s, 1 H), 1.1 (s, 9 H); $^{31}P\{^1H\}$ NMR (40.5 MHz, CD_2Cl_2 solution) 3.6 ppm upfield of 85% H_3PO_4; field desorption MS, *m/z* 900 (M^+).

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