(5) The products containing polychlorosilyl groups showed decomposition peaks on the GLPC column.

(6) Satisfactory elemental analyses and consistent NMR and ir spectral data were obtained for all the products reported here.

(7) The NMR and ir spectral data were reported previously: Y. Kiso, K. Tamao, and M. Kumada, *J. Organomet. Chem.*, **76**, 105 (1974).

(8) A small amount (~4% yield) of [possibly (*Z*)]-*n*-Bu(Me_3Si)C═C(Si-Me_2H)Bu-*n* was also formed owing to the concomitant H–Cl interchange on the silicon atom characteristic of the interaction of hydrochlorosilanes with nickel complexes; Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, *J. Organomet. Chem.*, **50**, 297 (1973); Y. Kiso, M. Kumada, K. Maeda, K. Sumitani, and K. Tamao, *ibid.*, **50**, 311 (1973).

(9) The present thermal isomerization and alkali–desilylation are based on the recent observations by Dr. H. Okinoshima; dissertation submitted to Kyoto University, 1975. We thank him for valuable suggestions.

(10) The empirical melting point rule strongly suggests the *Z* configuration for the liquid isomer: E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 326–327.

(11) Cf. C. C. Price and J. R. Sowa, *J. Org. Chem.*, **32**, 4126 (1967).

(12) Cf. J. A. Labinger, J. Schwartz, and J. M. Townsend, *J. Am. Chem. Soc.*, **96**, 4009 (1974).

(13) Hydrosilylation of internal acetylenes under such mild conditions as presently employed is also noteworthy.[14]

(14) M. F. Lappert, T. A. Nile, and S. Takahashi, *J. Organomet. Chem.*, **72**, 425 (1974).

(15) Although *n*-BuC≡CH readily reacted with $HSiCl_2Me$ under similar conditions, a mixture of several products was formed. None of them has yet been characterized, but see ref 14.

(16) The reaction of $HSiClMe_2$ with 5-decyne (~100 hr) gave 50–80% yield of 5-decene ($Z{:}E \simeq 80{:}20$) instead of the double silylation product, together with 50–20% yield of the hydrosilylation product. It has previously been recognized that silanes containing no chlorine atoms do not exhibit reactivity.[17]

(17) Y. Kiso, K. Tamao, and M. Kumada, *J. Organomet. Chem.*, **76**, 95 (1974).

(18) The nonstereoselective hydrosilylation might suggest an intervention of radical species; cf. I. Ojima, M. Kumagai, and Y. Nagai, *J. Organomet. Chem.*, **66**, C14 (1974).

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Solid Phase Organometallic Synthesis. Bis(di-*n*-butylchlorotin)tetracarbonylosmium

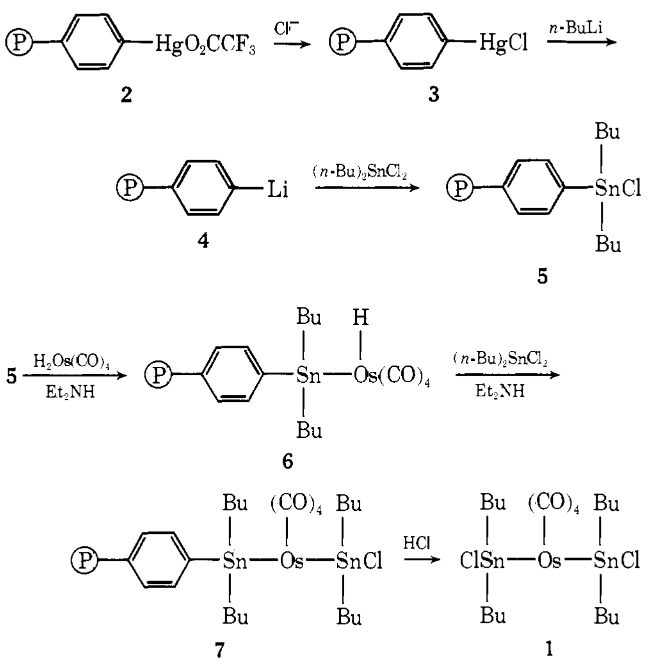
Sir:

Herein we describe the solid phase synthesis and subsequent isolation of the title compound, **1**, from di-*n*-butyltin dichloride and dihydridotetracarbonylosmium with diethylamine as the coupling agent (see Scheme I). Polymer attachment circumvented formation of bis(μ-dibutyltin-tetracarbonylosmium), the cyclic product from the known reaction of these components in solution.[1]

Since Merrifield's discovery of the solid phase method for peptide synthesis,[2] several useful applications have been found for polymer-bound reagents[3] and catalysts.[4] Repetitive, sequential-type syntheses using insoluble polymer supports have been described for peptides,[2] oligonucleotides,[5] and oligosaccharides.[6]

Multiple step syntheses with unprotected multifunctional reactants are much less common.[3b] Polymer "immobilized" ester enolates have been monoacylated[7] and several reactions of terephthalaldehyde have been described[8a] including its stepwise conversion to 4,4′-stilbenedicarbaldehyde.[8b] For these applications, relatively low levels of substitution limited reaction of one polymer-bound moiety with another.[7,8] In contrast, apparent chelate properties of phosphine-substituted copolymers have been attributed to polymer chain mobility.[9] While present information is inadequate to reconcile these seemingly contradictory observations, it is clear that intrapolymer reactions pose a significant threat to the success of any solid phase synthesis scheme that utilizes unprotected, multifunctional components.

Scheme I



The choice of a macroreticular styrene–20% divinylbenzene copolymer for this work was based upon observations by Grubbs and coworkers[10] that the higher degree of cross-linking in this porous polymer permits much less internal mobility than in the 2% cross-linked gels commonly used for peptide synthesis[11] and catalyst support.[9] Other important considerations were the requirements that the distance between substituents on the resin must be chosen to minimize intrapolymer reactions and the pores must be large enough to permit growth and removal of the product molecules.[12] The phenyl–tin bond served as the cleavable connecting link. To ensure its exclusive formation, aromatic mercuration[13] was selected for the initial functionalization.[14] Unpolymerized vinyl groups on the polymer were deactivated toward mercuration[16] by treatment with *n*-butyllithium (TMEDA complex)[17] followed by methanolysis. The dried resin was stirred in a dilute solution of $Hg(O_2CCF_3)_2$[18] at 0° for 18 hr and the resino-phenylmercuric trifluoroacetate[19] **2** was converted to the corresponding chloride **3** with excess tetramethylammonium chloride in methanol. Microscopic examination of a bisected bead from a portion of **3**, that had been reduced with lithium naphthalenide[21] in THF and quenched in methanol, revealed fairly even distribution of elemental mercury.[24]

Treatment of **3**[25] under argon with 0.75 *M* *n*-BuLi in toluene (1.5 mequiv/g) for 1 hr followed by exhaustive washing with toluene and ether gave resino-phenyllithium, **4**. This was quenched with excess $(n\text{-}Bu)_2SnCl_2$ (2.0 mmol/g) in ether.[26] The first metal-to-metal bond was formed when **5** (8.0 g having 0.022 mequiv of Cl/g) was stirred with a solution of $H_2Os(CO)_4$ (0.65 mmol) and diethylamine (1 ml) in 1:1.5 THF–CH_2Cl_2 for 2.5 hr under argon. The infrared spectrum of the washed and dried resin **6** (1% in KBr)[27] exhibited ν_{CO} at 2113 m, 2048 m, and 2026 vs cm^{-1}, similar to the spectrum of *cis*-$Ph_3SnOs(CO)_4H$;[1] a weak absorption at 1937 cm^{-1} is tentatively assigned to ν(Os–H). Treatment of **6** with $(n\text{-}Bu)_2SnCl_2$ (3.28 mmol) in CH_2Cl_2 (10 ml) containing Et_2NH (1 ml) as above gave the resino-trimetalide **7**[28] with an infrared spectrum (ν_{CO} 2048 vw and

2013 s cm^{-1}) characteristic of *trans*-bis(organotin)tetracarbonylosmium compounds.[1,29,30]

Cleavage of most of the trimetalide was accomplished with anhydrous HCl in CH_2Cl_2 (−15°, 30 min). The infrared spectrum of a hexane solution of the pale yellow residue, after removal of the solvent and excess HCl under vacuum, was essentially identical with that of **1** and indicated a yield of 35%.[31] Removal of the solvent and volatile by-products under vacuum at 40° and recrystallization from methanol gave pure **1** (18 mg, 17%) identified by infrared spectroscopy, melting point, and undepressed mixture melting point with an authentic sample.[1]

In a similar fashion, the coupling scheme was carried two steps beyond **7** to synthesize the analogous pentametalide. The residue from HCl cleavage contained two major high molecular weight components by GPC analysis.[32] The smaller of these was collected and identified as **1** by retention volume and ir spectrum. The larger (also collected) gave a mass spectrum with the highest observable multiplet peak centered at *m/e* 1316 ± 2 which probably arises from loss of a butyl group from the molecular ion of $[ClSnBu_2Os(CO)_4]_2SnBu_2$.[33] Further characterization of this component is in progress. The presence of **1** in this mixture suggests that some of the resino-trimetalides may be doubly attached and/or physically inaccessible. The sharp drop in the level of substitution from **5** to **7** favors the latter. Experiments in progress are designed to eliminate both potential problems and to extend the method to other multifunctional organometallics.

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(32) Gel permeation chromatographic analyses were performed using Waters Associates' 100 Å μ-Styragel columns.
(33) We observed that the base peak in the mass spectrum of **1** is (M − 57) corresponding to loss of one butyl group.

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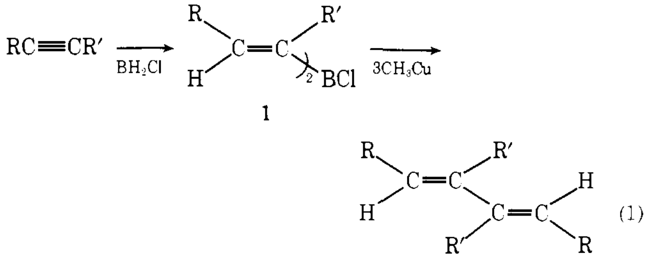
Methylcopper Induced Coupling of Dialkenylchloroboranes. A New Procedure for the Stereoselective Synthesis of *(E,E)*-1,3-Dienes

Sir:

Dialkenylchloroboranes (**1**), readily available through the reaction of acetylenes with chloroborane–ethyl etherate,[1] react rapidly at 0° with 3 molar equiv of methylcopper to produce (*E*,*E*)-1,3-dienes (**2**) in excellent yields (eq 1).



The stereochemical purity of the product is >99%. The present reaction, therefore, provides a facile and stereoselective transformation of acetylenes into the corresponding (*E*,*E*)-1,3-dienes and can even be extended to the accommodation of a functional group.

A number of metal salts react with organoboranes,[2] and such transmetalation reactions appear to hold promise for a noncarbanionic route to organo transition metallics.[3] During these investigations, we have discovered that methylcopper is a highly efficient coupling agent for dialkenylchloroboranes. The results are summarized in Table I.

To achieve the nearly quantitative conversion of borane into diene it was essential to utilize 3 molar equivalents of CH_3Cu as shown in Table II. Further increase of CH_3Cu did not exercise a significant influence on the yield. The reaction was quite rapid at 0°; the addition of the borane to CH_3Cu in ether caused an instantaneous change of color from yellow to black. The GLPC analysis after 5 min revealed formation of the diene in 70% yield. In contrast to alkenylboranes, trialkylboranes and dialkylchloroboranes