

AD-A222 990

(2)

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS						
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution list enclosed						
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)						
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			7a. NAME OF MONITORING ORGANIZATION Office of Naval Research						
6a. NAME OF PERFORMING ORGANIZATION Massachusetts Institute of Technology		6b. OFFICE SYMBOL (if applicable)	7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217						
6c. ADDRESS (City, State, and ZIP Code) 77 Massachusetts Avenue Cambridge, MA 02139			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0307						
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS						
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		<table border="1"> <tr> <td>PROGRAM ELEMENT NO.</td> <td>PROJECT NO.</td> <td>TASK NO.</td> <td>WORK UNIT ACCESSION NO.</td> </tr> </table>				PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.						
11. TITLE (Include Security Classification) The Synthesis and Structure of Stibaindoles									
12. PERSONAL AUTHOR(S) Stephen L. Buchwald, * Richard A. Fisher and Bruce M. Foxman									
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) June 6, 1990					
15. PAGE COUNT 6									
16. SUPPLEMENTARY NOTATION									
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)						
FIELD	GROUP	SUB-GROUP	main group metallacycles, solid state inorganic, metal polymers, sulfur						
19. ABSTRACT (Continue on reverse if necessary and identify by block number)									
SEE ATTACHED REPORT DISTRIBUTION STATEMENT A Approved for public release Distribution Unlimited DTIC ELECTE JUN 20 1990									
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified						
22a. NAME OF RESPONSIBLE INDIVIDUAL Stephen L. Buchwald			22b. TELEPHONE (Include Area Code) (617)253-1885		22c. OFFICE SYMBOL				

OFFICE OF NAVAL RESEARCH

Contract N00014-88-K-0307

R & T code 4135014

Technical Report No. 3

The Synthesis and Structure of Stibaindoles

by

Stephen L. Buchwald*, Richard A. Fisher and Bruce M. Foxman

Prepared for Publication

in

Angewandte Chemie

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

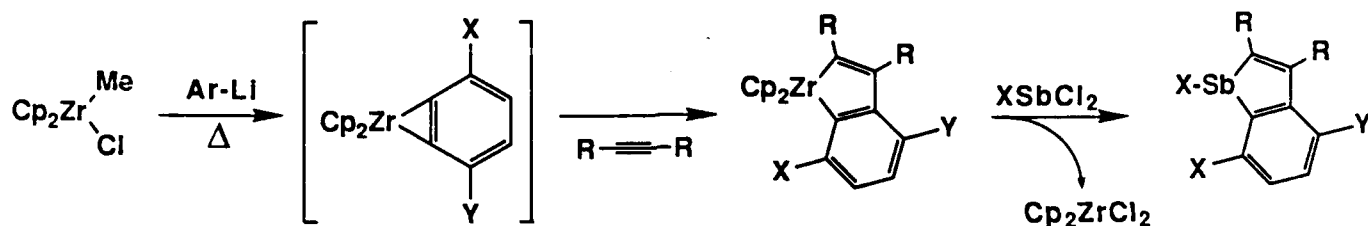
June 6, 1990

Reproduction in whole or part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

90 06 19 030

Recent applications of main group organometallic compounds in the materials sciences has dramatically increased the interest in developing new and more selective synthetic routes to main group organometallic compounds. The first synthesis and structural characterization of a new class of metalloid-heterocycle, stibaindoes, has been accomplished by the application of a transmetallation strategy from zirconium. The facile formation, and ready isolation, of these new compounds bodes well for the role early transition metal complexes may play in the discovery of new and valuable classes of main group compounds.



Accession For	
NTIS	CRA&I ☒
DTIC	TAB ☐
Unannounced ☐	
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

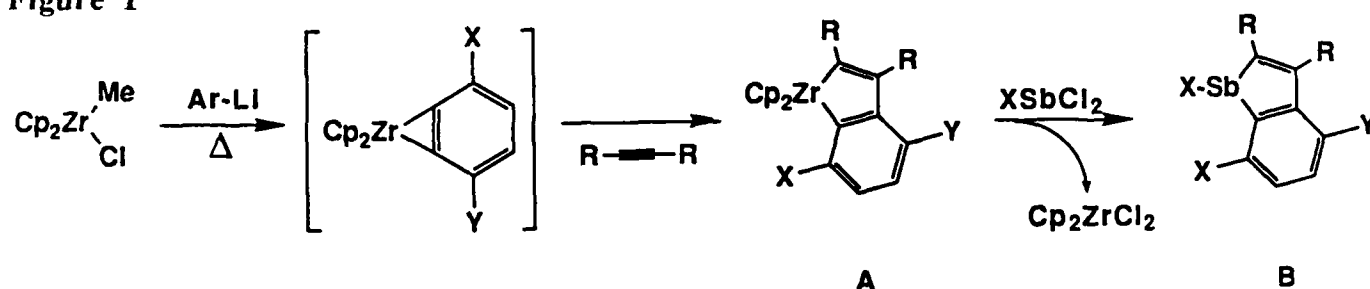
The Synthesis and Structure of Stibaindoles**

By Stephen L. Buchwald,* Richard A. Fisher, and Bruce M. Foxman

Heterocyclic compounds are ubiquitous in organic chemistry and have, consequently, been a popular synthetic target. The vast majority of these efforts have focused on naturally occurring heterocyclic skeletons containing second and third row elements with significantly less attention directed to their heavier main group analogs.^[1] As a consequence, an impressive array of useful reactions is available to the chemist wishing to construct heterocycles of N, O, P, and S, while methods for the synthesis of their heavier analogs are limited.^[2] In this communication, we report the synthesis and characterization of a series of new metalloid-heterocycles, benzo-[b]-stiboles.^[3]

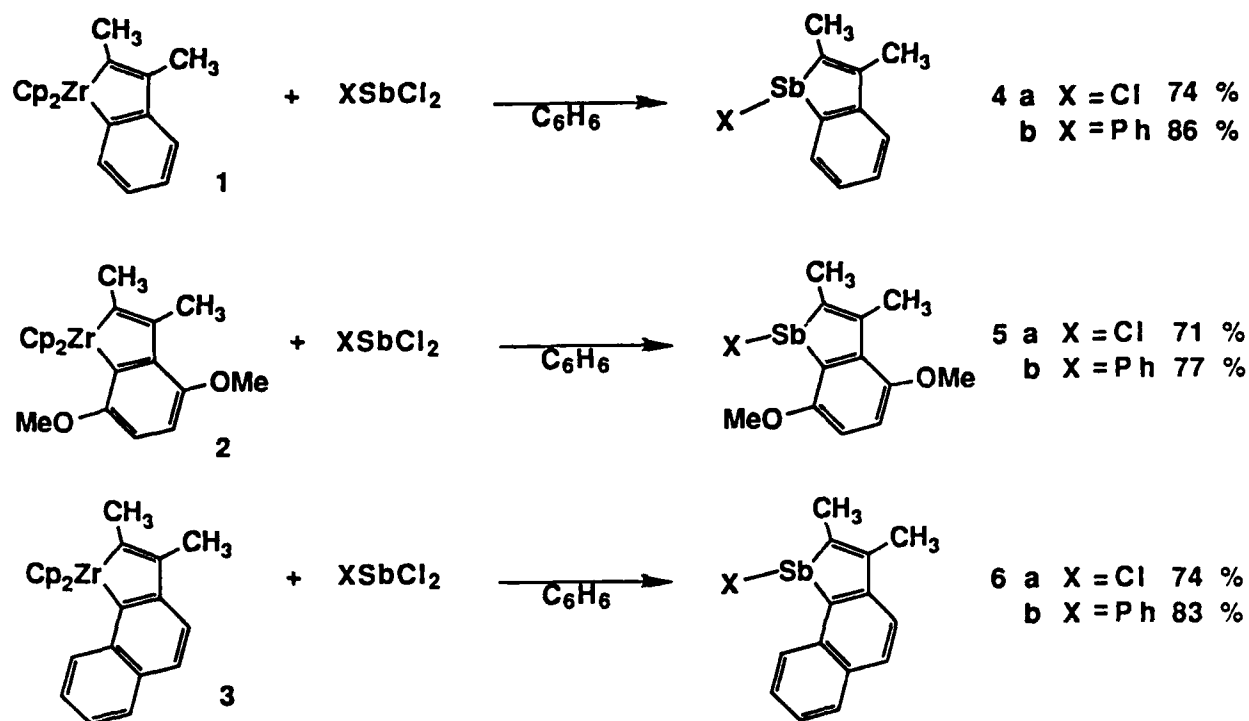
In the course of developing new zirconocene-based methodology for organic synthesis, we,^[4i-k] and others,^[4a-h] have established that sequential treatment of zirconocene(methyl) chloride with an aryl lithium and an alkyne, followed by heating, affords the metallacycle A (Figure 1). The generality of this

Figure 1



reductive coupling reaction is documented elsewhere.^[4] Treatment of benzene solutions of the zirconacycle (A) with one equivalent of XSbCl_2 ($\text{X} = \text{Cl}, \text{Ph}$) produces the benzo-[b]-stiboles (B).^[5] The only byproduct of the reaction, Cp_2ZrCl_2 , is removed by flash chromatography on alumina (III) or MgSO_4 (anhydrous).^[6] Our results are summarized in Figure 2.

Figure 2



The antimony metallacycles (4-6) are moderately air stable, crystalline solids. The 1-chloro derivatives slowly decompose, when stored for prolonged periods in air, to give as yet uncharacterized species. They may be stored indefinitely in a dry nitrogen atmosphere. The 1-phenyl derivatives are substantially more robust and may be stored in the laboratory atmosphere without detectable decomposition. Complexes 4-6 are all considerably more prone to decomposition in solution than in the solid state. All the compounds were characterized by ^1H , ^{13}C NMR, IR, and combustion analysis or HRMS. Solution molecular weight determinations indicate that the stibaindoles are monomeric in benzene solution.^[7]

An X-ray crystal structure determination was carried out on compound **5b**,^[8] and the structure is shown in Figure 3. The stibaindole ring is planar, as anticipated (no deviations greater than 0.03Å), and orthogonal to the plane of the phenyl ring. The shortest intermolecular Sb-Sb distance is 4.75Å. The highly pyramidalized geometry about the antimony atom, the bond distances, and bond angles are all in good agreement with other structurally characterized stibole derivatives.^[9]

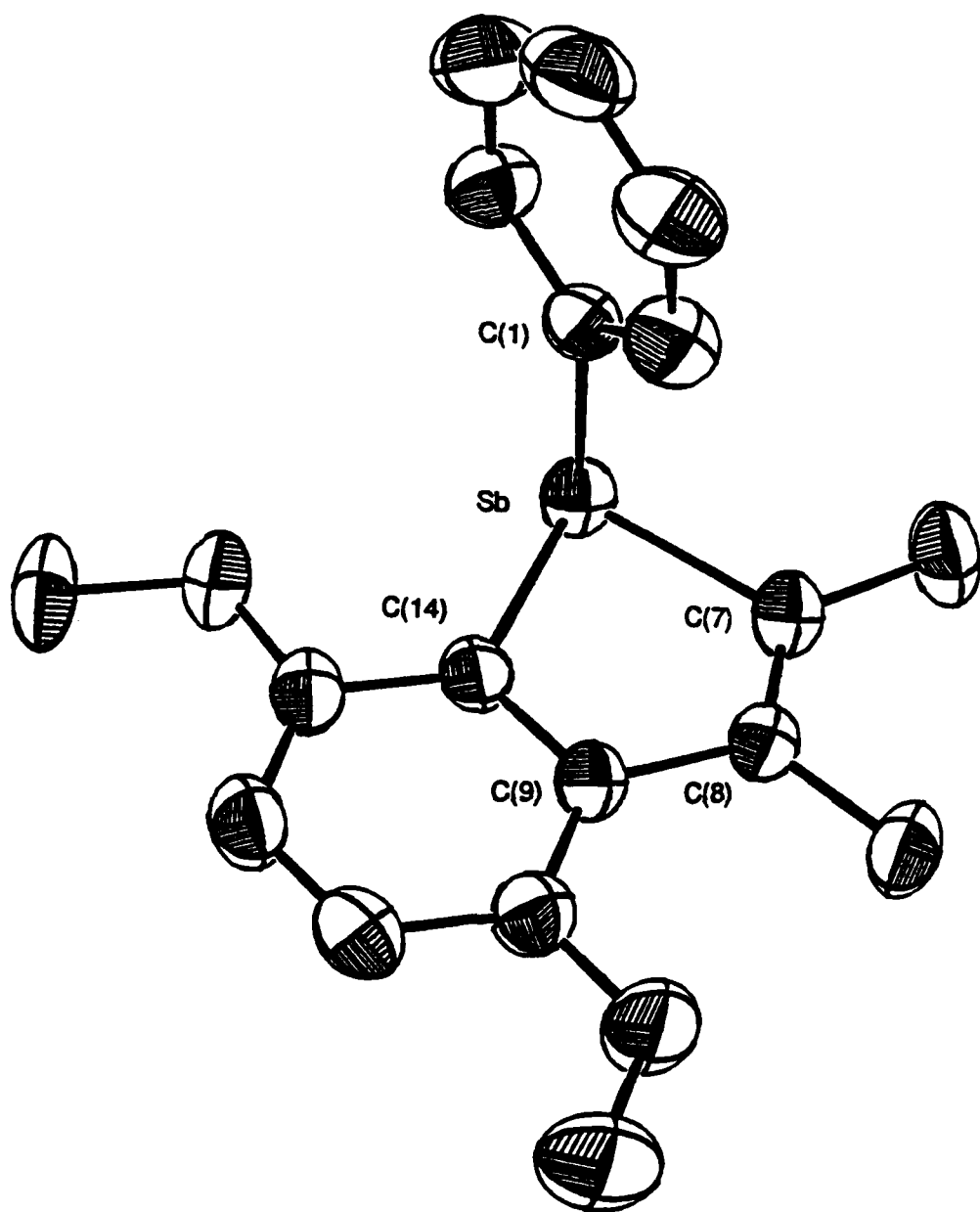
Figure 3

Molecular structure of **5b**. Bond Distances (Å): Sb-C1, 2.164(4); Sb-C7, 2.131(3); Sb-C14, 2.119(3); C7-C8, 1.334(4); C8-C9, 1.504(3); C9-C14, 1.387(4). Angles(°): C1-Sb-C7, 96.5(1); C1-Sb-C14, 95.5(1); C7-Sb-C14, 79.9(1).

Continued interest in heterocyclic compounds coupled with recent applications of main group organometallics in materials science provides a powerful incentive for the development of new and more selective synthetic routes to main group metallacycles. Results from this laboratory, and elsewhere, indicate that early transition metal complexes may play an important role in the discovery of new and valuable classes of main group compounds. Further investigations of the synthesis, reactivity and determination of the properties of other main group metallacycles are ongoing in our laboratory.

Experimental:

General procedure the preparation of Stibaindoles: The zirconacycle (1.00 mmol) was dissolved in 20 mL benzene in a nitrogen filled dry box. Either antimony trichloride (0.228 g, 1.00 mmol) or phenylantimony dichloride (0.270 g, 1.00 mmol), was added, all at once, as a solid. After 5 minutes, the flask was sealed with a septum, brought out of the dry box, and the solvent removed, *in vacuo*, on a Schlenk line. Zirconocene dichloride and the desired stibaindoles were the only species detectable in the crude reaction mixture as determined by ^1H NMR. The zirconocene dichloride was separated from the product by extraction with 10/1 hexanes/ether followed by rapid chromatography on either anhydrous MgSO_4 (**4a**, **5a**, **6a**) or alumina III (**4b**, **5b**, **6b**).



Footnotes and References:

- [*] Prof. Stephen L. Buchwald,
Richard A. Fisher
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
- Prof. Bruce M. Foxman
Department of Chemistry
Brandeis University
Waltham, Massachusetts 02254
- [**] This work was supported, in part, by the Office of Naval Research, and by Union Carbide, whom we gratefully acknowledge. SLB is a Fellow of the Alfred P. Sloan Foundation (1988-90), a Dreyfus Teacher-Scholar (1999-93), an American Cancer Society Junior Faculty Research Awardee (1987-89), an Eli Lilly Grantee (1988-89), and an awardee of the Union Carbide Innovation Recognition Program (1988, 89)
- [1] a) Aylett, B. J., *Organometallic Compounds, Fourth Edition, Part Two*, Wiley: New York, 1979. b) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Antimony*. Wiley: New York, 1970.
- [2] a) Atkinson, R. E. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, pp 539-560. b) Armitage, D. A. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, pp 614-617. c) Markl, G.; Hauptman, H.; Merz, A. J. *Organomet. Chem.* (1983), 249, 335.
- [3] To our knowledge, no previous reports of mono benzo-stiboles, stibaindoles, have appeared. Bis benzo-stiboles, stibafluorenes, are well known,^[3ab] and are readily synthesized using 2,2'-dilithiobiphenyl reagents.^[3c-e] a) Atkinson, R. E. *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, p 548. b) Aylett, B. J., *Organometallic Compounds, Fourth Edition, Part Two*, Wiley: New York, 1979, p 454. c) Meinema, H. A.; Martens, H. F.; Noltes, J. G.; Bertazzi, N.; Barbieri, R. J. *Organomet. Chem.* (1977), 136, 173. d) Meinema, H. A.; Noltes, J. G. *J. Organomet. Chem.* (1978), 160, 435. e) Hellwinkel, D.; Bach, M. J. *Organomet. Chem.* (1969), 17, 389. See also: f) Campbell, I. G. M. *J. Chem. Soc.* (1950); 3109. g) Campbell, I. G. M. *J. Chem. Soc.* (1952), 4448; h) Campbell, I. G. M. *J. Chem. Soc.* (1955), 1662 and references therein.
- [4] a) Erker, G.; Czisch, P.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem.* (1986), 98, 356. b) Erker, G.; Dorf, U.; Czisch, P.; Peterson, J. L. *Organometallics* (1986), 5, 668. c) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* (1983), 105, 3353. d) Skibbe, V.; Erker, G. *J. Organomet. Chem.* (1983), 241, 15. e) Erker, G.; Kropp, K. *Chem. Ber.* (1982), 115, 2437. f) Erker, G.; Kropp, K.; Krüger, C.; Chiang, A. P. *Chem. Ber.* (1982), 115, 2447. g) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* 1982, 224, 29. h) Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* (1980), 21, 1637. i) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* (1986), 108, 7411. j) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* (1987), 109, 7137. k) Buchwald, S. L.; King, S. K. manuscript in preparation.
- [5] a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* (1988), 110, 2310. b) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* (1988), 110, 2979. c) Buchwald, S. L.; Fisher, R. A.; Davis, W. M. *Organometallics* (1989), 8, 2082.