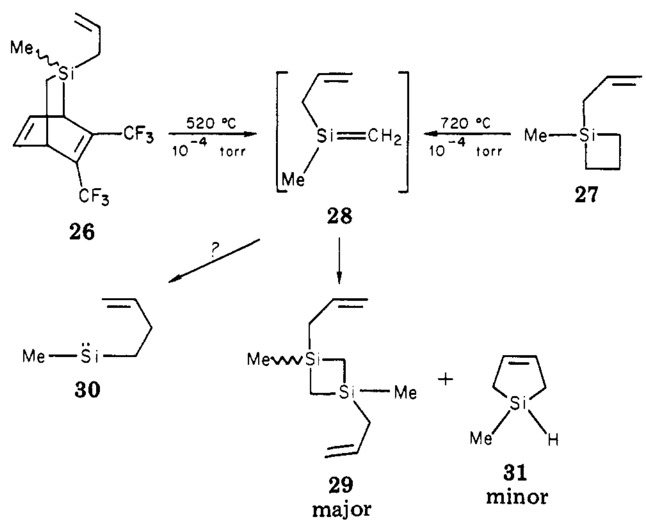
Scheme II



butadiene. After the hexafluoroxylene (74%), the major volatile product is silacyclohexene 24 (23%), the expected product of cycloaddition of 15 and the 1,3-diene. This result stands in stark contrast with the reported[6] copyrolysis of silacyclobutane 14 and 1,3-butadiene (vide supra). The flow pyrolysis of 22 also affords a small amount (5%) of 2-methyl-3-(dimethylsilyl)methyl-1,3-butadiene (25). Although we have previously observed this type of linear adduct from the reactions of silenes and butadienes,[11] it was conceivable that 26 arose from a stepwise radical addition of dimethylsilylene to dimethylbutadiene followed by hydrogen migration from carbon to silicon. This interpretation is rendered highly unlikely since pyrolysis of 22 in an excess of triethylsilane produced no 2,2-dimethyl-1,1,1-triethyldisilane, the normal product of silylene trapping by the Si-H bond.

Thus, as the evidence seems strong that pyrolysis of 22 does produce silene 15, the case for generation and rearrangement of 15 from silacyclobutane 14 is at best weakened. However, the picture is confused by the recent report of isomerization of 15 to Me_2Si: at 100 K.[7] This amazingly facile hydrogen migration is consistent neither with our results for 22 nor with the recent calculations of Schaefer[12] which predict that the activation energy for the essentially thermoneutral rearrangement $H_2Si{=}CH_2 \rightarrow H{-}\ddot{S}i{-}CH_3$ is about 40 kcal/mol.

In the hopes of finding a silene particularly predisposed to rearrange to a silylene, we have generated allylmethylsilene 28. This was accomplished by the flash vacuum pyrolyses (10^{-4} torr) of both silabicyclo[2.2.2]octadiene 26 and 1-allyl-1-methyl-1-silacyclobutane (27) (Scheme II). Pyrolysis of 26 (520 °C) was extremely clean, affording only hexafluoroxylene (83%) and 1,3-diallyl-1,3-dimethyl-1,3-disilacyclobutane (28, 85%). Pyrolysis of 27 required ~200 °C more than for 26, but still produced 29 in 27% yield. Thus, although silene 28 seemed an excellent candidate for rearrangement to silylene 30 through a cyclic six-electron process, it appears that this does not happen, as 28 simply dimerizes in the normal head-to-tail fashion. However, in the pyrolysis of 27 there is a small amount (2.3%) of 4-methyl-4-silacyclopentene (31) formed which may well arise from the cyclization of silylene 30 followed by transannular hydrogen migration. This interpretation is not demanded as it is also possible to imagine 31 arising from 28 through a di-π-methane sequence.

The many syntheses and structural proofs involved in this report will be incorporated with current work and complete details from ref 1 in a full paper.

Acknowledgment is made to the National Science Foundation and to Dow Corning Corporation for support of this work. We thank Procter and Gamble Co. for a fellowship to G.T.B. during this period. We are grateful to Professor Rob Conlin for sending us his report on the pyrolysis of 14 prior to publication.

Registry No. 2, 23290-58-6; **3**, 76410-87-2; **5**, 25261-26-1; **6**, 865-76-9; **7**, 3704-44-7; **8**, 78697-99-1; **11** isomer 1, 78698-00-7; **11** isomer 2, 78698-01-8; **12**, 78698-02-9; **13**, 78698-03-0; **15**, 38063-40-0; **21**, 78698-04-1; **22**, 78715-28-3; **23**, 1628-01-9; **24**, 78698-05-2; **26**, 78698-06-3; **27**, 3944-06-7; **28**, 78698-07-4; **29**, 78698-08-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; $F_3CC{\equiv}CCF_3$, 692-50-2.

---

[11] Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.

[12] Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 7644.

Rational Syntheses of Mixed Dialkylhaloboranes (R^AR^BBX) and Mixed Trialkylboranes ($R^AR^BR^CB$) via Stepwise Hydridation–Hydroboration of Alkyldihaloboranes

Surendra U. Kulkarni, D. Basavaiah, Marek Zaidlewicz, and Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received August 12, 1981

Summary: The stepwise hydridation of $R^ABBr_2{\cdot}SMe_2$ with $LiAlH_4$, followed by stepwise hydroboration of two different alkenes, provides a convenient route to the mixed organoboranes, $R^AR^BR^CB$, and to the products into which such mixed organoboranes can be transformed.

A rational synthesis of mixed dialkylhaloboranes (R^AR^BBX, 1) and trialkylboranes ($R^AR^BR^CB$, 2) has long eluded chemists. A convenient synthetic approach to such derivatives would greatly expand applications for the versatile organoboranes. We now wish to report the preparation of such mixed organoborane derivatives (1, 2) via the controlled hydridation of alkyldihaloboranes ($R^ABX_2{\cdot}SMe_2$, 3), followed by sequential hydroboration (eq 1).

$$\underset{\substack{3A,\ X = Cl\\ 3B,\ X = Br}}{R^ABX_2{\cdot}SMe_2} \rightarrow \underset{1}{R^AR^BBX{\cdot}SMe_2} \rightarrow \underset{2}{R^AR^BR^CB} \quad (1)$$

The increasing importance of organoboranes[1] as synthetic intermediates reveals a need for mixed dialkylhaloboranes and mixed trialkylboranes. Partially mixed trialkylboranes, $R^A{}_2R^BB$ (4), have been prepared by various methods.[2-6] Most of the earlier approaches involved use of the stable $R^A{}_2BH$ or R^BBH_2 reagents.[1,5] Recently, more general methods have been reported (eq 2).[4,6]

$$R^A{}_2BX \xrightarrow{MH} [R^A{}_2BH] \xrightarrow{\text{alkene B}} \underset{4}{R^A{}_2R^BB} \quad (2)$$

---

[1] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[2] Brown, H. C.; Negishi, E.; Gupta, S. K. *J. Am. Chem. Soc.* **1970**, *92*, 6648. For an early preparation of a partially mixed organoborane, *i*-Bu_2-*t*-BuB, see: Hennion, G. F.; McCusker, P. A.; Rutkowski, A. J. *J. Am. Chem. Soc.* **1958**, *80*, 617.

[3] Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1818.

[4] Maddocks, P. J.; Pelter, A.; Rowe, K.; Smith, K.; Subrahmanyam, C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 653.

[5] Whiteley, C. G. *J. Chem. Soc., Chem. Commun.* **1981**, 5.

[6] Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.*, in press.

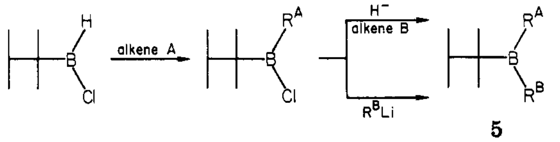
0276-7333/82/2301-0212$01.25/0

Table I. Preparation of Mixed Organoboranes and Their Carbon Analogs

$R^AR^BR^CB$ substituents			yield,[a] %	
R^A	R^B	R^C	ketone R^ACOR^B	carbinol $R^AR^BR^C$-COH
n-C_5H_{11}	n-C_6H_{13}	Br	84 (70)	
n-C_6H_{13}	n-$C_{12}H_{25}$	Br	87 (72)[b]	
n-C_6H_{13}	n-C_5H_{11}	n-C_8H_{17}		69[c]

[a] GC yields, determined by using a suitable internal standard. Isolated yields of >98% pure products are given in the parentheses. [b] Yield after double crystallization; >99% pure material, mp 47–48 °C. [c] Chemical purity 95%.

It is apparent that a general route to the totally mixed organoboranes, **2**, would require a practical synthesis of mixed dialkylhaloborane, **1**, or mixed dialkylboranes, R^AR^BBH. A general synthesis of totally mixed trialkylboranes, such as **5**, where R^C is the highly hindered 2,3-dimethyl-2-butyl (thexyl, Thx) group, has been reported recently (eq 3).[7,8] However, our attempts to obtain R^AR^BBH by the controlled elimination of 2,3-dimethyl-2-butene have thus far not been successful.[9,10] Consequently, we undertook to search for a simple procedure for preparing the hitherto inaccessible mixed dialkylhaloboranes (**1**) and mixed trialkylboranes (**2**).



(3)

5

Alkyldihaloboranes (**3**) are readily prepared by hydroboration of alkenes with dihaloborane–methyl sulfide ($HBX_2{\cdot}SMe_2$).[11,12] The addition of $LiAlH_4$ to **3** in the presence of alkene B provides $R^AR^B{}_2B$ (50%) and unreacted **3** (50%). Fortunately, the reaction of **3B** with the stoichiometric quantity of $LiAlH_4$ (borane:hydride ratio 1:1) in Et_2O affords the corresponding alkylbromoborane, $R^ABHBr{\cdot}SMe_2$ (**6B**).[13] The ^{11}B NMR spectrum of **6B** exhibits a doublet around δ 0.7 (J_{BH} 136 Hz); heteronuclear proton decoupling shows a single resonance. The IR spectrum exhibits an absorption at 2450 cm^{-1}, but none in the region of 1550 cm^{-1}, indicating the presence of a nonbridged boron hydride species (this implies both the existence of **6B** as a SMe_2 complex and the absence of R^ABH_2 dimer). The hydridation is relatively slow, requiring 3 h at 0 °C, followed by 1 h at room temperature.

Terminal alkenes are readily hydroborated by **6B** at 0 °C to provide the corresponding mixed dialkylbromoboranes (eq 4).[14] This procedure provides a simple synthetic route to the mixed dialkylbromoboranes, R^AR^BBBr.

$$\underset{\mathbf{6B}}{R^ABHBr{\cdot}SMe_2} \xrightarrow{\text{alkene B}} \underset{\mathbf{1B}}{R^AR^BBBr{\cdot}SMe_2} \qquad (4)$$

The absence of any significant disproportionation was established by converting the product, **1B**, into the borinate ester (R^AR^BBOMe, **7**) by treatment with methanol–sodium methoxide and converting the product into ketone, R^AR^BCO (**8**), via the DCME reaction (eq 5).[15] Examination of the product by GC analysis revealed the absence of $R^A{}_2CO$ and $R^B{}_2CO$ impurities (Table I).

$$1 \xrightarrow[\text{MeOH}]{\text{NaOMe}} \underset{\mathbf{7}}{R^AR^BBOMe} \xrightarrow[\text{2. [O]}]{\text{1. }Cl_2CHOMe,\ Et_3COLi} \underset{\mathbf{8}}{R^AC(=O)R^B} \qquad (5)$$

The reaction of **1** with 1 equiv of hydride ($^1/_4LiAlH_4$) in the presence of alkene C failed to provide the desired mixed organoborane **2**. Instead, the DCME reaction[16] revealed the presence of largely disproportionated boranes.[17] Possibly the presence of the byproduct, $LiAlBr_4$, facilitates redistribution.

This difficulty was overcome by treating the reaction mixture containing **1** with methanol–sodium methoxide, when **1** was converted into **7** and the salts were precipitated as sodium bromide and aluminum methoxide. Finally, **7** was converted into the mixed borane by treatment with alkene C and $LiAlH_4$ (eq 6).[2] GC analysis of the product revealed the presence of a single component (**9**, 69% yield based on **3**) in 95% purity.

$$7 \xrightarrow[^1/_3LiAlH_4]{\text{alkene C}} R^AR^BR^CB \xrightarrow[\text{2. [O]}]{\text{1. }Cl_2CHOMe,\ Et_3COLi} \underset{\mathbf{9}}{R^AR^BR^CCOH} \qquad (6)$$

Consequently, the present procedures make available both mixed R^AR^BBX and mixed $R^AR^BR^CB$ for the first time. The following procedures are representative.

To 3.18 g (10 mmol) of n-$C_6H_{13}BBr_2{\cdot}SMe_2$[11] was added 2.2 mL (30 mmol) of SMe_2 and 15 mL of Et_2O at 0 °C, followed by a slow addition of $LiAlH_4$ in Et_2O (2.5 mmol) with stirring. The reaction was allowed to proceed for 3 h at 0 °C, followed by 1 h at room temperature, and 1.2 mL (11 mmol) of 1-pentene was added at 0 °C. After 3 h, 4.48-mL solution of NaOMe in MeOH (17.5 mmol, 3.9 M) was added slowly. The mixture was stirred for 0.5 h at room temperature; solvents were removed under the aspirator vacuum (15 mmHg) and extracted with 2 × 15 mL of a 1:1 mixture of pentane and Et_2O. The solvents were removed, 15 mL of THF and 1.3 mL (5 mmol) of n-tetradecane (internal standard for GC analysis) were added, and the DCME reaction was carried out as described elsewhere.[15] The GC analysis on a 6 ft × $^1/_4$ in. column packed with 10% SE-30 on Chromosorb W indicated 84% yield of 6-dodecanone. From a 20-mmol scale reaction, 97% pure ketone was isolated in 70% yield: bp 85–87 °C (0.9 mm); $n^{20}{}_D$ 1.4315 [lit.[18] bp 125 °C (12 mm); $n^{20}{}_D$ 1.4339].

---

[7] Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 4542.

[8] Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919.

[9] Brown, H. C.; Kulkarni, S. U., unpublished results.

[10] Monoalkylborane–amine complexes have been prepared by the displacement of 2,3-dimethyl-2-butene, with amines, from thexylalkylboranes (ThxBRH): Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1972**, *94*, 5893.

[11] Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.

[12] The hydridation–hydroboration reaction works with alkyldichloroboranes as well. But the yields obtained from bromoboranes are better than those from chloroboranes. Besides, the alkyldibromoborane–methyl sulfide complexes can be prepared and handled more conveniently. Therefore, we employed mainly the alkyldibromoboranes during the present study.

[13] Attempted hydridation of **3B** with potassium triisopropoxyborohydride in THF formed the boronate esters, $R^AB(OR)_2$.

[14] A small amount of ether-cleaved product, R^AR^BBOEt (5–10%), was formed in this process. The ^{11}B NMR examination of the methanolysis product indicated the presence of >90% pure borinate ester **7** (δ 55), along with some boronate (δ 30, <5%) and borate (δ 18, <5%) esters as impurities.

[15] Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876.

[16] Brown, H. C.; Katz, J.-J.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 3968.

[17] The GC analysis revealed the formation of 5–10% R^AR^BCO (from R^AR^BBOEt) and several carbinols (from the corresponding redistributed boranes).

[18] Rabilloud, G. *Bull. Soc. Chim. Fr.* **1966**, 634.

For the preparation of **9**, the borinate ester **7** (10 mmol) was dissolved in 15 mL of THF and treated with 3.33 mmol of $LiAlH_4$ in the presence of 1.56 mL (10 mmol) of 1-octene at 0 °C. The reaction mixture was stirred for 3 h at room temperature, and the aluminum salts were removed by a slow addition of 0.65 g of H_2SO_4 (6.66 mmol) and 0.5 mL of water at 0 °C. The reaction mixture was extracted with pentane (2 × 20 mL), the combined organic extracts were dried over anhydrous K_2CO_3, solvents were removed under vacuum, and the resulting **2** was subjected to the DCME reaction.[16] GC analysis using n-dodecane as an internal standard showed a 69% yield of 7-pentylpentadecan-7-ol. Approximately 5% of impurities could be detected.

In summary, the bromine atoms of alkyldibromoboranes serve as effective and easily replaceable blocking groups for stepwise hydroboration. They can be sequentially replaced via the hydridation reaction.[6] Subsequent stepwise hydroboration provides the mixed dialkylbromoboranes and trialkylboranes. This process represents the first general synthesis for such hitherto inaccessible derivatives via the stepwise hydridation–hydroboration processes. Both the mixed organoboranes as well as the sequential hydridation–hydroboration process possess great synthetic potential, some of which we are presently exploring.

Acknowledgment. We thank the National Institutes of Health for the financial support through Grant GM 10937-19.

Registry No. **1B** ($R^A = n$-C_5H_{11}, $R^B = n$-C_6H_{13}), 79329-70-7; **1B** ($R^A = n$-C_6H_{13}, $R^B = n$-$C_{12}H_{25}$), 79357-03-2; **2** ($R^A = n$-C_6H_{13}, $R^B = n$-C_5H_{11}, $R^C = n$-C_8H_{17}), 79329-09-2; **3B** ($R^A = n$-C_6H_{13}), 79329-71-8; **6B** ($R^A = n$-C_5H_{11}), 79357-04-3; **6B** ($R^A = n$-C_6H_{13}), 79357-05-4; **7** ($R^A = n$-C_5H_{11}, $R^B = n$-C_6H_{13}), 79329-10-5; **7** ($R^A = n$-C_6H_{13}, $R^B = n$-$C_{12}H_{25}$), 79329-11-6; **8** ($R^A = n$-C_5H_{11}, $R^B = n$-C_6H_{13}), 6064-27-3; **8** ($R^A = n$-C_6H_{13}, $R^B = n$-$C_{12}H_{25}$), 79329-12-7; **9** ($R^A = n$-C_6H_{13}, $R^B = n$-C_5H_{11}, $R^C = n$-C_8H_{17}), 79329-13-8; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 1-dodecene, 112-41-4; 1-octene, 111-66-0.

Conversion of a Bridging Methylene Ligand to a Ketenylidene Moiety. Synthesis and Reactivity of $H_2Os_3(CO)_9(CCO)$

A. C. Sievert, D. S. Strickland, and J. R. Shapley*

Department of Chemistry and
Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801

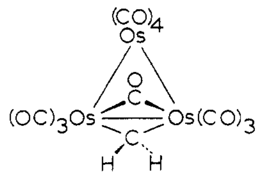
G. R. Steinmetz and G. L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

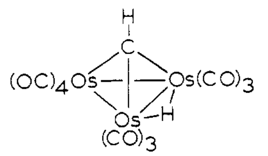
Received June 3, 1981

Summary: The product formed by thermally induced loss of carbon monoxide from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ is formulated as $H_2Os_3(CO)_9(\mu_3\text{-}1,2\text{-}\eta^2\text{-}CCO)$. The latter compound readily reacts with methanol to form the carbomethoxymethylidyne cluster, $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$.

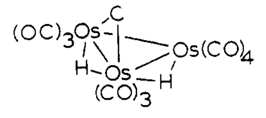
Recently a new triosmium methylene cluster, $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, was prepared by protonation of $[Os_3(CO)_{11}CHO]^-$ and was proposed to have structure I based on infrared and ^{13}C and ^1H NMR spectroscopy.[1]



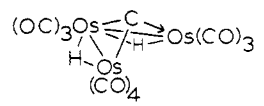
I



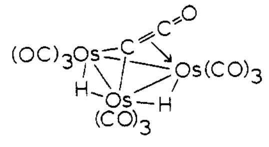
II



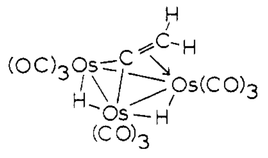
IIIa



IIIb



IV



V

The methylene cluster may also be obtained by treating $Os_3(CO)_{11}NCMe$ with CH_2N_2;[2] an X-ray crystallographic study of the trimethylsilyl derivative $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$ is consistent with structure I.[2] From hydrogenation of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ in refluxing benzene, a yellow byproduct having the stoichiometry "$Os_3(CO)_{10}(CH_2)$" was observed.[1] The same compound (mass spectrum, m/z 870 M^+ (^{192}Os); IR (ν(CO), C_6H_{12}) 2121 mw, 2086 s, 2064 vs, 2055 vs, 2034 mw, 2006 ms, 1994 m, 1984 mw) is prepared in 84% yield by refluxing a nitrogen-purged toluene solution of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.

Three formulations have been considered for "$Os_3(CO)_{10}(CH_2)$". The prospect of $HOs_3(CO)_{10}(\mu_3\text{-}CH)$ (II), analogous to the conversion of $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ into $H_3Os_3(CO)_9(\mu_3\text{-}CH)$,[3] is eliminated by the absence of a methylidyne ^1H NMR signal. A singlet hydride peak is seen at 25 °C (τ 29.73, CH_2Cl_2) and down to −80 °C. The $^{13}C\{^1H\}$ NMR spectrum of "$Os_3(CO)_{10}(^{13}CH_2)$" (90% ^{13}C enriched, from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}^{13}CH_2)$[2]) shows a singlet at δ 8.6 ($CDCl_3$, 25 °C); off-resonance decoupling establishes that the labeled carbon is not hydrogen substituted (the τ 29.73 signal is now a doublet, ^2J(C–H) = 2.9 Hz). A formula such as $H_2Os_3(CO)_{10}(C)$ seems unlikely, since compounds with either a divalent (IIIa) or a trivalent (IIIb) carbon atom are expected to be quite reactive and hence unstable. However, formulation of the yellow compound as a ketenylidene complex, $H_2Os_3(CO)_9(CCO)$ (IV), is consistent with all the available data. Thus, the IR spectrum (Nujol mull) shows a weak band at 1644 cm^{-1} which is assigned to ν(CCO) of the ketenylidene moiety. Furthermore, the ^{13}C NMR spectrum of a sample prepared from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ that was ca. 40% ^{13}C enriched at the carbonyls and 90% ^{13}C enriched at the methylene shows both the δ 8.6 singlet and a superimposed doublet (^1J(C–C) = 86 Hz) of ca. 40% total intensity. Simultaneously, a doublet with the same coupling constant, due to the ketenylidene carbonyl, appears at δ 160.3.

---

[1] Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278.

[2] Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.*, in press.

[3] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.