atmosphere was irradiated for 75 min in the photochemical reactor (temperature 25 °C).

Exchange Reactions between the Organotin Adducts and Me_3SnCl. C. Reaction of Methyl 2-Methyl-3-phenyl-3-(trimethylstannyl)propanoate (Isomer 3) with Me_3SnCl. Synthesis of Methyl 2-Methyl-3-phenyl-3-(dimethylchlorostannyl)propanoate (Isomer 11). Adduct 3 (5.42 g, 0.015 mol) was added to Me_3SnCl (3.58 g, 0.018 mol) with stirring under nitrogen. The reaction mixture was (a) left at room temperature for 20 h and (b) left for 12 h in the photochemical reactor. The ^1H NMR spectrum showed that under both reaction conditions a quantitative yield of compound 11 was obtained; solid; mp 88–90 °C (ethanol).

Acknowledgment. This work was carried out with financial support of CONICET (Argentina) and CIC (Province of Buenos Aires, Argentina). We wish to express our gratitude to the Alexander von Humboldt-Foundation (FRG) for a generous grant in equipment (J.C.P.). Helpful discussions with Prof. Dr. T. N. Mitchell (Dortmund University, FRG) are gratefully acknowledged.

Registry No. 1, 95798-64-4; 2, 95785-30-1; 3, 95798-65-5; 4, 95798-66-6; 5, 95798-67-7; 6, 95798-68-8; 7, 95798-69-9; 8, 95798-70-2; 9, 95841-18-2; 10, 95841-19-3; 11, 95798-71-3; 12, 95798-72-4; 13, 95798-73-5; 14, 95798-74-6; 15, 95798-75-7; 16, 95798-76-8; AIBN, 78-67-1; Me_3SnH, 1631-73-8; Me_2SnClH, 16561-41-4; Me_3SnCl, 1066-45-1; methyl (*E*)-2-methyl-2-butenoate, 6622-76-0; methyl (*E*)-2-methyl-3-phenyl-2-propenoate, 22946-43-6; methyl (*E*)-2-phenyl-2-butenoate, 50415-85-5; methyl (*E*)-2,3-diphenyl-2-butenoate, 36854-27-0.

A MNDO Study of Tin Radical Cations[1]

Michael J. S. Dewar,* Gilbert L. Grady,[2] and Daniel R. Kuhn

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received August 27, 1984

Radical cations derived from stannane and its alkyltrimethyl derivatives (Me_3SnR; R = Me, Et, *i*-Pr, *t*-Bu) have been studied, using MNDO. The calculated structures agree with experiment. Fragmentations of the radical cations have also been studied.

Introduction

ESR studies[3-5] of stannane radical cation 1 and its tetraalkyl derivatives have been reported in recent years. The results[3] for the tetramethyl derivative **2a** seemed to indicate a rather unusual C_{3v} structure (**3b**) with the tin and one methyl on the threefold axis of symmetry and the other three methyl groups coplanar with the tin. In the case of 1 both the C_{3v} structure **3a** and the C_{2v} structure **4a** have been observed.[3] No theoretical calculations seem as yet to have been reported for species of this kind other than some early ones for 1 by Hartmann et al.,[6] which, however, were based on an assumed geometry.

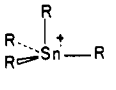
$SnH_4^{+\cdot}$
1

$Me_3SnR^{+\cdot}$
2a, R=Me
2b, R=Et
2c, R=*i*-Pr
2d, R=*t*-Bu

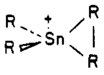
According to the Jahn–Teller theorem, 1 should undergo distortion from tetrahedral symmetry, like the analogous carbon species.[7] Here the distortion can be regarded in another light, as a way to maximize the bonding in an electron-deficient system where there are not enough electrons to form the requisite number of electron-pair bonds. In a molecule MX_4, M being a group 14[19] element, eight electrons are needed to form the four MX bonds. In the corresponding radical cation $MX_4^{+\cdot}$, only three such bonds can be formed. In cases of this kind, the optimum structure can usually be deduced by first forming the best possible set of two-electron bonds and then considering how the odd electron can best be used to bond the extra group. In the case of $MX_4^{+\cdot}$, six of the seven electrons will be used to form normal σ bonds to three of the ligands (X). Since a σ bond is stronger, the greater the s character of the AO's used to form it, the best arrangement is to use sp^2 hybrid AOs of M, the odd electron being left in a p AO. The fourth ligand (X^+) now has to be attached in the best way possible to the radical $\cdot MX_3$.

There are two possible solutions.

In the first type of structure 5, the singly occupied AO of M is used to form a one-electron bond to the fourth ligand, leading to a triangular pyramid of the kind **3b** postulated by Walther et al.[5] for **2a**. M should in fact lie above the base of the pyramid because this distortion will reduce the repulsions between the ligands and also strengthen the bond to the apical group by introducing s character into the p AO of M used to bind it. While an increase in s character of the apical AO of M will lead to a corresponding decrease in the s character of the three basal AOs, this should not significantly weaken the bonds formed by the latter.



3a R=H
b R=CH_3



4a R=H
b R=CH_3

The second alternative is to fuse the fourth ligand (X^+) into one of the existing CX bonds, interaction of the empty

---

[1] Part 71 of a series of papers reporting applications of quantum mechanical models to chemical problems. For part 70, see: Dewar, M. J. S. *J. Phys. Chem.*, in press.

[2] On sabbatical leave from St. Michael's College, Winooski, VT 05454.

[3] Hasegawa, A.; Kaminaka, S.; Wakabayashi, T.; Hayashi, M.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1199.

[4] Symons, M. C. R. *J. Chem. Soc. Chem. Commun.* **1982**, 869.

[5] Walther, B. W.; Williams, F.; Lau, W.; Kochi, J. K. *Organometallics* **1983**, *2*, 688.

[6] Hartmann, H.; Papula, L.; Strehl, W. *Theor. Chim. Acta.* **1971**, *21*, 69.

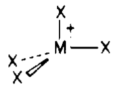
[7] (a) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432. (b) Pople, J. A. *Int. J. Mass. Spectrom. Ion. Phys.* **1976**, *19*, 89. (c) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017.

0276-7333/85/2304-1041$01.50/0

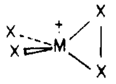
AO of X^+ with the two-center MX bond MO leading to a three-center two-electron bond and a C_{2v} (or C_{2v}-like) structure. The resulting structure can be regarded as a σ complex proper[8] (**6**) between X_2 acting as the donor and $X_2M^{+}\cdot$ as the acceptor.

If the apical (acceptor) group in a σ complex has an occupied p or π orbital available, back-coordination may further stabilize it, just as in the case of a π complex.[9] However, back-coordination is likely to be much less important in σ complexes than in π complexes because antibonding (σ^*) MOs are usually much higher in energy than analogous π MOs and should therefore be much less effective acceptors of electrons. Forward coordination is also more difficult in the case of a σ complex because σ electrons cannot easily interact with AOs of other atoms, being tucked away between the nuclei they are bonding. At least one of the basal atoms in a σ complex is therefore usually hydrogen, this being the smallest atom.

Which type of structure, **5** or **6**, is the more stable will depend on whether or not the difference in bond energy between the three-center (MX_2) bond in **6** and a normal two-center bond (MX) is greater than the bond energy of the one-electron MR bond in **5**. Since hydrogen is adept at forming three-center bonds, it is not surprising to find type **6** structures in methane and stannane. Steric considerations, on the other hand, would seem to preclude the formation of such a structure in **2a**, and therefore it seems reasonable that a type **5** structure is preferred.



5



6

Recent work[11] has led to the development of parameters for tin in the MNDO SCF MO procedure.[12] These have been used successfully in calculations for a variety of organotin compounds.[10] We have now used this approach to study the radical cation **1**, derived from stannane, and also alkyltrimethyl derivatives of **1** where the alkyl group is methyl (**2a**), ethyl (**2b**), isopropyl (**2c**), or *tert*-butyl (**2d**).

Procedure

The calculations were carried out by using the spin-unrestricted version[13] (UMNDO) of MNDO[11] as implemented in the MOPAC[14] package of computer programs. The geometries were fully optimized by the derivative procedures included in MOPAC. Transition states were located by the reaction coordinate method[15] and refined by minimizing the scalar gradient of the energy.[16] All stationary points were characterized by calculating force constants.[16]

Results and Discussion

In agreement with experiment,[3] two minima **3a** and **4a** were found for **1**, corresponding, respectively, to the structures **5** and **6** considered above. Their calculated heats of formation are shown in Table I and their geometries in Figure 1.

Table I. UMNDO Calculated ΔH_f's of SnH_4^+ (kcal/mol)

struct	ΔH_f
3a	291
4a	287
SnH_2^+-H_2	242

Table II. UMNDO Calculated ΔH_f's (kcal/mol) of Tetraalkyltin Radical Cations

struct	ΔH_f	struct	ΔH_f
3b	206	**8b**	189
8a	194	**9b**	201
9a	201		

Table III. UMNDO Calculated Geometric Parameters for 3b, 8a, and 8b

	bond lengths[a,b]		bond angles[c]	
struct	R_a-Sn	Me_b-Sn	Me_a-Sn-Me_b	Me_b-Sn-Me_b
3	2.34	2.07	101	117
8a	2.37	2.07	101	116
8b	2.47	2.07	103	117

[a] The subscripts a and b stand for apical and basal, respectively. [b] In angstroms. [c] In degrees.

The C_{2v} structure **4a** is predicted to be the more stable of the two by ~4 kcal/mol. As expected and as Figure 1 (**4a**) shows, the two hydrogen atoms involved in the three-center two-electron bond are close together (1.31 Å), the corresponding HSnH bond angle is small (46°), and the corresponding SnH bonds are long (1.69 vs. 1.59 Å in stannane). As in the case of the analogous radical cation from methane, this structure can be regarded as being derived from stannyl radical ($H_3Sn\cdot$) by replacing one hydrogen atom by the pseudoatom H_2^+.

In the less stable structure **3a**, the bond to the apical H is lengthened by 31% (2.01 vs. 1.59 Å) relative to that in stannane. As the arguments above suggest, the angle (92°) between the apical hydrogen atom and each basal hydrogen atom is slightly greater than 90°.

UMNDO predicts **4a** to decompose readily to $SnH_2^{+}\cdot$ and H_2, the reaction being very exothermic ($\Delta H = -46$ kcal/mol) and requiring virtually no activation ($\Delta H^{\ddagger} \approx 0.1$ kcal/mol).[17] The C_{3v} structure **3a** may also decompose with expulsion of H_2 via **4a**. The conversion of **3a** to **4a** occurs through a transition state of C_s symmetry (Figure 2) with a calculated enthalpy of activation of less than 0.1 kcal/mol.

It is of course true that no treatment of this type can claim accuracy to within the small values (0.1 kcal/mol) obtained above for the activation barriers. We may conclude, however, that these results are consistent with a low barrier for interconversion of **3a** and **4a** and that the C_{3v} structure **3a** is likely to decompose via the C_{2v} structure **4a**. The experimental (ESR) evidence[3] indicates, however, that **3a** and **4a** are both reasonably stable species, at least in a freon matrix, irradiation of stannane leading initially to a mixture of the two. Since the decomposition of **4a** must have a large positive volume of activation, it may take place less readily in a rigid matrix. Our calculations refer of course to the gas phase.

As expected on the basis of the arguments given above, no minimum corresponding to a C_{2v} (type **6**) structure

---

(8) I.e., a species involving a dative bond in which the donor is a filled σ MO; cf.[9] the term has unfortunately been used in a most improper way to describe the Wheland intermediate in aromatic substitutions.

(9) Dewar, M. J. S. *Bull Soc. Chim. Fr.* **1951**, *18*, C71.

(10) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 6773.

(11) Dewar, M. J. S.; Grady, G. L.; Stewart, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(13) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(14) QCPE Publication 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

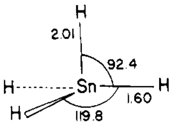
(15) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1971**, *93*, 4290.

(16) (a) McIver, J. W., Jr.; Komornicki, J. *J. Am. Chem. Soc.* **1972**, *94*, 2625. (b) McIver, J. W., Jr.; Komornicki, J. *Chem. Phys. Lett.* **1971**, *10*, 303.

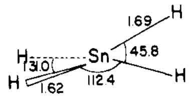
(17) Though **4a** has been shown to be a minimum on the UMNDO surface by a force constant calculation, The very low energy of activation and the extremely small (probable) geometric displacement has made it difficult to locate. The activation energy was estimated from a reaction path calculation.

Table IV. UMNDO Calculated Geometric Parameters for 9a and 9b

	bond lengths			bond angles			
struct	Me_a–Sn	Me_b–Sn	R–Sn	Me_a–Sn–Me_b	Me_b–Sn–Me_b	R–Sn–Me_a	R–Sn–Me_b
9a	2.35	2.07	2.10	100	116	99	117
9b	2.35	2.07	2.14	99	114	103	116



3a



4a

Figure 1. UMNDO calculated geometries for the C_{3v} (**3a**) and C_{2v} (**4a**) structures of the stannane radical cation.

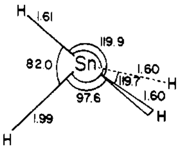


Figure 2. The UMNDO transition state (C_s symmetry) for interconversion of **3a** and **4a**.

could be found on the potential energy (PE) surface for **2a**. In agreement with experiment, the only stable species was a pyramidal C_{3v} (type **5**) structure, **3b**, analogous to the structure attributed to the neopentane radical cation on the basis of its ESR spectrum.[18] The calculated heats of formation and geometry of **3b** are shown in Tables II and III. As expected, the apical Sn–C bond is much longer than the basal ones (2.33 vs. 2.07 Å). The bond angle (100°) between the apicals and basal bonds is greater than in the case of the parent ion **3a**, as would also be expected, because the repulsions between the apical and axial methyl groups in **3b** must be greater than those between the apical and axial hydrogen atoms in **3a**. The angles (117°) between the axial bonds in **3b** are correspondingly less than 120°.

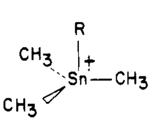
Similar conclusions follow from our calculations for the triethyl (**2b**) and triisopropyl (**2c**) derivatives of **2a**. The only stable species found were again of type **5**. Here, however, two isomers of this kind are possible, one (**8**) with alkyl and the other (**9**) with methyl, in the apical position. Since the strengths of C–alkyl bonds fall in the order Me > Et > *i*-Pr > *t*-Bu, the rule indicated above predicts **8** to be more stable and this indeed is what we found. The heats of formation calculated for **8a** and **8b** (Table II) are less positive than those for **9a** and **9b**. Their geometries are shown in Tables III and IV. Note that the apical bond lengths and the apical–axial bond angles increase along the series **3b** > **8a** > **8b**. This of course would be expected because the repulsions between the apical and axial groups will increase with their size.

Table V. UMNDO Calculated Heats (kcal/mol) for the Products of the Fragmentation of 3b, 8a, and 8b

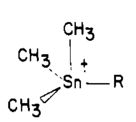
struct	ΔH_f	struct	ΔH_f
Me_3Sn^+	187	CH_3CH_2	11
CH_3	25	$(CH_3)_2CH$	-1

Table VI. Heats (kcal/mol) of Reaction and Activation for Reaction 1

R	ΔH_{rxn}	ΔH
CH_3	6	8
CH_3CH_2	4	6
$(CH_3)_2CH$	-3	1



8a R=CH_2CH_3
b R=$HC(CH_3)_2$

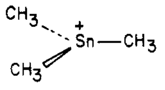


9a R=CH_2CH_3
b R=$HC(CH_3)_2$

As noted above, **4a** is predicted to decompose by loss of H_2. Type **5** species, when conversion to type **6** does not occur, are expected to decompose by loss of the apical group as a radical, the bond linking this to tin being formed in effect by only one electron; i.e.

$$R'_3SnR^{+\cdot} \rightarrow R'_3Sn^+ + \cdot R \qquad (1)$$

Table V shows the calculated (UMNDO) heats of formation of trimethylstannyl cation (**7**) and the methyl, ethyl,



7

and isopropyl radicals. The corresponding heats of reaction for dissociation of **3b**, **8a**, and **8b** into them are given in Table VI. As expected, the heats of reaction, corresponding to the bond strengths of the apical bonds, are quite small.

Symons has found[4] that upon slight warming of a freon matrix containing **2a**, the ESR signal of the radical cation disappeared and was replaced by that of methyl radical ($CH_3\cdot$), presumably generated by fragmentation (eq 1). The calculated (UMNDO) activation energy for this reaction is indeed only 8 kcal/mol, explaining nicely the experimental observations.

Table VI also shows the activation energies calculated for loss of the apical group in reaction 1. Again as expected, the values decrease with increase in the size of the axial group, Me > Et > *i*-Pr. Extrapolation suggests that the value for **8c** should be negative and indeed no minimum could be found on the potential surface for the trimethyl-*tert*-butylstannane radical cation **2d**. Curiously enough Walther et al.[5] obtained ESR signals for **2d** in a freon matrix although none were observed for the analogous ethyl (**2b**) and isopropyl (**2c**) derivatives. On any basis, **2d** would be expected to be the least stable of the three. This seems to support our suggestion that disso-

---

(18) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891.

(19) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

ciation reactions of this kind may be greatly retarded in solid matrices. The degree of retardation could well depend greatly on the experimental conditions.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Contract No. F49620-83-C-0024, and the Robert A. Welch Foundation, Grant No. 126. Calculations were carried out with a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. 1, 93529-24-9; **2a**, 84494-88-2; **2b**, 96041-38-2; **2c**, 96041-39-3; **2d**, 85005-13-6.

Hydrostannation of 1,1-Bis(trimethylstannyl)ethylene and Some Related Olefins: First Steps toward Constructing a Karplus-Type Curve for ^3J(Sn–Sn)

Terence N. Mitchell,* Werner Reimann, and Christa Nettelbeck

Abteilung Chemie, Universität Dortmund, Postfach 500 500, 4600 Dortmund 50, Federal Republic of Germany

Received July 5, 1984

Four trimethylstannyl-substituted alkenes, $Me_3SnCR{=}CH_2$ (R = Ph, *t*-Bu, Me_3Si, Me_3Sn), were hydrostannated by trimethyltin hydride. Though all four olefins reacted, that with R = *t*-Bu was consumed only very slowly. The major product was, as expected, the 1,2-distannylalkane $RCHSnMe_3CH_2SnMe_3$; however, for R = Me_3Sn 40% of the regioisomer $(Me_3Sn)_2CRCH_3$ was obtained compared with at most 5% in the other cases. On the basis of NMR data (^1H, ^{13}C, ^{29}Si, ^{119}Sn) for distannylalkanes and for $Me_3SnCH_2CH_2SiMe_3$ the preferred rotamers in solution ($CDCl_3$) at room temperature have been determined. The value of ^3J(Sn–Sn) corresponding to a dihedral angle of 180° is ca. 1100 Hz, while an angle of 90° apparently corresponds to a value near zero: values of this magnitude are shown by allene–hexamethylditin adducts. First results on bromodemethylated derivatives show that the effect of increasing the electronegativity of the tin moiety is not straightforward.

Introduction

Though the hydrostannation of alkynes and olefins containing only organic substituents was subject to extensive study some 20 years ago,[1] organotin-substituted alkynes and alkenes were at that time neglected. In 1976, Bulten[2] reported that the hydrostannation of vinyltrimethyltin with trimethyltin hydride gave a mixture of 1,1- and 1,2-distannylalkanes (eq 1). The corresponding triethyltin compounds gave 23% of the 1,1 and 77% of the 1,2 compound. At that time the formation of the 1,1 compounds was described by the authors as "unexpected".

$$\begin{aligned} &Me_3SnCH{=}CH_2 + Me_3SnH \rightarrow \\ &\qquad \underset{60\%}{Me_3SnCH_2CH_2SnMe} + \underset{40\%}{(Me_3Sn)_2CHCH} \quad (1) \end{aligned}$$

We were later able to show that hydrostannation of stannylalkenes, $RCH{=}CHSnMe_3$, generally leads to 1,1-distannylalkanes,[3] that hydrostannation of stannylalkynes $RC{\equiv}CSnMe_3$ normally gives 1,1-distannyl-1-alkenes, and that these in turn undergo hydrostannation to give 1,1,1-tristannylalkanes (eq 2–4).[4] In the course of this work, we were able indirectly to prepare the simplest 1,1-distannylalkene, 1,1-bis(trimethylstannyl)ethylene for the first time. We report here on its hydrostannation and that of some closely related stannyl olefins.

$$RCH{=}CHSnMe_3 + Me_3SnH \rightarrow RCH_2CH(SnMe_3)_2 \quad (2)$$

$$RC{\equiv}CSnMe_3 + Me_3SnH \rightarrow RCH{=}C(SnMe_3)_2 \quad (3)$$

$$RCH{=}C(SnMe_3)_2 + Me_3SnH \rightarrow RCH_2C(SnMe_3)_3 \quad (4)$$

Work in recent years has shown that a Karplus-type dependence of three-bond coupling constants on the subtended dihedral angle is quite normal;[5] in the field of organotin chemistry, Doddrell, et al.[6] established such a dependence for ^3J(SnCCC) some years ago, while Quintard et al.[7] have recently proposed an equation for the angle dependence of ^3J(SnCCD) and thus indirectly for ^3J(SnCCH). The lack of experimental data has previously precluded a search for an angle dependence of ^3J(SnCCSn), but the present work has provided some tin data which can, in combination with proton and carbon-13 data, be used for this purpose.

Spectral Data

These were obtained by using a Bruker AM-300 NMR spectrometer (^1H 300 MHz, other nuclei at corresponding frequencies) and are presented in Tables I–IV. Table I contains proton chemical shifts, Table II proton–proton and tin–proton coupling constants, Table III carbon-13 data, and Table IV tin-119 data.

With two exceptions, measurements were made at room temperature with solutions (^1H 5% v/v; other nuclei 50% v/v) of the compounds in $CDCl_3$; for ^{29}Si the DEPT technique[8] was used and for ^{119}Sn inverse gated decoupling. While the data contained in Tables III and IV could be

---

[1] Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.

[2] Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *111*, C33.

[3] Mitchell, T. N.; el-Behairy, M. *J. Organomet. Chem.* **1979**, *172*, 293. Mitchell, T. N.; el-Behairy, M. unpublished results.

[4] Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47.

[5] Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield Beach, 1982; p 114.

[6] Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpit, M.; Lee, C. H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

[7] Quintard, J.-P.; Degeuil-Castaing, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 41.

[8] Bendall, M. R.; Doddrell, D.; Pegg, D. T. *J. Magn. Reson.* **1983**, *53*, 229.

0276-7333/85/2304-1044$01.50/0