41. Ring-Opening Reaction of a Dihydrozirconafuran (= 2,5-Dihydro-1,2-oxazirconole): An Equilibrium Studied by NMR Methods, and Its Chemical Consequences

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The dihydrozirconafuran **3** (2,2-di(cyclopenta-2,4-dien-1-yl)-2,5-dihydro-5,5-dimethyl-3,4-bis(trimethylsilyl)-1,2-oxazirconole) is a valuable synthetic equivalent to the 14-electron fragment Cp_2Zr[1]). The reactions of this metallacycle suppose an equilibrium with an 'opened' form [$ZrCp_2(RC{\equiv}CR)$(acetone)], the latter paving the way to numerous ligand replacements. In a solution containing the dihydrozirconafuran and acetone, these reactions are reversible and degenerate, and can be studied by NMR methods: by two-dimensional spectroscopy and by observation of the isotope-induced chemical shifts that occur upon incorporation of (D_6)acetone into the metallacycle. The findings give an indirect proof of the described equilibrium.

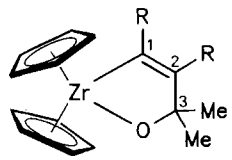
Introduction. – Most alkyne complexes of zirconocene coordinate a solvent or ligand molecule for the sake of electronic and coordinative saturation. The bis(trimethylsilyl)-ethyne zirconocene complex, *e.g.*, was prepared with tetrahydrofuran [1], pyridine [2], and acetone [3] as additional ligand L (see **1**–**3**; trimethylphosphane was also used [4]).

$[ZrCp_2(Me_3SiC{\equiv}CSiMe_3)L]$ **1** L = THF
2 L = pyridine
3 L = acetone

These complexes are valuable building blocks within organometallic reactions because they can be used to introduce the 14-electron fragment Cp_2Zr [5] under mild conditions [6]. Interestingly, it does matter whether **1**, **2**, or **3** are employed as sources of 'zirconocene' fragment in such reactions. *E.g.*, the reaction of buta-1,3-diynes $RC{\equiv}C{-}C{\equiv}CR'$ (R,R' = $SiMe_3$, Ph, *t*-Bu) with the THF complex mainly ended up in dinuclear alkynyl complexes [6] [7], the central single bond of the butadiynes was cleaved. Upon reaction with the pyridine or the acetone complex, metallacyclic cumulenes of one or two diyne molecules were formed instead [6] [8].

The earlier investigations [1–3] showed that L in **1**–**3** is easily exchangeable. Upon dissolution of the complexes in the corresponding deuterated solvents, L was liberated, a process detectable in the ^{1}H-NMR spectrum. With the acetone complex, this was some-

[1]) Throughout this paper, Cp = η^5-C_5H_5.



3 R = $SiMe_3$
4 R = Ph

what surprising, since X-ray crystallography [3] proved the alkyne and the acetone ligand to be covalently bound together (dihydrozirconafuran structure **3**). Therefore, a detailed NMR study on the solution behavior of **3** and the acetone exchange was carried out.

Results of NMR Investigations. – First, a complete assignment of all resonances was performed. The analysis of the ^{1}H-NMR spectrum by an NOE difference experiment is straightforward: Saturation of the acetone Me *s* (1.41 ppm) leads to an enhancement of the cyclopentadienyl (6.11 ppm) and the 2-(trimethylsilyl) (0.30 ppm) *s*'s (for numbering, see *Formula* **3**). By examination of the heteronuclear couplings (^{13}C and ^{29}Si satellites in the ^{1}H-NMR spectrum, ^{1}H-coupled ^{13}C- and ^{29}Si-NMR spectra) and by selective ^{13}C,^{1}H-correlation experiments [9], all other resonances can be assigned, except those of the two olefinic C-atoms. The low-field signal should, as commonly found in transition-metal vinyl or alkynyl systems, stem from C(1), and this is supported by the earlier [3] performed ^{13}C,^{1}H COLOC experiment. The data are compiled in the *Table*.

Table. *NMR Data of the Acetone Complex* **3**

	δ/ppm		J/Hz	Δ/Hz[a])	Δ/ppb[a])
	C_6D_6 solution	solid state			
^{1}H-NMR					
Me_3Si–C(1)	0.19		^1J(H,C) = 118		
			^2J(H,Si) = 6.0		
Me_3Si–C(2)	0.30		^1J(H,C) = 119	+1.2	+3.0
			^2J(H,Si) = 6.3		
2 Me–C(3)	1.41		^1J(H,C) = 125		
Cp	6.11		^1J(H,C) = 171		
^{13}C-NMR					
C(1)	213.3	213.9		−2.6	−26
C(2)	193.3	193.1			
C(3)	90.5	90.3	^2J(C,H) = 4	+25.1	+250
Me_3Si–C(1)	5.4	6.4	^1J(C,H) = 118		
			^1J(C,Si) = 49		
Me_3Si–C(2)	4.5	6.4	^1J(C,H) = 119	+3.1	+30
			^1J(C,Si) = 50		
2 Me–C(3)	29.0	31.3	^1J(C,H) = 125	+94.0	+934
		30.1	^3J(C,H) = 4		
Cp	113.4	114.7	^1J(C,H) = 171		
		114.3			
^{29}Si-NMR					
Me_3Si–C(1)	−22.9		^2J(Si,H) = 6.0		
Me_3Si–C(2)	−20.0		^2J(Si,H) = 6.3		

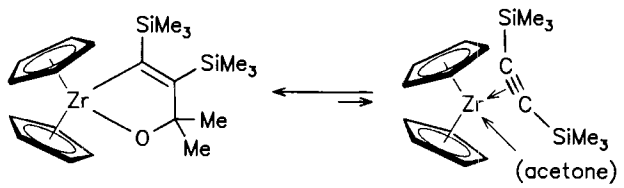
[a]) Δ is the shift occurring on replacement of the 2 Me–C(3) by 2 CD_3–C(3). A high-field shift is regarded to be positive [11], hence $\Delta = \delta(\mathbf{3}) - \delta((D_6)\text{-}\mathbf{3})$.

To link the solution NMR to the crystallographic data, a solid-state ^{13}C-NMR spectrum of **3** was recorded. No significant deviations from the solution data were found (*Table*), which means that the latter represent the same constitution as determined for the solid state. An interesting feature is the splitting of the cyclopentadienyl and 2 Me–C(3) resonances. This clearly resembles the lack of molecular symmetry in the crystalline state (point group C_1 in the X-ray analysis [3]): the five-membered ring is not planar, whereas in solution, an effective C_s symmetry is found, probably caused by rapid interconversion of the two possible enantiomers.

The solid-state spectrum is consistent with the assignment of the two olefinic C-atoms. The spinning sideband pattern of the low-field resonance, C(1), spreads over 230 ppm, whereas this pattern belonging to C(2) is less wide. The greater chemical-shift anisotropy of the former is likely to be due to the directly attached transition-metal centre.

The experiments conducted so far show that the dihydrozirconafuran is retained in solution. However, the chemical behavior of **3** [3] [6] suggests an equilibrium between the cyclic and another form, where no bond exists between the alkyne and the acetone ligand (*Scheme 1*). If one could establish a reversible exchange of the acetone, this would prove the existence of this equilibrium, because it required the 'breaking and making' of the C(2)–C(3) single bond.

Scheme 1



3

For this purpose, we prepared mixtures of the complex **3** and acetone, avoiding a great excess of the latter (see *Exper. Part*), and recorded the ^{1}H- and ^{13}C-NMR spectra in the temperature range from 23 to 67°. No changes in the lineshape are observed, all the lines of the probably exchanging groups remain sharp. The exchange – if any exists – must be slow on the NMR time scale. Thus, the two-dimensional NOE experiment (NOESY), being capable of detecting dynamic processes [10] even in the slow-exchange regime, was employed in the investigation. At room temperature, cross-peaks indicating chemical exchange could not be unambiguously identified, even with a mixing time of 2.5 s. But at 45°, exchange peaks between the Me resonances of the complexed and the free acetone are indeed detectable (*Fig. 1*).

For further experiments, we prepared a similar mixture of complex **3** and (D_6)acetone. Their ^{1}H-NMR spectrum exhibits two *s*'s for the Me groups of the acetone, one at 1.41 ppm (complexed) and one at 1.58 ppm (free). The integrals of both resonances, taken together, represent the required six protons. This means that in part acetone was replaced by (D_6)acetone (*Scheme 2*).

The most convincing proof of the incorporation of (D_6)acetone into complex **3** is the simultaneous observation of both isotopomers **3** and (D_6)-**3** in the mixture. The isotope

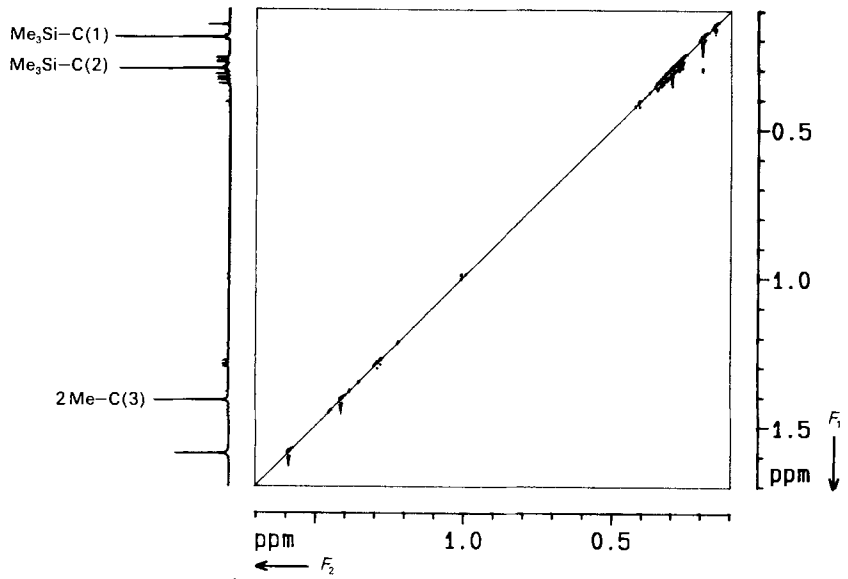
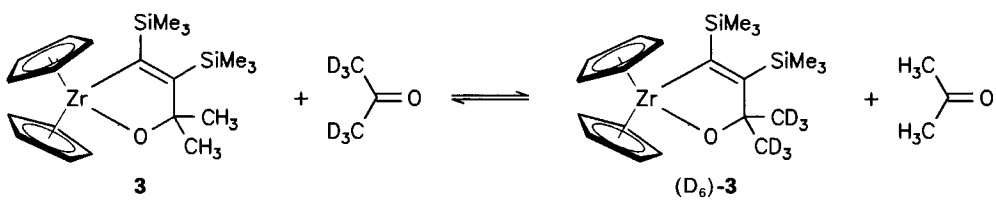


Fig. 1. *Phase-sensitive* (TPPI) *^{1}H-NOESY spectrum of the system* **3***/acetone* (*Sample A*) *at 45°*. Mixing time 2.5 s, width in both dimensions 690 Hz, 256 exp. in t_1, final data matrix 1024 × 512 points. The cross-peaks drawn above the diagonal (positive phase) indicate chemical exchange, those below indicate NOE (negative phase). The resonance of free acetone (benzene solution) appears at 1.58 ppm (additional signals on the diagonal arise from decomposition products).

Scheme 2



effect on the ^{13}C- and ^{1}H-NMR chemical shifts leads to a separation between the resonance lines of **3** and (D_6)-**3**. This D-induced shift Δ (see *Table*) is maximal for the methyl groups themselves (*ca.* 1 ppm high-field), but is still detectable at the resonances of C(1) and the 2-(trimethylsilyl) group (*Fig. 2*). This line splitting is maintained at elevated temperatures, a fact again indicating that the exchange occurs slowly with respect to the NMR time scale.

The same line splitting is observed if acetone is added to a solution of independently prepared (D_6)-**3**. It is also detected with mixtures of the complexes **3** and (D_6)-**3**. This proves that the splitting stems rather from the intrinsic isotope effect than from another effect. The shift for C(3) is positive[2]), whereas it is negative for the carbonyl

[2]) For the sign convention, see [11] and *Table*.

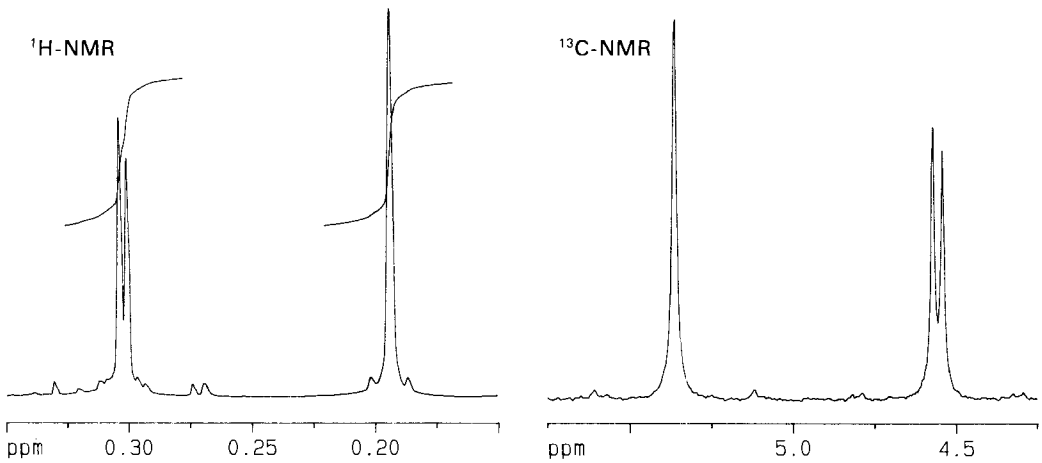
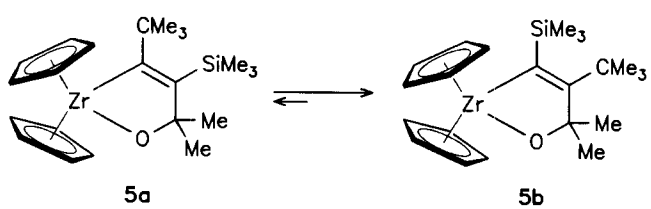


Fig. 2. *^{1}H- and ^{13}C-NMR Spectra* (high-field region) *of the system* **3**/*(D_6)acetone* (*Sample B*). The splitting of the Me_3Si–C(2) resonance is due to the intrinsic isotope effect.

C-atom in several ketones, carboxylic acids, and derivatives thereof [12] ((D_6)acetone: $^2\Delta^{13}C(D) = -329$ ppb). The complexed acetone, therefore, must be rather different from the free molecule which again makes the existence of a covalent bond between C(3) and the alkyne ligand most likely also in solution.

Discussion. – The presented results prove that an equilibrium according to *Scheme 1* indeed exists. It is shifted almost completely to the left-hand side, because only the cyclic form could be detected by spectroscopic methods employed in this and an earlier [3] work. Nevertheless, it is the basis for most reactions observed with **3**, *e.g.* alkyne exchange or ligand replacement. If a dihydrozirconafuran is prepared with the unsymmetrically substituted 1-(*tert*-butyl)-2-(trimethylsilyl)ethyne, two regioisomers are possible (*Scheme 3*).

Scheme 3



5a **5b**

Actually, both isomers **5a** and **5b** were found [13], and upon keeping the mixture in solution for some time, the ratio of the two forms changes from the initial value of 4:1 (representing the formation rates) to 1:3, the 1-(trimethylsilyl) form being the thermodynamically more stable. This isomerization is most likely to proceed *via* a ring-opening, followed by either a 180° turn of the now η^2-coordinated alkyne, or ligand exchange and subsequent ring closure, a process requiring an equilibrium analogous to that described for **3**.

For five-membered metallacycles, the lability of the C(2)–C(3) bond is not an uncommon feature. Metallacyclopentanes, -pentenes, and -pentadienes, especially of early transition metals, exhibit equilibria similar to the one discussed here [5]. This was deduced from the reactivities of such systems, *e.g.* replacement of ethylene units by alkynes in the reaction sequence metallacyclopentane – metallacyclopentene – metallacyclopentadiene [14d]. For metallacyclopentadienes, further evidence came from reactions in which the intermediates could be trapped [14e], or from isomerizations of unsymmetrically substituted titanacycles [4] [15]. The reversible opening and closing of the central C–C bond in 1,1-bis(η^5-cyclopentadienyl)titanacyclopentane [16] or 1,1-bis(η^5-cyclopentadienyl)-hafnacyclopentane [14d] was proven by labeling techniques, and such saturated systems were also subject to quantitative MO considerations [17].

The coupling of unsaturated hydrocarbons with carbonyl compounds at group-4 metallocenes has been observed for many years, for example by *Erker*'s or *Buchwald*'s group [14], but the resulting dihydrometallafurans were not always isolated and characterized. Instead, the products of subsequent hydrolysis were examined. So, little is known about the metallacycles. We now were able to show by NMR that their behavior is similar to that of five-membered metallacarbocycles, although a remarkable stability was pointed out for the oxa systems [14d].

The zirconocene-mediated coupling of unsymmetrically substituted alkynes with carbonyl compounds, leading to mixtures of regioisomers (*cf.* **5a**/**5b**), was also investigated by *Livinghouse* [18]. He isolated (after protolysis) mixtures of regioisomeric allylic alcohols. No effort was made to explore whether the ratios of regioisomers resulted from kinetic or from thermodynamic control (quenching either the initially formed or the energetically favoured dihydrozirconafuran), because isomerization of the organometallic intermediates (in analogy to *Scheme 3*) was not considered. Changing the reaction conditions might possibly also change the products' ratio.

The lability of the dihydrozirconafuran system **3** seems to be connected with the presence of the silyl substituents. If they are replaced by Ph groups (complex **4**), the reactivity is drastically reduced. Possible reasons for this behavior were already discussed [3]. But we must clearly distinguish the factors that determine *a*) the observed reactivity of the compounds **3** and **5** and *b*) the position of the equilibrium for **5**, depicted in *Scheme 3*. They need not be the same. The steric demands of a Me_3Si and a *t*-Bu group are almost equal. This follows from the fact that in the solid state, these two groups can cause disorders if they occupy similar molecular positions (see [7] for an example). However, small but appreciable differences might exist that would suffice to drive the equilibrium in *Scheme 3* to the right-hand side. The probably a bit bulkier Me_3Si group prefers the favorable, because less hindered 1-position at the end of the C-chain [13].

Experimental Part

Compounds. The preparation of *2,2-di(cyclopenta-2,4-dien-1-yl)-2,5-dihydro-5,5-dimethyl-3,4-bis(trimethylsilyl)-1,2-oxazirconole* (= *di(η^5-cyclopenta-2,4-dien-1-yl)[3,3-dimethyl-1,2-bis(trimethylsilyl)prop-1-en-1-yl-3-yl-oxy]zirconium*; **3**) was already described in [3], and (D_6)-**3** was prepared in an analogous manner. EI-MS (70 eV): *m/z* 456 (M^+), 390 ([M – (D_6)acetone]$^+$), 284 ([M – alkyne]$^+$).

Spectra. (D_6)Benzene (dried and deoxygenated) was used as solvent for all NMR experiments which were performed on a *Bruker-ARX-400* spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz; ^{29}Si, 79.49 MHz) at r.t., unless stated otherwise. Chemical shifts are given in ppm rel. to $SiMe_4$ but were referenced against the solvent signals (^{1}H,

δ 7.16 ppm; ^{13}C, δ 128.0 ppm). The shifts due to the intrinsic isotope effect, observed for *samples B–E* under various conditions, were reproducible within 0.2 Hz. The solid-state ^{13}C-NMR spectrum was recorded at 75.74 MHz (*Bruker MSL 300*) by the CP/MAS technique. The substance was placed in a zirconia rotor (4 mm o.d.) with *Kel-F* cap, the spinning rate was 3000 Hz, the contact time 2 ms and the recycle delay 5 s. Reference: external adamantane, $\delta(CH_2)$ 38.4 ppm.

Samples were prepared as follows. *Sample A* from 22 mg (0.05 mmol) of **3** in 0.5 ml of (D_6)benzene and a small amount of dry acetone (molar ratio complex/acetone 0.9:1.0, ^1H-NMR). *Sample B* from 68 mg (0.15 mmol) of **3** in 0.5 ml of (D_6)benzene and a small amount of dry (D_6)acetone (molar ratio complex/acetone 1.0:0.6, ^1H-NMR). *Sample C* from 25 mg (0.05 mmol) of (D_6)-**3** in 0.5 ml of (D_6)benzene and a small amount of dry acetone (molar ratio complex/acetone 1.0:7.5, ^1H-NMR). *Sample D* from 15 mg (0.03 mmol) of **3** and 38 mg (0.08 mmol) of (D_6)-**3** in 0.5 ml of (D_6)benzene. *Sample E* from 70 mg (0.16 mmol) of **3** and 15 mg (0.03 mmol) of (D_6)-**3** in 0.5 ml of (D_6)benzene. Complex **3**, if dissolved in acetone, rapidly decomposed. Thus, a great excess of free acetone had to be avoided. Despite the small amounts added for the exchange experiments, we observed partial decomposition, especially during long-term measurements or at elevated temp. None of the products could yet be identified. The tetrahydrofuran complex **1** formed, upon loss of L, a binuclear η^5:η^1-cyclopentadienediyl-bridged complex [1] whose resonance signals could *not* be detected in our mixtures.

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REFERENCES

[1] U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V.V. Burlakov, V.B. Shur, *Angew. Chem.* **1993,** *105,* 1228.
[2] U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V.V. Burlakov, V.B. Shur, *Z. Anorg. Allg. Chem.* **1995,** *621,* 77.
[3] U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V.V. Burlakov, V.B. Shur, *J. Organomet. Chem.* **1994,** *484,* 203.
[4] a) F. Langhauser, Doctoral Thesis, University of Kaiserslautern, 1991; b) P. Binger, P. Müller, F. Langhauser, F. Sandmeyer, P. Philipps, B. Gabor, R. Mynott, *Chem. Ber.* **1993,** *126,* 1541.
[5] E. Negishi, T. Takahashi, *Acc. Chem. Res.* **1994,** *27,* 124.
[6] A. Ohff, Doctoral Thesis, University of Rostock, 1995.
[7] U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V.V. Burlakov, *Organometallics* **1995,** *13,* 2903.
[8] U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V.V. Burlakov, *Angew. Chem.* **1994,** *106,* 1678.
[9] B. Godry, Doctoral Thesis, University of Dortmund, 1995.
[10] J. Jeener, B.H. Meier, P. Bachmann, R.R. Ernst, *J. Chem. Phys.* **1979,** *71,* 4546.
[11] O. Eppers, H. Günther, *Helv. Chim. Acta* **1990,** *73,* 2071.
[12] P.E. Hansen, F.M. Nicolaisen, K. Schaumburg, *J. Am. Chem. Soc.* **1986,** *108,* 625.
[13] C. Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov, U. Rosenthal, *J. Organomet. Chem.* **1995,** *501,* 189.
[14] a) G. Erker, F. Rosenfeldt, *J. Organomet. Chem.* **1982,** *224,* 29; b) V. Skibbe, G. Erker, *ibid.* **1983,** *241,* 15; c) K. Kropp, V. Skibbe, G. Erker, C. Krüger, *J. Am. Chem. Soc.* **1983,** *105,* 3353; d) G. Erker, U. Dorf, A.L. Rheingold, *Organometallics* **1988,** *7,* 138; e) G. Erker, R. Zwettler, *J. Organomet. Chem.* **1991,** *409,* 179; f) S.L. Buchwald, B.T. Watson, *J. Am. Chem. Soc.* **1986,** *108,* 7411; g) S.L. Buchwald, R.T. Lum, J.C. Dewan, *ibid.* **1986,** *108,* 7441.
[15] C. Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov, U. Rosenthal, H. Görls, *J. Organomet. Chem.* **1995,** *501,* 179.
[16] R.H. Grubbs, A. Miyashita, *J. Am. Chem. Soc.* **1978,** *100,* 1300.
[17] J.W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976,** *98,* 1729.
[18] B.C. van Wagenen, T. Livinghouse, *Tetrahedron Lett.* **1989,** *30,* 3495.