in a difference Fourier map phased with the W atoms. Almost all of the hydrogen atoms on the methyl groups were located in a later difference map. The four hydrogen atoms on the allene ligand were located in a subsequent difference map. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms.

The final difference Fourier map was essentially featureless except for two peaks of 1.5 and 1.2 e/Å^3 in the immediate vicinity of the two tungsten atoms.

$W_2(O\text{-}t\text{-}Bu)_6(C_3H_4)_2$ (2). A suitable crystal was located, transferred to the goniostat, and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. Data were corrected for absorption. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles.

A final difference Fourier was featureless, with several peaks of intensity 0.8–1.1 e/Å^3 lying near the metal atoms.

$W_2(O\text{-}t\text{-}Bu)_6(C_3H_4)(CO)_2$ (3). The crystalline sample consisted of "clumps" of black crystals with poorly defined faces. Several attempts were made before a suitable fragment was located. Many of the crystals examined were badly split (or twinned), as evidenced by numerous closely grouped peaks. The sample was maintained in a dry nitrogen atmosphere by using standard techniques employed by the Indiana University Molecular Structure Center.

A systematic search of a limited hemisphere of reciprocal spaces located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. It was apparent that a significant "pseudocell" was present, as seen in the intensity distribution. The $h0l$ zone, for example, is best described as present for $l = 4n$. Unfortunately, the exceptions to the "extinctions" were clearly present, so it was not possible to simply reduce the cell.

Data were collected by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. As expected, two independent molecules are present in the unique quadrant. Because of the pseudocell, less than half of the unique data were observed. For this reason, no attempt was made to refine anisotropically any atoms except the tungsten atoms.

The two molecules are nearly identical, as evidenced by their similar metric parameters.

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Supplementary Material Available: For the compounds $W_2(O\text{-}t\text{-}Bu)_6(C_3H_4)$, $W_2(O\text{-}t\text{-}Bu)_6(C_3H_4)_2$, and $W_2(O\text{-}t\text{-}Bu)_6(C_3H_4)(CO)_2$, complete listings of atomic coordinates, anisotropic thermal parameters, and bond distances and angles and stereoviews (50 pages); F_o and F_c values (38 pages). Ordering information is given on any current masthead page.

Dynamic Processes in the Solid State. Diene Flip and Ring Reorientation in Crystalline Zirconocene Complexes

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The dynamic processes that the zirconocene species $(C_5H_5)_2ZrCl_2$ (1), $(C_5H_4{}^tBu)_2ZrCl_2$ (2), $(C_5H_5)_2ZrC_4H_4Me_2$ (3), and $(C_5H_4{}^tBu)_2ZrC_4H_6$ (4) undergo in the solid state have been examined. The results of potential energy barrier calculations and packing analyses are discussed in light of the dynamic information obtained by ^{13}C magic angle spinning NMR spectroscopy. The potential energy barriers to reorientation of the C_5H_5 ligands in 1 and 3 are estimated, while the $C_5H_4{}^tBu$ groups in 2 and 4 are found to be blocked in their motion. An alternative interpretation of the diene flip, detected in 3 and 4 by the NMR experiments, is put forward.

Introduction

In previous papers[1] we have shown that the pairwise atom–atom potential energy method[2] can be fruitfully used to investigate the occurrence of dynamic processes in crystals of neutral organometallic molecules. The method affords a clear picture of the control exerted by the crystal packing on the reorientational motions that metal-bound molecular fragments can undergo in the solid state. A (semi)quantitative estimate of the potential energy (pe) barriers opposing the reorientational motions can also be attained in most cases. The potential energy approach becomes particularly useful when complementary information on the dynamic processes can be obtained from spectroscopic sources. ^{13}C CP/MAS NMR and ^1H wide-line experiments or spin–lattice relaxation time measurements are well-suited for the investigation of solid-state reorientational phenomena.[3] Successful correlations be-

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tween the results of NMR experiments and potential energy barrier calculations have been made, for example, in the cases of the cis and trans isomers of $(C_5H_5)_2Fe_2(CO)_4$,[1a] of the metallocene species $(C_5H_5)_2M$ (M = Ni, Fe, Ru),[1f] and of the arene complexes $(C_6H_6)_2Cr$, $(C_6H_6)M(CO)_3$ (M = Cr, Mo),[1b,g] $(C_6H_3Me_3)Cr(CO)_3$, and $(C_6H_2Me_4)Cr(CO)_3$.[1d] This approach has also been applied to larger polymetallic complexes of Ru and Os.[1c] In most cases the appreciation of the factors controlling the fragment reorientational freedom has allowed the establishment of the mechanistic features of the dynamic phenomena under investigation. Moreover, when the reorientations are low-energy processes, good fits between calculated potential energy barriers and the activation energies yielded by the spectroscopic experiments can also be obtained.

In this paper we extend our studies to the crystalline zirconocene complexes $(C_5H_5)_2ZrCl_2$[4] (1), $(C_5H_4{}^tBu)_2ZrCl_2$[5] (2), $(C_5H_5)_2ZrC_4H_4Me_2$[6] (3), and $(C_5H_4{}^tBu)_2ZrC_4H_6$[7] (4). The reason for this choice is 2-fold.

(i) ^{13}C CP/MAS experimental results for these complexes have recently become available.[8]

(ii) Beside the well-established reorientational freedom of the unsubstituted Cp rings, compounds 3 and 4 appear to undergo diene flip in the solid state.[8] This is a novel phenomenon on which our approach to solid-state problems can be tested further. The aim is to achieve a better understanding of the processes detected by the NMR technique and, possibly, to obtain an estimate of the energy cost of each dynamic behavior.

Results and Discussion

Our methodological approach has been extensively tested over a large and diversified range of applications and will not be described here. Readers interested in details of the computational procedures are directed to previous papers on this subject. In particular, refs 1a,c present a detailed discussion about the assumptions (and approximations) required when the atom–atom potential energy method[2] is applied to crystals of neutral transition-metal complexes. The coefficients for the calculation of the Buckingham function, describing the dependence of the packing potential energy (ppe) on the orientation of the fragment undergoing reorientation, are taken from the literature[9] (see also ref 1). Ionic contributions arising from bond polarities are not taken into account. The *inter*molecular and *intra*molecular potential energy barriers to motion (ΔE_{inter} and ΔE_{intra}) are calculated as ΔE = ppe − ppe_{min}, where ppe_{min} is the value of the function corresponding to the equilibrium ("static") structure of the molecule in the lattice. ΔE_{tot}, when discussed, is obtained as $\Delta E_{tot} = \Delta E_{inter} + \Delta E_{intra}$. In keeping with the basic assumption of the pairwise potential energy method, namely that interatomic interactions depend on the distances between atomic centers, the H atoms were added in calculated positions at 1.08 Å. Methyl groups in all species were treated as Cl atoms centered on the C(Me) positions. This was necessary to take into account the almost free rotational motion of the CH_3 groups in the solid. These procedures had been successfully tested in our previous studies of the reorientational motions in crystals of $(C_6Me_6)Mo(CO)_3$[1h] and of $(C_6H_2Me_4)Cr(CO)_3$ and $(C_6H_3Me_3)Cr(CO)_3$.[1d]

All calculations were carried out with the aid of a slightly modified version of the OPEC[10a] computer program. The program ROTENER[10b] was used to estimate the *intra*molecular barrier to simultaneous reorientation of the C_5H_5 ligands in 3. SCHAKAL88[11] was used for the graphical representation of the results.

Fractional atomic coordinates and crystallographic parameters for the species under investigation were obtained from the Cambridge Crystallographic Data Base or from the original structural reports.[4-7]

The results of ^{13}C CP/MAS experiments[8] for the species discussed herein can be summarized as follows.

(i) The unsubstituted Cp rings in 1 and 3 have been shown to undergo reorientational motion in the solid state at 300 K. Only one resonance is observed for the C atoms of the Cp rings in 1, while two distinct resonances are observed in the spectrum of 3. No estimate of the activation energies for these processes has been given. A higher rotational barrier for the Cp ring closer to the butadiene methyl groups in 3 has been proposed on the basis of the $T_1(^{13}C)$ values for the two rings.

(ii) The $C_5H_4{}^tBu$ ligands in 2 and 4 have been shown to be blocked in their motion. For 2, even at T = 360 K, there is no indication of chemical exchange; the five signals in the high-field region of the ^{13}C NMR spectrum have been assigned to the methine and quaternary C atoms, the two $C_5H_4{}^tBu$ ligands being made equivalent by crystallographic symmetry. Ten signals are otherwise observed for 4 (in spite of the fact that the asymmetric unit contains two independent molecules; see below).

(iii) The most interesting feature of the NMR spectra of 4 is the diene flip, which leads to equilibration of the central and terminal diene carbons of the C_4H_6 ligands. The activation energy for this process has been estimated to be ca. 14 kcal·mol^{-1}. No specific mention of the behavior of the $C_4H_4Me_2$ ligand in 3 is given, although it would appear that an analogous process is taking place. This is in contrast with our results, as will be discussed below.

Reorientational Motion of the C_5H_5 Ligands in 1 and 3. The study of the Cp reorientational motion in 1 poses an interesting problem because of the presence of two independent molecules in the asymmetric unit of the triclinic cell.[4] This requires an estimate of the reorientational barriers for all four independent Cp rings. Since each ring experiences a different crystalline environment,

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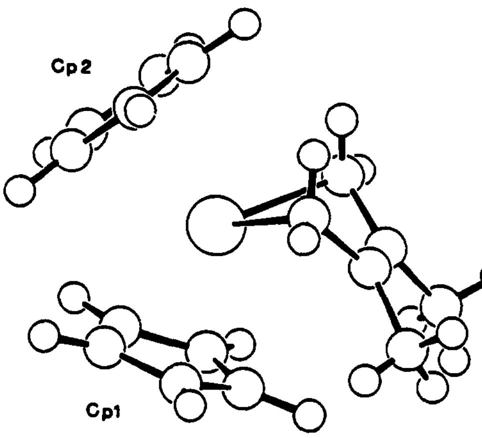

Figure 1. Molecular structure of $(C_5H_5)_2ZrC_4H_4Me_2$ (3).

the reorientational barriers are, in principle, not equivalent. Indeed, our calculations yield values of ca. 2.6, 1.6, 1.6, and 1.5 kcal·mol^{-1} for the four independent reorientational motions. These low values confirm that the Cp rings in 1 undergo rotational jumping motion in the solid state at room temperature. We were also able to determine that, while *intra*molecular contributions are usually very small in systems such as metallocenes and bis(arenes), where the reorienting fragments are parallel and far away, this is not the case for the zirconocene complexes. Due to the "bent" coordination of the Cp ligands, the *intra*molecular repulsions during reorientation are not negligible (from 0.6 to 1.3 kcal·mol^{-1}) and contribute to the determination of the total barriers.

Considering that ΔE barrier calculations within the atom–atom approach tend to give upper limits of the reorientational barriers ("static environment" approximation[12]), it is not surprising that the Cp jumping motions in 1 could not be frozen out in the NMR experiment.[8] It is worth recalling, at his stage, that the ΔE barriers for 1 are strictly comparable to those observed in crystals of the metallocene species $(C_5H_5)_2M$ (at room temperature: M = Ni, 1.5; M = Fe, 2.0; M = Ru, 3.4 kcal·mol^{-1}), in remarkable agreement with the potential barrier/activation energy values yielded by various spectroscopic techniques.[1f] The sensitivity of pe barrier calculations to small differences in crystalline environment is shown convincingly in the case of *cis*-$(C_5H_5)_2Fe_2(CO)_4$, where the values of the potential energy barriers for the motion of the two crystallographically independent Cp rings (1.9 and 4.2 kcal·mol^{-1})[1a] are in accord with the activation energies obtained by spin–lattice relaxation time mesaurements (1.5 and 3.3 kcal·mol^{-1}).[3h] The low reorientational barriers in 1 show up in the X-ray diffraction experiment in terms of a high rotational disorder of the Cp ligands.

The crystallographic symmetry in 3 (a mirror plane bisecting the C_5H_5 rings and passing through the middle of the butadiene ligand) makes the two unsubstituted C_5H_5 rings experience different environments in the lattice. Furthermore, one of the C_5H_5 ligands (Cpl in Figure 1) is in close proximity to the methyl substituents on the diene. Hence, both *intra*molecular and *inter*molecular constraints can be expected to affect the reorientational motion of the two C_5H_5 ligands in different manners. This is in agreement with the ^{13}C CP/MAS results (although the difference in $T_1(^{13}C)$ values between the two C_5 rings has been attributed to the motion of the methyl substituents). As a matter of fact, both ΔE_{intra} and ΔE_{inter} appear to be higher for Cpl than for Cp2 (2.1, 1.6 versus 0.8, 0.9 kcal·mol^{-1}), resulting in quite different ΔE_{tot} barriers (3.7 versus 1.7 kcal·mol^{-1}).

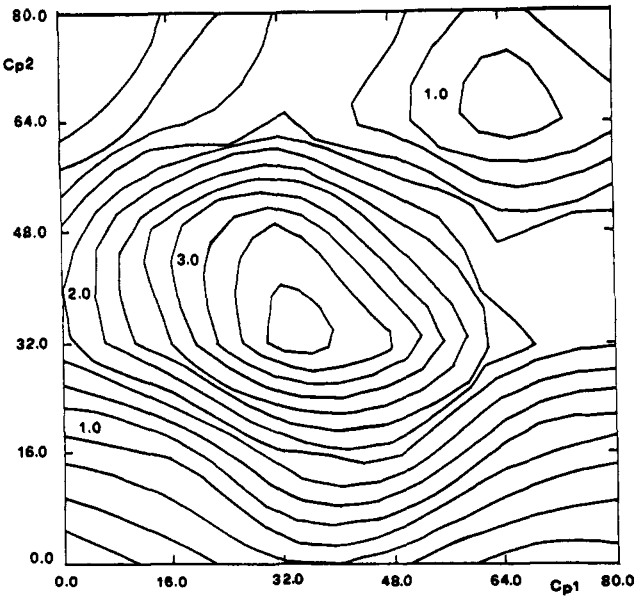

Figure 2. Topographic map for the combined rotations of the two independent C_5H_5 ligands in 3. Relative intramolecular potential energy levels (ΔE, kcal·mol^{-1}) are drawn at 2 kcal·mol^{-1} steps, the minimum being set at 0 for the original orientations of the two fragments.

At this stage, one may object that this reorientational model implicitly assumes that one ligand remains "static" during reorientation of the other one. In order to check the effect on the intramolecular barrier of a *simultaneous* reorientation of the two ligands, ΔE_{intra} was calculated for a complete reorientation of one ligand at each rotational step of the second one. As shown in Figure 2, when Cpl is midway (e.g. ca. 36° from its original position) the intramolecular reorientational barrier for Cp2 increases to about 4.1 kcal·mol^{-1}. In conclusion, the two ligands are not truly independent in their motion; rather, asynchronous rotational jumps (one ligand is in the state of jump, while the other is in a minimum) appear to facilitate the motion. Similar observations can be made for the reorientational motions in 1.

Motion of the ($C_5H_4{}^tBu$) Ligands in 2 and 4. In agreement with the spectroscopic findings, reorientation of the bulky $C_5H_4{}^tBu$ ligands in 2 appears to be forbidden by the upsurge of extremely high potential energy barriers (>50 kcal·mol^{-1}). As expected, the shape of this ligand is such that the fragment is tightly locked in place by the surrounding molecules in the crystal lattice. The potential energy well, however, is rather flat (ΔE < 15 kcal·mol^{-1} within the angular range ±40°), suggesting that the ligand can undergo some large-amplitude swinging motion. Identical behavior is shown by the $C_5H_4{}^tBu$ ligands in 4.

Diene Flip in 3 and 4. Far more interesting is the phenomenon of diene topomerization in the solid state, evidenced by the NMR experiment in the case of 4. Insights into such a dynamic process can be obtained by comparing the values of both inter- and intramolecular potential energies corresponding to the equilibrium structure (that "observed" in the crystal) with those corresponding to the alternative orientation of the diene ligand after diene flip. This motion (as in the case of 3 below) can be "simulated" by allowing a 180° reorientation of the diene fragment around an axis passing approximately through the Zr atom and the center of mass of the C_4 fragment. This procedure affords a crude estimate of the

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[12] Gavezzotti, A.; Simonetta, M. *Acta Crystallogr., Sect. A* **1976**, *32*, 997.

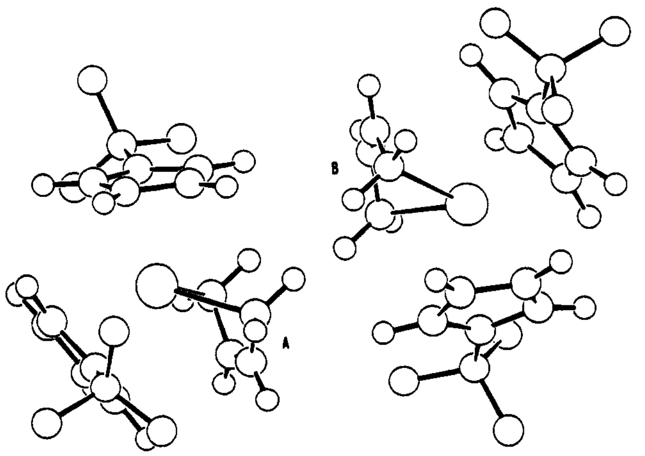
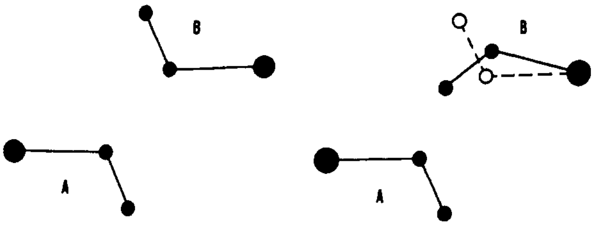


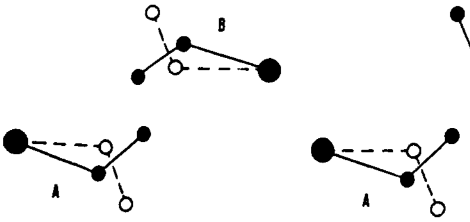
Figure 3. The two independent molecules present in the asymmetric unit of $(C_5H_4{}^tBu)_2ZrC_4H_6$ (4), showing how the two diene ligands face each other in the lattice.

Chart I



equilibrium A_{obs}, B_{obs}

$\Delta H_{inter}(A_{obs},B_{inv})$ 12.0
$\Delta H_{intra}(A_{obs},B_{inv})$ 0.6
$\Delta H_{tot}(A_{obs},B_{inv})$ 12.6



$\Delta H_{inter}(A_{inv},B_{inv})$ 72.1
$\Delta H_{intra}(A_{inv},B_{inv})$ 0.4
$\Delta H_{tot}(A_{inv},B_{inv})$ 72.5

$\Delta H_{inter}(A_{inv},B_{obs})$ 10.9
$\Delta H_{intra}(A_{inv},B_{obs})$ 0.4
$\Delta H_{tot}(A_{inv},B_{obs})$ 11.3

$\Delta H(A_x,B_x)$ = ppe(A_x,B_x) − ppe(A_{obs},B_{obs}) (kcal·mol^{-1})

difference in potential energy (ΔH) between the two alternative orientations of the fragment in the lattice. It should be stressed that the ΔH values bear no relationship to the potential energy barriers (ΔE) discussed so far; rather, they represent the enthalpy difference between the two different topomers in the solid state.

Let us focus our attention on the relative positions of the two independent molecules present in the asymmetric unit of 4 (see Figure 3). These two molecules appear to be almost face-to-face in the lattice, offering each other the C_4H_6 ligands. This is a relevant observation for the understanding of the diene-flip process. The results of our calculations are summarized in Chart I.

On the basis of our findings, it is possible to conclude that the molecular organization in crystals of 4 does not prohibit the flip of the diene ligands, *given that the two ligands do not move simultaneously.* It is also clear that the process does not lead to an alternative, energetically equivalent, position of the diene ligand in the solid state. Moreover, the values of $\Delta H_{tot}(A_{inv},B_{obs})$ and $\Delta H_{tot}(A_{obs},B_{inv})$ (11.7 and 13.2 kcal·mol^{-1}, respectively) are found to be only slightly lower than the activation energy (14 kcal·mol^{-1}) estimated on the basis of the NMR experiment, indicating that the reverse process (the diene returning to its "ground-state" orientation) requires much less energy. Therefore, the process detected by the NMR experiment should be better described as a rapid clicking motion, with very little residence time in the second orientation. This is in agreement with the fact that the solid-state structure of 4 does not show positional disorder for the diene atoms over two sites. It may well be that, as the temperature is increased, the second potential minimum also would become populated and would be observed in the diffraction experiment. A similar situation is known to occur in solid monoclinic sulfur.[13a] In this case, it was possible to "follow" the progressive increase in population (and depopulation) of an alternative molecular orientation, from the almost completely ordered structure (at 100 K) to the 50% disordered one (at room temperature), as the temperature was varied.

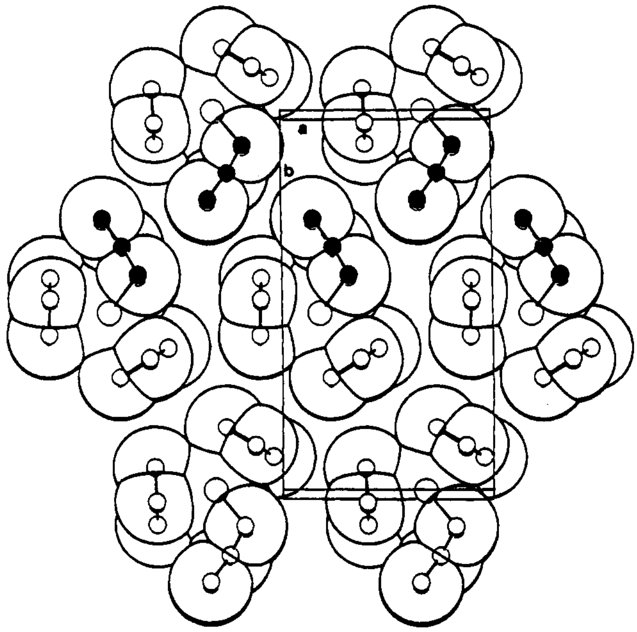


Figure 4. Section of the crystal packing of 3 parallel to the *ab* plane. The space-filling outline shows the molecular interlocking pattern.

Another example of exchange between nondegenerate structures in the solid state is shown by the Cope rearrangements of solid semibullvalenes.[13b]

It is not clear from the NMR results discussed in ref 8 whether a similar phenomenon is taking place in crystals of 3. We have evidence from our packing analysis that a similar flip would be a high-energy process at room temperature. There is, however, a number of aspects of the molecular organization in the lattice of 3 which deserve attention. Figure 4 shows a section of the crystal packing of 3 parallel to the *ab* plane. The space-filling outline shows the molecular interlocking pattern. The diene groups adopt a chevronlike distribution along the *a* axis. It is easy to appreciate that the topomerization of a single molecule is prevented by the energetically expensive process of the methyl groups "pushing past" the neighboring ones. Hence, a to-and-fro process of the kind discussed above for 4 does not appear to be feasible. The energy cost does, however, decrease (though not as much as to actually permit topomerization at room temperature) if this motion is accompanied by a similar motion of the neighboring

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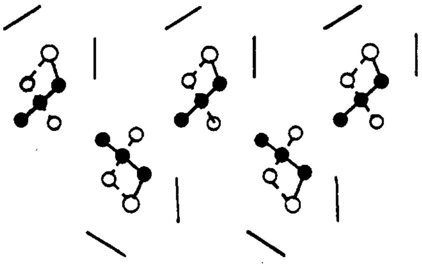
Chart II



molecules (a sort of clicking wave which propagates along the *a* axis as shown in Chart II[17]). This observation may be taken as indicating that a substantial lattice modification, perhaps an order–disorder phase transition above 300 K, is necessary to allow diene topomerization in 3.

The occurrence of order–disorder phase transitions seems to be a general feature of crystals made of structurally nonrigid neutral organometallic molecules. Besides those known to occur for ferrocene,[1f] transitions to plastic phases have been observed, for instance, in crystalline formylferrocene[14] and acetylferrocene[15] and in $(C_4H_4S)Cr(CO)_3$,[16] while the onset of reorientational motion of the arene fragments has been invoked to explain the behavior observed by ^1H spin–lattice NMR spectroscopy in crystalline $(1,2,3\text{-}C_6H_3Me_3)Cr(CO)_3$ and $(1,2,4,5\text{-}C_6H_2Me_4)Cr(CO)_3$.[1d]

Along this line of thinking, one may wish to speculate on the possibility of "predicting" the occurrence of phase transitions (or other lattice modifications) from a knowledge of the molecular assembly in the lattice and of the internal degrees of freedom of the molecules under investigation. It seems that crystals containing structurally nonrigid organometallic molecules are very likely to undergo *intermolecular* rearrangements as a function of the temperature. An increase in temperature (and the consequence loss of lattice cohesion) will tend to increase the motional freedom of the molecular fragments, particularly along low-energy intramolecular rearrangement pathways, up to a point beyond which the intramolecular modification will be able to "propagate" through the lattice, becoming an intermolecular rearrangement. The intermolecular pathways for processes of this kind can be seen as the result of the *combination* of lattice periodicity with intramolecular rearrangement pathways. On these premises, it should be clear that any hypothesis on solid-state intermolecular rearrangements and phase transition mechanisms must be based on an exact knowledge of the molecular organization in the crystal.

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[17] This simple model also necessitates that the molecules rotate slightly around their centers of mass in order to decrease the repulsive interactions between the methyl groups and the Cp ligands of next-neighboring molecules.

Synthesis, Structure, and Fluxional Behavior of 4-Sila-, 4-Germa-, and 4-Stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes

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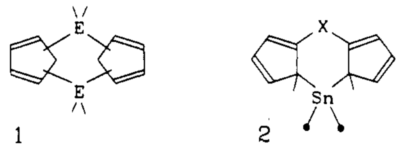
4-Elementa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes were obtained as a result of interaction of dilithiated dicyclopentadienyldimethylmethane with dichlorodimethylsilane, -germane, and -stannane, and their ^1H and ^{13}C NMR spectra were studied in detail. Tin and germanium derivatives in solution were found to be equilibrium mixtures of syn and anti isomers with respect to the mutual orientation of their allylic hydrogens at C(3a) and C(4a). The interconversion of these isomers occurs because of the elementotropic rearrangements. The mechanism of the processes was ascertained by use of 2D ACCORDION experiments, and the kinetic parameters were determined by means of complete line-shape analyses of the dynamic NMR spectra. Prototropic rearrangements were observed for 4-sila-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene.

Introduction

η^1-Cyclopentadienyl derivatives of the group IVA elements (Si, Ge, Sn, and Pb) are so-called fluxional compounds owing to the rapid intramolecular [1,5]-sigmatropic migration of the organometallic group over the cyclopentadienyl ring. Numerous experiments have been carried out to study such rearrangements.[1] These compounds including polymetalated cyclopentadienes have attracted recently the attention of synthetic chemists as the initial materials for the syntheses of various transition-metal derivatives of substituted cyclopentadienes.[2] Compounds

Scheme I



1 2

E = Si; Ge

X = CH_2; CMe_2; $SiMe_2$

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[1] Jutzi, P. *Chem. Rev.* 1986, *86*, 983.

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