tively, and regenerating the starting Rh(I) complex **1** (eq 2), thus

$$cis\text{-}\mathrm{RhH(CH_2COR)(PMe_3)_3Cl \rightarrow RhCl(PMe_3)_3 + CH_3COR} \qquad (2)$$

completing the catalytic cycle for the epoxide isomerization reaction. Isolation of the complexes **2** and **3** as the major Rh species in the catalytic reaction undoubtedly points out that the overall reductive elimination process **2**,**3** → **1** is rate determining in the catalytic cycle. Since this process proceeds by a prior slow PMe_3 dissociation from **2** (vide infra), this phosphine dissociation step is rate determining in the catalytic isomerization process. The mechanism of epoxide isomerization catalyzed by **1** is thus plausibly presented by Scheme I.

Kinetic measurements of the reductive elimination process of **2** were carried out by monitoring the concentration of **2** as well as that of the products, $ClRh(PMe_3)_3$ (**1**) and acetone by ^1H NMR and ^{31}P NMR in C_6D_6 between 27 and 44 °C. First-order plots for the disappearance of **2** are invariably linear for at least 3 half-lives and are unaffected by variations in the initial concentration of **2**. Activation parameters obtained from a linear Arrhenius plot of k_{obsd} are (31 °C) as follows: $E_a = 25.6$ kcal/mol, $\Delta H^{\ddagger} = 25.0$ kcal/mol, $\Delta G^{\ddagger} = 23.4$ kcal/mol, $\Delta S^{\ddagger} = 5.3$ eu. In the presence of added PMe_3, the reaction rate is inhibited and the stoichiometry is altered to that of eq 3.[11] Still, disappearance

$$cis\text{-}\mathrm{RhH(CH_2COCH_3)(PMe_3)_3Cl + PMe_3 \rightarrow CH_3COCH_3 + \underset{\textbf{6}}{[Rh(PMe_3)_4]^+Cl^-}} \qquad (3)$$

of **2** obeys first-order kinetics (Table I), and the reciprocal of k_{obsd} varies linearly with the concentration of added PMe_3. Also, in the presence of the "Phosphine sponge" $Rh(acac)(C_2H_4)_2$, a 15-fold increase in the rate of **2** disappearance is observed at 27 °C.

The reductive elimination reaction of **2** is *intramolecular*: decomposition of a toluene solution containing equimolar amounts of **2** and the *cis*-deuterioalkyl complex *mer*-$RhD(CD_2COCD_3)(PMe_3)_3Cl$ (**7**) (5×10^{-2} M each), obtained from reaction of **1** with hexadeuteriopropylene oxide, yielded a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 and no crossover products. Kinetic measurements of the rate of decomposition of **7** at 31 °C yield a small kinetic isotope effect $k^H_{obsd}/k^D_{obsd} = 1.3$.

The above evidence suggests that the reductive elimination of **2** occurs by a dissociative mechanism involving a rate-determining prior loss of PMe_3, as outlined in eq 4–7. Reaction 5 is practically

$$cis\text{-}\mathrm{RhH(CH_2COCH_3)(PMe_3)_3Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RhH(CH_2COCH_3)(PMe_3)_2Cl + PMe_3} \qquad (4)$$

$$\mathrm{RhH(CH_2COCH_3)(PMe_3)_2Cl} \xrightarrow{k_2} \mathrm{Rh(PMe_3)_2Cl + CH_3COCH_3} \qquad (5)$$

$$\mathrm{RhCl(PMe_3)_2 + PMe_3} \overset{\text{fast}}{\rightleftharpoons} \mathrm{RhCl(PMe_3)_3} \qquad (6)$$

$$\mathrm{RhCl(PMe_3)_3 + PMe_3} \xrightarrow{\text{fast}} \mathrm{[Rh(PMe_3)_4]^+Cl^-} \qquad (7)$$

irreversible; no reaction between acetone and **1** takes place at 31 °C, even over periods of weeks.

By employment of the steady-state approximation, the reductive elimination from **2** gives rate law 8. From the intercept of a linear

$$-\frac{d[\mathbf{2}]}{dt} = \frac{k_1k_2[\mathbf{2}]}{k_{-1}[\mathrm{PMe_3}] + k_2} = k_{obsd}\,[\mathbf{2}] \qquad (8)$$

plot of $1/k_{obsd}$ vs. $[PMe_3]$ follows $k_1 = 1.02 \times 10^{-4}$ s^{-1}, corresponding to an activation-free energy $\Delta G^{\ddagger}$ (31 °C) = 23.3 kcal/mol. This indicates that the PMe_3 ligands are very tightly bound to the Rh(III). For comparison, the rate constant for PPh_3 dissociation from *mer*-$RhH_2(PPh_3)_3Cl$ at 30 °C is approximately 4×10^2 s^{-1}.[12] The ratio $k_{-1}/k_2 = 1.83$ is obtained from the slope of this plot, indicating that the rate of the reductive elimination step (5) is comparable to that of the reassociation process.

Our studies demonstrate for the first time a requirement for ligand dissociation prior to intramolecular hydridoalkyl reductive elimination; the rate of reductive elimination from *cis*-$PtH(Me)(PPh_3)_2$ is not affected by added PPh_3.[3] Dialkyl reductive elimination from square-planar Pd[13,14] and Au[15] complexes also takes place by a dissociative mechanism and has been proposed theoretically[16] to proceed from a cis-"T"-shaped intermediate. Similar considerations may be applied to octahedral hydridoalkyl complexes by taking into account only the plane of the reductively eliminating groups.

Acknowledgment. I thank M. A. Cushing, Jr., for skilled technical assistance.

Registry No. 1, 36103-64-7; **2**, 82555-23-5; **3**, 82555-24-6; **4**, 82555-25-7; propylene oxide, 75-56-9; styrene oxide, 96-09-3; ethylene oxide, 75-21-8.

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[11] The C_6D_6-insoluble cationic complex **3**[6] is undoubtedly formed as a result of fast reaction between **1** and PMe_3; not even traces of **1** could be detected when reaction 3 was monitored by ^{31}P NMR.

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Simplification and Assignment of Carbon-13 Spectra by Using *J*-Resolved NMR Spectroscopy in Solids

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Received April 26, 1982

In the high-resolution solid-state ^{13}C NMR called CP/MAS,[1] signal assignment is usually made by referring to the spectrum in solution. However, some substances exhibit characteristic spectra in the solid state, and many others are insoluble in solvents or decompose on melting. Therefore, it is desirable to develop a method that is capable of signal assignment in solids. In a previous paper,[2] we reported that *J* multiplets can be observed under homonuclear decoupling with magic-angle sample spinning (MAS); this method provides an assignment aid in solids. In complex molecules, however, resonance lines in *J* spectra are usually overlapping each other so heavily that complete assignment is hampered. This communication describes a modification that facilitates the assignment of ^{13}C spectra in solids; the resonances always appear as sharp singlets, resulting in time saving.

The pulse sequence that we used for the simplification and assignment of ^{13}C spectra in solids is depicted in Figure 1; it is one of various possible alternatives. In the first τ interval, the homonuclear decoupling to the protons suppresses spin diffusion so that MAS is then able to remove ^{13}C–^1H dipolar and anisotropic *J* coupling but not the isotropic *J* coupling; in the second τ interval, all three of the heteronuclear interactions are removed. The evolution under chemical-shift interactions is refocused by a 180° pulse. Therefore, the ^{13}C magnetization *M* at the commencement of data acquisition depends only on the time evolution in the first τ interval under the isotropic ^{13}C–^1H *J* coupling:

$$M_n(\tau) = M_n(0)\cos^n(\pi SJ\tau) \qquad n = 0\text{–}3 \qquad (1)$$

where *S* designates the scaling factor of the used homonuclear decoupling and *n* is the number of protons that are directly bonded

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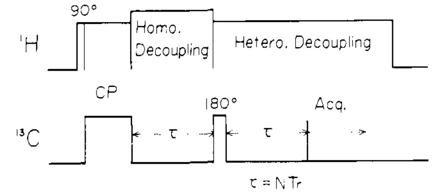

Figure 1. Pulse sequence for simplification and assignment of ^{13}C spectra in solids. The interval τ must be an integer multiple of the sample-spinning period T_r to observe the free-induction decay at the full amplitude.

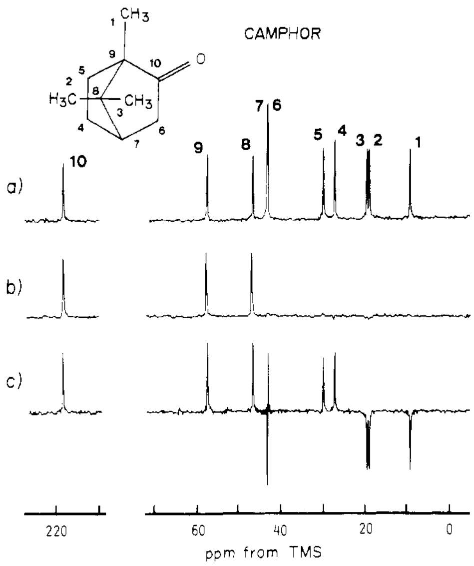

Figure 2. ^{13}C spectra of camphor: (a) normal CP/MAS spectrum; (b) nonprotonated carbons selectively observed by setting τ = 9.3 ms $\simeq$ $(2SJ)^{-1}$ in Figure 1; (c) signals of nonprotonated and methylene carbons are positive in sign and those of methine and methyl carbons are negative with τ = 18.6 ms $\simeq$ $(SJ)^{-1}$. The experiments were performed on a home-built spectrometer operating at 60 MHz for ^1H with an rf field of 25 G and a spinning frequency of 2.2 kHz. The homonuclear interaction was decoupled by the BR-24 pulse cycle[8] with a pulse interval of 4.7 μs.

to the observed carbon. As seen from eq 1, only nonprotonated carbons are observed with $\tau = (2SJ)^{-1}$, and the signals of nonprotonated and methylene carbons are observed 180° out of phase from those of methine and methyl carbons with maximum intensities with $\tau = (SJ)^{-1}$. Generally, the interval τ must be an integer multiple of the spinning period T_r; these rotational echoes due to heteronuclear dipolar interactions may be refocused so that the free-induction decay can be observed at the full amplitude.[3]

The observed ^{13}C spectra of camphor are shown in Figure 2. Spectrum a is a normal CP/MAS spectrum, and spectra b and c were obtained by the pulse sequence shown in Figure 1 with $\tau \simeq (2SJ)^{-1}$ and $(SJ)^{-1}$, respectively. As mentioned above, while only nonprotonated carbons appear in spectrum b, in spectrum c the signals of nonprotonated and methylene carbons are positive in sign, and those of methine and methyl carbons are negative. It should be noted that the overlapping lines 6 and 7 in a are distinctively observed in c. The fairly small dipolar interaction in camphor due to fast molecular motion allowed us to obtain the spectra in b and c without setting $\tau = NT_r$. Even in rigid solids selective observation of nonprotonated carbons is feasible also under $\tau \neq NT_r$, because $^{13}C-^1H$ dipolar interactons are weak for nonprotonated carbons. Indeed, we have been successful in selectively observing nonprotonated carbons in 1,5-dimethylnaphthalene under $\tau \neq NT_r$. Another method has been proposed by Opella et al.[4] for selective observation of nonprotonated carbons, based on the fact that $^{13}C-^1H$ dipolar interactions of nonprotonated carbons are especially weak. However, signals of methyl carbons may also appear, contrary to our method, since their dipolar interactions are rather weak. In order to observe such spectra as shown in Figure 2c in rigid solids, besides setting $\tau = NT_r$, we must adjust the magic angle much more critically and shorten the cycle time of multiple-pulse homonuclear decoupling sequences; work along these lines is in progress.

The experiment described here is also applicable to liquids, where homonuclear decoupling is unnecessary. Very recently, related experiments using a 90° pulse instead of cross polarization have been performed in liquids.[5,6] Our experiment is related to the pulse sequence used for heteronuclear two-dimensional J-resolved spectroscopy in liquids.[7] This type of two-dimensional NMR is feasible also in solids by using the pulse sequence given in Figure 1, separating overlapping multiplets; however, it is time consuming as assignment aid only.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research.

Registry No. Carbon-13, 14762-74-4; camphor, 76-22-2; 1,5-dimethylnaphthalene, 571-61-9.

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An Orbital Explanation for Pauling's Third Rule

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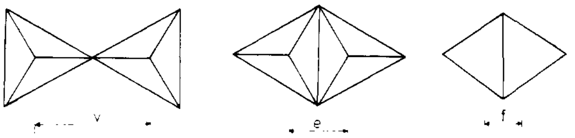
Received April 20, 1982

Pauling proposed a set of rules 50 years ago that governed the stability of the crystal structures of extended solid-state arrays. His third rule suggested that the coordination polyhedra surrounding the cations would be most stable if they shared vertices, less stable if they shared edges, and least stable if they shared faces.[2] In keeping with contemporary understanding of the forces holding such solids together, it was pointed out that the cations located at the polyhedra centroids were closest together if faces were shared and furthest apart if vertices only were shared (**1**).



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Thus, cation-cation electrostatic repulsions were expected to decrease in the order faces > edges > vertices, with a commensurate increase in stability. These repulsions were also expected to shorten any shared edges that might occur. In this note, we propose a very different explanation for the instability of edge sharing by using a purely orbital model. We note that earlier work of Tossell and Gibbs[3] showing that molecular orbital calculations predict shared edges, when present, to be shortened.

McLarnan and Baur[4] have recently enumerated the different ways of filling the tetrahedral holes of a hexagonal anion (X) close

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(1) Fellow of the Alfred P. Sloan Foundation and Camille and Henry Dreyfus Teacher-Scholar.

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