on annealing (Figure 1b). No hyperfine lines were visible when C_2D_4 was used, showing that the interactions were with the protons of C_2H_4. The $M_I = {}^1/_2$ line was an almost isotropic singlet, indicating that the $M_I = {}^1/_2$ interactions from C_2H_4/Al did not arise from the superposition of parallel and perpendicular features but from isotropic proton hyperfine interactions only. This line has been analyzed as a partially resolved quintet of quintets and was simulated with the ESR parameters, $a_H(4) = 4.0$, $a_H(4) = 2.5$, and $\Delta H_{pp} = 2.8$ G, identical with those of aluminocyclopentene.

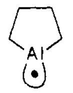
The large aluminum hyperfine interaction and two sets of magnetically equivalent proton interactions of the same magnitude as those in aluminocyclopentene strongly indicate that the spectrum is due to aluminocyclopentane formed by a coupling of two ethylene molecules by the aluminum atom whose orbital composition is sp^x and not pure p as in the aluminum atom itself. Insertion of the $a_\parallel$ and $a_\perp$ aluminum values into the relationships $a_\parallel = A_{iso} + 2A_{dip}$ and $a_\perp = A_{iso} - A_{dip}$ leads to $A_{iso} = 689.5$ MHz and $A_{dip} = 54.4$ MHz, assuming that $a_\parallel$ and $a_\perp$ are both positive. Combining these values with the predicted Al atomic parameters[8] $A = 3911$ and $P = 83.4$ MHz gives s- and p-unpaired spin populations of 0.18 and 0.65, respectively, and a total spin population of ~0.83 on the Al atom. An sp^3-hybridized orbital is indicated on the Al, but an sp^2 orbital cannot be excluded because of the inaccuracies in the predicted atom A and P parameters. The observation of two sets of four-proton interactions removes the possibility that the ESR carrier is a bridged aluminum monoethylene species but is consistent with the dimeric species in which the four protons on the two carbons adjacent to the aluminum have a 4-G interaction while the four protons of the β carbons have a 2.5-G interaction. As in aluminocyclopentene, aluminocyclopentane probably has an envelope-type structure of C_s symmetry with the Al atom below the C4 frame and is not a planar molecule of C_{2v} symmetry. The greater Al 3p orbital contribution to the SOMO in aluminocyclopentane is probably accompanied by more 3s character in the bonding orbitals directed toward the carbon atoms which itself may arise from smaller CCC bond angle at the central C–C single bond compared to those at the C=C double bond in aluminocyclopentene. The driving force for the involvement of the higher energy 3p orbitals of Al in this cyclometalation reaction is the formation of two strong C–Al σ bonds[9] that more than compensate for the s to p promotional energy.

At least two mechanisms for the cyclodimerization reaction are possible: (i) a consecutive three-step radical process (reactions 1–3) or (ii) a concerted process involving the two ethylene molecules reacting simultaneously with the Al atom. If the reaction

$$Al^{\bullet} + CH_2CH_2 \rightarrow AlCH_2CH_2^{\bullet} \qquad (1)$$

$$AlCH_2CH_2^{\bullet} + C_2H_4 \rightarrow AlCH_2CH_2CH_2CH_2^{\bullet} \qquad (2)$$

$$AlCH_2CH_2CH_2CH_2^{\bullet} \longrightarrow$$



(3)

proceeds via aluminoethyl and -butyl radicals, it is surprising that neither we nor Kasai[2,3] see any trace of these radicals in matrix ESR spectra. Furthermore, the fact that no metal atom addition reaction to a simple alkene has yet been observed also tends to argue against this mechanism. Mechanism ii could involve the rearrangement of a bis-ethylene aluminum complex although a direct route not involving a complex is feasible.

There are numerous examples of such cyclodimerization of alkenes in the presence of transition-metal complexes,[10,11] e.g., $Fe(CO)_5$, and the symmetry rules applicable to such reactions have been considered thoroughly by Stockis and Hoffmann.[12] The reactions usually require photoactivation and involvement of other ligands in addition to alkenes. We believe this is the first report of such a thermal reaction by a naked metal atom and provides direct evidence for the involvement of aluminocyclopentanes in aluminum–olefin reactions.[5] In conclusion, it is worth noting that both species A and B are remarkably stable up to 343 K in adamantane.

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Determination of Relaxation Pathways in Coupled Spin Systems by Two-Dimensional NMR Exchange Spectroscopy with Small Flip Angles

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Two-dimensional exchange spectroscopy (NOESY) has proven to be a remarkably useful method for studying cross-relaxation (nuclear Overhauser effects).[1-3] In most applications, the multiplet structure due to scalar couplings is not explicitly taken into account, and the integrated signal amplitudes only yield information about cross-relaxation rates[3-5] $\sigma_{ij} = W_2^{ij} - W_0^{ij}$ between spins I_i and I_j. This limitation makes it difficult to test various motional models,[6,7] to ascertain the importance of correlation between pairs of dipolar interactions,[8] and generally to study molecules with a correlation time $\tau_c \approx 1/\omega_0$, where the cross-relaxation rates σ_{ij} vanish.

It is the purpose of this communication to show that high-resolution 2D exchange spectra recorded with the "small flip angle NOESY" sequence $90°-t_1-10°-\tau_m-10°-t_2$ allow one to determine separately the zero-, single-, and double-quantum relaxation rates W_0^{rs}, W_1^{rs}, and W_2^{rs} between eigenstates $|r\rangle$ and $|s\rangle$. This method is related to *zz*-spectroscopy[9,10] and to spy relaxation studies.[11] If $\tau_m = 0$, this experiment is equivalent to *z*-filtered COSY:[12,13] only pairs of transitions that share a common energy level give rise to cross-peaks, which are positive or negative for progressive or regressive connectivities. Simple rules describe the amplitudes even in the presence of strong coupling.[13]

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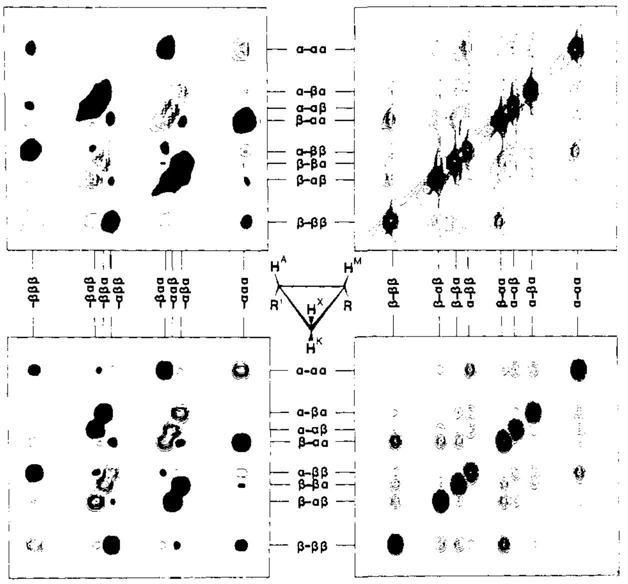

Figure 1. Multiplets taken from small flip angle NOESY spectra of *cis*-2-phenylcyclopropanecarboxylic acid ethyl ester (R = $COOCH_2CH_3$, R′ = C_6H_5). The cross-peak (left) is centered at $\omega_1 = \Omega_M$ and $\omega_2 = \Omega_A$; the diagonal peak (right) is centered at $\omega_1 = \omega_2 = \Omega_M$. Top: experimental multiplets. Bottom: simulations, calculated without initial rate or weak coupling approximations but neglecting correlation effects and motional anisotropy. Experimental parameters: sequence $90°–t_1–10°–\tau_m–10°–t_2$, zero-quantum signals shifted[16] by incrementing τ_m from 3.6 to 3.7 s; spectral width 770 Hz in both domains, data matrix 1K × 4K points before, 4K × 4K points after zero filling. Parameters in simulation: τ_c = 6.7 ps, hence extreme narrowing with $W_0^{ij}:W_1^{ij}:W_2^{ij}$ = 2:3:12. The dipolar contributions were calculated from known proton–proton distances:[15] W_2^{AM}, W_2^{AK}, W_2^{AX}, W_2^{KM}, W_2^{KX}, W_2^{MX} = 0.015, 0.003, 0.012, 0.003, 0.069, and 0.011 s^{-1}, respectively. Uncorrelated external random field contribution W_1^{ext} = 0.019 s^{-1} for all single-quantum transitions. Equidistant contours in experimental and simulated spectra at ±3%, ±6%, ...; ±99% of the maximum peak in corresponding diagonal multiplet. Filled contours on the left represent positive signals, all other peaks being negative, including the signals on the diagonal which appear with densely spaced contours.

If $\tau_m > 0$, the populations migrate between the 2^N eigenstates of the N-spin system:

$$\Delta \boldsymbol{P}(\tau_m) = \exp\{\mathbf{W}\tau_m\}\Delta \boldsymbol{P}(0) \approx \{\mathbf{1} + \mathbf{W}\tau_m\}\Delta \boldsymbol{P}(0) \qquad (1)$$

where $\Delta \boldsymbol{P}$ is the vector of the deviations of the populations from thermal equilibrium and **W** the matrix of transition probabilities. The equality holds for arbitrary duration of the mixing interval τ_m, while the approximation is restricted to the initial rate regime. Simulations of small flip angle NOESY spectra can be calculated by inserting eq 1 into our "Grandchild of Laocoon" program for simulating *z*-COSY spectra,[13] taking care that **W** must be expressed in the eigenbase.

The principle is illustrated in Figure 1, which shows multiplets taken from small flip angle NOESY spectra of a disubstituted cyclopropane derivative. The transitions are labeled by shorthand expressions for the corresponding products[5,14] of shift operators I^+, I^- and polarization operators I^α, I^β. Thus, $\{\alpha–\beta\alpha\}$ stands for $I_A^\alpha I_M^- I_K^\beta I_X^\alpha$ (the four spins always appear in the same order.) In the *diagonal multiplet* of spin *M* in Figure 1, the predominant off-diagonal peaks are due to the interactions of the geminal protons K and X (r_{KX} = 1.79 Å),[15] notably a strong peak connecting $\{\alpha–\alpha\alpha\}$ and $\{\alpha–\beta\beta\}$, proportional to W_2^{KX} in the initial rate approximation, since protons K and X must flip simultaneously. The peak connecting $\{\alpha–\alpha\alpha\}$ and $\{\beta–\alpha\beta\}$ is much weaker, reflecting a greater separation (r_{AX} = 2.44 Å), while there is no detectable peak connecting $\{\alpha–\alpha\alpha\}$ and $\{\beta–\beta\alpha\}$ (r_{AK} = 3.0 Å). Other peaks carry information about single-quantum transition probabilities, such as the peak connecting $\{\alpha–\alpha\alpha\}$ and $\{\alpha–\beta\alpha\}$ (proportional to W_{1K}). The *cross-peak multiplet* connecting A and M (left half of Figure 1) features strong signals between connected transitions, e.g., between $\{\alpha–\alpha\alpha\}$ and $\{–\alpha\alpha\alpha\}$, which occur in the absence of relaxation, like in *z*-COSY.[12,13] The peak between $\{\alpha–\alpha\alpha\}$ and $\{–\beta\beta\beta\}$ is proportional to W_2^{KX} (in the initial rate approximation), since, in addition to the permutation of A and M in the roles of active and passive spins, this peak reflects concerted flips of K and X. Other peaks have amplitudes that reflect the superposition of various pathways. For example, the amplitude of the signal correlating the transitions $\{\beta–\beta\alpha\}$ and $\{–\alpha\alpha\alpha\}$ can be rationalized as follows: since $\{\beta–\beta\alpha\}$ is converted into populations $\{\beta\alpha\beta\alpha\}$ and $\{\beta\beta\beta\alpha\}$, while the coherence $\{–\alpha\alpha\alpha\}$ is proportional to the difference of the populations $\{\alpha\alpha\alpha\alpha\}$ and $\{\beta\alpha\alpha\alpha\}$, there are three relaxation pathways that may contribute to the signal: W_2^{AK} connects $\{\beta\alpha\beta\alpha\}$ and $\{\alpha\alpha\alpha\alpha\}$, W_2^{MK} leads from $\{\beta\beta\beta\alpha\}$ to $\{\beta\alpha\alpha\alpha\}$, while W_1^K connects $\{\beta\alpha\beta\alpha\}$ to $\{\beta\alpha\alpha\alpha\}$. As a result, the cross-peak corresponding to the process $\{\beta–\beta\alpha\} \rightarrow \{–\alpha\alpha\alpha\}$ is proportional to $W_2^{AK} + W_2^{MK} - W_1^K$.

A quantitative evaluation of the **W** matrix requires a comparison of experimental and simulated multiplets. The dipolar contributions to the **W** matrix were calculated from known proton–proton distances.[15] Only the isotropic correlation time, τ_c, and the amount of external (uncorrelated) random field relaxation were adjusted empirically to obtain satisfying agreement between theory and experiment. No agreement could be found if the assignments of the K and X resonances were inverted. Thus, the small flip angle NOESY method allows one to solve stereochemical questions such as the distinction between cis and trans isomers in our example. With this experiment one obtains information about both scalar and dipolar couplings (COSY and NOESY information) in one single spectrum.

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Chemistry of Cationic Zirconium(IV) Benzyl Complexes. One-Electron Oxidation of d^0 Organometallics

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Cationic d^0 complexes $Cp_2M(R)^+$ ($Cp^- = C_5H_5^-$, M = Ti, Zr) have been implicated as active species in soluble Cp_2MCl_2/AlR_nCl_{3-n} Ziegler–Natta olefin polymerization catalyst systems.[1,2] We recently showed that the THF complex $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**1**) polymerizes ethylene in CH_2Cl_2 solvent under mild conditions.[2] The active species in this reaction is probably the "naked alkyl" $Cp_2Zr(R)^+$ since THF inhibits the polymerization, and **1** does not coordinate a second THF ligand.[3] We now report that the benzyl analogue of **1**, $[Cp_2Zr(CH_2Ph)(THF)][BPh_4]$ (**2**), can be prepared by a novel one-electron oxidation of d^0 $Cp_2Zr(CH_2Ph)_2$, and that **2** also polymerizes ethylene.

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