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Solution Behavior of $\mathrm{Zr}_{2}\left(\mathrm{OCMe}_{2} \mathrm{CMe}_{2} \mathrm{O}\right)_{2}\left(\mathrm{OCMe}_{2} \mathrm{CMe}_{2} \mathrm{OH}\right)_{4}$. At room temperature, the ${ }^{1} \mathrm{H}$ NMR of $\mathrm{Zr}_{2}\left(\mathrm{OCMe}_{2} \mathrm{CMe}_{2} \mathrm{O}\right)_{2}\left(\mathrm{OCMe}_{2} \mathrm{CMe}_{2} \mathrm{OH}\right)_{4}$ contains several broad overlapping peaks in the methyl region. However, at elevated temperatures $\left(65-85^{\circ} \mathrm{C}\right)$, the methyl region simplifies to four sharp resonances in an approximate 1:2:2:1 ratio. With a total of 24 methyls in the compound, this suggests a fluxional process which gives rise to $C_{2 h}$ symmetry. Scheme 1 (suppl.) shows two possible processes. Route A involves two separate motions; the proton transfer between axial ligands (which equilibrates four of the six ligands) and the swinging of the bridging ligands in the equatorial plane. If the latter does take place, there must be the restriction that the metal centers remain at least five-coordinate at all times or this would equilibrate all eight of the bridging ligand methyls. Route B is more simple and invokes only the proton transfer to the nonchelating oxygen of the bridging ligand. The bridging ligand then becomes monodentate and the geometry about the metal centers becomes trigonal prismatic. The two hydroxyl protons not shown in B will have equal probability to be on any of the four chelate ligands. Either of these routes could explain the observed symmetry and, at this time, we have no preference for one over the other.

Primary mechanism; explanation for expected isotopomer ratios. As stated in the paper, each deuterated ligand (see Scheme 3 of published text) has an equal chance to couple with a second deuterated ligand or a nondeuterated ligand. For example, using Scheme 3, assume that each deuterated ligand (in bold) (eq. 4) has equal probability of coupling to either ligand

$$
\begin{equation*}
(1 / 2 m) X+(n-1 / 2 m) Z=1 \tag{4}
\end{equation*}
$$

next to it. Then, for the four deuterated ligands, two should couple with each other (giving one fully-deuterated PMH) and two should couple with nondeuterated ligands (giving two partiallydeuterated PMH). This results in a minimum ratio of $1: 2$ expected for the fully-to-partiallydeuterated PMH (see eq. 4). As the initial mole fraction of the deuterated compound increases,
the incidence of neighboring deuterated subunits grows, yielding a relative rise in frequency of coupling of two deuterated ligands.





Scheme 1 suppl.

