methods required for their preparations. Finally, the reaction of $HfCp_2Cl$ with magnesium under the same conditions as above gave ESR spectra due to small fractions of the zirconium compound usually contained in the commercial product, in agreement with previous observations by Lappert and coworkers on their attempts to reduce hafnium(IV) metallocenes.[5]

Acknowledgment. I am grateful to Mrs. Hênique for efficient technical assistance.

Registry No. 6, 86569-04-2; $ZrCp_2Cl_2$, 1291-32-3; $ZrCp_2Br_2$, 1294-67-3; Mg, 7439-95-4; PhC≡CPh, 501-65-5; PhC≡CH, 536-74-3; styrene, 100-42-5; hex-1-ene, 592-41-6; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; benzophenone, 119-61-9; dibenzopinacol, 464-72-2.

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

"Lid-On" and "Lid-Off" Diastereoisomers of Lacunar Macrobicyclic Complexes As Identified by ^{13}C- and ^1H-Coupled ^{13}C NMR Spectroscopy

Norman Herron, Dennis L. Nosco, and Daryle H. Busch*

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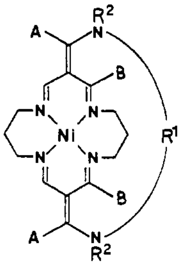
Isomers involving different orientations of R^1 and R^2 about the amide-like nitrogen of the lacunar macrobicycles of structure I have been noted several times in our previous publications.[1-3] These isomers have been designed "lid-on" (II) and "lid-off" (III) in reference to the orientation that the R^1 bridge occupies relative to the metal center.[1] While any given bridged molecule has, to date, a unique isomeric configuration,[1,2] the identification as to this being "lid-on" or "lid-off" has relied exclusively on X-ray crystal structures of isolated materials. Two such crystal structures have been reported that show dramatically the effect of going from a "lid-on" to a "lid-off" isomer type. The iron(II) complexes of I, in both of which R^1 = *m*-xylylene, have the "lid-on" configuration if R^2 = H and "lid-off" configuration if R^2 = CH_3.[3,4] The cavity of the former structure is 7.57 Å high and 5.20 Å wide while the latter is 5.02 Å high and 7.37 Å wide. The corresponding binding constants for carbon monoxide show that the "lid-on" isomer binds CO a factor of 10 times more strongly than the "lid-off" structure.



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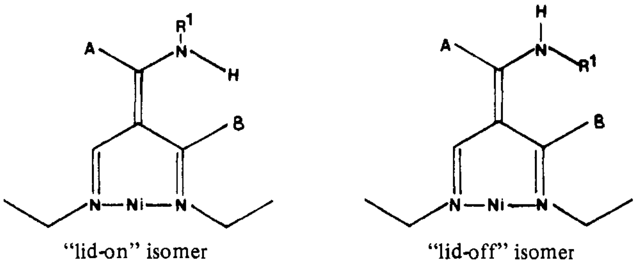

"lid-on" isomer
II

"lid-off" isomer
III

(structure I viewed from the side along the NiN_4 plane)

Table I. Coupling Constant Data for Lacunar Complexes I Where R^2 = H

R^1	$^3J_{^{13}C-^1H}$, Hz	isomer type predicted	isomer type obsd (X-ray)
$(CH_2)_6$	2.0	lid-off	
m-xylylene	7.8	lid-on	lid-on
m-xylylene (dimeric)[1]	6.5	lid-on	lid-on
trans-1,3-cyclohexanediylbis(methylene)	6.1	lid-on	
cis-1,3-cyclohexanediylbis(methylene)	6.1	lid-on	lid-on
p-xylylene	≤1.5	lid-off	lid-off
$(CH_2)_5$	≤1.5	lid-off	
$(CH_2)_4$	≤1.5	lid-off	

These and other data[4,5] have shown that the size and shape of the lacuna in these structures have a pronounced effect on the strength of binding of an axial ligand such as CO or O_2 within the cavity. It is clearly important that the "lid-on"/"lid-off" isomer type be easily identified in order to estimate the cavity dimensions of new structures without the necessity of a lengthy X-ray crystal structure analysis, and it is even more important to be able to assess such configurations in solution where the small-ligand binding is to take place.

A technique that allows this identification to be done rapidly in solution is ^{13}C NMR spectroscopy, particularly ^1H-coupled ^{13}C NMR spectroscopy for instances where R^2 = H. When R^2 = H, it is clear from structures II and III that the relationship between this R^2 proton and the vinylic methyl group carbon A is either cis ("lid-off") or trans ("lid-on") across the "amide-like" C–N bond. It is well-known in ^1H NMR spectra that the vicinal or three-bond $^1H-^1H$ coupling constants across such bonds reflect the classic Karplus equation,[6a] and the same ought to hold true for the three-bond coupling between the proton (R^2) on nitrogen and the carbon nucleus A.[6b] If so, then a cis/"lid-off" orientation will give a smaller coupling constant than a trans/"lid-on" orientation. In order to establish whether this was true, the fully ^1H-coupled ^{13}C NMR spectra of two model amide compounds were recorded and the $^3J_{^{13}C-^1H}$ coupling constants for cis and trans orientations of the coupling nuclei across the amide bond were determined. Acetamide has $^3J_{^{13}C-^1H}$ = 6.84 Hz and ≤1.0 Hz, dimethylformamide has $^3J_{^{13}C-^1H}$ = 6.82 Hz and ≤1.0 Hz for, presumably, the trans and cis coupling constants, respectively, in each case. These reflect the same trend as standard olefinic coupling constants: $^3J_{^1H-^1H(cis)}$ = 7–11 Hz, $^3J_{^1H-^1H(trans)}$ = 12–18 Hz;[6] i.e., $^3J_{trans} > {}^3J_{cis}$.

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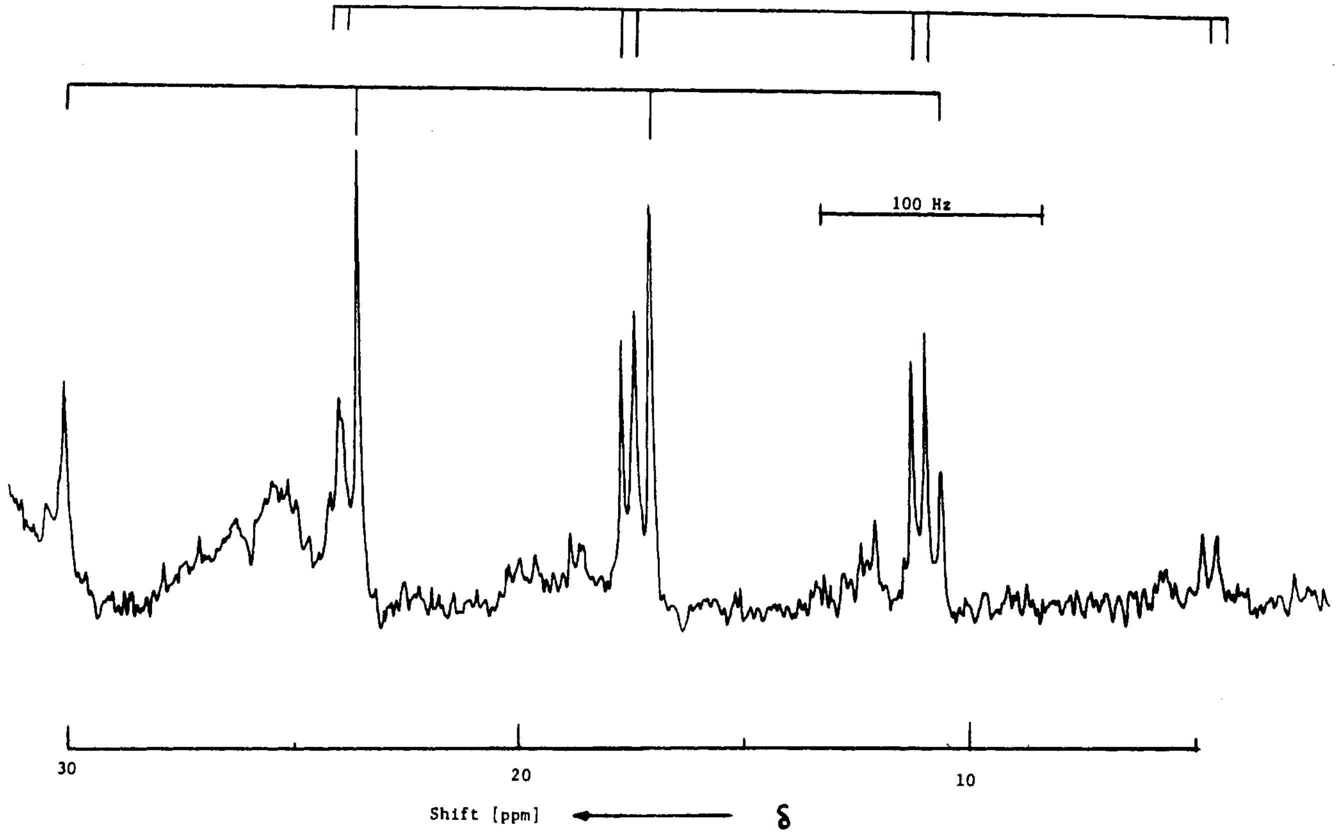

Figure 1. Fully ^1H-coupled ^{13}C NMR spectrum of I where R^2 = H and R^1 = *cis*-1,3-cyclohexanediylbis(methylene) in $C^2H_3NO_2$ with expansion of the 3–30 ppm region, showing the splitting of both methyl carbon resonances into quartets (^1J = 129.8 Hz) by directly attached protons and of one of these further into doublets by the R^2 proton (^3J = 6.1 Hz).

With this base, analysis of a series of lacunar complexes I where R^2 = H was undertaken by running fully coupled ^{13}C NMR spectra in $C^2H_3NO_2$ and looking for the $^3J_{^{13}C-^1H}$ coupling between the R^2 proton and the methyl group carbon A. Figure 1 illustrates one such ^{13}C NMR spectrum, and Table I lists the results for a series of compounds.

The results in Table I appear to validate the application of coupling information to the assignment of structure in that the deduced structure in all instances agrees with that observed in the X-ray structure of the same compound. This indicates that the X-ray structure is retained in solution, and as a general rule, ^3J = 6–8 Hz corresponds to a "lid-on" orientation while $^3J \leq 2$ Hz indicates a "lid-off" isomer.

One interesting and valuable observation from these data concerns the relative ^{13}C NMR shifts of the two methyl groups A and B of complexes I. When a "lid-on" isomer is predicted on the basis of the coupling data, it is found that the two methyl carbon resonances are separated by, typically, some 5 ppm with carbon A (the one showing ^3J coupling to the R^2 proton) occurring upfield at ~15 ppm.[1] On the other hand, when a "lid-off isomer is present, the two carbons are nearly coincident with shifts of ~20 ppm. It appears, therefore, that carbon A experiences an upfield shift of some 5 ppm on going from a "lid-off" to a "lid-on" isomer type. This is most probably a result of steric-compression shifting[7] due to the cis orientation of carbon A and the R^1 substituent across the amide-like C–N bond in the "lid-on" structure. Indeed, molelcular models show very close approach of these groups in the "lid-on" isomer.

This latter phenomenon is useful in predicting the isomer type of lacunar complexes where $R^2 \neq$ H and where no ^3J coupling information is accessible. The prediction is that the complex will be "lid-on" if $\Delta\delta(CH_3)$ is 5 ppm and "lid-off" if $\Delta\delta(CH_3)$ is 0 ppm, at least for moderately small R^2 groups such as H or CH_3.[8]

^{13}C NMR spectra have, therefore, been found to be a useful and rapid method for evaluating the "lid-on"/"lid-off" isomer type of lacunar complexes I. Application of simple shift and coupling information from ^{13}C NMR spectra has the potential for widespread use in the analysis of the structure of coordination compounds as the examples here demonstrate.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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