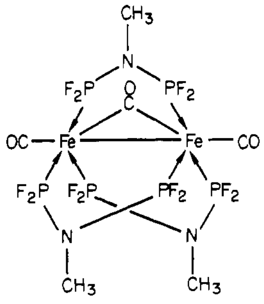
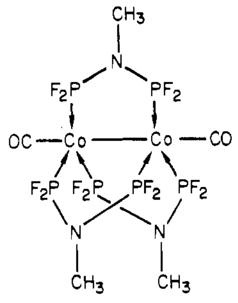
hydrolysis of $CH_3N(PF_2)_2Fe(CO)_4$ (I) to $CH_3NHPF_2Fe(CO)_4$ (II) on the usual chromatographic adsorbents such as Florisil and alumina.

B. The Binuclear Iron Carbonyl Derivative $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$. The thermal reaction of $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ produces $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ as a major product[2,4] whereas the photochemical reaction of excess $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ (i.e., a 6:1 mole ratio) produces $[CH_3N(PF_2)_2]_4Fe_2CO$ in up to 37% yield.[3] These binuclear iron carbonyl complexes are two of the three previously known members of the series $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ (n = 1,2, and 4), which may be regarded as formal substitution products of $Fe_2(CO)_9$, although significant structural changes occur upon successive pairwise substitution of CO groups with $CH_3N(PF_2)_2$ ligands. We now report conditions for the isolation of the previously missing member of the $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ series, namely $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ (n = 3), in ~2% yield from the reaction mixture obtained by photolysis of $CH_3N(PF_2)_2$ with $Fe_3(CO)_{12}$ in a 2.5:1 mole ratio.

Several structures for $[CH_3N(PF_2)_2]_3Fe(CO)_3$ are conceivable including a structure with three bridging $CH_3N(PF_2)_2$ ligands as in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$[13] a structure with two bridging $CH_3N(PF_2)_2$ ligands, one bridging PF_2 group, and one terminal CH_3NPF_2 group as in $[CH_3N(PF_2)_2]_4Fe_2CO$[3] and a structure with two bridging $CH_3N(PF_2)_2$ ligands and one terminal $CH_3N(PF_2)_2$ ligand related to that of $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$.[14] Unfortunately, the physically attractive red crystals of $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ do not appear to be readily suitable for X-ray crystallography.[15] The infrared ν(CO) spectrum of $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ is distinctive since it exhibits only one terminal ν(CO) frequency (1977 cm^{-1}) and one bridging ν(CO) frequency (1776 cm^{-1}). Structure V is therefore suggested for $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$. This structure has equivalent terminal CO groups on each iron atom and is related to the established structure VI for $[CH_3N(PF_2)_2]_3Co_2(CO)_2$[13] by addition of a bridging carbonyl group across the metal–metal bond.



V



VI

Acknowledgment. We gratefully acknowledge successive support of this research by Air Force Office of Scientific Research Grant AFOSR-75-2869 (1979), National Science Foundation Grant CHE-77-15991 (1980), and a grant from the Petroleum Research Fund, administered by the American Chemical Society (1981). The Finnegan gas chromatography–mass spectrometer used for this work was purchased with a major equipment grant from the National Science Foundation.

Registry No. I, 86669-56-9; II, 86669-57-0; III, 86669-58-1; V, 86669-59-2; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; Fe, 7439-89-6; $CH_3N(PF_2)_2$, 17648-18-9.

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Reduction of Zirconocene Dihalides with Magnesium Studied by ESR. Evidence of Zirconium(III) Hydride Formation by Hydrogen Transfer from the Cyclopentadienyl Ring

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Among the organometallic and coordination compounds of the early transition metals, those of Zr in its 3+ oxidation state are the most poorly documented and remain a scarcity. Their difficult access is due in part to the relatively low potential at which Zr(IV) reduces to Zr(III) ($-E_{1/2}$ = 1.6–2.09 V);[1] they are known also to have a marked tendency to dimerize, giving compounds with low paramagnetism.[2-4] However, very recently a number of cyclopentadienylzirconium compounds have been detected in solution by their ESR spectra as stable radical anions[5] or as intermediates in oxidative-addition reactions.[6,7]

When features due to metal and ligand hyperfine interactions are present, ESR techniques provide an excellent opportunity to monitor reaction sequences involving paramagnetic metal-centered radicals. In this work we report on the identification by ESR of Zr(III) species obtained by chemical reduction of zirconocene dihalides with metallic magnesium and on some of their chemical reactivities.[8] We also demonstrate that the formation of zirconium(III) hydride species proceeds by hydrogen transfer from the cyclopentadienyl ring.

Experimental Section

All manipulations were performed under argon. Grignard-quality magnesium was used for reduction; THF was distilled over sodium naphthalide and then on lithium aluminum hydride before use. ESR spectra were recorded on a JEOL ME SX X-band spectrometer with a Bruker B-A6 accessory for field calibration. $ZrCp_2Cl_2$ (Cp = η^5-C_5H_5) was purchased from Alfa Inorganics. $ZrCp_2Br_2$ was prepared by treating $ZrCp_2(CH_3)_2$ with dry HBr gas in ether.

Results and Discussion

In contrast with titanocene dihalides, which cleanly reduce to the monohalides with Al or Zn metals,[9] zirconocene dihalides are inert toward these reagents and the use of Na amalgam or metallic Li leads to Zr(II) species which have been isolated as zirconocene dicarbonyls or phosphine compounds.[10-12] It has been reported that reduction of $ZrCp_2Cl_2$ with metallic magnesium (0.5 mol) in THF affords a reddish

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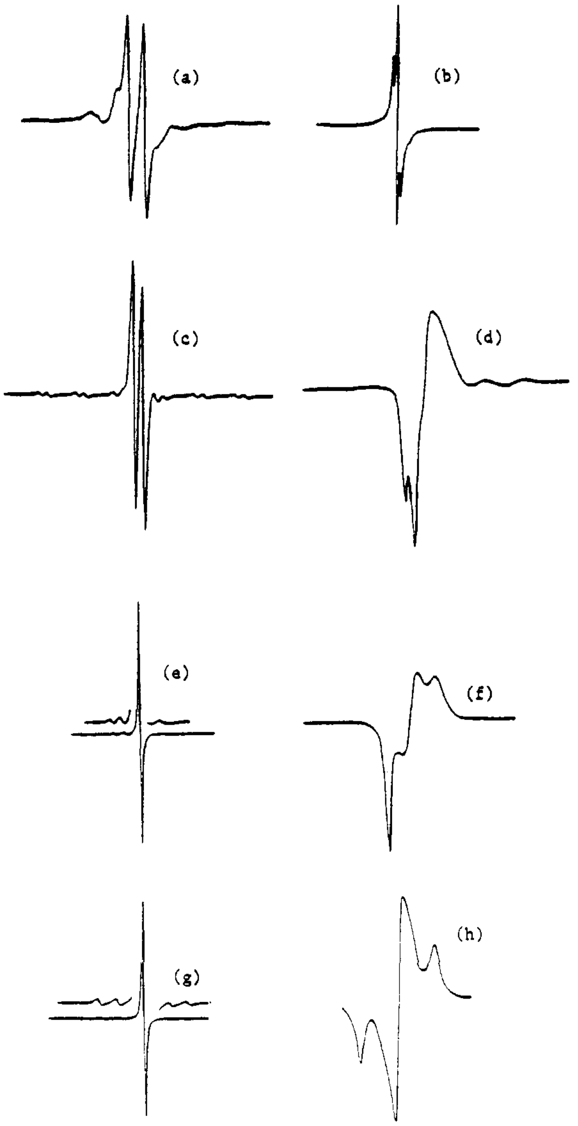

Figure 1. ESR spectra of solution I: (a) 48 h after mixing; (b) with C_5D_5 instead of C_5H_5 (g value same as in (a), outer lines due to partial deuteration of Cp); (c) 5 min after mixing with PhC≡CPh; (e) same as (c) after 6 h; (g) 5 min after mixing with styrene; (d, f, h) frozen-solution (THF) spectra of (c), (e), and (g), respectively. All room-temperature spectra were scanned at the same sweep range.

brown solution from which $ZrCp_2HCl$ can be recovered after several days,[13,14] but no details were mentioned about the mechanism by which the reaction proceeds. Obviously formation of the chlorohydride requires a chlorine removal step by Mg and a subsequent hydrogen transfer onto zirconium. We decided therefore to monitor the progress of the reaction by ESR.

When a 0.1 M solution of $ZrCp_2X_2$ (X = Cl, Br) is treated with excess magnesium (solution I), a reddish brown coloration develops after a short induction period; formation of Zr(III) paramagnetic species is revealed by the intense ESR spectrum obtained, which consists of a central singlet flanked by neatly resolved satellites due to hyperfine interaction of the unpaired electron with the ^{91}Zr nucleus ($I = {}^5/_2$, 11.23%). When the reaction is allowed to proceed further, the spectrum rapidly develops complex features due to ill-defined species, the number and intensity of which vary continuously. After the mixture is stirred for 48 h, the spectrum reduces to a doublet of 1:1 intensity with poorly resolved satellites (Figure 1a).

Table I. ESR Parameters of Solution I in the Absence and Presence of Substrates

		A_{av}-(Zr), G	A_{av}-(H), G	g_{av}	g_{aniso}
I	*a*	24.5		1.9760	
	b		7.4	1.9898	
I + PhC≡CPh	*c*	26.8	7.2	1.9945 1.9964^f	$g_1 = 2.0050$ $g_2 = 1.9955$ $g_3 = 1.9887$
	d	7.4		1.9905 1.9900^f	$g_1 = 2.0013$ $g_2 = 1.9912$ $g_3 = 1.9774$
I + PhC≡CH		8.8	6.4	*g*	
I + styrene	*e*	11.9		1.9825 1.9830^f	$g_1 = 2.0008$ $g_2 = 1.9825$ $g_3 = 1.9657$
I + hex-1-ene		17.8	5.8	*g*	

[a] Singlet after 5 min of reaction. [b] Corresponds to Figure 1a. [c] Corresponds to Figure 1c. [d] Corresponds to Figure 1e. [e] Corresponds to Figure 1g. [f] Calculated by using the expression $g_{av} = {}^1/_3(g_1 + g_2 + g_3)$. [g] Not measured.

This solution can be kept in a sealed tube for several months without loss in signal intensity. The amount of Mg consumed by this time is about 1.5 mol of Mg/mol of the dichloride. The doublet is easily attributed to a Zr(III) hydride since the proton hyperfine splitting (7.4 G) is very close to values obtained for other early transition-metal hydride complexes such as those of Nb or Ti.[15,16]

The reaction with diphenylacetylene was interesting to follow by ESR. Thus, if this alkyne is introduced into the $ZrCp_2Cl_2$/Mg/THF solution at the beginning of the reaction (in a ratio PhC═CPh:$ZrCp_2X_2$ = 2:1) a reddish coloration also develops rapidly and the ESR signal of the species formed after a few minutes exhibits an intense central doublet flanked by the expected number of satellites neatly resolved, indicating hyperfine interaction of the unpaired electron with both zirconium and hydrogen (Figure 1c). Interestingly, no other signals are present as was the case in the absence of diphenylacetylene. When the reaction is allowed to proceed for a few hours (6–8 h), the doublet disappears and is replaced by a very intense singlet, again with neat Zr hyperfine satellites but with a substantially different value of the hyperfine constant A(Zr) (Figure 1e).

This result incited us to investigate further the reaction of solution I with other olefins. In fact, in several other cases clear ESR spectra were obtained when those olefins were introduced at the beginning of the reaction, and in all cases only singlets or doublets of high intensity were observed, with A(Zr) varying in magnitude with the nature of the olefin (Figure 1 and Table I). Hyrolysis of solution aliquots with diphenylacetylene and styrene showed by GLC that hydrogenation of the substrate had occurred. With these convincing elements in hand in favor of the formation of a Zr(III) hydride, we sought to determine the origin of the hydrogen abstracted by the metal. Two sources are possible, the solvent or the cyclopentadienyl ring; the third possibility of having traces of moisture present was provisionally excluded. By conducting the reaction in THF-d_8, we obtained the same doublet at the end of the reaction, although the intermediate features of the spectrum were somewhat different.

A definitive proof was provided by conducting the reaction with $Zr(C_5D_5)_2Cl_2$.[17] The final ESR spectrum exhibited only a singlet (Figure 1d) with line width ≃ 3 G, which is the expected signal for a Zr(III)–D pattern since the sixfold re-

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(13) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405.

(14) Wailes, P. C.; Weigold, H. *Inorg. Synth.* **1979**, *19*, 226.

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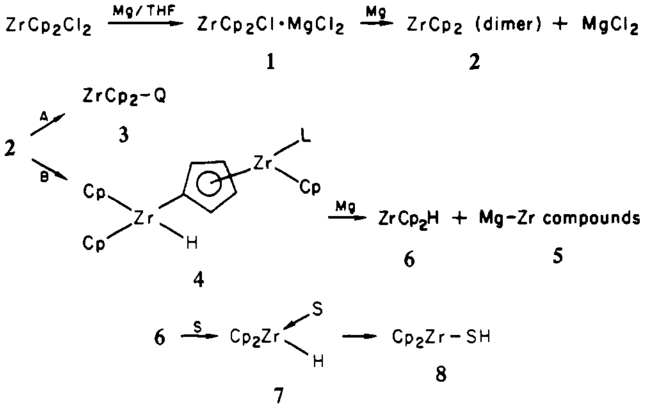
(17) Prepared from $Tl(C_5D_5)$ and $ZrCl_4$. For C_5D_5 see: Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.

Scheme I[a]



[a] Abbreviations: S = unsaturated substrate; L = THF; Q = THF fragments. **6**, **7**, and **8** are simple formulations of probably more complex structures (such as radical anions, for example).

duction of the proton hyperfine splitting would yield a nonresolved triplet. The same reaction conducted with $PhC\equiv CPh$ provided a confirmation to this result, the spectrum consisting of a singlet having nearly the same A(Zr) value as the doublet observed with $ZrCp_2Cl_2$ at the same stage of the reaction.

In Table I are gathered the ESR parameters, for liquid and frozen solutions, of all the spectra obtained from solution I in the absence and presence of substrates. It clearly shows that every system (solution I + olefin) has characteristic features so that, in the absence of more material evidence, such as the isolation of a well-defined species, one can safely assume that the compounds responsible for the signals are different from each other and therefore must contain in their structure the substrate unit introduced.

Scheme I summarizes the postulated mechanisms of the reactions observed: the dichloride (X = Cl) is first reduced to the monochloride (**1**), most probably a magnesium-bridged dimer (ESR singlet). Further reduction leads to product **2**.[18] This species reacts through pathway A, yielding **3**, where the metal is bound to hydrocarbon fragments resulting from cleavage of THF;[19] **3** is thought to be responsible for the complex signal that develops in the absence of substrates. This hypothesis is supported by the simpler intermediate features observed when THF-d_8 is used as solvent, again due to the reduction of proton hyperfine interaction. Dimer **2** can also react through pathway B, giving **4**, a formally mixed-valence species,[6] which yields **5** and **6**. **4** should be invoked to explain that hydrogen transfer to the metal occurs through a bimolecular mechanism. Secondary products **5** are postulated to account for the excess magnesium consumed relative to the stoichiometric requirements for the formation of $MgCl_2$, and **6** is the key ESR-active precursor responsible for the signals and the reactions that occur in the presence of unsaturated substrates. Signal c (Table I) with diphenylacetylene is attributed to species **7**, where the alkyne is coordinated to the metal hydride. In this case, pathway A is not detected by ESR due probably to the reaction of $PhC\equiv CPh$ with **3** to give diamagnetic species. Species **8** is subsequently formed through olefin cis insertion into the Zr–H bond, giving the singlet e (Table I). The reactions in the presence of $PhC\equiv CH$ and hex-1-ene follow the same initial processes, though they show different Zr hyperfine constants due to the different π-acidities of these substrates.[20] The particularly high A(Zr) value of the species generating spectrum c (Table I) is attributed to the high steric requirements of the phenyl rings in diphenylacetylene leading to loose coordination of this substrate on Zr, thus reducing spin density on the triple bond. With styrene, however, only an intense singlet (Figure 1g) is observed; the expected doublet relative to species **7** is probably too short-lived to be detected due to the high reactivity of the olefin toward hydrogenation. Indeed, under catalytic conditions the rate of hydrogen absorption is much faster than with other olefins.[21] It should be mentioned that mechanisms such as those resulting in **7** and **8** have been postulated to account for the ESR spectral changes in $NbCp_2H_2$/olefin systems[16] and generally for the conversion of alkenes or alkynes into transition-metal alkyl or alkenyl compounds.[22] The formation of $ZrCp_2HCl$ with system **1** can be explained by the reaction of **6** with $ZrCp_2Cl_2$ when only 0.5 mol of Mg is used.

Solution I shows interesting reactivities toward other organic substrates. Thus it isomerizes *cis*- into *trans*-stilbene and reacts with benzophenone to give dibenzopinacol. The latter reaction also occurs with reduced titanocene compounds[23] and is well-known to proceed by a free-radical pathway, the Zr(III) here acting as an electron source. It should not be excluded that electron-transfer mechanisms also govern the reactions of the present system with unsaturated substrates but that such pathways are not directly detectable by ESR.

The ESR data (Table I) call for some comments. The proton hyperfine interaction constant has the same value as in the species generated by photolysis of $ZrCp_2(CH_3)_2$.[24] It is, however, affected only to a small measure by olefin coordination, which shows a similar Zr–H interaction in all the cases examined. In contrast, the Zr hyperfine splitting appears to be sensitive to the metal environment to an appreciable extent, thus providing a qualitative measure of the importance of electron delocalization on the coordinated unsaturated ligand. The range of variation is surprisingly very wide if one takes also into account other data determined recently for Cp_2Zr^{III} species;[4] the low values of 8.5 and 7.4 G in the table are to be compared with A(Zr) = 8.5 G observed for $[Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}N_2)CH(SiMe_3)_2]$ attributed to extensive electron delocalization on the dinitrogen ligand.[25]

In the absence of structural evidence as to the identity of the species described, the frozen-solution spectra provide some information about their nature. The parameters for the glassy phase are the first well-defined values to be reported for a Zr(III) compound. They are all related to three-component tensors consistent with rhombic molecular symmetry and in agreement with the expected tetrahedral structure for a bent metallocene compound, with a g_1 value close to 2.0023 indicating that the unpaired electron lies in a d_{z^2} orbital.

We conclude therefore that the ESR-active species **6**, **7**, and **8** (Scheme I) contain mononuclear zirconocene units, probably associated with magnesium halide as radical anions; a dimeric structure is expected to lead to different ESR features, in some cases characteristic of a triplet state[26] or antiferromagnetic interaction. Other alternatives such as formation of mono- or tricyclopentadienyl compounds, though not to be completely excluded, are highly unlikely due to the more sophisticated

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(18) Formation of this dimer has been postulated earlier at several occasions; see, for instance: Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933.

(19) Reduced transition-metal compounds are known to cleave THF to give various hydrocarbons: Sobota, P.; Pluzinski, T.; Jesowska-Trebiatowska, B. *J. Organomet. Chem.* **1980**, *185*, 69.

(20) These two substrates show persistent doublets; the step leading to **8** (Scheme I) does not appear to occur easily.

(21) Samuel, E. *J. Organomet. Chem.* **1980**, *198*, C65.

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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.

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

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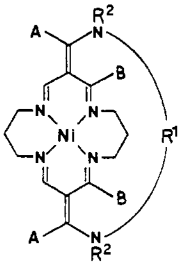
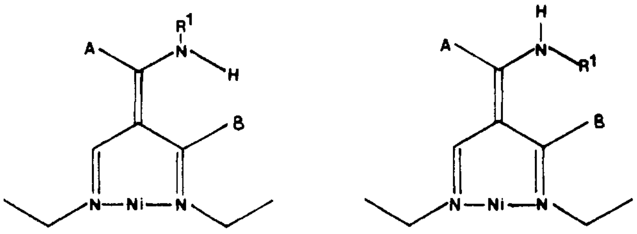
Isomers involving different orientations of R^1 and R^2 about the amide-like nitrogen of the lacunar macrobicycles of structure I have been noted several times in our previous publications.[1-3] These isomers have been designed "lid-on" (II) and "lid-off" (III) in reference to the orientation that the 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.



I



"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 ^{1}H-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 ^{1}H NMR spectra that the vicinal or three-bond ^{1}H–^{1}H 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 ^{1}H-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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