

Isotopic perturbation of resonance in a homologous series of metal complexes with allylic cation character

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ABSTRACT: Deuterium-induced isotope shifts in a series of ML_n (L = statistical mixture of 3-oxido-2-phenylpropenal- d_0 , -1- d and -1,3- d_2) were measured. The ^{13}C NMR isotope shifts, $\delta_{\text{C(D)}} - \delta_{\text{C(H)}}$, for the aldehydic CH of AlL_3 , $\text{Al}(\text{OiPr})_2\text{L}$, $(\text{CH}_3)_2\text{AlL}$, SiBr_3L , $\text{SiL}_3^+\text{HBr}_2^-$, $(\text{CF}_3)_3\text{GeL}$, $(\text{EtO})_4\text{NbL}$, $\text{Rh}(\text{CO})_2\text{L}$, PdL_2 , SbCl_4L and $(\text{EtO})_4\text{TaL}$ are small and positive. The positive isotope shifts are unusual, but since they are small and temperature independent they are intrinsic. A relationship between these isotope shifts and the chemical shifts can be discerned and attributed to isotopic perturbation of resonance in an allylic cation. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: resonance; isotopic perturbation; metal complexes; allylic cations

INTRODUCTION

Isotope shifts

Isotopic substitution leads to detectable changes in the NMR chemical shift of a reporter nucleus.¹ These have become readily accessible, owing to the ability of modern multinuclear high-field instruments to resolve signals due to isotopically substituted molecules. Such isotope shifts are a topic of much current research, providing a sensitive probe of molecular structure. They are especially useful in studies of tautomerization equilibria, where replacement of a hydrogen-bonded H by D often affects the position of the equilibrium.² They have provided surprising results about the symmetry of hydrogen bonds in solution.³ Replacement of CH by CD is synthetically more difficult, but can produce isotope shifts that provide further information about structure.⁴

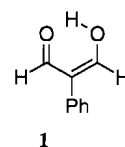
The deuterium-induced ^{13}C NMR isotope shift ${}^n\Delta$ is the chemical-shift difference between corresponding ^{13}C signals of deuterium- and protium-containing molecules:

$${}^n\Delta = \delta_{\text{C(D)}} - \delta_{\text{C(H)}} \quad (1)$$

It falls off rapidly with n , the number of bonds between the reporter nucleus and the isotope. As defined here, the isotope shift is usually <0 , but conventions differ.

Metal β -diketonates have been widely studied and

utilized.⁵ Usually these occur as chelates, with the metal coordinated to both oxygens. A quasi-aromaticity associated with the system of π -electrons has been proposed. In connection with an investigation of the symmetry of these complexes,⁶ we have measured isotope shifts in metal complexes (ML) of 3-hydroxy-2-phenylpropenal (HL) (**1**). This offers the advantage over the familiar 2,4-pentanedionate (acac) that the aldehyde permits α -deuterium labeling. The phenyl is for ease of synthesis and handling.



Isotope shifts lead to a resolvable splitting of the NMR signals of the aldehydic carbons of the isotopologues of ML. In a statistical mixture of ML- d_0 , -1- d and -1,3- d_2 (**2**, **2-d**, **2-d₂**), there are four signals in the carbonyl region of the ^2H -decoupled ^{13}C NMR spectrum, as illustrated in Fig. 1. Only two are observed without decoupling, because carbons attached to deuterium lack the nuclear Overhauser enhancement and they are split into a triplet. According to the known deuterium content of our samples, the taller of these two can be assigned as ML- d_0 . The other is the CH carbon of ML- d . With ^2H decoupling the two downfield signals persist. The two new signals are from carbons attached to ^2H , made visible by the decoupling. The taller is assigned to the CD of ML- d on the basis of the deuterium content. The weakest signal is from ML- d_2 .

Chemical shift differences are ${}^3\Delta$ and ${}^1\Delta + {}^3\Delta$, as labeled on Fig. 1. The separation between ML- d_0 and - d_2

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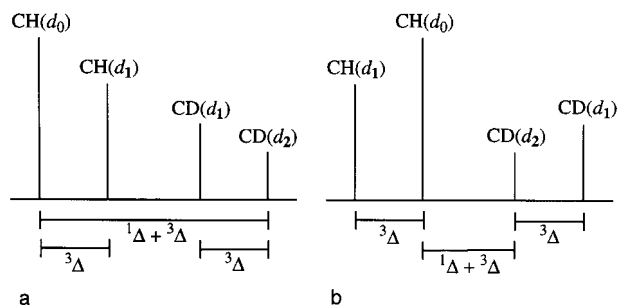
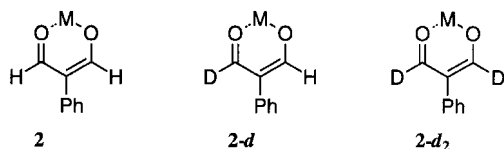


Figure 1. Expected ^{13}C NMR spectrum of metal chelates of a mixture of **1**, **1-d** and **1-d₂**: (a) if $^3\Delta < 0$; (b) if $^3\Delta > 0$. Peaks are assigned by intensities and ^2H content

signals is dominated by the large $^1\Delta$, arising from the directly bonded deuterium. There are two possible patterns [Fig. 1(a) or (b)], depending on whether $^3\Delta$ is negative or positive.



We are focusing on intrinsic isotope shifts, which arise simply from the averaging of the electronic shielding over the vibrational wavefunctions.¹ We ignore the possible contribution of an equilibrium isotope shift, which arises when ML is a mixture of two rapidly interconverting species.

EXPERIMENTAL

3-Hydroxy-2-phenylpropenal (HL, 1). This was synthesized by established procedures from dimethylformamide (DMF), POCl_3 and phenylacetic acid, precipitation as a perchlorate salt, hydrolysis with NaOH in aqueous methanol and acidification.⁷ A statistical mixture of HL isotopologues (HL- d_0 , -1- d and -1,3- d_2) was synthesized by the same procedures, except that DMF- d_7 provided a source of deuterium.⁸ The isotopic content was determined by mass spectrometry.

Preparation of metal complexes. Syntheses were conducted with dried solvents in a dry-box or using Schlenk techniques if necessary. Syntheses were adapted from known procedures: $\text{Al}(\text{bzac})_3$ or $(\text{CH}_3)_2\text{Al}(\text{acac})$,⁹ $\text{Si}(\text{acac})_3^+\text{Cl}^-$,¹⁰ $\text{Rh}(\text{CO})_2(\text{acac})$,¹¹ $\text{Pd}(\text{dbm})_2$,¹² $\text{SbCl}_4(\text{acac})$.¹³ More specifically, ML was prepared from HL and one of the following: 1/3 or 1 equiv. of $\text{Al}(\text{OiPr})_3$ in benzene, $(\text{CH}_3)_3\text{Al}$ in toluene, 1 or 1/3 equiv. of SiBr_4 in CDCl_3 , $(\text{CF}_3)_3\text{GeI}$ and Et_3N in pyridine, tetracarbonyl- μ -dichlorodirrhodium(I) and BaCO_3 in diethyl ether-THF, PdCl_2 and NaOAc in ethanol, SbCl_5 in CDCl_3 , or

Table 1. Aldehydic chemical shifts and isotope shifts for metal complexes of 3-oxido-2-phenylpropenal

Complex	Solvent	δ (ppm)	$^3\Delta$ (ppb)
$\text{Rh}(\text{CO})_2\text{L}$	CDCl_3	178.7	42
PdL_2	CDCl_3	178.9	43
$(\text{EtO})_4\text{NbL}$	C_6D_6	180.6	60
$(\text{EtO})_4\text{TaL}$	C_6D_6	180.8	61
SiBr_3L	CDCl_3	182.7	67
$\text{SiL}_3^+\text{HBr}_2^-$	CDCl_3	183.1	69
AlL_3	CDCl_3	183.4	67
$\text{Al}(\text{OiPr})_2\text{L}$	C_6D_6	183.4	67
$(\text{CH}_3)_2\text{AlL}$	C_6D_6	185.1	67
SbCl_4L	CDCl_3	186.3	79
$(\text{CF}_3)_3\text{GeL}$	Pyridine- d_5	187.2	85

$\text{Nb}(\text{OEt})_5$ or $\text{Ta}(\text{OEt})_5$ in benzene. Generally the reaction solvent was evaporated and the residue then dissolved in an NMR solvent. Further details are available.^{6,14}

Instrumentation. Air- or water-sensitive samples were kept in Teflon-valved NMR tubes. ^{13}C NMR spectra were recorded on a Varian Unity 500-MHz NMR spectrometer. Chemical shifts are relative to CDCl_3 (δ 77.0), C_6D_6 (δ 128.0) or pyridine- d_5 (δ 123.5).

RESULTS

One-bond isotope shifts

The isotope shifts $^1\Delta + ^3\Delta$ of the deuterium-bound carbons of the Al, Rh, and Pd complexes are between -310 and -350 ppm. For comparison, the corresponding isotope shift in K^+L^- is -395 ppb.⁶

Isotope shifts for reference compounds

For $\text{CH}_3\text{OCH}=\text{CPhCH}=\text{O-d}$ there are two aldehydic ^{13}C NMR signals, with an isotope shift $^3\Delta$ of -30 ppb for one and an unresolvable shift for the other.⁶ This represents the intrinsic shift from a distant isotope in a static asymmetric structure. The isotope shifts $^3\Delta$ of M^+L^- ($\text{M} = \text{Li}, \text{Na}, \text{K}$) are between -49 and -62 ppb, depending on solvent but not on M. These represent the intrinsic shift from a distant isotope in an unchelated L^- , which is a symmetric resonance hybrid with *E,anti* (extended) stereochemistry, according to a crystal structure.⁶ In both of these cases the negative (upfield) isotope shift is entirely expected.

Isotope shifts for metal chelates

Table 1 lists chemical shifts and isotope shifts for various

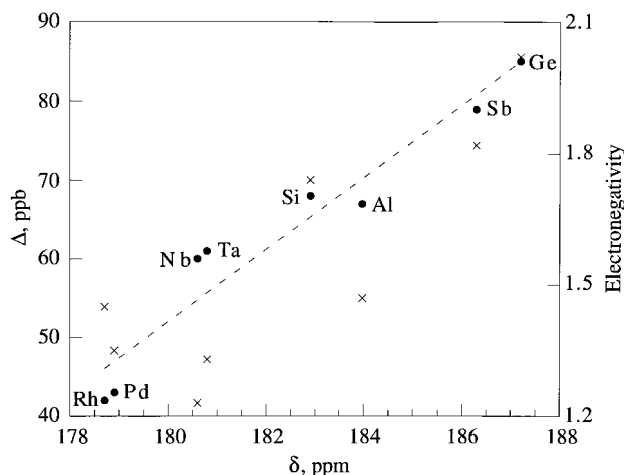


Figure 2. Relationships among isotope shift (●), electronegativity (×), and chemical shift for a series of metal chelates

ML_n chelates. From replicate determinations most isotope shifts are accurate to ± 1 – 2 ppb, except that broad peaks for $SiL_3^+ HBr_2^-$ and for Al complexes led to uncertainties up to ± 7 ppb. The positive (downfield) nature of the isotope shifts is unusual, but it is apparent from the pattern of intensities in the ^{13}C NMR spectra, which match Fig. 1(b). The isotope shifts for AlL_3 , $(CF_3)_3GeL$, $Rh(CO)_2L$ and PdL_2 are independent of temperature, down to $-30^\circ C$.

All ML_n might have been expected to exhibit the same $^3\Delta$, but the values in Table 1 do vary. The largest isotope shifts correspond to the most downfield signals, as shown in Fig. 2. In plotting these data, values for each metal have been averaged over all its complexes in Table 1.

DISCUSSION

The isotope shifts in Table 1 are small and positive for all the metal chelates. The positive nature might be taken as arising from the isotopic perturbation of an equilibrium between two equilibrating tautomers.¹ This would require these complexes to be asymmetric, with inequivalent M—O bonds. However, perturbation of equilibrium would produce considerably larger isotope shifts, as judged from the 0.76 ppm in HL,⁸ or from the 0.3–0.4 ppm seen in some unusual ML that are asymmetric.⁶ The substantially smaller values in Table 1 are consistent only with an intrinsic $^3\Delta$, arising from a distant isotopic substitution. Besides, since the isotope shifts are independent of temperature, there is no contribution from isotopic perturbation. We therefore conclude that these are intrinsic shifts from symmetric metal chelates.

The positive $^3\Delta$ is unusual for intrinsic shifts but is not unprecedented.¹⁵ It may be associated with the *Z,syn* configuration of L in a chelate, whereas the *E,anti* configuration in L^- produces a more normal negative $^3\Delta$.

This is consistent with the 180° CCCH dihedral angle in the chelates, just as $^3\Delta_F(D)$ in alkyl fluorides increases with the FCCH dihedral angle.¹⁶

Relationship between isotope shifts and chemical shifts

Not only do the largest isotope shifts in Table 1 correspond to the most downfield signals, but also the dependence of isotope shift on chemical shift is acceptably linear, as shown in Fig. 2. The slope is $(4.6 \pm 0.5) \times 10^{-3}$. The linear relationship is similar to that involving $^2\Delta$ in ketones and related molecules,¹⁷ where the slope is lower, only $(1.1$ – $1.2) \times 10^{-3}$ per D, even though the deuterium atom is one atom closer than in our case. The positive intrinsic isotope shift there was attributed to hyperconjugation, which is not operative here. Our slope is certainly much smaller in magnitude than the -95×10^{-3} (upfield, vs δ_H) observed for $^2\Delta$ in some *o*-hydroxy acyl aromatics.¹⁸ In that case the H or D is involved in a hydrogen bond, the NMR characteristics of which are sensitive to O—H and O—O distances.

The metal chelates in Table 1 form a homologous series with a continual structural variation that is manifested in chemical shifts. It is likely that the correlation in Fig. 2 arises from a dependence on electron density in the L fragment. The downfield shift (increasing δ) roughly parallels the Allred–Rochow electronegativities of the metals, which are also included in Fig. 2.¹⁹ The worst deviators are rhodium and palladium, which appear to be less electron withdrawing than as tabulated, perhaps as a result of back-donation of d electrons.

This behavior is similar to that seen in a series of $ArC(CD_3)_2^+$ and related carbocations, where $^2\Delta$ undergoes a sign change from negative to positive with increasingly electron-withdrawing groups in the aromatic ring.²⁰ The negative $^2\Delta$ is normal, and the positive $^2\Delta$ was attributed to isotopic perturbation of hyperconjugation, which weakens the bending and stretching force constants and effectively makes C—H a better electron donor than C—D. As a result, the carbon in the deuterated molecule is less electron rich, and therefore downfield.

It should be noted that this explanation is consistent with the Born–Oppenheimer approximation.²¹ The electronic wavefunction is independent of the nuclear masses, so that deuterium cannot itself reduce the electron density. Instead, isotopic substitution changes the vibrational wavefunction. Equation (2) relates the isotope shift [Eqn. (1)] to the distance-dependent shielding constant $\sigma(r)$, averaged over the vibrational wave functions ψ for H and D.²² The integrals can be expanded around the average interatomic distances $\langle r_H \rangle$ and $\langle r_D \rangle$, leading to Eqn. (3) as the leading term.

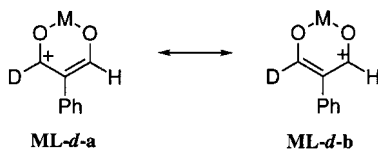
Then the anharmonicity and the higher zero-point energy of H lead to $\langle r_H \rangle$ greater than $\langle r_D \rangle$. Since $d\sigma/$

dr is usually <0 ,²³ Δ is then negative, corresponding to the D isotopologue being upfield. Similarly, a hyperconjugative C—H is longer than C—D. However, this permits greater electron donation from C—H to a carbocation, which shifts upfield, the reverse of the normal behavior.

$${}^n\Delta = \int \sigma(r)\psi^2(r_H)dr - \int \sigma(r)\psi^2(r_D)dr \quad (2)$$

$${}^n\Delta \approx \frac{d\sigma}{dr} (\langle r_H \rangle - \langle r_D \rangle) \quad (3)$$

The positive isotope shifts in ML_n can be attributed to an isotopic perturbation of resonance. Saunders and Kates first proposed this concept to account for the ${}^3\Delta$ of ~ 165 ppb in some allylic carbocations.²⁴ This isotope shift was originally explained by assuming that the more important resonance form is the one with positive charge on the carbon bearing the proton. The assumption seems to have been *ad hoc*, made to reach a conclusion in accord with the experimental result. It is not obvious that the more important resonance form is this one and not the one with positive charge on the carbon bearing the deuterium. Moreover, it is not clear exactly how this explanation is consistent with the Born–Oppenheimer approximation.



We now propose a detailed explanation for our isotope shifts, invoking isotopic perturbation of resonance. We consider $ML-d$ to be a resonance hybrid of the allylic cations $ML-d-a$ and $ML-d-b$. Although the ligand as a whole bears negative charge, the two aldehydic carbons are positive. Just as anharmonicity causes bond lengths, averaged over the zero-point motion, to be shorter for heavier isotopes, the bond shortening must also hold for the C=CD partial double bond in $ML-d$, because the effective mass of a CD fragment is greater than that of CH. This bond shortening causes the resonance form $ML-d-b$ where this bond is double, to contribute more. Consequently the CH is more cationic, and it is shifted downfield, whereas a distant deuterium would ordinarily shift the CH upfield. This conclusion is also derivable from HMO theory, which calculates a greater π bond order between atoms with a greater overlap integral S or greater (in magnitude) resonance integral β .²⁵ This explanation too is consistent with the Born–Oppenheimer approximation, since deuterium substitution acts by changing the average over the vibrational wavefunction.

The downfield isotope shift of the CH depends on the carbocationic character, which increases with the electronegativity of the metal, as reflected in the chemical

shift. The increase of ${}^3\Delta$ from $Rh(CO)_2L$ to $(CF_3)_3GeL$ thus parallels this cationic character, leading to the correlation in Fig. 2. The homology of the series reveals this regularity. It should be noted, though, that ${}^3\Delta$ never reaches the 165 ppb seen in true cations.

This interpretation can also account for why L^- itself exhibits the normal negative ${}^3\Delta$. This is simply because the cationic character is not developed. Yet the chemical shift is not far upfield, as expected for an electron-rich L^- . Consequently, L^- deviates widely from the correlation of Fig. 2, and has been excluded. However, we associate the downfield chemical shift of L^- with its different stereochemistry.

The concept of isotopic perturbation of resonance is a matter of controversy. Balzer and Berger observed that three-, four- or five-bond isotope shifts in cyclopentenyl cations and their 1,3-dimethyl and 1,3-di-*tert*-butyl derivatives decrease regularly from +163 to +75 to -10 ppb per D.²⁶ These values do not match those in the corresponding 1,3-disubstituted benzenes. They show a constant decrement of ~ 86 ppb from ${}^3\Delta$ to ${}^4\Delta$ to ${}^5\Delta$. The decreasing ${}^n\Delta$ parallels the downfield chemical shift of the carbocation carbon. It was therefore concluded that these are intrinsic isotope shifts peculiar to cations whose carbons are shifted far downfield. It was further concluded that the term isotopic perturbation of resonance should not be used.

We would agree that isotopic perturbation of resonance does not rationalize the effects of D, CD_3 and $C(CD_3)_3$ on cyclopentenyl cations. The sign reversal for $C(CD_3)_3$ shows that these three deuterated substituents cannot all have the same effect on stability of allylic carbocations. The decrease in ${}^n\Delta$ is not linear in the chemical shift of the carbocation carbon, so it is not clear how the far downfield cationic carbons account for the isotope shifts. Besides, it must be recognized that the constant decrement from ${}^3\Delta$ to ${}^4\Delta$ to ${}^5\Delta$ cannot extend to a ${}^6\Delta$, so it cannot be a key feature of the isotope shifts.

Just because isotopic perturbation of resonance cannot account for these data does not mean that it can never account for any data. Our data come from a homologous series of rigid allylic cations, with one deuterium fixed in the same location. The shortening of the C=CD bond favors the resonance form $ML-d-b$, making the CH more cationic and shifting it downfield. That shift increases with the carbocationic character, as reflected in the chemical shift, thus leading to the correlation in Fig. 2. These isotope shifts, although they arise from perturbation of resonance, are not equilibrium shifts but are intrinsic, from averaging the shielding over the vibrational wavefunction.

CONCLUSIONS

A homologous series of ML_n chelates shows small positive intrinsic isotope shifts that vary linearly with

chemical shifts. The linear relation is attributed to isotopic perturbation of resonance between two allylic cation structures, arising by shortening of the C=CD bond.

Acknowledgements

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