Symmetry of Metal Chelates

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Is a metal chelate symmetric, with the motion of the metal described by a single-well potential, or is it asymmetric, in a double-well potential? For hydrogen, this is the familiar question of the symmetry of a hydrogen bond. The molecular symmetry of ML_n complexes (M = Li, Na, K, Al, Pd, Rh, Si, Sn, Ge, Sb, etc.; L is the anion of 3-hydroxy-2-phenylpropenal) in solution is now probed with the method of isotopic perturbation of equilibrium. A statistical mixture of 3-hydroxy-2-phenylpropenal-d_0, -1-*d*, and -*1*,*3*-d_2 was synthesized and converted to various metal complexes. Some complexes show two aldehydic signals, which means that their ligands are monodentate. For LiL, NaL, and KL, the ^{13}C NMR isotope shifts, $\delta_{CH(D)} - \delta_{CH(H)}$, for the aldehydic CH groups are small and negative, consistent with L^- being a resonance hybrid. They are small and positive for AlL_3, PdL_2, $Rh(CO)_2L$, SiX_3L, $SiL_3{}^+X^-$, $(CF_3)_3GeL$, $SbCl_4L$, $(EtO)_4TaL$, and $(EtO)_4NbL$. The positive isotope shifts are unusual, but since they are small and temperature independent, they are intrinsic and indicate that these metal chelates are symmetric, as expected. Large positive isotope shifts, up to 400 ppb, are observed for Ph_3GeL, Me_3GeL, Ph_2GeL_2, Bu_3SnL, and Ph_4SbL. However, it is likely that these are monodentate complexes undergoing rapid metal migration, as judged from the X-ray crystal structures of Ph_3SnL and Ph_4SbL. NMR experiments indicate an intermolecular mechanism for exchange, which may be a bimolecular double metal transfer. It is remarkable that the isotope shifts in these five complexes demonstrate that they are asymmetric structures, even though they appear from other NMR evidence to be symmetric chelates.

Introduction

Metal β-diketonates have been widely studied.[1] The most familiar are those of 2,4-pentanedionate (acac). Most commonly they are bidentate chelates, with the metal coordinated to two oxygens and with a quasi-aromaticity. The question we ask is whether the motion of the metal is described by a single-well or double-well potential. Is the metal located midway between the two oxygens (Figure 1a) or is it closer to one and jumping between them (Figure 1b)?

Bidentate β-diketonates are firmly believed to be symmetric.[2] It might be thought foolish to propose otherwise, since many hundreds of crystal structures show two equal M−O bond distances, as well as C−C or C−O.[3] Yet these may be only an average of a static or dynamic mixture of asymmetric structures. Besides, symmetry cannot be universal, since some metal β-diketonates show unequal M−O distances.[4]

Must both M−O bonds be equivalent? In the extreme case, the metal may be so electron rich that there is no need to coordinate a second oxygen. Indeed, some β-diketonates bind monodentately, as in $Me_3Si(acac)$ and $Me_2Si(acac)_2$,[5] as well as in some complexes of Hg, Pt, and Cu.[6] When the silicon center is more electron deficient, the complex is octahedral, with bidentate acac.[7]

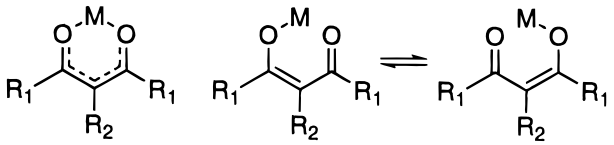

Figure 1. (a) Symmetric and (b) asymmetric metal β-diketonate chelates.

The interaction between the metal and acac is thus tunable from monodentate to symmetric,[5] conceivably via an asymmetric species (Figure 1b). We seek such a complex, where the second M−O bond is formed but is weaker than the first. Even if the metal is jumping back and forth quickly, this is a double-well potential, distinct from the monodentate and symmetric extremes.[8]

Molecular orbital theory is generally silent on this issue, symmetry being assumed as the starting geometry for a calculation,[9] except for $Pb(acac)_2$, where MNDO calculations indicate equal Pb−O bond lengths.[10] Aromaticity does not

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guarantee symmetry, since the symmetry of benzene is due to the σ system.[11] We avoid degenerate orbitals and Jahn−Teller reduction of symmetry.[12] Nor are we addressing cases such as $(RO)_2Ti(acac)_2$ and (η^2,η^1-4-cyclooctenyl)Pd(acac), where two acac oxygens are in different environments.[13]

The method of isotopic perturbation permits a judgment about molecular symmetry.[14] This method has been applied to carbocations[15] and to cyclohexane[16] and has also been used to distinguish whether $CpSn(CH_3)_3$ is η^5 or η^1.[17] It has been applied to the familiar question of the symmetry of the hydrogen bonds in 3-hydroxy-2-phenylpropenal[18] and monoanions of dicarboxylic acids.[19] The molecular symmetries of some metal β-diketonates in solution are now deduced by this method.

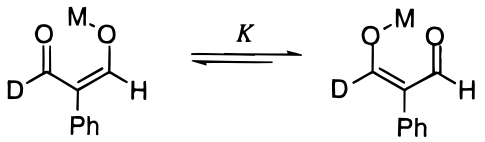
The simplest ligand to examine is 3-hydroxypropenal-*1-d*, with the deuterium closer to carbon than those in Zn(acac-*1-*d_3)$_2$, where no effect could be detected.[20] More suitable, for ease of synthesis and crystallinity, is 3-hydroxy-2-phenylpropenal (HL), **1**.

The splitting of the ^{13}C NMR signals of the aldehydic carbons of the isotopologues of ML is diagnostic. The observed isotope shift ($^n\Delta_{obs}$) is the chemical shift difference between CH signals of ML and ML-*d* (eq 1). This includes an intrinsic contribution

$$^n\Delta_{obs} = \delta_{CH(D)} - \delta_{CH(H)} \quad (1)$$

$^n\Delta_o$, which is usually <0 and falls off rapidly with *n*, the number of bonds between the reporter nucleus and the isotope.

If ML is a mixture of two species, there is an equilibrium isotope shift (Δ_{eq}) given by eq 2,[14,18] where *D* is the ^{13}C chemical



ML-*d*-a **ML-*d*-b**

shift difference between =CH−OM and −CH=O and *K* is the equilibrium constant [**ML-*d*-b**]/[**ML-*d*-a**].

$$\Delta_{eq} = \frac{D}{2}\frac{K-1}{K+1} \quad (2)$$

To assess feasibility, *D* can be estimated as 28 ppm from the carbonyls of $Me_3Si(acac)$.[21] Furthermore, *K* at 25 °C can be estimated as 1.2 from the zero-point energies of 2770- and 3020-cm^{-1} CH frequencies in aldehydes and enols.[22] These lead to an estimated Δ_{eq} of ca. +1 ppm. Although these are imperfect models, Δ_{eq} is certainly large and positive and is of greater magnitude than any $^3\Delta_o$, which is small for so distant an isotope. The observed isotope shift is the sum of these (eq 3).

$$\Delta_{obs} = \Delta_{eq} + {}^3\Delta_o \quad (3)$$

If ML is symmetric, only $^3\Delta_o$ is manifested. In contrast, if ML is asymmetric, then a large positive Δ_{eq} is dominant.

Experimental Section

Instrumentation. NMR spectra were recorded on a Varian Unity 500-MHz spectrometer. Chemical shifts for ^{13}C spectra are given in ppm relative to $CDCl_3$ (δ 77.0), dioxane (in D_2O, δ 67.5), DMSO-d_6 (δ 39.5), CD_3OD (δ 49.15), C_6D_6 (δ 128.0), toluene-d_8 (δ 20.4), or pyridine-d_5 (δ 123.5). Probe temperature was measured using methanol.[23] NMR experiments on air- or water-sensitive samples were conducted in Teflon-valved tubes (Wilmad).

A ^{2}H-decoupled ^{13}C NMR spectrum was obtained as follows: After normal locking and shimming, a ^{1}H NMR spectrum was recorded without a lock. The frequency of the aldehyde signal was converted to the ^{2}H frequency. A synthesized signal generator was fixed to that frequency, and a ^{13}C spectrum was obtained while the aldehyde deuteriums were selectively decoupled through the lock channel.

For the single-crystal X-ray structure determinations, a Siemens R3m/V four-circle diffractometer was used to collect the data using Mo Kα radiation. No absorption corrections were applied, and each of the structures was solved by direct methods (SHELXTL PLUS, PC version). All non-hydrogen atoms were refined anisotropically, while the hydrogens were fixed in idealized positions (d_{CH} = 0.96 Å). Crystallographic data are summarized in Table 1.

Synthesis of 3-Hydroxy-2-phenylpropenal (HL, 1). Both HL and the statistical mixture of HL isotopologues were synthesized by established procedures,[24] from dimethylformamide (DMF), $POCl_3$, and phenylacetic acid, i.e., precipitation as a perchlorate, hydrolysis with NaOH in aqueous methanol, and acidification, except that DMF-d_7 provided a source of deuterium.[18] The isotopic content of each batch was determined by mass spectrometry. NMR data for HL-d_0 are as follows. ^{1}H NMR ($CDCl_3$): δ 14.5 (s, OH, 1H), 8.6 (s, CHO, 2H), 7.2−7.6 (m, Ph, 5H). ^{13}C NMR: δ 181.3.

Synthesis of the *O*-Methyl Derivative (CH_3L). In methanol-d_4, HL was slowly ($t_{1/2}$ = days) converted to CD_3L. The reaction was acid catalyzed and base inhibited. In $CDCl_3$, 1 equiv of CH_3OH was sufficient. ^{1}H NMR ($CDCl_3$): δ 9.39 (s, 1H), 7.46−7.25 (m, 5H), 7.05 (s, 1H), 4.02 (s, 3H). ^{13}C NMR (CD_3OD): δ 193.4, 174.0.

Syntheses of the Metal Complexes. The preparations of the metal chelates were exploratory, without any attempt to obtain or characterize pure products. Generally, unpurified products gave good NMR signals. A few critical products were purified to obtain single crystals for X-ray crystallography.

All syntheses were adapted from known procedures for metal β-diketonates. Metal salts were obtained commercially and used without further purification. Deuterated solvents were obtained from Cambridge Isotope Laboratory. The solvents, including deuterated ones, were dried

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Table 1. Crystallographic Data for $Et_3NH^+L^-$, Ph_4SbL, and Ph_3SnL (L = 3-Oxido-2-phenylpropenal)

	$Et_3NH^+L^-$	Ph_4SbL	Ph_3SmL
empirical formula	$C_{30}H_{46}N_2O_4$	$C_{33}H_{27}O_2Sb$	$C_{27}H_{22}O_2Sn$
a, Å	16.534(6)	10.925(5)	9.512(5)
b, Å	8.592(3)	11.146(4)	16.656(8)
c, Å	21.152(7)	12.327(4)	14.724(6)
α, deg	90.00	99.37	90.00
β, deg	108.69	92.39	92.50
γ, deg	90.00	112.75	90.00
V, Å^3	2846.4(17)	1356.7(9)	2330.5(19)
Z	4	2	4
fw	498.69	577.30	497.14
space group	*C*2/*c*	*P*1	$P2_1/n$
T, K	188(2)	295(2)	296(2)
λ, Å	0.710 73	0.710 73	0.710 73
d g cm^{-3}	1.164	1.413	1.417
μ, mm^{-1}	0.076	1.044	1.115
$R(F_o)$, all data[a]	0.0686	0.0424	0.0590
$R(F_o)$, $I > 2\sigma(I)$[a]	0.0452	0.0355	0.0402
$R_w(F_o^2)$, all data[b]	0.1162	0.0926	0.1120
$R_w(F_o^2)$, $I > 2\sigma(I)$[b]	0.0998	0.0875	0.0989

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

and degassed with standard methods. Syntheses were conducted in a drybox or by using Schlenk techniques if necessary.

Usually the nondeuterated HL was used for the exploratory synthesis of a metal chelate, on a scale of 10−300 mg. If the reaction was successful and gave a good aldehyde ^{13}C NMR signal, then a mixture of HL, HL-*d*, and HL-d_2 was used instead of HL. The isotope shift was measured as the separation between the aldehydic signals of the d_0 and d_1 isotopologues.

Alkali Metal (Li, Na, K) Salts. The procedure was adapted from the preparation of alkali metal salts of acac.[25] The sodium salt of 3-hydroxy-2-phenylpropenal (NaL) was prepared by the reaction of HL (0.1 g, 0.7 mmol) with excess sodium hydride in dry THF. The potassium salt was prepared using 0.1 g of HL and 85% potassium hydroxide (0.06 g, 0.9 mmol) in methanol, and the lithium salt was prepared using 0.1 g of HL in THF and 0.5 mL (0.8 mmol) 1.6 M butyllithium in hexane. After evaporation of the solvents, the residual solids were dissolved in 1−2 mL portions of an NMR solvent.

TlL. This procedure was adapted from the preparation of Tl(bzac).[26] All manipulations were performed using drybox or Schlenk techniques. HL was dissolved in CH_2Cl_2, and TlOEt was added. The white solid that precipitated was insoluble in benzene, chloroform, or methylene chloride and soluble in pyridine-d_5.

PdL_2. This procedure was adapted from the preparation of Pd(dbm)$_2$.[27] HL (0.05 g, 0.34 mmol) and $NaOAc\cdot 3H_2O$ (0.5 g, 0.37 mmol) were dissolved in 40 mL of absolute ethanol, after which $PdCl_2$ (0.03 g, 0.17 mmol) was added. The solution turned from purple to blackish green after 3 h and deposited a precipitate, which was collected by filtration and dried. Mp: >270 °C.

$Rh(CO)_2L$. This procedure was adapted from the preparation of Rh(CO)$_2$(acac).[28] In a drybox, tetracarbonylbis(*μ*-chloro)dirhodium(I) (0.1 g), HL (0.18 g), and $BaCO_3$ (0.2 g) were dissolved in a mixture of ether (5 mL) and THF (20 mL). The reaction mixture was refluxed for 1 week and was then centrifuged to remove solid impurities. After column chromatography (silica gel; 2% methanol in CH_2Cl_2), orange-red crystals formed when hexane was added. Mp: 106−109 °C. ^1H NMR ($CDCl_3$): *δ* 8.54 (d, 2 Hz, 2H), 7.37 (t, 8 Hz, 2H), 7.30 (t, 7 Hz, 1H), 7.22 (d, 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): *δ* 183.5, 182.9 (d, $^1J_{RhC}$ = 74.1 Hz), 178.7.

Aluminum Complexes. All manipulations were performed using drybox or Schlenk techniques. The procedures were adapted from the preparations of Al(bzac)$_3$, $(CH_3)_2$Al(acac), and $AlCl_2$(acac).[29] Al(OiPr)$_3$ (0.02 g, 0.1 mmol) and HL (0.05 g, 0.3 mmol) were stirred for 15 min. in 5 mL of dry benzene, the solvent was then evaporated, and the white solid that remained was dried. Similarly, $(iPrO)_2$AlL, $AlCl_2L$, and $(CH_3)_2$AlL were prepared using HL and 1 equiv of Al(OiPr)$_3$ in benzene, 1 equiv of $AlCl_3$ in refluxing ether, or 1 equiv of $(CH_3)_3$Al in toluene, respectively.

Silicon Complexes. All manipulations were carried out under dry N_2 using Schlenk techniques or a drybox. Solvents were dried and degassed prior to use. All experiments were started with ca. 10 mg of HL in an oven-dried RotoTite NMR tube.

$(RO)_3SiL$. HL was dissolved in $CDCl_3$, and 1 equiv of Et_3N was added, followed by 1 equiv of $Si(OEt)_3Cl$. Alternatively, HL was dissolved in $CDCl_3$ and 1 equiv of $SiCl_4$ and 3 equiv of trifluoroethanol were added.

Reaction of $Si(OPh)_4$ and HL. HL was dissolved in $CDCl_3$, and 1 equiv of Et_3N was added, followed by 1 equiv of $Si(OPh)_4$. ^{13}C NMR ($CDCl_3$): *δ* 175.1, 192.7.

Alkylsilyl Derivatives. The procedure for **$RSiClL_2$** (R = tBu, Ph) was adapted from the preparation of PhSiCl(acac)$_2$.[30] HL and 1/2 equiv of $RSiCl_3$ were dissolved in $CDCl_3$, and the solution was heated to 80 °C for 5 days. The procedure for **Ph_2SiL_2** was adapted from the preparation of $Ph_2Si(acac)_2$.[31] HL and 1 equiv of imidazole were dissolved in C_6D_6, 1/2 equiv of Ph_2SiCl_2 was added, and the mixture was filtered to remove imidazole·HCl. The procedure for **Ph_3SiL** was adapted from the preparation of $(CH_3)_3SiL$.[32] HL and Ph_3SiCl were dissolved in C_6D_6, and Et_3N was added. ^1H NMR: *δ* 9.01 (s), 7.8−7.1 (m), 7.03 (s). To prepare **$C_6F_5(CH_3)_2SiL$**, HL was dissolved in $CDCl_3$, after which $C_6F_5(CH_3)_2SiNH_2$ was added.

$SiL_3^+HCl_2^-$ and $SiL_3^+HBr_2^-$. This procedure was adapted from the preparation of $Si(acac)_3^+HCl_2^-$.[33] HL was dissolved in $CDCl_3$, and 1/3 equiv of $SiCl_4$ or $SiBr_4$ was added.

$SiCl_3L$ and $SiBr_3L$. HL was dissolved in C_6D_6 or $CDCl_3$, and 1 equiv of $SiCl_4$ or $SiBr_4$ was added. The product from C_6D_6 precipitated, or $CDCl_3$ was pumped off, and the solid was dried.

Germanium Complexes. The most common synthesis for a germanium complex of a *β*-diketone is the reaction of a germanium halide with a thallium diketonate,[34] but TlL is too insoluble. Instead, a method that had been applied to several silicon and tin diketonates was adapted.[35] All manipulations were performed using drybox or Schlenk techniques.

Ph_3GeL. Ph_3GeCl was dissolved in dry methanol, and 1 equiv of NaOMe was added. After solvent removal, the white solid remaining was redissolved in CH_2Cl_2. NaCl was filtered off, and 1 equiv of HL was added. The solvent was pumped off, and the oily product was dried under vacuum. ^1H NMR (pyridine-d_5): *δ* 8.6.

Ph_2GeL_2. Ph_2GeCl_2 and 2 equiv of HL were dissolved in pyridine-d_5 or benzene, and 2 equiv of Et_3N was added. With benzene as the solvent, $Et_3NH^+Cl^-$ was filtered off, the solvent was evaporated, and pyridine-d_5 was added. **$Et_3NH^+L^-$** could be obtained as an additional byproduct. A clear crystal was grown from cold benzene. The solid was found to be very hygroscopic.

$(CH_3)_3GeL$ and $(CF_3)_3GeL$. In an NMR tube, $(CH_3)_3GeBr$ or $(CF_3)_3$-GeI and 1 equiv of HL were dissolved in pyridine-d_5, followed by 1 equiv of Et_3N.

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$(MeO)_3GeL$. HL was dissolved in $CDCl_3$, and 1 equiv of Et_3N was added, followed by $Ge(OMe)_4$ (1 or 2 equiv). ^1H NMR ($CDCl_3$, aldehyde region): δ 8.98 (1H), 8.8 (1H). ^{13}C NMR: δ 192.7, 192.3, 176.3, 176.1.

Tin Complexes. The conventional procedure for preparing tin β-diketonates is the reaction of tin halides with alkali metal or Tl salts of acac.[36] Alternatively, $Bu_2Sn(acac)_2$ and $Et_3Sn(acac)$ can be prepared from the corresponding tin alkoxides and Hacac.[37] These procedures were applied to the syntheses of tin complexes of HL. All manipulations were performed using drybox or Schlenk techniques.

$SnCl_2L_2$. HL and excess NaH were reacted in dry THF. The solution was decanted, and the solvent was evaporated. The residue and $^1/_2$ equiv of $SnCl_4$ were stirred in dry benzene. Sodium chloride was filtered off, and the solvent was evaporated. ^{13}C NMR ($CDCl_3$): δ 186.7, 187.8.

Bu_2SnL_2. HL was dissolved in C_6D_6, and $^1/_2$ equiv of $Bu_2Sn(OCH_3)_2$ was added, upon which the solution rapidly turned milky. The solvent was evaporated, leaving a white solid. Mp: 187−188 °C. ^1H NMR ($CDCl_3$): δ 8.5 (s), 7.2−7.5, 1.7, 1.4, 0.9. The aldehydic ^{13}C NMR signal is too broad to resolve the isotope shift, even at −20 °C or after recrystallization from benzene or with 2,6-di-*tert*-butyl-4-methylphenol to eliminate possible broadening due to free radicals.

Bu_3SnL. HL was dissolved in $CDCl_3$, and 1 equiv of Bu_3SnOCH_3 was added. ^1H NMR: δ 8.35 (s, broad at −70 °C), 7.75 (d), 7.35 (t), 7.20 (t), 1.65 (m), 1.3 (m), 0.9 (t). At 25 °C, the ^{13}C NMR aldehydic signal is too broad (width ~3 ppm) to resolve an isotope shift. In pyridine-d_5, this signal sharpens with increasing temperature in both the ^1H and the ^{13}C NMR spectra. The ^1H and ^{13}C isotope shifts are 22 and 118 ppb at 70 and 110 °C, respectively. The aldehydic ^1H signal does not decoalesce, even at −70 °C in toluene-d_8.

Ph_3SnL. Ph_3SnCl was dissolved in dry methanol, and 1 equiv of NaOMe was added. After solvent evaporation, the remaining white solid was redissolved in CH_2Cl_2, NaCl was filtered off, and CH_2Cl_2 was pumped off. The resulting solid white Ph_3SnOMe was dried under vacuum and then dissolved in CH_2Cl_2 with 1 equiv of HL. A white solid was obtained after removing the volatiles. A single crystal was obtained from methanol/methylene chloride at 4 °C. This material decomposed at 233−235 °C.

Ph_2SnL_2. Ph_2SnCl_2 was dissolved in dry methanol, and 2 equiv of NaOMe was added. The solvent was evaporated, and the white residue was redissolved in CH_2Cl_2. NaCl was filtered off, 2 equiv of HL was added, and a white solid precipitated.

Antimony Complexes. The syntheses of the Sb(V) complexes were adapted from the preparation of $R_nSbCl_{4-n}(acac)$.[38]

$SbCl_4L$. HL was dissolved in $CDCl_3$, and 1 equiv of $SbCl_5$ was added.

Ph_4SbL. Ph_4SbBr was dissolved in dry ethanol or methanol, and 1 equiv of sodium ethoxide or methoxide was added. The solution was warmed at 50 °C for 1 h and then stirred for 4 h at room temperature. The solvent was evaporated, the solid was dissolved in CH_2Cl_2, NaBr was filtered off, and the CH_2Cl_2 solvent was evaporated, leaving a white solid (Ph_4SbOEt or Ph_4SbOMe). HL and 1 equiv of of this solid were dissolved in C_6D_6. A crystal was obtained after addition of hexane and storage at 4 °C. Mp: 163−165 °C.

Ph_3SbClL. Ph_3SbCl_2 and 0.9 equiv of HL were dissolved in C_6D_6, and 0.9 equiv of triethylamine was added. ^1H NMR: δ 8.86 (s), 8.25 (d), 7.96 (d), 7.0 (m), 6.71 (s). ^{13}C NMR: δ 190.4, 170.3. Alternatively, a mixture of Ph_3SbCl_2 and 1 equiv of NaOMe was stirred for several hours in methanol at 50 °C. After the solvent was pumped off, the solid was dissolved in CH_2Cl_2, the solution was decanted, and 1 equiv of HL was added. The two preparations gave the same NMR spectra.

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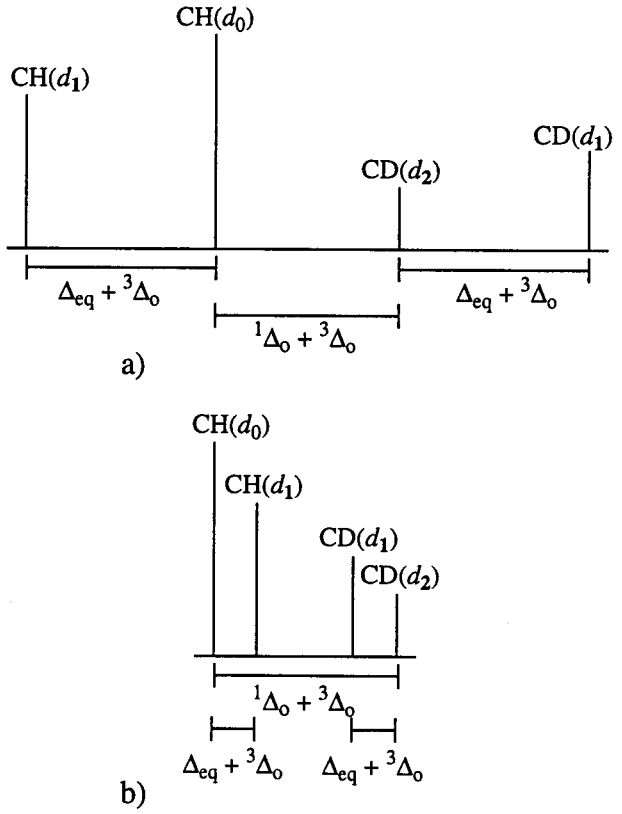

Figure 2. Expected ^{13}C NMR spectra for metal chelates of a mixture of **1**, **1-*d***, and **1-d_2**: (a) if $\Delta_{eq} + {}^3\Delta_o > 0$ (mixture of two asymmetric structures); (b) if $\Delta_{eq} + {}^3\Delta_o < 0$ ($\Delta_{eq} \sim 0$, symmetric structure). Peaks are assigned by intensities and ^2H content.

Other Transition-Metal Complexes. $(iPrO)_2TiL_2$. HL was dissolved in dry benzene, $^1/_2$ equiv of $Ti(OiPr)_4$ was added dropwise, and the solvent was evaporated.

$(EtO)_4TaL$ and $(EtO)_4NbL$. HL was dissolved in dry benzene, and 1 equiv of $Ta(OEt)_5$ or $Nb(OEt)_5$, respectively, was added very slowly. ^{13}C NMR: δ 180.8 and 180.6, respectively. The single aldehydic signal is consistent with $(EtO)_4ML$.

Other Attempts. Reaction of $Si(OAc)_4$ with 2 equiv of HL did not produce an NMR spectrum assignable to $(AcO)_2SiL_2$. Reaction of $EtOSiCl_3$, $(EtO)_2SiCl_2$, or $Sb(OEt)_3$ with HL gave primarily EtL. Some ^{13}C NMR signals at δ 181−184 seem to be associated with bidentate complexes such as $(AcO)_2SiL_2$ and $ROSiCl_2L$, but separation could not be accomplished. Attempts to obtain NMR spectra of ML_2 (M = Ni, Zn, Co) and ML_3 (M = Eu, La, Y, Yb) were unsuccessful. A serious limitation of this method is NMR line broadening due to paramagnetic metals, even as impurities. Attempts to obtain single crystals of Me_3GeL, Ph_3GeL, Ph_2GeL_2, and Bu_3SnL were unsuccessful.

Results

Signal Assignments and Isotope Shifts. Two ^{13}C NMR signals are observed in the carbonyl region for metal complexes of a mixture of **1**, **1-*d***, and **1-d_2**. From the relative amounts, the taller signal is assigned as ML-d_0. This is confirmed by adding ML. The other signal represents the CH carbon of ML-*d*.

By decoupling deuterium, it becomes possible to observe all carbons, including CD that are ordinarily split into a triplet. There are four signals in the carbonyl region of the ^2H-decoupled ^{13}C NMR spectra for metal complexes of the mixture of **1**, **1-*d***, and **1-d_2**. The two signals furthest downfield are the same as those observed without ^2H decoupling. The other two signals represent carbons attached to ^2H. The taller of these two is assigned to the CD of **ML-*d*** on the basis of the deuterium content. The weakest signal, sometimes undetectable above the noise, is from **ML-d_2**.

Table 2. Aldehydic Chemical Shifts and Isotope Shifts for 3-Hydroxy-2-phenylpropenal (HL), Its *O*-Methyl Derivative, and Its Alkali Metal and Thallium Salts

salt	solvent	δ, ppm	$\Delta_{eq} + {}^3\Delta_o$, ppb	${}^1\Delta_o + {}^3\Delta_o$, ppb
HL[a]	$CDCl_3$	181.3	+759	−251
CD_3L	CD_3OD	193.4, 174.0		
Li^+L^-	DMSO-d_6	188.3	−61	
Li^+L^-	D_2O	191.9	−49	
Na^+L^-	DMSO-d_6	188.3	−62	
Na^+L^-	D_2O	191.8	−50	
K^+L^-	DMSO-d_6	188.3	−65	
K^+L^-	D_2O	191.9	−49	−395
K^+L^-	CD_3OD	189.3	−55	−394
Tl^+L^-	pyridine-d_5	188.6	|< 30|	

[a] Reference 18.

Table 3. Aldehydic Chemical Shifts and Isotope Shifts for Complexes of Rhodium, Palladium, and Aluminum

complex	solvent	δ, ppm	$\Delta_{eq} + {}^3\Delta_o$, ppb	${}^1\Delta_o + {}^3\Delta_o$, ppb
PdL_2	$CDCl_3$	178.9	43	−340
$Rh(CO)_2L$	$CDCl_3$	178.7	42	−346
AlL_3	$CDCl_3$	183.4	67 ± 7	−310
AlL_3	C_6D_6	183.4	67 ± 7	−310
$Al(OiPr)_2L$	C_6D_6	183.4	67 ± 7	
$AlCl_2L$	C_6D_6	183.1	60 ± 7	
$(CH_3)_2AlL$	C_6D_6	185.1	67 ± 7	

The chemical shift differences between signals are $\Delta_{eq} + {}^3\Delta_o$ and ${}^1\Delta_o + {}^3\Delta_o$, as labeled in Figure 2. The separation between $\boldsymbol{d_0}$ and $\boldsymbol{d_2}$ signals is dominated by ${}^1\Delta_o$, so it is $\Delta_{eq} + {}^3\Delta_o$ that is diagnostic. Since Δ_{eq} and ${}^3\Delta_o$ are expected to be of opposite sign and since the magnitude of Δ_{eq} depends on whether the structure is symmetric ($\Delta_{eq} = 0$) or asymmetric ($\Delta_{eq} \gg 0$), there are two possible patterns (Figure 2a,b) for the ^{13}C NMR spectrum. Therefore, the appearance, either with or without ^2H decoupling, distinguishes symmetric complexes from asymmetric ones.

Isotope Shifts. HL, RL, Alkali Metal Salts, and Thallium Salts. Table 2 lists the chemical shifts and isotope shifts for these compounds. The observed isotope shift $\Delta_{eq} + {}^3\Delta_o$ for HL is +759 ppb. This is a measure of the isotope shift that can be expected for a mixture of two rapidly interconverting asymmetric structures. For CD_3L, the isotope shift ${}^3\Delta_o$ is −30 ppb for the downfield signal and is not resolvable for the upfield signal (|<30| ppb). These represent the intrinsic shifts that can be expected from a distant isotope in a static asymmetric structure.

The intrinsic isotope shift ${}^1\Delta_o + {}^3\Delta_o$ of K^+L^- is −395 ppb. The more diagnostic isotope shifts $\Delta_{eq} + {}^3\Delta_o$ of M^+L^- are all small and negative. There is a small solvent dependence but no difference between Li, Na, and K salts in the same solvent. The aldehydic ^{13}C signal of TlL is too broad to resolve the isotope shift, but it is definitely not large. These values are distinctly different from those for HL.

Rhodium, Palladium, and Aluminum Complexes. Table 3 lists the chemical shifts and isotope shifts of Rh(I), Pd(II), and Al(III) complexes. The intrinsic isotope shifts ${}^1\Delta_o + {}^3\Delta_o$ are between −310 and −350 ppm, somewhat smaller in magnitude than that of K^+L^-. The more diagnostic isotope shifts $\Delta_{eq} + {}^3\Delta_o$ of square planar Rh and Pd complexes are small and positive. For the octahedral AlL_3 complex, the isotope shift is slightly larger but much smaller than that of the parent HL. The isotope shifts for all three metal chelates are independent of temperature and of whether the aluminum center is electron rich, as in $(CH_3)_2AlL$, or electron deficient, as in $AlCl_2L$.

Silicon Complexes. Table 4 lists the chemical shifts and isotope shifts of silicon complexes. Although reactions of $(EtO)_nSiCl_{4-n}$ ($n = 1, 2$) with Et_3N + HL produce only EtL, reactions of $(RO)_3SiCl$ give NMR spectra consistent with $(RO)_3SiL$. The other silicon reagents have no alkoxy groups, so that they too form authentic Si−L complexes. Many of these have separate signals for aldehyde and enol carbons. The chemical shift difference between them is ∼30 ppm, larger than the 22−25 ppm difference for RL, which confirms their assignment as monodentate Si−L species. Electron-deficient silicon complexes such as SiL_3^+ and SiX_3L have a single aldehydic signal but only a small positive isotope shift.

Table 4. Aldehydic Chemical Shifts and Isotope Shifts for Silicon Complexes

complex	solvent	δ, ppm	$\Delta_{eq} + {}^3\Delta_o$, ppb	${}^1\Delta_o + {}^3\Delta_o$, ppb
$(EtO)_3SiL$	$CDCl_3$	175.1, 192.7		
$(CF_3CH_2O)_3SiL$	$CDCl_3$	166.3, 191.3	...,[a] −31	
$(PhO)_3SiL$	$CDCl_3$	175.1, 192.7	−43, −42	
$tBuSiClL_2$	$CDCl_3$	157.7, 191.1		
$PhSiClL_2$	$CDCl_3$	157.1, 191.1		
Ph_2SiL_2	C_6D_6	158.5, 189.9		
Ph_3SiL	C_6D_6	161.6, 190.3		
$C_6F_5(CH_3)_2SiL$	$CDCl_3$	2 peaks		
$SiL_3{}^+HCl_2{}^-$	$CDCl_3$	183.3	67 ± 6	−346
$SiL_3{}^+HBr_2{}^-$	$CDCl_3$	183.1	69 ± 3	−353
$SiCl_3L$	C_6D_6	181.7	73	
$SiBr_3L$	$CDCl_3$	182.7	67	

[a] Not observed.

Table 5. Aldehydic Chemical Shifts and Isotope Shifts for Germanium Complexes

complex	solvent	δ, ppm	Δ_{obs}, ppb
$(CF_3)_3GeL$	pyridine-d_5	187.2	+85
Me_3GeL	pyridine-d_5 (100 °C)	180.5	+400
Me_3GeL	pyridine-d_5 (110 °C)	180.3	+388
Ph_3GeL	pyridine-d_5	182.5	+310
Ph_3GeL	$CDCl_3$	169.4, 191.7	
Ph_2GeL_2	pyridine-d_5	182.3	+350
$(MeO)_3GeL$	$CDCl_3$	192.7, 192.3, 176.3, 176.1	

Germanium Complexes. Table 5 lists the chemical shifts and isotope shifts of Ge(IV) complexes. The isotope shift for the aldehydic carbon of $(CF_3)_3GeL$ is +85 ppb at all temperatures. Therefore, there is no Δ_{eq} and $(CF_3)_3GeL$ is symmetric. In contrast, $(MeO)_3GeL$ is a monodentate complex, perhaps in two different configurations.

The aldehydic ^1H NMR signal of Me_3GeL is too broad to be observed at room temperature. At 70 °C, it sharpens and is seen at δ 8.4. The aldehydic ^{13}C signal is also very broad at 25 °C, but at 100 °C, it sharpens, revealing a large isotope shift of 400 ppb, which is evidence for an asymmetric structure. No decoalescence is observed at low temperature.

In pyridine-d_5, the ^1H and ^{13}C aldehydic signals of Ph_3GeL are sharp, with no significant temperature dependence of the ^1H NMR line width from −30 to +50 °C. The ^{13}C isotope shift is +310 ppb at 25 °C. Similarly, the ^{13}C isotope shift of Ph_2GeL_2 is +350 ppb, again evidence for an asymmetric structure.

Tin Complexes. Table 6 lists the ^{13}C chemical shifts and isotope shifts for the tin complexes. In $CDCl_3$, the aldehydic signals of Bu_2SnL_2 and Bu_3SnL are too broad to resolve the isotope shifts. The aldehydic ^1H signal of Bu_3SnL does not decoalesce at −70 °C in toluene-d_8. At 110 °C in pyridine-d_5, the isotope shift for Bu_3SnL is 118 ppb, too large to be merely an intrinsic ${}^3\Delta_o$. Instead, this must be an equilibrium isotope shift, indicating that Bu_3SnL is not a single symmetric structure but a mixture of two tautomers.

At −35 °C, the ^1H NMR pattern of Ph_3SnL is concentration dependent, suggestive of a monomer−dimer (or oligomer)

Table 6. Aldehydic Chemical Shifts and Isotope Shifts for Tin Complexes

complex	solvent	δ, ppm	Δ_{obs}, ppb
Bu_2SnL_2	$CDCl_3$	183.3 (broad)	
Bu_3SnL	$CDCl_3$	188.6 (broad)	
Bu_3SnL	pyridine-d_5 (110 °C)	185.5	118 ± 9
Ph_3SnL	$CDCl_3$	190.3 (broad)	
Ph_3SnL	pyridine-d_5 (−35 °C)	180.0, 191.5	|<30|, |<30|
Ph_2SnL_2	pyridine-d_5	180.8, 192.6	|<30|, |<30|
Ph_2SnL_2	pyridine-d_5 (−30 °C)	192.4, 191.9, 183.0, 180.5	
$SnCl_2L_2$	$CDCl_3$	186.7, 187.8	

Table 7. Aldehydic Chemical Shifts and Isotope Shifts for Antimony Complexes

complex	solvent	δ, ppm	Δ_{obs}, ppb
$SbCl_4L$	$CDCl_3$	186.3	+79
Ph_4SbL	C_6D_6	183.4	+212
Ph_4SbL	pyridine-d_5	185.0	+152
Ph_4SbL	toluene-d_8 (48 °C)	183.1	+200
Ph_4SbL	toluene-d_8 (−27 °C)	183.8	+261
Ph_3SbClL	C_6D_6	170.3, 190.4	
Ph_3SbClL	pyridine-d_5	172.7, 191.3	

Table 8. Aldehydic Chemical Shifts and Isotope Shifts for Other Metal Complexes

complex	solvent	δ, ppm	$\Delta_{eq} + {}^3\Delta_o$, ppb	${}^1\Delta_o + {}^3\Delta_o$, ppb
$(iPrO)_2TiL_2$	$CDCl_3$ (0 °C)	178.3, 183.9	70 ± 3, 57 ± 5	-303 ± 6, -322 ± 10
$(EtO)_4TaL$	C_6D_6	180.8	61	−309
$(EtO)_4NbL$	C_6D_6	180.6	60	

equilibrium. This is supported by the X-ray crystal structure, which shows Ph_3SnL to be polymeric. At −35 °C in pyridine-d_5, there are two aldehydic ^{13}C signals, separated by 11.5 ppm. Similarly, at 25 °C, the two signals of Ph_2SnL_2 are separated by 11.8 ppm. The separations are similar to those for other tin β-diketonates[39] and considerably less than the 20−30 ppm seen in the spectra of monodentate silicon complexes. The two different carbons may be assigned to apical and basal L in monomeric Ph_3SnL, as in $Ph_3Sn(dbm)$,[40] or to cis and trans L in Ph_2SnL_2. The isotope shift for any of the signals is very small. The ^{13}C NMR spectrum of $SnCl_2L_2$ also shows two aldehydic signals, but they are separated by only 1.1 ppm. This complex also is cis, similar to $SnCl_2(acac)_2$.[39]

Antimony Complexes. According to the data in Table 7, the isotope shift for $SbCl_4L$ is +79 ppb. So low a value means that this compound is symmetric.

The isotope shifts of Ph_4SbL are significantly larger. The data in Table 7 are unambiguous evidence that Ph_4SbL is asymmetric, with a double-well potential. In toluene-d_8, a significant temperature dependence of the isotope shift can be observed. Moreover, the ^1H NMR isotope shift for the δ 8.0 signal is +35 ppb at room temperature and increases to +46 ppb at −50 °C. This signal does not decoalesce at −70 °C in toluene-d_8.

It is puzzling that Ph_3SbClL is monodentate, as judged by separate ^{13}C signals for aldehyde and enol carbons.

Other Metal Complexes. Table 8 shows ^{13}C data for other metal complexes. In the spectrum of $(iPrO)_2TiL_2$, there are two aldehydic signals not as widely separated as those of a monodentate complex. Like $SnCl_2L_2$, this compound may also be assigned as cis. The isotope shifts at both carbons are small and positive, as are those of the single carbons of $(EtO)_4TaL$ and $(EtO)_4NbL$.

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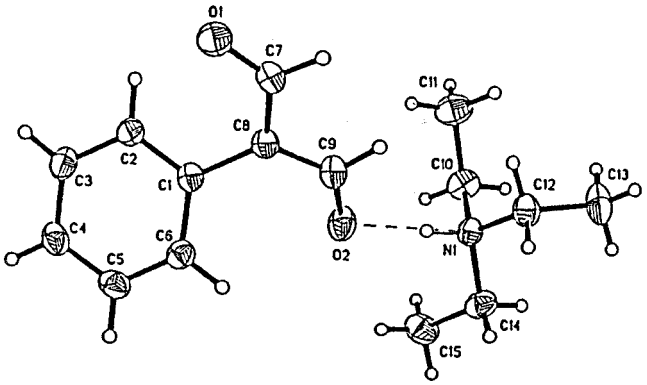


Figure 3. X-ray structure of $Et_3NH^+L^-$.

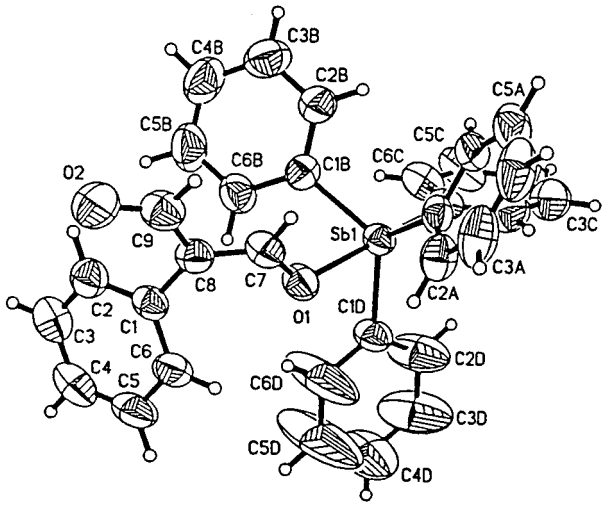


Figure 4. X-ray structure of Ph_4SbL.

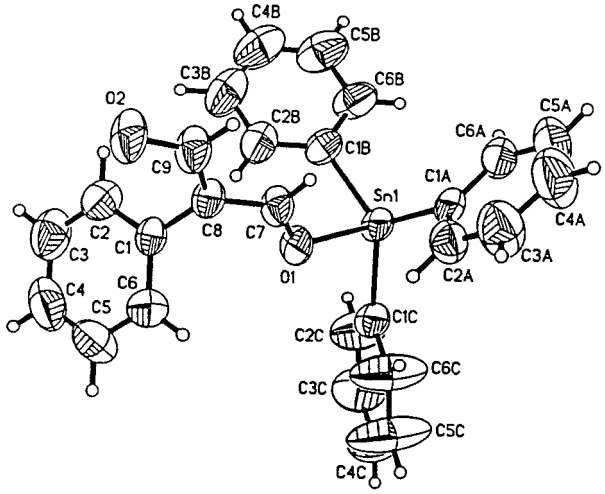


Figure 5. X-ray structure of Ph_3SnL.

X-Ray Analyses. The X-ray structures for $Et_3NH^+L^-$, Ph_4SbL, and Ph_3SnL are shown in Figures 3−5.

$Et_3NH^+L^-$. The stereochemistry of L^- is *E*,anti. Only one oxygen of L^- participates in hydrogen bonding to NH. The O(1)−C(7) and O(2)−C(9) distances are 1.267(2) and 1.241(2) Å, respectively. The C(7)−C(8) and C(8)−C(9) distances are also different, 1.394(2) and 1.417(2) Å, respectively. These differences are due to crystal packing forces, since L^- is a resonance hybrid and therefore intrinsically symmetric.

Ph_4SbL. The most notable feature is that the ligand L assumes an *E*,anti stereochemistry with a monodentate binding mode. The C=O and C−O bond lengths are 1.218(5) and 1.288(5) Å,

respectively. The C(7)−C(8) and C(8)−C(9) distances of L are also different, 1.357(5) and 1.430(5) Å, respectively.

Ph_3SnL. The most notable feature here is that L is *E*,anti and bridges two trigonal bipyramidal tin atoms, resulting in a polymeric structure. Two oxygens occupy opposite axial positions on a tin. The two Sn−O distances are different, 2.200(2) and 2.244(3) Å. The C(7)−C(8) and C(8)−C(9) distances are 1.389(5) and 1.396(5) Å, respectively, and the C−O distances are 1.262(4) and 1.257(5) Å.

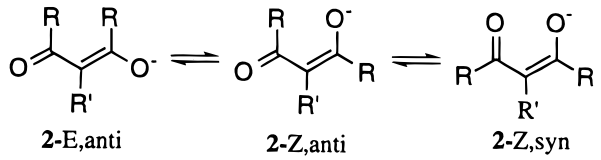
Exchange Studies. The ^{1}H and ^{13}C NMR spectra of a mixture of Bu_2SnL_2 and Ph_3SnL in $CDCl_3$ show individual signals from each complex. In contrast, a mixture of Bu_3SnL and Ph_3SnL shows averaged signals from L. When the molar ratio of Bu_3SnL/Ph_3SnL is changed from 9/1 to 1/1, the chemical shift of the averaged signal changes from δ 189.0 to δ 189.5. Likewise, mixtures of Bu_3SnL with Ph_4SbL or with Ph_3GeL show averaged signals.

Discussion

Alkali Metal Salts. The observed isotope shifts $\Delta_{eq} + {}^3\Delta_o$ in Table 2 for alkali metal salts are small and negative. The signs and magnitudes are both as expected from ${}^3\Delta_o$ alone. Therefore, there are no equilibrium isotope shifts and the structures are symmetric.

Symmetry is to be expected, inasmuch as these salts are ionic, each with an L^- ion that is a resonance hybrid. Indeed, not only the chemical shifts but also the isotope shifts are independent of the metal. Such constancy is inconsistent with a chelate. Instead, L^- is present as a free ion or as a solvent-separated ion pair, and the metal ion is not closely associated.

The isotope shifts and chemical shifts do vary with solvent. This variation may be attributed to an equilibrium among stereoisomers. Although L^- (**2**, R = H, R′ = Ph) is *E*,anti in the crystal, in agreement with calculations,[41] *Z*,anti and *Z*,syn stereoisomers could be present in polar solvents. According to evidence below, the intrinsic isotope shift ${}^3\Delta_o$ is less negative for these stereoisomers. More of these stereoisomers in polar solvents would account for the observed variation.



2-E,anti **2**-Z,anti **2**-Z,syn

To preclude the symmetry intrinsic to L^-, a metal ion that can chelate is needed. Thallium might be suitable, since some Tl chelates show unequal Tl−O distances.[4] Yet we find that TlL is symmetric, according to its small isotope shift. Alternatively, the small isotope shift may be from ion-paired L^-.

Symmetric Chelates. The isotope shifts for Pd, Rh, and Al chelates in Table 3 are small and positive. The positive nature might be taken as evidence for equilibrating asymmetric tautomers. If so, Δ_{eq} (eq 3) is only ca. +0.1 ppm, significantly smaller than the 1 ppm estimated. However, since the isotope shifts are not greater at −30 °C, there is no Δ_{eq}. We therefore conclude that these metal chelates are symmetric, without any contradiction of previous X-ray results.[1]

This judgment means that a positive isotope shift, if small, cannot be taken as evidence for an asymmetric structure. Even with silicon complexes SiL_3^+, $SiCl_3L$, and $SiBr_3L$, the isotope shift in Table 4 is only ∼70 ppb. Thus, these too are symmetric. Likewise, the electron-deficient complexes $(CF_3)_3GeL$, $SbCl_4L$, $(EtO)_4TaL$, and $(EtO)_4NbL$ are symmetric, according to the small isotope shifts. It is gratifying to confirm the expected result.

The positive ${}^3\Delta_o$ is unusual but not unprecedented.[42] The observation of both positive and negative ${}^3\Delta_o$ values for ML_n may be associated with two different configurations of L. Just as the magnitude of ${}^3\Delta_F(D)$ in alkyl fluorides increases with the HCCF dihedral angle,[43] the increased ${}^3\Delta_o$ in the *Z*,syn metal chelates can be associated with the higher CCCH dihedral angle.

Monodentate Complexes. To increase the electron density on silicon so as to attenuate the affinity for a second oxygen of L, the other ligands were changed from halide to alkoxy to alkyl. However, according to the data in Table 4, these all exhibit separate signals for aldehyde and enol, which means that they are monodentate.

Complexes with Large Isotope Shifts. The data in Tables 5−7 show that large positive isotope shifts can be found in certain Ge, Sn, and Sb complexes. Their magnitudes are close to the 1 ppm estimated above for Δ_{eq} and much too large to be intrinsic. Moreover, since some are temperature-dependent, these must be equilibrium shifts, arising from the variability of *K*. The important result is that such isotope shifts are conclusive evidence for a mixture of two tautomers and therefore for complexes that are necessarily asymmetric, even though only a single aldehydic carbon signal is seen. It is remarkable that the isotope shifts demonstrate that these are asymmetric structures, even though they appear by other NMR evidence to be symmetric chelates.

These isotope shifts, although large, are smaller than the 1 ppm estimated. They are also smaller than the 0.76 ppm for HL,[18] as is the temperature dependence. Because a metal−oxygen interaction is stronger than in those models, *D* or *K* (or both) in eq 2 could be diminished, resulting in the reductions.

The asymmetry of the R_3GeL and R_3SnL complexes might be ascribed to a trigonal bipyramid undergoing rapid pseudorotation. To the extent that the equatorial oxygen of L binds more tightly to the metal, this oxygen will resemble the enolic oxygen of Figure 1b. However, the difference between axial and equatorial oxygens is so slight that *K* in eq 2 is likely to be exceedingly small, leading to a Δ_{eq} much less than observed. Besides, a pseudorotating trigonal bipyramid cannot account for the asymmetry of Ph_4SbL.

Asymmetric Chelates or Monodentate Complexes? The large positive isotope shifts for Me_3GeL, Ph_3GeL, Ph_2GeL_2, Bu_3SnL, and Ph_4SbL show that these complexes must be asymmetric. This observation does not distinguish between a chelate with unequal M−O bonds (Figure 1b) and a pair of interconverting monodentate complexes (Scheme 1). If the latter, interconversion must be fast enough to render the aldehyde and enol carbons equivalent. The lack of NMR decoalescence at −70 °C indicates a barrier <10 kcal/mol.

The X-ray crystal structures in Figures 4 and 5 show that L in both Ph_3SnL and Ph_4SbL is *E*,anti. This extended stereochemistry prohibits chelation. Although the tin environment in Ph_3SnL is trigonal bipyramidal, this complex is polymeric, with two unequal M−O distances, as though it were a monodentate complex with intermolecular association. The more congested Ph_4SbL complex is genuinely monodentate. Therefore, the

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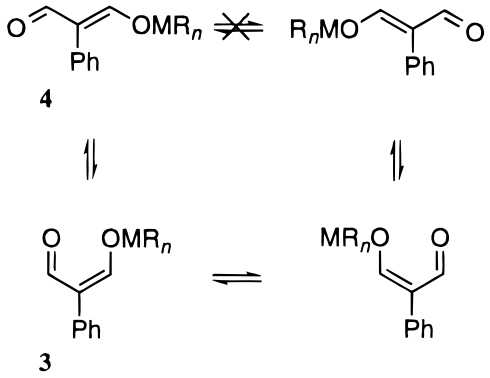
Scheme 1. Unimolecular Mechanism for Metal Transfer in a Monodentate Metal Complex



asymmetry of Ph_4SbL and Bu_3SnL (if analogous to Ph_3SnL) does not require a chelate with unequal M−O bonds but can be ascribed to a pair of interconverting monodentate complexes. This inference can be extended to Me_3GeL and Ph_3GeL.

We cannot be certain that the *E*,anti structure in these two crystals persists in solution. It might become *Z*,syn, to permit additional metal−oxygen bonding, just as HL is *E*,anti in the crystal but *Z*,syn in solution to permit intramolecular hydrogen bonding.[44] We could not obtain single crystals of Me_3GeL and Ph_3GeL, which may be *Z*,syn in solid and in solution. If so, these could be asymmetric chelates, which we cannot absolutely reject.

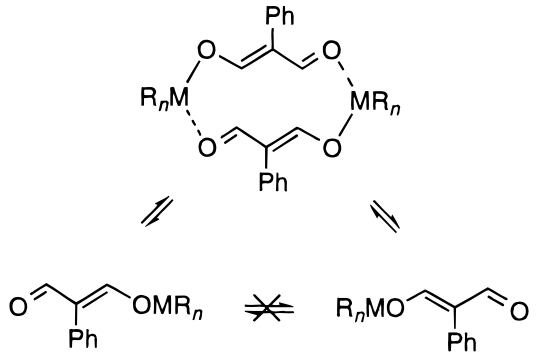
The best prospect for an asymmetric chelate is Ph_2GeL_2, since this complex is likely to be hexacoordinate, like $Bu_2Sn(acac)_2$.[45] If the phenyls are cis, like the chlorines in $Ge(acac)_2Cl_2$,[39] the axial and equatorial aldehydic carbons can interconvert by Bailar twists. However, perturbation by deuterium would not lead to an isotope shift as large as 350 ppb, since the difference between zero-point energies of axial and equatorial CH groups is so slight that *K* in eq 2 must be exceedingly small. If instead the phenyls are trans, as in $Ph_2Si(acac)_2$,[31] then this configuration would be an example of the asymmetric chelate that we seek. It is most unfortunate that a single crystal of Ph_2GeL_2 could not be obtained.

Metal Transfer. How can these complexes show rapid metal transfer from one oxygen to the other? A crucial consideration for the transfer is the stereochemistry of L. Only the *Z*,syn stereoisomer (**3** in Scheme 1) allows the two oxygens to be close enough to permit metal transfer. If L is *E*,anti (**4**), as seen in the two crystal structures, then the transfer would seem to require **3** as intermediate, as in Scheme 1. Yet formation of **3** requires rotation about the C═C partial double bond, whose barrier is well above 10 kcal/mol and which would be too slow to account for the rapid transfer.

Another mechanism for interconversion of monodentate complexes is a bimolecular double metal transfer, as shown in Scheme 2. This is an attractive mechanism for such complexes, especially since an oligomeric structure is readily accessible, as judged from the crystal structure of Ph_3SnL.

This mechanism would be operative even with two different metals or with different ligands on the metal. Indeed, a mixture of Bu_3SnL with Ph_3SnL, Ph_4SbL, or Ph_3GeL shows an averaged ^{13}C NMR signal. These results are not explained by the unimolecular mechanism of Scheme 1. Moreover, the lack of exchange in a mixture of Bu_2SnL_2 and Ph_3SnL is a consequence

Scheme 2. Bimolecular Mechanism for Metal Transfer in a Monodentate Metal Complex



of the double-exchange mechanism, which is blocked in hexacoordinated Bu_2SnL_2.

The bimolecular mechanism of metal exchange has long been proposed but never observed,[46] except perhaps for some brief and inconclusive reports.[47] Instead, exchange is usually catalyzed by a free ligand or a free metal ion, a process that continues to be studied.[48] We could not test the concentration dependence of the exchange because it proceeds too quickly to permit rate measurements, even at low temperatures. However, in our preparations the amount of free ligand, as a trace impurity, is much lower than the stoichiometric concentrations used to measure the kinetics. Nevertheless, transfers of L between Bu_3SnL and Ph_3SnL, Ph_4SbL, or Ph_3GeL, or the metal transfers from one oxygen to the other in Me_3GeL, Ph_3GeL, Ph_2GeL_2, Bu_3SnL, and Ph_4SbL, are much faster than the process as catalyzed by free ligand. We therefore conclude that transfer of metal from one oxygen to the other is intermolecular, and we suggest that it occurs by what may be the first case of a bimolecular double metal transfer (Scheme 2).

Conclusions

The alkali metal salts of 3-hydroxy-2-phenylpropenal (ML, M = Li, Na, K) exist as solvent-separated ions in CD_3OD, D_2O, or DMSO-d_6. The stereochemistry of L^- is *E*,anti, and a small negative $^3\Delta_o$ is observed. This anion possesses a single symmetric structure.

A large variety of ML_n compounds have been prepared. Most metal chelates of 3-hydroxy-2-phenylpropenal in solution are symmetric, with single-well potentials. This is in good agreement with previous X-ray structures and is in line with what is expected. Small positive intrinsic isotope shifts are observed for these chelates.

Many silicon complexes and Ph_3SbClL are monodentate, with only one oxygen of L bonded to the metal, whereas electron-deficient complexes such as SiL_3^+ are symmetric. Large positive isotope shifts due to isotopic perturbations of the equilibria are observed for Me_3GeL, Ph_3GeL, Ph_2GeL_2, Bu_3SnL, and Ph_4SbL.

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Therefore, these compounds are asymmetric, with double-well potentials. Nevertheless, it is concluded that these metal complexes are not asymmetric chelates but monodentate complexes. Since they show only a single aldehydic signal in their NMR spectra, they are undergoing rapid metal transfers from one oxygen to the other. It is remarkable to be able to distinguish that these are asymmetric complexes, since the NMR spectra alone would suggest that they are symmetric. Moreover, the interconversion may be occurring by a bimolecular double metal transfer.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of $Et_3NH^+L^-$, Ph_4SbL, and Ph_3SnL (L = 3-oxido-2-phenylpropenal). This material is available free of charge via the Internet at http://pubs.acs.org.

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