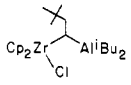
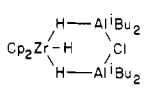
The significant question which remains to be answered centers on whether there is a suitable model system which is consistent with our $Zr(3d_{5/2})$ binding energy for either the initially formed catalyst or the second catalytic species. Not surprisingly, compounds such as **13**[12] and **14**[13] were shown to be "electron-rich"



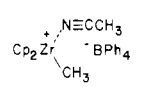
13

$Zr(3d_{5/2})$ = 181.0 eV



14

$Zr(3d_{5/2})$ = 181.3 eV

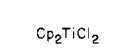


15

$Zr(3d_{5/2})$ = 181.5 eV

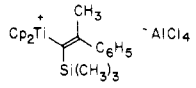
relative to both catalysts, as determined by the binding energies of 181.0 and 181.3 eV, respectively. Thus, structures closely related to **13** and **14** are not good models for either of the active species.

Recently, considerable attention has been devoted to the possible intermediacy of cationic zirconium[14] and titanium[15] species as active Ziegler–Natta polymerization catalysts.[16] In order to evaluate this concept, which was first proposed in 1965,[17] we studied the solvent complexed zirconium(IV) cationic species **15**,[14] which showed a $Zr(3d_{5/2})$ binding energy of 181.5 eV. While this compound is more electron deficient than either **13** or **14**, it does not approach the values observed for both of the catalytic species formed from **1**, **2**, and **3**. Perhaps the best model for the formation of the first catalytic species is provided by examination of the first member of the titanium triad. Comparison of **16** with Eisch's



16

$Ti(2p_{3/2})$ = 457.1 eV



17

$Ti(2p_{3/2})$ = 457.6 eV

stable cationic titanocene **17** shows a 0.5 eV change *to a more electron-deficient titanium derivative*. This can be compared to a change of 0.7 eV in converting **1** into the initially formed zirconocene-derived catalyst.

On the basis of our data, we wish to suggest that the first formed catalytic species is **18** and the second formed catalytic species is

18 **19** **20**

19 (formed by β-hydride elimination from the attached polymer), with the methylaluminoxane anion **20** as the counterion in both cases.[16-18] In support of our proposal of **19** as the secondary catalytic species, we have shown that exposure of the initially formed catalyst **18** to hydrogen gas gave a material with a binding energy for $Zr(3d_{5/2})$ equal to 182.2 eV.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this investigation.

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(15) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219 and references contained therein. We wish to express our sincere gratitude to Professor Eisch for providing a sample of **17**.

(16) For a discussion of related thorium catalysts, see: Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653. Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *Ibid.* **1987**, *109*, 4127. Toscano, P. J.; Marks, T. J. *Langmuir* **1986**, *2*, 820.

(17) Dyachkovskii, F. S. *Polym. Sci, USSR* **1965**, *7*, 121. Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci.* **1967**, *16*, 2333. See, also: Giannetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polymn. Sci,. Polym. Chem. Ed.* **1985**, *23*, 2117.

(18) Evolution of both hydrogen chloride gas and methane from the reaction of **1** with methylaluminoxanes, of methane from the reaction of **3** with methylaluminoxanes, of methane-d_3 from the reaction of **3**-d_6 with methylaluminoxanes, and of methane-d_1 from the reaction of **3** with methylaluminoxanes prepared from trimethylaluminum and deuterium oxide suggests, but does not prove, that the gegenion is an oxygen-based anion rather than an aluminum-based anion.

Asymmetric Hydrogenation of Trisubstituted Acrylic Acids Catalyzed by a Chiral (Aminoalkyl)ferrocenylphosphine–Rhodium Complex

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Received September 8, 1987

Although development of chiral phosphine–rhodium or ruthenium catalysts for asymmetric hydrogenation of olefins has resulted in so great a success as to make this reaction a practical approach to optically active compounds,[1-3] the olefinic substrates successfully used so far have been restricted, with a few exceptions,[4] to those containing a functional group such as carbonyl β to the olefinic double bond.[5-7] When designing chiral phosphine ligands, we have focused our particular attention on the selectivity being enhanced greatly by attractive interactions between functional groups on a substrate and on the chiral ligand.[8] Such reasoning prompted us to introduce an amino group on the chiral phosphine ligand that would provide an efficient catalyst for the rhodium-catalyzed asymmetric hydrogenation of unsaturated carboxylic acids. Here we report that chiral (aminoalkyl)ferrocenylphosphine ligands, (*R*)-*N*-methyl-*N*-[2-(dialkylamino)ethyl]-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamines (**1**),[9] give rise to high stereoselectivity as well as high catalytic activity in the hydrogenation of trisubstituted acrylic acids (tetrasubstituted olefins) where high stereoselectivity has

(1) For reviews: (a) Koenig, K. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 71. (b) Brown, J. M.; Chaloner, P. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; p 137. (c) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 175. (d) Bosnich, B.; Fryzuk, M. D. *Top. Stereochem.* **1981**, *12*, 119. (e) Nógrádi, M. *Stereoselective Synthesis*; VCH Verlag: Weinheim, 1987; p 53.

(2) For a recent report concerning rhodium-catalyzed hydrogenation: Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326.

(3) For a recent report concerning ruthenium-catalyzed hydrogenation: Noyori, R.; Ohta, M.; Hisao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117.

(4) Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596.

(5) The high stereoselectivity is ascribed mainly to the chelate coordination by the functional group as well as the olefin in the diastereomeric transition state.[1,6,7]

(6) For reviews: (a) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 41. (b) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Prenum: New York, 1979; Vol. 3, p 537.

(7) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746 and references cited therein.

(8) (a) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138. (b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395. (c) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191. (d) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.

(9) The ferrocenylphosphines **1** were prepared by treatment of (*R*)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate with 5–15 equiv of 2-(dialkylamino)ethyl-*N*-methylamines in refluxing methanol.[8] The specific rotations ($[\alpha]^{25}_D$ (*c* 0.2–0.4, chloroform)) of **1a**, **1b**, **1c**, and **1d** are −333, −368, −297, and −325°, respectively.

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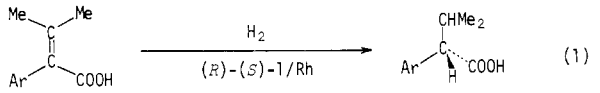
Table I. Asymmetric Hydrogenation of Trisubstituted Acrylic Acids Catalyzed by Chiral Ferrocenylphosphine–Rhodium Complexes[a]

entry	olefin	ligand	solvent	reaction time (h)	product	% ee[b] (config)	$[\alpha]_D^{25}$[c] ($CHCl_3$)
1	**2a**	**1a**	THF/MeOH (90/10)	30	**3a**	98.4 (*S*)	+61.7°[d]
2	**2a**	**1a**	THF/MeOH (80/20)	20	**3a**	97.6 (*S*)	+60.7°[d]
3	**2a**	**1a**	*i*-PrOH	20	**3a**	97.0 (*S*)	
4	**2a**	**1a**	MeOH	5	**3a**	95.8 (*S*)	
5	**2a**	**1b**	THF/MeOH (80/20)	20	**3a**	97.9 (*S*)	
6	**2a**	**1c**	THF/MeOH (80/20)	30	**3a**	98.1 (*S*)	
7	**2a**	**1d**	THF/MeOH (80/20)	30	**3a**	98.2 (*S*)	
8	**2b**	**1a**	THF/MeOH (80/20)	40	**3b**	97.4 (*S*)	+46.6°[d,e]
9	**2c**	**1a**	THF/MeOH (80/20)	40	**3c**	96.7 (*S*)	+51.6°[d,f]
10	**2d**	**1a**	THF/MeOH (80/20)	65	**3d**	97.3 (*S*)	+78.4°[d,g]
11[h]	(*E*)-**4a**	**1a**	*i*-PrOH	100	*l*-**5a**[i]	97.3 (2*S*,3*S*)	+43.5°
12[h]	(*E*)-**4b**	**1a**	THF/MeOH (80/20)	100	*u*-**5b**	92.1 (2*S*,3*R*)	+49.1°[j]

[a] The hydrogenation was carried out at room temperature and 50 atm of initial hydrogen pressure in the presence of 0.5 mol % of the rhodium catalyst, unless otherwise noted. The chemical yields are quantitative. [b] Determined by HPLC analysis of *N*-phenyl- or *N*-isopropylamides of the products with a chiral column (Sumitomo Chemical Co., Sumipax OA-1000, OA-4100, or OA-2000). [c] (*c* 1.5–1.7). [d] Literature rotations for optically pure (*S*)-**3a**, (*S*)-**3b**, (*S*)-**3c**, and (*R*)-**3d** are $[\alpha]_D^{25}$ +62.5° (chloroform) (ref 11), $[\alpha]_D^{21}$ +46.8° (chloroform) (ref 13b), $[\alpha]_D^{22}$ +52.8° (chloroform) (ref 13b), and $[\alpha]_D^{25}$ −76.20° (ethanol) (Piccolo, O.; Menicagli, R.; Lardicci, L. *Tetrahedron* **1979**, *35*, 1751), respectively. [e] $[\alpha]_D^{21}$. [f] $[\alpha]_D^{22}$. [g] $[\alpha]_D^{25}$ (ethanol). [h] Reaction with 1 mol % of the catalyst and at 100 atm of hydrogen pressure. [i] Contaminated with a small amount (3%) of *u*-5a. [j] $[\alpha]_D^{25}$ (*c* 1.0, acetone).

never been observed in spite of its wide applicability.

The results obtained for the asymmetric hydrogenation of 2-aryl-3-methyl-2-butenoic acids (**2**) (eq 1) are summarized in



(1)

2a: Ar = Ph
2b: Ar = 4-Cl-C_6H_4
2c: Ar = 4-MeO-C_6H_4
2d: Ar = 2-Naphthyl

(*S*)-**3a**-**d**

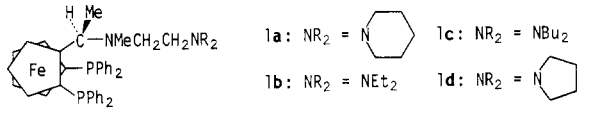
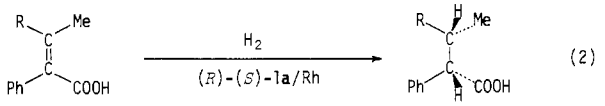


Table I. Hydrogenation of 2-phenyl-3-methyl-2-butenoic acid (**2a**) (1.0 mmol) was carried out in the presence of 0.5 mol % of a rhodium catalyst prepared in situ by mixing RhCl(NBD), $AgBF_4$, and chiral ligand (*R*)-(*S*)-**1a** in a ratio of 1:1:1.3 and 5 mol % of triethylamine[10] in 7 mL of a 90:10 mixture of THF and methanol at room temperature and 50 atm of initial hydrogen pressure (entry 1). The hydrogenation was complete in 30 h. Extraction of the carboxylic acid with 10% aqueous sodium hydroxide followed by acidification of the aqueous solution with concentrated hydrochloric acid gave a quantitative yield of the product (*S*)-**3a**; $[\alpha]^{25}_D$ +61.7° (*c* 1.5, chloroform).[11] The enantiomeric excess was determined to be 98.4% by HPLC analysis of the anilide of **3a** (aniline, DCC, ethyl acetate) with a chiral stationary phase column (Sumitomo Chemical Co., Sumipax OA-1000, hexane/dichloroethane/ethanol = 250/20/1). Similar results were obtained with the in situ rhodium catalyst prepared from $[Rh(NBD)_2]BF_4$ and **1a** or with preformed rhodium complex $[Rh(NBD)(\mathbf{1a})]BF_4$. Use of methanol as solvent in place of the mixed solvent increased the rate of hydrogenation, though the stereoselectivity was a little lower (95.8% ee) (entry 4). The acrylic acids including 4-chlorophenyl (**2b**),[12] 4-methoxyphenyl (**2c**), and 2-naphthyl (**2d**) also underwent the hydrogenation at the *re* face with high stereoselectivity to produce (*S*)-**3** of around 97% ee (entries 8–10). It is well documented that certain esters of the α-isopropylarylacetic acids (**3**) are effective insecticides and only the (*S*) isomers are their active components.[13]

The present asymmetric hydrogenation finds a useful application in the asymmetric synthesis of carboxylic acids containing two vicinal chiral carbon centers (eq 2). Thus, the hydrogenation



(2)

(*E*)-**4a**: R = Et
(*E*)-**4b**: R = Ph

(2*S*,3*S*)-**5a**
(2*S*,3*R*)-**5b**

of (*E*)-2-phenyl-3-methyl-2-pentenoic acid (**4a**) gave *l*-**5a**[14] (97% selectivity) as expected from the cis stereochemistry of hydrogenation. With the (*R*)-(*S*)-**1a**/Rh catalyst, the (+)-isomer was obtained in 97.3% ee, whose configuration is assumed to be (2*S*,3*S*) provided that hydrogen attacked the *re* face (entry 11). Similarly, hydrogenation of (*E*)-2,3-diphenyl-2-butenoic acid (**4b**) with (*R*)-(*S*)-**1a**/Rh produced diastereomerically pure (2*S*,3*R*)-**5b**[15] of 92.1% ee (entry 12).

Comparable selectivity and catalytic activity to **1a** was observed with the ferrocenylphosphine ligands **1b**, **1c**, and **1d**, all of which have a dialkylamino group at the terminal position on the ferrocene side chain (entries 5–7). The rhodium complexes with chiraphos,[16] pyrphos,[17] and ferrocenylphosphines lacking the aminoalkyl side chain, such as BPPFA,[8] were catalytically much less active for the present hydrogenation, the tetrasubstituted olefins **2** giving low optical yields (<25% ee) with low conversion even at higher reaction temperature. It is likely that the terminal amino group on ligand **1** forms an ammonium carboxylate with the olefinic substrate and consequently attracts the substrate to the coordination sphere of the catalyst to promote the hydrogenation.[18,19]

(10) The addition of the base is not necessarily required, but it can make the asymmetric hydrogenation highly reproducible.

(11) Aaron, C.; Dull, D.; Schmiegel, J. L.; Jaeger, D.; Ohashi, Y.; Mosher, H. S. *J. Org. Chem.* **1967**, *32*, 2797.

(12) Asymmetric hydrogenation of **2b** (50% conversion, 85% ee) with (*R*)-(*S*)-PPFA/Rh catalyst has been reported in a patent, but the result was not reproducible in our hands: U.S. Patent 4.409.397 (11. 10. 1983); *Chem. Abstr.* **1984**, *110*, 51098.

(13) (a) Ohno, N.; Fujimoto, K.; Okuno, Y.; Mizutani, T.; Hirano, M.; Itaya, N.; Honda, T.; Yoshioka, H. *Agr. Biol. Chem.* **1974**, *38*, 881. (b) Miyakado, M.; Ohno, N.; Okuno, Y.; Hirano, M.; Fujimoto, K.; Yoshioka, H. *Agr. Biol. Chem.* **1975**, *39*, 267.

(14) ^1H NMR (400 MHz in $CDCl_3$). *l*-**5a**: δ 0.661 (d, *J* = 6.7 Hz, 3 H), 0.944 (t, *J* = 7.4 Hz, 3 H), 1.223 (quint d, *J* = 7.4 and 13.4 Hz, 1 H), 1.605 (qdd, *J* = 7.4, 3.3, and 13.4 Hz, 1 H), 2.10–2.19 (m, 1 H), 3.249 (d, *J* = 10.6 Hz, 1 H), 7.21–7.34 (m, 5 H). *u*-5a: δ 0.765 (t, *J* = 7.3 Hz, 3 H), 1.045 (d, *J* = 6.6 Hz, 3 H), 0.83–0.95 (m, 1 H), 1.17–1.28 (m, 1 H), 2.10–2.20 (m, 1 H), 3.249 (d, *J* = 10.6 Hz, 1 H), 7.21–7.34 (m, 5 H).

(15) Auerbach, R. A.; Kingsbury, C. A. *Tetrahedron* **1971**, *27*, 2069.

(16) (*S*,*S*)-1,2-Bis(diphenylphosphino)butane: Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

(17) (*R*,*R*)-1-Benzyl-3,4-bis(diphenylphosphino)pyrrolidine.[2]

(18) Esters of the acrylic acids **2** did not undergo the hydrogenation with the **1a**/Rh catalyst, which may support the promotion of hydrogenation by the attractive interaction forming ammonium carboxylate.

(19) In the studies on asymmetric hydrogenation of (acylamino)acrylic acids and methylsuccinic acid precursors,[1] it has been proposed that the carboxylate generated by the addition of triethylamine has a much greater affinity to rhodium catalyst than the corresponding acid: Ojima, I.; Kogure, T.; Yoda, N. *J. Org. Chem.* **1980**, *45*, 4728.

The attractive interaction is also expected to effect the selective enantioface differentiation of the olefin to give high optical yields.[20]

(20) The (aminoalkyl)ferrocenylphosphines **1** were also found to be effective for the asymmetric hydrogenation of other types of acrylic acids such as atropic acid and α-methylcinnamic acid to give the products of over 80% ee.

Macrocycles Containing Tin. Through Space Cooperative Binding and High Size Selectivity in the Complexation of Chloride Ion by Lewis Acidic Macrobicyclic Hosts

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Received August 3, 1987

The interaction of basic macrocyclic and macrobicyclic hosts with cationic guests has been studied intensively in recent years. In contrast, the analogous complexation of anionic guests by Lewis acidic polydentate or macrocyclic hosts has received little attention.[1] Recently, we found low selectivity in binding of chloride ion in organic solvents by a series of macrocyclic hosts containing two Lewis acidic tin atoms.[2] We anticipated that the addition of more binding sites to or the incorporation of structural rigidity into our Lewis acidic macrocyclic hosts would result in more selective anion complexation. Creation of macrobicycles **1** appeared to be one way to build up binding site rigidity rapidly since Lewis acidic tin atoms containing one electron withdrawing group will complex donors in a trigonal-bipyramidal structure with the donor and withdrawing groups in the axial positions.[3] In this communication we report neutral Lewis acidic macrobicycles in which both the dynamics and energetics of binding of chloride anion are highly size dependent; this apparently represents selective binding of chloride within the host cavity in a manner directly analogous to the binding of cations by cryptands.[4]

The reaction sequence for preparation of macrobicyclic hosts **1** from macrocycles is shown in Scheme I. The starting macrocycles have been reported[5] as has the immediate precursor of **1b**.[6] The macrobicyclization reactions were effected in 20–30% yields for the precursors of **1b–d** but only in 4% yield for the (apparently) strained precursor to **1a**. The final HCl cleavage reactions were virtually quantitative. Sharp melting products **1** were characterized by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy.

The complexation of chloride by hosts **1** was studied by ^{119}Sn NMR spectroscopy.[7] Previously, we observed that macrocyclic hosts **2** exchanged chloride fast on the ^{119}Sn NMR time scale and that the first and second binding constants for hosts **2** were nearly

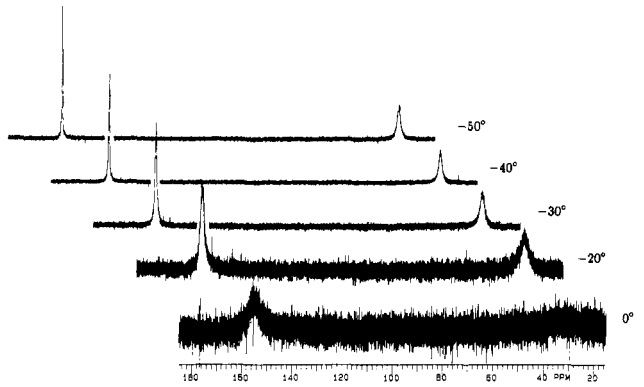
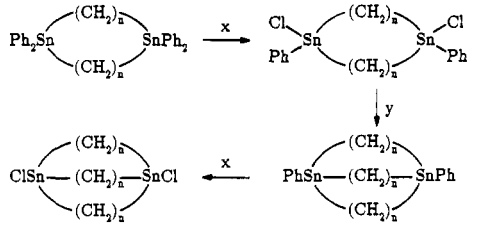


Figure 1. ^{119}Sn NMR spectra (149.2 MHz) of a $CDCl_3$ solution containing host **1b** and 0.5 equiv of tetrahexylammonium chloride.

Scheme I

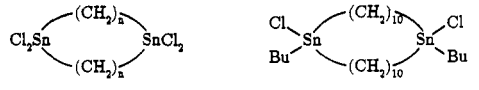


1

(a: n = 6, b: n = 8, c: n = 10, d: n = 12)

Reagents: x, HCl in CH_2Cl_2; y, $BrMg(CH_2)_nMgBr$ in THF.

the same for each host and varied little between hosts.[2] In this work, similar behavior was observed for macrocyclic model **3** in the binding of chloride in $CDCl_3$ solution; addition of increments of tetrahexylammonium chloride to a solution of **3** resulted in a smooth shift for the single sharp peak from +150 ppm (tetracoordinate) to −50 ppm (pentacoordinate).[8] Thus, model **3** (like hosts **2**) binds two chloride ions strongly and equilibrates rapidly ($k > 5 \times 10^6$ s^{-1}).



2 (n = 8, 10, 12) **3**

The ^{119}Sn NMR spectra of bicyclic hosts **1** showed dramatic differences in comparison to those of their macrocyclic counterparts when chloride ion was present. Unlike macrocycles **2** and **3**, bicyclic hosts **1b–d** in the presence of excess chloride bound only one chloride per host; the limiting chemical shifts were at about the midpoint of the tetra- and pentacoordinate tin shifts (one signal for the two tin atoms arises either from fast exchange within the complex or complexation of chloride by both tin atoms simultaneously). There was no indication that any host **1** bound a second chloride anion. Thus, since the tin atoms are insulated from one another by hydrocarbon chains, there is a through space cooperative binding effect in **1b–d** mandated by the structure.

The rates of binding of chloride by hosts **1** were substantially slower than those for cycles **2** and **3**. In the presence of 0.5 equiv of chloride ion per host, the ^{119}Sn NMR spectra of C-12 host **1d** at room temperature consisted of one broad signal that further broadened at lower temperatures. The spectrum of the C-10 host **1c** (plus 0.5 equiv of Cl^-) at room temperature contained one very broad signal, but at −50 °C broad signals at +150 ppm (uncomplexed) and +40 ppm (1:1 complex) were observed. The spectrum

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