"Thermochemical Kinetics"; Wiley: New York, 1968; pp 178–181. It is found that **5** (+ 2H⁺) is ~68 kcal mol⁻¹ less stable than **3–4** (+ 2H⁺). However, the energy difference between **5** and **3–4** should be considerably larger, because **5** has to accommodate the two negative charges in the vicinal position, whereas in **3–4** they are four bonds apart.
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Isotopomer Differentiation by Means of Inclusion

Sir:

Tetra(4-methylpyridine)nickel(II) thiocyanate (**1**) forms inclusion compounds with a variety of guest molecules, including *p*-xylene and naphthalene.[1] Sorption isotherms for many analogous systems have been studied,[2] the crystal structure of some inclusion compounds has been determined,[3,4] and the cavity shape has been discussed.[4] The competition between guests such as *p*-xylene and ethylbenzene for sites in the host lattice has been investigated quantitatively.[5] A similar, less marked, but potentially useful, competition is reported here for isotopomers with the same host. After **1** is shaken with an excess of a mixture of p-$(CH_3)_2C_6H_4$ (A) and p-$(CD_3)_2C_6D_4$ (B), of A and $(CD_3)_2C_6H_4$ (C), or of $C_{10}H_8$ (D) and $C_{10}D_8$ (E), dissolved in *n*-pentane, the inclusion compound forms which is shown below to have a higher D/H ratio; the mother liquor has a lower D/H ratio than that of the original mixture.

The host material, **1**, was prepared as described elsewhere.[6] Its composition corresponded closely to theoretical. The purities of the deuterated compounds were quoted by the manufacturer as follows: B, 98+; C, 99+; E, 99+ at. % deuterium. A was reagent grade material, purified further by stirring for several days with **1**, filtering off the resulting solid, and recovering A by dissolving the solid in dilute HCl, extracting it with *n*-pentane, and distillation over a 2 °C range. This procedure is intended to reduce the amounts of possible impurities such as ethylbenzene or other isomers which are far less included than A. D was reagent grade product recrystallized from ethanol.

Although the inclusion compound with *p*-xylene can be made in the absence of a diluent, the latter was used to increase the quantity of liquid phase (and thus the fluidity of the system) without excessive use of the deuterated compound, and pentane was chosen for the diluent to eliminate interference in the mass spectral range of interest.

Mixtures of A and B, of A and C, and D and E, all in pentane, were prepared as indicated in Table I using a syringe, and a small portion was set aside in a sealed tube for subsequent analysis. This is referred to below as the original mixture. The remainder of the mixture was added to a 10-mm Pyrex tube containing **1**, and the tube cooled in dry ice and sealed. The quantitites were chosen such that the resulting liquid phase (L) weighed 4–10 times that of the solid phase (S) and such that an excess of guest was always present. This ensured that all of **1** had been saturated with guest. For *p*-xylene and naphthalene, saturation occurs when the molar host/guest ratio is unity. The tubes were tumbled slowly at room temperature for several days to equilibrate, during which time the guests distributed themselves between liquid and solid phases. The tubes were then centrifuged, L was withdrawn and set aside, and S was air dried briefly. S was decomposed with 6 N HCl, and the liberated guests were extracted with pentane. A small portion of **1** was stirred with L, HCl was added to decompose it, and the guests were extracted with pentane, similar to the decomposition of S. (The addition of **1** to L was merely to provide a similar history for both L and S apart from the inclusion step.) The HCl, in addition to causing decomposition and dissolution of all of the products except the guests, prevents the 4-methylpyridine from being extracted.

The original solution and the pentane extracts from L and S were then analyzed with a CEC 21-104 analytical mass spectrometer in order to compare the areas of the parent peaks: A, 106; B, 116; C, 112; D, 128; E, 136 amu. After the background was checked, the instrument parameters including chart speed were adjusted so that the peaks in the range of interest were as large and as smooth as possible. The area of the larger of the two parent peaks was usually ~30 cm³. After the sample had been admitted, time was allowed for the pressure within the spectrometer to stabilize. At least four spectra were then taken consecutively for a given sample and the areas under the parent peaks measured with a high quality planimeter. The average ratio of the areas was taken as a measure of the relative amounts of the two isotopomeric guests. With the limitations of the spectrometer included it is estimated that these ratios are accurate to ~1%. Compound **1**, alone, decomposed with HCl and then extracted with pentane, gave no peaks in the region of interest. There is no isotope exchange between B and C and the other substances used; this is doubtless true also for E.

The mole ratios, determined as described, are given in Table I. For all of the experiments, the values for L, original solution, and S differ by considerably more than the experimental error. In all instances the deuterated isotopomer is included to a slightly greater extent than the protonated. The fact that the ratios for the original mixture lie between those of L and S shows that the results are internally consistent. The fractions given in the second last column were estimated by assuming the total absence of host in L, absence of pentane in S, and a guest/host ratio in S of unity. If one defines a separation factor for the deuterated species, s_d, as the mole ratio in S divided by the mole ratio in L, the values in the last column are obtained. Its magnitude, at least in the system A–B, appears to be the

Table I. Distribution of Isotopomers between Liquid and Solid Phases

guest mixture	quantities used			mole ratio (B/A, C/A, or E/D)			fraction of total guest pptd	s_d
	guest mixture mL	pentane. mL	host, g	L	orig	S		
A + B	0.45	2.0	0.15	0.808	0.863	0.899	0.08	1.11
	0.10	2.0	0.16	1.05	1.12	1.30	0.36	1.24
	0.20	2.0	0.17	1.17	1.22	1.30	0.10	1.11
	0.85	1.5	0.30	1.43	1.46	1.49	0.08	1.04
A + C	0.40	2.0	0.17	0.937	1.02	1.13	0.09	1.21
	0.40	2.0	0.15	0.933	1.04	1.13	0.08	1.21
	0.36	2.0	0.16	1.27	1.31	1.40	0.10	1.10
D + E	0.15[a]	2.1	0.10	1.96	2.02	2.04	0.17	1.04

[a] Gram.

larger the greater the value of the pentane/guest ratio, suggesting that the fractionation of deuterium would be more effective the more the system is diluted with pentane. The data also indicate that the preference of the host for the deuterated isotopomer over the protonated is greater in the *p*-xylene systems than in the naphthalene, and nearly the same for the two *p*-xylene systems. The explanation for these preferences is not yet clear.

Further work is being conducted to extend the concentration ranges and to apply the phenomenon to the liquid chromatographic fractionation of isotopomers where the effects of the differential inclusion are cumulative and prospects for practical applications are emerging.

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Synthesis, Characterization, and Molecular Structure of an Aluminum Pentamethylcyclopentadienyl Complex, [η³-(CH₃)₅C₅Al(Cl)CH₃]₂: An Organometallic Analogue of Benzvalene

Sir:

Several organoaluminum compounds play an important role in commercial olefin polymerization processes;[1,2] yet the fundamental structural chemistry, bonding, and rearrangement dynamics of discrete organoaluminum–olefin complexes remain incompletely defined and systematized. The chemistry of aluminum–olefin complexes has recently piqued our interest, and we report here on the formation and molecular structure of an unusual aluminum addition complex of pentamethylcyclopentadiene, $[\eta^3$-$(CH_3)_5C_5Al(Cl)CH_3]_2$ (**1**).

Compound **1** was prepared by combination of a toluene solution containing 1.95 g (10 mmol) of pentamethylcyclopentadienylmagnesium chloride[3] with 0.92 g (5 mmol) of $[(CH_3)_2AlCl]_2$ under a dry nitrogen atmosphere. The resulting yellow-white solid was extracted with hexane from which colorless crystals were obtained upon vacuum evaporation of the solvent (50% yield after crystallization).[4] The compound is extremely air and moisture sensitive; the solid material and the solutions turn dark purple upon exposure to protic sources. The mass spectrum (70 eV) of **1** displays a fragmentation pattern typical of $[RR'AlCl]_2$ compounds;[5] the most intense ions include *m/e* 232 ($^{35}Cl_2AlC_5(CH_3)_5{}^+$), 212 ($^{35}ClAlC_5(CH_3)_5(CH_3)^+$), 197 ($^{35}ClAlC_5(CH_3)_5{}^+$), and 177 ($CH_3AlC_5(CH_3)_5{}^+$). The 60-MHz ¹H NMR spectrum (32 °C, Me₄Si standard) of **1** in benzene shows a singlet at 1.60 ppm (area 5) which can be assigned to the protons on five
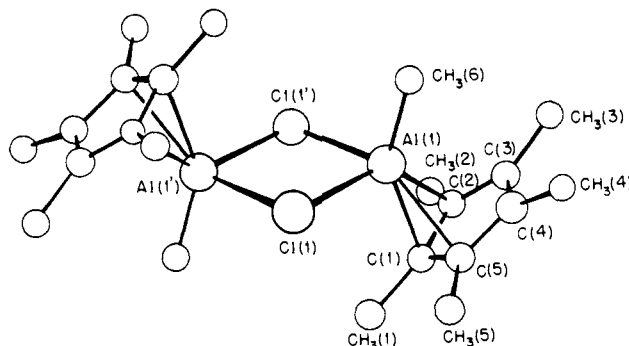

Figure 1. Molecular structure of $[\eta^3$-$(CH_3)_5C_5Al(Cl)CH_3]_2$.

equivalent cyclopentadienyl ring methyl groups, and a singlet at −0.85 ppm (area 1) which can be assigned to the equivalent protons of a methyl group bonded to the aluminum atom. The 25.2-MHz ¹³C{¹H} NMR spectrum (32 °C, Me₄Si standard) shows a singlet at 10.74 ppm assigned to the ring methyl carbon atoms and a singlet at 115.36 ppm assigned to the ring framework carbon atoms. The resonance for the methyl group bonded directly to the aluminum atom is not observed.[6] The stoichiometry involved in the synthesis of **1** and the mass spectrometric and NMR data are consistent with a reaction pathway involving the exchange of pentamethylcyclopentadienyl groups for two of the terminal methyl groups on the parent dimer $[(CH_3)_2AlCl]_2$. Upon first examination, the room temperature NMR spectra suggest that in solution the molecular structure of **1** contains fluxional monohapto $(CH_3)_5C_5$-Al units as are found in $(CH_3)_3Ge[(CH_3)_5C_5]$ and $(CH_3)_3Sn[(CH_3)_5C_5]$.[7] However, these data are inconclusive, and a single-crystal X-ray diffraction analysis has been carried out to provide the necessary structural description.

Compound **1** crystallizes in a monoclinic cell, $P2_1/c$, with two molecules per unit cell. Crystal data are as follows: $a = 8.657$ (2), $b = 8.914$ (2), $c = 16.208$ (2) Å; $\beta = 104.95$ (1)°; $V = 1208.4$ (4) Å³; $Z = 2$; $\rho_{calcd} = 1.17$ g cm⁻¹; Cu Kα radiation ($\lambda = 1.5418$ Å); μ (Cu Kα) = 10.8 cm⁻¹; $F(000) = 424$.[8] Each dimeric molecule of **1** possesses crystallographic C_i-$\bar{1}$ site symmetry and the molecule nearly conforms to an idealized C_{2h}-$2/m$ geometry. The molecular structure of **1** is shown in Figure 1, and the significant intramolecular bond angles and distances are summarized in Table I. Each alumi-

Table I. Selected Interatomic Distances (Ångstroms) and Angles (Degrees)

Contact Distances			
Al(1)–Cl(1)	2.378 (3)	C(1)–C(2)	1.43 (1)
Al(1)–Cl(1')	2.398 (2)	C(1)–C(5)	1.44 (1)
Al(1)–C(1)	2.095 (7)	C(2)–C(3)	1.39 (1)
Al(1)–C(2)	2.254 (8)	C(3)–C(4)	1.37 (1)
Al(1)–C(5)	2.279 (8)	C(4)–C(5)	1.38 (1)
Al(1)–CH₃(6)	1.916 (7)		

Nonbonded Distances			
Al(1)–C(3)	2.499 (6)	CH₃(6')–CH₃(2)	>5.0
Al(1)–C(4)	2.517 (7)	Al(1)–Al(1')	3.561 (3)
CH₃(1)–Cl(1)	3.878 (8)	Cl(1)–Cl(1')	3.182 (2)
CH₃(2)–Cl(1)	3.406 (10)	CH₃(6)–CH₃(3)	3.685 (10)
CH₃(6')–CH₃(1)	3.879 (11)	CH₃(6)–CH₃(4)	3.572 (11)

Bond Angles			
Cl(1)–Al(1)–Cl(1')	83.56 (8)	C(5)–C(1)–C(2)	107.1 (6)
Al(1)–Cl(1)–Al(1')	96.44 (9)	C(1)–C(2)–C(3)	106.9 (6)
Cl(1)–Al(1)–CH₃(6)	101.5 (2)	C(2)–C(3)–C(4)	109.1 (6)
Cl(1')–Al(1)–CH₃(6)	101.1 (2)	C(3)–C(4)–C(5)	110.4 (6)
Al(1')–Al(1)–C(1)	104.6 (2)	C(4)–C(5)–C(1)	106.5 (6)
Al(1')–Al(1)–CH₃(6)	105.2 (2)		