

Figure 1. Thermal conversion of **1** to **2** as followed by UV spectroscopy (methylcyclohexane, spectra taken every 5 s) at 90 °C. Curve a represents mixture of **1** and **2** after near thermal equilibration of UV cell; curve b represents equilibrium mixture of **1** and **2** at 90 °C.

mass spectral data alone, even with the FD technique, are not adequate for the molecular weight assignments of compounds of this type.

Photochemical Conversion of 1 into 2. Quantitative conversion to **2** can be achieved through photolysis of solutions of **1** (methylcyclohexane) at -78 °C using a Hanovia high-pressure lamp (pyrex filter). A ^1H NMR spectrum (250 MHz, methylcyclohexane- d_{14} , -68 °C) taken immediately after photolysis shows new signals at δ 0.93 (d, relative intensity 6), 1.16 (d, 12), 2.74 (sept, 1), 3.22 (m, 2), and 6.91 (s, 2) and are assigned to **2** as the sole product with no trace of **1**.¹² Prolonged photolysis of **2** at -78 °C leads to no photodecomposition; however, upon warming to 0 °C **2** is converted back cleanly to **1**. Unambiguous proof that **2** in solution exists solely as a dimeric¹ form is demonstrated by the ^{119}Sn NMR [100.74 MHz, -68 °C, ^1H decoupled, methylcyclohexane- d_{14}], δ (ppm from Me_4Sn)] A single resonance at +427.3 is accompanied by two tin-tin coupling satellites [1J (^{119}Sn - ^{117}Sn) = 2930 Hz] of relative peak intensities, 3.8% of parent peak, which are expected only for a structure possessing two directly bonded tin atoms.¹³ Solutions of **2** around -70 °C are intensely red, showing an absorption maximum λ_{max} 494 nm ($\log \epsilon$ 4.59),⁵ and are extremely air- and moisture-sensitive.

Thermal Equilibrium between 1 and 2. At 0 °C or lower temperatures to -78 °C, cyclotristannane **1** is thermodynamically stable in an inert solvent and **2** is converted to **1** only slowly, thus permitting one to record the spectra of **2** (see above). However, at room temperature or above, rapid equilibration between **1** and **2**, with **2** being favored at higher temperatures, occurs. This process can be followed by ^1H NMR and/or UV spectroscopy. For instance, Figure 1 shows the rate of formation of **2** (after thermal equilibration of the UV cell) at 90 °C as followed by UV spectroscopy: approximate equilibrium ratio of $[\mathbf{2}]/[\mathbf{1}] = 2.09$ at 90 °C and approximate time required for 95% completion of the equilibration, $\tau = 165$ s, starting with an initial concentration of **1** (solution prepared at 0 °C) = 2.18×10^{-3} M (at 50 °C equilibrium ratio 1.30, τ 300 s at 70 °C; 0.49, 1300 s). This equilibration phenomenon was totally unexpected and is perhaps unprecedented. Its simplest explanation may be offered by invoking the intermediacy of the corresponding stannylene **2a** ($\text{R} = 2,4,6$ -triisopropylphenyl in **3a**) which is generated relatively slowly from either **1** or **2** but rapidly adds to **2** or dimerized, as formulated by $2(\mathbf{1}) \rightleftharpoons [2(\mathbf{2}) + 2(\mathbf{2a})] \rightleftharpoons 3(\mathbf{2})$.¹⁴ This sequence

(12) Using an internal standard, this photoconversion is shown to produce 3 mol of **2** from 2 mol of **1**.

(13) 1J (^{119}Sn - ^{117}Sn) for $\text{Me}_3\text{Sn-SnMe}_3$ is 4211 Hz with similar satellite intensities observed for **2**: Mitchell, T. N. *J. Organomet. Chem.* **1974**, *70*, C1. (Also: Sita, L. R., unpublished results.)

(14) Although not spectroscopically detected, **2a** can indeed be trapped from solution mixtures of **1** and **2** with reagents such as 2,3-dimethyl-1,3-butadiene and tri-*n*-butyltin hydride at room temperature.

of reactions constitutes one possible route through which **1** is formed from **6** in this particular instance.^{4c,g}

A few comments on the spectral properties of **1** and **2** are in order. The remarkable low-field ^{119}Sn NMR chemical shift resulting from strongly deshielded tin atoms in **2** can be compared to the low-field ^{29}Si NMR chemical shifts observed for $\text{Si}=\text{C}^{15}$ and $\text{Si}=\text{Si}^{16}$ double bonds. The electronic spectrum of **2** is also characterized by the intense absorption in the visible region in a similar manner to those of tetrakis(2,6-diethylphenyl)disilene (**7**) [λ_{max} 272 nm ($\log \epsilon$ 3.84), 340 (3.44), 422 (3.80)]^{4c,e} and tetrakis(2,6-diethylphenyl)digermene (**8**) [λ_{max} 263 nm ($\log \epsilon$ 4.11), 412 (3.92)].^{4c,e} All of these dimetallenes, **2**, **7**, and **8**, retain structural integrity in solution, and these facts suggest the possibility that they might all have similar structural features. Since **7** and **8**^{4c,i} have twist-double-bond structures with no or little ($\chi_{\text{Ge}} = 15^\circ$) pyramidalization, respectively,¹⁷ the crystallographic analysis of **2** (which we intend to pursue) may not reveal as pronounced a trans-bent structure¹⁸ as that of **3** ($\chi_{\text{Sn}} = 41^\circ$).² Even for this reason alone, the crystal structure of **2** attracts great interest.

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Supplementary Material Available: Full experimental details of Scheme II, including spectral data of new compounds and copies of spectra of **1**, **2**, **7**, and **8** (8 pages). Ordering information is given on any current masthead page.

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NMR Spectra of $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_2\text{SiMe}_3\text{Li}(\text{pmdeta})$ and $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}(\text{pmdeta})$: The First Direct Observation of Resolved ^7Li - ^1H Coupling

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Observation of scalar spin-spin coupling between ^7Li and ^{13}C in the nuclear magnetic resonance spectra of these nuclei has been critical in determining degrees of oligomerization for organolithium species in solution.¹ Recently, coupling between ^7Li and ^{31}P nuclei was reported for a series of phosphidolithium dimers $[\text{LiPR}_2]_2$,

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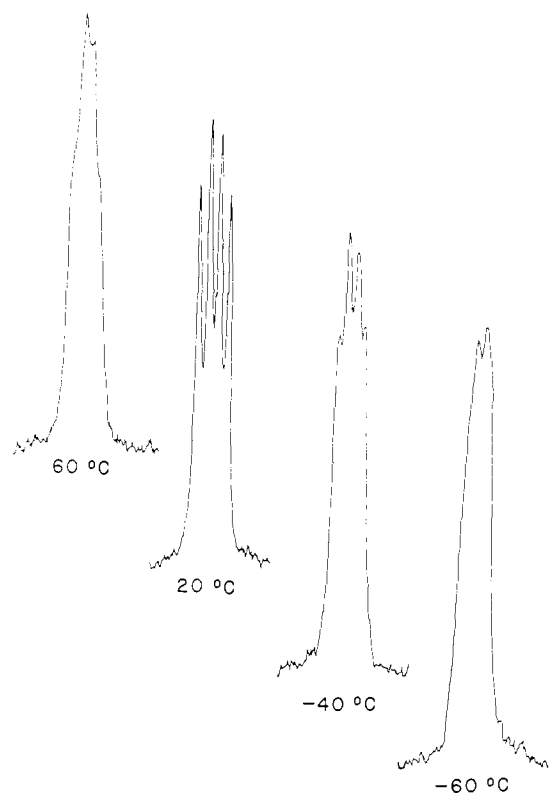


Figure 1. Experimental ^1H NMR spectra (300 MHz) of the hydride resonance ($\delta -20.15$) for complex **1** at various temperatures.

$\text{R} = \text{Ph}_2\text{CH}(\text{SiMe}_3)_2$.³ Surprisingly, however, coupling between ^7Li and ^1H nuclei has not been resolved in simple alkyl- and aryllithium complexes, although labeling and decoupling experiments strongly suggest such couplings exist.^{4,5}

We report the observation of significant ^7Li - ^1H spin-spin coupling between the hydrogen and lithium ligands in the complexes $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_2\text{SiMe}_3\text{Li}(\text{pmdeta})$ (**1**) (pmdeta = pentamethyldiethylenetriamine) and $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}(\text{pmdeta})$ (**2**), as well as temperature-dependence studies which bear upon the novelty of these results.

As a test of the generality of the deprotonation of (penta-methylcyclopentadienyl)iridium polyhydride compounds by *t*-BuLi/pmdeta,⁶ we treated a mixture of $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{SiMe}_3$ and pmdeta with *t*-BuLi in a minimum amount of *n*-hexane at -40°C . The pale yellow solution deposited white microcrystals over 24 h, yielding ca. 30% of the desired salt **1**. Removal of solvent from the mother liquor and recrystallization of the residue from hexane gave an additional 30% of analytically pure **1**. Data for **1**: ^1H NMR (C_6D_6 , 20°C , 300 MHz) δ 2.34 (s, 15 H, C_5Me_5), 2.04 (s, 3 H, internal amine methyl), 1.98 (s, 12 H, terminal amine methyl), 1.7 (br, 8 H, amine methylenes), 0.81 (s, 9 H, SiMe_3), -20.15 (1:1:1:1 quartet, $J_{\text{LiH}} = 8.4$ Hz, 2 H, Ir-H); $^1\text{H}\{^7\text{Li}\}$ NMR (C_6D_6 , 20°C , 300 MHz, hydride resonance only) $\delta -20.15$ (s, 2 H, Ir-H); ^7Li NMR (C_6D_6 , 20°C , 116 MHz) δ 3.2 (t, $J_{\text{LiH}} = 8.4$ Hz); $^7\text{Li}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C , 116 MHz) δ 3.2 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C , 75 MHz) δ 88.6 (s, C_5Me_5), 58.3, 57.0, 46.0, 43.2 (all br s, pmdeta), 12.5 (s, C_5Me_5), 11.7 (s, SiMe_3); IR (C_6D_6) $\nu_{\text{Ir-H}}$ 2069 cm^{-1} (very br). Anal. Calcd for $\text{C}_{20}\text{H}_{50}\text{N}_3\text{LiSiIr}$: C, 45.26; H, 8.63; N, 7.20. Found: C, 44.88; H, 8.37; N, 7.20.

As noted above, the ^1H NMR spectrum of a sufficiently dilute (ca. 0.01 M) solution of pure **1** shows an upfield resonance ($\delta -20.15$) due to the iridium-bound hydrides, which appears as a 1:1:1:1 quartet ($J = 8.4$ Hz), with the outermost peaks slightly reduced in intensity due to the significant linewidth (fwhh ~ 6 –7 Hz) (Figure 1, 20°C spectrum). The structure of the resonance proved to be independent of magnetic field strength over the range 200–500 MHz. Guessing that this feature was due to ^7Li - ^1H spin-spin coupling (^7Li has $s = 3/2$, 92.6% abundance), we performed a $^1\text{H}\{^7\text{Li}\}$ NMR experiment. Upon broad-band decoupling of the ^7Li frequency, the quartet collapsed to a singlet, indicating loss of ^7Li - ^1H coupling. No apparent differences between the downfield alkyl regions of the two spectra were noted.

Further confirmation of this coupling resolution resulted from the ^7Li NMR spectrum. This showed a broad triplet resonance (δ 3.2, $J = 8.4$ Hz), which collapsed to a broad singlet (fwhh ~ 8 –9 Hz) upon broadband irradiation of the proton frequency.

During these experiments we noted that the ability to resolve the ^7Li - ^1H coupling varied with temperature. In fact, resolution of the coupling for **1** is restricted to the temperature range -40 to $+40^\circ\text{C}$; outside this window the lines are broadened to the point where the quartet structure is lost (Figure 1).

Given this interesting result, we carefully reinvestigated the ^1H NMR spectrum of $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}(\text{pmdeta})$ (**2**)⁶ and found a similar window. Splitting of the hydride resonance could only be observed between -10 and -40°C . The most well-resolved spectrum occurred at -20°C and showed essentially the same features as those for complex **1**: ^1H NMR (toluene- d_8 , -20°C , 300 MHz, hydride resonance only) $\delta -19.27$ (1:1:1:1 quartet, $J_{\text{LiH}} = 6.4$ Hz, 3 H, Ir-H); $^1\text{H}\{^7\text{Li}\}$ NMR (toluene- d_8 , -20°C , 300 MHz, hydride resonance only) $\delta -19.27$ (s, 3 H, Ir-H); ^7Li NMR (toluene- d_8 , -20°C , 116 MHz) δ 5.0 (q, $J_{\text{LiH}} = 6.4$ Hz); $^7\text{Li}\{^1\text{H}\}$ NMR (toluene- d_8 , -20°C , 116 MHz) δ 5.0 (s).

These results conclusively demonstrate the resolution of scalar spin-spin ^7Li - ^1H coupling, with a coupling constant quite large compared to those observed in organic systems.

Although we do not know how many careful searches have been made for ^7Li - ^1H coupling in other systems, complexes **1** and **2** appear at present to be unique. We suggest the following reasons for this situation:

(1) We believe that both complexes are monomeric in solution. Because the proton resonance appears as a quartet, and not some more complex pattern, the hydride ligands must "see" only one lithium atom on the NMR time scale. Also, a Signer molecular weight determination on $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}(\text{pmdeta})$ indicated it to be monomeric in benzene solution.⁶ We presume this is due to the known ability of pmdeta to occupy three of four lithium coordination sites.⁷

(2) The ability to resolve the coupling seems quite sensitive to the concentration of **1**. As noted, the results described apply to 0.01 M solutions. While we have not explored this phenomenon in detail, at concentrations approaching 0.02 M, the hydride resonances broaden to doubletlike patterns with "fattening" of the peaks at the wings, and at concentrations >0.05 M, the peaks appear as broad singlets.

(3) The couplings are large enough that the inherent linewidth plus the quadrupolar broadening due to ^6Li and ^7Li cannot obscure the fine structure. Even though the ^7Li NMR resonances, for example, are 6–9 Hz wide at half-height, the total wing separations of 16 Hz for **1** and 18 Hz for **2** are easily large enough to overcome the broadening and show the appropriate multiplet pattern.

(4) The ability to resolve the coupling is clearly temperature-dependent. We cannot at this point determine the cause or causes of the temperature windows observed.⁸ However, we believe that

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(5) Oliver and co-workers suggest $J(^7\text{Li}-^1\text{H}) < 1$ Hz for (ethyl-, propyl-, and trimethylsilyl)lithium on the basis of decoupling experiments. Oliver, J. P., personal communication.

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(8) We are in agreement with referees' suggestions that the broadening at low temperatures is most likely due to faster ^7Li quadrupole relaxation and that at high temperatures to fast intermolecular exchange processes. Possible additional influences on the line broadening include viscosity effects and changes in molecular correlation time (cf.: Suzuki, M.; Kubo, R. *Mol. Phys.* **1963-1964**, 7 (3), 201).

the paucity of variable-temperature studies on organolithium complexes may be partly responsible for the novelty of our results.

In conclusion, we have observed the first examples of lithium-proton spin-spin coupling in two transition-metal lithium complexes. Attempts to understand the results on structural and chemical bases are continuing.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098. We are grateful to Drs. John Oliver, Gideon Fraenkel, and Theodore Brown for helpful discussions. Support for the NMR spectrometers used in this work was provided by NSF Equipment Grants CHE82-09580 (300 MHz) and CHE82-08994 (500 MHz).

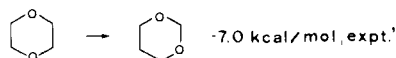
Do Anomeric Effects Involving the Second-Row Substituents Cl, SH, and PH₂ Exist? Stabilization Energies and Structural Preferences

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Despite being separated by a saturated carbon, two geminal substituents can interact strongly. This phenomenon has become known as the anomeric effect:³ the extensive literature has been well reviewed.^{4,5} Both energetic and structural consequences are often dramatically large. As early as 1937, Brockway noticed the progressive decrease in the C-F bond lengths along the series of fluorinated methanes, CH₃F > CH₂F₂ > CHF₃ > CF₄.⁶ Lemieux, in particular, attributed the preference of heteroatom substituents for axial rather than equatorial conformations in saturated heterocyclic ring systems (e.g., pyranose forms of sugars) to the stereoelectronic consequences of such interactions.³ Although quantitative experimental data is sparse, Benson has recorded several dramatic instances where two first-row heteroatoms attached to the same carbon produce large stabilizations.⁷ For example, even though the optimum conformations are not present, 1,3-dioxane is 7.0 kcal/mol more stable than the 1,4-isomer.



(1) University of Erlangen-Nürnberg.

(2) University of Hyderabad.

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(5) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141-1150 and references cited.

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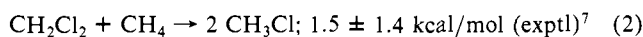
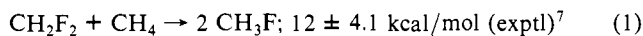
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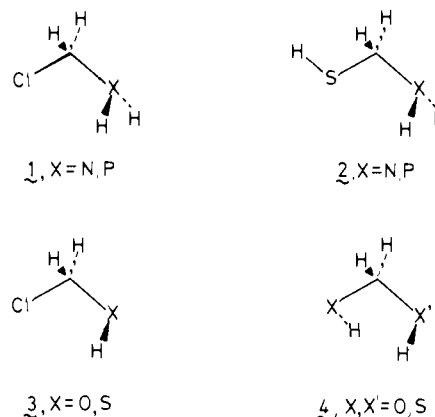
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These structural and energetic manifestations of the anomeric effect involving first-row substituents have been studied systematically theoretically,^{4,5,8,9} and the origin of the effect ("negative hyperconjugation")⁵ is well established. An electronegative atom or group, X in XCH₂Y, lowers the energy of the orbital designated π* CH₂X, because of its symmetry. π-Donation by lone pair electrons on Y into this orbital provides substantial stabilization. This also produces the bond length changes and conformational preferences observed experimentally^{4,6,10} and computationally.^{4,5,8,9}

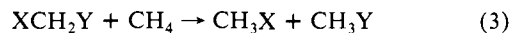
In view of the importance of the anomeric effect and the extensive studies involving first-row groups, the relative lack of information concerning the involvement of second-row substituents is surprising. Conformational effects, e.g., gauche and axial preferences of chlorine,^{4,10} are among the positive evidence for the operation of such effects. In contrast, the experimental energy data on CH₂Cl₂⁷ indicate the lack of any appreciable energetic effect (contrast eq 1 and 2).



As a consequence of the paucity of information, we have calculated the structures and energies of all possible first- and second-row disubstituted methanes, XCH₂Y (X, Y = F, OH, NH₂, Cl, SH, and PH₂). This extends similar earlier studies which were devoted to the interactions of first-row substituents.^{8,9} All principal conformations of the XCH₂Y molecules were examined. The 3-21G(*)//3-21G(*) methyl stabilization energies (e.g., 3)



presented in Table I refer to the lowest energy geometry of each species, but a more extensive set of data is given in the supplementary material.



For uniformity, all of the data are calculated at the 3-21G-(*)//3-21G(*) level.¹¹ This represents a split-valence basis set for the first-row atoms and hydrogen but a d-orbital augmented basis for all second-row atoms. Even for normal-valent second-row molecules, d-functions generally give better geometries and relative energies.¹¹ In many of the more critical instances (see Table I), the results were checked against experiment or the results of higher level calculations. Errors probably do not exceed 4 kcal/mol and in most instances are expected to be considerably less. The errors in the available experimental data are equally large.

In contrast to the very large methyl stabilization energies in XCH₂Y systems involving any combination of the first-row groups, F, OH, and NH₂ (Table I, top left),⁹ corresponding interactions are negligible when X and Y both involve second-row groups, Cl,

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