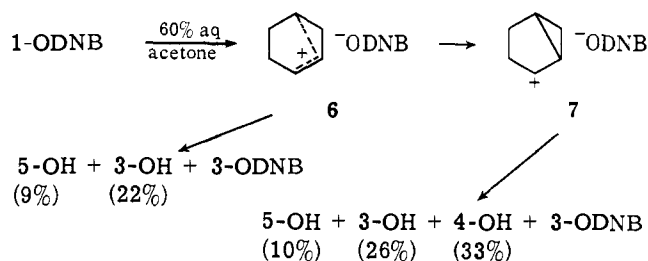


cyclopropylcarbinyl cation–dinitrobenzoate ion pair **7** described for solvolysis and **3-** and **4-**ODNB's.<sup>2b</sup> Reaction of **7** with solvent would produce **3-OH** and **4-OH**, and ion-pair return may produce **3-ODNB**.<sup>9</sup>

If we assume that the product distribution from **7** is the same as that found from **3-ODNB** and that all of alcohol **4-OH** is derived from **7**, the products from ion pair **6** are 22% **3-OH**, 9% **5-OH**, and probably the majority of the ion-pair return product, **3-ODNB**, using the 90° results for **3-ODNB**. This requires a reasonable lifetime and stability of **6** even though the configuration changes required for the conversion of **6** to **7** appear to be small.



Hanack and Keberle<sup>10</sup> reported that the buffered acetolysis of  $\Delta^3$ -cyclohexenyl tosylate (**5-OTs**) gave a small amount of [3.1.0] products, **3-OAc** and **4-OAc**, along with major amounts of **5-OAc** and  $\Delta^2$ -cyclohexenyl acetate. We have found that in buffered acetic acid 17% of a mixture of **3-OAc** and **4-OAc** is converted to **5-OAc** after 47 hr at 75° which gives a first-order rate constant of about  $1 \times 10^{-6} \text{ sec}^{-1}$  for this rearrangement. This requires that *ca.* 40% of the **3-OAc** and **4-OAc** produced from **5-OTs** would have rearranged during the 168-hr acetolysis period at 70.00°. The combined yield of **3-OAc** and **4-OAc** should then be considered to be a minimum of 11%. However, since the ratio of **3-OAc**/**4-OAc** from the acetolysis of **5-OTs** is 0.55,<sup>10</sup> it appears that these products are produced from the cyclopropylcarbinyl cation in **7**.<sup>11</sup>

At least two factors may account for the ability to enter the potential well of the homoallylic cation in **6** from **1-ODNB** but not from **5-OTs**: (1) the increased energy in the [2.2.0] system compared to the  $\Delta^3$ -cyclohexenyl system due to strain and/or (2) the marked increase in *Y* value and nucleophilicity in the solvent systems used with these two substrates (buffered acetic acid for **5-OTs** and *sym*-collidine buffered 60% aqueous acetone for **1-ODNB**). With respect to factor 2, we have found that **5-OH** is the only alcohol product from **5-OTs** in *sym*-collidine buffered 60% aqueous acetone at 50° after 24 hr. However, this result may only reflect the increased nucleophilicity of this solvent system compared to buffered acetic acid.

**Acknowledgments.** Support of this research by the National Science Foundation (GP-7818, GP-10691) is gratefully acknowledged.

(9) The benzoate ester of **1-OH** is stable to the solvolytic conditions which negates any **1-ODNB**  $\rightarrow$  **3-ODNB** by a direct acid-catalyzed rearrangement as found with **1-OAc**.<sup>4</sup>

(10) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963).

(11) In the  $\Delta^2$ -cyclohexenyl-cyclohexyl system,  $k_{\text{unsat}}/k_{\text{sat}} = 2.4$  is found for tosylate acetolysis; ref 10 and H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, **78**, 2735 (1956).

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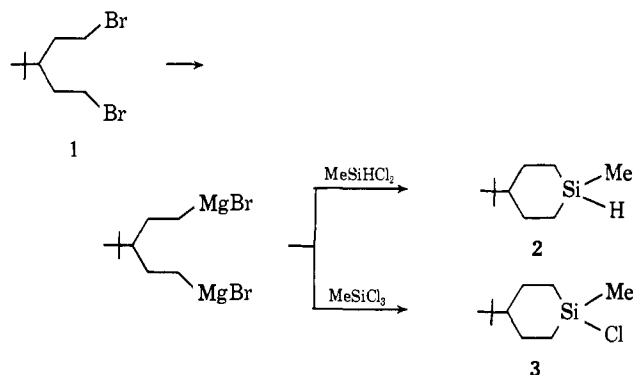
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## New Conformationally Stable 4-*tert*-Butyl-1-silacyclohexanes and Stereochemistry of Insertion of Dimethylsilylenes into the Silicon-Hydrogen Bond

Sir:

The stereochemistry of reactions on a silicon center has been studied mainly by using optically active 1-naphthylphenylmethylsilyl derivatives prepared first by Sommer and Frye.<sup>1,2</sup> However, it became necessary to look for other aliphatic silicon compounds suitable for the stereochemical study of certain reactions as the dimethylsilylene insertion into the Si-H bond reported in this paper. Accordingly, we have prepared the first conformationally stable 4-*tert*-butyl-1-silacyclohexane derivatives. Numerous stereochemical studies on the corresponding carbon analogs, 4-*tert*-butylcyclohexanes, have been published since the first proposal of the *tert*-butyl function as a holding group.<sup>3</sup>

3-*tert*-Butyl-1,5-dibromopentane (**1**), bp 98–99° (3 mm),<sup>4</sup> was prepared by a five-step synthesis from *p*-*tert*-butylphenol. The reaction of the di-Grignard reagent of **1** with methylchlorosilane and with methyltrichlorosilane afforded 1-methyl-4-*tert*-butyl-1-silacyclohexane (**2**, *cis/trans* = 1.0)<sup>5</sup> and 1-methyl-4-*tert*-butyl-1-chloro-1-silacyclohexane (**3**, *cis/trans* = 1/2.3), respectively.



By alcoholysis of **3** or of **2** catalyzed by palladium on charcoal, a number of alkoxy derivatives were prepared. The isopropoxysilane proved the most convenient for separation of *cis* and *trans* isomers by preparative glc. These isomeric alkoxy derivatives were then reduced to **2** with  $\text{LiAlH}_4$  stereospecifically (retention of configuration) as in reduction of optically active alkoxy silanes.<sup>2</sup> Several derivatives of **2** were prepared; nmr data for these compounds are listed in Table I.<sup>6</sup>

The structures of **2a** and **2b** were assigned from  $\text{SiHCH}_2$  coupling constants. Thus, irradiation of the  $\text{SiCH}_3$  signal of **2b** revealed  $J_{\text{SiH(ax)}-\text{CH(ax)}}$  and  $J_{\text{SiH(ax)}-\text{CH(eq)}}$  to be 6.5 and 1.7 Hz, respectively, and  $J_{\text{SiH(eq)}-\text{CH(ax)}}$  to be *ca.* 1.0 Hz for **2a**. The axial methyl

(1) L. H. Sommer and C. L. Frye, *J. Amer. Chem. Soc.*, **81**, 1013 (1959).

(2) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(3) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

(4) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 1109 (1965).

(5) Throughout the paper, *cis* and *trans* are defined with respect to 4-*tert*-butyl and 1-methyl groups. Suffix a is added to the *cis* compounds and b to the *trans*.

(6) Satisfactory elemental analyses and parent peaks ( $\text{M}^+$ ) in mass spectra were obtained for each isomer of **4**, **5**, **7**, and **8**, and for *cis-trans* mixtures of **2**, **3**, **6**, **9**, and **10**.

Table I. Proton Magnetic Resonance Data for 1-Methyl-4-*tert*-butyl-1-silacyclohexyl Derivatives

Compd <sup>b</sup>	X =	$\delta$ , ppm		
		SiCH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	Si-X
<b>2a</b>	H	0.12 (d, $J = 3.5$ Hz)	0.86 (s)	3.95–3.78 (m) <sup>d</sup>
<b>2b</b>	H	0.07 (d, $J = 3.5$ Hz)	0.86 (s)	3.93–3.53 (m) <sup>e</sup>
<b>3a<sup>c</sup></b>	Cl	0.42 (s)	0.86 (s)	
<b>3b<sup>c</sup></b>	Cl	0.38 (s)	0.87 (s)	
<b>4a</b>	OCH(CH <sub>3</sub> ) <sub>2</sub>	0.10 (s)	0.86 (s)	1.10 (d), 3.96 (sep) ( $J = 6.0$ Hz)
<b>4b</b>	OCH(CH <sub>3</sub> ) <sub>2</sub>	0.02 (s)	0.86 (s)	1.14 (d), 3.99 (sep) ( $J = 6.0$ Hz)
<b>5a</b>	OCH <sub>3</sub>	0.10 (s)	0.86 (s)	3.36 (s)
<b>5b</b>	OCH <sub>3</sub>	0.01 (s)	0.85 (s)	3.41 (s)
<b>6a</b>	OC(CH <sub>3</sub> ) <sub>3</sub>	0.13 (s)	0.86 (s)	1.21 (s)
<b>6b</b>	OC(CH <sub>3</sub> ) <sub>3</sub>	0.06 (s)	0.85 (s)	1.26 (s)
<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	0.35 (s)	0.96 (s)	7.63–7.22 (m)
<b>7b</b>	C <sub>6</sub> H <sub>5</sub>	0.26 (s)	0.84 (s)	7.73–7.25 (m)
<b>8a</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	0.27 (s)	0.89 (s)	7.37–7.41 (m)
<b>8b</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	0.12 (s)	0.80 (s)	7.42–7.44 (m)
<b>9a</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	0.22 (s)	0.84 (s)	7.31–7.34 (m)
<b>9b</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	0.09 (s)	0.77 (s)	7.36–7.42 (m)
<b>10a</b>	Si(CH <sub>3</sub> ) <sub>2</sub> H	0.10 (s)	0.84 (s)	0.10 (d), 3.56 (sep) ( $J = 4.5$ Hz)
<b>10b</b>	Si(CH <sub>3</sub> ) <sub>2</sub> H	0.04 (s)	0.84 (s)	0.16 (d), 3.69 (sep) ( $J = 4.5$ Hz)

<sup>a</sup> Nmr spectra were taken as carbon tetrachloride solutions with Varian Associates HA-100 and A60D spectrometers. <sup>b</sup> For the definition of *cis* and *trans*, see ref 5. <sup>c</sup> Isomers were not separated, chemical shifts being determined with a mixture. <sup>d</sup> The chemical-shift value ( $\delta$  3.91) was determined by decoupling. <sup>e</sup> The chemical-shift value ( $\delta$  3.80) was determined by decoupling.

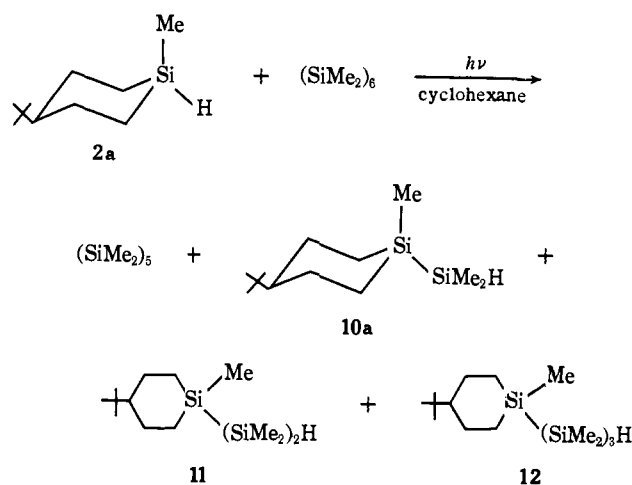
gives rise to a resonance at lower field ( $\delta$  0.12) than the equatorial methyl ( $\delta$  0.07), whereas the axial hydrogen ( $\delta$  3.80) appeared at higher field than the equatorial hydrogen ( $\delta$  3.91). A similar relationship has been observed for cyclohexane derivatives, and many observations show that the chemical shifts of protons in the functional groups attached to six-membered rings are related to their configuration and that these relations afford a reasonable basis for stereochemical assignments.<sup>7</sup> Therefore, the *cis* and *trans* structures listed in Table I were assigned assuming that the compound with a methyl signal appearing at lower field was the *cis* isomer. These assignments were further supported by several reactions. Thus, the stereochemical courses of reactions examined so far resemble exactly those of optically active silicon compounds.<sup>2</sup> Details of these compounds will be reported later with results of X-ray crystallographic analyses of both *cis* and *trans* *p*-bromophenyl derivatives (**8a** and **8b**) now in progress.

These compounds possess some advantages as substrates of the stereochemical study: (a) separation of *cis* and *trans* isomers is relatively easy; (b) the stereochemical course can be monitored by glc and/or nmr; hence each reaction requires only small amounts of reactants; (c) a mixture simply enriched with either of the two isomers can be used satisfactorily; (d) absence of the phenyl or naphthyl group makes some reactions, such as photolysis in the presence of **2**, possible.

In this communication we report the stereochemistry of insertion of photochemically generated dimethylsilylenes into the Si-H bond of **2**. This is one of the

most important problems in connection with the electronic state of silylenes.<sup>8–10</sup>

Irradiation of 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloheptane<sup>9</sup> or dodecamethylcyclohexasilane<sup>11</sup> in hydrosilanes gave insertion products. For example, 0.856 mmol of dodecamethylcyclohexasilane in cyclohexane irradiated with a 160-W low-pressure mercury arc lamp in the presence of 0.773 mmol of **2a** afforded a single mono insertion product (**10a**, 0.197 mmol) with retention of configuration. No *cis*–*trans* isomerization occurred in the recovered **2a** (0.280 mmol). In addition



(8) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(9) H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *ibid.*, **93**, 5272 (1971).

(10) For a pertinent review, see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(11) M. Ishikawa and M. Kumada, *Chem. Commun.*, 612 (1970).

(7) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, Chapters 3–8.

to the mono insertion product, higher homologs including di insertion (**11**, 0.103 mmol) and probably tri insertion products (**12**) were obtained.<sup>12</sup> The configuration of these compounds could not be judged by means of chemical shifts of the methyl protons, but the stepwise mechanism of dimethylsilylene insertion<sup>12</sup> is enough to suggest the same configuration. The trans isomer **2b** also gave **10b** in a similar stereospecific way. It is concluded, therefore, that the insertion of the photochemically generated dimethylsilylene into the Si-H bond took place with retention of configuration, as is also true for the dichlorocarbene.<sup>13</sup>

Results of other stereochemical studies including conformational analyses, homolytic aromatic silylation, and desilylation reactions will be published in forthcoming papers.

**Acknowledgment.** We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

(12) H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 4 (1969).

(13) L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, 90, 4486 (1968).

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### Organometallic Chalcogen Complexes. XXV. Structural and Magnetic Studies of

$\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{S})$ ,  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$ , and the  
Oxidized Monocation,  $[\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2]^+$ .

The Sensitivity of the Geometry of a Triangular  
Metal Cluster System to Antibonding Electrons

Sir:

We wish to present here the results of a stereochemical characterization of three compounds which not only substantiate predictions concerning the dominant influence of antibonding valence electrons on the metal-metal bond lengths of a metal cluster  $\text{M}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{XY}$  system but also provide evidence that its architecture can undergo a drastic Jahn-Teller deformation due to the effect of antibonding electrons. Previous X-ray analyses of  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$ ,<sup>1</sup>  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$ ,<sup>2,3</sup>  $\text{CoNi}_2(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$ ,<sup>3</sup> and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{O})$ <sup>4</sup> showed a basic averaged structure consisting of an equilateral triangle of metal atoms capped above and below by X and Y groups to give a trigonal-bipyramidal  $\text{M}_3\text{XY}$  fragment. With the assumption of cylindrical symmetry for each cyclopentadienyl ring pentahapto-coordinated to a metal atom, an idealized  $D_{3h}$  geometry was discerned when the triply bridging X and Y ligands are identical and an idealized  $C_{3v}$  geometry when the X and Y ligands are different. The prime characteristic of this particular metal cluster system is that with the assumption of electron-pair bonds between each pair of metal atoms the paramagnetic  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  molecule contains *five* electrons in

excess of the closed-shell electronic configuration of each metal atom, the paramagnetic  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  molecule *one* electron over the "magic number" of each nickel atom, and the  $\text{CoNi}_2(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{O})$  molecules a closed-shell electronic configuration for each metal atom. A qualitative LCAO-MO model (based on the nodal character of available metal orbitals and described elsewhere<sup>5</sup> for  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$ ) predicts that the *five* excess electrons in  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  and *one* unpaired electron in  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  occupy primarily the strongly antibonding metal symmetry orbitals essentially localized in the trimetal plane. On the basis that the corresponding bonding and antibonding electron-filled energy levels effectively cancel each other with respect to bonding effects, it follows from this bonding model that the net stabilization of the trimetal system is a consequence of only *one* bonding electron in the  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  molecule and *five* bonding electrons in the  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  molecule compared to *six* bonding electrons (corresponding to electron-pair metal-metal bonds) in the  $\text{CoNi}_2(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{O})$  molecules. The number of antibonding electrons in this localized symmetry-based bonding scheme is compatible with the observed average values of the metal-metal distances: (1) which are unusually long in  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  (2.801 (5) Å) but much shorter in  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  (2.389 (2) Å); (2) which are shorter in  $\text{CoNi}_2(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$  (2.358 (2) Å) than in  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$ ; and (3) which in  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{O})$  (2.365 (4) Å) are analogous with those in  $\text{CoNi}_2(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})_2$ .

The recently reported syntheses of  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{S})$  by Otsuka, Nakamura, and Yoshida<sup>6</sup> appeared to provide a critical test case of whether this apparent correlation of metal-metal bond lengths with the number of "extra" presumably strongly antibonding electrons is a valid one in that (with the reasonable assumption of their configurations being analogous to those of  $\text{Ni}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{O})$ ) the tricobalt disulfide molecule contains *two* electrons in excess of the magic number of each metal atom and the latter molecule *none*. An important bonus to this problem was provided by our subsequent discovery that the tricobalt disulfide molecule could be easily oxidized to give the  $[\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2]^+$  monocation. The resulting structural and magnetic investigations form the subject matter of this communication.

$\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{S})$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  were prepared and isolated according to Otsuka, *et al.*<sup>6-10</sup> In

(5) C. E. Strouse and L. F. Dahl, *ibid.*, 93, 6032 (1971); C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, No. 47, 93 (1969).

(6) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, 7, 261 (1968).

(7) A characterization of  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{S})$  by mass spectral, ir, <sup>1</sup>H nmr, and temperature-dependent magnetic susceptibility studies was reported elsewhere by Otsuka, Nakamura, and Yoshida.<sup>8</sup> From heat capacity measurements of  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  over a 15-270°K range, Sorai, *et al.*,<sup>9</sup> later discovered a crystalline phase transition (192.5°K) whose behavior they interpreted in terms of a cooperative coupling between the librational motion of the cyclopentadienyl rings in the crystalline lattice and the electronic states of the molecule. They also described their anomalous magnetic susceptibility data (which showed a maximum at 215°K) of  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  on the basis of the introduction of temperature-dependent energy parameters and the inversion of spin states at higher temperatures to the phenomenological model derived by Chesnut<sup>10</sup> for magnetic exciton systems. Since our physical measurements of  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_2$  and  $\text{Co}_3(\text{h}^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{S})$  were performed independently, we have outlined

(1) V. A. Uchtman, H. Vahrenkamp, and L. F. Dahl, *J. Amer. Chem. Soc.*, 90, 3272 (1968).

(2) A. A. Hock and O. S. Mills, *Proc. Int. Conf. Coord. Chem.*, 6th, 640 (1961).

(3) V. A. Uchtman and L. F. Dahl, to be published.

(4) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 3763 (1969).