

Two observations are pertinent to the mechanistic elucidation of the 2:1 adduct **3** formation: (1) the cyclobutanone **2** is not converted to **3** by heating with **1** at 75° (18 days in cyclohexane); (2) the reaction of norbornene with **1** in acetonitrile (70°, 20 days) furnishes not **3** but the second, more stable 2:1 adduct **6** in 16% yield along with **2**.

Two pathways for the initial step of **3** formation are conceivable, assuming that an unknown catalyst is not responsible for the conversion $2 + 1 \rightarrow 3$: (a) some zwitterion, **9**, is formed from the reactants in a process which competes with the concerted formation of **2** and **9** cyclizes to **10** which is the σ -complex formed in an electrophilic aromatic alkylation; (b) as a 1,3-diene, **1** combines with norbornene in a Diels-Alder reaction, and the strain relief of norbornene would favor the formation of the six-membered ring, **10**, rather than the annellation of the four-membered ring in **2**.

Conversion of the σ -complex **10** to the benzene derivative **5** includes a suprafacial 1,3-hydrogen shift which is forbidden by orbital symmetry to be concerted.² The interception of the cyclohexadiene derivative **10** with a second molecule of **1** to form **3** appears to be faster than the intermolecular prototropic shift $10 \rightarrow 5$. In acetonitrile, however, the reaction of **10** does proceed via **5** to the second 2:1 adduct **6**.

We have obtained from **1** and *cis*- β -methylstyrene a 2:1 adduct of a structure corresponding to that of **3**. In contrast to the behavior of the mentioned ketenophiles, the 2:1 adducts of **1** and α -methylstyrene⁷ or 1,1-diphenylethylene⁷⁻⁹ are of the enol ester type, like **6**.

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Optically Active Tris(dithiocarbamato)cobalt(III) Complexes

Sir:

There is considerable current interest in geometrical and optical (inversion) isomerism of tris-chelated transition metal complexes. Essentially two limiting mechanisms have been found in such systems. Isomerism and inversion occur *via* a trigonal bipyramidal transition state for unsymmetrical β -diketonato cobalt(III) complexes¹ while a trigonal prismatic transition state is favored for the corresponding tropolonato complexes.²

The results of recent studies on tris(*N,N*-disubstituted dithiocarbamato)metal(III, IV) complexes, $M^{III}(\text{dtc})_3$ and $M^{IV}(\text{dtc})_3\text{BF}_4$, where $M = \text{Fe(III), Fe(IV), Ru(III), Co(III), and Rh(III)}$, indicate a trigonal prismatic transition state which is achieved by a twisting motion of the trigonal antiprismatic reactant around the C_3

(1) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 5319 (1970).

(2) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972); (b) S. S. Eaton and R. H. Holm, *ibid.*, 93, 4913 (1971).

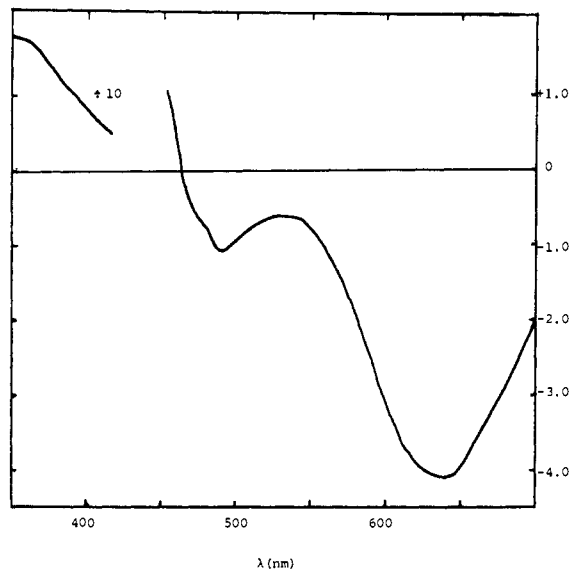


Figure 1. CD spectrum of $(+)_{546}\text{Co}(\text{Ph}_2\text{dtc})_3$.

axis. The rates of metal centered inversion ($\Delta \rightleftharpoons \Lambda$) have been shown to be strongly metal dependent.³

To date all inversion studies on the dithiocarbamate complexes have involved pmr line-shape analysis on racemic species containing diastereotopic groups which are used as a probe for the inversion reaction.³

The partial resolution of tris(*N-p*-hydroxyphenyl-*N*-methylthiocarbamate)cobalt(III) by preferential absorption of enantiomers on a starch substrate has been described. The compound was reported to racemize in 4 days at room temperature, but no thermodynamic parameters were detailed.⁴ We wish to report a general method for the preparation of optically active $\text{Co}^{III}(\text{dtc})_3$ complexes by a facile ligand exchange reaction between optically active $\text{K}[\text{CoEDTA}]$ or $\text{K}[\text{CoPDTA}]$ ⁵ and the sodium salt of the appropriate dithiocarbamate. Some preliminary details of metal-centered inversion obtained from *direct* polarimetric measurements on the optically active species are also discussed.

In a typical preparation, $\text{Na}[\text{Ph}_2\text{dtc}]$ (0.5 g) in acetone (10 ml) was added to an aqueous solution (10 ml) containing $(+)_{546}\text{-K}[\text{CoEDTA}]$ ⁶ (0.1 g; $[\alpha]_{546} + 980$). The solution was stirred rapidly and, after 10 min, the insoluble green, optically active $(+)_{546}\text{-Co}(\text{Ph}_2\text{dtc})_3$ ($[\alpha]_{546} + 1480^\circ$) was collected by filtration and washed thoroughly with water. The CD spectrum of the compound in toluene solution is shown in Figure 1.

The following $\text{Co}(\text{R,R-dtc})_3$ compounds have also been obtained in optically active form using this method: $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Bu, } i\text{-Bu, Bz, cych, pyr, pip}$. Full details of the preparations and optical activity studies including assignment of absolute configurations will be reported later.^{7,8}

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(5) Abbreviations used in this paper are: EDTA, ethylenediaminetetraacetic acid; PDTA, 1,2-propanediaminetetraacetic acid; R,R-dtc, *N,N*-disubstituted dithiocarbamate where $\text{R} = \text{Me, methyl; Et, ethyl; } i\text{-Pr, isopropyl; } n\text{-Bu, } n\text{-butyl; } i\text{-Bu, isobutyl; Ph, phenyl; Bz, benzyl; cych, cyclohexyl; R,R} = \text{pyr, pyrrolidyl; R,R} = \text{pip, piperidyl}$.

(6) F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, 2, 192 (1960).

(7) L. R. Gahan, J. G. Hughes, and M. J. O'Connor, investigations in progress. The reaction of optically active $\text{K}[\text{CoPDTA}]$ with excess

The optical inversion of $(+)_546\text{-Co}(\text{pyr-dtc})_3$ in chloroform solution has been studied over a temperature range (30–50°) by following the loss of optical activity by polarimetry at 546 nm. The thermodynamic data obtained were as follows: E_a , 24.0 ± 2.1 kcal/mol; ΔH^\ddagger , 23.4 ± 2.1 kcal/mol; ΔG^\ddagger , 23.7 ± 4.2 kcal/mol; ΔS^\ddagger , -0.8 ± 7.0 eu; A , 4.06×10^{12} sec $^{-1}$; k_{25° , 1.01×10^{-5} sec $^{-1}$. The near-zero entropy of activation is typical of the value previously found for a trigonal twist mechanism.³

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ethylenediamine leads to the stereospecific formation of the tris(ethylenediamine)cobalt(III) ion. The reaction with K[CoPDTA] described in the present paper appears not to be stereospecific since in a number of preparations the optical activity of the product is lower than that obtained using K[CoEDTA].⁸

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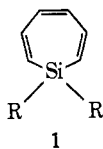
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Synthesis of

1,1-Dimethyl-2,7-diphenyl-1-silacyclohepta-2,4,6-triene. A Nonannulated Silepin

Sir:

Despite considerable activity in the area of heterocycloheptatrienes,¹ there have been no substantiated² reports of nonannulated³ silacycloheptatrienes, silepins (**1**), to date. Aside from the usual desire to study the



properties of a new ring system, interest in **1** is derived from its possible role as a precursor to the unknown¹¹

(1) For an excellent review of the syntheses and chemistry of azepines, oxepines, and thiepins, see L. A. Paquette in "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1970, pp 249–310.

(2) A hexaphenyldicarbomethoxysilepin structure has been tentatively suggested for the product from ethanol induced decomposition of a 7-silanorbornadiene: H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 5584 (1964).

(3) Annulated silepins known are the benzo[*d*]silepin,^{4,5} the dibenzo[*b,f*]silepin,^{6,7,8} and the tribenzo[*b,d,f*]silepin.^{9,10}

(4) L. Birkofer and H. Haddad, *Chem. Ber.*, **102**, 432 (1969); **105**, 2101 (1972).

(5) L. Birkofer, H. Haddad, and H. Zamarlik, *J. Organometal. Chem.*, **25**, C57 (1970).

(6) J. Y. Corey, M. Deuber, and B. Bichlmeir, *J. Organometal. Chem.*, **26**, 167 (1971).

(7) F. K. Cartledge and P. D. Mollere, *J. Organometal. Chem.*, **26**, 175 (1971).

(8) T. J. Barton, W. E. Volz, and J. L. Johnson, *J. Org. Chem.*, **36**, 3365 (1971).

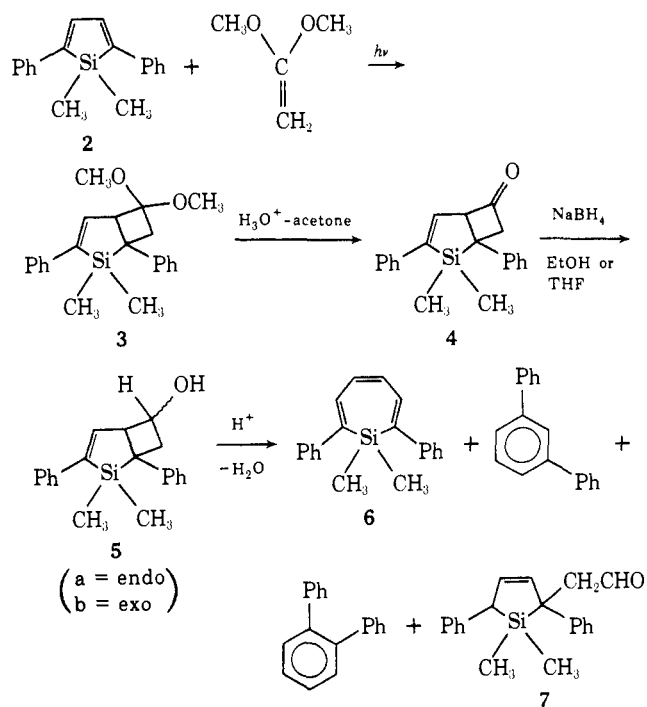
(9) K. A. Andrianov, L. M. Volkova, N. V. Delazari, and N. A. Chumaeski, *Khim. Geterotskil. Soedin.*, 435 (1967); *Chem. Abstr.*, **67**, 10869c (1967).

(10) J. Y. Corey and E. R. Corey, *Tetrahedron Lett.*, 4669 (1972).

(11) An exception to this is the frequent and abundant observation of $R_3\text{Si}^+$ in the mass spectra of various organosilanes.

silylenium ion ($R_3\text{Si}^+$) and as a model system in which to search for cyclic (p-d-p) π conjugation.¹²

Our synthesis starts with the photoaddition of 1,1-dimethoxyethylene to the readily available¹³ 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (**2**). Although plagued by the photolability of **2**,¹⁴ irradiation (N_2 , medium-pressure 450-W Hg arc through Pyrex) of **2** dissolved in 1,1-dimethoxyethylene (ca. 1 g/60 ml) affords ketal (**3**) in 70% yield (mp 86.5–87.5°; nmr¹⁵ (DCCl_3) δ 7.30–6.80 (m, 11 H), 3.70 (d, 1 H, $J = 3.5$ Hz), 3.09 (s, 6 H), 2.74 and 2.42 (AB, 2 H, $J = 12$ Hz), 0.41 (s, 3 H), -0.21 (s, 3 H)).¹⁶ Hydrolysis of **3** was effected with slightly acidic aqueous acetone to yield ketone **4** in 72% yield (mp 72–73°; nmr¹⁵ (CCl_4) δ 7.28–6.90 (m, 10 H), 6.86 (d, 2 H, $J = 4$ Hz), 4.49 (m, 1 H), 3.61 (d of d, 1 H, $J = 11$ and 2 Hz), 3.35 (d of d, 1 H, $J = 11$ and 1 Hz), 0.40 (s, 3 H), -0.11 (s, 3 H); ir $\nu_{\text{C=O}}$ (neat) 1785 cm^{-1}).¹⁶ Sodium borohydride reduction of **4** provided **5** as a ca. 1:1 epimeric mixture of alcohols in 52% yield. Tedious fractional recrystallization afforded pure endo alcohol (**5a**) (mp 115–116°; nmr¹⁵ (DCCl_3) δ 6.98–7.50 (m, 10 H), 6.94 (d, 1 H), 4.49 (br s, 1 H), 3.98 (d of d of d (apparent d of t), 1 H, $J = 2.5, 3,$ and 8.5 Hz), 2.82 (d of d of d, 1 H, $J = 12, 2.5,$ and 7.5 Hz), 2.43 (d of d, 1 H, $J = 7.5$ and 12 Hz), 1.82 (br s, 1 H, exchanges with D_2O), 0.42 (s, 3 H), -0.17 (s, 3 H)).¹⁶ The exo alcohol (**5b**) has not been obtained in pure form but has been completely characterized as the *p*-nitrobenzoate derivative.



The most successful method for dehydration of **5a** has been with a catalytic amount of *p*-toluenesulfonic

(12) An excellent, detailed discussion of (pd) π cyclic conjugation is provided by G. Hafelinger, *Fortschr. Chem., Forsch.*, **28**, 1 (1972).

(13) T. J. Barton and E. E. Gottsman, *Syn. Inorg. Metal-Org. Chem.*, **3**, 201 (1973).

(14) T. J. Barton and A. J. Nelson, *Tetrahedron Lett.*, 5037 (1969).

(15) Extensive discussion of the nmr spectra and mechanistic speculation is deferred to the complete manuscript.

(16) All new compounds reported here with the exception of **7** gave satisfactory elemental (C and H) analysis and consistent ir, nmr, and mass spectra. Aldehyde **7** was unstable, did not give reproducible values, and was characterized solely from spectral data.