to the mono insertion product, higher homologs including di insertion (**11**, 0.103 mmol) and probably tri insertion products (**12**) were obtained.[12] 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[12] 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.[13]

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.

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

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Received March 2, 1972

Organometallic Chalcogen Complexes. XXV. Structural and Magnetic Studies of $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, $Co_3(h^5\text{-}C_5H_5)_3S_2$, and the Oxidized Monocation, $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$. 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 $M_3(h^5\text{-}C_5H_5)_3XY$ 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 $Ni_3(h^5\text{-}C_5H_5)_3S_2$,[1] $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$,[2,3] $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$,[3] and $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$[4] 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 M_3XY 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 $Ni_3(h^5\text{-}C_5H_5)_3S_2$ molecule contains *five* electrons in excess of the closed-shell electronic configuration of each metal atom, the paramagnetic $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ molecule *one* electron over the "magic number" of each nickel atom, and the $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$ 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[5] for $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$)) predicts that the *five* excess electrons in $Ni_3(h^5\text{-}C_5H_5)_3S_2$ and *one* unpaired electron in $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ 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 $Ni_3(h^5\text{-}C_5H_5)_3S_2$ molecule and *five* bonding electrons in the $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ molecule compared to *six* bonding electrons (corresponding to electron-pair metal–metal bonds) in the $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$ 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 $Ni_3(h^5\text{-}C_5H_5)_3S_2$ (2.801 (5) Å) but much shorter in $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ (2.389 (2) Å); (2) which are shorter in $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$ (2.358 (2) Å) than in $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$; and (3) which in $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$ (2.365 (4) Å) are analogous with those in $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$.

The recently reported syntheses of $Co_3(h^5\text{-}C_5H_5)_3S_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ by Otsuka, Nakamura, and Yoshida[6] 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 $Ni_3(h^5\text{-}C_5H_5)_3S_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$) 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 $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation. The resulting structural and magnetic investigations form the subject matter of this communication.

$Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ and $Co_3(h^5\text{-}C_5H_5)_3S_2$ were prepared and isolated according to Otsuka, *et al.*[6–10] In

(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).

(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 $Co_3(h^5\text{-}C_5H_5)_3S_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ by mass spectral, ir, ^1H nmr, and temperature-dependent magnetic susceptibility studies was reported elsewhere by Otsuka, Nakamura, and Yoshida.[8] From heat capacity measurements of $Co_3(h^5\text{-}C_5H_5)_3S_2$ over a 15–270°K range, Sorai, *et al.*,[9] 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 $Co_3(h^5\text{-}C_5H_5)_3S_2$ 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[10] for magnetic exciton systems. Since our physical measurements of $Co_3(h^5\text{-}C_5H_5)_3S_2$ and $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ were performed independently, we have outlined

contrast to the diamagnetic $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, the tricobalt disulfide complex is paramagnetic at room temperature with $\mu_{eff} = 2.83$ BM[11] (characteristic of two unpaired electrons in the absence of orbital contributions). The cyclopentadienyl ^1H nmr resonance observed in carbon disulfide solution from 163 to 324°K indicated diamagnetism below 173°K where a sharp singlet at τ 5.33 was observed (*cf.* $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, τ 5.35 at ambient room temperature), but at temperatures greater than 173°K a paramagnetic shift was observed which considerably broadened the signal and moved it monotonically to higher field with increasing temperature.[12,13] Bulk susceptibility data measured[11] from 98 to 340°K exhibited Curie–Weiss law behavior at temperatures greater than 195°K, but at $T_N = 195$°K an abrupt discontinuity was observed such that $\chi_{M'}$ dropped to approximately one-half its maximum value within a 30° temperature range. A recent calorimetric study of $Co_3(h^5\text{-}C_5H_5)_3S_2$ by Sorai and coworkers[9] showed that a phase transition occurs at 192.5°K. The complementary magnetic data in solid state and in solution as well as the abnormally high transition entropy[9] provide conclusive evidence that this phase transition must be coupled with a change in spin states as a function of temperature. The Chesnut exciton theory[10] has provided a good model (modified by us only through inclusion of a TIP term) for our bulk susceptibility data of $Co_3(h^5\text{-}C_5H_5)_3S_2$.

$[Co_3(h^5\text{-}C_5H_5)_3S_2]^+I^-$ was prepared by the stoichiometric addition of I_2 to the neutral complex and was purified by repeated recrystallizations from acetonitrile. This ionic compound was analyzed by ir, solution conductivity, esr, and bulk susceptibility measurements. Esr studies both in CH_2Cl_2 solution and in polycrystalline form showed a broad resonance signal centered at $g = 2.05$ with no fine structure. Temperature-dependent susceptibility measurements[11] indicated that the cation is a simple paramagnet; for the iodide salt the effective magnetic moment was found to decrease linearly from 1.95 BM at 297°K to 1.77 BM at 83°K.[14]

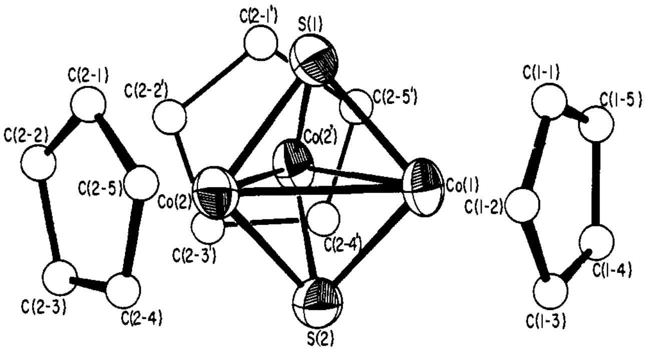

Figure 1. The $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation of the I^- salt. The monocation of idealized C_{2v}-2*mm* geometry has crystallographic site symmetry C_s-*m*.

Single-crystal X-ray diffraction investigations[15–18] revealed the following prominent structural features: (1) with the assumption of cylindrical symmetry for each cyclopentadienyl ring, the $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ molecule has an averaged C_{3v} geometry with three equivalent Co–Co distances of 2.452 (2) Å; (2) the $Co_3(h^5\text{-}C_5H_5)_3S_2$ molecule possesses an averaged D_{3h} geometry with three equivalent Co–Co distances of 2.687 (3) Å; (3) the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation (Figure 1) is significantly deformed to a C_{2v} geometry

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them in this communication. It is also noteworthy that our MO scheme used to rationalize the magnetic and X-ray data differs from that proposed by the Japanese workers[9] to account for their experimental results.

(8) S. Otsuka, A. Nakamura, and T. Yoshida, *Justus Liebigs Ann. Chem.*, **719**, 54 (1968).

(9) M. Sorai, A. Kosaki, H. Suga, S. Seki, T. Yoshida, and S. Otsuka, *Bull. Chem. Soc. Jap.*, **44**, 2364 (1971).

(10) D. B. Chesnut, *J. Chem. Phys.*, 40, 405 (1964).

(11) The magnetic susceptibility measurements were kindly performed initially by Dr. Michael Camp and later by Mr. James Kleppinger at the University of Wisconsin *via* the Faraday method.

(12) Three distinct regions of paramagnetic-shift dependence within the temperature range of 163–324°K can be differentiated: (1) a Curie range ($S \cong 1$) for $T \geq 260$°K where the paramagnetic shift varies linearly with $1/T$; (2) a region for $T \leq 173$°K where with temperature change the shift is zero which is characteristic of a diamagnetic species ($S = 0$); (3) an intermediate non-Curie region for $173 < T < 260$°K where an equilibrium exists between a singlet and triplet species. On the basis of the inherent assumptions that the equilibrium interconversion between the two species occurs at a sufficient rate such that the observed shifts are averaged over both species and that dipolar contributions (which presumbly are small due to the relative isotropy of the g values, *viz.*, $g_{||} \approx g_{\perp}$) to the shifts are essentially invariant to the nondrastic change in geometry, the dipolar term can be combined with the isotropic hyperfine contact term to give the equation $(\Delta H_i/\Delta H_0) = K[S/(S+1)/3][\exp(\Delta G/RT) + 1]^{-1}T^{-1}$, where K is a constant.[13] However, a least-squares analysis of this simple model did not fit the observed shifts in the non-Curie region; a much better fit to the observed data was obtained for an analogous empirical model for which a temperature dependence was introduced into the energy separation between the singlet and triplet states (*i.e.*, consistent with the premise that ΔG is a function of temperature).

(13) For an excellent review of the application of nmr paramagnetic shifts to an investigation of structures and structural equilibria of metal complexes, see R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

(14) The magnetic susceptibility of the corresponding SbF_6^- salt, containing a similarly distorted $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation (B. K. Teo, P. D. Frisch, and L. F. Dahl, to be published), also obeyed the Curie–Weiss law and gave a magnetic moment of $\mu_{eff} = 1.84$ BM at 272°K; this value remained unchanged within 0.02 BM over a temperature range from 272 to 83°K.

(15) $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$: hexagonal with $a = b = 9.184$ (1) Å, $c = 10.639$ (2) Å; $\rho_{obsd} = 1.88$ g cm^{-3} *vs.* $\rho_{calcd} = 1.85$ g cm^{-3} ($Z = 2$). $Co_3(h^5\text{-}C_5H_5)_3S_2$: hexagonal with $a = b = 9.417$ (1) Å, $c = 10.117$ (2) Å; $\rho_{obsd} = 1.88$ g cm^{-3} *vs.* $\rho_{calcd} = 1.86$ cm^{-3} ($Z = 2$). The structures of $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, which appears isomorphous with $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$, and $Co_3(h_5\text{-}C_5H_5)_3S_2$, which appears isomorphous with $Ni_3(h^5\text{-}C_5H_5)_3S_2$, were solved by the application of the Wei procedure[16] based on an incoherent twinning mechanism involving a single-crystal component of above unit cell dimensions and of symmetry $P6_3/m$. This space group requires the $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ and $Co_3(h^5\text{-}C_5H_5)_3S_2$ molecules to possess crystallographic site symmetry C_{3h}-3/*m* which necessitates for the $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ molecule that the sulfur and carbonyl ligands are disordered into each other. Our crystal model additionally assumes that each cyclopentadienyl ring possesses a twofold orientational disorder of half-weighted atoms such that the crystallographic site symmetry for each molecule of $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ and $Co_3(h^5\text{-}C_5H_5)_3S_2$ is increased to D_{3h}-$\bar{6}2m$. Anisotropic least-squares refinements of $Co_3(h\text{-}C_5H_5)_3(CO)(S)$ (197 independent observed diffractometry data) and $Co_3(h^5\text{-}C_5H_5)_3S_2$ (218 independent observed diffractometry data) converged to values of 6.0 and 10.3%, respectively, for $R_1(F^2)$ and values of 9.3 and 10.4%, respectively, for $R_2(F^2)$. No significant changes in Co–Co distances (*i.e.*, <0.002 Å) were observed on prior least-squares refinement from a completely isotropic thermal model (with data-to-parameter ratios of 11.5/1.0 for the tricobalt disulfur complex and 9.4/1.0 for the tricobalt sulfur–carbonyl complex) *vs.* the abovementioned refinements from a mixed anisotropic–isotropic thermal model (with data-to-parameter ratios of 5.2/1.0 for the tricobalt disulfur complex and 4.5/1.0 for the tricobalt sulfur–carbonyl complex). Attempted refinement under $P6_3$ symmetry of an ordered structure for $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ was not successful.

(16) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).

(17) $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+I^-$: monoclinic; $C2/m$; $a = 17.615$ (3) Å, $b = 9.930$ (2) Å, $c = 10.489$ (1) Å, $\beta = 107.77$ (1)°; $\rho_{obsd} = 2.14$ g cm^{-3} *vs.* $\rho_{calcd} = 2.12$ g cm^{-3} for $Z = 4$. Least-squares refinement gave $R_1(F) = 3.9\%$ and $R_2(F) = 5.5\%$ for 1322 independent observed diffractometry data.

(18) For computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-5082. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

with one short Co–Co distance of 2.474 (2) Å and two long Co–Co distances of 2.649 (1) Å resulting in an averaged value of 2.591 Å. The shorter Co–Co distance compares favorably with those in $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, while the two longer distances are similar to those in $Co_3(h^5\text{-}C_5H_5)_3S_2$. All of these variations in metal–metal distances are in complete accord with our bonding model[5] which assumes *no* antibonding electrons for $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, *one* such electron for the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation, and *two* such electrons for $Co_3(h^5\text{-}C_5H_5)_3S_2$. The 0.1-Å longer Co–Co distances in $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ compared to those in the electronically equivalent $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$ may be readily attributed to the influence of the larger triply bridging sulfur ligand.

The nontrivial singlet–triplet equilibrium indicated from the temperature-dependent magnetic measurements of $Co_3(h^5\text{-}C_5H_5)_3S_2$ together with the structural information that $Co_3(h^5\text{-}C_5H_5)_3S_2$ shows no detectable distortion of the Co_3S_2 fragment from D_{3h} geometry[19] at room temperature in contradistinction to the large C_{2v} deformation of this fragment in the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation illuminates a key point with regard to the electronic structures of these complexes. For $Co_3(h^5\text{-}C_5H_5)_3S_2$ the nmr paramagnetic shift data, which strongly indicate that the singlet–triplet energy separation in the non-Curie region is temperature dependent, may be rationalized on the basis that at $T > 260°$ the triplet state arising from double occupancy of a doublet degenerate level is more likely the ground state than one arising from occupancy of two close-lying energy levels (with one level nondegenerate and the other degenerate).[20] On the other hand, at $T < 260°K$ the observed nmr solution data can be explained in terms of two close-lying levels of which the lowest one is nondegenerate. This situation may arise if the antibonding $1a'_2$ level[5] is assumed to be lower in energy and therefore fully occupied at $T < 173°K$. With an increase in temperature the $1a'_2$ level is then presumed to be destabilized relative to the antibonding $3e'$ one[5] such that a crossover occurs to give the $3e'$ level as the occupied lower one at room temperature.[21] The solid-state magnetic data, whose interpretation is complicated by the observed phase transition,[7,9] are consistent with these bonding hypotheses. We feel (in harmony with Sorai, *et al.*[9]) that the change in electronic structure may be primarily a consequence of the metal–cyclopentadienyl interactions due to a vibronic effect caused by more restricted ligand motion at lower temperatures. The C_{2v} geometry of the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation may be explained by a Jahn–Teller splitting of a doublet ^2E ground state (which presumably would occur for a symmetrical triangular tricobalt cluster system. The unpaired electron would cause the $3e'$ (under D_{3h}) to break down into $a_1 + b_2$ (under C_{2v}), but it is not possible to predict which nondegenerate energy level is lower and hence the directional nature of the geometrical deformation. The observed one short and two long Co–Co distances are compatible with the unpaired electron occupying the a_1 orbital. This work will be reported in full upon completion of closely related studies which have included the preparation and structural characterization of $Rh_3(h^5\text{-}C_5H_5)_3(CO)(S)$, a complex which is isosteric with its electronically equivalent cobalt analog.

Acknowledgment. These investigations were made possible by the financial support of the National Science Foundation (No. GP-19175X). The use of the UNIVAC 1108 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of NSF and the Wisconsin Alumni Research Foundation administered through the University Research Committee. We also express special thanks to Mr. Boon Keng Teo at the University of Wisconsin, to Dr. C. H. Wei at Oak Ridge National Laboratory (Biology Division), and to Dr. H. Vahrenkamp at the Institut für Anorganische Chemie der Universität München for helpful consultations.

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[19] For all $P6_3/m$ twinned structures,[1,4] a significant distortion from D_{3h} (or C_{3v}) symmetry may be undetected due to the twinning as well as the added possibility of a threefold crystal disorder of an unsymmetrical metal triangle. For this reason we stress that the averaged geometry is D_{3h} (or C_{3v}). However, the thermal ellipsoids of the metal atoms in $Co_3(h^5\text{-}C_5H_5)_3S_2$ did not give an indication of either any distortion or crystalline disorder.

[20] A Jahn–Teller distortion of the molecule would be anticipated for such an electronic configuration (*e.g.*, the antibonding $1a'_2$ energy level being slightly lower than the antibonding $3e'$ one).

[21] Another possibility is that the $3e'$ level is lower, but the degeneracy is broken due to some unknown and structurally nondetectable change in the $Co_3(h^5\text{-}C_5H_5)_3S_2$ molecule from threefold symmetry (presumably involving the cyclopentadienyl rings and/or the Co_3S_2 cluster fragment).

Carbon-13 Spectra of Allenes

Sir:

As a result of technical advances carbon-13 nmr has finally begun to achieve its obvious place as a convenient and powerful tool for the elucidation of organic structures[1] and the probing of ground-state electronic distributions of molecules.[2] The unusual bonding situation in the allene functionality has prompted us to undertake a systematic study of this class of compounds.[3,4] Determination of the spectra[5] of over 50 allenes has provided data which show definite chemical-shift trends as a function of substitution. Moreover, these trends are correlated with theoretical calculations of electron density. Representative carbon-13 nmr chemical shifts for allenes with simple alkyl substituents are given in Table I.

In general, for allenes bonded to nonfunctionalized carbon, the sp-hybridized carbons are found in the sparsely populated region at lower field than CS_2 (−20 to −5 ppm) whereas the sp² carbons appear at slightly

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[1] (a) E. F. Mooney and P. H. Winson, *Annu. Rev. Nucl. Magn. Resonance Spectrosc.*, **2**, 153 (1969); (b) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

[2] Examination of electronic environments in aromatic compounds by carbon-13 nmr has been quite successful. See, for instance, R. J. Pugmire, M. J. Robins, D. M. Grant, and R. K. Robins, *J. Amer. Chem. Soc.*, **93**, 1887 (1971), and references therein.

[3] (a) R. A. Friedel and L. Retcofsky, *ibid.*, **85**, 1300 (1963); (b) R. Steur, J. P. C. M. van Dougen, M. J. A. de Bie, and W. Drenth, *Tetrahedron Lett.*, 3307 (1971).

[4] W. W. Conover, J. K. Crandall, and S. A. Sojka, paper presented at the International Symposium on Acetylenes, Allenes, and Cumulenes, Nottingham, England, July 5–8, 1971.

[5] Spectra were obtained by using equipment previously described: A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. T. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971).