Acknowledgment. The research of H.J.S. and J.A.P. was supported by the National Science Foundation (Grant CHE-8417548), the Charles and Johanna Busch Fund–Rutgers University, and a crystallographic instrumentation grant from the National Institutes of Health (Grant 1510 RRO 1486 01A1). The research of K.K.-J. was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (Grant GM 34111).

Supplementary Material Available: Tables of crystal and refinement data and lists of atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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Laser Spectroscopy of Calcium and Strontium Monocyclopentadienide

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Received April 22, 1986

The gas-phase reaction of Ca or Sr vapors with cyclopentadiene has resulted in the laser spectroscopic observation of the metal monocyclopentadienide free radicals, CaCp and SrCp (Cp = C_5H_5). The spectra are interpreted as arising from "open-faced sandwich" complexes of C_{5v} symmetry. Our experimental methods have general utility for the synthesis and characterization of inorganic free radicals.

The cyclopentadienyl ligand is one of the popular and fascinating ligands in inorganic chemistry.[1] The most celebrated molecule containing Cp is ferrocene, $Fe(Cp)_2$, which has a "sandwich" structure.[1] The alkali metals and the heavier alkaline-earth metals form ionic complexes with C_5H_5.[2-5] InCp[6] and TlCp[7] have C_{5v} symmetry in the gas phase. InCp and TlCp are the covalent closed-shell analogues of the ionic free radicals, Ca^+Cp^- and Sr^+Cp^-, that we have discovered.

We have recently observed a large number of Ca-, Sr-, and Ba-containing free radicals with only one ligand, ML (L = OH,[8-11] OCH_3, OCH_2CH_3, $OCH(CH_3)_2$, $O(CH_2)_2CH_3$, $OC(CH_3)_3$,[12] OCN,[13] CHO_2, CH_3CO_2[14,15]). The bonding and electronic structure in these molecules is well described by an M^+ ion perturbed by the L^- ligand. The M^+ ions are isoelectronic with the alkali atoms so the molecular states can be described in terms of one-electron metal-centered atomic orbitals.

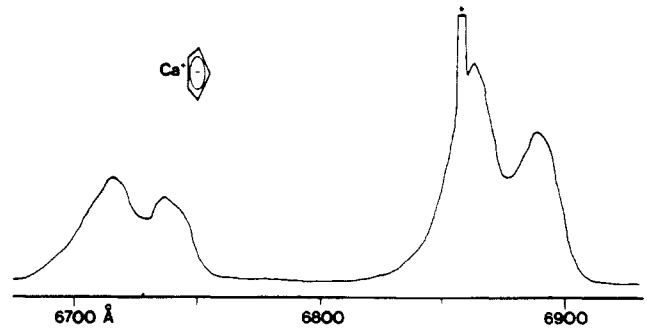

Figure 1. Resolved fluorescence spectrum showing laser-induced fluorescence from the $\tilde{A}$–$\tilde{X}$ transition of CaCp. The splitting between the strong features is due to spin–orbit coupling in the $\tilde{A}^2E_1$ state. The asterisk marks scattered light from the dye laser exciting the molecular transition.

Table I. $\tilde{A}$–$\tilde{X}$ and $\tilde{B}$–$\tilde{X}$ Vibronic Transition Frequencies for CaCp and SrCp in cm^{-1}

	CaCp			SrCp		
band	$\tilde{A}^2E_{1(1/2)}$	$\tilde{A}^2E_{1(3/2)}$	$\tilde{B}^2A_1$	$\tilde{A}^2E_{1(1/2)}$	$\tilde{A}^2E_{1(3/2)}$	$\tilde{B}^2A_1$
3–0	15 495	15 548		14 014[a]	14 300	
2–0	15 170	15 226		13 763[a]	14 039	
1–0	14 848	14 897	17 072	13 510[a]	13 782	15 106
0–0	14 518	14 575	16 772	13 268	13 523	14 846
0–1	14 237	14 282	16 470	13 040	13 289[a]	14 616
0–2	13 955	14 002		12 822	13 053[a]	
0–3	13 690	13 739				
0–4	13 458[a]	13 505[a]				

[a] Blended.

For the Cp^- ligand the ground 4s (Ca^+) or 5s (Sr^+) atomic orbital gives rise to the $\tilde{X}^2A_1$ ground state of MCp. The excited 3d (Ca^+) and 4d (Sr^+) atomic orbitals result in d_{z^2} ($^2A_1$); d_{xz}, d_{yz} ($^2E_1$); and d_{xy}, $d_{x^2-y^2}$ ($^2E_2$) states. The expected electronic transitions are $\tilde{B}^2A_1$–$\tilde{X}^2A_1$ and $\tilde{A}^2E_1$–$\tilde{X}^2A_1$. ($^2E_2$–$^2A_1$ is electric-dipole forbidden.) In fact, the $\tilde{B}^2A_1$ and $\tilde{A}^2E_1$ states are $3d_{z^2}$–$4p_z$ (Ca^+) and $4d_{z^2}$–$5p_z$ (Sr^+) mixtures because of d–p mixing induced by the C_{5v} ligand field.

MCp (M = Ca, Sr) molecules were produced in a Broida oven[16] by the reaction of the alkaline earth vapor with cyclopentadiene (C_5H_6). Pressures were approximately 1.5 torr of argon and 3 mtorr of cyclopentadiene. The cyclopentadiene was prepared from the Diels–Alder dimer by a simple distillation. The direct reaction of the dimer with Ca vapor was not successful.

A broad-band (1 cm^{-1}) CW dye laser beam was focused into the Broida oven in order to excite the molecular emission. A second broad-band (1 cm^{-1}) dye laser beam was always used to excite the alkaline earth $^3P_1$–$^1S_0$ atomic transition (6892 Å for Sr, 6573 Å for Ca). The reaction was greatly enhanced by electronic excitation of the metal. Two types of experiments were used to record the spectra.

Laser excitation spectra were obtained by scanning the dye laser probing the molecular transitions, and recording the fluorescence through red-pass filters selected to block the scattered laser light. The second dye laser, resonant with the metal atomic line, was chopped to modulate the molecular fluorescence for lock-in detection.

Spectra were also recorded by exciting the molecular emission and recording the resolved fluorescence with a monochromator. For these experiments the molecular emission was imaged onto the entrance slit of a 0.64-m monochromator. Scanning the monochromator (not the laser) provided resolved laser-induced fluorescence spectra.

Figure 1 is a portion of the $\tilde{A}^2E_1$–$\tilde{X}^2A_1$ spectrum of CaCp. This spectrum was recorded by resolving the fluorescence produced by a laser (marked with an asterisk) exciting the $\tilde{A}^2E_{1(3/2)}$–$\tilde{X}^2A_1$

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Table II. Vibrational Frequencies for CaCp and SrCp in cm^{-1}

state	CaCp	SrCp
$\tilde{X}^2A_1$	312[a]	223
$\tilde{A}^2E_1$	325	259
$\tilde{B}^2A_1$	300	260

[a] $\omega_e x_e = 8.9\ cm^{-1}$.

transition of the 0–0 (v'–v'') vibrational band. The partially resolved peak to the right is the 0–0 $\tilde{A}^2E_{1(1/2)}$–$\tilde{X}^2A_1$ transition. The pair of features between 6700 and 6750 Å correspond to the two spin components of the $\tilde{A}$ state in the $v' = 1$ level of the 1–0 transition. Only one mode is Franck–Condon active, and sequence structure was not resolved. The unequal intensities of the two spin components is due to incomplete collisional relaxation. In the laser excitation spectrum these two features have the same intensity, as expected for two spin components. If the $\tilde{A}^2E_{1(1/2)}$ component is excited then the intensity of the $^2E_{1(1/2)}$ spin components is enhanced. Thus, at our pressure of 1–2 torr there is some evidence of resonance fluorescence. The major part of the observed emission is produced by collisional relaxation, accounting for the observation of the 2–0 and 1–0 bands when the 0–0 band is pumped. This collisional redistribution of population in the excited electronic state is observed for all of the larger radicals[13] that we have prepared.

The corresponding spectra of the $\tilde{A}^2E_1$–$\tilde{X}^2A_1$ and $\tilde{B}^2A_1$–$\tilde{X}^2A_1$ transitions of SrCp were also observed. For SrCp the vibrational frequency accidentally matches the spin–orbit splitting so the vibrational and spin–orbit structures are overlapped. For example, the $^2E_{1(3/2)}$–$^2A_1$ 0–0 band overlaps the $^2E_{1(1/2)}$–$^2A_1$ 1–0 band at 7262 Å. The centers of the observed CaCp and SrCp bands are provided in Table I for both the $\tilde{B}$–$\tilde{X}$ and $\tilde{A}$–$\tilde{X}$ transitions.

The attribution of our spectra to CaCp and SrCp and the spectral assignments rest on the close similarily with the alkaline-earth monohalide, monohydroxide,[8-11] and monoalkoxide[12,13] spectra. The observed $\tilde{A}^2E_1$ spin–orbit splittings are 55 ± 5 cm^{-1} (CaCp) and 258 ± 5 cm^{-1} (SrCp) compared to 67 cm^{-1} for CaOH[9] and 264 cm^{-1} for SrOH.[10] The presence of five off-axis carbons and hydrogens hardly quenches the spin–orbit coupling and there is no evidence of a Jahn–Teller effect. This is probably because the molecular orbital for the $\tilde{A}^2E_1$ state (like the alkaline earth monohalide A state[17-19]) is polarized away from the ring so that the unpaired electron is separated from the Cp^- ring by the M^{2+} core.

The strongest features in the $\tilde{A}$–$\tilde{X}$ and $\tilde{B}$–$\tilde{X}$ transitions were attributed to the 0–0 vibrational band because of Franck–Condon arguments. The observed vibrational frequencies (ω_e's) are listed in Table II with estimated ±5-cm^{-1} errors. For the other alkaline-earth derivatives the metal–ligand stretch always had the largest Franck–Condon factor. Therefore we assign the observed mode to the M–Cp stretch of a_1 symmetry. The only possible alternate assignment is to the M–Cp tilt of e_1 symmetry. Since the bend is doubly degenerate only $\Delta v_B = \pm 2$ bands would appear, although a Jahn–Teller effect would allow electronic transitions with $\Delta v_B = \pm 1$.[20]

The techniques we have utilized in the discovery of the CaCp and SrCp molecules are quite general. Any metal can be vaporized by heating or by sputtering in an electrical discharge,[21] and any appropriate oxidant can be added to the system. One laser drives the chemistry by making M* from M while the second laser interrogates the product molecules formed by reaction of M* with the oxidant. It is very likely that many gas-phase metal alkyls, alkoxides, cyanates, cyanides, carboxylates, and cyclopentadienides can be synthesized and identified in this way.

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Acknowledgment. This research was supported by the National Science Foundation (CHE-8306504). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Partial support was also provided by the Office of Naval Research.

Sulfoxide Induced Acceleration and Enhancement of Geometric Selectivity of a [1,5]-Sigmatropic Hydrogen Shift

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Received April 22, 1986

The experimental delineation of the effects of substituents on the stereochemical course and on the rate of pericyclic processes is of utility in synthesis as well as in developing an understanding of the mechanism and theory of these processes. It is the purpose of this paper to describe the profound influence of a sulfoxide moiety, more specifically the phenylsulfinyl group, on the course of the vinylallene variant of the [1,5]-sigmatropic hydrogen shift.[1] The system chosen for study involved the competitive isomerization of vinylallene **1** to the conjugated trienes **2** plus **3** (Scheme I).

In typical initial preparative experiments,[2] a solution of PhSCl (0.28 mmol) in THF (0.25 mL) was added dropwise to a stirred solution of alkenynol **4** (0.25 mmol; prepared by reacting β-cyclocitral with the corresponding acetylide, RC_2Li[3]) and triethylamine (0.5 mmol) in dry THF (1 mL) cooled to −78 °C. After 1 h at −78 °C and 10 h at room temperature followed by workup, the observed products proved to be mainly the rearranged trienes **2a–e** (major) plus **3a–e** (minor) in a ratio which ranged from ~4:1 to >98:2 (63–91%). These triene sulfoxides are formed via the intermediacy of vinylallene **1** (formed via [2,3]-sigmatropic shift[4] of sulfenate ester **5** and isolable by rapid handling at or below room temperature) and these examples to our knowledge constitute the most facile examples of neutral, *acyclic* [1,5]-sigmatropic hydrogen shifts yet recorded. By way of comparison, the hydrocarbon **1g** is undetectably rearranged after 2 days of standing at room temperature; after 9 days it is only 23% rearranged to a mixture of **3g** plus **2g** with significantly lower geometric selectivity (~2:1 ratio).

Preparation of the hydrocarbon vinylallenes **1f** and **1g** and the derivatives **1h** and **1i**, which differ from **1a** only with respect to the oxidation level at sulfur, are shown in Scheme II.

In order to more quantitatively assess the nature of the unprecedented sulfoxide effect, a kinetic investigation of these isomerizations was undertaken. Table I compares the data for the sulfoxides **1a–1e**, with that of the hydrocarbons **1f** and **1g** as well as the phenyl sulfide **1h** and phenyl sulfone **1i**. The following are evident from the data in Table I: (a) The sulfoxide substituent imparts a significant directing group on the trajectory of the [1,5]-hydrogen shift[1a,5] (H favors migration anti to the sulfoxide).

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