dent on the initial concentration c_0 (Figure 2). Therefore, the following relation between the change of λ_{max} and the composition of the isomer mixture can be deduced

$$\Delta\lambda_{max} = \lambda_{max} - \lambda_{max}^0 = q_t c_t + q_c(c_0 - c_t) \quad (2)$$

Using eq 2, the composition of a mixture of the two isomers can be determined. Defining y_c as the fraction of the cis isomer, we find $y_c^{313} = 0.4$ and $y_c^{420} = 0.3$. The corresponding values found by Zimmermann, *et al.*,[13] are $y_c^{313} = 0.8$ and $y_c^{420} = 0.2$. The last value is in reasonable agreement with our result; the first value, however, is much larger. This discrepancy is most probably due to the large band width of our solution filter.

The cholesteric–isotropic transition temperature T_{iso} depends on the composition of the isomer mixture. A pure 35:65 by weight mixture of CC and CN has a transition temperature of 76°. T_{iso} is lowered to 63 and 50° for 0.27 and 0.54 *M* solutions of *cis*-azobenzene, respectively. However, T_{iso} is lowered to 52 and 35° for the corresponding concentrations of the trans isomer.

By dissolving *trans*-stilbene, λ_{max} increases with increasing concentration (q_t = 200 (nm l.)/mol). A shift of λ_{max} to shorter wavelength is observed when a trans–cis isomerization is induced by irradiation with light of λ 313 nm.

By the method described in this paper, selective uv irradiation produced sharp colored images without decomposing the liquid-crystal solvent. The image formation is reversible.

Since the change of *n* by the solute molecules is very small, it must be concluded that the change of the pitch is due to an intrinsic twisting power[10] of the solute molecules which do not have an asymmetric center.

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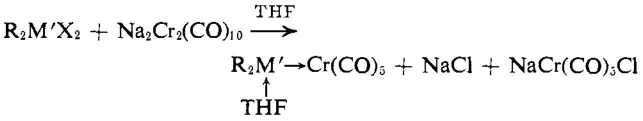
Dialkylgermylene- and -stannylene–Pentacarbonylchromium Complexes

Sir:

A great deal has been learned about chemically interesting, highly reactive molecules by studying their more accessible transition metal complexes.[1] Not only are the chemical and physiochemical properties of the complex informative as to the nature of the highly reactive species, but the complex may also serve as a convenient source for generation of the species. Divalent group IV radicals constitute an area in which there is considerable interest[2] and recently, the coordination compounds of divalent carbon have received much attention.[3] Also, a platinum complex of dichlorosilylene has been reported.[4] We wish to communicate here our synthetic results on pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes,[5] R_2Ge and R_2Sn, and to report some of the more interesting properties of these new complexes. This study represents the first reported synthesis of such coordination compounds.[6] Since these are directly related to pentacarbonylchromium–carbene complexes, which have been subjected to extensive chemical, spectroscopic, and structural examination,[3a,b] they are of special interest for comparative purposes, as part of a homologous series.

The low-temperature (−78°) reaction of $Na_2Cr_2(CO)_{10}$[7] in tetrahydrofuran with dialkylgermanium and -tin dihalides yields pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes.



$$R_2M'X_2 + Na_2Cr_2(CO)_{10} \xrightarrow{\text{THF}} \underset{\underset{\text{THF}}{\uparrow}}{R_2M'}\!\rightarrow Cr(CO)_5 + NaCl + NaCr(CO)_5Cl$$

Ia, R = CH_3; M′ = Ge
b, R = CH_3; M′ = Sn
c, R = t-C_4H_9; M′ = Sn

These complexes are isolated by crystallization from hexane solutions at −78° as extremely air-sensitive, pale-yellow, tetrahydrofuran adducts.[8] All attempts to carry out the reaction in noncoordinating solvents or to remove the tetrahydrofuran without decomposition of the complexes have failed. The approximate order of thermal stability of the complexes is Ic > Ib > Ia; only Ic is stable for any length of time at room temperature, hence it has so far proven the most amenable to complete purification and characterization.[9] *Anal.* Calcd for $C_{17}H_{26}O_6CrSn$: C, 41.07; H, 5.28; Cr, 10.46; mol wt, 497. Found: C, 40.98; H, 5.38; Cr, 11.08; mol wt, 475 (cryoscopic in benzene); pale yellow crystals;[10] mp,

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(1) An elegant example is Pettit's study of cyclobutadiene complexes: P. Reeves, T. Devon, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5890 (1969), and references therein.

(2) (a) P. L. Timms, *Prep. Inorg. React.*, **4**, 59 (1968); (b) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971); (c) J. D. Donaldson, *Progr. Inorg. Chem.*, **8**, 287 (1667); (d) W. H. Atwell and R. D. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969); (e) W. P. Neumann, *ibid.*, **2**, 165 (1963); (f) W. P. Neumann and K. Kühlein, *Justus Liebigs Ann. Chem.*, **683**, 1 (1965), and references therein; (g) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(3) (a) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Muller, and R. D. Fischer, *J. Organometal. Chem.*, **28**, 237 (1971), and references therein; (b) O. S. Mills, *Pure Appl. Chem.*, **20**, 127 (1969); (c) D. J. Cardin, B. Cetinkaya, M. F. Lappert, L. J. Manojlovic-Muir, and K. W. Muir, *Chem. Commun.*, 400 (1971), and references therein; (d) F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971).

(4) G. Schmid and H. J. Balk, *Chem. Ber.*, **103**, 2240 (1970).

(5) We follow the nomenclature rules which have been adopted for divalent silicon.[2d]

(6) A BF_3 adduct of $(h^5\text{-}C_5H_5)_2Sn$ has recently been reported: P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **92**, 2577 (1970).

(7) (a) E. Lindner, H. Behrens, and S. Birkle, *J. Organometal. Chem.*, **15**, 165 (1968); (b) W. C. Kaska, *J. Amer. Chem. Soc.*, **90**, 6340 1968); (c) R. G. Hayter, *ibid.*, **88**, 4376 (1966); (d) this reagent has previously been employed for the synthesis of a carbene complex: K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **7**, 950 (1968).

(8) (a) Reactions with dialkylsilicon dihalides yield only $Cr(CO)_6$ as the final hydrocarbon-soluble metal carbonyl product. Reactions with diarylgermanium and -tin dihalides are considerably more complex and will be discussed at a later date. (b) Contamination by unstable THF–$Cr(CO)_5$[8c,d] considerably complicates purification. (c) W. Strohmeier and K. Gerlach, *Chem. Ber.*, **94**, 398 (1961). (d) T. J. Marks, unpublished results.

(9) (a) In refluxing benzene, Ic reacts with triphenylphosphine to produce $(C_6H_5)_3PCr(CO)_5$. (b) The ^{19}Sn Mössbauer spectrum of Ic (IS = 2.11, QS = 4.14 mm/sec; we thank Professor J. J. Zuckerman for this measurement) is quite unlike spectra of Sn(IV)–transition metal compounds[9c] and will be discussed in detail at a later date. (c) J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 22 (1970). (d) Though we have not yet obtained complete analytical data for less stable Ib and Ia, the great similarity in spectral properties leads us to believe that Ia, Ib, and Ic have essentially the same structures.

(10) An X-ray study is in progress.

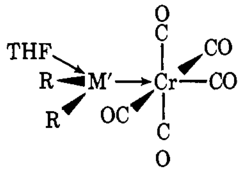
Table I. Spectroscopic Data For $R_2M'Cr(CO)_5 \cdot THF$ Molecules

R_2M'	ν_{CO}[a]			τ_{CH_3}[b]	$J_{Sn^{117,119}-CH_3}$[c]
	$A_1^{(2)}$	$A_1^{(1)}$	E		
$(t\text{-}C_4H_9)_2Sn$	2031 (s)	1938 (m)	1918 (s)	8.60	56.0
$(CH_3)_2Sn$	2038 (w)	1941 (m)	1920 (s)	9.20	23.0
$(CH_3)_2Ge$	2043 (w)	1942 (ms)	1922 (s)	9.00	

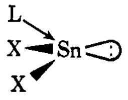
[a] In reciprocal centimeters, m = medium, s = strong, w = weak. Measured in hexane solutions. Band assignments follow ref 13. [b] Measured in toluene-d_8 solutions. [c] In hertz; measured at both 60 and 90 MHz.

120–122° dec. The mass spectrum[11] exhibits a parent ion corresponding to $(C_4H_9)_2SnCr(CO)_5^+$.[12]

Our particular structural formulation, A, is well supported by infrared and nmr data (Table I). The solution infrared spectra are in good accord with an approximately C_{4v} $LCr(CO)_5$ structure[13] and are, in fact, quite similar to those of the analogous carbene complexes.[3a] However, the lower frequencies of the C–O stretching vibrations indicate that the divalent germanium and tin ligands are stronger donors of electron density. In fact, the frequencies are qualitatively lower by 10–20 cm^{-1} than for any other neutrally charged $LCr(CO)_5$ molecule yet reported.[13–15] The positions of the $A_1^{(2)}$ and $A_1^{(1)}$ bands relative to the E mode, which serve as a rough gauge of the π-bonding ability of the group trans to the axial carbonyl,[13–15] indicate that the new ligands are at least as strong π acceptors as carbenes. Within the series Ia, Ib, Ic, the trend in frequencies is in accord with the trend in electronegativities of the group IV metals and the inductive effects of the alkyl groups.



A



B

The pmr spectra are in accord with the proposed formulation of the compounds and are also informative about electronic structure. The small magnitudes of the $J_{Sn^{117,119}-CH_3}$ values indicate that tin is in a low valent state,[16] as would be expected for a stannylene [formally tin(II)] complex. The values are far below the range observed for "normal" tin(IV) transition metal molecules, as for example ones in which a dimethyltin group bridges two transition metals ($J \approx$ 37–45 Hz).[16b,c] The nmr also reveals that the coordinated tetrahydrofuran is labile and rapidly exchanges with free tetrahydrofuran in solution at room temperature.

This work demonstrates that transition metal complexes of dialkylgermylenes and -stannylenes can be prepared, and these have properties distinctly different from the analogous carbene complexes and complexes of tetravalent germanium and tin. The divalent metals appear to function simultaneously as Lewis acids (to tetrahydrofuran) and strong Lewis bases (to chromium). This behavior is consistent with the structural chemistry of a number of tin(II) halides, B, in which the tin coordinates to a base (*e.g.*, H_2O) and is proposed to also possess a "stereochemically active" lone pair.[17] The chemistry of the divalent group IV metal–transition metal compounds and related species is under continuing investigation.[18]

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(11) Direct inlet spectrum at 80°, 20 eV. We thank Mr. D. A. Netzel for assistance with this measurement.

(12) This ion fragments by progressive loss of CO, which is typical of metal carbonyl compounds, and exhibits the complex multiplet structure expected from the presence of the various chromium and tin isotopes.

(13) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969).

(14) The next lowest is for a carbene complex,[3a] $(CO)_5CrC(OCH_3)$-[p-$(CH_3)_2NC_6H_4$] where $A_1^{(2)}$ = 2054, B_1 = 1976, $A_1^{(1)}$ = 1943, and E = 1935 cm^{-1}. We have been unable to observe the weak B_1 mode in our spectra, presumably due to higher local symmetry at the chromium. Traces of $Cr(CO)_6$ present as a decomposition product also interfere.

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(16) (a) N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, **85**, 1377 (1963); (b) H. R. Patil and W. A. G. Graham, *ibid.*, **87**, 673 (1965); (c) D. E. Fenton and J. J. Zukerman, *ibid.*, **90**, 6226 (1968).

(17) R. E. Rundle and D. H. Olson, *Inorg. Chem.*, **3**, 596 (1964).

(18) (a) T. J. Marks and A. M. Seyam, *J. Organometal. Chem.*, **31**, C62 (1971); (b) T. J. Marks, manuscript in preparation.

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Alternating Line-Width Effects in the Electron Spin Resonance Spectra of 2-Cyclohexenone Radical Anion and Its Simple Alkyl Derivatives

Sir:

Several recent reports exist of the electron spin resonance (esr) spectra of the radical anions of α,β-unsaturated ketones.[1–4] In particular, Russell and Stevenson,[1] by means of electrolytic reduction in dimethylformamide, have prepared and characterized the ketyls of several 2-cyclopentenones and 2-cyclohexenones in which all hydrogen atoms in positions α to the π system are substituted by methyl groups. They have also demonstrated that the reported esr spectrum of 4,4-dimethylcyclohexenone radical anion of Chen and Bersohn[2] is due to a semidione. A few examples of straight-chain ketyl radicals have been published by House, *et al.*,[3] and Harbour and Guzzo,[4] but in these cases, as with those of Russell and Stevenson,[1] observation of the often transient radical anion depends critically on substitution of key positions with blocking groups such as methyl, *tert*-butyl, or a cyclo-

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(3) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

(4) J. Harbour and A. V. Guzzo, *Mol. Phys.*, **20**, 565 (1971).