chloride and isopropylation of d_1-benzene, it was obvious that *o*-deuteriocumene had a sharp and intense absorption at 15.8 μ and *m*-deuteriocumene absorbed strongly at 15.0 μ. The isopropylation of d_1-benzene gave a product containing 86.0% d_1-cumene (by mass spectra). This material was used on an infrared standard with the assumption that two-fifths of the deuterium was in the *o*-position.

Products of the reaction of dimethyl sulfate with the cumyl anion were analyzed in the ethereal concentrate by gas–liquid chromatography employing a Perkin–Elmer model 154B Vapor Fractometer operating at 150° and using helium as a carrier gas. *t*-Butylbenzene and *p*-cymene were well separated by an "A"-column (purportedly di-*n*-decyl phthalate). *p*-Cymene would have been detected at a molar concentration $^1/_{500}$ that of the *t*-butylbenzene.

Solubility Measurements.—Treatment of 0.1 mole of cumyl methyl ether with sodium–potassium alloy for 7 hours in 700 ml. of ethyl ether at room temperature followed by filtration gave 550 ml. of an ether solution of the anion. Treatment of this solution with deuterium chloride gave a precipitate of alkali metal halide which was removed by filtration. The precipitate weighed 2.90 g. and was found to contain less than 0.03% sodium by flame photometry. From the ethereal solution 4.75 g. of cumene was recovered. The 550 ml. of filtrate thus gave 0.038 mole of potassium chloride and 0.039 mole of cumene and the solubility of the anion in ether is indicated to be 0.07 *M*.

Treatment of 0.1 mole of cumyl methyl ether with the alloy in the presence of 100 ml. of the dimethyl ether of ethylene glycol for 7 hours at room temperature did not give a homogeneous solution. The solution was allowed to settle and a sample of the homogeneous supernatant liquid was pipetted into methyl alcohol. The hydrolysate was analyzed for cumene, cumyl methyl ether and the dimethyl ether of ethylene glycol by gas–liquid chromatography at 100° in the "A"-column. The procedure was calibrated by prepared samples and the results indicated that more than 95% of the cumyl methyl ether had been destroyed. The ratio of cumene to dimethyl ether of ethylene glycol after hydrolysis indicated a solubility of the anion in this solvent of 0.42 *M*.

Reagents.—The cumyl methyl ether and *p*-bromocumene used have been described previously.[13] Deuterium oxide (>99.5%) was obtained from the Stuart Oxygen Co. Deuterium chloride was prepared by the reaction of deuterium oxide with benzoyl chloride[14] and should have possessed a purity of >95%. *d*-Acetic acid was prepared by the hydrolysis of acetyl chloride with deuterium oxide. The *d*-acetic acid was isolated by distillation. Its isotopic purity was never measured. Phillips 99 mole % minimum *n*-pentane was used without purification as was Mallinckrodt analytical grade ether (containing a trace of alcohol as a preservative). The dimethyl ether of ethylene glycol (Ansul Chem. Corp.) was refluxed over sodium until no further reaction occurred. Constant boiling material was stored over sodium and under nitrogen before use. All other solvents were dried by calcium hydride.

Acknowledgment.—Mass spectra were obtained by Mr. G. P. Schacher. Infrared absorptions were obtained by Mr. D. Harmes and Miss D. McClung. The Vapor Fractometer was operated by Mr. E. M. Hadsell. The cumyl methyl ether was prepared by Mr. W. Reuter.

(13) G. A. Russell, This Journal, **79**, 3871 (1957); **78**, 1047 (1956).

(14) H. C. Brown and C. Groot, *ibid.* **64**, 2223 (1942).

SCHENECTADY, N. Y.

COMMUNICATIONS TO THE EDITOR

INFRARED SPECTRA OF METAL CARBONYL HYDRIDES

Sir:

Several years ago this laboratory located the first vibration involving a hydrogen atom in metal carbonyl hydrides —703 cm.$^{-1}$ in $HCo(CO)_4$.(1) To take into account the range of possible consequences of the interaction expected between the hydrogen and the CO groups, a bonding model was proposed(1) containing a degree of freedom. In one limit the hydrogen was solely bonded to the metal and in the other limit to CO groups—the demonstration of the exact state requiring further experimentation.(1,2) Cotton has criticized this view and suggests that the 703 cm.$^{-1}$ band arises from a Co–H stretching vibration.(3,4)

This laboratory has now studied in detail the infrared spectrum of $DCo(CO)_4$, $H_2Fe(CO)_4$, $HDFe(CO)_4$, $HMn(CO)_5$, $DMn(CO)_5$, and a number of related compounds 2 to 33 μ obtained with appropriate prisms and small gratings. The 703 and 330 cm.$^{-1}$ bands of $HCo(CO)_4$ shift to 600 and 296 cm.$^{-1}$ in $DCo(CO)_4$ for frequency ratios of 1.17 and 1.12. These data establish that C and/or O atoms participate along with the H or D atom in the motions of this group of vibrations. Six vibrations of this character are observed between 300 and 800 cm.$^{-1}$ in $H_2Fe(CO)_4$, the typical hydrogen contribution being less than for $HCo(CO)_4$. Moreover, it appears that C–O bending motions primarily couple with the hydrogen motion in these modes.

The major components of the intense 5 μ band of $HMn(CO)_5$ are two overlapped bands with PQR structure apparently centering at 2028.8 and 2020 cm.$^{-1}$. A much weaker band has its Q branch at 1994.4 cm.$^{-1}$. Among the weaker satellites is a band at 1782 cm.$^{-1}$. The most intense bands at longer wave lengths occur at 735, 664, 615 and 458 cm.$^{-1}$. The stronger bands of $DMn(CO)_5$ are similar to those of $HMn(CO)_5$ except that the hydride bands at 735, 664 and 615 cm.$^{-1}$ seem to collapse into a deuteride band (doublet) at 676 cm.$^{-1}$; the weaker band at 1782 cm.$^{-1}$ is replaced by one at 1287 cm.$^{-1}$.

The 1782 and 1287 cm.$^{-1}$ bands are the Mn–H and Mn–D stretching vibrations! They correspond to a Mn–H force constant of *ca.* 1.87 md./Å. The following explanation is offered for the behavior of the bands near 15 μ. The 735 and 615 cm.$^{-1}$ bands result from the coupling of a weak, "pure" Mn–H bending mode with an intense C–O bending mode, both of which have (uncoupled) frequencies near a second C–O bending mode of different symmetry at 664 cm.$^{-1}$. The deuteration shift of the (uncoupled) Mn–H frequency (*ca.* $\sqrt{2}$) moves it

(1) W. Edgell, C. Magee and G. Gallup, This Journal, **78**, 4185 (1956).

(2) W. Edgell, *Ann. Rev. Phys. Chem.*, **8**, 353 (1957).

(3) F. Cotton and G. Wilkinson, *Chem. and Ind.* (*London*), 1305 (1956).

(4) F. Cotton, This Journal, **80**, 4425 (1958).

beyond the range of effective coupling with the C–O bending mode, which then appears together with the second C–O mode at *ca.* 676 cm.$^{-1}$. The *uncoupled* Mn–H bending frequency is thus fixed at *ca.* 665 cm.$^{-1}$!

Thus both Mn–H stretching and bending frequencies are established. They are consistent with the *metal–hydrogen bonding limit* of the model of Edgell, Magee and Gallup,[1] and with those of Hieber[5] and Cotton and Wilkinson.[3] While not definitely proven, the above findings imply that the bonding of the hydrogen in $HCo(CO)_4$ and $H_2Fe(CO)_4$ is similar to that in $HMn(CO)_5$ with greater hydrogen–CO coupling.

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[5] W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 745 (1932); *Die Chemie*, **55**, 25 (1942).

W. F. EDGELL
G. ASATO
W. WILSON
C. ANGELL
CHEMISTRY DEPARTMENT
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

RECEIVED MARCH 14, 1959

$D_{\infty h}$ LIGAND FIELDS AND "SANDWICH" COMPLEXES[1]

Sir:

Numerous molecular orbital treatments of ferrocene and its analogs have been published.[2-7] There is presented here a strong-field, ligand-field model for sandwich-type complexes with the general formula $M^{\mu}(R^{\nu})_2$. Here M^{μ} is a transition metal atom in its μth valence state and R^{ν} is a planar ring carrying a charge ν. The field on M^{μ} from rings R^{ν} is due to the formal charges on the ring and/or virtual charges arising from mutual polarization of M and R. It is assumed that the actual field is adequately reproduced by one of $D_{\infty h}$ symmetry and that the field uncouples the d electrons on the transition metal atom.[8] Since the field is axially symmetric, m remains a good quantum number, the d functions of different |m| are not mixed, and the five d orbitals have at most three different energies. Let $a = r \sin \theta$ be the coördinate perpendicular, and $z = r \cos \theta$ the coordinate parallel to the symmetry axis. The perturbing field contains no odd powers in z because of the symmetry plane through M^{μ}. The field is assumed to be continuous at the origin so that it contains no first power in a. To the second power

$$\begin{aligned} V &= V_0 + V_a a^2 + V_z z^2 \\ &= \{V_0 + V_a(a^2 + z^2)\} - (V_a - V_z)z^2 \end{aligned}$$

The portion of the perturbation in braces is spherically symmetric, produces no d splitting, and is neglected. With hydrogenic orbitals of effective charge Z, $E(e_{2g}) = -3Dd$, $E(e_{1g}) = -9Dd$, and $E(a_{1g}) = -11Dd$, where $Dd = 6(V_a - V_z)(Z/a_0)^2$ is the $D_{\infty h}$ ligand field strength. In Table I are listed the $D_{\infty h}$ electron configurations of some ferrocene analogs assuming $V_a > V_z$ and a formal charge of -1 on each ring. Also listed are the observed paramagnetic moments expressed as number of unpaired electrons.

TABLE I

Species[a]	Assignment ($D_{\infty h}$ field)	Unpaired electrons (obs.)[b]
$(Cy)_2Ti$	$(a_{1g})^2$	0
$[(Cy)_2Mo]^{+2}$	$(a_{1g})^2$	0
$(Cy)_2V$	$(a_{1g})^2(e_{1g})^1$	3
$[(Cy)_2Cr]^+$	$(a_{1g})^2(e_{1g})^1$	3
$(Cy)_2Cr$	$(a_{1g})^2(e_{1g})^2$	2
$[(Cy)_2Fe]^+$	$(a_{1g})^2(e_{1g})^3$	1
$(Cy)_2Mn$	$(a_{1g})^2(e_{1g})^3$	5
$(Cy)_2Fe$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Co]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Rh]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Ir]^+$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Ru$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Co$	$(a_{1g})^2(e_{1g})^4(e_{2g})^1$	1
$(Cy)_2Ni$	$(a_{1g})^2(e_{1g})^4(e_{2g})^2$	2

[a] Cy = C_5H_5. [b] Bibliography is given in reference 7.

The predictions agree with experiment except for $(Cy)_2V$, $(Cy)_2Cr^+$, and $(Cy)_2Mn$ which suggest that a weak field treatment may be required. The considerations given here should apply also to the benzene metal complexes. The author is indebted to Professor G. W. Watt for the suggestion of a field theory approach to the problem and for a preliminary correlation of the data.

DEPARTMENTS OF CHEMISTRY AND PHYSICS
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS
F. A. MATSEN

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

[2] H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953).

[3] W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

[4] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

[5] E. Ruch, *Rec. Trav. Chim.*, **75**, 638 (1956).

[6] M. Yamazaki, *J. Chem. Phys.*, **24**, 1260 (1956).

[7] A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957).

[8] See, for example, W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

SYNTHETIC STUDIES ON SPHINGOLIPIDS. V. THE SYNTHESIS OF DIHYDROCEREBROSIDES

Sir:

The structure of the cerebrosides has been established by Carter and co-workers[1-3] as Va, in which R is a long-chain fatty acid residue. We wish to report the synthesis of palmitoyl- and stearoyl-dihydrocerebrosides (Vb and Vc).

As key intermediate we employed the substituted *cis*-oxazoline I ($R^1 = CH_3(CH_2)_{14}$).[4] Hydrolysis with diluted hydrochloric acid gave *erythro*-3-O-benzoyldihydrosphinogosine (II), which was not isolated, but was acylated directly in the presence of sodium acetate to give the *erythro* form of the amidoester III. (IIIb: m.p. 74–75.5°; found: C, 76.8; H, 11.8; N, 2.2; IIIc: m.p. 73–75°; found: C, 76.9; H, 11.35; N, 2.0.)

When a benzene solution of III was shaken with tetraacetyl-α-D-galactosyl bromide[5] in the presence of freshly-prepared silver carbonate,[6] a 60% yield of IV was obtained. (IVb: m.p. 43–45°; found: C, 67.9; H, 9.7; N, 1.8; IVc: m.p. 43–45°; found: C, 67.9; H, 9.3; N, 1.6). Saponification

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[1] H. E. Carter, O. Nalbandov and P. A. Tavormina, *J. Biol. Chem.*, **192**, 197 (1951).

[2] H. E. Carter and F. L. Greenwood, *ibid.*, **199**, 283 (1952).

[3] H. E. Carter and Y. Fujino, *ibid.*, **221**, 879 (1956).

[4] D. Shapiro, H. M. Flowers and S. Spector-Shefer, THIS JOURNAL, in press.

[5] A. Robertson, *J. Chem. Soc.*, 1820 (1929).

[6] W. Koenigs and E. Knorr, *Ber.*, **34**, 957 (1901).