Fig. 1.—Idealized model in perspective of the sexadentate seven-coordinate aquo complex, $Fe(OH_2)Z^-$, with the twofold axis vertical. The complexed oxygen atoms, O_1 --- O_4, have coordinates measured parallel to the twofold axis from an origin at Fe as follows: O_1 and O_2, -0.11 Å.; O_3 and O_4, $+0.56$ Å.

(II).[5] That both of these conclusions can be valid simultaneously is demonstrated by our determination of structure, using three-dimensional X-ray analysis, of the calcium salt $Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$ containing the anionic Fe(III)–DCTA chelate, $Fe(OH_2)Z^-$.

$Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$ crystallizes in the monoclinic space group $C2/c$ with $a = 34.34 \pm 0.02$, $b = 8.844 \pm 0.011$, $c = 13.527 \pm 0.017$ Å., $\beta = 91.02 \pm 0.05°$, and a unit cell content of four Ca^{2+}, eight $Fe(OH_2)Z^-$, and thirty-six H_2O. Intensity data, measured by counter methods out to $(\sin \theta)/\lambda = 0.65$ with Mo $K\alpha$ radiation, were utilized in the heavy-atom technique for structure determination. Least-squares refinement of positional and anisotropic thermal parameters gives a residual of 0.094 for the approximately 92% of the data which are definitely above background.

The $Fe(OH_2)Z^-$ ion, as given by the analysis and illustrated in Fig. 1, is a sexadentate seven-coordinate aquo complex which approximates closely to the symmetry required by a twofold axis through OH_2, Fe, the midpoint of the C–C bond shared by the ethylenediamine and cyclohexane rings, and the midpoint of the opposite C–C bond in the cyclohexane ring. The atoms N_1, N_2, Fe, and O of H_2O are coplanar, but O_3 and O_4 are, respectively, -0.99 and $+0.99$ Å. from this plane in positions corresponding to a rotation of 29° about the twofold axis. Consequently, the coordination group of $Fe(OH_2)Z^-$ is geometrically intermediate between the NbF_7^{2-} configuration[6] which, suitably modified, is utilized[5] by $Mn(OH_2)Y^{2-}$, and the pentagonal bipyramid which, in an asymmetric form, is utilized[3] by $Fe(OH_2)Y^-$. The "chair" form with standard bond parameters is assumed by the cyclohexane ring. Ethylenediamine and glycinate ring

(5) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

(6) The coordination group about Ca^{2+} in $Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$, comprising five water molecules and two carbonyl oxygen atoms, approximates closely to the idealized $(C_{3v}-mm2)$ NbF_7^{2-} configuration as described by J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

geometry in $Fe(OH_2)Z^-$ is very like that in $Mn(OH_2)Y^-$, and is suggestive of slightly more cumulative strain than in $Fe(OH_2)Y^-$. Lengths of the complexing bonds in $Fe(OH_2)Z^-$ conform, nonetheless, to the pattern observed[3] in $Fe(OH_2)Y^-$. When averaged in agreement with C_2-2 symmetry, one obtains Fe–O (O_1 and O_2) $= 2.017$, Fe–OH_2 $= 2.090$, Fe–O (O_3 and O_4) $= 2.092$, Fe–N $= 2.29$ Å., all with $\sigma < 0.005$ Å. Passing over differences in detail, we note that the averaged length of the five Fe–O bonds comes out just 0.005 Å. larger for $Fe(OH_2)Z^-$ than for $Fe(OH_2)Y^-$, while the comparatively unimportant Fe–N bonds are 0.035 Å. shorter in the DCTA complex. Over-all comparisons of the two configurations suggest little or no difference in the energy of complex formation for the DCTA and EDTA chelates.

A principal source of stability[2] for both chelates is the large increase in entropy associated with the release during chelation of water molecules (five in the present case) from the hydrated $Fe(OH_2)_6^{3+}$. The accompanying and partially off-setting decrease in the (partial molar) entropy of the chelating agent is confidently expected to be of lower magnitude for DCTA than for EDTA primarily because the cyclohexane ring in DCTA functions as a relatively severe constraint of the number of configurations available to the *free* complexing species. The stability constant of $Fe(OH_2)Z^-$ is unreported, but a value of about 10^{27}, as compared with $10^{25.1}$ for $Fe(OH_2)Y^-$, is made plausible by the tabulated data[2] for the chelates of Mn^{2+} and many other ions.

(7) National Science Foundation Cooperative Fellow, 1962–1964.

(8) Author to whom communications should be addressed.

DEPARTMENT OF CHEMISTRY   GERSON H. COHEN[7]
CORNELL UNIVERSITY   J. L. HOARD[8]
ITHACA, NEW YORK

Kinetics of the Addition of Grignard Reagents to Ketones[1]

Sir:

The 1,2-addition of Grignard reagents to carbonyl groups has been the subject of extensive study for many years.[2] Recently data have been interpreted in terms of the product arising from a low concentration of a complex between a dimeric Grignard reagent and a ketone,[3,4] from a complex between dialkylmagnesium and ketone,[5] or from the reaction of a Grignard reagent with a 1:1 complex between a Grignard reagent and a ketone.[6] In this communication data are presented which are consistent with a mechanism involving product arising from a complex between ketone I and methylmagnesium bromide with an equilibrium constant for complex formation of 6.2 1./mole.

2,4-Dimethyl-4'-methylmercaptobenzophenone (I), m.p. 53–54°, displays a strong absorption with λ_{max} 315 mμ (ϵ 2.5 $\times$ 10^4) in diethyl ether. An additional band, λ_{max} 360 mμ, is observed when methylmagnesium

(1) Research supported by the U.S. Army Research Office (Durham).

(2) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954.

(3) J. Miller, G. Gregoriou, and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 3966 (1961).

(4) (a) N. M. Bikales and E. I. Becker, *Chem. Ind.* (London), **11**, 1831 (1961); (b) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963).

(5) H. O. House and D. D. Traficante, *J. Org. Chem.*, **28**, 355 (1963).

(6) M. Anteunis, *ibid.*, **26**, 4214 (1961); *ibid.*, **27**, 596 (1962).

bromide is present in the solution. Methylmagnesium bromide does not show an appreciable absorbance in this region. The longer wave length absorption which is present in solutions containing methylmagnesium bromide has been ascribed to a 1:1 complex between the ketone and the Grignard reagent.[7] The rate of disappearance of both the ketone band and the complex band obeys good first-order kinetics as is illustrated in Table I for the absorbance at 355 mμ

TABLE I

REACTION OF 10^{-4} M I WITH 0.107 M METHYLMAGNESIUM
BROMIDE IN DIETHYL ETHER AT $25.0°$

Time, sec.	Rel. A, 355 mμ	10^3k_1, sec.$^{-1}$, integrated
0	0.842	...
24	0.763	4.11
42	0.703	4.30
60	0.651	4.29
78	0.594	4.47
102	0.533	4.48
120	0.493	4.46
138	0.453	4.49
162	0.418	4.32
180	0.376	4.48
198	0.353	4.39
220	0.313	4.46
240	0.291	4.43
270	0.255	4.42
300	0.224	4.41
360	0.176	4.35
420	0.133	4.39
480	0.108	4.28
600	0.065	4.27

when 10^{-4} M ketone I and 0.01 to 0.4 M methylmagnesium bromide are employed. The rate constant calculated from data taken at 355 mμ divided by the rate constant obtained at 315 mμ is 1.04 ± 0.03, indicating that both the ketone and the complex disappear at the same rate.

The first-order rate constants, k_1, for the disappearance of either ketone or complex increase with increasing concentration of methylmagnesium bromide (Table II and Fig. 1). Below $ca.$ 0.1 M the reaction is approxi-

TABLE II

RATE OF REACTION OF KETONE I WITH METHYLMAGNESIUM
BROMIDE IN DIETHYL ETHER AT $25.0°$

I$_2$ titration	Grignard. M Total base	Total bromide	10^3k_1,^{a} sec.$^{-1}$
0.338	...	0.366	7.8 ± 0.2
0.208	0.219	0.242	6.6 ± 0.6
0.107	0.117	0.121	4.6 ± 0.2
0.0406	0.0452	0.0467	1.98 ± 0.02
0.0161	0.0188	0.0188	0.85 ± 0.01

^{a} Average of two runs at each concentration.

mately first order in Grignard, while at higher concentrations the apparent order in Grignard is less than one (Fig. 1). These results for ketone I may be quantitatively fitted, for the concentration region investigated, to the scheme[8]

$$\text{ketone} + \text{Grignard} \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k} \text{product}$$
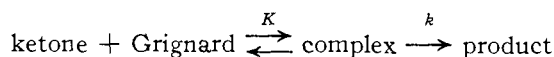
(7) S. G. Smith, *Tetrahedron Letters*, **7**, 409 (1963).
(8) Of course, the data also fit the scheme

$$\text{complex} \rightleftharpoons \text{ketone} + \text{Grignard} \longrightarrow \text{product}$$
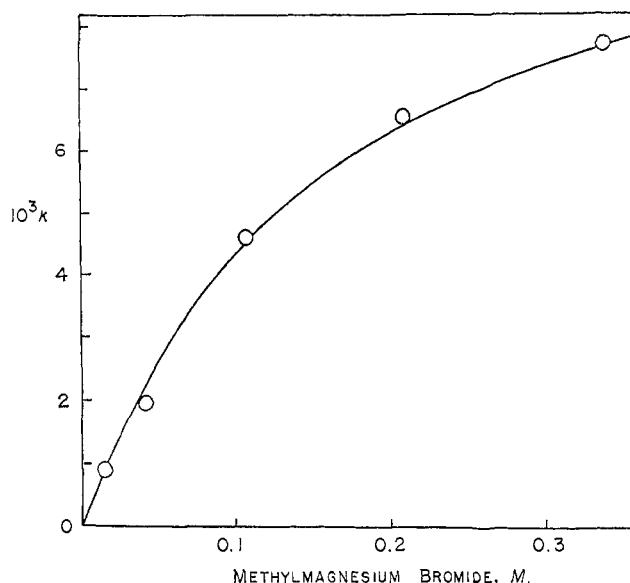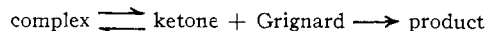

Fig. 1.—Plot of observed first-order rate constant for ketone I in an ether solution of methylmagnesium bromide at $25.0°$ vs. concentration of methylmagnesium bromide.

The line in Fig. 1 corresponds to an equilibrium constant, K, of 6.2 1./mole and a rate constant, k_1, for conversion of complex to product of 1.1×10^{-2} sec.$^{-1}$ at $25°$ in diethyl ether. To the extent that phenylmagnesium bromide[9] and ethylmagnesium bromide[10] may be used as models for the nature of methylmagnesium bromide these reactions would involve a monomeric Grignard reagent at the concentrations employed.

Acknowledgment.—We are indebted to the Dow Chemical Company for supplying the magnesium used in these experiments.

(9) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).
(10) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453 (1963).
(11) Alfred P. Sloan Fellow.

THE NOYES CHEMICAL LABORATORY   STANLEY G. SMITH[11]
UNIVERSITY OF ILLINOIS   GEORGE SU
URBANA, ILLINOIS

The Thermal Equilibration of cis- and trans-β-Decalones.
An Example of an Unusually Large Entropy of Isomerization

Sir:

In the course of our work on the hydrogenation of unsaturated ketones, it became necessary to determine the relative thermodynamic stabilities of cis- (I) and trans- (II) β-decalone. It was also felt that such data

I   II
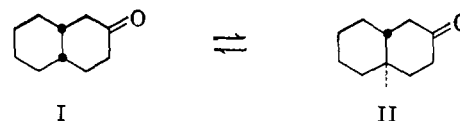
would afford more information concerning the 3-alkyl ketone effect first proposed by Klyne[1] and later evaluated by Allinger and Freiberg.[2]

I and II were equilibrated by heating in sealed ampoules over a Pd catalyst using the procedure described for the equilibration of 3,5-dimethylcyclohexa-

(1) W. Klyne, *Experientia*, **12**, 119 (1956).
(2) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **84**, 2201 (1962).