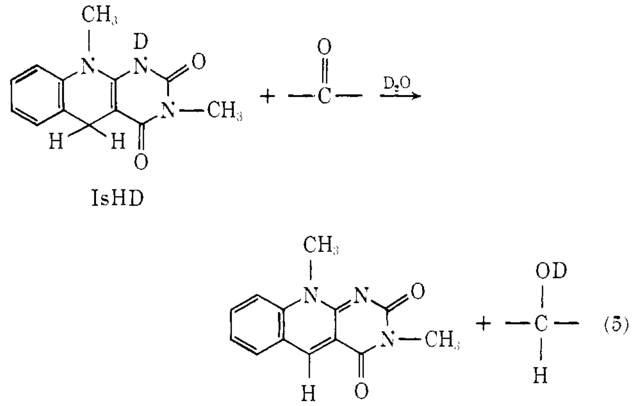

**Acknowledgment.** Supported by a grant from the National Science Foundation.

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[9] Postdoctoral Fellow.

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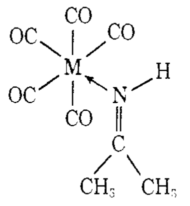
## Stabilization of Dimethylketimine by Metal Complex Formation

*Sir:*

Ketimines, RR′C=NR″, are stable compounds only when the R, R′, and R″ groups are relatively large.[1] Thus dimethylketimine, $(CH_3)_2C{=}NH$, the imine analog of acetone, has never been isolated and is apparently too unstable for isolation. This communication describes the preparation and characterization of the first stable metal complex of dimethylketimine.

A solution of $Na_2[Cr_2(CO)_{10}]$, prepared[2] by photolysis of a tetrahydrofuran solution of $Cr(CO)_6$ in the presence of excess dilute sodium amalgam with stirring, was treated with excess of a tetrahydrofuran solution of 2-bromo-2-nitrosopropane,[3] $(CH_3)_2C(NO)Br$. Evaporation of the solvent followed by chromatography on alumina ($CH_2Cl_2$ solution) and sublimation at ~55° (0.01 mm) gave a 3–5% yield of yellow crystalline $(CH_3)_2C{=}N(H)Cr(CO)_5$. *Anal.* Calcd for $C_8H_7CrNO_5$: C, 38.5; H, 2.8; Cr, 20.8; N, 5.6; O, 32.1; mol wt, 249. Found: C, 38.4; H, 2.8; Cr, 20.2; N, 5.5; O, 32.3; mol wt, 279 (vapor pressure lowering), mp 45–47°. The analogous yellow tungsten compound $(CH_3)_2C{=}N(H)W(CO)_5$, mp 66–67°, was similarly prepared from $Na_2[W_2(CO)_{10}]$ and 2-bromo-2-nitrosopropane.

The spectroscopic properties of $(CH_3)_2C{=}N(H)Cr(CO)_5$ were in accord with its formulation as the dimethylketimine complex I. The infrared spectrum ($CH_2Cl_2$ solution) exhibited $\nu$(CO) frequencies at 2073 (w), 1930 (vs), and 1896 (m) cm$^{-1}$ which may be assigned to the $A_1$, E, and $A_1$ modes, respectively, of an $LM(CO)_5$ molecule. A more intense infrared spectrum (KBr pellet) exhibited a sharp band at 3317 cm$^{-1}$ assigned to the $\nu$(NH) frequency and an extremely weak band at ~1645 cm$^{-1}$ which may be the $\nu$(C=N) frequency. The proton nmr spectrum ($(CD_3)_2CO$ solution) exhibited resonances at $\tau$ 0.66 (broad, width at half-height 13 Hz) and 7.87 (sharp singlet) of approximate relative intensities ~1:6 which may be assigned to the single imine proton and the six equivalent methyl protons, respectively.



I

The formation of the compounds $(CH_3)_2C{=}N(H)M(CO)_5$ (I: M = Cr and W) from 2-bromo-2-nitrosopropane and the corresponding metal carbonyl anions $[M_2(CO)_{10}]^{2-}$ clearly must involve debromination and deoxygenation of the halonitroso compound by the strongly reducing metal carbonyl anion. Since *gem*-halonitroso alkanes of the type RR′C(NO)X (X = Cl or Br) are available from the corresponding ketones RR′C=O through halogenation of their oximes,[4] the reaction outlined in this communication should be useful for the preparation of a wide range of ketimine–metal carbonyl complexes from the corresponding ketones.

Reactions of 2-bromo-2-nitrosopropane with other metal carbonyl anions and related compounds appear to give unusual products of other types such as the yellow iron carbonyl derivative $[(CH_3)_2C{=}NFe(CO)_3]_2$ (from $Fe(CO)_4{}^{2-}$) and the purple cyclopentadienylmolybdenum carbonyl derivative $(CH_3)_2C{=}NOMo(CO)_2C_5H_5$ (from $C_5H_5Mo(CO)_3{}^-$). Details of this chemistry will be presented in future publications.

**Acknowledgment.** We are indebted to the National Cancer Institute for partial support of this work under Grants CA12938-01 and CA-12938-02 and to Mr. K. C. Hodges for help with the infrared spectra.

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[1] S. Patai, Ed., "The Chemistry of the Carbon–Nitrogen Double Bond," Interscience, New York, N. Y., 1970.

[2] R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966).

[3] O. Piloty, *Ber.*, **31**, 452 (1898).

[4] J. H. Boyer in "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Interscience, New York, N. Y., 1969, pp 235–238.

[5] Postdoctoral research associate, 1971–1973.

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*Received May 14, 1973*

## Detailed Stereochemistry in Solution of a Macrocyclic Complex Having Eight Chiral Centers. Observation of an Intramolecular Nuclear Overhauser Effect

*Sir:*

Complexes of metal chelates that contain several chiral centers exhibit intricate stereochemistries and large numbers of possible isomers.[1] Powerful techniques are required to deduce the detailed structures of individual isomers of such species in solution. We report here the use of double resonance nmr measurements, including a novel example of an intramolecular nuclear Overhauser effect (NOE), combined with stereospecific deuteration and strain energy calculations to produce an exceptionally detailed description of the

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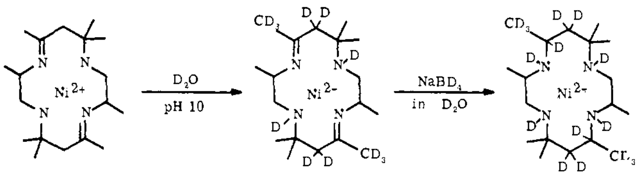
[1] See, for example, L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969).

total stereochemistry of a complex with a macrocyclic ligand having eight chiral centers. Nmr spectra were obtained at 100 MHz using a JEOL spectrometer, Model JNM-MH-100. The solutions used in the NOE measurements were deoxygenated.[2]

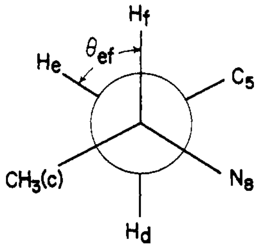
We have isolated five isomeric forms of the complex of structure I given in Figure 1 (isomer yields (%) $\alpha:\beta:\gamma:\delta:\epsilon$ = 60:15:18.5:1.2:1.8), all of which, because of the mode of synthesis, contain carbon atoms 2 and 9 having *R* chirality. The stereochemistry of the $\alpha$-isomer is the subject of this report. Nmr studies were conducted on the usual hydrogen-containing species and on the $d_{16}$ derivative (prepared according to Scheme I). The methyl signals (Figure 1) occur as two singlets (six protons each) and two doublets (six protons each). This requires that the structure of the $\alpha$-isomer have $C_2$ symmetry since the methyl groups are clearly pairwise equivalent. Spin-decoupling experiments produced unequivocal assignments of all resonances (Figure 1) and led to evaluation of all the H–H coupling constants.

**Scheme I**



From the values of the coupling constants[3] $J_{ac}$ (<0.5 Hz) and $J_{bc}$ (=5.0 Hz), it is concluded that the dihedral angle $\theta_{ac}$ is about 90° and $\theta_{bc}$ is less than 60° so that the five-membered chelate rings are very nearly eclipsed. This strongly suggests that the amines flanking this ring have their hydrogens on the same side of the coordinate plane. Further $CH_3$(d) is assigned an axial orientation on the basis of the coupling constants.

The coupling constants associated with the six-membered ring lead uniquely to structure II. $J_{ef}$ (=3.0 Hz) falls near the usual range for gauche hydrogen ($\theta \simeq 60°$; 3.8–4.4 Hz) while $J_{df}$ is consistent with trans hydrogen (11.0 as compared to a range from 10.0 to 12.4 Hz).[4–6] This requires $CH_3$(c) to be equatorial while $H_d$ is axial. The low field position of the $CH_3$(a) signal (2.36 ppm) justifies its assignments to an axial orientation, probably in a chair-form chelate ring.[7]



II

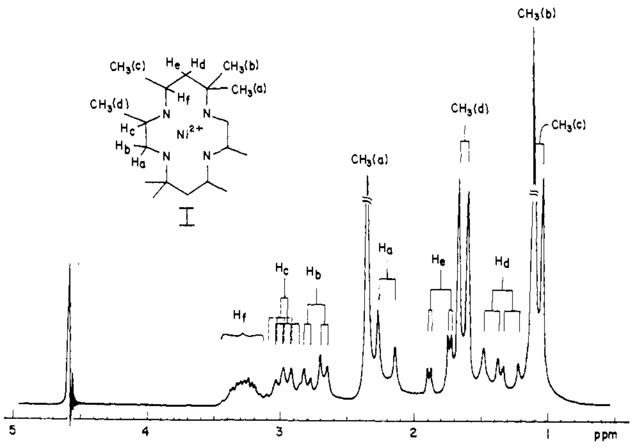
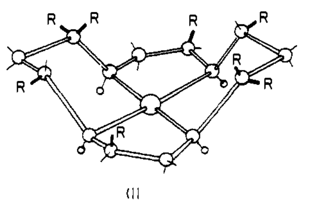


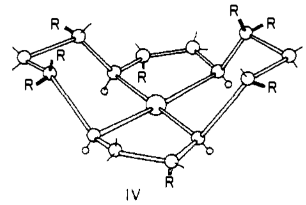
Figure 1. A 100-MHz pmr spectrum of the complex (chloride salt) in $D_2O$. Chemical shifts are expressed downfield from the internal standard sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

Confirmation of the chair-form of the six-membered rings and of the assignment of $CH_3$(a) to an axial site is found in an especially illuminating NOE experiment. This conformation, in contrast to a twist form, places the $H_f$ proton in close proximity to the axial methyl of the *gem*-dimethyl set. Using a scheme related to I, but reducing with $NaBH_4$ in $D_2O$, all of the protons on the six-membered ring and its substituents, except $H_f$ and those on the *gem*-dimethyl pair, were replaced with deuterium. Irradiation of the $CH_3$(a) singlet at 2.36 ppm caused the singlet due to $H_f$ at 3.28 ppm to increase in integrated intensity by 41 ± 5% with no decrease in band width at half-height, leaving all other signals unaffected. Irradiation of the $CH_3$(b) singlet was without effect. This result is consistent with a $CH_3$(a)–$H_f$ separation[8] of ~2.6 Å, a value very close to that required for the chair form of the six-membered ring (~2.5 Å). In contrast, a twist ring should expand the $CH_3$(a)–$H_f$ distance to 4.3–4.5 Å, leading to a negligible NOE intensity enhancement.[8]

The $C_2$ symmetry of complex I requires $C_7$ and $C_{14}$ to have the same chiralities. There are 20 possible $C_7$,$C_{14}$-racemic isomers and eight of these have $C_2$ symmetry.[2] However, only two of the eight, structures III and IV, have $CH_3$(c) equatorial, $CH_3$(d) axial, chair form six-membered rings, eclipsed five-membered rings. The application of strain energy calculations by the modified method of Boyd, as described elsewhere,[9] permits us to choose between these two structures because IV is predicted to be much more stable than III (9.0 kcal/mol difference in strain energy). The $\alpha$-isomer has been found to be stable toward isomerization under conditions where many related structures isomerize to more stable forms. In view of the fact that $C_2$ and $C_9$ have *R* chiralities, the remaining centers have the chiral



III



IV

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(2) Details will be reported elsewhere.

(3) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(4) T. Ito and M. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 155 (1970).

(5) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).

(6) T. Ito, H. Saito, and H. Ito, *Inorg. Nucl. Chem. Lett.*, **6**, 607 (1970).

(7) The downfield shift of axial methyl protons in planar $d^8$ derivatives has been related to the magnetic anisotropy associated with the metal ion: L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968).

(8) R. A. Bell and J. K. Saunders, *Can. J. Chem.*, **48**, 1114 (1970).

(9) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 2010 (1973).

forms $C_7$, *S*; $C_{14}$, *S*; $N_1$, *R*; $N_4$, *S*; $N_8$, *R*; and $N_{11}$, *S*.[10]

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[10] The financial support of the National Science Foundation is gratefully acknowledged.

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## Stable Carbocations. CLX.[1] The Relative Order of Charge Delocalization by Phenyl, Cyclopropyl, and Methyl Groups in Carbenium Ions Based on $^{13}C$ Nuclear Magnetic Resonance Studies

*Sir:*

In our continued study of carbocation intermediates we reported, on the basis of the $^{13}C$ chemical shifts of the carbenium ion centers in the phenyldimethylcarbenium ion, the cyclopropyldimethylcarbenium ion, and the trimethylcarbenium ion, that the relative effectiveness of the phenyl, methyl, and cyclopropyl groups to delocalize charge shows the order[2] $C_6H_5 >$ c-$C_3H_5 > CH_3$. Brown and Peters[3] took exception with our conclusion and suggested that $^{13}C$ nmr shifts of carbocations do not correlate with "stabilities of solvolytic transition states and the corresponding cationic intermediates." They based their contention mainly on the fact that our observed order of deshielding of chemical shifts in ions $R(CH_3)_2C^+$ (where R = $C_6H_5$, c-$C_3H_5$, and $CH_3$) is different from the rate order c-$C_3H_5 > C_6H_5 > CH_3$ observed in their solvolytic rate studies, as well as the stabilities of these ions deduced from equilibrium studies of the ions and their related alcohol (or olefin) precursors.

We now present extensive additional experimental evidence to show, based on $^{13}C$ nmr data, the trend in delocalization in related phenyl-, cyclopropyl-, and methyl-substituted ions is consistently indicated in our preceding studies. Brown and Peters[3] further did not consider the difference between spectroscopic (nmr) structural studies of carbocations which measure directly properties of the ions and conclusions based on kinetic and equilibrium data which relate only the relative stabilities, *i.e.*, energy differences between covalent precursors and carbenium ion like transition states and intermediates, respectively (in the involved tertiary systems).

Using methods developed in our laboratories the complete $^{13}C$ nmr spectra of several related series of phenyl-, cyclopropyl-, and methylcarbenium ions were obtained using fast Fourier transform nmr spectroscopy. Data are tabulated in Table I. $^{13}C$ chemical shifts cannot be directly equated with, although they obviously do reflect, the charge densities at carbons of similar hybridization and substitution.[4] The shielding constant ($\sigma$) for a particular atom is generally assumed to be composed of a paramagnetic term ($\sigma_p$) reflecting charge polarization, variation in bond order, and average excitation energy, a diamagnetic term ($\sigma_d$), and a term reflecting neighboring group effects ($\sigma' = \sigma - (\sigma_p + \sigma_d)$). The latter two terms for carbon-13 are considered to be much less significant than the paramagnetic term.[5] The chemical-shift differences between the carbenium centers of closely related ions (*i.e.*, comparing related secondary or tertiary systems) in Table I are too large to be accounted for solely by changes in $\sigma_d$ and $\sigma'$ terms. The differences in the carbon shifts on substituents in comparable ions, however, are much smaller, and may only reflect changes in the $\sigma_d$ and $\sigma'$ terms rather than different electron densities.[6] The $^{13}C$ chemical shifts of the carbenium centers in closely related series of carbocations thus clearly indicate the trend of charge delocalization by neighboring methyl, phenyl, and cyclopropyl groups.

In all systems studied the trend is that phenyl delocalizes charge from neighboring carbenium centers more than cyclopropyl, which in turn is much more effective than methyl. We feel that this order is, indeed, the expected one considering the nature of charge delocalization by these neighboring groups. The $\pi$-electron system of a phenyl group, when not hindered by steric effects, can conjugatively (*i.e.*, *via* p–$\pi$ interaction) delocalize charge more effectively than hyperconjugation with the bent $\sigma$ C–C bonds of the cyclopropane system, which in turn is more effective than C–H bond hyperconjugation by the methyl group.

We further feel, in contrast to Brown and Peters,[3] that there is no discrepancy at all with data of solvolytic rates and other observations, such as Deno's study of equilibrium constants of the related ions and their alcohol or olefin precursors in acid media.[8]

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[1] Part CLIX: G. A. Olah, G. Liang, P. W. Westerman, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, in press.

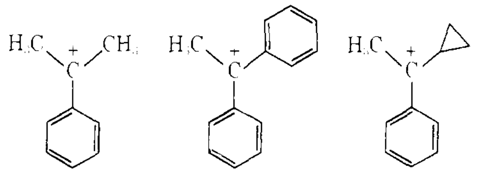
[2] G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

[3] H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973). We thank Professor Brown for a copy of his manuscript prior to publication.

[4] H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **468** (1961).

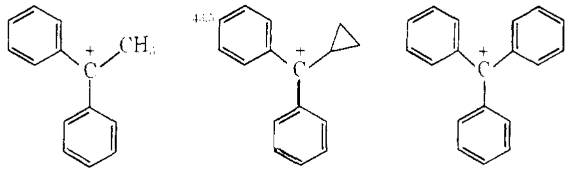
[5] M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

[6] In simple monosubstituted benzenes particular success has been achieved in correlating para carbon shifts with calculated charge densities.[7] Professor H. C. Brown, refereeing our communication, has noted *inter alia* that the para carbon shifts in the following ions seem to suggest that the ability of the cyclopropyl ring to delocalize charge is greater than the phenyl ring. We feel, however, that such comparison would neglect the effect that a cyclopropyl ring may have on the phenyl ring shifts.



37.8 45.6 48.2

When considering, for example, the para carbon shifts in the subsequently shown series of ions, one would arrive at the opposite conclusion. Significantly, the difference of 5 ppm in the para carbon shifts of the diphenylcyclopropylcarbenium ion, in which one phenyl ring lies in the face of the cyclopropyl ring, clearly shows substituent group effects ($\sigma'$) to be important even at the distant para position.



45.6 48.5 49.7

For similar reasons, in the cyclopropylmethylphenylcarbenium ion, the substituent group effects could cause the para shift to be more shielded than that expected from a consideration of the paramagnetic term alone.

[7] (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (b) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).