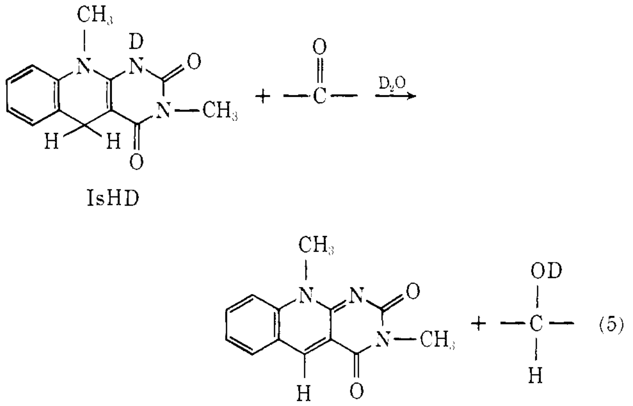

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(9) Postdoctoral Fellow.

Seiji Shinkai,[9] Thomas C. Bruice*
Department of Chemistry, University of California
Santa Barbara, California 93106

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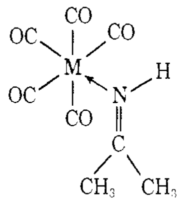
Stabilization of Dimethylketimine by Metal Complex Formation

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 ν(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 ν(NH) frequency and an extremely weak band at ~1645 cm^{-1} which may be the ν(C═N) frequency. The proton nmr spectrum ($(CD_3)_2CO$ solution) exhibited resonances at τ 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.



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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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(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.

R. B. King,* W. M. Douglas[5]
Department of Chemistry, University of Georgia
Athens, Georgia 30602

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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).