**Table II.** Values of Log $K^f_{IH^+}$ of Three Hammett Indicators and of $K^f_{CH_3COOH_2^+}$

| Acid system | Log $K^f_{IH^+}$ | | | |
|---|---|---|---|---|
| | 2-NA | 2-N-4ClA | 2-N-4,5Cl₂A | $K^f_{CH_3COOH_2^+}$ |
| HClO₄ | 4.9[a] (4.85)[b] | 4.2[c] (4.0)[a] (3.9)[b] | 3.1[c] | 12.0[c] |
| CH₃SO₃H | 4.9₅[c] (4.9)[d] | 4.2[c] | | 13.0,[e] 7[c] |

[a] Reference 2, considering protonation of acetic acid. [b] Reference 2, neglecting protonation of acetic acid. [c] Present work, spectrophotometric, average value of different determinations. [d] Reference 3, spectrophotometric, in mixtures of methanesulfonic acid and its tetraethylammonium salt. [e] This work, conductometric, in solutions of the acid.

The values of $K^f_{IH^+}$ of 2-NA and 2-N-4ClA were also obtained from [IH⁺]/[I] ratios found spectrophotometrically in fresh acetic acid free solutions of methanesulfonic acid, knowing $pK_{2HA}$ ($K_{2HA} = a_{H^+}a_{HA_2^-}/\{HA\}^2$). In this study $pK_{2HA}$ was redetermined conductometrically and found equal to 6.0₅, in agreement with that previously reported.[3] The value of $K^f_{CH_3COOH_2^+}$ was found conductometrically and also spectrophotometrically with 2-N-4ClA as indicator in methanesulfonic acid solutions containing acetic acid. In the calculation of [H$_s^+$], homoconjugation (HA$_2^-$) and heteroconjugation (A⁻···HOOCCH₃) were taken into account. The latter was found to be negligible under the experimental conditions. A summary of values of log $K^f_{IH^+}$ and $K^f_{CH_4COOH_2^+}$ obtained by the various methods is presented in Table II. The reason why the new value of $K^f_{IH^+}$ of 2-NA as determined in dilute perchloric acid is the same as that determined previously[1] is that the concentration of acetic acid added with the perchloric acid was so small the correction was negligible. Calculated values of $pa_H$ in 2-NA-perchloric acid mixtures used in the calibration of the glass electrode[5] are only 0.03–0.04 unit greater than previously reported at the highest acetic acid concentration encountered when the effect of the acid is taken into account.

From values of log $K^f_{BH^+}$ of acetonitrile (−10.1,[6] −10.8,[7] and ∼9.5[8]) and of acetic acid (−6.2,[9] −6.1[10]) referred to water as solvent, it is clear that the basicity of acetic acid in water is stronger than that of AN. Qualitatively, the same behavior is found in AN.

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## Mobility of Substituents in Metal Carbene Complexes about an FeC₆ or RuC₆ Core through Chelate Ring Formation

*Sir:*

The formation or rupture of chelate rings without breaking of a metal ligand bond is a relatively rare occurrence in transition metal chemistry, although such reactions have been frequently utilized in the construction of macrocyclic ligands.[1] Here we report on the importance of such a reaction in the chemistry of metal isocyanide complexes in which other chelate rings are not present to stabilize the metal–ligand bonds. Generally the reaction of a primary amine with an isocyanide complex results in the attack of the amine upon one isocyanide to yield a monodentate diaminocarbene ligand.[2] The results described below indicate that in certain cases the carbene and isocyanide substituents appended to the basic metal–carbon core may migrate in a reversible chelation process which can result in the conversion of the original amine nitrogen and its substituent into an isocyanide ligand.

When an amine adds to a six-coordinate isocyanide complex, either of the isomers **1** or **2** may be formed.
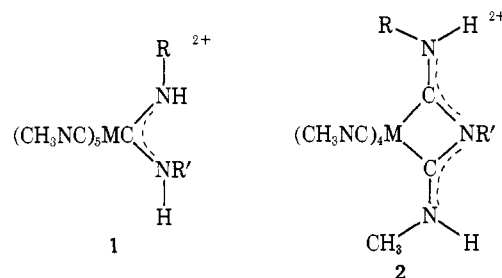


Steric effects appear to be dominant in determining which isomer is formed. The reaction of methylamine with hexakis(methyl isocyanide)ruthenium(II) in refluxing methanol for 15 min yields **1** (M = Ru; R = R' = CH₃). Spectroscopic data important to the characterization of this and other complexes are set out in Table I.[3] Longer reaction times produce a ruthenium complex containing two monodentate diaminocarbene ligands. Ethylamine also reacts with hexakis(methyl isocyanide)ruthenium(II) to yield **1** (M = Ru; R = CH₃, R' = C₂H₅; and R = C₂H₅, R' = CH₃) which exists in two isomeric forms due to steric constraints within the planar carbene ligand.[3] However, when methylamine is added to hexakis(methyl isocyanide)iron(II) chelative addition occurs to produce the complex cation **2** (M = Fe; R = R' = CH₃) which has been characterized by an X-ray diffraction study.[4] The formation of this complex probably proceeds through the normal attack of an amine on a coordinated isocyanide to yield the intermediate **1** (M = Fe; R = R' = CH₃). Due to the close proximity of ligands in this six-coordinate intermediate, the carbene ligand can then function as a nucleophile toward a second isocyanide and effect ring closure to give **2**. Similarly ethylamine reacts with hexakis(methyl isocyanide)iron(II) to yield the chelate complex **2** (M = Fe; R = CH₃,

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(2) For reviews on carbene ligands see: F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); P. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(3) In all cases the complex cations have been isolated as crystalline hexafluorophosphate salts. Satisfactory microanalytical data have been obtained for all new species. For comparison of spectroscopic data on other related carbene complexes see: A. L. Balch and J. Miller, *J. Amer. Chem. Soc.*, **94**, 417 (1972); J. S. Miller and A. L. Balch, *Inorg. Chem.*, **11**, 2069 (1972); W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *ibid.*, **12**, 451 (1973).
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**Table I.** Spectroscopic Data for Iron and Ruthenium Complexes

| Complex | Nmr data, τ (intensity) in acetonitrile-$d_3$ | | | | Infrared data, cm$^{-1}$ [a] | |
|---|---|---|---|---|---|---|
| | HNC$H_3$ [b] | CNC$H_3$ | NH | Other | $\nu_{N-H}$ | $\nu_{C\equiv N}$ |
| $(CH_3NC)_5RuC(NHCH_3)_2{}^{2+}$ | 7.20 (3), 6.90 (3) | 6.52 (15) | 3.45 (2) | | 3460 (m), 3395 (m) | 2268 (m), 2217 (s) |
| $(CH_3NC)_4Ru(C(NHCH_3)_2)_2{}^{2+}$ | 7.25 (6), 7.03 (6) | 6.57 (6), 6.55 (6) | 3.45 (4) | | 3476 (m), 3391 (m) | 2267 (m), 2212 (s) |
| $(CH_3NC)_5RuC(NHCH_3)NHC_2H_5{}^{2+}$ | 7.21 (1.9), 6.88 (1.1) | 6.57 (15) | 3.52 (2) | 8.83, 8.79 }(3)$^c$; 6.3 (2)$^d$ | 3461 (m), 3437 (m), 3405 (m), 3382 (w) | 2271 (m), 2218 (s) |
| $(CH_3NC)_4(C_2H_5NC)RuC(NHCH_3)_2{}^{2+}$ | 7.25 (3), 6.89 (3) | 6.55 (15) | 3.50 (2) | 8.63 (3)$^e$, 6.23 (2)$^f$ | 3461 (m), 3396 (m) | 2266 (m), 2214 (s) |
| $(CH_3NC)_5FeC(NH_2)NHCH_3{}^{2+}$ | 7.21 (3) | 6.53 (15) | 3.43, 3.20 }(3) | | 3538 (m), 3451 (m), 3414 (m) | 2239 (m), 2198 (s) |
| $(CH_3NC)_4FeC_2(NCH_3)(NHCH_3)_2{}^{2+}$ | 6.75 (6) | 6.62 (6), 6.59 (6) | 1.73 (2) | 7.13 (3)$^g$ | 3330 (m) | 2244 (m), 2205 (s) |
| $(CH_3NC)_4FeC_2(NC_2H_5)(NHCH_3)_2{}^{2+}$<br>$(CH_3NC)_4FeC_2(NCH_3)(NHCH_3)(NHC_2H_5)^{2+}$ | 6.72 (3.3) | 6.60, 6.57 }(12) | 1.62 (2) | 8.97 (0.27)$^e$, 8.70 (2.7)$^e$, 7.11 (2.7)$^g$, ~6.7 (2)$^d$ | 3329 (m) | 2243 (m), 2211 (s) |

$^a$ Fluorolube mull. $^b$ Doublet with $J_{H-N-C-H}$ of ca. 5 Hz. $^c$ Overlapping pair of triplets with $J_{H-C-C-H}$ of ca. 7 Hz (total intensity). $^d$ Complex methylene multiplet. $^e$ Triplet with $J_{H-C-C-H}$ of ca. 7 Hz. $^f$ Quartet with $J_{H-C-C-H}$ of ca. 7 Hz. $^g$ Interior chelate methyl.

R' = $C_2H_5$; and R = $C_2H_5$, R' = $CH_3$) which exists (as we have isolated it) as a mixture of two isomers, but ammonia reacts with the iron isocyanide complex to yield the complex 1 (M = Fe; R = H, R' = $CH_3$) with a monodentate diaminocarbene ligand. Thus it appears that a small central metal ion and increasing the size of the attacking amine favor chelative addition.

If $CD_3NH_2$ is allowed to react with hexakis(methyl isocyanide)ruthenium(II), the product is a mixture of the two isomers 1 (M = Ru; R = $CH_3$, R' = $CD_3$; and R = $CD_3$, R' = $CH_3$). The pmr spectrum of this complex is identical with that of the complex prepared from normal methylamine except that ratio of intensities of the methyl isocyanide ligands to the methyl groups of the carbene ligands is now 10:1:1. However, heating the deuterium labeled complex (dimethyl sulfoxide solution, 100°) results in the gradual decrease in intensity of the signal due to the methyl isocyanide ligands while the doublets at τ 7.20 and 6.90 increase in intensity (but the *total* intensity of all methyl groups remains unchanged). After 6 hr of heating the intensity ratio of resonances at 6.52, 6.90, and 7.20 is 5:1:1 (*i.e.*, that expected for statistical scrambling of the deuterated methyl group among the four positions in the cation). We propose that this scrambling results from ring closure to yield the isomer 2 as an intermediate which then can open to re-form 1 with the result that a substituent initially present on the entering amine (along with the amine nitrogen) may be incorporated into an isocyanide ligand. Similarly heating $(CH_3NC)_5RuC(NHC_2H_5)NHCH_3{}^{2+}$ in dimethyl sulfoxide for 6 hr results in isomerization to $(CH_3NC)_4(C_2H_5NC)RuC(NHCH_3)_2{}^{2+}$. Although the pmr spectrum of this complex is consistent with a trans geometry for the complex, the nmr parameters are probably insufficiently sensitive to distinguish cis and trans isomers since isocyanide ligands which are cis and trans to monodentate diaminocarbene ligands give rise to resonances which are accidentally degenerate.

When the iron complex 2 is prepared from $CD_3NH_2$ under the mildest conditions feasible (refluxing methanol, 20 min) the pmr spectrum of the product is the same as the pmr spectrum of 1 (M = Fe; R = R' = $CH_3$) except that the ratio of intensities in the methyl region is 3.1:3.1:2.2:1 with a total intensity of six-sevenths of that of the complex prepared from unlabeled methylamine. Consequently a single perdeuteriomethyl group has been introduced into the complex and it is largely localized on the chelate ring positions. However, some scrambling to other positions has already occurred in the time required to prepare the complex. Upon further heating (refluxing methanol for 6 hr) the labeled methyl group becomes randomly scrambled throughout the molecule. The intensities of the pmr resonances at 7.13 and 6.75 increase while the intensities of those at 6.62 and 6.59 decrease until the ratio finally stabilizes at 2:2:2:1; however, the total intensity does not change. Similarly the pmr spectrum of the mixture 2 (M = Fe; R = $CH_3$, R' = $C_2H_5$; and R = $C_2H_5$, R' = $CH_3$) undergoes a complex series of changes upon heating. These changes are consistent with scrambling of the ethyl group and the production of some coordinated ethyl isocyanide.

No reactions completely analogous to the situation described above have been previously discovered. Further experiments which are aimed at exploring the scope and at accurately measuring the kinetics of these ring opening and closing reactions are in progress. Probably the closest analogy to the behavior of these isocyanide complexes is found in complexes in which a coordinate nucleophile (an amino group or hydroxide ion) reacts with the uncoordinated nitrile of coordinated amino acetonitrile to yield tridentate or bidentate chelates. In the process the coordinated amine or hydroxide is converted to coordinated amidine or amide, respectively.[5] However, the reversibility of these ring closures has not been demonstrated. The possibility that chelate formation may be important in the chemistry of carbamoyl complexes[6] is under investigation.

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## Dipole-Stabilized Carbanions from a Methyl Thio Ester and a Methylamide

*Sir:*

Dipole-stabilized carbanions, species in which inductive stabilization of the negative charge on carbon is provided by an $\alpha$ heteroatom which is the positive end of a dipole, have been postulated as reaction intermediates in base-catalyzed hydrogen–deuterium exchanges,[1–13] base-promoted rearrangements,[14] metalations,[15–21] and decarboxylation.[22] The permanent dipole of amine oxides provides a number of examples of such an effect, and, for a variety of functions,[14–21] metalated species have been trapped by electrophiles in synthetically useful reactions. The formation and electrophilic trapping of a dipole-stabilized carbanion from dibenzylbenzamide reported by Fraser, *et al.*,[19] is an important advance in the synthetic use of carboxamide-stabilized carbanions; however, these are, at present, less useful than analogous species from nitrosoamines.[18]

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(11) W. W. Paudler and L. S. Helmick, *J. Org. Chem.*, **33**, 1087 (1968).
(12) L. K. Keefer and C. H. Fodor, *J. Amer. Chem. Soc.*, **92**, 5747 (1970).
(13) R. R. Fraser and Y. Y. Wigfield (*Tetrahedron Lett.*, 2515 (1971)) report that inductive stabilization is not a dominant factor for *N*-nitrosoamines and favor resonance stabilization of the anion in that case.
(14) T. Durst, R. Van Den Elzen, and M. J. LeBelle, *J. Amer. Chem. Soc.*, **94**, 9261 (1972).
(15) R. A. Abramovitch, R. T. Coutts, and E. M. Smith, *J. Org. Chem.*, **37**, 3584 (1972), and references cited therein.
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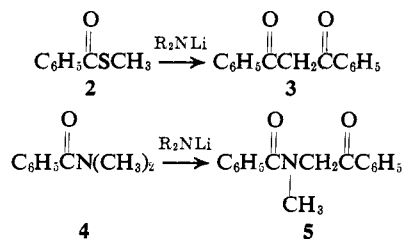(21) K. Hirai, H. Matsuda, and Y. Kishida, *Tetrahedron Lett.*, 4359 (1971).
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Although serious questions need to be raised about the contribution of inductive effects in each case,[1,13,23,24] there are experimental indications that carbanion stabilization may be provided by a number of mesomeric dipoles as generalized in formula **1**. The possible opera-

$$-\overset{|}{\underset{|}{C}}-\ddot{X}-Y{=}Z \longleftrightarrow -\overset{|}{\underset{|}{C}}-\overset{+}{X}{=}Y-\overset{-}{\ddot{Z}}$$

**1**
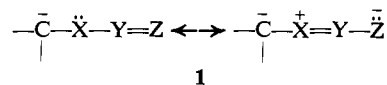
tion of such stabilization has been individually noted for carboxamides[2,3,14,19] and a vinylogous carboxamide[1] (**1**, X—Y=Z = -N—C=O), nitrosoamines[12,13,18] (**1**, X—Y=Z = -N—N=O), imidates which are part of polyazaheteroaromatic systems (**1**, X—Y=Z = -N—C=N-),[10,11,16] isonitriles[17] (**1**, X—Y=Z = -N=C:), and a vinylogous thio ester[2] (**1**, X—Y=Z = -S—C=O); this factor could be important for carbanions from isothiocyanates[20] (**1**, X—Y=Z = -N=C=S) and dithioimidates[21] (**1**, X—Y=Z = SC(S)=N-). We wish to draw attention to the formal correlation among carbanions stabilized by these different functions, to suggest that dipole-stabilized carbanions may be more accessible as reaction intermediates than previously suspected, and to provide two examples of novel reactions which appear to involve such species.

Reaction of methyl thiobenzoate (**2**) with lithium 2,2,6,6-tetramethylpiperidide[25] in tetrahydrofuran at ambient temperature gives a 64% yield[26] of dibenzoylmethane (**3**). Reaction of dimethylbenzamide (**4**) under the same conditions gives a 60% yield of methylphenacylbenzamide (**5**).[27]

$$\underset{\textbf{2}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}SCH_3} \xrightarrow{R_2NLi} \underset{\textbf{3}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5}$$

$$\underset{\textbf{4}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}N(CH_3)_2} \xrightarrow{R_2NLi} \underset{\textbf{5}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle CH_3}{|}}{N}CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5}$$

These transformations can be reasonably postulated to involve initial formation of the dipole-stabilized carbanion **6**. Conversion of **6** to products could follow at least two different routes: intramolecular rearrangement to give **7** which reacts with **2** or **4** to give **8**, or direct reaction of **6** with **2** or **4** to give **8**. The conversion of **8**, X = S, to **3** could involve intramolecular rearrangement of **8** or reaction with another molecule of **2** and cleavage of the $\alpha$ sulfur–carbon bond induced by the thiolate.[28]

The postulation of **6** (X = S) as a reaction intermediate appears to be the first suggestion that the thio ester function might act as a dipole-stabilizing function for a carbanion, although d-orbital effects may be impor-

(23) Inductive stabilization by different dipoles is generally noted as a possible contributor to anion stability: D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 2.
(24) For an excellent review of $\alpha$-heteroatom-substituted organometallic compounds, see D. J. Peterson, *Organometal. Chem. Rev., Sect. A*, **7**, 295 (1972).
(25) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973), and references cited therein.
(26) The crude yield is 84%, based on 3 mol of starting thio ester.
(27) The material is identical by melting point, mixture melting point, nmr, and ir spectral criteria with independently prepared material: D. G. Ott, F. N. Hayes, and V. N. Keir, *J. Amer. Chem. Soc.*, **78**, 1941 (1956).
(28) M. Oki, W. Funakoshi, and A. Nakamura, *Bull. Chem. Soc. Jap.*, **44**, 828 (1971).