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# NITROGEN CONFIGURATIONAL STABILITY: THE EFFECT OF A NEIGHBORING FERROCENE GROUP

ROBERT DAMRAUER
*Chemistry Department, University of Colorado Denver Center, Denver, Colorado 80202 (U.S.A.)*

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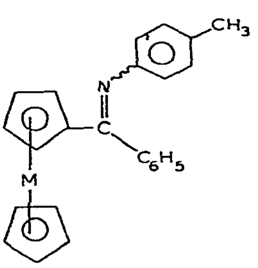
## SUMMARY

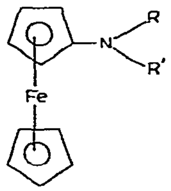
The diastereotopic benzyl group has been used to probe dynamic effects in systems where a ferrocene group and nitrogen are directly $\sigma$-bonded. We have studied the effect of a ferrocene group on nitrogen inversion as well as observing interesting rotational phenomena in *N*-ferrocenyl-benzamides and -acetamides.

## INTRODUCTION

We have been interested in the effect of organometallic groups on the configurational stability of neighboring nitrogen[1] largely because of a report by Schlögl and Mechter[2] that diferrocenylcarbodiimide had been resolved. Their report suggested a large effect by the ferrocene group since other carbodiimides are configurationally unstable at room temperature[3]*. To assess in depth the effect of the ferrocene group we began a program in which the ferrocene group was placed in different chemical environments with respect to nitrogen. Temperature-dependent NMR studies of the imines (I) and (II) showed that the metallocene group has little effect on *syn–anti* isomerization[1]. Thus, coalescence temperature data for (I) and (II) do not differ significantly from data in which the metallocene group is replaced by an aryl function[1]. In this paper we report on some dynamic aspects of the solution character of compounds (III)–(VI).



(I), M = Fe;
(II), M = Ru



(III)[4], $R{=}CH_2C_6H_5$ and $R'{=}COC_6H_5$;
(IV), $R{=}CH_2C_6H_5$ and $R'{=}COCH_3$;
(V), $R{=}CH_3$ and $R'{=}COC_6H_5$;
(VI)[4], $R{=}CH_2C_6H_5$ and $R'{=}CH_2CH_3$

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* Our investigation of the diferrocenylcarbodiimide system has led to the preliminary conclusion that Schlögl and Mechter's observation[2] is incorrect. See also footnote 5 in ref. 3.

## RESULTS

We have examined the NMR spectra of compounds (III)–(VI) over wide temperature ranges and have listed our observations in Table 1. The benzamide, (III), has been studied in the most detail. Examination of the benzyl hydrogen signal in toluene-$d_8$, dichlorodifluoromethane, and dimethyl ether show a distinct low temperature broadening of the benzyl singlet followed by disappearance of the signal. Further cooling results in the appearance of two benzyl signals. Only in dimethyl ether is the reappearance of the benzyl signal clearly discernable as an AB quartet. High temperature spectra in toluene-$d_8$ and diphenyl ether show no unusual effects.

TABLE 1

| Compound | Temp. range (°C) | Solvent | Comments on signal splitting |
|---|---|---|---|
| (III) | −80 to room temp. | Toluene-$d_8$ | $CH_2$'s sharp singlet at RT, broaden to −40°, signal disappears from −45° to −75°, at −80° signal reappears as two broad lines (Δν 211 Hz) |
| | −114 to room temp. | $CF_2Cl_2$ | $CH_2$'s sharp singlet at RT, broaden to −50°, signal disappears from −55° to −90°, at −94° reappears as two broad lines (Δν 191 Hz) |
| | −120 to room temp. | $(CH_3)_2O$ | $CH_2$'s sharp singlet at RT, broaden to −53°, signal disappears from −55° to −95°, reappears as AB quartet at −98° ($J=16$) (Δν 111 Hz) |
| | Room temp. to 130 | Toluene-$d_8$ | $CH_2$'s remain sharp singlet |
| | 160 | $(C_6H_5)_2O$ | $CH_2$'s remain sharp singlet |
| (IV) | −128 to room temp. | $(CH_3)_2O$ | $CH_2$'s singlet at RT, from RT to −58° signal sharpens, from −60 to −95° broadens, signal disappears from −98 to −105°, reappears at −108° as two broad signals, at −118° sharpens to AB quartet ($J=15$) (Δν 104 Hz) |
| | −118 to room temp. | $(CH_3)_2O$ | $CH_3$ remains singlet |
| | Room temp. to 120 | Toluene-$d_8$ | $CH_2$'s remain singlets |
| | 60 to 200 | $(C_6H_5)_2O$ | $CH_3$ and $CH_2$'s remain singlets |
| (V) | −120 to room temp. | $CH_2{=}CHCl$ | $CH_3$ sharp singlet to −100°, below −100° the whole spectrum broadens |
| | −87 to room temp. | Toluene-$d_8$ | $CH_3$ remains sharp singlet |
| | Room temp. to 120 | Toluene-$d_8$ | $CH_3$ remains sharp singlet |
| | 60 to 200 | $(C_6H_5)_2O$ | $CH_3$ remains sharp singlet |
| (VI) | −140 to −60 | $CH_2{=}CHCl$ | $CH_2$'s sharp singlet at −60°, broadens continuously to −140° |
| | −130 to −60 | $(CH_3)_2O$ | $CH_2$'s sharp singlet at −60°, broadens continuously to −130° |

Compound (IV) behaves in a similar manner. An AB quartet has been observed in dimethyl ether and no unusual effects have been found in spectra taken up to 180°. The added structural feature of the acetyl group in (IV) gives us a second probe to examine the dynamic aspects of these compounds. The methyl signal, however, remains a singlet through the entire temperature range of −128 to 200°.

Compound (V) has shown no spectral changes in the temperature ranges indicated in Table 1. Compound (VI) shows no splitting of the benzyl hydrogen signal at low temperatures. Significant broadening of the signal does, however, occur.

All of the dynamic phenomena suggested by the spectral changes outlined have been shown to be reversible. Quantitative analysis of the dynamic spectral changes has proved impossible. The necessity of employing solvents like dimethyl ether (*i.e.*, non-deuterated) has led to spectra which are unsuitable for line-shape analysis. Distortions of the signals to be analyzed caused by the solvent have led to rates (and ultimately to barrier heights) of a high degree of uncertainty.

## DISCUSSION

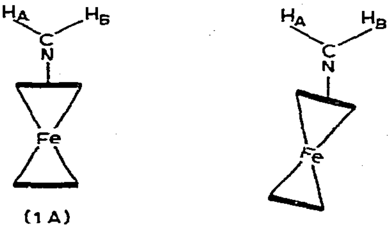
Although accurate determinations of barrier heights have proved impossible, we estimate barrier heights of $\simeq 8$ kcal/mole for the restricted process in compounds (III) and (IV) by analogy with NMR temperature studies of related compounds[5,6].

Data for the amides, (III)–(V), have been examined with particular attention to three dynamic processes: (1) rotation about N–CO (N–R′), (2) rotation about N–Fc (Fc-ferrocenyl), and (3) rotation about N-alkyl (N–R). The first of these is a well known phenomenon which is usually accessable to NMR temperature studies; *cis* and *trans* isomers have been assigned on the basis of NMR chemical shifts, coupling, and nuclear Overhauser effects[5,7]. Examination of our amide NMR data gives no indication of slow rotation about the N–CO bond: the methyl signals of (IV) and (V) remained singlets throughout the temperature range studied and we observed AB coupling in the benzyl signals of (III) and (IV) ($J = 16$ and 15 Hz, respectively) in low temperature spectra in dimethyl ether. These data suggest that it is unlikely that the dynamic process which is being slowed is N–CO rotation, since it is improbable that the *cis* and *trans* isomers of both (IV) and (V) would have accidentally equivalent methyl group chemical shifts. We suggest that amides (III)–(V) exist largely as single isomers. It is difficult from our data to rule out a rapidly rotating N–CO bond, but we feel that barrier data on other amides[5], coupled with the temperature range studied herein, make the possibility remote.

Restricted N–Fc rotation can result in benzyl hydrogen non-equivalence in compounds (III) and (IV). Two conformations shown in Fig. 1 serve to illustrate this. In A we see a conformation with a plane of symmetry passing through the molecule such that $H_A$ and $H_B$ are equivalent. Fig. 1B results from N–Fc rotation and points out the non-equivalence of $H_A$ and $H_B$. The data presented in Table 1 are consistent with restricted N–Fc rotation resulting in the population of a conformation like the one shown in Fig. 1B. It should be clear that when conformations like 1B are populated, $H_A$ and $H_B$ are always non-equivalent regardless of the rate $N{-}CH_2C_6H_5$ rotation.

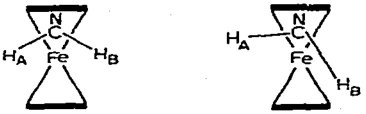
The data presented are also consistent with restricted $N{-}CH_2C_6H_5$ rotation. Reference to Fig. 2 indicates both a symmetrical and an unsymmetrical conformation when we focus our attention on rotation about the benzyl group. Thus, population of a conformer like 2B leads to non-equivalence of the benzyl hydrogens of (III) and (IV).

The complicated nature of the restricted dynamic process(es) is best seen using Fisher–Taylor–Hirschfelder models. We are unable, based on our data and with



(1 A)

(1 B)



(2A)

(2B)

Fig. 1. An end-on view of the $FcNCH_AH_B$ moiety. Neither the carbonyl substituent attached to N nor the $C_6H_5$ attached to C is shown. Both substituents can be symmetrically disposed in A.

Fig. 2. An end-on view of the $H_AH_BCNFc$ moiety. Neither the carbonyl substituent attached to N nor the $C_6H_5$ attached to C is shown. Both substituents can be symmetrically disposed in A.

reference to such models, to assess the relative importance of restricted N–Fc and/or $N–CH_2C_6H_5$ rotation. The models of (III) and (IV) indicate that steric interactions are of overwhelming importance, but, in addition, make it clear that because of the complexity of these interactions further analysis of the restricted process(es) would be quite tenuous. Suffice it to say that rotational constraints about either N–Fc or $N–CH_2C_6H_5$ (or both) give rise to benzyl hydrogen non-equivalence at low temperatures and that further analysis of such constraints appears very difficult*.

Our attempt to assess the effect of the ferrocenyl group on the inversional configurational stability of nitrogen has been unsuccessful. Although significant line broadening of the benzyl hydrogens occurred, we were unable to detect AB-type splitting. The broadening may be caused by non-equivalence of these hydrogens, but such broadening appears to be a common phenomenon in benzyl amines[6]. Our observations suggest that the ferrocenyl group is not strongly influencing nitrogen inversion (at least in a stabilizing way).

We conclude that the ferrocene group does not exercise any unusual electronic effects in the systems studied. Although dynamic processes have been isolated and studied, these are believed to be controlled very largely by steric considerations.

## EXPERIMENTAL

### *General comments*

Elemental analyses were performed by Huffman Laboratories (Wheatridge, Colorado). IR spectra were recorded using a Perkin–Elmer 237B grating IR spectrophotometer. The NMR spectra used for characterization purposes were recorded on either a Varian Associates A-60A or HA-100 spectrometer. All NMR temperature studies were performed using the HA-100 equipped with a Varian Associates 6040 Variable Temperature Controller. Temperature measurements were made using the methanol separation-calibration method (with extrapolation to very low temperatures). These measurements were carried out before and after each temperature run. Excellent agreement was found between the measurements. The mass spectra have been recorded on an AEI MS-12 Mass Spectrometer.

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* D. L. Weaver has undertaken X-ray crystallographic analysis of (III) and (IV).

### *Preparation of N-benzyl-N-ferrocenylbenzamide (III)*[4]

Compound (III) was prepared by the method outlined in ref. 5 by benzoylation of benzylferrocenylamine. The crude yield was quantitative. Purification was carried out by sublimation at 0.3 mm. Room temperature sublimation gives benzoic acid; as the temperature was raised to 130°, (III) sublimed. Purified yield: 67% with m.p. 130–131° (lit.[4] 134.5–135.5°).

The IR spectrum ($CCl_4$) showed principal bands at 3100–3000 w, 3000–2850 w, 1650 s, 1475 m, 1410 m, 1370 m, and 1300 m $cm^{-1}$. The NMR spectrum (HA-100) (toluene-$d_8$) consisted of peaks at 3.55(t) (2H), 3.79(t) (2H), 3.93(s) (5H), 5.28(s) (2H), and 6.85–7.50(m) (10H) ppm. The mass spectrum showed principal *m/e* (intensity) peaks at: molecular ion 395(100), 396(36), 397(5), 394(3), 393(8), 304(17), 224(11), 133(12), 121(17), 105(21), 91(63), and 77(20).

### *Preparation of N-benzyl-N-ferrocenylacetamide (IV)*

Into a 50 ml 1-necked flask equipped with a reflux condenser was charged 0.2 g (0.7 mmole) of benzylferrocenylamine[4] and 0.6 ml of acetic anhydride. The mixture was heated to reflux for 4–5 min. After addition of 6 ml of water, a yellowish oil separated. The oil was taken up in diethyl ether, separated, and dried over $MgSO_4$. The ether solution was rotary evaporated leaving 0.15 g (65%) of a yellow solid. This was sublimed at 0.1 mm/80° (initially some beads of liquid condensed and were removed) giving an analytical sample of (IV) melting at 87–88°. (Found: C, 68.43; H, 5.97. $C_{19}H_{19}FeNO$ calcd.: C, 68.48; H, 5.75%.)

The IR spectrum ($CCl_4$) had principal bands at 3100 w, 3075 w, 3030 w, 2930 m, 2860 w, 1660 s, 1465 m, 1400 w, 1375 m, and 1285 m $cm^{-1}$. The NMR spectrum (A-60A) ($CCl_4$) consisted of peaks at 1.97(s) (3H), 3.98(m) (2H), 4.07(s) (5H), 4.15(m) (2H), 5.06(s) (2H), and 7.30(s) (5H) ppm. The mass spectrum showed principal *m/e* (intensity) peaks at: molecular ion 333(100), 334(30), 335(4), 332(2), 331(11), 291(17), 268(31), 242(14), 228(11), 227(53), 202(33), 200(13), 199(15), 133(21), 121(48), and 91(48).

### *Preparation of crude N-methylferrocenylamine*[8]

Into a 250 ml 3-necked flask equipped with magnetic stirring bar, reflux condenser, dropping funnel, and nitrogen inlet system was charged 0.15 g (4.0 mmole) of lithium aluminum hydride[9] and 5 ml of dry diethyl ether. To this mixture 0.85 g (2.5 mmole) of the benzylurethane, $FcNHCO_2CH_2C_6H_5$[8,10], dissolved in 40 ml of diethyl ether was added. The addition was but slightly exothermic. After refluxing overnight, the mixture was poured into 40 ml of water. The ether layer was separated and dried over $MgSO_4$. Rotary evaporation (0.2 mm) gave 0.55 g of a brown semi-solid material used directly in the following procedure.

### *Preparation of N-ferrocenyl-N-methylbenzamide (V)*

Crude *N*-methylferrocenylamine (0.55 g; 2.5 mmole) and 3 ml of 10% NaOH were mixed in a stoppered 50 ml Erlenmeyer flask. The rapid addition of 1.41 g (10 mmole) of benzoyl chloride was exothermic. After shaking a few minutes a brown solid precipitated. The pH was adjusted to 2 and the mixture was allowed to stand overnight. Addition of diethyl ether caused a yellow precipitate to form. This was collected: 0.34 g (42% from the urethane), m.p. 120–121°. The crude amine was sublimed at 0.13

mm and room temperature to remove excess benzoic acid. When the temperature was raised to 90° an analytical sample of (V) was collected melting at 125–125.5°. (Found: C, 67.61; H, 5.43. $C_{18}H_{17}FeNO$ calcd.: C, 67.73; H, 5.37%.)

The IR spectrum ($CCl_4$) had principal bands at 3100 w, 3060 w, 3030 w, 2925 w, 1640 s, 1480 m, 1445 w, 1415 m, 1400 m, 1365 m, 1350 m, 1325 m, and 1285 m $cm^{-1}$. The NMR spectrum (HA-100) (toluene-$d_8$) consisted of peaks at 3.26(s) (3H), 3.62(t) (2H), 3.80(t) (2H), 3.92(s) (5H), and 6.80–7.40(m) (5H) ppm. The mass spectrum had principal *m/e* (intensity) peaks at: molecular ion 319(87), 320(30), 321(4), 318(3), 317(8), 254(45), 186(13), 121(24), 118(100), 105(18), and 77(28).

### *Preparation of benzylethylferrocenylamine (VI)*[4]

Compound (VI) was prepared by the method outlined in ref. 5 by the ethylation of benzylferrocenylamine with triethyloxonium tetrafluoroborate. We obtained a 26% yield of (VI), m.p. 44–46° (lit.[4] 48–48.5°).

The IR spectrum (KBr) had principal bands at 3100 w, 3070 w, 3030 w, 2980 m, 2940 m, 2900 m, 2875 m, 1510 m, 1465 w, 1450 m, 1400 w, 1375(2), 1305 w, 1255 m, 1130 s, and 1100 s $cm^{-1}$. The NMR spectrum (A-60A) ($CDCl_3$) consisted of peaks at 1.18(t) (3H), 3.06(q) (2H), 3.75(t) (2H), 3.89(t) (2H), 4.18(s) (7H)*, and 7.32(s) (5H) ppm. The mass spectrum had principal *m/e* (intensity) peaks at: molecular ion 319(100), 320(46), 321(6), 318(4), 317(14), 228(39), 214(15), 213(71), 212(17), 186(46), 121(45), and 91(24).

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* The benzyl hydrogens and the unsubstituted cyclopentadienyl both have absorptions at 4.18 ppm. As the temperature is lowered these signals separate.