

### Preliminary communication

## ELECTROPHILIC REACTIONS AT THE CYANOMETHYL LIGAND IN THE ELECTRON RICH COMPLEX FeCp(dppe)CH<sub>2</sub>CN

P.M. TREICHEL\*, D.W. FIRSICH, and T.H. LEMMEN

*Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)*

(Received August 1st, 1980)

### Summary

Protonation or alkylation (MeOSO<sub>2</sub>F) of the electron-rich complex FeCp(dppe)CH<sub>2</sub>CN (dppe = 1,2-bis(diphenylphosphine)ethane) is accompanied by an unexpected intramolecular rearrangement to give new carbene complexes. The interesting step in this rearrangement is believed to be the electrophilic attack of the methylene carbon of an η<sup>2</sup>-CH<sub>2</sub>CNR group at a cyclopentadienyl carbon atom; no precedent exists for this process. A crystal structure on the protonated complex (as the PF<sub>6</sub><sup>-</sup> salt) was carried out.

The reaction of FeCp(CO)<sub>2</sub>CH<sub>2</sub>CN (I) with acids was reported in 1963 [1] to give an η<sup>2</sup>-ketenimine complex of iron:



This is the only known complex having an η<sup>2</sup>-ketenimine ligand. Complexes of N,N-dialkylketenimmonium ligands have been reported [2]; however, their preparation was accomplished by a quite different synthetic method.

We were interested in learning what effect there might be in this reaction if the two carbonyl groups in the starting material were replaced by good donor ligands such as phosphines\*. In fact, samples of the compound FeCp(dppe)CH<sub>2</sub>CN (II) were available from earlier work\*\*. The preliminary view was that this precursor would be considerably more basic, a consequence

\*Substitution of CO's by good donor ligands would give electron-rich complexes. Such species have characteristic chemistry which contrasts to the chemistry of carbonyl complexes; see ref. 3.

\*\*Prepared by photolysis of FeCp(CO)<sub>2</sub>CH<sub>2</sub>CN with dppe in CH<sub>3</sub>CN [4].

of the good donor ability of the phosphine ligands relative to CO; we hoped to assess this by determining the  $pK_b$  for this species and comparing this value to the value of 13–14 estimated for  $\text{FeCp}(\text{CO})_2\text{CH}_2\text{CN}$ . This proved not to be possible however when it was determined that the reaction followed a different course to an unexpected product.

When  $\text{HBr}$  (g) was bubbled into a toluene solution of II a yellow precipitate formed. This was separated, and converted to a  $\text{PF}_6^-$  salt by metathesis using  $\text{NH}_4\text{PF}_6$  in acetone. This product, IIIa, crystallizes as yellow needles from  $\text{CH}_2\text{Cl}_2$ /heptane (30%). An infrared spectrum reveals peaks at 3355 ( $\nu(\text{NH})$ ) and at  $1530\text{ cm}^{-1}$  (associated with the carbene ligand); its NMR spectrum contains resonances at  $\delta$  2.45 (d, int. 4,  $\text{CH}_2\text{CH}_2$ ), 3.44 (s, int. 2,  $\text{CH}_2$ ), 4.21 (m, int. 2) and 5.46 (m, int. 2), and at 6.50 and 7.40 ppm (m, int. 20,  $\text{C}_6\text{H}_5$ ). A similar reaction between II and  $\text{MeOSO}_2\text{F}$  occurs to give, after  $\text{PF}_6^-$  metathesis, IIIb in 57% yield. Data on IIIb include IR absorptions at 3370 and  $1540\text{ cm}^{-1}$ , and NMR resonances at  $\delta$  2.30 (d, int. 3,  $\text{CH}_3$ ), 2.48 (d, int. 4,  $\text{CH}_2\text{CH}_2$ ), 3.43 (s, int. 2,  $\text{CH}_2$ ), 4.15 (m, int. 2), 5.47 (M, int. 2), 6.34 (Br, int. 1, NH) and 7.48 ppm (m, int. 20,  $\text{C}_6\text{H}_5$ ). Significant is the lack of an intensity = 5 cyclopentadienyl proton resonance and the appearance in each spectrum of two new resonances of intensity 2 at  $\delta \sim 4.2$  and  $\sim 5.5$  ppm.

A crystal structure study was undertaken on IIIa. Crystal data: Space group *Ibca*, one independent molecular unit in a unit cell with cell parameters  $a$  16.841(3),  $b$  27.167(4),  $c$  31.862(5) Å. A total of 3112 diffraction data ( $I >$

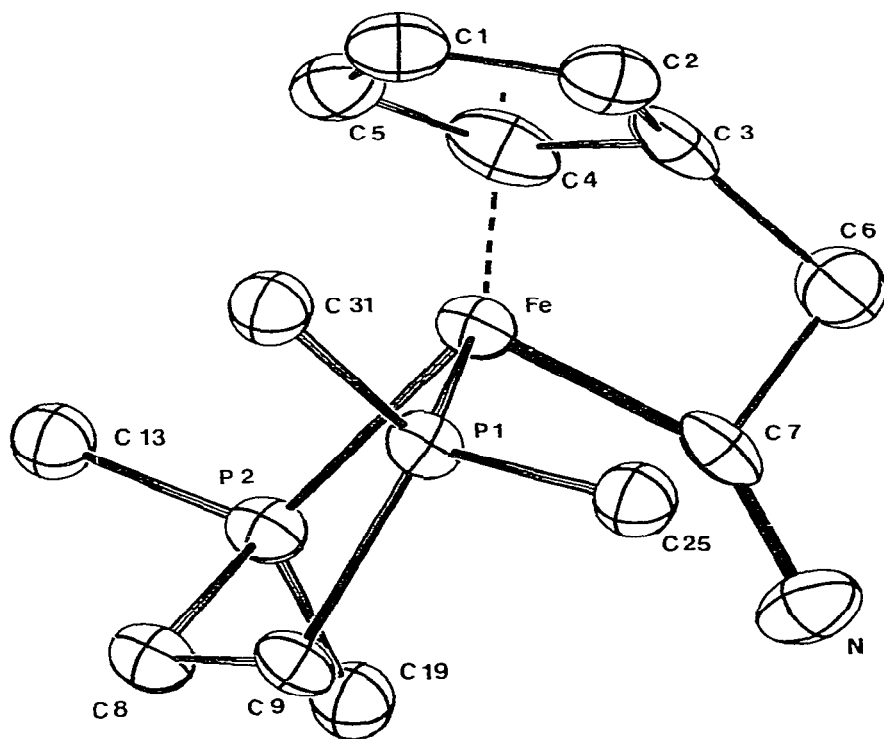


Fig. 1. Molecular structure of the cation,  $[\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{CNH}_2)(\text{dppe})]^+$ . Phenyl groups have been omitted for clarity.

$2\sigma(I)$ ) were collected. The structure was solved by heavy atom methods and refined by isotropic and anisotropic least squares programs to  $R_1 = 0.0868$ . The structure of the cation is displayed in Fig. 1. Bond lengths for the planar metal-carbene portion of the structure are: Fe—C(7), 1.862(14) Å; C(7)—N, 1.305(14) Å; C(7)—C(6), 1.515(15) Å; bond angles are: FeC(7)C(6), 98.9(9)°; FeC(7)N, 140.8(1.0)°; C(6)C(7)N, 119.2(1.3)°. The cyclopentadienyl ring is canted somewhat because of its attachment at C(3) to the coordinated carbene. Thus the ring-metal distances vary 2.016(12) Å for Fe—C(3) to 2.165(12) Å, the average value for Fe—C(1) and Fe—C(5). Other bond distances and angles are normal.

We believe that formation of IIIa and IIIb in these electrophilic reactions could occur by the route shown in the scheme (Fig. 2). Attack of  $H^+$  or  $R^+$  at nitrogen followed by rearrangement of an  $\eta^2$ -ketenimine complex seems a likely first step, considering the result for the dicarbonyl I and the expected basicity at this site. Rearrangement might then occur giving a second intermediate in which the carbon of the methylene group has some electrophilic character. This complex then rearranges by the intramolecular attack by this carbon on a ring carbon forming a cyclopentadiene complex. Transfer of  $H^+$  from the ring to the more basic nitrogen site would logically follow.

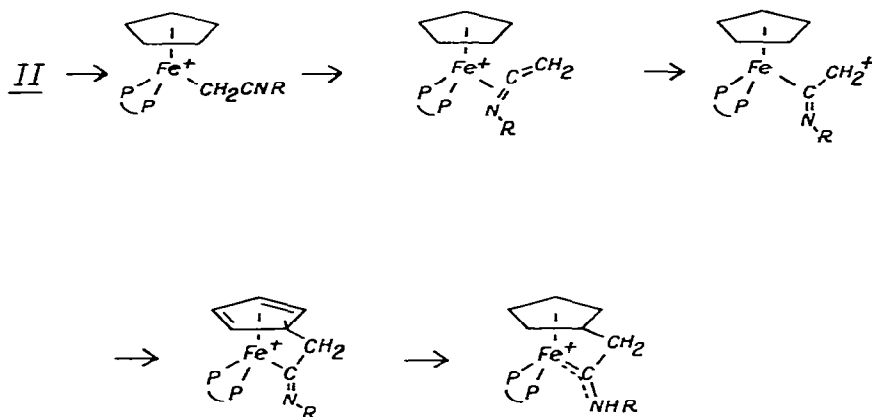


Fig. 2. Proposed mechanism for the formation of IIIa ( $R = H$ ) and IIIb ( $R = Me$ ).

Few intramolecular rearrangements involving transfer of a metal bonded group to a cyclopentadienyl ligand are known and these appear not closely related to this work. An *o*-carboranyl-acyliron species,  $Fe(C_5H_5)(CO)_2CO-(C_2B_{10}H_{11})$  is known to undergo an intermolecular rearrangement; nucleophilic attack at the cyclopentadienyl group may be involved in this example [5]. In addition pyrolyses of cyclopentadienyl-alkylmetal complexes sometimes yield alkylcyclopentadienyl species [6] via a presumed radical pathway. The rearrangement in this cyanomethyliron system seems rather more closely related to the intramolecular transfer of  $H^+$  from a metal to a coordinated hydrocarbon, a process which also involves intramolecular electrophilic attack.

We acknowledge the partial support for this work provided by the University of Wisconsin Graduate School.

## References

- 1 J.K.P. Ariyaratne and M.L.H. Green, *J. Chem. Soc.*, (1963) 2976.
- 2 R.B. King and K.C. Hodges, *J. Amer. Chem. Soc.*, 97 (1975) 2702.
- 3 P.M. Treichel, K.P. Wagner, and H.J. Mueh, *J. Organometal. Chem.*, 86 (1975) C13.
- 4 D.W. Firsich, Ph.D. Thesis, University of Wisconsin, 1979.
- 5 L.I. Zakharkin, L.V. Orlova, A.I. Kovredov, L.A. Federov, and B.V. Lokshin, *J. Organometal. Ch* 27 (1971) 95.
- 6 J.A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1963) 4096.