

The details of the experimental method, calculations and a complete discussion of their bearing on the concepts of chemical bonding in ferrocene proposed and discussed by various workers<sup>6,11-13</sup> will be published elsewhere.

The author wishes to thank the Research Corporation and the Monsanto Chemical Co. for supporting this work.

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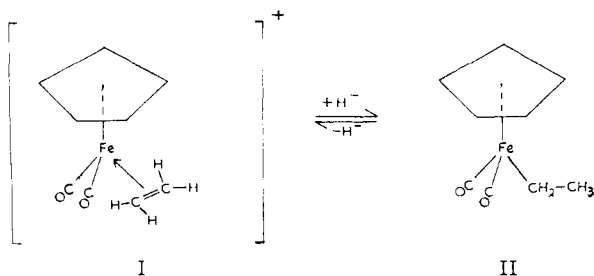
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### HYDRIDE ADDITION TO SOME $\pi$ -BONDED OLEFIN-IRON COMPLEXES

Sir:

We have noted previously the abstraction of a hydride ion from some  $\sigma$ -bonded iron-alkyl complexes.<sup>1</sup> We now report that this reaction is reversible and that reduction with sodium borohydride of tetrahydrofuran solutions of the cation perchlorates,  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2=\text{CHR}]^+\text{ClO}_4^-$  where R = H, Me,<sup>1,2,3</sup> forms  $\sigma$ -alkyl complexes. The cation (I), R = H, gives the ethyl complex



(II) in good yields. The product was identified by comparison of the infrared and proton magnetic resonance spectra with those of a sample of the ethyl compound prepared as previously reported.<sup>4</sup> Reduction of the cation (III), R = Me, gives the isopropyl complex (IV) in high yield. The isopropyl complex was identified by the comparison of the spectra with those of characterized samples of the isopropyl and *n*-propyl complexes prepared by the reaction of the sodium salt,  $\text{Na}^+[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with the propyl halides.<sup>5</sup> No *n*-propyl isomer was found in the reaction products. The major product of the reduction of the cation  $[\text{Mn}(\text{CO})_5\text{propene}]^+$ ,<sup>5</sup> under similar conditions, was manganese carbonyl. When the reduction of the cation (III) was carried out in the presence of a large excess of 1-hexene and also of butadiene only the isopropyl complex (IV) was formed. It therefore seems reasonable that the reaction proceeds by an internal mechanism rather than by the prior formation of the hydride  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}^6$  and

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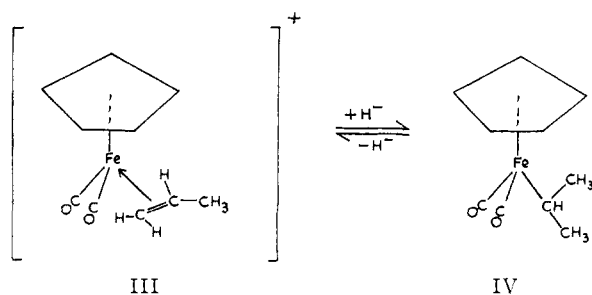
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expulsion of the propene, followed by the addition of the Fe-H across the olefinic double bond. This latter reaction has been shown separately.<sup>5</sup> The reaction may proceed by hydride ion attack either on the metal, as suggested for the reduction of the related cobalticinium cation,<sup>7</sup> or on the cyclopentadienyl group, with transfer from the intermediate cyclopentadiene complex to the ethylenic group,<sup>8</sup> or directly on the ethylenic group.

Since the propene cation (III) may be prepared readily from the *n*-propyl complex,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2n\text{-propyl}$ ,<sup>1</sup> and its reduction gives high yields of the isopropyl complex (IV), the isomerization of the *n*-propyl to isopropyl may be understood as a simple, two-step hydride removal and addition process. This mechanism is very similar to that put forward recently for the isomerization of olefins on metal surfaces.<sup>8</sup> Also this reversible conversion of alkyl to olefin complexes very clearly bears a strong relationship to the intermediate steps postulated to occur in the hydroformylation, Fischer-Tropsch and related reactions.<sup>8</sup>

**Acknowledgments.**—We thank the International Nickel Company (Mond) Ltd. for a gift of iron carbonyl, the Ethyl Corporation for a gift of manganese carbonyl and the Hungarian Relief Fund for financial support to P.L.I.N.

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### A NEW SYNTHESIS OF BARBITURIC ACIDS

Sir:

We wish to report that the reaction of carbodiimides with substituted malonic acids leads to barbiturates in many instances. Thus, when malonic acid and two moles of *N,N'*-dicyclohexylcarbodiimide were brought together in tetrahydrofuran solution, an exothermic reaction ensued with the separation of crystalline *N,N'*-dicyclohexylurea. On filtering off the urea and evaporating the tetrahydrofuran solution, a colorless crystalline compound I, m.p. 200–201°, was obtained in 65% yield (based on the malonic acid). *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_3$ : C, 65.72; H, 8.27; N, 9.58. Found: C, 66.00; H, 8.19; N, 9.39.

Partly on the basis of n.m.r. and infrared spectra, the barbituric acid structure I was assigned to this compound. The correctness of this assignment was later proved by the synthesis of I by the action of malonyl chloride on *N,N'*-dicyclohexylurea.