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Preliminary communication

THE INFLUENCE OF A CYANO-SUBSTITUENT ON AN ALKYLIRON ISOMERIZATION REACTION

D.L. REGER and P.J. McELLIGOTT
Department of Chemistry, University of South Carolina, Columbia, S.C. 29208 (U.S.A.)

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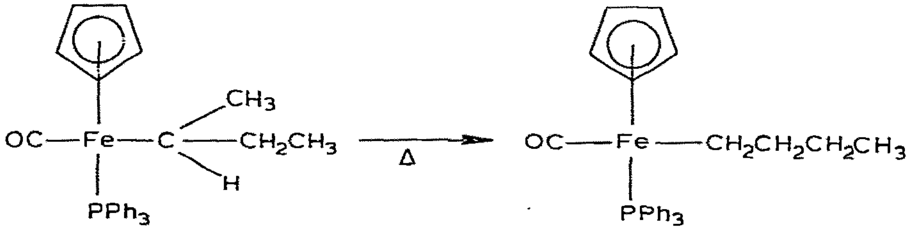
Summary

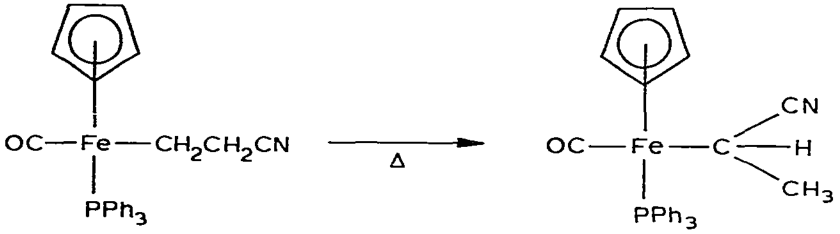
The complex $CpFe(CO)(PPh_3)(\sigma\text{-}CH_2CH_2CN)$ cleanly undergoes an isomerization reaction to $CpFe(CO)(PPh_3)(\sigma\text{-}CH(CH_3)CN)$ when heated in solution at 95°C. The electron-withdrawing cyano group thus stabilizes a secondary alkylmetal complex in preference to the isomer containing a primary carbon to iron bond.

The isomerization of an alkyl group in alkylmetal complexes is a potentially important process in many reactions catalyzed by transition metal-hydride compounds [1]. Previous work has shown that secondary alkylmetal ligands isomerize to a primary isomer [2,3]. Thus, for example, we have shown previously that the reaction shown in eq. 1 takes place readily in toluene solution [2a].



(1)

Bennett et al. [3], working with alkyliridium complexes, have suggested that the driving force for these reactions is mainly steric in nature. We are attempting to introduce substituents on the alkyl ligand to determine the importance of possible electronic effects on these isomerization reactions. Although partially frustrated by synthetic problems, we report here the first example of the exclusive isomerization of an alkylmetal complex containing a primary alkyl to a secondary alkyl isomer.



(I) (II) (2)

Heating the β-cyano-substituted complex I [4] at 95°C for 3 h in toluene solution causes the complete isomerization to the α-cyano isomer II (eq. 2). II can be isolated in good yield as a red solid. This isomerization reaction is easily followed by IR where the ν(CN) of I (2225 cm^{-1}) shifts 40 wave-numbers lower in II. The anomalously low ν(CN) of an α-cyano substituent in complexes of this type has been reported previously [4].

The ^{1}H NMR spectrum (60 MHz) of II is also very characteristic, showing the methyl group as a doublet (J 7.3 Hz) at δ 1.3 ppm and a complex resonance for the methine hydrogen atom at δ 0.8 ppm in addition to the expected Cp and PPh_3 resonances. Note that in reaction 2 a second chiral center forms α to the chiral center at the iron. It is believed that both possible diastereomers form in equal amounts because in the 400 MHz spectrum each half of the δ 1.3 ppm doublet was observed as two peaks separated by 1.2 Hz. In the 60 and 200 MHz spectra, this resonance is a simple doublet (a 1.0 Hz phosphorus coupling was resolved on the Cp resonance in these spectra). Also, the δ 0.8 ppm complex resonance assigned in the 60 MHz spectrum to the methine hydrogen atom is seen as a quintuplet (two overlapping quartets) at 400 MHz much different in appearance than at 60 MHz. Thus two complexes seem to be present, in this case, the two possible diastereomers.

Reaction 2 demonstrates that the electronic stabilizing effects of the electron-withdrawing cyano substituent is great enough to overcome any negative steric effects. Stabilization of alkylmetal complexes by α-cyano groups has been suggested previously by product isolation studies [5]. These results raise the possibility that isomerization reactions of unsubstituted alkylmetal complexes such as shown in eq. 1 could be caused (or partially caused) by potentially destabilizing electronic effects of the electron-donating alkyl substituents and that they are not totally dominated by steric effects.

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