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Preliminary communication

THE REACTIONS OF [Fe(CO)$_{5-n}$(CNAr)$_n$] (n = 1 OR 2; Ar = ARYL) WITH DICYCLOPENTADIENE

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Summary

Although [Fe(CO)$_3$(CNAr)$_2$] complexes fail to react with dicyclopentadiene at 140°C, under the same conditions [Fe(CO)$_4$(CNAr)] complexes give high yields of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNAr)] and [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(CNAr)$_2$], with the product ratios depending very much on the aryl group (Ar).

We have found that the reaction of dicyclopentadiene with [Fe(CO)$_5$] and various ArNC (Ar = aryl) at 140—150°C gives a mixture of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNAr)] (I) and [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(CNAr)$_2$] (II) together with smaller amounts of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] (III) and [Fe(CO)$_3$(CNAr)$_2$] (IV). At temperatures below 140°C, only IV and [Fe(CO)$_4$(CNAr)] are formed whilst on increasing the amounts of CNAr in the reaction mixtures, the yields of III decrease. As the thermal reaction of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] with ArNC gives solely [Fe$_2$(η-C$_5$H$_5$)$_2$(CNAr)$_4$] [1], it seems unlikely that our reaction proceeds with prior formation of III, and so we have looked at the thermal reactions of various [Fe(CO)$_{5-n}$L$_n$] (n = 1 or 2; L = organoisocyanide) with dicyclopentadiene.

[Fe(CO)$_4$(CNAr)] and [Fe(CO)$_3$(CNAr)$_2$ [2] were heated with dicyclopentadiene in an oil bath at 145°C. Although all of the [Fe(CO)$_3$(CNAr)$_2$] which we looked at failed to react, [Fe(CO)$_4$(CNAr)] gave mixtures of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] (n = 1 or 2) in high yield. Traces of III where n = 0 were formed in some reactions, but derivatives where n = 3 or 4 were never observed. There were no reactions between [Fe(CO)$_4$(CNAr)] and indene, or between [Fe(CO)$_4$(CNMe)] and dicyclopentadiene.

Our observations prompt speculation about the course of these reactions involving [Fe(CO)$_4$L] (L = CO or CNAr). The generally accepted mechanism when L = CO involves (a) the dissociation of dicyclopentadiene to cyclo-

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pentadiene, (b) the formation of $[(\eta^4\text{-}C_5H_6)Fe(CO)_2L]$, (c) its conversion to $(\eta^5\text{-}C_5H_5)Fe(CO)(L)H$ and (d) the thermal decomposition of the hydride to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [3]. This may also be the reaction pathway when L = CNAr with the understanding that in both steps (b) and (c) either CO or CNAr may be lost. However it is difficult to account for the absence of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ from the reaction products even though when e.g. L = $CNC_6H_3Me_2$-2,6 the principal product is $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(L)]$ and on the above mechanism free $[\eta\text{-}C_5H_5)Fe(CO)_2H]$ would have to be formed. Consequently we suggest tentatively that the reaction proceeds by way of olefin-bis-iron carbonyl complexes. In these, the two iron carbonyl moieties are coordinated to the dicyclopentadiene molecule before it dissociates, and they remain intimately associated throughout the reaction sequence which leads to the final products.

Further work is being carried out to clarify the reaction mechanism.

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