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ORGANOMETALLICS IN ORGANIC SYNTHESIS: FORMATION OF CIS 2-ALKENES BY REACTION OF TETRACARBONYLIRON CATIONIC COMPLEXES WITH ORGANO-CADMIUM REAGENTS

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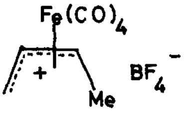
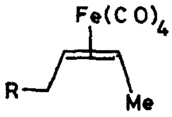
We have recently reported[1] the alkylation of tricarbonylcyclohexadienyliron cations with organo-cadmium and -zinc reagents. This reaction has now been extended to the acyclic tetracarbonyl(methyllallyl)iron complex (1), readily available by published procedures.[2,3]



1



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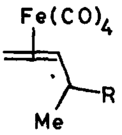
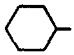


3

4

$RCHMeCH{=}CH_2$

5

R = Ph, $PhCH_2$, 

Slow addition of an ether or THF solution of the dialkyl cadmium reagent (R_2Cd, R = Ph, $PhCH_2$ and cyclohexyl, prepared from the corresponding Grignard reagent) to a stirred suspension of (1) in THF at 0°C under argon, followed by work-up with ammonium chloride solution, ether extraction and chromatography on silica yielded in each case a yellow oil which displayed bands characteristic of the $Fe(CO)_4$ group in the infra-red (e.g. 2, R = $PhCH_2$ ν_{max} cm^{-1} 2080, 2060, 1990, 1965). The compounds, probably (2) and (3), were unstable in solution, iron oxides being deposited on standing under air for a few hours. Subsequent filtration through alumina and removal of solvent gave (4) and (5) in 50 - 60% yield (not optimised) which could be further purified by preparative g.c. All final products gave satisfactory i.r., m.s. and n.m.r., the latter showing that 90% attack occurred at the unsubstituted terminus to give (4) as the major product in all cases, i.e., the reaction is regioselective. Some double bond migration occurred with R = Ph, to give a minor proportion (20 - 25%) of the corresponding styrene derivative.

Comparison of n.m.r. and i.r. of (4, R = $PhCH_2$) with an authentic sample of trans compound, prepared by reaction of benzyl magnesium bromide with trans crotyl chloride, established that (4) is the cis isomer, i.e., the reaction occurs with retention of the cisoid geometry of the allyl cation, as observed in the addition of other nucleophiles.[3] Thus, the trans compound shows the methyl resonance (CCl_4 solution) at τ 8.38,d, J = 3 cps, and ν_{max} 1635 and 970 cm^{-1}, whilst (4) gives τ 8.46,d, J = 5 cps and ν_{max} 1650 with no band at 970 cm^{-1} (characteristic of trans double bond).

The scope of the reaction is presently being investigated.

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