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ORGANOMETALLICS IN ORGANIC SYNTHESIS: ALKYLATIONS OF TRICARBONYLCYCLOHEXADIENYLIRON CATIONIC COMPLEXES WITH ORGANO-ZINC AND -CADMIUM REAGENTS

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Tricarbonylcyclohexadienyliron tetrafluoroborate and hexafluorophosphate salts (1) are readily prepared by hydride abstraction from the neutral tricarbonylcyclohexadieneiron complexes[1] or by the acid-promoted demethoxylation of the appropriate methoxy-substituted complex.[2] The salts react[3,4] readily with nucleophiles such as amines, hydroxide ion, phosphites, sulphites, enamines and ketones (as enols) but so far no direct alkylations have been described. Grignard reagents[1] and *n*-butyllithium have been shown to lead by reductive coupling to bis 5,5'(tricarbonylcyclohexadieneiron) complexes or to decomposition. Alkylations are possible using organo-zinc and -cadmium reagents prepared in ether or THF solution by reaction of the appropriate Grignard reagent with the metal chloride.

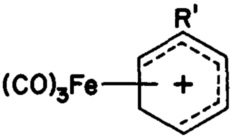
Excess alkylating reagent is added through a rubber septum to a stirred suspension of the salt in dry THF, cooled to 0°C under nitrogen. The resulting mixture is immediately poured into ammonium chloride solution and the product chromatographed on silica in petrol. Usually the cadmium reagents give superior (not yet optimised) yields (Table).

The reaction is regioselective in the 2-substituted salts (1, R' = Me or MeO), n.m.r. spectra showing greater than 90% addition to C-5 to give (2, R' = Me or MeO). All purified products gave satisfactory n.m.r., m.s. and i.r. spectra, a typical example being tricarbonyl (2-methyl-5-isopropylcyclohexa-1,3-diene)iron (2, R' = Me, R'' = Me_2CH), the major stereoisomer formed direct from α-phellandrene[3,5,6] with which it is identical (n.m.r., g.c.); τ ($CDCl_3$) 4.44, 1H m H-3; 6.9, 2H m H-1, H-4; 7.82, 3H s 2-Me; 8.0, 1H m and 8.64, 1H m H_2-6; 8.64, 2H m isopropyl CH and H-5; 9.12, 6H d J = 6Hz isopropyl Me_2. ν_{max} (neat) 2050 and 1970 $Fe(CO)_3$; M^+ 276.

Alkylation therefore occurs on the opposite side of the ring to the $Fe(CO)_3$ group, as is the case with most other irreversible nucleophiles.[3] Attack of a nucleophile from the same side as the $Fe(CO)_3$ appears to occur only when the reaction centre is substituted[5] or when the addition of the nucleophile is reversible. The hydroxy-derivative (2, R' = H, R'' = OH), obtainable by nucleophilic addition of hydroxide to (1, R' = H), and the diastereoisomer, obtainable by borohydride reduction of tricarbonylcyclohexadienoneiron, are equilibrated to the same mixture of the two under conditions where (1, R' = H) can be intermediate.[5]

TABLE

R'	R''	M	Yield %
H	CH_2=CH-CH_2	Cd	82
H	Me_2CH	Cd	52
H	MeCH=CH	Cd	40
H	Ph	Cd	83
H	$PhCH_2$	Cd	72
H	CH_2=CH-CH_2	Zn	65
Me	CH_2=CH-CH_2	Zn	50
OMe	CH_2=CH-CH_2	Zn	35
H	Me_2CH	Zn	35
Me	Me_2CH	Zn	50
OMe	Me_2CH	Zn	10
H	MeCH=CH	Zn	35
Me	MeCH=CH	Zn	45
OMe	MeCH=CH	Zn	40
H	Ph	Zn	67
H	$PhCH_2$	Zn	60



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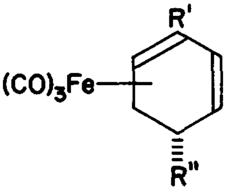

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