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ORGANOMETALLIC COMPOUNDS IN ORGANIC SYNTHESIS : ELECTROPHILIC REACTIONS OF SOME TRICARBONYLCYCLOHEXADIENYLIUM-IRON COMPLEXES WITH ALLYLTRIMETHYL SILANES.

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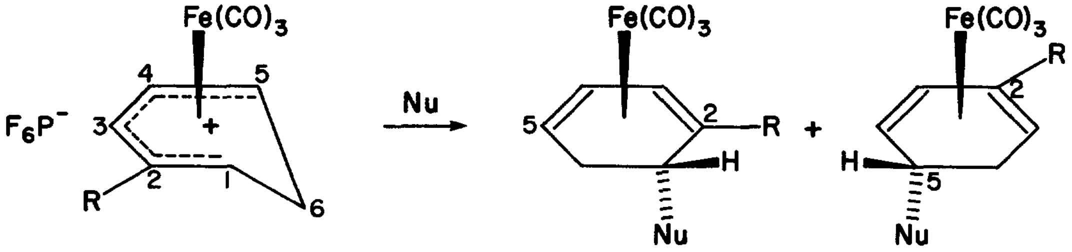
Summary: Allyltrimethylsilanes react with a range of tricarbonylcyclohexadienyl-iron complexes under mild conditions to form new carbon-carbon bonds in excellent yields.

Salts of tricarbonylcyclohexadienyl-iron cations have considerable potentialities in organic synthesis[1]. They react with a wide range of nucleophiles[2] to form new C-X bonds (X = O,S,N,P,C). New C-C bonds are formed using enols (from ketones[3], dicarbonyl derivatives[3]), trimethysilylenol-ethers[4], alkyls derived from boron[5], zinc[6], cadmium[6] and copper[7]. Attack of such reagents is completely stereospecific from the α-side [rear to $Fe(CO)_3$], but regiospecificity is more limited, one useful exception being 2-OMe which directs into an unsubstituted 5-position[3]. Some synthetic uses of the latter have been reported[8], including reactions at a substituted 5-position. Regiospecificity varies with the nucleophile[3] and is probably related partly to kinetic or thermodynamic control of products, partly to steric effects, and partly to charge-distribution in the cation which is assessed using ^{13}C NMR[9].

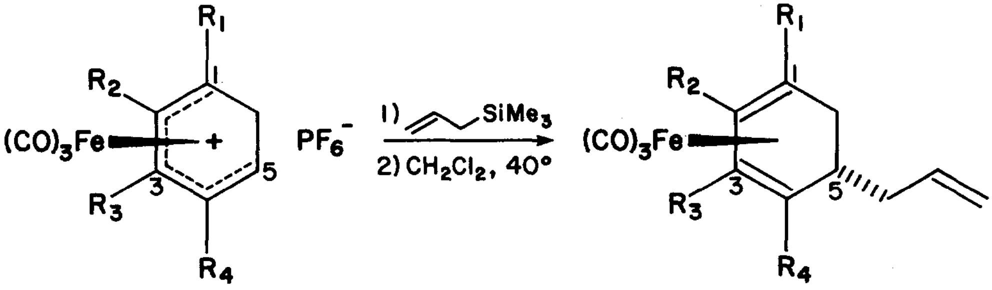
For 2-substituted salts the reactions are:



Nu = Nucleophile

We now describe a new reaction of considerable synthetic potential, offering advantages over previous processes involving organometallic allyl donors, employing allyltrimethylsilanes as shown below.

The advantages of the reagents are: (1) they are stable to air and water; (2) they do not undergo allylic isomerization[10]; (3) they contain an excellent electrofugal group $^{+}SiMe_3$[11]; (4) the double bond is highly nucleophilic[12] but is also capable of reacting with a range of electrophiles[13]. The result of the process shown is transfer of an allyl group to the terminus of a tricarbonylcyclohexadienyliron cation to give a dienyl complex in good yields (52-98%) under very simple experimental conditions.



SALTS		YIELDS (%)	COMPLEX	
(1)	$R_1 = R_2 = R_3 = R_4 = H$	(52)[a]	(6)	$R_1 = R_2 = R_3 = R_4 = H$
(2)	$R_1 = R_3 = R_4 = H;\ R_2 = Me$	(64)[b]	(7)	$R_1 = R_3 = R_4 = H;\ R_2 = Me$
(3)[14]	$R_1 = R_2 = R_4 = H;\ R_3 = OMe$	(77)[c]	(8)	$R_1 = R_2 = R_4 = H;\ R_3 = OMe$
(4)[14]	$R_1 = COOMe;\ R_2 = Me;\ R_3 = R_4 = H$	(80)[d]	(9)	$R_1 = COOMe;\ R_2 = Me;\ R_3 = R_4 = H$
(5)[14]	$R_1 = R_4 = H;\ R_2 \frown R_3 = -(CH_2)_4-$	(98)[e]	(10)	$R_1 = R_4 = H;\ R_2 \frown R_3 = -(CH_2)_4-$

[a] 1.1 equiv $SiMe_3$; CH_3CN, 60°, 8 hrs; [b] 36 hrs

[c] 20 hrs; [d] 1 hr; [e] 23 hrs.

The regiospecificity is high, reaction occurring at the less hindered position. The presence of a substituent such as COOMe is compatible with the process.

A typical experiment simply involves refluxing an excess of allyltrimethylsilane with the salt in dry CH_2Cl_2. As the reaction proceeds the insoluble salt goes into solution and completion of the reaction is monitored by the disappearance of $[Fe(CO)_3]^+$ bands at 2105, 2050 cm^{-1} and appearance of $[Fe(CO)_3]$ bands at 2040, 1980 cm^{-1} in the IR spectrum. After an appropriate reaction time, the excess silane and solvent are removed under vacuo and the neutral complex is obtained as a yellow liquid by a short chromatography over silica gel in hexane.

The structures of the products (6 → 10) are fully supported by their ^1H-NMR data (see Table) and other spectral characteristics (IR and Mass), including combustion values.

TABLE. ^{1}H-NMR Data[a] of Tricarbonylcyclohexadieniron-
Complexes (6 → 10)

Complex	CH_2=CH[b]	H-1	H-2	H-3	H-4	H-5	H-6(2H)		Allyl	Others
						endo	exo	endo	$C\underline{H}_2$	
6	4.78-5.84	3.04	5.3	5.3	3.04	1.6-2.1	1.26	1.8	1.95	-
7	4.76-5.82	2.95	-	5.16[c]	2,96[c]	2.04	1.24	1.9	1.9	C-2,Me 1.08(s)
8	4.78-5.86	2.56	5.08[c]	-	3.34	2.00	1.15	1.8	2.0	C-3,OMe 3.60(s)
9	4.78-5.86	-	-	5.12[d]	3.04[c]	2.2	1.04	2.2	1.96	C-1,COOMe 3.64(s); C-2,Me 2.48(s)
10	4.75-5.86	2.78	-	-	2.78	2.04	1.25	1.85	1.4-2.5	$(CH_2)_4$ 1.40-2.5

[a] Unless otherwise specified all signals are characteristic multiplets, which agree with accepted interpretation; Chemical shifts are in δ values.

[b] Characteristic multiplet; [c] dd, J=6 and 2 Hz; [d] doublet, J = 6Hz

endo - on the same face as [Fe(CO)$_3$]; *exo* - on the face opposite to [Fe(CO)$_3$].

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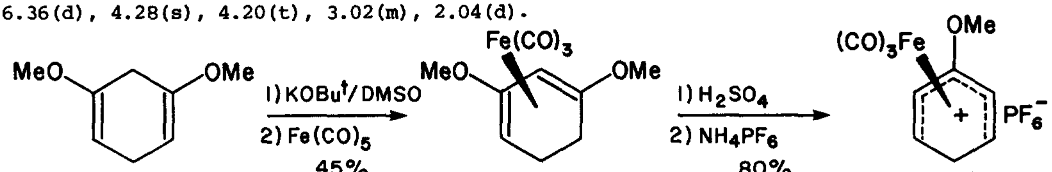
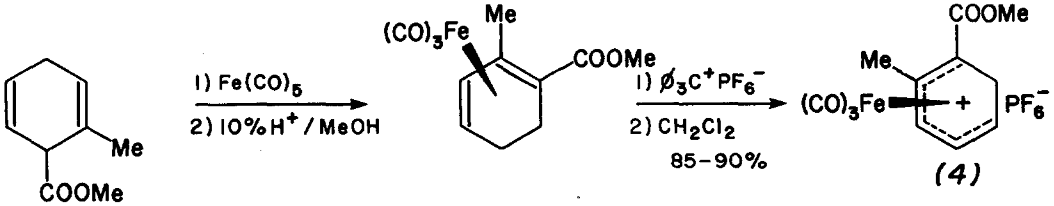
14. Salts 3,4 and 5 were prepared as follows:

Tricarbonyl-(3-methoxycyclohexadienyl)iron hexafluorophosphate (3): ^{1}H-NMR[δ,$(CD_3)_2CO$]^{15}: 6.36(d), 4.28(s), 4.20(t), 3.02(m), 2.04(d).



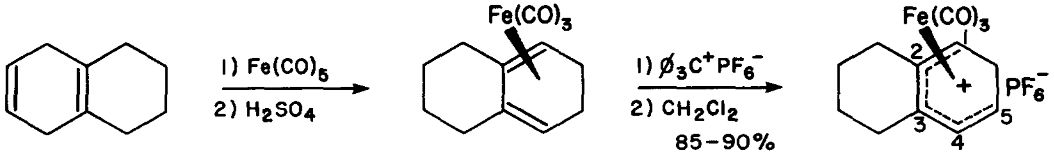
(3)

Tricarbonyl-(1-carbomethoxy-2-methylcyclohexadienyl)iron hexafluorophosphate (4): ^{1}H-NMR[δ,CD_3CN]^{16}: 7.04(d), 5.80(t), 4.66(t), 3.80(s), 3.20(dd), 2.48(s), 2.02(br,d).



(4)

Tricarbonyl-(1-5-η-bicyclo[4,4,0]decadienylium)iron hexafluorophosphate (5); ^{1}H-NMR[δ,CD_3CN]: 5.76(d) 4.30(t), 3.76(d), 1.8-3.2(m)



(5)

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