The Interaction of Cationic Metal π-Enyl Complexes with Aryltrimethyl -silanes and -stannanes. Novel Electrophilic Aromatic Substitutions

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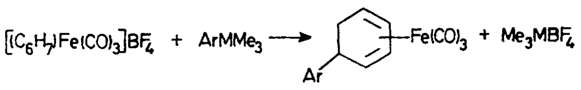
Summary The electrophile $[(C_6H_7)Fe(CO)_3]^+$ has been shown to react readily with a range of $ArMMe_3$ compounds (M = Si or Sn, Ar = XC_6H_4, X = H, *p*-MeO, or *p*-Me_2N, 2-furyl, or 2-thienyl) to give the corresponding diene-substituted aromatic compounds $[(ArC_6H_7)Fe(CO)_3]$.

The use of cationic π-enyl complexes such as $[(C_6H_7)Fe(CO)_3]^+$ (I) as electrophilic reagents towards aromatic substrates has recently been demonstrated.[1] A variety of diene-substituted heterocycles (*e.g.* II; Ar = indolyl, pyrrolyl, furyl, thienyl) and benzenoid derivatives (*e.g.* II; Ar = 1,3,5-trimethoxybenzyl, or 1,3-dimethoxybenzyl) were obtained. However, cation (I) was apparently not sufficiently electrophilic to attack anisole, alkylbenzenes or benzene.

It occurred to us that diene-substituted derivatives of the less activated arenes might by synthesised by using the reaction between (I) and aryl-$SiMe_3$ and aryl-$SnMe_3$ compounds, since these are known to be much more reactive towards electrophiles than the corresponding aryl-H compounds.[2,3] This has now been confirmed, and reaction (1) (M = Si,Sn) proceeds readily in acetonitrile or acetone using a wide variety of aryl groups (*e.g.* Ar = Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$). In most cases the reactions proceed to completion, shown by the disappearance of the original dienyl carbonyl bands at 2110 and 2065 cm^{-1}, and the growth of product peaks at 2050 and 1970 cm^{-1} characteristic of neutral tricarbonyl iron (diene) compounds.



(1)

(I) (II)

The compound (II; Ar = *p*-$Me_2NC_6H_4$) was isolated in *ca.* 50% yield as fine cream crystals (m.p. 116—117 °C) by evaporation of the acetone solvent, extraction with pentane, and cooling at −78 °C. Satisfactory elemental analyses were obtained. Its electron-impact mass spectrum revealed the expected parent peak at *m/e* 339, together with the step-wise loss of three carbonyl groups. Strong peaks were also observed at *m/e* 197 and 121, which can be assigned to $Me_2NC_6H_4$-Ph and $Me_2NC_6H_5$, respectively. The compound (II; Ar = *p*-$MeOC_6H_4$) has been similarly characterised.

TABLE, Reaction of $[(C_6H_7)Fe(CO)_3]BF_4$ (0·0065M) with trimethyl Si and Sn derivatives in MeCN at 45 °C.

Substrate	k_2[a] (M^{-1} s^{-1})	Relative rates
$PhSiMe_3$	$<10^{-7}$[b]	$<0{\cdot}1$
(*p*-MeO.C_6H_4)$SiMe_3$	$1{\cdot}1 \times 10^{-6}$	1
(*p*-$Me_2N.C_6H_4$)$SiMe_3$	$5{\cdot}8 \times 10^{-3}$	5,300
2-furyl $SiMe_3$	$1{\cdot}4 \times 10^{-4}$	127
2-thienyl $SiMe_3$	$1{\cdot}9 \times 10^{-6}$	1·7
$PhSnMe_3$	$3{\cdot}9 \times 10^{-6}$	3·5
(*p*-MeO.C_6H_4)$SnMe_3$	$6{\cdot}5 \times 10^{-5}$	60
(*p*-$Me_2N.C_6H_4$)$SnMe_3$	$3{\cdot}4 \times 10^{-2}$	30,000

[a] Obtained by following the disappearance of the dienyl carbonyl band at 2110 cm^{-1}. [b] No apparent reaction after 8 days.

We have shown reaction (1) as giving the Me_3MBF_4 species, but have not in fact identified the tin and silicon containing products. It is well known that for M = Si, the fluoroborate, if ever formed, rapidly breaks down to Me_3SiF and BF_3.

Similar reactions of $[(C_6H_7)Fe(CO)_3]^+$ have also been observed with 2-trimethylsilyl-furan and -thiophen. These reactions are considerably faster than those previously reported[1] involving interaction of (I) with furan and thiophen, and provide a more convenient route to diene-substituted heterocycles.

Preliminary kinetic data have been obtained for reaction (1) in acetonitrile (Table). Apart from the reaction with *p*-$Me_2NC_6H_4SnMe_3$, all reactions were studied under pseudo-first-order conditions by use of a large excess of the $ArMMe_3$ compounds. In each series of arene substrates the expected order of reactivity is observed, *i.e.* Ph < *p*-MeO·C_6H_4 < *p*-Me_2N·C_6H_4, which is obviously related to the increasing ease of electrophilic attack at the carbon atom of the Ar–M bond. Also the aryltin compounds are more readily attacked by (I) than the silicon analogues, as previously observed for a range of more familiar electrophiles.[3] However, the difference between the reactivities of the tin and silicon compounds (a factor of *ca.* 10) is exceptionally small in this reaction (*e.g.* towards acid, $PhSnMe_3$ is some 10^5 times as reactive as $PhSiMe_3$[2]), suggesting interesting mechanistic implications.

Preliminary tests indicate that other cationic π-enyl complexes such as $[(C_7H_7)Cr(CO)_3]BF_4$ and the acyclic dienyl $[(C_5H_7)Fe(CO)_3]BF_4$ also function as electrophiles in a manner analogous to reaction (1), indicating that the reaction may be useful for the synthesis of a variety of otherwise inaccessible compounds.

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