Journal of Organometallic Chemistry, 172 (1979) C47—C50
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Preliminary communication

ARENEIRON COMPLEXES FROM METAL ATOM EVAPORATION

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(Received February 5th, 1979)

Summary

Metal evaporation syntheses have given Fe(η^6-arene)L_2 and Fe(η^6-arene)(η^4-diene) complexes (where L = phosphorus ligand). Protonation and methylation of Fe(arene)L_2 complexes yield [Fe(arene)L_2H]$^+$ and [Fe(arene)L_2Me]$^+$ species, respectively. Protonation of Fe(arene)(η^4-triene) complexes yields [Fe(arene)(η^5-dienyl)]$^+$ salts.

Complexes of the type M(arene)L_2 have been known for some time. Skell's report [1] of Fe(toluene)$(PF_3)_2$ was followed shortly thereafter by Timms' preparation of Fe(benzene)$(PF_3)_2$ [2]. Recently, there has been a resurgence of interest in these and related classes of compounds [3]. This later work prompts us to report our own work in this area.

The co-condensation of iron atoms with toluene on a liquid nitrogen cooled surface gives a red-brown, very unstable mixture of "solvated" iron atoms (probably Fe$(arene)_2$, but see ref. 4). As the mixture warms to room temperature, it changes from red-brown to black as it decomposes to pyrophoric iron metal and free toluene. If the "solvated" iron atoms are treated with phosphorus ligands at low temperature before decomposition can occur, Fe(toluene)L_2 complexes are readily isolated. For example, using an apparatus and technique described in detail elsewhere [5], 14 g of iron and 200 ml of toluene were co-condensed over a period of 3.5 h. The resultant mixture was treated with 100 ml of $P(OMe)_3$ and after a workup which included chromatography of alumina, Fe(η^6-toluene)$[P(OMe)_3]_2$ (I) (15 g, 15%) was isolated as a dark red, air-sensitive, liquid. Its $^{31}P\{^1H\}$ NMR spectrum (toluene) consists of a singlet of 179.7 ppm. The ^1H NMR spectrum (toluene-d_8) consists of aromatic multiplets at 5.34 and 4.80 ppm, phosphite-methoxy at 3.55 ppm, and toluene-methyl at 2.25 ppm. Similar products were obtained with other phosphorus ligands.

When the tolueneiron co-condensation mixture was treated with dienes,

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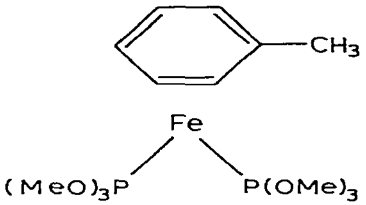
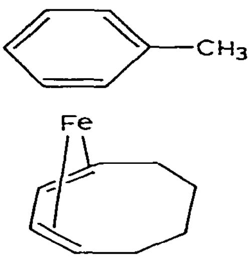
*Contribution No. 2644.



(I)



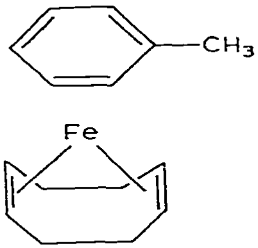
(II)

thermally unstable Fe(η^6-toluene)(η^4-diene) complexes could be isolated. Reaction with 1,3-cyclooctadiene (1,3-COD) gave II, a red oil which can be isolated analytically pure but which decomposes to iron metal, toluene, and 1,3-COD on standing at room temperature. The ^{1}H NMR spectrum of II (toluene-d_8) consists of toluene resonances at 4.92(1), 4.86(2), 4.72(2), and 1.95(3) ppm and COD resonances at 4.60(2), 2.68(2), 2.17(4), and 1.60(4) ppm.

Facile isomerization of polyolefins has been observed in other iron atom-diene systems [5—7], so it was not clear that reaction with 1,5-cyclooctadiene would necessarily give a product different from the preceding reaction with 1,3-COD. In fact, it does; Fe(η^6-toluene)(η^4-1,5-COD) (III) is a bright orange, crystalline product. The coordinated toluene shows ^{1}H NMR (toluene-d_8) resonances at 5.06(1), 4.37(2), 4.27(2) and 1.93(3) ppm, and the 1,5-COD at 2.81(4), 2.46(4), and 1.89(4) ppm.

The Fe(η^6-toluene)(η^4-cycloheptatriene) complex IV has the cycloheptatriene coordinated through adjacent olefinic groups and displays no exchange between the coordinated and non-coordinated groups. On the other hand, Fe(η^6-toluene)-(η^4-cyclooctatetraene) (V) undergoes rapid exchange of the coordinated and uncoordinated olefinic groups. At room temperature, the ^{1}H NMR spectrum of the η^4-COT consists of a single line at 5.23 ppm (toluene-d_8) with a relative intensity of eight.

Reactions with aromatic compounds (such as benzene, xylenes, or mesitylene) which have freezing points above ~−70°C, require new co-condensation techniques, since these solvents/reactants melt above the decomposition points of their respective "solvates." The phosphorus ligands or olefins may be co-con-



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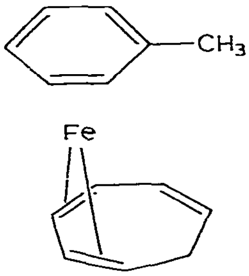

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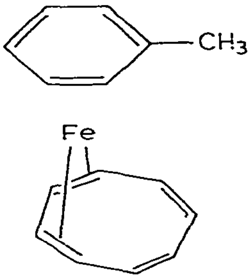
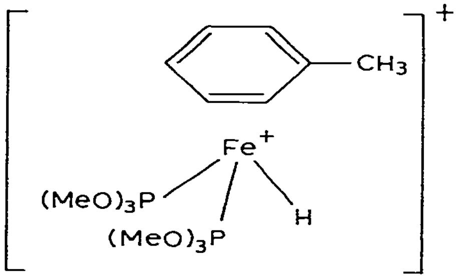


(V)

densed with the arene and iron atoms, or an inert, low-melting solvent such as methylcyclohexane may be included to fluidize the mixture at some lower temperature. Complexes isolated by these techniques include Fe(benzene)-[P(OMe)$_3$]$_2$ (VI), Fe(mesitylene)[P(OMe)$_3$]$_2$ (VII), and Fe(benzene)(η^4-1,3-cyclohexadiene) (VIII). The last, reported elsewhere [1,5] is remarkably stable when compared with any of the other Fe(arene)(diene) complexes which we have prepared to date.

The Fe(arene)[P(OR)$_3$]$_2$ complexes undergo both protonation and methylation reactions to yield products which are only slightly air sensitive. For example, reaction of I with methanolic HBF$_4$ yields [Fe(η^6-toluene)[P(OMe)$_3$]$_2$H] (IX) which is readily isolated in almost quantitative yield and analytical purity as the BPh$_4^-$ salt. The hydride is observed at 1930 cm^{-1} in the infrared and −13.27 ppm (triplet, J(PH) 98 Hz in CD$_2$Cl$_2$) in the ^{1}H NMR spectrum. The toluene ^{1}H NMR resonances are shifted downfield relative to the non-protonated precursor.



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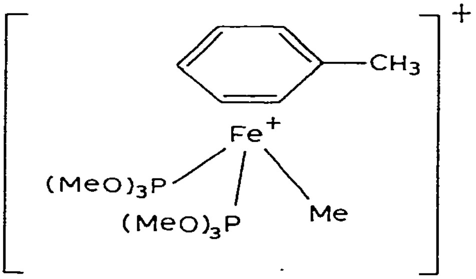
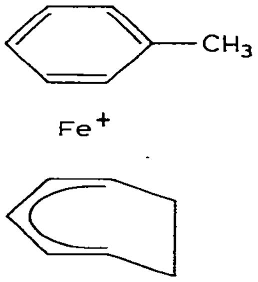


(X)

Reaction of I with [Me$_3$O][BF$_4$] in acetonitrile gives [Fe(η^6-toluene)-[P(OMe)$_3$]$_2$Me]$^+$ (X). The ^{1}H NMR spectrum of X is very similar to that of IX, except that the hydride resonance has been replaced by a methyl resonance 0.32 ppm below TMS, with J(PH) 4 Hz.

Protonation of IV in methanol yields XI which can be isolated as the PBh$_4^-$ salt in 80% yield. The ^{1}H NMR spectrum of XI (CD$_2$Cl$_2$) displays toluene resonances similar to those of IX and X. The cycloheptadienyl group has ^{1}H resonances at 6.88(1), 5.09(2), 4.88(2), 1.83(2), and 0.85(2) ppm.

Details of these reactions and others will be reported shortly.



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