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Alkyne Coupling Reactions Mediated by Iron(II) Complexes: Highly Chemo- and Regioselective Formation of η^6-Coordinated Arene and Pyridine Complexes

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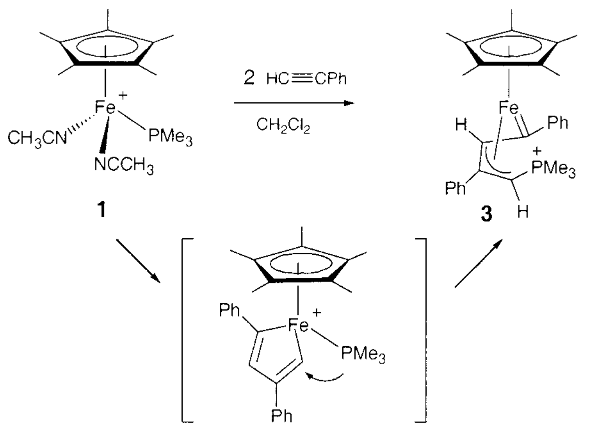
*Summary: Reaction of the bis(acetonitrile) complex **1** with HC≡CPh affords the (allyl)carbene complex **3**, which results from a head-to-tail coupling of two alkynes. The tris(acetonitrile) complex [Fe(C_5Me_5)(CH_3CN)$_3$][PF_6] (**2**) mediates highly chemo- and regioselective [2 + 2 + 2] cycloaddition reactions of C≡C and C≡N triple bonds, providing access to π-arene and -pyridine complexes. The pyridine complex **5a** has been characterized by an X-ray crystal structure.*

Activation of alkynes by transition-metal complexes has attracted considerable attention during the past few decades, allowing the discovery of new C−C bond-forming reactions. In this context, Ru-catalyzed reactions of alkynes and related stoichiometric reactions have been extensively developed.[1] In contrast, corresponding studies on related iron complexes have been less explored and the use of iron(II) complexes containing a cyclopentadienyl-based ligand has not been reported.[2] This led us to investigate the chemistry of the readily accessible iron bis(acetonitrile) and tris(acetonitrile) complexes [Fe(C_5Me_5)(CH_3CN)$_2$(PMe_3)][PF_6] (**1**)[3] and [Fe(C_5Me_5)(CH_3CN)$_3$][PF_6] (**2**)[3] in order to determine their potential utility in synthesis. We report that compounds **1** and **2** are able to promote C−C bond alkyne coupling reactions such as dimerization and [2 + 2 + 2] cycloaddition[4] reactions. The first iron(II)-mediated cycloaddition reactions of C≡C and C≡N triple bonds is presented. High chemoselectivity is observed, depending on the nature of the alkyne. These reactions selectively provide access to π-arene and the hitherto unknown π-pyridine complexes of iron. The convenient synthesis of iron sandwich complexes is very attractive, since they constitute an important class of molecules as organometallic "electron reservoirs" [5] and, when these complexes are attached to dendrimers, applications in anionic recognition were found.[6]

Scheme 1



Oxidative coupling of two alkynes can be mediated by the bis(acetonitrile) complex **1**. Treatment of **1** with phenylacetylene in CH_2Cl_2 affords the allylcarbene complex **3**, in which the phenyl substituents are exclusively located in the 1- and 3-positions (Scheme 1). As previously proposed for the related Ru complex,[7] the mechanism may involve a ferracyclopentadiene intermediate which results from a head-to-tail coupling of two molecules of alkynes; then PMe_3 migrates to the less hindered electrophilic carbon atom.

The presence of two labile ligands allows a dimerization reaction to occur, whereas cycloaddition takes place

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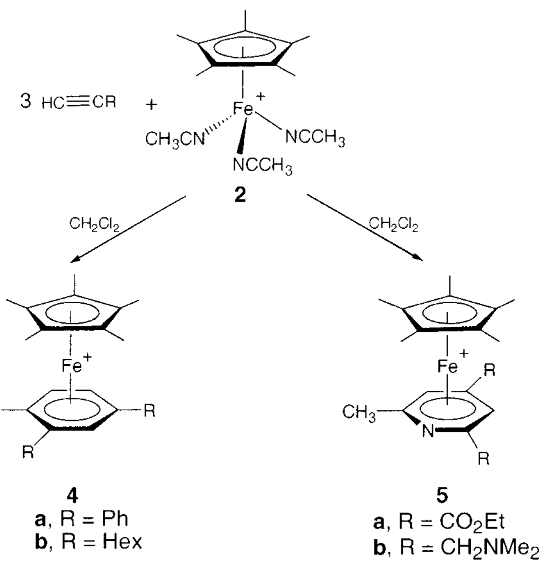
Scheme 2



in the case of the tris(acetonitrile) derivative **2**. Complex **2** reacts with 3 equiv of HC≡CR (R = Ph, Hex) in CH_2Cl_2 (room temperature) to give the arene complexes [Fe(C_5Me_5)(1,2,4-$C_6H_3R_3$)][PF_6] (R = Ph (**4a**), Hex (**4b**)) in 65% yield (Scheme 2). Despite the presence of acetonitrile in **2**, homocyclotrimerization of terminal alkynes occurs. NMR analyses of the crude reaction mixtures show that compounds **4** are formed with high selectivity (ca. 95%, based on Fe−arene protons by NMR). No reaction occurs with the disubstituted alkynes PhC≡CPh and EtC≡CEt, probably due to the steric bulk of the C_5Me_5 ligand.[8]

In sharp contrast, by using alkynes having a heteroatom bonded to the propargyl position such as ethyl propiolate and 1-(dimethylamino)-2-propyne, the reaction affords π-pyridine complexes instead of arene complexes. Treatment of **2** with HC≡CR (R = CO_2Et, CH_2NMe_2) in CH_2Cl_2 gives the π-2-Me-4,6-R_2-pyridine complex **5** (R = CO_2Et (**5a**), CH_2NMe_2 (**5b**)) (Scheme 2). Heterocyclotrimerization of two alkynes and one acetonitrile occurs; the latter comes from **2**. In both cases, the coordination of the heterocycle is characterized in the ^1H NMR spectra by an upfield shift of the aromatic protons. In the ^1H NMR spectrum ($CDCl_3$) of **5b**, the aromatic protons give rise to singlets at δ 6.00 and 5.89 in agreement with an asymmetrically 2,4,6-trisubstituted structure. The structure of the first π-pyridine of iron, **5a**, has been confirmed by an X-ray diffraction analysis (Figure 1).[9] The Fe−(C_5Me_5) centroid and Fe−(pyridine) centroid distances (1.688 and 1.542 Å, respectively) are very comparable to that of the arene complex [Fe(C_5Me_5)(η^6-C_6Et_5H)][PF_6].[8]

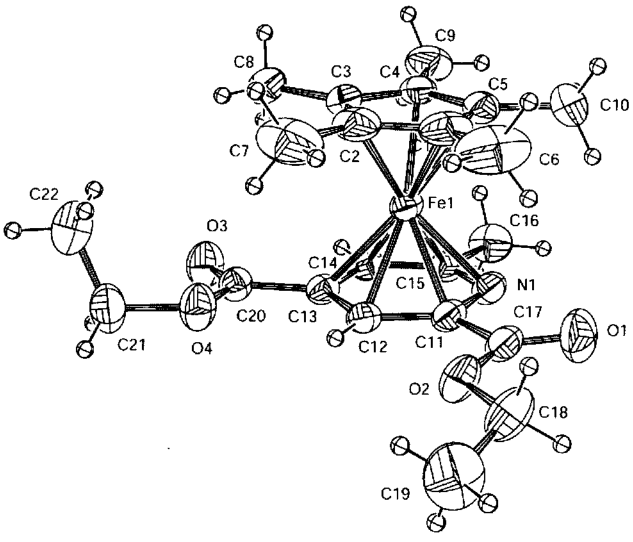
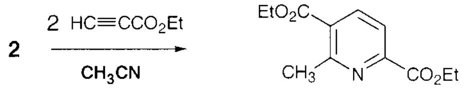


Figure 1. ORTEP drawing of **5a**. Selected bond distances (Å) and angles (deg): Fe−(C_5Me_5) centroid = 1.688, Fe−(pyridine ring) centroid = 1.542, Fe−C(pyridine ring) = 2.082 (range 2.044(3)−2.109(3)), Fe−N = 2.069(3), N−C(11) = 1.368(4), N−C(15) = 1.374(4); N−C(11)−C(17) = 114.8(3), C(12)−C(11)−C(17) = 122.1(3), C(14)−C(15)−C(16) = 122.5(3), C(16)−C(15)−N = 116.6(3), C(14)−C(13)−C(20) = 118.1(3), C(12)−C(13)−C(20) = 123.1(3).

Scheme 3



6

Complexes [Fe(C_5Me_5)(arene)]$^+$ are accessible from the bromo precursor [Fe(C_5Me_5)$(CO)_2$(Br)] under drastic reaction conditions, the presence of $AlCl_3$ being required.[5a] We found that complex **2** is inert toward ligand-exchange reactions involving hexamethylbenzene and 2,6-dimethylpyridine. Therefore, the above approach constitutes an alternative method to prepare mixed-sandwich iron(II) derivatives under mild conditions.

By using CH_3CN as solvent instead of CH_2Cl_2, no reaction occurs except with ethyl propiolate. The coordinating solvent acetonitrile inhibits alkyne complexation, but the presence of a better ligand such as a carbonyl group in HC≡CCO_2Et allows the reaction to proceed. Remarkably, the reaction of **2** in the presence of HC≡CCO_2Et (CH_3CN) leads to the formation of the free pyridine derivative [2-Me-3,6-$(CO_2Et)_2$−C_5H_2N] (**6**) in 73% yield vs **2** (Scheme 3). However, we were not able to idenfy any organometallic products from the reaction mixture. The nature of the solvent has a dramatic effect on the reaction product, and it is noteworthy that a different regioisomer of the pyridine ring is formed. The aromatic protons of **6** appear in the ^1H NMR spectrum ($CDCl_3$) as low-field doublets at δ 8.30 and 8.00.

The above results show that the formation of pyridines, as complexes or not, is controlled by the presence of a heteroatom. As suggested by the dimerization reaction, we assume that a metallacyclopentadiene intermediate, resulting from coupling of the two coordinated alkyne molecules, is initially formed.[10] However,

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(8) (a) Hamon, J.-R.; Saillard, J.-Y.; Toupet, L.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1662. (b) Hamon, J.-R.; Astruc, D. *Organometallics* **1989**, *8*, 2243.

(9) Crystal data for **5a**: yellow needles were grown by slow diffusion of Et_2O in an acetone solution of **5a**, $FeC_{22}H_{30}NO_4PF_6$, M_r = 573.29, monoclinic, space group $P2_1/n$, Z = 4, a = 7.9282(2) Å, b = 20.8095(4) Å, c = 15.3784(4) Å, β = 97.940(1)°, V = 2512.83 Å^3, T = 293 K, ρ_{calcd} = 1.515 g cm^{-3}, F(000) = 1184. A total of 5732 reflections were measured. The agreement factors for the 3376 observations with $I > 2\sigma(I)$ are R = 0.056 and R_w = 0.145. A Nonius Kappa CCD instrument was used, with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The whole structure was refined by full-matrix least-squares techniques on F^2, with hydrogens refined using the Riding mode.

coordination of the C≡C bond of the third molecule of alkyne could be inhibited by the presence of the heteroatom. Only a molecule of acetonitrile could interact and then insert into the Fe−C bond to afford the observed product.

The formation of the π-pyridine complexes **5** (CH_2Cl_2) is deduced to arise from an initial head-to-tail oxidative coupling step, whereas that of the iron-free pyridine **6** (CH_3CN) results from a tail-to-tail coupling, showing the crucial role of the solvent. For the π-arene complexes **4**, the regiochemistry of the metallacycloaddition should be similar to that of **5** and **3**, since all these reactions are performed in CH_2Cl_2.

In conclusion, we developed alkyne coupling reactions at an iron(II) center including highly chemo- and regioselective [2 + 2 + 2] cycloadditions, the formation of pyridine derivatives being heteroatom-assisted. These results show that labile complexes of iron, **1** and **2**, are promising candidates for other C−C bond-forming reactions, and this clearly opens up new prospectives for the development of iron chemistry.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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