

Preliminary communication

Palladium–Copper catalyzed coupling of iron σ -metalla-alkynes with aryl halides. A simple way to link electroactive organoiron complexes with aromatic structures

Raphaël Denis, Tania Weyland, Frédéric Paul, Claude Lapinte *

UMR CNRS 6509, Organométalliques et Catalyse: Chimie et Electrochimie Moléculaires, Université de Rennes 1, Campus de Beaulieu, Rennes 35042, Cedex, France

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Abstract

In the presence of catalytic amounts of bis(triphenylphosphine)dichloropalladium(II) $[(Ph_3P)_2PdCl_2]$ and copper iodide (CuI) in di-*iso*-propylamine, the terminal iron acetylide complex **1** $[(Cp^*)(dppe)Fe(C\equiv CH)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) can be coupled with various *para*- or *meta*-substituted aryl bromides or iodides **2a–g** to give the corresponding functionalized complexes **3a–g** $[(Cp^*)(dppe)Fe(C\equiv C-C_6H_4-G)]$ with fair yields (G = NO₂, CN, H, Br, ^tBu, OMe). © 1997 Elsevier Science S.A.

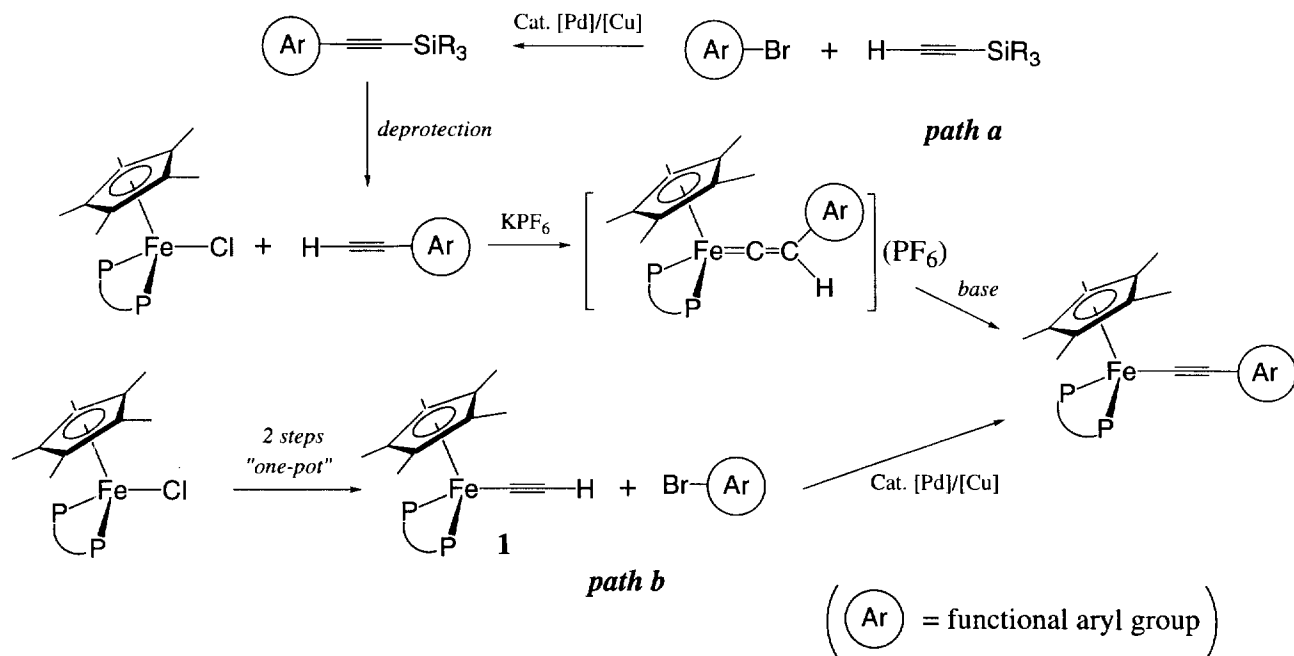
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Palladium–Copper catalyzed coupling of terminal alkynes with aryl bromides in presence of an amine, also referred as Sonogashira coupling [1,2], has found a wide synthetic application in organic chemistry [3]. This reaction constituted a straightforward access to complex organic architectures [4,5]. More recently, starting from metallated aromatic substrates, its use has also been extended to organometallic synthesis, and allowed isolation of metal-containing nanoscopic materials [6–10]. Our work strongly involves the study of organoiron poly- or di-nuclear molecules, where electroactive Cp*Fe(dppe) units are connected through an acetylenic core to an organic spacer. In such molecules, efficient electronic delocalization can take place depending on the spacer [11–15]. In this respect, aromatic ligands like benzene are particularly interesting since they allow multiple branching [15]. Indeed, such materials are very

promising for elaboration of electronic devices and new pathways to such compounds are highly desirable. The usual way to make those molecules was to synthesize independently the organic ligand in the first place and to complex it to the iron center afterwards, via the corresponding vinylidene complex (Scheme 1; *path a*) [16]. Using a Sonogashira-based coupling, we developed a new synthetic route toward such molecules, starting from the organoiron terminal alkynyl complex **1** [16] and the bromoaromatic precursor (Scheme 1; *path b*). While this work was in progress, Bruce et al. [17] reported briefly in a communication the use of a similar coupling between metallated diynylys and iodoaromatics. However, the metal centers in their complexes were electron-poor and presumably difficult to oxidize [17]. To our knowledge, it is the first time that a metallated alkyne directly σ -linked to an electron-rich and redox-active transition metal center is used in such a catalytic coupling.

Reaction of an excess of an aromatic bromide or iodide (**2a–g**) with compound **1** in di-*iso*-propylamine in presence of the palladium catalyst and the copper co-catalyst allows isolation of the corresponding cou-

* Corresponding author.



Scheme 1. Synthetic routes for coupling of a 'Cp*Fe(diphosphine)' unit with an aromatic moiety via the ethynyl spacer (Ar = aromatic group).

pled product (**3a–g**) in good yields.¹ Under those conditions, the use of a lower amount of palladium catalyst (5%) results usually in uncompleted conversion of **1**. Regarding the co-catalyst concentration, the use of a two-fold excess of copper iodide relative to the catalyst proved to be the most effective. Finally, heating of the reaction mixture is used to increase the rate of the coupling, since the reaction proceeds only very sluggishly at ambient temperature. With **2c**, for instance, approximately 15% of starting complex **1** are still present after 3 days at 20°C. Nevertheless, the reaction is quite versatile and stands various functional groups on the aromatic, as shown in Table 1. Better yields are usually achieved with electro-attracting substituents. In those cases, the reaction proceeds faster, whereas, longer reaction times and catalyst renewal are needed with

electron-donating ones.² For all reactions reported, all the starting complex **1** had reacted, even when the yield in product **3** was not quantitative (Scheme 2).

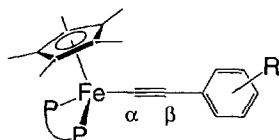
Interestingly, isolation of the complexes can be achieved without a chromatographic separation.¹ Depending on the aromatic substrate used, extraction in toluene and washing with *n*-pentane and methanol usually allow isolation of quite pure material. In worst cases, crude complexes can be further purified by an oxidation–reduction cycle permitting isolation of pure material.^{2,3} Most of the catalyst presumably decomposes at the end of the coupling and remains in the tarry materials left after extraction.

¹ Satisfactory elemental analyses were obtained for most compounds reported, the others being underways. A typical preparation is given hereafter for **3c**. In a Schlenk tube, 200 mg of complex **1** (0.325 mmol), 23 mg of bis(triphenylphosphine)dichloropalladium complex (0.032 mmol) and 13 mg of copper iodide (0.065 mmol) were introduced under argon. Subsequently, 0.163 ml of phenylbromide (1.625 mmol) and 10 ml of di-*iso*-propylamine were injected and the mixture was refluxed for 12 h. The solvent was then cryogenically trapped and the brown residue was extracted with toluene and filtered on a celite pad. Evaporation of the toluene and washing with small portions of *n*-pentane (2 × 5 ml) at –40°C and methanol (5 ml) at –40°C yielded 160 mg of the orange complex **3c** (0.231 mmol; 71%) after drying in vacuo. Further purification can be achieved by recrystallization from dichloromethane–ether mixture (the compound stays in solution) or as described in ².

² The reaction is performed under argon as described in ¹ from 200 mg of **1** (0.325 mmol), 23 mg of palladium complex (0.032 mmol), 13 mg of copper iodide (0.065 mmol) and 191 mg of 4-iodoanisole (0.810 mmol) in 10 ml of di-*iso*-propylamine. After 12 h and 18 h total reaction time, additional portions of palladium catalyst are added (2 × 23 mg, 0.032 mmol) after what the heating is maintained further during 12 h. Subsequent isolation of the product is similar as previously described. Yield of coupled product is estimated by NMR. The crude product is then dissolved in dichloromethane, oxidized with 37 mg of ferricinium hexa-fluoro-phosphate (0.111 mmol) and precipitated by addition of diethylether. After isolation by decantation and drying in vacuo, the green precipitate is redissolved in dichloromethane and reduced back to the starting complex with 16 mg of cobaltocene (0.085 mmol). Filtration of the cobaltocenium salt, evacuation of the diethylether and vacuum-drying yields 71 mg of pure orange complex **3g** (0.097 mmol; 30%).

³ All complexes **3a–g** are electroactive systems. A single reversible wave between 1.0 and –1.0 V vs. SCE can be observed each time.

Table 1
Yields and selected spectroscopic data for complexes **3**. ^{31}P , ^1H and ^{13}C spectra were recorded at 81 MHz, 200 MHz and 50 MHz, respectively



Complex Formed	Aromatic Substrate	Isolated Yield (%)	FTIR in CH_2Cl_2 (cm^{-1})	^{31}P in $\text{C}_6\text{D}_6/\text{H}_3\text{PO}_4$ (ppm)	^1H ($\text{C}_6\text{D}_6/\text{TMS}$, ppm)		^{13}C ($\text{C}_6\text{D}_6/\text{TMS}$, ppm)		
					Cp^*	R	$\alpha/\beta J_{\text{CP}}$ (Hz)	β	R
3a		64	2036, 2008 ^b	100.6	1.45	/	168.5 (38)	143.6	/
3b		51	2050, 2025 ^b	100.4	1.46	/	158.5 (38)	120.6	103.7
3c		71	2054	100.0	1.46	/	137.4 (40)	120.5	/
3d		73	2060, 2034 ^b	100.4	1.48	/	144.2 (40)	119.3	/
3e		50	2053	101.4	1.51	/	142.2 (39)	119.5	/
3f		20 ^a	2055	101.8	1.55	1.26	nd ^{c,d}	120.2 ^d	31.5 ^d
3g		30 ^a	2059	101.08	1.55	3.34	131.9 (40)	119.4	54.9

^a Isolated after purification by oxidation and reduction as described in ².

^b Two vibrational modes, presumably due to vibrational coupling, are observed for the acetylenic bond in those complexes.

^c Not distinguishable from other signals.

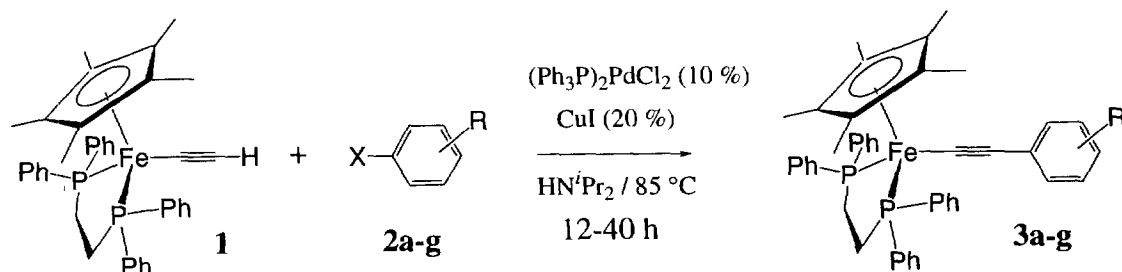
^d Measured in CD_2Cl_2 . Only CH_3 groups reported for ^1Bu ($^1J_{\text{CH}} = 125$ Hz).

In our chemistry, such a simple approach from the readily accessible alkynyl complex **1** proved to be very valuable. First, it constitutes a more general method since new functionalized complexes like **3a** or **3b**, possibly not accessible by the traditional route, were obtained in good yields. Then, the yields for more common products like **3c** compares well with the usual vinylidene route (**b**) [16].

From dibromoaromatics **2d**, **2e**, monosubstituted bromoaromatic complexes **3e**, **3f** could be selectively isolated with good yields, even in presence of a fivefold excess of dihalogenoaromatic. Thus, this reaction constitute an efficient mean to discriminate the two halogen functions in those organic substrates and allows further functionalization of the iron-substituted phenyl moiety. Complexes **3e** and **3f** constitute very interesting building blocks for elaboration of differentially substituted dinuclear complexes [18]. With monohalogeno substrates, the presence of other functional groups like the nitro in **3a**, which is a classic ONL-active substituent

for such molecules [19,20], or the cyano group in **3b**, that can be complexed to other metallic centers [21], should also give rise to interesting developments.

In conclusion, we have reported here an original, general and efficient method to couple the terminal alkynyl complex **1** with aromatic frameworks (Scheme 1; **b**). The interest of this reaction is two-fold. On the purely applied side, grafting electroactive iron-alkynyl moiety to various aromatic scaffolds constitute an efficient way to label those molecules, using the redox signature of the iron center. Additionally, for separatory purposes, the 'insolubilizing' power of the oxidized iron(III) complex can allow selective precipitation of metal-complexed molecules. On the more fundamental side, organometallic structures where electron rich metal centers are connected to functionalized aryl groups via an ethynyl spacer can lead to original molecular properties arising from electronic delocalization upon oxidation. In this respect, polynuclear organometallics possessing differentiated iron centers constitute promising



Scheme 2.

new targets for nanoscopic molecular device elaboration. We are currently working in this field and results will be reported in due course.

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