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Reaction of 1,3-diynes with the electron rich iron complex (η^5-C_5Me_5)(η^2-dppe)Fe–Cl. A new and direct access to the iron butadiynyl complex (η^5-C_5Me_5)(η^2-dppe)Fe–C≡CC≡CSiMe$_3$

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Abstract

The electron rich iron complexes (C_5Me_5)Fe(dppe)Cl (**3**) and (C_5Me_5)Fe(dppe)Br (**4**) do not react with Li(C≡C)$_n$SiMe$_3$ ($n = 1$, 2). Treatment of the chloro iron complex **3** with Me$_3$SiC≡C–C≡CSiMe$_3$ in methanol and in the presence of NaBPh$_4$ provides the binuclear complex (C_5Me_5)(dppe)FeC≡C–C≡C–Fe(dppe)(C_5Me_5) (**10**) as the unique product of this clean reaction (73%). Reaction of the chloro iron derivative **3** with one equivalent of trimethylsilyl(1,3-butadiyne) in triethylamine as a solvent and in the presence of NaBPh$_4$ yields 82% of the mononuclear iron trimethylsilyl-1,3-butadiyne compound. The triethylamine acts as a base to selectively deprotonate the putative butatrienylidene intermediate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: (C_5Me_5)(dppe)FeC≡C–C≡C–Fe(dppe)(C_5Me_5); (C_5Me_5)Fe(dppe)(C≡C–C≡CSiMe$_3$); Triethylamine

1. Introduction

Despite the wide interest of chemists pertaining to the reactions of alkynes with transition metal complexes, the expansion of this branch chemistry to diynes and polyynes is still in its infancy [1]. The products formed by the reaction of 1,3-diynes with transition metal complexes appear strongly dependent on the nature of the metal, its electron richness and steric environment. The lithium salt of the trimethylsilyl-protected 1,3-butadiyne, Me$_3$SiC≡C–C≡CLi·LiBr, readily obtained by treating the bistrimethylsilyl analogue Me$_3$SiC≡C–C≡CSiMe$_3$ with MeLi·LiBr [2,3] constitutes a very useful synthon to prepare [M]C≡C–C≡CSiMe$_3$ derivatives. As the relative nucleophilicity of Li(C≡C)$_n$SiMe$_3$ decreases with the carbon chain length, this reagent is less nucleophilic than LiC≡CSiMe$_3$. For instance, in contrast with this latter, it does not react with M(CO)$_6$ (M = Cr, W) [4]. However, it is nucleophilic enough to displace halide from many transition metal complexes allowing the preparation of a variety of transition metal compounds containing the trimethylsilyl 1,3-butadiyne ligand [1]. In the iron series, conversion of (C_5R_5)Fe(CO)$_2$X (R = H, Me, Ph) to the corresponding trimethylsilylbutadiynyl complexes has been achieved following this route (Scheme 1) [5–8]. On the other hand, terminal 1,3-diynes can oxidatively add to the electronically unsaturated metal centers, for instance, RhCl(PPr$^i_3$)$_2$ and HC≡CC≡CR gave the Rh(III)–diynyl complex RhHCl(C≡CC≡CR)(PPr$^i_3$)$_2$ [9,10]. Moreover, in the presence of NEt$_3$, HC≡CC≡CR reacts with *cis*-RuCl$_2$(dppe)$_2$ to give *trans*-RuCl(C≡CC≡CR)(dppe)$_2$ [11,12].

In connection with our ongoing interest in the synthesis and physical properties of molecular wires in which an all carbon chain is capped by two redox active metal termini, we need to find out reactions to prepare the mononuclear precursors containing polyynes ligands [13]. A few years ago, a three-step access to the binuclear complex (C_5Me_5)(dppe)FeC≡C–C≡C–Fe(dppe)(C_5Me_5) (**10**) [14] and a two-step route to (C_5Me_5)(dppe)Fe(C≡C–C≡CSiMe$_3$) (**11**) [7] were reported by our group. We now report the reactions of the electron rich (C_5Me_5)(dppe)FeCl complex with

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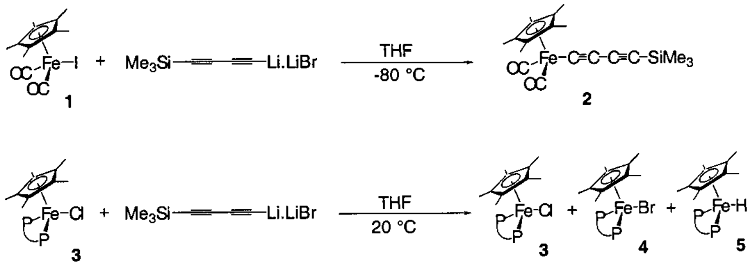
$Me_3SiC{\equiv}C{-}C{\equiv}CLi{\cdot}LiBr$, $Me_3SiC{\equiv}C{-}C{\equiv}SiMe_3$ and $Me_3SiC{\equiv}C{-}C{\equiv}CH$ in different experimental conditions. These investigations allowed us to find a one-step synthesis of the key compounds (**10**) and (**11**).

2. Results and discussion

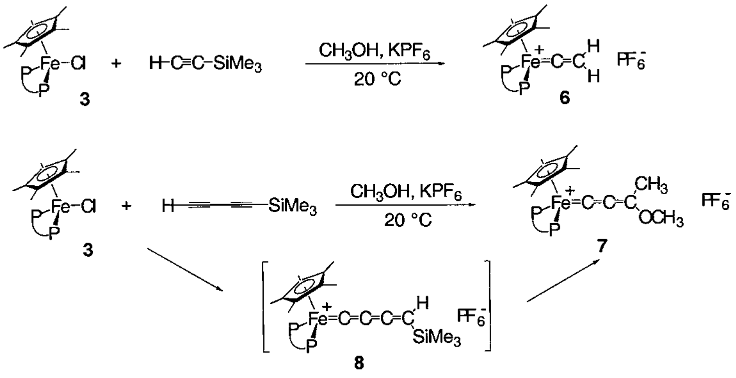
In contrast with $(C_5Me_5)Fe(CO)_2Br$ [7], $(C_5Me_5)Fe(dppe)Cl$ (**3**) or $(C_5Me_5)Fe(dppe)Br$ (**4**) do not react with $Li(C{\equiv}C)_xSiMe_3$. Indeed, when this reaction is carried out at low temperature in THF no reaction occurred. Nevertheless, at 20°C in THF, a color change from dark green to brown resulted from the treatment of **3** with $Me_3SiC{\equiv}C{-}C{\equiv}CLi{\cdot}LiBr$. After 4 h of reaction, three organoiron complexes are present in the reaction mixture: the halide derivatives **3** and **4** in the ratio 60:40 and a small amount (5%) of the known iron hydride $(C_5R_5)Fe(dppe)H$ (**5**) (Scheme 1) [15]. It is probable that the inertness of **3** toward $Li(C{\equiv}C)_2SiMe_3$ could be due to the weak electrophilic character of the iron center, but also to a strong steric protection around the metal provided by both the C_5Me_5 and dppe ligands [16]. So, alternative routes must be found to $(C_5Me_5)Fe(dppe)C{\equiv}C{-}C{\equiv}CSiMe_3$.

The deprotonation of vinylidene complexes constitutes one of the most general methods to prepare transition metal compounds featuring acetylide ligands, themselves being conveniently obtained from reactions of 1-alkynes with a wide variety of transition metal halides via a 1,2-H shift [17,18]. This reaction was extended to terminal 1,3-diynes to prepare transition metal complexes containing a 1,3-dyine ligand [11,12]. However, this extension is limited to a small number of complexes with an electron poor metal center. In the cases of more electron-rich fragments, 1,3-diynes tend to undergo a 1,4-H shift affording highly reactive butatrienylidene transition metal intermediates, which are not stable in the reaction conditions [1,19–22]. Thus, treatment of **3** with $Me_3SiC{\equiv}CH$ in methanol and in the presence of the potassium hexafluorophosphate salt, produces vinylidene $[(C_5Me_5)Fe(dppe)({=}C{=}CH_2)][PF_6]$ (**6**) in 95% yield [14] (Scheme 2), but the replacement of $Me_3SiC{\equiv}CH$ by $Me_3SiC{\equiv}C{-}C{\equiv}CH$ affords, in the same conditions, the allenylidene iron complex $[(C_5Me_5)Fe(dppe)({=}C{=}C{=}C(CH_3)OMe)][PF_6]$ (**7**) via butatrienylidene $[(C_5Me_5)Fe(dppe)({=}C{=}C{=}C{=}C(H)SiMe_3)]X$ (**8**) [21]. Similar to the reaction observed in the case of the vinylidene, the cleavage of the trimethylsilyl fragment should occur after the hydrogen 1,4-shift and a subsequent addition of a methanol molecule provides the allenylidene **7** (Scheme 2) [19].

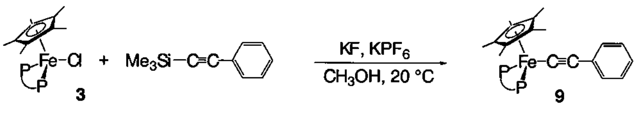
We also found that treatment of $Me_3SiC{\equiv}C{-}C_6H_5$ with one equivalent of **3** in the methanol–THF (10:1) mixture and in the presence of KF and KPF_6 ($NaBPh_4$ can also be used) salts produces the iron alkynyl derivative $(C_5Me_5)Fe(dppe)(C{\equiv}C{-}C_6H_5)$ (**9**) isolated in 80% yield (Scheme 3) [23]. In this one-step procedure the



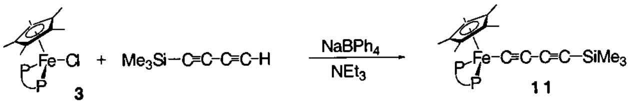
Scheme 1.



Scheme 2.



Scheme 3.

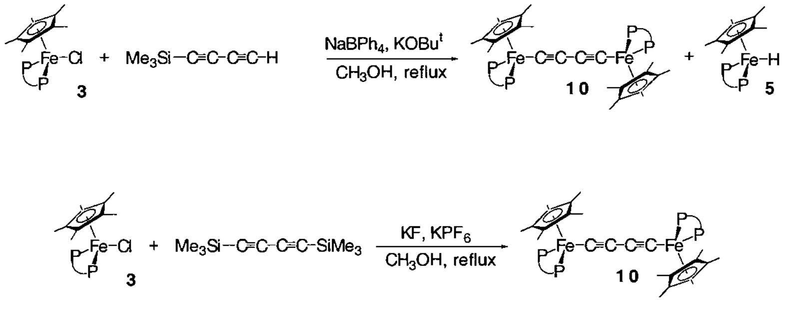


Scheme 5.

ethynyl benzene is in situ generated by the fluoride-induced cleavage of the terminal trimethylsilyl group. As extensively described, the PF_6 anion promotes the complexation of the terminal alkyne at the iron center giving the vinylidene derivative isolated in most cases as the final product of the reaction. However, in the above-defined conditions, the cleavage of the trimethylsilyl group is associated with the formation of a stoichiometric amount of a strong base namely MeOK. This base, in situ deprotonates the vinylidene intermediate, allowing the formation of **9** as the unique organoiron product of this sequence of reactions. By analogy, we though that treatment of the chloro iron complex **3** with $Me_3SiC\equiv C–C\equiv CSiMe_3$ in the same conditions, could give the 1,3-butadiynyl complex $(C_5Me_5)Fe(dppe)(C\equiv C–C\equiv CSiMe_3)$ (**11**). However, the mononuclear compound was not formed in these conditions. The known binuclear complex $(C_5Me_5)(dppe)FeC\equiv C–C \equiv C–Fe(dppe)(C_5Me_5)$ (**10**) constitutes the unique product of this clean reaction (Scheme 4). Interestingly, compound **10** is isolated in 73% yield. This reaction constitutes a new synthetic access to the binuclear complex **10** much more directly than the oxidative coupling of the iron alkynyl derivative $(C_5Me_5)Fe(dppe)(C\equiv CH)$ [14]. It is noteworthy, that the use of two or three equivalents of $Me_3SiC\equiv C–C\equiv CSiMe_3$ did not allow us to observe the presence of any mononuclear species. Assuming that the complexation of the second iron center could occur on the butatrienylidene intermediate, we tried to perform the reaction in the presence of one equivalent of potassium *tert*-butoxide and two equivalents of $Me_3SiC\equiv C–C\equiv CSiMe_3$ to favor both the formation of a mononuclear intermediate and its quick deprotonation. However, we did not observe the formation of $(C_5Me_5)(dppe)FeC\equiv C–C\equiv CSiMe_3$. The unique difference was the formation of a small amount of the hydride **5** beside the bis(iron) derivative **10** (Scheme 4).

Assuming that the formation of the iron allenylidene **7** results from the fast addition of a nucleophilic molecule of solvent onto the butatrienylidene **6** (Scheme 2), we thought that the use of a more basic and less nucleophilic solvent could avoid the nucleophilic addition. We and the others found that primary and secondary amines react with in situ generated butatrienyllidene complexes providing amino-allenylidenes [19,20,24]. However, the use of bulky and weakly nucleophilic amine should favor the deprotonation of the transient butatrienylidene intermediate with respect to the nucleophilic addition of the amine. Accordingly, we reacted the chloro iron compound **3** with one equivalent of trimethylsylil(1,3-butadiyne) in diethylamine as a solvent. Analysis of the products after the reaction indicates the presence of a neutral compound and several organoiron iron salts, which were not identified. The neutral compound was isolated in 33% yield from a CH_2Cl_2 liquor containing the reaction products after the precipitation of the salts by the addition of diethyl ether. It was identified as the desired derivative $(C_5Me_5)(dppe)Fe(C\equiv C–C\equiv CSiMe_3)$ (**11**). As the formation of salts should result from an initial nucleophilic addition of the secondary amine on the putative butatrienylidene intermediate, the reaction was reproduced in the same conditions, but using triethylamine as a solvent. In this case, the solvent selectively acts as a base and deprotonates the butatrienylidene intermediate, providing the target complex **11** in 82% yield (Scheme 5).

In conclusion, we found direct routes to $(C_5Me_5)(dppe)FeC\equiv C–C\equiv C–Fe(dppe)(C_5Me_5)$ (**10**) and $(C_5Me_5)Fe(dppe)(C\equiv C–C\equiv CSiMe_3)$ (**11**) which are now easily accessible in fair yield. Our results show that



Scheme 4.

terminal alkynes and diynes present a similar reactivity. The difference of behavior between these two families of compounds comes mainly from the high reactivity of butatrienylidene intermediates in comparison with the relative chemical inertness of the vinylidene derivatives. For this reason, the complexation of diynes at an electron rich metal center require accurately defined reaction conditions. Following the strategy reported here, we think that it should be possible to prepare butadiynyl complexes with different metal centers and a wide variety of 1,3-diynes [25].

3. Experimental

3.1. General data

All manipulations were carried out under argon atmosphere. Solvents or reagents were used as follows: Et_2O and *n*-pentane, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 and purged with argon; $HN(^iPr)_2$, and NEt_3, distilled from KOH and purged with argon. Complex **3** [26] and trimethylsilyl-1,3-butadiyne [27] were prepared following reported procedures. High field NMR spectra experiments were performed on multinuclear Bruker 300 or 200 MHz instruments (AM300WB and 200DPX). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H- and ^{13}C-NMR spectra, H_3PO_4 for ^{31}P-NMR spectra. Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer (400–4000 cm^{-1}). UV–vis spectra were recorded on an UVIKON 942 spectrometer. Cyclic voltammograms were recorded using a PAR 263 in CH_2Cl_2 (0.1 M $(n\text{-}Bu)_4N^+\ PF_6^-$) at 25°C at a platinum electrode, using a SCE reference electrode and ferrocene as internal calibrant (0.460 V) [28].

3.2. Reaction of TMSC≡CC≡CLi·LiBr with (η⁵-C₅Me₅)(η⁵-dppe)FeCl

In a Schlenk tube bis(trimethylsilyl)-1,3-butadiyne (0.117 g, 0.60 mmol) and THF (15 ml) were introduced. The resulting solution was cooled down to −80°C before adding MeLi·LiBr (1.65 ml, 0.75 mmol). The solution was then allowed to warm up to 20°C and stirred for 4 h. Separately, in another Schlenk tube, the green complex **3** (0.356 mg, 0.56 mmol), KPF_6 (0.112 g, 0.6 mmol) and 30 ml of methanol were introduced. This suspension was cooled down to −80°C and the solution of THF containing the trimethylsilyl-1,3-butadiynediyl lithium was transferred. The solution was allowed to warm up upon stirring for 16 h. Evaporation of the solvent under vacuum and extraction of the solid residue with CH_2Cl_2 provided a greenish brown powder containing the complexes $(\eta\text{-}C_5Me_5)Fe(dppe)Cl$ (**3**), $(\eta\text{-}C_5Me_5)Fe(dppe)Br$ (**4**), and $(\eta\text{-}C_5Me_5)Fe(dppe)H$ (**5**), in a 38:57:5 ratio. Complexes **3**, **4**, and **5** were identified by comparison of the ^1H-NMR spectra and cyclic voltammograms with those of authentic samples [26].

*3.3. (η⁵-C₅Me₅)(η⁵-dppe)Fe–C≡C–C≡C–Fe(η⁵-dppe)-(η⁵-C₅Me₅) (**10**)*

3.3.1. In a Schlenk tube the complex **3** (0.250 g, 0.40 mmol) and 20 ml of methanol were introduced. The suspension was cooled down to −25°C before adding 0.6 equivalents of trimethylsylyl-1,3-butadiyne (0.030 g, 0.24 mmol), 1.1 equivalents of $NaBPh_4$ (0.150 g, 0.44 mmol), and 1.1 equivalents of $KOBu^t$ (0.0493 mg, 0.44 mmol), successively. The mixture was allowed to warm up to 20°C in 16 h upon stirring. Initially dark green, the solution turned orange. Evaporation of the solvent under vacuum and extraction of the solid residue with a toluene–diethyl ether 1:1 mixture provided an orange solid residue. Comparison of the IR, ^1H, ^{31}P and CV data of the crude products with those of authentic samples indicated the formation of the two iron complexes $(\eta\text{-}C_5Me_5)Fe(dppe)H$ (**5**) [26] and $(C_5Me_5)(dppe)FeC{\equiv}C{-}C{\equiv}C{-}Fe(dppe)(C_5Me_5)$ (**10**) [14] in the 60:40 ratio as determined from the integration of the ^1H-NMR spectra.

3.3.2. In a Schlenk tube 1,4-bis(trimethylsilyl-1,3-butadiyne (0.055 g, 0.28 mmol) and 1 ml of THF were introduced. To this solution, complex **3** (0.350 g, 0.56 mmol), methanol (20 ml), KF (0.033 mg 0.56 mmol) and Na BPh_4 (0.191 g, 0.56 mmol) were successively introduced. The resulting suspension was stirred under reflux for 4 h. A slow color change from dark green to brown was observed. Evaporation of the solvent under vacuum and extraction of the crude residue with 4 × 5 ml of toluene provided a brown powder. After washing with 5 ml of diethyl ether the solid was identified as the pure binuclear complex (**10**) isolated in 73% yield.

*3.4. (η⁵-C₅Me₅)(η²-dppe)Fe–C≡C–C≡C–SiMe₃ (**11**)*

3.4.1. To a suspension of **3** [26] (0.300 g, 0.48 mmol) and $NaBPh_4$ (0.180 g, 0.58 mmol) in diethylamine (25 ml), 1.2 equivalents of trimethylsilylbutadiyne (0.070 g, 0.55 mmol) was added. The mixture is stirred at 20°C for 16 h. After evaporation of the solvent under reduced pressure, the crude residue was extracted with 4 × 5 ml CH_2Cl_2 and concentrated to 10 ml. After the precipitation of non-identified organoiron salts by the addition of diethyl ether and filtration, evaporation to dryness of the filtrate provide an orange powder identified by comparison with the data of an authentic sample as the pure compound **11** (33%) [7].

3.4.2. To a suspension of **3** [26] (0.300 g, 0.48 mmol) and $NaBPh_4$ (0.185 g, 0.54 mmol) in triethylamine (25 ml), 1.2 equivalents of trimethylsilylbutadiyne (0.070 g, 0.55 mmol) was added. While the mixture was stirred at 20°C for 16 h, the dark green color slowly turned to orange. After removal of the solvent, the solid residue was extracted with 30 ml (3 × 10 ml) of diethyl ether. The solvent was removed under reduced pressure and the resulting orange powder was dried under vacuum. The product was identified as a pure sample of **11** (82%) by comparison with the spectroscopic data of an authentic sample [7].

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