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Synthesis of Metal Acetylides via Palladium-Catalyzed Carbon-Metal Bond Formation[†]

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The iron complex $CpFe(CO)_2I$ (**1**) undergoes a clean coupling reaction of the Fe-I bond with the $Sn-C\equiv$ bond of various trialkyltin acetylides $R_3SnC\equiv CR'$ (R' = H, Pr, Bu, Ph) in the presence of a catalytic amount (5%) of $(CH_3CN)_2PdCl_2$ to give the corresponding σ-alkynyl metal complexes $CpFe(CO)_2C\equiv CR'$ [R' = H (**2**), Pr (**3**), Bu (**4**), Ph (**5**)] in 60-70% yields. Under the same conditions, 1 equiv of complex **1**, $CpFe(CO)_2I$, in the presence of palladium, reacts with the 1-(trimethylstannyl)-1,3-butadiyne $(CH_3)_3SnC\equiv CC\equiv CH$ (**8**) to form the iron complex $Cp(CO)_2FeC\equiv CC\equiv CH$ (**11**) and 2 equiv reacts with 1,4-bis(trimethylstannyl)-1,3-butadiyne, $(CH_3)_3SnC\equiv CC\equiv CSn(CH_3)_3$ (**10**), to yield the bimetallic complex $Cp(CO)_2FeC\equiv CC\equiv CFe(CO)_2Cp$ (**12**) possessing the $\eta^2(\sigma,\sigma)$-1,3-butadiyne-1,4-diyl ligand bridging the two iron atoms.

Introduction

The characteristic behavior of palladium causing oxidative addition of the C-X bond (X = halide, triflate) in organic electrophiles is a well-known phenomenon.[1] It is a key step which in the presence of an appropriate partner, with its subsequent evolution (i.e. transmetalation, isomerization, reductive elimination), has given a new powerful approach to synthetic organic strategies.

In fact, one of the most critical operations in the synthesis of organic molecules is the generation of a carbon-carbon bond. The greatest breakthrough in the use of palladium catalysts in organic synthesis has been the achievement of efficiently coupling together a wide variety of organic moieties under mild condition, by the reaction of organic electrophiles with organotin reagents. With this procedure it is possible to use tin reagents to couple with organic electrophiles and thus overcome the difficulty of using reagents that are difficult to prepare and store, since they may be air or moisture sensitive and uneasy to handle, and that are unusable in the presence of sensitive functionalities, such as Grignard and copper reagents or organozinc, organomercurial, organoboron, organoaluminum, and organozirconium compounds.[2]

The insertion of palladium, and group 10 metals in general, into other types of bonds has been less frequently investigated with respect to the well-known oxidative addition process of palladium with organic electrophiles.[3]

In an extensive review, Solokov and Reutov[4a] accounted for a large number of examples of oxidative addition of organometallic compounds to zerovalent complexes of the nickel triad metals. Organomercurials and organometallic derivatives of group 14 elements were examined. In the reaction with organomercurials, the corresponding transition metal-mercury σ-bonded species were isolated for some complexes with strong electron-withdrawing radicals, although demercuration easily occurs, leading to the formation of the corresponding organoplatinum and organopalladium derivatives. The reactions of organohalides and tetraorganoderivatives of Si, Ge, Sn, and Pb, mostly with Pt(0), were also largely reviewed. Usually the isolation of the corresponding heterodinuclear compounds, in which the transition metal is inserted into the organo or haloelement bond, was possible, as summarized in eq 1.

$$R_nMX + M' \longrightarrow R_nMMX \qquad (1)$$

M=Hg, Si, Ge, Sn, Pb
X=halogen
M'=Pt, Pd, Ni

Other reports on this topic followed,[4b-d] but no subsequent reaction was generally described for the organotransition metal compounds obtained.

We have recently reported[5] the unprecedented observation of a coupling reaction in the presence of palladium between an iron halide complex and a trialkyltin acetylide compound with formation of an iron acetylide complex. This intriguing result has prompted us to investigate the generality of this reaction in view of the fundamental importance that this could have with regards to the mechanistic and synthetic aspects of organometallic chemistry.

In this paper we report further evidence of the effectiveness of palladium in catalyzing the coupling of a variety of tin acetylides with the iron-halide complex $CpFe(CO)_2I$.

Experimental Section

All manipulations were carried out under a protective atmosphere of argon (deoxygenated with copper-based BTS catalyst (Fluka) and dried with 4-Å molecular sieves) in carefully dried equipment. Conventional vacuum line and/or Schlenk tube techniques were used. THF was distilled over sodium benzophenone; DMF was distilled under vacuum from CaH_2. Liquids were transferred by syringe or cannula.[6] Infrared spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using a 0.1-mm CaF_2 cell. ^1H-NMR spectra and the broad-band proton-decoupled ^{13}C NMR spectra were recorded in the Fourier transform mode on a Bruker WP-80 spectrometer

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and a Varian XL-300 spectrometer. The NMR chemical shifts are reported in parts per million vs Me_4Si, by assigning the ^1H impurity in the solvent ($CDCl_3$) at 7.24 ppm. The ^{13}C spectral chemical shifts are referenced to the ^{13}C triplet ($CDCl_3$) at 77.00 ppm. Melting points were determined in a open capillary on a Buchi 510 melting point apparatus. Elemental analyses were performed by the Servizio Microanalisi of the Area della Ricerca di Roma (Consiglio Nazionale delle Ricerche, Monterotondo). Mass spectral analyses were performed with a Hewlett-Packard 5890 GC–MS instrument equipped with an HP-1 cross-linked methyl silicone gum (12 m × 0.2 mm × 0.33 μm film thickness) capillary column. The GC parameters used were as follows: injection port, 240 °C; detector, 280 °C; oven, temperature ramp from 50 °C (hold 1 min) to 200 °C (hold 5 min), at 10 °C/min. Ionization was by electron impact, operating at 70 eV.

$(CH_3CN)_2PdCl_2$,[7] $(CH_3)_3SnCl$,[8] $Bu_3SnC{\equiv}CH$,[9] $Bu_3SnC{\equiv}C(CH_2)_2CH_3$,[10] $Bu_3SnC{\equiv}C(CH_2)_3CH_3$,[11] and $Bu_3SnC{\equiv}CC_6H_5$[12] were prepared according to the literature procedures. (*Z*)-1-methoxybut-1-en-3-yne (97% isomerically pure) is available from Aldrich as a 50% solution in methanol–water. It was purified according to the literature procedure.[13] $CpFe(CO)_2I$ (Strem Chemicals) was used as received. The active organometallic content of Bu-Li (Aldrich) was checked periodically by titration with 2,5-dimethoxybenzyl alcohol.[14]

General Procedure for the Coupling Reaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $Bu_3SnC{\equiv}CR$ (R = H, Pr, Bu, Ph) in the Presence of Palladium. In a typical reaction, 5 mol % of solid $(CH_3CN)_2PdCl_2$ was added to a stirred solution of 1.0 mmol of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and 1.2 mmol of $Bu_3SnC{\equiv}CR$ in 30 mL of DMF. The solution turned from deep red to dark brown, and the stirring was continued overnight at room temperature. After this time, 50 mL of diethyl ether was added to the reaction mixture, followed by 100 mL of a saturated solution of KF in water. The mixture was stirred rapidly for 30 min while argon was bubbled through the solution and then filtered by vacuum suction through a glass frit covered with a celite pad and transferred into a separating funnel. The aqueous phase was discarded, the solution was washed with water (3 × 50 mL), and the aqueous phase was back-extracted with diethyl ether (2 × 50 mL). The combined ether extracts were dried over magnesium sulfate and filtered, 20 g of Celite was added, and the mixture was evaporated to dryness in vacuo. The residue was added to a 3 × 40 cm column of silica gel (Kieselgel; Merck) and eluted with a mixture of 10% EtOAc in hexanes. Spectroscopic data for the iron acetylide complexes are listed in Table I and agree well with literature reports.[16-19]

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $Bu_3SnC{\equiv}CH$ in the Presence of $(CH_3CN)_2PdCl_2$. Isolation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{=}O)CH_3$. Using the method described above, 16 mg (0.05 mmol) of solid $(CH_3CN)_2PdCl_2$, 390 mg (1.27 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and 443 mg (1.44 mmol) of $Bu_3SnC{\equiv}CH$ were reacted in 30 mL of DMF. The chromatographic separation of the reaction mixture afforded first a small amount of an unidentified product and then the acyl compound. Evaporation of the solvent resulted in 90 mg (30%) of the product as a dark oil. IR (CCl_4, cm^{-1}): 2019.9, 1961.6, 1659.1. ^1H-NMR ($CDCl_3$, ppm): 2.56 (s, 3 H), 4.84 (s, 5 H). The spectroscopic data agreed with the literature values reported.[15]

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $Bu_3SnC{\equiv}C(CH_2)_2CH_3$ in the Presence of $(CH_3CN)_2PdCl_2$. Isolation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{=}O)(CH_2)_3CH_3$. Using the method described above, 30 mg (0.11 mmol) of solid $(CH_3CN)_2PdCl_2$, 506 mg (1.66 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and 718 mg (2.01 mmol) of $Bu_3SnC{\equiv}C(CH_2)_2CH_3$ were reacted in 30 mL of DMF. The chromatographic separation yielded 213 mg (50%) of the acyl compound as a red oil. IR (CH_2Cl_2, cm^{-1}): 2017.0, 1956.7, 1646.0. ^1H-NMR ($CDCl_3$, ppm): 0.85 (t, 3 H, J = 7.3 Hz), 1.23 (m, 2 H), 1.43 (p, 2 H, J = 7.4 Hz), 2.86 (t, 2 H, J = 7.5 Hz), 4.82 (s, 5 H). ^{13}C-NMR ($CDCl_3$, ppm): 13.82, 22.10, 27.27, 66.34, 86.27, 214.41, 256.72. Anal. Calcd for $C_{12}H_{14}O_3Fe$: C, 54.99; H, 5.38. Found: C, 54.83; H, 5.34.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}C(CH_2)_3CH_3$.[17] Using the method described above, 16 mg (0.06 mmol) of solid $(CH_3CN)_2PdCl_2$, 335 mg (1.1 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and 510 mg (1.37 mmol) of $Bu_3SnC{\equiv}C(CH_2)_3CH_3$ were reacted in 30 mL of DMF. The chromatographic separation afforded the coupled product (216 mg, 74%) as red oil.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CC_6H_5$.[17,18] Using the method described above, 23 mg (0.08 mmol) of solid $(CH_3CN)_2PdCl_2$, 530 mg (1.74 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and 830 mg (2.09 mmol) of $Bu_3SnC{\equiv}CC_6H_5$ were reacted in 30 mL of DMF. The chromatographic separation afforded 360 mg (74%) of the coupled product as an orange solid, mp 119–120 °C (lit.[17,18] mp 120–121 °C).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}C(CH_2)_2CH_3$. The isolation of the pure acetylide was possible by modification of the workup procedure described in the general procedure. Thus, 24 mg (0.09 mmol) of solid $(CH_3CN)_2PdCl_2$, 252 mg (0.83 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and 490 mg (1.23 mmol) of $Bu_3SnC{\equiv}C(CH_2)_2CH_3$ were reacted in 40 mL of DMF. After the overnight stirring, 50 mL of diethyl ether was added to the reaction mixture followed by 100 mL of a saturated solution of KF in water, previously adjusted to pH 9 with $NaHCO_3$. The subsequent treatment was performed as usual. The chromatographic separation afforded the product as a yellow oil (142 mg, 71%). Anal. Calcd for $C_{12}H_{12}O_2Fe$: C, 59.05; H, 4.96. Found: C, 58.85; H, 4.95.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CH$.[16] The isolation of this product required a different procedure from the above described, because even the alkaline workup led to the hydration of the alkyne. A 17-mg amount (0.06 mmol) of solid $(CH_3CN)_2PdCl_2$ was added to a stirred solution of 512 mg (1.68 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and 610 mg (1.94 mmol) of $Bu_3SnC{\equiv}CH$ in 30 mL of THF. The solution turned dark brown, and the stirring was continued at room temperature overnight. After this time, the solvent was removed under vacuum and the residue sublimed at 80 °C/2 × 10^{-2} mbar. After 5 h the yellow material collected on the cold finger was contaminated with an oily liquid. The sublimed material was collected on a glass frit, washed with pentane, and dried under vacuum. A 230-mg amount (67%) of pure product was obtained, mp 55–56 °C (lit.[16] mp 55–60 °C). Alternatively, the crude reaction mixture could be chromatographed on alumina with a mixture of 10% EtOAc in hexanes as eluent. But in this case a substantially lower yield (30%) of product was isolated.

Preparation of $(CH_3)_3SnC{\equiv}CC{\equiv}CH$. A solution of freshly distilled (*Z*)-1-methoxybut-1-en-3-yne (1.297 g, 0.016 mol) in THF (50 mL) was treated with butyllithium (21 mL, 0.032 mol) (1.5 M solution in hexane) at −25 °C. The mixture was stirred at low temperature for 1 h. Within this time, the initial clear solution became cloudy and light brown in color. $(CH_3)_3SnCl$ (6.96 g, 0.035 mol) was then added as a solid to the mixture, causing the cloudiness to disappear. After the addition of the tin compound the cold bath was removed, the reaction was allowed to reach room temperature, and the stirring was continued for a further 1 h. The solvent was then evaporated under vacuum and the residue loaded into a sublimation apparatus. The cold finger of the sublimator was connected to a circulating cryostat, and the temperature of the cooling fluid was set at −10 °C. At 70 °C/2 × 10^{-2} mmHg a white solid was collected (3.266 g, 97%). It had to be removed from the cold finger under a protective blanket of argon. At room temperature $(CH_3)_3SnC{\equiv}CC{\equiv}CH$ is an air-/moisture-sensitive

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deliquescent material. Owing to the unavoidable contamination of the compound with trace amounts of **10** and because of its sensitivity, satisfactory elemental analysis were not be obtained, mp above 100 °C (dec). IR (CH_2Cl_2, cm^{-1}): 3299.5, 2122.0, 2037.0. ^{1}H-NMR ($CDCl_3$, ppm): 3.75 (s, 1 H), 0.65 (d, 1.37 Hz, $Sn^{117-119}$ satellites), 0.28 (s, 9 H), -0.09 (d, 1.37 Hz, $Sn^{117-119}$ satellites). ^{13}C-NMR ($CDCl_3$, ppm): 156.32, 91.39, 85.67, 84.32, -7.91. Mass fragmentation pattern (reported for the most abundand Sn isotope Sn^{120}) (*m/e*): 214 (M^+); 199 ($M^+ - 15$, $-Me$); 184 ($M^+ - 30$, $-2Me$); 169 ($M^+ - 45$, $-3Me$).

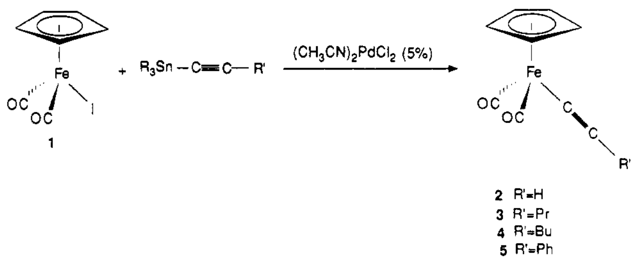
Preparation of $(CH_3)_3SnC{\equiv}CC{\equiv}CSn(CH_3)_3$. A THF (50 mL) solution of freshly distilled (*Z*)-1-methoxybut-1-en-3-yne (0.519 g, 0.006 mol) was cooled to -25 °C and treated with butyllithium (13 mL, 90.019 mol) (1.5 M solution in hexane). A tan precipitate formed immediately, and the mixture was stirred at low temperature for 1 h. $(CH_3)_3SnCl$ (3.90 g, 0.130 mol) was then added as a solid to the mixture, causing the rapid disappearance of the precipitate, with formation of a clear, pale yellow solution. The cold bath was removed, the reaction was allowed to reach room temperature, and the stirring was continued for an additional 1 h. During this time the color of the solution became progressively more intense. The reaction mixture was then poured into a saturated aqueous NH_4Cl (100 mL) solution and extracted with 3 × 100 mL portions of pentane. The combined organic phases were washed twice with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent left a tan solid, which was purified by sublimation at 70 °C/2 × 10^{-2} mmHg (2.12 g, 90%), mp above 100 °C (dec). IR (CH_2Cl_2, cm^{-1}): 2041.4. ^{1}H-NMR ($CDCl_3$, ppm): 0.66 (d, 1.22 Hz, $Sn^{117-119}$ satellites), 0.28 (s, 9 H), -0.084 (d, 1.22 Hz, $Sn^{117-119}$ satellites). ^{13}C-NMR ($CDCl_3$, ppm): 91.44, 84.50, -7.80. Mass fragmentation pattern (reported for the most abundant combination of 2 Sn isotopes, Sn^{118} and Sn^{120}) (*m/e*): 376 (M^+); 361 ($M^+ - 15$, $-Me$); 331 ($M^+ - 45$, $-3Me$). Anal. Calcd for $C_{10}H_{18}Sn_2$: C, 31.97; H, 4.83. Found: C, 30.72; H, 4.92.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2FeC{\equiv}CC{\equiv}CH$.[19] Solid $(CH_3CN)_2PdCl_2$ (0.070 g, 0.3 mmol) was added to a THF (50 mL) solution of $CpFe(CO)_2I$ (1.957 g, 0.006 mol) and $(CH_3)_3SnC{\equiv}C\text{-}C{\equiv}CH$ (1.636 g, 0.008 mol). The solution immediately turned dark and was allowed to stir overnight. The volume of the solution was then reduced in vacuo to 10 mL, Celite (10 g) was added, and the solvent was completely evaporated. The coated mixture was then transferred to a chromatographic column packed with Al_2O_3 and eluted with a mixture of 8/2 hexane/EtOAc. Two bands were collected, the first of which (0.70 g, 36%) was the unreacted $CpFe(CO_2)I$; the second one (0.74 g, 51%) is the product. Further purification was achieved by high-vacuum sublimation at 80 °C/4 × 10^{-6} mmHg, mp above 110 °C (dec).

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2FeC{\equiv}CC{\equiv}CFe(CO)_2(\eta^5\text{-}C_5H_5)$.[16,19] **(a) In THF.** Solid $(CH_3CN)_2PdCl_2$ (35 mg, 0.13 mmol) was added to a THF (50 mL) solution of $CpFe(CO)_2I$ (730 mg, 2.4 mmol) and $(CH_3)_3SnC{\equiv}CC{\equiv}CSn(CH_3)_3$ (450 mg, 1.2 mmol). The solution turned immediately dark and was allowed to stir overnight. The volume of the solution was then reduced to 10 mL in vacuo, Celite (10 g) was added, and the solvent was completely evaporated. The coated mixture was then transferred to a chromatographic column packed with SiO_2 and separated by a gradient eluition of a mixture of hexane/EtOAc. The coupled product was isolated (415 mg, 43%) as a red solid. Recrystallization by vapor diffusion of pentane into a concentrated THF solution gave red crystals of the product, mp dec. above 110 °C (dec).

(b) In DMF. A 25-mg amount (0.09 mmol) of solid $(CH_3CN)_2PdCl_2$ was added to a stirred solution of 533 mg (1.75 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and 328 mg (0.88 mmol) of $(CH_3)_3SnC{\equiv}CC{\equiv}CSn(CH_3)_3$ in 40 mL of DMF. The solution became dark brown, and the stirring was continued overnight at room temperature. After this time, the reaction mixture was transferred into a separating funnel, an additional 100 mL of water was added, and the mixture was treated with a 3 × 50 mL fraction of diethyl ether. The ethereal phase was discarded, and the aqueous solution was treated with 3 × 50 mL of CH_2Cl_2. The combined dichloromethane extracts were dried over magnesium sulfate, filtered, and evaporated to dryness in vacuo; 224 mg (34%) of product was obtained as a dark solid. The ^{1}H NMR analysis showed that the product was contaminated (8%) with unreacted $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$.

Scheme I



Blank Experiments, General Procedure. All the coupling reactions have been repeated under the identical conditions described above, with the only exception of excluding the addition of palladium in the reaction mixture and, in another run, adding 5 mol % of $PdCl_2$ ($PdCl_2$ required a few hours to completely dissolve in DMF). As a representative example the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $Bu_3SnC{\equiv}CPh$ has also been repeated without catalyst in refluxing THF and in DMF at 80 °C. The reaction time as well as the workup and the chromatographic separation were the same as reported for each coupling experiment. None of the blank reactions produced detectable amounts of the coupled product. From the chromatographic separation of the reaction mixture, the starting iron complex was recovered almost quantitatively.

Results and Discussion

σ-Alkynyl derivatives of transition metals are conventionally prepared by the reaction of metal halides with anionic alkynylating agents such as alkynyl compounds of alkali metals,[20] magnesium,[20] or copper.[21] Other preparations use the interaction of a neutral alkyne with transition metal complexes.[22] Recently, alkynyliodonium triflates have been used as alkynylating agents for organometallic systems.[23] These methods do offer accessibility to a wide variety of (σ-alkynyl)metal complexes[24] but often require cumbersome preparations of starting materials and/or careful handling of labile reactants. The advantage of our method relies on mild reaction conditions and on the use of the easily accessible transition metal halides and alkynylstannanes as coupling partners.

An example of an alkynylstannane being used to introduce a σ-alkynyl moiety in a metal complex has been reported.[25] Reaction of a rhenium tetrafluoborate salt and a trimethyltin acetylide compound resulted in a σ-alkynyl complex of rhenium, but only in very low yield (18%). In agreement with our unprecedented discovery of the formation of an iron acetylide complex under a palladium-catalyzed coupling reaction,[5] the reaction of the simple $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (**1**) with the trialkyltin acetylide derivatives $Bu_3SnC{\equiv}CR$ [R = H (**2**), Pr (**3**), Bu (**4**), Ph (**5**)] affords the corresponding η^1-alkynyl derivatives in the presence of the palladium catalyst (Scheme I).

These reactions were initially run under the identical conditions we used previously for the coupling of iodo–

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Table I. IR,[a] ^{1}H NMR,[b] and ^{13}C NMR[b] Data for the Iron Acetylide Complexes 2–5 and 11 and 12

compd	IR, cm^{-1}	^{1}H-NMR, δ	^{13}C-NMR, δ
$CpFe(CO)_2C{\equiv}CH$	3280.5 w, 2305.0 w, 2046.3 vs, 1994.4 vs	1.57 (s, 1 H) (Cp), 4.99 (s, 5 H) ($\equiv$CH)	85.17 (Cp), 84.13, 101.38 ($C{\equiv}C$), 212.13 (CO)
$CpFe(CO)_2C{\equiv}C(CH_2)_2CH_3$	2123.5 w, 2039.1 vs, 1989.2 vs	0.93 (t, 3 H, J = 4.7 Hz) ($-CH_3$), 1.24–1.61 (m, 2 H) ($-CH_2-$), 2.25 (t, 2 H, J = 6.8 Hz) ($Fe-CH_2-$), 4.94 (s, 5 H) (Cp)	13.26, 23.95, 24.05 (Pr), 67.34, 115.78 ($C{\equiv}C$), 84.97 (Cp), 213.26 (CO)
$CpFe(CO)_2C{\equiv}C(CH_2)_3CH_3$	2121.7 w, 2038.6 vs, 1988.0 vs	0.87 (t, 3 H, J = 7.1 Hz) ($-CH_3$), 1.34–1.43 (m, 4 H) ($-CH_2-CH_2-$), 2.28 (t, 2 H, J = 6.9 Hz) ($Fe-CH_2-$) 4.95 (s, 5 H) (Cp)	13.71, 21.86, 21.91, 32.93 (Bu), 67.11, 115.65 ($C{\equiv}C$), 84.90 (Cp), 212.84 (CO)
$CpFe(CO)_2C{\equiv}CPh$	2108.8 s, 2042.1 vs, 1994.4 vs	5.06 (s, 5 H), (Cp) 7.08–7.32 (m, 5 H) (–Ph)	125.28, 127.68, 127.79, 131.35 (Ph), 85.23 (Cp), 88.26, 116.41 ($C{\equiv}C$), 212.30 (CO)
$CpFe(CO)_2C{\equiv}CC{\equiv}CH$	3299.9 w, 2149.5 s, 2049.9 vs, 2002.5 vs	1.41 (s, 1 H) ($\equiv$CH), 5.02 (s, 5 H) (Cp)	54.35, 70.88, 89.85, 96.80 ($C{\equiv}CC{\equiv}C$), 85.37 (Cp), 211.37 (CO)
$Cp(CO)_2FeC{\equiv}CC{\equiv}CFe(CO)_2Cp$	2144.0 w, 2044.2 vs, 1995.7 vs	4.95 (s, 5 H) (Cp)	66.84, 101.58 ($C{\equiv}CC{\equiv}C$), 85.15 (Cp), 212.29 (CO)

[a] Recorded in CH_2Cl_2. [b] Recorded in $CDCl_3$. Abbreviations: w, weak; s, strong; vs, very strong.

cyclopentadienyl derivatives and trialkyltin acetylides.[26a–c] Typically, the $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (1) was stirred overnight with a slight excess of tributyltin acetylide in the presence of 5 mol % of $(CH_3CN)_2PdCl_2$ using DMF as the solvent. The reaction mixture was then treated with an aqueous solution of KF, in order to transform the byproduct Bu_3SnI into the insoluble Bu_3SnF. Following filtration, it was extracted with Et_2O/H_2O to transfer DMF into the aqueous phase and the coupled product into the ethereal solution. After removal of the solvent, the reaction mixture was then separated by chromatographic methods. By this procedure the coupled products $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}C(CH_2)_3CH_3$ (4) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CC_6H_5$ (5) were isolated in 74% and 60% yields, respectively, while products 2 and 3 only in the corresponding hydrated forms were isolated, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{=}O)CH_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{=}O)(CH_2)_3CH_3$. At first this inconvenience was attributed to the effect of the aqueous treatment of the reaction mixture on the alkyne. Therefore, even though the workup conditions were not acidic, $NaHCO_3$ was added to the aqueous KF solution to give an alkaline solution of pH 9. This procedure only prevented the hydration of 3, and after chromatographic separation the alkyne was recovered in 71% yield, but 2 was again obtained in the hydrated form. The reaction for the formation of 2 was then run in THF. When a sample of the reaction mixture examined by ^{1}H-NMR showed formation of the product, the solvent was evacuated and the mixture directly chromatographed over silica. Again $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{=}O)CH_3$ was the only product recovered, indicating that the silica itself can induce hydration. The use of alumina as a separating agent avoided this inconvenience, but the yield of the isolated product was quite low (30%). An acceptable yield of the alkyne 2 was finally obtained by running the reaction in THF, and after evaporation of the solvent, the crude reaction mixture was directly sublimed under high vacuum. The product 2 was collected on the cold finger along with some tributyltin iodide, which was easily washed out with pentane. By this procedure, pure $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CH$ was isolated in 68% yield. The ease of hydration of these alkynes is probably due to the ability of certain metals to catalyze the hydration of η^1-metal acetylides under neutral conditions.[27] In Table I are listed the spectroscopic data for all the iron acetylide compounds prepared.

It is interesting to note the difference in the ease of hydration of the series of the acetylide complexes (2–5). While 2 and 3 are quite sensitive toward water to a different extent, complexes 4 and 5 do not show any formation of the corresponding acyl compounds under same conditions. The difference in behavior of complexes 3 and 4 is significant. The addition of a simple methylene to the alkyl chain makes the iron acetylide compounds resistent toward hydration.

The palladium-catalyzed alkynylation reaction was then extended to the preparation of metal acetylyde complexes containing the 1,3-butadiyne ligand. A convenient preparation for these types of compounds can give easy access to the building blocks of the metal–polyyne polymers in which transition metal atoms are joined in the main chain by a metal–carbon σ-bond. These products are of relevant importance in electronics and material science.[28] The tin diyne compounds 8 and 10 were prepared by a simple modification of the synthetic route that lead to 1,4-bis(trimethylsilyl)-1,3-butadiyne from the commercially available (*Z*)-1-methoxybut-1-en-3-yne (5).[19] The corresponding 1,4-bis(trimethylstannyl)-1,3-butadiyne (10) was produced simply by replacing $(CH_3)_3SiCl$ with $(CH_3)_3SnCl$ in the quenching of dianion 9 (Scheme II).

By repeating the same synthetic route, using an enyne/BuLi–$(CH_3)_3SnCl$ ratio of 1/2, it was possible to trap the intermediate monolithiated butadiyne 7 with formation of 1-(trimethylstannyl)-1,3-butadiyne (8). While it is possible to isolate the bis(tin) diyne 10 in pure form by sublimation, the corresponding mono(tin) diyne 8 is unavoidably contaminated by a small amount (3–5%) of the bis(tin) analgue (10). This inconvenience is probably due to the difficulty to achieve the precise stoichiometry required in the treatment of the enyne 6 with BuLi to obtain 7 or 9. The tin compounds 8 and 10 were then reacted with the iron complex 1 in the presence of a catalytic amount (5%) of $(CH_3CN)_2PdCl_2$ (Scheme III). The reaction for the formation of 11 was run in THF while that for the formation of 12 was performed both in THF and DMF.

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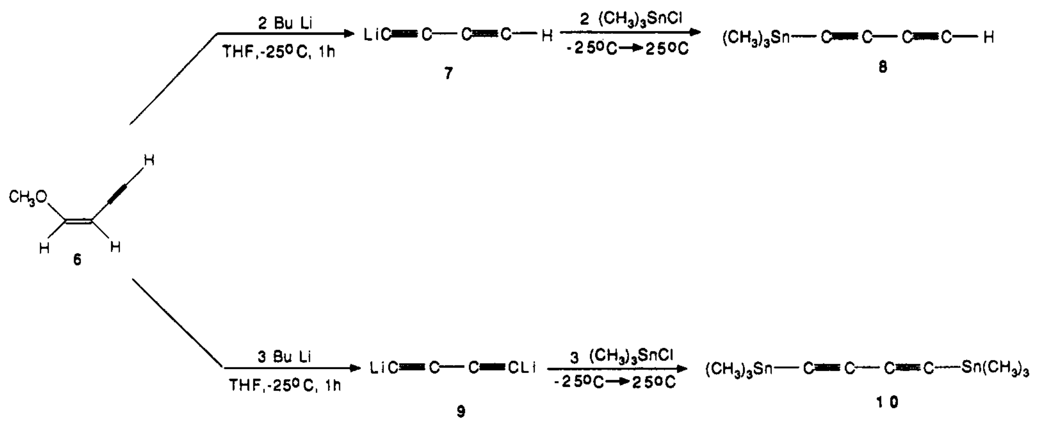
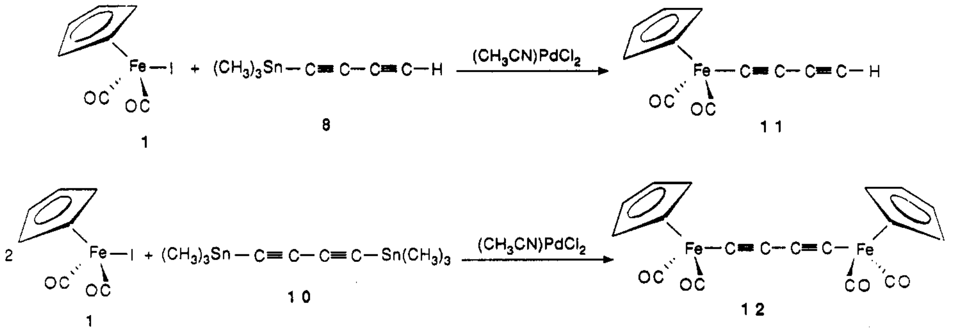
Scheme II



Scheme III



When the reactions were run in THF, the coupled products were isolated by chromatographic separation. In the formation of 12 in DMF, the reaction mixture was at first partioned between Et_2O and H_2O, to separate in the ethereal phase the unreacted $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and then the aqueous-DMF layer was treated with CH_2Cl_2 to extract the coupled product 12.

The procedure in DMF to form 12 is simpler than the one in THF, because the chromatographic separation can be avoided, but the yield is lower and the product is contaminated with a small amount of starting material. In THF, the coupled products 11 and 12 were recovered in 51% and 46% yields, respectively. Although these yields were not optimized, it is noteworthy to underline the effectiveness of this procedure for the preparation of complexes 11 and 12, in comparison with the known literature methods.[16,19] In these reports, compound 11 has been prepared in three steps starting from $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ with an overall yield of 59%,[19] and a further step is necessary to produce 12, with an overall yield of 32%. With our method, compounds 11 and 12 are both produced in *a single* step starting from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with comparable yields.

As shown before,[5] evidence for the role of palladium in these transformations came from the observation that these reactions, even under forcing conditions (see Experimental Section), do not lead to the formation of any product and the starting material is recovered unchanged when reactions were run in the absence of catalyst. Addition of the palladium as $PdCl_2$ to the mixture of the coupling partners also did not lead to the formation of any products. This is a further evidence that only Pd^0 is the species responsible for the promotion of metal-carbon bond formation. In support of this hypothesis, we found[5] that $Pd(PPh_3)_4$ is as effective, in terms of consumption of starting material and reaction rate, as $(CH_3CN)_2PdCl_2$. In fact $(CH_3CN)_2PdCl_2$ contains the metal as Pd^{II} and needs to be reduced in situ by a slight excess of the stannane[29] before it enters the catalytic cycle. However, $Pd(PPh_3)_4$ undergoes side reactions, such as substitution of CO ligands by PPh_3. The experimental results seem to suggest that the catalytic cycle involves the sequential addition-transmetalation-reductive elimination process, parallel to the pathways reported for the well-known palladium-catalyzed carbon-carbon bond formation.[2,3] To the best of our knowledge the oxidative addition of the palladium into the iron-iodine bond is unprecedented.

In conclusion, our method both offers a new entry for such coupling preparations and opens a hitherto unknown aspect of palladium chemistry. Further studies are under way to elucidate the reaction mechanism, to characterize possible intermediates that lead to the products, and to test the generality of the observed coupling reaction toward other transition metals and organic functionalities.

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