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Preliminary communication

Formation of Mo, W, Fe and Ru di(metal σ-acetylide) derivatives of 2.5-diethynylthiophene via palladium-catalyzed metal–carbon coupling

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Abstract

In the presence of catalytic amount of bis(acetonitrile)dichloropalladium(II) $[(CH_3CN)_2PdCl_2]$ the iodocyclopentadienylmetal complexes $[(\eta^5\text{-}C_5H_5)\,M(CO)_nI]$ (**1**, M = Mo, n = 3; **2**, M = W, n = 3; **3**, M = Fe, n = 2, **4**, M = Ru, n = 2) couple in a 2 to 1 ratio with 2,5-bis[(tributyltin)ethynyl]thiophene (**5**), to form the corresponding dimetal derivatives of general formula $[(\mu\text{-}C_4H_2SC{\equiv}C\text{-}2,5)\{(C_5H_5)M(CO)_n\}_2]$ (**6**, M = Mo, n = 3; **7**, M = W, n = 3; **8**, M = Fe, n = 2; **9**, M = Ru, n = 2).

Keywords: Thiophene diacetylides; Preparations; Molybdenum; Tungsten; Iron; Ruthenium

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σ-Acetylide complexes are currently receiving much attention due to the unique properties arising from electron delocalization from the metal to the unsaturated ligand, which could give rise to promising advanced polymeric materials [1]. Therefore new pathways to such compounds are highly desirable.

We have previously disclosed [2] that metal iodides and trialkyltin moieties can smoothly couple in the presence of palladium, to afford σ-acetylides in appreciable yields (Scheme 1). These results have stimulated interest in extending this procedure to the bridging between two metal residues of more complicated compounds such as diacetylides. In particular polyethynyl aromatics are of prime interest in view of their use as precursors and building blocks for polymeric organometallic materials [1,3].

We wish to report here the preparation of diacetylides bridging two metals by the coupling of 2,5-bis[(tributyltin)ethynyl]thiophene with cyclopentadienyl metal iodides of Mo, W, Fe and Ru. 2,5-Diethynylthiophene (CARE! All ethynyl aromatics should be treated as potentially explosive materials [4]), was prepared by the palladium/copper-catalyzed reaction between 2,5-dibromothiophene and (trimethylsilyl)acetylene, and subsequent removal of the trimethylsilyl groups by base hydrolysis [5]. The intermediate 2,5-bis((trimethylsilyl)ethynyl)thiophene was easily isolated, with comparable yield, by sublimation (110°C, 10^{-5} bar) of the crude reaction mixture, rather than by chromatography as described in the literature. Treatment of the 2,5-diethynylthiophene with two equivalents of Et_2NSnBu_3 replaced the acetylenic protons by tributyltin groups [6] (Scheme 2) quantitatively, forming the bis(tributyltin) derivative [7] (**5**). Beside its use in

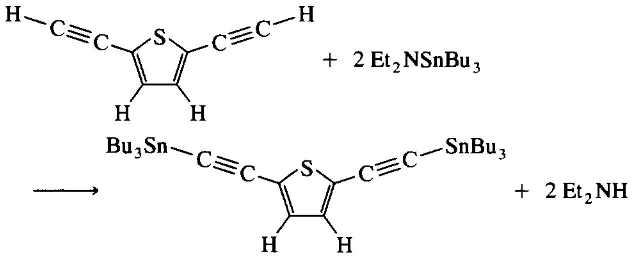
$$[\mathrm{Cp(CO)_nMI}] + \mathrm{Bu_3Sn{-}C{\equiv}C{-}R}$$

$$\mathrm{R = H, Pr, or\ Ph}$$

$$\xrightarrow{\text{“Pd”}} [\mathrm{Cp(CO)_nM{-}C{\equiv}C{-}R}]$$

$$\mathrm{M = W, Mo, Fe, or\ Ru}$$

Scheme 1.



Scheme 2.

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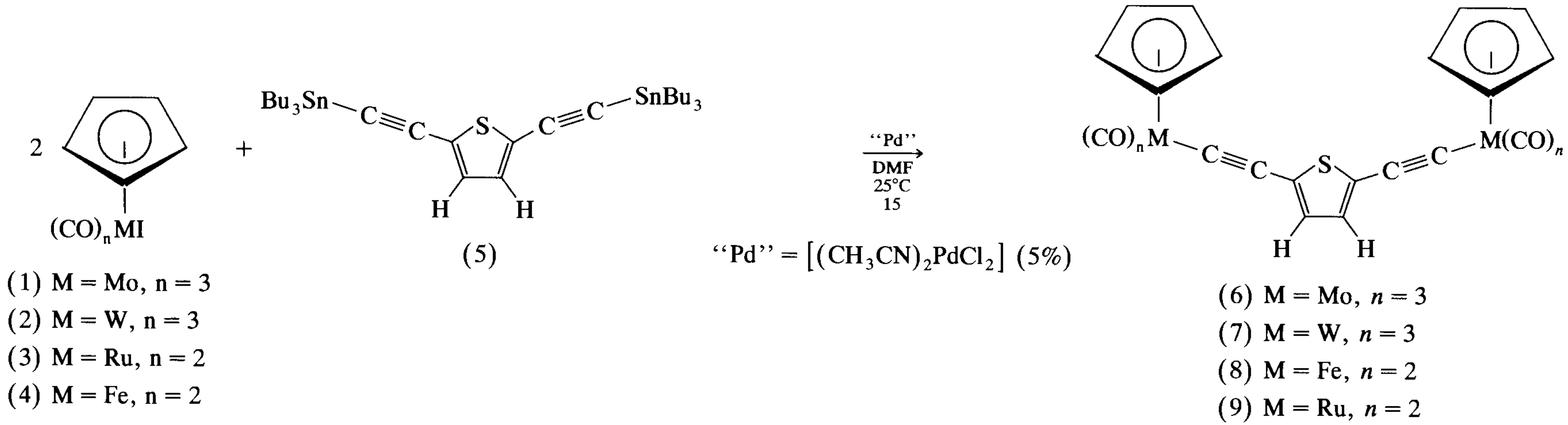

2
(CO)$_n$MI
(1) M = Mo, n = 3
(2) M = W, n = 3
(3) M = Ru, n = 2
(4) M = Fe, n = 2
+
Bu$_3$Sn—C≡C
S
C≡C—SnBu$_3$
H
H
(5)
"Pd"
DMF
25°C
15
"Pd" = [(CH$_3$CN)$_2$PdCl$_2$] (5%)
(CO)$_n$M—C≡C
S
C≡C—M(CO)$_n$
H
H
(6) M = Mo, n = 3
(7) M = W, n = 3
(8) M = Fe, n = 2
(9) M = Ru, n = 2

Scheme 3.

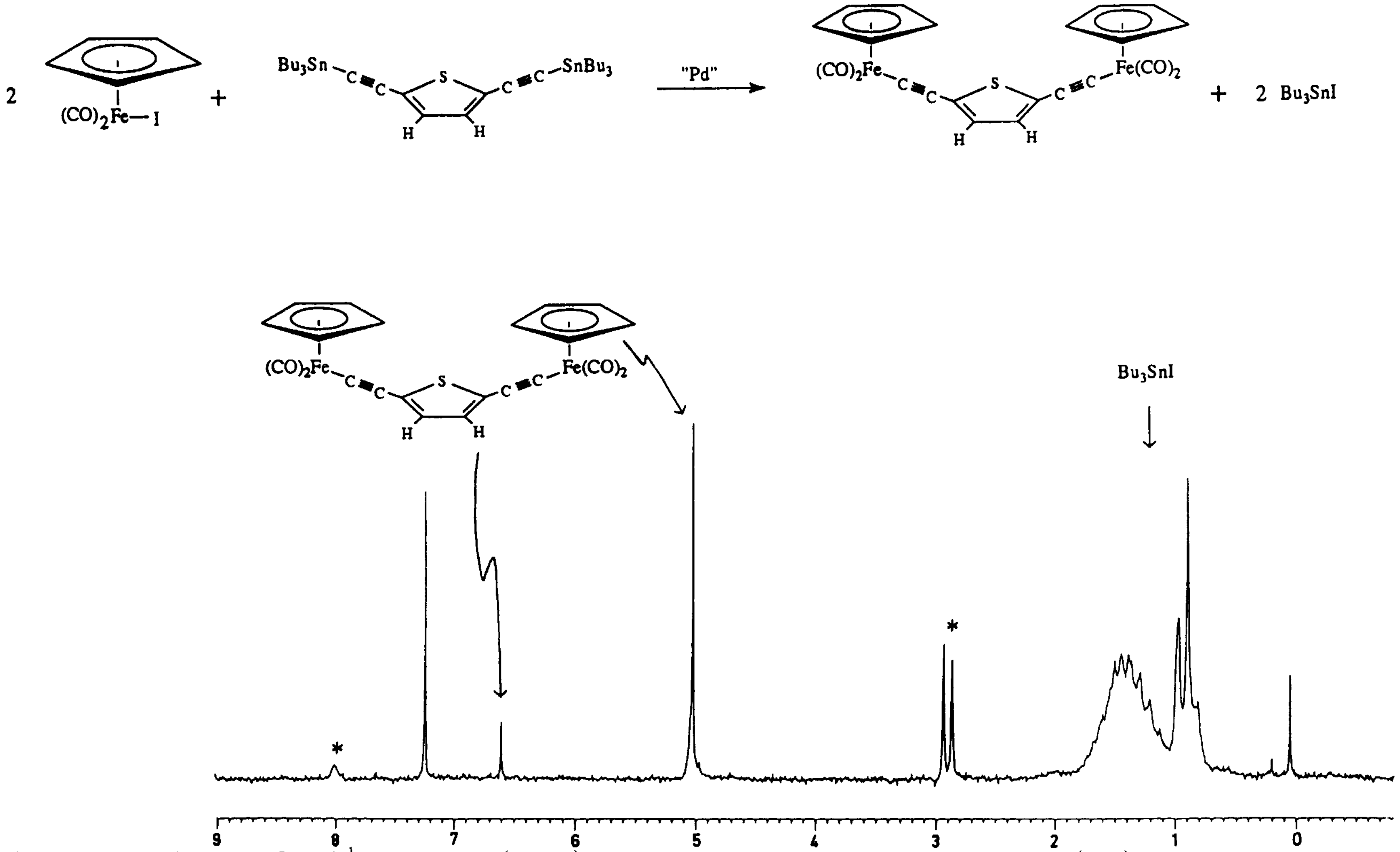
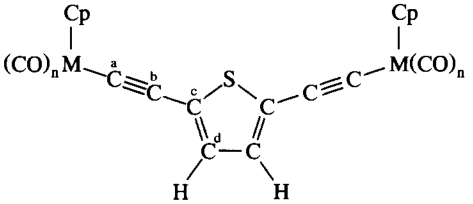
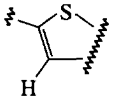


Fig. 1. Coupling reaction between **5** and **4**. ^{1}H-NMR spectrum (80 MHz) of the crude reaction mixture after evaporation of the solvent (DMF), and redissolution in $CDCl_3$. Asterisks indicate residual DMF.

Table 1
Spectroscopic data for compounds **6–9**. ^{1}H and ^{13}C-NMR were recorded at 300 MHz and 75 MHz, respectively.



Compound	$M(CO)_n$	IR (CH_2Cl_2, cm^{-1})	^{1}H ($CDCl_3$/TMS, ppm)		^{13}C ($CDCl_3$/TMS, ppm)					
			Cp		Cp	a	b	c	d	CO
6	$Mo(CO)_3$	1967.1, 2043.9	5.52, s, 10H	6.67, s, 2H	93.00	94.49	121.24	125.77	128.31	222.11, 238.36
7	$W(CO)_3$	1951.1, 2038.3	5.61, s, 10H	6.64, s, 2H	91.62	79.66	120.17	125.81	128.51	211.18, 228.48
8	$Fe(CO)_2$	1996.9, 2042.6, 2097.5	5.02, s, 10H	6.60, s, 2H	85.28	93.71	108.35	125.39	127.72	212.01
9	$Ru(CO)_2$	1998.8, 2048.8, 2107.4	5.43, s, 10H	6.65, s, 2H	87.98	98.35	102.56	125.12	128.10	196.47

the present work, this new stannane derivative may be a valuable intermediate for the widely used Stille coupling to form carbon–carbon bonds [8] and in the R_3Sn-alkynyl exchange route used to prepare transition metal σ-acetylide complexes [9].

Coupling reactions of **5** with the iodo derivatives **1–4** were carried out under standard condition [2a–c] of palladium catalysis. The metal iodides **1–4** and 2,5-bis[(tributyltin)ethynyl]thiophene **5** (in a 2 to 1.1 ratio) were allowed to react overnight [10] in the presence of bis(acetonitrile)dichloropalladium(II), $[(CH_3CN)_2PdCl_2]$, in DMF as shown in Scheme 3. Although we routinely used 5 mol% of catalyst, we found that this amount can be safely lowered to 2% with unchanged efficiency.

A slight excess of stannane, over the 2 to 1 stoichiometry is required in order to produce the active Pd(0) catalyst by the in situ reduction of $[(CH_3CN)_2PdCl_2]$ [2c]. Alternatively the excess of stannane can be avoided by the direct use of zerovalent palladium catalysts such as $[Pd(dba)_2]$ [11]. $[Pd(PPh_3)_4]$ must be avoided since concomitant replacement of CO by PPh_3 occurs. In the formation of complexes **6–9** monitored by ^{1}H-NMR spectroscopy of samples of reaction mixture, freed from the solvent, and redissolved in $CDCl_3$, there is complete consumption of starting materials and only peaks of the dimetal complex and of the byproduct Bu_3SnI could be detected (Fig. 1).

Despite the effectiveness of the coupling reaction in generating complexes **6–9** the low yields of the recovered products are a disappointment. After work up and chromatographic separation of the crude reaction mixture the yields of isolated product were 28% for Mo (**6**), 31% for W (**7**), 41% for Fe (**8**) and 25% for Ru (**9**). We believe that this heavy loss of material is due to the lability of the products under the work up/isolation conditions [2c]. Currently we are dedicating great efforts to find conditions to minimize the factors limiting this otherwise remarkable transformation.

References and notes

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[7] 2,5 diethynylthiophene (0.538 g, 4.07 mmol) and Et_2NSnBu_3 (3.16 g, 8.14 mmol) were mixed in a dry atmosphere in a 50 ml flask. After overnight stirring at room temperature, the flask was keept under vacuum for 2 h, and pure 2,5-bis[(tributyltin)ethynyl]thiophene was quantitatively obtained as yellow oil. ^{1}H-NMR ($CDCl_3$, ppm): 0.89 (t, 18H, $J = 7.2$ Hz) ($C\mathit{H}_3$-CH_2-CH_2-CH_2-), 1.00–1.10 (m, 12H) (CH_3-$C\mathit{H}_2$-CH_2-CH_2-), 1.25–1.40 (m, 12H) (CH_3-CH_2-$C\mathit{H}_2$-CH_2-), 1.54 (t, 12H, $J = 7.2$ Hz) (CH_3-CH_2-CH_2-$C\mathit{H}_2$-), 6.94 (s, 2H) (*H-Thioph.*). ^{13}C-NMR ($CDCl_3$, ppm): 11.24 ($\mathit{C}H_3$-CH_2-CH_2-CH_2-), 13.64 (CH_3-$\mathit{C}H_2$-CH_2-CH_2-), 26.95 (CH_3-CH_2-$\mathit{C}H_2$-CH_2-), 28.83 (CH_3-CH_2-CH_2-$\mathit{C}H_2$-), 99.54 (Sn-C≡), 101.81 ≡C–Thioph.), 124.47, 131.26 (*Thioph.*).

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[10] Satisfactory analyses were obtained for all compounds reported. Synthesis of (**6–9**). [$(CH_3CN)_2PdCl_2$] (5% mmol) was added as solid to a mixture of [$(\eta^5$-$C_5H_5)M(CO)_nI$] (2 mmol), and $(Bu_3Sn{-}C{\equiv}C{-})_2C_4H_2S$ (1.1 mmol), in DMF (20 ml). After stirring overnight at room temperature, 50 ml CH_2Cl_2 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 to a separatory funnel. The aqueous phase was separated, the organic solution was washed with water (3 × 50 ml), and the combined aqueous phases were back-extracted with CH_2Cl_2 (2 × 50 ml). The combined organic 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 and the product was isolated by elution with a mixture of hexane–dichlorometane (1 : 1).
The reaction can also be carried out in the presence of [$Pd(dba)_2$] catalyst, using a precise 2 : 1 stoichiometric ratio of metal iodide and stannane.

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