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Formation of Metal σ-acetylides of Mo, W, and Ru via Palladium-Catalyzed Metal–Carbon Coupling

Egidio Viola, Claudio Lo Sterzo *, Raffaella Crescenzi, Giuseppe Frachey

Centro CNR di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro, 5-00185 Roma, Italy

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Abstract

The cyclopentadienyl metal complexes $[(\eta^5\text{-}C_5H_5)M(CO)_nI]$ (**1**, M = Mo, $n = 3$; **2**, M = W, $n = 3$; **3**, M = Ru, $n = 2$) react with tributyltin acetylides $Bu_3Sn\text{–}C{\equiv}C\text{–}R$ (**4**, R = H; **5**, R = Pr; **6**, R = Ph) in the presence of 5 mol% of $[(CH_3CN)_2PdCl_2]$ to give the corresponding σ-alkynyl metal complexes $[(\eta^5\text{-}C_5H_5)M(CO)_n\text{–}C{\equiv}C\text{–}R]$ in good yield.

Keywords: Palladium; Catalysis; Molybdenum; Tungsten; Ruthenium; Acetylide

1. Introduction

Metal σ-acetylide compounds are of continuing interest in organometallic chemistry. Beside their "classical" role as unusual σ-organic derivatives of transition metals, in which the unique characteristic of the acetylide fragment linked to the metal allowed a large variety of important transformations and applications [1], there is an emerging and considerable interest in metal σ-acetylides as models and precursors for polyalkyne polymers containing transition metals in the main chain backbone, a feature of great importance in the advanced materials field [2].

Within this framework, new and efficient routes to such compounds are desirable. We have previously shown that a number of σ-acetylide complexes are conveniently synthesized by coupling tributyltin acetylide derivatives and $[CpFe(CO)_2I]$ (Cp = η^5-cyclopentadienyl) in the presence of a catalytic amount of palladium (Scheme 1) [3].

$$[Cp(CO)_2FeI] + R_3Sn\text{–}(C{\equiv}C)_n\text{–}R' \xrightarrow[Pd]{} [Cp(CO)_2Fe(C{\equiv}C)_nR']$$

$$R = Bu,\ n = 1,\ R' = H,\ Bu \text{ or } Ph$$

$$R = Me,\ n = 2,\ P' = H \text{ or } Fe(CO)_2Cp$$

Scheme 1.

This chemistry seems to parallel the well-known Pd-catalyzed carbon–carbon bond formation. Recently tin acetylides have received increasing attention in the preparation of transition metal acetylides. A number of efficient methods which use such derivatives as intermediates [4] or partners [5] to attach an acetylenic group to a metal have been reported.

The powerful tool that Pd-catalysis represents in organic chemistry [6], and the importance of transition metal acetylides, has prompted us to explore the effectiveness of this method in the organometallic field, by widening the selection of transition metals that can be introduced in this synthetic route.

2. Results and discussion

We report the results obtained from the reactions of tungsten, molybdenum and ruthenium iodide-complexes of the type $[CpM(CO)_nI]$ (**1**) M = Mo; $n = 3$, (**2**) M = W; $n = 3$, (**3**) M = Ru; $n = 2$) with some representative tributyltin acetylides $Bu_3Sn\text{–}C{\equiv}C\text{–}R$ (**4**) R = H, (**5**) R = Pr, (**6**) R = Ph in the presence of a catalytic amount (5% molar) of $[(CH_3CN)_2PdCl_2]$ (Scheme 2). In our procedure, the metal–carbon coupling reaction occurs smoothly at room temperature on stirring the cyclopentadienyliodo-metal derivatives **1–3** with 1.1 equivalent of tributyltin acetylide **4–6** and 5 mol% of bis(acetonitrile)dichloropalladium(II) in *N,N*-dimethylformamide (DMF) overnight.

The stannyl derivative is used in a slight excess in order to produce the active Pd catalyst by the in situ

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* Corresponding author.

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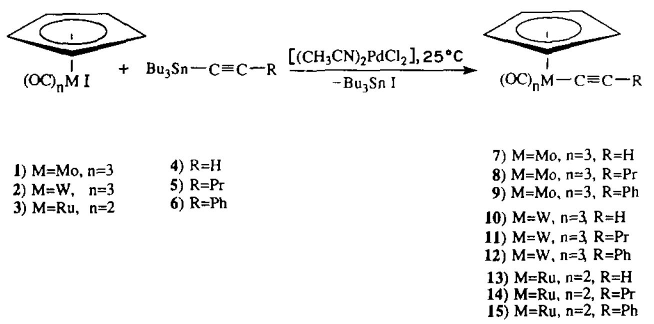

Scheme 2.

reduction of the [(CH$_3$CN)$_2$PdCl$_2$] [7]. As for the formation of the corresponding iron acetylides [3b], the essential role played by the palladium catalyst is shown by the fact that the coupling reaction does not take place and starting materials are recovered unchanged in absence of palladium, or even when PdCl$_2$, which is not reduced to Pd(O) under the reaction conditions, is used. Without Pd catalyst, even under forcing conditions, (DMF; 60°C, benzene; reflux) no coupling takes place, and only substantial decomposition of the starting materials occurs. Further evidence that Pd(O) is the active species in promoting the coupling reaction, comes from the direct use of a Pd(O) catalyst, such as [Pd(PPh$_3$)$_4$]. However, in this case, though σ-acetylides are formed, the reaction is complicated by the concurrent formation of products arising from substitution of the CO by phosphine in both starting materials and products [3b,8].

The results of our work are summarized in Table 1. The most significant aspects of these data are as follows: (i) In some cases (entries 3–6) the reaction gave a complete or very high conversion of starting material, while in other cases (entries 1 and 2, and 7–9) it proceeded to a less extent. (ii) There is generally a difference, in some case significant, between the percentage of converted starting material and the isolated

Table 1
Palladium-catalyzed coupling at metal iodides **1**–**3** and stannanes **4**–**6**

Entry	Metal iodide	Stannane	Product	%Conversion [a]	Yield (%) [b]
1	[CpMo(CO)$_3$I]	Bu$_3$Sn-C≡C-H	CpMo(CO)$_3$-C≡C-H	71	24
2	[CpMo(CO)$_3$I]	Bu$_3$Sn-C≡C-Pr	CpMo(CO)$_3$-C≡C-Pr	70	40
3	[CpMo(CO)$_3$I]	Bu$_3$Sn-C≡C-Ph	CpMo(CO)$_3$-C≡C-Ph	100	80
4	[CpW(CO)$_3$I]	Bu$_3$Sn-C≡C-H	CpW(CO)$_3$-C≡C-H	89	62
5	[CpW(CO)$_3$I]	Bu$_3$Sn-C≡C-Pr	CpW(CO)$_3$-C≡C-Pr	100	62
6	[CpW(CO)$_3$I]	Bu$_3$Sn-C≡C-Ph	CpW(CO)$_3$-C≡C-Ph	91	53
7	[CpRu(CO)$_2$I]	Bu$_3$Sn-C≡C-H	CpRu(CO)$_2$-C≡C-H	42	9
8	[CpRu(CO)$_2$I]	Bu$_3$Sn-C≡C-Pr	CpRu(CO)$_2$-C≡C-Pr	50	20
9	[CpRu(CO)$_2$I]	Bu$_3$Sn-C≡C-Ph	CpRu(CO)$_2$-C≡C-Ph	64	31

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b] Isolated yield of pure compound.

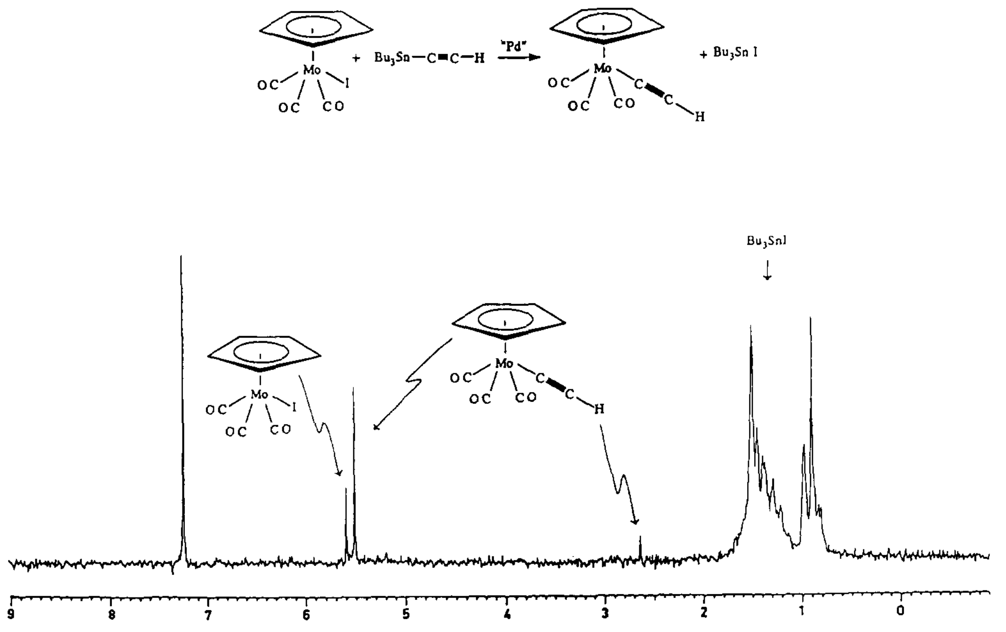

Fig. 1. Coupling reaction between **1** and **4** (Table 1, entry 1), ^{1}H NMR spectrum (80 MHz) of the crude reaction mixture after evaporation of the solvent (DMF), and redissolution in CDCl$_3$.

yield of coupled product. Both these aspects can be explained by the intrinsic instability of metal σ-acetylides [9]. For example, longer reaction times and the addition of fresh catalyst improved the percentage of starting material consumed, though not the isolated yield of the desired product. Decomposition of the product seems to be competitive with its formation at longer reaction times. Therefore the reaction cannot be usefully pushed to completion. Monitoring the reaction by ^{1}H NMR spectroscopy (Fig. 1), only showed starting materials and coupled product. No acyl derivative arising from the hydration of the metal σ-acetylide in the crude reaction mixture or in compounds eluted by column chromatography was ever detected. Hydration was an annoying inconvenience encountered in the preparation of some of the corresponding iron acetylides [3b].

With respect to the second point, the sensitivity of metal σ-acetylides accounts also for the significant loss of material during isolation, despite the high degree of conversion. We believe that on-column degradation during the chromatographic separation, performed to isolate the products, is one of the most important factors in causing this discrepancy. Although we took the precaution of using flash chromatography and degassed solvents, and we shielded the column from light, the product band, while running often produced an immobile tail.

Despite these limits we believe that the easy formation of this series of σ-acetylides, as well as the previously reported iron analogues, is noteworthy because of the simplicity, the effectiveness of the method, and the mild conditions. Compounds **7**, **9**, **10** and **12** are produced in a comparable yield to those of described methods [1e,10] but compounds **8**, **11**, **13**–**15** were unknown before the present work. Compounds **13**–**15** also add to the few existing examples of cyclopentadienyl(monoacetylide) ruthenium(II) derivatives. Moreover, the unreacted metal iodide is recovered during the chromatographic separation, and therefore can be used in a succeeding run.

By this methodology, although optimization is still required, we offered both a new entry relative to conventional methods of obtaining metal σ-acetylides, and confirmed that the palladium-catalyzed metal–carbon bond formation possesses the potential of being a new and fascinating feature of the already rich and well-appreciated palladium chemistry.

Further studies along these lines are in progress.

3. Experimental details

All preparations were carried out under argon using oven-dried (130°C) glassware. Conventional vacuum line and/or Schlenk tube techniques were used. DMF was distilled under vacuum from CaH_2 and stored on activated 4 Å molecular sieves. Liquids were transferred by syringe or cannula [11]. IR spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using a 0.1 mm CaF_2 cell. ^{1}H-NMR spectra and the broad-band proton-decoupled ^{13}C-NMR spectra were recorded in the Fourier-transform mode on Bruker WP-80 and AC300P spectrometers. The ^{1}H-NMR chemical shifts are reported in parts per million vs. Me_4Si, by assigning the ^{1}H impurity signal in the solvent ($CDCl_3$) at 7.24 ppm. The ^{13}C-NMR chemical shifts are referenced to the ^{13}C triplet of $CDCl_3$ at 77.00 ppm. Melting points were determined in an 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, Montelibretti).

$[(CH_3CN)_2PdCl_2]$ [12] $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ [13b], $[(\eta^5\text{-}C_5H_5)W(CO)_3]$ [13a,13b], $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$ [14], and $Bu_3SnC{\equiv}C{-}CH_2CH_2CH_3$ [15] were prepared according to the literature procedures. $Bu_3SnC{\equiv}CH$ and $Bu_3SnC{\equiv}C{-}C_6H_5$ were purchased from Aldrich, and were used as received.

Column chromatographic purifications of reaction mixtures were performed with Merk 60-mesh silica gel.

3.1. Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(\sigma\text{-}C{\equiv}C{-}H)]$ (7). General Procedure

Solid $[(CH_3CN)_2PdCl_2]$ (0.023 g, 0.07 mmol) was added to a mixture of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3I]$ (0.506 g, 1.36 mmol), and $Bu_3SnC{\equiv}CH$ (0.625 g, 1.98 mmol), in DMF (20 ml). After stirring overnight at room temperature, 50 ml of diethyl ether were 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 ethereal solution was washed with water (3 × 50 ml), and the aqueous phase 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 and eluted first with a mixture of hexane-dichloromethane (7:3), which gave a red fraction containing a small amount of unreacted $[(\eta^5\text{-}C_5H_5)Mo(CO)_3I]$ and then by hexane-dichloromethane (1:1) which gave a yellow fraction. Evaporation of the solvent from the latter left the product (0.087 g, 24%) as a yellow solid.

NMR in $CDCl_3$: $\delta(^1H) = 2.64$ (s, 1H, CH), 5.50 (s, 5H, Cp); $\delta(^{13}C) = 92.83$ (Cp); 83.75, 115.17 (C≡C); 222.82, 238.50 (CO).

Spectroscopic data are consistent with literature reports [1d,10]

3.2. *[(η^5-C_5H_5)Mo(CO)$_3$(σ-C≡C-$CH_2CH_2CH_3$)] (8)*

As described for (7), [$(CH_3CN)_2PdCl_2$] (0.055 g, 0.16 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)Mo(CO)$_3$I] (0.620 g, 1.66 mmol), and $Bu_3SnC{\equiv}C{-}CH_2CH_2CH_3$ (0.780 g, 2.18 mmol), in DMF (20 ml). Chromatographic separation of the reaction mixture afforded first a red fraction containing a small amount of unreacted [(η^5-C_5H_5)Mo(CO)$_3$I] and then a yellow fraction containing the coupled product. Evaporation of the solvent from the latter left the product (0.204 g, 40%) as a yellow solid.

Mp 69–70°C. IR(CH_2Cl_2); 2041.9, 1961.6 cm^{-1}, NMR in $CDCl_3$: $\delta(^1H) = 0.94$ (t, 3H, $J = 7{,}1$ Hz, CH_3), 1.47 (ses, 2H, $J = 7{,}1$ Hz, CH_2), 2.27 (t, 2H, $J = 7{,}1$ Hz, CH_2), 5.46 (s, 5H, Cp); $\delta(^{13}C) = 13.47$ (CH_3); 23.49 (CH_2); 24.54 (CH_2); 92.79 (Cp); 94.13, 129.97 (C≡C); 222.67, 240.22 (CO). Anal. Found: C, 49.82; H, 3.87. Calc.: C, 50.02; H, 4.13%.

3.3. *[(η^5-C_5H_5)Mo(CO)$_3$(σ-C≡C-C_6H_5)](9)*

As described for (7), [$(CH_3CN)_2PdCl_2$] (0.020 g, 0.11 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)Mo(CO)$_3$I] (0.500 g, 1.1 mmol), and $Bu_3SnC{\equiv}C{-}C_6H_5$ (0.585 g, 1.5 mmol), in DMF (20 ml). Chromatographic separation of the reaction mixture afforded first a red fraction containing a small amount of unreacted [(η^5-C_5H_5)Mo(CO)$_3$I] and then a yellow fraction containing the coupled product. Evaporation of the solvent from the latter left the product (0.304 g, 80%) as a yellow solid.

IR(CH_2Cl_2); 2038.3, 1951.7 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 5.50$ (s, 5H, Cp), 7.14–7.37 (m, 5H, Ph); $\delta(^{13}C) = 92.93$ (Cp); 87.83, 126.01, 127.14, 127.92, 129.39, 130.85 ($C{\equiv}O{-}C_6H_5$); 222.39, 238.78 (CO).

Spectroscopic data are consistent with literature reports [1e,10].

3.4. *[(η^5-C_5H_5)W(CO)$_3$(σ-C≡C-H)](10)*

As described for (7), [$(CH_3CN)_2PdCl_2$](0.023 g, 0.07 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)W(CO)$_3$I](0.750 g, 1.63 mmol), and $Bu_3SnC{\equiv}C{-}H$ (0.667 g, 2.12 mmol), in DMF (20 ml). Chromatographic separation of the reaction mixture afforded first a red fraction containing a small amount of unreacted [(η^5-C_5H_5)W(CO)$_3$I] and then a yellow fraction containing the coupled product. Evaporation of the solvent from the latter left the product (0.361 g, 62%) as a yellow solid.

IR(CH_2Cl_2); 2043.0, 1951.7 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 2.58$ (s, 1H, CH), 5.59 (s, 5H, Cp); $\delta(^{13}C) = 91.43$ (Cp); 95.43, 114.96 (C≡C); 211.85, 228.60 (CO).

Spectroscopic data are consistent with literature reports [10].

3.5. *[(η^5-C_5H_5)W(CO)$_3$(σ-C≡C-$CH_2CH_2CH_3$)](11)*

As described for (7), [$(CH_3CN)_2PdCl_2$] (0.028 g, 0.13 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)W(CO)$_3$I] (0.338 g, 0.73 mmol), and $Bu_3SnC{\equiv}C{-}CH_2CH_2CH_3$ (0.621 g, 1.74 mmol), in DMF (20 ml). Chromatographic separation of the reaction mixture afforded only a yellow fraction containing the coupled product. Evaporation of the solvent left the product (0.179 g, 62%) as a yellow solid.

Mp 86–87°C. IR(CH_2Cl_2); 2036.3, 1947.3 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 0.92$ (t, 3H, $J = 7.0$ Hz, CH_3), 1.45 (ses, 2H, $J = 7.0$ Hz, CH_2), 2.33 (t, 2H, $J = 7.0$ Hz, CH_2), 5.56 (s, 5H, Cp); $\delta(^{13}C) = 13.46$ (CH_3), 23.62 (CH_2), 24.33 (CH_2); 91.39 (Cp), 129.43 (C≡C); 211.85, 230.54 (CO).

Anal. Found: C, 39.20; H, 3.04. Calc.: C, 39.03; H, 3.02%.

3.6. *[(η^5-C_5H_5)W(CO)$_3$(σ-C≡C-C_6H_5)](12)*

As described for (7), [$(CH_3CN)_2PdCl_2$] (0.036 g, 0.14 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)W(CO)$_3$I] (0.506 g, 1.36 mmol), and $Bu_3SnC{\equiv}C{-}C_6H_5$ (0.738 g, 1.89 mmol), in DMF (20 ml). Chromatographic separation of the reaction mixture afforded only a yellow fraction containing the coupled product. Evaporation of the solvent left the product (0.311 g, 53%) as a yellow solid.

IR(CH_2Cl_2); 2044.1, 1965.3 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 5.54$ (s, 5H, Cp), 7.15–7.35 (m, 5H, Ph); $\delta(^{13}C) = 91.53$ (Cp); 126.06, 126.97, 127.86, 128.40, 129.16, 131.00 ($C{\equiv}C{-}C_6H_5$); 222.40, 238.79 (CO).

Spectroscopic data are consistent with literature reports [1e,10].

3.7 *[(η^5-C_5H_5)Ru(CO)$_2$(σ-C≡C-H] (13)*

As described for (7), [$(CH_3CN)_2PdCl_2$] (0.010 g, 0.04 mmol) was allowed to react with a mixture of [(η^5-C_5H_5)Ru(CO)$_2$I] (0.160 g, 0.46 mmol), and $Bu_3SnC{\equiv}C{-}H$ (0.187 g, 0.59 mmol), in DMF (5 ml). The solvent was then removed under vacuum and the residue sublimed at 70°C/1×10^{-1} mbar. After 10 h pink crystals were deposited on the cold finger, along with traces of an oily liquid. The sublimed material was collected on a glass frit, and, after washing with pentane, the pure product (0.009 g, 9%) was isolated.

IR(CH_2Cl_2); 2053.9, 2002.7 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 1.72$ (s, 1H, CH), 5.41 (s, 5H, Cp); $\delta(^{13}C) = 87.80$ (Cp); 95.74 (C≡C); 196.48 (CO).

Anal. Found: C, 44.01; H, 2.56. Calc.: C, 43.73; H, 2.45%.

3.8. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(\sigma\text{-}C{\equiv}C\text{-}CH_2CH_2CH_3)]$ (14)

As described for (7), $[(CH_3CN)_2PdCl_2]$ (0.010 g, 0.04 mmol) was allowed to react with a mixture of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ (0.105 g, 0.30 mmol), and $Bu_3SnC{\equiv}C\text{-}CH_2CH_2CH_3$ (0.139 g, 0.39 mmol), in DMF (10 ml). Dichloromethane instead of diethyl ether was used in this case to dilute the reaction mixture before the KF treatment, as well as in the subsequent extraction. Chromatographic separation of the reaction mixture afforded first an orange fraction containing unreacted $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ (0.042 g, 40%), and then a brown fraction containing the coupled product. Evaporation of the solvent from the latter left the product (0.017 g, 20%) as a yellow solid.

IR(CH_2Cl_2); 2045.6, 1929.9 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 0.89$ (t, 3H, $J = 7.0$ Hz, CH_3), 1.48 (ses, 2H, $J = 7.0$ Hz, CH_2), 2.27 (t, 2H, $J = 7.0$ Hz, CH_2), 5.38 (s, 5H, Cp); $\delta(^{13}C) = 13.49$ (CH_3); 23.62 (CH_2); 24.00 (CH_2); 87.73 (Cp); 109.30 ($C{\equiv}C$); 197.08 (CO).

Anal. Found: C, 50.93; H, 4.42. Calc.: C, 49.82; H, 4.18%.

3.9. $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(\sigma\text{-}C{\equiv}C\text{-}C_6H_5)]$ (15)

As described for (7), $[(CH_3CN)_2PdCl_2]$ (0.020 g, 0.08 mmol) was allowed to react with a mixture of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ (0.200 g, 0.57 mmol), and $Bu_3SnC{\equiv}C\text{-}C_6H_5$ (0.283 g, 0.72 mmol), in DMF (10 ml). Chromatographic separation of the reaction mixture afforded first an orange fraction containing unreacted $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ (0.060 g, 30%), and then, using pure CH_2Cl_2 as eluent, a dark-yellow fraction containing the coupled product. Evaporation of the solvent left the product (0.057 g, 31%) as a dark-yellow solid.

IR(CH_2Cl_2); 2050.0, 2000.1 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H) = 5.45$ (s, 5H, Cp), 7.06–7.34 (m, 5H, Ph); $\delta(^{13}C) = 87.94$ (Cp); 110.52, 125.47, 127.28, 127.83, 131.54 ($C{\equiv}C\text{-}C_6H_5$); 196.69 (CO).

Anal. Found: C, 54.8; H, 3.86. Calc.: C, 55.72; H, 3.12%.

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