Synthesis of triynylcarbene complexes and of bi- and trinuclear complexes with heptatriynylidene C$_7$-bridges

Cornelia Hartbaum, Helmut Fischer *

Fakultät für Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany

Abstract

The dimethylamino(trimethylsilylhexatriynyl)carbene complex [(CO)$_5$W=C(NMe$_2$)C≡CC≡CC≡CSiMe$_3$] (**2**) was synthesized by two different routes: (a) by sequential reaction of the ethynylcarbene complex [(CO)$_5$W=C(NMe$_2$)C≡CH] with *n*BuLi, CuI, and IC≡CC≡CSiMe$_3$ and (b) by Cl$_2$Pd(MeCN)$_2$-catalyzed coupling of [(CO)$_5$W=C(NMe$_2$)C≡CSn*n*Bu$_3$] with IC≡CC≡CSiMe$_3$. Desilylation of **2** with KF/THF/MeOH afforded the hexatriynylcarbene complex [(CO)$_5$W=C(NMe$_2$)C≡CC≡CC≡CH] (**4**). Deprotonation and coupling with ClSn*n*Bu$_3$ gave the *C*-stannylated carbene complex [(CO)$_5$W=C(NMe$_2$)C≡CC≡CC≡CSn*n*Bu$_3$] (**5**). Reaction of **5** with *n*BuLi and [ClRu(CO)$_2$Cp] afforded the heterobimetallic heptatriynylidene-bridged complex [(CO)$_5$W=C(NMe$_2$)C≡CC≡CC≡CRu(CO)$_2$Cp] (**6**). The trinuclear complex [(CO)$_5$W=C(NMe$_2$)C≡CC≡CC≡C–Hg–C≡CC≡CC≡C(Me$_2$N)C=W(CO)$_5$] (**7**) was obtained by reaction of **4** with *n*BuLi and HgCl$_2$. All new compounds are stable at room temperature. Spectroscopic data suggest weak interaction of the metal centers in **6** and **7**. © 1999 Elsevier Science S.A. All rights reserved.
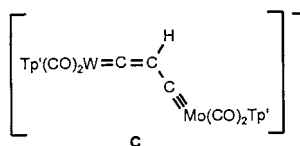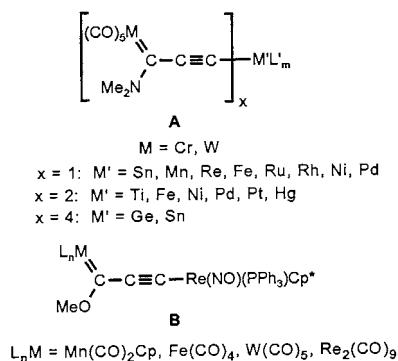
Keywords: Carbene complexes; Binuclear complexes; Tungsten; Ruthenium; Alkynyl complexes; Coupling reaction; Bridging ligands

Bi- and polynuclear transition-metal complexes containing unsaturated conjugated carbon bridges should exhibit potentially useful physical and chemical properties [1,2]. Carbon-bridged bimetallic π-conjugated complexes of the type [L$_n$MC$_m$M′(L′)$_{n'}$] have been proposed as a new class of one-dimensional molecular wires [2]. Rigid-rod polymers like [L$_n$MC≡C–X–C≡C]$_m$ (X = aryl) can exhibit both liquid crystalline [3] and nonlinear optical properties [4] similar to certain metal acetylides [5]. Binuclear complexes with different L$_n$M end groups at a conjugated π-system should exhibit second-order nonlinear optical (NLO) properties. Mononuclear π-systems such as highly ethynylated organic and organometallic compounds represent viable monomers for the synthesis of high carbon polymers. Transition metal σ-acetylide complexes [6] and ethynyl-substituted half sandwich complexes can be considered as building blocks in the synthesis of linear [7], star-shaped [7d, 8], and spheric [9] structures.

Different types of π-conjugated carbon bridges are conceivable. Examples of compounds with a 'naked' carbon chain [L$_n$MC$_m$M′(L′)$_{n'}$], include binuclear π-conjugated acetylide transition metal complexes. Until now, complexes with an even number of carbon atoms *m* (up to *m* = 20 [1f]) linking the metals are more readily accessible than those with an odd number of carbon atoms [1a], although a few complexes with a C$_3$ bridge [10] and a complex with a C$_5$ linkage [1e] have already been prepared.
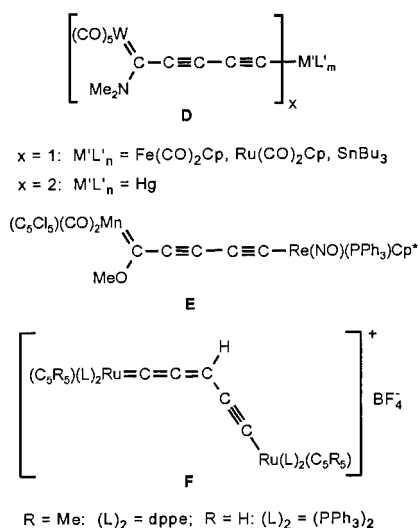
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* Corresponding author.

Scheme 1.

Scheme 2.

We now report on the synthesis of the first dimethyl-amino(triynyl)carbene complexes and on the synthesis of bi- and trinuclear C_7R-bridged heptatriynylidene complexes.

1. Results and discussion

### 1.1. Mononuclear heptatriynylidene complexes

The coupling of a $(CO)_5M[C_3R]$ or $L_nM[C_5R]$ fragment with a $M'(L')_{n'}$ fragment has turned out to be a convenient approach to C_3R- and C_5R-bridged bi- and polynuclear complexes, respectively [11,12,14]. Therefore, the coupling of a $(CO)_5M[C_7R]$ and a metal-ligand fragment also seemed to be the method of choice for the synthesis of C_7R-bridged complexes.

This route required hexatriynylcarbene complexes, $[(CO)_5M=C(XR)C\equiv CC\equiv CC\equiv CR']$ ($R' = H$, $SiMe_3$ or $SnnBu$), as the starting materials. Dimethylamino-substituted carbene complexes ($XR = NMe_2$) were chosen, as alkoxycarbene complexes ($XR = OR$) were expected to be much less stable. In earlier experiments alkoxy-substituted alkynylcarbene complexes such as $[(CO)_5W=C(OMe)C\equiv CH]$ proved to be very unstable and readily decomposed in solution even at low temperature. In contrast, the corresponding amino-(ethynyl)carbene complex $[(CO)_5W=C(NMe_2)C\equiv CH]$ was more stable due to the stabilizing effect of the amino-substituent at the carbene carbon atom, and could be isolated.

Hexatriynylcarbene complexes were unknown. Essentially three different routes for their synthesis were conceivable: synthesis by (a) sequential reaction of $[M(CO)_6]$ with $Li[C\equiv CC\equiv CC\equiv CSiMe_3]$, an alkylating agent, and $HNMe_2$, (b) coupling of a $[(CO)_5M=C(NMe_2)C\equiv C]^-$ with a $[C\equiv CC\equiv CSiMe_3]^+$ unit, and (c) coupling of a $[(CO)_5M=C(NMe_2)C\equiv CC\equiv C]^-$ with a $[C\equiv CSiMe_3]^+$ unit. Earlier it was observed that $Li[C\equiv CC\equiv CSiMe_3]$ did not react with $M(CO)_6$ (M = Cr, W) [14] in contrast to $Li[C\equiv CSiMe_3]$. This is presumably due to the reduced nucleophilicity of the butadiynide as compared to the acetylide. The anion $[C\equiv CC\equiv CC\equiv CSiMe_3]^-$ is even less nucleophilic than $[C\equiv CC\equiv CSiMe_3]^-$. Therefore, route (a) seemed unreasonable and was not attempted. Route (b) was expected to give the best overall results since $[(CO)_5M=C(NMe_2)C\equiv CH]$ complexes are more readily available and in higher yield than $[(CO)_5M=C(NMe_2)C\equiv CC\equiv CH]$ complexes.

The dimethylamino(trimethylsilylhexatriynyl)carbene complex **2** was obtained by a modification of the Cadiot–Chodkiewicz reaction [16] as well as by Stille coupling [17]. Deprotonation of $[(CO)_5W=C(NMe_2)C\equiv CH]$ (**1**) [18] with $nBuLi$ at $-80°C$ in diethyl ether gave $Li[(CO)_5W=C(NMe_2)C\equiv C]$. Subsequent reaction with

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We recently reported on the synthesis of a series of bi-, tri-, and pentanuclear π-conjugated C_3R-bridged complexes of type **A** (Scheme 1) [11,12]. In addition to these compounds, a few binuclear alkoxy (alkynyl)carbene complexes (**B**, Scheme 1) have been synthesized by Gladysz et al. [10a, 13]. The reaction of $[Tp'(CO)_2Mo\equiv C-CH_2-C\equiv W(CO)_2Tp']$ (Tp' = hydrido-tris(3,5-dimethylpyrazolyl)borate) with $KOtBu$ afforded an anionic complex (**C**, Scheme 1) with a $C-(CH)-C$-bridge [10b].

Some bi- and trinuclear π-conjugated C_5R-bridged complexes are also known: **D** [14], **E** [1e], and **F** [15] (Scheme 2).

one equivalent of CuI and, after 30 min, one equivalent of IC≡CC≡CSiMe₃ and chromatographic workup gave compound **2** as a red powder in only 5% yield (Eq. (1)). Alternatively complex **2** was obtained by Stille coupling of the dimethylamino(tributylstannylethynyl)carbene complex **3** [11] with an equimolar amount of IC≡CC≡CSiMe₃ at room temperature (r.t.) in toluene in the presence of 10 mol% of [Cl₂Pd(MeCN)₂]. The reaction proceeded rather slowly and was complete after only 10 h (Eq. (1)). Again, the isolated yield of **2** was 5%.

(1)
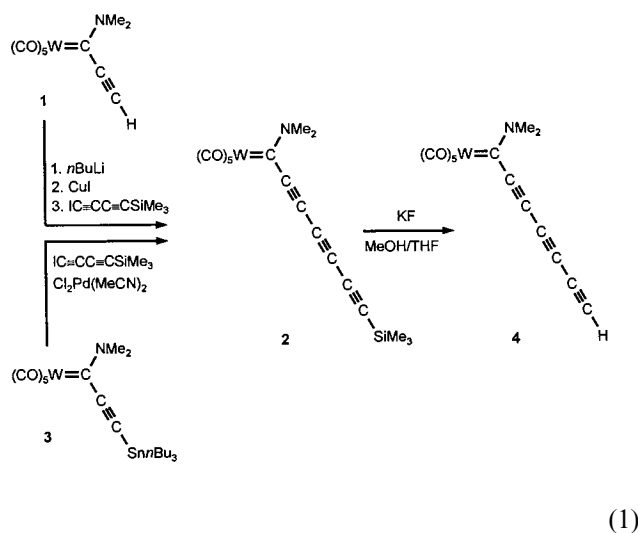
Desilylation of **2** with KF in MeOH/THF afforded the unsubstituted dimethylamino(hexatriynyl)carbene complex **4** in a 75% yield as a red powder (Eq. (1)).

Both hexatriynylcarbene complexes, **2** and **4**, were stable as solids at r.t. and in solution at temperatures below − 30°C. The ν(CO) absorptions of **2** and **4** in the IR spectra are almost identical with those of the corresponding ethynyl- and butadiynylcarbene complexes [(CO)₅W=C(NMe₂)(C≡C)ₓR] (x = 1, 2) [11,14, 18]. There is only a small shift towards higher energy indicating a slight increase in the backbonding properties in the series x = 1, 2, 3. As expected, the influence of increasing the chain length on the ν(C≡C) absorption is more pronounced. A shift towards smaller wavenumbers is observed.

In the ¹H-NMR spectra the resonances of the N–Me groups appear as two well separated singlets due to hindered rotation around the C(carbene)–N bond. With increasing chain length in [(CO)₅W=C(NMe₂)(C≡C)ₓH] the signal of the terminal hydrogen considerably shifts towards higher field ($\delta = 5.65$ (x = 1), 3.81 (x = 2), 2.96 (x = 3)). The ¹³C-NMR spectra of **2** and **4** are characterized by alternating high field/low field resonances of the sp-C atoms along the chain $C(NMe_2)–C^\alpha≡C^\beta–C^\gamma≡C^\delta–C^\varepsilon≡C^\xi–R$.
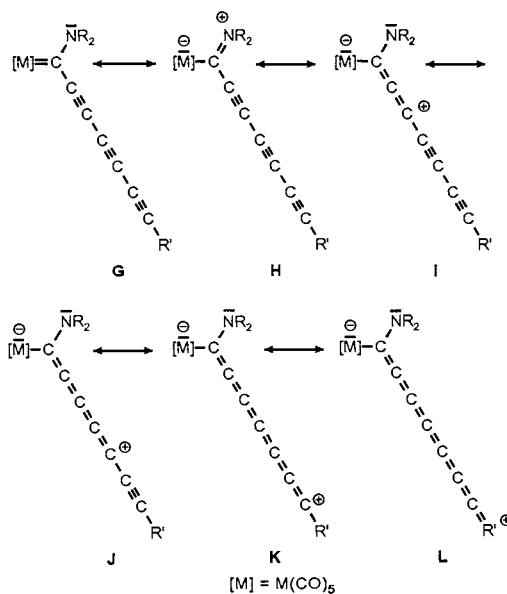

Scheme 3.

The resonances were assigned on the basis of the $^nJ(CH)$ coupling constants of **4** (n = 1, 2, 3) and by comparison with the data of the corresponding butadiynyl complexes [14]. The resonances of C^β, C^δ, and C^ξ are at lower field than the signals of C^α, C^γ, and C^ε. With increasing distance from the carbene carbon atom the difference $\Delta\delta$ for the resonances of the pairs C^α/C^β, C^γ/C^δ, and C^ε/C^ξ decreases. In addition, $\Delta\delta$ for corresponding pairs increases with increasing chain length (x = 1, 2, 3).

From this spectroscopic data it follows that **2** and **4** are best described as hybrids of the various resonance forms **G**–**L**, the dipolar structures **I**, **J**, and **K** significantly contributing to the overall description (Scheme 3).

1.2. Bi- and trinuclear complexes

Deprotonation of **4** with nBuLi in diethyl ether at − 80°C followed by reaction with ClSnnBu₃ afforded the binuclear complex **5** (Eq. (2)). After purification by column chromatography an orange–red **5** is obtained in a 47% yield.

Subsequent Cl₂Pd(MeCN)₂-catalyzed coupling [19] of **5** with [ClRu(CO)₂Cp] in toluene at r.t. gave the C₇(NMe₂)-bridged Ru(CO)₂Cp-substituted hexatriynylcarbene complex **6** (Eq. (2)). The reaction proceeded rather slowly and required 1 day for completion. After chromatographic workup of the reaction mixture, the bimetallic complex **6** was obtained in a 46% yield.

(2)
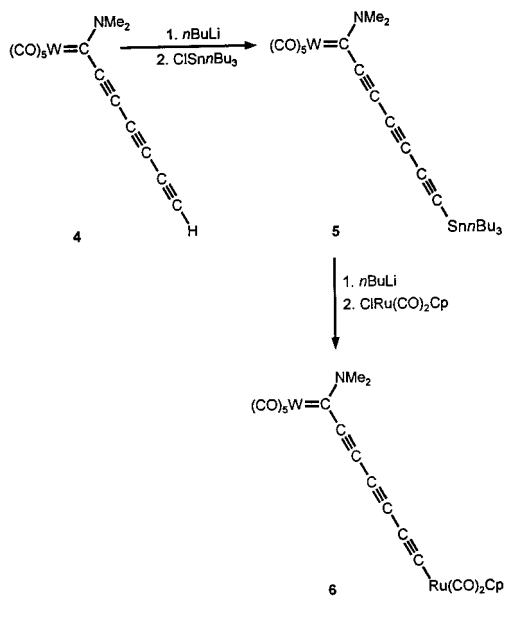
Trinuclear bis-[C$_7$(NMe$_2$)]-bridged complexes are likewise accessible. When **4** was deprotonated with one equivalent of *n*BuLi and then half an equivalent of HgCl$_2$ was added to the solution, the formation of the new complex **7** was observed by IR spectroscopy. Chromatography of the reaction mixture gave the orange complex **7** in a 23% yield (Eq. (3)).

(3)
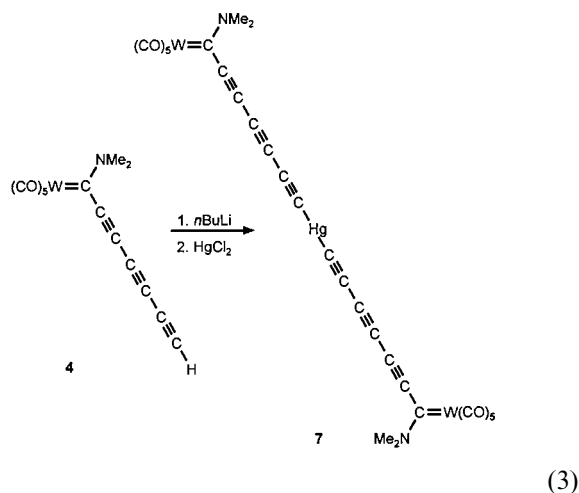
All new bi- and trinuclear complexes **5**–**7** are stable at r.t. Obviously, the introduction of a C$_2$ unit into the C$_5$R-bridge of [(CO)$_5$W=C(NMe$_2$)(C≡C)$_2$M'L'$_{n'}$] or of two C$_2$ units into the C$_3$R-bridge of [(CO)$_5$W=C(NMe$_2$)C≡CM'L'$_{n'}$] does not significantly alter the stability of these compounds.

The elongation of the carbon bridge in [(CO)$_5$W=C(NMe$_2$)(C≡C)$_x$M'L'$_{n'}$] ($x = 1 \rightarrow 2 \rightarrow 3$) diminishes the energy gap between the LUMO and the HOMO. Therefore, a bathochromic shift of the MLCT absorption at lowest energy is to be expected. This assumption is confirmed by the UV–vis spectra of the Ru(CO)$_2$Cp-

substituted complexes [M'L'$_{n'}$ = Ru(CO)$_2$Cp: λ_{max} = 373 nm ($x = 1$), 398 nm ($x = 2$), 428 nm ($x = 3$)], each in DMF. The MLCT absorption shifts towards shorter wavelengths when nonpolar or weakly polar solvents are replaced by more polar ones. However, the solvatochromic effect is only moderate and decreases with increasing chain length: $\Delta\tilde{v}$(toluene/DMF) = 1440 cm^{-1} ($x = 1$), 970 cm^{-1} ($x = 2$), 840 cm^{-1} ($x = 3$) (Fig. 1).

The v(CO) spectrum of the Sn*n*Bu$_3$-substituted complex **5** is similar to that of **2** and **4**. In contrast, the A^1(*trans*) and the E v(CO) absorptions of **6** and **7** are at significantly smaller wavenumbers. From the shift a weak interaction between the π basic fragments Ru(CO)$_2$Cp and Hg and the (CO)$_5$W fragment can be deduced indicating an enhanced contribution of the resonance form **L** (Scheme 3). The ^{13}C-NMR spectra of **5**–**7** are similar to those of **2** and **4**. Again, an alternation of the resonances along the chain is observed. The alternation is most pronounced with the Ru(CO)$_2$Cp-substituted complex **6**.

In summary, dimethylamino(hexatriynyl)carbene complexes are accessible by two different coupling routes from alkynyl(dimethylamino)carbene complexes and butadiyne derivatives. Both routes suffer from rather low yields. In contrast, the subsequent coupling of dimethylamino(hexatriynyl)carbene complexes with metal halides, XM'L'$_{n'}$, to form bi- and trinuclear complexes proceeds with moderate to high yield. The elongation of the chain in [(CO)$_5$W=C(NMe$_2$)(C≡C)$_x$M'L'$_{n'}$] ($x = 1, 2, 3$) does not significantly alter the stability of the compounds. Therefore, complexes with even longer chains C$_x$R should be isolable species provided that suitable precursors for their synthesis can be found.
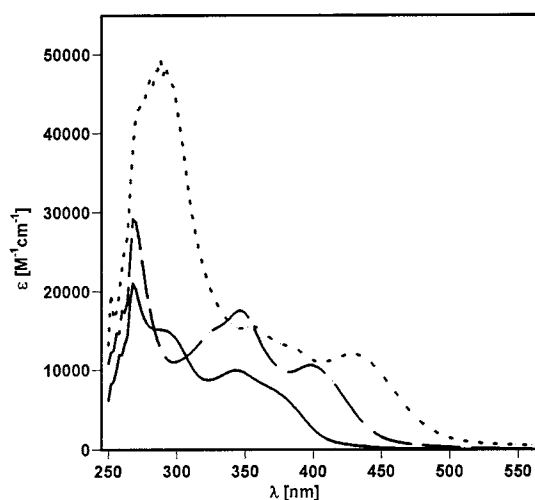

Fig. 1. UV–vis spectra of [(CO)$_5$W=C(NMe$_2$)(C≡C)$_x$Ru(CO)$_2$Cp] in DMF at room temperature [— ($x = 1$), –– ($x = 2$), --- ($x = 3$)].

2. Experimental

All operations were performed under argon by using standard Schlenk techniques. Solvents were dried by refluxing over CaH_2 (CH_2Cl_2) and sodium/benzophenone ketyl (pentane, Et_2O, THF) and were freshly distilled prior to use. The yields refer to analytically pure compounds and were not optimized. Silica gel used for column chromatography (Fa. J.T. Baker, silica gel for flash chromatography) was argon-saturated. The complexes **1** [18], **3** [11], [ClRu(CO)$_2$Cp] [20], and [Cl$_2$Pd(MeCN)$_2$] [21] as well as IC≡CC≡CSiMe$_3$ [22] were prepared according to literature procedures. nBu$_3$SnCl was purchased from Fa. Aldrich. NMR: Bruker AC 250; chemical shifts are reported relative to internal TMS. Unless specifically mentioned NMR spectra were recorded in CDCl$_3$ at r.t.—IR: Biorad FTS 60.—MS: Finnigan MAT 312.—Elemental analyses: Heraeus CHN-O-RAPID.

2.1. Pentacarbonyl[1-dimethylamino-7-trimethylsilyl-2,4,6-heptatriynylidene]tungsten (2)

2.1.1. Route A: via nucleophilic substitution

At $-80°C$ 5.00 mmol of nBuLi (3.13 ml of a 1.6 M solution of nBuLi in hexane) was added to a solution of 5.00 mmol (2.03 g) of **1** in 30 ml of Et$_2$O. The solution was stirred for 30 min at $-80°C$. Then 5.00 mmol (0.95 g) of CuI and 15 ml of THF were added and the solution was stirred for another 30 min at r.t. The solution was cooled again to $-80°C$, 5.00 mmol (1.24 g) of IC≡CC≡CSiMe$_3$ in 20 ml of THF was added. The temperature of the solution was allowed to rise to r.t. and the solution was stirred for 60 min. The solvent was removed in vacuo. The remaining sticky residue was dissolved in 60 ml of THF and filtered with 150 ml of THF:CH$_2$Cl$_2$ (1:1) over a 10 cm-layer of silica. The solvent of the filtrate was removed in vacuo, the residue dissolved in 40 ml of pentane, and chromatographed at $-40°C$ on silica. With pentane:CH$_2$Cl$_2$ (9:2) a red–orange band was eluted. Removal of the solvent in vacuo afforded **2** as a red powder. Yield: 0.13 g (5%, based on **1**).

2.1.2. Route B: via coupling

A solution of 5.00 mmol (3.47 g) of **3**, 5.00 mmol (1.24 g) of IC≡CC≡CSiMe$_3$, and 0.50 mmol (0.13 g) of [Cl$_2$Pd(MeCN)$_2$] in 20 ml of toluene was stirred at r.t. for 10 h. The solvent was removed in vacuo. The remaining dark brown residue was purified as described above (route A). Yield: 0.13 g (5%, based on **3**).

Dec. above 124°C. IR (pentane): v(C≡CC≡CC≡C) 2151 (vw) cm^{-1}; v(CO) 2065 (w), 1983 (w), 1946 (vs), 1937 (vs) cm^{-1}. ^{1}H-NMR: δ 0.24 (s, 9 H, SiCH$_3$), 3.55 (s, 3 H, NCH$_3$), 3.75 (s, 3 H, NCH$_3$). ^{13}C-NMR: δ -0.71 (SiCH$_3$), 47.61 (NCH$_3$), 51.51 (NCH$_3$), 58.08

(C$_\gamma$), 72.02 (C$_\alpha$), 87.14, 88.55 (C$_\delta$, C$_\varepsilon$), 100.42 (C$_\zeta$), 112.49 (C$_\beta$), 197.72 [^1J(WC) = 128 Hz, *cis*-CO], 203.62 [^1J(WC) = 88 Hz, *trans*-CO], 230.11 [^1J(WC) = 130 Hz, W≡C]. EI MS, m/z (%): 525 (47) [M$^+$], 497 (9), 469 (100), 441 (82), 413 (75), 385 (40) [M$^+$$-n$ CO, $n = 1–5$]. Anal.: Found C, 38.94; H, 2.72; N, 2.58%. C$_{17}$H$_{15}$NO$_5$SiW (525.3): Calc.: C, 38.87; H, 2.88; N, 2.67%.

2.2. Pentacarbonyl(1-dimethylamino-2,4,6-heptatriynylidene)tungsten (4)

A solution of 0.69 mmol (0.04 g) of KF and 2.00 mmol (1.05 g) of **2** in 20 ml of THF:MeOH (1:1) was stirred at r.t. for 10 min. Then, 40 ml of CH$_2$Cl$_2$ was added and the resulting yellow solution was extracted three times with 50 ml each of a saturated solution of NaHCO$_3$ in water. The organic phase was dried with Na$_2$SO$_4$, and the solvent was removed in vacuo. The residue was dissolved in 30 ml of pentane and chromatographed on silica at $-40°C$. An orange band was eluted with pentane:CH$_2$Cl$_2$ (5:1) which gave, after removal of the solvent in vacuo, a red solid. Yield: 0.68 g (75%, based on **2**). Dec. above 81°C. IR (pentane): v(CO) 2066 (m), 1983 (w), 1948 (s), 1938 (vs) cm^{-1}. IR (KBr): v(C≡CC≡CC≡C) 2164 (vw), 2143 (vw) cm^{-1}. ^{1}H-NMR: δ 2.96 (s, 1 H, C≡CH), 3.56 (s, 3 H, CH$_3$), 3.76 (s, 3 H, CH$_3$). ^{13}C-NMR (gated decoupled, DRX600): δ 47.74 [q, ^1J(CH) = 142 Hz, CH$_3$], 51.60 [q, ^1J(CH) = 140 Hz, CH$_3$], 57.15 (C$_\gamma$), 67.86 [d, ^2J(CH) = 52 Hz, C$_\varepsilon$], 71.24 (C$_\alpha$), 78.99 [d, ^1J(CH) = 261 Hz, C$_\zeta$], 87.80 [d, ^3J(CH) = 7 Hz, C$_\delta$], 111.85 (C$_\beta$), 197.86 [^1J(WC) = 128 Hz, *cis*-CO], 203.57 [^1J(WC) = 129 Hz, *trans*-CO], 230.26 [^1J(WC) = 85 Hz, W = C]. EI MS, m/z (%): 453 (80) [M$^+$], 425 (12), 397 (93), 369 (95), 341 (100), 313 (90) [M$^+$$-n$ CO, $n = 1–5$]. Anal.: Found: C, 37.11; H, 1.64; N, 3.31%. C$_{14}$H$_7$NO$_5$W (453.1): Calc.: C, 37.11; H, 1.56; N, 3.09%.

2.3. Pentacarbonyl[1-dimethylamino-7-tributyl-stannyl-2,4,6-heptatriynylidene]tungsten (5)

At $-80°C$, 2.00 mmol of nBuLi (1.25 ml of a 1.6 M solution in hexane) was added to 2.00 mmol (0.91 g) of **4** in 20 ml of Et$_2$O. The solution was stirred for 30 min at $-80°C$, 2.00 mmol (0.65 g) of nBu$_3$SnCl was then added and the solution was allowed to warm to r.t. After stirring was continued for another 30 min, the solvent was removed in vacuo. The residue was dissolved in 20 ml of pentane and chromatographed at $-40°C$ on silica. With pentane:CH$_2$Cl$_2$ (5:1) a yellow band was eluted. Removal of the solvent in vacuo afforded **5** as a red–orange powder. Yield: 0.70 g (47%, based on **4**). Dec. above 79°C. IR (pentane): v(C≡CC≡CC≡C) 2146 (vw); v(CO) 2064 (w), 1981 (w), 1944 (vs), 1935 (vs) cm^{-1}. ^{1}H-NMR: δ 0.92 [t,

^3J(HH) = 7.3 Hz, 9 H, CH$_2$CH_3], 1.06–1.10 (m, 6 H, SnCH$_2$), 1.30–1.39 (m, 6 H, SnCH$_2$CH_2), 1.54–1.62 (m, 6 H, CH_2CH$_3$), 3.54 (s, 3 H, NCH$_3$), 3.74 (s, 3 H, NCH$_3$). ^{13}C-NMR: δ 11.67 [s and 2 d, ^1J(^{117}SnC, ^{119}SnC) = 378 Hz, 361 Hz, SnCH$_2$], 13.60 (CH$_2$CH$_3$), 26.95 [s and d, ^2J($^{117/119}$SnC) = 60 Hz, SnCH$_2$CH$_2$], 28.81 [s and d, ^3J($^{117/119}$SnC) = 24 Hz, CH$_2$CH$_3$], 47.45 (NCH$_3$), 51.52 (NCH$_3$), 55.19 (C$_\gamma$), 71.33 (C$_\alpha$), 89.38 (C$_\delta$), 91.73 [s and d, ^2J($^{117/119}$SnC) = 43 Hz, C$_\epsilon$], 104.70 [s and d, ^1J($^{117/119}$SnC) = 213 Hz, C$_\xi$], 113.35 (C$_\beta$), 197.85 [^1J(WC) = 128 Hz, cis-CO], 203.72 [^1J(WC) = 129 Hz, trans-CO], 230.38 (W≡C). MS (FAB, NBOH), m/z (%): 743 (4) [M$^+$], 687 (39) [M$^+$ −2 CO]. Anal.: Found: C, 42.09; H, 4.49; N, 1.80%. C$_{26}$H$_{33}$NO$_5$SnW (742.1): Calc.: C, 42.08; H, 4.48; N, 1.89%.

2.4. Pentacarbonyl{7-[dicarbonyl(η^5-cyclopentadienyl)-ruthenio]-1-dimethylamino-2,4,6-heptatriynylidene}-tungsten (6)

A solution of 2.00 mmol (1.48 g) of **5**, 2.00 mmol (0.52 g) of [ClRu(CO)$_2$Cp], and 0.20 mmol (0.05 g) of [Cl$_2$Pd(MeCN)$_2$] in 10 ml of toluene was stirred at r.t. for 1 day. The solvent was removed in vacuo. The dark brown residue was dissolved in 5 ml of CH$_2$Cl$_2$ and chromatographed at −40°C on silica. With pentane:CH$_2$Cl$_2$ (1:1) an orange band was eluted. Removal of the solvent in vacuo gave **6** as an orange solid. Yield: 0.62 g (46%, based on **5**). Dec. above 154°C. IR (Et$_2$O): ν(C≡CC≡CC≡C) 2131 (m); ν(CO) 2061 (m), 2019 (sh), 2009 (m), 1977 (w), 1935 (vs), 1916 (sh) cm^{-1}. ^{1}H-NMR: δ 3.52 (s, 3 H, CH$_3$), 3.72 (s, 3 H, CH$_3$), 5.48 (s, 5 H, C$_5$H$_5$). ^{13}C-NMR: δ 46.92 (CH$_3$), 48.41 (C$_\gamma$), 51.34 (CH$_3$), 69.70 (C$_\alpha$), 88.16 (C$_5$H$_5$), 92.84, 93.39 (C$_\delta$, C$_\epsilon$), 107.44 (C$_\xi$), 116.28 (C$_\beta$), 194.96 (RuCO), 198.10 [^1J(WC) = 127 Hz, cis-WCO], 204.05 (trans-WCO), 230.42 [^1J(WC) = 87 Hz, W = C]. UV–vis: λ_{max} (lg ε) = 444 nm (4.063) [toluene], 428 nm (4.081) [DMF]. MS (FAB, NBOH), m/z (%): 675 (5) [M$^+$], 647 (3), 619 (14), 591 (4), 563 (2), 535 (3) [M$^+$ −n CO, n = 1–5]. Anal.: Found: C, 37.27; H, 1.77; N, 2.00%. C$_{21}$H$_{11}$NO$_7$RuW (674.2): Calc. C, 37.41; H, 1.64; N, 2.08%.

2.5. Bis[pentacarbonyl(1-dimethylamino-2,4,6-hepta-triynylidene)tungsten]mercury (7)

At −80°C, 1.50 mmol of nBuLi (0.94 ml of a 1.6 M solution in hexane) was added to a solution of 1.50 mmol (0.68) of **4** in 20 ml of Et$_2$O. After stirring for 30 min at −80°C, 0.75 mmol (0.20 g) of HgCl$_2$ in 5 ml of THF was added. The solution was allowed to warm to r.t. Stirring was continued for another 30 min. The solvent was removed in vacuo and the residue was dissolved in 5 ml of CH$_2$Cl$_2$. Chromatography at −

40°C on silica with pentane:CH$_2$Cl$_2$ (1:1) afforded a yellow–orange band. Removal of the solvent in vacuo gave **7** as an orange solid. Yield: 0.19 g (23%, based on **4**). Dec. above 151°C. IR (THF): ν(C≡CC≡CC≡C) 2151 (vw); ν(CO) 2062 (w), 1976 (w), 1933 (vs), 1914 (sh) cm^{-1}. ^{1}H-NMR: δ 3.61 (s, 6 H, CH$_3$), 3.78 (s, 6 H, CH$_3$). ^{13}C-NMR ([D$_8$]THF): δ 48.00 (CH$_3$), 52.12 (CH$_3$), 53.62 (C$_\gamma$), 70.87 (C$_\alpha$), 86.49, 88.05 (C$_\delta$, C$_\epsilon$), 110.42 (C$_\beta$), 128.17 (C$_\xi$), 198.67 [^1J(WC) = 127 Hz, cis-CO], 204.17 (trans-CO), 224.34 (W≡C). MS (FAB, NBOH), m/z (%): 1106 (17) [M$^+$], 1078 (7), 1050 (14), 1022 (4), 994 (8), 966 (7), 938 (9), 910 (8) [M$^+$ −n CO, n = 1–7]. C$_{28}$H$_{12}$HgN$_2$O$_{10}$W$_2$ (1104.7). It was not possible to obtain a correct elemental analysis.

Acknowledgements

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