

η^1 -Alkynyl and vinylidene transition metal complexes

10. Reaction of the metal-acetylide $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]\text{Li}$ with 1,2-diiodoethane as electrophile and with various nucleophiles[☆]

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Abstract

Treatment of the η^1 -acetylide complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]\text{Li}$ (**4**) with 1,2-diiodoethane in THF at -78°C , followed by the addition of $\text{Li}-\text{C}\equiv\text{C}-\text{R}$ [$\text{R} = \text{C}(\text{CH}_3)_3$, C_6H_5 , $\text{Si}(\text{CH}_3)_3$, **6a–6c**] or $n\text{-C}_4\text{H}_9\text{Li}$ and protonation with H_2O , afforded the corresponding oxametallacyclopentadienyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-\text{R})\text{CH}=\text{CC}(\text{CH}_3)_3]$ (**7a–7c**), **8c** and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(n\text{-C}_4\text{H}_9)\text{CH}=\text{CC}(\text{CH}_3)_3]$ (**9**). The formation of these metallafuran derivatives is rationalized by the electrophilic attack of 1,2-diiodoethane onto the metal center of **4** to form first the neutral complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]$ (**5**). Subsequent nucleophilic addition of $\text{Li}-\text{C}\equiv\text{C}-\text{R}$ **6a–6c** or $n\text{-C}_4\text{H}_9\text{Li}$ and a reductive elimination step followed by protonation leads to the products **7a–7c** and **9**. One reaction intermediate could be trapped with $\text{CF}_3\text{SO}_3\text{CH}_3$ and characterized by a crystal structure analysis. The identity of another intermediate was established by infrared spectroscopic data. The oxametallacyclopentadienyl complex **10** forms in the presence of excess 1,2-diiodoethane through an alternative pathway and crystallizes as a clathrate containing iodine.

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1. Introduction

Recently, we reported the reaction of tungsten-acetylide complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{R}]\text{Li}$ [**1**, $\text{R} = \text{C}(\text{CH}_3)_3$, C_6H_5 , $p\text{-CH}_3\text{-C}_6\text{H}_4$] with ethyliodoacetate that gives the oxametallacyclopentadienyl complex **2** after protonation with dilute acid (Scheme 1) [2].

For formation of **2**, we proposed a multi-step process as presented in Scheme 2. In the first step, the anionic

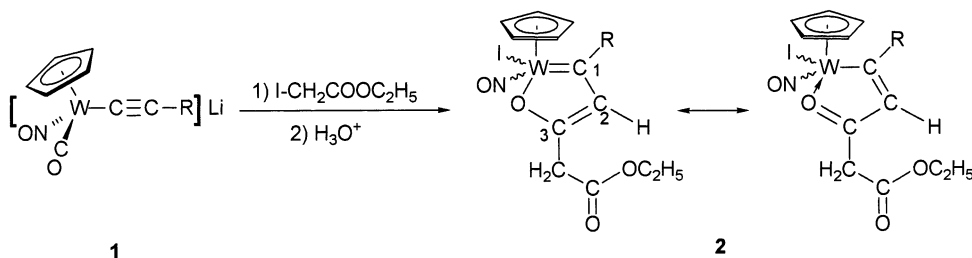
η^1 -acetylide complex **1** undergoes electrophilic iodination with ethyliodoacetate on the metal center. This leads to the neutral η^1 -acetylide complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{R}]$ **A**. Nucleophilic addition of the ester enolate anion $[\text{CH}_2\text{COOC}_2\text{H}_5]\text{Li}$, the leaving group in the first step, to the CO ligand of **A** generates the anionic η^1 -acetylide- η^1 -acyl complex **B**. The subsequent reductive elimination leads to the structures **C** and **D**, from which the oxametallacyclopentadienyl complex **2** forms after protonation and tautomerization (Scheme 2).

To support the mechanism, we attempted to isolate the neutral iodo complex **A** [$\text{R} = \text{C}(\text{CH}_3)_3$], but we were unsuccessful because of the apparently immediate attack of the ester enolate anion $[\text{CH}_2\text{COOC}_2\text{H}_5]\text{Li}$. Therefore,

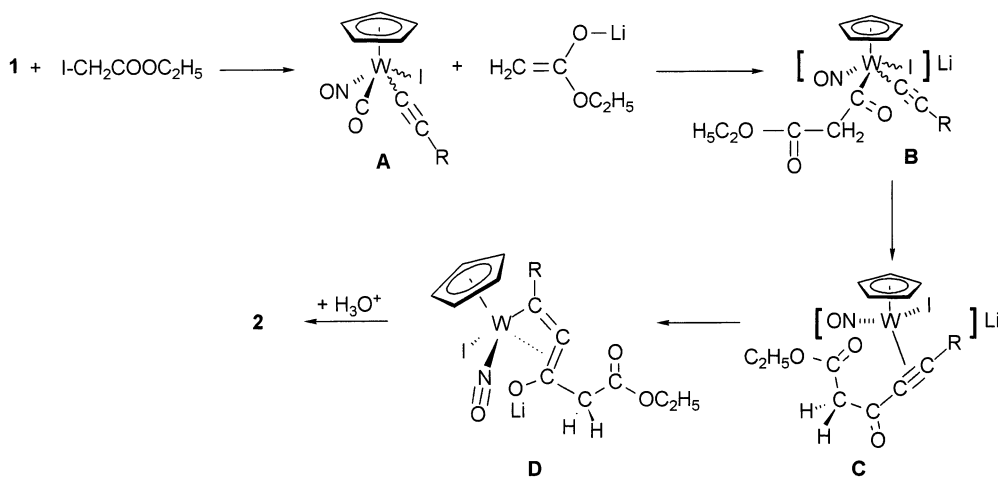
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[☆] See Ref [1].



Scheme 1.



Scheme 2.

we searched for another reagent that would give the neutral iodo complex **A** via a different route. Moreover, we intended to vary the substituent on C_3 in the oxametallacyclopentadienyl complex **2** by adding different nucleophiles to the intermediate **A**.

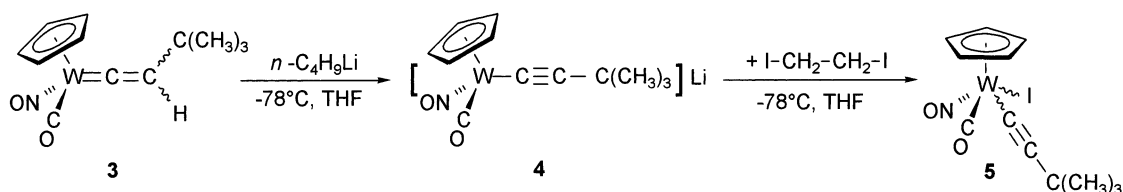
In this study, we report on replacing ethyliodoacetate with 1,2-diiodoethane giving the neutral intermediate $[(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]$ (**5**) [**A** with $\text{R} = \text{C}(\text{CH}_3)_3$] to which different nucleophiles could be added subsequently.

2. Results and discussion

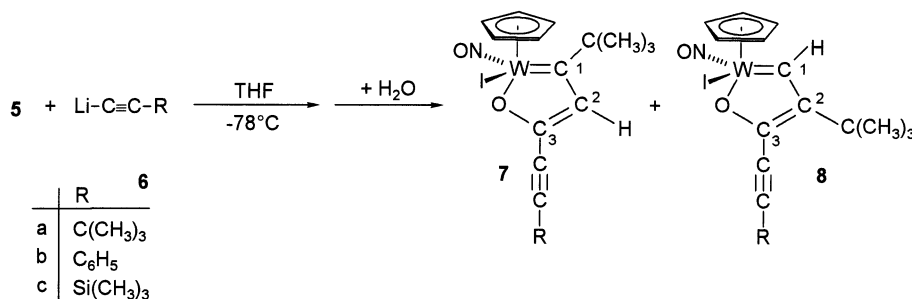
2.1. Synthesis of metallacycles **7a–7c**, **8c**, **9** and **10**

The emerald green solution of lithium metallate **4** was obtained, by treating the tungsten–vinylidene complex **3** with one equivalent of $n\text{-C}_4\text{H}_9\text{Li}$ in THF at -78°C [3].

Electrophilic iodination of **4** with 1,2-diiodoethane led to the formation of the neutral η^1 -acetylide iodo complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]$ (**5**) as a red solution in THF (Scheme 3). Due to the instability of **5**, we were not able to isolate this complex. To confirm its structure, we followed the reaction by IR spectroscopy at -62°C in THF under inert gas atmosphere. The tungsten–acetylide $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]\text{Li}$ (**4**) gives rise to intense absorption at 1860 cm^{-1} (CO) and 1450 cm^{-1} (NO). The red shift of the signals compared with the corresponding vinylidene complex **3** (carbonyl group at 1991 cm^{-1} and NO group at 1619 cm^{-1}) is due to the negative charge on the metal center. After the addition of 1,2-diiodoethane, the absorption for the stretching vibrations of the carbonyl as well as the nitrosyl group shifted to higher wavenumbers. $[(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{CO})(\text{NO})\text{W}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3]$ (**5**) shows a signal for the carbonyl group at 2073 cm^{-1} , indicating an electron-deficient highly electrophilic car-



Scheme 3.



Scheme 4.

bonyl complex [4]. The stretching vibration of the nitrosyl group (1684 cm^{-1}) confirms this observation.

Addition of lithium acetylide **6a–6c** as nucleophile to an in situ generated solution of **5** in THF at $-30\text{ }^{\circ}\text{C}$ led, after protonation with $\text{H}_2\text{O–THF}$ mixture (1:6), to the formation of the oxametallacyclopentadienyl complexes **7a–7c** and **8c** in 42–60% yields (Scheme 4). These compounds were isolated as red crystals and were characterized by elemental analysis and spectroscopic methods. Interestingly, the reaction of $\text{Li–C}\equiv\text{C–Si}(\text{CH}_3)_3$ with **5** afforded in addition to **7c** also a small amount of **8c** after hydrolysis in which the *tert*-butyl group is located on C_2 instead of on C_1 as found in complex **7c**. It was not possible to separate **8c** from **7c**, but the signal for the $\text{C}_\alpha\text{–H}$ atom in the $^1\text{H–NMR}$ spectrum appearing at very downfield (10.73 ppm, $^2J_{\text{W–H}} = 6.9\text{ Hz}$) is clear evidence for structure **8c** (see Section 2.5) [5].

A very similar result was obtained in the addition of $n\text{-C}_4\text{H}_9\text{Li}$ to a solution of **5** in THF at $-30\text{ }^{\circ}\text{C}$, which gave the metallacycle **9** after protonation in 45% yield (Scheme 5).

A surprising result was obtained when η^1 -acetylide complex **4** was reacted with an excess of 1,2-diiodoethane and then with one equivalent of lithium acetylide **6a**. After addition of two equivalents of 1,2-diiodoethane to η^1 -acetylide complex **4**, the solution color changed slowly from green to red. Addition of lithium acetylide **6a** gave the oxametallacyclopentadienyl complex **10** in 41% yield as a dark red compound (Scheme 5). In this complex, the *tert*-butyl group is found to be on C_2 just as observed for compound **8c**. The structure of complex **10** was fully characterized by

spectroscopic methods, elemental analysis and X-ray crystallography. The crystal structure of **10** reveals a clathrate complex containing an I_2 molecule as a guest. The iodine molecule coordinates on each side to the iodine atom bond to tungsten [6].

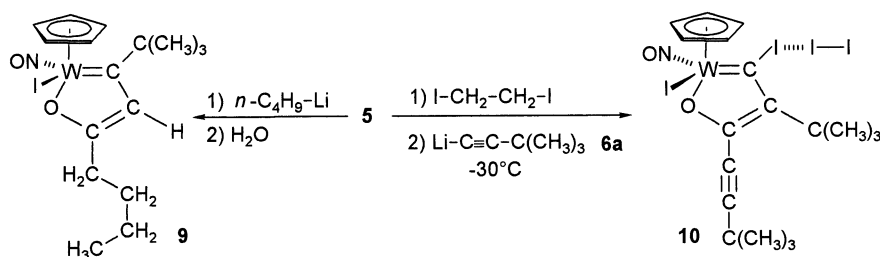
2.2. Mechanistic consideration

As a working hypothesis, we propose that the anionic acyl complex **E**, formed by nucleophilic addition of **6** or $n\text{-C}_4\text{H}_9\text{Li}$ to the highly electrophilic carbonyl group of **5**, is the key intermediate for the formation of both oxametallacyclopentadienyl complexes **7a–7c** and **9** as well as the products **8c** and **10**.

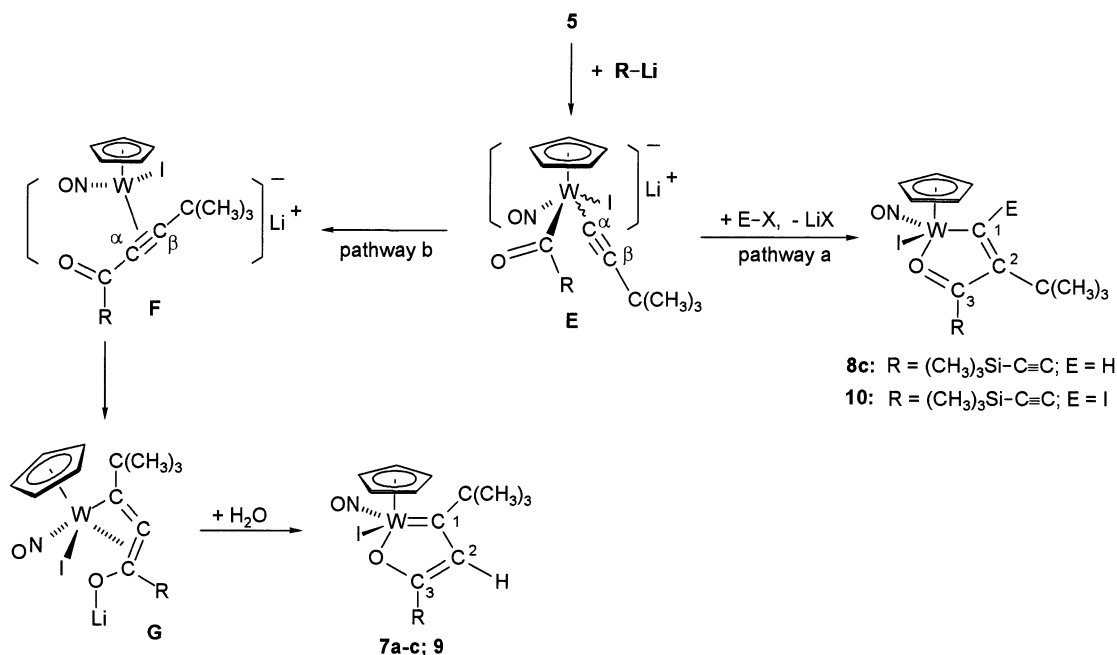
There are two different possibilities for complex **E** to react with electrophiles: in the presence of a soft electrophile such as 1,2-diiodoethane, the electrophilic attack occurs at C_α and subsequent bond formation between C_β and the carbonyl carbon atom of **E** would give rise to the formation of oxametallacyclopentadienyl complex like **10** (pathway a). In the absence of a reactive soft electrophile, **E** undergoes a reductive elimination reaction to the structures **F** and **G** (Scheme 6). Protonation of **G** and tautomerization would finally produce the oxametallacyclopentadienyl complexes such as **7a–7c** and **9** (pathway b).

2.3. Trapping of intermediate: synthesis of η^3 -allenyl complex **11**

The trapping of the intermediate **G** ($\text{R} = n\text{-C}_4\text{H}_9$) supports our mechanistic considerations proposed in Scheme 6. Using $\text{CF}_3\text{SO}_3\text{CH}_3$ instead of $\text{H}_2\text{O–THF}$ as



Scheme 5.



Scheme 6.

the electrophile after addition of *n*-C₄H₉Li to **5**, we obtained the η³-allenyl complex **11** in 64% yield as dark red crystals (Scheme 7). This solid compound can be stored under inert conditions at +3 °C without decomposition for several weeks. The structure of **11** was confirmed by spectroscopic and X-ray crystallographic studies as well as by elemental analysis [7]. Interestingly, complex **11** shows a temperature-dependent ¹H-NMR spectra (vide infra).

2.4. Characterization of 7a–7c, 8c and 9

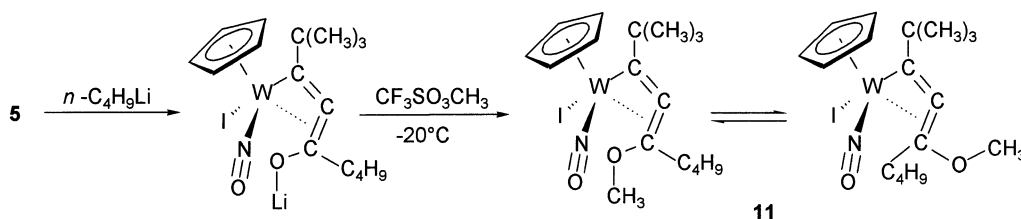
The ¹H-NMR and ¹³C-NMR spectra of compounds **7a–7c**, **8c** and **9** display sharp and well-resolved signals. The most characteristic features of the ¹H-NMR and ¹³C-NMR spectra are the signals for C₁ and H₂, respectively, with the corresponding satellite signals caused by the coupling with the ¹⁸³W atom (14% ¹⁸³W abundance, *I* = 1/2). For example, the proton on C₂ in the ¹H-NMR spectrum of **7a** appears as a singlet at δ = 7.21 ppm with ³*J*_{W-H} = 6 Hz. ¹³C-NMR for **7a** displays a singlet at δ = 269.1 ppm (¹*J*_{W-C} = 90.2 Hz) for C₁; C₂ and C₃ appear at δ = 136.4 and 184.2 ppm, respectively.

IR spectrum of **7a** shows a strong absorption at 1636 cm⁻¹ for the nitrosyl group and the C≡C stretching frequency gives rise to absorption at 2208 cm⁻¹. The band at 1560 cm⁻¹ is assigned to the coordinated carbonyl group, which is comparable with C=O absorption in similar metallacycles **5a** [8].

For structures **7c** and **8c**, we found an ¹H signal at δ = 7.29 ppm with ³*J*_{W-H} = 5.8 Hz for complex **7c** and at δ = 10.73 ppm (²*J*_{W-H} = 6.9 Hz) in **8c** which is typical for the C_α-H in similar complexes [5]. Likewise, complexes **7b**, **7c** and **9** show very similar absorption to those of **7a** in NMR and IR spectra (see Section 5) [9].

2.5. Spectroscopy of 10

The most interesting features of the ¹³C-NMR spectra of complex **10** are the signals for C₁, C₂ and C₃; C₁ displays a singlet at 205.6 ppm, and C₂ and C₃ show absorption at 159.4 and 178.8 ppm, respectively. IR spectrum of **10** shows a strong absorption at 1651 cm⁻¹ for the nitrosyl group and the C≡C stretching frequency gives rise to absorption at 2204 cm⁻¹.



Scheme 7.

2.6. Characterization and temperature-dependent behavior of **11**

As expected, the infrared spectrum of **11** shows absorption at 1864 cm^{-1} for the η^3 -allenyl group, and the $\text{N}=\text{O}$ stretching appears at 1591 cm^{-1} [10]. The most informative features in ^{13}C -NMR and ^1H -NMR spectra are the signals for C_1 , C_2 and C_3 , the carbon atoms of the η^3 -allenyl group and the methoxy group, respectively. In ^{13}C -NMR spectrum, C_1 is observed at $\delta = 111.6$, and the C_2 and C_3 signals appear at $\delta = 179.2$ and 175.3 ppm, respectively. The CH_3O group shows absorption at $\delta = 59.5$ ppm in ^{13}C -NMR spectrum and at $\delta = 3.13$ ppm in ^1H -NMR spectrum.

^1H -NMR spectrum of **11** shows the presence of two rotamers. A rotational barrier of $\Delta G^\ddagger \cong 15.4$ kcal mol $^{-1}$ was obtained, measured by temperature-dependent ^1H -NMR experiments. At $-22\text{ }^\circ\text{C}$, the CH_3O group gives rise to sharp absorption at 3.29 and 3.13 ppm (1:6 mixture). The peaks broaden and shift as the temperature was raised and finally coalesced into a very broad peak centered at 3.16 ppm at $54\text{ }^\circ\text{C}$. At this temperature, the *n*-butyl proton peaks also coalesce.

3. Molecular structure of complex **11**

Suitable single crystals of complex **11** were grown from a dichloromethane solution by slow diffusion of pentane at $-20\text{ }^\circ\text{C}$. The X-ray diffraction study confirmed the η^3 -allenyl structure. The ORTEP plot is shown in Fig. 1. The η^3 -allenyl fragment C_1 – C_2 – C_3 is linear ($176(1)^\circ$) and the bond distances C_1 – C_2 (1.29 Å) and

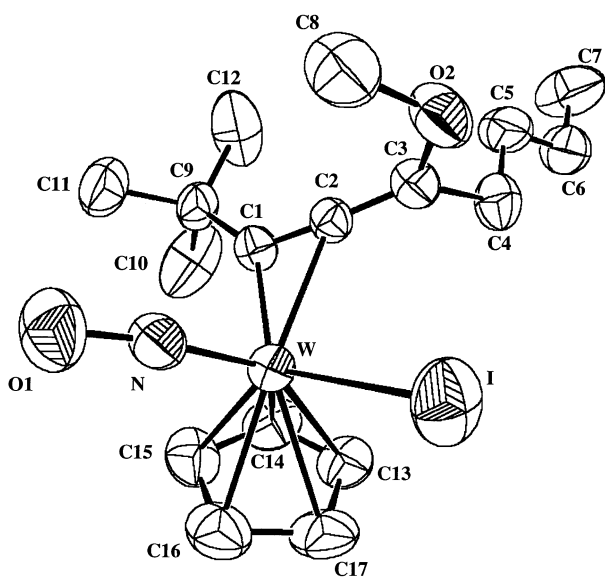


Fig. 1. ORTEP drawing of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^3\text{-C}(\text{CH}_3)_3\text{C}=\text{C}(\text{OCH}_3)(n\text{-C}_4\text{H}_9)]$ (**11**) with thermal ellipsoids shown at the 40% probability level.

Table 1
Selected bond distances (Å) and angles ($^\circ$) for **11**

W–C1	2.11 (1)	C1–W–I	124.7 (3)
W–C2	2.33 (1)	C1–C2–C3	176 (1)
W–I	2.78 (1)	C2–W–I	91.8 (2)
C1–C2	1.29 (1)	C2–C3–C4	125 (1)
C2–C3	1.31 (1)	C2–C1–C9	131 (1)
C3–C4	1.50 (2)	C2–C1–W	82.9 (7)
C3–O2	1.36 (1)	C2–C3–O2	124 (1)
C1–C9	1.53 (2)	C3–O2–C8	116 (1)
N–W–C1	95.1 (4)	C3–C4–C5	110 (1)
N–W–C2	104.2 (4)		
N–W–I	94.0 (3)		

C_2 – C_3 (1.31 Å) corroborate with their equal bond lengths the η^3 -allenyl structure **7a**. The iodo group is situated *trans* to the σ -bonded allenyl group W–C₁. For crystallographic data, selected bond distances and angles, see Tables 1 and 2.

4. Molecular structure of complex **10**

Complex **10** gave single crystals at $-20\text{ }^\circ\text{C}$ in hexane. The X-ray structure confirmed the oxametallacyclopentadienyl complex **10** and showed that the I_2 molecule is coordinated on each side to the iodine atom I_1 on the tungsten. The I_2 molecule has an intramolecular I–I distance of 2.74 Å, which is longer than the I–I distance in pure iodine (2.715(6) Å in the solid and 2.667(2) Å in gaseous state). The intermolecular I–I distance of 3.501(1) is within the range of what has been reported in polyiodide compounds [6]. The angle between I(1)–I(3)–I(3) of 177.7° and the dihedral angle I(1)–I(3)–I(3)–I(1) of 2.2° imply an almost linear connection (Fig. 3). The two organic moieties are twisted relative to each other by 102.2° . Of particular note is the short–long–short pattern of the $\text{C}(1)=\text{C}(2)\text{--}\text{C}(3)=\text{O}(2)$ fragment (1.36(1), 1.45(1) and 1.28(1) Å, respectively), which is typical for oxametallacyclopentadiene ring systems [2, 9a, 9c]. The ORTEP plot of complex **10** is shown in Figs. 2 and 3. For crystallographic data, selected bond distances and angles, see Tables 3 and 4.

5. Experimental

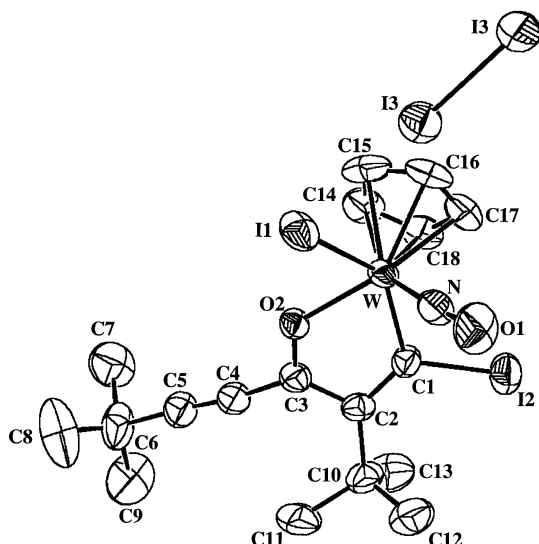
5.1. General considerations

All reactions were carried out under an argon atmosphere (99%, by Messer–Griesheim) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{W}=\text{C}=\text{CHR}]$. All other compounds were commercially available. NMR spectra were ob-

Table 2

Crystal data and conditions for crystallographic data collection and structure refinement for **11**

11	
Formula	C ₁₇ H ₂₆ INO ₂ W
fw	587.153
Color and habit	Red, transparent
Crystal system	Monoklin
Space group	C2/c
Lattice constants	a = 34.79 (1) Å, α = 90.0°; b = 9.26 (1) Å, β = 111.43 (1)°; c = 13.32(1) Å, γ = 90.0°
Volume	3993.34(1) Å ³
Formula units per unit cell	Z = 4
Density (calc.)	1.866 g cm ⁻³
Linear absorption coefficient	73.4 cm ⁻¹
Diffractometer	Image plate diffractometer system (STOE)
Radiation	Mo-K _α (λ = 0.71069 Å)
Monochromator	Graphite
Scan range	3.3° ≤ 2θ ≤ 52.1°, -42 ≤ h ≤ 42, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	14 596
R _{int}	0.074
Independent reflections	3835
Independent reflections with F ₀ > 4σ(F ₀)	2849
Applied corrections	Lorentz and polarization coefficients
Structure determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86 ^a); further atoms from F-synthesis (program SHELXL-93 ^b), structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; atomic scattering factors from ^c
Number of parameters	199
R(F ²)	0123
R(F)	0.063 for all 3835 reflections
R(F)	0.048 for 2849 reflections with F ₀ > 4σ(F ₀)

^a G.M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, Universität Göttingen, 1986.^b G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, Universität Göttingen, 1993.^c A.J.C. Wilson (Ed.), Int. Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.Fig. 2. ORTEP drawing of (η⁵-C₅H₅)W(I)(NO)[η²-O=C(C≡C-C(CH₃)₃)C(I)=CC(CH₃)₃] (**10**) with thermal ellipsoids shown at the 60% probability level.

tained on Bruker AM 400 and AC 200 spectrometers. Proton and carbon chemical shifts are referenced to tetramethylsilane. MS measurements (70 eV) were

performed on a Varian MAT 311-A. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on Carlo Erba 1104 elemental analyzer.

5.2. (η⁵-C₅H₅)W(I)(NO)[η²-O=C(C≡C-C(CH₃)₃)CH=CC(CH₃)₃] (**7a**)

At -78 °C, to a THF solution (20 ml) of tungsten-vinylidene complex [(η⁵-C₅H₅)(CO)(NO)]-W=C=C(H)[C(CH₃)₃] (**3**) (389 mg, 1 mmol) was added 1 mmol *n*-BuLi (a solution of 1.5 mmol ml⁻¹ in hexane) and the color changed immediately from orange to green. After the mixture was stirred for 0.5 h, a solution of 280 mg (1 mmol) of 1,2-diiodoethane in 10 ml THF was added drop-wise to the green reaction mixture, whereby the color changed slowly to red. The mixture was stirred for 1 h and then warmed to -30 °C. A precooled (0 °C) solution of (*tert*-butylethynyl)lithium in 10 ml THF was added drop-wise to the red solution. After 30 min, 1 ml of a precooled mixture of THF and water (6:1) was added. The solvent was removed under reduced pressure and the oily residue was first chromatographed (silica gel; pentane:ether = 2:1) and finally purified with HPLC to yield 304 mg (51%) of **7a**, as dark red crystals (m.p. 194–196 °C dec.) from CH₂Cl₂ and

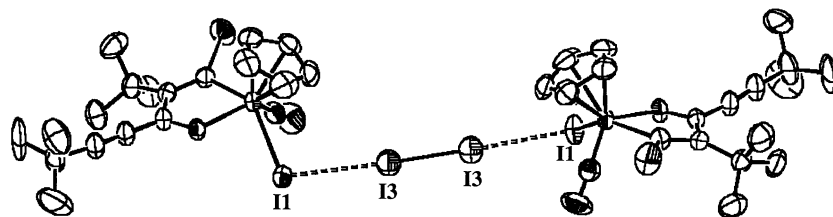


Fig. 3. ORTEP drawing of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3)\text{C}(\text{I})=\text{CC}(\text{CH}_3)_3]$ -dimer (**10**) with thermal ellipsoids shown at the 60% probability level.

Table 3
Selected bond distances (Å) and angles (°) for **10**

W–C1	2.15 (1)	C1–W–I1	138.3 (2)
W–N	1.79 (1)	C1–C2–C3	106.8 (6)
W–I1	2.81 (1)	C1–W–O2	71.9 (2)
W–O2	2.07 (1)	C1–W–I1	138.4 (2)
C1–C2	1.36 (1)	C2–C3–O2	118.5 (6)
C2–C3	1.45 (1)	C3–O2–W	120.3 (4)
C3–O1	1.28 (1)	O2–W–I1	79.4 (2)
I1–I3	3.50 (1)	W–C1–C2	120.6 (6)
N–W–C1	81.9 (3)	I1–I3–I3	177.7 (3)
N–W–I1	85.3 (2)		
N–W–O2	117.0 (3)		

NMR (400 MHz, CDCl_3) δ 7.21 (s, 1H, $\text{C}_\beta\text{-H}$, $^3J_{\text{W-H}} = 6$ Hz), 6.03 (s, 5H, Cp), 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C -NMR (400 MHz, CDCl_3) δ 269.1 (C_1 , $^1J_{\text{W-C}} = 90.2$ Hz), 184.3 (C_3), 136.4 (C_2), 112.2 and 78.9 (alkyne), 101.5 (C_5H_5), 49.0 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{C}(\text{CH}_3)_3$), 29.9 ($\text{C}(\text{CH}_3)_3$), 27.8 ($\text{C}(\text{CH}_3)_3$); IR (KBr), $\tilde{\nu}$ (cm^{-1}) 2207 ($\text{C}\equiv\text{C}$), 1636 ($\text{N}=\text{O}$); MS (70 eV) m/e 597 [M^+ , ^{184}W], 567 [$\text{M}^+ - \text{NO}$], 470 [$\text{M}^+ - \text{I}$].

5.3. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{CPh})\text{CH}=\text{CC}(\text{CH}_3)_3]$ (**7b**)

pentane. Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{INO}_2\text{W}$: C, 36.21; H, 4.05; N, 2.35. Found: C, 36.41; H, 3.78; N, 2.84%. ^1H -

The preparation was carried out as described for **7a** but instead of (*tert*-butylethynyl)lithium, (phenylethy-

Table 4
Crystal data and conditions for crystallographic data collection and structure refinement for **10**

10	
Formula	$\text{C}_{18}\text{H}_{23}\text{I}_2\text{NO}_2\text{W}$
fw	587.153
Color and habit	Red, transparent
Crystal system	Monoklin
Space group	$I2/a$
Lattice constants	$a = 18.32(1)$ Å, $\alpha = 90.0^\circ$; $b = 11.70(1)$ Å, $\beta = 96.44(2)^\circ$; $c = 2.49(1)$ Å, $\gamma = 90.0^\circ$
Volume	$4791.0(1)$ Å ³
Formula units per unit cell	$Z = 2$
Density (calc.)	2.357 g cm ⁻³
Linear absorption coefficient	87.0 cm ⁻¹
Diffractometer	Image plate diffractometer system (STOE)
Radiation	Mo–K α ($\lambda = 0.71073$ Å)
Monochromator	Graphite
Scan range	$3.3^\circ \leq 2\theta \leq 52.1^\circ$, $-42 \leq h \leq 42$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$
Reflections collected	17536
R_{int}	0.026
Independent reflections	4330
Independent reflections with $F_0 > 4\sigma(F_0)$	3695
Applied corrections	Lorentz and polarization coefficients
Structure determination and refinement	W positional parameters from Patterson synthesis (program SHELXS-86 ^a); further atoms from <i>F</i> -synthesis (program SHELXL-93 ^b), structure refinement by the anisotropic full-matrix least-squares procedure for all non-hydrogen atoms; atomic scattering factors from ^c
Number of parameters	253
$R(F^2)$	0.063
$R(F)$	0.031 for all 4330 reflections
$R(F)$	0.024 for 3695 reflections with $F_0 > 4\sigma(F_0)$

^a G.M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, Universität Göttingen, 1986.

^b G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, Universität Göttingen, 1993.

^c A.J.C. Wilson (Ed.), Int. Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.

nyl)lithium was used. Crystallization from CH_2Cl_2 and pentane yielded 259 mg (42%) of **7b** as dark red crystals, dec. temp. 202–205 °C. Anal. Calc. for $\text{C}_{20}\text{H}_{20}\text{INO}_2\text{W}$: C, 38.92; H, 3.27; N, 2.27. Found: C, 38.42; H, 2.96; N, 1.31%. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.61–7.3 (m, 5H, phenyl), 7.26 (s, 1H, $\text{C}_\beta\text{-H}$), 6.01 (s, 5H, Cp), 1.37 (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 270.7 (C_1), 182.9 (C_3), 136.5 (C_2), 132.8, 131.5, 128.7, 119.6 (arom C), 101.9 (C_5H_5), 101.0 and 87.8 (alkyne), 49.6 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{C}(\text{CH}_3)_3$); IR (KBr), $\tilde{\nu}$ (cm^{-1}) 2198 ($\text{C}\equiv\text{C}$), 1629 ($\text{N}=\text{O}$).

5.4. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3)\text{CH}=\text{CC}(\text{CH}_3)_3]$ (**7c**)

The preparation was carried out as described for **7a** but instead of (*tert*-butylethynyl)lithium, (trimethylsilylethynyl)lithium was used. Crystallization from CH_2Cl_2 and pentane yielded 318 mg (52%) of **7c** as dark red crystals, m.p. 178–179 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.29 (s, 1H, $\text{C}_\beta\text{-H}$, $^3J_{\text{W-H}} = 5.8$ Hz), 6.03 (s, 5H, Cp), 1.34 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.25 (s, 9H, $\text{Si}(\text{CH}_3)_3$); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 273.8 (C_1), 183.1 (C_3), 137.6 (C_2), 110.8 (alkyne), 102.7 (C_5H_5), 101.8 (alkyne), 50.3 ($\text{C}(\text{CH}_3)_3$), 32.8 ($\text{C}(\text{CH}_3)_3$), 0.89 ($\text{Si}(\text{CH}_3)_3$); IR (film), $\tilde{\nu}$ (cm^{-1}) 2148 ($\text{C}\equiv\text{C}$), 1635 ($\text{N}=\text{O}$).

5.5. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3)\text{C}(\text{C}(\text{CH}_3)_3)=\text{CH}]$ (**8c**)

During the reaction described for **7c**, **8c** is formed as a side product. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 10.73 (s, 1H, $\text{C}_2\text{-H}$, $^2J_{\text{W-H}} = 6.9$ Hz), 5.96 (s, 5H, Cp), 1.41 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.29 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

5.6. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-n\text{-C}_4\text{H}_9)\text{CH}=\text{CC}(\text{CH}_3)_3]$ (**9**)

The preparation was carried out as described for **7a** but instead of (*tert*-butylethynyl)lithium, *n*-BuLi was used. Crystallization from CH_2Cl_2 and pentane yielded 258 mg (45%) of **9** as dark red crystals, m.p. 154 °C. Anal. Calc. for $\text{C}_{16}\text{H}_{24}\text{INO}_2\text{W}$: C, 33.53; H, 4.22; N, 2.44. Found: C, 33.74; H, 3.81; N, 2.73%. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.12 (s, 1H, $\text{C}_\beta\text{-H}$, $^3J_{\text{W-H}} = 6$ Hz), 5.99 (s, 5H, Cp), 2.62 (t, 2H, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.69 (tt, 2H, $^3J = 7$ Hz, $^3J = 8$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.35 (qt, 2H, $^3J = 7$ Hz, $^3J = 8$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.92 (t, 3H, $^3J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 263.7 (C_1), 213.2 (C_3), 132.0 (C_2), 100.6 (C_5H_5), 47.6 ($\text{C}(\text{CH}_3)_3$), 37.6 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 31.1 ($\text{C}(\text{CH}_3)_3$), 27.1 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 21.6 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 12.7

($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); IR (KBr), $\tilde{\nu}$ (cm^{-1}): 1630 ($\text{N}=\text{O}$); MS (70 eV) *m/e* 573 [M^+ , ^{184}W], 543 [$\text{M}^+ - \text{NO}$].

5.7. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^2\text{-O}=\text{C}(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3)\text{CC}(\text{CH}_3)_3\text{C}(\text{I})]$ (**10**)

At -78 °C, after deprotonation of tungsten–vinylidene complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})-\text{W}=\text{C}=\text{C}(\text{H})-\text{C}(\text{CH}_3)_3]$ (**3**) (389 mg, 1 mmol), as described before, with 1 mmol BuLi (a solution of 1.5 mmol ml^{-1} in hexane), a solution of 560 mg (2 mmol) of 1,2-diiodoethane in 10 ml THF was added drop-wise to the green reaction mixture, whereby the color changed slowly to red. The mixture was stirred for 1 h and then a precooled (0 °C) solution of (*tert*-butylethynyl)lithium in 10 ml THF was added drop-wise to the red solution. After stirring at -30 °C for 1 h, the solvent was removed under reduced pressure and the oily residue was first chromatographed (silica gel; pentane:ether = 2:1) and finally purified with HPLC to yield 348 mg (41%) of **10** as dark red crystals (m.p. 161–162 °C dec.) from benzene and hexane. Anal. Calc. for $\text{C}_{18}\text{H}_{23}\text{I}_2\text{NO}_2\text{WI}_2$: C, 29.90; H, 3.21; N, 1.94. Found: C, 29.45; H, 3.03; N, 1.19%. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 6.0 (s, 5H, Cp), 1.66 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.33 (9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 205.6 (C_1), 178.9 (C_3), 159.4 (C_2), 116.1 and 81.3 (alkyne), 103.9 (C_5H_5), 37.1 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 29.4 ($\text{C}(\text{CH}_3)_3$); IR (KBr), $\tilde{\nu}$ (cm^{-1}) 2204 ($\text{C}\equiv\text{C}$), 1651 ($\text{N}=\text{O}$); MS (70 eV) *m/e* 723 [M^+ , ^{184}W], 693 [$\text{M}^+ - \text{NO}$], 596 [$\text{M}^+ - \text{I}$].

5.8. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{I})(\text{NO})[\eta^3\text{-C}(\text{CH}_3)_3=\text{C}=\text{C}(\text{OCH}_3)(n\text{-C}_4\text{H}_9)]$ (**11**)

The preparation was carried out as described for **9** but instead of protonation with $\text{H}_2\text{O}-\text{THF}$, 0.11 ml of $\text{CF}_3\text{SO}_3\text{CH}_3$ (160 mg, 1 mmol) was added at -20 °C. Crystallization from CH_2Cl_2 and pentane yielded 374 mg (64%) of **11** as dark red crystals, m.p. 65 °C. Anal. Calc. for $\text{C}_{17}\text{H}_{26}\text{INO}_2\text{W}$: C, 34.74; H, 4.46; N, 2.39. Found: C, 34.81; H, 4.09; N, 2.79%. Two rotamers: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.91 (s, 5H, Cp), 3.29 and 3.13 (2s, 1:6, 3H, OCH_3), 2.3 and 2.7 (2m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 2.05 and 1.95 (2m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.42 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.4–1.2 (2m 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 0.98–0.86 (2t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ 178.9 (C_2), 175.3 (C_3), 111.6 (C_1), 99.8 (Cp), 59.5 (OCH_3), 40.8 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 31.4 ($\text{C}(\text{CH}_3)_3$), 27.2 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 22.3 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.6 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); IR (KBr), $\tilde{\nu}$ (cm^{-1}), 1864 ($\text{C}=\text{C}=\text{C}$), 1591 ($\text{N}=\text{O}$); MS (70 eV) *m/e* 587 [M^+ , ^{184}W], 557 [$\text{M}^+ - \text{NO}$].

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