

Alkynylcarbyne complexes containing various tri- and bidentate ligands such as cyclopentadienide, tris(pyrazolyl)borate, bis(pyrazolyl)acetate and tmeda: synthesis and spectroscopic properties

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Abstract

The (alkynylcarbyne)tungsten complexes $[L_3(CO)_2W\equiv C-C\equiv C-R]$ (**3a,b**–**6a,b**) [L_3 = hydro[tris(3,5-dimethylpyrazol-1-yl)]borato (Tp', **3**), hydro[tris(pyrazol-1-yl)]borato (Tp, **4**), cyclopentadienyl (Cp, **5**), bis(3,5-dimethylpyrazol-1-yl)acetato (bdmpza, **6**); R = SiMe₃ (**a**), Ph (**b**)] were prepared in a stepwise fashion from $[W(CO)_6]$ and $Li[C\equiv CR]$, $(CF_3CO)_2O$ and $M[L_3]$ (M = Na, K). The formation of **6a,b** was highly selective, only complexes with a *trans* arrangement of the carboxylate group of bdmpza and the alkynylcarbyne ligand were detected. The reaction of $[W(CO)_6]$ with $Li[C\equiv CR]$, $C_2O_2Cl_2$ and tmeda afforded *trans*- $[Cl(CO)_2(tmeda)W\equiv C-C\equiv C-R]$ (**7a,b**). The electron-donating potential of the different tripodal ligands L_3 was studied by IR- and ¹³C-NMR spectroscopy and compared to that of the ligand combination Cl/tmeda. The IR data suggest that in these complexes bdmpza is a weaker electron donor than Tp' and Tp but displays stronger electron-donating abilities than Cp. The structures of **6b** and **7b** were established by X-ray structural analyses. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbyne complexes; Tripodal ligands; Tungsten; Electron donating ability

1. Introduction

Organometallic compounds with extended π -conjugated ligands have attracted considerable interest [1], since bi- and polynuclear complexes containing π -unsaturated conjugated bridges are expected to exhibit potentially useful physical and chemical properties. In such bi- and polynuclear complexes the metal–ligand fragment L_nM can occupy an internal or/and a terminating position in the chain. Various types of bridging ligands have been proposed. In recent years attention has focused on complexes with carbon-rich bridges, $[LnM(C)_mM'L'_n]$ [2]. Until now, complexes with an even number of carbon atoms linking the metals (m up to 20 [3]) are more readily accessible than those with an odd number of carbon atoms. Usually, complexes with

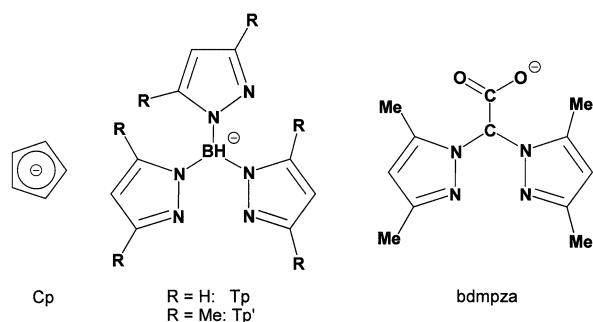
an even number of carbon atoms are derived from alkynes and alkynyl complexes via coupling reactions. In contrast, precursors for the synthesis of complexes with an odd number of bridging carbon atoms are much less readily available.

Alkynylcarbyne complexes (alkynylidyne complexes), $L_nM\equiv C-(C\equiv C)_m-R$, might be suitable starting compounds for the synthesis of complexes with an odd number of bridging carbon atoms. In addition, they also might constitute interesting terminating groups. However, until now there are only a few reports on alkynylcarbyne complexes. The first complexes, *trans*- $X(CO)_4W\equiv C-C\equiv C-Ph$ (X = Cl, Br, I), were prepared by Fischer et al. already in 1974 [4]. Since then, only a few more alkynylcarbyne complexes containing bi- and tridentate ligands, $L_nM\equiv C-C\equiv C^rBu$ (M = Mo, W), have been reported by Stone and coworkers [5].

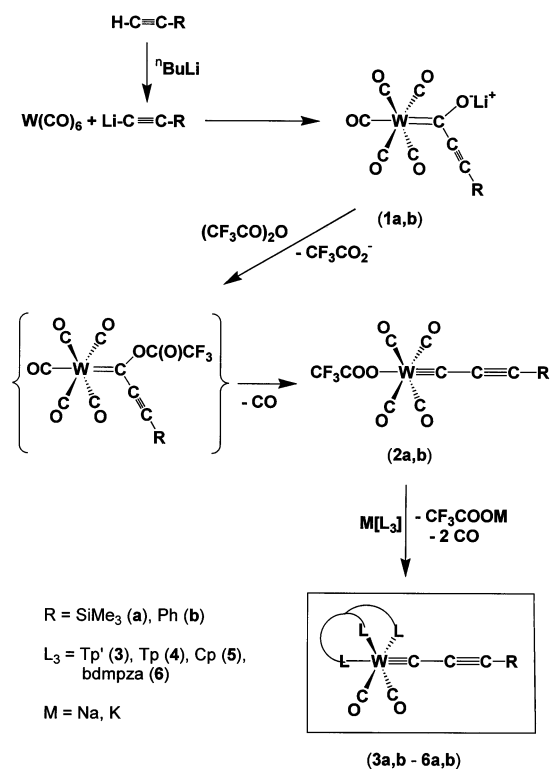
We now report on the synthesis and the spectroscopic properties of a series of alkynylcarbyne complexes of tungsten containing tripodal ligands,

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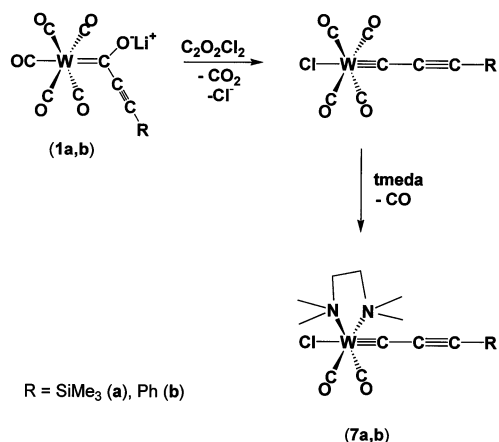
E-mail address: helmut.fischer@uni-konstanz.de (H. Fischer).



Scheme 1.



Scheme 2.



Scheme 3.

$L_3(CO)_2W\equiv C-C\equiv CR$, as well as of two tmeda complexes. To have a rather broad range of electronic properties available, in addition to cyclopentadienide (Cp), hydro[tris(pyrazol-1-yl)]borate (Tp), hydro[tris(3,5-dimethylpyrazol-1-yl)]borate (Tp') [6] and the new scorpionate ligand bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) recently reported by Otero et al. [7] and Burzlaff and coworkers [8] were used as coligands (Scheme 1). The alkynylcarbyne substituent R (SiMe₃, Ph) was chosen in such a way as to be able to further functionalize the complexes and use them as precursors for the synthesis of bi- and polynuclear complexes.

2. Results and discussion

Fischer-type carbyne complexes are usually prepared by either one of the two following pathways:

- transformation of carbene into carbyne complexes by reaction with trihalides of Group III elements (B [9], Al [10], Ga [11]) or
- abstraction of an oxide, O²⁻, from an acyl metalate by e.g. Ph₃PBr₂ [12], SOCl₂ [13], COCl₂, oxalyl halides, or (CF₃CO)₂O [14].

For the synthesis of alkynylcarbyne complexes pathway (b) turned out to be more efficient than pathway (a) affording higher yields. Addition of Li[C≡C-R] to [W(CO)₆] in THF or Et₂O gave the acyl tungstates **1a,b** [15,16]. Subsequent oxide abstraction with trifluoroacetic anhydride at -80 °C [14] afforded the *trans*-tetracarbonyl(trifluoroacetato)tungsten complexes **2a,b**. The trifluoroacetato ligand is only weakly coordinated and, therefore, is easily replaced by other anions. The tetracarbonyl complexes **2a,b** were not isolated but immediately transformed at -50 °C into the complexes **3a,b-6a,b** (Scheme 2) by reaction with the sodium or potassium salts of the tripodal ligand (NaTp', KTp, NaCp or K[bdmpza]). The reaction was accompanied by CO evolution. Column chromatography of the crude products of **3a,b-5a,b** finally afforded the pure complexes in moderate yield (14–56% overall yield, three steps). Deviating from this purification procedure complexes **6a,b** were obtained in 83 and 91% yield by precipitation from the reaction mixture (addition of pentane to solutions in diethyl ether) and subsequent recrystallization.

All complexes are poorly soluble in unpolar organic solvents but readily soluble in polar solvents. In the solid state, all compounds are stable at room temperature. At -30 °C, they can be stored under inert gas for prolonged periods without noticeable decomposition. In solution at room temperature, however, complexes **3a,b-5a,b** slowly decompose.

For comparison, additionally the alkynylcarbyne complexes **7a,b** containing a bidentate ligand (tmeda) were synthesized from [W(CO)₆] and Li[C≡C-R] (R =

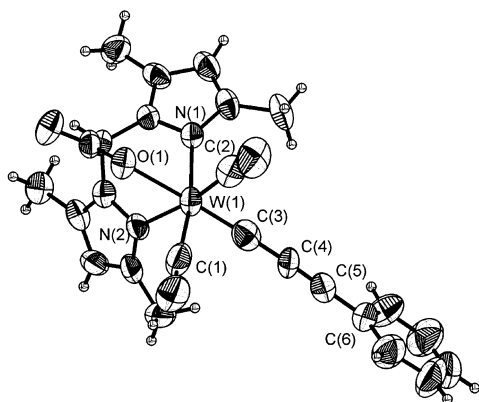


Fig. 1. Molecular structure of complex **6b** in the crystal (solvent molecule omitted for clarity).

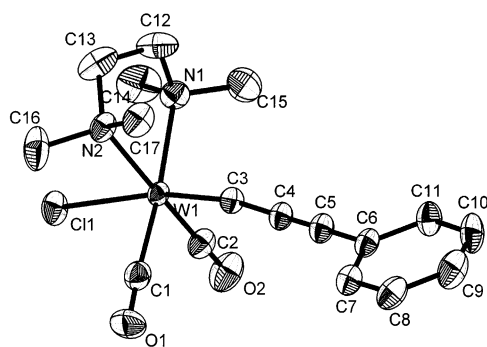


Fig. 2. Molecular structure of complex **7b** in the crystal (hydrogen atoms and solvent molecule are omitted for clarity).

Table 1
Selected bond distances and angles in **6b** and **7b**

	6b	7b
<i>Bond lengths</i>		
W(1)–C(1)	2.032(14)	1.986(6)
W(1)–C(2)	2.024(13)	1.983(5)
W(1)–C(3)	1.839(13)	1.834(5)
W(1)–N(1)	2.247(8)	2.304(4)
W(1)–N(2)	2.233(9)	2.300(4)
W(1)–O(3)	2.222(7)	
W(1)–Cl(1)		2.5098(14)
C(3)–C(4)	1.429(16)	1.376(6)
C(4)–C(5)	1.216(15)	1.204(7)
C(5)–C(6)	1.457(15)	1.427(6)
<i>Bond angles</i>		
C(3)–W(1)–C(1)	88.6(5)	82.4(2)
C(3)–W(1)–C(2)	85.1(5)	88.3(2)
C(3)–W(1)–N(1)	99.7(4)	100.16(19)
C(3)–W(1)–N(2)	102.8(4)	97.27(17)
W(1)–C(3)–C(4)	178.1(10)	168.4(4)
C(3)–C(4)–C(5)	177.3(12)	175.7(5)
C(4)–C(5)–C(6)	179.2(12)	176.9(5)

SiMe₃, Ph), oxalyl chloride and tmeda (Scheme 3). After chromatography, **7a** was obtained in 22%, **7b** in 24% overall yield. Compounds **7a,b** are less stable than

3a,b–6a,b. Nevertheless, they can be heated to at least 80 °C but start to decompose quickly above ca. 120 °C.

The metal in these complexes **3a,b–6a,b** and **7a,b** is pseudo-octahedrally coordinated, the tripodal ligand in **3a,b–6a,b** occupying a facial position. In contrast to **3a,b–5a,b**, two isomers are conceivable for complexes **6a** and **6b**: there is either a *trans* arrangement of a 3,5-dimethylpyrazolyl group and the alkynylcarbyne ligand (isomer **A**) or of the carboxylate and the alkynylcarbyne ligand (isomer **B**). IR, ¹H- and ¹³C-NMR spectra indicate that a single isomer is formed. The ¹H-NMR spectra of **6a** and **6b** exhibit a single set of resonances for the pyrazolyl groups (e.g. two Me peaks). In contrast, for **3a** and **3b** four *N*-methyl resonances are observed. The ¹³C-NMR spectra show only one peak for the two CO ligands at a position [$\delta = 225.9$ (**6a**) and 226.0 ppm (**6b**)] similar to that of the CO resonances in **3a,b** and **4a,b** ($\delta = 226.1–227.3$ ppm). From these observation it follows that in solution isomer **B** is present. The conclusion is supported by the results of the X-ray analysis of complex **6b**. Until now, there is no solid-state structure of a complex with a terminally bonded alkynylcarbyne ligand available. Only a complex featuring a bridging C≡C–CMe₃ ligand [17] and a binuclear Re–W complex with a nearly linear C₃ bridge, [Cp*(PPh₃)(NO)Re–C≡C–C≡W(O^tBu)₃] (**8**) [18], have been characterized by X-ray structural analyses. Therefore, the structure of **7b** was also established by an X-ray analysis.

In both complexes, **6b** (Fig. 1) and **7b** (Fig. 2), the coordination octahedron is slightly distorted. The CO ligands are bent towards the alkynylcarbyne ligand. Conversely, the C(carbyne)–W–N angle is > 90°. As has already been deduced from the NMR spectra the carboxylate in **6b** occupies the position *trans* to the alkynylcarbyne ligand. The W≡C(carbyne) distance is equal in both compounds [1.839(13) Å in **6b**, 1.834(5) Å in **7b**] (Table 1) and compares well with that in the tolylcarbyne complex [Tp*(CO)₂W≡C–C₆H₄Me-*p*] ((1.829(3) Å) [19]. Obviously, the *trans* ligand (RCOO[−], Cl[−], pyrazolyl) does not significantly influence the W≡C(carbyne) bond length. However, the (^tBuO)₃W≡C distance in **8** is significantly shorter (1.769(8) Å) [18]. Due to the π -acceptor properties of the pyrazolyl ligands in **6b** the W–CO distances in **6b** is longer than in **7b** (2.024–2.032(14) Å in **6b**, 1.983–1.986(6) Å in **7b**). The C(3)–C(4) distance in **6b** (1.429(16) Å) and **7b** (1.376(6) Å) compares well with the median value for a C(sp)–C(sp) single bond (1.377 Å [20]). The C(4)–C(5) distance (1.216(15) Å in **6b** and 1.204(7) Å for **7b**) is also in the range usually observed for C≡C bonds (1.183 Å [20]). Whereas the WCCC fragment in **6a** is nearly linear (W–C–C 178.1(10)°, C–C–C 177.3(12)°), that in **7b** is slightly bent (W–C(3)–C(4) 168.4(4)°,

C(3)–C(4)–C(5) 175.7(5)°). The deviation from linearity is presumably due to packing effects in the crystal.

All alkynylcarbyne complexes display two $\nu(\text{CO})$ absorptions of similar intensity as expected for *cis*-[L₄M(CO)₂] complexes. An additional weak absorption at 2050–2057 cm⁻¹ in the spectra of the trimethylsilylethynylcarbyne complexes **3a–7a** is assigned to the $\nu(\text{C}\equiv\text{C})$ vibration. The corresponding absorption of the phenylethynylcarbyne complexes is at about 50 cm⁻¹ higher wavenumbers indicating stronger π -acceptor properties of C–C≡C–SiMe₃ compared to C–C≡C–Ph. The conclusion agrees with the observation that the $\nu(\text{CO})$ absorptions of the phenylethynylcarbyne complexes **3b–7b** are at slightly smaller wavenumbers than those of **3a–7a**.

From the shift in the $\nu(\text{CO})$ absorptions (Table 1) we can deduce a decrease in the electron donating ability in the order Tp' > Tp > Cp. The same order has been reported before by Stone and coworkers [5] for *t*-butylethynylcarbyne complexes of molybdenum. A higher electron-donating potential of Tp compared to Cp has also been observed by McElwee-White and coworkers [21] with some molybdenum carbyne complexes.

Replacement of one strongly σ -donating pyrazolyl group in Tp by the electronegative C(=O)O⁻ group (**4** → **6**) should reduce the electron-donating properties of the tripodal ligand, although the effect should be less pronounced for a substitution *cis* to CO than *trans* to CO. The assumption is confirmed by the $\nu(\text{CO})$ absorptions: the influence of the new bdmmpza tripodal ligand on the carbonyl vibrations is intermediate between that of Tp and Cp. Thus, with respect to the electronic influence of various tripodal ligands on the metal bdmmpza fills in the gap between Tp and Cp. Based on the $\nu(\text{CO})$ spectra the σ -donor/ π -acceptor ratio of the tripodal bdmmpza ligand is comparable to the ligand combination tmeda/Cl⁻.

Table 2
 $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$ absorptions of the complexes **3a,b–7a,b** (in cm⁻¹) in THF

Complex	A ₁	B ₁	$\nu(\text{C}\equiv\text{C})$
[Tp'(CO) ₂ W≡C–C≡C–SiMe ₃] (3a)	1982	1896	2052
[Tp(CO) ₂ W≡C–C≡C–SiMe ₃] (4a)	1991	1906	2056
[Cp(CO) ₂ W≡C–C≡C–SiMe ₃] (5a)	1995	1923	2057
[(bdmpza)(CO) ₂ W≡C–C≡C–SiMe ₃] (6a)	1995	1912	2052
[Cl(tmeda)(CO) ₂ W≡C–C≡C–SiMe ₃] (7a) ^a	1997	1908	2050
[Tp'(CO) ₂ W≡C–C≡C–Ph] (3b)	1979	1893	2101 ^b
[Tp(CO) ₂ W≡C–C≡C–Ph] (4b)	1988	1904	2102
[Cp(CO) ₂ W≡C–C≡C–Ph] (5b)	1992	1920	2105
[(bdmpza)(CO) ₂ W≡C–C≡C–Ph] (6b)	1992	1910	2097 ^b
[Cl(tmeda)(CO) ₂ W≡C–C≡C–Ph] (7b)	1993	1909	

^a In CH₂Cl₂.

^b In KBr.

From the IR data it also follows that bdmmpza is stronger electron-donating than Cp. This result contradicts data published earlier by Burzlaff et al. [22]. Based mainly on the shorter M–CO distances in [Tp'M(CO)₃] and [CpM(CO)₃] than in [(bdmpza)M(CO)₃] (M = Mn, Re) they concluded that bdmmpza would be less electron-donating than Cp and Tp'. However, a change in donor capacity of Tp', Tp and Cp in compounds of transition metals belonging to different groups has been recognized before [23]. Apparently this dependence of the electron-donor ability on the metal also holds true for bdmmpza.

The carbonyl and the carbyne resonances in the ¹³C-NMR spectra are rather insensitive to changes in the tripodal ligand (Tp', Tp and bdmmpza) and appear at $\delta = 226.6 \pm 0.7$ and $\delta = 250.4 \pm 3.1$ ppm (Table 2). The same applies to both alkynyl carbon atoms. Surprisingly, substitution of carboxylate for the *trans*-pyrazolyl group does not significantly affect the W≡C resonance. In contrast, in the *trans*-chloro complexes **7a,b** all carbon resonances (CO, W≡C–C≡C) are shifted towards higher field, the resonance of the carbyne carbon even by ca. 20 ppm.

When the pyrazole-containing tripodal ligands are replaced by cyclopentadienide a significant shift towards higher field for the carbonyl resonance and, conversely, towards lower field for the carbyne resonance is observed.

Thus, several metal–ligand fragments are now available for modifying the properties of the alkynylcarbyne ligand. Furthermore, due to the C=O functionality, a fine-tuning of the electronic properties of the new bdmmpza group should be possible through addition of Lewis acids. These new alkynylcarbyne complexes should constitute good starting compounds for chain extensions and for the synthesis of binuclear complexes with an odd number of bridging carbon atoms. The high thermal stability of the complexes **3a,b–7a,b** should make coupling reactions feasible which usually require elevated temperatures. Preliminary results already indicate that **7a** can be desilylated by e.g. [NBu₄]F–THF (Table 3).

3. Experimental

3.1. General

All operations were carried out under either nitrogen or Ar by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone ketyl or CaH₂ and were freshly distilled prior to use. The silica gel used for chromatography (J.T. Baker, silica gel for flash chromatography) was saturated with Ar. The yields refer to analytically pure compounds and were not optimized. NaTp [6] and

Table 3
Selected ^{13}C -NMR resonances (in ppm) of complexes **3a,b–7a,b**

Complex	$\delta(\text{CO})$	$\delta(\text{W}=\text{C})$	$\delta(\text{C}_\alpha)$	$\delta(\text{C}_\beta)$
[Tp'(CO) ₂ W≡C–C≡C–SiMe ₃] (3a) ^a	226.1	247.3	120.4	79.5
[Tp(CO) ₂ W≡C–C≡C–SiMe ₃] (4a) ^b	226.5	253.4	120.9	80.7
[Cp(CO) ₂ W≡C–C≡C–SiMe ₃] (5a) ^b	222.2	266.3	123.0	86.1
[(bdmpza)(CO) ₂ –W≡C–C≡C–SiMe ₃] (6a) ^b	225.9	244.1	121.1	78.8
[Cl(tmeda)(CO) ₂ –W≡C–C≡C–SiMe ₃] (7a) ^a	222.0	232.4	118.8	68.2
[Tp'(CO) ₂ W≡C–C≡C–Ph] (3b) ^b	227.3	247.3	122.5	71.4
[Tp(CO) ₂ W≡C–C≡C–Ph] (4b) ^b	226.7	251.4	122.3	72.1
[Cp(CO) ₂ W≡C–C≡C–Ph] (5b) ^b	222.4	264.2	122.3	76.7
[(bdmpza)(CO) ₂ –W≡C–C≡C–Ph] (6b) ^b	226.0	248.9	122.3	69.8
[Cl(tmeda)(CO) ₂ –W≡C–C≡C–Ph] (7b) ^a	222.4	230.4	105.2	68.2

^a In CDCl₃.

^b In *d*₆-acetone.

KTp' [24] were prepared according to literature procedures. K[bdmpza] [8] was supplied by Dr N. Burzlaff. Trimethylsilylacetylene (Fluka), phenylacetylene (Merck), *n*-BuLi (Chemetall), [W(CO)₆] and trifluoroacetic anhydride (Aldrich) were commercial products and were used without further purification. IR: Bio-Rad FT-IR spectrophotometer. ¹H-NMR, ¹³C-NMR: Bruker AC 250, Bruker DRX 600. Unless specifically mentioned, ¹H-NMR spectra were recorded at 250 MHz and ¹³C-NMR at 151 MHz at room temperature (r.t.). Chemical shifts are reported relative to the residual solvent peaks [CD₃COCD₃; $\delta = 2.04$ (¹H) and 29.8 ppm (¹³C), CDCl₃; $\delta = 7.24$ (¹H) and 77.0 ppm (¹³C)]. MS: Finnigan MAT 312 (EI) or Finnigan MAT 312/AMD5000 (FAB).

3.2. General procedure for the synthesis of the complexes **3–6**

At -30 °C, 5.0 mmol of trimethylsilylacetylene and phenylacetylene, respectively, in 30 ml of THF was lithiated with a 15% solution of *n*-BuLi in hexane. After 0.5 h, 5.0 mmol of [W(CO)₆] was added to the solution. The resulting red solution was stirred at r.t. for 1 h and then cooled to -80 °C. (CF₃CO)₂O (5.0 mmol) of was added. CO evolution was observed. The solution was warmed to -50 °C and 5.0 mmol of NaTp', KTp and NaCp, respectively, was added. When the CO evolution stopped after warming to r.t. the solvent was removed in vacuo. The dark brown residue

was dissolved in THF and chromatographed at -20 °C on silica gel.

3.2.1. Dicarbonyl[hydro(tris-3,5-dimethylpyrazol-1-yl)borato](trimethylsilylpropynylidyne)-tungsten (**3a**)

Chromatography with pentane afforded a purple band. Removal of the solvent from the purple fraction yielded complex **3a** as a red–purple microcrystalline powder. Yield: 900 mg (28% relative to [W(CO)₆]). Dec. > 208 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2052 w, $\nu(\text{CO})$ 1982 s, 1896 s. ¹H-NMR (CDCl₃): $\delta = 0.15$ (s, 9H, Si(CH₃)₃), 2.28 (s, 3H, pz-C₃Me), 2.33 (s, 9H, pz-C₅Me), 2.55 (s, 6H, pz-C₃Me), 5.71 (s, 1H, pz-C₄H), 5.88 (s, 2H, pz-C₄H). ¹³C-NMR (CDCl₃): $\delta = -0.5$ (Si(CH₃)₃), 12.6 (pz-C₅Me), 15.1 (pz-C₃Me), 16.4 (pz-C₃Me), 79.5 (C_β), 106.4 (pz-C₄), 120.4 (C_α), 144.4 (pz-C₃), 145.2 (pz-C₃), 151.8 (pz-C₅), 152.2 (pz-C₅), 226.1 (t, $J(\text{WC}) = 162$ Hz, CO), 247.3 (t, $J(\text{WC}) = 198$ Hz, W≡C). FABMS (NBA); m/z (%): 646 (4) [M⁺], 618 (10) [M⁺ – CO], 590 (9) [M⁺ – 2CO], 73 (100) [Si(CH₃)₃]. Anal. Found: C, 42.89; H, 4.90; N, 12.65. Calc. for C₂₃H₃₁BN₆O₂SiW (646.3): C, 42.74; H, 4.83; N, 13.00%.

3.2.2. Dicarbonyl[hydro(tris-3,5-dimethylpyrazol-1-yl)borato](phenylpropynylidyne) tungsten (**3b**)

Chromatography with pentane–CH₂Cl₂ (4:1) gave a purple band. Removal of the solvent from the purple fraction afforded complex **3b** as a red–purple microcrystalline powder. Yield: 520 mg (14% relative to [W(CO)₆]). Dec. > 182 °C. IR (THF, cm⁻¹) $\nu(\text{CO})$ 1979 s, 1893 s. ¹H-NMR (CDCl₃): $\delta = 2.30$ (s, 3H, pz-C₅Me), 2.35 (s, 3H, pz-C₃Me), 2.36 (s, 6H, pz-C₅Me), 2.59 (s, 6H, pz-C₃Me), 5.73 (s, 1H, pz-C₄H), 5.89 (s, 2H, pz-C₄H), 7.15–7.50 (m, 5H, C₆H₅). ¹³C-NMR: $\delta = 12.6$ (s, pz-C₅Me), 12.6 (s, pz-C₅Me), 15.3 (s, pz-C₃Me), 16.5 (s, pz-C₃Me), 71.4 (C_β), 106.6 (C₁, Ph), 107.5 (s, pz-C₄), 107.7 (s, pz-C₄), 122.5 (C_α), 129.7 (Ph), 129.9 (Ph), 133.2 (Ph), 146.0 (s, pz-C₃), 146.9 (s, pz-C₃), 152.7 (s, pz-C₅), 152.9 (s, pz-C₅), 227.3 (t, $J(\text{WC}) = 160$ Hz, CO), 247.3 (W≡C). FABMS (NBA); m/z (%): 650 (8) [M⁺], 622 (10) [M⁺ – CO], 594 (10) [M⁺ – 2CO]. Anal. Found: C, 48.00; H, 4.18; N, 12.75. Calc. for C₂₆H₂₇BN₆O₂W (650.2): C, 48.03; H, 4.19; N, 12.93%.

3.2.3. Dicarbonyl[hydro(trispyrazol-1-yl)borato](trimethylsilylpropynylidyne) tungsten (**4a**)

Chromatography with pentane–CH₂Cl₂ (9:1) gave a red band. Removal of the solvent from the red fraction afforded complex **4a** as a red microcrystalline powder. Yield: 870 mg (31% relative to [W(CO)₆]). Dec. > 164 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2056 w, $\nu(\text{CO})$ 1991 s, 1906 s. ¹H-NMR (CDCl₃): $\delta = 0.18$ (s, 9H, Si(CH₃)₃), 6.13 (t, $J^3 = 2.1$ Hz, 1H, pz-C₄H), 6.24 (t, $J^3 = 2.2$ Hz, 2H, pz-C₄H), 7.58 (d, 1H, pz-C₅H), 7.60 (d, 1H, pz-C₃H), 7.64 (d, $J^3 = 2.2$ Hz, 2H, pz-C₅H), 8.01 (d,

$J^3 = 1.9$ Hz, 2H, pz-C₃H). ¹³C-NMR: $\delta = -0.4$ (Si(CH₃)₃), 80.7 (t, $J^3 = 4$ Hz, C _{β}), 107.2 (pz-C₄), 120.9 (t, $J^2 = 28$ Hz, C _{α}), 137.1 (pz-C₃), 145.2 (pz-C₅), 146.2 (pz-C₅), 226.5 (t, $J(\text{WC}) = 164$ Hz, CO), 253.4 (t, $J(\text{WC}) = 200$ Hz, W \equiv C). FABMS (NBA); m/z (%): 562 (38) [M⁺], 534 (24) [M⁺ – CO], 73 (68) [Si(CH₃)₃], 68 (43) [C₃H₄N₂]. Anal. Found: C, 37.19; H, 3.89; N, 14.59. Calc. for C₁₇H₁₉BN₆O₂SiW (562.1): C, 36.32; H, 3.41; N, 14.95%.

3.2.4. Dicarboxyl[hydro(trispyrazol-1-yl)borato](phenylpropynylidyne)tungsten (**4b**)

Chromatography with pentane–CH₂Cl₂ (4:1) gave a red band. Removal of the solvent from the red fraction afforded complex **4b** as a red microcrystalline powder. Yield: 780 mg (28% relative to [W(CO)₆]). Dec. > 135 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2102 vw, $\nu(\text{CO})$ 1988 s, 1904 s. ¹H-NMR: $\delta = 6.30$ (t, $J^3 = 2.1$ Hz, 1H, pz-C₄H), 6.40 (t, $J^3 = 2.3$ Hz, 2H, pz-C₄H), 7.20–7.60 (m, 5H, Ph), 7.83 (d, $J^3 = 2.0$ Hz, 1H, pz-C₅H), 7.90 (d, $J^3 = 2.2$ Hz, 1H, pz-C₃H), 7.96 (d, $J^3 = 2.3$ Hz, 2H, pz-C₅H), 8.11 (d, $J^3 = 1.9$ Hz, 2H, pz-C₃H). ¹³C-NMR: $\delta = 72.1$ (C _{β}), 107.2 (pz-C₄), 107.4 (C₁, Ph), 122.3 (C _{α}), 129.7 (Ph), 130.0 (Ph), 133.2 (Ph), 137.1 (pz-C₃), 137.3 (pz-C₃), 145.0 (pz-C₅), 146.2 (pz-C₅), 226.7 (t, $J(\text{WC}) = 64$ Hz, CO), 251.4 (W \equiv C). EIMS; m/z (%): 566 (5) [M⁺], 538 (6) [M⁺ – CO], 512 (4) [M⁺ – 2CO]. Anal. Found: C, 43.66; H, 3.23; N, 14.12. Calc. for C₂₀H₁₅BN₆O₂W (566.0): C, 42.44; H, 2.67; N, 14.85%.

3.2.5. Dicarboxyl(cyclopentadienyl)(trimethylsilylpropynylidyne)tungsten (**5a**)

Chromatography with pentane–CH₂Cl₂ (4:1) gave a red band. Removal of the solvent from the red fraction afforded complex **5a** as a red microcrystalline powder. Yield: 1160 mg (56% relative to [W(CO)₆]). Dec. > 115 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2057 w, $\nu(\text{CO})$ 1995 s, 1923 s. ¹H-NMR: $\delta = 0.15$ (s, 9H, Si(CH₃)₃), 5.87 (s, 5H, C₅H₅). ¹³C-NMR: $\delta = -0.8$ (Si(CH₃)₃), 86.1 (C _{β}), 93.6 (C₅H₅), 123.0 (C _{α}), 222.2 (CO), 266.3 (W \equiv C). FABMS (NBA); m/z (%): 414 (11) [M⁺], 386 (5) [M⁺ – CO], 358 (12) [M⁺ – 2CO], 73 (100) [Si(CH₃)₃]. Anal. Found: C, 38.05; H, 3.59. Calc. for C₁₃H₁₄O₂SiW (414.2): C, 37.70; H, 3.41%.

3.2.6. Dicarboxyl(cyclopentadienyl)(phenylpropynylidyne)tungsten (**5b**)

Chromatography with pentane–CH₂Cl₂ (4:1) gave a red band. Removal of the solvent from the red fraction afforded complex **5b** as a red microcrystalline powder. Yield: 794 mg (38% relative to [W(CO)₆]). Dec. > 136 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2105 w, $\nu(\text{CO})$ 1992 s, 1920 s. ¹H-NMR: $\delta = 5.89$ (s, 5H, C₅H₅), 7.3–7.5 (m, 5H, C₆H₅). ¹³C-NMR: $\delta = 76.7$ (C _{β}), 93.3 (C₅H₅), 109.6 (C₁, Ph), 122.3 (C _{α}), 129.6 (Ph), 130.3 (Ph), 132.5 (Ph), 222.4 (t, $J(\text{WC}) = 194$ Hz, CO); 264 (t, $J(\text{WC}) = 226$

Hz, W \equiv C). EIMS; m/z (%): 418 (43) [M⁺], 390 (3) [M⁺ – CO], 362 (100) [M⁺ – 2CO]. Anal. Found: C, 45.73; H, 2.71. Calc. for C₁₆H₁₀O₂W (418.1): C, 45.96; H, 2.41%.

3.3. General procedure for the synthesis of the complexes **6a** and **6b**

At –30 °C, 5.0 mmol of trimethylsilylacetylene and phenylacetylene, respectively, in 30 ml of Et₂O was lithiated with a 15% solution of *n*-BuLi in hexane. After 0.5 h, 5.0 mmol of [W(CO)₆] was added to the solution. The resulting red solution was stirred at r.t. for 1 h and then cooled to –80 °C. (CF₃CO)₂O (5.0 mmol) of was added. CO evolution was observed. The solution was warmed to –50 °C and 5.0 mmol of the K[bdmpza] was added. When the CO evolution stopped after warming to r.t. ca. 50ml of pentane was added. A pale red precipitate formed. The precipitate was washed 3 × with 50 ml of pentane each to remove [W(CO)₆]. The powder was dried in vacuo and then recrystallized from THF.

3.3.1. Bis(3,5-dimethylpyrazol-1-yl)acetato(dicarboxyl)(trimethylsilylpropynylidyne)tungsten (**6a**)

Yield: 2.5 g (83% relative to [W(CO)₆]). Dec. > 205 °C. IR (THF, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2052 w, $\nu(\text{CO})$ 1995 s, 1912 s, 1693 m. ¹H-NMR: $\delta = 0.14$ (s, 9H, Si(CH₃)₃), 2.59 (s, 6H, pz-CMe), 2.60 (s, 6H, pz-CMe), 6.36 (s, 2H, pz-C₄H), 6.62 (s, 1H, CH). ¹³C-NMR: $\delta = -0.4$ (Si(CH₃)₃), 11.0 (pz-CMe), 16.1 (pz-CMe), 69.0 (CH), 78.8 (C _{β}), 108.9 (pz-C₄), 121.1 (t, $J^2(\text{WC}) = 27$ Hz; C _{α}), 144.2 (pz-C₅), 154.7 (pz-C₃), 163.7 (CO₂), 225.9 (t, $J(\text{WC}) = 172$ Hz, CO), 244.1 (t, $J(\text{WC}) = 196$ Hz; W \equiv C). FABMS (NBA); m/z (%): 603 (12) [M⁺ + Li], 596 (14) [M⁺], 496 (22) [M⁺ – 2CO – CO₂], 455 (52) [M⁺ – 2CO – CO₂ – C₂H₃N], 108 (100) [C₆H₈N₂]. Anal. Found: C, 39.77; H, 4.09; N, 9.16. Calc. for C₂₀H₂₄N₄O₄SiW (596.4): C, 40.28; H, 4.06; N, 9.39%.

3.3.2. Bis(3,5-dimethylpyrazol-1-yl)acetato(dicarboxyl)(phenylpropynylidyne)tungsten (**6b**)

Yield: 2.7 g (91% relative to [W(CO)₆]). Dec. > 206 °C. IR (KBr, cm⁻¹) $\nu(\text{C}\equiv\text{C})$ 2097; (THF, cm⁻¹) $\nu(\text{CO})$ 1992 s, 1910 s, 1692 m. ¹H-NMR: $\delta = 2.61$ (s, 6H, Me), 2.64 (s, 6H, Me), 6.37 (s, 2H, C₄H), 6.63 (s, 1H, CH), 7.3–7.5 (m, 5H, C₆H₅). ¹³C-NMR: $\delta = 11.0$ (C₅Me), 16.2 (C₃Me), 69.1 (CH), 69.8 (C _{β}), 107.4 (C₁, Ph), 108.9 (pz-C₄), 122.3 (C _{α}), 129.6 (Ph), 129.9 (Ph), 133.2 (Ph), 144.2 (pz-C), 154.7 (pz-C), 163.6 (CO₂), 226.0 (CO), 248.9 (W \equiv C). FABMS (NBA); m/z (%): 600 (4) [M⁺], 500 (2) [M⁺ – 2CO – CO₂], 459 (4) [M⁺ – 2CO – CO₂ – C₂H₃N]. Anal. Found: C, 46.18; H, 3.46; N, 9.33. Calc. for C₂₃H₂₀N₄O₄W (600.3): C, 46.02; H, 3.36; N, 9.33%.

3.4. Dicarbonyl(chloro)(trimethylsilylpropynylidyne)-(tetramethylethylenediamine)tungsten (**7a**)

At $-80\text{ }^{\circ}\text{C}$, 5.0 mmol of 1.6M solution of *n*-BuLi in hexane were added dropwise to a solution of 5.0 mmol of trimethylsilylacetylene in 30 ml of THF. The solution was stirred for 10 min and then gradually warmed to r.t. A suspension of 5.0 mmol of $[\text{W}(\text{CO})_6]$ in 50 ml of THF cooled to $-5\text{ }^{\circ}\text{C}$ was added. The solution immediately turned orange. It was cooled to $-80\text{ }^{\circ}\text{C}$ and a solution of 5.0 mmol of $\text{C}_2\text{O}_2\text{Cl}_2$ in 20 ml of THF was added dropwise. The color of the solution changed to red–brown and a CO evolution was observed. The solution was warmed to $-60\text{ }^{\circ}\text{C}$ and 5.0 mmol of tmeda was added. When the CO evolution had ceased the solution was heated at $40\text{ }^{\circ}\text{C}$ for 1 h. The solvent was removed in vacuo. The light brown residue was dissolved in 25 ml of CH_2Cl_2 and solution filtered over a 15 cm layer of silica gel. A red–brown band was eluted which was subsequently chromatographed at $-20\text{ }^{\circ}\text{C}$ on silica gel. With CH_2Cl_2 three fractions were obtained: the first, yellow–brown one contained $[\text{W}(\text{CO})_6]$, the second, yellow–orange one $[(\text{CO})_4\text{W}(\text{tmeda})]$ and the third, orange fraction finally gave complex yellow–orange **7a** as a microcrystalline powder. Yield: 600 mg (24% relative to $[\text{W}(\text{CO})_6]$). M.p. $> 124\text{ }^{\circ}\text{C}$. IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{C}\equiv\text{C})$ 2050 vw, br; $\nu(\text{CO})$ 1997 s, 1908 vs. $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.16$ (s, 9H, SiCH₃), 2.90 (s, 6H, NCH₃), 2.91 (s, 4H, NCH₂), 3.18 (s, 6H, NCH₃). $^{13}\text{C-NMR}$ (CDCl_3): $\delta = -0.0$ (SiCH₃), 52.3, 58.2, 61.2 (NCH₃, CH₂), 68.2 (C_β), 118.8 ($J^2(\text{WC}) = 28.9\text{ Hz}$, C_α), 222.0 ($J(\text{WC}) = 173\text{ Hz}$, CO), 232.4 ($J(\text{WC}) = 210\text{ Hz}$, W≡C). FABMS (NBA); m/z (%): 500 (18) [M^+], 472 (59) [$\text{M}^+ - \text{CO}$], 465 (45) [$\text{M}^+ - \text{Cl}$], 444 (58) [$\text{M}^+ - 2\text{CO}$], 409 (14) [$\text{M}^+ - 2\text{CO} - \text{Cl}$], 115 (100) [tmeda-H⁺]. Anal. Found: C, 34.44; H, 5.34; N, 5.28. Calc. for $\text{C}_{14}\text{H}_{25}\text{ClN}_2\text{O}_2\text{SiW}$ (500.8): C, 33.58; H, 5.03; N, 5.59%.

3.5. Dicarbonyl(chloro)(phenylpropynylidyne)-(tetramethylethylenediamine)tungsten (**7b**)

At $-80\text{ }^{\circ}\text{C}$, 5.0 mmol of phenylacetylene were lithiated in 30 ml of THF by dropwise adding a 15% solution of *n*-BuLi in hexane. After 5 min of stirring the cooling bath was removed and the solution stirred until r.t. was reached. At $-5\text{ }^{\circ}\text{C}$, this solution was combined with 5.0 mmol of a solution of $[\text{W}(\text{CO})_6]$ in 50 ml of THF. The resulting red solution was stirred for ca. 20 min while warming to $0\text{ }^{\circ}\text{C}$ and then cooled to $-80\text{ }^{\circ}\text{C}$. 5.0 mmol of $\text{C}_2\text{O}_2\text{Cl}_2$ was added dropwise. The color of the solution changed to red–brown and a CO evolution was observed. The solution was warmed to $-60\text{ }^{\circ}\text{C}$ and 5.0 mmol of tmeda was added. When the CO evolution had ceased after warming the solution to r.t. and successive heating to $40\text{ }^{\circ}\text{C}$ for 1 h, the

solvent was removed in vacuo. The light brown residue was dissolved in THF and chromatographed at $-20\text{ }^{\circ}\text{C}$ on silica gel. Chromatography with pentane– CH_2Cl_2 (1:0) gave a red band. Removal of the solvent from the red fraction afforded complex **9** as a red microcrystalline powder. Yield: 550 mg (22% relative to $[\text{W}(\text{CO})_6]$). M.p. $> 120\text{ }^{\circ}\text{C}$ (dec.). IR (THF, cm^{-1}) $\nu(\text{CO})$ 1993 s, 1909 vs. $^1\text{H-NMR}$ (CDCl_3): $\delta = 2.92$ (s, 6H, CH₃), 2.93 (s, 4H, CH₂), 3.22 (s, 6H, CH₃), 7.23–7.45 (m, 5H, C₆H₅). $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 52.31$, 58.21, 61.21 (CH₃, CH₂), 68.2 (C_β), 105.2 ($J^2(\text{WC}) = 30\text{ Hz}$, C_α), 121.8, 128.5, 128.6, 132.7 (Ph), 222.4 ($J(\text{WC}) = 172\text{ Hz}$, CO), 230.4 ($J(\text{WC}) = 212\text{ Hz}$, W≡C). FABMS (NBA); m/z (%): 504 (21) [M^+], 476 (59) [$\text{M}^+ - \text{CO}$], 469 (37) [$\text{M}^+ - \text{Cl}$], 448 (56) [$\text{M}^+ - 2\text{CO}$], 115 (100) [tmeda-H⁺], 89 (21) [C-Ph]. Anal. Found: C, 39.63; H, 4.54; N, 5.07. Calc. for $\text{C}_{17}\text{H}_{21}\text{ClN}_2\text{O}_2\text{W}$ (504.7): C, 40.46; H, 4.19; N, 5.55%.

3.6. X-ray structural analyses of **6b** and **7b**

6b. $\text{C}_{27}\text{H}_{28}\text{N}_4\text{O}_5\text{W}$, molecular mass (672.38), crystal size $0.2 \times 0.2 \times 0.05\text{ mm}^3$ (obtained by recrystallization from THF); crystal system monoclinic, space group $P2_1/c$, $a = 20.617(15)\text{ \AA}$, $b = 9.680(8)\text{ \AA}$, $c = 15.743(14)\text{ \AA}$, $\beta = 111.99(5)^\circ$; $V = 2913.3(41)\text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.533\text{ g cm}^{-3}$, absorption coefficient 4.005 mm^{-1} , $F(000) 1328$; scan type: adaptive ω , θ range $2.13\text{--}25.0^\circ$, scan range 1.6° , scan rate variable $4.0\text{--}30.0^\circ$ per minute in ω ; 5119 independent reflections, 3478 reflection with $I > 2\sigma(I)$; 334 refined parameters; $R_1 = 0.0600$, $wR_2 = 0.1507$. Largest difference peak and hole: $+1.818$ and -1.676 e \AA^{-3} .

7b. $\text{C}_{18}\text{H}_{23}\text{Cl}_3\text{N}_2\text{O}_2\text{W}$, molecular mass (589.58), crystal size $0.3 \times 0.2 \times 0.3\text{ mm}^3$ (obtained by recrystallization from CH_2Cl_2); crystal system triclinic, space group $P\bar{1}$, $a = 7.704(2)\text{ \AA}$, $b = 11.921(3)\text{ \AA}$, $c = 12.961(3)\text{ \AA}$, $\alpha = 101.30(1)^\circ$, $\beta = 105.21(2)^\circ$, $\gamma = 105.68(1)^\circ$; $V = 1059.3(5)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.848\text{ g cm}^{-3}$, absorption coefficient 5.848 mm^{-1} , $F(000) 572$; scan type: adaptive ω , θ range $2.12\text{--}27.05^\circ$, 4579 independent reflections, 4344 reflection with $I > 2\sigma(I)$; 220 refined parameters; $R_1 = 0.0301$, $wR_2 = 0.0775$. Largest difference peak and hole: $+1.220$ and -1.452 e \AA^{-3} .

The measurements were performed at -38 (**6b**) and $-42\text{ }^{\circ}\text{C}$ (**7b**) with a crystal mounted in a glass capillary on a Siemens P4 diffractometer (graphite monochromator, Mo–K_α radiation, $\lambda = 0.71073\text{ \AA}$). The structures were solved by direct methods using the SHELX-97 program package [25]. The positions of the hydrogen atoms were calculated by assuming ideal geometry and their coordinates were refined together with those of the attached C atoms as ‘riding model’. The positions of all other atoms were refined anisotropically by the full-matrix least-squares method. Complex **6b** crystallized with one equivalent of THF, complex **7b** with one equivalent

of CH₂Cl₂. The solvent molecules were refined anisotropically.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 166390 and 166389 for compounds **6b** and **7b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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