Symmetric and Non-Symmetric Dinuclear Alkenyl-Bridged Carbene Complexes of Chromium and Tungsten

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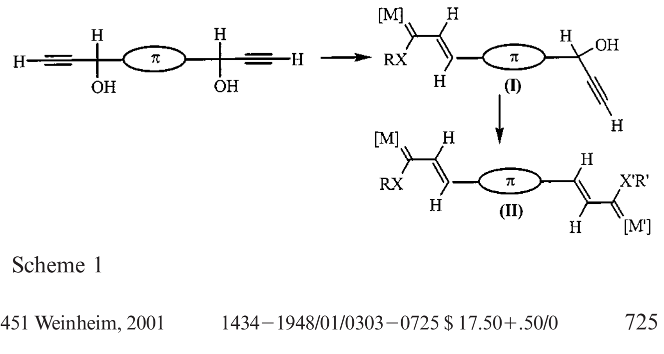
Treatment of $(CO)_5W{=}C(NMe_2)CH{=}CH{-}Ar{-}(OH)(H)C{\equiv}CH$ (**1a**–**b**) [**a**: $-Ar- = 1,4\text{-}C_6H_4-$; **b**: $-Ar- = 2,5\text{-}C_4H_2S-$] with $W(CO)_5(THF)$ in methanol yields the nonsymmetrical bis(alkenylcarbene)-bridged ditungsten complexes $(CO)_5W{=}C(NMe_2)CH{=}CH{-}Ar{-}CH{=}CH(OMe)C{=}W(CO)_5$ (**3a**–**b**). Similarly, the symmetrical bis(methoxycarbene)ditungsten derivative $[(CO)_5W{=}C(OMe)CH{=}CH-]_2(1,4\text{-}C_6H_4-)$ (**4a**) is obtained in a low yield from the precursor $(CO)_5W{=}C(OMe)CH{=}CH{-}C_6H_4{-}(OH)(H)C{\equiv}CH$ (**2a**). Complexes **3a** and **3b** undergo aminolysis reactions with diamines such as piperazine and ethylenediamine to produce the corresponding bis[alkenyl(amino)carbene]ditungsten complexes **5a**–**b** and **6a**–**b**. The reaction of **1a** with $Cr(CO)_5(THF)$ affords the heterobimetallic (W–Cr) bis(carbene) complex $(CO)_5W{=}C(NMe_2)CH{=}CH{-}Ar{-}CH{=}CH(OMe)C{=}Cr(CO)_5$ (**3′a**). This complex, as well as the bis(methoxycarbene) derivative **4′a**, can also be obtained by treatment of $(CO)_5W{=}C(XR)CH{=}CH{-}C_6H_4{-}CHO$ [**1c**: XR = NMe_2; **2c**: XR = OMe] with $(CO)_5Cr{=}C(OMe)CH_2^{-}Li^{+}$. All the new compounds have been characterized by analytical and spectroscopic methods, and the single-crystal structures of **3a**, **4a**–**b**, and **4′a** have been established.

Introduction

During the last decade, binuclear transition-metal complexes with unsaturated organic spacers such as polyynes have been the subject of considerable investigations due to their potential applications in molecular electronics or nonlinear optics.[1,2] A wide range of bis(carbene) complexes have also been reported. Thus, symmetrical bis(carbene) complexes of Groups 6 and 7 metals containing aryl[3,4] and thienyl[5,6] bridges are accessible from dilithiated aromatic precursors by the classic Fischer method. A series of alkenyl- or polyenyl-bridged bis(carbene) complexes have been prepared either by condensation reactions of dialdehydes with the methyl group of (alkoxy)methylcarbene complexes,[7,8,9] or by oxidative coupling of $[M]{=}C(OR)CH_2Li$.[10,11] The synthesis of a symmetrical bis(carbene) complex with an ammonium pentadienide bridge has also been described.[12] The formation of bis(aminocarbene)dichromium complexes[13] has been achieved by reaction of arylbis(amides) with $Cr(CO)_5^{2-}$. Recently, H. Fischer et al. reported an efficient synthesis of symmetrically substituted alkynediyl-bridged aminocarbene complexes by Pd coupling of two $(CO)_5M{=}C(NR_2)(C{\equiv}C)_n$ units (n = 1,2,3).[14] The same precursors were also used to prepare polynuclear complexes of the type $[(CO)_5M{=}C(NR_2)(C{\equiv}C)]_xM'L_n$.[15] By contrast, nonsymmetrical bis(carbene) complexes are scarce. A bis(aminocarbene)chromium−iron complex has been prepared in two steps by the reaction of a diamide with $Cr(CO)_5^{2-}$ and $Fe(CO)_4^{2-}$.[13] An ethyne-bridged (alkoxycarbene)(aminocarbene)ditungsten complex was also recently obtained by the Fischer route starting from an ethynylcarbene complex.[14] We have previously described a convenient route to alkenyl(alkoxy)- and -(amino)carbene complexes of Groups 6 and 8 metals, by activation of propargyl alcohol derivatives.[16,17] With the use of dialkynols, this procedure was recently applied to the synthesis of alkenylcarbene complexes **I** containing a free propargyl alcohol substituent (Scheme 1).[18] In this paper we report a new synthetic route to a series of dinuclear π-conjugated bridged carbenechromium(0) and -tungsten(0) complexes. We show that this methodology, which is based on the sequential activation of dialkynols, opens the route to nonsymmetrical bis(carbene) complexes **II**. Preliminary results of this work have already been reported.[19]



Scheme 1

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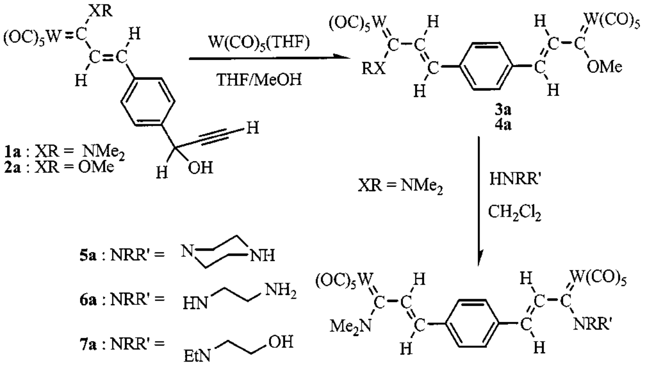
Results and Discussion

Synthesis of Bis(carbene)-Bridged Ditungsten Complexes

When solutions of the [alkenyl(dimethylamino)carbene]-tungsten complex **1a** and of the photogenerated W(CO)$_5$(THF) adduct in methanol/tetrahydrofuran were combined at room temperature, the color gradually changed from red to dark red. The reaction proceeded rather slowly and required 3 d for completion. The bimetallic complex **3a** was obtained in a 60% yield after chromatographic workup (Scheme 2). Under similar conditions, the symmetrical binuclear bis(methoxycarbene) derivative **4a** was isolated from **2a** in a lower yield (30%) as violet microcrystals. This latter complex was already obtained as a by-product (9%) during the synthesis of **2a** from the dialkynol 1,4-[H−C≡CH(OH)]C$_6$H$_4$.[18]



Scheme 2

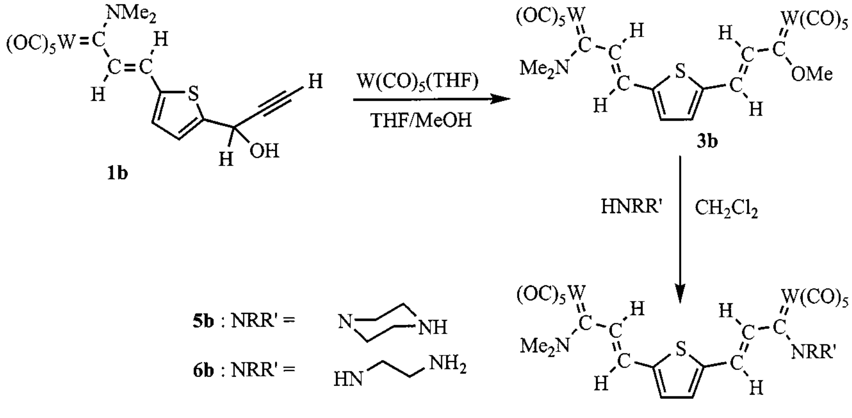
The same protocol was applied to **1b** to prepare the thienyl-bridged bimetallic complex **3b** in a 61% yield (Scheme 3). The new complexes **3a** and **3b** were unequivocally characterized by means of standard spectroscopic techniques (IR, ^{1}H and ^{13}C{^{1}H} NMR). The structures of **3a**, the symmetrical bis(methoxycarbene) derivative **4a** and its thienyl analog **4b**[18] were also confirmed by X-ray diffraction studies (vide supra). The stereoselective formation of the new CH=CH bond was easily deduced by the coupling constants, $^3J_{\text{H-H}} \approx 16-17$ Hz, which is indicative of an (*E*) configuration. For each alkenyl fragment, the ^{1}H and ^{13}C shifts of the β-proton and β-carbon atom appear upfield from the shift of the α-proton and α-carbon atom, respectively (Table 1). This trend was previously observed for monometallic alkenyl(alkoxy)- and -(amino)carbene complexes.[16,20] The ^{1}H and ^{13}C NMR spectra show two N*Me* signals as expected by the restricted rotation around the C(carbene)−NMe$_2$ bond. The ^{13}C NMR spectra also display two carbene resonances at δ ≈ 300 and 250, in the range characteristic for (alkoxycarbene)- and (aminocarbene)tungsten complexes, respectively. Thus, these data suggest that there is apparently no π delocalization occurring along the alkenyl bridges, in contrast to the recently described π-conjugated ethyne-bridged bis(carbene) complex (CO)$_5$W=C(NMe$_2$)−C≡C−(OMe)C=W(CO)$_5$ where the carbene resonances were found shifted upfield by more than 60 ppm [δ = 235.9 and 181.7].[14]

Complexes **3a** and **3b** could be easily transformed into bis(aminocarbene) complexes by the classical aminolysis route. For example, addition of excess of piperazine, ethylenediamine or 2-(ethylamino)ethanol (3−5 equiv.) in dichloromethane at room temperature led to the isolation of the bis(aminocarbene) complexes **5a−b**, **6a−b** [(*E*)/(*Z*) ≈ 9:1], or **7a** in good yields (Scheme 2 and Scheme 3).

Spectroscopic data clearly reveal the presence of two alkenyl(amino)carbene fragments (see Table 1 and Exp. Sect.). We note in particular the presence of two characteristic low-field singlet resonances for the carbene carbon atoms (δ ≈ 250). As these complexes contain a free amine site, a second aminolysis reaction was attempted in order to prepare tetrametallic tetrakis(aminocarbene) complexes. However, after stirring a 1:1 mixture of **6b** and **3a** in dichloromethane at room temperature, no reaction occurred, even after 1 d. The starting complexes were recovered.

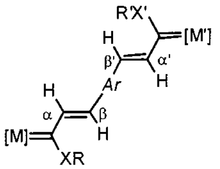
Synthesis of Bis(carbene)-Bridged Tungsten−Chromium Complexes

Treatment of **1a** with Cr(CO)$_5$(THF) at room temperature, and after 18 h of stirring, afforded the new heterobimetallic (W−Cr) bis(carbene) complex **3′a** in a modest yield, up to 30% (Scheme 4). Prolonged reaction times were found to decrease the yield. This observation reflects the reduced thermal stability of both Cr(CO)$_5$(THF) and **3′a**, which slowly decompose in solution. Efforts to prepare the analogous bis(methoxycarbene) complex **4′a** starting from the less reactive compound **2a** failed.



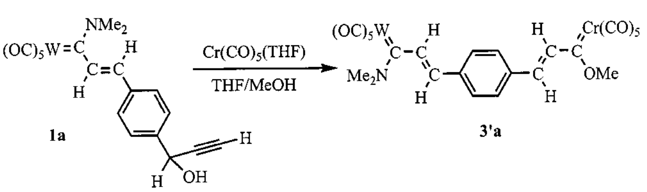
Scheme 3

Table 1. Selected ^1H and ^{13}C NMR spectroscopic data for the bimetallic complexes in $CDCl_3$



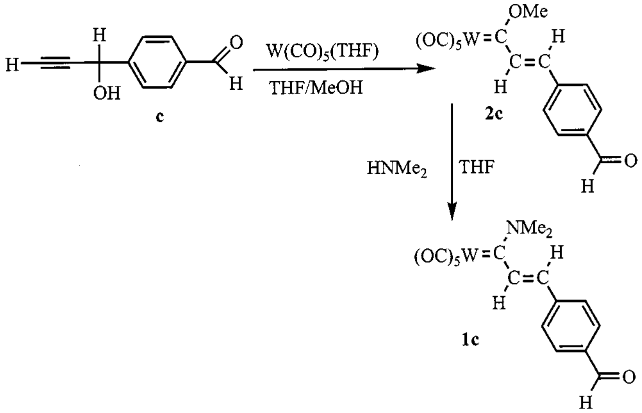
Complex	M	XR	M′	X′R′	−*Ar*−	M=C	M′=C	$C_{\alpha,\alpha'}$ ($H_{\alpha,\alpha'}$)	$C_{\beta,\beta'}$ ($H_{\beta,\beta'}$)
4a	$W(CO)_5$	OMe	$W(CO)_5$	OMe	$-C_6H_4-$	307.0	–	144.2 (7.85)	131.8 (7.10)
4b	$W(CO)_5$	OMe	$W(CO)_5$	OMe	$-C_4H_2S-$	304.2	–	143.6 (7.68)	134.7 (7.22)
–[a]	$Cr(CO)_5$	OMe	$Cr(CO)_5$	OMe	$-C_6H_4-$	333.4	–	140.0 (7.95)	127.4 (6.90)
3a	$W(CO)_5$	OMe	$W(CO)_5$	NMe_2	$-C_6H_4-$	306.5	252.1	143.3 (7.81), 139.6 (7.05)	133.3 (7.12), 122.0 (5.86)
3b	$W(CO)_5$	OMe	$W(CO)_5$	NMe_2	$-C_4H_2S-$	303.1	250.9	139.8 (7.56), 135.4 (6.90)	135.2 (7.28), 117.3 (6.11)
4′a	$W(CO)_5$	OMe	$Cr(CO)_5$	OMe	$-C_6H_4-$	306.9	333.4	144.2 (7.89), 140.0 (7.97)	131.9 (7.12), 127.4 (6.85)
3′a	$Cr(CO)_5$	OMe	$W(CO)_5$	NMe_2	$-C_6H_4-$	332.7	252.3	139.5 (7.93), 139.3 (7.09)	128.6 (6.92), 121.9 (5.93)

[a] Ref.[18]



Scheme 4

An alternative synthetic approach to **3′a** and **4′a** is the use of the Aumann's procedure which allows the condensation of aldehydes with the Fischer-type (methoxy)methylcarbene derivative $(CO)_5Cr=C(OMe)Me$.[7] The [alkenyl(methoxy)carbene]tungsten complex **2c**, containing a *p*-phenylaldehyde group, was generated in a 40% yield on activation of the propargyl alcohol derivative **c** with $W(CO)_5(THF)$. Subsequent addition of dimethylamine afforded, almost quantitatively, the corresponding (dimethylamino)carbene complex **1c** (Scheme 5).



Scheme 5

When complex **2c** was combined with $(CO)_5Cr=C(OMe)-Me$ and treated with Et_3N/Me_3SiCl the heterobimetallic complex **4′a** was obtained in a 33% yield after chromatographic workup (Scheme 6). The same route was also employed for the synthesis of **3′a**, but the isolated yield was lower (20%).

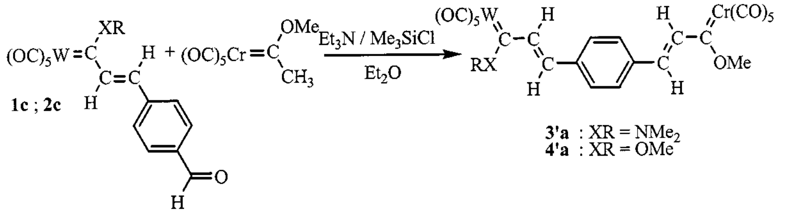
Spectroscopic data are in agreement with the proposed nonsymmetric structures. The ^1H NMR spectrum of **4′a** exhibits two singlets for the two nonequivalent O*Me* groups, and two AB systems for the α,β- and α′,β′-alkenyl protons, respectively. The ^{13}C NMR spectrum consists of distinct signals for the two alkenyl and methoxy carbon atoms, and the carbene resonances are found in the range typical for [(methoxy)carbene]chromium and -tungsten. The unsymmetrical alkenyl-bridged [(dimethylamino)carbene](methoxycarbene) complex **3′a** also exhibits two distinct sets of proton and carbon atom resonances (Table 1 and Exp. Sect.).

Molecular Structures of 3a, 4a, 4b, and 4′a

The structures of the carbene complexes **3a**, **4a**, **4b**, and **4′a** were determined by single-crystal X-ray diffraction. The molecular structures are displayed in Figures 1−4. Selected bond lengths and angles are listed in Table 2. In all cases, the environment about the metal atoms is octahedral. The (*E*) configuration of the alkenyl double bond in these molecules was confirmed. Moreover, in all cases the carbon chain adopts a *s-trans* stereochemistry with respect to the $C_{carb}-C_\alpha$ bond.

Structure of 4b

The two "$W(CO)_5$" fragments are on the same side of the thiophene bridge, a feature already observed for the dinuclear chromium complex $[Cr(CO)_5(=C(OEt)-]_2(C_4H_2S)$ (Figure 1).[5] However, by contrast to the latter species, the sulfur atom of the ring in **4b** is directed towards the metal units. The W=C bond length [2.166(9) Å] is similar to that found in other W−(alkoxycarbene) complexes.[21] The C−C and S−C bond lengths of the thiophene ring [1.360(12), 1.365(12), 1.368(12); 1.713(9), and 1.719(9) Å] compare well with those of thiophene-containing complexes.[5,22,23] The



Scheme 6

Table 2. Selected bond lengths [Å] and angles [°] for **4b**,**4a**, **3a**, and **4′a**

4b		**4a**		**3a**		**4′a**	
W1−C7	2.166(9)	W1−C7	2.165(6)	W1−C6	2.256(7)	W(Cr)−C7	2.111(6)
W2−C16	2.190(8)	C7−C8	1.464(7)	W2−C19	2.181(7)	C7−C8	1.438(8)
C7−C8	1.435(11)	C8−C9	1.320(7)	C6−C9	1.489(10)	C8−C9	1.333(8)
C8−C9	1.336(13)	C9−C10	1.433(7)	C9−C10	1.315(10)	C9−C10	1.452(8)
C9−C10	1.453(11)	C7−O6	1.329(7)	C10−C11	1.463(10)		
C13−C14	1.440(12)			C19−C18	1.472(10)		
C14−C15	1.349(12)			C18−C17	1.315(10)		
C15−C16	1.455(11)			C17−C14	1.444(10)		
S1−C10	1.713(9)			C6−N	1.315(9)		
S1−C13	1.719(9)			C19−O6	1.309(9)		
W1−C7−O6	130.6(6)	W1−C7−O6	131.0(4)	W1−C6−N1	130.7(5)	W(Cr)−C7−O6	130.7(4)
W1−C7−C8	121.0(6)	W1−C7−C8	121.2(4)	W1−C6−C9	113.6(5)	W(Cr)−C7−C8	121.3(5)
C7−C8−C9	125.2(8)	C7−C8−C9	124.2(5)	N1−C6−C9	115.7(7)	C7−C8−C9	124.5(6)
O6−C7−C8	108.4(7)	O6−C7−C8	107.8(5)	W2−C19−O6	131.8(5)	O6−C7−C8	107.9(5)
W2−C16−O7	130.6(6)			W2−C19−C18	120.0(5)		
W2−C16−C15	119.6(6)			O6−C19−C18	108.2(6)		
C16−C15−C14	122.6(8)						
O7−C16−C15	109.8(7)						

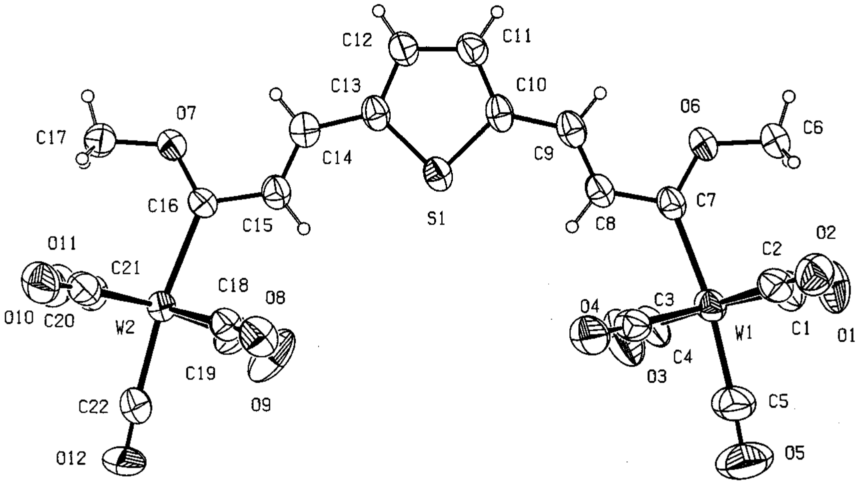


Figure 1. Molecular structure of (CO)$_5$W=C(OMe)CH=CH−C$_4$H$_2$S−CH=CH(OMe)C=W(CO)$_5$ (**4b**)

pattern of bond lengths in **4b** [W−C7 2.166(9), C7−C8 1.435(11), C8−C9 1.336(13), C9−C10 1.453(11) Å], indicates a limited π delocalization in the ground state.[24] Remarkably, the thiophene ring, the alkenyl, the carbene carbon and the tungsten atoms are in a plane (mean deviation from the plane 0.06 Å).

Structure of Complexes 4a, 3a, and 4′a

As observed in **4b**, in all cases the two metal units are in a *cis* configuration with respect to the benzene ring. The W=C(O) bond length [2.165(6) Å] in **4a** (Figure 2) is normal. The alkenyl portion in **4a** exhibits an alternating C−C single-bond, double-bond, and single-bond sequence [1.464(7), 1.320(7), 1.433(7) Å].

Complex **3a** (Figure 3) exhibits a W=C(N) distance of 2.256(7) Å, which is rather long relative to that of typical aminocarbene complexes [W−C 2.186(22) Å in (CO)$_5$W=C(NHMe)Ph)].[25,26] The C(carbene)−N bond [1.315(9) Å] is somewhat short indicating a double-bond character.[14] These values compare well with those reported for

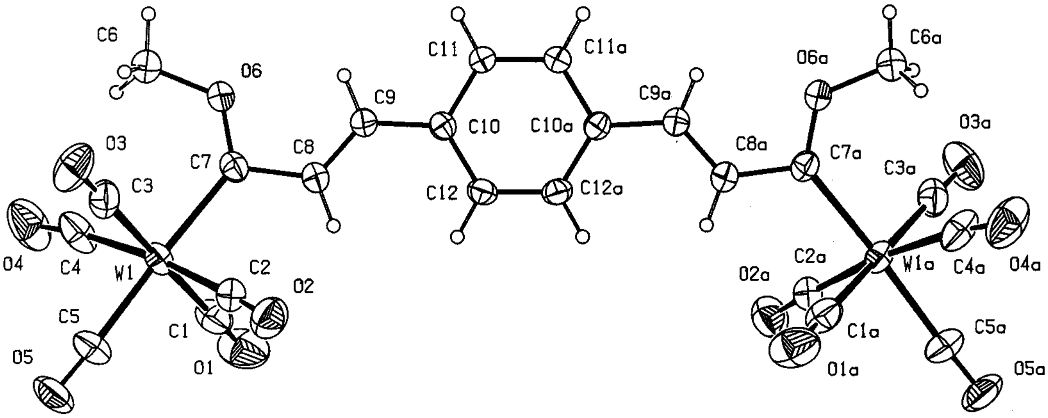


Figure 2. Molecular structure of $(CO)_5W=C(OMe)CH=CH-C_6H_4-CH=CH(OMe)C=W(CO)_5$ (**4a**)

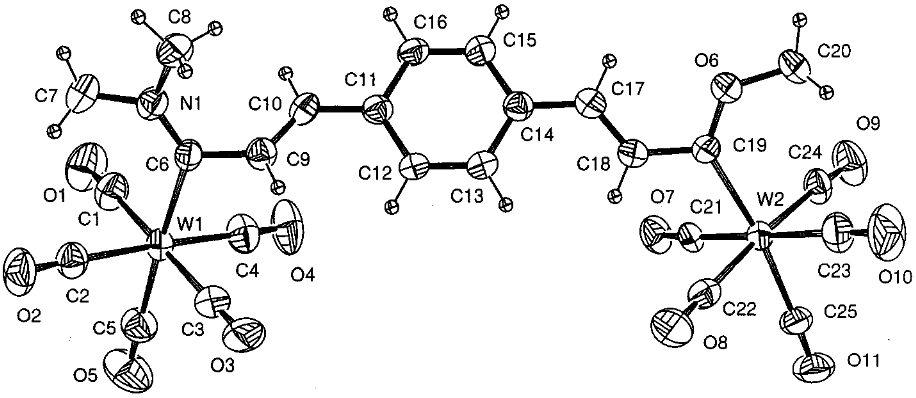


Figure 3. Molecular structure of $(CO)_5W=C(NMe_2)CH=CH-C_6H_4-CH=CH(OMe)C=W(CO)_5$ (**3a**)

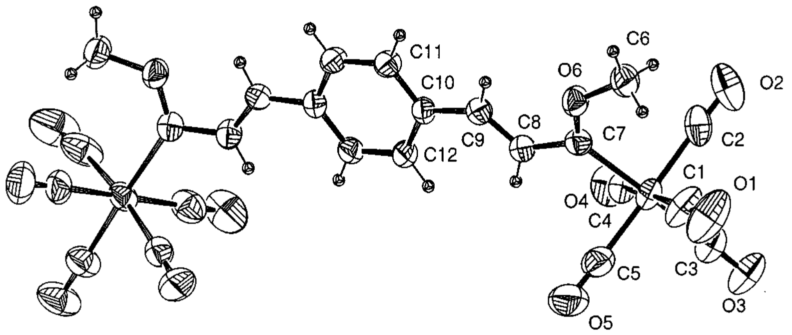


Figure 4. Molecular structure of $(CO)_5W=C(OMe)CH=CH-C_6H_4-CH=CH(OMe)C=Cr(CO)_5$ (**4′a**)

$(CO)_5W=C(NMe_2)-(NMe_2)C=W(CO)_5$ [W=C 2.295(7), 2.281(7); $C_{carb}-N$ 1.310(8), 1.314(9) Å],[14] $[(CO)_5W=C(NMe_2)C{\equiv}C-Hg-C{\equiv}CC(NMe_2)=W(CO)_5]$, and $[(CO)_5W=C(NMe_2)C{\equiv}C-TiCp_2-C{\equiv}CC(NMe_2)=W(CO)_5]$.[15] This is consistent with the magnetically nonequivalent methyl substituents in the NMR spectra. The W−C(O) distance [2.181(7) Å] is in the range of that of the above structures. As for **4a**, the C−C bond chain is alternated [1.489(10), 1.315(10), 1.463(10); 1.472(10), 1.315(10), 1.444(10) Å]. The bridging carbon chain is planar (mean deviation from the plane 0.087 Å); however, the two metal units deviate from this plane by 23° and 65° for the C(alkoxy)- and C(amino)carbene parts, respectively.

The molecular structure of the heterodimetal (Cr−W) complex **4′a** (Figure 4) is disordered for the metal positions (W,Cr), a feature which is also observed for $(CO)_5Cr\{=C(COMe)CH_2CH_2C(OMe)C=\}W(CO)_5$.[27] It is worth noting that the orientation of the aromatic ring contrasts with that in the (Cr−Fe) complex $[(CO)_5Cr\{=C(NMe_2)(m\text{-}C_6H_4)C(NMe_2)=\}Fe(CO)_4]$ in which the phenyl bridge is perpendicular to the plane of the metal−carbene bond.[13]

Conclusion

This study shows that binuclear alkenylcarbene-bridged complexes can be conveniently prepared by sequential activation of bis(propargyl alcohol) derivatives. This route allows the synthesis of nonsymmetrical bis(carbene) complexes containing either two different tungsten−carbene fragments (amino- and alkoxycarbene) or two different metallic centers (Cr and W). This opens up an entry to novel "push-pull" heterobimetallic bis(carbene) compounds, for instance with Groups 6 and 8 metals since they are both known to activate propargyl alcohols. Moreover, the reactivity of alkenylcarbene complexes is known to depend on the nature of the metal (Cr vs. W) and the substituent (alkoxy vs. amino) in typical reactions such as annulations and Diels−Alder cycloadditions. Studies on the reactivity of our nonsymmetric complexes, particularly with regard to the ability to discriminate the two metal−carbene fragments, are in progress.

Experimental Section

General: All manipulations were carried out under argon with Schlenk techniques. Solvents were dried and distilled before use by standard techniques. − NMR spectra were recorded with Bruker DPX-200 and Bruker AM-300 spectrometers. − Infrared spectra were obtained with a Nicolet FT-IR spectrometer. − High resolution mass spectra were obtained with Varian MAT 311 and Micromass ZABSpec TOF spectrometers at the C.R.M.P.O., University of Rennes 1. − Microanalyses were performed by the "Centre de Microanalyse du CNRS" at Vernaison, France.

Procedures for the Preparation of Bis(carbene)-Bridged Ditungsten Complexes

$(CO)_5W{=}C(NMe_2)CH{=}CH{-}C_6H_4{-}CH{=}CH(MeO)C{=}W(CO)_5$ (3a): A solution of $W(CO)_6$ (0.421 g, 1.2 mmol) in 60 mL of THF was irradiated for 6 h at room temperature by using a Rayonet and a Pyrex photochemical reactor. The yellow solution of $W(CO)_5(THF)$ was then transferred into a Schlenk flask containing a solution of **1a** (0.537 g, 1 mmol) in 30 mL of methanol. The reaction mixture was stirred for 3 d at room temperature. After evaporation of the solvent under vacuum, the red residue was chromatographed on silica gel. Elution with dichloromethane/pentane (1:3) gave the bimetallic complex **3a** as a red solid in a 60% yield (0.525 g). − IR (CH_2Cl_2): ν_{CO} = 2059 (m), 1905 (s); $\nu_{C=C}$ = 1581 (w), 1546 (w) cm^{-1}. − ^1H NMR (300.133 MHz, $CDCl_3$): δ = 7.81 (d, 1 H, $^3J_{HH}$ = 15.4 Hz, C*H*=), 7.54 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, C_6H_4-), 7.36 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, C_6H_4-), 7.12 (d, 1 H, $^3J_{HH}$ = 15.4 Hz, C*H*=), 7.05 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 5.86 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 4.57 (s, 3 H, O*Me*), 3.77 [s, 3 H, N*Me* (*Z*)], 3.36 [s, 3 H, N*Me* (*E*)]. − ^{13}C {^1H} NMR (75.469 MHz, $CDCl_3$): δ = 306.5 (W=*C*), 252.1 (W=*C*), 203.9, 203.4 (*C*O), 198.3, 197.6 (*C*O), 143.3 (*C*H=), 139.6 (*C*H=), 138.6, 134.3 (C_6H_4−), 133.3 (*C*H=), 129.9, 127.3 (C_6H_4−), 122.0 (*C*H=), 69.05 (O*Me*), 53.5 [N*Me* (*Z*)], 44.5 [N*Me* (*E*)]. − $C_{27}H_{17}NO_{11}W_2$ (874.98): C 34.31, H 1.96, N 1.60; found C 34.97, H 2.19, N 1.61. − HRMS (FAB^+): calcd. for $C_{27}H_{17}NO_{11}{}^{184}W_2$ 874.9821; found 874.9834.

$(CO)_5W{=}C(OMe)CH{=}CH{-}C_6H_4{-}CH{=}CH(MeO)C{=}W(CO)_5$ (4a): The synthesis followed the method outlined for the synthesis of **3a**. Compound **4a** was obtained from $W(CO)_6$ (0.417 g, 1.1 mmol) and **2a** (0.520 g, 0.99 mmol) as a red dark powder in a 30% yield (0.250 g). − IR (CH_2Cl_2): ν_{CO} = 2065 (m), 1941 (s) cm^{-1}. − ^1H NMR (300.133 MHz, $CDCl_3$): δ = 7.85 (d, 2 H, $^3J_{HH}$ = 15.5 Hz, C*H*=), 7.50 (s, 4 H, C_6H_4−), 7.10 (d, 1 H, $^3J_{HH}$ = 15.5 Hz, C*H*=), 4.55 (s, 6 H, OCH_3). − ^{13}C\{^1H\} NMR (200.131, $CDCl_3$): δ = 307.0 (W=*C*), 203.8, 197.4 (*C*O), 144.2 (*C*H=), 137.1 (C_6H_4-), 131.8 (*C*H=), 129.0 (C_6H_4−), 69.1 (OCH_3).

$(CO)_5W{=}C(NMe_2)CH{=}CH{-}C_4H_2S{-}CH{=}CH(OMe)C{=}W(CO)_5$ (3b): The synthesis followed the method outlined for the synthesis of **3a**. Compound **3b** was obtained from $W(CO)_6$ (0.320 g, 0.91 mmol) and **1b** (0.370 g, 0.68 mmol)as a red dark oil in a 61% yield (0.370 g). − IR (CH_2Cl_2): ν_{CO} = 2064 (m), 1931 (s) cm^{-1}. − ^1H NMR (200.131 MHz, $CDCl_3$): δ = 7.56 (d, 1 H, $^3J_{HH}$ = 15.0 Hz, C*H*=), 7.28 (d, 1 H, $^3J_{HH}$ = 15.0 Hz, C*H*=), 6.90 (d, 1 H, $^3J_{HH}$ = 16.3 Hz, C*H*=), 7.28 (d, 1 H, $^3J_{HH}$ = 3.7 Hz, C_4H_2S), 6.95 (d, 1 H, $^3J_{HH}$ = 3.7 Hz, C_4H_2S), 6.11 (d, 1 H, $^3J_{HH}$ = 16.3 Hz, C*H*=), 4.57 (s, 3 H, O*Me*), 3.81 [s, 3 H, N*Me* (*Z*)], 3.40 [s, 3 H, N*Me* (*E*)]. − ^{13}C\{^1H\} NMR (50.322 MHz, $CDCl_3$): δ = 303.1 (W=*C*), 250.9 (W=*C*), 203.8, 203.1 (*C*O), 198.1, 197.5 (*C*O), 146.2, 142.3 (C_4H_2S), 139.8 (*C*H=), 139.4 (*C*H=), 135.4 (*C*H=), 129.0, 126.8 (C_4H_2S), 117.3 (*C*H=), 68.7 (O*Me*), 53.4 [N*Me* (*Z*)], 44.7 [N*Me* (*E*)]. − HRMS (FAB^+): calcd. for $C_{23}H_{15}NO_{11}S^{184}W_2$ 880.9385; found 880.9411.

$(CO)_5W{=}C(NMe_2)CH{=}CH{-}C_6H_4{-}CH{=}CH(MeO)C{=}Cr(CO)_5$ (3′a): In a procedure analogous to the synthesis of **3a**, $Cr(CO)_6$ (0.2 g, 0.9 mmol) was irradiated in THF at −10 °C for 6 h. The yellow solution of $Cr(CO)_5(THF)$ was then transferred into a Schlenk flask containing a solution of **1a** (0.3 g, 0.6 mmol) in 30 mL of methanol. The reaction mixture was stirred for 18 h at room temperature. After evaporation of the solvent under vacuum, the red residue was chromatographed on a silica gel column. Elution with dichloromethane/pentane (1:3) gave the bimetallic complex **3′a** as a red oil in a 30% yield (0.132 g). − IR (CH_2Cl_2): ν_{CO} = 2056 (m), 1944 (s), 1928 (s) cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.93 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 7.57 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, C_6H_4−), 7.42 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, C_6H_4−), 7.09 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 6.92 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 5.93 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 4.80 (s, 3 H, O*Me*), 3.83 [s, 3 H, N*Me* (*Z*)], 3.42 [s, 3 H, N*Me* (*E*)]. − ^{13}C\{^1H\} NMR (75.469 MHz, $CDCl_3$): δ = 332.7 (Cr=*C*′), 252.3 (W=*C*), 216.9, 203.4 (*C*O), 216.6, 197.6 (*C*O), 139.5 (*C*H=), 139.3 (*C*H=), 138.6, 134.1 (C_6H_4-), 129.9 (*C*H=), 128.6, 127.1 (C_6H_4-), 121.9 (*C*H=′), 53.4 (O*Me*), 49.5 [N*Me* (*Z*)], 44.4 [N*Me* (*E*)]. − HRMS (FAB^+): calcd. for $C_{25}H_{17}NO_{11}CrW$ 743; found 742.97.

$(CO)_5W{=}C(OMe)CH{=}CH{-}C_6H_4{-}CHO$ (2c): A solution of $W(CO)_6$ (2.6 g, 7.4 mmol) in 60 mL of THF was irradiated for 6 h at room temperature by using a Rayonet and a Pyrex photochemical reactor. The yellow solution of $W(CO)_5(THF)$ was then transferred into a Schlenk flask containing a solution of the dialkynol derivative **c** (1 g, 6.2 mmol) in 30 mL of methanol. The reaction mixture was then stirred for 18 h at room temperature. After evaporation of the solvent under vacuum, the red residue was chromatographed on a silica gel column. Elution with dichloromethane/pentane (1:3) gave the red monometallic complex **2c** as a red oil in a 38% yield (1.19 g). − IR (CH_2Cl_2): ν_{CO} = 2066 (m), 1939 (s) cm^{-1}. − ^1H NMR (200.131 MHz, $CDCl_3$): δ = 10.0 (s, 1 H, C*HO*), 7.91 (d, 1 H, $^3J_{HH}$ = 15.5 Hz, C*H*=), 7.65 (m, 4 H, C_6H_4−),7.11 (d, 1 H, $^3J_{HH}$ = 15.5 Hz, C*H*=), 4.65 (s, 3 H, O*Me*). − ^{13}C\{^1H\} NMR (75.46 MHz, $CDCl_3$): δ = 307.8 (W=*C*), 203.7, 197.2 (*C*O), 145.4 (*C*H=), 140.6 (*C*H=), 137.2, 130.5 (C_6H_4−), 129.4 (C_6H_4−), 69.3 (O*Me*). − HRMS (FAB^+): calcd. for $C_{16}H_{10}O_7{}^{182}W$ 497.9939; found 497.9937.

$(CO)_5W{=}C(OMe)CH{=}CH{-}C_6H_4{-}CH{=}CH(MeO)C{=}Cr(CO)_5$ (4′a): Equimolar quantities of **2c** (0.252 g, 0.5 mmol) and the complex $(CO)_5Cr(OCH_3)(CH_3)$ (0.126 g, 0.5 mmol) were dissolved in ether (30 mL) with triethylamine (0.280 mL, 2 mmol) and trimethylsilyl chloride (0.250 mL, 1.5 mmol), and the resulting mixture was stirred for 6 h at room temperature. The solvent was removed under vacuum, and the red-brown residue was chromatographed on a silica gel column. Elution with dichloromethane/pentane (1:3) gave the bimetallic complex **4′a** in a 33% yield (0.012 g). − IR

(CH_2Cl_2): ν_{CO} = 2067, 2057 (m), 1943 (s) cm^{-1}. − ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 7.97 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 7.89 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 7.59 (m, 4 H, C_6H_4−), 7.12 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 6.85 (d, 1 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 4.81 (s, 3 H, O*Me*), 4.63 (s, 3 H, O*Me*). − ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 333.4 (Cr=*C*), 306.9 (W=*C*), 224.3, 216.5 (*C*O), 203.4, 197.3 (*C*O), 144.2 (*C*H=), 140.0 (*C*H=), 138.6, 134.1 (C_6H_4−), 129.9 (*C*H=), 128.6, 127.1 (C_6H_4−), 121.9 (*C*H=), 69.1 (O*Me*), 66.6 (O*Me*). − HRMS (FAB$^+$): calcd. for $C_{24}H_{14}O_{12}Cr^{182}W$ 730.21; found 729.8.

General Procedure for the Preparation of Bis[alkenyl(amino)carbene]ditungsten Complexes: To a solution of **3a** (0.874 g, 1 mmol) in 20 mL of dichloromethane at room temperature was added 3−5 equiv. of amine. The color rapidly changed from red to orange. After stirring for 20 min, the solvent was removed in vacuo and the crude product was chromatographed on a silica gel column using pentane/dichloromethane (1:2) as the eluent. Evaporation of the solvent gave the bis(aminocarbene) complexes as orange solids in good yields.

$(CO)_5W=C[N(-CH_2CH_2-)_2NH]CH=CH-C_6H_4-CH=CH-(Me_2N)C=W(CO)_5$ (5a): Yield 54% (0.501 g). − IR (paraffin): ν_{CO} = 2061 (m), 1894 (s); $\nu_{C=C}$ = 1530 (f) cm^{-1}. − ^{1}H NMR (300.135 MHz, [D$_6$]acetone): δ = 7.54 (s, 4 H, C_6H_4−), 7.32 (d, 2 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 6.15 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 6.10 (d, 1 H, $^3J_{HH}$ = 16.8 Hz, C*H*=), 4.36 and 4.10 (m, 4 H, C*H*$_2$), 3.94 [s, 3 H, N*Me* (*Z*)], 3.59 [s, 3 H, N*Me* (*E*)], 3.20 and 3.01 (m, 4 H, C*H*$_2$). − ^{13}C{^{1}H} NMR (75.469 MHz, [D$_6$]acetone): δ = 248.3, 245.0 (W=*C*), 204.7, 204.5 (*C*O), 199.5, 199.3 (*C*O), 140.3, 139.4 (*C*H=), 136.9, 136.8, 127.9 (C_6H_4−), 124.3, 122.9 (*C*H=), 65.2 and 56.7 (*C*H$_2$), 54.3 [N*Me* (*Z*)], 48.5 and 48.2 (*C*H$_2$), 44.92 [N*Me* (*E*)]. − $C_{28}H_{23}N_3O_{10}W_2$ (929): C 36.17, H 2.50, N 4.52; found C 36.41, H 2.62, N 4.48. − HRMS (FAB$^+$): calcd. for $C_{28}H_{23}N_3O_{10}{}^{184}W_2$ 929.0399; found 929.0400.

$(CO)_5W=C[N(-CH_2CH_2-)_2NH]CH=CH-C_4H_2S-CH=CH-(Me_2N)C=W(CO)_5$ (5b): Yield 50% (0.440 g). − IR (CH_2Cl_2): ν_{CO} = 2061 (m), 1925 (s) cm^{-1}. − ^{1}H NMR (200.135 MHz, [D$_6$]-acetone): δ = 7.02 (d, 2 H, $^3J_{HH}$ = 16.4 Hz, C*H*=), 7.0 (m, 2 H, C_4H_2S), 6.20 (d, 2 H, $^3J_{HH}$ = 16.4 Hz, C*H*=), 4.39 and 4.14 (m, 4 H, C*H*$_2$), 3.86 [s, 3 H, N*Me* (*Z*)], 3.52 [s, 3 H, N*Me* (*E*)], 2.94 and 2.88 (m, 4 H, C*H*$_2$).

$(CO)_5W=C[N(H)(CH_2-CH_2NH_2)]CH=CHC_6H_4CH=CH-(Me_2N)C=W(CO)_5$ (6a): Yield 75% (0.677 g). − IR (KBr): ν_{CO} = 2062 (m), 1895 (s) cm^{-1}. − ^{1}H NMR (300.134 MHz, CD_2Cl_2): δ = 7.38 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, C_6H_4−), 7.21 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, C_6H_4−), 7.03 (d, 2 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 5.95 (d, 2 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 3.80 [s, 3 H, N*Me* (*Z*)], 3.36 [s, 3 H, N*Me* (*E*)], 2.88 (m, 2 H, C*H*$_2$), 2.73 (t, 2 H, C*H*$_2$). − ^{13}C{^{1}H} NMR (75.469 MHz, [D$_6$]acetone): δ = 248.4 (W=*C*), 204.4, 202.5 (*C*O), 199.3, 199.1 (*C*O), 140.8 (C_6H_4−), 139.8 (*C*H=), 135.4, 129.4, 127.7 (C_6H_4−), 124.7 (*C*H=), 65.2 (NH*C*H$_2$), 54.3 [N*Me* (*Z*)], 44.9 [N*Me* (*E*)], 33.1 (*C*H$_2$NH$_2$). − $C_{26}H_{21}N_3O_{10}W_2$ (903): C 34.55, H 2.34, N 4.65; found C 30.09, H 1.96, N 3.83. − HRMS (FAB$^+$): calcd. for $C_{26}H_{21}N_3O_{10}{}^{184}W_2$ 903.0246; found 903.0240.

$(CO)_5W=C[N(H)(CH_2-CH_2-NH_2]CH=CH-C_4H_2S-CH=CH(Me_2N)C=W(CO)_5$ (6b): Yield 70% (0.636 g). − IR (CH_2Cl_2): ν_{CO} = 2061 (m), 1924 (s) cm^{-1}. − ^{1}H NMR (200.131 MHz, $CDCl_3$): δ = 6.84 (d, 1 H, $^3J_{HH}$ = 3.5 Hz, C_4H_2S), 6.74 (d, 1 H, $^3J_{HH}$ = 3.5 Hz, C_4H_2S), 6.67 (d, 2 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 6.14 (d, 2 H, $^3J_{HH}$ = 15.3 Hz, C*H*=), 3.80 [s, 3 H, N*Me* (*Z*)], 3.40 [s, 3 H, N*Me* (*E*)], 3.09 (m, 2 H, C*H*$_2$), 2.82 (m, 2 H, C*H*$_2$). − ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2): δ = 204.19, 202.07 (*C*O), 198.8, 198.2 (*C*O), 54.5 [N*Me* (*Z*)], 49.1 [N*Me* (*E*)]. − HRMS (FAB$^+$): calcd. for $C_{24}H_{19}N_3O_{10}S^{184}W_2$ 908.9810; found 908.9815.

$(CO)_5W=C[N(CH_2CH_2OH)CH_2CH_3]CH=CH-C_6H_4-CH=CH(Me_2N)C=W(CO)_5$ (7a): Yield 81% (0.755 g). − IR (CH_2Cl_2):

Table 3. Crystallographic data for **4b**,**4a**, **3a**, and **4′a**

	4b	**4a**	**3a**	**4′a**
Empirical formula	$C_{22}H_{12}O_{12}SW_2$	$C_{24}H_{14}O_{12}W_2$	$C_{25}H_{17}NO_{11}W_2$	$C_{24}H_{14}CrO_{12}W$
Molecular mass	868.08	862.05	875.10	730.20
Crystal size [mm]	0.45 × 0.33 × 0.33	0.32 × 0.15 × 0.12	0.40 × 0.26 × 0.12	0.47 × 0.34 × 0.22
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
a [Å]	7.408(15)	14.792(5)	9.045(2)	14.785(3)
b [Å]	10.313(4)	16.610(5)	13.997(4)	16.478(5)
c [Å]	17.802(4)	12.274(5)	22.425(6)	12.228(4)
α [°]	99.42(2)	90.000(5)	90	90
β [°]	98.92(5)	114.822(5)	92.648(2)	115.04(2)
γ [°]	96.32(7)	90.000(5)	90	90
V [Å^3]	1313(3)	2737.1(17)	2836.0(13)	2699.1(13)
Z	2	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	2.196	2.092	2.050	1.797
T [K]	293(2)	293(2)	293(2)	293(2)
μ [mm^{-1}] (Mo-K_α)	8.896	8.458	8.163	4.721
Absorption correction	psi scan	psi scan	psi scan	psi scan
F(000)	808	1608	1640	1408
θ_{range} [°]	1.18 to 26.97	1.95 to 26.99	1.72 to 27.84	1.96 to 26.98
Index ranges	$0 \le h \le 9$	$0 \le h \le 18$	$0 \le h \le 11$	$0 \le h \le 18$
	$-13 \le k \le 13$	$0 \le k \le 21$	$-18 \le k \le 17$	$0 \le k \le 21$
	$-22 \le l \le 22$	$-15 \le l \le 14$	$-29 \le l \le 29$	$-15 \le l \le 14$
Number of reflections collected	6170	3097	12043	3049
Number of independent reflections	5718	2984	6706	2936
Numbers of reflections with $I > 2\ \sigma(I)$	4071	2219	5347	1888
Number of parameters	518	173	353	173
R_1 [$I > 2\sigma(I)$]	0.0476	0.0292	0.0474	0.0473
R_1 (all data)	0.0768	0.0576	0.0659	0.0963
wR_2 (all data)	0.1383	0.0762	0.1289	0.1180
Largest different peak/hole, min./max. [eÅ^{-3}]	1.993/−2.150	0.777/−0.527	1.563/−2.064	0.746/−0.926

ν_{CO} = 2061 (m) 1924 (s) cm^{-1}. − ^{1}H NMR (200.131 MHz, CDCl$_3$): δ = 7.36 (s, 4 H, C_6H_4−), 7.08 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 7.02 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 5.95 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 5.89 (d, 1 H, $^3J_{HH}$ = 16.7 Hz, C*H*=), 4.23 (q, 2 H, $^3J_{HH}$ = 7.3 Hz, NCH_2CH_3), 4.09 (t, 2 H, CH_2), 3.94 (m, 2 H, CH_2OH), 3.82 [s, 3 H, N*Me* (*Z*)], 3.40 [s, 3 H, N*Me* (*E*)], 1.44 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.25 (t, 1 H, O*H*). − ^{13}C {^{1}H} NMR (75.469 MHz, CDCl$_3$): δ = 254.0, 252.5 (W=*C*), 203.6, 203.5 (*C*O), 198.4, 198.3 (*C*O), 139.2, 138.5 (*C*H=), 135.8, 135.4, 127.0, 126.9 (C_6H_4−), 123.0, 122.1 (*C*H=), 60.2 (O*Me*), 58.1 (N*C*H$_2$), 53.5 [N*Me* (*Z*)], 53.3 NCH_2CH_2, 44.3 [N*Me* (*E*)], 14.1 (*C*H$_3$), 13.9 (CH$_2$). − HRMS (FAB$^+$): calcd. for $C_{28}H_{24}N_2O_{11}{}^{184}W_2$ 932.0399; found 932.0403.

X-ray Crystal Structure Analysis: Crystals, data collection, and refinement parameters for complexes **3a**, **4a**, **4b**, and **4′a** are given in Table 3. Crystals were obtained by slow concentration of a dichloromethane solution. All X-ray data were collected with an automatic diffractometer CAD4 NONIUS (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). After Lorentz and polarization corrections, the structures were solved with SIR-97,[27] which reveals the non-hydrogen atoms of the structure and a statistical disorder between Cr and W atoms (complex **4′a**). After anisotropic refinement, a Fourier difference map reveals all the hydrogen atoms. The whole structures were refined with SHELXL97 by the full-matrix least-squares technique (use of *F* square magnitude; *x*, *y*, *z*, β_{ij} for Cr, W, C, and O atoms, *x*, *y*, *z* in riding mode for H atoms).[28] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146553 (**4b**), -146554 (**4a**), -146555 (**3a**), -146556 (**4′a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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