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Aminomethylene complexes of molybdenum(IV) and tungsten(IV) bearing 1,2-dithiolato ligands

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Abstract

The syntheses, spectroscopic data and the structures of molybdenum(IV) and tungsten(IV) aminomethylene complexes bearing 1,2-dithiolato ligands are presented. Oxidative decarbonylation of $Cp^*(CO)_2M\equiv CNEt_2$ (**1a**,**b**) (**a**: M = Mo; **b**: M = W; Cp* = pentamethylcyclopentadienyl) with $PhICl_2$ affords the aminocarbyne complexes *cis*-$Cp^*(Cl)_2(CO)M\equiv CNEt_2$ (**2a**,**b**), which react with the 1,2-dithiolates $Na_2(mnt) \times DMF$, (mnt^{2-} = 1,2-dicyanoethene-1,2-dithiolate), $Li_2(bdt)$ (bdt^{2-} = 1,2-benzenedithiolate) and $Li_2(Mebdt)$ ($Mebdt^{2-}$ = 4-methyl-1,2-benzenedithiolate) to afford the substitution products $Cp^*(mnt)(CO)M\equiv CNEt_2$ (**3a**,**b**), $Cp^*(bdt)(CO)M\equiv CNEt_2$ (**4a**,**b**) and $Cp^*(Mebdt)(CO)W\equiv CNEt_2$ (**5b**), respectively. Treatment of **3b** with HCl yields, after elimination of CO, the 16-electron aminomethylene complex $Cp^*(Cl)(mnt)W{=}C(H)NEt_2$ (**6b**). Addition of HCl to the M–C triple bond of complexes **4a**,**b** and **5b** affords the 18-electron aminomethylene complexes $Cp^*(Cl)(bdt)(CO)M{=}C(H)NEt_2$ (**7a**,**b**) and $Cp^*(Cl)(Mebdt)(CO)W{=}C(H)NEt_2$ (**8b**), which upon heating lose carbon monoxide to afford the 16-electron aminomethylene complexes $Cp^*(Cl)(bdt)M{=}C(H)NEt_2$ (**9a**,**b**) and $Cp^*(Cl)(Mebdt)W{=}C(H)NEt_2$ (**10b**), respectively. An alternative approach to **9b** offers the nucleophilic substitution reaction of $Cp^*(Cl)_3W{=}C(H)NEt_2$ with $Li_2(bdt)$. Complexes **2a**–**10b** have been fully characterized and the crystal structures of the complexes **3b**, **6b** and **9b** are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Carbyne complexes; Cyclopentadienyl complexes; 1,2-Dithiolato ligands; Molybdenum; Tungsten

1. Introduction

Aminomethylene complexes of chromium(0) [1,2] have been shown to be useful reagents for organic synthesis. Photolysis of these compounds generates chromium ketene intermediates [3], which can be trapped by imines to give β-lactams [4], by olefins to give cyclobutanones [5], and by alcohols and amines to afford α-amino acid derivatives [6]. Thermal reactions of these compounds with alkynes follow a common pathway involving chromium enaminoketene and nitrogen ylide intermediates to produce pyrrolinones, pyrrols or aminofurans [7], whereas their reactions with electron deficient olefins afford cyclopentanes [8]. The course of these C–C coupling reactions should be strongly dependent on the oxidation state, d-electron configuration and coordinative saturation of the metal center. Therefore reactivity studies of aminomethylene complexes of Group 6 metals in higher oxidation states are particularly appealing. However, only few compounds of this type have been reported so far and include the chromium(II) complexes $[(\eta^5\text{-}C_5R_5)(L)(CO)_2Cr{=}C(H)N^iPr_2][PF_6]_n$ [R = H, Me; $n = 0$: L = Cl, Br; $n = 1$: L = EtNC, ^{t}BuNC, PMe_3, $P(OMe)_3$] [9] and the related molybdenum(II) and tungsten(II) compounds $[Cp(CO)_3M{=}C(H)NMe_2][CpM(CO)_3]$ (Cp = cyclopentadienyl, M = Mo, W) [2a,c], $Cp(Cl)(CO)_2W{=}C(H)NEt_2$ [10], $Cp^*(X)(CO)(L)W{=}C(H)NEt_2$ (X = Br, I; L = CO, EtNC, ^{t}BuNC, PMe_3) [11] and $(RCS_2)_2(CO)_2M{=}C(H)N^iPr_2$ (R = NMe_2, NEt_2, $N(CH_2)_4$, OEt; M = Mo, W) [12]. Most of these complexes were prepared upon protonation of Fischer-type aminocarbyne complexes [1,9–12]. We have shown recently that this methodology can be extended to Schrock-type aminocarbyne complexes providing first tungsten(IV) aminomethylene complexes [1,13]. An al-

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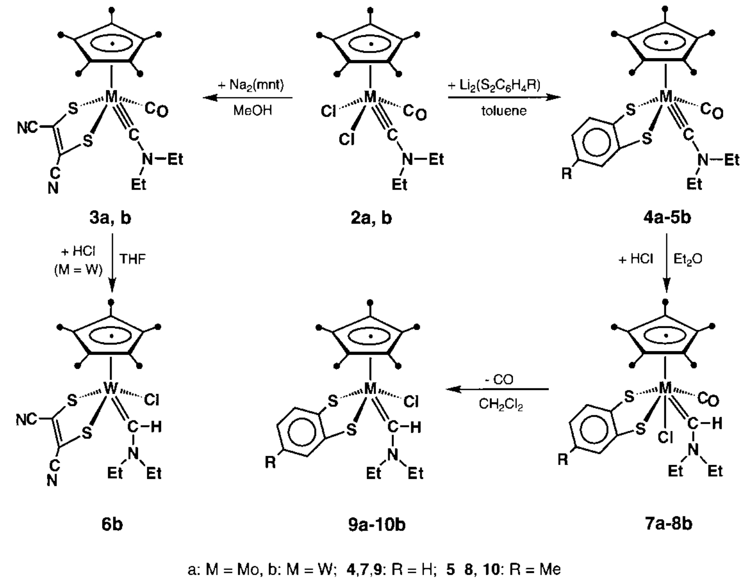


Scheme 1. Syntheses of aminocarbyne and aminomethylene complexes (**3a**–**10b**) starting from **2a**,**b**. Only one of the several possible geometrical isomers of **7a**–**8b**, and one of the two isomers of **5b**, **8b** and **10b** (**5b$_1$**, **8b$_1$** and **10b$_1$**) differing in the position of the methyl group in the phenyl ring is depicted.

ternative approach to compounds of this type involving proton-abstraction from an azatungstenacyclopentane has been also reported recently [14]. In continuation of our studies in this field, we report here on the syntheses and structures of 16- and 18-electron molybdenum(IV) and tungsten(IV) aminomethylene complexes bearing 1,2-dithiolato ligands.

2. Results and discussion

Starting materials for the reactions described below were the aminocarbyne complexes of Cp*(CO)$_2$M≡CNEt$_2$ (**1a**,**b**) (**a**: M = Mo; **b**: M = W) [15,16]. Oxidative decarbonylation of **1b** with one equivalent PhICl$_2$ has been shown previously to give the dichloro complex **2b** in high yield (Scheme 1) [13]. In an analogous reaction, the molybdenum compound **2a** was now prepared from **1a** and isolated as a red–violet, microcrystalline solid in quantitative yield (Scheme 1).

Complex **2a** is thermally less robust than the analogous tungsten compound **2b** [m.p. (dec.) = 176°C] and decomposes upon heating at 136°C. Treatment of **2a**,**b** with the nucleophile Na$_2$(mnt) × DMF (DMF = *N*,*N*-dimethylformamide) in refluxing methanol affords the 1,2-dithiolato complexes **3a**,**b** as slightly air-sensitive, brown (**3a**) and rust-colored solids (**3b**) in good yields (75–81%) (Scheme 1). Complexes **3a** and **3b** are readily soluble in CH$_2$Cl$_2$, MeOH and THF, sparingly soluble in diethylether and insoluble in pentane. They show a remarkable thermal stability and decompose at 180°C (**3a**) and 192°C (**3b**).

A similar ligand substitution reaction occurs when **2a**,**b** are reacted with a slight excess of the 1,2-dithiolate Li$_2$(bdt) in toluene at an ambient temperature to afford selectively the 18e-aminocarbyne complexes **4a**,**b** (Scheme 1). These were isolated in good yields as brown solids, which melt at 149 and 123°C, respectively. Using the dilithium salt of 4-methyl-1,2-benzenedithiolate as a nucleophile, the analogous red–brown tungsten compound **5b** was obtained starting from **2b** (Scheme 1). Complex **5b** was isolated in 79% yield as a mixture of the two positional isomers **5b$_1$** and **5b$_2$** (Fig. 1) and melts at 80°C. The ratio of the isomers is approximately 1:1. Complexes **4a**–**5b** show a higher solubility in organic solvents than **2a**, **3a** and **3b**. They are readily soluble in CH$_2$Cl$_2$, toluene and diethylether and sparingly soluble in pentane.

No evidence was found for the formation of the 16-electron aminocarbyne complexes Cp*(L$_2$)M≡CNEt$_2$ (L$_2$ = mnt, bdt, Mebdt) in the substitution reactions mentioned above. Similarly, treatment of **2b** with 1,2-ethanedithiolate or 3,5-di-*tert*-butyl catecholate, which as mnt^{2-} and bdt^{2-} form five-membered ring chelates, affords the 18-electron aminocarbyne complexes

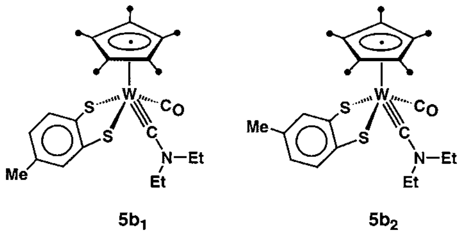


Fig. 1. Positional isomers of complex **5b**.

$Cp^*(X_2)(CO)W{\equiv}CNEt_2$ ($X_2 = SCH_2CH_2S$, 3,5-^{t}Bu$_2$-$C_6H_2O_2$) [17]. The reaction of **2b** with two equivalents of potassium cyanide or lithium phenylselenolate produces also the 18-electron monocarbonyl complexes *cis*-$Cp^*(CN)_2(CO)W{\equiv}CNEt_2$ and *cis*-$Cp^*(PhSe)_2(CO)W{\equiv}CNEt_2$, respectively [17]. In comparison, substitution of the chloro ligands in **2b** by monodentate alkyl or arylthiolates such as $(EtS)^-$, $(^tBuS)^-$ and $(4\text{-}MeC_6H_4S)^-$ is accompanied by elimination of CO to yield selectively, the 16-electron aminocarbyne complexes $Cp^*(RS)_2W{\equiv}CNEt_2$ (R = Et, ^{t}Bu, 4-MeC_6H_4) [17]. The reaction of **2b** with 1,4-butanedithiolate, which forms seven-membered ring chelates, affords also the 16-electron aminocarbyne complex $Cp^*(S(CH_2)_4S)W{\equiv}CNEt_2$ [17]. DFT calculations at the B3LYP/DZP level offer a good explanation for these observations and show that the CO dissociation energy of the 18-electron model complexes $Cp(X)_2(CO)W{\equiv}CNH_2$ (X = Cl, EMe, E = O, S, Se; $(X)_2 = ECH_2CH_2E$, E = O, S, Se) depends strongly on the ligating atom X and decreases upon widening of the angle X-W-X, the latter occurring during the dissociation process (relaxation energy) to give the 16-electron complexes $Cp(X)_2W{\equiv}CNH_2$ [17].

Compounds **2a**–**5b** form a rare class of carbyne complexes [13,16,18], which have the metal center in the same oxidation state as Schrock-type carbyne complexes [1,19] and contain carbonyl ligands as Fischer-type carbyne complexes [1,19]. The stability of these compounds is remarkable in view of the observation that Schrock-type carbyne complexes react with CO to give various C–C coupling products derived from the carbyne group [20]. This stability can be rationalized with the specific electronic properties of aminocarbyne ligands. Thus, these ligands bear only one π-acceptor MO comparable in energy to those of alkyl and arylcarbyne ligands. This orbital lies in the ligand plane and is largely localized on the carbyne-carbon atom [19]. The other π-acceptor orbital of an aminocarbyne ligand appears at higher energy due to the strong interaction of the empty p orbital of the carbon atom [1] with the filled p orbital (lone pair) of the adjacent nitrogen atom [19]. This is expressed in valence bond terms by the resonance formula **B** {$M{\equiv}C{-}NEt_2$ (**A**) ↔ $M^{(-)}{=}C{=}N^{(+)}Et_2$ (**B**)}. Comprehensive MO analyses have shown that only two metal d orbitals are available for π-backbonding in four-legged piano-stool complexes such as **2a**–**5b**. The one is primarily z^2 in character and the other is an xy-based orbital [21]. Both orbitals are filled with two electrons in **2a**–**5b** given the d^4 electron configuration of the metal center in these complexes [1]. DFT studies at the B3LYP/DZP level of the model compounds $Cp(X)_2(CO)W{\equiv}CNH_2$ (X = Cl, EMe, E = O, S, Se; $(X)_2 = ECH_2CH_2E$, E = O, S, Se) show that an optimum interaction of the dπ metal orbitals with the π-acceptor orbitals of the aminocarbyne and the carbonyl ligand results in case of a *cis* disposition of the aminocarbyne and the carbonyl ligand. Moreover, the aminocarbyne ligand adopts an almost orthogonal orientation relative to the Cp ligand. This is shown by the dihedral angle of the carbyne ligand plane and the Cp ring plane, which ranges in the minimum structures from 77.03° ($Cp(SCH_2CH_2S)(CO)W{\equiv}CNH_2$) to 89.04° ($Cp(SeCH_2CH_2Se)(CO)W{\equiv}CNH_2$) [17]. The DFT studies imply the existence of an electronic barrier to rotation of the amino group about the $C_{carbyne}$–N bond. All calculations agree well with the spectroscopic data of **2a**–**5b** as well as the crystal structure data of **3b** and related 18-electron aminocarbyne complexes. Thus, the solution IR spectra of **2a**–**5b** display one ν(CO) absorption at 1968–2001 cm^{-1} and one characteristic absorption in the range of 1584–1607 cm^{-1}, which is assigned to the $\nu(C_{carbyne}\overset{\cdots}{-}N)$ vibration (Table 1).

The frequency of the $\nu(C_{carbyne}\overset{\cdots}{-}N)$ vibration is slightly lower than that of immonium ions $[R_2C{=}NR_2]^+$, ($\nu(C{=}N) = 1640$–$1690\ cm^{-1}$) [22] indicating that the metal–aminocarbyne bond in **2a**–**5b** is best represented by the resonance formula **B**. This is supported by the molecular structures of **3b** and related aminocarbyne complexes revealing long M–$C_{carbyne}$ bonds, short $C_{carbyne}$–N bonds and planar amino groups (Table 3). The frequency of the $\nu(C_{carbyne}\overset{\cdots}{-}N)$ vibration is also strongly dependent on the electronic situation of the metal center. For example, the $\nu(C_{carbyne}\overset{\cdots}{-}N)$ absorption band of **2a**–**5b** appears at higher wavenumbers than that of the 16-electron complexes $Cp^*(RS)_2W{\equiv}CNEt_2$ (R = Et, ^{t}Bu, 4-MeC_6H_4) and that of the 18-electron complexes $Cp^*(Cl)_2(L)M{\equiv}CNEt_2$ (M = Mo, W; L = ^{t}BuNC, $P(OMe)_3$), in which the carbonyl ligand has been replaced by a weaker π-acceptor ligand L (Table 1). This suggests a stronger contribution of the resonance formula **B** to the metal–aminocarbyne bond in **2a**–**5b** than in $Cp^*(RS)_2W{\equiv}CNEt_2$ (R = Et, ^{t}Bu, 4-MeC_6H_4) and $Cp^*(Cl)_2(L)M{\equiv}CNEt_2$ (M = Mo, W; L = ^{t}BuNC, $P(OMe)_3$). Further evidence for this is given by the molecular structures. These show the tungsten–carbon multiple bond of **3b** and other carbonyl-containing tungsten(II) aminocarbyne complexes to be longer, and the $C_{carbyne}$–N bond to be shorter than that of the 16-electron complexes $Cp^*(^tBuS)_2W{\equiv}CNEt_2$ or $Tp'(Br)_2W{\equiv}CNEt_2$ (Tp′ = HB(3,5-$Me_2pz)_3$; 3,5-Me_2pz = 3,5-dimethylpyrazol-1-yl) (Table 3) [23].

An additional spectroscopic tool to identify the M^{II} aminocarbyne complexes **2a**–**5b** is the carbyne-carbon resonance in the $^{13}C\{^1H\}$-NMR spectra, which appears at considerably lower field (δ 301.8–313.4) than those of the M^0 complexes **1a** (δ 274.6) [15] and **1b** (δ 268.6) [16], and the 16-electron tungsten(II) complexes $Cp^*(RS)_2W{\equiv}CNEt_2$ (R = Et: δ 258.7 (toluene-d_8); R = ^{t}Bu: δ 260.8 (C_6D_6)) [17]. This resonance is accompanied, in the case of the tungsten compounds, by

Table 1
ν(CO) and $\nu(C_{carbyne}\overset{\cdots}{-}N)$ absorptions (cm^{-1}) of high oxidation state molybdenum and tungsten diethylaminocarbyne complexes bearing a Cp* ligand

Complex	ν(CO)	$\nu(C_{carbyne}\overset{\cdots}{-}N)$	Solvent	Reference
cis-Cp*(Cl)$_2$(CO)Mo≡CNEt$_2$ (**2a**)	2006 (vs)	1596 (s)	CH$_2$Cl$_2$	This work
cis-Cp*(Cl)$_2$(CO)W≡CNEt$_2$ (**2b**)	1986 (vs)	1600 (s)	CH$_2$Cl$_2$	[13]
cis-Cp*(CN)$_2$(CO)W≡CNEt$_2$	2009 (vs)	1618 (s)	CH$_2$Cl$_2$	[17]
Cp*(Cl)(GeCl$_3$)(CO)W≡CNEt$_2$	2018 (vs)	1599 (s)	CH$_2$Cl$_2$	[17]
Cp*(mnt)(CO)Mo≡CNEt$_2$ (**3a**)	2001 (vs)	1603 (s)	CH$_2$Cl$_2$	This work
Cp*(mnt)(CO)W≡CNEt$_2$ (**3b**)	1987 (vs)	1607 (s)	CH$_2$Cl$_2$	This work
Cp*(bdt)(CO)Mo≡CNEt$_2$ (**4a**)	1983 (vs)	1584 (s)	CH$_2$Cl$_2$	This work
Cp*(bdt)(CO)W≡CNEt$_2$ (**4b**)	1969 (vs)	1592 (s)	CH$_2$Cl$_2$	This work
Cp*(Mebdt)(CO)W≡CNEt$_2$ (**5b**)	1968 (vs)	1591 (s)	CH$_2$Cl$_2$	This work
cis-Cp*(PhSe)$_2$(CO)W≡CNEt$_2$	1968 (vs)	1590 (s)	CH$_2$Cl$_2$	[17]
Cp*(SCH$_2$CH$_2$S)(CO)W≡CNEt$_2$	1971 (vs)	1586 (s)	CH$_2$Cl$_2$	[17]
cis-Cp*(Cl)$_2$(^{t}BuNC)Mo≡CNEt$_2$	–	1567 (s)	CH$_2$Cl$_2$	[17]
cis-Cp*(Cl)$_2$(^{t}BuNC)W≡CNEt$_2$	–	1571 (s)	CH$_2$Cl$_2$	[13]
cis-Cp*(Cl)$_2$[P(OMe)$_3$]Mo≡CNEt$_2$	–	1544 (s)	CH$_2$Cl$_2$	[17]
cis-Cp*(Cl)$_2$[P(OMe)$_3$]W≡CNEt$_2$	–	1547 (s)	CH$_2$Cl$_2$	[13]
Cp*(4-MeC$_6$H$_4$S)$_2$W≡CNEt$_2$	–	1502 (s)	Et$_2$O	[17]
Cp*(EtS)$_2$W≡CNEt$_2$	–	1502 (s)	Et$_2$O	[17]
Cp*(^{t}BuS)$_2$W≡CNEt$_2$	–	1496 (s)	Pentane	[17]

satellites due to coupling with the ^{183}W nucleus. It is interesting to note, that the ^1J(W,C) coupling constant of **2b** (210.0 Hz) [13] and of **3b** (189.4 Hz) is considerably smaller than those of Cp*(RS)$_2$W≡CNEt$_2$ (R = Et: 273.2 Hz; R = ^{t}Bu: 271.8 Hz; R = 4-MeC$_6$H$_4$S: 267.5 Hz) [17]. This suggests that the W–C$_{carbyne}$ bond of the 18-electron monocarbonyl complexes (**2b**, **3b**) is weaker than that of the 16-electron congeners in agreement with the IR and crystal structure data (Tables 1 and 3). However, the most striking spectroscopic feature of **2a**–**5b** is the temperature dependence of their ^{1}H- and ^{13}C{^{1}H}-NMR spectra [13]. This can be traced back to the hindered rotation of the amino group about the C$_{carbyne}$–N bond, which makes the ethyl groups inequivalent in the low exchange limit spectra of **2a**–**5b**. For example, the ^{1}H-NMR spectrum of **3a** in CDCl$_3$ displays at 222 K, two triplets for the methyl protons at δ 1.09 and 1.29 and two quadruplets for the methylene protons of the aminocarbyne ligand at δ 3.26 and 3.35 [24]. The ^{13}C{^{1}H}-NMR spectrum of **3a** also shows a double set of resonances for the ethyl groups at 222 K (δ (CH$_3$) = 13.6 and 14.4; δ (CH$_2$) = 49.4 and 49.7) giving additional evidence for a frozen-in rotation of the amino group. As the temperature is increased, the methyl proton signals broaden, coalesce at $T_c = 269$ K (300 MHz) and appear as one triplet at δ 1.22 in the fast exchange limit spectrum of **3a** at 298 K. Similarly, one multiplet resonance at δ 3.31 is observed for the methylene protons of **3a** at 298 K, and the methyl and methylene carbon atoms give rise to one singlet resonance at δ 14.0 and 49.7, respectively, in the fast exchange limit ^{13}C{^{1}H} spectrum of **3a** at 298 K. The free energy of activation $\Delta G^{\neq}$ (T_c) for the site exchange of the ethyl groups of **3a** was calculated at the coalescence temperature T_c of the methyl proton resonances to be 54.6 kJ mol^{-1}. A similar temperature dependence was observed for the methyl and methylene proton resonances of the aminocarbyne complexes **2a** and **3b**–**4b** leading to the activation barriers $\Delta G^{\neq} < 38.7$ kJ mol^{-1} ($T_c < 167$ K) (**2a**), $\Delta G^{\neq} = 55.6$ kJ mol^{-1} ($T_c = 272$ K) (**3b**), $\Delta G^{\neq} = 49.7$ kJ mol^{-1} ($T_c = 245$ K) (**4a**), and $\Delta G^{\neq} = 51.9$ kJ mol^{-1} ($T_c = 256$ K) (**4b**). Complexes **2a**–**5b** differ thereby from molybdenum(0) and tungsten(0) aminocarbyne complexes, such as **1a** and **1b**

Table 2
Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **3b**

Bond lengths			
W–C(1)	231.1(6)	S(1)–C(13)	175.0(7)
W–C(2)	244.3(6)	S(2)–C(15)	175.0(6)
W–C(3)	248.1(6)	C(6)–N(1)	128.6(8)
W–C(4)	236.0(5)	C(7)–N(1)	149.6(8)
W–C(5)	229.6(6)	C(9)–N(1)	148.2(8)
W–C(6)	188.1(6)	C(12)–O	113.2(8)
W–C(12)	200.5(7)	C(13)–C(14)	144.4(9)
W–C$_g$ [a]	204.4	C(13)–C(15)	133.7(9)
W–C$_f$ [a]	203.4	C(15)–C(16)	143.4(9)
W–S(1)	244.9(2)	C(14)–N(2)	114.2(9)
W–S(2)	245.1(2)	C(16)–N(3)	115.6(8)
Bond angles			
S(1)–W–S(2)	82.01(6)	W–S(1)–C(13)	103.0(2)
S(1)–W–C(6)	118.9(2)	W–S(2)–C(15)	103.1(2)
S(1)–W–C(12)	81.9(2)	W–C(6)–N(1)	176.0(5)
S(2)–W–C(6)	80.9(2)	C(6)–N(1)–C(7)	121.8(6)
S(2)–W–C(12)	139.5(2)	C(6)–N(1)–C(9)	121.0(6)
C(6)–W–C(12)	75.0(3)	C(7)–N(1)–C(9)	117.1(5)

[a] C$_g$ denotes the center of the Cp* ring and C$_f$ the foot of the tungsten-to-ring normal.

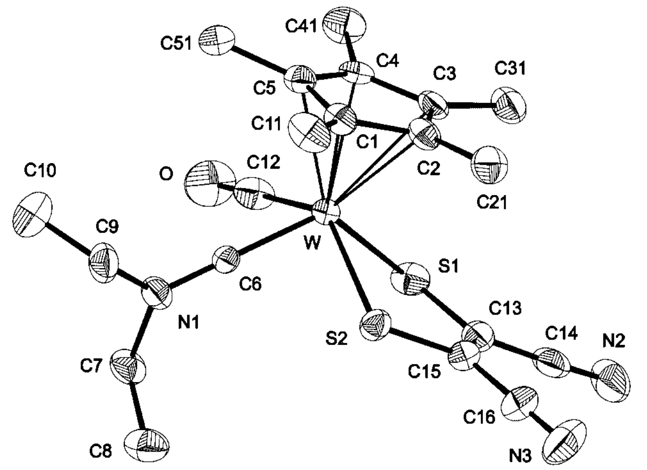


Fig. 2. ZORTEP plot of the molecular structure of **3b** with the thermal ellipsoids drawn at the 50% probability level.

[1], in which the barrier to rotation of the amino group about the $C_{carbyne}$–N bond is too small to be detected with solution NMR spectroscopy [15]. The NMR data match well to the DFT calculations of the model compounds Cp(X)$_2$(CO)W≡CNH$_2$ (X = Cl, EMe, E = O, S, Se; (X)$_2$ = ECH$_2$CH$_2$E, E = O, S, Se), which predict an electronic barrier to rotation of the amino group and an almost perpendicular arrangement of the aminocarbyne and the Cp ligand. In order to determine the latter experimentally, a single-crystal X-ray diffraction study of **3b** was carried out. Dark-red single crystals of **3b** were obtained upon slow evaporation of a THF solution. The molecular structure of **3b** is shown in Fig. 2 and selected bond lengths and angles are listed in Table 2.

Complex **3b** shows the expected coordination geometry of a 'four-legged piano-stool complex' [21a], which can be described as square-pyramidal with the Cp* ligand at the apex of the pyramid. The tungsten atom resides at a distance of 203.4 pm from the Cp* ring plane and of 91.9 pm from the basal plane of the pyramid defined by the ligating atoms S(1), S(2), C(6) and C(12). The dihedral angle between these planes is 5.7°. The W–$C_{carbyne}$ bond length of 188.1(6) pm is similar to those found in other 18-electron tungsten(II) aminocarbyne complexes bearing a carbonyl ligand (Table 3). This bond is, however, longer than that of the 16-electron complexes Cp*(^{t}BuS)$_2$W≡CNEt$_2$ and Tp′(Br)$_2$W≡CNEt$_2$ (Table 3). In addition, the $C_{carbyne}$–N bond of **3b** is with 128.6(8) pm slightly shorter than that of Cp*(^{t}BuS)$_2$W≡CNEt$_2$ or Tp′(Br)$_2$W≡CNEt$_2$ (Table 3) and corresponds to a C–N double bond. These structure data suggest the presence of a weaker W–$C_{carbyne}$ bond and a stronger $C_{carbyne}$–N bond in **3b** than in Cp*(^{t}BuS)$_2$W≡CNEt$_2$ and Tp′(Br)$_2$W≡CNEt$_2$, which agrees also well with the IR and NMR data (vide supra). Further evidence for the strong contribution of the resonance formula **B** (vide supra) is given by the planarity of the amino group (the sum of the bond angles of the nitrogen atom is 359.9°). The carbyne ligand is arranged almost perpendicular to the Cp* ligand with a dihedral angle of 78.7° between the carbyne ligand plane, defined by the atoms C(6), N(1), C(7) and C(9), and the Cp* ring plane (Table 3). The same orientation is also found in other tungsten(II) aminocarbyne complexes bearing a carbonyl ligand, the good agreement between observed dihedral angles (Table 3) and calculated dihedral angles for the model compounds Cp(X)$_2$(CO)W≡CNH$_2$ (X = Cl, EMe, E = O, S, Se; (X)$_2$ = ECH$_2$CH$_2$E, E = O, S, Se) (Cp/CNH$_2$ = 77.03–89.04° (B3LYP/DZP)) being remarkable.

The aminocarbyne complexes **3a**–**5b** are useful starting materials for the synthesis of 16-, and 18-electron M(IV) aminomethylene complexes (Scheme 1). Thus, treatment of the mnt-derivative **3b** with HCl in THF leads, after elimination of CO, to the 16-electron aminomethylene complex **6b** (Scheme 1). This was purified by column chromatography on silanized silica and isolated in 74% yield as an ocherous solid, that is readily soluble in CH$_2$Cl$_2$, THF, moderate soluble in diethylether and insoluble in pentane (Scheme 1). In comparison, the bdt- and Mebdt-substituted aminocarbyne complexes **4a**, **4b** and **5b** add HCl to the metal–carbon triple bond to afford the 18-electron aminomethylene complexes **7a**, **7b** and **8b**, respectively

Table 3
Selected bonding parameters of tungsten(II) diethylaminocarbyne complexes bearing a Cp* or Tp′ ligand [1]

Complex	W–$C_{carbyne}$ [a]	W–CO [a]	$C_{carbyne}$–N [a]	Cp*/CNEt$_2$ [b]	Reference
3b	188.1(6)	200.5(7)	128.6(8)	78.7	This work
Cp*(Cl)(GeCl$_3$)(CO)W≡CNEt$_2$	187.1(12)	198.9(14)	131.0(18)	86.9	[17]
cis-Cp*(PhSe)$_2$(CO)W≡CNEt$_2$	185.1(12)	200.6(12)	130.4(14)	85.2	[17]
Cp*(3,5-^{t}Bu$_2$-C$_6$H$_2$O$_2$)(CO)W≡CNEt$_2$	185.0(8)	198.4(9)	132.7(9)	81.4	[17]
Cp*(^{t}BuS)$_2$W≡CNEt$_2$	181.3(5)	–	133.7(7)	–	[17]
Tp′(Br)$_2$W≡CNEt$_2$	176.3(8)	–	134.5(8)	–	[23]

[a] Bond lengths are given in pm and estimated standard deviations in parentheses.

[b] Cp*/CNEt$_2$ denotes the dihedral angle (°) between the least square planes of the Cp* ligand (ring-carbon atoms) and the aminocarbyne ligand ($C_{carbyne}$,N and $C_{methylene}$ atoms).

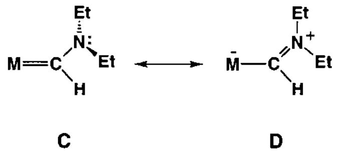


Fig. 3. Resonance formulas for the metal–aminomethylene bond.

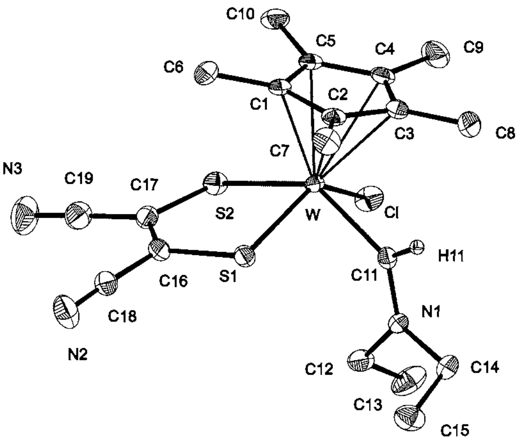


Fig. 4. ZORTEP plot of the molecular structure of **6b** with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons except that bonded to the carbon atom C11.

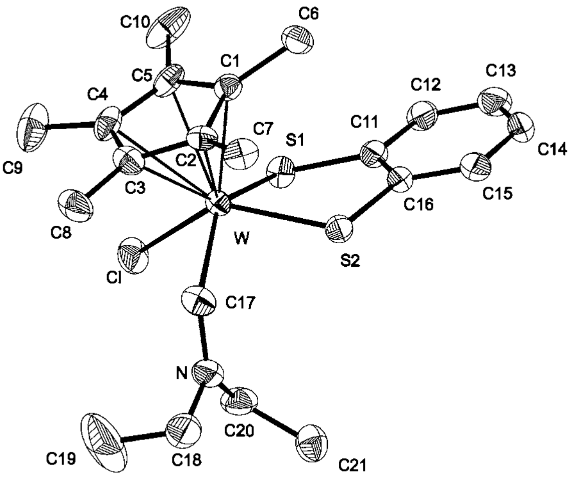
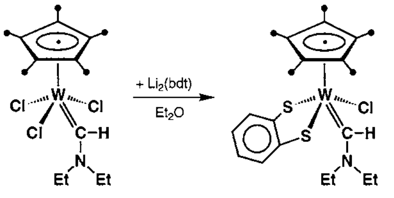


Fig. 5. ZORTEP plot of the molecular structure of **9b** with the thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

(Scheme 1). These were isolated in high yield as brown (**7a**, **8b**) and golden-brown (**8a**) solids, that are soluble in CH_2Cl_2 and THF and insoluble in pentane. Complexes **7a**–**8b** lose carbon monoxide to afford selectively the 16-electron aminomethylene complexes **9a**–**10b** (Scheme 1). Decarbonylation occurs slowly in CH_2Cl_2 at ambient temperature and is fast in refluxing THF. This reaction also takes place in the solid-state as shown by the conversion of **7b** to **9b** in vacuo at 90°C (see Section 4). Compounds **9a**–**10b** were isolated in high yield as brown (**9a**) and olive-green (**9b**, **10b**) thermally stable solids, which are more soluble in organic solvents than their precursors **7a**, **8a** and **8b**. The compounds **8b** and **10b** were obtained as an approximately 1:1 mixture of the two isomers $\mathbf{8b_1}/\mathbf{8b_2}$ and $\mathbf{10b_1}/\mathbf{10b_2}$ differing in the position of the methyl group in the phenyl ring (Scheme 1, Fig. 1). An alternative approach to **9b** offers the nucleophilic substitution reaction of $Cp^*(Cl_3)W{=}C(H)NEt_2$ with $Li_2(bdt)$ in diethyl ether at ambient temperature (Eq. (1)).



9b (1)

Complexes **6b**–**10b** were fully characterized. Thus, the compounds are distinguished in the solution IR spectra by an absorption of medium intensity in the range of 1503–1551 cm^{-1}, which can be assigned to the $\nu(C_{carbene}\overset{...}{-}N)$ vibration. The high frequency of this vibration suggests a strong π-interaction of the amino group with the metal–carbon double bond, which in valence bond terms means a strong contribution of the resonance formula **D** (Fig. 3). Additional evidence for this is given by the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **6b**–**10b** and the molecular structures of **6b** and **9b**. The NMR spectra show that rotation about the $C_{carbene}$–N bond is frozen in, giving rise to a double set of resonances for the inequivalent ethyl groups, and the molecular structures show short $C_{carbene}$–N bonds.

The ^1H-NMR spectra of **6b**–**10b** display a characteristic singlet resonance at low field (δ 10.55–10.82) for the proton bound to the carbene-carbon atom. Accordingly, the carbene carbon resonances appearing at low field (239.6–264.2) should be split into doublets in the proton-coupled ^{13}C-NMR spectra. This was verified for **8b**, **9a** and **10b**. The $^1J(C,H)$ coupling constants of the 16-electron complexes **9a** (134.8 Hz) and **10b** (136.4 Hz) have similar values to that of the 18-electron complex **8b** (137.3 Hz) excluding any agostic interaction of the C–H bond with the metal center in the 16-electron complexes [25]. This is also confirmed by the crystal structures of **6b** and **9b** showing non-distorted aminomethylene ligands.

Suitable single crystals of **6b** and **9b** were obtained upon slow evaporation of a CD_2Cl_2 (**6b**) and C_6D_6 solution (**9b**) at room temperature. ZORTEP plots of the molecular structures of **6b** and **9b** are depicted in Figs. 4 and 5, and selected bond lengths and angles are listed in Tables 4 and 5.

Both complexes are as **3b** square pyramidal with the Cp* ligand occupying one coordination site at the apex of the pyramid. The tungsten is located at a distance of 200.8 pm (**6b**) and 202.0 pm (**9b**) from the Cp* ring plane (C_f), and a distance of 89.0 pm (6**b**) and 87.4 pm (**9b**) from the basal plane of the pyramid. The dihedral angle of these planes is 2.6° (**6b**) and 5.6° (**9b**). The five-membered chelate rings, formed from the 1,2-dithiolato ligands, are fold with a folding angle of 15.1° (**6b**) and 23.5° (**9b**) (24.8° for **3b**). The aminomethylene ligand is arranged almost perpendicular to the Cp* ligand as shown by the dihedral angle of 85.7° (**6b**) and 84.2° (**9b**) between the best plane passing through the atoms $\mathrm{C_{carbene}}$, N, $\mathrm{C_{methylene1}}$ and $\mathrm{C_{methylene2}}$ and the Cp* ring plane. The W–$\mathrm{C_{carbene}}$ bond is with 210.9(2) pm (**6b**) and 207.9(7) pm (**9b**) similar in length to that of the $\mathrm{W^{IV}}$ complex $\mathrm{Cp^*(Cl)_3W{=}C(H)NEt_2}$ (W–C = 206.5(7) pm) [13], but shorter than that of the $\mathrm{W^{II}}$ complex *cis*-$\mathrm{Cp^*(Cl)(CO)_2W{=}C(H)NEt_2}$ (W–C = 214.1(3) pm) [26] probably due to the smaller covalent radius of $\mathrm{W^{IV}}$ [27]. The aminomethylene ligand deviates only slightly from planarity with the best planes passing through the atoms W, $\mathrm{C_{carbene}}$, N and the atoms $\mathrm{C_{carbene}}$, N, $\mathrm{C_{methylene1}}$, $\mathrm{C_{methylene2}}$ to form an angle of 7.0° (**6b**) and 2.2° (**9b**). In addition, the $\mathrm{C_{carbene}}$–N bond lengths of 131.1(3) (**6b**) and 131.8(9) pm (**9b**) are only slightly larger than that of a C–N double bond (127 pm) [22], which indicates in agreement with the IR and NMR data the strong π-conjugation of the amino group with the metal–carbon double bond.

Table 4
Selected bond lengths (pm) and bond angles (°) with estimated standard deviation for **6b**

Bond lengths			
W–C(1)	225.1(2)	C(16)–C(17)	136.8(3)
W–C(2)	231.7(2)	C(14)–N(1)	148.5(3)
W–C(3)	243.6(2)	C(12)–N(1)	148.1(3)
W–C(4)	244.5(2)	C(11)–N(1)	131.1(3)
W–C(5)	233.3(2)	S(2)–C(17)	173.8(2)
W–C(11)	210.9(2)	S(1)–C(16)	174.9(2)
W–C_g [a]	201.9	C(16)–C(18)	143.7(3)
W–C_f [a]	200.8	C(17)–C(19)	144.2(3)
W–Cl	244.8(1)	C(18)–N(2)	114.9(3)
W–S(1)	233.2(9)	C(19)–N(3)	114.0(3)
W–S(2)	237.8(7)		
Bond angles			
S(1)–W–S(2)	82.49(2)	W–S(1)–C(16)	108.14(8)
S(1)–W–Cl	132.70(3)	W–S(2)–C(17)	106.91(8)
S(2)–W–Cl	79.31(2)	W–C(11)–N(1)	132.5(2)
S(1)–W–C(11)	78.79(6)	C(11)–N(1)–C(12)	123.8(2)
S(2)–W–C(11)	136.72(7)	C(11)–N(1)–C(14)	121.1(2)
Cl–W–C(11)	85.39(6)	C(12)–N(1)–C(14)	115.0(2)

[a] C_g denotes the center of the Cp* ring and C_f the foot of the tungsten-Cp*-ring normal.

Table 5
Selected bond lengths (pm) and bond angles (°) with estimated standard deviation for **9b**

Bond lengths			
W–C(1)	226.1(6)	S(1)–C(11)	176.0(6)
W–C(2)	229.4(6)	S(2)–C(16)	175.6(6)
W–C(3)	240.9(7)	C(17)–N	131.8(9)
W–C(4)	247.4(7)	C(18)–N	147.9(9)
W–C(5)	234.9(8)	C(20)–N	149.1(9)
W–C(17)	207.9(7)	C(11)–C(16)	138.6(9)
W–C_g [a]	202.2	C(11)–C(12)	140.1(9)
W–C_f [a]	201.0	C(15)–C(16)	142.3(9)
W–Cl	245.7(2)	C(12)–C(13)	138.0(10)
W–S(1)	237.2(2)	C(14)–C(15)	136.9(11)
W–S(2)	233.4(2)	C(13)–C(14)	138.6(12)
Bond angles			
S(1)–W–S(2)	82.04(8)	W–S(1)–C(11)	106.1(2)
S(1)–W–Cl	78.82(7)	W–S(2)–C(16)	107.3(2)
S(2)–W–Cl	135.29(8)	W–C(17)–N	134.4(4)
S(1)–W–C(17)	135.4(2)	C(17)–N–C(18)	120.5(6)
S(2)–W–C(17)	80.4(2)	C(17)–N–C(20)	122.2(6)
Cl–W–C(17)	85.6(2)	C(18)–N–C(20)	117.3(6)

[a] C_g denotes the center of the Cp* ring and C_f the foot of the tungsten-Cp*-ring normal.

Several configuration isomers can be envisaged for the pseudooctahedral complexes **7a**–**8b**, only one isomer being present in solution according to IR and NMR spectroscopy. A simplified MO picture of **7a**–**8b** predicts a *cis*-orientation of both the aminomethylene and the CO ligand relative to the Cp* ligand in this isomer. Unfortunately, suitable single crystals could not be obtained so far, to determine unambiguously the structure of this isomer. The NMR spectra of **7a**–**8b** show further, that either one rotamer with respect to the M–$\mathrm{C_{carbene}}$ bond is present in solution, or that rotation of the carbene ligand about the M–$\mathrm{C_{carbene}}$ bond is fast on the NMR time scale. Given the d^2 metal configuration and the presence of two potential π-acceptor ligands in these compounds an electronic barrier to rotation of the carbene ligand is conceivable. Studies addressing this question are currently in progress.

3. Conclusions

The aminocarbyne complexes *cis*-$\mathrm{Cp^*(Cl)_2(CO)M{\equiv}CNEt_2}$ (M = Mo, W) react selectively with various nucleophiles upon substitution of the chloro ligands and are therefore valuable starting materials for various $\mathrm{M^{II}}$ aminocarbyne complexes. This has been demonstrated in the present work by the syntheses of the 18-electron 1,2-dithiolato complexes $\mathrm{Cp^*(mnt)(CO)M{\equiv}CNEt_2}$, $\mathrm{Cp^*(bdt)(CO)M{\equiv}CNEt_2}$ and $\mathrm{Cp^*(Mebdt)(CO)W{\equiv}CNEt_2}$. Spectroscopic and crystal structure data indicate a weaker M–$\mathrm{C_{carbyne}}$ and a stronger $\mathrm{C_{carbyne}}$–N bond in these compounds than in the 16-electron complexes $\mathrm{Cp^*(RS)_2M{\equiv}CNEt_2}$ (R = alkyl, aryl). They also show in agreement with DFT calculations a preferred orientation of the aminocarbyne ligand relative to the Cp* ligand and a hindered rotation of the amino group about the $C_{carbyne}$–N bond in these compounds. Addition of HCl to the metal–carbon triple bond affords selectively 18-, or 16-electron aminomethylene complexes, e.g. Cp*(Cl)(bdt)(CO)-M=C(H)NEt_2, Cp*(Cl)(bdt)M=C(H)NEt_2 (M = Mo, W) and Cp*(Cl)(mnt)W=C(H)NEt_2. The compounds Cp*(Cl)(bdt)CO)M=C(H)NEt_2 form a new class of metal carbenes, which have the metal center in the same oxidation state as Schrock-type carbene complexes [1] and bear a carbonyl ligand as Fischer-type carbene complexes [28]. Studies of the reactions of the 16-, and 18-electron aminomethylene complexes with alkynes are of specific interest given the rich alkyne chemistry of Fischer-type carbene complexes. These are currently in progress.

4. Experimental

4.1. General

Standard inert-gas atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane over CaH_2, diethylether, THF and toluene over Na–benzophenone, CH_2Cl_2 over Sicapent and Na–Pb alloy and MeOH over Mg), distilled under nitrogen and stored over 4 Å molecular sieves (MeOH: 3 Å). Column chromatography was carried out on a silanized silica support (Merck 7719; 0.063–0.200 mm) as the stationary phase in a thermostated column of 15 cm length and 2 cm diameter. The silanized silica was dried in vacuo at 150°C prior to use. The complexes **1a** [15], **1b** [16], and **2b** [13] were prepared as previously described. The compounds $PhICl_2$ [29], Na_2(mnt) [30] and 1,2-benzenedithiol [31] were obtained following literature procedures. The salts Li_2(bdt) and Li_2(Mebdt) were prepared upon treating the corresponding 1,2-dithiols with two equivalents of Li^nBu in pentane and isolated as white solids, which were dried thoroughly to remove adhesive solvent. All other chemicals were commercially available. Elemental analyses were obtained from the Central Analytical Group of the Chemistry Department of the Humboldt-Universität zu Berlin. Solution IR spectra were recorded in the region of 2200–1500 cm^{-1} on a Bruker IFS-55 spectrometer using a NaCl cell; the intensities of the absorption bands are given in parentheses (vs = very strong, s = strong, m = medium). All ^1H-NMR (300 MHz) and $^{13}C\{^1H\}$-NMR spectra (75.5 MHz) were recorded on a Bruker AM-300 spectrometer in dry, deoxygenated methylene-d_2 chloride, chloroform-d_1 or benzene-d_6. The ^1H- and $^{13}C\{^1H\}$-NMR spectra were calibrated against the internal residual proton and natural abundance ^{13}C resonances of the deuterated solvent (methylene-d_2 chloride, δ_H 5.32 and δ_C 53.8 ppm; chloroform-d_1, δ_H 7.24 and δ_C 77.0 ppm; benzene-d_6,δ_H 7.15 and δ_C 128.0 ppm). The complicated splitting pattern of the NMR signals of the 1,2-benzenedithiolato ligand protons was simulated in the case of **9b** using the program WIN-DAISY from Bruker (1995) to give the chemical shifts and the J(H,H) coupling constants (vide infra). The following abbreviations are used for the signal multiplicities: s = singlet, t = triplet, q = quadruplet, dq = doublet of quadruplets, m = multiplet, br = broad. Mass spectra were obtained with a Hewlett–Packard 5995A or a Varian MAT 311 A spectrometer using an ionization energy of 70eV; m/z values are given relative to the ^{98}Mo, ^{184}W, ^{32}S and ^{35}Cl isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed under vacuum in capillary tubes and heated with a rate of 3 K min^{-1} to a temperature, which was lower by 10 K than the melting point or the temperature of starting decomposition. Heating was then continued slowly until the samples melted or started to decompose. IR spectra of the heated samples were recorded and compared with those of authentic samples to determine whether the compounds had decomposed.

4.2. Synthesis of cis-$Cp^*(Cl)_2(CO)Mo\equiv CNEt_2$ (**2a**)

Compound **1a** (1.230 g, 3.31 mmol) was dissolved in 50 ml of CH_2Cl_2 and the solution cooled to −78°C. A solution of 910 mg (3.31 mmol) of freshly prepared $PhICl_2$ in 30 ml of CH_2Cl_2 was added slowly. The reaction mixture was allowed to warm to room temperature (r.t.). Evolution of gas was observed and the color of the solution changed from intense yellow to red–violet. After 1 h stirring at ambient temperature, an IR spectrum of the solution was recorded to confirm the complete conversion of **1a** to **2a**. Afterwards the solution was evaporated to dryness and the resulting residue was washed twice with 15 ml of diethyl ether and 15 ml of C_5H_{12} and dried in vacuo. Red–violet, microcrystalline solid; m.p. (dec.) 136°C. Yield: 1.371 g (quantitative). Anal. Calc. for $C_{16}H_{25}Cl_2MoNO$ (414.23): C, 46.39; H, 6.08; Cl, 17.12; N, 3.38. Found: C, 46.56; H, 6.16; Cl, 17.22; N, 3.33%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2006 (vs) [ν(CO)], 1596 (s) [$\nu(C_{carbyne}\overset{\cdots}{=}N)$]. IR (MeOH): $\tilde{\nu}$ [cm^{-1}] = 2006 (vs) [ν(CO)], 1604 (s) [$\nu(C_{carbyne}\overset{\cdots}{=}N)$]. ^1H-NMR ($CDCl_3$, 298 K): δ = 1.34 (t, ^3J(H,H) = 7.3 Hz, 6H, $N(CH_2CH_3)_2$), 1.93 (s, 15H, C_5Me_5), 3.42 (dq, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 7.3 Hz, 2H, $N[C(H_A)(H_B)CH_3]_2$), 3.48 (dq, ^2J(H,H) = 13.3 Hz, ^3J(H,H) = 7.3 Hz, 2H, $N[C(H_A)(H_B)CH_3]_2$). $^{13}C\{^1H\}$-NMR: ($CDCl_3$, 298 K): δ = 11.7 (C_5Me_5), 14.3 ($N(CH_2CH_3)_2$), 49.4 ($N(CH_2CH_3)_2$), 111.7 (C_5Me_5), 229.3 (CO), 313.4 ($Mo\equiv C$). EIMS: m/z = 387 [M^+ − CO], 358 [M^+ − CO − Et], 303 [M^+ − CO − Et − EtNC].

4.3. Synthesis of Cp*(mnt)(CO)Mo≡CNEt$_2$ (**3a**)

A solution of 264 mg (0.64 mmol) of **2a** in 30 ml of MeOH was treated at ambient temperature with 181 mg (0.70 mmol) of Na_2(mnt) × DMF. The wine-red solution was refluxed for 20 min. The resulting brown suspension was allowed to cool to ambient temperature and an IR spectrum of the solution was recorded revealing that the ν(CN) absorption of Na_2(mnt) × DMF at 2191 cm^{-1} and the ν(CO) absorption of **2a** at 2006 cm^{-1} had been replaced by those of the product at 2212 and 2203 cm^{-1} [ν(CN)] and 1999 cm^{-1} [ν(CO)]. The suspension was evaporated to dryness and the residue extracted twice with 15 ml of CH_2Cl_2. The extracts were filtered from NaCl, combined and concentrated in vacuo to a few milliliters. Addition of 20 ml of a diethyl ether–C_5H_{12} (1:1) mixture afforded precipitation of **3a** as a brown solid. The supernatant solution was rejected and the precipitate washed twice with 5 ml of diethyl ether and with 10 ml of C_5H_{12} and dried in vacuo. Brown solid. m.p. (dec.) 180 °C. Yield: 250 mg (81%). Anal. Calc. for $C_{20}H_{25}MoN_3OS_2$ (483.51): C, 49.68; H, 5.21; N, 8.69. Found: C, 49.00; H, 5.41; N, 8.47%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2210 (m) and 2200 (m) [ν(C≡N)], 2001 (vs) [ν(CO)], 1603 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($CDCl_3$, 298 K): δ = 1.22 (t, ^3J(H,H) = 7.3 Hz, 6H, N(CH$_2$C*H*$_3$)$_2$), 1.83 (s, 15H, C$_5$*Me*$_5$), 3.31 (m, 4H, N[C(*H*$_A$)(*H*$_B$)CH$_3$]$_2$). ^{1}H-NMR ($CDCl_3$, 222 K): δ = 1.09 (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.29 (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.80 (s, 15H, C$_5$*Me*$_5$), 3.26 (q, ^3J(H,H) = 7.3 Hz, 2H, C*H*$_2$CH$_3$), 3.35 (q, ^3J(H,H) = 7.3 Hz, 2H, C*H*$_2$CH$_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 298 K): δ = 11.5 (C$_5$*Me*$_5$), 14.0 (N(CH$_2$*C*H$_3$)$_2$), 49.7 (N(*C*H$_2$CH$_3$)$_2$), 110.8 (*C*$_5$Me$_5$), 117.1 and 117.4 (*C*≡N), 127.0 and 129.3 (*C*=*C*), 227.7 (*C*O), 305.1 (Mo≡*C*). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 222 K): δ = 11.5 (C$_5$*Me*$_5$), 13.6 and 14.4 (CH$_2$*C*H$_3$), 49.4 and 49.7 (*C*H$_2$CH$_3$), 110.4 (*C*$_5$Me$_5$), 117.3 and 117.6 (*C*≡N), 126.9 and 128.8 (*C*=*C*), 227.2 (*C*O), 304.8 (Mo≡*C*). EIMS: *m*/*z* = 457 [M$^+$ − CO] 373 [M$^+$ − CO − Et − EtNC].

4.4. Synthesis of Cp*(mnt)(CO)W≡CNEt$_2$ (**3b**)

A solution of 271 mg (0.54 mmol) of **2b** in 25 ml of MeOH was treated at ambient temperature with 154 mg (0.59 mmol) of Na_2(mnt) × DMF and the violet solution was refluxed for 15 min. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CN) absorption of Na_2(mnt) × DMF at 2191 cm^{-1} by those of the product at 2214 and 2205 cm^{-1} in MeOH). The resulting red–brown suspension was worked up in an analogous way followed for **3a** to afford complex **3b** as a rust-coloured solid. M.p. (dec.) 192°C. Yield: 230 mg (75%). Anal. Calc. for $C_{20}H_{25}N_3OS_2W$ (571.42): C, 42.04; H, 4.41; N, 7.35; S, 11.22. Found: C, 41.50; H, 4.47; N, 7.27; S, 11.24%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2212 (m) and 2202 (m) [ν(C≡N)], 1987 (vs) [ν(CO)], 1607 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. IR (MeOH): $\tilde{\nu}$ [cm^{-1}] = 2214 (m) and 2205 (m) [ν(C≡N)], 1986 (vs) [ν(CO)], 1614 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($CD_2Cl_2$, 298 K): δ = 1.24 (br, 6H, N(CH$_2$C*H*$_3$)$_2$), 2.00 (s, 15H, C$_5$*Me*$_5$), 3.37 (q, 4H, N(C*H*$_2$CH$_3$)$_2$). ^{1}H-NMR (CD_2Cl_2, 222 K): δ = 1.07 (t, ^3J(H,H) = 7.4 Hz, 6H, CH$_2$C*H*$_3$), 1.28 (t, ^3J(H,H) = 7.4 Hz, 3H, CH$_2$C*H*$_3$), 1.94 (s, 15H, C$_5$*Me*$_5$), 3.30 (q, 2H, ^3J(H,H) = 7.4 Hz, C*H*$_2$CH$_3$), 3.37 (q, 2H, ^3J(H,H) = 7.4 Hz, C*H*$_2$CH$_3$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): δ = 11.6 (C$_5$*Me*$_5$), 14.5 (N(CH$_2$*C*H$_3$)$_2$), 50.6 (N(*C*H$_2$CH$_3$)$_2$), 109.0 (*C*$_5$Me$_5$), 117.5 and 117.9 (*C*≡N), 130.3 and 132.7 (*C*=*C*), 222.5 (*C*O, ^1J(W,C) = 126.6 Hz), 301.8 (W≡*C*, ^1J(W,C) = 189.4 Hz). EIMS: *m*/*z* = 571 [M$^+$], 543 [M$^+$ − CO], 514 [M$^+$ − CO − Et], 459 [M$^+$ − CO − Et − EtNC], 438 [M$^+$ − CO − Et − CS$_2$], 383 [M$^+$ − CO − Et − EtNC–CS$_2$].

4.5. Synthesis of Cp*(bdt)(CO)Mo≡CNEt$_2$ (**4a**)

Compound **2a** (472 mg, 1.14 mmol) and 200 mg (1.30 mmol) of freshly prepared Li_2(bdt) were weighed in a Schlenk tube, the mixture was suspended in 30 ml of toluene and the suspension stirred for 2 h at ambient temperature. During this time the color of the solution changed from red–violet to brown and precipitation of a white solid (LiCl) was observed. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorption of the starting material at 1997 cm^{-1} by that of **4a** at 1976 cm^{-1}). The solvent was removed in vacuo and the oily residue extracted twice with 20 ml of diethyl ether. The extracts were filtered from LiCl, combined and evaporated to dryness. The residue obtained was washed twice with 10 ml of cold (−78°C) C_5H_{12} and dried in vacuo at 20°C to afford **4a** as a brown solid. M.p. (dec.) 149°C. Yield: 290 mg (53%). Anal. Calc. for $C_{22}H_{29}MoNOS_2$ (483.55): C, 54.65; H, 6.05; N, 2.90. Found: C, 54.41; H, 6.30; N, 2.72%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1983 (vs) [ν(CO)], 1584 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. IR (toluene): $\tilde{\nu}$ [cm^{-1}] = 1976 (vs) [ν(CO)], 1580 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($CDCl_3$, 298 K): δ = 1.24 (t, ^3J(H,H) = 7.3 Hz, 6H, N(CH$_2$C*H*$_3$)$_2$), 1.82 (s, 15H, C$_5$*Me*$_5$), 3.28 (dq, ^2J(H,H) = 13.1 Hz, ^3J(H,H) = 7.3 Hz, 2H, N[C(*H*$_A$)(H$_B$)CH$_3$]$_2$), 3.35 (dq, ^2J(H,H) = 13.1 Hz, ^3J(H,H) = 7.3 Hz, 2H, N[C(H$_A$)(*H*$_B$)CH$_3$]$_2$), 6.65 and 6.70 (m each, 1H each, *H*4/*H*5, bdt), 7.28 and 7.45 (m, 1H each, *H*3/*H*6, bdt). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 298 K): δ = 10.5 (C$_5$*Me*$_5$), 14.3 (N(CH$_2$*C*H$_3$)$_2$), 49.2 (N(*C*H$_2$CH$_3$)$_2$), 109.5 (*C*$_5$Me$_5$), 121.1 and 121.7 (*C*4/*C*5, bdt), 128.3 and 128.8 (*C*3/*C*6, bdt), 144.8 and 148.1 (*C*1/*C*2, bdt), 231.5 (*C*O), 308.0 (Mo≡*C*). EIMS: *m*/*z* = 485 [M$^+$], 457 [M$^+$ − CO], 428 [M$^+$ − CO − Et], 373 [M$^+$ − CO − Et − EtNC], 333 [M$^+$ − CO − Et − EtNC–C$_3$H$_4$].

4.6. Synthesis of Cp(bdt)(CO)W≡CNEt$_2$ (**4b**)*

Compound **2b** (556 mg, 1.11 mmol) and 203 mg (1.32 mmol) of freshly prepared Li$_2$(bdt) were suspended in 30 ml of toluene and the suspension stirred vigorously for 48 h at ambient temperature. During this time the color of the solution changed from red–violet to red–brown. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorption of the starting material at 1980 cm^{-1} by that of **4b** at 1963 cm^{-1}). The suspension was worked up as described for **4a** to afford complex **4b** as a brown, microcrystalline solid. M.p. 123°C. Yield: 540 mg (85%). Anal. Calc. for $C_{22}H_{29}NOS_2W$ (571.46): C, 46.24; H, 5.12; N, 2.45; S, 11.22. Found: C, 45.83; H, 5.29; N, 2.33; S, 11.25%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1969 (vs) [ν(CO)], 1592 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. IR (toluene): $\tilde{\nu}$ [cm^{-1}] = 1963 (vs) [ν(CO)], 1589 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($CDCl_3$, 298 K): $\delta = 1.24$ (t, ^3J(H,H) = 7.2 Hz, 6H, N(CH$_2$C*H*$_3$)$_2$), 1.92 (s, 15H, C$_5$*Me*$_5$), 3.31 (dq, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 7.2 Hz, 2H, N[C(*H*$_A$)(H$_B$)CH$_3$]$_2$), 3.37 (dq, ^2J(H,H) = 13.2 Hz, ^3J(H,H) = 7.2 Hz, 2H, N[C(H$_A$)(*H*$_B$)CH$_3$]$_2$), 6.62 and 6.67 (m each, 1H each, *H*4/*H*5, bdt), 7.35 and 7.51 (m each, 1H each, *H*3/*H*6, bdt). ^{1}H-NMR (CD_2Cl_2, 184 K): $\delta = 1.06$ (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.25 (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.86 (s, 15H, C$_5$*Me*$_5$), 3.27 (m, 2H, C(*H*$_A$)(*H*$_B$)CH$_3$), 3.34 (m, 2H, C(*H*$_A$)(*H*$_B$)CH$_3$), 6.58 and 6.62 (m each, 1H each, *H*4/*H*5, bdt), 7.24 and 7.40 (m each, 1H each, *H*3/*H*6, bdt). ^{13}C{^{1}H}-NMR ($CDCl_3$, 298 K): $\delta = 11.5$ (C$_5$*Me*$_5$), 14.6 (N(CH$_2$*C*H$_3$)$_2$), 49.7 (N(*C*H$_2$CH$_3$)$_2$), 107.5 (*C*$_5$Me$_5$), 121.4 and 122.0 (*C*4/*C*5, bdt), 128.6 and 129.2 (*C*3/*C*6, bdt), 145.6 and 149.5 (*C*1/*C*2, bdt), 226.3 (*C*O), 304.7 (W≡*C*). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 184 K): $\delta = 11.1$ (C$_5$*Me*$_5$), 13.5 (CH$_2$*C*H$_3$), 14.6 (CH$_2$*C*H$_3$), 48.9 (*C*H$_2$CH$_3$), 49.4 (*C*H$_2$CH$_3$), 106.6 (*C*$_5$Me$_5$), 120.8 and 121.4 (*C*4/*C*5, bdt), 128.0 and 128.4 (*C*3/*C*6, bdt), 145.2 and 149.1 (*C*1/*C*2, bdt), 226.5 (*C*O), 303.6 (W≡*C*). EIMS: *m*/*z* = 571 [M$^+$], 543 [M$^+$ − CO], 514 [M$^+$ − CO − Et], 459 [M$^+$ − CO − Et − EtNC].

4.7. Synthesis of Cp(Mebdt)(CO)W≡CNEt$_2$ (**5b**)*

Following the way described for the synthesis of **4a**, the mixture of isomers of **5b** (**5b$_1$**/**5b$_2$**) was isolated as a red–brown solid after treating 543 mg (1.08 mmol) of **2b** with 195 mg (1.16 mmol) of freshly prepared Li$_2$(Mebdt) in 40 ml of toluene for 12h at ambient temperature. M.p. 80°C. Yield: 497 mg (79%). Anal. Calc. for $C_{23}H_{31}NOS_2W$ (585.49): C, 47.18; H, 5.34; N, 2.39; S, 10.95. Found: C, 46.24; H, 5.59; N, 2.37; S, 10.23%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1968 (vs) [ν(CO)], 1591 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. IR (toluene): $\tilde{\nu}$ [cm^{-1}] = 1963 (vs) [ν(CO)], 1589 (s) [$\nu(C_{carbyne}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($C_6D_6$, 298 K): $\delta = 0.87$ (t, ^3J(H,H) = 7.3 Hz, 12H, N(CH$_2$C*H*$_3$)$_2$), 1.80 (s, 30H, C$_5$*Me*$_5$), 2.10 and 2.14 (s each, 3H each, *Me*bdt), 2.71 (m, 8H, N[C(*H*$_A$)(*H*$_B$)CH$_3$]$_2$), 6.59 and 6.65 (dd each, 1H each, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.1 Hz, *H*5, Mebdt), 7.68 and 7.82 (d each, 1H each, ^4J(H,H) = 1.1 Hz, *H*3, Mebdt), 7.75 and 7.90 (d each, 1H each, ^3J(H,H) = 7.7 Hz, *H*6, Mebdt). ^{1}H-NMR ($CDCl_3$, 298 K): $\delta = 1.23$ (t, ^3J(H,H) = 7.3 Hz, 12H, N(CH$_2$C*H*$_3$)$_2$), 1.93 (s, 30H, C$_5$*Me*$_5$), 2.16 and 2.18 (s each, 3H each, *Me*bdt), 3.35 (m, 8H, N[C(*H*$_A$)(*H*$_B$)CH$_3$]$_2$), 6.46 and 6.50 (dd each, 1H each, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.1 Hz, *H*5, Mebdt), 7.17 and 7.33 (d each, 1H each, ^4J(H,H) = 1.1 Hz, *H*3, Mebdt), 7.22 and 7.39 (d each, 1H each, ^3J(H,H) = 7.7 Hz, *H*6, Mebdt). ^{13}C{^{1}H}-NMR ($CDCl_3$, 298 K): $\delta = 11.5$ (C$_5$*Me*$_5$), 14.5 (N(CH$_2$*C*H$_3$)$_2$), 20.3 and 20.6 (*Me*bdt), 49.6 (N(*C*H$_2$CH$_3$)$_2$), 107.4 (*C*$_5$Me$_5$), 122.5 and 123.1 (*C*5, Mebdt), 128.1, 128.6, 129.2, 129.7 (*C*3/*C*6, Mebdt), 130.8 and 131.4 (*C*4, Mebdt), 142.0, 145.4, 146.1 and 149.5 (*C*1/*C*2, Mebdt), 226.4 (*C*O), 304.3 (W≡*C*). EIMS: *m*/*z* = 585 [M$^+$], 557 [M$^+$ − CO], 528 [M$^+$ − CO − Et].

4.8. Synthesis of Cp(Cl)(mnt)W=C(H)NEt$_2$ (**6b**)*

A solution of 274 mg (0.48 mmol) of **3b** in 30 ml of THF was treated at 0°C with a 1 M solution of HCl (0.48 ml, 0.48 mmol) in diethyl ether. The red–brown solution was allowed to warm to r.t. and stirred for 6 h. Afterwards an IR spectrum of the solution was recorded revealing the presence of an intense band at 1515 cm^{-1} ($\nu(C_{carbene}\overset{\cdots}{-}N)$ absorption of **6b**) and the complete consumption of the starting material. The solvent was removed in vacuo, the residue dissolved in 10 ml of CH_2Cl_2, the solution cooled to −78°C and treated with approximately 10 g of silanized silica gel. The suspension was evaporated to dryness at ambient temperature and the resulting powder transferred into a thermostated chromatographic column, which was filled with silanized silica in pentane and kept at 0°C. The product was eluted with diethyl ether, the brown eluate evaporated to dryness and the residue washed with C_5H_{12} and dried in vacuo to afford complex **6b** as an ocherous solid. Yield: 205 mg (74%). Anal. Calc. for $C_{19}H_{26}ClN_3S_2W$ (579.87): C, 39.36; H, 4.52; Cl, 6.11; N, 7.25. Found: C, 39.87; H, 4.79; Cl, 6.20; N, 7.04%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2218 (m) and 2209 (s) [ν(C≡N)], 1516 (vs) [$\nu(C_{carbene}\overset{\cdots}{-}N)$]. ^{1}H-NMR ($CD_2Cl_2$, 298 K): $\delta = 1.04$ (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.34 (t, ^3J(H,H) = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.96 (s, 15H, C$_5$*Me*$_5$), 2.92 (q, ^3J(H,H) = 7.3 Hz, 2H, C*H*$_2$CH$_3$), 3.67 (dq, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 7.3 Hz, 1H, C(*H*$_A$)(H$_B$)CH$_3$), 3.73 (dq, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 7.3 Hz, 1H, C(H$_A$)(*H*$_B$)CH$_3$), 5 (s, 1H, W=C*H*). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 298 K): $\delta = 12.6$ (C$_5$*Me*$_5$), 15.4 and 16.2 (CH$_2$*C*H$_3$), 52.7 and 56.3 (*C*H$_2$CH$_3$), 105.4 (*C*$_5$Me$_5$), 116.7 and 117.4 (*C*≡N), 139.7 and 142.1 (*C*=*C*), 249.1 (W=*C*, ^1J(W,C) = 108.2 Hz).

4.9. Synthesis of $Cp^*(Cl)(bdt)(CO)W{=}C(H)NEt_2$ (**7b**)

A red–brown solution of 490 mg (0.86 mmol) of **4b** in diethyl ether was treated at −35°C with 0.55 ml of a 1 M solution of HCl in diethyl ether and stirred at −35°C. Precipitation of a brown solid was observed. After 2 h an IR spectrum of the supernatant solution was recorded, which revealed that the ν(CO) and $\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$ absorption of the starting material at 1968 and 1588 cm^{-1} had disappeared. The supernatant solution was decanted off and the precipitate washed twice at ambient temperature with 10 ml of diethyl ether and once with 10 ml of C_5H_{12} and dried in vacuo. Golden-brown solid. M.p. (dec. to **9b**) 89°C. Yield: 485 mg (93%). IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2008 (vs) [ν(CO)], 1547 (m) [$\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$]. ^{1}H-NMR ($CD_2Cl_2$, 298 K): δ = 0.82 (t, ^3J(H,H) = 7.2 Hz, 3H, CH_2CH_3), 1.32 (t, br, ^3J(H,H) = 7.2 Hz, 3H, CH_2CH_3), 2.09 (s, 15H, C_5Me_5), 2.25 (dq, ^2J(H,H) = 13.5 Hz, ^3J(H,H) = 7.2 Hz, 1H, $C(H_A)(H_B)CH_3$), 2.31 (dq, ^2J(H,H) = 13.5 Hz, ^3J(H,H) = 7.2 Hz, 1H, $C(H_A)(H_B)CH_3$), 3.88 and 4.01 (br each, 1H each, $C(H_A)(H_B)CH_3$), 7.41 and 7.47 (m each, 1H each, *H*4/*H*5, bdt), 8.25 and 8.32 (m each, 1H each, *H*3/*H*6, bdt), 10.69 (s, 1H, W=C*H*). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): δ = 12.0 and 16.1 (CH_2CH_3), 12.7 (C_5Me_5), 54.2 and 58.1 (CH_2CH_3), 107.0 (C_5Me_5), 125.1 and 126.6 (*C*4/*C*5, bdt), 131.1 and 131.6 (*C*3/*C*6, bdt), 153.5 and 155.0 (*C*1/*C*2, bdt), 216.3 (*C*O, ^1J(W,C) = 131.2 Hz), 240.0 (W=*C*, ^1J(W,C) = 103.8 Hz).

4.10. Synthesis of $Cp^*(Cl)(Mebdt)(CO)W{=}C(H)NEt_2$ (**8b**)

Following the procedure described for **7b**, the mixture of isomers of **8b** (**8b$_1$**/**8b$_2$**) was obtained as a brown solid after treating 207 mg (0.35 mmol) of **7b** with 0.35 ml of a 1 M solution of HCl in diethyl ether at −78°C. Yield: 199 mg (90%). Anal. Calc. for $C_{23}H_{32}ClNOS_2W$ (621.95): C, 44.42; H, 5.19; N, 2.25; S, 10.31. Found: C, 43.67; H, 5.76; N, 2.40; S, 10.38%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2007 (vs) [ν(CO)], 1546 (m) [$\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$]. ^{1}H-NMR ($CD_2Cl_2$, 298K): δ = 0.83 (t, ^3J(H,H) = 7.1 Hz, 6H, CH_2CH_3), 1.33 (t, ^3J(H,H) = 7.1 Hz, 6H, CH_2CH_3), 2.09 (s, 30H, C_5Me_5), 2.32 (q, br, 4H, ^3J(H,H) = 7.1 Hz, CH_2CH_3), 2.54 and 2.55 (s each, 3H each, *Me*bdt), 3.88 and 3.99 (br each, 2H each, $C(H_A)(H_A)CH_3$), 7.26 and 7.31 (dd each, 1H each, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, *H*5, Mebdt), 8.06 and 8.13 (s, br each, 1H each, *H*3, Mebdt), 8.12 and 8.19 (d each, 1H each, ^3J(H,H) = 8.0 Hz, *H*6, Mebdt), 10.65 and 10.67 (s each, 1H each, W=C*H*). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): δ = 11.9 and 15.9 (CH_2CH_3), 12.5 (C_5Me_5), 20.7 and 20.8 (*Me*bdt), 58.1 (CH_2CH_3), 106.8 (C_5Me_5), 126.8, 128.4, 130.4, 130.9, 131.3 (*C*5/*C*3/*C*6, Mebdt), 135.7 and 137.5 (*C*4, Mebdt), 151.0, 152.7, 153.9 and 155.4 (*C*1/*C*2, Mebdt), 216.4, 216.6 (CO), 239.6, 239.7 (W=*C*, ^1J(W,C) = 110.4 Hz, ^1J(C,H) = 137.3 Hz). EIMS: m/z = 593 [$M^+ - CO$], 538 [$M^+ - CO - EtNC$], 508 [$M^+ - CO - EtNC - C_2H_6$], 473 [$M^+ - CO - EtNC - EtH - Cl$], 389 [$M^+ - CO - EtNC - C_2H_6 - Cl - C_4H_4S$].

4.11. Synthesis of $Cp^*(Cl)(bdt)(CO)Mo{=}C(H)NEt_2$ (**7a**) and $Cp^*(Cl)(bdt)Mo{=}C(H)NEt_2$ (**9a**)

A solution of 163 mg (0.34 mmol) of **4a** in 30 ml of diethyl ether was treated at −30°C with a 1 M solution of HCl in diethyl ether (0.34 ml, 0.34 mmol). The mixture was allowed to warm to r.t. and stirred. IR monitoring of the reaction revealed a gradual decrease in intensity of the ν(CO) absorption of **4a** at 1980 cm^{-1}. Precipitation of a brown solid was also observed. After 3 h the reaction was complete and the solvent was removed in vacuo at low temperature. The residue was washed twice with 15 ml of C_5H_{12} and dried in vacuo to afford **7a** as a brown solid. Yield: 173 mg (99%). Compound **7a** was contaminated with some paramagnetic impurity giving rise to broad signals in the ^{1}H-NMR spectrum at 199 K. Compound **7a** could be, however, characterized by IR and $^{13}C\{^1H\}$-NMR spectroscopy. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2020 (vs) [ν(CO)], 1551 (m) [$\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$]. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 199 K): δ = 11.6 and 15.1 (CH_2CH_3), 13.0 (C_5Me_5), 52.6 and 55.1 (CH_2CH_3), 107.8 (C_5Me_5), 123.9 and 125.2 (*C*4/*C*5, bdt), 129.7 and 130.0 (*C*3/*C*6, bdt), 154.8 and 155.3 (*C*1/*C*2, bdt), 221.7 (*C*O), 248.1 (Mo=*C*).

The crude product was dissolved in 20 ml of CH_2Cl_2 and the solution stirred at ambient temperature. IR-monitoring of the reaction revealed a continuous, slow replacement of the absorptions of **7a** by the $\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$ absorption of the product **9a** at 1516 cm^{-1}. After 7 days, complex **7a** had almost been consumed and the solvent was stripped off. The residue was dissolved in diethyl ether and the solution was treated at −78°C with approximately 10 g of silanized silica. The suspension was evaporated to dryness and the resulting powder transferred into a chromatographic column, which was filled with a suspension of silanized silica in C_5H_{12} and kept at 0°C. Elution with C_5H_{12} afforded a small mauve fraction, which was discarded. The product was then eluted with a diethyl ether–C_5H_{12} mixture (1/1) and the orange eluate evaporated to dryness. The residue was washed with 10 ml of C_5H_{12} and dried in vacuo to afford **9a** as a brown solid. Yield: 155 mg (93% rel. to **4a**). Anal. Calc. for $C_{21}H_{30}ClMoNS_2$ (492.00): C, 51.27; H, 6.15; Cl, 7.21; N, 2.85. Found: C, 50.75; H, 6.20; Cl, 6.81; N, 2.75%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1516 (s) [$\nu(\mathrm{C_{carbene}} \stackrel{\cdots}{=} \mathrm{N})$]. ^{1}H-NMR ($CD_2Cl_2$, 298 K): δ = 1.03 (t, ^3J(H,H) = 7.3 Hz, 3H, CH_2CH_3), 1.35 (t, ^3J(H,H) = 7.3 Hz, 3H,

CH_2CH_3), 1.66 (s, 15H, C_5Me_5), 3.02 (q, ^3J(H,H) = 7.3 Hz, 2H, CH_2CH_3), 3.63 (q, ^3J(H,H) = 7.3 Hz, 2H, CH_2CH_3), 7.17 and 7.23 (m each, 1H each, $H4/H5$, bdt), 7.88 and 7.93 (m each, 1H each, $H3/H6$, bdt), 10.82 (s, 1H, Mo = C*H*). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): $\delta = 12.4$ (C_5Me_5), 14.6 and 15.7 (CH_2CH_3), 52.6 and 55.7 (CH_2CH_3), 105.8 (C_5Me_5), 122.8 and 123.8 ($C4/C5$, bdt), 129.1 and 129.5 ($C3/C6$, bdt), 154.7 and 157.0 ($C1/C2$, bdt), 264.2 (Mo=*C*, ^1J(C,H) = 134.8 Hz).

4.12. Synthesis of Cp(Cl)(bdt)W=C(H)NEt$_2$ **(9b)***

4.12.1. Method 1

A solution of 127 mg (0.21 mmol) of **7b** in 20 ml of THF was refluxed for 4 h. During this time the color of the solution changed from brown to greenish. An IR spectrum of the solution was recorded and revealed the presence of a strong band at 1503 cm^{-1} ($\nu(C_{carbene}\overset{\cdots}{-}N)$ absorption of **9b**). The solvent was then removed in vacuo and the residue dissolved in 15 ml of diethyl ether. The solution was filtered and the filtrate evaporated to dryness. The residue was washed twice with 5 ml of C_5H_{12} and dried in vacuo to afford **9b** as olive-green solid. M.p.: 203°C. Yield: 100 mg (83%). Anal. Calc. for $C_{21}H_{30}ClNS_2W$ (579.90): C, 43.50; H, 5.21; Cl, 6.11; N, 2.42. Found: C, 43.43; H, 5.42; Cl, 6.35; N, 2.15%. IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1503 (s) [$\nu(C_{carbene}\overset{\cdots}{-}N)$]. The ^1H-NMR spectrum of the product was identical to that of **9b** obtained following method 3 (vide infra).

4.12.2. Method 2

A Schlenk tube was charged with 136 mg (0.22 mmol) of **7b**, evacuated and placed in an oil bath, which was preheated to 90°C. The Schlenk tube was heated for 30 min. After cooling to r.t. an IR spectrum of a small sample of the solid was recorded in CH_2Cl_2 and revealed that most of **7b** (ν(CO) absorption at 2008 cm^{-1}) had transformed into **9b** ($\nu(C_{carbene}\overset{\cdots}{-}N)$ absorption at 1504 cm^{-1}). Extraction with diethyl ether afforded an olive-green solution, which was concentrated in vacuo to approximately 2 ml, treated with 10 ml of C_5H_{12} and cooled to −30°C. The precipitate obtained was separated from the supernatant solution and dried in vacuo to afford **7b** as an olive-green solid. Yield: 85 mg (66%). The product was characterized by IR spectroscopy.

4.12.3. Method 3

A Schlenk tube was charged with a mixture of 260 mg (0.51 mmol) of $Cp^*(Cl)_3W{=}C(H)NEt_2$ and 94 mg (0.56 mmol) of Li_2bdt and the mixture was suspended in 50 ml of diethyl ether. The red–brown suspension was treated with ultrasound in a water bath for 0.5 h at ambient temperature. The resulting greenish solution was filtered, the residue consisting mainly of LiCl washed once with 10 ml of diethylether and the wash solution combined with the filtrate and evaporated to dryness. The residue was extracted twice with 10 ml of CH_2Cl_2 and the combined extracts were evaporated to dryness in vacuo. The solid obtained was suspended in 10 ml of C_5H_{12}, the suspension stirred for 0.5 h at ambient temperature and then cooled to −40°C. The supernatant solution was discarded and the solid dried in vacuo to afford **9b** as an olive-green solid. Yield: 252 mg (85%). IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 1504 (s) [$\nu(C_{carbene}\overset{\cdots}{-}N)$]. ^1H-NMR ($CDCl_3$, 298 K): $\delta = 1.02$ (t, ^3J(H,H) = 7.1 Hz, 3H, CH_2CH_3), 1.33 (t, ^3J(H,H) = 7.1 Hz, 3H, CH_2CH_3), 1.88 (s, 15H, C_5Me_5), 3.11 (m, 2H, $C(H_A)(H_B)CH_3$), 3.60 (dq, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 7.1 Hz, 1H, $C(H_A)(H_B)CH_3$), 3.66 (dq, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 7.1 Hz, 1H, $C(H_A)(H_B)CH_3$), 7.05 and 7.14 (m, 1H each, ^3J(H3,H4) ≈ ^3J(H5,H6) = 7.8 Hz, ^3J(H4,H5) = 7.0 Hz, ^4J(H3,H5) ≈ ^4J(H4,H6) = 1.2 Hz, $H4/H5$, bdt), 7.88 and 8.01 (m, 1H each, ^3J(H3,H4) ≈ ^3J(H5,H6) = 7.8 Hz, ^4J(H3,H5) ≈ ^4J(H4,H6) = 1.2 Hz, ^5J(H3,H6) = −0.6 Hz, $H3/H6$, bdt), 10.65 (s, 1H, W = C*H*). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 298 K): $\delta = 12.2$ (C_5Me_5), 15.4 and 16.2 (CH_2CH_3), 52.0 and 54.7 (CH_2CH_3), 103.3 (C_5Me_5), 122.8 and 123.8 ($C4/C5$, bdt), 129.2 and 129.5 ($C3/C6$, bdt), 152.7 and 157.2 ($C1/C2$, bdt), 254.4 (W=*C*, ^1J(W,C) = 110.6 Hz). EIMS: $m/z = 579$ [M$^+$], 494 [M$^+$ − EtNC − EtH].

4.13. Cp(Cl)(Mebdt)W=C(H)NEt$_2$ **(10b)***

A solution of **8b** in CD_2Cl_2 was monitored by ^1H- and ^{13}C-NMR spectroscopy at ambient temperature. Decarbonylation of **8b** to give the mixture of isomers of **10b** (**10b$_1$**/**10b$_2$**) occurs slowly and takes several days to go to completion. ^1H-NMR (CD_2Cl_2, 298K): $\delta = 1.02$ (t, ^3J(H,H) = 7.1 Hz, 6H, CH_2CH_3), 1.32 (t, ^3J(H,H) = 7.1 Hz, 6H, CH_2CH_3), 1.86 (s, 30H, C_5Me_5), 2.41 and 2.42 (s each, 3H each, *Me*bdt), 3.10 (q, ^3J(H,H) = 7.1 Hz, 4H, CH_2CH_3), 3.62 (dq, ^2J(H,H) = 13.7 Hz, ^3J(H,H) = 7.1 Hz, 2H, $C(H_A)(H_B)CH_3$), 3.68 (dq, ^2J(H,H) = 13.7 Hz, ^3J(H,H) = 7.1 Hz, 2H, $C(H_A)(H_B)CH_3$), 6.92 and 6.97 (dd each, 1H each, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.7 Hz, $H5$, Mebdt), 7.69 and 7.75 (s, br each, 1H each, $H3$, Mebdt), 7.73 and 7.80 (d each, 1H each, ^3J(H,H) = 8.0 Hz, $H6$, Mebdt), 10.63 and 10.64 (s each, 1H each, W = C*H*). $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 298 K): $\delta = 12.3$ (C_5Me_5), 15.7 (CH_2CH_3), 16.4 (CH_2CH_3), 20.5 and 20.6 (*Me*bdt), 52.1 (CH_2CH_3), 55.2 (CH_2CH_3), 103.6 (C_5Me_5), 124.6 and 125.5 ($C5$, Mebdt), 128.8, 129.4, 129.5, 130.0 ($C3/C6$, Mebdt), 133.0 and 134.0 ($C4$, Mebdt), 150.2, 153.3, 155.0 and 157.9 ($C1/C2$, Mebdt), 255.0 and 255.1 (W=*C*, ^1J(W,C) = 110.6 Hz, ^1J(C,H) = 136.4 Hz).

Table 6
Summary of crystallographic data for the complexes **3b**, **6b** and **9b**

	3b	**6b**	**9b**
Empirical formula	$C_{20}H_{25}N_3OS_2W$	$C_{19}H_{26}ClN_3S_2W$	$C_{21}H_{30}ClNS_2W$
Molecular weight	571.40	579.85	579.88
Crystal color	Dark red	Brown	Green
Crystal size (mm^3)		$0.40\times0.40\times0.40$	$0.64\times0.60\times0.56$
Temperature (K)	200(2)	180(2)	180(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no 2)	$P\bar{2}_1/c$ (no 14)	Pn (no 7)
Unit cell dimensions			
a (Å)	7.971(3)	13.081(3)	8.247(5)
b (Å)	11.710(5)	12.522(3)	17.271(11)
c (Å)	12.963(4)	14.363(3)	8.627(3)
α (°)	95.18(3)	90	90
β (°)	103.30(3)	114.04(2)	115.89(3)
γ (°)	106.69(3)	90	90
V (Å^3)	1111.9(7)	2148.6(8)	1105.4(10)
Z	2	4	2
ρ_{calc} (g cm^{-3})	1.707	1.793	1.742
μ_{Mo-K_α}	5.194	5.703	5.540
$F(000)$	560	1136	572
2Θ min./max. (°)	5.54/52.28	6.22/50.50	4.72/54.88
hkl range	-9, 9/-14, 14/0, 15	-15, 15/-15, 15/-17, 17	-10, 10/0, 22/-10, 10
Total data	10657	13738	4290
Data unique [a]	4034	3864	4270
Data for refinement	3941	3864	4270
R_{int}	0.0784	0.0329	0.0098
Min./max. density [b]	1.800/-2.591	0.749/-0.858	1.107/-0.942
Parameters refined	244	339	236
R_1 [c] [$I>2\sigma(I)$]	0.0368	0.0165	0.0277
wR_2 [d] (all data)	0.1590	0.0379	0.0727
Goodness-of-fit [e] (all data)	1.072	1.044	1.038

[a] [$I>2\sigma(I)$].

[b] e A^{-3}.

[c] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$.

[d] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[e] Goodness of fit $=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$; $F_c^*=kF_c[1+0.001\times F_c^2\lambda^3/\sin(2\Theta)]^{-1/4}$.

4.14. Crystal structure determination of compounds **3b**, **6b** and **9b**

A summary of the crystal data, data collection and refinement for the structures of the complexes **3b**, **6b** and **9b** is given in Table 6. The X-ray structure analyses were performed on a STOE-STADI4 four-circle diffractometer (**9b**) and on a STOE-IPDS diffractometer (**3b**, **6b**) using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda=0.71073$ Å). Ψ-scan was carried out for **9b** (extinction coefficient = 0.0016(3)). Structure solution was performed with direct methods (SHELXS-97, SHELXS-86) and subsequent Fourier-difference synthesis (SHELXL-93, SHELXL-97) without restraints (**9b**: two restraints). Refinement on F^2 was carried out by full-matrix least-square techniques. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined in **3b** isotropically ($U_{iso}=0.08$) and in **6b** free. In **9b** the hydrogen atoms were included using a riding model. Geometrical calculations were performed with PLATON [32] and illustrations with ZORTEP [33].

5. Supplementary data

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 149852 (**3b**), 149853 (**6b**) and 149854 (**9b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www.http:/www.ccdc.cam.ac.uk).

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[1] The following formal electronic classification of the ligands was used resulting in the metal oxidation states of the complexes mentioned in this work: aminomethylene: neutral 2-electron donor ligand bearing an empty π-acceptor orbital; aminocarbyne (aminomethylidyne): cationic 2-electron donor ligand bearing a pair of orthogonal π-acceptor orbitals at different energies; cyclopentadienide: anionic 6-electron donor ligand; halide: 2-electron donor ligand; 1,2-dithiolates: dianionic 4-electron donor ligands. Given this formalism, the metal oxidation state is + IV in the aminomethylene complexes **6b**–**10b**, zero in the aminocarbyne complexes **1a**,**b** and + II in the aminocarbyne complexes **2a**–**5b**, $Cp^*(X)_2W{\equiv}CNEt_2$ (X = EtS, ^{t}BuS, 4-MeC_6H_4S) and $Cp^*(Cl)_2(L)M{\equiv}CNEt_2$ (M = Mo, W; L = ^{t}BuNC, $P(OMe)_3$). Following this formalism Fischer-type Group 6 metal carbene and carbyne complexes have the metal center in the oxidation state 0, Schrock-type Group 6 metal carbene complexes have the metal center in the oxidation state + IV, and Schrock-type Group 6 metal carbyne complexes have the metal center in the oxidation state + II.

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