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Selective synthesis of four- and five-membered metallaheterocycles via C–C bond-forming reactions of η^2-iminoacyl and η^3-1-azaallyl complexes of tungsten with alkyl isocyanides

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Abstract

Efficient procedures for the synthesis of four- and five-membered tungstenaheterocycles are reported, starting from the readily accessible η^2-iminoacyl and η^3-1-azaallyl complexes $Cp^{\star}(CO)_2W[\eta^2\text{-}C(NEt)Me]$ (**1**) and $Cp^{\star}(CO)_2W[\eta^3\text{-}CH_2{\cdots}CH{\cdots}NEt]$ (**2**) ($Cp^{\star} = \eta^5\text{-}C_5Me_5$), respectively. A clean isocyanide insertion into the metal–iminoacyl-carbon bond occurs when **1** is heated with RNC (R = Me, Et), leading to the η^2-1,4-diaza-3-methylbutadien-2-yl complexes $Cp^{\star}(CO)_2\overline{W[C(NR)C(N}Et)Me]$ (**3**: R = Me; **4**: R = Et). Similarly complex **2** reacts with RNC (R = Me, Et), by insertion of the isocyanide into the metal–azaallyl-carbon bond, to afford the metallacyclic aminocarbene complexes $Cp^{\star}(CO)_2\overline{W[C(NHR)C(H)C(H)N}Et]$ (**5**: R = Me; **6**: R = Et). A tautomeric equilibrium between the aminocarbene complexes and their imino counterparts $Cp^{\star}(CO)_2\overline{W[C(NR)CH_2C(H)N}Et]$ (R = Me, Et) is suggested by the H/D exchange of the amino and one vinyl hydrogen observed in the acid-catalyzed reaction of **5** with D_2O to yield $Cp^{\star}(CO)_2\overline{W[C(NDR)C(D)C(H)N}Et]$ (**5′**). Determination of the solid-state structure of **6** by a single-crystal X-ray diffraction study has revealed a "four-legged piano stool" complex with a planar five-membered metallaheterocycle. The intraannular bond lengths indicate π-electron delocalization within the cycle. A close analogy between **5** and **6** and 3-aminopyrroles is discussed in terms of reactivity and spectroscopic and structural data.

Introduction

We previously reported the syntheses and reactions of the electron-rich isocyanide metallates $Na[(\eta^5\text{-}C_5R_5)M(CO)_n(EtNC)_{3-n}]$ (R = H, Me; M = Mo, W; $n = 1, 2$) with carbon-based electrophiles [1–4]. We showed that the course of these reactions is strongly influenced by the nature of the electrophile. "Hard" electrophiles react with the metallates at the isocyanide nitrogen to yield aminocarbyne complexes. Illustrative examples of this approach are the regioselective ethylation of the tungsten compounds $Na[Cp^{\star}W(CO)_n(EtNC)_{3-n}]$ ($n = 1, 2$) with Et_3OBF_4 to yield the diethylaminocarbyne complexes $Cp^{\star}(CO)_n(EtNC)_{2-n}W{\equiv}CNEt_2$ [1,2]. In contrast, "soft" electrophiles react with the metallates at the metal center, as

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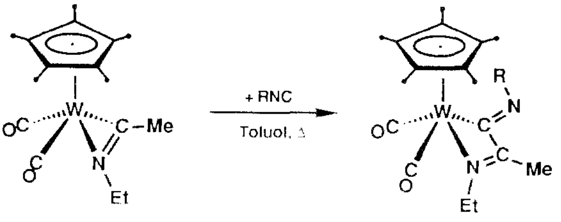
demonstrated by the regioselective methylation of Na[Cp*M(CO)$_2$(EtNC)] (M = Mo, W) with MeI to give the M^{II} methyl complexes *cis/trans*-Cp*M(CO)$_2$-(EtNC)(Me) [3,4].

Both types of product, i.e. aminocarbyne and alkyl complexes, show new and versatile reaction patterns. The diethylaminocarbyne complexes (η^5-C_5R_5)(CO)$_2$M≡CNEt$_2$ (R = H, Me; M = Mo, W) when treated with one equivalent of X_2 (X = Br, I) undergo partial decarbonylation to yield (η^5-C_5R_5)(X)$_2$(CO)-M≡CNEt$_2$ [1,5]. The latter compounds belong to a new class of transition-metal carbyne derivatives that combine features of both Schrock-type alkylidyne and Fischer-type carbyne complexes [6,7]. This is demonstrated by their ability to undergo (like Schrock-type alkylidyne complexes) reductive elimination reactions to give low-valent metal diethylaminocarbyne compounds [8–10] and (like Fischer-type carbyne complexes) oxidative decarbonylation reactions with halogens to give carbonyl-free high-valent metal species [11]. Representative examples of these two types of reactions are the reduction of (η^5-C_5R_5)(Br)$_2$(CO)W≡CNEt$_2$ (R = H, Me) with Na/Hg and R′NC (R′ = Me, Et, ^{t}Bu) to afford the electron-rich diethylaminocarbyne complexes (η^5-C_5R_5)(CO)(R′NC)W≡CNEt$_2$ [2,12], and the oxidation of (η^5-C_5R_5)(Br)$_2$(CO)M≡CNEt$_2$ (R = H, Me; M = Mo, W) with Br$_2$ to yield the 2-azavinylidene compounds (η^5-C_5R_5)(Br)$_4$MCNEt$_2$ [13].

In comparison, the alkyl complexes *cis/trans*-Cp*M(CO)$_2$(EtNC)(R) (M = Mo, W; R = Me, Et) undergo a migratory insertion of the isocyanide ligand into the metal–alkyl bond [14,15]. In the case of molybdenum this insertion results in the exclusive formation of the η^2-iminoacyl complexes Cp*(CO)$_2$Mo[η^2-C(NEt)R] [4]. In contrast, for M = W a mixture of the η^2-iminoacyl and η^3-1-azaallyl complexes Cp*(CO)$_2$W[η^2-C(NEt)R] and Cp*(CO)$_2$W[η^3-CH(R′)⋯CH⋯NEt] (R′ = H, Me) is obtained [3]. Moreover, the η^2-iminoacyl-complexes Cp*(CO)$_2$M[η^2-C(NEt)R] rearrange thermally, via an intramolecular hydrogen shift, to the η^3-1-azaallyl compounds Cp*(CO)$_2$M[η^3-CH(R′)⋯CH⋯NEt] (M = Mo, W; R′ = H, Me) [3,4]. We have continued this work with the goal of devising a metal-mediated preparation of heterocycles, and we report here the high yield syntheses of four- and five-membered tungstenaheterocycles, taking advantage of facile C–C bond forming reactions of the η^2-iminoacyl and η^3-1-azaallyl complexes Cp*(CO)$_2$W[η^2-C(NEt)Me] (**1**) and Cp*(CO)$_2$W[η^3-CH$_2$⋯CH⋯NEt] (**2**) with alkylisocyanides.

Results and discussion

When the η^2-iminoacyl complex **1** is heated with an excess of RNC (R = Me, Et) in toluene at 90 °C an isocyanide insertion in the tungsten–iminoacyl-carbon bond occurs, leading to the four-membered metallaheterocycles **3** and **4** (eq. a). After



(a)

1

3 : R = Me
4 : R = Et

removal of the solvent *in vacuo* and recrystallization from n-pentane, the compounds **3** and **4** are isolated as thermally stable, slightly air-sensitive, red-brown solids in 84 and 81% yields, respectively. They are soluble in CH_2Cl_2, toluene and Et_2O, but only sparingly soluble in n-pentane (especially at low temperature). IR spectroscopic investigation of the reaction solutions indicates the formation of another product in low yield. The two strong ν(CO) absorption bands of the starting material in toluene at 1905 and 1803 cm^{-1} are replaced at the end of the reaction by the two strong ν(CO) absorption bands of the insertion products (**3** and **4**) at 1912 and 1817 cm^{-1}, the latter being accompanied by a weak shoulder on the high energy side ($\sim$ 1830 cm^{-1} in both cases). Separation of the minor product from the four-membered metallacycle **3** or **4** is easy owing to the much higher solubility of the minor product in n-pentane (see Experimental section). Separation was also achieved by column chromatography on an alumina support at 0 °C; the minor product was eluted first with Et_2O and isolated as a yellow microcrystalline solid in $<$ 10% yield, and the main product **3** (**4**) was then eluted with THF. However, use of this purification method results in a slight decrease in the yield of the main product **3** (**4**), apparently due to slow decomposition of the metallacycles **3** and **4** on the alumina column [16].

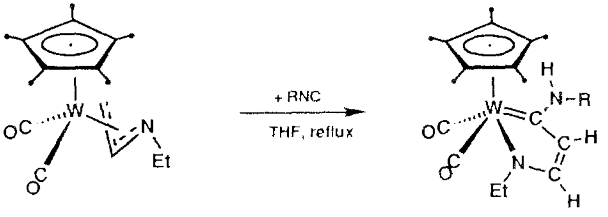
The minor product was identified on the basis of the spectroscopic properties as the metallacyclic carbene complex **5** or **6**, respectively. These compounds are the exclusive products of the reaction of the η^3-1-azaallyl complex **2** with RNC (R = H, Me) (eq. b). The formation of **5** and **6** can be accounted for in terms of a two-step reaction sequence, which involves a slow isomerization of **1** to **2** [3], followed by a rapid isocyanide insertion reaction of **2** with RNC (R = Me, Et) to give **5** and **6**, respectively. The isomerization of **1** to **2** competes with the reaction of **1** with RNC to afford **3** and **4** (eq. a). The low yield of **5** and **6** indicates that the isomerization is slow compared with the insertion reaction.

Experimental evidence for the two-step reaction sequence from **1** to **5** or **6** is provided by (a) the slow rearrangement of **1** to **2** in the absence of RNC in refluxing toluene [3], and (b) the fast reaction of **2** with RNC in refluxing THF to give **5** or **6** (eq. b). An alternative pathway, involving initial formation of **3** and **4** from **1** followed by a slow isomerization of **3** to **5** and **4** to **6**, is excluded, since the four-membered metallacycles **3** and **4** remain unchanged when their solutions in toluene are refluxed for several days.

The molybdenum complex $Cp^\star(CO)_2Mo[\eta^2\text{-}C(NEt)Me]$ has previously been shown to undergo a similar isocyanide insertion reaction with MeNC and EtNC to afford the four-membered molybdenaheterocycles $Cp^\star(CO)_2\overline{Mo[C(NMe)C(N}Et)Me]$ and $Cp^\star(CO)_2\overline{Mo[C(NEt)C(N}Et)Me]$, analogous to **3** and **4**, respectively [4]. The presence of a planar four-membered metallacyclic ring has been confirmed in the case of $Cp^\star(CO)_2\overline{Mo[C(NEt)C(N}Et)Me]$ in the solid state by a single-crystal X-ray diffraction determination. This further showed that the planar skeleton of the dihapto-bonded 1,4-diaza-3-methylbutadien-2-yl ligand (also alternatively described as an (α-imino)iminoacyl ligand) adopts an *anti-s-trans-anti* conformation with alternating single and double bonds [4,17,18]. The spectroscopic properties of the molybdenum complexes closely match those of the tungsten analogues **3** and **4** (see "Spectroscopic investigations") [4]. These results are consistent with the structures suggested in eq. a for the tungsten compounds **3** and **4**.

The η^3-1-azaallyl complex **2** reacts with excess RNC (R = Me, Et) in refluxing

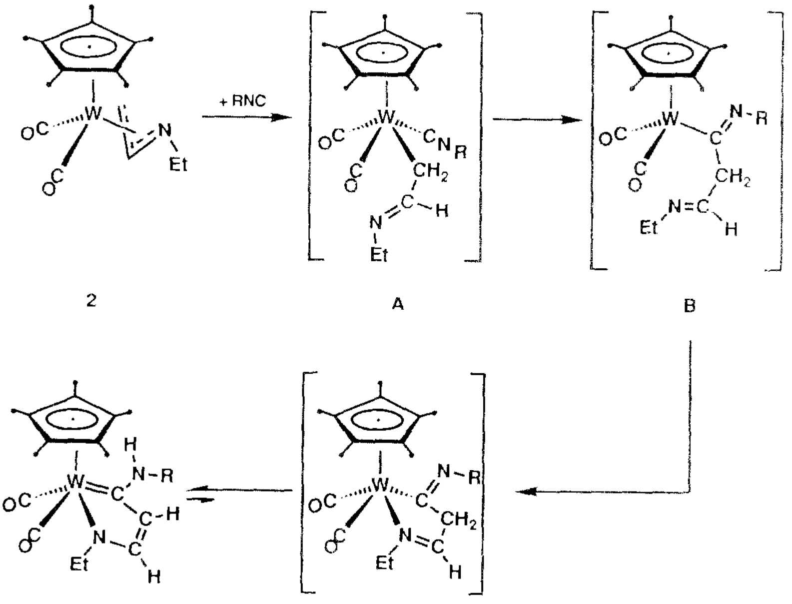
THF to form the metallacyclic aminocarbene complexes **5** and **6** (eq. b). IR spectroscopic monitoring of the reaction shows that there is a quantitative conversion of the 1-azaallyl complex into the five-membered tungstenacycles **5** and **6**, respectively. Thus the two strong ν(CO) absorptions of the starting material in THF at 1927 and 1843 cm^{-1} are replaced by the two strong ν(CO) absorptions of the products at 1915 and 1826 cm^{-1} (**5** and **6**). The compounds **5** and **6** were isolated after purification by column chromatography on alumina as thermally stable, moderately air sensitive, yellow, microcrystalline solids in 92 and 96% yield, respectively. They are soluble in all common organic solvents.



(b)

2

5 : R = Me
6 : R = Et



2 A B

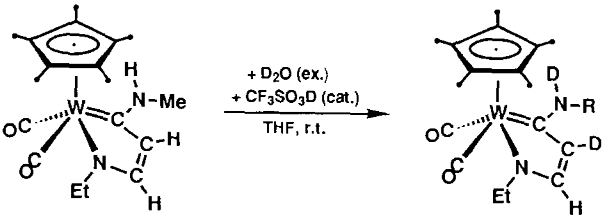
5, 6 C

Scheme 1.

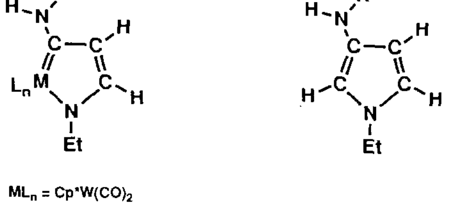
A plausible pathway for the conversion of **1** into **5** and **6** is depicted in Scheme 1. The first step involves displacement of the coordinated azallyl-nitrogen in **2** by the alkyl isocyanide, to give the carbon-bound tungsten enamide **A**. An analogous reaction process was previously reported for the reaction of η^3-oxaallyl complex Cp(CO)$_2$W[η^3-CH$_2$=C(OEt)=O] with PPh$_3$ to give the carbon-bound tungsten enolate Cp(CO)$_3$WCH$_2$C(O)OEt, a complex closely related to the enamide **A** [19].

The intermediate **A** would be then expected to undergo a rapid insertion of the isocyanide ligand into the W–alkyl bond to afford the 16e η^1-iminoacyl complex **B** (an alternative description of **B** is that of a carbon-bound imine complex of tungsten). There is a precedent for such a reaction in the thermal isomerization of the W^{II}-methyl complexes *cis*- and *trans*-$Cp^\star W(CO)_2(EtNC)(Me)$ to yield a mixture of the η^2-iminoacyl and η^3-azaallyl complexes $Cp^\star(CO)_2W[\eta^2\text{-}C(NEt)Me]$ (**1**) and $Cp^\star(CO)_2W[\eta^3\text{-}CH_2\stackrel{..}{-}CH\stackrel{..}{-}NEt]$ (**2**) [3]; this rearrangement is assumed to proceed via the 16e iminoacyl intermediate $Cp^\star(CO)_2W[\eta^1\text{-}C(NEt)Me]$ analogous to **B** (Scheme 1). Finally, coordination of the remote imino-nitrogen to the tungsten center would afford the 18e carbon-bound imine complex **C**, which would then tautomerize to the aminocarbene complex **5** or **6**.

Experimental evidence for the presence of a tautomeric equilibrium between the aminocarbene complex **5** (**6**) and the imine complex **C** (Scheme 1) was provided by the slow, acid-catalyzed reaction of **5** with an excess of D_2O in THF, which resulted in an H/D exchange, at the same rate, of both the NH proton and the proton of the CH group attached to the carbene-carbon, leading to **5′** (eq. c). The equilibrium is shifted well towards the aminocarbene tautomer **5** (**6**) (Scheme 1, last step). This is demonstrated by the IR and NMR spectra, which give no evidence for the presence of the imine tautomer **C**. The prototropic tautomerization of **5** and **6** can be compared with the well known imine–enamine isomerization of organic and transition-metal carbon-bound imines [20–22]. It can also be related to the prototropic tautomerism of heteroaromatic compounds containing amino groups [23,24]. This relationship becomes evident by using for **5** and **6** the well known isolobal analogy between the $Cp^\star W(CO)_2$ fragment and a CH group [25,26]. Thereafter the metallacyclic aminocarbene complexes **5** and **6** can alternatively be viewed as inorganic analogues of the 3-alkylamino-1-ethylpyrroles (Fig. 1).



5 **5′** (c)



5, 6 **a**

Fig. 1. Analogy between aminocarbene complexes **5** and **6** 3-alkylamino-1-ethylpyrrols.

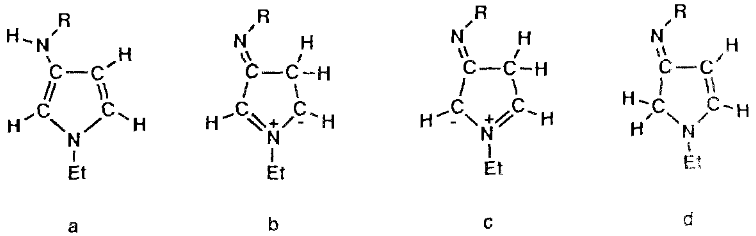


Fig. 2. Possible tautomeric for 3-alkylamino-1-ethylpyrrols.

Experimental evidence for this analogy is provided by the solid-state structure of **6**, which is shown to involve a planar five-membered metallaheterocycle with intraannular bond lengths that indicate that bond delocalization occurs within the ring, as observed for organic pyrroles (see discussion of crystal structure of **6** below). Further support for this analogy is provided by the fact that aminopyrroles are also involved in prototropic tautomerism [23,24,27,28]. It is noteworthy that theoretical studies on 3-aminopyrroles by the SCF-MO π approximation method indicate the amino (enamine) tautomer **a** (analogous to **5** and **6**) to be considerably more stable than the imino (ketimine)-counterparts **b**–**d** (Fig. 2), the tautomers **b** and **c** being analogous to complex **C** (Scheme 1) [24]. These conclusions were supported by experimental work on 2,4,5-trisubstituted 3-aminopyrroles [29–31].

Spectroscopic investigations

IR spectra

Consistent with the formulation of **3**–**6** as "four-legged piano-stool" complexes containing two mutually *cis*-oriented carbonyl ligands, two ν(CO) absorption bands of almost equal intensity are observed in the IR-spectra of the metallacycles. The higher frequency, more intense, band is assigned to the symmetric CO stretching mode (Table 1) [32–34]. These bands are shifted to lower frequency as the solvent polarity is increased (Table 1) [2–4]. A similar trend was observed previously for the ν(CO) absorptions of the tungsten compounds **1** and **2** and the molybdenum complexes $Cp^{\star}(CO)_2Mo[C(NR)C(NEt)Me]$ (R = Me, Et), the latter being analogous to **3** and **4** [3,4].

The four-membered metallacycles **3** and **4** exhibit two characteristic absorptions at low frequency (~ 1630 and 1585 cm^{-1}) that are assigned to the two ν(C=N) vibrations of the dihapto bonded 1,4-diaza-3-methylbutadien-2-yl ligand (Table 1). The position of these bands is not influenced by the solvent polarity, in keeping with previous observations for the analogous molybdenum compounds [4]. In comparison, the aminocarbene complexes **5** and **6** are distinguished by a weak absorption at 1550 cm^{-1} (CH_2Cl_2) that is assigned to the C(carbene)–N stretching vibration. This band reveals the strong interaction of the lone electron pair of nitrogen with the *p*-orbital of the carbene carbon atom; this interaction is represented in valence bond terms by the zwitterionic resonance form **f** (Fig. 3).

Comparable low frequency absorptions have been observed in the IR spectra of other aminocarbene complexes [35,36]. Some characteristic examples are $(CO)_{5-n}L_nM[C(NHMe)Me]$ ($n = 0, 1$; L = PPh_3; M = Cr, W) [ν(CN) in nujol mull: 1530–1580 cm^{-1}] [37], *trans*-$Cp(CO)_2(M'Ph_3)W[C(NHEt)Ph]$ (M′ = Ge, Sn)

Table 1

ν(NH), ν(CO) and ν(CN) absorptions of the tungsten complexes **3**–**6** in cm^{-1}, solvent n-pentane (a), toluene (b), THF (c) and CH$_2$Cl$_2$ (d)

Complex	ν(NH) ν(ND)	ν(CO)	ν(CN)	Solvent
Cp*(CO)$_2$W[C(NMe)C(NEt)Me] (**3**)	–	1923 vs, 1832 vs	1634 w, 1589 vw	a
		1912 vs, 1817 vs	1633 w, 1589 vw	b
		1906 vs, 1804 vs	1635 w, 1590 vw	d
Cp*(CO)$_2$W[C(NEt)C(NEt)Me] (**4**)	–	1921 vs, 1831 vs	1631 w, 1585 vw	a
		1912 vs, 1817 vs	1630 w, 1584 vw	b
		1905 vs, 1803 vs	1631 w, 1583 vw	d
Cp*(CO)$_2$W[C(NHMe)C(H)C(H)NEt] (**5**)	3441 [a]	1926 vs, 1844 vs	1548 w	a
		1915 vs, 1826 vs	1550 w	c
		1912 vs, 1818 vs	1550 w	d
Cp*(CO)$_2$W[C(NDMe)C(D)C(H)NEt] (**5'**)	2549 [a]	1926 vs, 1843 vs	1540 w	a
		1914 vs, 1826 vs	1540 w	c
Cp*(CO)$_2$W[C(NHEt)C(H)C(H)NEt] (**6**)	3426 [a]	1925 vs, 1843 vs	1549 w	a
		1915 vs, 1826 vs	1550 w	c
		1912 vs, 1819 vs	1550 w	d

[a] In KBr.

[ν(CN) in KBr: 1498 cm^{-1}] [38] and (CO)$_5$Cr[C(NEt$_2$)SeR] (R = aryl) [ν(CN) in KBr: 1512–1521 cm^{-1}] [39].

Further experimental evidence for the significant contribution of the resonance form **f** to the overall structure of the aminocarbene complexes is provided by the solid-state structure of **6**, which has a longer W–C(carbene) bond than expected for a typical W=C double bond and a shorter C(carbene)–N bond than expected for a C(sp^2)–N(sp^2) single bond (see discussion of the crystal structure of **6** below).

Finally the aminocarbene complexes **5** and **6** show sharp absorptions at 3441 and 3426 cm^{-1}, respectively (KBr spectra), arising from the ν(NH) stretching vibration of the alkylamino group. This absorption is shifted in the deuterated aminocarbene complex **5'** to 2549 cm^{-1} [ν(N–D)].

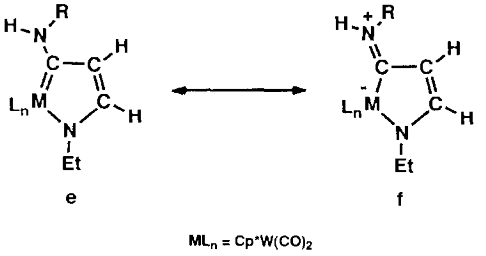


Fig. 3. Resonance forms for the aminocarbene complexes **5** and **6**.

Table 2

^{1}H NMR data for the complexes **3**–**6** in CD_2Cl_2 (a) or C_6D_6 (b) at +20 °C; relative intensities and multiplicities in parentheses, coupling constants in hertz

Komplex	NCH_2CH_3	Cp*	CCH_3	NCH_3	NCH_2CH_3	NH	CH	Solvent
3	1.09 (3,t) ^3J(HH) 7.3	1.99 (15,s)	1.83 (3,s)	3.42 (3,s)	3.12 (1,dq) $^2J(H_BH_A)$ 12.2 $^3J(H_BH_X)$ 7.3; 3.47 (1,dq) $^2J(H_AH_B)$ 12.2 $^3J(H_AH_X)$ 7.3	–	–	a
4	1.10 (3,t) [a] ^3J(HH) 7.3; 1.28 (3,t) ^3J(HH) 7.3	1.98 (15,s)	1.84 (3,s)	–	3.17 (1,dq) [a] $^2J(H_BH_A)$ 12.2 $^3J(H_BH_X)$ 7.3; 3.47 (1,dq) [a] $^2J(H_AH_B)$ 12.2 $^3J(H_AH_X)$ 7.3; 3.36 (1,dq) $^2J(H_BH_A)$ 12.7 $^3J(H_BH_X)$ 7.3; 3.61 (1,dq) $^2J(H_BH_A)$ 12.7 ^3J(H H) 7.3	–	–	a

5	1.13 (3,t) ^3J(HH) 7.3	1.68 (15,s)	–	2.52 (3,d) ^3J(HH) 4.9	3.45 (1,dq) $^2J(H_BH_A)$ 13.1 $^3J(H_BH_X)$ 7.3; 3.55 (1,dq) $^2J(H_AH_B)$ 13.1 $^3J(H_AH_X)$ 7.3	5.09 (1,br)	5.56 (1,d) [b] ^3J(HH) 2.5; 7.50 (1,d) ^3J(HH) 2.5	b
5	1.13 (3,t) ^3J(HH) 7.3	1.68 (15,s)	–	2.51 (3,s)	3.45 (1,dq) $^2J(H_BH_A)$ 13.1 $^3J(H_BH_X)$ 7.3; 3.55 (1,dq) $^2J(H_AH_B)$ 13.1 $^3J(H_AH_X)$ 7.3		7.50 (1,s)	b
6	0.92 (3,t) ^3J(HH) 7.3; 1.13 (3,t) [a] ^3J(HH) 7.3	1.70 (15,s)	–	–	2.97 (2,m); 3.45 (1,dq) [a] $^2J(H_BH_A)$ 12.8 $^3J(H_BH_X)$ 7.3; 3.56 (1,dq) [a] $^2J(H_AH_B)$ 12.8 $^3J(H_AH_X)$ 7.3	5.09 (1,br)	5.58 (1,d) [b] ^3J(HH) 2.5; 7.50 (1,d) ^3J(HH) 2.5;	b

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[a] Methyl and methylene protons of the metal-bonded NCH_2CH_3-group. [b] Proton resonance of the CH group attached to the carbene-carbon.

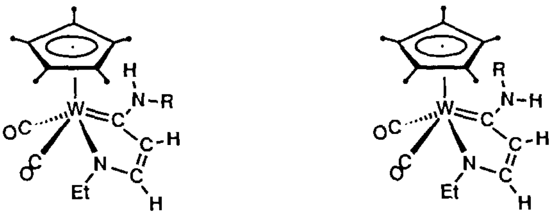
^1H NMR spectra

The ^1H NMR spectra are also consistent with the proposed structures for **3**–**6** (Table 2). All the complexes have a chiral metal center, and so the methylene protons of all ethyl groups are diastereotopic, giving rise to two separate doublets of quartets, as expected for the AB-part of an ABX_3 spin system [$^2J(H_AH_B)$ = 12–13 Hz and $^3J(H_AH_X)$ = $^3J(H_BH_X)$ = 7.3 Hz] [40]. The only exception is provided by the methylene protons of the ethylamino group in **6**, which appear in C_6D_6 as a multiplet centered at δ 2.97. Analysis of this multiplet resonance was achieved with complete spin-decoupling of the methyl protons by irradiation at δ 0.92. The decoupled spectrum of the diastereotopic methylene protons in toluene-d_8 at +20 °C shows two doublets of doublets at δ 2.90 (H_A) and δ 2.94 (H_B) that result from the *geminal* spin–spin coupling between these protons ($^2J(H_AH_B)$ = 12.2 Hz) and the *vicinal* spin–spin coupling between the methylene protons and the NH proton [$^3J(H_AH_X)$ = 5.2 Hz; $^3J(H_BH_X)$ = 4.3 Hz].

The ^1H NMR spectrum of **4** shows two triplets for the methyl protons at δ 1.10 and 1.28, and four doublets of quartets for the diastereotopic methylene protons of the two different N-bonded ethyl groups at δ 3.17, 3.36, 3.47 and 3.61. The resonances at δ 1.10, 3.17 and 3.47 are unequivocally assigned to the methyl and methylene protons of the tungsten bonded NCH_2CH_3 group; this assignment is based on comparison of the ^1H NMR spectra of **3** and **4** and on double resonance experiments (double irradiation of the methyl protons at δ 1.10 converts the methylene proton resonances at δ 3.17 and 3.47 into doublets). Use of the same method also allows the methyl and methylene proton resonances of the two different NCH_2CH_3 groups in **6** to be unequivocally assigned (Table 2).

The ^1H NMR spectra of the aminocarbene complexes **5** and **6** display two characteristic doublet resonances for the protons of the chemically non-equivalent CH groups at δ 5.56 and 7.50 (**5**) and 5.58 and 7.50 (**6**), the two protons being coupled to each other [$^3J(HH)$ = 2.5 Hz]. The higher field doublet is unequivocally assigned to the CH group next to the carbene-carbon (Table 2). This assignment is based on comparison of the ^1H NMR spectra of **5** and **5′**, the latter showing only one singlet resonance at δ 7.50 for the CH proton next to the NCH_2CH_3 group (Table 3). It is noteworthy that similar chemical shifts are observed for the H-2 and H-3 protons in organic pyrroles. Moreover, the *vicinal* coupling constant between these protons ($^3J(23)$ ~ 2.6 Hz) is essentially equal to that between the two CH protons in **5** and **6** [28]. This spectroscopic similarity gives further support to the description of the aminocarbene complexes **5** and **6** as inorganic pyrrole analogues (see Fig. 1, and earlier discussion). The methyl protons of the methylamino group in **5** appear as a doublet at δ 2.52 owing to spin–spin coupling with the NH proton, the latter giving rise to a broad resonance (unresolved quartet) at δ 5.09. These results indicate slow exchange of the amino proton relative to the NMR time scale. The vicinal coupling constant ($^3J(HH)$ = 4.9 Hz) is found in the range observed for other aminocarbene complexes with a H–C–N–H fragment [37,41,42]. By comparison, the analogous methyl protons of the deuterated aminocarbene complex **5′** give rise to a singlet at δ 2.51, in which the $^3J(HD)$ coupling is not resolved (Table 2).

Hindered rotation of the alkylamino group about the C(carbene)–N bond is expected for the aminocarbene complexes **5** and **6**, leading to rotational isomers (Fig. 3, Fig. 4). Rotational barriers higher than 25 kcal/mol have been observed for other aminocarbene complexes, e.g. the M^0 derivatives $(CO)_5M[C(NHR)R']$ (M =



cis *trans*

Fig. 4. Two possible isomers for the aminocarbene complexes **5** and **6**.

Cr, W; R, R′ = alkyl), allowing isolation of rotamers with different spectroscopic and physical properties [36,37,41–43]. The ^{1}H NMR spectra of **5** and **6** in toluene-d_8 are not temperature dependent within the range −80 to +20 °C. Moreover, they indicate the presence of only one isomer, which on the basis of the X-ray diffraction study of **6** can be assumed to have a *cis* structure (Fig. 4).

These results are consistent with the solution IR spectra of **5** and **6**, which show only two ν(CO) absorptions (see discussion of the IR spectra). This implies that the *cis*-isomer is the thermodynamically favored one, perhaps for steric reasons. This implication is supported by a molecular model study of **6** by use of the program MACMOMO with the bond lengths and angles of **6** obtained from the solid-state structure determination (see results on crystal structure of **6**) [44]. This indicates that there is severe steric repulsion between the methylene group of the ethylamino substituent and one CO ligand in the *trans*-isomer (Fig. 4).

^{13}C NMR spectra

Further support for the assigned structures of **3–6** is provided by the ^{13}C NMR spectra (Table 3). Two different environments are observed for the inequivalent carbonyl ligands in **3–6**. Both CO resonances are accompanied by satellites arising from ^{183}W–^{13}C coupling. The ^1J(WC) coupling constant (146–160 Hz) are found within the range observed for other tungsten carbonyl complexes [45,46].

The four-membered metallacycles **3** and **4** are characterized by two low-field resonances for the imino-carbons at δ 179.3 and 190.6 (**3**) and 176.7 and 190.7 (**4**). The higher field signal (**3**: δ 179.3; **4**: δ 176.7) is accompanied by tungsten satellites (**3**: ^1J(WC) = 61.0 Hz; **4**: ^1J(WC) = 60.5 Hz) and is therefore unequivocally assigned to the tungsten bonded imino-carbon (Table 3). The five-membered metallacycles **5** and **6** are characterized by one low-field resonance for the aminocarbene-carbon at δ 222.6 [^1J(WC) = 89.1 Hz] and 221.8 [^1J(WC) = 89.1 Hz], respectively. Comparable chemical shifts of the carbene carbons and ^1J(WC) coupling constants have been found for other low-valent tungsten aminocarbene complexes, such as $(CO)_5W[C(NMe_2)Me]$ [δ_C 253.3 ($CDCl_3$, r.t.); ^1J(WC) = 92.8 Hz] [47], $(CO)_5W[C(NMe_2)C(H)C(Ph)NMe_2]$ [δ_C 242.7 ($CDCl_3$, r.t.); ^1J(WC) = 89.1 Hz] [47], $[Cp(CO)_3W[C(H)NMe_2]]BF_4$ [δ_C 215.5 ($(CD_3)_2SO$, r.t.); ^1J(WC) = 70 Hz] [48] and *cis*-$[Cp^*(CO)_2(EtNC)W[C(H)NEt_2]]PF_6$ [δ_C 232.6 (CD_2Cl_2, r.t.); ^1J(WC) = 85.4 Hz] [49]. In addition the aminocarbene complexes **5** and **6** display two resonances at δ 105.2 and 166.6 (**5**) and 105.5 and 166.6 (**6**) for the CH units of the five-membered ring. Both resonances appear as doublets in the ^{1}H-coupled ^{13}C NMR spectrum of **6**, the ^1J(CH) coupling constant (155.8 and 155.3 Hz) being indicative of a C(sp^2)–H bond

Table 3

^{13}C NMR data for the complexes **3–6** in CD_2Cl_2 (a) or C_6D_6 (b) at +20 °C

Complex	$C_5(\mathit{C}H_3)_5$	$C\mathit{C}H_3$	$NCH_2\mathit{C}H_3$	$N\mathit{C}H_2CH_3$; $N\mathit{C}H_3$	$\mathit{C}_5(CH_3)_5$	$\mathit{C}H$	C=N; W=C	CO	Solvent
3	11.4	12.4	14.0	47.8; 48.0	104.9	–	179.3 [a]; ^1J(WC) 61.0; 190.6	252.1 ^1J(WC) 159.9; 257.4 ^1J(WC) 155.0	a
4	11.4	12.4	14.0 [b]; 16.3	48.1 [b]; 55.4	104.9		176.7 [a] ^1J(WC) 60.5; 190.7	252.3 ^1J(WC) 159.5; 257.7 ^1J(WC) 155.4	a
5	10.3	–	17.5	33.4 57.2 [b]	102.3	105.2; 166.6	222.6 ^1J(WC) 89.1	250.8 ^1J(WC) 146.5; 251.6 ^1J(WC) 148.9	b
5′	10.2	–	17.5	33.4 57.2 [b]	102.4	105.2 ^1J(CD) 24.1; 166.6	222.4	250.7 251.5	b
6	10.2 ^1J(CH) 127.0		14.5 ^1J(CH) 126.5 17.5 [b] ^1J(CH) 126.4	41.4 ^1J(CH) 136.4; 57.2 [b] ^1J(CH) 136.1	102.3	105.5 ^1J(CH) 155.8; 166.6 ^1J(CH) 155.3	221.8 ^1J(WC) 89.1	250.6 ^1J(WC) 146.5; 251.5 ^1J(WC) 148.9	b

[a] Signal for the tungsten-bonded imino-carbon. [b] Methyl- and methylene-carbon resonance of the tungsten-bonded NCH_2CH_3-group.

Table 4

Mass spectra of the complexes **4** and **6**; m/z values relative to the ^{14}W isotope

Complex	m/z	tentative assignment
4	500	M^+
	472	$[M-\mathrm{CO}]^+$
	445	$[M-\mathrm{EtNC}]^+$
	444	$[M-2\,\mathrm{CO}]^+$
	417	$[M-\mathrm{CO}-\mathrm{EtNC}]^+$
	389	$[M-2\,\mathrm{CO}-\mathrm{EtNC}]^+$
	387	$[M-\mathrm{CO}-\mathrm{EtNC}-\mathrm{C_2H_6}]^+$ (base peak)
	359	$[M-2\,\mathrm{CO}-\mathrm{EtNC}-\mathrm{C_2H_6}]^+$
6	500	M^+
	472	$[M-\mathrm{CO}]^+$
	444	$[M-2\,\mathrm{CO}]^+$ (base peak)
	442	$[M-\mathrm{CO}-\mathrm{C_2H_6}]^+$

[50]. An unequivocal assignment of the upfield shifted signal at δ 105.2 (**5**) and 105.5 (**6**) to the CH group attached to the carbene carbon is achieved by comparison of the ^{13}C{^{1}H} NMR spectra of **5** and **5′**. The latter is distinguished by a triplet resonance at δ 105.2, which is assigned to the carbene-carbon attached CD-group [^1J(CD) = 24.1 Hz].

Mass spectra

The four-membered tungstenacycle **4** gives, under EI conditions, a similar fragmentation pattern to that of the molybdenum analogue $\mathrm{Cp^{\star}(CO)_2\overline{Mo[C(NEt)}}$-$\mathrm{\overline{C}(NEt)Me]}$ [4]. It involves loss of the CO ligands, the inserted ethylisocyanide group, and ethane (Table 4). For the metallacyclic aminocarbene complex **6** there is successive loss of the two CO ligands from the parent molecule ion M^+ (m/z = 500), followed by elimination of ethane.

Crystal structure of **6**

The molecular structure of **6** was determined by a single crystal X-ray diffraction study. An ORTEP plot of the compound with the atom numbering scheme is given in Fig. 5. Selected bond distances and angles are listed in Table 5 and fractional coordinates in Table 6. The coordination geometry around the tungsten atom in **6** can be conveniently described as square pyramidal, with the Cp* ligand at the apex. The basal plane of the pyramid is defined by the carbonyl carbons C(1) and C(2) and the tungsten-ligated atoms of the metallacycle N(1) and C(5) (the maximal deviation from the least squares plane is 0.4 pm). This plane is essentially parallel to the Cp* ring plane, the dihedral angle between the two planes being 3°. The orthogonal distance of the tungsten atom from the basal plane is 92.8 pm and that from the Cp* ring plane 200.2 pm, the latter distance being typical for complexes containing a $\mathrm{Cp^{\star}W(CO)_2}$ fragment [51,52]. The *cis* OC–W–CO and L–W–L′ bond angles [C(1)–W–C(2) = 75.0(3)°; N(1)–W–C(5) = 74.3(2)°] and the *trans* OC–W–L and OC–W–L′ bond angles [N(1)–W–C(1) = 125.1(3)°; C(2)–W–C(5) = 126.3(3)°] of **6** are also within the range found for other "four-legged piano-stool" complexes of the type *cis*-$\mathrm{CpM(CO)_2LL'}$ [53]. The Cp* ring is slightly slipped,

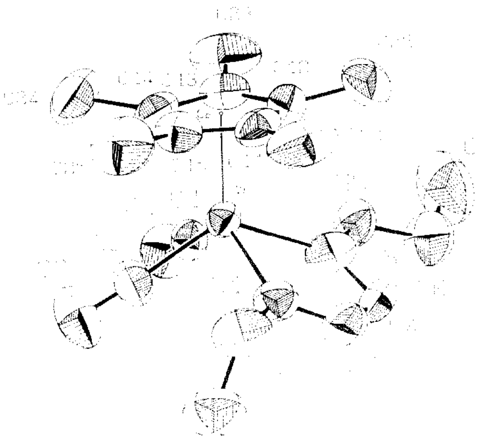


Fig. 5.

probably owing to the *trans* effect of the carbonyl ligands; this is indicated by the lengthening of the W–ring-carbon distances *trans* to the carbonyls [W–C(11) and W–C(12)]. Such ring-slip distortions have been previously reported for other Cp* complexes and treated theoretically [53–56].

The metal carbonyl linkages are approximately linear, the W–C(1)–O(1) and W–C(2)–O(2) bond angles being 177.1(6)° and 175.0(8)°, respectively. The W–C_{CO} bond distances [W–C(1) = 189.9(7) pm; W–C(2) = 195.3(7) pm] are found to be quite close to those of the η^3-1-azaallyl complex **2** [3]. They are, however, consider-

Table 5

Selected bond distances (pm) and bond angles (°) for **6**, with estimated standard deviations [a]

W–N(1)	216.0(5)	N(1)–W–C(1)	125.1(3)
W–C(1)	189.9(7)	N(1)–W–C(2)	83.7(3)
W–C(2)	195.3(7)	N(1)–W–C(5)	74.3(2)
W–C(5)	217.9(6)	C(1)–W–C(2)	75.0(3)
W–C(11)	239.0(6)	C(1)–W–C(5)	78.9(3)
W–C(12)	236.2(7)	C(2)–W–C(5)	126.3(3)
W–C(13)	231.9(6)	Cp*–W–C(1)	120
W–C(14)	227.5(6)	Cp*–W–C(2)	119
W–C(15)	232.2(6)	Cp*–W–N(1)	115
W–Cp*	201	Cp*–W–C(5)	114
C(1)–O(1)	119.8(8)	W–N(1)–C(3)	116.5(5)
C(2)–O(2)	114.7(8)	W–N(1)–C(8)	126.4(5)
N(1)–C(3)	130.8(9)	W–C(1)–O(1)	177.1(6)
N(1)–C(8)	146.6(9)	W–C(2)–O(2)	175.0(8)
C(3)–C(4)	137(1)	C(3)–N(1)–C(8)	117.1(6)
C(4)–C(5)	141.9(9)	N(1)–C(3)–C(4)	120.1(7)
N(2)–C(5)	134.5(7)	C(3)–C(4)–C(5)	114.3(7)
N(2)–C(6)	144.9(9)	C(4)–C(5)–N(2)	121.3(6)
		W–C(5)–C(4)	114.5(5)
		W–C(5)–N(2)	123.9(5)
		C(5)–N(2)–C(6)	124.7(6)

[a] Cp* denotes the center of the pentamethylcyclopentadienyl ring.

Table 6

Fractional atomic coordinates and their estimated standard deviations for non-hydrogen atoms in **6** [a]

Atom	x	y	z	U_{eq}
W	0.01837(1)	−0.26368(1)	0.15379(3)	0.042
O1	0.1013(3)	−0.2306(3)	−0.1163(6)	0.080
C1	0.0685(3)	−0.2420(3)	−0.0119(8)	0.052
C2	−0.0168(4)	−0.3111(3)	−0.0116(8)	0.065
O2	−0.0332(3)	−0.3399(3)	−0.1119(7)	0.095
N1	−0.0775(2)	−0.2351(3)	0.1876(7)	0.063
C3	−0.0869(4)	−0.1751(4)	0.2129(9)	0.071
C4	−0.0371(4)	−0.1340(4)	0.2098(9)	0.067
N2	0.0742(3)	−0.1281(2)	0.1689(9)	0.066
C5	0.0210(3)	−0.1621(3)	0.1740(8)	0.081
C6	0.0773(4)	−0.0613(3)	0.197(1)	0.088
C7	0.1402(7)	−0.0415(5)	0.217(1)	0.133
C8	−0.1332(3)	−0.2752(4)	0.180(1)	0.078
C9	−0.1708(4)	−0.2681(5)	0.041(1)	0.102
C11	0.0136(4)	−0.3022(4)	0.4023(7)	0.058
C12	0.0649(4)	−0.2626(4)	0.3914(7)	0.061
C13	0.1075(3)	−0.2885(3)	0.2884(8)	0.057
C14	0.0792(3)	−0.3444(3)	0.2323(8)	0.056
C15	0.0215(3)	−0.3519(3)	0.3044(8)	0.057
C21	−0.0422(5)	−0.2959(5)	0.504(1)	0.093
C22	0.0789(6)	−0.2092(5)	0.489(1)	0.094
C23	0.1729(4)	−0.2685(4)	0.257(1)	0.094
C24	0.1115(5)	−0.3921(4)	0.132(1)	0.094
C25	−0.0181(5)	−0.4100(4)	0.291(1)	0.098
Cp*	0.057	−0.310	0.325	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix.

ably shorter than the W–C_{CO} bond distance of $W(CO)_6$ [W–C_{CO} = 205.8(3) pm], which indicates extensive $d\pi$–$p\pi^*$ back-bonding to the carbonyls in **6** [57]. These results are consistent with the appearance in the IR spectra of **5** and **6** of ν(CO) absorptions at rather low frequency. The W–C bond distance for the carbonyl *trans* to the carbene ligand is longer than that for the carbonyl located *trans* to the imino nitrogen, owing to the lower σ-donor/π-acceptor ratio of the carbene moiety [36].

A striking feature of the structure is the planarity of the five-membered metallacycle, the maximal deviation from the least squares plane being 4 pm. The planarity of the five-membered metallacycle is also reflected in the sum of 540° for the five intraannular bond angles, this value being that for an ideal planar pentagon. The amino-nitrogen and methylene-carbon atoms of the ethylamino group N(2) and C(6) as well as the N(1)-attached methylene-carbon atom C(8) also lie in the plane of the metallacycle (maximal deviation from the least-squares plane defined by the atoms W, N(1), N(2), C(3), C(4) C(5), C(6) and C(8) is 8 pm).

The W–C(carbene) bond length [W–C(5) = 217.9(6) pm] is long in comparison with the corresponding distances in non-heteroatom stabilized W^{II} carbene complexes such as *trans*-$Cp(CO)_2(SnPh_3)W[C(H)Tol]$ [W–C(carbene) = 203.2(7) pm] [58] and $Cp_2W[C(H)Ph]$ [W–C(carbene) = 205(2) pm] [59]. The adjacent C(carbene)–N bond [N(2)–C(5) = 134.5(7) pm] is intermediate in length between that expected for a C(sp^2)–N(sp^2) single (144 pm) and a C(sp^2)=N(sp^2) double bond (127 pm) [60–62]. Both of these features reflect reduced back-bonding from tungsten to carbene-carbon and a high degree of π-bonding between the carbene-carbon and amino-nitrogen atom, which in valence bond terms implies a strong contribution of the zwitterionic resonance form **f** to the overall structure of **6** (Fig. 3). The sum of angles around the carbene carbon is 360°, consistent with a sp^2-hybridized carbon atom. The C(4)–C(5) bond distance (141.9(9) pm) is shorter and the C(3)–C(4) bond distance (137(1) pm) slightly longer than that expected for a C(sp^2)–C(sp^2) single (148 pm) and a C(sp^2)=C(sp^2) double bond (134 pm), respectively [63–65]. Similarly, the N(1)–C(3) bond (130.8(9) pm) is intermediate in length between that expected for a C(sp^2)–N(sp^2) single (144 pm) and a C(sp^2)=N(sp^2) double bond (127 pm) (see C(carbene)–N bond distance above). The W–N(1) bond length (216.0(5) pm) is similar to that in the η^3-1-azaallyl complex **2** (218.6(5) pm) [3]. The sum of the angles around N(1) is 360°, indicating sp^2 hybridization of the nitrogen atom. These results provide structural evidence for π electron delocalization in the metallacyclic ring, and illustrate the close relationship between **6** and an organic pyrrole.

Conclusion

The η^2-iminoacyl complex **1** and the η^3-1-azaallyl complex **2** can be readily obtained by methylation of the tungsten(0) metallate Na[Cp*W(CO$_2$(EtNC)] with MeI. Both compounds undergo clean insertion reactions with alkyl isocyanides to form tungstenaheterocycles.

In a reaction fully analogous to that of the corresponding molybdenum compound, complex **1** affords the η^2-1,4-diaza-3-methylbutadien-2-yl complexes Cp*(CO)$_2$W[C(NR)C(NEt)Me] (**3**, **4**) when treated with RNC (R = Me, Et). Preliminary studies show that these four-membered metallaheterocycles are selectively alkylated at the exocyclic imino-nitrogen to yield 1-metalla-2-azacyclobutadiene complexes [16]. The latter compounds are of particular interest because they are isoelectronic with metallacyclobutadiene complexes, which are important intermediates in the metathesis of alkynes [66,67].

By contrast, the η^3-1-azaallyl complex **2** reacts with RNC to yield the five-membered tungstenacycles Cp*(CO)$_2$W[C(NHR)C(H)C(H)NEt] (**5**, **6**). These compounds can be regarded as inorganic pyrrole analogues in terms of reactivity and spectroscopic and structural data. Further aspects of this analogy, with a view to the metal-mediated synthesis of heterocycles, are currently under investigation.

Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane, toluene, Et$_2$O and THF over Na/benzophenone), distilled under nitrogen and stored over 4-Å molecular sieves prior to use. All column chromatography was performed on neutral alumina (Merck, activity I, 0.063–0.2 mm, dried *in vacuo* and stored under nitrogen) as the stationary phase in a thermostated column of 30 cm length and 1.5 cm diameter.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were recorded on a Nicolet DX 5 FT spectrophotometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded in dry, deoxygenated methylene-d_2 chloride, benzene-d_6, or toluene-d_8 on a Jeol GX 400 instrument. Chemical shifts were referenced to residual solvent signals (CD_2Cl_2 δ_H 5.32 and δ_c 53.8 ppm; C_6D_6 δ_H 7.15 and δ_C 128.0 ppm; C_7D_8 δ_H 2.03 and δ_C 20.4 ppm). Mass spectra were obtained with Finnigan MAT 311 A and MAT 90 spectrometers.

The synthesis of $Cp^{\star}W(CO)_2[\eta^2\text{-}C(NEt)Me]$ (**1**) and $Cp^{\star}(CO)_2W[\eta^3\text{-}CH_2{\overset{\dots}{-}}CH{\overset{\dots}{-}}NEt]$ (**2**) has been described previously [3]. MeNC and EtNC were prepared by published procedures [68,69], distilled, and stored under nitrogen at −30 °C.

1. $Cp^{\star}(CO)_2\overline{W[C(NMe)C(N}Et)Me]$ *(3)*

A solution of 240 mg (0.54 mmol) of **1** in 100 ml of toluene was treated with 0.088 ml (1.62 mmol) of MeNC and the mixture heated at 90 °C until the reaction was complete (IR monitoring). The resulting red-brown solution was evaporated to dryness, the residue suspended in 20 ml pentane, and the suspension cooled to −78 °C. The pale orange solutions was decanted and the residual red-brown solid dried *in vacuo* at room temperature, M.p.: 168 °C (dec.). Yield: 220 mg (84%). Found: C, 44.02; H, 5.35; N, 5.61; O, 7.04; W, 37.34. $C_{18}H_{26}N_2O_2W$ (486.26) calc.: C, 44.46; H, 5.39; N, 5.76; O, 6.58; W, 37.81%.

2. $Cp^{\star}(CO)_2\overline{W[C(NEt)C(N}Et)Me]$ *(4)*

A solution of 230 mg (0.52 mmol) of **1** in 40 ml of toluene was treated with 0.10 ml (1.35 mmol) of EtNC and the mixture heated at 90–100 °C until reaction was complete (IR monitoring). The resulting red-brown solution was worked up as described in *1* to give complex **4** as a red-brown solid. M.p.: 109 °C. Yield: 210 mg (81%). Found: C, 45.79; H, 5.76; N, 5.53; O, 6.57; W, 36.21. $C_{19}H_{28}N_2O_2W$ (500.29) calc.: C, 45.61; H, 5.64; N, 5.60; O, 6.40; W, 36.75%.

3. $Cp^{\star}(CO)_2\overline{W[C(NHMe)C(H)C(H)N}Et]$ *(5)*

To a solution of 190 mg (0.43 mmol) of **2** in 30 ml of THF was added 0.046 ml (0.85 mmol) of MeNC and the mixture was refluxed for 2 h. The resulting yellow solution was evaporated to dryness and the residue purified by chromatography on alumina at 0 °C. Elution with Et_2O afforded a yellow band, from which complex **5** was isolated as a yellow, microcrystalline solid after evaporation of the solvent and crystallization of the residue from the minimum amount of pentane. M.p.: 167 °C. Yield: 190 mg (92%). Found: C, 44.83; H, 5.51; N, 5.67; O, 6.96; W, 36.90. $C_{18}H_{26}N_2O_2W$ (486.26) calc.: C, 44.46; H, 5.39; N, 5.76; O, 6.58; W, 37.81%.

4. $Cp^{\star}(CO)_2\overline{W[C(NDMe)C(D)C(H)N}Et]$ *(5′)*

A solution of 100 mg (0.21 mmol) of **5** in 15 ml THF was treated with 0.1 ml (5.53 mmol) D_2O and 0.9 μl (0.01 mmol) CF_3SO_3D and the mixture stirred for several days at room temperature. The resulting slightly cloudy solution was evaporated to dryness and the residue dissolved in pentane. The solution was filtered and the solvent removed from the filtrate under reduced pressure to yield **5′** as a yellow solid. Yield: 90 mg (90%). The product was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

5. $Cp^{\star}(CO)_2\overline{W[C(NHEt)C(H)C(H)NEt]}$ (**6**)

A solution of 260 mg (0.58 mmol) of **2** in 30 ml of THF was treated with 0.092 ml (1.24 mmol) of EtNC and the mixture refluxed until the reaction was complete ((IR monitoring). The resulting yellow solution was evaporated to dryness and the residue purified by column chromatogaphy as described under **3** to yield complex **6** as a yellow microcrystalline solid. M.p.: 127 °C. Yield: 280 mg (96%). Found: C, 46.04; H, 5.71; N, 5.59; W, 36.29. $C_{19}H_{28}N_2O_2W$ (500.29) calc.: C, 45.61; H, 5.64; N, 5.60; W, 36.75%.

6. *Structure determination of* **6**

Suitable crystals were obtained as red plates upon cooling a saturated n-pentane solution of **6** from room temperature to −78 °C. Complex **6** crystallizes in the tetragonal space group $P\bar{4}2_1c$ (Int. Tables. No. 114). Unit cell constants were obtained by centering and least squares refinement of 15 reflections at high θ values ($a = b = 2234.5(2)$ pm, $c = 902.7(1)$ pm; $V = 4113 \times 10^6$ pm^3, $Z = 8$, $\rho_{calc} = 1.62$ g/cm^3).

Data collection was performed on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 71.073$ pm) at room temperature (23 ± 3 °C). Intensity data for 7941 reflections in the range $1.0° \leq \theta \leq 25.0°$ ($-h$, $\pm k$, l) were collected by an ω-scan range of 0.9° and a stationary background determination at 0.7 °C from each reflection. Scan speed ranged from 0.7 to 29.3°/min. The intensity data were corrected for Lorentz and polarisation effects and for absorption (empirical correction, 9 reflections, $\mu = 53.8$ cm^{-1}). During data collection a decay of 5% was observed but not corrected. After merging, 3615 of 3622 unique reflections ($I > 0.0$) were used in the refinement. The structure was solved by the Patterson method and subsequent least-squares refinement cycles and difference Fourier syntheses. All atoms are refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions (C–H = 95 pm) and included in the structure factor calculation but not refined (254 parameters). Refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$ and converged yielding R-values of $R = 0.036$ and $R_w = 0.025$. A refinement in the enantiomorphous setting gave R-values of $R = 0.046$ and $R_w = 0.038$. Residual electron density maxima and minima were 1.06 and -0.94 e$^-$/Å^3 near the tungsten atom. Atomic scattering parameters were taken from ref. 70. Anomalous dispersion effects were included for all non-hydrogen atoms [71]. All calculations were performed on a MicroVAX 3100 computer with standard programs [72–75]. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55499, the names of the authors, and the journal citation.

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