Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 3700–3713
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Bis(amino)allenylidene complexes by displacement of the MeO group in methoxy allenylidene complexes of chromium and tungsten. Synthesis, DFT calculations and solid-state structures of new bis(amino)allenylidene complexes

Matthias Drexler, Thomas Haas, Sze-Man Yu, Henning S.g. Beckmann, Bernhard Weibert, Helmut Fischer *

Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany

Received 4 February 2005; received in revised form 17 March 2005; accepted 17 March 2005
Available online 15 June 2005

Abstract

Pentacarbonyl dimethylamino(methoxy)allenylidene tungsten, $[(CO)_5W{=}C{=}C{=}C(OMe)NMe_2]$ (**1b**), reacts with one equivalent of *primary* amines, H_2NR, by selectively replacing the methoxy group to give dimethylamino(amino)allenylidene complexes, $[(CO)_5W{=}C{=}C{=}C(NHR)NMe_2]$. When the amine is used in excess both terminal groups, OMe as well as NMe_2, are replaced by the *primary* amino group giving $[(CO)_5W{=}C{=}C{=}C(NHR)_2]$. The NHR substituent in these complexes may be modified by deprotonation with LDA followed by alkylation. The replacement of the methoxy group in **1b** by a *secondary* amino group, NR_2, can be achieved by a stepwise process. Addition of $Li[NR_2]$ to the C_γ atom of **1b** affords an alkynyl tungstate. Subsequent OMe^- elimination induced by TMS-Cl/SiO_2 yields the allenylidene complexes $[(CO)_5W{=}C{=}C{=}C(NR_2)NMe_2]$. When bidentate diamines are used instead of monoamines both substituents, OMe and NMe_2, are replaced and allenylidene complexes are formed in which C_γ constitutes part of a 5-, 6-, or 7-membered heterocycle. The reaction of $[(CO)_5Cr{=}C{=}C{=}C(OMe)NMe_2]$ (**1a**) with diethylene triamine affords an allenylidene complex with a heterocyclic endgroup carrying a dangling $CH_2CH_2NH_2$ substituent. All reactions follow a strict regioselective attack of the nucleophile at C_γ and proceed with good to excellent yields. The addition of N–H to the $C_\alpha{=}C_\beta$ bond is not observed. By applying either one of these routes nearly any substitution pattern in bis(amino)allenylidene complex can be realized.

Keywords: Allenylidene complexes; Chromium; Tungsten; Substitution; Propadienylidene complexes

1. Introduction

The synthesis of the first transition metal allenylidene complexes was reported in 1976 simultaneously by Fischer et al. [1] and by Berke [2]. Since then, the chemical and physico-chemical properties of this class of compounds have attracted increasing interest [3] as these complexes show great potential for applications in synthesis, catalysis, and other areas. The allenylidene ligand can easily be transformed into other groups by C–C and C–X bond forming reactions. Some ruthenium allenylidene complexes have turned out to be powerful precatalysts, for instance in olefin metathesis [4]. Therefore, several new routes to allenylidene complexes have been developed over the years.

Most synthetic routes to allenylidene complexes involve the reaction of suitable transition metal complexes with 1,1-disubstituted propargylic alcohols bearing alkyl

* Corresponding author. Tel.: +49 7531 882783/052; fax: +49 7531 883136.
E-mail address: helmut.fischer@uni-konstanz.de (H. Fischer).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.03.070

or aryl groups following the method introduced by Selegue [5]. Until recently, synthetic pathways to heteroatom-stabilized allenylidene complexes were scarce [6] although this type of allenylidene complexes should constitute an interesting target for the synthesis of organometallic push–pull systems for opto-electronic applications.

Recently we developed a simple one-pot method for the synthesis of various monoamino-substituted allenylidene complexes by using deprotonated propynoic acid amides or *C*-ethynylimines as C_3-fragments [7]. The reaction with [$(CO)_5$M-THF] (M=Cr, W) followed by alkylation of the resulting metalates with Meerwein salts afforded the corresponding amino-allenylidene complexes. The carbon atoms in such π-donor-substituted allenylidene ligands constitute alternating electrophilic and nucleophilic centers.

The reactions of allenylidene complexes with nucleophiles and electrophiles have been studied in some detail, especially those of bisaryl-substituted allenylidene complexes [8]. Various calculations at different levels of theory have been used [9] to predict the regioselectivity of reactions with nucleophiles such as, e.g., amines. Based on these theoretical studies, nucleophiles should attack at the metal-bound C_α atom of the allenylidene ligand. This has been confirmed by various experiments. Until recently, the addition of the amine to the C_α atom, hence following the predicted pathway, has been found almost exclusively [6,10]. An exception was the addition of ammonia to the C_γ atom of the rhenium allenylidene complex [(triphos)$(CO)_2$Re=C=C=C$(Ph)_2$]$^+$OTf$^-$ [11].

Recently, we observed that dimethylamine reacts, as expected, with the amino(phenyl)allenylidene complex [$(CO)_5$Cr=C=C=C(NMe_2)Ph] by addition of the amine across the C_α=C_β bond via initial C_α attack to give the alkenyl(amino)carbene complex [$(CO)_5$Cr=C(NMe_2)—CH=C(NMe_2)Ph]. The corresponding reaction of dimethylamine with the amino(methoxy)allenylidene complex [$(CO)_5$Cr=C=C=C(NMe_2)OMe] (**1a**), however, proceeded by addition of the amine to the C_γ atom and subsequent elimination of methanol to form the substitution product [$(CO)_5$Cr=C=C=C$(NMe_2)_2$] (Scheme 1) [7].

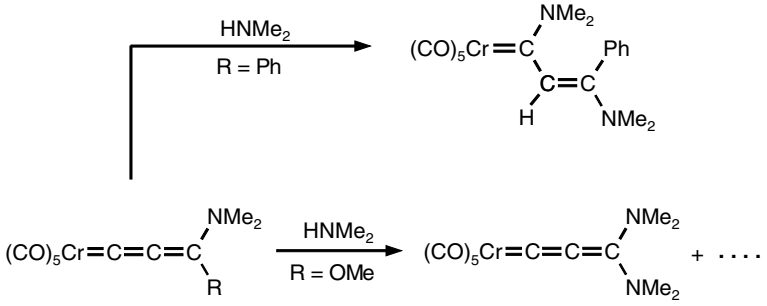
We now report that, starting out from dimethylamino(*methoxy*)allenylidene complexes, [$(CO)_5$M=C=C=C(NMe_2)OMe] (M=Cr (**1a**), W (**1b**)), various bis(amino)-substituted allenylidene complexes are likewise readily accessible by simple substitution processes. Thus, the π-donor propensity of the terminal group in these organometallic push–pull systems can easily and conveniently be modified.

2. Preparative results

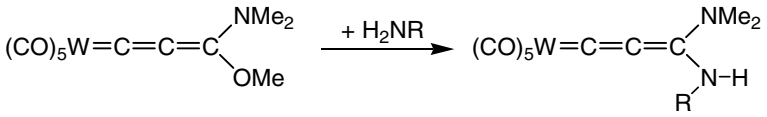
For the synthesis of bis(amino)-substituted allenylidene complexes dimethylamino(methoxy)allenylidene complexes, [$(CO)_5$M=C=C=C(NMe_2) OMe] (M=Cr (**1a**), W (**1b**)) have turned out to be convenient starting complexes. They are readily accessible by reaction of [$(CO)_5$M-THF] with lithiated propynoic acid dimethylamide followed by alkylation of the resulting metalate with trimethyloxonium tetrafluoroborate [7].

Addition of one equivalent of ammonia, allylamine or *iso*-propylamine to solutions of the pentacarbonyl dimethylamino(methoxy)allenylidene tungsten complex **1b** in THF gives rise to the formation of the bis(amino)allenylidene complexes **2**–**4** (Scheme 2) by displacement of the methoxy group. The new allenylidene complexes carrying two different amino substituents at C_γ are usually obtained in high yields. The reactions are highly selective. Products derived from addition of H_2NR to the C_α=C_β bond of the allenylidene ligand or from displacement of the dimethylamino group by N(H)R, simultaneously or in addition to OMe, have not been observed under these reaction conditions.

At room temperature the reactions are complete within minutes to a few hours. The driving force is most probably the thermodynamically favorable replacement of the weak π-donor OMe by the much stronger π-base N(H)R. Since the elimination product methanol also is a very weak nucleophile, follow-up reactions such as addition of methanol to the C_α=C_β bond of the allenylidene ligand are not to be expected. The experimental results are in accord with theoretical calculations. According to DFT calculations the reaction of **1b** with ammonia



Scheme 1.



Scheme 2.

in THF at 298 K is exergonic by about 31 kJ/mol. The ^{1}H NMR spectrum of **2** shows two N–Me and two N–*H* resonances indicating restricted rotation around both C_γ–N bonds. In contrast, only one N–*H* signal is observed for complexes **3** and **4**. Therefore within detection limits, only one isomer of **3** and **4** is present in solution. For steric reasons, the *E* conformer as shown in Scheme 2 (for the various conformations see also Scheme 8 below) is expected to be the preferred isomer (see below the structure of complex **8**, Fig. 1).

The reaction of **1b** with 2,2-dimethylaziridine deviates from the pattern of Scheme 2. Instead of the expected dimethylamino(dimethylaziridinyl)allenylidene complex analogous to **2**-**4** an approximate 1:1 mixture of the starting complex and of **5** (Scheme 3) is obtained. Chromatographic work-up of the mixture affords complex **5** in 44%. The yield of **5** increases to 77% when two equivalents of 2,2-dimethylaziridine are employed. According to the ^{1}H NMR spectrum, complex **5** is present in solution as the *E* isomer only.

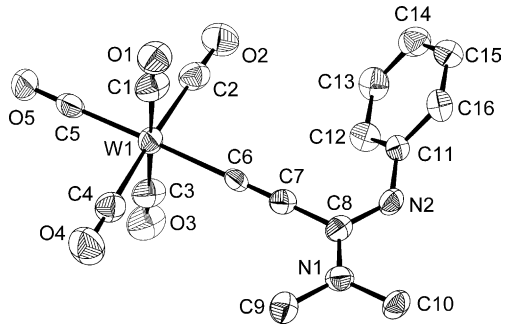
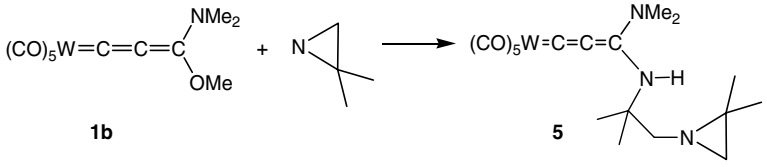


Fig. 1. Structure of complex **8** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) are: W(1)–C(6) 2.158(9), C(6)–C(7) 1.179(13), C(7)–C(8) 1.420(12), C(8)–N(1) 1.323(12), C(8)–N(2) 1.337(12); W(1)–C(6)–C(7) 179.3(9), C(6)–C(7)–C(8) 179.0(10), C(7)–C(8)–N(1) 119.7(9), C(7)–C(8)–N(2) 120.5(9).

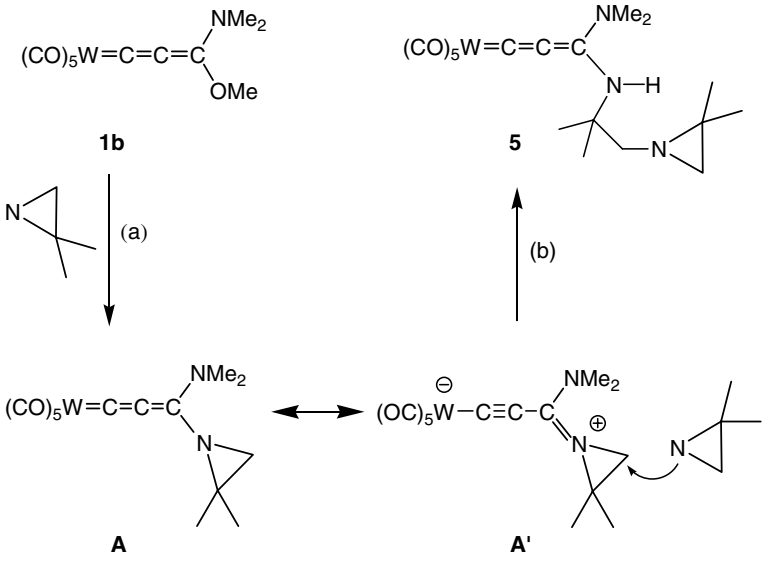
Presumably, the first step in the reaction of **1b** with 2,2-dimethylaziridine involves substitution of the methoxy group for aziridine (step a in Scheme 4). In the resulting complex **A**/**A**′ the aziridinyl substituent is activated towards nucleophiles (see resonance form **A**′) due to the electron-withdrawing properties of the "$(CO)_5$W-C=C=C" fragment. Nucleophilic attack of a second molecule of 2,2-dimethylaziridine at the aziridinyl substituent of **A**/**A**′, ring opening, and rearrangement finally produce the isolated product **5** (step b in Scheme 4). From the product distribution it follows that step b must be considerably faster than step a. The failure to spectroscopically detect complex **A**/**A**′ in the course of the reaction is in accord with such a conclusion.

Less reactive N-nucleophiles, like aniline, do not react with **1b** even when the mixtures are stirred for several days. The problems connected with the reduced nucleophilic reactivity of the substrate can be circumvented by using the corresponding lithium amides. Thus, addition of lithium anilide to solutions of **1b** gives, via nucleophilic addition of the anilide to the C_γ atom of the allenylidene ligand, the trisubstituted propynyl metalate **6**. Elimination of methoxide from **6** is achieved by addition of trimethylchlorsilane and filtration through silica gel. Thus, the allenylidene complex **8** (Scheme 5) is obtained in 73% yield. Analogously, addition of dimethylamide to **1b** to form **7**, followed by reaction with trimethylchlorsilane and filtration through silica gel affords the bis(dimethylamino)allenylidene complex **9**.

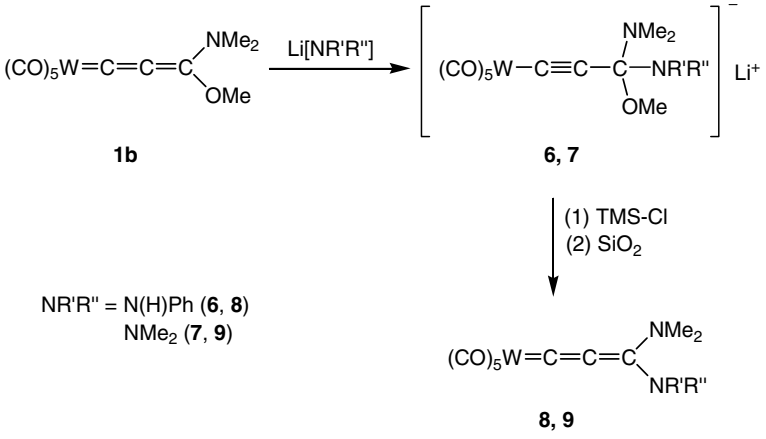
Complex **9** has already been prepared by a different route [12]. Its ^{1}H and ^{13}C NMR spectra exhibit only one resonance for each of the four *N*-bound methyl groups. In contrast, the two Me groups in the complexes **2**–**5** and **8** carrying one NMe_2 and a N(H)R substituent at C_γ are inequivalent giving rise to two Me signals. From these observations a significant double-bond character of the C_γ–NMe_2 bond can be deduced (see **D** in Scheme 6). However, only one set of signals is



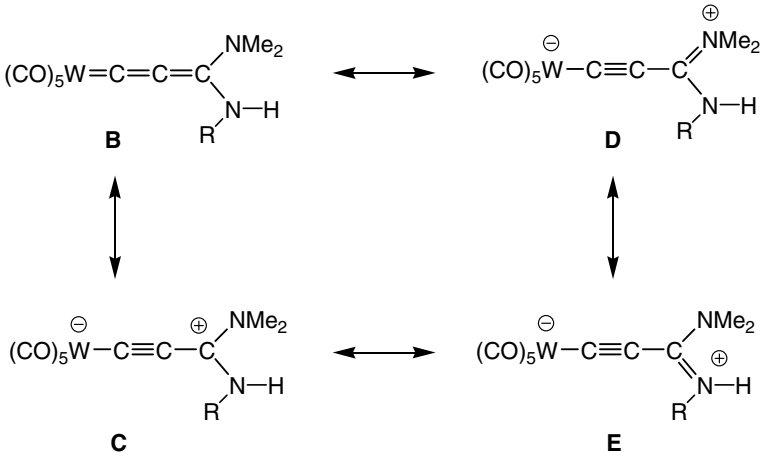
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

observed for the substituent R. Therefore, either only one isomer (with respect to the C_γ–N(H)R bond) is present in solution or there is rapid rotation around the C_γ–N(H)R bond. The former option is more likely. Steric considerations suggest that the *E* conformer as shown in Scheme 6 is the preferred isomer. From the appearance of the *ν*(CO) absorptions in the IR spectra at rather low energy it follows that dipolar resonance forms (**C**–**E** in Scheme 6) considerably contribute to the overall bond description. Consequently, the *ν*(CCC) absorption is at high energy (in the range 2024–2031 cm^{-1}) in accordance with a significant triple-bond character of the C_α–C_β bond (resonance form **C**–**E**).

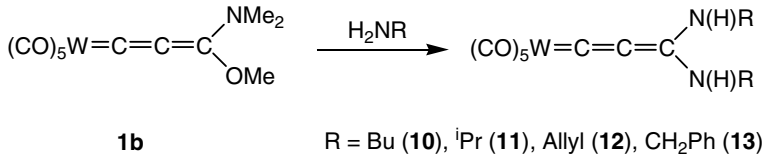
The results of the X-ray structural analysis of complex **8** (Fig. 1, Table 1) confirm the *E* arrangement of NMe_2 and Ph at the C(8)–N(2) bond. Both amino planes are within error limits coplanar (torsion angles: C(7)–C(8)–N(1)–C(9) 1.1°, C(7)–C(8)–N(2)–C(11) −2.6°) thus allowing optimal π-interaction with the "$(CO)_5$W-C═C═C" fragment. The triple-bond character of the C_α–C_β bond also shows up in the very short C_α–C_β distance (1.179(13) Å) in the solid-state structure of **8**. The C_α–C_β bond is even shorter than that in **9** (1.205(11) Å [12]) and, as expected, also shorter than that in monoamino-substituted allenylidene pentacarbonyl complexes (usually about 1.23 Å) [1,7,10a,12–14]. Conversely, the C_β–C_γ distance (1.420(12) Å) is rather long and is longer than that in monoamino-substituted allenylidene pentacarbonyl complexes (1.37–1.40 Å). In accord with the importance of the resonance forms **D** and **E** the C–N distances are shorter than those usually observed for $C(sp^2)$–$N(sp^2)$ single bonds [15].

In all of these reactions (Schemes 2, 3 and 5), using one equivalent of the N-nucleophile, the displacement of exclusively the methoxide substituent is observed. However, when the amine is employed in excess (at least two equivalents) the dimethylamino substituent is exchanged as well. Thus, the reactions of **1b** with *n*-butylamine, allylamine, *iso*-propylamine, and benzylamine, respectively, afford the symmetrically *N*,*N*-disubstituted allenylidene complexes **10**–**13**, usually in excellent yields (85–95%) when the amine is used in large excess (Scheme 7).

Again, addition of the amine to the C_α–C_β bond of the allenylidene ligand to give alkenyl(amino)carbene complexes is not observed. These results in combination with the experiments with equimolar amounts of allenylidene complex **1b** and amine (Scheme 2) indicate that there is a strong preference for exchange of the methoxide over the amino ligand. Therefore, these double substitution processes must proceed by a step-wise fashion. Due to restricted rotation around the C_γ–N bonds three isomers are conceivable that differ by the relative orientation of the (N)C–N(R) fragments: *E*/*E*, *E*/*Z*, and *Z*/*Z* (Scheme 8). Only two isomers are detected by ^1H and ^{13}C NMR spectra for **11**–**13** in solution: *E*/*E* and *E*/*Z*. The ratios *E*/*E*:*E*/*Z* as calculated from the relative

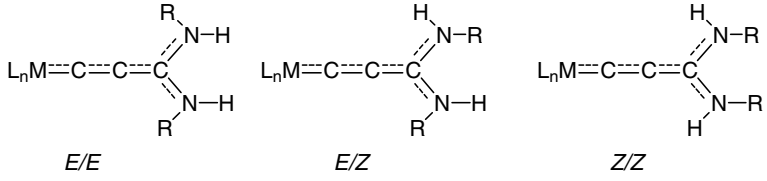
Table 1
Crystal data and refinement details for compounds **8**, **11** and **18**

	8	**11**	18
Formula	$C_{16}H_{12}N_2O_5W$	$C_{14}H_{16}N_2O_5W$	$C_{12}H_{11}CrN_3O_5$
M_r	496.13	476.14	329.24
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	11.097(5)	9.015(11)	9.560(4)
b (Å)	7.327(3)	9.595(4)	11.779(4)
c (Å)	20.496(9)	10.869(9)	13.701(4)
α (°)	90	87.67(4)	90
β (°)	97.129(15)	68.37(4)	108.52(3)
γ (°)	90	87.32(3)	90
V (Å^3)	1653.5(12)	872.7(13)	1462.9(9)
Z	4	2	4
Crystal size (mm^3)	0.3 × 0.4 × 0.5	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.4
ρ_{calc} (g cm^{-3})	1.993	1.812	1.495
μ (mm^{-1})	7.014	6.640	0.806
F(000)	944	456	672
T (K)	188(2)	188(2)	188(2)
Max. 2*Θ* (°)	54	54	54
Index range	$-14 \leqslant h \leqslant 13$	$-11 \leqslant h \leqslant 11$	$0 \leqslant h \leqslant 12$
	$-9 \leqslant k \leqslant 9$	$-12 \leqslant k \leqslant 12$	$0 \leqslant k \leqslant 15$
	$-26 \leqslant l \leqslant 26$	$-13 \leqslant l \leqslant 12$	$-17 \leqslant l \leqslant 16$
No. of data	6545	7687	3381
No. of unique data	3594	3794	3191
Parameters	217	199	190
$R(F)$ for $I > 2\sigma(I)$	0.0518	0.0357	0.0413
$wR_2(F)$ for all data	0.1316	0.0890	0.1074
Goodness-of-fit on F^2	1.044	1.106	1.049



1b R = Bu (**10**), ^{i}Pr (**11**), Allyl (**12**), CH_2Ph (**13**)

Scheme 7.



E/E *E/Z* *Z/Z*

Scheme 8.

intensities of the resonances of N–*H* and the substituents R are 1:0.7 (**11**) and ca. 1:1 (**12** and **13**). Surprisingly, all three isomers are detectable for complex **10** (ratio ca. 1:1:1).

Crystals of the major isomer of **11** suitable for an X-ray structural analysis could be obtained from the isomeric mixture. Fig. 2 clearly shows the *E*/*E* orientation of the *iso*-propylamino substituents. The various distances along the WC_3N_2 fragment are similar to those of **8** although in **11** the C6–C7 bond seems to be slightly longer and the C7–C8 bond slightly shorter than the corresponding bonds in **8**. The atoms C7, C8, N1, N2, C11, and C12 lie almost within one plane (torsion angles C7–C8–N1–C11 −4.5°, C7–C8–N2–C12 −4.0°)

When bidentate *N*,*N*-dinucleophiles are used instead of monodentate amines double substitution offers a convenient access to such allenylidene complexes where the terminal carbon atom is a constituent of a *N*-heterocycle. For instance, by reaction of **1b** with 1,2-diaminoethane complex **14** is obtained in almost quantitative yield (Scheme 9). Ring formation considerably accelerates the second substitution step: the formation of **14**

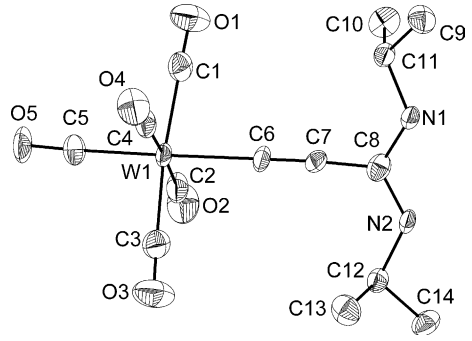
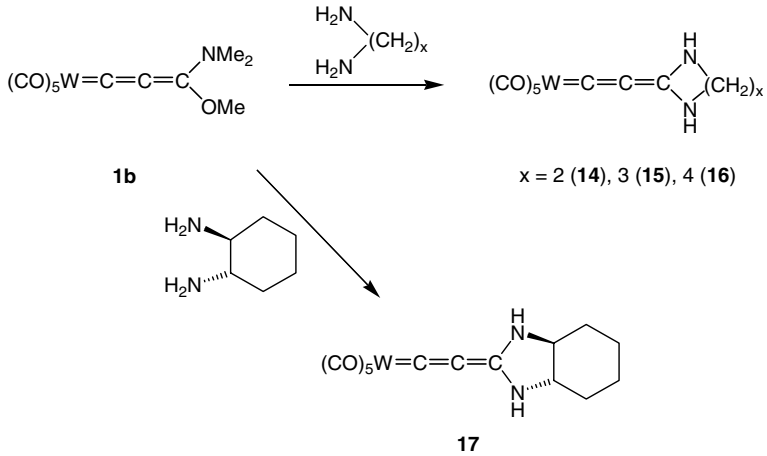


Fig. 2. Structure of complex **11** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) are: W(1)–C(6) 2.155(6), C(6)–C(7) 1.200(8), C(7)–C(8) 1.390(8), C(8)–N(1) 1.337(8), C(8)–N(2) 1.316(8); Cr(1)–C(6)–C(7) 178.6(5), C(6)–C(7)–C(8) 176.7(6), C(7)–C(8)–N(1) 118.7(6), C(7)–C(8)–N(2) 121.1(6).

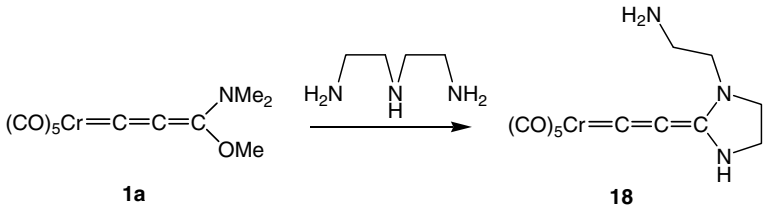
is complete within a few minutes. Analogously, the reaction of **1b** with 1,3-diaminopropane, 1,4-diaminobutane, and *trans*-1,2-diaminocyclohexane affords the complexes **15**–**17** featuring 2-tetrahydropyrimidin-2-ylidene,



1b x = 2 (**14**), 3 (**15**), 4 (**16**)

17

Scheme 9.



1a 18

Scheme 10.

[1,3]diazepan-2-ylidene, and octahydro-benzoimidazol-2-ylidene end groups, again nearly quantitatively (Scheme 9). Ring closure by addition of the "second" NH_2 group of the α,ω-diamine to the C_α–C_β bond giving 7-, 8- and 9-membered bis-*N*-heterocyclic carbene ligands is not observed. When two equivalents of a *cis*/*trans*-mixture of 1,2-diaminocyclohexane (ratio 1:4) are employed instead of the neat *trans* isomers, the isomeric mixture obtained of **17** reflects the initial ratio of isomers (approximately 1:4).

The reaction using the corresponding chromium precursor **1a** and diethylenetriamine as educts affords complex **18**, which contains an additional pending amine functional group (see Scheme 10).

The structure of complex **18** has been confirmed by its IR and NMR spectra and additionally by an X-ray structural analysis (Fig. 3, Table 1). The bond lengths C_α–C_β, C_β–C_γ, and C_γ–N are similar to those in **8**, although C_α–C_β is somewhat longer. The imidazolidin-2-ylidene ring is planar and eclipsed with respect to the *cis* CO ligands (torsion angle C(1)–Cr(1)–C(8)–N(2) 57.7°). The significantly shorter Cr–$(CO)_{trans}$ distance compared to the mean of the Cr–$(CO)_{cis}$ bonds confirms the pronounced donor properties of bis(amino)allenylidene ligands as already deduced from the IR spectra.

Due to the electron-withdrawing properties of the "$(CO)_5M$=C=C=C" fragment, the hydrogen atoms at the amino groups are acidic. This can be used for further derivatization. For instance, deprotonation of complex **10** with lithium di-*iso*-propylamide followed by alkylation with $[R_3O]BF_4$ (R = Me, Et) affords the corresponding alkylated allenylidene complexes **19** and **20** (Scheme 11). Although four conformers are possible, differing by the arrangement of H, Bu, and Me with respect to the partial N–C double bonds, only one isomer is detected by ^{1}H NMR spectroscopy. Presumably, the isomer shown in Scheme 11 is the one present in solution.

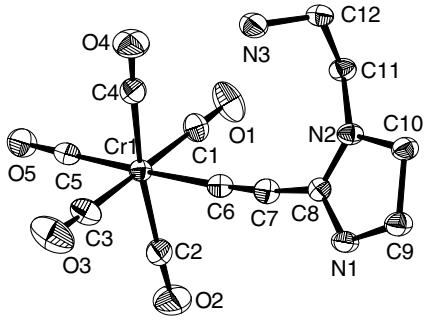
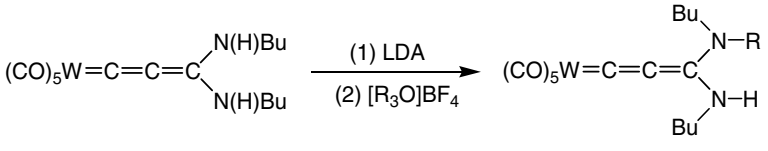


Fig. 3. Structure of complex **18** in the crystal (ellipsoids drawn at 50% level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) are: Cr(1)–C(6) 2.030(3), C(6)–C(7) 1.214(4), C(7)–C(8) 1.411(4), C(8)–N(1) 1.324(3), C(8)–N(2) 1.336(3); Cr(1)–C(6)–C(7) 175.8(2), C(6)–C(7)–C(8) 173.1(3), C(7)–C(8)–N(1) 124.9(2), C(7)–C(8)–N(2) 123.5(2).

3. Discussion

From the results obtained so far it follows that the reactivity of allenylidene pentacarbonyl complexes towards N-nucleophiles strongly depends on the substituents at the allenylidene ligand, on the N-nucleophile and on the reaction conditions. Diaryl-substituted allenylidene complexes generally add N–H nucleophiles such as primary and secondary amines, imines, hydrazines, and hydroxylamines to the C_α–C_β bond giving alkenyl(amino)carbene, alkenyl(imino)carbene, or alkenyl (hydrazino)carbene complexes [10d,10e,10f]. Depending on the nucleophile, the α,β-addition is followed by cyclization affording 5-membered heterocyclic carbene ligands (pyrazolidinylidene [10e] or isoxazolidinylidene



10 R = Me (**19**), Et (**20**)

Scheme 11.

ligands [10f]). When N-substituted imines are employed cycloaddition of the C=N bond to the C_α–C_β bond yields azetidinylidene complexes [10d].

Aryl[di(organyl)amino]allenylidene complexes likewise add dimethylamine to the C_α–C_β bond giving alkenyl(amino)carbene complexes [10a,17]. However, no reaction is observed when dimethylamine is replaced by diethyl amine [10a]. In contrast, aryl[mono(organyl)amino]allenylidene complexes are deprotonated by amines [16,17]. For instance, addition of dimethylamine to solutions of $[(CO)_5Cr{=}C{=}C{=}C(NHMe)Ph]$ rapidly generates the iminoalkynyl chromate $[(CO)_5Cr{-}C{\equiv}C{-}C(=NMe)Ph]^-$ [17]. Contrary to the secondary amine $NHMe_2$, primary amines H_2NR in large excess do not add to the C_α–C_β bond of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ but rather displace the dimethylamino substituent yielding $[(CO)_5Cr{=}C{=}C{=}C(NHR)Ph]$ complexes [17].

Dimethylamine likewise does not add to the C_α–C_β bond of the alkoxy(amino)allenylidene complex $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)OMe]$ but replaces the methoxy substituent ([7], this work). In di(amino)allenylidene complexes even the amino substituent may be displaced by other amines (this work).

In summary, four different reaction patterns have been observed in the reactions of allenylidene pentacarbonyl complexes with N-nucleophiles:

(a) addition of N–H to the C_α–C_β bond,
(b) cycloaddition of N=C to the C_α–C_β bond,
(c) deprotonation of a terminal N(H)R substituent,
(d) displacement of one or even both terminal substituents by amines.

Reaction paths (a) and (b) are initiated by attack of the nucleophile at the C_α atom, path (d) obviously by an initial attack at C_γ. To get any hints as to the preferred site of attack DFT calculations were carried out on a series of differently substituted allenylidene pentacarbonyl chromium complexes $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$ (R^1, R^2 = Ph, OMe, NMe_2). In these complexes the LUMO is predominantly localized in the allenylidene ligand and oriented perpendicular to the allenylidene plane. The LUMO+1 is localized within the $(CO)_5Cr$ fragment. The breakdowns of the contributions from the metal and the carbon atoms along the chain to the LUMO are listed in Table 2. In all substituted complexes the LUMO is mainly localized at C_α and C_γ. The contributions of C_α and C_γ to the LUMO are similar, C_γ generally contributing slightly more than C_α. The difference of the C_α and C_γ contribution is almost independent of the substituent at C_γ. From these data a clear preference for a nucleophilic attack at either C_α or C_γ cannot be deduced.

Table 2
Contributions from chromium and the chain carbon atoms to the LUMO of $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$

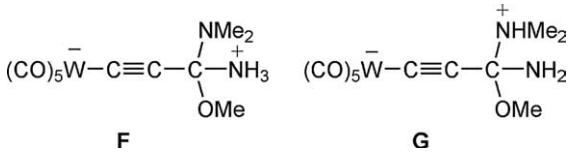
M	Substituents R^1/R^2	M	C_α	C_β	C_γ
Cr	Ph/Ph	11	20	5	25
	Ph/OMe	8	21	2	26
	NMe_2/OMe	6	28	1	33
	NMe_2/NMe_2	6	26	1	32

Table 3
Partial atomic charges of the chain carbon atoms in $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$

M	Substituents R^1/R^2	C_α	C_β	C_γ
Cr	Ph/Ph	0.12	−0.18	0.06
	Ph/OMe	0.14	−0.31	0.41
	NMe_2/OMe	0.13	−0.38	0.57
	NMe_2/NMe_2	0.11	−0.34	0.43

The partial atomic charges along the chain obtained from the natural bond orbital analysis are listed in Table 3 (for calculations on allenylidene pentacarbonyl complexes, see [9c,9e]). The C_β atom in all complexes carries a negative and the C_α atom a slightly positive partial charge. With the exception of $[(CO)_5Cr{=}C{=}C{=}CPh_2]$ the positive partial charges at C_α and C_γ differ significantly, the charge at C_γ being considerably higher than that at C_α. In $[(CO)_5Cr{=}C{=}C{=}CPh_2]$ the charges are similar, the partial atomic charge at C_α being even somewhat higher than at C_γ. Therefore since the contribution to the LUMO of C_α and C_γ are very similar the site of nucleophilic addition of N-nucleophiles might predominantly be determined by the partial atomic charges: addition to the C_α atom for $[(CO)_5Cr{=}C{=}C{=}CPh_2]$ and addition to C_γ for all other donor-substituted allenylidene complexes. These expectations agree with the experimental results. Whether dimethylamine initially also adds to C_γ of $[(CO)_5Cr{=}C{=}C{=}CPh_2]$ and the adduct subsequently rearranges to the C_α adduct is unknown at present. The addition of ammonia to the C_γ atom of bisaryl-substituted allenylidene rhenium complexes followed by slow rearrangement into the C_α adduct has recently been reported [11].

By addition of amines to the C_γ atom zwitterionic alkynyl pentacarbonyl metalates are formed. Thus, addition of NH_3 to $[(CO)_5W{=}C{=}C{=}C(OMe)NMe_2]$ (**1b**) gives **F**. According to the DFT calculations (298 K, in THF) the reaction is endergonic by 24 kJ/mol. Tautomer **G** ($NHMe_2$-adduct of $[(CO)_5W{-}C{=}C(OMe)NH_2]$) is less stable by 28 kJ/mol.



Elimination of $HNMe_2$ from **F** is exergonic by 45 kJ/mol and of MeOH (to give **2**) by 55 kJ/mol. The system

"$[(CO)_5W{=}C{=}C{=}C(NMe_2)NH_2]$ + MeOH" is more stable by 10 kJ/mol than "$[(CO)_5W{=}C{=}C{=}C(OMe)NH_2]$ + $NHMe_2$" thus explaining the selectivity (OMe vs. NMe_2 displacement) in the reaction of NH_3 with **1b**. The observation that primary amines are able to displace secondary amines may be explained by reducing unfavorable steric interaction between the π-donor substituents at C_γ through such a substitution process. Reducing unfavorable steric interaction allows for a better overlap between the lone pair at the donor substituents and the carbon chain and thus for enhanced electron donation from terminal substituents to the $(CO)_5M$ acceptor fragment. This is evident in the IR spectra and the barriers to rotation around the C_γ–NMe_2 bond in $[(CO)_5W{=}C{=}C(NMe_2)R]$ (R = NH_2 (**2**) or NMe_2 (**9**)). Compared to **9** the *ν*(CO) absorptions of **2** are at lower wave numbers and the cumulene vibration is at higher energy indicating enhanced contribution of dipolar resonance structures such as **D** and **E** (Scheme 6) to the overall bonding description. The barrier to rotation around the C_γ–NMe_2 in **9** is less than 35 kJ/mol [12], however, that in **2** is higher than 75 kJ/mol [7] in indicating enhanced double-bond character in **2**.

Unfavorable steric interactions between two NMe_2 substituents are also indicated by the solid-state structure of **9**. To reduce steric congestion the dimethylamino groups in **9** are tilted by about 20° against the plane formed by C_γ and the nitrogen atoms. The tilt is well reproduced by the DFT calculation of the ground-state structure. In contrast to **9**, the NH_2 and the NMe_2 plane in **2** are calculated to be coplanar, the C_γ–NMe_2 distance being slightly shorter in **2** than in **9** in accord with an increased contribution of resonance forms **D** and **E** and with the IR data.

Several routes for the modification of the substitution pattern of allenylidene complexes are now available. The alkoxy substituent can easily be replaced by NH_2, NHR, and NR_2. Secondary amino groups, NR_2, are readily replaced by primary amino groups, NHR. Via deprotonation followed by alkylation, primary amino groups can again be transferred into NRR′. Thus, by applying either one of the different routes described above nearly any substitution pattern can be realized.

4. Experimental

4.1. General

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane, Et_2O) and sodium (THF). The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitrogen-saturated. The reported yields refer to analytically pure compounds and are not optimized. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer at room temperature. Chemical shifts are reported relative to the residual solvent or tetramethylsilane peaks. IR: Biorad FTS 60. UV–Vis: Hewlett–Packard diode array spectrophotometer 8453. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. The precursor allenylidene complexes **1a**–**b** were prepared according to literature procedures [7]. 2,2-Dimethylaziridine was obtained by the method of Meyers et al. [18]. All other amines were commercially available and used as supplied.

4.2. General procedure for the preparation of the allenylidene complexes 2–5

At room temperature 1.1 mmol (2.1 mmol in the case of **5**) of the corresponding amine was added to a solution of 0.435 g (1.0 mmol) of **1b** in 2 mL of THF. The solution was stirred until the starting complex was consumed (as indicated by IR spectroscopy). The solvent was removed in vacuo and the remaining residue was purified either by column chromatography or by recrystallization (as specified).

4.2.1. Pentacarbonyl(3-amino-3-dimethylamino-propa-1,2-dienylidene)tungsten (2)

Yellow solid. Yield: 0.35 g (83%) after recrystallization from CH_2Cl_2; m.p. 143–146 °C (dec.). IR (THF, cm^{-1}): *ν*(CO) = 2089 vw, 1921 vs, 1893 m; *ν*(CCC) = 2031 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): *δ* = 3.22 (s, 3H, $N(CH_3)_2$), 3.46 (s, 3H, $N(CH_3)_2$), 7.83, 8.18 (br, 2H, NH_2). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): *δ* = 38.6 ($N(CH_3)_2$), 43.4 ($N(CH_3)_2$), 102.7 (C_β), 148.5 (C_γ), 154.3 (C_α, $^1J_{WC}$ = 102.7 Hz), 199.7 (*cis*-CO, $^1J_{WC}$ = 124.2 Hz), 224.0 (*trans*-CO, $^1J_{WC}$ = 133.3 Hz). MS(FAB), *m/z* (%): 420 (65) [M^+], 392 (62) [$(M - CO)^+$], 364 (40) [$(M - 2CO)^+$]. UV–Vis: λ_{max} (nm) (log *ε*) [solvent]: 388 (3.900) [$CHCl_3$], 374 (3.928) [CH_2Cl_2], 362 (3.707) [DMF]. Anal. Found: C, 28.71; H, 2.38; N, 6.72. Calc. for $C_{10}H_8N_2O_5W$ (420.0): C, 28.60; H, 1.92; N, 6.67%.

4.2.2. Pentacarbonyl(3-allylamino-3-dimethylamino-propa-1,2-dienylidene)tungsten (3)

Deep-red oil. Yield: 0.46 g (99%), without further purification. IR (THF, cm^{-1}): *ν*(CO) = 2086 vw, 1957 vw, 1921 vs, 1894 m; *ν*(CCC) = 2028 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): *δ* = 2.86 (s, 3H, $N(CH_3)_2$), 3.26 (s, 3H, $N(CH_3)_2$), 4.06 (br, 1H, NCH_2CH), 4.25 (m, 2H, NCH_2), 5.18–5.30 (m, 2H, NCH_2CHCH_2), 8.27 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): *δ* = 34.8 ($N(CH_3)_2$), 39.8 ($N(CH_3)_2$), 45.9 (CH_2), 100.0 (C_β), 118.0 (=CH_2), 133.3 (—CH=), 146.7 (C_γ), 157.7 (C_α), 199.5 (*cis*-CO, $^1J_{WC}$ = 124.4 Hz), 203.3

(*trans*-CO). MS(FAB), *m/z* (%): 460 (30) [M^+], 320 (20) [$(M - 5CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 387 (3.966) [$CHCl_3$], 372 nm (3.929) [CH_2Cl_2], 340 nm (3.871) [DMF]. Anal. Found: C, 34.42; H, 2.81; N, 6.24. Calc. for $C_{13}H_{12}N_2O_5$ W (460.1): C, 33.94; H, 2.63; N, 6.09%.

4.2.3. Pentacarbonyl(3-isopropylamino-3-dimethylamino-propa-1,2-dienylidene)tungsten (**4**)

Yellow solid. Yield: 0.11 g (23%) after recrystallization from pentane/CH_2Cl_2 (1:1); m.p. 152–154 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2087 vw, 1921 vs, 1893 m; ν(CCC) (cm^{-1}) 2028 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 1.31 (d, 6H, ^{i}Pr–CH_3, $^3J_{HH}$ = 6.6 Hz), 3.15 (br, 3H, $N(CH_3)_2$), 3.44 (s, 3H, $N(CH_3)_2$), 4.42 (sept, 1H, ^{i}Pr–CH, $^3J_{HH}$ = 6.6 Hz), 7.38 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 23.7 (^{i}Pr–CH_3), 38.4 ($N(CH_3)_2$), 43.5 ($N(CH_3)_2$), 51.1 (^{i}Pr–CH), 101.2 (C_β), 147.6 (C_γ), 161.1 (C_α), 199.7 (*cis*-CO, $^1J_{WC}$ = 126.0 Hz), 203.4 (*trans*-CO). MS(FAB), *m/z* (%): 462 (22) [M^+], 434 (31) [$(M - CO)^+$], 406 (28) [$(M - 2CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 379 (3.520) [$CHCl_3$], 372 (3.887) [CH_2Cl_2], 354 (3.765) [DMF]. Anal. Found: C, 33.80; H, 3.76; N, 5.44. Calc. for $C_{13}H_{14}N_2O_5$ W (462.1): C, 33.79; H, 3.05; N, 6.06%.

4.2.4. Pentacarbonyl(3-dimethylamino-3-[2-methyl-1-{2,2-dimethylaziridin-1-yl} propan-2-amino]-propa-1,2-dienylidene)tungsten (**5**)

Yellow solid. Yield: 0.42 g (77%) after recrystallization from pentane/CH_2Cl_2 (1:1); m.p. 90–92 °C. IR (THF, cm^{-1}): ν(CO) = 2086 vw, 1922 vs, 1894 m; ν(CCC) = 2028 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 1.11 (s, 6H, $C(CH_3)_2$), 1.29 (s, 6H, $C(CH_3)_2$), 1.56 (s, 2H, CH_2), 3.20 (s, 3H, $N(CH_3)_2$), 3.47 (s, 3H, $N(CH_3)_2$), 3.56 (s, 2H, CH_2), 7.37 (br 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 23.2 ($C(CH_3)_2$), 33.5 ($C(CH_3)_2$), 36.1 ($N(CH_3)_2$), 41.8 ($N(CH_3)_2$), 56.1 (CH_2), 57.8 (CH_2), 100.0 (C_β), 146.7 (C_γ), 159.4 (C_α), 198.0 (*cis*-CO, $^1J_{WC}$ = 124.1 Hz), 201.6 (*trans*-CO). MS(FAB), *m/z* (%): 546 (100) [M^+], 518 (30) [$(M - CO)^+$], 490 (20) [$(M - 2CO)^+$], 462 (35) [$(M - 3CO)^+$], 434 (44) [$(M - 4CO)^+$], 406 (75) [$(M - 5CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 400 (4.049) [pentane], 382 (4.169) [$CHCl_3$], 369 (4.051) [CH_2Cl_2], 362 (3.903) [DMF]. Anal. Found: C, 39.32; H, 4.23; N, 7.68. Calc. for $C_{18}H_{23}N_2O_5$ W (545.2): C, 39.65; H, 4.25; N, 7.71%.

4.3. General procedure for the preparation of the allenylidene complexes **8** and **9**

At 0 °C 0.435 g (1.0 mmol) of **1b** was added to a solution of 5.0 mmol of the corresponding lithium amide in 50 mL of dry THF. The solution was stirred at 0 °C until starting complex was consumed (as indicated by IR spectroscopy). Then, 0.38 mL (3.0 mmol) of chlorotrimethylsilane was added and the solution was filtered through silica gel. The silica was washed several times with dry THF. Chromatographic workup afforded the products.

4.3.1. Pentacarbonyl(3-dimethylamino-3-phenylamino-propa-1,2-dienylidene)tungsten (**8**)

Yellow solid. Yield: 0.36 g (73%) after chromatography on silica gel by using mixtures of pentane and CH_2Cl_2 (1:1 to 1:4); m.p. 142–143 °C. IR (THF, cm^{-1}): ν(CO) = 2087 vw, 1923 vs, 1895 m; ν(CCC) = 2024 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 3.41 (s, 3H, $N(CH_3)_2$), 3.57 (s, 3H, $N(CH_3)_2$), 7.28 (t, 1H, Ph-*p*-H, $^3J_{HH}$ = 7.4 Hz), 7.39 (t, 2H, Ph-*m*-H, $^3J_{HH}$ = 8.0 Hz), 7.54 (t, 2H, Ph-*o*-H, $^3J_{HH}$ = 8.1 Hz), 9.30 (s, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 39.4 ($N(CH_3)_2$), 43.9 ($N(CH_3)_2$), 102.6 (C_β, $^2J_{WC}$ = 24.6 Hz), 126.3 (Ph-*o*-C), 128.3 (Ph-*p*-C), 130.4 (Ph-*m*-C), 139.7 (Ph-*i*-C), 146.0 (C_γ), 167.0 (C_α, $^1J_{WC}$ = 99.6 Hz), 199.4 (*cis*-CO, $^1J_{WC}$ = 124.2 Hz), 203.4 (*trans*-CO, $^1J_{WC}$ = 133.7 Hz). MS(FAB), *m/z* (%): 496 (21) [M^+], 468 (23) [$(M - CO)^+$], 412 (15) [$(M - 3CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 407 (4.085) [$CHCl_3$], 400 (4.109) [CH_2Cl_2], 369 (3.910) [DMF]. Anal. Found: C, 38.90; H, 2.54; N, 5.56. Calc. for $C_{16}H_{12}N_2O_5$ W (496.0): C, 38.74; H, 2.44; N, 5.65%.

4.3.2. Bis(dimethylamino)-propa-1,2-dienylidene(penta carbonyl)tungsten (**9**)

Yellow solid. Yield: 0.31 g (69%) after chromatography on silica gel using mixtures of pentane and CH_2Cl_2 (2:1 to 1:2). Identification by comparison of its spectroscopic data with those published in the literature [12].

4.4. General procedure for the preparation of the allenyl idene complexes **10–13**

At room temperature 10 mmol of the corresponding amine was added to a solution of 0.435 g (1.0 mmol) of **1b** in 2 mL of THF. The solution was stirred until all of the starting complex was consumed (as indicated by IR spectroscopy). The solvent was removed in vacuo. The products were purified either by column chromatography or by recrystallization (as specified).

4.4.1. Pentacarbonyl[3,3-bis(butylamino)-propa-1,2-dienylidene]tungsten (**10**)

Yellow solid. Yield: 0.43 g (85%) after chromatography on silica gel using mixtures of pentane and CH_2Cl_2 (2:1 to 1:4); m.p. 105–107 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2086 vw, 1961 vw, 1921 vs, 1894 m; ν(CCC) = 2029 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 0.94 (t, $^3J_{HH}$ = 7.2 Hz, 6H, $NCH_2CH_2CH_2CH_3$),

1.39 (tq, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.5 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.66 (tt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.8 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 3.15, 3.44, 3.55, 3.62 (t, 4H, $NCH_2CH_2CH_2CH_3$), 7.77, 7.95, 8.23, 8.48 (2H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 14.8, 15.0, 15.1, 15.2 ($NCH_2CH_2CH_2CH_3$), 21.3, 21.5, 21.6, 22.1 ($NCH_2CH_2CH_2CH_3$), 33.6, 33.7, 33.7 ($NCH_2CH_2CH_2CH_3$), 46.4, 46.9, 48.5 ($NCH_2CH_2CH_2CH_3$), 100.1, 101.0, 101.5 (C_β), 147.7, 148.4 (C_γ), 161.1 (C_α, $^1J_{WC}$ = 99.0 Hz), 199.6 (*cis*-CO, $^1J_{WC}$ = 124.2 Hz), 203.5 (*trans*-CO). MS(FAB), *m/z* (%): 504 (45) [M^+], 476 (85) [$(M - CO)^+$], 448 (100) [$(M - 2CO)^+$], 420 (35) [$(M - 3CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 402 nm (3.976) [pentane], 385 (4.148) [$CHCl_3$], 373 (4.077) [CH_2Cl_2], 340 (3.993) [DMF]. Anal. Found: C, 37.85; H, 4.20; N, 5.56. Calc. for $C_{16}H_{20}N_2O_5W$ (504.2): C, 38.12; H, 4.00; N, 5.56%.

4.4.2. Pentacarbonyl[3-bis(isopropylamino)-propa-1,2-dienylidene]tungsten (**11**)

Yellow solid. Yield: 0.45 g (95%) after recrystallization from pentane/CH_2Cl_2; m.p. 111–112 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2087 vw, 1961 vw, 1921 vs, 1893 m; ν(CCC) = 2028 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 1.27, 1.31 (br, 12H, $CH(CH_3)_2$), 3.93, 4.30, 4.44 (br, 2H, CH $(CH_3)_2$), 7.35, 7.59, 8.11 (br, 2H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 22.8, 23.5, 23.7 ($CH(CH_3)_2$), 46.0, 49.4, 50.6 ($CH(CH_3)_2$), 101.2 (C_β), 145.66, 147.5 (C_γ), 161.1 (C_α), 199.6 (*cis*-CO, $^1J_{WC}$ = 124.3 Hz), 203.4 (*trans*-CO). MS(FAB), *m/z* (%): 462 (22) [M^+], 434 (31) [$(M - CO)^+$], 406 (28) [$(M - 2CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 381 (3.490) [$CHCl_3$], 375 (4.033) [CH_2Cl_2], 361 (3.857) [DMF]. Anal. Found: C, 35.41; H, 3.42; N, 6.08. Calc. for $C_{14}H_{16}N_2O_5$ W (476.1): C, 35.32; H, 3.39; N, 5.88%.

4.4.3. Pentacarbonyl[3-bis(allylamino)-propa-1,2-dienylidene]tungsten (**12**)

Deep-red oil. Yield: 0.56 g (92%) after washing with CH_2Cl_2/pentane (1:1). IR (THF, cm^{-1}): ν(CO) = 2087 vw, 1922 vs, 1895 m; ν(CCC) = 2028 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 4.02, 4.20, 4.23 (m, 4H, NCH_2), 5.16 (m, 4H, $CHCH_2$), 5.90 (m, 2H, $CHCH_2$), 7.26, 7.50, 8.17 (br, 2H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 45.8, 48.9, 49.2 (N–CH_2), 100.3, 101.1, 101.5 (C_β), 118.6 ($CH{=}CH_2$), 133.0, 135.0, 135.2 ($CH{=}CH_2$), 147.5, 149.4 (C_γ), 155.8 (C_α), 199.4 (*cis*-CO, $^1J_{WC}$ = 124.5 Hz), 203.2 (*trans*-CO). MS(FAB), *m/z* (%): 472 (22) [M^+], 444 (3) [$(M - CO)^+$], 416 (5) [$(M - 2CO)^+$], 388 (28) [$(M - 3CO)^+$], 360 (12) [$(M - 4CO)^+$], 332 (18) [$(M - 5CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 392 (3.491) [$CHCl_3$], 387 nm (3.939) [CH_2Cl_2], 365 nm (3.823) [DMF]. Anal. Found: C, 36.08; H, 3.14; N, 6.25. Calc. for $C_{14}H_{12}N_2O_5W$ (472.1): C, 35.62; H, 2.56; N, 5.93%.

4.4.4. Pentacarbonyl[3,3-bis(benzylamino)-propa-1,2-dienylidene]tungsten (**13**)

Yellow oil. Yield: 0.26 g (46%) after chromatography on silica gel using CH_2Cl_2 as eluent. IR (THF, cm^{-1}): ν(CO) = 2086 vw, 1922 vs, 1895 m; ν(CCC) = 2026 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 4.64, 4.82, 4.85 (s, 4H, NCH_2), 7.33-7.36 (m, 6H, Ph), 7.45 (m, 4H, Ph), 8.36, 8.44, 8.92 (2H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 50.4, 50.5, 50.6 (NCH_2), 102.3, 102.1 (C_β), 129.3–130.5 (Ph), 137.0 (Ph), 139.3, 139.4 (C_{ipso}), 149.1 (C_γ), 157.6 (C_α), 199.4 (*cis*-CO), 203.1 (*trans*-CO). MS(FAB), *m/z* (%): 571 (50) [M^+], 543 (25) [$(M - CO)^+$], 487 (100) [$(M - 3CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 397 (3.561) [CH_2Cl_2]. Anal. Found: C, 45.73; H, 2.89; N, 4.90. Calc. for $C_{22}H_{16}N_2O_5$ W (572.2): C, 46.18; H, 2.82; N, 4.90%.

4.5. General procedure for the preparation of the allenylidene complexes **14–18**

1.1 mmol of the diamine was added to a solution of 1.0 mmol of complex **1a** or **1b** in 2 mL of THF. The solution was stirred until all of the starting complex was consumed (as indicated by IR spectroscopy). The solvent was removed in vacuo. Purification either by column chromatography (on silica gel) or by recrystallization (as specified) afforded the products.

4.5.1. Pentacarbonyl(4,7-diaza-cyclo[$0^{3,7}$]-hepta-1,2-dien-1-ylidene)tungsten (**14**)

Yellow solid. Yield: 0.40 g (96%) after recrystallization from pentane/CH_2Cl_2 (1:2); m.p. 168–170 °C. IR (THF, cm^{-1}): ν(CO) = 2091 vw, 1961 vw, 1922 vs, 1896 m; ν(CCC) = 2032 m. ^{1}H NMR (250 MHz, [D$_6$]-acetone): δ = 3.96 (s, 4H, CH_2), 8.68 (br, 2H, NH). ^{13}C NMR (62.9 MHz, [D$_6$]-acetone): δ = 45.7 (CH_2), 97.6 (C_β), 150.8 (C_γ), 158.0 (C_α), 199.6 (*cis*-CO, $^1J_{WC}$ = 125.8 Hz), 202.8 (*trans*-CO). MS(FAB), *m/z* (%): 418 (32) [M^+], 390 (20) [$(M - CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 357 (3.751) [$CHCl_3$], 383 (3.674) [CH_2Cl_2], 340 (2.974) [DMF]. Anal. Found: C, 28.76; H, 1.45; N, 6.84. Calc. for $C_{10}H_6N_2O_5$ W (418.0): C, 28.73; H, 1.45; N, 6.70%.

4.5.2. Pentacarbonyl(4,8-diaza-cyclo[$0^{3,8}$]-octa-1,2-dien-1-ylidene)tungsten (**15**)

Yellow solid. Yield: 0.43 g (98%) after recrystallization from pentane/CH_2Cl_2 (1:2); m.p. 166–167 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2089 vw, 1919 vs, 1892 m; ν(CCC) = 2034 m. ^{1}H NMR (250 MHz, [D$_6$]-acetone): δ = 1.27 (m, 4H, CH_2), 3.75 (m, 4H, NCH_2), NH not detected. ^{13}C NMR (62.9 MHz, [D$_6$]-acetone): δ = 20.0 (NCH_2CH_2), 40.8 (NCH_2CH_2), 102.4 (C_β), 145.2 (C_γ), 158.0 (C_α), 199.6 (*cis*-CO), 202.7 (*trans*-CO). MS(FAB), *m/z* (%): 432 (7) [M^+], 403 (8)

[(M − CO)$^+$], 375 (7) [(M − 2CO)$^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 377 (3.997) [CH_2Cl_2], 363 (3.776) [DMF]. Anal. Found: C, 30.47; H, 2.10; N, 6.49. Calc. for $C_{11}H_8N_2O_5W$ (432.0): C, 30.58; H, 1.87; N, 6.48%.

4.5.3. Pentacarbonyl(4,9-diaza-cyclo[$0^{3,9}$]-nona-1,2-dien-1-ylidene)tungsten (**16**)

Yellow solid. Yield: 0.29 g (66%) after column chromatography using a mixture of pentane/CH_2Cl_2 (1:2) as eluent; m.p. 184–186 °C (dec.). IR (THF, cm^{-1}): ν(CO) = 2085 vw, 1959 vw, 1918 vs, 1891 m; ν(CCC) = 2030 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 1.99 (m, 4H, CH_2), 3.58 (m, 4H, NCH_2), 8.38 (br, 2H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 28.2 (CH_2), 46.0 (NCH_2), 104.8 (C_β), 146.9 (C_γ), 151.3 (C_α), 199.8 (*cis*-CO, $^1J_{WC}$ = 124.2 Hz), 202.8 (*trans*-CO). MS(FAB), *m/z* (%): 446 (27) [M$^+$], 418 (30) [(M − CO)$^+$], 390 (19) [(M − 2CO)$^+$], 362 (8) [(M − 3CO)$^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 380 (3.613) [$CHCl_3$], 367 (3.715) [DMF]. Anal. Found: C, 32.73; H, 2.47; N, 6.25. Calc. for $C_{12}H_{10}N_2O_5$ W (446.1): C, 32.31; H, 2.26; N, 6.28%.

4.5.4. Pentacarbonyl(4,11-diaza-dicyclo[$0^{3,11}$. $0^{5,10}$]-undeca-1,2-dien-1-ylidene)tungsten (**17**)

Yellow solid. Yield: 0.94 g (99%) after column chromatography using mixtures of pentane/THF (2:1 to 1:3) as eluent; m.p. 178–180 °C. IR (THF, cm^{-1}): ν(CO) = 2090 vw, 1961 vw, 1922 vs, 1897 m; ν(CCC) = 2027 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 1.34–1.62 (m, 4H, NCHCH$_2$CH_2, *cis* and *trans* adduct), 1.85–2.22 (m, 4H, NCHCH_2CH$_2$, *cis* and *trans* adduct), 3.46 (m, 1.6H, NCH, *trans* adduct), 4.21 (m, 0.4H, NCH, *cis* adduct), 8.74 (br, 0.4H, NH, *cis* adduct), 8.92 (br, 1.6H, NH, *trans* adduct). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 21.1, 25.5, 27.9, 31.7 (CH_2, *cis* and *trans* adduct), 57.4 (NCH, *cis* adduct), 66.1 (NCH, *trans* adduct), 98.5 (C_β, *cis* adduct), 99.6 (C_β, *trans* adduct), 150.5 (C_γ, *cis* adduct), 152.2 (C_γ, *trans* adduct), 161.7 (C_α, *cis* adduct), 161.7 (C_α, *trans* adduct), 199.5 (*cis*-CO, *cis* adduct), 199.5 (*cis*-CO, $^1J_{WC}$ = 124.4 Hz, *trans* adduct), 202.7 (*trans*-CO, *cis* adduct), 202.8 (*trans*-CO, $^1J_{WC}$ = 132.0 Hz, *trans* adduct). MS(FAB), *m/z* (%): 472 (68) [M$^+$], 444 (52) [(M − CO)$^+$], 416 (32) [(M − 2CO)$^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 403 (3.437) [pentane], 395 (4.192) [$CHCl_3$], 395 (4.024) [CH_2Cl_2], 365 nm (3.976) [DMF]. Anal. Found: C, 35.75; H, 2.75; N, 5.94. Calc. for $C_{14}H_{12}N_2O_5$ W (472.1): C, 35.62; H, 2.56; N, 5.93%.

4.5.5. Pentacarbonyl(4,7,10-triaza-cyclo[$0^{3,7}$]-deca-1,2-dien-1-ylidene)chromium (**18**)

Yellow solid. Yield: 0.31 g (94%) after recrystallization from CH_2Cl_2; m.p. 140–145 °C. IR (THF, cm^{-1}): ν(CO) = 2086 vw, 1968 vw, 1929 vs, 1902 m; ν(CCC) = 2023 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 3.54 (t, $^3J_{HH}$ = 6.2 Hz, 2H, NCH_2CH$_2$NH$_2$), 3.80 (t, $^3J_{HH}$ = 6.2 Hz, 2H, NCH$_2$CH_2NH$_2$), 3.86 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 10.9 Hz, 2H, CH_2), 4.07 (dd, $^3J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 11.8 Hz, 2H, CH_2), NH not detected. ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 42.3 (NCH$_2$CH$_2$NH$_2$), 48.0 (CH_2), 49.4 (NCH$_2$$CH_2NH_2$), 49.4 ($CH_2$), 97.2 ($C_\beta$), 147.5 ($C_\gamma$), 179.7 ($C_\alpha$), 218.7 (*cis*-CO), 222.0 (*trans*-CO). MS(FAB), *m/z* (%): 330 (100) [(M + H)$^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 387 (3.949) [$CHCl_3$], 382 (4.078) [CH_2Cl_2], 352 (3.680) [DMF]. Anal. Found: C, 43.69; H, 3.66; N, 12.61. Calc. for $C_{12}H_4CrN_3O_5$ (329.2): C, 43.78; H, 3.37; N, 12.76%.

4.6. General procedure for the preparation of the allenylidene complexes **19** and **20**

At −80 °C, 0.55 mL of LDA (1.8 M in hexane) was slowly added to a solution of 0.50 g (1.0 mmol) of **10** in 5 mL of THF. After stirring for 30 min at −80 °C, the solvent was removed in vacuo. The residue was dissolved in 5 mL of CH_2Cl_2 and cooled to 0 °C. 1.0 mmol of the corresponding Meerwein salt was added. The solution was stirred at 0 °C until all starting material was consumed (as indicated by TLC). After filtration over silica gel at −10 °C and removal of the solvent in vacuo, the crude product was purified by column chromatography (SiO_2, −10 °C) using mixtures of pentane and CH_2Cl_2 as the eluent (2:1 to neat CH_2Cl_2).

4.6.1. Pentacarbonyl[3-butylamino-3-methyl(butyl)amino-propa-1,2-dienylidene]tungsten (**19**)

Yellow solid. Yield: 0.16 g (33%); m.p. 65–67 °C. IR (THF, cm^{-1}): ν(CO) = 2086 vw, 1922 vs, 1894 m; ν(CCC) = 2026 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 0.95 (m, 6H, NCH$_2$CH$_2$CH$_2$CH_3), 1.39 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.63 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 3.16 (s, 3H, NCH_3), 3.65, 3.86 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 7.72 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 15.0, 15.1 (NCH_2CH$_2$CH$_2$$CH_3$), 21.4, 21.5 (NCH$_2CH_2$$CH_2CH_3$), 32.0, 33.9 (NCH$_2$$CH_2CH_2CH_3$), 44.3, 47.4 (N$CH_2CH_2CH_2CH_3$), 54.7 ($NCH_3$), 101.0 ($C_\beta$), 147.2 ($C_\gamma$), 160.0 ($C_\alpha$), 199.6 (*cis*-CO, $^1J_{WC}$ = 124.2 Hz), 203.4 (*trans*-CO). MS(FAB), *m/z* (%): 518 (58) [M$^+$], 490 (92) [(M − CO)$^+$], 462 (73) [(M − 2CO)$^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 374 (3.966) [CH_2Cl_2]. Anal. Found: C, 40.19; H, 4.51; N, 5.20. Calc. for $C_{17}H_{22}N_2O_5$ W (518.2): C, 39.40; H, 4.28; N, 5.41%.

4.6.2. Pentacarbonyl(3-butylamino-3-ethyl[butyl]amino-propa-1,2-dienylidene)tungsten (**20**)

Yellow solid. Yield: 0.30 g (57%); m.p. 55–56 °C. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2087 vw, 1966 vw, 1923 vs, 1890 m; ν(CCC) = 2023 m. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 0.95 (m, 6H, NCH$_2$CH$_2$CH$_2$CH_3), 1.23 (m, 3H, Et-CH_3), 1.41 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$),

1.67 (m, 4H, $NCH_2CH_2CH_2CH_3$), 3.55 (m, 4H, $NCH_2CH_2CH_2CH_3$), 3.81 (m, 2H, Et-CH_2), 7.73 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D_6]-acetone): δ = 13.0 (Et-CH_3), 15.0, 15.1 ($NCH_2CH_2CH_2CH_3$), 21.4, 21.5 ($NCH_2CH_2CH_2CH_3$), 32.0, 33.8 ($NCH_2CH_2CH_2CH_3$), 44.1, 47.4 ($NCH_2CH_2CH_2CH_3$), 54.7 (Et-CH_2), 101.0 (C_β), 147.2 (C_γ), 160.0 (C_α), 199.6 (*cis*-CO), 203.4 (*trans*-CO). MS(FAB), *m/z* (%): 532 (46) [M^+], 504 (96) [$(M - CO)^+$], 476 (77) [$(M - 2CO)^+$]. UV–Vis: λ_{max} (nm) (log ε) [solvent]: 372 (3.992) [CH_2Cl_2]. Anal. Found: C, 40.51; H, 4.31; N, 4.98. Calc. for $C_{18}H_{24}N_2O_5W$ (532.2): C, 40.62; H, 4.55; N, 5.26%.

4.7. X-ray structural analyses

Single crystals suitable for X-ray structural analyses were obtained by slow evaporation of the solvent at 4 °C. The measurements were performed at 188(2) K with a crystal mounted on a glass fiber on a Siemens P4 diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.71073 Å). For crystal data and refinement details see Table 1. The structures were solved by direct methods using the SHELXTL-97 program package [19]. The positions of the hydrogen atoms were calculated by assuming ideal geometry and their coordinates were refined together with those of the attached carbon atoms as ''riding model''. All other atoms were refined anisotropically.

4.8. DFT-calculations

All DFT calculations were performed using JAGUAR [20] (version 5.5.016) running on Linux 2.4.20 – 28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. Known X-ray structures were used as initial geometries for a geometry optimization using the LACVP* basis set (ECP basis set for Cr and W, N31G6* basis set for all other atoms) and the BP86 density functional. The structures were shown to be ground-state structures since no large imaginary frequencies were obtained after calculation of the second derivative. Partial charges were calculated using the NBO program [21] (version 5.5) and the breakdown of molecular orbital contributions were obtained using the AOMix [22] program package. The solvation energies (in THF) were obtained by using the self-consistent reaction field (SCRF) method implemented in *Jaguar*. Gibbs free energies in solution (THF) were acquired by numerical calculation of the vibrational modes.

5. Supplementary material

Crystallographic data for the structural analyses of complexes **8**, **11**, and **18** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-262379 (**8**), CCDC-262380 (**11**) and CCDC-262381 (**18**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or http://ccdc.com.ac.uk).

Tables listing the data of the calculated structures, energies, population analyses, and molecular orbital coefficients are available free of charge from the authors.

Acknowledgments

We thank the Wacker-Chemie GmbH for a gift of chemicals.

References

[1] E.O. Fischer, H.J. Kalder, A. Frank, F.H. Köhler, G. Huttner, Angew. Chem. 88 (1976) 683;
Angew. Chem. Int., Ed. Engl. 15 (1976) 623.
[2] H. Berke, Angew. Chem. 88 (1976) 684;
Angew. Chem. Int., Ed. Engl. 15 (1976) 624.
[3] (a) For reviews on allenylidene complex chemistry see: M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem. 22 (1983) 59;
(b) M.I. Bruce, Chem. Rev. 91 (1991) 197;
(c) M.I. Bruce, Chem. Rev. 98 (1998) 2797;
(d) V. Cadierno, P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571.
[4] (a) A. Fürstner, M. Picquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998) 1315;
(b) M. Bassetti, F. Centola, D. Sémeril, C. Bruneau, P.H. Dixneuf, Organometallics 22 (2002) 4459, and literature cited therein.
[5] J.P. Selegue, Organometallics 1 (1982) 217.
[6] (a) Recent reviews on π-donor-substituted allenylidene complexes: H. Fischer, N. Szesni, Coord. Chem. Rev. 248 (2004) 1659;
(b) R.F. Winter, S. Záliš, Coord. Chem. Rev. 248 (2004) 1565.
[7] H. Fischer, N. Szesni, G. Roth, N. Burzlaff, B. Weibert, J. Organomet. Chem. 683 (2003) 301.
[8] (a) M.A. Esteruelas, A.V. Gomez, A.M. López, E. Onate, N. Ruiz, Organometallics 17 (1998) 2297;
(b) M.A. Esteruelas, A.V. Gomez, A.M. López, M. Oliváu, E. Onate, N. Ruiz, Organometallics 19 (2000) 4;
(c) M.A. Esteruelas, A.V. Gomez, A.M. López, E. Onate, Organometallics 17 (1998) 3567;
(d) M.A. Esteruelas, A.V. Gomez, A.M. López, E. Onate, N. Ruiz, Organometallics 18 (1999) 1606;
(e) D.J. Bernad, M.A. Esteruelas, A.M. López, M. Olivan, E. Onate, M.C. Puerta, P. Valerga, Organometallics 19 (2000) 4327.
[9] (a) H. Berke, G. Huttner, J. von Seyerl, Z. Naturforsch. B 36 (1981) 1277;
(b) V. Cadierno, M.P. Gamasa, J. Gimeno, M. Gonzalez-Cueva, E. Lastra, J. Borge, S. Garcia-Granda, E. Pérez-Carreno, Organometallics 15 (1996) 2137;
(c) A. Marrone, N. Re, Organometallics 21 (2002) 3562;
(d) M. Baya, P. Crochet, M.A. Esteruelas, E. Gutierrez-Puebla, A.M. López, J. Modrego, E. Onate, N. Vela, Organometallics 19 (2000) 2585;
(e) N. Re, A. Sgamellotti, C. Floriani, Organometallics 19 (2000) 1115.

[10] (a) F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, Organometallics 12 (1993) 2556;
(b) M.A. Esteruelas, A.V. Gomez, A.M. López, E. Onate, Organometallics 17 (1998) 3567;
(c) D.J. Bernard, M.A. Esteruelas, A.M. López, J. Modrego, M.C. Puerta, P. Valerga, Organometallics 18 (1999) 4995;
(d) H. Fischer, G. Roth, D. Reindl, C. Troll, J. Organomet. Chem. 454 (1993) 133;
(e) H. Fischer, G. Roth, J. Organomet. Chem. 490 (1995) 229;
(f) G. Roth, H. Fischer, J. Organomet. Chem. 507 (1996) 125.
[11] N. Mantovani, L. Marvelli, R. Rossi, V. Bertolasi, C. Bianchini, I. de los Rios, M. Peruzzini, Organometallics 21 (2002) 2382.
[12] G. Roth, H. Fischer, Organometallics 15 (1996) 1139.
[13] R. Aumann, B. Jasper, R. Fröhlich, Organometallics 14 (1995) 3173.
[14] G. Roth, D. Reindl, M. Gockel, C. Troll, H. Fischer, Organometallics 17 (1998) 1393.
[15] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) S1.
[16] R. Aumann, Chem. Ber. 127 (1994) 725.
[17] N. Szesni, B. Weibert, H. Fischer, Inorg. Chim. Acta 358 (2005) 1645.
[18] A.I. Meyers, D.L. Temple, D. Haidukewych, E.D. Mihelich, J. Org. Chem. 39 (1974) 2787.
[19] G.M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), 1997.
[20] JAGUAR 5.5, Schrödinger, LLC, Portland, Oregon, 2003
[21] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, F. Weinhold, NBO 5.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001
[22] (a) S.I. Gorelsky, AOMix program Available from: <http://www.stanford.edu/~gorelsky/>;
(b) S.I. Gorelsky, A.B.P. Lever, J. Organomet. Chem. 635 (2001) 187.