A convenient route to six-membered heterocyclic carbene complexes: Reactions of aminoallenylidene complexes with 1,3-bidentate nucleophiles

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Abstract

Pentacarbonyl dimethylamino(*methoxy*)allenylidene complexes of chromium and tungsten, $[(CO)_5M=C=C=C(NMe_2)OMe]$ (M = Cr (**1a**), W (**1b**)), react with 1,3-bidentate nucleophiles such as amidines and guanidine, $H_2N–C(=NH)R$ (R = Ph, $C_6H_4NH_2$-4, $C_6H_4NO_2$-3, NH_2), by displacing the methoxy substituent to give exclusively dimethylamino(imino)-allenylidene complexes, $[(CO)_5M=C=C=C\{N=C(NH_2)R\}NMe_2]$ (**2a**–**5a**, **2b**). Treatment of the chromium complexes **2a**–**5a** with catalytic amounts of hydrochloric acid or HBF_4 gives rise to an intramolecular cyclization. Addition of the terminal NH_2 substituent to the C_α–C_β bond of the allenylidene chain affords pyrimidinylidene complexes **6**–**9** in high yield. In contrast to the chromium complexes **2a**–**5a**, the corresponding tungsten complex **2b** could not be induced to cyclize due to the lower electrophilicity of the α-carbon atom in **2b**. The dimethylamino(*phenyl*)allenylidene complex $[(CO)_5Cr=C=C=C(NMe_2)Ph]$ (**10**) reacts with benzamidine or guanidine similarly to **1a**. However, the second reaction step – cyclization to give pyrimidinylidene complexes – proceeds much faster. Therefore, the formation of an imino(phenyl)allenylidene complex as an intermediate is established only by IR spectroscopy. The analogous reaction of **10** with 3-amino-5-methylpyrazole affords, via a formal [3+3]-cycloaddition, a pyrazolo[1,5a]pyrimidinylidene complex **13**. Compound **13** is obtained as two isomers differing in the relative position of the N-bound proton (1H or 4H). The related reaction of **10** with thioacetamide yields a thiazinylidene complex and additionally an alkenyl(amino)carbene complex.
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1. Introduction

Allenylidene complexes have attracted a great deal of attention in recent years [1]. This is mostly due to their versatile chemical and physico-chemical properties. Additionally, allenylidene complexes have turned out to be valuable building blocks for C–C and C–X bond formation [2–9] and have found application in catalytic processes [10,11]. The presence of a linear unsaturated carbon chain makes them potentially useful as one-dimensional wires [12] and for opto-electronic applications [13].

The allenylidene ligand in such complexes is characterized by a sequence of electrophilic and nucleophilic sites. From theoretical [2a,14] and experimental studies it follows that the atoms C_α and C_γ exhibit electrophilic character whereas C_β is a nucleophilic center. Therefore, nucleophiles either add to the metal-bound or the terminal carbon atom of the allenylidene backbone. The regioselectivity of nucleophilic addition is determined by the Lewis acidity and the steric requirements of the metal fragment, the π-donor properties of the terminal substituents of the allenylidene backbone, and by the properties of the nucleophile [1–9].

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Until now, the majority of known allenylidene complexes are either bis(aryl)- or bis(alkyl)-substituted. They are readily obtained by a method introduced by Selegue [15] using substituted propargylic alcohols as the C_3 source and suitable transition metal precursors. Therefore, most reactivity studies have been performed with these types of allenylidene complexes. We recently demonstrated that the bonding and the reactivity of π-donor substituted allenylidene complexes strongly deviates from that of their non-donor substituted counterparts.

For instance, non-donor substituted allenylidene complexes show a distinct preference for the addition of amines across the C_α–C_β bond of the allenylidene chain to give α,β-unsaturated aminocarbene complexes or azabutadienyl complexes, respectively [2b,5,7b,16]. Until now, only one example for the addition of ammonia to the terminal carbon atom is known, namely that of the rhenium allenylidene complex [(triphos) (CO)$_2$-Re=C=C=C(Ph)$_2$][OTf] [5]. In contrast, in π-donor-substituted allenylidene complexes addition of amines to the α-carbon atom of the allenylidene ligand is only of minor importance [17]. In most cases amines add to the terminal carbon atom of the allenylidene ligand [18,19].

The presence of two electrophilic centers in the allenylidene chain offers access to cyclic ligands through reactions with bidentate nucleophiles. Esteruelas and co-workers [20] recently demonstrated that cationic ruthenium allenylidene complexes readily undergo diheterocyclization reactions with 1,2- and 1,3-dinucleophiles yielding five- and six-membered heterocycles. In previous investigations, we were able to synthesize pyrazolidinylidene [21] and isoxazolidinylidene complexes [22] of chromium and tungsten from bis(aryl)allenylidene pentacarbonyl complexes and hydrazines or hydroxy-lamines.

We now report on the reactions of π-donor-substituted allenylidene complexes with a series of dinucleophiles and on the synthesis and characterization of various unsaturated heterocyclic carbene ligands coordinated to chromium.

2. Results and discussion

Addition of a slight excess of an amidine or guanidine to solutions of the pentacarbonyl dimethylamino(methoxy)allenylidene chromium complex 1a in THF almost quantitatively afforded the dimethylamino(imino)allenylidene complexes 2a–5a (Scheme 1). The reactions proceeded quickly and were complete within from a few minutes to a maximum of 2 h, depending on the amidine (guanidine). Product formation is highly selective, only the amino(imino)allenylidene complexes 2a–5a were isolated. They were derived from 1a by substitution of an amidine (guanidine) for the methoxy group. Neither the formation of bis(amino)allenylidene or imino(methoxy)allenylidene complexes nor the addition of the nucleophile across the C_α–C_β bond of the allenylidene ligand to give α,β-unsaturated carbene complexes could be observed. After recrystallization, the complexes 2a–5a were obtained in an analytically pure form in 92–98% yield. The reaction of the tungsten allenylidene complex 1b with benzamidine proceeded similarly and gave the corresponding dimethylamino(imino)allenylidene tungsten complex 2b in 94% yield (Scheme 1).

The new allenylidene complexes were fully characterized by spectroscopic means and by elemental analyses. The IR spectra show in addition to the typical pentacarbonyl pattern in the region 1800–2100 cm^{-1} a $v(CCC)$ absorption between 2007 and 2020 cm^{-1}. As observed previously [1h,1k,23], the exact position of the cumulenylidene absorption depends on the donor capacity of the terminal substituents of the allenylidene ligand. The $v(CCC)$ absorption of 2–5 is found at a lower wavenumber compared to bis(amino)allenylidene complexes but at a higher wavenumber than that in amino(alkoxy)allenylidene complexes. From these data a donor capacity of the terminal substituents in 2–5 can be deduced that is intermediate in between that of amino(alkoxy)allenylidene and bis(amino)allenylidene complexes. This indicates a significant contribution of the zwitterionic iminium alkynyl resonance structure II (Scheme 2) to the overall bonding. The conclusion is confirmed
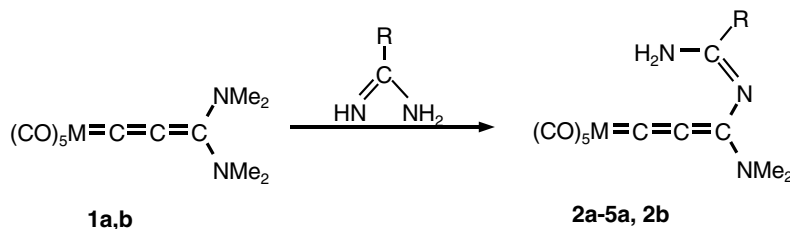
M = Cr (**a**), W (**b**)

R = Ph (**2**), C$_6$H$_4$NH$_2$-4 (**3**), C$_6$H$_4$NO$_2$-3 (**4**), NH$_2$ (**5**)

Scheme 1.
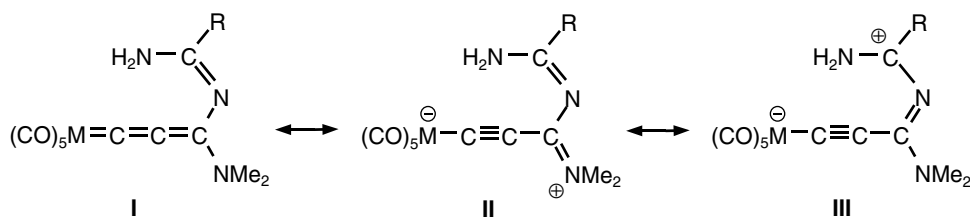
Scheme 2.

by the position of the C_α resonance of the allenylidene ligand in the ^{13}C NMR spectra at rather high field. From the observation of two signals for the dimethylamino group in the ^1H and the ^{13}C NMR spectra a significant double bond character of the C_γ-N-bond can be deduced. All other data are in agreement with known aminoallenylidene complexes of chromium or tungsten.

The structure of **2b** was additionally established by an X-ray structural analysis (Fig. 1, Table 1). Due to the double bond character of the N2–C9 bond (1.313(7) Å) four orientations of the amidoyl moiety relative to the allenylidene spine and the partial C9–N1 bond are possible. In the crystal the imidoyl group is orientated toward the metal center in a (Z)-s-cis-conformation thus reducing unfavourable steric interactions with the dimethylamino substituent. The spectroscopic data of **2**–**5** indicate that in solution these complexes also adopt a (Z)-s-cis conformation. The extended π-system [W-C6≡C7–C8(=N1)–N2=C9] is essentially planar indicating strong π-delocalisation. Bonding distances and angles of the allenylidene backbone are similar to those reported for other aminoallenylidene pentacarbonyl complexes [18,23–25]: the bonds C6–C7 (1.207(8) Å) and C8–N1 (1.333(7) Å) are short and the bonds W1–C6 (2.173(6) Å) and C7–C8 (1.426(8) Å) are long. These

data once more confirm that delocalisation of the electron pair at nitrogen toward the metal plays an important role in stabilizing these complexes.

Several mechanisms are conceivable to account for the formation of **2**–**5**. A likely one is shown in Scheme 3. In general, the observed reaction should be similar to that of **1b** with ammonia, primary and secondary amines [19]. The reaction is initiated by addition of the nucleophile to the γ-carbon atom of the allenylidene chain. In contrast to amines, two nucleophile centers are present in amidines. Since the NH_2 group is more nucleophilic than the HN=C group, an addition of the amidine via the NH_2 terminus is most likely. The subsequent tautomerization of **A** to give the vinylidene complex **B** is followed by methanol elimination to form **C**. Another tautomerization and rearrangement of the
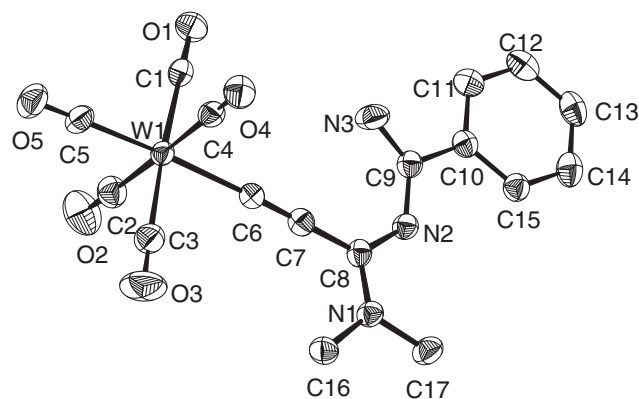

Fig. 1. Structure of complex **2b** in the crystal (ellipsoids drawn at 50% level, hydrogens omitted for clarity). Selected bond length (Å) and angles (°): W1–C1 2.036(6), W1–C2 2.066(7), W1–C3 2.055(7), W1–C4 2.028(6), W1–C5 2.015(6), W1–C6 2.173(6), C6–C7 1.207(8), C7–C8 1.426(8), C8–N1 1.333(7), C8–N2 1.365(7), N2–C9 1.313(7), C9–N3 1.338(7); W1–C6–C7 176.1(5), C6–C7–C8 179.3(6), C7–C8–N1 118.6(5), C7–C8–N2 125.6(5), N2–C9–N3 127.8(5), N2–C9–C10 115.6(5), N3–C9–C10 116.5(5).

Table 1
Crystal data and refinement details for compounds **3b** and **9**

| Complex	**3b**	**9**
Formula	$C_{17}H_{13}N_3O_5W$	$C_{17}H_{13}CrN_3O_5$
M_r	523.15	391.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	6.4540(16)	10.862(5)
b (Å)	21.431(6)	6.930(2)
c (Å)	13.310(4)	23.236(7)
α (°)	90	90
β (°)	95.57(3)	99.15(4)
γ (°)	90	90
V (Å^3)	1832.2(9)	1726.7(11)
Z	4	4
Crystal size (mm^3)	$0.50 \times 0.30 \times 0.20$	$0.50 \times 0.40 \times 0.30$
ρ_{calc} (g cm^{-3})	1.897	1.505
μ (mm^{-1})	6.336	0.696
$F(000)$	1000	800
Diffractometer	Siemens P4	Siemens P4
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71073	0.71073
T (K)	188(2)	183(2)
Maximum 2Θ (°)	54	54
Index range	$-8 \leqslant h \leqslant 0$,	$-13 \leqslant h \leqslant 13$,
	$-27 \leqslant k \leqslant 27$,	$-8 \leqslant k \leqslant 5$,
	$-16 \leqslant l \leqslant 16$	$-29 \leqslant l \leqslant 29$
Number of data	4475	4733
Number of unique data	3992	3756
Parameters	235	235
$R(F)$ for $I > 2\sigma > (I)$	0.0344	0.0362
$wR_2(F^2)$ for all data	0.0838	0.0852
Goodness-of-fit on F^2	1.046	1.031
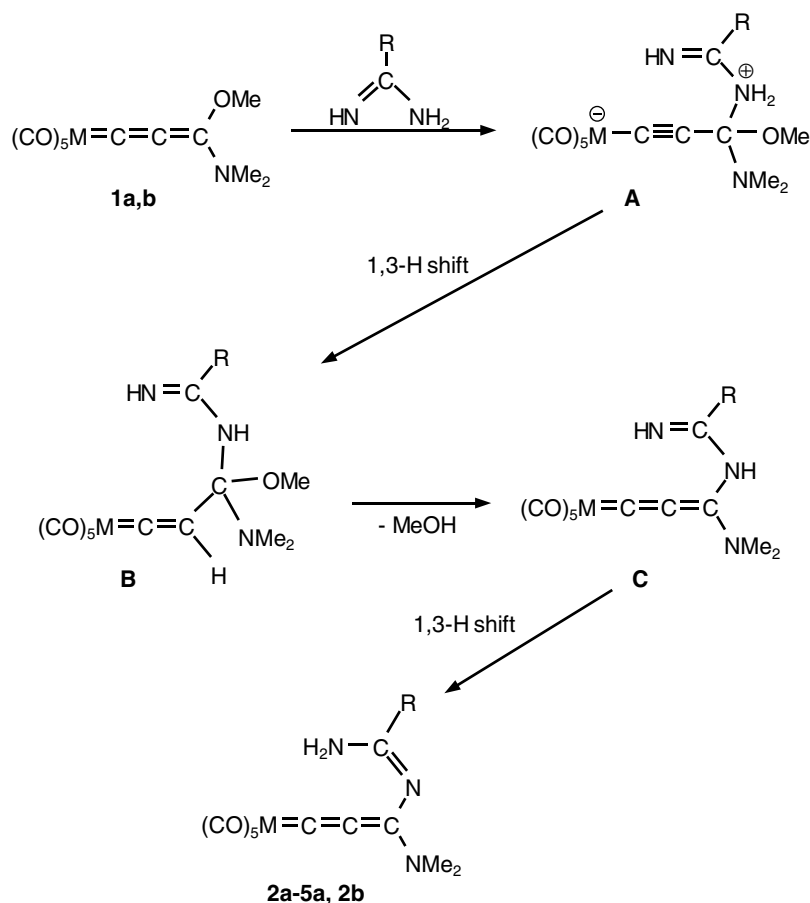
Scheme 3.

π-system finally afford the product complexes **2**–**5**. Formation of the thermodynamically favored conjugated π-system is presumably the driving force for the rearrangement. Alternatively, methanol elimination from **A** followed by a 1,3-H shift would likewise produce the complexes **2**–**5**. A similar reaction sequence has been proposed by Gimeno et al. for the displacement of a terminal amino substituent by carbon nucleophiles [24].

The complexes **2a**–**5a** were stable in solution at ambient temperature. Addition of acids like hydrochloric acid or HBF$_4$, however, induced cyclization and formation of the pyrimidinylidene complexes **6**–**9** (Scheme 4). The new complexes were obtained in 78–96% yield. In

contrast to chromium compounds, all attempts to cyclize tungsten allenylidene complex **2b** failed. Even adding of large amounts of hydrochloric acid, HOAc or HBF$_4$ to solutions of **2b** only led to decomposition of the compound.

The complexes **6**–**9** are the product of an intramolecular addition of the free NH$_2$ group to the C$_\alpha$–C$_\beta$ bond of the allenylidene ligand. Very likely, the initial reaction step is protonation of the nucleophilic C$_\beta$ atom of the allenylidene chain. This agrees with the results of theoretical studies on the electronic structure of a series of pentacarbonyl allenylidene chromium and tungsten complexes [(CO)$_5$M=C=C=C(R^1)R^2; M = Cr, W;

R = Ph (**2a, 6**), C$_6$H$_4$NH$_2$-4 (**3a, 7**), C$_6$H$_4$NO$_2$-3 (**4a, 8**), NH$_2$ (**5a, 9**)
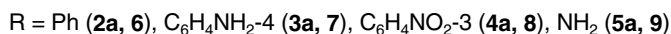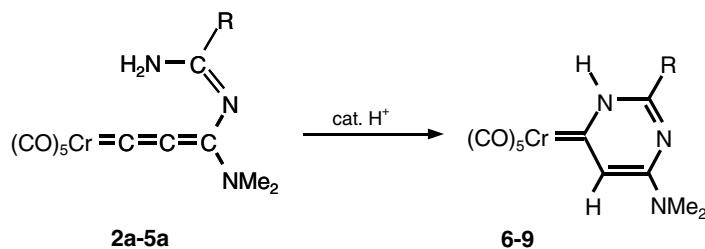
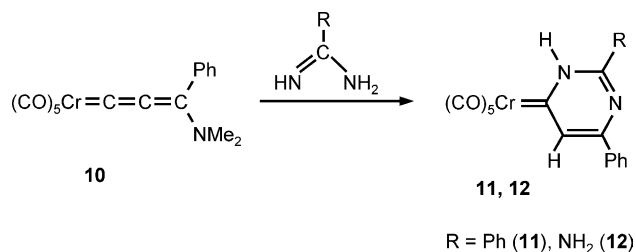Scheme 4.

R^1 = Ph, OMe, NMe$_2$; R^2 = Ph, OMe, NMe$_2$]. These calculations [19] indicate that the HOMO is predominantly localized at the metal and at C$_\beta$. The C$_\beta$ atom is the prefered site for an electrophilic attack. The proposal of an initial protonation at C$_\beta$ is also supported by the observation that, on addition of acids to neutral allenylidene complexes of manganese, osmium and ruthenium, cationic alkenylcarbyne complexes are formed [14d,26]. Protonation of **2–5** is followed by cyclization and deprotonation. Nevertheless, other pathways are also conceivable and cannot be excluded since deuteration experiments (cyclisation intiated by DCl) were inconclusive.

When solutions of benzamidine or guanidine were added to the amino(*phenyl*)allenylidene complex **10** and the reaction solutions then worked up analogously to those of **2a–5a**, we were unable to isolate imino-(phenyl)allenylidene chromium complexes related to **2a–5a**. Filtration of the crude reaction mixtures over silica at −20 °C instantaneously led to the formation of the pyrimidinylidene complexes **11** and **12** (Scheme 5). However, the presumed allenylidene intermediate in the reaction of **10** with guanidine could be observed by IR spectroscopy when the filtration was carried out at −80 °C. The v(CO) absorptions (1932 vs, 1904 sh cm^{-1} in THF) were, as expected, at somewhat higher wavenumbers than those of the isolated amino(imino) allenylidene complexes **2a–5a** and the v(CCC) band (1984 m cm^{-1}) was found at lower wave numbers. The enhanced reactivity of the imino(*phenyl*)allenylidene intermediates, when compared to **2a–5a**, is readily explained by the absence of the strong π-donor NMe$_2$ at the terminal position of the allenylidene ligand. π-Donor-substituents considerably contribute to the stabilization of these complexes.

The new complexes containing a heterocyclic carbene ligand were obtained as yellow to red solids and were characterized by spectroscopic means and elemental analyses. The spectroscopic data were in accord with those of the few pyrimidinylidene complexes reported until now [27]. From the IR spectra, it follows that the cyclic aminocarbene ligand in **6a–9a**, **11**, and **12** exhibits higher σ-donor/π-acceptor properties than the aminoallenylidene ligand in **2a–5a**. A prominent feature is also the pronounced low-field shift of the metal-bound C$_\alpha$

atom in the ^{13}C NMR spectra on cyclization. In the ^{1}H NMR spectra the C$_\beta$–H resonance appears as a singlet in the range 6.4–8.5 ppm. The position strongly depends on the substituents at the pyrimidine ring. Donor substituents give rise to an upfield shift of the H$_\beta$ signal. The complexes **6–9** exhibit two broad resonances for the C6-bound dimethylamino group in the NMR spectra indicating double bond character of the C6–N bond due to the delocalisation of the electron pair at this nitrogen atom towards the metal center (Scheme 6). From the temperature dependence of the NMR spectrum of **7** a barrier of $\Delta G^{\neq} = 61.9 \pm 0.5$ kJ/mol to rotation around the C–NMe$_2$ bond was calculated.

The molecular structure of complex **6** was additionally confirmed by an X-ray structural analysis (Fig. 2, Table 1). As expected, the cyclic aminocarbene (pyrimidinylidene) ligand is essentially planar (torsion angles: C6–N1–C9–N2 2.8(3)°, C8–N2–C9–N1 0.3(3)°) and adopts a staggered conformation with respect to the *cis*-CO ligands (torsion angle N1–C6–Cr1–C2 = 62.3(2)°). Both rings (pyrimidinylidene and phenyl ring)
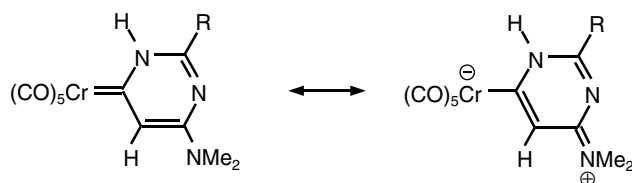
Scheme 6.

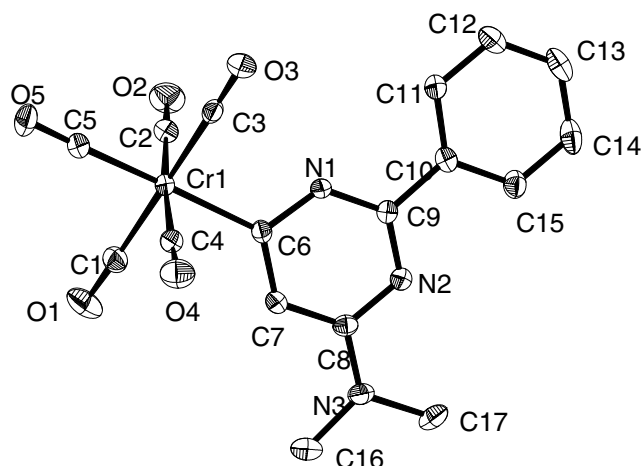Fig. 2. Structure of complex **6** in the crystal (ellipsoids drawn at 50% level, hydrogens omitted for clarity). Selected bond lengths (Å) and angles (°): Cr1–C1 1.926(2), Cr1–C2 1.897(2), Cr1–C3 1.882(2), Cr1–C4 1.913(2), Cr1–C5 1.869(2), Cr1–C6 2.114(2), C6–C7 1.381(3), C7–C8 1.416(3), C8–N3 1.346(3), C8–N2 1.371(3), N2–C9 1.309(3), C9–N1 1.354(3), N1–C6 1.398(3); Cr1–C6–C7 128.5(2), C6–C7–C8 121.4(2), C7–C8–N3 133.7(2), C7–C8–N2 121.5(2), C8–N2–C9 117.2(2), N2–C9–N1 122.1(2), C9–N1–C6 125.0(2), N1–C6–C7 112.6(2).

Scheme 5.

R = Ph (**11**), NH$_2$ (**12**)

as well as the pyrimidinyl ring and the dimethylamino group are coplanar (torsion angles: N1–C9–C10–C11 −0.2(3)°, C16-N3–C8-C7 0.7(3)°). The bonds N3–C8 and C6–C7 are short and even shorter than the corresponding bonds in 2,6-diamino-4(3H)-pyrimidinone [28]. In turn, C7–C8 is rather long and is longer than the C=C bond in 2,6-diamino-4(3H)-pyrimidinone [28] or 6-hydroxy-4(3H)-pyrimidinone [29]. These data confirm that there is considerable electron transfer from the nitrogen atom to the metal center.

Complexes with a bicyclic carbene ligand are likewise accessible through reaction of allenylidene complexes with dinucleophiles. For instance, the pyrazolopyrimid-inylidene complex 13 was formed when solutions containing 10 and 3-amino-5-methylpyrazole in THF were stirred at 60 °C for five days. The pyrazolopyrimidiny-lidene complex 13 was obtained after chromatography in 74% yield as a chromatographically non-separable mixture of the 1H- and 4H-isomer (Scheme 7).

The IR spectrum of the mixture shows only one set v(CO) of absorptions. In contrast, the NMR spectra exhibit two sets of resonances. Analogously to the comparable carbon atom (C7) in related organic compounds [30], the resonance of the metal-bound (Cα) carbon atom in 1H-13 is observed at higher field ($\delta = 203.8$) than that of 4H-13 ($\delta = 234.0$). From this observation and from
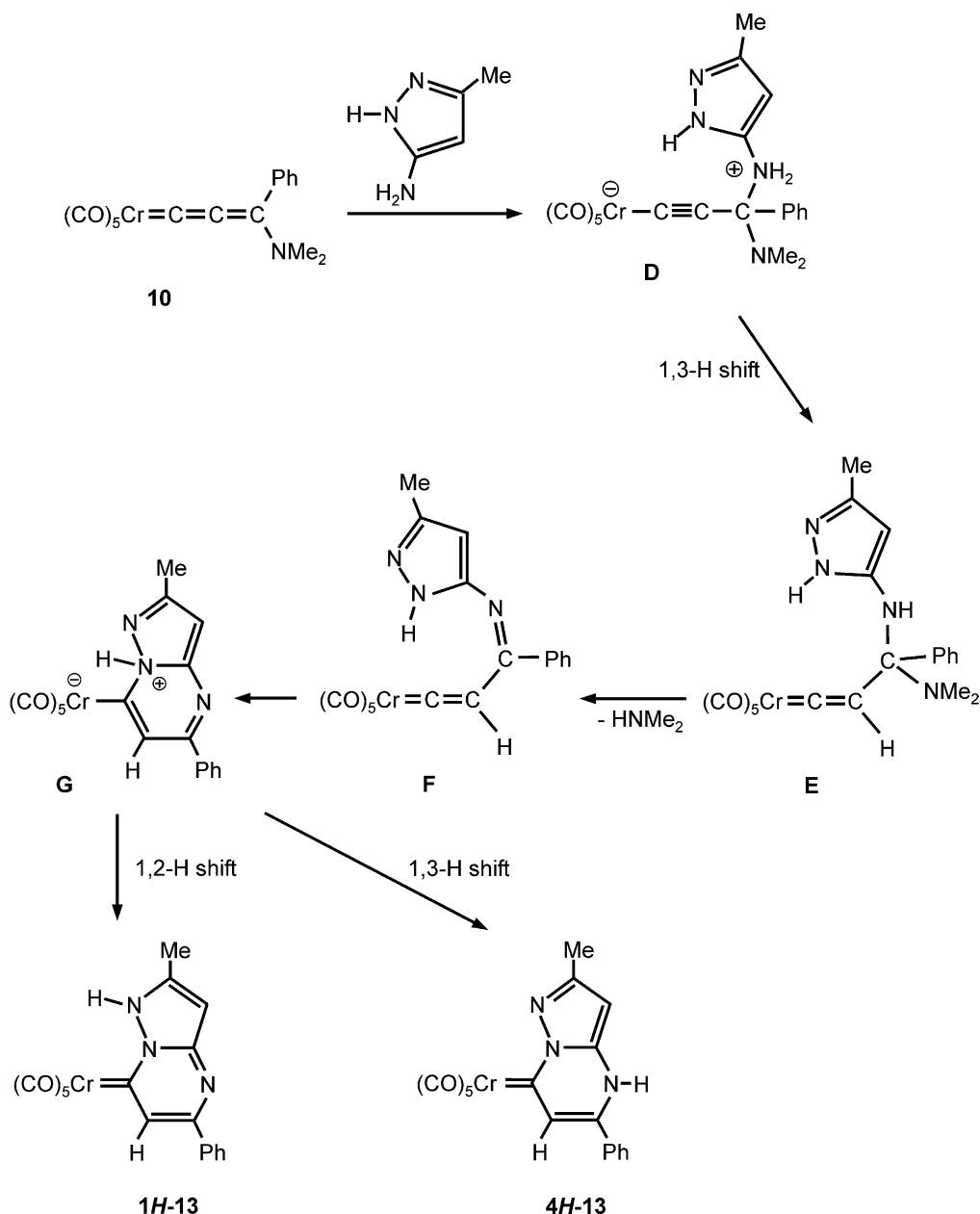
Scheme 7.

the relative intensity of the Me resonance in the ^{1}H NMR spectrum the ratio of isomers is calculated to be ca. 4:1.

A possible mechanism for the formation of **13** is shown in Scheme 7: addition of the amino group of 3-amino-5-methylpyrazole to the terminal carbon atom of the allenylidene chain (**10 → D**) is followed by tautomerisation to give a vinylidene intermediate **E** and thermally induced intramolecular cyclisation (**E → F → G**). Subsequent 1,2- or 1,3-H shift finally affords the two isomeric product complexes **1H-13** and **4H-13**. Alternatively, elimination of HNMe$_2$ from **D** followed by cyclization could directly produce **4H-13**.

Compared to the reactions of complex **10** with benzamidine, guanidine, and 3-amino-5-methylparazole, the reaction with thioacetamide in THF proceeded much slower. After 24 h of stirring a mixture of the starting compound **10**, the thiazinylidene complex **14** and the aminocarbene complex **15** was obtained (Scheme 8). Chromatographic workup of the mixture yielded 40% of **10**, 15% of **14** and 34% of **15**. Extending the reaction times led only to decomposition of the cycloadduct **14**. Obviously, complex **14** is unstable under the reaction conditions employed.

Carbene complex **15** results from addition of dimethylamine to the C$_\alpha$–C$_\beta$ bond of **10**. Dimethylamine in turn is formed as the co-product in the reaction of **10** with thioacetamide. The formation of **15** shows that – in contrast to the reactions of **1a**, **1b**, and **10** with amidines, guanidine, and 3-amino-5-methylpyrazole – α,β-addition of dimethylamine successfully competes with displacement of the C$_\gamma$-bound dimethylamide.

1,3-Dinucleophiles such as acetamide, 2-aminopyridine or ureas that are even weaker nucleophiles than amidines, guanidine, 3-amino-5-methylpyrazole, and thioacetamide did not react with **1a**, **1b**, and **10**.

Our results demonstrate that π-donor-substituted allenylidene complexes are suitable synthons for the preparation of complexes containing six-membered heterocyclic carbene ligands. Due to the large variability of of 1,3-dinucleophiles and their substitution pattern, a broad range of heterocyclic carbene complexes should be accessible. Problems connected with low reactivity of some allenylidene complexes towards weaker nucleophiles can possibly be circumvented by using more activated alkoxyallenylidene complexes like for instance [(CO)$_5$M=C=C=C(OMe)Ph].

3. Experimental

3.1. General

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH$_2$ (CH$_2$Cl$_2$) LiAlH$_4$ (pentane) and sodium (THF). The silica gel used for chromatography (Baker, silica for flash chromatography) was argon saturated. The yields refer to analytically pure compounds and are not optimized. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded with Jeol JNX 400 or a Varian Inova 400 spectrometer at ambient temperature. Chemical shifts are relative to the residual solvent or tetramethylsilane peaks. IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. Complexes **1a**, **1b** and **10** [23], propynoic acid dimethylamide [31], and 3-methylimino-3-phenyl-propyne [32] were prepared according to literature procedures. All other chemicals were commercial products and used as supplied.

3.2. General procedure for the reaction of 1a and 1b with amidines

At room temperature a solution of 1.1 mmol of the corresponding amidine or guanidine (prepared in situ by adding an equimolar amount of a concentrated NaOH solution to a solution of the amidine hydrochlorides at 0 °C) in 2 ml of degassed water was added to a solution of 1.0 mmol of **1a** or **1b** in 2 ml of THF. The progress of the reaction was monitored by TLC. When all of the starting compound was consumed the crude reaction mixture was filtered at −20 °C over silica gel using CH$_2$Cl$_2$ as the eluent. The solvent was removed in vacuo and the remaining residue was purified by recrystallisation from a mixture of pentane/CH$_2$Cl$_2$ (1:1).

3.2.1. Pentacarbonyl(3-benzamidino-3-dimethylamino-1,2-propadienylidene)chromium (2a)

Red solid. Yield: 0.36 g (92%). M.p. 136–137 °C. IR (THF, cm^{-1}): v(CO) = 2075 vw, 1931 vs, 1907 m; v(CCC) = 2008 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ = 3.47 (s, 3H, NCH$_3$), 3.57 (s, 3H, NCH$_3$), 7.55 (t, $^3J_{HH}$ = 7.6 Hz, 2H, ArH), 7.66 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, ArH), 8.13 (dt, $^3J_{HH}$ = 7.1 Hz,
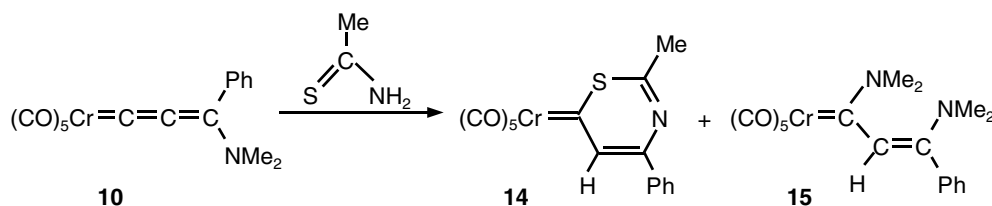
Scheme 8.

$^4J_{HH} = 1.2$ Hz, 2H, ArH), 8.97 (br, 2H, NH$_2$). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 39.3$ (NCH$_3$), 41.9 (NCH$_3$), 110.4 (C$_\beta$), 129.8, 130.6, 134.6, 136.0 (ArC), 149.7 (C$_\gamma$), 166.5 (N=C–NH$_2$), 187.0 (C$_\alpha$), 220.0 (*cis*-CO), 224.0 (*trans*-CO). MS (FAB), *m/z* (%): 391 (48) [M$^+$], 363 (12) [(M – CO)$^+$], 335 (28) [(M – 2CO)$^+$], 307 (36) [(M – 3CO)$^+$], 279 (100) [(M – 4CO)$^+$], 251 (26) [(M – 5CO)$^+$]. UV–Vis (λ_{max}/ nm (log ε) [solvent]): 496 (4.122) [pentane], 454 (4.039) [CH$_2$Cl$_2$], 414 (3.971) [DMF]. Anal. Found: C, 52.06; H, 3.34; N, 10.71. Calc. for C$_{17}$H$_{13}$CrN$_3$O$_5$ (391.3): C, 52.18; H, 3.35; N, 10.74%.

3.2.2. Pentacarbonyl(3-benzamidino-3-dimethylamino-1,2-propadienylidene)tungsten (2b)

Red solid. Yield: 0.49 g (94%). M.p. 141–142 °C. IR (THF, cm^{-1}): v(CO) = 2080 vw, 1968 vw, 1926 vs, 1903 m; v(CCC) = 2011 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): $\delta = 3.46$ (s, 3H, NCH$_3$), 3.57 (s, 3H, NCH$_3$), 7.55 (tt, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.7$ Hz, 2H, ArH), 7.66 (tt, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, ArH), 8.10 (dt, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.4$ Hz, 2H, ArH), 9.13 (br, 2H, NH$_2$). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 39.3$ (NCH$_3$), 42.1 (NCH$_3$), 108.4 (C$_\beta$), 129.9, 130.6, 134.7, 136.0 (ArC), 151.7 (C$_\gamma$), 166.5 (C$_\alpha$), 167.0 (N=C–NH$_2$), 199.3 (*cis*-CO, $^1J_{WC} = 121.3$ Hz), 203.3 (*trans*-CO). MS (FAB), *m/z* (%): 523 (100) [M$^+$], 495 (38) [(M – CO)$^+$], 439 (54) [(M – 3CO)$^+$], 383 (20) [(M – 5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 472 (3.628) [pentane], 441 (4.141) [CH$_2$Cl$_2$], 403 (4.029) [DMF]. Anal. Found: C, 38.77; H, 2.43; N, 7.93. Calc. for C$_{17}$H$_{13}$N$_3$O$_5$W (523.1): C, 39.03; H, 2.50; N, 8.29%.

3.2.3. Pentacarbonyl[3-(4-amino-benzamidino)-3-dimethylamino-1,2-propadienylidene]-chromium (3a)

Orange solid. Yield: 0.40 g (98%). M.p. 138–140 °C (dec.). IR (THF, cm^{-1}): v(CO) = 2075 vw, 1929 vs, 1903 m; v(CCC) = 2012 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): $\delta = 3.40$ (s, 3H, NCH$_3$), 3.51 (s, 3H, NCH$_3$), 5.56 (s, 2H, NH$_2$), 6.74 (d, $^3J_{HH} = 8.8$ Hz, 2H, ArH), 7.94 (d, $^3J_{HH} = 8.8$ Hz, 2H, ArH), 8.60 (br, 1H, NH$_2$), 9.38 (br, 1H, NH$_2$). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 38.9$ (NCH$_3$), 41.5 (NCH$_3$), 110.2 (C$_\beta$), 115.2, 122.2, 131.9 (ArC), 149.4 (C$_\gamma$), 155.5 (ArC), 166.2 (N=C–NH$_2$), 182.9 (C$_\alpha$), 220.2 (*cis*-CO), 224.1 (*trans*-CO). MS (FAB), *m/z* (%): 406 (6) [M$^+$], 378 (3) [(M – CO)$^+$], 350 (6) [(M – 2CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 443 (4.286) [CH$_2$Cl$_2$], 412 (4.289) [DMF]. Anal. Found: C, 50.04; H, 3.64; N, 13.30. Calc. for C$_{17}$H$_{14}$CrN$_4$O$_5$ (406.3): C, 50.25; H, 3.47; N, 13.79%.

3.2.4. Pentacarbonyl[3-(3-nitro-benzamidino)-3-dimethylamino-1,2-propadienylidene]chromium (4a)

Deep-red solid. Yield: 0.42 g (96%). M.p. 152–155 °C (dec.). IR (THF, cm^{-1}): v(CO) = 2075 vw, 1930 vs, 1909 m; v(CCC) = 2007 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone):

$\delta = 3.51$ (s, 3H, NCH$_3$), 3.61 (s, 3H, NCH$_3$), 7.88 (t, $^3J_{HH} = 8.0$ Hz, 1H, ArH), 8.49 (ddd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.2$ Hz,$^5J_{HH} = 0.8$ Hz, 1H, ArH), 8.54 (dt, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, ArH), 8.54 (t, $^4J_{HH} = 2.0$ Hz, 1H, ArH), 9.41 (br, 2H, NH$_2$). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 39.3$ (NCH$_3$), 41.9 (NCH$_3$), 110.7 (C$_\beta$), 129.8, 130.6, 134.6, 136.0 (ArC), 149.7 (C$_\gamma$), 164.4 (N=C–NH$_2$), 189.8 (C$_\alpha$), 220.0 (*cis*-CO), 224.0 (*trans*-CO). MS (FAB), *m/z* (%): 436 (6) [M$^+$], 408 (3) [(M – CO)$^+$], 296 (23) [(M – 5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 531 (2.985) [pentane], 471 (3.731) [CH$_2$Cl$_2$], 395 (3.931) [DMF]. Anal. Found: C, 46.51; H, 2.91; N, 12.62. Calc. for C$_{17}$H$_{12}$CrN$_4$O$_7$ (436.3): C, 46.80; H, 2.77; N, 12.84%.

3.2.5. Pentacarbonyl(3-guanidino-3-dimethylamino-1, 2-propadienylidene)chromium (5a)

Red solid. Yield: 0.294 g (89%). M.p. 173–174 °C. IR (THF, cm^{-1}): v(CO) = 2076 vw, 1926 vs, 1900 m; v(CCC) = 2020 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): $\delta = 3.17$ (s, 3H, NCH$_3$), 3.40 (s, 3H, NCH$_3$), 7.26 (br, 4H, NH). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 36.4$ (NCH$_3$), 39.3 (NCH$_3$), 106.9 (C$_\beta$), 148.5 (C$_\gamma$), 161.4 (C$_\alpha$), 173.4 (N=C–NH$_2$), 218.8 (*cis*-CO), 222.3 (*trans*-CO). MS (FAB), *m/z* (%): 331 (100) [M$^+$]. UV– Vis: (λ_{max}/nm (log ε) [solvent]): 420 nm (3.625) [pentane], 400 (4.013) [CHCl$_3$], 396 (4.012) [CH$_2$Cl$_2$], 364 (4.111) [DMF]. Anal. Found: C, 40.04; H, 3.21; N, 16.99. Calc. for C$_{11}$H$_{10}$CrN$_4$O$_5$ (330.2): C, 40.01; H, 3.05; N, 16.97%.

3.3. General procedure for the cyclisation of allenylidene complexes 2a–5a

At room temperature two drops of diluted hydrochloric acid (2 M) (or a minimum amount of HBF$_4$) were added to a solution of 1.0 mmol of the corresponding allenylidene complex in 5 ml of THF. The course of the reaction was monitored by TLC. When all of the starting compound was consumed the solvent was removed in vacuo and the remaining residue was purified as specified below.

3.3.1. Pentacarbonyl(6-dimethylamino-2-phenyl-3H-pyrimidin-4-ylidene)chromium (6)

Yellow solid. Yield: 0.31 g (78%) after chromatographic workup using a mixture of pentane/CH$_2$Cl$_2$ (1:1) as eluant. M.p. 168–169 °C. IR (THF, cm^{-1}): v(CO) = 2049 vw, 1959 vw, 1923 vs, 1900 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): $\delta = 3.23$ (s, 3H, NCH$_3$), 3.36 (s, 3H, NCH$_3$), 7.03 (s, 1H, C$_\beta$H), 7.58 (t, $^3J_{HH} = 7.3$ Hz, 2H, ArH), 7.65 (t, $^3J_{HH} = 7.3$ Hz, 1H, ArH), 8.04 (d, $^3J_{HH} = 7.1$ Hz, 2H, ArH), 11.80 (br, 2H, NH). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): $\delta = 36.5$ (NCH$_3$), 37.6 (NCH$_3$), 115.5 (C$_\beta$), 128.4, 128.9.3, 132.3, 132.9 (ArC), 154.2 (N=C–NH), 156.5 (C$_\gamma$), 213.9 (C$_{carbene}$), 219.5 (*cis*-CO), 223.8 (*trans*-CO). MS (FAB), *m/z* (%):

391 (100) [M$^+$], 363 (22) [(M – CO)$^+$], 335 (30) [(M – 2CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 358 (3.936). Anal. Found: C, 52.34; H, 3.78; N, 10.77. Calc. for C$_{17}$H$_{13}$CrN$_3$O$_5$ (391.3): C, 52.18; H, 3.35; N, 10.74%.

3.3.2. Pentacarbonyl[2-(4-aminophenyl)-6-dimethylamino-3H-pyrimidin-4-ylidene]chromium (7)

Yellow solid. Yield: 0.39 g (96%) after recrystallisation from CH$_2$Cl$_2$. M.p. >250 °C. IR (HCCl$_3$, cm^{-1}): v(CO) = 2049 w, 1964 vw, 1917 vs. ^{1}H NMR (250 MHz, [D$_6$]-acetone, 25 °C): δ = 3.21 (br s, 3H, NCH$_3$), 3.31 (br s, 3H, NCH$_3$), 5.53 (br, 2H, NH$_2$), 6.79 (d, 2H, Ph-m-H, $^3J_{H,H}$ = 8.7 Hz), 6.88 (s, 1H, H-3) , 7.86 (d, 2H, Ph-o-H, $^3J_{H,H}$ = 8.7 Hz), 11.22 (br, 1H, NH); (400 MHz, [D$_6$]-acetone, −20 °C): δ = 3.21 (s, 3H, NCH$_3$), 3.34 (s, 3H, NCH$_3$), 5.79 (br, 2H, NH$_2$), 6.80 (d, 2H, Ph-m-H, $^3J_{H,H}$ = 8.6 Hz), 6.89 (s, 1H, H-3) , 7.87 (d, 2H, Ph-o-H, $^3J_{H,H}$ = 8.2 Hz), 11.55 (br, 1H, NH). ^{13}C NMR (63 MHz, [D$_6$]-acetone): δ = 39.8 (br, NCH$_3$), 117.2 (C$_\beta$), 117.7 (Ph-m-C), 123.2 (Ph-i-C), 133.0 (Ph-m-C), 156.5 (Ph-p-C), 159.4 (amidine-C), 163.0 (C$_\gamma$), 190.4 (C$_{carbene}$), 223.1 (cis-CO), 227.3 (trans-CO). FAB-MS m/z (%): 406 (60) [M$^+$], 378 (33) [(M – CO)$^+$], 350 (68) [(M – 2CO)$^+$], 322 (64) [(M – 3CO)$^+$], 294 (100) [(M – 4CO)$^+$], 266 (75) [(M – 5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 370 (3.958) [CH$_2$Cl$_2$]. Anal. Found: C, 49.08; H, 3.99; N, 12.83. Calc. for C$_{17}$H$_{14}$CrN$_4$O$_5$ (406.3). Calc.: C, 50.25; H, 3.47; N, 13.79%.

3.3.3. Pentacarbonyl[6-dimethylamino-2-(3-nitrophenyl)-3H-pyrimidin-4-ylidene]chromium (8)

Yellow solid. Yield: 0.38 g (87%) after recrystallisation from pentane/CH$_2$Cl$_2$(1:1). M.p. 142–143 °C (dec.). IR (THF, cm^{-1}): v(CO) = 2049 vw, 1922 vs, 1900 m. ^{1}H NMR (250 MHz, [D$_6$]-acetone, r. t.): δ = 3.27 (br s, 3H, NCH$_3$), 3.35 (br s, 3H, NCH$_3$), 7.10 (s, 1H, H-3), 7.92 (t, 1H, Ph-m-H, $^3J_{H,H}$ = 8.0 Hz), 8.49 (d, 1H, Ph-p-H, $^3J_{H,H}$ = 8.0 Hz), 8.50 (d, 1H, Ph-o-H, $^3J_{H,H}$ = 8.0 Hz), 8.87 (t, 1H, Ph-o-H, $^4J_{H,H}$ = 1.9 Hz), 12.15 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_8$]-THF): δ = 35.1 (NCH$_3$), 38.1 (NCH$_3$), 117.0 (C$_\beta$), 124.3 (Ph-o-C), 127.0 (Ph-p-C), 130.8 (Ph-m-C), 135.0 (Ph-i-C), 135.8 (Ph-o-C), 149.4 (Ph−m-C), 154.6 (Amidine-C), 155.7 (C$_\gamma$), 217.4 (C$_{carbene}$), 220.2 (cis-CO), 224.0 (trans-CO). FAB-MS m/z (%): 436 (46) [M$^+$], 380 (40) [(M – 2CO)$^+$], 352 (42) [(M – 3CO)$^+$], 324 (100) [(M – 4CO)$^+$], 296 (90) [(M – 5CO)$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 368 (3.597) [CH$_2$Cl$_2$]. Anal. Found: C, 47.01; H, 2.97; N, 12.77. Calc. for C$_{17}$H$_{12}$CrN$_4$O$_7$ (436.3): C, 46.80; H, 2.77; N, 12.84%.

3.3.4. Pentacarbonyl(2-amino-6-dimethylamino-3H-pyrimidin-4-ylidene)chromium (9)

Yellow solid. Yield: 0.28 (85%) after recrystallisation from CH$_2$Cl$_2$. M.p. 154–158 °C. IR (THF, cm^{-1}):

v(CO) = 2046 vw, 1958 vw, 1918 vs, 1896 m. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ = 3.09 (br, 6H, NCH$_3$), 6.43 (s, 1H, C$_\beta$H), 10.27 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [D$_6$]-acetone): δ = 37.9 (br, NCH$_3$), 38.7 (br, NCH$_3$), 110.6 (C$_\beta$), 155.7 (N=C–NH), 158.1 (C$_\gamma$), 210.7 (C$_{carbene}$), 221.3 (cis-CO), 225.4 (trans-CO). MS (FAB) m/z (%): 331 (100) [M$^+$]. UV–Vis: (λ_{max}/nm (log ε) [solvent]): 359 (3.986) [CH$_2$Cl$_2$]. Anal. Found: C, 39.71; H, 3.22; N 16.48. Calc. for C$_{11}$H$_{10}$CrN$_4$O$_5$ (330.2): C, 40.01; H, 3.05; N, 16.97%.

3.4. General procedure for the reaction of 10 with benzamidine and guanidine

At room temperature a solution of 20 mmol of the corresponding amidine in 5 ml of degassed water (prepared in situ by adding an equimolar amount of a concentrated NaOH solution to a solution of the commercially available amidine hydrochlorides at 0 °C) was added to a solution of 1.0 mmol (0.35 g) of 10 in 5 ml of THF. The progress of the reaction was monitored by TLC. When all of the starting compound was consumed the solvent was removed in vacuo and the remaining residue was chromatographed on silica gel at −20 °C using mixtures of pentane/CH$_2$Cl$_2$/acetone.

3.4.1. Pentacarbonyl(2,6-diphenyl-3H-pyrimidin-4-ylidene)chromium (11)

Orange solid. Yield: 0.27 g (64%). M.p. 111–113 °C. IR (THF, cm^{-1}): v(CO) = 2051 m, 1968 vw, 1930 vs, 1923 vs, 1911 sh. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ = 7.45–7.61 (m, 6H, ArH), 8.08 (m, 2H, ArH), 8.21 (m, 2H, ArH), 8.51 (s, 1H, C$_\beta$H), 13.39 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): δ = 129.1, 129.6, 129.6, 129.9, 132.6 (ArC), 133.1 (C$_\beta$), 133.1, 133.2, 136.2 (ArC), 153.0 (C$_\gamma$), 158.8 (N=C–N), 218.9 (cis-CO), 224.3 (trans-CO), 235.8 (C$_\alpha$). MS (FAB), m/z (%): 424 (100) [M$^+$], 368 (41) [(M – 2CO)$^+$], 340 (36) [(M – 3CO)$^+$], 312 (95) [(M – 4CO)$^+$], 284 (61) [(M – 5CO)$^+$]. UV–Vis (λ_{max}/nm (log ε) [solvent]): 371 (3.875), 461 (3.832) [CH$_2$Cl$_2$]. Anal. Found: C, 59.31; H, 2.83; N 6.72. Calc. for C$_{21}$H$_{12}$N$_2$O$_5$Cr (424.33): C, 59.44; H, 2.85; N, 6.60%.

3.4.2. Pentacarbonyl(2-amino-6-phenyl-3H-pyrimidin-4-ylidene)chromium (12)

Orange oil. Yield: 0.24 g (66%). IR (THF, cm^{-1}): v(CO) = 2050 m, 1966 vw, 1923 vs, 1906 sh. ^{1}H NMR (400 MHz, [d$_8$]-THF): δ = 6.89 (br, 2H, NH$_2$), 7.45 (m, 3H, ArH), 7.74 (s, 1H, C$_\beta$H), 8.04 (m, 2H, ArH), 11.52 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [d$_8$]-THF): δ = 123.9, 127.8, 128.4 (3 ArC), 131.0 (C$_\beta$), 136.6 (ArC), 155.9 (C$_\gamma$), 156.4 (N=C–N), 218.7 (cis-CO), 223.0 (trans-CO), 228.8 (C$_\alpha$). MS (FAB), m/z (%): 363 (19) [M$^+$], 335 (7) [(M – CO)$^+$], 307 (100)

$[(M - 2CO)^+]$, 279 (16) $[(M - 3CO)^+]$, 251 (34) $[(M - 4CO)^+]$, 223 (30) $[(M - 5CO)^+]$. UV–Vis (λ_{max}/ nm (log ε) [solvent]): 434 (3.927) [CH$_2$Cl$_2$]. Anal. Found: C, 50.75; H, 3.34; N 10.08. Calc. for C$_{15}$H$_9$N$_3$O$_5$Cr (363.25): C, 49.60; H, 2.50; N, 11.57%.

3.5. Pentacarbonyl(2-methyl-5-phenyl-1H-pyrazolo[1,5a]pyrimidin-7-ylidene)chromium (**1H-13**) and pentacarbonyl(2-methyl-5-phenyl-4H-pyrazolo[1,5a]pyrimidin-7-ylidene)chromium (**4H-13**)

1.69 g (20 mmol) of 2-amino-5-methylpyrazole is added to a solution of 0.35 g (1 mmol) of complex **2** in 5 ml of THF. The suspension is stirred for 5 days at 60 °C. The reaction is followed by TLC or IR spectroscopy. When all of the starting material is consumed the solvent is removed in vacuo and the remaining residue chromatographed on sica gel at −20 °C using mixtures of pentane/CH$_2$Cl$_2$/acetone as the eluent.

Orange oil. Yield: 0.30 g (74%). IR (THF, cm^{-1}): v(CO) = 2050 m, 1976 vw, 1930 vs, 1905 sh. ^{1}H NMR (400 MHz, [d$_6$]-acetone, mixture of isomers): **1H-13** (minor isomer): δ = 2.49 (s, 3H, CH$_3$), 6.18 (s, 1H, C$_\beta$H), 7.48–7.81 (m, 5H, ArH), 8.01 (s, 1H, PyrH), 10.64 (br, 1H, NH); **4H-13** (major isomer): δ = 2.01 (s, 3H, CH$_3$), 6.24 (s, 1H, C$_\beta$H), 7.48–7.81 (m, 5H, ArH), 7.99 (s, 1H, PyrH), 11.03 (br, 1H, NH). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone, mixture of isomers): **1H-13** (minor isomer): δ = 13.4 (CH$_3$), 87.8 (PyrC), 122.7 (C$_\beta$), 127.9, 129.4, 131.3, 132.4 (4 ArC), 137.9, 143.1 (2 PyrC), 153.7 (C$_\gamma$), 218.1 (*cis*-CO), 223.1 (*trans*-CO), 234.0 (C$_\alpha$); **4H-13** (major isomer): δ = 13.9 (CH$_3$), 88.8 (PyrC), 120.9 (C$_\beta$), 128.3, 130.2 131.5, 132.4 (2 × 5 ArC), 134.7, 136.2 (4 PyrC), 156.5 (C$_\gamma$), 203.8 (C$_\alpha$), 218.9 (*cis*-CO), 225.5 (*trans*-CO). MS (FAB), m/z (%): 401 (50) [M$^+$], 373 (38) $[(M - CO)^+]$, 345 (32) $[(M - 2CO)^+]$, 317 (26) $[(M - 3CO)^+]$, 289 (100) $[(M - 4CO)^+]$, 261 (48) $[(M - 5CO)^+]$. UV–Vis (λ_{max}/nm (log ε) [solvent]): 480 (3.954) [CH$_2$Cl$_2$]. Anal. Found: C, 53.81; H, 3.64; N 9.10. Calc. for C$_{18}$H$_{11}$N$_3$O$_5$Cr (401.98): C, 53.87; H, 2.67; N, 10.47%.

3.6. Pentacarbonyl(2-methyl-6-phenyl-3H-thiazin-4-ylidene)chromium (**14**)

1.26 g (20 mmol) of thioacetamide is added to a solution of 0.35 g (1 mmol) of complex **10** in 5 ml of THF. The suspension is stirred for 24 h at ambient temperature. The solvent is removed and the remaining residue chromatographed on sica gel at −20 °C using mixtures of pentane/CH$_2$Cl$_2$ as the eluent. The first yellow fraction contains the carbene complex **15** (0.13 g, 0.34 mmol, 34%) [25], the following red band the starting compound **2** (0.14 g, 0.4 mmol, 40%) and the final deep blue fraction the thiazinylidene complex **14**.

Complex **14**: Blue oil. Yield: 0.06 g (15%). IR (THF, cm^{-1}): v(CO) = 2052 m, 1978 w, 1941 vs, 1932 sh. ^{1}H NMR (400 MHz, [d$_6$]-acetone): δ = 2.78 (s, 3H, CH$_3$), 7.49–7.57 (m, 3H, ArH), 8.21 (d, $^3J_{HH}$ = 7.2 Hz, 2H, ArH), 9.01 (s, 1H, C$_\beta$H). ^{13}C NMR (100.5 MHz, [d$_6$]-acetone): δ = 32.6 (CH$_3$), 131.9 (C$_\beta$), 130.2, 130.6, 133.5, 137.3 (ArC), 144.2 (C$_\gamma$), 189.9 (S–C=N), 217.9 (*cis*-CO), 226.1 (*trans*-CO), 270.1 (C$_\alpha$). MS (FAB), m/z (%): 379 (63) [(M)$^+$], 351 (17) $[(M - CO)^+]$, 323 (67) $[(M - 2CO)^+]$, 295 (33) $[(M - 3CO)^+]$, 267 (100) $[(M - 4CO)^+]$, 239 (92) $[(M - 5CO)^+]$. UV–Vis (λ_{max}/nm (log ε) [solvent]): 332 (4.340), 586 (3.908) [CH$_2$Cl$_2$]. Anal. Found: C, 49.58; H, 2.30; N, 3.55. Calc. for C$_{16}$H$_9$NO$_5$SCr (379.31): C, 50.67; H, 2.39; N, 3.69%.

3.7. X-ray structural analyses of **2b** and **6**

Single crystals suitable for X-ray structural analyses were obtained by slow evaporation of the solvent from a solution of **2b** and **6** in CH$_2$Cl$_2$ at 4 °C. The measurements were performed with a crystal mounted on a glass fibre on a Siemens P4 diffractometer (graphite monochromator, Mo Kα, radiation, λ = 0.71073 Å). For the data collection the Wykhoff technique was used. Semiempirical absorption correction (ψ scan with 12 reflections) was performed. The structures were solved by direct methods using the SHEXTL-97 program package [33]. The position 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. Supplementary material

Crystallographic data for the structural analyses of complexes **2b** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 272844 (**2b**) and CCDC 272844 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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