Synthesis of Benzannulated *N*-Heterocyclic Carbene Ligands by a Template Synthesis from 2-Nitrophenyl Isocyanide

F. Ekkehardt Hahn,* César García Plumed, Marco Münder, and Thomas Lügger[a]

Abstract: The reaction of 2-nitrophenyl isocyanide **2** with $[M(CO)_5(thf)]$ (M = Cr, Mo, W) yields the isocyanide complexes $[M(CO)_5(\mathbf{2})]$ (**3**: M = Cr; **4**: M = Mo; **5**: M = W). Complexes **3**–**5** react with elemental tin under reduction of the nitro function of the isocyanide ligand to give the complexes with the unstable 2-aminophenyl isocyanide ligand. The coordinated 2-aminophenyl isocyanide ligand in all three complexes reacts spontaneously under intramolecular nucleophilic attack of the primary amine at the isocyanide carbon atom to yield the complexes with the NH,NH-benzimidazol-2-ylidene ligand (**6**: M = Cr; **7**: M = Mo; **8**: M = W). An incomplete reduction of the nitro group in **3**–**5** is observed when hydrazine hydrate is used instead of tin. Here the formation of complexes with a coordinated 2-hydroxylamine-functionalized phenyl isocyanide $[(CO)_5M\text{-}CN\text{-}C_6H_4\text{-}2\text{-}N(H)\text{-}OH]$ is postulated and this unstable ligand again undergoes intramolecular cyclization to give the NH,NOH-stabilized benzimidazol-2-ylidene complexes **9**–**11**. The tungsten derivative **11** can be allylated stepwise by a deprotonation/alkylation sequence first at the OH and then at the NH position to yield the monoallylated and diallylated species **12** and **13**. The molecular structures of **3**–**5** and **12**–**13** were established by X-ray crystallography.

Keywords: carbene ligands · chromium · isocyanide ligands · molybdenum · tungsten

Introduction

The nucleophilic attack at the carbon atom of a coordinated isocyanide ligand is a standard method to generate metal–carbene complexes.[1–3] Protic nucleophiles such as alcohols and primary or secondary amines have been particularly useful in this reaction. This carbene synthesis was first applied, although unintentionally, in 1915 when Tschugajeff and Skanawy-Grigorjewa reacted tetrakis(methyl isocyanide)platinum(II) with hydrazine.[4] The reaction products were 50 years later recognized as carbene complexes.[5]

The addition of proton-containing bases HX to coordinated isocyanides usually leads to the formation of complexes with acyclic carbene ligands. However, employment of functional isocyanides, which contain both the isocyanide group and the nucleophile in the same molecule, gives access to complexes with heterocyclic carbene ligands through an intramolecular 1,2-addition across the C≡N triple bond. Fehlhammer et al. introduced readily available and stable 2-hydroxyalkyl isocyanides such as $C{\equiv}NCH_2CH_2OH$, in which the nucleophile and the isocyanide group are already linked before coordination to the metal center. If suitably activated by coordination to transition metals in higher oxidation states these ligands spontaneously cyclize to form oxazolidin-2-ylidenes[6] allowing even the isolation of homoleptic tetra-[7] and hexacarbene complexes.[8]

In β-functional aryl isocyanides the electrophilic isocyanide and the nucleophilic substituent are not only linked, but are also suitably arranged in one plane for an intramolecular cycloaddition reaction. This geometry together with the aromaticity of the resulting cyclic carbene ligand could lead to an even greater tendency to form heterocyclic ylidenes. Contrary to aliphatic 2-hydroxyethyl isocyanide,[6–8] free 2-hydroxyphenyl isocyanide is not stable and cyclizes to give benzoxazole.[9] However, lithiation of benzoxazole and subsequent reaction with Me_3SiCl yields 2-(trimethylsiloxy)-phenyl isocyanide,[10] a synthon for 2-hydroxyphenyl isocyanide. The O-protected 2-(trimethylsiloxy)phenyl isocyanide can coordinate to transition metals and a series of complexes of type **A** (Scheme 1) have been prepared.[11–16] Cleavage of the Si–O bond in these complexes is best achieved by stirring in methanol with a catalytic amount of KF under formation of complexes **B** with the 2-hydroxyphenyl isocyanide ligand. Subsequently, complexes containing the benzoxazol-2-ylidene ligand **C** can be formed by intramolecular nucleophilic attack if the isocyanide is sufficiently activated (or insufficiently deactivated) towards intramolecular

[a] Prof. Dr. F. E. Hahn, C. García Plumed, Dr. M. Münder, Dr. T. Lügger
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstraße 36, 48149 Münster (Germany)
Fax: (+49) 251-833-3108
E-mail: fehahn@uni-muenster.de

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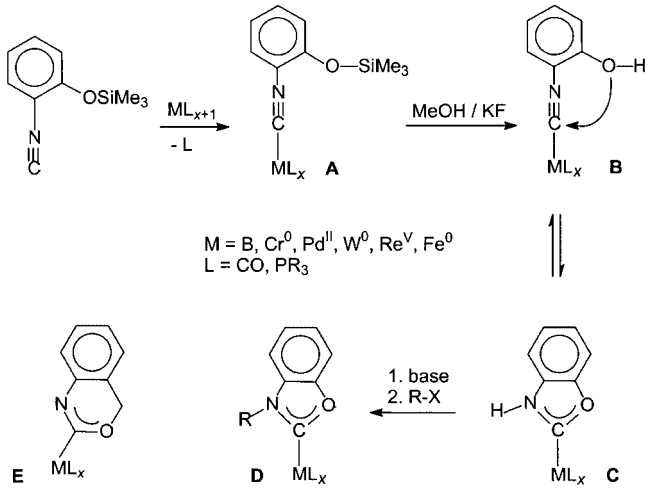


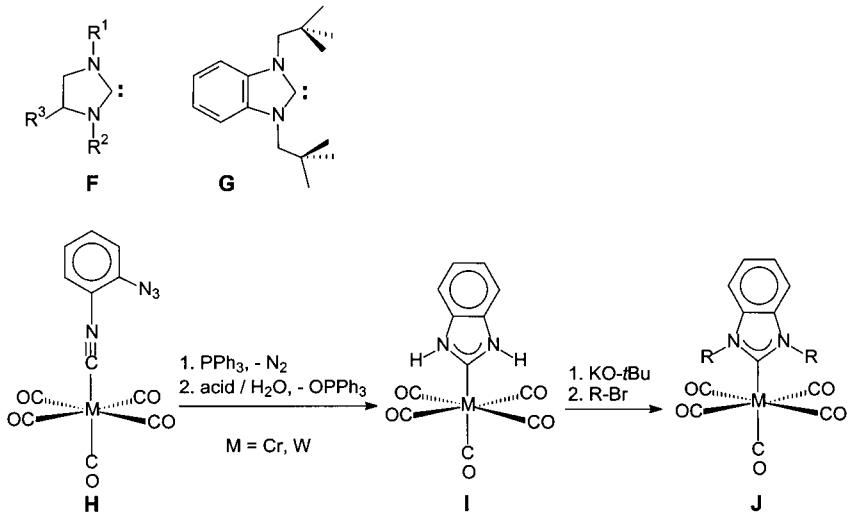
Scheme 1. Template synthesis of NH,O- and NR,O-stabilized carbene ligands from coordinated 2-(trimethylsiloxy)phenyl isocyanide.

nucleophilic attack by the hydroxy group at the isocyanide carbon atom. Different observations are made during the cyclization reaction depending on the nature of the transition-metal complex fragment ML_x.[17,18] Strong M→L backbonding stabilizes the hydroxyphenyl isocyanide ligand (**B**), whereas weak backbonding leads to the formation of the complex **C** with an NH,O-stabilized carbene ligand (Scheme 1).

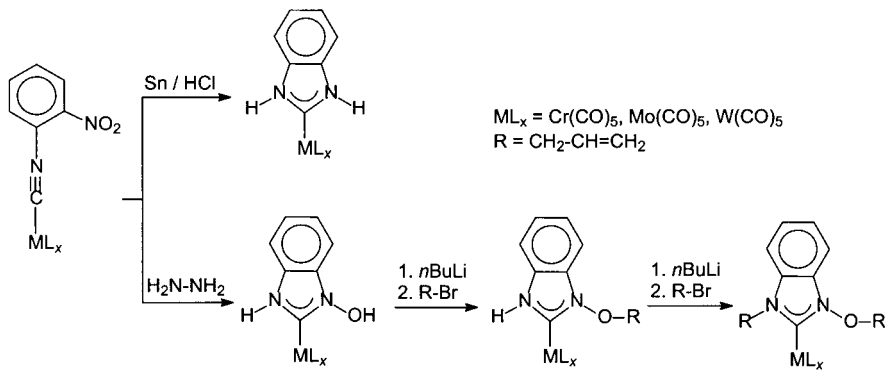
Various methods have been reported to shift the equilibrium between the 2-hydroxyphenyl isocyanide complex **B** and the NH,O-carbene complex **C** to either one side.[17,19] Finally, the NH,O-heterocarbene complexes **C** are easily N-alkylated by NH-deprotonation and reaction with alkyl halides to give ylidene complexes of type **D**.[12,20] The cyclization reaction **A**→**B**→**C** is of general nature and has recently been employed to generate benzoxazin-2-ylidene complexes **E** in which the carbene carbon atom is part of a six-membered ring.[21] General methods for the template-controlled preparation of *N*-heterocyclic carbenes from coordinated isocyanides[22] and the the coordination chemistry and reactivity of coordinated 2-(trimethylsiloxy)phenyl isocyanide have recently been reviewed.[23]

NH,O and NR,O-stabilized carbene ligands generated as depicted in Scheme 1 are not stable when liberated from the metal center, in contrast to the known NR,NR-stabilized *N*-heterocyclic carbenes.[24] Free saturated unsymmetrically substituted imidazolin-2-ylidenes **F**[25] and benzannulated *N*-heterocyclic carbenes of type **G**[26] show an interesting reactivity.[27] However, the synthesis of the benzannulated free carbenes is difficult and time consuming.[26] Based on the template synthesis for NH,O-stabilized carbene ligands presented in Scheme 1, we developed the template-controlled synthesis of complexes with NH,NH-stabilized (**I**) and NR,NR-stabilized carbene ligands (**J**) starting from complexes with the 2-azidophenyl isocyanide ligand (**H**), which is a synthon for the unknown 2-aminophenyl isocyanide (Scheme 2).[28] A similar method was used by Michelin et al. for the preparation of *N*-heterocyclic carbenes with a benzannulated six-membered *N*-heterocyclic ring.[29]

Since 2-azidophenyl isocyanide is difficult to prepare and explosive under certain circumstances, we searched for new 2-substituted phenyl isocyanide ligands that could be converted into NH,NH-stabilized carbene ligands in a template reaction. Here we present the preparation of 2-nitrophenyl isocyanide, its pentacarbonyl metal complexes, and the reduction of the nitro group in the coordinated ligand to give different carbene complexes depending on the reducing agent used (Scheme 3).



Scheme 2. Template-controlled synthesis of complexes with *N*-heterocyclic carbene ligands.



Scheme 3. Reduction of the nitro group in complexes with the 2-nitrophenyl isocyanide ligand.

Results and Discussion

Coordinated 2-hydroxyphenyl isocyanide (**B** in Scheme 1) cyclizes spontaneously to give the NH,O-stabilized carbene ligand. To generate NH,NH-stabilized carbene ligands it appears neccessary to generate, at least in situ, the complex with the freely unknown 2-aminophenyl isocyanide ligand which is supposed to immediately cyclize by intramolecular nucleophilic attack of the amine group at the isocyanide carbon atom. We intended to generate the 2-aminophenyl isocyanide ligand from coordinated 2-nitrophenyl isocyanide by reduction of the nitro group of the coordinated ligand.

Synthesis of 2-nitrophenyl isocyanide 2 and of complexes [M(CO)$_5$(2)] (3: M = Cr; 4: M = Mo; 5: M = W): Ligand **2** was prepared by reaction of commercially available nitroaniline with acetyl formate to yield 2-nitrophenyl formamide **1** (Scheme 4). Dehydration of **1** with diphosgene in basic solution[30] gives the isocyanide **2** in about 90% yield.

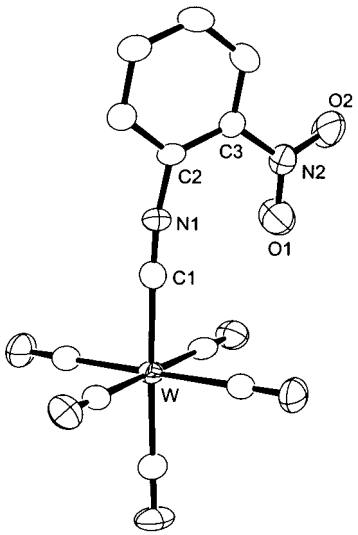
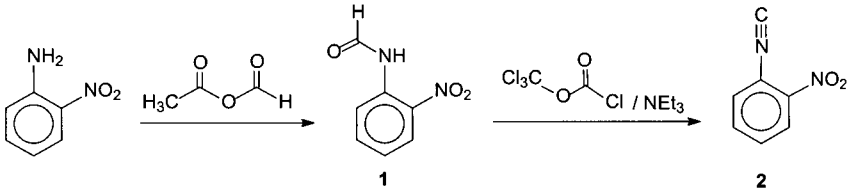


Figure 1. Molecular structure of **5** (the Cr and Mo derivatives **3** and **4**, respectively, are isostructural).



Scheme 4. Preparation of 2-nitrophenyl isocyanide **2**.

Isocyanide **2** is an off-white solid with the typical smell of phenyl isocyanides. The N≡C stretching frequency in **2** is observed in the IR spectrum at $\tilde{\nu} = 2129\ cm^{-1}$, slightly lower than reported for 2-azidophenyl isocyanide ($\tilde{\nu} = 2142\ cm^{-1}$).[28] The resonance of the isocyanide carbon atom in ^{13}C NMR spectrum appears as a broad signal[31] at $\delta = 173.6$ ppm.

Coordination of **2** to photochemically generated [M(CO)$_5$(thf)] (M = Cr, Mo, W) in THF gives the isocyanide complexes [M(CO)$_5$(**2**)] (**3**: M = Cr; **4**: M = Mo; **5**: M = W) as red solids in good yield. Complexes **3–5** are air-stable but light sensitive. The molecular structures of complexes **3–5** were determined by X-ray diffraction (Figure 1).

Bond lengths and angles in **5** fall in the range observed for carbonyl tungsten complexes with a phenyl isocyanide ligand in the *trans* position to CO (Table 1).[3,26,28,32] The tungsten atom is coordinated in a slightly distorted octahedral fashion. The C≡N–C group of the isocyanide ligand exhibits an almost linear geometry. It deviates, however, more from linearity than observed for the pentacarbonyl tungsten complex with the 2-azidophenyl isocyanide ligand.[28] This can be attributed to the stronger electron-withdrawing capability of the nitro group compared to the azido group leading to a slightly stronger W→C backbonding.

In general, the IR spectroscopic data for complexes **3–5** are indicative of only weak M→C backbonding. This is corroborated by the virtually unchanged wavenumber for the N≡C stretching frequency upon coordination of **2** (Table 2). Clearly, the isocyanide ligands in **3–5** are activated for a nucleophilic attack at the isocyanide carbon atom.[23]

Table 1. Selected bond lengths [Å] and angles [°] for complexes **3–5**.

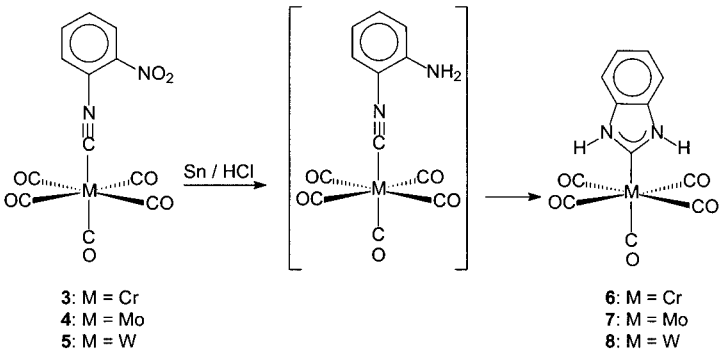
	3	**4**	**5**
M–CN	1.953(3)	2.090(4)	2.073(5)
M–CO$_{trans}$	1.903(4)	2.043(4)	2.038(5)
M–CO$_{cis}$	1.905(4)–1.910(4)	2.045(5)-2.062(5)	2.036(6)–2.073(5)
C1–N1	1.159(4)	1.166(4)	1.157(6)
N1–C2	1.377(4)	1.385(4)	1.382(6)
N2–C3	1.466(4)	1.459(5)	1.454(7)
C1-M-CO$_{cis}$	88.66(13)–90.82(14)	88.21(15)–90.70(15)	88.7(2)–90.9(2)
C1-M-CO$_{trans}$	178.18(14)	178.02(15)	178.0(2)
M-C1-N1	176.7(3)	176.5(3)	177.3(4)
C1-N1-C2	171.3(3)	172.8(4)	171.6(5)

Reduction of the nitro group in 3–5 with Sn/HCl: Complexes **3–5** react in diethyl ether with tin and aqueous hydrochloric acid to give the complexes **6–8** with an NH,NH-stabilized carbene ligand (Scheme 5). We propose the complexes with a 2-aminophenyl isocyanide ligand as an intermediate in this reaction. Intramolecular nucleophilic attack of the amine group at the isocyanide carbon atom leads to the NH,NH-carbene ligand. We have obtained complexes **6** and **8** previously by Staudinger reaction followed by hydro-

Table 2. Selected spectroscopic data for **2** and complexes **3–14**.

Compound	$\tilde{\nu}$ [cm^{-1}][a]			^{13}C NMR[δ][b]		
	C≡N	N–H	O–H	M–C	*trans*-CO	*cis*-CO
2	2129			173.6[c]		
3	2134			183.9	215.8	213.9
4	2133			174.0	205.6	203.1
5	2134			163.2	195.4	193.3
6[d]		3466		200.8	222.9	219.3
7		3467		194.1	213.1	208.3
8[d]		3463		182.8	202.6	199.0
9		3460	3623	198.1	223.4	219.1
10		3462	3626	191.7	219.3	213.3
11		3458	3623	182.5	203.5	199.4
12		3413		182.7	202.7	199.2
13				187.7	201.2	197.6
14[e]			196.9	200.5	198.2	

[a] Measured as KBr pellets. [b] 50.3 MHz, measured in $CDCl_3$ (for **2–5** and **13**) or [D_8]THF (for **6–12**). [c] Data for the free isocyanide ligand. [d] The spectroscopic data for **6** and **8** are identical within experimental error to those reported for identical complexes obtained from 2-azidophenyl isocyanide complexes.[28] [e] Data for **14** (Scheme 8, 62.9 MHz, $CDCl_3$) were taken from reference.[26]



3: M = Cr
4: M = Mo
5: M = W

6: M = Cr
7: M = Mo
8: M = W

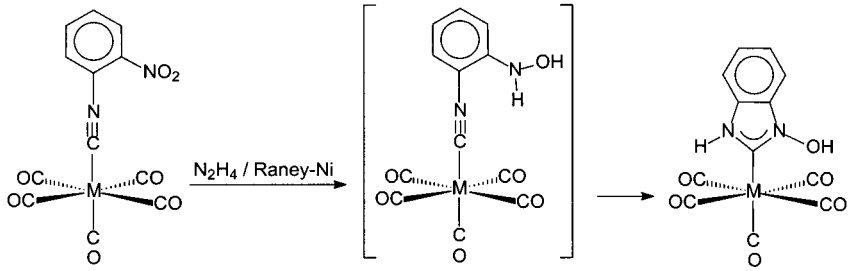
Scheme 5. Preparation of carbene complexes **6–8** by reduction of the nitro group in complexes **3–5**.

The cleavage of the O–$SiMe_3$ bond in $M(CO)_5$ complexes of the 2-(trimethylsiloxy)phenyl isocyanide ligand (Scheme 1) leads to a mixture of the isocyanide complex **B** and the NH,O-carbene complex **C**.[17] Owing to the enhanced nucleophilicity of the amine group in 2-aminophenyl isocyanide compared with the hydroxy group in 2-hydroxyphenyl isocyanide no such equilibrium is observed upon reduction of the nitro group in complexes **3–5**. However, the reduction/cyclization reaction of complex **3** to give complex **6** is particularly slow and the transient 2-aminophenyl isocyanide complex (^{1}H NMR: $\delta = 4.90$ ppm NH_2; IR: $\tilde{\nu} = 2151$ cm^{-1} for the transient 2-aminophenyl isocyanide complex versus $\tilde{\nu} = 2134$ cm^{-1} for **3**) can be observed together with the carbene complex **6** after a reaction time of only 6 h. After 17 h complete conversion to the NH,NH-carbene complex **6** has occurred.

Reduction of the nitro group in 3–5 with hydrazine/Raney nickel: The reaction of complexes **3–5** in methanol with hydrazine hydrate and a small amount of Raney nickel does not yield the NH,NH-carbene complexes **6–8**. Instead complexes **9–11** are obtained. They exhibit the resonance typical for the carbene-carbon atom ($\delta = 182.5$–198.1 ppm) in their ^{13}C NMR spectra. Surprisingly, the ^{13}C NMR spectra show six resonances for the benzene ring instead of the expected three resonances for a C_2-symmetrical carbene ligand. In addition both an NH and one OH absorption are observed in the IR spectra (Table 2). Mass spectra showed molecular weights that were always 16 amu higher than those found for complexes **6–8**. The analytical data strongly indicate that complexes **9–11** contain an unsymmetrically NH,NOH-substituted carbene ligand (Scheme 6). All analytical data are in agreement with the representation of **9–11** in Scheme 6. The chemical shifts for the carbene carbon atoms in **9–11** compare well to the equivalent parameters in the complexes with NH,NH-stabilized carbene ligands **6–8** (Table 2). Complexes **9–11** show one N–H and one O–H absorption each in the IR spectrum (Table 2). While the wavenumbers for the N–H absorptions is similar to those for the complexes with NH,NH-stabilized carbene ligands, the O–H absorption appears at a much higher wavenumber around $\tilde{\nu} = 3620$ cm^{-1} (Table 2).

lysis from complexes with an 2-azidophenyl isocyanide ligand (Scheme 2).[28] The method presented here appears superior, since the 2-nitrophenyl isocyanide is much easier to synthesize than 2-azidophenyl isocyanide and the reduction is a simple conversion compared to the Staudinger reaction.

The carbene complexes **6–8** were characterized by spectroscopy (Table 2). No absorptions due to an isocyanide function could be detected in the IR spectra. The NH,NH-carbene ligands show the characteristic IR absorption for the N–H bond around 3465 cm^{-1}.[28] In the ^{1}H NMR spectra the strong deshielding of the N-H protons is confirmed by their resonance as broadened singlets around $\delta = 12$ ppm. The spectroscopic data for **6** and **8** are identical within experimental error to those reported for the same compounds obtained from the 2-azidophenyl isocyanide complexes (Scheme 2).[28]



3: M = Cr
4: M = Mo
5: M = W

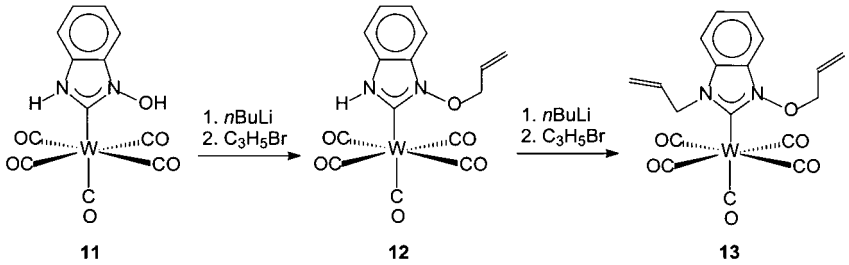
9: M = Cr
10: M = Mo
11: M = W

Scheme 6. Preparation of carbene complexes **9–11** by reduction of the nitro group in complexes **3–5** with hydrazine hydrate/Raney nickel.

Apparently, the reduction of the nitro groups in complexes **6–8** proceeds via an unstable hydroxylamine derivative (Scheme 6) that can undergo an intramolecular cyclization to give the carbene complexes **9–11**. This behavior was not observed upon reduction with the stronger reducing agent Sn/HCl.

Alkylation of complexes 9–11: Complexes with NH,NH-stabilized carbene ligands such as **6–8** can be deprotonated and alkylated at the nitrogen atoms.[28] The carbene ligands in complexes **9–11** contain two functional groups (NH and OH) that both possess acidic protons and that both can be alkylated. Previous studies with complexes containing the 4-hydroxybenzoxazol-2-ylidene ligand have shown, that stepwise alkylation yields first the N- and then the O-alkylation product.[19,33]

The tungsten complex **11** reacts with one equivalent of *n*BuLi and subsequently with one equivalent of allyl bromide to give exclusively the O-alkylated complex **12**. If the deprotonation/alkylation procedure is repeated, the N,O-dialkylated complex **13** is obtained (Scheme 7).



Scheme 7. Stepwise O- and N-alkylation of the carbene ligand in complex **11**.

Complexes **12** and **13** were identified spectroscopically by the lack of absorptions due to O–H and N–H and groups in the IR spectra and by the characteristic coupling pattern of the allylic protons in the ^{1}H NMR spectra. In addition, both complexes were characterized by X-ray diffraction. The molecular structure of complex **12** is shown in Figure 2. It confirms that indeed the monoalkylated O-allylated species has formed upon reaction of **11** with one equivalent of base and one equivalent of allyl bromide.

Bond parameters in **12** are comparable to equivalent parameters found for $W(CO)_5$ complexes of NR,NR-[26] and NH,NH-stabilized[28] benzannulated *N*-heterocyclic carbenes. The carbene-carbon atom is efficiently stabilized by (p-p)πN→C donation. The nitrogen atoms of the *N*-heterocyclic ring are almost perfectly planar and the bond lengths within the five-membered ring fall in a small range (1.348(4)–1.396(5) Å). The C1–N1 and C1–N2 separations are almost equidistant indicating that the type of substituent at the nitrogen atoms is not significant for the N–C bond lengths within the *N*-heterocyclic ring.

The molecular structure of complex **13** is shown in Figure 3. Here both the nitrogen atom and the oxygen atom are substituted with allyl groups. Equivalent bond parameters do not differ significantly between **12** and **13**. Again both nitrogen atoms are almost planar (sum of angles 359.6° for N1 and 360.0° for N2). The N-C-N angle at the carbine-carbon atom C1 is almost identical for **12** and **13**.

The order of alkylation in **11** and **12** (first O-alkylation,

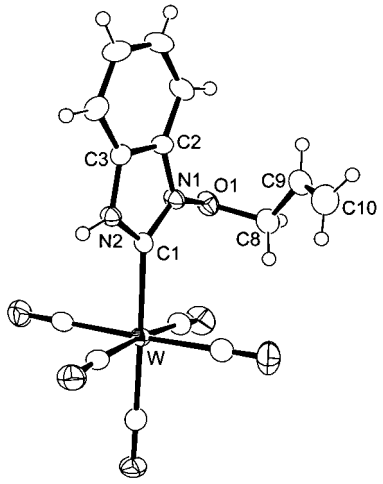


Figure 2. Molecular structure of complex **12**. Selected bond lengths [Å] and angles [°]: W–C1 2.232(4), W–CO_{cis} 2.036(4)–2.047(4), W–CO_{trans} 1.983(4), N1–C1 1.357(5), N1–C2 1.394(5), N2–C1 1.348(4), N2–C3 1.396(5), C2–C3 1.382(5), N1–O1 1.374(4), O1–C8 1.471(5); C-W-C_{cis} 85.83(15)–91.98(14), C-W-C_{trans} 174.31(15)–178.0(2), W-C1-N1 132.0(3), W-C1-N2 124.7(3), N1-C1-N2 103.3(3), C1-N1-C2 113.0(3), C1-N1-O1 125.4(3), C2-N1-O1 121.1(3), C1-N2-C3 112.9(3), N1-O1-C8 111.3(3).

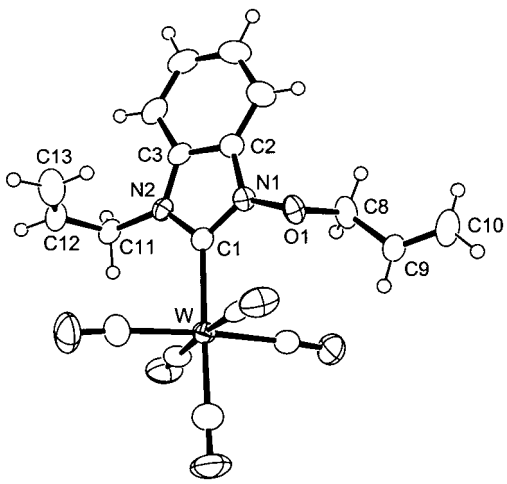
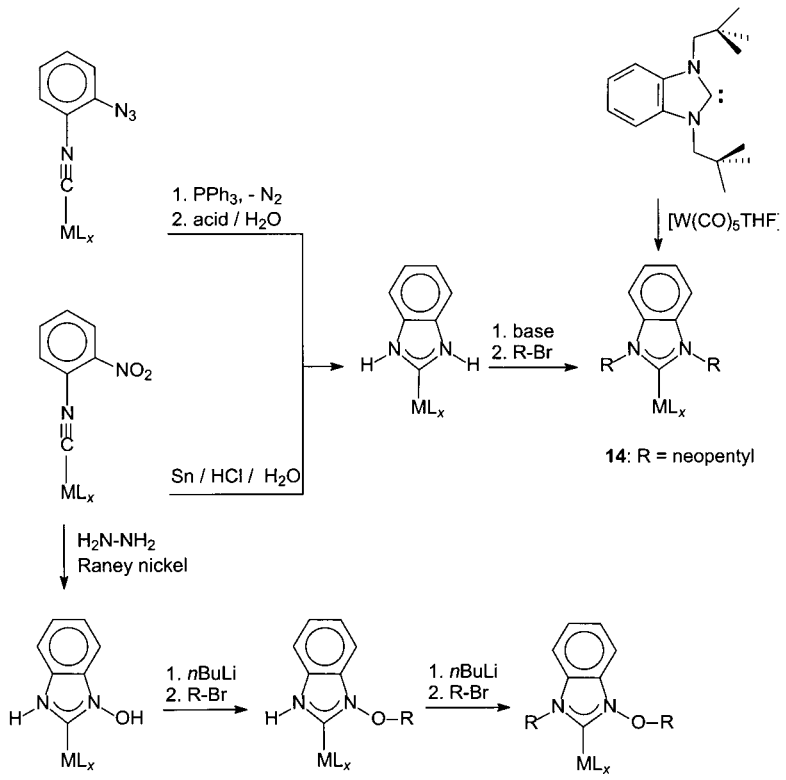


Figure 3. Molecular structure of complex **13**. Selected bond lengths [Å] and angles [°]: W–C1 2.242(3), W–CO_{cis} 2.023(4)–2.047(4), W–CO_{trans} 2.001(4), N1–C1 1.352(4), N1–C2 1.388(4), N2–C1 1.370(4), N2–C3 1.391(4), C2–C3 1.382(5), N1–O1 1.380(3), O1–C8 1.468(4), N2–C11 1.457(4); C-W-C_{cis} 86.3(2)–93.5(1), C-W-C_{trans} 175.0(2)–176.2(2), W-C1-N1 126.3(2), W-C1-N2 130.8(2), N1-C1-N2 102.9(3), C1-N1-C2 114.6(3), C1-N1-O1 122.8(3), C2-N1-O1 122.4(3), C1-N2-C3 111.3(3), C1-N2-C11 126.2(3), C3-N2-C11 122.5(3), N1-O1-C8 110.3(2).

second N-alkylation) is inverted compared to that for complexes with the 4-hydroxybenzoxazol-2-ylidene ligand. Obviously, the hydroxy group in the hydroxylamine derivative **11** is more nucleophilic and thus much more easily alkylated than a hydroxy group bound to the aromatic ring. This behavior allows the stepwise alkylation and the preparation of unsymmetrically substituted NR,NOR-stabilized carbene ligands in a template synthesis.

Conclusion

Previously we have demonstrated that pentacarbonyl metal complexes with a benzannulated *N*-heterocyclic carbene ligand are accessible by substitution of a CO ligand for a stable *N*-heterocyclic carbene ligand in hexacarbonyl metal complexes (preparation of **14** in Scheme 8)[26] or by addition of the stable carbenes to metal salts.[34] Similar complexes can be generated by the reaction of *N*,*N*′-dialkylbenzimidazolium salts with metal salts containing basic anions[35,36] or in the presence of an external base.[37] Alternatively, the opening of dibenzotetraazafulvalenes by electrophilic metal centers yields carbene complexes.[27a,38] All these methods utilize free or in situ generated benzimidazol-2-ylidenes in a substitution-type reaction. Here we present a method to generate the benzannulated *N*-heterocyclic carbene ligand at a metal template starting from 2-nitrophenyl isocyanide ligand (Scheme 8).



Scheme 8. Preparation of benzannulated *N*-heterocyclic carbene ligands by template synthesis.

This method involves the reduction of the nitro group in coordinated 2-nitrophenyl isocyanide with Sn/HCl and the cyclization of the intermediate, unstable 2-aminophenyl isocyanide ligand to give the complex with an NH,NH-stabilized carbene ligand. Such complexes were previously prepared by Staudinger reaction followed by template-controlled cyclization of 2-azidophenyl isocyanide.[28] The reaction starting from 2-nitrophenyl isocyanide has the advantage that this ligand is easily prepared and that the reduction reaction with Sn/HCl is straightforward compared to the Staudinger reaction of 2-azidophenyl isocyanide. The NH,NH-stabilized carbene ligand can be alkylated to give the complex with an NR,NR-stabilized carbene, a carbene ligand that is stable in the free state for certain substituents R.

Pentacarbonyl metal complexes of 2-nitrophenyl isocyanide also react with hydrazine hydrate/Raney nickel under incomplete reduction of the nitro group. After cyclization complexes with an unsymmetrically substituted NH,NOH-stabilized carbene ligand are obtained. Such complexes can be alkylated in a stepwise fashion first under O-alkylation and then under N-alkylation (Scheme 8).

The template-controlled formation of NH,NH- and NH,NOH-stabilized carbene ligands allows the preparation of complexes with carbene ligands that are not stable in the free state. These ligands can be alkylated and thus carbene ligands that are stable without coordination to a transition metal can be obtained. Even when the carbene ligand obtained by template synthesis is not stable in the free state it can still be transferred to other metals by ligand transfer reactions.[39] In summary: the template reaction described here gives access to transition-metal complexes bearing carbene ligands that do not exist in the free state.

Experimental Section

General: All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Varian U 600 (600 MHz) spectrometer and are reported relative to TMS as internal standard. IR spectra were recorded on a Bruker Vector 22 FT spectrometer. Mass spectra were taken on Varian MAT 212 (EI, 70 eV), Varian MAT 8200 (EI, 70 eV) or Quattro LCZ (ESI, 50 eV) instruments. Elemental analyses were obtained with a Vario EL III Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälischen Wilhelms-Universität Münster.

Nitrophenyl formamide (1): Sodium formate (19.7 g, 0.29 mol) was dried at 60 °C under vacuum for 8 h. After cooling to room temperature it was suspended in diethyl ether (100 mL) and acetyl chloride (10.3 mL, 0.145 mol) was added. The suspension was stirred for 12 h at ambient temperature. The resulting acetyl formate was added to nitroaniline (10.0 g, 72 mmol) and the resulting mixture was stirred for 0.5 h at ambi-

ent temperature. Removal of the solvent at reduced pressure afforded a yellow solid, which was washed with acetone and dried in vacuum to give **1** (11.8 g, 98%) as a yellow powder. ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta =$ 10.30 (br s, 1H; NH), 8.79 (d, 1H; Ar-H), 8.58 (s, 1H; NC(O)H), 8.26–7.27 ppm (m, 3H; Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta =$159.5 (CO) 136.0, 133.6, 125.8, 123.9, 122.9 ppm (Ar-C) (only five of the six expected Ar-C signals could be resolved); IR (KBr pellet): $\tilde{\nu} =$3285 (s, NH), 1684 (vs, CO), 1507 (vs, NO_2), 1337 cm^{-1} (s, NO_2); elemental analysis calcd (%) for $C_7H_6N_2O_3$ (166.14): C 50.61, H 3.64, N 16.86; found: C 50.62, H 3.70, N 16.31.

2-Nitrophenyl isocyanide (2): A solution of **1** (3.39 g, 20.4 mmol) in CH_2Cl_2 (140 mL) was treated with triethylamine (11.0 mL, 78.2 mmol) and then cooled down to 0°C. Diphosgene (2.5 mL, 20.7 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 0.5 h and then at room temperature for 2 h. The brown solution was poured into a saturated aqueous potassium carbonate solution (100 mL). The organic layer was separated, and washed several times with the potassium carbonate solution and subsequently with water. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. The resulting oily product was purified by column chromatography on neutral Al_2O_3 (4% H_2O) with ethyl acetate/*n*-hexane (1:4, v/v) as eluent to give **2** (2.70 g, 89%) as a brownish solid. ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta =$ 8.14 (m, 1H; Ar-H), 7.79–7.63 ppm (m, 3H; Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta =$173.6 (br; Ar-C-N*C*), 144.1 (Ar-*C*-NC), 136.0, 134.5, 130.3, 129.8, 125.5 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu} =$2129 (vs, NC), 1532, 1345 cm^{-1} (vs, NO_2); elemental analysis calcd (%) for $C_7H_4N_2O_2$ (148.12): C 56.76, H 2.72, N 18.91; found: C 56.76, H 2.97, N 18.61.

Pentacarbonyl(2-nitrophenyl isocyanide)chromium(0) (3): A solution of $[Cr(CO)_6]$ (2.03 g, 9.2 mmol) in THF (150 mL) was irradiated for 6 h in a photoreactor (high-pressure mercury vapour lamp) to give $[Cr(CO)_5(thf)]$. Isocyanide **2** (1.30 g, 8.8 mmol) dissolved in toluene (10 mL) was added to the $[Cr(CO)_5(thf)]$ solution with a syringe. The resulting orange solution was stirred overnight at ambient temperature. The solvent was removed under reduced pressure and the dark red residue was purified by column chromatography on neutral Al_2O_3 (4% H_2O) with dichloromethane/petrol ether (1:3, v/v) as eluent. The deep red fraction was collected and the solvents were removed to yield **3** (1.93 g, 65%) as a red solid. ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta =$8.19 (d, 1H; Ar-H), 7.75–7.50 ppm (m, 3H; Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta =$ 215.8 (*trans*-CO), 213.9 (*cis*-CO), 183.9 (br, Ar-C-N*C*), 144.2 (Ar-*C*-NC), 134.7, 129.2, 129.1, 126.1 ppm (Ar-C) (only five of the expected six Ar-C resonances could be resolved); IR (KBr pellet):$\tilde{\nu} =$2134 (s, CN), 2046 (vs, CO), 2000 (sh, CO), 1934 (vs, CO), 1530 (s, NO_2), 1332 cm^{-1} (s, NO_2); MS (70 eV, EI): *m/z* (%): 340 (54) $[M]^+$, 284 (8) $[M-2CO]^+$, 256 (19) $[M-3CO]^+$, 228 (44) $[M-4CO]^+$, 200 (42) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{12}H_4N_2CrO_7$ (340.17): C 42.37, H 1.19, N 8.24; found: C 42.33, H 1.47, N 8.16.

Pentacarbonyl(2-nitrophenyl isocyanide)molybdenum(0) (4): Complex **4** was prepared as described for **3** from $[Mo(CO)_6]$ (3.06 g, 11.6 mmol) and **2** (1.55 g, 10.5 mmol). Complex **4** was obtained as a red, light-sensitive powder (2.61 g, 65%). ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta =$8.18 (d, 1H; Ar-H), 7.73–7.56 ppm (m, 3H; Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta =$205.6 (*trans*-CO), 203.1 (*cis*-CO), 174.0 (br; Ar-C-N*C*), 144.3 (Ar-*C*-NC), 134.7, 129.4, 129.4, 126.1 ppm (Ar-C) (only five of the six expected Ar-C resonances could be resolved); IR (KBr pellet): $\tilde{\nu} =$2133 (s, CN), 2048 (vs, CO), 2005 (sh, CO), 1938 (vs, CO), 1531 (s, NO_2), 1335 cm^{-1} (s, NO_2); MS (70 eV, EI): *m/z* (%): 384 (33) $[M]^+$, 356 (20) $[M-CO]^+$, 328 (6) $[M-2CO]^+$, 300 (6) $[M-3CO]^+$, 272 (11) $[M-4CO]^+$, 244 (66) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{12}H_4N_2MoO_7$ (384.11): C 37.52, H 1.05, N 7.29; found: C 37.58, H 1.27, N 7.50.

Pentacarbonyl(2-nitrophenyl isocyanide)tungsten(0) (5): Complex **5** was prepared as described for **3** from $[W(CO)_6]$ (2.74 g, 7.8 mmol) and **2** (1.10 g, 7.4 mmol). Complex **5** was obtained as a red, light-sensitive powder (2.86 g, 82%). ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta =$8.18 (d, 1H; Ar-H), 7.82–7.55 ppm (m, 3H; Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): $\delta =$195.4 (*trans*-CO), 193.3 (*cis*-CO), 163.2, (br; Ar-C-N*C*), 144.1 (Ar-*C*-NC), 134.5, 129.2, 129.2, 125.9 ppm (Ar-C) (only five of the six expected Ar-C resonances could be resolved); IR (KBr pellet): $\tilde{\nu} =$2134 (s, CN), 2044 (vs, CO), 1995 (sh, CO), 1928 (vs, CO), 1530 (s, NO_2), 1334 cm^{-1} (s, NO_2); MS (70 eV, EI): *m/z* (%): 472 (50) $[M]^+$, 332 (100) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{12}H_4WN_2O_7$ (472.02): C 30.53, H 0.85, N 5.93; found: C 30.89, H 1.00, N 5.93.

Pentacarbonyl(benzimidazol-2-ylidene)chromium(0) (6): Tin powder (3.250 g, 27 mmol) was added to a solution of **3** (1.323 g, 3.9 mmol) in diethyl ether (90 mL). The solution was cooled to 0°C and aqueous (37%) HCl (7.6 mL) was added. After the reaction mixture was stirred for 1 h at 0°C and for 16 h at ambient temperature, the yellow solution was filtered. The solvent was removed under reduced pressure, and the yellow residue was purified by column chromatography on neutral silica gel (4% H_2O) with ethyl acetate/*n*-hexane (1:4, v/v) as eluent. The light yellow fraction was collected and the solvents were stipped in vacuo to yield **6** (1.082 g, 89%) as pale yellow powder. ^{1}H NMR ([D$_8$]THF, 200.1 MHz): $\delta =$12.07 (s, 2H; NH), 7.38 (m, 2H; Ar-H), 7.20 ppm (m, 2H; Ar-H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz): $\delta =$222.9 (*trans*-CO), 219.3 (*cis*-CO), 200.8 (NCN), 135.6 (Ar-C-N), 123.5, 111.1 cm^{-1} (Ar-C); IR (KBr pellet): $\tilde{\nu} =$3466 (s, NH), 2059 (vs, CO), 1919 (vs, CO), 1889 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 310 (25) $[M]^+$, 282 (6) $[M-CO]^+$, 254 (8) $[M-2CO]^+$, 226 (13) $[M-3CO]^+$, 198 (17) $[M-4CO]^+$, 170 (100) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{12}H_6N_2CrO_5$ (310.19): C 46.47, H 1.95, N 9.03; found: C 46.64, H 1.83, N 8.86. The spectroscopic and microanalytical data for **6** are identical within experimental error to those reported for **6** obtained from the 2-azidophenyl isocyanide complex.[28]

Pentacarbonyl(benzimidazol-2-ylidene)molybdenum(0) (7): Complex **7** was prepared as described for **6** from **4** (316 mg, 0.8 mmol), tin powder (685 mg, 5.8 mmol) and aqueous (37%) HCl (1.65 mL) in diethyl ether (40 mL). Complex **7** was obtained as a pale yellow solid (122 mg, 42%). ^{1}H NMR ([D$_8$]THF, 200.1 MHz): $\delta =$11.96 (s, 2H; NH), 7.38 (m, 2H; Ar-H), 7.18 ppm (m, 2H; Ar-H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz): $\delta =$ 213.1 (*trans*-CO), 208.3 (*cis*-CO), 194.1 (NCN), 135.5 (Ar-C-N), 124.0, 111.5 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu} =$3467 (s, NH), 2066 (vs, CO), 1922 (vs, CO), 1889 (vs, CO).

Pentacarbonyl(benzimidazol-2-ylidene)tungsten(0) (8): Complex **8** was prepared as described for **6** from **5** (492 mg, 1 mmol), tin powder (890 mg, 7.5 mmol) and aqueous (37%) HCl (2.2 mL) in diethyl ether (45 mL). Complex **8** was obtained as a pale yellow solid (402 mg, 87%). ^{1}H NMR ([D$_8$]THF, 200.1 MHz): $\delta =$11.97 (s, 2H; NH), 7.31 (m, 2H; Ar-H), 7.12 ppm (m, 2H; Ar-H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz): $\delta =$ 202.6 (*trans*-CO), 199.0 (*cis*-CO), 182.8 (NCN), 135.1 (Ar-C-N), 123.8, 111.3 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu} =$3463 (s, NH), 2065 (vs, CO), 1921 (vs, CO), 1895 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 442 (82) $[M]^+$, 414 (65) $[M-CO]^+$, 386 (100) $[M-2CO]^+$, 358 (92) $[M-3CO]^+$, 330 (73) $[M-4CO]^+$, 302 (86) $[M-5CO]^+$. The spectroscopic data for **8** are identical within experimental error to those reported for **8** obtained from the 2-azidophenyl isocyanide complex.[28]

Pentacarbonyl(1-hydroxy-3-hydro-benzimidazol-2-ylidene)chromium(0) (9): To obtain complex **9** the reduction of the nitro group in **3** was carried out with hydrazine hydrate instead of tin powder. $N_2H_4{\cdot}H_2O$ (1.65 mL, 34 mmol) and a small amount of Raney nickel (ca. 15 mg) were added to a solution of **3** (825 mg, 2.6 mmol) in methanol (50 mL). The mixture was stirred 0 C for 1 h and then at room temperature for 3 h. The cloudy red solution was filtered and the solvent was removed under reduced pressure. The dark red residue obtained was purified by column chromatography on neutral silica gel (4% H_2O) with ethyl acetate/*n*-hexane (1:4, v/v) as eluent. The pale yellow fraction was collected and the solvents were removed to give **9** as yellow solid (200 mg, 25%). ^{1}H NMR ([D$_8$]THF, 200.1 MHz): $\delta =$11.85 (s, 1H; NH), 10.92 (s, 1H; OH), 7.45–7.34 ppm (m, 4H; Ar-H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz): $\delta =$223.4 (*trans*-CO), 219.1 (*cis*-CO), 198.1 (NCN), 133.6 (Ar-C-N), 133.4 (Ar-C-N), 124.2, 123.6, 111.5, 109.1 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu} =$3623 (s, OH), 3460 (s, NH), 2058 (vs, CO), 1943 (sh, CO), 1888 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 326 (22) $[M]^+$, 270 (11) $[M-2CO]^+$, 242 (13) $[M-3CO]^+$, 214 (24) $[M-4CO]^+$, 186 (100) $[M-5CO]^+$.

Pentacarbonyl(1-hydroxy-3-hydro-benzimidazol-2-ylidene) molybdenum(0) (10): The complex was obtained as described for the synthesis of **9** from $N_2H_4{\cdot}H_2O$ (0.70 mL, 14 mmol), Raney nickel (15 mg) and **4** (398 mg, 1 mmol) in methanol (50 mL). Complex **10** was isolated as a yellow powder (276 mg, 72%). ^{1}H NMR ([D$_8$]THF, 200.1 MHz): $\delta =$11.79 (s, 1H; NH), 10.88 (s, 1H; OH), 7.49–7.25 ppm (m, 4H; Ar-H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz): $\delta =$219.3 (*trans*-CO), 213.3 (*cis*-CO), 191.7

(NCN), 133.6 (Ar-C-N), 133.0 (Ar-C-N), 124.4, 123.8, 111.9, 109.6 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu}=3626$ (s, OH), 3462 (s, NH), 2066 (vs, CO), 1938 (sh, CO), 1888 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 371 (100) $[M-H]^+$, 343 (30) $[M-CO-H]^+$, 325 (31) $[M-CO-H_2O]^+$, 314 (31) $[M-2CO-H]^+$, 259 (62) $[M-4CO-H]^+$.

Pentacarbonyl(1-hydroxy-3-hydro-benzimidazol-2-ylidene)tungsten(0) (11): Complex **11** was prepared as described for **9** from **5** (1.202 g, 2.5 mmol), $N_2H_4{\cdot}H_2O$ (1.73 mL, 36 mmol) and Raney nickel (15 mg) in methanol (50 mL). After column chromatography complex **11** was obtained as a pale yellow solid (835 mg, 73%). ^1H NMR ([D$_8$]THF, 200.1 MHz): $\delta=11.87$ (s, 1H; NH), 10.94 (s, 1H; OH), 7.49–7.25 ppm (m, 4H; Ar-H); $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 50.3 MHz): $\delta=203.5$ (*trans*-CO), 199.4 (*cis*-CO), 182.5 (NCN), 134.0 (Ar-C-N), 133.0 (Ar-C-N), 124.4, 123.8, 111.9, 109.6 ppm (Ar-C); IR (KBr pellet): $\tilde{\nu}=3623$ (s, OH), 3458 (s, NH), 2065 (vs, CO), 1908 (vs, CO), 1884 cm^{-1} (vs, CO); MS (50 eV, ESI): *m/z* (%): 457 (100) $[M-H]^+$, 429 (14) $[M-CO-H]^+$, 401 (7) $[M-2CO-H]^+$, 347 (17) $[M-3CO-H]^+$; elemental analysis calcd (%) for $C_{12}H_6N_2O_6W$ (458.04): C 31.47, H 1.32, N 6.12; found: C 31.82, H 1.48, N 6.00.

Pentacarbonyl(1-allyloxy-3-hydro-benzimidazol-2-ylidene)tungsten(0) (12): Complex **11** (416 mg, 0.9 mmol) in THF (20 mL) was deportonated with *n*BuLi (0.43 mL of a 2.5 M solution in *n*hexane) at −78 °C. After the reaction mixture had been stirred for 2 h, allyl bromide (0.09 mL, 1.1 mmol) was added at 0 °C and the solution was stirred overnight. The solvent was removed under reduced pressure and the oily brownish residue was dissolved in diethyl ether. The insoluble LiBr was separated by filtration and the soluble fraction was purified by column chromatography on neutral Al_2O_3 (4% H_2O) with ethyl acetate/*n*-hexane (1:16, v(v) as eluent to yield **12** as a pale yellow solid (402 mg, 89%). ^1H NMR ([D$_8$]THF, 200.1 MHz): $\delta=12.22$ (s, 1H; NH), 7.37 (m, 4H; Ar-H), 6.23 (m, 1H, C*H*=CH$_2$), 5.50 (m, 2H, CH=C*H*$_2$), 4.87 ppm (m, 2H, O-CH$_2$); ^{13}C NMR ([D$_8$]THF, 50.3 MHz): $\delta=202.7$ (*trans*-CO), 199.2 (*cis*-CO), 182.7 (NCN), 134.0 (Ar-C-N), 131.9 (Ar-C-N), 131.2 (HC=CH$_2$), 125.3 (Ar-C), 124.6 (Ar-C), 122.6 (HC=*C*H$_2$), 112.6 (Ar-C), 110.3 (Ar-C), 80.3 ppm (O-CH$_2$); IR (KBr pellet): $\tilde{\nu}=3413$ (s, NH), 2066 (vs, CO), 1919 (vs, CO), 1879 (vs, CO), 1863 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 498 (37) $[M]^+$, 442 (7) $[M-2CO]^+$, 414 (11) $[M-3CO]^+$, 386 (8) $[M-4CO]^+$, 358 (94) $[M-5CO]^+$.

Pentacarbonyl(1-allyloxy-3-allyl-benzimidazol-2-ylidene)tungsten(0) (13): The alkylation procedure to prepare **12** from **11** was repeated with the **12** obtained in the previous reaction. Complex **13** was obtained as a yellow powder (381 mg, 78%). ^1H NMR ($CDCl_3$, 600 MHz): $\delta=7.38$ (m, 4H; Ar-H), 6.26 (m, 1H, O-CH$_2$-C*H*=CH$_2$), 6.06 (m, 1H, N-CH$_2$-C*H*=CH$_2$), 5.66 −5.63 (m, 2H, O-CH$_2$-CH=C*H*$_2$), 5.35–5.14 (m, 2H, N-CH$_2$-CH=C*H*$_2$), 5.20 (m, 2H, N-CH$_2$), 4.87 ppm (m, 2H, O-CH$_2$); ^{13}C NMR ($CDCl_3$, 150.6 MHz): $\delta=201.2$ (*trans*-CO), 197.6 (*cis*-CO), 187.7 (NCN), 132.5, 132.0 (Ar-C-N), 130.5, 129.7 (CH$_2$-H*C*=CH$_2$), 124.1, 123.9 (Ar-C), 122.1 (O-CH$_2$-HC=*C*H$_2$), 118.4 (N-CH$_2$-HC=*C*H$_2$), 111.5, 109.3 (Ar-C), 79,0 (O-CH$_2$), 52.6 ppm (N-CH$_2$); IR (KBr pellet): $\tilde{\nu}=2064$ (vs, CO), 1965 (vs, CO), 1909 cm^{-1} (vs, CO); MS (70 eV, EI): *m/z* (%): 538 (53) $[M]^+$, 510 (17) $[M-CO]^+$, 454 (34) $[M-3CO]^+$, 426 (52) $[M-4CO]^+$, 398 (54) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{18}H_{14}N_2O_6W$ (538.17): C 40.17, H 2.62, N 5.21; found: C 40.54, H 2.41, N 5.22.

X-ray crystallography: Single crystals suitable for X-ray analysis were obtained by recrystallization from acetone at 0 °C (**3**–**5**) or from ethyl acetate at 0 °C (**12, 13**). They were mounted on glass fibers using two-component glue or mineral oil. X-ray intensities were measured by using a Bruker AXS Apex system equipped with a rotating anode. All data were measured with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Data reduction was performed with the Bruker SMART[40] program package. For further crystal and data collection details see Table 3. All crystal structures were solved by using SHELXS-97[41] by heavy-atom methods and refined with SHELXL-97[42] using anisotropic thermal parameters for all none hydrogen atoms. Hydrogen positions were calculated and thermally fixed to 1.3 U_{eqv} of the parent atom (exception atom H(2N) in **12** whose positional parameters were identified from a difference Fourier map and which were refined). The C=C portion of one of the allyl groups in **13** is disordered. Ortep-3 for Windows[43] has been used for all plots. CCDC-197035 (**3**), CCDC-235843 (**4**), CCDC-197036 (**5**), CCDC-235844 (**12**), and CCDC-235845 (**13**) contain the supplementary crstallographic data for this paper. These data can be free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44)1223-336033; or deposit@ccdc.ac.uk).

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Table 3. Selected crystal and data collection details for **3**–**5** and **12**–**13**.

	3	**4**	**5**	**12**	**13**
formula	$C_{12}H_4N_2CrO_7$	$C_{12}H_4N_2MoO_7$	$C_{12}H_4N_2O_7W$	$C_{15}H_{10}N_2O_6W$	$C_{18}H_{14}N_2O_6W$
M_r	340.17	384.11	472.02	498.10	538.16
a [Å]	6.2511(3)	6.5466(7)	6.4755(4)	6.8366(4)	10.5020(10)
b [Å]	26.5422(12)	27.944(3)	27.633(2)	19.1135(12)	9.7299(10)
c [Å]	8.0857(4)	7.6700(8)	7.6282(5)	12.1643(7)	18.491(2)
α [°]	90.0	90.0	90.0	90.0	90.0
β [°]	95.749(2)	92.409(3)	92.9130(10)	99.2400(10)	94.576(2)
γ [°]	90.0	90.0	90.0	90.0	90.0
V [Å^3]	1334.81(11)	1401.9(3)	1363.22(15)	1568.9(2)	1883.4(3)
T [K]	153(2)	153(2)	123(2)	173(2)	173(2)
ρ_{calcd} [g cm^{-3}]	1.693	1.820	2.300	2.109	1.898
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4	4
μ [mm^{-1}]	0.895	0.972	8.511	7.397	6.170
theta limits [°]	$5.2\le2\theta\le50.0$	$5.5\le2\theta\le55.1$	$3.0\le2\theta\le50.0$	$5.4\le2\theta\le60.0$	$4.4\le2\theta\le60.1$
unique data	2329	3212	2386	4557	5475
obs data [$I>2\sigma(I)$]	2120	2451	2243	4046	4413
*R*1 (obs) [%]	5.11, *wR*1 = 10.30	4.70, *wR*1 = 9.24	2.77, *wR*1 = 5.11	3.02, *wR*1 = 6.36	3.15, *wR*1 = 5.80
*R*2 (all) [%]	5.90, *wR*2 = 10.59	7.16, *wR*2 = 9.98	3.12, *wR*2 = 5.20	3.68, *wR*2 = 6.58	4.67, *wR*2 = 6.21
GOF	1.267	1.066	1.337	1.118	1.015
no. of variables	199	199	199	221	263
res. el. density [e Å^{-3}]	0.368/−0.221	0.779/−0.296	0.883/−0.605	1.677/−1.413	1.343/−0.930

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