# Template Synthesis of Benzannulated N-Heterocyclic Carbene Ligands

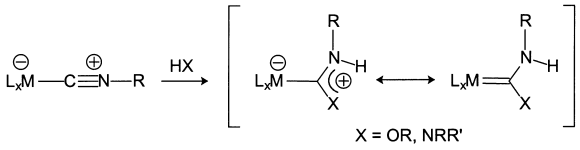
**F. Ekkehardt Hahn,*[a] Volker Langenhahn,[a] Nicole Meier,[a] Thomas Lügger,[a] and Wolf Peter Fehlhammer[b]**

**Abstract:** The reaction of 2-azidophenyl isocyanide (**7**) with $[M(CO)_5(thf)]$ (M = Cr, W) yields the isocyanide complexes $[M(CO)_5(\mathbf{7})]$ (M = Cr **8**, M = W **9**). Complexes **8** and **9** react with tertiary phosphines such as triphenylphosphane at the azido function of the isocyanide ligand to give the 2-triphenylphosphiniminophenyl isocyanide complexes **10** (M = Cr) and **11** (M = W). The polar triphenylphosphiniminophenyl function in complexes **10** and **11** can be hydrolyzed with $H_2O$/HBr to afford triphenylphosphane oxide and the complexes containing the unstable 2-aminophenyl isocyanide ligand. This ligand spontaneously cyclizes by intramolecular nucleophilic attack of the primary amine at the isocyanide carbon atom to yield the 2,3-dihydro-1*H*-benzimidazol-2-ylidene complexes **12** (M = Cr) and **13** (M = W). Double deprotonation of the cyclic NH,NH-carbene ligands in **12** and **13** with KO*t*Bu and reaction with two equivalents of allyl bromide yields the *N*,*N*′-dialkylated benzannulated N-heterocyclic carbene complexes **14** (M = Cr) and **15** (M = W). The molecular structures of complexes **9** and **11**–**15** were confirmed by X-ray diffraction studies.

**Keywords:** carbene ligands · chromium · isocyanide ligands · structure elucidation · tungsten

## Introduction

Nucleophilic attack at the carbon atom of a coordinated isocyanide 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 (Scheme 1). This carbene synthesis was first discovered, although unintentionally, in 1915 by Tschugajeff and Skanawy–Grigorjewa who treated platinum(II) tetrakis-(methyl isocyanide) with hydrazine.[4] The reaction products were only recognized as carbene complexes 50 years later.[5]




Scheme 1. Carbene formation by nucleophilic attack on coordinated isocyanides.

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While the addition of HX to coordinated isocyanides usually leads to the formation of complexes with acyclic carbene ligands, the use 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 bond. Fehlhammer et al. have 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 high oxidation states, these ligands spontaneously cyclize to form oxazolidin-2-ylidenes;[6] this even allows the isolation of homoleptic tetra-[7] and hexacarbene complexes.[8]

In $\beta$-functionalized aryl isocyanides, the electrophilic isocyanide and the nucleophilic substituent are not only linked, but are also suitably oriented in one plane for an intramolecular cycloaddition reaction to occur. This geometry together with the aromaticity of the resulting 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] which is a synthon for 2-hydroxyphenyl isocyanide (Scheme 2).

The O-protected 2-(trimethylsiloxy)phenyl isocyanide can coordinate to transition metals and a series of such complexes have been prepared.[11–16] Cleavage of the Si–O bond in these

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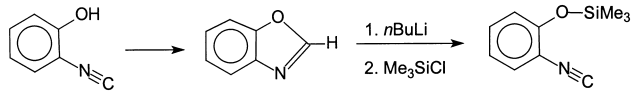
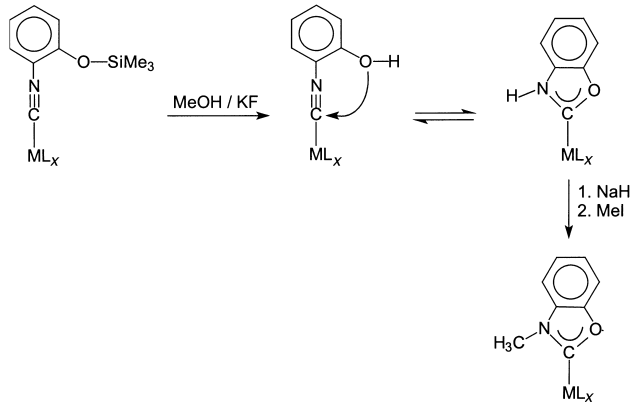



Scheme 2. Cyclization of 2-hydroxyphenyl isocyanide and synthesis of 2-(trimethylsiloxy)phenyl isocyanide from benzoxazole.

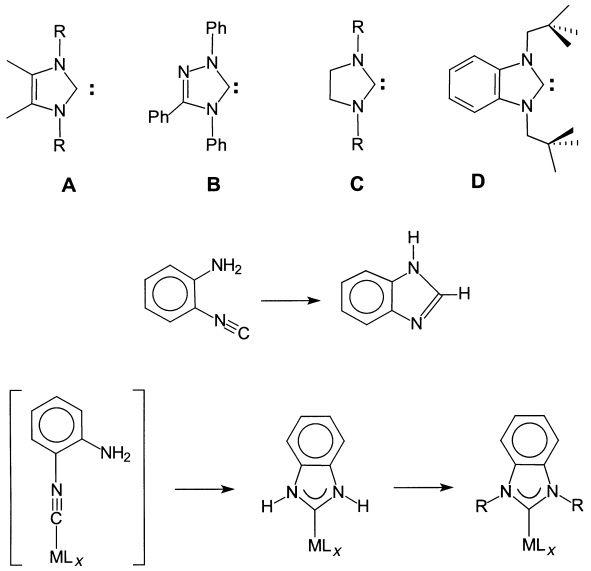
complexes is best achieved by stirring in methanol with a catalytic amount of KF. Subsequently, complexes containing the benzoxazol-2-ylidene ligand can form, if the isocyanide is sufficiently activated (or insufficiently deactivated) towards intramolecular nucleophilic attack by the hydroxyl group at the isocyanide carbon atom. Different observations have been made during the cyclization reaction depending on the nature of the transition metal complex fragment.[17, 18] Strong M → L backbonding stabilizes the hydroxyphenyl isocyanide ligand, while weak backbonding leads to the formation of the NH,O-carbene complex (Scheme 3).




Scheme 3. Template-controlled formation of NH,O-stabilized cyclic carbene ligands.

Various methods have been reported to shift the equilibrium between the 2-hydroxyphenyl isocyanide complex and the NH,O-carbene complex to either side.[17, 19] Finally, NH,O-heterocarbene complexes are easily *N*-alkylated by NH-deprotonation and reaction with alkyl halides.[12, 20] The coordination chemistry and reactivity of coordinated 2-(trimethylsiloxy)phenyl isocyanide has recently been reviewed.[21]

NH,O- and NR,O-stabilized carbene ligands generated according to Scheme 3 are not stable when liberated from the metal center in contrast to the known NR,NR-stabilized carbenes of types **A**–**C**, [22], and **D**[23] (Scheme 4). The benzannulated N,N′-stabilized carbenes of type **D** have interesting reactivities[24] but their synthesis is difficult and time consuming.[23] We therefore started a program to study the preparation of coordinated carbenes of type **D** in a template synthesis at suitable metal centers from coordinated $\beta$-functionalized isocyanides based on the template synthesis for N,O-stabilized carbene ligands presented in Scheme 3. Our synthesis involves the template-based cyclization of 2-aminophenyl isocyanide to give the complex with an NH,NH-carbene ligand. However, 2-aminophenyl isocyanide is not stable as a free molecule and cyclizes to give benzimidazole. Here we report a synthon which can be converted at a metal template into 2-aminophenyl isocyanide; this allows the template-controlled cyclization of coordinated 2-aminophenyl isocyanide to an NH,NH-carbene ligand and the double *N*,*N*′-alkylation of this ligand to give coordinated carbenes of type **D** (Scheme 4).

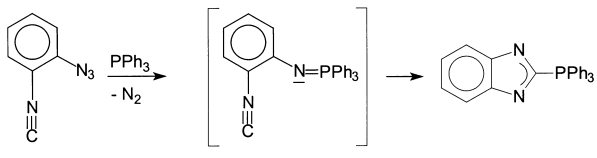



Scheme 4. N-Heterocyclic carbenes (top) and proposed template-controlled cyclization of 2-azidophenyl isocyanide (bottom).

## Results and Discussion

Since free 2-aminophenyl isocyanide spontaneously cyclizes to give benzimidazole, we searched for a synthon that would allow the in situ generation of 2-aminophenyl isocyanide. Benzimidazole cannot be opened with *n*BuLi to yield the 2-*N*-lithiated phenyl isocyanide by analogy with the O-lithiation of benzoxazole (Scheme 2). Thus, the preparation of an N-protected 2-aminophenyl isocyanide is not possible. However, 2-azidophenyl isocyanide (**7**) is a suitable synthon for 2-aminophenyl isocyanide. Isocyanide **7** can be activated at the azido function; thus, reaction of **7** with triphenylphosphane leads to nitrogen liberation[25] and formation of an unstable iminophosphorane which cyclizes with $PPh_3$ migration to yield a benzimidazole derivative (Scheme 5).[26] We have explored the reaction of metal-coordinated **7** with tertiary phosphines with the intention of generating a coordinated benzimidazol-2-ylidene.

**Synthesis of 2-azidophenyl isocyanide (7)**: The preparation of 2-azidophenyl isocyanide (**7**) has been mentioned in the literature.[27] However, the briefly reported synthesis proved




Scheme 5. Reaction of 2-azidophenyl isocyanide with triphenylphosphane leading to cyclization.

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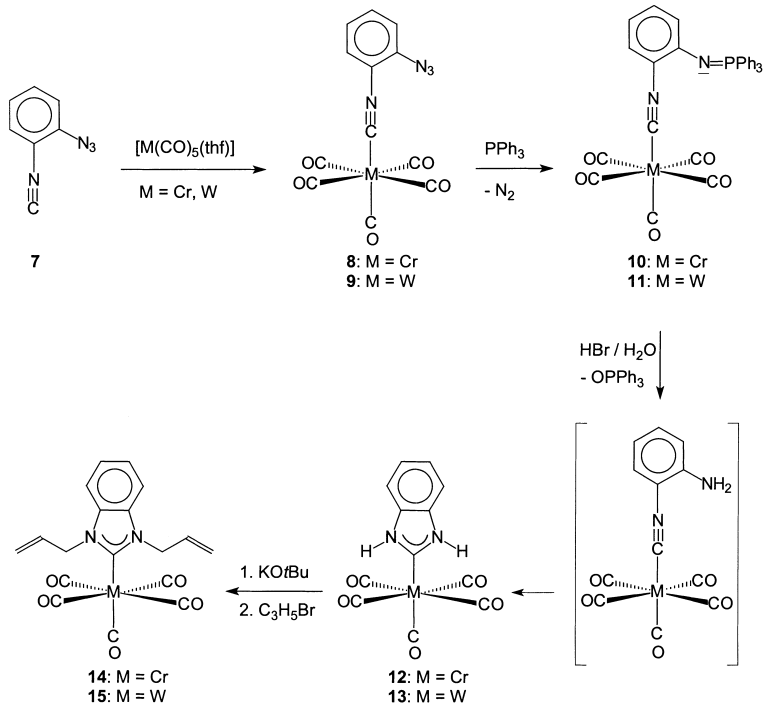
irreproducible in our hands and no analytical data for **7** were given. We have therefore developed a synthesis for 2-azidophenyl isocyanide derived from the literature procedure as shown in Scheme 6.

Thus, commercially available anthranilic acid (**1**) was treated with $NaNO_2$ to yield the diazonium salt **2**. Compound **2** was not isolated but directly treated with $NaN_3$ to give 2-azidobenzoic acid (**3**).[28] The acid **3** was converted with ethyl chloroformate into the mixed anhydride which reacts with ammonia to give 2-azidobenzoic amide (**4**). The benzamide **4** was subjected to a Hofmann degradation[29] leading to the azidoaniline **5**. Reaction of **5** with commercially available phenyl formate gave N-formyl-2-azidoaniline (**6**).[30] Compound **6** forms amido–imido tautomers in solution which can be detected by NMR spectroscopy; tautomer **6** is the major isomer (80%). 2-Azidophenyl isocyanide is finally obtained from **6** by a classical Ugi isocyanide synthesis[31] by using diphosgene and triethylamine for the dehydration. Isocyanide **7** is a low-melting (35 °C) crystalline solid with the typical bad smell associated with phenyl isocyanides. It is light sensitive and should be stored in the dark. The N≡C stretching frequency was observed in the infrared spectrum at 2142 $cm^{-1}$, a value typical for O-functionalized phenyl isocyanides.[3, 10] The signal for the isocyanide carbon atom appears, as expected,[32] as a broad singlet at $\delta = 168.8$ ppm in the $^{13}C$ NMR spectrum.

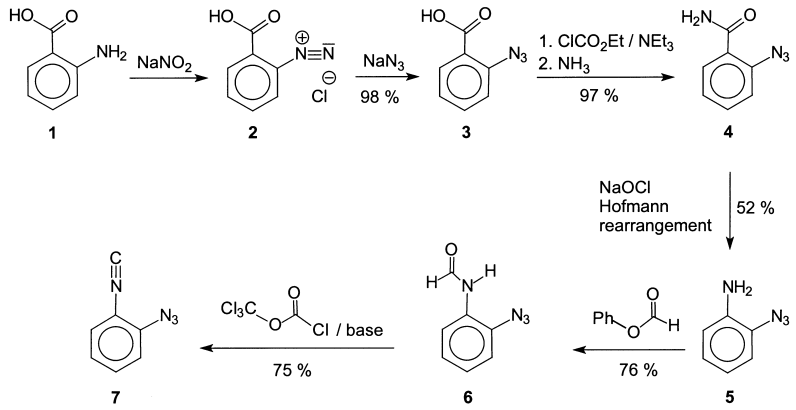



Scheme 7. Synthesis of the carbene complexes **14** and **15** from the isocyanide complexes **8** and **9**.

**Template synthesis of carbene complexes**: 2-Azidophenyl isocyanide (**7**) reacted like other phenyl or alkyl isocyanides with photochemically generated $[Cr(CO)_5(thf)]$ or $[W(CO)_5(thf)]$ in THF to give the monoisocyanide complexes $[M(CO)_5(\mathbf{7})]$ (M = Cr **8**, M = W **9**) in good yield (Scheme 7). Both complexes are air stable and light sensitive.

The molecular structure of complex **9** was determined by X-ray diffraction (Figure 1). The bond lengths and angles fall into the range observed for carbonyl tungsten complexes with phenyl isocyanide ligands in the *trans* position to CO (Figure 1).[3, 33] The tungsten atom in **9** is coordinated in a slightly distorted octahedral fashion. The C≡N–C group of the isocyanide ligand has a linear geometry which is indicative of weak W→C backbonding. This is corroborated by the virtually unchanged wavenumber for the N≡C stretching frequency upon coordination of **7** (Table 1). Clearly, the isocyanide ligands in **8** and **9** are activated towards nucleophilic attack at the isocyanide carbon atom.[14, 17]

The azido function of the isocyanide ligand in **8** and **9** reacts with triphenylphosphane in a Staudinger-type[25] reaction with liberation of dinitrogen to give the complexes with an iminophosphorane function[34] **10** and **11** (Scheme 7). The new isocyanide complexes **10** and **11** can be easily identified by the strong IR absorptions caused by the C≡N stretching mode and by the characteristic IR absorptions for the P=N bond (1348 $cm^{-1}$ for **10**; 1350 $cm^{-1}$ for **11**). The conversion of the azido function into an iminophosphorane does not significantly affect the N≡C bond of the isocyanide as judged by the minimal change of wavenumber for the N≡C stretching mode in the IR spectrum (Table 1). As in **9**, all W–CO distances in **11** are shorter than the W–CN distance; this means that CO is a better π acceptor than phenyl isocyanide.




Scheme 6. Synthesis of 2-azidophenyl isocyanide (**7**).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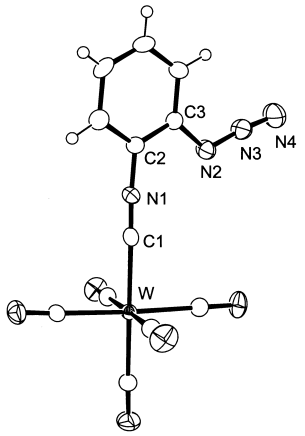


Figure 1. Molecular structure of complex **9** with the crystallographic numbering scheme. Selected bond lengths [Å] and angles [°]: W–C1 2.104(4), W–$CO_{cis}$ 2.036(5)–2.062(5), W–$CO_{trans}$ 2.025(4), C1–N1 1.161(5), N1–C2 1.383(5), C2–C3 1.382(6), C3–N2 1.412(5), N2–N3 1.242(5), N3–N4 1.130(6); C-W-C (*cis*) 88.4(2)–92.7(2), C-W-C (*trans*) 176.6(2)–179.0(2), W-C1-N1 178.9(4), C1-N1-C2 175.6(4), C3-N2-N3 116.0(4), N2-N3-N4 172.6(5).

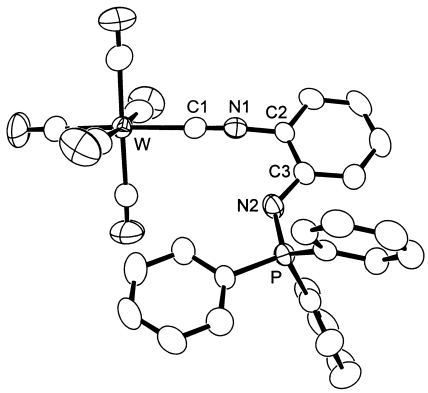


Figure 2. Molecular structure of complex **11** with the crystallographic numbering scheme. Selected bond lengths [Å] and angles [°]: W–C1 2.134(5), W–$CO_{cis}$ 2.019(6)–2.043(6), W–$CO_{trans}$ 2.009(6), C1–N1 1.147(5), N1–C2 1.400(6), C2–C3 1.403(6), C3–N2 1.376(5), N2–P 1.564(4), P–$C_{Ph}$ 1.799(4)–1.815(4); C-W-C (*cis*) 87.0(2)–94.8(2), C-W-C (*trans*) 174.7(2)–177.9(2), W-C1-N1 175.3(4), C1-N1-C2 173.6(4), C3-N2-P 129.7(3), N2($C_{Ph}$)-P-$C_{Ph}$ 105.3(2)–116.1(2).

Table 1. Selected spectroscopic data for **7** and complexes **8**–**16**.

| Compound | $\tilde{\nu}$(C≡N) [$cm^{-1}$][a] | $^{13}$C NMR [δ][b] | | |
|---|---|---|---|---|
| | | M–C | *trans*-CO | *cis*-CO |
| **7** | 2142 | 168.8 | | |
| **8** | 2145 | 179.1 | 216.5 | 214.3 |
| **9** | 2141 | 158.9 | 196.1 | 193.8 |
| **10** | 2148 | 167.1 | 217.8 | 215.1 |
| **11** | 2147 | 148.7 | 197.3 | 194.6 |
| **12** | | 200.6 | 222.7 | 219.0 |
| **13** | | 182.8 | 202.5 | 198.9 |
| **14** | | 206.2 | 221.2 | 216.9 |
| **15** | | 193.2 | 200.4 | 197.2 |
| **16**[c] | | 196.9 | 200.5 | 198.2 |

[a] Measured in $CH_2Cl_2$ solution (**7**) or as KBr pellets (**8**–**11**). [b] 150.6 MHz for **7**, 50.3 MHz for **8**–**15**, 62.9 MHz for **16**, measured in [$D_6$]DMSO (**7**), $CDCl_3$ (**8**–**11** and **14**–**16**), or [$D_8$]THF (**12**–**13**). [c] Data for this carbene complex (Scheme 8) were taken from ref. [23].

The IR data of complexes **10** and **11** suggest that the 2-phosphiniminophenyl isocyanide ligand shows no tendency for an intramolecular cyclization by attack of the negatively polarized iminophosphorane nitrogen atom at the isocyanide carbon atom. This contrasts the behavior of 2-phosphiniminophenyl isocyanide, which is not stable in the free state but instead spontaneously cyclizes by an intramolecular nucleophilic attack to give a benzimidazole derivative (Scheme 5). Presently we do not know if the steric demand or electronic factors (M→L backbonding) of the $W(CO)_5$ moiety are responsible for the change in reactivity of coordinated 2-phosphiniminophenyl isocyanide compared with the free ligand. This inertness towards intramolecular cyclization is unequivocally demonstrated with the molecular structure of **11** (Figure 2). Complex **11** contains an essentially octahedrally coordinated tungsten atom. The W–CN bond is slightly elongated and the C≡N bond is slightly shorter than in the 2-azidophenyl isocyanide complex **9**. This indicates that the isocyanide ligand in **11** is more electron-rich than the one in **9** and that it acts exclusively as a σ donor with no W→C≡N backbonding present. This assumption is backed by the slight increase of the wavenumber for the C≡N stretching mode in **10** and **11** compared to **8**, **9**, and the free ligand **7**. The most remarkable feature in the molecular structure of **11** is the P=N2 bond length of 1.565(4) Å. This value is typical for P=N bonds and it is in good agreement with P=N bond lengths found in other aromatic-substituted triphenylphosphiniminophosphoranes with an $sp^2$-hybridized nitrogen atom.[34] The angle C3-N2-P of 129.7(3)° is also consistent with an $sp^2$-hybridized nitrogen atom.

The 2-phosphiniminophenyl isocyanide ligand in **10** and **11** was hydrolyzed with aqueous methanol containing a catalytic amount of HBr. This led to elimination of triphenylphosphane oxide and formation of the 2-aminophenyl isocyanide complex (Scheme 7). As with the corresponding 2-hydroxyphenyl isocyanide complexes (Scheme 3); this complex is not stable. The amino group of the coordinated 2-aminophenyl isocyanide ligand attacks the isocyanide carbon atom which leads to the NH,NH-carbene complexes **12** and **13**.

Carbene complexes **12** and **13** were initially characterized spectroscopically. No absorptions due to an isocyanide function could be detected in the IR spectra. The NH,NH-carbene ligands have characteristic IR absorptions for the N–H bond (3463 $cm^{-1}$ for **12** and 3461 $cm^{-1}$ for **13**).[11, 12, 14–16] In the $^1$H NMR spectra, the strong deshielding of the N–H protons is confirmed by their resonance as broadened singlets in the range $\delta = 11.9-12.15$ ppm. The aromatic protons of the 2,3-dihydro-1*H*-benzimidazol-2-ylidene ligand in **12** and **13** give two multiplets in the range $\delta = 7.0-7.5$ ppm. This is in agreement with a system comprising an aromatic ring with two identical substituents in the 1,2-positions.

Complexes **12** and **13** were crystallized and their molecular structures were determined by X-ray diffraction (Figure 3). The crystal structure analyses confirmed that **12** and **13** contain NH,NH-heterocyclic carbene ligands. The W–C1 bond length in **13** is significantly longer than the W–CN distance in the isocyanide complexes **9** and **11**. In the series of formal $C^{II}$ ligands, CO is the strongest π acceptor

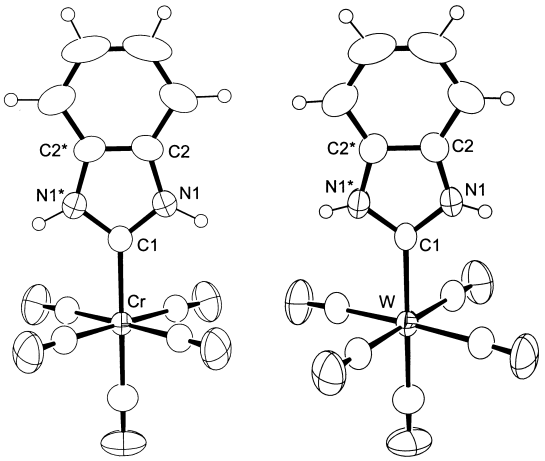


Figure 3. Molecular structure of complexes **12** (left) and **13** (right) with the crystallographic numbering scheme. Starred atoms represent symmetry equivalent positions. Complex **12** resides on a crystallographic mirror plane and is bisected by a twofold axis along the Cr–C1 vector. Complex **13** is bisected by a twofold axis along the W–C1 vector. Selected bond lengths [Å] and angles [°] for **12** [**13**]: M–C1 2.075(4) [2.203(4)], M–$CO_{cis}$ 1.887(3) [2.022(4)–2.029(4)], M–$CO_{trans}$ 1.853(5) [1.995(6)], C1–N1 1.343(4) [1.356(4)], N1–C2 1.389(5) [1.376(4)], C2–C2* 1.336(7) [1.385(6)]; C-M-C (*cis*) 89.3(2)–90.7(2) [88.7(1)–90.3(1)], C-M-C (*trans*) 179.5(2)–180.0(1) [177.4(2)–180.0(1)], M-C1-N1 128.3(2) [128.6(2)], N1-C1-N1* 103.3(4) [102.8(4)], C1-N1-C2 112.2(3) [113.1(3)].

followed by R–N≡C, and the N-heterocyclic carbene is the weakest one. This order of π-acceptor capability has been demonstrated previously with tungsten complexes containing CO, isocyanides, and carbene ligands.[35] On the other hand, the NH,NH-carbene ligand is a better σ donor than the isocyanide. In **12** and **13** this causes a significant shortening of the M–CO distance for the *trans*-CO ligand compared with the *cis*-CO ligands. In the isocyanide complexes **9** and **11** the M–CO distances of the *cis* and *trans* carbonyls are identical within experimental error.

In **13** the W–C1 bond length is longer than in the related complex with an NH,O-stabilized heterocyclic annulated carbene ligand (2.185(10) Å, Scheme 3).[12] Owing to the higher electronegativity of oxygen, the carbene carbon atom of the latter ligand is not as efficiently stabilized by pπ–pπ N→C interactions as the NH,NH-carbene ligand in **13**. On the other hand, the efficient pπ–pπ donation of the nitrogen atoms in the carbene ligand of **13** prevents any significant backdonation from the metal center to the carbene carbon atom. This electronic situation manifests itself in the $^{13}C$ NMR spectra, in which the C2 resonance for the coordinated NH,O-carbene ligand ($\delta = 211.6$ ppm) is shifted to lower field by about 30 ppm relative to the C2 resonance for **13** ($\delta =$ 182.8 ppm).[36]

The intramolecular cyclization of 2-hydroxyphenyl isocyanide at the $W(CO)_5$ complex fragment leads to a mixture of the isocyanide complex (15%) and the NH,O-carbene complex (85%).[17] Due to the enhanced nucleophilicity of the amino group in 2-aminophenyl isocyanide compared with the hydroxyl group in 2-hydroxyphenyl isocyanide, no equilibrium between the isocyanide complex and the NH,NH-carbene complex was observed by NMR spectroscopy during the hydrolysis and cyclization of complexes **10** and **11**.[17, 19]

An important property of the carbene complexes **12** and **13** is their insolubility in solvents such as dichloromethane or chloroform. However, they dissolve well in polar solvents containing oxygen donor groups like diethyl ether or THF; this is apparently caused by the ability of the NH protons to form hydrogen bridges to oxygen atoms of the solvent.

The acidity of the NH protons in **12** and **13** facilitates the generation of N-alkyl-substituted derivatives. In a typical reaction, **12** or **13** were treated with KO*t*Bu in DMF. The resulting monodeprotonated intermediate was quenched with allyl bromide and the deprotonation/quenching sequence was repeated for a second time without isolation of the mono-allylated product. The complexes with the dialkylated carbene ligand **14** and **15** could be isolated in good yield. Complexes with N-allylated carbene ligands are useful starting materials for the preparation of carbene/olefin complexes, and the substitution of a CO ligand by a carbene-bound allyl group has been demonstrated with a $W(CO)_5$ complex and an N(allyl),O-carbene ligand.[20]

Complexes **14** and **15** were identified spectroscopically by the lack of absorptions due to NH groups in the IR spectra and by the characteristic coupling pattern of the allylic protons in the $^1H$ NMR spectra. In addition, both complexes were characterized by X-ray diffraction (Figure 4).

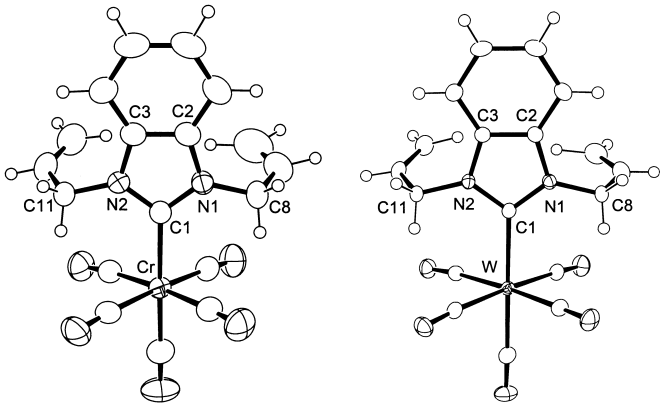


Figure 4. Molecular structure of complexes **14** (left) and **15** (right) with the crystallographic numbering scheme. Selected bond lengths [Å] and angles [°] for **14** [**15**]: M–C1 2.135(2) [2.256(3)], M–$CO_{cis}$ 1.880(2)–1.918(2) [2.017(3)–2.061(3)], M–$CO_{trans}$ 1.856(2) [2.002(3)], C1–N1 1.372(3) [1.375(4)], C1–N2 1.365(3) [1.372(3)], N1–C2 1.387(3) [1.390(4)], N2–C3 1.386(3) [1.384(4)], C2–C3 1.376(3) [1.388(4)], N1–C8 1.460(3) [1.458(4)], N2–C11 1.459(3) [1.456(4)]; C-M-C (*cis*) 86.85(10)–95.15(9) [87.01(13)–94.75(13)], C-M-C (*trans*) 174.79(9)–178.87(9) [174.99(11)–179.37(11)], M-C1-N1 128.26(14) [128.8(2)], M-C1-N2 127.76(14) [127.1(2)], N1-C1-N2 103.9(2) [104.0(2)], C1-N1-C2 111.50(2) [111.7(2)], C1-N1-C8 127.6(2) [126.9(2)], C2-N1-C8 120.8(2) [121.3(2)], C1-N2-C3 112.0(2) [111.8(2)], C1-N2-C11 127.3(2) [126.8(3)], C3-N2-C11 120.6(2) [121.4(2)].

The carbene carbon atoms in both complexes are stabilized by strong pπ–pπ N→C interactions from the essentially planar ring nitrogen atoms (sum of angles at N for both **14** and **15** is 359.9°). The NR,NR-carbene ligands are even stronger σ donors than the carbene ligands in **12** and **13**. This leads to a further elongation of the M–C1 bond length (2.135(2) Å for **14**, 2.256(3) Å for **15**) compared with the complexes with the NH,NH-carbene ligands in **12** and **13**. In addition, the


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$^{13}$C NMR spectra of complexes **14** and **15** have the largest $\Delta\delta$ differences between the *trans*- and *cis*-CO resonances of all complexes reported here.

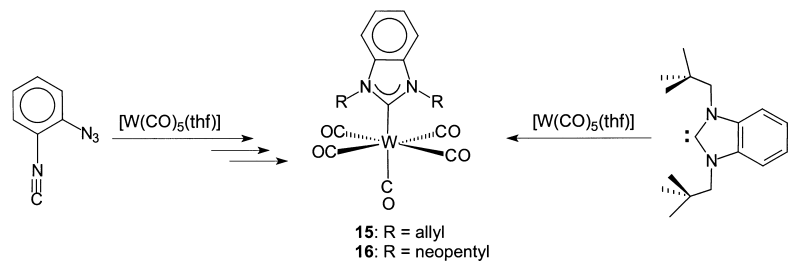
The W–C1 distance in **15** compares well with the equivalent distance in a reported tungsten complex with a benzannulated NR,NR-heterocyclic carbene ligand (2.229(7) and 2.216(7) Å.[37] The W–C1 distance in **15** is shorter than the equivalent distance in complex **16** (2.27(1) and 2.29(1) Å) which also contains a benzannulated NR,NR-carbene ligand (Scheme 8).[23] However, the carbene ligand in complex **16** is *N*,*N*′-substituted with sterically very demanding substituents which even force the metal out of the plane of the carbene ligand.

The C–N bond lengths within the carbene ring in **14** and **15** fall in a narrow range (1.365(3)–1.390(4) Å) and are indicative of p$\pi$–p$\pi$ N → C interactions between the nitrogen and carbon atoms. As expected, these C–N bonds are significantly shorter than the N–$CH_2$ bonds (range 1.456(4)–1.460(3) Å). The N–C–N bond angles at the carbene carbon atom are almost identical in both complexes (103.9(2)° and 104.0(2)°) and are typical for benzimidazol-2-ylidene complexes.

## Conclusion

Previously we have demonstrated that pentacarbonyl metal complexes with a benzannulated N-heterocyclic carbene ligand are accessible by substitution of a CO ligand in hexacarbonyl metal complexes (preparation of **16** in Scheme 8).[23] Similar complexes can be generated by the reaction of *N*,*N*′-dialkylbenzimidazolium salts with metal salts containing basic anions[37–39] or by the opening of dibenzotetraazafulvalenes by electrophilic metal centers.[24a] All these methods utilize free or in situ generated benzimidazol-2-ylidenes in a substitution-type reaction. Here, we present for the first time a method to generate the benzannulated N-heterocyclic carbene ligand at a template metal starting from a $\beta$-functionalized phenyl isocyanide ligand (preparation of **15** in Scheme 8).

This new method offers several advantages. It gives access to complexes with the NH,NH-heterocyclic carbenes, a ligand type which is not stable in the free state. The NH,NH-carbene ligand can be alkylated stepwise to give access to unsymmetrically *N*,*N*′-substituted carbene ligands. The generation of a benzannulated N-heterocyclic carbene ligand from a coordinated 2-azidophenyl isocyanide might allow the generation of new Grubbs-type catalysts by cyclization of 2-azidophenyl isocyanide at Ru$^{II}$[41] and of polycarbene ligands by bridging alkylation of the carbene ligands in poly(NH,NH-carbene) complexes. While it is known that free benzannulated N-heterocyclic carbenes exhibit different properties to "Arduengo-type" N-heterocyclic carbenes (**A** in Scheme 4),[23, 24] the pentacarbonyl tungsten complex of a typical "Arduengo-carbene"[40] exhibits structural parameters which are quite similar to **15** and **16**.




Scheme 8. Synthesis of complexes with benzannulated N-heterocyclic carbene ligands by substitution (right) and by template-controlled generation of a carbene ligand (left).

## 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. NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Varian U 600 spectrometer (600 MHz) and are reported relative to TMS as internal standard. IR spectra were recorded on a Bruker Vector 22 or on a Beckman IR 12 double-beam infrared spectrometer. Mass spectra (EI, 70 eV and 80 eV) were recorded on Finnigan MAT 711 or Varian MAT 212 instruments. Elemental analyses (C,H,N) were performed on a Heraeus CHN-Rapid elemental analyzer or a Vario EL III elemental analyzer.

**2-Azidobenzoic acid (3)**: A suspension of anthranilic acid (**1**) (100 g, 0.73 mol) in water (500 mL) and concentrated hydrochloric acid (185 mL) was cooled to −5 °C, and a solution of sodium nitrite (52.6 g, 760 mmol) dissolved in water (150 mL) was added dropwise. The resulting solution was stirred for 30 min at −5 °C. The diazonium salt **2** was not isolated, but the reaction mixture was poured into a mixture of sodium azide (53 g, 820 mmol) dissolved in water (150 mL) and ice (1000 g). A pale yellow precipitate formed immediately. The reaction mixture was set aside overnight. By then, the development of nitrogen had ceased. A pale yellow precipitate was isolated by filtration. The precipitate was washed with water and dried in vacuo to afford compound **3** (117 g, 98 %). $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta$ = 13.12 (s, 1H; OH), 7.76–7.24 (m, 4H; Ar-H); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150.6 MHz): $\delta$ = 166.4 (CO), 138.7, 133.1, 131.1, 124.9, 124.0, 120.8 (Ar-C); IR (KBr pellet): $\tilde{\nu}$ = 3000–2500 (m, OH), 2128, 2107, 2083 (vs, $N_3$), 1692 (s, C=O) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 163 (74) $[M]^+$, 135 (100) $[M-N_2]^+$, 119 (72) $[M-CO_2]^+$; elemental analysis calcd (%) for $C_7H_5N_3O_2$ (163.13): C 51.54, H 3.09, N 25.76; found: C 51.36, H 2.90, N 25.71.

**2-Azidobenzoic amide (4)**: A three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel was charged with **3** (117 g, 0.72 mol), dichloromethane (1000 mL), and triethylamine (105 mL, 830 mmol). The resulting suspension was cooled to −15 °C and ethyl chloroformate (72 mL, 0.75 mol) was added dropwise; the temperature must not exceed 0 °C during the addition. A precipitate of triethylammonium chloride formed during the addition. After completion of the addition, the reaction mixture was stirred for 1 h at 0 °C. Subsequently, the reaction mixture was cooled to −35 °C and gaseous ammonia was added for about 40 min. The resulting pale yellow suspension was stirred overnight. Removal of the solvent afforded a solid, which was washed with water (400 mL) and dried in vacuo to give **4** (113 g, 97 %) as pale yellow needles. $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta$ = 8.38–7.70 (m, 4H; Ar-H), 7.51 (br s, 2H; $NH_2$); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150.6 MHz): $\delta$ = 176.6 (CO), 148.0, 142.7, 141.8, 137.0, 135.3, 129.7 (Ar-C); IR (KBr pellet): $\tilde{\nu}$ = 3375, 3163 (m, NH), 2131, 2101 (vs, $N_3$), 1654 (C=O) cm$^{-1}$; elemental analysis calcd (%) for $C_7H_6N_4O$ (162.15): C 51.85, H 3.73, N 34.55; found: C 51.61, H 3.41, N 34.57.

**2-Azidoaniline (5)**: Freshly prepared aqueous NaOCl (1.0 L, 1.1M) was added to a suspension of **4** (113 g, 0.70 mol) in an aqueous NaOH solution (200 mL, 10 %) at 0 °C. The reaction mixture was stirred for 6 h during which the temperature was

kept below 20 °C. The resulting dark brown solution was stirred overnight at room temperature. The reaction mixture was then filtered to remove unreacted **4**. Compound **5** was precipitated from the filtrate by addition of a saturated aqueous solution of ammonium chloride (100 mL) and isolated by filtration. Purification was achieved by redissolving in diethyl ether together with activated charcoal. A brown solution was isolated after filtration. Removal of the diethyl ether solvent yielded **5** (48.6 g, 52 %) as brownish microcrystals. $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta = 7.47 - 7.14$ (m, 4H; Ar-H), 5.02 (br s, 2H; NH$_2$); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150.6 MHz): $\delta = 150.3$, 136.2, 134.5, 128.8, 128.1, 125.9 (Ar-C); IR (KBr pellet): $\tilde{\nu} = 3387$, 3295, 3188 (m, NH), 2129 (vs, N$_3$), 2080 (m, N$_3$) cm$^{-1}$. Compound **5** was fully characterized by NMR and IR spectroscopy.

***N*-Formyl-2-azidoaniline (6)**: Azide **5** (6.5 g, 0.05 mol) was dissolved in diethyl ether (100 mL) and cooled to 0 °C. Phenyl formate (7.14 mL, 0.065 mol) was then added dropwise at this temperature. The solution was then stirred at room temperature overnight. The solvent and phenol formed were removed in vacuo. The crude oily product was purified by recrystallization from dichloromethane/methanol (3:1) to give **6** (5.97 g, 76 %) as brownish crystals. $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta = 9.67$ (s, 1H; NH, major tautomer 80 %), 8.48 (s, 1H; N=C*H*(OH), minor tautomer), 8.30 (d, 1H; C(O)H, major tautomer), 8.10 – 7.13 (m, 4H; Ar-H, both tautomers), 3.41 (br s; N=C–OH, minor tautomer); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150.6 MHz): $\delta = 168.7$ (N=C–OH), 165.3 (N–C=O), 134.0, 133.9, 130.4, 130.1, 127.2, 124.2 (Ar-C); IR (KBr pellet): $\tilde{\nu} = 3000 - 2500$ (br m, NH and OH), 2107 (vs, N$_3$), 1692 (s, C=O) cm$^{-1}$; elemental analysis calcd (%) for $C_7H_6N_4O$ (162.15): C 51.85, H 3.73, N 34.55; found: C 51.73, H 3.47, N 34.34.

**2-Azidophenyl isocyanide (7)**: Compound **6** (3.0 g, 18.5 mmol) and triethylamine (10.3 mL, 74 mmol) were dissolved in dichloromethane (50 mL). The solution was cooled to 0 °C and diphosgene (1.2 mL, 10 mmol) was added dropwise with a syringe. The reaction mixture was stirred for 1 h at 0 °C and then at ambient temperature overnight. The brown solution was then poured into a saturated aqueous potassium carbonate solution (100 mL) and the mixture was stirred for 30 min. The organic layer was separated, washed several times with water, and dried over sodium sulfate. Removal of the solvent gave **7** as a brown oil. This was purified by chromatography on neutral $Al_2O_3$ (4 % $H_2O$) with diethyl ether as the eluent to give **7** (2.0 g, 74.9 %) as brownish crystals. Isocyanide **7** should be stored in the dark at low temperature. M.p. 35 °C; $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta = 7.58$ (dd, 1H; H-6), 7.53 (dt, 1H; H-4), 7.46 (dd, 1H; H-3) 7.24 (dt, 1H; H-5); $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150.6 MHz): $\delta = 168.8$ (br, N≡C), 136.1 (C–N$_3$), 131.0 (C-4), 127.9 (C-6), 125.5 (C-5), 120.1 (C-3), 116.6 (C-1); IR ($CH_2Cl_2$ solution): $\tilde{\nu} = 2142$ (s, C≡N), 2121, (s, N$_3$) cm$^{-1}$. Due to the light sensitivity of **7**, no elemental analysis was performed.

**Pentacarbonyl(2-azidophenyl isocyanide)chromium(0) (8)**: A solution of [Cr(CO)$_6$] (880 mg, 4 mmol) in THF (300 mL) was irradiated for 8 h in a photoreactor (high-pressure mercury vapor lamp). A solution of **7** (560 mg, 3.9 mmol) in toluene (4 mL) was added with a syringe to the resulting orange solution and this then stirred overnight with the exclusion of light. The solvent was removed in vacuo, and the resulting dark yellow residue was purified by column chromatography (neutral $Al_2O_3$, 4 % $H_2O$) with dichloromethane as eluent. The second pale yellow fraction was collected and the solvent was removed. Recrystallization of the yellow residue (diethyl ether/*n*hexane 2:1) at −20 °C yielded **8** (0.865 mg, 65 %) as yellow, light-sensitive crystals. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.52 - 7.12$ (m, 4H; Ar-H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 216.5$ (*trans*-CO), 214.3 (*cis*-CO), 179.1 (CNR), 137.4, 129.8, 129.5, 126.9, 125.2, 119.4 (Ar-C); IR ($CH_2Cl_2$ solution): $\tilde{\nu} = 2145$ (s, CN), 2126 (s, N$_3$), 2054, 1958 (vs, CO) cm$^{-1}$; elemental analysis calcd (%) for $C_{12}H_4N_4CrO_5$ (335.18): C 42.87, H 1.20, N 16.67; found: C 42.90, H 1.30, N 17.24.

**Pentacarbonyl(2-azidophenyl isocyanide)tungsten(0) (9)**: Complex **9** was prepared as described for **8** from [W(CO)$_6$] (1410 mg, 4 mmol) and **7** (560 mg, 3.9 mmol). Complex **9** (1179 mg, 63 %) was obtained as yellow, light-sensitive crystals. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.47 - 7.14$ (m, 4H, Ar-H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 196.1$ (*trans*-CO), 193.8 (*cis*-CO), 158.9 (CNR), 137.6, 130.1, 127.2, 125.2, 119.3, 118.9 (Ar-C); IR ($CH_2Cl_2$ solution): $\tilde{\nu} = 2141$ (s, CN), 2122 (s, N$_3$), 2056, 1953 (vs, CO) cm$^{-1}$; elemental analysis calcd (%) for $C_{12}H_4N_4O_5W$ (468.03): C 30.79, H 0.86, N 11.97; found: C 30.81, H 0.85, N 11.92.

**Pentacarbonyl(2-triphenylphosphiniminophenyl isocyanide)chromium(0) (10)**: Triphenylphosphane (1060 mg, 4.04 mmol) in THF (10 mL) was added to a solution of **8** (1341 mg, 4 mmol) in THF (200 mL). The yellowish solution was stirred for 6 h at ambient temperature until the evolution of dinitrogen ceased. The solvent was stripped in vacuo and the resulting dark yellow residue was purified by column chromatography (neutral $Al_2O_3$, 4 % $H_2O$) with diethyl ether/*n*hexane (1:1) as eluent. The second pale yellow fraction was collected and the solvent mixture was removed in vacuo. Recrystallization of the remaining residue (diethyl ether/*n*hexane 2:1) at −20 °C yielded **10** (1825 mg, 80 %) as pale yellow, air-stable crystals. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.65 - 6.36$ (m, 19H; Ar-H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 217.8$ (*trans*-CO), 215.1 (*cis*-CO), 167.1 (CNR), 148.4 (Ar–C–N=P), 132.5, 132.3, 132.0 (P–Ar–C), 130.8 (CN–Ar–*C*), 129.0, 128.8, 128.5 (P–Ar–C), 127.2, 121,8, 121.6, 116.6 (CN–Ar–*C*); $^{31}$P{$^1$H} NMR ($CDCl_3$, 81 MHz): $\delta = 8.02$ (s); IR (KBr pellet): $\tilde{\nu} = 2148$ (s, CN), 2059, 1990, 1937 (vs, CO), 1348 (s, P=N) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 570 (3) $[M]^+$, 514 (5) $[M - 2\,CO]^+$, 486 (2) $[M - 3\,CO]^+$, 458 (16) $[M - 4\,CO]^+$, 430 (100) $[M - 5\,CO]^+$; elemental analysis calcd (%) for $C_{30}H_{19}N_2CrO_5P$ (570.31): C 63.15, H 3.33, N 4.91; found: C 62.78, H 3.60, N 4.84.

**Pentacarbonyl(2-triphenylphosphiniminophenyl isocyanide)tungsten(0) (11)**: Complex **11** was prepared as described for **10** from **9** (1872 mg, 4 mmol) and triphenylphosphane (1060 mg, 4.04 mmol). Compound **11** (2100 mg, 75 %) was obtained as yellow, air-stable crystals. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.85 - 6.51$ (m, 19H; Ar-H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 197.3$ (*trans*-CO), 194.6 (*cis*-CO), 148.7 (CNR and Ar–C–N=P), 132.5, 132.4, 132.1 (P–Ar–C), 130.7 (CN–Ar–*C*), 129.3, 128.9, 128.6 (P–Ar–C), 127.4, 121,9, 121.7, 116.8 (CN–Ar–*C*); $^{31}$P{$^1$H} NMR ($CDCl_3$, 81 MHz): $\delta = 5.09$ (s); IR (KBr pellet): $\tilde{\nu} = 2147$ (s, CN), 2065, 1993, 1942 (vs, CO), 1350 (s, P=N) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 702 (5) $[M]^+$, 646 (7) $[M - 2\,CO]^+$, 618 (3) $[M - 3\,CO]^+$, 590 (10) $[M - 4\,CO]^+$, 562 (64) $[M - 5\,CO]^+$; elemental analysis calcd (%) for $C_{30}H_{19}N_2O_5PW$ (702.16): C 51.31, H 2.70, N 3.98; found: C 51.74, H 3.01, N 4.08.

**Pentacarbonyl(2,3-dihydro-1*H*-benzimidazol-2-ylidene)chromium(0) (12)**: Aqueous HBr (0.1 mL, 47 %) was added to a solution of **10** (1140 mg, 2 mmol) in a mixture of methanol (10 mL) and water (1 mL). After stirring the reaction mixture for 24 h, a saturated aqueous $NaHCO_3$ solution (1 mL) was added. The solvents were stripped in vacuo. The remaining residue was suspended several times in water (25 mL) to remove the inorganic salts. The organic residue was filtered, dissolved in diethyl ether (20 mL), and dried over $Na_2SO_4$. The salt was removed by filtration and the filtrate was evaporated to dryness. Complex **12** was purified by column chromatography (silica gel 60, 4 % $H_2O$) with diethyl ether/methanol (25:1) as the eluent. Removal of the solvent yielded **12** as an off-white solid. Recrystallization from diethyl ether/*n*hexane (1:1) at −20 °C yielded **12** (527 mg, 85 %) as pale yellow, air-stable crystals. $^1$H NMR ([D$_8$]THF, 200.1 MHz): $\delta = 11.90$ (s, 2H; NH), 7.21 (m, 2H; Ar-H), 7.02 (m, 2H; Ar-H); $^{13}$C{$^1$H} NMR ([D$_8$]THF, 50.3 MHz): $\delta = 222.7$ (*trans*-CO), 219.0 (*cis*-CO), 200.6 (NCN), 135.3, 123.7, 110.8 (Ar-C); IR (KBr pellet): $\tilde{\nu} = 3463$ (m, NH), 2058, 1951 (vs, CO) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 310 (10) $[M]^+$, 282 (3) $[M - CO]^+$, 254 (5) $[M - 2\,CO]^+$, 226 (5) $[M - 3\,CO]^+$, 198 (12) $[M - 4\,CO]^+$, 170 (100) $[M - 5\,CO]^+$; elemental analysis calcd (%) for $C_{12}H_6N_2CrO_5$ (310.14): C 46.47, H 1.94, N 9.03; found: C 46.85, H 2.12, N 9.16.

**Pentacarbonyl(2,3-dihydro-1*H*-benzimidazol-2-ylidene)tungsten(0) (13)**: Complex **13** was prepared as described for **12** from **11** (1404 mg, 2 mmol). Complex **13** (689 mg, 78 %) was obtained as yellow, air-stable crystals. $^1$H NMR ([D$_8$]THF, 200.1 MHz): $\delta = 12.15$ (s, 2H; NH), 7.45 (m, 2H; Ar-H), 7.20 (m, 2H; Ar-H); $^{13}$C{$^1$H} NMR ([D$_8$]THF, 50.3 MHz): $\delta = 202.5$ (*trans*-CO), 198.9 (*cis*-CO), 182.8 (NCN), 135.1, 121.6, 111.2 (Ar-C); IR (KBr pellet): $\tilde{\nu} = 3461$ (m, NH), 2064, 1869 (vs, CO) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 442 (71) $[M]^+$, 414 (11) $[M - CO]^+$, 386 (6) $[M - 2\,CO]^+$, 358 (18) $[M - 3\,CO]^+$, 330 (27) $[M - 4\,CO]^+$, 302 (100) $[M - 5\,CO]^+$; elemental analysis calcd (%) for $C_{12}H_6N_2O_5W$ (441.99): C 32.60, H 1.35, N 6.33; found: C 32.69, H 1.78, N 6.42.

**Pentacarbonyl(1,3-bisallylbenzimidazol-2-ylidene)chromium (14)**: Potassium *tert*-butanolate (245 mg, 2.2 mmol) was added to a solution of **12** (620 mg, 2 mmol) in DMF (10 mL) and at −20 °C. After stirring for 4 h at room temperature, allyl bromide (1.8 mL, 2.1 mmol) was added and the solution was stirred overnight. This procedure was repeated as described above to achieve the second alkylation. The solvent was stripped in vacuo,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and the oily brownish residue was dissolved in diethyl ether. The inorganic salt was filtered off, and column chromatography (neutral $Al_2O_3$, 4% $H_2O$) with *n*hexane/$CH_2Cl_2$ (10:1) as eluent gave complex **14** (507 mg, 65%) as a pale yellow solid. Recrystallization from *n*hexane/diethyl ether (3:1) at −20 °C afforded yellow, air-stable crystals of **14**. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.27-7.11$ (m, 4H; Ar-H), 6.0 (ddt, $^3J = 16$, 10, 4 Hz, 2H; $CH_2-CH{=}CH_2$), 5.32–5.29 (m, 4H; $CH{=}CH_2$), 5.02 (d, $^3J = 4$ Hz, 4H; $N-CH_2$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 221.2$ (*trans*-CO), 216.9 (*cis*-CO), 206.2 (NCN), 135.2 (Ar-C), 132.3 ($CH_2-CH{=}CH_2$), 122.9 (Ar–C), 117.9 ($CH_2-CH{=}CH_2$), 110.9 (Ar-C), 51.5 ($N-CH_2$); IR (KBr): $\tilde{\nu} = 2057$, 1980, 1903 (vs, CO) cm$^{-1}$; MS (80 eV, EI): *m*/*z* (%): 390 (8) $[M]^+$, 362 (11) $[M-CO]^+$, 334 (15) $[M-2CO]^+$, 306 (12) $[M-3CO]^+$, 278 (21) $[M-4CO]^+$, 250 (100) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{18}H_{14}N_2CrO_5$ (390.20): C 55.40, H 3.58, N 7.15; found: C 55.85, H 4.11, N 7.52.

**Pentacarbonyl(1,3-bisallylbenzimidazol-2-ylidene)tungsten(0) (15)**: Complex **15** was prepared as described for **14** from **13** (882 mg, 2 mmol). Complex **15** (678 mg, 65%) was obtained as yellow, air-stable crystals. $^1$H NMR ($CDCl_3$, 200.1 MHz): $\delta = 7.41-7.26$ (m, 4H; Ar-H), 6.02 (ddt, $^3J = 16$, 10, 4 Hz, 2H; $CH_2-CH{=}CH_2$), 5.34–5.23 (m, 4H; $CH{=}CH_2$), 5.09 (d, $^3J = 4$ Hz, 4H; $N-CH_2$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 50.3 MHz): $\delta = 200.4$ (*trans*-CO), 197.2 (*cis*-CO), 193.2 (NCN), 134.6 (Ar-C), 132.1 ($CH_2-CH{=}CH_2$), 123.3 (Ar-C), 118.0 ($CH_2-CH{=}CH_2$), 111.3 (Ar-C), 52.9 ($N-CH_2$); IR (KBr pellet): $\tilde{\nu} = 2063$, 1977, 1900 (vs, CO) cm$^{-1}$; MS (70 eV, EI): *m*/*z* (%): 522 (26) $[M]^+$, 494 (16) $[M-CO]^+$, 466 (15) $[M-2CO]^+$, 438 (22) $[M-3CO]^+$, 410 (100) $[M-4CO]^+$, 382 (63) $[M-5CO]^+$; elemental analysis calcd (%) for $C_{18}H_{14}N_2O_5W$ (522.16): C 41.40, H 2.70, N 5.36; found: C 41.37, H 2.61, N 5.17.

**X-ray crystallography**: Single crystals suitable for X-ray analysis were mounted on glass fibers by using two-component glue or mineral oil. X-ray intensities were measured at room temperature (**11**–**14**) with a Nonius CAD-4 equipped with a seal tube or at 153 K by using a Bruker AXS Apex system equipped with a rotating anode (**9**, **15**). All data were measured with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data reduction was performed with either X-CAD[42] or the Bruker SMART[43] program packages, respectively. For further crystal and data collection details see Table 2. All crystal structures were solved with SHELXS-97[44] by heavy atom methods and were refined with SHELXL-97[45] by using anisotropic thermal parameters for all non-hydrogen atoms. With the exception of **12**, all hydrogen positions were determined by Fourier techniques and were refined with isotropic thermal parameters. Hydrogen positions in **12** were calculated and thermally fixed to 1.3 Ueqv of the parent atom. Ortep3 for Windows[46] was used for all plots. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC-192094–192099 contain the supplementary crystallographic data for this paper. These data can be obtained 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.cam.uk).

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[1] a) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, **1983**; b) B. Crociani, in *Reactions of Coordinated Ligands*, *Vol. 1* (Ed.: P. S. Braterman), Plenum, New York, **1986**, p. 553.
[2] Reviews on coordination chemistry of isocyanides: a) E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.* **1983**, *22*, 209; b) P. M. Treichel, *Adv. Organomet. Chem.* **1973**, *11*, 21.
[3] F. E. Hahn, *Angew. Chem.* **1993**, *105*, 681; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 650.
[4] a) L. Tschugajeff, M. J. Skanawy–Grigorjewa, *J. Russ. Chem. Soc.* **1915**, *47*, 776; b) L. Tschugajeff, M. Skanawy–Grigorjewa, A. Posnjak, *Z. Anorg. Chem.* **1925**, *148*, 37.
[5] a) A. Burke, A. L. Balch, J. H. Enemark, *J. Am. Chem. Soc.* **1970**, *92*, 2555; b) W. M. Butler, J. H. Enemark, *Inorg. Chem.* **1971**, *10*, 2416; c) W. M. Butler, J. H. Enemark, J. Parks, A. L. Balch, *Inorg. Chem.* **1973**, *12*, 451.
[6] a) W. P. Fehlhammer, H. Hoffmeister, H. Stolzenberg, B. Boyadjiev, *Z. Naturforsch.* **1989**, *44b*, 419; b) W. P. Fehlhammer, H. Hoffmeister, B. Boyadjiev, T. Kolrep, *Z. Naturforsch.* **1989**, *44b*, 917; c) U. Kernbach, W. P. Fehlhammer, *Inorg. Chim. Acta* **1995**, *235*, 299; d) W. P. Fehlhammer, K. Bartel, B. Weinberger, U. Plaia, *Chem. Ber.* **1985**, *118*, 2220.
[7] W. P. Fehlhammer, K. Bartel, U. Plaia, A. Völkl, A. T. Liu, *Chem. Ber.* **1985**, *118*, 2235.
[8] a) U. Plaia, H. Stolzenberg, W. P. Fehlhammer, *J. Am. Chem. Soc.* **1985**, *107*, 2171; b) R. Fränkel, U. Kernbach, M. Bakola–Christianopoulou, U. Plaia, M. Suter, W. Ponikwar, H. Nöth, C. Moinet, W. P. Fehlhammer, *J. Organomet. Chem.* **2001**, *617/618*, 530.
[9] J. P. Ferris, F. R. Antonucci, R. W. Trimmer, *J. Am. Chem. Soc.* **1973**, *95*, 919.
[10] P. Jutzi, U. Gilge, *J. Organomet. Chem.* **1983**, *246*, 159.
[11] F. E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* **1993**, 842.

Table 2. Selected crystal and data collection details for **9** and **11**–**15**.

| | **9** | **11** | **12** | **13** | **14** | **15** |
|---|---|---|---|---|---|---|
| formula | $C_{12}H_4N_4O_5W$ | $C_{30}H_{19}N_2O_5PW$ | $C_{12}H_6NCrO_5$ | $C_{12}H_6N_2O_5W$ | $C_{18}H_{14}N_2O_5Cr$ | $C_{18}H_{14}N_2O_5W$ |
| $M_r$ | 468.04 | 702.29 | 310.19 | 442.04 | 390.31 | 522.16 |
| $a$ [Å] | 7.0986(5) | 9.4320(10) | 11.768(3) | 11.909(3) | 8.7850(10) | 8.825(4) |
| $b$ [Å] | 16.7591(12) | 23.547(2) | 14.794(2) | 14.940(3) | 9.842(2) | 9.800(4) |
| $c$ [Å] | 11.9553(9) | 12.678(2) | 7.318(2) | 7.517(2) | 10.748(2) | 10.672(4) |
| $\alpha$ [°] | 90.0 | 90.0 | 90.0 | 90.0 | 80.0200(10) | 99.88(3) |
| $\beta$ [°] | 93.713(2) | 98.1300(10) | 90.0 | 92.18(2) | 77.4100(10) | 102.68(3) |
| $\gamma$ [°] | 90.0 | 90.0 | 90.0 | 90.0 | 89.4600(10) | 90.13(4) |
| $V$ [Å]$^3$ | 1419.3(2) | 2787.4(6) | 1274.0(5) | 1336.5(6) | 892.8(3) | 886.3(6) |
| $T$ [K] | 153(2) | 293(2) | 293(2) | 293(2) | 293(2) | 153(1) |
| $\rho_{calcd}$ [g cm$^{-1}$] | 2.190 | 1.673 | 1.617 | 2.197 | 1.452 | 1.957 |
| space group | $P2_1/c$ | $P2_1/n$ | $Cmcm$ | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $Z$ | 4 | 4 | 4 | 4 | 2 | 2 |
| $\mu$ [mm$^{-1}$] | 8.168 | 4.243 | 0.918 | 8.662 | 0.671 | 6.548 |
| unique data | 4092 | 4875 | 637 | 1164 | 3127 | 5056 |
| obs data [$I > 2\sigma(I)$] | 3617 | 3873 | 501 | 1037 | 2678 | 4794 |
| $R1$ (obs.) [%] | 3.51, $wR1 = 9.10$ | 2.84, $wR1 = 7.13$ | 3.34, $wR1 = 8.28$ | 1.30, $wR1 = 3.18$ | 3.43, $wR1 = 9.09$ | 2.59, $wR1 = 5.86$ |
| $R2$ (all) [%] | 4.03, $wR2 = 9.44$ | 4.73, $wR2 = 7.75$ | 5.09, $wR2 = 8.95$ | 1.69, $wR2 = 3.26$ | 4.49, $wR2 = 9.75$ | 2.74, $wR2 = 5.91$ |
| GOF | 1.041 | 0.994 | 1.091 | 1.066 | 1.087 | 1.016 |
| no. of variables | 215 | 352 | 68 | 105 | 292 | 291 |
| res. el. density [e Å$^{-3}$] | 2.544/−2.777 | 0.940/−0.811 | 0.344/−0.329 | 0.398/−0.507 | 0.317/−0.202 | 2.113/−1.679 |

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[12] F. E. Hahn, M. Tamm, *J. Organomet. Chem.* **1993**, *456*, C11.
[13] F. E. Hahn, T. Lügger, *J. Organomet. Chem.* **1994**, *481*, 189.
[14] F. E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* **1995**, 569.
[15] M. Tamm, T. Lügger, F. E. Hahn, *Organometallics* **1996**, *15*, 1251.
[16] U. Kernbach, T. Lügger, F. E. Hahn, W. P. Fehlhammer, *J. Organomet. Chem.* **1997**, *541*, 51.
[17] F. E. Hahn, M. Tamm, *Organometallics* **1995**, *14*, 2597.
[18] F. E. Hahn, L. Imhof, *Organometallics* **1997**, *16*, 763.
[19] F. E. Hahn, M. Tamm, T. Lügger, *Angew. Chem.* **1994**, *106*, 1419; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1356.
[20] M. Tamm, F. E. Hahn, *Inorg. Chim. Acta* **1999**, *288*, 47.
[21] M. Tamm, F. E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175.
[22] a) A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361; b) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, *107*, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021; c) A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027; d) M. K. Denk, A. Thadani, K. Hatano, A. J. Lough, *Angew. Chem.* **1997**, *109*, 2719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607; e) for a review on N-heterocyclic carbenes, see W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.
[23] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931.
[24] a) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551; *Angew. Chem. Int. Ed.* **2000**, *39*, 541; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, B. Wibbeling, *Angew. Chem.* **2000**, *112*, 2393; *Angew. Chem. Int. Ed.* **2000**, *39*, 2307.
[25] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635.
[26] *Isonitrile Chemistry* (Ed.: I. Ugi), Academic Press, New York, **1971**.
[27] T. El-Shini, R. Herrmann, *Z. Naturforsch.* **1986**, *41b*, 132.
[28] P. Cledera, C. Avendano, J. C. Menendez, *Tetrahedron* **1998**, *54*, 12349.
[29] E. S. Wallis, J. F. Lane, *Org. React.* **1946**, *3*, 267.
[30] H. L. Yale, *J. Org. Chem.* **1971**, *36*, 3238.
[31] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, K. Offermann, *Angew. Chem.* **1965**, *77*, 492; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 472.
[32] I. Morishima, A. Mizuno, T. Yonezawa, *J. Chem. Soc. Chem. Commun.* **1970**, 1321.
[33] a) F. E. Hahn, M. Tamm, *J. Organomet. Chem.* **1990**, *398*, C19; b) F. E. Hahn, M. Tamm, *Organometallics* **1992**, *11*, 84; c) F. E. Hahn, M. Tamm, *J. Organomet. Chem.* **1994**, *467*, 103; d) for comparison with alkyl isocyanides see F. E. Hahn, M. Tamm, *Organometallics* **1994**, *13*, 3002.
[34] M. J. E. Hewlins, *J. Chem. Soc. (B)* **1971**, 942.
[35] M. P. Guy, J. T. Guy, Jr., D.-W. Bennett, *Organometallics* **1986**, *5*, 1696.
[36] C. G. Kreiter, V. Formacek, *Angew. Chem.* **1972**, *84*, 155; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 141.
[37] K. Öfele, W. A. Herrmann, D. Mihailos, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, *J. Organomet. Chem.* **1995**, *498*, 1.
[38] F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241.
[39] K. M. Lee, C. K. Lee, I. J. B. Lin, *Angew. Chem.* **1997**, *109*, 1936; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1850.
[40] N. Kuhn, T. Kratz, R. Boese, D. Bläser, *J. Organomet. Chem.* **1994**, *470*, C8.
[41] a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18; b) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236.
[42] CAD4, Enraf-Nonius, **1995**.
[43] SMART, Bruker AXS, **2000**.
[44] SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
[45] SHELXL-97, G. M. Sheldrick, Universität Göttingen (Germany), **1997**.
[46] ORTEP-3, L. J. Farrugia, University of Glasgow (Scotland), **1999**.

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