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Reactions of β-functional phenyl isocyanides

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Contents

Abstract

Aspects of the coordination chemistry of β-functional phenyl isocyanides are reviewed, with emphasis on research involving 2-hydroxyphenyl isocyanide and derivatives thereof, which has been carried out in our Berlin group during the last few years. The driving force of coordinated 2-hydroxyphenyl isocyanide to form carbene complexes with 2,3-dihydrobenzoxazol-2-ylidene ligands depends on the attached metal fragment and can be

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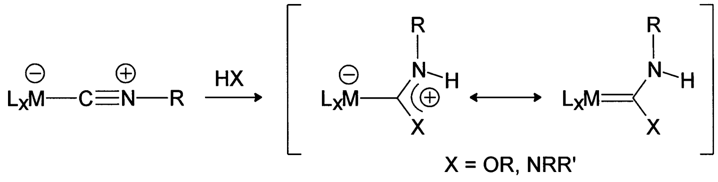
used as a probe for the π-electron release ability of the metal center. Related work on N- and C-functional phenyl isocyanides aimed towards the synthesis of 2,3-dihydro-1*H*-imidazol-2-ylidene and 2,3-dihydro-1*H*-indol-2-ylidene complexes is also described.

Keywords: Isocyanides; Carbenes; Complexes; Cycloadditon; Heterocycles

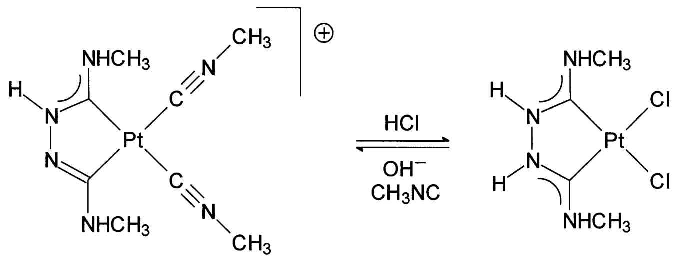
1. Introduction

Isocyanides coordinated to metal centers in higher oxidation states may undergo nucleophilic attack at the terminal carbon atom by a variety of reagents [1–3]. In particular, with protic nucleophiles, such as alcohols or primary and secondary amines, the reaction yields metal–carbene complexes (Scheme 1)[1].



Scheme 1. Nucleophilic addition of alcohols or amines to coordinated isocyanides.

Unintentionally, this method was first applied as early as 1915 when Tschugajeff and Skanawy-Grigorjewa treated tetrakis(methyl isocyanide)platinum(II) with hydrazine and isolated a red salt with the formulation $[Pt(N_2H_3)(MeNC)_4]Cl_2$, which was very likely the first carbene complex to be synthesized in pure form [4]. By treatment with hydrochloric acid this complex was converted into a yellow compound, which could be transformed back to the red form by addition of methyl isocyanide and base. However, these products were assigned wrong dimeric structures with six-coordinate platinum(II). Only in 1970, well after Fischer and Maasböl's first successfully planned synthesis and characterization of a stable tungsten carbene complex [5], these complexes were recognized as carbene complexes **1** and **2** [6] (Scheme 2).



1 **2**

Scheme 2. Constitution of Tschugajeff's red (left), yellow complexes (right).

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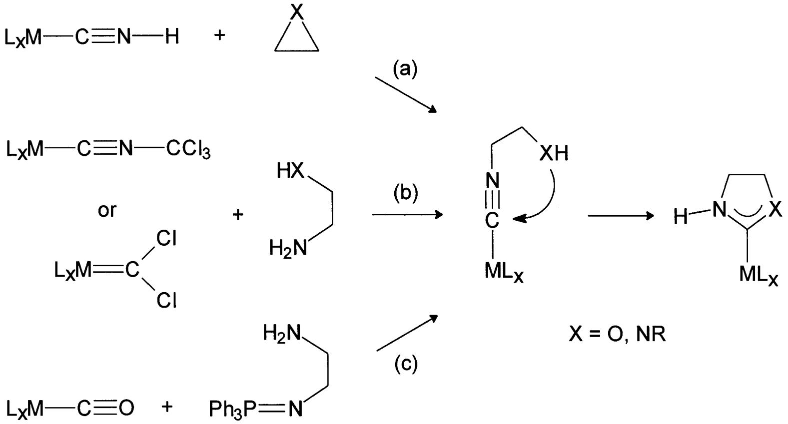
[1] Throughout the text formal charges at isocyanide or carbene ligands will not be drawn, unless necessary for the correct description of different mesomeric forms.

Whereas the addition of nucleophiles HX to coordinated isocyanides usually leads to the formation of acyclic carbene complexes, the employment of functional isocyanides, which contain both the isocyanide group and the nucleophile in the same molecule, gives access to complexes with heterocyclic carbenes through an intramolecular 1,2-addition across the CN triple bond. Various synthetic methods have been developped to generate such functional aliphatic isocyanides at the metal center [7]. Selected examples are: (a) the reaction of cyanometal acids with epoxides [8][2], [9][3], [10,11] and aziridines [12], (b) the reaction of ethylenediamine or ethanolamine with trichloromethyl isocyanide [13] or dichlorocarbene complexes [14] and (c) the reacion of metal carbonyls with aminophosphinimines [15] (Scheme 3). Also α-metallation of coordinated isocyanides followed by reaction with 1,2-dipolar substrates such as aldehydes, ketones, CS_2 or isocyanates has been reported several times [16,17]. This resembles the organic route to heterocycles employed by Schöllkopf and Hoppe from α-metalated isocyanides [18].



Scheme 3. Formation of carbene complexes from coordinated β-functional aliphatic isocyanides.

Alternatively, Fehlhammer et al. have introduced readily available and stable 2-hydroxyalkyl isocyanides such as $CNCH_2CH_2OH$, in which the nucleophile and the isocyano 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 [19–23] allowing even the isolation of homoleptic tetra- [24] and hexacarbene complexes [25].

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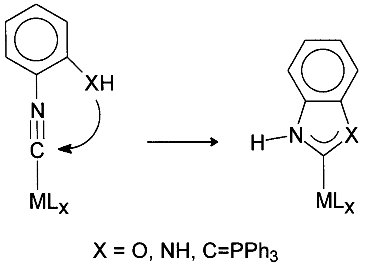
[2] It should be noted, that the chemistry of functional isocyanides probably started as early as 1901, when Baeyer and Villiger studied the reaction of $H_4Fe(CN)_6$ with ethylene oxide and isolated an ice-like compound, the characterization of which should be performed after the onset of the cooler season [9]. Similar experiments more than eight decades later suggest that this material contained at least 2-hydroxyethyl isocyanide if not carbene ligands [10].

[3] Quotation, p. 2689: “Aethylenoxid giebt mit dem in einem Kältegemisch abgekühlten Ferrocyanreagens eine eisähnliche Verbindung, die möglicher Weise auch ein Hydrat des Aethylenoxids sein könnte. Beim Verreiben verwandelte sie sich in ein weisses Krystallpulver. Die nähere Untersuchung sollte nach Eintritt der kühleren Jahreszeit erfolgen.”

In β-functional aryl isocyanides (Scheme 4) the electrophilic isocyanide and the nucleophilic substiutent are not only linked, but also suitably oriented in one plane for an intramolecular cycloaddition reaction. This geometry together with the aromaticity of the resulting ligand could lead to an even greater tendency to form heterocyclic ylidenes. Therefore, we initiated a program to study the coordination chemistry of aromatic isocyanides with functional groups in the *ortho*-position, and the present review summarizes predominantly the results obtained during the last few years in our group including related work on benzannelated heterocyclic carbene complexes.



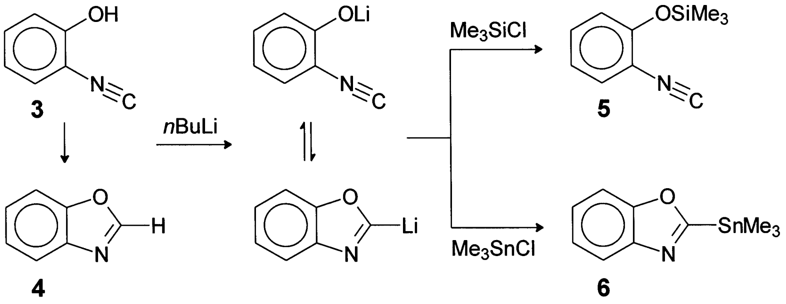
Scheme 4. Formation of carbene complexes from coordinated β-functional phenyl isocyanides.

2. *O*-functional phenyl isocyanides

2.1. Coordination to metal(0) centers

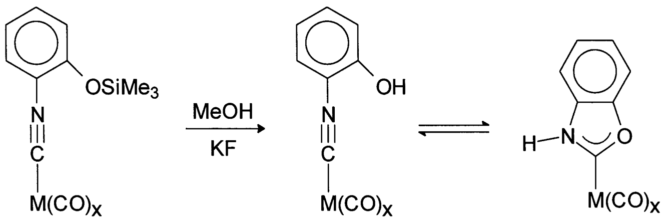
2.1.1. Complexes with 2-hydroxyphenyl isocyanide

We became interested in the coordination chemistry of 2-hydroxyphenyl isocyanide (**3**) in order to evaluate reactions at the hydroxy group possibly leading to a template synthesis for aromatic tripodal triisocyanides [3,26]. Contrary to aliphatic 2-hydroxyethyl isocyanide [19–25] free **3** is not stable and cyclizes to benzoxazole (**4**) [27]. Lithiation of **4** leads to an equilibrium between lithiated **3** and **4**. Reaction of this mixture with Me_3SiCl yields regiospecifically 2-(trimethylsiloxy)phenyl isocyanide (**5**), while reaction with Me_3SnCl gives *C*-metallated 2-trimethylstannylbenzoxazole (**6**) [28] (Scheme 5).



Scheme 5. Preparation of 2-(trimethylsiloxy)phenyl isocyanide (**5**).

The masked isocyanide (**5**) can be readily coordinated to transition metal fragments by carbonyl substitution reactions, and a series of complexes of the type [(**5**)M(CO)$_x$] (**7**) ($x = 4$, M = Fe; $x = 5$, M = Cr, Mo, W) has been prepared [29–31]. Cleavage of the Si–O bond is best achieved by stirring in methanol with a catalytic amount of KF for approximately two days releasing complexes [(**3**)M(CO)$_x$] (**8**) with the 2-hydroxyphenyl isocyanide ligand. Subsequently, complexes **9** containing the 2,3-dihydrobenzoxazol-2-ylidene ligand (for nomenclature see [32a] can form, if the isocyanide is sufficiently activated (or insufficiently deactivated) towards intramolecular nucleophilic attack by the hydroxy group (Scheme 6).



7a, M = Fe, x = 4
7b, M = Cr, x = 5
7c, M = Mo, x = 5
7d, M = W, x = 5

8a, M = Fe, x = 4
8b, M = Cr, x = 5
8c, M = Mo, x = 5
8d, M = W, x = 5

9a, M = Fe, x = 4
9b, M = Cr, x = 5
9c, M = Mo, x = 5
9d, M = W, x = 5

Scheme 6. Equilibrium between isocyanide, carbene complexes **8**, **9**.

Different observations are made depending on the nature of the transition metal fragment. Coordinated to the Fe(CO)$_4$ group 2-hydroxyphenyl isocyanide completely cyclizes to give the carbene complex **9a**, which is the only product detectable by NMR spectroscopy [29]. On the other hand, hydrolysis of the Si–O bond in [(**5**)M(CO)$_5$] (**7b**, M = Cr; **7c**, M = Mo, **7d**, M = W) gives mixtures of isocyanide complexes **8b**–**d** and ylidene complexes **9b**–**d** with the 2,3-dihydrobenzoxazol-2-ylidene ligand [33]. In these mixtures complexes **8** can be identified by the CN stretching frequencies (2132–2141 cm^{-1}), while complexes of type **9** show a strong IR absorption for the N–H bond around 3430 cm^{-1}. The O*H* resonance for complexes **8b**–**d** is found between 5.6 and 6.1 ppm in the ^{1}H NMR spectrum (in CDCl$_3$), whereas the N*H* resonance for complexes of type **9** appears around 10.5 ppm. Comparison of the integrals for these two resonances allows the determination of the relative abundance of the two components in a mixture of **8** and **9** indicating that the equilibrium resides mostly on the side of the ylidene complexes **9** (Table 1, vide infra).

Single crystals of **9d** were obtained by cooling a solution of **8d**/**9d** in ethanol. The result of an X-ray crystal structure determination is depicted in Fig. 1

Table 1
Physical, IR spectroscopic data for mixtures of complexes **8**, **9**[a]

ML_x	Complex	Ratio (%)		IR $\tilde{\nu}$ (cm^{-1})	k(CN) N m^{-1}
		Isocyanide	Ylidene		
$Fe(CO)_4$	**9a**	0	100	2169[b]	1791
$W(CO)_5$	**8d/9d**	15	85	2141	1746
$Mo(CO)_5$	**8c/9c**	24	76	2137	1739
$Cr(CO)_5$	**8b/9b**	29	71	2132	1731
cis-$[W(CO)_4PPh_3]$	**8e**	100	0	2117	1706
cis-$[W(CO)_4CRR']$	**8f**	100	0	2108	1692

[a] Ref. [33].

[b] See footnote 4 in the text.

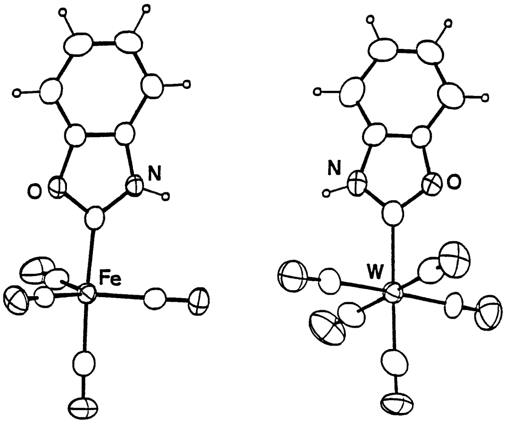
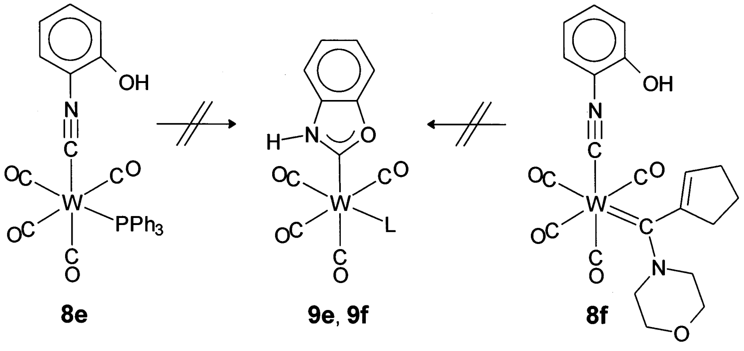


Fig. 1. Molecular structures of **9a** (left), of **9d** in **9d**·EtOH (right).

(right) together with the molecular structure of the iron derivative **9a** (left). The ^1H NMR spectrum taken from redissolved crystals of **9d** in $CDCl_3$ again shows the same ratio between complexes **8d**/**9d**.

Substituted isocyanide tetracarbonyl tungsten derivatives have been prepared [33,34]. The *cis*-configurated 2-hydroxyphenyl isocyanide complexes **8e** [33] and **8f** [34] are obtained after hydrolysis of the corresponding *O*-silylated precursors. Here, the situation is reverse to that found for coordination to the $Fe(CO)_4$ fragment (vide supra), and the equilibrium resides completely on the side of the open isocyanide form with no observable amounts of the hypothetical carbene complexes **9e** and **9f** (Scheme 7).



Scheme 7. *Cis*-configurated 2-hydroxyphenyl isocyanide complexes.

Comparison of the reactivity of complexes **8a**–**f** shows, that the tendency of coordinated 2-hydroxyphenyl isocyanide to form 2,3-dihydrobenzoxazol-2-ylidene varies with the metal fragment ranging from complete carbene formation in **8a** to complete isocyanide stabilization in **8e** and **8f**. It has been shown that the electrophilicity of coordinated carbonyl or isocyanide ligands can be related to the IR absorption frequencies or to the force constants of the CO or CN bonds, respectively [35]. The force constant can be directly correlated with the positive charge on the carbon atom, e.g. with its susceptibility to nucleophilic attack [36]. Table 1 summarizes the IR stretching frequencies and force constants calculated by the method of Cotton and Kraihanzel [37] of complexes **8** together with the observed isocyanide: carbene ratios.

The highest force constant ($k = 1791$ N m^{-1}) is calculated for the iron derivative **8a**[4] indicating that metal-to-ligand ($d \rightarrow \pi^*$)-backbonding is the weakest in the series of complexes **8a**–**f**. Here, the lack of sufficient stabilization causes the 2-hydroxyphenyl isocyanide to undergo complete carbene formation at the $Fe(CO)_4$ metal fragment. A decrease in k by 45 N m^{-1} relatively to **8a** is calculated for the tungsten complex **8d**, and this enhanced backdonation from the metal center already results in partial suppression of the cycloaddition reaction. Comparison of the data obtained for the pentacarbonyl complexes **8b**–**d** and **9b**–**d** illustrates, how sensitive the isocyanide/ylidene equilibrium is to marginal changes in the electronic properties of the metal fragment allowing almost a fine-tuning of the isocyanide: carbene ratio (Table 1).

Substitution of one *cis*-carbonyl ligand in the tungsten complex **8d** by the much weaker π-acceptors triphenylphosphane PPh_3 in **8e** or the (amino)ylidene ligand in **8f** (Scheme 7) increases the π-basicity of the metal center thus leading to enhanced ($d \rightarrow \pi^*$)-backbonding to the remaining 2-hydroxyphenyl isocyanide as clearly shown by the much smaller force constants ($k = 1706$ and 1692 N/m). These low values indicate complete deactivation of the isocyanide carbon in **8e** and **8f** for

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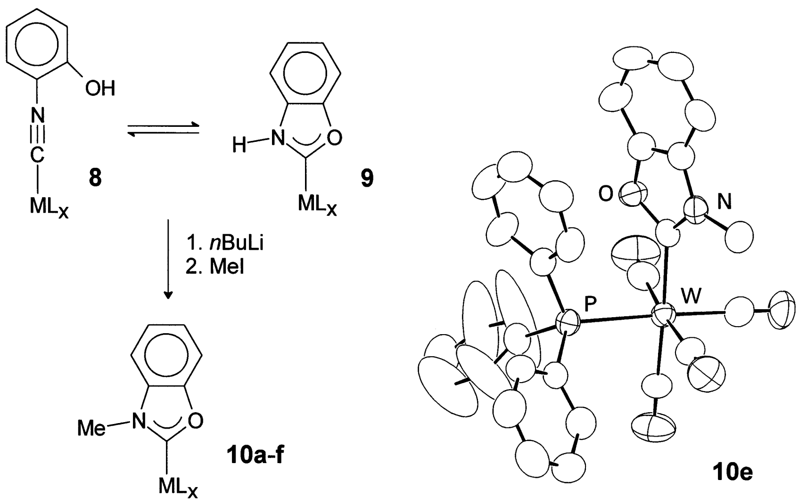
[4] The wave number for the 2-(timethylsiloxy)phenyl isocyanide derivative (**7a**), as the complex **8a** was not observed.

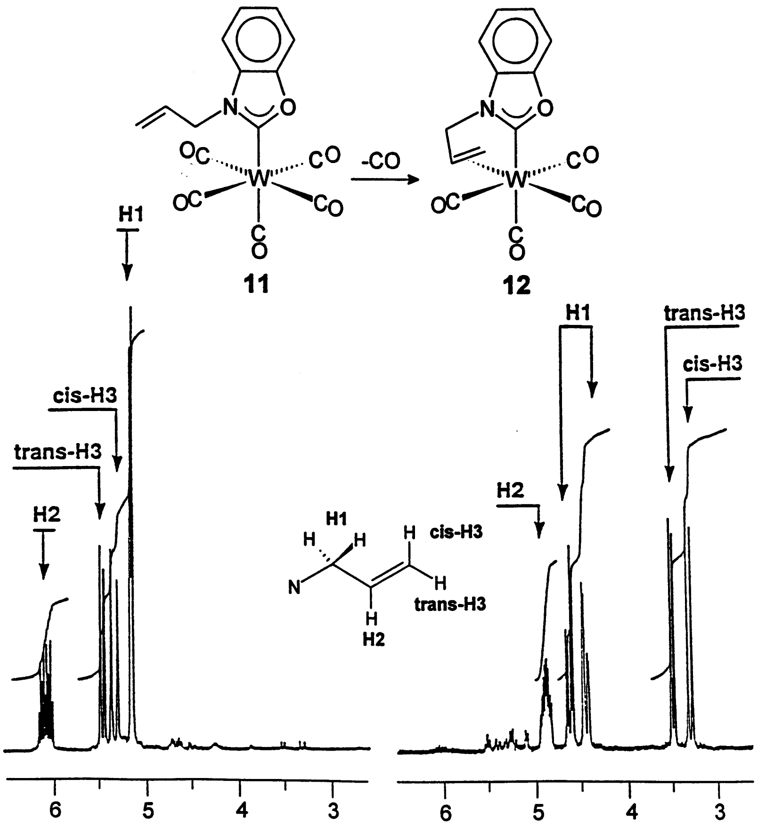


Scheme 8. Preparation of 3-methyl-2,3-dihydrobenzoxazol-2-ylidene complexes, molecular structure of **10e**.

intramolecular nucleophilic attack and explains why no ylidene complexes **9e** and **9f** can be identified spectroscopically.

Even eletronically stabilized isocyanide complexes of the type **8** are converted to ylidene derivatives by deprotonation and subsequent alkylation. In deprotonated **8** the phenolate oxygen atom is a stronger nucleophile causing complete cyclization. *N*-methylation of the resulting monoanionic benzoxazol-2-yl complexes results in the formation of stable complexes with 3-methyl-2,3-dihydrobenzoxazol-2-ylidene ligands **10a**–**f** [29–31,33,34] (Scheme 8). No 2-methoxyphenyl isocyanide derivatives have ever been isolated from the reaction mixture. Scheme 8 also shows an ORTEP presentation of the molecular structure of the triphenylphosphine complex **10e**. The molecular structure of the bisylidene derivative **10f** [34] offers the possibility to compare three types of metal-carbon bonds in the same molecule [38].

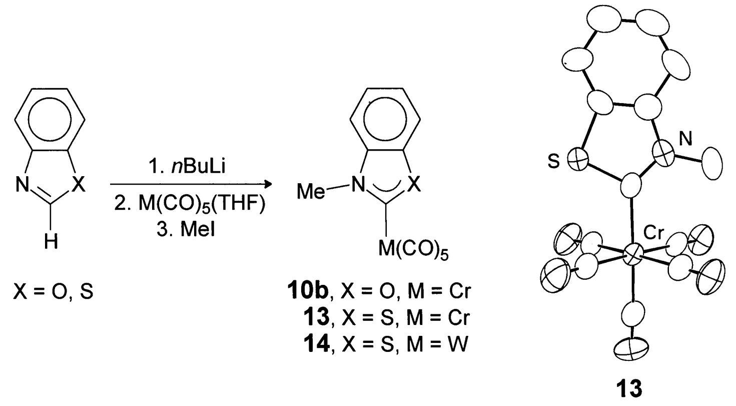
Furthermore, this route also allows the introduction of functionalized substituents at the ylidene nitrogen atom, and for example the use of allyl bromide yields the 3-allyl-2,3-dihydrobenzoxazol-2-ylidene complex **11** (Scheme 9) [39]. The carbene ligand in **11** is a potentially tridentate ligand, as coordination of the alkene moiety of the allyl substituent can lead to the formation of alkene-carbene complexes. Several examples with acyclic [40] and cyclic [41] carbenes have been reported, and their role as intermediates in several catalytic processes such as olefin metathesis, cyclopropanation of alkenes and heterogenous Ziegler–Natta polymerization of alkenes has been outlined extensively [40–42]. Heating **11** in toluene under reflux for three days results in the formation of **12** containing an η^2:η^1-(3-allyl-2,3-dihydrobenzoxazol-2-ylidene) ligand. Intramolecular chelation is detected easily by ^{1}H NMR spectroscopy, and the ^{1}H NMR spectra of **11** and **12** showing only the allylic resonances are depicted in Scheme 9.



Scheme 9. ^{1}H NMR spectra (allylic resonances only) of complexes **11**, **12**.

It should be noted that employment of **5** is not the only possibility for the synthesis of *N*-alkylated 2,3-dihydrobenzoxazol-2-ylidene complexes. Alternatively, a one-pot reaction starting directly from benzoxazole has been developed for the synthesis of the methylated chromium complex **10b** [31]. An anionic benzoxazol-2-yl complex is formed on addition of lithiated benzoxazole to [Cr(CO)$_5$(THF)], which can subsequently be methylated with methyl iodide to give **10b** in relatively low yield (22%) (Scheme 10). However, this one-pot method is an interesting alternative, as it is considerably time-saving and as the four-step route employing **5** gives **10b** in just comparable yield (31%).

For the synthesis of corresponding 2,3-dihydrobenzothiazol-2-ylidene complexes metalation of benzothiazole is even the method of choice due to the absence of an *S*-functional phenyl isocyanide, and Raubenheimer et al. have used benzothiazol-2-yllithium for the preparation of various copper(I) [43], gold(I) [44] and iron(II) complexes [45]. Accordingly, the pentacarbonyl chromium and tungsten complexes **13** and **14** have been obtained in a one-pot reaction using lithiated benzothiazole and [M(CO)$_5$(THF)] [46,47]. The molecular structure of **13** is shown in Scheme 10.

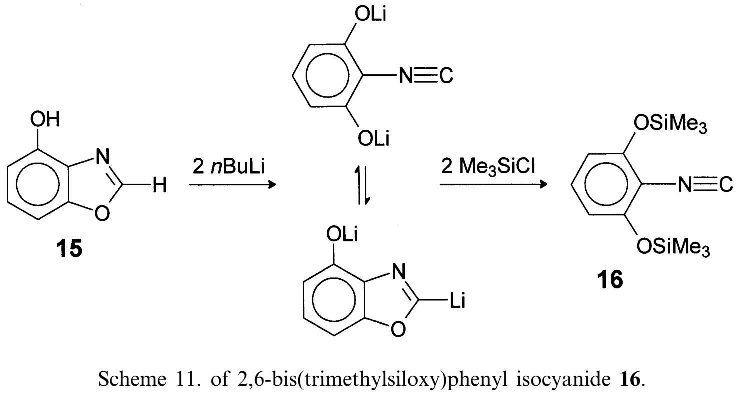


Scheme 10. One-pot synthesis of carbene complexes, molecular structure of **13**.

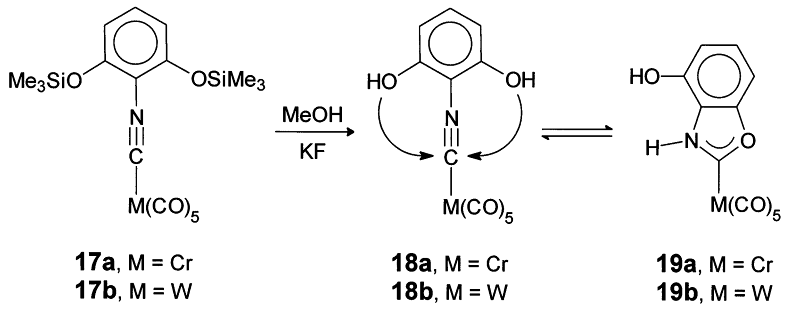
2.1.2. Complexes with 2,6-dihydroxyphenyl isocyanide

We became interested in the coordination chemistry of doubly functionalized 2,6-dihydroxyphenyl isocyanide due to its potential for the preparation of chelating polycarbene ligands (vide infra). It can be synthesized as the silylated derivative **16** by double deprotonation of 4-hydroxybenzoxazole **15** and regiospecific reaction with two equivalents of trimethylchlorosilane (Scheme 11) [48]. Treatment of **16** with photochemically generated [M(CO)$_5$(THF)] (M = Cr, W) leads to complexes **17**, which react after cleavage of the Si–O bonds to give a mixture containing the isocyanide complexes **18** and the carbene complexes **19** (Scheme 12) [48,49].

As shown for the corresponding monofunctional system **8**/**9**, the mixtures **18**/**19** can be characterized quantitatively by ^{1}H NMR spectroscopy (Fig. 2). Comparison of the integrals for the N*H* resonances in **19a**,**b** and for the O*H* resonances in **18a**,**b**



Scheme 11. of 2,6-bis(trimethylsiloxy)phenyl isocyanide **16**.



Scheme 12. Equilibrium between isocyanide, carbene complexes **18**, **19**.

and in **19a**,**b** shows, that the chromium complexes **18a**/**19a** form a 59:41 mixture, whereas a nearly inverse ratio of 40:60 is observed for the tungsten derivatives **18b**/**19b**. Again, these differences can be easily rationalized by comparison of the force constants for the CN stretching frequencies in **18a** and in **18b**. For **18a** the IR absorption is observed at lower wave numbers (k(CN) = 1724 N m^{-1}) than for **18b** (k(CN) = 1752 N m^{-1}) indicating that the Cr(CO)$_5$ metal fragment stabilizes the 2,6-dihydroxyphenyl isocyanide ligand more effectively by (d → π^*)-backbonding

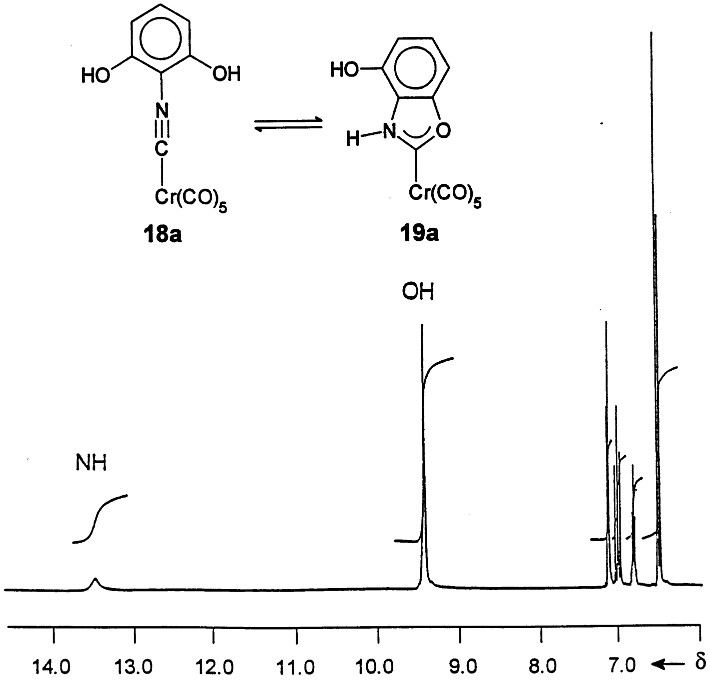
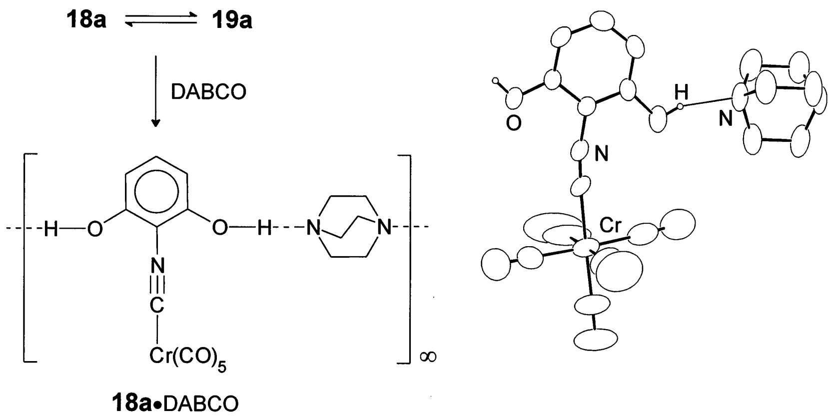


Fig. 2. ^{1}H NMR spectrum of **18a**/**19a**.

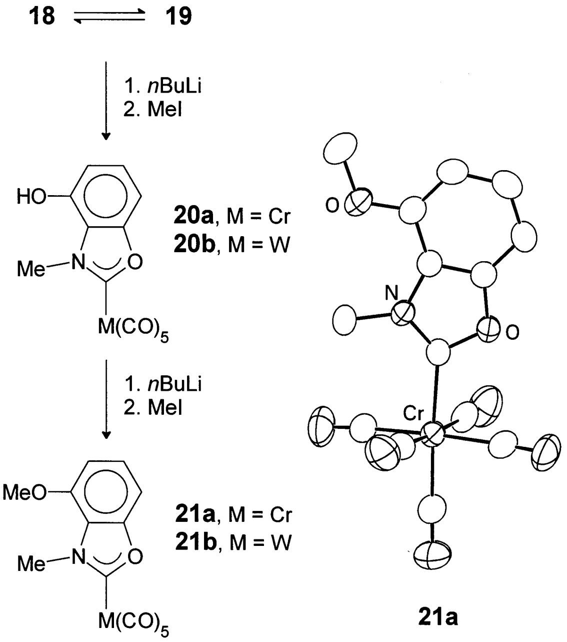


Scheme 13. Synthesis, molecular structure of **18b**·DABCO.

than the $W(CO)_5$ group. This result is in agreement with the observations made for the monohydroxyphenyl isocyanide complexes.

Normally, nucleophilic attack at coordinated isocyanides can be promoted by bases, and it has been shown, for instance, that amines and pyridines catalyze carbene formation [50]. If two equivalents of triethylamine or one equivalent of 1,4-diazabicyclo[2.2.2]octane (DABCO) are added to a solution of **18a**/**19a** the expected shift in equilibrium to the carbene side is not observed (Scheme 13). On the contrary, spectroscopic data indicate the exclusive formation of amine adducts **18a**·$2NEt_3$ and $[\mathbf{18a}\cdot\mathrm{DABCO}]_\infty$ [48]. The isocyanide complex **18a** is obviously stabilized by the addition of these amines to such an extent that the equlibrium **18a**/**19a** is shifted completely to the side of the pentacarbonyl(2,6-dihydroxyphenyl isocyanide)chromium-amine adducts. In order to understand the mechanism of this unusual stabilization, X-ray structure analyses were carried out [48]. The molecular structure of **18a**·DABCO is depicted in Scheme 13 showing that these crystals contain a hydrogen-bridged polymer. Obviously, the use of weak bases (the pK_s values of phenol and the tertiary amines employed are of the same order of magnitude) does not lead to deprotonation of the hydroxy groups and an increase in their nucleophilicity, but rather to the formation of OH···N hydrogen bridges and thus to the stabilization of the isocyanide complex **18a**.

Attempts to shift the equilibrium to the carbene side must therefore be carried out with stronger bases which are capable of completely deprotonating the hydroxy groups. If mixtures of complexes **18**/**19** are treated with one equivalent of KO^tBu followed by methyl iodide the *N*-methylated complexes **20** can be obtained (Scheme 14). The employment of two equivalents of base and MeI gives the *N*,*O*-dimethylated complexes **21** [48,49]. After deprotonation, the phenolic oxygen atoms are sufficiently nucleophilic to allow the intramolecular cycloaddition to proceed to completion. The subsequent alkylation prevents the reverse reaction, and a complete shift of the **18**/**19** equilibrium to the side of the mono- or dimethylated carbene complexes is achieved. The molecular structure of the respective chromium derivative **21a** is shown in Scheme 14, also.

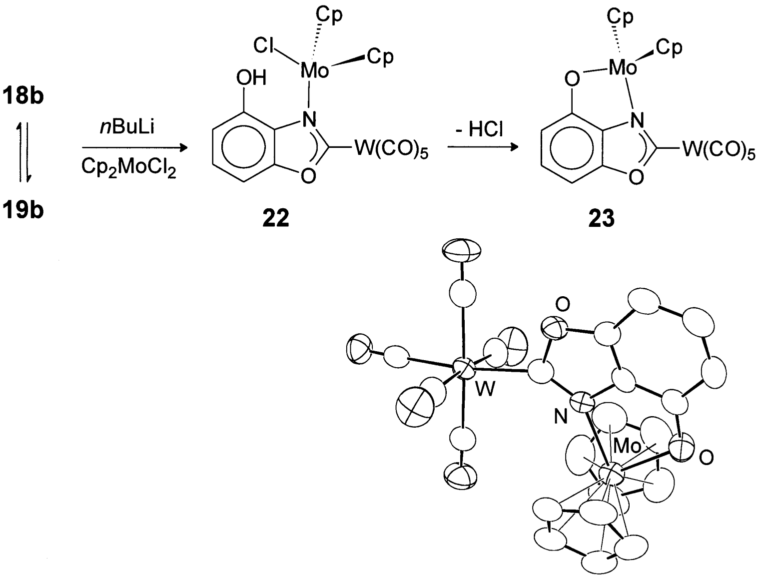


Scheme 14. Synthesis of carbene complexes **20**, **21**, molecular structure of **21a**.

The nitrogen and oxygen atoms in the ylidene complexes **19** can not only be involved in organic alkylation reactions but are also suitable donor atoms for the syntheses of heterobimetalic chelate complexes. In fact, treatment of **18b**/**19b** with one equivalent of ^{n}BuLi followed by the addition of molybdocene dichloride results in the formation of the molybdenum–tungsten complex **23** incorporating a μ-η^1:η^2-ylidene ligand. This reaction proceeds via the intermediate **22**, which may quickly eliminate hydrogen chloride [51]. The molecular structure of **23** (Scheme 15) reveals that the carbene ligand is not coordinated without strain if one compares the relatively small intraring bond angles to those observed for the monometallic complexes **20b** and **21b** (Scheme 14). This situation would become even more unfavourable upon employment of smaller metal ions, and with titanocene dichloride no chelate formation can be observed. In general, the synthesis of heterobimetallic complexes by this route combining transition metals in high and low oxidation states might lead to complexes with interesting electronic and optical properties which will be further investigated.

2.2. Coordination to metals in higher oxidation states

The results in Section 2.1 show, that 2-hydroxyphenyl isocyanide has an unusual strong tendency to form cyclic carbene complexes even at relatively electron-rich

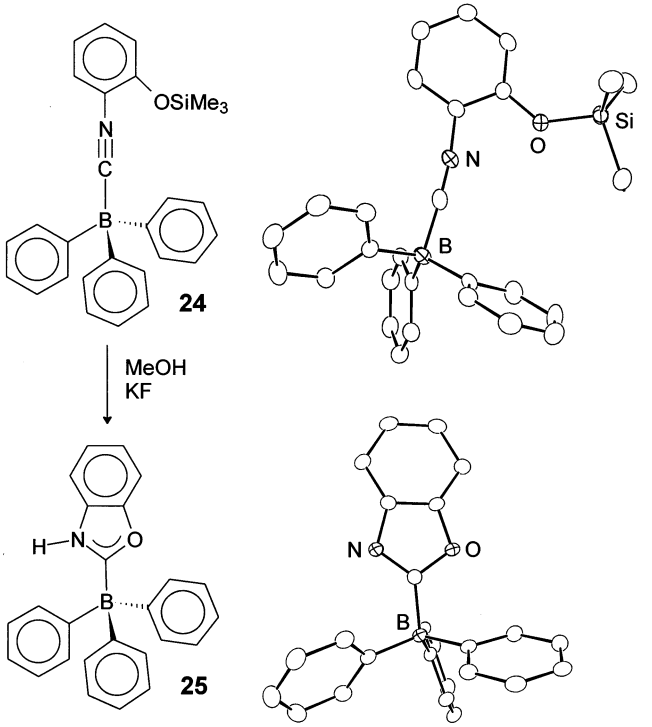


Scheme 15. Synthesis, molecular structure of the heterobimetallic complex **23**.

metal fragments. Enhancement of (d → π^*)-backbonding from the metal center can nevertheless suppress carbene formation completely. On the contrary, complete carbene formation will occur, if there is only little or no backdonation from the metal, which holds for early transition metals in high oxidation states with d^0-electron configurations or for late transition metals in medium or high oxidation states with low-energy d-orbitals.

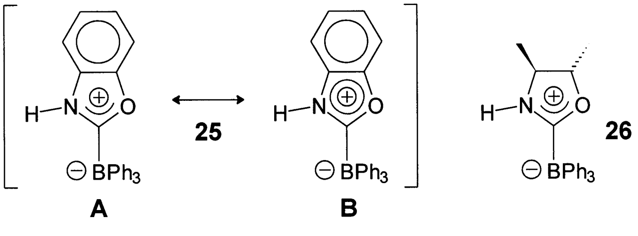
Triphenylboron can be regarded as a simple metal substitute with no d-electrons and has been used as a Lewis acid in the formation of adducts with isocyanides [20,52]. In order to study how 2-trimethylsiloxyphenyl isocyanide (**5**) reacts after hydrolysis if coordinated mainly as a σ-donor, we synthesized the borane adduct **24** from **5** and BPh_3 at low temperature (Scheme 16) [53]. The molecular structure of **24** is shown in Scheme 16 representing so far the only crystallographically characterized isocyanide adduct of a triorganoborane Lewis acid.

In **24** the absorption for the CN stretching frequency (2244 cm^{-1}) is shifted to significantly higher wavenumbers compared to the free isocyanide (2120 cm^{-1}), and the force constant for the C≡N bond in **24** is calculated to be 1918 $N\ m^{-1}$ which illustrates, that coordination to BPh_3 actually activates the isocyanide towards nucleophilic attack. Consequently, **24** reacts in methanol in the presence of a catalytic amount of KF to give the ylidene complex **25** [53]. Independently of our approach, **25** has also been synthesized by the alternative route employing *C*-lithiation of benzoxazole followed by hydrolysis of the intermediate benzoxazol-2-yl-triphenylborate [54].



Scheme 16. Synthesis, molecular structures of borane adducts **24**, **25**.

The molecular structure of **25** is also depicted in Scheme 16 [53,54]. Comparison of the structural parameters of the ylidene ligand in **25** to those found in low-valent transition metal complexes with the 2,3-dihydrobenzoxazol-2-ylidene ligand (vide supra) reveals little sensitivity[5] towards the attached metal fragment no matter to which extent backbonding is feasible or not [55]. Thus, from a structural point of view, **25** can be conceived as a true main-group carbene complex. Furthermore, the structural characterization of **25** allows a direct comparison of its molecular parameters with those of the (oxazolidin-2-ylidene)BPh_3 complex **26** (Scheme 17)



Scheme 17. Mesomeric structures for boron complexes **25**, **26.**

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[5] Theoretical calculations on OC–BH_3 [55] and on (2,3-dihydrooxazol-2-ylidene)BH_3 [54] suggest, that backbonding can not be neglected in isocyanide and carbene borane adducts, and pronounced hyperconjugation of the σ(B–H) bonds into empty ligand π^*-, σ^*-orbitals must be considered.

formed after hydrolysis and cyclization of the aliphatic isocyanide in $[Me_3SiOCH_2CH_2NC\text{-}BPh_3]$ [21]. Whereas the boron–C(ylidene) distances are almost identical, **25** contains longer C(ylidene)–heteroatom distances and shorter distances between the heteroatoms and the other attached carbon atoms than in **26**. This indicates for **25** less stabilization of the carbene center by $(p \rightarrow p)\pi$ bonding from the heteroatoms (Scheme 17, **A**) and increased π-delocalization in the carbene ring due to contributions of the aromatic mesomeric structure **B** (Scheme 17). Such an aromatic stabilization is not possible in **26** which contains apart from the carbene carbon only saturated carbon atoms in the five-membered ring.

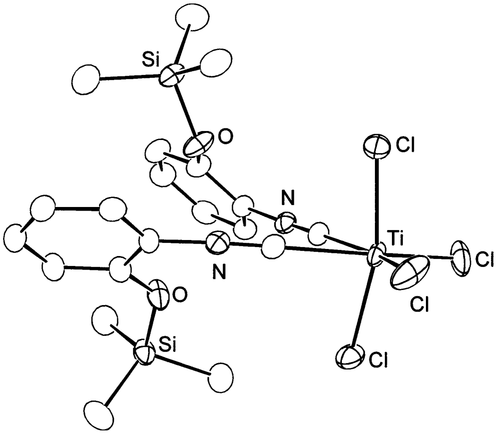
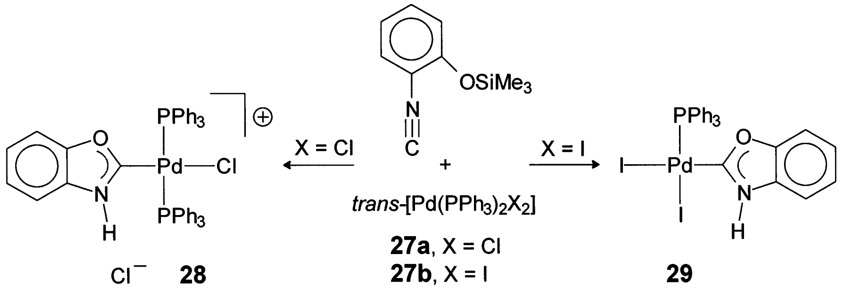


Fig. 3. Molecular structure of *cis*-$[TiCl_4(\mathbf{5})_2]$.

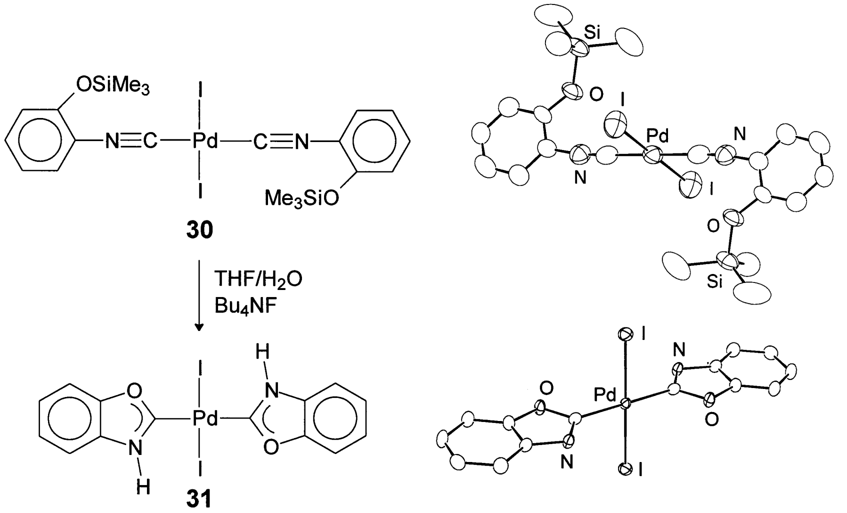
Ti(IV) is a true transition metal center with no d-elctrons available for backbonding and coordination should give strongly activated isocyanides. Preliminary results have been reported on the reaction of **5** with $TiCl_4$ giving complex *cis*-$[TiCl_4(\mathbf{5})_2]$ in excellent yield [56]. The structure has been unequivocally assigned by means of an X-ray structure analysis and the result is shown in Fig. 3. Surprisingly, the IR spectrum exhibits just one absorption for the CN stretching frequencies at 2200 cm^{-1}, which nevertheless indicates strong activation of the isocyanide. However, cleavage of the Si–O bonds in *cis*-$[TiCl_4(\mathbf{5})_2]$ has not yet been achieved, as normal hydrolytic conditions will also destroy the titanium–chloride bonds.

Palladium(II) and platinum(II) are among the most widely used transition metal centers for the synthesis of carbene complexes from coordinated isocyanides [1,57]. Mono(2,3-dihydrobenzoxazol-2-ylidene) Pd(II) complexes can be obtained from the reaction of **5** with *trans*-$[Pd(PPh_3)_2X_2]$ (**27a**, X = Cl; **27b**, X = I) without isolation of the intermediate isocyanide complexes. Depending on the halogen atom the reaction proceeds in different ways (Scheme 18). The reaction of **5** with the dichloride **27a** results in substitution of one chloride ligand and in the formation of the cationic *trans*-configurated complex **28**. According to the HSAB principle the Pd–I bond is significantly more stable than the Pd–Cl bond [58], and reaction of **5** with the diiodide **27b** leads to substitution of one triphenylphosphine instead of one iodo ligand and to the formation of the *cis*-configurated complex **29**. The molecular strucutres of both products have been established by means of X-ray structure determinations [59].



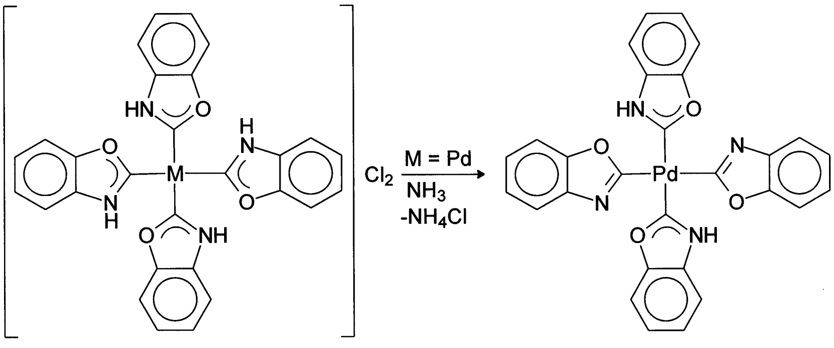
Scheme 18. Palladium(II) monocarbene complexes.

The stability of the Pd–I bond is also obvious from the reaction of excessive **5** with neat PdI_2, which adds only two isocyanide molecules without further substitution of the remaining iodides [60]. In aqueous THF the complex *trans*-[Pd(**5**)$_2$I$_2$] **30** was desilylated with formation of the bisylidene complex **31** (Scheme 19) [61].



Scheme 19. Synthesis of a bisylidene complex from PdI_2. Molecular structures of **30**, **31**.

Employment of $[PdCl_2(NCPh)_2]$ or $[PtCl_2(NCPh)_2]$ facilitates complete substitution and leads to homoleptic tetrakis(2,3-dihydrobenzoxazol-2-ylidene) palladium(II) and platinum(II) complexes **32** and **33** on reaction with four equivalents of **5** (Scheme 20) [61]. The ^{13}C NMR chemical shift of the carbene carbon atom in **33** (188.5 ppm) appears at higher field than in the related complexes with similar aliphatic carbene ligands [24]. Addition of an aqueous ammonia solution to a



32, M = Pd
33, M = Pt

34

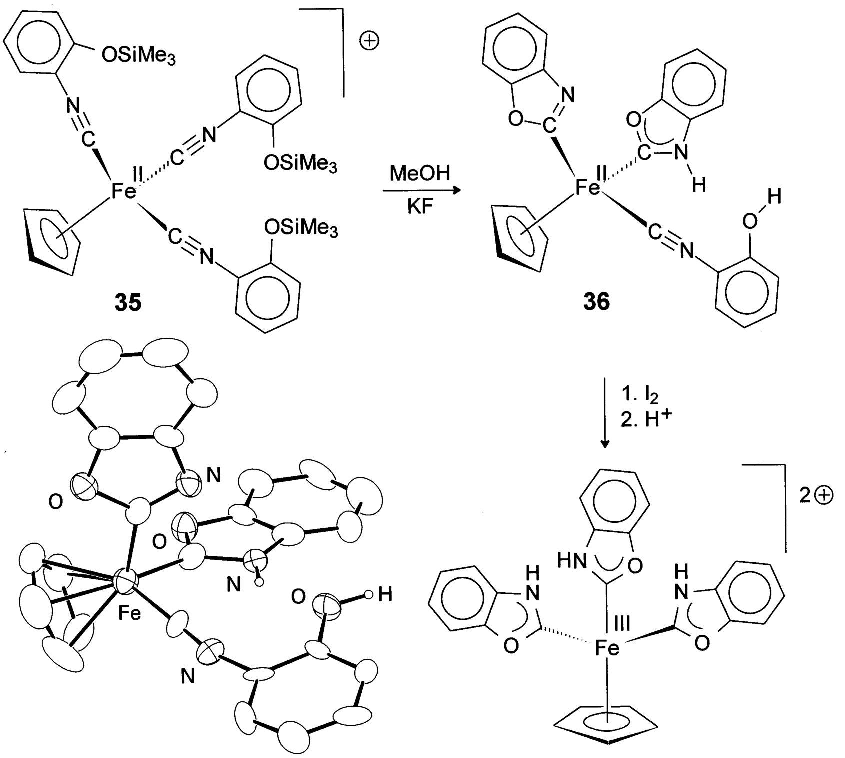
Scheme 20. Homoleptic palladium(II), platinum(II) tetracarbene complexes.

solution of **32** leads to the precipitation of the neutral complex **34** as a white solid, which contains two neutral ylidene and two anionic benzoxazol-2-yl ligands. Complex **34** can be reprotonated with mineral acids giving back the starting compound **32** [61].

The coexistence of protonated and deprotonated 2,3-dihydrobenzoxazol-2-ylidene species in the same ligand sphere has also been demonstrated for an iron(II) complex [62]. Desilylation of the cationic triisocyanide complex $[CpFe(\mathbf{5})_3]^+$ (**35**) in methanol with a catalytic amount of potassium fluoride yields the neutrally charged complex **36**, which assembles all three possible intermediates for the conversion of coordinated isocyanides into ylidenes: the open chain, the cyclic carbenoid and the cyclic carbanionic form (Scheme 21). This is a particularly illustrative example of a borderline case between cyclization and non-cyclization or sufficient and insufficient C≡N activation, respectively, and the formation of this unusual complex can be rationalized by comparison of the σ-donor/π-acceptor properties of the ligands in **35** and **36**.

Phenyl isocyanides are considered to be significantly better π-acceptors than heterocyclic ylidenes. Thus, stepwise intramolecular conversion of the 2-hydroxyphenyl isocyanides into a 2,3-dihydrobenzoxazol-2-ylidene ligands does continuously increase the electron density at the metal center. Thereby, $(d \rightarrow \pi^*)$-backbonding to the remaining isocyanides will increase and the nucleophilic attack of the hydroxy oxygen atom at the isocyanide carbon becomes more and more hampered. Eventually, backbonding becomes so strong, that the reaction stops before all isocyanides are converted into ylidenes. For the remaining isocyanide in **36** a force constant $k(\mathrm{CN}) = 1659\ \mathrm{cm}^{-1}$ can be calculated clearly indicating complete deactivation (vide supra).

To allow complete ylidene formation in **36** $(d \rightarrow \pi^*)$-backbonding from the metal center must be reduced. This is best achieved by oxidizing Fe(II) in **36** to Fe(III). As expected chemical oxidation of **36** with I_2 yields the cationic tricarbene complex



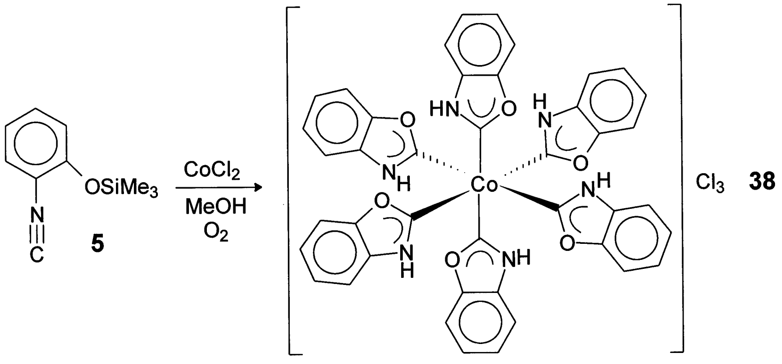
Scheme 21. Synthesis of iron ylidene complexes, molecular structure of **36**.

37, which shows no absorptions for isocyanides in the IR spectrum (Scheme 21) [62].

Preliminary results show, that even the synthesis of a homoleptic hexacarbene complex is possible with the use of 2-(trimethylsiloxy)phenyl isocyanide **5**. The cobalt(III) complex **38**·4H_2O is obtained by reaction of **5** with $CoCl_2$ in methanol with passing air through the solution (Scheme 22) [31]. Complex **38** has been fully characterized and the spectroscopic data compare well with those reported for the corresponding hexakis(oxazolidin-2-ylidene)cobalt(III) complexes [25]. The resonance for the carbene carbon atoms is observed at 208.8 ppm in the ^{13}C NMR spectrum of **38**.

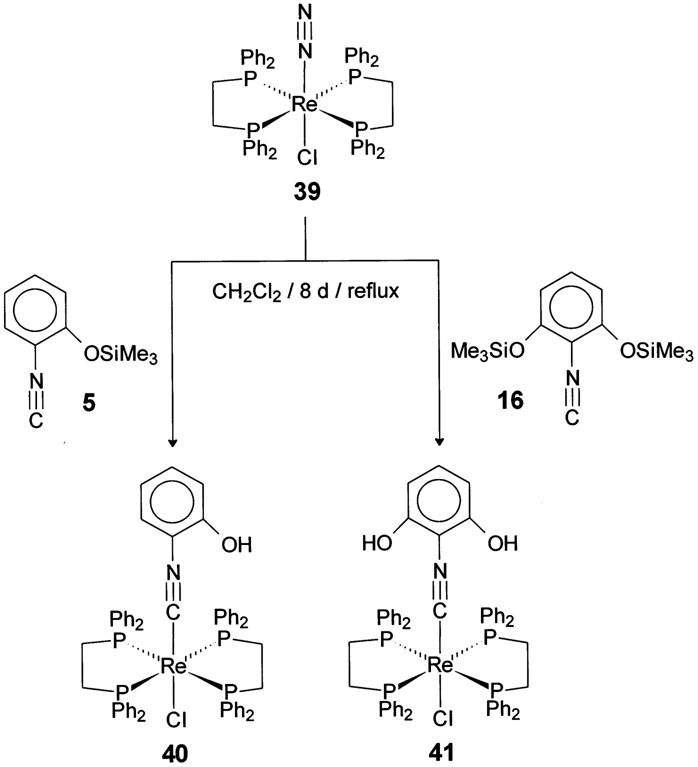
2.3. Rhenium complexes

An important feature of the chemistry of rhenium is the existence of a large number of easily accessible and stable oxidation states which interconvert under mild redox conditions [63]. Therefore, rhenium isocyanide complexes are particu-



Scheme 22. Formation of a homoleptic cobalt(III) hexacarbene complex.

larly suitable for studying the coordination chemistry of **3** depending on the oxidation state of the metal center, and complexes of **3** with rhenium in the +I, +III and +V oxidation state have thus been prepared [64,65].



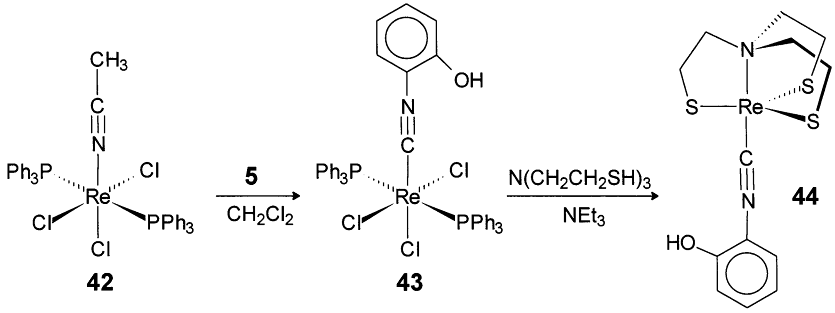
Scheme 23. Rhenium(I) isocyanide complexes.

2.3.1. Rhenium(I) complexes

An ideal starting material for the preparation of Re(I) isocyanide complexes is *trans*-[ReCl(N_2)(dppe)$_2$] **39** which allows displacement of dinitrogen by aliphatic [66] and aromatic isocyanides [67]. The reaction of the silylated derivatives 2-(trimethylsiloxy)phenyl isocyanide **5** and 2,6-bis(trimethylsiloxy)phenyl isocyanide **16** with **39** in boiling CH_2Cl_2 for 8 days yields directly the monoisocyanide complexes **40** and **41** already containing free hydroxy groups (Scheme 23) [64]. Apparently, trace amounts of HCl are responsible for the desilylation reaction if the reaction time is sufficiently long. The IR absorption for the CN stretching vibration is observed at 1858 cm^{-1} in **40** and at 1862 cm^{-1} in **41**. The corresponding force constants k(CN) were calculated to $k(CN) = 1315$ and 1320 N m^{-1}, respectively. As complete deactivation for the intramolecur cycloaddition reaction has already been observed for k(CN) values at about 1700 N m^{-1} (vide supra) these extremely low force constants indicate how effectively the electron-rich *trans*-[Re(I)(dppe)$_2$Cl] metal fragment stabilizes the 2-hydroxyphenyl isocyanides.

2.3.2. Rhenium(III) complexes

The reaction of *mer*-[ReCl$_3$(NCCH$_3$)(PPh$_3$)$_2$] (**42**) with isocyanides proceeds with acetonitrile substitution to yield complexes *mer*-[ReCl$_3$(CNR)(PPh$_3$)$_2$] [68]. Accordingly, after refluxing a solution of **42** with **5** in CH_2Cl_2 for 2 days the Re(III) complex **43** is obtained, again without isolation of the intermediate silylated derivative (Scheme 24) [64].



Scheme 24. Rhenium(III) isocyanide complexes.

The rhenium(III) atom in **43** is much less electron releasing than in the Re(I) complexes **40** and **41**, and consequently, the IR absorption for the CN stretch appears at much higher wavenumber ($\nu = 2107$ cm^{-1}). However, the force constant ($k(CN) = 1690$ N m^{-1}) clearly shows that backbonding is still strong enough for complete deactivation of the coordinated ligand against intramolecular nucleophilic attack. The molecular structure of **43** is shown in Fig. 4 (left). Note that the Re–C–N angle is almost perfectly linear (178(1)°)

The syntheses of a series of technetium(III) and rhenium(III) isocyanide complexes with the tetradentate tripodal ligand 2,2′,2″-nitrilotris(ethanthiol) has been reported [69]. Similarly, *mer*-[ReCl$_3$(**3**)(PPh$_3$)$_2$] **43** reacts with N(CH$_2$CH$_2$SH)$_3$ in the

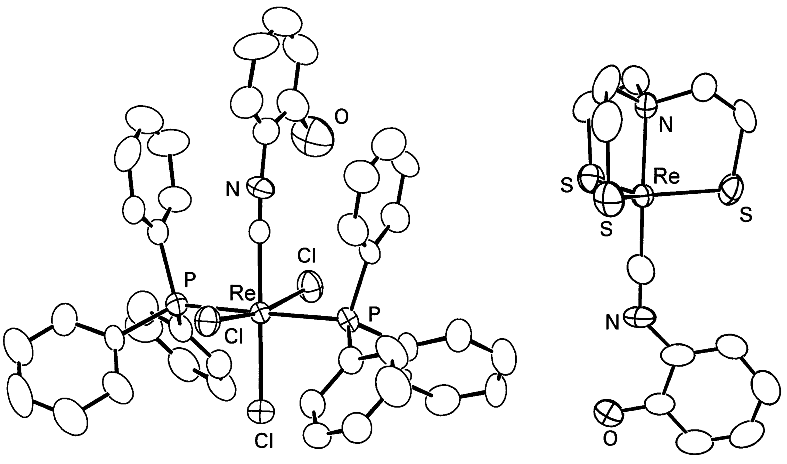
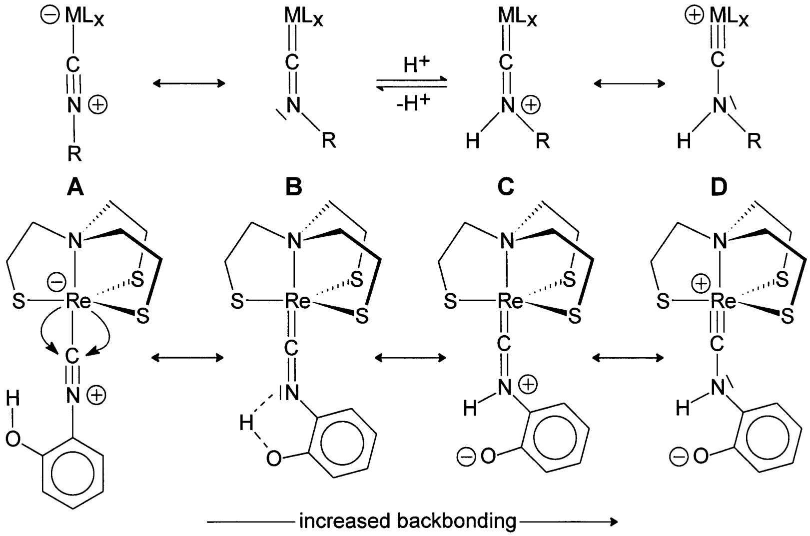


Fig. 4. Molecular structures of rhenium(III) complexes **43** (left), **44** (right).

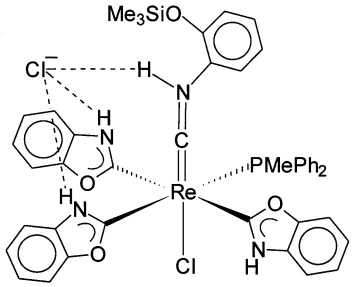
presence of NEt_3 to give the trigonal-bipyramidal complex **44** (Scheme 24). Compared with the octahedral Re(III) complex **43** the absorption for the CN stretching frequency ($\nu = 1882$ cm^{-1}) is shifted to significantly lower wavenumbers indicating much stronger backbonding from the metal center. Crystals of **44** contain trigonal-bipyramidal molecules with the nitrogen atom and the isocyanide ligand adopting axial coordination sides. The isocyanide ligand displays a bent geometry with an unexpectedly small C–N–C angle of 133.5(1)° [70]. Bent geometries have been reported for isocyanides coordinated to very electron-rich metal centers with a high



Scheme 25. Mesomeric structures for complex **44**.

π-electron release ability. These ligands possess an electronic charge localized at the nitrogen atom (mesomeric form **B**, Scheme 25) and might therefore undergo electrophilic attack (by proton, carbon cation or Lewis acid) to give aminocarbyne complexes (mesomeric forms **C** and **D**) [71]. In complex **44** the proton at the hydroxy group is such a potential electrophile, which can attack the nitrogen atom intramolecularly to form an ylidic aminocarbyne complex. Thus, in **44** the reactivity of 2-hydroxyphenyl isocyanide is reverse to that observed at electron-poor metal centers. This description is supported by the observation of the ^{13}C NMR resonance for the carbyne carbon atom at $\delta = 196.9$ ppm which is substantially lower field than expected for a coordinated isocyanide. However, as the position of the proton could not be refined, an umambigious distinction between the four conceivable structures shown in Scheme 25 is not possible.

Although not fully understood, the formation of complex **45** is a particularly nice example, where the coordinated isocyanides must have displayed both electrohilic



45

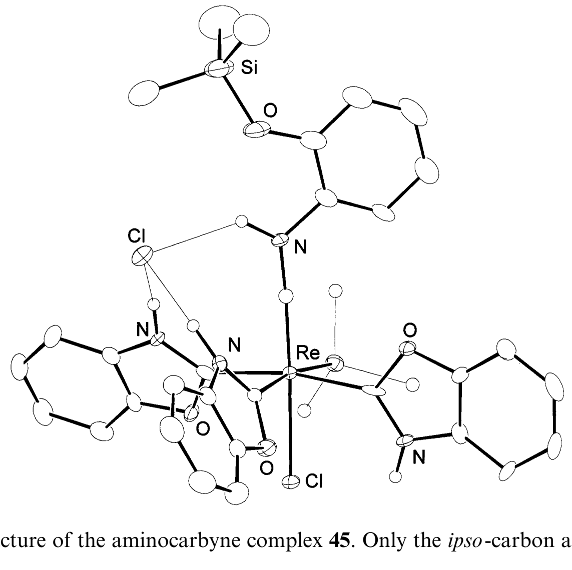
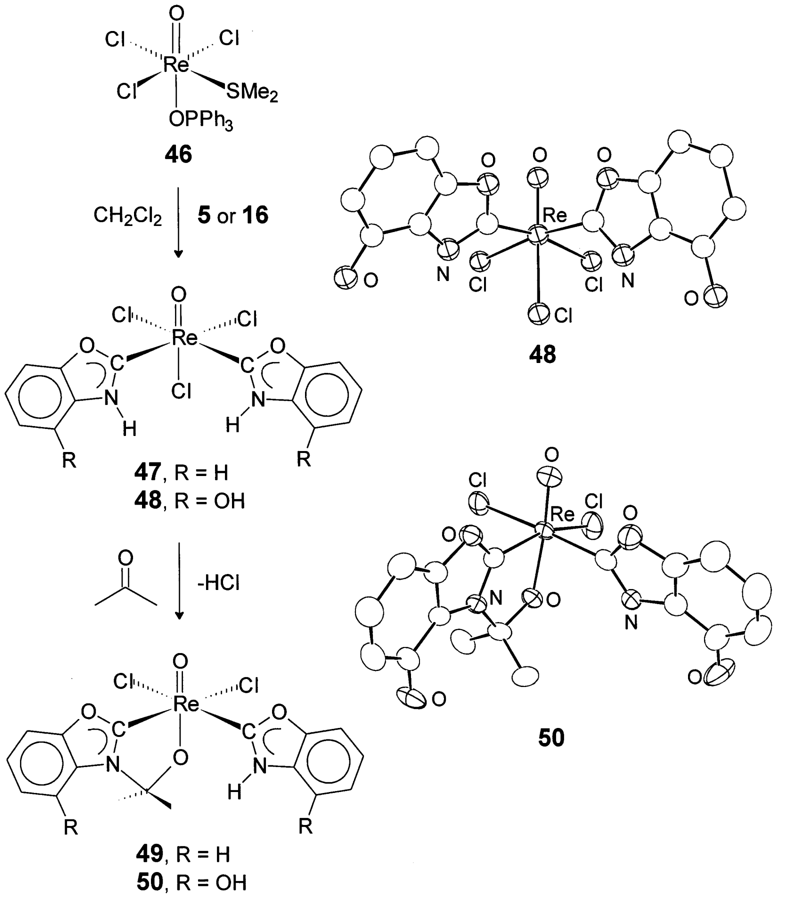


Fig. 5. Molecular structure of the aminocarbyne complex **45**. Only the *ipso*-carbon atoms of the $PMePh_2$ are shown.

and nucleophilic reactivity. Starting from *mer*-[ReCl$_3$(PMePh$_2$)$_3$] and complex **5** the crystalline rhenium(I) complex **45** can be isolated. The molecular structure is presented in Fig. 5 revealing an octahedral geometry at the metal center with a meridional arrangement of three 2,3-dihydrobenzoxazol-2-ylidene ligands. In *trans*-position to the chloro ligand **45** also contains an aminocarbyne ligand formed by protonation of coordinated 2-(trimethylsiloxy)phenyl isocyanide. The chloride counter anion is engaged in hydrogen bonding with the aminocarbyne and two of the carbene ligands [72].

2.3.3. Rhenium(V) complexes

mer-[Re(O)Cl$_3$(SMe$_2$)(OPPh$_3$)] (**46**) is a suitable starting material for the synthesis of rhenium(V) oxo carbene complexes. Reactions of **46** with two equivalents of the silylated isocyanides **5** or **16** give the dicarbene complexes **47** and **48** after cleavage of the Si–O bonds (Scheme 26). As expected for the coordination to electron-poor



Scheme 26. Synthesis of bisylidene complexes, molecular structures of **48**, **50**.

metal centers in high oxdation state the ylidene formation is complete, although the intermediate occurence of an isocyanide carbene complex could be proved spectroscopically. The molecular structures of **47**·$OPPh_3$ and of **48**·$2OPPh_3$ (Scheme 26) have been established by X-ray crystallography confirming the facial geometry of the coordination sphere [64,65].

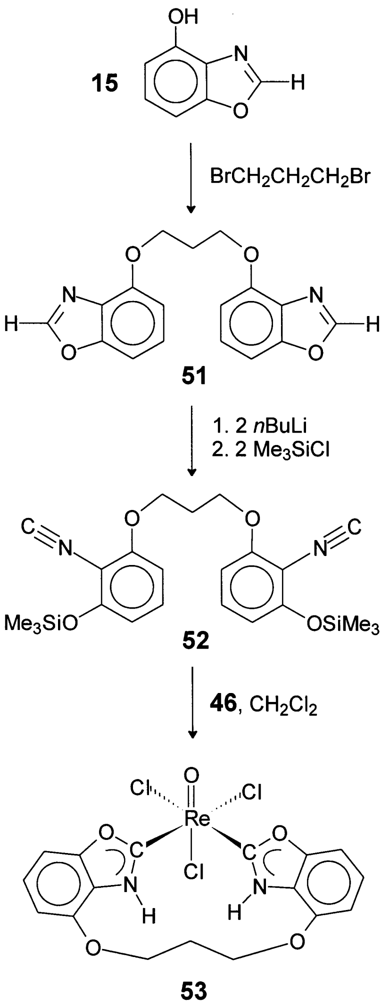
Originally, the *cis*-arrangement of the ylidene ligands in complexes **47** and **48** encouraged us to attempt a template synthesis of chelating bidentate carbene ligands. Bridging of the ligands could be either achievd through the nitrogen atoms in **47** and **48** or via the oxygen atoms of the hydroxy groups in **48**. Although attempts to introduce suitable links have failed so far, a new reaction was discovered leading to complexes with chelating carbene alkoxide ligands [65]. If **47** and **48** are stirred in acetone for a couple of days crystalline **49** and **50** precipitate from the reaction mixture in high yield. Scheme 26 shows the molecular strucure of **50** with one ylidene ligand bearing an *iso*-propoxide residue, which has substituted the chloro ligand in *trans*-position to the oxo group. Formally, these complexes have formed by insertion of acetone into one NH bond followed by the elimination of HCl.

The difficulties encountered with the template synthesis of chelating ylidene ligands has lead to the development of alternative strategies whereby the β-functional isocyanides are linked before coordination to the metal center. Williamson coupling of **15** with 1,3-dibromopropane gives the bridged benzoxazole **51**. As shown for the syntheses of the silylated derivatives **5** and **16** the reaction with *n*-butyllithium and Me_3SiCl yields regiospecifically the diisocyanide ligand **52** (Scheme 27) [65]. **52** had previously been employed by Angelici et al. for the synthesis of complexes such as homoleptic $[Rh(\mathbf{52})_2]PF_6$ incorporating two chelating isocyanides [73].

Analogously to the preparation of **47** and **48** the isocyanide **52** reacts readily with **46**. The monomeric structure of the resulting chelate complex **53** is unequivocally confirmed by NMR, IR and mass spectroscopy [65]. The route presented in Scheme 27 is potentially useful for the preparation of a wide variety of complexes with chelating polycarbene ligands, of which only few examples are known to date [74].

3. *N*-functional isocyanides

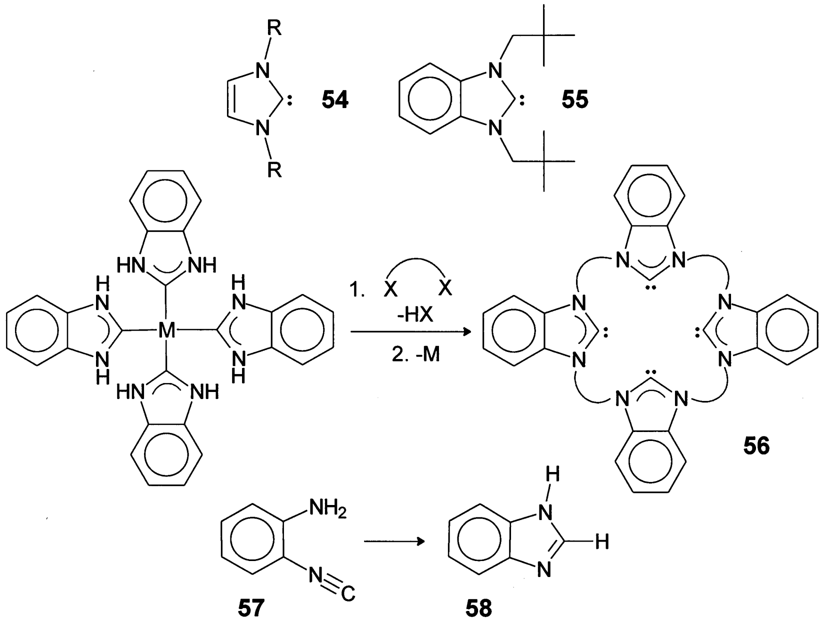
The chemistry of *N*,*N*-heterocyclic carbenes has experienced an incredible renaissance [75] in recent years starting in 1991 with the isolation of 2,3-dihydro-1*H*-imidazol-2-ylidenes of type **54** by Arduengo et al. (Scheme 28) [76]. Since then the employment of free and stable carbenes can be regarded as the method of choice for the synthesis of transition metal complexes with aromatic *N*,*N*-heterocyclic carbene ligands, as the reactivity can be studied in the absence of any byproducts from carbene generation [32]. The corresponding 2,3-dihydro-1*H*-benzimidazol-2-ylidenes have also been generated by deprotonation of benzimidazolium salts followed by in situ reaction with appropriate metal complexes ([74]d, [77]). Furthermore, the introduction of bulky substituents increases the stability of these carbenes, and the free and stable 1,3-bis(2,2-dimethylpropyl)-



Scheme 27. Rhenium(V) complexes with chelating carbene ligands.

2,3-dihydro-1*H*-benzimidazol-2-ylidene (**55**) could be isolated and has been structurally characterized only recently [78].

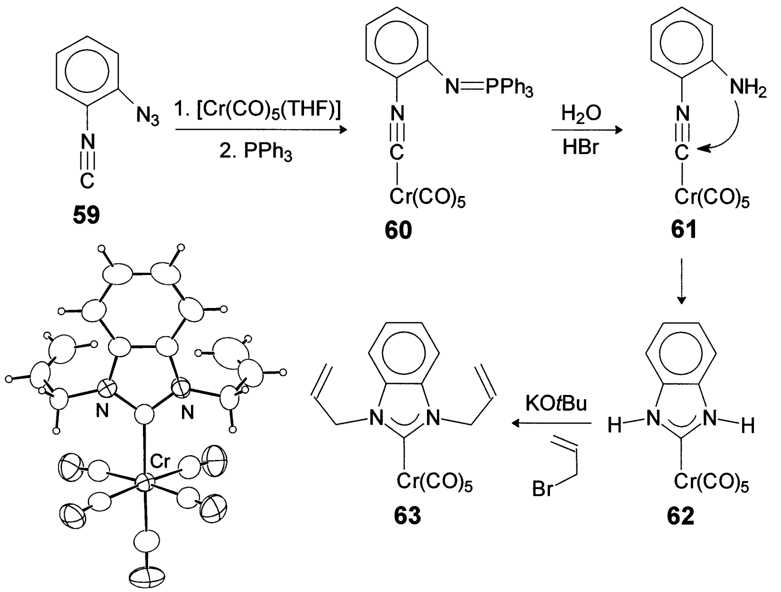
However, the availability of free carbenes is limited to 1,3-disubstituted derivatives which do not allow further reactions at the nitrogen atoms. One of our main aims is the development of synthetic strategies towards the synthesis of cyclic multidentate carbene ligands of type **56** which can be regarded as carbacrownethers. In order to perform a template synthesis for such a system a method for the preparation of 2,3-dihydro-1*H*-benzimidazol-2-ylidenes bearing just protons at the nitrogen atoms is needed (Scheme 28).



Scheme 28. Free *N*,*N*-heterocyclic carbenes, template synthesis of a hypothetical chelating tetracarbene ligand.

Complexes with *N*,*N*-carbene ligands can be prepared by nucleophilic addition of amines to coordinated isocyanides [1]. Consequently, the preparation of *N*-unsubstituted 2,3-dihydro-1*H*-benzimidazol-2-ylidenes requires a synthetic route to 2-aminophenyl isocyanide (**57**) which like **3** is not stable and cyclizes immediatedly to benzimidazole (**58**) (Scheme 28). Therefore, we have choosen 2-azidophenyl isocyanide (**59**) [79] as a suitable starting material for the generation of metal coordinated **57**.

Complex **59** easily forms [Cr(**59**)$(CO)_5$] upon reaction with photochemically generated $[Cr(CO)_5(THF)]$ (Scheme 29). Azides can undergo the Staudinger reaction with tertiary phosphines to give phosphinimines [15,80]. Accordingly, the addition of PPh_3 results in the evolution of dinitrogen and crystalline **60** can be isolated in high yield. The phosphinimino group in *ortho*-position to the coordinated isocyanide is readily hydrolyzed in aqueous methanol with catalytic amounts of HBr. Thereby, Ph_3PO is formed with release of the 2-aminophenyl isocyanide complex [Cr(**57**)$(CO)_5$] (**61**) which immediatedly cyclizes to give **62** containing the 2,3-dihydro-1*H*-benzimidazol-2-ylidene ligand [81]. Due to the higher nucleophilicity of the amino nitrogen atom in **57** compared with the hydroxy oxygen atom in **3**, the equilibrium resides completely on the side of the ylidene derivative **62**. In order to evaluate the possibility to functionalize **62** at the nitrogen atoms, it was treated with two equivalents of KO^{t}Bu followed by the additon of allyl bromide. The doubly allylated ylidene complex **63** was thus obtained. Its molecular structure is depicted in Scheme 29 [81].

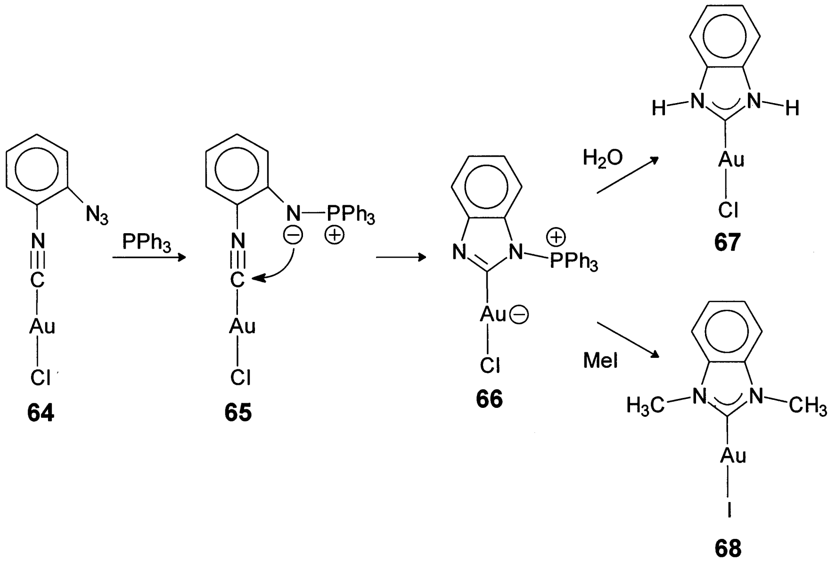


Scheme 29. Synthesis of *N*,*N*-heterocyclic chromium(0) carbene complexes, molecular structure of **63**.

Different reactivity is observed at the electron-poor AuCl metal fragment. Complex **64** can be synthesized by reaction of $(Me_2S)AuCl$ with **59**. Contrary to $Cr(CO)_5$ the AuCl metal fragment does not stabilize the phosphinimino functionalized isocyanide, and the intramolecular cycloadditon does already occur if **64** is treated with PPh_3. (Note that the ylidic presentation for the phosphinimino group is shown in Scheme 30 to simply elucidate the nucleophilicity of the nitrogen atom in **65**). The resulting complex **66** which contains an ylidic phosphonio substituted imidazol-2-yl ligand can either be hydrolyzed to give the parent 2,3-dihydro-1*H*-benzimidazol-2-ylidene complex **67**. Alternatively, it can be directly converted into the *N*,*N*-dimethylated derivative **68** by treatment with excess methyl iodide. Applying the above mentioned reactions to homoleptic tetracoordinate palladium(II) or platinum(II) complexes will eventually open up the template synthesis of carbacrownethers of type **56** presented in Scheme 28.

4. *C*-functional isocyanides

Michelin et al. have reported on the synthesis of β-functional isocyanides of the type $2\text{-}(XCH_2)C_6H_4NC$ ($X = Cl$, Br, I) and have used the isocyanide and halomethyl functions to selectively interact with appropriately choosen metal substrates to give mononuclear or polynuclear complexes [82]. Substitution reac-



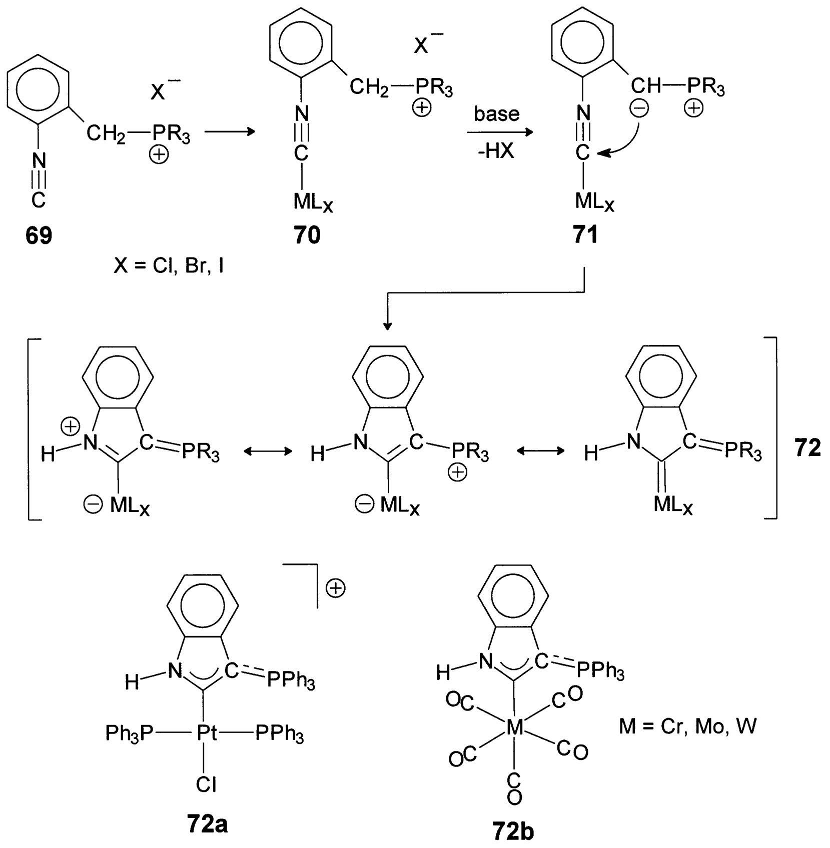
Scheme 30. *N*,*N*-heterocyclic gold(I) carbene complexes.

tions with tertiary phosphines result in the formation of phosphonium substituted isocyanides of type **69** (Scheme 31). The phosphines employed comprise PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 [83]. Coordination of **69** to transition metal fragments gives phosphonium isocyanide complexes **70** which are a suitable source for the corresponding phosporous ylides (or phosphoranes) **71**. Note that the ligand in **71** is isoelectronic with the phophinimine isocyanide in complexes **60** and **65** (Schemes 29 and 30). Complex **71** might undergo an intramolecular cycloaddition reaction with the formation of metal coordinated 3-(phosphonio)-2,3-dihydro-1*H*-indol-2-ylidenes of type **72**, if the isocyanide is sufficiently activated towards nucleophilic attack by the negatively charged ylide carbon atom [83,84]. Scheme 31 presents some possible (not all) mesomeric structures for compounds **72**.

For instance, coordination of **69** ($PR_3 = PPh_3$) to *trans*-$[Pt(PPh_3)_2Cl]$ followed by the addition of triethylamine gives the platinum(II) complex **72a** [57,83]. The preparation of the pentacarbonyl derivatives **72b** from $[M(\mathbf{69})(CO)_5]$ (M = Cr, Mo, W) requires the use of a stronger base such as $Na[N(SiMe_3)_2]$ in order to guarantee a complete cyclization reaction [84]. This observation is in agreement with the fact that here the isocanide is much less activated towards nucleophilic attack than in the corresponding platinum(II) derivative.

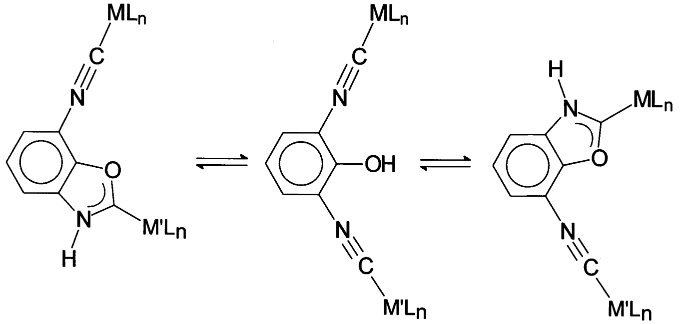
5. Prospects

Our activities in the area of β-functional phenyl isocyanides have originally arisen from the quest for a template synthesis of tripodal aromatic triisocyanides



Scheme 31. Synthesis of 2,3-dihydro-1*H*-indol-2-ylidene complexes.

[3,26]. Our initial failure lead to a new field of organometallic research in our group involving several dedicated students during the last couple of years [31,46,49,59,65]. Our contributions presented in this review are based on our work which had started at the Technische Universität Berlin and was then continued at the Freie Universität Berlin. Since April 1998 the group resides at the Westfälische Wilhelms-Universität Münster, where future efforts in the area of β-functional phenyl isocyanides will be directed towards the synthesis of multifunctional polyisocyanide and polycarbene derivatives. These systems comprise isocyanides such as 2-hydroxyphenyl-1,3-diisocyanide. Its complexes **73** (Scheme 32) have already been studied for $ML_n = M'L_n = Cr(CO)_5$ showing an ylidene to isocyanide ratio of 60:40 [49]. In heterobimetallic complexes ($ML_n \neq M'L_n$) of type **73** discrimination between the two metal centers will be possible and nucleophilic attack will occur at the metal center with the lower π-electron release ability. Redox reactions might reverse the equilibrium, and therefore systems such as **73** could be used as molecular switches.

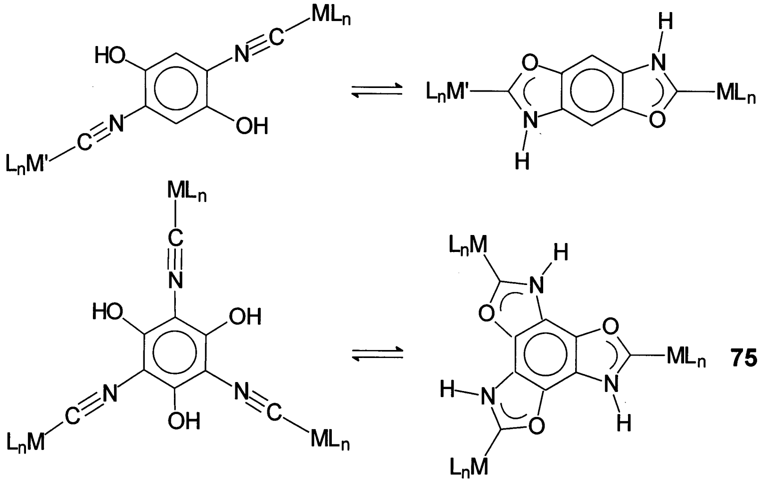


73

Scheme 32. Complexes with 2-hydroxyphenyl-1,3-diisocyanide.

Homo- and heterobimetallic complexes of type **74** will allow bridging of two metal centers in a linear fashion, and interesting electronic as well as otical and nonlinear optical properties might be expected from these derivatives. Last but not least, use of a trihydroxyphenyl triisocyanide can lead to the equilibrium between planar triisocyanide and tricarbene complexes of type **75** which could ultimatively allow the construction of organometallic dendrimers (Scheme 33).

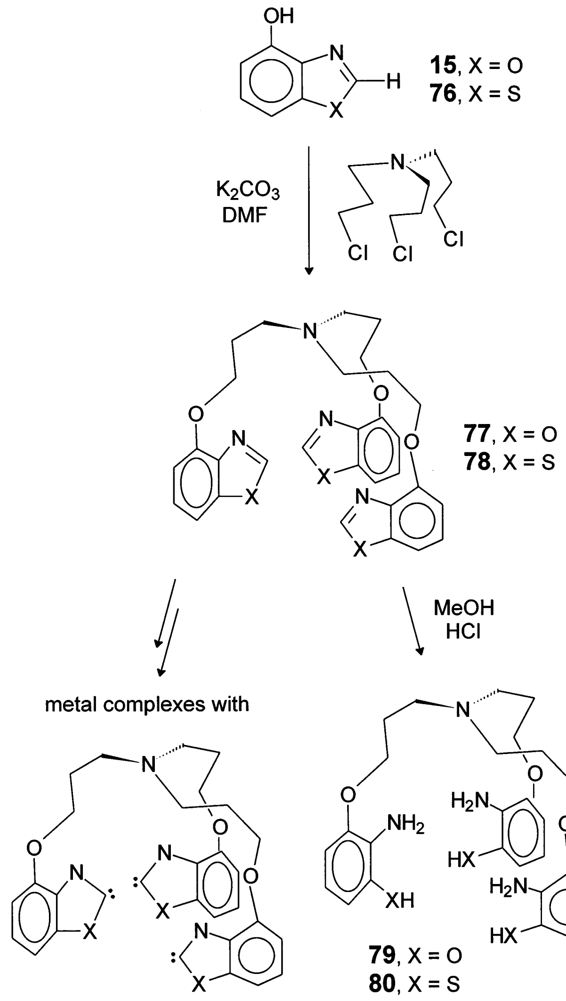
Some of the organometallic results have had an impact on our work which is focused on more classical coordination chemistry involving mainly polydentate tripodal ligands with *N*-, *O*- and *S*-coordination sites [85–89]. As for instance **15** and **76**, which can be used for the synthesis of carbene complexes, have also been employed for the preparation of tripodal hexadentate ligands with N,O- and N,S-donor groups (Scheme 34). Williamson coupling of **15** and **76** with tris(3-chloropropyl)amine gives the heterocyclic derivatives **77** and **78** which can be used for the synthesis of complexes with chelating carbene ligands following the methods



74

75

Scheme 33. Hypothetical complexes with β-functional polyisocyanides.



Scheme 34. Poly(benzoxazole) ligands as precursors for the preparation of polycarbenes or hexadentate chelate ligands.

outlined in this review. Alternatively, acidic hydrolysis yields the tripodal hexadentate ligands **79** and **80** [46]. Thus, the results presented in Scheme 34 build a bridge between organometallic and coordination chemistry with both areas stimulating each other.

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