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Cyclic Polycarbene Ligands with Crown Ether Structure

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ABSTRACT: *The cyclization reaction of coordinated β-functional phenyl isocyanides was used to generate coordinated anellated N-heterocyclic carbenes. Coordinated 2-trimethylsiloxyphenyl isocyanide reacts, after Si—O bond cleavage, to yield a complex with a coordinated benzoxazol-2-ylidene ligand. The cyclization reaction of coordinated 2-aminophenyl isocyanide, obtained in situ from 2-azidophenyl isocyanide, yields the coordinated benzimidazol-2-ylidene. Both ylidenes can be alkylated at the nitrogen atoms. Attempts to generate four benzimidazol-2-ylidenes at Pt^{II} and to bridge them by N-alkylation leading to a crown ether-like ligand with carbene donors are presented here. Free N-heterocyclic carbenes derived from benzimidazole with large N-substituents exist as monomers while they dimerize to dibenzotetraazafulvalenes when substituted with sterically less-demanding substituents at the ring nitrogen atoms. A chemical equilibrium between the monomeric carbene and its dimerized enetetraamine exists for the N,N′-isopropyl substituted derivative.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:540–549, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10099

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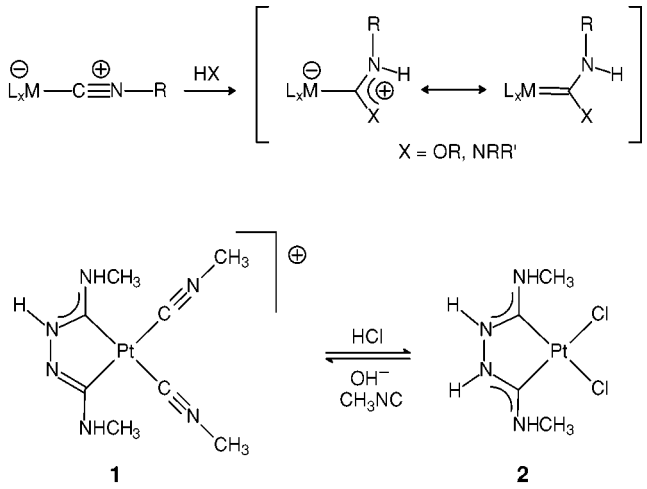
The nucleophilic attack at the carbon atom of a coordinated isocyanide is a standard method to generate metal carbene complexes [1–3]. Protic nucleophiles such as alcohols or primary or secondary amines have been particularly useful in this reaction (Scheme 1). This carbene synthesis was first applied, although unintentionally, in 1915 when Tschugajeff and Skanawy-Grigorjewa reacted tetrakis(methyl isocyanide) platinum(II) with hydrazine [4]. A red salt with the formula $[Pt(N_2H_3)(MeNC)_4]Cl_2$ **1** was isolated, which was very likely the first carbene complex to be synthesized in pure form [4]. Treatment of **1** with hydrochloric acid yielded a yellow complex **2**, which could be transformed back to the red form by addition of methyl isocyanide and base. The red and yellow complexes were initially assigned wrong, dimeric structures with six-coordinated Pt^{II}. Fifty years later, these were recognized as the carbene complexes **1** and **2** [5].

While the addition of nucleophiles HX to coordinated isocyanides usually leads to the formation of complexes with acyclic carbene ligands, the employment of functional isocyanides, which contain both the isocyanide group and the nucleophile in the same molecule, gives access to complexes with heterocyclic carbene ligands through an intramolecular 1,2-addition across the CN triple bond. Various synthetic methods have been developed to generate such functional aliphatic isocyanides at the metal center [6]. Alternatively, Fehlhammer et al. have introduced readily available and stable 2-hydroxyalkyl isocyanides such as $CNCH_2CH_2OH$, in which the nucleophile and the isocyanide group are already



SCHEME 1 Nucleophilic addition of alcohols and amines to coordinated isocyanides and constitution of Tschugajeff's red (**1**) and yellow (**2**) complex.

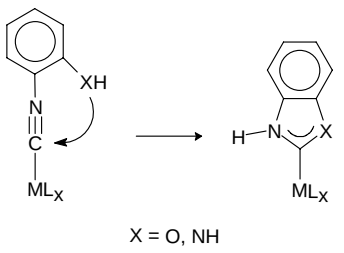
linked before coordination to the metal center. If suitably activated by coordination to transition metals in higher oxidation states these ligands spontaneously cyclize to form oxazolidin-2-ylidenes [7] allowing even the isolation of homoleptic tetra- [8] and hexacarbene complexes [9].

In β-functional aryl isocyanides (Scheme 2) the electrophilic isocyanide and the nucleophilic substituent are not only linked, but are also suitably oriented in one plane for an intramolecular cycloaddition reaction. This geometry together with the aromaticity of the resulting carbene ligand could lead to an even greater tendency to form heterocyclic ylidenes. Therefore, we studied the coordination chemistry of aromatic isocyanides with functional groups in the ortho-position and their cyclization to NH,X-stabilized carbene ligands [10].

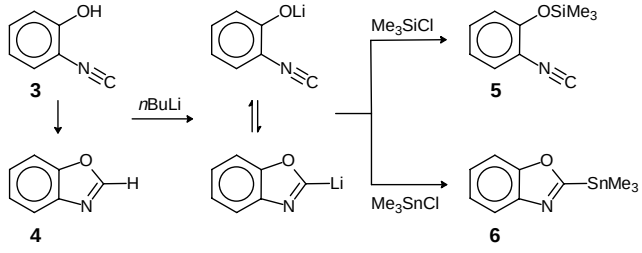
We became interested in the coordination chemistry of 2-hydroxyphenyl isocyanide **3** in order to evaluate reactions at the hydroxy group possibly leading to a template synthesis for aromatic tripodal triisocyanides [3,11]. Contrary to aliphatic 2-hydroxyethyl isocyanide [7–9], free **3** is not stable and cyclizes to benzoxazole **4** [12]. 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-(trimethylstannyl)benzoxazole **6** [13] (Scheme 3).

The O-protected isocyanide **5** can readily be coordinated to transition-metal complex 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 [14–16]. Cleavage of the Si—O bond in complexes of type **7** is best achieved by stirring in methanol with a catalytic amount of KF for approximately 2 days releasing complexes [(**3**)M(CO)$_x$] **8** with the 2-hydroxyphenyl isocyanide ligand. Subsequently, complexes **9** containing the benzoxazol-2-ylidene ligand can form, if the isocyanide is sufficiently activated (or insufficiently deactivated) towards intramolecular nucleophilic attack by the hydroxy group (Scheme 4).

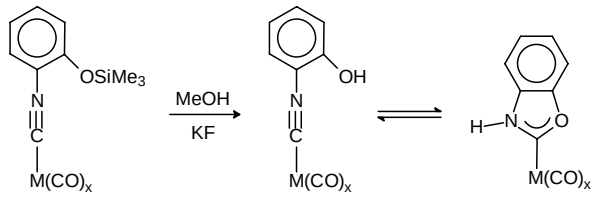
Different observations were made during the cyclization reaction **8** → **9** depending on the nature of the transition-metal complex fragment. Coordinated to the Fe(CO)$_4$ group 2-hydroxyphenyl isocyanide completely cyclizes to give the carbene complex **9a**, which is the only product detectable by NMR spectroscopy [14]. 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** [16]. 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** was 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** appeared around 10.5 ppm. Comparison of the integrals for these two resonances allows to determine the relative abundance of the two components in a mixture of **8**



SCHEME 2 Formation of N,X-stabilized carbene complexes from coordinated β-functional phenyl isocyanides.



SCHEME 3 Preparation of 2-(trimethylsiloxy)phenyl isocyanide (**5**).



7a, M = Fe, x = 4 **8a**, M = Fe, x = 4 **9a**, M = Fe, x = 4
7b, M = Cr, x = 5 **8b**, M = Cr, x = 5 **9b**, M = Cr, x = 5
7c, M = Mo, x = 5 **8c**, M = Mo, x = 5 **9c**, M = Mo, x = 5
7d, M = W, x = 5 **8d**, M = W, x = 5 **9d**, M = W, x = 5

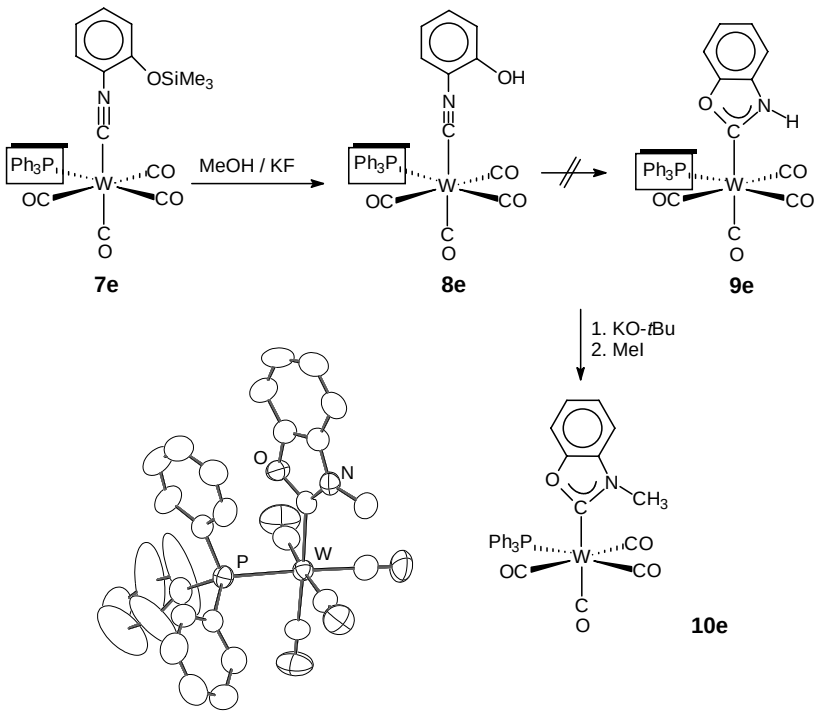
SCHEME 4 Equilibrium between isocyanide complexes **8** and carbene complexes **9**.

and **9** indicating that the equilibrium resides mostly on the side of the ylidene complexes **9** (Table 1).

The cis-configurated 2-hydroxyphenyl isocyanide complex **8e** was obtained after hydrolysis of the corresponding O-silylated precursor **7e**. Here, the situation is reverse to that found for coordination to the $Fe(CO)_4$ complex and the equilibrium resides completely on the side of the "open" isocyanide form with no observable amounts of the hypothetical carbene complexes **9e** (Scheme 5) [16].

Comparison of the reactivity of complexes **8a–e** (Table 1) shows, that the tendency of coordinated 2-hydroxyphenyl isocyanide to form the benzoxazol-2-ylidene varies with the complex fragment ranging from complete carbene formation in **8a** to complete isocyanide stabilization in **8e**. 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 [17]. The force constant can be directly correlated with the positive charge on the carbon atom, for example, with its susceptibility to nucleophilic attack [18]. Table 1 summarizes the IR stretching frequencies and force constants calculated by the method of Cotton and Kraihanzel [19] of complexes **8** together with the observed isocyanide/carbene ratios.

The highest force constant ($k = 1791$ N/m) is calculated for the iron derivative **8a** indicating that metal-to-ligand ($d \rightarrow \pi^*$)-backbonding is the weakest in the series of complexes **8a–e**. Here, the lack of sufficient stabilization causes the 2-hydroxyphenyl isocyanide to undergo complete carbene formation at the $Fe(CO)_4$ complex fragment. A decrease in k by 45 N/m relatively to **7a** is calculated for the tungsten complex **8d**, and this already enhanced backdonation from the metal center 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



SCHEME 5 Preparation of the N-methylated carbene complex **10e** from electronically stabilized **8e** and molecular structure of **10e**.

TABLE 1 Physical and IR Spectroscopic Data for Mixtures of Complexes **8** and **9**

		Ratio (%)			
ML_x	Complex	Isocyanide	Ylidene	IR $\tilde{\nu}$, cm^{-1}	k (CN) N/m
$Fe(CO)_4$	**9a**	0	100	2169[a]	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

[a]Wave number for complex **7a**, the O-desilylated complex **8a** could not be detected.

changes in the electronic properties of the complex 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-acceptor triphenylphosphane PPh_3 in **8e** increases the π-basicity of the metal center thus leading to enhanced (d → π*)-backbonding to the 2-hydroxyphenyl isocyanide as clearly shown by the much smaller force constant ($k = 1706$ N/m). This low value indicates complete deactivation of the isocyanide carbon atom in **8e** for intramolecular nucleophilic attack and explains why no ylidene complexes **9e** can be identified spectroscopically (Scheme 5).

Even electronically stabilized isocyanide complexes of the type **8e** can be converted into ylidene derivatives by deprotonation and subsequent N-alkylation. In deprotonated **8e** 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 the complex with the 3-methyl-2,3-dihydrobenzoxazol-2-ylidene ligand (Scheme 5) [16].

Furthermore, this route also allows the introduction of functionalized substituents at the ylidene nitrogen atom and, for example, the reaction of **9d** with allyl bromide yields the 3-allyl-2,3-dihydrobenzoxazol-2-ylidene complex (**10d**) (Scheme 6) [20]. The carbene ligand in **10d** is a potentially tridentate ligand, as coordination of the alkene moiety of the allyl substituent can lead to the formation of an alkene–carbene complex. Heating **10d** in toluene under reflux for 3 days resulted in the formation of **11d** containing an $\eta^2:\eta^1$-(3-allyl-2,3-dihydrobenzoxazol-2-ylidene) ligand. Intramolecular chelation is easily detected by ^1H NMR spectroscopy [20].

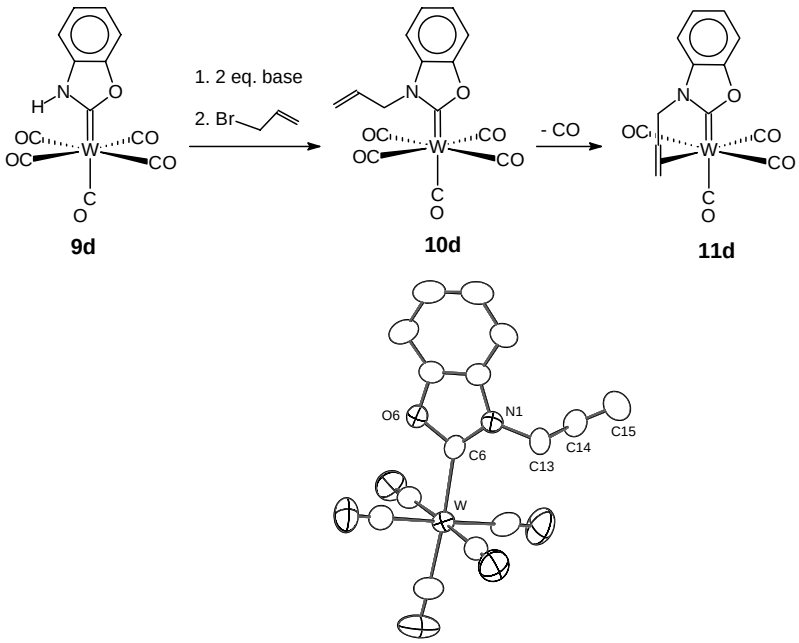
The relation of the amount of M → L backbonding and the course of the cyclization reaction can be illustrated with additional examples. In general, 2-hydroxyphenyl isocyanide has an unusual strong tendency to form cyclic carbene complexes even at relatively electron-rich complex fragments. Enhanced (d → 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 back-donation 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 [21]. To study how 2-(trimethylsiloxy)phenyl isocyanide **5** reacts after hydrolysis if coordinated mainly as a σ-donor, we synthesized the borane adduct **12** from **5** and BPh_3 at low temperature [22]. The molecular structure of **12** is shown in Scheme 7, representing so far the only crystallographically characterized isocyanide adduct of a triorganoborane Lewis acid.

In **12** the absorption for the CN stretching frequency (2244 cm^{-1}) is shifted to significantly higher wave numbers compared to the free isocyanide (2120 cm^{-1}), and the force constant for the CN bond in **12** was calculated to be 1918 N/m, which illustrates that the coordination to BPh_3 actually activates the isocyanide towards nucleophilic attack. Consequently, **12** reacts in methanol in the presence of a catalytic amount of KF to give the ylidene complex **13** (Scheme 7) [22].

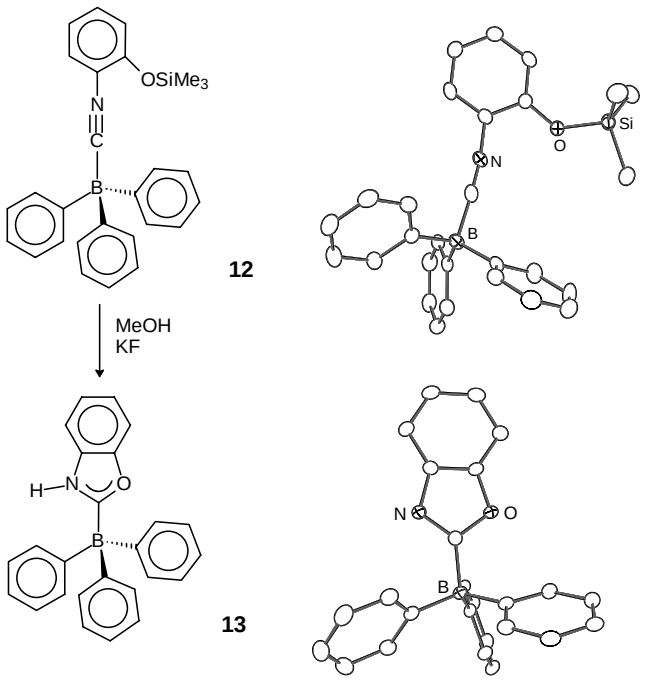
Reaction of an excess of **5** with PdI_2 leads to complex *trans*-$[Pd(\mathbf{5})_2I_2]$ **14** [23]. In aqueous THF complex **14** was O-desilylated under formation of the bisylidene complex **15** (Scheme 8) [24].

The coexistence of *N*-protonated and *N*-deprotonated benzoxazol-2-ylidene together with 2-hydroxyphenyl isocyanide in the same coordination sphere has been demonstrated for an iron(II) complex [25]. Desilylation of the cationic triisocyanide complex $[CpFe(\mathbf{5})_3]^+$ **16** in methanol with a catalytic amount of potassium fluoride yields the neutral complex **17**, which assembles all three



SCHEME 6 Preparation of complex **10d** with an *N*-functional benzoxazol-2-ylidene ligand and molecular structue of **10d**.

possible intermediates for the conversion of a coordinated isocyanides into ylidenes: the open chain isocyanide, the cyclic carbenoid ligand, and the cyclic carbanionic ligand (Scheme 9). This is a particularly illustrative example of a borderline case between



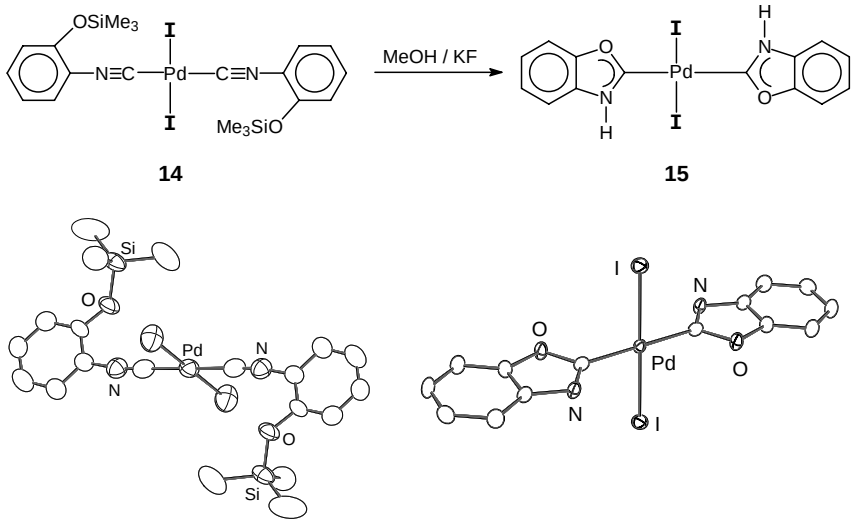
SCHEME 7 Synthesis and molecular structures of the triphenylborane adducts **11** and **12**.

cyclization and noncyclization or sufficient and insufficient CN 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 **16** and **17**.

Phenyl isocyanides are considered to be significantly better π-acceptors than heterocyclic ylidenes. Thus, stepwise intramolecular conversion of the 2-hydroxyphenyl isocyanides into benzoxazol-2-ylidene ligands in **16** 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 increasingly hampered. Eventually, backbonding becomes so strong, that the reaction stops before all isocyanides are converted into ylidenes. For the remaining isocyanide in **17**, a force constant $k(\mathrm{CN}) = 1659\ \mathrm{cm}^{-1}$ was calculated clearly indicating the complete deactivation of this isocyanide for cyclization.

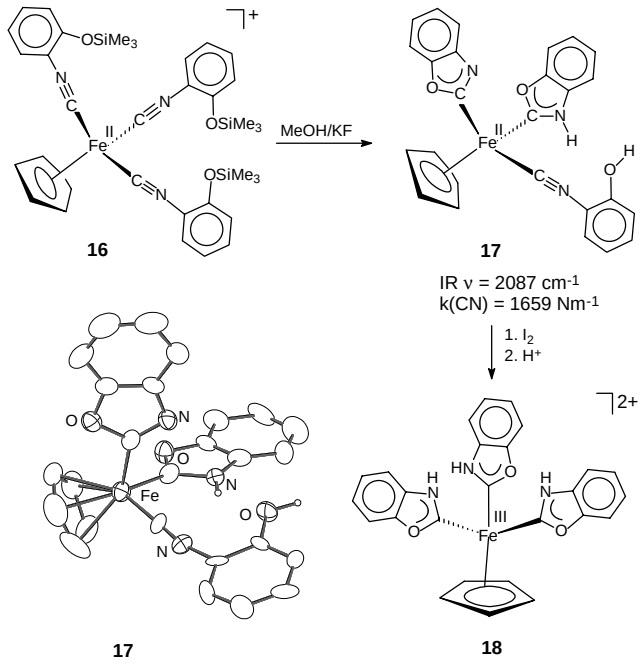
To allow complete ylidene formation $(d \rightarrow \pi^*)$-backbonding from the metal center in **17** must be reduced. This is best achieved by oxidizing Fe^{II} in **17** to Fe^{III}. As expected chemical oxidation of **17** with I_2 yields the cationic tricarbene complex **18**, which shows no absorptions for isocyanides anymore in the IR spectrum (Scheme 9).

An important feature of the chemistry of rhenium is the existence of a large number of easily accessible and stable oxidation states that interconvert under mild redox conditions [26]. Therefore,



SCHEME 8 Preparation of the bisylidene complex **15** and molecular structures of **15** and the precursor **14**.

rhenium isocyanide complexes are particularly suitable for studying the coordination chemistry of 2-hydroxyphenyl isocyanide **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 [27]. The isocyanide ligands in the rhenium(V) complex **19** undergo cyclization to yield the biscarbene complex **20**, immediately after Si—O bond cleavage. No such cyclization was observed for the isocyanide ligand in the electron-rich Re^{III} complex **21**, where strong backbonding from the metal center causes complete isocyanide deactivation which, after Si—O bond cleavage, leads to complex **22**, containing a 2-hydroxyphenyl isocyanide ligand (Scheme 10) [27].

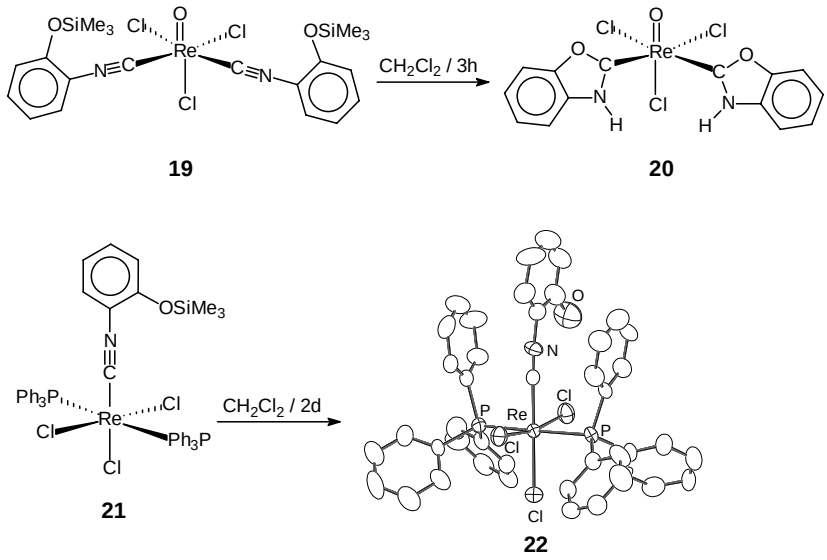


SCHEME 9 Synthesis of the iron ylidene complexes **17** and **18** and molecular structure of **17**.

While the reactivity of coordinated 2-hydroxyphenyl isocyanide is mostly determined by the electronic situation at the metal center, it should be noted that an alternative method for shifting the equilibrium between carbene and isocyanide exists for mixtures composed of about equal amounts of *N,O*-heterocarbene and 2-hydroxyphenyl isocyanide complex. Addition of weak bases such as NEt_3 to such mixtures stabilizes the isocyanide complex by engaging the hydroxyl group in hydrogen bonds, while stronger bases will deprotonate the hydroxy function, making the oxygen atom more nucleophilic and thereby shifting the equilibrium to the carbene complex side [28].

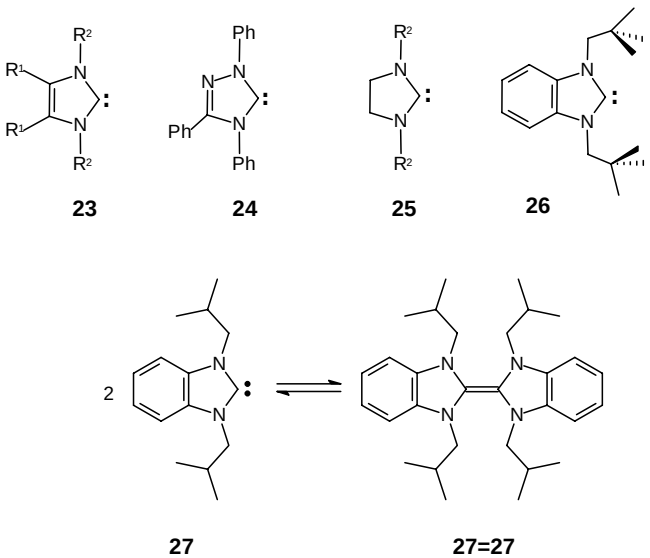
So far only *N,O*-heterocarben ligands obtained by cyclization of 2-hydroxyphenyl isocyanide have been presented. However, even *N,N*-heterocyclic carbenes can be prepared by the intramolecular cyclization of β-functional isocyanides.

The chemistry of *N,N*-heterocyclic carbenes has experienced an "incredible renaissance" [29] in recent years starting in 1991 with the isolation of 2,3-dihydro-1*H*-imidazol-2-ylidenes of type **23** by Arduengo et al. (Scheme 11) [30]. Since then additional types of stable *N,N*-heterocyclic carbenes such as **24** and **25** and new methods



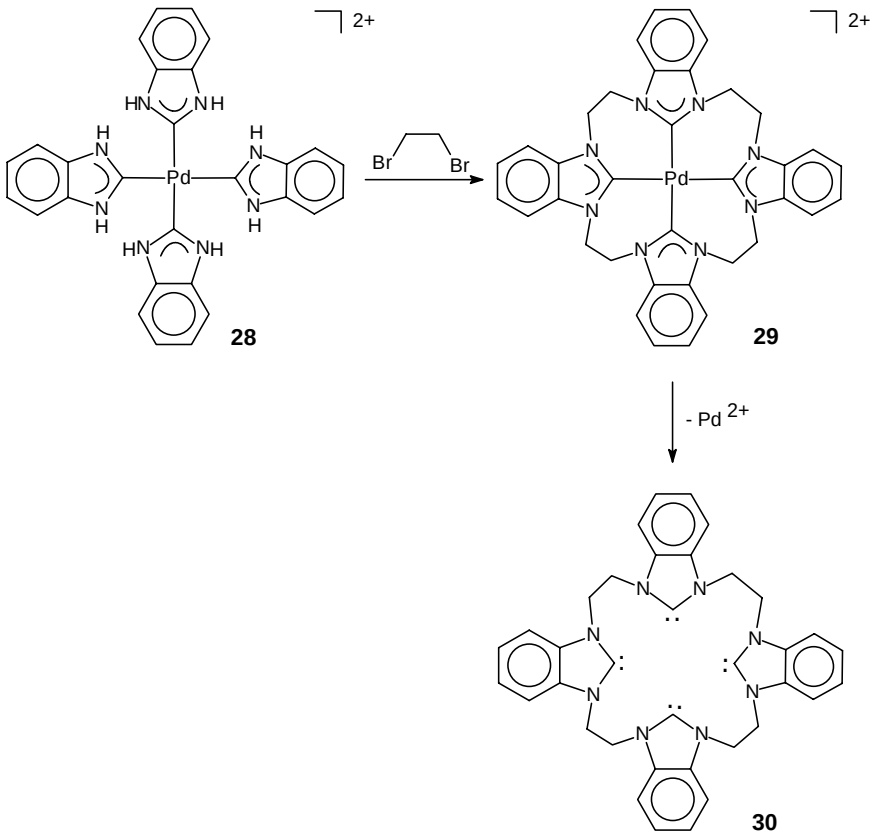
SCHEME 10 Reactivity of rhenium isocyanide complexes and molecular structure of complex **22**.

for their preparation have been reported [31]. The employment of free, stable carbenes can be regarded as the method of choice for the synthesis of transition metal carbene complexes, as their reactivity can be studied in the absence of any byproducts from carbene generation. The significance of *N*-heterocyclic carbenes in catalysis has recently been reviewed [32]. Complexes of the corresponding anellated 2,3-dihydro-1*H*-benzimidazol-2-ylidenes have also been generated in situ by deprotonation of benzimidazolium salts followed by reaction with appropriate metal complexes [33]. Furthermore, the introduction of bulky N-substituents increases the stability of the anellated *N*-heterocyclic carbenes, and the first stable anellated N-heterocyclic carbene 1,3-bis(2,2-dimethylpropyl)-2,3-dihydro-1*H*-benzimidazol-2-ylidene **26** was isolated only recently (Scheme 11) [34]. Anellated *N*-heterocyclic carbenes show an interesting chemistry, which distinguishes them from the nonanellated derivatives. Among the unusual features, not seen with carbenes of the Arduengo type, is the formation of an equilibrium between the carbene **27** and its dimer dibenzotetraazafulvalene **27**=**27** [35], the formation of unusual ring systems in the reaction with phosphaalkynes [36] and the facile cleavage of the dimer in the presence of Lewis acids [37].



SCHEME 11 *N*,*N*-heterocyclic carbenes and reactivity of the anellated carbene **27**.

However, the availability of free *N*-heterocyclic carbenes is limited to 1,3-disubstituted derivatives, which do not allow further reactions at the nitrogen atoms. One of our main aim was the development of synthetic strategies towards the synthesis of cyclic multidentate carbene ligands of type **30**, which can be regarded as crown ethers with carbon donor atoms (carbacrowns). To perform a template synthesis for such a ligand, a method for the preparation of 2,3-dihydro-1*H*-benzimidazol-2-ylidenes bearing just protons at the nitrogen atoms is needed (Scheme 12). Four of these ligands in a square-planar complex of type **28** could then be linked together by double N-alkylation to yield complex **29**, which would, after removal of the metal atom, lead to the carbacrown **30**.

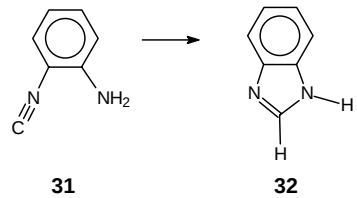


28 **29** **30**

SCHEME 12 Synthetic strategy for the preparation of the carbacrown ligand **30**.

Complexes with *N*,*N*-stabilized cyclic carbene ligands can be prepared by nucleophilic addition of amines to coordinated isocyanides [1]. Consequently, the preparation of complexes with N-unsubstituted 2,3-dihydro-1*H*-benzimidazol-2-ylidenes like **28** is best achieved by cyclization of 2-aminophenyl isocyanide **31** at a suitable metal center. Unfortunately, 2-aminophenyl isocyanide is not stable and cyclizes, even in the absence of metal ions, in analogy to the reaction **3** → **4** (Scheme 3) to give benzimidazole **32** (Scheme 13).

Therefore, we chose 2-azidophenyl isocyanide as a synthon for the in situ generation of metal-coordinated 2-aminophenyl isocyanide. In a preliminary study [38] we coordinated 2-azidophenyl isocyanide to the $Cr(CO)_5$ complex fragment to obtain complex **33**. This complex can be reacted with PPh_3 in a Staudinger-type [39] reaction to yield the iminophosphorane complex **34**. Hydrolysis with water/HBr yielded $OPPh_3$ and the unstable 2-aminophenyl isocyanide complex **35**, which cyclizes to give complex **36** with the 2,3-dihydro-1*H*-benzimidazol-2-ylidene ligand (Scheme 14). A similar reaction sequence has been used to generate saturated *N*,*N*-heterocyclic carbenes at group 6 metal centers [40].

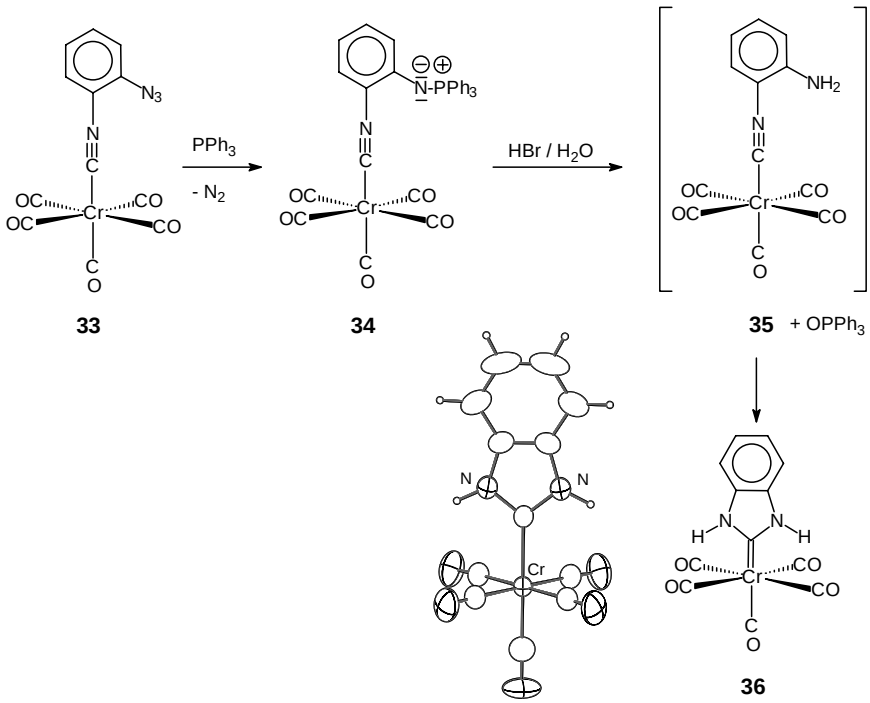


31 **32**

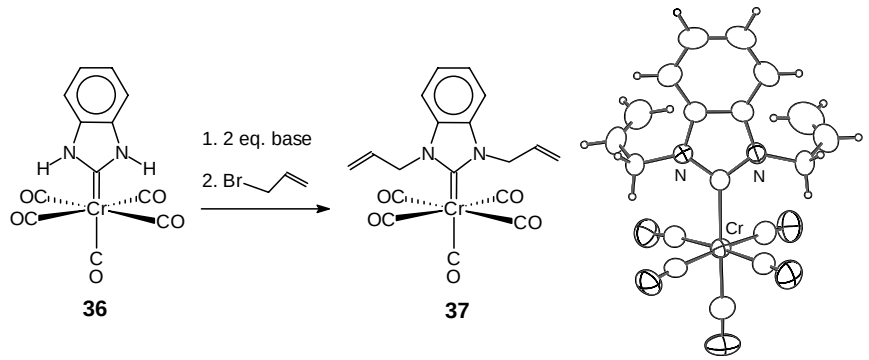
SCHEME 13 Cyclization of 2-aminophenyl isocyanide **31** to benzimidazole **32**.

In order to evaluate the possibility to functionalize **36** at the nitrogen atoms, it was treated with 2 equiv. KO*t*Bu followed by the addition of allyl bromide. The doubly *N*,*N*-allylated ylidene complex **37** was thus obtained. Its molecular structure is depicted in Scheme 15.

With the reaction sequence **33** → **36** we have developed the tools to generate 4 NH,NH-heterocyclic carbene ligands at a square planar metal center. The alkylation of these carbenes has been demonstrated with the sequence **36** → **37**. We have attempted to



SCHEME 14 Template synthesis of complex **36** with an NH,NH-stabilized cyclic carbene ligand and molecular structure of **36**.



SCHEME 15 N,N-alkylation of carbene complex **36** and molecular structure of **37**.

bind 4 equiv. 2-azidophenyl isocyanide at a Pt^{II} ion, liberate the amino groups, cyclize the four ligands, and then bridge them by N-alkylation.

REFERENCES

[1] (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. Transition Metal Carbene Complexes; Verlag Chemie: Weinheim, 1983; (b) Crociani, B. In Reactions of Coordinated Ligands; Braterman, P. S. (Ed.); Plenum: New York, 1986, Vol. 1, p. 553.

[2] Reviews on coordination chemistry of isocyanides: (a) Singleton, E.; Oosthuizen, H. E. Adv Organomet Chem 1983, 22, 209; (b) Treichel, P. M. Adv Organomet Chem 1973, 11, 21.

[3] Hahn, F. E. Angew Chem 1993, 105, 681; Angew Chem Int Ed Engl 1993, 32, 650.

[4] (a) Tschugajeff, L.; Skanawy-Grigorjewa, M. J Russ Chem Soc 1915, 47, 776; (b) Tschugajeff, L.; Skanawy-Grigorjewa, M.; Posnjak, A. Z Anorg Alg Chem 1925, 148, 37.

[5] (a) Burke, A.; Balch, A. L.; Enemark, J. H. J Am Chem Soc 1970, 92, 2555; (b) Butler, W. M.; Enemark, J. H. Inorg Chem 1971, 10, 2416; (c) Butler, W. M.; Enemark, J. H.; Parks, J.; Balch, A. L. Inorg Chem 1973, 12, 451.

[6] (a) Fehlhammer, W. P.; Fritz, M. Chem Rev 1993, 1993, 1243; (b) Beck, W.; Weigand, W.; Nagel, U.; Schaal, M. Angew Chem 1984, 96, 377; Angew Chem Int Ed Engl 1984, 23, 377; (c) Weigand, W.; Nagel, U.; Beck, W. Z Naturforsch 1988, 43b, 328; (d) Bär, E.; Völkl, A.; Beck, F.; Fehlhammer, W. P. J Chem

Soc, Dalton Trans 1986, 863; (e) Kunz, R.; Le Grel, P.; Fehlhammer, W. P. J Chem Soc, Dalton Trans 1996, 3231; (f) Fehlhammer, W. P.; Bär, E.; Boyadjiev, B. Z Naturforsch 1986, 41b, 1023; (g) Fehlhammer, W. P.; Beck, G. J Organomet Chem 1989, 369, 105; (h) Beck, G.; Fehlhammer, W. P. Angew Chem 1988, 100, 1391; Angew Chem Int Ed Engl 1988, 27, 1344.

[7] (a) Fehlhammer, W. P.; Hoffmeister, H.; Stolzenberg, H.; Boyadjiev, B. Z Naturforsch 1989, 44b, 419; (b) Fehlhammer, W. P.; Hoffmeister, H.; Boyadjiev, B.; Kolrep, T. Z Naturforsch 1989, 44b, 917; (c) Kernbach, U.; Fehlhammer, W. P. Inorg Chim Acta 1995, 235 , 299; (d) Fehlhammer, W. P.; Bartel, K.; Weinberger, B.; Plaia, U. Chem Ber 1985, 118, 2220.

[8] Fehlhammer, W. P.; Bartel, K.; Plaia, U.; Völkl, A.; Liu, A. T. Chem Ber 1985, 118, 2235.

[9] Plaia, U.; Stolzenberg, H.; Fehlhammer, W. P. J Am Chem Soc 1985, 107, 2171.

[10] Tamm, M.; Hahn, F. E. Coord Chem Rev 1999, 182, 175.

[11] (a) Hahn, F. E.; Tamm, M. J Organomet Chem 1990, 398, C19; (b) Hahn, F. E.; Tamm, M. Angew Chem 1991, 103, 213; Angew Chem Int Ed Engl 1991, 30, 203; (c) Hahn, F. E.; Tamm, M.; Dittler-Klingemann, A.; Neumeier, R. Chem Ber 1991, 124, 1683; (d) Hahn, F. E.; Tamm, M. Organometallics 1992, 11, 84; (e) Hahn, F. E.; Tamm, M. J Organomet Chem 1994, 467, 103; (f) Hahn, F. E.; Tamm, M.; Imhof, L.; Lügger, T. J. Organomet Chem 1996, 526, 149.

[12] Ferris, J. P.; Antonucci, F. R.; Trimmer, R. W. J Am Chem Soc 1973, 95, 919.

[13] Jutzi, P.; Gilge, U. J Organomet Chem 1983, 246, 159.

[14] Hahn, F. E.; Tamm, M. J Chem Soc, Chem Commun 1993, 482.

[15] Hahn, F. E.; Tamm, M. J Organomet Chem 1993, 456, C11.

[16] Hahn, F. E.; Tamm, M. Organometallics 1995, 14, 2597.

[17] (a) Singh, M. M.; Angelici, R. J. Inorg Chem 1984, 23, 2691; (b) Singh, M. M.; Angelici, R. J. Inorg Chem 1984, 23, 2699; (c) Chatt, J.; Richards, R. L.; Royston, G. H. D. J Chem Soc, Dalton Trans 1973, 1433; (d) Darensbourg, D. J.; Darensbourg, M. Y. Inorg Chem 1970, 9, 1691.

[18] Sarapu, A. C.; Fenske, R. F. Inorg Chem 1975, 14, 247.

[19] Cotton, F. A.; Kraihanzel, C. S. J Am Chem Soc 1962, 84, 4432.

[20] Tamm, M.; Hahn, F. E. Inorg Chim Acta 1999, 288, 47.

[21] (a) Hesse, G.; Witte, H.; Bittner, G. Liebigs Ann Chem 1965, 687, 1; (b) Hesse, Witte, H. Ann Chem 1965, 687, 9.

[22] Tamm, M.; Lügger, T.; Hahn, F. E. Organometallics 1996, 15, 1251.

[23] Hahn, F. E.; Lügger, T. J Organomet Chem 1994, 481, 189.

[24] Kernbach, U.; Lügger, T.; Hahn, F. E.; Fehlhammer, W. P. J Organomet Chem 1997, 541, 51.

[25] Hahn, F. E.; Tamm, M. J. Chem Soc, Chem Commun 1995, 569.

[26] Rouschias, G. Chem Rev 1974, 74, 531.

[27] Hahn, F. E.; Imhof, L. Organometallics 1997, 16, 763.

[28] Hahn, F. E.; Tamm, M.; Lügger, T. Angew Chem 1994, 106, 1419; Angew Chem Int Ed Engl 1994, 33, 1356.

[29] Regitz, M. Angew Chem 1996, 108, 791; Angew Chem Int Ed Engl 1996, 35, 725.

[30] (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J Am Chem Soc 1991, 113, 361; (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. J Am Chem Soc 1992, 114, 5530.

[31] Herrmann, W. A.; Köcher, C. Angew Chem 1997, 109, 2256; Angew Chem Int Ed Engl 1997, 36, 2162.

[32] Herrmann, W. A. Angew Chem 2002, 114, 1342; Angew Chem Int Ed Engl 2002, 41, 1290.

[33] (a) Lee, K. M.; Lee, C. K.; Lin, I. J. B. Angew Chem 1997, 109, 1936; Angew Chem Int Ed Engl 1997, 36, 1850; (b) Hahn, F. E.; Foth, M. J Organomet Chem 1999, 585, 241.

[34] Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. Chem Eur J 1999, 5, 1931.

[35] Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. Angew Chem 2000, 112, 551; Angew Chem Int Ed Engl 2000, 39, 541.

[36] Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R.; Wibbeling, B. Angew Chem 2000, 112, 2393; Angew Chem Int Ed 2000, 39, 2307.

[37] Hahn, F. E.; Wittenbecher, L.; Kühn, M.; Lügger, T.; Fröhlich, R. J Organomet Chem 2001, 617/618, 629.

[38] Hahn, F. E.; Langenhahn, V.; Lügger, T.; Fehlhammer, W. P. Chem Eur J, submitted.

[39] Staudinger, H.; Meyer, J. Helv Chim Acta 1919, 2, 635.

[40] Liu, C. Y.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. Organometallics 1996, 15, 1055.