ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 600 (2000) 12–22

Journal of Organometallic Chemistry

Review

N-Heterocyclic carbenes: state of the art in transition-metal-complex synthesis☆

Thomas Weskamp [1], Volker P.W. Böhm, Wolfgang A. Herrmann *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 29 November 1999; accepted 8 December 1999

Abstract

Recently, transition-metal complexes containing nucleophilic *N*-heterocyclic carbenes (NHCs) have been receiving increased attention in the literature, largely due to their favorable application in homogeneous catalysis. This article reviews the principles of known preparative procedures of such complexes that have been developed over the past 30 years since the independent isolation of chromium and mercury imidazolin-2-ylidene complexes by Öfele and Wanzlick. The discussion will focus exclusively on the preparation of complexes of nitrogen heterocycles and makes no claim to be exhaustive. These complexes exhibit all the principles of NHC ligands and appear most frequently in the literature.

Keywords: Transition-metal complexes; *N*-Heterocyclic carbenes; Synthesis

1. Introduction

It is now more than 30 years since Öfele and Wanzlick independently published the first structures and preparations of complexes containing *N*-heterocyclic carbenes (NHCs) [1,2]. Both reports used the deprotonation of an imidazolium salt by a basic metal precursor to form the imidazolin-2-ylidene complexes shown in Scheme 1. Lappert subsequently extended the methodology to complexes containing imidazolidin-2-ylidene ligands [3]. In 1991 Arduengo et al. succeeded in crystallizing the first free carbene, which was prepared by deprotonation of 1,3-bis(adamantyl)imidazolium chloride [4]. This allowed the preparation of metal–NHC complexes directly from the preformed, free carbene, leading to an enormous revival in the interest in the preparation of free carbenes and their metal complexes [5–15]. The focus on transition-metal compounds of heterocyclic carbenes has its roots in the unique properties of this type of carbenes when attached to a metal.

NHCs are σ-donating ligands and are more comparable to P-, N- or O-donating ligands rather than to classical Fischer- or Schrock-type carbenes. In contrast to the 'conventional' carbene ligands, the metal–carbon bond is much longer and is chemically and thermally more inert towards cleavage. In striking contrast to many other heteroatom donating ligands, NHCs show very high dissociation energies. This phenomenon has been quantified by theoretical calculations for different metals, e.g. in comparison to phosphine ligands [16,17]. This article focuses on the synthetic methods for the preparation of NHC complexes that bear nitrogen as the only heteroatom in the ring system. The properties of these complexes have been reviewed before and will not be discussed in detail here [3,18–20].

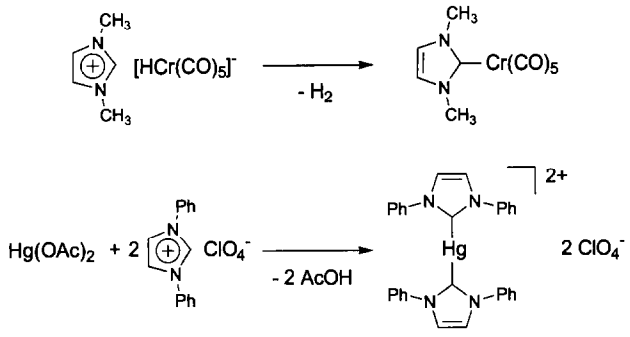
☆ Essays on organometallic chemistry. Part 11. For Part 10, see Ref. [45].

* Corresponding author. Tel.: +49-89-28913080; fax: +49-89-28913473.

E-mail address: lit@arthur.anorg.chemie.tu-muenchen.de (W.A. Herrmann)

[1] Present address: Symyx Technologies, 3100 Central Expressway, Santa Clara, CA 95051, USA.

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00035-8



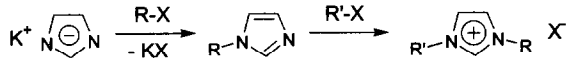
Scheme 1. Preparation of the first transition metal complexes of NHCs by Öfele and Wanzlick.

2. Synthesis of azolium salts as carbene precursors

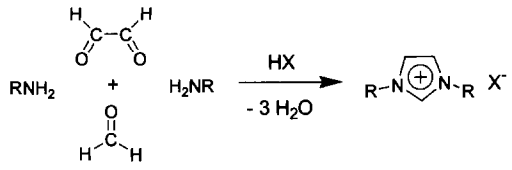
Generally, the synthesis of NHC complexes starts with *N*-substituted azolium salts. These precursors are generally accessible by two complementary synthetic routes: (i) nucleophilic substitution starting at the imidazole heterocycle and (ii) a multi-component reaction, building up the heterocycle with the appropriate substituents in one step.

In the first procedure, potassium imidazolide is reacted with one equivalent of alkyl halide in toluene to give the 1-alkylimidazole [21]. Subsequent alkylation at the 3-position is easily effected by the addition of another equivalent of alkyl halide (Scheme 2) [22–24]. The drawback of this simple route is that only primary alkyl halides can be reacted to produce the imidazolium salts in satisfactory yields, as reactions with secondary and tertiary alkyl halides result in substantial amounts of elimination by-products.

In order to introduce other substituents at the 1- and 3-positions of the imidazolium salt, the reaction of primary amines with glyoxal and formaldehyde in the presence of an acid can be used [25–27]. Variation of the amine used allows the preparation of imidazolium salt libraries, which can be further diversified by using different acids in order to change the anion of the imidazolium salt (Scheme 3) [28]. By synthesizing the bisimine prior to the ring closure with formaldehyde and an acid in a two-step sequence, it is possible to



Scheme 2. Preparation of imidazolium salts from imidazole.



Scheme 3. Preparation of imidazolium salts by ring formation.

form imidazolium salts derived from bulky anilines that do not bear a *para*-substituent [29,30].

A method reported by Gridnev et al. allows the combination of both strategies: (i) synthesis of 1-alkylimidazole by a multi-component reaction starting from glyoxal, formaldehyde, a primary amine and ammonium chloride and (ii) subsequent alkylation by a primary alkyl halide to give the imidazolium salt [31]. Direct coupling of imidazole with iodoarenes in the presence of copper(II) triflate giving 1-aryl-imidazole and the alkylation in a second step follows the same synthetic scheme [32].

The reaction of an *ortho*-ester, e.g. $HC(OEt)_3$, with a secondary bisamine in the presence of an ammonium salt yields symmetrical imidazolidinium salts [33,34]. Treatment of 2,3-dihydro-1*H*-benzimidazoles with trityl tetrafluoroborate generates the benzimidazolium salt and triphenylmethane [35].

The importance of the azolium salt synthesis for NHC chemistry has its roots in the fact that the synthesis of NHC complexes involves the use of the protonated ligand except for few examples (vide infra). But in this respect, progress in the synthesis of appropriate ligand precursors can help to increase the applications of and the interest in not only *N*-heterocyclic, but all types of heterocyclic carbenes.

3. Synthesis of transition-metal complexes

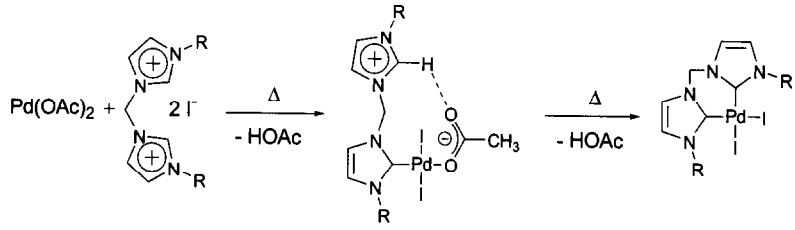
Although NHC complexes of almost all metals of the periodic table are known, access to all these compounds is mainly based on three routes: the in situ deprotonation of ligand precursors, the complexation of the free, pre-isolated NHC and the cleavage of electron-rich olefins. A variety of other methods, mainly of importance in special cases, will be discussed at the end of this review.

3.1. In situ deprotonation of ligand precursors

The in situ complexation of the ligand has the advantage of not having to prepare the free NHC. In cases where the carbene is unstable or difficult to handle, this approach offers the only means to prepare the desired complex.

3.1.1. Deprotonation by basic metallates

Azolium cations can be deprotonated in situ by Brönstedt basic metallate anions upon heating. The metal of the base functions as the ligand acceptor at the same time. Öfele prepared the first $(NHC)Cr(CO)_5$ complexes by this method (Scheme 1) [1,36]. This route has also been used to prepare complexes from benzimidazolium, pyrazolium, triazolium and tetrazolium salts [37]. The limit of this method is the availability of the



Scheme 4. Preparation of palladium(II) complexes with NHC by deprotonation of imidazolium salts.

appropriate metallate precursor, which is determined by the nature and oxidation state of the central metal atom of the new complex as well as its ligand environment.

3.1.2. Deprotonation by basic anions

Brönstedt basic anions either on the metal precursor or the azolium salt can provide the desired ligand in situ by deprotonation. Commercially available acetate salts and acetylacetonate salts or metal alkoxides, which are simple to prepare, are frequently used. In the cases of coordinating anions on the azolium salt, this anion is incorporated into the new complex. To avoid this incorporation, non-coordinating perchlorate, hexafluorophosphate or tetrafluoroborate azolium salts have to be used.

Wanzlick introduced the use of acetate salts in his synthesis of a mercury bis-NHC complex starting from mercury(II) diacetate (Scheme 1) [2]. More than 25 years later, this method proved to be especially valuable for palladium(II) and nickel(II) complexes starting from the corresponding metal(II) diacetates and imidazolium or triazolium salts [38–42]. For palladium, it is possible to apply the in situ deprotonation method even without solvent [38,39], but use of THF or even better DMSO provides enhanced yields of the complexes [41,42]. Additionally, a variety of palladium and nickel complexes with methylene bridged, chelating NHCs were accessible only by this route (Scheme 4) [17,41,43–46] until these bidentate ligands were isolated as free carbenes recently [47]. The in situ deprotonation can be extended to other azolium precursors like benzimidazolium or triazolium salts and their palladium complexes, respectively [35,41,48–50].

For rhodium(I) and iridium(I) compounds alkoxo ligands take over the role of the basic anion. Using μ-alkoxo complexes of (η^4-cod)rhodium(I) and iridium(I) — formed in situ by adding the μ-chloro bridged analogues to a solution of sodium alkoxide in alcohol — with azolium salts leads to the corresponding NHC complexes at room temperature (Scheme 5) [39,51]. Using imidazolium ethoxide with $[(\eta^4\text{-cod})RhCl]_2$ provides a way to the same complexes [51]. By this method, it is also possible to prepare benzimidazolin-2-ylidene complexes of rhodium(I) [51,52]. Furthermore, this method can be extended to triazolium- and tetrazolium salts [53]. The ruthenium(II) complex $[Cp^*Ru(OCH_3)]_2$ undergoes dimer cleavage on reaction with imidazolium salts and allows isolation of the stable 16-electron complex Cp*(NHC)RuCl [54].

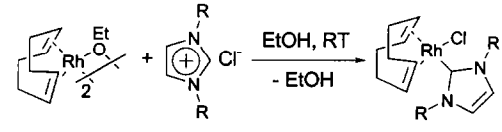
The use of μ-hydroxo μ-alkoxo bridged polynuclear complexes of chromium, molybdenum, tungsten and rhenium in this synthetic approach leads to the formation of monomeric bis(NHC) complexes (Scheme 6) [55–57]. Chelating and non-chelating imidazolium salts as well as benzimidazolium and tetrazolium salts can be used.

Basic silver(I) oxide is a convenient precursor to silver(I) bis(NHC) complexes [29,58]. The reaction is performed in CH_2Cl_2 at room temperature. The cationic complex precipitates and is a useful NHC transfer agent (vide infra).

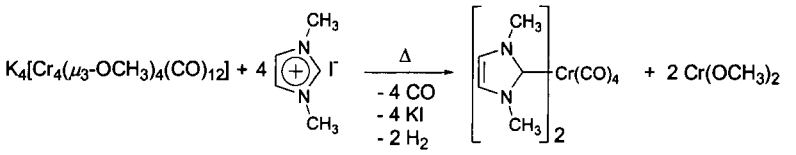
Loosely bound η^5-cyclopentadienyl anions can also serve as the base to deprotonate imidazolium salts. When chromocene is reacted with an imidazolium salt in THF, the metal precursor loses one molecule of cyclopentadiene to form the 14-electron complex Cp(NHC)CrCl (see Scheme 14) [59]. This complex can be further oxidized by $CHCl_3$ to $Cp(NHC)CrCl_2$.

3.1.3. Deprotonation by external base

The addition of external base for the in situ deprotonation of the azolium salts can lead to different products as compared with the use of metal salts with basic anions. As an example, the use of potassium *tert*-butoxide with an imidazolium perchlorate and one equivalent of palladium(II) diacetate in the presence of sodium iodide forms a dimeric mono(NHC) complex (Scheme 7) [60]. This method can also be used with triazolium salts [60]. The dimeric mono(NHC) complexes are valuable precursors for the introduction of other ligands by dimer cleavage, e.g. phosphines or different NHCs [27,61]. It is also possible to deprotonate imidazolium salts in the presence of $[(\eta^4\text{-cod})RhCl]_2$ with lithium *tert*-butoxide in THF at room temperature [27]. Using



Scheme 5. Preparation of imidazolin-2-ylidene complexes of rhodium(I) from a metal alkoxide.



Scheme 6. Synthesis of imidazolin-2-ylidene complexes of chromium by a redox reaction.

potassium *tert*-butoxide and sodium hydride in THF also generates the desired NHC from imidazolium salts (vide infra). The ligands can be coordinated e.g. to $Cr(CO)_6$ and to $W(CO)_6$ in situ [62].

Imidazolium salts can further be deprotonated with a phosphazene base at 0°C in THF and trapped by e.g. $[(\eta^4\text{-cod})IrCl]_2$ [63]. The lower temperature allows the use of more sensitive imidazolium salts, such as those derived from natural products. By using phase-transfer catalysts like tetrabutylammonium bromide it is possible to generate NHC complexes with a diluted, aqueous sodium hydroxide solution. For example, benzimidazolium bromides and $(Me_2S)AuCl$ react in CH_2Cl_2–H_2O at room temperature in this way to give $[(NHC)_2Au]Br$ [64].

Triethylamine in THF can be used as the external base to deprotonate triazolium salts. The resulting NHCs were complexed in situ, e.g. to $[(\eta^6\text{-cymene})RuCl_2]_2$, $[(\eta^4\text{-cod})RhCl]_2$, and $[Cp^*RhCl_2]_2$ [65,66].

Addition of butyl lithium to a suspension of palladium(II) diiodide and methylene-bridged bisimidazolium salts leads to the in situ complexation of the NHC and formation of the cationic $[(chelate)_2Pd]I_2$ in low yield [67]. Higher yields are obtained by deprotonation with acetate anions in DMSO (vide supra). By deprotonation with butyl lithium in THF it is also possible to prepare an NHC analogous ligand of Trofimenko's tris(pyrazolyl)borate [68]. Reaction with iron(II) chloride leads to the formation of a homoleptic hexa(NHC)iron(III) complex. The same methodology works with benzimidazolium salts [50].

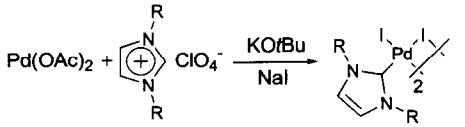
3.1.4. Elimination of small molecules from neutral ligand precursors

The elimination of an alcohol from a neutral 2-alkoxy-1,2-dihydro-1*H*-imidazole, i.e. a cyclic diaza-*ortho*-ester, leads to the formation of NHCs. By 1961 these compounds had already attracted much attention [69]. The cyclic carbene precursors are prepared by the reaction of vicinal diamines with an *ortho*-ester like $HC(OEt)_3$ [69–71]. Upon heating, the elimination of ethanol forms the NHC, which in most cases dimerizes to the corresponding tetraaminoethylene derivative (vide infra). By a variation of the *ortho*-ester method it is possible to prepare imidazolidinium salts in the presence of ammonium salts [33]. These can then be deprotonated by a base [14,35,70] or transformed into the corresponding 1,3-substituted 2-alkoxy-imidazolidines by alkaline alkoxide in alcohol (Scheme 8) [72]. The reaction of triazolium salts with sodium methoxide in methanol yields 5-methoxy-4,5-dihydro-1*H*-triazoles, which also eliminate methanol upon heating in vacuo. The formed triazolin-5-ylidenes can then either be isolated or trapped by an appropriate metal precursor [6,72]. Imidazolium and benzimidazolium salts can also be transformed into the neutral diaza-*ortho*-esters by this method [72]. Imidazolidin-2-ylidene complexes of ruthenium were prepared in situ by this method at elevated temperatures in connection with the exchange of a phosphine ligand [34]. The variation of aromatic substituents on the nitrogen atoms in the ring system is easily possible by palladium catalyzed Buchwald–Hartwig amination of the vicinal diamines before the ring-closing reaction [73].

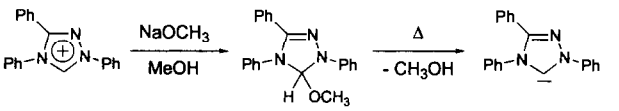
It is also possible to eliminate chloroform from trichloromethyl substituted heterocycles. For example, *N*,*N*′-dianilinoethane reacts with chloral to form 1,3-diphenyl-2-(trichloromethyl)imidazolidin which loses one molecule of chloroform upon heating (see Scheme 15). The 1,3-diphenylimidazolidin-2-ylidene dimerizes spontaneously to form an electron rich tetraaminoethylene [69–71,74].

3.2. Complexation of the preformed, free NHCs

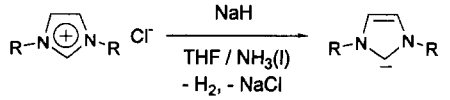
Since the isolation of free, stable NHCs by Arduengo et al., the direct application of these compounds has attracted much attention in complex synthesis [4,5,19]. The use of isolated NHCs has the advantage that a large variety of metal precursors without special re-



Scheme 7. Preparation of dimeric imidazolin-2-ylidene complexes of palladium(II).



Scheme 8. Preparation of 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-triazole and thermal elimination of methanol.



Scheme 9. Preparation of free NHCs from imidazolium salts.

quirements regarding the ligand sphere and the oxidation state can be used for the preparation of NHC complexes.

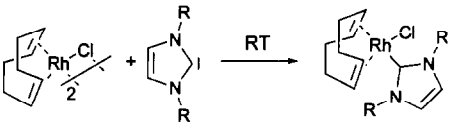
Various methods have been developed to prepare the NHCs from suitable precursors. Azolium salts can be deprotonated by NaH and KO*t*Bu or dimsyl-anions ($DMSO^-$) in THF [4,5]. The generation of NHCs by reaction with NaH in a mixture of liquid ammonia and THF is a high-yield and the most general method (Scheme 9) [26,39]. In the case of *N,N'* methylene-bridged bisimidazolium salts the preparation of the free dicarbene is only possible by the use of potassium hexamethyldisilazide (KHMDS) as the base in toluene [47]. With the other methods deprotonation occurs also at the methylene bridge [42].

Cyclic thiourea derivatives like 1,3,4,5-tetramethylimidazole-2(3*H*)-thione — prepared by condensation of substituted thioureas with α-hydroxyketones — can be converted into the corresponding imidazolin-2-ylidene by elemental sodium or potassium (Scheme 10) [75]. This method was adopted for the preparation and isolation of 1,3-bis-*neo*-pentylbenzimidazolin-2-ylidene through reaction with Na–K [13]. With lithium diisopropylamide (LDA) as the base it is also possible to generate free benzimidazolin-2-ylidenes in solution [35].

As mentioned above, triazolium salts can be converted into 5-methoxy-4,5-dihydro-1*H*-triazoles by the reaction with sodium methanolate in methanol. The heterocycles eliminate methanol upon heating in vacuo (Scheme 8) [72] and the formed triazolin-5-ylidenes can then be isolated in certain cases [51]. The same method works with imidazolium and benzimidazolium salts [34,72].

3.2.1. Cleavage of dimeric complexes

Nucleophilic NHCs can cleave dimeric complexes with bridging ligands such as halides, carbon monoxide or acetonitrile. Examples for this type of complex formation are the reaction of $[(\eta^4\text{-cod})MCl]_2$ or $[Cp^*MCl_2]_2$ (M = Rh, Ir) with free NHCs (Scheme 11) [26,39,76–78]. By the use of less sterically demanding NHCs it is also possible to incorporate two NHC ligands in a then cationic rhodium complex [39]. Cleaving $[Rh(CO)_2Cl]_2$ with NHCs leads to the formation of a bis-ligated complex $(NHC)_2Rh(CO)Cl$ [39]. Dimer cleavage and incorporation of one NHC occurs also with $[(\eta^6\text{-cymene})RuCl_2]_2$ [26,39,79] and $[Os(CO)_3Cl_2]_2$ [39]. Higher nuclear clusters can also be cleaved, e.g. $[Cp^*RuCl]_4$ is cleaved to yield Cp*Ru(NHC)Cl by free NHC [80]. The same compound is obtained from $[Cp^*RuCl_2]_n$ with 1.5 equivalents of free NHC [54].



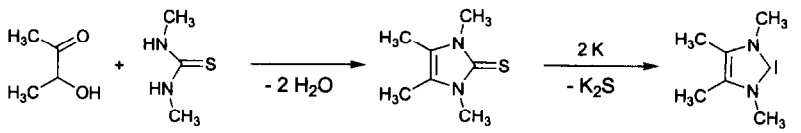
Scheme 11. Cleavage of dimeric complexes by imidazolin-2-ylidenes.

A special case of 'dimer cleavage' is the reaction of NHCs with oligomeric metal salts to form mononuclear complexes. It is possible to break up bridging anions in $TiCl_4$ in pentane as the solvent resulting in $(NHC)TiCl_4$ [81]. The coordination of one NHC is complementary to the reaction of the solvent adduct $(thf)_2TiCl_4$ with two NHC ligands (vide infra). Analogously, the mono(NHC) complexes are obtained from $Y[N(SiMe_3)_2]_3$ and $La[N(SiMe_3)_2]_3$ in hexane [82].

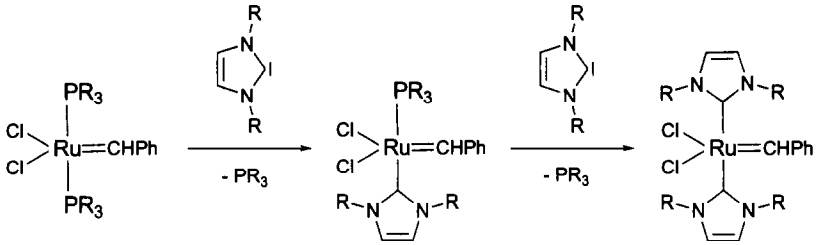
3.2.2. Exchange of phosphine ligands

Phosphines and other ligands (vide infra) can be exchanged for NHCs. As most phosphines are simple to exchange even below room temperature, this method is an important means of NHC complex preparation. In certain cases it has been found that a sequential exchange of phosphines can lead to the clean formation of mixed phosphine–NHC complexes. On the olefin metathesis catalyst dichloro-bis(tricyclohexylphosphine)benzylidene ruthenium(II) both phosphines can be displaced for various NHCs without affecting the benzylidene moiety (Scheme 12) [83]. The use of bulky NHCs leads to the substitution of only one of the phosphines to yield a mixed phosphine–NHC complex [16,80,84,85]. The exchange also works for Cp*-Ru(PCy_3)Cl [80]. The substitution of triphenylphosphine on $(Ph_3P)_3RuCl_2$ with an excess of NHC results in the formation of $(NHC)_4RuCl_2$ [86].

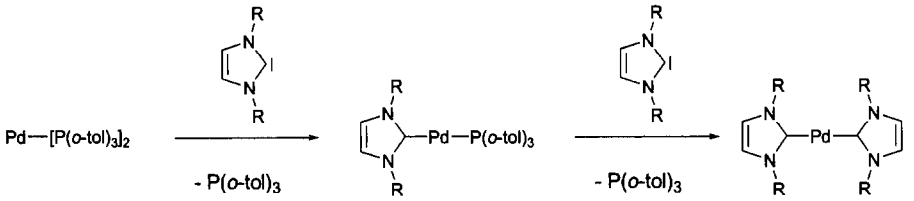
The same approach allows the formation of palladium(0) complexes of various NHCs. Starting from bis(tri-*ortho*-tolylphosphine)palladium(0) quantitative ligand exchange provides the formation of bis-(NHC)palladium(0) complexes (Scheme 13) [87]. Again, by the use of sterically more demanding NHCs



Scheme 10. Preparation of imidazolin-2-ylidenes from thiourea derivatives.



Scheme 12. Phosphine exchange on ruthenium(II) benzylidene complexes.



Scheme 13. Preparation of palladium(0) NHC complexes by phosphine exchange.

like 1,3-diadamantylimidazolin-2-ylidene just one of the phosphines is displaced [88]. Only tri-*ortho*-tolylphosphine gave a clean substitution reaction, but not triphenylphosphine or tricyclohexylphosphine.

Nickel complexes can also be prepared by phosphine exchange. Both triphenylphosphines can be displaced by NHC ligands in $(Ph_3P)_2NiCl_2$ [40]. Substitution of trimethylphosphine in $(Me_3P)_2NiCl_2$ is possible by chelating NHCs [47]. The reaction yields either the monocationic [(Me_3P)Ni(chelate)Cl]Cl or the dicationic [Ni(chelate)$_2$]Cl_2 depending on the reaction conditions.

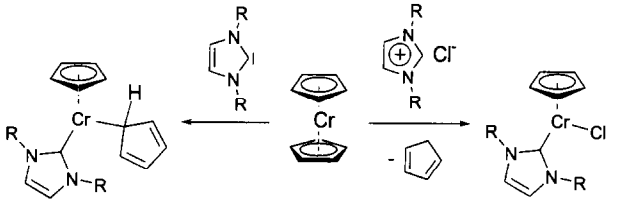
3.2.3. Exchange of other ligands

In carbonyl complexes like $Cr(CO)_6$, $W(CO)_6$, $Fe(CO)_5$ or $Ni(CO)_4$ one or two carbon monoxide molecules can be displaced by NHC ligands [26,62,76,89]. Further substitution requires photolysis conditions [90].

Exchange of coordinated solvent molecules like THF in $Cp^*_2M(thf)$ (M = Sm, Yb) by free NHC leads to the more stable mono imidazolin-2-ylidene complex [91–93]. The same exchange methodology is possible with $(thf)_{3.25}ErCl_3$ to coordinate three NHCs and with $(thf)_2Y[N(SiHMe_2)_2]_3$ resulting in different degrees of exchange dependent on the stoichiometry of the reaction [82]. $(thf)_2NiCl_2$ is a valuable precursor to the bis(NHC) complexes of nickel(II) [40]. The bis(thf)tetrachloro complexes of titanium, zirconium, hafnium, niobium and tantalum allow the exchange of both solvent molecules for NHC ligands [94]. In $(thf)W(CO)_5$ the solvent molecule can be exchanged for an NHC ligand selectively [35]. All three acetonitrile molecules can be exchanged by imidazolin-2-ylidenes in $(CH_3CN)_3M(CO)_3$ (M = Cr, Mo, W) to give only *fac*-$(NHC)_3M(CO)_3$ [62]. Reacting silver(I) and copper(I) triflates in THF with free NHCs can be regarded as well as an exchange of THF molecules but without the isolation of the solvent complexes [95].

Amines have also been exchanged by NHC in some complexes. For example TMEDA can be replaced by two NHCs in $(tmeda)_2VCl_2$ [62], and pyridine by one NHC in complexes of chromium, molybdenum and tungsten [94].

Olefins like 1,5-cyclooctadiene can also be subject to ligand exchange if no other ligands can be replaced (vide supra). Bis(NHC) complexes of nickel(0) and platinum(0) have been prepared from Ni(η^4-cod)$_2$ and Pt(η^4-cod)$_2$, respectively [96]. The preparation of the corresponding palladium(0) complexes is impossible by this route and has to be achieved by exchange of phosphine ligands (Scheme 13) [87]. The exchange of η^4-1,5-cyclooctadiene ligands on palladium(0) is possible if an electron-deficient alkene like tetracyanoethylene or maleic anhydride is present [97]. But this does not result in homoleptic palladium(0)–NHC complexes as the acceptor olefin is not replaced. Starting at (η^4-cod)Pd(CH_3)Cl the olefin can be exchanged by one or two NHCs to form [(NHC)Pd(CH_3)Cl]$_2$ or $(NHC)_2Pd(CH_3)Cl$, respectively [98]. Attempts to exchange dibenzylideneacetone ligands from $Pd_2(dba)_3$ by free NHCs have failed in the isolation of well-defined palladium(0) complexes [38,98]. In certain cases it is also possible to replace anionic ligands by neutral NHC ligands. Nickelocene and chromocene undergo a cyclopentadienyl shift from η^5 to η^1-coordination upon coordination of one imidazolin-2-ylidene ligand (Scheme 14) [99]. Under certain conditions it is possible to remove a cyclopentadienyl ligand completely with another equivalent of NHC to form, e.g. the cationic [Cp(NHC)$_2$Ni]Cp complex with a non-coordinating cyclopentadienyl anion [99]. This complements the deprotonation of imidazolium salts by cyclopentadienyl



Scheme 14. Reaction of chromocene with imidazolin-2-ylidenes and imidazolium salts.

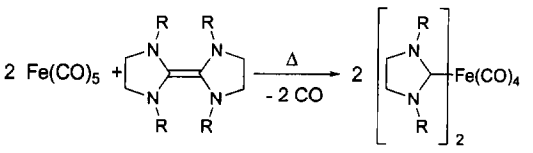
anions where one of the ligands is removed totally from the metal center (vide supra) [59].

3.3. Cleavage of electron-rich olefins

Electron-rich olefins are nucleophilic and therefore subject to thermal cleavage by various transition-metal complexes. As the formation of tetraaminoethylenes, i.e. enetetramines, is possible by different methods there are various precursors to imidazolidin-2-ylidene complexes readily available [100]. Dimerization of non-stable NHCs is one of the routes used to obtain these electron-rich olefins (Scheme 15) [74]. The existence of an equilibrium between free NHC monomers and the olefinic dimer was proved recently [15]. In addition to the above-mentioned methods, it is possible to deprotonate imidazolidinium salts with Grignard reagents in order to prepare tetraaminoethylenes [70]. The isolation of stable imidazolidin-2-ylidenes was achieved by deprotonation of the imidazolidinium salt with potassium hydride in THF [7].

Heating of tetraaminoethylenes in refluxing toluene in the presence of complex precursors such as manganese, iron, ruthenium, cobalt and nickel carbonyls yields the corresponding NHC complexes [3,101,102]. Generally, one or two carbon monoxide molecules are replaced by imidazolidin-2-ylidene ligands (Scheme 16). Higher substitution is nevertheless possible in certain cases [103]. In the case of $[Ru_3(CO)_{12}]$ the exchange of one of the carbonyl ligands occurs without disruption of the cluster structure [101]. The exchange of phosphine ligands is also possible, e.g. in the Wilkinson catalyst $(Ph_3P)_3RhCl$ or in $(Ph_3P)_3RuCl_2$ [86,103–105]. Dimeric complexes can also be subjected to this procedure and react under monomerization, e.g. $[(\eta^4\text{-cod})RhCl]_2$ [103,104].

Benzimidazolin-2-ylidene complexes are conveniently prepared from the corresponding enetetramines or from



Scheme 16. Complex preparation by transition-metal attack on tetraaminoethylenes.

benzimidazolium salt precursors (vide supra). In refluxing toluene the enetetramine is attacked, e.g. by $[(\eta^4\text{-cod})RhCl]_2$ to form the mono(NHC) or the bis(NHC) complex depending on the reaction conditions [106].

3.4. Other methods

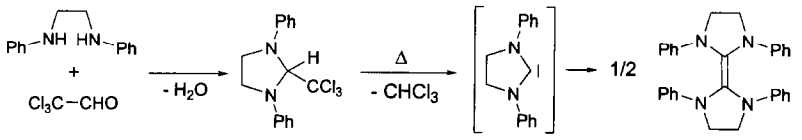
In addition to the above-mentioned most common methods, some less frequently used reactions have also led to NHC complexes of different metals. In all these cases certain requirements for the metal, the complex precursor or the NHC itself have prevented broad application in the preparation of more examples.

3.4.1. Vapor-phase synthesis

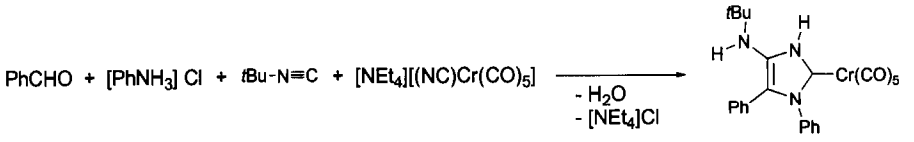
In the case of sublimable NHCs, the vapor deposition method can lead to the formation of desired complexes. In the case of 1,3-di-*tert*-butylimidazolin-2-ylidene and Group 10 metals, this method was successfully applied in the preparation of the corresponding homoleptic bis(1,3-di-*tert*-butylimidazolin-2-ylidene)metal(0) complexes of nickel, palladium and platinum [107].

3.4.2. The metalla-Ugi reaction

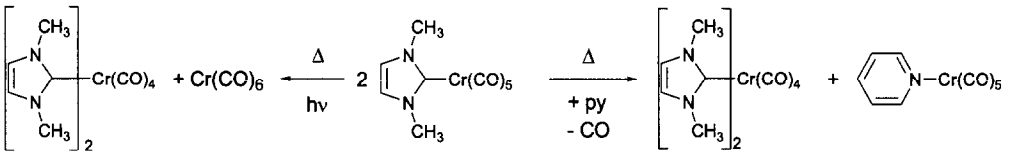
The isolobal analogy of oxygen and a d^6-transition-metal complex fragment ML_5 is the idea behind the application of the *Ugi*-4-component condensation for hydantoins in complex synthesis [108]: anionic cyano complexes are reacted with an aldehyde, an isocyanide and an ammonium salt to form the desired NHC complexes. The drawback of this route is the fact that the coordinated NHC is limited to a hydrogen substituent at the 3-position. This principle has been demonstrated for various metals, e.g. chromium and tungsten (Scheme 17) [109]. The imidazolin-2-ylidene ligands in turn can easily be displaced from the metal by pyridine due to the protonation in 3-position to afford the substituted parent imidazole derivative. It is also possible to start the reaction sequence from a



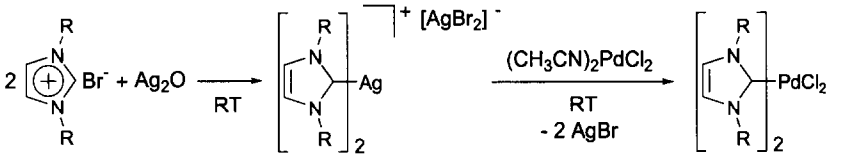
Scheme 15. Synthesis of electron-rich tetraaminoethylenes.



Scheme 17. Metalla-*Ugi*-4-component condensation.



Scheme 18. Disproportionation of $(NHC)Cr(CO)_5$.



Scheme 19. Complex preparation by transfer of imidazolin-2-ylidene ligands from silver(I).

defined isocyanide complex, e.g. with platinum as the central metal [110]. The α-H atom of the isocyanide is attacked by an amine base; subsequent cycloaddition of a dipolarophile to the ylid structure gives the desired imidazolin-2-ylidene complex. If the isocyanide ligand is replaced by an *N*-isocyanimine ligand, this reaction leads to triazolin-5-ylidene complexes [111].

3.4.3. Ligand transfer reactions

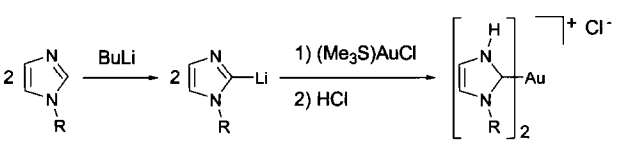
NHC ligands can be transferred in an intermolecular way from one metal complex to another in certain cases. The first examples of this reaction were found in a disproportionation reaction of (1,3-dimethylimidazolin-2-ylidene)$Cr(CO)_5$. The complex was heated under photolysis conditions to form (1,3-dimethylimidazolin-2-ylidene)$_2Cr(CO)_4$ and $Cr(CO)_6$ (Scheme 18) [36]. The same reaction type is possible with molybdenum and tungsten [112]. Thermally induced disproportionation of $(NHC)Cr(CO)_5$ complexes occurs in the presence of other donor ligands such as pyridine or tricyclohexylphosphine (Scheme 18) [113]. Further substitution requires photolysis conditions [36,62,113].

NHC transfer from imidazolidin-2-ylidene complexes of chromium, molybdenum and tungsten pentacarbonyl is possible. The NHC ligands have been successfully transferred to rhodium(I), palladium(II), platinum(II), copper(I), silver(I) and gold(I) [114,115]. Reacting $(NHC)W(CO)_5$ with $(PhCN)_2PdCl_2$ results in mono- or bisligated complexes depending on the conditions used. Starting at $(PhCN)_2PtCl_2$, the complex $(NHC)Pt(CO)Cl_2$ is obtained indicating that a carbonyl transfer is also possible by this method. Using $(Me_2S)AuCl$ leads to the formation of the cationic $[(NHC)_2Au]Cl$ and dimeric $[Rh(CO)_2Cl]_2$ gives $(NHC)_2Rh(CO)Cl$.

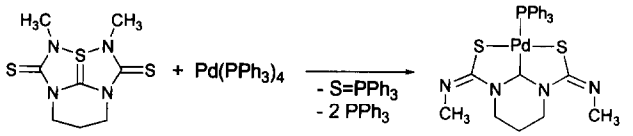
Cationic bis(imidazolin-2-ylidene)silver(I) complexes can also be used to transfer both NHC ligands to $(CH_3CN)_2PdCl_2$ or $(Me_2S)AuCl$ in CH_2Cl_2 at ambient temperature (Scheme 19) [58]. Furthermore, it is possible to form the silver(I) complex from Ag_2O in situ without isolation prior to the transfer reaction [116]. The silver(I) halide that forms during the transfer can be filtered off the product solution and recycled to give the donor complex in a phase-transfer catalytic reaction under basic conditions (vide supra). In certain cases it has been advantageous to use a mixture of CH_2Cl_2 and ethanol as the solvent in this reaction [117].

3.4.4. Rare examples

2-Lithioimidazoles — prepared from 1-substituted imidazoles with butyl lithium at low temperatures — can be transmetallated by (L)AuCl with $L = Me_2S$ or PPh_3, for example, and can subsequently be quenched by HCl to give a 3-hydrolmidazolin-2-ylidene complex (Scheme 20) [118]. This method has the disadvantage of resulting in a hydrogen substitution on one of the nitrogen atoms of the NHC ligand.



Scheme 20. Preparation of imidazolin-2-ylidene complexes with hydrogen substitution.

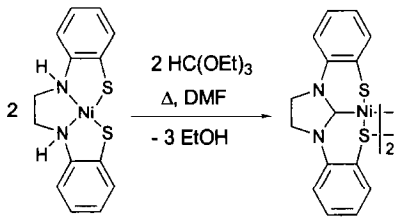


Scheme 21. Complex preparation by transition-metal attack on a thiourea derivative.

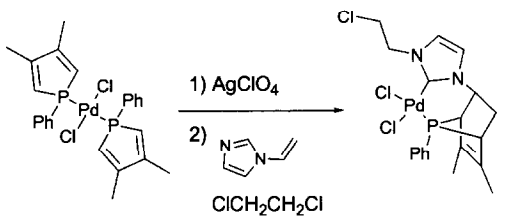
The reaction of thiourea derivatives with a complex precursor to form NHC complexes is a combination of the carbene formation from thioureas with potassium and the cleavage of electron-rich olefins by complex precursors. In the literature example, a stabilized 10-*S*-3-tetraazapentalene derivative is cleaved by $Pd(PPh_3)_4$ and $(Ph_3P)_3RhCl$ (Scheme 21) [119].

A variation on the thermal elimination of an alcohol from the neutral 2-alkoxy-1,2-dihydro-1*H*-imidazole is the preformation of a chelate *vic*-bisamine complex, which is subsequently attacked by an *ortho*-ester to form the desired NHC complex. This principle has been demonstrated with nickel and platinum (Scheme 22) [120,121]. The reverse sequence is also possible, as demonstrated by the attack of a *vic*-bisamine on a tungsten carbonyl cation $[(PhCCPh)_3W(CO)]^+$ [122].

Certain transition-metal complexes can serve as templates for the synthesis of chelating NHC ligands. It is necessary to have functional groups present in the template that allow the build up of an intermediate imidazolium moiety, which is then subject to NHC formation. For example, 1-phenylphosphole complexes of palladium(II) are attacked in a Diels–Alder reaction by 1-vinylimidazole [123]. If 1,2-dichloroethane is used as the solvent the imidazole is quaternized in situ and is then subjected to a spontaneous carbometallation reaction (Scheme 23).



Scheme 22. Synthesis of NHC complexes by the attack of an *ortho*-ester on a chelate precursor.



Scheme 23. Template synthesis of a chelate NHC-phosphine palladium(II) complex.

4. Conclusions

This survey on published synthetic routes to NHC transition-metal complexes shows that there exists a broad variety of different approaches to this class of complexes. In general, the preparation by cleavage of dimeric metal precursors or exchange of other ligands with free NHCs is the most convenient and general approach. In most examples the maximum number of NHC ligands on the metal is achieved by this method despite of some contrary examples. The major limitation of this approach is the necessity to prepare the free NHCs.

In cases where this is not possible, the complex formation has to be accomplished in situ from a ligand precursor, e.g. the imidazolium salt in the case of imidazolin-2-ylidenes. Using this method there is often the chance to prepare complexes that do not have the maximum number of NHC ligands attached to the metal center, allowing further substitution and complex variation. Cleavage of tetraaminoethylenes has been used extensively in the preparation of imidazolidin-2-ylidene complexes.

NHC transfer from one metal to another appears to be a simple alternative for the preparation of new metal complexes which have not yet been accessible. But still this method relies on the preparation of the ligand-donating complexes in advance and can therefore be limited by the access to this essential precursor. Further methods such as vapor-phase synthesis or template synthesis have only achieved importance in cases where the other methods have failed.

Observations of NHC complex stability to date suggest that the low and medium oxidation states 0, + I, + II and + III are stabilized best by this type of ligand. Both higher and lower oxidation states have presented preparation and isolation difficulties in many cases, although some extreme cases such as rhenium(VII) are known. Nevertheless, NHC complexes have been prepared for almost all the transition and a number of Main Group metals in a wide variety of oxidation states.

Acknowledgements

The work of our group was supported by the former Hoechst AG, now Aventis R&T and Celanese AG, the Deutsche Forschungsgemeinschaft (DFG), the Bayerischer Forschungsverbund Katalyse (FORKAT), Degussa-Hüls AG (precious metal salt grants), the Alexander von Humboldt-Stiftung (fellowship for M.G. Gardiner) and the Fonds der Chemischen Industrie (studentships for V.P.W.B. and T.W. as well as L.J. Gooßen, J. Schwarz and M. Steinbeck). The authors thank F. Bielert, K. Denk, C.W.K. Gstöttmayr, F.J.

Kohl, M. Mühlhofer, M. Prinz and J. Schwarz from TU München, as well T. Boussie, G. Diamond and K. Hall from Symyx Technologies for helpful discussions. Assistance by and discussions with our pioneer in NHC complexes, K. Öfele, are gratefully acknowledged.

References

[1] K. Öfele, J. Organomet. Chem. 12 (1968) 42.
[2] (a) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154; Angew. Chem. Int. Ed. Engl. 7 (1968) 141. (b) P. Luger, G. Ruban, Acta Crystallogr. Sect. B 27 (1971) 2276.
[3] M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.
[4] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[5] A.J. Arduengo III, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530.
[6] D. Enders, K. Breuer, G. Raabe, J. Runsink, J.H. Teles, J.-P. Melder, K. Ebel, S. Brode, Angew. Chem. 107 (1995) 1119; Angew. Chem. Int. Ed. Engl. 34 (1995) 1021.
[7] A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, J. Am. Chem. Soc. 117 (1995) 11027.
[8] R.W. Alder, P.R. Allen, M. Murray, A.G. Orpen, Angew. Chem. 108 (1996) 1211; Angew. Chem. Int. Ed. Engl. 35 (1996) 1121.
[9] G.A. McGibbon, J. Hrušák, D.J. Lavorato, H. Schwarz, J.K. Terlouw, Chem. Eur. J. 3 (1997) 232.
[10] A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, Liebigs Ann. (1997) 365.
[11] R.W. Alder, C.P. Butts, A.G. Orpen, J. Am. Chem. Soc. 120 (1998) 11526.
[12] G. Maier, J. Endres, Chem. Eur. J. 5 (1999) 1590.
[13] F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931.
[14] R.W. Alder, M.E. Blake, C. Bortolotti, S. Bufali, C.P. Butts, E. Linehan, J.M. Oliva, A.G. Orpen, M.J. Quayle, Chem. Commun. (Cambridge) (1999) 241.
[15] (a) Y. Liu, P.E. Lindner, D.M. Lemal, J. Am. Chem. Soc. 121 (1999) 10626; (b) F.E. Hahn, L. Wittenbacher, D. LeVan, R. Fröhlich, Angew. Chem. 112 (2000) 551; Angew. Chem. Int. Ed. Engl. 39 (2000) 541.
[16] T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Angew. Chem. 111 (1999) 2573; Angew. Chem. Int. Ed. Engl. 38 (1999) 2416.
[17] J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J., in press.
[18] M.F. Lappert, J. Organomet. Chem. 100 (1975) 139.
[19] W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256; Angew. Chem. Int. Ed. Engl. 36 (1997) 2162.
[20] M. Regitz, Angew. Chem. 108 (1996) 791; Angew. Chem. Int. Ed. Engl. 35 (1996) 725.
[21] P. Fournan, P. de Cointet, E. Laviron, Bull. Chem. Soc. Fr. (1968) 2438.
[22] B.K.M. Chan, N.-H. Chang, M.R. Grimmett, Aust. J. Chem. 30 (1977) 2005.
[23] M.R. Haque, M. Rasmussen, Tetrahedron 50 (1994) 5535.
[24] M.R. Grimmett, Imidazole and Benzimidazole Synthesis, Academic Press, London, 1997, p. 201.
[25] A.J. Arduengo III, US Patent No. 5 077 414 (Du Pont), 1991.
[26] W.A. Herrmann, C. Köcher, L.J. Gooßen, G.R.J. Artus, Chem. Eur. J. 2 (1996) 1627.
[27] W.A. Herrmann, L.J. Gooßen, M. Spiegler, J. Organomet. Chem. 547 (1997) 357.
[28] V.P.W. Böhm, T. Weskamp, C.W.K. Gstöttmayr, W.A. Herrmann, Angew. Chem. 112 (2000) in press; Angew. Chem. Int. Ed. Engl. 39 (2000) in press.
[29] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K.-H. Ongania, G. Opromolla, P. Zanello, Organometallics 18 (1999) 4325.
[30] J. Huang, S.P. Nolan, J. Am. Chem. Soc. 121 (1999) 9889.
[31] A.A. Gridnev, I.M. Mihaltseva, Synth. Commun. 24 (1994) 1547.
[32] A. Kiyomori, J.-F. Marcoux, S.L. Buchwald, Tetrahedron Lett. 40 (1999) 2657.
[33] S. Saba, A.M. Brescia, M.K. Kaloustian, Tetrahedron Lett. 32 (1991) 5031.
[34] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953.
[35] B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongania, K. Wurst, J. Organomet. Chem. 572 (1999) 177.
[36] K. Öfele, M. Herberhold, Angew. Chem. 82 (1970) 775; Angew. Chem. Int. Ed. Engl. 9 (1970) 739.
[37] (a) K. Öfele, C.G. Kreiter, Chem. Ber. 105 (1972) 529. (b) K. Öfele, Angew. Chem. 81 (1969) 936; Angew. Chem. Int. Ed. Engl. 8 (1969) 515. (c) K. Öfele, E. Roos, M. Herberhold, Z. Naturforsch. Teil B 31 (1976) 1070.
[38] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 107 (1995) 2602; Angew. Chem. Int. Ed. Engl. 34 (1995) 2371.
[39] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Chem. Eur. J. 2 (1996) 772.
[40] W.A. Herrmann, G. Gerstberger, M. Spiegler, Organometallics 16 (1997) 2209.
[41] W.A. Herrmann, J. Schwarz, M.G. Gardiner, M. Spiegler, J. Organomet. Chem. 575 (1999) 80.
[42] W.A. Herrmann, J. Schwarz, M.G. Gardiner, Organometallics 18 (1999) 4082.
[43] W.A. Herrmann, C.-P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.
[44] M.G. Gardiner, W.A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.
[45] W.A. Herrmann, V.P.W. Böhm, C.-P. Reisinger, J. Organomet. Chem. 576 (1999) 23.
[46] G. Bertrand, E. Díez-Barra, J. Fernández-Baeza, H. Gornitzka, A. Moreno, A. Otero, R.I. Rodríguez-Curiel, J. Tejeda, Eur. J. Inorg. Chem. (1999) 1965.
[47] R.E. Douthwaite, K. Haüssinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Danopoulos, Organometallics 18 (1999) 4584.
[48] W.A. Herrmann, J. Fischer, K. Öfele, G.R.J. Artus, J. Organomet. Chem. 530 (1997) 259.
[49] F.E. Hahn, M. Foth, J. Organomet. Chem. 585 (1999) 241.
[50] B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongama, K. Wurst, J. Organomet. Chem. 552 (1998) 45.
[51] C. Köcher, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 261.
[52] M. Mühlhofer, Diplomarbeit, Technische Universität München, 1999.
[53] M. Prinz, Diplomarbeit, Technische Universität München, 1997.
[54] W. Baratta, W.A. Herrmann, P. Rigo, J. Schwarz, J. Organomet. Chem. 593–594 (2000) 489.
[55] K. Ackermann, P. Hofmann, F.H. Köhler, H. Kratzer, H. Krist, K. Öfele, H.R. Schmidt, Z Naturforsch. Teil B 38 (1983) 1313.
[56] W.A. Herrmann, D. Mihalios, K. Öfele, P. Kiprof, F. Belmedjahed, Chem. Ber. 125 (1992) 1795.
[57] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1.

[58] H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.
[59] M.H. Voges, C. Rømming, M. Tilset, Organometallics 18 (1999) 529.
[60] D. Enders, H. Gielen, G. Raabe, J. Runsink, J.H. Teles, Chem. Ber. 129 (1996) 1483.
[61] T. Weskamp, V.P.W. Böhm, W.A. Herrmann, J. Organomet. Chem. 585 (1999) 348.
[62] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 459 (1993) 177.
[63] J.H. Davis Jr., C.M. Lake, M.A. Bernard, Inorg. Chem. 37 (1998) 5412.
[64] K.M. Lee, C.K. Lee, U.B. Lin, Angew. Chem. 109 (1997) 1936; Angew. Chem. Int. Ed. Engl. 36 (1997) 1850.
[65] D. Enders, H. Gielen, G. Raabe, J. Runsink, J.H. Teles, Chem. Ber. 130 (1997) 1253.
[66] D. Enders, H. Gielen, J. Runsink, K. Breuer, S. Brode, K. Boehn, Eur. J. Inorg. Chem. (1998) 913.
[67] W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, J. Organomet. Chem. 490 (1995) 149.
[68] U. Kernbach, M. Ramm, P. Luger, W.P. Fehlhammer, Angew. Chem. 108 (1996) 333; Angew. Chem. Int. Ed. Engl. 35 (1996) 310.
[69] H.-W. Wanzlick, H.-J. Klemer, Angew. Chem. 73 (1961) 493.
[70] D.M. Lemal, K.I. Kawano, J. Am. Chem. Soc. 84 (1962) 1761.
[71] H.-W. Wanzlick, F. Esser, H.-J. Kleiner, Chem. Ber. 96 (1963) 1208.
[72] J.H. Teles, J.-P. Melder, K. Ebel, R. Schneider, E. Gehrer, W. Harder, S. Brode, D. Enders, K. Breuer, G. Raabe, Helv. Chim. Acta 79 (1996) 61.
[73] I. Cabanal-Duvillard, P. Mangeney, Tetrahedron Lett. 40 (1999) 3877.
[74] H.-W. Wanzlick, E. Schikora, Angew. Chem. 72 (1960) 494.
[75] N. Kuhn, T. Kratz, Synthesis (1993) 561.
[76] W.A. Herrmann, L.J. Gooßen, C. Köcher, G.R.J. Artus, Angew. Chem. 108 (1996) 2980; Angew. Chem. Int. Ed. Engl. 35 (1996) 2805.
[77] W.A. Herrmann, L.J. Gooßen, G.R.J. Artus, C. Köcher, Organometallics 16 (1997) 2472.
[78] M. Prinz, M. Grosche, E. Herdtweck, W.A. Herrmann, Organometallics, in press.
[79] L. Jafarpour, J. Huang, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 3760.
[80] J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674.
[81] N. Kuhn, T. Kratz, D. Bläser, R. Boese, Inorg. Chim. Acta 238 (1995) 179.
[82] W.A. Herrmann, F.C. Munck, G.R.J. Artus, O. Runte, R. Anwander, Organometallics 16 (1997) 682.
[83] T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. 110 (1998) 2631; Angew. Chem. Int. Ed. 37 (1998) 2490.
[84] T. Weskamp, F.J. Kohl, W.A. Herrmann, J. Organomet. Chem. 582 (1999) 362.
[85] M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247.
[86] M. Steinbeck, Dissertation, Technische Universität München, 1999.
[87] V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, J. Organomet. Chem. 595 (2000) 186.
[88] C.W.K. Gstöttmayr, V.P.W. Böhm, M. Grosche, T. Weskamp, W.A. Herrmann, in preparation.
[89] N. Kuhn, T. Kratz, R. Boese, D. Bläser, J. Organomet. Chem. 470 (1994) C8.
[90] C. Köcher, Dissertation, Technische Universität München, 1997.
[91] H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, Angew. Chem. 106 (1994) 1829; Angew. Chem. Int. Ed. Engl. 33 (1994) 1733.
[92] H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, Chem. Ber. 127 (1994) 2369.
[93] A.J. Arduengo III, M. Tamm, S.T. McLain, C.T. Calabrese, F. Davidson, W.J. Marshall, J. Am. Chem. Soc. 116 (1994) 7927.
[94] W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, J. Organomet. Chem. 480 (1994) C7.
[95] A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405.
[96] A.J. Arduengo III, S.F. Gamper, J.C. Calabrese, F. Davidson, J. Am. Chem. Soc. 116 (1994) 4391.
[97] D.S. McGuinness, K.J. Cavell, B.W. Skelton, A.H. White, Organometallics 18 (1999) 1596.
[98] D.S. McGuiness, M.J. Green, K.J. Cavell, B.W. Skelton, A.H. White, J. Organomet. Chem. 565 (1998) 165.
[99] C.D. Abernethy, J.A.C. Clyburne, A.H. Cowley, R.A. Jones, J. Am. Chem. Soc. 121 (1999) 2329.
[100] H.E. Winberg, J.E. Carnahan, D.D. Coffman, M. Brown, J. Am. Chem. Soc. 87 (1965) 2055.
[101] M.F. Lappert, P.L. Pye, J. Chem. Soc. Dalton Trans. (1977) 2172.
[102] P.B. Hitchcock, M.F. Lappert, P.L. Pye, J. Chem. Soc. Dalton Trans. (1978) 826.
[103] A.W. Coleman, P.B. Hitchcock, M.F. Lappert, R.K. Maskell, J.H. Miffler, J. Organomet. Chem. 296 (1985) 173.
[104] E. Çetinkaya, I. Özdemir, P.H. Dixneuf, J. Organomet. Chem. 534 (1997) 153.
[105] (a) M.F. Lappert, P.L. Pye, J. Chem. Soc. Dalton Trans. (1978) 837. (b) P.B. Hitchcock, M.F. Lappert, P.L. Pye, J. Chem. Soc. Chem. Commun. (1976) 644.
[106] B. Çetinkaya, P.B. Hitchcock, H. Küçükbay, M.F. Lappert, S. Al-Juaid, J. Organomet. Chem. 481 (1994) 89.
[107] P.L. Arnold, F.G.N. Cloke, T. Geldbach, P.B. Hitchcock, Organometallics 18 (1999) 3228.
[108] I. Ugi, K. Offermann, Isonitrile Chemistry, vol. 20, Academic Press, London, 1971.
[109] D. Rieger, S.D. Lotz, U. Kembach, S. Schröder, C. André, W.P. Fehlhammer, Inorg. Chim. Acta 222 (1994) 275.
[110] W.P. Fehlhammer, K. Bartel, A. Vökl, D. Achatz, Z. Naturforsch. Teil B 37 (1982) 1044.
[111] B. Weinberger, F. Degel, W.P. Fehlhammer, Chem. Ber. 118 (1985) 51.
[112] C.G. Kreiter, K. Öfele, G.W. Wieser, Chem. Ber. 109 (1976) 1749.
[113] K. Öfele, M. Herberhold, Z. Naturforsch. Teil B 28 (1973) 306.
[114] S.-T. Liu, T.-Y. Hsieh, G.-H. Lee, S.-M. Peng, Organometallics 17 (1998) 993.
[115] R.-Z. Ku, J.-C. Huang, J.-Y. Cho, F-M. Kiang, K.R. Reddy, Y.-C. Chen, K.-J. Lee, J.H. Lee, G.-H. Lee, S.-M. Peng, S.-T. Liu, Organometallics 18 (1999) 2145.
[116] C.K. Lee, J.C.C. Chen, K.M. Lee, C.W. Liu, U.B. Lin, Chem. Mater. 11 (1999) 1237.
[117] H.M.J. Wang, C.Y.L. Chen, U.B. Lin, Organometallics 18 (1999) 1216.
[118] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147.
[119] N. Matsumura, J.-I. Kawano, N. Fukunishi, H. Inoue, J. Am. Chem. Soc. 117 (1995) 3623.
[120] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, Organometallics 11 (1992) 2346.
[121] D. Sellmann, W. Prechtel, F. Knoch, M. Moll, Inorg. Chem. 32 (1993) 538.
[122] R.-Z. Ku, D.-Y. Chen, G.-H. Lee, S.-M. Peng, S.-T. Liu, Angew. Chem. 109 (1997) 2744; Angew. Chem. Int. Ed. Engl. 36 (1997) 2631.
[123] H. Lang, J.J. Vittal, P.-H. Leung, J. Chem. Soc. Dalton Trans. (1998) 2109.