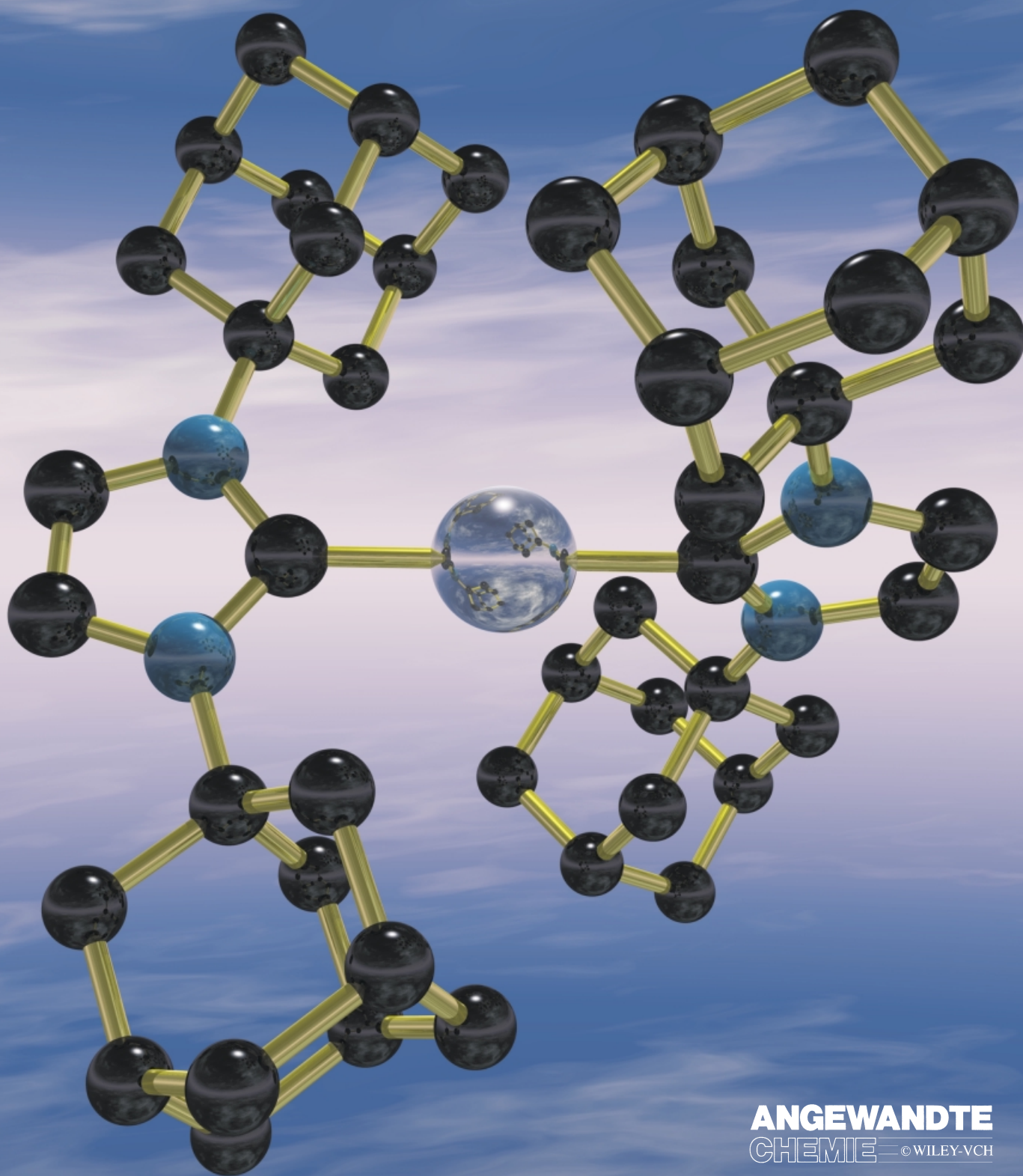# N-Heterocyclic carbenes as ligands for metal complexes – challenging phosphane ligands in homogeneous catalysis

N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis**

Wolfgang A. Herrmann*

In memory of John Osborn

N-Heterocyclic carbenes have become universal ligands in organometallic and inorganic coordination chemistry. They not only bind to any transition metal, be it in low or high oxidation states, but also to main group elements such as beryllium, sulfur, and iodine. Because of their specific coordination chemistry, N-heterocyclic carbenes both stabilize and activate metal centers in quite different key catalytic steps of organic syntheses, for example, C−H activation, C−C, C−H, C−O, and C−N bond formation. There is now ample evidence that in the new generation of organometallic catalysts the established ligand class of organophosphanes will be supplemented and, in part, replaced by N-heterocyclic carbenes. Over the past few years, this chemistry has been the field of vivid scientific competition, and yielded previously unexpected successes in key areas of homogeneous catalysis. From the work in numerous academic laboratories and in industry, a revolutionary turning point in oraganometallic catalysis is emerging.

Keywords: carbene ligands · carbenes · heterocycles · homogeneous catalysis

1. Introduction

Since the first report by Öfele in 1968,[1a] the metal coordination chemistry of N-heterocyclic carbenes **A** – **C**, derived from imidazole, pyrazole, and triazole has had a long, steady history in our laboratory. Numerous metal compounds

A   **B**   **C**   **D**
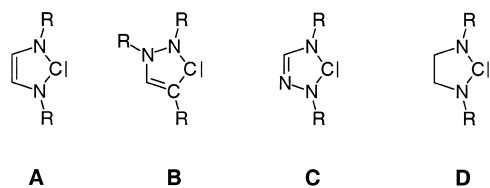
were synthesized and characterized before the free carbene ligands became available through the important work of Arduengo et al.[2] A series of Ph.D. theses[3, 4] yielded a large number of publications. The related C−C-saturated carbenes **D** (e.g., R = neopentyl) resulting from "Wanzlick dimers"[5] were investigated in terms of their organometallic chemistry by Lappert and his associates.[6]

The ylidenes **A** – **D** are nucleophilic singlet carbenes. They have been attached to metals either from the corresponding azolium salts (**A** – **D**) or from "Wanzlick dimers" (**D**), ever since the pioneering work of Öfele[1a] and Wanzlick[1b] appeared in the literature. Since N-heterocyclic carbenes are now available as "bottle-able compounds" (a phenyl-substituted triazole-derived ylidene of type **C**[21] is the first carbene to be commercially available[**]), their inorganic and organometallic chemistry has gained enormously in versatility and depth.[7]

2. Early Breakthroughs

In 1992/93, we noted the striking similarity of electron-rich organophosphanes PR_3 and N-heterocyclic carbenes (NHCs) in terms of their metal coordination chemistry, particularly the ligand properties and metal complex synthesis.[8–10] It was pointed out that both low- and high-oxidation-state transition metals are compatible with the "Wanzlick – Öfele carbenes,"[***] with typical examples being represented by the well characterized species **1** – **4**.

[**] Acros Organics, Dat. No. 30226-0010.

[***] Hans Werner Wanzlick (Berlin) and Karl Öfele (Munich) published the first transition metal complexes (Hg and Cr, respectively) back in 1968.[1a,b] Inspite of Arduengo's breakthrough isolation of the free carbene (1991), we assign the term "Wanzlick – Öfele carbenes" to recognize their pioneering work in this area.

$$\text{(1)}$$

$$\text{(2)}$$
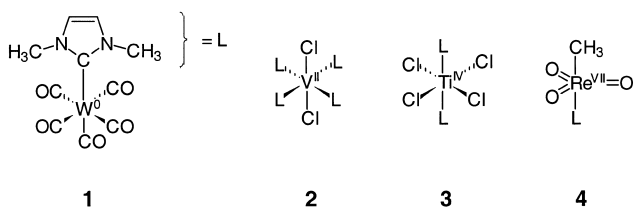
Spectroscopic studies revealed the close relationship of NHCs and organophosphanes.[9–12] They are both pronounced σ-donor ligands with only little backbonding character. Regarding the theory of their bonding, the NHCs are best treated as "diaza–allyl systems", with little π aromaticity being present in the C–C and CN unsaturated species **A – C**.

Four initial key patents were filed with priority of December 29, 1994.[13–16] They cover transition metal complexes of Group 8 – 10 elements exhibiting N-heterocyclic carbenes including imidazole- and pyrazole-derived carbenes as well as chelating dicarbene ligands.[13] A catalytic procedure to generate aldehydes by hydroformylation with catalysts containing N-heterocyclic carbenes was disclosed in the second patent.[14] The catalytic C–C coupling to make aromatic aldehydes with the same catalysts (e.g., hydroformylation and related coupling reactions) is covered by the third patent,[15] and the fourth reports novel complexes of the lanthanoid metals including scandium and yttrium.[16]

Somewhat later, the generation and large-scale synthesis of pure N-heterocyclic carbenes was described ("ammonia method"):

Liquid ammonia or mixtures of liquid ammonia with organic amines or polar-aprotic solvents were used as solvents,

- to smoothly and quantitatively deprotonate the corresponding azolium salts
- with reagents such as metal hydrides, -amides, -alkoxides, and -carboxylates
- at temperatures between − 75 and 0 °C.[17]

This technique following Equation (1) also applies to large-scale syntheses. It includes deprotonation agents such as the commercial $K^+[(CH_3)_3SiNSi(CH_3)_3]^-$ and $Li^+[N(iC_3H_7)_2]^-$ that, for example, selectively generate chelating dicarbenes but leave methylene and other hydrocarbon bridges intact[18] [Eq. (2)]. The high-yielding synthesis of novel, functionalized
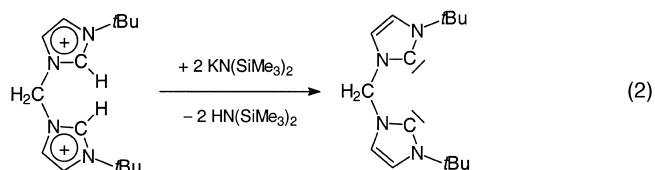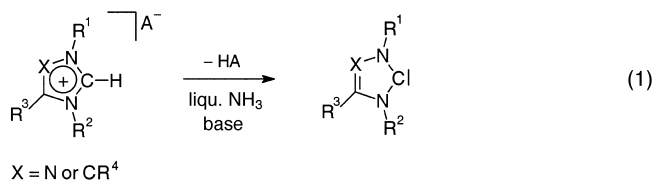
N-heterocyclic carbenes in liquid ammonia was described in detail as the standard literature technique in 1996.[19] Other techniques include the use of potassium hydride or potassium *tert*-butylate in THF to deprotonate the azolium precursor cations.[2c] Care has to be taken with the choice of the deprotonating agent, because certain hydrides yield imidazolidines $(+ H^-)$ instead of the carbene.[2c]

3. Easy Access

Most easily available are stable carbenes derived from imidazole, not least because numerous imidazolium precursor compounds can be made along various reliable routes. The one-pot synthesis starting from glyoxal, primary amine, and formaldehyde is straightforward (Scheme 1a), its variation (Scheme 1b) allows unsymmetrically N-substituted derivatives (R^1, R^2) to be made, while in another route (Scheme 1c) the imidazolide anion is alkylated by reactive alkyl-/aryl halides (or -triflate derivatives). The orthoformate route (Scheme 1d) converts the easily accessible 1,2-diamines (e.g. from Pd-catalyzed Buchwald coupling) into the aryl-substituted imidazolium salts. The heterocycle synthesis according to Scheme 1a and b was previously mentioned in the literature.[20] The desulfurization of the cyclic thiourea derivatives (Scheme 1e) depends on relatively drastic conditions but works well in many cases, for example, benzimidazolin-2-ylidenes from the corresponding 2-thiones.[5b] Vacuum ther-

Wolfgang A. Herrmann was born 1948 in Kelheim/Donau (Germany) and received his organometallic academic education with E. O. Fischer (Munich), H. Brunner (Regensburg), and P. S. Skell (Pennsylvania State University) before he became a professor of chemistry at the university of Regensburg (1979) and then Frankfurt (1982). In 1985 he was appointed the professor of inorganic chemistry at Technische Universität München to succeed E. O. Fischer. His research is focused on homogeneous catalysis, with a strong synthetic, spectroscopic, and structural background. He has authored approximately 550 scientific publications, numerous patents, and a number of review articles. He holds honorary doctorates from the Lyon, Veszprém, and South Carolina universities (1990/1995/1999) as well as numerous scientific awards, for example the Leibniz Award of the DFG, the Wilhelm Klemm Award of the German Chemical Society, the Alexander von Humboldt Award, the Max Planck Research Award, the Bundesverdienstkreuz, and the Ordre d'Houneur of the President of France. Professor Herrmann is a member of the editorial board of Angewandte Chemie.

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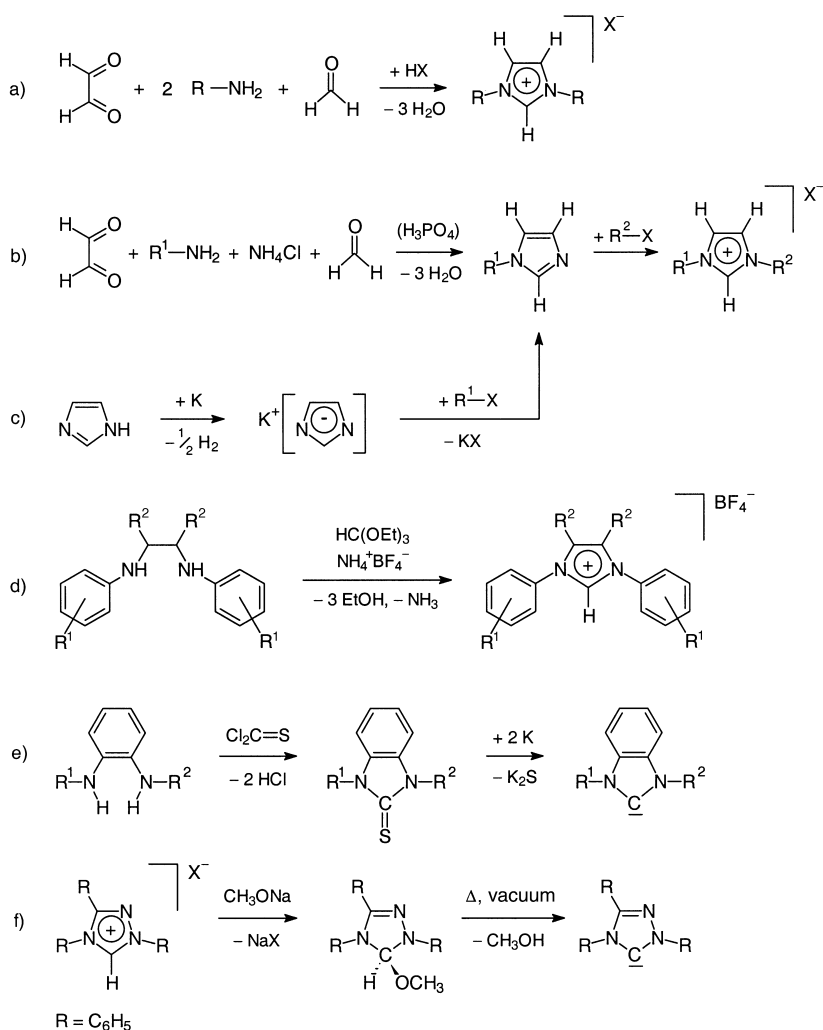
Scheme 1. Convenient synthetic routes to imidazolium salts and imidazolin(2)-ylidenes derived therefrom.

Examples are the "titration" of $TiCl_4 \cdot 2\,PR_3$ with two NHC equivalents to give $TiCl_4 \cdot 2\,NHC$, or of $VCl_2 \cdot 4\,NR_3$ with four equivalents to yield $VCl_2 \cdot 4\,NHC$.[26a] The typical examples **1–4** result from the free carbenes. The complexation to beryllium chloride[11] is typical in that the analogy to other σ-donor ligands is evident [Eq. (3)]. Other alkaline-earth metal complexes of NHCs were described by Schumann et al.[33]

Metal complexes of alkylidene-bridged dicarbenes followed soon.[12] Also, the first chemistry occurring at the five-membered heterocycles was reported, for example, the OsO_4-addition to the C–C unsaturation [Eq. (4)].[4b, 23] This latter reaction once again indicates that there is little to no π-aromaticity in the five-membered ring, quite consistent with recent charge-density studies.[34]

Numerous molecular structures were determined by single-crystal X-ray diffraction. It was shown that there is little or no variation in the geometrical details of the NHC ligands from case to case. The metal–carbene bonds are rather long (> 210 pm), while in Fischer- and Schrock-type complexes these distances are significantly below 200 pm because of pronounced backbonding ("double bond"). An excellent benchmark structure is the olefin metathesis catalyst **5** which exhibits both types of carbenes (Figure 1). As a result of this particular bonding situation, nucleophilic NHCs can, depending on the steric situation, rotate around the metal–carbon axis.

molysis of methoxy derivatives (Scheme 1 f) yields carbenes in good yields, as well, for example, 4,5-dihydro-1*H*-1,2,4-triazol-5-ylidenes.[21]

The free carbenes **A** and **D** are stable to air. Their "air sensitivity" is in fact hydrolysis. It is reported that **D** hydrolyzes instantaneously, while **A** is much more robust because of "aromatic stabilization".[22] Hydrolysis yields acyclic products by C–N bond cleavage.[22]
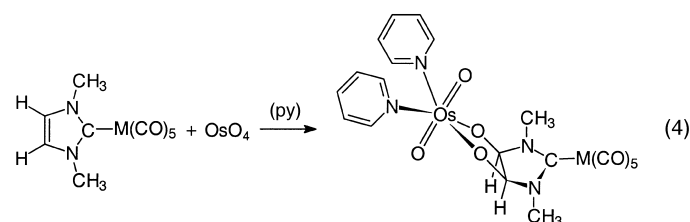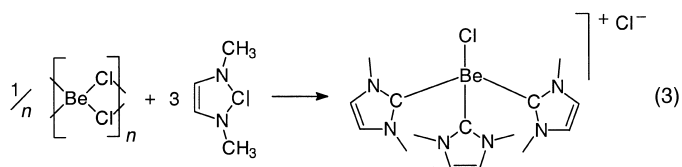
4. Metal Coordination Chemistry

N-heterocyclic carbenes in fact behave like typical σ-donor ligands that can substitute classical $2\,e^-$ donor ligands such as amines, ethers, and phosphanes in metal coordination chemistry.[23–32] It was determined in 1993 that "heterocarbenes show bonding properties similar to those of trialkylphosphanes and alkylphosphinates".[9] Nolan et al. concluded from structural and thermochemical studies that "in general these ligands behave as better donors than the best phosphane donor ligands with the exception of the sterically demanding (adamantyl) carbene".[118]
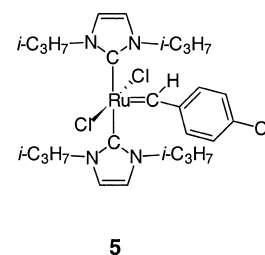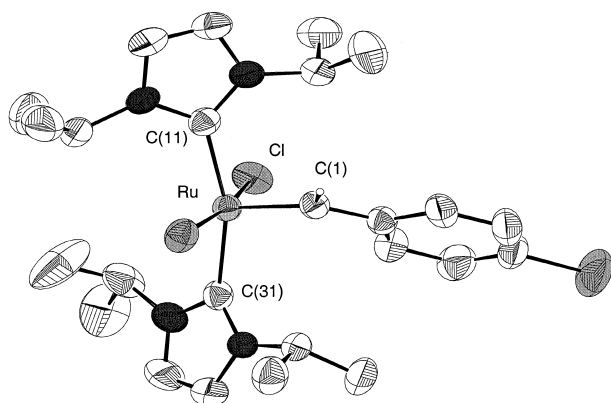
$$(3)$$

$$(4)$$

M = Cr, Mo, W; py = pyridine

5

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Figure 1. ORTEP representation of the molecular structure of the olefin metathesis catalyst **5**. Selected bond lengths [pm]: Ru-C(11) 210.7(3), Ru-C(31) 211.5(3), Ru-C(1) 182.1(3).[4k]

Full reports on the synthesis of metal complexes that are relevant to catalysis appeared in 1996 and the following year.[24–32] While in most cases imidazolin-2-ylidene complexes were described, several triazol-derived systems were reported, too.[21, 95] Salt metathesis and elimination reactions represent the prevailing synthetic access to NHC and related metal complexes. Regitz gave a first review in 1996.[35] A recent exploitation of the azolium route now covers metallocenes, such as **6** [Eq. (5)], and works for both nickelocene and chromocene. Another field of application has thus been opened.[36]
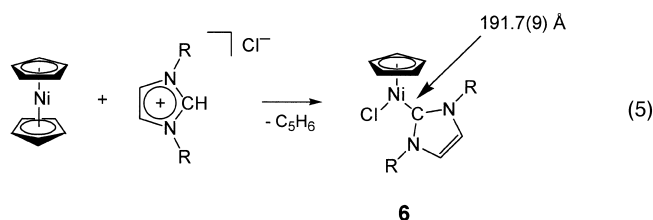

The first carbene-linked cyclophane **8** was made by Youngs et al.[37] from the ionic bis(imidazolium) precursor compound **7**, which results from a straightforward alkylation reaction of 2,6-bis(imidazolemethyl)pyridine [Eq. (6)]. Silver oxide was used to deprotonate **7** and, at the same time, introduce the metal center which adopts a linear coordination environment in the binuclear complex **9a** (X-ray diffraction study).[37] Monomeric and dimeric silver halide complexes **9b** and **9c**, respectively, are obtained in the same way,[38] while the existence of NHC–copper(I) complexes, such as **9d**, seems to depend on chelating properties of the ligands.[39] A tetranuclear, ionic complex of formula [Ag₄L₂][PF₆]₄ is derived from the N,N,C,C-macrocycle **8**.[40]

Special NHC-transfer reagents are the silver(I) complexes of type **9e**. They are formed in a simple way by treatment of Ag₂O with imidazolium salts[41] and transfer their NHC ligands to other metals, for example, palladium.[42] This technique seems to be particularly effective in the case of functionalized NHCs with "dangling" substituents. Related nickel and palladium cyclophane-type complexes of the NHC series have recently been made.[43]
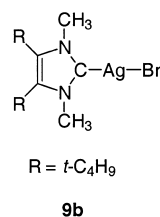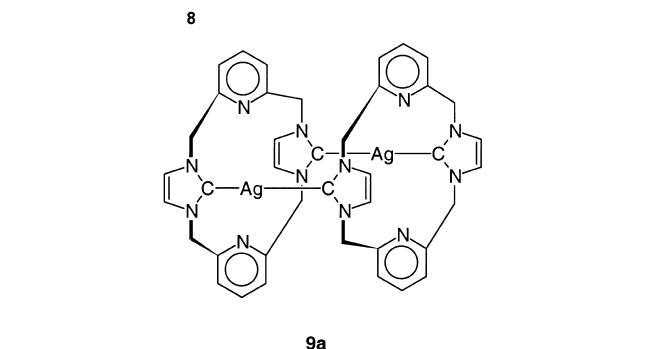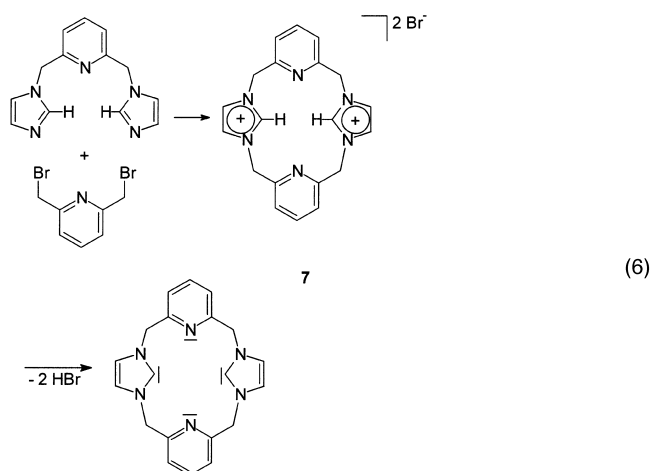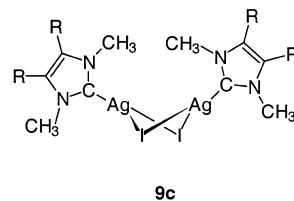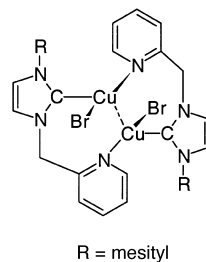
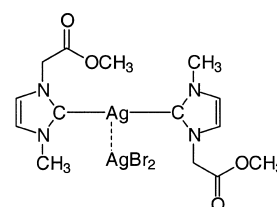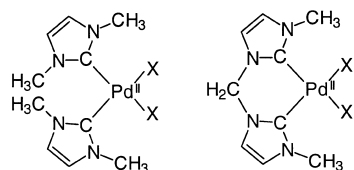## 5. Catalytic Properties

After the initial patent reports, catalytic data were released in a series of publications, the first of which appeared in 1995.[44]

5.1. Heck and Suzuki Coupling

First, the Heck coupling of aryl bromides and aryl chlorides was communicated: Complexes **10** and **11** are active upon
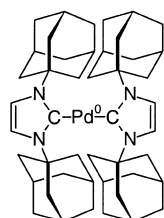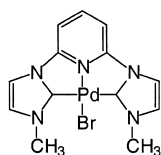
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smooth reduction with formate or hydrazine, thus generating the active Pd^0 species. Unexpected were the low catalyst loadings (ca. 10^{-3} mol %) necessary to obtain yields > 99 % in the case of bromides, and 0.1 – 1 mol % for aryl chlorides.[44] The advantageous properties of the "New structural principle
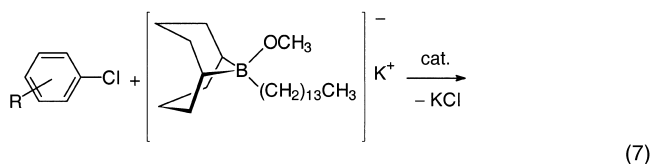

10a-c   **11a-c**

a: X = Cl; **b**: X = Br; **c**: X = I

for catalysts in homogeneous catalysis"[44] was stated as follows: "The new catalyst type described here has a series of advantageous properties and potential for development: a) high thermal and hydrolytic durability resulting from exceptionally stable M–C bonds (long shelf-life, stability to oxidation); b) easy accessibility, and c) no need for an excess of the ligand. The prospects for derivatization to water-soluble catalysts (two-phase catalysis), immobilization, and chiral modification seem promising because of the constitution of the ligands."[44] These predictions have since been shown to be correct.
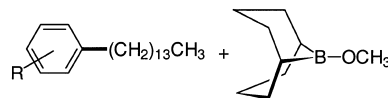
The phosphane-free NHC catalyst **12a**, either as the isolated complex or generated in situ, represents the most active coupling agent for aryl chlorides to form (substituted) biphenyls in the Suzuki cross-coupling. Reaction times between two and 48 h are sufficient at room temperature, while at 80 °C the productivity is approximately six times better.[45] The stability of the active catalyst **12b** is a result of the "pincer-type" tridentate C,N,C-ligand.[122]

(7)

R = H, 3,5-(OCH$_3$)$_2$, 4-CO$_2$CH$_3$

cat. = Pd(OAc)$_2$ + **14c**
          (2 mol%)   (4 mol%)

Highly active and very stable catalysts for Heck, Suzuki, and Sonogashira coupling reactions were discovered in certain palladium(II) complexes of NHCs with "dangling" N-substituents: Catalyst **13a** performed particularly well, giving turnover numbers (TONs) of 1.7×10^6 (Heck) and 1.1×10^5 (Suzuki) at > 85 % conversion of 4-bromoacetophenone with butyl acrylate and phenylboronic acid, respectively.[42]

After first reports on the Suzuki cross-coupling activity of carbene ancillary ligands involving aryl bromides and activated aryl chlorides,[47] non-activated, functionalized aryl chlorides were coupled successfully.[48] Typical examples are shown in Equation (8); dba = *trans,trans*-dibenzylideneacetone. The sterically demanding 1,3-bis(mesityl)imidazolinylidene (generated in situ from the imidazolium chloride **14b**) proved to be the best choice of ligand at palladium(II) centers. The C–C saturated azolium salt **14d** is now commercially available.[*]

[*] Strem Chemicals, Inc. (Kehl, Germany).

12a   **12b**

A general and user-friendly procedure for Suzuki reactions with aryl chlorides is now based on easy-to-make NHC – palladium catalysts. As shown by Fürstner et al.,[46] subtle steric effects in the NHC ligands govern the *B*-alkyl Suzuki – Miyaura coupling,[129] with the best results being obtained from the 1,3-di-2-propyl derivative [Eq. (7)], as "imidazolium additive". In several cases, the in situ technique is more efficient than the use of the preformed palladium catalyst. Other borate complexes with *c*-C$_3$H$_5$, C≡C-C$_6$H$_5$, and CH$_2$CH=CH$_2$ in place of (CH$_2$)$_{13}$CH$_3$, perform similarly well.

14a   **14b**

14c   **14d**

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$$R{-}\boxed{}{-}Cl + (OH)_2B{-}\boxed{} \xrightarrow[\substack{80\,°C,\ 1.5\ h \\ Cs_2CO_3 \\ dioxane \\ -\,[ClB(OH)_2]}]{\text{cat.}} R{-}\boxed{}{-}\boxed{} \quad \geqslant 96\% \qquad (8)$$

R = H, CH$_3$, CO$_2$CH$_3$

cat. = [Pd$_2$(dba)$_3$] + **14b**
(1.5 mol%)

High efficiencies in Heck reactions of aryl bromides were reported by the Nolan group[49] who used palladium in the presence of C,P-chelating NHC ligands derived from the sterically demanding imidazolium salt **14a**. A catalyst loading of 0.5 mol% based on palladium was sufficient to obtain good yields. Cesium carbonate turned out to be the most efficient base, much better than KOtC$_4$H$_9$, NaOAc, and K$_2$CO$_3$.[49]

Exceptionally stable nickel and palladium complexes derive from imidazolium-linked *ortho*-cyclophanes.[43] They catalyze Heck and Suzuki coupling reactions of aryl bromides and iodides with remarkable activities (TONs $7.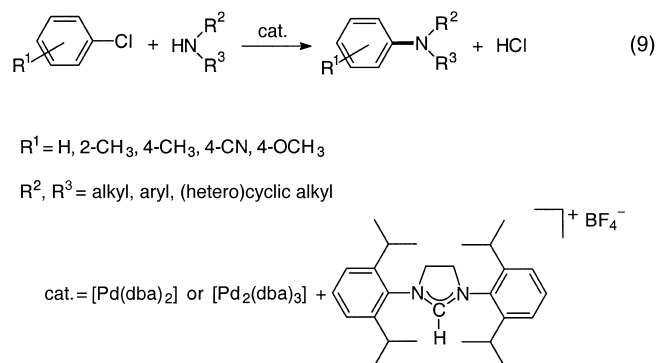1 \times 10^6$ for iodobenzene/n-butylacrylate at 140 °C; 6.8×10^5 for 4-bromo-nitrobenzene/n-butylacrylate at 140 °C).

Mixed NHC–phosphane complexes of palladium(II) provide an excellent means of increasing both the activity and stability of the active species in C−C coupling reactions of this type. An important feature seems to be the necessity of bulky NHC ligands, whereas the phosphane has to be optimized for each type of reaction.[119]

Numerous papers confirm the extraordinarily high thermal robustness of NHC catalysts. For example, the bis(carbene)–palladium(II) catalyst **13c** (X-ray diffraction study) maintains activity in the Heck coupling at least of aryl bromides at 184 °C (!) in air.[124]

5.2. Aryl Amination

Through the use of NHC catalysts the palladium-catalyzed amination of aryl halides has experienced remarkable advances in substrate scope and reaction rates. Aryl chlorides are the most desired starting materials, simply for economic reasons. Nolan et al. have introduced a sterically hindered version of imidazolylidenes in the presence of palladium(0) complexes, albeit elevated temperatures are necessary to achieve good results.[50] Instead, Hartwig's group used the dihydroimidazolylidene, see Equation (9), and obtained

$$R^1{-}\boxed{}{-}Cl + HN{\diagdown}{\overset{R^2}{\underset{R^3}{}}} \xrightarrow{\text{cat.}} R^1{-}\boxed{}{-}N{\diagdown}{\overset{R^2}{\underset{R^3}{}}} + HCl \qquad (9)$$

R^1 = H, 2-CH$_3$, 4-CH$_3$, 4-CN, 4-OCH$_3$

R^2, R^3 = alkyl, aryl, (hetero)cyclic alkyl

cat. = [Pd(dba)$_2$] or [Pd$_2$(dba)$_3$] +

yields near quantitative at room temperature when strong bases such as NaOtC$_4$H$_9$ were used to deprotonate the ligand precursor [Eq. (9)].[51] TONs as high as 5×10^3 were obtained at elevated temperatures for the reaction of morpholine with an unactivated aryl chloride, for example, chlorotoluene (7 h, 100 °C). Catalyst precursor ligands of type **14d** were used (2,6-diisopropyl instead of mesityl).

Readily available heteroaryl halides were used in the catalytic coupling with 7-azabicyclo[2.2.1]heptane. This useful type of cross-coupling amination once again employs NHC-based catalysts.[52] A typical example is given in Equation (10).

$$(10)$$

R = aryl

cat. = [Pd$_2$(dba)$_3$] or Pd(OAc)$_2$ +
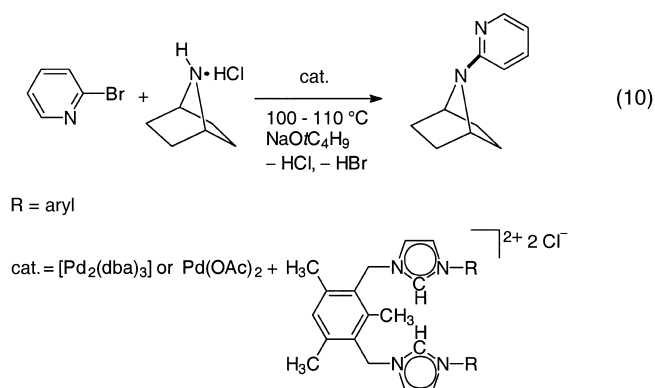
This reaction also works with heteroaryl chloride, albeit less efficiently. Any other ligand system tested so far (e.g., P(C$_6$H$_5$)$_3$, diphosphane ligands) is inferior under comparable conditions. Yields around 70% were achieved.[52] The synthetic utility of the catalyst system seems to be broad and useful for the synthesis of *N*-arylamines. Also [Ni(acac)$_2$] in combination with sterically hindered NHC ligands catalyzes the amination of aryl chlorides.[53] Future work must be aimed at avoiding the use of sodium hydride to regenerate the catalytically active nickel species.

5.3. Amide α-Arylation

Sterically hindered N-heterocyclic carbenes have become the ligands of choice for the palladium-catalyzed α-arylation of amides.[54] The Hartwig group showed in an extensive study that cyclization reactions following Equation (11) give an

$$(11)$$

cat. = Pd(OAc)$_2$ + **14b**
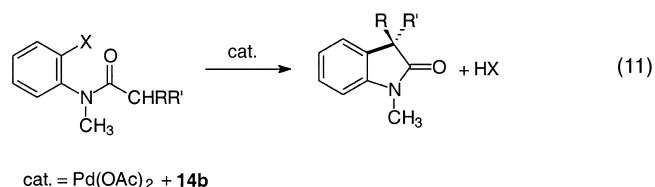
excellent performance—conversions and yields up to quantitative—when the bulky ligand precursor **14b** was employed in the presence of palladium(II) acetate. Enantiomeric excesses up to 67% were obtained when the chiral imidazolium salt **15** was used as a ligand precursor in the

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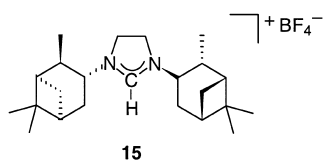
cyclization of amides where $R^1 \neq R^2$. Chiral oxindoles, important substructures in numerous biologically active molecules, are thus catalytically accessible by easy means.[54]
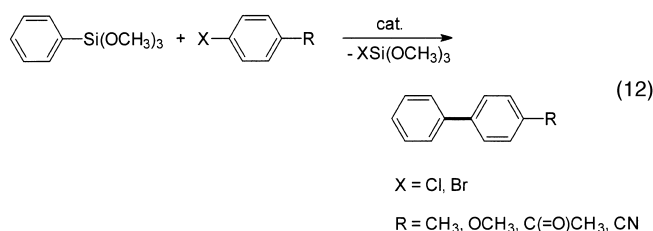
In an extension of common cross-coupling reactions, Nolan et al. have found that methoxysilanes $RSi(OCH_3)_3$ (R = vinyl, phenyl) react with aryl bromides and electron-deficient aryl chlorides according to Equation (12). Also, 2-halopyridines

$$\text{Ph-Si(OCH}_3)_3 \; + \; X\text{-C}_6\text{H}_4\text{-R} \; \xrightarrow[-\,XSi(OCH_3)_3]{\text{cat.}} \; \text{Ph-C}_6\text{H}_4\text{-R} \tag{12}$$

X = Cl, Br

R = CH_3, OCH_3, $C(=O)CH_3$, CN

can be coupled to give 2-aryl pyridines.[55] The catalyst is formed in situ from $Pd(OAc)_2$ (3 mol%) and the equimolar amount of bulky imidazolium salt **14b** (also **14c**, isopropyl in place of mesityl). The new catalysts seem to work in reactions of vinyltrimethoxysilane.[55] As in the majority of papers in this field, no turnover numbers and frequencies (TONs and TOFs) are reported, so comparison with other catalysts is not easily possible.

5.4. Hydrosilylation

Chiral N-heterocyclic carbenes, their metal complexes, and their successful applications in catalysis appeared in 1996.[56a] As an example, the hydrosilylation of acetophenone with rhodium catalysts (**16**) was used. The enantiomeric excesses reported at that time (>30%) were subsequently raised

$R^* = CH(CH_3)C_6H_5$

16

$R^1 = CH_3$, t-C_4H_9; $R^2 = CH_2C_6H_5$, i-C_3H_7

17
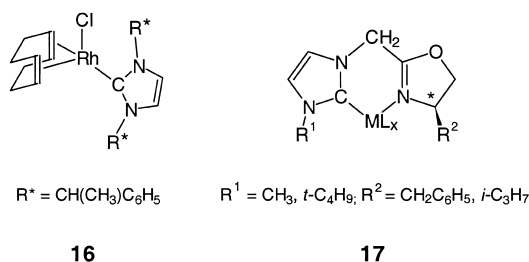
in the Ph.D. thesis work of M. Steinbeck to >70%.[4h] Simple chiral N-substituents, such as $C^*H(CH_3)C_6H_5$, were sufficient to generate significant optical induction into the prochiral substrates. Chelate complexes **17** exhibiting chiral oxazoline building blocks became available in 1998.[56b] They are made from the free imidazole $C_3N_2H_3R$ by stepwise treatment with $ClCH_2C\equiv N$, C_2H_5OH, and chiral β-aminoalcohols $HOCH_2C^*HR'NH_2$.

5.5. Olefin Metathesis

Catalytic Heck-type reactions[44, 47, 57a–e] and a new generation of olefin metathesis catalysts[57f–n] were reported in 1998/99. On both topics, NHC ligands amply demonstrated their excellence over standard phosphane ligands in homogeneous catalysis. Therefore, these subjects became a major focus of our research.[7, 57] Typical catalysts with N-heterocyclic ligands for the olefin metathesis are **18–21**, for the Heck coupling **22** and **23**. Catalysts of type **21** (mixed-metal systems) are described in ref. [56].

18

19

20

R = aryl, alkyl; R' = CH_3, cyclohexyl

21

22

23
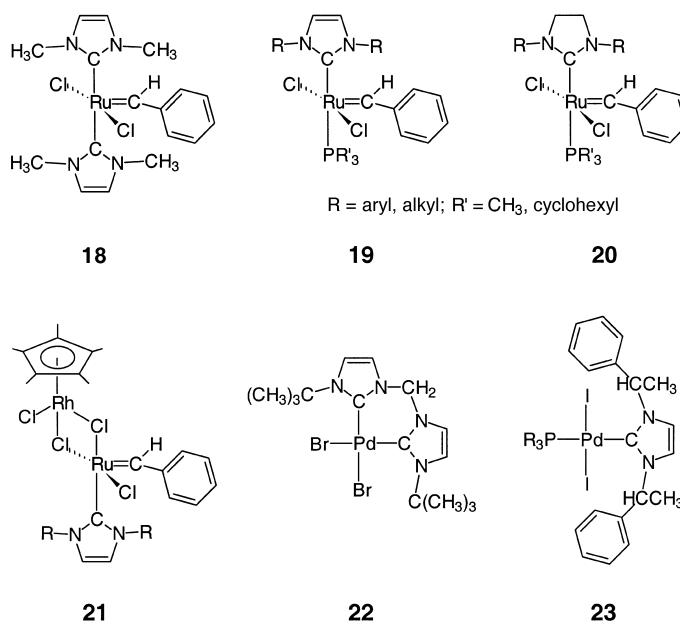
Ring-opening polymerization (ROMP), acyclic diene metathesis (ADMET), and ring-closing metathesis (RCM) are the best understood metathesis varieties as yet. Overviews on the rapid development in this area were given by Grubbs[58] and Fürstner.[59] It is clear by now that N-heterocyclic carbenes have made ruthenium the most promising "olefin-metathesis metal", predominantly because of the high tolerance to functional groups and the mild reaction conditions (normally room temperature).

In an extensive comparative study, Fürstner et al. have adjusted the metathesis catalysts of types **19** and **20** by changing the electronic and steric properties of the NHC ligands.[59b] They made a comprehensive series of new derivatives, which included those with Ru=CHR entities tethered to form a metallacycle, for example, the structurally investigated compound **21**. It was concluded that "No single catalyst outperforms all others in all possible applications".[59b] We conclude that the great structural versatility of the catalysts of types **19** and **20** is thus all the more important.

The mixed-ligand olefin metathesis catalysts such as those of types **19** and **20** were first patented[57k] and then communicated at the XVIIIth International Conference on Organometallic Chemistry in Munich,[60] before appearing in the journals in 1999.[57i] Papers by Grubbs'[61] and Nolan's groups[62] on the same subject followed a little later.[63] A

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series of patents by Grubbs et al. covers some of this work including the synthesis of the corresponding ruthenium NHC catalysts.[64a–e]

The mixed carbene/phosphane ruthenium catalysts **24** and **25** were subjected to density functional theory (DFT) calculations. They showed low dissociation barriers of the NHC ligands compared to the phosphanes.[57i] The same overall picture was obtained from palladium(0) species of the type [(NHC)Pd⁰(PR₃)].[65]

24   **25**
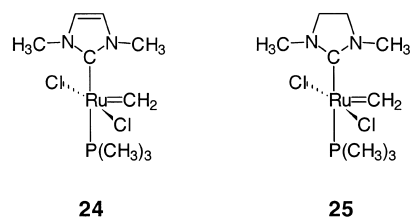
Ligand-exchange studies, however, revealed that the π-bonding of the olefin (associative mechanism) may be the decisive factor.[66] Phosphane dissociation is facilitated in [Ru(PR₃)₂Cl₂(=CHC₆H₅)], but the resulting 14e-intermediate binds the olefin better in **20**. As seen in Scheme 2, the carbene
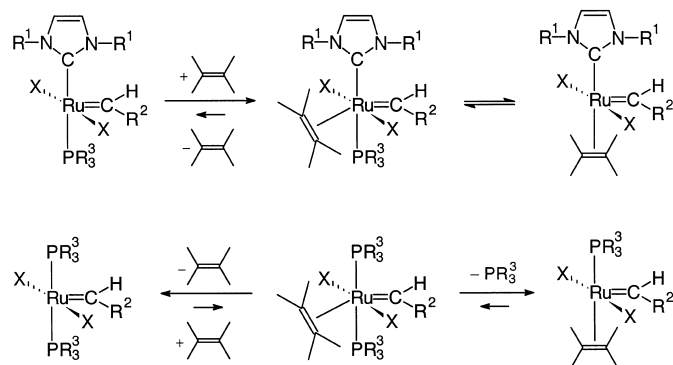
Scheme 2. Equilibria govern the activities of the ruthenium catalysts in olefin metathesis: olefin association versus phosphane dissociation; R¹ = alkyl, aryl; R² = C₆H₅; R³ = alkyl, cycloalkyl.

strengthens the olefin binding to the metal, a fact which is thought to account for the excellent activities of catalysts **19**–**21**.[66] Better olefin association may explain why the bis(NHC) complex **18** is more active than the corresponding bis(phosphane) catalyst [Ru(PCy₃)₂Cl₂(=CHC₆H₅)]. In the bis(NHC) case, the associated olefin (step 1) could strongly labilize one of the NHC ligands for subsequent dissociation. The mixed-metal catalyst **21** is more ROMP-active than its mononuclear counterpart **19** by an order of magnitude.

The C–C saturated derivatives **20** were published later in the year 1999.[67–69] Catalysts **20** exhibit excellent activities, working at monomer:catalyst ratios of up to 1 000 000:1 for ROMP. However, the stability of type **20** catalysts is clearly lower than that of their C–C unsaturated counterparts. Various applications in the ring-closing metathesis of olefins were reported recently, thus showing the great interest in this field.[69–71]

As a further exploitation of the outstanding carbene effects, the ruthenium complex **28** was recently generated in situ by Grubbs et al.[72] and successfully employed in the olefin metathesis. For this purpose, a η¹-vinylidene precatalyst **27** was generated by a standard method from the *p*-cymene complex **26** and converted into the active catalyst by a olefin metathesis reaction itself (Scheme 3). The major advantages
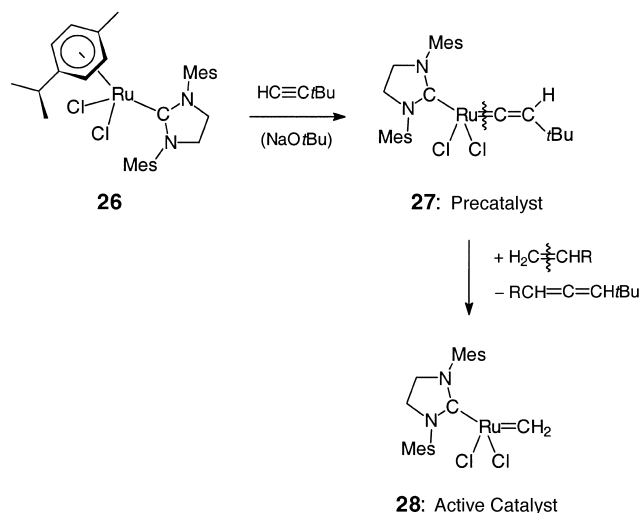
Scheme 3. Generation of the active CH₂ complex **28** by olefin metathesis of the vinylidene precursor compound **27**.

of these catalysts are that they are compatible with functional groups (heteroatoms) and protic solvent systems, and that they work under mild conditions, normally at room temperature. Contributions in the area of olefin metathesis came also from Blechert's group.[73] In a joint effort, the stereoselective ring-closing metathesis (RCM) following Equation (13) was developed with catalysts **18** and **19**, with the latter (R = CH(CH₃)C₆H₅; R′ = cyclo-C₆H₁₁) yielding 40% enantiomeric excess.[4k, 4n, 73] This results holds promise for an improvement of the desymmetrization of prochiral olefins.

R = C₆H₅

(13)
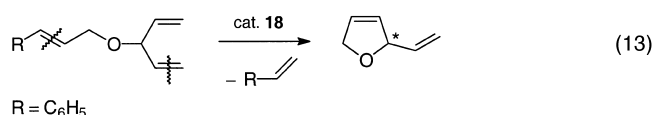
In a similar approach, methylene complexes of type **25** were treated with 1,1-difluorethylene, with the result that the metathesis exchange reaction $L_xRu=CH_2 + F_2C=CH_2 \rightleftharpoons L_xRu=CF_2 + H_2C=CH_2$ occurred.[74] This method is an easy means to generate dihalocarbene metal complexes that are rare in organometallic chemistry.

5.6. Metathesis Cross-Coupling

Not only has the synthesis of trisubstituted and functionalized olefins become possible through the catalyst **29a**,[75] there is also the cross-metathesis of α,β-saturated amides with terminal olefins, for example, styrene, is also catalyzed by this

29a   **29b**
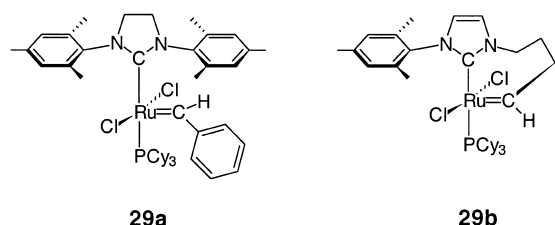
compound.[70] Equation (14) shows one out of numerous examples (THP = tetrahydropyranyl). More electron-rich amides give poorer yields because of carbonyl chelation at the catalytic center. Nevertheless, this is at present the most
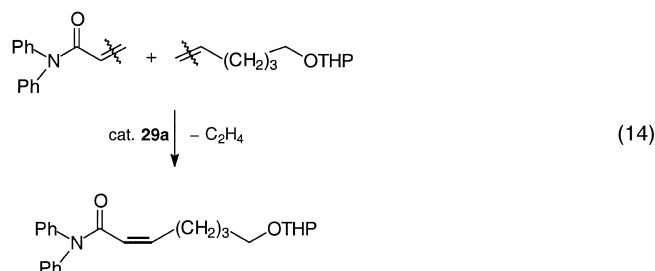
promising approach to a difficult reaction. The chelate congener **29b** of type **19** catalysts combines the steric bulk (N-mesityl) with enhanced thermal stability and steric constraints.[59b]

This type of catalyst was recently used to cyclize N-allyl-N-isopropyl acrylamide by ethylene release (α, ω) in a metathetical approach.[120] The first product is N-isopropyl-3-pyrrolin-2-one. Upon warming, a radical reaction with the same catalyst leads to a chlorinated product.[120]

5.7. Sonogashira Coupling
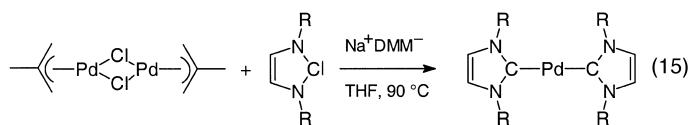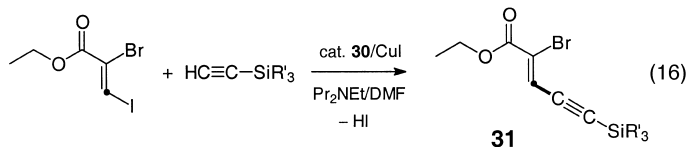
The palladium(0) species **30**, which is active in the Heck and Suzuki C–C-coupling,[76] can also be employed to furnish a Sonogashira-type coupling to make the bromo-eneyne **31**, a common building block of natural products [Eq. (16)]. The

DMM⁻ = dimethylmalonate; R = t-C₄H₉   **30**

analogy with the standard catalyst [Pd{P(C₆H₅)₃}₄] was noted by the authors who, at the same time, presented a new, simple synthesis of Pd⁰ bis(carbene) complexes: (π-allyl)pallad-

ium(II) chloride is treated with the free carbene under reducing conditions [Eq. (15)]. Copper-free conditions were reported for the Sonogashira coupling of aryl bromides with alkynylsilanes on Pd(OAc)₂/**14b** or **14d**.[121]

5.8. Ethylene/Carbon Monoxide Copolymerization

Yet another catalytic application was found in 1999: dicationic palladium(II) NHC complexes such as **32** catalyze the copolymerization of C₂H₄ and CO to give high molecular

R = mesityl, X = PF₆
R = CH₃, X = BF₄

32
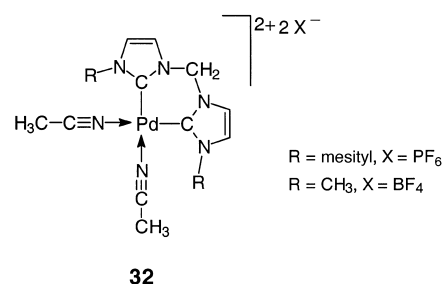
weight, strictly alternating poly(C₂H₄-alt-CO) under mild conditions and low pressure.[77] Polyketones play a considerable role in numerous technical applications, particularly in the car industries.

5.9. Kumada Coupling (Grignard Cross-Coupling)

A promising entry into the Grignard cross-coupling of aryl chlorides as sketched in Equation (17) was opened by NHC catalysts of nickel.[78] Generated in situ from [Ni(acac)₂] and
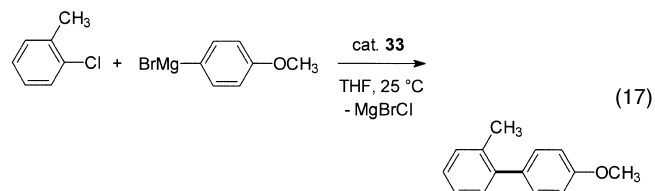
imidazolium salts, the catalysts—very likely zero-valent nickel species such as **33 a, b**—effect the C–C coupling even at room temperature (3 mol% Ni). All previous catalysts required

33a   R = CH₃, i-C₃H₇   **33b**
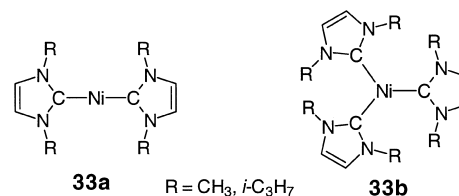
much higher temperatures, with the result that they suffer from insufficient selectivity because of the formation of numerous side products. The related palladium(0) catalysts mentioned by Nolan et al.[79] are less active than the nickel(0)

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systems; they require higher temperatures, typically around 80 °C.

The first case of catalytic C−F bond activation in conjunction with selective C−C bond formation was observed with NHC−nickel catalysts.[80] Once again, a sterically demanding carbene **14c**, was successful and simply generated in situ from [Ni(acac)$_2$] and the azolium salt [Eq. (18)]. The yields of the desired heterocoupling products were as high as 97 % (R^1 = CF$_3$). Both the product selectivity and the Hammett correlation suggest a polar reaction and disfavor the radical pathways seen to participate when NiCl$_2$ alone is used as a coupling reagent.[80]

$$R^1 \!-\!\!\!\!\bigcirc\!\!\!\!-F \;+\; BrMg\!-\!\!\!\!\bigcirc\!\!\!\!-R^2 \xrightarrow[\substack{25\,°C,\,18h \\ -MgBrF}]{cat.} R^1\!-\!\!\!\!\bigcirc\!\!-\!\!\bigcirc\!\!\!\!-R^2 \tag{18}$$

R^1 = H, CF$_3$, OCH$_3$

R^2 = H, 4-t-C$_4$H$_9$, 2,4,6-(CH$_3$)$_3$

cat. = [Ni(acac)$_2$] + **14c**
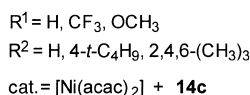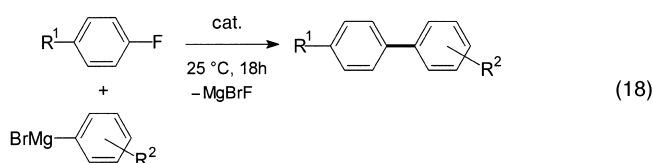
5.10. Stille Coupling

Another common type of C−C coupling, named after John Stille, works with catalysts that were generated from Pd(OAc)$_2$ and imidazolium salts.[81] Equation (19) shows a typical example, which works well in 1,4-dioxane at 100 °C (12 h) in the presence of tetrabutylammonium chloride.

$$(19)$$

cat. = Pd(OAc)$_2$ + **14c**

5.11. C−H Activation

Certain NHC complexes of iridium have a strong tendency to undergo C−H activation. For example, the dimethyl iridium(I) species **34** undergoes loss of methane under protolytic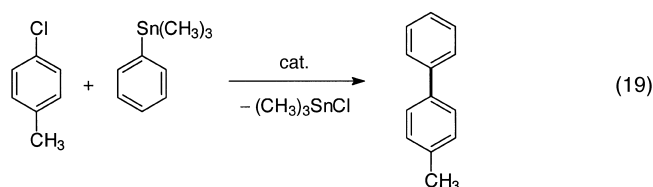 conditions, and forms the internal π-olefin complex **35** in a stepwise manner and in high yields by β-H migration [Eq. (20)].[82] The related process occurs with the isopropyl derivative **36** [Eq. (21)].[82] However, the stable dicationic **39** can be generated without CH activation from the dichloro complex (**38**) instead of the dimethyl precursor compound [Eq. (22)].[82] This story tells us that 1) chelate structures of NHC−metal complexes can spontaneously occur by C−H activation, and 2) the latter reaction is principally feasible with NHC−metal catalysts.

$$(20)$$

34 → **35**

$$(21)$$

36 → **37**

$$(22)$$

R = CH(CH$_3$)$_2$, cyclohexyl

38   **39**
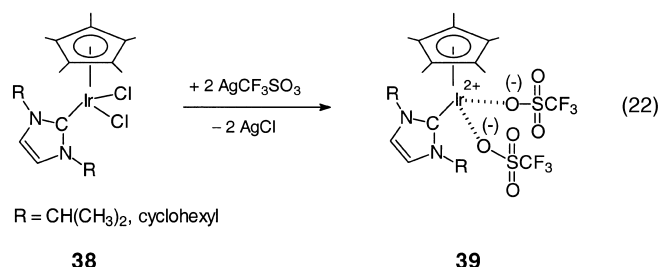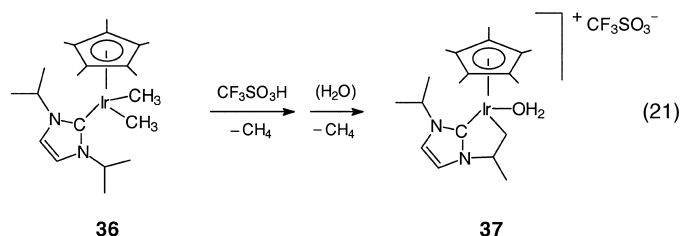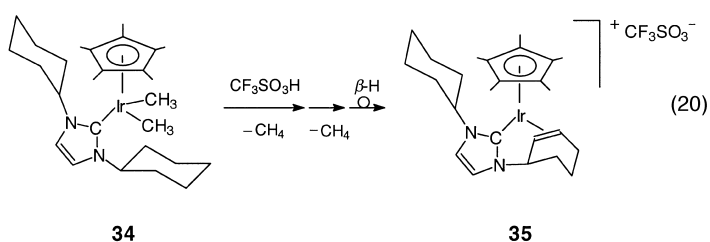
As a matter of fact, a new approach to the activation of the greenhouse gas methane was opened by virtue of the NHC−palladium complex **11b** (tC$_4$H$_9$ in place of CH$_3$): Trifluoroacetic anhydride yielded the methyl ester upon treatment with methane in the presence of potassium peroxodisulfate[83, 84] according to Equtions (23a) and (23b). Remarkable are the

$$CH_4 + \substack{CF_3C\!\!=\!\!O \\ CF_3C\!\!=\!\!O} \xrightarrow{(CF_3CO_2H)} CF_3C\substack{=O \\ OCH_3} + CF_3C\substack{=O \\ OH} \tag{23a}$$

$$\tfrac{1}{2} K_2S_2O_8 \quad\quad KHSO_4 \tag{23b}$$
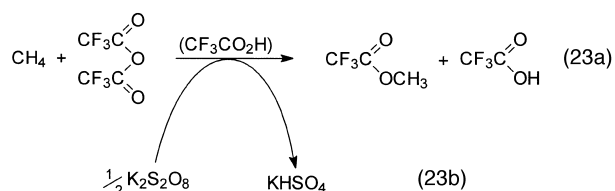
relatively mild reaction conditions: 20–30 bar CH$_4$, 80–90 °C. The peroxodisulfate provides the redox equivalents necessary to balance the conversion CH$_4$ → H$^+$ + CH$_3^+$ + 2 e$^-$/ O$_2^{2-}$ + 2 e$^-$ → 2 O^{2-}. Neither the Periana (Pt) nor the Sheldon system (Pd) gives any methane activation under such conditions.

5.12. Hydrogenation, Hydroformylation

These olefin functionalization reactions work with rhodium(I) catalysts of type **16**, as mentioned in previous reviews[7, 56] based on the Ph.D. theses of M. Steinbeck,[4h] J. Fischer,[4d] and C. Köcher.[4g, 29] Detailed investigations are

required in this promising, industrially relevant area. The concept of two-phase catalysis has plenty of potential here, especially since successes were achieved with this principle in the industrial Ruhrchemie/Rhône-Poulenc process.[85, 86] Water-soluble NHC–metal complexes are known, too.[30]

Recent reports predict a great future of NHC catalysts in alkene hydrogenation: Using sterically hindered ligands, the Nolan group achieved TONs up to 2.4×10^5 at only 4 bar hydrogen pressure at $100\,^\circ$C for the substrate 1-hexene.[87] However, the ruthenium(II) catalysts tested work well only at elevated temperatures but not under the mild conditions typical of the classical Wilkinson (Rh) catalyst. Also, the replacement of phosphane by the carbene [Eq. (24)] does not dramatically improve the catalyst's activity. The 14e intermediate [HRu(CO)(Cl)L] is thought to be the active species, the formation of which is enhanced by addition of $HBF_4 \cdot O(C_2H_5)_2$.[87] Catalyst **40** has a distorted trigonal-pyramidal structure in the solid state.[87]

(24)
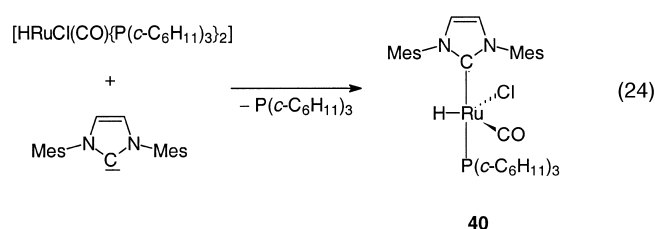
Based on our results,[29] vinylarenes were subjected to hydroformylation with NHC-rhodium catalysts. High selectivities were obtained for the branched isomer,[88] possible candidates in the synthesis of important pharmaceuticals, such as ibuprofen. Branched-to-linear ratios of up to 97:3 were obtained with styrene and some of its derivatives in the presence of square-planar catalysts **41a** or **41b** made by ligand exchange from Wilkinson's catalyst $[RhCl\{P(C_6H_5)_3\}_3]$. Unfortunately, the catalytic activities are still low (TOF $< 10\,h^{-1}$), in accord with earlier reports on catalyst **16**.[4g, 29]

41a L = $P(C_6H_5)_3$
41b L = CO

R = bulky substituent, e. g. mesityl
41c
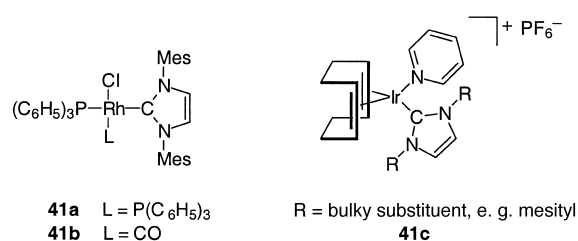
Cationic NHC–iridium(I) catalysts of type **41c** were used in olefin hydrogenation[89] and in transfer hydrogenation with ketones.[90] The catalyst stability is at the expense of activity in these cases. However, increased hydrogen pressure at $50\,^\circ$C gives acceptable results.[89]

5.13. Furan Synthesis and Alkyne Coupling

A quasi-catalytic furan synthesis by the rearrangement reaction following Equation (25) was reported by Dixneuf

(25)

42

43
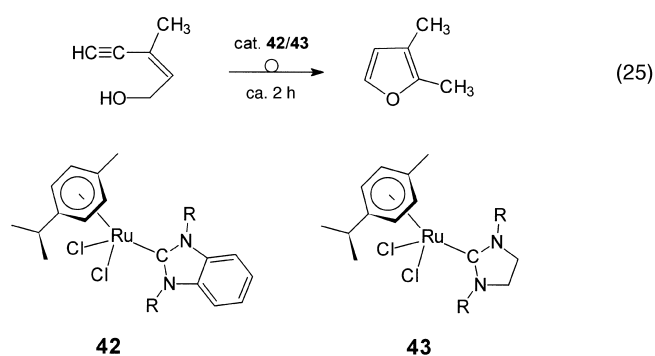
et al.[91] The catalyst **42** is a benzimidazolin-2-ylidene complex of ruthenium.[91a] Yields of around 80% were reported (1 mol% cat., $80\,^\circ$C, 25 h). In a subsequent paper, the improved catalyst **43** was used.[91b]

An alkyne coupling reaction following Equation (26 a) was described by Herrmann and Baratta.[27a] Once again, ruthenium is required as the mediating metal. The NHC complex **45** used for this purpose[27b] associates 2e ligands such as phosphanes and carbenes to form tetracoordinate adducts **46**, [Eq. (26b)]. The π addition of alkynes clearly facilitates the

(26a)

44a (trans)   **44b** (cis)   **44c**

(26b)

45

46

R = cyclohexyl, mesityl

L = CO, $P(C_6H_5)_3$, NC_5H_5, $CH(CO_2Et)$
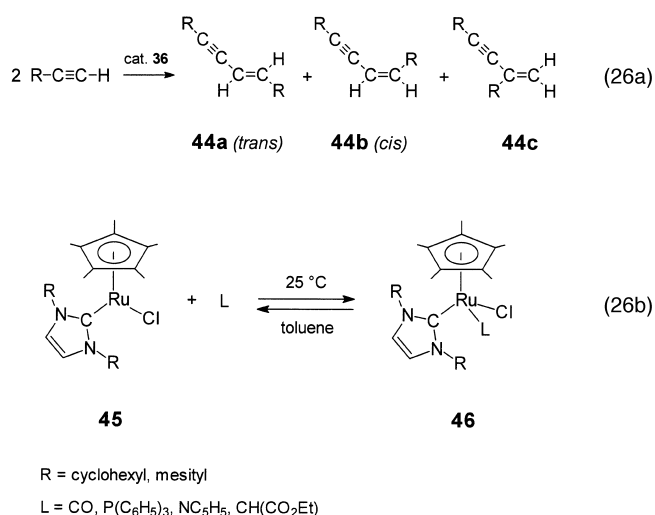
consecutive C–C-coupling. Conversions as high as quantitative were achieved with R = C_6H_5, C_6H_4-p-CH_3, $SiMe_3$ within 5–10 min. In most cases, the *trans*-coupling product **44a** dominated, with the exception of R = $SiMe_3$ where the α-olefin **44c** was formed $>92\%$. Maximum turnovers of TOF $= 10\,320$ (TON $= 860$) were reported so far.[27a]

Highly functionalized enones are accessible from readily available acyclic precursor compounds when NHC–ruthenium metathesis catalysts such as **20** (R = mesityl) are applied. Combined with efficient protodesilylations, this process gives conversions up to 98% at $60\,^\circ$C, starting from appropriate siloxyalkynes.[126] Equation (27) represents an excellent example of an alkene–siloxyalkyne metathesis.

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(27)
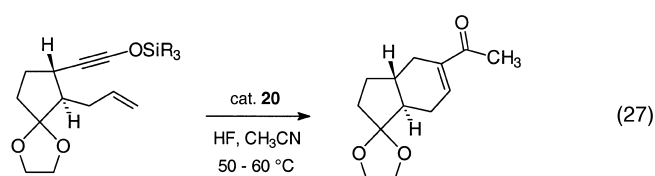
5.14. Olefin Cyclopropanation

Rhodium(I) and ruthenium(II) complexes **47** containing NHCs with hemilabile, dangling ether moieties were successfully used as catalysts for the cyclopropanation of olefins with diazoalkanes, [Eq. (28)].[92] This reaction is of industrial use in the synthesis of insecticides.

(28)

cat. =

47a   **47b**

R = alkyl; L = P(C$_6$H$_5$)$_3$
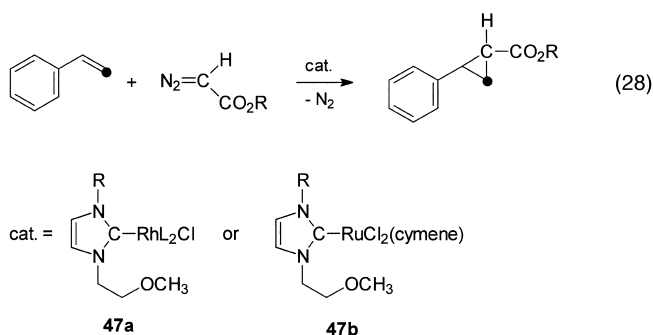
5.15. Arylation and Alkenylation of Aldehydes

A convenient, user-friendly method for the addition of aryl or alkenyl boronic acids to aldehydes employs a catalyst formed in situ from RhCl$_3$ · 3 H$_2$O, the bulky imidazolium salt **14b**, and inexpensive aqueous bases.[93] The addition is chemoselective for aldehydes and compatible with many functional groups in both reaction partners. Secondary aldehydes—possibly asymmetric varieties in the future—are thus formed according to Equation (29) in good to excellent yields.[93]

(29)

R^1= alkyl, aryl   cat. = RhCl$_3$ • 3H$_2$O + **14b**
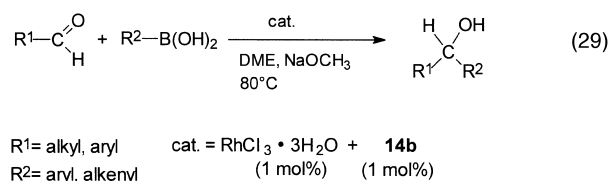R^2= aryl, alkenyl   (1 mol%)   (1 mol%)

5.16. Reduction of Aryl Halides

Dehalogenation of aryl halides was performed when nickel(0) catalysts (3 mol %) of bulky N-heterocyclic carbenes were used in the presence of β-hydrogen containing alkoxides, with the latter acting as reducing agents.[128] Most efficient once again was the carbene derived from the imidazolium salt **14b** by in situ deprotonation by the alkoxide (normally

NaOiC$_3$H$_7$). Mild reaction conditions (THF, 65 °C, 1–3 h) are convincing indications that this new way of replacing halides (F, Cl, Br, I) by hydrogen can find practical use through further improvement.

5.17. Atom-Transfer Radical Polymerization

Styrene and methyl methacrylate undergo atom transfer radical polymerization (ATRP) in the presence of catalysts possessing donating NHC ligands. Thus, the tetrahedral iron(II) complex **48**, reported by Grubbs et al.,[94] works at 85 °C for styrene to provide a polymer with low polydispersities ($M_w/M_n \approx 1.1$). ATRP is a method to control free-radical polymerizations. Compound **48** gives the highest polymerization rates seen for ATRP in organic solvents to date.[94]

48
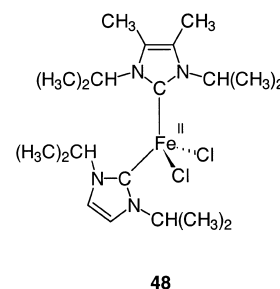
5.18. Asymmetric Catalysis

Apart from a few examples, stereoselective synthesis has to date not been generally investigated with NHC catalysts. The number of reported successes in correspondingly small. In the Enders' group in particular, however, triazolinylidene ligands have developed a convincing potential.[95] Chiral catalysts such as **49** and **50** (BARF = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) gave moderate optical inductions up to 44 %

49a   **49b**

R* = CH(CH$_3$)(C$_6$H$_5$),

50   **51**
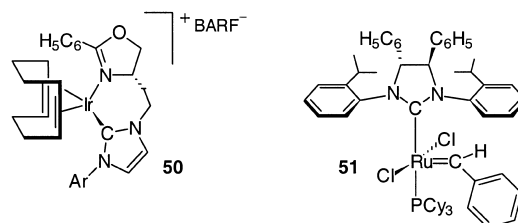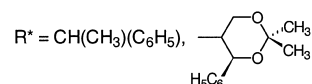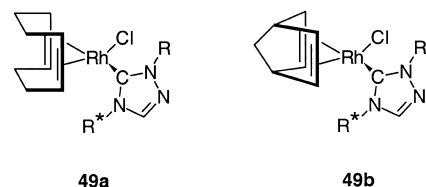
in hydrosilylation reactions.[95a, d, 96] A number of optically pure, both soluble and immobilized rhodium, ruthenium, and palladium complexes were synthesized and characterized.[95] Catalyst **51** was used for the desymmetrization of *meso*

compounds. For example the asymmetric catalyst effects the conversion of 4-allyloxy-3,5-dimethyl-2,5-heptadiene into (2S)-((2Z)-buten-2-yl)-3-methyl-2,5-dihydrofuran in 90% enantiomeric excess.[120]

Good to excellent stereoselectivities in the hydrogenation especially of trisubstituted alkenes (25°C, 50 bar H_2) were obtained by virtue of the NHC-chelate iridium(I) catalyst 50.[123] The cationic catalyst is modeled after the basic structure of 41c.[90] This was the first report of high optical induction using electron-rich carbene ligands in catalytic processes.

Chiral silver(I) diaminocarbenes act as carbene transfer agents to copper salts. The products catalyze the addition of diethylzinc to c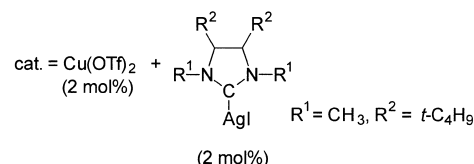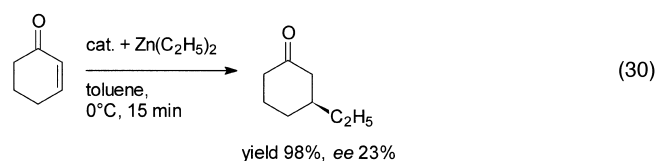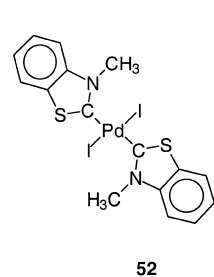yclohexanone[97] according to Equation (30). The optical yields are certainly subject to further improvement but the easy generation of the catalyst is striking indeed.

(30)

cat. = Cu(OTf)₂ (2 mol%) + [diaminocarbene AgI structure] $R^1 = CH_3$, $R^2 = t\text{-}C_4H_9$ (2 mol%)

Imidazolium salts are among the best investigated ionic liquids. Their beneficial effects in catalytic processes may in part originate from their easy conversion into NHC-metal complexes, since coligands of reasonable basicity are known to induce deprotonation.[24, 29] Reactions following Equation (31) to convert the imidazolium metallate 53a into the

(31)

53a   53b

NHC complex 53b may then occur under a pseudo "ionic liquid effect". A Russian report is indicative of the chemistry following Equation (31) but the product was not unambiguously characterized because of concomitant decomposition reactions.[101] Similarly, the alkoxy rhodium complex 54a undergoes spontaneous formation of the NHC derivative 54b [Eq. (32)] a reaction which is now a standard synthesis[19].

(32)

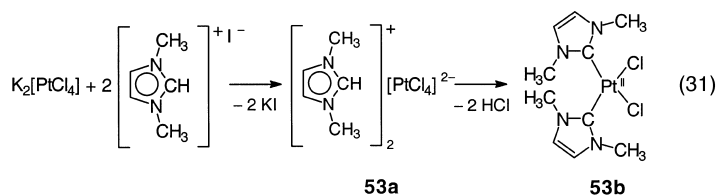R = C₂H₅ 54a   54b

6. Ionic Liquid Effects

Great progress in catalytic C–C coupling reactions was recently made with non-aqueous ionic liquids ("NAIL").[98] As demonstrated for the Heck coupling of aryl halides, molten tetraalkylammonium halides (particularly [N(C₄H₉)₄]Br) improved both the stability and activity of almost every known palladium catalyst system compared to standard solvents such as DMF, N,N-dimethyl acetamide, or 1-methyl 2-pyrrolidone.[98b] Remarkably, the yield with the NHC catalysts 10 improves from 20% to >99% for the coupling of bromobenzene with styrene. Effects of similar magnitude were reported for low reactive chloroarenes.[98b]

Ionic solvents are relatively expensive. However, they can be recycled, without loss of catalyst. In the mechanistic considerations, anionic catalyst species of type [Br-Pd⁰-Ligand]⁻ are invoked, at least for the NHC- and palladacycle catalyst systems Pd^{II}, albeit Pd^{II}/Pd^{IV} equilibria cannot be ruled out.[98b]
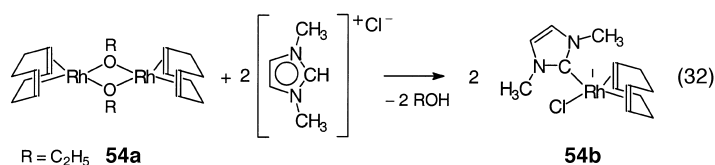
52

The ionic-liquid concept[98] was taken up by the Italian group of Calò.[99, 100] They used related palladium complexes of benzothiazole carbene ligands 52[99b] in a melt of tetra(n-butyl)ammonium salts to carry out the coupling of aryl bromides with 3-hydroxy-2-methylene alkanoates. β-Aryl-ketones are thus formed in good yields.

7. Avoiding Catalyst Leaching

Polymer-supported NHC catalysts were published in 2000: Good results in the Heck coupling reactions were achieved with polymers on the basis of the Wang resin (4-bromomethyl)phenoxymethylpolystyrene. Hardly any catalyst leaching was observed, which supported earlier proposals that the NHCs are strongly bound to the catalyst metal center.[7] The methodology is outlined in Scheme 4 and described in full detail in refs. [41, 65]

An alternative strategy was pursued by Blechert et al. to obtain a polymer-supported olefin metathesis catalyst. In this case, the polymer-anchored ligand precursor was built up first and then treated with the catalyst metal compound. Scheme 5 outlines this straightforward methodology.[102] Excellent results were obtained in the ring-closing metathesis and the cross-metathesis, for example, yne–ene metathesis.[102] Yao developed a soluble poly(ethylene glycol) (PEG) bound polymer catalyst of type 18 which is immobilized through the phenylalkylidene moiety to a PEG support.[103]

Four consecutive ring-closing metathesis steps were achieved by Barrett et al. with the help of recyclable catalysts of type 55.[104] Here, the classical carbene that initiates the metathesis is itself anchored to the vinylated polystyrene resin by a metathetical step as shown in Equation (33). This catalyst is more efficient in olefin metathesis, especially in RCM, than the congener derived from the bis(phosphane) ruthenium complex [(PR₃²)₂RuCl₂(=CHR³)]. The working principle of

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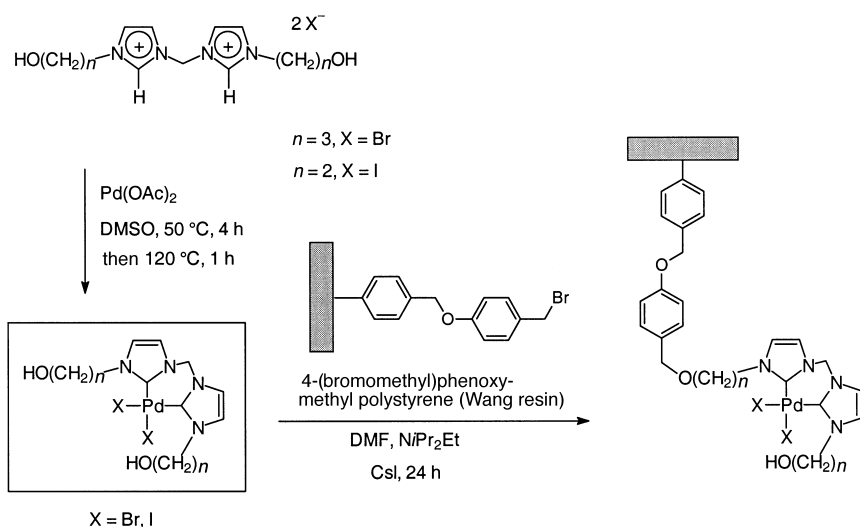
Scheme 4. Immobilization of a NHC palladium catalyst according to Herrmann et al.[65]
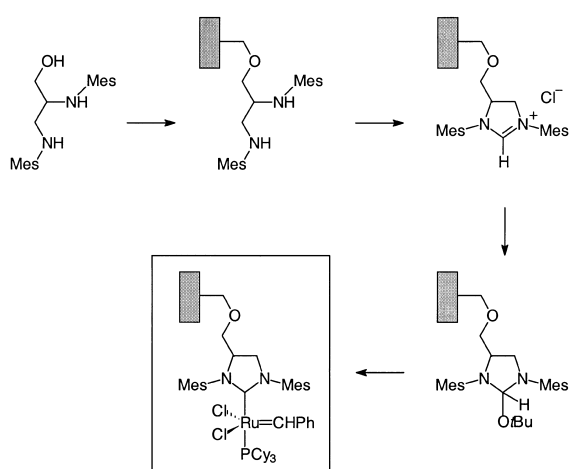
Scheme 5. Immobilization of a NHC ruthenium catalyst according to Blechert et al.[102]
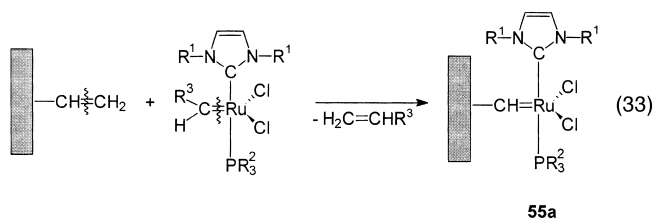
R^1 = mesityl; R^2 = c-C_6H_{11}; R^3 = C_6H_5

this new type of "boomerang" catalyst is based on the reversible release of the metallacarbene moiety into the solution phase from the resin, and recovery by the support after reaction. The ruthenium contamination of the products is thus minimized. Beyond that, catalyst recovery and recyclability are improved.[104]

An elegant approach to immobilized olefin-metathesis catalysts was reported by Buchmeister et al.[125] They prepared monolithic materials exhibiting a particle diameter of 1.5 ± 0.5 μm, by the metathetic copolymerization of appropriate olefins. The monolithic carrier is then functionalized

by "living" NHC-ruthenium termini (from animidazolium precursor and $[Cl_2Ru(PCy_3)_2=CHC_6H_5]$). The catalyst 55b (Ad = adamantyl) thus formed shows high activities in both the ring-closing and ring-opening metathesis, with cis/trans ratios in the polymeric products that correspond exactly to what has been seen in homogeneous catalysis. The lack of any microporosity in the catalysts 55b minimizes diffusion effects to a large extent, thus giving high turnover frequencies often beyond those of homogeneous catalysts.
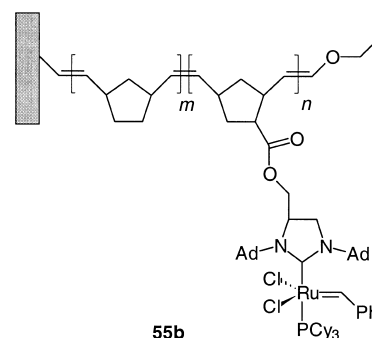
An alternative concept—immobilization of olefin metathesis NHC-catalysts on a monolithic material prepared by a sol–gel technique—was presented by Hoveyda et al.[127] They made ruthenium-containing glass pellets that efficiently promote olefin metathesis reactions. The catalysts are robust and stable in air.

8. 2,3-Dihydro-1H-imidazol-2-ylidenes

C−C saturated N-heterocyclic carbenes are expected to be yet stronger σ-donor ligands than their C−C unsaturated counterparts. While the five- and six-membered compounds 56 and 57, respectively, have been documented in metal

R^1 = CH_3, t-C_4H_9

R^2 = CH_3, cyclohexyl

X = Cl, Br
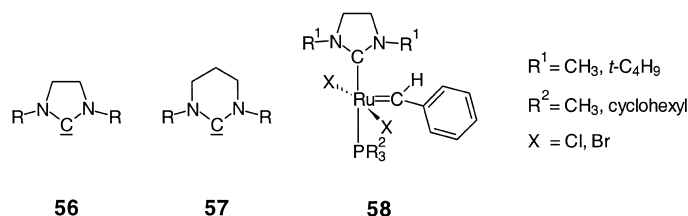
complexes for quite some time.[105] Thus, the examples 58 were independently reported by the research groups of Grubbs[68] and Herrmann,[67] and showed that the activity for the olefin metathesis is—with the reactions investigated—higher than that of the C−C unsaturated analogues. However, the catalyst stability seems generally lower.

1304

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9. Acyclic Bis(amino)carbenes

A new approach in catalysis is the use of the "open-chained" bis(amino)carbenes **59–61**. They are accessible from the corresponding formamidinium salts according to

59   **60**   **61**
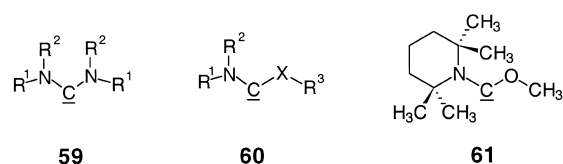
R^1, R^2 = alkyl, aryl; R^3 = aryl; X = O, S

Equation (34), as shown by Alder et al.[107] It was found that the free carbenes are stable for a number of substituents R^1 and R^2, with the most investigated members of **59** carrying

$$ (34) $$

59
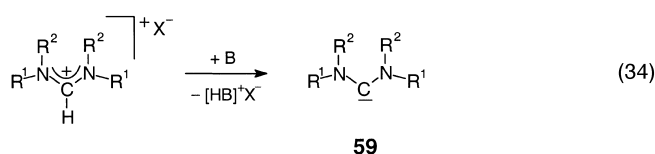
two diisopropylamino or two piperidyl substituents.[108] Neutral and anionic deprotonation agents can be used, preferentially Li[N(iC$_3$H$_7$)$_2$] or K[N(SiMe$_3$)$_2$] in liquid ammonia, to generate this specific subgroup of N-functionalized carbenes. Several metal complexes were synthesized with these ligands, for example **62**.[106, 108] The stable aminooxy- and aminothiocarbenes such as **60** described recently by Alder et al.[107b] are close to the classical Fischer-type carbene complexes.

σ-coordination   π-coordination
                   (side on)

62   **63**
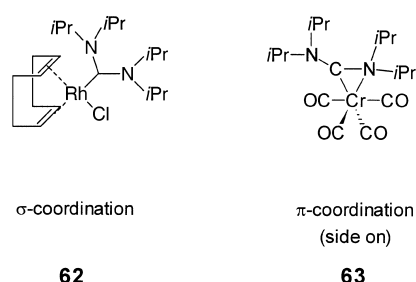
It is worth of mention that bis(amino)carbenes can (side-on) coordinate to transition metals. For example, the tetra-carbonylchromium(0) complex **63** has a η^2(C,N)-coordination, with bond lengths of 192.0(1) pm for the carbene–chromium bond and 220.7(1) pm for the nitrogen–chromium bond. Accordingly, the respective C–N bonds differ by around 15 pm.[34] This effect may very well stabilize the under-coordinated "resting state" of N-heterocyclic carbene catalysts.

10. Theoretical Studies

The bonding theory of N-heterocyclic carbenes with regard to their cyclic structure and their metal bonding has been the subject of theoretical studies that are covered in previous review articles.[7] Experimental and theoretical charge-density studies revealed that free NHCs have somewhat less π-electron delocalization than in their metal complexes.[34] Acyclic bis(amino)carbenes (e.g., **59**) donate significantly more electron density to metals than their cyclic counterparts.[108a] Here, the nitrogen lone pairs can participate in intramolecular coordination to the metal.[34] Recent density functional theory (DFT) studies predict that oxidative addition of imidazolium salts to platinum(0) is an exothermic process.[109] This result is consistent with the experimental finding that a hydridoplatinum(II) NHC complex is thus formed.

Kinetic and DFT studies on alkyl-carbene elimination from NHC–palladium(II) complexes revealed a new type of reductive elimination with implications for catalysis:[110] Elimination of methylimidazolium cations from **64** [Eq. (35)] proceeds in a concerted way and suggests similarities in the reactivity of M–R and M–N(NHC) bonds. This finding once again highlights the principal differences between conventional metal–carbenes [L$_x$M=CR^{1}R^2] and N-heterocyclic carbenes.[110]

$$ (35) $$

64

R = C$_6$H$_5$, c-C$_6$H$_{11}$, OC$_6$H$_5$
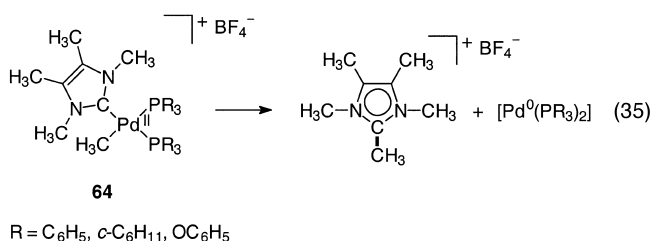
11. Perspectives

What have we learned from the foregoing discussion? N-Heterocyclic carbenes (NHCs) clearly are not just "phosphane mimics" as they are sometimes called in the literature. They are more than that, they are versatile and easy-to-make ligands with great potential in homogeneous catalysis. There is increasing experimental evidence that NHC–metal catalysts surpass their phosphane congeners in both activity and scope of application. The most convincing and best studied example so far has been olefin metathesis, for which reaction ruthenium–NHC catalysts were exploited independently by two research groups. Here, it became evident that organo-phosphanes—ubiquitous standard ligands in organometallic chemistry—give poorer catalytic performance than NHC ligands in structurally analogous catalysts. The NHC–ruthenium complexes are the most active catalysts of olefin metathesis known to date. They tolerate functional groups, and work at ambient temperature. NHCs strongly bind to typical catalyst metals, but do not undergo ligand dissociation, at least in the hitherto investigated cases.

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Structural versatility is a great strength of N-heterocyclic carbenes (Scheme 6): chirality (a), functionalization (b), immobilization (c), water solubility (d), and chelate effects (e) can be achieved by easy means. All these varieties have principally been verified, and stable transition metal complexes were described in all cases.[4, 7]
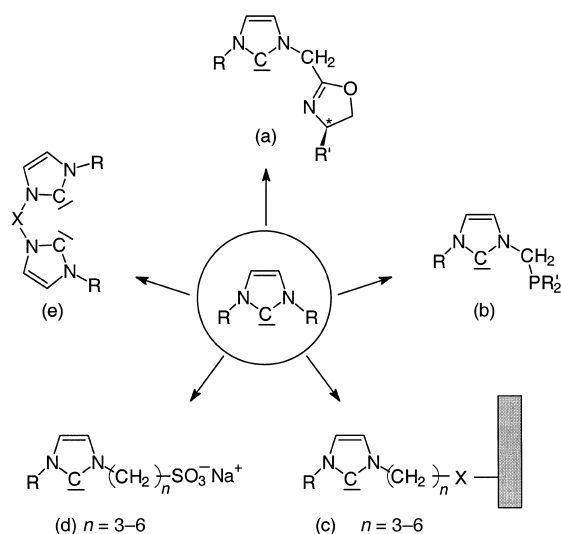
Scheme 6. The versatility of ylidenes derived from imidazolium compounds.

Numerous new varieties of NHC-metal complexes were reported within a short period of time, among them the first alkaline earth complexes,[33] the silver salt **65** with its strained structure,[111] the pyridyl – NHC palladium chelate **66**,[112] the nine-membered rhodium complex **68**[29] and the eleven-membered chiral palladium complex **69**.[113] The electronic effects in chelating NHC – metal complexes may also be adjusted for certain purposes by changing the bridging groups.
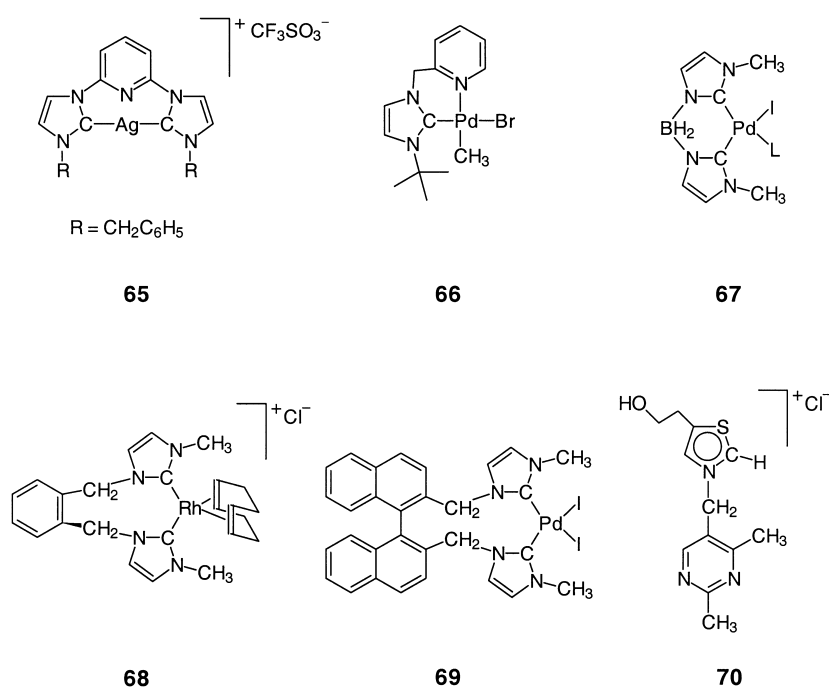
For example, the formally anionic BH_2^- group in complex **67** can replace the isoelectronic standard CH_2 moiety, thus changing the charge of the metal.

Some of the ionic-liquid effects in organometallic catalysis are likely to arise from NHC catalysts, be it as free carbenes or as their metal complexes; both can be readily formed in situ from azolium salts. It is also reasonable to assume in biological systems similar phenomena occur when the ubiquitous imidazolium groups interact with metal ions. We know from the foregoing discussion that NHC ligands are compatible with literally any kind of metal in low and high oxidation states. The naturally occurring thiazolium salt thiamine **70**, the coenzyme of vitamin B_1, catalyzes the decarboxylation of pyruvate, with the deprotonated ylidene form of **70** known to be the active catalyst.[114] The biochemistry of NHC – metal complexation lies ahead of us like an uncharted sea.[131] This is also true for the chemistry of the homologous and isoelectronic congeners **E**, **F**, and **G** metal compounds of which have
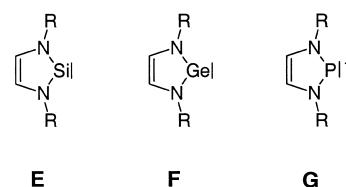
been described in some detail,[22, 115] including the C—C saturated derivatives of the silylenes and germylenes. Now that the heavier congeners of carbenes are available, this field is also ready to be developed in organometallic catalysis. As a matter of fact, the μ-silylene palladium complex **71** has just
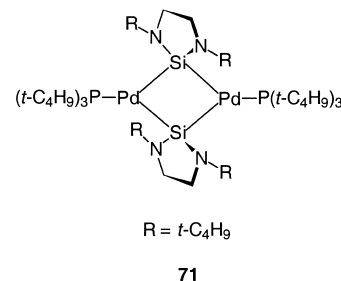
been made and structurally characterized.[116a] It dissociates in solution to form low-coordinate mononuclear palladium species. The analogous compound of the C—C unsaturated silylene was reported, and has moderate activity in the Suzuki coupling (aryl bromides).[116b]

Beyond catalysis, N-heterocyclic carbenes are going to gain relevance in materials science. For example, Liu et al. just reported on the first thermally stable liquid crystals based on NHC – palladium complexes such as **72**.[117] The arrangement of this type of rodlike molecule results in

1306

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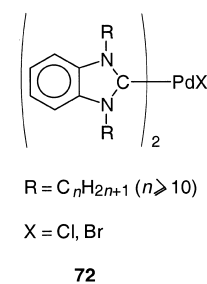
the preferential formation of a monolayered lamellar structure. The mesophases of **72** and related compounds have a mosaic texture. The new liquid crystalline phases are thermally stable up to the isotropic temperatures without decomposition. Once again, the ease of preparation, the thermal stability, and the structural versatility are unique features, as in catalysis.

Addendum: Dinitroxide Carbenes

A peculiar class of N-heterocyclic carbenes was recently described by Weiss et al.[130] Although unstable in the free state, the nitroxide carbene **73** could coordinate to a palladium(II) center, to form the cationic, diamagnetic complex **74** [Eq. (36)]. These carbenes can be regarded as
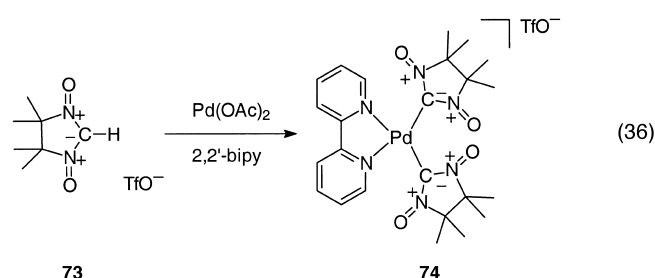
nitronyl–nitrosonium systems. A reversed-polarity singlet structure is stabilized here, with the carbene acting as π-donor and as π-acceptor ligand at the same time ("Autoumpolung" concept). The Pd−C bond of 197.7(4) pm (X-ray diffraction study) is in the typical range as in related NHC complexes. The variable electronic nature of the dinitroxide carbenes predisposes them as electronically flexible ligands. Complexes of Ag(I), Au(I), and Hg(II) were also obtained.[130]

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