Dissertation zur Erlangung des
naturwissenschaftlichen Doktorgrades
der Julius-Maximilians-Universität
Würzburg

Studies on

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the Reactivity of Iridium Bis(phosphinite) Pincer Complexes towards Phosphines, Boranes and their Lewis Adducts

and on

the Reactivity of Cyclic (Alkyl)(Amino) Carbenes and Nickel Complexes thereof

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vorgelegt von
Ursula Sofia Désirée Paul
aus Hausen
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Eingereicht bei der Fakultät für Chemie und Pharmazie am

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Gutachter der schriftlichen Arbeit:

1. Gutachter: Prof. Dr. Udo Radius

2. Gutachter: Prof. Dr. Holger Braunschweig

Prüfer des öffentlichen Promotionskolloquiums:

1. Prüfer: Prof. Dr. Udo Radius

2. Prüfer: Prof. Dr. Holger Braunschweig

3. Prüfer: ....

Tag des öffentlichen Promotionskolloquiums:

....

Doktorurkunde ausgehändigt am:

....

„Nur die Richtung ist Realität, das Ziel ist immer eine Fiktion, auch das erreichte –
und dieses oft ganz besonders.“

– Arthur Schnitzler –

Die vorliegende Arbeit wurde im Zeitraum von Oktober 2012 bis April 2017 am Institut für Anorganische Chemie der Julius-Maximilians-Universität Würzburg unter Anleitung von Prof. Dr. Udo Radius und in Kooperation mit Prof. Dr. Holger Braunschweig durchgeführt.

Abbreviations

substituents:

Ar	aryl substituent
R	alkyl substituent
X	halide substituent
Me	methyl
nBu	*n*butyl
*t*Bu	*tert*butyl
Cy	cyclohexyl
Cp	cyclopentadienyl
Ph	phenyl
*p*Tol	*para*tolyl = 4-methylphenyl
Mes	mesityl = 2,4,6-trimethylphenyl
Dur	duryl = 2,3,5,6-tetramethylphenyl
Dipp	2,6-di*iso*propylphenyl
OTf	trifluoromethanesulfonate
pin	pinacolato
*t*BuPCP	κ^3-C_6H_3-1,3-(CH_2–P*t*Bu$_2$)$_2$
*t*BuPOCOP	κ^3-C_6H_3-1,3-(OP*t*Bu$_2$)$_2$

compounds:

9-BBN	9-borabicyclo[3.3.1]nonane
COD	1,5-cyclooctadiene
DCM	dichloro methane
aDC	acyclic diaminocarbene
cAAC	cyclic (alkyl)(amino) carbene
NHC	N-heterocyclic carbene
*i*Pr$_2$Im	1,3-di*iso*propyl imidazoline-2-ylidene
*t*Bu$_2$Im	1,3-di*tert*butyl imidazoline-2-ylidene
Ad$_2$Im	1,3-diadamantyl imidazoline-2-ylidene
Dipp$_2$Im	1,3-bis(2,6-di*iso*propylphenyl) imidazoline-2-ylidene
Dipp$_2$Im^{H4}	1,3-bis(2,6-di*iso*propylphenyl) imidazolidine-2-ylidene
Mes$_2$Im	1,3-dimesityl imidazoline-2-ylidene
Mes$_2$Im^{H4}	1,3-dimesityl imidazolidine-2-ylidene
LDA	lithium di*iso*propylamide

other:

DFT	density functional theory
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
rt	room temperature
TOF	turn over frequency [s^{-1}]
TON	turn over numbers
TEP	Tolman electronic parameter
PDI	polydispersity index
$\%V_{bur}$	percent buried volume
VE	valence electron

Table of Content

Chapter I.

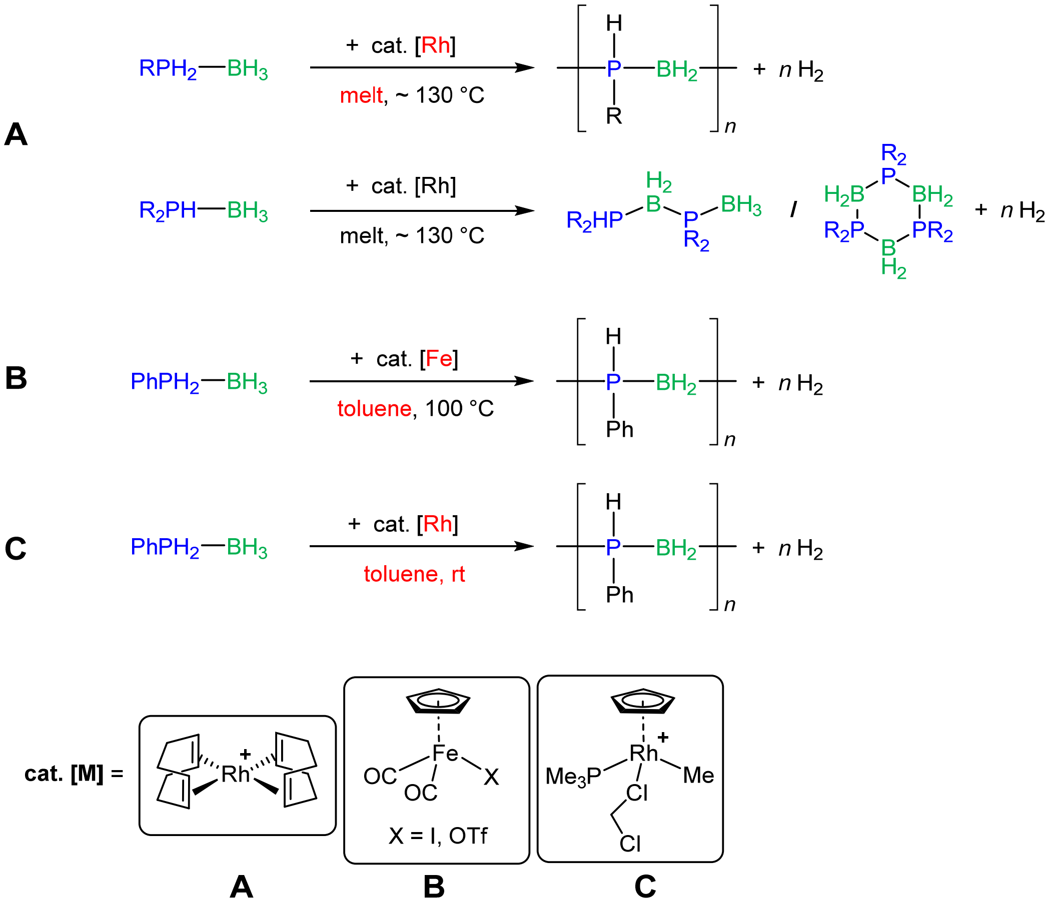
Reactivity of Iridium Bis(phosphinite) Pincer Complexes towards Phosphines, Boranes and their Lewis Adducts

1. Introduction

1.1. Dehydrogenative Coupling of Phosphine-Borane Adducts

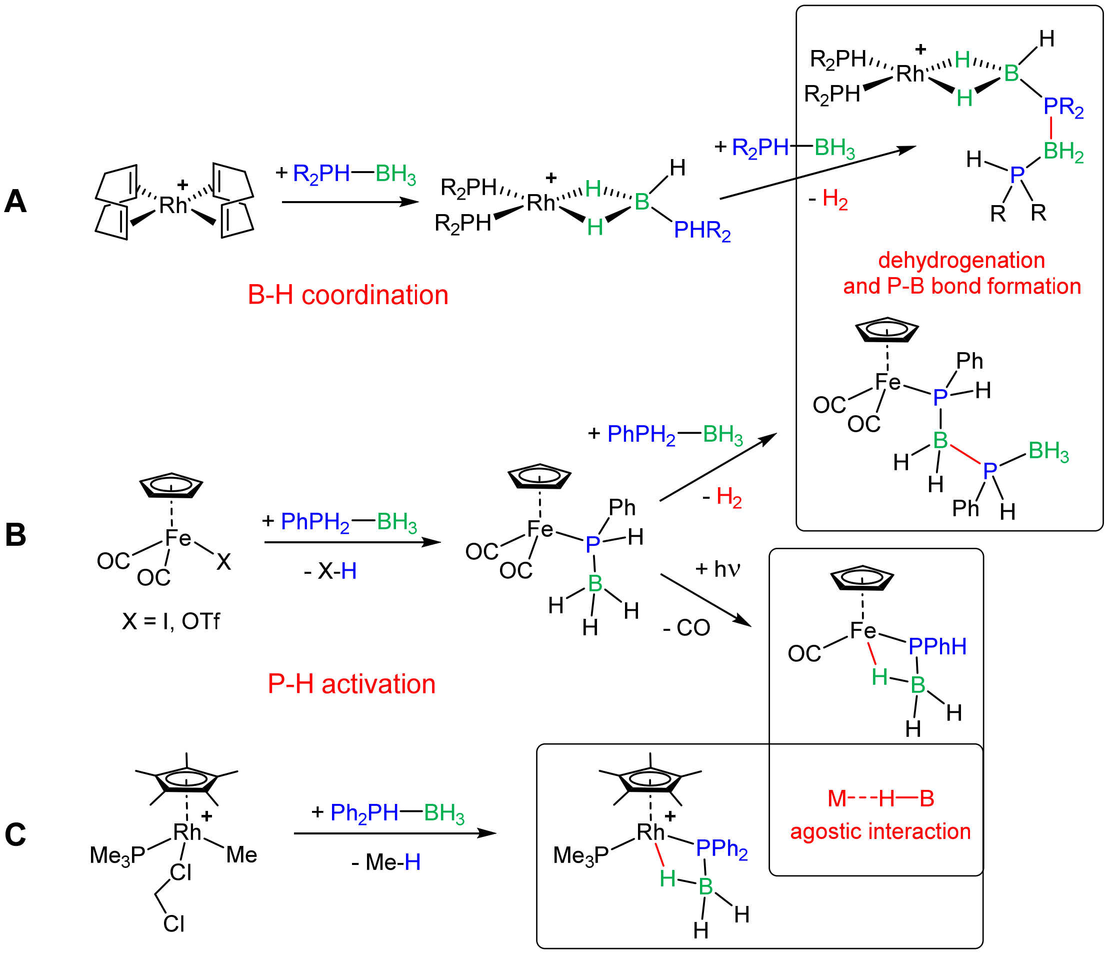
Catalysis is defined as a lowering of activation energy for a desired chemical transformation by participation of an additional compound, the so called catalyst, which itself is not consumed by the reaction. This concept has been applied at a vast number of novel synthetic pathways under feasibly mild reaction conditions, especially in (macro-)molecular organic chemistry. Accordingly, seminal advances in catalytic C–C bond formation reactions, including olefin polymerization, olefin metathesis and palladium-catalyzed cross-coupling reactions have been recognized with the award of Nobel Prizes in 1963, 2005 and 2010.[1] However, the development of catalytic routes to corresponding main group compounds and materials has been comparably slow. The formation of such main group element-element bonds has traditionally been achieved using methods such as salt metathesis and reductive coupling. Catalytic routes to form relatively strong homonuclear (E–E) und heteronuclear (E–E') bonds between lighter main group elements (E = B, N, Al, Si, P, S), are mainly based on dehydrocoupling of main group element hydrides (E–H).[2]

In the case of the classical group 13/15 Lewis adducts, namely phosphine and amine boranes, which are isoelectronic with alkanes, such a dehydrogenation results in the formation of poly(phosphinoborane) and poly(aminoborane) materials, respectively, and can thus be compared with olefin polymerization reactions. It should be noted here, that due to the different electronegativities of phosphorus (or nitrogen) and boron, the P–H (or N–H) and B–H bonds of phosphine (or amine) boranes are oppositely polarized to give protic (δ+) and hydridic (δ-) hydrogen substituents. Therefore, dehydrogenation of phosphine-borane adducts can also proceed via thermal induction, though this requires remarkably higher temperatures (compared to the more E–H bond-polarized amine boranes) and yields and molecular weights of the obtained poorly characterized polymers were reported to be generally very low.[3] However, detailed studies on rhodium-catalyzed dehydrocoupling of a broad range of primary and secondary phosphine boranes have been reported by Manners *et al.* since the early 2000s.[4] These catalytic protocols used mainly primary phosphine–BH_3 adducts as substrates and $[Rh(COD)_2][OTf]$ as catalyst precursor and yielded polydisperse, soluble, branched polymers (M_n > 10 000) as well as cross-linked, swellable, but insoluble materials, depending on the specific reaction conditions and substituents at the phosphorus atom. Satisfactory conversion and weight distribution were only obtained when the polymerization was carried out as a melt reaction at elevated temperatures (Scheme 1.1.1, **A**).[4] Utilizing $[CpFe(X)(CO)_2]$ (X = I/OTf) as precatalyst, instead, enabled dehydrocoupling of phenylphosphine borane in solution at elevated temperatures to yield a readily soluble polymeric material with control over the molecular weight (M_n 42 000 to 80 000) by simple variation of the catalyst loading (Scheme 1.1.1, **B**).[5b] Inspired by these results, Weller *et al.* developed $[Cp^*Rh(Me)(PMe_3)(DCM)]^+$, which adopts similar structural motifs, namely a d^8-{CpM} complex fragment bearing a further anionic (I or Me) and initially two neutral co-ligands (CO or PMe_3 and DCM). One of these neutral ligands dissociates in the course of catalyst activation in order to provide a vacant site for the substrate. This cationic rhodium complex was found to catalyze dehydrogenation of $PhPH_2$–BH_3 to moderate-molecular weight polymers (M_n 15 000) in solution even at room temperature (Scheme 1.1.1, **C**).[6b]



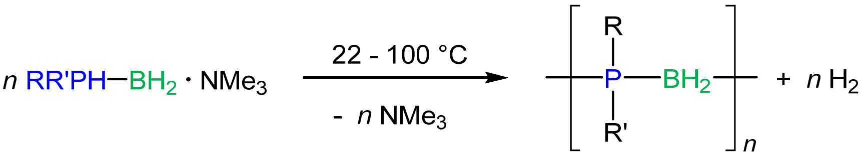
Scheme 1.1.1: Examples for rhodium- (**A**, **C**) and iron-(**B**) catalyzed dehydrocoupling of primary and secondary phosphine boranes.

Mechanistic studies on a stoichiometric reaction scale were carried out for the three catalytic systems mentioned above. They have in common, that P–H as well as B–H bond activation products could be isolated and subsequently transformed via P–B bond formation to phosphido borane dimer-ligated rhodium[6] or iron[5] complexes (Scheme 1.1.2). Thus, these B–H and P–H activated phosphine trihydroborate and phosphido borane species were proposed to be key intermediates in the catalytic cycles. However, an analysis of the mechanism of polymer growth is rather complicated and quite specific for each of the investigated complexes **A-C**. For example, the iron-catalyzed dehydrocoupling of phenylphosphine borane **C** was reported to proceed via a chain-growth coordination-type mechanism, based on the observed molecular weights of the polymers depending on the catalyst loading and conversion. Accordingly, molecular weights were found to decrease with increasing catalyst loading, high-molecular weight polymers were detected even at an early stage of the catalysis (low conversions ~ 35 %) and prolonged reaction times after consumption of the starting materials did not result in higher molecular weights, i.e. no further condensation of the polymer chains. All these findings account for the proposed chain-growth mechanism.[5b]



Scheme 1.1.2: Isolated intermediates from catalytic transformations and stoichiometric reactions of phosphine-borane adducts with different rhodium (**A**, **C**) and iron (**B**) precatalysts.

Interestingly, the substrate scope of this dehydrogenative coupling reaction is limited to aryl substituted phosphine boranes, as these possess the required polarity of the P–H bond through the electron-withdrawing effect of the aryl moiety at the phosphorus. Catalytic dehydrogenation of alkylphosphine boranes led for very few examples via typically slow reactions under harsh conditions to rather ill-defined branched as well as cross-linked polymeric materials with only moderate molecular weights but high polydispersity. Well-defined alkyl substituted poly(phosphinoboranes) are alternatively accessible through metal-free addition/polymerization of suitable Lewis base-stabilized monomeric phosphinoboranes (Scheme 1.1.3).[7]

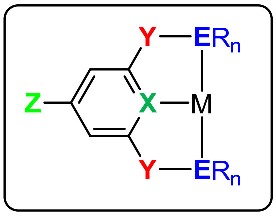


$$n\ RR'PH{-}BH_2 \cdot NMe_3 \xrightarrow[-\ n\ NMe_3]{22\ -\ 100\ °C} \left[\overset{R}{\underset{R'}{P}}{-}BH_2 \right]_n + n\ H_2$$

Scheme 1.1.3: Oligomerization and polymerization of Lewis base (NMe3)-stabilized monomeric phosphinoboranes.

1.2. Synthesis and Reactivity of Iridium Pincer Complexes

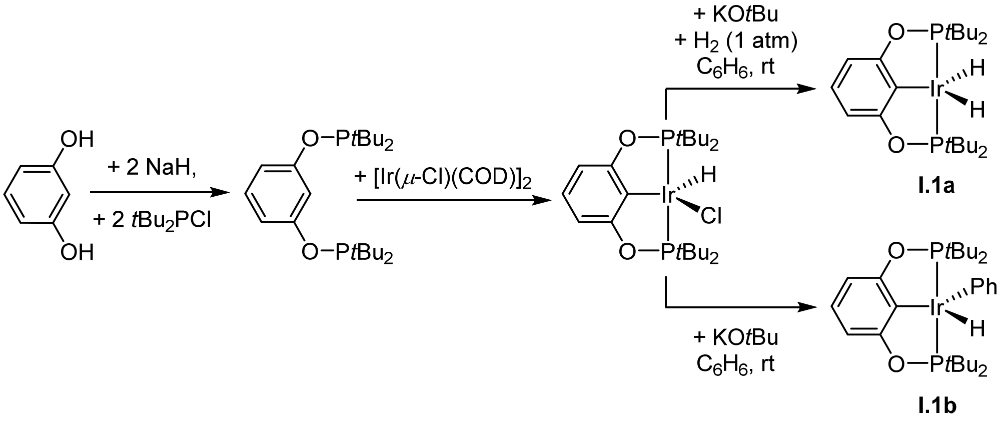
Since the pioneering work of Shaw *et al.* in the 1970s[8] the chemistry of transition-metal complexes bearing pincer ligands has attracted much attention and has found various applications[9]. The tridentate coordination mode of a pincer ligand results in a strong binding to the metal center, and the rigidity of the generally in *mer* configuration bound ligand framework rather prevents cyclometalation at terminal groups of the pincer ligand, thus explaining the extraordinary high thermal stability of the resulting pincer-metal fragment. Furthermore, the modular design of the pincer ligand allows a facile fine-tuning and optimization of the steric as well as electronic properties of the corresponding transition metal complex fragment[10] according to the specific requirements for its application, e.g. in catalysis (Figure 1.2.1).



group:		**influence on:**
ER$_n$	e.g. **PR$_2$**, NR$_2$, OR	sterics (ligands R variable) lability (electron-donating/-withdrawing effects of E)
X	e.g. **C**, N, B	electronic properties (trans influence)
Z	e.g. halide, **H**, OR	electron density (of X by remote -M/+M effects) solubility
Y	e.g. **O**, CH$_2$, NH	sterics (indirectly by affecting the bite-angle) electron density (at E)

Figure 1.2.1: Possibilities and resulting effects of ligand modulation at a pincer-metal fragment.

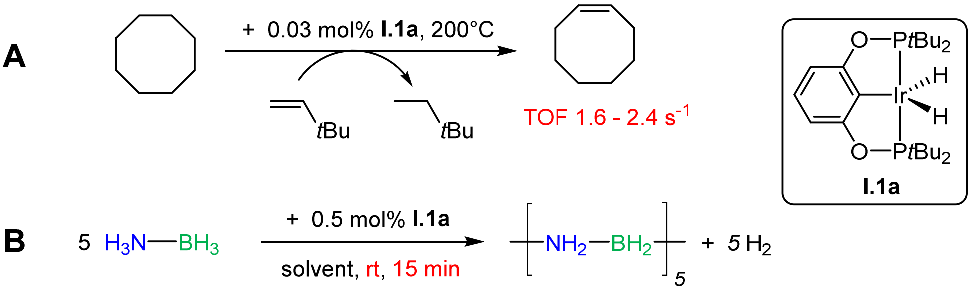
Especially one class of such pincer-ligated transition metal compounds gained a growing interest throughout the last years, namely iridium complexes bearing the bis(phosphinite) pincer ligand *t*BuPOCOP (κ^3-C_6H_3-1,3-(OP*t*Bu$_2$)$_2$). Their most important representatives **I.1a** and **I.1b** are synthesized in three steps from readily available reagents following a straight forward procedure developed by Brookhart *et al.* in 2004[11] (Scheme 1.2.1).



Scheme 1.2.1: Synthesis of bis(phosphinite) pincer-ligated iridium complexes [(*t*BuPOCOP)IrH$_2$] (**I.1a**) and [(*t*BuPOCOP)IrHPh] (**I.1b**).

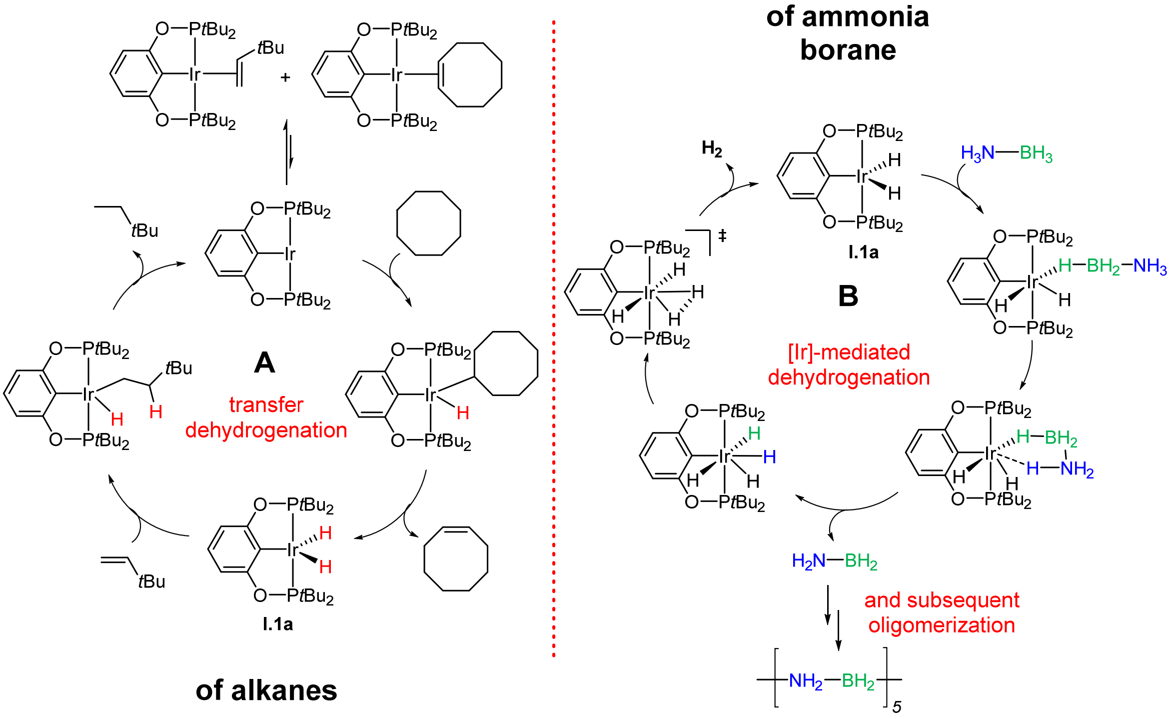
These iridium complexes **I.1a,b** have shown unique activities in the homogeneous transfer dehydrogenation of alkanes, such as cyclooctane with *tert*-butylethylene (Scheme1.2.2, **A**), providing turn overs of about one magnitude higher than the benchmark catalytic system for this reaction, namely the closely related *t*BuPCP-pincer complex [(κ^3-C_6H_3-1,3-(CH$_2$–P*t*Bu$_2$)$_2$)IrH$_2$] by Jensen, Kaska *et al.*[12].

Since alkanes are isoelectronic with amine boranes, which had been envisioned for quite a while as promising candidates for hydrogen-storage materials due to their high percentage by weight of available hydrogen and the reversibility of such hydrogen-release reactions, the reactivity of dihydrido iridium(**III**) complex **I.1a** was also investigated towards several amine-borane adducts. Remarkably high rates at mild conditions were reported for the dehydrogenation of ammonia borane NH_3–BH_3 yielding the cyclic pentamer $[NH_2–BH_2]_5$ upon release of one equivalent of hydrogen each[13] (Scheme 1.2.2, **B**).



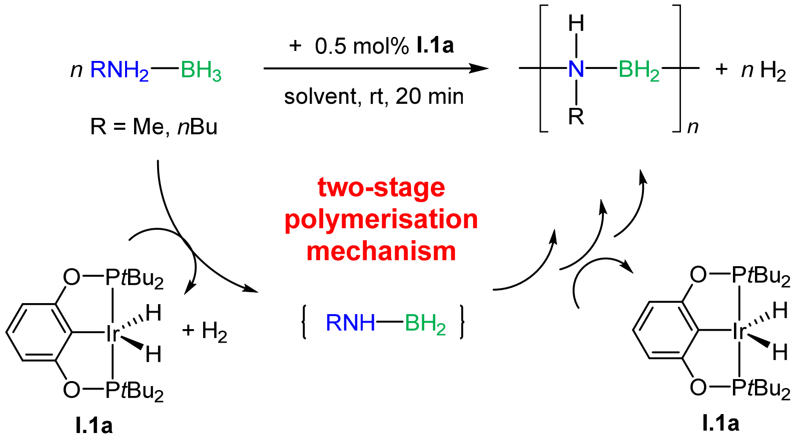
Scheme 1.2.2: Examples for (transfer) dehydrogenation of alkenes and isoelectronic amine boranes using [(*t*BuPOCOP)IrH_2] (**I.1a**) as precatalyst.

Though transforming both alkanes and isoelectronic amine borane NH_3–BH_3 with high rate and high selectivity to the desired products, the mechanisms of these dehydrogenation reactions differ fundamentally (Scheme 1.2.3). In the transfer dehydrogenation of alkanes (**A**) the 14VE complex [(*t*BuPOCOP)Ir] was postulated as catalytically active species, whereas for the dehydrogenative oligomerization of ammonia borane (**B**) the substrate was calculated to directly react with 16VE complex [(*t*BuPOCOP)IrH_2] (**I.1a**) without prior release of H_2.[13b,c] The latter reaction is able to circumvent the endothermic initial loss of dihydrogen due to the polarized nature of the present N–H and B–H bonds.[14]



Scheme 1.2.3: Proposed mechanisms for **A** cyclooctane/ *tert*-butylethylene transfer dehydrogenation and **B** ammonia borane dehydrogenation using [(*t*BuPOCOP)IrH_2] (**I.1a**) as (pre)catalyst.

Encouraged by these results, Manners *et al.* were also able to show that [(*t*BuPOCOP)IrH$_2$] (**I.1a**) readily catalyzes the dehydrocoupling of primary alkylamine boranes (RNH$_2$–BH$_3$) to yield soluble high molecular weight poly(aminoboranes) [RNH–BH$_2$]$_n$ (Scheme 1.2.4, top),[13g] contrary previous studies on different catalytic systems yielding only borazines and/or poorly characterized insoluble and branched oligomeric material.[15] As these poly(aminoboranes) are a novel class of inorganic polymer materials, their facile synthetic accessibility as well as a reproducible product quality (molecular weight distribution) are of high importance for envisioned applications, such as being percursors for B–N ceramics.[3b] Based on the observed dependency of the molecular weight (of the polymer obtained) from a given catalyst loading and the reaction times (conversion), the mechanism of this reaction was proposed to differ from that of ammonia borane dehydrogenation by the fact that both the dehydrogenation and the coupling of the so formed aminoborane monomers proceed iridium metal-assisted[13g] (Scheme 1.2.4, bottom).

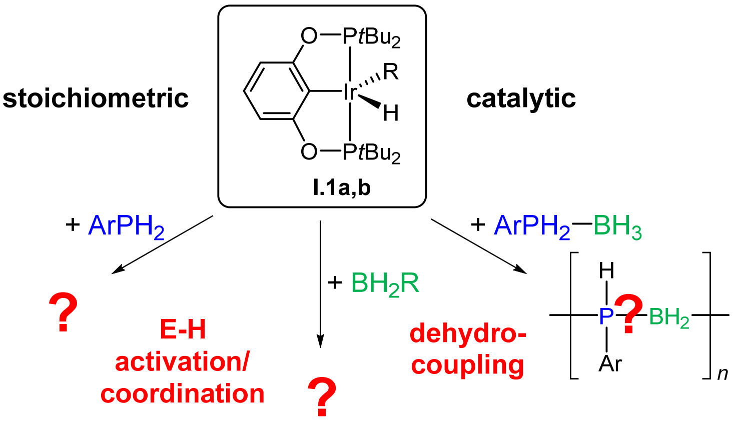


Scheme 1.2.4: Dehydropolymerization of primary alkylamine boranes using [(*t*BuPOCOP)IrH$_2$] (**I.1a**) as precatalyst and postulated two-stage reaction mechanism.

Furthermore, [(*t*BuPOCOP)IrH$_2$] (**I.1a**) proved to be an active (pre)catalyst in the (transfer) dehydrogenation of alcohols[16a] and amines[16b] and was utilized in several further catalytic as well as stoichiometric transformations of organic substrates.[16c-h]

1.3. Motivation

Throughout the last years, we have successfully been developing several protocols for the formation of homonuclear main group element–element bonds by either transition metal-catalyzed, acceptorless dehydrogenation[17a] or by stoichiometric reductive coupling of element hydrides in the presence of a hydrogen acceptor.[17b] Due to their specific properties, including inertness against air and moisture, as well as the presence of reactive P–H and B–H bond, which allow further functionalization of the obtained polymers, poly(phosphinoboranes) are envisioned as highly interesting inorganic soft materials. Recently, applications of these compounds as precursors for luminescent semiconductor boron phosphide and as electron-beam resists for lithography have been reported.[4d,e] We were thus encouraged to our investigations on novel synthetic strategies to access poly(phosphinoboranes) via dehydrogenation of the parent phosphine borane adducts. Thereby, we wanted to focus on iridium complexes bearing the bis(phosphinite) pincer ligand *t*BuPOCOP (κ^3-C_6H_3-1,3-($OPtBu_2$)$_2$),[11] as these compounds have already shown unique activities in various homogeneous catalytic transformations involving dehydrogenation processes. For example, complex [(*t*BuPOCOP)IrH_2] (**I.1a**) proved to catalyze at high rates and under mild conditions dehydrogenative coupling of amine boranes to readily soluble, high-molecular weight polymers.[13g] This was of particular interest, as previous studies revealed that other catalysts mostly led to poorly characterized insoluble and branched oligomeric material.[15] Also the established synthetic protocols for the formation of poly(phosphinoboranes) still make use of rather harsh reaction conditions (melt reactions at elevated temperatures) and often yield insoluble, cross-linked materials, what hampers sufficient characterization and further transformation of these polymers. There have only been two reports on “low temperature” dehydrocoupling of phosphine boranes in solution yet. One of these is the iron complex [Cp(CO)$_2$FeI], which is also a rare example[18] of a catalyst being successfully applied in the dehydrogenation of both amine-[5a] and phosphine-borane[5b] adducts, a fact that further encouraged us to our studies on the iridium bis(phosphinite) pincer system.



Scheme 1.3.1: Possible stoichiometric and catalytic reactions of [(*t*BuPOCOP)IrHR] (R = H **I.1a**, Ph **I.1b**) with primary phosphines, boranes as well as the Lewis adducts thereof.

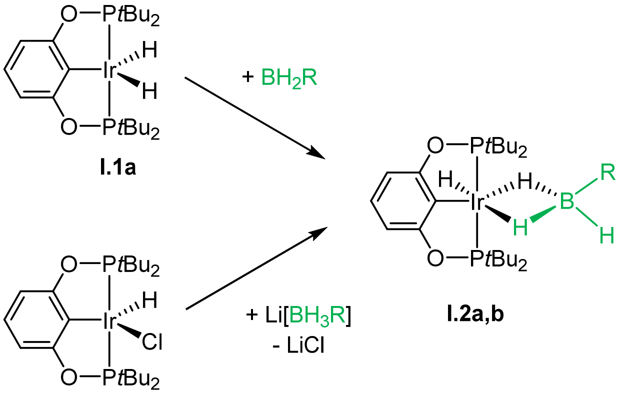
Furthermore, to gain some insight into the mechanism of this reaction, we wanted to study the reactivity of the pincer complexes [(*t*BuPOCOP)IrH_2] (**I.1a**) and [(*t*BuPOCOP)IrHPh] (**I.1b**) towards individual primary phosphine and borane moieties (Scheme 1.3.1).

2. Results and Discussion

This chapter summarizes the crucial aspects of the publications prepared during the course of this dissertation. The bibliographic data of the complete manuscripts can be found in chapter 4.

2.1. Reactions with primary Boranes

We investigated the synthesis and characterization of iridium pincer complexes, which are coordinated by aryl dihydroborate ligands. The distorted octahedrally coordinated complexes [(*t*BuPOCOP)IrH(κ^2-H_2BHR)] (R = Mes **I.2a**, Dur **I.2b**) were obtained either from the reaction of dihydrido complex [(*t*BuPOCOP)IrH_2] (**I.1a**) with a stoichiometric amount of an arylborane BH_2R or from reacting chlorido monohydrido complex [(*t*BuPOCOP)IrHCl] with the lithium salt of the corresponding borohydride Li[BH_3R] (Scheme 2.1.1).



Scheme 2.1.1: Synthesis of dihydrido borate complexes [(*t*BuPOCOP)IrH(κ^2-H_2BHR)] (R = Mes **I.2a**, Dur **I.2b**).

There are several different possibilities for borohydrides to interact with a transition metal center (Figure 2.1.1), namely the formation of boryl (**A**), σ-borane (**B**) or dihydroborate (**C**) complexes.[19] Taking into account both synthetic approaches that have been applied, the formed products can most likely be described as either borane (BH_2R) adducts of the neutral, 16VE complex [(*t*BuPOCOP)IrH_2] (**B**) or borohydride ($[BH_3R]^-$) adducts of the cationic, formally 14VE species $[(tBuPOCOP)IrH]^+$ (**C**).

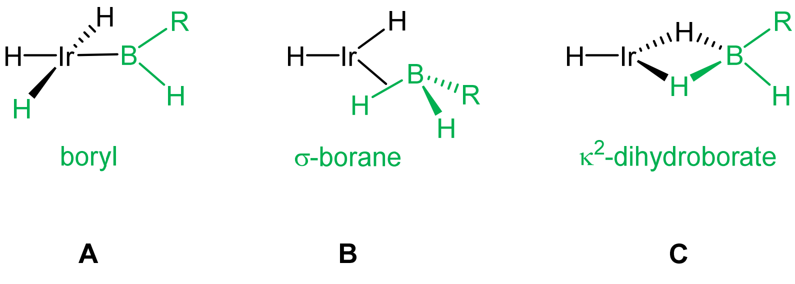


Figure 2.1.1: Structural motifs resulting from the coordination of BH_2R to an iridium(III) dihydrido complex fragment.

The solid state structure of **I.2b** obtained from X-ray diffraction studies (Figure 2.1.2) as well as NMR spectroscopic data reveal a bidentate κ^2 binding mode of the arylborate ligands with indications for significant Ir–B interactions and thus the presence of two bridging hydrogen atoms and one terminal iridium-bound hydrido ligand (Figure 2.1.1, **C**). This finding compares well with closely related iridium(**III**) and osmium(**II**) complexes bearing a durylborane ligand (κ^2-σ:σ-H_2BDur).

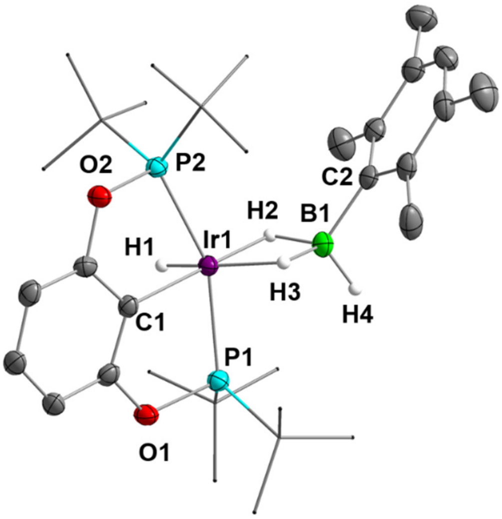
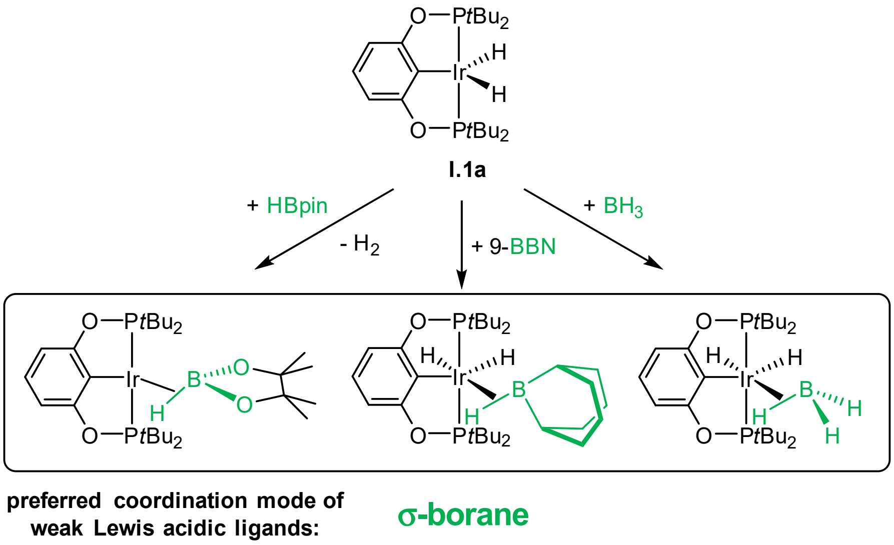


Figure 2.1.2: Molecular structure of dihydro borate complex [(*t*BuPOCOP)IrH(κ^2-H_2BHDur)] (**I.2b**) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

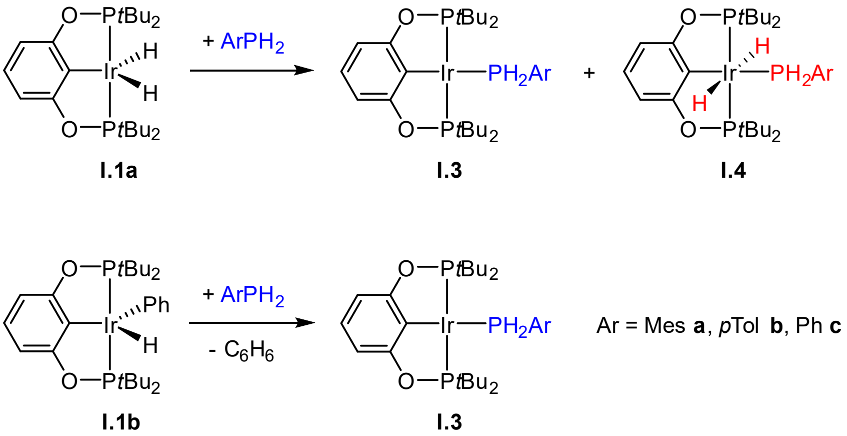
Contrarily, Goldberg and Heinekey have obtained σ-borane iridium complexes (Figure 2.1.1, **B**) as products of the reaction of the very same iridium complex [(*t*BuPOCOP)IrH_2] (**I.1a**) with BH_3, HBpin and 9-BBN, instead[16e] (Scheme 2.1.2). This clearly reflects that the coordination behavior of borane ligands is not only dependent on the choice of the transition metal and ancillary ligands but also the same way, very critically on the properties of the borane itself, i.e. the Lewis acidity of the borane which is imposed by the respective substituent on the boron atom.[20]



Scheme 2.1.2: Reactions of [(*t*BuPOCOP)IrH_2] (**I.1a**) with less Lewis acidic boranes BH_3, HBpin and 9-BBN yielding σ-borane iridium complexes, instead.

2.2. Reactions with primary Phosphines

We furthermore aimed out for first studies on the reactivity of [(*t*BuPOCOP)IrH$_2$] (**I.1a**) and its highly reactive precursor [(*t*BuPOCOP)IrHPh] (**I.1b**) towards different primary phosphines ArPH$_2$ (Ar = Mes, *p*Tol, Ph) (Scheme 2.2.1). While reactions of dihydrido complex **I.1a** with one equivalent of ArPH$_2$ resulted in the formation of a mixture of iridium(I) and iridium(III) phosphine complexes **I.3a-c** and **I.4a-c**, the hydrido phenyl complex [(*t*BuPOCOP)IrHPh] (**I.1b**) was transformed selectively and quantitatively into phosphine-ligated iridium(I) complexes **I.3a-c** (Figure 2.2.1) with reductive elimination of benzene.



Scheme 2.2.1: Reaction of primary phosphines ArPH$_2$ with the complexes [(*t*BuPOCOP)IrH$_2$] (**I.1a**) and [(*t*BuPOCOP)IrHPh] (**I.1b**) to give the iridium(I) phosphine **I.3a-c** and iridium(III) dihydrido phosphine complexes **I.4a-c**, respectively.

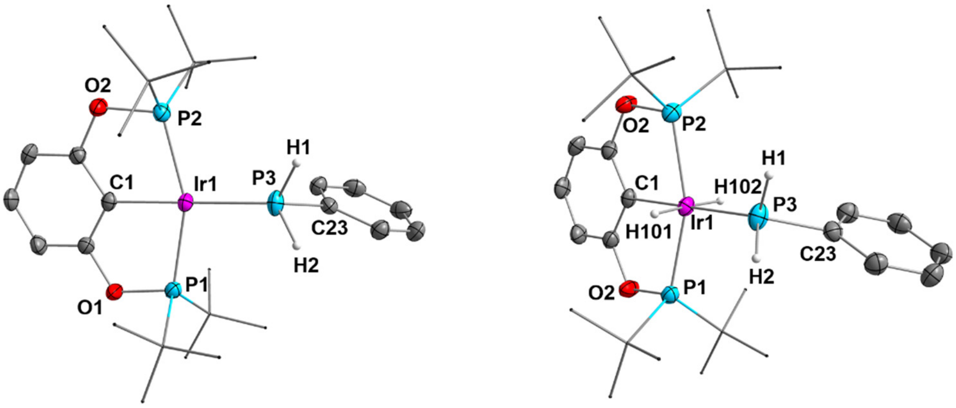
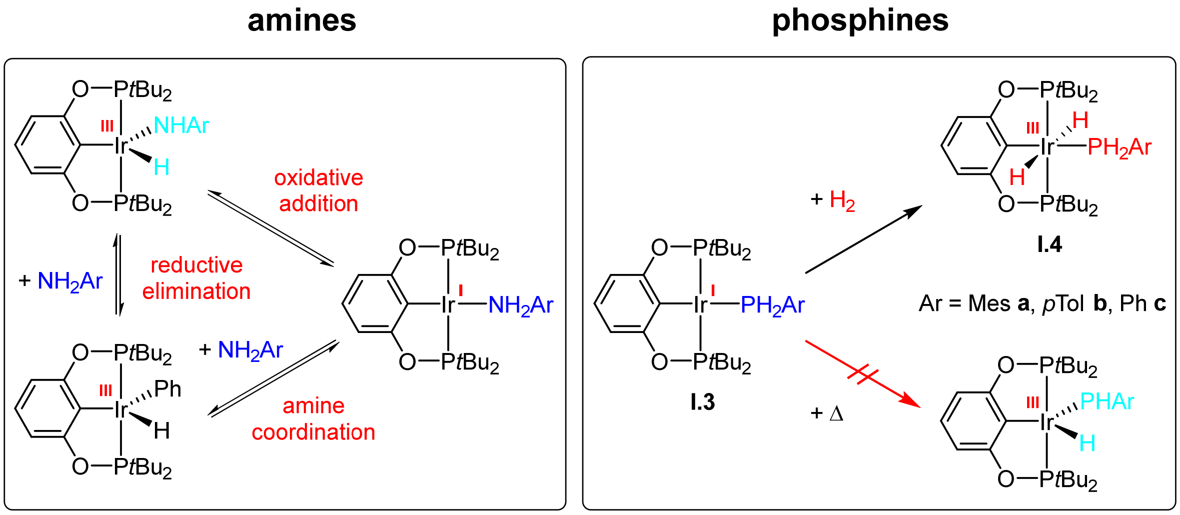


Figure 2.2.1: Molecular structures of iridium(I) phosphine complex [(^{t}BuPOCOP)Ir(PH$_2$Ph)] (**I.3c**) (left) and iridium(III) dihydrido phosphine complex [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ph)] (**I.4c**) (right) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

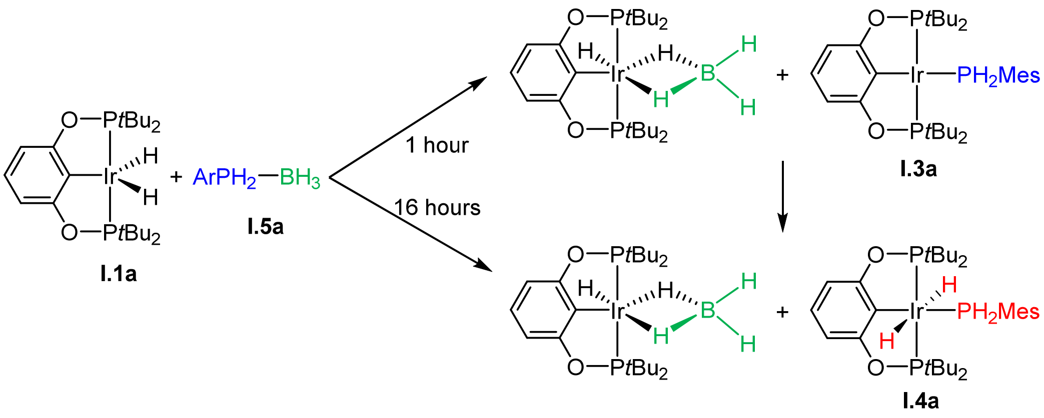
Subsequent treatment of these complexes with dihydrogen resulted in the formation of the iridium(III) dihydrido phosphine complexes **I.4a-c** (Scheme 2.2.2, right and Figure 2.2.1, right). However, no indications for a conversion of the iridium(I) compounds [(tBuPOCOP)Ir(PH$_2$Ar)] (**I.4a-c**) to iridium(III) complexes [(tBuPOCOP)IrH(PHAr)] by oxidative addition of a P–H bond could be observed (Scheme 1.2.2). This is in marked contrast with the results obtained for the reactivity of bis(phosphinite) pincer ligated iridium complexes, like [(*t*BuPOCOP)IrHPh], with primary anilines and benzamides.[16c] Anilines yield equilibrium mixtures of the starting materials, Lewis base coordination adducts [(*t*BuPOCOP)Ir(NH_2Ar)] and oxidative addition products [(*t*BuPOCOP)IrH(NHAr)] depending on the Lewis basicity of the amine employed (Scheme 2.2.2, left), whereas benzamides were found to exclusively undergo oxidative addition to give the iridium(III) complexes [(*t*BuPOCOP)IrH(NHCOAr)].



Scheme 2.2.2: Reactivity of primary phosphine-coordinated iridium(I) complexes [(*t*BuPOCOP)Ir(PH_2Ar)] (**I.3a-c**) (right) in comparison with the related primary amine-ligated complexes (left).

2.3. Dehydrocoupling of Phosphine-Borane Adducts

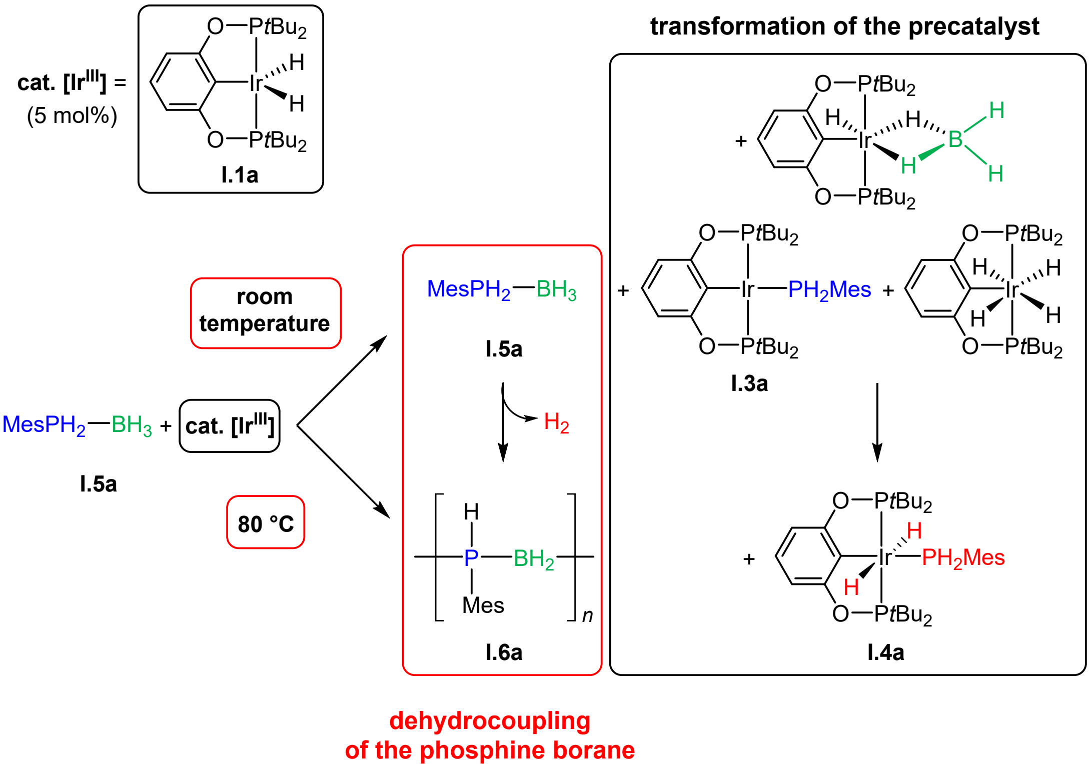
With respect to a further application of iridium pincer complexes [(*t*BuPOCOP)IrH$_2$] (**I.1a**) and (*t*BuPOCOP)IrHPh] (**I.1b**) as precatalysts in the dehydrogenation of phosphine boranes, we aimed out for first studies on the reactivity of these iridium(**III**) compounds towards primary phosphine-borane adducts. Treatment of **I.1a** with stoichiometric amounts of MesPH$_2$–BH$_3$ (**I.5a**), for example, resulted immediately in a complete consumption of the starting materials with the formation of two products, namely the σ-borane complex [(*t*BuPOCOP)Ir(H)$_2$(η^2-H–BH$_2$)][16e] as well as the phosphine complex [(^{t}BuPOCOP)Ir(PH$_2$Mes)] (**I.3a**). The latter is converted into the dihydrido phosphine complex [(tBuPOCOP)Ir(H)$_2$(PH$_2$Mes)] (I.4a) within 16 hours at room temperature (Scheme 2.3.1).



Scheme 2.3.1: Stoichiometric reaction of [(*t*BuPOCOP)IrH$_2$] (**I.1a**) with mesityl-substituted phosphine borane MesPH$_2$–BH$_3$ (**I.5a**)

Thus, the Lewis adducts are cleaved when treated with the iridium(**III**) pincer complex **I.1a** and react like the corresponding free acid and base, respectively, instead of being activated at one of the B–H or P–H functionalities to yield boryl- or phosphido-borane complexes, which were proposed as the catalytic intermediates that undergo the P–B bond formation processes in the rhodium- and iron-based systems.[5, 6]

Furthermore, we treated the phosphine-borane adduct MesPH$_2$–BH$_3$ (**I.5a**) with catalytic amounts (5 mol%) of [(*t*BuPOCOP)IrH$_2$] (**I.1a**) (Scheme 1.3.2). At room temperature the iridium complex **I.1a** is transformed, as already described above, into the borane complex [(*t*BuPOCOP)Ir(H)$_2$(η^2-H–BH$_2$)], the phosphine complex [(^{t}BuPOCOP)Ir(PH$_2$Mes)] (**I.3a**) and additionally into minor amounts of the tetrahydride [(*t*BuPOCOP)IrH$_4$],[11a] whereas the excess of the phosphine borane **I.5a** remains unchanged in solution. Upon heating this reaction mixture to 80 °C solely one iridium-containing compound remains in solution, namely the dihydrido mesitylphosphine complex [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] (**I.4a**), while the phosphine-borane adduct **I.5a** is quantitatively converted via dehydrogenative coupling to the poly(phosphinoborane) **I.6a** within 24 hours.

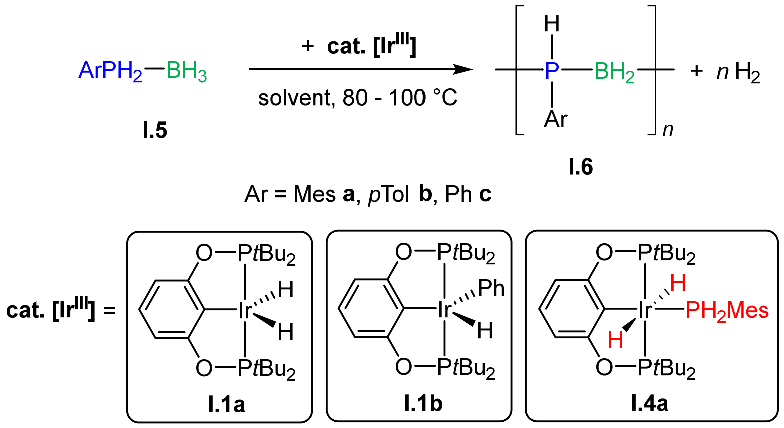


Scheme 2.3.2: Catalytic reaction of [(*t*BuPOCOP)IrH$_2$] (**I.1a**) with mesitylphosphine borane MesPH$_2$–BH$_3$ (**I.5a**) as substrate.

Interestingly, the observed reactivity of the iridium pincer complex **I.1a** with the primary phosphine borane MesPH$_2$–BH$_3$ (**I.5a**) differs drastically from that of amine boranes, like NH$_3$–BH$_3$, though both classes of borane adducts are found to undergo homogeneous catalytic dehydrocoupling to the polymeric phosphino- and aminoboranes with **I.1a** as precatalyst. [(*t*BuPOCOP)IrH$_2$] (**I.1a**) reacts with an excess of ammonia borane to the tetrahydrido complex [(*t*BuPOCOP)IrH$_4$] and only at prolonged reaction times [(*t*BuPOCOP)Ir(H)$_2$(η^2-H–BH$_2$)] was formed, whereas no amine- or amide-ligated iridium species was observed. Furthermore, the isolated σ-borane complex was postulated as a dormant form of the iridium catalyst as itself did not show any catalytic activity in the dehydrogenation of ammonia borane.[13a] Contrarily, both iridium(I) and iridium(III) complexes [(^{t}BuPOCOP)Ir(PH$_2$Mes)] (**I.3a**) and [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] (**I.4a**) were successfully utilized as precatalysts for the polymerization of MesPH$_2$–BH$_3$ (**I.5a**) and thus can be described as resting states of the catalytically active species rather than deactivation products.

Thermal dehydrogenative coupling utilizing [(*t*BuPOCOP)IrH$_2$] (**I.1a**) as catalyst was also achieved for further primary arylphosphine boranes, like *p*TolPH$_2$–BH$_3$ (**I.5b**) and PhPH$_2$–BH$_3$ (**I.5c**). The best results, however, were obtained for the initially investigated adduct MesPH$_2$–BH$_3$ (**I.5a**) (Table 2.3.1, entries 1-3). Therefore, the catalysis was optimized for **I.5a** as starting material by variation of the reaction conditions.

Table 2.3.1: Iridium-catalyzed dehydrocoupling of primary arylphosphine-borane adducts **5a-c** to poly(phosphinoboranes) **6a-c**.



entry	adduct	catalyst (mol%)	method[a]	time	M_n/M_w	Dispersity[b]
1	**5a**	**I.1a** (5)	**A**	24 h	10 000/ 300 000	30.0
2	**5b**	**I.1a** (5)	**A**	24 h	5 000/ 66 000	13.2
3	**5c**	**I.1a** (5)	**A**	24 h	10 000/ 216 000	21.6
4	**5a**	**I.1a** (2.5)	**A**	24 h	5 000/ 13 000	2.6
5	**5a**	**I.1a** (2.5)	**B**	24 h	33 000/ 59 000	1.8
6	**5a**	**I.1a** (2.5)	**B**	6 h	20 000/ 116 000	5.8
7	**5a**	**I.1b** (2.5)	**B**	24 h	34 000/ 71 000	2.1
8	**5a**	**I.4a** (2.5)	**B**	24 h	67 000/ 233 000	3.5
9	**5a**	**I.1a** (0.5)	**B**	24 h	5 000/ 10 000	2.0

[a] Reaction conditions for method **A**: 5 mL of toluene, 100 °C and **B**: 0.6 mL of benzene, 80 °C. [b] Formerly denoted as PDI.

Accordingly, the highest molecular weight polymers were produced when using 5 mol% of precatalyst **I.1a**. Lowering of the catalyst loading to 2.5 and 0.5 mol% resulted in lower molecular weights of the polymer **I.6a** with a narrower molecular weight distribution (Table 2.3.1, entries 4-5 and 9). This dependence of the molecular weights on the catalyst loading would be consistent with a step-growth mechanism of the catalyzed dehydrocoupling reaction, whereas the formation of high molecular weight polymers even at low substrate conversion (of circa 36 %, Table 2.3.1, entry 6) rather suggests a chain-growth character of this reaction. These contrary results would be consistent with a two-stage polymerization mechanism, as already reported for the dehydrogenative coupling of primary amine boranes.[13g] In the first step dehydrogenation proceeds slowly through concerted hydrogen cleavage from the parent phosphine borane by the respective iridium pincer complex. In the second step the formed monomer phosphinoborane ArPH–BH$_2$ undergoes a most-likely metal assisted, fast chain-growth polymerization to the corresponding poly(phosphinoborane) [ArPH–BH$_2$]$_n$ **I.6a-c**. In such a reaction sequence the availability of the monomer phosphinoborane would be the limiting factor for the progress of the polymerization, which would also explain the observed dependence of the molecular weight on the catalyst loading.

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4. Publications

This chapter provides the bibliographic details of the publications summarized in this part (**Chapter I**) of the present thesis to facilitate the retrieval of the complete manuscripts and supporting information.

All results, which have been illustrated and placed into their scientific context within Sections "**2. Results and Discussion**" and "**Summary and Outlook**", are enclosed in the following two publications in peer-reviewed journals:

I. *Aryldihydroborane Coordination to Iridium and Osmium Hydrido Complexes*
N. Arnold, S. Mozo, U. Paul, U. Radius, H. Braunschweig, *Organometallics* **2015**, *34*, 5709-5715.

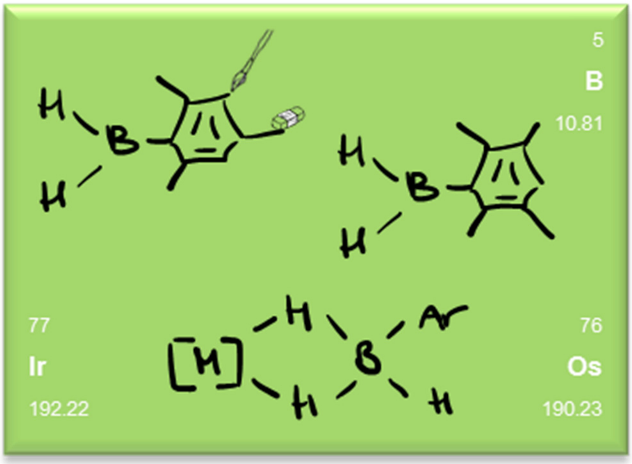
II. *Iridium-catalysed dehydrocoupling of aryl phosphine–borane adducts: synthesis and characterisation of high molecular weight poly(phosphinoboranes)*
U. S. D. Paul, H. Braunschweig, U. Radius, *Chem. Commun.* **2016**, *52*, 8573-8576.

4.1. Publication I.

Aryldihydroborane Coordination to Iridium and Osmium Hydrido Complexes

Nicole Arnold, Silvia Mozo, Ursula Paul, Udo Radius, Holger Braunschweig,

Organometallics **2015**, *34*, 5709-5715.



Aryldihydroborane Coordination to Iridium and Osmium Hydrido Complexes

Nicole Arnold, Silvia Mozo, Ursula Paul, Udo Radius, Holger Braunschweig,

Organometallics

Journal Impact Factor: 4.186 (ISI Journal Citation Reports © Ranking: 2015)

Contribution to this publication: 30 %

3. Author

DOI: 10.1021/acs.organomet.5b00788

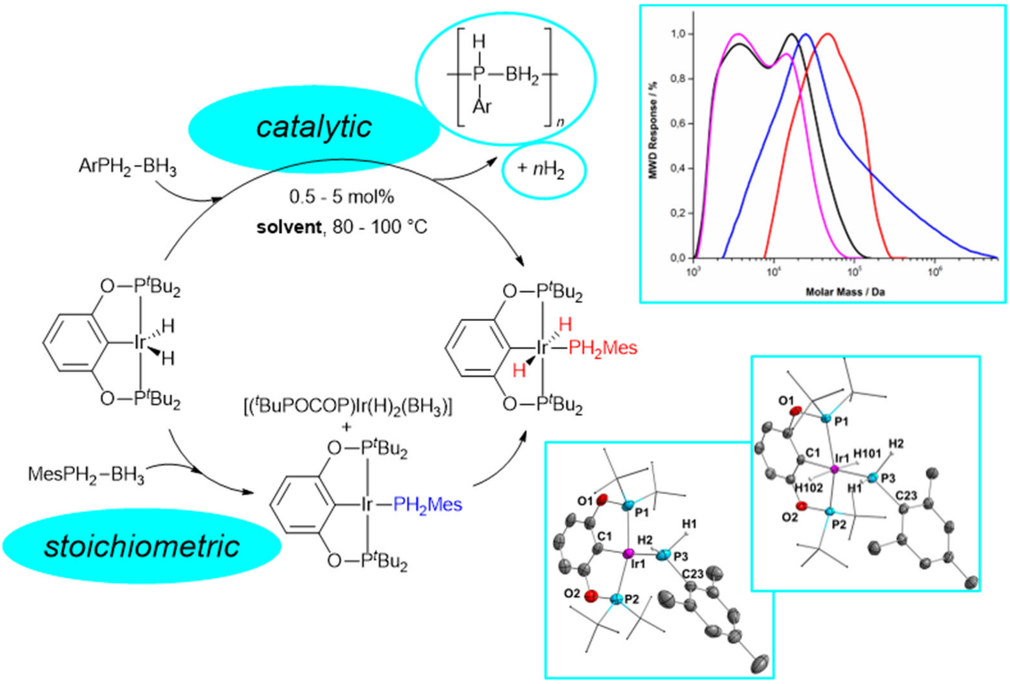
Hyperlink: http://pubs.acs.org/doi/abs/10.1021/acs.organomet.5b00788

4.2. Publication II.

Iridium-catalysed dehydrocoupling of aryl phosphine–borane adducts: synthesis and characterisation of high molecular weight poly(phosphinoboranes)

Ursula S. D. Paul, Holger Braunschweig, Udo Radius

Chem. Commun. **2016**, *52*, 8573-8576.



Iridium-catalysed dehydrocoupling of aryl phosphine–borane adducts: synthesis and characterisation of high molecular weight poly(phosphinoboranes)

Ursula S. D. Paul, Holger Braunschweig, Udo Radius

Chemical Communications

Journal Impact Factor: 6.567 (ISI Journal Citation Reports © Ranking: 2015)

Contribution to this publication: 90 %

1. Author

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Chapter II.

Reactivity of Cyclic (Alkyl)(Amino) Carbenes and Nickel Complexes thereof

1. Introduction

1.1. Synthesis and Characteristics of Cyclic (Alkyl)(Amino) Carbenes

It took more than quarter of a century from the pioneering work of Wanzlick *et al.*[1] until Arduengo *et al.* finally succeeded in the synthesis and isolation of the first stable crystalline N-heterocyclic carbene (NHC), 1,3-diadamantyl imidazoline-2-ylidene, in 1991.[2] Since then, NHCs have not only become a considerable alternative to phosphines as ancillary ligands in transition-metal chemistry, especially in homogeneous catalysis,[3] but also have found versatile applications on their own, for example in organocatalysis.[4] Their efficiency is mostly attributed to the sterically demanding structure and strong σ-donor properties.[4a, 5] In 2005, more than a decade after this breakthrough in NHC chemistry, Bertrand *et al.* reported of the synthesis of first representatives of another class of stable carbenes, which has attracted increasing study in recent years.[6] These cyclic (alkyl)(amino) carbenes (cAACs) arise from the replacement of one of the electronegative amino substituents of NHCs by a more electropositive alkyl group. The steric profile of cAAC ligands is largely variable with an almost unlimited choice of the substituents at the quaternary carbon atom in α-position to the carbene center.[7] Furthermore, DFT calculations revealed that cAACs are more electron rich, i.e. more nucleophilic, than the parent NHCs (Figure 1.1.1).

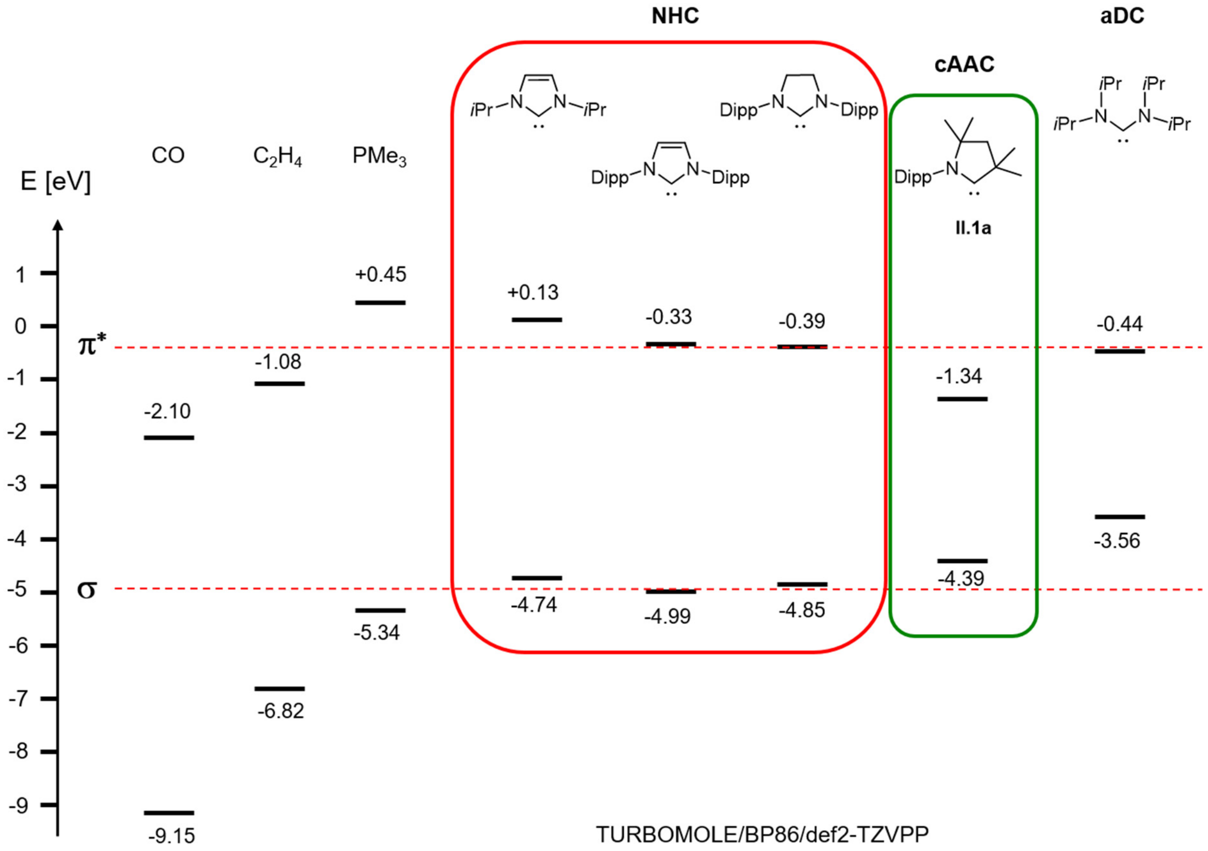
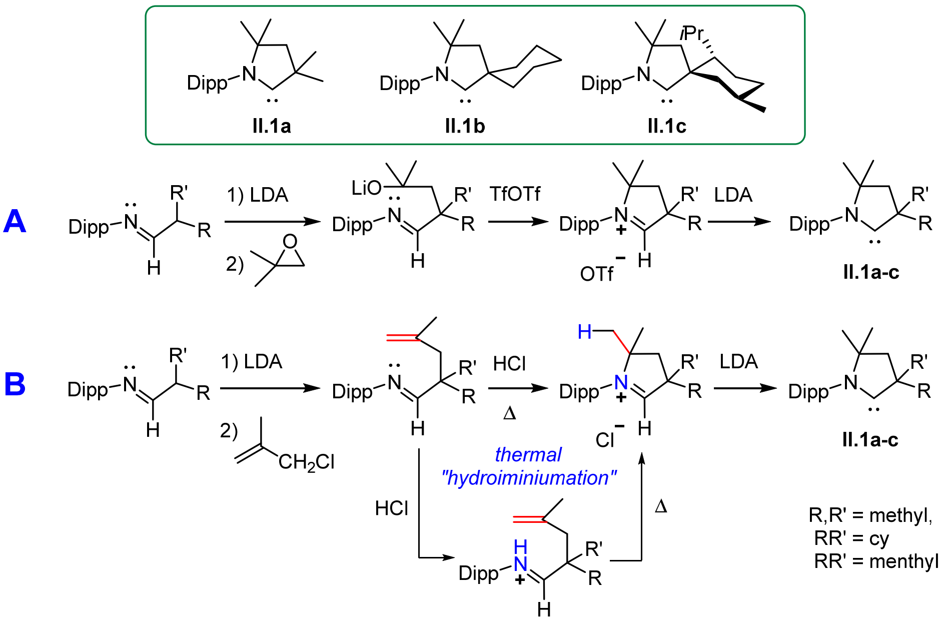


Figure 1.1.1: The calculated energies of the HOMO and LUMO (in eV) of common ligands in transition metal chemistry, such as CO, ethylene, PMe3, selected NHCs (*i*Pr2Im, Dipp2Im, Dipp2Im^{H4}), cAAC^{methyl} (**II.1a**) and an acyclic diaminocarbene (aDC). Geometry optimizations were performed using the DFT (def2-TZVPP/BP86) implementation of the TURBOMOLE set of programs.

Accordingly, the HOMO of the methyl-substituted cAAC **II.1a** is slightly higher in energy (-1.34 eV) than that of related NHCs, like saturated $Dipp_2Im^{H4}$ (-4.85 eV), and common tertiary phosphines, like PMe_3 (-5.34 eV). On the other hand, cAAC ligands have a smaller singlet–triplet energy gap due to a significantly lower energy carbene π^* orbital (-1.34 eV) and thus are also considerably more electrophilic than NHCs or phosphines (Figure 1.1.1). This finding is clearly reflected in the ability of cAACs to activate small molecules, such as CO,[8] H_2,[9] and P_4[10] as well as enthalpically strong bonds, such as C–H,[11] Si–H, B–H, N–H, P–H[9, 12] and even B–C,[13] very recently. It also serves as explanation for the stabilization of a range of main-group element radicals[14] as well as the stabilization of non-transition metal centers with unusual oxidation states, as most impressively exemplified in the isolation of beryllium(0) compound $[Be(cAAC^{methyl})_2]$ by Braunschweig *et al.*. [15]

The first synthetic approach to access the methyl-, cyclohexyl- and menthyl-substituted cAACs **II.1a-c** was published by Bertrand *et al.* in 2005, in which an aldimine (that is already bearing the desired substituents in α position) is deprotonated and reacted with 1,2-epoxy-2-methylpropane to yield an alkoxy aldimine (Scheme 1.1.1, **A**).[6] Cyclization to the corresponding aldiminium salt is achieved by treatment with triflic anhydride. This compound can be deprotonated with LDA to afford the respective free carbene **II.1a-c** as colorless solid. A more facile and economic synthesis of these cAACs was reported two years later by the same group (Scheme 1.1.1, **B**).[7] This "hydroiminiumation" route makes use of the same aldimine as starting material, which is deprotonated and reacted with 3-chloro-2-methylpropene to afford an alkenyl aldimine, instead. Heating a solution of this compound in the presence of two equivalents of HCl/Et_2O results in a cyclization under formation of the carbene precursor, which can be deprotonated accordingly to the corresponding free cAAC **II.1a-c**.

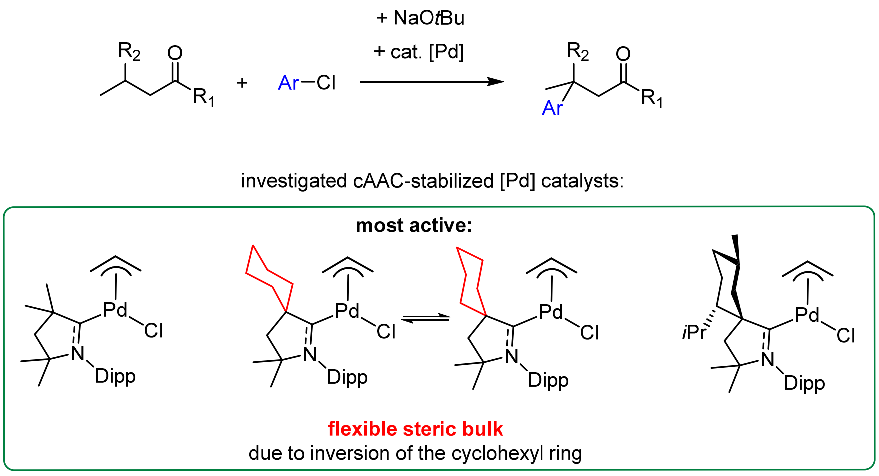


Scheme 1.1.1: Synthetic strategies for $cAAC^{RR'}$ (R,R' = methyl **II.1a**, RR' = cy = **II.1b**, RR' = menthyl **II.1c**).

While the choice of the amino substituent was found to be restricted to electron-withdrawing groups (e.g. 2,6-di*iso*propylphenyl, Dipp), the substituents at the quaternary carbon atom in α-position to the carbene center can be chosen deliberately. This offers the possibility to create any desired steric congestion around the carbene carbon atom and even to generate enantiomerically pure carbenes in the case of cAAC^{menthyl} (**II.1c**).

1.2. Cyclic (Alkyl)(Amino) Carbenes as Ligands in Transition Metal-mediated Catalysis

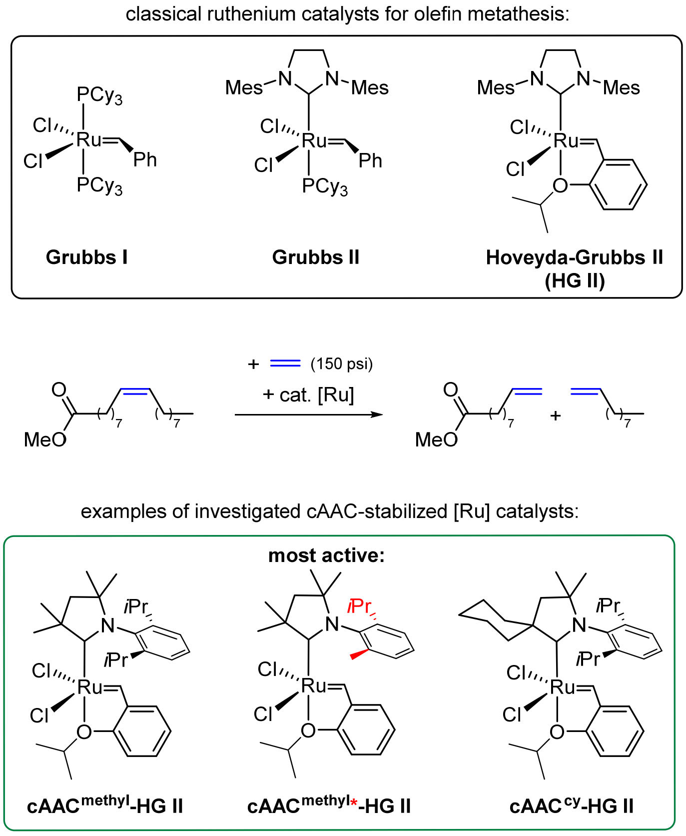
Their tunable steric and outstanding electronic properties make cAACs to perfect candidates for homogeneous catalytic applications that require transition metal complexes coordinated by electron-rich ligands with a specific bulkiness at the transition metal center. Accordingly, cAACs could be successfully employed as ligands in the palladium-catalyzed α-arylation of carbonyl compounds (Scheme 1.2.1).[6]



Scheme 1.2.1: Palladium-catalyzed α-arylation of carbonyls, utilizing cAACs **II.1a-c** as ligands.

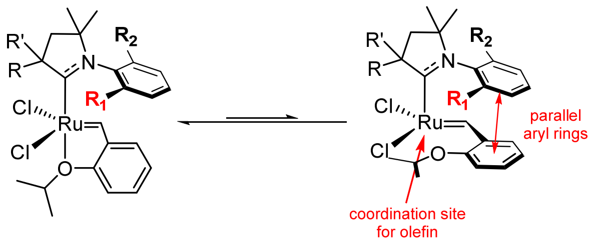
The air-stable pre-catalysts $[PdCl(\eta^3\text{-}H_2C{=}CH\text{–}CH_2)(cAAC^{RR'})]$ (RR' = methyl, cyclohexyl, menthyl) were prepared by treatment of dinuclear allyl chlorido complex $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2C{=}CH\text{–}CH_2)_2]$ with cAAC **II.1a-c**. Interestingly, the cAAC^{cy}-substituted complex revealed the highest catalytic activity with a turn over number (TON) of up to 7200 at room temperature. This is presumably due to its flexible steric bulk (when undergoing a ring flip), which enables oxidative addition of the aryl chlorides but also favours reductive elimination of the arylation products. Analogous NHC-stabilized palladium complexes have so far not resulted in comparable TONs at mild reaction conditions.[16] The high efficiency of the cAAC^{cy}-coordinated catalyst at ambient temperature allows even for a selective α-arylation of aldehydes, like *iso*butanal. This reaction is in general likely to be hampered by a competing aldol condensation in the presence of a base especially at elevated temperatures, which was not observed using cAAC-stabilized catalysts at room temperature.

Furthermore, cAACs have been intensively investigated as ligands in ruthenium-catalyzed olefin metathesis.[17] Presumably one of the greatest advances in transition metal catalysis had been achieved by the exchange of one phosphine ligand of the first generation Grubbs or Hoveyda-Grubbs catalysts with a more nucleophilic NHC ligand,[18] which was acknowledged with Grubbs, Schrock and Chauvin being awarded the Nobel Prize in 2005. As cAACs are proposed to be better σ-donors than NHCs it was of high interest, if their coordination would result in higher catalytic activities compared to these second generation Grubbs or Hoveyda-Grubbs catalysts (Scheme 1.2.2).[17]



Scheme 1.2.2: Ruthenium-catalyzed enolysis of methyl oleate, utilizing cAACs as ligands.

The air-stable cAAC-coordinated precatalysts were prepared from the first generation Hoveyda-Grubbs complex by substitution of PCy_3 and successfully utilized in several different metathesis reactions. The best results were obtained for the ethenolysis of methyl oleate with TONs approaching 200 000 to 330 000, when sterically few demanding 2-methyl-6-*iso*propylphenyl substituted $cAAC^{methyl*}$ is bound to the ruthenium catalyst. The observed structure-activity relationship is attributed to the catalyst initiation in which the ether moiety dissociates from the metal center under rotation of its benzylidene ring parallel to the N-aryl group.[17e] Minimizing the steric bulk of the cAAC ligand both at nitrogen as well as at the quaternary carbon atom in α-position to the carbene carbon facilitates this reaction and thus leads to an increase in catalytic activity.[17a]



Scheme 1.2.3: Proposed catalyst initiation with coplanar arrangement of the aryl rings.

Probably the most thoroughly investigated catalytic system bearing cAAC ligands is, however, the cationic gold(I) complexes, like [Au(cAAC^{adamantyl})(η^2-toluene)][B(C_6F_5)$_4$][19] or Werner-type complex [Au(cAAC^{adamantyl})(NH_3)][B(C_6F_5)$_4$],[20] and the closely related cAAC-stabilized gold(I) halides[21] (Figure 1.2.1).

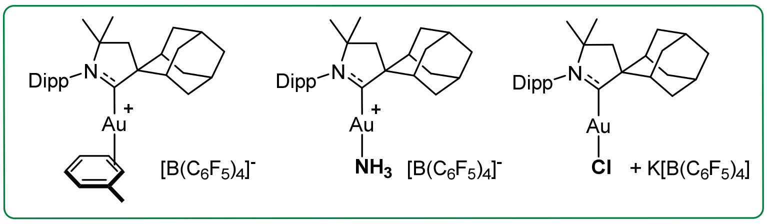
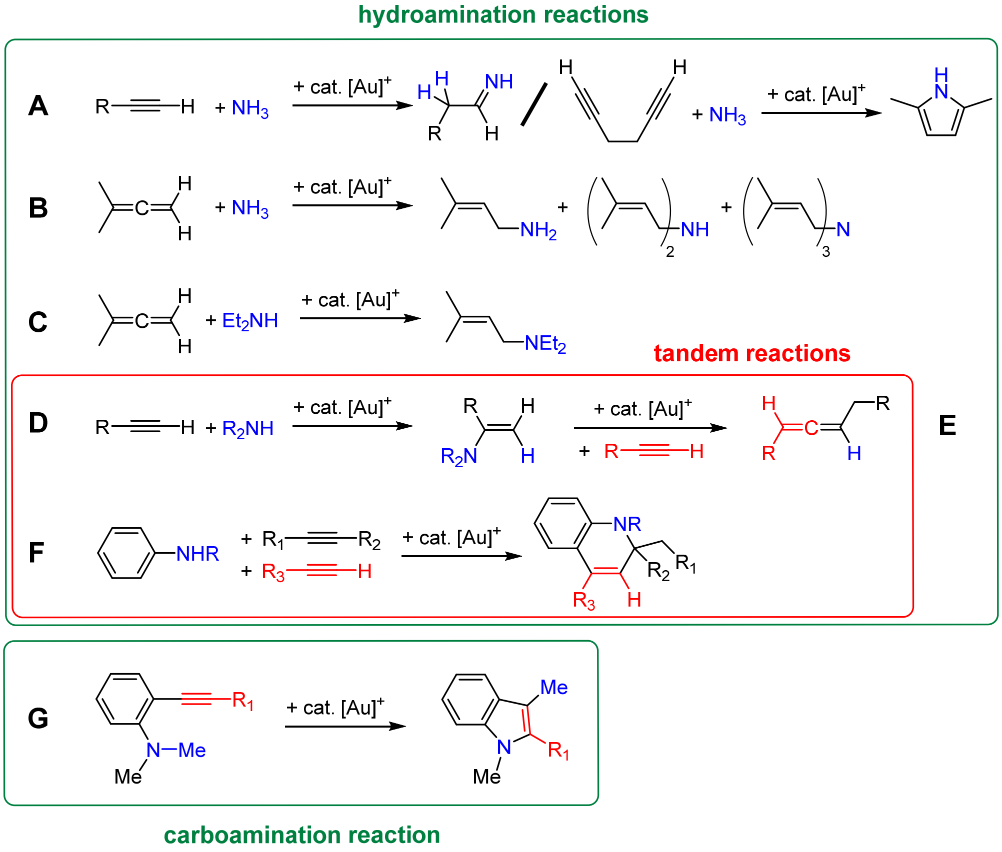


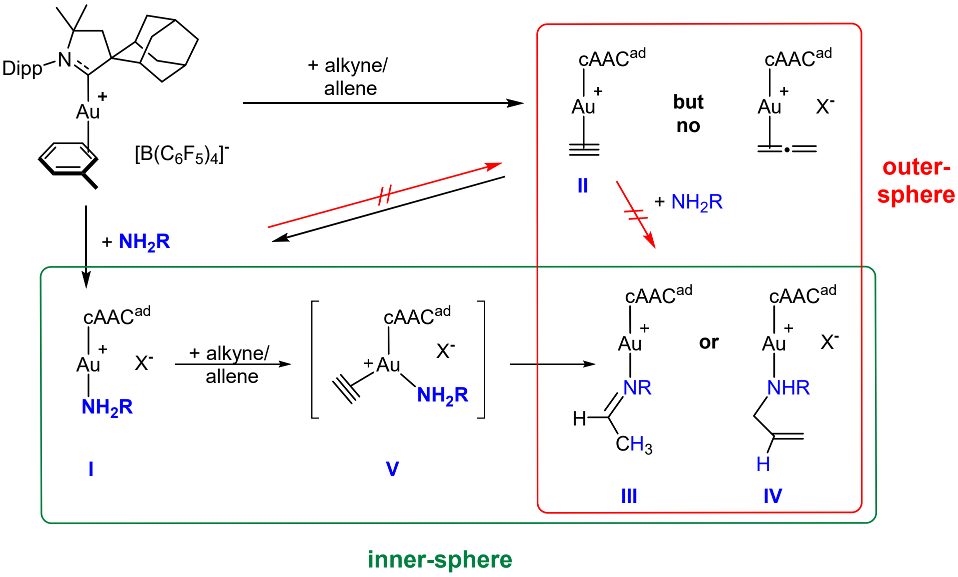
Figure 1.2.1: Examples of investigated cAAC-stabilized [Au] catalysts.

Like their phosphine- or NHC-coordinated congeners, they proved to be highly active catalysts for a broad range of hydroamination reactions[19-20, 22] (Scheme 1.2.4) though displaying thermal robustness and high functional-group tolerance as well as low air and moisture sensitivity. The most outstanding example might be the efficient addition of ammonia to a variety of unactivated alkynes (**A**) and allenes (**B**).[20] The activation and subsequent functionalization of readily available and thus inexpensive ammonia still remains one of the main challenges of transition metal and catalytic chemistry as there are still very few examples reported in literature.[23] On the other hand, the desired transformation products, like amines, imines and nitrogen-containing heterocycles, are important compounds for organic synthesis, natural products chemistry and industrial applications arising thereof.



Scheme 1.2.4: Gold-catalyzed hydroamination (**A-D**), homo-/cross-coupling tandem (**E, F**) and carboamination (**G**) reactions, utilizing the adamantyl-substituted cAAC as ligand.

Furthermore, the cAAC-stabilized gold complexes were utilized in the catalytic hydroamination of alkynes to enamines (**D**) and allenes to allylic amines (**C**) with a variety of substrates, such as primary and secondary amines as well as hydrazines.[22a, 22c, 22e] The latter reaction was found to produce regioselectively the respective secondary and tertiary allylamines as products of a Markovnikov hydroamination.[22a] As the gold-catalyzed coupling of enamines and terminal alkynes to allenes with the loss of imines had been reported earlier,[19] Bertrand *et al.* were also able to develop a one-pot synthesis of such allenes, starting directly from the respective internal and/or terminal alkynes and secondary amines in a 2:1 ratio (**E**).[22c] The same cationic gold(**I**) catalyst was furthermore used for promoting a tandem hydroamination-hydroarylation reaction, in which an arylamine adds to an internal alkyne in the first step. Then a terminal alkyne inserts into an adjacent C–H bond of the amino arene ring while being coupled to the hydroaminated alkene (**F**). [22b] Remarkably cAAC-stabilized gold complexes were not only found to catalyze the addition of N–H bonds (hydroamination) across C–C multiple bonds but also to catalyze the intramolecular addition of N–C bonds (carboamination) across the C–C triple bonds of 2-alkynyl-*NN'*-dimethylanilines (**G**).[22d]



Scheme 1.2.5: Mechanistic investigations on the hydroamination of alkynes and allenes, proposing an inner-sphere reaction pathway.

Mechanistic investigations revealed that the cationic gold(**I**) complexes initially react with ammonia or amines to Werner-type complexes $[Au(cAAC^{adamantyl})(NH_3)][B(C_6F_5)_4]$ (Scheme 1.2.5, **I**). In the presence of an excess of an alkyne or allene the amino ligand is not replaced with the olefin to give an η^2-alkyne or η^2-allene complex (**II**), but the respective imine- (**III**) or allylamino-ligated complexes (**IV**) are formed instead.[20, 22e] Therefore, an inner-sphere insertion mechanism would be most likely, involving a tri-coordinate gold(I) intermediate (**V**), similarly postulated for the gold-catalyzed hydroamination of alkynes and allenes with arylamines by Tanaka and Yamamoto using $[Au(CH_3)(PPh_3)]$ or $[AuBr_3]$ as pre-catalysts.[24] However, no such an amino η^2-olefin complex (**V**) could be identified within the intramolecular hydroamination of 2-alkynyl-*N*-methylanilines or the methylamination of 2-alkynyl-*NN'*-dimethylanilines (Scheme 1.2.4, **G**),[22d] thus leaving the validation of the proposed mechanism as an important object of the ongoing research in this field of cAAC chemistry.

1.3. Cyclic (Alkyl)(Amino) Carbenes stabilizing low-valent Transition Metal Species

The ready accessibility of stable though comparably low-coordinated complexes is a rather general feature of cAAC-stabilized transition metal chemistry and a useful prerequisite for applications of these complexes in catalytic processes, as shown in chapter 1.2. The-solvent coordinated cationic gold(I) complex $[Au(cAAC^{adamantyl})(\eta^2\text{-toluene})][B(C_6F_5)_4]$, for example, is obtained by halide abstraction from the parent chloride complex $[AuCl(cAAC^{adamantyl})]$.[19] Although the toluene is η^2-coordinated to the metal, X-ray diffraction experiments revealed only minor perturbations of the aromatic ring, and thus the complex might be described as a pseudo-naked $[Au(cAAC)]^+$ cation. However, this compound is reported to be indefinitely stable in solution and solid state and shows high thermal stability, what made it a perfect candidate for catalytic applications. Although activity and selectivity of $[Au(L)]^+$ species in catalysis have been studied extensively,[25] there are only few examples in literature for the isolation of such compounds.[26]

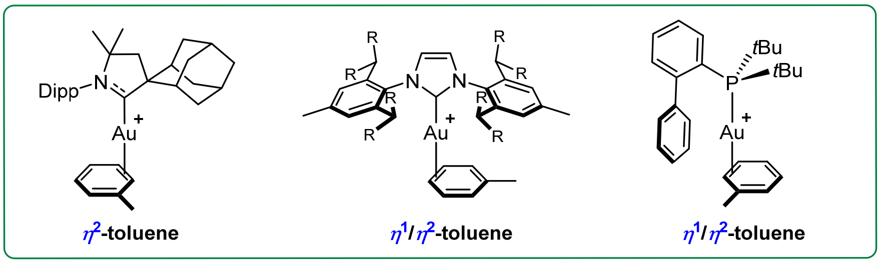
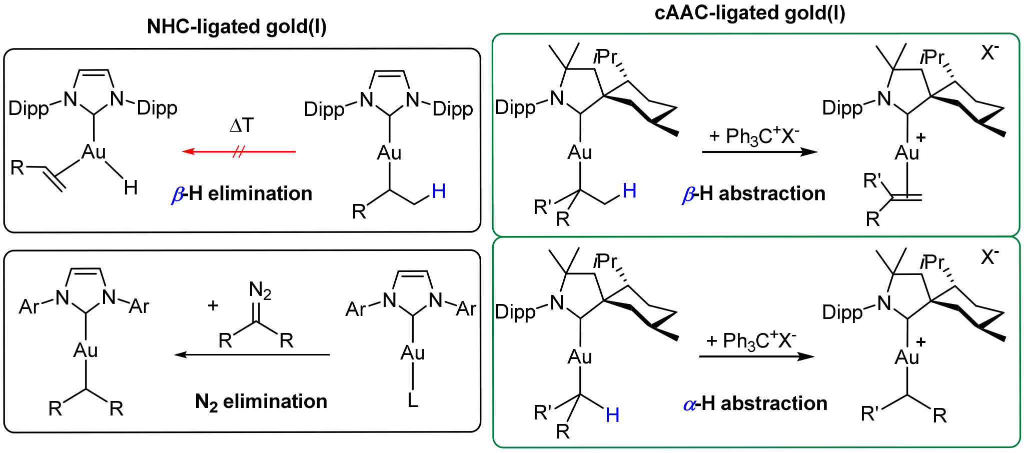


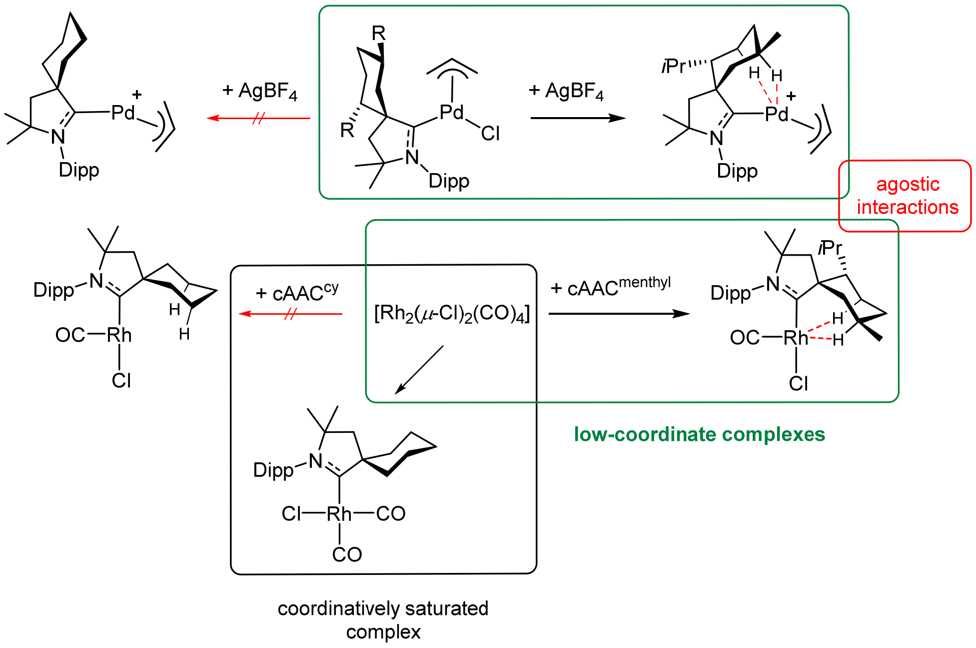
Figure 1.3.1: Examples of weakly solvent-coordinated and thus pseudo-naked $cAAC^{adamantyl}$- (left), NHC- (IPr**, R = *p*-*t*Bu-C_6H_4, middle) or phosphine- (JohnPhos, right) stabilized gold(I) cations.

These complexes have in common, that the cationic metal center requires high electronic donation as well as steric shielding by the ligand (L), what can be implemented by the use of very bulky tertiary phosphines (e.g. JohnPhos)[26a] or carbenes (e.g. $cAAC^{adamantyl}$, IPr**)[26c] (Figure 1.3.1).



Scheme 1.3.1: Differences in reactivity of NHC- (left) and cAAC-stabilized (right) gold(I) alkyl complexes.

Similar cationic cAAC-stabilized alkene complexes were obtained by *β*-hydride abstraction from a gold(I) alkyl precursor $[Au(butyl)(cAAC^{menthyl})]$[27] (Scheme 1.3.1, top). Contrary to experimental and theoretical results on β-hydride elimination from related NHC-stabilized systems,[28] this reaction was facilitated due to the strong electron-donor properties of the cAAC ligand. In the same way, α-hydride abstraction was also feasible and resulted in the formation of novel bis-carbene-stabilized gold(I) complexes [27] (Scheme 1.3.1, bottom). Furthermore the preparation of cAAC-supported multinuclear, mixed valence gold(I)-gold(0) as well as gold(I)-gold(I) clusters and their role in the catalytic carbonylation of amines has been reported by Bertrand *et al.*.[29] Hetero bimetallic compounds resulting from the coordination of cAAC-stabilized gold, silver and copper cations to an anionic dimetalloborylene $[(\eta^5\text{-}C_5H_5)(CO)Mn{=}B{=}Mn(CO)(\eta^5\text{-}C_5H_5)]^-$ have been reported by Braunschweig *et al.*.[30]

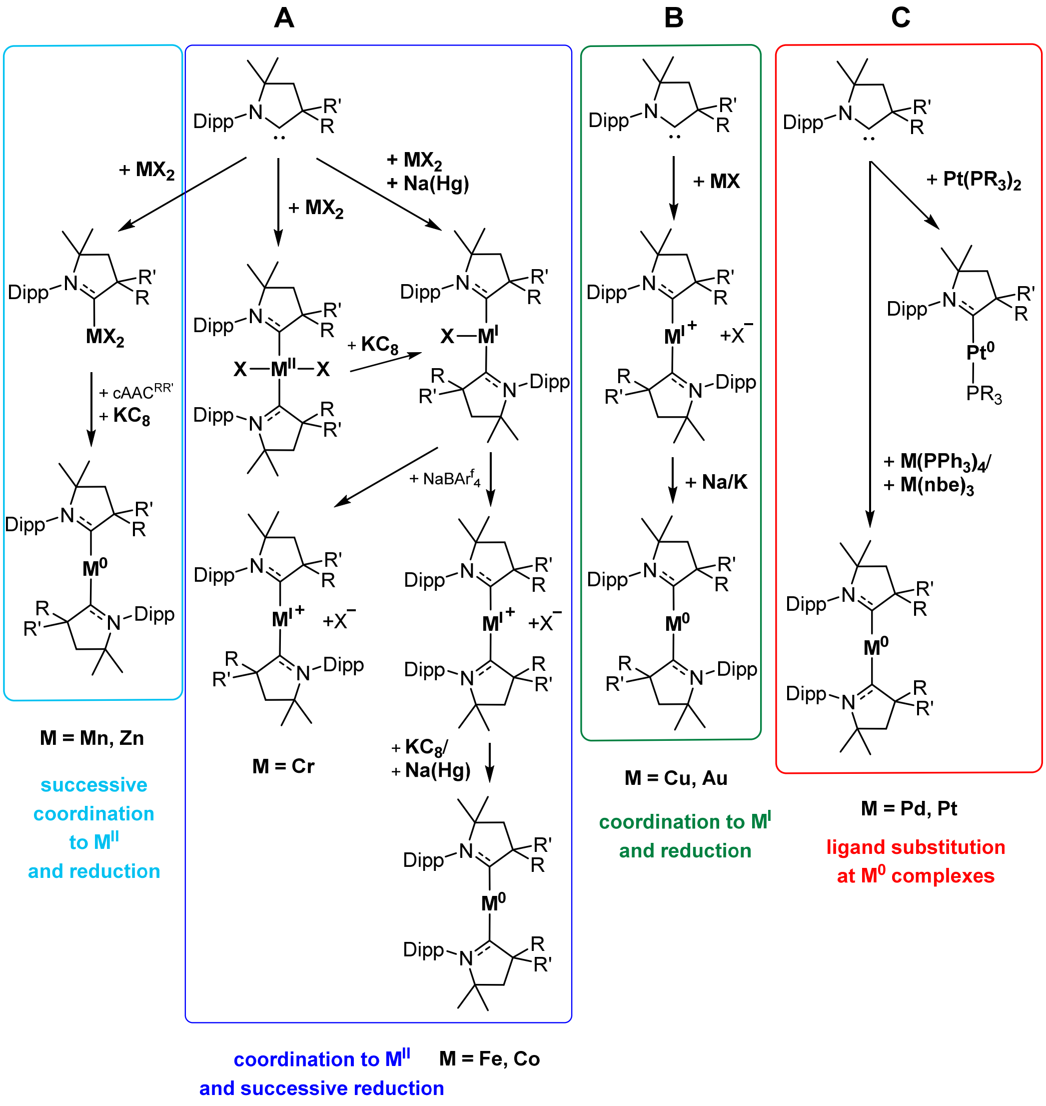


Scheme 1.3.2: Stabilization of low-coordinate palladium(II) and rhodium(I) complexes by the sterically demanding cAAC$^{\text{menthyl}}$ ligand.

The accessibility of stable complexes of catalytically relevant transition metals in their common oxidation but unexceptional low coordination state by utilizing cAACs as ligands has furthermore been reported for the 14VE species $[RhCl(CO)(cAAC^{menthyl})]$ and $[Pd(\eta^3\text{-}H_2C{=}CH\text{–}CH_2)(cAAC^{menthyl})]^+$[31] (Scheme 1.3.2). The formation of comparable compounds bearing the sterically less demanding cAAC$^{\text{cy}}$ ligand, however, was not possible, reflecting its flexible and thus remarkably reduced steric bulk (see Scheme 1.2.1). The surprising stability of these low-coordinated complexes can not only be explained by the high steric shielding and electron-donating ability of the cAAC$^{\text{menthyl}}$ (**II.1c**) ligand, but predominantly by the presence of agostic interactions with H atoms of the cyclohexyl ring of the menthyl substituent.

A recent but noteworthy application of cAACs in transition metal chemistry is, that they provide access to bis-cAAC-stabilized diamagnetic and paramagnetic complexes with the metal center in low or even the zero oxidation state. Such low-valent $[M(L)_2]^{n+}$ species have been envisioned as key intermediates in catalytic processes (especially for late transition metals) and thorough studies on stability and reactivity of such compounds are therefore of high importance. Since the first syntheses of a homoleptic cationic bis-cAAC-coordinated gold(I) complex in 2008[21] and a homoleptic neutral bis-cAAC-stabilized zinc(0) compound in 2013,[32] a considerable number of stable $[M(cAAC)_2]^{n+}$ species of Group 6 to Group

12 metals (M) have been reported[33] mainly by the groups of Bertrand [34a] [35] [36] and Roesky.[34b, 34d, 34e] [37] [38] [39a]



Scheme 1.3.3: Synthesis of [M(cAAC)$_2$]$^+$, [M(cAAC)$_2$], and [M(cAAC)(PR$_3$)] by **A** coordination of cAACs to a M(II) metal center and subsequent reduction, **B** coordination of cAACs to a M(I) metal center and subsequent reduction or **C** ligand substitution at a M(0) complex (nbe = norbornene).

With the exception of the palladium(0)[39a] and platinum(0)[39b] representatives, these compounds have been obtained following the same synthetic strategy (Scheme 1.3.3), namely the adduct formation of cAAC with the respective metal halide **A** MX$_2$ (for M = Cr,[37] Mn,[38] Fe, Co,[34] Zn[32]) or **B** MX (for M = Cu,[35] Au[21]) in the first step and a subsequent transformation of these products by a suitable reducing agent to the desired low-valent [M(cAAC)$_2$] complexes. In some cases also homoleptic compounds [M(cAAC)$_2$]$^+$ with the metal in non-zero oxidation state could be obtained as final products (M = Cr)[37] or intermediates (M = Fe, Co, Cu, Au) from partial reduction and halide abstraction reactions. Contrarily, two-coordinate homoleptic palladium and platinum complexes [M(cAAC)$_2$] as well as heteroleptic [Pt(cAAC)(PR$_3$)] have been obtained by **C** ligand exchange from the respective phosphine- or olefin-ligated Pd(0) or Pt(0) precursors.[39]

Evaluation of the structural parameters and magnetic properties obtained from experimental data as well as theoretical studies on the electronic situations revealed, however, fundamental differences between the investigated $[M(cAAC)_2]^{n+}$ systems with a strong dependence of the metal center and that the respective bonding and electronic situation of these is largely unpredictable without the interaction of experimental and theoretical studies. Due to their electronic configuration ($d^5 – d^9$ and $d^{10}s^1$) the formal Cr(I), Mn(0), Fe(0), Co(0) and Cu(0)/Au(0) compounds are paramagnetic and the magnetic susceptibility measurements suggest S = 5/2 (Cr^+),[37] S = 3/2 (Mn),[38] S = 1 (Fe), S = ½ (Co),[34] S = ½ (Cu)[35] and S = ½ (Au)[36] spin ground states for the corresponding $[M(cAAC)_2]^{n+}$ compounds.

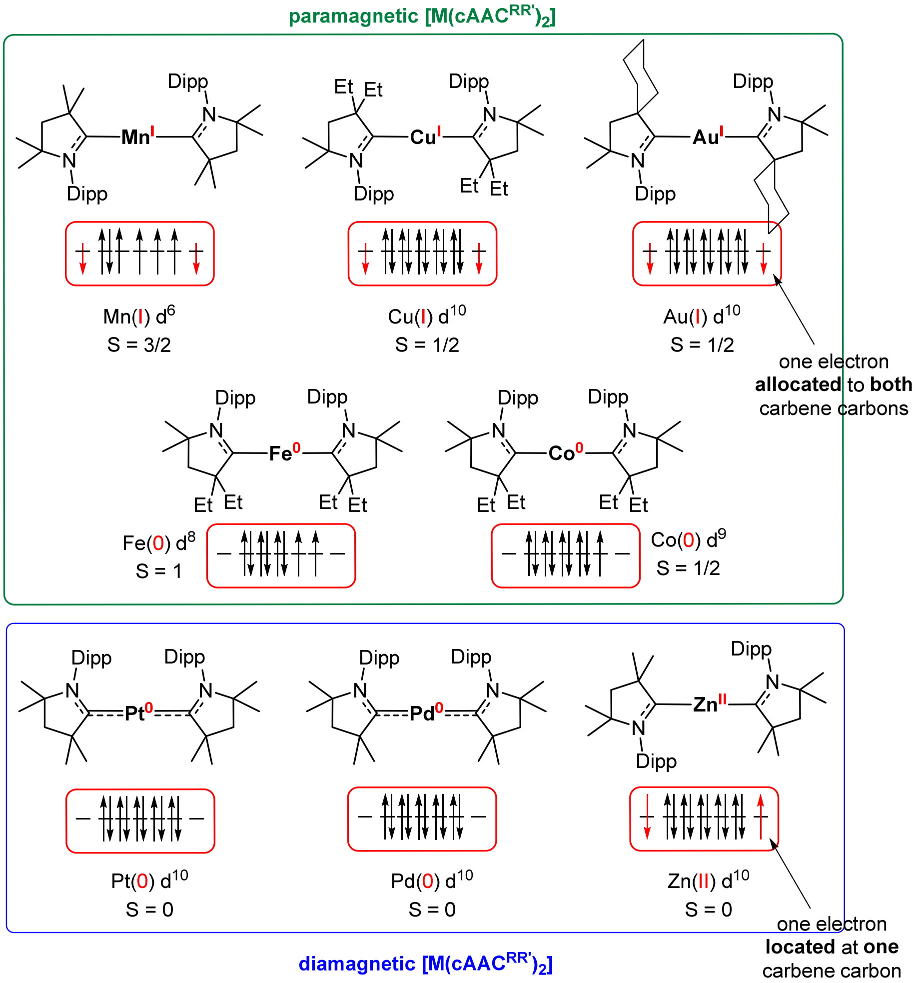
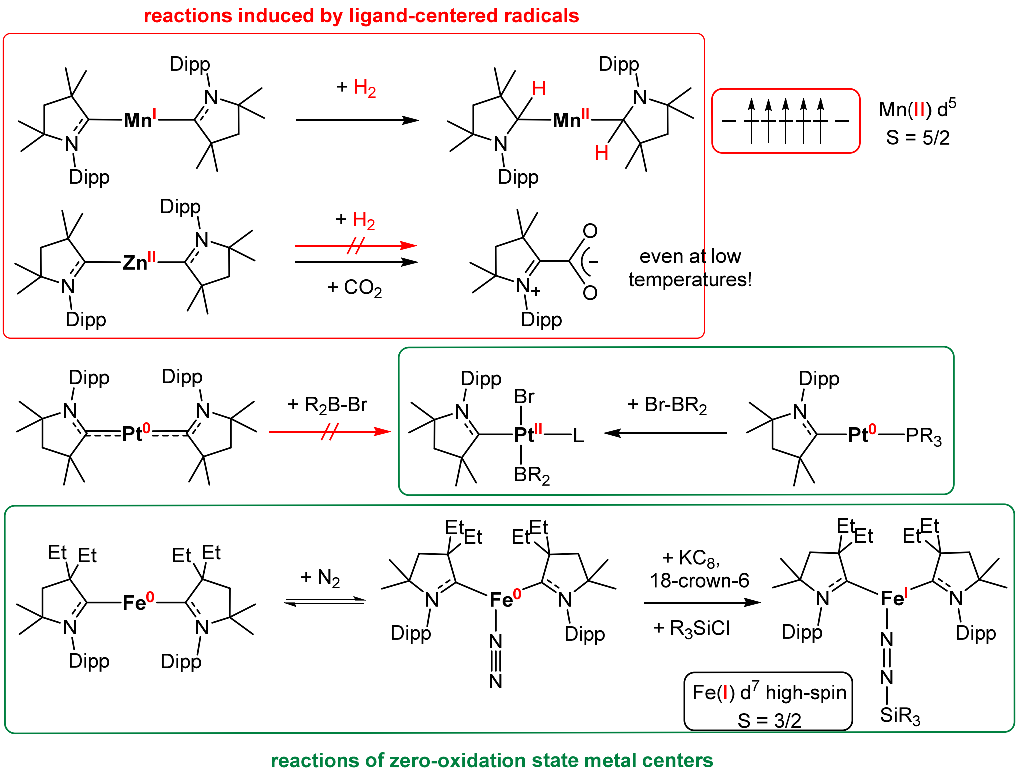


Figure 1.3.2: Electronic configuration and spin ground states (S) of neutral, homoleptic bis-cAAC-coordinated complexes $[M(cAAC^{RR'})_2]$ of Group 7 to Group 12 metals (M).

While this correlates well with the expected values for chromium(I), iron(0) and cobalt(0), a prediction of the spin ground state based on linear coordination of zero oxidation state metals with given d-electron configuration fails for manganese, copper and gold (Figure 1.3.2). Theoretical investigations confirmed that a non-zero oxidation state, namely Mn(I), prevails for the neutral $[Mn(cAAC)_2]$ complex and that one radical electron is delocalized over the two adjacent carbene carbon atoms, what results in a S = 3/2 ground state due to antiferromagnetic coupling. This radical center character of both cAAC carbon atoms was supported by the finding, that dihydrogen is cleaved homolytically by $[Mn(cAAC)_2]$ to result in $[Mn^{II}(cAACH)_2]$ with the hydrogen atoms attached to the former carbene carbons instead of the metal atom (Scheme 1.3.4).[38] Likewise, [Cu(cAAC)$_2$] and [Au(cAAC)$_2$] should formally be described as Cu(I) and Au(I) complexes, with one unpaired electron delocalized over the p(π) orbitals of the ligands and the metal (thus resembling in a way a d^{10}s^{0}p^1 Cu(0)/Au(0) configuration).[35-36] Similar results have also been obtained from theoretical studies on the diamagnetic compound [Zn(cAAC)$_2$] indicating a singlet biradicaloid instead of the expected singlet closed-shell ground state, what is reflected with the high reactivity of this bis-cAAC-stabilized formal Zn(II) complex towards CO$_2$ (Scheme 1.3.4).[32] Although for diamagnetic Group 10 metal complexes [Pd(cAAC)$_2$] and [Pt(cAAC)$_2$] no such a radical formation and delocalization could be observed, DFT calculations revealed significant π-backdonation from the respective metal center to the cAAC ligands. Thus these compounds were found to be essentially inert against Lewis acids, such as halo boranes, whereas the related heteroleptic complexes [Pt(cAAC)(PR$_3$)] undergo B–X bond activation reactions with bromo boranes and even form a metal-only Lewis pair with GaCl$_3$ (Scheme 1.3.4).[39b] The only (homoleptic) examples for the majority of the spin density remaining on the metal center and only moderate backbonding to the carbene ligands are the iron and cobalt complexes [M^0(cAAC)$_2$].[34a] Remarkably, the iron complex [Fe(cAAC)$_2$] is able to bind dinitrogen at low temperatures, what was substantiated by reductive trapping of the [Fe(cAAC)$_2$(N$_2$)] species as a diazenido complex [Fe(cAAC)$_2$(N$_2$SiR$_3$)] (Scheme 1.3.4), and to catalyze the reductive transformation of N$_2$ to NH$_3$.[40]

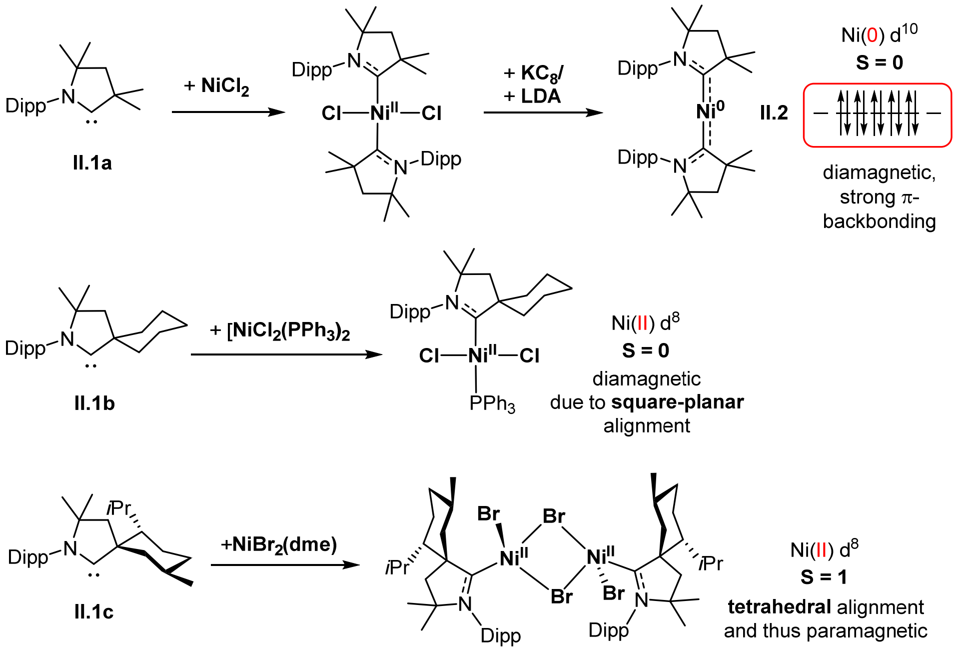


Scheme 1.3.4: Examples for characteristic reactions of [M(cAAC)$_2$] with the metal in +I/+II or zero oxidation state.

The stability and reactivity of the above mentioned low-valent transition metal complexes can to a great extend be attributed to the steric and especially the outstanding electronic properties of the cAAC ligands. A comparably small singlet–triplet energy gap enables the delocalization of radical electrons into the ligand-based orbitals. Furthermore, the high polarizability of the cAACs results in the stabilization of various (unusual) metal species by either pure donor or any required combination of donor and acceptor bonding.

1.4. Cyclic (Alkyl)(Amino) Carbene-coordinated Nickel Complexes

While there have been numerous great advances in cAAC-ligated transition metal chemistry, especially in the fields of catalysis (chapter 1.2) and stabilization of low-valent metal species (chapter 1.3), the respective nickel complexes were unknown until the first synthesis of such a cAAC-coordinated compound $[Ni_2Br_2(\mu\text{-}Br)_2(cAAC^{menthyl})_2]$ in 2013.[41] Since then, there have only been two further reports focusing mainly on the ligation of nickel(II) halides[42] and the synthesis and characterization of a first bis-cAAC-stabilized nickel(0) complex $[Ni(cAAC^{methyl})_2]$[43] (**II.2**) (Scheme 1.4.1).



Scheme 1.4.1: Synthesis of cAAC-stabilized nickel(II) and nickel(0) complexes.

Though all investigated carbenes **II.1a-c** are known to possess strong electron-donating and the same way accepting properties, the reaction of $cAAC^{menthyl}$ (**II.1c**) with nickel bromide affords dinuclear $[Ni_2Br_2(\mu\text{-}Br)_2(cAAC^{menthyl})_2]$ with each nickel atom being tetrahedrally coordinated by three bromido and one carbene ligand.[41] By means of crystal field splitting a square planar coordination mode should prevail over a tetrahedral, and indeed the sterically less demanding cAACs **II.1a-b** form diamagnetic *trans*-$[NiCl_2(cAAC^{methyl})_2]$ and *trans*-$[NiCl_2(cAAC^{cy})(PPh_3)]$ upon treatment with nickel(II) chlorides. [42-43] This different outcomes of similar reactions can be explained with the extraordinary high steric demand of the $cAAC^{menthyl}$ ligand together with bulkier bromido (compared to chlorido) ligands around a comparably small first-row transition metal cation, which results in the formation of a tetrahedral complex as favored product due to sterics.

Furthermore, Roesky *et al.* reported of a reduction of bis-$cAAC^{methyl}$-coordinated *trans*-$[NiCl_2(cAAC^{methyl})_2]$ to the zero-oxidation state $[Ni(cAAC^{methyl})_2]$ (**II.2**) by KC_8 or LDA as reductants

(Scheme 1.4.1, top).[43] The latter is a diamagnetic, dark purple colored compound with a singlet closed-shell spin ground state and significant contributions of π-backdonation to the carbene–metal bonds. Theoretical studies revealed additionally the presence of a low lying, singlet biradical exited state with nickel in the formal oxidation number of +I and the presence of one radical electron being delocalized over both carbene carbons (compare to biradical [Zn(cAAC^{methyl})$_2$], Figure 1.3.2). The intense color of product **II.2** is similar to that of related NHC-stabilized complexes, like [Ni(Dipp$_2$Im)$_2$] (deep purple) and [Ni(Dipp$_2$Im^{H4})$_2$] (purple), and stands in line with the absorption bands at 533, 611 and 807 nm, observed in the UV/Vis spectrum, which were assigned mainly to HOMO → LUMO, HOMO-2 → LUMO and HOMO-3 → LUMO excitations. The molecular structure of [Ni(cAAC^{methyl})$_2$] (**II.2**) in the solid state was obtained from X-ray diffraction experiments (Figure 1.4.1) and shows a slightly distorted linear coordination of two cAAC^{methyl} ligands to the nickel(0) center. Reduction of the nickel(**II**) precursor *trans*-[NiCl$_2$(cAAC^{methyl})$_2$] to nickel(0) complex **II.2** is accordingly accompanied with a shortening of the Ni–carbene carbon bonds and an elongation of the N–carbene carbon bonds, what indicates significantly increased π-backbonding from the metal to the carbene ligands in the latter compound. Furthermore, the N1-C1-C3-N2 torsion angle is reduced from 180 ° in the chlorido precursor to 76 ° in [Ni(cAAC^{methyl})$_2$] (**II.2**), with both N–Dipp groups oriented to the same side with respect to the nickel atom. This is in agreement with a general trend,[39a] which has been observed for the alignment of the carbene rings in complexes of the type [M(cAAC)$_2$]. While in complexes of M = Mn, Cu, Au and Zn (with radical electrons delocalized over the carbene carbons) the respective Dipp groups are aligned on opposite sides, complexes of M = Fe, Co, Ni, Pd and Pt show both Dipp groups at the same side (thus rather enabling π-backdonation to some extend). The orientation of the N-aryl rings thus might have a huge influence on the spin ground state and electronic structure of low-valent cAAC-stabilized transition metal complexes, and *vice versa*.

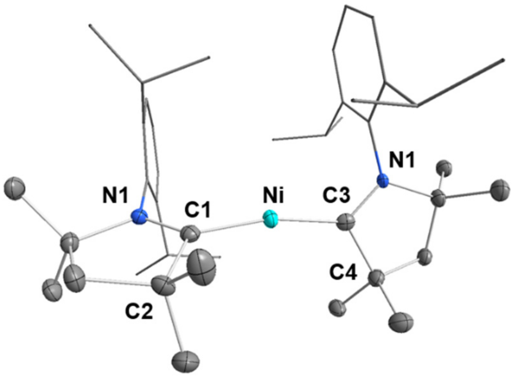
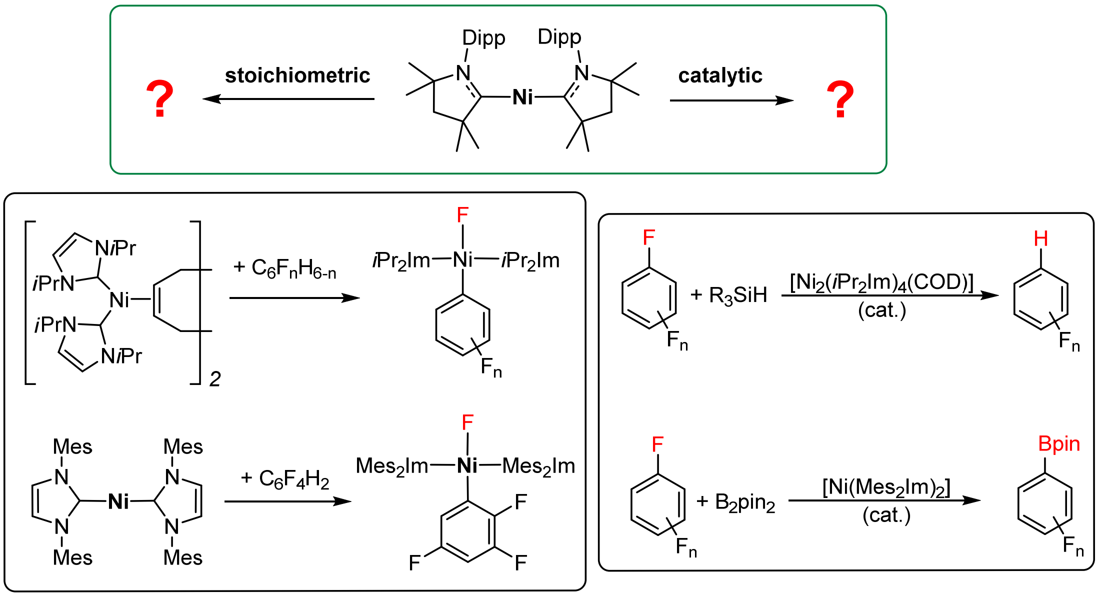


Figure 1.4.1: Molecular structure of [Ni(cAAC^{methyl})$_2$] (**II.2**), prepared according to literature.[43]

First catalytic investigations of Ni(cAAC^{methyl})$_2$] (**II.2**) were successfully carried out at the base- (LDA) mediated cross-coupling between unactivated aryl fluorides/chlorides and aryl Grignard reagents.[43] The mixed carbene-phosphine-ligated nickel(**II**) complex *trans*-[NiCl$_2$(cAAC^{cy})(PPh$_3$)] was, however, very recently reported to be rather inefficient as catalyst for Suzuki-coupling, hydrosilylation and α-arylation reactions.[42]

1.5. Motivation

Based on these very few initial results in cAAC-coordinated nickel chemistry, we wanted to explore in more depth the reactivity of the highly interesting low-valent nickel(0) complex $[Ni(cAAC^{methyl})_2]$ (**II.2**), with a focus on C–F and C–H bond activation reactions as we have been thoroughly investigating stoichiometric as well as catalytic reactions of the closely related NHC-stabilized nickel(0) complexes with partially- and perfluorinated reagents, over the last decades (Scheme 1.5.1).[44] $[Ni_2(\textit{i}Pr_2Im)_4(\mu\text{-}COD)]$, which serves as synthon for otherwise not accessible $\{Ni^0(NHC)_2\}$ species, was found to undergo oxidative addition with a series of fluorinated arenes to form complexes of the type *trans*-$[Ni(C_6F_nH_{6-n})F(\textit{i}Pr_2Im)_2]$ and readily catalyzes subsequent transformations, such as hydrodefluorination and Suzuki-Miyaura cross-coupling. [44a-g] Furthermore, we recently reported the $[Ni(Mes_2Im)_2]$-catalyzed borylation of fluoroarenes via C–F bond cleavage and were able to isolate *trans*-$[Ni(C_6F_3H_2)F(Mes_2Im)_2]$ as intermediate in the catalytic cycle of this reaction.[44h] Replacement of the NHCs by a much stronger σ-donor cAAC ligand should be very promising for these reactions, as the cleavage of the enormous strong C–F bond via oxidative addition usually requires the use of an electron-rich reagent.



Scheme 1.5.1: Possible stoichiometric and catalytic reactions of $[Ni(cAAC^{methyl})_2]$ (**II.2**) with fluoroaromatic reagents in comparison to that of the closely related NHC-stabilized nickel(0) complexes.

We also aimed to investigate the reactivity of cAACs with respect to fluorinated arenes, as they are known to be non-innocent ligands due to their ability to activate small molecules, as well as a range of common organic as well as inorganic substrates.

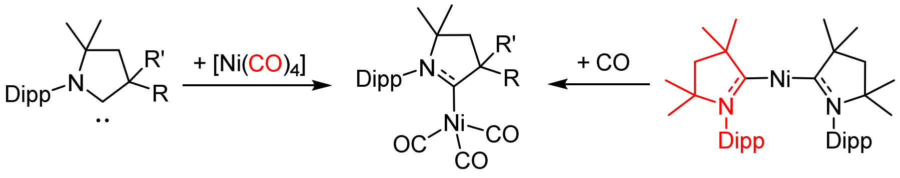
Furthermore, we were interested in the synthesis and first studies on the reactivity of cAAC-coordinated nickel carbonyl complexes. As already established as routine method for the NHC-ligated congeners, $[Ni(CO)_3(cAAC^{RR'})]$ would serve as direct measure for evaluating the overall electron-donating properties and the steric demand of these carbenes and would thus allow to compare the obtained experimental data with those previously reported from theoretical studies (e.g. DFT calculations).

2. Results and Discussion

This chapter summarizes the crucial aspects of the publications prepared during the course of this dissertation. The bibliographic data of the complete manuscripts can be found in chapter 4.

2.1. Cyclic (Alkyl)(Amino) Carbene-stabilized Nickel Carbonyl Complexes

We investigated the synthesis and characterization of nickel carbonyl complexes which are coordinated by one and two cyclic (alkyl)(amino) carbene (cAAC) ligands, respectively. The coordinatively saturated 18VE complexes $[Ni(CO)_3(cAAC^{RR'})]$ (R,R' = methyl **II.3a**, RR' = cy = cyclohexyl **II.3b**, RR' = menthyl **II.3c**) were obtained either from the reaction of carbene **II.1a-c** with a slight excess of $[Ni(CO)_4]$ or from reacting bis-cAAC-ligated complex $[Ni(cAAC^{methyl})_2]$ (**II.2**) with an excess of CO (Scheme 2.1.1).



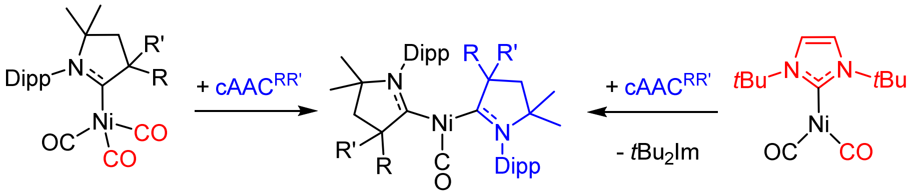
R,R' = methyl **II.1a**
RR' = cy **II.1b,**
RR' = menthyl **II.1c**

R,R' = methyl **II.3a**
RR' = cy **II.3b,**
RR' = menthyl **II.3c**

II.2

Scheme 2.1.1: Synthesis of $[Ni(CO)_3(cAAC^{RR'})]$ (R,R' = methyl **II.3a**, RR' = cy = **II.3b**, RR' = menthyl **II.3c**).

The result of the latter reaction, however, was surprising as bis-NHC-stabilized complexes, like $[Ni_2(iPr_2Im)_4(\mu\text{-}COD)]$, are known to give the corresponding bis-NHC-ligated nickel(0) carbonyl complexes $[Ni(CO)_2(NHC)_2]$ upon reaction with carbon monoxide.[44e, 45] Formation of analogous bis-cAAC-coordinated complexes $[Ni(CO)(cAAC^{RR'})_2]$ (R,R' = methyl **II.4a**, RR' = cy = cyclohexyl **II.4b**) was achieved by substitution of two further carbonyl ligands with $cAAC^{RR'}$ **II.a,b** from the parent mono-cAAC compounds **II.3a,b** (Scheme 2.1.2). An alternative synthetic strategy for the formation of complexes **II.4a,b** using $[Ni(CO)_2(tBu_2Im)]$[46] as starting material, instead, is depicted in Scheme 2.1.2.



R,R' = methyl **II.3a**,
RR' = cy **II.3b**

R,R' = methyl **II.4a**,
RR' = cy **II.4b**

Scheme 2.1.2: Synthesis of $[Ni(CO)(cAAC^{RR'})_2]$ (R,R' = methyl **II.4a**, RR' = cy = **II.4b**).

Both reactions are in marked contrast to the results obtained in studies on nickel carbonyl complexes, which are ligated by the closely related moderately bulky NHCs $Dipp_2Im$ or Mes_2Im. Their four-coordinate 18VE carbonyl complexes [Ni(CO)$_3$(NHC)] are known to be more or less inert against any kind of replacement of a carbonyl ligand.[47] Thus a bis-carbene-coordination is only achieved by substituting the bulky *t*Bu$_2$Im ligand in the coordinatively unsaturated complex [Ni(CO)$_2$(*t*Bu$_2$Im)] with formation of a four-coordinate 18VE bis-carbonyl complex, like [Ni(CO)$_2$(Mes$_2$Im)$_2$].[48] Contrarily, in the case of cAAC^{methyl} (**II.1a**) and cAAC^{cy} (**II.1b**) both release of CO and/or substitution of the NHC ligand *t*Bu$_2$Im was feasible and led to the formation of a three-coordinate 16VE mono-carbonyl complex [Ni(CO)(cAAC$^{RR'}$)$_2$] **II.4a,b** (Figure 2.1.1).

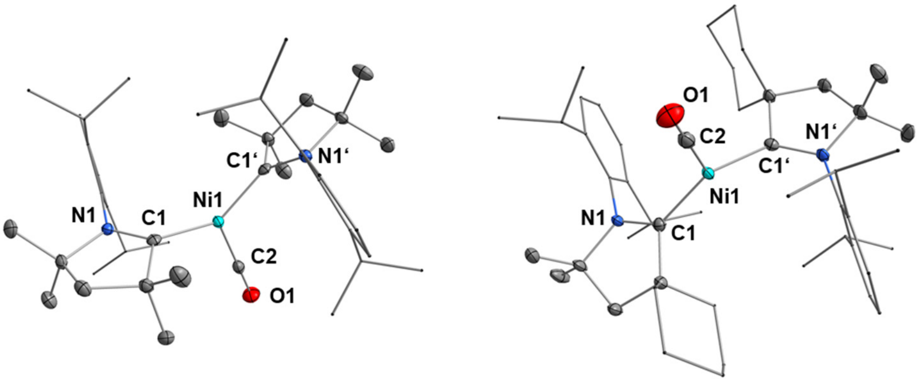


Figure 2.1.1: Molecular structures of bis-cAAC compounds [Ni(CO)(cAAC^{methyl})$_2$] (**II.4a**) (left) and [Ni(CO)(cAAC$^{cy'}$)$_2$] (**II.4b**) (right) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

Among the cAACs investigated within our studies, cAAC^{menthyl} (**II1c**) possesses an exceptional position. Reaction with [Ni(CO)$_4$] leads in the same way as described above to the formation of mono-cAAC-coordinated complex [Ni(CO)$_3$(cAAC^{menthyl})] (**II.3c**). However, only with this carbene no bis-cAAC-coordinated product [Ni(CO)(cAAC^{menthyl})$_2$] was accessible as neither a further substitution of the CO ligands by the carbene, nor an alternative replacement of *t*Bu$_2$Im at [Ni(CO)$_2$(*t*Bu$_2$Im)] occurred. Furthermore, solely cAAC^{menthyl} (**II1c**) did not produce any side-product (Figure 2.1.2) in the reaction depicted in Scheme 2.1.1. In the case of cAAC^{methyl} (**II.1a**) and cAAC^{cy} (**II.1b**) the formation of 3,3-diamino-2-aryloxyacrylimidamide **II.5a,b** (Figure 2.1.2) as side-reaction was observed when CO ligands were released from [Ni(CO)$_4$] or [Ni(CO)$_3$(cAAC$^{RR'}$)] (**II.3a,b**) in the presence of uncoordinated carbenes **II.1a** or **II.1b**.

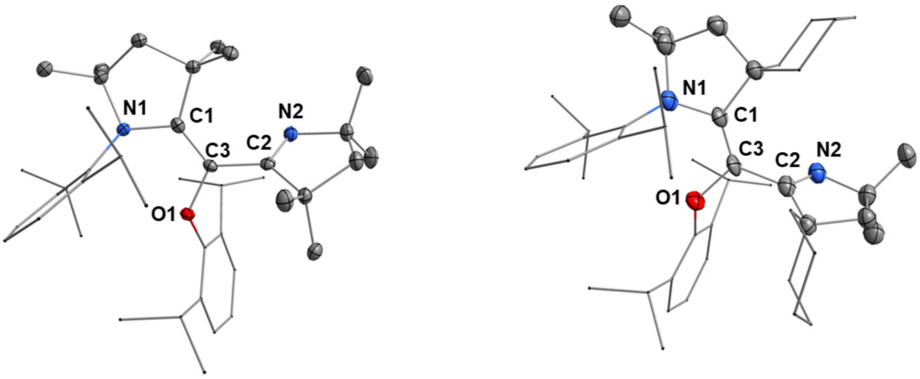
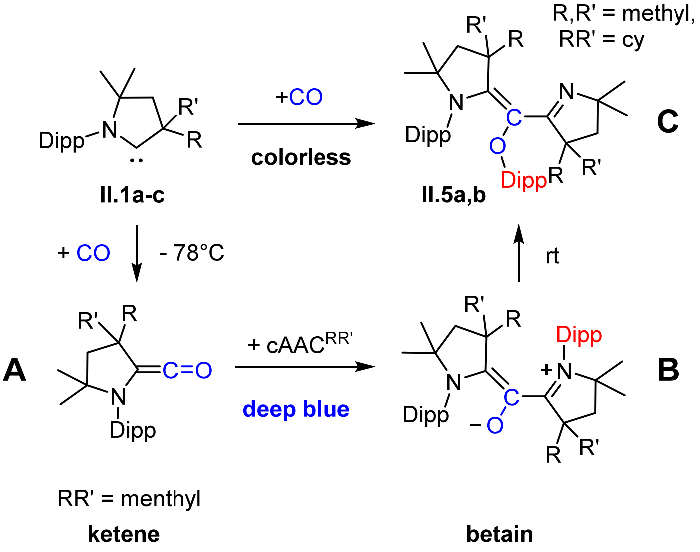


Figure 2.1.2: Molecular structures of 3,3-diamino-2-aryloxyacrylimidamides **II.5a** (left) and **II.5b** (right) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

These CO activation products were also selectively prepared by bubbling CO through a solution of cAAC$^{RR'}$ **II.1a,b**. The formation of **II.5a,b** is meant to proceed *via* the reaction of two equivalents of cAAC with CO and subsequent migration of one Dipp entity.



Scheme 2.1.3: Carbonylation of cAACs **II.1a-c** leading to a ketene **A** (RR' = menthyl) or a 3,3-diamino-2-aryloxyacrylimidamide **C** (R,R' = methyl **II.5a**, RR' = cy **II.5b**).

In the first step the electrophilic carbene adds to CO to give an amino ketene **A**, which is an isolable and stable product of the reaction of cAAC^{menthyl} with carbon monoxide.[8] In the case of cAAC^{methyl} and cAAC^{cy} a second equivalent of the carbene adds to this adduct **A** to give betain **B**, [11a] [49] which rearranges to the final product **C**, i.e. a 3,3-diamino-2-aryloxyacrylimidamide, by migration of the Dipp group to the (former) carbonyl oxygen atom [50] (Scheme 2.1.3).

2.2. Steric and Electronic Properties of Cyclic (Alkyl)(Amino) Carbenes

With the mono-cAAC complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] (**II.3a-c**) in hands, we were interested to determine the steric demand[51] as well as the electronic properties[52] of cAAC^{methyl} (**II.1a**), cAAC^{cy} (**II.1b**) and cAAC^{menthyl} (**II.1c**) and wanted to compare them with the large array of data available for the related NHCs. These results are summarized in Figure 2.2.1.

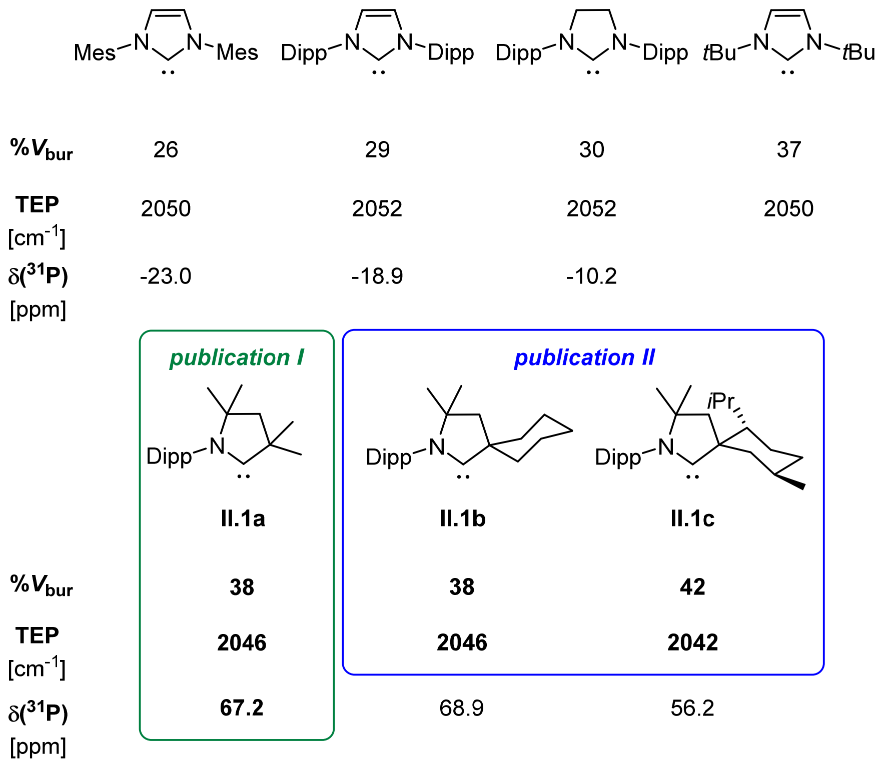
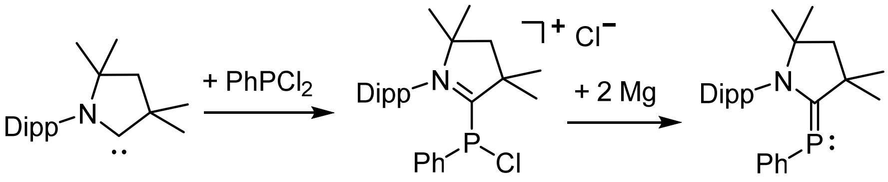


Figure 2.2.1: Comparison of NMR spectroscopic data and TEP values of selected NHCs and cAACs$^{RR'}$ **II.1a-c** as well as the calculated %V_{bur} from the respective nickel carbonyl complexes [Ni(CO)$_3$(carbene)].

The most frequently used method[47, 53] to describe the donor strength of carbene ligands, is based on the measurement of the A$_1$ carbonyl stretching frequencies of complexes of the type [Ni(CO)$_3$(L)] (L = 2 VE donor ligand, e.g. carbene), commonly known as the Tolman electronic parameter (TEP).[54] This relies on the theory that the ligand L passes electron density not only to the metal center but also to the π^* orbitals of the carbonyl ligands, thus weakening the C–O bond. The TEP values obtained from [Ni(CO)$_3$(cAAC^{methyl})] (**II.3a**) (**2046** cm^{-1}), [Ni(CO)$_3$(cAAC^{cy})] (**II.3b**) (**2046** cm^{-1}) and [Ni(CO)$_3$(cAAC^{menthyl})] (**II.3c**) (**2042** cm^{-1}) are similar to those observed for NHC-ligated complexes such as [Ni(CO)$_3$(Mes$_2$Im)] (2050 cm^{-1}), [Ni(CO)$_3$(Dipp$_2$Im)] (2052 cm^{-1}) and [Ni(CO)$_3$(Dipp$_2$Im^{H4})] (2052 cm^{-1}).[47]

The TEP, however, only reflects the overall electron density at the metal center and gives no information on conceivable contributions of π-backbonding. These π-acceptor properties of carbenes can, for example,[55] be assessed by the ^{31}P NMR shifts of carbene–phosphinidene adducts,[56] which are highly sensitive to the exact polarity of the P–C^{carbene} bond in these adducts. For this reason, we prepared the corresponding compound cAAC^{methyl}–PPh (**II.6a**) according to a literature procedure (Scheme 2.2.1).[56a]



II.1a **II.6a**

Scheme 2.2.1: Preparation of the cAAC^{methyl}–phenylphosphinidene adduct **II.6a**.

Like its bulkier cAAC-substituted congeners (δ_P = 56.2 – 68.9 ppm),[56a] product **II.6a** gave rise to a significantly low-field shifted resonance in the ^{31}P NMR spectrum (δ_P = 67.2 ppm). Accordingly, cAAC^{methyl} (**II.1a**), cAAC^{cy} (**II.1b**) and cAAC^{menthyl} (**II.1c**) were proposed to be notably stronger σ-donors than common NHCs, such as Dipp$_2$Im or Mes$_2$Im, as they gave rise to similar TEP values of 2042 - 2046 cm^{-1}, while possessing superior π-acceptor properties (Figure 2.2.1), which are only surpassed by those of acyclic (alkyl)(amino) carbenes and the so-called Bielawski-type carbenes.[56b] This high electrophilicity of cAACs$^{RR'}$ (**II.1a-c**) is also reflected by their reactivity against carbon monoxide. Whereas classical NHCs are not electrophilic enough for this reaction, cAACs$^{RR'}$ (**II.1a-c**) form stable mono- or bis-carbene adducts with CO, probably in dependence of the steric demand of the cAAC$^{RR'}$.

Quantification of the steric demand of cAAC^{methyl} (**II.1a**), cAAC^{cy} (**II.1b**) and cAAC^{menthyl} (**II.1c**) was achieved by analysis of the percent buried volume (%V_{bur}),[51] which was calculated from the X-ray crystallographic data of the carbonyl complexes [Ni(CO)$_3$(cAAC^{methyl})] (**II.3a**), [Ni(CO)$_3$(cAAC^{cy})] (**II.3b**) and [Ni(CO)$_3$(cAAC^{menthyl})] (**II.3c**) using the Samb*V*ca web application.[57] The obtained values of the %V_{bur} of 38 - 42 % are even higher than those obtained for very bulky NHCs, like *t*Bu$_2$Im[47] (Figure 2.2.1). Irrespective of their %V_{bur}, all three cAACs afforded the saturated four-coordinated complexes [Ni(CO)$_3$(cAAC$^{RR'}$)], when they were reacted with [Ni(CO)$_4$]. Contrarily, the bulky NHC *t*Bu$_2$Im replaces two carbonyl ligands yielding the three-coordinate complex [Ni(CO)$_2$(*t*Bu$_2$Im)], instead.[46] The individual steric demand is, however, of importance for the formation of complexes [Ni(CO)(cAAC$^{RR'}$)$_2$] as only the bulkiest representative cAAC^{menthyl} (**II.1c**) proved to be too demanding to yield any bis-carbene-ligated compound.

It should be noted here, that the procedure of the %V_{bur} calculation needs to be challenged to some extend when applied for cAAC-coordinated metal complexes. The Samb*V*ca program has originally been developed for NHCs and makes use of the coordinates of the carbene carbon atom and a putative center of mass, in the middle of the two NHC nitrogen atoms, and places the metal center on a line passing through this two points.[57] An (alkyl)(amino) carbene is, however, not symmetrically substituted at the carbene carbon atom and the middle of the adjacent carbon atom C2 and the nitrogen atom N1 does not longer describe a center of mass. Thus, the routine of the Samb*V*ca program assumes a bending of the carbene ring into the examined hypothetic sphere around the metal atom and therefore may significantly over-estimates the volume that is occupied by the cAAC$^{RR'}$ ligand (%V_{bur}), as depicted in Figure 2.2.2 for cAAC^{methyl} (**II.1a**).

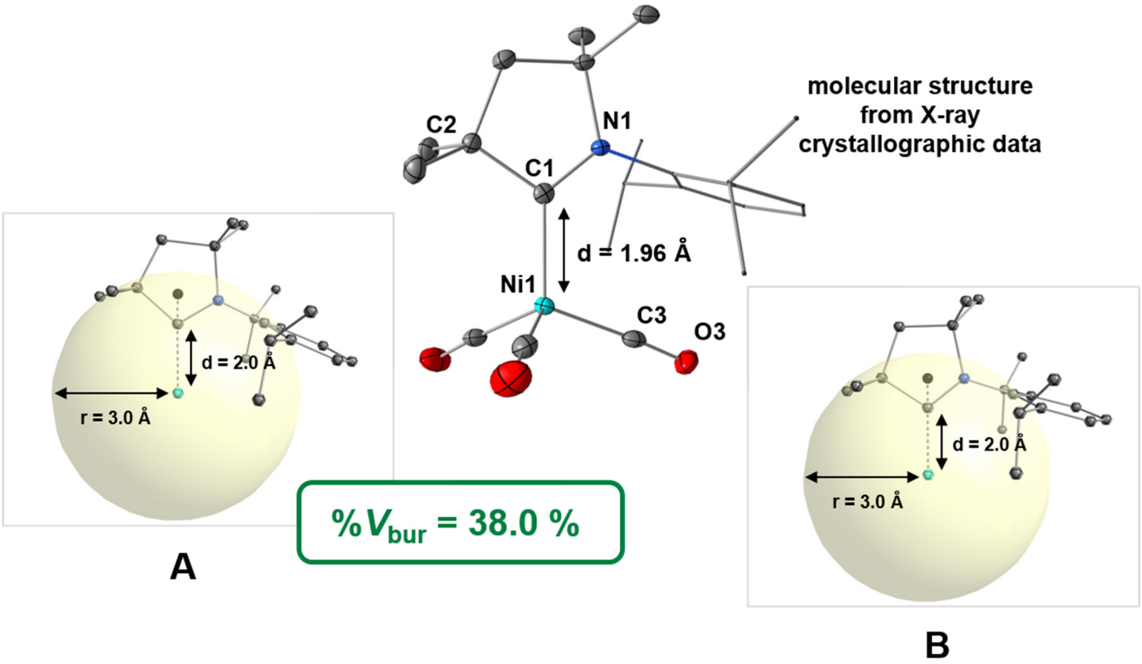
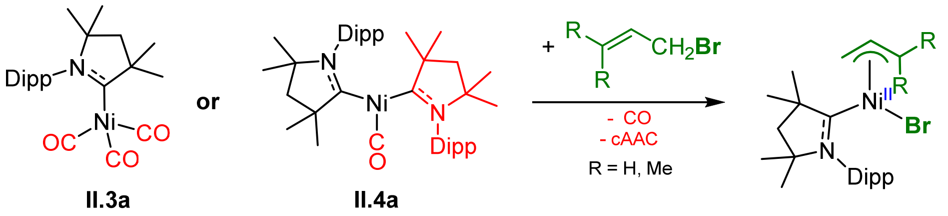


Figure 2.2.2: Molecular structure of [Ni(CO)$_3$(cAAC^{methyl})] (**II.3a**) (middle) with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms are omitted for clarity) and comparison between the coordination mode of cAAC^{methyl} (**II.1a**) within the hypothetic coordination sphere around a nickel atom **A:** modelled for the calculation of %V_{bur} according to literature (left) and **B:** derived from the solid state structure (right).

2.3. Reactivity of the Cyclic (Alkyl)(Amino) Carbene Nickel Complexes

We furthermore aimed for first studies on the reactivity of the cAAC stabilized nickel carbonyl complexes $[Ni(CO)_3(cAAC^{methyl})]$ (**II.3a**) and $[Ni(CO)(cAAC^{methyl})_2]$ (**II.4a**) with respect to π-acidic substrates.[58] We were especially interested in reactions with allyl halides, since oxidative addition of these substrates to $[Ni(CO)_3(cAAC^{RR'})]$ would provide a convenient entry into novel nickel allyl chemistry. NHC-stabilized nickel allyl complexes[47, 59] as well as the closely related cyclopentadienyl complexes[60] have attracted considerable attention over the last years, due to various catalytic applications[61] [62] of these substances and for their use as starting materials to give to very interesting, highly reactive yet isolable Ni(I) radical species.[63] Introducing cAACs as ligands, instead, appears quite promising as these are known to stabilize a broad range of main group element radicals as well as highly reactive paramagnetic transition metal species (see chapter 1.3).

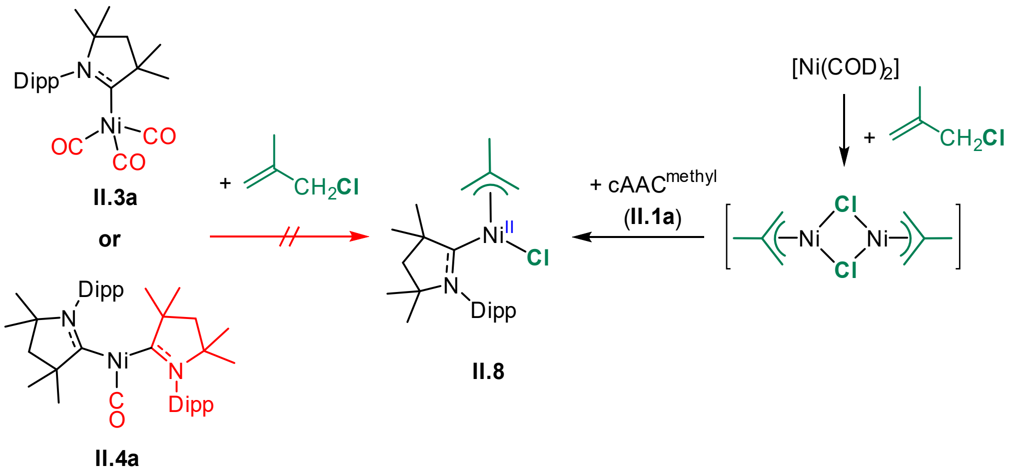
Both $[Ni(CO)_3(cAAC^{methyl})]$ (**II.3a**) and $[Ni(CO)(cAAC^{methyl})_2]$ (**II.4a**) afforded nickel(II) cAAC allyl halide complexes $[NiBr(\eta^3\text{-}H_2C{=}CH{-}CH_2)(cAAC^{methyl})]$ (**II.7a**) and $[NiBr(\eta^3\text{-}H_2C{=}CH{-}CMe_2)(cAAC^{methyl})]$ (**II.7b**) when treated with allyl bromides *via* oxidative addition of the allyl halide with CO loss (Scheme 2.3.1).



R = H **II.7a**,
R = Me **II.7b**

Scheme 2.3.1: Synthesis of allyl bromido complexes $[NiBr(\eta^3\text{-}H_2C{=}CH{-}CH_2)(cAAC^{methyl})]$ (**II.7a**) and $[NiBr(\eta^3\text{-}H_2C{=}CH{-}CMe_2)(cAAC^{methyl})]$ (**II.7b**).

Contrarily, in the case of the related NHC complexes only the use of the coordinatively unsaturated, three-coordinate 16VE complexes $[Ni(CO)_2(NHC)]$ led to reaction with allyl halides, whereas saturated 18VE complexes $[Ni(CO)_3(NHC)]$ were reported to be inert against any kind of CO substitution.[47] However, NHC-stabilized nickel carbonyls $[Ni(CO)_2(NHC)]$ reacted both with allyl chlorides and allyl bromides, while no reaction of cAAC-ligated nickel compounds **II.3a** or **II.4a** with allyl chlorides was observed. To obtain the allyl chlorido complex $[NiCl(\eta^3\text{-}H_2C{=}CMe{-}CH_2)(cAAC^{methyl})]$ (**II.8**), we followed an alternative synthetic strategy in which first the allyl chloride is oxidatively added to a nickel(0) center to give the dinuclear allyl chlorido complex $[Ni_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2C{=}CH{-}CH_2)_2]$.[59a, 59b] Afterwards, the carbene ligand is introduced into the coordination sphere of the nickel(II) intermediate by *in situ* addition of $cAAC^{methyl}$ (**II.1a**) which results in the formation of the desired mononuclear complex **II.8** (Scheme 2.3.2).



Scheme 2.3.2: Synthesis of allyl chlorido complex [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC$^{\text{methyl}}$)] (**II.8**)

The allyl halide complexes [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC$^{\text{methyl}}$)] (**II.7a**), [NiBr(η^3-H$_2$*C*=*C*H–*C*Me$_2$)(cAAC$^{\text{methyl}}$)] (**II.7b**) and [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC$^{\text{methyl}}$)] (**II.8**) have been isolated and characterized, but show decomposition at room temperature in solution as well as in solid state. This decomposition is accompanied by a color change of the yellow or orange allyl nickel halides to give a purple product.[59a, 59b] For compound **II.7a** the decomposition product **II.9** was isolated and characterized by single-crystal X-ray diffraction (Figure 2.3.1, right).

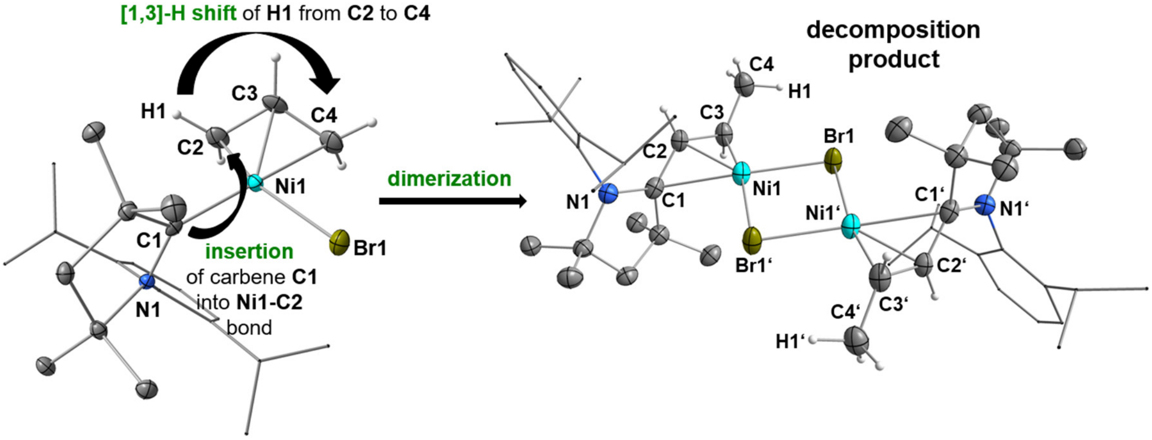
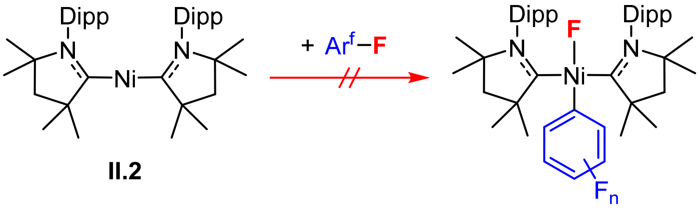


Figure 2.3.1: Molecular structures of [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC$^{\text{methyl}}$)] (**II.7a**) (left) and its decomposition product [Ni$_2$(μ-Br)$_2$(η^3-(*cAAC*$^{\text{methyl}}$)=*C*H–*C*H(CH$_3$))$_2$] (**II.9**) (right) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms except of those bound to the allyl ligand are omitted for clarity.

As depicted in Figure 2.3.1, in decomposition product **II.9** the former cAAC$^{\text{methyl}}$ ligand is incorporated into the allyl ligand with a concomitant [1,3]-H shift (from C2 to C4) to form the dinuclear allyl nickel bromido complex [Ni$_2$(μ-Br)$_2$(η^3-(*cAAC*$^{\text{methyl}}$)=*C*H–*C*H(CH$_3$))$_2$] **II.9**.

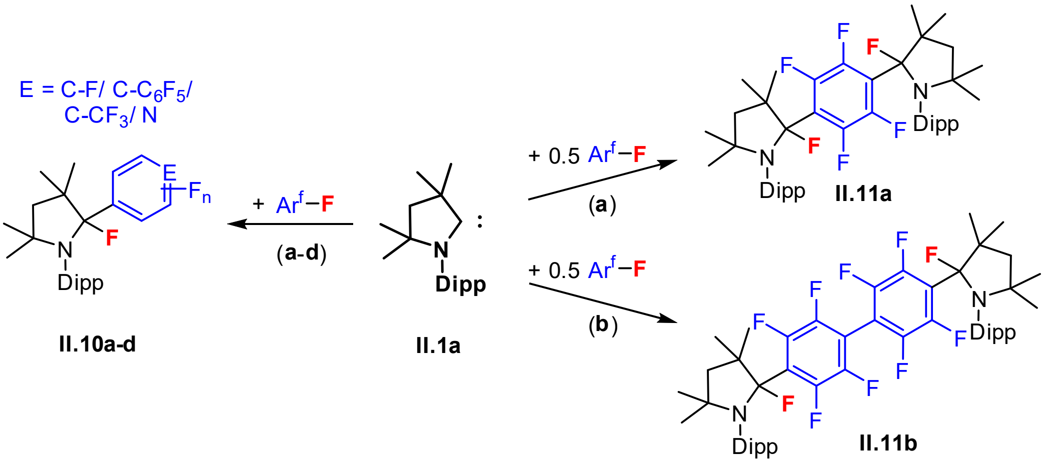
2.4. Cyclic (Alkyl)(Amino) Carbenes in C–F and C–H Bond Activation Reactions

We initially aimed for studies on the C–F bond activation of polyfluoroaromatics using the cAAC-stabilized nickel(0) complex [Ni(cAAC^{methyl})$_2$] (**II.2**) as the Radius group has thoroughly investigated stoichiometric as well as catalytic reactions of analogous NHC-stabilized nickel(0) complexes over the last decade, such as reactions of [Ni$_2$(*i*Pr$_2$Im)$_4$(μ-COD)] and [Ni(Mes$_2$Im)$_2$] with partially- and perfluorinated reagents.[44] The cleavage of the enormous strong C–F bond via oxidative addition is mostly achieved by highly nucleophilic reagents, which are typically low-valent transition metal centers that are stabilized with strongly electron-donating ligands.[64] As our evaluation of the electronic properties (see chapter 2.2) revealed cAACs to be notably stronger σ-donors than common NHCs (as they give rise to a similar TEP value while having superior π–acceptor properties), cAAC^{methyl} (**II.1a**) should be a promising ligand for nickel-mediated C–F bond activation reactions. However, [Ni(cAAC^{methyl})$_2$] (**II.2**) did not undergo any reaction with the fluorinated arenes used within our studies (Scheme 2.4.1).



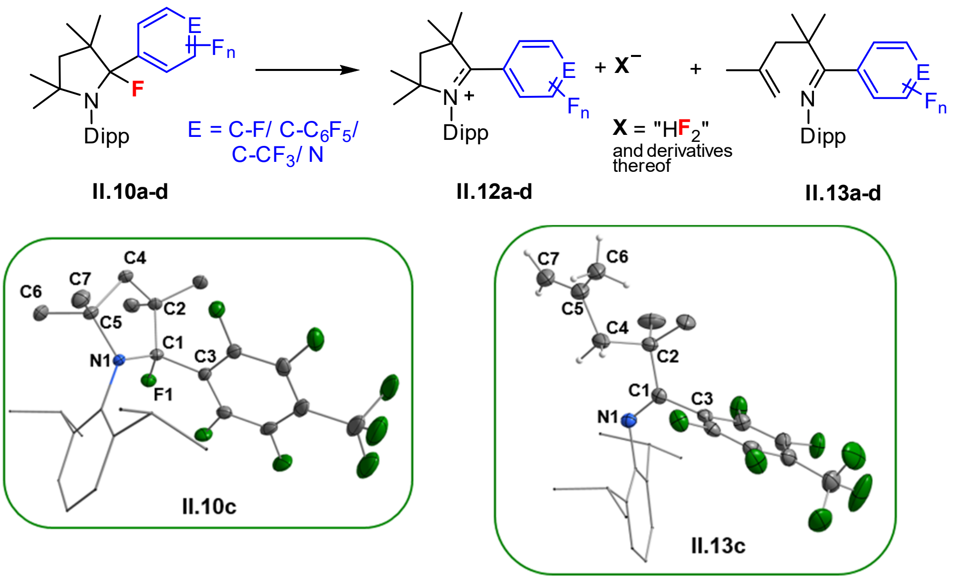
Scheme 2.4.1: Treatment of [Ni(cAAC^{methyl})$_2$] (**II.2**) with fluoroarenes.

However, addition of perfluoroarenes to the highly nucleophilic carbene cAAC^{methyl} (**II.1a**), itself, led instantly to a C–F bond activation reaction. The carbene carbon atom of cAAC^{methyl} (**II.1a**) inserts regioselectively into the C–F bond in 4-position of aryl fluorides C_5F_5E (E = C–F **a**, C–C_6F_5 **b**, C–CF_3 **c**, N **d**) with formation of the products (cAAC^{methyl})F(Ar^f) **II.10a-d**. As the cAAC bound fluoroarene of (cAAC^{methyl})F(C_6F_5) (**II.10a**) and (cAAC^{methyl})F(C_6F_4–C_6F_5) (**II.10b**) is activated towards a second nucleophilic aromatic substitution in *para*-position to the cAAC moiety we also obtained the double activation products (cAAC^{methyl})F(C_6F_4)F(cAAC^{methyl}) (**II.11a**) and (cAAC^{methyl})F(C_6F_4–C_6F_4)F(cAAC^{methyl}) (**II.11b**) depending on the stoichiometry of cAAC^{methyl} (Scheme 2.4.2). Unlike NHCs, which produce perfluoroaryl substituted imidazolium salts,[65] all these neutral products **II.10a-d** and **II.11a,b** may be considered as the products of an oxidative addition of the fluoroarene to the carbene carbon atom.[11b, 66] Similar to the oxidative addition of fluoroarenes to transition metals with an increase in coordination number and oxidation state by 2 units, the number of substituents increases here by 2 units and the formal oxidation state at the (former) cAAC carbene carbon atom (C1) raises as well.



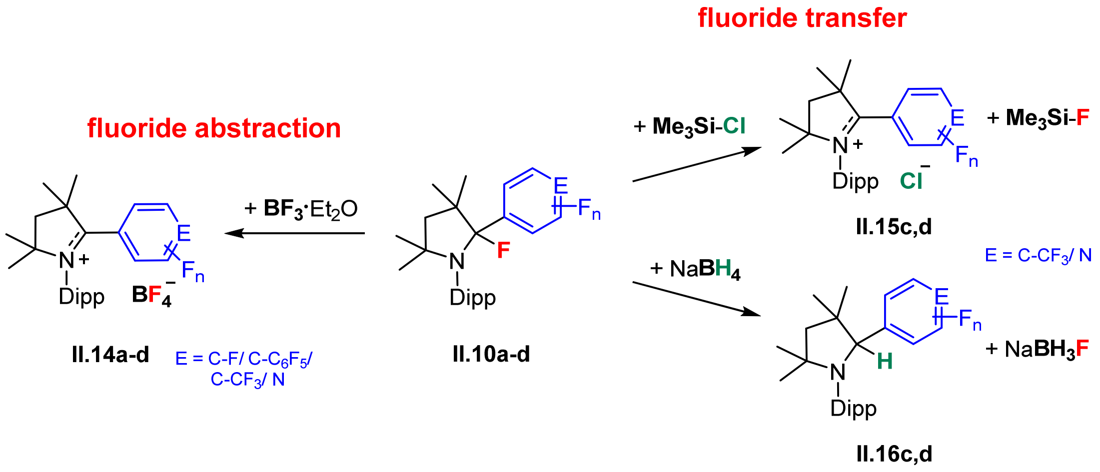
Scheme 2.4.2: Synthesis of mono C–F activation products (cAAC^{methyl})F(Ar^f) **II.10a-d** (left) and double C–F activation products (cAAC^{methyl})F(C_6F_4)F(cAAC^{methyl}) (**II.11a**) and (cAAC^{methyl})F(C_6F_4–C_6F_4)F(cAAC^{methyl}) (**II.11b**) (right).

The compounds (cAAC^{methyl})F(Ar^f) **II.10a-d** were found to feature a quite elongated and therefore presumably week bond between the former carbene carbon atom C1 and the fluoride substituent F1 (see Scheme 2.4.3) and thus fragment in solution to ionic iminium salts [(cAAC^{methyl})(Ar^f)][X] **II.12a-d** *via* cleavage of this C1–F1 bond, accompanied by elimination of HF and opening of the cAAC^{methyl} ring to yield also the neutral alkenyl perfluoroaryl imine species **II.13a-d** (Scheme 2.4.3).



Scheme 2.4.3: Decomposition of (cAAC^{methyl})F(Ar^f) **II.10a-d** due to C1–F1 bond cleavage, as illustrated with the molecular structures of (cAAC^{methyl})F(C_6F_4–CF_3) (**II.10c**) and the resulting alkenyl perfluorotolyl imine **II.13c**.

Accordingly, compounds (cAAC^{methyl})F(Ar^f) **II.10a-d** can be utilized as mild fluoride source in fluoride abstraction or fluoride transfer reactions.[66-67] Fluoride abstraction has been exemplified by the reaction with BF_3 etherate as fluoride acceptor to yield the respective iminium salts [(cAAC^{methyl})(Ar^f)][BF_4] **II.14a-d** (Scheme 2.4.4).



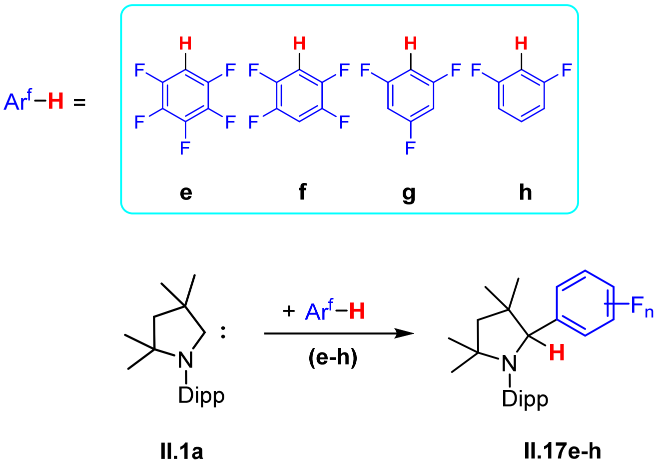
Scheme 2.4.4: Application of compounds (cAAC^{methyl})F(Ar^{f}) **II.10a-d** in fluoride abstraction (left) and fluoride transfer reactions (right) to chlorotrimethylsilane (top) and sodium borohydride (bottom), respectively.

Fluoride transfer has also been achieved starting from (cAAC^{methyl})F(C_6F_4–CF_3) (**II.10c**) or (cAAC^{methyl})F(C_5F_4N) (**II.10d**) to selected substrates such as sodium borohydride, chlorotrimethylsilane (Scheme 2.4.4) and different organo halides. The results of the fluoride transfer reactions from (cAAC^{methyl})F(C_6F_4–CF_3) (**II.10c**) (entries 1-4) and (cAAC^{methyl})F(C_5F_4N) (**II.10d**) (entries 5-8) are summarized in Table 2.4.1.

Table 2.4.1: Fluoride transfer from (cAAC^{methyl})F(C_6F_4–CF_3) (**II.10c**) or (cAAC^{methyl})F(C_5F_4N) (**II.10d**) to selected substrates.

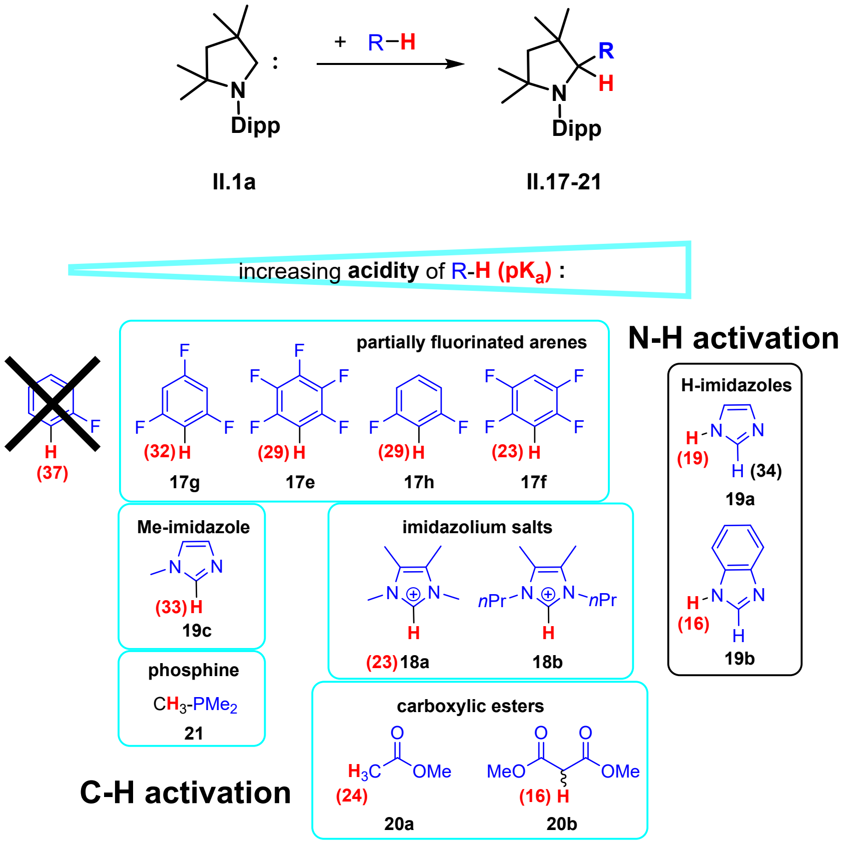
entry	substrate	fluorination reagent	conditions	conversion	product
1	Me_3Si–**Cl**	**II.10c**	C_6D_6, rt	100 %	**II.15c**
2	benzoyl–**Cl**	**II.10c**	C_6D_6, rt	100 %	**II.15c**
3	benzyl–**Br**	**II.10c**	C_6D_6, rt - 80 °C	/	/
4	*iso*propyl–**I**	**II.10c**	C_6D_6, rt - 80 °C	/	/
5	Me_3Si–**Cl**	**II.10d**	C_6D_6, rt	100 %	**II.15d**
6	benzoyl–**Cl**	**II.10d**	C_6D_6, rt	100 %	**II.15d**
5	tosyl–**Cl**	**II.10d**	C_6D_6, rt	100 %	**II.15d**
8	$NaBH_4$	**II.10d**	thf, rt	100 %	**II.16d**

Since cAAC^{methyl} (**II.1a**) activates the C–F bond of different perfluorinated arenes C_5F_5E (E = C–F, C–C_6F_5, C–CF_3, N) **a-d** with high regioselectivity at the *para*-position to the E group, we were furthermore interested in investigating the chemoselectivity of the reactions of carbene **II.1a** with partially fluorinated arenes $C_6F_nH_{6-n}$ **e-i**. Instead of C–F bond activation, exclusively insertion of the cAAC carbon atom into a C–H bond was observed with formation of the neutral products (cAAC^{methyl})H(Ar^{f}) (Ar^{f} = C_6F_5 **II.17e**,[11b] 2,3,5,6-C_6F_4H **II.17f**, 2,4,6-$C_6F_3H_2$ **II.17g** and 2,6-$C_6F_2H_3$ **II.17h**) (Scheme 2.4.5).



Scheme 2.4.5: Synthesis of C–H activation products (cAAC^{methyl})H(Ar^{f}) **II.17e-h.**

The finding that the least C–H acidic fluoroarene used, fluorobenzene C_6FH_5 ($pK_a \approx 37$), did not react, encouraged us to further investigations on scope and limitations of this carbene mediated C–H bond activation reaction. Therefore, cAAC^{methyl} (**II.1a**) was treated with reagents of different C–H acidity, commonly used to examine the basicity of organic and organometallic compounds (Scheme 2.4.6).

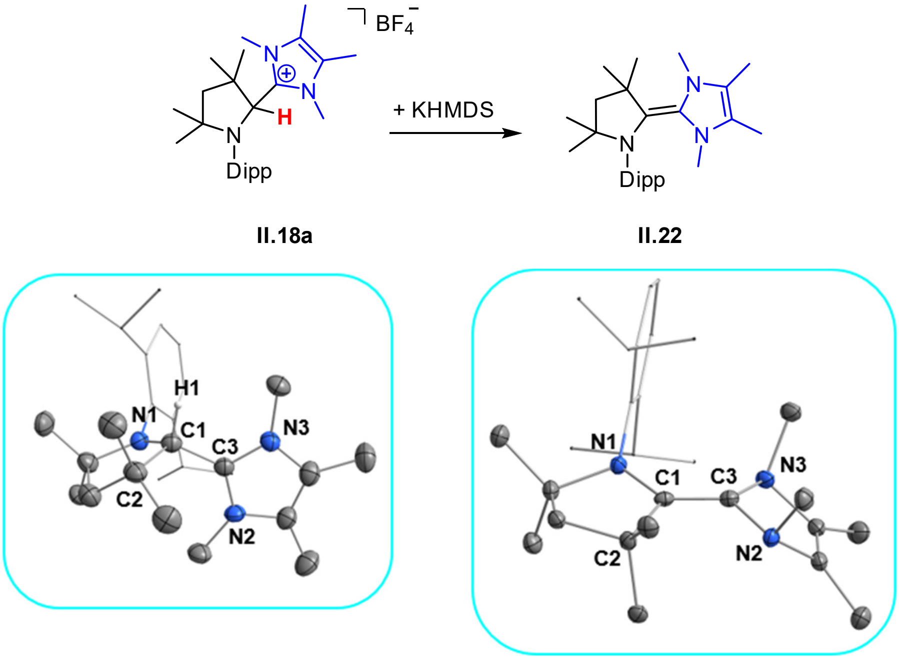


Scheme 2.4.6: Reactivity of cAAC^{methyl} (**II.1a**) towards several compounds classes, affording different activation products of partially fluorinated arenes (**II.17e-h**), imidazolium ions (**II.18a,b**), imidazoles (**II.19a-c**), esters (**II.20a,b**) and tertiary phosphines (**21**), depending on their C–H acidity.

As depicted in Scheme 2.4.6, cAAC^{methyl} (**II.1a**) was found to react readily with imidazolium salts (**II.18a,b**), imidazoles (**19a-c**), esters (**II.20a,b**) and even trimethylphosphine (**21**), though for imidazole

($C_3H_4N_2$) (**II.19a**) and benzimidazole ($C_7H_7N_2$) (**II.19b**) insertion into the more acidic N–H bond prevails over C–H bond activation.

Remarkably, all reactions afforded the neutral products ($cAAC^{methyl}$)H(R) (**II.17-21**) of a C–H or N–H bond insertion rather than abstraction of the acidic protons. Contrarily, in the course of C–H bond activation of, for example, esters with the closely related adamantly-substituted NHC (Ad_2Im) such a formation of an imidazolium cation $[(Ad_2Im)(H)]^+$ and the respective enolat anions, which can further react to Claisen condensation anions, was reported by Nolan *et al.*.[68] This stands in line with the results reported by Arduengo *et al.* in their studies on the mechanism of C–H bond activation through strongly nucleophilic carbenes.[69] Backbone-saturated NHCs (e.g. $Mes_2Im^{H_4}$) were found to undergo C–H bond insertions, whereas NHCs with an unsaturated backbone (e.g. $Me_2Im^{Me_2}$) formed exclusively ionic products, i.e. imidazolium salts, stemming from proton abstraction. The cationic part of the latter is proposed to be too well-stabilized through extensive π-delocalization to be attacked at the C1-position by the initially formed carbanions (e.g. enolat anions).[69-70]



II.18a **II.22**

Scheme 2.4.7: Synthesis of carbene heterodimer ($cAAC^{methyl}$)=($Me_2Im^{Me_2}$) (**II.22**).

Unlike C–F bond activation products ($cAAC^{methyl}$)F(Ar^f) **II.10a-d**, the C–H bond insertion products **II.17-21** are stable in solution and cannot be utilized for thermal R–H elimination with regeneration of the free carbene **II.1a**, as reported for several alkane adducts of backbone saturated NHCs.[71] Furthermore, they are not accessible for hydride abstraction, nor for deprotonation reactions,[72] except for the ionic imidazolium salt insertion product (**II.18a**). $[(cAAC^{methyl})H(Me_2Im^{Me_2})][BF_4]$ (**II.18a**) was deprotonated by KHMDS at the former cAAC carbon atom, resulting in the formation of a novel $cAAC^{methyl}$–NHC heterodimer (**22**) (Scheme 2.4.7).[72b, 73] Compound **22** did not show any indications for dissociation into the carbenes $cAAC^{methyl}$ (**II.1a**) and $Me_2Im^{Me_2}$.

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4. Publications

This chapter provides the bibliographic details of the publications summarized in this part (**Chapter II**) of the present thesis to facilitate the retrieval of the complete manuscripts and supporting information.

All results, which have been illustrated and placed into their scientific context within Sections “**2. Results and Discussion**” and “**Summary and Outlook**”, are enclosed in the following three publications in peer-reviewed journals:

I. *Cyclic (Alkyl)(Amino)Carbene Complexes of Rhodium and Nickel and Their Steric and Electronic Parameters*
U. S. D. Paul, C. Sieck, M. Haehnel, K. Hammond, T. B. Marder, U. Radius, *Chem. Eur. J.* **2016**, 22, 11005-11014.

II. *Synthesis and Reactivity of Cyclic (Alkyl)(Amino)Carbene stabilized Nickel Carbonyl Complexes*
U. S. D. Paul, U. Radius, *Organometallics*, **2017**, *36*, 1398-1407.

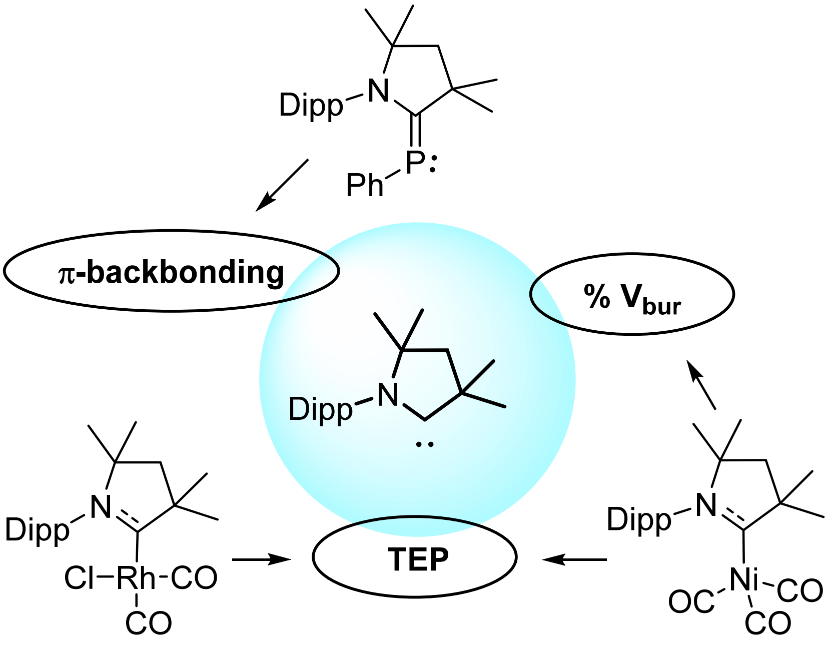
III. *Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino) Carbene*
U. S. D. Paul, U. Radius, *Chem. Eur. J*. **2017**, *23*, 3993-4009.

4.1. Publication I.

Cyclic (Alkyl)(Amino)Carbene Complexes of Rhodium and Nickel and Their Steric and Electronic Parameters

Ursula S. D. Paul, Carolin Sieck, Martin Haehnel, Kai Hammond, Todd B. Marder, Udo Radius

Chem. Eur. J. **2016**, 22, 11005-11014.



Cyclic (Alkyl)(Amino)Carbene Complexes of Rhodium and Nickel and Their Steric and Electronic Parameters

Ursula S. D. Paul, Carolin Sieck, Martin Haehnel, Kai Hammond, Todd B. Marder, Udo Radius

Chemistry – A European Journal

Journal Impact Factor: 5.771 (ISI Journal Citation Reports © Ranking: 2015)

Contribution to this publication: 50 %

1. Author

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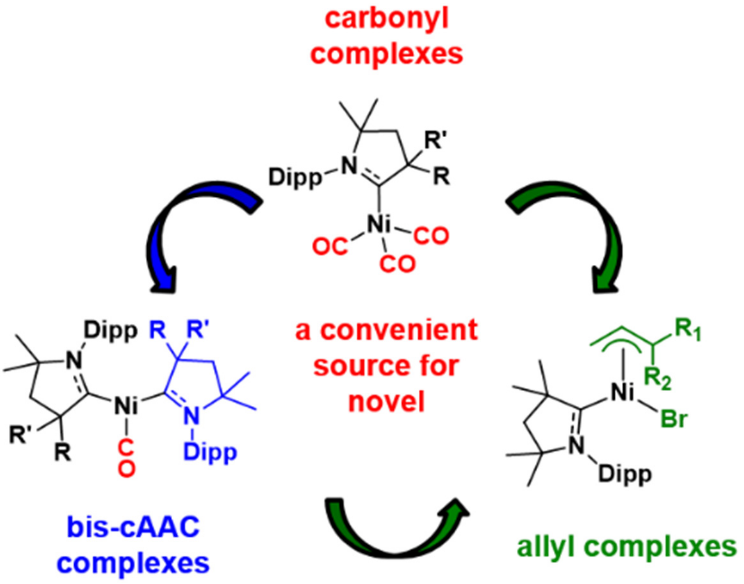
Hyperlink: http://onlinelibrary.wiley.com/doi/10.1002/chem.201601406/abstract

4.2. Publication II.

Synthesis and Reactivity of Cyclic (Alkyl)(Amino)Carbene stabilized Nickel Carbonyl Complexes

Ursula S. D. Paul, Udo Radius

Organometallics **2017**, *36*, 1398-1407.



Synthesis and Reactivity of Cyclic (Alkyl)(Amino)Carbene stabilized Nickel Carbonyl Complexes

Ursula S. D. Paul, Udo Radius

Organometallics

Journal Impact Factor: 4.186 (ISI Journal Citation Reports © Ranking: 2015)

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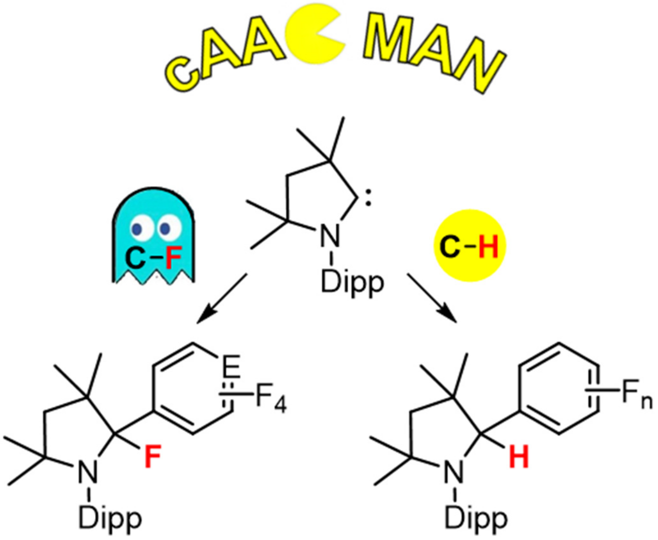
4.3. Publication III.

Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino) Carbene

Ursula S. D. Paul, Udo Radius

Chem. Eur. J. **2017**, *23*, 3993-4009.



Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino) Carbene

Ursula S. D. Paul, Udo Radius

Chemistry – A European Journal

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Summary and Outlook

Chapter I

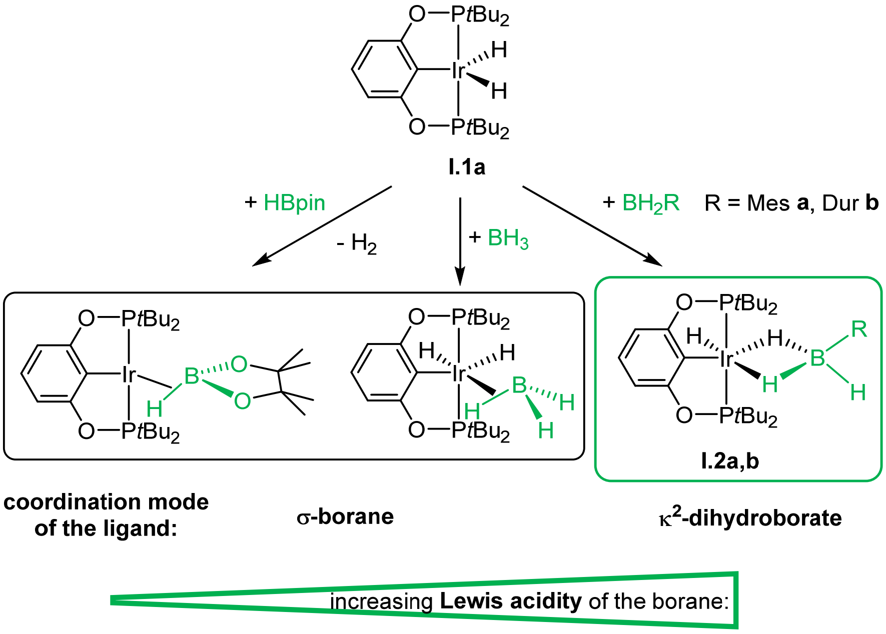
The first part of the present work provides an insight into the chemistry of iridium complexes bearing the bis(phosphinite) pincer ligand *t*BuPOCOP (κ^3-C_6H_3-1,3-(OP*t*Bu_2)$_2$) towards primary boranes and phosphines as well as phosphine-borane Lewis adducts. It furthermore encloses some more detailed studies on their application as catalyst for the dehydrogenative coupling of the latter compounds. The results presented herein can be divided into three sections:

I. synthesis and characterization of aryl dihydroborate ligated iridium(**III**) complexes

II. and aryl phosphine coordinated iridium(**I**) and dihydrido iridium(**III**) complexes,

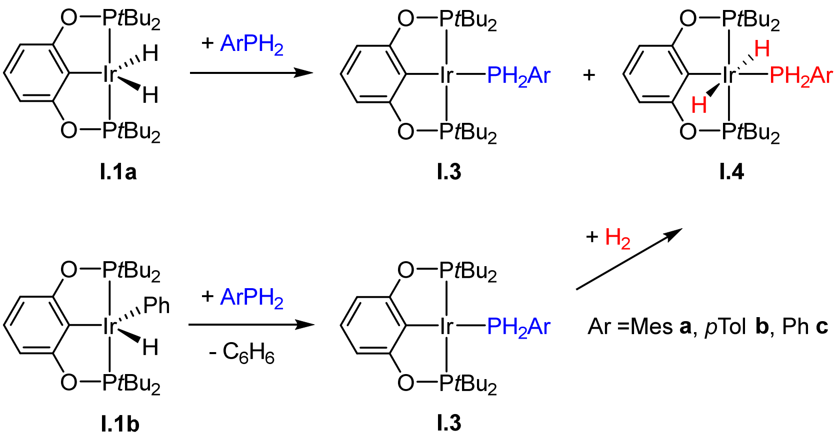
III. as well as studies on the reactivity of the parent iridium pincer complexes towards BH_3 adducts of primary phosphines, which led to first results in the homogeneous catalytic dehydrocoupling of P-aryl substituted phosphine boranes mediated by such iridium pincer complexes.

Treatment of [(*t*BuPOCOP)IrH_2] (**I.1a**) with mesityl- and durylborane resulted in the formation of κ^2-σ:σ-dihydroborate complexes [(*t*BuPOCOP)IrH(κ^2-H_2BHMes)] (**I.2a**) and [(*t*BuPOCOP)IrH(κ^2-H_2BHDur)] (**I.2b**). These primary arylboranes thus coordinate to the iridium complex fragment as bidentate borohydrido ligands, whereas BH_3, 9-BBN and HBpin were reported to give η^2-bound σ-borane complexes, which is in line with the different Lewis acidity of the borane substrates used (Scheme 1.1).



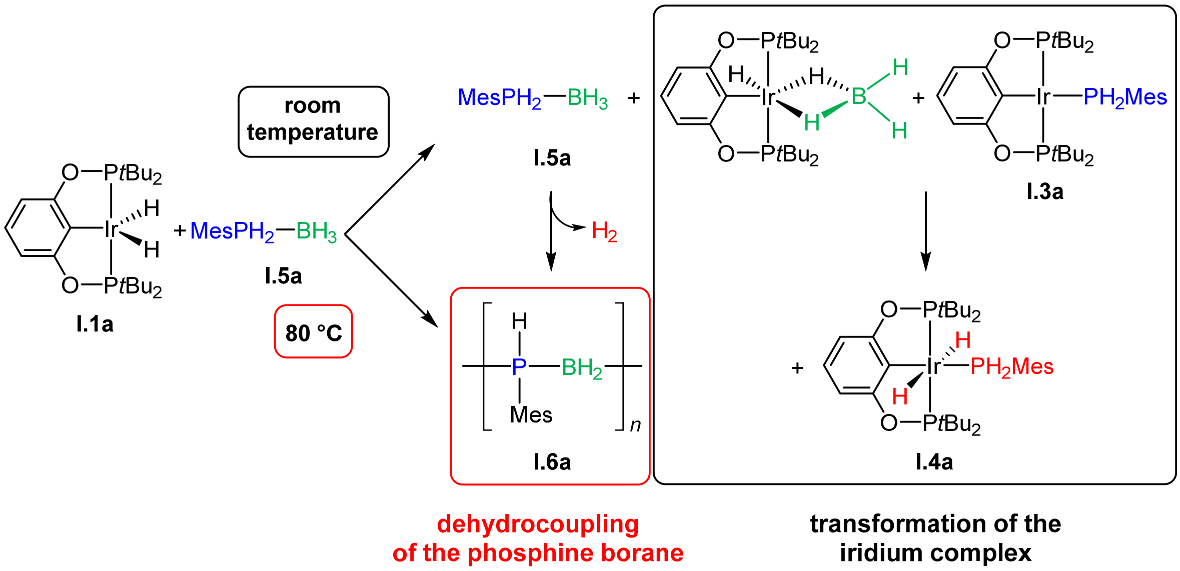
Scheme 1.1: Reactivity of iridium pincer complex **I.1a** towards different boranes, yielding dihydro borate complexes [(*t*BuPOCOP)IrH(κ^2-H_2BHR)] (R = Mes **I.2a**, Dur **I.2b**) with primary arylboranes as substrates.

Furthermore, primary arylphosphines were found to react with [(*t*BuPOCOP)IrH_2] (**I.1a**) and [(*t*BuPOCOP)IrHPh] (**I.1b**) upon coordination of the Lewis bases to the transition metal center and formation of iridium(I) phosphine complexes [(*t*BuPOCOP)Ir(PH_2Ar)] (Ar = Mes **I.3a**, *p*Tol **I.3b**, Ph **I.3c**) or iridium(III) dihydrido phosphine complexes [(*t*BuPOCOP)Ir$(H)_2$(PH_2Ar)] (Ar = Mes **I.4a**, *p*Tol **I.4b**, Ph **I.4c**) without any indications for oxidative addition of the primary phosphines or an alternative P–H bond activation step (Scheme 1.2).



Scheme 1.2: Synthesis of primary arylphosphine coordinated iridium(I) **I.3a-c** and iridium(III) dihydrido complexes **I.4a-c**.

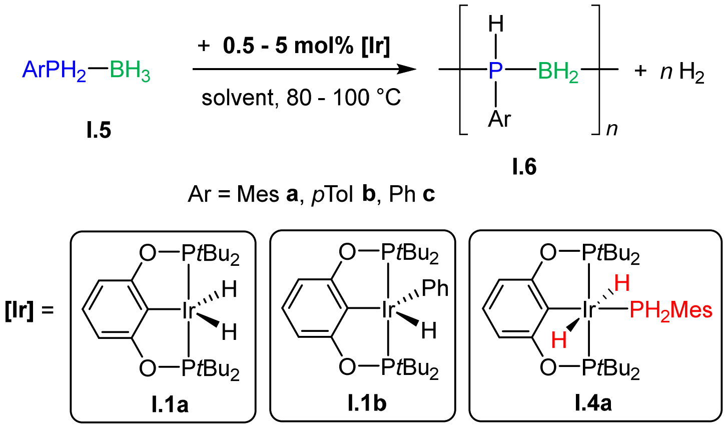
The same products were obtained from reactions of [(*t*BuPOCOP)IrH_2] (**I.1a**) with BH_3-based monoaryl phosphine boranes as starting materials (Scheme 1.3).



Scheme 1.3: Reaction of [(*t*BuPOCOP)IrH_2] (**I.1a**) with mesitylphosphine borane MesPH_2–BH_3 (**I.5a**) as substrate.

Accordingly, treatment of **I.1a** with stoichiometric amounts or an excess of $MesPH_2–BH_3$ (**I.5c**) results in cleavage of the Lewis adduct and formation of both the σ-borane complex [(*t*BuPOCOP)Ir$(H)_2(\eta^2$-H–$BH_2)$] as well as the phosphine complex [(*t*BuPOCOP)Ir(PH_2Mes)] (**I.3a**). The latter is converted into the dihydrido phosphine complex [(*t*BuPOCOP)Ir$(H)_2(PH_2Mes)$] (**I.4a**) within 16 hours at room temperature or upon heating to 80 °C, which also leads to a complete consumption of borane complex **I.3a** and dehydrogenative polymerization of the exceeding starting material to high-molecular weight (M_n 33 000, M_w 59 000) poly(phosphinoborane) **I.6a**.

This very promising catalytic protocol was optimized for $MesPH_2–BH_3$ (**I.5c**) as substrate and also successfully applied at further primary phosphine-borane adducts *p*Tol$PH_2–BH_3$ (**I.5b**) and $PhPH_2–BH_3$ (**I.5c**) (Scheme 1.4).



Scheme 1.4: Iridium-catalyzed dehydrocoupling of primary arylphosphine-borane adducts **5a-c** to poly(phosphinoboranes) **6a-c**.

First studies on the mechanism of this iridium pincer complex-catalyzed dehydrocoupling revealed similarities to the analogous transformation of amine-borane substrates, which is proposed to proceed via a two-stage polymerization mechanism. However, unlike reported for these substrates, in the course of phosphine borane dehydrogenation no formation of [(*t*BuPOCOP)Ir$(H)_2(\eta^2$-H–$BH_2)$] by catalyst deactivation was observed, but generation of catalytically active phosphine complexes, like [(*t*BuPOCOP)Ir$(H)_2(PH_2Mes)$] (**I.4a**), which can thus be described as resting states of the yet unidentified catalytically active species. Contrary to earlier reports on rhodium- or iron-based precatalysts, no boryl, phosphido or phosphido-borane complexes were formed as catalytic intermediates. Hence, further investigations are necessary to gain a deeper understanding of the iridium-mediated P–B bond formation process as well as reliable informations on the sequence of P–H and B–H bond cleavage.

Chapter II

The second part of the present work provides an insight into the chemistry of cyclic (alkyl)(amino) carbene-stabilized nickel complexes as well as it encloses some more detailed studies on the properties and reactivity of the free carbenes itself. The results presented herein can be divided into four sections:

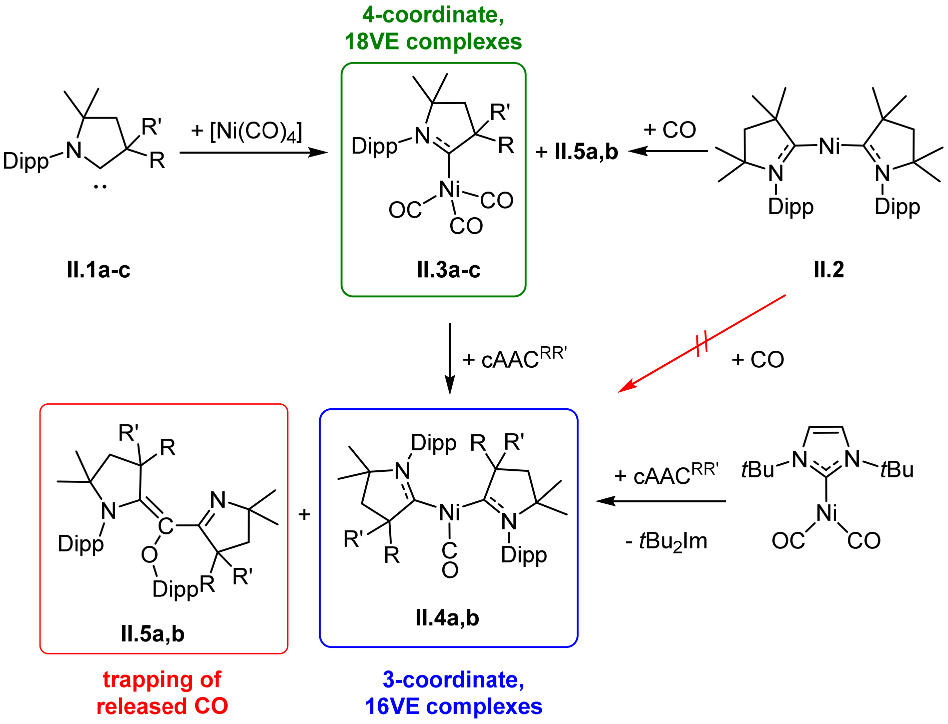
I. synthesis and characterization of cyclic (alkyl)(amino) carbene-stabilized nickel carbonyl complexes,

II. which allow the evaluation and quantification of the steric and electronic properties of these cyclic (alkyl)(amino) carbenes,

III. first studies on the reactivity of these novel nickel complexes, and

IV. investigations on C–F and C–H bond activation at the carbene center of cyclic (alkyl)(amino) carbenes.

Two different types of (alkyl)(amino) carbene-stabilized nickel carbonyl complexes were synthesized, the coordinatively saturated, 18VE mono-cAAC-ligated complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] (R,R' = methyl **II.3a**, RR' = cy **II.3b**, RR' = menthyl **II.3c**) as well as coordinatively unsaturated, 16VE bis-cAAC-ligated complexes [Ni(CO)(cAAC$^{RR'}$)$_2$] (R,R' = methyl **II.4a**, RR' = cy **II.4b**) (Scheme 2.1).



Scheme 2.1: Synthetic strategies developed for the preparation of mono-cAAC complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] (**II.3a-c**) (R,R' = methyl **a**, RR' = cy **b**, RR' = menthyl **c**) and bis-cAAC compounds [Ni(CO)(cAAC$^{RR'}$)$_2$] (**II.4a,b**) (R,R' = methyl **a**, RR' = cy **b**).

The latter display an unprecedented coordination pattern, as related three-coordinate NHC-stabilized nickel carbonyl complexes have only been realized so far by coordination of one sterically very demanding carbene. Furthermore, the intriguing side-products of these reactions, the 3,3-diamino-2-aryloxyacrylimidamides (R,R' = methyl **II.5a**, RR' = cy **II.5b**), were identified and selectively synthesized from the reaction of carbon monoxide with the carbene cAAC^{methyl} (**II.1a**) and cAAC^{cy} (**II.1b**).

The complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] (R,R' = methyl **II.3a**, RR' = cy **II.3b**, RR' = menthyl **II.3c**) were used to determine the steric demand as well as the electronic properties of the carbenes cAAC^{methyl} (**II.1a**), cAAC^{cy} (**II.1b**) and cAAC^{menthyl} (**II.1c**). Accordingly, cAACs **II.1a-c** were proposed to be notably stronger σ-donors than common NHCs, such as Dipp$_2$Im or Mes$_2$Im, as they give rise to similar TEP values of 2042 - 2046 cm^{-1}, while possessing superior π-acceptor properties. The accepting properties can be verified using the corresponding phosphinidene adducts, which give rise to significantly low-field shifted resonances in the ^{31}P NMR spectrum ($\delta_P = 67.2$ ppm) (Figure 2.1). Furthermore, complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] **II.3a-c** were used for quantification of the steric demand of cAACs **II.1a-c** by analysis of the percent buried volume (%V_{bur}). The values obtained of 38 - 42 % (Figure 2.1) are higher than those of the bulky NHCs, like *t*Bu$_2$Im. However, all three cAACs afforded four-coordinate mono-carbene complexes upon reaction with [Ni(CO)$_4$]. The steric demand is of importance for the formation of bis-carbene complexes [Ni(CO)(cAAC$^{RR'}$)$_2$] **II.4** and the bis-carbene adducts of CO **II.5** as only the bulkiest representative cAAC^{menthyl} (**II.1c**) failed to give such products (Scheme 2.1).

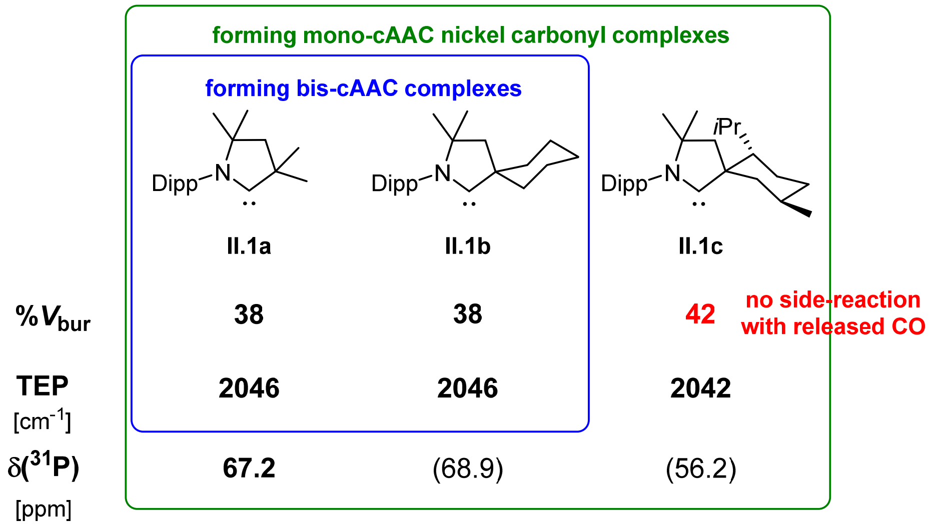
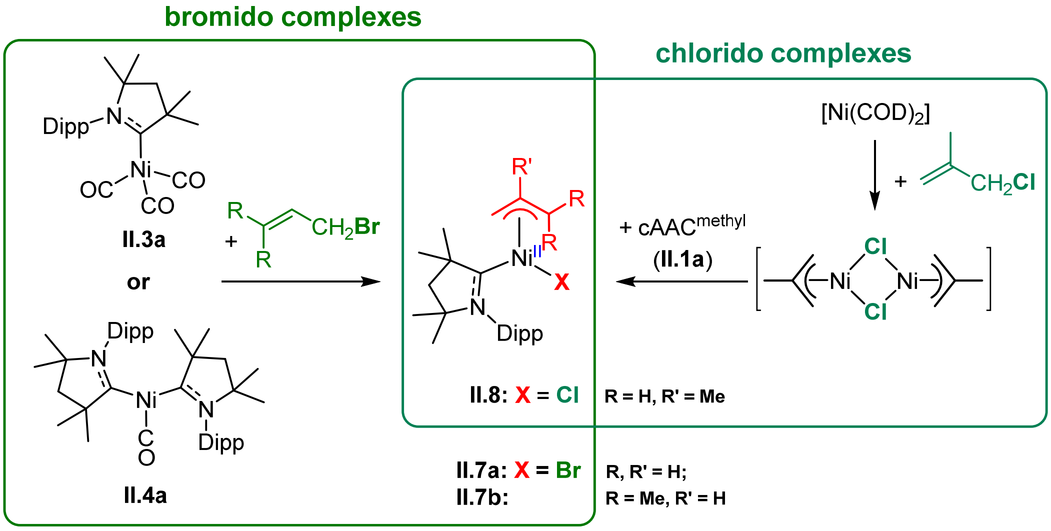


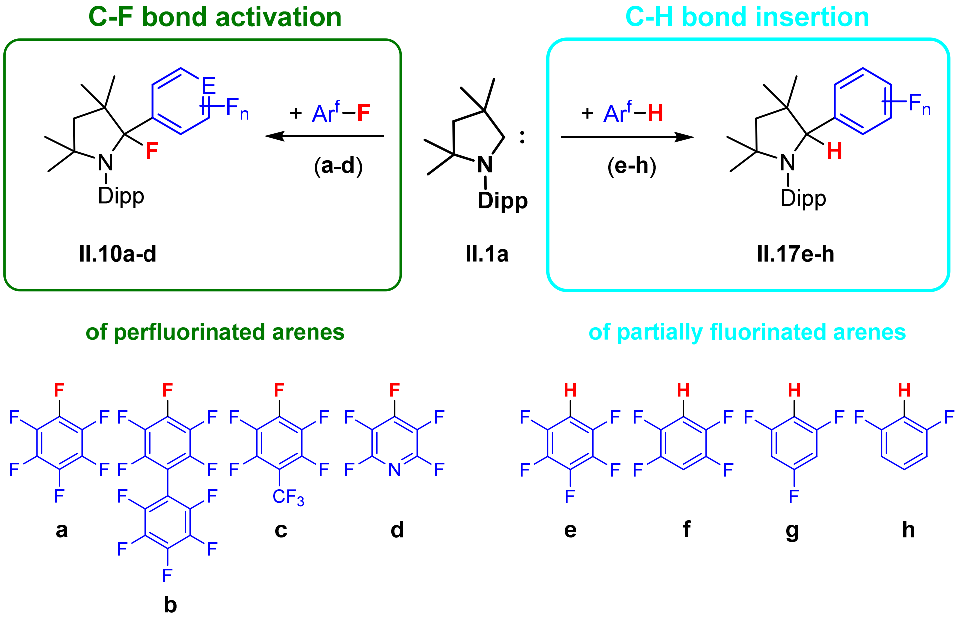
Figure 2.1: Conspectus of NMR spectroscopic data and TEP values of investigated cAACs$^{RR'}$ **II.1a-c** as well as the calculated %V_{bur} from the respective nickel carbonyl complexes [Ni(CO)$_3$(cAAC$^{RR'}$)] **II.3a-c**.

In first investigations on the reactivity of the cAAC-stabilized nickel carbonyl complexes, allyl halide complexes [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC^{methyl})] (**II.7a**) and [NiBr(η^3-H$_2$*C*=*C*H–*C*Me$_2$)(cAAC^{methyl})] (**II.7b**) are obtained *via* the oxidative addition of allyl bromides with CO extrusion. Since the carbonyl complexes [Ni(CO)$_3$(cAAC^{methyl})] (**II.3a**) and [Ni(CO)(cAAC^{methyl})$_2$] (**II.4a**) proved to be inert against allyl chlorides, [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC^{methyl})] (**II.8**) was synthesized following an alternative synthetic strategy (Scheme 2.2).



Scheme 2.2: Overview over the synthetic strategies developed for the preparation of allyl bromido complexes [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC^{methyl})] (**II.7a**) and [NiBr(η^3-H$_2$*C*=*C*H–*C*Me$_2$)(cAAC^{methyl})] (**II.7b**) and allyl chlorido complex [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC^{methyl})] (**II.8**).

The conversion of fluoroaromatics into novel fluorinated organic molecules plays an important role in the development of pharmaceuticals, agrochemicals and materials and therefore is investigated with ongoing interest. We thus aimed for studies on C–F bond activation of fluorinated arenes using the cAAC-stabilized nickel(0) complex [Ni(cAAC^{methyl})$_2$] (**II.2**). However, this complex proved to be unreactive with respect to polyfluoroarenes, but the free carbene cAAC^{methyl} (**II.1a**) itself was found to insert easily into the C–F bond of perfluoroarenes (Scheme 2.3).



Scheme 2.3: Reactivity of cAAC^{methyl} (**II.1a**) towards per- and partially fluorinated aromatic substrates, affording the respective C–F (**II.10a-d**, left) and C–H bond insertion products (**II.17e-h**, right).

To investigate the regio- as well as the chemoselectivity of this reaction a series of per- and partially fluorinated arenes was treated with **II.1a** to yield the novel compounds (cAAC^{methyl})F(Ar^f) **II.10a-d**, products of a regioselective C–F bond insertion in 4-position of the aryl fluorides C_5F_5E (E = C–F **a**, C–C_6F_5 **b**, C–CF_3 **c**, N **d**). Contrarily, reactions with partially fluorinated arenes exclusively resulted in C–H bond activation, affording compounds (cAAC^{methyl})H(Ar^f) **II.17e-h** (Ar^f = C_6F_5 **e**, 2,3,5,6-C_6F_4H **f**, 2,4,6-$C_6F_3H_2$ **g** and 2,6-$C_6F_2H_3$ **h**) (Scheme 2.3). Further investigations revealed that cAAC^{methyl} (**II.1a**) readily reacts with a broad range of (moderately) C–H acidic substrates, such as imidazolium salts (**II.18a,b**), imidazoles (**19a-c**), esters (**II.20a,b**) and even trimethylphosphine (**21**), though for imidazole ($C_3H_4N_2$) (**II.19a**) and benzimidazole ($C_7H_7N_2$) (**II.19b**) insertion into the more acidic N–H bond prevails over C–H bond activation.

First studies on the reactivity of the products obtained have, most interestingly, revealed that fluoro-substituted compounds (cAAC^{methyl})F(Ar^f) **II.10a-d** can be utilized as mild fluoride source in fluoride abstraction or fluoride transfer reactions. We therefore envisioned compounds **II.10a-d** as promising starting point for further, more detailed investigations on cAAC-mediated fluorine transfer reactions, as such examples for non-metal- and especially carbene-mediated fluorine transfer reactions are rather exceptional.

Zusammenfassung

Kapitel I

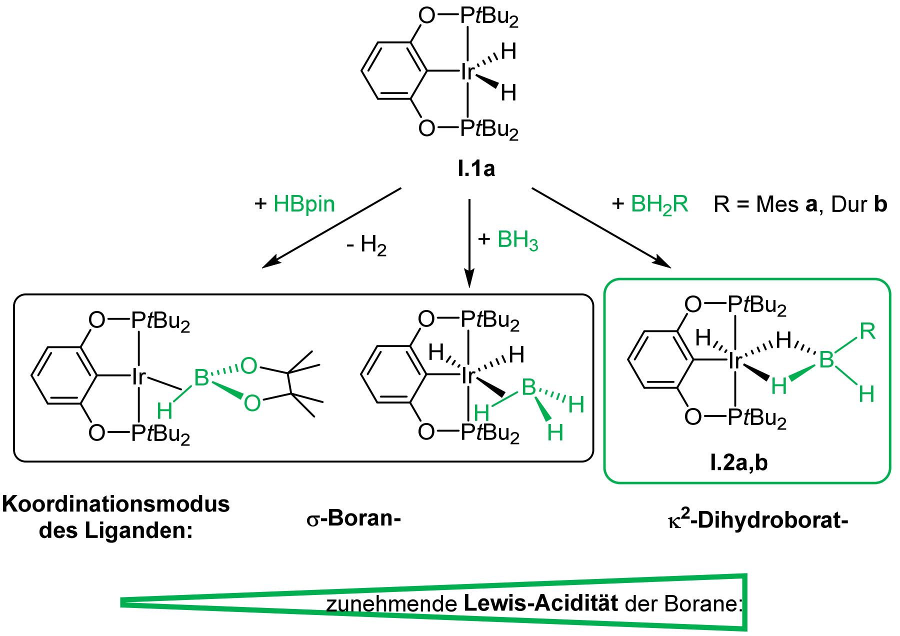
Der erste Abschnitt der vorliegenden Arbeit gibt einen vertieften Einblick in die Reaktivität von Iridiumkomplexen, die den bis(Phosphinit)-Pincer *t*BuPOCOP (κ^3-C_6H_3-1,3-(OP*t*$Bu_2)_2$) als Liganden aufweisen, gegenüber primären Boranen und Phosphanen sowie gegenüber Phosphan-Boran-Lewis-Paaren. Desweiteren sind detailliertere Untersuchungen zu deren Anwendung als Katalysator zur dehydrogenativen Kupplung von Phosphanboranen enthalten. Die erhaltenen Ergebnisse lassen sich in drei Teilbereiche gliedern:

I. Synthese und Charakterisierung von Iridium(III)-Komplexen, die Aryldihydroboratliganden tragen,

II. Arylphosphan-koordinierte Iridium(I)- und Iridium(III)-Komplexe,

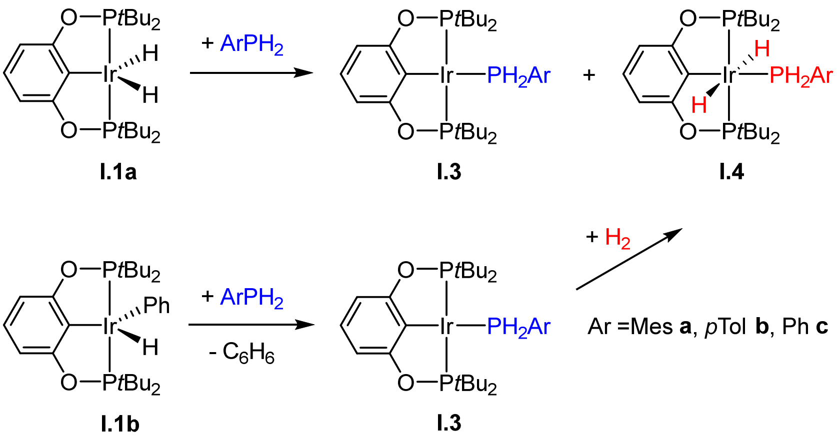
III. sowie Studien zur Reaktivität der zugrundeliegenden Iridiumpincerkomplexe gegenüber BH_3-Addukten von primären Phosphanen. Diese führten zu ersten Ergebnissen in der homogen-katalytischen Dehydrokupplung von Phosphanboranen unter Verwendung der Iridiumpincerkomplexe als Katalysator.

Umsetzungen von [(*t*BuPOCOP)IrH_2] (**I.1a**) mit Mesitylboran und Durylboran führten zur Bildung der κ^2-σ:σ-Dihydroboratkomplexe [(*t*BuPOCOP)IrH(κ^2-H_2BHMes)] (**I.2a**) und [(*t*BuPOCOP)IrH(κ^2-H_2BHDur)] (**I.2b**). Die primären Arylborane koordinieren folglich als zweizähnige Borhydridliganden an das Iridiumkomplexfragment. Im Gegensatz dazu reagieren BH_3, 9-BBN und HBpin zu η^2-gebundenen σ-Borankomplexen, was durch die unterschiedlichen Lewis-Aciditäten der eingesetzten Borane erklärt werden kann. (Schema 1.1).



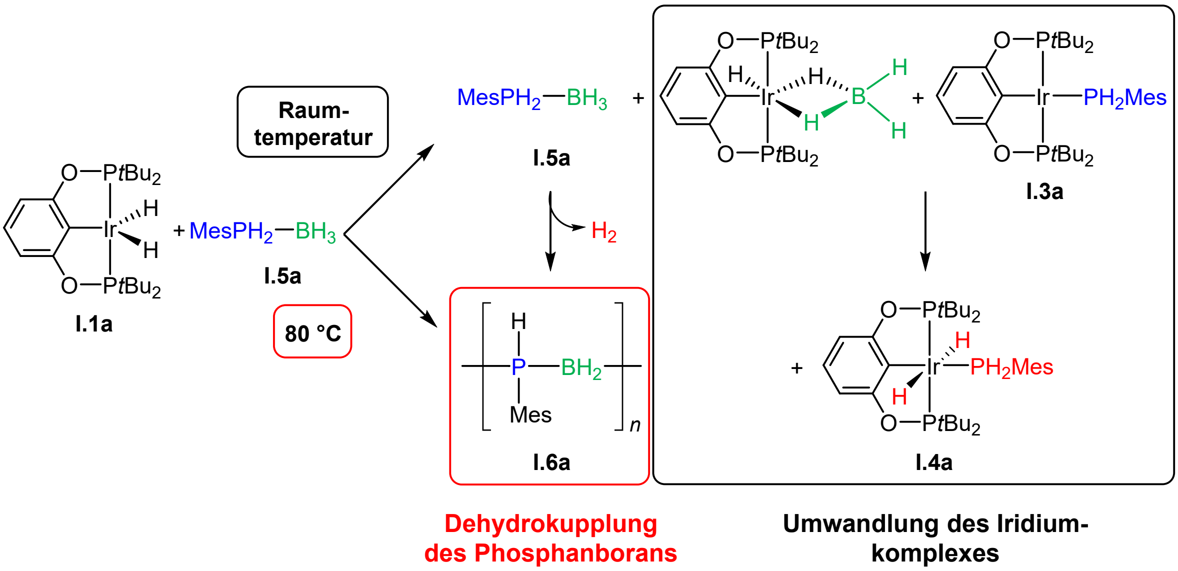
Schema 1.1: Reaktivität des Iridiumpincerkomplexes **I.1a** gegenüber verschiedenen Boranen, unter Ausildung der Dihydroboratkomplexe [(*t*BuPOCOP)IrH(κ^2-H_2BHR)] (R = Mes **I.2a**, Dur **I.2b**).

Desweiteren reagieren primäre Arylphosphane mit [(*t*BuPOCOP)IrH$_2$] (**I.1a**) und [(*t*BuPOCOP)IrHPh] (**I.1b**) unter Koordination als Lewis-Base an das Übergangsmetallatom, was zur Ausbildung von Iridium(I)-Phosphankomplexen [(*t*BuPOCOP)Ir(PH$_2$Ar)] (Ar = Mes **I.3a**, *p*Tol **I.3b**, Ph **I.3c**) oder Iridium(III)-Dihydridophosphankomplexen [(*t*BuPOCOP)Ir(H)$_2$(PH$_2$Ar)] (Ar = Mes **I.4a**, *p*Tol **I.4b**, Ph **I.4c**) führt. Dabei gab es keinerlei Anzeichen für eine etwaige P–H-Aktivierung der eingesetzten primären Phosphane (Schema 1.2).



Schema 1.2: Darstellung von Arylphosphan-stabilisierten Iridium(I)- **I.3a-c** und Iridium(III)-Dihydridokomplexen **I.4a-c**.

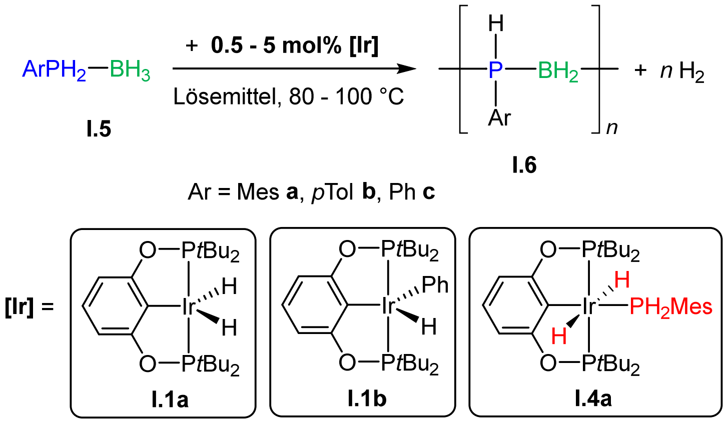
Selbige Produkte wurden auch aus der Umsetzung von [(*t*BuPOCOP)IrH$_2$] (**I.1a**) mit den Monoarylphosphan–BH$_3$-Lewis-Addukten erhalten (Schema 1.3).



Schema 1.3: Reaktivität von [(*t*BuPOCOP)IrH$_2$] (**I.1a**) gegenüber MesPH$_2$–BH$_3$ (**I.5a**).

Demnach führt die Umsetzung von **I.1a** mit äquimolaren Mengen oder einem Überschuss an $MesPH_2–BH_3$ (**I.5c**) zur Adduktspaltung und Bildung sowohl des σ-Borankomplexes $[(t\mathrm{BuPOCOP})\mathrm{Ir(H)_2}(\eta^2\text{-H–BH}_2)]$ als auch des Phosphankomplexes $[(t\mathrm{BuPOCOP})\mathrm{Ir(PH_2Mes)}]$ (**I.3a**). Letzterer wandelt sich bei Raumtemperatur nach einiger Zeit in den entsprechenden Dihydridophosphankomplex $[(t\mathrm{BuPOCOP})\mathrm{Ir(H)_2(PH_2Mes)}]$ (**I.4a**) um. Dieselbe Umwandlung kann ebenfalls durch Erhitzen auf 80 °C erzielt werden, wobei hierbei auch der Borankomplexes **I.3a** vollständig abreagiert und es zur dehydrogenativen Polymerisation von überschüssigem Startmaterial **I.5c** zu hochmolekularem (M_n 33 000, M_w 59 000) Poly(phosphinoboran) **I.6a** kommt.

Die Katalyse wurde für $MesPH_2–BH_3$ (**I.5c**) als Substrat optimiert und konnte erfolgreich auf weitere primäre Phosphanborane, wie pTolPH$_2$–BH$_3$ (**I.5b**) und $PhPH_2–BH_3$ (**I.5c**), übertragen werden (Schema 1.4).



Schema 1.4: Iridium-katalysierte Dehydrokupplung von primären Arylphosphan-Boran-Addukten **5a-c** zu Poly(phosphinoboranen) **6a-c**.

Erste Untersuchungen bezüglich des Mechanismus dieser Iridiumpincerkomplex-katalysierten Dehydrokupplung zeigten deutliche Parallelen zur analogen Umwandlung von Aminboranen. Für diese wurde ein zweistufiger Polymerisationsmechanismus postuliert. Im Gegensatz dazu kommt es aber bei der Wasserstoffabspaltung von Phosphanboranen (unter Katalysebedingungen, d.h. Erhitzen) nicht zu einer Ausbildung von $[(t\mathrm{BuPOCOP})\mathrm{Ir(H)_2}(\eta^2\text{-H–BH}_2)]$ durch Deaktivierung des Katalysators. Es werden stattdessen Phosphankomplexe, wie $[(t\mathrm{BuPOCOP})\mathrm{Ir(H)_2(PH_2Mes)}]$ (**I.4a**), gebildet, welche selbst katalytisch aktiv sind und somit als „Ruhezustand" der bisher nicht identifizierten, tatsächlich aktiven Katalysatorspezies beschrieben werden können. Im Gegensatz zu Vorarbeiten an Rhodium- oder Eisen-basierten Systemen konnten zudem Boryl-, Phosphido- oder Phosphidoborankomplexen als Zwischenstufen des Katalysezyklus nicht beobachtet werden. Daher sind weitere Untersuchungen erforderlich, um ein tieferes Verständnis für die elementaren Prozesse der Dehydrokupplung von Phosphan-Boran-Addukten zu erhalten, welche den Mechanismus und die Abfolge von P–H- und B–H-Bindungsaktivierung sowie die P–B-Bindungsbildung umfassen.

Kapitel II

Der zweite Abschnitt der vorliegenden Arbeit gibt einen Einblick in die Chemie von Nickelkomplexen, die durch zyklische (Alkyl)(Amino) Carbene (cAACs) stabilisiert werden. Desweiteren sind Untersuchungen zu den Eigenschaften und zur Reaktivität der freien Carbene selbst enthalten. Die erhaltenen Ergebnisse lassen sich in vier Teilbereiche gliedern:

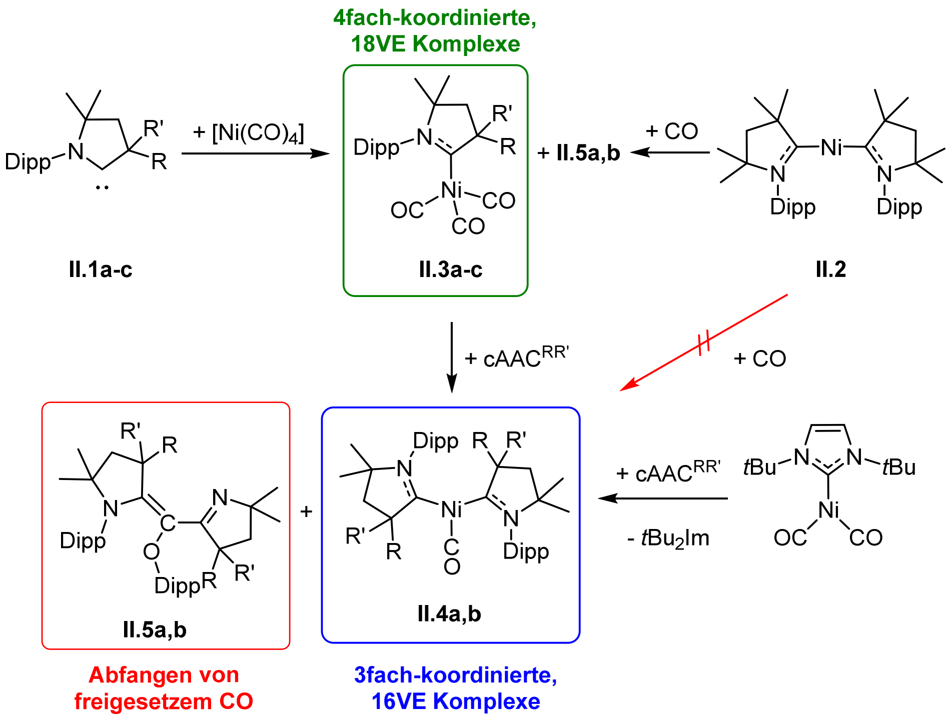
I. Synthese und Charakterisierung von Nickelkomplexen, die durch zyklische (Alkyl)(Amino) Carbene stabilisiert werden,

II. welche die Bestimmung und Quantifizierung von deren sterischen und elektronischen Eigenschaften zulassen,

III. erste Studien zur Reaktivität dieser neuartigen Nickelkomplexe, sowie

IV. Untersuchungen zur C–F- und C–H-Bindungsaktivierung am Carbenkohlenstoffatom der entsprechenden zyklische (Alkyl)(Amino) Cabene.

Zwei verschiedenen Arten von cAAC-stabilisierten Nickelcarbonylkomplexen konnten dargestellt werden, nämlich die koordinativ-abgesättigten, 18VE mono-cAAC-Komplexe $[Ni(CO)_3(cAAC^{RR'})]$ (R,R' = methyl **II.3a**, RR' = cy **II.3b**, RR' = menthyl **II.3c**) sowie die koordinativ-ungesättigten, 16VE bis-cAAC-Komplexe $[Ni(CO)(cAAC^{RR'})_2]$ (R,R' = methyl **II.4a**, RR' = cy **II.4b**) (Schema 2.1).



Schema 2.1: Synthesestrategien, die entwickelt wurden zur Darstellung von mono-cAAC-Komplexen $[Ni(CO)_3(cAAC^{RR'})]$ (**II.3a-c**) (R,R' = methyl **a**, RR' = cy **b**, RR' = menthyl **c**) und bis-cAAC-Komplexen $[Ni(CO)(cAAC^{RR'})_2]$ (**II.4a,b**) (R,R' = methyl **a**, RR' = cy **b**).

Letztere weisen ein außergewöhnliches Koordinationsmuster auf, da vergleichbare dreifach-koordinierte NHC-stabilisierte Nickelcarbonylkomplexe bisher lediglich durch Koordination eines äußerst sterisch anspruchsvollen Liganden zugänglich waren. Desweiteren konnten die 3,3-Diamino-2-aryloxyacrylimidamide (R,R' = methyl **II.5a**, RR' = cy **II.5b**) als faszinierende Nebenprodukte dieser Reaktionen identifiziert und auch gezielt durch Umsetzung von Kohlenmonoxid mit cAAC$^{\text{methyl}}$ (**II.1a**) und cAAC$^{\text{cy}}$ (**II.1b**) dargestellt werden.

Die Komplexe [Ni(CO)$_3$(cAAC$^{\text{RR'}}$)] (R,R' = methyl **II.3a**, RR' = cy **II.3b**, RR' = menthyl **II.3c**) wurden zur Bestimmung des sterischen Anspruchs und der elektronischen Eigenschaften der gebundenen Carbene cAAC$^{\text{methyl}}$ (**II.1a**), cAAC$^{\text{cy}}$ (**II.1b**) and cAAC$^{\text{menthyl}}$ (**II.1c**) herangezogen. Demnach können die cAACs **II.1a-c** verglichen mit geläufigen NHCs, wie Dipp$_2$Im oder Mes$_2$Im, als deutlich stärkere σ-Donoren bezeichnet werden, da sie ähnliche TEP-Werte von 2042 - 2046 cm^{-1} hervorrufen aber zugleich viel höhere π-Akzeptoreigenschaften aufweisen. Diese Akzeptoreigenschaften wurden mittels entsprechender Phosphiniden-Addukte bestimmt, welche deutlich Tieffeld-verschobene Resonanzen im ^{31}P NMR Spektrum (δ_P = 67.2 ppm) (Abbildung 2.1) aufweisen. Desweiteren wurden die Komplexe [Ni(CO)$_3$(cAAC$^{\text{RR'}}$)] **II.3a-c** zur Quantifizierung des sterischen Anspruchs der cAAC-Liganden **II.1a-c** durch Analyse des jeweiligen prozentualen verdeckten Volumens (%V_{bur}) verwendet. Die erhaltenen Werte von 38 - 42 % (Abbildung 2.1) sind noch höher als diejenigen sperriger NHC-Liganden, wie z.B. *t*Bu$_2$Im. Die Umsetzungen der cAACs mit [Ni(CO)$_4$] führten jedoch in allen Fällen zur Bildung von vierfach-koordinierten mono-Carbenkomplexen. Im Gegensatz dazu war der sterische Anspruch bei der Darstellung der bis-Carbenkomplexe [Ni(CO)(cAAC$^{\text{RR'}}$)$_2$] **II.4** und der bis-Carben-Addukte von CO **II.5** durchaus von Bedeutung, insbesondere da letztere lediglich für den sperrigsten Vertreter cAAC$^{\text{menthyl}}$ (**II.1c**) nicht zugänglich waren (Schema 2.1).

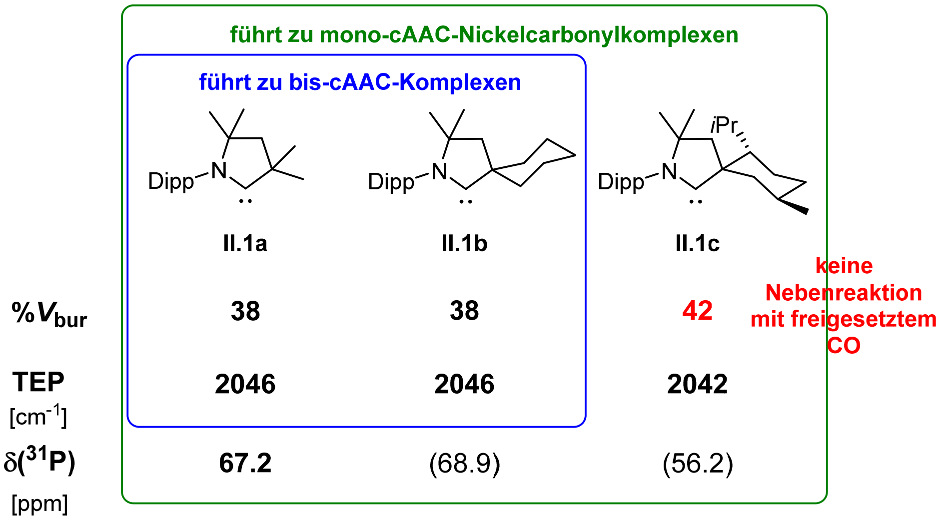
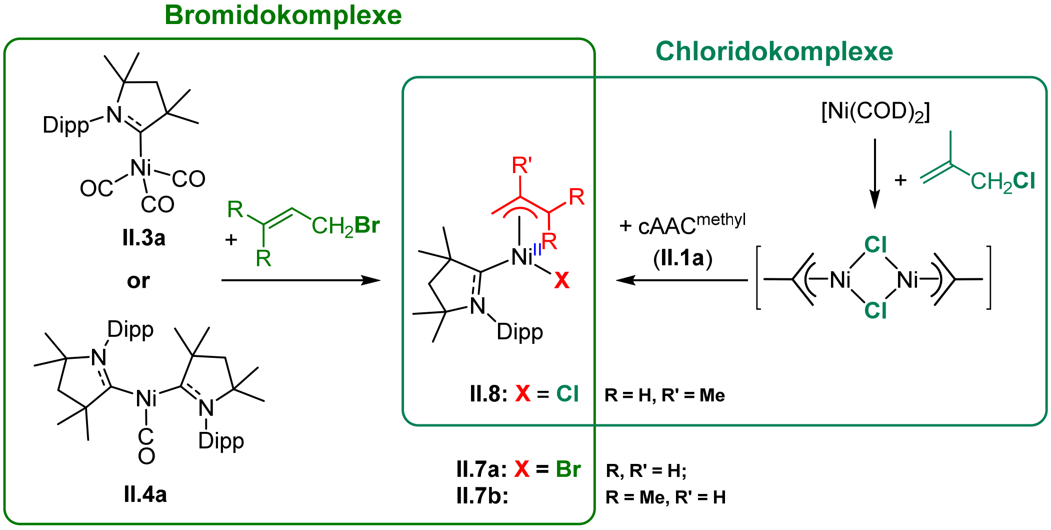


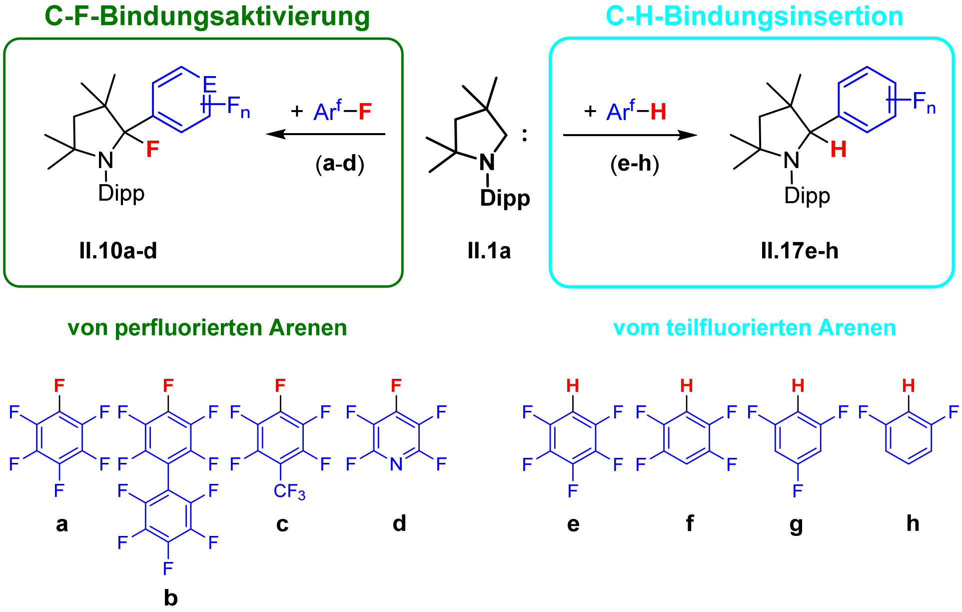
Abbildung 2.1: Übersicht über NMR-spektroskopische Daten und TEP-Werte der untersuchten Liganden cAACs$^{\text{RR'}}$ **II.1a-c** sowie berechnete %V_{bur} ausgehend von den entsprechenden Komplexen [Ni(CO)$_3$(cAAC$^{\text{RR'}}$)] **II.3a-c**.

Erste Untersuchungen zur Reaktivität der cAAC-stabilisierten Nickelcarbonylkomplexe lieferten die Allylhalogenidkomplexe [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC$^{\text{methyl}}$)] (**II.7a**) und [NiBr(η^3-H$_2$*C*=*C*H–*C*Me$_2$)(cAAC$^{\text{methyl}}$)] (**II.7b**) durch oxidative Addition der entsprechenden Allylbromide unter Freisetzung von CO. Da sich die Carbonylkomplexe [Ni(CO)$_3$(cAAC$^{\text{methyl}}$)] (**II.3a**) und [Ni(CO)(cAAC$^{\text{methyl}}$)$_2$] (**II.4a**) als inert gegenüber Allylchloriden erwiesen, musste Verbindung [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC$^{\mathrm{methyl}}$)] (**II.8**) über eine alternative Syntheseroute dargestellt werden (Schema 2.2).



Schema 2.2: Übersicht über die Synthesestrategien, die zur Darstellung der Allylbromidokomplexe [NiBr(η^3-H$_2$*C*=*C*H–*C*H$_2$)(cAAC$^{\mathrm{methyl}}$)] (**II.7a**) und [NiBr(η^3-H$_2$*C*=*C*H–*C*Me$_2$)(cAAC$^{\mathrm{methyl}}$)] (**II.7b**) beziehungsweise des Allylchloridokomplexes [NiCl(η^3-H$_2$*C*=*C*Me–*C*H$_2$)(cAAC$^{\mathrm{methyl}}$)] (**II.8**) entwickelt wurden.

Die Umwandlung von Fluoraromaten in neuartige fluorierte organische Moleküle spielt eine wichtige Rolle in der Entwicklung von Pharmazeutika, Agrochemikalien und Materialien und wird daher mit anhaltendem Interesse erforscht. Aus diesem Grund sollte auch untersucht werden, inwiefern sich der cAAC-stabilisierte Nickel(0)-Komplex [Ni(cAAC$^{\mathrm{methyl}}$)$_2$] (**II.2**) zur C–F-Bindungsaktivierung von Polyfluorarenen eignet. Jedoch zeigte dieser keine Reaktivität gegenüber diesen Substraten, wohingegen das freie Carben cAAC$^{\mathrm{methyl}}$ (**II.1a**) selbst bereitwillig in C–F-Bindungen von Perfluoraromaten insertiert (Schema 2.3).



Schema 2.3: Reaktivität von cAAC$^{\mathrm{methyl}}$ (**II.1a**) gegenüber fluorierten Aromaten, was zur Bildung der entsprechenden C–F- (**II.10a-d**, links) oder C–H-Bindungsinsertionsprodukte (**II.17e-h**, rechts) führt.

Zur Untersuchung der Regio- und der Chemoselektivität dieser Reaktion wurden verschiedenste fluorierte Aromaten mit **II.1a** umgesetzt, was zur Darstellung neuartiger Verbindungen des Typs (cAAC^{methyl})F(Ar^{f}) **II.10a-d** führte. Dabei handelt es sich um Produkte einer regioselektiven C–F-Bindungsaktivierung von perfluorierten Aromaten durch Insertion in die 4-Position von C_5F_5E (E = C–F **a**, C–C_6F_5 **b**, C–CF_3 **c**, N **d**). Im Gegensatz dazu reagiert **II.1a** mit teilfluorierten Arenen ausschließlich unter C–H-Bindungsaktivierung zu Verbindungen des Typs (cAAC^{methyl})H(Ar^{f}) **II.17e-h** (Ar^{f} = C_6F_5 **e**, 2,3,5,6-C_6F_4H **f**, 2,4,6-$C_6F_3H_2$ **g** und 2,6-$C_6F_2H_3$ **h**) (Schema 2.3). Weitere Untersuchungen zeigten, dass cAAC^{methyl} (**II.1a**) bereitwillig Reaktionen mit einer Vielzahl an (mäßig) C–H-aciden Substraten, wie Imidazoliumsalzen (**II.18a,b**), Imidazolen (**19a-c**), Estern (**II.20a,b**) und sogar Trimethylphosphan (**21**) eingeht, wobei für Imidazol ($C_3H_4N_2$) (**II.19a**) und Benzimidazol ($C_7H_7N_2$) (**II.19b**) die Insertion in die acidere N–H-Bindung gegenüber einer möglichen C–H-Bindungsaktivierung vorherrscht.

Erste Studien zur Reaktivität der erhaltenen Produkte, haben interessanterweise ergeben, dass sich die Fluor-substituierten Verbindungen (cAAC^{methyl})F(Ar^{f}) **II.10a-d** als milde Fluoridquellen in Fluoridübertragungsreaktionen eignen. Die Verbindungen **II.10a-d** sollten deshalb einen vielversprechenden Startpunkt für weitere, eingehende Untersuchungen zur cAAC-vermittelten Fluoridübertragung darstellen, da solche nicht-Metall- und inbesondere Carbene-vermittelten Fluorübertragungsreaktionen immer noch eine Ausnahme darstellen.

Appendix

1. Reprint Permissions

1.1. ACS Publications

All manuscripts of the following publications:

Aryldihydroborane Coordination to Iridium and Osmium Hydrido Complexes
Nicole Arnold, Silvia Mozo, Ursula Paul, Udo Radius, Holger Braunschweig, *Organometallics* **2015**, *34*, 5709-5715.
DOI: 10.1021/acs.organomet.5b00788

Synthesis and Reactivity of Cyclic (Alkyl)(Amino)Carbene stabilized Nickel Carbonyl Complexes
Ursula S. D. Paul, Udo Radius, *Organometallics* **2017**, *36*, 1398-1407.
DOI: 10.1021/acs.organomet.7b00109

were reproduced with permission from the American Chemical Society. The detailed bibliographic data and the corresponding hyperlinks of the respective articles can be found in chapter 4 of each part of the present work.

1.2. RSC Publications

The manuscript of the following publication:

Iridium-catalysed dehydrocoupling of aryl phosphine–borane adducts: synthesis and characterisation of high molecular weight poly(phosphinoboranes)
U. S. D. Paul, H. Braunschweig, U. Radius, *Chem. Commun.* **2016**, *52*, 8573-8576.
DOI: 10.1039/C6CC04363A

was reproduced with permission from the Royal Society of Chemistry. The detailed bibliographic data and corresponding hyperlink of the respective article can be found in chapter 4 of the first part of the present work.

1.3. Wiley Publications

All manuscripts of the following publications:

Cyclic (Alkyl)(Amino)Carbene Complexes of Rhodium and Nickel and Their Steric and Electronic Parameters
U. S. D. Paul, C. Sieck, M. Haehnel, K. Hammond, T. B. Marder, U. Radius, Chem. Eur. J. **2016**, *22*, 11005-11014.
License number: 4050170273056

Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino) Carbene
U. S. D. Paul, U. Radius, *Chem. Eur. J*. **2017**, *23*, 3993-4009.
License number: 4096620118681

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2. List of Publications

Publications in peer-reviewed journals:

2017:

"Synthesis and Reactivity of Cyclic (Alkyl)(Amino)Carbene stabilized Nickel Carbonyl Complexes"

U. S. D. Paul, U. Radius, *Organometallics* **2017**, *36*, 1398-1407.

"Ligand versus Complex: C–F and C–H Bond Activation of Polyfluoroaromatics at a Cyclic (Alkyl)(Amino) Carbene"

U. S. D. Paul, U. Radius, *Chem. Eur. J.* **2017**, *23*, 3993-4009.

"B–B Bond Activation and NHC Ring-expansion Reactions of Diboron(4) Compounds, and Accurate Molecular Structures of $B_2(NMe_3)_4$, B_2eg_2, B_2neop_2 and B_2pin_2"

M. Eck, S. Würtemberger-Pietsch, A. Eichhorn, J. H. J. Berthel, R. Bertermann, U. S. D. Paul, H. Schneider, A. Friedrich, C. Kleeberg, U. Radius, T. B. Marder, *Dalton Trans.* **2017**, *46*, 3661-3680.

2016:

"Synthesis and Thermal Properties of Novel NHC-Stabilized Cobalt Carbonyl Nitrosyl Complexes"

F. Hering, J. H. J. Berthel, K. Lubitz, U. S. D. Paul, H. Schneider, M. Haerterich, U. Radius, *Organometallics* **2016**, *35*, 2806-2821.

"Preparing (Multi)Fluoroarenes as Building Blocks for Synthesis: Nickel-Catalyzed Borylation of Polyfluoroarenes via C–F Bond Cleavage"

J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. Du, T. B. Marder, U. Radius, *J. Am. Chem. Soc.* **2016**, *138*, 5250-5253.

"Iridium-catalysed dehydrocoupling of aryl phosphine-borane adducts: synthesis and characterisation of high molecular weight poly(phosphinoboranes)"

U. S. D. Paul, H. Braunschweig, U. Radius, *Chem. Commun.* **2016**, *52*, 8573-8576.

“Cyclic (Alkyl)(Amino)Carbene Complexes of Rhodium and Nickel and Their Steric and Electronic Properties”

U. S. D. Paul, C. Sieck, M. Haehnel, K. Hammond, T. B. Marder, U. Radius, *Chem. Eur. J.* **2016**, *22*, 11005-11014.

2015:

“Room temperature ring expansion of N-heterocyclic carbenes and B-B bond cleavage of diboron(4) compounds”

S. Pietsch, U. Paul, I. A. Cade, M. J. Ingleson, U. Radius, T. B. Marder, *Chem. Eur. J.* **2015**, *21*, 9018-9021.

“Bite-angle bending as a key for understanding group-10 metal reactivity of $d^{10}[M(NHC)_2]$ *complexes with sterically modest NHC ligands”*

F. Hering, J. Nitsch, U. Paul, A. Steffen, F. M. Bickelhaupt, U. Radius, *Chem. Sci.* **2015**, *6*, 1426-1432.

“Aryldihydroborane Coordination to Iridium and Osmium Hydrido Complexes”

N. Arnold, S. Mozo, U. Paul, U. Radius, H. Braunschweig, *Organometallics* **2015**, *34*, 5709-5715.

2011:

“Gold(I) “click” 1,2,3-triazolylidenes: synthesis, self-assembly and catalysis”

K. J. Kilpin, U. S. D. Paul, A.-L. Lee, J. D. Crowley, *Chem. Commun.* **2011**, *47*, 328-330.

Poster presentations and talks given at conferences:

poster and short presentation: *„Eigenschaften und Reaktivität von zyklischen Alkylaminocarbenen (CAACs) und deren Nickelcarbonylkomplexe“*

U. Paul, U. Radius, ChemSyStM 2016, Julius-Maximilians-Universität Würzburg, Würzburg, 06.12.2016.

poster and short presentation: *„Eigenschaften und Reaktivität von zyklischen Alkylaminocarbenen (CAACs) und deren Nickelcarbonylkomplexe“*

U. Paul, U. Radius, 18. Vortragstagung der Wöhler-Vereinigung, Freie Universität Berlin, Berlin, 26.09. – 28.09.2016.

poster: *“Iridium catalysed dehydrocoupling of primary phosphine-borane adducts”*

U. S. D. Paul, U. Radius, 2016 Würzburg Summer School on Molecular Boron Chemistry, Julius-Maximilians-Universität Würzburg, Würzburg, 25 – 29.07.2016.

poster and short presentation: *“Iridium catalysed dehydrocoupling of primary phosphine-borane adducts”*

U. S. D. Paul, U. Radius, 9th CaRLa Winter School 2016, Heidelberg, 21 – 26.02.2016.

poster: *„Reaktivität von Iridium-Pincer Komplexen gegenüber Phosphanen“*

U. Paul, U. Radius, 17. Vortragstagung der Wöhler-Vereinigung, Universität des Saarlandes, Saarbrücken, 24.09. – 26.09.2014.

oral presentation: *„Reaktivität von Ir(III)-Pincer Komplexen gegenüber Phosphanen, Boranen und deren Lewis Paaren“*

U. Paul, Wissenschaftliches Kolloquium von Arbeitsgruppen für Anorganische Chemie 2013, Hirschegg (Kleinwalsertal), 26.08.2013.

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