Nucleophilic and electrophilic platinum compounds for C-H bond activation
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Chapter 1
General Introduction

1.1 Organometallic Chemistry

Organometallic chemistry is the discipline dealing with compounds containing at least one direct metal-carbon bond.\[^1\] The bonding interaction may be ionic or covalent, localized or delocalized between one or more carbon atoms of an organic group or molecule and transition, lanthanide, actinide, or main group metal atom.\[^2\]

The development of transition-metal organometallic chemistry dates back to 1827 when Zeise\[^3\] reported the first transition-metal organometallic compound, the ethylene-platinum complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$. Subsequent developments in the area of organometallic chemistry arose not in orderly steps from this original discovery but from several other initially unrelated discoveries, as the discovery of nickel tetracarbonyl in 1890 by Mond, Langer and Quincke,\[^4\] and the discovery of polyphenylchromium compounds in 1919 by Hein.\[^5\] Although these compounds were investigated in some laboratories, and a few complexes of other olefins (e.g. butadiene) with transition metals were also prepared, the importance was not recognized until after 1950, when their structures could be adequately explained.\[^1,6\]

Organometallic chemistry leaped forward in the early 1950s when the structure of ferrocene, $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$ was found.\[^7,8\] This area was developed further by E.O. Fischer and G. Wilkinson into an extensive chapter of organometallic chemistry. This discovery and the recognition of a new type of bonding between metals and organic unsaturated molecules stimulated an enormous interest in these compounds, and resulted in the present state of organometallic chemistry. This was aided by the rapid development of physical methods of investigation, in particular single crystal X-ray spectroscopy and NMR spectroscopy, which afforded detailed information about the structure and bonding in organometallic compounds and facilitated the understanding of their behavior.
1.2 C-H Bond Activation of Hydrocarbons

1.2.1 C-H bond activation of hydrocarbons in homogeneous media

General aspects

The formation of new carbon-carbon bonds is a key step in synthesis. The traditional approach concerns direct reactions between organic molecules, such as radical reactions or Diels-Alder reactions and of stoichiometric reactions involving main group organometallic compounds, such as organomagnesium and organolithium compounds with functionalized organic molecules. The introduction of transition metal catalysts has made a variety of pathways accessible for the catalytic, selective formation of new carbon-carbon bonds.\(^ {2,9-11}\)

\[
\begin{align*}
R-Y + [M] & \quad \rightarrow \quad R-[M]-Y \\
R-[M]-Y + R'-X & \quad \rightarrow \quad R-R' + [M]XY
\end{align*}
\]

**Scheme 1.1 C-C bond forming reactions**

During the last decades the quest for more economic ways for the formation of C-C bonds has become a matter of increasing importance for both industrial and academic research. From the point of view of atom economy,\(^ {9}\) reduction of waste and reduction of the number of reaction steps it would be desirable to circumvent the formation of salt ([M]XY in Scheme 1.1), hence avoid the use of carbon-halogen containing compounds, esters, and the like. Substrates which contain a reactive C-H bond rather than a C-X bond (X = halide) are very interesting alternatives for synthetic purposes.\(^ {12-15}\)

\[
\begin{align*}
\begin{array}{c}
Y \\
H
\end{array} + [M] & \quad \rightarrow \quad \begin{array}{c}
\begin{array}{c}
Y \\
[M]H
\end{array}
\end{array} \\
\begin{array}{c}
\begin{array}{c}
Y \\
[R]
\end{array}
\end{array} & \quad \rightarrow \quad \begin{array}{c}
\begin{array}{c}
Y \\
H
\end{array}
\end{array}
\end{align*}
\]

\([M] = \text{transition metal complex}, Y = \text{coordinating group}\)

**Scheme 1.2 C-C bond forming via ortho-metallation**

C-H bond activation can be very successful when chelation of an adjacent heteroatom (e.g. O, N) is involved, in which case the reaction is commonly referred to as orthometalation, for instance as it is known for metal catalyzed reactions of mainly Ru, Pd, Rh.\(^ {16}\) After coordination of the metal center to the heteroatom, the C-H bond at the α- or 2-position is activated and addition of alkenes, alkynes or carbonyls can occur to form a new C-C bond with good regioselectivity.\(^ {17-19}\)
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Scheme 1.3 Carbonylation of N-(2-pyridyl)pyrrolidine as developed by Murai et al.\[^{[19]}\]

When no heteroatom for coordination is available, C-H bond activation becomes much more difficult or just lacks selectivity towards one particular C-H bond. However, there are some promising systems, such as the Pd-catalyzed oxidative coupling of benzene with an alkene displayed in Scheme 1.4.\[^{[20]}\]

Scheme 1.4 Oxidative coupling of benzene and ethyl (E)-cinnamate

Despite the efforts that have been made, the turnover number is still not high enough for economic application. Moreover, the use of peroxide oxidants and acetic acid solvents in these "non-chelation-assisted" reactions is problematic.\[^{[16]}\] Reported systems for C-H bond activations of alkanes are still rare and are mainly based on Shilov-type of catalysis (see below).\[^{[15]}\]

Platinum is a promising metal for C-H activation reactions of "non-chelation-assisted" hydrocarbons, because platinum hydride bonds can be quite strong compared to Pd and Ni.\[^{[2]}\] In the next paragraphs, nucleophilic platinum(0)- and electrophilic platinum(II)/platinum(IV)-systems in C-H bond activation processes will be discussed.

1.2.2 C-H bond activation of hydrocarbons by Pt(0)-systems

General aspects

A method to activate C-H bonds of hydrocarbons is the in situ generation of a coordinatively unsaturated electron-rich platinum(0) center. The main routes to achieve this reactive electron-rich intermediate by removal of groups of ligands from suitable precursors are thermolysis, photochemical irradiation or chemical methods. After generation of the coordinatively unsaturated platinum(0) center the C-H bond of the hydrocarbon can oxidatively add to the platinum center
forming often a stable platinum alkyl hydride. However, for C-H bond activation, only thermolysis is known to be able to create a Pt(0)-system that is reactive towards hydrocarbons.

**C-H bond activation using in situ generated unsaturated platinum(0) by thermolysis**

In 1988 Whitesides published a phosphine-stabilized platinum complex that cleanly reacts with hydrocarbons.[21,22] When *cis*-hydridoneopentyl platinum(II)[bis(dicyclohexylphosphino)ethane] is heated in benzene solution, neopentane is reductively eliminated. Oxidative addition of a C-H bond of benzene produces *cis*-hydridophenyl platinum(II)[bis(dicyclohexylphosphino)ethane]. The intermediate responsible for oxidative addition is believed to be [bis(dicyclohexylphosphino)ethane] platinum(0).[22] This electron-rich d^14 fragment can react with a variety of saturated and unsaturated hydrocarbons.[21]

![Scheme 1.5 Generation of an unsaturated platinum(0) by thermolysis](image)

If thermolysis of [bis(dicyclohexylphosphino)ethane]hydridoneopentylplatinum(II) is carried out in alkanes, platinum alkyl hydrides are formed; even methane is activated. The bidentate *cis*-coordinating PP-ligand is needed, otherwise no C-H activation is observed, e.g. employing the linear Pt(PR$_3$)$_2$ does not work since its frontier orbitals are ill-disposed for overlap with $\sigma_{C-H}$ and $\sigma^*_{C-H}$ orbitals of the hydrocarbons.[21,23,24] Thermolysis in alkenes and alkynes gave almost exclusively coordination of the alkenes and alkynes, and no C-H activation products.

Modifications in the PP-ligand can dramatically change the reactivity of the intermediate after thermolysis. Diminishing the P-Pt-P angle, for instance by using bis(di-tert-butylphosphino)methane instead of bis(dicyclohexylphosphino)ethane as ligand, eliminates the activity of the Pt$^0$P$_2$ complex towards alkanes and even benzene,[25] only the Si-C bond of tetramethylsilane can be activated. Introduction of oxygen,[26,27] and nitrogen-donors[27] as substituents on phosphorus retains the activity towards C-H groups of hydrocarbons, only platinum-platinum dimer formation limits yields of C-H activated products.[27]
1.2.3 C-H activation by cationic platinum(II) species

The Shilov System

In 1969 Shilov\textsuperscript{[28]} and co-workers demonstrated that Pt(II) salts were capable of activating alkane C-H bonds. Some years later, Shilov\textsuperscript{[29]} also reported that catalytic conversion of alkanes (including methane) to mixtures of the corresponding chlorides and alcohols could be achieved by employing aqueous solutions of Pt(II) and Pt(IV) salts.\textsuperscript{[15]}

\[
\text{R-H + Pt}^{IV} + \text{HX} \xrightarrow[120 \degree C]{\text{Pt}^{III} \text{(cat.)}} \text{R-X + Pt}^{II} + 2 \text{H}^+ \\
X = \text{OH, Cl}
\]

Scheme 1.6 Functionalization of alkanes catalyzed by Pt(II)

The Shilov system is clearly unprecedented in many respects. First the reaction is performed in aqueous solution and is unaffected by the presence of molecular oxygen. Second, the reaction exhibits an unusual chemoselectivity; alkanes are activated at equal or even faster rate than the produced alcohols or alkyl chlorides. Third, the order of regioselectivity (primary C-H > secondary C-H > tertiary C-H) is the reverse of what is normally found for electrophilic and radical oxidations of hydrocarbons. It is, therefore, in principle a very interesting and promising reaction. However, due to the use of expensive Pt\textsuperscript{IV} as stoichiometric oxidant, poor turnover numbers and sometimes unsatisfactory selectivity, the Shilov system is not suitable for practical applications.

Platinum(II) complexes: Applications of the Shilov system

In recent years several new alkane oxidations have been discovered that utilize electrophilic late transition metals in strongly acidic media (e.g. CF<sub>3</sub>CO<sub>2</sub>H, H<sub>2</sub>SO<sub>4</sub>).\textsuperscript{[30-35]} A good application of the Shilov system in these acidic media has been demonstrated by Periana et al.,\textsuperscript{[33]} who improved the stability of the catalyst by adding the bidentate nitrogen ligand bipyrimidine. By doing so, methane is selectively converted into methanol with quite high turnover numbers in the presence of air. The catalytic cycle proposed by Periana is presented in Scheme 1.7.
Understanding the mechanism of the Shilov system and new C-H activation systems

After the report by Shilov, much research has been directed at the mechanism of the selective conversion of alkanes into alcohols in order to better understand this remarkable reactivity.\[15,30,31,34-45\] The C-H activation appears to determine both the rate and the selectivity of the alkane oxidation, thus providing significant motivation to understand the details of its mechanism. Unfortunately, this step has proven to be the most difficult one to study. The reaction stoichiometry involves electrophilic displacement of a proton of the alkane by Pt$^{II}$. For this reaction, two different mechanisms have been proposed: oxidative addition of the C-H bond at Pt$^{II}$ yielding an alkyl(hydrido)platinum(IV) complex which is subsequently deprotonated, or deprotonation of an intermediate Pt(II)-alkane $\sigma$-adduct.

**Scheme 1.7 Proposed mechanism for the functionalization of methane by Periana et al.**
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Scheme 1.8 Oxidative addition/reductive elimination or σ-bond metathesis?

Strong support has been presented for the pathway in which activation of the alkane C-H bond occurs by oxidative addition to a Pt(II) species and generation of a Pt(IV) alkyl hydride as an undetected intermediate.\(^{40,41}\) C-H bond activation was clearly established by observation of Pt(II) alkyl/aryl exchange products,\(^{40,41,43}\) but Pt(IV) alkyl hydrides were not directly observed. In the reported system, (tmeda)Pt(Me)(NC\(_5\)F\(_3\))\(^+\), the reactive three-coordinate Pt(II) species should produce a five coordinate Pt(IV) alkyl hydride that is not stable and indeed immediately gave rise to elimination of methane and a Pt(II) alkyl species.\(^{41}\)

![Scheme 1.8 Oxidative addition/reductive elimination or σ-bond metathesis?](image)

**Scheme 1.9 Stable Pt(IV) alkyl hydrides formed via C-H activation.**

Wick and Goldberg\(^{46}\) reported the first example of C-H activation of Pt(II) to form stable Pt(IV) alkyl hydrides (see Scheme 1.9). Reaction of B(C\(_6\)F\(_5\))\(_3\) with K[Tp'Pt(Me)]\(_2\) (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) resulted in abstraction of the methyl group from the platinum(II) and generated in situ a three-coordinate platinum(II) species with could activate hydrocarbons (e.g. benzene, cyclohexane, pentane). This resulted in the five-coordinate intermediate Pt(IV) (alkyl)(hydride) species that now could be trapped by coordination of the third pyrazolyl ring, producing a stable six-coordinate Pt(IV) species Tp'PtMe(alkyl)(hydride).

Johansson and Tilseth\(^{47,48}\) extended these studies by Bercaw\(^{37-43,49}\) and Goldberg\(^{46}\) and showed hydrocarbon activation at a cationic platinum(II) complex under mild conditions. The Pt\(^{II}\) complex [(N\(^f\)-N\(^f\))Pt(CH\(_3\))(OH\(_2\))]\(^+\)BF\(_4\) \(^-\) (N\(^f\)-N\(^f\) = Ar\(^f\)=C(CH\(_3\))C(CH\(_3\))=NAr\(^f\), Ar\(^f\) = 3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\)) is able to activate benzene at 25 °C and methane C-H bonds at 45 °C, in 2,2,2-trifluoroethanol. This solvent has a low nucleophilicity and is quite polar and appears to be excellent for carrying out C-H activating reactions.
Unlike alkanes, aromatic compounds can coordinate to the metal center, resulting in interaction with the cationic platinum center. Recently Tilset et al. [48,50] showed by NMR-studies and calculations that the reaction path for C-H activation involves an η²-benzene adduct, which decreases the activation barrier of the C-H activation process for benzene relative to methane.

### 1.3 Ligands Systems used in this Study

#### 1.3.1 Imine ligands

Part of the studies in our research group have been aimed at the organometallic chemistry of late transition metals involving didentate nitrogen ligands, and in particular those based on α-diimines (e.g. Ar-BIAN, R-DAB).

![Scheme 1.10 C-H activation at mild conditions by Johansson et al.](image)

Scheme 1.10 C-H activation at mild conditions by Johansson et al.

Pioneering work regarding the coordination chemistry of diaza(buta)dienes has been carried out notably by Vrieze and Van Koten, tom Dieck, Schurig, Frühauf. A number of R-DAB-complexes of low-valent transition metals, often with CO as co-ligand, have been prepared. [52-61]
Compared to phosphine ligands, these compounds usually combine better σ-donor and π-acceptor properties, and are thus capable of stabilizing both higher and lower oxidation state of a transition metal. Another advantage of these α-diimines is the facile tunability of their electronic and steric properties, as well as the straightforward synthesis of these ligands. Recently, also a trans-coordinating diimine ligand, the so-called isophthalaldimine ligand was prepared in our group. These tridentate NCN ligands afford stable trans-diimine transition metal complexes with platinum, palladium and rhodium, but their reactivity towards certain functional groups is diminished compared to cis-diimine transition metal complexes.

Especially the class of rigid α-diimines like Ar-BIAN, designed in our laboratory, has been the subject of many studies. This stems largely from the excellent suitability of their late transition metal complexes as (pre)catalysts for a number of selective carbon-element coupling reactions, such as Suzuki/Negishi type C-C bond formation, allylic amination of unactivated olefins, three-component coupling reactions, and stereoselective cis-hydrogenation of alkynes (Scheme 1.12).

![Scheme 1.12](image)

Scheme 1.12 Stereoselective Pd(BIAN)-catalyzed cis-hydrogenation of alkynes to (Z)-alkenes.

In the field of co-polymerization and polymerization, a discovery in the group of Brookhart has attracted a lot of attention: cationic nickel(II) and palladium(II) species bearing bulky aryl-substituted α-diimine ligands (including Ar-BIAN) are excellent catalysts for the polymerization of ethylene, α-olefins, and internal and cyclic olefins to high molecular weight polymers.

Concerning platinum complexes, α-diimines have been used as ligands in the extremely mild C-H bond activation reactions by cationic Pt(II)-complexes and Pt(0) complexes stabilized with Ar-BIAN’s are moderately active in hydrosilation reactions as has been shown by our group.

### 1.3.2 N-Heterocyclic Carbene ligands

N-Heterocyclic carbenes (NHC’s) are being applied more and more frequently as ligands in organometallic chemistry and homogeneous catalysis. As opposed to imines and α-diimines, NHC’s are excellent σ-donors and poor π-acceptors. NHC complexes are Fischer-type carbene
complexes and contain two strong \( \pi \)-donor substituents on the carbene carbon, which enforce a nucleophilic character at the carbene carbon of the free carbene ligand. The bonding of the singlet N-heterocyclic carbenes to transition metals is mainly described by \( \sigma \)-donation with negligible \( \pi \)-back bonding. In fact, these carbene ligands can substitute classical 2\( e^- \) donor ligands as amines, ethers, and phosphines. The ligand properties and also the coordination chemistry can be best compared with electronrich trialkylphosphines as far as the metal coordination chemistry is concerned.\(^{[74]}\) However, Nolan concluded from structural and thermochemical studies that NHC-ligands behave as better donors compared to the most Lewis basic phosphine ligands, with the exception of the sterically demanding (adamantyl)carbene.\(^{[75]}\)

The research in this field of NHC-ligands started in the late sixties. Öfele\(^{[76]}\) and Wanzlick\(^{[77]}\) have in 1968 independently published the structures and preparations of the first metal complexes containing \( N \)-heterocyclic carbenes. Both reported the deprotonation of an imidazolium salt by a basic metal precursor to form the complexes of the unsaturated NHC: imidazol-2-ylidene, as is shown in Scheme 1.13.

\[
\begin{align*}
\text{Scheme 1.13 & Preparation of the first transition metal complexes of NHC's by Öfele and Wanzlick respectively.} \\
\end{align*}
\]

The related C-C saturated NHC can be derived from “Wanzlick dimers”, (tetraaminoethylenes) as displayed in Scheme 1.14. The resulting saturated imidazolidin-2-yldene ligands, developed by Lappert \textit{et al.}\(^{[78]}\) are more electron-rich and have different chemistry compared to the unsaturated analogues.

\[
\begin{align*}
\text{Scheme 1.14 & The Wanzlick equilibrium} \\
\end{align*}
\]

Innovative work in the area of NHC chemistry has been done by Arduengo and co-workers,\(^{[79]}\) who succeeded in the synthesis of the first stable free carbene. The free carbene (Scheme 1.15) is obtained in high yield when the corresponding imidazolium salt is treated with 1 equivalent of
sodium hydride in the presence 5 mol% potassium tert-butoxide in tetrahydrofuran. This discovery, the synthesis of the easily handled, nucleophilic imidazol-2-ylidene class of carbenes, which can be stored “in a bottle”\(^\dagger\), paved the way for the preparation of metal-NHC complexes directly from the free carbene. Stable carbenes are obtained most easily from imidazole, but nowadays several routes are known for the straightforward synthesis of imidazolium precursor compounds\([80-82]\) for instance the one-pot synthesis starting from glyoxal, a primary amine and formaldehyde. Unsymmetrically N-substituted imidazolium salts can be easily prepared by a small deviation from this route and aryl substituted imidazolium salts can be synthesized from 1,2-diamines and orthoformate.

\[ \text{Scheme 1.15 Synthesis of the free carbene by Arduengo} \]

As noted above, the field of NHC really expanded since the discovery of the “free” carbene by Arduengo\([79]\). Gradually, more reports about NHC stabilized complexes with low valent late transition metals appeared in the literature\([73]\). Hermann,\([83]\) Nolan\([84]\) and Grubbs\([85]\) demonstrated some excellent examples of the benefit of NHC’s in catalysis. They used NHC’s in the ruthenium-catalyzed olefin metathesis reaction, which reaction was accelerated with the development of these NHC-based ruthenium catalysts (2nd generation Grubbs’ catalysts, see Figure 1.16).

\[ \text{Scheme 1.16 Ruthenium catalysts containing the NHC-ligands (2nd generation Grubbs’)} \]

Ruthenium has become the most employed metathesis metal, because of the stability of these 2nd generation Grubbs’ catalysts, predominantly because of the high tolerance to functional groups and the mild reaction temperatures (normally room temperature) compared to the 1st generation Grubbs’ catalyst \([\text{Ru(PCy}_3\text{)}_2\text{Cl}_2(=\text{CHC}_6\text{H}_3)]\). The first two examples by Hermann and Nolan did not

\(^\dagger\) The free carbene reacts slowly with oxygen, but very fast with water, so Schlenk-techniques are needed to avoid moisture.
improve the 1st generation Grubbs' catalyst that much, but especially the use of the saturated NHC-ligand did improve the activity of the metathesis catalyst (monomer:catalyst ratios up to 1000000:1 for ring-opening polymerization).

NHC-stabilized complexes have been reported for almost all d10-metals that are able to catalyze reactions such as Heck and Suzuki coupling (Pd, Ni),[86-90] aryl amination (Pd, Ni),[91,92] hydrosilylation (Pt),[93,94] Grignard cross-coupling (Ni) and Stille coupling (Pd).[95] These new NHC-catalysts have advantages and potential for the future.[87] They exhibit high thermal and hydrolytic durability resulting from exceptionally stable M-C bonds (long shelf-life, stability to oxidation); they are readily accessible and do not need an excess of the ligand.

![Scheme 1.17 Pt(0) NHC-complexes reported by Markó and Arduengo](attachment:image)

R = Me, Cy, βBu

**Scheme 1.17 Pt(0) NHC-complexes reported by Markó and Arduengo**

Until recently, the only carbene-containing platinum(0) known was reported by Arduengo et al., who describes the synthesis of a platinum(0) biscarbene.[97] Although this complex is formally a 14-electron species, this complex is rather stable, which is probably due to the large mesityl-substituents on the N-atoms of the imidazolium-based carbene. In order to induce more activity for this kind of complexes, we envisaged that one of the NHC's should be replaced by a more labile ligand. While this thesis was in progress, Markó[93] reported a NHC Pt0 complex that is active in hydrosilation, demonstrating the advantages of NHC's in platinum(0)-catalyzed H-element activation and the need of labile ligand(s) in combination with the quite stable carbene-platinum bond.

### 1.4 Aim, Scope and Outline of this Thesis

The aim of this work has been the synthesis of novel late transition metal compounds that are able to activate C-H bonds of hydrocarbons in an intermolecular way. It is known from the literature that platinum hydrides can be very stable entities, therefore platinum seems to be a good transition metal to attempt further C-H activation processes. This can be done via two pathways; one concerns the in situ generation of an unsaturated platinum(0) center which is reactive towards C-H bonds of hydrocarbons in a nucleophilic way. A different approach is the development of cationic
platinum(II) complexes, which are reactive towards C-H bonds of hydrocarbons in an electrophilic way.

In chapter 2 the synthesis and properties of new Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene)-complexes are described. Various Pt\(^0\) precursors are employed for the synthetic route and several methods are compared. The reactivity of these Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene)-complexes towards protic acids has been investigated with the aim to obtain readily accessible electrophilic Pt-centers for bond activation reactions.

The synthesis of the first examples of zerovalent platinum mono-carbene bis(alkene) complexes is described in chapter 3. These Pt\(^0\) complexes react under mild conditions with dihydrogen to form neutral hydrido platinum(II) carbene complexes with a hemilabile coordinating carbonyl moiety. The zerovalent platinum mono-carbene bis(alkene) complexes were destined to be reactive towards C-H bonds of certain imidazolium salts in a nucleophilic way. Their reactivity towards such C-H bonds is described in chapter 4. Indeed complete conversion to hydrido platinum(II) bis(carbene) compounds has been observed. Furthermore, in situ formation of cationic hydrido platinum(II) bis(carbene) complexes and their reactivity towards C-H bonds of hydrocarbons in an electrophilic way is described.

Chapter 5 deals with the development of 2-pyridinecarboxaldimine-based NNO-ligands, which should have stabilizing properties in neutral and cationic platinum(II) complexes. The reactivity of the neutral [Pt\(^{II}\)(Me)(NNO)] and cationic [Pt\(^{II}\)(Me)(NNO)]BF\(_4\) complexes towards C-H bonds of hydrocarbons is discussed.

1.5 References

Chapter 1


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