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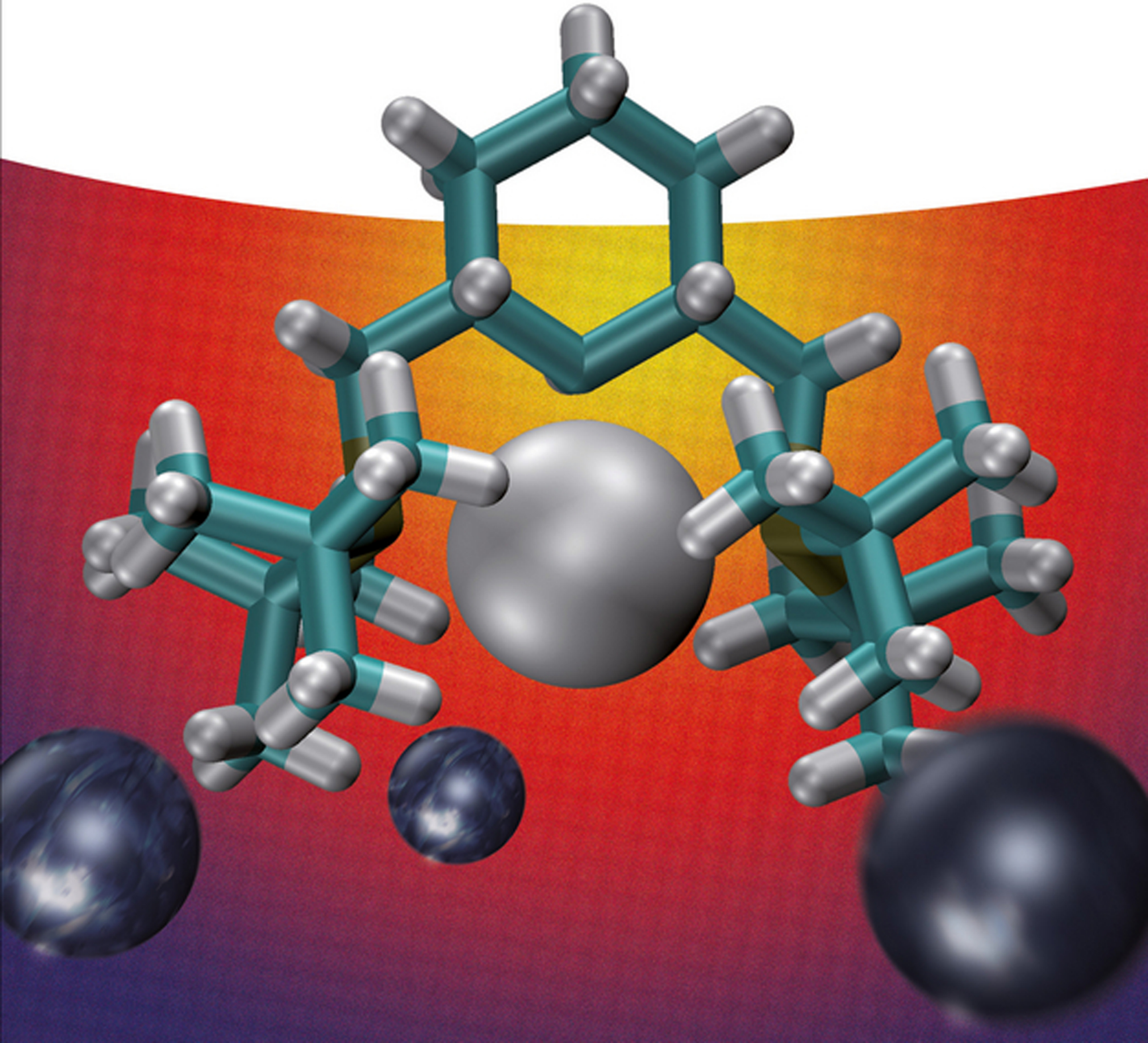
Pincer and Pincer-Type Complexes

Applications in Organic Synthesis and Catalysis



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Pincer and Pincer-Type Complexes

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Contents

Preface

Transition metal catalysis has become one of the most important tools in organic synthesis, important reasons being the high selectivities and high levels of atom economy usually achieved in catalytic transformations. Pincer and pincer-like complexes is an important class of catalysts employed in organic synthesis. The main advantage of these species is the well-defined stoichiometry, which allows conscious catalyst design and fine-tuning of the reactivity and selectivity of the catalyst. Also, the tri-dentate pincer ligand gives the metal complexes an unusual thermal stability. These properties contribute to the improvement of the usual catalytic properties of the commonly used catalysts and sometimes this can give unique catalytic features, which cannot be presented without the pincer framework of the system.

The book aims to help synthetic chemists to choose and apply pincer- complex catalysts in organic transformations. It also points out the most important pincer architectures that can be used efficiently in selective synthesis. Furthermore, it discusses reactivity and mechanisms in the elementary steps of catalytic transformation, which increases our understanding thereby pointing toward completely new applications.

Chapter 1 by Milstein and Chidambaram describes a unique pincer-complex catalyzed transformation for synthesis of esters, amides, and peptides using the aromatization–dearomatization ability of the pincer ligands. Several chapters focus on the possibility of using pincer complexes to stabilize the unusual oxidation state of the metal central atom. Chapter 2 by Campora and Melero analyze the possibilities of bringing palladium to Pd(IV) and nickel to Ni(III) states during the catalytic process. Chapter 10 by Frech is focused on application of a Pd(II)–Pd(IV) catalytic cycle in cross-coupling reactions. Chapter 3 by Szymczak and Moore describes an entirely new application area of pincer complexes, namely as scaffolds for appended functionalities, such as Lewis acids or Lewis bases (even both of these functionalities in the same complex). Another promising novel application is using saturated pincer frameworks for catalysis as described by Jonasson and Wendt in Chapter 8. Chapter 4 by Szabó is focused on pincer-complex catalyzed functionalization of imines and some C–H functionalizations including asymmetric catalysis. Chapter 5 by Adhikary and Guan describes the use of nickel pincer complexes in cross-coupling reactions and shows how these can be complementary to the traditional palladium systems. Pincer complexes have shown very promising reactivity in the activation of small molecules, and in the contribution by Bailey, Parkes, Kemp, and Goldberg (Chapter 11), the possibilities for generation of reactive intermediates in oxidation and reduction reactions are described. In the last decade, a number of new pincer frameworks have appeared and a few of these are described in the final chapters. Although they have not always shown a lot of applications they hold a promise for completely novel transformations. Thus, Chirik in Chapter 7 describes how redox activity of the ligands can be understood and give unprecedented reactivity to base metal complexes. The use of Si, Ge, or Sn with their exceptional trans influence as the central ligating atom is explored in two chapters. Turculet in Chapter 6 gives an overview of PSiP pincer chemistry, showing the unique features of this chemistry and Takaya and Iwasawa in Chapter 9 describes the application of heavier group 14 based pincer palladium complexes in hydrocarboxylation and borylation reactions.

Hopefully, the new aspects of pincer-complex catalysis reviewed in the above chapters will contribute to a broadening of the applications of pincer complexes in organic synthesis as well as to the study of reaction mechanisms.

We would like to acknowledge the authors of this book for their enthusiasm and for sharing their knowledge on pincer chemistry with the readers and for their help in realizing the present book on applications of pincer-complex catalysis in organic synthesis.

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1
Catalysis by Pincer Complexes: Synthesis of Esters, Amides, and Peptides

Chidambaram Gunanathan and David Milstein

1.1
Introduction and Background

Esters, amides, amines, acetals, and peptides are important industrial chemicals. Production of these chemicals is based on multistep processes using stoichiometric amounts of acid or base promoters and coupling reagents, and involves reactive intermediates derived from alcohols or acids (Scheme 1.1), which leads to very large amounts waste [1]. Controlling overoxidation of substrates in the synthetic methods of these products is a challenge, and hence stepwise syntheses are performed (see below) [2]. Thus, green processes that can circumvent stoichiometric reagents and the generation of reactive intermediates, such as acid chlorides, and directly deliver stable and useful industrial products, such as esters and amides, in an atom-economical, selective manner without producing waste are needed.

Pincer ligands, that is, tridentate ligands that enforce meridional geometry upon complexation to transition metals, result in pincer complexes which possess a unique balance of stability versus reactivity [3]. Transition-metal complexes of bulky, electron-rich ''pincer'' ligands have found important applications in synthesis, bond activation, and catalysis [4, 5]. Among these, pincer complexes of ^{i}Pr-PNP (2,6-bis-(di-*iso*-propylphosphinomethyl)pyridine), ^{t}Bu-PNP (2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine), and PNN ((2-(di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl)pyridine), PNN-BPy (6-di-*tert*-butylphosphinomethyl-2,2′-bipyridine) ligands exhibit diverse reactivity [6–8]. These bulky, electron-rich pincer ligands can stabilize coordinatively unsaturated complexes and participate in unusual bond activation and catalytic processes.

In most processes, homogeneously catalyzed by metal complexes, the ligands, while imparting critical properties on the metal center, do not participate directly in bond-making and -breaking processes with the substrates. In recent years, complexes in which the ligands actively cooperate with the metal center in bond-activation processes have been developed [9]. We have devised novel catalytic systems based on pincer complexes in which the pincer ligands cooperate with the metal center in a synergistic manner and their interplay facilitates the chemical processes. The pincer complexes are based on new pyridine- and acridine-type

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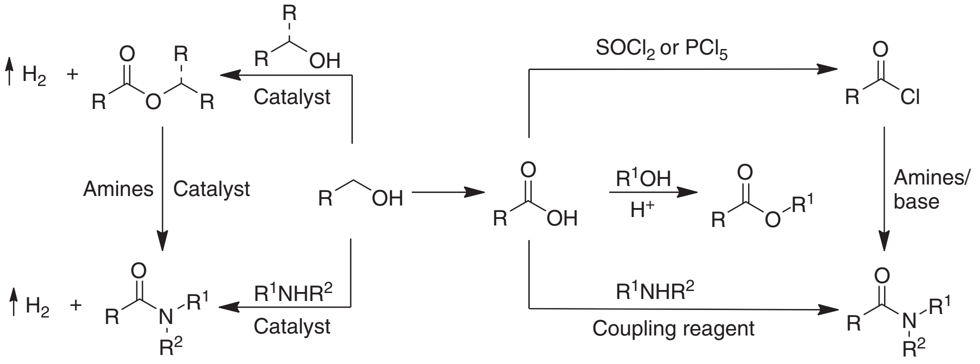
pincer ligands, which undergo bond-breaking and -making processes, involving aromatization–dearomatization of the pincer ligands [8]. Such cooperative pincer complexes catalyze several unique processes, as summarized in recent reviews [6–8, 10]. Here we concentrate on the selective synthesis of esters [11–13], amides [14, 15], acetals [16], amines [17], and imines [18], directly from alcohols. Using diols, polyesters were obtained [19]; diols and diamines provided polyamides [20, 21], and aminoalcohols resulted in formation of pyrazines and peptides [22]. Cooperative pincer complexes have also catalyzed the reverse reactions of esterification and amidation; thus, hydrogenation of esters [23, 24], formates, and carbonates [25] provides the corresponding alcohols, whereas amides give amines and alcohols [26] and urea provides methanol and amines [27]. Carbon dioxide also undergoes hydrogenation to formate salts [28] by pincer catalysts.



Scheme 1.1 Conventional versus catalytic synthesis of esters and amides.

Deprotonation of a pyridinylmethylenic proton of pyridine- and bipyridine-based pincer complexes can lead to dearomatization. The dearomatized complexes can then activate a chemical bond (H–Y, Y = H, OH, OR, NH_2, NR_2, C) by cooperation between the metal and the ligand, thereby regaining aromatization (Figure 1.1). The overall process does not involve a change in the metal's oxidation state [6–8]. In this chapter, we describe the novel, environmentally benign catalytic synthesis of esters, amides, and peptides that operate via this new metal–ligand cooperation based on aromatization–dearomatization processes.

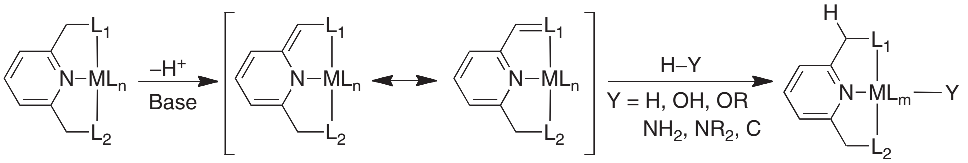
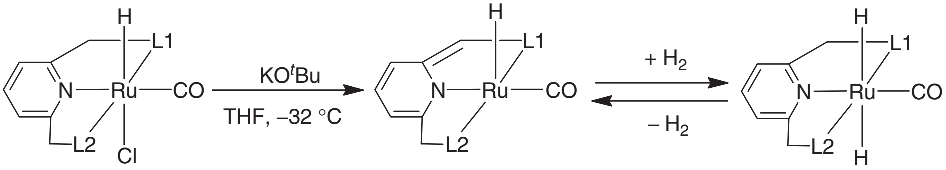


Figure 1.1 Metal–ligand cooperation based on aromatization–dearomatization.

1.2
Bond Activation by Metal–Ligand Cooperation

We have discovered a new mode of bond activation by metal–ligand cooperation based on aromatization–dearomatization of pyridine- and acridine-based heteroaromatic pincer complexes (Figure 1.1) [6–8, 29]. Recently, we have observed that bipyridine-derived PNN-Bipy ligands also exhibit similar metal–ligand cooperativity (Scheme 1.2) [13, 24–27]. Such reactivity, which is not possible with the corresponding aryl-based PCP pincer complexes, is made possible in pyridine-based pincer complexes by (i) the relatively low resonance energy of pyridine (28 kcal mol^{-1}; compared to benzene, 36 kcal mol^{-1}), (ii) the acidity of pyridinyl methylene protons in the pyridine-based pincer complexes, and (iii) stabilization of the dearomatized ligand by the metal center.



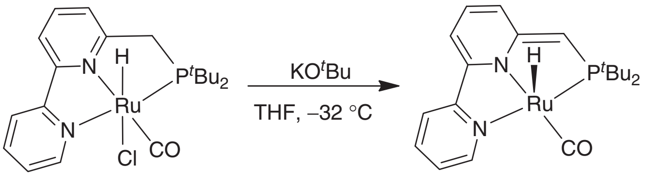
1: L1, L2 = P^{i}Pr$_2$
4: L1, L2 = P^{t}Bu$_2$,
7: L1 = P^{t}Bu$_2$, L2 = NEt$_2$

2: L1, L2 = P^{i}Pr$_2$
5: L1, L2 = P^{t}Bu$_2$,
8: L1 = P^{t}Bu$_2$, L$_2$ = NEt$_2$

3: L1, L2 = P^{i}Pr$_2$
6: L1, L2 = P^{t}Bu$_2$,
9: L1 = P^{t}Bu$_2$, L2 = NEt$_2$

Scheme 1.2 Preparation of dearomatized pyridine-based PNP and PNN pincer complexes and their reversible reaction with H$_2$.

For example, the pyridine-based pincer complexes **1**, **4**, **7**, and **10** undergo smooth deprotonation to provide complexes **2**, **5**, **8**, and **11** (Schemes 1.2 and 1.3). NMR studies of **2**, **5**, **8**, and **11** indicate dearomatization, as the pyridine protons are shifted to lower frequency (olefinic region). Moreover, the structure of complex **2** is unequivocally corroborated by single-crystal X-ray diffraction studies [23]. Importantly, the dearomatized complexes of **2**, **5**, and **8** activate dihydrogen by cooperation between the ruthenium center and the deprotonated phosphine arm, resulting in aromatization to quantitatively yield the ruthenium *trans*-dihydride complexes of **3**, **6**, and **9**, respectively (Schemes 1.2). The magnetically equivalent

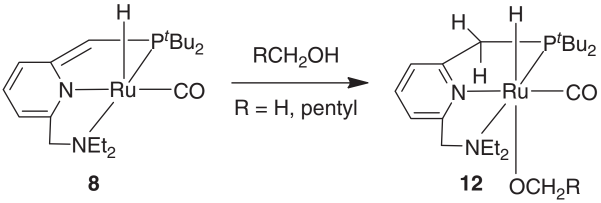


10 **11**

Scheme 1.3 Preparation of dearomatized bipyridine-derived PNN pincer complex **11**.

trans-dihydrides resonate as triplets in complexes **3** and **6** at −4.96 ppm ($^2J_{PH} = 20.0$ Hz) and −4.90 ppm ($^2J_{PH} = 17.0$ Hz), respectively, whereas they display doublets at −4.06 ppm ($^2J_{PH} = 17.0$ Hz) for complexes **9**. The *trans*-dihydride complexes **3**, **6**, and **9** slowly lose H_2 at room temperature to regenerate complexes **2**, **5**, and **8**, respectively.

In addition to the activation of dihydrogen [29d, 30], the dearomatized pyridine-derived pincer complexes also activate O−H bonds of alcohols [11–18, 31] and water [29e, 32], N−H bonds of amines and ammonia [29f,h], sp^3 C−H [29c] and sp^2 C−H bonds [29a,g], and carbon dioxide [33]. Among these various bond-activation reactions, of particular interest here is the O−H bond activation of alcohols, as complex **8** reacts with alcohols to provide the aromatic coordinatively saturated hydrido-alkoxy complexes **12** (Scheme 1.4), indicating the possibility of catalytic transformations based on dehydrogenation of alcohols.



Scheme 1.4 O−H activation by the dearomatized PNN pincer complex **8**.

Such dearomatization and aromatization of these electron-rich ligand systems in cooperation with metal centers present new opportunities for homogeneous catalysis.

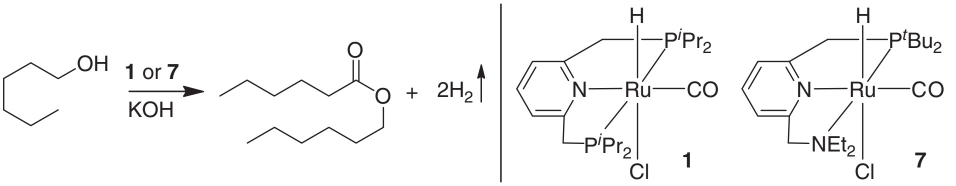
1.3
Synthesis of Esters

Esterification is an important reaction in organic synthesis. It has an assortment of applications in the production of synthetic intermediates, biologically active natural products, fragrances, polymers, polyesters, plasticizers, fatty acids, paints, and pharmaceuticals. Environmentally benign esterification methods catalyzed by pincer complexes that operate via metal–ligand cooperation are described in this section.

1.3.1
Synthesis of Esters from Primary Alcohols

When primary alcohols were heated with a catalytic amount of complex **1**, in the presence of a catalytic amount of base, an unusual dehydrogenative coupling to form esters with evolution of H_2 was observed [11]. Thus, refluxing a hexanol (bp 157 °C) solution containing complex **1** and KOH (0.1 mol% each) under argon in

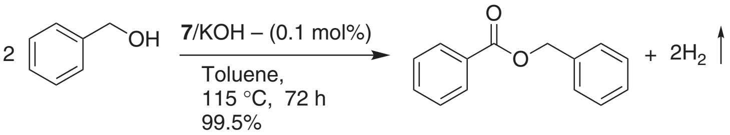
Table 1.1 Catalytic conversion of alcohols to esters by PNP (**1**) and PNN (**7**) complexes in the presence of catalytic base.



Catalyst	Solvent	Time	Temperature (°C)	Yield (%)	TON
1/KOH (0.1 mol%)	—	24	157	67	670
7/KOH (0.1 mol%)	Toluene	24	115	95	950

an open system for 24 h resulted in formation of hexyl hexanoate in 67% yield. The PNN complex **7**, which possesses a hemilabile amine "arm," was a significantly better catalyst (still in the presence of an equivalent of base) than the corresponding PNP complex **1**, leading to 95% (950 turnovers) hexyl-hexanoate after 24 h at 115 °C (Table 1.1) [11].

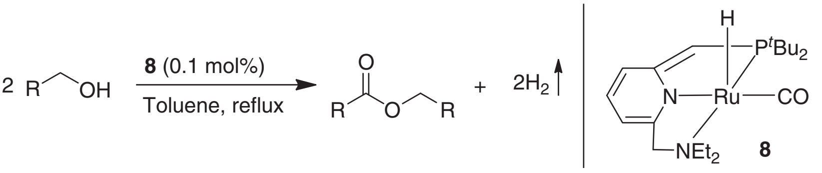
Good turnover numbers (TONs) and yields of esters were obtained with various alcohols at 115 °C. Reaction follow-up with benzyl alcohol indicated that 91% benzyl benzoate was formed already after 6 h, with turnover frequency (TOF) reaching 333 h^{-1} at the level of 50% benzyl benzoate. Formation of the ester became very slow after 6 h, perhaps because of retardation of the reaction by the high ester concentration. However, almost quantitative formation of benzyl benzoate was obtained (Scheme 1.5).



Scheme 1.5 Catalytic conversion of benzyl alcohol to benzyl benzoate by PNN complex **7**.

Further improvement in the reaction was possible by exclusion of the need for base. Thus, reaction of complex **7** with KO^{t}Bu resulted in the formation of the coordinatively unsaturated, 16e$^-$ Ru(II) neutral complex **8**. Indeed, **8** is an excellent catalyst for the dehydrogenative coupling of alcohols to esters and the reaction proceeds with liberation of H_2 under neutral conditions [11]. Table 1.2 provides a few examples. GC analysis of the reaction mixtures indicated that aldehydes were formed only in trace amounts. This catalytic reaction provided a new "green" pathway for the synthesis of esters directly from alcohols. Considerably less efficient methods had been reported previously for this transformation [34].

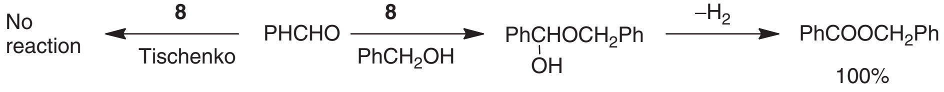
Table 1.2 Examples of dehydrogenative coupling of alcohols to form esters and dihydrogen catalyzed by dearomatized Ru PNN complex **8**.



Entry	R	Ester	Time (h)	Ester (%)
1[a]	Propyl	Butyl butyrate	5	90
2	Pentyl	Hexyl hexanoate	6	99
3	Ph	Benzyl benzoate	4	92

Conditions: 0.01 mmol catalyst **8**, 10 mmol alcohol, and toluene (2 ml) were refluxed (115 °C) under Ar flow.
[a] Neat reaction, heated at 117 °C.

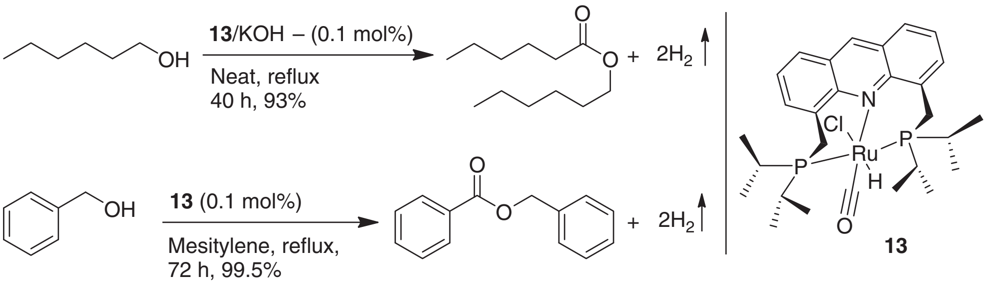
There are two potential pathways by which an ester can be formed, both involving an intermediate aldehyde, namely a Tischenko-type condensation [35] or hemiacetal formation followed by its dehydrogenation [34]. Our results establish that the second pathway is operative, at least in the case of benzyl alcohol [11]. Thus, employing benzaldehyde (in absence of alcohol) did not yield any ester. On the other hand, reaction of benzaldehyde with 1 equivalent of benzyl alcohol led to quantitative formation of benzyl benzoate (Scheme 1.6).



Scheme 1.6 Formation of ester via hemiacetal intermediary.

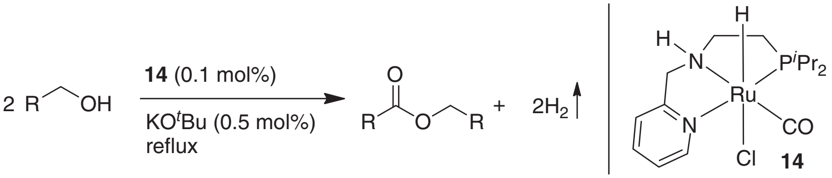
Using the acridine-derived PNP pincer complex **13**, primary alcohols can be directly transformed into acetals under neutral conditions [16, 36]. When the reactions were carried out in the presence of 1 equivalent of base (relative to complex **13**, 0.1 mol%), the corresponding esters were obtained in very good yields (Scheme 1.7). Mechanistic studies revealed that a β-hydrogen is essential for the acetal formation; thus, alcohols such as benzyl alcohol provided benzyl benzoate in 99.5% yield, rather than acetal, even under neutral conditions [16].

Recently, Gusev and coworkers [37] reported the PNN ruthenium pincer complex **14** with an aliphatic backbone, which displayed impressive catalytic activity in the presence of a base (KO^{t}Bu, 0.5 mol%) for the conversion of simple alcohols such as ethanol and propanol. Although the reactions worked at temperatures below 100 °C, good conversions required heating at higher temperatures (Table 1.3,



Scheme 1.7 Esterification of primary alcohols by acridine PNP ruthenium pincer complex **13**.

Table 1.3 Dehydrogenative coupling of alcohols to form esters and dihydrogen catalyzed by the Ru PNN complex **14**.



Entry	R	T (°C)	Time (h)	Conversion (%)
1	Me	78	7.5	30
2	Et	96	8	73
3	Pr	118	3	78
4	*i*-Amyl	131	2.5	92
5	Hexyl	158	1	86

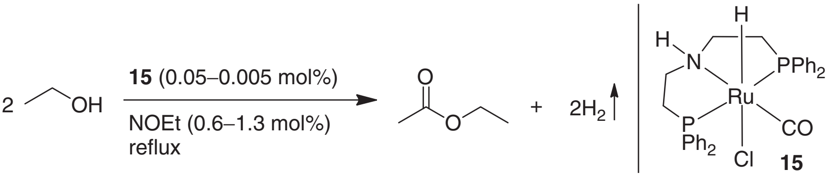
entries 4–5). An analogous dehalogenated osmium-based dimeric pincer complex was also reported to have comparable activity to that of complex **14**.

Though in moderate yield, the reported conversion of ethanol to ethyl acetate by complex **14** and a related osmium dimer complex [37] by Gusev generated interest in the catalytic synthesis of ethyl acetate from ethanol because it is a widely used fine chemical. Very recently, Beller *et al.* [38] screened the catalytic activity of various known pincer complexes for this transformation and found that Takasago's complex **15**, known as *Ru-MACHO catalyst*, is very efficient and the reaction in the presence of a base resulted in very good TON (Table 1.4).

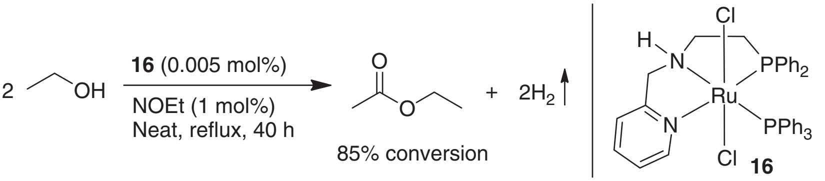
Simultaneously, Spasyuk and Gusev [39] also reported a similar finding; among the various screened pincer complexes, complex **16** showed impressive reactivity with 85% conversion of ethanol (Scheme 1.8).

In addition to these transformations by well-defined pincer complexes, the complexes assembled *in situ* from the metal precursor [Ru(COD)(methylallyl)$_2$] (COD, cyclooctadiene) and PNP or PNN pincer ligands (used for complexes

Table 1.4 Synthesis of ethyl acetate from ethanol by Ru-MACHO catalyst.



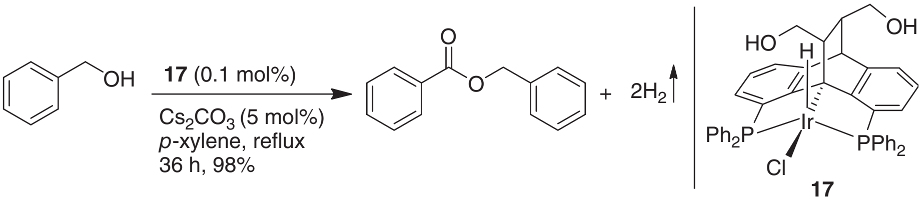
Entry	15 (mol%)	NaOEt (mol%)	Time (h)	*T* (°C)	Yield (%)	TON
1	0.05	1.3	6	90	81	1 620
2	0.05	1.3	24	70	70	1 400
3	0.005	0.6	46	90	77	15 400



Scheme 1.8 Synthesis of ethyl acetate from ethanol by the PNN ruthenium pincer complex **16**.

4 and 7, respectively) also catalyzed the dehydrogenative coupling of alcohol into esters successfully [40]. The catalytically active complex (which could be complex **8**, the CO ligand generated from intermediate aldehyde) displayed similar reactivity as that of complex **8**. PNP and PNN ruthenium(II) hydrido borohydride complexes [(PNX)RuH(BH$_4$), X = P, N] [41] and PNS ruthenium complexes [(PNS$^{t\mathrm{Bu}}$)RuHCl(CO)] [42], analogs to complex **7**, also show catalytic reactivity for the esterification of alcohols.

In 2011, Gelman and coworkers [43] reported a PC$_{\mathrm{SP}}{}^{3}$P iridium pincer complex (**17**), which exhibited efficient catalytic activity for the conversion of benzyl alcohol to benzyl benzoate (Scheme 1.9) and was suggested to operate via a novel metal–ligand cooperation mode. Both electron-withdrawing and electron-donating substituents



Scheme 1.9 Acceptor-less dehydrogenative coupling of benzyl alcohols to form esters and dihydrogen catalyzed by the Ir(III) PC$_{\mathrm{SP}}{}^{3}$P complex **17**.

on the aromatic ring are tolerated, and the corresponding esters were obtained in good yields (88–97%).

1.3.2
Synthesis of Cross-Esters from Primary and Secondary Alcohols

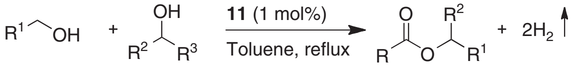
When a toluene solution of complex **11** (1 mol%) was refluxed with equimolar amounts of 1-hexanol and cyclohexanol, cyclohexyl hexanoate was obtained in 79% yield, together with 16% hexyl hexanoate, resulting from self-coupling of 1-hexanol, and 12% of cyclohexanone by dehydrogenation of cyclohexanol [13]. Despite the use of equimolar amounts of primary and secondary alcohols, the formation of the ester cyclohexyl hexanoate as the major product from dehydrogenative cross-esterification is noteworthy. The yield of the cross-esterification products significantly improved when an excess of secondary alcohols was used in the reaction. Thus, in a similar reaction, refluxing a toluene solution containing cyclohexanol and 1-hexanol in a molar ratio of 2.5/1 with complex **11** (1 mol%), cyclohexyl hexanoate was obtained in 93% yield (based on 1-hexanol). Cyclohexanone (34%) was also formed, and the products were isolated by column chromatography. The synthetic potential and substrate scope of this selective dehydrogenative cross-esterification process were demonstrated [13] with various cyclic and acyclic secondary alcohols and other primary alcohols, and the results are summarized in Table 1.5.

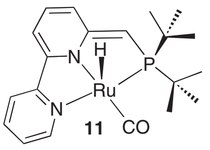
1.3.3
Synthesis of Esters by Acylation of Secondary Alcohols Using Esters

The transesterification reaction is a useful transformation that converts esters to other esters upon reaction with alcohols, as a result of exchange of alkoxy groups, avoiding the use of air- and moisture-sensitive reagents, such as acid chlorides. Further, ester-to-ester transformation is particularly useful when the carboxylic acid and their activated derivatives are not readily available [44]. In general, transesterification of secondary alcohols is slower than that of primary alcohols. The reaction is not atom-economical, as it produces, in addition to the desired ester, an equivalent of alcohol. Circumventing this undesired path, we have devised a novel method for transesterification in which dihydrogen is formed as the only byproduct, rather than alcohols, upon reaction of symmetrical esters with secondary alcohols.

Thus, refluxing a benzene solution of complex **8** (1 mol%), ethyl acetate (5 mmol) and cyclohexanol (15 mmol) under an argon atmosphere for 28 h resulted in complete consumption of ethyl acetate [12]. Cyclohexyl acetate was the only product formed (95%, Table 1.6) as observed by GC analysis and further confirmed by characterization of the isolated product. Similarly, refluxing a toluene solution containing 1 equivalent of an ester, such as hexyl hexanoate, pentyl pentanoate, and butyl butyrate, and 3 equivalent of various secondary alcohols in the presence of 1 mol% of complex **8** resulted in cross-esters in very good yields (Table 1.6). Somewhat lower yields of products were obtained when only 2 equivalent of secondary alcohols was used.

Table 1.5 Dehydrogenative cross-coupling of primary and secondary alcohols catalyzed by **11**.[a]





11

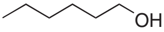
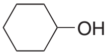
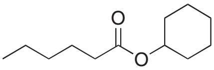
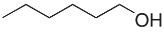
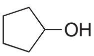
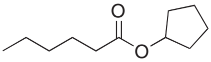
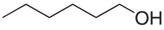
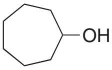
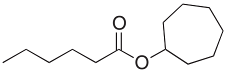
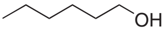
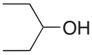
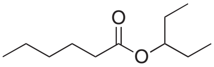
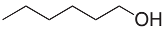
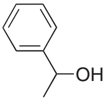
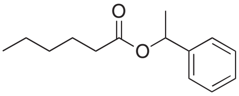
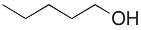
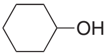
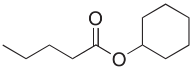
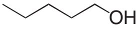
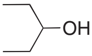
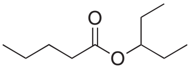
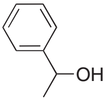
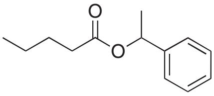
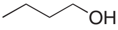
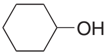
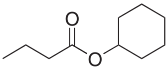
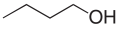
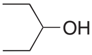
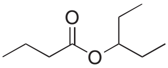
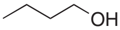
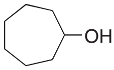
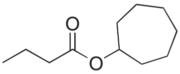
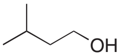
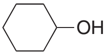
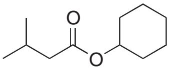
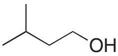
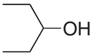
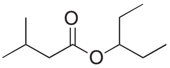
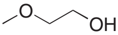
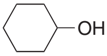
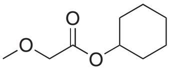
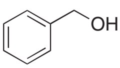
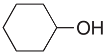
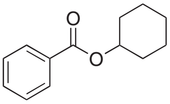
Entry	1° alcohol	2° alcohol	Cross ester	Time (h)	Yield (%)
1				24	93
2				26	63
3				26	90
4				26	93
5				26	58
6				25	95
7				24	96
8				38	46
9				25	95
10				26	93

Table 1.5 (*Continued*)

Entry	1° alcohol	2° alcohol	Cross ester	Time (h)	Yield (%)
11				26	70
12				25	99
13				25	95
14				24	98
15				24	91

[a] Complex **11** (0.03 mmol), primary alcohol (3 mmol), secondary alcohol (7.5 mmol), and toluene (2 ml) were refluxed under argon. Yields of products were determined by GC using *m*-xylene as an internal standard.

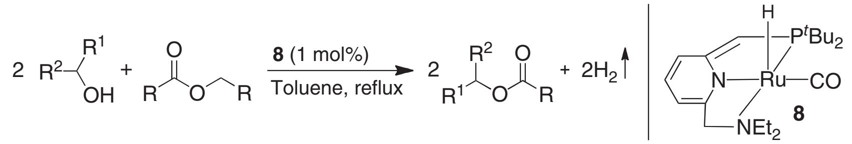
When the unsymmetrical ester ethyl butyrate was reacted with 3-pentanol in the presence of **8** (1 mol%) under refluxing toluene, 75% conversion of ethyl butyrate took place to yield 73% of 3-pentyl butyrate (entry 14, Table 1.6). 3-Pentyl acetate, which was expected to be formed from the ethanol intermediate, was observed only in trace amounts, perhaps as a result of the loss of ethanol under reflux conditions. Likewise, the reaction of methyl hexanoate with cyclohexanol results in 42% conversion with the formation of 42% cyclohexyl hexanoate (entry 15).

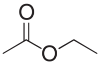
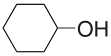
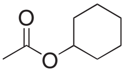
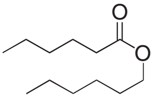
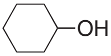
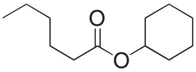
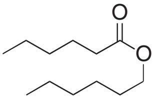
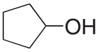
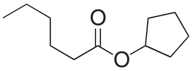
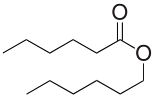
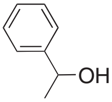
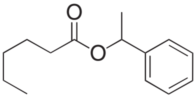
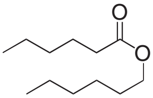
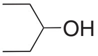
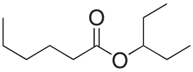
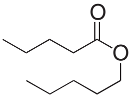
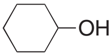
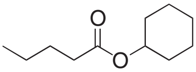
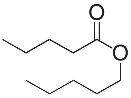
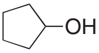
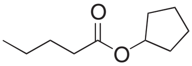
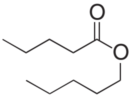
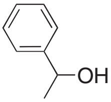
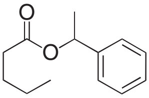
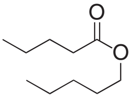
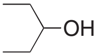
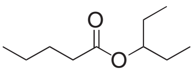
Dehydrogenation of the secondary alcohol to the corresponding ketone is a slower reaction than the dehydrogenative coupling of the primary alcohol to ester, and thus most of the secondary alcohol reacts with the ester, although some ketone formation is observed as excess of alcohol is used. When symmetrical esters are used, both acyl and alkoxy parts of the substrate ester are incorporated into the product ester with liberation of hydrogen, providing an atom-economical and environmentally benign method for the transesterification reactions [12].

1.3.4
Synthesis of Polyesters from Diols

Polyesters are generally synthesized by a step-growth polycondensation reaction or through chain-growth ring-opening polymerization. However, achieving high molecular weights by the known methods for the synthesis of polyesters is

Table 1.6 Acylation of secondary alcohols catalyzed by the complex **8**.[a]



Entry	Ester	Alcohol	Cross-esters	Time	Conversion	Yield (%)
1[b]				28	100	95
2				26	96	95
3				26	71	70
4				36	50	49
5				26	91	90
6				36	93	93
7				36	87	85
8				18	51	49
9				26	91	90