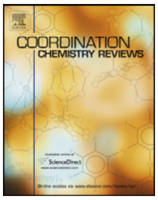
Coordination Chemistry Reviews 255 (2011) 1991–2024

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Recent advances in metal catalysts with hybrid ligands

Wen-Hua Zhang[a], Sheau Wei Chien[a], T.S. Andy Hor[a,b,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore
[b] Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research, 3 Research Link, 117602, Singapore

Contents

ARTICLE INFO

Article history:
Received 22 February 2011
Accepted 26 May 2011
Available online 8 July 2011

Keywords:
Hybrid ligand
Hemilabile
Chelating ligand
Homogenous catalysis
Transition metal

ABSTRACT

This review summarises some recent developments of the metal complexes of hetero-functional hybrid ligands of C-, N-, O-, P- and S-donors. It highlights the ligand designs, synthetic pathways, structural motifs and catalytic prowess of these complexes.

---

* Corresponding author at: Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore.
E-mail address: andyhor@nus.edu.sg (T.S.A. Hor).

0010-8545/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2011.05.018

1. Introduction

Hybrid ligands are bi- or polydentate ligands that contain at least two different types of chemical functionality capable of binding to metal centres. They range from ligands that differ by their donating atoms (e.g. NR_3 and PR_3) ("hetero-donating hybrids") to those that are chemically different although they have the same donor atom (e.g. amine and imine) ("homo-donating hybrids"). These donor functions are often chosen to be inherently contrasting so that bonding phenomena such as hemilability and *trans*-influence can be exemplified and harnessed [1–8]. In many cases, the hybrid donors introduce new features that are not found in pure homo-ligands. Since many of these properties also govern, or at least affect, the functional behaviour of the complexes such as in catalysis, the use of hybrid ligands to influence the functional outcome in metal complexes has proven to be a powerful means to design molecular complexes for technological applications. As the behaviour of the hybrid ligands also depends on the electronic and geometric states of the metal upon which the ligands are coordinated, the overall design often requires a synchronised adjustment of both ligand and metal features.

Recent years have seen an influx of research endeavours in applying hybrid ligands in transition metal-based homogenous catalysis. The field is too broad and diverse to be covered in a single review. There are also other excellent reviews on some specialised topics in this area, such as oxazoline-based systems [1,9,10], pyridine-2,6-bis(oxazolines) [11], planar-chiral ferrocene-based ligands [9,12–15], bis(imino)pyridines [16], chiral thiophosphoramide and thioamide [17], phosphoramidite [18,19] etc. We herein limit to the most abundant donor sets in the 2*p* and 3*p* series and confine to recent developments within the last 5 years. These are primarily ligand sets with different permutations of C, N, O, P and S donors. Other donors such as B, Si and Se are outside the present scope and will be captured only for comparative purpose. Hybrid ligands that are based on N-heterocyclic carbenes (NHCs) [20–33] hybridised with an X (X = C or a heteroatom) donor, tridentate pincer complexes [32,34,35], and [N, O]-Schiff-base (mostly salen, salan and salanen) hybrids [36–40] have been sufficiently reviewed and hence are also excluded in this account.

2. [C, N, O] hybrids

With the current flourish of N-heterocyclic carbenes (NHCs), the design and application of [C,X]-ligands (X = heteroatom) has been well explored [20–33]. The development of bi- or polydentate NHCs containing different carbene scanfolds is tempting but uncommon [41,42] probably due to the technical challenges not only in the ligand syntheses but also purification of the precursors. Very few O-centric hybrids have been reported so far due to their notably weak donation ability. A mixed set of weak to moderate donors could however be used to enhance the substrate selectivity of metal complexes through selective ligand ejection [43–45]. N-based hybrid ligands are however ubiquitous, as they are abundant and cover a broad range of ligand types. Their synthesis and complexation are generally convenient and facile. Very significantly, N-donors are adaptable in different metal environments and compatible with other donor functions. Hence there are many established methods to bring them together into single molecular entities [16,46]. The design, synthesis and structure of various metal complexes with N-based hybrid ligands are described in Section 2.1. The following Section 2.2 will cover the catalytic systems of these complexes.

2.1. Design, synthesis and structures

The quest of a suitable catalyst hinges on a successful combination of an active metal and a compatible and synergistic ligand. Such a simple principle is best reflected in N-based hybrid ligands since nitrogen donors have the propensity to almost all metal states, especially those of transition metals. The metals summarized herein span from Group 3 Sc^{III} (**1**) [47–50] (including La^{III} (**2**) [51] and Ce^{IV} (**3**) [52]) to Group 11 Cu^{I} (**17**) [53] and from 3*d* to 5*d* metals.

The great diversity of ligand types, from bidentate to multidentate, and from achiral to chiral, etc., also adds to their popularity. Their synthesis and subsequent complexation are rather simple and straightforward under relatively mild conditions, as well as with often predictable structural outcomes. Table 1 lists a series of representative examples of recent metal complexes of N-based hybrid ligands.

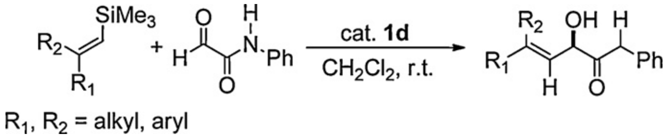
For example, the synthesis of pyridine-2,6-bis(oxazolines) (pybox) by Nishiyama et al. [54] has established a standard synthetic methodology for others. The complexation of pybox with many metals presents a model of a versatile ligand. As seen in complexes **1–3**, **10** and **13**, pybox is distinctive in that the two peripheral oxazoline rings make a chiral and C_2-symmetrical concave, which allows the two bulky substituents on the oxazoline ring to be positioned close to the reaction site thus serving as "chiral fences"[54].

The design of **5**, **6** and **9** is inspired by nature in mimicking the heme [55,56] or histidine [57]. Complex **16** on the other hand can mimic the synthetic benzimidazole-derived carbene complexes [58].

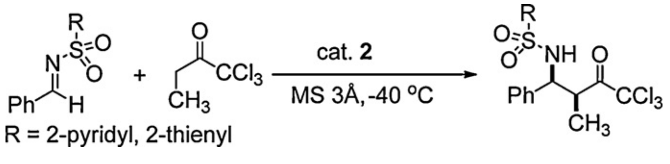
Chirality of complexes **7** and **12** can be achieved by installing a chiral centre in the pyridylimine or pyridylamido ligands [59,60]. The synthesis of water soluble cationic Ru^{III} complex **8** can be accomplished by oxidation of its neutral Ru^{II} counterpart by *t*-BuOOH in the presence of $NaBF_4$ in CH_2Cl_2 [61]. Other ligands are designed to have hemilability that can potentially provide a dynamic "on and off" [1] chelating effect for the metal centre during the catalytic cycle.

2.2. Catalysis

Asymmetric synthesis catalysed by transition metal complexes of enantiopure pybox has experienced a pronounced growth in recent years [11]. The use of pybox in Rh^{III}-based asymmetric hydrosilylation of ketones [54] gives higher optical yields than many chiral phosphine catalysts. Recently, Evans et al. have synthesized a series of Sc^{III}-pybox complexes **1** for enantioselective Friedel–Crafts alkylations [47], vinylsilane additions [48], enantio- and diastereo-selective Sakurai–Hosomi reaction [49] and pyrrolealkylations of α,β-unsaturated 2-acyl imidazoles [50]. It is



Scheme 1. Enantioselective alkenylation using air- and moisture-stable trimethylvinylsilanes catalysed by **1d** (Ref. [48]).



Scheme 2. Mannich-type reaction catalysed by **2** (Ref. [51]).

Table 1
A selected list of metal complexes of N-based hybrid ligands and their catalytic reactions.

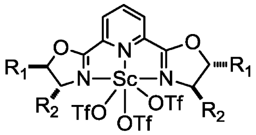
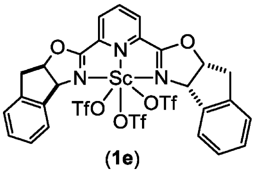
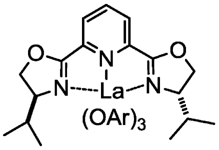
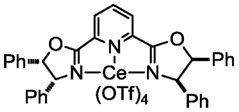
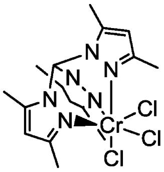
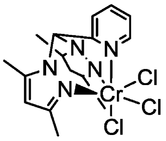
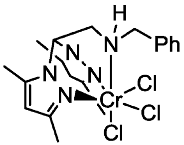
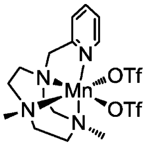
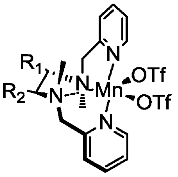
M	Compound	Preparation	Catalytic reactions	Authors	Reference
Sc	 R_1 = H, R_2 = Ph (**1a**) R_1 = H, R_2 = i-Pr (**1b**) R_1 = H, R_2 = CH_2Ph (**1c**) R_1 = Ph, R_2 = Me (**1d**)  (**1e**)	Sc(OTf)$_3$ and L in CH_2Cl_2	Friedel–Crafts alkylations, vinylsilane additions, Sakurai–Hosomi reaction, pyrrole alkylation of α,β-unsaturated 2-acyl imidazoles	Evans	[47–50]
La	 (Ar = 4-MeO-C_6H_4-) (**2**)	La(OAr)$_3$, L and LiOAr in toluene/THF	Mannich-type reactions	Matsunaga and Shibasaki	[51]
Ce	 (**3**)	Ce(OTf)$_4$ and L in EtOAc	Nitrone cycloadditions of α,β-unsaturated 2-acyl imidazoles	Evans	[52]
Cr	 (**4a**)  (**4b**)  (**4c**)	[$CrCl_3(THF)_3$] with L in THF	Ethylene trimerization	Hor	[62,63]
Mn	 (**5a**)  R_1 = R_2 = H (**5b**) (R_1R_2) = c-C_4H_8 (**5c**)	Mn(OTf)$_2$ with L in THF	Olefin epoxidation	Ribas and Costas	[64,65]

Table 1 (*Continued*)

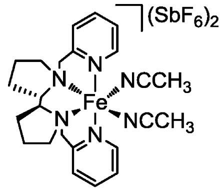
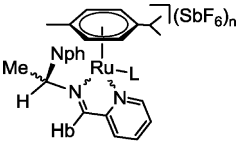
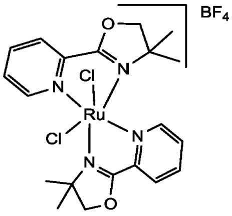
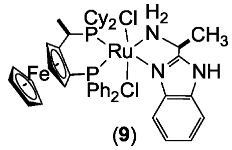
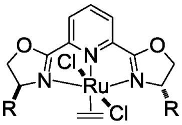
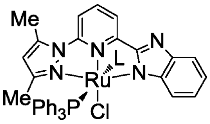
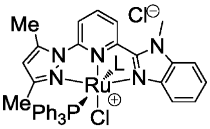
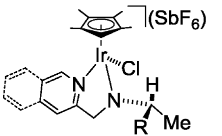
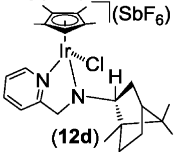
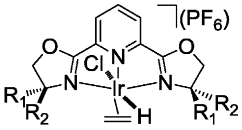
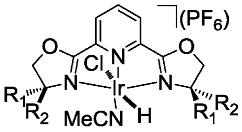
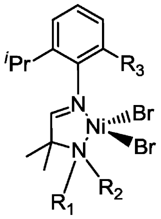
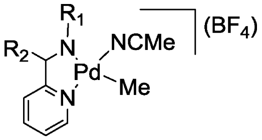
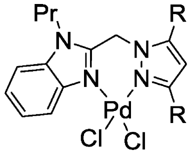
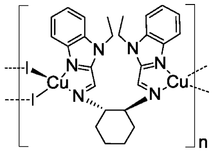
M	Compound	Preparation	Catalytic reactions	Authors	Reference
Fe	 **(6)**	$FeCl_2$ $4H_2O$ with L in MeCN at r.t. followed by chloride extraction using $AgSbF_6$	Selective secondary or tertiary C–H bond oxidation	White	[55,56]
Ru	 L = Cl, *n* = 1 (**7a**) L = H_2O, *n* = 2 (**7b**)	$[\{RuCl(\eta^6\text{-arene})\}_2(\mu\text{-Cl})_2]$ with L and $NaSbF_6$ in MeOH	1,3-dipolar cycloaddition of nitrones with methacrolein	Carmona	[59]
	 (**8**)	$[RuCl_2(cod)]_x$ (cod = cycloocta-1,5-diene) with L in ClC_2H_4Cl at 100 °C followed by oxidation using $NaBF_4$/*t*-BuOOH in CH_2Cl_2	C–H bond oxidation of arylalkanes	Yi	[61]
	 (**9**)	Ru-phosphine precursor with L in toluene at 100 °C	Hydrogenation of aryl ketones	Sandoval	[57]
	 R = ^{i}Pr (**10a**) R = Ph (**10b**)	$[RuCl_2(\eta^6\text{-benzene})]_2$ with L in the presence of 1 atm ethylene in CH_2Cl_2	C–H amination	Blakey	[66]
	 L = DMSO (**11a**)  L = DMSO (**11b**)	$RuCl_2(PPh_3)_3$ with L in toluene at 110 °C giving $RuCl_2(L)(PPh_3)$. Substitution reactions giving other complexes	Transfer hydrogenation of aryl ketones	Yu	[67]
Ir	 R = Ph (**12a**), 1-Nph (**12b**), Cy(**12c**)  (**12d**)	$[(IrClCp^*)_2(\mu\text{-Cl})_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and L in the presence of $NaSbF_6$ in MeOH	Diels–Alder reactions	Carmona and Lamata	[60]

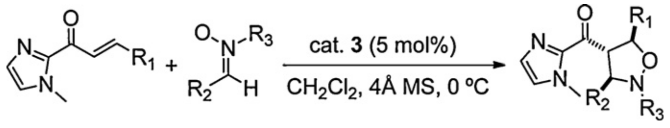
Table 1 (*Continued*)

M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 R_1 = H, R_2 = ^{i}Pr (**13a**) R_1 = Ph, R_2 = H (**13b**)  R_1 = H, R_2 = ^{i}Pr (**13c**) R_1 = Ph, R_2 = H (**13d**)	$[Ir(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_2$ with L and ethylene in MeOH at −40 °C followed by anion exchange with NaX (X = PF_6, SbF_6) giving $[Ir(\eta^2\text{-}C_2H_4)_2(L)](X)$, and then treatment with $HCl(OEt_2)$ in THF at 0 °C	Transfer hydrogenation of aryl ketones	Gamasa	[68]
Ni	 R_1 = R_2 = Me (**14b**) R_1 = R_2 = Et (**14c**) R_1 = R_2 = ^{n}Pr (**14d**) (R_1R_2) = c-C_3H_6 (**14e**) (R_1R_2) = c-C_4H_8 (**14f**)	$NiBr_2$(dme) (dme = 1,2-dimethoxyethane) with L in CH_2Cl_2	Ethylene polymerization	Chen	[69]
Pd	 R1 = H, R_2 = Me (**15**)	PdMeCl(cod) with L in Et_2O at r.t.	Ethylene–norbornene copolymerization	Chen	[70]
	 R = H, Me, ^{t}Bu (**16a-c**)	$K_2[PdCl_4]$ and L in MeOH at r.t.	Suzuki, Heck and Sonogashira reactions	Hor	[58]
Cu	 (**17**)	CuI and L in MeCN at r.t.	N-arylation and azide–alkyne cycloaddition	Hor	[53]

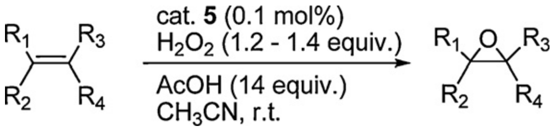
further expanded to Ce^{IV}-pybox complexes **3** in enantioselective nitrone cycloadditions with β-substituted α,β-unsaturated 2-acyl imidazoles [52]. La^{III}-pybox complexes **2** have been applied to catalytic asymmetric Mannich-type reactions [51]. Blakey et al. extended this to Ru^{II}-pybox complexes **10** for enantioselective C–H amination [66] while Gamasa et al. applied Ir^{I}- and Ir^{III}-pybox complexes **13** for asymmetric transfer hydrogenation of ketones [68].

For example, **1d** can effectively catalyze enantioselective alkenylation using air- and moisture-stable trimethylvinylsilanes under mild conditions (Scheme 1). It also represents the first example of intermolecular Lewis acid-catalysed alkenylation. The products formed are highly crystalline solids, ideally suited for industrial process chemistry [48].

Asymmetric Mannich-type reaction can be achieved by using **2** as catalyst (Scheme 2). The $La(OAr)_3$-^{i}Pr-pybox + LiOAr system gives products in >72–99% yield and 92–98% ee. The La^{III}-OAr moiety in the $La(OAr)_3$-^{i}Pr-pybox plays a key role in promoting the reaction compared to $La(OTf)_3$-^{i}Pr-pybox [51].



Scheme 3. Asymmetric endoselective nitrone cycloadditions catalysed by **3** (Ref. [52]).

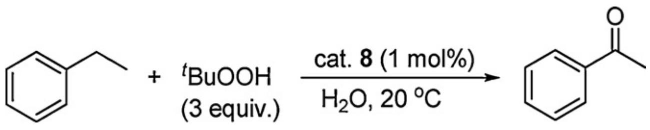


Scheme 4. Clean oxidation of olefins catalysed by **5** (Ref. [65]).

Ce^{IV}-Ph-pybox complex **3** catalyzes asymmetric endoselective nitrone cycloaddition with a range of α,β-unsaturated 2-acylimidazoles substrates under mild conditions (Scheme 3). This chemistry is amenable to the efficient asymmetric synthesis of highly functionalized β′-hydroxy-β-amino acid derivatives [52].

The catalytic reactions based on amino/amido-pyridine (**5**, **6**, **12**, **15**) [55,56,59,60,64,65,70], imino-pyridine (**7**) [59], amino/imino-imidazole (**9**, **17**) [53,57] and imine-amine (**14**) [69] hybrids have also been widely explored since they are adaptable to a range of catalytically active metals. Ribas and Costas have developed the Mn^{II} based tetradentate amino-pyridine catalysts **5a** [64,65] as efficient epoxidation catalysts towards the oxidation of a broad range of olefins using H_2O_2 or CH_3CO_3H as clean oxidants (Scheme 4). These catalysts exhibit unusual chemoselectivity that allows regioselective monoepoxidation of diolefins [64,65]. White et al. have pursued Fe^{II} catalyst **6** for site-selective oxidations of unactivated secondary and tertiary C–H bonds [55,56]. Such catalyst may be capable of discriminating the subtle electronic and steric differences between C–H bonds in complex molecules even in some complicated natural products (Schemes 5 and 6). They also show better selectivity than enzymatic oxidation [55,56].

Other catalytic reaction such as 1,3-dipolar cycloaddition (**7**) [59], hydrogenation (**9**) [57] for Ru^{II} complexes, Diels–Alder reaction for Ir^{III} complex (**12**) [60], ethylene polymerization for Ni^{II} (**14**) [69] and Cr^{III} (**4**) complexes [62,63] or ethylene–norbornene copolymerization for Pd^{II} (**15**) [70], N-arylation and "click" reaction for Cu^{I} (**17**) [53] have also been reported.

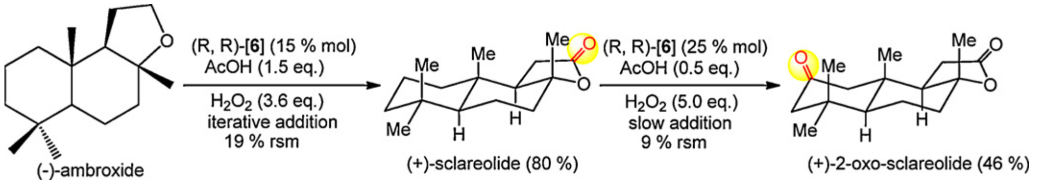


Scheme 7. C–H bond oxidation of ethylbenzene with *t*-BuOOH catalysed by **8** (Ref. [61]).

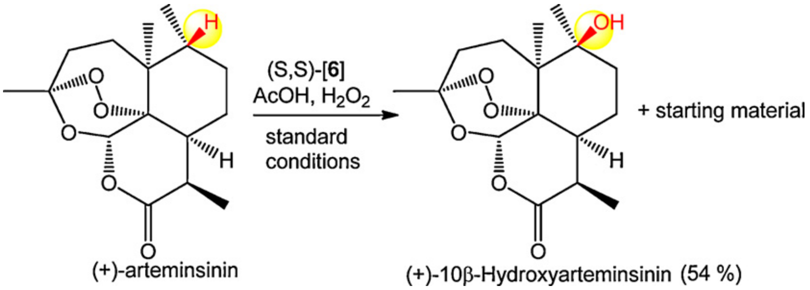
Pyridyl-oxazoline, imidazole-pyrazole and more complicated pyridyle-imidazole-pyrazole ligands have also been conveniently synthesized for metal-catalysed transformations. While high-valent metal-oxo species have been invoked in both non-heme and Gif-type oxidations [71,72], catalytic C–H bond oxidation reactions mediated by well-defined Ru^{III} complexes have been rarely reported [73,74]. Yi et al. have developed cationic Ru^{III} complex **8** for effective C–H bond oxidation reaction of arylalkanes in water (Scheme 7). The treatment of ethylbenzene with *t*-BuOOH (3 equiv.) and 1.0 mol% **8** in water cleanly produced $PhCOCH_3$ at r.t. A large kinetic isotope effect ($K_H/K_D = 14$) and a relatively large Hammett value ($\rho = -1.1$) suggest a solvent-caged oxygen rebounding mechanism via a Ru^{IV}-oxo intermediate species [61]. Complex **16** developed by Hor et al. represents a new class of hybrid ligands which are "carbene-mimics" and can efficiently catalyze Suzuki, Heck and Sonogashira reactions with a broad scope of substrates (Scheme 8)[58]. The cross-coupling of unactivated aryl bromides and 5- or 6-membered heteroaryl bromides with arylboronic acids at r.t. with turnover frequencies (TOF) reaching as high as 60,000 h^{-1} which is significantly better than that of the C–N carbene-imidazole analogue. These results suggested that these Pd^{II} complexes with N-based hybrid ligands are versatile and efficient catalysts for different types of cross-coupling reactions under aerobic conditions. It points a way forward to design NHC-carbene mimics in a similar manner that carbene could mimic phosphine.

3. [C, N], [C, O] and [N, O] hybrids

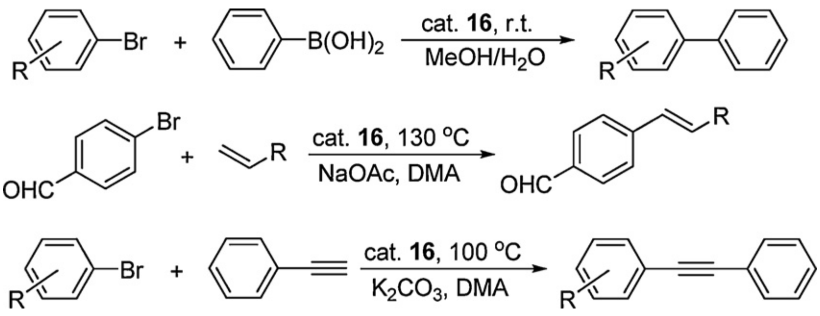
One of the most prevailing organometallic complexes today is functionalized or hybridised heterocyclic carbenes [20–33]. Among the most notable are the [C, O]-heterodonating Grubbs–Hoveyda catalyst [75–83]. Cyclometalated [84] and pincer complexes [32,34,35] represent other common forms of carbon hybrids. One important class of [N,O] hybrid ligands is found in Schiff-base derivatives [36–40], especially the salen, salan and their hybrid



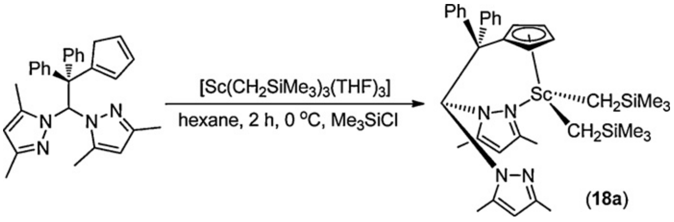
Scheme 5. Selective secondary C–H bond oxidation in (−)-ambroxide catalysed by **6** (Ref. [56]) (rsm = recovered starting materials).



Scheme 6. Selective tertiary C–H bond oxidation in (+)-arteminsinin catalysed by **6** (Ref. [55]).



Scheme 8. Suzuki, Heck and Sonogashira reactions catalysed by **16** (Ref. [58]).



Scheme 9. Synthetic scheme for **18a** (Ref. [93]).

(salalen). Shibasaki et al. have also developed salen type complexes with additional oxygen functionality that can support dinuclear homo- or heterometallic complexes [85–90]. Some recent representative complexes from [C, N], [C,O], and [N, O] hybrid ligands are compiled in Table 2.

3.1. Design, synthesis and structures

Within the last few years the design of heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane has been extended because these systems can be adapted to a range of metals. These multidentate hybrid ligands can also be sterically and electronically tuned [91,92]. The functions of the complexes formed are strongly influenced by the design of the scorpionate ligands. Complexation is generally straightforward. For example, **18a** is isolated from direct reaction of the scorpionate ligand with $[Sc^{III}(CH_2SiMe_3)_3(THF)_3]$ in hexane at 0 °C (Scheme 9) [93]. Complex **18a** is fluxional in solution even at −90 °C (NMR), probably due to an exchange between the coordinated and uncoordinated pyrazole rings, and hence interconversion between the stereoisomers (Scheme 10). Complex **18a** reacts with an alkyl sponge $[Ph_3C][B(C_6F_5)_4]$ to give its cationic form **18e** in good yield (70%) (Scheme 11).

Complexes **20** and **21** are photoredox catalysts designed by Stephenson et al. [90] and MacMillan et al. [94], respectively. Preliminary mechanistic studies of photoredox catalysis for reductive dehalogenation reactions [95] suggested that iminium ions are likely byproducts in the reactions of tertiary amines (Scheme 12) [96]. Complex **20** serves as a photoredox catalyst in generating $[Ru^{I}(bpy)_3]^+$ (bpy = 2,2′-bipyridine) as reductant after reductive quenching. The latter in turn oxidizes imine to iminium ions in the presence of alkyl halides which functions as oxidizing reagent to regenerate **20** [90].

In the catalytic cycle proposed by MacMillan et al. [94] (Scheme 13), **21** should readily accept a photon from room light to populate the $[^*Ir(ppy)_2(dtbbpy)]^+$ (ppy = 2-phenylpyridinato-N, $C^{2'}$; dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine) excited state. Given its known tendency towards reductive quenching, $[^*Ir(ppy)_2(dtbbpy)]^+$ would readily accepts a single electron from a sacrificial quantity of enamine to form a strong reductant $Ir(ppy)_2(dtbbpy)$. This electron-rich iridium system would participate in single electron transfer (SET) with trifluoromethyl iodide to render the electrophilic trifluoromethyl radical in the organocatalytic cycle while regenerating the photoredox catalyst **21**. Further development of such novel ideas of cooperation of organo- and photoredox catalytic cycles could lead to a new generation of catalysts [90,94,97–104].

Complexes **22–25** were also developed based on relatively simple [C, N] hybrids. Easy preparation and functional modification offer a distinct advantage to this system [105–108]. For example, complex **24** developed by Shaughnessy et al., bears hydrophilic functional groups which enables the Pd^{II} complex to catalyze Suzuki reactions in aqueous solutions [107].

The planar-chiral palladacycles based on iron- or cobalt-based metallocenes were independently reported by Uemura [109], Richards [110] and Sammakia [111] in 1995. This topic is extensively studied recently by Wu (**26–29**) [112–117], Peters (**31–33**) [15,118–121], Overman (**34**) [122] and Richards (**35**) [14,123]. Complexation using this type of [C, N] ligands usually takes place in two steps, *viz*: ligand addition to a suitable metal substrate (e.g. Na_2PdCl_4) giving a dinuclear palladacyclic complex, and then cleavage by an incoming ligand (e.g. PPh_3) to yield the mononuclear complex (Scheme 14). The cyclometalated [C, N] ligand is chelated to the sq. planar Pd(II).

Trost et al. and Hui et al. have developed pentadentate [N, O] hybrid ligand bis-ProPhenol which reacts with Et_2Zn to give a dinuclear Zn(II) in which the metal atoms in proximity are chemically distinctive (**51**) [124–131] (Scheme 15). The complementary reactivity of these two metal centres could promote dual activation of the substrate whereas conformational rigidity would enable chiral recognition. Ding et al. further reported the reaction of **51** with *p*-nitrophenol, giving **52**, in which *p*-nitrophenol inserts between the metals as phenoxide (eliminating ethane), thereby giving two hetero-phenoxo bridges (from bis-ProPhenol and *p*-nitrophenol) while maintaining the dinuclear core and keeping the central Zn_2O_2 ring to be planar (e.s.d. 0.002 Å) (Zn···Zn 3.178(1) Å). The Zn^{II} adopts a sq. pyramidal geometry with two coordinated THF molecules protruding in opposite directions out of the plane (Fig. 1) [132].

Catalyst **24** was designed to be water soluble [107]. Different ligands are used to adjust the electronic and steric properties of **38–46** [133–142].

3.2. Catalysis

The planar-chiral palladacycles **26–35** are catalytically active towards a range of reactions such as Suzuki and Sonogashira coupling [112–115,117], amination of aryl chlorides [116,147], aza-Claisen rearrangement [15,118,120,121], Friedel–Crafts reaction [119] and allylicimidate rearrangement [123]. Complex **32** enables the enantioselective intramolecular Friedel–Crafts alkylation of indoles having disubstituted internal olefins (Scheme 16) [119]. A highly strained planar-chiral platinacycle is sufficiently reactive, presumably providing an accelerated olefin coordination step. Catalyst **34** gives the first catalytic asymmetric allylic esteri-

Table 2
A selected list of metal complexes of [C, N], [C, O] and [N, O] hybrid ligands and their catalytic reactions.

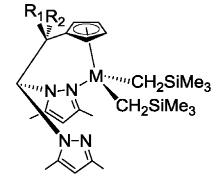
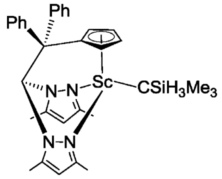
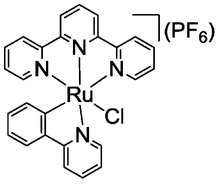
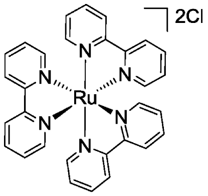
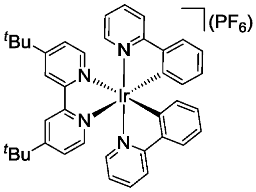
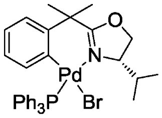
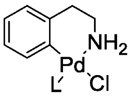
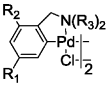
M	Compound	Preparation	Catalytic reactions	Authors	Reference
[C, N] hybrids					
Sc, Y	 $R_1 = R_2 =$ Ph, M = Sc, Y (**18a**,**b**) $R_1 = {}^t$Bu, R_2 = H, M = Sc, Y (**18c**,**d**)  (**18e**)	$[M(CH_2SiMe_3)_3(THF)_3]$ (M = Sc, Y) with L in hexane at 0 °C	Ring-opening polymerization of ε-caprolactone	Otero	[93,143–145]
Ru	 (**19**)	$[RuCl_3(trpy)]$ and 2-phenylpyridine in refluxing DMF	Oxidative dehydrogenation of 2-substituted imidazolines	Kanbara	[146]
	 (**20**)	$RuCl_2$ with bpy in DMF	Aza-Henry reactions	Stephenson	[90]
Ir	 (**21**)	$[IrCl(ppy)_2]_2$ with L in 1,2-ethanediol at 150 °C	α-Trifluoromethylation of aldehydes	MacMillan	[94]
Pd	 (**22**)	Palladacycle dimer with PPh_3 in CH_2Cl_2	Ring-opening of oxabicyclic alkenes with organozinc halides	Hou	[105]
	 L = ^{t}BuXPhos (**23a**) XPhos (**23b**) SPhos (**23c**) BrettPhos (**23d**)	$PdMe_2$(tmeda) (tmeda = N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine), and 2-(2-chlorophenyl)ethylamine and phosphine L in methyl tert-butyl ether at 50 °C	Cross-coupling reaction of aryl chlorides and dimethylamine	Buchwald	[106]
	 R_1 = OH, R_2 = H, R_3 = Me (**24a**) R_1 = H, R_2 = SO_3Na, R_3 = Me (**24b**) $R_1 = R_2$ = H, R_3 = $(CH_2)_3SO_3Na$ (**24c**)	$PdCl_2$ and the appropriate L in the presence of NaOAc in MeOH	Suzuki coupling	Shaughnessy	[107]

Table 2 (*Continued*)

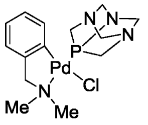
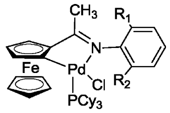
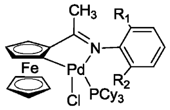
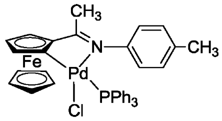
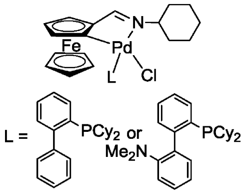
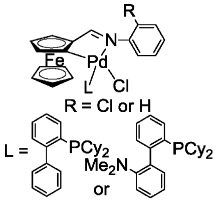
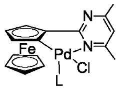
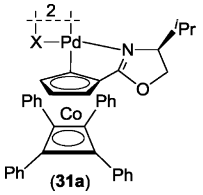
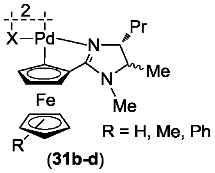
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 **(25)**	$[Pd(\mu\text{-}Cl)(dmba)]_2$ with PTA (dmba = N,C-chelating 2-(dimethylaminomethyl)phenyl; PTA = 1,3,5-triaza-7-phosphaadamantane) in CH_2Cl_2 at r.t.	Sonogashira reaction	Ruiz	[108]
	 R_1 = Cl, R_2 = H (**26a**) R_1 = Cl, R_2 = H (**26b**)  R_1 = Cl, R_2 = H (**26c**) R_1 = Cl, R_2 = H (**26d**)	Dinuclear palladacycle with PCy_3 in CH_2Cl_2 at r.t.	Suzuki coupling	Wu	[112]
	 **(27)**	Dinuclear palladacycle with PPh_3 in CH_2Cl_2 at r.t.	Suzuki and Sonogashira couplings, coupling of arylboronic acids with terminal alkynes	Wu	[113–115]
	 **(28a-b)**	Palladacyclic dimers with PPh_3 in CH_2Cl_2 at r.t.	Amination of aryl chlorides	Gong and Wu	[116]
	 R = Cl or H **(29a-d)**	Palladacyclic dimers with phosphine ligand in CH_2Cl_2 at r.t.	Suzuki coupling	Gong and Wu	[117]
	 L = PPh_3 (**30a**), PCy_3 (**30b**) (Dicyclohexylphosphanyl)biphenyl (**30c**), 2-(Dicyclohexylphosphanyl -2'-(N,N,-dimethylamino)biphenyl (**30d**)	Palladacyclic dimers with phosphine ligand in CH_2Cl_2 at r.t.	Amination of aryl chlorides	Xu and Ji	[147]
	 **(31a)**  R = H, Me, Ph **(31b-d)**	Na_2PdCl_4 with L in the presence of MeOH, followed by reaction with PPh_3 or Na(acac) (acac = acetylacetonate) in MeOH/benzene	Aza-Claisen rearrangement	Peters	[15,118]

Table 2 (*Continued*)

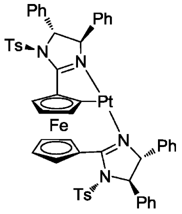
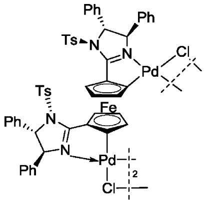
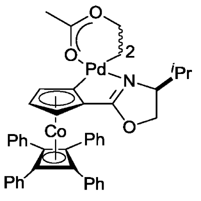
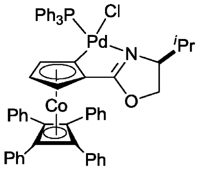
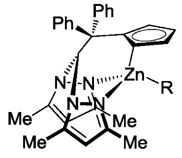
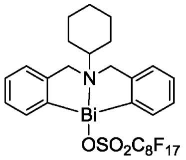
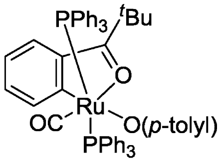
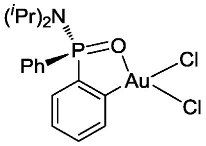
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 (**32**)	K[$PtCl_3(H_2C{=}CH_2)$] with L in the presence of base in MeOH/benzene followed by treatment of Na(acac) and LiCl/HCl	Friedel–Crafts alkylation of indoles	Peters	[119]
	 (**33**)	$Na_2[PdCl_4]$ with L in the presence of NaOAc in $MeOH/CH_2Cl_2$	Aza-Claisen rearrangement, Michael Additions	Peters	[120,121]
	 (**34**)	$Pd(OAc)_2$ with L in HOAc at 95 °C	Synthesis of allylic aryl ethers	Overman	[122]
	 (**35**)	Palladacyclic dimers with PPh_3 ligand in CH_2Cl_2 at r.t.	Allylicimidate rearrangement	Richards	[123]
Zn	 R = Me, Et, ^{t}Bu, CH_2SiMe_3 (**36a-d**)	$Zn(CH_2SiMe_3)_2$ and L in toluene at −70 °C. Reaction 2,4,6-trimethylphenol $ZnEt_2$ and L in THF at −40 °C	Ring-opening polymerization of ε-caprolactone	Sánchez-Barba and Otero	[148]
Bi	 (**37**)	Chloride precursor with $AgOSO_2C_8F_{17}$	Mannich-type reactions	Yin, Au and Wong	[149]
[C, O] hybrids					
Ru	 (**38**)	$RuH_2(CO)(PPh_3)_3$ with [2′-(4-methylphenoxy)pivalophenone	C–H alkenylation	Kakiuchi	[133,134]
Au	 (**39**)	Reaction of $SnMe_3$(L) with K[$AuCl_4$] in MeCN at 90 °C	Three component coupling of aldehyde, amine and alkyne	Ortiz	[135]

Table 2 (*Continued*)

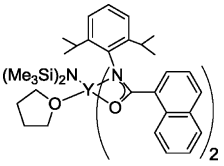
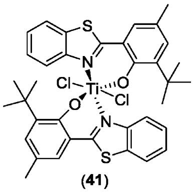
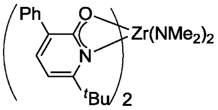
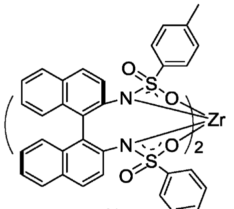
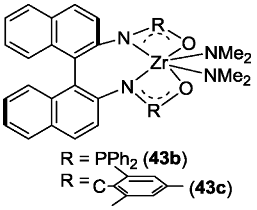
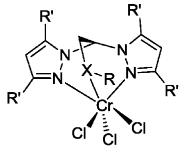
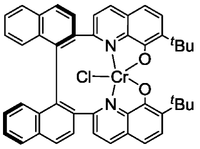
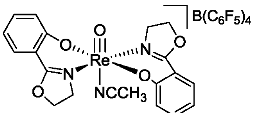
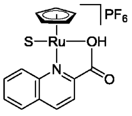
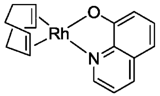
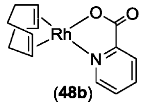
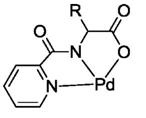
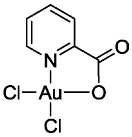
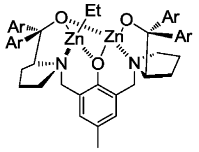
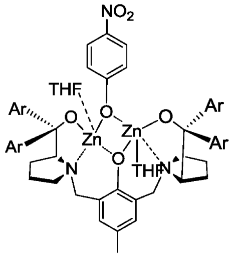
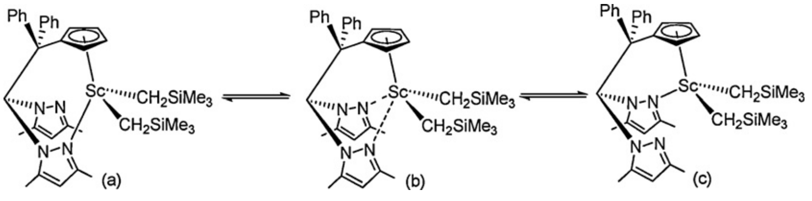
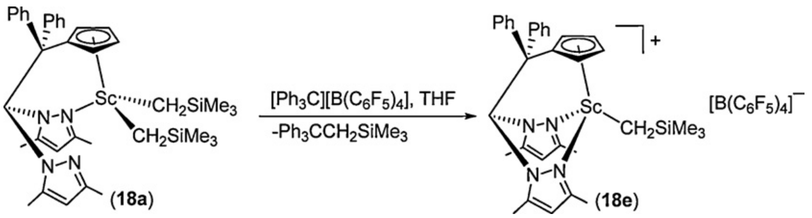
M	Compound	Preparation	Catalytic reactions	Authors	Reference
[N, O] hybrids					
Y	 (**40**)	$Y(N(SiMe_3)_2)_3$ and N-(diisopropylphenyl)naphthyl amide in toluene at 90 °C	Hydroamination of aminoalkenes	Schafer	[136]
Ti,Zr	 (**41**)	$TiCl_4(THF)_2$ with L in toluene at −78 °C or $ZrCl_4$ with L in THF at −78 °C	Ethylene polymerization	Jin	[137]
	 (**42**)	$Zr(NMe_2)_4$ with 6-tert-butyl-3-phenyl-2-pyridone in benzene	Aminoalkene cyclohydroamination	Schafer	[138]
	 (**43a**)  R = PPh_2 (**43b**) R = C (**43c**)	$M(NMe_2)_4$ (M = Ti, Zr) and L in toluene	Hydroamination	Zi and Fang	[140]
Cr	 X = O; R′ = Me; R = Et (**44a**) X = O; R′ = Me; R = ^{i}Pr (**44b**) X = O; R′ = Me; R = Hexyl (**44c**) X = O; R′ = Me; R = Ph (**44d**) X = O; R′ = H; R = Hexyl (**44e**)	$[CrCl_3(THF)_3]$ with L in THF	Ethylene trimerization	Hor	[139]
	 (**45**)	$CrCl_2$ and L in refluxing THF, followed by air oxidation	Nozaki–Hiyamaallylation	Yamamoto	[141]
Re	 (**46**)	Cl extraction from the precursor complex using $[Et_3Si]^+$	Converting vicinal diols and aldehydes to cyclic acetals	Abu-Omar	[142]
Ru	 S = solvent, substrate, product (**47**)	$[RuCp(CH_3CN)_3]PF_6$, 2-quinolinecarboxylic acid and 2-propen-1-ol in acetone	Deallylation of allyl ethers, dehydrativeallylation of alcohols, dehydrative S-allylation of thiols and thioic S-acids	Kitamura	[150,151]

Table 2 (*Continued*)

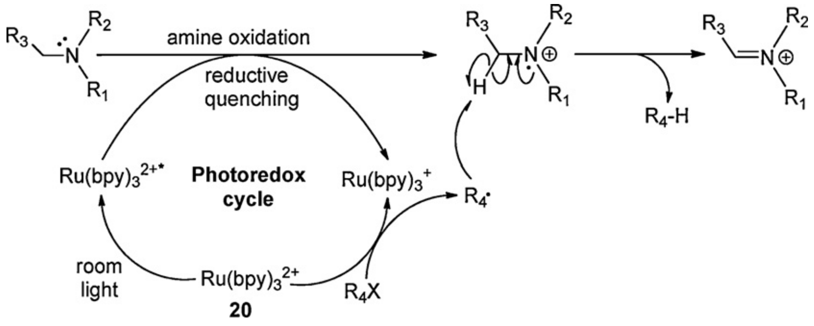
M	Compound	Preparation	Catalytic reactions	Authors	Reference
Rh	 (**48a**)  (**48b**)	$[RhCl(cod)]_2$ with L in methanol at r.t.	Polymerization of carbenes	de Bruin	[152]
Pd	 R = $CH(CH_3)_2$, $CH_2C_6H_5$ (**49a-b**)	$Pd(OAc)_2$ with L in THF at r.t.	Suzuki and Heck reaction	Kantam and Likhar	[153]
Au	 (**50**)	$Na[AuCl_4]\cdot 2H_2O$ and pyridine-2-carboxylic acid in H_2O	Cycloisomerization of 1,5-enynes and acyl migration of propargylic esters	Zhang	[154,155]
Zn	 Ar = Phenyl, 4-Biphenyl, b-Naphthyl (**51**)  Ar = Phenyl, 4-Biphenyl, b-Naphthyl (**52**)	$ZnEt_2$ with L in THF	Michael reaction; Mannich-type reaction, Aza-Henry reaction, Friedel–Crafts alkylation of pyrroles with nitroalkenes, aza-Friedel–Crafts reaction	Trost, Hui and Ding	[126–132]



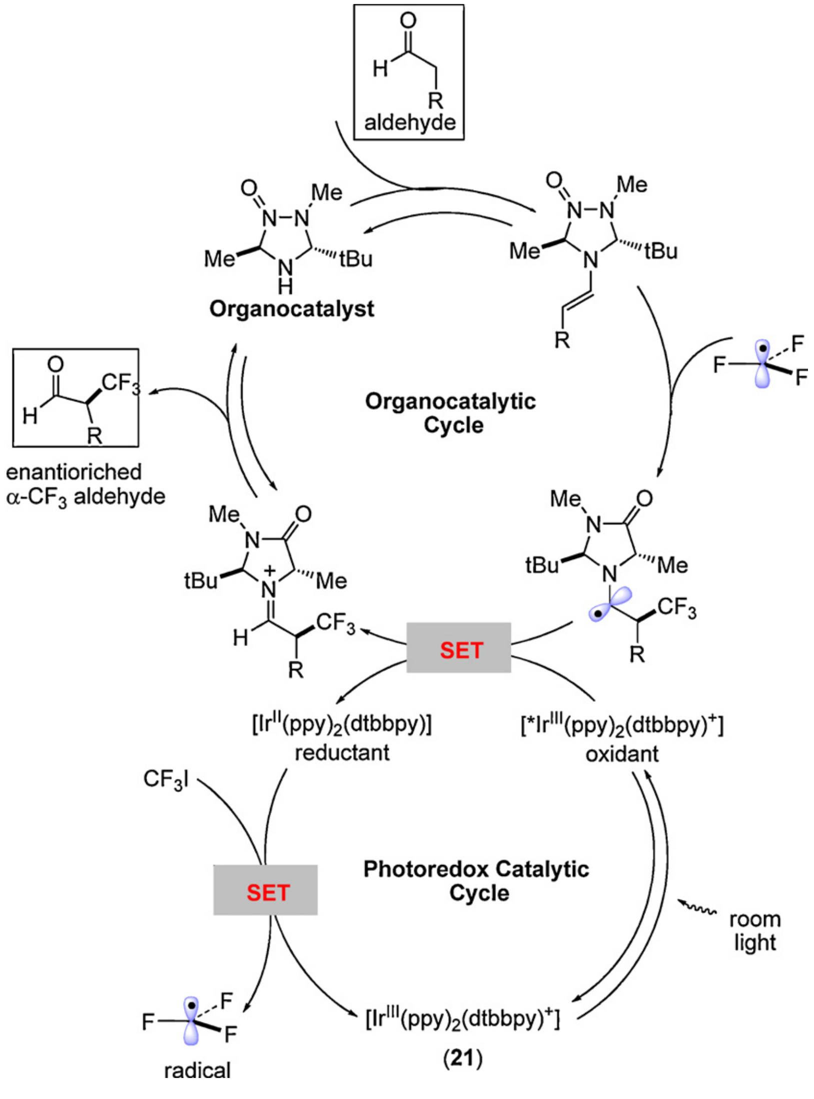
Scheme 10. Schematic representation of the fluxional process of **18a** involving Sc-pyrazole bond making and breaking (Ref. [93]).



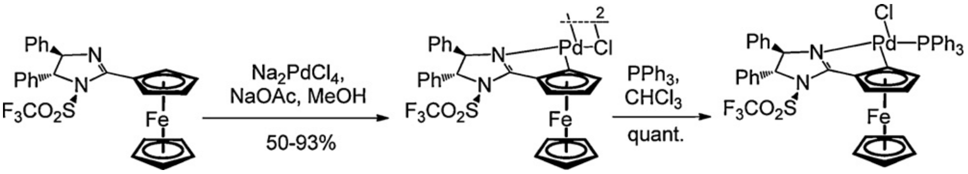
Scheme 11. Conversion of neutral **18a** to cationic **18e** (Ref. [93]).



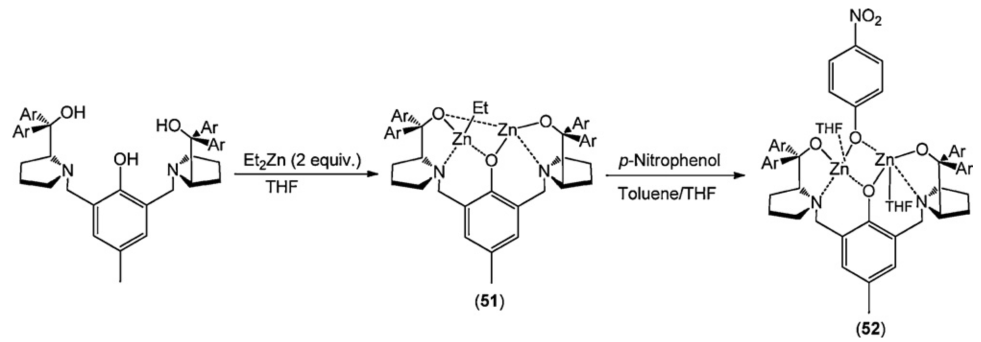
Scheme 12. Iminium ion generation using photoredox catalyst **20**.
(Adapted from Ref. [90]).



Scheme 13. Proposed cooperative organocatalytic and photoredox catalytic cycles for CF_3 alkylation using catalyst **21** (SET = Single Electron Transfer).
(Adapted from Ref. [94]).



Scheme 14. Preparative route of the planar-chiral mononuclear palladacyclic complexes via its dinuclear analogue (Ref. [118]).



Scheme 15. Preparation of the dinuclear Zn complexes **51** and **52** (Refs. [125] and [132]).

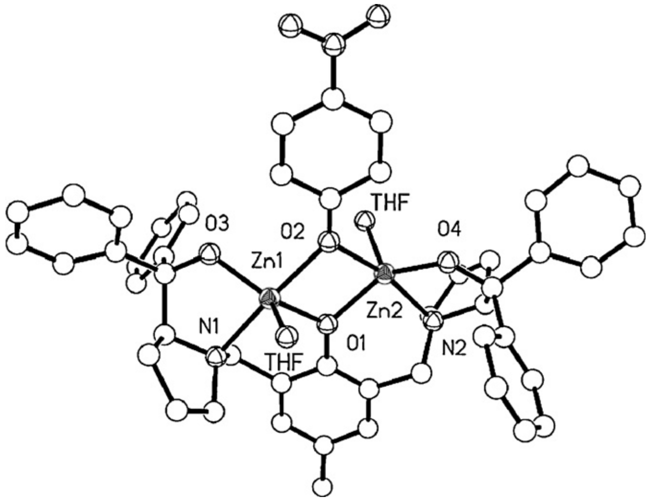
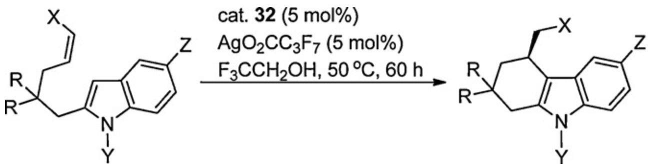


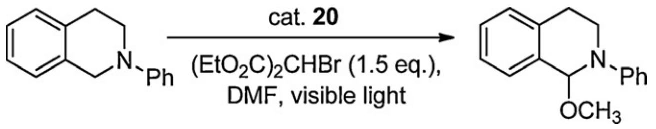
Fig. 1. Structure of **52** with hydrogen atoms and solvent molecules omitted for clarity.
(Structure reproduced from Ref. [132]).



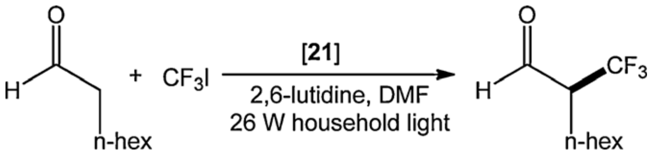
Scheme 16. Friedel–Crafts alkylation of indoles catalysed by **32** (Ref. [119]).

fication reaction with high stereo-induction (Scheme 17) [122]. It proceeds readily at r.t. under low catalyst loadings (1 mol%).

Use of cyclometalating Ru^{II} and Ir^{III} complexes as (co)catalyst is an emerging area. They are widely used in solar cells (SCs) and organic light emitting diodes (OLEDs). Kanbara et al. have used the cyclometalated ruthenium complex **19** as an effective catalyst for the oxidative dehydrogenation of 2-substituted imidazolines under aerobic oxidation conditions giving imidazole derivatives [146].



Scheme 18. Oxidative iminium ion formation catalysed by **20** (Ref. [90]).



Scheme 19. α-Trifluoromethylation and α-perfluoroalkylation of aldehydes using **21** as catalyst (Ref. [94]).

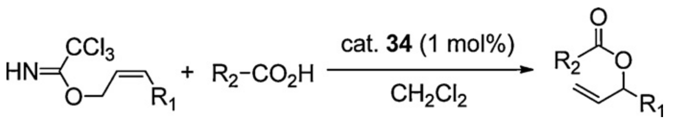
Stephenson et al. reported the Ru(II) mixed-ligand catalyst **20** in an experimentally simple method for the oxidative coupling of nitroalkanes with tertiary N-arylamines under visible light (Scheme 18). The reaction proceeds in high chemical yield with only 1 mol% catalyst and visible light without the need for an external oxidant [90].

Similarly MacMillan et al. reported the first enantioselective, organocatalytic α-trifluoromethylation and α-perfluoroalkylation of aldehydes using the readily available iridium photocatalyst **21** and a chiral organocatalyst imidazolidinone. A range of α-trifluoromethyl and α-perfluoroalkyl aldehydes are obtained from commercially available perfluoroalkyl halides with high efficiency and enantioselectivity (Scheme 19) [94].

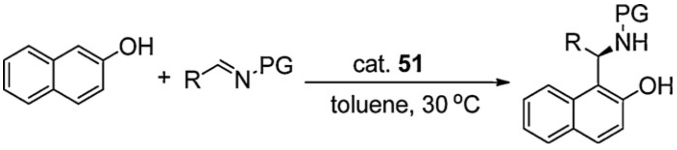
Complex **51** developed by Trost et al. have proven a robust catalyst towards various types of reactions, such as Michael [126,130], Mannich-type [127], aza-Henry [128] and Friedel–Crafts reactions [129]. Hui et al. further extended the use of **51** to the first asymmetric aza-Friedel–Crafts reaction of 2-naphthol with tosylimines (up to 98% ee) (Scheme 20) [131].

4. [P, S] hybrids

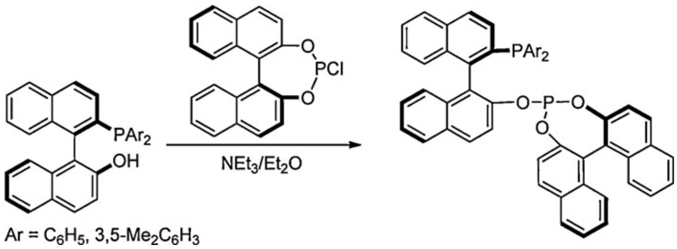
[P, X] and [S, X] (X = C, N, O) ligands are typical “hard-soft” hybrid pairs and most frequently used ligands for catalytic reactions. The hybrids between 2*p* and 3*p* elements are highlighted in Sections 5–8. Numerous P-based hybrid ligands such as phosphine–phosphoramidite [156–160] and phosphine–phosphonite [161] ligands are widely applied to var-



Scheme 17. Enantioselective formation of allylic esters from (Z)-allylictrichloroacetimidates and carboxylic acids catalysed by **34** (Ref. [122]).



Scheme 20. Asymmetric aza-Friedel–Crafts reaction of 2-naphthol with tosylimines catalysed by **51** (Ref. [131]).



Scheme 21. One-step synthesis of a phosphine–phosphite hybrid ligand (Ref. [164]).

ious enantioselective catalytic reactions. However, most of these complexes are catalytically generated *in situ*, and their structures optimized using computational methods [156,157,160,162].

[P, S] type ligands have been more explored compared to their [X, P] and [X, S] (X = hard donor) relatives. Although both are considered soft donors, they are sufficiently different to work well as hybrid pairing. For example, phosphines are generally regarded as σ-donors and π-acceptors while the sulfur ligands are poorer σ-donor and π-acceptor ligands. Their combination could target at regio- and enantiofacial discrimination. A handful of examples of planar-chiral complexes with [P, S] hybrid ligands have been recently reviewed by Chan et al. [163]. Some recent representative complexes from [P, S] hybrid ligands are compiled in Table 3.

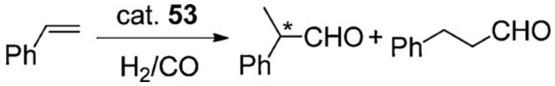
4.1. *Design, synthesis and structures*

Complexes with homoatomic P-based hybrid ligand are effective catalysts compared to their conventional mono- or bidentate analogues by showing high activity, selectivity and stability for a number of transformations. In **53** and **55** with phosphine–phosphonite ligands, the σ-donating phosphine and π-accepting phosphonite, bearing a chiral auxiliary, are designed to create a highly asymmetric environment at the catalytic centre [160,161]. This demonstrates a key thrust of research in hybrid ligands. The ligand synthesis is facile and straightforward – a hybrid phosphine–phosphite ligand binaphos, for example, developed by Takaya et al. requires only simple workup and is formed in high yield (Scheme 21) [164,165].

Another advantage offered by hybrid ligands is found in **53–55** in which the two phosphorus atoms are structurally locked at the *cis*-position and form a rigid and steric chiral pocket for asymmetric reactions.

4.2. *Catalysis*

Zhang et al. reported the synthesis of Rh^{I} complex **53** as a catalyst for hydroformylation reaction of styrene derivatives and vinyl acetate with excellent enantioselectivities (up to 99% ee) (Scheme 22). The performance is significantly enhanced compared to the benchmark ligands, binaphos [160]. Reek et al. also developed a set of chiral phosphine–phosphoramidite ligands based on indole backbone [157]. However, the enantioselectivity (up to 72% ee) of their rhodium complexes **54** was a shade lower compared to the catalysts reported by Zhang. Complex **55** could also catalyze asymmetric hydroformylation of heterocyclic olefins with high enantioselectivity (~91%) and excellent region-selectivities [161].



Scheme 22. Asymmetric hydroformylation of styrene catalysed by **53** (Ref. [160]).

5. [C, P] hybrids

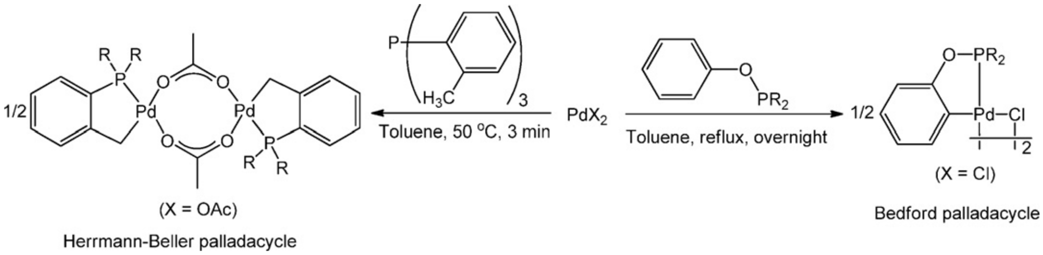
Several types of [C, P] hybrid ligands have been designed and applied in transition metal-based catalysis such as the phosphine–olefin hybrids, Herrmann–Beller type palladacycle [168], Bedford type catalyst [169–173] and various carbene–phosphine hybrids. Some recent representative complexes from [C,P] hybrid ligands are listed in Table 4.

5.1. *Design, synthesis and structures*

The phosphine–olefin couples in **58** and **59** are promising alternatives to the phosphorus- and/or nitrogen-based ligands as dienes are known in some cases to be highly effective and superior to some conventional diphosphine ligands [174]. The presence of a strong M–P bond, unlike dienes, could also improve the catalyst stability. For example, Lei et al. have successfully used a phosphine hybridised with electron deficient ethylene to accomplish Negishi coupling in good yields under facile conditions [175]. Other types of [C, P] hybrid ligands include the Herrmann–Beller palladacycle **61** and **62** [168,176,177] and Bedford palladacycle **63–65** [169–171,173] which are widely used because of their facile preparation. Both systems can be accessed in one step under relatively mild conditions using simple metal sources $Pd(OAc)_2$ or $PdCl_2$ (Scheme 23). The [C, P] hybrid ligands in Herrmann–Beller palladacycle shows a *syn-anti* arrangement [168], while in the Bedford palladacycle the two [C, P] ligands across the coordination plane are *anti* to each other [173] (Fig. 2).

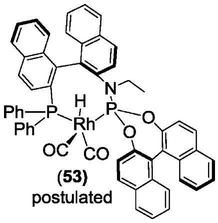
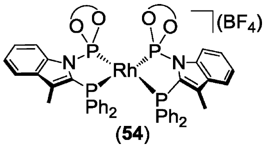
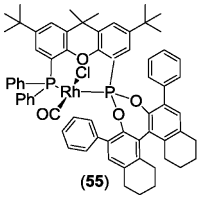
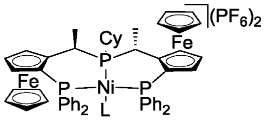
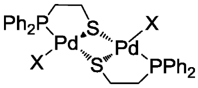
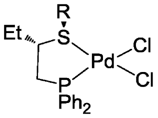
5.2. *Catalysis*

Phosphapalladacycles are powerful catalysts, promoting reactions under low catalyst loading with high turnover numbers (TON). Recent examples include ring-opening reaction of oxabicyclic alkenes with arylboronic acids [176], addition of alkynes to norbornadienes [177], allylation of aldehydes [169,170], Suzuki coupling [177,183] and 1,4-conjugate additions [169]. Complex **61** shows high catalytic activity and asymmetric induction ability in ring-opening reaction of oxabicyclic alkenes with arylboronic acids (Scheme 24) [176], providing corresponding products in high yields (70–99%) and high ee (69–83%). Complex **62** selectively catalyzes the addition of terminal alkynes across one double bond of norbornadiene to afford *exo*-5-alkynyl-bicyclo[2.2.1]hept-2-enes

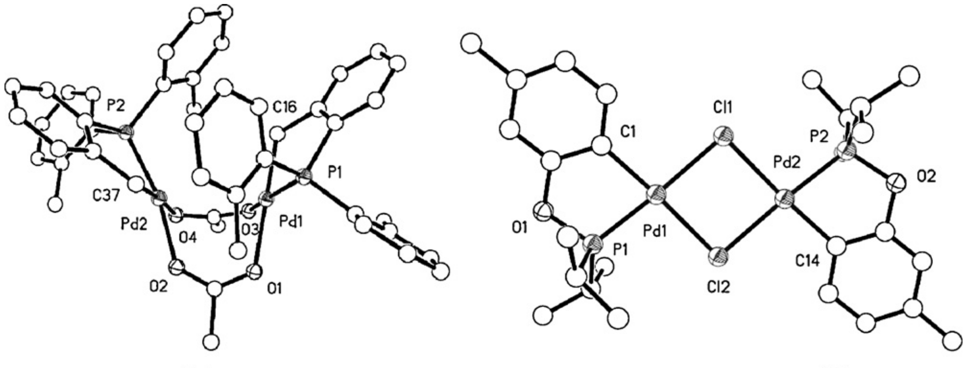


Scheme 23. Preparative routes to Herrmann–Beller palladacycle and Bedford palladacycle (Refs. [168] and [173] respectively).

Table 3
A selected list of metal complexes from [P, S] hybrid ligands, their preparation and catalytic reactions.

M	Compound	Preparation	Catalytic reactions	Authors	Reference
Rh	 (53) postulated	$[Rh(\mu\text{-}Cl)(CO)_2]_2$ with L in CH_2Cl_2	Hydroformylation	Zhang	[160]
	 (54)	$[Rh(nbd)_2]BF_4$ (nbd = 2,5-norbornadiene) with L in $CHCl_3$ at r.t.	Hydrogenation and hydroformylation	Reek	[157]
	 (55)	$[Rh(\mu\text{-}Cl)(CO)_2]_2$ with L in CH_2Cl_2 at r.t.	Hydroformylation	Reek	[161]
Ni	 (56)	NiX_2 (X = Cl, ClO_4) with L in EtOH/toluene (X = Cl), THF or MeCN/Et_2O. $TlPF_6$ is used together with $NiCl_2$	Hydroamination	Fadini	[166]
Pd	 X = Cl (57a), I (57b)  (57c)	$PdCl_2(PhCN)_2$ with L in CH_2Cl_2 at r.t.	Suzuki coupling	Dervisi	[167]

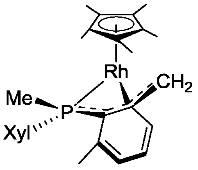
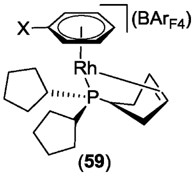
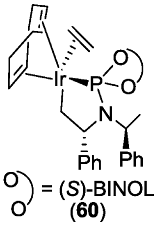
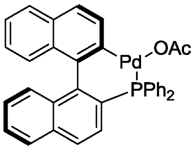
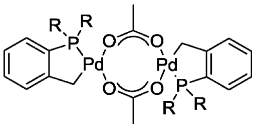
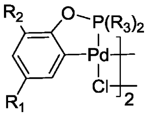
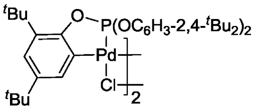
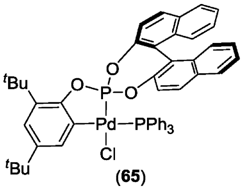
(Scheme 25) [177]. The reaction exhibits extraordinary generality with respect to the alkyne. This constitutes the first addition of a C(sp)-H bond to an unactivated isolated double bond under neutral conditions. Complex **65** exhibits good activity in 1,4-conjugate additions using boronic acid and aldehyde allylations with allylstannanes (Scheme 26) but the stereoselectivity is poor [169]. This is probably due to ineffective projection of BINOLate chirality over the active site.



(a) (b)

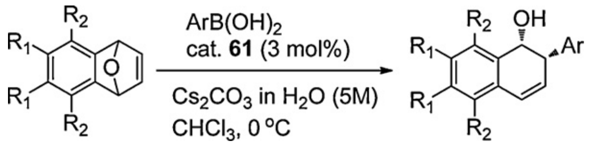
Fig. 2. Structure of: a) Herrmann–Beller palladacycle, and b) bedfordpalladacycle. All hydrogen atoms were omitted for clarity. (Structures reproduced from Ref. [168] and [173] respectively).

Table 4
A selected list of metal complexes from [C, P] hybrid ligands, their preparation and catalytic reactions.

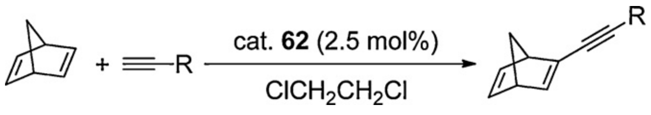
M	Compound	Preparation	Catalytic reactions	Authors	Reference
Rh	 (**58**)	$[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ with $PMeXyl_2$ at −40 °C and then $ZnCp^*_2$ at −20 °C, followed by treatment with CH_2Cl_2 and anion change with NaBArF	Hydrogen isotope exchange in hydrosilanes	Carmona	[178]
	 (**59**)	Intramolecular dehydrogenation of RhCl(nbd)(PCy_3) in the presence of NaBArF in PhF	1,4-additions	Frost	[179]
Ir	 (**60**)	$[IrCl(cod)]_2$ andL in THF. Then Cl was extracted using pyrrolidine for substitution reactions	Allylic substitution	Hartwig	[180–182]
Pd	 (**61**)	$Pd(OAc)_2$ with L in toluene at 50 °C	Ring-opening reaction of oxabicyclic alkenes with arylboronic acids	Hou	[176]
	 R = *o*-Tol (**62**)	$Pd(OAc)_2$ with L in toluene at 50 °C	Addition of alkynes to norbornadienes	Tenaglia	[177]
	 $R_1 = R_2 = {}^tBu$, R_3 = Ph (**63a**) $R_1 = R_2 = {}^tBu$, $R_3 = {}^iPr$ (**63b**) R_1 = H, $R_2 = R_3$ = Ph (**63c**) R_1 = H, R_2 = Ph, $R_3 = {}^iPr$ (**63d**)	$PdCl_2$ and L in refluxing toluene	Suzuki coupling	Eppinger	[183]
	 (**64**)	$PdCl_2$ and L in refluxing toluene	Allylation of aldehydes	Bedford	[170]
	 (**65**)	$PdCl_2(MeCN)_2$ and L in refluxing toluene	1,4-conjugate additions	Bedford	[169]

6. [N, P] hybrids

[N, P] hybrids are by far the most abundant types of hybrid ligands. Their complexes are highly effective catalytic precursors towards a variety of reactions such as hydrogenation [184,185], allylic alkylation [186], and many others [9,13,187–189]. Armed with mixed donor characteristics, they can stabilize intermediate oxidation states or geometries in a catalytic cycle. For example, metal in a low oxidation state can be stabilized by the π-acceptor character of a phosphorus donor while maintaining its amenity



Scheme 24. Ring-opening reaction of oxabicyclic alkenes with arylboronic acids catalysed by **61** (Ref. [176]).



Scheme 25. Addition of alkynes to norbornadienes catalysed by **62** (Ref. [177]).

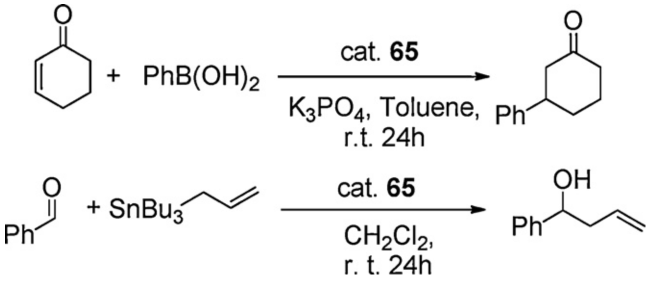
towards oxidative addition supported by the nitrogen σ-ability [1,3,190,191]. The most successful ligands contain a phosphine, phosphinite or phosphite as P-donor and an oxazoline, oxazole, thiazole or pyridine as N-donor group. Numerous reviews have been dedicated in recent years on this topic [9,10,12,13,187–190]. Some recent representative complexes from [N, P] hybrid ligands are listed in Table 5.

6.1. *Design, synthesis and structures*

Many designs of [N, P] donors, including polydentate ligands, are based on modification or optimization of the earlier successful catalysts. A good example is the [Ru^{II}(η^6-arene)] containing diamines or aminoalcohols, discovered by Noyori et al. [192,193] for transfer hydrogenation. The planar ligands in **68–69** and **75–80** coordinated with octahedral Fe^{II} or Ru^{II} centre create a more open coordination environment for nucleophilic attack at an antiperiplanar fashion, which may facilitate ionization and nucleophilic attack [186].

Iridium complexes **85–94** containing chiral phosphine–oxazoline ligands have been intensively studied by Andersson et al. (**85–88**) [194–199], Pfaltz et al. (**89**, **90**) [200–203], Li et al. (**91**) [204], Zhou et al. (**92**) [205,206], Hou (**93**) [207], and Mazet et al. (**94**) [208] following the successful application of Ir^{I} complexes for achiral catalysis by Crabtree et al. [209,210] and for chiral catalysis using [N, P] ligand by Pfaltz et al. [211,212]. The [N, P] hybrid ligands are used to mimic the coordination environments of Crabtree's catalyst intermediates which bear one N (pyridine) and one P (P(^{i}Pr)$_3$ or PCy$_3$) in *cis* configuration [209,210]. The lower cost of Ir compared to Rh is also a factor that favors its use.

Ni complexes **95–101** have been used by Jones et al. [213], Braunstein et al. [214,215], Hor et al. [216–219] and others for alkene (co-)polymerization or oligomerizations. Ferrocenediyliminophosphine derivatives serve as highly flexible ligands in **98–101**. The ferrocenyl core plays the important role of a spectator in giving the difunctional donors the desirable coordinative mobility and serving as an electronic reservoir needed for pendant/donating switches. The redox-active Fe^{II} provides an additional electronic buffer that allows the catalytic metal to remain active in different redox stages. The hemilability of the donors allows the metal to "pick and choose" its donors [5,216]. The reactions of the ferrocenediyliminophosphine ligands give a dynamic library of Ni complexes with different oxidation states from Ni^0 to Ni^{III}, and structural types depending on the reaction conditions (Scheme 27). An additional advantage on Ni are its diverse geometries thus helping to cope with different ligand demands e.g. tetrahedral Ni^0_P and Ni$^0_{N,P}$, sq. planar Ni$^{II}_{N,P}$ and trigonal planar Ni$^{I}_{N,P}$ and Ni$^{I}_{C,N,P}$ etc.



Scheme 26. 1,4-conjugate additions catalysed by **65** (Ref. [169]).

6.2. *Catalysis*

6.2.1. *Hydrogenation*

Asymmetric hydrogenation of ketones has been recognised as a valuable way to obtain chiral secondary alcohols as ketones are one of the most common families of unsaturated substrates [242–246]. Enantioselective reduction of prochiral ketones leading to optically pure secondary alcohols is accordingly a subject of considerable interest [185,246–248]. The asymmetric hydrogenation pioneered by Noyori uses ruthenium complexes of the highly effective BINAP ligands [249,250]. Hydrogenation reactions using Ru^{II} complexes with hybrid ligands continue to advance in a blistering pace [229,245,251–254]. Ir^{I} complexes **85–93** are featured heavily. A broad scope of substrates beyond conventional ketones has also been examined, such as N-acylcarbamates and amides [227,235], imides [228], aldehydes, esters, imines [197,203,207,230], carboxylic esters [234], enolphosphinates [194,196], olefins [195,204], diphenylvinylphosphine oxides and vinylphosphonate [199], unfunctionalized enamines and 4H-chromenes [200–202] as well as α,β-unsaturated carboxylic acids [205,206]. There are also recent reviews on Ir catalysed asymmetric hydrosilylation, transfer hydrogenation and hydrogenation of ketones [184,185]. Complexes **68–70**, **73**, **76**, **80**, **84–93** are also active towards asymmetric hydrogenation while **72** and **76** have been applied for asymmetric transfer hydrogenation reactions.

Recently, Morris et al. have synthesized Fe^{II} complexes **68** and **69** as cheap and environmentally friendly catalytic compounds [222,223]. They are suitable precatalysts for the transfer hydrogenation of ketones at r.t. (Scheme 28), giving turnover frequencies of up to 2600 h^{-1} with very low catalyst loadings (0.025–0.17%). For sterically demanding prochiral ketones, excellent enantioselectivities can be obtained (up to 96% ee).

6.2.2. *Olefin oligomerization and polymerization*

Hou et al. have demonstrated that a cationic rare earth metal alkyl species **66** can serve as an excellent catalyst for the living *cis*-1,4 polymerization of both isoprene and butadiene as well as for the living *cis*-1,4 copolymerization of isoprene and butadiene (Scheme 29) [220]. This system affords, for the first time, polyisoprene, polybutadiene, and poly(isoprene-butadiene) with both extremely high *cis*-1,4 content (ca. 99%) and narrow molecular-weight distribution (M_w/M_n = 1.13). Such excellent selectivity and activity can be maintained even at elevated temperatures (up to 80 °C). The catalyst system is one of the best systems for the exclusive *cis*-1,4 polymerization and copolymerization of isoprene and butadiene.

Nickel complexes **96–101** are catalytically active towards olefin oligomerization or polymerization. Complex **96** and **97** return with high activities in oligomerization of ethylene with AlEtCl$_2$ or MAO as cocatalyst [214,215]. Hor et al. demonstrated that the hemilabile iminophosphanyl ferrocene ligand can stabilize catalytically active low-valent nickel [216] and the resulting complexes **98–101** can be directly used to catalyze ethylene oligomerization [216–219]. In some cases the use of an alkyne stabilized catalyst can be viewed

Table 5
A selected list of metal complexes from [N, P] hybrid ligands, their preparation and catalytic reactions.

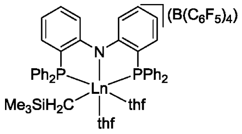
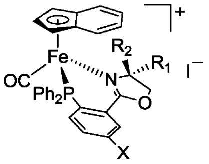
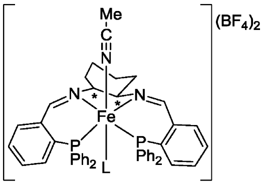
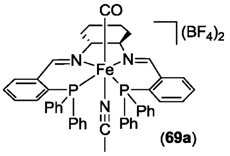
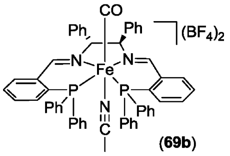
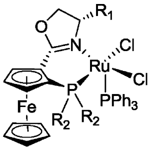
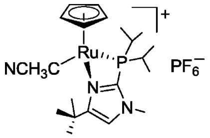
M	Compound	Preparation	Catalytic reactions	Authors	Reference
Sc, Y, Lu	 Ln = Sc (**66a**), Y (**66b**), Lu (**66c**)	$[Ln(CH_2SiMe_3)_3(THF)_2]$ with L in THF at r.t.	*cis*-1,4-polymerization and copolymerization of isoprene and butadiene	Hou	[220]
Fe	 X = H, R_1 = R_2 = CH_3 (**67a**) X = H, R_1 = H, R_2 = Ph (**67b**) X = CF_3, R_1 = R_2 = CH_3 (**67c**)	$FeI(Indenyl)(CO)_2$ with L in refluxing pentane	Mukaiyama aldol reaction	Bauer	[221]
	 L = CO (**68a**) L = ^{t}BuNC (**68b**)	$[Fe(H_2O)_6](BF_4)_2$ with L in CH_3CN followed by reaction with ^{t}BuCN or CO in acetone or refluxing $CHCl_3$	Asymmetric transfer hydrogenation	Morris	[222]
	 (**69a**)  (**69b**)	$[Fe(H_2O)_6](BF_4)_2$ with L in CH_3CN, then react with CO in acetone	Asymmetric transfer hydrogenation of ketones	Morris	[223]
Ru	 R_1 = ^{i}Pr, R_2 = Ph (**70a**) R_1 = ^{t}Bu, R_2 = Ph (**70b**) R_1 = Ph, R_2 = Ph (**70c**) R_1 = ^{i}Pr, R_2 = 3,5-Me_2Ph (**70d**) R_1 = Ph, R_2 = 4-CF_3Ph (**70e**) R_1 = ^{i}Pr, R_2 = 3,5-Me_2-4-MeOPh (**70f**)	$RuCl_2(PPh_3)_3$ with L in toluene at r.t.	Hydrogenation of α-alkoxy substituted ketone	Tellers	[224]
	 (**71**)	$[RuCp(CH_3CN)_3]^+[PF_6]^-$ and L in degassed acetone overnight	Isomerization of alkenes	Grotjahn	[225]

Table 5 (*Continued*)

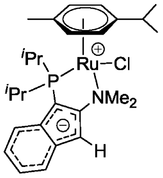
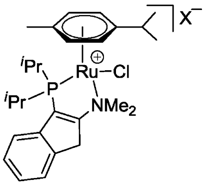
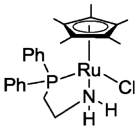
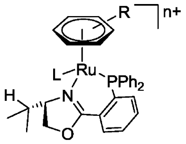
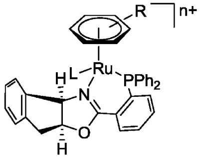
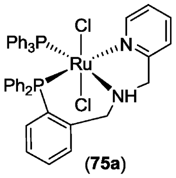
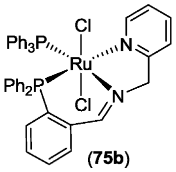
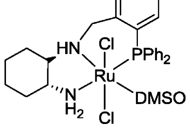
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 **(72a)**  **(72b)**	Cationic: $[Ru(p\text{-}cymene)Cl_2]_2$ with L, $AgBF_4$, $AgSO_3CF_3$, $Li(Et_2O)_{2.5}B(C_6F_5)_4$ in CH_3CN; Zwitterionic: $[RuCl_2(p\text{-}cymene)]_2$ with L in CH_2Cl_2 then with K_2CO_3 in THF	Transfer hydrogenation of ketones	Stradiotto	[226]
	 **(73)**	$RuClCp^*$ (isopropene) with L in CH_2Cl_2	Hydrogenation of N-acylcarbamates and N-acylsulfonamides.Hydrogenation of imides	Ikariya	[227,228]
	 L = Cl, n = 1 R = H_6 **(74b)**, Me_6 **(74b)** L = H_2O, n = 2 R = H_6, Me_6, *p*-Me^{i}Pr **(74c-e)**  L = Cl, n =1 R = H_6 **(74f)**, Me_6 **(74g)** L = H_2O, n = 2 R = H_6, Me_6, *p*-Me^{i}Pr **(74h-j)**	$[RuCl(\eta^6\text{-}arene)]_2(\mu\text{-}Cl)_2$ with L and $NaPF_6$ in MeOH	1,3-dipolar cycloaddition of nitrones with methacrolein	Carmona	[59]
	 **(75a)**  **(75b)**	$RuCl_2(PPh_3)_3$ with L in CH_2Cl_2 at r.t. for 1 h or in toluene at 90 °C for 20 min	Transfer hydrogenation	Zotto and Baratta	[229]
	 **(76)**	$RuCl_2(DMSO)_4$ with L in THF at 120 °C	Hydrogenation of aldehydes, esters, imines and ketones. Transfer hydrogenation	Clarke	[230,231]

Table 5 (*Continued*)

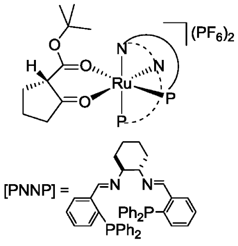
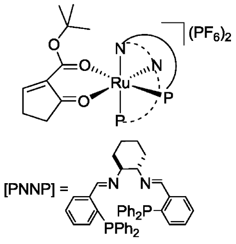
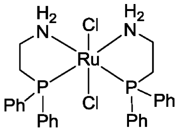
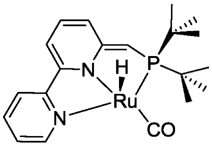
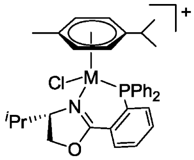
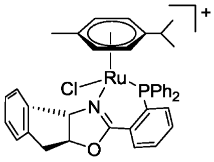
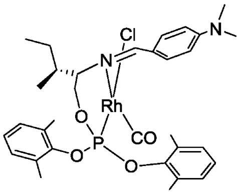
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 (**77**)	$RuCl_2(L)$ with $(Et_3O)PF_6$ in CH_2Cl_2 at r.t. then with 2-tertbutoxycarbonylcyclopentanone in CH_2Cl_2 at r.t.	Asymmetric electrophilic fluorination of 1,3-dicarbonyl compounds	Togni and Mezzetti	[232]
	 (**78**)	$RuCl_2(L)$ with $(Et_3O)PF_6$ in CH_2Cl_2 at r.t. then with 2-tertbutoxycarbonylcyclopentanone in CH_2Cl_2 at r.t.	Asymmetric Diels–Alder reactions of unsaturated β-ketoesters	Mezzetti	[233]
	 (**79**)	$RuCl_2(DMSO)_4$ with L in toluene	Reduction of carboxylic esters to alcohols	Saudan	[234]
	 (**80**)	$RuHCl(PPh_3)_3(CO)$ with L in THF at 65 °C	Hydrogenation of amides to alcohols and amines	Milstein	[235]
Ru, Os	 M = Ru (**81a**), Os (**81b**)  M = Ru (**81c**), Os (**81d**)	$[MCl_2(\eta^6\text{-cymene})]_2$, L and NaX in MeOH at r.t. (M = Ru, Os; X = SbF_6, BF_4, CF_3SO_3, PF_6)	Diels–Alder reaction.	Carmona	[236]
Rh	 (**82**)	$[RhCl(CO)]_2$ and L in $CHCl_3$ or CH_2Cl_2 at 20 °C	Enantioselective hydrosilylation	Korostylev	[237]

Table 5 (*Continued*)

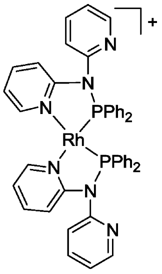
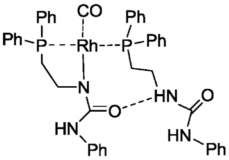
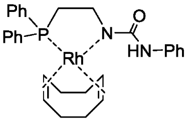
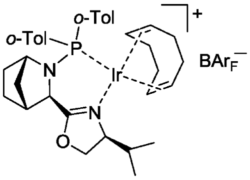
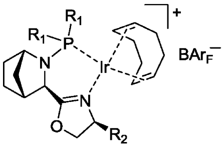
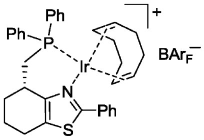
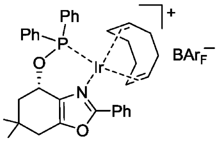
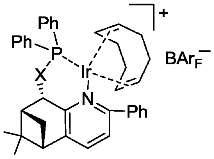
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 (**83**)	$[RhCl(cod)]_2$ and L in THF at r.t.	Arylation of arenes	Kempe	[238]
	 (**84a**)  (**84b**)	$[RhCl(cod)]_2$ and L in CH_2Cl_2 at r.t.	Asymmetric hydrogenation	Reek	[239]
Ir	 (**85**)	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment with NaBArF and H_2O	Asymmetric hydrogenation of enolphosphinates	Andersson	[194]
	 R_1 = *o*-Tol, R_2 = ^{i}Pr (**86a**) R_1 = Ph, R_2 = ^{i}Pr (**86b**) R_1 = Ph, R_2 = Ph (**86c**)  (**86d**)  (**86e**) (**85d,e**)	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment with NaBArF and H_2O	Asymmetric hydrogenation of fluorinated olefins;asymmetric hydrogenation of di and trisubstitutedenolphosphinates; asymmetric hydrogenation of imines	Andersson	[195–197]
	 X = CH_2 (**87a**) X = O (**87b**)	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment with NaBArF and H_2O	Asymmetric hydrogenation	Andersson	[198]

Table 5 (*Continued*)

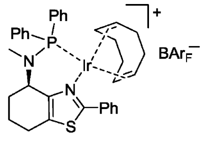
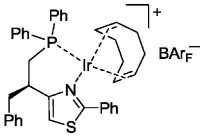
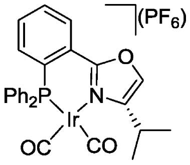
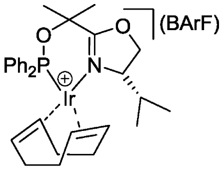
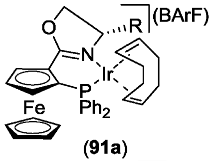
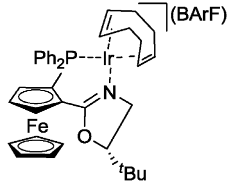
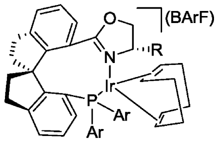
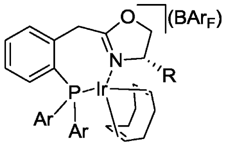
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 **(88a)**  **(88b)**	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment with NaBArF and H_2O	Hydrogenation of diphenylvinylphosphine oxides and vinylphosphonates	Andersson	[199]
	 **(89)**	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment of $NaPF_6$ at r.t. then with CO in THF	Pauson–Khand reactions; hydrogenation of unfunctionalized enamines and 4H-chromenes	Pfaltz	[200–202]
	 **(90)**	$[IrCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment of NaBArF and then with CO in THF at r.t.	Asymmetric hydrogenation of imines	Pfaltz	[203]
	 **(91a)**  **(91b)**	$[IrCl(cod)]_2$ and L in CH_2Cl_2 at r.t. followed by treatment with NaBArF or $NaPF_6$	Hydrogenation of olefins	Li	[204]
	 **(92)**	$[IrCl(cod)]_2$, L, NaBArF in refluxing CH_2Cl_2	Hydrogenation of α,β-unsaturated carboxylic acids	Zhou	[205,206]
	 Ar = Ph, R = ^{i}Pr **(93a)** Ar = Ph, R = ^{t}Bu **(93b)**	$[IrCl(cod)]_2$, L and NaBArF in CH_2Cl_2 at r.t.	Asymmetric hydrogenation of imines	Hou	[207]

Table 5 (*Continued*)

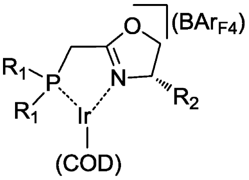
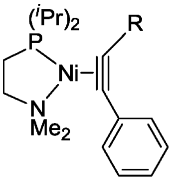
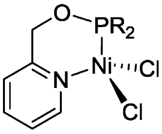
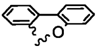
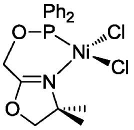
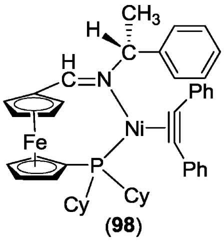
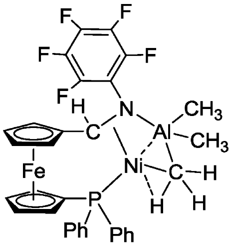
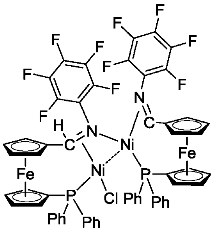
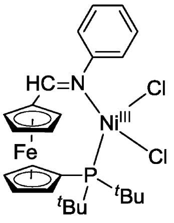
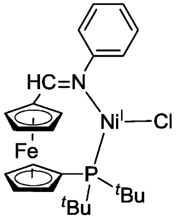
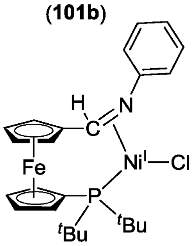
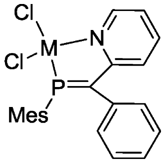
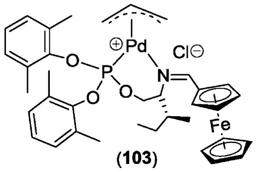
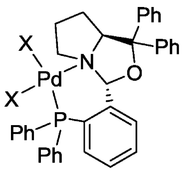
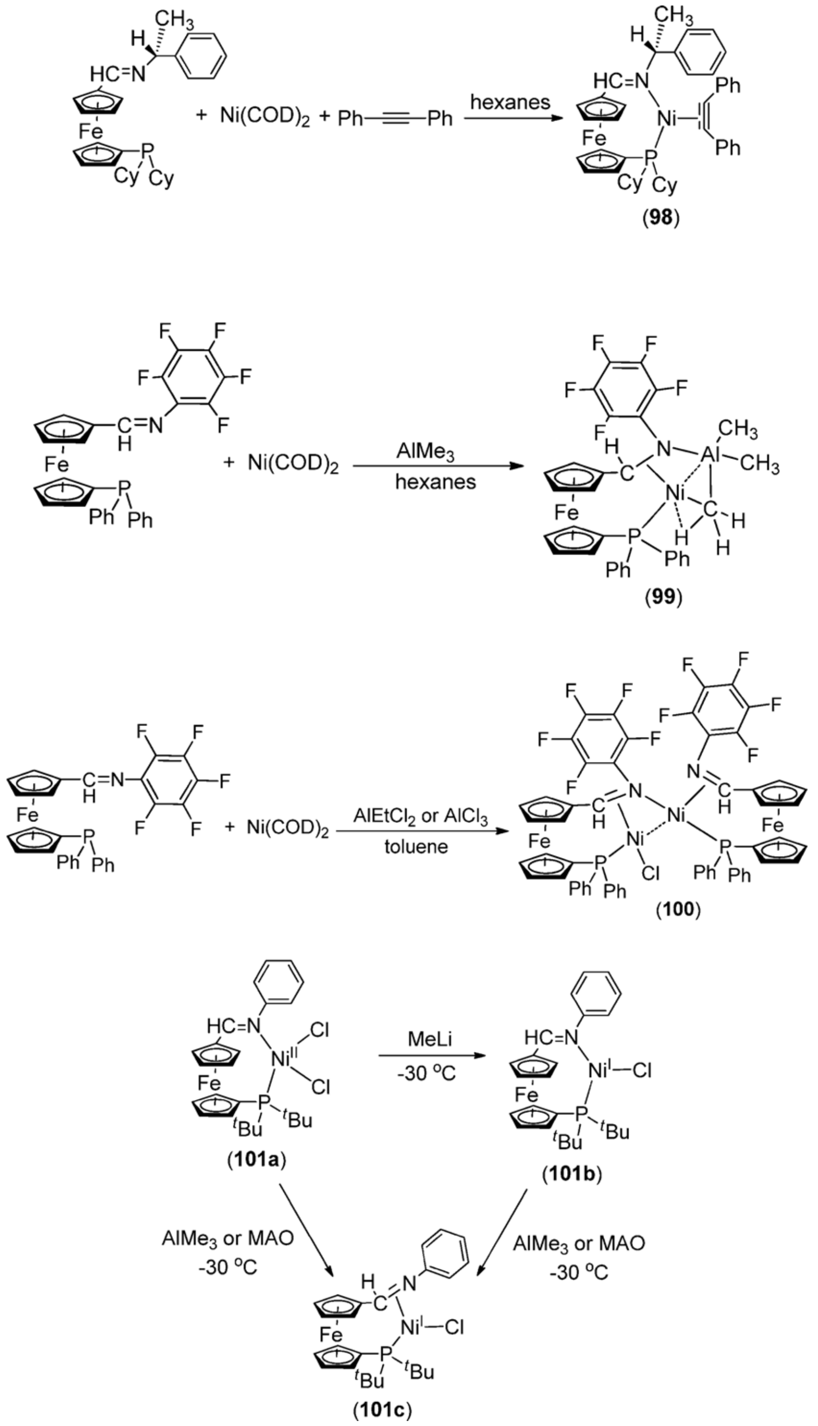
M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 R_1, R_2 = alkyl, aryl (**94**)	$[IrCl(cod)]_2$ and L in CH_2Cl_2 at 48 °C, followed by treatment with NaBArF at r.t.	Isomerization of primary allylic alcohols	Mazet	[208]
Ni	 R = ^{t}Bu (**95a**) R = CF_3 (**95b**)	$Ni(cod)_2$ and L in pentane followed by treatment PhCCR (R = Ph, ^{t}Bu, CF_3, CtCPh) at r.t.	C–C bond activation in biphenylene and cyclotrimerization of alkynes	Jones	[213]
	 R = Ph (**96a**) R = ^{t}Bu (**96b**) R =  (**96c**)	$NiCl_2(dme)$ and L in CH_2Cl_2	Oligomerization of ethylene	Braunstein	[214]
	 (**97**)	$Ni(cod)_2$ and L in toluene at r.t. followed by treatment with $AlEtCl_2$ in toluene at r.t.	Ethylene and propylene oligomerization	Giambastiani and Braunstein	[215]
	 (**98**)	$NiCl_2(dme)$ and L in THF followed by treatment with MeLi in THF at −30 °C and then $AlMe_3$ or MAO at r.t.	Ethylene oligomerization	Hor	[216]
	 (**99**)	$Ni(cod)_2$ and L in hexane at r.t and then with CO or diphenylacetylene at r.t.	Ethylene oligomerization	Hor	[217]

Table 5 (*Continued*)

M	Compound	Preparation	Catalytic reactions	Authors	Reference
	 (**100**)	Ni(cod)$_2$ with L in hexane at r.t. followed by treatment with AlMe$_3$ in toluene at r.t.	Ethylene oligomerization	Hor	[218]
	 (**101a**)  (**101b**)  (**101c**)	NiCl$_2$(dme) and L in CH$_2$Cl$_2$ at r.t.	Ethylene oligomerization	Hor	[219]
Pd,Pt	 M = Pd (**102a**) M = Pt (**102b**)	[MCl$_2$(cod)] and L in CH$_2$Cl$_2$ at r.t.	Overman–Claisen rearrangement	Dake and Gates	[240]
	 (**103**)	PdCl$_2$(cod)/[Pd(allyl)Cl]$_2$ and L in CH$_2$Cl$_2$ at r.t.	Allylic alkylation and sulfonylation	Korostylev	[237]
	 X = BF$_4$ (**104a**) X = PF$_6$ (**104b**) X = SbF$_6$ (**104c**) X = ClO$_4$ (**104d**)	PdCl$_2$ and L in CH$_2$Cl$_2$ at r.t. followed by treatment with AgOTf/AgSbF$_6$/AgClO$_4$ at r.t.	Diels–Alder reactions	Nakano	[241]

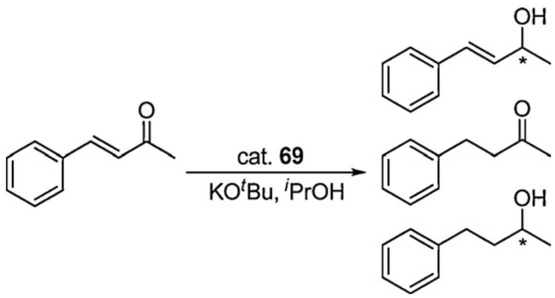


Scheme 27. Reactions of ferrocenediyliminophosphine derivatives with Ni substrates (Ref. [216–219]).

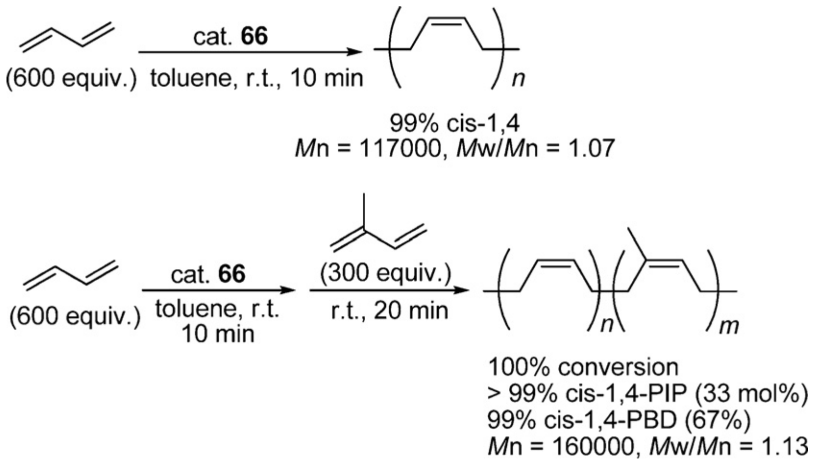
as a mimic for olefin entry to Ni-promoted olefin oligomerization. They provide new insight in catalyst design for polymerization [217].

6.2.3. Other reactions

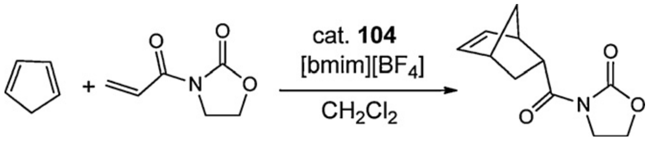
Palladium complexes **102a**, **103** and **104** are also active in promoting other types of reactions, such as Overman–Claisen rearrangement [240], allylic alkylation and sulfonylation [237] and Diels–Alder reactions [241]. Chiral cationic palladium–phosphinooxazolidine catalysts **104** in ionic liquid [bmim][BF$_4$] afforded excellent enantioselectivity in Diels–Alder reactions and the catalyst is easily recycled eight times without any significant decrease in chemical yields or enantioselectiv-



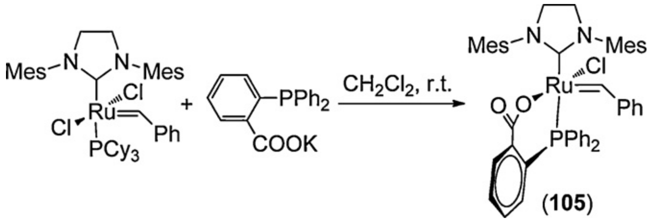
Scheme 28. Transfer hydrogenation of the α,β-unsaturated ketone catalysed by **69** (Ref. [223]).



Scheme 29. Living *cis*-1,4-polymerization of butadiene and its block copolymerization with isoprene catalysed by **66** (Ref. [220]).



Scheme 30. Diels–Alder reactions in ionic liquid catalysed by **104** (Ref. [241]).



Scheme 32. Synthesis of **105** (Ref. [257]).

ity (89–99%, 88–99% ee) [241] (Scheme 30). The asymmetric Diels–Alder reactions catalysed by **104** in ionic liquid are economically and environmentally practical processes.

7. [O, P] hybrids

[O, P]-type hybrid ligands are typical representations of soft-hard couples for hemilabile applications [190,255]. The P donor site usually provides a firm anchor whereas the M–O bond can cleave reversibly. This dynamic behaviour helps the catalyst switch between different states during the catalytic cycles and thus improving the turnovers, at least in principle. Some recent representative complexes from [O, P] hybrid ligands are listed in Table 6.

7.1. Design, synthesis and structures

Decomposition products of olefin-metathesis catalysts have been shown to be responsible for unwanted side reactions such as olefin isomerization in addition to loss of activity [256] (Scheme 31). The chelating [O, P] ligand in **105** is designed to protect the 14-electron methylidene species $(H_2IMes)Cl_2Ru^{II}{=}CH_2$ from decomposition during the catalytic process involving terminal olefins [44], as the chosen [O, P] hybrid is structurally and electronically closely related to PPh_3, which is known to readily dissociate in $[(H_2IMes)(PPh_3)Cl_2Ru^{II}{=}CHPh]$ [257]. Complex **105** can be easily synthesized in 75% yield from the potassium salt of the ligand with the Ru precursor in CH_2Cl_2 (Scheme 32).

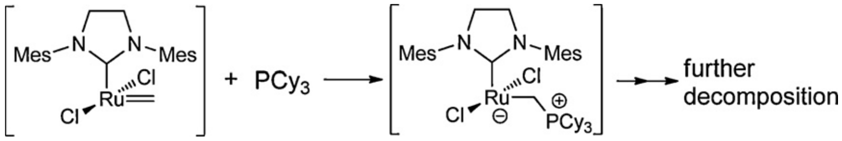
In **106** and **108**, the [O, P] ligands are expected to show different coordination modes such as κ^1-*P*, κ^2-*P,N*, κ^2-*P,O*, and κ^3-*P,N,O* [258]. The hemilabile behaviour of these ligands have been catalytically harnessed in e.g. hydrogenation of olefins [259], olefin oligomerization [260], transfer hydrogenation of ketones [261], and cross-coupling of secondary amines with aryl halides [262].

7.2. Catalysis

Complex **105** is poorly active towards ring-closing metathesis (RCM) at 30 °C, perhaps because of the stable chelate. It can be initiated by addition of CuCl with initial rates comparable to their non-chelating analogues. However, the introduction of CuCl does not lead to a more stable catalytic system, but rather a deviation from first-order kinetics for more challenging substrates [44]. Catalysts **109** are efficient towards C–Cl activation in Suzuki–Miyaura couplings. The flexible coordination behaviour inherent in a hybrid ligand system thus offers the metal several options to gain stability without compromising on its vital reactivity [264].

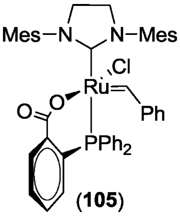
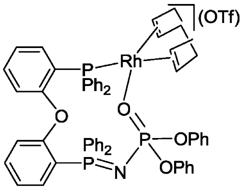
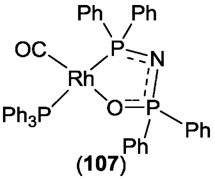
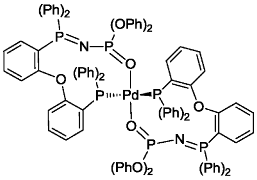
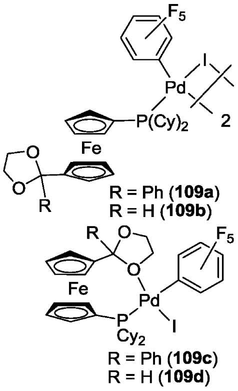
8. [C, S], [N, S] and [O, S] hybrids

The soft sulfur donor, like phosphorus, should show higher affinity to soft metals. Accordingly, the [X, S] (X = C, N, O) hybrids may mirror the functions of their [X, P] counterparts. Sulfur ligands are generally poorer σ-donor and π-acceptor ligands compared with phosphines and hence they are less used. However, organosulfur



Scheme 31. Decomposition pathway for $(H_2IMes)Cl_2Ru{=}CH_2$ (Ref. [256]).

Table 6
A selected list of metal complexes from [O, P] hybrid ligands, their preparation and catalytic reactions.

M	Compound	Preparation	Catalytic reactions	Authors	Reference
Ru	 **(105)**	2-(diphenylphosphino)benzoic acid and KH in THF at 50 °C followed by treatment with $RuCl_2(PCy_3)(NHC)(CHPh)$ in CH_2Cl_2 at r.t.	Metathesis reaction	Grubbs	[44]
Rh	 **(106)**	$[RhCl(cod)]_2$, L and AgOTf in CH_2Cl_2 at r.t.	Hydrogenation of olefins	Balakrishna	[258]
	 **(107)**	$[RhCl(cod)]_2$ and L in CH_2Cl_2 followed by treatment with ${}^tBuOK$ in CH_3OH and then with CO in CH_2Cl_2 and finally with PPh_3 at r.t.	Hydroformylation of styrene	Kostas and Kyritsis	[263]
Pd	 **(108)**	$Pd_2(dba)_3$ (dba = dibenzylideneacetone) and L in toluene at r.t.	Suzuki coupling	Balakrishna	[258]
	 R = Ph **(109a)** R = H **(109b)** R = Ph **(109c)** R = H **(109d)**	$Pd_2(dba)_3$, L and C_6F_5I in THF at r.t.	Suzuki coupling	Hor	[264]

compounds are readily available and stable, allowing easy storage and handling with aliphatic thiols being an exception. Moreover, sulfide is an exceptionally stable bridging atom, as demonstratedin many giant sulfide clusters [265–267]. The design, synthesis and catalytic reactions of sulfur based hybrids have been reviewed recently [268–271]. Some recent representative complexes from [C, S], [N, S] and [O, S] hybrid ligands are compiled in Table 7.

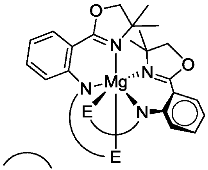
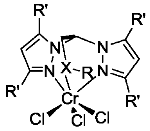
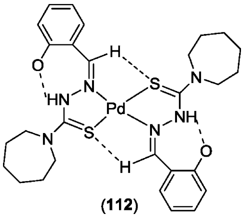
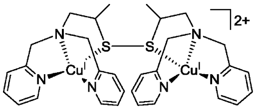
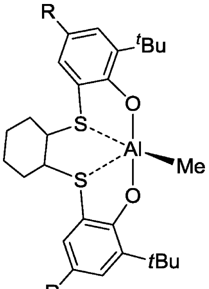
8.1. Design, synthesis and structures

Metal selectivity and hemilability of [N, S] hybrid ligand are among the key motives behind the synthesis of **110–112** and **114**. In **113**, the ligand [N-(2-mercaptopropyl)-N,N-bis(2-pyridylmethyl)amine] and its complexation is designed to mimic the behaviour of an enzyme superoxide dismutase which neutralizes superoxide in living cells [272]. Complex **113** is synthesized from $Cu^{II}(acac)_2$, the [N, S] hybrid ligand, and HBF_4 in CH_3CN at r.t. In this process, the ligand is oxidized by Cu^{II} (which reduces to Cu^{I}) to form a S–S bond.

8.2. Catalysis

Metal complexes based on [X, S] (X = C, O, N) ligands exhibit diverse applications in organic reactions [17,163,271]. One of the most promising examples is the dinuclear Cu^{I} complex **113** reported by Bouwman et al. An electrocatalytic system is

Table 7
A selected list of metal complexes from [C, S], [N, S] and [O, S] hybrid ligands, their preparation and catalytic reactions.

M	Compound	Preparation	Catalytic reactions	Authors	Reference
Mg	 E = $(CH_2)_2OMe$ (**110a**) $(CH_2)_2StBu$ (**110b**) 2-methoxy-Ph (**110c**) 2-methylthio-Ph (**110d**)	Mg^nBu_2 and L in hexane at 0 °C and then r.t.	Ring-opening polymerization of L-lactide	Chen	[273]
Cr	 X = S; R' = Me; R = Me (**111a**) X = S; R' = Me; R = CH_2Ph (**111b**) X = S; R' = Me; R = Decyl (**111c**)	$CrCl_3(THF)_3$ and L in THF at r.t.	Ethylene oligomerization	Hor	[139]
Pd	 (**112**)	K_2PdCl_4 and L in H_2O/MeOH at pH 9.0–9.5	Suzuki coupling	Kostas, Heropoulos and Kovala-Demertzi	[274]
Cu	 (**113**)	$Cu(acac)_2$, L and HBF_4 in CH_3CN at r.t.	Electrocatalytic conversion of CO_2 to oxalate	Bouwman	[272]
Al	 (**114**)	$AlMe_3$ and Lin pentane at 0 °C and then r.t.	MMA, isoprene, benzofuran and *rac*-lactide polymerization	Okuda	[275]

devised based on **113** which is able to activate and convert CO_2 selectively into oxalate (Scheme 33) [272]. It has a significant implication in environmental CO_2 remediation. Complexes **111** reported by Hor et al. are active towards ethylene trimerization to 1-hexene with high selectivity [139]. Complex **112** is inactive towards the Suzuki–Miyaura coupling under aerobic condition. However, microwave irradiation promotes the coupling of aryl bromides and chlorides with phenylboronic acid in DMF/H_2O [274].

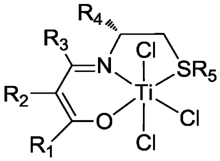
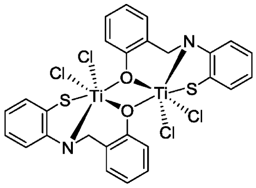
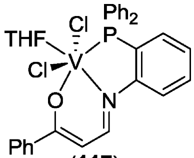
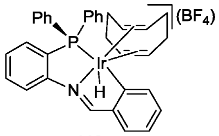
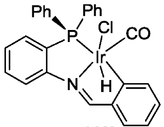
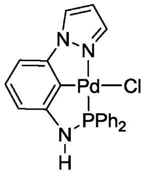
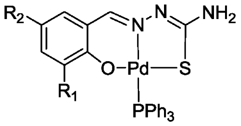
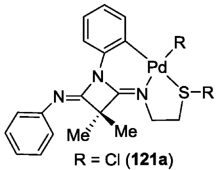
9. Hybrid ligands with mixed donors

Hybrid ligands with mixed donor set (≥3 different donors) inherently give a multitude of permutations and donor flexibility. Apart from the expected gain from multidentate coordination, a range of metal geometries and structures could also be tolerated. The asymmetric trait inherent of a hybrid ligand could also result in higher level of substrate selectivity and chiral differentiation or induction. These ligands however can be synthetically challenging and post-synthetic workups may also be tedious. Imahori and Matano et al. have developed synthetic methods to synthesize phosphole-containing calixphyrins which is [P, N_2, X] (X = N, O, S) hybrid. This ligand can bind to different metals such as Pd [276–279], Rh [277,278], Au [277,279], Pt [279,280] and their catalytic properties have been investigated. The phosphole-containing calixphyrins complexes have been recently reviewed by Imahori and Matano [281] and will not be described in this review. Some recent representative complexes from mixed donor hybrid ligands are listed in Table 8.

9.1. Design, synthesis and structures

The hemilability of the ligand and the catalytic activity of the metal are two major issues in **115–121**. The

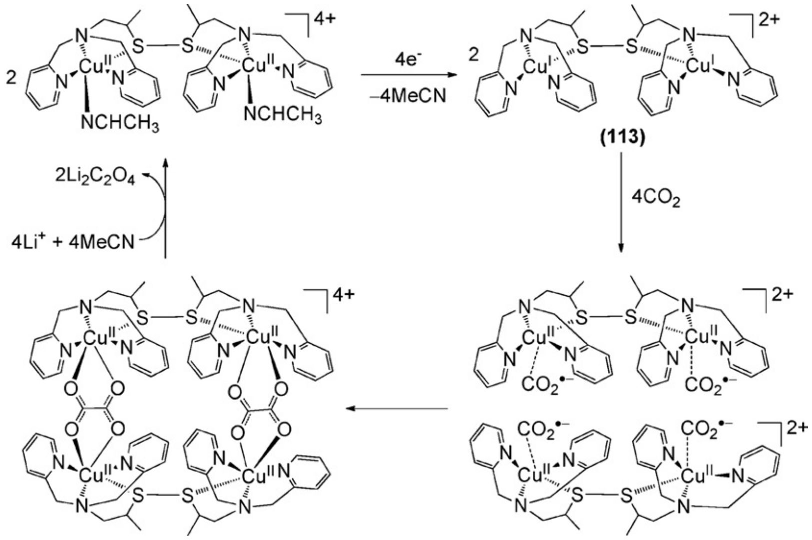
Table 8
A selected list of metal complexes from mixed donor hybrid ligands, their preparation and catalytic reactions.

M	Compound	Preparation	Catalytic reactions	Authors	Reference
Ti	 **(115)**	$TiCl_4$ and L in toluene at −78 °C then r.t.	Ethylene homo- and copolymerization	Sun and Tang	[284]
	 (**116**)	$TiCl_4$ and L in toluene at −78 °C then r.t. followed by treatment with trace H_2O	Ethylene polymerization	Jin	[285]
V	 **(117)**	NaH and L in THF at −78 °C then r.t. followed by treatment with $VCl_3(THF)_3$ at r.t.	Olefin polymerization	Li	[286]
Ir	 **(118a)**  **(118b)**	$IrCl_2$(cod) and L in THF at r.t. followed by treatment with $AgBF_4$ at r.t. or $IrCl_2$(cod) and L in the presence of CO in THF at r.t.	Hydroamination of alkynes, reductive amination of aldehydes	Liu	[287,288]
Pd	 **(119)**	$PdCl_2$(cod) and L in refluxing toluene	Suzuki, Sonogashira and Hiyama couplings	SanMartin and Domínguez	[183,289]
	 R_1 = ^{t}Bu, R_2 = H (**120a**) R_1 = OCH_3, R_2 = H (**120b**) R_1 = H, R_2 = Cl (**120c**)	$PdCl_2(PPh_3)_2$, L and Et_3N in EtOH	Mizoroki–Heck reaction	Mao and Smith	[290]
	 R = Cl (**121a**) R = OAc (**121b**)	$Pd(OAc)_2$, L in THF followed by treatment with LiCl in MeOH	Suzuki and Heck coupling	Chen	[291]

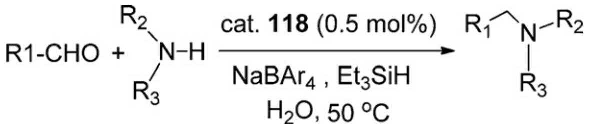
ligand denticity may also play an important role in influencing the stability of these complexes. Tridentate or polydentate ligands generally serve as better shields for catalytically active metal centres [282,283]. The syntheses of **115–121** are facile and straightforward and their structures are as expected.

9.2. Catalysis

Complex **115–117** show high activity towards ethylene polymerizations [284–286]. In addition, α-alkene and cycloalkenes such as cyclopentene and norbornenecan also be efficiently incorporated into polymerization using **115** as catalyst [284]. Ir^{III} complex **118**



Scheme 33. Proposed electrocatalytic cycle that converts CO_2 to oxalate promoted by **113** (Ref. [272]).



Scheme 34. Reductive amination of aldehyde in aqueous media catalysed by **118** (Ref. [288]).

was reported by Liu et al. to be active towards hydroamination of alkynes and reductive amination of aldehydes in aqueous media (Scheme 34) [287,288], while **119–121** were reported to be active towards various coupling reactions which is typical for Pd catalysts [289–291].

10. Summary and outlook

This review only touches the tip of an iceberg of catalytic reactions promoted by complexes using hybrid ligands. Many heterogeneous systems promoted by such ligands have also not been included in this review [37,292–295]. Nevertheless, in the vast majority of documented examples, the role or uniqueness of the hybrid ligand is not clearly defined or experimentally proven. Even the expected hemilability or chiral inductive effects are generally assumed but not specifically demonstrated with concrete data [1,5,8,296,297]. Verifications of such would certainly help to elevate the level of activities in this system. Modification of the hybrid ligands at the synthetic stage would continue to provide the most direct means to tune the electronic, steric, and stereochemical properties of their molecular complexes. However, such modification needs to be more systematic and predictive, and on this front, better integration with computational capability would be needed [298–301]. The precious platinum metals understandably dominate the use of these hybrid ligands but, as we continue to advance on sustainable catalysis, we should expect more innovative research in more abundant and bio-compatible metals such as Mn, Fe, Cu and Zn [55,56,64,65,129,130,272]. Their uses will also require a new breed of hybrid ligands that can offer higher stability and enhancing catalytic prowess to these 3*d* metals. The catalytic activation or initiation should go beyond chemical and thermal means. We need to design and develop hybrids that are photo-sensitive [90,94,97–104], notably on sunlight or room light, and very importantly demonstrate reversibility under controlled photo conditions, e.g. using different wavelengths. A better use of magneto- and electrocatalytically active hybrid ligands can be expected [272,302–308]. Direct adaption of natural materials as ligands which can induce chirality of the molecular substrates would be challenging but valuable. Hybrids venturing into other heteroatoms such as Al, Bi and even the more amenable alkaline earth metals especially for application in aqueous media could also push this field to new frontiers. Integration of these new systems with other emerging materials systems (e.g. carbon nanotubes, graphene, meso-porous silica, metal surface, etc.) will elevate the overall impact of catalytic science and technology.

Acknowledgements

Financial support from the Ministry of Education (R143-000-364-305) and A*Star is acknowledged. We acknowledge Ni-Ni Ding for helpful discussions.

References

[1] P. Braunstein, F. Naud, Angew. Chem. Int. Ed. 40 (2001) 680.
[2] J. Podlahova, B. Kratochvil, V. Langer, Inorg. Chem. 20 (1981) 2160.
[3] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[4] A.D. Burrows, Sci. Prog. 85 (2002) 199.
[5] Z.Q. Weng, S.H. Teo, T.S.A. Hor, Acc. Chem. Res. 40 (2007) 676.
[6] H. Grützmacher, Angew. Chem. Int. Ed. 47 (2008) 1814.
[7] F. Speiser, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784.
[8] M. Bassetti, Eur. J. Inorg. Chem. (2006) 4473.
[9] Y. Miyake, Y. Nishibayashi, S. Uemura, Synlett (2008) 1747.
[10] Y.X. Li, Y.L. Zheng, F.T. Tian, Y.J. Zhang, W.B. Zhang, Chin. J. Org. Chem. 29 (2009) 1487.
[11] G. Desimoni, G. Faita, P. Quadrelli, Chem. Rev. 103 (2003) 3119.
[12] O.B. Sutcliffe, M.R. Bryce, Tetrahedron: Asymmetry 14 (2003) 2297.
[13] R.G. Arrayás, J. Adrio, J.C. Carretero, Angew. Chem. Int. Ed. 45 (2006) 7674.
[14] H. Nomura, C.J. Richards, Chem. Asian J. 5 (2010) 1726.
[15] D.F. Fischer, A. Barakat, Z.Q. Xin, M.E. Weiss, R. Peters, Chem. Eur. J. 15 (2009) 8722.
[16] V.C. Gibson, C. Redshaw, G.A. Solan, Chem. Rev. 107 (2007) 1745.
[17] W. Zhang, M. Shi, Synlett (2007) 19.
[18] F. Boeda, T. Beneyton, C. Crévisy, Mini-Rev. Org. Chem. 5 (2008) 96.
[19] J.F. Teichert, B.L. Feringa, Angew. Chem. Int. Ed. 49 (2010) 2486.
[20] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.
[21] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978.
[22] R.E. Douthwaite, Coord. Chem. Rev. 251 (2007) 702.
[23] H.M. Lee, C.C. Lee, P.Y. Cheng, Curr. Org. Chem. 11 (2007) 1491.
[24] O. Kühl, Chem. Soc. Rev. 36 (2007) 592.
[25] I.J.B. Lin, C.S. Vasam, Coord. Chem. Rev. 251 (2007) 642.
[26] S. Díez-González, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612.
[27] G.C. Vougioukalakis, R.H. Grubbs, Chem. Rev. 110 (2009) 1746.
[28] L. Gu, G. Zhu, H. Song, G. Zi, Chin. J. Org. Chem. 29 (2009) 1499.
[29] J.C.Y. Lin, R.T.W. Huang, C.S. Lee, A. Bhattacharyya, W.S. Hwang, I.J.B. Lin, Chem. Rev. 109 (2009) 3561.

[30] M. Poyatos, J.A. Mata, E. Peris, Chem. Rev. 109 (2009) 3677.
[31] O. Schuster, L. Yang, H.G. Raubenheimer, M. Albrecht, Chem. Rev. 109 (2009) 3445.
[32] D. Pugh, A.A. Danopoulos, Coord. Chem. Rev. 251 (2007) 610.
[33] S. Monsaert, A. Lozano Vila, R. Drozdzak, P. Van Der Voort, F. Verpoort, Chem. Soc. Rev. 38 (2009) 3360.
[34] C. Federsel, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 49 (2010) 6254.
[35] N. Selander, K.J. Szabó, Chem. Rev. 111 (2011) 2048.
[36] R. Drozdzak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan, F. Verpoort, Adv. Synth. Catal. 347 (2005) 1721.
[37] C. Baleizão, H. Garcia, Chem. Rev. 106 (2006) 3987.
[38] K. Matsumoto, B. Saito, T. Katsuki, Chem. Commun. (2007) 3619.
[39] A. Zulauf, M. Mellah, X. Hong, E. Schulz, Dalton Trans. 39 (2010) 6911.
[40] S.J. Wezenberg, A.W. Kleij, Angew. Chem. Int. Ed. 47 (2008) 2354.
[41] F.E. Hahn, Angew. Chem. Int. Ed. 45 (2006) 1348.
[42] F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122.
[43] O. Coutelier, G. Nowogrocki, J.F. Paul, A. Mortreux, Adv. Synth. Catal. 349 (2007) 2259.
[44] J.S.M. Samec, R.H. Grubbs, Chem. Eur. J. 14 (2008) 2686.
[45] A. Friedrich, U. Radius, Eur. J. Inorg. Chem. (2004) 4300.
[46] C.A. Caputo, N.D. Jones, Dalton Trans. (2007) 4627.
[47] D.A. Evans, K.R. Fandrick, H.J. Song, K.A. Scheidt, R. Xu, J. Am. Chem. Soc. 129 (2007) 10029.
[48] D.A. Evans, Y. Aye, J. Am. Chem. Soc. 128 (2006) 11034.
[49] D.A. Evans, Y. Aye, J. Wu, Org. Lett. 8 (2006) 2071.
[50] D.A. Evans, K.R. Fandrick, Org. Lett. 8 (2006) 2249.
[51] H. Morimoto, G. Lu, N. Aoyama, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 129 (2007) 9588.
[52] D.A. Evans, H.J. Song, K.R. Fandrick, Org. Lett. 8 (2006) 3351.
[53] F.W. Li, T.S.A. Hor, Chem. Eur. J. 15 (2009) 10585.
[54] H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, Organometallics 8 (1989) 846.
[55] M.S. Chen, M.C. White, Science 318 (2007) 783.
[56] M.S. Chen, M.C. White, Science 327 (2010) 566.
[57] Y. Li, K. Ding, C.A. Sandoval, Org. Lett. 11 (2009) 907.
[58] F.W. Li, T.S.A. Hor, Adv. Synth. Catal. 350 (2008) 2391.
[59] D. Carmona, M.P. Lamata, F. Viguri, J. Ferrer, N. García, F.J. Lahoz, M.L. Martín, L.A. Oro, Eur. J. Inorg. Chem. 16 (2006) 3155.
[60] D. Carmona, M.P. Lamata, F. Viguri, R. Rodríguez, F.J. Lahoz, I.T. Dobrinovitch, L.A. Oro, Dalton Trans. (2007) 1911.
[61] C.S. Yi, K.H. Kwon, D.W. Lee, Org. Lett. 11 (2009) 1567.
[62] J. Zhang, A.F. Li, T.S.A. Hor, Organometallics 28 (2009) 2935.
[63] J. Zhang, A.F. Li, T.S.A. Hor, Dalton Trans. (2009) 9327.
[64] I. Garcia-Bosch, A. Company, X. Fontrodona, X. Ribas, M. Costas, Org. Lett. 10 (2008) 2095.
[65] I. Garcia-Bosch, X. Ribas, M. Costas, Adv. Synth. Catal. 351 (2009) 348.
[66] E. Milczek, N. Boudet, S. Blakey, Angew. Chem. Int. Ed. 47 (2008) 6825.
[67] F. Zeng, Z. Yu, Organometallics 28 (2009) 1855.
[68] P. Paredes, J. Díez, M.P. Gamasa, Organometallics 27 (2008) 2597.
[69] F.Z. Yang, Y.C. Chen, Y.F. Lin, K.H. Yu, Y.H. Liu, Y. Wang, S.T. Liu, J.T. Chen, Dalton Trans. (2009) 1243.
[70] Y.C. Lin, K.H. Yu, S.L. Huang, Y.H. Liu, Y. Wang, S.T. Liu, J.T. Chen, Dalton Trans. (2009) 9058.
[71] W. Nam, Acc. Chem. Res. 40 (2007) 522.
[72] L. Que, Acc. Chem. Res. 40 (2007) 493.
[73] H. Ohtake, T. Higuchi, M. Hirobe, J. Am. Chem. Soc. 114 (1992) 10660.
[74] J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961.
[75] A.H. Hoveyda, P.J. Lombardi, R.V. O'Brien, A.R. Zhugralin, J. Am. Chem. Soc. 131 (2009) 8378.
[76] R.E. Giudici, A.H. Hoveyda, J. Am. Chem. Soc. 129 (2007) 3824.
[77] J.J. Van Veldhuizen, J.E. Campbell, R.E. Giudici, A.H. Hoveyda, J. Am. Chem. Soc. 127 (2005) 6877.
[78] D.G. Gillingham, O. Kataoka, S.B. Garber, A.H. Hoveyda, J. Am. Chem. Soc. 126 (2004) 12288.
[79] J.J. Van Veldhuizen, D.G. Gillingham, S.B. Garber, O. Kataoka, A.H. Hoveyda, J. Am. Chem. Soc. 125 (2003) 12502.
[80] P.G. Clark, E.N. Guidry, W.Y. Chan, W.E. Steinmetz, R.H. Grubbs, J. Am. Chem. Soc. 132 (2010) 3405.
[81] K.M. Kuhn, J.B. Bourg, C.K. Chung, S.C. Virgil, R.H. Grubbs, J. Am. Chem. Soc. 131 (2009) 5313.
[82] G.C. Vougioukalakis, R.H. Grubbs, J. Am. Chem. Soc. 130 (2008) 2234.
[83] H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S.P. Nolan, Angew. Chem. Int. Ed. 46 (2007) 6786.
[84] M. Albrecht, Chem. Rev. 110 (2010) 576.
[85] N.E. Shepherd, H. Tanabe, Y. Xu, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 132 (2010) 3666.
[86] S. Mouri, Z. Chen, H. Mitsunuma, M. Furutachi, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 132 (2010) 1255.
[87] M. Shibasaki, S. Matsunaga, N. Kumagai, Synlett (2008) 1583.
[88] S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga, M. Shibasaki, Angew. Chem. Int. Ed. 47 (2008) 3230.
[89] M. Shibasaki, S. Matsunaga, Chem. Soc. Rev. 35 (2006) 269.
[90] A.G. Condie, J.C. González-Gómez, C.R.J. Stephenson, J. Am. Chem. Soc. 132 (2010) 1464.
[91] C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 663.
[92] C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 525.
[93] A. Otero, J. Fernández-Baeza, A. Antiñolo, A. Lara-Sánchez, E. Martínez-Caballero, J. Tejeda, L.F. Sánchez-Barba, C. Alonso-Moreno, I. López-Solera, Organometallics 27 (2008) 976.
[94] D.A. Nagib, M.E. Scott, D.W.C. MacMillan, J. Am. Chem. Soc. 131 (2009) 10875.
[95] J.M.R. Narayanam, J.W. Tucker, C.R.J. Stephenson, J. Am. Chem. Soc. 131 (2009) 8756.
[96] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[97] T.P. Yoon, M.A. Ischay, J. Du, Nat. Chem. 2 (2010) 527.
[98] S.D. Tilley, M. Cornuz, K. Sivula, M. Gratzel, Angew. Chem. Int. Ed. 49 (2010) 6405.
[99] S. Tanaka, S. Masaoka, K. Yamauchi, M. Annaka, K. Sakai, Dalton Trans. 39 (2010) 11218.
[100] R.S. Stoll, S. Hecht, Angew. Chem. Int. Ed. 49 (2010) 5054.
[101] S. Losse, J.G. Vos, S. Rau, Coord. Chem. Rev. 254 (2010) 2492.
[102] M.A. Ischay, Z. Lu, T.P. Yoon, J. Am. Chem. Soc. 132 (2010) 8572.
[103] A. Inagaki, M. Akita, Coord. Chem. Rev. 254 (2010) 1220.
[104] W.C. Ellis, N.D. McDaniel, S. Bernhard, T.J. Collins, J. Am. Chem. Soc. 132 (2010) 10990.
[105] T.K. Zhang, K. Yuan, X.L. Hou, J. Organomet. Chem. 692 (2007) 1912.
[106] B.K. Lee, M.R. Biscoe, S.L. Buchwald, Tetrahedron Lett. 50 (2009) 3672.
[107] R. Huang, K.H. Shaughnessy, Organometallics 25 (2006) 4105.
[108] J. Ruiz, N. Cutillas, F. López, G. López, D. Bautista, Organometallics 25 (2006) 5768.
[109] Y. Nishibayashi, S. Uemura, Synlett (1995) 79.
[110] C.J. Richards, T. Damalidis, D.E. Hibbs, M.B. Hursthouse, Synlett (1995) 74.
[111] T. Sammakia, H.A. Latham, D.R. Schaad, J. Org. Chem. 60 (1995) 10.
[112] C. Xu, J.F. Gong, S.F. Yue, Y.J. Zhu, Y.J. Wu, Dalton Trans. (2006) 4730.
[113] N. Ma, Z. Zhu, Y. Wu, Tetrahedron 63 (2007) 4625.
[114] F. Yang, X. Cui, Y. Li, J. Zhang, G. Ren, Y. Wu, Tetrahedron 63 (2007) 1963.
[115] F. Yang, Y. Wu, Eur. J. Org. Chem. (2007) 3476.
[116] C. Xu, J.F. Gong, Y.J. Wu, Tetrahedron Lett. 48 (2007) 1619.
[117] C. Xu, J.F. Gong, T. Guo, Y.H. Zhang, Y.J. Wu, J. Mol. Catal. A: Chem. 279 (2008) 69.
[118] M.E. Weiss, D.F. Fischer, Z.Q. Xin, S. Jautze, W.B. Schweizer, R. Peters, Angew. Chem. Int. Ed. 45 (2006) 5694.
[119] H. Huang, R. Peters, Angew. Chem. Int. Ed. 48 (2009) 604.
[120] S. Jautze, P. Seiler, R. Peters, Angew. Chem. Int. Ed. 46 (2007) 1260.
[121] S. Jautze, R. Peters, Angew. Chem. Int. Ed. 47 (2008) 9284.
[122] S.F. Kirsch, L.E. Overman, N.S. White, Org. Lett. 9 (2007) 911.
[123] H. Nomura, C.J. Richards, Chem. Eur. J. 13 (2007) 10216.
[124] B.M. Trost, H. Ito, J. Am. Chem. Soc. 122 (2000) 12003.
[125] B.M. Trost, H. Ito, E.R. Silcoff, J. Am. Chem. Soc. 123 (2001) 3367.
[126] B.M. Trost, S. Hisaindee, Org. Lett. 8 (2006) 6003.
[127] B.M. Trost, J. Jaratjaroonphong, V. Reutrakul, J. Am. Chem. Soc. 128 (2006) 2778.
[128] B.M. Trost, D.W. Lupton, Org. Lett. 9 (2007) 2023.
[129] B.M. Trost, C. Müller, J. Am. Chem. Soc. 130 (2008) 2438.
[130] B.M. Trost, J. Hitce, J. Am. Chem. Soc. 131 (2009) 4572.
[131] L.F. Niu, Y.C. Xin, R.L. Wang, F. Jiang, P.F. Xu, X.P. Hui, Synlett (2010) 765.
[132] Y. Xiao, Z. Wang, K. Ding, Chem. Eur. J. 11 (2005) 3668.
[133] S. Ueno, T. Kochi, N. Chatani, F. Kakiuchi, Org. Lett. 11 (2009) 855.
[134] S. Ueno, E. Mizushima, N. Chatani, F. Kakiuchi, J. Am. Chem. Soc. 128 (2006) 16516.
[135] P. Oña-Burgos, I. Fernández, L. Roces, L. Torre Fernández, S. García-Granda, F. Lopez Ortiz, Organometallics 28 (2009) 1739.
[136] L.J.E. Stanlake, L.L. Schafer, Organometallics 28 (2009) 3990.
[137] A.Q. Jia, G.X. Jin, Dalton Trans. (2009) 8838.
[138] J.A. Bexrud, L.L. Schafer, Dalton Trans. 39 (2010) 361.
[139] J. Zhang, P. Braunstein, T.S.A. Hor, Organometallics 27 (2008) 4277.
[140] G. Zi, F. Zhang, L. Xiang, Y. Chen, W. Fang, H. Song, Dalton Trans. 39 (2010) 4048.
[141] G. Xia, H. Yamamoto, J. Am. Chem. Soc. 128 (2006) 2554.
[142] B.L. Wegenhart, M.M. Abu-Omar, Inorg. Chem. 49 (2010) 4741.
[143] A. Otero, J. Fernandez-Baeza, A. Antinolo, J. Tejeda, A. Lara-Sanchez, L.F. Sanchez-Barba, M. Sanchez-Molina, C. Bo, M. Urbano-Cuadrado, Inorg. Chim. Acta 362 (2009) 2909.
[144] A. Otero, J. Fernandez-Baeza, A. Antinolo, J. Tejeda, A. Lara-Sanchez, L.F. Sanchez-Barba, M. Sanchez-Molina, A.M. Rodriguez, C. Bo, M. Urbano-Cuadrado, Organometallics 26 (2007) 4310.
[145] A. Otero, J. Fernandez-Baeza, A. Lara-Sanchez, J. Tejeda, L.F. Sanchez-Barba, Eur. J. Inorg. Chem. (2008) 5309.
[146] A. Taketoshi, A. Tsujimoto, S. Maeda, T. Koizumi, T. Kanbara, ChemCatChem 2 (2010) 58.
[147] C. Xu, Z.Q. Wang, W.J. Fu, X.H. Lou, Y.F. Li, F.F. Cen, H.J. Ma, B.M. Ji, Organometallics 28 (2009) 1909.
[148] A. Garces, L.F. Sanchez-Barba, C. Alonso-Moreno, M. Fajardo, J. Fernandez-Baeza, A. Otero, A. Lara-Sanchez, I. Lopez-Solera, A.M. Rodriguez, Inorg. Chem. 49 (2010) 2859.
[149] X. Zhang, S. Yin, R. Qiu, J. Xia, W. Dai, Z. Yu, C.T. Au, W.Y. Wong, J. Organomet. Chem. 694 (2009) 3559.
[150] S. Tanaka, H. Saburi, M. Kitamura, Adv. Synth. Catal. 348 (2006) 375.
[151] S. Tanaka, P.K. Pradhan, Y. Maegawa, M. Kitamura, Chem. Commun. 46 (2010) 3996.

[152] D.G.H. Hetterscheid, C. Hendriksen, W.I. Dzik, J.M.M. Smits, E.R.H. van Eck, A.E. Rowan, V. Busico, M. Vacatello, V. Van Axel Castelli, A. Segre, E. Jellema, T.G. Bloemberg, B. de Bruin, J. Am. Chem. Soc. 128 (2006) 9746.
[153] M.L. Kantam, P. Srinivas, J. Yadav, P.R. Likhar, S. Bhargava, J. Org. Chem. 74 (2009) 4882.
[154] S. Wang, L. Zhang, J. Am. Chem. Soc. 128 (2006) 14274.
[155] S. Wang, L. Zhang, J. Am. Chem. Soc. 128 (2006) 8414.
[156] X. Zhang, B. Cao, Y. Yan, S. Yu, B. Ji, X. Zhang, Chem. Eur. J. 16 (2010) 871.
[157] J. Wassenaar, J.N.H. Reek, Dalton Trans. (2007) 3750.
[158] Q.H. Zeng, X.P. Hu, Z.C. Duan, X.M. Liang, Z. Zheng, Tetrahedron: Asymmetry 16 (2005) 1233.
[159] X.P. Hu, Z. Zheng, Org. Lett. 7 (2005) 419.
[160] Y. Yan, X. Zhang, J. Am. Chem. Soc. 128 (2006) 7198.
[161] S.H. Chikkali, R. Bellini, G. Berthon-Gelloz, J.I. van der Vlugt, B. de Bruin, J.N.H. Reek, Chem. Commun. 46 (2010) 1244.
[162] W. Zhang, Y. Chi, X. Zhang, Acc. Chem. Res. 40 (2007) 1278.
[163] F.L. Lam, F.Y. Kwong, A.S.C. Chan, Chem. Commun. 46 (2010) 4649.
[164] N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033.
[165] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 119 (1997) 4413.
[166] L. Fadini, A. Togni, Tetrahedron: Asymmetry 19 (2008) 2555.
[167] A. Dervisi, D. Koursarou, L.L. Ooi, P.N. Horton, M.B. Hursthouse, Dalton Trans. (2006) 5717.
[168] W.A. Herrmann, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. 34 (1995) 1844.
[169] R.B. Bedford, H. Dumycz, M.F. Haddow, L.T. Pilarski, A.G. Orpen, P.G. Pringle, R.L. Wingad, Dalton Trans. (2009) 7796.
[170] R.B. Bedford, L.T. Pilarski, Tetrahedron Lett. 49 (2008) 4216.
[171] R.B. Bedford, M. Betham, J.P.H. Charmant, M.F. Haddow, A.G. Orpen, L.T. Pilarski, S.J. Coles, M.B. Hursthouse, Organometallics 26 (2007) 6346.
[172] R.A. Baber, R.B. Bedford, M. Betham, M.E. Blake, S.J. Coles, M.F. Haddow, M.B. Hursthouse, A.G. Orpen, L.T. Pilarski, P.G. Pringle, R.L. Wingad, Chem. Commun. (2006) 3880.
[173] R.B. Bedford, S.L. Hazelwood, P.N. Horton, M.B. Hursthouse, Dalton Trans. (2003) 4164.
[174] R. Shintani, W.L. Duan, T. Nagano, A. Okada, T. Hayashi, Angew. Chem. Int. Ed. 44 (2005) 4611.
[175] X. Luo, H. Zhang, H. Duan, Q. Liu, L. Zhu, T. Zhang, A. Lei, Org. Lett. 9 (2007) 4571.
[176] T.K. Zhang, D.L. Mo, L.X. Dai, X.L. Hou, Org. Lett. 10 (2008) 3689.
[177] A. Tenaglia, L. Giordano, G. Buono, Org. Lett. 8 (2006) 4315.
[178] J. Campos, A.C. Esqueda, J. López-Serrano, L. Sánchez, F.P. Cossio, A. de Cozar, E. Álvarez, C. Maya, E. Carmona, J. Am. Chem. Soc. 132 (2010) 16765.
[179] T.M. Douglas, J. Le Notre, S.K. Brayshaw, C.G. Frost, A.S. Weller, Chem. Commun. (2006) 3408.
[180] M. Ueda, J.F. Hartwig, Org. Lett. 12 (2009) 92.
[181] L.M. Stanley, J.F. Hartwig, J. Am. Chem. Soc. 131 (2009) 8971.
[182] C.A. Kiener, C. Shu, C. Incarvito, J.F. Hartwig, J. Am. Chem. Soc. 125 (2003) 14272.
[183] A.N. Marziale, S.H. Faul, T. Reiner, S. Schneider, J. Eppinger, Green Chem. 12 (2010) 35.
[184] O. Pàmies, P.G. Andersson, M. Diéguez, Chem. Eur. J. 16 (2010) 14232.
[185] R. Malacea, R. Poli, E. Manoury, Coord. Chem. Rev. 254 (2010) 729.
[186] B.M. Trost, M.R. Machacek, A. Aponick, Acc. Chem. Res. 39 (2006) 747.
[187] L.C. Liang, Coord. Chem. Rev. 250 (2006) 1152.
[188] I.D. Kostas, Curr. Org. Synth. 5 (2008) 227.
[189] J.I. van der Vlugt, J.N.H. Reek, Angew. Chem. Int. Ed. 48 (2009) 8832.
[190] P. Braunstein, Chem. Rev. 106 (2006) 134.
[191] H.A. McManus, P.J. Guiry, Chem. Rev. 104 (2004) 4151.
[192] K.J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 36 (1997) 285.
[193] M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466.
[194] P. Cheruku, S. Gohil, P.G. Andersson, Org. Lett. 9 (2007) 1659.
[195] M. Engman, J.S. Diesen, A. Paptchikhine, P.G. Andersson, J. Am. Chem. Soc. 129 (2007) 4536.
[196] P. Cheruku, J. Diesen, P.G. Andersson, J. Am. Chem. Soc. 130 (2008) 5595.
[197] A. Trifonova, J.S. Diesen, P.G. Andersson, Chem. Eur. J. 12 (2006) 2318.
[198] J.J. Verendel, P.G. Andersson, Dalton Trans. (2007) 5603.
[199] P. Cheruku, A. Paptchikhine, T.L. Church, P.G. Andersson, J. Am. Chem. Soc. 131 (2009) 8285.
[200] Z.L. Lu, E. Neumann, A. Pfaltz, Eur. J. Org. Chem. (2007) 4189.
[201] C. Valla, A. Baeza, F. Menges, A. Pfaltz, Synlett (2008) 3167.
[202] A. Baeza, A. Pfaltz, Chem. Eur. J. 15 (2009) 2266.
[203] A. Baeza, A. Pfaltz, Chem. Eur. J. 16 (2010) 4003.
[204] X. Li, Q. Li, X. Wu, Y. Gao, D. Xu, L. Kong, Tetrahedron: Asymmetry 18 (2007) 629.
[205] S. Li, S.F. Zhu, C.M. Zhang, S. Song, Q.L. Zhou, J. Am. Chem. Soc. 130 (2008) 8584.
[206] H. Li, Y. Wu, Appl. Organomet. Chem. 22 (2008) 233.
[207] W.J. Lu, X.L. Hou, Adv. Synth. Catal. 351 (2009) 1224.
[208] L. Mantilli, D. Gérard, S. Torche, C. Besnard, C. Mazet, Angew. Chem. Int. Ed. 48 (2009) 5143.
[209] R. Crabtree, Acc. Chem. Res. 12 (1979) 331.
[210] R.H. Crabtree, H. Felkin, G.E. Morris, J. Organomet. Chem. 141 (1977) 205.
[211] P. Schnider, G. Koch, R. Prétôt, G. Wang, F.M. Bohnen, C. Krüger, A. Pfaltz, Chem. Eur. J. 3 (1997) 887.
[212] A. Lightfoot, P. Schnider, A. Pfaltz, Angew. Chem. Int. Ed. 37 (1998) 2897.
[213] C. Müller, R.J. Lachicotte, W.D. Jones, Organometallics 21 (2002) 1975.
[214] A. Kermagoret, P. Braunstein, Organometallics 27 (2008) 88.
[215] P. Chavez, I.G. Rios, A. Kermagoret, R. Pattacini, A. Meli, C. Bianchini, G. Giambastiani, P. Braunstein, Organometallics 28 (2009) 1776.
[216] Z. Weng, S. Teo, L.L. Koh, T.S.A. Hor, Angew. Chem. Int. Ed. 44 (2005) 7560.
[217] Z. Weng, S. Teo, T.S.A. Hor, Organometallics 25 (2006) 4878.
[218] Z. Weng, S. Teo, L.L. Koh, T.S.A. Hor, Chem. Commun. (2006) 1319.
[219] Z. Weng, S. Teo, Z.P. Liu, T.S.A. Hor, Organometallics 26 (2007) 2950.
[220] L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, Angew. Chem. Int. Ed. 46 (2007) 1909.
[221] M. Lenze, S.L. Sedinkin, N.P. Rath, E.B. Bauer, Tetrahedron Lett. 51 (2010) 2855.
[222] C. Sui-Seng, F. Freutel, A.J. Lough, R.H. Morris, Angew. Chem. Int. Ed. 47 (2008) 940.
[223] N. Meyer, A.J. Lough, R.H. Morris, Chem. Eur. J. 15 (2009) 5605.
[224] D.M. Tellers, M. Bio, Z.J. Song, J.C. McWilliams, Y. Sun, Tetrahedron: Asymmetry 17 (2006) 550.
[225] D.B. Grotjahn, C.R. Larsen, J.L. Gustafson, R. Nair, A. Sharma, J. Am. Chem. Soc. 129 (2007) 9592.
[226] R.J. Lundgren, M.A. Rankin, R. McDonald, G. Schatte, M. Stradiotto, Angew. Chem. Int. Ed. 46 (2007) 4732.
[227] M. Ito, L.W. Koo, A. Himizu, C. Kobayashi, A. Sakaguchi, T. Ikariya, Angew. Chem. Int. Ed. 48 (2009) 1324.
[228] M. Ito, A. Sakaguchi, C. Kobayashi, T. Ikariya, J. Am. Chem. Soc. 129 (2007) 290.
[229] A. Del Zotto, W. Baratta, M. Ballico, E. Herdtweck, P. Rigo, Organometallics 26 (2007) 5636.
[230] M.L. Clarke, M.B. Díaz-Valenzuela, A.M.Z. Slawin, Organometallics 26 (2007) 16.
[231] M.B. Díaz-Valenzuela, S.D. Phillips, M.B. France, M.E. Gunn, M.L. Clarke, Chem. Eur. J. 15 (2009) 1227.
[232] M. Althaus, C. Becker, A. Togni, A. Mezzetti, Organometallics 26 (2007) 5902.
[233] C. Schotes, A. Mezzetti, J. Am. Chem. Soc. 132 (2010) 3652.
[234] L.A. Saudan, C.M. Saudan, C. Debieux, P. Wyss, Angew. Chem. Int. Ed. 46 (2007) 7473.
[235] E. Balaraman, B. Gnanaprakasam, L.J.W. Shimon, D. Milstein, J. Am. Chem. Soc. 132 (2010) 16756.
[236] D. Carmona, C. Vega, N. García, F.J. Lahoz, S. Elipe, L.A. Oro, M.P. Lamata, F. Viguri, R. Borao, Organometallics 25 (2006) 1592.
[237] K.N. Gavrilov, O.G. Bondarev, R.V. Lebedev, A.A. Shiryaev, S.E. Lyubimov, A.I. Polosukhin, G.V. Grintselev-Knyazev, K.A. Lyssenko, S.K. Moiseev, N.S. Ikonnikov, V.N. Kalinin, V.A. Davankov, A.V. Korostylev, H.J. Gais, Eur. J. Inorg. Chem. (2002) 1367.
[238] S. Proch, R. Kempe, Angew. Chem. Int. Ed. 46 (2007) 3135.
[239] J. Meeuwissen, R. Detz, A.J. Sandee, B. de Bruin, M.A. Siegler, A.L. Spek, J.N.H. Reek, Eur. J. Inorg. Chem. (2010) 2992.
[240] J. Dugal-Tessier, G.R. Dake, D.P. Gates, Organometallics 26 (2007) 6481.
[241] K. Takahashi, H. Nakano, R. Fujita, Chem. Commun. (2007) 263.
[242] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.
[243] T. Ikariya, A.J. Blacker, Acc. Chem. Res. 40 (2007) 1300.
[244] X. Wu, J. Xiao, Chem. Commun. (2007) 2449.
[245] S.E. Clapham, A. Hadzovic, R.H. Morris, Coord. Chem. Rev. 248 (2004) 2201.
[246] H.U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 345 (2003) 103.
[247] Y.M. He, Q.H. Fan, Org. Biomol. Chem. 8 (2010) 2497.
[248] J.P. Genet, Acc. Chem. Res. 36 (2003) 908.
[249] R. Noyori, M. Ohta, Y. Hsiao, M. Kitamura, T. Ohta, H. Takaya, J. Am. Chem. Soc. 108 (1986) 7117.
[250] R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi, S. Akutagawa, J. Am. Chem. Soc. 109 (1987) 5856.
[251] D. Amoroso, A. Jabri, G.P.A. Yap, D.G. Gusev, E.N. dos Santos, D.E. Fogg, Organometallics 23 (2004) 4047.
[252] N. Arai, K. Suzuki, S. Sugizaki, H. Sorimachi, T. Ohkuma, Angew. Chem. Int. Ed. 47 (2008) 1770.
[253] M. Aydemir, N. Meric, A. Baysal, C. Kayan, M. Togrul, B. Gumgum, Appl. Organomet. Chem. 24 (2010) 215.
[254] F. Bie, Y. Li, W. Cao, C.A. Sanboval, Chin. J. Chem. 27 (2009) 2309.
[255] F.Y. Kwong, A.S.C. Chan, Synlett (2008) 1440.
[256] S.H. Hong, D.P. Sanders, C.W. Lee, R.H. Grubbs, J. Am. Chem. Soc. 127 (2005) 17160.
[257] J.A. Love, M.S. Sanford, M.W. Day, R.H. Grubbs, J. Am. Chem. Soc. 125 (2003) 10103.
[258] R. Venkateswaran, M.S. Balakrishna, S.M. Mobin, Eur. J. Inorg. Chem. (2007) 1930.
[259] D.J. Law, R.G. Cavell, J. Mol. Catal. 91 (1994) 175.
[260] R.G. Cavell, B. Creed, L. Gelmini, D.J. Law, R. McDonald, A.R. Sanger, A. Somogyvari, Inorg. Chem. 37 (1998) 757.
[261] V. Cadierno, P. Crochet, J. Díez, J. García-Álvarez, S.E. García-Garrido, J. Gimeno, S. García-Granda, M.A. Rodríguez, Inorg. Chem. 42 (2003) 3293.
[262] P. Molina, A. Arques, A. García, M.C.R. de Arellano, Tetrahedron Lett. 38 (1997) 7613.
[263] K.A. Chatziapostolou, K.A. Vallianatou, A. Grigoropoulos, C.P. Raptopoulou, A. Terzis, I.D. Kostas, P. Kyritsis, G. Pneumatikakis, J. Organomet. Chem. 692 (2007) 4129.
[264] S. Teo, Z. Weng, T.S.A. Hor, Organometallics 25 (2006) 1199.
[265] D. Fenske, C. Persau, S. Dehnen, C.E. Anson, Angew. Chem. Int. Ed. 43 (2004) 305.

[266] G. Li, Z. Lei, Q.M. Wang, J. Am. Chem. Soc. 132 (2010) 17678.
[267] T.K.M. Lee, N.Y. Zhu, V.W.W. Yam, J. Am. Chem. Soc. 132 (2010) 17646.
[268] H. Pellissier, Tetrahedron 63 (2007) 1297.
[269] M. Mellah, A. Voituriez, E. Schulz, Chem. Rev. 107 (2007) 5133.
[270] B.F. Bonini, M. Fochi, A. Ricci, Synlett (2007) 360.
[271] M. Bierenstiel, E.D. Cross, Coord. Chem. Rev. 255 (2011) 574.
[272] R. Angamuthu, P. Byers, M. Lutz, A.L. Spek, E. Bouwman, Science 327 (2010) 313.
[273] M.T. Chen, P.J. Chang, C.A. Huang, K.F. Peng, C.T. Chen, Dalton Trans. (2009) 9068.
[274] I.D. Kostas, G.A. Heropoulos, D. Kovala-Demertzi, P.N. Yadav, J.P. Jasinski, M.A. Demertzis, F.J. Andreadaki, G. Vo-Thanh, A. Petit, A. Loupy, Tetrahedron Lett. 47 (2006) 4403.
[275] B. Lian, H. Ma, T.P. Spaniol, J. Okuda, Dalton Trans. (2009) 9033.
[276] Y. Matano, T. Miyajima, T. Nakabuchi, H. Imahori, N. Ochi, S. Sakaki, J. Am. Chem. Soc. 128 (2006) 11760.
[277] Y. Matano, T. Miyajima, N. Ochi, T. Nakabuchi, M. Shiro, Y. Nakao, S. Sakaki, H. Imahori, J. Am. Chem. Soc. 130 (2008) 990.
[278] Y. Matano, M. Fujita, T. Miyajima, H. Imahori, Organometallics 28 (2009) 6213.
[279] T. Nakabuchi, Y. Matano, H. Imahori, Organometallics 27 (2008) 3142.
[280] Y. Matano, T. Nakabuchi, T. Miyajima, H. Imahori, Organometallics 25 (2006) 3105.
[281] Y. Matano, H. Imahori, Acc. Chem. Res. 42 (2009) 1193.
[282] G. Aharonian, K. Feghali, S. Gambarotta, G.P.A. Yap, Organometallics 20 (2001) 2616.
[283] G.P. Clancy, H.C.S. Clark, G.K.B. Clentsmith, F.G.N. Cloke, P.B. Hitchcock, J. Chem. Soc. Dalton Trans. (1999) 3345.
[284] X.H. Yang, Z. Wang, X.L. Sun, Y. Tang, Dalton Trans. (2009) 8945.
[285] A.Q. Jia, G.X. Jin, Organometallics 28 (2009) 1872.
[286] J.Q. Wu, L. Pan, Y.G. Li, S.R. Liu, Y.S. Li, Organometallics 28 (2009) 1817.
[287] R.Y. Lai, K. Surekha, A. Hayashi, F. Ozawa, Y.H. Liu, S.M. Peng, S.T. Liu, Organometallics 26 (2007) 1062.
[288] R.Y. Lai, C.I. Lee, S.T. Liu, Tetrahedron 64 (2008) 1213.
[289] B. Inés, R. SanMartin, F. Churruca, E. Domiĭnguez, M.K. Urtiaga, M.I. Arriortua, Organometallics 27 (2008) 2833.
[290] G. Xie, P. Chellan, J. Mao, K. Chibale, G.S. Smith, Adv. Synth. Catal. 352 (2010) 1641.
[291] M.T. Chen, C.A. Huang, C.T. Chen, Eur. J. Inorg. Chem. (2006) 4642.
[292] J.M. Fraile, J.I. Garcia, C.I. Herrerias, J.A. Mayoral, Chem. Commun. (2005) 4669.
[293] C. Copéret, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem. Int. Ed. 42 (2003) 156.
[294] K. Ding, Pure Appl. Chem. 78 (2006) 293.
[295] J.W. Park, C.H. Jun, J. Am. Chem. Soc. 132 (2010) 7268.
[296] H.V. Huynh, C.H. Yeo, G.K. Tan, Chem. Commun. (2006) 3833.
[297] M. Bassetti, A. Capone, M. Salamone, Organometallics 23 (2004) 247.
[298] C.N. Rowley, T.K. Woo, Can. J. Chem. 87 (2009) 1030.
[299] T.J.M. de Bruin, L. Magna, P. Raybaud, H. Toulhoat, Organometallics 22 (2003) 3404.
[300] S. Tobisch, T. Ziegler, Organometallics 23 (2004) 4077.
[301] W.J. van Rensburg, C. Grove, J.P. Steynberg, K.B. Stark, J.J. Huyser, P.J. Steynberg, Organometallics 23 (2004) 1207.
[302] A. Taher, J.B. Kim, J.Y. Jung, W.S. Ahn, M.J. Jin, Synlett (2009) 2477.
[303] P. Sobota, Coord. Chem. Rev. 248 (2004) 1047.
[304] F.C. Pigge, Synthesis (2010) 1745.
[305] X.H. Ho, S.I. Mho, H. Kang, H.Y. Jang, Eur. J. Org. Chem. (2010) 4436.
[306] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, ChemCatChem 2 (2010) 724.
[307] P.A. Jacques, V. Artero, J. Pecaut, M. Fontecave, Proc. Natl. Acad. Sci. 106 (2009) 20627.
[308] G. Centi, S. Perathoner, Top. Catal. 52 (2009) 948.