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Applications of transition metal complexes containing 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine ligand to transfer hydrogenation of ketones

Murat Aydemir*, Nermin Meric, Akın Baysal

Department of Chemistry, Dicle University, TR-21280 Diyarbakır, Turkey

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ABSTRACT

Hydrogen transfer reduction processes are attracting increasing interest from synthetic chemists in view of their operational simplicity. 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine, $(Ph_2PNH)_2C_{10}H_6N_2$, was prepared through a single step reaction of 3,3′-diamino-2,2′-bipyridine with diphenylchlorophosphine. Reaction of $(Ph_2PNH)_2C_{10}H_6N_2$ with $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ or $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ gave a range of new bridged dinuclear complexes $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**, respectively. All new complexes have been fully characterized by analytical and spectroscopic methods. $^1H^{31}P\{^1H\}$ NMR, $^1H^{13}C$ HETCOR or $^1H^1H$ COSY correlation experiments were used to confirm the spectral assignments. **1**, **2** and **3** are suitable catalyst precursors for the transfer hydrogenation of acetophenone derivatives. Notably $[Ru((Ph_2PNH)_2C_{10}H_6N_2)(\eta^6\text{-benzene})Cl_2]$, **1** acts as an excellent catalyst, giving the corresponding alcohols in 98–99% yields in 10 min at 82 °C (TOF $\leq$600 h^{-1}) for the transfer hydrogenation reaction in comparison to analogous rhodium or iridium complexes. This transfer hydrogenation is characterized by low reversibility under these conditions.

1. Introduction

Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen [1]. Transfer hydrogenation of ketones by *iso*-PrOH is convenient in large-scale synthesis since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents [2]. Today, the catalytic transfer hydrogenation [3] of prochiral ketones is one of the most attractive methods for synthesizing optically active secondary alcohols, which form an important class of intermediates for fine chemicals and pharmaceuticals [4,5]. There are several metal sources available that have to mediate the hydride transfer from the donor to the substrate. Even if main-group metals like aluminum have historically been used in the transfer hydrogenation reactions [6,7], today's catalysts of choice are transition metal complexes predominantly of ruthenium, rhodium [8] or iridium [9–11].

Synthesis of new aminophosphines to stabilize transition metals in low valent states is considered to be a most challenging task in view of their potential utility in a variety of metal-mediated organic transformations [12]. To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [13]. The effect of ligand type on structure and reactivity of transition metal complexes is an important topic of research in coordination and organometallic chemistry [14]. Ligands containing direct phosphorus–nitrogen bonds are quite attractive as structural modifications can be introduced via simple P–N bond formation [15] and they have proved to be versatile ligands, and varying the substituents on both P- and N-centers gives rise the changes in the P–NH angle and to conformation around the P-centers [16]. Small variations in these ligands can cause significant changes in their coordination behavior and the structural features of the resulting complexes [17,18]. The use of tertiary phosphines is widespread in organometallic chemistry and in homogeneous catalysis as these ligands can be used to fine tune the metal reactivity and selectivity. The complexes incorporating this ligand type are of considerable interest because of their potential use in many processes such as reductive elimination and oxidative addition for making and breaking C–H bonds [19,20], formation and cleavage of N–H and O–H bonds [21]. Also their extensive use in classical catalytic processes such as allylic alkylation [22], Heck [23,24], Suzuki [25–

* Corresponding author. Tel.: +90 412 248 8550; fax: +90 412 248 8300.
E-mail address: aydemir@dicle.edu.tr (M. Aydemir).

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27], hydrogenation [28,29], isomerization, decarbonylation, etc. [30,31] cannot be ignored.

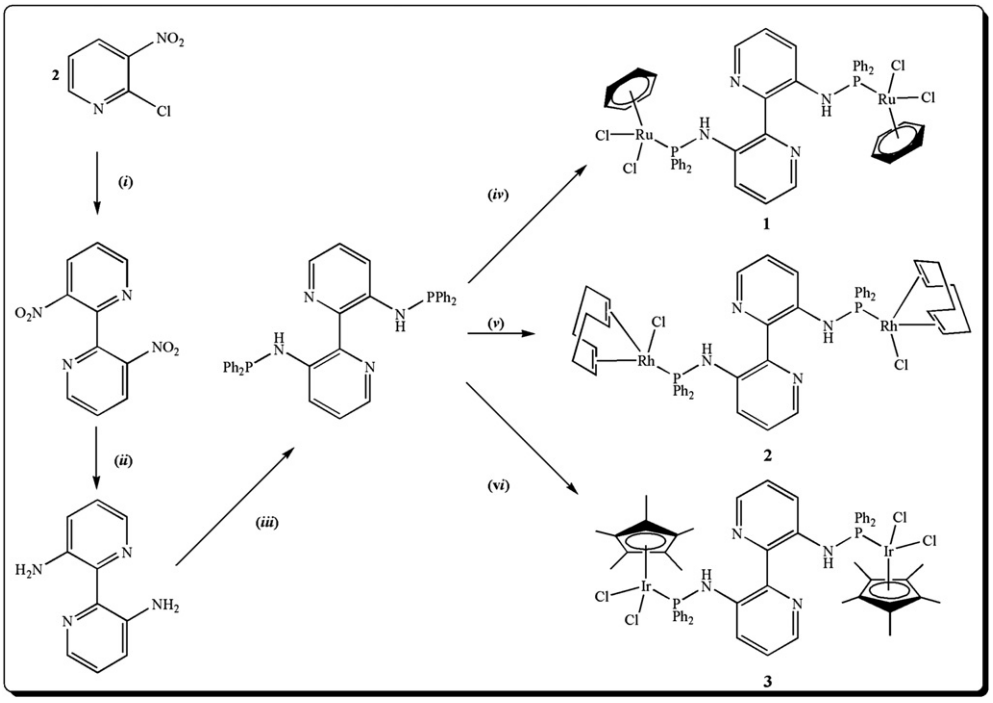
Recently, we have reported that the novel half-sandwich complexes, based on the ligands with P–N backbone, are active catalysts in the reduction of aromatic ketones [32–35]. By choosing an appropriate ligand system it is possible to fine tune the electronic and steric properties of the donor centers to bind to metals in desired oxidation state with a specific coordination number so that a catalyst may be generated for a specific organic transformation. In this context, aminophosphines play a major role because of easy and high yield synthetic methodologies and flexibility in their reactivity toward transition metals in their various oxidation states [36–40]. The above considerations prompted us to study the research program on the aminophosphine complexes. We previously reported the preparation of the 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine and its $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$ complex [41]. As part of our research program we report here, the synthesis and full characterization of three novel aminophosphine complexes $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**, and their catalytic evaluation in the transfer hydrogenation of acetophenone derivatives.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

Although aminolysis of chlorophosphines is an efficient method for preparing $R_2PN(H)R'$ or $(R_2P)_2NR'$ it has not widely been exploited yet, in part possibly because of the associated instability of the P–N bonds in these ligands [42,43]. Synthesis and characterization of bis(aminophosphine) ligand with rigid backbone, prepared from the starting material 3,3′-diamino-2,2′-bipyridine by the aminolysis method were previously reported [32] (Scheme 1). The ^{31}P NMR spectrum of $(Ph_2PNH)_2C_{10}H_6N_2$ showed a single resonance at δ(P) 26.82 ppm, similar to those found for closely related compounds, indicative of both phosphorus being equivalent as a result of the symmetry (C_2 symmetry) of the molecule (Fig. 1) [44]. 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine is unstable and decomposes rapidly on exposure to air or moisture. When the reactions were monitored by ^{31}P NMR spectroscopy, the formation of $P(O)Ph_2PPh_2$ was observed, as indicated by signals at δ 35.20 (d) ppm and δ −23.60 (d) ppm, $\{^1J(PP)$ 228 Hz$\}$. Solution of $(Ph_2PNH)_2C_{10}H_6N_2$ in $CDCl_3$, prepared under anaerobic conditions, is also unstable and decomposes gradually to give oxide and tetraphenylbiphosphine monoxide $[P(O)Ph_2PPh_2]$ derivatives. Because the $(Ph_2PNH)_2C_{10}H_6N_2$ is not stable enough in solution, the transition metal complexes were synthesized *in-situ*.

The ability of dimers $\{[Ru(arene)(\mu\text{-}Cl)Cl]_2\}$ to form mononuclear complexes of general formula $[Ru(\eta^6\text{-arene})Cl_2L]$ is well-known [45]. Thus, the reaction of $[Ru(\eta^6\text{-benzene})(\mu\text{-}Cl)Cl]_2$ and $(Ph_2PNH)_2C_{10}H_6N_2$ gives $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1** in high yield, which is an air stable, red microcrystalline powder (Scheme 1). Analysis by $^{31}P\{^1H\}$ NMR exhibits a unique signal in the spectrum, indicative of both phosphorus being equivalent as a result of the high symmetry of the complex. The chemical purity of the complex **1** was confirmed by a single $^{31}P\{^1H\}$ NMR signal at 52.03 ppm (Fig. 1). This complex is highly soluble in CH_2Cl_2 and slightly soluble in hexane so it can be crystallized from CH_2Cl_2/hexane solution. Analysis of complex **1** by ^1H NMR exhibits multiplet signals corresponding to the aromatic rings for **1** at 8.03–7.40 ppm and the C_6H_6 protons as a singlet at 5.47 ppm. In the ^1H NMR spectrum, the NH resonance of **1** was observed as a slightly doublet at 12.75 ppm (d, $^2J_{NHP}$ = 10.40 Hz) due to the multiple coupling $^2J_{NHP}$ which was confirmed by H/D exchange experiment. By H/D exchange experiment the signal of the NH simply disappears from the spectrum or more commonly is replaced by a weak signal close to δ 4.80 coming from suspended droplets of HDO.



Scheme 1. Synthesis of the $(Ph_2PNH)_2C_{10}H_6N_2$ ligand and its $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3** complexes. (i) Cu, DMF, 110 °C (ii) $SnCl_2$, concd. HCl, ½ h; (iii) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (iv) 1 equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-}Cl)Cl]_2$, thf; (vi) 1 equiv. $[Rh(\mu\text{-}Cl)(cod)]_2$, thf; (vii) 1 equiv. $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$, thf.

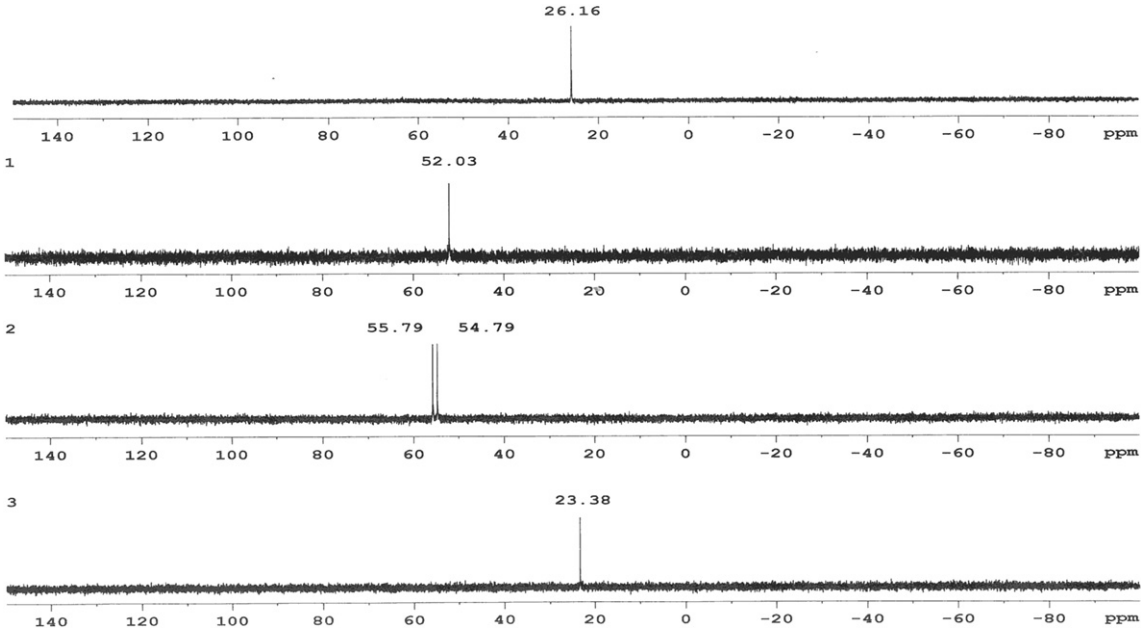


Fig. 1. ^{31}P NMR spectra of $(Ph_2PNH)_2C_{10}H_6N_2$ and its complexes.

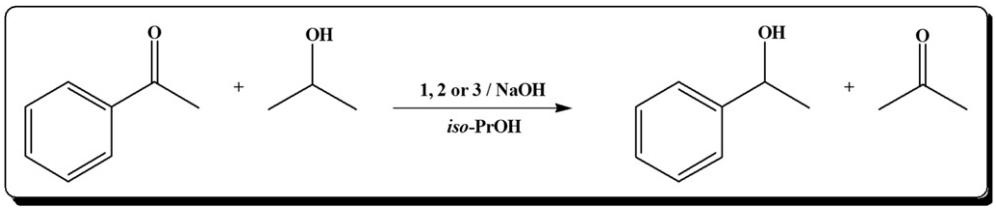
Furthermore in the ^{13}C $\{^1H\}$ NMR spectrum of **1**, $J(^{31}P^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values [46,47] (for details see Experimental section). The structural composition of the complex **1** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

The coordination chemistry of $(Ph_2PNH)_2C_{10}H_6N_2$ with $[Rh(\mu\text{-}Cl)(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ precursors was investigated as well. Reactions of $(Ph_2PNH)_2C_{10}H_6N_2$ with $Rh(\mu\text{-}Cl)(cod)]_2$ or $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ in tetrahydrofuran in a ratio of 1:1 at room temperature for 2 h gave microcrystalline precipitate of neutral complexes **2** and **3**, respectively. Complexation reactions, with coordination to rhodium or iridium were carried out at room temperature easily. Bridge cleavage of the dimer $[Rh(\mu\text{-}Cl)(cod)]_2$ with $(Ph_2PNH)_2C_{10}H_6N_2$ gave the dinuclear compound $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2**, in good yield. The coordination of the ligand through the P donor was confirmed by the ^{31}P $\{^1H\}$ NMR spectroscopy. The spectrum recorded in deuterated chloroform at room temperature shows a doublet centered at δ(P) 55.35 ppm with a ^1J(RhP) = 163.6 Hz [48,49] (Fig. 1). IR spectroscopy and elemental analysis of product **2** are consistent with the suggested molecular formula. ^1H and ^{13}C NMR spectra of compound **2** display all the signals of coordinated ligands. The ^1H NMR spectrum **2** displays the anticipated multiplets at δ 7.83–7.37 ppm for the protons of phenyls, broad singlets at δ 5.57, 2.12 and 2.00 ppm for cod protons, a broad multiplet at 12.65 ppm for NH. In the ^{13}C $\{^1H\}$ NMR spectrum of compound **2**, $J(^{31}P^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values [50] (for details see Experimental section). In the ^{31}P $\{^1H\}$ NMR, a singlet at 23.38 ppm was assigned to compound $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**, in-line with the values previously observed for similar compounds [51,52]. Analysis by ^1H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings for **3** at 8.21–7.35 ppm. Furthermore in the ^{13}C $\{^1H\}$ NMR spectrum of **3**, $J(^{31}P^{13}C)$ coupling constants of the carbons of the phenyl rings were observed. The structure of the **3** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values (for details see Experimental section).

2.2. Catalytic transfer hydrogenation of ketones

To the best of our knowledge Ronan Le Lagadec et al. [53] have reported the first crystallographic determination of a bimetallic bridged structure using this sort of ligands. Furthermore, a related structure has been invoked by Balakrishna et al. [54] for the formation of the ruthenium complex where the ligands also serve as bridge between two metal centers, however no crystallographic evidence was presented. Most recently [55] a similar structure has been determined for a BINAP-based phosphinite ligand BINAPO, whereas in the case for complexes **1**–**3**, it is noted by the authors that compounds bearing binaphtyl-based ligands bridging two metal centers are very rare. The observed activity of these complexes has encouraged us to investigate other analogous ligands and other transition metal complexes of these ligands. Furthermore, a complex with sp^3-hybridized nitrogens containing N–H bonds displays higher reaction rate. In this context, complexes **1**, **2** and **3** were selected as catalysts, *iso*-PrOH/NaOH as the reducing system, and acetophenone as a model substrate (Scheme 2) and the results are listed in Table 1.

In a preliminary study, when the reaction temperature was increased to 82 °C smooth reduction of acetophenone into 1-phenylethanol occurred, with conversion ranging from 98 to 99% after 10 min for **1**, 1 h for **2** and 3 h for **3** (Table 1, Entries 1–3). The choice of base, such as KOH and NaOH, had little influence on the conversions. In addition, optimization studies of the catalytic reduction of acetophenone in 2-propanol showed that a good activity was obtained with a base/ligand ratio of 5:1. From the results observed, it is noteworthy that the complexes **1**, **2** and **3** display the differences in reactivity. Complex **1** is the most active, quantitatively converting acetophenone with a high TOF of 594 h^{-1}. It should be pointed out that complex **1** is far more active than the corresponding precursor: $[Ru(\eta^6\text{-benzene})(\mu\text{-}Cl)Cl]_2$ (37% maximum yield in 24 h) [56]. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 1, Entries 4–6). As can be inferred from the Table 1 (Entries 7–9) the catalysts as well as the presence of NaOH are necessary to observe appreciable conversions. The base facilitates the formation of alkoxide by abstracting proton of the alcohol and subsequently alkoxide



Scheme 2. Hydrogen transfer from *iso*-PrOH to acetophenone.

undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [57,58]. In addition, the replacement of the reaction atmosphere from an inert gas to an ambient atmosphere had no negative effect on the activity of the catalyst (Table 1, Entries 10–12). Therefore, the coupling reactions were performed in air. Unfortunately, performing the reaction with the addition of water slowed the reaction but did not affect conversion of the product (Table 1, Entries 13–15). As shown in Table 1, increasing the substrate-to-catalyst ratio do not lower the conversions of the product in most cases except the time lengthened. Remarkably, the transfer hydrogenation of acetophenone could be achieved with up to 99% conversion even when the substrate-to-catalyst ratio reached to 1000:1 (Table 1).

The catalytic reductions of acetophenone derivatives were all tested with the conditions optimized for acetophenone and the results are summarized in Table 2. The fourth column in Table 2 illustrates conversions of the reduction performed in a 0.1 M of *iso*-PrOH solution containing **1**, **2** or **3** and NaOH (Ketone:Ru:NaOH = 100:1:5).

As already stated, electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone caused the changes in the reduction rate. An *ortho*- or *para*-substituted acetophenone with an electron-donor substituent, i.e., 2-methoxy or 4-methoxy is reduced more slowly than acetophenone (Table 2, Entries 4, 5, 9, 10, 14 and 15) [59]. In addition, the introduction of electron withdrawing substituents, such as F, Cl and Br to the *para*-position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved giving rise to easier hydrogenation [60,61]. We also carried out further experiments to investigate the effect of bulkiness of the alky groups on the catalytic activity and the results were given in Table 3 (entries 1–12). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols. It was found that the activity is highly dependent on the steric bulk of the alkyl group. The reactivity gradually decreased by increasing the bulkiness of the alkyl groups [62–65].

Encouraged by the high catalytic activities obtained in these preliminary studies, we next extended our investigations to include hydrogenation of various simple ketones (Table 4). Although, ruthenium-based catalysts have usually been applied in the hydrogenation of simple ketones [66–68], rhodium or iridium complexes have also been employed and found to be efficient catalyst in several processes [69,70]. So, we investigated and compared catalytic activity of ruthenium, rhodium and iridium complexes of $((Ph_2PNH)_2C_{10}H_6N_2)$ ligand. Investigation of catalytic activity of these complexes has shown that they are efficient catalysts affording almost quantitative transformation of the ketones in short times and **1** is more active than **2** and **3** (Table 4). For instance hydrogenations of cyclohexanone could be achieved in 20 min, 1.5 h and 4 h by $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**, respectively (Table 4, Entries 1–3). Conversion of methyl isobutyl ketone occurred in 1 h, 3 h and 8 h by **1**, **2** and **3**, respectively, while that of diethyl ketone occurred in 2 h, 5 h and 12 h by **1**, **2** and **3**, respectively (Table 4, Entries 7–12). Furthermore, in order to investigate the evolution of the catalyst, **1**–**3**, $^{31}P\{^1H\}$ NMR spectra were recorded periodically after the catalytic reaction. The singlet observed at 21.50 ppm at the end of third day in the spectrum is corresponding to hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$ [71–73].

Table 1
Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**.

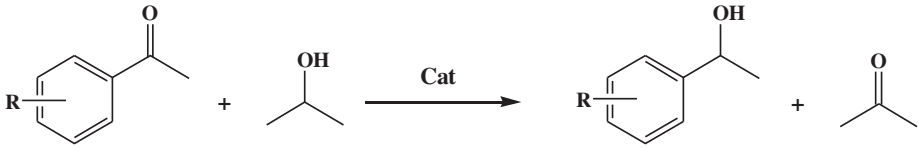
Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[i]	TOF (h^{-1})[k]
1	**1**[a]	**100:1:5**	10 min	99	594
2	**2**[a]	**100:1:5**	1 h	99	50
3	**3**[a]	**100:1:5**	3 h	98	33
4	**1**[b]	**100:1:5**	1 h	trace	–
5	**2**[b]	**100:1:5**	1 h	trace	–
6	**3**[b]	**100:1:5**	1 h	trace	–
7	**1**[c]	**100:1**	1 h	<5	–
8	**2**[c]	**100:1**	1 h	<5	–
9	**3**[c]	**100:1**	1 h	<5	–
10	**1**[d]	**100:1:5**	10 min	96	576
11	**2**[d]	**100:1:5**	1 h	99	99
12	**3**[d]	**100:1:5**	3 h	97	32
13	**1**[e]	**100:1:5**	2 h	98	49
14	**2**[e]	**100:1:5**	5 h	99	20
15	**3**[e]	**100:1:5**	11 h	98	<10
16	**1**[f]	**500:1:5**	30 min	99	198
17	**2**[f]	**500:1:5**	4 h	98	25
18	**3**[f]	**500:1:5**	10 h	97	10
19	**1**[g]	**1000:1:5**	1 h	97	97
20	**2**[g]	**1000:1:5**	8 h	98	12
21	**3**[g]	**1000:1:5**	16 h	99	<10

[a] Reaction condition: Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[b] Reaction condition: At room temperature; acetophenone/Ru/NaOH, 100:1:5.
[c] Reaction condition: Refluxing in *iso*-PrOH; acetophenone/Ru, 100:1, in the absence of base.
[d] Reaction condition: Refluxing the reaction in air.
[e] Reaction condition: Added 0.1 mL of H_2O.
[f] Reaction condition: Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 500:1:5.
[g] Reaction condition: Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 1000:1:5.
[i] Reaction condition: Determined by GC (three independent catalytic experiments).
[k] Reaction condition: Referred at the reaction time indicated in column; TOF = (mol product/mol Ru(II)Cat.) × h^{-1}.

3. Conclusions

In summary, we have synthesized a series of selected bridged dinuclear transition metal (Ru(II), Rh(I), Ir(III)) complexes based 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine bidendate ligand. We have found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent yields. Furthermore, the Ru(II)–aminophosphine complex showed strong catalytic activity in the transfer hydrogenation reaction than the

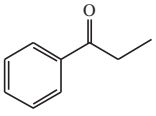
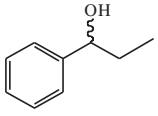
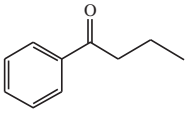
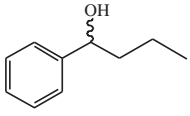
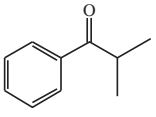
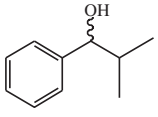
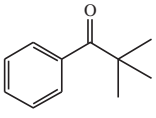
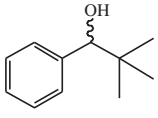
Table 2
Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from $((Ph_2PNH)_2C_{10}H_6N_2)$ and $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$.[a]



Entry	R	Time	Conversion (%)[b]	TOF (h^{-1})[c]
Cat: Ru(II) complex, **1**				
1	4-F	5 min	99	495
2	4-Cl	5 min	98	490
3	4-Br	10 min	98	588
4	2-MeO	20 min	97	291
5	4-MeO	15 min	95	380
Cat: Rh(I) complex, **2**				
6	4-F	1 h	99	99
7	4-Cl	1 h	98	98
8	4-Br	2 h	96	48
9	2-MeO	4 h	95	24
10	4-MeO	3 h	93	31
Cat: Ir(III) complex, **3**				
11	4-F	1 h	98	98
12	4-Cl	1 h	97	97
13	4-Br	3 h	96	32
14	2-MeO	5 h	94	19
15	4-MeO	4 h	92	23

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, respectively, the concentration of acetophenone derivatives is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

Table 3
Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems prepared from $((Ph_2PNH)_2C_{10}H_6N_2)$ and $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$.[a]

Entry	Catalyst	Time	Substrate	Product	Conversion (%)[b]	TOF (h^{-1})[c]
1	**1**	15 min			98	392
2	**2**	2 h			98	20
3	**3**	5 h			99	49
4	**1**	20 min			98	294
5	**2**	4 h			99	25
6	**3**	12 h			98	<10
7	**1**	30 min			98	196
8	**2**	5 h			97	20
9	**3**	15 h			97	<10
10	**1**	1 h			98	98
11	**2**	12 h			98	<10
12	**3**	24 h			97	<10

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, respectively, the concentration of alkyl phenyl ketones is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

analogous Rh(I) and Ir(III) complexes. The modular construction of these catalysts and their flexibility toward transfer hydrogenation make these systems to pursue.

4. Experimental

4.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glass-ware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl and 2-chloro-3-nitropyridine are purchased from Fluka and were used as received. The starting materials 3,3′-diamino-2,2′-bipyridine [74], 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine [75], $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ [76], $Rh(\mu\text{-Cl})(cod)]_2$ [77], $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ [78] were prepared according to literature procedures. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P $\{^1H\}$ NMR spectra (162.0 MHz) were recorded on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by Gallenkamp Model apparatus with open capillaries.

4.2. GC analyses

GC analyses were performed on a Shimadzu 2010 Plus Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of ketones were as follows; initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 °C/min; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

4.3. Syntheses of transition metal complexes

4.3.1. Synthesis of $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**

To a solution of $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ (92.8 mg, 0.180 mmol) in THF, a solution (THF 30 mL) of $(Ph_2PNH)_2C_{10}H_6N_2$, (100 mg, 0.180 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 3 h. After this time, the solution was filtered off and the solvent evaporated under vacuum, the solid residue thus obtained was washed with diethyl ether (3 × 15 mL) and then dried under vacuum (Scheme 1). Following recrystallization from diethylether/CH_2Cl_2, a red powder was obtained (yield 170 mg, 89.4%), m.p. >200 °C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$) δ = 12.75 (d, 2H, $^2J_{NHP}$ = 10.40 Hz, N**H**–P), 8.12 (d, 2H, J = 4.24, **H**-6), 8.03 (dd, 8H, J = 8.48 and 8.64 Hz, *o*-protons of phenyls), 7.55–7.40 (m, 12H, *m*- and *p*-protons of phenyls), 7.35 (d, 2H, J = 8.40, **H**-4), 6.86 (dd, 2H, J = 4.48 and 8.40, **H**-5), 5.47 (d, 12H, ^3J = 4.8 Hz, aromatic protons of benzene), ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 89.33 (d, ^2J = 3.00 Hz, aromatic carbons of benzene), 122.81 (**C**-5), 127.50 (**C**-4), 128.40 (d, J = 10.40 Hz, *m*-carbons of phenyls), 130.99 (s, *p*-carbons of phenyls), 132.50 (d, J = 10.10 Hz, *o*-carbons of phenyls), 134.90 (d, J = 34.00 Hz, *i*-carbons of phenyls), 137.54 (**C**-6), 142.12 (**C**-2), 148.40 (**C**-3); assignment was based on the $^1H^{13}C$ HETCOR and $^1H^1H$ COSY spectra; ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 52.03 (s); IR, (KBr): υ = 928 (P–NH), 1435 (P–Ph), 1584 (C=N), 3460 (N–H) cm^{-1}; $C_{46}H_{40}N_4P_2Ru_2Cl_4$ (1054.748 g/mol): calcd. C 52.34, H 3.82, N 5.31; found C 51.86, H 3.76, N 5.25%.

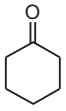
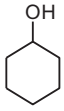
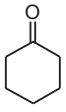
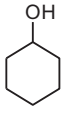
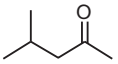
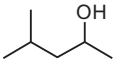
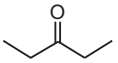
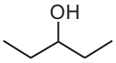
4.3.2. Synthesis of $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2**

A mixture of $[Rh(\mu\text{-Cl})(cod)]_2$ (90.6 mg, 0.180 mmol) and $(Ph_2PNH)_2C_{10}H_6N_2$, **1** (100 mg, 0.180 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 2 h. The volume of the solvent was then reduced to 0.5 mL before addition of diethyl ether (10 mL). The precipitated product was filtered off and dried *in vacuo* yielding **2** as a yellow microcrystalline solid (Scheme 1). Yield 166 mg, 88.1%, m.p. >200 °C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$) δ = 12.65 (d, 2H, $^2J_{NHP}$ = 10.80 Hz, N**H**–P), 8.04 (d, 2H, J = 3.60, **H**-6), 7.95 (d, 2H, J = 8.00, **H**-4), 7.83 (dd, 8H, J = 4.12 and 10.12 Hz, *o*-protons of phenyls), 7.47–7.37 (m, 12H, *m*- and *p*-protons of phenyls), 6.99 (dd, 2H, J = 4.80 and 6.00, **H**-5), 5.57 (br, 8H, C**H** of cod), 2.12 (br, 8H, C**H$_2$** of cod), 2.00 (br, 8H, C**H$_2$** of cod); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.59 (**C**H$_2$ of cod), 33.01 (–**C**H$_2$–), 106.79 (**C**H of cod), 122.23 (**C**-5), 126.60 (**C**-4), 128.37 (d, J = 11.07 Hz, *m*-carbons of phenyls), 130.31 (s, *p*-carbons of phenyls), 132.16 (d, J = 12.07 Hz, *o*-carbons of phenyls), 133.24 (d, J = 46.60 Hz, *i*-carbons of phenyls), 136.46 (C-6), 141.98 (**C**-2), 145.50 (**C**-3); assignment was based on the $^1H^{13}C$ HETCOR and $^1H^1H$ COSY spectra; ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 55.35 (d, ^1J ($^{103}Rh^{31}P$) = 163.62 Hz); IR, (KBr): υ = 905 (P–NH), 1435 (P–Ph), 1582 (C=N), 3418 (N–H) cm^{-1}; $C_{50}H_{52}N_4P_2Rh_2Cl_2$ (1047.652 g/mol): calcd. C 57.32, H 5.00, N 5.35; found C 56.96, H 4.88, N 5.27%.

4.3.3. Synthesis of $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**

A mixture of $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ (149.4 mg, 0.180 mmol) and $(Ph_2PNH)_2C_{10}H_6N_2$, **1** (100 mg, 0.180 mmol) in 20 mL of tetrahydrofuran was stirred at room temperature for 2 h. The volume of the solvent was then reduced to 0.5 mL before addition of diethyl ether (10 mL). The precipitated product was filtered off and dried *in vacuo* yielding **3** as an orange microcrystalline solid (Scheme 1). Yield 224 mg, 92.0%, m.p. >250 °C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$)

Table 4
Transfer hydrogenation of various simple ketones with *iso*-PrOH catalyzed by $[C_{10}H_6N_2\{NHPPh_2Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1**, $[C_{10}H_6N_2\{PPh_2NHRh(cod)Cl\}_2]$, **2** and $[C_{10}H_6N_2\{NHPPh_2Ir(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$, **3**.[a]

Entry	Catalyst	Substrate	Product	Time	Conversion (%)[b]
1	**1**			20 min	98
2	**2**			1.5 h	97
3	**3**			4 h	98
4	**1**			20 min	99
5	**2**			1.5 h	98
6	**3**			4 h	98
7	**1**			1 h	99
8	**2**			3 h	98
9	**3**			8 h	97
10	**1**			2 h	99
11	**2**			5 h	99
12	**3**			12 h	98

[a] Reaction condition: Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[b] Reaction condition: Determined by GC (three independent catalytic experiments). Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.

δ = 12.94 (d, 2H, $^2J_{NHP}$ = 8.00 Hz, N**H**–P), 8.21 (dd, 8H, J = 3.84 and 7.60 Hz, *o*-protons of phenyls), 8.03 (d, 2H, J = 4.28, **H**-6), 7.86 (d, 2H, J = 8.40, **H**-4), 7.40–7.35 (m, 12H, *m*- and *p*-protons of phenyls), 7.06 (dd, 2H, J = 4.40 and 8.32, **H**-5), 1.36 (d, 30H, ^4J = 2.0 Hz, C**H$_3$** of Cp* (C_5Me_5)); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 8.19 (C_5**Me**$_5$), 93.61 (**C**$_5Me_5$), 123.30 (**C**-5), 128.48 (**C**-4), 128.03 (d, J = 10.06 Hz, *m*-carbons of phenyls), 130.78 (s, *p*-carbons of phenyls), 132.85 (d, J = 11.07 Hz, *o*-carbons of phenyls), 132.00 (d, J = 38.20 Hz, *i*-carbons of phenyls), 136.73 (**C**-6), 143.41 (**C**-2), 146.68 (**C**-3), assignment was based on the ^{1}H^{13}C HETCOR and ^{1}H^{1}H COSY spectra; ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 23.38 (s); IR, (KBr): υ = 924 (P–NH), 1438 (P–Ph), 1559 (C=N), 3415 (N–H) cm^{-1}; $C_{54}H_{58}N_4P_2Ir_2Cl_4$ (1351.227 g/mol): calcd. C 48.00, H 4.33, N 4.15; found C 47.86, H 4.27, N 4.12%.

4.3.4. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of complexes [$C_{10}H_6N_2${$NHPPh_2Ru(\eta^6$-benzene)Cl_2}$_2$], **1**, [$C_{10}H_6N_2${PPh_2NHRh(cod)Cl}$_2$], **2** and [$C_{10}H_6N_2${$NHPPh_2Ir(\eta^5$-C_5Me_5)Cl_2}$_2$], **3** (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) were refluxed for 10 min for **1**, 1 h for **2** and 3 h for **3**. After this period a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. Conversions obtained are related to the residual unreacted ketone.

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References

[1] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129–170.
[2] H. Jiang, Q.D. Qiao, H. Gong, Kinet. Catal. Lett. 65 (1998) 193–197.
[3] S. Gladiali, G. Mestroni, in: M. Beller, C. Bolm (Eds.), Transition Metal for Organic Synthesis, vol. 2, Wiley-VCH, Weinheim, 1998, pp. 97–119.
[4] H. Siegel, V. Himmele, Angew. Chem. 92 (1980) 182–187.
[5] C. Botteghi, S. Paganelli, A. Schionato, M. Marchetti, Chirality 3 (1991) 355–369.
[6] K. Nishide, M. Node, Chirality 14 (2002) 759–767.
[7] T. Ooi, T. Ichikawa, K. Maruoka, Angew. Chem. Int. Ed. 113 (2001) 3722–3724.
[8] Y.Y. Kuo, M.F. Haddow, A. Perez-Rodondo, G.R. Owen, J. Chem. Soc. Dalton Trans. 39 (2010) 6239–6248.
[9] H.U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 345 (2003) 103–151.
[10] T. Ikariya, K. Murata, R. Noyori, Biomol. Chem. 4 (2006) 393–406.
[11] S. Gladiali, E. Alberico, Chem. Soc. Rev. 35 (2006) 226–236.
[12] (a) L.H. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983, pp. 137–165;
(b) P.W.N.M. Van Leeuwen, Organometallics 16 (1997) 3027–3037;
(c) T.J. Kwok, D.J. Wink, Organometallics 12 (1993) 1954–1959;
(d) I. Suisse, H. Bricout, A. Mortreux, Tetrahedron Lett. 35 (1994) 413–416;
(e) D. Gleich, R. Schmid, W.A. Herrmann, Organometallics 17 (1998) 2141–2143;
(f) S. Ganguly, R.M. Roundhill, Organometallics 12 (1993) 4825–4832;
(g) B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177–186.
[13] (a) J.T. Mague, J. Krinsky, Inorg. Chem. 40 (2001) 1962–1971;
(b) A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Rev. (1998) 1537–1540;
(c) K.V. Katti, V.S.R. Reddy, P.R. Singh, Chem. Soc. Rev. (1995) 97–107.
[14] P.C.J. Kamer, P.W.N.M. Leeuwen, J.N.H. Reek, Acc. Chem. Res. 34 (2001) 895–904.
[15] (a) N. Biricik, C. Kayan, F. Durap, B. Gümgüm, Z. Fei, R. Scopelliti, P.J. Dyson, N. Gürbüz, İ. Özdemir, Inorg. Chim. Acta 363 (2010) 1039–1047;
(b) K.G. Gaw, M.B. Smith, J.W. Steed, J. Organomet. Chem. 664 (2002) 294–297.
[16] H.J. Chen, J.M. Barendt, R.C. Haltiwanger, T.G. Hill, A.D. Norman, Sulfur 26 (1986) 155–162.
[17] P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1) (1995) 3367–3388.
[18] M. Aydemir, A. Baysal, B. Gümgüm, Appl. Organomet. Chem. 693 (2008) 3810–3814.
[19] S.D. Ittel, C.A. Tolman, A.D. English, J.P. Jesson, J. Am. Chem. Soc. 100 (1978) 7577–7585.
[20] M. Antberg, L. Dahlenberg, Angew. Chem. Int. Ed. 25 (1986) 260–261.
[21] J.F. Hartwig, R.A. Anderson, R.G. Bergman, Organometallics 10 (1991) 1710–1719.
[22] Y. Wang, X. Li, K. Ding, Tetrahedron Lett. 43 (2002) 159–161.
[23] D.P. Catsoulocas, B.R. Steele, G.A. Herapoulos, M. Micha-Screttas, C.G. Screttas, Tetrahedron Lett. 44 (2003) 4575–4578.
[24] M. Aydemir, A. Baysal, G. Öztürk, B. Gümgüm, Appl. Organomet. Chem. 23 (2009) 108–113.
[25] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Appl. Organomet. Chem. 23 (2009) 467–475.
[26] M.L. Clarke, D.J. Cole-Hamilton, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2001) 2721–2723.
[27] M. Aydemir, F. Durap, A. Baysal, O. Akba, B. Gümgüm, S. Özkar, L.T. Yıldırım, Polyhedron 28 (2009) 2313–2320.
[28] R. Spogliarich, J. Kaspar, M. Graziani, J. Organomet. Chem. 306 (1986) 407–412.
[29] A.M. Maj, M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, Tetrahedron: Asymmetry 10 (1999) 831–835.
[30] P.R. Hoffman, K.G. Caulton, J. Am. Chem. Soc. 97 (1975) 4221–4228.
[31] M.S. Balakrishna, R. Panda, D.C. Smith Jr., A. Klaman, S.P. Nolan, J. Organomet. Chem. 599 (2000) 159–165.
[32] C. Kayan, N. Meric, M. Aydemir, A. Baysal, D. Elma, B. Ak, E. Sahin, N. Gürbüz, İ. Özdemir, Polyhedron 42 (2012) 142–148.
[33] M. Aydemir, A. Baysal, N. Meric, C. Kayan, B. Gümgüm, S. Özkar, E. Sahin, J. Organomet. Chem. 696 (2011) 2584–2588.
[34] M. Aydemir, A. Baysal, N. Meric, C. Kayan, M. Toğrul, B. Gümgüm, Appl. Organomet. Chem. 24 (2010) 215–221.
[35] M. Aydemir, A. Baysal, Polyhedron 29 (2010) 1219–1224.
[36] R.J. Haines, M. Laing, E. Meintjies, P. Sommerville, J. Organomet. Chem. 215 (1981) C17–C19.
[37] M.S. Balakrishna, V.S.R. Reddy, S.S. Krishnamurthy, J.C.T.R. Burckette St Laurent, J.F. Nixon, Coord. Chem. Rev. 129 (1994) 1–90.
[38] M.S. Balakrishna, S.S. Krishnamurthy, Inorg. Chim. Acta 230 (1995) 245–248.
[39] M.S. Balakrishna, B. Santarsiero, R.G. Cavel, Inorg. Chem. 33 (1994) 3079–3084.
[40] M.S. Balakrishna, S.S. Krishnamurthy, R. Murugavel, M. Netaji, I.I. Mathews, J. Chem. Soc. Dalton Trans. (1993) 477–482.
[41] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, J. Organomet. Chem. 694 (2009) 2488–2492.
[42] K.G. Gaw, M.B. Smith, A.M.Z. Slawin, New J. Chem. 24 (2000) 429–435.
[43] F. Durap, N. Biricik, B. Gümgüm, S. Özkar, W.H. Ang, Z. Fei, R. Scopelliti, Polyhedron 27 (2008) 196–202.
[44] A.D. Burrows, M.F. Mahon, M.T. Palmer, J. Chem. Soc. Dalton Trans. (2000) 1669–1677.
[45] H. Le Bozec, D. Touchard, P.H. Dixneuf, Adv. Organomet. Chem. 29 (1989) 163–247.
[46] M. Aydemir, A. Baysal, N. Gürbüz, İ. Özdemir, B. Gümgüm, S. Özkar, N. Çaylak, L.T. Yıldırım, Appl. Organomet. Chem. 24 (2010) 17–24.
[47] M. Hariharasarma, C.H. Lake, C.L. Watkins, G.M. Gray, J. Organomet. Chem. 580 (1999) 328–338.
[48] Q. Zhang, G. Hua, P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2003) 3250–3257.
[49] P. Bhattacharyya, T.Q. Ly, A.M.Z. Slawin, J.D. Woollins, Polyhedron 20 (2001) 1803–1808.
[50] F. Majoumo, P. Lönnecke, O. Kühl, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 630 (2004) 305–308.
[51] H.L. Milton, M.V. Wheatley, A.M.Z. Slawin, J.D. Woollins, Polyhedron 23 (2004) 3211–3220.
[52] A.M.Z. Slawin, J. Wheatley, J.D. Woollins, Polyhedron 23 (2004) 2569–2574.
[53] R. Ceron-Camacho, V. Gomez-Benitez, R. Le Lagadec, D. Morales-Morales, R.A. Toscano, J. Mol. Catal. A: Chem. 247 (2006) 124–129.
[54] M.S. Balakrishna, P.P. George, S.M. Mobin, Polyhedron 24 (2005) 475–480.
[55] T.J. Geldbach, A.B. Chaplin, K.D. Hanni, R. Scopelliti, P.J. Dyson, Organometallics 24 (2005) 4974–4980.
[56] R. Tribo, S. Munoz, J. Pons, R. Yanez, A. Alvarez-Larena, J.F. Piniella, J. Ros, J. Organomet. Chem. 690 (2005) 4072–4079.
[57] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F.A. England, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 37 (1998) 1703–1707.
[58] H. Zhang, B.C. Yang, Y.Y. Li, Z.R. Donga, J.X. Gao, H. Nakamura, K. Murata, T. Ikariya, Chem. Commun. (2003) 142–143.
[59] R. Guo, X. Chen, C. Elphelt, D. Song, R.H. Morris, Org. Lett. 7 (2005) 1757–1759.
[60] P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, Organometallics 24 (2005) 5836–5844.
[61] J.W. Faller, A.R. Lavoie, Organometallics 20 (2001) 5245–5247.
[62] J.X. Gao, X.D. Yi, P.P. Xu, C.L. Tang, H.L. Wan, T. Ikariya, J. Organomet. Chem. 592 (1999) 290–295.
[63] J.X. Gao, H. Zhang, X.D. Yi, P.P. Xu, C.L. Tang, H.L. Wan, K.R. Tsai, T. Ikariya, Chirality 12 (2000) 383–388.
[64] J.S. Chen, Y.Y. Li, Z.R. Dong, B.Z. Li, J.X. Gao, Tetrahedron Lett. 45 (2004) 8415–8418.
[65] Z.R. Dong, Y.Y. Li, J.S. Chen, B.Z. Li, Y. Xing, J.X. Gao, Org. Lett. 7 (6) (2005) 1043–1045.
[66] R. Noyori, T. Ohkuma, Angew. Chem. Int. Ed. 40 (2001) 40–73.
[67] J. Canivet, G. Labat, H. Stockli-Evans, G. Süss-Fink, Eur. J. Inorg. Chem. (2005) 4493–4500.
[68] P. Stepnicka, J. Ludvíc, J. Canivet, G. Süss-Fink, Inorg. Chim. Acta 359 (2006) 2369–2374.
[69] S.C. Stinson, Chem. Eng. News 77 (1999) 101–120.
[70] H.U. Blaser, F. Spindler, M. Studer, Appl. Catal. A 221 (2001) 119–143.
[71] Z. Fei, R. Scopelliti, P.J. Dyson, Inorg. Chem. 42 (2003) 2125–2130.
[72] Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 530–537.

[73] S. Berger, S. Braun, H.O. Kolinowski, NMR-Spektroskopie von Nichtmetallen Band 3, ^{31}P NMR-Spektroskopie, Georg Theime Verlag, Stuttgart, New York, 1993.
[74] (a) S. Kanoktanaporn, J.A. Hugh-MacBride, J. Chem. Soc. Perkin 1 (1978) 1126–1131; (b) L. Kaczmarek, P. Nontha-Namirski, Acta Pol. Pharm. XXXVI (1979) 629–634.
[75] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Polyhedron 26 (2007) 3373–3378.
[76] R.A. Zelonka, M.C. Baird, J. Organomet. Chem. 35 (1972) C43–C46.
[77] G. Giordano, R.H. Crabtree, Inorg. Synth. 28 (1990) 88–90.
[78] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228–234.