A comparison of catalytic activity for imine hydrogenation using Ru ditertiary phosphine complexes, including chiral systems

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Abstract

A family of ruthenium ditertiary phosphine complexes was investigated for catalytic activity toward imine hydrogenation. The diphosphines (PP) used include chiral (chiraphos, diop, binap) and achiral (dppe, dppb) systems (chiraphos = $Ph_2PCH(Me)CH(Me)PPh_2$; diop = $Ph_2PCH_2CHOCMe_2OCHCH_2PPh_2$; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; $Ph_2P(CH_2)_nPPh_2$ ($n=2$, dppe; $n=4$, dppb)). Activity was observed in MeOH at low catalyst concentrations (0.77 mM Ru), under moderate conditions (room temperature (r.t.), 1000 psi H_2). The air-stable $Ru_2Cl_5(PP)_2$ complexes were more active than the commonly used dimeric $Ru_2(II,II)$ systems to which they give rise *in situ*. Asymmetric induction in the prochiral ketimine $PhCH_2N=C(Me)Ph$ was consistent, though modest, within the diop and binap series of neutral complexes, implying a common catalytic intermediate within each series. A maximum e.e. of 27% was found using $Ru_2Cl_5(chiraphos)_2$ as catalyst; this represents a non-optimized figure for asymmetric induction, as no other prochiral ketimines were screened.

Key words: Catalysis; Imine hydrogenation; Nitrile complexes; Ruthenium complexes; Phosphine complexes

Introduction

Mechanistic studies of homogeneous hydrogenation using Ru catalysts from this laboratory have demonstrated that maximum activity, as well as optimum efficiency in utilization of the phosphine ligand, is realized by use of systems in which the metal center is bound to a single diphosphine ligand [1, 2]. The present paper describes the use of a family of mono- and diruthenium complexes, most of them containing the RuCl(PP) unit (PP = chiral and achiral diphosphines; Fig. 1), for catalytic hydrogenation of imines, specifically some aldimines (eqn. (1)) and a prochiral ketimine (eqn. (2)).

$$RN=C(H)Ph \xrightarrow{H_2} RNHCH_2Ph \quad (1)$$

(R = alkyl, aryl)

$$PhCH_2N=C(Me)Ph \xrightarrow{H_2} PhCH_2NHCH(Me)Ph \quad (2)$$

The accessibility of pathways relating these closely similar systems permitted assessment of the effect on catalyst activity and enantioselectivity of minor molecular modification, a feature frequently cited as one of the principal advantages of soluble over bulk catalyst systems, but less often investigated. We chose to examine the utility of these systems for imine hydrogenation under standard sets of conditions, in an effort to extend

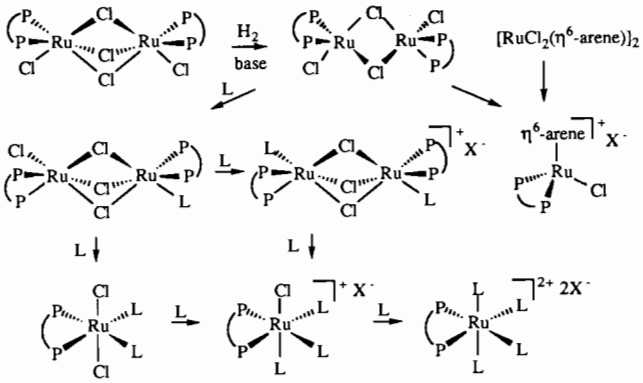

Fig. 1. Summary of some complexes prepared and investigated for catalytic activity; PP = dppe, dppb, chiraphos, diop, or binap; L = MeCN or PhCN; X = Cl or PF_6. Not shown here are $[Ru(H)Cl(dppb)]_3$, $Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$, $[RuCl_2(dppb)]_2$-(μ-dppb), $[RuCl_2(C_6H_6)]_2$(μ-dppe) and $RuCl_2(PP)(PPh_3)$ (PP = diop, binap) (see text).

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the useful range of such catalyst systems while at the same time establishing a basis for their comparison. Part of this work has been presented at meetings [3].

Promising results, in terms of both activity and (for the chiral systems) enantioselectivity, have been reported for several of these catalysts in homogeneous hydrogenation of various olefinic or ketonic substrates, principally with dinuclear complexes such as $Ru_2Cl_4(PP)_2$ (PP = dppb, diop, chiraphos) [4, 5] and $Ru_2Cl_4(binap)_2(NEt_3)$ [6–10]. Mononuclear complexes such as $RuCl(binap)(arene)^+X^-$ and $RuCl_2(binap)(PhCN)_2$, though less frequently used, have given good results in similar applications [11, 12]. While the activity of a number of the binap complexes has been investigated, as these results indicate, wide variations in the conditions and substrates employed preclude comparison. Many of the remaining complexes in Fig. 1 are either novel [13, 14] or have been neglected as potential catalysts.

Homogeneous hydrogenation of carbon–nitrogen double bonds, though more difficult and consequently less developed than the corresponding reduction of carbon–carbon and carbon–oxygen double bonds, has been the focus of much recent attention [15–21]. Most of the catalysts used for imine hydrogenation to date have been based on Rh and Ir systems; high activity and in some cases e.e. values of >90% have been achieved [16–21]. Use of ruthenium catalysts for this purpose remains little explored, despite the wider applicability demonstrated by ruthenium systems in the reduction of a wide range of olefin and carbonyl functionalities [22–24]. Few reports of ruthenium-catalyzed imine hydrogenations have appeared [3, 21, 25–28], and these include a single, promising, example of asymmetric hydrogenation (>99% e.e. was found for hydrogenation of a specific imine substrate (a sultam precursor) using an *in situ* catalyst presumed to be $Ru_2Cl_4(binap)_2(NEt_3)$ [26]).

Experimental

Solvents were dried and degassed by distillation under N_2, from Mg/I_2 or K_2CO_3 (alcohols) or sodium-benzophenone (C_6H_6). NMR spectra were recorded on a Varian XL-300 spectrometer. Hydrogenation experiments were conducted in a stainless steel autoclave equipped with a high-pressure regulator and connected to a vacuum line. Oxygen was removed from the system by evacuating the autoclave and refilling with N_2 three times, then H_2, and purging three times with H_2 before adjusting to the desired pressure. Conversions were determined by ^1H NMR, and e.e. values were measured by NMR spectra of diastereomers formed with α-mandelic acid [20]. Imines were prepared by condensation of the appropriate aldehyde or ketone with amine and stored under Ar in the dark. The syntheses and characterization of the ruthenium complexes have been described elsewhere: $Ru_2Cl_5(PP)_2$ [29, 30], $Ru_2Cl_4(PP)_2$ [29, 31], $[Ru(H)Cl(dppb)]_3$ [4, 23], $Ru_2Cl_4(PP)_2(L)$ (L = RCN [14, 32], $NH(CH_2Ph)_2$ [14, 32]), $Ru_2Cl_3(dppb)_2(RCN)_2^+PF_6^-$ [14, 31, 32], $RuCl_2(PP)(PhCN)_2$ [14, 32], $RuCl(PP)(RCN)_3^+PF_6^-$ [14, 31, 32], $Ru(dppb)(MeCN)_4^{2+}2PF_6^-$ [14, 32], $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ [33], $RuCl(PP)(C_6H_6)^+PF_6^-$ [13, 34], $[RuCl_2(C_6H_6)]_2(\mu\text{-dppe})$ [13, 34], *trans*-$RuCl_2(dppe)_2$ [35], $RuCl_2(PP)(PPh_3)$ [29, 36].

Results and discussion

Several factors influence the reproducibility of the reaction rates in the systems under study. Conversions are very sensitive to the presence of trace oxygen. Displacement of air from the autoclave assembly by a stream of N_2 was inefficient; variable, low conversions were obtained unless the autoclave assembly was evacuated as described above. Catalyst poisoning by reduction products, cited as a potential problem in catalytic hydrogenation of carbonyl groups and imines [37–40], was not observed; for example, addition of dibenzylamine (7.65 mM, 10 equiv. per Ru) caused no rate inhibition in reduction of $PhCH_2N{=}C(H)Ph$ using $Ru_2Cl_5(dppb)_2$ (**1**) as catalyst (1000 psi H_2, r.t., MeOH, 0.77 mM Ru, 0.153 M imine), see Tables 1 and 2. The steric bulk of this amine may hamper its coordination to the metal center (relative to imine). Decreases in conversion were, however, observed on use of samples of imine which had undergone partial hydrolysis over several weeks' exposure to air. As the reduction rate of $PhCH_2N{=}C(H)Ph$ using **1** was unaffected by addition of benzaldehyde (7.65 mM, 10 equiv. per Ru), this must be due to inhibition by small amounts of the primary amine derived from imine hydrolysis. Addition of benzylamine (7.65 mM, 10 equiv. per Ru) did in fact cause a sharp decrease in conversion, from 98 to 77% over 1 h (Table 2). Reaction of **1** with benzylamine yields $RuCl_2(dppb)(NH_2CH_2Ph)_2$ [14]; as high conversions were found using the isolated complex as a catalyst for reduction of aldimine (Table 2), the activity of this

TABLE 1. Dependence of conversion on N-substituent of imine in reduction of $RN{=}C(H)Ph$ using $Ru_2Cl_5(dppb)_2$ as catalyst[a]

Substituent R	Me	CH_2Ph	$CHMe_2$	cyclohexyl	Ph
Conversion (%)	53	84	30	25	10

[a]1000 psi H_2, r.t., 10 ml MeOH, 0.77 mM Ru (expressed as monomer concentration), [imine] = 0.153 M (imine added before MeOH), 0.5 h reaction time.

TABLE 2. Conversion data (%) for reduction of $PhCH_2N{=}C(R)Ph$ using Ru catalysts[a]

Entry	Catalyst	R = H[b]	R = Me[c]
1	$Ru_2Cl_5(dppb)_2$ (**1**)	98[d]	78
2	$Ru_2Cl_4(dppb)_2$ (**2**)	87	76
3	$[Ru(H)Cl(dppb)]_3$		61
4	$Ru_2Cl_4(dppb)_2(MeCN)$	84	76
5	$Ru_2Cl_4(dppb)_2(PhCN)$	81	74
6	$Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$	0[e]	35
7	$RuCl_2(dppb)(NH_2CH_2Ph)_2$	90	
8	$RuCl_2(dppb)(PhCN)_2$	6	51
9	$RuCl(dppb)(MeCN)_3{}^+PF_6{}^-$	8	43
10	$RuCl(dppb)(PhCN)_3{}^+PF_6{}^-$		56
11	$Ru(dppb)(MeCN)_4{}^{2+}2PF_6{}^-$	3	38
12	$Ru_2Cl_3(dppb)_2(MeCN)_2{}^+PF_6{}^-$	10	63
13	$Ru_2Cl_3(dppb)_2(PhCN)_2{}^+PF_6{}^-$	8	65
14	$[RuCl_2(dppb)]_2(\mu\text{-dppb})$	10	12
15	$RuCl(dppb)(C_6H_6)^+PF_6{}^-$	7[f]	46

[a]1000 psi H_2, r.t., 10 ml MeOH, 0.77 mM Ru, [imine] = 0.153 M. In all cases the imine was added directly to the catalyst, followed by MeOH. [b]Conversion measured after 1.0 h reaction. [c]Conversion measured after 24 h reaction. [d]Conversion measured after 24 h for different solvents: MeOH (100%), 5% C_6H_6 in MeOH (100), EtOH (70), C_6H_6 (4), MeCN (2); after 1 h, for 5% C_6H_6 in MeOH (97%). [e]Conversion was 85% after 24 h. [f]Conversion was 100% after 24 h; cf. 83% for the corresponding complex of dppe, 35% for $[RuCl_2(C_6H_6)]_2(\mu\text{-dppe})$, and 1% for *trans*-$RuCl_2(dppe)_2$. In EtOH or ^{i}PrOH, using $RuCl(dppb)(C_6H_6)^+PF_6{}^-$, the conversions were 100 and 70% in 24 h, respectively.

species must be governed by dissociation of amine, which is inhibited in the presence of excess amine. Careful purification and storage of the imine are clearly crucial for maintenance of an accurate standard for assessment of catalytic activity.

The sequence of addition of reagents was also important for liquid imines. Conversions were 15% lower after 1 h reaction time when solvent was added directly to catalyst **1**, followed by imine; the reverse order of addition perhaps promotes formation of Ru(imine) species. Kinetic studies carried out with $Ru_2Cl_5(dppb)_2$ as catalyst and the imines $RN{=}C(H)Ph$ (R = Ph or CH_2Ph; 1000 psi H_2, r.t., MeOH) are consistent with an unsaturate route in which a Ru^{II}(imine) species reacts with H_2 in a rate-determining step: conversions are essentially independent of [imine] and show an approximately first-order dependence on $[H_2]$ [14]. The reduction rate is sensitive to the bulk of the imine, showing a reactivity sequence (Table 1) largely consistent with expected steric effects, highest conversions being found for the least bulky substrates, presumably owing to their more facile binding to the Ru center; the data could again be rationalized invoking an unsaturate route. The high reactivity of the N-benzyl, relative to the N-methyl, imine may indicate an electronic contribution not yet understood. The slower rate of reduction of the ketimine $PhCH_2N{=}C(R)Ph$, R = Me, versus the aldimine, R = H, seems reasonable on steric grounds. A more subtle factor that can influence the conversions observed with both this ketimine and the aldimine $PhN{=}C(H)Ph$ over shorter reaction times may be their phase. As contact between the Ru species and a solid imine is limited until the imine dissolves, the effective order of addition of reagents for these two solid substrates was MeOH then imine (see above).

Conversions depend strongly on the solvent employed; as earlier found with rhodium systems [17, 21, 41], maximum activity requires alcohol solvents, possibly because of an alcohol-binding step in the catalytic cycle. The probable reactivity sequence MeOH > EtOH > ^{i}PrOH (Table 2, footnotes d and f) may indicate a sensitivity to the steric bulk of the alcohol ligand. Low conversions result from use of neat C_6H_6 (Table 2, footnote d), though catalyst poisoning by small amounts of added C_6H_6 noted in some Rh systems [41] is not observed in the $Ru_2Cl_5(dppb)_2/PhCH_2N{=}C(H)Ph$ system (Table 2, footnote d).

Comparative catalytic activity toward reduction of the aldimine $PhCH_2N{=}C(H)Ph$ and the corresponding ketimine $PhCH_2N{=}C(Me)Ph$ was measured under standard conditions, as shown in Table 2. The most active of the catalyst systems studied is the readily accessible, air-stable, Ru_2(II,III) species $Ru_2Cl_5(dppb)_2$ (**1**), which is reduced *in situ* to the Ru_2(II,II) species $Ru_2Cl_4(dppb)_2$ (**2**). A somewhat lower conversion is observed using $Ru_2Cl_4(dppb)_2$ directly (entry 2), probably because of its air-sensitivity, and consequent difficulties in handling, especially with liquid imine. The imine itself, or amine product, may function as the base necessary to effect reduction of **1** and abstraction of HCl [4], eqn. (3).

$$Ru_2Cl_5(PP)_2 + \tfrac{1}{2}H_2 \xrightarrow{\text{base}} Ru_2Cl_4(PP)_2 + \text{base}\cdot HCl \qquad (3)$$

Further abstraction of HCl, leading to Ru_2 chlorohydrido species, including $[Ru(H)Cl(dppb)]_3$, which has been isolated via such chemistry [4], appears unlikely; not only is the comparative activity of the isolated trimer relatively low (entry 3), but the tetrachloro complex $Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$ has been identified as the sole ruthenium product under related reaction conditions, though at higher [Ru] [14] (i.e. from solutions of **1** and $PhCH_2N{=}C(H)Ph$ under H_2).

An investigation of the kinetics of hydrogenation of $RN{=}C(H)Ph$ (R = CH_2Ph, Ph) using **1** as catalyst indicated a metal dependence that goes from first to half-order with increasing [Ru] [14]. This suggests dissociation to an active mononuclear Ru species, most likely a catalyst precursor of the type $RuCl_2(dppb)S_2$, where S = MeOH. The Ru_2(II,II) species **2** may be expected to behave in the same way, while the nitrile derivatives $Ru_2Cl_4(dppb)_2(RCN)$ could dissociate to give $RuCl_2(dppb)(MeOH)_2$ and $RuCl_2(dppb)(MeOH)$-

(RCN) species. Facile loss of nitrile from the latter is implied by the close correspondence between the activity of these nitrile complexes and **2** itself (entries 2, 4, 5), and is consistent with the usual view of nitriles as weak donor ligands [42]. These results contrast strongly with the lower activity of $RuCl_2(dppb)(PhCN)_2$ (entry 8), however, and perhaps imply a much lower lability for the nitrile ligand in the latter complex, relative to the coordinated nitrile in $RuCl_2(dppb)(MeOH)(RCN)$ (as well as, more predictably [42], to coordinated MeOH). The mononuclear cationic species, particularly the dication, are also generally less active, perhaps because the positive charge further reduces the lability of the donor ligands. The intermediate conversions observed for $Ru_2Cl_3(dppb)_2(RCN)_2^+$ could thus result from breakdown to an active neutral, nitrile-containing fragment and a less active cationic species.

The zero conversion found with the amine adduct $Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$ for the aldimine after 1 h reaction time is anomalous within this series. Some loss in activity might result from lower lability of the dibenzylamine ligand, but this should at most halve the conversion relative to the corresponding nitrile complexes, assuming dissociation to monomers occurs. The zero activity observed suggests either that the dibenzylamine ligand inhibits dissociation into mononuclear species, or that some other, as yet unknown, factor is involved (such as slow dissolution/dissociation of the complex, which would lead to an 'induction period'; note that significant conversions are realized for both the aldimine and the ketimine after 24 h). If the problem arises from a property of the amine ligand, this point may be of more general significance, given the similarity between this complex and the well-known binap species $Ru_2Cl_4(binap)_2(NEt_3)$ [22, 24, 26]. Use of the readily accessible nitrile analogues, or indeed of the air-stable species $Ru_2Cl_5(binap)_2$ (with added base, for non-basic substrates) may permit a substantial improvement in activity, without adversely affecting the high enantioselectivities attainable with the triethylamine complex. Studies are now in hand to test this suggestion.

The phosphine-bridged complex $[RuCl_2(dppb)]_2(\mu$-dppb) (entry 14) provides a useful contrast to these systems. Despite its coordinative unsaturation at both metal sites, the activity of this species is no higher than that of the six-coordinate complexes, and is considerably lower than that of the halide-bridged dimer **2**. It is possible that the phosphine-bridged structure is less able to accommodate incoming ligands (including substrates) than the corresponding halide-bridged system, perhaps because the integrity of the dinuclear structure is retained.

The η^6-benzene species $RuCl(dppb)(C_6H_6)^+PF_6^-$ (entry 15) displays an activity toward aldimine and ketimine reduction comparable to that of the cationic tris(nitrile) complexes (entries 9 and 10). The corresponding dppe complex (footnote f) gives lower conversions for the more easily reduced aldimine substrate. The dinuclear dppe-bridged species is even less active, while the bis(diphosphine) species *trans*-$RuCl_2(dppe)_2$ is virtually inert (footnote f). These empirical data support the widely accepted view, and earlier kinetic findings from this laboratory [1, 2], that a Ru:(PP) ratio of 1:1 is optimum for catalytic hydrogenation.

The above reasoning concerning the conversion data of Table 2 is clearly quite speculative, but such findings can lead to the design of better catalysts.

The comparative utility of catalysts of the types shown in Fig. 1 and $RuCl_2(PP)(PPh_3)$ species for asymmetric hydrogenation of imines was examined using the prochiral ketimine $PhCH_2N{=}C(Me)Ph$ as substrate (Table 3). Conversions are generally lower than with the dppb catalysts, especially for the binap systems, probably because of the greater steric bulk of the phosphine. Poor conversions were found on use of $RuCl_2(PP)(PPh_3)$ (cf. the lower activity observed with the PP = dppb species, relative to $RuCl_2(PPh_3)_3$, in transfer hydrogenation of imines [27]); the five-coordinate $RuCl_2(PP)(PPh_3)$ complexes, at least in benzene solution, provide a useful *in situ* source of $Ru_2Cl_4(PP)_2$ species via equilibrium (4) [29], and it is clear from the data of Table 3 that the presence of PPh_3 not surprisingly inhibits activity of the dinuclear catalysts.

$$2RuCl_2(PP)(PPh_3) \rightleftharpoons Ru_2Cl_4(PP)_2 + 2PPh_3 \qquad (4)$$

Only modest enantioselectivities are observed, a maximum e.e. value of 27% being found using $Ru_2Cl_5(chiraphos)_2$, which was also the most active

TABLE 3. Conversion and e.e. data for reduction of $PhCH_2N{=}C(Me)Ph$ using various chiral catalysts[a]

Entry	Catalyst	Conversion (%)	e.e. (%)
1	$Ru_2Cl_5(chiraphos)_2$	97	27
2	$Ru_2Cl_5(diop)_2$	61	16
3	$Ru_2Cl_5(binap)_2$	32	18
4	$Ru_2Cl_4(diop)_2$	59	13
5	$Ru_2Cl_4(binap)_2$	26	19
6	$Ru_2Cl_4(diop)_2(PhCN)$	57	17
7	$Ru_2Cl_4(binap)_2(PhCN)$	28	19
8	$RuCl_2(diop)(PhCN)_2$	24	14
9	$RuCl_2(binap)(PhCN)_2$	17	18
10	$RuCl(diop)(PhCN)_3^+PF_6^-$	37	11
11	$RuCl(chiraphos)(C_6H_6)^+PF_6^-$	24	13
12	$RuCl(diop)(C_6H_6)^+Cl^-$	27	10
13	$RuCl(binap)(C_6H_6)^+PF_6^-$	6	10
14	$RuCl_2(diop)(PPh_3)$	9	
15	$RuCl_2(binap)(PPh_3)$	8	

[a]1000 psi H_2, r.t., 10 ml MeOH, 0.77 mM Ru, [imine] = 0.075 M, reaction time = 24 h; imine added before MeOH.

catalyst. Values of *c.* 70% e.e. have been reported for reduction of this imine under closely comparable conditions (20 °C, 70 bar H_2) with rhodium systems [17, 43]. It should be noted that no other prochiral imines were screened, so the e.e. data for the Ru catalysts are not optimized in terms of imine structure.

Of more general significance is the invariance of e.e. values with catalyst structure within the neutral diop and binap series of complexes, which provides further evidence for a common catalytic intermediate within each series. This implies a basis for comparison of superficially distinct catalyst species. Thus, the enantioselective abilities of complexes such as $Ru_2Cl_4(PP)_2(NEt_3)$, $RuCl_2(PP)(RCN)_2$ and $RuCl_2(PP)$(diene), for example, with the important PP = binap systems [12, 22, 24], may be directly related, and indeed there is evidence that this is so for at least the first two species listed [12]. This finding highlights the importance of developing mechanistic understanding as a basis for catalyst design, especially in view of the considerable effort devoted to development of apparently novel systems. Preparation and use of air-sensitive, Ru(II) complexes with (PP):Ru = 1 not only involve unnecessary synthetic complications, but impair the activity of the catalyst system. In terms of both accessibility and activity, the mixed valence dimers $Ru_2Cl_5(PP)_2$ are particularly attractive, being readily synthesized from $RuCl_3(PR_3)_2$ and PP [29, 30]. In the presence of a basic substrate, as in the current imine work, these complexes appear to generate a direct source of $RuCl_2(PP)(solvent)_2$; with non-basic substrates such as prochiral olefins and ketones, small amounts of added base should initiate effective catalysis.

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References

1 B.R. James, R.S. McMillan, R.H. Morris and D.K.W. Wang, *Adv. Chem. Ser., 167* (1978) 127.
2 B.R. James and D.K.W. Wang, *Can. J. Chem., 58* (1980) 245.
3 (a) D.E. Fogg, A.M. Joshi, K.S. MacFarlane and B.R. James, *Proc. 8th Int. Symp. Homogeneous Catalysis, Amsterdam, Netherlands, 1992,* Abstr. O-7; (b) D.E. Fogg and B.R. James, *Proc. 15th Conf. Catal. of Org. Reactions, Phoenix, AZ, 1994,* Poster 3.
4 B.R. James, A. Pacheco, S.J. Rettig, I.S. Thorburn, R.G. Ball and J.A. Ibers, *J. Mol. Catal., 41* (1987) 147.
5 A.M. Joshi and B.R. James, *J. Chem. Soc., Chem. Commun.,* (1989) 1785.
6 T. Ikariya, Y. Ishii, H. Kawano, T. Arai, M. Saburi, S. Yoshikawa and S. Akutagawa, *J. Chem. Soc., Chem. Commun.,* (1985) 922.
7 H. Kawano, Y. Ishii, T. Ikariya, M. Saburi, S. Yoshikawa, Y. Uchida and H. Kumobayashi, *Tetrahedron Lett., 28* (1987) 1905.
8 M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Ohta, H. Takaya and R. Noyori, *J. Am. Chem. Soc., 110* (1988) 629.
9 H. Kawano, T. Ikariya, Y. Ishii, M. Saburi, S. Yoshikawa, Y. Uchida and H. Kumobayashi, *J. Chem. Soc., Perkin Trans. 1* (1989) 1571.
10 D.F. Taber and L.J. Silverberg, *Tetrahedron Lett., 32* (1991) 4227.
11 K. Mashima, K.-H. Kusano, T. Ohta, R. Noyori and H. Takaya, *J. Chem. Soc., Chem. Commun.,* (1989) 1208.
12 L. Shao, K. Takeuchi, M. Ikemoto, T. Kawai, M. Ogasawara, H. Takeuchi, H. Kawano and M. Saburi, *J. Organomet. Chem., 435* (1992) 133.
13 D.E. Fogg and B.R. James, *J. Organomet. Chem., 462* (1993) C21.
14 D.E. Fogg, *Ph.D. Thesis,* The University of British Columbia, Canada, 1994.
15 C.A. Willoughby and S.L. Buchwald, *J. Am. Chem. Soc., 114* (1992) 7562.
16 M.J. Burk and J.E. Feaster, *J. Am. Chem. Soc., 114* (1992) 6266.
17 (a) A.G. Becalski, W.R. Cullen, M.D. Fryzuk, B.R. James, G.-J. Kang and S.J. Rettig, *Inorg. Chem., 30* (1991) 5002; (b) G.E. Ball, W.R. Cullen, M.D. Fryzuk, W.J. Henderson and B.R. James, *Inorg. Chem., 33* (1994) 1464.
18 Y.N. Chan and J.A. Osborn, *J. Am. Chem. Soc., 112* (1990) 9400.
19 C. Lensink and J.G. de Vries, *Tetrahedron: Asymmetry, 3* (1992) 235.
20 J. Bakos, A. Orosz, B. Heil, M. Laghmari, P. Lhoste and D. Sinou, *J. Chem. Soc., Chem. Commun.,* (1991) 1684.
21 B.R. James, *Chem. Ind.,* in press.
22 R. Noyori, *Science, 248* (1990) 1194.
23 B.R. James, A.M. Joshi, P. Kvintovics, R.H. Morris and I.S. Thorburn, *Chem. Ind., 40* (1990) 11.
24 R. Noyori, *Chem. Soc. Rev., 18* (1989) 187.
25 S. Bhaduri, N. Sapre, K. Sharma, P.G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.,* (1990) 1305.
26 W. Oppolzer, M. Wills, C. Starkemann and G. Bernardinelli, *Tetrahedron Lett., 31* (1990) 4117.
27 G.-Z. Wang and J.-E. Bäckvall, *J. Chem. Soc., Chem. Commun.,* (1992) 980.
28 P. Krasik and H. Alper, *Tetrahedron: Asymmetry, 3* (1992) 1283.
29 A.M. Joshi, I.S. Thorburn, S.J. Rettig and B.R. James, *Inorg. Chim. Acta, 198–200* (1992) 283.
30 I.S. Thorburn, S.J. Rettig and B.R. James, *Inorg. Chem., 25* (1986) 234.
31 I.S. Thorburn, S.J. Rettig and B.R. James, *J. Organomet. Chem., 296* (1985) 103.
32 D.E. Fogg and B.R. James, to be published.
33 M. Bressan and P. Rigo, *Inorg. Chem., 14* (1975) 2286.
34 F. Faraone, G.A. Loprete and G. Tresoldi, *Inorg. Chim. Acta, 34* (1979) L251.

35 R. Mason, D.W. Meek and G.R. Scollary, *Inorg. Chim. Acta, 16* (1976) L11.
36 D.K.W. Wang, *Ph.D. Thesis,* The University of British Columbia, Canada, 1978.
37 G. Mestroni, A. Camus and G. Zassinovich, *Asp. Homog. Catal., 4* (1981) 71.
38 B. Heil, L. Markó and S. Torös, in L.H. Pignolet (ed.), *Homogeneous Catalysis with Metal Phosphine Complexes,* Plenum, New York, 1983, p. 317.
39 C.S. Chin and B. Lee, *Catal. Lett., 14* (1992) 135.
40 C. Lensink and J.G. de Vries, *Tetrahedron: Asymmetry, 4* (1993) 215.
41 C.J. Longley, T.J. Goodwin and G. Wilkinson, *Polyhedron, 5* (1986) 1625.
42 J.A. Davies and F.R. Hartley, *Chem. Rev., 81* (1981) 79.
43 J. Bakos, I. Toth, B. Heil, G. Szalontai, L. Parkanyi and V. Fulop, *J. Organomet. Chem., 370* (1989) 263.