# Coordination Chemistry and Catalytic Activity of Ruthenium Complexes of Terdentate Phosphorus−Nitrogen−Phosphorus (PNP) and Bidentate Phosphorus−Nitrogen (PNH) Ligands

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Structures of *trans*-dichlororuthenium(II) complexes of aminodiphosphines $RN(CH_2CH_2PPh_2)_2$ (**1a**−**d**, PNP) and aminophosphines $RN(H)CH_2CH_2PPh_2$ (**2a**−**d**, PNH) ligands are examined. The comparative reactivity of these metal complexes in ruthenium-catalyzed transfer hydrogenation reactions is subsequently evaluated.



In earlier papers we described the synthesis of a range of aminodiphosphine (PNP) ligands **1**, their hemilabile coordination to palladium complexes,[1] and their catalytic behavior in the Heck arylation reaction.[2] During the course of this work, we developed a simple two-step procedure for the synthesis of a series of the ligands **1** (PNP) and **2** (PNH) from readily available amines (Scheme 1).[3]

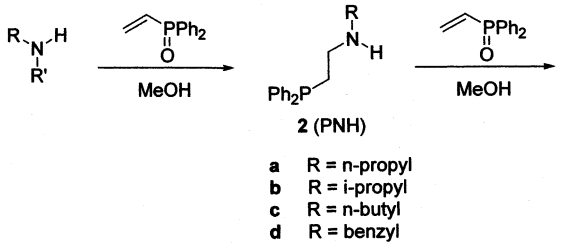
In an earlier study, a *cis,fac*-$[RuCl_2(PNP)(PPh_3)]$ complex was reported to be formed by refluxing a mixture of $PhCH_2N(CH_2CH_2PPh_2)_2$ (**1d**) and $[RuCl_2(PPh_3)_3]$ in hexane, and the assignment was made, based chiefly on infrared and $^1H$ NMR spectroscopic data.[4] In contrast, Bianchini and co-workers isolated a *trans,mer*-$[RuCl_2(PNP)(PPh_3)]$ complex by refluxing $[RuCl_2(PPh_3)_3]$ and ligand **1a** in THF.[5,6] As the two systems differ only in the substitution at nitrogen, the contrasting results led us to reexamine the ruthenium complexes of these amino (di)phosphine ligands. In particular, we wish to investigate the effect of the nitrogen substitution on the coordination and catalytic chemistry.

Adopting previously described procedures, the amino diphosphine ligands (**1a**−**1d**) were refluxed with $[RuCl_2(PPh_3)_3]$ in hexane (Scheme 2).[4] In all cases, the reaction mixtures recorded an $AX_2$ spin system ($J_{PP} \approx 27$ Hz) in their $^{31}P\{^1H\}$ NMR spectra, in addition to two displaced triphenylphosphine ligands ($\delta P$ −5 ppm), which is consistent with Bianchini's structure in which the PNP ligand adopts a *mer*-configuration around the metal center.

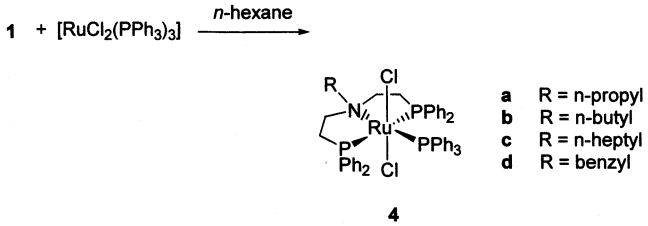
Single crystals of **4b** and **4d** suitable for X-ray diffraction analysis were obtained by slow diffusion of petroleum ether into solutions of the complexes in dichloromethane. Both structures showed meridonal arrangement of the PNP ligands around the octahedral metal centers, with the chloride ligands occupying the apical positions (Figure 1), i.e. a *trans,mer*-configuration. The preferred geometry affords the least sterically congested coordination sphere, while also placing ligands with comparable *trans*-effects ($Cl^-$, $RPPh_2$) in mutually *trans*-configurations.

The solid-state structures of **4b** and **4d** reveal noticeable differences in their coordination spheres induced by the different nitrogen substituents (Table 1). Al-

**Scheme 1. Aminodiphosphine (PNP) and Aminophosphine (PNH) Ligands**




**Scheme 2. Coordination of PNP Ligands to $[RuCl_2(PPh_3)_3]$**

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(4) Khan, M. M. T.; Reddy, V. V. S. *Inorg. Chem.* **1986**, *25*, 208−214.
(5) Bianchini, C.; Innocenti, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Gazz. Chim. Ital.* **1992**, *122*, 461−470.
(6) Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 2514.

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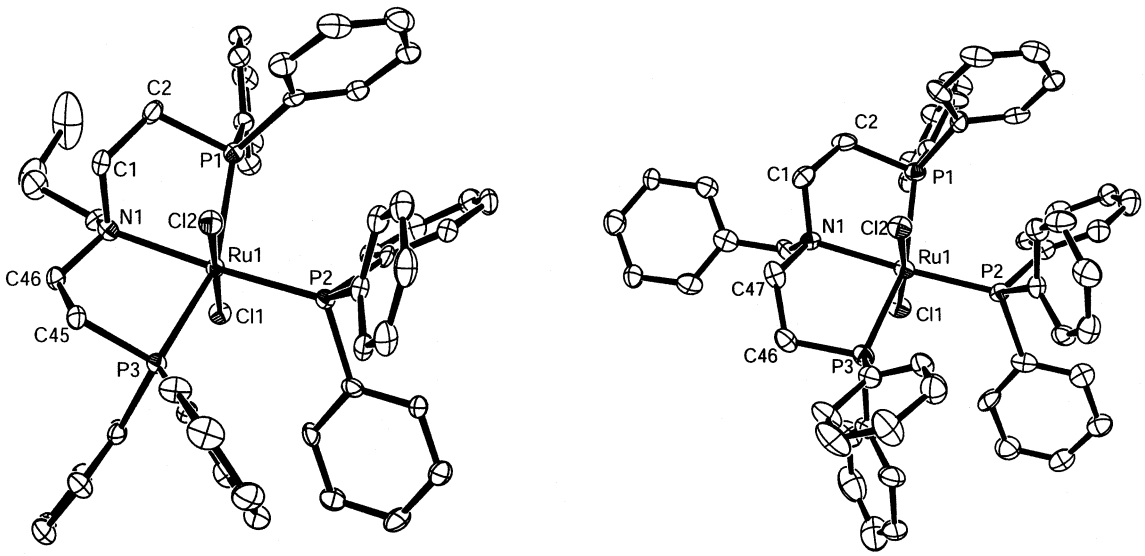



**Figure 1.** ORTEP diagrams of complexes **4b** (left) and **4d** (right) at 50% probability. Solvent molecules and hydrogen atoms are omitted for clarity.

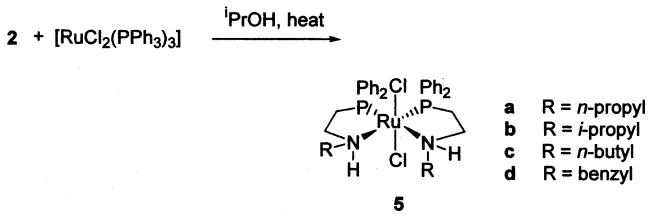
**Table 1. Selected Bond Lengths and Bond Angles for Complexes 4b and 4d**

| complex **4b** | | complex **4d** | |
|---|---|---|---|
| Selected Bond Lengths (Å) | | | |
| Ru(1)−P(2) | 2.309(2) | Ru(1)−P(2) | 2.319(2) |
| Ru(1)−N(1) | 2.315(5) | Ru(1)−N(1) | 2.317(7) |
| Ru(1)−P(1) | 2.365(2) | Ru(1)−P(1) | 2.394(2) |
| Ru(1)−P(3) | 2.371(1) | Ru(1)−P(3) | 2.382(2) |
| Ru(1)−Cl(2) | 2.437(2) | Ru(1)−Cl(1) | 2.414(2) |
| Ru(1)−Cl(1) | 2.438(2) | Ru(1)−Cl(2) | 2.413(2) |
| Selected Bond Angles (deg) | | | |
| N(1)−Ru(1)−P(2) | 176.74(11) | N(1)−Ru(1)−P(2) | 177.40(18) |
| N(1)−Ru(1)−P(1) | 79.18(11) | N(1)−Ru(1)−P(1) | 80.48(18) |
| N(1)−Ru(1)−P(3) | 81.22(11) | N(1)−Ru(1)−P(3) | 81.93(18) |
| P(2)−Ru(1)−P(1) | 97.85(5) | P(2)−Ru(1)−P(1) | 97.24(8) |
| P(2)−Ru(1)−P(3) | 101.33(5) | P(2)−Ru(1)−P(3) | 100.20(9) |
| P(1)−Ru(1)−P(3) | 156.18(6) | P(1)−Ru(1)−P(3) | 161.47(9) |
| N(1)−Ru(1)−Cl(1) | 91.43 (12) | N(1)−Ru(1)−Cl(1) | 91.30(18) |
| N(1)−Ru(1)−Cl(2) | 89.75 (12) | N(1)−Ru(1)−Cl(2) | 83.56 (18) |
| Cl(2)−Ru(1)−Cl(1) | 177.07(5) | Cl(2)−Ru(1)−Cl(1) | 174.41(9) |

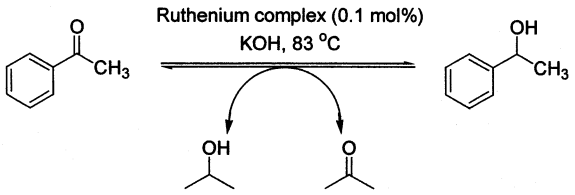
though the Ru−N bonds appear to be unaffected, complex **4d** displays very slight increase and decrease in the Ru−P and Ru−Cl bond lengths compared to **4b**, as will be expected to result from reduced electron donation by the amino group. More significantly, the Cl−Ru−Cl angle in complex **4d** deviates significantly from linearity, due entirely to the distortion of one of the chloride ligands, manifested by the observed N(1)−Ru(1)−Cl(2) bond angle of 83.5° compared to N(1)−Ru(1)−Cl(1) of 91.3 °C. Such a difference is not observed in complex **4b**, where these bond angles are virtually orthogonal: N(1)−Ru(1)−Cl(2) = 89.7°; N(1)−Ru(1)−Cl(1) = 91.4 °C. We propose that this difference of the two Ru−Cl bonds in complex **4d** effectively destroys the molecular symmetry, leading to the observation of two $\nu$(Ru−Cl) IR absorption bands and, consequently, an erroneous assignment of a *cis,fac*-structure in the previous report.[4] Indeed, subsequent examination of far-infrared absorption of the isolated ruthenium complexes **4a**−**4d** showed complex **4d** to be the only compound of this series that exhibits two bands in this region.

**Ruthenium(II) Complexes of Aminophosphine Ligands 2.** Two molar equivalents of the bidentate PNH ligands **2** displaced triphenylphosphine from [$RuCl_2$-($PPh_3$)$_3$] in refluxing 2-propanol, to furnish orange solids

**Scheme 3. Coordination of PNH Ligands to [$RuCl_2(PPh_3)_3$]**




**Scheme 4. Ruthenium-Catalyzed Transfer Hydrogenation of Ketones to Alcohols**




with the molecular composition [$Ru(PNH)_2Cl_2$]. The isolated complexes gave rise to singlet resonances at ca. 60 ppm in their $^{31}P\{^1H\}$ NMR spectra, consistent with the formation of symmetrical bis-ligated structures (Scheme 3). The molecular structures were determined by the isolation of suitable crystals of complexes **5a** and **5d** for X-ray crystallography by recrystallization from dichloromethane/hexane (two molecules of complex **5a** were found in the asymmetric part of the unit cell).

The structures have distorted octahedral geometries around the metal centers with a *cis,trans*-configuration, i.e., with the two phosphorus and nitrogen atoms *cis* to each other and the mutually *trans*-dichloride ligands adopting the apical positions (Figure 2). A striking feature is the highly distorted Cl−Ru−Cl bonds (ca. 167°). As no other [$(PNH)_2RuCl_2$] complexes were reported prior to this work, the data were compared to similar crystal structures retrieved from the Cambridge Crystallographic Database using QUEST and VISTA.[7] Searches were restricted to complexes of *cis,trans*-

(7) Cambridge Structural Database System, October 2001 Release: Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1 and 31.

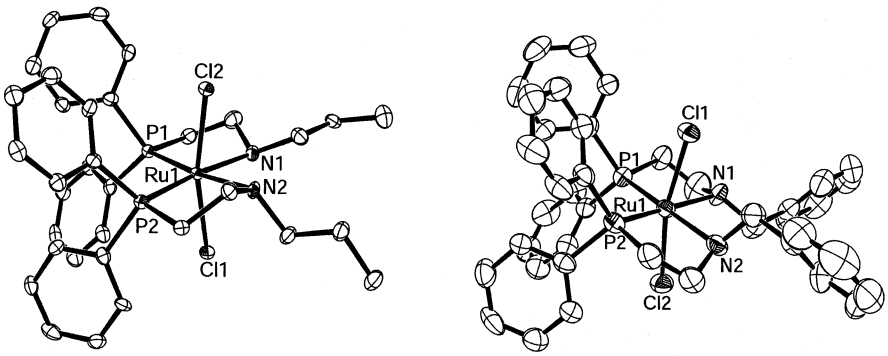



**Figure 2.** ORTEP representations of **5a** (left) and **5d** (right) at 50% probability. Solvent molecules and hydrogen atoms are omitted for clarity.

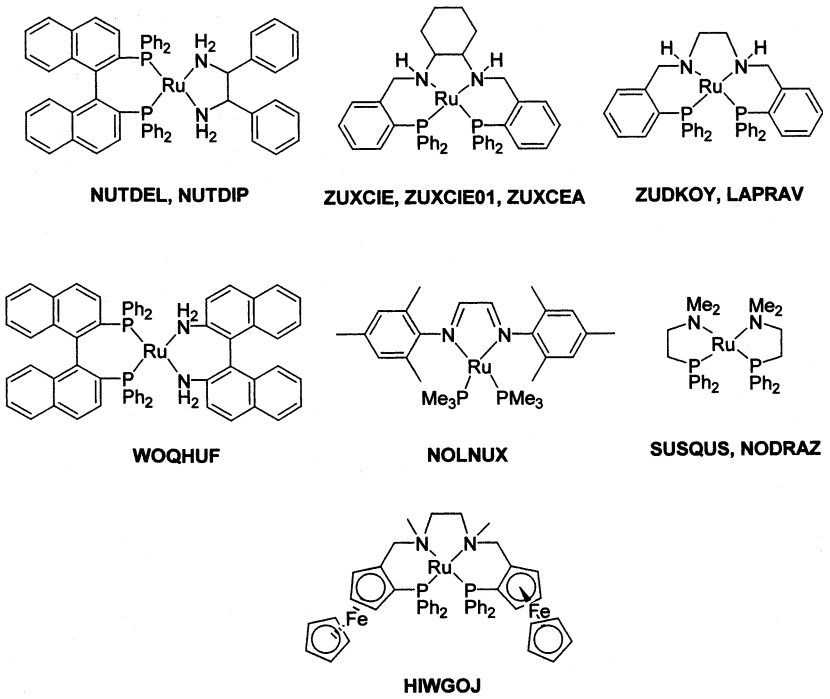



**Figure 3.** Types of *cis,trans*-$[RuP_2N_2Cl_2]$ complexes previously reported. *Trans*-chloride ligands are omitted for the sake of clarity.



$[RuCl_2P_2N_2]$ complexes containing two nitrogen and two phosphorus donor groups (chelation between donor groups is optional and could be in any combination), with *R* factor < 10%. Surprisingly, few crystal structures of this type were reported: only a total of 15 data sets representing seven distinct compounds were found (Figure 3).

Even within this relatively modest data set, it is clear that distortions are not uncommon in these complexes (Table 2), with the Cl−Ru−Cl bond angles ranging between 163° and 173°. Examination of the interatomic distances shows that the nitrogen substituent affects the structure of these compounds in an entirely different way from that observed previously with the PNP complexes: Ru−Cl and Ru−P bond lengths are fairly insensitive to the nature of the nitrogen donor. However, the Ru−N bonds are shorter by about 0.2 Å in complexes **5a** and **5d** (containing a NH moiety), compared to those containing tertiary amino groups (HIWGOJ, NODRAZ, and SUSQUS, Table 2). Perhaps as a result of closer atomic contacts in the equatorial plane, greater repulsion is experienced between the chloride ligands and the aromatic rings, resulting in the greater displacement of the dichloride ligands toward the nitrogen donors. Indeed, the Cl−Ru−Cl distortion appears to increase in the following order: tertiary amine < imine < secondary NH.

Another interesting feature is the chemical environment of the Ru−Cl bonds, reflected through the difference in Cl−Ru−N torsion angles. The Ru−Cl bonds in complexes **5a** and **5d** appear to be distinctly different, N(2)−Ru(1)−Cl deviating from N(1)−Ru(1)−Cl by as much as >8° (Table 2). This contrasts sharply with the other structures that show deviations of less than 2.6° between the two values. These differences again destroy the C2 symmetrical structure and are manifested in the appearance of two $\nu$(Ru−Cl) far-infrared absorption bands for complexes **5a**−**5d**.

**Ruthenium-Catalyzed Transfer Hydrogenation Reactions.** Catalytic transfer hydrogenation reaction is an attractive reaction protocol for the reduction of ketones to alcohols.[8,9] By using 2-propanol as the

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(9) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40−73.

**Table 2. Selected Bond Angles (deg) and Bond Lengths of $[P_2N_2RuCl_2]$ Complexes**

| REFCODE | ClRuCl | $Cl^1RuN^1$ | $Cl^2RuN^1$ | $Cl^2RuN^2$ | $Cl^1RuN^2$ | $\|\Delta(ClRuN^1)\|$ | $\|\Delta(ClRuN^2)\|$ | M−Cl | M−P | M−N |
|---|---|---|---|---|---|---|---|---|---|---|
| NUTDEL[17a] | 162.939 | 82.497 | 83.051 | 84.301 | 83.884 | 0.554 | 0.417 | 2.42, 2.42 | 2.282, 2.274 | 2.196, 2.185 |
| | 162.958 | 82.951 | 83.245 | 83.518 | 83.806 | 0.294 | 0.288 | 2.426, 2.409 | 2.28, 2.27 | 2.183, 2.188 |
| NUTDIP[17a,b] | 163.002 | 84.236 | 83.123 | 83.536 | 82.821 | 1.113 | 0.715 | 2.408, 2.425 | 2.276, 2.295 | 2.142, 2.189 |
| | 163.21 | 83.848 | 83.418 | 82.418 | 84.266 | 0.43 | 1.848 | 2.412, 2.416 | 2.301, 2.275 | 2.187, 2.14 |
| ZUXCIE01[18c] | 164.125 | 86.949 | 79.037 | 88.807 | 81.513 | 7.912 | 7.294 | 2.41, 2.432 | 2.3, 2.289 | 2.158, 2.163 |
| ZUXCIE[12c] | 164.213 | 81.787 | 88.536 | 78.777 | 87.285 | 6.749 | 8.508 | 2.409, 2.43 | 2.297, 2.29 | 2.14, 2.164 |
| ZUDKOY[19d] | 165.33 | 80.075 | 87.47 | 82.769 | 87.627 | 7.395 | 4.858 | 2.444, 2.409 | 2.303, 2.304 | 2.167, 2.163 |
| LAPRAV[20d] | 169.976 | 86.975 | 84.287 | 89.259 | 84.501 | 2.688 | 4.758 | 2.418, 2.427 | 2.292, 2.297 | 2.094, 2.097 |
| NOLNUX[21] | 165.676 | 97.684 | 93.654 | 98.303 | 93.349 | 4.03 | 4.954 | 2.365, 2.365 | 2.42, 2.398 | 2.025, 2.033 |
| WOQHUF[22] | 165.34 | 88.077 | 81.796 | 88.344 | 79.454 | 6.281 | 8.89 | 2.418, 2.4 | 2.273, 2.269 | 2.228, 2.263 |
| **5a**[a] | 166.82 | 83.46 | 85.69 | 80.99 | 91.91 | 2.23 | 10.92 | 2.402, 2.419 | 2.249, 2.251 | 2.242, 2.249 |
| | 166.10 | 82.51 | 85.92 | 82.12 | 90.72 | 3.41 | 8.6 | 2.408, 2.417 | 2.248, 2.252 | 2.233, 2.253 |
| **5d** | 166.76 | 81.68 | 87.16 | 82.05 | 91.13 | 5.48 | 9.08 | 2.407, 2.412 | 2.251, 2.253 | 2.242, 2.246 |
| ZUXCEA[12e] | 171.654 | 89.459 | 84.767 | 89.235 | 83.899 | 4.692 | 5.336 | 2.439, 2.403 | 2.295, 2.288 | 2.099, 2.091 |
| HIWGOJ[23] | 172.713 | 87.143 | 87.015 | 86.251 | 88.457 | 0.128 | 2.206 | 2.415, 2.405 | 2.301, 2.311 | 2.375. 2.332 |
| NODRAZ[24f] | 172.139 | 84.396 | 90.41 | 83.759 | 90.872 | 6.014 | 7.113 | 2.41, 2.395 | 2.255, 2.251 | 2.402, 2.377 |
| SUSQUS[25a,f] | 171.87 | 88.961 | 85.463 | 88.238 | 86.319 | 3.498 | 1.919 | 2.41, 2.412 | 2.257, 2251 | 2.414, 2.377 |
| | 173.159 | 86.255 | 89.611 | 86.518 | 88.327 | 3.356 | 1.809 | 2.402, 2.418 | 2.255, 2.241 | 2.404, 2.368 |

[a] Two molecules found in the asymmetric unit cell. [b] Stereoisomer of NUTDEL. [c,d,f] Identical structures, reported independently/in different solvents. [e] Stereoisomer of ZUXCIE.

**Table 3. Catalytic Activity of Complexes 4a−5d[a]**

| entry | catalyst | % conversion (h) | final % conversion (h) |
|---|---|---|---|
| 1 | $RuCl_2(PPh_3)_3$ | 41 (4) | 49 (8) |
| 2 | **4a** | 22 (8) | 85 (72) |
| 3 | **4b** | 15 (8) | 81 (72) |
| 4 | **4c** | 17 (8) | 68 (72) |
| 5 | **4d** | 13 (8) | 55 (72) |
| 6 | **5a** | 67 (4) | 87 (8) |
| 7 | **5b** | 59 (4) | 76 (8) |
| 8 | **5c** | 88 (4) | 94 (8) |
| 9 | **5d** | 39 (4) | 55 (8) |

[a] Reactions were carried out in duplicate, using a Radley's reaction carousel system under a nitrogen atmosphere, using 1 mol % of catalyst at 83 °C. % conversions monitored by GC.



reductant, $H^-$ and $H^+$ are delivered simultaneously to the carbonyl functionality, thus avoiding the use of stoichiometric, hazardous reducing reagents such as $NaBH_4$ and $LiAlH_4$. Impressive stereoselectivity could also be achieved by the use of chiral ligands in recent years. The most efficient catalysts reported for the reaction contain bifunctional ligands, e.g., $\beta$-amino alcohols, *N*-tosylated diamines, oxazoline-phosphines.[10,11] Among the nitrogen−phosphorus ligands, the tethered aminophosphine PNNP complexes such as ZUXCIE (Figure 3) is able to catalyze the reaction of aryl alkyl ketones at mild reaction temperatures while delivering high ee's.[12−14] As these complexes are not too dissimilar to complexes **5a**−**5d**, we decided to investigate the comparative reactivity of these complexes. Using the isolated complexes **4a**−**4d** and **5a**−**5d** as catalytic precursors, acetophenone was subjected to transfer hydrogenation reactions in a refluxing 2-propanol solution (Scheme 3). The results are summarized in Table 3.

The PNH complexes **5** generally catalyze reactions faster than $[RuCl_2(PPh_3)_3]$ (Table 3, entries 1 and 6−9), which is in turn a better catalyst than the PNP complexes **4** (entries 2−5 and 10). As expected, the presence of the NH functionality makes a dramatic difference to the turnovers of the reactions (entries 2−5 vs 6−10). This fits in well with the well-established observation that an NH group is essential in the rate-determining hydride transfer step.[11] We found that a reaction temperature of at least 60 °C is required in order for complexes **5a**−**5d** to achieve any observable turnover. This, compared to the lower reaction temperature required for complexes ZUXICE (ca. 30−40 °C), suggests that the N−N tether imbues special reactivity to the PNNP system.

Within each ligand class, the reactivity of the metal complexes is dependent on the nitrogen substituents. For the PNP complexes **4a**−**4d**, the higher homologues induced lower reaction turnover and yield (entries 2, 3, and 4), with the **4d** displaying the lowest activity. In contrast, the PNH complexes **5a**−**5d** seem to display the opposite trend: the butyl-substituted **5c** had higher activity than the propyl homologue **5a** (entries 6 and 8). Increasing the steric bulk of the *N*-substituent decreased the reactivity (entry 7), and the benzyl-substituted **5d** was the least reactive (entry 9).

## Conclusion

Amino phosphines and diphosphine ligands **1** and **2** have been prepared and their coordination chemistry on dichlororuthenium(II) complexes was evaluated. Complexes of the PNP terdentate ligand (**4a**−**4d**) were found to have a *trans,mer* arrangement around the metal center, whereas the bidentate PN(H) ligands form *cis,trans* complexes (**5a**−**5d**) in a highly sterically strained octahedral arrangement. The effect of nitrogen substituent on the overall geometry of these metal complexes was discussed. In catalytic transfer hydrogenation reactions the reactivity was found to be PNH (**5c** > **5a** > **5b** > **5d**) > PNP (**4a** > **4b** > **4c** > **4d**).

Chiral variants of the PNP and PNH ligands are being developed in our laboratory and evaluated in asymmetric catalytic reactions. The results will be reported elsewhere.

## Experimental Section

All reactions involving phosphorus(III) ligands were carried out under inert atmospheres of nitrogen or argon using

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(14) Gao, J. X.; Zhang, H.; Yi, X. D.; Xu, P. P.; Tang, C. L.; Wan, H. L.; Tsai, K. R.; Ikariya, T. *Chirality* **2000**, *12*, 383−388.

**Table 4. Crystal Data and Structure Refinement for Complexes 4b and 4d**

| complex **4b** | | complex **4d**·$2CH_2Cl_2$ | |
|---|---|---|---|
| empirical formula | $C_{50}H_{52}Cl_2NP_3Ru$ | empirical formula | $C_{53}H_{50}Cl_2NP_3Ru{\cdot}2CH_2Cl_2$ |
| fw | 931.81 | fw | 1135.67 |
| temperature | 100(2) K | temperature | 100(2) K |
| wavelength | 0.71073 Å | wavelength | 0.71073 Å |
| cryst syst | $P\bar{1}$ | cryst syst | $P21/c$ |
| space group | triclinic | space group | monoclinic |
| unit cell dimens | $a = 10.5452(3)$ Å, $\alpha = 87.473(2)°$<br>$b = 18.7436(6)$ Å, $\beta = 76.456(2)°$<br>$c = 22.5033(7)$ Å, $\gamma = 89.987(2)°$ | unit cell dimens | $a = 14.1873(10)$ Å, $\alpha = 90°$<br>$b = 14.5637(6)$ Å, $\beta = 106.374(4)°$<br>$c = 25.5349(15)$ Å, $\gamma = 90°$ |
| volume | 4319.8(2) $Å^3$ | volume | 5062.0(5) $Å^3$ |
| $Z$ | 4 | $Z$ | 4 |
| density (calcd) | 1.433 $Mg/m^3$ | density (calcd) | 1.490 $Mg/m^3$ |
| abs coeff | 0.635 $mm^{-1}$ | abs coeff | 0.760 $mm^{-1}$ |
| $F(000)$ | 1928 | $F(000)$ | 2328 |
| cryst size | $0.20 \times 0.10 \times 0.02$ $mm^3$ | cryst size | $0.20 \times 0.15 \times 0.10$ $mm^3$ |
| $\theta$ range for data collection | 1.40 to 25.00° | $\theta$ range for data collection | 2.36 to 25.00° |
| index ranges | $-12 \le h \le 12$, $-22 \le k \le 22$,<br>$-26 \le l \le 26$ | index ranges | $-16 \le h \le 16$,$-16 \le k \le 17$,<br>$-30 \le l \le 30$ |
| no. of reflns collected | 25 256 | no. of reflns collected | 15 463 |
| no. od ind reflns | 15193 [$R$(int) = 0.1063] | no. of ind reflns | 8721 [$R$(int) = 0.1302] |
| completeness to $\theta = 25.00°$ | 99.8% | completeness to $\theta = 25.00°$ | 98.0% |
| max. and min. transmn | 0.9874 and 0.8836 | max. and min. transmn | 0.9278 and 0.8628 |
| refinement method | full-matrix least-squares on $F^2$ | refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/ params | 15193/0/1030 | no. of data/restraints/ params | 8721/0/596 |
| goodness-of-fit on $F^2$ | 1.043 | goodness-of-fit on $F^2$ | 1.037 |
| final $R$ indices [$I>2\sigma(I)$] | R1 = 0.0665, wR2 = 0.1000 | final $R$ indices [$I>2\sigma(I)$] | R1 = 0.0911, wR2 = 0.2012 |
| $R$ indices (all data) | R1 = 0.1273, wR2 = 0.1156 | $R$ indices (all data) | R1 = 0.1529, wR2 = 0.2442 |
| extinction coeff | 0.00098(14) | extinction coeff | 0.0036(5) |
| largest diff peak and hole | 0.666 and −0.671 e $Å^{-3}$ | largest diff peak and hole | 1.532 and −1.164 e $Å^{-3}$ |

**Table 5. Crystal data and Structure Refinement for complexes 5a and 5d**

| complex **5a** | | complex **5d** | |
|---|---|---|---|
| empirical formula | $C_{34}H_{42}Cl_2N_2P_2Ru$ | empirical formula | $C_{42}H_{44}Cl_2N_2P_2Ru$ |
| fw | 712.61 | fw | 810.70 |
| temperature | 100(2) K | temperature | 293(2) K |
| wavelength | 0.71073 Å | wavelength | 0.71073 Å |
| cryst syst | $P\bar{1}$ | cryst syst | $P\bar{1}$ |
| space group | triclinic | space group | triclinic |
| unit cell dimens | $a = 11.5098(6)$ Å, $\alpha = 82.246(3)°$<br>$b = 15.8943(8)$ Å, $\beta = 72.680(3)°$<br>$c = 19.2179(8)$ Å, $\gamma = 77.757(2)°$ | unit cell dimens | $a = 10.9686(6)$ Å, $\alpha = 97.173(4)°$<br>$b = 12.1947(8)$ Å, $\beta = 107.402(4)°$<br>$c = 16.7431(11)$ Å, $\gamma = 110.999(4)°$ |
| volume | 3270.3(3) $Å^3$ | volume | 1926.2(2) $Å^3$ |
| $Z$ | 4 | $Z$ | 2 |
| density (calcd) | 1.447 $Mg/m^3$ | density (calcd) | 1.398 $Mg/m^3$ |
| abs coeff | 0.767 $mm^{-1}$ | abs coeff | 0.661 $mm^{-1}$ |
| $F(000)$ | 1472 | $F(000)$ | 836 |
| cryst size | $0.20 \times 0.10 \times 0.10$ $mm^3$ | cryst size | $0.10 \times 0.10 \times 0.05$ $mm^3$ |
| $\theta$ range for data collection | 1.11 to 26.00° | $\theta$ range for data collection | 2.70 to 25.00° |
| index ranges | $-14 \le h \le 13$, $-19 \le k \le 19$,<br>$-23 \le l \le 21$ | index ranges | $-12 \le h \le 13$, $-14 \le k \le 13$,<br>$-19 \le l \le 19$ |
| no. of reflns collected | 20 328 | no. of reflns collected | 11 260 |
| no. of ind reflns | 12739 [$R$(int) = 0.0843] | no. of ind reflns | 6748 [$R$(int) = 0.1110] |
| completeness to $\theta = 25.00°$ | 99.0% | completeness to $\theta = 25.00°$ | 99.6% |
| max. and min. transmn | 1.0000 and 0.8617 | max. and min. transmn | 0.9677 and 0.9369 |
| refinement method | full-matrix least-squares on $F^2$ | refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/ params | 12739/0/743 | no. of data/restraints/params | 6748/0/447 |
| goodness-of-fit on $F^2$ | 1.054 | goodness-of-fit on $F^2$ | 1.078 |
| final $R$ indices [$I>2\sigma(I)$] | R1 = 0.0672, wR2 = 0.1108 | final $R$ indices [$I>2\sigma(I)$] | R1 = 0.0765, wR2 = 0.1062 |
| $R$ indices (all data) | R1 = 0.1211, wR2 = 0.1271 | R indices (all data) | R1 = 0.1333, wR2 = 0.1210 |
| largest diff peak and hole | 1.343 and −1.152 e $Å^{-3}$ | largest diff peak and hole | 0.817 and −0.510 e $Å^{-3}$ |



standard Schlenk line techniques. Commercially available reagents were purchased from Avocado, Lancaster, or Aldrich chemical companies and used as received. Diphenylvinylphosphine oxide and $[RuCl_2(PPh_3)_3]$ were prepared according to published procedures.[15,16] The preparation of ligands **1a**−**1d** and **2a**−**2d** was reported previously.[3]

Melting points were determined on Electrothermal Gallenhamp melting point apparatus and are uncorrected. Far-infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer, and samples were suspended in Nujol sandwiched between polyethylene disks. NMR spectra were recorded using Bruker AM360 or AVANCE 400 or 500 spectrometers in deuteriochloroform, unless otherwise stated. $^1H$ and $^{13}C$ spectra were referenced to TMS, and $^{31}P$ NMR

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spectra were referenced to $H_3PO_4$ ($\delta = 0$ ppm). The chemical shifts ($\delta$) are in parts per million (ppm). The coupling constants ($J$) are in hertz (Hz). The following abbreviations are used: s (singlet), t (triplet), q (quartet), m (multiplet), d (doublet), br (broad). Mass spectra (MS and HRMS) were recorded using FAB technique by the Mass Spectrometry Service within The University of London's Intercollegiate Research Services (ULIRS) or The EPSRC Mass Spectrometry Service at Swansea, Wales. Elemental analysis was carried out at The University of North London.

Catalytic reactions were carried out using a Radley's 12-placed reaction carousel under reflux and an inert atmosphere. A Unicam 6100 system with a JW Scientific DB 250 column and FID detector was used for GLC analysis.

**X-ray Crystal Structural Analysis.** Crystals of **4b**, **4d**, **5a**, and **5d** were obtained by recrystallization from $CH_2Cl_2$/hexane at room temperature. Data were collected in wide-slicing mode using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 30 mm. Crystal data and details of data collection and refinement are given as Supporting Information.

**General Procedure for the Preparation of [$RuCl_2$(PNP)($PPh_3$)] Complexes. Dichloro(triphenylphosphine){bis-(2-(diphenylphosphino)ethyl)benzylamine}ruthenium-(II), 4d.** The ligand bis[2-(diphenylphosphino)ethyl]benzylamine (0.11 g, 2 mmol) was added to a solution of [$RuCl_2(PPh_3)_3$] (96 mg, 1 mmol) in hexane (10 mL), and the reaction mixture was refluxed for 4 h. Upon cooling to room temperature, the product deposited as an orange solid, which was collected by filtration and washed with acetone/ether. Yield: 72 mg, 75%. $^1$H NMR (360 MHz, $CDCl_3$): $\delta$ 2.69−2.86 (m, 4H, $CH_2$P), 3.10−3.35 (dm, 4H, N$CH_2CH_2$P), 4.77 (s, 2H, $C_6H_5CH_2$N), 6.68−8.16 (m, 40H, *Ph*). $^{31}$P NMR (145 MHz, $CD_2Cl_2$): $\delta$ 24.8 (d, $J_{PP}$ = 28 Hz), 47.0 (t, $J_{PP}$ = 28 Hz). $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 36.3 (virtual triplet, $^1J_{PC}$ = 11.5 Hz, NCH$_2CH_2$P), 52.9 (s, N$CH_2CH_2$P), 59.2 (s, $C_6H_5CH_2$N), 126.7−141.90 (aromatic region). HRMS: exact mass calcd for $C_{53}H_{50}Cl_2NP_3Ru$ 973.2203, found 973.2245. Far-IR $\nu$(Ru−Cl): 312, 270 cm$^{-1}$.

**Dichloro(triphenylphosphine){bis(2-(diphenylphosphino)ethyl)-*n*-propylamine}ruthenium(II), 4a.** A microanalytical sample was prepared by recrystallization from $CH_2Cl_2$/$CH_3OH$. The crystals contain $CH_2Cl_2$ solvent molecules, as verified by NMR and X-ray crystal analysis. Yield: 85%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.72 (t, 3H, $J$ = 7.2 Hz, $CH_3CH_2$), 1.44 (m, 2H, $CH_3CH_2$), 2.43 (m, 2H, $CH_2$P), 2.73−2.77 (m, 2H, N$CH_2CH_2$P), 2.95−299 (m, 2H, NCH$_2CH_2$P), 3.38−3.49 (4H, m, N$CH_2CH_2$P and $CH_3CH_2CH_2$N), 6.64−8.01 (m, 35H, *Ph*). $^{31}$P NMR (145.7 MHz, $CD_2Cl_2$): $\delta$ 26.0 (d, $J_{PP}$ = 27.5 Hz), 48.0 (t, $J_{PP}$ = 27.5 Hz, NCH$_2CH_2$P). $^{13}$C NMR (90.5 MHz, $CD_2Cl_2$): $\delta$ 12.3 (s, $CH_3CH_2$), 14.1 (s, $CH_3CH_2$), 36.5 (virtual triplet t, $^1J_{PC}$ = 11.7 Hz, NCH$_2CH_2$P), 54.0 (s, N$CH_2CH_2$P), 59.7 (s, $CH_3CH_2CH_2$N), 127.18−140.0 (aromatic region). HRMS: exact mass calcd for $C_{49}H_{50}Cl_2NP_3Ru$ 917.1577, found 917.1615. Far-IR $\nu$(Ru−Cl): 310 cm$^{-1}$. Anal. Found: C, 59.90; H, 5.52; N, 1.26. $C_{49}H_{50}Cl_2NP_3Ru\cdot CH_2Cl_2$ requires: C, 59.90; H, 5.23; N, 1.40.

**Dichloro(triphenylphosphine){bis(2-(diphenylphosphino)ethyl)-*n*-butylamine}ruthenium(II), 4b.** Yield: 75%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.71 (t, 3H, $J$ = 7.0 Hz, $CH_3CH_2$), 1.14 (m, 2H, $CH_3CH_2CH_2$), 1.38 (m, 2H, $CH_3CH_2CH_2$), 2.43 (m, 2H, NCH$_2CH_2$P), 2.77 (m, 2H, N$CH_2CH_2$P), 2.98 (m, 2H, NCH$_2CH_2$P), 3.39 (dm, 4H, N$CH_2CH_2$P, $CH_3CH_2CH_2CH_2$N), 6.60−8.00 (m, 35H, *Ph*). $^{31}$P NMR (145 MHz, $CDCl_3$): $\delta$ 26.09 (d, $J_{PP}$ = 27 Hz), 48.10 (t, $J_{PP}$ = 27 Hz). $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 13.2 (s, $CH_3CH_2$), 20.1 (s, $CH_3CH_2$), 21.7 (s, $CH_3CH_2CH_2$), 35.2 (virtual triplet, $^1J_{PC}$ = 12.0 Hz, NCH$_2CH_2$P), 56.6 (s, N$CH_2CH_2$P), 60.1 (s, $CH_3CH_2CH_2CH_2$N) 121.3−141.0 (aromatic). HRMS: exact mass calcd for $C_{50}H_{52}Cl_2NP_3Ru$ 931.1733, found 931.1749. Far-IR $\nu$(Ru−Cl): 310 cm$^{-1}$. Anal. Found: C, 62.65; H, 5.01; N, 1.32. $C_{50}H_{52}Cl_2NP_3Ru.CH_2Cl_2\cdot 0.5CH_2Cl_2$ requires: C, 62.25; H, 5.48; N, 1.44.

**Dichloro(triphenylphosphine){bis(2-(diphenylphosphino)ethyl)-*n*-heptylamine}ruthenium(II), 4c.** Yield: 85%. $^1$H NMR (400 MHz, toluene-$d_8$): $\delta$ 0.93 (t, 3H, $J$ = 8.0 Hz, $CH_3CH_2$), 1.06−1.62 (m, 10H $CH_3CH_2CH_2CH_2CH_2CH_2$), 2.49−2.55 (m, 2H, NCH$_2CH_2$P), 2.58−2.77 (m, 2H, N$CH_2CH_2$P), 3.04−3.08 (m, 2H, NCH$_2CH_2$P), 3.46−3.52 (m, 2H, N$CH_2CH_2$P), 3.79−3.84 (m, 2H $C_6H_{13}CH_2$N), 6.75−8.45 (m, 35H, *Ph*). $^{31}$P NMR (161.9 MHz, toluene-$d_8$): $\delta$ 26.1 (d, $J_{PP}$ = 27.5 Hz), 49.4 (t, $J_{PC}$= 27.5 Hz). $^{13}$C NMR (90.5 MHz, toluene-$d_8$): $\delta$ 14.7, 20.5, 23.5, 27.9, 29.7, 32.6, 36.6, (virtual triplet, $^1J_{PC}$ = 11.8 Hz, $CH_2$P) 53.6, (s, N$CH_2CH_2$P), 59.1 (s, $C_6H_{13}CH_2$N) (aromatic region). HRMS: exact mass calcd for $C_{53}H_{58}Cl_2NP_3Ru$ 973.2203, found 973.2245. Far-IR $\nu$(Ru−Cl): 310 cm$^{-1}$. Anal. Found: C, 61.63; H, 5.90; N, 1.38. $C_{53}H_{58}Cl_2NP_3Ru.CH_2Cl_2$ requires: C, 61.25; H, 5.71; N, 1.32.

**General Procedure for the Preparation of [$RuCl_2$(PN)$_2$] Complexes: Bis[*n*-propyl{2-(diphenylphosphino)-ethyl}amine]ruthenium(II) Dichloride, 5a.** [2-(Diphenylphosphino)ethyl]-*n*-propylamine·HCl salt (2 mmol) was neutralized (pH = 10) with aqueous NaOH (2M) in 2-propanol, extracted with DCM, dried ($MgSO_4$), and evaporated. The resultant oil was then dissolved in 2-propanol (2 mL) and added to a solution of [$RuCl_2(PPh_3)_3$] (96 mg, 1 mmol) in 2-propanol (10 mL). The reaction mixture was then refluxed for 4 h, cooled to room temperature, and reduced to 5 mL, whereupon the product precipitated as an orange solid, which was collected by filtration and washed with ether. Yield: 78%. A sample for microanalysis was recrystallized from $CH_2Cl_2$/$CH_3OH$. As before, the crystals tend to incorporate the $CH_2Cl_2$ solvent. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.89 (t, 6H, $J$ = 7.4 Hz, $CH_3CH_2$), 1.47−1.57 (m, 2H, $CH_3CH_2$), 1.84−1.87 (m, 2H, $CH_3CH_2$), 2.52−2.68 (m, 2H, N$CH_2CH_2$P), 2.70−2.94 (m, 6H, NCH$_2CH_2$P and $CH_3CH_2CH_2$N), 2.94−3.01 (m, 2H, $CH_3CH_2CH_2$N), 3.42−3.47 (m, 2H, N$CH_2CH_2$P), 3.69 (br s, 2H, *NH*), 6.91−7.19 (m, 20H, P$Ph_2$). $^{31}$P NMR (145 MHz, $CD_2Cl_2$): $\delta$ 59.2. $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 10.5 (s, $CH_3CH_2$), 21.6 (s, $CH_3CH_2$) 30.5 (virtual triplet, $^1J_{PC}$ = 14.4 Hz, NCH$_2CH_2$P), 46.9 (s, N$CH_2CH_2$P), 53.2 (s, $CH_3CH_2CH_2$N), 126.3−136.0 (aromatic region). HRMS: exact mass calcd for $C_{34}H_{44}Cl_2N_2P_2Ru$ 713.1322, found 713.1317. Far-IR $\nu$(Ru−Cl): 312, 280 cm$^{-1}$. Anal. Found: C, 52.93; H, 5.91; N, 3.35. $C_{34}H_{44}Cl_2N_2P_2Ru\cdot CH_2Cl_2$ requires: C, 52.57; H, 5.80; N, 3.50.

**Bis[isopropyl-{2-(diphenylphosphino)ethyl}amine]-ruthenium(II) Dichloride, 5b.** Yield: 84%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 1.32 (d, 6H, $J$ = 6.3 Hz, $CH_3$), 1.44 (d, 6H, $J$ = 6.3 Hz, $CH_3$), 2.79 (br. d, 4H, NCH$_2CH_2$P), 3.04 (br s, 2H, N$CH_2CH_2$P), 3.36 (br s, 2H, N$CH_2CH_2$P), 3.64−3.67 (m, 1H, *CH*), 4.19 (br s, 2H, *NH*), 7.00−7.31 (m, 20H, P$Ph_2$). $^{31}$P NMR (145 MHz, $CD_2Cl_2$): $\delta$ 64.4. $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 19.4 (s, $CH_3$), 23.7 (s, $CH_3$), 32.7 (virtual triplet, $^1J_{PC}$ = 12.0 Hz, $CH_2$P), 40.2 (s, $CH_2CH_2$P), 50.9 (s, *CH*), 126.5−138.79 (aromatic region). HRMS: exact mass calcd for $C_{34}H_{44}Cl_2N_2P_2Ru$ 713.1322, found 713.1317. Exact-IR $\nu$(Ru−Cl): 305, 270 cm$^{-1}$. Anal. Found: C, 54.87; H, 5.81; N, 3.55. $C_{34}H_{44}Cl_2N_2P_2Ru\cdot 0.5CH_2Cl_2$ requires: C, 54.73; H, 5.99; N, 3.70.

**Bis[*n*-butyl{2-(diphenylphosphino)ethyl}amine]-ruthenium(II) Dichloride, 5c.** Yield: 88%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 0.87 (t, 6H, $J$ = 7.4 Hz, $CH_3CH_2$), 1.21−1.39 (m, 4H, $CH_3CH_2$), 1.42−1.53 (m, 2H, $CH_3CH_2CH_2$), 1.79−1.90 (m, 2H, $CH_3CH_2CH_2$), 2.46−2.59 (m, 2H, N$CH_2CH_2$P), 2.69−2.79 (m, 6H, $CH_2$P and $CH_3CH_2CH_2CH_2$N), 2.91−2.98 (m, 2H, $CH_3CH_2CH_2CH_2$N), 3.33−3.42 (m, 2H, N$CH_2CH_2$P), 3.64 (br. s, 2H, N*H*), 6.90−7.63 (m, 20H, P$Ph_2$). $^{31}$P NMR (161.9 MHz,

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$CD_2Cl_2$): $\delta$ 59.4. $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 14.2 (s, $CH_3$-$CH_2$), 20.9 (s, $CH_3CH_2$), 31.5 (virtual triplet, $^1J_{PC}$ = 12.9 Hz, $NCH_2CH_2P$), 48.2 (s, $NCH_2CH_2P$), 52.3 (s, $CH_3CH_2CH_2CH_2N$), 127.3−137.8 (aromatic region). HRMS: exact mass calcd for $C_{36}H_{48}N_2Cl_2P_2Ru$ 741.1635, found 741.1642. Far-IR $\nu$(Ru−Cl): 305, 280 cm$^{-1}$. Anal. Found: C, 54.05; H, 6.38; N, 3.12. $C_{36}H_{48}N_2Cl_2P_2Ru\cdot CH_2Cl_2$ requires: C, 53.70; H, 6.09; N, 3.38.

**Bis[benzyl{2-(diphenylphosphino)ethyl}amine]-ruthenium(II) Dichloride, 5d.** Yield: 94%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.50−2.75 (m, 6H, $NCH_2CH_2P$ and $NCH_2$-$CH_2P$), 3.15−3.25 (m, 2H, $NCH_2CH_2P$), 4.24 (m, 6H, $C_6H_5CH_2N$ and N*H*), 6.94−7.28 (m, 30H, $PPh_2$). $^{31}$P NMR (145 MHz, $CDCl_3$): $\delta$ 59.5. $^{13}$C NMR (90.5 MHz, $CDCl_3$): $\delta$ 29.5 (virtual triplet, $^1J_{PC}$ = 12.7 Hz, $NCH_2CH_2P$), 46.1 (s, $NCH_2CH_2P$), 54.1 (s, $C_6H_5$ $CH_2N$), 127.5−138.1 (aromatic region). HRMS: exact mass calcd for $C_{42}H_{44}Cl_2N_2P_2Ru$ 808.1244, found 808.1264. Far-IR $\nu$(Ru−Cl): 305, 270 cm$^{-1}$.

Catalytic reactions were conducted using Radley's 12-placed reaction carousel. The apparatus is composed of two mounted metal blocks, separated by a 5 cm gap. The bottom block is positioned on a stirrer hotplate, and the temperature is controlled via a digital thermostat. The top block is cooled by circulating water and fitted with a central inlet/outlet for vacuum and gas combined with a radial gas distribution to the reaction tubes. The carousel can accommodate 12 glass reaction tubes, with a reaction volume of 3−25 mL. The tubes are fitted with screw caps, each containing an adjustable valve to control the gas flow into the reaction tube. Addition and extraction of solution to and from the reaction tube are conducted via fitted rubber septa.

**Typical Catalytic Runs.** The ruthenium complexes (0.1 mmol, 1 mol %) were introduced into reaction tubes, each equipped with stirrer bar. The tubes were then placed on a Radley's carousel and were evacuated with vacuum and purged with argon before the addition of anhydrous 2-propanol (8 mL). At the appropriate temperature, acetophenone (10 mmol, 1.17 mL) was added, and the reaction was initiated by the addition of KOH (2.9 mL, 0.05M solution in 2-propanol, 0.15 mmol). Reactions were monitored by extracting 0.1 mL aliquots of the reaction mixture periodically, which were analyzed by GLC. Retention times for acetophenone and 2-phenylethanol are 3.9 and 4.2 min, respectively. The results were duplicated to within ±5% accuracy.

The full details of the crystallographic data are deposited with the Cambridge Crystallographic Data Centre: CCDC186508 (**4b**), CCDC186509 (**4d**), CCDC186510 (**5a**) and CCDC186511 (**5d**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

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**Supporting Information Available:** Crystallographic data of the structures of compounds **4b**, **4d**, **5a**, and **5d** are given in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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