Atypical and Asymmetric 1,3-P,N Ligands: Synthesis, Coordination and Catalytic Performance of Cycloimino phosphanes

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Abstract: Novel seven-membered cyclic imine-based 1,3-P,N ligands were obtained by capturing a Beckmann nitritium ion intermediate generated in situ from cyclohexanone with benzo triazole, and then displacing it by a secondary phosphane under triflic acid promotion. These “cycloimino phosphanes” possess flexible non-isomerizable tetrahydroazepine rings with a high basicity; this sets them apart from previously reported iminophosphanes. The donor strength of the ligands was investigated by using their P-κ1- and P-N-κ2-, tungsten(0) carbonyl complexes, by determining the IR frequency of the trans-CO ligands. Complexes with [RhCp*Cl]2 demonstrated the hemilability of the ligands, giving a dynamic equilibrium of κ1 and κ2 species; treatment with AgOTf gives full conversion to the κ2 complex. The potential for catalysis was shown in the RuII-catalyzed, solvent-free hydration of benzonitrile and the RuII- and IrII-catalyzed transfer hydrogenation of cyclohexanone in isopropanol. Finally, to enable access to asymmetric catalysts, chiral cycloimino phosphanes were prepared from L-meth thione, as well as their P,N-κ2-RhII and a P-κ1-RuII complexes.

Introduction

Ligand-based reactivity can enhance the activity of transition metal catalysts, [1] as is the case for hybrid ligands, [2] which combine the properties of different heteroatoms to enable hemilability, redox non-innocence, proton shuffling, and substrate coordination. [3–7] 1,3-P,N ligands are particularly subject to diverse binding modes (N-κ1, P-κ1, P-κ1η2, κ1, and μ; Figure 1) and their complexes have found application in homo/heterogeneous catalysis, bio-inorganic chemistry, and photoluminescence. [3–7] Most of these 1,3-P,N complexes are based on pyridyl- and imidazolyl-based ligands A and B, which have structural limitations that are inherent to their syntheses. [4,6,7] Recently we reported on the highly tunable iminophosphanes C and their tautomers phosphaamidines D that can be independently substituted on the P, C, and N atoms. [5,8] These 1,3-P,N ligands are readily accessible from (base-stabilized) nitritium trflate precursors and even though they are obtained as (dynamic) E/Z isomer mixtures, the equilibrium shifts to the desired Z conformer on coordination to metals (Figure 2). [6] The hapticity in κ1/κ2-[(P,N)RhCp*Cl]2 complexes and the favorable performance in (κ1-1,P,N)-RuII-catalyzed nitrile hydration correlated with the electronic properties of the ligands [6d] and the basicity of the nitrogen donor (Figure 3). [3,4]

Iminophosphanes C are accessed from nitritium ion precursors, which are known both as reactive synthons and intermediates. [2,8] Illustrative is the Beckmann rearrangement of cyclohexanone oxime to the ring-expanded seven-membered
nitrilium intermediate (with an iminium resonance form), which hydrolyzes to the ε-caprolactam that is used as the building block for the commercial production of nylon-6 (Figure 4, top).\[9,10\] The intermediate can also be trapped by nucleophiles, for instance by benzotriazole,\[11\] which under Lewis acid promotion can be displaced by other nucleophiles.\[11a\] This reactivity mirrors our reported nitrilium triflate approach for the synthesis of $C$ and might be suitable to access novel 7-membered cyclic iminophosphanes (Figure 4E). Such “cycloiminophosphanes” would be conformationally locked, that is, unable to undergo $E/Z$ isomerization, which could boost their efficiency (Figure 5). Moreover, the ring might carry chiral groups as the required chiral cyclohexanone precursors are readily available from terpenoids used in, for instance, the flavoring and perfume industry.\[12\]

In this study, we report both the synthesis of these novel cyclic 1,3-P,N ligands and their surprising electronic properties that set them apart from noncyclic iminophosphanes. We explore their coordination to early and late transition metals in $\kappa^1/\kappa^2$ complexes and assess their performance in catalytic nitrile hydration and transfer hydrogenation. Crystal structures are provided for the (asymmetric tetrahydroazepine synths, ligands, and a W complex.

**Results and Discussion**

The synthesis of the cyclic ligands is discussed first, followed by an analysis of their donor capacity using IR- and $^{31}$P NMR spectroscopy on W$^0$ carbonyl complexes and dynamic Rh$^{III}$ complexes, respectively. Next, Ru$^I$ species are examined to evaluate the ligands’ performance in homogeneous catalysis. We also discuss analogous asymmetric ligands with a natural product-derived backbone.

**Precursor synthesis**

Our synthetic strategy is based on reacting phosphane with a seven-membered ring nitrilium ion, that is, the 3,4,5,6-tetrahydro-azepinium ion.\[10\] Because this ion could not be accessed by our established methodology in which amides are reacted to imidoyl halides with subsequent halide to triflate exchange,\[6\] as the activating agents converted ε-caprolactam to thick intractable mixtures of presumably protonated imidoyl chloride, dimers and/or nylon like polymers,\[13,14\] we decided to generate the desired nitrilium ion in situ using the Beckmann rearrangement and trap it with benzotriazole.\[11\]

Treating neat cyclohexanone with hydroxylamine·HCl salt by grinding them together in a mortar, while slowly adding NaOH, yielded the corresponding pure oxime conveniently, even on large scale (120 mmol, 82%; Scheme 1).\[15\] Next, under an atmosphere of nitrogen, the oxime was activated in situ as the corresponding methylsulfonate with methylsulfonyl chloride and triethylamine in MeCN at 0°C.\[11c,16\] Benzotriazole was added and the mixture was heated to reflux for 2 h to facilitate the ring expansion and trap the nitrilium ion. The reported work-up\[11d\] was significantly simplified by adding

![Figure 2. Synthesis of iminophosphanes and hemilabile metal coordination.](image2)

![Figure 3. Catalyzed nitrile hydration.](image3)

![Figure 4. Cycloiminophosphane synthesis from the Beckmann nitrilium intermediate.](image4)

![Figure 5. Non-isomerizable cycloiminophosphanes.](image5)
Scheme 1. Synthesis of benzotriazolyl-tetrahydroazepine.

water to the crude mixture to precipitate pure 4 as a white solid in good yield (60%); alternatively, evaporation, extraction into Et₂O and filtration over neutral alumina also provides 4 (58%). Single crystals suitable for X-ray diffraction analysis were obtained from Et₂O and revealed a remarkably flat conformation {N1–C1–N2–N3 = 179.54(8); C6–C1–N2–N3 = −0.37(12)}.

Figure 6. Displacement ellipsoid plot of benzotriazolyl tetrahydroazepine 4 at the 50% probability level. Hydrogen atoms are omitted for clarity, with the exception of H6A and H11. Selected bond lengths [Å] and angles [°]: C1–N1 = 1.2643(13), N1–C1 = 1.3746(11), N3···H6A = 2.29, N1···H11 = 2.50, N1–C1–N2 = 114.81(9), N1–C1–C6 = 129.01(9), N2–C2–C1 = 116.18(8), C1–N1–C2 = 118.88(9), N1–C1–N2–N3 = 179.54(8), C6–C1–N2–N3 = −0.37(12).

Scheme 2. The activation of 4 for Ph₂PH introduction.

Table 1. Lewis acid induced exchange of the benzotriazolyl group of 4 for Ph₂PH.

| Promoter | Loading (mol %) | Solvent | t [min.] | Conversion to E [%] | Selectivity for E [%] |
|----------|-----------------|---------|----------|---------------------|----------------------|
| 1\[a\]  | AlCl₃ | 10% | CHCl₃ | 10 | 25 | 100 |
| 2  | AlCl₃ | 10% | CHCl₃ | 90 | 40 | 95 |
| 3  | AlCl₃ | 10% | CHCl₃ | 300 | 57 | 88 |
| 4  | AlCl₃ | 25% | CHCl₃ | 90 | 64 | 93 |
| 5  | AlCl₃ | 100% | CHCl₃ | 90 | 99 | 99\[b\] |
| 6  | SnCl₄ | 100% | CHCl₃ | 90 | 70 | 95 |
| 7  | SnCl₄ | 100% | CHCl₃ | 300 | 72 | 97 |
| 8  | SnCl₄ | 100% | Toluene | 300 | 36 | 63 |
| 9  | SnCl₄ | 100% | CHCl₃ | 300 | 50 | 50 |
| 10 | BF₃·OEt₂ | 100% | CHCl₃ | 300 | 76 | 92 |
| 11\[c\] | HOTf | 100% | CHCl₃ | 10 | 100 | 100 |

[a] Conditions: 1 equiv. Ph₂PH, solvent (0.35 M), reflux. [b] Determined by ³¹P NMR spectroscopy. [c] 7 = 80°C, μW conditions, 0.25 M. [d] Conversion to the AlCl₃ adduct of 6. [e] RT, 0.5 M.

Phosphane introduction

In analogy to the formation of 4, we tried to capture the in situ generated 3,4,5,6-tetrahydro-azepinium ion directly with a phosphane to obtain the desired cycloiminophosphane ligand E, but to no avail. Instead, the benzotriazole group of 4 could be replaced for diphenylphosphane using Lewis acid promotion, which we examined under a variety of conditions (Scheme 2, Table 1). We started with a microwave reaction employed in related displaced relations by N nucleophiles,[11a] but this reaction using 10 mol% AlCl₃ (entry 1) proved to be less effective than regular heating under reflux (entries 2 and 3). The still modest conversion, probably due to Lewis pair interaction with the phosphane,[17] could be enhanced by increasing the amount of AlCl₃ (entries 4 and 5). Using equimolar amounts, AlCl₃ proved to be more selective than SnCl₄, SnCl₆ and BF₃ (entries 5–10) and resulted in 99% conversion to an Al adduct of the desired ligand, which on treatment with water gave the protonated ligand and a mixture of oxy aluminum anions. However, the by far most effective and convenient manner to obtain the protonated ligand was found to be the direct activation of 4 through protonation with triflic acid (entry 11).

Treatment of 4 with 1 equiv. of triflic acid at 0°C resulted instantly in a suspension from which its iminium form 5 could be isolated by filtration (Scheme 3). Whereas 5 is subject to decomposition over time, both in solution and as an isolated solid, it reacted cleanly upon immediate resuspension with phosphines to give 6 within minutes. After work-up, diphenyl derivative 6a was obtained in 77% as an air-stable solid. The aliphatic derivatives 6b and 6c (conversion 85% (nBu) and 66% (Cy)) could not be purified satisfactorily until after the subsequent deprotonation step (see below). Bulky substituents may hinder the formation of 6, as suggested by the lower selectivity found for 6c. Crystals suitable for X-ray diffraction could be obtained for 6a and 6c by slow diffusion of pentane into a THF solution. The molecular structures show a chair conformation for the tetrahydroazepine rings, with the P-lone pair facing away from the imine (Figure 7). Generally, the structures are comparable to those reported for noncyclic...
products show sets of two distinct iminophosphane ligands. To provide the desired novel ligands (83%), pentane was needed to generate the 1,3-P,N product (93%; δ(HP) = 6.7 (E), −13.2 (Z)), whereas NEt₃ (pKₐ ≈ 11) sufficed for previously reported ligands. The unexpected high basicity of 7 seems akin to that of structurally related 1,3-N,N bases such as DBU.²¹

**Coordination chemistry and catalysis**

The donor strength of P,N ligands affects their efficiency in cooperative reactions.²⁴ To examine the influence of 7 in transition metal complexes, we synthesized the tungsten carbonyl complexes 10 and 11 as the IR frequency of their trans-CO ligands reflect the ligand’s P,N donor strength.²² Treating ligand 7a with either [W(CO)₅(MeCN)] or [W(CO)₅] provided, respectively, k³-complex 10 (82%) and k²-complex 11 (83%; Scheme 5). IR spectroscopic analysis of the trans-CO ligands indicated increasing electron donation to the metal for 10 (2069, 2008 cm⁻¹) with respect to 10 (2069 (trans), 1904, 1873 cm⁻¹). Compared to the analogous W complexes of the widely applied Ph₃P,N ligand (Figure 1, A; k²: 2050, 1980, 1920 cm⁻¹; k¹: 2017, 1890, 1870, 1826 cm⁻¹)²²⁻²³ 7a appears to be a far stronger N donor. Of note is that the CO stretches for k²-complex 11 are weaker than those of k³-complex 10, which illustrates that the additional coordination of the strong N donor provides a more electron-rich metal center with stronger W==O backdonation. Single crystals of 10 were obtained by cooling a toluene solution. The molecular structure (Figure 9) shows a tight bond of the metal center with the trans-CO [W1−C19 = 2.0058(18) Å; W−C(avg) = 2.046 Å] and a slightly weakened CO triple bond [C19−O1 = 1.142(2) Å; C−O(avg) = 1.139 Å]. The W1−P1 distance (2.563(3) Å) is comparable to the one in analogous PPh₃ and Ph₃P,Py complexes.²²⁻²³ Further parameters of the ligand are similar to those for 6a.

The influence of P substituents was apparent in [(7) Rh(Cp')Cl₂] complexes, which can equilibrate between P-k¹ and P,N-k² forms with characteristic ³¹P NMR chemical shifts and coupling constants, as has been shown for related iminophosphane (generally: ¹JRh,P ≈ 146 Hz; ¹JRh,N ≈ 114 Hz; for example [(Me-NC(PH)P(3-Me-Ph))RhCp*Cl₂] (P-k¹: δ = 34.7 ppm, ¹JRh,P ≈ 144.6 Hz; P,N-k²: δ = −12.1 ppm, ¹JRh,N ≈ 114.7 Hz; see also Figure 2). To obtain the complexes, 7 was reacted with 8.

**Scheme 4.** Synthesis of 8, the noncyclic analogue of 7a.

**Scheme 5.** Analysis of the donor capacity of 7a by using W(CO)₅ complexes.
resonances suggests the presence of flipfamers or rotamers; the absence of $^{31}$P, $^{31}$P couplings rules out bridged complexes (μ coordination).

Surprisingly, Rh complexation of phenyl ligand 7a did not give a clean P-κ'/κ" mixture. The $^{31}$P NMR spectrum of complex 12a showed a mixture of two broad signals (δ 36.9 ppm, δ 142.5 Hz, (42%); δ 30.1 ppm, br s, (58%)) that resolved into three doublets on lowering the temperature to −94 °C (Figure 10). Their coupling constants suggests a mixture of two P-κ' complexes (δ 38.0 ppm, $J_{3P,3P} = 139.3$ Hz (31%); δ 36.5 ppm, $J_{3P,3P} = 137.7$ Hz (54%)) and possibly an N-κ' complex, as it has a strikingly different P–Rh coupling and other coordination modes are unlikely due to the lack of additional P and/or Rh couplings (δ 27.5 ppm, $J_{2P,2P} = 153.9$ Hz (15%)). The N-monodentate coordination mode of 1,3-P,N ligands has been reported only for Mn$^{II}$ and Fe$^{II,III}$ and not for rhodium. Apparently, the two P-κ' and one N-κ' bonding modes interchange rapidly at room temperature.

The competing P-κ'/N-κ1 coordination modes for 12a can be attributed to the C,N-dialkyl-P-phenyl substitution pattern of ligand 7a. Its aryl groups reduce the donating property of the phosphine group as compared to 7b and 7c, and the cyclic alkyl chain makes its imine a stronger donor than in reported iminophosphanes.31

For comparison, we synthesized the Rh complexes of noncyclic ligand 9 (Scheme 4), which is similarly substituted as 7a. The low temperature $^{31}$P NMR spectrum showed the P-κ' complex (δ 39.1 ppm, $J_{3P,3P} = 144.2$ Hz (55%); δ 27.7 ppm, $J_{3P,3P} = 132.8$ Hz (29%)) together with small amounts of both the N-κ' complex (δ 33.9 ppm, $J_{3P,3P} = 152.3$ Hz (4%) and the P-N-κ' complex (δ −15.0 ppm), $J_{3P,3P} = 115.0$ Hz (6%)) before AgOTf converted it fully to the κ' complex (72% yield, $\delta$($^{31}$P) = −15.5 (δ, $J_{3P,3P} = 114.6$ Hz. Even though the amount of observed N-coordination is lower for 9 than for 7a, these results highlight the influence of the C,N,P substituents of 9 on the P,N coordination mode.

All Rh-complexes 12a-c could be fully converted to the bidentate complex 13 upon chloride abstraction with AgOTf (Scheme 6; 13a: 82% yield, $\delta$($^{31}$P) = −16.8 ppm, $J_{3P,3P} = 113.9$ Hz; 13b: 83% yield, $\delta$($^{31}$P) = −19.7 ppm, $J_{3P,3P} = 110.0$ Hz; 13c: 76% yield, $\delta$($^{31}$P) = −2.6 ppm, $J_{3P,3P} = 106.8$ Hz). Next, we explored the coordination to Ru$^{II}$ (Scheme 6) and the catalytic activity($^{14}$) of the resulting complexes. Reacting 7a,b with [Ru(p-cym)]$_2$P,$^2_2$C=C$m$ = p-cymene) provided the P-κ' complex 14b (66%, $\delta$($^{31}$P) = 27.3 ppm). Complex 14a could not be isolated from the reaction mixture that showed the presence of two products ($\delta$($^{31}$P) = 31.2 (27%), 23.4 (73%) ppm), which we tentatively assign to the N-κ' and P-κ' complexes, respectively, in analogy to Rh$^{II}$ complex 12a (see above).

Next, three Ru$^{III}$ complexes of ligands 7a–c were preliminarily tested for their effectiveness as catalysts in the solvent-free, closed-vessel hydration of benzonitrile$^{29}$ at 180 °C for 3 h (Table 2). Surprisingly, 14a generated in situ with the phenyl substituted ligand 7a proved to be quite an active catalyst, yielding 79% product. In situ generated 14b with the n-butyl substituted ligand 7b offered a somewhat lower yield of 59%, which could be enhanced to 70% by preforming the catalyst.
(entries 2 and 3, respectively). The least effective catalyst was the Ru\textsuperscript{ii} complex of ligand 7c, giving a hydration yield of only 15% that may have its origin in the more limiting steric factors. Even though the catalytic conditions were not optimized in this brief screen, it is rewarding that a hydration yield as high as 79% was obtained for P-\textsuperscript{1-methylimidazole} and ligand 7b, which resembles the highest yield of 82% found for the comparable Ru catalyst with an acyclic iminophosphane.\textsuperscript{[20]} Both perform much better than the analogous Ru complex of the established Ph\textsubscript{2}PPy ligand, which gives a hydration yield of 6%.\textsuperscript{[6d]}

As complex 14b performed only modestly in the hydration of benzonitrile, we chose to further screen its potential by preliminarily exploring the transfer hydrogenation of cyclohexanone in iPrOH, under conditions adapted from Jalón et al., who used the analogous complex of 2-PPPh\textsubscript{1}-1-methylimidazolate to obtain a hydrogenation yield of 21% on using a KOH/catalyst ratio of 333:1 and a substrate/catalyst ratio of 2000:1.\textsuperscript{[26,27]}

Table 2 summarizes the effect of changes in catalyst loading, reaction time, and the addition of KOH. After in situ generation of the catalyst, at 3 mol% catalyst loading the conversions were slow (up to 20 h; entries 1–3), but similar to the catalyst of Jalón et al.,\textsuperscript{[28]} the catalyst was substantially more active in presence of KOH (entries 4 and 5). Even the corresponding \(\kappa^2\)-complex of 14b, obtained by ion exchange with NaBF\textsubscript{4}, was active under these conditions (entry 7). With 0.5 mol% catalyst and 2.5 mol% KOH, a reaction time of 2 h still resulted in the quantitative hydrogenation of cyclohexanone (entry 8). Last, as iridium(\textit{I}) complexes are generally very active hydrogenation catalysts,\textsuperscript{[29]} we also explored the in situ generation of [(7b) Ir(COD)Cl\textsubscript{2}], which showed a similar trend as the Ru\textsuperscript{ii} complexes (entries 9–11).

These preliminary screenings demonstrate that the conveniently in situ generated \(\kappa^1\) and \(\kappa^2\) complexes of Ru\textsuperscript{ii} and Ir of cyclic 1,3-P,N ligand 7 are active catalysts that warrant further scrutiny.

### Chirality

As, to the best of our knowledge, no asymmetric 1,3-P,N-ligand-based catalysts have been reported,\textsuperscript{[4]} the synthesis of such ligands may be valuable. With a synthetic route toward cyclic iminophosphanes at hand, we pursued substituting the backbone with a chiral group by using an inexpensive terpenoid as asymmetric starting point. The readily available terpenoid l-menthone\textsuperscript{[12]} is well-suited for this purpose, since its sizeable (2S)-\textit{P} group is expected to be favorable for asymmetric induction.\textsuperscript{[29]} Following the synthesis of the chiral ligands, we report their Ru and Rh complexes and briefly reflect on their catalytic potential.

The asymmetric derivatives of 7 were pursued in analogy to the parent compound, albeit that the solventless oxime synthesis was not effective, but reacting l-menthone with the hydroxylamine-HCl salt in an EtOH/H\textsubscript{2}O mixture did provide oxime 16 as a colorless liquid after purification by crystallization at 5°C (73%; Scheme 7).\textsuperscript{[30]}

Table 3 summarizes the effect of changes in catalyst loading, reaction time, and the addition of KOH. After in situ generation of the catalyst, at 3 mol% catalyst loading the conversions were slow (up to 20 h; entries 1–3), but similar to the catalyst of Jalón et al.,\textsuperscript{[28]} the catalyst was substantially more active in presence of KOH (entries 4 and 5). Even the corresponding \(\kappa^2\)-complex of 14b, obtained by ion exchange with NaBF\textsubscript{4}, was active under these conditions (entry 7). With 0.5 mol% catalyst and 2.5 mol% KOH, a reaction time of 2 h still resulted in the quantitative hydrogenation of cyclohexanone (entry 8). Last, as iridium(\textit{I}) complexes are generally very active hydrogenation catalysts,\textsuperscript{[29]} we also explored the in situ generation of [(7b) Ir(COD)Cl\textsubscript{2}], which showed a similar trend as the Ru\textsuperscript{ii} complexes (entries 9–11).

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Subsequent treatment with MeCl, NEt\textsubscript{3}, and benzoazolide induced the Beckmann rearrangement via 17 to the desired benzoazolyl azepine adduct 19, which was isolated as an orange liquid (90%).

Whereas the ring expansion could have generated either or both regioisomers 18 and 19 (Scheme 7, pathways A and B), the NMR spectra showed only a single set of signals for the Me and iPr CH\textsubscript{3} groups (\(\delta^1\text{H}) 1.11, 1.08, 1.06 \text{ ppm}; \delta\text{C}) 24.2, 20.1, 17.7 ppm), indicating the formation of a single isomer. Based on the reported selectivity of related asymmetric cyclohexanone substrates in the Beckmann rearrangement,\textsuperscript{[31]} we expected the formation of 19 to be favored. Whereas crystals of 19, grown in a MeCN solution at −20°C, were too temperature sensitive to isolate for X-ray crystallography, protonation with HOTT in CHCl\textsubscript{3} gave a thermally stable salt (20, 79%) in sharp contrast to the highly unstable unsubstituted azepinium triflate 5. Crystals

### Table 2. Solvent-free catalyzed hydration of benzonitrile with precatalyst [Ru(p-cym)Cl\textsubscript{2}]\textsuperscript{[6d]}

| Ligand (L) | T [°C] | t [h] | Yield [\%] |
|-----------|--------|-------|------------|
| 7a        | 180    | 3     | 79         |
| 7b        | 180    | 3     | 59         |
| 7b\textsuperscript{[1]} | 180 | 3 | 70 |
| 7c        | 180    | 3     | 15         |
| PyPPh\textsubscript{2} | 180 | 3 | 60\textsuperscript{[6d]} |

[a] Reaction conditions: Ph\textsubscript{2}C=N (3.6 mmol), H\textsubscript{2}O (7.2 mmol), 1.4 mol% [Ru(p-cym)Cl\textsubscript{2}] and ligand 7. [b] Determined by GC. [c] Preformed catalyst (14b).

### Table 3. Catalytic transfer hydrogenation of cyclohexanone.

| Precatalyst [M] | L     | Cat. Loading (mol%) | t [h] | Yield [\%] | Additives |
|----------------|-------|---------------------|-------|------------|-----------|
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 3                   | 2     | 3          | –         |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 3                   | 3     | 20         | –         |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 1                   | 20    | quant.     | –         |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 1                   | 4     | quant.     | 5 mol% KOH |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 1                   | 4     | 0          | 1 mol% NaBF\textsubscript{4} |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 1                   | 4     | quant.     | 5 mol% KOH, 1 mol% NaBF\textsubscript{4} |
| [Ru(p-cym)Cl\textsubscript{2}] | 7b    | 0.5                 | 2     | quant.     | 2.5 mol% KOH |
| [Ir(COD)Cl] | 7b    | 1                   | 4     | 2          | –         |
| [Ir(COD)Cl] | 7b    | 1                   | 4     | 84         | 5 mol% KOH, 1 mol% NaBF\textsubscript{4} |

Reaction conditions: cyclohexanone in i-PrOH (2 M), reflux. [a] Determined by GC.
suitable for X-ray analysis were obtained by slow diffusion of pentane into a CHCl₃ solution of 20. Its molecular structure (Figure 11) concurs with the anticipated (25,5R)-2-IPr-5-Me regioisomer 19 with both alkyl groups in equatorial positions. Compared to the non-protonated 4 (Figure 6), the benzotriazolyl group of 20 is rotated by 155° and tilted with respect to the imine group [20: N1–C1–N2–N3 = −25.9(3); 4: N1–C1–N2–N3 = 179.54(8)]. Clearly, protonation of the imine group prevents the intramolecular H-bonding that facilitated the planar conformation of 4; the N1–H1 hydrogen interacts only with the triflate anion (H1–O1 = 1.97(2) Å). The positively charged N1 presumably causes the slightly tighter benzotriazolyl bonding [20: C1–N2 = 1.384(3), N2–N3 = 1.403(3) Å; 4: C1–N2 = 1.4334(12), N2–N3 = 1.3746(11) Å]. The parameters of the iminium group [C1–N1 = 1.280(3) Å, N1–C1–C6 = 122.68(19)°, C1–N1–C2 = 125.01(19)°] are comparable to those for 6a and 6c (Figure 6).

The introduction of the phosphane group on the chiral ring could not be achieved in analogy with the synthesis of the non-chiral ligands 7 (Scheme 3); surprisingly, treatment of the protonated precursor 20 with diphenylphosphine yielded its dehydrocoupling product tetraphenyldiphosphane.[32–34] Instead, the phosphane group was introduced by treating 19 with lithium phosphides LiPR₂ (R = Ph, nBu) in THF to give the desired chiral cycloiminophosphane 21 in 53%, after purification by an acid/base work-up involving salt 22 (Scheme 8). The ³¹P NMR spectrum showed a single resonance at δ 6.6, thus indicating the absence of flippamers, which was attributed to the reduced flexibility of the ring on which the iPr and Me substituents favor equatorial positions.

Single crystals of 22 suitable for an X-ray structure determination were obtained by slow diffusion of pentane into a saturated CHCl₃ solution. The molecular structure (Figure 12) shows a tetrahydroazepine chair similar to the one in 20 with the (25)-iPr and (5)-Me indeed in equatorial positions and confirms that the stereochemical information of the menthone is retained over the synthesis. The conformation and bonding parameters of 22 compare closely to that of the achiral, unsubstituted 6a (Figure 7) (22: C1–N1 = 1.289(2) Å, C1–N2 = 1.4334(12), N2–N3 = 1.3746(11) Å).
P1–C1 = 1.8252(18) Å, N1–C1–P1 = 121.79(14)°; 6a: N1–C1 = 1.2858(16) Å, P1–C1 = 1.8269(13) Å, N1–C1–P1 = 123.06(10)°.

Coordination of chiral ligand 21 to Ru(II) gave the corresponding P-k⁺ complexes 23 (Scheme 9; 19%, δ(P) 24.8 ppm). Likewise, coordination of 21 to Rh(III) afforded k⁻-Rh(III) complex 24 that showed, akin to complex 12a (see above), a broad ³¹P NMR signal at room temperature, which resolved at −90°C into a series of doublets with two major P-k⁺ resonances (δ 34.3 ppm, J(140P) = 140.9 Hz, 38%; δ 22.8 ppm, J(140P) = 142.5 Hz, 42%; Figure 13) and four minor ones with couplings indicative of P-k⁻ and k⁻ bonding (δ 29.9 ppm, J(140P) = 140.9 Hz, 7%; δ 26.5 ppm, J(140P) = 137.7 Hz, 7%; δ 24.7 ppm, J(140P) = 137.7 Hz, 4%; δ 20.7 ppm, J(140P) = 115.0 Hz, 2%).

The P-k⁺ signals likely reflect different rotamers, as the absence of ³¹P, ³¹P couplings rules out μ-complexation. In contrast to 12a, no N-k⁻ signal was detected for 24, presumably because the adjacent iPr group discourages coordination at this site. Chloride abstraction converted 24 and its isomers to k⁻⁻ 25 (δ(P) 11.3 ppm, J(140P) = 106.6 Hz), which was calculated to be energetically favored by 3.1 kcal mol⁻¹ over its epimer 25* (δ(P) = 34.3 ppm, J(140P) = 137.7 Hz). The obtained chiral transition metal complexes might be useful for asymmetric catalytic reactions, but such investigations were outside the scope of the present study. Based on the performance of ligands 7 (see above), asymmetric transfer hydrogenation seems a promising starting point.

### Conclusion

This study reports the synthesis of cyclic 2-phospha-tetrahydropyrazepines as novel 1,3-P,N ligands with the intent of opening new opportunities in coordination chemistry and catalysis. This class of cycloiminophosphanes contains a seven-membered allaphic imine ring with which it complements other classes of 1,3-P,N ligands, including the aromatic 2-pyridyl- and 2-imidazolyl-phosphanes, as well as the recently reported acyclic iminophosphanes and phosphamidines. The ligands were readily obtained in a one-pot process through a Beckmann rearrangement of cyclohexanones to reactive nitrosole ion intermediates, which were trapped with benzotriazole. The benzotriazole was then quantitatively replaced with a secondary phosphane (R=Ph, nBu, Cy), facilitated by triflic acid activation. With respect to other 1,3-P,N ligands, these cycloiminophosphanes distinguish themselves by their high N-basicity and their flexible backbone, as ³¹P NMR spectroscopy of the neutral ligands reveals the presence of flippamers, indicative of dynamic conformational behavior of the tetrahydropyrazine ring. The ligands coordinate in both a P-k⁺ and a P,N-k⁻ fashion to W(carbonyl) complexes, which were analyzed by IR spectroscopy to quantify the ligands’ donor strength. Coordination to [RhCpCl₂]₂ gave a dynamic mixture of k⁻⁻ and k⁻ complexes that, on treatment with silver triflate, lead only to the k⁻⁻ complexes. Treatment with [RuCl(C₆H₅)][PF₆] selectively provides P-k⁺ complexes, which were also effective catalysts for the hydration of benzonitrile (1.4 mol%, 180 °C, 3 h, up to 79%) and the transfer hydrogenation of cyclohexanone (0.5 mol%, 83 °C, 2 h, quant.); for the latter reaction iridium(III) could also be used (1 mol%, 83 °C, 4 h, quant.). Finally, as a preamble to asymmetric catalysis, a chiral cycloiminophosphane could be accessed from the natural precursor l-menthol in a selective Beckmann rearrangement. It was characterized by X-ray crystallography, and used to access Rh(III) and Ru(II) complexes. These chiral ligands form promising candidates for the future study of asymmetric 1,3-P,N catalysis.

### Experimental Section

**Preparation of compounds:** The syntheses and full characterization of 4–7, 9–14, 19–25, the Lewis acid catalyst screening of 4, and the P-k⁺ and k⁻⁻ Rh(III) complexes of 9 are described in full detail (14 pages) in the Supporting Information, which also contains their ¹H, ¹³C(¹H), ¹⁹F(¹H), and ³¹P NMR spectra (37 pages).

**Computational procedure:** Density functional calculations were performed at the B97X-D level of theory using Gaussian09, revision A.02. Geometry optimizations were performed using the 6-31G(d,p) basis set (Def2-TZVP for Rh(III)) and the nature of each stationary point (see the Supporting Information) was confirmed by frequency calculations.

**X-ray crystallography:** Deposition Numbers 2084404 (for 4), 2084405 (for 6a), 2084406 (for 6c), 2084407 (for 10), 2084408 (for 6b).
This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/ CW). We thank T. van Dijk for measuring high resolution mass-spectra and for fruitful discussions. M. K. Jongkind and R. Hoogendoorn are acknowledged for contributing to the synthesis of 9, A. Chirila and M. M. Heeren contributed to screening suitable Beckmann rearrangement substrates.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: cooperative effects · coordination modes · homogeneous catalysis · ligand design · N,P ligands

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