Ruthenium PNN(O) Complexes: Cooperative Reactivity and Application as Catalysts for Acceptorless Dehydrogenative Coupling Reactions

de Boer, S.Y.; Korstanje, T.J.; La Rooij, S.R.; Kox, R.; Reek, J.N.H.; van der Vlugt, J.I.

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Ruthenium PNN(O) Complexes: Cooperative Reactivity and Application as Catalysts for Acceptorless Dehydrogenative Coupling Reactions

Sandra Y. de Boer, Ties J. Korstanje, Stefan R. La Rooij, Rogier Kox, Joost N. H. Reek, and Jarl Ivar van der Vlugt

Homogeneous, Supramolecular & Bio-inspired Catalysis, van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

Supporting Information

ABSTRACT: The novel tridentate PNN(O) pincer ligand \( L^H \) features a reactive 2-hydroxypyridine functionality as well as a bipyridyl-methylphosphine skeleton for meridional coordination. This proton-responsive ligand coordinates in a straightforward manner to \( \text{RuCl}_2(\text{CO})(\text{H})(\text{PPh}_3)_3 \) to generate complex 1. The methoxy-protected analogue \( L^\text{Me} \) was also coordinated to \( \text{Ru}^{\text{II}} \) for comparison. Both species have been crystallographically characterized. Site-selective deprotonation of the 2-hydroxypyridine functionality to give 1’ was achieved using both mild (DBU) and strong bases (\( \text{KOTBu} \) and \( \text{KHMDS} \)), with no sign of involvement of the phosphinomethyl side arm that was previously established as the reactive fragment. Complex 1’ is catalytically active in the dehydrogenation of formic acid to generate CO-free hydrogen in three consecutive runs as well as for the dehydrogenative coupling of alcohols, giving high conversions to different esters and outperforming structurally related PNN ligands lacking the N(OH) fragment. DFT calculations suggest more favorable release of \( \text{H}_2 \) through reversible reactivity of the hydroxypyridine functionality relative to the phosphinomethyl side arm.

INTRODUCTION

Reactive ligand design has opened up fundamentally novel pathways for bond activation, small-molecule functionalization, and homogeneous catalysis. Tridentate pincer ligands that feature a reactive site have gained a great deal of interest during the past decade. Among several design types, lutidine-based PNP systems (Figure 1a) and analogues thereof have particularly gained momentum as ligands of choice for a range of transformations, because of their ability to undergo facile and reversible deprotonation of the phosphinomethyl side arm, generating a formally dearomatized \( \text{N} \)-heterocycle. Recently, also bis(pyrazole)-appended pyridines (Figure 1b) have attracted much attention as pH-responsive pincer frameworks in the context of metal–ligand bifunctional catalysis.

All three systems can be qualified as outer-sphere reactive ligands, as the proton-responsive (C–H, N–H, or O–H) functionality is not located directly in the first coordination sphere of the metal center. This sets these systems apart from ligands that demonstrate reversible amino/amido reactivity. However, the overall geometric features as well as the steric and electronic characteristics of e.g. PN vs. N(OH) frameworks are different, with respect to both acidity, orientation, and location of the protic hydrogen relative to the metal center geometry and distance to bound substrate or hydride fragments on the metal. Next to the design of symmetric reactive pincer ligands, nonsymmetric tridentate systems that incorporate ligand...
reactivity have shown potential application in cascade catalysis.\textsuperscript{10,11} There is currently no system that combines both PN and N\textsuperscript{OH} reactive ligand-based functionalities or studies that compare both functionalities with respect to activation and catalytic performance.

Ruthenium complexes bearing reactive pincer ligands have demonstrated catalytic competence in a substantial variety of reactions, including acceptorless dehydrogenation of alcohols into ketones, the hydrogenation of amides into alcohols and amines, and the reverse reaction: i.e., amide formation from alcohols and amines.\textsuperscript{12} In these catalytic reactions metal–ligand cooperativity is crucial, as reversible deprotonation of the phosphinomethyl arm is required during the catalytic cycle. In order to address the catalytic competence of a rigid pincer unit incorporating both the well-established PN coordination mode and the reactive N\textsuperscript{OH} fragment, and related to ongoing studies in our group on the application of reactive ligands for substrate activation and catalysis,\textsuperscript{13} we herein introduce the new ligand LH based on 6-(di-tert-butylphosphinomethyl)-6′-hydroxy-2,2′-bipyridine (Figure 2). Coordination of this ligand to Ru(Cl)-(CO)(H)(PPh\textsubscript{3})\textsubscript{3} has enabled stoichiometric reactivity studies with various bases and Ru-catalyzed dehydrogenative (coupling) reactions. We show the added value of this skeleton relative to other reactive PNN scaffolds for these reactions.

\section*{RESULTS AND DISCUSSION}

\textbf{Synthesis of Tridentate PNN(O) Ligand LH and Coordination to Ru(II).} The synthesis of ligand LH was straightforward, despite the multistep approach, and comparable to the synthesis of bipyridine PNN ligands.\textsuperscript{4d} Intermediate A was synthesized according to a literature procedure\textsuperscript{14} via a Stille coupling using 2-bromo-6-methoxypyridine and 2-methyl-6-(tributylstannyl)pyridine (Scheme 1). Monolithiation of the Stille coupling using 2-bromo-6-methoxypyridine and 2-methyl-6-methoxy-3,5-di-tert-butylpyridine (Scheme 1) was synthesized according to a literature procedure\textsuperscript{14} via a Stille coupling using 2-bromo-6-methoxypyridine and 2-methyl-6-(tributylstannyl)pyridine (Scheme 1). Monolithiation of the Stille coupling using 2-bromo-6-methoxypyridine and 2-methyl-6-methoxy-3,5-di-tert-butylpyridine (Scheme 1). 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as KOtBu or KHMDS). Addition of 1 equiv of NEt₃ (pKₐ value in DMSO: 9)¹⁵ to complex 1 did not lead to proton transfer, according to ¹H NMR spectroscopy, but reaction with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (pKₐ value in DMSO: 12) gave an immediate color change from orange to brown-red, providing selective deprotonation of the 2-hydroxypyridine unit to generate complex 1' (Scheme 2). Using 1 equiv of KOtBu or KHMDS at −32 °C also led to 1', indicating that the 2-hydroxypyridine is the ultimate site for deprotonation.¹⁶ Addition of acid to a solution of 1' regenerates 1.

The transformation of 1 into 1' coincides with only a small shift in the ³¹P NMR spectrum to 102.7 ppm (Δδ = 1.7 ppm), suggesting that the overall donor capabilities of the pyridone unit are fairly similar to that of the parent 2-hydroxypyridine unit. In the ¹H NMR spectrum a doublet is observed at δ −19.47 (J_HP = 25 Hz) for the hydride and an ABX system centered around 3.80 and 3.63 ppm supports an intact methylene spacer.

Catalytic Activity of 1 in the Dehydrogenation of HCOOH. Hydrogen is potentially one of the major energy carriers for the future, and formic acid has been demonstrated to provide an interesting storage-release system for the reversible storage of dihydrogen.¹⁷ Formic acid dehydrogenation is typically performed using (sub)stoichiometric equivalents of base, but this negatively affects the hydrogen content of this storage material. Thus, catalytic dehydrogenation ideally would not require base or other additives. Ruthenium complexes bearing other types of pH-responsive ligands have been shown to be efficient catalysts for the reversible hydrogenation of CO₂ to formic acid.¹⁸ Complex 1' was found to be a competent catalyst for the base-free dehydrogenation of HCOOH (Scheme 3).¹⁹,²⁰ When only 1 equiv of formic acid was added to complex 1', generated in situ from 1 and KOtBu, a slight color change was observed from brown-red to orange-red, concomitant with the evolution of small bubbles of gas from the solution and detection of species 1' in the ³¹P NMR spectrum. We postulate the intermediacy of dihydride species 1HH, generated by proton and hydride transfer from formic acid to 1'.

Next, a catalytic experiment was performed using 10 mol% of 1', generated in situ from 1 and base, in dioxane as solvent at 75 °C. The dehydrogenation of formic acid was monitored volumetrically for three consecutive catalytic runs (Figure 4).

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dehydrogenation of formic acid with complex 1′ (Scheme 4).

Initially, HCOOH coordinates to deprotonated species 1′. The protic hydrogen of formic acid binds via a hydrogen bond to the ligand pyridonato group, which induces activation of the O−H bond, while the C═O fragment coordinates to the Ru center via the neutral oxygen. As there is likely no available vacant site on the metal (dissociation of a reprotonated pyridone group by Ru−N bond breaking is unlikely but cannot be ruled out on the basis of these data), β-H elimination is deemed not preferred. Therefore, a rearrangement is necessary that involves a rotation around the O−H bond to generate a species in which the formate hydrogen (HCOO−) atom coordinates to the ruthenium, concomitant with proton transfer to the pyridonato oxygen. This direct hydride transfer or ligand-assisted direct hydride transfer generates the release of carbon dioxide, which is accompanied by the formation of complex 1HH. In the final step the deprotonated species 1′ is regenerated, concomitant with the release of H₂.

**Catalytic Activity of 1′ in the Acceptorless Dehydrogenative Coupling of Alcohols.** Ruthenium pincer complexes have previously been successfully applied in the bifunctional activation of O−H bonds, a feature that can subsequently be used in dehydrogenative coupling reactions: e.g., to generate esters from alcohols with release of H₂.²¹ We were interested in probing the catalytic competence of the reactive ligand scaffold in 1 and to find out how this system compares with known Ru(PNN) systems in the acceptorless catalytic dehydrogenative coupling of alcohols to esters, given the different geometric and electronic features of the reactive pyridone C═O. Having established the O−H bond activation of BzOH, this substrate was subjected to literature conditions to afford 90% conversion to benzyl benzoate in 15 h without any formation of the aldehyde (based on GC and NMR analysis), thereby outperforming a RuH(Cl)(CO)(PNN) complex bearing a 2-(diethylaminomethyl)-6-(di-tert-butylphosphinomethyl)pyridine PNN ligand (95% conversion in 24 h).²² Complex 1Me shows only 52% conversion to benzyl benzoate after 16 h, indicating the positive effect of the availability of the pyridone C═O unit on the catalysis. The derivative 1MeCN is inactive under these conditions, likely due to strong binding of acetonitrile, preventing substrate coordination, while complex 1 is also active at 70 °C (74% conversion in 28 h), but no conversion is observed at room temperature. In the presence of DBU as external base, surprisingly, no turnover was obtained after 20 h at 117 °C. Although the deprotonation of complex 1 occurred smoothly with DBU in THF, the lack of activity could be caused by the reduced base strength of DBU in toluene due to the lower polarity of the medium.²³ We also studied the dehydrogenative coupling of 1-butanol to generate butyl butyrate. Catalyst 1 (1 mol %) gave full conversion to the desired product after 15 h at 117 °C with 1 mol % of KOTBu in toluene, thus outperforming the reaction with benzyl alcohol. The benchmark RuH(Cl)(CO)(PNN) complex again requires 72 h to achieve 92% conversion.

On the basis of the above data and the well-known reactivity of the PNP and PNN pincer complexes with a reactive methylene spacer in the ligand backbone, we propose a plausible catalytic cycle for the dehydrogenative coupling of alcohols by preactivated complex 1′, involving the hydroxypyridine functionality (Scheme 5). Initially, activation of the alcohol O−H bond results in ligand side arm rearomatization, to form alkoxide complex 2. In the following step 1HH is formed, presumably via dissociation of the reprotonated pyridone group by Ru−N bond breaking, concomitant with

**Scheme 5. Proposed Catalytic Cycle for the Dehydrogenative Coupling of Alcohols to Esters Using Complex 1 as Precatalyst and Involving 1′ in the Cycle**
formation of the aldehyde. Elimination of dihydrogen then regenerates complex 1'. The aldehyde condenses with alcohol directly or condenses in a metal-catalyzed fashion to form the hemiacetal, which (upon reaction with complex 1') leads to aromatized complex 2'. Dehydrogenation via β-H elimination eliminates the ester and generates trans-dihydride complex 1HH, from which another equiv of dihydrogen is then liberated to regenerate complex 1", completing the catalytic cycle. Alternatively, inner-sphere formation of the hemiacetal by coupling of the bound alkoxide with alcohol from solution may proceed as well.

**Computational Investigations into Dihydrogen Formation.** As can be seen in the above proposed catalytic cycles, the central complex formed is 1HH, concomitant with the release of CO2 (formic acid dehydrogenation) or aldehyde/ester (dehydrogenative coupling of alcohols). To date, no direct comparison has been made between the reactive 2-hydroxy-pyridine and phosphinomethyl-based functionalities with respect to H2 release via dehydrogenative pathways. Hence, we decided to perform DFT calculations (BP86, def2-TZVP, disp3), and the obtained energy profiles are displayed in Figure 5. The aromatized trans-dihydride complex 1HH was used as a reference point (0.0 kcal mol$^{-1}$). Starting from this complex, transition state TS' (H2 formation over the pyridone) is 5.0 kcal mol$^{-1}$ higher in free energy, while the barrier for TS" (H2 formation over the phosphon methyl) is 22.5 kcal mol$^{-1}$. However, proton shuttling via tBuOH, obtained from protonation of KOtBu, could be involved, which could lower the barrier significantly. Remarkably, the barrier of TS'PS' is lowered only marginally and is thus still much higher (17.3 kcal mol$^{-1}$) in energy than TS'. Subsequent formation of intermediate Int' is thermoneutral in comparison to 1HH, whereas species Int" is slightly uphill in energy by 4.7 kcal mol$^{-1}$. Liberation of dihydrogen is found to be exergonic by roughly 4 kcal mol$^{-1}$ for both complexes. Overall, the formation of dihydrogen is exergonic by $-4.1$ kcal mol$^{-1}$ for 1' and slightly endergonic by 0.9 kcal mol$^{-1}$ for 1", demonstrating that the pathway is both kinetically and thermodynamically favored via the hydroxy-pyridine species.

**CONCLUSIONS**

The novel rigid dual-mode reactive PNN$^{\text{OHH}}$ pincer ligand $^L$ bearing two different cooperative sites is easily synthesized, and coordination to ruthenium allows access to Ru(Cl)(CO)(H)-L(1H) complex 1, which was crystallographically characterized as the MeCN adduct. Reaction of complex 1 with DBU leads to selective deprotonation of the hydroxy-pyridine functionality, providing activated complex 1'. An excess of this weak base did not induce dearomatization via deprotonation of the phosphinomethyl side arm functionality. Application of complex 1 in the dehydrogenation of formic acid produces CO-free dihydrogen with a turnover frequency of 30 h$^{-1}$ for several consecutive runs, demonstrating catalyst robustness. Despite the ease of deprotonation of 1 relative to other complexes bearing proton-responsive ligands, only moderate catalytic activity in formic acid dehydrogenation was obtained under these unoptimized conditions. Complex 1 is also catalytically active in the dehydrogenative coupling of alcohols into esters, resulting in 90% conversion for benzyl alcohol and full conversion for 1-butanol. As such, this system outperforms related Ru(PNN) species, illustrating the beneficial role of the 2-hydroxy-pyridine reactive side arm. DFT calculations suggest an active role for the pyridine side arm in H2 liberation in these catalytic conversions.

**EXPERIMENTAL SECTION**

**General Procedures.** Solvents were either distilled over suitable drying agents or dried using an MBraun SPS (Solvent Purification System). All experiments were carried out under an inert-gas atmosphere using standard Schlenk techniques. All chemicals were dried under standard Schlenk techniques.
commercially available and used without further purification, unless
described otherwise. The H, 3H1P, 3P3H, and 3C1'H NMR spectra were
recorded at room temperature on Bruker AV400 (at 400, 162, and 100 MHz, respectively) and Bruker DRX500 instruments (at 500, 202, and 126 MHz, respectively) and calibrated to the residual proton and carbon signals of the solvent20 or to 85% H3PO4 externally. H1 and 3C NMR solution 1H NMR spectra were recorded on a JEOL AccuTOF GC v 4g, JMS-T100GC mass spectrometer (FD) and on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer (CSI). IR spectra were recorded with a Bruker Alpha-p FT-IR spectrometer operated in

### Syntheses and Characterization. 2-Methyl-6-(tributylstannyl)pyridine. This synthesis was based on a literature procedure. 22

2-Bromo-6-methylpyridine (7.56 g, 43.9 mmol) was dissolved in THF
(20 mL) and cooled to –78 °C. A 2.5 M solution of n-BuLi in hexanes (17.6 mL, 43.9 mmol) was added over the course of 20 min and the mixture was stirred for 3 h more at –78 °C. Tributylmagnesium (14.3 g, 43.9 mmol) was added, and the mixture was allowed to warm to room temperature overnight. The reaction was quenched with saturated NaHCO3 solution (40 mL) and extracted with ethyl acetate
(3 × 100 mL). The combined organic layers were washed with water and brine (both 50 mL), dried over Na2SO4, and concentrated in vacuo to give a yellow oil (16.58 g, quantitative). 1H NMR (300 MHz, chloroform-d, ppm): δ 7.39 (t, J = 7.5 Hz, 1H, pyH), 7.20 (d, J = 7.5 Hz, 1H, pyH), 6.98 (dd, J = 7.1, 1.1 Hz, 1H, pyH), 2.57 (s, 3H, CH3), 1.64–1.54 (m, 6H, SnBu), 1.36 (h, J = 7.2 Hz, 6H, SnBu). 13C NMR (75 MHz, chloroform-d, ppm): δ 173.04 (s, pyC), 158.57 (s, pyC), 133.23 (s, pyC), 129.33 (s, pyC), 121.45 (s, pyC), 29.13 (s, CH3), 27.57 (s, CH3), 24.93 (s, CH3), 13.47 (s, CH3), 9.85 (s, CH3). MS (FD–): [C12H12N2O]+ m/z calculated 383.197166 [M]+; found, 383.19725 [M]+.

### Compound A, 6-Methoxy-6'-methyl-2,2'-bipyridine. This synthesis was based on a literature procedure. 23

2-Methoxy-6-bromopyridine (8.2 g, 43.4 mmol), Pd(PPh3)4 (0.5 g, 0.434 mmol), LiCl (3.8 g, 96.8 mmol), and 2-methyl-6-(tributylstannyl)pyridine (43.4 mmol) were dissolved in diethyl ether (20 mL) and then cooled to –78 °C. In a separate flask, Pd(OAc)2 (1.012 g, 69%). 1H NMR (500 MHz, CD2Cl2, ppm): δ 7.92 (s, 1H, OCH3), 7.17 (d, J = 7.8 Hz, 1H, pyH), 7.04 (s, 1H, OCH3), 7.09 (d, J = 7.8 Hz, 1H, pyH), 6.72 (d, J = 7.1 Hz, 1H, pyH). 13C NMR (75 MHz, CD2Cl2, ppm): δ 163.8 (s, pyC), 163.2 (d, J = 15.0 Hz, pyC), 147.0 (s, pyC), 141.7 (s, pyC), 137.7 (s, pyC), 125.5 (d, J = 9.5 Hz, pyC), 121.3 (s, pyC), 117.1 (d, JPC = 1.5 Hz, pyC), 103.9 (s, 1C, pyC), 132.3 (d, JPC = 22.5 Hz, P(ICH2)2), 31.8 (d, JPC = 25.3 Hz, CH3), 29.8 (d, JPC = 32.0 Hz, P(ICH2)2), 19.0 (s, 1H, P(ICH2)2). MS (FD–): [C12H12N2O]+ m/z calculated 383.197166 [M]+; found, 383.19725 [M]+.

### Complex 1, RuCl(CO)(H)(H)[H]+. RuCl(CO)(H)(PPh3) (342.7 g, 0.36 mmol) and L6 (1118.8 g, 0.36 mmol) were dissolved in 10 mL of THF. The solution was heated to 50 °C and stirred overnight. The reddish orange suspension was cooled to room temperature and filtered. The solid was washed with cold Et2O (3 × 5 mL), and the product was obtained as a yellow solid (120.1 g, 67%). 1H NMR (500 MHz, CD2Cl2, ppm): δ 7.20 (d, J = 16.5 Hz, Ru-CO), 167.0 (s, pyC), 164.2 (d, JPC = 4.6 Hz, pyC), 158.3 (s, pyC), 156.6 (s, pyC), 141.5 (s, pyC), 129.5 (s, pyC), 124.8 (d, JPC = 8.9 Hz, pyC), 121.0 (s, pyC), 115.0 (s, pyC), 114.3 (s, pyC), 37.67 (d, JPC = 25.4 Hz, CH3P), 37.63 (d, JPC = 17.2 Hz, PC6H4(CH2)), 37.59 (d, JPC = 16.9 Hz, PC6H4(CH2)), 29.6 (d, JPC = 4.2 Hz, PC6H4(CH2)). MS (FD–): [C12H12N2O]+ m/z calculated 461.0937 [M + Cl]+; found, 461.0936 [M + Cl]+.

### Complex 2, RuCl(CO)(H)(H)[H]+. This complex was synthesized in the same manner as complex 1, but from L6 (115.2 g, 0.334 mmol) and RuCl(CO)(H)(PPh3) (318.2 g, 0.334 mmol), and was obtained as an orange-red powder (155.0 g, 91%). 1H NMR (400 MHz, acetone-d6, ppm): δ 8.17 (d, J = 8.1 Hz, 1H), 8.12 (t, J = 8.1 Hz, 1H).
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Hz, 1H), 8.04 (t, (J = 8.1 Hz, 1H)), 7.94 (d, (J = 7.8 Hz, 1H)), 7.63 (d, (J = 7.6 Hz, 1H)), 7.25 (d, (J = 8.6 Hz, 1H)), 4.16 (s, 3H), 3.87 (dd, (J = 17.4, 11.3 Hz, 1H)), 3.73 (dd, (J = 17.3, 7.9 Hz, 1H)), 1.42 (d, (J = 13.7 Hz, 9H)), 1.22 (d, (J = 13.7 Hz, 9H)), −14.93 (d, (J = 24.3 Hz, 1H)). 19F NMR (162 MHz, acetonitrile-d6, ppm): δ 105.9 (s). 31C NMR (126 MHz, CD3OD, ppm): δ 208.71 (d, (J = 15.5 Hz)), 164.83 (s), 161.75 (s), 155.52 (d, (J = 32.3 Hz)), 139.51 (s), 136.08 (s), 128.84 (s), 122.64 (d, (J = 9.0 Hz), 119.68 (s), 115.21 (s), 107.53 (s), 56.81 (s), 37.53−37.13 (m), 36.33 (d, (J = 24.7 Hz)), 29.79 (d, (J = 4.3 Hz)), 28.74 (d, (J = 3.4 Hz)).

The red solution was analyzed by GC and 1H NMR spectroscopy. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00111.

NMR spectra of new compounds, computational data, and crystallographic details (PDF)

Computational data (XYZ)

Crystallographic data (CIF)

Notes

The authors declare no competing financial interest.

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