

Novel Rhodium N-Heterocyclic Carbene Complexes: Catalysts for Green Chemistry

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E=mc² Journal Submission

Personal Section

I have always been interested in the physical sciences, particularly chemistry, from a very young age. I started to seriously pursue this interest in middle school and jumped headlong into the exciting world of scientific research. My very first science fair project, completed in the spring of my seventh grade year, dealt with the harmful effects of acid rain on a variety of common transition metals. This project laid the foundation of my dual interests in inorganic transition metal chemistry and the environmental applications of chemistry. One year later, my research switched gears towards the medical applications of transition metal chemistry. I devised an original recipe for baking powder by eliminating a standard ingredient, sodium aluminum sulfate, which has been identified as a possible chemical trigger of Alzheimer's disease, and replacing it with a variety of transition metal compounds that are essential to the body. Entering high school, I naturally wanted to combine my interests in both environmental and medical issues while still focusing on the area of inorganic/transition metal chemistry. After talking to various mentors and exploring a range of literature, I was pointed in the direction of *green chemistry*, a sub-field of chemistry that combined my two interests perfectly. Green chemistry, at its core, is a field aimed at creating, from the ground up, specialized catalysts, chemical agents, reactions, and other processes that minimize or even eliminate toxicity and harm to the environment and human health. Given these ambitious aims, a large part of green chemistry

involves novel synthesis of various compounds that can potentially end up as important catalysts in a variety of important reactions. This is the “vein” of green chemistry my project fell into: the synthesis of novel complexes (and useful catalysts) using the metal rhodium. The catalytic activity of the complexes was discovered after a series of tests, and I found them especially pertinent to pharmaceutical synthesis reactions.

I conducted the research for this project over the course of three years, and what stood out to me the most throughout that time was that while the actual, physical lab work of chemical synthesis is extremely challenging, it is also an intrinsically exciting process. It was seldom, however, smooth sailing; I, like most people working in a laboratory, had my fair share of failures and setbacks. I was forced to adapt my research many times, procedurally and conceptually. Thanks to invaluable guidance from my mentors in the lab, these “shifts” turned up exciting new avenues of experimentation and discovery. In short, utmost flexibility is paramount in research. Often, due to the nature of the project, I was learning relevant concepts as I worked. On the one hand, this is challenging, yet witnessing a concept first hand in the lab cemented my understanding of a concept with absolute clarity. For anyone who has the chance to do research, embrace this way of learning a concept, tackling it from every conceivable angle. Finally, keep the most detailed, meticulous, accurate written record of your work that you possibly can. As I quickly learned, it is absolutely indispensable. Adherence to these few principles, at least in my experience, is the key to success in any endeavor doing scientific research.

Abstract

N-Heterocyclic carbenes (NHCs) and their role as universal spectator ligands in transition metal compounds have recently sparked a wide interest in the broader field of Green Chemistry because of their astounding catalytic properties in reactions involving organic synthesis. This project dealt specifically with the synthesis of new Rhodium NHC complexes, derived from triazole, via high-yielding air stable procedures. Six of these Rhodium complexes were successfully synthesized, three neutral complexes, **2a-c**, by transmetallation from Ag(I) complexes and subsequently three more cationic complexes, **3a-c**, were isolated by treating the neutral complexes **2a-c** with triphenylphosphine and silver tetrafluoroborate, as shown in **reaction schemes 2 and 3**. They were characterized by elemental analysis and multi-nuclear NMR, and the structure of compounds **2c** and **3a-c** were further determined by x-ray diffraction. The complexes display a square planar geometry and the Rh-C_{NHC} distances between the NHC ligand and the Rhodium atom range from 2.017-2.034 Å. Most significantly, complex **3b** yielded two polymorphs displaying the first structural evidence of rotation about the metal-carbene bond. The complexes synthesized in this experiment, with their application to industrial and pharmaceutical processes such as alkene metathesis and transfer hydrogenation, have a great potential to be effective Green Chemistry catalysts.

Introduction

In recent years, N-heterocyclic carbenes (NHCs) and their transition metal complexes have emerged as efficient ligands in a great variety of catalytic processes, including alkene metathesis and transfer hydrogenation.¹⁻³ The first metal-NHC complexes were reported in 1968 by Wanzlick and Schönherr⁴ and by Öfele⁵ and the first stable free carbenes was isolated in 1991

by Arduengo et al.,⁶ These carbenes form strong bonds to metal centers⁷⁻¹¹ which makes them particularly beneficial for their use as ligands in organometallic catalysts. Contemporary NHC research is both vigorous and diverse; NHCs' fascinating molecular and electronic structures, uniquely challenging synthesis, and versatile properties resulted in their transition metal complexes' label as "a new generation of catalysts in organic synthesis." and many metal-NHC complexes of many transition elements have been reported.

Carbenes are neutral 2 electron donors, thermodynamically and kinetically unstable, and form very strong bonds with metal atoms. NHCs specifically are Fischer type carbenes. Steric tuning of NHCs is possible by changing the R₁ and R₂ substituents at nitrogen, and previous studies have indicated¹²⁻¹⁶ that the barrier to metal-NHC bond rotation is largely steric in nature.

NHC based catalysts display unusually high thermal stability and retain their catalytic activity even under extreme reaction conditions.

Rhodium complexes with several N-heterocyclic carbene ligands have been synthesized in the past and their electronic properties studied.¹⁷⁻²¹ However, triazole-based NHC ligands (Figure 1) have not been

extensively studied with rhodium. One facet of this work was to successfully synthesize new air stable triazole-based rhodium (I) NHC complexes in high yield. The iridium analogues of the rhodium complexes **3a-c** synthesized in this work have previously shown some catalytic activity for the transfer hydrogenation of C=C, C=N, and C=O bonds.^{22, 23} However, the novel Rh-NHC complexes synthesized in this work have shown equal, if not more vigorous, catalytic activity in the transfer hydrogenation of C=O, and especially C=N. It is usually held that the more polar

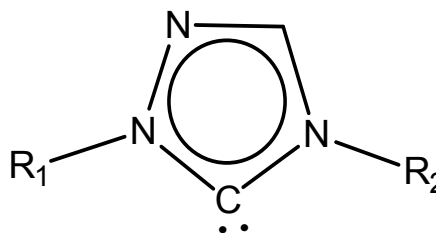
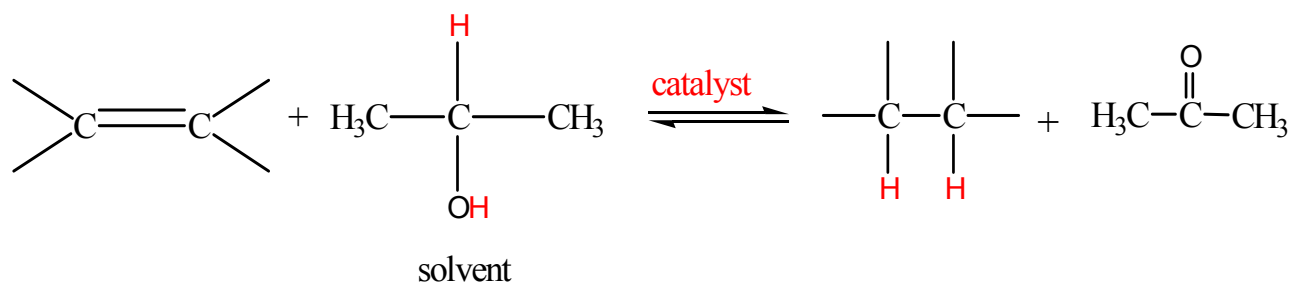


Figure 1: Triazole (an NHC carbene ligand)

C=O bond is easily reduced compared to the less polar C=N bond and the nonpolar C=C bonds by these organometallic catalysts, yet the rhodium complexes synthesized in this research exhibit an opposite trend with the better catalytic reduction of imines. These attributes of the newly synthesized rhodium complexes indicate a very promising and strong application for catalysis in numerous organic synthesis reactions and commercially important processes. The reduction of the C=N bond specifically is of great interest to the pharmaceutical industry because amine functional groups are present in many drugs.

Catalytic reduction is preferred to stoichiometric reduction by Hydrogen gas for large scale industrial use because it presents considerable safety hazards. However, the use of a solvent that can donate hydrogen overcomes these difficulties and comes closer to developing more green methods (**Scheme 1**).

Scheme 1. Transfer Hydrogenation with Isopropanol.



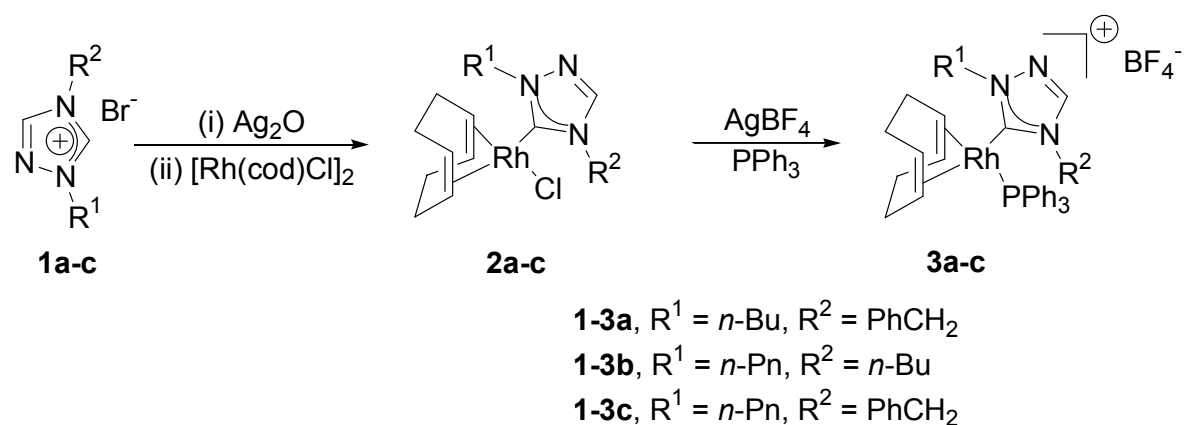
For example, isopropanol is a popular reactive solvent for the transfer hydrogenation reaction because it is easy to handle, relatively non-toxic, environmentally benign, and inexpensive. The volatile co-product acetone can also be easily removed to shift any unfavorable equilibrium. Many organometallic catalysts contribute to more environmentally safe and inexpensive methods of organic synthesis. Specifically, the rhodium NHC complexes

synthesized in this work have potential importance in developing greener synthesis in the pharmaceutical industry.

Results and Discussion:

Synthesis and Characterization. Rhodium (I) triazole based NHC complexes **2a-c** and **3a-c** were obtained in high yields by simple methods in the presence of air.

Scheme 2: Overall Reaction Scheme.



1,2,4-triazolium salts **1a-c** were prepared by treating the appropriate 1-neopentyl(*n*-Pn) or 1-*n*-butyl (*n*-Bu) triazole with *n*-butyl or benzyl bromide in toluene at reflux for 16 hours followed by isolation with diethyl ether. These triazolium salts have characteristic resonance in the ^1H NMR near 8.9 ppm ($\text{C}_3\text{-H}$ triazole proton) and 11.8 ppm ($\text{C}_5\text{-H}$ triazole proton).

The metal complexes **2a-c** were prepared by in situ transmetallation from silver carbene complexes of compounds **1a-c** (**Scheme 2**). Treatment with Ag_2O in CH_2Cl_2 at room temperature formed the intermediate silver carbene compounds, which were added directly to the $[\text{Rh}(\text{cod})\text{Cl}]_2$ in CH_2Cl_2 to yield the light yellow solids **2a-c**. These were recrystallized in

CH₂Cl₂/pentane to give crystals of **2a-c** in high yield. The structure of **2c** was determined by x-ray diffraction. All of the isolated complexes lack the C₅-H triazole proton resonance, but show a signal for the C₃-H triazole proton at 7.68–7.86 ppm.

The corresponding ionic complexes **3a-c** were synthesized by treating **2a-c** with 1 equivalent of triphenylphosphine and AgBF₄ in CH₂Cl₂ in the dark under nitrogen at room temperature (**Scheme 2**). They were recrystallized in CH₂Cl₂/pentane to yield the yellow-orange solids **3a-c** in high yield. Compound **3b** formed two polymorphs, and the structure of these polymorphs and compounds **3a** and **3c** were determined by x-ray diffraction.

The chemical shifts δ of the carbene carbon and the coupling constants $J(\text{Rh-C})$ in the ¹³C NMR of complexes **2a-c** and **3a-c** (**Table 1**) show a systematic order. There was no considerable difference in the chemical shift of the carbene carbon and the $J(\text{Rh-C})$ by varying the R₁ and R₂ groups in the NHCs.

Table 1. ¹³C NMR Chemical Shifts δ and Rh-C_{Carbene} Coupling Constants J and % yield of complexes **2a-c** and **3a-c**.

Complex	δ C _{Carbene} [ppm]	$J(\text{Rh-C}_{\text{Carbene}})$ [Hz]	Yield [%]
2a	185.46	51.56	97
2b	186.03	51.40	90
2c	186.59	50.86	94
3a	181.98	46.90	97
3b	182.30	46.50	91
3c	182.99	52.50	94

The chemical shifts δ of the phosphorus and the coupling constants $J(\text{Rh-P})$ in the ³¹P NMR of complexes **3a-c** (**Table 2**) show a similar systematic order.

Table 2. ³¹P NMR Chemical Shifts δ and Rh-P Coupling Constants J of complexes **3a-c**.

Complex	δ P [ppm]	$J(\text{Rh-P})$ [Hz]
3a	24.99	152.77
3b	24.93	153.41
3c	24.76	152.77

Structural Study. The structures of compounds of **2c** and **3a-c** were determined using single crystal x-ray diffraction (**Figures 2-5**). All the compounds display square planar geometries. As expected for NHCs, the Rh-C_{Carbene} bond lengths of 2.017-2.034 Å suggest a single bond. A selection of characteristic bond angles and bond distances are given in **Table 3**. A summary of relevant crystal and data parameters is presented in **Table 4**.

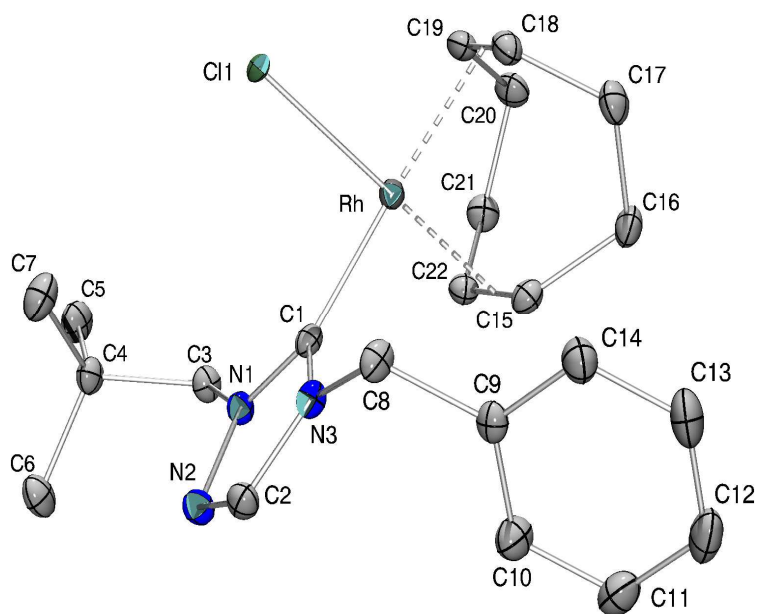


Figure 2. Ortep style plot of **2c** in the solid state. Thermal ellipsoids are drawn at 50% probability level and Hydrogen atoms are omitted for clarity.

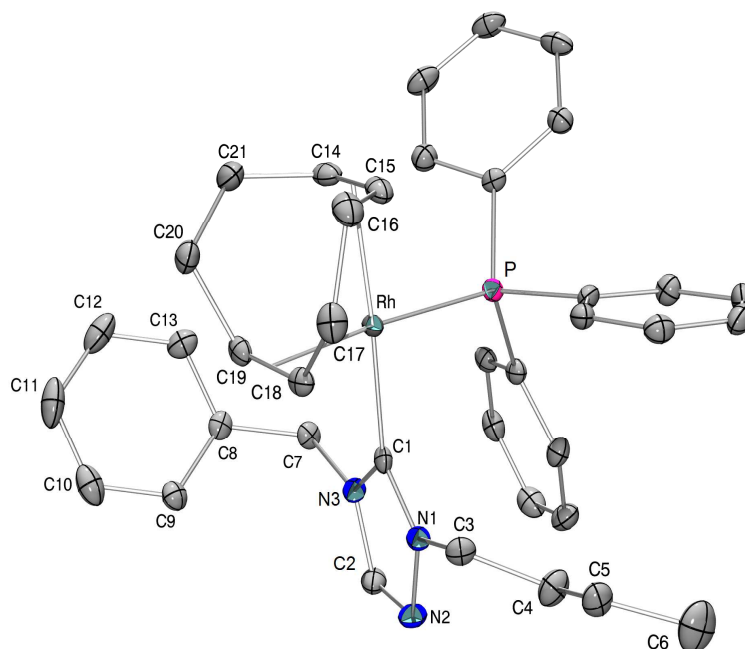


Figure 3. Ortep style plot of **3a** in the solid state. Thermal ellipsoids are drawn at 50% probability level and Hydrogen atoms are omitted for clarity.

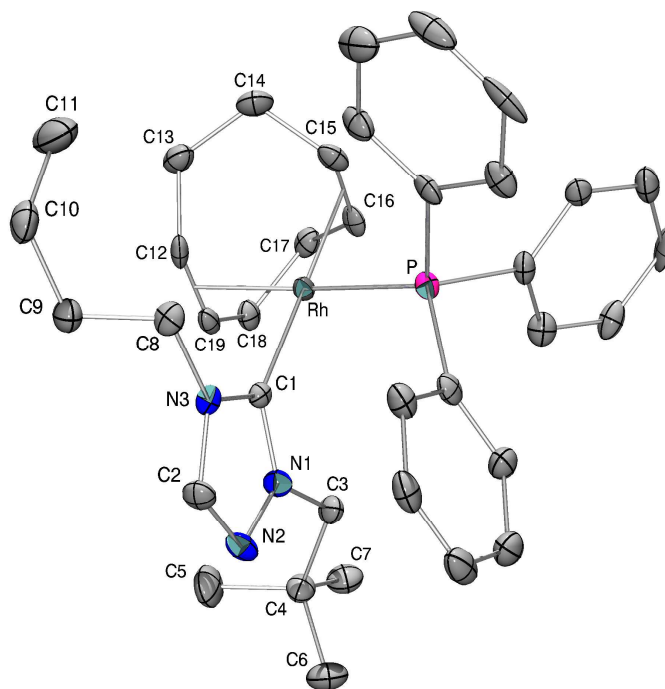


Figure 4a. Ortep style plot of a polymorph of **3b** in the solid state and the packing of **3b** in an orthorhombic unit cell. Thermal ellipsoids are drawn at 50% probability level and Hydrogen atoms are omitted for clarity.

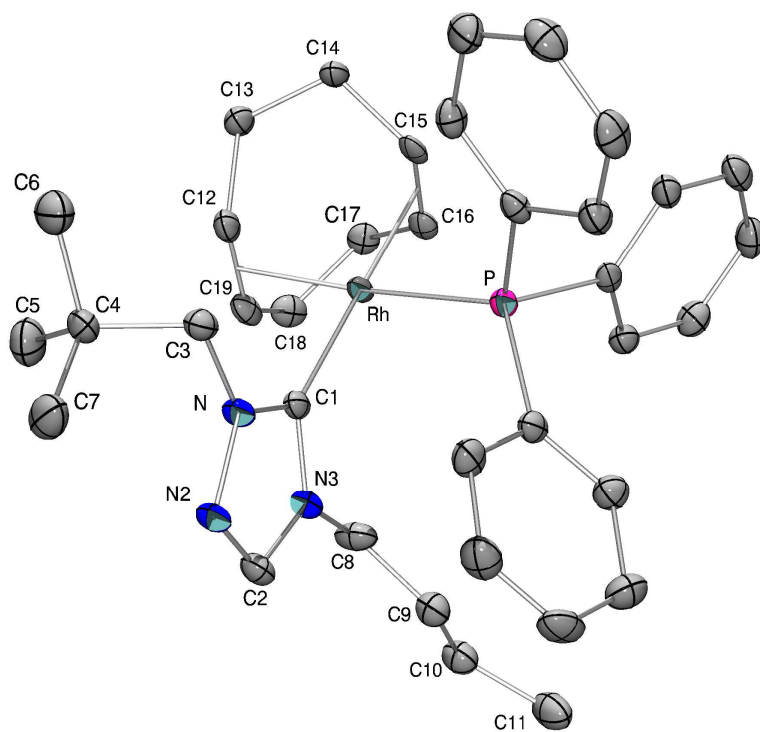


Figure 4b. Ortep style plot of a polymorph of **3b** in the solid state and the packing of **3b** in a monoclinic unit cell. Thermal ellipsoids are drawn at 50% probability level and Hydrogen atoms are omitted for clarity.

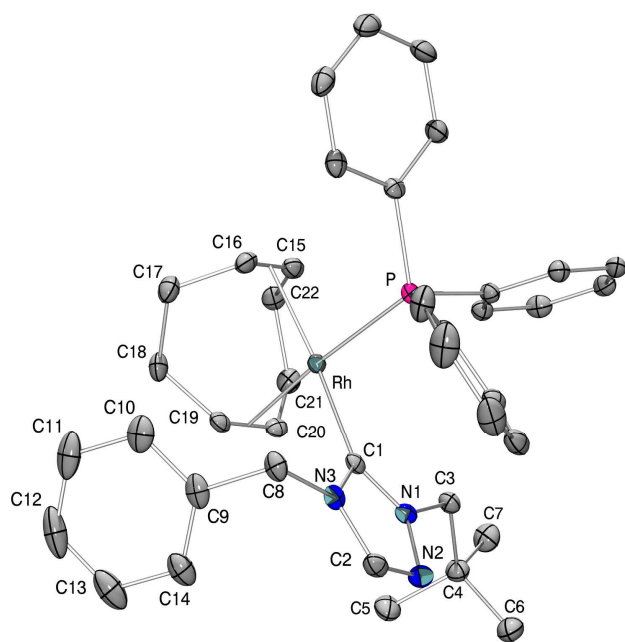


Figure 5. Ortep style plot of **3c** in the solid state. Thermal ellipsoids are drawn at 50% probability level and Hydrogen atoms are omitted for clarity.

Table 3. Selected bond distances (Å), and bond & torsion angles (deg) for **2c** and **3a-c**.

Complex	Rh-C1 _{Carbene}	N1-C1 _{Carbene} -N3	Cl-Rh-C1 _{Carbene}	N1-C1 _{Carbene} -Rh-Cl
2c	2.017 (3)	102.6 (3)	88.09 (8)	98.3
3a	Rh-C1 _{Carbene} 2.017 (3)	N1-C1 _{Carbene} -N3 102.6 (2)	P-Rh-C1 _{Carbene} 88.20 (8)	N1-C1 _{Carbene} -Rh-P 95.1 (3)
3b (ortho)	2.019 (4)	103.6 (4)	88.64 (12)	-87.9 (4)
3b (mono)	2.034 (3)	103.2 (3)	91.17 (9)	91.0 (3)
3c	2.034 (2)	102.27 (18)	89.50 (6)	-87.27 (19)

The two polymorph crystals of **3b** gave rise to two different structures and space groups; one in the rare orthorhombic chiral space group, and the other in a more common monoclinic centro-symmetric space group. This is the first structural evidence of free rotation about the Rh-C_{Carbene} bond. It is interesting to note that the C8-C9-C10-C11 torsion angles are 65.0 (6)° for the orthorhombic structure, but 165.6 (6)° for the monoclinic structure.

Table 4. Crystal Data and Structure Refinement Details for **2c** and **3a-c**

Identification code	2c	3a	3b orthorhombic	3b monoclinic	3c
Crystal color and size	yellow, 0.26 × 0.15 × 0.09 mm ³	yellow, 0.28 × 0.19 × 0.16 mm ³	orange, 0.24 × 0.24 × 0.14 mm ³	yellow, 0.31 × 0.13 × 0.07 mm ³	yellow, 0.27 × 0.18 × 0.07 mm ³
Empirical formula (total)	C ₂₃ H ₃₃ Cl ₃ N ₃ Rh	C ₃₉ H ₄₄ BF ₄ N ₃ PRh	C ₃₇ H ₄₈ BF ₄ N ₃ PRh	C ₃₇ H ₄₈ BF ₄ N ₃ PRh	C ₄₀ H ₄₆ BF ₄ N ₃ PRh
Formula weight	560.78	775.46	755.47	755.47	789.49
Temperature	100(2) K	100(2) K	100(2) K	100 (2) K	100(2) K
Radiation, wavelength	MoK α , 0.71073 Å	MoK α , 0.71073 Å	MoK α , 0.71073 Å	MoK α , 0.71073 Å	MoK α , 0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$	Monoclinic, P21	Orthorhombic, Pca21	Monoclinic, P21/n	Triclinic, P $\bar{1}$
Unit cell parameters	a = 10.664(3) Å b = 11.0892(14) Å c = 12.1804(16) Å α = 116.310(2) ^o β = 101.264(3) ^o γ = 101.292(3) ^o	a = 9.7209(5) Å b = 17.2947(8) Å c = 11.2937(5) Å α = 90 ^o β = 111.3(10) ^o γ = 90 ^o	a = 17.5796(17) Å b = 10.7382(10) Å c = 18.8487(17) Å α = 90 ^o β = 90 ^o γ = 90 ^o	a = 9.5515(8) Å b = 18.8196(19) Å c = 20.417(2) Å α = 90 ^o β = 101.769(2) ^o γ = 90 ^o	a = 11.1111(7) Å b = 13.0077(7) Å c = 13.3407(8) Å α = 87.6230(10) ^o β = 80.4350(10) ^o γ = 75.4090(10) ^o
Cell volume	1199.2(4) Å ³	1769.00(15) Å ³	3558.1(6) Å ³	3593.0(6) Å ³	1840.00(19) Å ³
Z	2	2	4	4	2
Calculated density	1.553 g/cm ³	1.456 g/cm ³	1.410 g/cm ³	1.397 g/cm ³	1.425 g/cm ³
Reflections for cell refinement	5527 (θ range 2.4 to 27.1 ^o)	7480 (θ range 2.4 to 28.3 ^o)	815 (θ range 2.5 to 19.7 ^o)	6428 (θ range 2.3 to 25.6 ^o)	9938 (θ range 2.3 to 28.4 ^o)
Data / restraints / parameters	5015 / 0 / 274	7758 / 1 / 444	6473 / 1 / 429	7428 / 31 / 439	8725 / 0 / 500
Final R indices [F ₂ >2 σ]	R1 = 0.0343, wR2 = 0.0895	R1 = 0.0295, wR2 = 0.0659	R1 = 0.0410, wR2 = 0.0887	R1 = 0.0352, wR2 = 0.0655	R1 = 0.0330, wR2 = 0.0762
R indices (all data)	R1 = 0.0406, wR2 = 0.0930	R1 = 0.0325, wR2 = 0.0674	R1 = 0.0535, wR2 = 0.0953	R1 = 0.0738, wR2 = 0.0792	R1 = 0.0427, wR2 = 0.0803
Goodness-of-fit on F ₂	1.048	1.017	1.007	1.049	1.030
Largest diff. peak and hole	1.61 and -0.50 e Å ⁻³	0.61 and $\bar{0}$.38 e Å ⁻³	0.76 and $\bar{0}$.66 e Å ⁻³	0.62 and -0.61 e Å ⁻³	1.39 and -0.34 e Å ⁻³

The ionic complexes **3a-c** were tested for catalytic properties in a transfer hydrogenation reaction toward ketones and imines. The study suggests that these are effective catalysts in the reduction of the C=O bond in acetophenone through transfer hydrogenation with isopropanol, and the reduction of the C=N bond in N-Benzylideneaniline through transfer hydrogenation with isopropanol.

Scheme 3: Transfer Hydrogenation of Acetophenone.

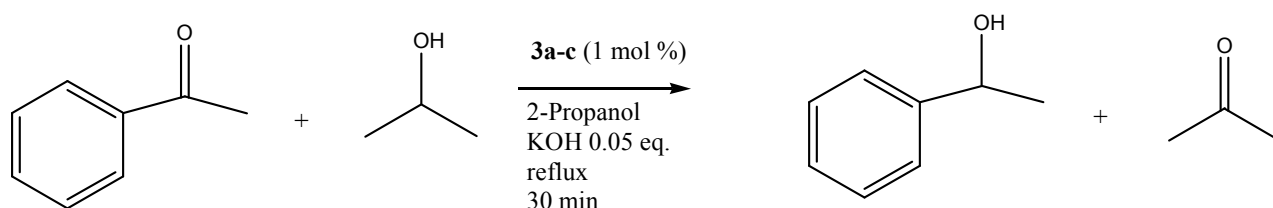


Table 5. Catalytic Transfer Hydrogenation of C₆H₅COCH₃ by **3a-c**.

Catalyst	3a	3b	3c
Yield ^a	40%	85%	66%

^a Based on average of 2 trials.

Scheme 4. Transfer Hydrogenation of N-benzylideneaniline.

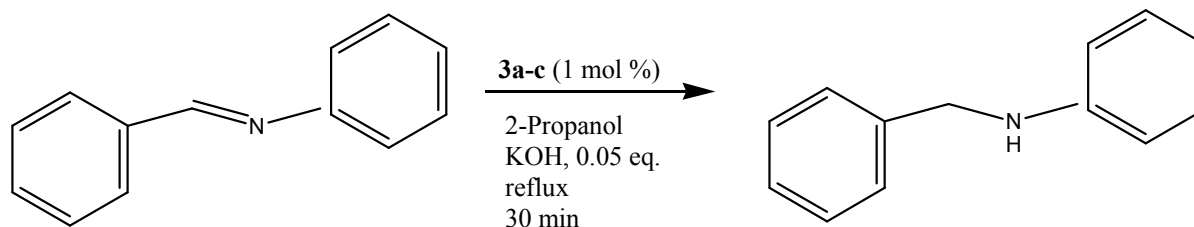


Table 6. Catalytic Transfer Hydrogenation of PhCH=NPh by **3a-c**.

Catalyst	3a	3b	3c
Yield ^a	100%	100%	100%

^a Based on average of 2 trials.

Conclusions

The compounds [(cod)Rh(NHC)Cl], (NHC = 1-butyl-4-benzyltriazol-5-ylidene(**2a**), 1-neopentyl-4-butyltriazol-5-ylidene(**2b**), 1-neopentyl-4-benzyltriazol-5-ylidene(**2c**)) by in situ transmetallation from silver carbene complexes of compounds **37,38(C-1)** as shown in the reaction scheme. The triazolium salts **1a-c** were treated with Ag₂O in room temperature, the silver-carbene complex formed readily reacted with [Rh(cod)Cl]₂ to yield yellow metal carbene compounds **2a-c**. These were crystallized in CH₂Cl₂/pentane to give [(cod)Rh(NHC)Cl] in good yield. All of the isolated complexes lack the C₅-H triazole proton resonance and show a signal for C₃-H triazole proton in the 7.68-7.86 ppm. The structure of **2c** was determined by x-ray diffraction. The corresponding ionic compounds **3 a-c** were made by treating **2 a-c** with 1 equivalent of triphenylphosphine and AgBF₄ in CH₂Cl₂ in the dark under nitrogen. The mixture is stirred 1 hour, followed by filtration through Celite and removal of solvent under vacuum to yield yellow-orange solids **3 a-c** in high yield. In the ³¹P NMR of compounds **3 a-c**, the signal due to the triphenylphosphine ligand was found in the 24.76-24.99 ppm and the ³¹P coupling to ¹⁰³Rh was observed with a coupling constant of 152.77-153.41 Hz. The compounds were crystallized in CH₂Cl₂/pentane and were air stable both as solids and in solution. Compound **3b** formed two polymorphs and the structure of these and compounds **3a** and **3c** were determined by x-ray diffraction. The three complexes **3a-c** showed catalytic properties in the transfer hydrogenation reduction of acetophenone, a ketone, but proved to be much more effective catalysts in the transfer hydrogenation reduction of N-benzylideneaniline, an imine.

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