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Article

Multifaceted Coordination of Naphthyridine−Functionalized N-Heterocyclic Carbene: A Novel "$Ir^{III}(C^{\wedge}N)(C^{\wedge}C)$" Compound and Its Evaluation as Transfer Hydrogenation Catalyst

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The 1,8-naphthyridine−functionalized N-heterocyclic carbene 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (BIN) has been successfully coordinated to Pd(II), W(0), Rh(I), and Ir(III), exhibiting its diverse binding modes. Reaction of BIN·HBr with Ag_2O, followed by transmetalation with $PdCl_2(COD)_2$ provides a cis complex $PdCl_2(\kappa C_2\text{-BIN})_2$ (**1**). Treatment of BIN·HBr with $W(CO)_4(piperidine)_2$ in acetonitrile affords a chelate complex $W(CO)_4(\kappa^2C_2,N_1'\text{-BIN})$ (**2**). Reaction of $\{RhCl(COD)\}_2$ with KO^{t}Bu and subsequent treatment with BIN·HBr in 1:2 and 1:1 ratio results in the mono and dinuclear complexes [Rh(COD)Br(κC_2-BIN)] (**3**) and [$\{Rh(COD)Br\}_2(\kappa N_8':\kappa C_2\text{-BIN})$] (**4**), respectively. In complex **3**, the "Rh(COD)Br" unit is coordinated to the carbene center, whereas an additional "Rh(COD)Br" unit is attached to naphthyridine nitrogen in complex **4** in an anti arrangement. Under identical reaction condition, a novel Ir(III) complex [$Ir(\kappa^2C_2,N_1'\text{-BIN})(\kappa^2C_3',C_2\text{-BIN})(H_2O)Br$]Br (**5**) has been synthesized. Complex **5** is proved to be catalytically active in hydrogen transfer reaction from ^{i}PrOH. All complexes have been characterized by spectroscopic methods and X-ray crystallography.

Introduction

N-heterocyclic carbene (NHC) ligands have emerged as a useful class of ligands in the development of highly effective organometallic[1] and organic catalysts.[2] The robust and thermally stable NHC based catalysts are considered as alternatives for their phosphine counterparts with enhanced catalytic performances.[3] The prospect of introducing various substituents at N atoms of imidazole has brought about a new dimension in NHC chemistry.[4] Heteroarene substituted NHC ligands exhibit wide diversity in ligand topology and binding mode, offering greater control over the coordination environment of metal and its catalytic activities.[5] The motivation for incorporating a 1,8-naphthyridine (NP) unit stems from our

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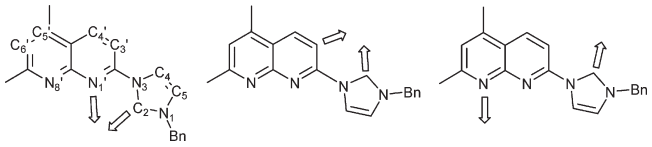
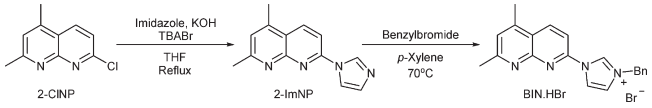
Scheme 1. Different Ligating Faces of BIN and the Numbering Scheme



Scheme 2. Synthesis of 1-Benzyl-3-(5,7-dimethylnaphthyrid-2-yl)imidazolium Bromide (BIN·HBr)



recent applications of NP-based ligands in the field of organometallic and coordination chemistry.[6] The NP appendage on a NHC core offers the prospect of making diverse metal-carbene complexes by virtue of its multiple binding sites and topological flexibility.[7] We report herein a NP-NHC hybrid ligand 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene (BIN), presenting a multitude of ligating faces as shown in Scheme 1. Exploiting these binding sites, a host of metal-BIN complexes incorporating Pd, W, Rh, and Ir are synthesized, and the catalytic activity of a novel "Ir^{III}-(C^N)(C^C)" complex in transfer hydrogenation reaction is evaluated.

Results and Discussions

Ligand Synthesis and Characterization. The synthetic procedure for the ligand precursor 1-benzyl-3-(5,7-dimethylnaphthyrid-2-yl)imidazolium bromide (BIN·HBr) is given in Scheme 2. Treatment of 2-chloro-1,8-naphthyridine (2-ClNP) with imidazole in presence of KOH and catalytic amount of tetrabutylammonium bromide provides 2-imidazolyl-1,8-naphthyridine (2-ImNP).[8] Quaternization of 2-ImNP with benzyl bromide in *p*-xylene at 70 °C results in the NHC ligand precursor BIN·HBr. The ^{1}H NMR spectrum of BIN·HBr exhibits a characteristic singlet at δ 10.5 ppm, assigned to the C_2 proton of the imidazole ring. X-ray structure of BIN·HBr has been determined. The molecular structure is shown in Figure 1, and important bond parameters are given in the corresponding figure caption. The N3−C13 and N4−C13 distances are 1.331(5) Å and 1.309(5) Å, respectively, and the N3−C13−N4 angle is 109.4(3)°. The naphthyridine and the imidazolium rings tend to be coplanar as reflected in the torsional angle ϕ C9−C10−N3−C13 of −8.1(5)°.

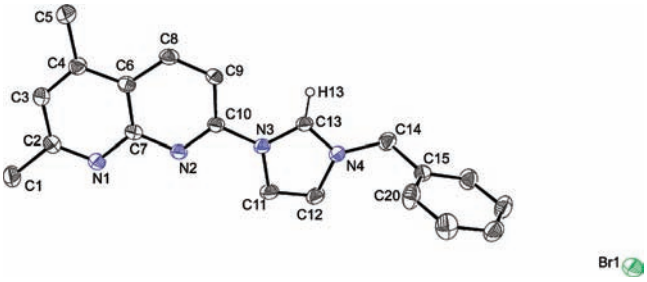
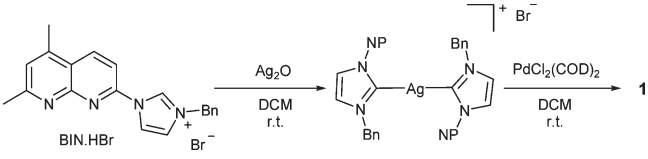


Figure 1. ORTEP diagram (50% probability thermal ellipsoids) of BIN·HBr with important atoms labeled. Hydrogen atoms except that on the C13 atom of imidazole are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): N3−C13 1.331(5), N4−C13 1.309(5), N3−C11 1.389(5), N4−C12 1.378(5), C11−C12 1.341(6), N3−C10 1.431(5), N4−C14 1.466(5), N2−C10 1.302(5), N2−C7 1.368(5).; N3−C13−N4 109.4(3), N2−C10−N3 115.3(3), C13−N3−C11 107.6(3), C13−N3−C10 126.4(3), C13−N4−C12 108.7(3), C13−N4−C14 125.0(3), C11−C12−N4 107.2(3), C12−C11−N3 107.0(4), C13−N3−C10 126.4(3). Dihedral angle (deg): C9−C10−N3−C13 −8.1(5).

Scheme 3. Synthesis of **1**



Synthesis and Characterization of $PdCl_2(\kappa C_2\text{-BIN})_2$ (1). The complexation protocols in NHC chemistry are mainly based on the following routes: (1) the complexation of the free, preisolated NHC; (2) in situ deprotonation of the azolium salt by base, either exogenous or embedded in the metal precursor, and subsequent metal-complexation; (3) use of basic Ag_2O to generate a Ag-NHC complex, followed by NHC transfer to a late transition metal via transmetalation.[9] Several other procedures have been developed in recent years.[10] Our choice of method is governed by the nature of the metal precursor used.

The palladium complex $PdCl_2(\kappa C_2\text{-BIN})_2$ (**1**) was synthesized via transmetalation route. Room temperature treatment of Ag_2O with BIN·HBr in dichloromethane provides the silver complex $[Ag(BIN)_2]Br$ which has been characterized by spectroscopic methods. Absence of a C_2-proton in ^{1}H NMR spectra indicates the complexation. The ESI-MS exhibits a molecular ion signal at m/z 737. Treatment of $[Ag(BIN)_2]Br$ with $PdCl_2(COD)_2$ in dichloromethane at room temperature provides **1** (Scheme 3) in good yield (81%). The molecular structure of **1**, determined by the X-ray crystallography, shows a square planar cis complex comprising two BIN ligands and two chlorine atoms (Figure 2). The palladium atom binds to the carbene centers (Pd1−C13 = 1.986(5) Å; Pd1−C33 = 1.997(4) Å) of two ligands, while the naphthyridine nitrogens remain uncoordinated, disposing away from the metal center. Two syn-disposed naphthyridine rings are parallel to each other. The angles constituting two cis oriented ligating atoms and the palladium are in the range of 88−94°. Most of the known $(NHC)_2PdX_2$ (X = halogen) type complexes reveal trans orientation of

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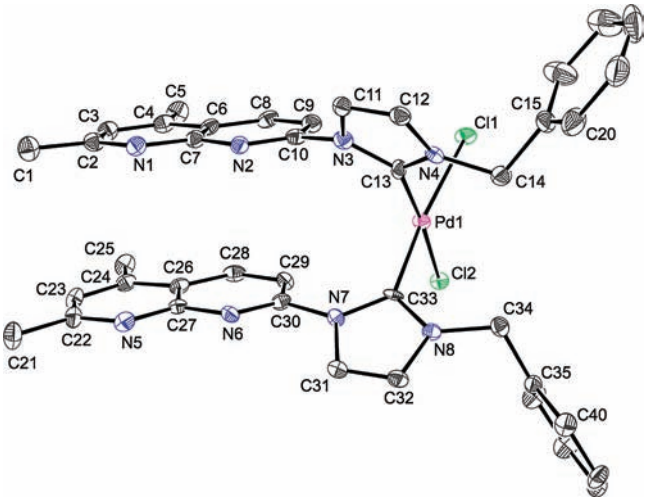

Figure 2. ORTEP diagram (50% probability thermal ellipsoids) of $PdCl_2(\kappa C_2\text{-BIN})_2$ (**1**) with important atoms labeled. Hydrogen atoms omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1−C13 1.986(5), Pd1−C33 1.997(4), Pd1−Cl1 2.3917(12), Pd1−Cl2 2.3618(12), C13−N4 1.335(7), C13−N3 1.358(6), C10−N3 1.427(7), N4−C14 1.471(7), C33−N7 1.363(6), C33−N8 1.344(6), N7−C30 1.435(6), C34−N8 1.465(6), H9···Cl1 2.637, H29···Cl2 2.801, Pd···H29 2.846, Pd···H9 2.935, Pd···H14A 2.896, Pd···H34B 2.766; C13−Pd1−C33 88.29(18), C13−Pd1−Cl1 88.41(14), C33−Pd1−Cl2 89.41(13), Cl1−Pd1−Cl2 94.38(4), N4−C13−N3 105.8(4), N8−C33−N7 105.2(4), C13−N3−C11 110.2(4), C13−N4−C12 110.3(4), C33−N7−C31 109.8(4), C33−N8−C32 111.0(4). Dihedral angle (deg): C33−N7−C30−C29 28.6(7), C13−N3−C10−C9 −45.2(7), C13−N3−C10−N2 137.4(5), C33−N7−C30 N6 −156.8(5).

ligands;[11] however, complex **1** adopts a cis configuration.[12] We attribute this unusual geometry to a combination of Pd···H interactions and intramolecular $\pi-\pi$ stacking of the NP rings. The intercentroid distance between two naphthyridine rings is 3.732 Å which is in the range of $\pi-\pi$ stacking interactions.[13]

ESI-MS of the product exhibits a signal at m/z 769 corresponding to the fragment $[M - Cl]^+$ (100%). In addition, a signal at m/z 815, attributed to $[Pd(BIN)_2Br]^+$ on the basis of simulated mass and isotope distribution pattern, appears in 30% abundance. The bromide present in the Ag-BIN precursor gets exchanged with chloride in **1** giving rise to the higher mass signal. However, X-ray and elemental analysis data of isolated crystals confirm the identity of **1**.

All ligand protons have been assigned in the ^1H NMR spectra for complex **1**. Protons of the coordinated BIN show marginal shifts reflecting its coordination to the metal, except one of the protons of each methylene group and C_3' protons which exhibit larger shifts. An upfield shift differences of $\Delta\delta$ 1.65 ppm is observed for methylene protons. This diamagnetic shift is ascribed to the Pd···H(C*H*) agostic interaction[14] having Pd···H distances 2.896 Å (H14A) and 2.766 Å (H34B). Further, the methylene protons undergo geminal coupling ($^2J_{HH}$ = 14 Hz), appearing as two doublets, which indicate their inequivalent chemical environment. In contrast, C_3' proton exhibits a downfield shift difference $\Delta\delta$ 1.68 ppm relative to the ligand precursor. Such large downfield shift is credited to its interaction with the coordinated chlorine (H9···Cl1 = 2.637 Å; H29···Cl2 = 2.801 Å). A comparison of bond parameters involving Pd and C−H units (aromatic and methylene) is shown in Supporting Information, Scheme S1. It reveals that the aromatic protons exhibit longer Pd···H distances (Pd···H29 = 2.846; Pd···H9 = 2.935 Å) than the methylene protons; however, the nature of Pd···H interaction (agostic or preagostic)[14,15] between C_3-hydrogen and palladium cannot be ascertained.

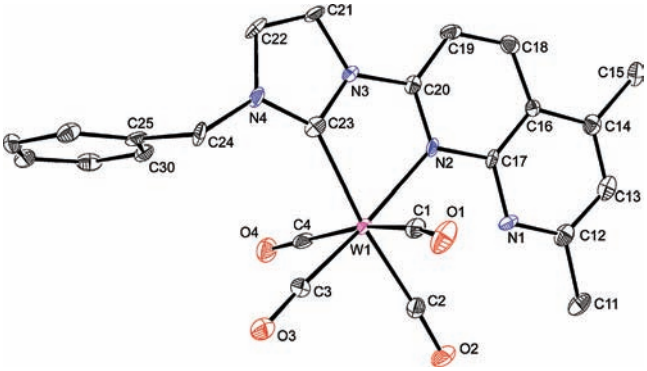

Figure 3. ORTEP diagram (50% probability thermal ellipsoids) of $W(CO)_4(\kappa^2C_2,N_1'\text{-BIN})$ (**2**) with important atoms labeled. Hydrogen atoms omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): W1−C23 2.196(6), W1−N2 2.336(5), W1−C1 2.022(7), W1−C2 2.015(6), W1−C3 1.937(6), W1−C4 2.055(7), O1−C1 1.159(8), C2−O2 1.164(8), C3−O3 1.185(8), O4−C4 1.150(8), N3−C23 1.395(8), N4−C23 1.347(8), N3−C21 1.401(7), N4−C22 1.390(8), N3−C20 1.393(8), N2−C20 1.339(8), N2−C17 1.379(8); C23−W1−N2 72.1(2), C1−W1−C4 167.1(2), C3−W1−N2 173.3(2), C1−W1−C4 167.1(2), C23−W1−N2 72.1(2), N4−C23−N3 103.3(5), C20−N3−C23 120.2(5), N2−C20−N3 115.3(5). Dihedral angle (deg): C23−N3−C20−N2 7.3(8).

Synthesis and Characterization of $W(CO)_4(\kappa^2C_2,N_1'\text{-BIN})$ (2). Reaction of BIN·HBr with $W(CO)_4(pip)_2$ (pip = piperidine) in acetonitrile provides $W(CO)_4(\kappa^2C_2,N_1'\text{-BIN})$ (**2**) in high yield (90%). The molecular structure of **2**, depicted in Figure 3, reveals a chelate binding of the ligand involving C_2(C23) carbene carbon and N_1'(N2) of the NP unit. Remaining four sites of tungsten are occupied by four carbonyl ligands. The W1−C23 bond distance is 2.196(6) A°. The W1−C2 bond (2.015(6) A°), being trans to the carbene carbon, is longer than W1−C3 distance (1.937(6)°) which is opposite to NP nitrogen. ESI-MS of

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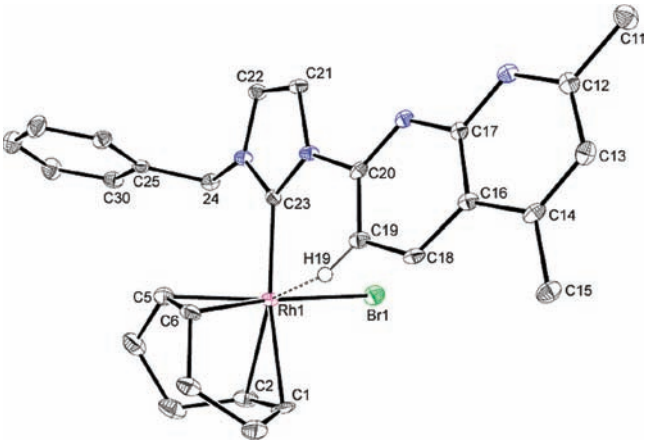

Figure 4. ORTEP diagram (50% probability thermal ellipsoids) of [Rh(COD)(κC_2-BIN)Br] (**3**) with important atoms labeled. Hydrogen atoms, except H29, are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Rh1−C23 2.033(4), Rh1−Br1 2.4900(7), Rh1−C1 2.191(4), Rh1−C2 2.217(4), Rh1−C5 2.111(5), Rh1−C6 2.132(4), C1−C2 1.378(7), C6−C5 1.396(6), C23−N3 1.372(5), N4−C23 1.356(5), C21−N3 1.400(5), N4−C22 1.386(5), C20−N3 1.424(5), Rh1···H19 2.4701; N4−C23−N3 104.0(3), C23−N3−C20 126.4(3), C23−N4−C22 111.6(3), C23−N3−C21 110.8(3), C23−Rh1−Br1 88.14(11), N3 C23 Rh1 131.0(3). Dihedral angle (deg): C19−C20−N3−C23 −20.

2 exhibits a signal at m/z 611 which corresponds to the molecular ion peak.

Synthesis and Characterization of Mono and Dinuclear Rh(I) Complexes [Rh(COD)Br(κC_2-BIN)] (3) and [{(Rh(COD)Br}$_2$($\kappa N_8'$:κC_2-BIN)] (4). Reaction of {RhCl(COD)}$_2$ with excess KO^{t}Bu and subsequent treatment with 2 equiv of BIN·HBr in tetrahydrofuran (THF) provides an 1:1 metal to ligand complex [Rh(COD)Br(κC_2-BIN)] (**3**) in good yield (81%). The molecular structure is shown in Figure 4, and important metrical parameters are provided in the corresponding figure caption. X-ray structure reveals the coordination of "Rh(COD)Br" to carbene carbon as expected. The Rh atom binds to the C_2 carbene center (C23) while the N atoms of NP remain uncoordinated and disposed away from the metal ions resulting in a square planar complex. The Rh1−C23 distance is 2.033(4) Å.

A dinuclear Rh(I) complex [{Rh(COD)Br}$_2$($\kappa N_8'$:κC_2-BIN)] (**4**) has been synthesized following a procedure similar to the synthesis of **3** using 1 equiv of BIN·HBr in moderate yield (75%). The molecular structure of **4** consists of two independent {Rh(COD)Br} units attached to BIN. One of the Rh atoms binds to the C_2 carbene center (C33) while the other Rh is coordinated to N_8' of NP (N1). The carbene carbon and the NP nitrogen atoms are in anti arrangement resulting in a rhodium dimer (Figure 5). Bimetal complexes with similar arrangement are rare for heteroarene substituted NHCs, though they are well documented for bis-carbene ligands.[16] Both Rh

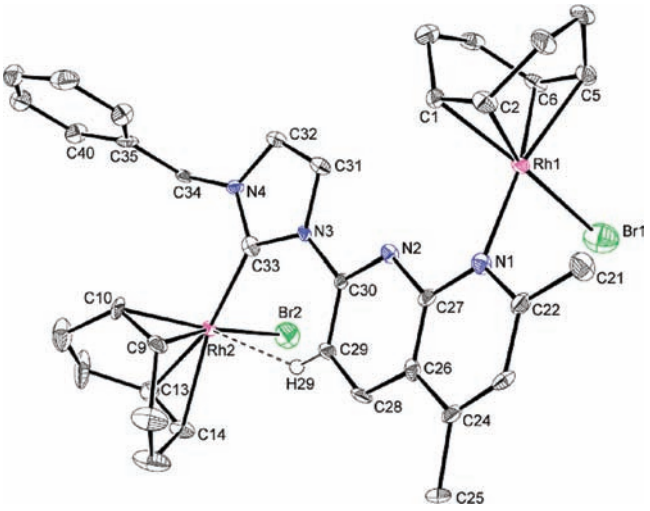

Figure 5. ORTEP diagram (50% probability thermal ellipsoids) of [{Rh(COD)Br}$_2$($\kappa N_8'$:κC_2-BIN)] (**4**) with important atoms labeled. Hydrogen atoms, except H29, are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Rh2−C33 2.014(9), Rh1−N1 2.150(7), Rh1−C5 2.140(9), Rh1−C6 2.127(8), Rh2−C13 2.199(9), Rh2−C14 2.202(9), C1−C2 1.369(12), C6−C5 1.391(12), C9−C10 1.406(12), C13−C14 1.381(13), N4−C33 1.353(10), N3−C33 1.386(10), C34−N4 1.448(10), N3−C31 1.406(10), N3−C30 1.427(10), N2−C30 1.309(10), N2−C27 1.369(10), C27−N1 1.373(11), C22−N1 1.350(11); N4−C33−N3 102.6(7), N3−C33−Rh2 131.7(6), C22−N1−C27 118.0(7), C30−N2−C27 117.9(7), C33−Rh2−Br2 89.3(2), N1−Rh1−Br1 86.26(19). Dihedral angle (deg): C29−C30−N3−C33 6.8.

atoms are in a square planar environment coordinated to one COD, one bromide, and a ligating atom from BIN. The Rh2−C33 and Rh1−N1 distances are 2.014(9) Å and 2.150(7) Å, respectively, consistent with literature values.[17] The Rh2−C13/C14 (2.199(9) Å/ 2.202(9) Å) bond distances are longer than Rh1−C5/C6 (2.140(9) Å/ 2.127(8) Å) distances, an illustration of the stronger trans effect of the carbene carbon in comparison to arene nitrogen. The Rh−C_2 (carbene) distance in **4** is marginally shorter than the corresponding distance in **3**, and other metrical parameters are comparable.

The ^{1}H NMR of **3** exhibits four sets of multiplets for COD protons. In contrast, multiple broad signals (δ 1.5−3.2 ppm) appear for COD in **4**, an indication that two ligands are in different chemical environment. The NMR signal for C_3' proton undergoes considerable downfield shift for both compounds **3** and **4**, albeit at a varying degree. This shift of C_3' proton is credited to its "preagostic"[14] interaction with rhodium. The shift differences ($\Delta\delta$) of 2.95 ppm, relative to the BIN·HBr, is significantly larger in the dimeric complex **4** than the corresponding shift differences observed for **3** ($\Delta\delta$ 2.18 ppm). A shorter Rh2−H29 distance (2.44 Å) and smaller torsional angle ϕ C29−C30−N3−C33 (6.8°) for **4**, in comparison to the corresponding values (2.47 Å and −20°) in **3**, are attributed for different NMR responses. It is, however, not obvious why naphthyridine and imidazole rings tend to be more planar upon coordination of the second "Rh(COD)Br" in **4**. The singlet methylene proton signal in complexes **3** and **4** indicates the absence of any M···H interaction. This is in sharp contrast to complex **1** in which both methylene and aromatic protons interact with Pd (Supporting Information, Scheme S1). Presumably the bulky COD around Rh does not allow

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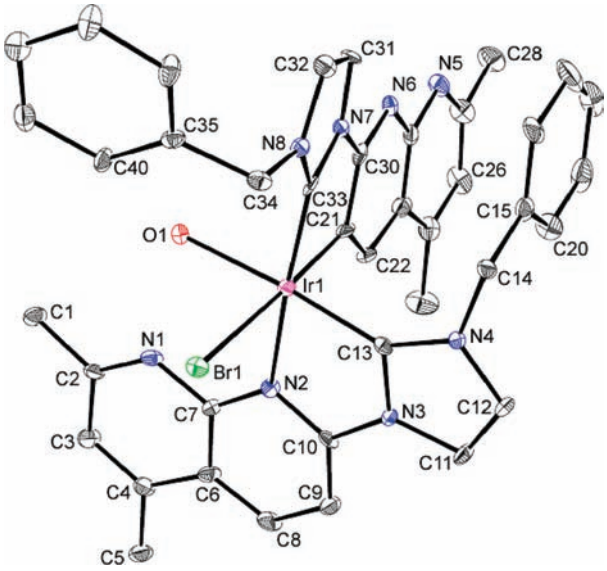

Figure 6. ORTEP diagram (30% probability thermal ellipsoids) of the cationic unit [Ir(κ^2C$_2$,N$_1$-BIN)(κ^2C$_3$′,C$_2$-BIN)(H$_2$O)Br]$^+$ in compound **5** with important atoms labeled. Hydrogen atoms omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−C13 1.929(10), Ir1−N2 2.129(8), Ir1−C21 2.041(12), Ir1−C33 1.980(11), Ir1−O1 2.159(6), Br1−H34B 2.6115, C13−N4 1.361(11), C13−N3 1.407(11), N3−C10 1.384(11), N2−C10 1.344(12), C33−N8 1.345(12), C33−N7 1.352(11), N7−C30 1.442(12), C21−C30 1.394(14), C21−C22 1.353(15), C30−N6 1.326(13); N4−C13−N3 102.2(8), C10−N3−C13 118.7(8), C10−N2−C7 115.3(8), N2−C10−N3 112.3(9), N8−C33−N7 101.8(9), C33−N7−C30 113.5(9), C21−C30−N7 114.1(10), C22−C21−C30 116.5(11), C13−Ir1−C33 99.8(4), C13−Ir1−C21 89.5(4), C33−Ir1−C21 78.7(4), C13−Ir1−Br1 93.4(3), C33−Ir1−Br1 103.2(3). Dihedral Angle (deg): N2−C10−N3−C13 1.5(13), C21−C30−N7−C33 0.1(13).

both of these hydrogens to interact with the metal. The preference of Rh···H19/Rh···H29 interactions in complexes **3** and **4**, respectively, is understandable since the metal−hydrogen interaction is stronger for aromatic proton in comparison to the methylene proton.[18]

ESI-MS of **3** and **4** are dominated by two signals at mass-to-charge (m/z) ratios of 541 and 417, assigned for [{Rh(BIN)Br(CH$_3$CN)}+H]$^+$ and [Rh(BIN)]$^+$, respectively, derived from simulated mass and isotopic distribution patterns. No signal for a dimetal compound could be identified in the ESI-MS spectrum of **4**, indicating weak interaction of Rh to arene nitrogens. Furthermore, facile detachment of COD is noticed under mass spectroscopic condition when Rh is attached to carbene.

Synthesis and Characterization of [Ir(κ^2C$_2$,N$_1$′-BIN)(κ^2C$_3$′,C$_2$-BIN)(H$_2$O)Br]Br (5). Reaction of {IrCl(COD)}$_2$ with [BIN·HBr], following an identical procedure employed in the synthesis of **3**, results in an unique complex [Ir(κ^2C$_2$,N$_1$′-BIN)(κ^2C$_3$′,C$_2$-BIN)(H$_2$O)Br]Br (**5**) in high yield (87%). Although complex **5** was obtained invariably at different metal-to-ligand stoichiometry, maximum yield and higher purity is achieved when 1:2 metal-to-ligand ratio is maintained. The molecular structure of **5** has been established by X-ray crystallography. The coordination geometry of iridium is best described as pseudo octahedral comprising of two cis oriented BIN ligands, one water molecule, and a bromide (Figure 6). One of the BIN (C^N) ligands chelates to the metal through the carbene carbon C$_2$ (C13) and the NP nitrogen N$_1$′(N2). The second BIN (C^C) chelates to iridium employing carbene carbon C$_2$ (C33) and C$_3$′(C21) of the NP core. The Ir1−C13 and Ir1−N2 bond distances of the C^N BIN are 1.929(10) Å and 2.129(8) Å; the Ir1−C33 (carbene) and Ir1−C21 (aryl) bond distances of C^C BIN are 1.980(11) Å and 2.041(12) Å. Longer Ir−N bond length of 2.129(8) Å compared to those present in Ir-bipyridyl complexes[19] is noted. The coordinated water molecule is trans to the carbene carbon C13, and the Ir1−O1 distance is 2.159(6) Å.

The electrospray ionization mass spectrometry (ESI-MS) spectrum of **5** reveals the molecular ion signal at m/z 917. An additional prominent signal attributed to the dehydrated molecular ion [M−H$_2$O]$^+$ at m/z 899 reaffirms the presence of water as one of the co-ligand.

Four imidazole protons and five aromatic NP protons from two BIN ligands are assigned in the ^{1}H NMR spectrum of compound **5**. A doublet at δ 8.15 ppm appears for the C$_3$′(C9) proton of C^N-BIN. The corresponding proton for the C^C-BIN (C21) is absent indicating cyclometalation. The C$_4$′(C22) proton of the C^C BIN is shifted upfield by $\Delta\delta$ 1.42 ppm while other aromatic proton signals shift marginally relative to the free ligand, reflecting the metalation of the adjoined carbon C21. Four methylene protons of the benzyl groups undergo geminal coupling appearing as four doublets ($^2J_{HH}$ = 15 Hz). One of the methylene protons, belonging to C^C-BIN, shifts downfield by $\Delta\delta$ 1.3 ppm which is attributed to its interaction with the bromide with H34B···Br1 distance of 2.611 Å calculated from X-ray geometry. Accordingly, the C^C-BIN methylene protons exhibit AX pattern whereas C^N-BIN methylene protons exhibit AB pattern (Supporting Information, Figure S1). The different patterns allow their unambiguous assignment. The cyclometalated carbon (C21) exhibits a downfield shift from the ligand precursor (BIN·HBr) in the ^{13}C NMR spectrum.

Two BIN ligands utilize different ligating faces (C^C and C^N) to bind iridium in complex **5**. Base-assisted deprotonation and subsequent cyclometalation[20] is a possibility since the reaction is carried out in presence of KO^{t}Bu. However, the formation of complex **5** involves the oxidation of the metal from Ir^{I} to Ir^{III}, clearly suggesting an "oxidative addition" step in the mechanism. A tentative reaction pathway involving a stepwise mechanism is proposed in Scheme 4. It is likely that the species **I**, an Ir analogue of **3**, is formed initially which undergoes rapid oxidative addition of the aryl C$_3$′−H bond leading to a "rollover" cyclometalated Ir(III)-hydride complex **II**.[21] Recent isolation of a similar complex

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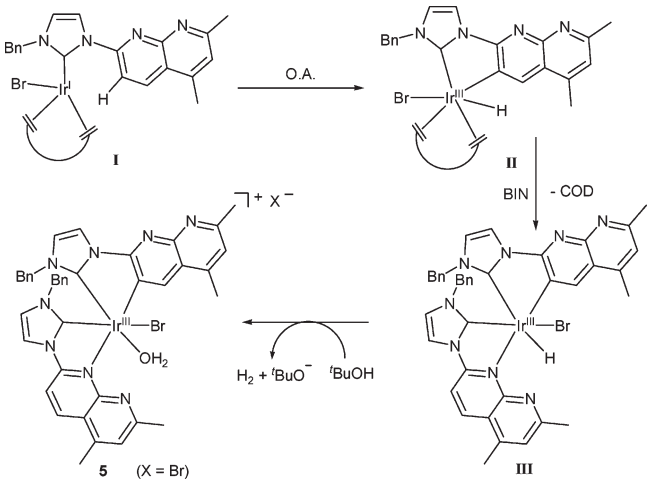
Scheme 4. Proposed Pathway for the Formation of **5**



$[Ir^{III}(H)(Cl)(COD)(py\text{-}NHC)]$ by Danopoulos and coworkers[22] supports the intermediacy of **II** in this reaction. It should be noted here that the oxidative addition/cyclometalation occurs when the central metal is Ir but not for Rh under identical reaction conditions. The same observation was also noted in the work of Danopoulos.[22] In the subsequent step, the free BIN, generated in situ from BIN·HBr and KOtBu, replaces the COD and chelates to the iridium forming **III**. It is our assertion that the presence of two strong σ-donor carbenes at iridium center increases the hydridic character, thereby facilitating the elimination of hydride as molecular hydrogen aided by ^{t}BuOH present in the reaction medium. The incipient vacant site is occupied by adventitious water providing **5**.

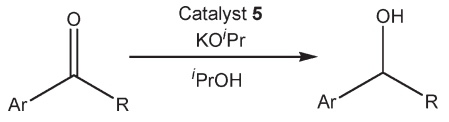
To the best of our knowledge, compound **5** is the rare example of an Ir^{III} complex incorporating NHC based C^C and C^N type ligands together. Furthermore, the ancillary water and bromide offer prospects for catalysis.

Catalytic Transfer Hydrogenation Reaction. Complex **5** successfully catalyzes the transfer hydrogenation reaction of aromatic and heteroaromatic ketones in presence of KOH/^{i}PrOH at room temperature. The ketones were converted into corresponding alcohols in good yield (Table 1) within a period of 1.5 h. In cases of aromatic ketones, we essentially got quantitative yield irrespective of substituents on the phenyl groups. The catalyst exhibits diminished activities toward the heteroaromatic ketones with moderate yields for acetylpyridine and acetylthiazole at elevated temperature. No conversion was observed for acetylpyrrole even after prolonged heating.

Concluding Remarks

We have achieved complexation of BIN with a host of metal ions demonstrating diverse binding modes of the naphthyridine-functionalized NHC ligand. A Ag(I) mediated transmetalation route is adapted for the synthesis of a cis complex $PdCl_2(\kappa C_2\text{-BIN})_2$ (**1**). Reaction of $W(CO)_4(piperidine)_2$ with BIN·HBr has afforded a chelate complex $W(CO)_4(\kappa^2C_2,N_1'\text{-BIN})$ (**2**). Mono and dinuclear complexes [{Rh(COD)Br-(κC_2-BIN)] (**3**) and [{(Rh(COD)Br}$_2$($\kappa N_8'$:κC_2-BIN)] (**4**) are synthesized from the reaction of in situ generated {Rh(O^{t}Bu)(COD)}$_2$ with BIN·HBr in 1:2 and 1:1 ratio, respectively. The mononuclear complex **3** presents an opportunity to access different homo and heterobimetallic complexes of interest which is being investigated in our laboratory. Complex **5** exhibits C^C and C^N bound BIN, along with cis oriented water and bromide at the metal, and proved to be catalytically active in transfer hydrogenation reaction of ketone. Mono and bidentate coordination of BIN has been demonstrated amply in this work. The prospect of exploiting the third binding site appears appealing. We are working vigorously to achieve just that.

Table 1. Transfer Hydrogenation Reaction of Ketones Catalyzed by **5**[a]



entry	ketone	yield (%)[b]	conversion (%)[c]	TON
1	acetophenone	83	98	978
2	3-nitroacetophenone	85	99	989
3	2-fluoroacetophenone[d]	90	100	999
4	4-methoxyacetophenone	90	97	969
5	2-methylacetophenone	90	99	989
6	benzophenone[e]	85	97	969
7	acetylpyridine[f]	62	69	689
8	acetylthiazole[g]	76	85	849
9	acetylpyrrole[h]	0	–	–

[a] Reaction conditions: 2 mmol substrate, 0.002 mmol **5**, 0.5 mL 0.1 M KOH in *i*-PrOH, 30 °C, 1.5 h, unless mentioned otherwise. [b] Isolated yield. [c] Determined by GC after reaction. [d] 0.5 h. [e] 1 h. [f] 3 h, 80 °C. [g] 2 h, 80 °C. [h] 24 h, 80 °C.

Experimental Section

General Procedures. All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum line techniques. ^{1}H NMR spectra were obtained on JEOL JNM-LA 400 and 500 MHz spectrometers. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl ether, and dried in vacuum for at least 48 h prior to elemental analyses. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. ESI-MS of all complexes were recorded in acetonitrile.

Materials. Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use.[23] $RhCl_3\cdot xH_2O$ and $IrCl_3\cdot xH_2O$ were purchased from Arora Matthey, India. KO^{t}Bu and $W(CO)_6$ were purchased from Sigma-Aldrich. The compounds $[RhCl(COD)]_2$,[24] $[IrCl(COD)]_2$,[25] $W(CO)_4(piperidine)_2$[26] and 2-chloro-1,8-naphthyridine[27] were synthesized following the literature procedures.

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Synthesis. 2-Imidazolyl-5,7-dimethyl-1,8-naphthyridine. Imidazole (1.8 g, 26.5 mmol), potassium hydroxide (1.24 g, 22.1 mmol), and tetrabutylammonium bromide (0.5 g, 1.55 mmol) were placed in a round-bottom flask and suspended in 200 mL of THF. The mixture was stirred at room temperature for 15 min. After which, 2-chloro-1,8-naphthyridine (4 g, 26.5 mmol) was added and heated at reflux for 4 h. The resulting mixture was cooled to room temperature, and solvent was removed under vacuo. Water was added to the residue and extracted three times with 100 mL of dichloromethane. After washing with water, the combined organic phases were dried over anhydrous $MgSO_4$, filtered, and volatiles were removed under reduced pressure. The crude solid was purified by column chromatography (silica gel, CH_3OH/CH_2Cl_2: 3/97) to afford pale pink solid. Yield: 3.5 g (70%). ^{1}H NMR (500 MHz, DMSO-d_6, 294 K): δ 8.76 (s, 1H, Im), 8.70 (d, J = 8 Hz, 1H, NP), 8.16 (s, 1H, Im), 8.04 (d, J = 8 Hz, 1H, NP), 7.36 (s, 1H, NP), 7.19 (s, 1H, Im), 2.67−2.63 (d, 6H, Me). ^{13}C NMR (125.7 MHz, DMSO-d_6, 294 K): 163.7 (NCN_{NP}), 154.6 (NCC_{NP}), 149.8 (NCC_{NP}), 146.5 (CCC_{NP}), 138.4 (CH_{NP}), 136.2 ($NCHN_{Im}$), 131 (CH_{Im}), 123.5 (CH_{NP}), 119.8 (CCC_{NP}), 117.3 (CH_{NP}), 112.1 (CH_{Im}), 25.4 (CH_3), 18.1 (CH_3). Anal. Calcd for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.57; H, 5.33; N, 24.79.

1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium Bromide. Benzyl bromide (45 mL) was added to a solution of 2-imidazolyl-1,8-naphthyridine (1 g, 4.46 mmol) in 50 mL of *p*-xylene, and the solution was heated at 70 °C for 6 h with stirring. A bluish green precipitate started to form during the course of reaction. After cooling, the solid was collected by filtration and washed thoroughly with benzene, diethyl ether and dried under vacuo. Yield: 1.6 g (90%). ^{1}H NMR (500 MHz, DMSO-d_6, 294 K): δ 10.58 (s, 1H, Im), 8.95 (d, J = 10 Hz, 1H, NP-C_4), 8.747 (d, J = 2 Hz, 1H, Im), 8.21 (d, J = 10 Hz, 1H, C_3), 8.115 (d, J = 2 Hz, 1H, Im), 7.57 (d, J = 10 Hz, 2H, Ph), 7.51 (s, 1H, NP-C_6), 7.46−7.4 (m, 3H, Ph), 5.58 (s, 2H, methylene), 2.73 (s, 3H, Me), 2.68 (s, 3H, Me). ^{13}C NMR (125.7 MHz, DMSO-d_6, 294 K): 164.8 (NCN_{NP}), 153.3 (NCC_{NP}), 150.8 (NCC_{NP}), 147.9 (CCC_{NP}), 140 ($NCHN_{Im}$), 136.5 (CH_{NP}), 134.9 (C_{Ph}), 129.6 (C_{Ph}), 129.5 (C_{Ph}), 129.1 (C_{Ph}), 125 (CH_{NP}), 124.2 (CH_{Im}), 121.6 (CCC_{NP}), 120.5 (CH_{NP}), 112.7 (CH_{Im}), 53.2 (CH_2Ph), 25.3 (CH_3), 18.4 (CH_3). Anal. Calcd for $C_{20}H_{19}N_4Br$: C, 60.77; H, 4.84; N, 14.17. Found: C, 60.71; H, 4.69; N, 14.11.

Bis[1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene]silver(I) Bromide. 1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (0.14 g, 0.354 mmol) was added to a dichloromethane slurry of Ag_2O (0.04 g, 0.173 mmol) and stirred at room temperature for 4 h under exclusion of light. The resulting mixture was filtered through a small pad of Celite, and the filter cake was washed thrice with 5 mL of dichloromethane. Pale yellow filtrate was concentrated under reduced pressure. Diethyl ether was added to induce precipitation. Off white solid was washed with diethyl ether and dried under vacuo. Yield: 0.075 g, (53%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.75−8.73 (d, J_2 = 10 Hz, 2H, NP), 8.60−8.58 (d, J_2 = 10 Hz, 2H, NP), 8.33−8.32 (d, J_2 = 5 Hz, 2H, Im), 7.46−7.32 (m, 10H, Ph), 7.27 (s, 2H, NP), 7.12−7.11 (d, J_2 = 5 Hz, 2H, Im), 5.47 (s, 4H, methylene), 2.78 (s, 6H, Me), 2.71 (s, 6H, Me). ^{13}C NMR (125.7 MHz, $CDCl_3$, 294 K): 182.4 (NCN_{Im}), 164.2 (NCN_{NP}), 154.2 (NCC_{NP}), 151.6 (NCC_{NP}), 145.9 (CCC_{NP}), 137.1 (CH_{NP}), 135.1 (C_{Ph}), 129.1 (C_{Ph}), 128.65 (C_{Ph}), 124 (C_{Ph}), 123.9 (CH_{NP}), 121.5 (CH_{Im}), 121.1 (CCC_{NP}), 120.5 (CH_{NP}), 113.9 (CH_{Im}), 56.7 (CH_2Ph), 25.6 (CH_3), 18.1 (CH_3). ESI-MS, m/z: 737 $[Ag(BIN)_2]^+$. Anal. Calcd for $C_{40}H_{36}N_8BrAg$: C, 58.96; H, 4.46; N, 13.76. Found: C, 58.83; H, 4.38; N, 13.66.

Dichloro-*cis*-[bis{1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)-imidazol-2-ylidene}]palladium(II) (1). The silver complex (0.05 g, 0.061 mmol) was added to a dichloromethane solution of Pd(COD)Cl_2 (0.018 g, 0.063 mmol). White precipitate of silver halide appeared immediately. After stirring at room temperature for 12 h, the mixture was filtered through a small pad of Celite. Pale yellow filtrate was concentrated under reduced pressure. Diethyl ether was added to induce precipitation. Off white solid was washed with diethyl ether and dried under vacuo. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated dichloromethane solution of the compound. Yield: 0.04 g (81%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 9.89 (d, J = 8.5 Hz, 2H, NP-C_3), 8.67 (d, J = 8.5 Hz, 2H, NP-C_4), 7.74 (d, J = 2 Hz, 2H, Im), 7.29 (d, J = 2 Hz, 2H, Im), 7.055 (m, 6H, Ph), 6.73 (dd, J = 7.5 Hz, J = 1.75, 4H, Ph), 6.503 (s, 1H, NP-C_6), 6.498 (s, 1H, NP-C_6), 5.502 (d, J = 14 Hz, 2H, methylene), 3.933 (d, J = 14 Hz, 2H, methylene), 2.835 (s, 6H, Me), 2.61 (s, 6H, Me). ^{13}C NMR (125 MHz, DMSO-d_6, 294 K): 165.0 (NCN_{NP}), 159.4 (NCN_{Im}), 153.3 (NCC_{NP}), 151.3 (NCC_{NP}), 147.1 (CCC_{NP}), 139.9 (CH_{NP}), 137.4 (C_{Ph}), 129.6−128.5 (C_{Ph}), 124.5 (CH_{NP}), 123.6 (CH_{Im}), 121.5 (CCC_{NP}), 120.6 (CH_{NP}), 112.4 (CH_{Im}), 55.5 (CH_2Ph), 25.6 (CH_3), 18.4 (CH_3). ESI-MS, m/z: 769 $[Pd(BIN)_2Cl]^+$, 815 $[Pd(BIN)_2Br]^+$, 457 $[Pd(BIN)Cl]^+$. Anal. Calcd for $C_{40}H_{36}N_8Cl_2Pd$: C, 59.60; 4.50; 13.90. Found: 59.93; 4.43; 13.55.

Tertacarbonyl-[1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)-imidazol-2-ylidene]tungsten(0) (2). 1-Benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (0.035 g, 0.11 mmol) was added to an acetonitrile solution of $W(CO)_4$(piperidine)$_2$ (0.05 g, 0.11 mmol) and stirred at room temperature for 7 h. The resulting red mixture was filtered through a small pad of Celite. The solvent was removed under reduced pressure, and the residue was dissolved in minimum amount of dichloromethane. Hexane was added to the solution to induce precipitation. The red solid was washed with hexane and dried under vacuo. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated benzene solution of the compound. Yield: 0.06 g (90%). ^{1}H NMR(400 MHz, $CDCl_3$, 292 K): δ 8.74−8.72 (d, J = 9 Hz, 1H, NP-C_4), 8.61 (s, 1H, Im), 8.498−8.476 (d, J = 9 Hz, 1H, NP-C_3), 7.53 (s, 1H, Im), 7.42−7.26 (m, 6H, NP-C_6, Ph), 5.68 (s, 2H, methylene), 2.73 (s, 3H, Me), 2.69 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$, 294 K): 218.6 (CO), 214.8 (CO), 206.9 (CO), 200.9 (NCN_{Im}), 164.8 (NCN_{NP}), 155.1 (NCC_{NP}), 154.1 (NCC_{NP}), 145.4 (CCC_{NP}), 136.1 (C_{Ph}), 135.6 (CH_{NP}), 129.8 (C_{Ph}), 129.4 (C_{Ph}), 129.1 (C_{Ph}), 128.4 (C_{Ph}), 124.7 (CH_{NP}), 123 (CH_{Im}), 118.9 (CCC_{NP}), 116.5 (CH_{NP}), 108.8 (CH_{Im}), 55.9 (CH_2Ph), 24.4 (CH_3), 18.3 (CH_3). ESI-MS, m/z: 611 $[M]^+$. Anal. Calcd for $C_{24}H_{18}N_4O_4W$: C, 47.21; H, 2.97; N, 9.18. Found. C, 47.02; H, 2.57; N, 9.31.

Bromo-(η^4-1,5-cyclooctadiene)-[1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene]rhodium(I) (3). $Rh_2Cl_2(COD)_2$ (0.04 g, 0.081 mmol) and ^{t}BuOK (0.022 g, 0.196 mmol) were stirred in THF at room temperature for 30 min. The resulting mixture was added slowly to a suspension of 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (0.066 g, 0.166 mmol) in THF at −78 °C. The mixture was allowed to attain room temperature overnight and then refluxed for 3 h. Bright yellow mixture was filtered through a small pad of Celite. The filtrate was evaporated to dryness and dissolved in minimum amount of dichloromethane. Fifteen milliliters of hexane was added with stirring to induce precipitation. Yellow solid was washed with hexane and dried under vacuo. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated benzene solution of the compound. Yield: 0.04 g (81%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 10.396 (d, J = 8.55 Hz, 1H, NP-C_3), 8.65 (d, J = 8.5 Hz, 1H, NP-C_4), 8.15 (s, 1H, Im), 7.49 (d, J = 7.2 Hz, 2H, Ph), 7.4207−7.3540 (m, 3H, Ph), 7.28 (s, 1H, Im), 6.84 (d, J = 2 Hz, 1H, NP-C_6), 6.07 (s, 2H, methylene), 3.05 (br, 2H, COD), 2.776 (d, J = 2.75 Hz, 6H, Me), 2.31−2.28 (m, 2H, COD), 2.00−1.87 (m, 4H, COD), 1.67−1.55 (m, 4H, COD). ^{13}C NMR (125.7 MHz, $CDCl_3$, 294 K): 185 (d, $^1J_{RhC}$ = 50 Hz, NCN_{Im}), 163.7 (NCN_{NP}), 154.5 (NCC_{NP}), 152.9 (NCC_{NP}), 145.9 (CCC_{NP}), 135.8 (C_{Ph}), 134.9 (CH_{NP}), 129.1 (C_{Ph}), 128.7 (C_{Ph}), 128.5 (C_{Ph}), 123.8 (CH_{NP}), 121.6 (CH_{Im}), 121.2 (CCC_{NP}), 120.5 (CH_{NP}), 116.9 (CH_{Im}), 98.1 (CH_{cod}), 70.6 (CH_{cod}), 56.7 (CH_2Ph), 32.5 (($CH_2)_{cod}$), 29.13 (($CH_2)_{cod}$), 25.7 (CH_3), 18.4 (CH_3). ESI-MS, m/z: 541 $[RhL(CH_3CN)Br + H]^+$. Anal. Calcd for

$C_{28}H_{30}N_4BrRh$: C, 55.55; H, 4.99; N, 9.25. Found. C, 55.61; H, 5.13; N, 9.35.

Dibromobis(η^4-1,5-cyclooctadiene)[1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene]dirhodium(I) (4). This compound was synthesized by following the procedure for **3**, except 1 equiv of ligand was used. Yield: 0.055 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 11.17 (d, J = 10 Hz, 1H), 8.77 (d, J = 10 Hz, 1H), 8.36 (d, J = 2.5 Hz, 1H), 8.52 (s, 1H), 7.46−7.29 (m, J = 10 Hz, 5H), 6.85 (d, J = 2.5 Hz, 1H), 5.57 (s, 2H), 3.24 (s, 3H), 3.18 (m, 2H), 2.98 (s, 3H), 2.82 (m, 2H), 2.36 (m, 6H), 2.2−2.16 (m, 2H), 2.00−1.88 (m, 8H), 1.78−1.76 (m, 3H), 1.56 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 294 K): 194.5 (d, $^1J_{RhC}$ = 45.5 Hz, N*C*N$_{Im}$), 164.9 (N*C*N$_{NP}$), 155.3 (N*C*C$_{NP}$), 153.8 (N*C*C$_{NP}$), 146.9 (C*C*C$_{NP}$), 137.3 (*C*$_{Ph}$), 135.6 (*C*H$_{NP}$), 129.3 (*C*$_{Ph}$), 128.8 (*C*$_{Ph}$), 128.6 (*C*$_{Ph}$), 124.2 (*C*H$_{NP}$), 122.7 (*C*H$_{Im}$), 120.1 (C*C*C$_{NP}$), 117.2 (*C*H$_{NP}$), 110.9 (*C*H$_{Im}$), 101.6 (*C*H$_{cod}$), 90.1 (*C*H$_{cod}$), 78.6 (*C*H$_{cod}$), 67.9 (*C*H$_{cod}$), 55.4 (*C*H$_2$Ph), 40.7 ((*C*H$_2$)$_{cod}$), 35.7 ((*C*H$_2$)$_{cod}$), 33.9 ((*C*H$_2$)$_{cod}$), 29.3 ((*C*H$_2$)$_{cod}$), 25.2 (*C*H$_3$), 18.1 (*C*H$_3$). ESI-MS, m/z: 541 [RhL(CH$_3$CN)Br + H]$^+$. Anal. Calcd for $C_{36}H_{42}N_4Br_2Rh_2$: C, 48.24; H, 4.72; N, 6.25. Found: C, 48.12; H, 4.65; N, 6.18.

Aquabromo[(κ^2*C*,*N*){1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazol-2-ylidene}][(κ^2*C*,*C*){1-benzyl-3-(5,7-dimethyl-1,8-naphthyrido-2-yl)imidazol-2-ylidene}]iridium(III) Bromide (5). $Ir_2Cl_2(COD)_2$ (0.05 g, 0.074 mmol) and ^{t}BuOK (0.035 g, 0.312 mmol) were stirred in THF at room temperature for 30 min. The resulting mixture was added slowly to a suspension of 1-benzyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl)imidazolium bromide (0.12 g, 0.303 mmol) in THF at −78 °C. The mixture was allowed to attain room temperature overnight and then refluxed for 3 h. The red mixture was filtered through a small pad of Celite. The filtrate was concentrated under vacuum, and 15 mL of diethyl ether was added with stirring to induce precipitation. The solid residue obtained was washed with diethyl ether and dried in vacuum. Crystals suitable for X-ray diffraction were grown by layering petroleum ether over a concentrated dichloromethane solution of the compound. Yield: 0.065 g (87%). ^{1}H NMR (500 MHz, CD_3CN, 292 K): δ 9.02 (d, J = 9 Hz, 1H, NP-C$_4'$), 8.15 (d, J = 9 Hz, 1H, NP-C$_3'$), 8.09 (d, J = 2.5 Hz, 1H, Im), 7.84 (d, J = 2.5 Hz, 1H, Im), 7.53 (s, 1H, NP-C$_3$), 7.43−7.30 (m, 5H, Ph), 7.28 (d, J = 2.5 Hz, 1H, Im), 7.20−7.02 (m, 6H, Ph, Im), 6.83 (d, J = 15 Hz, 1H, NP-methylene (C^C-BIN)), 6.65 (s, 1H, NP-C$_6'$), 6.64 (s, 1H, NP-C$_6$), 4.815 (d, J = 15 Hz, 1H, NP-methylene (C^C-BIN)), 4.69 (d, J = 15 Hz, 1H, NP-methylene (C^N-BIN)), 4.49 (d, J = 15 Hz, 1H, NP-methylene (C^N-BIN)), 2.85 (s, 3H, Me), 2.58 (s, 3H, Me), 2.52 (s, 3H, Me), 2.00 (s, 3H, Me). ^{13}C NMR (125.7 MHz, $CDCl_3$, 294 K): 185.2 (N*C*N$_{Im}$), 181.1 (N*C*N$_{Im}$), 165.2 (N*C*N$_{NP}$), 164.5 (N*C*N$_{NP}$), 156.2 (N*C*C$_{NP}$), 155.5 (N*C*C$_{NP}$), 153.7 (N*C*C$_{NP}$), 153.4 (N*C*C$_{NP}$), 147.3 (C*C*C$_{NP}$), 145.7 (C*C*C$_{NP}$), 137.8 (C*C*C$_{NP\text{-cyclometalated}}$), 135.9 (*C*$_{Ph}$), 135.6 (*C*$_{Ph}$), 131.3 (*C*H$_{NP}$), 130.2 (*C*H$_{NP}$), 129.8−128.7 (*C*$_{Ph}$), 126 (*C*H$_{NP}$), 124.4 (*C*H$_{NP}$), 123.8 (*C*H$_{Im}$), 122.4 (*C*H$_{Im}$), 122 (*C*H$_{NP}$), 121.7 (C*C*C$_{NP}$), 119.2 (*C*H$_{NP}$), 117.1 (*C*H$_{Im}$), 117 (*C*H$_{Im}$), 55.2 (*C*H$_2$Ph), 53.5 (*C*H$_2$Ph), 25.2 (*C*H$_3$), 24.9 (*C*H$_3$), 18.3 (*C*H$_3$), 18.2 (*C*H$_3$). ESI-MS, m/z: 917 [M]$^+$, 899 [M − H$_2$O]$^+$. Anal. Calcd for $C_{40}H_{37}N_8OBr_2Ir$: C, 48.19; H, 3.74; N, 11.25. Found: C, 48.10; H, 3.63; N, 11.15.

Transfer Hydrogenation. Aromatic ketone (2 mmol) and Ir catalyst (2 mg, 0.002 mmol) were placed in a Schlenk flask, and the vessel was flushed with nitrogen. A 12 mL portion of 2-propanol was added to the mixture and stirred for 5 min. A 0.5 mL portion of 0.1 M KOH in 2-propanol was added to the mixture. The reaction was continued under the conditions mentioned in Table 1. After completion of reaction, as monitored by GC, the reaction mixture was evaporated and the crude product was purified by silica gel column chromatography using 10% ethyl acetate/petroleum ether.

X-ray Data Collections and Refinement. Single crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2)K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated and scaled using SMART and SAINT software package,[28] and the data were corrected for

Table 2. Crystallographic Data and Pertinent Refinement Parameters for compounds **1**·2CH_2Cl_2, **2**, **3**, **4**, and **5**·CH_2Cl_2

	1·2CH_2Cl_2	**2**	**3**
empirical formula	$C_{42}H_{38}Cl_6N_8Pd$	$C_{24}H_{18}N_4O_4W$	$C_{28}H_{30}BrN_4Rh$
formula weight	973.90	610.27	605.38
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.7787(9)	8.0628(13)	6.9091(13)
b (Å)	12.8169(10)	10.2021(16)	12.842(3)
c (Å)	15.0948(12)	14.552(2)	14.458(3)
α (deg)	89.1670(10)	104.785(2)	100.294(3)
β (deg)	74.2740(10)	91.721(2)	94.061(3)
γ (deg)	77.9100(10)	108.532(2)	103.084(3)
V (Å^3)	2142.7(3)	1089.3(3)	1221.1(4)
Z	2	2	2
ρ_{calcd} (g cm^{-3})	1.510	1.861	1.647
μ (mm^{-1})	0.849	5.342	2.360
F(000)	988	592	612
reflections			
collected	14071	6101	10451
independent	10053	4270	5687
observed [$I > 2\sigma(I)$]	8816	3913	4574
no. of variables	512	300	309
GoF	1.120	1.026	1.056
R_{int}	0.0194	0.0292	0.0315
final R indices	R1 = 0.0660	R1 = 0.0392	R1 = 0.0482
[$I > 2\sigma(I)$][a]	wR2 = 0.1438	wR2 = 0.0833	wR2 = 0.1229
R indices (all data)[a]	R1 = 0.0837	R1 = 0.0448	R1 = 0.0641
	wR2 = 0.1767	wR2 = 0.0855	wR2 = 0.1345

	4	**5**·CH_2Cl_2	BIN·HBr
empirical formula	$C_{36}H_{42}N_4Br_2Rh_2$	$C_{41}H_{37}N_8OBr_2Cl_2Ir$	$C_{20}H_{19}N_4Br$
formula weight	896.38	1080.71	395.30
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	10.4180(13)	23.431(4)	7.4940(13)
b (Å)	13.2320(17)	14.773(3)	11.2896(19)
c (Å)	13.9807(17)	26.948(5)	11.612(2)
α (deg)	105.890(2)	90.00	80.327(3)
β (deg)	100.108(2)	97.863(4)	75.561(3)
γ (deg)	110.761(2)	90.00	72.375(3)
V (Å^3)	1651.7(4)	9240(3)	902.2(3)
Z	2	8	2
ρ_{calcd} (g cm^{-3})	1.802	1.554	1.455
μ (mm^{-1})	3.451	4.774	2.288
F(000)	892	4224	404
reflections			
collected	12341	41384	5969
independent	6125	11395	4260
observed [$I > 2\sigma(I)$]	4771	4676	3292
no. of variables	394	500	228
GoF	1.036	0.840	1.069
R_{int}	0.0399	0.1781	0.0177
final R indices	R1 = 0.0666	R1 = 0.0687	0.0491
[$I > 2\sigma(I)$][a]	wR2 = 0.1884	wR2 = 0.1221	0.1228
R indices (all data)[a]	R1 = 0.0842	R1 = 0.1719	0.0705
	wR2 = 0.2051	wR2 = 0.1546	0.1542

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$; $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum|F_o^2|^2]^{1/2}$.

(28) *SAINT+ Software for CCD difractometers*; Bruker AXS: Madison, WI, 2000.

absorption using the SADABS program.[29] The structures were solved and refined using SHELX suite of programs[30] while additional crystallographic calculations were performed by the programs PLATON.[31] Pertinent crystallographic data and refinement parameters are provided in Table 2. Figures were drawn using ORTEP32.[32] The hydrogen atoms were included into geometrically calculated positions in the final stages of the refinement and were refined according to "riding model". The dichloromethane solvent molecule in **1** was found to be disordered and was modeled satisfactorily. Hydrogen atoms of the coordinated water in **5** were not located. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **4**, all non-hydrogen atoms except C13 were refined with anisotropic thermal parameters. Anisotropic treatment of this particular atom resulted non-positive definite displacement tensors and was therefore subjected to isotropic refinement. The "SQUEEZE" option in PLATON was used to remove a disordered solvent molecule from the overall intensity data of compound **5**.

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Supporting Information Available: Full X-ray crystallographic data in CIF format; tables of metrical parameters for **1**, **2**, **3**, **4**, **5**, and BIN·HBr; Scheme S1, and ^{1}H NMR data for transfer hydrogenation products. This material is available free of charge via the Internet at http://pubs.acs.org.