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Complexes of Pd(II), η^6-C_6H_6Ru(II), and η^5-Cp*Rh(III) with Chalcogenated Schiff Bases of Anthracene-9-carbaldehyde and Base-Free Catalytic Transfer Hydrogenation of Aldehydes/Ketones and *N*-Alkylation of Amines

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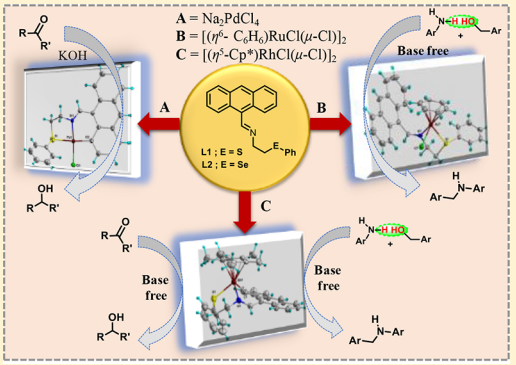
Supporting Information

ABSTRACT: The condensation of 2-(phenylsulfanyl)ethylamine and 2-(phenylselenyl)ethylamine with anthracene-9-carbaldehyde resulted in Schiff bases $[PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$(**L1**) and $[PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ (**L2**), respectively. $Na_2[PdCl_4]$ treatment of **L1**/**L2** in acetone−water mixture for 3 h at room temperature gave palladacycle $[PdCl(C^-, N, S/Se)]$ (**1**/**2**; **L1**/**L2**−H = $(C^-, N, S)/(C^-, N, Se)$). The reaction of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with **L1**/**L2** in methanol for 8 h at room temperature (followed by addition of NH_4PF_6) afforded half-sandwich complex $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl][PF_6]$, **3**/**4**: (**L** = **L1**/**L2** ≡ (N, E) ligand). The reaction of $[(\eta^5\text{-Cp*})RhCl(\mu\text{-}Cl)]_2$ with **L1** /**L2** in the presence of CH_3COONa at 50 °C (followed by treatment with NH_4PF_6) resulted in $[(\eta^5\text{-Cp*})Rh(\mathbf{L}\text{-}\mathbf{H})][PF_6]$, **5**/**6**: (**L** = **L1**/**L2**). On carrying out the reaction of $[(\eta^5\text{-Cp*})RhCl(\mu\text{-}Cl)]_2$ with these ligands at room temperature and in the absence of CH_3COONa, complex $[(\eta^5\text{-Cp*})Rh(\mathbf{L})Cl][PF_6]$, **7**/**8** (**L** = **L1**/**L2** ≡ (N, E) ligand), was formed. Complexes **1**−**8** were authenticated with ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectroscopy, high-resolution mass spectrometry, elemental analyses, and single-crystal X-ray diffraction. The moisture- and air-insensitive complexes of Pd(II) (**1**, **2**), Ru(II) (**3**, **4**) and Rh(III) (**5**−**8**) were thermally stable. Palladium and rhodium (under base-free condition) species efficiently catalyzed transfer hydrogenation (propan-2-ol as H-source). At room temperature conversion was 90% in TH catalyzed with 0.2 mol % of **2**. *N*-Alkylation of aniline with benzyl alcohol under base-free condition was promoted by **3**−**8**. The **7** was most efficient for the two base-free catalytic reactions. For TH optimum loading of **1**−**2** and **5**−**8** as catalyst is 0.05−0.2 and 0.2−0.5 mol % respectively. The optimum temperatures are 80 and 100 °C for TH and *N*-alkylation, respectively. The optimum loading of **3**−**8** for *N*-alkylation is 0.5 mol %. Mercury poisoning test supported homogeneous pathway for the two catalytic reactions. The rhodacycles probably gave real catalytic species by losing a Cp* group.



INTRODUCTION

Anthracene derivatives are reported important for designing phosphorescent, electroluminescent and semiconducting materials.[1,2] Anthracene-based ligands are versatile.[3−5] They are reported[3] for synthetic modeling of mono-[Fe] hydrogenase and discrimination of biologically important species. The synthesis, structure, and properties of metal complexes of a variety of anthracene based ligands have been reported.[6] The *ortho*-metalation of benzene[7] is well-known. However, such reports on naphthalene[8] are few, and those on anthracene[9] are scanty. Moreover, the metal complexes of anthracene-based ligands are rarely evaluated as a catalyst.[10] The architecture of ligand and its arrangement around the metal center play an important role in catalytic efficiency.[11] Thus, use of anthracene backbone in place of benzene frame in ligands can be gratifying. Consequently, transition metal complexes of anthracene based ligands are expected to be promising as homogeneous catalysts for several organic reactions including C−H activation and therefore are envisioned as worth exploring for diverse applications.[12] The organochalcogen ligands are known to form more air stable and moisture insensitive transition metal complexes compared to their phosphine analogs.[13] As a catalyst, such complexes are efficient.[13] There is combination of anthracene and chalcogen donor site in Schiff bases $[PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$(**L1**) and $[PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ (**L2**). Consequently, they are worth exploring. Of their complexes with Pd(II), Rh(III), and Ru(II) reported herein for the first time, **1**−**2** and **5**−**8** show good performance as catalysts for transfer hydrogenation (base-free in case of Rh). The Ru(II) and Rh(III) complexes (**3**−**8**) were efficient catalysts for *N*-alkylation reaction of amines with benzyl alcohol under base-free condition.

The palladacycles including those having metal−chalcogen bond are well-known for Suzuki−Miyaura,[14,15] Sonogashira,[15] and Heck coupling[16] and allylation of alkenes.[15a,16] However,

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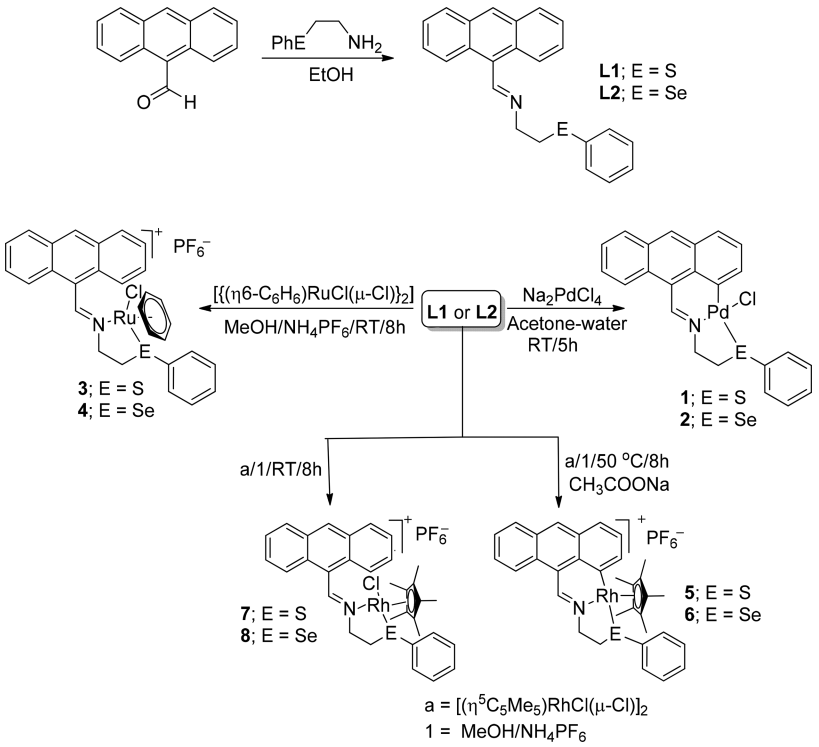
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of 1−8



transfer hydrogenation (TH) by palladacycles having a metal−chalcogen bond is not to our knowledge. TH based on a hydrogen source like 2-propanol, glycerol, cyclopentanol, or formic acid for reduction and a catalyst[17] has drawn attention due to its simplicity. Moreover, these low-cost hydrogen donors are environmentally friendly and have the ability to dissolve many organic compounds. The important cations used to design catalysts for TH[17] are Ru(II), Rh(III), Ir(III), and Ir(I). TH by species having common transition metals, viz., Fe, Mn, Co, and Ni is also reported.[18] Some of the species based on ruthenium are very efficient,[19] as within few minutes very good conversion is achieved in the presence of base with 0.03 to 0.005 mol % loading of the catalyst. However, none of them is base-free. The single Pd(II) catalyst reported so far for TH[20] was designed by incorporating air- and moisture-sensitive phosphine-based pincer complex of Pd into a MOF. Its optimum loading was reported as 5 mol % Pd. The TH of carbonyl compounds catalyzed with Pd(II) complexes of anthracene-based chalcogen ligands was rewarding, as optimum loading reduced to 0.05−0.2 mol %. In TH, undesirable decarbonylation and aldol condensation of base-sensitive ketones and aldehydes, mediated by metal and alkali, respectively, are matter of concern.[21] Base-free TH thus has wider scope and is less corrosive, important characteristics for use on industrial scale.[22] The catalysts carrying out TH efficiently under base-free mild conditions are not common. Cp*Rh−guanidinato complexes are reported to catalyze base-free TH.[23] The activation of TH (H source: 2-propanol) by complexes of Cp*Rh with anthracene-based chalcogen ligands reported herein is base-free and 0.2−0.5 mol % loading of the complexes as a catalyst is enough to give good to excellent yield.

The catalysts based on Au,[24] Ag,[25] Pd,[26] Rh,[27] Os,[28] Cu,[29] Ni,[30] Co,[31] Fe,[32] Mn,[33] Re,[34] Ru,[35] and Ir[36] have been reported for *N*-alkylation of amines with benzyl alcohols. The base is generally required for such *N*-alkylation. Some Ir species[37a,b] are known to be efficient for the *N*-alkylation but are expensive. Some catalysts based on Ru and Ir require forcing conditions.[37] However, Cp*$IrCl_2$[38] and $Ru_3(CO)_{12}$ (2 mol %) with bulky phosphines[39a] and $CpRuCl(PPh_3)_2$[39b] are examples of catalysts for which working conditions used are mild. Some ruthenium species are known to catalyze base-free *N*-alkylation[40] of amines with benzyl alcohols. For one such species, $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ reported by Williams et al.,[40a] the optimum loading is 2.5 mol %, and the presence of an excess of bulky phosphine ligand is essential. The only Rh species known to catalyze base-free *N*-alkylation of amines is $[RhH(PPh_3)_4]$.[41] Half-sandwich complexes of Ru(II) and Rh(III) with anthracene-based chalcogenated ligands (**L1** and **L2**) reported herein, catalyze *N*-alkylation reaction of amines with benzyl alcohols under base-free conditions. The catalytic activities of Ir(III) complexes of **L1** and **L2** have been reported by our group recently.[13b] The reaction time with Rh complexes as catalysts is half that of of their Ir analogues.

RESULTS AND DISCUSSION

The syntheses of Pd(II), Ru(II), and Rh(III) complexes (**1−4**, **7−8**) carried out at room temperature are summarized in Scheme 1. **L1** and **L2** were prepared by a reported method.[15b] Their palladation with Na_2PdCl_4 in acetone and water mixture (5:2) has resulted in **1** and **2**, respectively, where **L1**/**L2** behaves as a (C^-, N, E) pincer ligand. Complexes **3−4** and **7−8** were formed by chloro bridge cleavage of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ and $[(\eta^5\text{-}Cp^*)RhCl(\mu\text{-}Cl)]_2$ respectively, followed by reaction with **L1** or **L2** at room temperature, facilitated by anion exchange with NH_4PF_6. **5** and **6** resulted in the reaction of $[(\eta^5\text{-}Cp^*)RhCl(\mu\text{-}Cl)]_2$ with **L1** and **L2**, respectively, carried out in the presence of CH_3COONa at 50 °C.

At room temperature (as well as on heating up to 70 °C) but in the absence of sodium acetate, the reaction of $[(\eta^5\text{-}$

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Organometallics XXXX, XXX, XXX−XXX

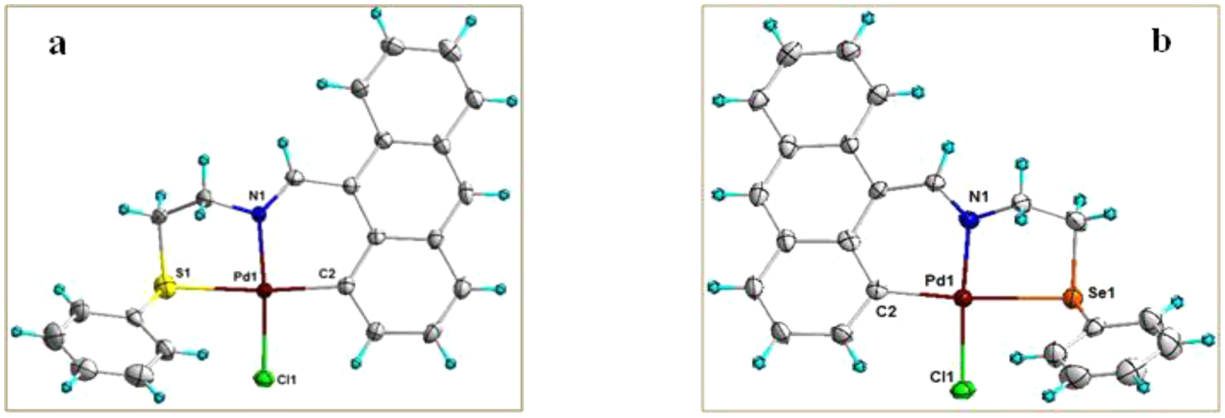

Figure 1. (a) ORTEP of **1**. Bond lengths (Å): Pd(1)−S(1) 2.4255(18), Pd(1)−Cl(1) 2.3364(16), Pd(2)−C(2) 1.998(6), Pd(1)−N(1) 1.982(5). Bond angles (deg): S(1)−Pd(1)−Cl(1) 88.9(2), Cl(1)−Pd(1)−N(1) 174.57(16), Cl(1)−Pd(1)−C(2) 95.52(18), C(2)−Pd(1)−S(1) 174.27(18), C(2)−Pd(1)−N(1) 88.9(2), N(1)−Pd(1)−S(1) 85.37(15). (b) ORTEP of **2**. Bond lengths (Å): Pd(1)−Se(1) 2.5231(9), Pd(1)−Cl(1) 2.3402(18), Pd(1)−C(2) 1.992(7), Pd(1)−N(1) 1.981(6). Bond angles (deg): Se(1)−Pd(1)−Cl(1) 90.08(5), Cl(1)−Pd(1)−N(1) 175.58(18), Cl(1)−Pd(1)−C(2) 95.3(2), C(2)−Pd(1)−Se(1) 174.1(2), C(2)−Pd(1)−N(1) 88.7(3), N(1)−Pd(1)−Se(1) 85.81(17).

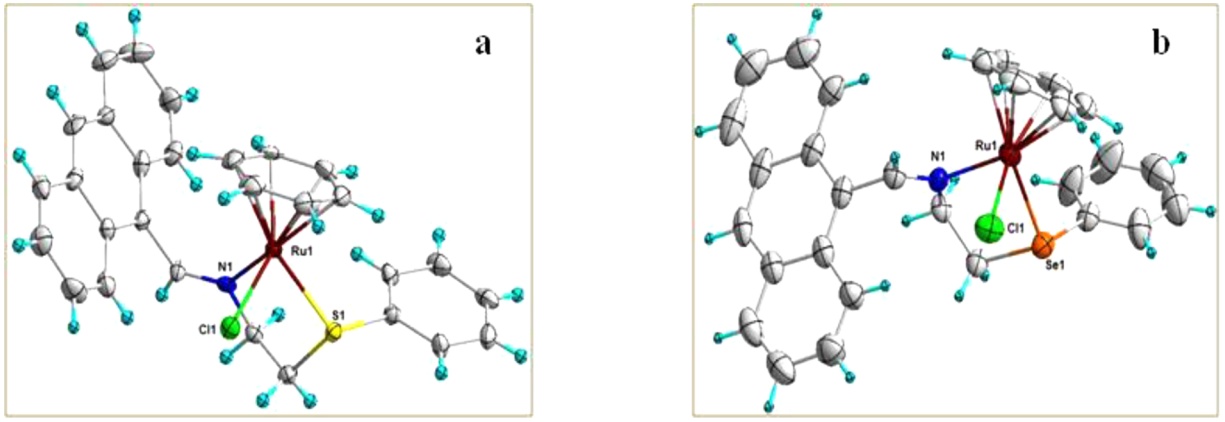

Figure 2. (a) ORTEP of **3**. Bond lengths (Å): Ru(1)−S(1) 2.367(3); Ru(1)−Cl(1) 2.386(3); Ru(1)−C(24) 2.217(15); Ru(1)−N(1) 2.134(10). Bond angles (deg): N(1)−Ru(1)−S(1) 83.6(3); N(1)−Ru(1)−Cl(1) 86.1(3); S(1)−Ru(1)−Cl(1) 78.81(11). (b) ORTEP of **4**. PF_6 anion has been omitted for clarity. Bond lengths (Å): Ru(1)−Se(1) 2.4911(10); Ru(1)−N(1) 2.091(6); Ru(1)−Cl(1) 2.397(2); Ru(1)−C(24) 2.159(11). Bond angles (deg): N(1)−Ru(1)−Se(1) 81.82(16); N(1)−Ru(1)−Cl(1) 85.31(16); Se(1)−Ru(1)−Cl(1) 83.84(6).

Cp*)RhCl(μ-Cl)]$_2$ with **L1** and **L2** has given **7** and **8**, respectively.

Palladium complexes **1** and **2** have good solubility in DMSO and DMF but moderate solubility in $CHCl_3$, CH_2Cl_2, and CH_3CN. The solubilities of **3**−**8** are good in CH_3CN, but they are sparingly soluble in CH_2Cl_2, $CHCl_3$, and CH_3OH. Complexes **1**−**8** could be stored for 6 months without noticeable decomposition, as revealed by their ^{1}H NMR spectra.

Spectral Characterization. The ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H}NMR and mass spectra [see Figures S9−S26] of **1**−**8** are in agreement with their molecular structures depicted in Scheme 1. In the case of **8**, ^{13}C{^{1}H} and ^{77}Se{^{1}H}NMR spectra could not be recorded due its inadequate solubility in all available solvents. The ^{77}Se{^{1}H} NMR spectra of **2**, **4**, and **6**, have depicted one signal in each case at 321.4, 424.1, and 379.8 ppm respectively (see Figures S13, S18, and S23) and were deshielded (56.4, 159.1, and 114.8 ppm respectively) compared to the signal of free **L2** in its ^{77}Se{^{1}H} NMR spectrum, indicating the coordination of selenium with the metal center. The signal of >CH═N− in ^{1}H NMR spectra of **1**−**8** was noted as deshielded up to 0.88 ppm in comparison to those of free ligands,[13b] supporting the coordination of azomethine nitrogen with Pd/Ru/Rh. The ^{13}C{^{1}H} NMR spectra of complexes **1** and **2** have new quaternary carbon signals at 144.4 and 144.8 ppm respectively (see Figures S10 and S12) implying the palladation of **L1** and **L2**. In ^{1}H NMR spectra of **1**−**8**, each proton of two CH_2 groups becomes diasterotopic, which results in multiplets of different pattern, appearing from δ 2.29 to 4.93 (Figures S9, S11, S14, S16, S19, S21, S24, and S26) supporting M−N and M−S/Se bond (M = Pd, Ru, or Rh) formation which prevents the free rotation in $-CH_2-CH_2-$. The total number of protons in the spectra of **1**, **2**, **5**, and **6** is lowered by one relative to those of **L1** and **L2** respectively, due to formation of M−C bond via C−H activation, i.e., metallacycle. In ^{13}C{^{1}H} NMR spectra of **1** and **2**, >CH═N− signals were shielded relative to those of free **L1** and **L2** by 3.52 and 6.15 ppm, respectively. In contrast, the >CH═N− signals in ^{13}C{^{1}H} NMR spectra of **3**−**7**, were deshielded (∼2−16.0 ppm) relative to those of free **L1** or **L2** due to coordination of this group with Ru/Rh(III). In both ^{1}H and ^{13}C{^{1}H} NMR spectra of **5**−**8**, the signals of η^5-pentamethylcyclopentadienyl group (singlet in ^{1}H NMR) were shielded (maximum shift ∼0.3 and 2.1 ppm, respectively) with respect to that of [(η^5-Cp*)RhCl(μ-Cl)]$_2$. This may be due to substitution of Cl with less electronegative S and Se.

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Organometallics XXXX, XXX, XXX−XXX

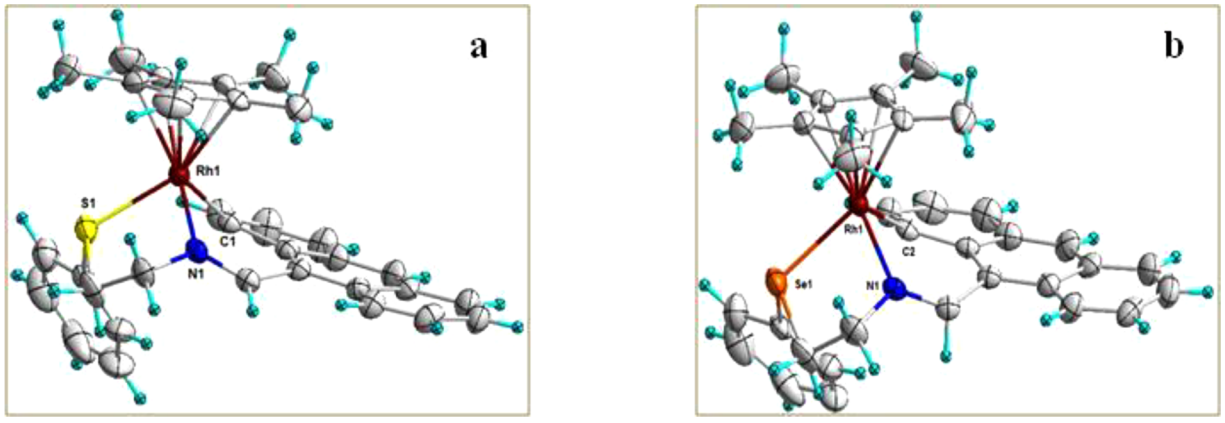

Figure 3. (a) ORTEP of **5**. Selected bond lengths (Å): Rh(1)−S(1), 2.347(16), Rh(1)−N(1), 2.039(5), Rh(1)−C(12), 2.030(6), Rh−C 2.158(6)−2.243(6). Selected bond angles (deg): C(12)—Rh(1)—S(1) 98.47(15), N(1)—Rh(1)—S(1) 82.15(14), C(12)—Rh(1)—N(1) 85.4(3). (b) ORTEP of **6**. Selected bond lengths (Å): Rh(1)−Se(1), 2.4559(7), Rh(1)−N(1), 2.041(4), Rh(1)−C(12), 2.030(5), Rh−C 2.174−2.554. Selected bond angles (deg): C(12)—Rh(1)—Se(1) 98.51(13), N(1)—Ir(1)—Se(1) 82.63(12), C(12)—Rh(1)—N(1) 86.15(18).

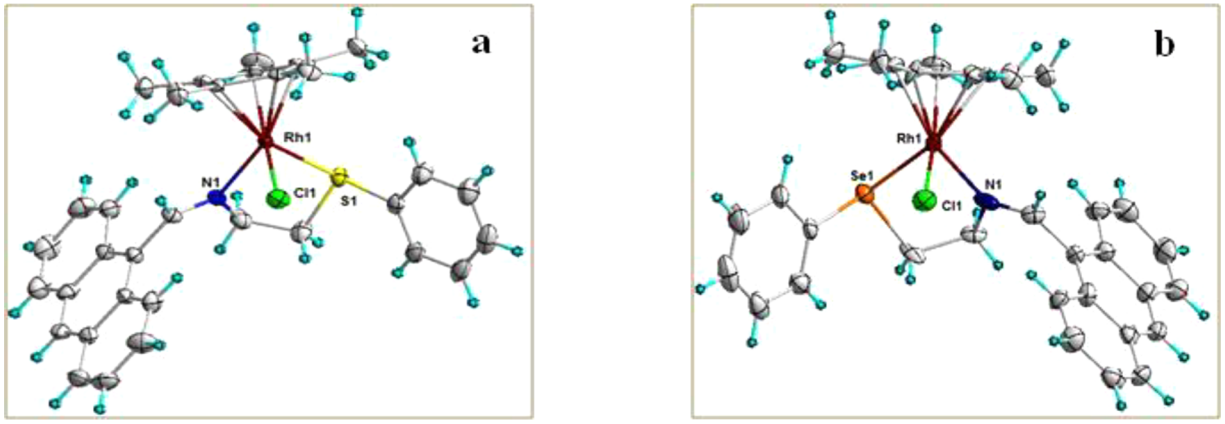

Figure 4. (a) ORTEP of **7**. Selected bond lengths (Å): Rh(1)−S(1), 2.3761(9), Rh(1)−N(1), 2.100(2), Rh(1)−Cl(1), 2.4026(9), Rh−C 2.153(3)−2.183(3). Selected bond angles (deg): Cl(1)—Rh(1)—S(1) 93.52(3), N(1)—Rh(1)—S(1) 82.88(8), Cl(1)—Rh(1)—N(1) 84.00(8). (b) ORTEP of **8**. Selected bond lengths (Å): Rh(1)−Se(1), 2.476(15), Rh(1)−N(1), 2.068(9), Rh(1)−Cl(1), 2.393(3), Rh−C 2.107(10)−2.186(11). Selected bond angles (deg): Cl(1)—Rh(1)—Se(1) 94.11(9), N(1)—Rh(1)—Se(1) 82.9(3), Cl(1)—Rh(1)—N(1) 86.4(2).

The signals of η^6-benzene in both ^{1}H and ^{13}C{^{1}H} NMR spectra appear deshielded with respect to that of [Ru(η^6-benzene)Cl$_2$]$_2$.

The high-resolution mass spectra (HR-MS) of complexes **1**−**8** were recorded. The cationic fragments of $[M - Cl]^+$ were noted in the HR-MS spectra of **1** and **2** (Figures S1and S2). However, in the HR-MS spectra of **3**−**8**, the cationic fragments of $[M - PF_6]^+$ were noticed (Figures S3−S8). These observations authenticate these complexes.

Crystal Structures. Single crystals of **1**−**8** were grown by slow evaporation of their solutions. **1** and **2** were dissolved in $CHCl_3$, and **3**−**8** were dissolved in diethyl ether−acetonitrile (1:3; v/v) mixture. The crystallographic data and refinement parameters are given in Tables S1−S3. The molecular structures (ellipsoids at 30% probability) of complexes **1**−**8** determined with single crystal X−ray diffraction are shown in Figures 1−4.

Complexes **1** and **2** crystallized with one molecule of chloroform, whereas in the case of **3** and **4**, two molecules of complex crystallized with two molecules of hexafluorophosphate anion in their crystal lattice. The crystal of **4** also has one molecule of chloroform. The $CHCl_3$, (in case of **1** and **2**) and PF_6^- anion have been omitted for clarity. **L1** and **L2** exhibit monoanionic tridentate (S/Se, N, C$^-$) bonding mode in **1** and **2**, i.e., six- and five-membered chelate rings are formed by their coordination with Pd, which shows distorted square planar geometry. The selected bond lengths of each complex are given below its molecular structure (Figures 1−4). In complexes **1** and **2**, bond lengths (Å) of Pd−C (1.998(6) and 1.992(7)), Pd−N (1.982(5) and 1.981(6)), and Pd−Cl (2.3364(16) and 2.3402(18)) are consistent with the values reported for palladacycles of chalcogenated Schiff bases,[13a14a] their reduced forms, tridentate selenated[14b] and indole-based Schiff bases,[16] and trinuclear Pd complexes of chalcogenated NHCs.[15b] The Pd−S bond length in **1**, 2.4255(18) Å, is somewhat longer than the reported value of 2.3179(19) Å[15b] for trinuclear Pd complex of sulfated NHC and is consistent with the value of 2.428(2) Å[14a] reported for a palladacycle of a sulfated Schiff base. The Pd−Se bond length in **2**, 2.5231(9) Å, is somewhat higher than the value reported (2.370(1) Å),[13a] for a complex of tridentate chalcogenated Schiff base and close to value of 2.528(11) Å[14b] reported for a complex of reduced chalcogenated Schiff base.

In the crystals of complexes **1** and **2**, intermolecular C−H···Cl noncovalent interactions exist as shown in Figures S27 and S28. They result in a three-dimensional framework. In the

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Organometallics XXXX, XXX, XXX−XXX

crystal of **2**, intermolecular Se···H−C7 interactions have been noted (Figure S28). The C−H···Cl distances are given in Table S6.

Ligands **L1** and **L2** coordinate with Ru in a neutral bidentate (S/Se, N) mode forming a five-membered chelate ring in complexes **3** and **4**, as corroborated by their single crystal structures. The geometry of ruthenium is pseudo-octahedral half-sandwich "piano-stool" type. The chlorine and η^6-C_6H_6 group complete the coordination sphere of ruthenium.

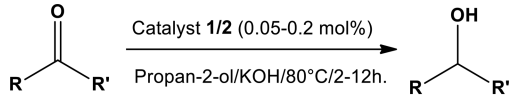
The length of the Ru−S bond in **3**, 2.367(3) Å, is shorter than the value of 2.4079(6) Å[13d] reported for ruthenium complex of (phenylthio)methyl-2-pyridine. The Ru−N bond lengths of **3** and **4** are 2.153(7) and 2.097(6) Å, respectively, consistent with the values [2.075(3)−2.104(6) Å] reported for several other species.[13d,e] The Ru−Se bond length in **4** is 2.4901(11) Å, consistent with the values 2.4859(9)−2.497(5) Å reported[13c] for Ru(II) complex of a 1,2,3-triazole based ligand. In the crystals of **3** and **4**, C−H···F secondary interactions due to PF_6^- anion (Figures S29 and S30) have been noted. The C−H···F distances are given in Table S6.

In complexes **5** and **6**, six- and five-membered chelate rings (one each) are formed due to coordination of **L1** and **L2** with rhodium in (C^-, S/Se, N) form, whereas only one five-membered chelate ring is formed in **7** and **8** due to their coordination with Rh via S/Se and N. In all four complexes **5**−**8**, there is a pseudo-octahedral half-sandwich "piano stool" type disposition of donor atoms around Rh. The centroid of η^5-Cp* ring occupies the center of three octahedral sites making a triangle. The, S/Se, N, and C^- or chlorine complete the coordination sphere. The Rh−S bond lengths in **5** and **7** [2.349(3) and 2.3761(9) Å, respectively] are somewhat shorter than values reported for complexes [η^5-Cp*RhCl-(1,1′-(1,2-ethanediyl)bis(3-methylimidazole-2-thione)]Cl [2.3967(11) Å],[42a] [η^5-Cp*RhCl{2-(phenylthiomethyl)pyridine}]PF_6 [2.383(2) Å],[42b] and [η^5-Cp*RhCl{η^2-S,P-Ph_2P-(S)NHPPh_2}]BF_4 [2.404(3) Å].[42c] The Rh−C bond lengths of **5** and **6** [2.030(6) and 2.030(5) Å, respectively] are consistent with the values reported for rhodacycles of *N*-benzylidenemethylamine and 2-phenylpyridine [2.0285(13) and 2.0361(13) Å, respectively][42d] and longer than the value reported for Rh−(NHC) complex [2.013(3) Å].[42e] The Rh−Se bond lengths of complexes **6** and **8** [2.4559(7) and 2.4732(6) Å, respectively] are somewhat shorter than the values reported for half-sandwich complexes of Rh(III) with 2-(phenylselenomethyl)pyridine [2.487(1) Å][42f] and [η^5-Cp*RhCl{η^2-(SePPh_2)$_2$N}]BF_4 [2.5266(8) Å][42g] but somewhat longer than the values reported for a half-sandwich complex of Rh(III) with 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand [2.3833(5)−2.4706(6) Å].[42h] The involvement of PF_6^- in C−H···F secondary interactions in **5**−**8** (Figures S31−S34) results in chains in the crystal structures. The C−H···F distances are given in Table S7.

Applications of Complexes 1−8 in Catalysis. *Catalytic Transfer Hydrogenation (TH).* The catalysis of TH of various aldehydes/ketones using 2-PrOH as a hydrogen donor with complexes **1** and **2** (0.05−0.2 mol %) was explored (Scheme 2). The KOH was the best base for this purpose,[43] as the catalytic TH is sensitive to the nature of base, e.g., performance in the presence of K_2CO_3, Cs_2CO_3, KHMDS, *t*-BuOK, or HCOONa[17,44] is not the same.

The reaction conditions for TH were optimized using 4-anisaldehyde as a model substrate and taking **2** as a catalyst. The optimum reaction temperature emerged as 80 °C (Table 1, entry 3). At room temperature, 90% conversion occurred on carrying out TH with 0.2 mol % of **2** as a catalyst for 12 h (Table 1, entry 1), whereas with 0.1 mol % of **2**, conversion was reduced to 45% (Table 1, entry 2). The conversion in TH of 4-anisaldehyde to the desired product was reduced on lowering the amount of KOH (Table 1, entry 4). In the absence of either **2** or KOH, there was no TH reaction (Table 1, entries 5 and 12). The combinations glycerol + KOH, 2-propanol + HCOONa, and HCOOH + HCOONa gave moderate conversions only (Table 1, entries 6, 8, and 9), whereas the combination of glycerol with HCOONa did not work at all (Table 1, entry 7). When TH reaction was performed using ethanol as a substitute of 2-propanol, keeping other conditions at optimum, the conversion was low (Table 1, entry 10). The conversion of model substrate did not increase when the loading of the catalyst was made 0.2 mol % (Table 1, entry 11). However, on decreasing the loading of the catalyst to 0.05 mol %, conversion diminished (Table 1, entry 13). TH attempted with Na_2PdCl_4 under conditions optimized for **1** and **2** gave poor conversion to the desired product (Table 1, entry 14), indicating the role of ligand in the catalytic activity. The optimum loading of **1** and **2** as a catalyst, TH at 80 °C was 0.1 mol % (Table 2). The overall optimized conditions can be summarized as KOH (40 mol %), **2** (0.05−0.2 mol %), and 2-propanol (5 mL) (Table 2, entry 1). Complex **1** was somewhat less efficient than **2**. The scope of optimized protocols as summarized in Scheme 2 has been explored, and results are shown in Table 2.

Scheme 2. Transfer Hydrogenation of Carbonyl Compounds



R = R'= Alkyl/Aryl/H

The presence of electron-withdrawing or -donating groups on benzaldehyde affects its TH. The former has gaven better yield/conversion. The conversions of benzaldehyde with deactivating groups (Table 2, entry 2−5) into desired product were up to 97% when loading of **1** or **2** as a catalyst was 0.05 mol %. In the presence of activating groups on benzaldehyde (Table 2, entry 6 and 7), conversion to desired product was up to 90% only, even with 0.1 mol % loading of the catalyst. **1** and **2** were somewhat less efficient for ketones than aldehydes. Aromatic (Table 2, entry 11−13) and aliphatic (Table 2, entry 14) ketones were reduced to corresponding alcohol in good yield by using 0.2 mol % loading of **1** or **2**. Thus, **1** and **2** can be labeled as more efficient catalysts (its required loading is low and reaction time short) than the entity designed by incorporation into MOF of a pincer complex of Pd which required loading as a catalyst of 5 mol %.[20] The TH reaction was subjected to mercury and triphenylphosphine poisoning tests.[45] TH of 4-anisaldehyde was catalyzed with **2** in the presence of excess Hg(0)/PPh_3 under optimum conditions. The reaction was unaffected and progressed to completion. Thus, complexes **1** and **2** behave as homogeneous catalysts.

The time profile of transfer hydrogenation under optimum conditions given in Figure S35 has revealed linear increase in the conversion up to 3 h without induction period.

Base-Free Catalytic Transfer Hydrogenation. For catalysis of TH of aldehydes/ketones to the corresponding alcohols by

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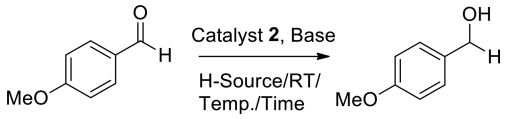
Table 1. Optimization of Reaction Conditions for Transfer Hydrogenation Using 2[a]



no.	base	solvent (mL)	temperature (°C)	time (h)	catalyst (mol %)	yield (%)/TOF (h^{-1})[b]
1.	KOH	2-PrOH	RT	12	0.2	90 (37.5)
2	KOH	2-PrOH	RT	12	0.1	45 (37.5)
3	KOH	2-PrOH	80	5	0.1	91 (182)
4[c]	KOH	2-PrOH	80	5	0.1	20 (40)
5	none	2-PrOH	80	5	0.1	nd
6	KOH	glycerol	80	5	0.1	40 (80)
7[d]	HCOONa	glycerol	80	5	0.1	<5
8[d]	HCOONa	2-PrOH	80	5	0.1	60 (120)
9[e]	HCOONa	HCOOH	80	5	0.1	51 (102)
10	KOH	C_2H_5OH	80	5	0.1	55 (110)
11	KOH	2-PrOH	80	5	0.2	91 (91)
12	KOH	2-PrOH	80	5	none	nd
13	KOH	2-PrOH	80	5	0.05	38 (152)
14[f]	KOH	2-PrOH	80	5	0.1	8 (6)

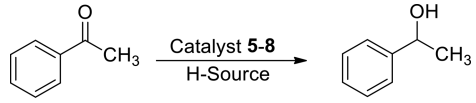
[a]Reaction conditions: 4-anisaldehyde, 1 mmol; 2-propanol, 5 mL; KOH, 0.2 mmol. [b]^{1}H NMR % yield. [c]Using 0.1 mmol of KOH. [d]HCOONa, 1 mmol. [e]At a ratio of 1:3 (HCOONa/HCOOH). [f]Na_2PdCl_4 as a catalyst. nd; not detected.

Table 2. Transfer Hydrogenation of Aldehyde/Ketone Catalyzed with 1 and 2[a]

				conversion (%)/isolated yield	
no.	substrate	catalyst (mol %)	time (h)	1	2
1	benzaldehyde	0.05	2	95/85	97/89
2	4-nitrobenzaldehyde	0.05	2	92/80	96/87
3	4-bromobenzaldehyde	0.05	2	93/82	94/85
4	4-chlorobenzaldehyde	0.05	2	90/81	91/80
5	4-fluorobenzaldehyde	0.05	2	89/79	93/85
6	4-anisaldehyde	0.1	5	89/77	91/83
7	4-methylbenzaldehyde	0.1	5	87/78	90/81
8	2-bromobenzaldehyde	0.05	5	89/76	92/80
9	3-anisaldehyde	0.1	5	85/74	90/78
10	2-pyridinecarboxaldehyde	0.2	5	88/79	91/76
11	acetophenone	0.2	12	70/61	75/63
12	propiophenone	0.2	12	65/58	66/54
13	4-methylacetophenone	0.2	12	61/50	69/56
14	octan-2-one	0.2	12	60/53	64/53

[a]Reaction conditions: aldehyde/ketone, 1 mmol; KOH, 40 mol %; 2-propanol, 5 mL; bath temperature, 80 °C.

Table 3. Optimization of Conditions for Catalysis of TH with Complexes 5−8[a]



no.	complex	mol % Rh	solvent/H-source (5 mL)	t (h)	yield %[b] (TOF (h^{-1}))
1	7	0.5	2-PrOH	2	88 (79)
2	7	0.25	2-PrOH	2	15 (30)
3	7	0.5	glycerol	2	<5
4	7	0.5	*t*-butyl alcohol	2	nd
5[c]	7	0.5	2-PrOH	2	4 (4)
6	**5**	0.5	2-PrOH	2	79 (79)
7	**6**	0.5	2-PrOH	2	76 (76)
8	**8**	0.5	2-PrOH	2	83 (83)
9	7	1	2-PrOH	2	88 (44)
10	7	0.5	2-PrOH	10	88 (17.6)
11	$[Cp^*RhCl_2]_2$	0.5	2-PrOH	24	12 (1)

[a]Reaction conditions: acetophenone, 1 mmol, temp., 80 °C. [b]Monitored with ^{1}H NMR; nd; not detected. [c]RT.

complexes **5**−**8**, base was not essential. Acetophenone was chosen as a model substrate to optimize conditions of the catalysis. Complexes **5**−**8** catalyzed its reduction (in aerobic base-free condition) with 2-PrOH to 1-phenylethanol, at 80 °C. The detailed results are shown in Table 3.

The conversion reached maximum in 2 h with 0.5 mol % **7** (Table 3, entry 1). 2-PrOH was the best solvent cum H-source for TH as reported earlier[17] (Table 3, entry 1). In the absence of **5**−**8**, no conversion was noticed. On lowering the amount of **7** below optimum value, conversion became poor (Table 3, entry 2). On using 0.5 mol % **7** as a catalyst at room temperature, only 4% conversion to the desired product was observed after 2 h (Table 3, entry 5). When glycerol or *t*-butyl alcohol was used in place of 2-propanol for TH (under optimized other conditions) no conversion was detected (Table 3, entry 3 and 4). On using **6** as a catalyst under optimum conditions, the conversion observed was lower (76%) compared to that achieved with **5**, **7**, and **8** (Table 3, entry 7). Overall order of catalytic efficiency for the base-free TH is **7** > **8** > **5** > **6** (Table 3, entries 5−8). On increasing the reaction time and amount of **7** as a catalyst beyond the optimized value, conversion to the reduced product was not improved (Table 3, entries 9). TH attempted with 0.5 mol % $[Cp^*RhCl_2]_2$ at 80 °C for 24 h has given only 12% conversion to the desired product (Table 3, entry 11).

The scope of TH catalyzed with **5**−**8** was studied using several aromatic aldehydes/ketones and aliphatic ketones. The optimum reaction conditions were used in each case. The results are summarized in Table 4. The catalytic TH of benzaldehyde using any one of complexes **5**−**8** (0.3 mol %) in the presence of 2-propanol under optimum conditions has resulted in good conversion (Table 4, entry 1). TH of aromatic

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Table 4. Transfer Hydrogenation of Aldehyde/Ketone Using 5−8[a]

			conversion (%)/isolated yield[b]			
no.	substrate	catalyst (mol %)	5	6	7	8
1	benzaldehyde	0.3	81/71	78/70	94/87	91/80
2	4-nitrobenzaldehyde	0.2	85/76	79/71	97/85	92/82
3	4-bromobenzaldehyde	0.2	84/72	78/69	94/83	88/79
4	4-chlorobenzaldehyde	0.2	82/70	74/65	92/81	84/75
5	4-anisaldehyde	0.3	79/70	72/63	90/80	81/72
6	4-methylbenzaldehyde	0.3	76/69	70/61	89/78	78/67
7	2-pyridinecarboxaldehyde	0.3	72/66	74/63	88/75	80/71
8	acetophenone	0.5	79/68	76/67	88/79	83/70
9	4-methylacetophenone	0.5	75/64	72/64	83/74	78/67
10	4-chloroacetophenone	0.5	80/72	78/69	94/85	88/79
11	propiophenone	0.5	79/70	76/66	88/79	81/70
12	cyclopentanone	0.5	74/65	73/61	84/75	78/66
13	octan-2-one	0.5	68/60	63/55	74/65	69/58

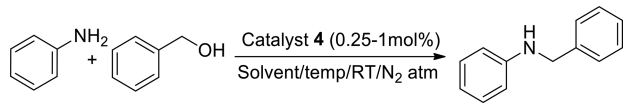
[a]Reaction conditions: aldehyde/ketone, 1 mmol; 2-propanol, 5 mL; bath temperature, 80 °C. [b]Monitored with ^{1}H NMR/isolated yield.

aldehydes having electron-rich (entries 5−6) as well as electron-poor (entries 2−4) substituents has been catalyzed with **5**−**8**. The reactivity varied with the substituent on benzene ring of carbonyl compound. The presence of electron-withdrawing groups like NO_2 on benzaldehyde has resulted in high conversion in a short time, even with 0.2 mol % loading of any one of complexes **5**−**8** as a catalyst. In the presence of electron-donating groups such as OCH_3 and CH_3 on benzaldehyde, 0.3 mol % loading of a complex from **5**−**8** as a catalyst was essential for comparable conversion. Complexes **5**−**8** as catalysts were somewhat less efficient for ketones compared to aldehydes. Both aromatic (Table 4, entry 8−10) and aliphatic (Table 4, entry 11−13) ketones were reduced to corresponding alcohols in good yield by using 0.5 mol % loading of any complex from **5**−**8** as a catalyst. In the presence of electron-rich substituent on an aromatic ketone (Table 4, entry 9), conversion to the reduced product was up to 83% after 2 h when loading of any one of complexes **5**−**8** as a catalyst was 0.5 mol %. For TH of aliphatic ketones complexes **5**−**8** were also efficient as catalysts as the yield given was good (Table 4, entries 11−13). The earlier reported η^5-Cp*Rh(III) guanidianto complexes are less efficient than the present ones as their reported loading for catalysis is high even for reaction time of 4 h.[23] The comparison of the performance of complexes **5**−**8** as catalysts for TH with their iridium analogues has revealed that the time taken is reasonably low with **5**−**8**. **5** and **6** were less efficient as catalysts than were **7** and **8**. The mercury and PPh_3 poisoning tests[45] made on TH catalyzed with **7** were negative as expected for homogeneous catalysis.

The time profiles of TH catalyzed under optimum conditions with complexes **5** and **7**, shown in Figure S36, have revealed that there is an induction period of 0.5 h. The conversion was increased almost linearly up to 2 h and reached maximum in the same time for both **5** and **7**. The induction period of ∼0.5 h has indicated that the **5** or **7** is not catalyzing TH directly and that formation of real catalytic species takes some time. This is consistent with the proposed catalytic species of $[Cp^*RhL]^{2+}$ and $Rh(L\text{-}H)]^{2+}$ for complexes **5** and **7**, respectively.

Base-Free Catalytic N-Alkylation of Aniline with Benzyl Alcohol. *N*-Alkylation of aniline with benzyl alcohol (Scheme 3) was base-free when complexes **3**−**8** were employed as catalysts.

Scheme 3. *N*-Alkylation of Aniline with Benzyl Alcohol



This *N*-alkylation is environmentally friendly as water is the byproduct. Optimization studies have shown that toluene (0.3 mL) is the best solvent for 1 mmol of the substrate under N_2 in the presence of any one of the complexes **3**−**8** (optimum loading: 0.5 mol %). Other optimum conditions are temperature of 100 °C and times of 6 h for **3**−**4** and 4 h for **5**−**8**. The overall results of optimization are summarized in Table 5.

The influence of different solvents on the formation of *N*-benzylaniline is given in Table 5 (entries 2−7). The catalytic efficiency of complex **3** was lower than that of **4**. Only 10% product was formed by using complex **7** as a catalyst under solvent-free condition (Table 5, entry 1). No product was obtained by using complex **4** as a catalyst under a similar condition (Table 5, entry 1). On using 0.25 mol % complex **4** or **7** as a catalyst, the conversion was poor (Table 5, entry 8). No significant difference in conversion was observed when catalytic reaction was carried out by using 1 mol % of complex **4** or **7** (Table 5, entry 9). On lowering the temperature to 50 °C (Table 5, entry 10) the conversion was reduced to 24 and 10% when the reaction was catalyzed with complexes **4** and **7**, respectively. At room temperature no conversion was detected (Table 5, entry 11). In the absence of catalyst (**4** or **7**), *N*-alkylation of aniline with benzyl alcohol was not observed (Table 5, entry 12). Under optimum conditions, and in the presence of $[(\eta^5\text{-}Cp^*)RhCl(\mu\text{-}Cl)]_2$ and $[Ru(\eta^6\text{-benzene})Cl_2]$, conversion was 12 and 6%, respectively, even on using 1 mol % loading catalyst and carrying out the reaction for 48 h (Table 5, entry 13).

The scope of *N*-alkylation of aniline and its derivatives with aromatic benzyl alcohols was explored (Table 6). The alcohols with electron-donating and -withdrawing substituents at para position reacted with anilines forming *N*-alkylated aniline derivatives in high yield (Table 6, entries 1−5). The presence of electron-donating (OCH_3 and CH_3) or electron-withdrawing groups (Br and Cl) marginally affects the reaction rate. However, the presence of former has given somewhat better yield. Complex **4** with a selenated ligand was more efficient than **3**, an analogue of sulfated ligand **L1**, as observed

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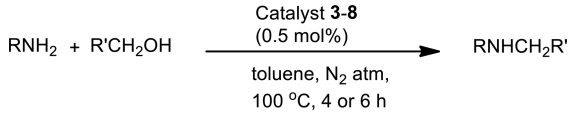
Table 5. Optimization of Reaction Conditions for Base-Free *N*-Alkylation of Aniline with Benzyl Alcohol Catalyzed by 4 and 7[a]

					yield (%)/TOF (h^{-1})[b]	
no.	solvent	catalyst	mol % Rh/Ru	*T*/°C	Rh	Ru
1	none	**7**/**4**	0.5/0.5	100	10 (5)	nd
2	THF	**7**/**4**	0.5/0.5	100	12 (6)	8 (2.6)
3	1,4-dioxane	**7**/**4**	0.5/0.5	100	23 (11.5)	20 (6.6)
4	fluorobenzene	**7**/**4**	0.5/0.5	100	22 (11)	15 (5)
5	toluene	**7**/**4**	0.5/0.5	100	98 (49)	96 (32)
6	1,2-dichlorobenzene	**7**/**4**	0.5/0.5	100	50 (25)	38 (12.6)
7	dimethoxyethane	**7**/**4**	0.5/0.5	100	21 (10.5)	15 (5)
8	toluene	**7**/**4**	0.25/0.25	100	30 (30)	22 (14.6)
9	toluene	**7**/**4**	1/1	100	96 (24)	94 (15.6)
10	toluene	**7**/**4**	0.5/0.5	50	24 (12)	10 (3.3)
11	toluene	**7**/**4**	0.5/0.5	RT	nd	nd
12	toluene	none	none	100	nd	nd
13[c]	toluene	$[Cp^*RhCl_2]_2/[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$	1	100	12 (0.25)	6 (0.12)

[a]Reaction conditions: $PhNH_2$ (1 mmol); $PhCH_2OH$ (1 mmol); toluene (0.3 mL); time, 4 h for **7** and 6 h for **4**; N_2 atmosphere. [b]Monitored with ^1H NMR. [c]Time, 48 h; nd: not detected.

Table 6. *N*-Alkylation of Aromatic Benzyl Alcohol and Aniline Catalyzed with 3−8[a]



			conversion (%)/isolated yield[b]					
entry no.	substrate (1)	substrate (2)	**3**	**4**	**5**	**6**	**7**	**8**
1	benzyl alcohol	aniline	93/83	96/89	88/77	83/74	98/90	92/80
2	4-methoxybenzyl alcohol	aniline	90/82	93/83	90/81	84/71	98/89	94/83
3	4-methylbenzyl alcohol	aniline	91/79	92/80	89/78	80/72	95/82	92/81
4	4-bromobenzyl alcohol	aniline	89/76	90/79	83/74	76/68	92/79	89/77
5	4-chlorobenzyl alcohol	aniline	81/73	87/77	80/71	75/63	89/81	85/73
6	benzyl alcohol	4-methoxyaniline	89/80	92/81	90/79	84/75	94/82	90/79
7	benzyl alcohol	4-methylaniline	87/76	89/80	88/76	82/71	93/79	91/76
8	benzyl alcohol	4-bromoaniline	80/71	85/73	90/80	86/77	96/84	94/85
9	benzyl alcohol	4-chloroaniline	75/66	79/68	90/73	88/79	97/86	95/84
10	benzyl alcohol	4-fluoroaniline	71/60	76/63	76/67	78/67	89/76	80/71

[a]Reaction conditions: RNH_2 (1 mmol), RCH_2OH (1 mmol), toluene (0.3 mL), Ru catalyst 0.5 mol %; time, 6 h for **3**−**4**; catalyst, Rh catalyst, 0.5 mol %; time, 4 h for **5**−**8**; nitrogen atmosphere. [b]Monitored with ^1H NMR/isolated yield.

earlier.[43b−d] The optimum loading of complexes **3** and **4** for catalysis of base-free *N*-alkylation is lower than the values reported for Ru-NHC complexes[40b] and pyridine-based Ru complexes.[40c] Grigg et al. have reported *N*-methylation of pyrrolidine with methanol catalyzed with *in situ* generated 1 mol % of complex $[RhH(PPh_3)_4]$.[41] Overall order of catalytic efficiency of the present complexes for base-free *N*-alkylation is **7** > **8** > **4** > **3** > **5** > **6**. The efficiency of complexes **5**−**8** as catalysts for N-alkylation is comparable to those of Ir complexes of anthracene based chalcogen ligands,[13b] but for complexes **3** and **4** it is quite lower than those of their Ir analogs.[13b]

The time profile of *N*-alkylation of aniline with benzyl alcohol with ruthenium complexes under optimum conditions shown in Figure S37 has revealed that slow initial conversion accelerates after 1 h. In 6 h, yield reaches maximum, and there is an induction period of ∼1 h. The time profile of *N*-alkylation catalyzed by Rh complexes under optimum conditions (Figure S38) shows induction period of 1 h. These results suggest that neither Ru nor Rh complexes are as such catalytic species.

The time profiles of *N*-alkylation of aniline with benzyl alcohol catalyzed with **5** and **7** under optimum conditions shown in Figure S38 indicate that the conversion is initially slow but accelerates after 1 h. The yield has reached maximum in 4 h with the induction period of ∼1 h. This is consistent with the generation of a real catalytic species different from **5** or **7** as proposed. The *N*-alkylation of aniline with benzyl alcohol was catalyzed separately with **4** and **7** (0.5 mol %) in the presence of Hg ([Ru/Rh]/Hg; 1:500)[13e] or 5.0 mol % of PPh_3 under optimum conditions. The inhibition of conversion was not noticed. Thus, the present catalysis of *N*-alkylation appears to be homogeneous.

Tentative Mechanisms. *Transfer Hydrogenation Catalyzed by 1 and 2.* The tentative mechanistic pathway for catalytic TH with **1** and **2** is shown in Scheme 4. **1** and **2** are precatalysts and are first converted to the isopropanolate, a key species of catalytic cycle (Scheme 4) with help of base KOH, essential for catalysis.

Thereafter β-elimination of acetone affords the hydride species. The emergence of acetone signal in the ^1H NMR spectrum of the reaction mixture supports this step. However,

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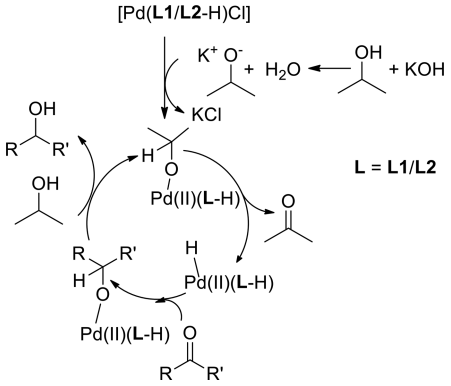
Scheme 4. Tentative Mechanism for TH with Catalyzed with 1

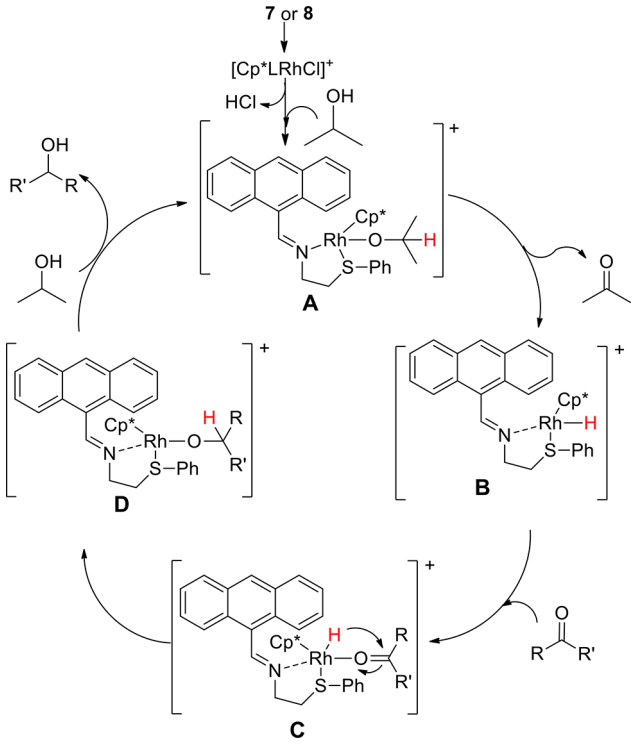


this hydride intermediate species could not be isolated. 1,2-Insertion of the aldehyde/ketone,[46] followed by transfer of alcoholic proton of isopropyl alcohol to alkoxy group attached to Pd, affords C−OH bond, resulting alcohol as a product. The TH reaction catalyzed with **1** was monitored with ^{1}H NMR spectroscopy during its progress. A new signal at $\delta \approx -7.36$ ppm (Figure S39) observed in the spectrum supports the formation of a metal−hydride species[47] proposed in the mechanism.

Transfer Hydrogenation Catalyzed by Complexes 5−8. A tentative mechanism (Scheme 5; complex **7** is used as representative catalyst) in which the partial decoordination of azomethine nitrogen/cleavage of M-N bond, HCl loss and isopropanolate[48] formation is proposed as a first step for TH catalyzed with complexes **7** and **8** in the absence of base.

The decoordination, probably an effect of bulky anthracenyl group, in part facilitates the interaction of a 2-propanol

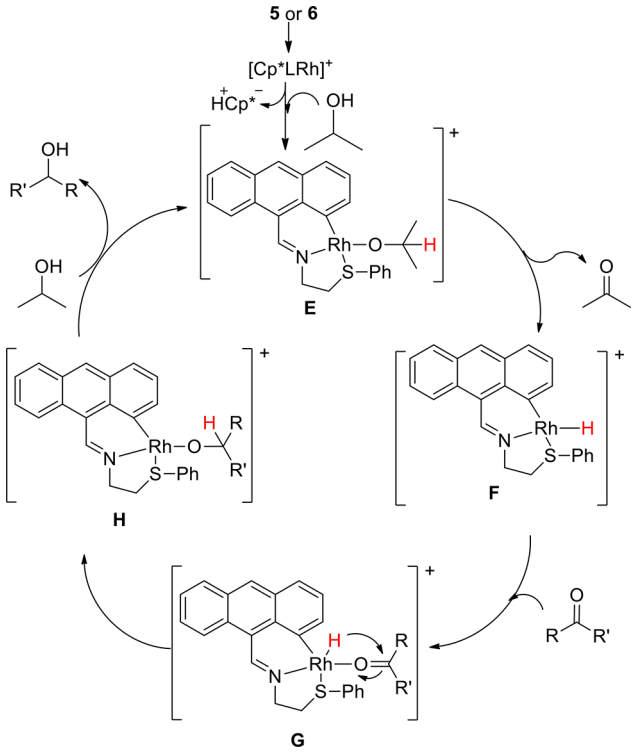
Scheme 5. Tentative Mechanism for Base-Free TH Catalyzed with 7



molecule with the Rh center resulting in intermediate **A** (Scheme 5), and proton transfer from the alcohol to the Rh center results in intermediate **B** (Scheme 5). The partially decoordinated nitrogen of ligand probably acts as an internal base. The β-hydride elimination gives a hydride complex with concomitant acetone loss (Scheme 5). The coordination of carbonyl group to intermediate **B** (metal hydride species) results in intermediate **C**. The proton transfer from metal to carbonyl group in **C** gives intermediate **D** which reacts with 2-propanol to give alcohol as a product and regenerate the real catalytically active alkoxo moiety. The formation of a metal hydride complex as a key intermediate (Scheme 5), is supported by a new signal grown with time at δ −10.23 ppm in ^{1}H NMR spectrum of the reaction mixture having **7** as a catalyst (Figure S40). Intermediate **B** (Scheme 5) is supported by ESI-MS (Figure S41) of complex **7** catalyzed TH reaction mixture. The spectrum of the mixture recorded after 30 min progress of the reaction has peak at m/z 580.1686 which may be ascribed to **B** $[C_{33}H_{35}RhNS]^+$.

The tentative mechanism of catalytic TH with complexes **5** and **6** is shown in Scheme 6, using **5** as a representative catalyst. It is expected to be different from that of **7**/**8**.

Scheme 6. Tentative Mechanism for Base-Free TH Catalyzed with 5



In the first step, the addition of alcohol to catalyst complex **5** proceeds with the loss of [Cp*] resulting in intermediate **E**. The [Cp*] is cleaved without change in oxidation state as reported earlier,[49] even for TH catalyzed with Cp*Rh based complex.[13f] The liberated [Cp*] probably acts as an in situ generated base and promotes the base-free TH.[49,50] Thereafter, **F** is formed by β-hydrogen elimination from alkoxo moiety **E**, with the loss of acetone molecule. Further steps in TH catalyzed with complex **5**/**6** are similar to those of **7**/**8**. The ESI-MS of reaction mixture of TH catalyzed with complex **5**

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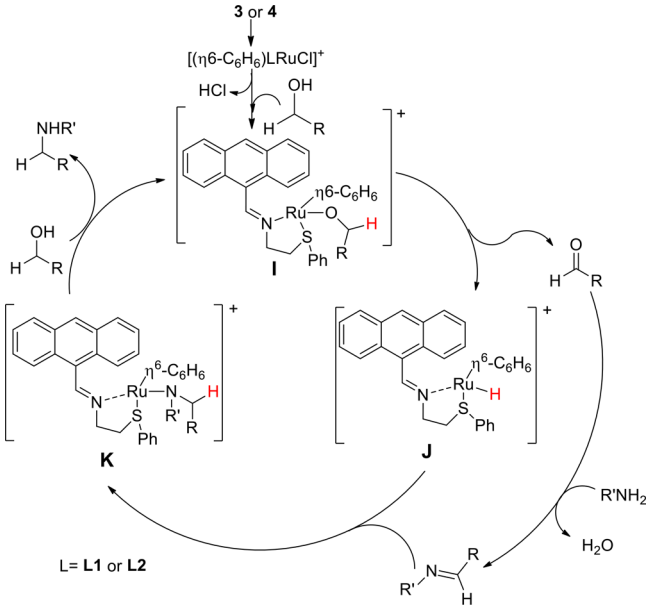
Organometallics XXXX, XXX, XXX−XXX

was recorded (Figure S42). There is peak at m/z = 137.0421 which may be ascribed to $[(Cp^*H) + H]^+$, formed by cleaved $[Cp^*]^-$. The appearance in the ESI-MS of the reaction mixture (Figure S42) recorded after 1 h a peak at m/z 502.3760 appears to be due to $[\mathbf{E}]^+ = [C_{26}H_{25}RhNOS]^+$.

The singlet at 1.40 and 1.46 ppm (due to Cp*Rh) observed in ^{1}H NMR spectra (see Figure S43) of catalytic reaction mixtures having complex **5** and **6**, respectively, disappeared completely after 1 h, supporting the proposed Cp* free species as a real catalyst. However, signals due to ligand of complex **5** were intact in ^{1}H NMR spectrum of reaction mixture recorded after 1 h (see Figure S45).

*N-Alkylation of Aniline with Benzyl Alcohol Catalyzed by **3**–**8**.* The tentative mechanism of base-free *N*-alkylation catalyzed with complexes **3** and **4** is depicted in Scheme 7

Scheme 7. Tentative Mechanism for Base-Free *N*-Alkylation Catalyzed with 4

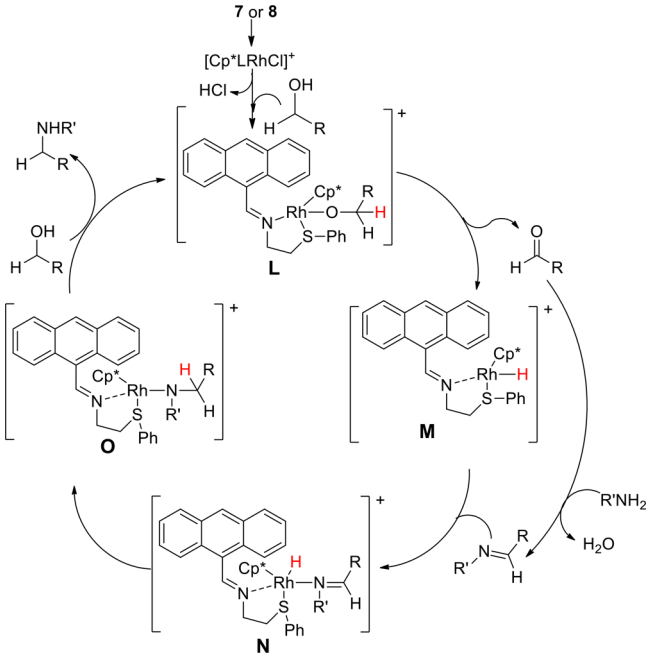


using **3** as a representative species. The bulky anthracenyl group partly decoordinates nitrogen of azomethine or cleaves M–N bond, which facilitates release of HCl, resulting in the formation of **I**. A β-elimination from the isopropoxide group and the elimination of acetone from **I** generate hydride **J**, which gives **K** by its addition to C=N bond. Thereafter, **K** reacts with alcohol to give *N*-alkylated product and regenerates catalytically active alkoxo moiety **I**.

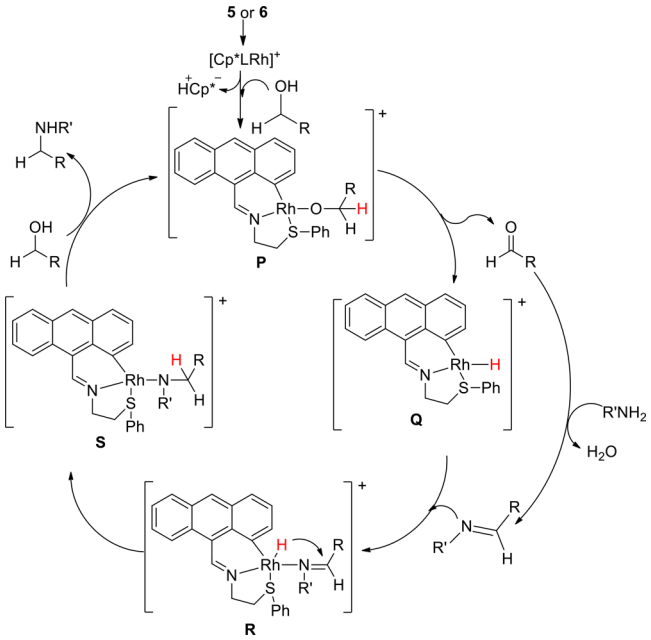
The ^{1}H NMR spectrum of reaction mixture (Catalyst: complex **4**) exhibits a new signal at δ −15.31 ppm (Figure S44), which indicates the formation of ruthenium hydride species **J** as an intermediate. On monitoring after 1 h, the reaction mixture of 4-methoxybenzyl alcohol, aniline and **4** with ESI-MS (Figure S45), a peak at m/z = 742.1030 assignable to $[\{\mathbf{I}\} + (2H_2O)]^+ = [\{C_{37}H_{34}NO_2RuSe\} + (2H_2O)]^+$ was noticed, supporting the mechanism of Scheme 7.

The tentative mechanistic pathways of base-free *N*-alkylation catalyzed with complexes **5**–**8** are shown in Schemes 8 and 9. For complexes **7** and **8**, the pathway is similar to that of complex **3**/**4**. The ^{1}H NMR spectrum (Figure S46) of reaction mixture (Catalyst: complex **7**) recorded with the progress of

Scheme 8. Tentative Mechanism for Base-Free *N*-Alkylation Catalyzed with 7



Scheme 9. Tentative Mechanism for Base-Free *N*-alkylation with Catalyzed with 5



reaction shows new signal at δ −9.33 ppm due to formation of rhodium-hydrido species (**M**).

On monitoring reaction mixture of aniline, 4-methoxybenzylalcohol and complex **7** with ESI-MS a peak (Figure S47) corresponding to $[\mathbf{M}]^+ = [(\eta^5\text{-Cp}^*)Rh(C_{23}H_{20}SN)]^+$ (m/z 508.1424) was noticed after 1 h, supporting the mechanism of Scheme 8. The mechanism of catalytic base-free *N*-alkylation with complexes **5** and **6** is expected to be different from that of complex **7** or **8** (Scheme 9). With the loss of $[Cp^*]$ complex **5**/**6**, is converted into rhodium-alkoxo moiety (intermediate **P**). The $[Cp^*]$ acts as an base generated in situ and promotes *N*-alkylation free from external base.[49,50] It may take proton

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Organometallics XXXX, XXX, XXX–XXX

from alcohol resulting alkoxide, another base. Thereafter, **Q** is formed by β-hydrogen elimination from alkoxo moiety **P**. Condensation of amine with aldehyde (or ketone) results imine. The addition of Rh−H to C═N bond results in **S**[51,36h] which reacts with alcohol to give *N*-alkylated product and regenerates catalytically active alkoxo moiety **P**.[51,38a]

On monitoring reaction mixture of aniline, 4-methoxybenzylalcohol and complex, **5** when reaction progressed for 2 h with ESI-MS, intermediate species **P** [$C_{31}H_{27}RhNO_2S$] and **Q** [$C_{23}H_{19}RhNS$], were identified by the appearance of peaks at m/z 603.3896 [{**P** + (Na)}$^+$] and 445.0936 [{**Q** + (H)}$^+$] (Figure S48) respectively. The peak at m/z = 137.0421 observed in ESI-MS of the reaction mixture of catalytic *N*-alkylation with complex **5**, is assignable to [{(Cp*) H$^+$} + H$^+$]. The singlet at 1.40 ppm (due to Cp*Rh) observed in ^{1}H NMR spectrum of catalytic reaction mixture of *N*-alkylation with **5**, disappeared after 1 h (see Figure S49), supporting the Cp* free species as a real catalyst. However, signals due to ligand in ^{1}H NMR of the *N*-alkylation reaction mixture were observed intact after 1h

CONCLUSION

The palladacycle [Pd(**L1/L2**−**H**)Cl] (**1/2**), ruthenium complexes [(η^6-C_6H_6)Ru(**L1/L2**)Cl][PF_6] (**3/4**), rhodacycles [(η^5-Cp*)Rh(**L1/L2**−H)(PF_6)] (**5/6**), and half-sandwich complexes [(η^5-Cp*)Rh(**L1/L2**)(Cl)(PF_6)] (**7/8**) of bulky ligands **L1/L2** having anthracenyl group were synthesized, characterized with multinuclei NMR, HR-MS, and single-crystal X-ray diffraction, and explored for their catalytic applications (TH and *N*-alkylation). Complexes **3**−**8** are only precatalysts as supported by time profiles of catalytic reactions. In catalysis with rhodadacycles the real catalytic species probably result by the loss of [Cp*]$^-$. The TH catalyzed by rhodium complexes **5**−**8** and *N*-alkylation of anilines with benzyl alcohols catalyzed by complexes **3**−**8** do not require base. The optimum loading of complexes **5**−**8** required to catalyze base-free transfer hydrogenation of various aldehydes/ketones with 2-propanol (H source) under ambient conditions is 0.2−0.5 mol %. The yield in base-free *N*-alkylation of anilines with aromatic benzyl alcohols in the inert atmosphere catalyzed with 0.5 mol % complexes **5**−**8** is good. Complex **7** shows maximum catalytic activity for both the reactions. The poisoning experiments for transfer hydrogenation and *N*-alkylation of anilines with benzyl alcohols show that the two catalytic processes are predominantly homogeneous. The alkoxide and M−H bond formation is proposed in the tentative mechanism of the two catalytic reactions on the basis of ^{1}H NMR spectra and ESI-MS of the reaction mixture recorded when reaction progressed for 1−2 h.

EXPERIMENTAL SECTION

Physical Measurement. A Bruker Spectrospin DPX-300 NMR spectrometer was used to record ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectra at 300.13, 75.47, and 57.24 MHz, respectively. The chemical shifts are reported in ppm relative to internal standards. The C, H, and N analyses were carried out with a PerkinElmer 2400 Series II C, H, and N analyzer. Single-crystal diffraction data of **1**, **2**, **3**, and **4** were collected on Bruker AXS SMART Apex CCD diffractometer at 298(2) K using Mo Kα radiations (λ = 0.71073 Å) radiations. Frames were collected by ω, φ, and 2θ-rotations with full-quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. All data were processed using the programs SAINT routine in APEX3. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-2014/7 program.[52] Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. High-resolution mass spectral measurements were performed with a Bruker Micro TOF-Q II instrument based on electron spray ionization (10 eV, 180 °C source temperature, sodium formate as a reference), taking sample in CH_3CN. Fourier transform-infrared spectra in KBr pellets were recorded on a Nicolet, Protege 460 FT-IR spectrometer. Commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4 and KOH pellets. Nitrogen atmosphere was created with Schlenk techniques. Yield refers to isolated yield of the compound which has purity of ≥95% [established by ^{1}H NMR]. All reactions were carried out in glassware dried in an oven, under ambient conditions.

Chemical and Reagents. Diphenyldiselenide, sodium borohydride, sodium tetrachloropalladate, and NH_4PF_6 procured from Sigma-Aldrich (USA) were used as received. Thiophenol, 9-antharacenecarboxaldehyde aldehydes, ketones, and alcohols were procured locally. The reported methods were used to synthesize [{(η^6-C_6H_6)RuCl(μ-Cl)}$_2$],[53] [{(η^5-Cp*)RhCl(μ-Cl)}$_2$][54] and **L1/L2**.[13b] All the solvents were dried and distilled by standard procedures before use.[55] Other chemicals and reagents used were available commercially within the country.

Syntheses of Complexes [Pd(L−H)Cl] (1/2; L = L1/L2). $Na_2[PdCl_4]$ (0.147 g, 0.5 mmol) was dissolved in 2 mL of water, and the solution of ligand **L1** (0.170 g, 0.5 mmol)/**L2**(0.170 g, 0.5 mmol) made in 5 mL of acetone was added to it with vigorous stirring. The mixture was further stirred for 2 h. The orange red solution was extracted with chloroform. The chloroform layer was washed with water, dried with anhydrous Na_2SO_4, and evaporated to dryness under vacuum to obtain **1** and **2** as an yellow/orange red colored powder. The single crystal of complex **1** and **2** was grown from $CHCl_3$ mixtures over a week.

1. Yield: (0.207 g, 86%; mp 156 °C). Anal. Found: C, 57.21; H, 3.74; N, 2.83%. Calcd for $C_{23}H_{18}ClNPdS$: C, 57.27; H, 3.76; N, 2.90%. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) = 3.32 (bs, 2 H, SCH_2 mixed with dmso solvent), 4.43 (s, 2 H, NCH_2), 7.39−7.41 (t, 1H, Ar−H), 7.47−7.56 (m, 3H, Ar−H), 7.60−7.62 (m, 1H, Ar−H), 7.65−7.77 (d, 1H, Ar−H), 8.17−8.23 (t, 3H, Ar−H) 8.30 (s, 1H, $CHCl_3$), 8.48−8.50 (d, 1H, Ar−H), 8.77−8.81 (d, 1H, Ar−H), 8.97 (s, 1 H, Ar−H), 9.75(s, 1H, C*H*═N). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 35.8 (SCH_2), 66.7 (NCH_2), 79.6 ($CHCl_3$ in DMSO-d_6) 123.6, 125.3, 125.5, 125.8, 127.0, 127.4, 128.9, 129.4, 129.8, 130.0, 130.5, 131.2, 132.2, 134.0, 137.2, 139.7, (Ar−C), 144.4 (C10, Ar−C), 157.9 (N═CH). HR-MS (CH_3CN) [$C_{23}H_{18}NPdS$]$^+$ (m/z) = 446.0192; calcd value for [$C_{23}H_{18}NPdS$]$^+$ = 446.0197 (ppm error δ: −1.3). IR (KBr, cm^{-1}): 2968 [m; $\nu_{C-H\ (aliphatic)}$)] 3058 (m; $\nu_{C-Haromatic}$), 1670 (m; $\nu_{C=Naromatic}$), 1423 (m; $\nu_{C=Caromatic}$), 755 (m; $\nu_{C-Haromatic}$). Single crystals of **1** having one molecule of chloroform were used to record NMR.

2. Yield: (0.232 g, 88%; mp 162 °C). Anal. Found: C, 52.17; H, 3.40; N, 2.63%. Calcd for $C_{23}H_{18}ClNPdSe$: C, 52.20; H, 3.43; N, 2.65%. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) = 3.27 (s, 2 H, SeCH_2), 3.43 (s, 1 H, NCH_2 mixed with dmso solvent), 4.59 (bs, 1H, NCH_2), 7.35−7.40 (t, 1H, Ar−H), 7.44−7.53 (m, 3H, Ar−H), 7.58−7.63 (m, 1H, Ar−H), 7.72−7.77 (m, 1H, Ar−H), 7.93−7.96 (d, 1H, Ar−H), 8.18−8.21 (m, 3H, Ar−H) 8.31 (s, 1H, $CHCl_3$;), 8.39−8.41 (d, 1H, Ar−H), 8.73−8.83 (d, 1H, Ar−H), 8.93 (s, 1H, Ar−H), 9.66 (s, 1H, C*H*═N). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 25 °C, TMS) δ (ppm) = 29.0 (SeCH_2), 68.1 (NCH_2), 79.6 ($CHCl_3$ in DMSO-*d6*) 123.7, 125.3, 125.8, 127.2, 127.3, 128.9, 129.5, 129.8, 130.2, 130.5, 131.1, 133.5, 133.9, 137.0, 139.3, (Ar−C), 144.8 (C10, Ar−C), 158.4 (N═CH). ^{77}Se{^{1}H}NMR (57 MHz, DMSO-d_6, 25 °C, Me_2Se) δ (ppm): 321.40. HR-MS (CH_3CN) [$C_{23}H_{18}NPdSe$]$^+$ (m/z) = 493.9615; calcd value for [$C_{23}H_{18}NPdSe$]$^+$ = 493.9647 (ppm error δ: 3.6). IR (KBr, cm^{-1}): 2951 [m; $\nu_{C-H\ (aliphatic)}$)] 3045 (m; $\nu_{C-Haromatic}$), 1635 (m; $\nu_{C=Naromatic}$), 1475

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Organometallics XXXX, XXX, XXX−XXX

(m; $\nu_{C=Caromatic}$), 748 (m; $\nu_{C-Haromatic}$). Single crystals of **2** having one molecule of chloroform were used to record NMR.

Syntheses of Complex [(η^6-C_6H_6)Ru(L)Cl][PF_6] (3/4; L = L1/L2). To a solution of **L1** (0.091 g, 0.2 mmol)/**L2** (0.082 g, 0.2 mmol) made in CH_3OH (5 mL) was added a solution of [{(η^6-C_6H_6)RuCl(μ-Cl)}$_2$] (0.050 g, 0.1 mmol) in CH_3OH (5 mL). The mixture was stirred for 8 h at room temperature. The resulting orange solution was filtered, and the volume of the filtrate was reduced (~7 mL) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the orange microcrystalline solid resulting instantaneously was filtered, washed with 5 mL of ice-cold CH_3OH, and dried in vacuo. Single crystals of each of the two complexes (**3**/**4**) were obtained from a mixture (1/4) of diethyl ether and CH_3CN.

3. Yield: (0.126 g, 90%; mp 220 °C). Anal. Found: C, 46.66; H, 3.57; N, 1.96%. Calcd for $C_{29}H_{25}ClF_6NPRuS$: C, 46.68; H, 3.59; N, 2.00%. ^{1}H NMR (300 MHz, CD_3CN, 25 °C) δ (ppm) = 2.44−2.57 (m, 1H, SCH_2), 2.92−2.99 (m, 1H, SCH_2), 3.78−3.89 (m, 2H, NCH_2), 5.89 (s, 6 H, η^6-C_6H_6), 7.46−7.48 (m, 1H, Ar−H), 7.62−7.73 (m, 5H, Ar−H), 7.83−7.98 (m, 3H, Ar−H), 8.04−8.07 (d, 1H, Ar−H), 8.19−8.26 (m, 3H, Ar−H), 8.82 (s, 1H, Ar−H), 10.25 (s, 1H, CH=N). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN, 25 °C, TMS) δ (ppm) = 37.4 (SCH_2), 60.4 (NCH_2), 87.7 (η^6-C_6H_6) 123.7, 124.5, 126.1, 126.3, 127.9, 128.5, 129.1, 129.4, 130.2, 130.3, 130.9, 131.2 (Ar−C), 180.2 (N=CH). HR-MS (CH_3CN) [$C_{29}H_{25}ClNRuS$]$^+$ (m/z) = 556.0452; calulated value for [$C_{29}H_{25}ClNRuS$]$^+$ = 556.0438 (δ: −2.5 ppm). IR (KBr, cm^{-1}): 2958 [m; $\nu_{C-H\ (aliphatic)}$] 3064 (m; $\nu_{C-Haromatic}$), 1646 (m; $\nu_{C=Naromatic}$), 1433 (m; $\nu_{C=Caromatic}$), 764 (m; $\nu_{C-Haromatic}$).

4. Yield: (0.224 g, 88% ; mp 200 °C). Anal. Found: C, 46.56; H, 3.34; N, 1.85%. Calcd for $C_{29}H_{25}ClF_6NPRuSe$: C, 46.57; H, 3.37; N, 1.87%. ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ (ppm) = 2.29−2.40 (m, 1 H, SeCH_2), 2.88−2.94 (m, 1H, SeCH_2), 3.71−3.77 (m, 1H, NCH_2), 4.22−4.27 (m, 1H, NCH_2), 5.93 (s, 6H, η^6-C_6H_6), 7.60−7.67 (m, 5H, Ar−H), 7.70−7.72 (m, 1H, Ar−H), 7.82−7.85 (m, 3H, Ar−H), 8.02−8.05 (d, 1H, Ar−H), 8.19−8.25 (m, 3H, Ar−H), 8.81 (s, 1 H), 10.24 (s, 1H, CH=N). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN, 25 °C, TMS) δ (ppm) = 29.8 (SCH_2), 61.1 (NCH_2), 86.6 (η^6-C_6H_6) 123.3, 124.1, 125.8, 125.9, 127.0, 127.6, 128.1, 128.8, 129.0, 130.1, 130.4, 130.7 (Ar−C), 180.2 (N=CH). ^{77}Se {^{1}H} NMR (57 MHz, CD_3CN, 25 °C, Me_2Se) δ (ppm) = 424.15. HR-MS (CH_3CN) [$C_{29}H_{25}ClNRuSe$]$^+$ (m/z) = 603.9836; calulated value for [$C_{29}H_{25}ClNRuSe$]$^+$ = 603.9886 (δ: −8.4 ppm). IR (KBr, cm^{-1}): 2919 [m; $\nu_{C-H\ (aliphatic)}$] 3048 (m; $\nu_{C-Haromatic}$), 1648 (m; $\nu_{C=Naromatic}$), 1421 (m; $\nu_{C=Caromatic}$), 766 (m; $\nu_{C-Haromatic}$).

Syntheses of Rh{(η^5-Cp*}(L-H)]PF_6 (5/6; L = L1/L2). To a solution of **L1** (0.068 g, 0.2 mmol)/**L2** (0.077 g, 0.2 mmol) and CH_3COONa (0.016 g, 0.2 mmol) made in CH_3OH (5 mL) was added a solution of [(η^5-Cp*RhCl(μ-Cl)]$_2$ (0.080 g, 0.1 mmol) prepared in CH_3OH (5 mL). The mixture was stirred for 8 h at 50 °C. The resulting yellow solution was filtered, and the filtrate reduced in volume (~5 mL) with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the resulting yellow microcrystalline solid was filtered, washed with 5 mL of ice-cold CH_3OH, and dried in vacuo. For single crystals of **5**/**6**, their concentrated solutions made in an acetonitrile−diethyl ether mixture (1:4 v/v) were evaporated slowly.

5. Yield: 0.130 g, 90%. Anal. Calcd for $C_{33}H_{33}F_6RhNPS$: C, 54.78; H, 4.60; N, 1.94. Found: C, 54.76; H, 4.58; N, 1.92. Mp: 180.0 °C. ^{1}H NMR (CD_3CN, 25 °C vs TMS) δ (ppm) 1.40 {(s, 15H, Me(Cp)}, 2.77−2.85 (m, 1H, CH_2−S), 373−3.79 (m, 1H, CH_2−S), 4.03−4.05 (m, 1H, CH_2−N), 4.63−4.69 (m, 1H, CH_2−N), 6.81 (s, 1H), 6.95−7.00 (m, 1H), 7.12−7.21 (m, 4H), 7.31−7.36 (m, 1H), 7.61−7.65 (m, 2H), 7.67−7.78 (m, 1H), 8.15−8.18 (m, 1H), 8.44−8.45 (m, 1H), 8.78 (s, 1H), 9.39 (s, 1H). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs TMS): 7.9 {C of Me(Cp*)}, 39.7 (C of CH_2−S), 65.3 (C of CH_2−N), 100.3 (C of Cp*) 122.8, 124.1, 125.8, 126.5, 126.7, 128.5, 128.9, 129.0, 129.5, 129.6, 130.5, 130.6, 132.1, 133.1, 136.5, 140.2, 140.2, 164.1 (C of CH=N). HR-MS (CH_3CN) [$C_{33}H_{33}RhNS$]$^+$ (m/z) = 578.1378; calculated value for [$C_{33}H_{33}RhNS$]$^+$ = 578.1383 (δ: −0.5 ppm). IR (KBr, cm^{-1}): 2918 [m; $\nu_{C-H\ (aliphatic)}$] 3065 (m; $\nu_{C-Haromatic}$), 1617 (m; $\nu_{C=Naromatic}$), 1470 (m; $\nu_{C=Caromatic}$).

6. Yield: 0.130 g, 85% Anal. Calcd for $C_{33}H_{33}F_6RhNPSe$: C, 51.44; H, 4.32; N, 1.82. Found: C, 51.43; H, 4.31; N, 1.81. Mp: 190.0 °C. ^{1}H NMR (CD_3CN, 25 °C vs TMS) δ (ppm) 1.46 {(s, 15H, Me(Cp)}, 2.57−2.66 (m, 1H, CH_2−N), 3.88−3.96 (m, 2H, CH_2−Se), 4.89−4.93 (m, 1H, CH_2−N), 6.88−6.90 (m, 2H), 6.98−7.00 (m, 4H), 7.23−7.21 (m, 1H), 7.58−7.65 (m, 2H), 7.72−7.77 (m, 1H), 8.14−8.17 (m, 1H), 8.46−8.49 (m, 1H), 8.76 (s, 1H), 9.43 (s, 1H). ^{13}C{^{1}H} NMR (CD_3CN, 25 °C vs TMS): 7.7 {C of Me(Cp*)}, 34.0 (C of CH_2−Se), 66.1 (C of CH_2−N), 99.5 (C of Cp*), 122.7, 123.8, 124.7, 125.0, 125.7, 126.4,128.4, 128.8, 129.3, 129.5, 130.3, 130.5, 131.0, 131.5, 132.0, 133.2, 136.6, 140.8, 164.3 (C of CH=N). ^{77}Se{^{1}H} NMR (CD_3CN, 25 °C, Me_2Se) δ (ppm): 379.8. HR-MS (CH_3CN) [$C_{33}H_{33}RhNSe$]$^+$ (m/z) = 626.0822; calulated value for [$C_{33}H_{33}ClRhNSe$]$^+$ = 626.0830 (δ: −1.2 ppm). IR (KBr, cm^{-1}): 2916 [m; $\nu_{C-H\ (aliphatic)}$] 3042 (m; $\nu_{C-Haromatic}$), 1609 (m; $\nu_{C=Naromatic}$), 1446 (m; $\nu_{C=Caromatic}$).

Syntheses of [Rh{(η^5-Cp*}Cl(L)]PF_6 (7/8; L = L1/L2). The **L1** (0.068 g, 0.2 mmol)/**L2** (0.077 g, 0.2 mmol) and [(η^5-$C_5(CH_3)_5RhCl(\mu\text{-}Cl)]_2$ (0.080 g, 0.1 mmol) were dissolved in CH_3OH (10 mL). The mixture was stirred for 8 h at room temperature. The resulting yellow solution was filtered, and the volume of the filtrate reduced to ~5 mL with a rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol), and the resulting yellow microcrystalline solid was filtered, washed with 5 mL of ice-cold CH_3OH, and dried in vacuo. Single crystals of **7**/**8** were grown by slow evaporation of their concentrated solutions made in an acetonitrile−diethyl ether mixture (1:4 v/v).

7. Yield: 0.129 g, 85% Anal. Calcd for $C_{33}H_{34}ClF_6RhNPS$: C, 52.15; H, 4.51; N, 1.84. Found: C, 52.13; H, 4.50; N, 1.82. Mp: 185.0 °C. ^{1}H NMR (CD_3CN, 25 °C vs TMS) δ (ppm) 1.48 {(s, 15H, Me(Cp)}, 2.72−2.76 (bs, 1H, CH_2), 3.09−3.25 (bs, 1H, CH_2), 3.55. (bs, 1H, CH_2), 3.82−3.86 (bs, 1H, CH_2), 7.52−7.67 (m, 7H), 7.70−7.67 (m, 2H), 7.73−7.78 (m, 1H), 8.17−8.25 (m, 2H), 8.39−8.41 (m, 1H), 8.97 (s, 1H), 9.76 (s, 1H). ^{13}C{^{1}H}NMR (CD_3CN, 25 °C vs TMS): 8.6 {C of Me(Cp*)}, 38.2 (C of CH_2−Se), 56.9 (C of CH_2−N), 99.7 (C of Cp*), 122.5, 123.5, 124.0, 126.0, 126.3, 127.3, 127.8, 128.5, 129.1, 129.6, 130.9, 130.9, 131.1, 177.9 (C of CH=N). HR-MS (CH_3CN) [$C_{33}H_{34}ClRhNS$]$^+$ (m/z)= 614.1179; calulated value for [$C_{33}H_{34}ClRhNS$]$^+$ = 614.1150 (δ: −4.8 ppm). IR (KBr, cm^{-1}): 2850 [m; $\nu_{C-H\ (aliphatic)}$] 3050 (m; $\nu_{C-Haromatic}$), 1606 (m; $\nu_{C=Naromatic}$), 1420 (m; $\nu_{C=Caromatic}$).

8. Yield: 0.145 g, 90%. Anal. Calcd for $C_{33}H_{34}ClF_6RhNPSe$: C, 49.12; H, 4.25; N, 1.74. Found: C, 49.13; H, 4.26; N, 1.75. Mp: 190 °C. ^{1}H NMR (CD_3CN, 25 °C vs TMS) δ (ppm) 1.68 {(s, 15H, Me(Cp)}, 2.58−2.66 (m, 1H, CH_2), 3.37−3.66 (m, 1H, CH_2), 3.93−4.09 (m, 1H, CH_2), 4.31−4.35 (m, 1H, CH_2), 7.48 (s, 1H), 7.59−7.66 (m, 6H), 7.74−7.83 (m, 2H), 7.89−7.92 (m, 1H), 8.21−8.23 (m, 2H), 8.33−8.45 (m, 1H), 8.81 (s, 1H), 9.48 (s, 1H). HR-MS (CH_3CN) [$C_{33}H_{34}ClRhNSe$]$^+$ (m/z) = 662.0610; calulated value for [$C_{33}H_{34}ClRhNSe$]$^+$ = 662.0594 (δ: −2.3 ppm). IR (KBr, cm^{-1}): 2885 [m; $\nu_{C-H\ (aliphatic)}$] 3042 (m; $\nu_{C-Haromatic}$), 1607 (m; $\nu_{C=Naromatic}$), 1416 (m; $\nu_{C=Caromatic}$).

Procedure for Catalysis of Transfer Hydrogenation with 1 and 2. Aldehyde/ketone (1 mmol), KOH (0.2 mmol) and catalyst **1**/**2** (0.05−0.2 mol %) were refluxed in 5 mL of 2-propanol for 2/5/12 h. After cooling the mixture to 25 °C, the 2-propanol was removed with a rotary evaporator, and the formed product was extracted with 50 mL of ethyl acetate. The solvent from the extract was evaporated off, resulting in a residue which was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (20:1) as eluent. The ^{1}H NMR of the purified product were recorded and matched with literature values.

Procedure for Catalysis of Transfer Hydrogenation with 5−8. Aldehyde/ketone (1 mmol) and catalyst **5**−**8** (0.2−0.5 mol %) were refluxed in 5 mL of 2-propanol for 2 h. After cooling the mixture to 25 °C, the 2-propanol was removed with a rotary evaporator. The hydrogenated product was extracted with 50 mL of ethyl acetate. The solvent of the extract was evaporated off, resulting in a residue which

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Organometallics XXXX, XXX, XXX−XXX

was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (20:1) as an eluent. The ^{1}H NMR of the purified product were recorded and matched with literature values.

Procedure for Catalytic of *N*-Alkylation. Complex **3**/**4** (0.5 mol %) or **5**−**8** (0.5 mol %) taken in 0.3 mL of toluene was mixed with the alcohol (1.2 mmol) and aniline (1 mmol). The mixture was refluxed for 6 (**3**/**4**) or 4 h (**5**−**8**). Thereafter solvent was evaporated off using a rotary evaporator. The residue was extracted with 20 mL of ethyl acetate. The organic layer was washed with water (3 × 50 mL) and dried over anhydrous Na_2SO_4. The solvent from the extract was evaporated off, and the residue was purified by column chromatography on silica gel using mixture of hexane and ethyl acetate (10:1) as eluent. The ^{1}H NMR of the purified product were recorded and matched with literature values.

Hg Poisoning Test. In an excess of Hg (Hg: Pd/Ru/Rh: 400:1) taken in a reaction flask. The TH and *N*-alkylation reactions were carried out optimum conditions. After standardized work up, conversion was unaffected.

PPh_3 Poisoning Test. The PPh_3 (5 mol %) was taken in the reaction flask. The TH or *N*-alkylation was carried in this flask out under optimum conditions. After standardized work up conversion remained nearly unchnaged.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00908.

Structural refinement parameters, selected bond lengths and bond angles of complexes **1**−**8**, distances [Å] of inter- and intramolecular interactions, ^{1}H and ^{13}C NMR spectra, mass spectra (PDF)

Accession Codes

CCDC 1865930−1865937 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX