Inorganic Chemistry Communications 37 (2013) 138–143

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Ruthenium(II) supported by phosphine-functionalized *N*-heterocyclic carbene ligands as catalysts for the transfer hydrogenation of ketones

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ARTICLE INFO

Article history:
Received 1 July 2013
Accepted 23 September 2013
Available online 1 October 2013

Keywords:
N-heterocyclic carbene
Transfer hydrogenation
Ruthenium(II) complexes
Ortho-metalation

ABSTRACT

We have prepared and characterized two ruthenium(II) complexes supported by phosphine-functionalized *N*-heterocyclic (NHC) ligands. One of the complexes (**2a**) underwent *ortho*-metalation of the *N*-phenyl moiety giving rise to a tridentate $PC_{NHC}C^-$ coordinating ligand whereas **2b** bears an *N*-mesityl group in order to prevent C–H activation of the aryl ring thereby enforcing a PC_{NHC} bidentate binding mode. Both **2a** and **2b** were shown to catalyze transfer hydrogenation of ketones at 82 °C in 2-propanol in the presence of KO^{t}Bu albeit with vastly different catalytic activities. Catalytic transfer hydrogenation by **2b** was shown to proceed at room temperature and in air using unpurified 2-propanol as solvent and hydrogen donor. Time studies revealed unique kinetic profiles for the two precatalysts; this may shed light on the difference in their catalytic activities.

Arduengo's discovery demonstrating that *N*-heterocyclic carbenes (NHCs) are isolable using common air- and moisture-free techniques [1] led early pioneers like Herrmann [2–5], Enders [6,7], Dixneuf, Çetinkaya [8], Nolan [9], and Grubbs [10,11] to employ NHCs as ligands supporting catalytically competent transition metal centers during the mid to late 1990s. Since this time the number of catalytic applications using metal–NHC complexes has increased rapidly. Due to their strong σ-donating ability, NHCs effectively stabilize numerous transition metal centers [12]. However, several common decomposition pathways exist for metal–NHC complexes; this limits the ability of monodentate NHC ligands to effectively stabilize metal centers at the high temperatures employed in some catalytic applications. Chelating, donor-functionalized NHCs have been developed to circumvent decomposition and have expanded the utility of metal–NHC catalysts for use in higher temperature applications [13].

The transfer hydrogenation of aldehydes, ketones, and imines is an industrially relevant reaction often conducted in refluxing 2-propanol or formic acid using ruthenium-based catalysts [14,15]. Under these conditions the ability of chelating, donor-functionalized NHCs to stabilize metal centers while preventing decomposition is quite valuable. Examples of ruthenium complexes supported by chelating, donor-functionalized NHCs have been reported and their efficacy as transfer hydrogenation catalysts has been explored. Thus far ruthenium complexes supported by chelating NHC ligands bearing nitrogen [16–27], anionic carbon [28,29], oxygen [30,31], phosphorous [32,33], arene [34–36], and alkene [30] donors have been used as transfer hydrogenation catalysts. Compared to other donor-functionalized NHC complexes, phosphine-functionalized NHC ruthenium(II) complexes are underdeveloped. To our knowledge, there have been only two reports of transfer hydrogenation catalyzed by ruthenium complexes of phosphine-functionalized chelating NHCs. Chiu and Lee [32] have reported on the synthesis and catalytic behavior of tridentate $PC_{NHC}P$ complexes of ruthenium(II), and Miranda-Soto and co-workers [33] have reported on a ruthenium(II) cyclopentadienyl complex supported by a phosphine-functionalized NHC bearing an N–H moiety. We set out to explore ruthenium(II) complexes supported by bidentate phosphine-functionalized NHCs bearing *N*-aryl groups and unexpectedly generated a ruthenium(II) complex supported by a tridentate $PC_{NHC}C^-$ ligand as a result of intramolecular C–H activation of the *N*-phenyl group (**2a**, Scheme 1). In order to explore the effects of *ortho*-metalation on catalytic transfer hydrogenation activity, we prepared the *N*-mesityl analogue (**2b**) and evaluated both **2a** and **2b** as catalysts for the transfer hydrogenation of several ketones.

The phosphine-functionalized bisimidazolium salts (**1a,b**) were prepared according to the method reported by Zhou and co-workers [37] with one minor modification; in the coupling reaction between *o*-(diphenylphosphino)benzyl chloride and 1-arylimidazoles, *N,N*-dimethylformamide was used as the solvent and the reaction was heated to 90 °C. In our hands, this modification allowed us to avoid the complicating factors introduced when ethanol was used as

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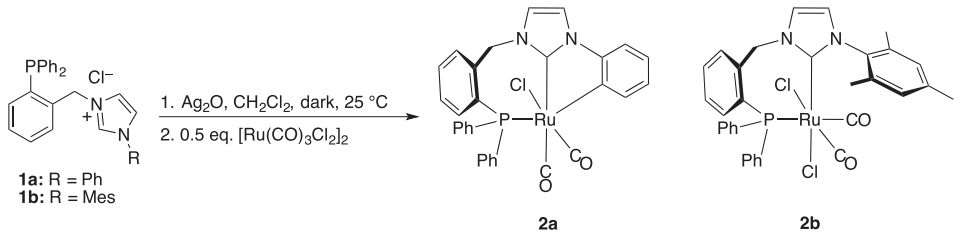
http://dx.doi.org/10.1016/j.inoche.2013.09.046



Scheme 1. Preparation of **2a** and **2b**.

Table 1
Crystal data and structure refinement for **2a**.

Empirical formula	$C_{31}H_{24}Cl_3N_2O_2PRu$
Formula weight	694.91
Temperature [K]	210(2)
Wavelength [Å]	0.71073
Crystal system, space group	Triclinic, P_{-1}
Unit cell dimensions	a = 8.1600(9) Å α = 100.109(5)° b = 12.1940(13) Å β = 93.560(5)° c = 14.9713(16) Å γ = 93.469(5)°
Volume [Å^3]	1459.9(3)
Z, Calculated density [mg/m^3]	2, 1.581
Absorption coefficient [mm^{-1}]	0.899
F(000)	700
Crystal size [mm]	0.17 x 0.08 x 0.03
θ range for data collection [°]	2.77 to 27.84
Limiting indices	$-10 \le h \le 10$, $-16 \le k \le 15$, $-19 \le l \le 19$
Reflections collected/unique	24,026/6906 [R_{int} = 0.0481]
Completeness to θ = 27.84	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9735 and 0.8622
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6906/22/383
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0417, wR_2 = 0.0742
R indices (all data)	R_1 = 0.0773, wR_2 = 0.0863
Largest diff. peak and hole [*e*/Å]	0.656 and −0.644

Table 2
Crystal data and structure refinement for **2b**.

Empirical formula	$C_{34}H_{31}Cl_4N_2O_2PRu$
Formula weight	773.45
Temperature [K]	190(2)
Wavelength [Å]	0.71073
Crystal system, space group	Monoclinic, $C_{2/c}$
Unit cell dimensions	a = 22.539(3) Å α = 90° b = 16.4065(17) Å β = 111.004(5)° c = 19.852(2) Å γ = 90°
Volume [Å^3]	6853.2(13)
Z, Calculated density [mg/m^3]	8, 1.499
Absorption coefficient [mm^{-1}]	0.849
F(000)	3136
Crystal size [mm]	0.21 × 0.20 × 0.19
θ range for data collection [°]	2.97 to 27.50°
Limiting indices	$-29 \le h \le 29$, $-20 \le k \le 21$, $-25 \le l \le 25$
Reflections collected/unique	53,042/7865 [R_{int} = 0.0433]
Completeness to θ = 27.50	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8553 and 0.8418
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7865/0/402
Goodness-of-fit on F^2	1.077
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.0860
R indices (all data)	R_1 = 0.0568, wR_2 = 0.0966
Largest diff. peak and hole [*e*/Å]	0.983 and −0.994

solvent. Specifically, ethanol acts as a competitive nucleophile for *o*-(diphenylphosphino)benzyl chloride thereby leading to an undesired side product and requiring chromatographic purification of the desired imidazolium salt [38]. The ruthenium(II) complexes were prepared via transmetalation from the Ag–NHC complex to $[Ru(CO)_3Cl_2]_2$ dimer (Scheme 1.) The orthometalated *N*-phenyl complex (**2a**) [39] furnished a disappointing 5.4% yield while the *N*-mesityl complex (**2b**) [40] was isolated as a crystalline solid in 49.9% yield. The low yield of **2a** may be due to its higher solubility in the crystallization solvent system since crude yields were higher (ca. 70%).

Single crystals suitable for X-ray diffraction studies of both **2a** and **2b** were grown via vapor diffusion of diethyl ether into a saturated dichloromethane solution of the product isolated after column chromatography. The full details of the X-ray diffraction studies have been reported previously by Domski and co-workers [41,42]. Crystal data, refinement, and data collection details are presented in Tables 1 (**2a**) and 2 (**2b**). Selected bond length and bond angle data are presented in Tables 3 (**2a**) and 4 (**2b**). The unit cell of both compounds includes one dicholoromethane molecule of crystallization. Both compounds adopt distorted octahedral coordination geometry in the solid state (Figs. 1; **2a** and 2; **2b**). For **2a** the bond angles of the *cis*-substituents at ruthenium range from 77.19° to 95.70°. For **2b** the bond angles of the *cis*-substituents at ruthenium

Table 3
Selected bond lengths (Å) and angles (°) for **2a**.

Bond lengths (Å)		Bond angles (°)	
Ru(1)–C(1)	1.858(4)	C(1)-Ru(1)–C(2)	91.18(14)
Ru(1)–C(2)	1.933(4)	C(1)–Ru(1)–C(3)	87.44(13)
Ru(1)–C(3)	2.066(3)	C(1)–Ru(1)–C(11)	89.85(12)
Ru(1)–C(11)	2.129(3)	C(2)–Ru(1)–C(11)	93.56(13)
Ru(1)–P(1)	2.4267(8)	C(3)–Ru(1)–C(11)	77.77(12)
Ru(1)–Cl(1)	2.4735(8)	C(1)–Ru(1)–P(1)	95.28(10)
		C(2)–Ru(1)–P(1)	93.05(10)
		C(3)–Ru(1)–P(1)	95.72(9)
		C(2)–Ru(1)–Cl(1)	92.23(10)
		C(3)–Ru(1)–Cl(1)	88.50(8)
		C(11)–Ru(1)–Cl(1)	85.40(8)
		P(1)–Ru(1)–Cl(1)	89.08(3)

Table 4
Selected bond lengths (Å) and angles (°) for **2b**.

Bond lengths (Å)		Bond angles (°)	
Ru(1)–C(1)	1.849(3)	C(1)–Ru(1)–C(2)	88.15(13)
Ru(1)–C(2)	1.934(3)	C(1)–Ru(1)–C(3)	92.46(11)
Ru(1)–C(3)	2.071(3)	C(2)–Ru(1)–C(3)	97.13(11)
Ru(1)–P(1)	2.4325(8)	C(1)–Ru(1)–P(1)	89.86(9)
Ru(1)–Cl(1)	2.4515(7)	C(3)–Ru(1)–P(1)	96.87(7)
Ru(1)–Cl(2)	2.4529(8)	C(2)–Ru(1)–Cl(1)	85.46(9)
		C(3)–Ru(1)–Cl(1)	84.81(7)
		P(1)–Ru(1)–Cl(1)	97.20(3)
		C(1)–Ru(1)–Cl(2)	93.92(9)
		C(2)–Ru(1)–Cl(2)	82.72(9)
		P(1)–Ru(1)–Cl(2)	83.52(3)
		Cl(1)–Ru(1)–Cl(2)	88.80(3)

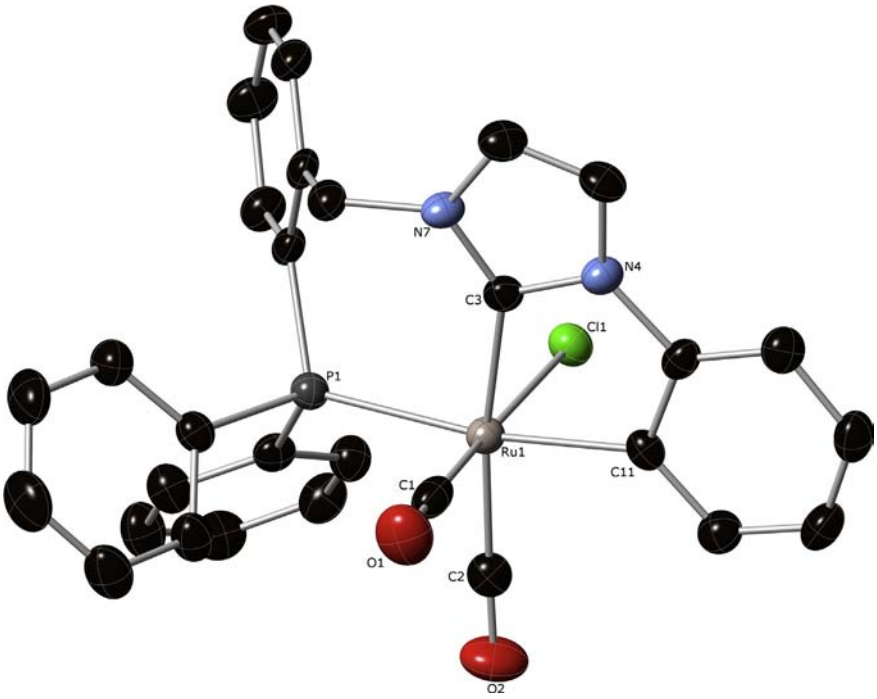


Fig. 1. ORTEP diagram of **2a**; thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and dichloromethane molecule of crystallization omitted for clarity.

range from 82.72 to 97.20°. For both complexes the Ru–CO bond lengths are inequivalent. In the structure of **2a** the Ru–C1 bond is 0.072 Å shorter than the Ru–C2 bond which is in agreement with the stronger *trans*-influence of the NHC compared to the chloride ligand. For **2b** the Ru–C1 bond is 0.085 Å shorter than the Ru–C2 bond in agreement with the stronger *trans*-influence of phosphines compared to chloride ligands. The Ru–C11 bond distance (2.129 Å) in **2a** is well within the range of a Ru–C covalent bond. The Ru–C11 bond is retained in solution as evidenced by the doublet centered at 154.44 ppm in the ^{13}C NMR spectrum; the splitting of this signal is consistent with ^{13}C –^{31}P coupling.

The ^{1}H NMR spectrum of **2a** is difficult to interpret due to extensive overlapping of peaks in the aromatic region. One noteworthy feature is that the signal for the methylene protons appears as two doublets due to the fact that these protons are diastereotopic. The ^{1}H NMR spectrum of **2b** exhibits an identical signature for the methylene protons. Additionally, the protons of the *ortho*-methyl groups on the mesityl ring resonate at different frequencies suggesting that rotation about the N–C_{Mes} bond is restricted in solution.

Both **2a** and **2b** catalyzed the transfer hydrogenation of acetophenone at 82 °C with 2-propanol as solvent and hydrogen donor in the presence of KO^{t}Bu [43]. Since **2b** was isolated in a much higher yield than **2a**, the majority of catalytic trials were conducted using **2b**; the results of these trials are reported in Table 5. At loadings of 213:1 ([ketone]:[[2]**b**]) at 82 °C under a dry nitrogen atmosphere, acetophenone, cyclohexanone,

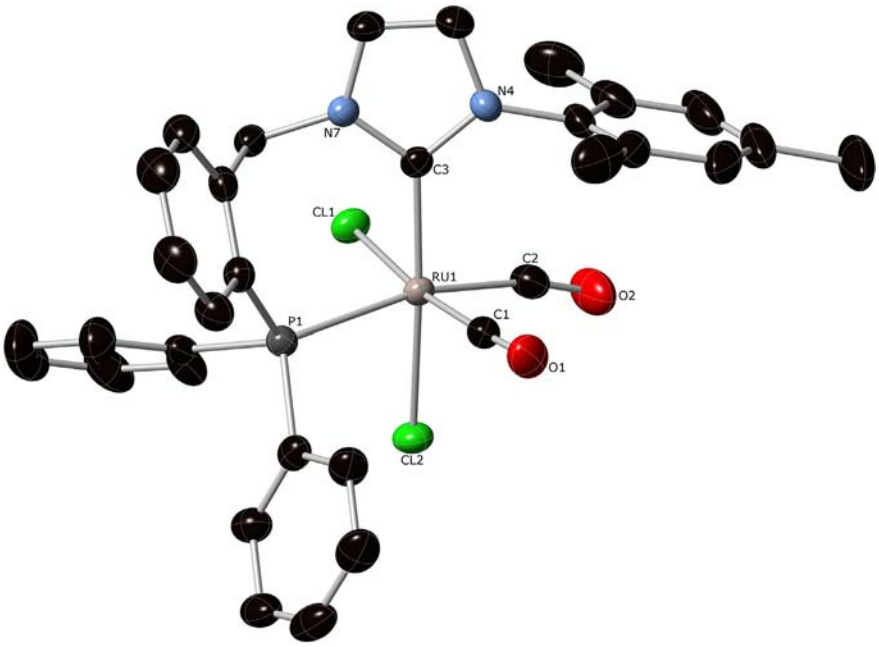
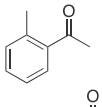
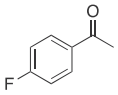
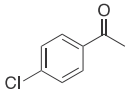
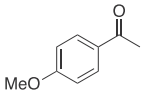


Fig. 2. ORTEP diagram of **2b**; thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and dichloromethane molecule of crystallization omitted for clarity.

Table 5
Results of catalytic trials with **2b**.

Trial[a]	Ketone	[ketone]:[Ru]	Temperature (°C)	Conversion[b] (%)	TOF[c] (h^{-1})
1		213:1	82	93.7	199
2[d]		213:1	82	90.5	192
3[e]		1000:1	82	45.8	456
4		213:1	25	25.6	54.3
5		213:1	82	96.7	206
6		213:1	82	61.3	130
7		213:1	82	53.6	114
8		213:1	82	62.3	133
9		213:1	82	99.5	211

[a] General conditions: **2b** (16 μmol) was dissolved in 5.0 mL of dry, degassed 2-propanol along with KO^{t}Bu (99 μmol) in an N_2 atmosphere. The ketone (3.4 mmol) was added to the reaction flask then the reaction mixture was heated to 82 °C with stirring. The reaction duration in each case was 60 min. [b]Determined via gas chromatography. [c]mol alcohol/mole Ru/h. [d]This reaction was conducted using unpurified solvents in air. [e]16.0 mmol of ketone was used.

and 2-methylacetophenone were converted to the corresponding alcohols with ≥93.7% conversion in 60 min (entries 1, 5, and 9). The turn over frequency (TOF) for the conversion of acetophenone to 1-phenylethanol with **2b** was at least 1.6 times higher than previously reported examples of transfer hydrogenation catalyzed by ruthenium(II) complexes supported by phosphine-functionalized NHCs under similar conditions [32,33].

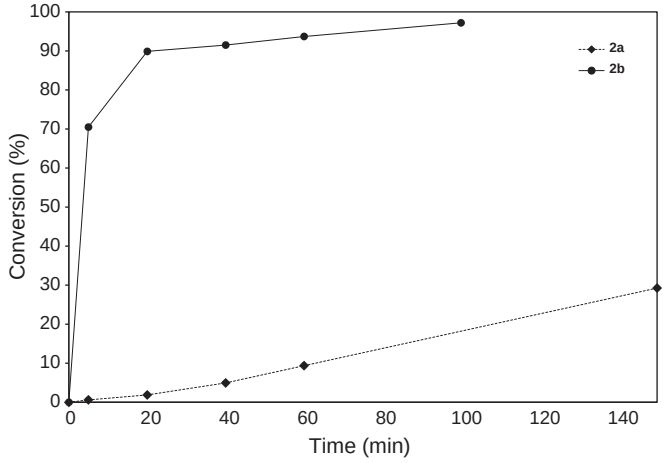


Fig. 3. Transfer hydrogenation of acetophenone to form 1-phenylethanol: % conversion vs. time for **2a** and **2b**.

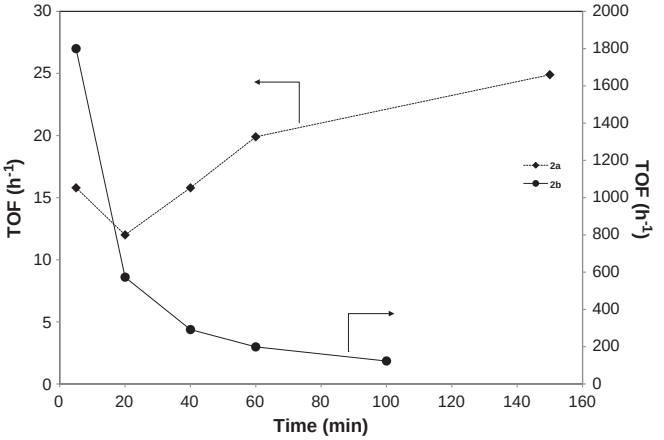


Fig. 4. Transfer hydrogenation of acetophenone to form 1-phenylethanol: turn over frequency (TOF) vs. time for **2a** and **2b**.

Somewhat unexpectedly, given the high steric demand near the carbonyl moiety, transfer hydrogenation of 2-methylacetophenone led to the highest conversion among the acetophenones. It is possible that the *ortho*-methyl group forces the ketone to adopt a conformation that decreases the steric interactions between the ketone and the ligand as the ketone approaches the Ru(II)-center. Substitution at the *para*-position led to lower catalytic activity (entries 6 – 8); the electron donating or withdrawing nature of the *para*-substituent did not seem to have a significant effect on catalytic activity (entry 6 vs. 8).

Other noteworthy features of **2b**'s catalytic behavior include: its ability to catalyze the transfer hydrogenation of acetophenone at ambient temperature (entry 4) and in air using unpurified 2-propanol with only a minor loss of catalytic activity (entry 2). In the solid state and in solution, **2b** is stable for at least one week and likely longer. These two observations combined suggest that **2b** is a robust pre-catalyst for transfer hydrogenation.

The percent conversion of acetophenone to 1-phenylethanol was monitored over time for **2a** and **2b**; the results of the time studies are summarized in Figs. 3 and 4. The data in Fig. 3 reveal that **2b** initiates rapidly and that the reaction reaches 90% conversion within 20 min while the activity of **2a** under identical conditions is much lower. As expected the TOF for **2b** diminishes over time as acetophenone is consumed (Fig. 4). Interestingly, the TOF of **2a** increases steadily from 20 min to 150 min suggesting that initiation of **2a** is slow (Fig. 4). One potential explanation for this observation is that the tridentate ligand of **2a** exerts extra steric demand at the active site thereby slowing initiation.

We have prepared and characterized two ruthenium(II) complexes supported by phosphine-functionalized NHC ligands and have evaluated their behavior as transfer hydrogenation catalysts. To our knowledge, this is the first report of transfer hydrogenation catalyzed by a ruthenium(II) complex supported by an *ortho*-metalated, phosphine-functionalized NHC ligand. The *ortho*-metalated complex, **2a**, showed low catalytic activity and an increase in TOF over time suggesting slow initiation. Notably, **2b** showed much higher activity catalyzing the transfer hydrogenation of several ketones to high conversion. Additionally, **2b** was shown to be a viable pre-catalyst at room temperature and in the presence of air using unpurified 2-propanol as the solvent and hydrogen donor.

Acknowledgments

GJD thanks Augustana College and the American Chemical Society's Petroleum Research Fund New Investigator Award program (PRF #

51217-UNI3) for financial support. The authors thank Dr. Mary Ellen Biggin for assistance with gas chromatography.

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[39] Synthesis of **2a**: Under a nitrogen atmosphere in the absence of light, 1-phenyl-3-(2-diphenylphosphinobenzyl)-1*H*-imidazol-3-ium chloride (**1a**) (0.36 g, 0.79 mmol) was allowed to react with Ag_2O (0.19 g, 0.79 mmol) in dry, degassed dichloromethane; 4 Å molecular sieves (approximately 0.5 g) were added to the mixture at the beginning of the reaction. After 24 h, the reaction mixture was filtered through Celite™ under an atmosphere of nitrogen into a flask containing $[Ru(CO)_3Cl_2]_2$ (0.21 g, 0.40 mmol); the reaction mixture was allowed to stir for 24 h in the dark. After stirring overnight, the reaction mixture was filtered through Celite™ under an atmosphere of dry nitrogen and all volatiles were removed *in vacuo*. The solid residue was purified via column chromatography (SiO_2, 40:1 CH_2Cl_2/MeOH) to furnish a yellow solid. Single crystals (0.025 g, 5.2%) were grown by dissolving the crude product in the minimum amount of dry dichloromethane and allowing diethyl ether to slowly evaporate, condense, and diffuse into the dichloromethane solution. ^{1}H NMR (d_6-DMSO): δ 8.12 (d, J = 0.46 Hz, 1 H, imid-*H*), 7.79 (m, 2 H, imid/Ar-*H*), 7.73 (m, 4 H, Ar-*H*), 7.57–7.47 (m, 10H, Ar-*H*), 7.27 (t, J = 1.93 Hz, 1 *H*), 7.05 (td, J = 0.37, 1.88, 1 H, Ar-*H*), 6.97 (t, J = 1.84 Hz, 1 H, Ar-*H*), 6.48 (t, J = 2.24 Hz, 1 H, Ar-*H*), 5.72 (s, 2 H, CH_2Cl_2), 5.28 (d, J = 3.57 Hz, 1 H, CH_2N), 5.10 (d, J = 3.57 Hz, 1 H, CH_2N). ^{13}C NMR (d_6-DMSO): δ 199.37 (d, J = 7.65 Hz, *C*O), 197.17 (d, J = 6.89 Hz, *C*O), 180.70 (d, J = 9.18 Hz, NCN), 154.44 (d, J = 12.25 Hz, metalated C_6H_4), 146.03, 140.34, 138.50, 138.37, 135.25, 135.14, 134.57, 134.54, 134.21, 133.79, 133.43, 132.80, 132.45, 132.37, 132.29, 131.62, 131.57, 131.45, 129.88, 129.79, 129.28, 129.22, 129.13, 125.98, 125.92, 124.27, 122.94, 116.43, 113.32, 55.46 (CH_2Cl_2), 52.20 (d, J = 1.65, CH_2N) ^{31}P{^{1}H}NMR (d_6-DMSO): δ 20.25 (1 P). Anal. Calcd for $C_{30}H_{22}ClN_2O_2PRu{\bullet}CH_2Cl_2$: C, 53.58; H 3.48; N 4.03. Found: C, 53.28; H, 3.73; N, 4.00.

[40] Synthesis of **2b**: In a nitrogen-filled glove box, a Schlenk flask was charged with 1-mesityl-3-(2- diphenylphosphinobenzyl)-1*H*-imidazol-3-ium chloride (**1b**) (0.76 g, 1.6 mmol), Ag_2O (0.37 g, 1.6 mmol), and 4 Å molecular sieves (*ca.* 0.5 g). The solids were suspended in dry, degassed dichloromethane and allowed to stir overnight in the dark. After 24 h, the reaction mixture was filtered through Celite™ into a Schlenk flask that had been charged with $[Ru(CO)_3Cl_2]_2$ (0.41 g, 0.79 mmol) under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature in the dark overnight. After 24 h, the reaction mixture was filtered through Celite™ and the volatiles were removed *in vacuo* to furnish a yellow solid. The crude product was purified by column chromatography (SiO_2, 40:1 CH_2Cl_2/MeOH). Single crystals (0.545 g, 49.9%) of the title compound were obtained by slow diffusion of diethyl ether onto a concentrated solution of the yellow powder isolated via column chromatography in dichloromethane. ^{1}H NMR (d_6-DMSO): δ 7.99 (d, J = 1.8 Hz, 1 H, imid-*H*), 7.88 (m, 3 H, imid/Ar-*H*), 7.62 (pseudo-t, J = 7.52 Hz, 1 H, Ar-*H*), 7.49–7.33 (m, 10 H, Ar-*H*), 7.18 (pseudo-t, J = 8.24 Hz, 1 H, Ar-*H*), 7.07 (s, 1 H, 2,4,6-$Me_3C_6H_2$), 7.03 (s, 1 H, 2,4,6-$Me_3C_6H_2$), 6.28 (d, J = 14.6 Hz, 1 H, CH_2N), 5.72 (s, 2 H, CH_2Cl_2), 5.06 (d, J = 14.6 Hz, 1 H, CH_2N), 2.28 (s, 3 H, *para*-CH_3), 1.95 (s, 3 H, *ortho*-CH_3), 1.69 (s, 3 H, *ortho*-CH_3). ^{13}C{^{1}H} NMR (d_6-DMSO): δ 195.27, 195.13 (d, J = 14 Hz, *C*O), 192.81, 192.68(d, J = 13 Hz, *C*O), 166.73, 166.61, (d, J = 12 Hz, NCN), 143.04, 142.90, 140.19, 136.82, 136.22, 136.09 (2C), 134.02, 133.93, 133.90, 132.73, 131.67, 131.58, 131.51, 131.17, 131.08, 130.86, 130.81, 130.58, 129.81 (d, J = 5.36 Hz), 129.59 (2C, d, J = 6.88 Hz), 128.50 (2C, d, J = 9.95 Hz), 127.49, 127.08, 125.32,

124.72, 55.46 (CH_2Cl_2), 52.63 (d, CH_2N, $J = 11.48$ Hz), 21.21 (*para*-CH_3), 18.59 (*ortho*-CH_3), 18.29 (*ortho*-CH_3). $^{31}P\{^1H\}$NMR (d_6-DMSO): δ 20.25 (1 P). Anal. Calcd for $C_{33}H_{29}Cl_2N_2O_2PRu{\bullet}CH_2Cl_2$: C, 52.80; H, 4.04; N, 3.62. Found: C, 52.77; H, 4.22; N, 3.56.

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[43] General procedure for catalytic trials: Under an atmosphere of nitrogen, the catalyst precursor (16 μmol) was added to a Schlenk flask with KO^{t}Bu (99 μmol) along with 5.0 mL of dry, degassed 2-propanol. To the reaction mixture was added 3.4 mmol of ketone. The reaction mixture was heated to 82 °C with stirring for 60 min. After the reaction period, the reaction mixture was filtered through a 0.45 μm syringe filter under ambient conditions and immediately analyzed via gas chromatography to determine the percent conversion.