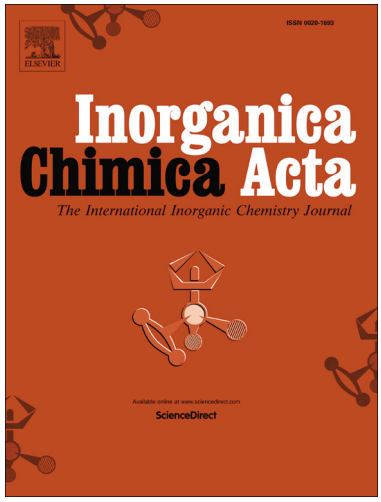

Research paper

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Ruthenium (II) and Iridium (III) Complexes of N-Heterocyclic Carbene and Pyridinol Derived Bidentate Chelates: Synthesis, Characterization, and Reactivity

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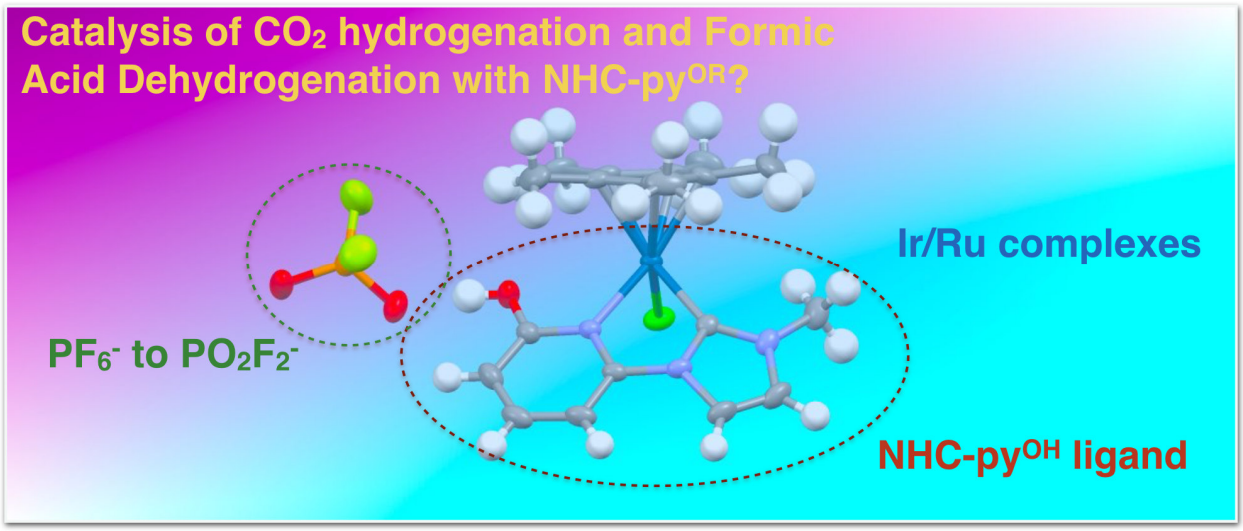
Abstract

We report the synthesis and characterization of new ruthenium(II) and iridium(III) complexes of a new bidentate chelate, $NHC^{R'}$-py^{OR} (OR = OMe, OtBu, OH and R' = Me, Et). Synthesis and characterization studies were done on the following compounds: four ligand precursors (**1**-**4**); two silver complexes of these $NHC^{R'}$-py^{OR} ligands (**5**-**7**); six ruthenium complexes of the type $[\eta^6$-(p-cymene)Ru($NHC^{R'}$-py^{OR})Cl]X with R' = Me, Et and R = Me, tBu, H and X = OTf^-, PF_6^- and $PO_2F_2^-$ (**8**-**13**); and two iridium complexes, [Cp*Ir(NHC^{Me}-py^{OtBu})Cl]PF_6 (**14**) and [Cp*Ir(NHC^{Me}-py^{OH})Cl]PO_2F_2 (**15**). The complexes are air stable and were isolated in moderate yield. However, for the PF_6^- salts, hydrolysis of the PF_6^- counter anion to $PO_2F_2^-$ during t-butyl ether deprotection was observed. Most of the complexes were characterized by ^{1}H and ^{13}C-NMR, MS, IR, and X-ray diffraction. The ruthenium complexes [η^6-(p-cymene)Ru(NHC^{Me}-py^{OR})Cl]OTf (R = Me (**8**) and tBu (**9**)) were tested for their ability to accelerate CO_2 hydrogenation and formic acid dehydrogenation. However, our studies show that the complexes transform during the reaction and these complexes are best thought of as pre-catalysts.

Graphic Abstract



Keywords: N-heterocyclic carbenes; pyridinol; protic ligands; transition metal complexes; carbon dioxide hydrogenation; X-ray crystallography

Highlights:

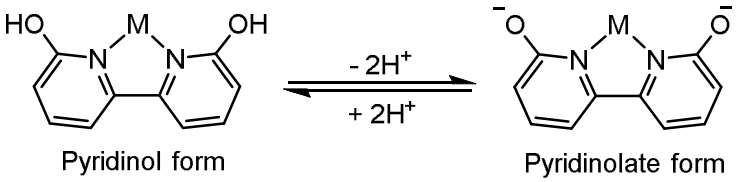
- Eight new complexes of a recently reported bidentate ligand are described, wherein the ligand merges an N-heterocyclic carbene with a pyridinol derived ring containing a proximal OH group.
- Silver, ruthenium, and iridium complexes of a new bidentate ligand have been synthesized and fully characterized by spectroscopic, analytical, and crystallographic methods.
- These complexes have been used as pre-catalysts for carbon dioxide hydrogenation and formic acid dehydrogenation.
- We observe transformations in the PF_6^- anion (to form $PO_2F_2^-$) associated with the metal complexes.

1. Introduction

Ruthenium complexes have been instrumental in advancing many fields including medicine and catalysis. Ruthenium is used in medicinal research because many ruthenium complexes are cytotoxic and have anti-proliferative properties. Ruthenium complexes can bind to iron transporters (which are up-regulated in cancer cells) to enhance drug uptake.[1] Thus far, three ruthenium complexes have entered clinical trials and some ruthenium complexes are cytotoxic towards cisplatin resistant cell lines.[2-7] Ruthenium complexes are also known for light harvesting properties. O'Regan and Grätzel pioneered the use of ruthenium complexes as photosensitizers in dye-sensitized solar cells,[8] and Ru-based sensitizers have also been used for artificial photosynthesis, as luminescent molecular probes, as photo responsive molecular devices, and for photo-catalysis.[9-17] Furthermore, ruthenium complexes also figure prominently as catalysts for (de)hydrogenation reactions[18, 19] and other types of catalysis (e.g. metathesis).[20-22] Among hydrogenation reactions, CO_2 is a challenging substrate to activate. Nonetheless, several groups worldwide have achieved CO_2 hydrogenation and the reverse reaction, formic acid dehydrogenation, using transition metals (e.g. Ir, Ru, Fe and others) ligated by N-heterocyclic carbene (NHC) ligands,[23] pyridinol-derived ligands,[24-27] and other ligands.[28-35]

Our group and others have previously studied the ligand 6,6'-dihydroxybipyridine (6,6'-dhbp) (Scheme 1) because of its unique advantages. Dhbp is a proton responsive ligand: upon deprotonation of hydroxyl group the electron-donating ability of the ligand is increased. Other pyridinol derived monodentate and chelating ligands have similar proton responsive properties and can form metal-ligand bifunctional catalysts.[36-43] Importantly, the catalytic activity of dhbp metal complexes can be tuned with changes in pH.[44-46] Frequently, the deprotonated

metal complexes of 6,6'-dhbp have an enhanced ability to catalyze various reactions including transfer hydrogenation and water oxidation.[44, 47] Ruthenium complexes of 6,6'-dhbp can allow for cancer selective cytotoxicity by low pH triggered photo-dissociation in acidic regions of cancer cells.[48] Thus, in some cases, 6,6'-dhbp ligand can be labile especially when bound to a first row transition metal (e.g. Cu) and under very acidic or basic conditions.[49]

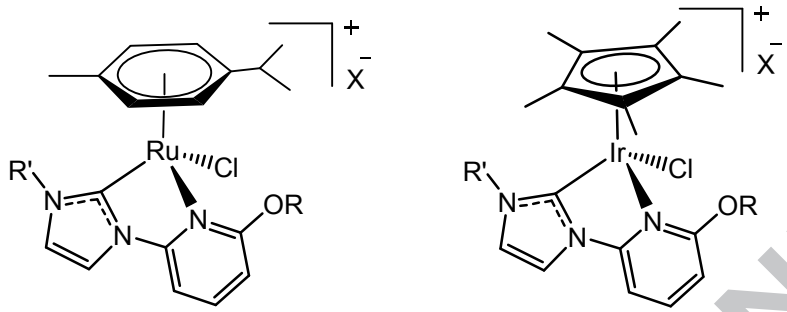


Scheme 1: Acid-base equilibrium of 6, 6'-dihydroxy-2, 2'-bipyridine (6, 6'-dhbp) complexes.

Likewise, N-heterocyclic carbenes (NHC) are a well-known ligand class that has been used to create many successful homogenous catalysts.[50-55] The stability of the NHC ligand derives from it being a strong σ-donor that can generate a robust M-C bond. Through synthesis, NHCs are readily modified to tune the steric and electronic properties of the ligands. [56-59] Previously, our group designed catalysts containing NHC ligands which catalyzed transfer hydrogenation reactions.[60, 61]

Many ruthenium complexes for the above applications have included pyridine or N-heterocyclic carbene ligands (NHCs). Also, some bidentate and tridentate ligands have combined NHC and pyridine rings on one scaffold.[62-76] However, prior to our recent work, no ligands have combined NHC and pyridinol rings in a chelate.[27] As a result, we envisioned that by combining an NHC ring with a pyridinol ring, we would introduce a new ligand class that would combine the strong donor properties of the NHC moiety with the proton responsive pyridinol

moiety. Recently, our group has reported new NHC-py^{OR} ligands and Ir complexes thereof which serve as pre-catalysts for CO_2 hydrogenation and formic acid dehydrogenation.[27] Here, we are reporting the synthesis and characterization of the Ru (**8-13**) and Ir (**14-15**) analogues supported by (NHC$^{R'}$-py^{OR}) ligands (OR = OMe, OtBu, OH; R' = Me, Et) with different counter anions, $(PF_6)^-$ and $(OTf)^-$. We also briefly describe the reactivity of these Ru complexes.



OR = OMe, OtBu, OH R' = Me , Et X = PF_6, PO_2F_2, OTf

Scheme 2: General structure of complexes **8-15**.

2. Experimental Section

2.1. General Procedures

All ligand and metal complex were synthesized under nitrogen atmosphere in a glove box or by utilizing standard Schlenk line techniques with oven dried glassware. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were acquired at room temperature on a Bruker AV360 360 MHz or AV500 500 MHz spectrometers, or on Varian 400 or 500 MHz spectrometers, and referenced to the solvent. Mid-IR spectra were collected on a Bruker Alpha ATR-IR spectrometer. Mass spectrometric data were collected on a Waters AutoSpec-Ultima NT spectrometer with electron ionization method. Elemental analyses were performed by NuMega Resonance Labs, Inc., San Diego, CA. Electronic spectra were measured on a Perkin Elmer Lambda 35 UV-visible spectrometer. Pressurized gas reactions were performed in a Parr reaction vessel.

2.2. Materials

Dry solvents were obtained via the Glass Contour Solvent System built by Pure Process Technology, LLC. All reagents were used as purchased and degassed under vacuum as needed. The compounds NHC-Py^{OR} (R = Me, tBu), [Im^{Me}-Py^{OtBu}]OTf (**4**), [Ag(NHC^{Me}-py^{OtBu})$_2$]OTf (**6**), and [Ag(NHC^{Me}-py^{OMe})$_2$]OTf (**7**) were prepared according to previously published procedures.[27] High purity grade (> 97%) formic acid was used as purchased from AMRESCO, Inc. The compressed gases CO_2 and 50/50 vol CO_2/H_2 were purchased from Airgas and used without further purification.

2.3. Synthesis of (Im^{Me}-py^{OtBu})I (1)

Dry THF (20 mL) was added via cannula to an evacuated flask containing 2-(methoxy)-6-(1H-imidazol-1-yl)pyridine (1.054 g, 4.85 mmol, 1 equiv) and a stir bar. Methyl iodide (MeI) (1.2 mL, 19.28 mmol, 4 equiv) was added dropwise with stirring at 0 °C. The reaction mixture was stirred for 12 h under nitrogen at room temperature. Some solid precipitated out after 12 h, and upon addition of Et_2O more solid precipitated. The solid was collected on a frit using suction and washed with more Et_2O. The white solid was further dried under vacuum to yield the product (Im^{Me}-py^{OMe})I (1.2477 g, 3.47 mmol, 71.7%). ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 10.95 (s, 1H), 8.01 (t, 1 H, $^3J_{HH}$ = 2.0 Hz), 7.79 (t, 1 H, $^3J_{HH}$ = 8.0 Hz), 7.66 (t, 1 H, $^3J_{HH}$ = 2.0 Hz), 7.74 (d, 1 H, $^3J_{HH}$ = 7.7 Hz), 6.78 (d, 1 H, $^3J_{HH}$ = 7.9 Hz), 4.31 (s, 3 H), 1.61 (s, 9 H). Anal. Calcd. for $C_{13}H_{18}IN_3O$ (359.21): C, 43.47%; H, 5.05%; N, 11.70%. Found: C, 42.44%; H, 5.22%; N, 11.52%.

2.4. Synthesis of (Im^{Me}-py^{OtBu})PF_6 (2)

An aqueous solution of NH_4PF_6 (6.001 g, 36.82 mmol) was added to 300 mL aqueous solution of (Im^{Me}-py^{OtBu})I (8.7433 g, 24.34 mmol) to produce some precipitate. The precipitate solid was collected on a fine frit, washed with Et_2O, and then further dried under vacuum to obtain an off-white solid (8.039 g, 21.31 mmol, 87.6%). Note that forming the (Im^{Me}-py^{OtBu})I solution required some heat to enhance the solubility of the solid, and this solution needed to be cooled prior to addition of the NH_4PF_6 solution in order to avoid oiling out of the product. All the spectroscopic characterization data were similar to those previously reported for (Im^{Me}-py^{OtBu})OTf.[27] Anal. Calcd. for $C_{13}H_{18}F_6N_3OP$ (377.27): C, 41.39%; H, 4.81%; N, 11.14%. Found: C, 41.26%; H, 4.64%; N, 11.34%.

2.5. Synthesis of (Im^{Et}-py^{OMe})Br (3)

A Schlenk flask with a stir bar was charged with NaOMe (4.7g, 87 mmol) and sealed with a rubber septum, and THF (200 mL) was added via cannula. Under N_2(g) atmosphere, 2,6-diflouropyridine (5.0 g, 43 mmol) was added dropwise to the stirring solution via syringe to form 2-(methoxy)-6-fluoropyridine. This reaction was stirred overnight (approximately 12 h) then THF was removed under reduced pressure. The flask containing crude product was evacuated and under positive N_2(g), approximately 100 mL of DMF was added, followed by the addition of imidazole (3.575 g, 52.5 mmol) and NaH (1.9 g, 160 mmol) at 0 °C. The flask was allowed to warm to room temperature and with positive nitrogen flow, a reflux condenser was attached and the flask was heated to 80 °C overnight with stirring. The reaction flask was cooled to room temperature, the DMF was removed from the mixture via rotary evaporator, and the remaining reaction mixture was transferred to a separatory funnel with 25 mL CH_2Cl_2. The organic phase

was washed with water (25 mL x 3), dried over $MgSO_4$, filtered, and the filtrate was concentrated to dryness via rotary evaporator.

The crude Im-py^{OMe} was dissolved in 200 mL of DMF and ethyl bromide (5.2 g, 48 mmol) was added dropwise with stirring. Under positive pressure of N_2(g), a reflux condenser was attached and the flask was heated to 120 °C overnight. The reaction flask was cooled to room temperature and the red oily product was obtained after solvent removal. Upon column chromatography purification with 90:10 ratio of MeOH : CH_2Cl_2, 42% (5.233g, 18.4 mmol) of product was obtained. ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 11.60 (s, 1H), 8.16 (t, 1H, Im, $^3J_{HH}$ = 1.8 Hz), 7.88 (t, 1H, py, $^3J_{HH}$ = 8.0 Hz), 7.46 (t, 1H, Im, $^3J_{HH}$ = 1.8 Hz), 7.93 (d, 1H, py, $^3J_{HH}$ = 8.1 Hz), 6.86 (d, 1H, py, $^3J_{HH}$ = 8.1 Hz), 4.67 (q, 2H, C*H*$_2$CH$_3$, $^3J_{HH}$ = 7.4 Hz), 1.73 (t, 3H, CH$_2$C*H*$_3$, $^3J_{HH}$ = 7.4 Hz), 4.03 (s, 3H, OC*H*$_3$). ^{13}C NMR (125.76 MHz, $CDCl_3$, ppm): δ 164.26 (py), 144.11 (py), 142.64 (py), 135.10 (im), 123.12 (im), 119.50 (im), 112.35 (py), 106.58 (py), 54.91 (OMe), 46.51 (N***C***H$_2$CH$_3$ of cationic imidazolium), 16.25 (NCH$_2$***C***H$_3$ of cationic imidazolium)). EI-MS (EI$^+$): m/z 176.1 (Im-pyOMe)$^+$.

2.6. Synthesis of [Ag(NHC^{Me}-py^{OtBu})$_2$]PF$_6$ (5)

An oven dried round-bottom Schlenk flask with stir bar was loaded with (Im^{Me}-py$^{O\mathit{t}Bu}$)PF_6 (1.5001 g, 3.976 mmol, 1 equiv) and Ag_2O (0.464 g, 2.00 mmol, 0.5 equiv) in a glovebox and sealed with a rubber septum. Dry CH_2Cl_2 (25 mL) was added via cannula at the Schlenk line to make a black slurry. The flask was covered in foil to block light. Aqueous NaOH (1.0 mL, 2.00 mmol, 0.5 equiv) was added dropwise via syringe with stirring. The reaction mixture was stirred for 24 h at room temperature. Excess Ag_2O was removed by suction filtration over Celite, which was washed with CH_2Cl_2 (40 mL). The organic phase of the filtrate was washed with DI water 3

times, dried over $MgSO_4$, filtered, and the filtrate concentrated to dryness. The resulting white solid was further dried under high vacuum to yield 1.3751 g of **5** (1.92 mmol, 96.4% yield). ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.66 (d, 2 H, $^3J_{HH}$ = 1.8 Hz), 7.56 (t, 2 H, $^3J_{HH}$ = 7.8 Hz), 7.39 (d, 2 H, $^3J_{HH}$ = 7.8 Hz), 7.28 (d, 2 H, $^3J_{HH}$ = 1.8 Hz), 6.71 (d, 2 H, $^3J_{HH}$ = 7.8 Hz), 3.99 (s, 6 H), 1.56 (s, 18 H).^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, ppm): δ 179.47 (d, $^1J_{AgC}$ = 198 Hz, NHC carbene carbon), 163.37 (py), 148.65 (py), 140.88 (py), 123.57 (NHC), 120.67 (NHC), 113.52 (py), 107.30 (py), 81.05 (O***C***$(CH_3)_3$), 39.54 (NMe), 28.75 (OC(***C***$H_3)_3$). FT-IR (ATR, cm^{-1}): 3187 (w), 3153 (w), 2979 (w), 2927 (w), 1601 (w), 1566 (m), 1453 (s), 1393(m), 1366 (w), 1297 (m), 1227 (w), 1165 (m), 1096 (m), 1044(m), 983 (m), 938 (m), 834 (s), 730 (m), 547 (m). A sample from another run gave correct combustion data for a hydrate. Anal. Calcd. for $C_{26}H_{34}AgF_6N_6O_2$ (715.42): C, 43.65%; H, 4.79%; N, 11.75%. Found: C, 42.84%; H, 5.10%; N, 11.46%. Anal. Calcd. for $C_{26}H_{34}AgF_6N_6O_2 + H_2O$ (733.43): C, 42.58%; H, 4.95%; N, 11.75%.

2.7.Synthesis of [(*p*-cym)RuCl(NHC^{Me}-py^{OMe})]OTf (8)

In a glovebox, an oven dried Schlenk flask with stir bar was loaded with $[(p\text{-cym})RuCl_2]_2$ (0.1932 g 0.315 mmol, 1 equiv), AgOTf (0.0809 g, 0.315 mmol, 1 equiv), [Ag(NHC^{Me}-py^{OMe})$_2$]OTf (0.2001 g, 0.315 mmol, 1 equiv), and dry CH_2Cl_2 (20 mL). An immediate color change from orange to yellow was observed. The reaction mixture was protected from light and stirred for 18 h resulting in the accumulation of a tan precipitate (AgCl). The reaction mixture was filtered over Celite with suction and was washed with 10 mL of CH_2Cl_2. The product was recrystallized by layering the filtrate with Et_2O. The resulting orange block crystals were collected by suction filtration and washed with ether yielding the desired product [(*p*-cym)RuCl(NHC^{Me}-py^{OMe})]OTf (**7**) (0.329 g, 0.540 mmol, 85.8% yield). ^{1}H NMR (500 MHz,

CD_3CN, ppm): δ 8.06 (t, 1 H, $^3J_{HH}$ = 8.3 Hz), 7.82 (d, 1 H, $^3J_{HH}$ = 2.3 Hz), 7.42 (d, 1 H, $^3J_{HH}$ = 2.4 Hz), 7.37 (d, 1 H, $^3J_{HH}$ = 7.8 Hz), 7.00 (d, 1 H, $^3J_{HH}$ = 8.4 Hz), 6.19 (d, 1 H, $^3J_{HH}$ = 6.4 Hz), 6.17 (d, 1 H, $^3J_{HH}$ = 6.0 Hz), 5.94 (d, 1 H, $^3J_{HH}$ = 6.6 Hz), 5.41 (d, 1 H, $^3J_{HH}$ = 5.9 Hz), 4.22 (s, 3 H), 4.06 (s, 3H), 2.32-2.34 (m, 1 H), 2.15 (s, 3 H), 0.91 (d, 3H, $^3J_{HH}$ = 7.2 Hz), 0.85 (d, 3H, $^3J_{HH}$ = 6.9 Hz).$^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2, ppm): δ 184.95 (NHC carbene carbon), 165.91 (py), 151.25 (py), 144.24 (py), 126.63 (NHC), 121.46 (q, $^1J_{CF}$ = 317.08 Hz, triflate), 117.14 (NHC), 110.14 (cym), 106.24 (cym), 105.00 (py), 104.30 (py), 92.14 (cym), 88.82 (cym), 87.66 (cym), 80.09 (cym), 58.30 (OMe), 38.76 (NMe), 31.58 (***C***H of cym), 22.71 (***C***H_3 of iPr on cym), 22.34 (***C***H_3 of iPr on cym), 19.40 (***C***H_3 of Me on cym). ^{19}F NMR (338.86 MHz, CD_3CN, ppm): δ -78.77. FT-IR (ATR, cm^{-1}): 3100 (w), 2968 (w), 2324 (w), 1619 (m), 1579 (w), 1487 (w), 1391 (m), 1258 (m), 1148 (w), 1029 (m), 975 (m), 866 (w), 791 (m), 738 (w), 688 (w), 636 (s), 571 (m), 516 (m). ESI-MS: m/z 460 [(*p-cym*)RuCl(NHC^{Me}-py^{OMe})]$^+$, 422 [(*p-cym*)Ru(NHC^{Me}-py^{OMe})]$^+$. Anal. Calcd. for $C_{21}H_{25}N_3O_4F_3SClRu$: C, 41.38%; H, 4.14%; N, 6.89%. Found: C, 40.98%; H, 4.50%; N, 6.85%.

2.8. Synthesis of [(*p*-cym)RuCl(NHC^{Me}-py^{OtBu})]OTf (9)

An oven dried Schlenk flask with stir bar was charged with [(*p*-cym)$RuCl_2]_2$ (0.4261 g 0.695 mol, 1 equiv), AgOTf (0.1786 g, 0.695 mmol, 1 equiv), and [Ag(NHC^{Me}-py^{OtBu})$_2$]OTf (0.5003 g, 0.695 mmol, 1 equiv) under $N_{2(g)}$. Dry CH_2Cl_2 (50 mL) was dispensed via cannula. An immediate color change from orange to yellow was observed. The reaction mixture was stirred for 18 h resulting in the accumulation of a tan precipitate (AgCl). The reaction mixture was filtered over Celite with suction and then was washed with 10 mL of CH_2Cl_2. The product was recrystallized by layering the filtrate with 80 mL of Et_2O. The resulting orange crystals were

collected by suction filtration and washed with ether yielding the desired product [(*p*-cym)RuCl(NHC^{Me}-py$^{O\mathit{t}Bu}$)]OTf (**9**) (0.6143 g, 0.943 mmol, 96.5 % yield). Pure microcrystalline product was also collected by quickly adding Et_2O to the filtrate. ^{1}H NMR (360 MHz, CD_3CN, ppm): δ 7.97 (t, 1 H, $^3J_{HH}$ = 7.9 Hz), 7.79 (d, 1 H, $^3J_{HH}$ = 2.3 Hz), 7.42 (d, 1 H, $^3J_{HH}$ = 2.3 Hz), 7.34 (d, 1 H, $^3J_{HH}$ = 8.0 Hz), 7.18 (d, 1 H, $^3J_{HH}$ = 8.1 Hz), 6.12-6.08 (m, 2 H), 5.94 (d, 1 H, $^3J_{HH}$ = 5.3 Hz), 5.53 (d, 1 H, $^3J_{HH}$ = 5.4 Hz), 4.05 (s, 3 H), 2.22 (m, 1 H), 2.14 (s, 3 H), 1.69 (s, 9 H), 0.85 (d, 3H, $^3J_{HH}$ = 7.1 Hz), 0.79 (d, 3H, $^3J_{HH}$ = 7.0 Hz). ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN, ppm): δ 185.68 (NHC carbene carbon), 165.66 (py), 152.12 (py), 143.75 (py), 127.32 (NHC), 122.22 (q, $^1J_{CF}$ = 320.50 Hz), 117.71 (NHC), 111.49 (py), 109.14 (cym), 105.45(py), 103.46 (cym), 94.29 (cym), 93.00 (cym), 87.04 (cym), 86.91 (O***C***$(CH_3)_3$), 80.81 (cym), 38.84 (NMe), 31.81 (***C***H of cym), 29.49 (OC(***C***$H_3)_3$), 22.66 (***C***H_3 of iPr on cym), 22.27 (***C***H_3 of iPr on cym), 19.18 (***C***H_3 of Me on cym). FT-IR (ATR, cm^{-1}): 3115 (w), 2977 (w), 1615 (m), 1572 (w), 1563 (w), 1473 (m), 1458 (m), 1397 (w), 1372 (m), 1275 (m), 1260 (s), 1223 (m), 1146 (s), 1028 (s), 908 (m), 846 (m), 822 (m), 757 (m), 739 (m), 716 (m), 691 (m), 634 (s), 571 (m), 515 (m), 453 (w). ESI-MS: m/z 502.1 [(*p*-cym)RuCl(NHC^{Me}-py$^{O\mathit{t}Bu}$)]$^+$, 446.0 [(*p*-cym)RuCl(NHC^{Me}-py^{OH})]$^+$, 410.0 [(*p*-cym)Ru(NHC^{Me}-py^{OH})]$^+$. Anal. Calcd. for $C_{24}H_{31}N_3O_4F_3SClRu + H_2O$: C, 43.04%; H, 4.97%; N, 6.28%. Found: C, 42.23%; H, 4.73%; N, 6.08%.

2.9. Synthesis of [(*p*-cym)RuCl(NHC^{Me}-py^{OH})]OTf (10)

An oven dried 25 mL Schlenk tube with Teflon plug was loaded with crystalline solid [(*p*-cym)RuCl(NHC^{Me}-py^{OtBu})]OTf (**9**) (0.5037 g, 0.774 mmol) and 10 mL of dry CH_2Cl_2. The atmosphere of the flask was removed by three cycles of freeze-pump-thaw. The evacuated flask was super-heated at 90 °C for 3 days. The resulting solution was micro-filtered to remove

insoluble black precipitate and layered with dry Et_2O to give orange crystals. The recrystallization is sensitive to the conditions and occurs best when kept air and moisture free. Alternatively, the product can be dried to a powder or a residue if the solid crashes out quickly. ^{1}H NMR (360 MHz, CD_3CN, ppm): δ 10.48 (broad s, 1H), 7.89 (t, 1 H, $^3J_{HH}$ = 7.9 Hz), 7.77 (d, 1 H, $^3J_{HH}$ = 2.4 Hz), 7.41 (d, 1 H, $^3J_{HH}$ = 2.3 Hz), 7.24 (d, 1 H, $^3J_{HH}$ = 8.9 Hz), 6.96 (d, 1 H, $^3J_{HH}$ = 8.9 Hz), 6.18 (d, 1 H, $^3J_{HH}$ = 6.3 Hz), 6.15 (d, 1 H, $^3J_{HH}$ = 6.2 Hz), 6.03 (d, 1 H, $^3J_{HH}$ = 6.2 Hz), 5.41 (d, 1 H, $^3J_{HH}$ = 6.3 Hz), 4.06 (s, 3 H), 2.32 (m, 1 H), 2.15 (s, 3 H), 0.89 (d, 3H, $^3J_{HH}$ = 6.9 Hz), 0.84 (d, 3H, $^3J_{HH}$ = 6.9 Hz).

2.10. Synthesis of [(*p*-cym)RuCl(NHC^{Me}-py^{OtBu})]PF_6 (11)

The same procedure was followed as for the synthesis of [(p-cym)RuCl(NHC^{Me}-py^{OtBu})]OTf with the following differences. The reagents and the amounts used were [Ag(NHC^{Me}-py^{OtBu})$_2$]PF_6 (0.500 g, 0.696 mmol, 1 equiv), [(p-cym)$RuCl_2$]$_2$ (0.427 g, 0.697 mmol, 1 equiv), and $AgPF_6$ (0.176 g, 0.697 mmol, 1 equiv). A color change of orange to light orange occurred with the addition of solvent. Orange crystals were grown from CH_2Cl_2 layered with ether yielding **11** (0.833 g, 1.29 mmol, 92.4% yield). ^{1}H NMR (360 MHz, CD_3CN, ppm): δ 7.97 (t, 1H, $^3J_{HH}$ = 8.5 Hz), 7.81 (d, 1 H, $^3J_{HH}$ = 2.0 Hz), 7.34 (d, 1 H, $^3J_{HH}$ = 8.0 Hz), 7.17 (d, 1 H, $^3J_{HH}$ = 8.2 Hz), 6.11 (m, broad, 2H), 5.94 (d, 1H, $^3J_{HH}$ = 6.2 Hz), 5.53 (d, 1H, $^3J_{HH}$ = 5.4 Hz), 4.05 (s, 3H), 2.14 (s, 3H), 1.69 (s, 9H), 0.84 (d, 3H, $^3J_{HH}$ = 6.8 Hz), 0.79 (d, 3H, $^3J_{HH}$ = 6.8 Hz). ^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN, ppm): δ 185.61 (NHC carbene carbon), 165.62 (py), 152.10 (py), 143.67 (py), 127.30 (NHC), 117.70 (NHC), 111.42 (py), 109.09 (cym), 105.41(py), 103.40 (cym), 94.25 (cym), 93.11 (cym), 86.98 (O***C***$(CH_3)_3$), 86.89 (cym), 80.84 (cym), 38.77 (NMe), 31.78 (***C***H of cym), 29.41 (OC(***C***$H_3)_3$), 22.58 (***C***H_3 of iPr on cym), 22.20 (***C***H_3 of iPr on cym),

19.12 (***C***H_3 of Me on cym). FT-IR (ATR, cm^{-1}): 3100 (w), 2969 (w), 2870 (w), 1629 (w), 1569 (w), 1485 (m), 1447 (w), 1399 (w), 1363 (w), 1291 (m), 1243 (w), 1135 (m), 1025 (w), 906 (w), 833 (s), 723 (w), 663 (w), 556 (m), 484 (m).

2.11. Synthesis of [(*p*-cym)RuCl(NHC^{Et}-py^{OMe})]PF_6 (12)

[Im^{Et}-py^{OMe}]Br (0.100g, 0.352 mmol) was added to Ag_2O (0.260g, 1.12 mmol) in 15 mL of water and allowed to stir at room temperature for 30 minutes in the absence of light. The solution was filtered and NH_4PF_6 (1.00 g, 6.13 mmol) was added and allowed to stir. A brown precipitate quickly formed and was collected by filtration. The resulting solid was washed twice with 20 mL of diethyl ether. The presumed [Ag(NHC^{Et}-py^{OMe})$_2$]PF_6 (crude, 0.0795 g, 0.174 mmol, 27%) was dissolved in 10 mL of dichloromethane and [(*p*-cymene)$RuCl_2$]$_2$ (0.050g, 0.0813 mmol) was added and the mixture was allowed to stir at room temperature for 18 h. The resulting silver chloride was removed by filtration and the solvent was removed under vacuum to yield product (0.048 g, 0.0943 mmol, 58%). An orange block crystal was grown from methanol and diethyl ether. ^{1}H NMR (360 MHz, $CDCl_3$, ppm)**:** δ 7.50 (d, 1 H, NHC, $^3J_{HH}$ = 2.1 Hz), 7.25 (t, 1 H, py, $^3J_{HH}$ = 8.1 Hz), 6.95 (d, 1 H, NHC, $^3J_{HH}$ = 2.1 Hz), 6.85 (d, 1 H, py, $^3J_{HH}$ = 7.9 Hz), 6.25 (d, 1 H, py, $^3J_{HH}$ = 8.4 Hz), 5.41 (m, 2 H, Ar-cym, $^3J_{HH}$ = 5.4 Hz), 5.20 (d, 1 H, Ar-cym, $^3J_{HH}$ = 5.9 Hz), 4.65 (d, 1 H, Ar-cym, $^3J_{HH}$ = 5.5 Hz), 3.60 (q, 2 H, C***H*****$_2$**CH_3, $^3J_{HH}$ = 6.7 Hz), 3.40 (s, 3 H, OC***H*****$_3$,**), 1.49 (m, 1 H, C***H***$(CH_3)_2$-cymene, $^3J_{HH}$ = 7.0 Hz), 1.35 (s, 3H, C***H*****$_3$**-cymene), 0.70 (t, 3H, CH_2C***H*****$_3$,** $^3J_{HH}$ = 7.2 Hz), 0.05 (m, 6H, CH(***CH*****$_3$**$)_2$-cymene, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$, ppm): δ 182.5 (NHC carbene carbon), 165.0 (py), 151.1 (py), 144.0 (py), 124.1 (NHC), 116.5 (NHC), 104.0 (py), 103.1 (py), 91.0 (cym), 87.5 (cym), 58.2 (OMe), 47.0 (N***C***H_2CH_3), 31.0 (***C***H of cym), 22.5 (***C***H_3 of iPr on cym), 22.0 (***C***H_3 of iPr on cym), 18.0

($NCH_2\boldsymbol{C}H_3$), 16.1 ($\boldsymbol{C}H_3$ of Me on cym), note that some sp^2 ^{13}C NMR signals of the cymene ligand were not detected and they may be under the $CDCl_3$ solvent peak or some may coincidentally occur at the same chemical shift (see the Supporting Information for the labelled spectrum). ESI-MS: m/z 474.1 $[M\text{-}Cl]^+$ (matches with the expected isotopic pattern).

2.12. Synthesis of [Cp*IrCl(NHC^{Me}-py^{OtBu})]PF_6 (14)

An oven dried Schlenk flask with stir bar was loaded with $[Cp^*IrCl_2]_2$ (0.535g, 0.672 mmol, 1 equiv), $AgPF_6$ (0.1766 g, 0.698 mmol, 1.04 equiv), and $[Ag(NHC^{Me}\text{-}py^{OtBu})_2]PF_6$ (0.4996 g, 0.696 mmol, 1.04 equiv) under $N_{2(g)}$. Dry CH_2Cl_2 (40 mL) was dispensed via cannula. An immediate color change from orange to yellow was observed. The reaction mixture was stirred and protected from light for 18 h resulting in the accumulation of a tan precipitate (AgCl). The reaction mixture was filtered over Celite with suction, which was washed with CH_2Cl_2 (10 mL). The product was recrystallized by layering the filtrate with Et_2O. The resulting yellow crystals were collected by suction filtration and washed with ether yielding the desired product [Cp*IrCl(NHC^{Me}-py^{OtBu})]PF_6 (**14**) (0.8087 g, 1.09 mmol, 81.4% yield). ^1H NMR (360 MHz, $CDCl_3$, ppm): δ 8.05 (d, 1H, $^3J_{HH}$ = 2.4 Hz), 8.00 (t, 1H, $^3J_{HH}$ = 8.1 Hz), 7.67 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 7.33 (d, 1H, $^3J_{HH}$ = 2.3 Hz), 7.03 (d, 1H, $^3J_{HH}$ = 8.4 Hz), 4.02 (s, 3H), 1.72 (s, 15H), 1.57 (s, 9H). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, ppm): δ 166.49 (NHC carbene carbon), 163.92 (py), 151.42 (py), 143.79 (py), 125.71 (NHC), 118.32 (NHC), 111.48 (py), 104.80 (py), 92.29 (Cp* ring carbons), 86.84 ($O\boldsymbol{C}(CH_3)_3$), 37.25 (NMe), 29.19 ($OC(\boldsymbol{C}H_3)_3$), 9.68 (CH_3 of Cp*). FT-IR (ATR, cm^{-1}): 3092 (w), 2983 (w), 1623 (m), 1562 (m), 1472 (m), 1400 (w), 1378 (w), 1293 (m), 1249 (w), 1149 (m), 1120 (m), 1026 (w), 909 (w), 880 (w), 824 (s), 735 (m), 685 (m), 674 (w), 562 (s), 500 (m). Anal. Calcd. for $C_{24}H_{35}ClF_6IrN_3OP$ (739.15): C, 35.64%; H, 4.68%; N, 5.42%. Found: C, 35.32%; H, 4.10%; N, 5.28%.

2.13. Synthesis of [Cp*IrCl(NHC^{Me}-py^{OH})]PO_2F_2 (15)

An oven dried heavy wall Schlenk tube with stir bar was charged with [Cp*IrCl(NHC^{Me}-py^{OtBu})]PF_6 (**14**) (0.2003 g, 0.271 mmol). The tube was evacuated and 6 mL of dry CH_2Cl_2 was added via cannula. The tube containing the mixture was subjected to 3 cycles of freeze-pump-thaw to remove O_2 and then heat to 80 ^oC. After 4 days, the solution was brought to room temperature and recrystallization was done by slow diffusion of Et_2O into the NMR sample in CD_3CN (0.1460 g, 0.2285 mmol, 84.3 % yield). ^1H NMR (360 MHz, CD_3CN, ppm): δ 7.87 (t, 1H, $^3J_{HH}$ = 8.1Hz), 7.78 (d, 1H, $^3J_{HH}$ = 2.0 Hz), 7.37 (d, 1H, $^3J_{HH}$ = 2.2 Hz), 7.23 (d, 1H, $^3J_{HH}$ = 8.1 Hz), 6.97 (d, 1H, $^3J_{HH}$ = 8.1 Hz), 3.95 (s, 3H), 1.74 (s, 15H). Anal. Calcd. for $C_{20}H_{27}ClF_2IrN_3O_3P$ (639.05): C, 33.80%; H, 4.18%; N, 6.22%. Found: C, 33.8%; H, 3.78%; N, 6.24%.

2.14. Single Crystal X-ray Diffraction for **8** – **12**, **14**, and **15**

Single crystals of complexes **8** – **12**, **14**, and **15** were mounted on a glass filament on a Bruker Apex2 CCD-based X-ray diffractometer[77] equipped with an Oxford N-Helix Cryosystem and a fine focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power (50 kV, 40 mA). X-ray intensities were measured at 173 K or 100 K with the detector placed at a distance of 6.000 cm from the crystal. The frames were integrated with the Saint[78] software package using a narrow-frame algorithm. Multi-scan absorption corrections were applied using SADABS.[79] The space groups were assigned using XPREP of the Bruker ShelXTL[80] software package. The structures were solved using ShelXT[80] and refined using SHelXL[80] and the graphical user interface ShelXle.[81] All non-hydrogen atoms were refined anisotropically. H atoms on carbon were positioned geometrically and constrained to ride on their parent atom. Additional crystallographic information is provided in the Supplemental Information. Structures of

complexes **8** – **12**, **14**, and **15** were deposited with the Cambridge Crystallographic Database and have reference numbers CCDC 1547999-1548003, 1548004, and 1548005, respectively. The cif files are also available as Supplementary Information.

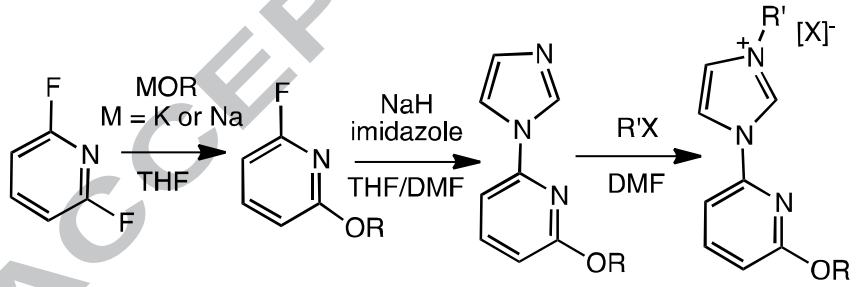
3. Result and Discussion

3.1. The synthesis of the compounds (1-15)

The N-heterocyclic carbene and pyridinol derived ligand precursors ($Im^{R'}$-py^{OR})X (Table 1, **1**-**4**) were readily synthesized by displacement of one *ortho*-fluorine from 2,6-difluoropyridine with NaOR followed by the substitution of the second *ortho*-fluorine with imidazole from sodium imidazolate.[82] The alkylation of the (Im-py^{OR}) compound with CH_3I, CH_3OTf, or CH_3CH_2Br resulted in the formation of imidazolium salts (Im^{R}-py^{OtBu})X , that differ in the R' and OR groups on the imidazole and pyridine ring, respectively, where R' = Me, Et and OR = O^{t}Bu, OMe (Table 1). Variation in the counter anion gave four compounds: (Im^{Me}-py^{OtBu})I (**1**), (Im^{Me}-py^{OtBu})PF_6 (**2**), (Im^{Et}-py^{OMe})Br (**3**), and (Im^{Me}-py^{OtBu})OTf (**4**) (Table 1). The purpose of the ^{t}Bu ether moiety was to serve as a protected form for obtaining the OH derivative in the metal complexes. Counter anion exchange was achieved readily by stirring the halide salt (**1**) in NH_4PF_6 or KPF_6 solution to form **2** (Scheme 3), by modifying literature procedures.[62]

Table 1: A numbering scheme for the compounds studied here. [a]These compounds (**4**, **6**, **7**) were synthesized in our previous work in reference [27].

Compound	Formula
1	$(Im^{Me}\text{-}py^{OtBu})I$
2	$(Im^{Me}\text{-}py^{OtBu})PF_6$
3	$(Im^{Et}\text{-}py^{OMe})Br$
4	$^{a}(Im^{Me}\text{-}py^{OtBu})OTf$
5	$[Ag(NHC^{Me}\text{-}py^{OtBu})_2]PF_6$
6	$^{a}[Ag(NHC^{Me}\text{-}py^{OtBu})_2]OTf$
7	$^{a}[Ag(NHC^{Me}\text{-}py^{OMe})_2]OTf$
8	$[(p\text{-}cym)Ru(NHC^{Me}\text{-}py^{OMe})Cl]OTf$
9	$[(p\text{-}cym)Ru(NHC^{Me}\text{-}py^{OtBu})Cl]OTf$
10	$[(p\text{-}cym)Ru(NHC^{Me}\text{-}py^{OH})Cl]OTf$
11	$[(p\text{-}cym)Ru(NHC^{Me}\text{-}py^{OtBu})Cl]PF_6$
12	$[(p\text{-}cym)Ru(NHC^{Et}\text{-}py^{OMe})Cl]PF_6$
13	$[(p\text{-}cym)Ru(NHC^{Me}\text{-}py^{OH})Cl]PO_2F_2$
14	$[Cp^*Ir(NHC^{Me}\text{-}py^{OtBu})Cl]PF_6$
15	$[Cp^*Ir(NHC^{Me}\text{-}py^{OH})Cl]PO_2F_2$



Scheme 3: The synthesis the imidazolium salts (**1**-**4**), $(Im^{R'}\text{-}py^{OR)}$. OR = tBu, Me; R' = Me, Et; $[X]^-$ = $[I]^-$, $[Br]^-$, $[OTf]^-$, $[PF_6]^-$. The first two steps were reported previously.[27]

The synthesis of $NHC^{R'}\text{-}py^{OR}$ metal complexes **5-15** is shown in Scheme 4. The imidazolium C2 position is readily deprotonated to generate an NHC. Upon treatment of the ligand precursors

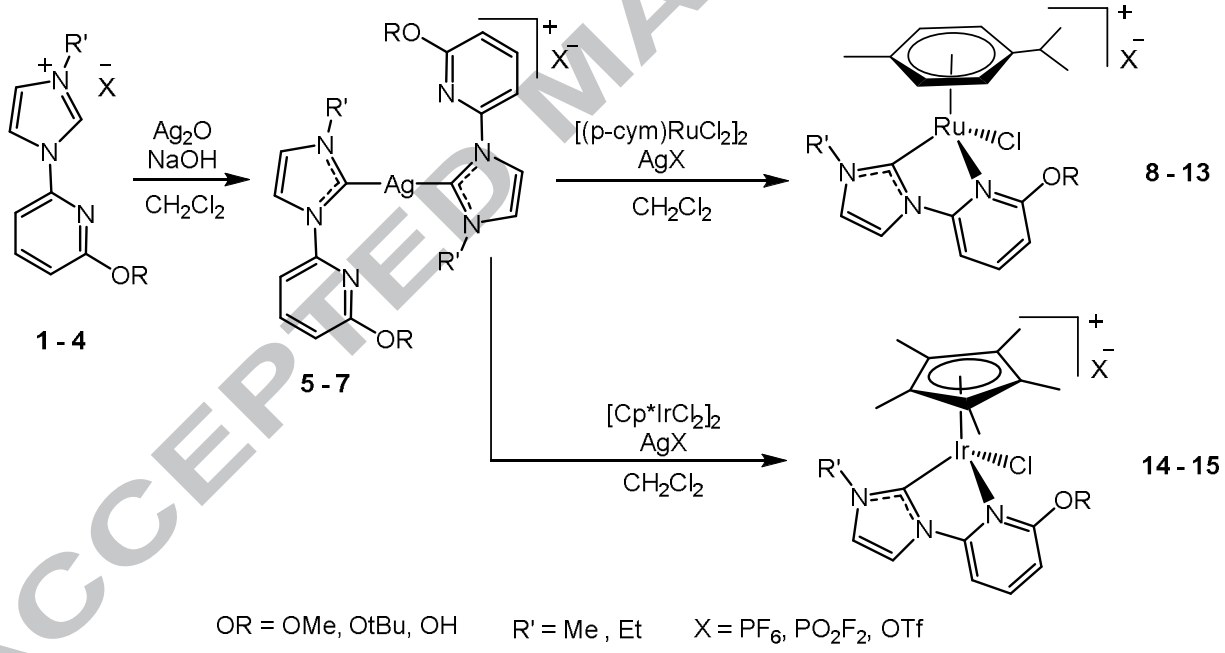
2 and **4** with Ag_2O and NaOH in the absence of light, silver bis(carbene) complexes were formed as $[Ag(NHC^{Me}\text{-}py^{OtBu})_2]PF_6$ (**5**) and $[Ag(NHC^{Me}\text{-}py^{OtBu})_2]OTf$ (**6**), respectively. $[Ag(NHC^{Me}\text{-}py^{OMe})_2]OTf$ (**7**) was made similarly, as reported previously.[27] The crystal structures of (**6**) and (**7**) have been reported previously, and we believe that (**5**) has a similar geometry based upon similar spectral features.[27]

Transmetallation of the silver bis(carbene) complex **5**, **6,** and **7** with the chloro-bridged dimeric ruthenium precursors $[(p\text{-cym})RuCl_2]_2$ and one equivalent of AgX afforded the chelate complexes $[(p\text{-cym})Ru(NHC^{Me}\text{-}py^{OMe})Cl]OTf$ (**8**), $[(p\text{-cym})Ru(NHC^{Me}\text{-}py^{OtBu})Cl]OTf$ (**9**), and $[(p\text{-cym})Ru(NHC^{Me}\text{-}py^{OtBu})Cl]PF_6$ (**11**) by use of X = $[OTf]^-$ or $[PF_6]^-$ as appropriate. The complex $[(p\text{-cym})Ru(NHC^{Et}\text{-}py^{OMe})Cl]PF_6$ (**12**) was made similarly from **3**, but in this case we did not isolate the silver carbene complex. The ^{t}Bu ether deprotection of **9** to form $[(p\text{-cym})Ru(NHC^{Me}\text{-}py^{OH})Cl]OTf$ (**10**) was achieved by superheating a CH_2Cl_2 solution or reflux of a CH_3CN solution. The driving force for the deprotection reaction is elimination of isobutene. Finally, for Ir species, similar to the synthesis of **8-13**, $[Cp^*IrCl_2]_2$ was used as our iridium source to obtain $[Cp^*Ir(NHC^{Me}\text{-}py^{OtBu})Cl]PF_6$ (**14**).

However, attempts to deprotect complex **11** by a similar procedure led to the isolation of $[(p\text{-cym})Ru(NHC^{Me}\text{-}py^{OH})Cl]PO_2F_2$ (**13**) (see Figure S27 for synthetic details and spectra). The formation of $[PO_2F_2]^-$ counter anion appears to be due to the hydrolysis of the $[PF_6]^-$ anion using adventitious water or the *in situ* formed OH group as a proton source (eq. 1). The hydrolysis of PF_6 was also observed when **14** was de-protected to form $[Cp^*Ir(NHC^{Me}\text{-}py^{OH})Cl]PO_2F_2$ (**15**). For several of these complexes, the hydrolysis of PF_6^- leads to the appearance of multiple peaks in the ^{19}F NMR. It is plausible that these peaks represent $PO_2F_2^-$ and species on the way to this product (see the supporting information).

$[PF_6]^-$ + $2H_2O$ → $[PO_2F_2]^-$ + 4 HF (1)

The literature shows that $[PF_6]^-$ can be thermally decomposed to PF_5 and F^-, and PF_5 can be further transformed to $O{=}PF_3$ in the presence of water.[83-85] In our case, it appears that the $O{=}PF_3$ was formed *in situ* and reacted further with water to form $[PO_2F_2]^-$ and HF. Others have observed similar reactions.[86-90] While we did not characterize the HF formed in this reaction, we did note that the glassware appeared to etch after running these reactions. Due to the hydrolysis of the $[PF_6]^-$ anion, we have preferred to use the $[OTf]^-$ salts for reactivity studies.



Scheme 4: The synthesis of NHC-py^{OR} metal complexes **5-15**

3.2. NMR spectroscopy of ruthenium and iridium complexes

The protons of the aromatic cymene ligand in complexes **8-13** are shifted downfield due to the chelation of the NHC-py^{OR} group. The methyl groups of the isopropyl substituent on cymene are inequivalent by ^{1}H-NMR, that is consistent with the central metal being a stereogenic element. The chemical shifts of the protons of the pyridine ring in complexes **8-10** are sensitive to the deprotection that converts py^{OtBu} to py^{OH} (Figure S20). These protons are shifted upfield by as much as 0.22 ppm by ^{1}H NMR when comparing **10** (OH group) to its methoxy (**8**) and t-butoxy (**9**) analogs. Complexes **9** and **11** only differ in counter anion, and there are no significant differences in ^{1}H-NMR spectra between these complexes (Figure S28).

3.3. Crystal structures of complexes 8-15

The crystal structures of the complexes **8**-**12** and **14**-**15** are shown as molecular diagrams in Figures 1, 2, and 3 with bond lengths and angles in Table 2. We were able to recrystallize all of the Ru and Ir complexes, except for [(*p*-cym)Ru(NHC^{Me}-py^{OH})Cl]PO_2F_2 (**13**). Crystals suitable for X-ray diffraction were typically obtained by layering a solution of dichloromethane with ether. All of the Ru-complexes **8**-**12** display piano stool structures with the cymene ligand η^6 coordinated to the Ru(II) center. The Ru-$C_{carbene}$, Ru-N, and Ru-Cl bond distances are all quite similar to each other and to similar complexes in the literature.[91-96] The C-Ru-N bite angles are all similar and range from 76.0(1)° to 76.5(1)°.

Both complexes **14** and **15** feature a half sandwich structure with the Cp* ligand η^5 coordinated to the Ir(III) metal center. The bond lengths and angles of these complexes are similar to each other (Table 2) and to other Ir(III) complexes including those in our recently published work.[27] The average M-$C_{carbene}$ distance are shorter than the M-N bond (despite N

(75 pm) having a smaller covalent radius than C (77 pm)) for all of the complexes (**8-15**) due to the strong σ donating and moderate π accepting properties of the NHC ligand.[97]

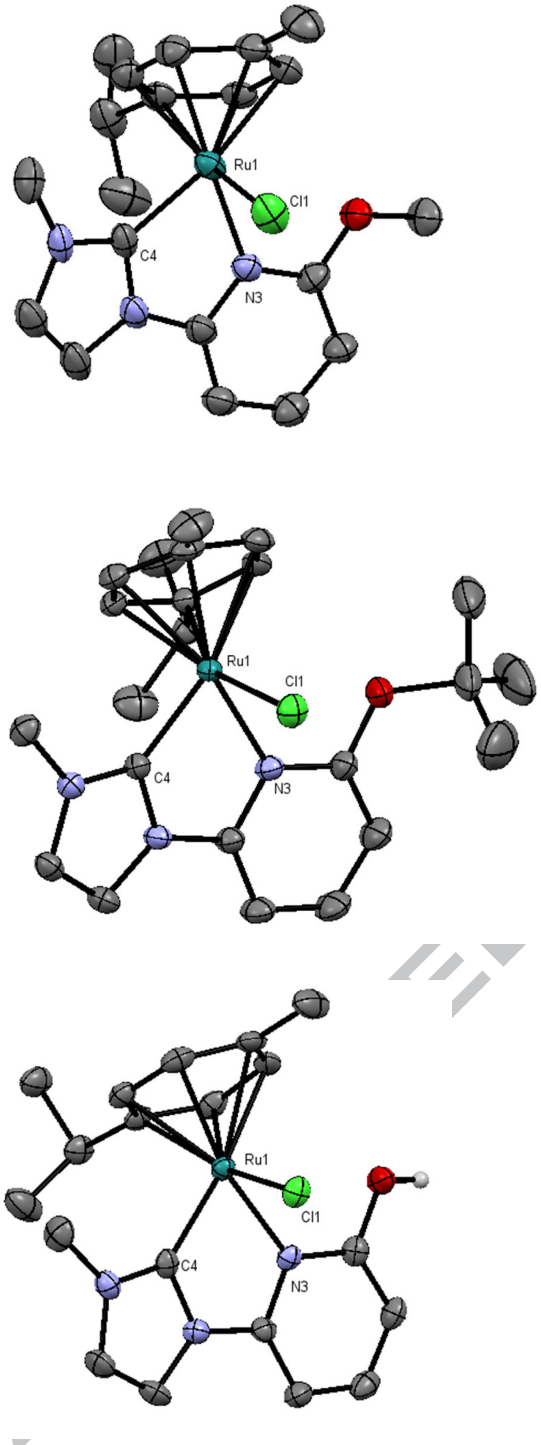


Figure 1: The ORTEP diagrams with 50% probability ellipsoids of [(*p*-cym)Ru(NHC^{Me}-py^{OMe})Cl]OTf **8** (top), [(*p*-cym)Ru(NHC^{Me}-py^{OtBu})Cl]OTf **9** (middle), and [(*p*-cym)Ru(NHC^{Me}-py^{OH})Cl]OTf **10** (bottom). Hydrogen atoms (except for the H of the OH group in **10**) and counter anions are omitted for clarity. Atom color codes are carbon (gray) and oxygen (red). These structures are oriented such that the chloride is forward from the plane of the bidentate ligand. Structural parameters are included in the Supporting Information. Complexes **8** and **10**

are disordered with regards to the position of NHC and pyridine rings, and that disorder is omitted here for clarity.

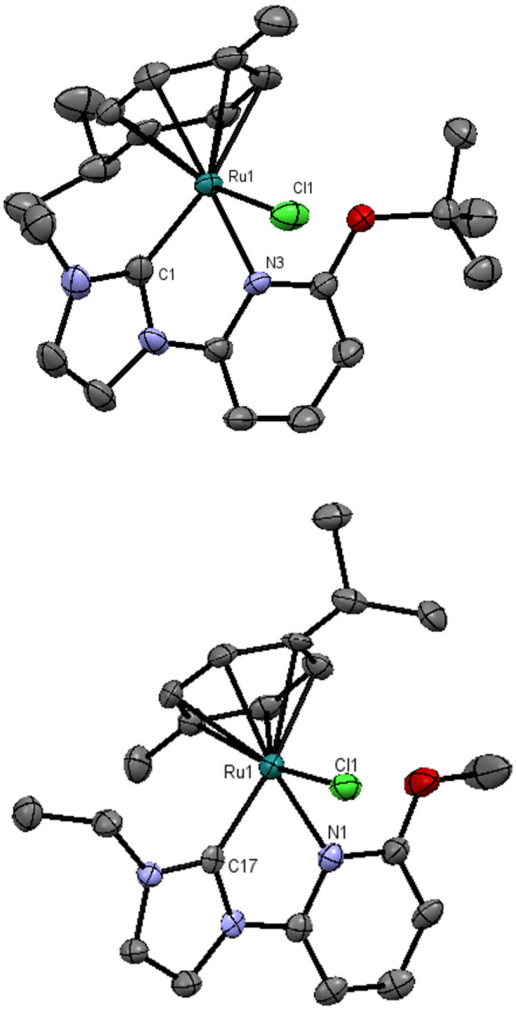


Figure 2: The ORTEP diagrams with 50% probability ellipsoids of [(*p*-cym)Ru(NHC^{Me}-py^{OtBu})Cl]PF_6 **11** (top) and [(*p*-cym)Ru(NHC^{Et}-py^{OMe})Cl]PF_6 **12** (bottom). Hydrogen atoms and counter anions are omitted for clarity. Atom color codes are carbon (gray) and oxygen (red). These structures are oriented such that the chloride is forward from the plane of the bidentate ligand. Structural parameters are included in the Supporting Information. Complex **12** is disordered with regards to the position of the NHC and pyridine rings, and that disorder is omitted here for clarity.

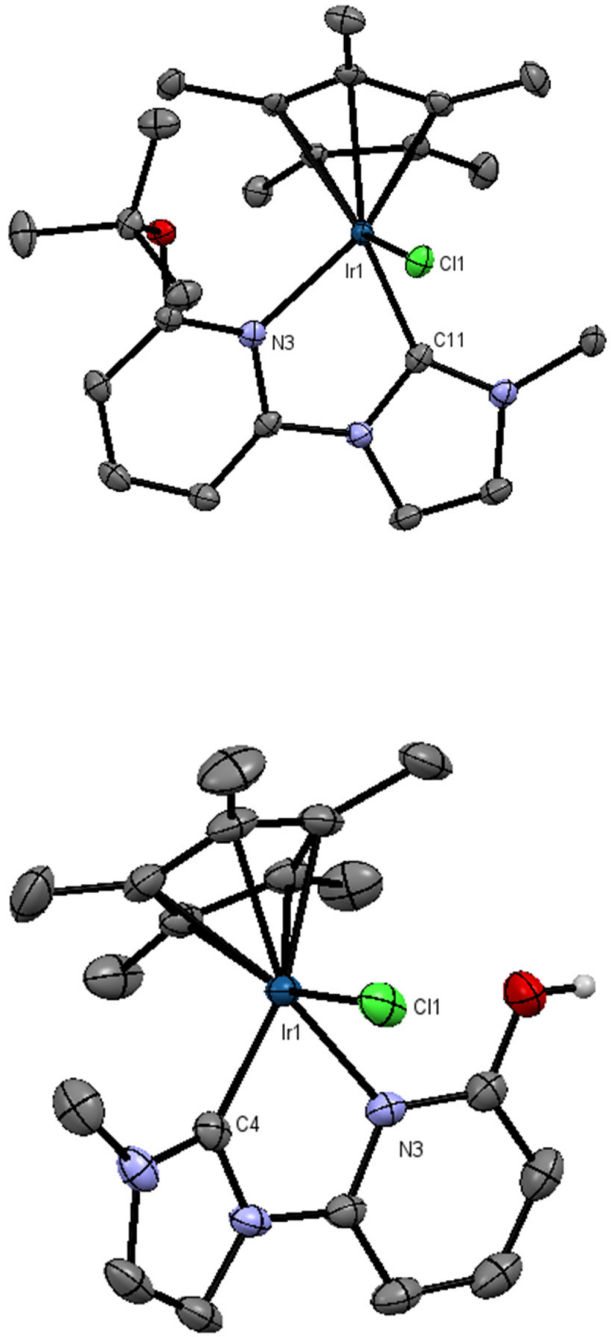


Figure 3: The ORTEP diagrams with 50% probability ellipsoid of [Cp*Ir(NHC^{Me}-py^{OtBu})Cl]PF_6 **14** (top) and [Cp*Ir(NHC^{Me}-py^{OH})Cl]PO_2F_2 **15** (bottom). Hydrogen atoms (except for the H of the OH group in **15**) and counter anions are omitted for clarity. Atom color codes are carbon (gray) and oxygen (red). These structures are oriented such that the chloride is forward from the plane of the bidentate ligand. Structural parameters are included in the Supporting Information.

Table 2: Selected bond lengths and angles of the complexes **8-15**.

Compound[a]	Bite Angle (°)	Bond Length (Å) Ru-Cl	Ru-N	Ru-$C_{carbene}$
8[b]	76.3(2)	2.398(1)	2.102(4)	2.049(5)
9	76.5(1)	2.407(1)	2.135(1)	2.013(1)
10[c]	76.2(2)	2.402(1)	2.137(4)	2.015(5)
11	76.2(1)	2.404(1)	2.130(3)	2.019(4)
12[d]	76.0(1)	2.415(2)	2.09(2)	2.09(2)
	Avg = 76.2(1)	**Avg = 2.405(1)**	**Avg = 2.119(5)**	**Avg = 2.037(5)**
		Ir-Cl	Ir-N	Ir-$C_{carbene}$
14	76.5(1)	2.409(1)	2.149(3)	2.008(4)
15	75.7(1)	2.408(1)	2.116(2)	2.017(2)
	Avg = 76.1(1)	**Avg = 2.408(1)**	**Avg = 2.133(1)**	**Avg = 2.013(1)**

[a]Compound **8** contains two independent molecules in the unit cell and contains flip disorder of the bidentate ligand, which results in four moieties, A/C and B/D. Compound **10** contains two independent molecules in the unit cell, which results in two moieties, 1/2. Compound **12** contains flip disorder of the bidentate ligand, which results in two moieties, A/B. [b]Bite angle and bond distances are for moiety A. [c]Bite angle and bond distances are for moiety 1. [d]Bite angle and bond distances are for moiety A.

3.4. Reactivity

Ruthenium complexes are known to catalyze many reactions including hydrogenation and dehydrogenation.[98, 99] We were interested in exploring the reactivity of our ruthenium complexes towards the hydrogenation of CO_2 and the dehydrogenation of formic acid. We chose to study complexes **8** and **9** as pre-catalysts because the triflate counter anion is stable and does not undergo unwanted transformations.

CO_2 hydrogenation was studied by dissolving the pre-catalysts **8** or **9** (at 0.3mM) in 1.0 M aqueous $NaHCO_3$ and then pressurizing the vessel with 300 psi of 1:1 CO_2:H_2 for 18 h at 115 °C. The literature has shown that both CO_2 and $NaHCO_3$ serve as substrates in this reaction, and removal of either component decreases the turnover numbers in our experience.[27, 100-102] Indeed, upon dissolving in aqueous solution, carbon dioxide forms CO_3^{2-} and HCO_3^- as aqueous ions. Sodium bicarbonate also serves as a base to raise the pH of the solution to around 8, which enhances the thermodynamic driving force for CO_2 hydrogenation because the product formed is formate rather than formic acid.[43] The extent of sodium formate production was measured by ^{1}H NMR spectroscopy with an internal standard. This allowed use to calculate turnover numbers (TON) and turnover frequency (TOF) (Table 3).

For formic acid (FA) dehydrogenation, the reaction was done by heating 1.02 M formic acid with 0.29 mM of the pre-catalyst **8** or **9** at 60°C for 3 h. The extent of reaction was determined by measuring the gas collected over water and using the ideal gas law to determine TON and TOF by assuming that the products formed are 1:1 CO_2 and H_2 (Table 3).

The order of reactivity for both reactions is that complex **8** is more active than **9**. Both complexes are best considered pre-catalysts as there were significant color changes and a small amount of brown precipitate observed at the end of the reaction. This observation indicates changes that may involve de-coordination of the cymene ligand from the complex.[61, 103, 104] Furthermore, our recent work has shown that iridium NHC-py^{OR} complexes are prone to cyclometallation reactions, and similar transformations may occur here as well.[27] The transformations seen for complexes **8** and **9** as well as iridium NHC-py^{OR} complexes[27] dissuaded us from undertaking a fully study of all the new metal complexes (including **10**)

reported herein. Nonetheless, the ligand system NHC-py^{OR} may be more promising with a metal less prone to cyclometallation and other side reactions.

Table 3: Catalytic CO_2 hydrogenation and FA dehydrogenation of complex **8** and **9**.[a]

	Hydrogenation		Dehydrogenation	
Catalysts	**TON**	**TOF(h^{-1})**	**TON**	**TOF (h^{-1})**
[(p-cym)Ru(NHC^{Me}-py^{OMe})Cl]OTf (**8**)	1440 (69)	80	180 (76)	60
[(p-cym)Ru(NHC^{Me}-py^{OtBu})Cl]OTf (**9**)	240 (36)	13	79 (69)	26

[a]Reaction conditions: All TON were calculated for 18 h for CO_2 hydrogenation and 3 h for FA dehydrogenation, and are an average of at least 2 trials. For hydrogenation, the reaction was performed in 25 mL of an aqueous solution of 0.3 mM pre-catalyst and 1 M $NaHCO_3$ at 115 °C and 300 psi of H_2/CO_2 (1:1). For dehydrogenation, aqueous formic acid (1.02 M) was treated with 0.29 mM of pre-catalyst at 60 °C.

4. Conclusion

In summary, we have synthesized new NHC$^{R'}$-py^{OR} complexes of Ru(II) and Ir(III) with various substituents on the pyridine and NHC rings and two different counter anions, $[OTf]^-$ and $[PF_6]^-$. [(*p*-cym)Ru(NHC^{Me}-py^{OR})Cl]$^+$ (**8-13**) and [Cp*Ir(NHC^{Me}-py^{OR})Cl]$^+$ (**14-15**) were synthesized in good yields by transmetallation of the bidentate ligand from [Ag(NHC^{Me}-py^{OR})$_2$]$^+$ at room temperature. The deprotection reaction of the t-butoxy group to form the hydroxy group shows that the $[PF_6]^-$ is unstable under the reaction conditions. The formation of $[PO_2F_2]^-$ is most likely due to the hydrolysis of $[PF_6]^-$ by adventitious moisture. A preliminary catalytic reactivity screening indicates that the ruthenium complexes **8** and **9** undergo further transformations when heated. Ruthenium catalysts derived from NHC-py^{OR} appear to be less robust than dhbp complexes. [27]

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Appendix A. Supplementary data. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/###. This includes spectra for all new compounds and crystallographic data (PDF). The atomic coordinates for these structures have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 1547999-1548005. These crystal structures are available as supporting information CIF format.

References

[1] C.S. Allardyce, P.J. Dyson, Platinum Met. Rev., 45 (2001) 62-69.
[2] Y.K. Yan, M. Melchart, A. Habtemariam, P.J. Sadler, Chem.Commun., (2005) 4764-4776.
[3] M. Galanski, V.B. Arion, M.A. Jakupec, B.K. Keppler, Curr. Pharm. Des., 9 (2003) 2078-2089.
[4] D.K. Heidary, B.S. Howerton, E.C. Glazer, J. Med. Chem., 57 (2014) 8936-8946.
[5] E. Wachter, A. Zamora, D.K. Heidary, J. Ruiz, E.C. Glazer, Chem.Commun., 52 (2016) 10121-10124.
[6] C. Moucheron, New J. Chem., 33 (2009) 235-245.
[7] F. Caruso, M. Rossi, A. Benson, C. Opazo, D. Freedman, E. Monti, M.B. Gariboldi, J. Shaulky, F. Marchetti, R. Pettinari, C. Pettinari, J. Med. Chem., 55 (2012) 1072-1081.
[8] B. O'Regan, M. Graetzel, Nature (London), 353 (1991) 737-740.
[9] W. Wu, S. Ji, W. Wu, J. Shao, H. Guo, T.D. James, J. Zhao, Chem. - Eur. J., 18 (2012) 4953-4964, S4953/4951-S4953/4929.
[10] K. Kalyanasundaram, Coord. Chem. Rev., 46 (1982) 159-244.
[11] M.R. Gill, J. Garcia-Lara, S.J. Foster, C. Smythe, G. Battaglia, J.A. Thomas, Nat. Chem., 1 (2009) 662-667.
[12] W. Chen, F.N. Rein, R.C. Rocha, Angew. Chem., Int. Ed., 48 (2009) 9672-9675, S9672/9671-S9672/9632.
[13] L. Sun, M. Burkitt, M. Tamm, M.K. Raymond, M. Abrahamsson, D. LeGourrierec, Y. Frapart, A. Magnuson, P.H. Kenez, P. Brandt, A. Tran, L. Hammarstroem, S. Styring, B. Aakermark, J. Am. Chem. Soc., 121 (1999) 6834-6842.
[14] J. Gu, J. Chen, R.H. Schmehl, J. Am. Chem. Soc., 132 (2010) 7338-7346.
[15] V.W. Manner, J.M. Mayer, J. Am. Chem. Soc., 131 (2009) 9874-9875.
[16] J. Zhao, S. Ji, W. Wu, W. Wu, H. Guo, J. Sun, H. Sun, Y. Liu, Q. Li, L. Huang, RSC Adv., 2 (2012) 1712-1728.
[17] K. Cao, J. Lu, J. Cui, Y. Shen, W. Chen, G. Alemu, Z. Wang, H. Yuan, J. Xu, M. Wang, Y. Cheng, J. Mater. Chem. A, 2 (2014) 4945-4953.
[18] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, Organometallics, 23 (2004) 1480-1483.
[19] R. Noyori, S. Hashiguchi, Acc. Chem. Res., 30 (1997) 97-102.
[20] C. Samojlowicz, M. Bieniek, K. Grela, Chem. Rev., 109 (2009) 3708-3742.
[21] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc., 114 (1992) 3974-3975.
[22] R.H. Grubbs, Angew. Chem., Int. Ed., 45 (2006) 3760-3765.
[23] S. Sanz, A. Azua, E. Peris, Dalton Trans., 39 (2010) 6339.
[24] M.Z. Ertem, Y. Himeda, E. Fujita, J.T. Muckerman, ACS Catal., 6 (2016) 600-609.
[25] J.F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D.J. Szalda, J.T. Muckerman, E. Fujita, Nature Chem., 4 (2012) 383-388.
[26] W.-H. Wang, J.F. Hull, J.T. Muckerman, E. Fujita, Y. Himeda, Energy Environ. Sci., 5 (2012) 7923-7926.
[27] S. Siek, D.B. Burks, D.L. Gerlach, G. Liang, J.M. Tesh, C.R. Thompson, F. Qu, J.E. Shankwitz, R.M. Vasquez, N.S. Chambers, G.J. Szulczewski, D.B. Grotjahn, C.E. Webster, E.T. Papish, Organometallics, 36 (2017) 1091-1106.
[28] R. Tanaka, M. Yamashita, L.W. Chung, K. Morokuma, K. Nozaki, Organometallics, 30 (2011) 6742-6750.
[29] R. Tanaka, M. Yamashita, K. Nozaki, J. Am. Chem. Soc., 131 (2009) 14168-14169.
[30] J.J.A. Calaje, Z. Lu, E.A. Kedzie, N.J. Terrile, J.N. Lo, T.J. Williams, Nature Commun., (2016) 11308-11313.
[31] P. Hu, Y. Diskin-Posner, Y. Ben-David, D. Milstein, ACS Catal., 4 (2014) 2649-2652.

[32] R. Langer, Y. Diskin-Posner, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, Angew. Chem., Int. Ed., 50 (2011) 9948-9952.
[33] Q. Liu, L. Wu, S. Gülak, N. Rockstroh, R. Jackstell, M. Beller, Angew. Chem. Int. Ed., 53 (2014) 7085-7088.
[34] E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge, M. Beller, Angew. Chem. Int. Ed., 52 (2013) 14162-14166.
[35] S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, Acc. Chem. Res., 48 (2015) 1995-2003.
[36] A.M. Royer, T.B. Rauchfuss, D.L. Gray, Organometallics, 29 (2010) 6763-6768.
[37] K.-i. Fujita, R. Kawahara, T. Aikawa, R. Yamaguchi, Angew. Chem., 127 (2015) 9185-9188.
[38] R. Kawahara, K.-i. Fujita, R. Yamaguchi, J. Am. Chem. Soc., 134 (2012) 3643-3646.
[39] K.-i. Fujita, N. Tanino, R. Yamaguchi, Org. Lett., 9 (2007) 109-111.
[40] C.M. Moore, B. Bark, N.K. Szymczak, ACS Catal., 6 (2016) 1981-1990.
[41] C.M. Moore, D.A. Quist, J.W. Kampf, N.K. Szymczak, Inorg. Chem., 53 (2014) 3278-3280.
[42] C.M. Moore, N.K. Szymczak, Chem. Commun., 49 (2013) 400-402.
[43] Y. Himeda, Eur. J. Inorg. Chem., 2007 (2007) 3927-3941.
[44] I. Nieto, M.S. Livings, J.B. Sacci, L.E. Reuther, M. Zeller, E.T. Papish, Organometallics, 30 (2011) 6339-6342.
[45] C.M. Conifer, R.A. Taylor, D.J. Law, G.J. Sunley, A.J.P. White, G.J.P. Britovsek, Dalton Trans., 40 (2011) 1031-1033.
[46] R. Kawahara, K.-i. Fujita, R. Yamaguchi, J. Am. Chem. Soc., 134 (2012) 3643-3646.
[47] J. DePasquale, I. Nieto, L.E. Reuther, C.J. Herbst-Gervasoni, J.J. Paul, V. Mochalin, M. Zeller, C.M. Thomas, A.W. Addison, E.T. Papish, Inorg. Chem., 52 (2013) 9175-9183.
[48] K.T. Hufziger, F.S. Thowfeik, D.J. Charboneau, I. Nieto, W.G. Dougherty, W.S. Kassel, T.J. Dudley, E.J. Merino, E.T. Papish, J.J. Paul, J. Inorg. Biochem., 130 (2014) 103-111.
[49] D.L. Gerlach, S. Bhagan, A.A. Cruce, D.B. Burks, I. Nieto, H.T. Truong, S.P. Kelley, C.J. Herbst-Gervasoni, K.L. Jernigan, M.K. Bowman, S. Pan, M. Zeller, E.T. Papish, Inorg. Chem., 53 (2014) 12689-12698.
[50] A.J. Arduengo, III, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc., 114 (1992) 5530-5534.
[51] A.J. Arduengo, III, R.L. Harlow, M. Kline, J. Am. Chem. Soc., 113 (1991) 361-363.
[52] C.M. Crudden, D.P. Allen, Coord. Chem. Rev., 248 (2004) 2247-2273.
[53] C.W. Bielawski, R.H. Grubbs, Angew. Chem., Int. Ed., 39 (2000) 2903-2906.
[54] Y. Mizuhata, T. Sasamori, N. Tokitoh, Chem. Rev., 109 (2009) 3479-3511.
[55] D. Gnanamgari, E.L.O. Sauer, N.D. Schley, C. Butler, C.D. Incarvito, R.H. Crabtree, Organometallics, 28 (2009) 321-325.
[56] J.A. Mata, M. Poyatos, E. Peris, Coord. Chem. Rev., 251 (2007) 841-859.
[57] E. Peris, R.H. Crabtree, Coord. Chem. Rev., 248 (2004) 2239-2246.
[58] S. Diez-Gonzalez, S.P. Nolan, Coord. Chem. Rev., 251 (2007) 874-883.
[59] T. Droege, F. Glorius, Angew. Chem., Int. Ed., 49 (2010) 6940-6952.
[60] J. DePasquale, N.J. White, E.J. Ennis, M. Zeller, J.P. Foley, E.T. Papish, Polyhedron, 58 (2013) 162-170.
[61] J. DePasquale, M. Kumar, M. Zeller, E.T. Papish, Organometallics, 32 (2013) 966-979.
[62] H.-S. Chen, W.-C. Chang, C. Su, T.-Y. Li, N.-M. Hsu, Y.S. Tingare, C.-Y. Li, J.-H. Shie, W.-R. Li, Dalton Trans., 40 (2011) 6765-6770.
[63] A.A. Danopoulos, D. Pugh, H. Smith, J. Saßmannshausen, Chem. Eur. J., 15 (2009) 5491-5502.
[64] S.P. Downing, A.A. Danopoulos, Organometallics, 25 (2006) 1337-1340.
[65] D. Pugh, J.A. Wright, S. Freeman, A.A. Danopoulos, Dalton Trans., (2006) 775-782.
[66] A.A. Danopoulos, N. Tsoureas, J.A. Wright, M.E. Light, Organometallics, 23 (2004) 166-168.
[67] A.A. Danopoulos, J.A. Wright, W.B. Motherwell, S. Ellwood, Organometallics, 23 (2004) 4807-4810.
[68] A.A. Danopoulos, A.A.D. Tulloch, S. Winston, G. Eastham, M.B. Hursthouse, Dalton Trans., (2003) 1009-1015.

[69] R.E. Douthwaite, D. Hauessinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Danopoulos, Organometallics, 18 (1999) 4584-4590.
[70] G.F. Caramori, A.O. Ortolan, R.L.T. Parreira, E.H. da Silva, J. Organomet. Chem., 799-800 (2015) 54-60.
[71] Y. Cheng, H.-J. Xu, J.-F. Sun, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, Dalton Trans., (2009) 7132-7140.
[72] J.M. Darmon, R.P. Yu, S.P. Semproni, Z.R. Turner, S.C.E. Stieber, S. DeBeer, P.J. Chirik, Organometallics, 33 (2014) 5423-5433.
[73] R.P. Yu, J.M. Darmon, J.M. Hoyt, G.W. Margulieux, Z.R. Turner, P.J. Chirik, ACS Catal., 2 (2012) 1760-1764.
[74] R.P. Yu, J.M. Darmon, C. Milsmann, G.W. Margulieux, S.C.E. Stieber, S. DeBeer, P.J. Chirik, J. Am. Chem. Soc., 135 (2013) 13168-13184.
[75] A. Raba, M. Cokoja, S. Ewald, K. Riener, E. Herdtweck, A. Poethig, W.A. Herrmann, F.E. Kuehn, Organometallics, 31 (2012) 2793-2800.
[76] K. Riener, M.J. Bitzer, A. Poethig, A. Raba, M. Cokoja, W.A. Herrmann, F.E. Kuehn, Inorg. Chem., 53 (2014) 12767-12777.
[77] Bruker, in: Apex2 2013.10-0, Bruker AXS Inc, Madison, Wisconsin USA, 2007.
[78] Bruker, in: Saint Plus 8.34A, Bruker AXS Inc, Madison, Wisconsin USA, 2007.
[79] Bruker, in: SADABS 2012/1, Bruker AXS Inc, Madison, Wisconsin USA, 2001.
[80] G.M. Sheldrick, Acta Cryst., A64 (2008) 112-122.
[81] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Cryst., 44 (2011) 1281-1284.
[82] M. Schlosser, T. Rausis, Helv. Chim. Acta, 88 (2005) 1240-1249.
[83] T.C. Ehlert, M.-M. Hsia, J. Chem. Eng. Data, 17 (1972) 18-21.
[84] K.G. Rutherford, W.A. Redmond, J. Org. Chem., 28 (1963) 568-571.
[85] K.S. Gavritchev, G.A. Sharpataya, A.A. Smagin, E.N. Malyi, V.A. Matyukha, J. Therm. Anal. Calorim., 73 (2003) 71-83.
[86] R. Fernandezgalan, B.R. Manzano, A. Otero, M. Lanfranchi, M.A. Pellinghelli, Inorg. Chem., 33 (1994) 2309-2312.
[87] D.H. Gibson, Y. Ding, R.L. Miller, B.A. Sleadd, M.S. Mashuta, J.F. Richardson, Polyhedron, 18 (1999) 1189-1200.
[88] O.V. Gusev, A.M. Kalsin, M.G. Peterleitner, P.V. Petrovskii, K.A. Lyssenko, N.G. Akhmedov, C. Bianchini, A. Meli, W. Oberhauser, Organometallics, 21 (2002) 3637-3649.
[89] I. Ino, J.C. Zhong, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, Y. Kitamori, Inorg. Chem., 39 (2000) 4273-4279.
[90] S. Kitagawa, S. Kawata, Y. Nozaka, M. Munakata, Journal of the Chemical Society-Dalton Transactions, (1993) 1399-1404.
[91] S. Sanz, A. Azua, E. Peris, Dalton Trans., 39 (2010) 6339-6343.
[92] C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy, M. Albrecht, Organometallics, 28 (2009) 5112-5121.
[93] S. Hohloch, L. Suntrup, B. Sarkar, Organometallics, 32 (2013) 7376-7385.
[94] K. Ogata, S. Inomata, S.-i. Fukuzawa, Dalton Trans., 42 (2013) 2362-2365.
[95] M. Delgado-Rebollo, D. Canseco-Gonzalez, M. Hollering, H. Mueller-Bunz, M. Albrecht, Dalton Trans., 43 (2014) 4462-4473.
[96] S. Horn, C. Gandolfi, M. Albrecht, Eur. J. Inorg. Chem., 2011 (2011) 2863-2868.
[97] A.J. Arduengo, Acc. Chem. Res., 32 (1999) 913-921.
[98] V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, Coord. Chem. Rev., 251 (2007) 765-794.
[99] M. Poyatos, J.A. Mata, E. Falomir, R.H. Crabtree, E. Peris, Organometallics, 22 (2003) 1110-1114.
[100] W.-H. Wang, Y. Himeda, J.T. Muckerman, G.F. Manbeck, E. Fujita, Chem. Rev., 115 (2015) 12936-12973.
[101] J. Elek, L. Nadasdi, G. Papp, G. Laurenczy, F. Joo, Appl. Catal. A 255 (2003) 59–67.
[102] I. Jószai, F. Joó, J. Mol. Catal. A: Chem., 224 (2004) 87-91.
[103] R. Castarlenas, M.A. Esteruelas, E. Onate, Organometallics, 24 (2005) 4343-4346.

[104] R. Noyori, M. Yamakawa, S. Hashiguchi, J. Org. Chem., 66 (2001) 7931-7944.

Highlights:

- Eight new complexes of a recently reported bidentate ligand are described, wherein the ligand merges an N-heterocyclic carbene with a pyridinol derived ring containing a proximal OH group.
- Silver, ruthenium, and iridium complexes of a new bidentate ligand have been synthesized and fully characterized by spectroscopic, analytical, and crystallographic methods.
- These complexes have been used as pre-catalysts for carbon dioxide hydrogenation and formic acid dehydrogenation.
- We observe transformations in the PF_6^- anion (to form $PO_2F_2^-$) associated with the metal complexes.