DOI: 10.1002/chem.201101557

Preparation of Mononuclear, Homodinuclear, and Heterotrinuclear Complexes by Salicylaldiminato-Functionalized Imidazolium Salt: Approach to Multifunctional Catalysts

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Dedicated to Professor Zu-En Huang on the occasion of his 80th birthday

Abstract: A salicylaldiminato imidazolium salt that bears both a Schiff base and imidazolium salt moiety was used to synthesize heterometallic compounds that could serve as multifunctional catalysts in certain reactions. The successful preparation of seven mononuclear compounds with a variety of transition metals (Pd, Ir, Ru, Zn, Ni) illustrated the high versatility of this class of ligands, which is crucial for the design of catalysts. Synthesis of homodinuclear compounds and heterotrinuclear compounds provided practical methods to connect multiple metal fragments through these ligands. The heterotrinuclear complex (Ni/Ir) was employed as a catalyst in the reaction of dehalogenation/transfer hydrogenation of halo-acetophenones. The preliminary catalytic study showed that this heterometallic species is more active than a combination of the corresponding monometallic species.

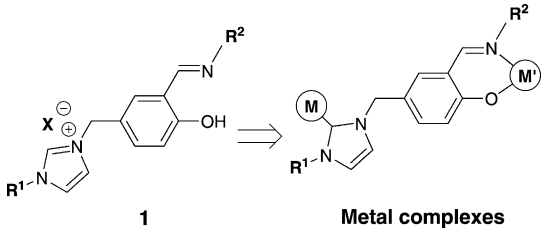
Keywords: heterometallic complexes · nitrogen heterocyclic carbenes · Schiff bases · tandem reactions · transition metals

Introduction

The classical approach for catalyst design is to develop highly selective catalysts for a single step in a specific reaction. However, increasing demands for environmentally benign and economical synthetic processes have necessitated the development of one-pot multiple catalytic transformations to obtain desired products in the most efficient ways.[1] Among the new approaches for organic transformations, developments of a single catalyst to mediate two or more reactions in a single synthetic operation provide one solution to achieve high catalytic efficiency and low environmental impact.[2] The advantages of such catalysts are evident, as the use of single multifunctional catalysts will save large amounts of time, solvents, reagents, and reaction workups during the preparations of both catalysts and the catalytic processes.[3]

To prepare a catalyst for a multistep process, highly versatile and stabile ligands are essential. N-Heterocyclic carbenes (NHCs), ubiquitous ligands for homogeneous catalysts, can bind to a wide range of metals with different oxidation states, thereby affording transition-metal compounds that are generally resistant to decomposition.[4] In the past few years, a number of NHC-based homometallic and heterometallic complexes with biscarbene ligands have been developed,[5] and the triazolium biscarbene heterometallic complexes have been successfully applied as multifunctional catalysts in catalyzing certain tandem processes.[6] However, homometallic and heterometallic complexes based on the same coordination manner, such as NHC–metal coordination, could face limitations in catalyzing multiple reactions that are fundamentally different in nature. Therefore, it is necessary to develop new ligands with different coordination manners to obtain more versatile catalysts for a wider range of reactions.

With these in mind, we envisioned that ligands (**1**, Scheme 1) that contained both a Schiff base and imidazolium salt moiety (precursor for in situ generating NHC) could be suitable candidates for the synthesis of multifunctional catalysts. Thus, we decided to develop a practical methodology to obtain heterometal complexes. Herein we describe the synthesis of ligands **1a–c** and their coordination with transition metals to afford monometal, homodimetal and heterotrimetal complexes of Ir, Ru, Pd, Ni, and Zn. We also report the preliminary results of the catalytic activity of heterotrimetal complex **7b** (Ni/Ir) in a tandem reaction.



Scheme 1. Salicylaldiminato imidazolium salt **1**.

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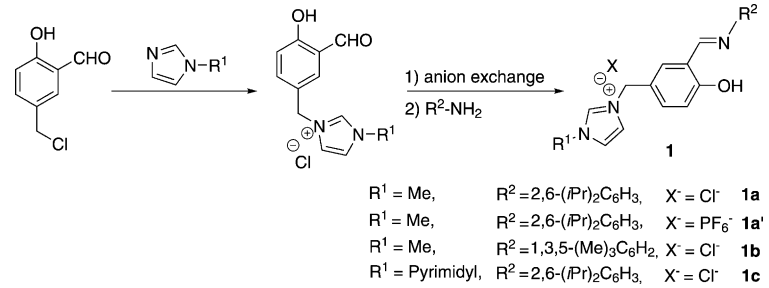
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201101557.

Results and Discussion

Synthesis and characterization of ligands: Ligands (**1a–c**) with both a Schiff base and imidazolium salt moiety were prepared by using two different amines (mesitylamine and 2,6-diisopropylaniline) and two substituted imidazoles [1-methylimidazole and 2-(1-imidazolyl)pyrimidine] (Scheme 2).[7] Compound **1a′**, an anion-exchange product, was obtained by using NH_4PF_6 as the anion-exchange reagent. All the ligands were characterized by NMR spectroscopy, elemental analysis, and in the case of the ligand **1a′**, by X-ray diffraction studies.

The molecular structure of ligand **1a′** (Figure 1) shows that the plane created by the phenolic aryl ring is roughly perpendicular to the both imidazole and diisopropylphenyl rings, as indicated by the dihedral angles (97.4 and 99.1°, respectively). This structure also suggests that the N,O-chelating moiety and the imidazole moiety could not coordinate to the same metal ion due to the rigidity of the phenyl ring.



Scheme 2. Synthesis of ligands **1a–c**.

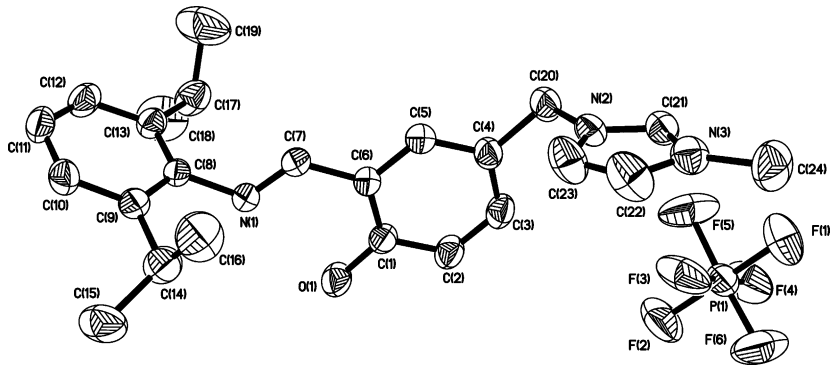
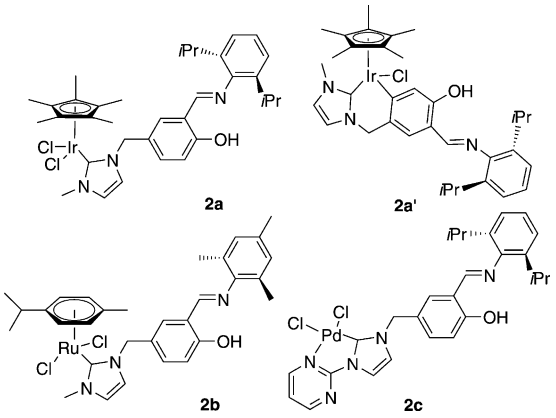


Figure 1. X-ray structure of compound **1a′**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–C(12) 1.270(3), N(3)–C(2) 1.307(3), N(2)–C(2) 1.316(3), N(3)–C(2) 1.307(3), O(1)–C(9) 1.336(3); N(2)-C(5)-C(6) 112.65(19), C(12)-N(1)-C(13) 117.74(18), N(1)-C(12)-C(10) 122.8(2).

Synthesis and characterization of monometal NHC complexes: To explore the coordination properties of these ligands, monometal NHC complexes (**2a–c**) were prepared by in situ transmetalation from the silver carbene complexes of ligands **1a–c** with different transition-metal complexes.[8] In the reaction between ligand **1a** and [{Cp*$IrCl_2$}$_2$] (Cp* = pentamethylcyclopentadiene), we also isolated a minor product **2a′**, which could arise from intramolecular C–H activation. All four compounds were characterized by NMR spectroscopy, elemental analysis, and in the case of the complex **2a**, by X-ray diffraction studies.



The ^{1}H NMR spectra of **2a–c** showed the absence of the downfield-shifted NC*H*N resonance, thus indicating the deprotonation of the acidic proton of **1a–c**. The $^{13}C\{^1H\}$ NMR spectra provide more direct evidence of the metalation, as seen by the signal at $\delta = 156.20$ and 156.68 ppm, assigned to the Ir–$C_{carbene}$ of **2a** and **2a′**; $\delta = 173.84$ ppm, assigned to the Ru–$C_{carbene}$ of **2b**; and $\delta = 156.78$ ppm, assigned to the Pd–$C_{carbene}$ of **2c**. Furthermore, the protons of the CH_2 of benzyl group of these two Ir complexes **2a** and **2a′** are diastereotopic and display signals at $\delta = 6.35$ and 4.77 ppm ($J = 14.0$ Hz) for **2a** and at $\delta = 4.85$ and 4.67 ppm ($J = 13.6$ Hz) for **2a′**, which are consistent with the research of Peris et al.[8a] Crystals of compound **2a** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of **2a** in CH_2Cl_2. The X-ray structure of **2a** can be regarded as a three-legged piano-stool (Figure 2). Together with the NHC moiety, two chloro atoms and a Cp* ring complete the coordination sphere about the Ir center. The plane of imidazole ring and the plane of phenol ring is perpendicular with a dihedral angle of 93.8°. The distances of Ir–$C_{carbene}$ (2.033 Å), Ir–Cl (2.414 and 2.426 Å), and Ir–Cp*(centroid) (1.790 Å) are in the range of other analogous [Cp*Ir(NHC)] complexes.[8a,9]

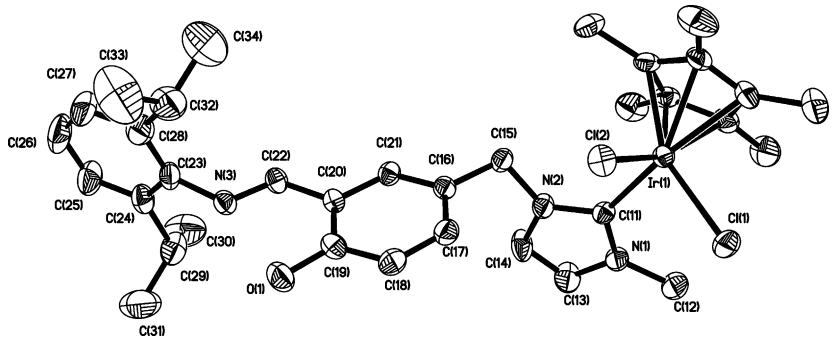
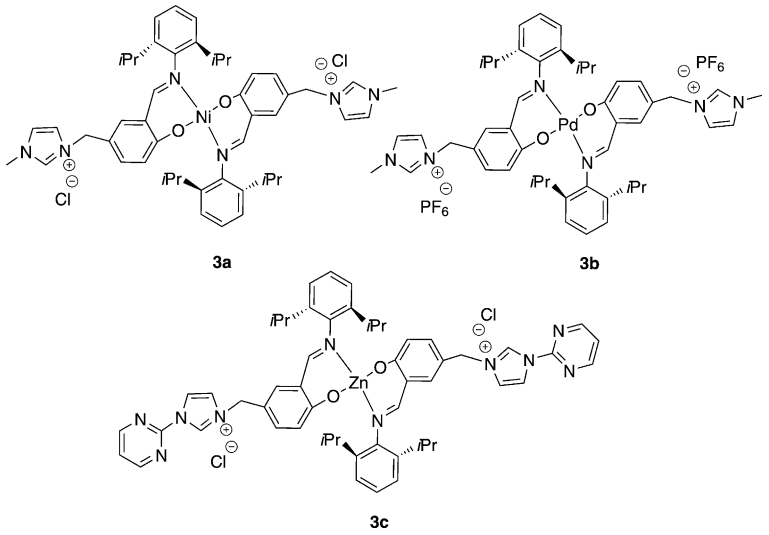


Figure 2. X-ray structure of compound **2a**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(11) 2.032(7), Ir(1)–Cl(1) 2.426(2), Ir(1)–Cl(2) 2.414(2), Ir(1)–Cp*(centroid) 1.790; C(11)-Ir(1)-Cl(1) 93.2(2), C(11)-Ir(1)-Cl(2) 92.1(2), N(2)-C(15)-C(16) 112.2(6), C(22)-N(3)-C(23) 121.3(7), N(3)-C(22)-C(20) 122.2(7).

Synthesis and characterization of monometal Schiff base complexes: By the treatment of ligands **1a**, **1a′**, or **1c** with metal acetates, we isolated a series of monometal Schiff base complexes (**3a**–**c**).[10] All of these complexes **3a**–**c** were characterized by NMR spectroscopy, elemental analysis, and in the case of complex **3b**, by X-ray diffraction studies.



The ^{1}H NMR spectra of compounds **3a**–**c** show the resonances of the NC*H*N protons and the disappearance of the O*H* protons, thereby indicating that the coordination has occurred in the Schiff base moiety. The X-ray structure of **3b** (Figure 3) shows an ideal square-planar geometry around the Pd center, which is similar to other analogous Schiff base Pd complexes.[10d,11] The plane of the phenolic aryl ring is roughly perpendicular to the planes of both imidazole and diisopropylphenyl rings (dihedral angle of 98.2 and 93.9°, respectively).

Unlike the reaction of ligand **1a′** with $Pd(OAc)_2$, we failed to obtain Schiff base Pd complex by the reaction of ligand **1a** and $Pd(OAc)_2$ due to the possible reaction of the imidazolium salt moiety and $Pd(OAc)_2$. Reaction of **1a** with $Co(OAc)_2$ in methanol heated to reflux in the presence of NaOMe yielded unexpected complex **4** (Scheme 3), which had a pentacoordinated Co center with the axial coordination site occupied by a free 1-methylimidazole ligand, produced by the displacement of the imidazole moiety in ligand **1a** with MeO^-. Reaction of **1a** with $[\{Cp^*IrCl_2\}_2]$ in THF in the presence of KO*t*Bu yielded complex **5** (Scheme 3). The structures of **4** and **5** were confirmed by elemental analysis and X-ray diffraction studies (Figure 4) and in the case of **5** by NMR spectroscopy. The formation of **4** and **5** revealed that ligand **1a** with counteranion Cl^- was not suitable for strong alkaline reaction conditions because the C–N bond between the imidazole group and the benzyl group was susceptible to nucleophilic attack.

Synthesis and characterization of homodimetal complexes: To further explore the reactivity of these ligands towards metal ions, we synthesized a series of homodimetallic complexes by reactions of ligand **1a′** with $[\{Cp^*IrCl_2\}_2]$ or $[\{IrCl(cod)\}_2]$ (cod = cyclooctadiene) in the presence of base. Two air-stable dinuclear complexes **6a** and **6b** were synthesized, as shown in Scheme 4.

The ^{1}H NMR spectrum of **6a** shows the disappearance of the resonances of the NC*H*N protons and Ph–O*H* protons, thus suggesting that double coordination has occurred. The ^{13}C NMR spectrum also confirms this with two signals at $\delta = 180.62$ and 165.97 ppm (Ir^I-O-*C* and Ir^I–$C_{carbene}$, respectively), similar to related iridium(I) complexes.[12] Crystals of **6a** suitable for X-ray diffraction were obtained from slow evaporation of dichloromethane/hexane (1:6) solution. Figure 5 shows the X-ray structure of **6a** and the most representative distances and angles. The structure reveals the expected square-planar arrangement of the ligands at both Ir^I centers. The NHC plane lies close to perpendicular to the $Ir_{carbene}$ coordination plane with a dihedral angle of 80.0°. The six-membered chelating ring Ir(1)-O(1)-C(27)-C(22)-C(21)-N(3) is located in the same plane. The distances of Ir–O, Ir–N, and Ir–$C_{carbene}$ are 2.009, 2.056, and 2.019 Å.

The ^{1}H NMR spectrum of **6b** shows the two singlets from two Cp* ligands ($\delta = 1.46$ and 1.74 ppm). The orthometalation could be observed by the benzyl methylene ($-CH_2-$) resonance at $\delta = 4.82$ and 4.69 ppm ($J = 14.4$ Hz). The $^{13}C\{^1H\}$ NMR spectrum confirms the double metalation, with two signals at $\delta = 172.19$ and 155.17 ppm (Ir^{III}-O-*C* and Ir^{III}–$C_{carbene}$, respectively). The ^{31}P NMR spectrum of **6b** also exhibits a septet signal of $\delta = -136.76$ to -150.83 ppm. The X-ray structure of **6b** (Figure 6) reveals that **6b** is a cationic compound with a PF_6^- as anion. It also shows that one Cp^*Ir^{III} is coordinated by the NHC ligand through the carbene and phenyl fragment; the other Cp^*Ir^{III} is coordinated by the O and N atoms of the salicylaldiminato fragment. The structure also indicates that the orthometalation of the phenyl ring of the imidazolylidene ligand has occurred, thus leading to a chelate coordination of the ligand with a bite angle of 84.5°. The Ir–O distance of 1.966 Å is shorter than in previous reports by the groups of Suzuki[13] and Meng,[14] which can be rationalized on the basis of steric repulsions between the Cp* ring and the isopropyl group. This steric hindrance may also lead to the loss of Cl^- from the iridium atom, but to form a more stable cationic compound with a weak coordinating anion, such as PF_6^-. The Ir–$C_{carbene}$ and Ir–C_{phenyl} distances are 2.02 and 2.06 Å, respectively, similar to other related [Cp*Ir(NHC)] complexes. The $Ir_{carbene}$–Cl (2.41 Å) and $Ir_{carbene}$–Cp*(centroid) (1.828 Å) distances lie in the expected range for other known [Cp*Ir(NHC)] complexes.[8a,9]

The successful preparation of **6a** and **6b** reveals that ligand **1a′** is more stable than ligand **1a** in strong alkaline conditions.

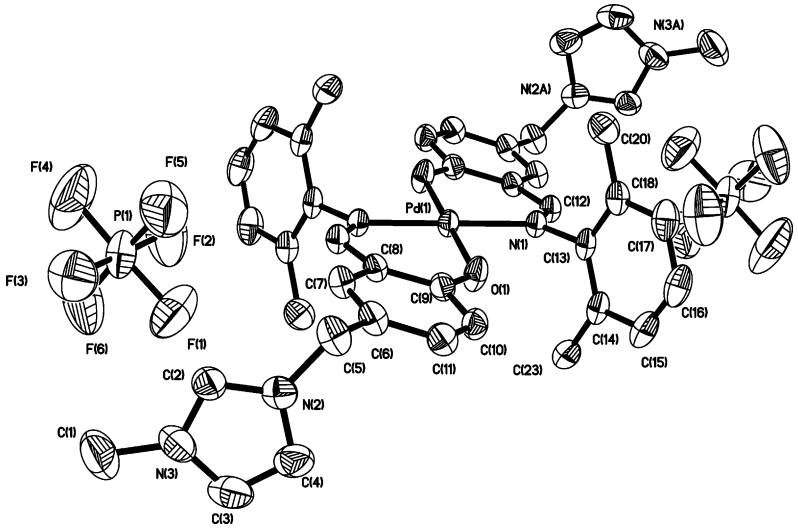
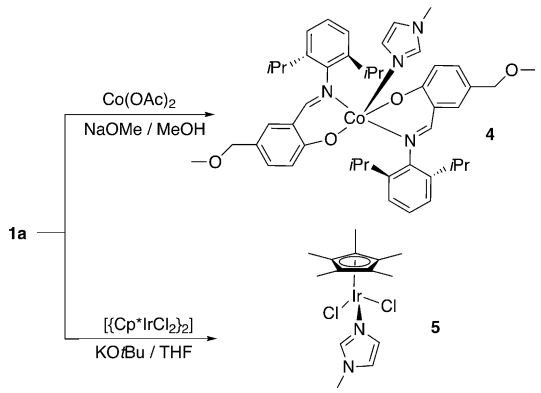


Figure 3. X-ray structure of compound **3b**. Ellipsoids at the 30% probability level. Hydrogen atoms and part of the isopropyl group have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–O(1) 1.968(3), Pd(1)–N(1) 2.017(3), N(1)–C(12) 1.280(5), N(1)–C(13) 1.461(4), O(1)–C(9) 1.304(5); N(2)-C(5)-C(6) 110.4(3), C(12)-N(1)-C(13) 118.3(3), N(1)-C(12)-C(8) 127.2(3), O(1)-Pd(1)-N(1) 91.54(11) C(9)-O(1)-Pd(1) 127.3(2), C(12)-N(1)-Pd(1) 124.2(2).



Scheme 3. The generation of complexes **4** and **5** from ligand **1a**.

Synthesis and characterization of heterotrimetal complexes: On the basis of the synthesis of monometal complexes, we carried out the synthesis of heterometallic complexes. As shown in Scheme 5, complexes **7a** and **7b** can be obtained by transmetalation of **3a** from the silver carbene derivative to $[\{Ru(p\text{-cymene})_2Cl_2\}_2]$ and $[\{Cp^*IrCl_2\}_2]$ in good yield (57 and 54%).

Complexes **7a** and **7b** were characterized by NMR spectroscopy, elemental analysis, and in the case of **7a**, by X-ray diffraction studies. The ^{1}H NMR spectra of **7a** and **7b** show the disappearance of the resonances of the NC*H*N protons as the first indication that metalation takes place. The only one resonance due to N–CH_3 of **7a** and **7b**, respectively, reveals that the transmetalation has occurred in two imidazolium salt moieties of **3a** to form symmetrical structures of **7a** and **7b**. The $^{13}C\{^1H\}$ NMR spectra provide more direct evidence of the metalation, as seen by the signal at $\delta = 173.62$ and 155.95 ppm, assigned to the Ru–$C_{carbene}$ of **7a** and Ir–$C_{carbene}$ of **7b**. The X-ray structure of **7a** shows an ideal square-planar geometry of the Ni center (Figure 7), with both ligands including NHC–Ru moiety *trans* to each other, thereby suggesting that the two NHC–Ru fragments are symmetry related. This means the two imidazole rings are essentially coplanar, with an *anti* configuration of the two NHC–Ru fragments along the Ru-Ni-Ru axis. The imidazole ring plane and the Ni coordination plane are roughly perpendicular with a dihedral angle of 98.7°. The Ru–$C_{carbene}$ distance is 2.125 Å, similar to the distance in other cymene–Ru NHC complexes.[5e,15] The Ni–O (1.810 Å), and the Ni–N (1.930 Å) distances are in the range of other analogous Schiff base Ni complexes.[16]

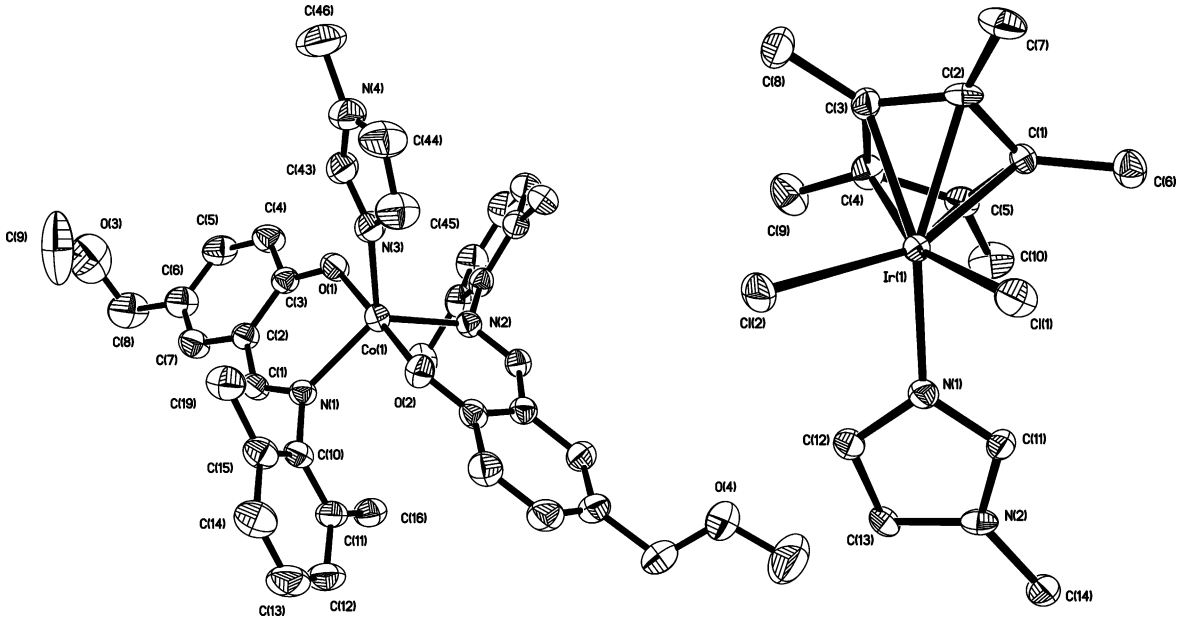
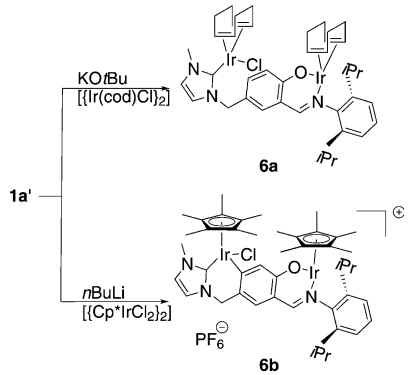


Figure 4. X-ray structure of compound **4** (left) and **5** (right). Ellipsoids at the 30% probability level. Hydrogen atoms and part of the isopropyl group have been omitted for clarity.



Scheme 4. Synthesis of homodimetal complexes **6a**,**b**.

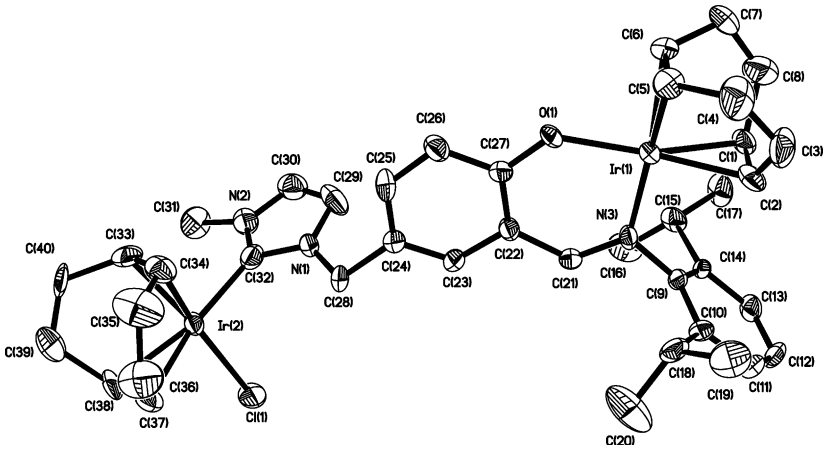
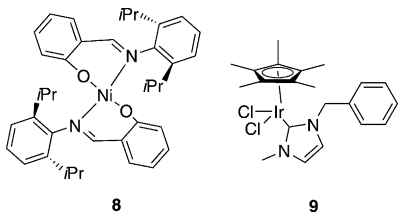


Figure 5. X-ray structure of compound **6a**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(1) 2.009(10), Ir(1)–N(3) 2.056(13), Ir(2)–C(32) 2.019(18), Ir(2)–Cl(1) 2.343(4), N(3)–C(21) 1.305(16), O(1)–C(27) 1.328(17); O(1)-Ir(1)-N(3) 91.1(4), C(27)-O(1)-Ir(1) 129.0(9), C(21)-N(3)-Ir(1) 124.0(10), C(32)-Ir(2)-Cl(1) 89.8(5), N(1)-C(28)-C(24) 111.4(13).

Attempts to obtain other heterometallic complexes by treating the monometal NHC complexes **2a** or **2c** with transition-metal acetates such as $Pd(OAc)_2$ and $Zn(OAc)_2$ failed to afford heterotrimetal complexes, presumably due to the high reactivity of the monometal NHC complexes.

Catalytic studies: With heterometallic complexes **7a** and **7b** in hand, we decided to test their catalytic activity in reactions that contained multiple organic transformations, which require catalytic activities of different transition-metal centers. First we decided to study the dehalogenation/transfer hydrogenation of halo-acetophenones in one pot catalyzed by compound **7b**, because the Ni center could catalyze the dehalogenation process[17] and the Ir center could catalyze transfer-hydrogenation reactions.[18] The halo-acetophenones were convenient starting substrates, which have been used in Pd/Ir catalytic systems by Peris and co-workers.[6c] The monometallic compounds **8**[16a] and **9**[8a] were also used in this catalytic process for comparison. Our preliminary results are summarized in Table 1.

4-Iodoacetophenone was used to see the effect of a base on the reaction in *i*PrOH (Table 1, entry 1–3). All the substrate of these three reactions was completely converted into the transfer-hydrogenation



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products **B** and **C** in various ratios. KO*t*Bu was the best base for the formation of prodcut **C** (entry 3). We then tested the less-reactive substrates 4-bromoacetophenone and 4-chloroacetophenone in the presence of KO*t*Bu for 24 h (entry 4 and 5). A complete conversion of 4-bromoacetophenone to **B** (31%) and **C** (66%) was obtained, whereas the reaction of 4-chloroacetophenone produced only hydrogenation-transfer product **B** (89%). In view of this, 4-bromoacetophenone was used to carry out the comparative study (entries 6–9). As expected, a higher conversion of product **C** could be achieved by using a higher catalyst loading of **7b** (5 mol%) in 24 h (entry 6). By contrast, the combination of complex **8** (5 mol%) and **9** (10 mol%) resulted in an ineffective system (entry 7) with only 16% conversion of **C**. Furthermore, complexes **8** and **9** were also used for this catalytic process, respectively (entries 8 and 9); both reactions generated moderate amounts of product **C**. Given that Ni/NHC complexes are effective in the transfer-hydrogenation processes[19] and Cp*Ir/NHC is an effective catalyst in the dehalogenation of aryl chlorides,[6c] the same reactions might be catalyzed by the Ni complex **8** and Ir complex **9**, respectively. However, this preliminary result suggests that the two metal fragments of the heterometallic complex **7b** may have some catalytic cooperativity, which may lead to a better catalytic performance of **7b** than a combination of the corresponding monometallic species in this tandem process.

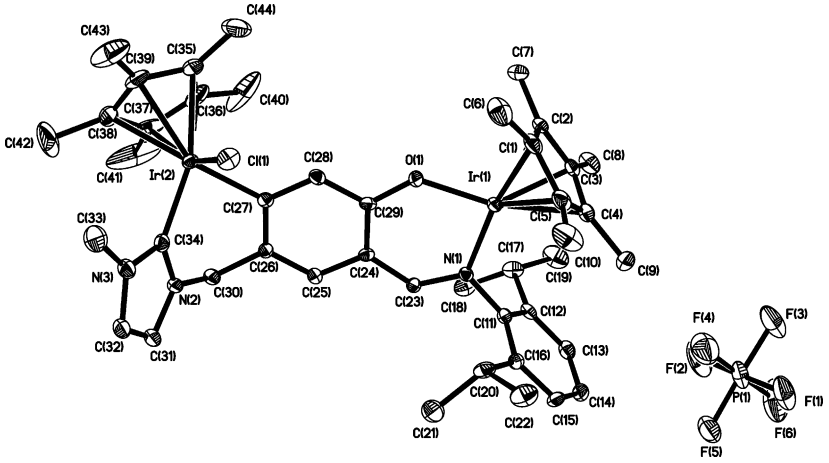
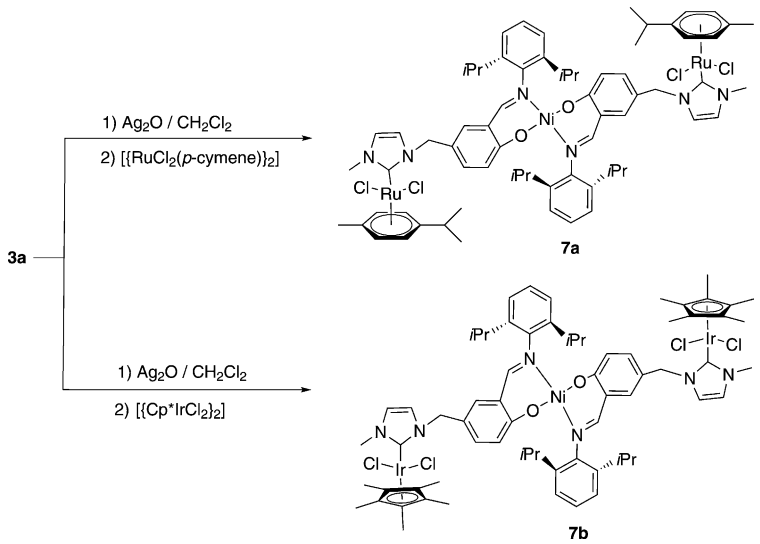


Figure 6. X-ray structure of compound **6b**. Ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(1) 1.966(3), Ir(1)–N(1) 2.036(4), Ir(2)–C(27) 2.058(5), Ir(2)–C(34) 2.017(5), Ir(2)–Cl(1) 2.4084(12), O(1)–C(29) 1.328(6), N(1)–C(23) 1.328(6); O(1)-Ir(1)-N(1) 89.34(15), C(34)-Ir(2)-C(27) 84.48(18), C(34)-Ir(2)-Cl(1) 90.04(14), C(27)-Ir(2)-Cl(1) 87.19(13), N(2)-C(30)-C(26) 109.7(4).



Scheme 5. Synthesis of heterodimetal complexes **7a**,**b**.

Conclusion

In summary, four salicylaldiminato-containing imidazolium salts **1a**–**c** were synthesized efficiently, from which we were able to obtain ligands with different reactivity, structures, and coordination modes. The synthesis of mononuclear compounds with a set of transition metals (Pd, Ir, Ru, Zn, Ni) is direct evidence of the high versatility of this series of ligands, which is critical for the design of catalysts. Furthermore, the effect of counteranions on the stability and reactivity of the ligands was also observed,[20] which allows us to choose suitable ligands with certain counteranions according to different reaction conditions. The successful preparations of homodinuclear metal complexes **6a**,**b** and heterotrinuclear metal complexes **7a**,**b** provided us with easy access to complexes that contained multiple metal fragments, which may open the possibility for a wide range of homometallic and heterometallic combinations. Finally, the

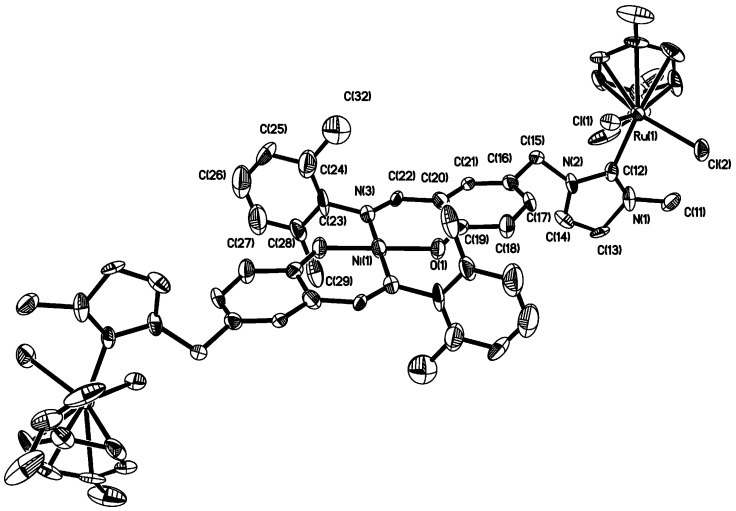
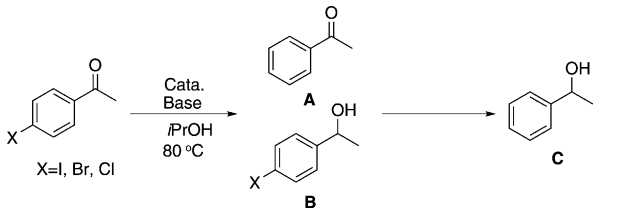


Figure 7. X-ray structure of compound **7a**. Ellipsoids at the 30% probability level. Hydrogen atoms, solvent molecules and parts of isopropyl have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)−C(12) 2.125(14), Ru(1)−Cl(1) 2.412(4), Ru(1)−Cl(2) 2.445(4), Ni(1)−O(1) 1.810(9), Ni(1)−N(3) 1.930(12), O(1)−C(19) 1.263(15), N(3)−C(22) 1.314(16); O(1)-Ni(1)-N(3) 93.3(4), C(12)-Ru(1)-Cl(1) 89.3(3), C(12)-Ru(1)-Cl(2) 89.0(4), Cl(1)-Ru(1)-Cl(2) 85.65(14); C(22)-N(3)-Ni(1) 125.5(9), C(19)-O(1)-Ni(1) 130.8(9), N(2)-C(15)-C(16) 109.9(10).

Table 1. Dehalogenation/transfer hydrogenation of halo-acetophenones by **7b**[a,b].



Entry	Catalyst	X	Base	A	B	C
1	**7b**	I	K_2CO_3	0	>99	0
2	**7b**	I	K_3PO_4	0	70	29
3	**7b**	I	KO*t*Bu	0	0	>99
4[c]	**7b**	Br	KO*t*Bu	0	31	66
5[c]	**7b**	Cl	KO*t*Bu	0	89	0
6[c,d]	**7b**	Br	KO*t*Bu	6	0	94
7[c,e,f]	**8+9**	Br	KO*t*Bu	9	75	16
8[c,e]	**8**	Br	KO*t*Bu	8	72	19
9[c,f]	**9**	Br	KO*t*Bu	7	51	42

[a] Reaction conditions: 4-haloacetophenone (0.25 mmol), base (0.50 mmol), anisole as internal reference (0.25 mmol), catalyst (1 mol%) and 2-propanol (3 mL), 80°C, nitrogen atmosphere, 12 h. [b] Yields determined by gas chromatography. [c] Reaction for 24 h. [d] 5 mol% catalyst. [e] 5 mol% **8**. [f] 10 mol% **9**.

preliminary catalytic study of **7b** in dehalogenation/transfer hydrogenation of halo-acetophenones showed us the catalyst with heterometallic species might improve its catalytic performance due to possible catalytic cooperativity between different metals, or at least it avoids any possible interference between two different catalysts.

Further development of new heterometallic catalysts and their application in other tandem processes is currently underway in our laboratory.

Experimental Section

General procedures: All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, THF, toluene) or calcium hydride (dichloromethane), and methanol was distilled over Mg/I_2. The starting materials 2-(1-imidazolyl)pyrimidine,[21] $[\{RuCl_2(p\text{-cymene})\}_2]$,[22] $[\{Pd(cod)Cl\}_2]$,[23] $[\{Cp^*IrCl_2\}_2]$,[24] and complexes **8**[10] and **9**[8a] were synthesized according to the literature procedures. Other chemical reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded using Bruker spectrometers operating at 400 or 500 (^1H), 162 (^{31}P), and 100 or 125 MHz (^{13}C), respectively. NMR spectra were recorded at room temperature in $CDCl_3$ and $[D_6]DMSO$, unless otherwise stated. Elemental analysis was performed using an Elementar Vario EL III analyzer. A gas chromatograph (HP-GC-6890 series)/mass spectrometer (HP-MS-5974) was also used.

Synthesis of 1a–c: The corresponding amines (12.00 mmol) were added dropwise to a solution of imidazolium salts (10.00 mmol) in methanol (10 mL) with constant stirring at room temperature. The resulting solution was stirred at room temperature for 12–48 h. All volatiles were then removed under high vacuum, and the residue was washed with ether (3× 5 mL) and dried under vacuum to afford corresponding ligands.

Compound ***1a***: Yellow solid, yield: 86%; ^1H NMR ($CDCl_3$, 500 MHz): $\delta=13.42$ (s, 1H; O*H*), 10.58 (s, 1H; NC*H*N), 8.36 (s, 1H; imine *H*), 7.71 (d, $J=2.0$ Hz, 1H; Ph), 7.60 (d, $J=8.0$ Hz, 1H; Ph), 7.51 (s, 1H; C*H*, imidazole), 7.49 (s, 1H; C*H*, imidazole), 7.18 (s, 3H; Ph), 7.04 (d, $J=8.0$ Hz, 1H; Ph), 5.60 (s, 2H; $-CH_2-$Ph), 4.05 (s, 3H; CH_3-imidazole), 2.93 (sept, 2H; $J=7.0$ Hz, *i*Pr C*H*), 1.16 ppm (d, 12H; $J=7.00$ Hz, *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=166.02$ (*C*=N), 162.04 (*C*−OH), 145.51 (*C*−N), 138.42 (Ph), 137.63(Ph), 133.87(Ph), 133.27 (Ph), 125.64 (Ph), 123.91 (Ph), 123.51 (*C*H imidazole), 123.19 (Ph), 121.79 (*C*H imidazole), 118.85 (Ph), 118.36 (Ph), 52.47 (CH_2−Ph), 36.53 (N−CH_3), 28.03 (*i*Pr *C*H), 23.40 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{24}H_{30}N_3ClO$: C 69.97, H 7.34, N 10.20; found: C 70.09, H 7.41, N 10.17.

Compound ***1a′***: Yellow solid, yield: 91%; ^1H NMR ($CDCl_3$, 500 MHz): $\delta=13.52$ (s, 1H; O*H*), 8.58 (s, 1H; NC*H*N), 8.31 (s, 1H; imine *H*), 7.52 (d, $J=2.0$ Hz, 1H; Ph), 7.41 (d, $J=8.5$ Hz, 1H; Ph), 7.21 (s, 2H; C*H*, imidazole), 7.17 (s, 3H; Ph), 7.06 (d, $J=8.5$ Hz, 1H; Ph), 5.24(s, 2H; $-CH_2-$Ph), 3.86 (s, 3H; CH_3-imidazole), 2.93 (sept, $J=7.0$ Hz, 2H; *i*Pr C*H*), 1.15 ppm (d, $J=7.00$ Hz, 12H; *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=166.17$ (*C*=N), 162.27 (*C*−OH), 145.47 (*C*−N), 138.56 (Ph), 135.99 (Ph), 133.71 (Ph), 133.43 (Ph), 125.70 (Ph), 123.61 (Ph), 123.25 (*C*H-imidazole), 122.83 (Ph), 121.71 (*C*H-imidazole), 119.04 (Ph), 118.54 (Ph), 52.82 (CH_2−Ph), 36.20 (N−CH_3), 28.07 (*i*Pr *C*H), 23.43 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{24}H_{30}N_3F_6OP$: C 55.28, H 5.80, N 8.06; found: C 55.33, H 5.81, N 8.17.

Compound ***1b***: Yield: 84%; ^1H NMR ($CDCl_3$, 500 MHz): $\delta=13.55$ (s, 1H; O*H*), 10.61 (s, 1H; NC*H*N), 8.39 (s, 1H; imine *H*), 7.74 (d, $J=2.0$ Hz, 1H; Ph), 7.58 (d, $J=2.0$ Hz, 1H; C*H*, imidazole), 7.56 (d, $J=2.0$ Hz, 1H; C*H*, imidazole), 7.55 (s, 1H; Ph), 7.48 (s, 1H; Ph), 7.01 (d, $J=8.5$ Hz, 1H; Ph), 6.89 (s, 2H; Ph), 5.58 (s, 2H; $-CH_2-$Ph), 4.04 (s, 3H; CH_3-imidazole), 2.28 (s., 3H; Ph−CH_3), 2.13 ppm (s, 6H; Ph−CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=166.09$ (*C*=N), 162.05 (*C*−OH), 144.94 (*C*−N), 137.56 (Ph), 134.64 (Ph), 133.62 (Ph), 133.27 (Ph), 128.99 (Ph), 127.98 (Ph), 123.80 (*C*H imidazole), 123.45 (Ph), 121.86 (*C*H imidazole), 119.06 (Ph), 118.18 (Ph), 52.46 (CH_2−Ph), 36.49 (N−CH_3), 20.67 (Ph−CH_3), 18.35 ppm (Ph−CH_3); elemental analysis calcd (%) for $C_{21}H_{24}N_3ClO$: C 68.19, H 6.54, N 11.36; found: C 68.36, H 6.62, N 11.57.

Compound ***1c***: Yield: 76%; ^1H NMR ($CDCl_3$, 500 MHz): $\delta=13.48$ (s, 1H; O*H*), 11.33 (s, 1H; NC*H*N), 8.86 (d, $J=5.0$ Hz, 2H; pyrimidine) 8.36 (s, 1H; imine *H*), 7.95–7.92 (m, 2H; Ph and pyrimidine), 7.78 (d, $J=8.5$ Hz, 1H; C*H*, imidazole), 7.51 (t, $J=5.0$ Hz, 1H; pyrimidine), 7.17 (s, 3H; Ph), 7.05 (d, $J=8.5$ Hz, 1H; C*H*, imidazole), 6.14 (s, 2H; $-CH_2-$Ph), 2.93 (sept, $J=13.6$ Hz, 2H; *i*Pr C*H*), 1.16 ppm (d, $J=7.00$ Hz, 12H *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=166.21$ (*C*=N), 162.17 (*C*−OH), 159.67 (pyrimidine), 152.26 (pyrimidine), 145.51 (*C*−N), 138.40 (Ph),

136.39 (NCN, imidazole), 134.45 (Ph), 134.06 (Ph), 125.62 (Ph), 123.97 (Ph), 123.50 (CH, imidazole), 123.17 (Ph), 122.08 (CH, imidazole), 118.93 (pyrimidine), 118.50 (Ph), 118.31 (Ph), 53.12 (CH_2–Ph), 36.20 (N–CH_3), 28.05 (*i*Pr CH), 23.40 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{27}H_{30}N_5ClO$: C 68.13, H 6.35, N 14.71; found: C 68.32, H 6.48, N 15.03.

Synthesis of 2a–c: A suspension of the ligands **1a**, **1b**, or **1c** (0.25 mmol) and silver oxide (0.6 equiv, 0.15 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature in the dark for 4–8 h. The mixture was then filtered to a solution of metal precursors (0.12 mmol [{Cp*$IrCl_2$}$_2$] or [{$RuCl_2$(*p*-cymene)}$_2$], 0.23 mmol [{Pd(cod)Cl}$_2$]) in dichloromethane (5 mL). After the mixture was stirred at room temperature for another 4 h, it was filtered. Then the filtrate was concentrated and the residue was purified by column chromatography or recrystallization. Compounds **2a** and **2a′** were isolated in a ratio of 5:1 by column chromatography. Complexes **2b** and **2c** were obtained in good yields upon recrystallization from dichloromethane/hexane.

Compound ***2a***: Orange solid, yield: 43%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, 1H; imine *H*), 7.63 (d, *J* = 2.0 Hz, 1H; Ph), 7.46 (d, *J* = 2.0 Hz, 1H; C*H*, imidazole), 7.17 (s, 3H; Ph), 7.03 (d, *J* = 8.4 Hz, 1H; C*H*, imidazole), 6.90 (d, *J* = 1.6 Hz, 1H; Ph), 6.74 (d, *J* = 1.6 Hz, 1H; Ph), 6.35 (d, *J* = 14.0 Hz, 1H; –CH_2–Ph), 4.77 (d, *J* = 14.0 Hz, 1H; –CH_2–Ph), 3.99 (s, 3H; CH_3-imidazole), 2.95 (sept, *J* = 6.8 Hz, 2H; *i*Pr C*H*), 1.66 (s, 15H; CH_3, Cp*), 1.16 ppm (d, *J* = 6.8 Hz, 12H; *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.50 (*C*=N), 161.14 (*C*–OH), 156.20 ($C_{carbene}$–Ir), 145.74 (*C*–N), 138.46 (Ph), 134.01 (Ph), 133.17 (Ph), 126.92 (Ph), 125.45 (Ph), 123.40 (CH imidazole), 123.12 (Ph), 121.71 (CH imidazole), 121.43 (Ph), 118.68 (Ph), 117.38, 88.79 ($C_5(CH_3)_5$), 52.82 (CH_2–Ph), 36.20 (N–CH_3), 28.01 (*i*Pr CH), 23.43 (*i*Pr CH_3), 9.19 ppm ($C_5(CH_3)_5$); elemental analysis calcd (%) for $C_{34}H_{44}N_3Cl_2OIr$: C 52.77, H 5.73, N 5.43; found: C 52.81, H 5.56, N 5.45.

Compound ***2a′***: Orange solid, yield: 9%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (s, 1H; imine *H*), 7.43 (s, 1H; Ph), 7.15 (s, 3H; C*H*, imidazole and Ph), 6.95 (d, *J* = 1.6 Hz, 1H; Ph), 6.91 (d, *J* = 1.6 Hz, 1H; Ph), 6.88 (s, 1H; Ph), 4.85 (d, *J* = 13.6 Hz, 1H; –CH_2–Ph), 4.67 (d, *J* = 13.6 Hz, 1H; –CH_2–Ph), 3.91 (s, 3H; CH_3-imidazole), 3.01 (sept, 2H; *J* = 6.8 Hz, *i*Pr C*H*), 1.73 (s, 15H; CH_3, Cp*), 1.14 ppm (d, *J* = 7.2 Hz, 12H; *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.05 (*C*=N), 159.22 (*C*–OH), 156.68 ($C_{carbene}$–Ir), 147.20 (*C*–N), 139.06 (Ph), 130.74 (Ph), 129.81 (Ph), 126.43 (Ph), 124.67 (Ph), 123.00 (CH imidazole), 121.26 (Ph), 120.18 (CH imidazole), 113.85 (Ph), 112.08 (Ph), 90.61 ($C_5(CH_3)_5$), 56.59 (CH_2–Ph), 36.94 (N–CH_3), 27.93 (*i*Pr CH), 23.55 (*i*Pr CH_3), 9.47 ppm ($C_5(CH_3)_5$); elemental analysis calcd (%) for $C_{34}H_{43}N_3Cl_2OIr$: C 52.84, H 5.61, N 5.44; found: C 52.90, H 5.66, N 5.48.

Compound ***2b***: Yield: 56%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 13.38 (s, 1H; O*H*), 8.29 (s, 1H; imine *H*), 7.53 (d, *J* = 2.0 Hz, 1H; C*H*, imidazole), 7.36 (d, *J* = 2.5 Hz, 1H; Ph), 7.02 (d, *J* = 8.0 Hz, 1H; C*H*, imidazole), 6.95 (d, *J* = 2.0 Hz, 1H; Ph), 6.89 (s, 2H; Ph), 6.82 (d, *J* = 2.0 Hz, 1H; Ph), 5.40 (s, 2H; –CH_2–Ph), 5.12 (d, *J* = 6.0 Hz, 4H; cymene-C_6H_4), 4.03 (s, 3H; CH_3-imidazole), 2.94 (sept, *J* = 7.0 Hz, 2H; *i*Pr C*H*), 2.28 (s, 3H; cymene-CH_3), 2.14 (s, 6H; Ph–CH_3), 2.09 (s, 3H; Ph–CH_3), 1.26 ppm (d, *J* = 5.6 Hz, 6H; cymene-CHCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 173.84 ($C_{carbene}$–Ru), 166.43 (*C*=N), 161.06 (*C*–OH), 145.16 (*C*–N), 134.62 (Ph), 134.50 (Ph), 133.26 (Ph), 132.68 (Ph), 128.96 (Ph), 127.03 (Ph), 123.88 (CH imidazole), 122.19 (Ph), 118.94 (CH imidazole), 117.29 (Ph), 108.55 (Ph), 99.20 (Ph), 53.92 (CH_2–Ph), 39.67 (N–CH_3), 30.80 (*i*Pr CH), 22.60 (*i*Pr CH_3), 20.72 (Ph–CH_3), 18.70 (Ph–CH_3), 18.40 ppm (Ph–CH_3); elemental analysis calcd (%) for $C_{31}H_{37}N_3Cl_2ORu$: C 58.21, H 5.83, N 6.57; found: C 58.15, H 5.78, N 6.63.

Compound ***2c***: Yield: 68%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.69 (dd, *J* = 5.6 Hz, 1H; pyrimidine), 8.85 (dd, *J* = 5.6 Hz, 1H; pyrimidine), 8.32 (s, 1H; imine *H*), 7.77 (d, *J* = 8.5 Hz, 1H; C*H*, imidazole), 7.56 (m, 2H; Ph and pyrimidine), 7.46 (t, *J* = 5.2 Hz, 1H; pyrimidine), 7.18 (s, 3H; Ph), 7.07(s, 1H; Ph), 7.02 (d, *J* = 8.5 Hz, 1H; C*H*, imidazole), 6.03(s, 2H; –CH_2–Ph), 2.94 (sept, *J* = 4.8 Hz, 2H; *i*Pr C*H*), 1.16 ppm (d, *J* = 4.8 Hz, 12H; *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.16 (*C*=N), 161.66 (*C*–OH), 160.47 (pyrimidine), 158.90 (pyrimidine), 156.78 (Pd–$C_{carbene}$), 153.17 (pyrimidine), 145.66 (*C*–N), 138.44 (Ph), 133.76 (Ph), 132.75 (Ph), 125.61 (CH imidazole), 125.48 (Ph), 123.44 (Ph), 123.18 (Ph), 119.55 (pyrimidine), 118.74 (Ph), 118.14 (Ph), 117.26 (CH imidazole), 52.79 (CH_2–Ph), 28.07 (*i*Pr CH), 23.44 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{27}H_{29}N_5Cl_2OPd$: C 52.57, H 4.74, N 11.35; found: C 52.35, H 4.63, N 11.29.

Synthesis of 3a–c: Ligands **1a**, **1a′**, or **1c** (0.5 mmol) were dissolved in THF (20 mL), and the resulting solution was added dropwise at room temperature to metal acetate (0.24 mmol, $Ni(OAc)_2$·4H_2O, $Pd(OAc)_2$, or $Zn(OAc)_2$ in THF (10 mL)). The reaction mixture was stirred overnight at room temperature. The resulting precipitate was filtered, washed with THF (10 mL × 3), and vacuum-dried to give monometal Schiff base compounds.

Compound ***3a***: Yield: 78%; ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 9.16 (s, 2H; NC*H*N), 7.84 (s, 2H; imine *H*), 7.68 (d, *J* = 8.0 Hz, 4H; Ph), 7.35 (d, *J* = 1.5 Hz, 2H; C*H*, imidazole), 7.28 (t, 2H; Ph), 7.17–7.16 (m, 4H; Ph), 7.01 (dd, *J* = 1.5 Hz, 2H; C*H*, imidazole), 5.43 (d, *J* = 8.5 Hz, 2H; Ph), 5.14 (s, 4H; –CH_2–Ph), 4.08 (sept, 4H; *J* = 6.5 Hz, *i*Pr C*H*), 3.80 (s, 3H; CH_3-imidazole), 1.38–1.19 ppm (dd, *J* = 7 Hz, 24H; *i*Pr CH_3); ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 164.92 (*C*=N), 162.48 (*C*–O), 144.87 (*C*–N), 141.13 (Ph), 136.32 (Ph), 134.08 (Ph), 135.48 (Ph), 133.22 (Ph), 126.01 (Ph), 123.75 (CH imidazole), 122.56 (Ph), 122.06 (CH imidazole), 120.62 (Ph), 118.75 (Ph), 51.26 (CH_2–Ph), 35.71 (N–CH_3), 28.42 (*i*Pr CH), 23.94 (*i*Pr CH_3), 23.09 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{48}H_{58}N_6O_2Cl_2Ni$: C 65.47, H 6.64, N 9.54; found: C 65.51, H 6.71, N 9.57.

Compound ***3b***: Yield: 86%; ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 9.05 (s, 2H; NC*H*N), 7.96 (s, 2H; imine *H*), 7.68 (s, 4H; Ph), 7.65 (s, 2H; Ph), 7.45 (d, *J* = 1.6 Hz, 2H; C*H*, imidazole), 7.35(t, 2H; Ph), 7.24–7.25 (m, 4H; Ph), 7.15 (dd, *J* = 1.6 Hz, 2H; C*H*, imidazole), 5.83 (d, *J* = 8.5 Hz, 2H; Ph), 5.15 (s, 4H; –CH_2–Ph), 3.80 (s, 6H; CH_3-imidazole), 1.23–1.13 ppm (dd, *J* = 7.0 Hz, 24H; *i*Pr CH_3); ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 164.89 (*C*=N), 163.96 (*C*–O), 144.43 (*C*–N), 141.94 (Ph), 136.80 (Ph), 135.66 (Ph), 135.48 (Ph), 127.20 (Ph), 124.26 (Ph), 123.05 (CH imidazole), 122.59 (Ph), 120.81 (CH imidazole), 120.72 (Ph), 119.71 (Ph), 51.74 (CH_2–Ph), 36.20 (N–CH_3), 28.49 (*i*Pr CH), 24.32 (*i*Pr CH_3), 23.31 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{48}H_{58}N_6O_2F_{12}P_2Pd$: C 50.25, H 5.10, N 7.32; found: C 50.33, H 5.21, N 7.27.

Compound ***3c***: Yield: 67%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 10.27 (s, 2H; NC*H*N), 9.04 (d, *J* = 5.0 Hz, 4H; pyrimidine), 8.89 (d, *J* = 3.5 Hz, 2H; imine *H*), 8.46 (s, 2H; Ph), 8.11 (s, 2H; Ph), 7.99 (m, 2H; Ph and pyrimidine), 7.76 (t, *J* = 5.0 Hz, 2H; pyrimidine), 7.46 (s, 2H; Ph), 7.43 (d, *J* = 8.5 Hz, 2H; C*H*, imidazole), 7.20 (m, 6H; Ph), 6.70 (d, *J* = 8.5 Hz, 2H; C*H*, imidazole), 5.39 (s, 4H; –CH_2–Ph), 3.21 (br, 4H; *i*Pr C*H*), 1.12 ppm (br, 24H *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.06 (*C*=N), 159.90 (*C*–OH), 159.48 (pyrimidine), 153.61 (pyrimidine), 152.07 (*C*–N), 140.82 (Ph), 136.86 (NCN, imidazole), 135.95 (Ph), 135.64 (Ph), 129.71 (Ph), 123.34 (Ph), 123.26 (CH, imidazole), 122.98 (Ph), 122.26 (CH, imidazole), 120.10 (pyrimidine), 119.49 (Ph), 116.94 (Ph), 52.18 (CH_2–Ph), 27.58 (*i*Pr CH), 23.11 ppm (*i*Pr CH_3); elemental analysis calcd (%) for $C_{54}H_{58}N_{10}O_2Cl_2Zn$: C 63.87, H 5.76, N 13.79; found: C 64.03, H 5.91, N 13.68.

Synthesis of 4: $Co(OAc)_2$·4H_2O (0.12 mmol) and NaOH (0.25 mmol) were added to a solution of ligand **1a** (0.25 mmol) in MeOH (10 mL), The reaction mixture was heated at reflux for 24 h under nitrogen atmosphere. After reaction, the solvent was evaporated. The residue was dissolved in dichloromethane (5 mL) and filtered. The filtrate was dried under reduced pressure and the residue was washed with ether (3 × 5 mL) and dried under vacuum to afford purple compound **4**. Yield: 25%. Elemental analysis calcd (%) for $C_{46}H_{58}N_4O_4Co$: C 69.94, H 7.40, N 7.09; found: C 69.98, H 7.48, N 7.12.

Synthesis of 5: *t*BuOK (0.5 mmol) was added to a solution of **1a** (0.4 mmol) in THF (10 mL). After stirring for 30 min, the mixture was cannulated to a suspension of [{Cp*$IrCl_2$}$_2$] (0.2 mmol) in THF (10 mL). The mixture was stirred at room temperature for an additional 24 h and filtered. The filtrate was dried under high vacuum and the resulting solid purified by recrystallization from THF/hexane (1:4) to give orange **5**. Yield: 46%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.929 (s, 1H; NC*H*N), 7.15 (s, 1H; imidazole), 6.85 (s, 1H; imidazole), 3.70 (s, 3H; CH_3-imidazole),

1.58 ppm (s, 15H; Cp*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.06 (NC*H*N), 130.62 (*C*H imidazole), 121.44 (*C*H imidazole), 85.35 ($C_5(CH_3)_5$), 34.88 (N−*C*H$_3$), 9.05 ppm ($C_5(CH_3)_5$); elemental analysis calcd (%) for $C_{14}H_{21}N_2Cl_2Ir$: C 35.00, H 4.41, N 5.83; found: C 35.23, H 4.57, N 5.90.

Synthesis of 6a: A solution of *t*BuOK in THF (1.0 M, 0.26 mL) was added dropwise to a stirred suspension of ligand **1a′** (0.25 mmol) in THF (15 mL) at room temperature. After the mixture was stirred for 30 min, [{Ir(cod)Cl}$_2$] (0.24 mmol) was added in one portion. The reaction mixture was stirred for an additional 16 h. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent to afford **6a** as an orange-red solid. Yield: 65%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (s, 1H; imine *H*), 7.53 (d, *J* = 8.8 Hz, 1H; imidazole), 7.24–7.21 (m, 4H; Ph), 7.22 (s, 3H; Ph), 7.12 (d, *J* = 8.8 Hz, 1H; imidazole), 6.76 (d, *J* = 2.0 Hz, 1H; Ph), 6.59 (d, *J* = 2.0 Hz, 1H; Ph), 5.76 (d, *J* = 14.4 Hz, 1H; −C*H*$_2$−Ph), 5.39 (d, *J* = 14.4 Hz, 1H; −C*H*$_2$−Ph), 4.60 (m, 2H; cod), 4.45 (m, 2H; cod), 3.96 (s, 3H; C*H*$_3$-imidazole), 3.33 (sept, *J* = 6.8 Hz, 2H; *i*Pr C*H*), 2.97 (m, 1H; cod), 2.93(m, 1H; cod), 2.68 (m, 2H; cod), 2.22–2.12 (m, 8H; cod), 1.74–1.59 (m, 8H; cod), 1.04 (d, *J* = 6.8 Hz, 6H; *i*Pr C*H*$_3$), 1.01 ppm (d, *J* = 6.8 Hz, 6H; *i*Pr C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 180.62 ($C_{carbene}$−Ir), 165.94 (*C*-O-Ir), 164.12 (*C*=N), 153.72 (*C*−N), 145.76 (Ph), 140.98(Ph), 135.89 (Ph), 127.51 (Ph), 123.67 (Ph), 123.43 (Ph), 120.44 (Ph), 123.18 (*C*H imidazole), 122.08 (*C*H imidazole), 119.63 (Ph), 118.96 (Ph), 84.74 (d, cod), 70.09 (d, cod), 56.84 (d, cod), 53.47 (*C*H$_2$−Ph), 51.67 (d, cod), 37.61 (N−*C*H$_3$), 33.72 (d, cod), 32.31(d, cod), 29.79 (d, cod), 28.01 (*i*Pr *C*H), 25.78 (d, cod), 22.49 ppm (*i*Pr *C*H$_3$); elemental analysis calcd (%) for $C_{40}H_{52}N_3ClIr_2$: C 48.30, H 5.27, N 4.22; found: C 48.39, H 5.29, N 4.30.

Synthesis of 6b: A solution of *n*BuLi (1.6 M, 0.31 mL, 0.5 mmol) in hexane was added dropwise to a stirred solution of ligand **1a′** (0.25 mmol) in THF (10 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 3 h. Then the mixture was cannulated to a suspension of [{Cp*IrCl$_2$}$_2$] (0.24 mmol) in THF (10 mL) and stirred overnight. After concentration the residue was purified by column chromatography to afford **6b** as a red solid. Yield: 28%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (s, 1H; imine *H*), 7.97 (s, 1H; Ph), 7.36 (m, 3H; Ph and C*H*, imidazole), 7.07 (d, *J* = 1.6 Hz, 1H; Ph), 7.01 (s, 1H; Ph), 6.91 (s, 1H; Ph), 4.82 (d, *J* = 14.4 Hz, 1H; −C*H*$_2$−Ph), 4.69 (d, *J* = 14.4 Hz, 1H; −C*H*$_2$−Ph), 3.89 (s, 3H; C*H*$_3$-imidazole), 2.96 (sept, *J* = 6.4 Hz, 1H; *i*Pr C*H*), 2.58 (sept, *J* = 6.4 Hz, 1H; *i*Pr C*H*), 1.74 (s, 15H; Cp*), 1.46 (s, 15H; Cp*), 1.05 (d, *J* = 6.4 Hz, 6H; *i*Pr C*H*$_3$), 0.90 ppm (d, *J* = 6.4 Hz, 6H; *i*Pr C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.19 (*C*-O-Ir), 164.89 (*C*=N), 155.17 ($C_{carbene}$−Ir), 151.45 (*C*−N), 140.88 (Ph), 140.77 (Ph), 134.70 (Ph), 131.80 (Ph), 128.61 (Ph), 127.47 (Ph), 125.23 (Ph), 123.88 (*C*H imidazole), 121.61 (*C*H imidazole), 120.84 (Ph), 109.64 (Ph), 92.30 ($C_5(CH_3)_5$, 92.11 ($C_5(CH_3)_5$, 56.47 (*C*H$_2$−Ph), 36.91 (N−*C*H$_3$), 26.35 (*i*Pr *C*H), 26.28 (*i*Pr *C*H), 22.61 (*i*Pr *C*H$_3$), 22.69 (*i*Pr *C*H$_3$), 9.48 ($C_5(CH_3)_5$), 9.30 ppm ($C_5(CH_3)_5$); ^{31}P NMR ($CDCl_3$, 202 MHz): δ = −136.76 to −150.83 ppm (sep); elemental analysis calcd (%) for $C_{44}H_{57}N_3F_6ClOPIr_2$: C 43.72, H 4.75, N 3.48; found: C 43.89, H 4.96, N 3.45.

Synthesis of 7a and 7b: A suspension of the compound **3a** (0.1 mmol) with silver oxide (0.13 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature in the dark for 10 h. The mixture was then filtered to a solution of [{RuCl$_2$(*p*-cymene)}$_2$] (for compound **7a**) or [{Cp*IrCl$_2$}$_2$] (for compound **7b**) (0.1 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature overnight and filtered. After concentration, the resulting solid was washed by toluene (3×10 mL), and then purified by recrystallization from dichloromethane/hexane (1:9, 10×3 mL) to give the complexes **7a** and **7b**, respectively.

Compound ***7a***: Reddish-brown solid, yield: 57%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (s, 2H; imine *H*), 7.28 (s, 2H; Ph), 7.13–7.11 (m, 4H; Ph), 6.96 (d, *J* = 1.6 Hz, 2H; C*H*, imidazole), 6.90–6.97 (br, 4H; Ph), 6.79 (d, *J* = 1.6 Hz, 2H; C*H*, imidazole), 5.55 (d, *J* = 8.8 Hz, 2H; Ph), 5.30 (m, 8H; cymene-C$_6H_4$), 5.02 (s, 4H; −C*H*$_2$−Ph), 4.20 (sept, *J* = 6.4 Hz, 4H; *i*Pr C*H*), 3.99 (s, 6H; C*H*$_3$-imidazole), 2.90 (d, *J* = 6.8 Hz, 2H; cymene-C*H*CH$_3$), 2.01 (s, 6H; cymene-C*H*$_3$), 1.44 (d, *J* = 6.8 Hz, 12H; cymene-CHC*H*$_3$), 1.22 ppm (d, *J* = 6.8 Hz, 24H; *i*Pr C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 173.62 ($C_{carbene}$−Ru), 163.83 (*C*=N), 163.29 (*C*−OH), 145.38 (*C*−N), 141.65 (Ph), 134.01 (Ph), 131.92 (Ph), 126.05 (Ph), 123.56 (Ph), 123.16 (Ph), 122.83 (*C*H imidazole), 122.79 (Ph), 122.50 (Ph), 121.43 (Ph), 118.75 (*C*H imidazole), 108.50 (Ph), 99.01 (Ph), 53.89 (*C*H$_2$−Ph), 39.61 (N−*C*H$_3$), 30.70 (*i*Pr *C*H), 29.62 (*i*Pr *C*H), 28.80 (*i*Pr *C*H), 24.33 (*i*Pr *C*H$_3$), 23.42 (*i*Pr *C*H$_3$), 18.60 ppm (Ph−*C*H$_3$); elemental analysis calcd (%) for $C_{68}H_{84}N_6Cl_4O_2NiRu_2$: C 57.51, H 5.96, N 5.92; found: C 57.54, H 6.09, N 5.96.

Compound ***7b***: Yellow-green solid, yield: 54%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32 (s, 2H; imine *H*), 7.23–7.18 (br, 4H; Ph), 7.09 (br, 4H; Ph), 7.01 (s, 2H; Ph), 6.93 (d, *J* = 9.0 Hz, 2H; Ph), 6.80 (d, *J* =

Table 2. X-ray crystallographic data for **1a′**, **2a·CH$_2$Cl$_2$**, **3b**, and **4**.

	1a′	**2a·CH$_2$Cl$_2$**	**3b**	**4**
formula	$C_{24}H_{30}F_6N_3OP$	$C_{35}H_{46}Cl_4IrN_3O$	$C_{48}H_{58}F_{12}N_6O_2P_2Pd$	$C_{46}H_{58}CoN_4O_4$
M_r	521.48	858.75	1147.34	789.89
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	14.965(3)	16.556(2)	14.565(3)	12.2281(18)
b [Å]	9.7123(17)	14.1137(17)	10.0661(19)	12.8516(18)
c [Å]	19.323(3)	16.2376(19)	18.573(4)	16.912(4)
α [°]	90	90	90	96.314(2)
β [°]	108.912(2)	103.428(2)	100.018(2)	107.595(2)
γ [°]	90	90	90	114.313(2)
V [Å^3]	2656.9(8)	3690.5(8)	2681.6(9)	2223.0(7)
Z	4	4	4	2
μ [mm^{-1}]	0.166	3.938	0.490	0.430
ρ_{calcd} [mg m^{-13}]	1.304	1.546	1.421	1.180
F [000]	1088	1720	1176	842
T [K]	296(2)	296(2)	296(2)	293(2)
θ range [°]	2.23 to 25.00	1.26 to 27.00	1.42 to 25.50	1.81 to 25.01
reflns collected/indep reflns	12793/4680	20756/7917	13407/4982	12026/7744
$R_{(int)}$	0.0289	0.0580	0.0393	0.0176
data/restraints/params	4680/0/378	7917/22/394	4982/0/328	7744/0/515
GOF	1.021	1.016	0.957	1.025
$R_1(I>2\sigma(I))$	0.0503,	0.0475	0.0470	0.0480
wR_2	0.1244	0.1123	0.1215	0.1396

Table 3. X-ray crystallographic data for **5**, **6a**·CH_2Cl_2, **6b**·CH_2Cl_2, and **7a**·CH_2Cl_2.

	5	**6a**·CH_2Cl_2	**6b**·CH_2Cl_2	**7a**·CH_2Cl_2
formula	$C_{14}H_{21}Cl_2IrN_2$	$C_{40}H_{52}ClIr_2N_3O$	$C_{45}H_{59}Cl_3F_6Ir_2N_3OP$	$C_{69}H_{86}Cl_6N_6NiO_2Ru_2$
M_r	480.43	1010.70	1293.67	1504.99
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	7.3275(7)	8.274(3)	15.7170(9)	14.447(7)
b [Å]	14.0818(13)	14.826(5)	15.4757(9)	17.302(8)
c [Å]	15.5413(15)	17.521(6)	20.1623(12)	17.543(8)
α [°]	90	86.497(6)	90	74.636(7)
β [°]	91.6740(10)	86.139(5)	103.8930(10)	65.689(7)
γ [°]	90	78.435(5)	90	70.552(8)
V [Å^3]	1602.9(3)	2098.5(11)	4760.6(5)	3726(3)
Z	4	2	4	2
μ [mm^{-1}]	8.651	6.430	5.848	0.910
ρ_{calcd} [mg m^{-13}]	1.991	1.600	1.805	1.341
F [000]	920	984	2528	1552
T [K]	296(2)	296(2)	296(2)	296(2)
θ range [°]	1.95 to 26.99	1.40 to 25.00	1.68 to 26.00	1.60 to 25.10
reflns collected/indep reflns	8922/3426	12523/7278	30532/9315	18020/12633
$R_{(int)}$	0.0267	0.0733	0.0195	0.0861
data/restraints/params	3426/0/178	7278/0/424	9315/3/550	12633/6/752
GOF	1.118	0.994	1.012	1.133
$R_1(I>2\sigma(I))$	0.0244	0.0545	0.0291	0.0905
wR_2	0.0540	0.1289	0.1042	0.2130

1.5 Hz, 2H; C*H*, imidazole), 6.65 (d, J=1.5 Hz, 2H; C*H*, imidazole), 5.92 (d, J=14.0 Hz, 2H; −CH_2–Ph), 5.52 (d, J=8.5 Hz, 2H; Ph), 4.71 (d, J=14.0 Hz, 2H; −CH_2–Ph), 4.22 (m, 4H; *i*Pr C*H*), 3.94 (s, 6H; CH_3-imidazole), 1.59 (s, 30H; CH_3, Cp*), 1.43 (d, J=7.0 Hz, 12H; *i*Pr CH_3), 1.21 ppm (d, J=7 Hz, 12H; *i*Pr CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ= 163.94 (*C*=N), 163.42 (*C*–OH), 155.95 ($C_{carbene}$–Ir), 145.48 (*C*–N), 141.74 (Ph), 134.64 (Ph), 132.70 (Ph), 128.19 (Ph), 126.00 (Ph), 123.00 (*C*H imidazole), 123.12 (Ph), 121.59 (*C*H imidazole), 121.36 (Ph), 118.80 (Ph), 88.67 ($C_5(CH_3)_5$), 53.58 (*C*H$_2$–Ph), 38.60 (N−*C*H$_3$), 28.81 (*i*Pr *C*H), 24.37 (*i*Pr *C*H$_3$), 23.47 (*i*Pr *C*H$_3$), 9.196 ppm ($C_5(CH_3)_5$); elemental analysis calcd (%) for $C_{68}H_{86}N_6Cl_4O_2NiIr_2$: C 50.91, H 5.40, N 5.24; found: C 50.99, H 5.53, N 5.25.

Typical catalysis procedure: In a typical run, a capped vessel that contained a stirrer bar was charged with 4-haloacetophenone (0.25 mmol), base (0.5 mmol), anisole as internal reference (0.25 mmol), catalyst (1–10 mol%), and 2-propanol (3 mL). The reaction mixture was stirred at 80°C for the appropriate time. Reactions were monitored and yields were determined by gas chromatography (GC). Products were characterized by GC/MS.

X-ray crystallography: Diffraction data of **1a′**, **2a**, **3b**, **4**, **5**, **6a**, **6b**, and **7a** were collected using a Bruker SMART APEX (at 293 K) or a Bruker SMART APEX (II) (at 296 K) diffractometer with a CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.71073 Å). The determination of crystal class and unit cell was carried out by using the SMART program package. All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).[25] The raw frame data were processed using SAINT[26] and SADABS[27] to yield the reflection data file. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. A summary of the crystallographic data and selected experimental information are given in Table 2 and Table 3.

CCDC-823615 (**1a′**), 823616 (**2a**), 823617 (**3b**), 823620 (**4**), 823621 (**5**), 823619 (**6a**), 823618 (**6b**) and 823622 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support by the National Science Foundation of China (grant nos. 20871032, 20971026), and by the Shanghai Leading Academic Discipline Project (project no. B108) is gratefully acknowledged.

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Received: May 20, 2011
Published online: August 23, 2011

