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Heterobimetallic Complexes Bridged by Imidazol{[4,5-*f*][1,10]-phenanthrolin}-2-ylidene: Synthesis and Catalytic Activity in Tandem Reactions

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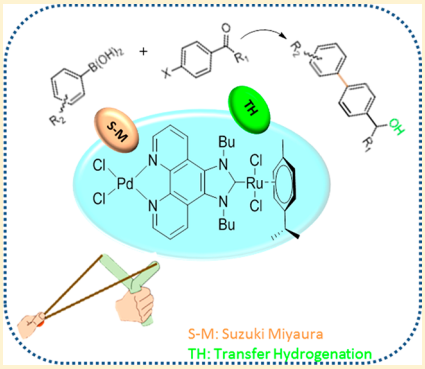
Supporting Information

ABSTRACT: A series of monometallic complexes obtained by metalation of the phenanthrolin donor in 1,3-dibutyl-1H-imidazol[4,5-*f*][1,10]phenanthrolin}ium hexafluorophospate **1** (M = Pd **2**, Ru **3**, Ir **4**) have been prepared. Subsequently, the imidazolium moiety of complexes **2**−**4** was metalated with M′, leading to the heterobimetallic phenanthroline/NHC complexes (M/M′ = Pd/Rh **5**, Pd/Ir **6**, Pd/Ru **7**, Ru/Pd **8**, Ir/Pd **9**) and the homobimetallic complex (M/M′ = Ir/Ir **10**). The new complexes were characterized by elemental analysis, FTIR, UV−vis, and NMR spectroscopy. The molecular structures of the heterobimetallic complexes **5** and **6** were determined by X-ray diffraction studies. The catalytic activity of the heterobimetallic complexes **5**−**9** were tested in selected tandem reactions (dehalogenation/transfer hydrogenation and Suzuki−Miyaura coupling/transfer hydrogenation). It was found that the M/M′ heterobimetallic complexes display higher catalytic activities when compared to equimolar mixtures of the mononuclear complexes M and M′, thus indicating that an increase in the number of metal atoms in one complex leads to an increased activity in the tandem reactions.



INTODUCTION

Bimetallic complexes, particularly heterobimetallic ones, have played a significant role in the development of coordination chemistry and recently they have emerged as a hot topic as catalysts in tandem reactions.[1−3] They are of interest in areas as disparate as bioinorganic chemistry, materials science, photophysics and artificial photosynthetic systems, redox and photoactive polymers, dendrimer chemistry, nanoscience, catalysis, and sensors.[4] The synthesis of heterobimetallic complexes requires the use of a ditopic ligand, meaning the ligand functions as a donor possessing two binding sites for the coordination to metal atoms. Ditopic ligands capable of binding metals at two separate sites in principle allow the creation of well-ordered extended complexes containing different metal atoms.[5] The use of ditopic ligands featuring a central rigid structure has been demonstrated for diverse applications.[6−8] The interplay of coordination geometry, thermodynamic, and kinetic properties of the metal ions and the structural features of the ligands results in one single or a set of well-defined polynuclear architectures. Most of the research in this area focused on the coordination chemistry of easily prepared, heterobifunctional ligands containing a mixed hard-soft donor set used for discrimination between metal ions. The design of ligands capable of binding two different metal ions potentially allows the utilization of synergistic effects of these metals.[9]

Tandem reactions can provide high value organic products via multiple chemical transformations proceding in a one-pot reaction.[10−13] A significant benefit of such transformations is the atom economy of the strategy. Research toward improved activity and selectivity of tandem systems greatly reduces the amount of waste, costs, energy consumption, and time.[14,15] Particularly useful are organic tandem transformations that are performed in an environmentally friendly medium. These advantages make tandem reactions particularly attractive.

The catalytic activity of a given dinuclear complex depends on the appropriate selection of the bridging ligand which provides electronic and steric stabilization to the metal centers. Various reviews deal with suitable catalysts for tandem reactions[16,17] and water-soluble organometallic complexes.[18]

We have prepared phenanthroline ligands fused with an *N*-alkyl imidazole group. Upon coordination of the phenanthroline nitrogen atoms in a chelation fashion, a series of ruthenium(II) complexes have been prepared. The catalytic properties of these complexes were investigated in the transfer hydrogenation of ketones.[19] Di- and trinuclear palladium

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complexes obtained from the related imidazol{[4,5-*f*][1,10]-phenanthrolin}-2-ylidene were applied in C−C cross-coupling reactions.[20]

In order to explore the catalytic activity of heterobimetallic complexes obtained from an N-heterocyclic carbene (NHC) annulated phenanthroline in selected tandem reactions (dehalogenation/Suzuki−Miyaura coupling reactions and transfer hydrogenation/Suzuki−Miyaura coupling reaction), we have prepared a series of novel Pd/Rh, Pd/Ir, Pd/Ru, Ru/Pd, and Ir/Pd complexes. The position of the different metals in the heterobimetallic complexes (N,N-chelate at the phenanthroline or metalated NHC) has a significant effect on the reactivity and selectivity in the tandem reactions studied. The mixed-donor ligand 1,3-dibutylimidazol{[4,5-*f*][1,10]-phenanthrolin}-2-ylidene, featuring an extended π-electron system and the ability to interact with metal centers via pπ-dπ overlap, exerts a significant effect on the electronic properties of the bimetallic complexes obtained from this ligand.

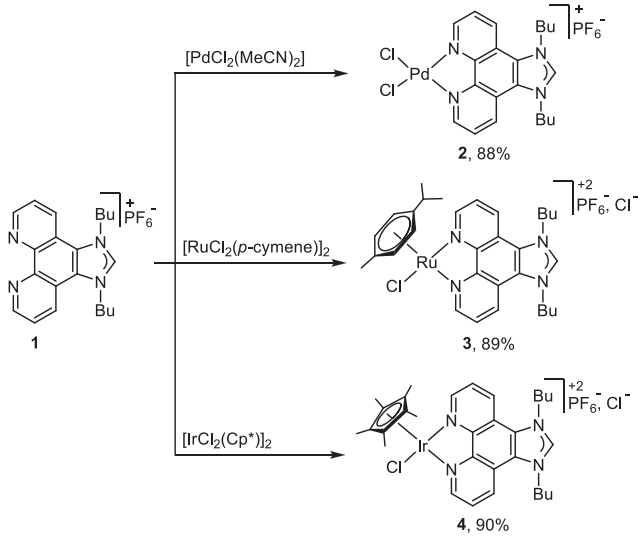
RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. As depicted in Scheme 1, the monometallic complexes **2**−**4** have been prepared by the reaction of the previously described imidazolium salt **1**[20] with equimolar amounts of $[PdCl_2(MeCN)_2]$, $[RuCl_2(p\text{-cymene})]_2$, and $[IrCl_2(Cp^*)]_2$, respectively, in CH_2Cl_2. In all cases, proligand **1** coordinates with the two phenanthroline nitrogen atoms to the metal center. The monometallic complexes **2**−**4** were obtained in good yields and were characterized by spectroscopic methods. ^{1}H NMR spectra of **3** and **4**, for example, feature the imidazolium N−CH−N resonance at δ 10.30 and 10.36 ppm, respectively. These resonances are slightly downfield shifted in comparison to the equivalent resonace in imidazolium salt **1** (δ 10.17 ppm). Attempts to prepare monometallic complexes analogous to **2**−**4** but featuring an N^N coordinated {M(COD)} complex fragment (M = Rh or Ir, COD = cyclooctadiene) failed under various reaction conditions, and only insoluble or intractable mixtures were obtained.

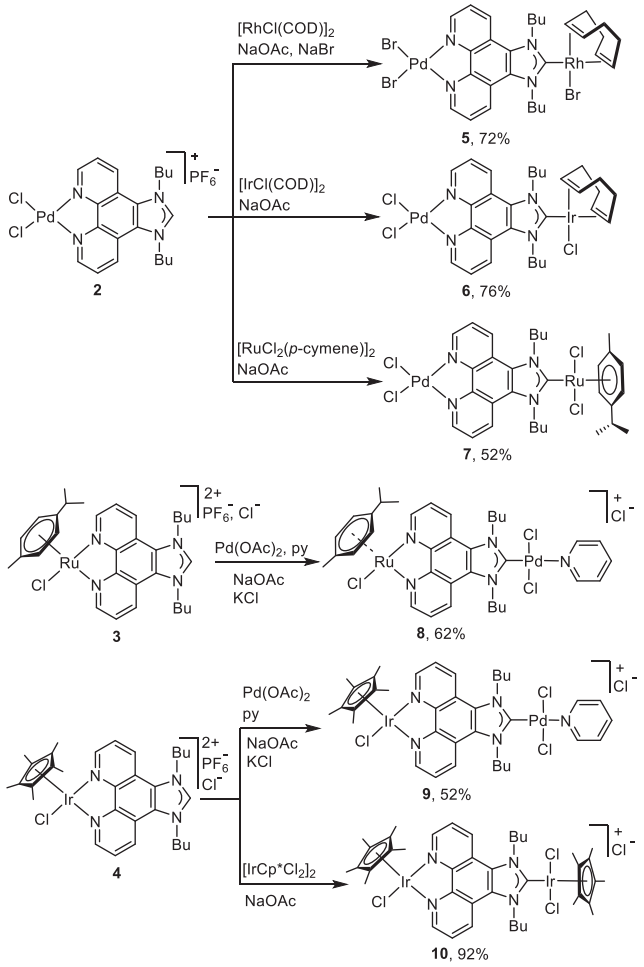
The monometallic complexes **2**−**4** were used as a precursors for the synthesis of heterobimetallic complexes. The reaction of palladium N^N-chelate complex **2** with $[MCl(COD)]_2$ (M = Rh, Ir) in the presence of NaOAc in CH_3CN affords complexes **5** (M = Rh, addition of NaBr necessary) and **6** (M = Ir) in high yields (Scheme 2, top). The heterobimetallic Ru/Pd complex **7** was prepared by metalation of the diamino-heterocycle of **2** with $[RuCl_2(p\text{-cymene})Cl_2]_2$ in THF using NaOAc as base. In addition, reaction of **3** or **4** with an equimolar amount of $[Pd(OAc)_2]$ in the presence of NaOAc, KCl, and an excess of pyridine affords the heterobimetallic complexes **8** (Ru/Pd) and **9** (Ir/Pd) featuring a Pd-NHC moiety (Scheme 2, bottom). The homobimetallic Ir/Ir complex **10** was prepared by reaction of the dinuclear complex $[IrCp^*Cl_2]_2$ with **4**. Complexes **5**−**10** can be handled in air and were purified by column chromatography on silica gel. They are rather stable toward air and moisture. The solubility of the complexes in acetone or halogenated solvents is rather low.

The heterobimetallic complexes **5**−**9** were characterized by spectroscopic methods and elemental analysis, but unfortunately, the ^{13}C NMR spectra of **5** and **6** could not be recorded due to the low solubility of the complexes. However, single crystals of **5** and **6** suitable for X-ray diffraction analyses were obtained by slow evaporation of the solvent from dichloromethane solutions of the complexes. These studies confirmed that **5** and **6** feature a planar three dentate imidazol{[4,5-

Scheme 1. Synthesis of Monometallic Complexes 2−4



Scheme 2. Synthesis of Heterobimetallic Complexes 5−10



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f][1,10]-phenanthrolin}-2-ylidene ligand bridging two metal centers (Pd/Rh or Pd/Ir, Figure 1).

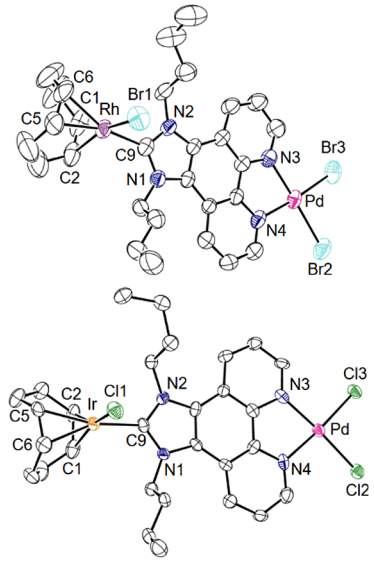
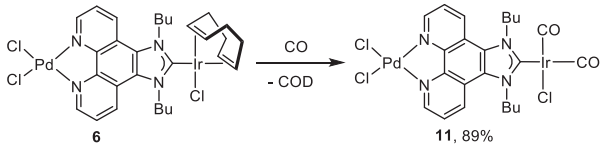


Figure 1. Molecular structures of **5** (top) and **6** (bottom). Hydrogen atoms have been omitted for clarity, and displacement ellipsoids are drawn at the 50% probability level.

Formation of the heterobimetallic complexes **7**–**9** and the homobimetallic complex **10** was confirmed by ^{1}H NMR spectroscopy where the downfield resonance for the N–CH–N protons of the monometallic complexes **2**–**4** was not observed anymore. The ^{13}C NMR spectra showed the characteristic C_{NHC} resonance at δ 178.6 (**7**), 164.9 (**8**), 154.2 (**9**), and 192.2 ppm (**10**).

In geneal, NHC ligands display good σ-donor and weak π-acceptor properties.[21] For an approximate evaluation of the electronic situation at a given metal center, metal bound carbonyl ligands have proved useful. Measuring of the carbonyl stretching frequencies of {M(CO)(NHC)} complexes allows an evaluation of the donor properties of NHC ligands, which is an important factor for homogeneous catalysis.[22−24] In order to evaluate the donor properties of the NHC ligand in **6**, for example, CO was bubbled through a solution of the complex in dichloromethane at ambient temperature to give complex **11** in good yield (Scheme 3). The reaction resulted in a quantitative

Scheme 3. Synthesis of Complex 11



substitution of the COD ligand by two CO ligands. The wavenumbers of the CO stretching modes were recorded at ν = 2067 and 1987 cm^{-1}, and these values are consistent with known [IrCl(CO)$_2$(NHC)]-type complexes.[13]

The IR data of the complexes **2**–**10** are summarized in Table 1. The spectra showed bands of varying intensities in the range of 4000–400 cm^{-1} clearly indicating the presence of the diaminoheterocycle with ν(C–N) vibrations between ν = 1411 and 1744 cm^{-1}.

Table 1. Selected IR, UV-vis, and NMR Spectroscopic Data for Compexes 2–10

entry	complex	IR (ν, cm^{-1})	UV–vis (λ, nm)	$\delta(C_{NHC})$ (ppm)
1	**2**	3346, 1411, 1352	383, 334, 291, 224	
2	**3**	3404, 1716, 1361	385, 305, 220, 205	
3	**4**	3366, 1696, 1489	330, 305, 230, 205	
4	**5**	3675, 1741, 1364	395, 320, 255, 240	not recorded
5	**6**	3582, 1631, 1405	398, 330, 240, 215	not recorded
6	**7**	3597, 1603, 1313	445, 390, 340, 290	178.6
7	**8**	3506, 1744, 1482	435, 375, 360, 290	164.9
8	**9**	3460, 1522, 1316	410, 351, 304, 268	154.2
9	**10**	3469, 1532, 1421	421, 386, 314, 276	192.2

The electronic absorption spectra of the monometallic complexes **2**–**4** and the heterobimetallic complexes **5**–**9** in dimethyl sulfoxide at ambient temperature are also summarized in Table 1. The monometallic complexes **2**–**4** exhibited intense bands due to ligand centered transitions and metal-to-ligand charge transfer transitions (MLCT) bands with the most intense bands recorded in the λ = 383–410 nm range. With the addition of the second metal by metalation of the NHC, perceptible changes in the absorption spectra were observed. For example, the absorption maximum of the monometallic complex **3** appeared at λ = 385 nm while that of the bimetallic complex **8**, now containing the {NHC–Pd} complex fragment, exhibited the strongest absorption at λ = 435 nm. Generally, the absorption maxima of the bimetallic complexes are shifted to higher wavelengths compared to the monometallic derivatives.

Molecular Structures of 5 and 6. The coordination geometry around the rhodium atom (in **5**) or the iridium atom (in **6**) is distorted square-planar with two coordination sites occupied by the midpoints of the double bonds of the cycloocta-1,5-diene (COD) ligand while the remaining two sites are occupied by the C_{NHC} atom and a halogeno ligand (Figure 1). The parameter τ_4 has been used to describe the coordination geometry of ML_4 complexes.[25,26] For a square-planar complex, τ_4 is zero, while it becomes one for a tetrahedral complex. For the iridium atom of the heterobimetallic complex **6**, the τ_4 value of 0.07 confirms the square-planar coordination geometry, while a τ_4 value of 0.04 was calculated for the rhodium atom in heterobimetallic complex **5**.

In complex **6**, the NHC ligand and the halogeno ligand are bound *cis* to each other and in *trans* positions to the centroids of the COD double bonds. This leads to two short Ir–C_{olefin} (*trans* to chloride) and two longer Ir–C_{olefin} (*trans* to NHC) bond distances due to the differences in *trans* influence of the halogeno and the NHC ligands. The Ir–C_{COD} distances range from 2.087(9) to 2.197(6) Å, and these values fall in the range reported for related IR-cod complexes.[27−29] The Ir–Cl1 bond length is also close to values reported for this separation in the literature.[30,31] (Table 2). The two chloride ligands and the two nitrogen atoms from the phenanthroline (phen) donor form an approximately square-planar polyhedron around the palladium atom of **6**, which lies 0.008(2) Å out of the least-squares plane defined by the atoms N3, N4, Cl2, and Cl3. The bond lengths and angles in the coordinated phen ligand of complexes **5** and **6** are slightly different from those found in the free phen ligand.[32] In the both complexes, the two nitrogen atoms are arranged closer to each other (2.639 Å in **5**, 2.620 Å in **6**, 2.720

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes 5 and 6

	5 (M = Rh, X = Br)	6 (M = Ir, X = Cl)
M−X1	2.512 (8)	2.374 (2)
M−C1	2.101 (6)	2.104 (9)
M−C2	2.105 (6)	2.087 (9)
M−C5	2.197 (6)	2.196 (8)
M−C6	2.202 (6)	2.160 (9)
M−C9	2.016 (5)	2.025 (8)
Pd1−X2	2.404 (8)	2.281(2)
Pd1−X3	2.392 (8)	2.286(2)
Pd1−N3	2.041 (4)	2.014(7)
Pd1−N4	2.047 (4)	2.017(7)
X1−M1−C9	89.1 (1)	90.2 (2)
X1−M1−D1[a]	91.1 (2)	89.8 (2)
X1−M1−D2	176.2 (2)	175.2 (2)
C9−M1−D1	177.0 (2)	174.9 (2)
C9−M1−D2	92.8(2)	95.3 (2)
D1−M1−D2	87.1 (2)	86.9 (3)
X2−Pd1−X3	90.4 (3)	90.7 (8)
X2−Pd1−N3	175.1 (1)	175.1 (2)
X2−Pd1−N4	97.4(1)	94.1(2)
X3−Pd1−N3	94.5 (1)	94.1 (2)
N3−Pd1−N4	80.4(2)	81.0(3)

[a]D1 and D2 are the midpoints of the C5═C6 and C1═C2 double bonds.

Å in the free ligand), most likely a consequence of the chelating coordination to the palladium atom.

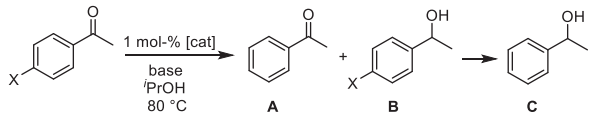
In complex **5**, the angle between the NHC plane and the coordination plane Br1/D1/D2 (D1, D2 are the midpoints of the COD double bonds) measures 86.1(3)°, which is slightly smaller than dihedral angles reported for related complexes.[33,34] The COD ring adopts a boat conformation, with the Rh−C_{COD} distances in the range 2.101(6)−2.202(6) Å. These distances agree well with the values reported in the literature for related complexes.[34−37] Similarly to complex **6**, the Rh−C1 and Rh−C2 bond distances in **5** (*trans* to Br1) are shorter than Rh−C5 and Rh−C6 distances (*trans* to C_{NHC}). The Rh−Br1 separation is close to the values reported in the literature for related complexes.[34−37]

Catalytic Studies. Transition metal catalyzed processes have enabled various transformations in modern organic synthesis. The power and efficiency of such methods is limited by the conventional focus on chemical reactions as discrete events. Peris and co-workers, however, studied polydentate N-heterocyclic carbene ligands and triazoldiylidene bridged heterobimetallic complexes of palladium, rhodium, iridium, and ruthenium as catalysts for tandem reactions, such as the dehalogenation/transfer hydrogenation and the Suzuki coupling/transfer hydrogenation.[12,13,16]

We have developed the heterobimetallic complexes **5**−**9** as catalysts for selected tandem reactions. These complexes, containing two different metal centers, were investigated in tandem reactions such as the dehalogenation/transfer hydrogenation and the Suzuki−Miyaura coupling/transfer hydrogenation. We also compared the catalytic properties of the dinuclear complexes to the activity of mixtures of related mononuclear complexes.

In order to obtain some basic information on the catalytic activity of the heterobimetallic complexes, we first studied their use in the dehalogenation/transfer hydrogenation of 4-haloacetophenone in the presence of ^{i}PrOH and KOH at 80 °C (Table 3, entries 1−5). In a related study, Peris and co-

Table 3. Dehalogenation/Transfer Hydrogenation of 4-Haloacetophenone[a]



				yield (%)		
entry	catalyst	X	base	A	B	C
1	**5**	Br	KOH	20	14	66
2	**6**	Br	KOH	10	18	72
3	**7**	Br	KOH	18	26	56
4	**8**	Br	KOH	0	0	>99
5	**9**	Br	KOH	0	10	88
6	**8**	Br	Cs_2CO_3	28	5	66
7	**9**	Br	Cs_2CO_3	33	9	58
8	**8**	Br	KO^{t}Bu	0	>99	0
9	**8**	Cl	KOH	0	87	13
10	**10** + **12**	Br	KOH	34	10	56
11[b]	**8**	Br	KOH	0	0	92

[a]Reaction conditions: 4-haloacetophenone (0.36 mmol), base (1.08 mmol), catalyst (1 mol %), 2-propanol (2.0 mL), 80 °C, 2 h. Yields determined by gas chromatography. [b]The reaction was carried out in the presence of a drop of Hg^0.

workers used heterobimetallic complexes and Cs_2CO_3 as a base.[16] As can be seen from the data in Table 3, the best results regarding formation of the desired compound **C** were obtained by using complexes **8** and **9** (entries 4 and 5). Complexes **5**−**7** gave product mixtures containing larger amounts of **A** and **B**. In the presence of a strong base such as KO^{t}Bu, complex **8** catalyzed only the transfer hydrogenation to give **B** and no dehalogenation was observed (entry 8). For the chlorinated acetophenone, this type of reaction was also observed with complex **8** and KOH as the base (entry 9). When two homodimetallic complexes (Ir/Ir complex **10**, Scheme 2, and known Pd/Pd complex **12**;[20] see Figure 2) were used in

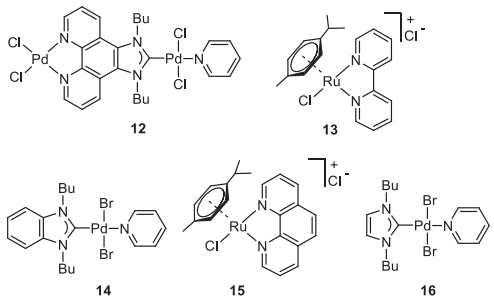


Figure 2. Known homobimetallic complex **12** and monometallic complexes **13**−**16** used in catalytic studies.[19,20,38]

equimolar ratio (base KOH), the yield of **C** decreased (entry 10) relative to the heterobimetallic Ir/Pd complex **9** (entry 5). In order to establish the homogeneous character of the catalytic transformation, a Hg^0 poisoning test was performed (entry 11). No change of the catalytic activity was observed in the presence of mercury for complex **8**, indicative for a homogeneous catalytic reaction.

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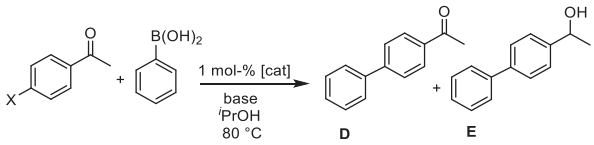
Table 4 shows representative data for the Suzuki coupling of 4-haloacetophenone with phenylboronic acid using various of

Table 4. Suzuki Coupling/Transfer Hydrogenation of 4-Haloacetophenone[a]



				yield (%)	
entry	catalyst	X	base	D	E
1	**5**	Br	KOH	26	14
2	**6**	Br	KOH	12	19
3	**7**	Br	KOH	24	5
4	**8**	Br	KOH	1	99
5	**9**	Br	KOH	12	88
6	**8**	Br	Cs_2CO_3	44	56
7	**8**	Br	KO^{t}Bu	8	30
8	**8**	Br	NaOH	21	79
9	**8**	Cl	KOH	86	14
10	**10** + **12**	Br	KOH	33	48
11	**13** + **14**	Br	KOH	85	8
12	**15** + **16**	Br	KOH	97	2

[a]Reaction conditions: 4-bromoacetophenone (0.36 mmol), KOH (0.72 mmol), phenylboronic acid (0.55 mmol), 2-propanol (2.0 mL), 80 °C, 2 h. Yields were determined by gas chromatography.

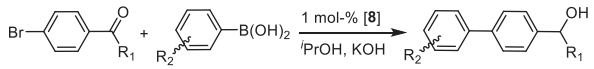
the prepared catalysts. Several bases (KOH, Cs_2CO_3, KO^{t}Bu, and NaOH) were employed. The best results were obtained in ^{i}PrOH at 80 °C. As can be seen from Table 4, the C−C coupling/transfer hydrogenation is best catalyzed by complexes **8** and **9** where it is completed within 2 h if formation of **E** is considered. The best results were obtained with complex **8** (entry 4). In contrast, the analogues of **8** and **9**, complexes **6** and **7**, containing the same metals, but at opposite coordination sites, give lower yields of **E** (entries 2 and 3). These results indicate that the coordination of an identical set of metals, but differing sites (N^N chelate or NHC), influences the catalytic performance of the complexes. The highest yields of **E** were always obtained when the palladium atom was bound to the NHC donor and the second metal (Ru or Ir) by the N^N chelate site.

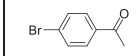
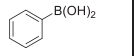
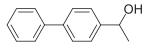
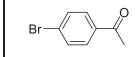
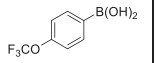
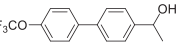
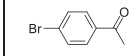
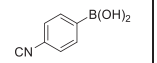
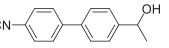
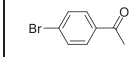
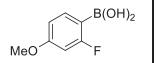
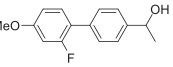
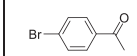
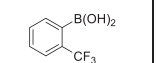
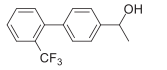
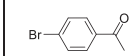
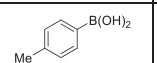
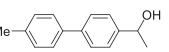
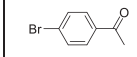
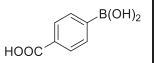
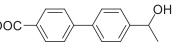
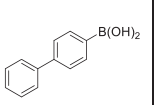
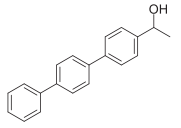
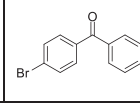
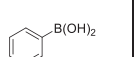
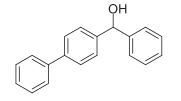
Interestingly, when 4-chloroacetophenone was used as substrate, C−C coupling and formation of compound **D** was observed as the major reaction product (catalyst **8**, entry 9). The mixture of two homobimetallic complexes (**10** + **12**) also gave a lower yield of **E** when compared to **9** (entry 10). Under the reaction conditions used, no dehalogenation products were observed, indicating that the coupling reaction is faster than the reduction of the 4-haloacetophenones.

In order to evaluate the effect of the heterobimetallic complexes compared to equimolar mixtures of homometallic ones, the known monometallic complexes **13** (Ru-N^N-chelate), **14** (Pd-NHC), **15** (Ru-N^N-chelate), and **16** (Pd-NHC) were prepared (Figure 2). As shown in Table 4, a significant decrease in catalytic activity of mixtures of two monometallic complexes **13** + **14** (entry 11) and **15** + **16** (entry 12) regarding the production of compound **E** was observed in comparison to the heterobimetallic Ru-N^N-chelate/Pd-NHC complex **8** (entry 4). While the reasons for this observation are not fully understood at this time, this may be a consequence of the higher local concentration of metal centers in the heterobimetallc complexes. In addition, subtle differences in the coordination of the bridging ligand may produce important differences in its electron-donating and steric properties. However, the data in Table 4 clearly show that the bridging ligand plays an essential role in the tandem reaction.

Using the most active catalyst **8**, the scope of the catalytic Suzuki coupling/transfer hydrogenation was studied with 4-bromobenzophenone and various boronic acids, affording the corresponding biphenyl alcohols in excellent yields (88−99%) (Table 5). The reaction tolerated a variety of functional

Table 5. Tandem Suzuki−Miyaura/Transfer Hydrogenation of 4-Bromoacetophenone Derivatives[a]



Entry	Ar-Br	ArB(OH)$_2$	Product	Yield [%]
1				99
2				96
3				98
4				82
5				88
6				99
7				99
8				94
9				90

[a]Reaction conditions: ketone (0.36 mmol), KOH (0.72 mmol), arylboronic acid (0.55 mmol), 2-propanol (2.0 mL), 80 °C, 2 h. Yields were determined by gas chromatography.

groups, including OMe, Me, and COOH, CN, OCF_3, and Ph, in varying substitution patterns, enabling a benign and efficient two-step synthesis of various organic compounds.

CONCLUSION

We have prepared a series of heterobimetallic complexes (Pd/Rh **5**, Pd/Ir **6**, Pd/Ru **7**, Ru/Pd **8**, and Ir/Pd **9**) bridged by the mixed donor set 1,3-dibutylimidazol{[4,5-*f*][1,10]-phenanthrolin}-2-ylidene ligand in which the metals coordinated to different donors of the ligand. The heterobimetallic complexes **5**−**9** were synthesized in a stepwise procedure and were used

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as catalysts in the tandem reactions (dehalogenation/transfer hydrogenation and Suzuki–Miyaura coupling/transfer hydrogenation). It was observed that the heterobimetallic complex **8** is the most active catalyst for the preparation of biphenyl alcohols. However, the analogue with an inverted coordination of the metals (complex **7**) only catalyzed cross-coupling reactions.

EXPERIMENTAL SECTION

All reactions were performed under air. The solvents were used as received, and the reagents were purchased from Sigma-Aldrich, Merck, Alfa Aesar, and Acros Organics. When required, solvents were dried by standard techniques. Compounds **1**, **2**, **12**,[20] **15**,[19] and **13**[38] were synthesized according to published procedures. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Varian AS 400 Mercury instrument, and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. FT-IR spectra were obtained on a PerkinElmer Spectrum 100 series spectrometer, and UV spectra were recorded on a PG T60 UV–vis spectrophotometer. Elemental analyses were performed with a PerkinElmer PE 2400 elemental analyzer.

Synthesis of Complex 3. A mixture of $[RuCl_2(p\text{-cymene})]_2$ (26 mg, 0.1 mmol) and proligand **1** (48 mg, 0.1 mmol) in THF (5 mL) was stirred for 2 h at ambient temperature. The resulting cream colored precipitate was isolated by filtration. The crude solid product was washed with diethyl ether (2 × 5 mL) and dried *in vacuo*. Yield: 69 mg (0.08 mmol, 89%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 1 H, N-CH-N), 10.11 (d, J = 4.8 Hz, 2 H, phen-H), 9.32 (d, J = 4.8 Hz, 2 H, phen-H), 8.32 (m, 2 H, phen-H), 6.41 (d, J = 5.2 Hz, 2 H, cymene-H), 6.16 (d, J = 6.0 Hz, 2 H, cymene-H), 4.99 (t, J = 6.8 Hz, 4 H, butyl-CH_2), 2.65 (m, 1 H, cymene-H), 2.18 (s, 3 H, cymene-H), 2.01 (m, 4 H, butyl-CH_2), 1.48 (m, 4 H, butyl-CH_2), 0.95 (m, 12 H, cymene-H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.9, 144.9, 143.9, 133.9, 127.7, 125.8, 120.4, 105.6, 104.0, 86.8, 85.0, 50.4, 31.0, 30.4, 22.2, 19.2, 18.5, 13.9. Anal. Calcd for $C_{31}H_{39}N_4Cl_2F_6PRu$ (M = 784.61): C, 47.45; H, 5.01; N, 7.14. Found: C, 47.41; H, 5.09; N, 7.11.

Synthesis of Complex 4. A mixture of $[IrCl_2Cp^*]_2$ (26 mg, 0.1 mmol) and proligand **1** (48 mg, 0.1 mmol) in CH_3CN (5 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was washed with diethyl ether (2 × 5 mL) and dried *in vacuo*. Yield: 79 mg (0.09 mmol, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.36 (s, 1 H, N-CH-N), 9.52 (d, J = 4.8 Hz, 2 H, phen-H), 9.38 (d, J = 4.8 Hz, 2 H, phen-H), 8.41 (m, 2 H, phen-H), 5.02 (t, J = 7.2 Hz, 4 H, butyl-CH_2), 2.01 (m, 4 H, butyl-CH_2), 1.73 (s, 15 H, Cp*-CH_3), 1.49 (m, 4 H, butyl-CH_2), 0.96 (t, J = 7.6 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.4, 144.4, 134.4, 128.5, 125.8, 120.4, 97.9, 50.9, 30.7, 19.3, 13.9, 8.9. Anal. Calcd for $C_{31}H_{40}N_4Cl_2F_6IrPIr$ (M = 876.76): C, 42.47; H, 4.60; N, 6.39. Found: C, 42.36; H, 4.43; N, 6.21.

Synthesis of Complex 5. A mixture of complex **2** (100 mg, 0.15 mmol), $[Rh(COD)Cl]_2$ (36 mg, 0.075 mmol), NaOAc (38 mg, 0.45 mmol), and NaBr (46 mg, 0.45 mmol) in MeCN (5 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was washed with diethyl ether (3 × 5 mL). The orange residue was recrystallized from CH_2Cl_2. Yield: 96 mg (0.10 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 5.2 Hz, 2 H, phen-H), 8.56 (d, J = 5.2 Hz, 2 H, phen-H), 7.69 (m, 2 H, phen-H), 5.78 (m, 2 H, butyl-CH_2), 5.23 (br, 2 H, COD-CH), 5.18 (m, 2 H, butyl-CH_2), 3.77 (br, 2 H, COD-CH), 2.46 (m, 6 H, COD-CH_2), 2.11 (m, 4 H, butyl-CH_2), 1.91 (m, 2 H, COD-CH_2), 1.78 (m, 4 H, butyl-CH_2), 1.22 (t, J = 8.4 Hz, 6 H, butyl-CH_3). The ^{13}C NMR spectrum could not be recorded due to the low solubility of the complex. Anal. Calcd for $C_{29}H_{36}N_4Br_3PdRh$ (M = 887.79): C, 39.23; H, 4.09; N, 6.31. Found: C, 39.18; H, 4.23; N, 6.21%.

Synthesis of Complex 6. A mixture of **2** (100 mg, 0.15 mmol), $[IrCl(COD)]_2$ (50 mg, 0.075 mmol), and NaOAc (38 mg, 0.45 mmol) in CH_3CN (5 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was washed with diethyl ether (3 × 5 mL). The orange residue was recrystallized from CH_2Cl_2. Yield: 96 mg (0.11 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, J = 5.2 Hz, 2 H, phen-H), 8.86 (d, J = 5.2 Hz, 2 H, phen-H), 7.80 (m, 2 H, phen-H), 5.76 (t, J = 6.8 Hz, 2 H, butyl-CH_2), 5.03 (t, J = 5.2 Hz, 2 H, butyl-CH_2), 4.87 (br, 2 H, COD-CH), 3.29 (br, 2 H, COD-CH), 2.34 (m, 8 H, COD-CH_2, butyl-CH_2), 1.81 (m, 8 H, COD-CH_2, butyl-CH_2), 1.17 (t, J = 8.0 Hz, 6 H, butyl-CH_3). The ^{13}C NMR spectrum could not be recorded due to the low solubility of the complex. Anal. Calcd for $C_{29}H_{36}N_4Cl_3IrPd$ (M = 845.59): C, 41.19; H, 4.29; N, 6.62. Found: C, 41.01; H, 4.38; N, 6.51.

Synthesis of Complex 7. A mixture of **2** (100 mg, 0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (46 mg, 0.075 mmol), and NaOAc (38 mg, 0.45 mmol) in THF (10 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was washed with diethyl ether (3 × 5 mL). Yield: 64 mg (0.07 mmol, 52%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (d, J = 8.4 Hz, 1 H, phen-H), 9.06 (d, J = 8.4 Hz, 1 H, phen-H), 8.52 (d, J = 8.4 Hz, 1 H, phen-H), 8.25 (d, J = 8.4 Hz, 1 H, phen-H), 7.94 (t, J = 8.4 Hz, 1 H, phen-H), 7.76 (t, J = 8.4 Hz, 1 H, phen-H), 5.72 (m, 2 H, butyl-CH_2), 5.23 (d, J = 6.0 Hz, 1 H, cymene-H), 5.10 (d, J = 6.0 Hz, 1 H, cymene-H), 5.04 (m, 2 H, cymene-H), 4.59 (m, 2 H, butyl-CH_2), 2.76 (m, 1 H, cymene-H), 2.35 (s, 3 H, cymene-H), 2.08 (m, 8 H, butyl-CH_2), 1.68 (d, J = 7.6 Hz, 6 H, cymene-H), 1.07 (t, J = 7.2 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.6, 151.3, 144.9, 134.6, 127.8, 126.3, 120.6, 106.3, 104.7, 88.3, 83.7, 50.8, 31.7, 30.2, 22.7, 19.8, 18.4, 12.8. Anal. Calcd for $C_{31}H_{38}N_4Cl_4PdRu$ (M = 815.92): C, 45.63; H, 4.69; N, 6.87. Found: C, 45.13; H, 4.68; N, 4.59.

Synthesis of Complex 8. A mixture of **3** (100 mg, 0.13 mmol), $Pd(OAc)_2$ (29 mg, 0,13 mmol), KCl (38 mg, 0.52 mmol), pyridine (1.0 mL), and NaOAc (38 mg, 0.45 mmol) in CH_3CN (5 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was purified by column choromatography (eluent: CH_2Cl_2/MeOH). Yield: 72 mg (0.08 mmol, 62%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.97 (d, J = 4.8 Hz, 2 H, phen-H),), 9.21 (t, J = 4.8 Hz, 2 H, phen-H), 8.91 (d, J = 5.2 Hz, 2 H, py-H), 8.28 (m, 2 H, phen-H), 8.02 (t, J = 5.2 Hz, 1 H, py-H), 7.62 (t, J = 5.2 Hz, 2 H, py-H), 6.33 (d, J = 6.8 Hz, 1 H, cymene-H), 6.30 (d, J = 6.8 Hz, 1 H, cymene-H), 6.09 (m, 2 H, cymene-H), 5.50 (br, 4 H, butyl-CH_2), 2.65 (m, 1 H, cymene-H), 2.17 (m, 4 H, butyl-CH_2, 3 H, cymene-H), 1.75 (m, 4 H, butyl-CH_2), 1.12 (d, J = 7.6 Hz, 6 H, cymene-H), 0.95 (t, 6 H, J = 8.4 Hz, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.9, 152.5, 150.9, 144.8, 139.4, 134.0, 127.7, 127.0, 125.8, 120.4, 105.5, 104.0, 87.0, 84.9, 50.4, 30.9, 30.6, 22.2, 19.3, 18.7, 13.9. Anal. Calcd for $C_{36}H_{43}N_5Cl_4PdRu$ (M = 895.02): C, 48.31; H,4.84; N, 7.83. Found: C, 48.36; H, 5.04; N, 7.91.

Synthesis of Complex 9. A mixture of **4** (100 mg, 0.11 mmol), $Pd(OAc)_2$ (25 mg, 0,11 mmol), KCl (38 mg, 0.52 mmol), pyridine (1.0 mL), and NaOAc (38 mg, 0.45 mmol) in CH_3CN (5 mL) was stirred for 2 h at ambient temperature. The resulting yellow colored precipitate was isolated by filtration. The crude solid product was purified by column choromatography (eluent: CH_2Cl_2/MeOH). Yield: 56 mg (0.05 mmol, 52%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (d, J = 8.8 Hz, 2 H, phen-H), 9.21 (d, J = 8.8 Hz, 2 H, phen-H), 8.87 (d, J = 7.6 Hz, 2 H, py-H), 8.34 (m, 2 H, phen-H), 8.02 (t, J = 7.6 Hz, 1 H, py-H), 7.64 (t, J = 7.6 Hz, 2 H, py-H), 5.55 (br, 4 H, butyl-CH_2), 2.15 (m, 4 H, butyl-CH_2,), 1.75 (m, 4 H, butyl-CH_2), 1.52 (m, 15 H, Cp*-CH_3), 1.10 (t, J = 7.6 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.2, 153.1, 151.4, 145.3, 145.2, 145.1, 135.2, 134.9, 129.4, 128.0, 127.7, 126.7, 126.5, 121.3, 120.1, 98.8, 51.3, 31.5, 20.2, 14.8, 9.9. Anal. Calcd for $C_{36}H_{44}N_5Cl_4IrPd$ (M = 987.17): C, 43.80; H, 4.49; N, 7.10. Found: C, 43.82; H, 4.62; N 7.13.

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Synthesis of Complex 10. A mixture of **4** (100 mg, 0.11 mmol), $[IrCp^*Cl_2]_2$ (45 mg, 0.05 mmol), and NaOAc (38 mg, 0.45 mmol) in THF (10 mL) was stirred under argon for 2 h at ambient temperature. The mixture was then heated to reflux for 24 h. The solvent was removed under reduced pressure. The orange solid product was recrystallized from CH_2Cl_2. Yield: 114 mg (0.10 mmol, 92%). ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.36 (d, 2 H, J = 5.6 Hz, phen-H), 9.13 (d, J = 8.0 Hz, 2 H, phen-H), 8.33 (dd, ^1J = 6.4 Hz, ^1J = 5.6 Hz, 2 H, phen-H), 5.61 (td, ^1J = 12.9 Hz, ^2J = 4.8 Hz, 1 H, butyl-CH_2), 5.15 (td, ^1J = 12.9 Hz, ^2J = 4.8 Hz, 1 H, butyl-CH_2), 4.62 (s, br, 1 H, butyl-CH_2), 3.08 (s, br, 1 H, butyl-CH_2), 2.27 (s, br, 2 H, butyl-CH_2), 2.01 (m, 2 H, butyl-CH_2), 1.93−1.57 (m, 34 H, butyl-CH_2, Cp*-CH_3), 1.07 (t, J = 7.2 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.2, 151.5, 144.1, 133.5, 128.3, 127.3, 119.9, 89.9, 85.4, 65.4, 53.0, 50.5, 33.6, 31.1, 29.6, 19.7, 15.7, 14.0, 8.6. Anal. Calcd for $C_{41}H_{54}N_4Cl_4Ir_2$ (M = 1129.12): C, 43.61; H, 4.96; N, 4.96. Found: C, 43.62; H, 4.96; N, 4.91.

Synthesis of Complex 11. Complex **6** (0.1 mmol) was dissolved in MeOH (5 mL), and CO gas was bubbled through the solution for 1 h. The color of the solution changed from bright yellow to pale yellow. The solution was concentrated to 1 mL and pentane (5 mL) was added. A pale yellow solid precipitated and was isolated by filtration and was washed with pentane. Yield: 71 mg (0.08 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 2 H, phen-H), 8.44 (d, J = 8.4 Hz, 2 H, phen-H), 7.76 (m, 2 H, phen-H), 5.26 (m, 2 H, butyl-CH_2), 4.83 (m, 2 H, butyl-CH_2), 2.09 (m, 2 H, butyl-CH_2), 1.88 (m, 2 H, butyl-CH_2), 1.63 (m, 4 H, butyl-CH_2), 1.10 (t, J = 6.8 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 180.3, 167.3, 148.5, 144.0, 133.3, 127.0, 126.2, 119.9, 51.9, 31.2, 19.9, 13.6. Anal. Calcd for $C_{23}H_{24}N_4Cl_3IrO_2Pd$ (M = 793.43): C, 34.81; H, 3.05; N, 7.06. Found: C, 34.58, H, 3.41, N, 6.96.

General Procedure for the Preparation of Complexes 14 and 16. The appropriate azolium salt (0.5 mmol) and $Pd(OAc)_2$ (0.5 mmol) were suspended in anhydrous pyridine (10 mL), and the mixture was stirred at 65 °C for 4 h. The residual pyridine was then removed *in vacuo* at room temperature. The complexes were purified by column chromatography on silica gel. Removal of the solvent and crystallization from CH_2Cl_2/diethyl ether afforded **14** and **16**.

*Complex **14**.* Yield: 200 mg (0.34 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (dd, J = 8.0 Hz, 2 H, py-H), 8.71 (t, J = 8.0 Hz, 1 H, py-H), 7.79 (m, 2 H, py-H), 7.37 (m, 2H, Ar-H), 7.24 (t, J = 16.0 Hz, 2 H, Ar-H), 4.71 (t, J = 16.0 Hz, 4 H, butyl-CH_2), 2.22 (m, 4 H, butyl-CH_2), 1.59 (m, 4 H, butyl-CH_2), 1.08 (t, J = 8.0 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 178.2, 159.5, 153.8, 134.8, 122.6, 110.3, 49.3, 30.3, 20.4, 13.8. Anal. Calcd for $C_{20}H_{27}N_3Br_2Pd$ (M = 575.64): C, 41.73; H, 4.73; N, 7.30. Found: C, 41.84; H, 4.68; N, 7.21.

*Complex **16**.* Yield: 162 mg (0.03 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, J = 8.0 Hz, 2 H, py-H), 8.89 (d, J = 8.0 Hz, 1 H, py-H), 7.76 (t, J = 8.0 Hz, 2 H, py-H), 7.33 (t, J = 8.0 Hz, 2 H, im-CH), 4.51 (t, J = 16.0 Hz, 4 H, butyl-CH_2), 2.07 (m, 4 H, butyl-CH_2), 1.47 (m, 4 H, butyl-CH_2), 1.03 (t, J = 16.0 Hz, 6 H, butyl-CH_3). ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 160.6, 154.3, 138.3, 124.9, 120.9, 51.1, 32.2, 20.0, 13.8. Anal. Calcd for $C_{16}H_{25}N_3Br_2Pd$ (M = 525.59): C, 36.56; H, 4.79; N, 7.99; Found: C, 36.60; H, 4.82; N, 8.03%.

General Procedure for the Tandem Dehalogenation/Transfer Hydrogenation of Haloacetophenones. In a typical run, a reaction vessel containing a stirring bar was charged with the 4-haloacetophenone (0.36 mmol), base (1.08 mmol), catalyst (1 mol %), phenylboronic acid (0.55 mmol), diethylene glycol-di-*n*-butylether (0.6 mmol, internal standard), and 2 mL of 2-propanol. The reaction mixture was stirred at 80 °C for the 2 h. For reaction monitoring, a small amount of sample was periodically withdrawn by syringe and conversion was analyzed by GC chromatography.

General Procedure for the Tandem Suzuki Coupling/Transfer Hydrogenation of Haloacetophenones. In a typical run, a capped vessel containing a stirring bar was charged with the ketone (0.36 mmol), base (0.72 mmol), catalyst (1 mol %), arylboronic acid (0.55 mmol), diethylene glycol-di-*n*-butylether (0.6 mmol, internal standard), and 2 mL of 2-propanol. The reaction mixture was stirred at 80 °C for 2 h. Yields were determined by GC chromatography and NMR spectroscopy.

X-ray Diffraction Studies. Single-crystal data were collected at 293(2) K for **5** and at 100 K for **6** using the ω-scan technique on a Rigaku-Oxford Xcalibur diffractometer with an Eos CCD area detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The data collection, cell refinement, and data reduction were performed using the CrysAlis^{Pro} program.[39] Analysis of the structures was performed using the OLEX2 programs,[40,41] and the structure models were refined by the full-matrix least-squares method based on F^2 against all reflections using the SHELXL.[42] All non-hydrogen atoms were refined anisotropically. The carbon-bound hydrogen atoms were included on idealized positions and were refined riding on their parent carbon atoms with C−H = 0.93, 0.96, 0.97, and 0.98 Å for aryl, methyl, methylene, and methine hydrogen atoms, respectively, with U_{iso}(H) = 1.5U_{eq}(methyl carbon) and 1.2U_{eq}(nonmethyl carbon). Geometrical calculations were performed using PLATON.[43] The figures were made using ORTEP.[44] A summary of the crystal data, experimental details, and refinement results for complexes **5** and **6** is presented (see the Supporting Information, Table S1).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00882.

NMR spectra of all compounds (PDF)

Accession Codes

CCDC 1584349 and 1584351 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Buchwalter, P.; Rosé, J.; Braunstein, P. Multimetallic Catalysis Based on Heterometallic Complexes and Clusters. *Chem. Rev.* **2015**, *115*, 28−126.

(2) (a) Peris, E. Polyaromatic N-heterocyclic carbene ligands and π-stacking. Catalytic consequences. *Chem. Commun.* **2016**, *52*, 5777−5787. (b) Zhou, J. Recent Advances in Multicatalyst Promoted Asymmetric Tandem Reactions. *Chem. - Asian J.* **2010**, *5*, 422−434.

DOI: 10.1021/acs.organomet.8b00882
Organometallics XXXX, XXX, XXX−XXX

(3) Burton, J. J., Garten, R. L., Eds. *Advanced Materials in Catalysis*; Academic Press: New York, 1977; p 129.
(4) McCleverty, J. A., Meyer, T. J., Eds. *Comprehensive Coordination Chemistry II*; Elsevier Pergamon: Oxford, U.K., 2004.
(5) Kharisov, B. I.; Martínez, P. E.; Jiménez-Pérez, V. M.; Kharissova, O. V.; Martinez, B. N.; Pérez, N. Recent advances on ditopic ligands. *J. Coord. Chem.* **2010**, *63*, 1−25.
(6) Jones, C. J. Transition metals as structural components in the construction of molecular containers. *Chem. Soc. Rev.* **1998**, *27*, 289−300.
(7) Würthner, F.; You, C. C.; Saha-Möller, C. R. Metallosupramolecular squares: from structure to function. *Chem. Soc. Rev.* **2004**, *33*, 133−146.
(8) Bencini, A.; Lippolis, V. 1,10-Phenanthroline: A versatile building block for the construction of ligands for various purposes. *Coord. Chem. Rev.* **2010**, *254*, 2096−2180.
(9) Böhmer, M.; Kampert, F.; Tan, T. T. Y.; Guisado-Barrios, G.; Peris, E.; Hahn, F. E. Ir^{III}/Au^{I} and Rh^{III}/Au^{I} Heterobimetallic Complexes as Catalysts for the Coupling of Nitrobenzene and Benzylic Alcohol. *Organometallics* **2018**, *37*, 4092−4099.
(10) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. Concurrent Tandem Catalysis. *Chem. Rev.* **2005**, *105*, 1001−1020.
(11) Ajamian, A.; Gleason, J. L. Two Birds with One Metallic Stone: Single-Pot Catalysis of Fundamentally Different Transformations. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754−3760.
(12) Zanardi, A.; Mata, J. A.; Peris, E. Well-Defined Ir/Pd Complexes with a Triazolyl-diylidene Bridge as Catalysts for Multiple Tandem Reactions. *J. Am. Chem. Soc.* **2009**, *131*, 14531−14537.
(13) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. Y-Shaped Tris-N-Heterocyclic-Carbene Ligand for the Preparation of Multifunctional Catalysts of Iridium, Rhodium, and Palladium. *Organometallics* **2012**, *31*, 5606−5614.
(14) Dehury, N.; Maity, N.; Tripathy, S. K.; Basset, J.-M.; Patra, S. Dinuclear Tetrapyrazolyl Palladium Complexes Exhibiting Facile Tandem Transfer Hydrogenation/Suzuki Coupling Reaction of Fluoroarylketone. *ACS Catal.* **2016**, *6*, 5535−5540.
(15) (a) Bitzer, M. J.; Kühn, F. E.; Baratta, W. Tandem Suzuki−Miyaura/transfer hydrogenation reaction catalyzed by a Pd−Ru complex bearing an anionic dicarbene. *J. Catal.* **2016**, *338*, 222−226. (b) Dehury, N.; Tripathy, S. K.; Sahoo, A.; Maity, N.; Patra, S. Facile tandem Suzuki coupling/transfer hydrogenation reaction with a bis-heteroscorpionate Pd−Ru complex. *Dalton Trans* **2014**, *43*, 16597−16600.
(16) Mata, J. A.; Hahn, F. E.; Peris, E. Heterometallic complexes, tandem catalysis and catalytic cooperativity. *Chem. Sci.* **2014**, *5*, 1723−1732.
(17) Zhang, D.; Xu, J.; Zhao, Q.; Cheng, T.; Liu, G. A Site-Isolated Organoruthenium-/Organopalladium-Bifunctionalized Periodic Mesoporous Organosilica Catalyzes Cascade Asymmetric Transfer Hydrogenation and Suzuki Cross-Coupling. *ChemCatChem* **2014**, *6*, 2998−3003.
(18) Zhang, G.; Liu, R.; Chou, Y.; Wang, Y.; Cheng, T.; Liu, G. Multiple Functionalized Hyperbranched Polyethoxysiloxane Promotes Suzuki Coupling Asymmetric Transfer Hydrogenation One-Pot Enantioselective Organic Transformations. *ChemCatChem* **2018**, *10*, 1882−1888.
(19) Gök, L.; Türkmen, H. Half-sandwich η^6-arene−ruthenium(II) complexes bearing 1-alkyl(benzyl)-imidazo[4,5-*f*][1,10]-phenanthroline (IP) derivatives: the effect of alkyl chain length of ligands to catalytic activity. *Tetrahedron* **2013**, *69*, 10669−10674.
(20) Gök, L.; Günnaz, S.; Şahin, Z. S.; Pelit, L.; Türkmen, H. The {[4,5-f][1,10]-phenanthrolin}l-2-ylidene and its palladium complexes: Synthesis characterization, and application in C-C cross-coupling reactions. *J. Organomet. Chem.* **2017**, *827*, 96−104.
(21) Hahn, F. E.; Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172.
(22) Türkmen, H.; Çetinkaya, B. *N*-heterocyclic carbene complexes of Rh(I) and electronic effects on catalysts for 1,2-addition of phenylboronic acid to aldehydes. *Appl. Organomet. Chem.* **2011**, *25*, 226−232.
(23) Türkmen, H.; Çetinkaya, B. 1,3-Diarylimidazolidin-2-ylidene (NHC) complexes of Pd(II): Electronic effects on cross-coupling reactions and thermal decompositions. *J. Organomet. Chem.* **2006**, *691*, 3749−3759.
(24) Leuthäußer, S.; Schwarz, D.; Plenio, H. Tuning the Electronic Properties of N-Heterocyclic Carbenes. *Chem. - Eur. J.* **2007**, *13*, 7195−7203.
(25) Jiang, A.; Krüger, C.; Pfeil, B. Structure of Dichloro(4,7-diphenyl-1,10-phenanthroline)palladium(II). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 2334−2338.
(26) Yang, L.; Powell, D. R.; Houser, R. P. Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index, τ_4. *Dalton Trans* **2007**, 955−964.
(27) Theron, M.; Purcell, W.; Basson, S. S. (η4-Cycloocta-1,5-diene)(2-pyridinethiolato-N-oxide-κO,κS)iridium(I). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *C52*, 336−338.
(28) Hälg, W. J.; Öhrström, L. R.; Rüegger, H.; Venanzi, L. M.; Gerfin, T.; Gramlich, V. The Dynamic Behaviour and NMR Solution Structures of Complexes of the Type (Bisphosphine)(cycloocta-1,5-diene)iridium(I) and the X-Ray Crystal Structure of (Cycloocta-1,5-diene)((−)-norphos)iridium(I) Hexafluorophosphate. *Helv. Chim. Acta* **1993**, *76*, 788−803.
(29) Wehman-Ooyevaar, I. C. M.; Luitwieler, I. F.; Vatter, K.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. Intramolecular C−H activation and oxidative addition reactions of iridium complexes containing arylamines with bulky substituents on nitrogen; X-ray structures of $[Ir^{I}(C_6H_4CH_2NEt_2\text{-}2\text{-}C,N(cod)]$ and $[Ir^{III}(C_6H_4CH_2NEt(CHMe)\text{-}2\text{-}C,N,C')I(cod)]$ (cod = cycloocta-1,-5-diene). *Inorg. Chim. Acta* **1996**, *252*, 55−69.
(30) Choate, M. M.; Peters, R. G.; Baughman, R. G. Chlorido(η4−1,5-cyclooctadiene)[(penta-fluoroethyl)diphenylphosphane]iridium-(I). *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *E67*, m72.
(31) Nichol, G. S.; Walton, D. P.; Anna, L. J.; Rajaseelan, E. [2-Butyl-4-(4-tert-butylbenzyl)-1,2,4-triazol-3-ylidene]chlorido[(1,2,5,6-η)-cycloocta-1,5-diene]iridium(I). *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2012**, *E68*, m158−m159.
(32) Nishigaki, S.; Yoshioka, H.; Nakatsu, K. The Crystal and Molecular Structure of *o*-Phenanthroline. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 875−879.
(33) Dinçer, M.; Özdemir, N.; Günay, M. E.; Çetinkaya, B.; Büyükgüngör, O. [1,3-Bis(2-ethoxyphenyl)imidazolidin-2-ylidene]-bromo(cycloocta-1,5-diene)rhodium(I). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2005**, *C61*, m373−m375.
(34) Dinçer, M.; Özdemir, N.; Gülcemal, S.; Çetinkaya, B. [1,3-Bis(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]bromido(η^4-cycloocta-1,5-diene)rhodium(I). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2007**, *C63*, m228−m230.
(35) Dinçer, M.; Özdemir, N.; Gülcemal, S.; Çetinkaya, B.; Büyükgüngör, O. Bromo(η^4-cycloocta-1,5-diene)[1-(2,3,4,5,6-pentafluorobenzyl)-3-(2,4,6-trimethylbenzylbenzimidazol-2-ylidene]-rhodium(I). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2006**, *C62*, m252−m254.
(36) Mayr, M.; Wurst, K.; Ongania, K.; Buchmeiser, M. R. 1,3-Dialkyl- and 1,3-Diaryl-3,4,5,6-tetrahydropyrimidin-2-ylidene Rhodium(I) and Palladium(II) Complexes: Synthesis, Structure, and Reactivity. *Chem. - Eur. J.* **2004**, *10*, 1256−1266.
(37) Pawar, G. M.; Wurst, K.; Wang, D.; Buchmeiser, M. [μ-3,3′-Diisopropyl-1,1′-(propane-1,3-di-yl)bis-(1,3-diazinan-2-ylidene)]bis-[bromido-(η^4-cycloocta-1,5-diene)rhodium(I)]. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2014**, *E70*, m71−m72.
(38) Türkmen, H.; Kani, İ.; Çetinkaya, B. Transfer Hydrogenation of Aryl Ketones with Half-Sandwich Ru^{II} Complexes That Contain Chelating Diamines. *Eur. J. Inorg. Chem.* **2012**, *2012*, 4494−4499.
(39) *CrysAlis PRO and CrysAlis RED*; Agilent Technologies: Yarnton, Oxfordshire, England, 2002.

DOI: 10.1021/acs.organomet.8b00882
Organometallics XXXX, XXX, XXX−XXX

(40) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.
(41) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment − *Olex2* dissected. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *A71*, 59−75.
(42) Sheldrick, G. M. Crystal Structure refinement with *SHELXL*. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3−8.
(43) Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.
(44) Farrugia, L.J. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012**, *45*, 849−854.

DOI: 10.1021/acs.organomet.8b00882
Organometallics XXXX, XXX, XXX−XXX