Syntheses, Structures and Catalytic Properties of Dinuclear Iridium(I) Complexes with a Hexadentate Macrocyclic Diamine-Tetracarbene Ligand

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ABSTRACT: Two dinuclear macrocyclic Ir(I)-NHC complexes $[Ir_2(L^1)(COD)_2](PF_6)_2$ (**1**, COD = 1,5-cyclooctadiene) and $[Ir_2(L^1)(COD)Cl]Cl$ (**2**) have been prepared from the reaction between $[Ir(COD)Cl]_2$ and macrocyclic N-heterocyclic carbene (NHC) ligand precursor $(H_4L)(PF_6)_4$ containing four benzimidazolium and two secondary amine groups. Furthermore, **1** and **2** have been carbonylated into $[Ir_2(L^1)(CO)_4](PF_6)_2$ (**3**) and $[Ir_2(L^1)(CO)_2Cl]Cl$ (**4**), respectively. Notably, **1** can capture the chloride ion to turn itself into **2** accompanying with the transformation from *cis* to *trans* configuration of ? due to the flexibility of macrocyclic ligand. **2** is unusual with a five-coordinate Ir(I) center exhibiting a distorted tetragonal pyramid geometry because such five-coordination is rarely reported for Ir(I)-NHC complexes. The catalytic properties of **1**, **2** and a related mononuclear Ir(I) complex $[(L^2)Ir(COD)](PF_6)$ (**5**, L^2 = bis-NHC ligand) have been evaluated in 1,4 conjugate addition reactions of arylboronic acids to cyclohexen-2-one. These three complexes are the first examples of Ir(I)-NHC species showing such catalytic properties for 1,4-addition reactions, which possess higher catalytic activities than the reported Ir(I) complex.

INTRODUCTION

Since the isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo and co-workers,[1] NHCs have been extensively employed as ancillary ligands in organometallic chemistry due to the facile tuning of the ligand's electronic and steric effects via the introduction of the substituents on the heterocyclic rings.[2] In the past decades, metal complexes with various type of macrocyclic NHC ligands[2l] including bidentate,[3] tridentate,[4] tetradentate[5-11] macrocyclic ligands and those high-dentate with more than four donors[12-13] have been reported, some of which have found potential applications as luminescent materials,[3a] medicines,[4a] and catalysts.[8c,10c]

Among the various NHC-containing macrocyclic ligands, the macrocyclic tetracarbene ligands with different linkers have been extensively studied in coordination to various transition metal ions. The resulting complexes exhibit diverse conformations due to the flexibility of macrocyclic ligands.[2l,6-12] They can be roughly classified into two types. The first type contains the exclusive four NHC groups, which have been substantially employed to prepare many metal complexes.[6-11] The second type is those with more than four donors atoms including donor atoms other than the four NHC groups.[12] The first macrocyclic tetra(NHC) platinum(II) complex (**A**, Chart 1) was synthesized via a template controlled reaction by Hahn et al..[6a] Subsequently, a variety of macrocyclic tetra(NHC) metal complexes have been obtained using *in situ* deprotonation or transmetalation method.[6-12] Most of tetracarbene metal complexes are mononuclear with coordination number 4-6, especially for the first type tetraNHC ligands.[6-11] The dinuclear or multinuclear structures are found for Au(I), Ag(I) or Cu(I) complexes, in which each metal ion is coordinated with two NHC donors in a linear fashion (example **B** in Chart 1).[6b-6d,7a,8b,10a,12] It should be noted that the combination of the four NHC groups and additional donor atoms such as nitrogen could give rise to various macrocyclic functionalized NHC ligands. However, the number of the reported examples is small.[12] Pyridine group has been combined with four NHC donors to give several mixed pyridine-NHC ligand precursors, from which very interesting macrocyclic metal-NHC complexes have been synthesized (examples **C**, **D**, Chart 1).[12a,12b] Recently we have designed a 26-membered macrocyclic diamine-tetracarbene ligand (L^1) and synthesized several metal complexes including the first example of dinuclear Ni(II) complex with a singly bridging oxo group and Ni(II) complex with Ni_2N_2 core formed by two bridging amides (example **E**, Chart 1).[14]

The Ir-NHC complexes have been extensively investigated as outstanding catalysts for, e.g., transfer hydrogenation[15] and N-alkylation catalysts.[16] Most of Ir(I,III)-NHC catalysts are supported by mono-NHC, poly-NHC or functionalized NHC ligands containing other donor group.[15-17] However, the example of the Ir complex with macrocyclic NHC-containing ligand is extremely rare. The only known example is a heterobimetallic complex, in which the Au(I) ion is located in the cavity of the tetra-NHC ligand and each of the two Ir(I) atom is coordinated with one carbene donor hanging outside the ligand (**F**, Chart 1).[6d]

As an extension of our study of coordination chemistry of our diamine-tetracarbene ligand L^1,[14] we have attempted to prepare Ir(I) complexes with L^1. Here we report dinuclear Ir(I) complexes $[Ir_2(L^1)(COD)_2](PF_6)_2$ (**1**) and $[Ir_2(L^1)(COD)Cl]Cl$ (**2**), $[Ir_2(L^1)(CO)_4](PF_6)_2$ (**3**) and $[Ir_2(L^1)(CO)_2Cl]Cl$ (**4**). **2** and **4** are unusual binuclear complexes containing a rare five-coordinate Ir(I) center. **1** can switch its configuration from *cis* to *trans* form by capturing chloride ion to form **2**. **1** and **2** display considerable catalytic activities for 1,4 addition reactions of arylboronic acids to α, β-unsaturated ketones.

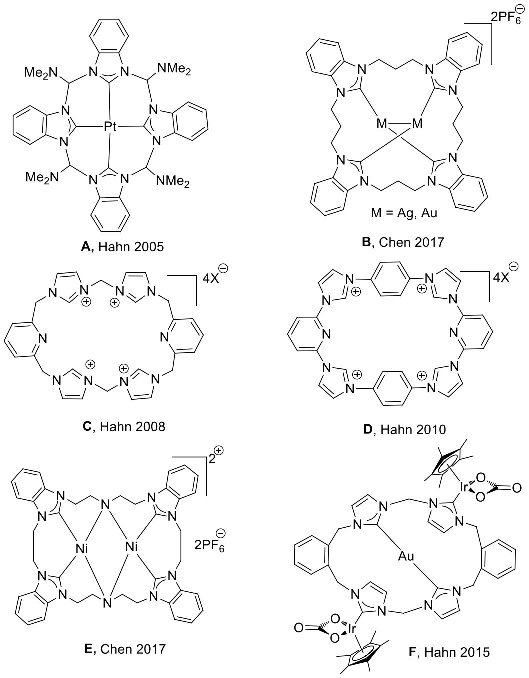


Chart 1. Selected examples of tetra-NHC ligands and metal complexes

RESULTS AND DISCUSSIONS

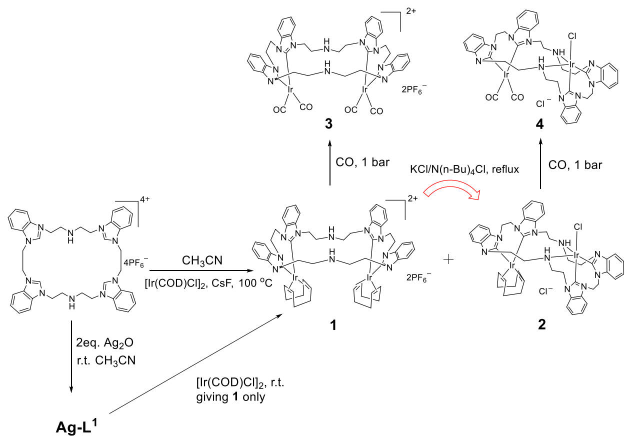
Synthesis and Characterization of Metal Complexes. The macrocyclic salt $(H_4L^1)(PF_6)_4$ was prepared using a reported three-step procedure.[14] Complex $[Ir_2L^1(COD)_2](PF_6)_2$ (**1**) is prepared in 42% yield as the major product by reacting $(H_4L^1)(PF_6)_4$ with $[Ir(COD)Cl]_2$ in the presence of CsF in acetonitrile at 100 °C (Scheme 1). A minor product is also isolated as $[Ir_2L(COD)Cl]Cl$ (**2**) in 15% yield from the same reaction pot. **1** and **2** are separated by column chromatography.

Ag(I)-NHC complexes are often used as transmetalation reagent to prepare other transition metal NHC complexes.[18] **1** can also be synthesized by transmetalation reaction from Ag(I) complex Ag-L^1 formed *in situ*, from which a binuclear species was isolated and characterized in our previous work.[14] The reaction was carried out between $[Ir(COD)Cl]_2$ and 0.5 equiv of Ag-L^1 formed *in situ* in CH_3CN, affording **1** in 56% yield. In this reaction, **1** is the only isolated product because of the absence of free Cl^- ion, which was used by Ag^+ to form AgCl precipitate.

1 and **2** can be carbonylated by bubbling a stream of CO into an acetonitrile solution to yield the carbonylated complexes $[Ir_2(L^1)(CO)_4](PF_6)_2$ (**3**) and $[Ir_2(L^1)(CO)_2Cl]Cl$ (**4**) in high yield**,** respectively.

1-**4** have been characterized by NMR, electrospray ionization mass spectrometry (ESI-MS) and IR spectroscopy. No resonance for 2*H*-benzimidazium protons of $(H_4L^1)(PF_6)_4$ was detected in **1**-**4**, indicating the coordination of the carbene carbon to the Ir(I) ions. The ^1H NMR spectrum of **1** reveals a highly symmetrical structure, which displays four resonances for 16 aromatic protons, one singlet signal at 4.72 ppm for the protons of two equivalent ethylene linkers between two benzimidazolylidene units, and two signals at 4.84−5.12 ppm and 3.16−3.41 ppm for the ethylene bridges between benzimidazolylidene and secondary amine. The ^{13}C NMR spectrum of **1** exhibits the characteristic peak of the carbene carbon at 185.63 ppm, which is similar to those of the reported Ir(I)-NHC complexes.[15-17] In contrast with **1**, the ^1H NMR spectrum of **2** is more complicated, in accordance with lower symmetrical structure. Twelve ^1H NMR signals appear at 3.32-6.23 ppm, which are due to 12 methylene groups of ethylene linkers. The ^{13}C NMR spectrum shows two resonances at 185.31 and 186.38 ppm, corresponding to two magnetic inequivalent carbene carbons. There are also two sets of ^{13}C NMR resonances at 110.32-135.48 ppm for aromatic carbons, corresponding to two inequivalent aromatic moieties. No resonances of 1,5-cyclooctadiene at 2.0-2.75 ppm are found in the ^1H NMR spectra of **3** and **4**, indicating that COD has been replaced by CO. The new signals at 174.94 and 168.84 ppm in ^{13}C NMR spectra are due to the carbonyl groups. The IR spectra show infrared stretching frequencies of carbonyl groups at 2078 cm^{-1}, 1999 cm^{-1} for **3** and 2092 cm^{-1}, 2010 cm^{-1} for **4**. ESI-MS data show their respective $[\mathbf{1}\text{-}PF_6]^+$ and $[\mathbf{1}\text{-}2PF_6]^{2+}$, $[\mathbf{2}+H]^+$ and $[\mathbf{2}\text{-}2Cl]^{2+}$, $[\mathbf{3}\text{-}PF_6]^+$ and $[\mathbf{4}+H]^+$ fragments, respectively, in agreement with their bimetallic macrocyclic structures.

Scheme 1. Synthesis of 1-4



It is found that the yield of **2** is enhanced with the addition of $n\text{-}NBu_4Cl$ at the beginning of the reaction. When more than 2 equiv NBu_4Cl is added, **2** is the only isolated product. Based on this observation, we postulated that **1** can be converted into **2** in the presence of chloride ion. Thus, a reaction between **1** and 2 equiv $n\text{-}NBu_4Cl$ in CH_3CN was carried out, which indeed yielded **2**. This conversion proceeds slowly at ambient temperature, but finishes in half an hour with heating the solution to reflux. In the conversion from **1** to **2**, one COD group in **1** is lost and the simultaneous coordination of amine and chloride results in a switch from *trans*- to *cis*-configuration on one half of the molecule.

The solid-state structures of **1** and **2** have been determined by single-crystal X-ray diffraction on the single crystal grown from slow evaporation of the acetone solution of each complex (Figs. 2-3 with the selected bond lengths and angles in the captions). As expected, both **1** and **2** display a dinuclear macrocyclic structure. In the crystal lattice, there are two crystallographically independent molecules of **1** with similar structural parameters. Therefore, only structural data for one molecule are discussed here. **1** exhibits a C_{2v} symmetry, which is in good agreement with the NMR data. Each Ir(I) center is coordinated with two carbene donors and a COD ligand. Therefore **1** can be regarded as two mono Ir(I) units connected by two diethyleneamino bridges. The two Ir(I) centers lie on the same side of the macrocyclic ring, adopting a *cis*-configuration. The Ir-C_{NHC} distances (2.008(17) Å), Ir-C_{COD} distances (2.169(17), 2.179(14) Å), and C_{NHC}-Ir-C_{NHC} angle (87.2(8)°) are comparable to the reported precedents.[15-16]

In **2** (Fig. 3), the two Ir(I) centers are located on the opposite sides of the macrocyclic ring. Ir2 is four-coordinated with two benzimidazole carbene donors and a COD ligand, which is similar to **1**. Interestingly, the other metal atom Ir1 adopts a distorted tetragonal pyramid geometry (τ = 0.107)[19] with two benzimidazole carbene donors and two nitrogen atoms in the equatorial plane and one chloride in the apical position. Despite a large number of Ir(I)-NHC complexes reported, examples of five-coordinate Ir(I)-NHC complexes remain rare[17] probably due to the high electron-donor ability of NHC ligands favoring a four-coordinate planar geometry over five-coordination. Due to the different coordination modes of two Ir(I) centers in **2**, the dihedral angle between two benzimidazoles of Ir1 (115.21°) is larger than that in Ir2 (106.84°). The Ir1-C_{NHC} distances are 1.88(2) and 2.022(16) Å, while Ir2-C_{NHC} distances are 1.97(2) and 2.04(2) Å. The Ir1-N distances are 2.240(13) and 2.243(15) Å. The Ir1-Cl1 distance is 2.513(4) Å, which is similar to the Ir-Cl distance in other reported Ir(I)-NHC complexes.[17c,17f]

It is found that there are hydrogen bonds between the chloride anions and the hydrogen atoms. The coordinated Cl1 formed four hydrogen bonds with four hydrogen atoms. Similar hydrogen bonds are formed between Cl2 and hydrogen atoms (Figure S14). The π-π stacking interactions of benzimidazole rings exist in the crystal lattices of **1** and **2**, which results in a one-dimensional supramolecular chain with face to face distance of 3.644 Å in **1** but two neighboring molecules in **2** with face to face distance of 3.468 Å ~~in 2~~ (Figure S12).

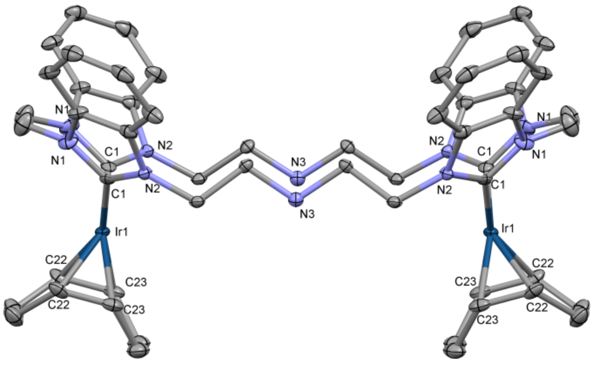


Figure 2. Structure of **1** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1-C1 2.008(17), Ir1-C22 2.179(14), Ir1-C23 2.169(17), C1-Ir1-C1 87.2(8), C22-Ir1-C22 80.6(8), C23-Ir-C23 80.5(8), C22-Ir1-C23 36.7(6) 92.0(6).

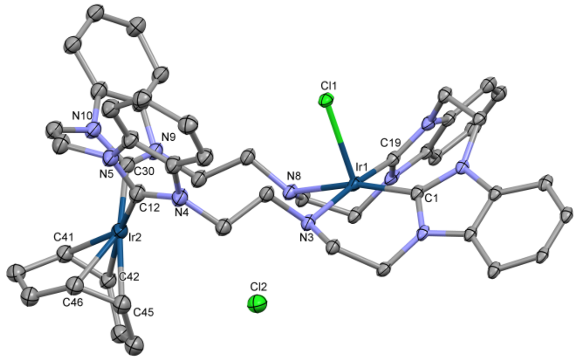


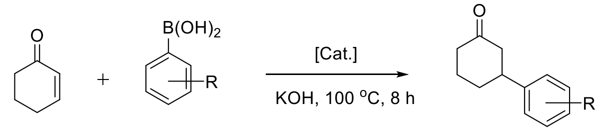
Figure 3. Structure of **2** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1-C1 2.022(16), Ir1-C19 1.88(2), Ir1-Cl1 2.513(4), Ir1-N8 2.240(13), Ir1-N3 2.243(15), Ir2-C12 1.97(2), Ir2-C30 2.04(2), C1-Ir1-C19 89.9(7), C1-Ir1-N8 166.2(7), C19-Ir1-N3 172.6(7), C12-Ir2-C30 88.8(9).c

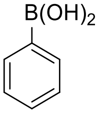
Catalytic Performances of 1 and 2. The construction of carbon-carbon bond has received much attention in organic chemistry. It has been reported that a large number of NHC-metal complexes can induce the reactions of C-C bond formation.[20]

Recent research shows that 1,4 addition of arylboronic acids to α, β-unsaturated ketones are normally catalyzed by Rh[21-22] and Pd complexes.[23] It is found some Rh-NHC complexes show good activities and chemoselectivities.[22] Only few Ir complexes have been reported to be able to catalyze the 1,4-addition reactions despite the lower cost of Ir.[24] To the best of our knowledge, there is no report on the evaluation of Ir-NHC complexes in this addition reaction. Herein, we have evaluated the catalytic properties of **1** and **2** in 1,4-addition of arylboronic acids to cyclohexen-2-one.

The general procedure for catalytic reactions refers to the reported Rh-catalyzed 1,4-addition reaction,[22d] and we have optimized the solvent. The substrates and 1-2 mol% loading of **1** or **2** were dissolved in the solvent at refluxing within 8 h and KOH was used as the base. Four solvents have been tested and yields are shown in Table 1. The mixed solvent toluene/water (2:1) is the best solvent for our reactions. Therefore this mixed solvent (Table 1) was used as the solvent to study the catalytic performances of **1** and **2** towards the addition of five different arylboronic acid to cyclohexen-2-one. The results are summarized in Table 2. Comparison of the yields obtained with **1** and **2** under the same catalytic conditions (Entries 1 vs 2, 7 vs 8, 13 vs 14, 19 vs 20, 25 vs 26) show that both **1** and **2** exhibit a definite catalytic activity, and **1** affords better catalytic outcomes than **2**. This suggests that the four-coordinate Ir(I) center with two NHC units and COD displays higher activity than the five-coordinate Ir(I) center. The lower activity of catalyst **2** could be due to the presence of the five-coordinate Ir(I) center. When the amount of catalyst **2** was doubled, the yields of reactions catalyzed by **2** reached the level of **1** as expected (Entries 3, 9, 15, 21, 27; Table 2).

Table 1. Optimization of the Solvent of Arylboronic Acids to Cyclohex-2-one[a]

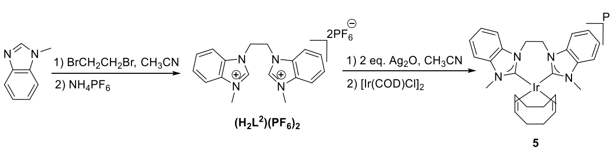


Entry	Catalyst	Solvent	Arylboronic	Yield (%)[b]
1	**1**	Toluene		28
2	**1**	THF		12
3	**1**	THF/water (2:1)		10
4	**1**	Toluene/water (2:1)		70

[a]Conditions: cyclohexen-2-one (0.5 mmol), [Ir] (1 mol%), KOH (0.01 mmol), $ArB(OH)_2$ (0.6 mmol); [b]Isolated yields.

In order to test if the two mononuclear Ir(I) units in **1** show a cooperative performance in the catalytic reactions, a related mononuclear Ir(I) complex $(L^2)Ir(COD)](PF_6)$ (**5**) has been synthesized and applied to the addition reaction. **5** was prepared by the reaction between $[Ir(COD)Cl]_2$ and the Ag-L^2 species formed *in situ* in CH_3CN (Scheme **2**). The crystals of **5** were obtained by slow evaporation of an acetone solution of **5**. The molecular structure of **5** was found to have a similar coordination geometry as **1** (Fig. 4) and Ir2 in **2**. The Ir-C_{NHC} distances are 2.033(3), and 2.012(4) Å and C_{NHC}-Ir-C_{NHC} angle is 84.18(13)°, which are close to those in **1** and Ir2 in **2**.

Scheme 2. Synthesis of 5



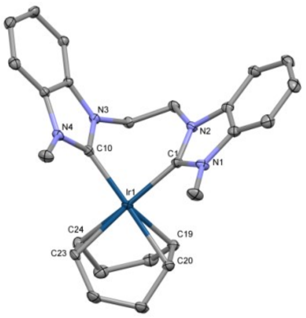
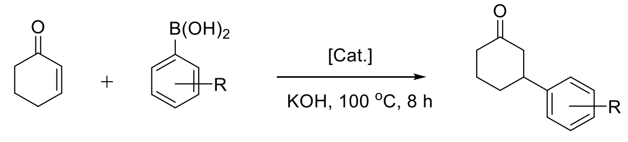
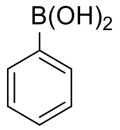
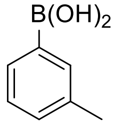
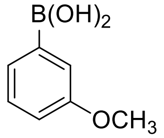
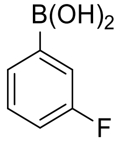
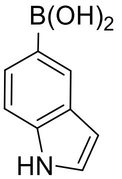


Figure 4. Structure of complex **5** showing 30 % probability ellipsoids. Hydrogen atoms and the hexafluorophosphate anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1-C1 2.033(3), Ir1-C10 2.012(4), Ir1-19 2.165(4), Ir1-20 2.214(4), Ir1-23 2.189(4), Ir1-24 2.191(4), C1-Ir1-C10 84.18(13).

The catalytic results indicate that the yield of reaction catalyzed by **5** is close to **2** with the same catalyst loading (Table 2, entries 5, 11, 17, 23 and 29), but lower than **1**. When increasing the catalyst loading of **5** to 2 mol%, the yields are similar to **1** (Table 2, entries 6, 12, 18, 24 and 30). These results show that the two Ir(I) centers in **1** could be regarded as two independent catalytic centers, while the five-coordinate Ir(I) unit in **2** is probably inactive for this catalytic reaction.

Table 2. 1,4 Addition of Arylboronic Acids to Cyclohex-2-one[a]



Entry	Catalyst	[Ir] [%]	Arylboronic	Yield (%)[b]
1	1	1		70
2	2	1		50
3	**2**	2		68
4	$[Ir(COD)Cl]_2$	1		23
5	5	1		49
6	5	2		65
7	1	1		88
8	2	1		48
9	**2**	2		82
10	$[Ir(COD)Cl]_2$	1		31
11	5	1		44
12	5	2		75
13	1	1		92
14	2	1		59
15	**2**	2		88
16	$[Ir(COD)Cl]_2$	1		23
17	5	1		55
18	5	2		85
19	1	1		42
20	2	1		26
21	**2**	2		40
22	$[Ir(COD)Cl]_2$	1		12
23	5	1		23
24	5	2		35
25	1	1		84
26	2	1		53
27	**2**	2		83
28	$[Ir(COD)Cl]_2$	1		27
29	5	1		49

30	5	2	80

[a]Conditions: cyclohexen-2-one (0.5 mmol), [Ir] (1 mol%), KOH (0.01 mmol), $ArB(OH)_2$ (0.6 mmol), Toluene/water (2:1) mixed solvent (2 mL). [b]Isolated yields.

Sweigart's group have reported a simple mononuclear Ir(I) complex, which has a considerable catalytic activity for the same reaction.[24] Our Ir(I)-NHC complexes exhibit nearly twice the activity of this reported complex. The higher yields are tentatively attributed to the π-π stacking between substrates and macrocyclic ligand.[22d]

The catalytic activity of the iridium precursor $[Ir(COD)Cl]_2$ is also investigated under the same reaction condition for comparison. The yields are similar to the reported mononuclear Ir(I) complex.[24]

From Table 2, the arylboronic acids with electron-donating substituent (3-Me, 3-OMe) have higher yields than the electron-donating substituent (3-F, benzazole). However, all the tested Ir(I) complexes **1**, **2**, **5** and $[Ir(COD)Cl]_2$ cannot achieve the efficiency level of Rh(I) complexes.

CONCLUSION

In this work, four dinuclear Ir(I)-NHC complexes **1**-**4** with macrocyclic diamine-tetracarbene ligand have been synthesized and characterized by NMR, ESI-MS and single X-ray diffraction. **1** contains two Ir(I)-centers coordinated by two NHC groups and one COD ligand, which are in a *cis* arrangement. **2** exhibits a *trans* configuration, which has one four-coordinate Ir(I) center similar to **1** and the other five-coordinate Ir(I) ion exhibiting a rare tetragonal pyramid geometry. **3** and **4** are the carbonylation products of **1** and **2**, in that the COD moieties are replaced by CO. **1** is found to convert into **2** in the presence of chloride ions.

1, **2** and related mononuclear complex **5** have been found to exhibit catalytic performances toward 1,4-addtion of arylboronic acids to cyclohexen-2-one. They presents the first examples on Ir-NHC complexes with the catalytic activity for this addition reaction.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all reactions and manipulations were performed under a dry nitrogen atmosphere using the standard Schlenk techniques. Solvents were dried using conventional methods and freshly distilled before use. NMR spectra were recorded on a Bruker AM-400 spectrometer. ESI-MS were recorded on a Bruker MaXis mass spectrometer. Elemental analysis was performed in a Perkin-Elmer 240C analytic instrument. Macrocyclic tetra-NHC ligand precursor $(H_4L^1)(PF_6)_4$,[14] $(H_2L^2)(PF_6)_2$[25] and the Ir(I) precursor $[Ir(COD)Cl]_2$[26] were synthesized according to the reported procedures.

One-Pot Synthesis of $[Ir_2(L^1)(COD)_2](PF_6)_2$ (1) and $[Ir_2(L^1)(COD)Cl]Cl$ (2). $(H_4L)(PF_6)_4$ (0.1246 g, 0.1 mmol), $[Ir(COD)Cl]_2$ (0.0671 g, 0.1 mmol) and CsF (0.076 g, 0.5 mmol) were suspended in 5 mL of acetonitrile with vigorously stirring at 100 °C for 18 h. After cooling to room temperature, the precipitate was removed by centrifugation. The red solution was evaporated in vacuum and the residue was purified by column chromatography (with acetone/DCM = 1:6) to afford the desired product **1** as red solid (0.069 g, yield: 42.5 %) and **2** as orange solid (0.019 g, yield: 12.4%).

1. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.67-7.69 (d, $^2J_{H,H}$ = 8 Hz 4H, Ph-*H*), 7.52-7.54 (d, $^2J_{H,H}$ = 8 Hz 4H, Ph-*H*), 7.35 (t, 4H, Ph-*H*), 7.25 (t, 4H, Ph-*H*), 5.94-5.95 (m, 4H, COD-*H*), 5.14-5.17 (m, 4H, COD-*H*), 5.10-5.12 (m, 4H, NCH_2), 4.79-4.86 (m, 4H, NCH_2), 4.72 (s, 8H, CH_2), 3.39-3.43 (m, 4H, NCH_2), 3.67 (br, 4H, NCH_2), 2.71-2.74 (m, 4H, COD-*H*), 2.39-2.47 (m, 8H, COD-*H*), 2.08-2.12 (m, 4H, COD-*H*). ^{13}C NMR (100 MHz, acetone-d_6, 25 °C): δ 185.63 (Ir-C_{carbene}), 134.34 (imidazole-ring-*C*), 123.18 (Ph*C*), 111.34 (Ph*C*), 110.14 (Ph*C*), 80.11 (COD-*C*), 77.12 (COD-*C*), 50.09 (N-*C*H_2), 49.15 (N-*C*H_2), 44.27 (N-*C*H_2), 31.45 (N-*C*H_2), 30.95 (N-*C*H_2). MS (ESI): m/z $[M-PF_6]^+$: 1409.50, Anal. Calcd for $C_{56}H_{66}N_{10}F_{12}Ir_2P_2$ (1553.55 g mol^{-1}): C, 43.29; H, 4.28; N, 9.02. Found: C, 43.58; H, 3.94; N, 9.32.

2. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.69-7.72 (m, 4H, Ph-*H*), 7.52-7.54 (dt, $^2J_{H,H}$ = 8 Hz, 8 Hz, 4H, Ph-*H*), 7.36-7.39 (t, 4H, Ph-*H*), 7.31 (t, 2H, Ph-*H*), 7.23 (t, 2H, Ph-*H*), 6.18-6.23 (m, 2H, CH_2), 5.96-6.02 (m, 2H, CH_2), 5.46 (m, 2H, CH_2), 5.25 (m, 2H, CH_2), 5.07-5.11 (m, 2H, CH_2), 4.79-4.89 (m, 4H, COD-*H*), 4.63 (br, 2H, CH_2), 4.52 (br, 2H, CH_2), 4.07-4.18 (m, 4H, CH_2), 3.32-3.45 (m, 4H, CH_2), 2.80-2.90 (m, 2H, COD-*H*), 2.28-2.41 (m, 4H, COD-*H*), 2.09-2.13 (m, 2H, COD-*H*). ^{13}C NMR (100 MHz, acetone-d_6, 25 °C): δ 186.30 (Ir-C_{carbene}), 185.31 (Ir-C_{carbene}), 134.97 (imidazole-ring- *C*), 133.70 (imidazole-ring-*C*), 123.60 (Ph*C*), 123.32 (Ph*C*), 111.66 (Ph*C*), 110.32 (Ph*C*), 81.38 (COD-*C*), 78.62 (COD-*C*), 53.53 (N-*C*H_2), 50.29 (N-*C*H_2), 47.94 (N-*C*H_2), 47.74 (N-*C*H_2), 44.81 (N-*C*H_2), 44.48 (N-*C*H_2), 31.16 (COD-*C*), 30.07 (COD-*C*), 29.45 (COD-*C*), 22.56 (COD-*C*). MS (ESI): m/z $[M + H]^+$: 1227.58, Anal. Calcd for $C_{48}H_{54}N_{10}Cl_2Ir_2$ (1226.35 g mol^{-1}): C, 47.01; H, 4.44; N, 11.42. Found: C, 47.33; H, 4.14; N, 11.55.

Synthesis of $[Ir_2(L^1)(COD)_2](PF_6)_2$ (1) Using Ag_2O. $(H_4L)(PF_6)_4$ (0.1246 g, 0.1 mmol) and Ag_2O (0.0463 g, 0.2 mmol) were suspended in 5 mL of acetonitrile with vigorously stirring in the dark for 12 h at ambient temperature. The excess Ag_2O was then removed by centrifugation and $[Ir(COD)Cl]_2$ (0.036 g, 0.053 mmol) was added into the solution with vigorously stirring for further 3 h at ambient temperature. The red solution was filtered through Celite to remove the AgCl precipitate. The solvent was removed in vacuum and the residue was purified by column chromatography (with acetone/DCM = 1:6) to afford the desired product **1** as red solid (0.046 g, yield: 55.8%).

Synthesis of $[Ir_2(L^1)(COD)Cl]Cl$ (2) in the Presence of NBu_4Cl. $(H_4L)(PF_6)_4$ (0.1246 g, 0.1 mmol), cesium fluoride (0.076 g, 0.5 mmol), NBu_4Cl (0.055 g, 0.2 mmol) and $[Ir(COD)Cl]_2$ (0.0671 g, 0.1 mmol) were suspended in 5 mL acetonitrile with vigorously stirring for 18 h at 100 °C. After cooling to room temperature, the resulting precipitate was removed by centrifugation. The red solution was evaporated in vacuum and the residue was purified by column chromatography (with acetone/DCM = 1:3) to afford the desired product **2** as orange solid (0.058 g, Yield: 47.2%). The crystals of **2** suitable for X-ray diffraction studies were obtained by slow evaporated the acetone solution of **2**.

Conversion of 1 into 2. In a round-bottomed flask, **1** (0.046g, 0.029 mmol, 1 equiv) was dissolved in 5 mL of CH_3CN, followed by addition of KCl (0.022g, 0.3 mmol, 10 equiv). The mixture was stirred at 90 °C for 30 min, and the solution gradually turns from red to orange. Subsequently, the solution was filtered through Celite and the solvent was removed in vacuum. The residue was redissolved in CH_3CN and purified by flash column chromatography (with acetone/DCM = 1:3) to afford **2** as orange solid (0.032 g, yield: 88.6%).

Synthesis of $[Ir_2(L^1)(CO)_4](PF_6)_2$ (3). In a Schlenk tube, **1** (0.046 g, 0.029 mmol) was dissolved in 5 mL of CH_3CN. A stream of CO was continued to bubble through the solution for 30 min at room temperature. The red solution rapidly turned into bright yellow. Then the gas stream was stopped and the solution was stirred for another 30 min. After that, the solvent was evaporated under reduced pressure. The yellow residue was purified by column chromatography (with EA/DCM = 1:4) to afford **3** as bright yellow solid (0.027g, yield: 72.6 %). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.69-7.71 (d, $^2J_{H,H}$ = 8

Hz, 2H, Ph-*H*), 7.63-7.65 (d, $^{2}J_{\mathrm{H,H}}$ = 8 Hz, 2H, Ph-*H*), 7.54-7.59 (m, 4H, Ph-*H*), 7.29-7.33 (t, 2H, Ph-*H*), 7.23-7.27 (m, 6H, Ph-*H*), 6.06-6.12 (m, 2H, C*H*$_2$), 5.52-5.56 (m, 2H, C*H*$_2$), 4.99-5.31 (m, 6H, C*H*$_2$), 4.66-4.79 (m, 4H, C*H*$_2$), 3.94-4.04 (m, 2H, C*H*$_2$), 3.30-3.36 (m, 2H, C*H*$_2$), 3.14-3.21 (t, 2H, C*H*$_2$), 4.52 (br, 2H, C*H*$_2$), 4.07-4.18 (m, 4H, C*H*$_2$), 3.32-3.45 (m, 4H, C*H*$_2$), 2.74-2.82 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, acetone-*d*$_6$, 25 °C): δ 180.93 (Ir-*C*$_{\mathrm{carbene}}$), 174.94 (Ir-*C*O), 133.88 (imidazole-ring-*C*), 132.50 (imidazole-ring-*C*), 122.33 (Ph*C*), 123.61 (Ph*C*), 111.34 (Ph*C*), 109.21 (Ph*C*), 55.22 (N-*C*H$_2$), 52.77 (N-*C*H$_2$), 48.73 (N-*C*H$_2$), 47.99 (N-*C*H$_2$), 46.78 (N-*C*H$_2$), 44.11 (N-*C*H$_2$), 43.40 (COD-*C*). IR (cm^{-1}): 2078, 1999; MS (ESI): m/z [M–PF$_6$]$^+$, [M–2CO–PF$_6$]$^+$: 1303.25, 1247.25, Anal. Calcd for $C_{44}H_{42}N_{10}F_{12}Ir_2O_4P_2$ (1449.23 g mol^{-1}): C, 36.47; H, 2.92; N, 9.66. Found: C, 36.22; H, 3.14; N, 9.96.

Synthesis of [Ir$_2$(L^1)(CO)$_2$Cl]Cl (4). In a Schlenk tube, **2** (0.036 g, 0.029 mmol) was dissolved in 5 mL of CH_3CN. A stream of CO was continued to bubble through the solution for 30 min at room temperature. The red solution rapidly turned into bright yellow. Then the gas was stopped and the solution was stirred for another 30 min. After that, the solvent was evaporated under reduced pressure, the yellow-green residue was purified by column chromatography (with EA/DCM = 1:2) to afford **4** as green solid (0.022g, yield: 64.2%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25 °C): δ 7.88-7.90 (d, $^{2}J_{\mathrm{H,H}}$ = 8 Hz, 2H, Ph-*H*), 7.79-7.81 (dt, $^{2}J_{\mathrm{H,H}}$ = 8 Hz, 8 Hz, 2H, Ph-*H*), 7.69-7.71 (m, 4H, Ph-*H*), 7.35-7.45 (m, 8H, Ph-*H*), 7.31 (t, 2H, Ph-*H*), 7.23 (t, 2H, Ph-*H*), 6.18-6.23 (m, 2H, C*H*$_2$), 5.95-6.01 (m, 2H, C*H*$_2$), 5.39 (m, 2H, C*H*$_2$), 5.17 (m, 2H, C*H*$_2$), 4.95-5.03 (m, 8H, C*H*$_2$), 4.73 (m, 2H, C*H*$_2$), 3.88 (m, 2H, C*H*$_2$), 3.21 (m, 2H, C*H*$_2$), 2.75-2.92 (m, 2H, C*H*$_2$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25 °C): δ 181.99 (Ir-*C*$_{\mathrm{carbene}}$), 175.96 (Ir-*C*$_{\mathrm{carbene}}$), 168.84 (Ir-*C*O) 134.96 (imidazole-ring-*C*), 133.60 (imidazole-ring-*C*), 124.76, 124.70, 123.86, 123.43 (Ph*C*), 112.54, 112.42, 110.83, 110.30 (Ph*C*), 68.97 (N-*C*H$_2$), 56.30 (N-*C*H$_2$), 53.81 (N-*C*H$_2$), 49.87 (N-*C*H$_2$), 49.20 (N-*C*H$_2$), 47.88 (N-*C*H$_2$), 45.19 (N-*C*H$_2$), 44.49 (N-*C*H$_2$). IR (cm^{-1}): 2092, 2010; MS (ESI): m/z [M + H]$^+$: 1175.33, Anal. Calcd for $C_{42}H_{42}N_{10}Cl_2Ir_2O_2$ (1174.19 g mol^{-1}): C, 42.96; H, 3.61; N, 11.93. Found: C, 42.55; H, 3.92; N, 11.75.

[(L^2)Ir(COD)](PF$_6$) (5). (H$_2$L^2)(PF$_6$)$_2$ (0.0582 g, 0.1 mmol) and Ag_2O (0.0463 g, 0.2 mmol) were suspended in 5 mL of acetonitrile with vigorously stirring in the dark for 12 h at ambient temperature. The excess Ag_2O was then removed by centrifugation and [Ir(COD)Cl]$_2$ (0.0368 g, 0.05 mmol) was added, the solution was stirred for further 6 h. The red solution was filtered and the solvent was removed under vacuum. The red residue was purified by column chromatography (with EA/DCM = 1:5) to afford **5** as red solid (0.047 6g, yield: 62.1%). ^{1}H NMR (400 MHz, acetone-*d*$_6$, 25 °C): δ 7.61-7.63 (d, $^{2}J_{\mathrm{H,H}}$ = 8 Hz, 2H, Ph-*H*), 7.48-7.50 (d, $^{2}J_{\mathrm{H,H}}$ = 8 Hz, 2H, Ph-*H*), 7.29-7.32 (m, 4H, Ph-*H*), 5.82-5.88 (m, 2H, COD-*H*), 5.11-5.16 (m, 2H, COD-*H*), 4.67-4.70 (m, 2H, C*H*$_2$), 4.58-4.61 (m, 2H, C*H*$_2$), 4.18 (s, 6H, C*H*$_3$), 2.56-2.60 (m, 2H, COD-*H*$_2$), 2.31-2.39 (m, 4H, COD-*H*$_2$), 2.05-2.10 (m, 2H, COD-*H*$_2$). ^{13}C NMR (100 MHz, acetone-*d*$_6$, 25 °C): δ 188.25 (Ir-*C*$_{\mathrm{carbene}}$), 137.17, 136.83 (imidazole-ring-*C*), 125.00, 124.94 (imidazole-ring-*C*), 112.32, 111.67 (Ph*C*), 81.69 (COD), 79.28 (COD), 45.92 (COD), 36.90 (N-*C*H$_2$), 32.78 (N-*C*H$_3$). MS (ESI): m/z [M–PF$_6$]$^+$: 623.50, Anal. Calcd for $C_{28}H_{38}F_6IrN_4P$ (767.81 g mol^{-1}): C, 43.80; H, 4.99; N, 7.30. Found: C, 44.33; H, 4.52; N, 7.08.

General Procedure for Iridium-Catalyzed 1,4 Addition Reaction. 2-Cyclohexen-1-one, arylboronic acid, potassium hydroxide and the catalyst (1-2 mol %) were suspended in 5 mL of the solvent mixture (toluene/H$_2$O at 2:1) in a 25 mL Schlenk tube. The mixture was stirred at 100 °C for 8 h. The solution was then filtered and the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography (with EA/DCM = 1:10) to afford the corresponding desired products.

Crystal Structure Determination. Single crystal X-ray diffraction data were collected for **1**, **2** and **5** on a Bruker APEX DUO diffractometer with a CCD area detector (Mo Kα radiation, λ = 0.71073 Å).[27] The APEXII program was used to obtain frames of data and determining lattice parameters. SAINT was used to integrate the data. The absorption corrections were applied using SADABS.[28] The structures were solved using SHELXS-97[29] and subsequently completed via Fourier recycling using SHELXL 2014 program.[30] All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were set at the calculated position and generated by the riding model.

ASSOCIATED CONTENT

Supporting Information

*Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI:
Table for the summary of crystal data and refinement; NMR spectra; ESI-MS spectra; Crystal packing; Additional structural data in CIF format (CIF).

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Notes

The authors declare no competing financial interest.

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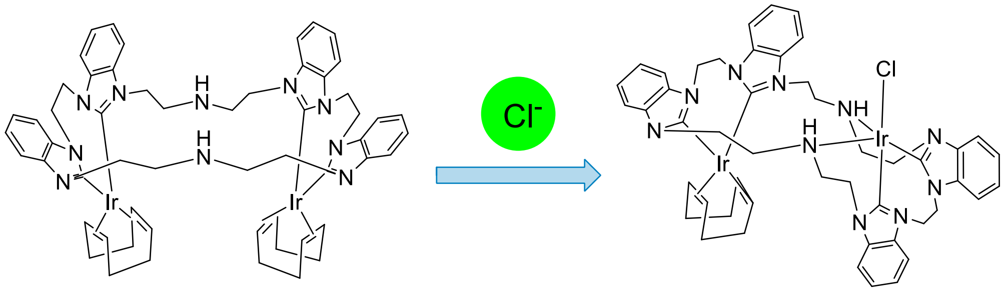
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