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Efficient formation of organoiridium macrocycles *via* C–H activation directed self-assembly†

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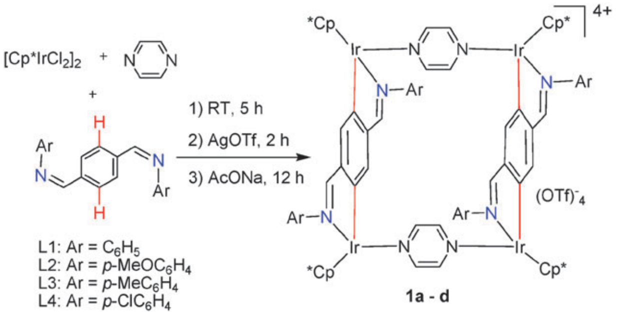
Received 9th November 2009, Accepted 11th March 2010
First published as an Advance Article on the web 13th April 2010
DOI: 10.1039/b923335k

Versatile and efficient procedures for the construction and modification of organometallic macrocycles with half-sandwich Ir corners *via* C–H activation and self-assembly have been developed.

The construction of new nanoscopic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1–3] Synthetic routes including stepwise and self-assembly strategies have been developed by many groups, and such structures are also used to build up organometallic half-sandwich molecular rectangles, prisms and cages,[4] however, a simple one-pot approach for preparing molecular rectangles from half-sandwich metal corners and two different rigid or semi-rigid bifunctional ligands is a challenge. Aromatic C–H activation mediated by transition metals is an important process in many well-known organic reactions.[5] Although *ortho*-metallation is a fairly common and expectable phenomenon in iridium chemistry, and iridium complexes have been extensively used in the study of the mechanisms of C–H activation,[6] using this process to construct nanoscopic macrocycles has hardly been explored.[7]

Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes,[8] we have initiated a new one-pot approach for preparing heterotopic organometallic macrocycles. In this contribution, we report an efficient one-pot method for synthesizing molecular macrocycles of half-sandwich iridium complexes *via* C–H activation directed muticomponent self-assembly under very mild conditions. Also an approach for postsynthetic modification (PSM)[9] of organometallic macrocycles through dimethylacetylene dicarboxylate (DMAD) insertion has been employed.

As shown in Scheme 1, $[Cp^*IrCl_2]_2$ was first treated with pyrazine in dichloromethane at room temperature to afford the μ-pyrazine bridged dinuclear complexes,[8a] to which 4 equiv. of AgOTf (Tf = O_2SCF_3) was then added. After the mixture was stirred at room temperature for 2 h, sodium acetate and terephthal-bis-imine ligand **L1** were added and keep stirring for additional 12 h. A tetranuclear macrocycle $[Cp^*_4Ir_4(\mu\text{-pyrazine})_2(\mu\text{-}\mathbf{L1})_2](OTf)_4$ (**1a**) was obtained simply by extracting with CH_2Cl_2.† X-Ray structural analysis revealed, to our surprise, that four half-sandwich cyclometalated iridium corners are formed.†



Scheme 1 Synthesis of tetranuclear complexes **1a–d**.

As shown in Fig. 1 (left), the cation of **1a** indeed adopts a rectangular structure with dimensions of 6.96 × 6.98 Å according to Ir···Ir non-bonding distances. The $Ir–N_{CH=N}$, $Ir–C_{Ar}$ bond lengths and the $C_{Ar}–Ir–N_{CH=N}$ chelate bite angle are similar in related Cp*Ir cyclometallated complexes.[6]

The isolation of the tetranuclear macrocycles generally formulated as $[Cp^*_4Ir_4(\mu\text{-pyrazine})_2(\mu\text{-L})_2](OTf)_4$ (**L** = **L2** (**1b**), **L3** (**1c**), **L4** (**1d**)) demonstrated the compatibility of this reaction with other terephthal-bis-imine ligands **L2–L4**. The products have been fully characterized by NMR, elemental analyses, and the formation of half-sandwich cyclometalated iridium corners were confirmed by X-ray structural analyses of **1b** and **1c** (Fig. 1 (right)).‡

With the intent of exploring the scope of our synthetic approach toward different organometallic macrocycle systems and to demonstrate the regioselectivity in the C–H activation

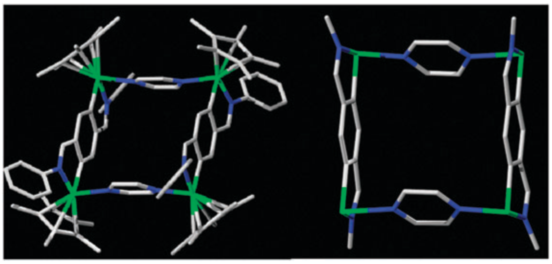


Fig. 1 Left: complex of **1a** in stick mode. Triflate anions, solvent molecules and hydrogen atoms are omitted for clarity. Right: the cores of **1a–c** in stick mode illustrating the formation of five-membered iridium(III) rings. Triflate anions, solvent molecules, Cp* rings, the substitutions of nitrogen atoms and hydrogen atoms are omitted for clarity. Carbon atoms are shown as dark gray, nitrogen as blue, and iridium as green.

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† Electronic supplementary information (ESI) available: Experimental details and crystal structure determination. CCDC 744136 (**1a**), CCDC 744137 (**1b**), CCDC 744138 (**1c**), CCDC 744142 (**2a**), CCDC 744133 (**3a**), CCDC 744134 (**3b**), CCDC 744140 (**4a**) and CCDC 744141 (**4b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b923335k

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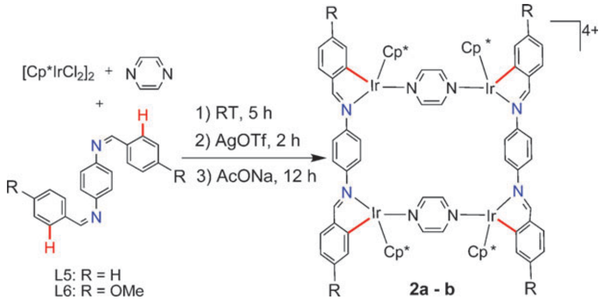


Scheme 2 Synthesis of tetranuclear complexes **2a** and **2b**.

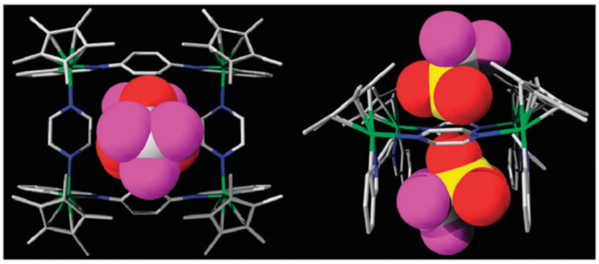
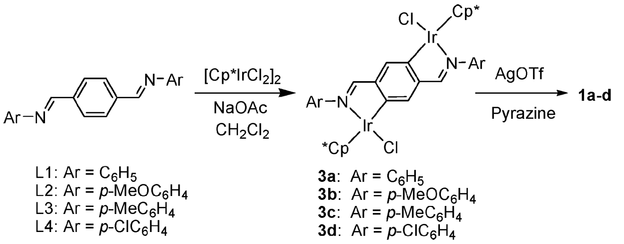


Fig. 2 Left: side views of **2a** in stick mode. Right: top view of the **2a** in stick mode. Triflate anions in space-filling mode. Two triflate anions, solvent molecules and hydrogen atoms are omitted for clarity. Carbon atoms are shown as dark gray, nitrogen as blue, sulfur as yellow, fluorine as pink and iridium as green.

step. *N*,*N′*-bisbenzylidenebenzene-1,4-diamine ligands **L5** or **L6** were introduced to these reactions. Treatment of **L5** or **L6** with the previously described iridium-catalyzed C–H activation conditions resulted in the formation of **2a** and **2b** in 68 and 71% yields, respectively (Scheme 2). All of imine moieties are coordinated to Cp*Ir fragments by a C–H activation reaction in *ortho*-position with respect to imine groups. The structure of **2a**, which contains Cp*Ir-based five-membered metallacycles and pyrazine ligands was established by X-ray structure analysis (Fig. 2).† The complex cation of **2a** has a rectangular cavity with dimensions of 8.4 × 7.0 Å according to Ir···Ir separations. Interestingly, in the solid state the macrocycle exhibits an arrangement in which the Cp* rings exist in *cis* conformation. A remarkable feature of the structure is that two of the four triflate anions are located above and below the macrocycle accommodated by the cavity in different ways.

On the basis of these observations, we hypothesized that the multi-component self-assembly and C–H activation can be accomplished in the process. The mechanism of aromatic C–H activation at [Cp*Ir] fragments has been studied using density functional theory by Davies and Macgregor,[6e,h] and although the computed C–H activation barriers are not consistent with the reactivity patterns of experimental studies, a range of carboxylates and triflates were found to effect cyclometallation. As further experimental evidence, it is worth noting that the C–H activation in our system can be carried out without additional sodium acetate, indicating that triflate can promote C–H activation.[10]

Organoiridium macrocycles **1a–d** could also be prepared by an alternative "C–H activation before self-assembly" stepwise synthetic pathway, by first creating the stable bimetallic edges **3a–d** using two-site aromatic C–H activation in double-Schiff-base ligands **L1–L4** with $[Cp^*IrCl_2]_2$, and then reaction with pyrazine in the presence of AgOTf (Scheme 3).[11] While the electron-withdrawing substituent (*p*-Cl) inhibits C–H activation, electron-donating substituents (*p*-OMe or *p*-Me) favour C–H activation. The ^{1}H NMR spectra of products **3a–d** in $CDCl_3$ exhibited similar two singlets in a 1 : 1 intensity ratio due to the imine and the central phenyl ring, respectively, indicative of highly symmetric structures. The structures of **3a** and **3b** containing two five-membered cyclometalated rings was confirmed by X-ray structure analyses.† An ORTEP view of the molecular structure of **3a** is shown in Fig. 3, with selected bond lengths and angles listed. It revealed that the complex has a dimeric structure containing two five-membered cyclometalated rings. The M–N, M–C bond lengths and the C–M–N chelate bite angles are similar to related Cp*Ir cyclometallated complexes.[6e,f] The reactions of *N*,*N′*-bisbenzylidenebenzene-1,4-diamines ligands **L5** or **L6** with $[Cp^*IrCl_2]_2$ leads to the formation of binuclear iridium-based "organometallic clip" linear moieties **4a,b** in high yields. Detailed structures of **4a,b** were established by X-ray single crystal analyses,‡ and as shown in Fig. 4, both imine moieties are coordinated to Cp*Ir fragments by a C–H activation reaction in *ortho*-position with respect to the imine group. Analogously, organoiridium macrocycles **2a,b** which contain Cp*Ir-based five-membered metallacycles and pyrazine ligands, were prepared by direct reactions of **4a,b** with pyrazine in the presence of AgOTf, respectively (Scheme 4).



Scheme 3 Stepwise formation of **1a–d**.

PSM is an important methodology due to its potential for accessing advanced materials.[9] Taking into account that some functionalized alkynes, such as DMAD, can be employed to expand metallacycles through DMAD insertion into metal–aryl of cyclometalated compounds[6f] PSM of our metallacycles was attempted by reacting DMAD with the tetranuclear cyclometalated complexes **1a** and **1b** at room temperature. In these cases, only one single alkyne insertion in each Ir–aryl

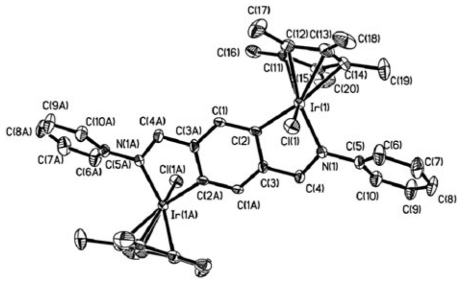


Fig. 3 ORTEP view of **3a** (ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–C(2) 2.029(4), Ir(1)–N(1) 2.102(4); C(2)–Ir(1)–N(1) 77.54(15), C(4)–N(1)–Ir(1) 115.8(3).

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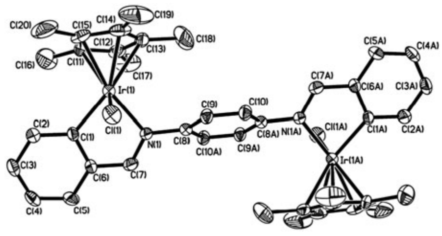
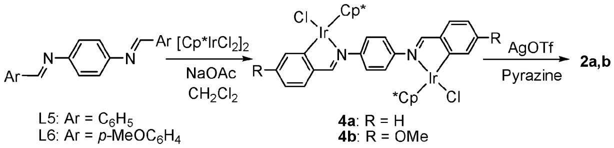
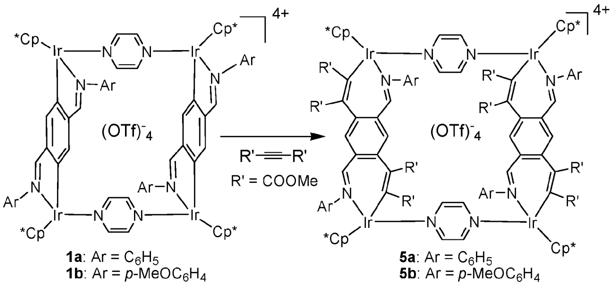


Fig. 4 ORTEP view of **4a** (ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 2.030(6), Ir(1)–N(1) 2.092(4), N(1)–C(7) 1.292(7); C(1)–Ir(1)–N(1) 78.1(2).



Scheme 4 Stepwise formation of **2a,b**.



Scheme 5 Postsynthetic modification of **1a,b** by alkyne insertion.

has been determined by ^{1}H NMR spectra and elemental analyses of **5a,b** (Scheme 5).

In summary, we have developed an efficient procedure for the construction of a series of organometallic macrocycles *via* C–H activation directed muticomponent self-assembly. The procedure avoided the separation problems and product loss that occurred in previous stepwise-formation procedures, and the desired organometallic macrocycles were readily obtained in good yields. The dimensions of these discrete organometallic macrocycles could be expanded through the insertion of unsaturated molecules into the five-membered cyclometalation corners. This synthetic approach might be efficiently applied to the construction and PSM of novel multi-metallic discrete macrocycles or cages *via* C–H activation directed self-assembly under very mild conditions.

This work was supported by the National Science Foundation of China (20721063, 20771028), Shanghai Leading Academic Discipline Project (B108), Shanghai Science and Technology Committee (08DZ2270500, 08DJ1400103) and the National Basic Research Program of China (2009CB825300).

Notes and references

‡ Two of the four triflate anions in complexes **1a**, **2a** and some unknown solvents in complexes **1a**, **1c**, **2a**, **4a**, are strongly disordered and cannot be refined properly, as a result, the SQUEEZE algorithm was used to omit all of these disordered fragments. Details of the crystallographic analyses are provided in the ESI†.

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10 When the mixture was stirred at 55 °C for 12 h in the absence of sodium acetate, the products could be obtained in moderate yields.
11 See ESI† for additional details.