Stepwise Formation of a Molecular Square with Bridging NH,O-Substituted Dicarbene Building Blocks

Fabian M. Conrady,[†] Roland Fröhlich,[‡] Christian Schulte to Brinke,[†] Tania Pape,[†] and F. Ekkehardt Hahn[*,†]

[†]Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany
[‡]Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

S *Supporting Information*

ABSTRACT: The β,β'-bis(triisopropylsiloxy)phenyl-1,4-diisocyanide **3** and $[Ir(Cp^*)Cl_2]_2$ were used for the stepwise assembly of the $[Ir(Cp^*)Cl]$ cornered molecular square $[6](Cl)_4$. Synthesis of the tetrakis(diisocyanide) bridged molecular square $[Ir(Cp^*)Cl(3)]_4(BF_4)_4$ **5**$(BF_4)_4$ followed by cleavage of the O—Si(i-Pr)$_3$ bonds of the diisocyanide bridges with HCl/i-PrOH led to an intramolecular attack of the liberated hydroxyl groups at the isocyanide carbon atoms with formation of molecular square $[6](Cl)_4$ featuring four dicarbene linkers.

Scheme 1. Synthesis of Complex [2]

The self-assembly of metallosupramolecular structures has become a field of intensive research after Lehn et al. demonstrated the spontaneous formation of dinuclear helicates from bipyridine and Cu^I.[1] Subsequently, a large number of metallosupramolecular assemblies have been described.[2] Most of these compounds are built up from metal centers coordinated by nitrogen and/or oxygen donor atoms of polydentate ligands, and some have been used as molecular hosts for the encapsulation and selective chemical transformation of small molecules.[3] Molecular squares built from end-capped Pd^{II} and 4,4'-bipyridine building blocks have been among the first metallosupramolecular assemblies to be studied in detail by the groups of Fujita,[4] Stang,[5] and others.[6] Related architectures featuring polydentate ligands with carbon donor atoms are rare although some examples with bridging diisocyanide,[7] acyclic diaminocarbene,[8] or NHC ligands[9] have been described.

N-Heterocyclic carbenes (NHCs) are C^{II} donor ligands which form stable M—C bonds.[10] A number of poly-NHC ligands have been described,[11] but only recently have the first metallosupramolecular structures emerged which are held together by poly-NHC ligands. Among these are molecular squares[12] featuring rigid ditopic benzobis-NHCs[13] and 4,4'-bipyridine linkers as well as cylindrical assemblies obtained from macrocyclic[14] and other poly-NHC ligands.[15]

We have studied the metal template controlled transformation of β-functionalized isocyanides into N,O-[16] and N,N-substituted NHC ligands.[17] Here we present a novel β,β'-disubstituted phenyl-1,4-diisocyanide,[18] its use for the generation of a molecular square featuring four bridging diisocyanide ligands, and the template controlled intramolecular conversion of the bridging diisocyanides into four bridging dicarbene ligands.

First we studied the conversion of two isocyanide ligands into NH,O-NHCs at the iridium template by reacting $[Ir(Cp^*)Cl_2]_2$ with 4 equiv of 2-trimethylsilyloxyphenyl isocyanide **1**[19]
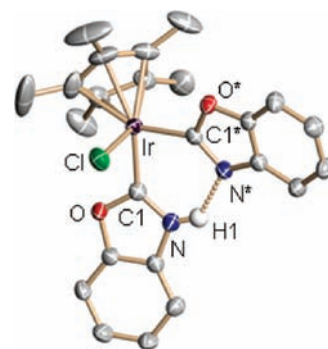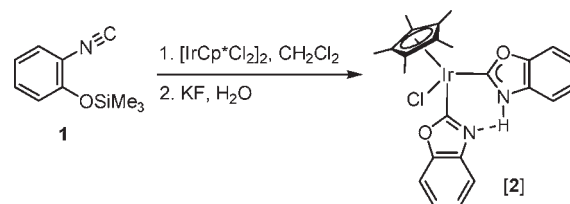

Figure 1. Molecular structure of [**2**]; hydrogen atoms (except NH) are omitted for clarity. The complex resides on a mirror plane passing through atoms Ir and Cl. Selected bond lengths (Å) and angles (deg): Ir1—C1 2.004(3), Ir1—Cl 2.4244(13); C1—Ir1—C1* 88.8(2).

(Scheme 1; see Supporting Information (SI)). The initially formed diisocyanide complex was not isolated but instead treated with KF/H$_2$O which caused cleavage of the O—SiMe$_3$ bonds followed by intramolecular nucleophilic attack of the liberated hydroxyl groups at the isocyanide carbon atoms with generation of the di-NHC complex [**2**]. Complex [**2**] was identified by ^{1}H NMR spectroscopy revealing the characteristic resonance for the N—H proton at 10.04 ppm and by ^{13}C NMR spectroscopy showing the resonance for the heterocarbene C2 carbon atom at 178.7 ppm.

An X-ray diffraction analysis (Figure 1) confirmed the formation of [**2**]. The metric parameters found in [**2**] fall in the range previously described for Ir—NHC complexes.[20] The angle C1—Ir—C1* measures 88.8(2)° which is a perfect value for the construction of a molecular square with $\{[Ir(Cp^*)Cl(NHC)_2\}$
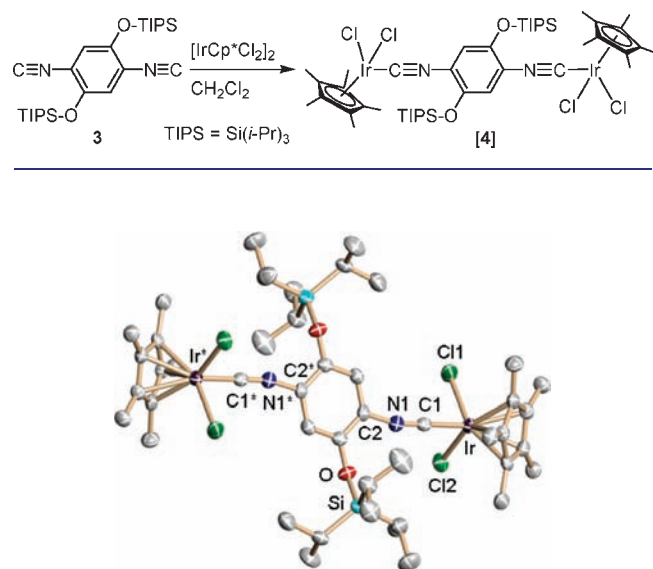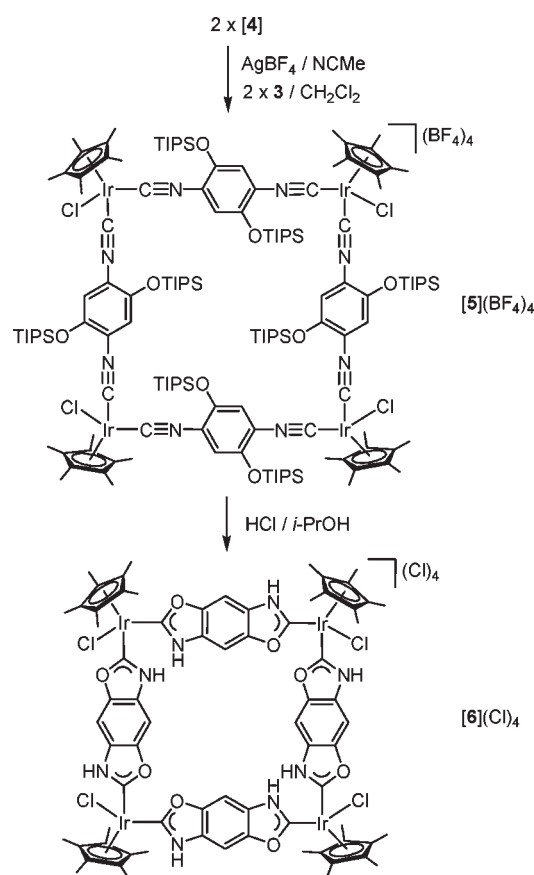
Scheme 2. Synthesis of Complex [4]

Figure 2. Molecular structure of one molecule of [4]; hydrogen atoms are omitted for clarity. The complex resides on a crystallographic inversion center. Selected bond lengths (Å) and angles (deg): Ir–C1 1.918(5), Ir–Cl1 2.4097(13), Ir–Cl2 2.4039(13), C1–N1 1.163(6), Ir···Ir* 11.5787(8); Cl1–Ir–Cl2 89.88(5), Cl1–Ir–C1 87.13(14), Cl2–Ir–C1 87.30(15), Ir1–C1–N1 177.1(5), C1–N1–C2 164.8(5).

building blocks. The two NHC ligands share one NH proton via a N–H···N hydrogen bond. Similar behavior, allowing the formation of a neutral complex, has been observed before.[16c,21]

Next the β,β'-functionalized phenyl-1,4-diisocyanide **3** was prepared starting from 2,5-diaminohydroquinone dihydrochloride (see SI). This diisocyanide could only be prepared with the sterically demanding tris(isopropyl)silyl (TIPS) protection groups instead of the trimethylsilyl groups used for **1**. Reaction of **3** with 1 equiv of $[Ir(Cp^*)Cl_2]_2$ in CH_2Cl_2 yielded the dinuclear complex [4] in almost quantitative yield (Scheme 2; see SI). The progress of the reaction can be monitored by IR spectroscopy where the wavenumber for the isocyanide stretching vibration shifts from $\tilde{v} = 2130$ cm^{-1} for free **3** to $\tilde{v} = 2152$ cm^{-1} for [4]. ^{13}C NMR spectroscopy also confirmed the formation of [4] showing the resonance for the isocyanide carbon atom at 136.0 ppm compared to the corresponding signal for the free ligand at 169.8 ppm.[18]

An X-ray diffraction analysis confirmed the composition of [4] (the asymmetric unit contains two essentially identical independent halves of [4]; only one molecule of [4] is shown in Figure 2). Complex [4] features an Ir–C1 separation of 1.918(5) Å and a slightly bent C1–N1–C2 (164.8(5)°) isocyanide group. The Cp* ligands are oriented pseudo-*trans* to each other, and the Ir···Ir* separation measures 11.5787(8) Å.

Cleavage of the O–Si(*i*-Pr)$_3$ bonds in [4] with tetrabutylammonium fluoride in fluorobenzene converts the bridging diisocyanide ligand into a bridging di-NHC ligand featuring two NH, O-substituted heterocarbene donors. The bridging dicarbene ligand was detected by the characteristic resonances for the N–H protons at 12.12 ppm and the resonance for the carbene carbon atoms at 185.2 ppm which is similar to the chemical shift for the equivalent resonance for the carbene carbon atoms in complex [2] (178.7 ppm).

Scheme 3. Synthesis of the Molecular Squares [5](BF$_4$)$_4$ and [6](Cl)$_4$

The dinuclear complex with just one bridging di-NHC ligand was not studied further. Instead, the tetranuclear iridium complex featuring four bridging diisocyanide ligands [5](BF$_4$)$_4$ was synthesized from 2 equiv of [4] and 2 equiv of the diisocyanide **3** using the method described by Tatsumi for related diisocyanide-bridged molecular squares (Scheme 3; see SI).[7]

Due to the cationic nature of complex cation [5]$^{4+}$, the IR spectrum shows the isocyanide stretching vibration at a slightly higher wavenumber ($\tilde{v} = 2166$ cm^{-1}) compared to the neutral complex [4] ($\tilde{v} = 2152$ cm^{-1}). The ^{13}C NMR spectrum of [5](BF$_4$)$_4$ reveals the resonance for the isocyanide carbon atom at 124.6 ppm, slightly upfield from the equivalent resonance in [4] (136.0 ppm). The HR-ESI mass spectrum shows a peak at $m/z = 1142.7933$ for the molecular ion $[[5](BF_4)]^{3+}$ (calcd 1142.7920).

Dissolving complex [5](BF$_4$)$_4$ in a 5 M isopropanolic hydrogen chloride solution and stirring the mixture for 12 h at 100 °C yielded the molecular square [6](Cl)$_4$ as a yellow, air-stable solid in excellent yield (Scheme 3). In this one-step reaction all eight O–Si(*i*-Pr)$_3$ bonds of [5](BF$_4$)$_4$ are cleaved and the generated hydroxyl groups attack the isocyanide carbon atoms in their α-position in an intramolecular nucleophilic fashion under formation of eight new NH,O-NHC donor groups (see SI). The result is compound [6](Cl)$_4$, the first molecular square exclusively bridged by ditopic dicarbene ligands.

The formation of [6](Cl)$_4$ was confirmed by NMR spectroscopy. The ^{1}H NMR spectrum shows the characteristic signal for
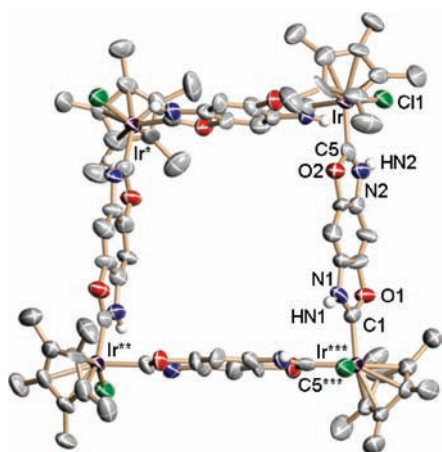
Figure 3. Molecular structure of $[6]^{4+}$ in $[6](Cl)_4$ with hydrogen atoms, except for N−H, omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir−C5 2.013(11), Ir1***−C1 2.001(10), Ir−Cl1 2.399(3), C1−O1 1.366(13), C1−N1 1.321(4), C5−O2 1.351(13), C5−N2 1.292(15); C1−Ir1***−C5*** 85.7(4), Ir···Ir 10.5000(9).

the N−H protons at 15.05 ppm. The carbene carbon resonance was observed at 180.3 ppm in the ^{13}C NMR spectrum. This value is similar to the chemical shift of the carbene carbon atom in the mononuclear complex [**2**]. In addition to correct microanalytical data, the MALDI mass spectrum shows the peak for the molecular ion $[6−Cl]^+$ m/z = 2057 which is formed by removal of one chloro ligand from the tetracation $[6]^{4+}$.

Single crystals of $[6](Cl)_4$ were analyzed by X-ray diffraction. The molecular structure of the tetracation is depicted in Figure 3. Tetracation $[6]^{4+}$ resides on a crystallographic 4-fold axis. It is built from four {Ir(Cp*)Cl} vertices linked together by four dicarbene ligands. All metric parameters in $[6]^{4+}$ fall in the typical range for related Ir−NHC complexes.[20] The four Ir···Ir separations measure 10.5000(9) Å. This value is significantly shorter than the Ir···Ir separation in the diisocyanide complex [**4**](11.5787(8) Å) demonstrating that the transformation of the bridging diisocyanide ligands in [**4**] (and [**5**]$^{4+}$) into bridging dicarbene ligands in $[6]^{4+}$ proceeds with a reduction of the Ir···Ir separation and thus with a general shrinkage of the molecular square.

We have demonstrated that the bridging β,β'-bis(triisopropylsiloxy)-substituted phenyl-1,4-diisocyanide ligand **3** can be converted in an Ir^{III} template controlled reaction into a bridging di-(NH,O)-NHC ligand via the intermediate β,β'-dihydroxyphenyl-1,4-diisocyanide. The transformation of the diisocyanide into the dicarbene proceeds with a reduction of the Ir···Ir separation. We have previously demonstrated that the template controlled transformation of β-hydroxyphenyl isocyanides into NH,O-NHCs is a reversible reaction which is controlled by the electronic situation at the template metal center.[16,22] In principle, the transformation of a dicarbene bridged molecular square into a β,β'-dihydroxyphenyl-1,4-diisocyanide bridged complex would give access to molecular squares which change their size depending on the oxidation state of the metal atoms at the vertices. However, this carbene→isocyanide transformation is not feasible with $[6]^{4+}$ as the $Ir^{III}→Ir^I$ reduction would lead to changes to the coordination number (6 to 4) and coordination geometry (octahedral to square-planar) of the metal centers. Therefore, we are now studying molecular squares similar to $[6]^{4+}$ built from metal centers which form stable octahedral isocyanide and/or

NHC complexes in different oxidation states like the couples Fe^{II}/Fe^{III} and Re^I/Re^{III}.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental details for the synthesis of all compounds and X-ray crystallographic files for compounds [**2**], [**4**], and $[6](Cl)_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
fehahn@uni-muenster.de

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