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Beta-Diketone and -Ketoenamine-Based Organic Building Blocks for Porous Metal Organic-Materials

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BETA-DIKETONE AND -KETOENAMINE-BASED ORGANIC BUILDING BLOCKS FOR POROUS METAL-ORGANIC MATERIALS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
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in
The Department of Chemistry

by
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ABSTRACT

This dissertation focuses on synthesis of multifunctional β-diketone and β-ketoenamine ligands and their reaction with metal ions, mainly Cu^{2+}. Several new bi-, tri-, and tetrafunctional organosilicon β-diketone building blocks with β-diketone groups at approx. 109° (tetrahedral) were successfully synthesized. New thiophene based bifunctional ligands where the β-diketones are at about 145° are also reported here. We also prepared a range of new aryl-β-ketoenamines from their analogous β-diketones in very high yield using a simple microwave-assisted procedure.

Reactions of organosilicon tris(β-diketone)s LH_3 with Cu^{2+} were explored quite intensively. These ligands form metal-organic-polyhedra (MOPs) that are soluble in organic solvents, and insoluble metal-organic polymers, upon reaction with Cu^{2+}.

The possibility of self-correction of the structure of Cu β-diketones was also studied. It was found that microwave irradiation of the insoluble material (likely polymeric $[Cu_3L_2]_n$) in dichloromethane generates a green soluble species (15%). AFM images of the newly generated materials reveal molecules that are ca. 5 nm in size, which matches the expected size of a metal-organic dodecahedron $Cu_{30}L_{20}$ as estimated by molecular modeling. This indicates that β-diketone-based metal-organic materials can undergo self-correction of their structure under microwave-assisted heating.

CHAPTER 1

INTRODUCTION-POROUS MATERIALS

1.1 Zeolites

Porous materials have been of great importance to humankind for a very long time. Natural zeolites are one of the earliest known porous crystalline materials. They are formed when a volcanic ash released during volcanic eruption chemically reacts with salt water. The Greek word zeolite means "a stone that boils" and was first given by a Swedish mineralogist Axel Fredrik Cronstedt, in 1756, when he noticed that this kind of stone dances about when it is heated.[1-3] This occurred due to the release of the water molecules in the pores of the rock. This can be regarded as one of the earliest examples of host-guest chemistry. Natural zeolites, because of their highly porous nature, have found diverse applications in our world as in catalysts in petrochemical industries, storage of heat energy, water softening, removal of heavy metal ions in mine waste water and fission products, adsorption and separation of gases, and removal of odor.[3] Their ability to selectively filter molecules based on their size and shape has led to the name "molecular sieves."[4]

Natural zeolites are hydrated aluminosilicates of group IA and IIA elements. Their empirical formula can be represented as $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$ where y is 2 or larger, n is the cation valence and w represents the water contained in the cavity of the zeolite. The framework is built from corner-sharing SiO_4 and AlO_4 tetrahedra. The many applications of natural zeolites inspired scientists such as Barrer, Milton, Breck and their colleagues to come up with synthetic approaches of making zeolites in the late 1940s.[5,6] Since then, many synthetic zeolites of various topologies and chemical composition (Al/Si ratios) were made. In the 1980s, Flanigen, Bedrad and coworkers[7,8] reported the synthesis of aluminophosphates and open framework sulfides, classes of porous materials similar to zeolites. This decade also marked the beginning of the development of the long-sought-after porous materials with predetermined structure.

1.2 Porous Metal-Organic Materials

Porous metal-organic materials are built from combination of metal ions or metal ion clusters and organic building blocks in a synthetically predictable way. These materials could be porous discrete molecules or extended solids containing uniformly distributed pores. Some of the earliest rationally designed porous metal-organic materials were reported by Maverick and coworkers in 1984,[9] Robson and coworkers in 1989[10] and 1990,[11] and Fujita and coworkers in 1990.[12] It is important to note that many porous metal-organic materials were known much earlier but lack deliberate design of porosity (size and shape) and framework topology. In the 1984 paper, Maverick and coworkers reported the synthesis of a well defined discrete porous metal-organic molecule, $Cu_2(m\text{-XBA})_2$, using a bis(β-diketone) building block and Cu^{2+}, as shown in Figure 1.1.[9]

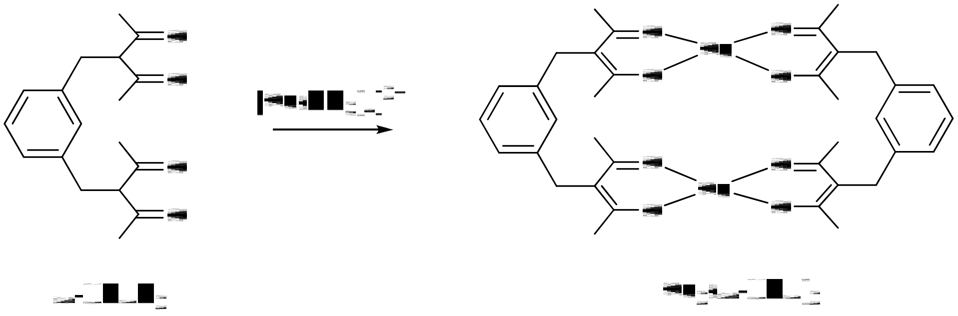


Figure 1.1 m-$XBAH_2$ in CH_2Cl_2 reacts with aqueous $[Cu(NH_3)_4]^{2+}$ to form $Cu_2(m\text{-XBA})_2$.

Five years later, the first rationally designed extended porous metal-organic material was reported by Robson and coworkers. In their report, they demonstrated the construction of a rationally designed extended porous metal-organic network (Figure 1.2) by reaction of Cu(I) with the tetrahedral nitrile organic building block $C(C_6H_4CN)_4$.

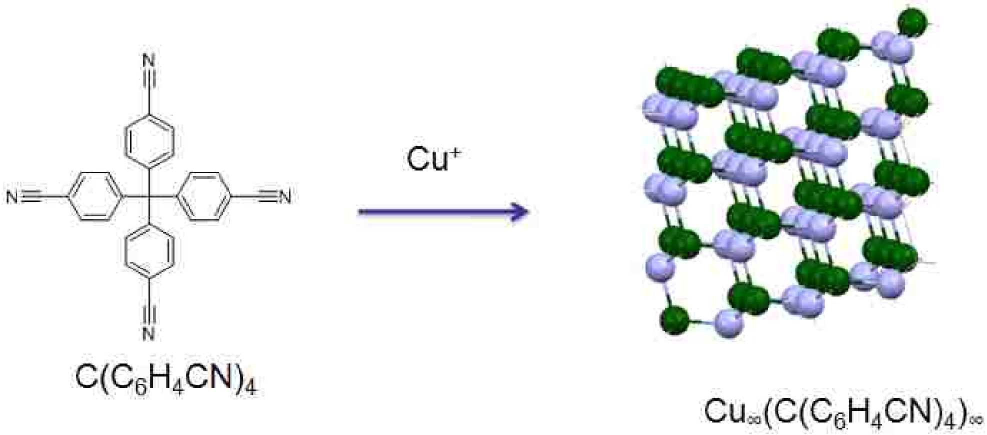


Figure 1.2 Reaction of the tetranitrile $C(C_6H_4CN)_4$ with $Cu(CH_3CN)_4BF_4$ affords the intended diamond-like network $[(C(C_6H_4CN)_4)(Cu)]_n$. A part of the structure is shown here.[13]

In 1990, Fujita and coworkers successfully made a metal-organic square using $(en)PdCl_2$ and bpy (Figure 1.3).[12] Four years later, they also made 2D network, $[Cd(4,4'\text{-bpy})_2(NO_3)_2]_n$, and demonstrated the clathrate and catalytic property of the materials.[14]

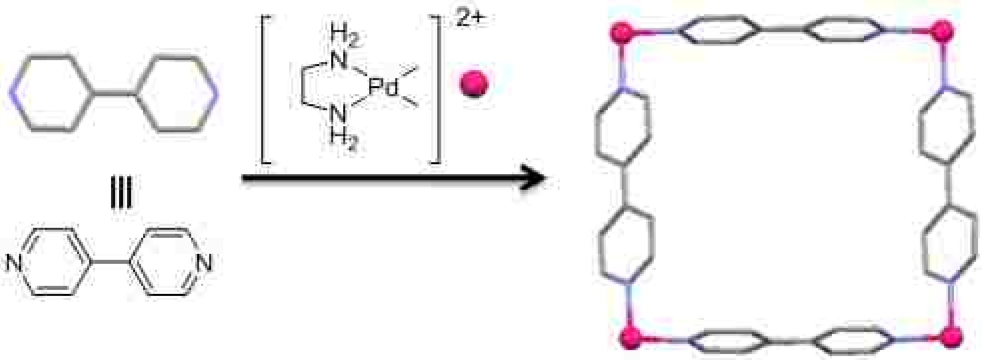


Figure 1.3 Reaction of $(en)Pd(NO_3)_2$ and bpy afforded a molecular square.[12]

The name MOF (metal-organic framework) and the popularity of these materials seemed to flourish when Yaghi and coworkers synthesized several porous metal-organic materials from carboxylate based organic linkers and metal ion clusters beginning in 1995.[15,16] Many carboxylate-based MOFs have been reported since then by many scientists from all over the world, and this area has been reviewed.[17-20]

Another related class of materials that are built in a similar fashion is the so-called metal-organic polyhedra (MOPs), which are discrete 3D porous metal-organic molecules. The first example of a MOP was reported in 1995 by Fujita and coworkers, see Figure 1.4.[21] It was made by the self-assembly reaction of the tridentate ligand 1,3,5-tris(pyridin-4-ylmethyl)benzene and (en)Pd(NO$_3$)$_2$.

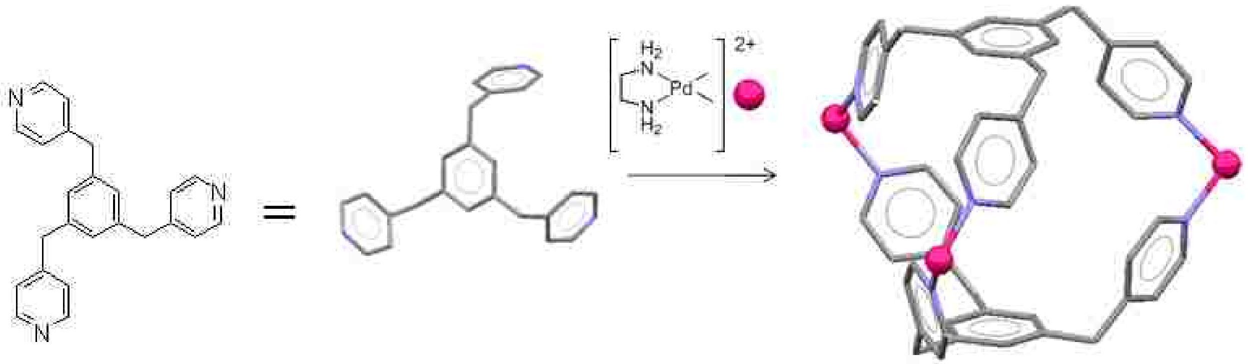


Figure 1.4 Preparation of the first metal-organic polyhedron, Pd$_3$(1,3,5-tris(pyridin-4-ylmethyl)benzene)$_2^{6+}$, as reported by Fujita and coworkers in 1995.

In the same year Fujita reported the synthesis of a metal-organic octahedron (Figure 1.5) using the same metal ion, (en)Pd(NO$_3$)$_2$, and a similar, tridentate, building block 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine.[22] Many MOPs have been reported since then. [23-29]

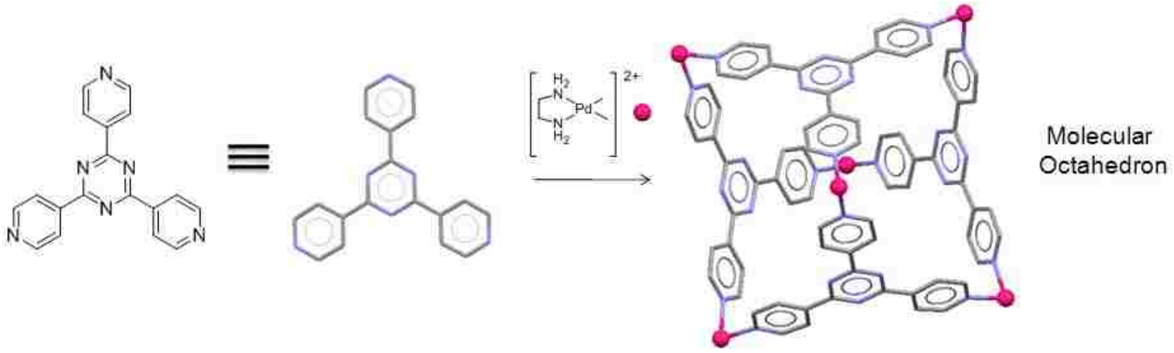


Figure 1.5 Metal-oragnic octahedron, constructed from ten species: four ligands and six metal ions.

Stang and Olenyuk have prepared a general molecular architecture library (Figure 1.6) for preparing discrete metal-organic molecules, polygons and polyhedral.[78]

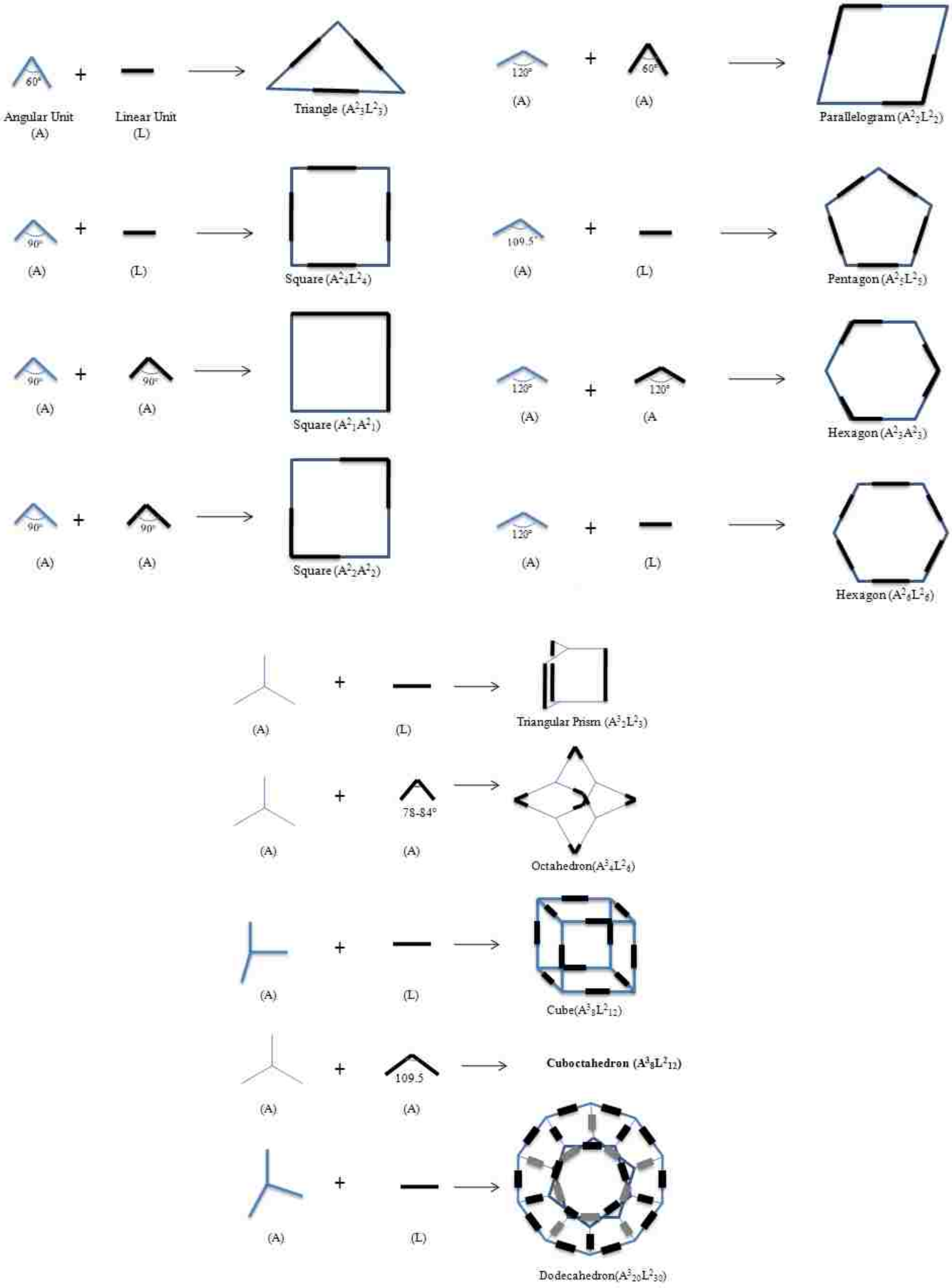


Figure 1.6 Peter Stang's molecular architecture for making discrete molecules.

Theoretically, the angle and number of the binding sites in the ligand and the open sites in the metal ion should determine the topology of the product. Synthetic conditions (pH, type of solvent, concentration, and temperature) also play a great role in shaping the final structure. There are several reports that demonstrated the formation of different structures from the same starting materials under different conditions.[30-36] For instance, MOF-2 ($Zn(BDC)(DMF)(H_2O)$),[37] MOF-3 ($Zn_3(BDC)_3{\cdot}6CH_3OH$),[38] and MOF-5 ($(Zn_4O)$-$(BDC)_3(DMF)_8(C_6H_5Cl)$)[39] ($BDC^{2-}$ is 1,4-benzenedicarboxylate) are all made from Zn^{2+} and BDC^{2-} under different conditions. One has, therefore, to consider these things when intending to synthesize MOFs.

An interesting subclass of MOFs is the so called zeolite like MOFs. It has been the objective of many scientists to make zeolites with tailorable pore size and shape. Self assembly reactions of transition metal ions and imidazolate organic linkers seem to provide a good way to achieve the objective. It turned out that the nitrogen groups in imidazoles are at an angle close to 145°, the Si-O-Si angle in zeolites, Figure 1.7. So if the Si atom in zeolites is replaced by a transition metal ion that is capable of making tetrahedral coordination geometry, it should be possible, theoretically, to make metal-organic material with a framework topology like that of a zeolite.

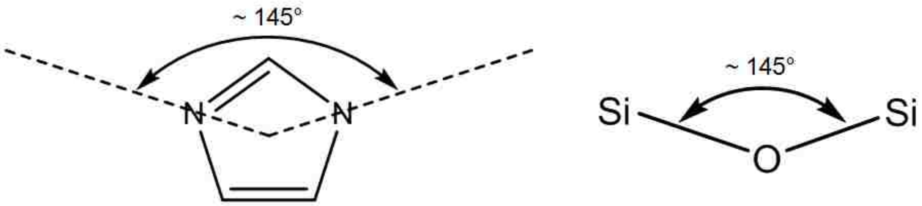


Figure 1.7 The metal-N-N-metal bond in imidazole and Si-O-Si bond in zeolites form nearly equal angles (~ 145°)

Some single crystal studies on metal imidazolate frameworks $[Cu(im)_2]_\infty$, $[Co(im)]_\infty$ and, $[Zn(im)_2]_\infty$ have been reported between 1960 and 2002.[40-43] These crystalline materials, however, didn't display open frameworks. In 2002, You and coworkers synthesized a Co-imidazolate (Figure 1.8) having a zeolite topology. They circumvented the lack of pore opening in previous reports by employing piperazine as structure directing agent. Later in 2003, You and coworkers reported the preparation of five polymorphous frameworks of Co-imidazolate.[44]

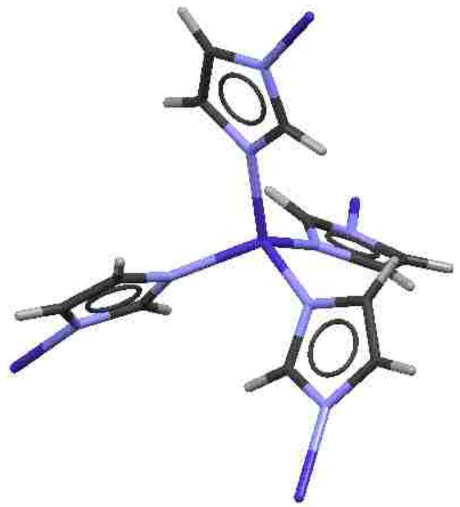


Figure 1.8 Part of the zeolite-like Co-imidazolate framework crystal structure reported by You and coworkers is shown here. The Cobalt (blue) ions occupy the tetrahedral center.

More recently, Yaghi and coworkers have reported the preparation of many zeolite-like metal-organic frameworks from Zn and functionalized imidazoles, Figure 1.9, using high throughput techniques. They are called ZIFs (zeolitic imidazolate frameworks).[45-47]

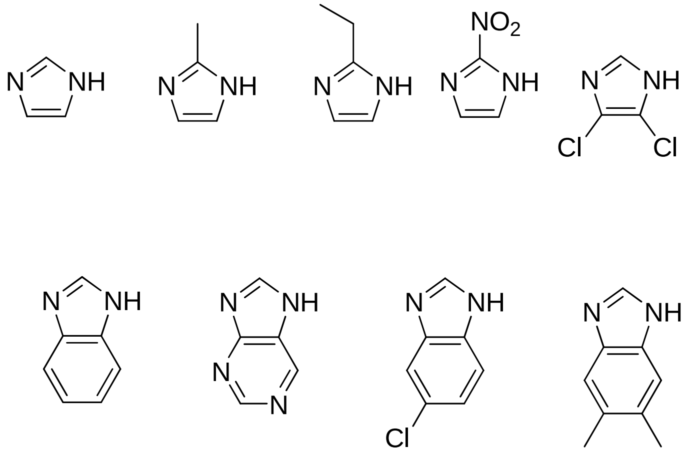


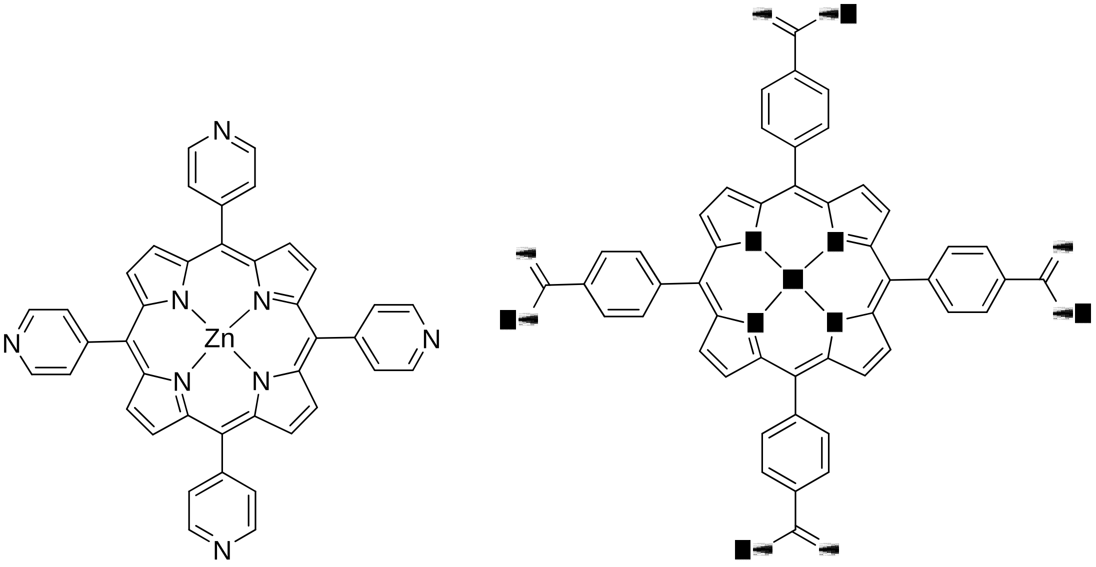
Figure 1.9 Imidazole and functionalized imidazoles used by Yaghi for making ZIFs.

According to the analysis of Bu and Feng,[48] zeolites and MOFs can be considered as complementary rather than competing classes. For instance, unlike zeolites, which usually have negatively charged frameworks, MOFs are mostly positively charged or neutral. So if zeolites are used as cation exchangers, MOFs could be used as anion exchangers. Hydrophilicity is tuned in zeolites by adjusting the charge density of the framework (varying the Si/Al ratio). In case of MOFs, it may be accomplished by introducing different functional groups.

MOFs do contain some desirable features that may not exist in zeolites. For example, the metals in MOFs are usually transition metals as opposed to zeolites, which are mostly made up of main group elements. MOFs, therefore, might have a better capacity to bind guest molecules through coordinatively unsaturated metal sites. Furthermore, by starting with larger organic building blocks or metal ion clusters, MOFs can form relatively large pores. It is also possible to make chiral MOFs directly from chiral organic building blocks.[49] This can be a much better alternative to the challenging task of using chiral directing agents to build chiral inorganic frameworks.[49]

Another advantage to this field is the ability to use porphyrins as building blocks to make porphyrin-based porous metal-organic materials. In 1994, Goldberg and coworkers reported one of the earliest crystal structures of a 3D porous tetra(4-pyridyl) porphyrin (TPyP), Figure 1.9, based material.[50, 51] The 3D structure was made possible through bonding of the lone pair on the pyridyl nitrogen with the central metal ion, Zn^{2+} in the presence of some guest solvents.

Since then, several other porphyrin-based porous materials have been reported. One of the most commonly used class of porphyrins for such purpose is the *meso*-tetra(p-carboxyphenyl)porphy-rins, TCPPs, see Figure 1.10.[51] The recent report by Choe and coworkers is a good example that demonstrates the richness of coordination sites that can be available in porphyrins.[52] They were able to make three different porphyrin-based MOFs by a one pot solvothermal reaction (involves heating the starting materials in a certain solvent) of TCPP or PdTCPP, metal nitrates (Co or Zn), and bpy in the DMF/ethanol solvent mixture at 80 °C, Figure 1.11.



ZnTPyP M(TCPP)

Figure 1.10 ZnTPyP (tetra(4-pyridyl) porphyrin) and M-TCPP (tetra(p-carboxyphenyl) porphyrins).

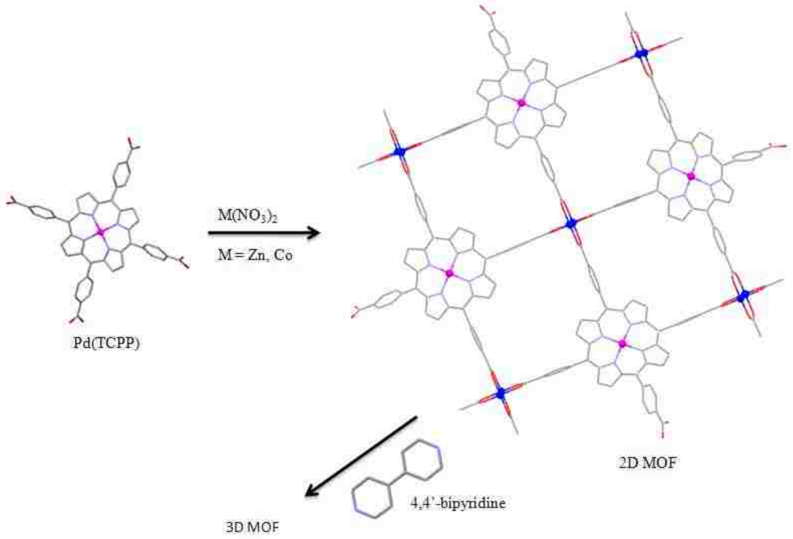


Figure 1.11 TCPP or Pd(TCPP) reacts with nitrates of Co or Zn, blue color, in the presence of bpy in DMF/ethanol at 80 ^{o}C to form a porphyrin-based 3D MOF.

The ability to build deliberately designed materials which seem to be materialized in MOFs has been a long-sought-after goal for many materials scientists.

1.3 Covalent Organic Frameworks (COFs)

COFs are covalently bonded porous crystalline organic materials. Yaghi and coworkers pioneered the synthesis of this interesting class of materials.[53] In their report, they successfully demonstrated the synthesis of COF-1 (Figure 1.12). They were also able to build several 3D COFs.[54] Since these materials are constructed through strong covalent bonds, they have very high thermal stabilities (400 to 500 °C).

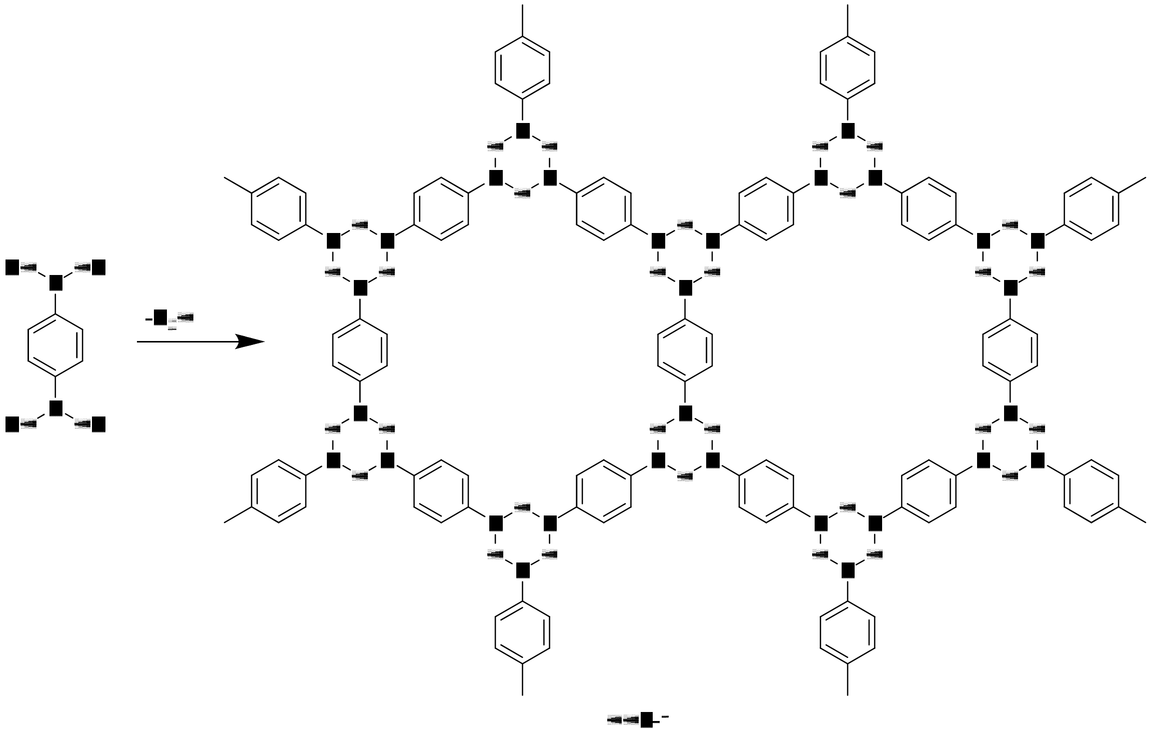


Figure 1.12 COF-1 was synthesized by heating 1,4-benzenediboronic acid in a sealed tube.

1.4 Potential Applications of Porous Metal-Organic Materials

One application of these porous materials that is under extensive study is the possibility of using them for storing hydrogen gas.[55,56] Hydrogen is one of the promising candidates to substitute for fossil fuels that we use currently. Hydrogen contains three times more energy than an equal weight of gasoline.[57] When hydrogen burns, it releases water, as opposed to the environmentally hazardous carbon dioxide in the case of fossil fuels. However, at room temperature and pressure hydrogen is gaseous and would require an efficient containment system to hold enough hydrogen in a reasonable volume. For instance, at atmospheric pressure, a 20 gallon tank full of hydrogen gas can only propel a car for 500 feet.[57] Porous materials, because of their very large surface area, could theoretically accommodate much more hydrogen gas, adsorbed on their surfaces, than an empty cylinder of the same volume would. As a tank in automobiles, these materials should hold sufficient hydrogen to support today's acceptable travel range, about 300 miles, without compromising passenger or luggage room.[57] The Department of Energy's (DOE) target for 2010 is for storage systems that are capable of storing 6.5% by weight of hydrogen. Currently many scientists are working towards this end.[55] Table 1.1 includes some of the best storage materials and their hydrogen storage capacities so far achieved.[58] We have included the $Cu(m\text{-pba})_4$ made in our lab for comparison.

Using the same principle, many scientists have shown the ability of these materials to store other gases such as methane and carbon dioxide. Yaghi and coworkers recently found that one of their zeolitic imidazolate frameworks called ZIF-69 will store 83 times its volume in CO_2 at 1 atm and 273K.[45,47] MOFs have also shown promising applications in separation of gasses such as CO/CO_2, CH_4/CO_2, N_2/CO_2.[47]

Porous metal-organic materials have also shown potential application in catalysis. Several metallacycles and MOPs (cages), either by themselves or with an encapsulated organometallic catalyst, have shown catalytic activity.[65,66] For instance, Raymond and co-workers have recently shown a highly shape/size-selective allylic isomerization with an organometallic catalyst encapsulated in a supramolecular framework.[67]

Table 1.1 Hydrogen adsorption data for selected porous materials

Material	H_2 uptake at 77 K, 1 atm (wt %)	Maximum H_2 uptake at 77 K (wt %)	Maximum H_2 uptake at 298 K (wt %)
MOF-177[55,59] $Zn_4O(btb)$	1.25	7.5, 70 bar	
MOF-505[60, 61] $Cu_2(bptc)$	2.59	4.2	
HKUST-1[62, 63] $Cu_3(btc)_2$	2.54	3.6, 10 bar	0.35, 65 bar
$Cu_4(m\text{-pba})_4$[64]		4.3, 43 bar	0.65, 75 bar

Fujita and coworkers have also recently reported a highly regioselective Diels-Alder coupling of anthracene and phthalimide guests using an organopalladium cage. This cage promotes reaction at the terminal (1,4) position of the anthracene framework (Figure 1.13), different from the well established coupling at the center (9,10) position in the absence of the host.[68-70]

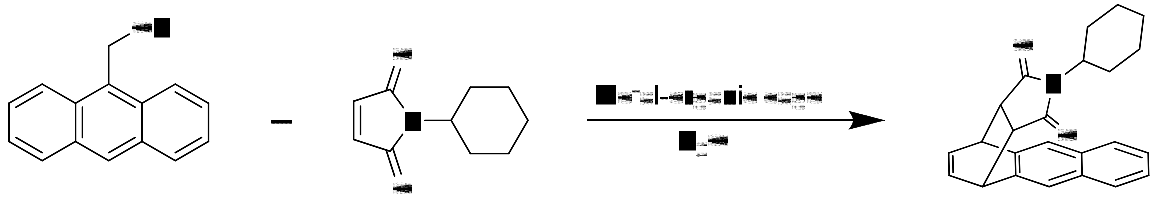


Figure 1.13 Diels-Alder coupling of 9-hydroxymethylanthracene and *N*-cyclohexylphthalimide within a metal-organic cage results in a 1,4 adduct.

1.5 β-Diketone-Based Building Blocks for Making Porous Metal-Organic Materials

Because of the rich and interesting coordination chemistry they provide upon reaction with a range of *d*- and *f*-block metal ions, β-diketoneates have been studied for a long time. β-diketones are uninegatively charged chelating oxygen donors. There are several examples in the literature where β-diketone based ligands have been used as building blocks to make porous metal-organic materials.[71] In their free state, unbound with metal ions, β-diketones are known to tautomerize between the keto and enol forms. This is shown for acetylacetone (2,4-pentanedione, or acacH) Figure 1.14.

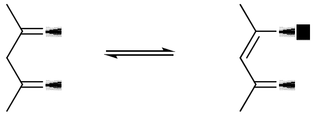


Figure 1.14 Keto and enol tautomers of acetylacetone.

To generate a β-diketone based porous material, one should start with a multi functional β-diketonate ligand. The earliest example of a rationally designed β-diketone based metal-organic molecule was prepared from a bis(β-diketone) ligand and Cu(II), figure 1.1. Further work on this compound has shown the ability to tune functionalities (use of ketoenamine binding sites instead of diketones and addition of *t*-butyl on the benzene spacer) with out disturbing the topology of the original molecule, Figure 1.15 a.[72] In a different report, the shape and size of the pore was inceased by changing the spacer into naphthalene which enabled the accommodation of guest molecules, pyrazine and Dabco, inside the cavity of the molecule, Figure 1.15 b.[73]

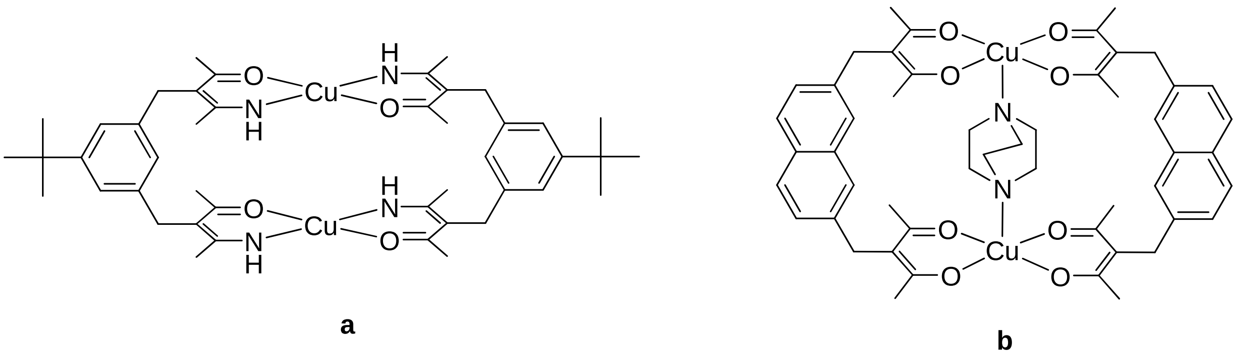


Figure 1.15 Metal-organic molecules with different organic building units **a**. ketoenamine binding sites **b**. $Cu_2(NBA)_2$ made from a larger 2,7-naphthalenediylbis-(methylene) spacer.

One of the most important advantages of β-diketone building blocks is their ability to form coordinatively unsaturated metal sites upon reaction with some transition metals, which means they provide an opportunity for the guest molecules to bind with the metal directly. This phenomenon is not commonly observed with the other building blocks. Due to their chelating nature, β-diketones also provide an opportunity for the construction of robust materials.

Compared to the other organic building blocks commonly employed in this field, such as pyridines or carboxylate based ligands, not many β-diketone based porous metal-organic materials have been reported. For example, excluding interpenetrated structures, only very few β-diketone based 3D MOFs[74, 75] and MOPs[75-77] are known. The purpose of the experiments in this dissertation is to study the possibility of making 3D MOFs and MOPs using β-diketone based building blocks and to explore their applications.

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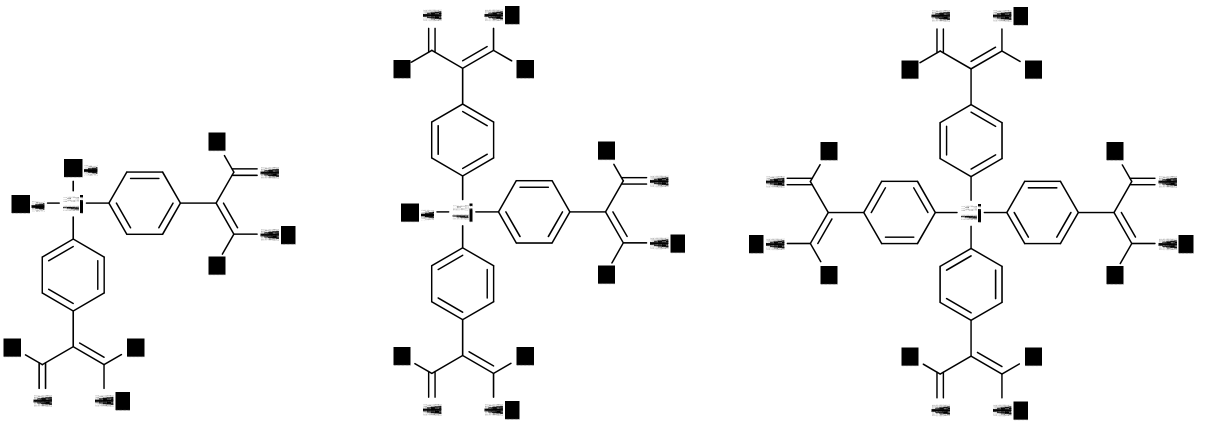
CHAPTER 2

SYNTHESIS OF ORGANOSILICON-BASED MULTIDENTATE β-DIKETONES*

2.1 Introduction

In the course of designing porous metal-organic materials, synthesis of a well chosen organic building block can be considered as a stepping stone to the entire process. The angle between the binding sites, the size and shape of the organic building block, and, of course, the type of metal ion to be used, help to determine the shape, size, and porosity of the metal-organic material to be built. Because of this, the first step in our approach is to carefully design an appropriate organic building block and synthesize it. Once the synthesis of this building block is accomplished successfully, we can pass on to the second step, namely reaction with metal ions.

In this chapter, we will focus on the synthesis of multifunctional organosilicon β-diketone building blocks and their (nonporous) Ir/Rh complexes. Herein, we report the synthesis of $Me_2Si(phacH)_2$ (**1**), $Me_2Si(phprH)_2$ (**2**), $MeSi(phacH)_3$ (**3**), $MeSi(phprH)_3$ (**4**), $Si(phacH)_4$ (**5**), and $Si(phprH)_4$ (**6**), shown in Figure 2.1.



1 ($Me_2Si(phacH)_2$, R = Me) **3** ($MeSi(phacH)_3$, R = Me) **5** ($Si(phacH)_4$, R = Me)
2 ($Me_2Si(phprH)_2$, R = Et) **4** ($MeSi(phprH)_3$, R = Et) **6** ($Si(phprH)_4$, R = Et)

Figure 2.1 Multifunctional organosilicon building blocks.

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If a transition metal ion favors square planar coordination geometry, then its reaction with the bis(β-diketone) (**1** or **2**), tris(β-diketone) (**3** or **4**), and tetrakis(β-diketone) (**5** or **6**) building blocks should generate a metal-organic pentagon, metal-organic dodecahedron, and a 3D metal-organic framework respectively (see Figure 2.2). However, based on our experience with other β-diketone building blocks, metal-organic products smaller than the proposed structures wouldn't be surprising.

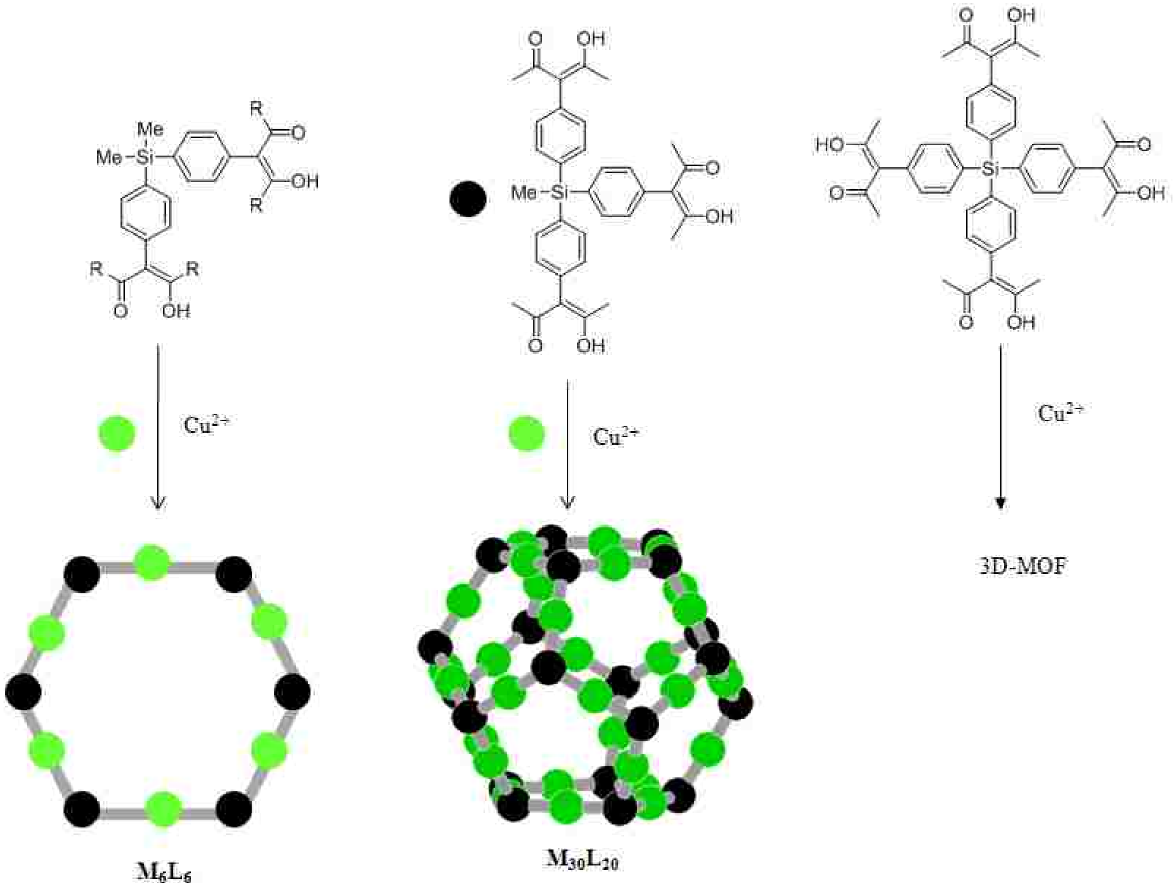


Figure 2.2 Possible metal-organic structures that can be obtained from the new ligands.

We decided to use β-diketone ligands because of their ability to bind readily with almost all metal ions and their ability to form coordinatively unsaturated metal centers upon reaction with certain metal ions such as Cu^{2+}. Furthermore, the chelating nature of β-diketones may be advantageous, because once the desired product is achieved, the two metal-ligand bonds will increase the thermal stability of the final product.

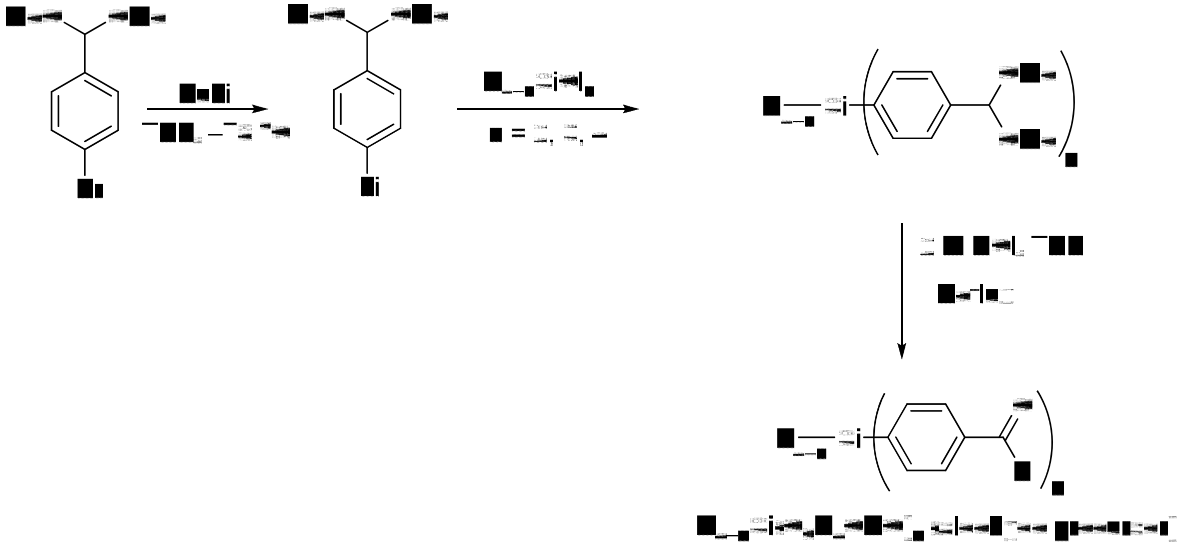
2.2 Results and Discussion

Multifunctional ligands with approximately tetrahedral angles between the ligand moieties can be derived from di-, tri-, and tetraphenylmethane. However, the Si analogs (di-, tri-, and tetraphenylsilanes, as in **1**-**6**) are generally easier to synthesize, because of the availability of coupling reactions between aryllithium compounds and chlorosilanes.[1-12] Thus, tetraphenylsilane is considerably easier to prepare than tetraphenylmethane. Still, even among the oligoarylsilanes, some derivatives have presented synthetic challenges: for example, Wuest et al. reported that tetrakis(4-formylphenyl)silane was difficult to prepare in pure form.[1] We recently used[13] the method of Ramirez et al.[14-16] to prepare new aromatic bis(β-diketones) from the analogous aldehydes. For the present work, we wished to prepare a family of bis-, tris-, and tetrakis(β-diketones) with approximately tetrahedral angles, for reaction with metal ions. To do this, we needed the corresponding di-, tri-, and tetraaldehydes (i.e. bis-, tris-, and tetrakis(4-formylphenyl)silanes) as starting materials.

2.2.1 Synthesis of Aldehydes

Lithiation of 4-bromobenzaldehyde dimethyl acetal, followed by treatment with Me_2SiCl_2, produces a bis(acetal) which yields bis(4-formylphenyl)dimethylsilane ($Me_2Si(C_6H_4CHO)_2$) on hydrolysis.[17] We carried out analogous reactions with $MeSiCl_3$ and $SiCl_4$, and obtained the other needed aldehydes, tris(4-formylphenyl)methylsilane ($MeSi(4\text{-}C_6H_4CHO)_3$, liquid) and tetrakis(4-formylphenyl)silane ($Si(4\text{-}C_6H_4CHO)_4$, crystalline solid). This synthesis is summarized in Scheme 1.

Scheme 1



The formation of an aldehyde can easily be noticed by a ^{1}H NMR peak at around 10 ppm due to the aldehyde proton, see Figure 2.3. The tris(aldehyde) MeSi(phCHO)$_3$ is easily oxidized in air to the analogous carboxylic acid over a few days.

2.2.2 Synthesis of β-Diketones

The aldehydes prepared here react with 4,5-dimethyl-(scheme 2, R′ = Me) or 4,5-diethyl-2,2,2-trimethoxy-1,3,2-dioxaphospholene (R′ = Et) at ambient temperature under N$_2$ to produce dioxaphospholanes, which on refluxing in methanol yield the new β-diketones (**1-6**). These compounds contain either two (Me$_2$Si(phacH)$_2$, **1**; Me$_2$Si(phprH)$_2$, **2**), three (MeSi(phacH)$_3$, **3**; MeSi(phprH)$_3$,**4**), or four (Si(phacH)$_4$, **5**; Si(phprH)$_4$, **6**) β-diketone substituents; in the abbreviations, "ac" and "pr" represent the β-diketone moieties acetylacetone and dipropionylmethane (3,5-heptanedione) respectively.

The formation of these β-diketone linkers can be easily be noticed by the formation of a new enolic peak near 16.7 ppm and the disappearance of the aldehyde peak near 10.0 ppm in the

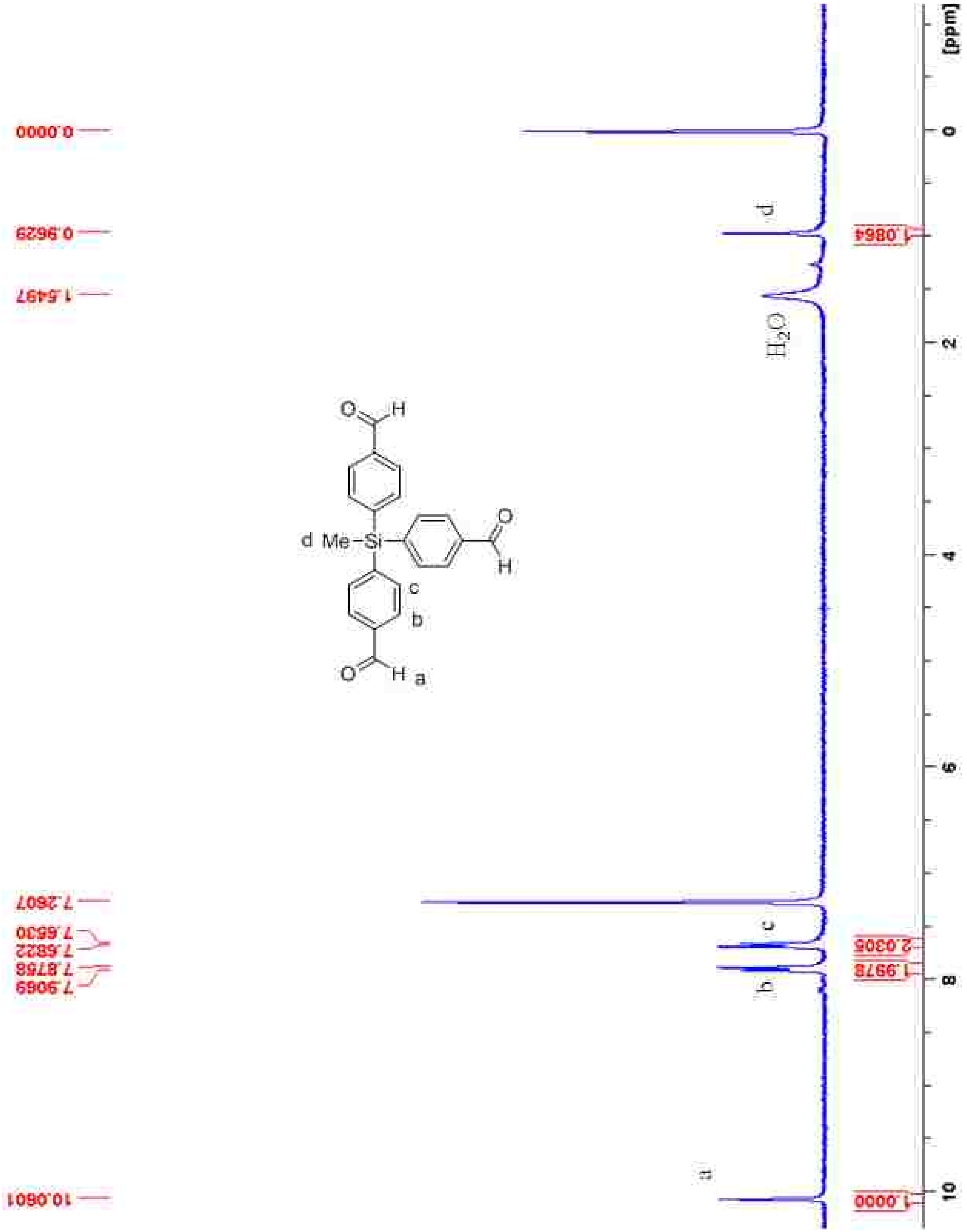


Figure 2.3 ^{1}HNMR spectrum of MeSi(phCHO)$_3$.

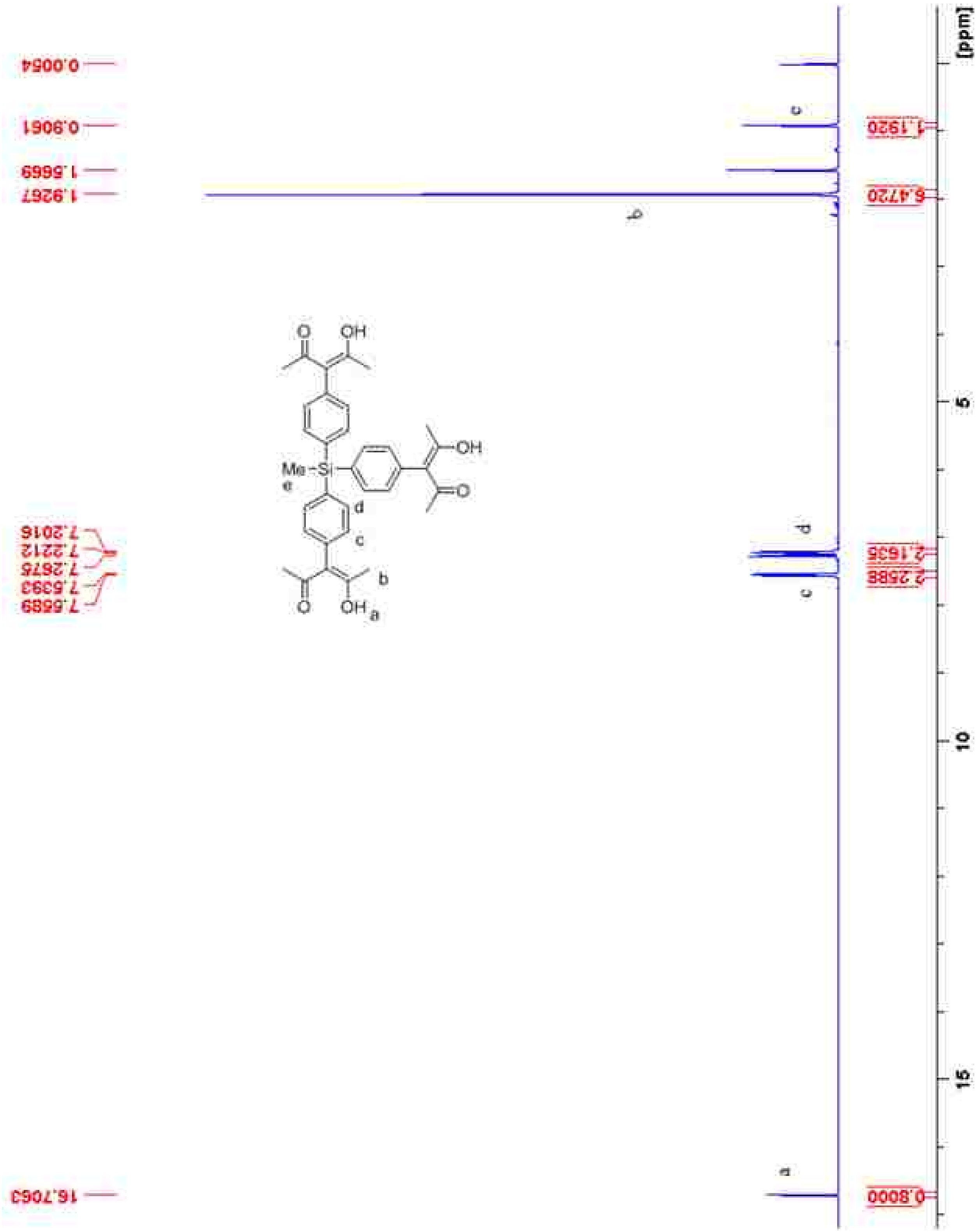
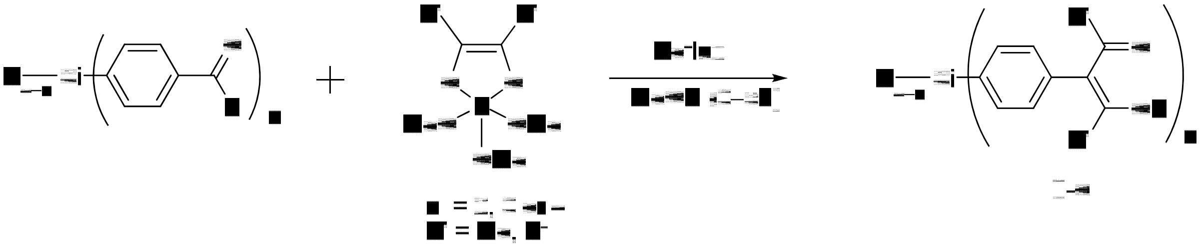


Figure 2.4 ^{1}HNMR spectrum of MeSi(phacH)$_3$ (**3**).

Scheme 2



^{1}H NMR, Figure 2.4. No keto-enol tautomerism (Figure 2.5) was observed in our β-diketone molecules; only the enolic form was observed in the ^{1}H NMR.

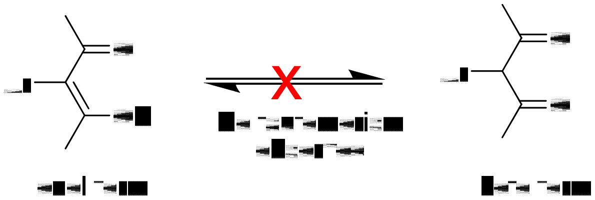


Figure 2.4 No tautomerism between the enol and keto forms.

2.2.3 Crystal Structure Analyses of β-Diketones

Compounds **2-4** were also structurally characterized by single crystal X-ray diffraction. Selected data from these studies are given in Table 1. ORTEP diagrams for **2-4** are shown in Figures 2.6-2.8.

All of the β-diketones **2-4** are in the enol form in their crystals, in agreement with the results of ^{1}H NMR spectral measurements in solution. In all of these structures, the refined positions for the enol H atoms are closer to one O atom than the other, and there is also slight alternation of bond lengths in the O-C-C-C-O chelate rings. Only intramolecular O–H···O hydrogen bonds, and no unusual intermolecular contacts, were observed in these structures. A search of the Cambridge Structural Database[18] [Database version 5.29, updated to November 2007] revealed thirteen compounds in which one or more β-diketone moieties are directly

Table 2.1 Crystal Data and Structure Refinement for Multifunctional β-Diketones **2**-**4**.

	2	**3**	**4**
formula	$C_{28}H_{36}O_4Si$	$C_{34}H_{36}O_6Si$	$C_{40}H_{48}O_6Si$
fw	464.66	568.72	652.87
cryst size, mm	0.25x0.11x0.10	0.25x0.10x0.07	0.27x0.22x0.07
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	9.845(4)	7.3493(10)	13.336(2)
b, Å	16.663(3)	22.714(5)	22.955(3)
c, Å	17.247(4)	18.640(5)	25.885(4)
α, deg	68.294(10)	90	70.796(8)
β, deg	89.725(8)	91.177(7)	78.854(8)
γ, deg	83.072(9)	90	89.768(9)
V, Å^3	2607.1(10)	3119.2(12)	7326.8(18)
Z	4	4	8
D_{calc}, Mg/m^{-3}	1.184	1.211	1.184
T, K	110	105	110
θ range, deg	2.5-24.4	2.5-27.5	2.5-23.0
μ, mm^{-1}	0.120	0.118	0.109
no. of measd reflns	16020	59143	86197
no. of indep reflns	8538	7145	20205
no. of reflns $I > 2\sigma(I)$	4921	3753	9984
no. of params	623	387	1726
goodness of fit	1.022	1.003	1.028
R ($I > 2\sigma(I)$)	0.060	0.056	0.095
wR_2	0.134	0.134	0.287
lgst diff, e Å^{-3}	0.22	0.30	0.93

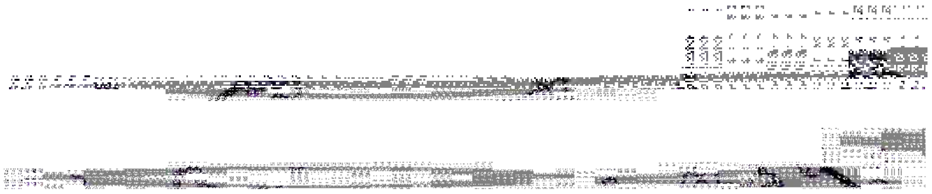


Figure 2.6 Molecular structure of $Me_2Si(phprH)_2$ (**2**) (ellipsoids shown at the 50% probability level). One of two crystallographically independent molecules in the asymmetric unit is shown.

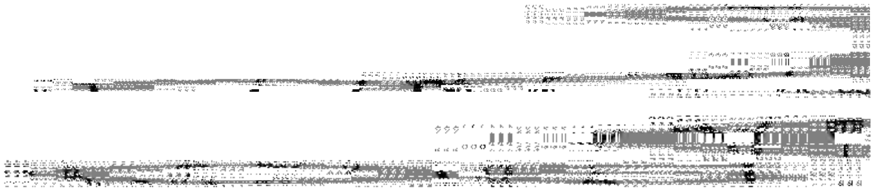


Figure 2.7 Molecular structure of MeSi(phacH)$_3$ (**3**) (ellipsoids shown at the 50% probability level).

attached to aromatic rings. Like the present compounds, all of the previous examples are in the enol form. Enolic β-diketones typically show some alternation among C–O and C–C bond lengths around the rings: average values for all structures (including those reported here) are C–O, 1.321 ± 0.019; C–C, 1.383 ± 0.012; C–C, 1.425 ± 0.019; and C–O, 1.274 ± 0.015 Å. These

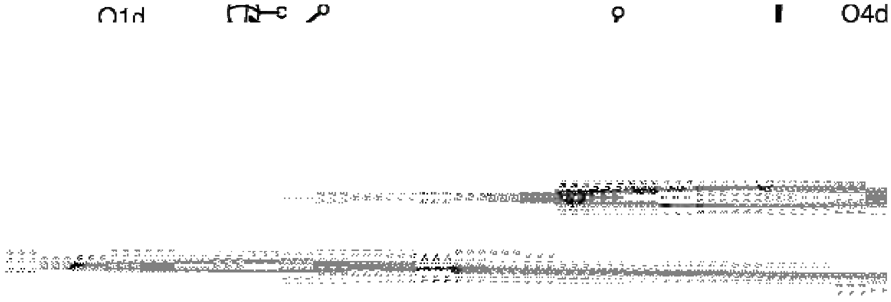


Figure 2.8 Molecular structure of MeSi(phprH)$_3$ (**4**) (ellipsoids shown at the 20% probability level). One of four crystallographically independent molecules in the asymmetric unit is shown.

values represent relatively small differences in length between the formal single and double bonds of the enol structure. This effect has been discussed in terms of resonance-assisted hydrogen bonding: for β-diketones in the enol form, which have O···O distances between 2.4 and 2.5 Å, the strength of the OH···O hydrogen bond, and the resulting amount of resonance, are large, leading to a high degree of delocalization and a small amount of bond length alternation.[19,20]

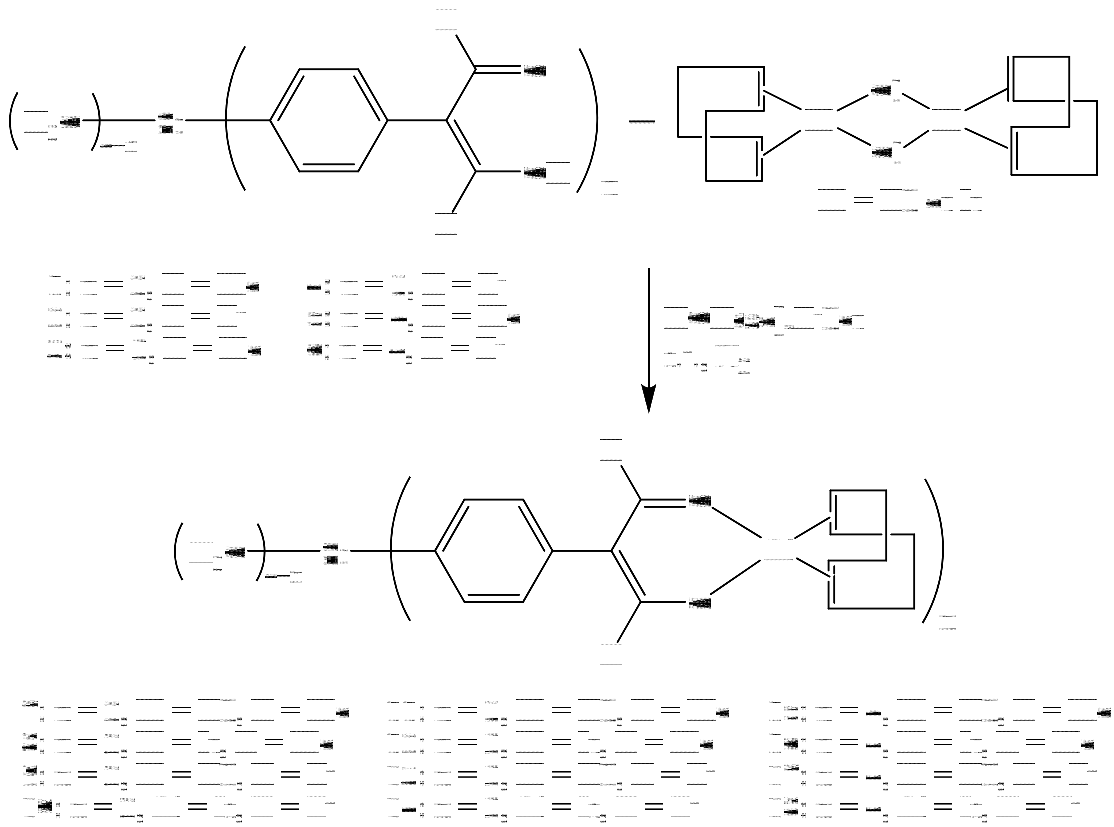
2.2.4 Rhodium(I) and Iridium(I) Complexes

Early preparations of (acac)M(COD) were reported by Chatt and Venanzi[21] and by Bonati and Wilkinson[22] (M = Rh), and by Platzer et al.[23] (M = Ir). The reaction of [M(COD)(μ-Cl)]$_2$ (M = Rh and Ir) with simple bis(β-diketones) to form binuclear complexes was reported by Whitmore and Eisenberg.[24] (Among more recent studies of related complexes is that of Tokitoh et al., who prepared Rh β-ketophosphenates and β-ketoiminates.[25]) We used a similar procedure to prepare Rh and Ir complexes of the new silicon-based multifunctional β-diketones. Compounds **1−6** react with [M(COD)(μ-Cl)]$_2$ (M = Rh and Ir) in the presence of added base to form multimetallic silicon-bridged Rh and Ir complexes (Scheme 3), which are soluble in common organic solvents. The spectral properties of the new multinuclear metal complexes are similar to those of the simpler Rh and Ir complexes, with (for example) both aromatic and aliphatic ^{1}H resonances showing slight upfield shifts compared to the uncomplexed β-diketones.

2.3 Experimental

General Considerations. Reagents were used as received: 4-bromobenzaldehyde dimethyl acetal and SiCl$_4$ (Aldrich), dimethyldichlorosilane and methyltrichlorosilane (Gelest Inc.), CDCl$_3$ (Fisher), [Rh(COD)(μ-Cl)]$_2$ (Strem), and [Ir(COD)(μ-Cl)]$_2$ (COD = 1,5-cyclooctadiene) (Pressure Chemicals). Column chromatography was carried out with Sorbent Technologies silica gel (230−450 mesh). NMR spectra were recorded on Bruker (250, 300, or 400 MHz) or Varian (500 MHz) spectrometers, with $CDCl_3$ as solvent unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl-[26]and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene,[13] and bis(4-formylphenyl)dimethylsilane ($Me_2Si(4\text{-}C_6H_4CHO)_2$),[17] were prepared by literature methods.

Scheme 3. Synthesis of Rhodium(I) and Iridium(I) Complexes **7-18**



Tris(4-formylphenyl)methylsilane ($MeSi(C_6H_6CHO)_3$). 4-Bromobenzaldehyde dimethyl acetal (12.02 g, 52.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 32.5 mL, 52 mmol) was added at −78 °C over 40 min. After stirring for an additional 90 min at −78 °C, methyltrichlorosilane (1.40 mL, 13.2 mmol) was slowly added to the above suspension. The reaction mixture was stirred for an additional 2 h at −78 °C and then overnight while it returned to room temperature. The reaction mixture was quenched with 2 M

HCl (60 mL) and extracted with ether (3 × 50 mL). The ether solution was washed with brine, dried over $MgSO_4$, and evaporated to give the oily intermediate acetal MeSi(4-$C_6H_4CH(OCH_3)_2)_3$, which was hydrolyzed without purification. The oil was dissolved in 100 mL of THF/2 M HCl (1:1 v/v) and the mixture refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured into saturated $NaHCO_3$(aq) (50 mL) and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure, giving an oil. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give tris(4-formylphenyl)methylsilane as a colorless liquid, 2.67 g (56%). ^{1}H NMR: δ 10.07 (s, 3H, C*H*O); 7.90, 7.68 (*AB*, 12H, aromatic C*H*); 0.97 (s, 3H, SiCH_3). ^{13}C NMR: δ 192.6, 142.63, 137.4, 135.9, 129.2, −3.7. ^{29}Si NMR: −11.3. FTIR: 3030, 2831, 1698, 1595, 1209, 838 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_3Si$ (M = 358.46): C, 73.71; H, 5.06. Found: C, 73.45; H, 5.11.

Tetrakis(4-formylphenyl)silane ($Si(C_6H_6CHO)_4$). 4-Bromobenzaldehyde dimethyl acetal (12.02 g, 52.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 32.5 mL, 52 mmol) was added slowly at −78 °C over 45 min. After stirring the mixture for 2 h at −78 °C, tetrachlorosilane (1.14 mL, 10 mmol) was slowly added to the above suspension. The remainder of the procedure up to the isolation of the crude product was the same as that for $CH_3Si(phCHO)_3$, except that the crude $Si(phCHO)_4$ was obtained as an off-white solid. This was recrystallized from hexane/ethyl acetate (3:1) to give (Si(4-$C_6H_4CHO)_4$) as a white solid, 3.40 g (75%), mp 200-204 °C. ^{1}H NMR: δ 10.09 (s, 4H, C*H*O); 7.94, 7.73 (*AB*, 16H, aromatic C*H*). ^{13}C NMR: δ 192.3, 139.7, 137.9, 137.0, 129.3. ^{29}Si NMR: −16.9. FTIR: 3057, 2830, 1701, 1597, 1208, 837 cm^{-1}. Anal. Calcd for $C_{28}H_{20}O_4Si$ (M = 448.54): C, 74.98; H, 4.49. Found: C, 74.72; H, 4.60.

3,3′-[Dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedione), $Me_2Si(phacH)_2$ (1). A mixture of bis(4-formylphenyl)di-methylsilane (2.19 g, 8.16 mmol) and 2,2,2-trimethoxy- 4,5-dimethyl-1,3,2-dioxaphospholene (4.29 g, 20.4 mmol) was stirred at room temperature under argon. After 24 h, 50 mL of methanol was added, and the mixture was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **1** as a white solid, 1.95 g (58%), mp 155-157 °C. ^{1}H NMR: δ 16.70 (s, 2H, O*H*); 7.55, 7.18 (*AB*, 8H, aromatic C*H*); 1.92 (s, 12H, CH_3); 0.60 (s, 6H, $SiCH_3$). ^{13}C NMR: δ 191.1, 137.9, 137.8, 134.8, 130.7, 115.3, 24.5, −2.0. ^{29}Si NMR: δ 10.0. Anal. Calcd for $C_{24}H_{28}O_4Si$ (M = 408.55): C, 70.55; H, 6.91. Found: C, 70.70; H, 7.02.

4,4′-[Dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedione), $Me_2Si(phprH)_2$ (2). A mixture of bis(4-formylphenyl)di-methylsilane (1.00 g, 3.73 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (2.66 g, 11.2 mmol) was stirred at room temperature under argon. After 18 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **2** as a white solid, 0.71 g (41%), mp 98-99 °C. ^{1}H NMR: δ 16.72 (s, 2H, O*H*); 7.52, 7.15 (*AB*, 8H, aromatic C*H*); 2.11 (m, 8H, CH_2) 1.01 (t, 12H, CH_3); 0.56 (s, 6H, $SiCH_3$). ^{13}C NMR: δ 194.1, 137.2, 137.0, 134.5, 130.7, 113.8, 29.9, 9.6, −2.2. ^{29}Si NMR: δ 13.1. Anal. Calcd for $C_{28}H_{36}O_4Si$ (M = 464.66): C, 72.37; H, 7.81. Found: C, 72.21; H, 7.64.

3,3′,3″-[Methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedione), $MeSi(phacH)_3$ (3). A mixture of tris(4-formylphenyl)methylsilane (1.76 g, 4.91 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (4.60 g, 21.9 mmol) was stirred at room temperature under argon. After 20 h, 60 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid formed. It was collected and air-dried. The filtrate was concentrated under reduced pressure to about 10 mL and filtered, giving a second crop of product. The combined product was recrystallized from methanol to give **3** as a white solid, 1.56 g (56%), mp 212-215 °C. ^{1}H NMR: δ 16.71 (s, 3H, O*H*); 7.55, 7.21 (*AB*, 12H, aromatic C*H*); 1.93 (s, 18H, C*H*$_3$); 0.91 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 191.1, 138.4, 135.8, 135.1, 130.9, 115.3, 24.5, −2.9. ^{29}Si NMR: δ 12.5. Anal. Calcd for $C_{34}H_{36}O_6Si$ (M = 568.72): C, 71.80; H, 6.38. Found: C, 72.00; H, 6.47.

4,4′,4″-[Methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedione), MeSi(phprH)$_3$ (4). A mixture of tris(4-formylphenyl)methylsilane (0.390 g, 1.09 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (1.00 g, 4.20 mmol) was stirred at room temperature under argon. After 20 h, 10 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. Then solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **4** as a white solid, 0.385 g (54%), mp 130-132 °C. ^{1}H NMR: δ 16.76 (s, 3H, O*H*); 7.55, 7.21 (*AB*, 12H, aromatic C*H*); 2.16 (m, 12H, C*H*$_2$) 1.05 (t, 18H, C*H*$_3$), 0.91 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 194.0, 137.7, 135.6, 134.8, 130.8, 113.7, 30.0, 9.6, −3.0. ^{29}Si NMR: δ 12.4. Anal. Calcd for $C_{40}H_{48}O_6Si$ (M = 652.87): C, 73.58; H, 7.41. Found: C, 73.47; H, 7.37.

3,3′,3″,3‴-[Silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedione), Si(phacH)$_4$ (**5**). A mixture of tetrakis(4-formylphenyl)silane (2.00 g, 4.46 mmol) and 2,2,2-trimethoxy- 4,5-dimethyl-1,3,2-dioxaphospholene (5.60 g, 26.8 mmol) was stirred at room temperature under argon. After 20 h, 60 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid appeared. After cooling, the mixture was filtered, giving solid **5** as a pure white solid compound, 1.91 g (59%), mp >220 °C. ^{1}H NMR: δ 16.72 (s, 4H, O*H*); 7.61, 7.26 (*AB*, 16H, aromatic C*H*), 1.94 (s, 24H, C*H*$_3$). ^{13}C NMR: δ 191.0, 138.8, 136.9, 133.1, 131.0, 115.2, 24.5. ^{29}Si NMR: δ 16.6. Anal. Calcd for $C_{44}H_{44}O_8Si$ (M = 728.90): C, 72.50; H, 6.08. Found: C, 72.36; H, 6.25.

4,4′,4″,4‴-[Silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedione), Si(phprH)$_4$ (**6**). A mixture of tetrakis(4-formylphenyl)silane (0.80 g, 1.78 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (3.20 g, 13.43 mmol) was stirred at room temperature under argon. After 20 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid appeared, which was collected and dried under vacuum. Yield: 0.925 g (62%), mp 152-155 °C. ^{1}H NMR: δ 16.74 (s, 4H, O*H*); 7.57, 7.25 (m, 16H, aromatic C*H*); 2.14 (m, 16H, CH_2); 1.04 (m, 24H, CH_3). ^{13}C NMR: δ 194.2, 138.4, 136.1, 133.0, 130.4, 113.9, 30.2, 9.1. ^{29}Si NMR: δ 16.9. Anal. Calcd for $C_{52}H_{60}O_8Si$ (M = 841.11): C, 74.25; H, 7.19. Found: C, 73.89; H, 6.99.

General Synthesis of the Complexes 7-18. The required [M(COD)(μ-Cl)]$_2$ (M = Rh or Ir) (0.200 mmol) and a stoichiometric amount of β-diketone (chosen from **1**−**6**) were combined under N_2 in diethyl ether (20 mL), and aqueous KOH (1 mL, 1 M) was then added. The solution was stirred for 25-45 min. During this time a yellow solid precipitated. It was collected and washed with 2-propanol and pentane and dried. The crude product was recrystallized either from diethyl ether or a diethyl ether/$CHCl_3$ mixture.

Bis(1,5-cyclooctadiene)[μ-[3,3′-[dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedionato)]dirhodium, Me$_2$Si(phac-Rh(COD))$_2$ (7). Yield: 0.135 g (81%); dec 240 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*), 4.13 (s, 8H, =C*H*), 2.50 (m, 8H, CH_2), 1.87 (m, 8H, CH_2), 1.72 (s, 12H, CH_3), 0.55 (s, 6H, SiCH_3). ^{13}C NMR: δ 185.8, 142.8, 136.4, 134.7, 131.2, 114.4, 76.8, 30.5, 28.6, −1.9. ^{29}Si NMR: δ 8.8. Anal. Calcd for $C_{40}H_{50}O_4Rh_2Si$ (M = 828.72): C, 57.97; H, 6.08. Found: C, 58.06; H, 5.96.

Bis(1,5-cyclooctadiene)[μ-[3,3′-[dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedionato)]diiridium, $Me_2Si(phac\text{-}Ir(COD))_2$ (8). Yield: 0.117 g (58%); dec 280 °C. ^{1}H NMR: δ 7.52, 7.13 (*AB*, 8H, aromatic C*H*), 4.04 (s, 8H, =C*H*), 2.31 (m, 8H, CH_2), 1.78 (s, 12H, CH_3), 1.70 (m, 8H, CH_2), 0.56 (s, 6H, SiCH_3). ^{13}C NMR: δ 185.7, 141.8, 136.9, 134.9, 131.0, 116.1, 59.9, 31.4, 28.6, −1.9. ^{29}Si NMR: δ 10.0. Anal. Calcd for $C_{40}H_{50}O_4Ir_2Si$ (M = 1007.30): C, 47.69; H, 5.00. Found: C, 47.90; H, 4.99.

Bis(1,5-cyclooctadiene)[μ-[4,4′-[dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedionato)]dirhodium, $Me_2Si(phpr\text{-}Rh(COD))_2$ (9). Yield: 0.135 g (76%); dec 198 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*); 4.13 (s, 8H, =C*H*), 2.50 (m, 8H, CH_2), 1.92 (m, 16H, CH_2 and CH_2CH_3); 0.85 (t, 12H, CH_3); 0.56 (s, 6H, SiCH_3). ^{13}C NMR: δ 188.6, 142.1, 135.7, 134.4, 131.6, 113.2, 76.9, 33.2, 30.5, 10.4, −2.6. ^{29}Si NMR: δ 13.8. Anal. Calcd for $C_{44}H_{58}O_4Rh_2Si$ (M = 884.83): C, 59.73; H, 6.61. Found: C, 59.52; H, 6.70.

Bis(1,5-cyclooctadiene)[μ-[4,4′-[dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedionato)]diiridium, $Me_2Si(phpr\text{-}Ir(COD))_2$ (10). Yield: 0.120 g (56%); dec 190 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*); 4.04 (s, 8H, =C*H*), 2.31 (m, 8H, CH_2), 1.99 (q, 8H, CH_2CH_3), 1.70 (d, 8H, CH_2), 0.93 (t, 12H, CH_3); 0.57 (s, 6H, SiCH_3). ^{13}C NMR: δ 188.5, 141.3, 136.6, 135.1, 132.2, 115.0, 60.8, 33.3, 31.4, 10.9, −3.1. ^{29}Si NMR: δ 12.3. Anal. Calcd for $C_{44}H_{58}O_4Ir_2Si$ (M = 1063.45): C, 49.69; H, 5.50. Found: C, 49.90; H, 5.49.

Tris(1,5-cyclooctadiene)[μ-[3,3′,3″-[methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedionato)]trirhodium, $MeSi(phac\text{-}Rh(COD))_3$ (11). Yield: 0.147 g (92%); dec 288 °C. ^{1}H NMR: δ 7.46, 7.14 (*AB*, 12H, aromatic C*H*), 4.14 (s, 12H, =C*H*), 2.49 (m, 12H, CH_2), 1.87 (m, 12H, CH_2), 1.73 (s, 18H, CH_3), 0.83 (s, 3H, SiCH_3). ^{13}C NMR: δ 185.7, 143.1, 135.8, 134.3, 131.3, 114.3, 76.8, 30.5, 28.6, −2.7. ^{29}Si NMR: δ 13.3. Anal. Calcd for $C_{58}H_{69}O_6Rh_3Si$ (M = 1198.97): C, 58.10; H, 5.80. Found: C, 57.92; H, 5.81.

Tris(1,5-cyclooctadiene)[μ-[3,3′,3″-[methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedionato)]triiridium, MeSi(phac-Ir(COD))$_3$ (12). Yield: 0.141 g (72%); dec 276 °C. ^{1}H NMR: δ 7.50, 7.15 (*AB*, 12H, aromatic C*H*), 4.04 (s, 12H, =C*H*), 2.31 (m, 12H, CH_2), 1.80 (s, 18H, CH_3), 1.70 (m, 12H, CH_2), 0.85 (s, 3H, SiCH_3). ^{13}C NMR: δ 185.7, 142.2, 136.0, 134.8, 131.2, 116.1, 60.0, 31.4, 28.7, −2.7. ^{29}Si NMR: δ 13.6. Anal. Calcd for $C_{58}H_{69}Ir_3O_6Si$ (M = 1466.88): C, 47.49; H, 4.74. Found: C, 47.39; H, 4.70.

Tris(1,5-cyclooctadiene)[μ-[4,4′,4″-[methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedionato)]trirhodium, MeSi(phpr-Rh(COD))$_3$ (13). Yield: 0.164 g (95%); dec 220 °C. ^{1}H NMR: δ 7.47, 7.14 (*AB*, 12H, aromatic C*H*); 4.11 (s, 12H, =C*H*), 2.50 (m, 12H, CH_2), 1.92 (m, 24H, CH_2 and CH_2CH$_3$); 0.85 (m, 21H, CH_3 and SiCH_3). ^{13}C NMR: δ 188.6, 142.1, 135.7, 134.3, 131.6, 113.2, 76.8, 33.2, 30.5, 10.4, −2.6. ^{29}Si NMR: δ 12.6. Anal. Calcd for $C_{64}H_{81}Rh_3O_6Si$ (M = 1283.13): C, 59.91; H, 6.36. Found: C, 59.73; H, 6.33.

Tris(1,5-cyclooctadiene)[μ-[4,4′,4″-[methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedionato)]triiridium, MeSi(phpr-Ir(COD))$_3$ (14). Yield: 0.141 g (68%); dec 290 °C. ^{1}H NMR: δ 7.51, 7.15 (*AB*, 12H, aromatic C*H*); 4.05 (s, 12H, =C*H*), 2.31 (m, 12H, CH_2), 2.00 (m, 12H, CH_2CH$_3$) 1.68 (m, 12H, CH_2); 0.91 (m, 21H, CH_3 and SiCH_3). ^{13}C NMR: δ 188.6, 136.7, 135.1, 132.3, 130.8, 115.0, 60.8, 33.4, 31.4, 11.0. ^{29}Si NMR: δ 13.0. Anal. Calcd for $C_{64}H_{81}Ir_3O_6Si$ (M = 1551.06): C, 49.56; H, 5.26. Found: C, 49.70; H, 5.49.

Tetrakis(1,5-cyclooctadiene)[μ-[3,3′,3″,3‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedionato)]tetrarhodium, Si(phac-Rh(COD))$_4$ (15). Yield: 0.071 g (45%); mp 168−174 °C. ^{1}H NMR: δ 7.51, 7.16 (*AB*, 16H, aromatic C*H*), 4.13 (s, 16H,

=C*H*), 2.48 (m, 16H, CH_2), 1.88 (m, 16H, CH_2), 1.74 (s, 24H, CH_3). This compound was not sufficiently stable in $CDCl_3$ solution for recording a high-quality ^{13}C NMR spectrum. ^{29}Si NMR: δ 16.0. Anal. Calcd for $C_{76}H_{88}O_8Rh_4Si$ (M = 1569.21): C, 58.17; H, 5.65. Found: C, 57.88; H, 5.76.

Tetrakis(1,5-cyclooctadiene)[μ-[3,3′,3″,3‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedionato)]tetrairidium, Si(phac-Ir(COD))$_4$ (16). Yield: 0.113 g (58%). ^{1}H NMR: δ 7.55, 7.18 (*AB*, 16H, aromatic C*H*), 4.04 (s, 16H, =C*H*), 2.31 (m, 16H, CH_2), 1.82 (s, 24H, CH_3), 1.71 (m, 16H, CH_2). This compound was not sufficiently stable in $CDCl_3$ solution for recording high-quality ^{13}C or ^{29}Si NMR spectra. Anal. Calcd for $C_{76}H_{88}Ir_4O_8Si$ (M = 1926.46): C, 47.38; H, 4.60. Found: C, 47.01; H, 4.73.

Tetrakis(1,5-cyclooctadiene)[μ-[4,4′,4″,4‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedionato)]tetrarhodium, Si(phpr-Rh(COD))$_4$ (17). Yield: 0.148 g (88%); dec 246 °C. ^{1}H NMR: δ 7.52, 7.17 (*AB*, 16H, aromatic C*H*), 4.14 (s, 16H, =C*H*), 2.50 (m, 16H, CH_2), 2.00 (m, 16H, CH_2), 1.90 (q, 16H, CH_2CH_3), 0.86 (t, 24H, CH_3). ^{13}C NMR: δ 188.5, 142.5, 136.8, 132.6, 131.8, 113.2, 76.1, 33.2, 30.5, 10.4. ^{29}Si NMR: δ 17.2. Anal. Calcd for $C_{84}H_{104}O_8Rh_4Si$ (M = 1681.43): C, 60.00; H, 6.23. Found: C, 60.33; H, 6.45.

Tetrakis(1,5-cyclooctadiene)[μ-[4,4′,4″,4‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedionato)]tetrairidium, Si(phpr-Ir(COD))$_4$ (18). Yield: 0.108 g (53%); dec 204 °C. ^{1}H NMR: δ 7.53, 7.17 (*AB*, 16H, aromatic C*H*), 4.04 (s, 16H, =C*H*), 2.33 (m, 16H, CH_2), 2.04 (q, 16H, CH_2CH_3), 1.72 (m, 16H, CH_2), 0.93 (t, 24H, CH_3). ^{13}C NMR: δ 188.4, 141.6, 138.3, 136.9, 131.6, 114.9, 60.0, 33.4, 30.2, 10.2. ^{29}Si NMR: δ 15.9. Anal. Calcd for $C_{84}H_{104}Ir_4O_8Si$ (M = 2038.67): C, 49.49; H, 5.14. Found: C, 49.25; H, 4.95.

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CHAPTER 3

METAL-ORGANIC POLYMERS AND POLYHEDRA FROM ORGANOSILICON-BASED MULTIDENTATE β-DIKETONES, AND THEIR ANALYSIS BY SCANNING-PROBE MICROSCOPY

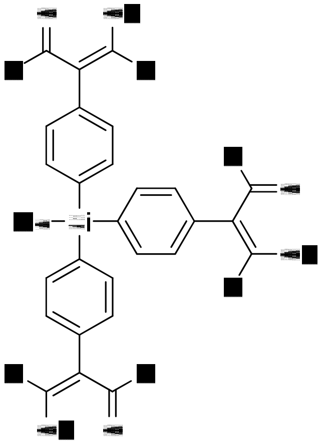
3.1 Introduction

Since the discovery of zeolites, a class of porous materials, and their wide spectrum of applications, many scientists have been motivated to investigate the synthesis of porous materials in a systematic way. To date, a great deal of energy, time and resources have been invested in these materials, especially in investigating ways to prepare them with pores of controlled size and shape. The efforts are still continuing and were successful to a certain degree. In the last two or three decades, however, different classes of rationally designed porous materials have emerged. Metal-organic frameworks (MOFs), metal-organic polyhedra (MOPs), zeolitic imidazolate frameworks (ZIFs), and covalent organic frameworks (COFs) are some of the famous classes of rationally designed porous materials.

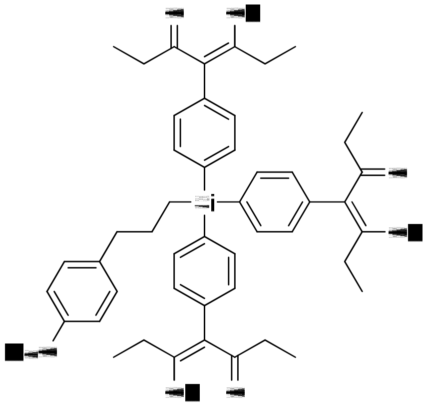
Since there are many metal ions of different central geometry (linear, tetrahedral, square planar, octahedral) and since there are many choices of organic ligands, it should be possible to make a broad range of metal-organic compounds with predefined shapes and sizes.[1] These materials have pores (with uniform size and shape) that are uniformly distributed throughout the material and are built by connecting organic building blocks using metal ion linkers. These porous metal-organic materials have potential application in catalysis,[2,3] hydrogen gas storage,[4-6] separation,[7-9] drug delivery,[10,11] host-guest chemistry[12,13] and others. This chapter discusses the synthesis and properties of metal-organic polyhedra (MOPs) derived from tetrahedral-based β-diketone ligands.

According to our approach, synthesis of metal-organic materials is carried out in two steps. The first step is to synthesize a well chosen organic building block (ligand) and the second step involves reactions of the ligand with an appropriate metal ion. The synthesis of several Si-based multifunctional β-diketone organic building blocks was discussed in the previous chapter. Here, we will focus on the second step, ligand-metal ion reactions.

This chapter discusses reactions of tetrahedral based tris(β-diketone) organic building blocks (**1**-**3**), Figure 3.1, and Cu^{2+}. Based on the angle between the β-diketone moieties in the ligand and the expected square planar geometry around Cu^{2+}, it is anticipated that copper complexes of **1**-**3** would produce a metal-organic dodecahedron, a subclass of MOPs. The edges of a dodecahedron make an angle of 108°, which is nearly equal to the tetrahedral angle, ~109.5°, in the building block.



1 $MeSi(phacH)_3$, R=Me
2 $MeSi(phprH)_3$, R=Et



3 $mppSi(phprH)_3$, R=Et

Figure 3.1 Tris(β-diketone) building blocks

Based on our experience with other β-diketones, it won't be surprising if a smaller polyhedron (cube) is formed instead of dodecahedron. We have recently reported that *m*-$pbaH_2$ (Figure 3.2) with a 120° between the β-diketone moieties made a metal-organic square instead of the expected hexagon upon reaction with Cu^{2+}.[12]

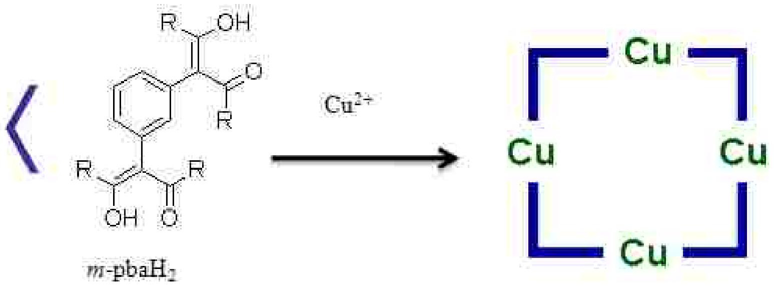


Figure 3.2 Reaction of *m*-pbaH_2 with Cu^{2+} generates a metal-organic square, Cu_4(*m*-pba)$_4$ instead of the expected metal-organic heaxagon, Cu_6(*m*-pba)$_6$.

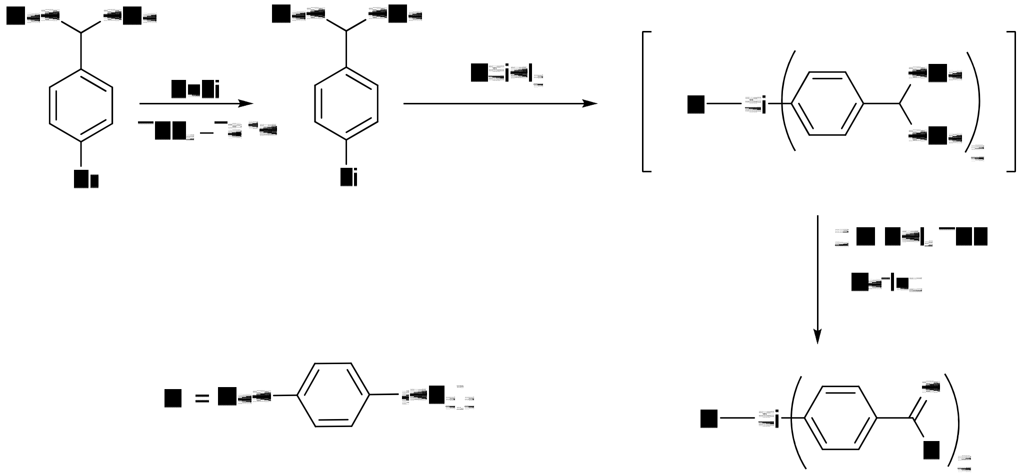
The chelating ability of β-diketone ligands is expected to make the metal-organic products more stable because of the increased metal-ligand bond strength; it has a negative impact on the building process though. Strong bonds make self correction of the structure difficult, which is not desirable in the self assembly process because whatever is formed at first is more likely to remain as the final product. Under normal circumstances of self assembly, various intermediate structures might form but should re-arrange themselves to the most stable structure during the course of reaction. This is a major challenge that needs to be addressed in the chemistry of rationally designed porous metal-β-diketonate materials.

We have chosen Cu^{2+} as our metal ion linker because of its ability to make coordinatively unsaturated square planar complexes readily upon reaction with β-diketones. Several studies have shown enhanced guest adsorption upon the use of a host that is built from coordinatively unsaturated metal ions.[14] One problem with Cu^{2+}, however, is its paramagnetic nature, which makes NMR measurements difficult or impossible.

3.2 Results and Discussion

The synthesis of building blocks **1** and **2** was discussed in the previous chapter. Compound **3** was made similarly, except that (3-(p-methoxyphenyl)propyl)trichlorosilane (Scheme 3.1) was used as starting material instead of CH_3SiCl_3. The purpose of changing the methyl substituent to this longer tail was to increase the solubility of the metal complexes. It also turned out that the corresponding new tris(aldehyde) is a solid at room temperature, which makes the whole separation/purification process much easier. The new β-diketone mppSi(phprH)$_3$ (**3**) was prepared by treating the tris(aldehyde) with 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene in N_2 and refluxing in methanol afterwards. Substituents; in the abbreviations, “mpp” and “pr” represent 3-(p-methoxyphenyl)propyl and dipropionylmethane (3,5-heptanedione) respectively.

Scheme 3.1. Synthesis of a Si-based tris(aldehyde) with a longer tail.



Reaction of compound **1** with Cu^{2+} forms mostly polymeric insoluble material (~ 80%). The soluble part (~ 20%) is not very stable in solution. It decomposes if left in solution for a few hours. The relative amount of the soluble/insoluble products also depends upon the rate of stirring. The highest yields of soluble products, in all of our reactions, were made under gentle stirring. If the mixture of ligand (in dichloromethane) and $[Cu(NH_3)_4]^{2+}$ (in H_2O) is stirred vigorously, insoluble materials are almost exclusively made . Reaction of compound **2** and **3** produced about 60% and 70% of soluble material respectively upon reaction with $[Cu(NH_3)_4]^{2+}$. Compounds **1**, **2** and **3** form almost exclusively insoluble materials upon reaction with $Cu(NO_3)_2$ in DMF, no base was added. See Table 3.1 for a summary of the metal-ligand reactions.

Table 3.1 Metal-ligand reactions under different conditions

Ligand	Reaction conditions	Cu reactant	Overall yield (%)	Soluble yield (%) Mild/vigorous stirring	Insoluble yield (%) Mild/vigorous stirring
1	2-phase (CH_2Cl_2/H_2O),	$[Cu(NH_3)_4]^{2+}$	~100	20/0	80/100
2	2-phase (CH_2Cl_2/H_2O),	$[Cu(NH_3)_4]^{2+}$	~100	60/0	40/100
3	2-phase (CH_2Cl_2/H_2O),	$[Cu(NH_3)_4]^{2+}$	~100	70/0	30/100
1,2, or 3	both ligand and metal salt dissolved in DMF	$Cu(NO_3)_2$	~100	<3	>97

Elemental analyses of both soluble and insoluble materials indicate 3:2 metal-ligand ratios [Cu_3L_2]. However, this doesn't distinguish between dodecahedron, decahedron, or cube. In our case, it is even hard to tell the difference between a polymer and a discrete molecule based on elemental analysis since the metal-ligand ratio is likely to be about the same.

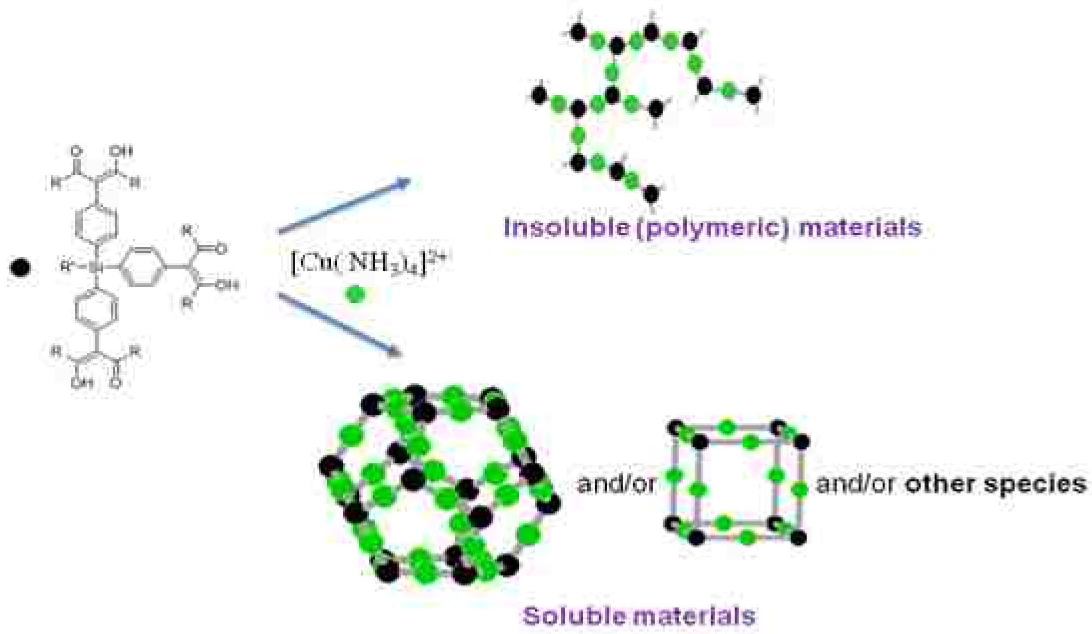


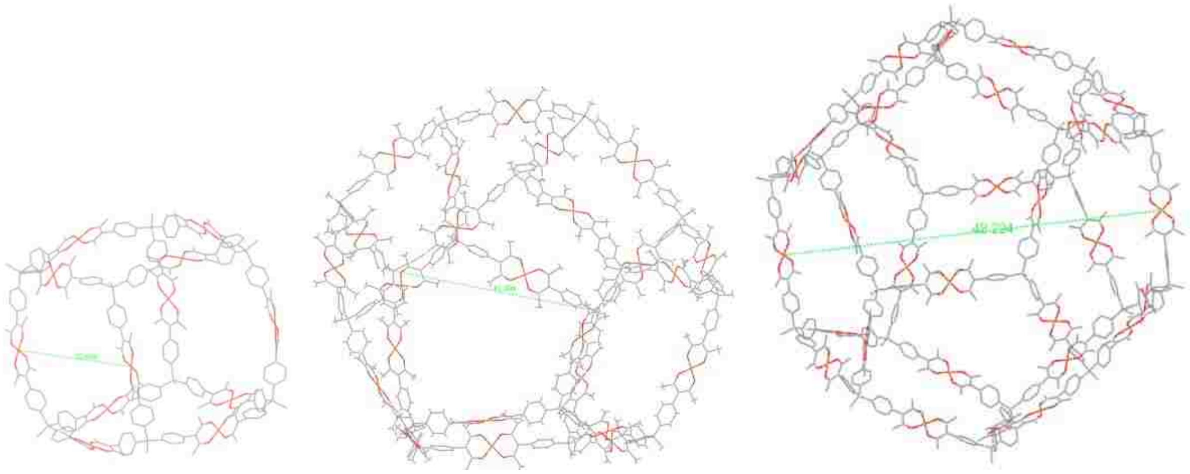
Figure 3.3 Reaction of tris(β-diketones) with Cu^{2+} results in insoluble (polymeric) and soluble species that might contain a metal-organic dodecahedron and/or cube and /or other species

We think the insoluble materials have polymeric structures, whereas the soluble materials have molecular structures; this is illustrated schematically in Figure 3.3. AFM analysis of the soluble materials is discussed below. The insoluble materials may be considered as the kinetic product, forming on initial reaction of the ligands and metal ions. In typical self-assembly processes, such initial products can rearrange over a longer period of time to form the desired (molecular) product. However, the strong bonds that the chelating ligands form with the metal ion in our case are likely to hinder the breaking and re-assembly of metal-ligand bonds to form the desired molecular structure.

The three tris(β-diketone) ligands, and different reaction conditions, yield varying proportions of soluble and insoluble Cu complexes, as listed in Table 3.1. In addition to modifying ligand structure and reaction conditions to maximize the yield of soluble products, we explored refluxing and microwave-assisted procedures for breaking up and re-assembling the insoluble materials. Refluxing insoluble $[Cu_3(MeSi(phac)_3)_2]_n$ (1st row in Table 3.1), in dichloromethane for 3-5 h produces olive green, soluble material in ~ 5% yield.

These newly generated materials, like the other soluble Cu(II) complexes prepared here, did not form crystals, so we could not use X-ray analysis to determine their structure. Also, we attempted to characterize them by mass spectrometry, gel permeation chromatography (coupled with DLS detector), and TEM, but these experiments did not useful results. Instead, they were analyzed by atomic force microscopy (AFM). AFM should be able to differentiate among the possible products. Molecular modeling of the possible metal-organic polyhedra is given in Figure 3.4.

Adsorbates of the soluble material, generated by refluxing of $[Cu_3(MeSi(phac)_3)_2]_n$ in dichloromethane, formed isolated nanostructures of different sizes on glass surfaces as displayed in the AFM topographs in Figure 3.5. The successive zoom-in views of AFM topography



Cube (2 nm) Decahedron (3.5 to 4.5 nm) Dodecahedron (5 nm)

Figure 3.4 Structures of the molecular cube $(MeSi(phac)_3)_8Cu_{12}$ (diameter ca. 2 nm), molecular decahedron$(MeSi(phac)_3)_{16}Cu_{24}$, (diameter ca. 3.5-4.5 nm), and molecular dodecahedron $(MeSi(phac)_3)_{20}Cu_{30}$, (diameter ca. 5 nm), that could form on reaction of $MeSi(phac)_3H_3$ (**1**) with Cu. The structures were obtained via molecular modeling with HyperChem version 7.01.

images displays tall features with brighter colors, whereas shallow features are darker. The AFM probe is much larger than the surface features and thus, due to tip-sample convolution the lateral resolution is limited to several nanometers. However, the **z** resolution of AFM is on the order of a few Angstroms, and can be useful for evaluating dimensions of molecular adsorbates. Approximately 3% of the surface is covered with the nanostructures within the 2.7 × 2.7 μm^2 area of Figure 3.5A. The structures range from 2-15 nm in height. The size of the larger structures corresponds to the dimensions of aggregates of several molecules. A magnified view of the surface structures of these materials is presented in Figure 3.5B. The characteristic morphology of the underlying glass substrate is visible in both images. A representative cursor profile of four of the nanostructures (Figure 3.5C) shows a height of approximately 5 nm. Analysis of 200 nanostructures reveals that 50% of the features measure between 4 and 6 nm in height (Figure 3.5D). These results are in good agreement for the predicted 5 nm dimensions of the dodecahedron structure $(MeSi(phac)_3)_{20}Cu_{30}$).

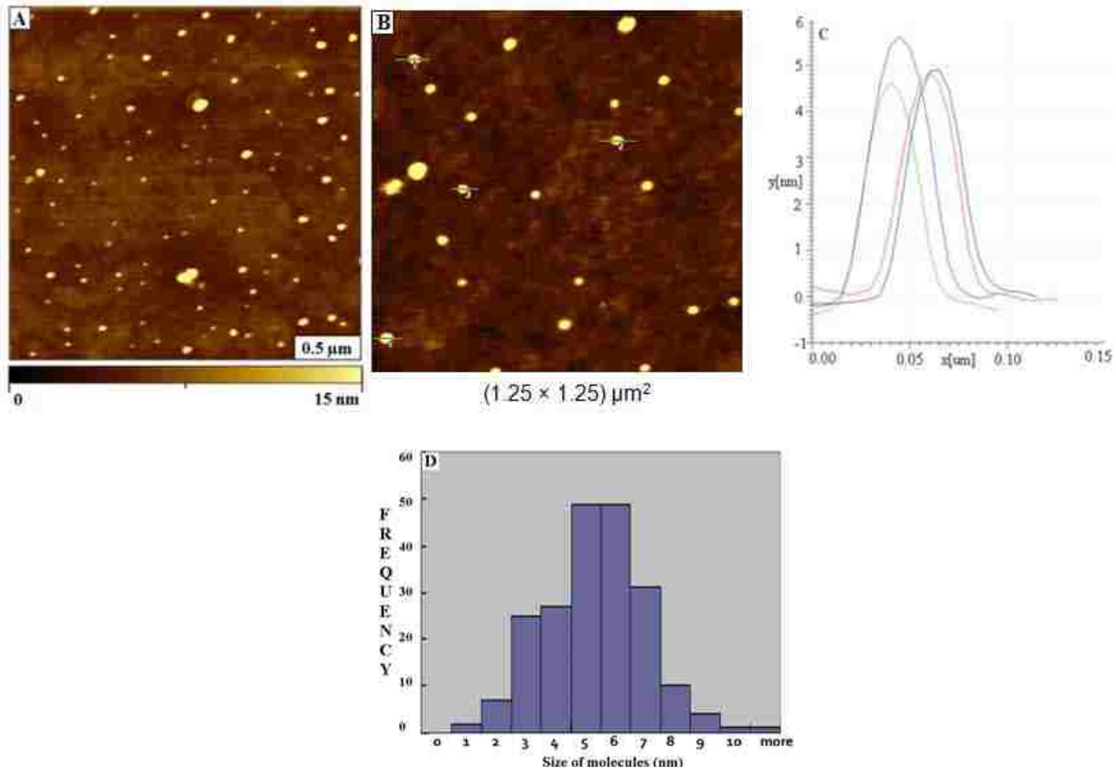


Figure 3.5 Metal-organic dodecahedra, $[(MeSi(phac)_3)_{20}Cu_{30}]$, generated from polymeric material under refluxing conditions. A) Tapping mode AFM image of $[(MeSi(phac)_3)_{20}Cu_{30}]$, B) enlargement of a portion of (A); C) size analysis of four representative molecules; and D) histogram of 200 molecules.

Because of their ability to produce intense local heating in a very short time (which helps minimize the possibility of decomposition), microwave assisted procedures seem to offer a great advantage. Thus, we suspended the insoluble polymeric product $[Cu_3(MeSi(phpr)_3)_2]_n$ formed from $Cu(NO_3)_2$ and **2** (4th row in Table 3.1) in dichloromethane, and exposed the mixture to microwave radiation (400 W, ca. 30 min, 150 °C). By the end of the irradiation, the colorless dichloromethane solution turned olive green, indicating the formation of new green soluble species. By repeating the same procedure with the unconverted insoluble material, several crops of these soluble species can be harvested with an overall yield of ~ 15%. These materials formed polydisperse nanostructures, as viewed in the AFM of Figure 3.6. A higher surface coverage (8 %) is apparent for this sample, prepared on atomically flat mica substrates. The nanostructures range from 2.4 to 28 nm in height, with an overall average size of 5.4 ± 1.6 nm. Thus, a large fraction of the molecules in this sample also match the expected molecular dimensions (5 nm) of the dodecahedron. The zoom-in view displays fairly regular shapes and sizes for 11 nanostructures within the 2.5 × 2.5 μm^2 area of Figure 3.6B. A representative line profile for two nanostructures exhibits heights measuring 5 nm (Figure 3.6C).

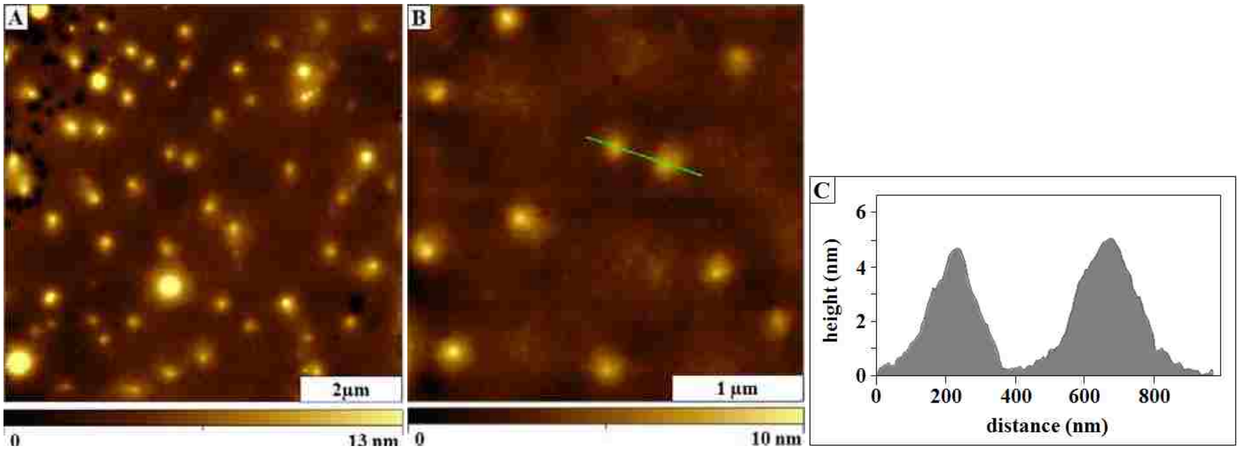


Figure 3.6 AFM images of soluble $[(MeSi(phpr)_3)_2Cu_3]_n$ generated by microwave irradiation of insoluble (polymeric) material. A) Tapping mode AFM image. B) Enlargement of a portion of the image, showing location of line profile. C) Line profile of two molecules; heights are ca. 5 nm, as expected for the metal-organic dodecahedron $[(MeSi(phpr)_3)_{20}Cu_{30}]$.

Microwave irradiation of the insoluble portion from reaction of $[Cu(NH_3)_4]^{2+}$ and **2** (2nd row in Table 3.1) also produced green soluble species. The surface morphology of this material is quite different from the previous samples. The sample displays globular protrusions of varied sizes, arranged randomly throughout the surface. The surface has saturation coverage without exposing uncovered areas of the mica substrate (Figure 3.7A). Throughout the surface there are nanopores or channels interspersed within the globular nanostructures, which are more clearly apparent in the phase image of Figure 3.7B. The AFM probe is too wide to fully penetrate within the narrow nanopores; however the phase images confirm the locations of the nanopores. A cursor profile across two of the larger nanopores is presented in Figure 3.7C, revealing a depth of about 3 nm. The globular nanostructures observed in the topographs (Figures 3.7A and 3.7D) range from 1.5 to 14 nm in height. The expected dimension is about 5 nm. A closer view is presented in Figure 3.7D which shows the variations in sizes. The shapes of the nanostructures are apparent in the phase image of Figure 3.7E. It reveals nanostructures with and without nanopores. The globular nanostructures along the cursor line range from 4 to 6 nm in height (Figure 3.7F).

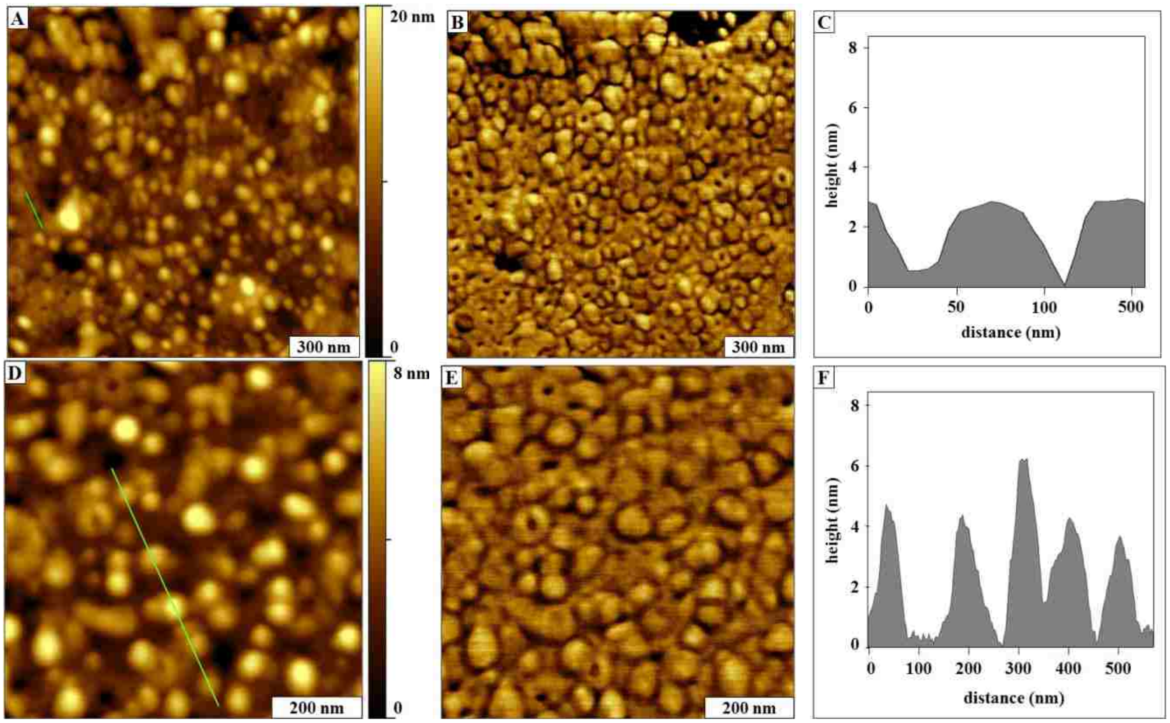


Figure 3.7 AFM images of metal-organic dodecahedra, [MeSi(phpr)$_{20}$Cu$_{30}$], generated through microwave irradiation of insoluble polymeric materials (obtained from reaction of [Cu(NH$_3$)$_4$]$^{2+}$ and MeSi(phprH)$_3$).

To help us compare these images with known systems, AFM images of our previously synthesized molecular square, Cu$_4$(*m*-pba)$_4$ (Figure 3.8), were studied.[12] According to the crystal structure of this compound, the methyl groups on opposite faces are about 6.3 Å apart.

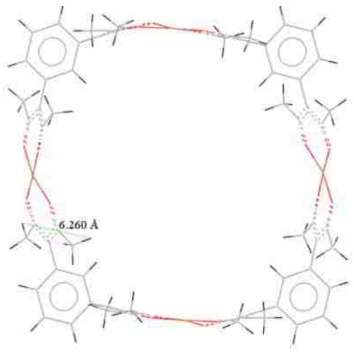


Figure 3.8 Structure of $Cu_4(m\text{-pba})_4$, taken from Reference 12. The molecule is ca. 14 Å in diameter, and the β-diketone methyl groups on opposite faces are ca. 6.3 Å apart.

This sample, $Cu_4(m\text{-pba})_4$, formed ring nanostructures, as shown in Figure 3.9. Six ring structures are visible within the 1.2 × 1.2 μm^2 area. The rings are fairly uniform in size and shape. The cavity in the center of each ring is more clearly apparent in the simultaneously acquired phase image of Figure 3.9B.

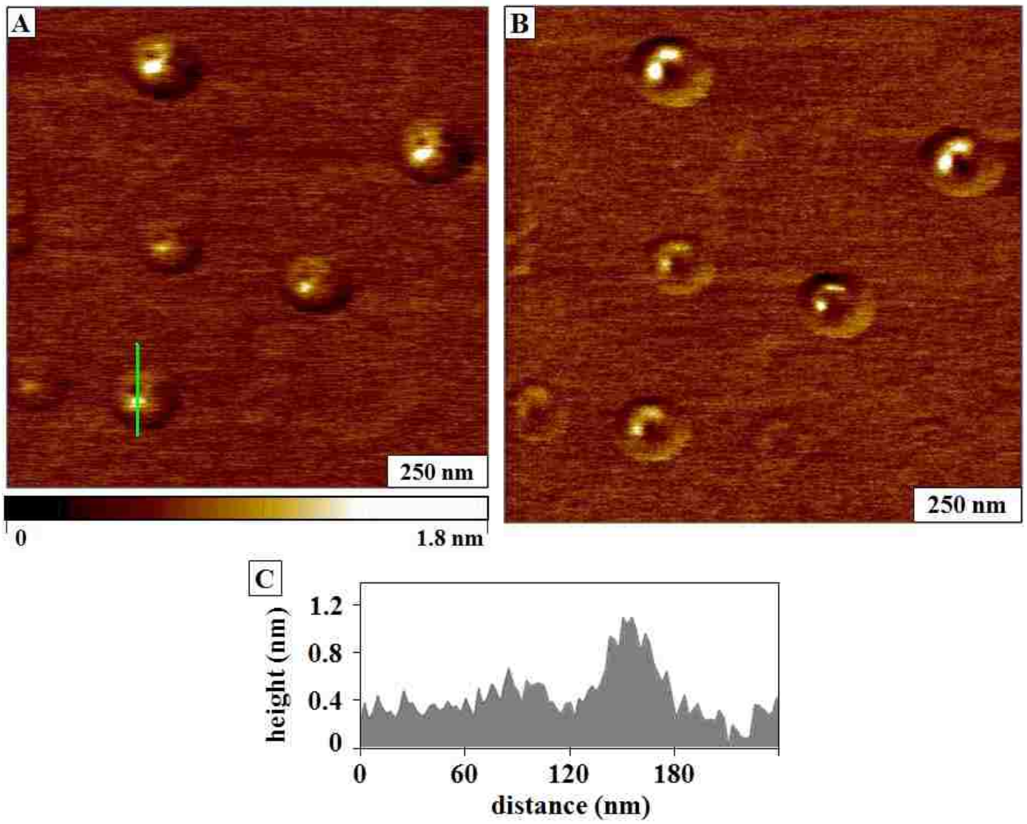


Figure 3.9 AFM images of molecular squares, $Cu_4(m\text{-pba})_4$, and height profile for one molecular square.

The height of the structures measured 1.4 ± 0.3 nm referencing the uncovered areas of mica as a baseline. The lateral dimensions are distorted by tip-sample convolution. The height of an individual ring structure measures 1.2 nm as shown by a representative cursor profile (Figure 3.9C).

3.3 Conclusion

Based on the AFM studies shown here, it is reasonable to conclude that metal–β-diketone bonds can undergo structural self correction under refluxing and microwave irradiation conditions. A large portion of the solublized material falls in the range of 4 to 6 nm in size. These are most likely the metal-organic dodecahedra that were proposed in the beginning of this project. The smaller globular features could be decahedra or cubic structures, which according to molecular modeling (see Figure 3.3) should have diameters that range between 2 and 4.5 nm. It is not surprising to see structures smaller than the "ideal" geometries. This is particularly true in metal–β-diketonate porous compounds. Our recently reported molecular square, $Cu_4(m\text{-pba})_4$ is a good example of this phenomenon. The m-pbaH_2 ligand with β-diketone moieties at 120° was expected to give a metal-organic hexagon upon complexation with Cu^{2+}, but ended up with a smaller structure, metal-organic square.

3.4 Experimental Section

General Syntheses Considerations. Reagents were used as received: 4-bromobenzaldehyde dimethyl acetal, 3-(p-methoxyphenyl)propyltrichlorosilane and $CDCl_3$ (Aldrich). Column chromatography was carried out with Sorbent Technologies silica gel (230-450 mesh). NMR spectra were recorded on Bruker (250, 300 or 500 MHz) spectrometers, with $CDCl_3$ as solvent unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl-[15] and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene[12] were prepared by literature methods.

mppSi($C_6H_6CHO)_3$. A solution of n-BuLi/hexanes (1.6 M, 37.5 mL, 60.0 mmol) was added dropwise over 1 h to a solution of 4-bromobenzaldehyde dimethyl acetal (13.8 g, 60.0 mmol, dissolved in 130 mL THF) at –78 °C. After stirring the reaction mixture for 5 h at the same temperature, 3-(p-methoxyphenyl)propyltrichlorosilane (4.25 g, 15.0 mmol) was added and the reaction mixture was allowed to warm to room temperature with constant stirring for about 48 h. It was quenched with about 25 mL of 2 M HCl. The mixture was extracted with ether (2 x 50 mL) and the organic layer dried over Na_2SO_4 and concentrated. The oily residue was refluxed for about 3 h with THF/2 M HCl (1:1, 50 mL, and the refluxed mixture was allowed to cool and added to saturated $NaHCO_3$(aq), ~ 50 mL. The mixture was extracted with ether (2 x 50 mL), and the ether extracts washed with brine, dried (Na_2SO_4), filtered and concentrated. The final product was purified using gradient elution chromatography on silica gel. 1:5, 1:4 and 1:3 ratios of ethyl acetate to hexane solvent mixtures were used as mobile phase. 5.70 g (77% yield) of the product was collected.^{1}H NMR ($CDCl_3$): 3.77 (s, 3H, OMe), 6.91, 7.14 (*AB*, 4H, aromatic C*H*), 1.45-2.62 (m, 6H, Si($CH_2)_3$), 7.73, 7.53 (*AB*, 12H, aromatic C*H*), 10.03 (s, 3H, C*H*O).

mppSi(PhprH)$_3$. $MeOC_6H_4(CH_2)_3Si(C_6H_4CHO)_3$ (2.50 g, 5.07 mmol) was combined with **7** (3.80 g, 16.1 mmol) in the glove box and the mixture was stirred for about 20 h in the presence of 5 mL dichloromethane. It was then refluxed with methanol (13 mL) for 4 h followed by concentration over the rotavap. The crude product was dissolved in methanol and put in the refrigerator overnight. 1.52 g (46% yield) of a white precipitate was collected. Anal. Calcd for $C_{40}H_{48}O_6Si$: C, 73.58; H, 7.41. Found: C, 73.47; H, 7.37. ^{1}H NMR ($CDCl_3$): 3.76 (s, 3H, OMe), 6.81, 7.04 (*AB*, 4H, aromatic C*H*), 1.41-2.62 (m, 6H, Si(CH_2)$_3$), 7.52, 7.19, (*AB*, 12H, aromatic C*H*), 1.02 (t, 18H, CH_2CH$_3$), 2.13 (q, 12H, CH$_2$CH_3), 16.73(s, 3H, O*H*).

Reaction of MeSi(PhprH)$_3$ with [Cu(NH$_3$)$_4$]$^{2+}$(aq): $CuSO_4·5H_2O$ (98 mg, 0.39 mmol) was dissolved in 35 mL of water and concentrated NH_3(aq) was added to the solution until the precipitate that formed with the first few drops disappeared completely and the solution adopted a dark purple color. Then 25 mL of dichloromethane was added into the Cu^{2+}solution followed by dropwise addition of MeSi(PhprH)$_3$ (114 mg, 0.18 mmol) solution in dichloromethane (75 mL). After the reaction mixture was stirred gently for about 6 h, a dark green solution and insoluble green materials were obtained. After filtration and evaporation of the solvent, 80 mg (62% yield) of the soluble material was collected. Anal. Calcd for [(MeSi(phac)$_3$)$_2$Cu$_3$]$_n$: C, 64.47; H, 6.09. Found: C, 64.64; H, 6.00.

Reaction of mppSi(phprH)$_3$ with [Cu(NH$_3$)$_4$]$^{2+}$(aq). $CuSO_4·5H_2O$ (80 mg, 0.33 mmol) was used to prepare [Cu(NH$_3$)$_4$]$^{2+}$ as above. Then 25 mL of dichloromethane was added into the Cu^{2+} solution followed by dropwise addition of mppSi(phprH)$_3$ (150 mg, 0.20 mmol) solution in dichloromethane (75 mL). After the reaction mixture was stirred for about 6 h, a dark green solution and insoluble green materials was obtained. After filtration and evaporation of the solvent, 121 mg (73% yield) of the soluble material was collected. Anal. Calcd for [(mppSi(Phpr)$_3$)$_2$Cu$_3$]$_n$ C, 66.93; H, 6.30. Found: C, 67.20; H, 6.20.

Reaction of MeSi(PhprH)$_3$ with Cu(NO$_3$)$_2$: $Cu(NO_3)_2·3H_2O$ (72 mg, 0.3 mmol) was dissolved in 30 mL of DMF. MeSiPhprH$_3$ (100 mg, 0.15 mmol) dissolved in DMF (30 mL) was added dropwise with stirring. After about 3 h stirring, a green insoluble material (> 97%) was filtered out.

AFM Sample Preparation. Samples for AFM characterizations were prepared by depositing a drop (10 μL) of solution onto a cleaned glass slide or onto freshly cleaved pieces of ruby muscovite mica (S & J Trading Co., NY). The glass surface was cleaned by immersion in piranha solution (sulfuric acid and 30% hydrogen peroxide, 3:1 v/v) for 1 h and dried in air. (Caution is needed when using piranha solution since it is a highly reactive and corrosive mixture, wear appropriate acid-resistant gloves and eye protection.) Solutions of copper tris(β-diketonate) complexes (0.0075 mM in CH_2Cl_2 (Aldrich)) and of Cu_4(*m*-pba)$_4$ (0.001 mM in chloroform (EMD)), were deposited on the substrates and dried for at least 12 h before AFM imaging.

Scanning Probe Microscopy. Surface characterizations were accomplished in ambient conditions using a model 5500 scanning probe microscope equipped with Picoscan v5.3.3 software (Agilent Technologies, Inc., Chandler, AZ). Tapping mode AFM images were acquired at a scan rate of 3.0 nm/s for 256 lines/frame for Figures 3.5-3.7; and Figure 3.9 was obtained with 512 lines/frame. Point probe plus silicon (PPP-NCL) tips from Nanosensors (Neuchatel, Switzerland**)** were used for AFM experiments, with an average force constant of 48 N/m and resonant frequency of 172 kHz.

Image Analysis. Data processing was accomplished using SPIP Version 3.2.2.0 (Image Metrology, Hørsholm, Denmark) and also with Gwyddion (version 2.5) supported by the Czech Metrology Institute **(**http://gwyddion.net/). Estimates of surface coverage were obtained with UTHSCA Image Tool.[16] Images were first converted to grayscale bitmaps and a threshold value was selected visually for conversion to black and white pixels. Relative estimates of surface coverage were obtained from the percentage of colored pixels.

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CHAPTER 4

MICROWAVE-ASSISTED CONVERSION OF MULTIDENTATE ARYL-β-DIKETONES INTO β-KETOENAMINES

4.1 Introduction

β-Ketoenamine based ligands have potential application in the development of porous metal-organic materials. There are more β-diketone based porous metal-organic materials than those based on β-ketoenamines. In the previous chapter, we have observed that copper complexes of the organosilicon β-diketones are not stable for long periods in solution. β-Ketoenamines are similar to β-diketones in that they are chelating and mostly form square planar coordination geometry with Cu^{2+} and Ni^{2+}, but have a different binding site, which might result in better stability for metal complexes. Herein, we report several new β-ketoenamine building blocks prepared using a simple and high yield microwave-assisted procedure from their analogous β-ketoenamines. The geometry of these building blocks is suitable for making porous metal-organic materials.

A simple and high-yield procedure for the preparation of β-ketoenamines was reported by Litvic.[1] According to this procedure, acetylacetone and ammonium carbamate (NH_2COONH_4) were mixed together in methanol at room temperature for about 10 min to yield 95% of the expected product, as shown in Figure 4.1. Using the same procedure, with slight changes in reaction times, they were able to successfully convert several β-keto esters into β-amino-α,β-unsaturated esters.

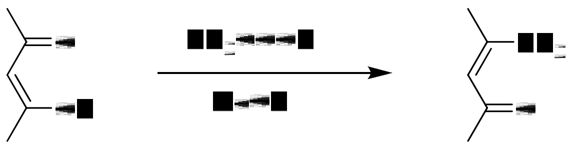


Figure 4.1 Litvic procedure for converting acetylacetone to its ketoenamine.

Conversions of aryl-β-diketones into their corresponding β-ketoenamines, however, seem to occur at much lower yield. For instance, when we attempted to use the Litvic procedure with some of our compounds (*m*-pbaH$_2$ and Me$_2$Si(phacH)$_2$; see Figure 4.2) we obtained less than 5% yield even after several days of refluxing. Therefore, we searched for alternate methods.

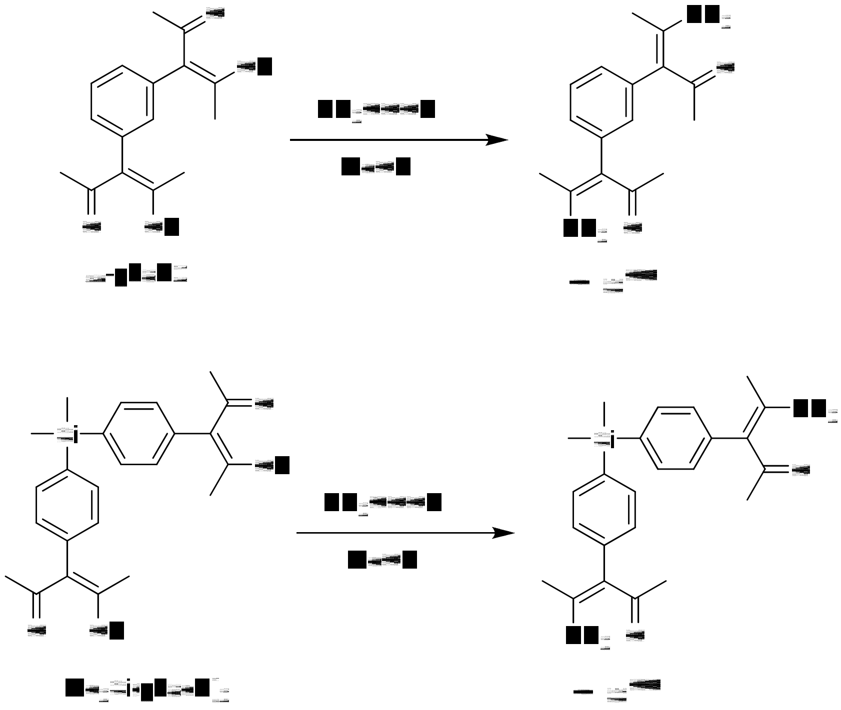


Figure 4.2 Reactions of aromatic β-diketones with ammonium carbamate give only low yields of the corresponding β-ketoenamines.

Previous examples of the conversion of β-diketones into β-ketoenamines have often employed NH$_3$ as a reactant, which needs somewhat special setup and handling procedure. One of these was reported by our group in 1989 in the preparation of 5-*tert*-butyl-*m*-xylenebis(acetylacetone imine), BBIH$_2$, see Figure 4.3.[2]

Microwave-assisted procedures have been reported previously in the conversion of β-diketones to β-ketoenamines.[3,4] For example, Briabante and coworkers converted acetylacetone to ketoenamines using a domestic microwave oven.[3] They dispersed their reactants, acetylacetone and CH$_3$COONH$_4$, in montmorillonite clay K-10 and applied microwave radiation

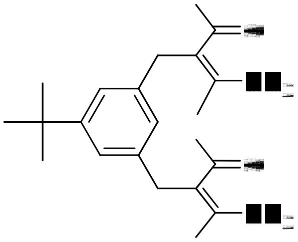
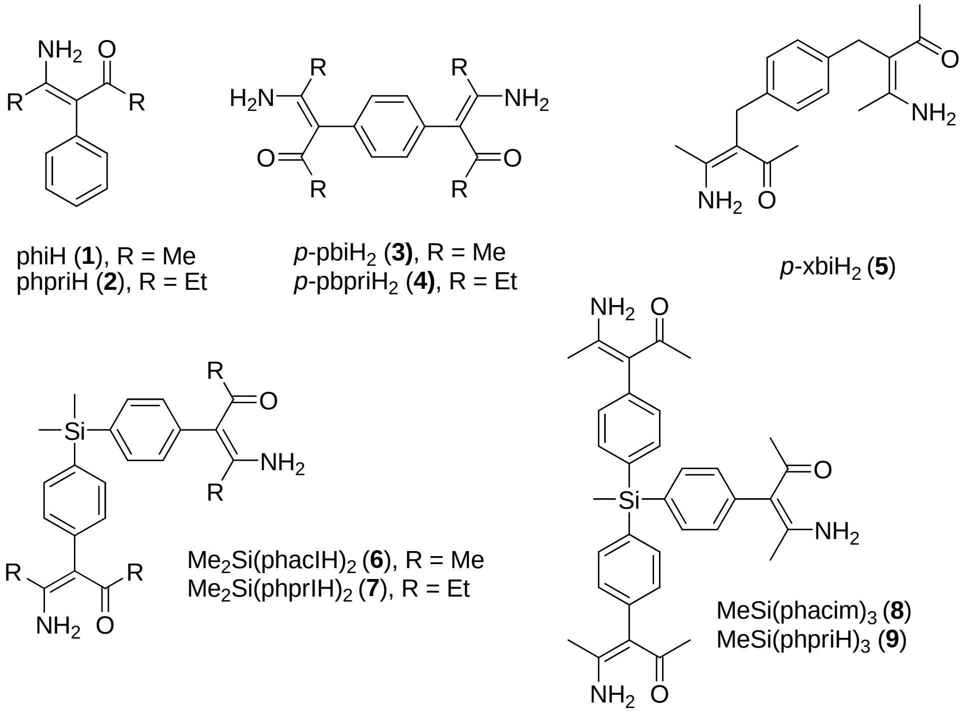


Figure 4.3 5-*tert*-Butyl-*m*-xylenebis(acetylacetone imine), $BBIH_2$.

to get their desired products. Hamelin and coworkers had earlier reported microwave-assisted amine-aldehyde condensation using K-10 and SiO_2 as a solid support with and without a catalyst.[4] Based on these studies, we explored microwave-assisted reactions in our system.

Using a microwave oven that is optimized for synthesis, including the capacity for carrying out reactions in sealed containers that withstand elevated temperatures and pressures, we have successfully prepared several β-ketoenamines shown in Figure 4.4 from the analogous β-diketones.



phiH (**1**), R = Me
phpriH (**2**), R = Et

p-pbiH_2 (**3**), R = Me
p-pbpriH_2 (**4**), R = Et

p-xbiH_2 (**5**)

$Me_2Si(phaclH)_2$ (**6**), R = Me
$Me_2Si(phprlH)_2$ (**7**), R = Et

$MeSi(phacim)_3$ (**8**)
$MeSi(phpriH)_3$ (**9**)

Figure 4.4. Newly synthesized aromatic-based β-ketoenamines

4.2 Discussion

The β-diketone precursors required for these reactions are shown in Figure 4.5. All are reported compounds with the exception of PhprH$_2$(**11**) and *p*-pbprH$_2$ (**13**). They are prepared either from the analogous aldehydes (using the dioxaphospholene method of Ramirez and coworkers;[5] all except **14**) or from 1,4-bis(bromomethyl)benzene.

All of the new ketoenamines (**1-9**) were obtained by reaction of β-diketones with ammonium acetate in toluene under microwave irradiation. The reactions were complete in 45 min or less. The products can easily be identified by ^{1}H NMR: (a) the enol peaks in the starting β-diketones (ca. 16.7 ppm) are replaced by two broad NH peaks (ca. 5.0, 10.6 ppm); and (b) the peaks for the R groups (see Figure 4.6) are split. The β-ketoenamines can be purified by washing or re-crystallizing from toluene, or by column chromatography; they are less soluble in toluene than their analogous β-diketones and are more soluble in methanol.

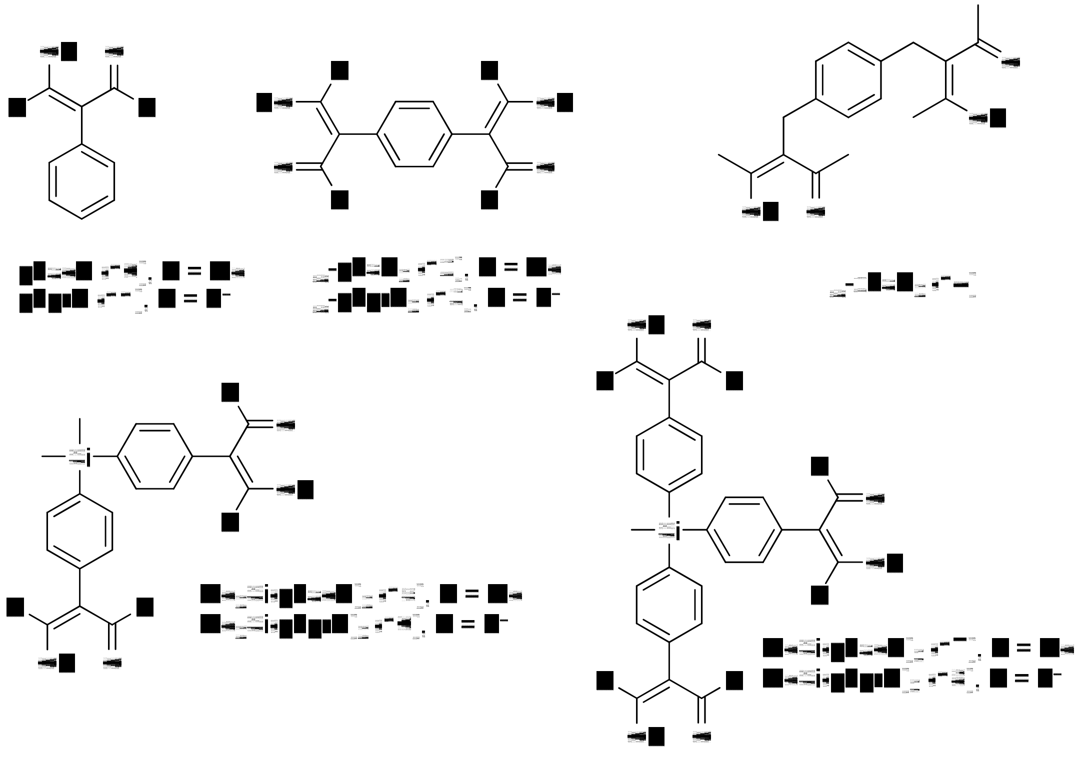


Figure 4.5 β-diketones used as starting materials

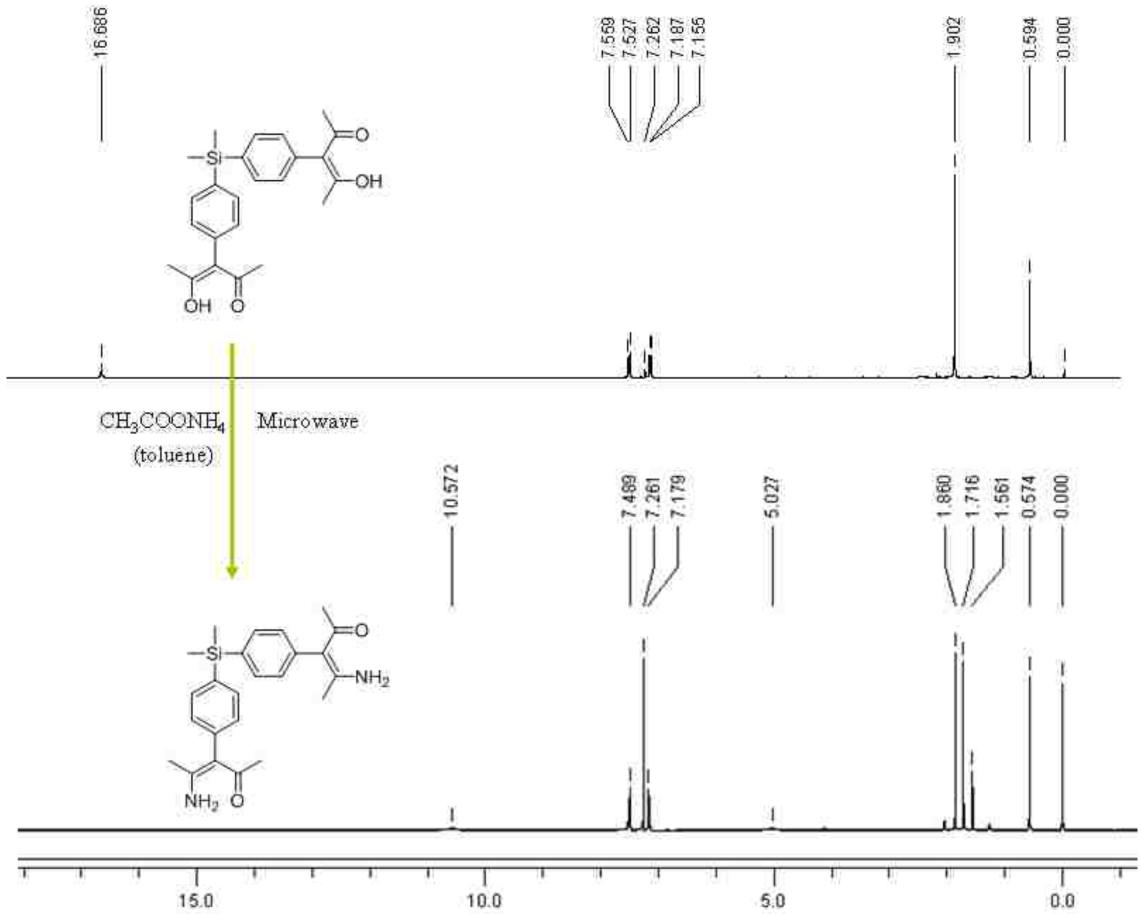


Figure 4.6. ^{1}H NMR spectra illustrating the microwave-assisted conversion of the bis(β-diketone) $Me_2Si(phacH)_2$ (**15**) into the bis(β-ketoenamine) $Me_2Si(phiH)_2$ (**6**).

4.3 Metal-Ligand Reactions

Some metal–β-ketoenamine reactions were examined. Reaction of Cu^{2+} with **9** produced almost exclusively insoluble green materials. The monofunctional ligand **2**, however, formed exclusively olive green soluble species upon reaction with $Cu(NO_3)_2$. Generally, Cu^{2+} complexes of the multifunctional β-ketoenamines are less soluble than their β-diketone counterparts.

4.4 Conclusion

It has been shown that microwave-assisted conversion of β-diketones to their corresponding β-ketoenamines produce a much higher yield as compared to refluxing the reactants in a solvent.

Using the microwave procedure, a higher temperature (~150 °C) and pressure was easily applied to the reaction system. This could possibly be one of the reasons why such a big difference in the yield was observed. Furthermore, the microwave assisted reactions took much shorter time to complete, less than 45 min, as opposed to several days and smaller overall yield in case of refluxing. So, for this particular group of ligands, where the β-diketone moieties are directly bonded to the aromatic ring through α-carbon (except **5**), microwave-assisted conversion has proved to be efficient.

4.5 Experimental

General Considerations. Reagents were used as received: Ammonium acetate (Amresco), benzaldehyde and terephthalaldehyde (Fisher), and $CDCl_3$ (Aldrich). NMR spectra were recorded on Bruker DPX-250 and DPX-400 spectrometers, with $CDCl_3$ as solvent unless otherwise noted. For many of reactions below, no further purification was undergone after extraction and solvent evaporation. The initial yield for those reactions is almost quantitative (> 97%). However, purity of the product is reported. The % purity was estimated by comparing the integration values of the unreacted β-diketone (enol peak) versus the newly formed amine peak. % yield is given instead of % purity for procedures that employed further purification steps (column chromatography or washing), because this resulted in the disappearance of all the unreacted β-diketones.

General procedure for microwave irradiation. For each of the β-ketoenamine syntheses described below (**1-9**), the reactants and solvent were placed in a microwave reaction vessel (or two vessels, if the total volume was >30 mL) with stirring, and the mixture was irradiated at 400 W and 140 °C for the specified length of time. The products were extracted from the vessel using dichloromethane (3×50 mL), and the resulting extract treated further as described in the individual procedures.

PhiH (**1**). Ammonium acetate (0.54 g, 7.0 mmol), phacH (**10**) (0.50 g, 2.8 mmol) and toluene (30 mL); irradiation 30 min. Evaporation of the extract resulted in solid white material, which was further purified by washing with cold toluene to give PhiH (**6**) as a white solid, 0.52 g (95% yield), mp 98-99 °C. ^{1}H NMR: δ 10.54, 5.05 (br, 2H, N*H*$_2$); 7.36-7.16 (m, 5H, aromatic C*H*); 1.85 (s, 3H, C*H*$_3$CO); 1.70 (s, 3H, C*H*$_3$CNH$_2$). ^{13}C NMR: δ 196.8, 159.6, 140.5, 131.9, 128.5, 126.6, 110.2, 29.4, 22.2. Anal. Calcd for $C_{11}H_{13}NO$ (M = 175.10): C, 75.40; H, 7.48; N, 7.99. Found: C, 75.39; H, 7.35; N, 8.13.

PhpriH (**2**). Ammonium acetate (1.54 g, 20.0 mmol), phprH (**11**) (2.0 g, 9.8 mmol) and toluene (60 mL); 45 min. Evaporation of solvent resulted in solid white material, which is 97% pure according to ^{1}H NMR. mp 72-75 °C. ^{1}H NMR: δ 10.66, 5.09 (br, 2H, N*H*$_2$); 7.37-7.16 (m, 5H, aromatic C*H*); 2.07 (q, 2H, CH$_3$C*H*$_2$CO); 1.96 (q, 2H, CH$_3$C*H*$_2$CNH$_2$); 1.00 (t, 3H, C*H*$_3$CH$_2$CO); 0.94 (t, 3H, C*H*$_3$CH$_2$CNH$_2$).

***p*-pbiH$_2$** (**3**). Ammonium acetate (0.69 g, 9.0 mmol), *p*-pbaH$_2$ (**12**) (0.50 g, 1.8 mmol) and toluene (30 mL); irradiation 30 min. The solvent was removed under reduced pressure to give *p*-pbiH$_2$ (**3**) as a white solid, 97% pure, mp > 260 °C. ^{1}H NMR (DMSO): δ 10.38, 7.57 (br, 4H, N*H*$_2$); 7.12 (s, 4H, aromatic C*H*); 1.70 (s, 6H, C*H*$_3$CO); 1.65 (s, 6H, C*H*$_3$CNH$_2$). ^{13}C NMR: δ 193.5, 160.6, 138.7, 131.9, 108.2, 28.7, 20.9.

***p*-pbpriH$_2$** (**4**). Ammonium acetate (0.69 g, 9.0 mmol), *p*-pbprH$_2$ (**13**) (0.50 g, 1.5 mmol) and toluene(30 mL); irradiation 45 min. The solvent was removed under reduced pressure to give *p*-pbpriH$_2$ (**4**) as a white solid, 95% pure, mp 256-257 °C. ^{1}H NMR: δ 10.69, 5.10 (br, 4H, N*H*$_2$); 7.16 (s, 4H, aromatic C*H*); 2.13 (q, 4H, CH$_3$C*H*$_2$CO); 2.01 (q, 4H, CH$_3$C*H*$_2$CNH$_2$); 1.03 (t, 6H,

CH_3CH_2CO); 0.97 (t, 6H, $CH_3CH_2CNH_2$). ^{13}C NMR: δ 200.2, 164.0, 138.1, 132.3, 108.7, 33.9, 27.8, 11.9, 9.1.

***p*-xbiH$_2$** (**5**) Ammonium acetate (0.61 g, 7.9 mmol), *p*-xbaH$_2$ (**14**) (0.40 g, 1.3 mmol) and toluene (30 mL); irradiation 40 min. The solvent was removed under reduced pressure, to give *p*-xbiH$_2$ (**5**) as light yellow solid, 84 % pure. ^{1}H NMR: δ 10.56, 4.98 (br, 4H, NH_2); 7.07 (s, 4H, aromatic CH); 3.63 (s, 4H, aromatic CH_2); 2.06 (s, 6H, CH_3CO); 1.91 (s, 6H, CH_3CNH_2). ^{13}C NMR: δ 197.9, 160.7, 138.7, 127.7, 102.5, 33.7, 29.64, 21.5, 29.4.

$Me_2Si(PhiH)_2$ (**6**). Ammonium acetate (0.94 g, 12.2 mmol), $Me_2Si(phacH)_2$ (**15**) (0.50 g, 1.2 mmol) and toluene (30 mL); irradiation 35 min. Evaporation of solvent resulted in a solid white material, which was further purified by column chromatography (hexane/ethyl acetate, 1:1) to give $Me_2Si(phiH)_2$ (**6**) as a white solid, 0.43 g (85% yield), mp 204-206. ^{1}H NMR: δ 10.57, 5.03 (br, 4H, NH_2); 7.49, 7.18 (*AB*, 8H, aromatic CH); 1.86 (s, 6H, CH_3CO); 1.72 (s, 6H, CH_3CNH_2); 0.57 (s, 6H, $SiCH_3$). ^{13}C NMR: δ 196.8, 159.5, 141.1, 136.2, 134.3, 131.3, 110.1, 29.4, 22.4, −2.1.

$Me_2Si(PhpriH)_2$ (**7**). Ammonium acetate (0.94 g, 12.2 mmol), $Me_2Si(phprH)_2$ (**16**) (0.50 g, 1.0 mmol) and toluene (30 mL); irradiation 40 min. Evaporation of solvent resulted in a light yellow solid material, $Me_2Si(phpriH)_2$ (**7**), 93% pure. mp 150-156. ^{1}H NMR: δ 10.68, 5.14 (br, 4H, NH_2); 7.50, 7.18 (*AB*, 8H, aromatic CH); 2.09 (q, 4H, CH_3CH_2CO); 1.98 (q, 4H, $CH_3CH_2CNH_2$); 1.01 (t, 6H, CH_3CH_2CO); 0.96 (t, 6H, $CH_3CH_2CNH_2$); 0.58 (s, 6H, $SiCH_3$). ^{13}C NMR: δ 200.1, 164.0, 140.4, 136.2, 134.5, 131.5, 108.9, 34.0, 27.7, 12.0, 9.1, −2.1.

$MeSi(PhiH)_3$ (**8**). Ammonium acetate (0.60 g, 7.7 mmol), $MeSi(phacH)_3$(**17**) (0.50 g, 0.90 mmol) and toluene (30 mL); irradiation 40 min. The solvent was evaporated to give $MeSi(phiH)_3$ (**8**) as a white solid, 98% pure. ^{1}H NMR: δ 10.56, 5.04 (br, 6H, NH_2); 7.50, 7.19 (*AB*, 12H, aromatic C*H*); 1.87 (s, 9H, C*H*$_3$CO); 1.73 (s, 9H, C*H*$_3$CNH$_2$); 0.88 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 196.7, 159.5, 141.5, 135.4, 134.2, 131.4, 110.1, 29.4, 22.3, −3.0.

MeSi(PhpriH)$_3$ (9). Ammonium acetate (0.60 g, 7.7 mmol), MeSi(phprH)$_3$(**18**) (0.50 g, 0.8 mmol) and toluene (30 mL); irradiation 40 min. The solvent was evaporated to give MeSi(PhpriH)$_3$ (**9**) as a light yellow solid, 95% pure. ^{1}H NMR: δ 10.52, 5.24 (br, 6H, N*H*$_2$); 7.51, 7.20 (*AB*, 12H, aromatic C*H*); 2.12 (q, 6H, CH$_3$C*H*$_2$CO); 1.99 (q, 6H, CH$_3$C*H*$_2$CNH$_2$); 1.03 (t, 9H, C*H*$_3$CH$_2$CO); 0.93 (t, 9H, C*H*$_3$CH$_2$CNH$_2$); 0.88 (s, 3H, SiC*H*$_3$).

PhprH (**11**). A mixture of benzaldehyde (3.00 g, 28.3 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (7.15 g, 30.0 mmol) was stirred at room temperature under argon. After 24 h, 15 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was purified using column chromatography (hexane/ethyl acetate, 3:1) to give PhprH (**11**) as a brown liquid, 3.93 g (68%). ^{1}H NMR: δ 16.70 (s, 1H, O*H*); 7.42-7.15 (m, 5H, aromatic C*H*); 2.12 (q, 4H, C*H*$_2$CH$_3$); 1.02 (t, 6H, CH$_2$C*H*$_3$). ^{13}C NMR: δ 194.0, 136.3, 131.2, 128.6, 127.3, 113.8, 29.8, 9.4.

***p*-PbprH$_2$** (**13**). A mixture of terephthaldehyde (5.00 g, 37.3 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (18.70 g, 82.1 mmol) was stirred at room temperature under argon. After 24 h, 15 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, re-crystallized from methanol to give p-pbprH$_2$ (**13**) as a white solid, 3.83 g (31%), mp 137-140 °C. ^{1}H NMR: δ 16.77 (s, 2H, O*H*); 7.21 (s, 4H, aromatic C*H*); 2.17 (q, 8H, C*H*$_2$CH$_3$); 1.06 (t, 12H, CH$_2$C*H*$_3$). ^{13}C NMR: δ 194.0, 135.7, 131.6, 113.3, 29.8, 9.5. Anal. Calcd for $C_{20}H_{26}O_4$ (M = 330.18): C, 72.70; H, 7.93. Found: C, 72.91; H, 7.69.

Reaction of PhpriH (2) with Cu(NO$_3$)$_2$. Cu(NO$_3$)$_2$·2H$_2$O (55 mg, 0.25 mmol) and phpriH (100 mg, 0.49 mmol), dissolved in 15 mL of MeOH, were stirred for 3 h.The reaction mixture turned olive green. The solvent was evaporated. Olive green solid (130 mg, ~ 100%) was obtained.

Reaction of MeSi(PhpriH)$_3$ (9) with [Cu(NH$_3$)$_4$]$^{2+}$. CuSO$_4$·5H$_2$O (60 mg, 0.25 mmol) was dissolved in 50 mL of water and concentrated NH$_3$(aq) was added to the solution until the precipitate that formed with the first few drops disappeared completely and the solution adopted a dark purple color. Then 30 mL of dichloromethane was added into the Cu^{2+} solution followed by dropwise addition of **1** (100 mg, 0.15 mmol) solution in dichloromethane (60 mL). After the reaction mixture was stirred gently for about 4 h, a dark green solution obtained. After filtration and evaporation of the solvent, 110 mg (97% yield) of the soluble material was collected. The compound starts to form insoluble precipiates if it is kept in solution for more than a day.

4.6 References

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CHAPTER 5

META-SUBSTITUTED MULTIFUNCTIONAL ORGANOSILICON β-DIKETONES

5.1 Introduction

Synthesis of Si-based multifunctional β-diketones in which the β-diketone moieties are at tetrahedral angles was previously reported.[1] These compounds react with Cu^{2+} to form mixtures of insoluble (likely polymeric) and soluble (molecular) species, as described in chapter 3. We also showed that the polymeric material can reassemble under microwave irradiation to form molecular species, as confirmed by AFM.

Herein, we report the synthesis of geometrically modified new Si-based β-diketone building blocks, Figure 5.1. These new species are expected to form smaller metal-organic porous materials upon reaction with appropriate transition metal ions. The geometric

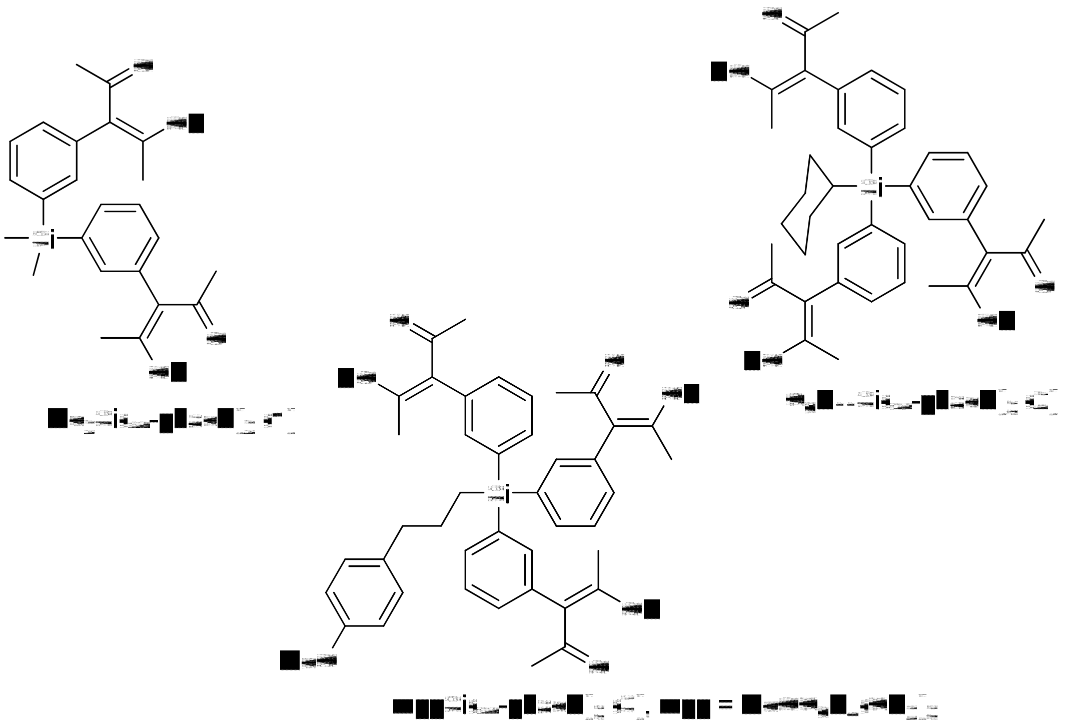
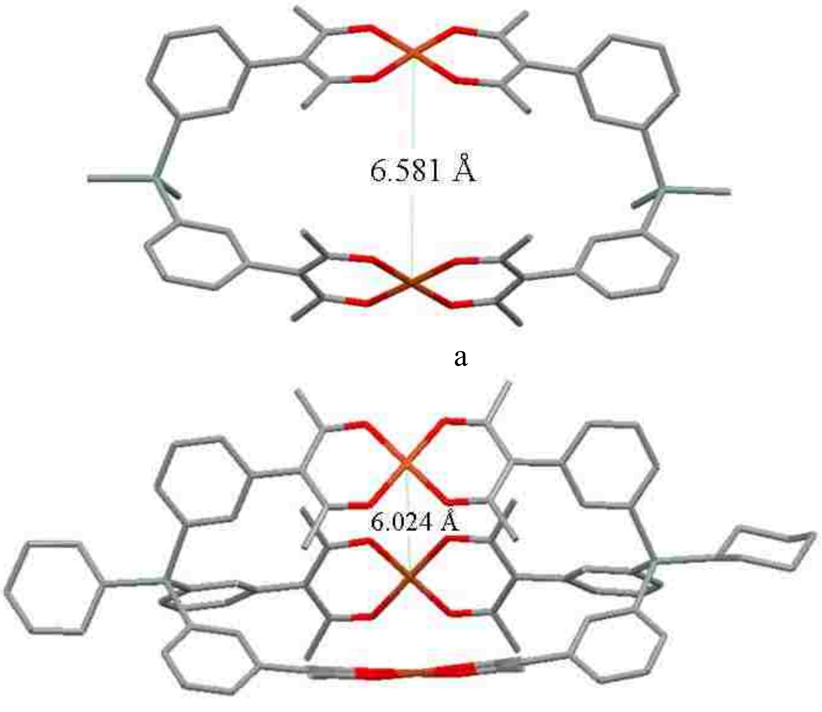


Figure 5.1 *Meta*-substituted organosilicon β-diketones. $Me_2Si(m\text{-phacH})_2$ (**1**), $C_6H_{11}Si(m\text{-phacH})_3$ (**2**) and $mppSi(m\text{-phacH})_3$ (**3**).

modification is placing the β-diketone moiety in the meta position instead of para as in our former ligands.[1] The cyclohexyl substituent on **2** was introduced because it may help promote crystallization of the final metal-organic product. Geometrically, **1** is expected to form a dimer with a pore size of about 6.5 Å (Figure 5.2, a) upon reaction with Cu^{2+} or any other metal ion that forms square planar coordination geometry with β-diketones. **2** and **3** should form a cage M_3L_2 (Figure 5.2**,** b).



a

b

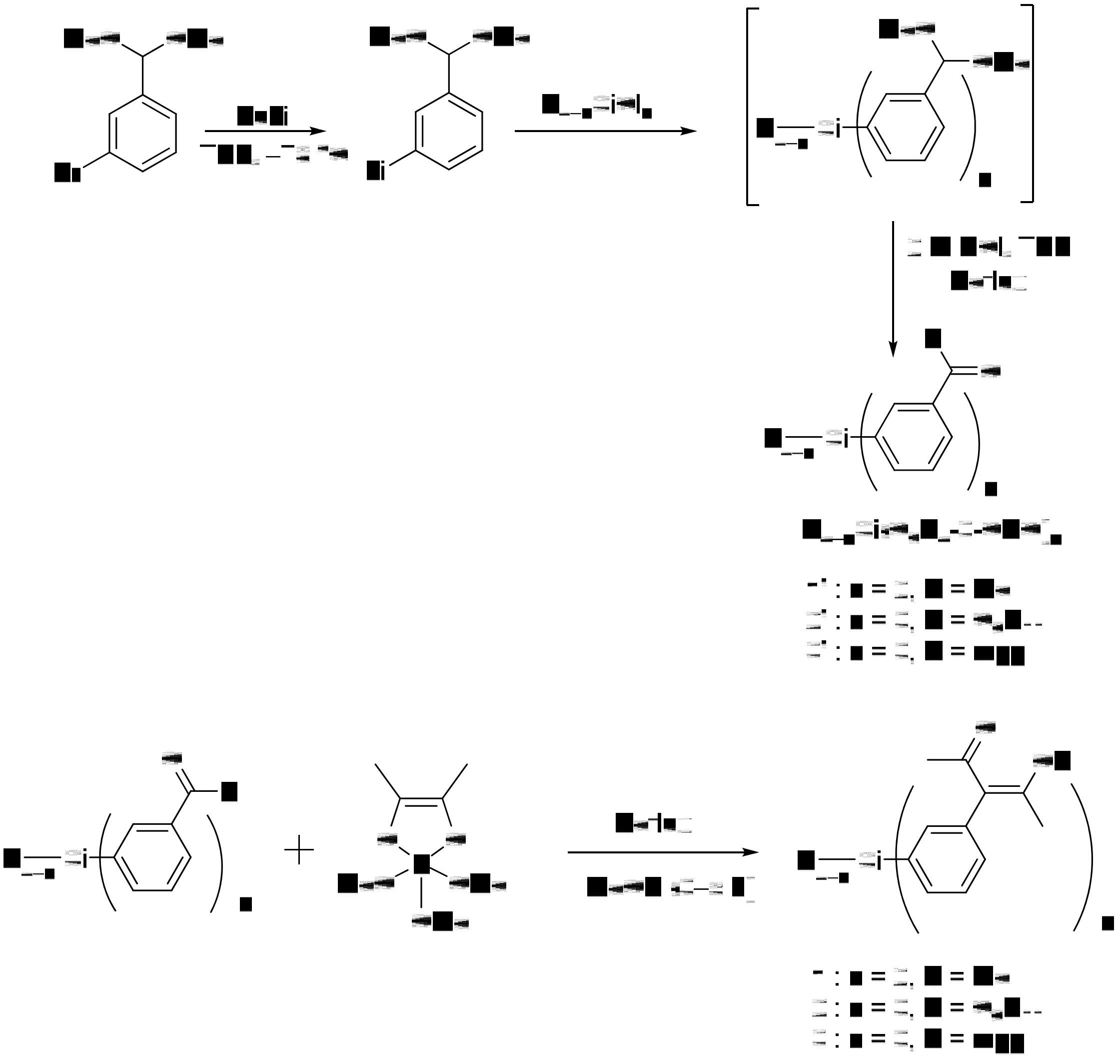
Figure 5.2 Structures (optimized with HyperChem version 7.01) of metal complexes that are predicted to form with the new ligands: (a) $Cu_2(Me_2Si(m\text{-phac})_2)_2$ (b) $Cu_3(C_6H_{11}Si(m\text{-phac})_3)_2$.

5.2 Results and Discussion

Like our previously reported Si-based ligands, these new ligands were also prepared through coupling of aryllithium compounds and chlorosilanes. The difference, however, is that the β-diketone moieties are placed in the meta position instead of para in the aromatic ring. The first step in the process was to make an aldehyde precursor through lithiation of 3-

bromobenzaldehyde diethyl acetal, followed by treatment with Me_2SiCl_2, to produce a bis(acetal) which yields bis(3-formylphenyl)dimethylsilane (**1'**) on hydrolysis. Similar reactions with $C_6H_{11}SiCl_3$ and $mppSiCl_3$ were carried out to produce the other aldehydes. The term "mpp" is used in place of 3-(p-methoxyphenyl)propyl. Different from the previous procedure, the aldehydes were not isolated except in case of **3'**.

Scheme 1. Synthesis of (**1**) $Me_2Si(m\text{-phacH})_2$, (**2**) $C_6H_{11}Si(m\text{-phacH})_3$ and (**3**) $mppSi(m\text{-phacH})_3$.



Attempts to isolate the aldehydes led to extensive oxidation to the carboxylic acids. The second major step was the preparation of the β-diketones by reacting the aldehydes with 2,2,2-

trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene[2] at room temperature under argon to produce dioxaphospholanes, which on refluxing in methanol yield the new β-diketones (**1**, **2**, and **3**).

Single crystals of both **1** and **2** (Figure 5.3 and 5.4) were grown by slow evaporation of solutions in a mixture of ethyl acetate and hexane. The crystal structures (Figure 5.3 and 5.4) contain enol tautomers, in agreement with solution NMR data.

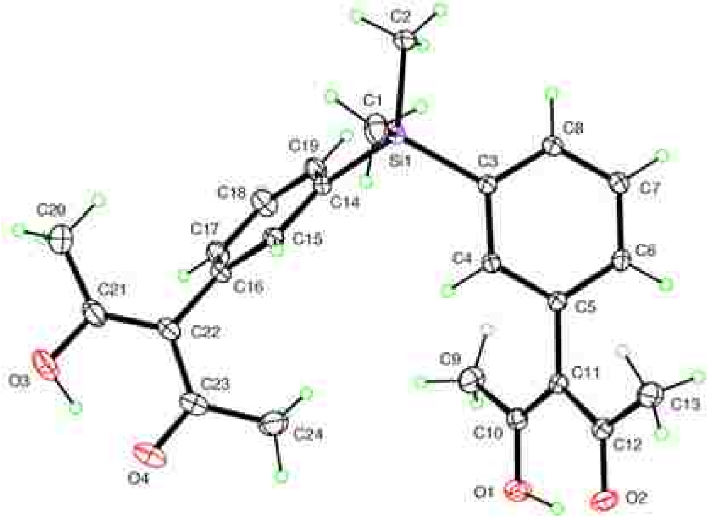


Figure 5.3 Crystal structure of $Me_2Si(m\text{-phacH})_2$.

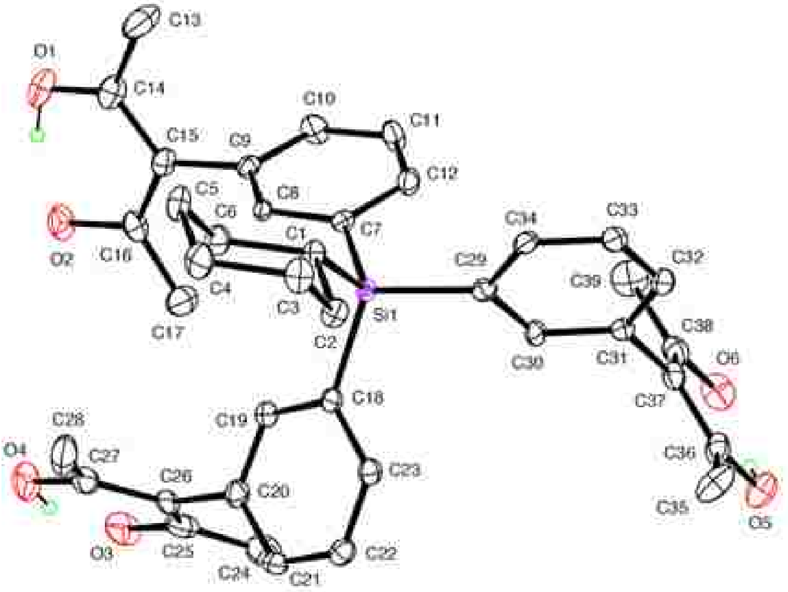


Figure 5.4 Crystal structure of $C_6H_{11}Si(m\text{-phacH})_3$. Enolic hydrogen atoms are showing others are removed for clarity.

5.3 Metal-Ligand Reactions

Reactions of **1**, **2** and **3** with Cu^{2+} were studied. Two-phase reactions of **1**, **2** and **3** (in dichloromethane) and $[Cu(NH_3)_4]^{2+}$(aq) turned out to be very similar to those of the previously reported ligands (para isomers). **2** and **3** formed mostly green insoluble material (~ 80%). The soluble part is not stable in solution. Once the solvent is removed, only a fraction of the soluble material can dissolve back in the solvent. Reaction of **1** with Cu^{2+} forms mostly soluble species (~70%), but this material decomposes in solution in ~24 h. We were unable to grow single crystals from these materials.

5.4 Organic Cages

Preliminarily studies on condensation reactions of **3'** and *p*-phenylenediamine were also done. There are few recent examples in the literature where syntheses of organic cages through aldehyde-amine condensation were reported.[3,4] Theoretically, **3'** is a suitable building block for making an organic cage in the presence of a linear spacer, Figure 5.5.

To that end, condensation reactions of 1,4-phenylenebisamine, a linear spacer, and **3'** were explored under different conditions (refluxing with different solvents, microwave reactions and solvothermal reaction under programmed oven heating). All the attempts produced mostly insoluble material (likely polymeric). Microwave irradiation of these insoluble materials suspended in dichloromethane produced soluble species (~ 5%). ^1H NMR of these soluble species (Figure 5.7) suggests the possible formation of the desired organic cage. Further work is needed to explore conditions under which a higher yield of these species might be generated from the byproducts (polymers).

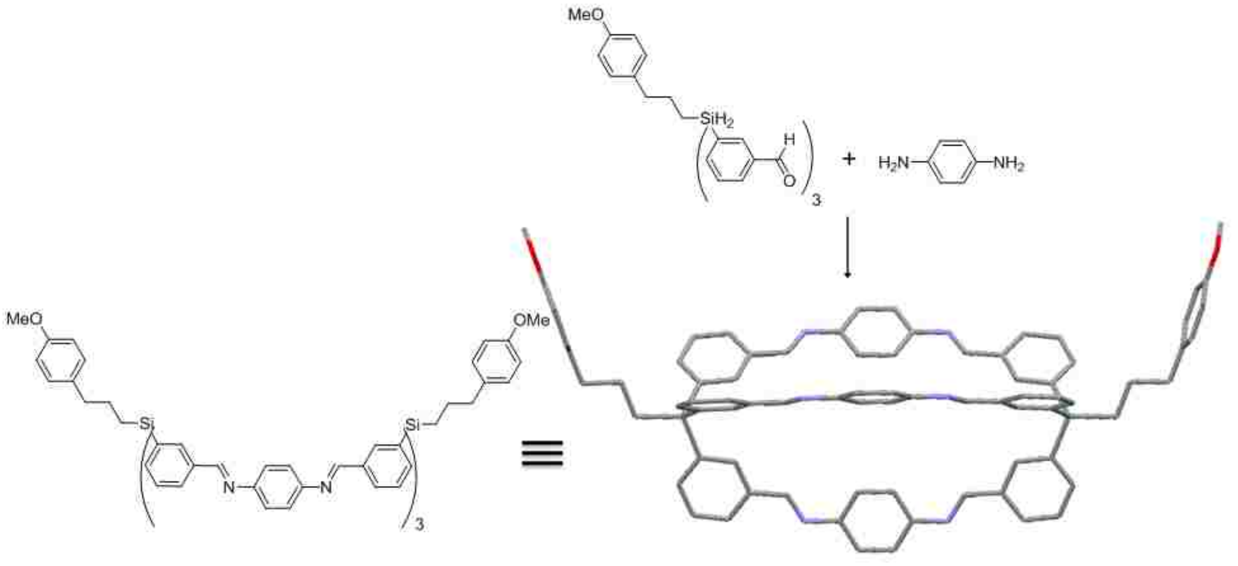


Figure 5.5 Organic cage. HyperChem modeled structure of the expected organic cage that can possibly form from condensation of **3'** and 1,4-phenylenediamine.

5.5 Carboxylic Acid Building Blocks

The carboxylic acid byproducts (Figure 5.6) that are formed by oxidation of the aldehydes in air can be good building blocks for making 3D porous materials. For instance, the bis(carboxylic) ligand may be able to form a cage upon reaction with Cu^{2+}. HyperChem modeling shows that the two adjacent Cu and eight oxygen atoms from the four carboxylates expected to form a "paddlewheel" structure as in copper acetate ($Cu_2(CH_3COO)_4$), Figure 5.8.

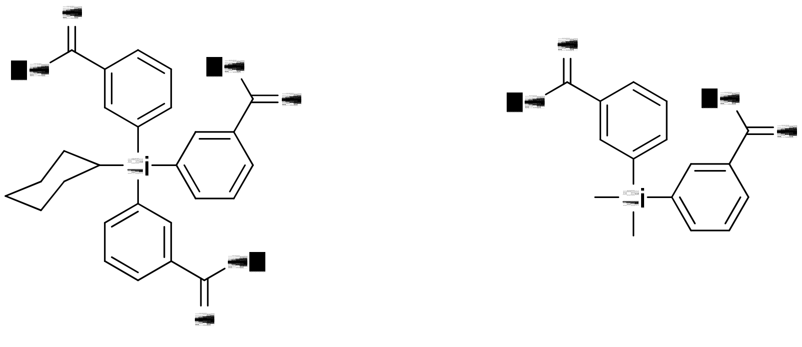


Figure 5.6 Carboxylic acid byproducts: $(C_6H_{11})Si(m\text{-}C_6H_4COOH)_3$ and $Me_2Si(m\text{-}C_6H_4COOH)_2$

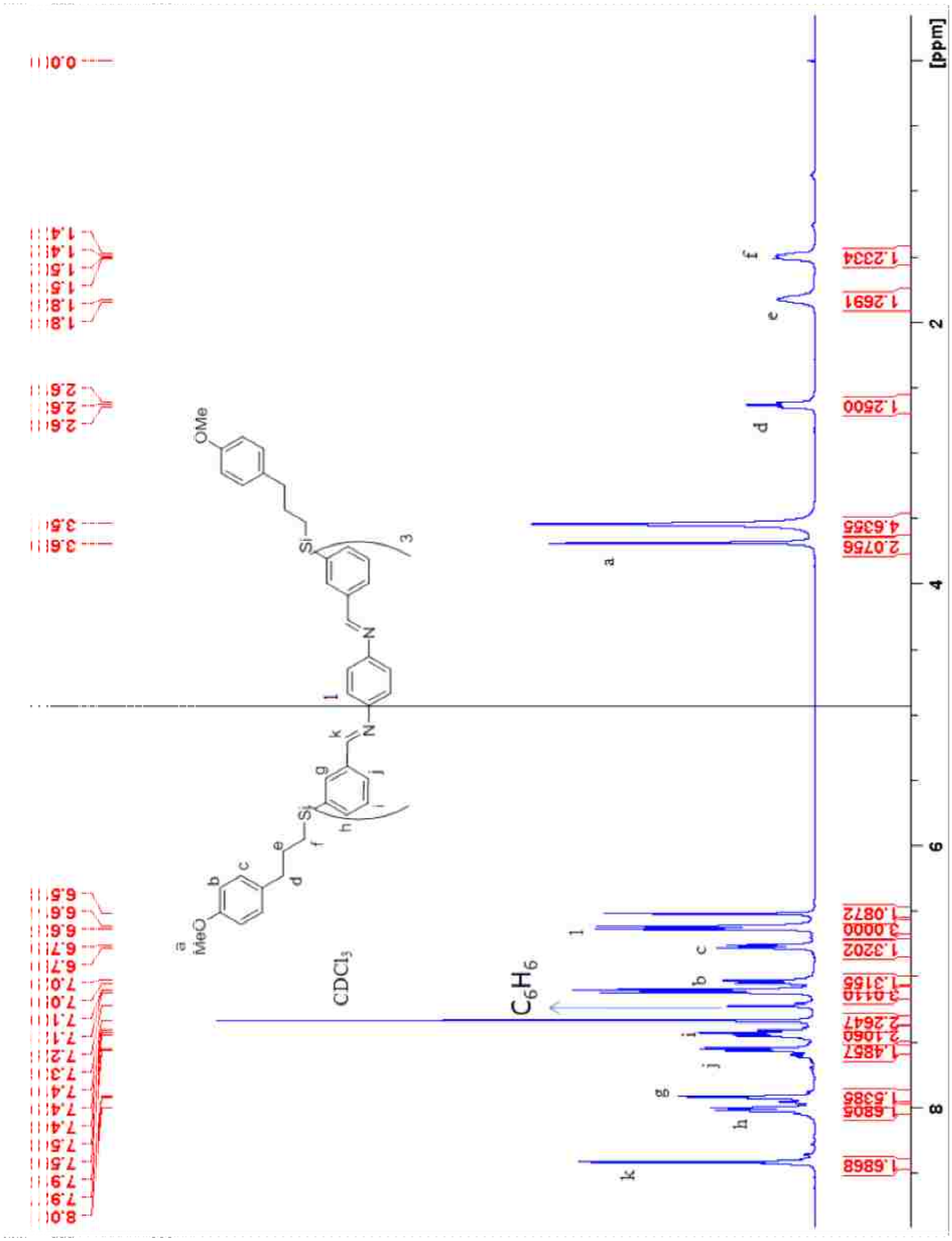


Figure 5.7 ^{1}HNMR spectrum of the soluble material derived from microwave irradiation of the **3'** and 1,4-phenylenediamine polymer.

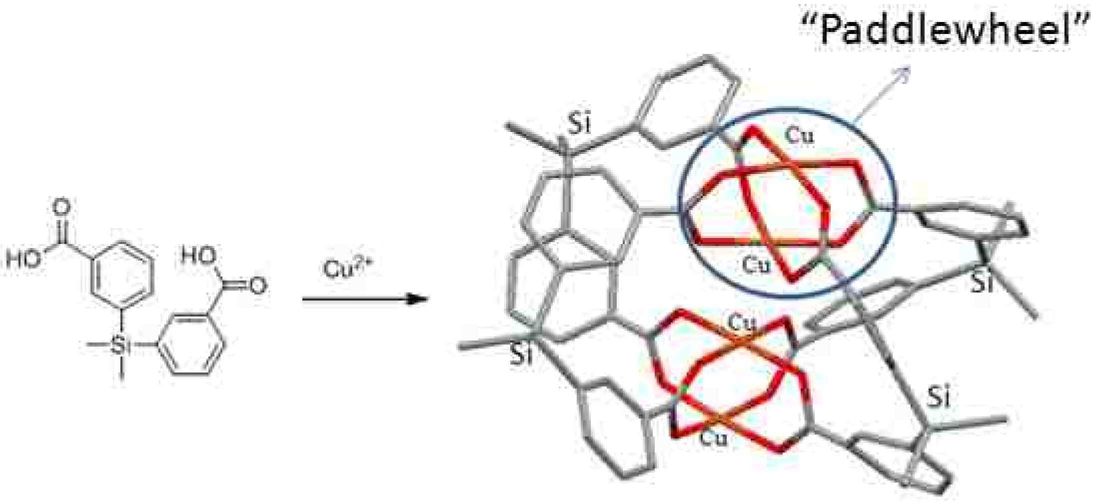


Figure 5.8 HyperChem optimized structure of the expected metal-organic product $Cu_4(Me_2Si(m\text{-}C_6H_4COO)_2)_4$.

Solvothermal test reactions between the carboxylic acids and Cu^{2+} were carried out. The normal procedure involved heating both the ligand and metal salt, $Cu(NO_3)_2$, in DMSO or DMF inside a tightly capped 20 mL vial for about 24 h at 100 °C and cooling it down slowly at a rate of 0.1 °C/min. All the attempted experiments produced green insoluble materials. Experimental procedures attempted so far have not been successful in producing single crystals of the metal complexes of the carboxylic acids. The insoluble products might be polymers and it might be interesting to explore the possibility of generating molecular species from these materials by microwave irradiation as in chapter 3.

5.6 Experimental

General Considerations. Reagents were used as received: 3-bromobenzaldehyde diethyl acetal and $CDCl_3$ (Aldrich), dimethyldichlorosilane, cyclohexyltrichlorosilane and 3-(*p*-methoxyphenyl)propyltrichlorosilane (Gelest Inc.). Column chromatography was carried out with Sorbent Technologies silica gel (230−450 mesh). NMR spectra were recorded on Bruker (250, or 400 MHz) spectrometers, with $CDCl_3$ as solvent unless otherwise noted. 2,2,2-trimethoxy-4,5-

dimethyl-1,3,2-dioxaphospholene was prepared by the literature method.[2] Bis(3-formylphenyl)dimethylsilane ($Me_2Si(C_6H_4$-3-$CHO)_2$) (**1**), an intermediate in the synthesis of Me_2Si(*m*-phacH)$_2$, was prepared according to a literature method.[5]

Me_2Si(*m*-phacH)$_2$ (1). 3-Bromobenzaldehyde dimethyl acetal (10.40 g, 40.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 25.0 mL, 40.0 mmol) was added at −78 °C over 40 min. After stirring for an additional 4 h at −78 °C, dimethyl-dichlorosilane (2.00 g, 15.5 mmol) was slowly added to the above suspension. The reaction mixture was stirred for an additional 2 h at −78 °C and then overnight while it returned to room temperature. The reaction mixture was quenched with 2 M HCl (30 mL) and extracted with ether (3 × 50 mL). The ether solution was washed with brine, dried over $MgSO_4$, and evaporated to give the oily intermediate acetal, $Me_2Si(C_6H_4$-3-$CH(OCH_3)_2)_2$, which was hydrolyzed without purification. The oil was dissolved in 100 mL of THF/2 M HCl (1:1 v/v) and the mixture refluxed under N_2 for 2 h. After cooling to room temperature, the reaction mixture was poured into saturated $NaHCO_3$(aq) (50 mL) and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure, giving an oil which was then treated with excess 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (7.50 g, 35.7 mmol) and stirred at room temperature under argon. After 18 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate, 5:1) to give a white solid (Me_2Si(*m*-phacH)$_2$), 0.65 g (10%), mp 106-112 °C. ^{1}H NMR: δ 16.76 (s, 2H, O*H*); 7.49-7.20 (m, 8H, aromatic C*H*); 1.88 (s, 12H, CH_3); 0.59 (s, 6H, $SiCH_3$). ^{13}C NMR: δ 191.0, 138.6, 136.5, 136.0, 133.0, 131.8, 128.2, 115.1, 24.2, −2.6.

$C_6H_{11}Si(\textit{m}\text{-}phacH)_3$ (2). 3-Bromobenzaldehyde dimethyl acetal (12.71 g, 49.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 31.0 mL, 49.6 mmol) was added at −78 °C over 40 min. After stirring for an additional 4 h at −78 °C, cyclohexyltrichlorosilane (2.83 g, 13.0 mmol) was slowly added to the above suspension. The reaction mixture was stirred for an additional 2 h at −78 °C and then overnight while it returned to room temperature. The reaction mixture was quenched with 2 M HCl (30 mL) and extracted with ether (3 × 50 mL). The ether solution was washed with brine, dried over $MgSO_4$, and evaporated to give the oily intermediate acetal $(C_6H_{11})Si(3\text{-}C_6H_4CH(OCH_3)_2)_3$, which was hydrolyzed without purification. The oil was dissolved in 100 mL of THF/2 M HCl (1:1 v/v) and the mixture refluxed under N_2 for 2 h. After cooling to room temperature, the reaction mixture was poured into saturated $NaHCO_3$(aq) (50 mL) and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure, giving an oil which was then treated with excess 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (17.78 g, 78.0 mmol) and stirred at room temperature under argon. After 18 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **2** as a white solid, 5.10 g (62%), mp 150-151 °C. ^1H NMR: δ 16.60 (s, 3H, O*H*); 7.51-7.22 (m, 12H, aromatic C*H*); 1.94-1.17 (m, 11H, C_6H_{11}) 1.84 (s, 18H, C*H*$_3$). ^{13}C NMR: δ 190.7, 138.5, 136.4, 135.0, 134.9, 132.2, 128.5, 115.2, 28.3, 28.0, 26.9, 23.7.

$mppSi(C_6H_4\text{-}3\text{-}CHO)_3$ (3'). 3-Bromobenzaldehyde dimethyl acetal (13.8 g, 60.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. *n*-BuLi solution in hexane (1.6 M, 37.5 mL, 60.0 mmol) was added at −78 °C over 40 min. After stirring for an additional 90 min at −78 °C, methyltrichlorosilane (3.46 mL, 15.0 mmol) was slowly added to the above suspension. The reaction mixture was stirred for an additional 2 h at −78 °C and then overnight while it returned to room temperature. The reaction mixture was quenched with 2 M HCl (60 mL) and extracted with ether (3 × 50 mL). The ether solution was washed with brine, dried over $MgSO_4$, and evaporated to give the oily intermediate acetal, mppSi(C_6H_4-3-CH(OCH_3)$_2$)$_3$, which was hydrolyzed without purification. The oil was dissolved in 100 mL of THF/2 M HCl (1:1 v/v) and the mixture refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured into saturated $NaHCO_3$ (aq) (50 mL) and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure, giving oil. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give mppSi(C_6H_4-3-CHO)$_3$ as a colorless liquid, 5.20 g (70%). ^{1}H NMR: δ 9.98 (s, 3H, C*H*O); 7.96-6.80, (m, 16H, aromatic C*H*); 3.78 (s, 3H, OC*H*$_3$); 2.68-1.48, (m, 6H, Si(C*H*$_2$)$_3$). ^{13}C NMR: δ 192.2, 157.6, 141.1, 136.5, 135.7, 134.8, 133.3, 131.0, 129.3, 128.8, 113.6, 55.0, 38.1, 25.5, 11.5.

mppSi(*m*-phacH)$_3$ (3). A mixture of mppSi(*m*-C_6H_4CHO)$_3$ (2.60 g, 5.3 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (4.1 g, 18.0 mmol) was stirred at room temperature under argon. After 18 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (hexane/ethyl acetate, 3:1) to give **3** as a colorless liquid, 2.0 g (54%). ^{1}H NMR: δ 16.51 (s, 3H, O*H*); 7.42-6.77 (m, 16H, aromatic C*H*); 2.61 (t, 2H, C*H*$_2$CH$_2$CH$_2$Si) 1.75 (m, 2H, CH$_2$C*H*$_2$CH$_2$Si); 1.42 (t, 2H, CH$_2$CH$_2$C*H*$_2$Si).

Me$_2$Si(*m*-C$_6$H$_6$COOH)$_2$. This compound was made accidentally when the oily Me$_2$Si(*m*-phCHO)$_2$ was exposed to air for several hours.

Reaction of Me_2Si(*m*-phacH)$_2$ (1) and $[Cu(NH_3)_4]^{2+}$. $CuSO_4{\cdot}5H_2O$ (67 mg, 0.27 mmol) was dissolved in 50 mL of water and concentrated NH_3(aq) was added to the solution until the precipitate that formed with the first few drops disappeared completely and the solution adopted a dark purple color. Then 30 mL of dichloromethane was added into the Cu^{2+}solution followed by dropwise addition of **1** (100 mg, 0.25 mmol) solution in dichloromethane (60 mL). After the reaction mixture was stirred gently for about 4 h, the organic layer was a dark green solution. This was separated filtered, dried over Mg_2SO_4, evaporated to give 110 mg (96% yield) of soluble material. The compound starts to form insoluble precipiates if it is kept in solution for more than a day.

Reaction of $C_6H_{11}Si$(*m*-phacH)$_3$ (2) and $[Cu(NH_3)_4]^{2+}$. $CuSO_4{\cdot}5H_2O$ (60 mg, 0.25 mmol) was used to prepare $[Cu(NH_3)_4]^{2+}$ as above. Then 25 mL of dichloromethane was added into the Cu^{2+}solution followed by dropwise addition of **2** (100 mg, 0.16 mmol) solution in dichloromethane (60 mL). After the reaction mixture was stirred for about 6 h, an insoluble green material (81 mg, 70% yield) was filtered out. A green soluble material (32 mg, 28% yield) was obtained after evaporation of the solvent from the filtrate. The soluble material starts to form an insoluble precipatates if it is kept in solution for more than a day.

Reaction of mppSi(*m*-phacH)$_3$ (3) and $[Cu(NH_3)_4]^{2+}$. $CuSO_4{\cdot}5H_2O$ (60 mg, 0.25 mmol) was used to prepare $[Cu(NH_3)_4]^{2+}$ as above. Then 25 mL of dichloromethane was added into the Cu^{2+}solution followed by dropwise addition of **3** (100 mg, 0.15 mmol) solution in dichloromethane (60 mL). After the reaction mixture was stirred for about 6 h, an insoluble green material (84 mg, 74% yield) was filtered out. A green soluble material (20 mg, 17% yield) was obtained after evaporation of the filtrate. The soluble material starts to form insoluble materials if it is kept in solution for more than a day.

Reaction of $Me_2Si(C_6H_4\text{-3-COOH})_2$ with $Cu(NO_3)_2$. $Cu(NO_3)_2 \cdot 2H_2O$ (30 mg, 0.13 mmol) and $Me_2Si(C_6H_4\text{-3-}CH_3COOH)_2$ (30 mg, 0.10 mmol) were dissolved in a 6 mL, 1:1 mixture of DMSO and DMF in a 20 mL vial. The reaction mixture was heated for 23 h at 100 °C and cooled down at a rate of 0.1 °C/min to 30 °C. A blue green precipitate (~ 90%) and light green solution were obtained.

Reaction of $mppSi(C_6H_4\text{-3-CHO})_3$ (3') and 1,4-phenylenediamine. 3' (500 mg, 1.0 mmol) and 1,4-phenyldiamine (162 mg, 1.5 mmol), dissolved in 50 mL of benzene with a catalytic amount of acetic acid, were refluxed overnight. A rubber-like light yellow material (600 mg, 98% yield) was obtained. The yellow material (200 mg), suspended in benzene (50 mL), was irradiated by microwave for 30 m at 150 °C. A yellow solution was obtained. A yellow viscous material (~ 15 mg, 5%) was obtained after evaporation of the solvent. ^1H NMR is shown in Figure 5.6, page 67.

5.7 References

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CHAPTER 6

THIOPHENE BASED β-DIKETONATE BUILDING BLOCKS

6.1 Introduction

The ability to place multiple metal binding sites at various angles and distances on organic compounds is one of the key reasons why there are so many different porous metal-organic structures available today. The availability of many metal ions makes the library of porous metal-organic materials even richer. Sometimes, different reaction conditions produce different metal-organic structures even when the starting materials are the same.

Bis(β-diketones), whose diketones are at 120° were synthesized in our group and their copper complex are metal-organic squares (Figure 6.1). With 120°, they were expected to form metal-organic hexagons.[1] In the previous chapters, we have also discussed bifunctional organosilicon ligands whose diketone sites are placed at approximately tetrahedral angles.[2] However, their copper complexes are not stable in solution and thus, were not well characterized.

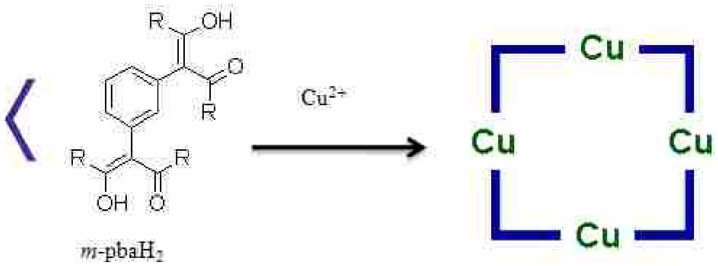


Figure 6.1 Reaction of *m*-pbaH_2 with Cu^{2+} generates a metal-organic square, Cu_4(*m*-pba)$_4$, where the ligand occupies the corners of the square.

Herein, we report the synthesis of a new thiophene based building blocks having two β-diketone sites at about 145°, Figure 6.2. This building block is expected to form a bigger metal-organic polygon upon reaction with Cu^{2+} or other metal ions that form square planar coordination geometry with β-diketones.

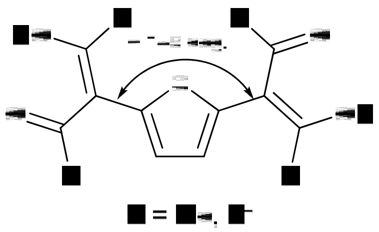


Figure 6.2 New thiophene based β-diketones. ThacH_2, R = Me and thprH_2, R = Et.

According to HyperChem modeling (Figure 6.3), a metal-organic decamer, consisting of ten ligands and ten metal ions, would have approximately the expected angles between its thiophene molecules. The expected structure of $Cu_{10}(thac)_{10}$ is shown in Figure 6.3.

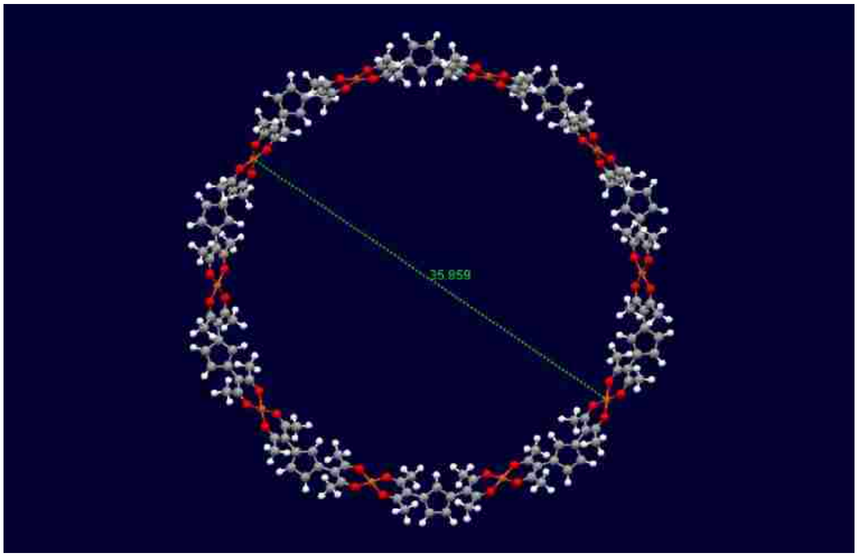


Figure 6.3 HyperChem geometry optimization of one possible thiophene based diketonate-Cu complex, namely metal-organic decamer ($Cu_{10}(thac)_{10}$). This large metallocycle is expected to have a diameter of ca. 3.6 nm.

Again, the angle afforded by this species is similar to that of imidazolates, which were shown to form porous solids with zeolite-type topologies upon reaction with Zn or Co.[3-6] We expect that these ligands might also form a zeolite-type structure upon reaction with bigger metal ions (such as Zr and Sn) that are capable of coordinating to four β-diketonates at a tetrahedral geometry.

6.2 Results and Discussion

The new thiophene based β-diketones were synthesized from their aldehyde precursors and phospholene using the Ramirez's method (Scheme 1).[7] Unlike our previously mentioned building blocks, these compounds needed from a week to ten days of stirring for the completion of the reaction. Normally phospholene-aldehyde reactions are complete overnight and they normally require refluxing in methanol for the formation of diketones from the intermediates. $ThacH_2$ and $thprH_2$, however, don't need methanol refluxing. The enol peak appears as stirring continues (Figure 6.4).

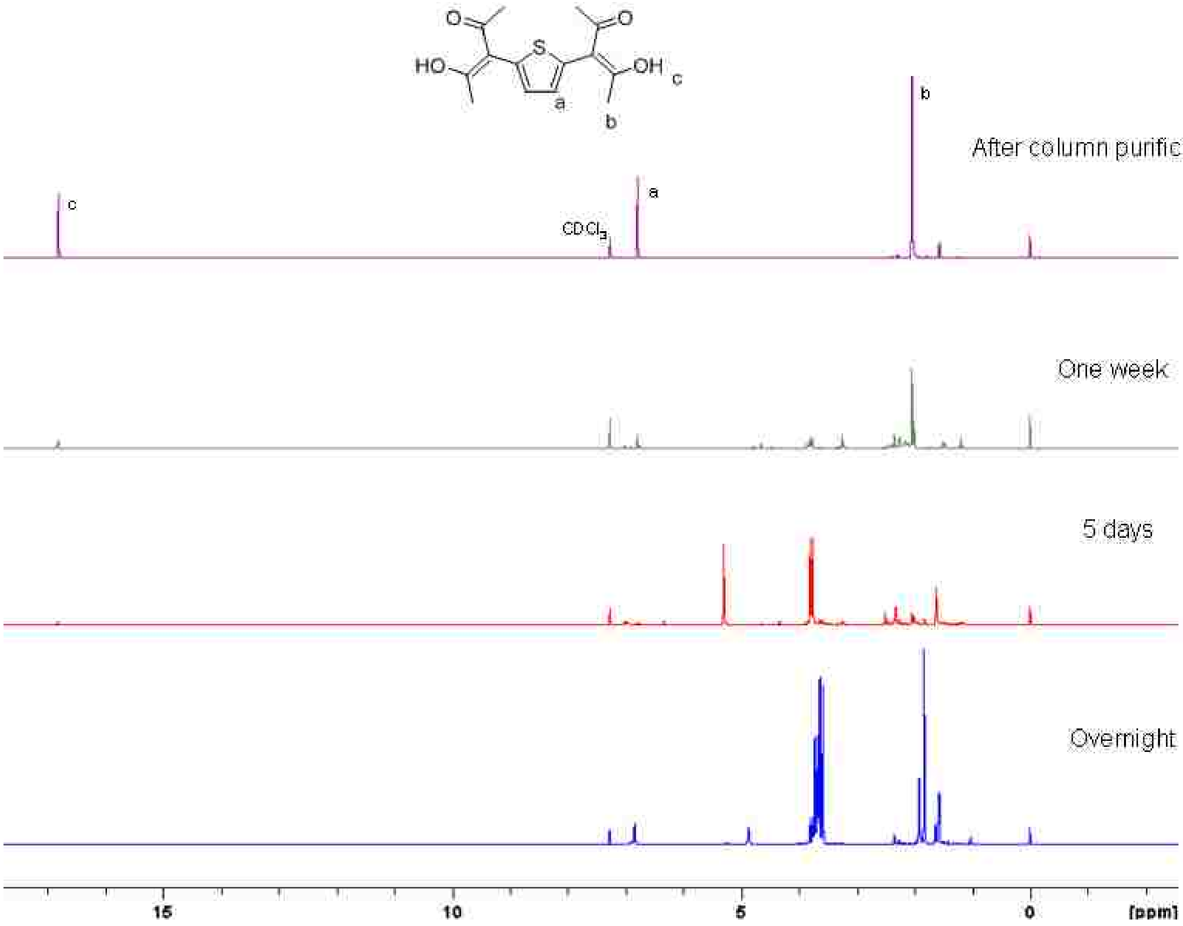
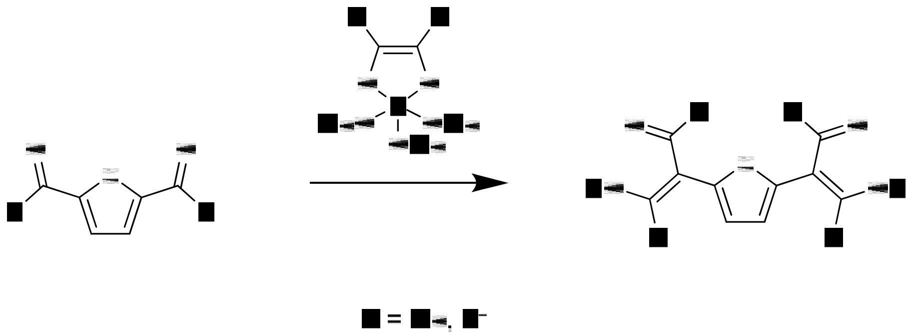


Figure 6.4 ^{1}HNMR spectra of reaction mixture of phospholene and 2,5-thiophenedicarboxaldehyde vs. time.

Single crystals of thacH$_2$ were obtained by slow evaporation of an ethyl acetate-hexanes solution, see drawing in Figure 6.5. In agreement with the results observed in ^{1}HNMR measurements in solution, the ligand is also in its enol form in the solid state.

Scheme 1. ThacH$_2$ and thprH$_2$ were prepared using Ramirez method from the 2,5-thiophenedicarboxaldehyde.[7]



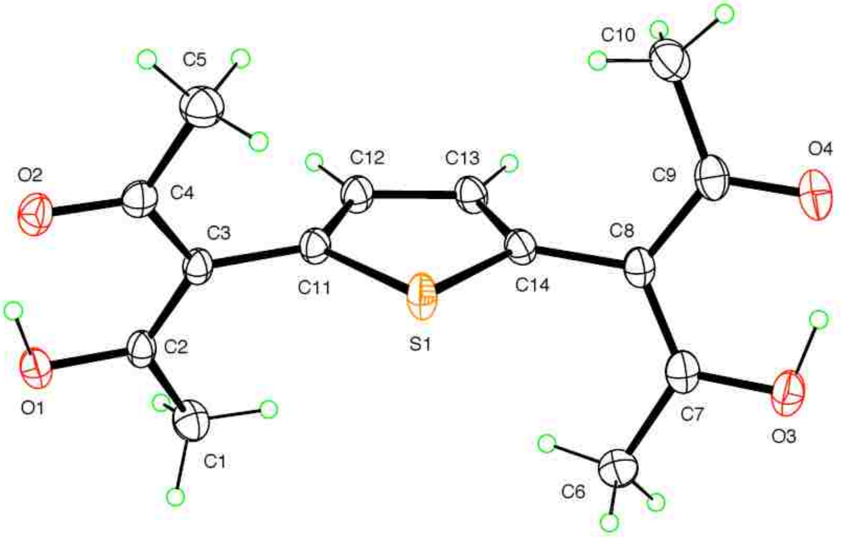


Figure 6.5. Crystal structure of thacH$_2$.

Reactions of these ligands with Cu^{2+} tend to form a green solution which turns yellowish within ca. 1h. The initial green color is similar to that observed in many other Cu(II) β-diketonate complexes; the change to yellowish may indicate an undesirable reaction involving the thiophene S atoms that leads to decomposition.

Solvothermal reactions of these ligands with Zr^{4+} were also attempted. Zr^{4+} was chosen because of its ability to bind to four β-diketones.[7-9] Such coordination is necessary to build a zeolite-type metal-organic framework using β-diketone ligands. Since **1** and **2** have two β-diketone mioties that are ~145° (like that of Si-O-Si bond in zeolites) and if these mioties form a tetrahedral coordination around Zr (like O around Si in zeolites) it is likely that the final framework will have a zeolitic topology. With this understanding, the reaction was carried out.

Both the ligand and $ZrCl_4$ were dissolved in DMF (12 mL) in a programmable oven; the temperature gradients employed are shown in Figure 6.6. The purpose of the slow heating was to encourage the growth of crystals. Such techniques are common in reactions of carboxylate ligands and metal ions..

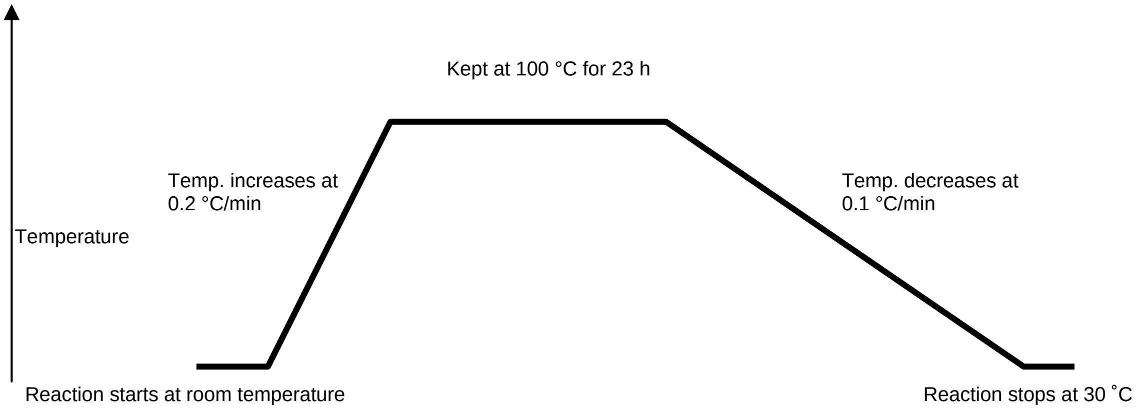


Figure 6.6. Temperature profile used for solvothermal reactions of $thacH_2$ (or $thprH_2$) with $ZrCl_4$ in DMF.

All of the reactions produced an insoluble materials, which is expected since our product is polymeric. However, none of the efforts to grow crystals of metal complexes of these new species has been successful. We believe further exploration of this chemistry is needed. These ligands might result in a very interesting new class of metal-organic zeolites.

6.3 Experimental

General Considerations. Reagents were used as received: 2,5-thiophenedicarboxaldehyde (Aldrich). Column chromatography was carried out with Sorbent Technologies silica gel (230-450 mesh). NMR spectra were recorded on Bruker (250, or 400 MHz) with $CDCl_3$ as solvent unless otherwise noted. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl- and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene were prepared by literature methods.[1,10]

ThacH$_2$ (**1**) A mixture of 2,5-thiophenedicarboxaldehyde (0.59 g, 4.2 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (1.96 g, 9.3 mmol) dissolved in dichloro-methane (5 mL) were stirred at room temperature under argon for one week. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give **1** as a white solid, 0.51 g (43%), mp 120-121 °C. ^1H NMR: δ 16.80 (s, 2H, O*H*); 6.79 (s, 2H, C*H*); 2.04 (s, 12H, CH_3). ^{13}C NMR: δ 192.3, 139.7, 129.5, 106.8, 23.9.

ThprH$_2$ (**2**) A mixture of 2,5-thiophenedicarboxaldehyde (0.50 g, 3.6 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (2.0 g, 8.4 mmol) dissolved in dichloro-methane (5 mL) were stirred at room temperature under argon for 11 days. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give **2** as a brown gel, 0.27 g (23%). ^1H NMR: δ 16.80 (s, 2H, O*H*); 6.77 (s, 2H, C*H*); 2.32 (q, 8H, CH_2CH_3); 1.10 (t, 12H, CH_3). ^{13}C NMR: δ 195.7, 139.2, 129.5, 105.4, 29.8, 9.8

Reaction of ThacH$_2$ (1) with $[Cu(NH_3)_4]^{2+}$. $CuSO_4 \cdot 5H_2O$ (75 mg, 0.30 mmol) was dissolved in 20 mL of water and concentrated $NH_3(aq)$ was added to the solution until the precipitate that formed with the first few drops disappeared completely and the solution adopted a dark purple color. Then 30 mL of dichloromethane was added into the Cu^{2+}solution followed by dropwise addition of **1** (75 mg, 0.27 mmol) solution in dichloromethane (30 mL) with stirring. A green solution which turns yellowish within ca. 1h was observed.

Reaction of ThacH$_2$ (1) with [Cu(NH$_3$)$_4$]$^{2+}$ ZrCl$_4$ (20 mg, 0.054 mmol) and thacH$_2$ (30 mg, 0.11 mmol) were dissolved DMF(10 mL), in a 20 mL vial. The reaction mixture was heated for 23 h at 100 °C and cooled down at a rate of 0.1 °C/min to 30 °C. A yellow precipitate (~ 100%) was obtained.

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CHAPTER 7

CONCLUSION AND PROSPECTS

7.1 Introduction

This dissertation focuses on the synthesis of multifunctional β-diketone and β-ketoenamine ligands and their reaction with metal ions, mainly Cu^{2+}. Copper(II) was our first metal ion choice because of the coordinatively unsaturated square planar center that it can form upon reaction with β-diketones. Furthermore, the chelating nature of β-diketones provides an opportunity for building robust materials due to the strong metal-ligand bonds. The new ligands that are reported in this dissertation are geometrically suitable building blocks for making porous metal-organic materials. Most of our metal-ligand studies focused on preparation of metal-organic polyhedra (MOPs) from silicon-based tris(β-diketone) and Cu^{2+}. MOPs are a class of metal-organic materials with enormous potential application in gas storage, separation, catalysis, drug delivery and host-guest chemistry. To date, very few (less than five) β-diketone based MOPs are known.

7.2 Synthesis of Ligands

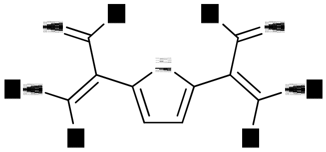
The number of ligand groups, β-diketones or β-ketoenamines in our case, and the angle between these sites play a great role in determining the topology of the porous material to be built. In this dissertation, several new β-diketone and β-ketoenamine-based ligands are reported, as shown in figure 7.1: organosilicon-based bi-, tri-, and tetradentate ligands (**1**-**7**) with β-diketone groups at about 109.5° (tetrahedral angle); their modified version (**8**-**10**), where the β-diketones are placed meta to the Si in the aromatic ring; and thiophene based bidentate ligands (**11** and **12**) where the β-diketones are at about 145°.

a)

1 (n = 2, R = R’ = Me) **2** (n = 2, R = Me, R’ = Et)
3 (n = 3, R = R’ = Me) **4** (n = 3, R = Me, R’ = Et)
5 (n = 4, R’ = Me) **6** (n = 4, R’ = Et)
7 (n = 3, R = $(CH_2)_3C_6H_4OMe$, R’ = Me)

b)

8 (n = 2, R = Me, R’ = Et
9 (n = 3, R = cyclohexyl, R’ = Me)
10 (n = 3, R = $(CH_2)_3C_6H_4OMe$, R’= Et)



c)

11) R=Me **12**) R=Et

Figure 7.1 Multifunctional β-diketones reported in this dissertation, using a) p-substituted organosilicon, b) m-substituted organosilicon, and c) thiophene linkages.

The aryl-β-diketones were prepared using Ramirez’s method from the corresponding aldehydes. β-ketoenamine-based ligands were also explored. These ligands were prepared from their analogous β-diketones and ammonium acetate using microwave-irradiation.

Based on our results with the microwave-assisted procedures, we highly recommend, if possible, that synthetic Chemists to try microwave assisted heating for low-yield or slow reactions. We have observed, both in the hydrolysis step of β-diketone preparation and in the conversion of β-diketones to β-ketoenamines, that microwave-assisted heating resulted in a purer product in a much shorter reaction time compared to refluxing.

Using the procedure that was employed to prepare the organosilicon β-diketone ligands, a similar family of pyridine-based ligands may be prepared as shown in Figure 7.2.[1] Pyridine based ligands are attractive in that they can undergo self correction during metal-organic self assembly process due the relatively weaker metal-ligand bond.

Figure 7.2 Possible organosilicon-based pyridine ligands that can be made using procedures employed in this dissertation.

7.3 Metal-Ligand Reactions

Reactions of organosilicon tris(β-diketone)s with Cu^{2+} were explored quite intensively. These reactions are expected to form β-diketone-based MOPs, which have been much less explored than β-diketone-based MOFs and metal-organic polygons (or rings). Two phase reactions of compound **3** (in dichloromethane) and $[Cu(NH_3)_4]^{2+}$(aq) produce soluble (~20%) and insoluble material (80%) under mild stirring. The insoluble material can be obtained almost quantitatively under vigorous stirring. Based on this observation, we suggest that stirring rate may be important in determining product yield, especially in two-phase metal-ligand reactions.

The depth of a hole made on a monolayer surface of the soluble material, according to AFM studies, turned out to be about 5 nm, which matches the expected size of a metal-organic dodecahedron according to HyperChem. This indicates that we are generating a metal-organic dodecahedron as we proposed. However, a major problem exists with all the copper complexes of the β-diketone ligands reported here: the materials are not stable for extended periods in solution. This makes their characterization and purification difficult, and it is a challenge that needs to be addressed in the future.

A metal-organic dodecahedron that might be relatively more stable in solution might be prepared using a commercially available bis(terpyridine) ligand and an organosilicon-based tris(pyridine), as shown in Figure 7.3. This will be similar to Peter Stang's metal-organic dodecahedron,[2] but with coordinatively unsaturated metal sites for binding guest species.

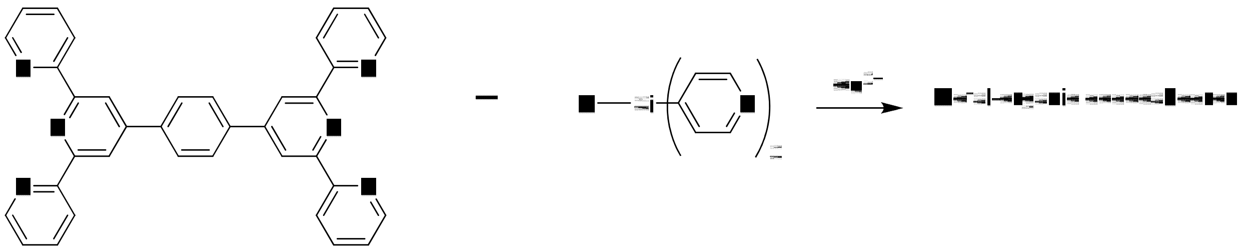


Figure 7.3 Reaction of bis(terpyridine)**,** Si-tris(pyridine), and Cu^{2+} is expected to form a metal-organic dodecahedron.

It is worth noting that stability in solution may not be a requirement at the application level depending on the purpose for which these materials are intended to be used. For instance, a material doesn't have to be stable in solution or even soluble to be used for gas storage or separation purposes. Therefore, the capacity of the porous materials reported here to store hydrogen gas or other gases such as methane and carbon dioxide should be explored in the future. Furthermore, even though the insoluble materials are not well characterized, they are likely to be porous metal-organic polymers. Their gas storage capacity should be explored in the future.

When the insoluble material is refluxed in an organic solvent for several hours, it generates a green soluble material (5%). AFM images of these species reveal molecules that are 5 nm in size, which matches the expected size of the metal-organic dodecahedron. The percent yield of the soluble species that are generated from the insoluble materials is increased to 15% using microwave irradiation. This indicates that β-diketone-based metal-organic materials can undergo self-correction of their structure under refluxing or microwave-assisted heating conditions. Self-correction of structure is highly desirable in supramolecular self-assembly process to generate a final product of a specific structure.

Reactions of metal ions with other ligands were also studied. The organosilicon bis(β-diketones) **1** and **2** produce soluble copper complexes. However, we have not been able to characterize these species well, and they decompose over time in solution. Organosilicon tetrakis(β-diketones), such as **5** and **6**, were expected to form MOFs upon reaction with Cu^{2+}. Experimentally, these reactions produce only insoluble material, as expected for MOFs. Generally, copper complexes of the β-ketoenamine ligands studied here are less soluble than those of the analogous β-diketones.

Reaction of thiophene based β-diketone ligands with copper(II) generates green soluble species that quickly turn to yellow, possibly due to decomposition. Square planar copper complexes of β-diketones are normally green in color. The decomposition could be due to some reactions between the copper and sulfur in the thiophene. This challenge might be avoided if the thiophene moiety were oxidized to a sulfone, as shown in figure 7.3.

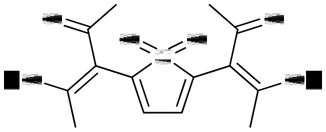


Figure 7.4 Thiophene-*S,S*-dioxide-based bis(β-diketone).

Preliminarily studies on reactions of Zr^{+4} with the thiophene based ligand **11** were also done. These reactions produce an insoluble material. No crystal of these species has been grown yet. Reactions of Zr^{+4} or Sn^{+4} with **11** and **12** might result in a very interesting new class of metal-organic zeolites. Yaghi and co-workers recently reported a zeolitic imidazolate framework (ZIF) that is capable of storing 83 times its volume in CO_2 at 1 atm and 273 K.[3] We believe further exploration of this chemistry is worthy due to potential applications in gas storage.

7.4 Conclusion

This dissertation reports the synthesis of several new multifunctional organosilicon and thiophene based β-diketones. A simple and high yielding microwave-assisted conversion of aromatic based β-diketones to their analogous β-ketoenamines is also reported. Based on AFM studies, a new β-diketone based metal-organic dodecahdrom was made. Furthermore, it was shown that β-diketone based metal-organic materials can undergo self-correction of structure under refluxing or microwave irradiation. Gas storage capacity of both the metal-organic dodecahedron and the polymeric byproducts should be explored in the future.

7.5 References

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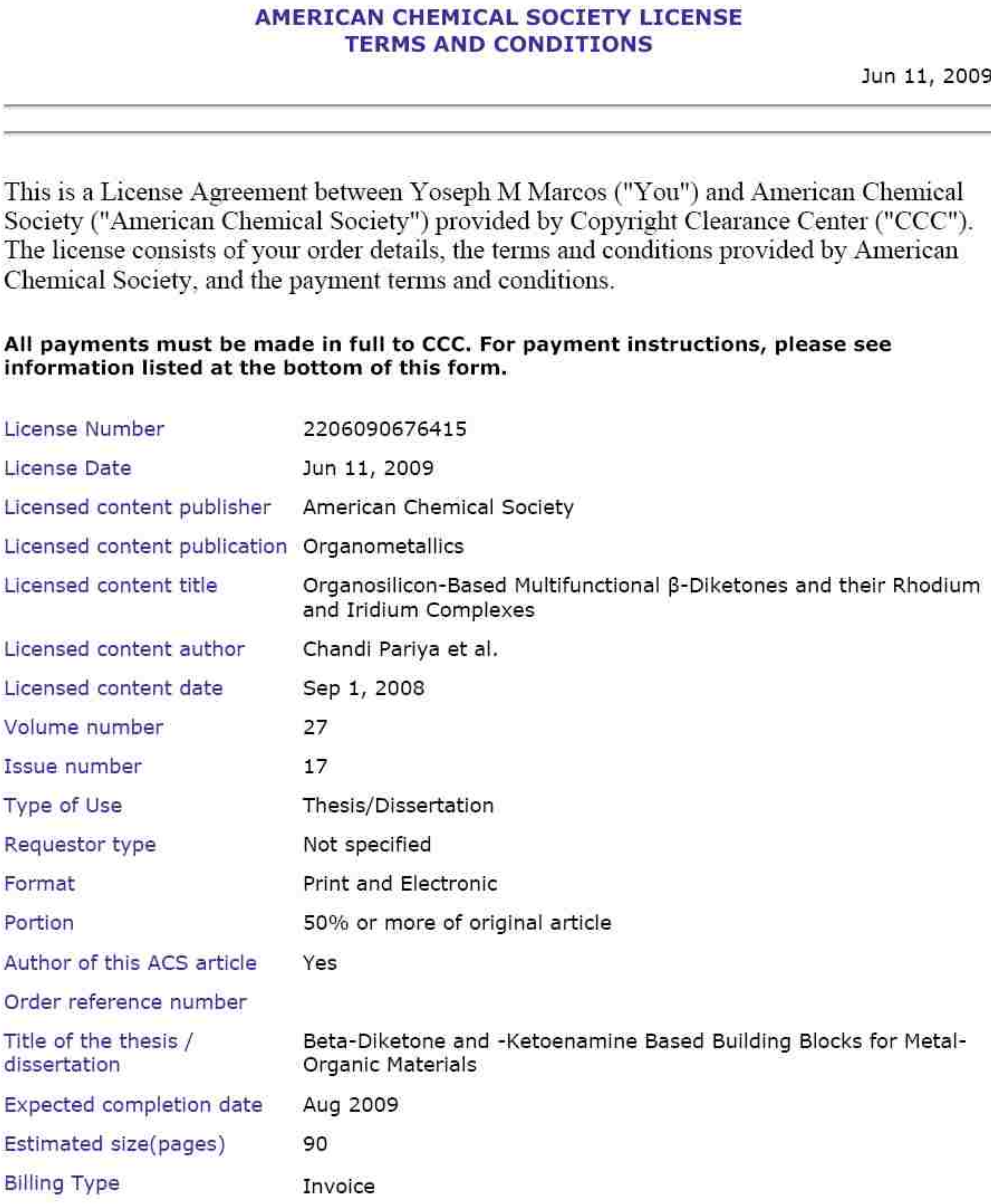

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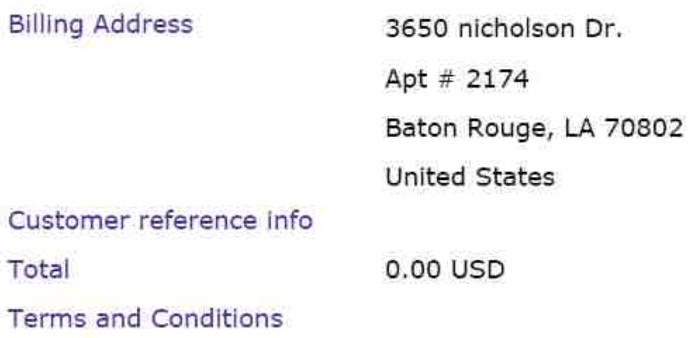

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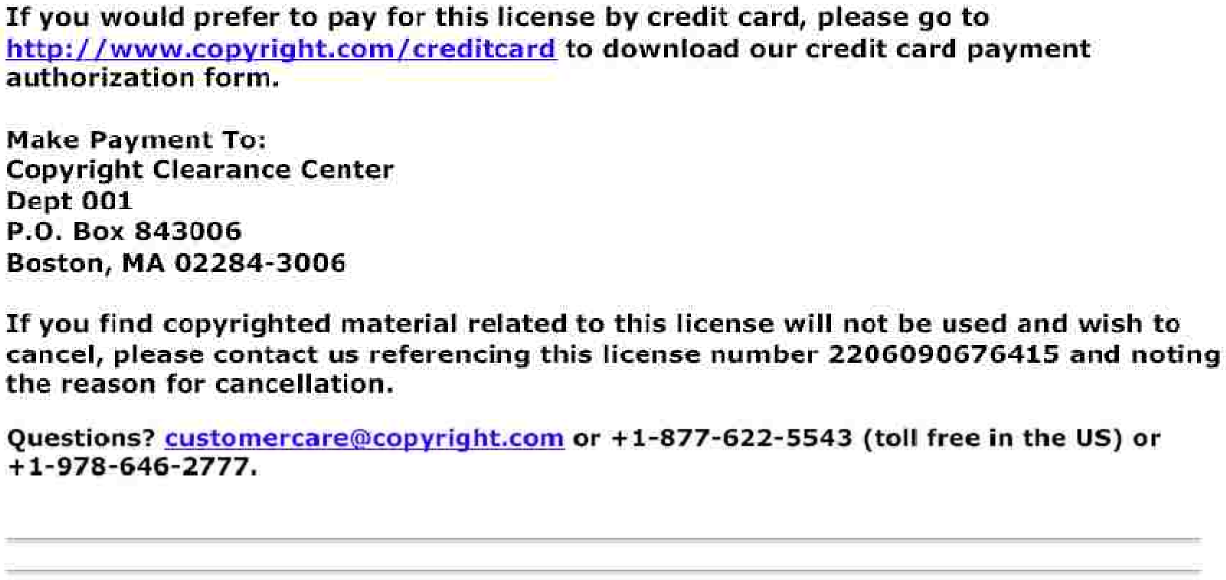

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