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A One-Pot Diastereoselective Self Assembly of C-Stereogenic Copper(I) Diphosphine Clusters

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P ligands, copper, cluster compounds, self-assembly, chirality

C-chirogenic diphosphine-based clusters with 8-membered "chair-like" $\text{Cu}_4\text{Cl}_4\text{L}_2$ and 12-membered "drum-like" $\text{Cu}_6\text{Cl}_6\text{L}_3$ (L = diphosphine) frameworks were prepared in one-pot from chiral diphosphines which were synthesized *via* the double hydrophosphination reaction in excellent enantio- and diastereo-selectivity. Excellent control over the final molecular architecture of the cluster (drum *vs* chair) could be achieved by the judicious selection of the source of the copper atoms employed in the synthetic protocol. Each cluster has been characterized by single crystal X-ray crystallography, ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The generated clusters have been found to exhibit catalytic activity in the hydroboration reaction of α,β -unsaturated enones with excellent yields albeit with low enantioselectivity.

INTRODUCTION

Copper is arguably one of the most inexpensive and abundant metal that is extremely versatile from a coordination standpoint, with its complexes readily accessing the coordination numbers

of two to six¹ dependant on factors such as the valency of the metal center and nature of the ligands. This attribute, together with its coordinative lability, have led to the widespread application of copper complexes in areas such as organic synthesis,² homogeneous catalysis³ and in the generation of metal-organic coordination complexes.⁴ In recent years, copper clusters have been widely studied due to their unusual yet interesting structural, magnetic and photophysical properties,⁵ for example Che⁶ discovered a highly luminescent Cu(I) diphosphine cluster that is strongly luminescent with a good quantum yield. Some other work involving copper clusters include their applications in optics,^{5m} catalysis⁷ and biological applications such as enzyme modeling.^{4d, 5h-i} The coordination driven self assembly reactions often result in unusual architectures such as helicates, tetrahedra, mesocates and many others.⁸ However majority of such structures involve polydentate ligands that contains nitrogen and/or oxygen donor atoms.⁹ Although phosphines have been widely employed in coordination chemistry in view of their unique electronic and stereochemical properties, their involvement in copper clusters remains limited possibly due to their irregular shapes and bulky substituents which often lead to more complex geometries and lower probability of forming well-defined structures.¹⁰ Copper clusters with cubane type, $\text{Cu}_4\text{X}_4\text{L}_4$ (X = halogen, L = ligand) and "drum-like" $\text{Cu}_6\text{X}_6\text{L}_6$ cores have been reported since the 1960's (Figure 1).¹¹ However a lack of applications as well as challenges faced in the synthesis of such compounds¹² led to a decline in their interest until the catalytic properties of such clusters were recognized.^{7c-d, 13} Copper clusters bearing phosphine ligands of the type PR_3 (R = Et, NMe_2 , Ph, *tert*-butyl),¹⁴ PPh_2R^1 (R^1 = Me, cyclohexyl)^{15a-b} and diphosphine ligands^{5g, 6, 15c-e} have been described in literature, showing a growing interest towards copper-phosphine clusters. Synthesis of chiral phosphine ligands involving catalytic protocols are however very limited,¹⁶ and they usually rely on expensive optically pure phosphines¹⁷ or tedious

resolution processes.¹⁸ Furthermore, most phosphines are sensitive to oxygen and therefore difficult to handle, which indirectly affects the overall efficiency of these often step-wise protocols. The development of an efficient and facile one-pot methodology which provides access to enantioenriched phosphines and their subsequent coordination to form copper clusters along with the ability to control their architecture is therefore of paramount importance in order to generate a viable molecular library for these types of compounds.

Figure 1. Structural representations of cubane unit Cu_4X_4 (1) and "drum-like" unit Cu_6X_6 (2) in copper clusters (Ligands are omitted for clarity).

Herein, we report the one-pot syntheses of chiral 12 membered "drum-like" and 8 membered "chair like" copper clusters bearing bridging diphosphine ligands with two C-stereogenic centers. By utilizing the newly developed synthetic method, we have successfully circumvented the challenges that may be faced in the possible synthesis of copper-phosphine clusters such as (i) the need for prior synthesis of air and moisture-sensitive tertiary phosphines (or the protection and subsequent de-protection of their adducts) and their resolution and/or purification, as well as (ii) the tedious separation techniques that are necessary for the isolation of the final complexes. In order to demonstrate the versatility of the method, we repeated the same experimental procedures on a variety of diphosphine ligands, and in each instance, we obtained our desired product in 72-89% isolated yield. Several X-ray quality crystals of the products were obtained and the solid state structures studied in greater detail along with a preliminary study conducted to

gauge the potential of the generated cluster in asymmetric hydroboration reaction of α,β -unsaturated enones.

RESULTS AND DISCUSSION

Synthesis of Optically Active Copper-Phosphine Clusters

We had recently developed a new method for the generation of optically pure diphosphine ligands utilizing a highly efficient palladacycle catalyzed asymmetric hydrophosphination reaction (Scheme 1).¹⁹ The enantiomeric excess (*ee*) and diastereomeric excess (*de*) obtained were determined to be >98 % and >94% respectively, thus providing facile access to optically pure diphosphines such as ligands **5** and **6**. The availability of these *tertiary* diphosphine skeletal frameworks prompted the current study to explore the possibility of the direct addition of CuCl into the crude diphosphines without the need for prior purification or optical resolution of the isomers. It needs to be highlighted that the excellent stereocontrol achieved coupled with low Pd catalyst loading and the capability to directly generate *tertiary* diphosphines (as opposed to oxide/sulfide or borane adducts which entail additional protection, de-protection sequence) allows a hitherto unexplored one-pot sequence. Upon refluxing the diphosphines with CuCl in acetone for 10 hours, the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR for the complete conversion of the diphosphine ligand. Upon completion the crude reaction mixture was directly loaded onto silica gel columns and afforded white solids of their respective copper-phosphine clusters **7a-e** in 72-89% isolated yields. Single crystal X-ray diffraction quality crystals of all the copper-diphosphine clusters **7a-e** were subsequently recrystallized from a dichloromethane solution layered with *n*-hexanes. An example of the molecular structure of the tetra-coordinated copper(I) cluster **7a** is shown in Figures 2 and 3. The individual single crystal X-ray structures of clusters **7a-e** and their pertinent bonding related information is given in SI (Figures D-H).

Scheme 1. Enantio- and diastereo-selective synthesis of diphosphine ligands and subsequent *in-situ* generation of $\text{Cu}_6\text{Cl}_6\text{L}_3$ copper cluster.

Table 1. Synthesis of Copper(I) Clusters.^a

Entry	3/4	5/6 ^b	7	Yield ^c (%)
1 ^d	3a (R = Ph)	(<i>S,S</i>)- 5a	7a	72
2	3b (R = 4-FC ₆ H ₄)	(<i>R,R</i>)- 5b	7b	77
3	3c (R = 4-MeC ₆ H ₄)	(<i>R,R</i>)- 5c	7c	72
4	3d (R = 2-Furyl)	(<i>R,R</i>)- 5d	7d	89
5	4	(<i>R,R</i>)- 6	7e	85

^aConditions: 6 mol % of cat. (*S*)-**8**, solvent (**3a**, **3b**, **3c** toluene, **3d** THF, **4** DCM). ^bAbsolute configurations were determined by X-ray crystallographic data of clusters **7a-e**; see SI Figures D-H. The *ee* and *de* of each ligands **5a-d** were determined previously,¹⁹ whereas the *ee* and *de* for ligand **6** was determined using the same technique (see SI Figure C.). ^cIsolated yield after

silica gel column chromatography and calculated based on copper atoms. ^d6 mol % of cat. (*R*)-**8** was used instead.

Figure 2. ORTEP representation of Complex **7a**. Hydrogen atoms except H(C13), H(C28), H(C61), H(C76), H(C109) and H(C124) on chiral centers were omitted for clarity.

Figure 3. Coordination Sphere around the Copper Centers in Complex **7a**. The carbon backbone of the bridging diphosphine ligand is omitted for clarity.

The large bite angle of the diphosphine ligands employed is the main contributing factor towards the formation of the cluster architecture. It is seen that each chiral diphosphine ligand skeleton wraps itself around the drum core in such a way that one of the phosphines coordinate to a Cu atom in the upper hexagonal face while the other coordinates to a Cu atom in the lower drum face (for ex. bidentate diphosphine P(1)-P(2) attaches to Cu(1) in the upper face and Cu(2) in the lower face as seen in Figure 3). This in turn leads to the generation of a "paddle wheel" structure for the overall molecular cluster. From the perspective of future catalytic applications it needs to be noted that the chiral C-centers in the ligand framework retain close proximity towards the nearest Cu centre of the core with only two bonds separating them thus offering the possibility of exertion of stereogenic control on the adjacent metal reaction sites during asymmetric protocols. As seen from the crystallographic data, the 12-membered "drum-like" core comprises 2 interconnecting Cu_3Cl_3 hexagonal faces with 3 diphosphine ligands extending outwards from the inner core (Figure 3). Each of the 6 copper centers Cu(X) adopt a distorted-tetrahedral geometry with their neighboring ligand atoms P(X), Cl(X), Cl(Y) and Cl(Z). The Cl atoms act as bridges connecting the Cu centers both within the individual hexagonal faces and also between the two faces thus forming the "drum-like" core. Complex **7a** crystallizes in the monoclinic C2 space group, complex **7c** in the cubic P23 and complexes **7b**, **d-e** in the trigonal R3 space group. Selected bond lengths and angles of cluster **7a-e** are provided in Table 2.

Table 2. Selected Bond Lengths and Angles of the Tetracoordinate Cu(I) complexes **7a-e**.^a

Complex	Average Cu←P (Å)	Range of Cu←P ^b (Å)	Average Cu-Cl (Å)	Range of Cu-Cl ^b (Å)	Average P→Cu-Cl (°)	Average Cl-Cu-Cl (°)
7a	2.206	2.202(2)-2.213(2)	2.414	2.345(2)-2.470(2)	118.50	98.89
7b	2.199	2.189(15)-2.219(12)	2.405	2.345(4)-2.471(4)	118.69	99.03
7c	2.201	2.167(18)-2.234(11)	2.395	2.377(7)-2.413(7)	119.70	99.20
7d	2.200	2.199(2)-2.201(2)	2.416	2.350(2)-2.456(2)	118.82	98.41
7e	2.195	2.194(2)-2.195(2)	2.409	2.342(2)-2.446(2)	119.24	97.90

^aAverage bond lengths and angles are calculated with the respective data provided in the crystal structures. ^bRange of bond lengths are determined based on the shortest and longest bond length.

Based on examples of other four-coordinate phosphine-based copper(I) chloride complexes obtained from the Cambridge Structural Database (CSD), the average bond distances of Cu(I)←P and Cu(I)-Cl is ~2.30 and ~2.35 Å, which indicates that the clusters **7a-e** are in good agreement with other structurally stable tetra-coordinated copper(I) chloride complexes previously synthesized. Assuming that the core of the cluster is a right regular hexagonal prism, we derived the approximate cavity volume of each complexes **7a-e** as 37, 36, 36, 38 and 37 Å³ respectively. The Cu···Cu distances averaged 3.19 (**7a**), 3.26 (**7b**), 3.22 (**7c**), 3.22 (**7d**), and 3.20 Å (**7e**); these values were determined from the cif files using Mercury 3.1 software. The Cu···Cu distances are longer than the sum of the van der Waals radii (2.80 Å) of Cu(I), but they are close to reported structures which shows near infrared (NIR) emissions due to Cu···Cu interactions,^{5n-o} hence indicating the presence of weak cuprophilic interactions.

Spectroscopic and Spectrometric Analysis

To examine the persistence of the clusters in solution, ¹H, ¹³C and ³¹P{¹H} NMR studies were conducted. The ¹H NMR spectra of complexes **7a-d** are distinct and may be assigned to their respective protons of the diphosphine backbone, the ¹³C NMR spectra of the same complexes

indicates that they are highly symmetrical due to the presence of 1 set of ligand signals. However, for complex **7e**, the relatively broader ^1H and ^{13}C NMR signals might be attributed to dynamic motions of the flexible aliphatic chains on the diphosphine ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of all 5 complexes show a slightly broadened signal in the region of -1.2 to 2.4 ppm, and this arise from relatively weak $\text{Cu}\leftarrow\text{P}$ bonds, resulting in a dynamic behavior.²⁰ It is also interesting to note that the ^{31}P chemical shift values of each clusters **7a-e** are similar to their corresponding free diphosphine ligands **5a-d** and **6**. This seems to imply that the phosphorous centers are experiencing a similar electronic environment before and after coordination to the copper ions and is indicative of the inherent overall symmetry in the structure. A search of the literature revealed that a tri-coordinated and tetra-coordinated Cu(I) complexes^{21a} having the same dipyrrolylmethane-based phosphine ligands possess similar ^{31}P chemical shift values at -6.6 and -6.2 ppm respectively. In our case, it is probable that even if multiple species of the "drum-like" clusters are present in solution, NMR data might not be sufficient to determine the persistence of the clusters in solution. However, the positive mode high-resolution ESI-MS analysis of clusters **7a-e** suggest the presence of the intact clusters in solution.

Attempted Synthesis of Other Cu-X Complexes

Motivated by these results, we proceeded to examine the possibilities of forming other clusters by: (i) varying the mole ratio of the diphosphine ligand to Cu(I) ratio, and (ii) using other Cu(I) compounds such as CuOTf, CuOAc, CuNO₃ and CuI. A recent literature report^{21a} has shown that in a 1:1 mole ratio of dipyrrolylmethane-based diphosphine ligand to CuI, a tri-coordinate Cu(I) complex can be formed. However when the mole ratio was changed to 1:2, a tetra-coordinate Cu(I) cluster was formed instead. However, our attempts at modifying the mole ratio of ligand to CuCl (through 1:4, 1:10 and 1:20) in EtOH, MeOH, acetone or acetonitrile afforded the same

clusters **7a-e**. The replacement of CuCl with CuOTf, CuOAc and CuNO₃ gave numerous products that could neither be isolated nor identified. However, the reaction between stoichiometric amount of diphosphine ligand **5a** with CuI in acetone at 60°C for 22 hours generated a major product (³¹P{¹H}: -12.6) with a well-defined ¹H NMR spectrum (SI Figures A and B). The positive mode high-resolution ESI-MS exhibited a peak at 3273.4280 which corresponds to [M+H]⁺ (calculated [M+H]⁺ *m/z* 3273.4272), indicative of the formation of a "drum-like" cluster. However, attempts to recrystallise the product was unsuccessful.

Attempted Formation of Cu(II) Clusters

Compared to their Cu(I) counterparts, polynuclear Cu(II) complexes are relatively scarce.²² To explore the formation of an optically active Cu(II) complex with the diphosphine ligands **5a-d** and **6**, ligand **5a** was refluxed with CuCl₂ in a 1:2 mole ratio for 10 hours in ethanol. The crude ³¹P{¹H} NMR spectrum showed 3 signals at 44.4, 32.1 and -1.2 ppm in approximately 1 : 40 : 30 ratio. Upon further examination, it was revealed that the peaks at 32.1 ppm belonged to the oxidized diphosphine ligand and -1.2 ppm coincided with the cluster **7a**. We were intrigued by three observations: (i) the copper centers of cluster **7a** are in the +1 oxidation state, but the source of copper (CuCl₂) is in the +2 oxidation state, (ii) the large proportion of oxidized phosphine, and (iii) the identity of the peak at 44.4 ppm.

From the standpoint of Cu(II)-phosphine chemistry, it has been observed by Corain²³ that Cu(II) ions may be reduced to Cu(I) ions in the presence of phosphine ligands. Following an extensive literature search, it was found that the reduction of CuCl₂ by carbonyl compounds²⁴ was also plausible. Hence, we postulated that by providing an alternative source of reducing agent such as a carbonyl compound, the sacrificial role of the phosphine could be replaced. To test our theory, we decided to attempt the one pot *in-situ* reduction of CuCl₂ by acetone and the

subsequent coordination of the diphosphine ligand. The experiment was initially conducted with the ligand **5a** and CuCl₂ in a 1:2 mole ratio in acetone at room temperature, and no product formation was observed. After refluxing the mixture overnight, 2 peaks at 44.4 and -1.2 ppm in a 1:50 ratio was observed without the formation of the oxidized phosphine at 32.1 ppm. The major product **7a** was isolated in 62% yield. The minor product **9** (44.4 ppm) was isolated and characterized by NMR spectroscopy. Due to the low yield (5%) of complex **9**, the synthesis was repeated on a larger scale with the racemic catalyst **8**. An X-ray quality crystal of racemic complex **9** was obtained and the molecular structure is depicted in Figures 4 and 5.

Figure 4. ORTEP Representation of Complex **9**. All hydrogen atoms were omitted for clarity.

Figure 5. Coordination Sphere around the Copper Centers in Complex **9**. The carbon backbone of the bridging diphosphine ligand backbone are omitted for clarity.

Complex **9** crystallized in the triclinic P-1 space group in a distorted 8-membered chair conformation comprising of 4 Cu(I) centers and 4 Cl atoms acting as bridging ligands. The Cu(1) and Cu(1A) copper atoms possess 18 valence electrons whilst Cu(2) and Cu(2A) have 16 valence electrons each. Selected bond lengths and angles are summarized in Table 3.

Table 3. Selected Bond Lengths (Å) and Angles (°) for Complex **9**.

Cu(1)–Cl(1)	2.3783(16)	Cu(1)←P(1)	2.1976(15)
Cu(2)–Cl(2)	2.3748(16)	Cu(2)←P(2)	2.1812(16)
Cu(1)–Cl(2)	2.5336(15)	Cu(1)–Cu(2)	2.7911(10)
Cu(1)–Cl(2A)	2.3844(14)	Cu(1A)–Cl(2)	2.3844(14)
Cu(2)–Cl(1)	2.2366(16)		
P(1)→Cu(1)–Cl(1)	127.09(6)	Cl(2A)–Cu(1)–Cu(2)	130.26(5)
P(1)→Cu(1)–Cl(2)	119.44(5)	Cl(2)–Cu(1)–Cu(2)	52.70(4)
P(1)→Cu(1)–Cl(2A)	113.03(6)	P(2)→Cu(2)–Cl(1)	137.93(7)
Cl(1)–Cu(1)–Cl(2)	92.31(5)	P(2)→Cu(2)–Cl(2)	120.49(6)
Cl(1)–Cu(1)–Cl(2A)	102.99(5)	Cl(1)–Cu(2)–Cl(2)	100.40(6)
Cl(2)–Cu(1)–Cl(2A)	96.30(5)	P(2)→Cu(2)–Cu(1)	139.93(5)

P(1)→Cu(1)–Cu(2)	116.14(4)	Cl(1)–Cu(2)–Cu(1)	55.14(4)
Cl(1)–Cu(1)–Cu(2)	50.50(4)	Cl(2)–Cu(2)–Cu(1)	58.07(4)

The average Cu←P and Cu–Cl bond lengths in cluster **9** are 2.19 Å and 2.38 Å respectively, which are slightly shorter compared to those in the clusters **7a-e**. The bond lengths of the "Cu₄Cl₄" framework are "normal" in comparison with Cu←P (2.18 Å) and Cu–Cl (2.44 Å) bond lengths reported for cubane complexes.^{21b} The Cu(I) atoms are not equally bridged by the Cl atoms, in particular, Cu(1)–Cl(1) is 2.3783(16) Å and Cu(1)–Cl(2) is 2.5336(15) Å. This could be due to the large bite angle of the diphosphine ligands which caused an elongation of the Cu(1)–Cl(2) and Cu(1A)–Cl(2A) bond lengths. The Cu(1) and Cu(1A) atoms adopt a distorted tetrahedral geometry whereas Cu(2) and Cu(2A) atoms exhibit a pseudotrigonal planar geometry with a torsion angle of 169.75°. The Cu···Cu distance measured 2.7911(10) Å, which indicates weak metal-metal interactions. The total cavity area within the "Cu₄Cl₄" skeleton is estimated to be 17 Å³.

Spectrometric Analysis of Complex **9**

¹H, ¹³C and ³¹P{¹H} NMR spectroscopic analysis were performed. The ¹H and ¹³C NMR spectra shows sharp peaks arising from their respective nuclei, and the absence of excessive signals indicates that complex **9** is highly symmetrical. ³¹P{¹H} NMR of the complex showed a sharp distinct peak at 44.4 ppm, which seems to suggest that the Cu←P bonds are stronger than those present in clusters **7a-e**. Strangely, the chemical shift is very different from other clusters reported in literature. A previously reported tetranuclear dipyrrolylmethane-based diphosphine Cu₄I₄^{21a} has a ³¹P signal at -6.2 ppm and (1-(diphenylphosphino)butan-2-yl)oxy)diphenylphosphine) Cu₂I₂ complex²⁵ shows up at -23.0 ppm. In addition, the ³¹P chemical shift of known di-, tetra- and octa-nuclear halide and hydride copper(I) complexes^{5g, 5k, 20, 21a}

bearing diphosphines of different electronic structures and possible bite angles remains in a rather narrow range from -3.1 to -21.9 ppm. We do not have any reasonable explanation for this phenomenon, but the ^{31}P chemical shift of phosphine complexes can differ depending on the metal, ions and also coordination number. As a further confirmation the positive mode high-resolution ESI-MS analysis was conducted and it confirmed the presence of the intact cluster **9** ($[\text{M}+\text{H}]^+ m/z$ 1818.1033, calculated $[\text{M}+\text{H}]^+ m/z$ 1818.1023). With all the spectroscopic data collected, it was determined that complex **9** indeed persist in solution in the same form as its solid state structure indicated.

Formation of Different Structural Clusters

From our experimental observations in the formation of clusters **7a** and **9**, we proposed the following pathways for their syntheses. The addition of CuCl_2 to the diphosphine **5a** proceeds *via* 2 pathways, the first being the *in-situ* reduction of CuCl_2 to CuCl by acetone, which is effectively the same as adding CuCl , followed by the subsequent coordination of the ligand **5a** to form complex **7a**. The second pathway involves the initial coordination of the ligand to CuCl_2 , then a sequential reduction of the Cu(II) to Cu(I) resulting in the formation of complex **9**. From this, we hypothesized that if the *in-situ* reduction could be impeded, the formation of complex **9** could be increased. Instead of refluxing the ligand **5a** and CuCl_2 in acetone, the solvent was replaced by methanol (cluster **7a**: 58% isolated yield, cluster **9**: 4% isolated yield), acetonitrile (cluster **7a**: 61%, cluster **9**: 4%), chloroform (cluster **7a**: 26%, cluster **9**: 2%), tetrahydrofuran (cluster **7a**: 22%, cluster **9**: 2%) and methyl ethyl ketone (cluster **7a**: 56%, cluster **9**: 4%). In the case of methanol, acetonitrile and methyl ethyl ketone, negligible amounts of phosphine oxide at 32.1 ppm ($^{31}\text{P}\{^1\text{H}\}$ NMR) was observed, which indicates that these solvents are also capable of reducing CuCl_2 to CuCl . Indeed, it has been reported by Hume^{24b} and Owsley^{24c} that CuCl has

been obtained from boiling solution of CuCl₂ in acetonitrile and methanol. In addition, methyl ethyl ketone behaves similarly to acetone albeit with slightly lower yields. However, when chloroform and tetrahydrofuran were used as the solvent, a significant amount of phosphine oxide was isolated, which inevitably affected the yields of both clusters **7a** and **9**. These experiments provide preliminary evidence on the reducing ability of the phosphine ligand in the absence of a suitable "sacrificial" solvent. Even though carbonyl functionalities are present on the phosphine ligand, we do not observed their participation in the reduction of Cu(II) to Cu(I) from ¹H and ³¹P{¹H} NMR studies of the crude reaction mixture.

Application in Catalytic Hydroboration

In the last decade, numerous reports on the application of Cu(I)←phosphine²⁶ and Cu(I)-NHC²⁷ complexes in hydroboration have emerged. The presence of a cavity within the clusters synthesized in this work could essentially control the stereoselectivity of such reaction by virtue of the close proximity of the adjacent chirality directing centers on the diphosphine backbone.

Table 4. Catalytic Hydroboration of Chalcone.

Entry	Cat.	Solvent	Base	t (hr)	Yield ^a (%)	ee ^b (%)
1	7a	THF	Cs ₂ CO ₃	1	97	3
2	7a	DEE	Cs ₂ CO ₃	1	97	4
3	7a	EA	Cs ₂ CO ₃	2	96	14
4	7a	EA	KO ^t Bu	0.5	97	11
5	7a	DCM	Cs ₂ CO ₃	1	98	7
6	7b	EA	Cs ₂ CO ₃	2	99	8
7	7c	EA	Cs ₂ CO ₃	2	99	5

8	7d	EA	Cs ₂ CO ₃	3	98	10
9	7e	EA	Cs ₂ CO ₃	2	99	9

^aIsolated yield after column chromatography. ^b*ee* was determined by chiral HPLC.

The hydroboration of an α,β -unsaturated enone using bis(pinacolato)diboron was carried out efficiently in the presence of 1 mol % of cluster **7a**. The reaction proceeded smoothly at room temperature with excellent yields. However the enantioselectivities achieved was below par when compared to Yun^{26a} (up to 94% *ee*) and Fernández^{26d} (up to 99% *ee*). Efforts to improve on the stereoselectivity by optimization of the reaction conditions as well as the application of the catalyst system to other asymmetric synthesis scenarios are currently being pursued.

CONCLUSION

We have successfully developed a methodology for the direct diastereoselective one-pot synthesis of optically pure "drum-like" hexanuclear Cu(I) complexes incorporating a chiral diphosphine backbone in up to 89% isolated yield. All synthesized complexes were characterized by ¹H, ¹³C and ³¹P NMR as well as by single crystal X-ray diffraction analysis. The substitution of CuCl with CuCl₂ resulted in the formation of an unexpected tetranuclear Cu(I) cluster by a separate pathway, which exhibits stronger Cu...Cu interactions than its hexanuclear counterpart. The small cavity volume of the generated clusters along with the presence of chiral directing centers on the phosphine backbone might offer an opportunity to investigate potential cooperative catalysis especially in an asymmetric manner as indicated by an exploratory study conducted on the use of the "drum-like" clusters in the hydroboration reaction of α,β -unsaturated enones.

EXPERIMENTAL SECTION

General Information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. Solvents were purchased from their respective companies and used as supplied. Where necessary, solvents were degassed prior to use. A Low Temp Pairstirrer PSL-1800 was used for controlling low temperature reactions. Column chromatography was done on Silica gel 60 (Merck). Melting points were measured using SRS Optimelt Automated Point System SRS MPA100. Optical rotations were measured with JASCO P-1030 Polarimeter in the specified solvent in a 0.1 dm cell at 22.0°C. NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers. Chemical shifts were reported in ppm and referenced to an internal SiMe₄ standard (0 ppm) for ¹H NMR, chloroform-d (77.23 ppm) for ¹³C NMR, and an external 85% H₃PO₄ for ³¹P{¹H} NMR. All X-ray quality crystals were obtained *via* recrystallization from a dichloromethane solution layered with *n*-hexanes.

The palladacycle (*S*)-**8**¹⁹ was prepared according to literature methods. All other reactants and reagents were used as supplied.

Caution! Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.

Preparation of Copper(I) Clusters **7a-c**

To a solution of Ph₂PH (2.2 equiv) in toluene (10 mL) was added catalyst (*R*)- or (*S*)-**8** (6 mol %) and stirred for 10 minutes before cooling to -80°C. Diunsaturated alkene (1.0 equiv) was added followed by NEt₃ (2.0 equiv) in toluene (1 mL) dropwise. The solution was stirred at -80°C and the completion of the reaction was monitored by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the ³¹P{¹H} NMR spectrum. Upon

completion, the solution was allowed to room temperature. Volatiles were removed under reduced pressure. The crude product was redissolved in acetone (10 mL) and CuCl (2.0 equiv) was added. The mixture was refluxed overnight and on cooling, concentrated to give the crude complex, which was purified *via* silica gel column chromatography (DCM or 9 DCM : 1 EA) to afford white solid of the clusters **7a-c**.

7a

The hydrophosphination step was completed in 8 h. (72% yield based on Cu atoms). $[\alpha]_D = -48.6$ (*c* 0.1, DCM). Mp: 206-208°C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 202 MHz): δ -1.2; ^1H NMR (CDCl_3 , 500 MHz): δ 9.03 (brs, 1H, Ar), 8.19-8.17 (m, 4H, Ar), 8.02-8.00 (m, 4H, Ar), 7.67-7.36 (m, 16H, Ar), 6.94-6.76 (m, 9H, Ar), 4.73-4.69 (m, 2H, PCHCHH), 4.59-4.54 (m, 2H, PCHCHH), 3.31 (dd, 2H, $J = 18.1$ Hz, 12.8 Hz, PCHCHH); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.8 (d, 2C, $^3J_{\text{PC}} = 14.9$ Hz, C=O), 140.1-128.0 (42C, Ar), 44.0 (d, 2C, $^2J_{\text{PC}} = 13.0$ Hz, PCHCH₂), 38.9 (d, 2C, $^1J_{\text{PC}} = 25.5$ Hz, PCH). HRMS (ESI, m/z ($\text{M} + \text{H}$)⁺) calcd for $\text{C}_{144}\text{H}_{121}\text{O}_6\text{P}_6\text{Cu}_6\text{Cl}_6$ 2727.1472, found 2727.1477. Elemental analysis calcd (%) for $\text{C}_{144}\text{H}_{120}\text{O}_6\text{P}_6\text{Cu}_6\text{Cl}_6$: C 63.44, H 4.44; found: C 63.48, H 4.49.

7b

The hydrophosphination step was completed in 45 h. (77% yield based on Cu atoms). $[\alpha]_D = +38.9$ (*c* 0.1, DCM). Mp: 226-228°C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 202 MHz): δ -0.8; ^1H NMR (CDCl_3 , 500 MHz): δ 8.99 (brs, 1H, Ar), 8.15-8.11 (m, 4H, Ar), 7.99-7.95 (m, 4H, Ar), 7.68-7.64 (m, 4H, Ar), 7.38-7.33 (m, 6H, Ar), 6.97-6.85 (m, 13H, Ar), 4.68-4.63 (m, 2H, PCHCHH), 4.47-4.41 (m, 2H, PCHCHH), 3.30-3.24 (m, 2H, PCHCHH); ^{13}C NMR (CDCl_3 , 125 MHz): δ 196.3 (2C, C=O), 166.7 (1C, CF), 164.7 (1C, CF), 140.1-115.4 (40C, Ar), 43.6 (2C, PCHCH₂), 38.8

(2C, PCH). HRMS (ESI, m/z ($M + H$)⁺) calcd for C₁₄₄H₁₁₅O₆P₆F₆Cu₆Cl₆ 2835.0906, found 2835.0898.

7c

The hydrophosphination step was completed in 72 h. (72% yield based on Cu atoms). [α]_D = +44.5 (c 0.1, DCM). Mp: 249-251°C. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ -1.0; ¹H NMR (CDCl₃, 500 MHz): δ 9.00 (brs, 1H, Ar), 8.18-8.14 (m, 4H, Ar), 7.88-7.86 (m, 4H, Ar), 7.67-7.63 (m, 4H, Ar), 7.33-7.32 (m, 6H, Ar), 7.12-7.11 (m, 4H, Ar), 6.93-6.81 (m, 9H, Ar), 4.71-4.66 (m, 2H, PCHCHH), 4.46-4.41 (m, 2H, PCHCHH), 3.32 (dd, 2H, J = 17.1 Hz, 13.5 Hz, PCHCHH), 2.34 (s, 6H, C₆H₄CH₃); ¹³C NMR (CDCl₃, 125 MHz): δ 197.5 (2C, C=O), 143.6-128.0 (42C, Ar), 43.9 (2C, PCHCH₂), 38.8 (2C, PCH), 29.8 (1C, C₆H₄CH₃), 21.7 (1C, C₆H₄CH₃). HRMS (ESI, m/z ($M + H$)⁺) calcd for C₁₅₀H₁₃₃O₆P₆Cu₆Cl₆ 2811.2415, found 2811.2430.

Preparation of Copper(I) Cluster 7d

The preparation is similar as above but THF was used in place of toluene. The hydrophosphination step was completed in 36 h. (89% yield based on Cu atoms). [α]_D = +42.0 (c 0.1, DCM). Mp: 265-268°C. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ -0.6; ¹H NMR (CDCl₃, 300 MHz): δ 9.02 (brs, 1H, Ar), 8.15-8.10 (m, 4H, Ar), 7.73-7.67 (m, 4H, Ar), 7.44-7.33 (m, 9H, Ar), 7.12-7.05 (m, 7H, Ar), 6.93-6.83 (m, 3H, Ar), 6.23 (brs, 2H, Ar), 4.63-4.55 (m, 2H, PCHCHH), 4.19-4.08 (m, 2H, PCHCHH), 3.12-3.03 (m, 2H, PCHCHH); ¹³C NMR (CDCl₃, 125 MHz): δ 186.3 (2C, C=O), 152.0 (2C, C(O)C-O), 146.8 (2C, O-CH=C), 139.7-128.2 (30C, Ar), 119.6 (2C, C(O)C=CH), 112.1 (2C, O-CH=CH), 43.0 (2C, PCHCH₂), 29.7 (2C, PCH). HRMS (ESI, m/z ($M + H$)⁺) calcd for C₁₃₂H₁₀₉O₁₂P₆Cu₆Cl₆ 2667.0222, found 2667.0217.

Preparation of Copper(I) Cluster 7e

The preparation is similar as above but DCM was used as the solvent. The hydrophosphination step was completed in 12 h. (85% yield based on Cu atoms). $[\alpha]_D = -19.5$ (c 0.1, DCM). Mp: 221-224°C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz): δ 2.4; ^1H NMR (CDCl_3 , 300 MHz): δ 8.08-7.98 (m, 9H, Ar), 7.44-7.39 (m, 13H, Ar), 6.69-6.66 (m, 1H, Ar), 6.40 (brs, 1H, Ar), 4.71-4.64 (m, 2H, PCH), 4.49-4.45 (m, 2H, PCHCH), 3.04 (brs, 12H, CO_2CH_3); ^{13}C NMR (CDCl_3 , 100 MHz): δ 167.7 (4C, C=O), 137.9-127.6 (30C, Ar), 53.8 (2C, PCHCH), 52.3 (4C, CO_2CH_3), 44.1 (2C, PCH). HRMS (ESI, m/z ($\text{M} + \text{H}$) $^+$) calcd for $\text{C}_{126}\text{H}_{121}\text{O}_{24}\text{P}_6\text{Cu}_6\text{Cl}_6$ 2799.0549, found 2799.0552.

Preparation of Copper(I) Cluster 9

The preparation is similar as for cluster **7a** but CuCl_2 was added instead of CuCl . The mixture was refluxed overnight and on cooling, concentrated to give the crude complex, which was purified *via* silica gel column chromatography (DCM or 9 DCM : 1 EA) to afford white solid of the cluster **9**. 3% yield based on Cu atoms. $[\alpha]_D = +39.5$ (c 0.1, DCM). Mp: 257-259°C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 202 MHz): δ 44.4; ^1H NMR (CDCl_3 , 300 MHz): δ 8.04-8.02 (m, 4H, Ar), 7.92-7.89 (m, 4H, Ar), 7.41-7.33 (m, 19H, Ar), 7.16 (t, 4H, $^3J = 7.7$ Hz, 12.8 Hz, Ar), 7.05 (d, 2H, $^3J = 7.5$ Hz, Ar), 6.79 (t, 1H, $^3J = 7.3$ Hz, Ar), 4.91-4.90 (m, 2H, PCHCHH), 3.42-4.25 (m, 2H, PCHCHH), 3.07-2.96 (m, 2H, PCHCHH); ^{13}C NMR (CDCl_3 , 125 MHz): δ 198.0 (2C, C=O), 135.1-124.7 (42C, Ar), 48.0 (2C, PCHCH₂), 44.8 (2C, PCH). HRMS (ESI, m/z ($\text{M} + \text{H}$) $^+$) calcd for $\text{C}_{96}\text{H}_{81}\text{O}_4\text{P}_4\text{Cu}_4\text{Cl}_4$ 1818.1023, found 1818.1033.

General Procedure for Catalytic Hydroboration

Under a nitrogen atmosphere, Cu(I) cluster **7a** (2.7 mg, 1.0 μmol , 1 mol %), base (10 mol %) and B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv.) in solvent (2 mL) was stirred for 10 mins. Enone (20.8 mg, 0.10 mmol, 1.0 equiv.) and MeOH (8.1 μL , 0.20 mmol, 2.0 equiv.) was added consecutively and stirred. The completion of the reaction was determined by TLC analysis and

confirmed by ^1H NMR. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to afford the desired product. The data were consistent with the literature.^{32b} The *ee* was determined on a Daicel Chiralpak AD-H column with n-hexane/2-propanol = 97/3, flow = 0.9 mL/min, wavelength = 210 nm. Retention times: 8.7 min, 12.4 min.

ASSOCIATED CONTENT

Supporting Information.

NMR, X-ray structures, refinement data, crystallographic data (cif files) and HPLC spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TABLE OF CONTENTS

12-membered "drum-like" $\text{Cu}_6\text{Cl}_6\text{L}_3$ and an 8-membered "chair-like" $\text{Cu}_4\text{Cl}_4\text{L}_2$ diphosphine-based clusters were prepared in one-pot from the optically pure diphosphine ligands synthesized *via* the catalytic double hydrophosphination reaction in excellent enantio- and diastereo-selectivity. The clusters were characterized by ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as well as single crystal X-ray crystallography.