

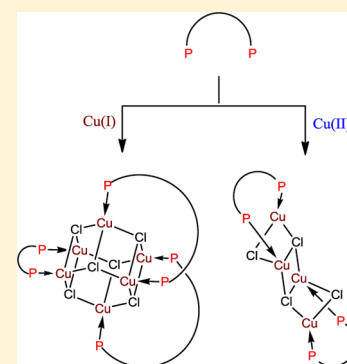
A One-Pot Diastereoselective Self Assembly of C-Stereogenic Copper(I) Diphosphine Clusters

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Supporting Information

ABSTRACT: C-chirogenic diphosphine-based clusters with 8-membered “chairlike” $\text{Cu}_4\text{Cl}_4\text{L}_2$ and 12-membered “drumlike” $\text{Cu}_6\text{Cl}_6\text{L}_3$ (L = diphosphine) frameworks were prepared in one-pot syntheses from chiral diphosphines, which were generated in situ via the double hydrophosphination reaction in excellent enantio- and diastereoselectivity. 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 was characterized by single-crystal X-ray crystallography, ^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The synthesized clusters were 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 metals that is extremely versatile from a coordination standpoint, with its complexes readily accessing the coordination numbers of two to six¹ dependent on factors such as the valency of the metal center and nature of the ligands. This attribute, together with its coordinative lability, has led to the widespread application of copper complexes in areas such as organic synthesis,² homogeneous catalysis,³ 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} catalysis,⁷ 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, the majority of such structures involve polydentate ligands that contain 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 “drumlike” $\text{Cu}_6\text{X}_6\text{L}_6$ cores have been reported since the 1960s (Figure 1).¹¹ However, a lack of applications as well as challenges faced in the synthesis of such compounds¹² led to a

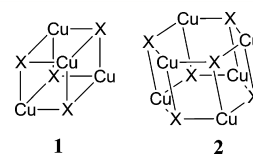


Figure 1. Structural representations of cubane unit Cu_4X_4 (1) and “drumlike” unit Cu_6X_6 (2) in copper clusters (ligands are omitted for clarity).

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, NMe₂, Ph, *tert*-butyl),¹⁴ PPh_2R^1 (R^1 = Me, cyclohexyl),^{15a,15b} and diphosphine ligands^{5g,6,15c–e} have been described in literature, showing a growing interest toward 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 are therefore difficult to handle, which indirectly affects the overall efficiency of these often stepwise protocols. The development of an efficient and facile one-pot methodology that 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 to generate a viable molecular library for these types of compounds.

Herein, we report the one-pot syntheses of chiral 12-membered “drumlike” and 8-membered “chairlike” copper

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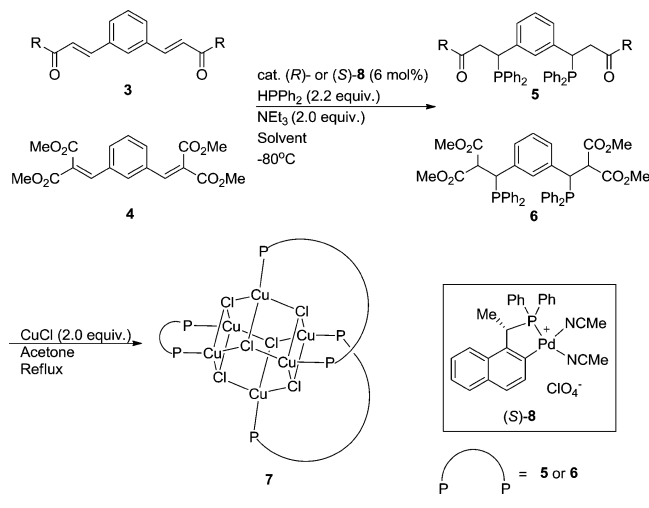
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clusters bearing bridging diphosphine ligands with two C-stereogenic centers. By utilizing the newly developed synthetic method, we successfully circumvented the challenges that may be faced in the possible synthesis of copper-phosphine clusters such as (i) the need for prior synthesis of air and moisture-sensitive tertiary phosphines (or the protection and subsequent deprotection 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. 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 were 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 have 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*)

Scheme 1. Enantio- and Diastereoselective Syntheses of Diphosphine Ligands and Subsequent *In Situ* Generation of Cu₆Cl₆L₃ Copper Cluster



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, deprotection sequence) allows a hitherto unexplored one-pot sequence. Upon refluxing the diphosphines with CuCl in acetone for 10 h, the reaction was monitored by ³¹P{¹H} 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 high isolated yields (Table 1). X-ray diffraction quality crystals of all

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 catalyst (*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 Supporting Information Figures D–H. The *ee* and *de* of each ligand 5a–d were determined previously,¹⁹ whereas the *ee* and *de* for ligand 6 was determined using the same technique (see Supporting Information Figure C). ^cIsolated yield after silica gel column chromatography and calculated based on copper atoms. ^d6 mol % of catalyst (*R*)-8 was used instead.

the copper-diphosphine clusters 7a–e were subsequently recrystallized from dichloromethane solutions layered with *n*-hexanes. An example of the molecular structure of the tetracoordinated 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 Supporting Information (Figures D–H).

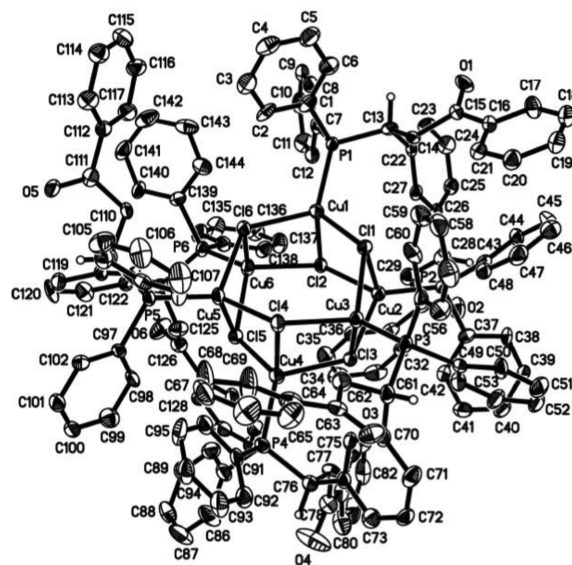


Figure 2. ORTEP representation of Complex 7a. Hydrogen atoms except H(C13), H(C28), H(C61), H(C76), H(C109), and H(C124) on chiral centers were omitted for clarity.

The large bite angle of the diphosphine ligands employed is the main contributing factor toward 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 (e.g., bidentate diphosphine P(1)–P(2) attaches to Cu(1) in the upper face and to 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

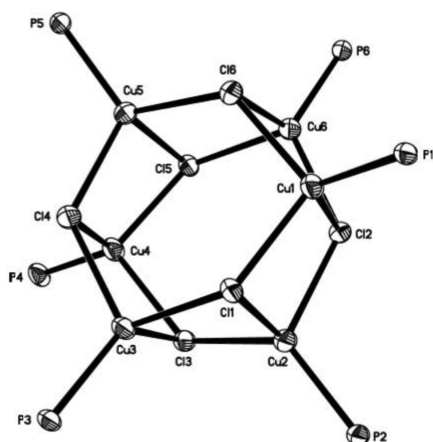


Figure 3. Coordination sphere around the copper centers in complex 7a. The carbon backbone of the bridging diphosphine ligand is omitted for clarity.

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 toward the nearest Cu center 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 two interconnecting Cu_3Cl_3 hexagonal faces with three diphosphine ligands extending outward from the inner core (Figure 3). Each of the six copper centers $\text{Cu}(X)$ adopt a distorted-tetrahedral geometry with their neighboring ligand atoms $\text{P}(X)$, $\text{Cl}(X)$, $\text{Cl}(Y)$, and $\text{Cl}(Z)$. 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 “drumlike” 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 clusters 7a–e are provided in Table 2.

On the basis of examples of other four-coordinate phosphine-based copper(I) chloride complexes obtained from the Cambridge Structural Database (CSD), the average bond distances of $\text{Cu}(\text{I})\leftarrow\text{P}$ and $\text{Cu}(\text{I})\text{—Cl}$ are ~ 2.30 and ~ 2.35 Å, which indicates that the clusters 7a–e are in good agreement with other structurally stable tetracoordinated copper(I) chloride complexes previously synthesized. Assuming that the core of the cluster is a right regular hexagonal prism, we derived the approximate cavity volumes of the complexes 7a–e as 37, 36, 36, 38, and 37 Å³, respectively. The $\text{Cu}\cdots\text{Cu}$ 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 $\text{Cu}\cdots\text{Cu}$ 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 that show near-infrared (NIR) emissions due to $\text{Cu}\cdots\text{Cu}$ interactions;^{5n,o} hence, they indicate 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 indicate that they are highly symmetrical due to the presence of one set of ligand signals. However, for complex 7e, the relatively broader ¹H and ¹³C NMR signals might be attributed to dynamic motions of the flexible aliphatic chains on the diphosphine ligand. The ³¹P{¹H} NMR spectra of all five complexes show slightly broadened signals in the region of -1.2 to 2.4 ppm, arising from relatively weak $\text{Cu}\leftarrow\text{P}$ bonds, resulting in a dynamic behavior.²⁰ It is also interesting to note that the ³¹P chemical shift values of the clusters 7a–e are similar to their corresponding free diphosphine ligands 5a–d and 6. This seems to imply that the phosphorus 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 tricoordinated and tetracoordinated Cu(I) complexes^{21a} having the same dipyrrolylmethane-based phosphine ligands possess similar ³¹P chemical shift values at -6.6 and -6.2 ppm, respectively. In our case, it is probable that even if multiple species of the “drumlike” 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 electrospray ionization mass spectrometry (ESI-MS) analysis of clusters 7a–e suggests 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 , CuNO_3 , and CuI . A recent literature report^{21a} has shown that in a 1:1 mol ratio of dipyrrolylmethane-based diphosphine ligand to CuI , a tricoordinate Cu(I) complex can be formed. However, when the mole ratio was changed to 1:2, a tetracoordinate 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 CuNO_3 gave numerous products that could neither be isolated nor identified. However, the reaction between a stoichiometric amount of diphosphine ligand 5a with

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 (deg)	average Cl–Cu–Cl (deg)
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.

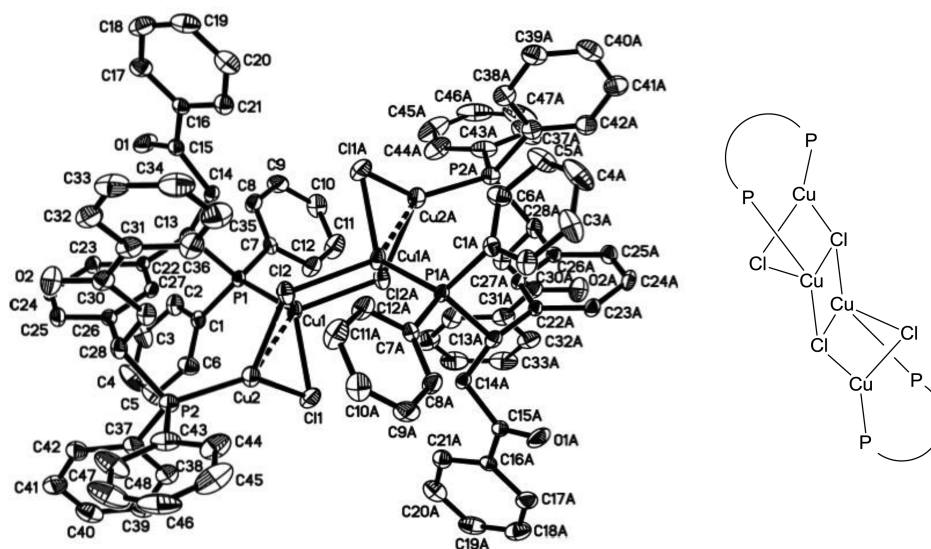


Figure 4. ORTEP representation of complex **9**. All hydrogen atoms were omitted for clarity.

CuI in acetone at 60 °C for 22 h generated a major product ($^{31}\text{P}\{^1\text{H}\}$: -12.6) with a well-defined ^1H NMR spectrum (Supporting Information Figures A and B). The positive-mode high-resolution ESI-MS exhibited a peak at 3273.4280, which corresponds to $[\text{M} + \text{H}]^+$ (calculated $[\text{M} + \text{H}]^+ m/z$ 3273.4272), indicative of the formation of a “drumlike” cluster. Unfortunately, attempts to recrystallize the product were 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 CuCl_2 in a 1:2 mol ratio for 10 h in ethanol. The crude $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed three signals at 44.4, 32.1, and -1.2 ppm in approximately a 1:40:30 ratio. Upon further examination, it was revealed that the peaks at 32.1 ppm belonged to the oxidized diphosphine ligand, and the peak at -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 (CuCl_2) 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 CuCl_2 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 CuCl_2 by acetone and the subsequent coordination of the diphosphine ligand. The experiment was initially conducted with the ligand **5a** and CuCl_2 in a 1:2 mol ratio in acetone at room temperature, and no product formation was observed. After refluxing the mixture overnight, two peaks at 44.4 and -1.2 ppm in a 1:50 ratio were 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. Because of 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.

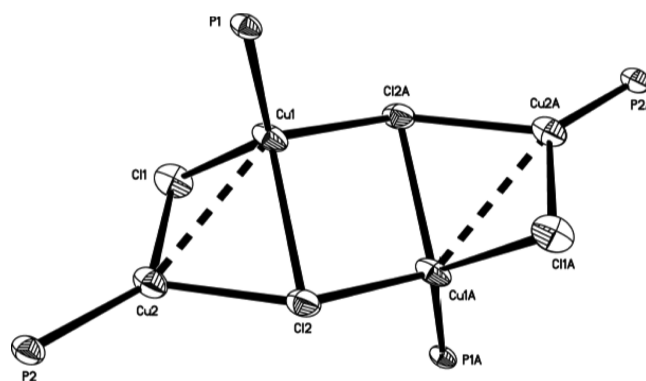


Figure 5. Coordination sphere around the copper centers in complex **9**. The carbon backbone of the bridging diphosphine ligand backbone was omitted for clarity.

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

The average Cu←P and Cu–Cl bond lengths in cluster **9** are 2.19 and 2.38 Å, respectively, which are slightly shorter compared to those in the clusters **7a–e**. The bond lengths of the “ Cu_4Cl_4 ” 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

Table 3. Selected Bond Lengths (Å) and Angles (deg) 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)

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 analyses were performed. The ¹H and ¹³C NMR spectra show 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 octanuclear halide and hydride copper(I) complexes^{5g,k,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 ³¹P chemical shift of phosphine complexes can differ depending on the metal, ions, and also the 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 ([M + H]⁺ *m/z* 1818.1033, calculated [M + H]⁺ *m/z* 1818.1023). With all the spectroscopic data collected, it was determined that complex 9 indeed persists 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 CuCl₂ to the diphosphine 5a proceeds via two pathways, the first being the in situ reduction of CuCl₂ 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 CuCl₂, 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 CuCl₂ 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 (THF) (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 (³¹P{¹H} NMR) were observed, which indicates that these solvents are also capable of reducing CuCl₂ to CuCl. Indeed, it has been reported by Hume^{24b} and Owsley^{24c} that CuCl has been obtained from boiling a 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 THF 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 past 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.

The hydroboration of an α,β-unsaturated enone using bis(pinacolato)diboron was carried out efficiently in the

Table 4. Catalytic Hydroboration of Chalcone

entry	catalyst	solvent ^a	base	<i>t</i> (hr)	yield ^b (%)	<i>ee</i> ^c (%)
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

^aDEE: diethyl ether, EA: ethyl acetate. ^bIsolated yield after column chromatography. ^c*ee* was determined by chiral HPLC.

presence of 1 mol % of cluster **7a**. The reaction proceeded smoothly at room temperature with excellent yields (Table 4). However, the enantioselectivities achieved were below par when compared to those of 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 syntheses of optically pure “drum-like” hexanuclear Cu(I) complexes incorporating chiral diphosphine backbones 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 exhibited 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 “drumlike” 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 the solution was stirred for 10 min before it was cooled 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 phosphorus signal attributed to diphenylphosphine (–40 ppm) in the ³¹P{¹H} NMR spectrum. Upon completion, the solution was allowed to warm 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, once cooled, 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). [α]_D = –48.6 (c 0.1, DCM). Mp: 206–208 °C. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ –1.2; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 197.8 (d, 2C, ³J_{PC} = 14.9 Hz, C=O), 140.1–128.0 (42C, Ar), 44.0 (d, 2C, ²J_{PC} = 13.0 Hz, PCHCH₂), 38.9 (d, 2C, ¹J_{PC} = 25.5 Hz, PCH). High-resolution mass spectrometry (HRMS) (ESI, *m/z* (M + H)⁺) calcd for C₁₄₄H₁₂₁O₆P₆Cu₆Cl₆: 2727.1472, found 2727.1477. Elemental analysis calcd (%) for C₁₄₄H₁₂₀O₆P₆Cu₆Cl₆: 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). [α]_D = +38.9 (c 0.1, DCM). Mp: 226–228 °C. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ –0.8; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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). [α]_D = –19.5 (c 0.1, DCM). Mp: 221–224 °C. ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 2.4; ¹H NMR (CDCl₃, 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, CO₂CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 167.7 (4C, C=O), 137.9–127.6 (30C, Ar), 53.8 (2C, PCHCH), 52.3 (4C, CO₂CH₃), 44.1 (2C, PCH). HRMS (ESI, *m/z* (M + H)⁺) calcd for C₁₂₆H₁₂₁O₂₄P₆Cu₆Cl₆: 2799.0549; found: 2799.0552.

Preparation of Copper(I) Cluster **9.** The preparation is similar as for cluster **7a**, but CuCl₂ was added instead of CuCl. The mixture was refluxed overnight and, once cooled, 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. [α]_D = +39.5 (c 0.1, DCM). Mp: 257–259 °C. ³¹P{¹H} NMR (CDCl₃, 202 MHz): δ 44.4; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 ($M + H$)⁺] calcd for C₉₆H₈₁O₄P₄Cu₄Cl₄: 1818.1023; found: 1818.1033.

General Procedure for Catalytic Hydroboration. Under a nitrogen atmosphere, Cu(I) cluster **7a** (2.7 mg, 1.0 μ mol, 1 mol %), base (10 mol %), and B₂pin₂ (27.9 mg, 0.11 mmol, 1.1 equiv) in solvent (2 mL) was stirred for 10 min. Enone (20.8 mg, 0.10 mmol, 1.0 equiv) and MeOH (8.1 μ L, 0.20 mmol, 2.0 equiv) was added consecutively and stirred. The completion of the reaction was determined by thin-layer chromatography 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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Notes

The authors declare no competing financial interest.

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