Copper(I) Diphosphine Catalysts for C−N Bond Formation: Synthesis, Structure, and Ligand Effects

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A series of copper(I) complexes containing bis(diarylphosphino)propane, bis(diarylphosphino)ethane, bis(diarylphosphino)methane, and *N,N*-bis(diarylphosphino)amine ligands (Aryl = Ph, 2-C_6H_4(Me) or 2-C_6H_4(*i*-Pr)) has been synthesized. Crystal structures of selected chloride derivatives are reported. The complex structures proved to be very sensitive to both the backbone and P-substituents of the chelating ligand. The complexes have been screened for catalytic amidation reactions. Although in most cases only very low activity is observed, comparable with simple copper halide salts, notable exceptions are catalysts based on *N,N*-bis(diphenylphosphino)amine ligands, where a significant improvement in catalyst efficiency is observed. We propose the unusual electronic properties of these ligands may be the cause of their distinctive performance in these and other catalytic reactions where hard donor ligands have previously been employed.

1. Introduction

Palladium-catalyzed C−N bond formation has developed into a versatile way of producing aryl amines and amides from aryl halides,[1] probably the best known methodology being the Buchwald−Hartwig amination reaction, which makes use of palladium complexes supported by strong σ-donor phosphine or N-heterocyclic carbene (NHC) ligands.[2] However, there has also been recent progress in revisiting the much older Ullmann and Goldberg copper-mediated methodologies,[3,4] so that Buchwald and co-workers have demonstrated that efficient catalytic systems operating at much lower temperatures than traditionally employed with copper can be attained by judicious choice of supporting ligand.[5] These copper-based systems show advantages over palladium catalysts with certain substrates, and the two catalyst families are in many ways complementary.

Bidentate chelating phosphines have been used as ligands for copper-catalyzed amination of aryl halides with aryl amines. [6] However their activity is generally surpassed by supporting ligands based on "hard" N and/or O donor chelates. This is in contrast to palladium-catalyzed coupling, where softer donors are usually the ligand of choice. To our knowledge no reports exist on the use of phosphines as ligands in copper-catalyzed amidation, and this lack of results for copper phosphine systems is maybe surprising given the ubiquitous role of P-donor ligands in virtually all catalysis with late transition metals. We have a long standing interest in the application of small bite angle diphosphines as ligands for catalysis and have previously shown that such ligands can lead to active systems in, for example, olefin polymerization with late transition metals, another area where hard donors dominate.[7] We describe here the synthesis of a range of copper(I) diphosphine complexes and their screening for the amidation of aryl halides.

2. Results and Discussion

A focused library of diphosphine ligands was targeted in which the chelate length is systematically varied and an *ortho* aryl substitutent added (Figure 1). The latter factor proved to be crucial in previous catalysis with such ligands.[7,8] We also utilized the related *N,N*-bis(diarylphosphino)amines, which have a track record of success in other reactions often associated with harder donor sets.[8]

2.1. Synthesis of Copper Diphosphine Complexes: 13−24. Copper diphosphine complexes with the general stoichiometries $[\mathbf{L}CuCl]_n$ (n = 1−3), $[\mathbf{L}(CuCl)_2]$, or $[\mathbf{L}_2Cu]Cl$ were synthesized in a straightforward manner by reaction of ligand with CuCl in toluene (Scheme 1), with products being obtained as white or off-white microcrystalline solids in moderate to good yields (48−96%). One equivalent of

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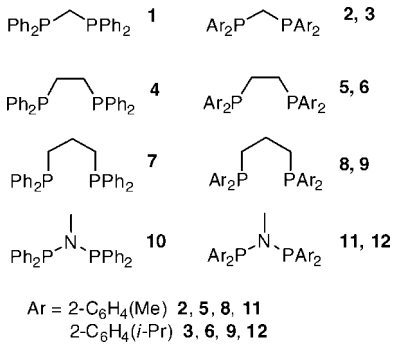

Figure 1. Diphosphine ligand library.

Scheme 1. Complex Synthesis

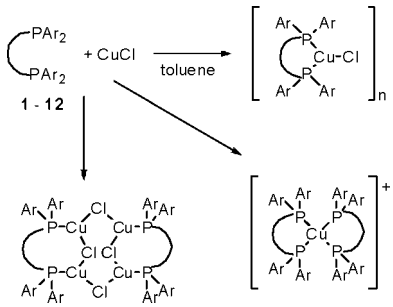

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 13

Cu1−Cl1	2.4490(11)	Cu3−P4	2.2966(11)
Cu1−Cl2	2.3848(11)	Cu3−P6	2.2513(11)
Cu1−P1	2.2680(12)	Cu1−Cl1−Cu2	74.28(4)
Cu1−P3	2.2524(10)	Cu1−Cl2−Cu2	75.78(3)
Cu2−Cl1	2.4212(11)	Cu1−Cl2−Cu3	103.34(4)
Cu2−Cl2	2.4032(12)	Cu2−Cl2−Cu3	105.82(4)
Cu2−P2	2.2302(11)	P1−C1−P2	112.62(18)
Cu2−P5	2.2295(11)	P3−C26−P4	116.02(17)
Cu3−Cl2	2.4697(11)	P5−C51−P6	113.58(18)
Cu3−Cl3	2.3055(11)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 16

Cu1−Cl1	2.4027(19)	Cu2−P2	2.2463(19)
Cu1−Cl2	2.436(2)	Cu2−P3	2.235(2)
Cu2−Cl1	2.409(2)	Cu3−P4	2.214(2)
Cu2−Cl2	2.374(2)	Cu3−P6	2.231(2)
Cu3−Cl3	2.2134(19)	P1−C13−C14−P2	−112.6(4)
Cu1−P1	2.2401(19)	P3−C39−C40−P4	172.4(4)
Cu1−P5	2.2351(19)	P5−C65−C66−P6	166.7(3)

diphosphine ligand per copper was used in each case, even though this did not always lead to the expected stoichiometry for the final product.

In general, elemental analyses data are consistent with the formation of complexes of the type $[\mathbf{L}CuCl]_n$. It has been reported that such complexes (specifically **13** and **16**) are not simple mononuclear species, the number of copper atoms being sensitive to both ligand effects and solvent in solution.[9] It therefore seems likely that higher nuclearity species are formed; X-ray crystallography (see below) and mass spectrometry show this is the case. Ligand **3** does not react smoothly with copper(I) chloride to give a $[(\mathbf{3})CuCl]_n$ complex. After mixing ligand **3** with copper(I) chloride in toluene at room temperature the ^{31}P NMR spectrum shows a broad peak at δ −22.0 indicating copper complexation, but a large amount of unreacted ligand is also present (δ −49.5). Heating this mixture at reflux for several days resulted in no change to the product distribution, but the addition of a further equivalent of copper(I) chloride led to the consumption of the remaining free ligand. Elemental analysis and mass spectrometry suggest a complex (**15**) with the composition $[(\mathbf{3})_2Cu_4Cl_4]$ in the solid state (see Experimental Section). 1,3-Bis(diphenylphosphino)propane (**7**) also does not react to give the complex [(**7**)CuCl]. In this case two broad resonances are observed in the ^{31}P NMR spectrum, in line with the report of Pettinari et al., proposing this is due to an equilibrium between $[(\mathbf{7})_2Cu_2(\mu\text{-}Cl)_2]$ and $[(\mathbf{7})_2Cu]Cl$.[10] Elemental analysis and electrospray mass spectrometry confirm the presence of $[(\mathbf{7})_2Cu]Cl$ (**19**).

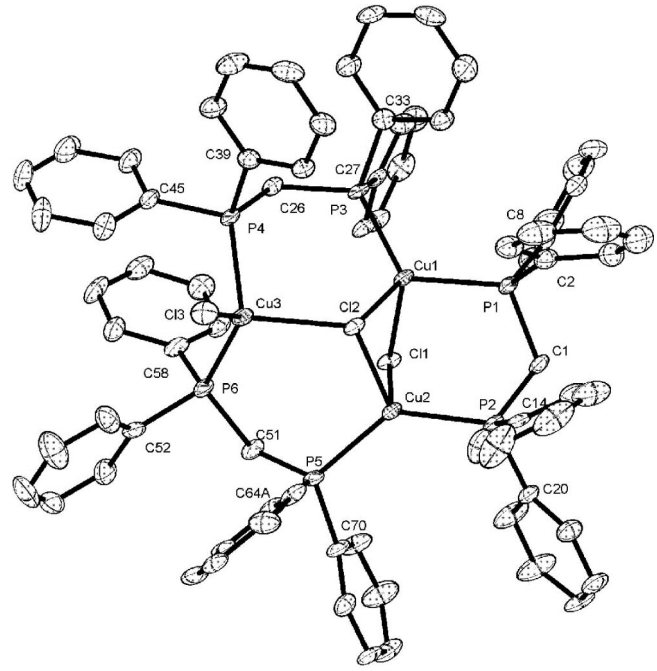

Figure 2. Crystal structure of $[(Ph_2PCH_2PPh_2)CuCl]_3$ (**13**). Hydrogens and solvent are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 14

Cu1−Cl1	2.2316(15)	Cu1−P1−C1−C2	−56.3(4)
Cu1−P1	2.2524(14)	Cu1−P1−C8−C9	178.4(4)
Cu1−P3	2.2490(15)	Cu2−P2−C16−C17	−175.4(4)
Cu2−Cl2	2.2327(14)	Cu2−P2−C23−C24	79.4(4)
Cu2−P2	2.2623(14)	Cu1−P3−C30−C31	71.6(4)
Cu2−P4	2.2746(15)	Cu1−P3−C37−C38	−172.7(4)
P1−Cu1−P3	118.87(6)	Cu2−P4−C45−C46	174.4(4)
P2−Cu2−P4	119.32(5)	Cu2−P4−C52−C53	−59.1(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 17

Cu1−Cl1	2.1697(17)	P1−C1−C2−P2	49.0(7)
Cu1−P1	2.2471(16)	Cu1−P1−C3−C4	23.25.4(6)
Cu1−P2	2.2617(18)	Cu1−P1−C10−C11	−67.0(5)
P1−Cu1−P2	92.98(6)	Cu1−P2−C17A−C18A	−13.7(10)
C17A−P2−C24A	103.8(5)	Cu1−P2−C24A−C25A	−69.0(5)

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 23

Cu1−Cu2	2.7750(13)	Cl1−Cu1−Cl3	105.44(4)
Cu1−Cu3	2.8699(10)	Cl1−Cu2−Cl4	95.31(4)
Cu2−Cu4	2.8726(9)	Cl2−Cu2−Cl4	91.22(5)
Cu3−Cu4	2.7526(13)	Cl1−Cu2−Cl2	85.75(4)
Cu1−Cl1	2.3045(10)	Cl2−Cu3−Cl3	105.57(4)
Cu1−Cl3	2.2932(14)	Cl2−Cu4−Cl4	94.78(4)
Cu2−Cl1	2.4982(12)	P1−N1−P2	121.60(14)
Cu2−Cl4	2.3393(10)	P3−N2−P4	120.36(14)
Cu2−Cl2	2.5579(13)	Cu1−P1−C2−C3	42.9(3)
Cu3−Cl2	2.3414(12)	Cu1−P1−C9−C10	62.9(2)
Cu3−Cl3	2.3355(10)	Cu2−P2−C16−C17	65.4(3)
Cu4−Cl2	2.4490(10)	Cu2−P2−C23−C24	46.9(3)
Cu4−Cl4	2.3085(13)	Cu3−P3−C31−C32	58.5(3)
Cu1−P1	2.1756(10)	Cu3−P3−C38−C39	44.3(3)
Cu2−P2	2.1920(10)	Cu4−P4−C45−C46	28.9(3)
Cu3−P3	2.1866(10)	Cu4−P4−C52−C53	75.4(3)
Cu4−P4	2.1867(9)		

The reactivity patterns for bis(diarylphosphino)methylamine ligands are similarly complex. The *ortho* tolyl derivative for which we were able to obtain structural characterization (**23**) is confirmed to have four copper chloride units and a ligand:Cu ratio of 0.5 in the solid state. Other analysis is consistent with this formulation. Electrospray mass spectrometry suggests other derivatives to have trimeric or tetrameric structures. We have had difficulty in obtaining satisfactory elemental analysis for these derivatives (data presented in Experimental Section for information), which we propose is due to contamination with small amounts of substoichiometric ligand:Cu species.

Providing a general rationale for the observed reactivity and structural patterns is challenging, as remarked in previous studies.[11] Less sterically encumbered, smaller bite-angle ligands tend to form lower nuclearity species, although the interplay of these factors is difficult to predict. Increasing steric bulk also leads the copper atoms to adopt a more linear arrangement. The influence of cuprophilic interactions also cannot be ruled out.[12] It should also be noted that although these chloride complexes are useful models in defining general trends, it is the amide derivatives, formed under catalytic conditions, which are believed to be the active species.

2.1.1. Crystal Structure of $[(Ph_2PCH_2PPh_2)CuCl]_3 \cdot 2C_2H_4Cl_2$ (13). The dichloroethane solvate **13** crystallizes in the space group $P\bar{1}$ and has one molecule of complex and two of dichloroethane in the asymmetric unit. The complex consists of a triangle of copper(I) atoms, each edge of which is bridged by a bis(diphenylphosphino)methane (dppm) ligand, creating

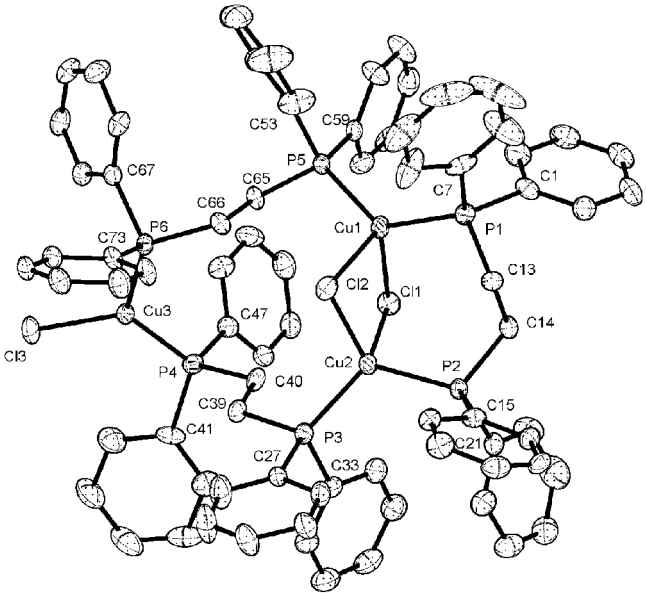


Figure 3. Crystal structure of $[(Ph_2PCH_2CH_2PPh_2)CuCl]_3$ (**16**) (hydrogens omitted for clarity).

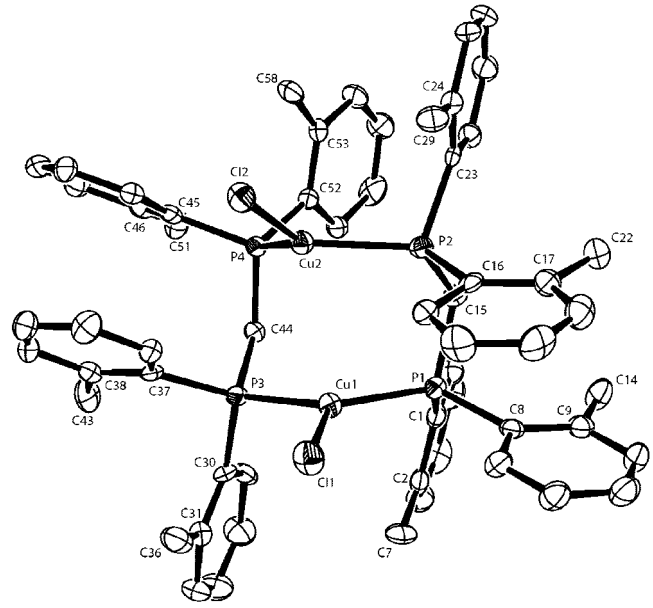


Figure 4. Crystal structure of $[(Ar_2PCH_2PAr_2)CuCl]_2$ {Ar = 2-C_6H_4(Me)} (**14**) (hydrogens and solvent omitted for clarity).

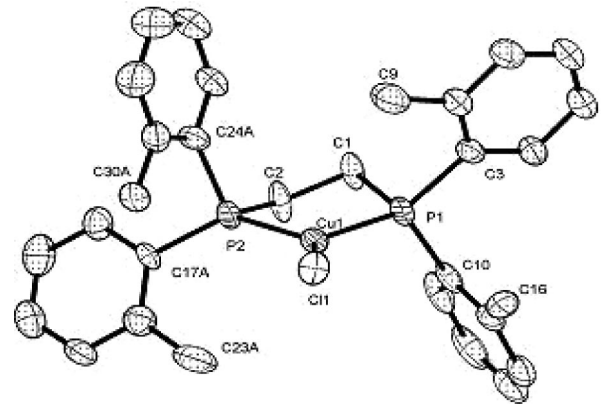


Figure 5. Crystal structure of $[(Ar_2PCH_2CH_2PAr_2)CuCl]$ {Ar = 2-C_6H_4(Me)} (**17**) (hydrogens omitted for clarity).

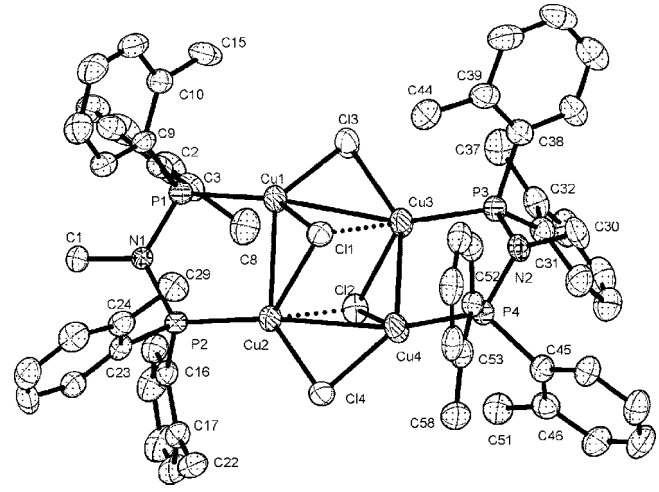
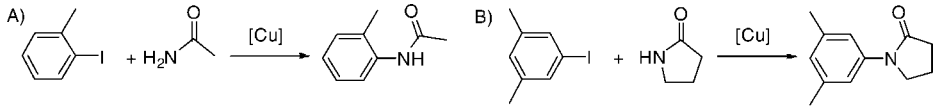


Figure 6. Crystal structure of $[(Ar_2PN(Me)PAr_2)Cu_2Cl_2]_2$ {Ar = 2-C_6H_4(Me)} (**23**) (hydrogens and solvent omitted for clarity).

Table 6. Catalytic Amidation Results



run[a]	catalyst	yield[b] (%)	run[a]	catalyst	yield[b] (%)
1	**13**	10	18[c]	CuI +**9**	6
2[c]	CuI + **1**	11	19	**22**	9
3	**14**	11	20[c]	CuI + **10**	34
4[c]	CuI + **2**	15	21[d]	CuI + **10** + Et_3N	29
5	**15**	10	22	**23**	14
6[c]	CuI + **3**	10	23[c]	CuI + **11**	18
7	**16**	6	24	**24**	13
8[c]	CuI + **4**	7	25[c]	CuI + **12**	10
9	**17**	5	26[c]	CuI + $Me(H)N(CH_2)_2N(H)Me$	80
10[c]	CuI + **5**	11	27	CuI	8
11	**18**	11	28[e]	CuCl + **10**	40
12[c]	CuI + **6**	6	29	CuCl	5
13	**19**	6	30[c]	CuI + **25**	37
14[c]	CuI + **7**	2	31[c]	CuI + **26**	28
15	**20**	10	32[c]	CuI + **27**	7
16[c]	CuI + **8**	8	33[f]	CuI + **10**	34
17	**21**	6	34[f]	CuI + **25**	31

[a] Conditions: Reaction A: 2-iodotoluene (1.0 mmol), acetamide (1.5 mmol), K_3PO_4 (2.0 mmol), complexes **13**−**24** (0.05 mmol), 1 mL of DMF, 80 °C, 23 h. [b] Determined by GC, average of two runs. [c] Reaction A: As run 1 only CuI (0.05 mmol), ligands **1**−**12**, **25**−**27** (0.1 mmol). [d] Reaction A: As run 1 only CuI (0.05 mmol), ligand **10** (0.05 mmol), Et_3N (0.5 mmol). [e] Reaction A: As run 1 only CuCl (0.05 mmol) and ligand **10** (0.1 mmol). [f] Reaction B: 1,3-Dimethyl-5-iodobenzene (1.0 mmol), 2-pyrrolidinone (1.5 mmol), K_3PO_4 (2.0 mmol), ligands **10**, **25** (0.1 mmol), CuI (0.05 mmol), 1 mL of toluene, 80 °C, 23 h.

Table 7. Crystallographic Details

	13·$2C_2H_4Cl_2$	**14**·$2C_2H_4Cl_2$	**16**	**17**	**23**·$3CH_2Cl_2$
color, habit	colorless block	colorless plate	colorless irregular block	colorless flat stalk	colorless block
size/mm	0.10 × 0.08 × 0.04	0.40 × 0.40 × 0.10	0.4 × 0.3 × 0.3	0.20 × 0.07 × 0.01	0.5 × 0.4 × 0.4
empirical formula	$C_{79}H_{74}Cl_7Cu_3P_6$	$C_{62}H_{68}Cl_6Cu_2P_4$	$C_{78}H_{72}Cl_3Cu_3P_6$	$C_{30}H_{32}ClCuP_2$	$C_{61}H_{68}Cl_6Cu_4N_2P_4$
M	1647.97	1276.82	1492.15	553.49	1561.83
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	13.596(3)	11.886(2)	26.080(4)	9.0865(18)	14.551(3)
b/Å	14.178(3)	12.866(2)	15.074(3)	21.048(4)	14.640(3)
c/Å	19.478(4)	22.334(4)	19.347(5)	14.503(3)	16.927(3)
α/deg	90.24(3)	81.31(4)	90	90	86.56(3)
β/deg	90.30(3)	78.59(5)	109.63(3)	100.17(3)	79.15(3)
γ/deg	90.96(3)	63.63(4)	90	90	64.59(3)
V/Å^3	3754.2(13)	2991.6(9)	7164(3)	2730.1(10)	3198.1(14)
Z	2	2	4	4	2
μ/mm^{-1}	4.822	1.125	1.171	1.032	1.7
T (K)	100	173	100	100	173
reflns: total/indep/R_{int}	29 546/12 807/0.0592	26 598/10 544/0.0962	80 379/16400/0.0789	30 759/6252/0.1357	34 227/14 518/0.0477
final R_1 and wR_2	0.0530, 0.1503	0.0532, 0.1114	0.0841, 0.2210	0.0921, 0.1774	0.0432, 0.0957
largest peak, hole	1.235, −0.687	0.474, −0.510	1.764, −0.683	0.680, −0.500	0.549, −0.615
ρ_{calc}/g cm^{-3}	1.458	1.42	1.384	1.347	1.445

a 12-membered-ring structure (Figure 2, Table 1). The structure also contains three chloride ligands: one terminal (Cl3) coordinated to Cu3, one that bridges Cu1 and Cu2 (Cl1), and one that bridges all three copper atoms (Cl2), so that all three copper atoms are tetrahedrally coordinated. The three dppm ligands, the three copper atoms, and the μ_3-bridging chloride make a fused ring system containing three six-membered rings. The ring containing Cu1, Cu3, P3, and P4 adopts a chair conformation, as does that containing Cu1, Cu2, P1, and P2, which also has the μ^2-1,3-bridging chloride. The third ring, containing Cu2, Cu3, P5, and P6 adopts an envelope conformation where five of the atoms are essentially planar and the sixth atom (P5) lies out of this plane. The Cu−Cl bond lengths vary from 2.31 Å (Cu3−Cl3) to 2.47 Å (Cu3−Cl2).

2.1.2. Crystal Structure of [($Ph_2PCH_2CH_2PPh_2$)CuCl]$_3$ (16). Complex **16** has a similar coordination geometry to **13**; each pair of the three copper(I) atoms is bridged by a bis(diphenylphosphino)ethane (dppe) ligand (Figure 3, Table 2). However, the different bridging ligand (dppe in **16**, cf. dppm in **13**) and the extended conformation it adopts result in long Cu3···Cu distances and two μ_2-bridging chlorides on the Cu1···Cu2 edge of the Cu_3 triangle. Both Cu1 and Cu2 are tetrahedrally coordinated, while Cu3, which is trigonal, carries one terminal chloride ligand. The C_2 backbones of the two dppe ligands complexed to Cu3 both have *anti* conformations (P3−C39−C40−P4 = 172° and P5−C65−C66−P6 = 167°), whereas the dppe ligand bridging Cu1 and Cu2 adopts a distorted *gauche* conformation (P1−C13−C14−P2 = −113°). The Cu−Cl bond length of the terminal chloride is much shorter (2.21 Å) than the equivalent bond length in the crystal structure of **13** and is likely a reflection of the lower coordination number of the copper(I) in **16**.

2.1.3. Crystal Structure of [($Ar_2PCH_2PAr_2$)CuCl]$_2$·$2C_2H_4Cl_2$ {Ar = 2-C_6H_4(Me)} (14). The crystal structure of the dichloroethane solvate **14** has the space group $P\bar{1}$ with one molecule of complex and two molecules of dichloroethane in

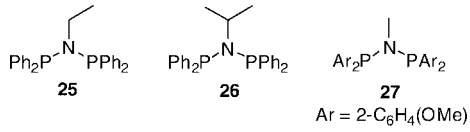


Figure 7. *N,N*-Bis(diarylphosphino)amine ligands used.

the asymmetric unit. In this structure, the two diphosphine ligands bridge a pair of copper(I) atoms, forming an eight-membered ring (Figure 4, Table 3). Each copper carries one terminal chloride ligand, and trigonal coordination results. The Cu−Cl bond lengths are both around 2.23 Å. All four di-*o*-tolylphosphino moieties are oriented such that one *o*-tolyl is close to *anti* and one is close to *gauche* with respect to the metal.

2.1.4. Crystal Structure of [(Ar$_2$PCH$_2$CH$_2$PAr$_2$)CuCl] {Ar = 2-C$_6$H$_4$(Me)} (17). Complex **17** contains a trigonal copper(I) atom coordinated by terminal chloride and chelating dppe derivative ligands (Figure 5, Table 4). The five-membered chelate ring adopts a δ twist conformation, with the torsion angle P1−C1−C2−P2 = 49°. Both *o*-tolyl groups on P2 are disordered and have been modeled as lying over two orientations about the P−C bond. One *o*-tolyl ring (C17) is disordered such that the torsion angle Cu−P2−C17−C18 is either −14° (about 67%) or 174° (the remainder). The tolyl group at C24 shows a slight disorder, which probably results from the disorder in the neighboring tolyl group. The two tolyl groups on P1 have torsion angles Cu1−P1−C3−C4 and Cu1−P1−C10−C11 = −25° and −67°. The Cu−Cl bond length is 2.17 Å, which is shorter than the terminal chloride bond lengths in either **13** or **16**.

2.1.5. Crystal Structure of [(Ar$_2$PN(Me)PAr$_2$)Cu$_2$Cl$_2$]$_2$·3CH$_2$Cl$_2$ {Ar = 2-C$_6$H$_4$(Me)} (23). The dichloromethane solvate **23** crystallizes in the space group $P\bar{1}$ with one molecule of complex and approximately three molecules of dichloromethane in the asymmetric unit. The complex consists of a distorted octahedron of four copper(I) atoms and two chloride atoms, with the four copper atoms in one plane and the chlorides in apical sites (Figure 6, Table 5). Pairs of copper atoms on each edge around the plane are bridged either by a further chloride or by a diphosphine ligand. The two chlorine atoms that lie at the apexes of the octahedron are not fully coordinated to all four copper atoms; the Cu−Cl distances vary from 2.30 to 3.19 Å, the latter being beyond a normal bond length. Both of these chloride atoms have two "short" Cu−Cl distances (in the range 2.30−2.50 Å) and two longer distances. The Cu−Cu distances vary from 2.75 to 2.87 Å, close to twice the van der Waals radius of copper. The nitrogen that links the phosphorus atoms in the bridging diphosphine ligand is planar (N2 sum of angles around nitrogen 360.0°) or very close to planar (N1, 358.9°), indicating delocalization of the lone pair.

2.2. Catalytic C−N Bond Formation. As a test reaction, the catalytic coupling of 2-iodotoluene and acetamide under previously reported conditions was screened with complexes **13**−**24**.[5b] In order to benchmark our systems against known catalysts, runs in which a methodology reminiscent of these previous reports, formation of a catalyst *in situ* with CuI and ligands **1**−**12**, were also attempted. Although the structural chemistry of copper(I) iodide complexes is likely to be different from copper(I) chloride complexes of the same ligands, in both cases halide must be replaced to generate the Cu(I) monoamidinate species, which Buchwald and co-workers have demonstrated to be the active catalysts in such reactions.[5c] Our results (*vide infra*) and those of others with N-donor ligands indicate the same trend in results irrespective of the halide used, suggesting the same active species is formed in either case. Results are presented in Table 6.

With one notable exception, similarly low activity is seen in all cases, in general preformed complexes **13**−**24** giving 5−14% yields and *in situ* catalysts 2−18%. The similarity of these values across a range of ligand structures leads to the conclusion that catalysis is not being influenced by these particular ligands,[6] corroborated by the similar result obtained in run 27, when only CuI is used (8%). The exception to this trend is the *N,N*-bis(diphenylphosphino)amine ligand **10** (run 20), which, when reacted with CuI *in situ*, gives an improved yield of 34%. This is double the figure of merit for other ligands, although still some way short of the value obtained with the previously reported diamine catalysts (run 26). Changing the metal salt to CuCl (run 28) gives a yield of 40%. This is similar to the CuI result, suggesting the same active species is formed in each case, and is again significantly higher than the metal salt alone (run 29: 5%). Performance being independent of halide used is in line with previous studies for copper diamine systems.[5b] The reason for the higher activity of a catalyst system formed *in situ* compared to using the preformed complex **22** is not clear, although solubility issues cannot be ruled out. Increasing the *ortho* aryl steric bulk of this diphosphine in **11** again yields a catalyst in which ligand control is not exerted. Experiments in which 1 equiv of **10** was used in conjunction with 1 equiv of triethylamine rather than 2 equiv of **10** gave similar results (run 21).

This promising result for ligand **10** led us to screen several other *N,N*-bis(diarylphosphino)amines (Figure 7). Similar results are obtained in the amidation of an aryl iodide as the N-substituent of the ligand is increased in bulk (runs 30−31); however, increasing the bulk of the P-aryl *ortho* substituent has a detrimental effect on catalysis, results now matching the ligand-free system (run 32). Ligands **10** and **25** were also found to be active in amidation reaction B (Table 6, runs 33−34).

3. Conclusions

Copper complexes of *N,N*-bis(diphenylphosphino)amine ligands show moderate activity for amidation reactions, the first reported copper phosphine systems to do so. This is in contrast to other diphosphines which give only, within error, the same yields achieved in the absence of any phosphine. It is noteworthy that *N,N*-bis(diphenylphosphino)amines are also the most successful diphosphines for nickel-catalyzed ethene polymerization, another area where hard donor ligands predominate. We have previously ascribed the distinctive performance of these ligands to a combination of their small and rigid chelates and their unusual electronic structure, the formal lone pair of the backbone nitrogen being delocalized over the entire P−N−P backbone. Buchwald and co-workers have demonstrated that chelating ligands are crucial in their systems by preventing multiple amidation and facilitating the formation of the active Cu(I) monoamidinate species. It is plausible that the role of the diphosphine ligand in this study is similarly to generate a Cu(I) monoamidinate species under catalytic conditions. Given the variations in structure observed for copper(I) chloride complexes by subtle modification of the diphosphine used, the specific ligand utilized is likely to have a crucial role in this regard.

4. Experimental Section

4.1. General Comments. All procedures were carried out under an inert (N_2) atmosphere using standard Schlenk line techniques or in an inert atmosphere (Ar) glovebox. Chemicals were obtained

from Sigma Aldrich, Fisher Scientific, Acros, Fluka, or Alfa Aesar and used without further purification unless otherwise stated. All solvents were purified using an Anhydrous Engineering Grubbs-type solvent system.[13] Ligands **1**, **4**, and **7** are commercially available. Ligands **2**, **3**, **5**, **6**, **8**−**12**, and **25**−**27** were synthesized according to previously published methods.[8]

NMR spectra were recorded on JEOL GX270, ECP 300, Lambda 300, or GX400 spectrometers, ^{1}H NMR chemical shifts are referenced relative to the residual solvent resonances in the dueterated solvent, and ^{31}P{^{1}H} NMR spectra are referenced relative to high frequency of 85% H_3PO_4. Mass spectra were recorded on a VG Analytical Quattro spectrometer. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol.

4.2. Synthesis of Copper(I) Diphosphine Chloride Complexes: 13−24. Synthesis of [(Ph$_2$PCH$_2$PPh$_2$)CuCl] (13). A solution of **1** (373 mg, 0.97 mmol) in toluene (20 mL) was added to solid copper(I) chloride (96 mg, 0.97 mmol), and the resulting mixture was stirred for 20 h at room temperature. During this time a white precipitate formed. The solvent was removed under reduced pressure to give a pale pink solid. **13** was obtained by recrystallization from a mixture of toluene and hexane as a white microcrystalline solid. This was isolated by filtration, washed with 2 × 5 mL of hexane, and dried *in vacuo*. Yield: 469 mg, 75%. X-ray-quality crystals of [(**1**)$_3$Cu$_3$Cl$_3$]·2C$_2$H$_4$Cl$_2$ were formed from 1,2-dichloroethane/hexane.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.21 (s, 2H, CH_2), 6.95 (m, 8H, ArH), 7.11 (m, 12H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −14.4 (s). Anal. Calcd for $C_{25}H_{22}CuClP_2$ (%): C 62.1, H 4.6. Found: C 58.6, H, 4.5. This composition is consistent with the empirical formula $C_{25}H_{22}CuClP_2 \cdot 0.5C_2Cl_2H_4$ (C 58.6, H 4.5), 0.5 mol of solvent present for every mol of [(**1**)CuCl] in the crystal structure. MS (ESI): 1413 [(**1**)$_3$Cu$_3$Cl$_2$]$^+$.

Synthesis of [(2-C$_6$H$_4$(Me))$_2$PCH$_2$P(2-C$_6$H$_4$(Me))$_2$)CuCl] (14). This was synthesized in essentially the same way as complex **13** using ligand **2** (200 mg, 0.45 mmol) and copper(I) chloride (45 mg, 0.45 mmol) to give **14** as a white microcrystalline solid. Yield: 230 mg, 76%. X-ray-quality crystals of [(**2**)$_2$Cu$_2$Cl$_2$]·2C$_2$H$_4$Cl$_2$ were formed from 1,2-dichloroethane/hexane.

^{1}H NMR (CDCl$_3$, 270 MHz): δ 1.66 (v br, 8H, ArCH_3), 2.03 (br, 4H, ArCH_3), 3.62 (br, 2H, CH_2), 6.64−7.43 (br m, 16H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −18.4 (s). Anal. Calcd for $C_{29}H_{30}CuClP_2$ (%): C 64.6, H 5.6. Found: C 59.9, H 5.4. This composition is consistent with the empirical formula $C_{29}H_{30}CuClP_2 \cdot 0.75C_2Cl_2H_4$ (C 59.7, H 5.4), 1,2-dichloroethane present in the crystal structure. MS (ESI): 1043 [(**2**)$_2$Cu$_2$Cl]$^+$.

Synthesis of [(2-C$_6$H$_4$(*i*-Pr))$_2$PCH$_2$P(2-C$_6$H$_4$(*i*-Pr))$_2$)Cu$_2$Cl$_2$] (15). A solution of **3** (106 mg, 0.19 mmol) in toluene (15 mL) was added to solid copper(I) chloride (19 mg, 0.19 mmol), and the resulting mixture was stirred for 20 h at room temperature. The reaction was monitored by ^{31}P{^{1}H} NMR, which showed a large amount of unreacted ligand (δ = −49.5 (s), −22.0 (br, s)). The mixture was heated at reflux for several days without any change in the ^{31}P NMR spectrum. The solvent was removed under reduced pressure, and the resulting solid was washed with hexane to remove the excess ligand. The white solid **15** was dried *in vacuo*. Yield: 45 mg, 63%.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.66 (d, 12H, CH(CH_3)$_2$), 0.85 (d, 12H, CH(CH_3)$_2$), 3.16 (t, 2H, CH_2), 3.70 (m, 4H, CH(CH$_3$)$_2$) 6.91 (t, 4H, ArH), 7.10−7.40 (m, 10H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −17.7 (s, br). Anal. Calcd for $C_{37}H_{46}Cu_2Cl_2P_2$ (%): C 59.2, H 6.2. Found: C 60.6, H 6.4. MS (ESI): 1465 [(**3**)$_2$Cu$_4$Cl$_3$]$^+$.

Synthesis of [(Ph$_2$P(CH$_2$)$_2$PPh$_2$)CuCl] (16). This was synthesized in essentially the same way as complex **13** using ligand **4** (415 mg, 1.04 mmol) and copper(I) chloride (103 mg, 1.04 mmol) to give **16** as a white solid. Yield: 495 mg, 96%. X-ray-quality crystals of [(**4**)$_3$Cu$_3$Cl$_3$] were formed by cooling a toluene solution of **16**. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.43 (br, 4H, CH_2), 7.09 (m, 8H, ArH); 7.21 (m, 12H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −9.8 (s). Anal. Calcd for $C_{26}H_{24}CuClP_2$ (%): C 62.8, H 4.9. Found: C 65.4, H 5.1. MS (ESI): 959 [(**4**)$_2$Cu$_2$Cl]$^+$, 859 [(**4**)$_2$Cu]$^+$.

Synthesis of [(2-C$_6$H$_4$(Me))$_2$P(CH$_2$)$_2$P(2-C$_6$H$_4$(Me))$_2$)CuCl] (17). A solution of **5** (153 mg, 0.34 mmol) in toluene (5 mL) was added to a suspension of copper(I) chloride (33 mg, 0.34 mmol) in toluene (5 mL). The mixture was stirred overnight, and during this time a white solid precipitated. The solid was isolated by filtration, washed with hexane (2 × 5 mL), and dried *in vacuo* to give **17** as a white solid. Yield: 115 mg, 62%. X-ray-quality crystals of [(**5**)CuCl] were formed by cooling a toluene solution of **17**.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.35 (t, 4H, CH_2), 2.43 (s, 12H, ArCH_3), 7.11 (m, 8H, ArH), 7.26 (m, 8H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −28.7 (s). Anal. Calcd for $C_{30}H_{32}CuClP_2$ (%): C 65.1, H 5.8. Found: C 65.0 H 5.7. MS (ESI): 1071 [(**5**)$_2$Cu$_2$Cl]$^+$.

Synthesis of [(2-C$_6$H$_4$(*i*-Pr))$_2$P(CH$_2$)$_2$P(2-C$_6$H$_4$(*i*-Pr))$_2$)CuCl] (18). This was synthesized in essentially the same way as complex **13** using ligand **6** (201 mg, 0.35 mmol) and copper(I) chloride (35 mg, 0.35 mmol) to give **18** as a white microcrystalline solid. Yield: 142 mg, 61%.

^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.88 (d, 12H, CH(CH_3)$_2$), 0.96 (d, 12H, CH(CH_3)$_2$), 2.33 (t, 4H, CH_2), 3.71 (m, 4H, CH(CH$_3$)$_2$), 7.09 (m, 4H, ArH), 7.28 (m, 12H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −31.7 (s). Anal. Calcd for $C_{38}H_{48}CuClP_2$ (%): C 68.6, H 7.3. Found: C 68.4, H 7.2. MS (ESI): 1353 Na$^+$[(**6**)$_2$Cu$_2$Cl$_2$], 1295 [(**6**)$_2$Cu$_2$Cl]$^+$.

Synthesis of [(Ph$_2$P(CH$_2$)$_3$PPh$_2$)$_2$Cu]Cl (19). A solution of **7** (223 mg, 0.54 mmol) in toluene (20 mL) was added to solid copper(I) chloride (53 mg, 0.54 mmol), and the resulting mixture was stirred for 4 h. The solvent was removed under reduced pressure, and the residue was triturated with diethyl ether (2 × 10 mL) to give **19** as a white solid. **19** was recrystallized from hot acetonitrile. Yield: 235 mg, 94%.

^{1}H NMR (CDCl$_3$, 270 MHz): δ 1.83 (br, 2H, CH_2), 2.38 (br, 4H, PCH_2), 7.10−7.79 (m, 20H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −5.0 (br), –12.0 (br). Anal. Calcd for $C_{54}H_{52}CuClP_4$ (%): C 70.2, H 5.7. Found: C 70.5, H 5.6. MS (ESI): 887 [(**7**)$_2$Cu]$^+$.

Synthesis of [(2-C$_6$H$_4$(Me))$_2$P(CH$_2$)$_3$P(2-C$_6$H$_4$(Me))$_2$)CuCl] (20). This was synthesized in essentially the same way as complex **17** using ligand **8** (100 mg, 0.213 mmol) and copper(I) chloride (21 mg, 0.213 mmol) to give **20** as a white solid. Yield: 90 mg, 74%.

^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 1.92 (m, 2H, CH_2), 2.37 (apparent s, 16H, ArCH_3, and PCH_2 obscured), 7.11−7.31 (m, 16H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −27.9 (s). Anal. Calcd for $C_{31}H_{34}CuClP_2$ (%): C 65.6, H 6.0. Found: C 65.6, H 6.2. MS (ESI): 1099 [(**8**)$_2$Cu$_2$Cl]$^+$, 631 [(**8**)Cu$_2$Cl]$^+$, 531 [(**8**)Cu]$^+$.

Synthesis of [(2-C$_6$H$_4$(*i*-Pr))$_2$P(CH$_2$)$_3$P(2-C$_6$H$_4$(*i*-Pr))$_2$)CuCl] (21). This was synthesized in essentially the same way as complex **17** using ligand **9** (226 mg, 0.389 mmol) and copper(I) chloride (39 mg, 0.389 mmol) to give **21** as a white solid. Yield: 238 mg, 90%.

^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.84 (d, 12H, CH(CH_3)$_2$), 1.01 (d, 12H, CH(CH_3)$_2$), 2.03 (m, 2H, CH_2), 2.46 (br s, 4H, PCH_2), 3.68 (m, 4H, CH(CH$_3$)$_2$), 7.11−7.46 (m, 16H, ArH). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): δ −28.1 (s). Anal. Calcd for $C_{39}H_{50}CuClP_2$

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(%): C 68.9, H 7.4. Found: C 71.5, H 7.7. This composition is consistent with the empirical formula $C_{39}H_{50}CuClP_2 \cdot C_7H_8$ (C 71.5, H 7.7) with toluene observed in the ^{1}H NMR spectrum. MS (ESI): 1323 $[(\mathbf{9})_2Cu_2Cl]^+$.

Synthesis of [(Ph$_2$PN(Me)PPh$_2$)CuCl] (22). This was synthesized in essentially the same way as complex **17** using ligand **10** (100 mg, 0.25 mmol) and copper(I) chloride (25 mg, 0.25 mmol) to give **22** as a white solid. Yield: 60 mg, 48%.

^{1}H NMR ($CDCl_3$, 270 MHz): δ 1.98 (br, 3H, NCH_3), 6.99−7.30 (m, 20H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 58.5 (s); Anal. Calcd for $C_{25}H_{23}CuClNP_2$ (%): C 60.3, H 4.7, N 2.8. Found: C 58.4, H 4.8, N 2.8. MS (ESI): 1458 $[(\mathbf{10})_3Cu_3Cl]^{2+}$.

Synthesis of [(2-C$_6$H$_4$(Me))$_2$PN(Me)P(2-C$_6$H$_4$(Me))$_2$)CuCl] (23). Reaction in toluene: This was synthesized in essentially the same way as **17** using **11** (54 mg, 0.12 mmol) and copper(I) chloride (12 mg, 0.12 mmol) to give **23** as a pale yellow solid. Yield: 39 mg, 59%. X-ray-quality crystals of $[(\mathbf{11})_2Cu_4Cl_4] \cdot 3CH_2Cl_2$ were formed from dichloromethane.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.09 (br, 6H, ArCH_3), 2.30 (br, 6H, ArCH_3), 2.82 (br, 3H, NCH_3), 6.83−7.42 (br m, 16H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 55.7 (s). Anal. Calcd for $C_{29}H_{31}CuCl_2NP_2$ (%): C 59.0, H 5.3, N 2.4. Found: C 59.8, H 5.7, N 2.7. MS (ESI): 1271 $[(\mathbf{11})_2Cu_4Cl_3]^+$, 973 $[(\mathbf{11})_2Cu]^+$.

Synthesis of [(2-C$_6$H$_4$(*i*-Pr))$_2$PN(Me)P(2-C$_6$H$_4$(*i*-Pr))$_2$)CuCl] (24). A solution of **12** (70 mg, 0.123 mmol) in toluene (5 mL) was added to a solution of copper(I) chloride (12 mg, 0.123 mmol) in toluene, and the resulting mixture was stirred overnight. The solvent was removed under reduced pressure, and the residue was triturated with hexane (2 × 5 mL) to give **24** as a white solid. Yield: 64 mg, 74%.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.60−1.34 (br m, 24H, CH(CH_3)$_2$), 2.43−2.93 (br m, 3H, NCH_3), 3.24−3.82 (br m, 4H, CH(CH$_3$)$_2$), 6.74−7.58 (br m, 16H, ArH). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 61.9 (s). Anal. Calcd for $C_{37}H_{47}CuClNP_2$ (%): C 66.7, H 7.1, N 2.1. Found: C 64.6, H 7.5, N 2.0. MS (ESI): 1460 $[(\mathbf{12})_2Cu_4Cl_2]^{2+}$.

4.3. X-ray Crystallography. X-ray diffraction experiments on **16** and **17** were carried out at 100 K on a Bruker SMART APEX diffractometer, and experiments on **14** and **23** were carried out at 173 K on a Bruker SMART diffractometer, both using Mo Kα X-radiation (λ = 0.71073 Å). A Bruker PROTEUM diffractometer using Cu Kα radiation (λ = 1.54157 Å) was used for **13**. All experiments were performed using a single crystal coated in paraffin oil mounted on a glass fiber.[14] All three diffractometers used a CCD area detector, and intensities were integrated[15] from several series of exposures, each exposure covering 0.3° in ω. Absorption corrections were based on multiple and symmetry-equivalent measurements done with SADABS V2.10.[16] Structures were refined using SHELXTL[17] against all F_o^2 data with hydrogen atoms riding in calculated positions, with isotropic displacement parameters equal to 1.5 times (methyl hydrogen atoms) or 1.2 times (all other hydrogen atoms) that of their attached atom. Complex neutral-atom scattering factors were used.[18]

In **13**, one phenyl ring (C64−C69) is disordered and has been modeled as lying over two orientations. The displacement ellipsoids for one of the other phenyl rings (C14−C19) indicate that it may also be disordered, but no satisfactory model with two or more ring positions could be obtained. The chlorine atoms in one of the dichloroethane solvent molecules are also disordered and have been modeled as lying over two positions.

The crystal structure of **23** contained residual electron density that could not be satisfactorily identified and was modeled using the SQUEEZE algorithm incorporated into the PLATON suite. This found an extra 78 electrons in a void of 278 Å^3, which corresponds to approximately two further molecules of dichloromethane in the asymmetric unit in addition to one ordered solvent molecule. Except as discussed above, refinement proceeded smoothly to give the shown structures.

4.4. Catalytic Screening. Coupling of 2-Iodotoluene with Acetamide. A Schlenk tube was charged with acetamide (90 mg, 1.52 mmol) and K_3PO_4 (430 mg, 2.03 mmol). The tube was evacuated and backfilled with nitrogen several times, and then either copper(I) iodide (9.6 mg, 0.05 mmol) or copper(I) chloride (5.0 mg, 0.05 mmol) and the appropriate ligand (0.10 mmol) or the appropriate preformed copper(I) chloride complex (0.05 mmol) was added followed by 2-iodotoluene (128 μL, 1.01 mmol) and dimethylformamide (1.0 mL). The tube was heated to 80 °C, sealed, and stirred for 23 h. The resulting suspension was allowed to cool to room temperature and filtered through a 0.5 × 1 cm plug of silica gel, eluting with 10 mL of ethyl acetate. Mesitylene (139 μL, 1.00 mmol) was added as a standard, and the solution was analyzed by GC.

Coupling of 1,3-Dimethyl-5-iodobenzene with 2-Pyrrolidinone. A Schlenk tube was charged with copper(I) iodide (9.6 mg, 0.05 mmol) and K_3PO_4 (430 mg, 2.03 mmol). The tube was evacuated and backfilled with nitrogen several times, and the appropriate ligand (0.10 mmol) was added followed by 2-pyrrolidinone (116 μL, 1.52 mmol), 1,3-dimethyl-5-iodobenzene (146 μL, 1.01 mmol), and toluene (1.0 mL). The tube was heated to 80 °C, sealed, and stirred for 23 h. The resulting suspension was allowed to cool to room temperature and filtered through a 0.5 × 1 cm plug of silica gel, eluting with 10 mL of ethyl acetate. Mesitylene (139 μL, 1.00 mmol) was added as a standard, and the solution was analyzed by GC.

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Supporting Information Available: Crystallograpic data (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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