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Synthesis and characterization of three dinuclear copper(I) complexes of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane

Daopeng Zhang, Jianmin Dou*, Shuwen Gong, Dacheng Li and Daqi Wang

Department of Chemistry, Liaocheng University, Liaocheng 252059, People's Republic of China

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Three dinuclear copper(I) complexes, $[Cu_2(\mu\text{-}Cl)_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})_2]\cdot 2CH_2Cl_2$ (1), $[Cu_2(\mu\text{-}Br)_2(1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10})_2]\cdot 2THF$ (2) and $\{Cu_2(\mu\text{-}I)_2[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]_2\}$ (3) have been synthesized by the reactions of CuX (X = Cl, Br and I) with the *closo* ligand $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. All these complexes were characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopy and X-ray structure determination. Single crystal X-ray structure determinations show that every complex contained di-μ-X-bridged structure involving a crossed parallelogram plane formed by two Cu atoms and two X atoms (X = Cl, Br, I). The geometry at the Cu atom was a distorted tetrahedron, in which two positions were occupied by two P atoms of the PPh_2 groups connected to the two C atoms of carborane (Cc), and the other two resulted from two X atoms which bridged the other Cu atom at the same time. To the best of our knowledge, this is the first example of copper(I) complexes with 1,2-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane as ligand characterized by X-ray diffraction. The catalytic property of the complex 3 for the amination of iodobenzene with aniline was also investigated. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: synthesis and characterization; copper(I) complex; crystal structure; 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane; catalytic property

INTRODUCTION

Organic or organo-element derivatives of dicarba-*closo*-dodecaborane have been given much attention due to their interesting chemical and physical properties. These compounds can be used as catalysts,[1,2] precursors for ceramic materials[3] and in medical fields.[4,5] The 1,2-dicarba-*closo*-dodecaborane is an icosahedral cluster with the two carbon atoms in adjacent positions, whose tertiary phosphine derivatives were first reported in 1963.[6] Since then, these types of compounds have been employed as ligands in transition metal chemistry and starting materials for the preparation of other 1,2-dicarba-*closo*-dodecaborane-containing organophosphorus compounds.[7] A great deal of complexes of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ with transition metals such as nickel, cobalt, gold, platinum, palladium, chromium, molybdenum, tungsten, iron, manganese, copper and silver have been reported.[8–18] As far as is known, although many metal complexes of the above ligand have been synthesized, there has been no report about the copper(I) complexes of $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ characterized by X-ray diffraction. With this and the point that copper complexes can exhibit both biological and catalytic activity[19–24] in mind, our interests concentrated on the synthesis of Cu(I) complexes of 1,2-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane. Three new dinuclear copper(I) complexes with the formula $Cu_2(\mu\text{-}X)_2[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]_2$ (X = Cl, Br and I), which were obtained by the reactions of CuX (X = Cl, Br, I) with $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ in ethanol under reflux conditions, are reported in this paper.

EXPERIMENTAL

Materials

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen. Dichloromethane, ethanol,

*Correspondence to: Jianmin Dou, Department of Chemistry, Liaocheng University, Liaocheng 252059, People's Republic of China.
E-mail: jmdou@lctu.edu.cn
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tetrahydrofuran and *n*-hexane were dried with appropriate drying agents and distilled under dinitrogen prior to use. 1,2-Dicarba-*closo*-dodecaborane was provided by Professor Vladimir I. Bregadze. 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane was synthesized according to a literature procedure.[6] Chlorodiphenylphosphine (98%) was obtained from J&K Chemical Ltd. CuCl, CuBr and CuI are common inorganic compounds.

Measurements

Fourier transform infrared spectra were measured on a Nicolet-460 FT-IR spectrophotometer in the range 4000–400 cm^{-1} as KBr pellets. Elemental analysis (C, H) was performed with a Perkin-Elemer 2400 II elemental analyzer. The ^{1}H- and ^{13}C-NMR were recorded on a Varian Mercury 400 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard at 400.15 and 100.63 MHz, respectively. The spectra were acquired at room temperature (298 K) unless specified otherwise. The ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in units of parts per million (ppm) with respect to the references and are stated relative to external TMS for ^{1}H and ^{13}C NMR.

Synthesis procedures

Complex 1

To a suspension of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.1 mmol) in ethanol (10 ml) was added CuCl (10.0 mg, 0.1 mmol). The mixture was refluxed for 3 h with the protection of dry N_2, and then a yellow solid formed. The solid was filtered off, washed with hot ethanol, and dried in vacuum (40.0 mg 65.4%). The yellow solid was dissolved in dichloromethane, and then crystals suitable for X-ray diffraction were obtained after partial evaporation of the solvent 3 weeks later (m.p. > 300 °C; decomposition). FT-IR ν_{KBr} (cm^{-1}): 3054m, 2578m, 1634s, 1432m, 1095m, 745m, 700s, 497m. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ 7.251–7.456 ppm (40H); ^{13}C NMR (100.63 MHz, $CDCl_3$): 127.887–136.518 ppm (48C), 77.501 ppm (4C). Anal. calcd for $C_{54}H_{64}B_{20}Cl_6Cu_2P_4$: C, 46.52; H, 4.59; found: C, 46.38; H, 4.47%.

Complexes 2 and 3

The synthesis procedures were similar to those of complex **1**, with CuBr (14.4 mg, 0.1 mmol) or CuI (19.1mg, 0.1 mmol) to replace CuCl reacted with 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.1 mmol) in ethanol (10 ml). The yields were 35.6 mg, 54.3% for **2** and 44.3 mg, 63% for **3**, respectively. Suitable crystals for complexes **2** and **3** for X-ray diffraction were grown from a tetrahydrofuran–*n*-hexane solution. (m.p. > 300 °C; decomposition). Complex **2**: FT-IR ν_{KBr} (cm^{-1}): 3040m, 2570m, 1618s, 1445m, 1109m, 750m, 687s, 491m. ^{1}H NMR (400.15MHz, $CDCl_3$): δ 7.200–7.587 ppm (40H); ^{13}C NMR (100.63 MHz, $CDCl_3$): δ 125.997–134.994 ppm (48C), 77.203 ppm (4C). Anal. calcd for $C_{60}H_{76}B_{20}Br_2Cu_2O_2P_4$: C, 49.44; H, 5.22; found: C, 49.58; H, 5.31%. Complex **3**: FT-IR ν_{KBr} (cm^{-1}): 3027m, 2588m, 1646s, 1423m, 1090m, 732m, 710s, 485m. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ 7.128–7.508 ppm (40H); ^{13}C NMR (100.63 MHz, $CDCl_3$): 128.816–137.789 ppm (48C), 77.909 ppm (4C). Anal. calcd for $C_{52}H_{60}B_{20}Cu_2I_2P_4$: C, 44.41; H, 4.27; found: C, 43.68; H, 4.08%.

X-ray structure determination

Crystals of complexes **1, 2** and **3** suitable for X-ray were obtained using two methods. For complex **1** they were obtained from a dichloromethane solution by non-artificial volatilization, while for complexes **2** and **3** the method of diffusion was employed. The collection of crystallographic data for the complexes **1**–**3** was carried out on a Bruker Smart-1000 CCD diffractometer, using graphite-monochromatized Mo–K_α ($\lambda = 0.71073$ Å) at 298(2)K. The unit cell parameters for the three complexes were determined by least-squares refinement of 25 carefully centered reflections. A total of 9676, 9998 and 16 251 reflections collected for complexes **1**–**3**, giving 6446 unique reflections ($R_{int} = 0.0572$) for **1**, 6642 ($R_{int} = 0.0547$) for **2**, and 5534 ($R_{int} = 0.0365$) for **3** were collected by $\omega/2\theta$ scan mode, respectively. The data obtained were corrected for Lorentz and polarization effects. Correction for semi-empirical absorption was also applied. The structures were solved by direct method and expanded using Fourier difference techniques with SHELXTL-97 program package.[25] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. All the H atoms were located in a difference Fourier map and thereafter refined isotropically. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and spectra characterization

These three complexes were obtained by reactions of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with CuX in ethanol under reflux. According to previous work,[17,26] the *closo* structure of 1,2-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane could be degraded to *nido*- [7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$ by the reaction of transition metal complexes with 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ in ethanol or methanol. This degradation process could typically take place in the reactions of 'electron rich' d^{10} metal complexes, such as $Cu(PPh_3)_2Cl$,[26] $Ag(PPh_3)ClO_4$,[27] $Au(PPh_3)Cl$[28] and $Au(AsPh_3)Cl$,[29] with the *closo*-1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ in ethanol. However, when free CuX (X = Cl, Br or I) with no other ligand reacted with 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ in ethanol, the *closo* structure of the carborane skeleton could be preserved.

All these three complexes were characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The IR spectra of these complexes were very similar to each other and exhibited absorptions characteristic of terminal B-H vibrations at 2578, 2570, and 2588 cm^{-1} for X = Cl, Br and I, respectively, which appeared in the normal range of B–H vibration from 2625 to 2450 cm^{-1}.[30,31] The absorptions at 3054, 3040 and 3027 cm^{-1}

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Table 1. Details of the crystal parameters, data collection and refinement for complexes **1**, **2** and **3**

Crystal data	**1**	**2**	**3**
Empirical formula	$C_{54}H_{64}B_{20}Cl_6Cu_2P_4$	$C_{60}H_{76}B_{20}Br_2Cu_2O_2P_4$	$C_{52}H_{60}B_{20}Cu_2I_2P_4$
Formula weight	1392.91	1456.19	1405.96
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	C2/c
a (Å)	10.727(6)	10.765(4)	5.2460(16)
b (Å)	12.317(6)	12.721(5)	11.118(3)
c (Å)	16.249(8)	16.322(7)	10.295(3)
α (deg)	69.736(8)	68.992(6)	90
β (deg)	71.260(9)	71.300(6)	119.304(2)
γ (deg)	81.152(9)	79.0947(7)	90
V (Å^3)	1905.1(17)	1971.9(14)	6276.4(14)
Z	1	1	2
D (mg m^{-3})	1.214	1.226	1.913
F(000)	708	740	2784
Crystal size (mm)	0.43 × 0.41 × 0.38	0.38 × 0.31 × 0.21	0.44 × 0.41 × 0.39
Theta range (deg)	1.87–25.01	1.83–25.01	1.75–25.81
Limiting indices	$-8 \le h \le 12$, $-14 \le k \le 14$, $-15 \le l \le 19$	$-12 \le h \le 12$, $-9 \le k \le 15$, $-18 \le l \le 19$	$-30 \le h \le 19$, $-19 \le k \le 15$, $-18 \le l \le 20$
Independent reflection	6446	6642	5534
Completeness to theta = 25.01	95.8%	95.4%	100%
Maximum and minimum transmission	0.7297 and 0.7021	0.7205 and 0.5694	0.5405 and 0.5049
Goodness-of-fit on F^2	1.000	1.001	1.010
$R[I > 2\sigma(I)]$	$R_1 = 0.0809$	$R_1 = 0.0758$	$R_1 = 0.0429$
	$wR_2 = 0.1902$	$wR_2 = 0.1722$	$wR_2 = 0.1062$
R (all data)	$R_1 = 0.1602$	$R_1 = 0.1710$	$R_1 = 0.0576$
	$wR_2 = 0.2433$	$wR_2 = 0.2271$	$wR_2 = 0.1142$
Largest difference peak and hole ($\times 10^2$ electrons Å^{-3})	1.242 and −0.575	0.664 and −0.821	0.673 and −0.805

may be attributed to the ν_{C-H} stretching vibration of benzene rings. There are three to four peaks from 1646 to 1423 cm^{-1}, which may be assigned to V_C=c stretching vibration. The peak at ca. 1430 cm^{-1} is the inplane deformation mode of the benzene ring, and the peak at ca. 1100 cm^{-1} is the absorption of $\nu_{C(phenyl)-P}$, which is slightly shifted in keeping with phosphorus coordination to the 1,2-$C_2B_{10}H_{10}$ moiety. The absorption at approximately 740 cm^{-1} shows the existence of the deformation cage. The ^{1}H NMR spectra (400.15 MHz) of these complexes displayed a complex pattern of resonance at about 7.2–7.5 ppm, which can be attributed to the phenyl-H of the diphenylphosphine ligands. In the ^{13}C NMR spectra (100.63 MHz), resonance at ca. $\delta = 130$ ppm can be assigned to the benzene ring C atoms, and $\delta = 77.0$ are the carborane cage C atoms.[32]

Crystal structure

Crystal structures of complexes **1–3** are shown in Figs 1–3. Selected bond lengths and angles are given in Table 2. The figures show that the structures of the three complexes are very similar to one another. Their structures are symmetrical, and the symmetry transformations used to generate equivalent atoms are $-x+1, -y+2, -z$ for comple x **1**, $-x, -y+2, -z$ for **2** and $-x+1/2, -y+3/2, -z+1$ for **3,** respectively. The same two structure units, Cu[1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$], are bridged by two Cl, Br or I atoms. Comparison of the configuration of the free ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ and that of the three complexes reveals differences. The P(1)–C(1)–C(2)–P(2) torsion angle is 10.6(3)° in the free ligand.[33] However, after the ligand is coordinated to CuX, this torsion angle is largely altered with the value 2.1(6), 2.9(7) and 3.3(2)° in the three complexes from **1** to **3**, respectively. The two Cc–Cc–P angles in the free ligand are 116.6(2) and 111.07(19)° for C(2)–C(1)–P(1) and C(1)–C(2)–P(2), while these two angles in the complexes tend to become equivalent to each other, as shown in Table 2. These data show that the symmetry of

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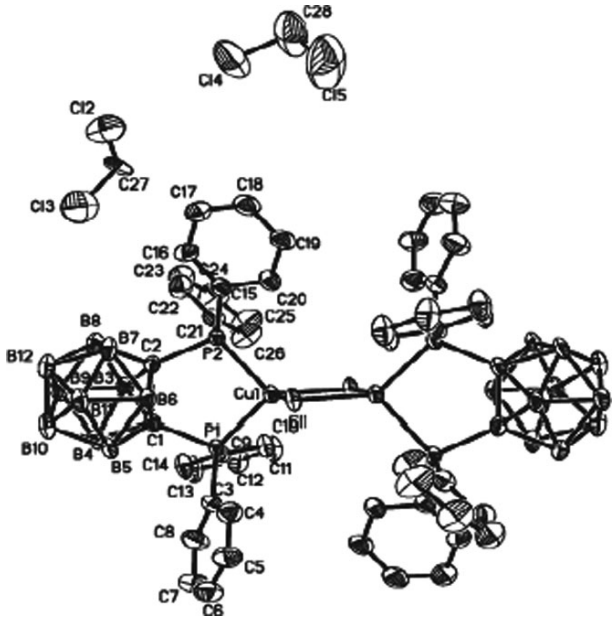

Figure 1. The crystal structure of complex **1.** The H atoms have been omitted for clarity.

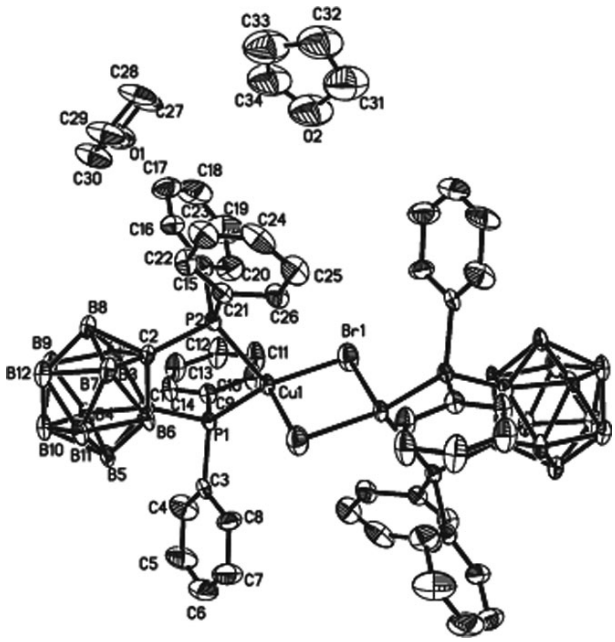

Figure 2. The crystal structure of complex **2.** The H atoms have been omitted for clarity.

the moiety 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ in the three complexes has a tendency to approach C_{2v} comparison to the free *closo* ligand. The average bond lengths of Cc–P in the three complexes 1.892, 1.884 and 1.882 Å are in agreement with the corresponding distance 1.885 Å in 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$, indicating that the coordinating to the metal atom has no influence on this distance.

For either of the complexes, the coordination sphere of the Cu atom is a distorted tetrahedron formed by

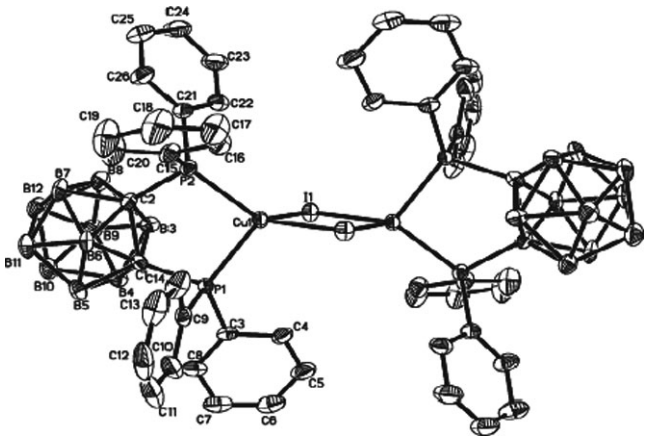

Figure 3. The crystal structure of complex **3.** The H atoms have been omitted for clarity.

two phosphorus atoms of PPh_2 groups and two X atoms that bridge the other Cu atom at the same time. As for the five-member chelating ring, due to the Cu atom out of the PCcCcP plane by the value 0.83–0.85 Å, there inevitably forms an envelope conformation between Cu and the above plane. The average distances of P–Cu in complexes **1–3** are 2.254, 2.255 and 2.276 Å, respectively, which are close to the corresponding bond lengths 2.236 in the $(PPh_3)_2CuCl_2Cu(PPh_3)$,[34] 2.261 in $[CuBr(PMePh_2)]_2$[35] and 2.276 Å in $Cu_2I_2(PPh_2Me)_4 \cdot SO_2$.[36] The angle of P(1)–Cu(1)–P(2) is almost equal in the three complexes with the value 93.63(8), 94.11(8) and 93.57(5)° from **1** to **3**, and this angle in $Cu(PPh_3)$[7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$](Me_2CO)[30] is 90.9(1)°. The central Cu_2X_2 unit forms a cross parallelogram plane, which is almost vertical to the PCcCcP plane with the dihedral angle between these two planes 92.6, 92.9 and 92.5° in the three complexes, respectively. The distances of Cu–X are 2.312(2), 2.3986(16) and 2.6802(7) Å, respectively. The corresponding bond lengths in the complexes with similar structure to the above three complexes are as follows—2.3055(8) in $(LCuCl)_2$ [L = $PPh_2CH_2CH(CH_2CH_3)OPPh_2$],[37] 2.4034(4) in $CuBr[P(CH_2Ph)_3]_2$,[38] and 2.6921(3) Å in [{Cu(μ-I)(dppf-P, P′)}$_2$].[39]

Catalytic property of complex 3

It is well known that copper halide, with or without ligand, can act as catalyst in many reactions.[40–44] CuI in the presence of the ligand is active for amination reactions with potassium tertiary butoxide (KO^tBu) as a base.[45] Taking into account that 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ is a chelating ligand, we investigated the amination of iodobenzene with aniline in the absence or presence of the complex **3** as a model reaction. The stoichiometric reaction is shown in Scheme 1.

The reaction was carried out under dry oxygen-free dinitrogen. A typical experiment is as follows. Toluene (5 ml) was charged to the reaction vessel followed by iodobenzene (3.30 mmol), aniline (1.57 mmol),

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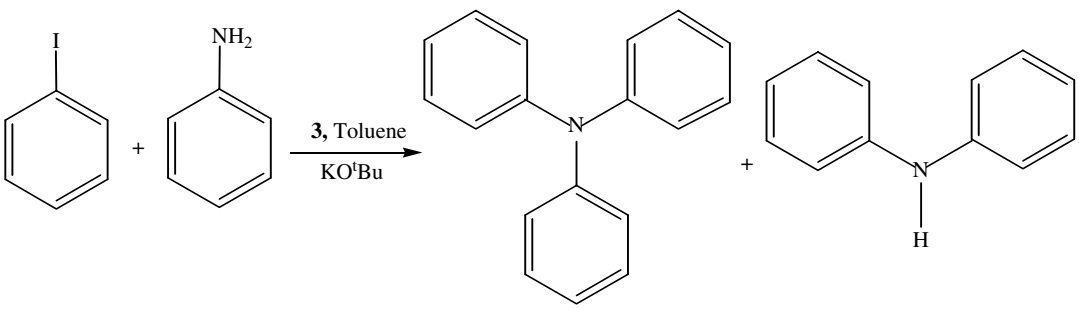
Table 2. Selected bond lengths (Å) and angles (deg) for complexes **1**, **2** and **3**

1		2		3	
Cu(1)–P(1)	2.247(2)	Cu(1)–P(1)	2.251(2)	Cu(1)–P(1)	2.2739(14)
Cu(1)–P(2)	2.262(2)	Cu(1)–P(2)	2.259(2)	Cu(1)–P(2)	2.2776(14)
Cu(1)–Cl(1)#1	2.407(2)	Cu(1)–Br(1)#1	2.4831(16)	Cu(1)–I(1)#1	2.6211(7)
Cu(1)–Cl(1)	2.312(2)	Cu(1)–Br(1)	2.3986(16)	Cu(1)–I(1)	2.6802(7)
P(1)–C(1)	1.886(7)	P(1)–C(1)	1.879(7)	P(1)–C(1)	1.875(5)
P(2)–C(2)	1.898(7)	P(2)–C(2)	1.889(8)	P(2)–C(2)	1.889(5)
C(1)–C(2)	1.722(10)	C(1)–C(2)	1.736(9)	C(1)–C(2)	1.752 (7)
P(1)–Cu(1)–P(2)	93.63(8)	P(1)–Cu(1)–P(2)	94.11(8)	P(1)–Cu(1)–P(2)	93.57(5)
P(1)–Cu(1)–Cl(1)#1	122.34(9)	P(1)–Cu(1)–Br(1)#	114.66(7)	P(1)–Cu(1)–I(1)#1	109.33
P(2)–Cu(1)–Cl(1)#1	119.01(8)	P(2)–Cu(1)–Br(1)#1	110.40(7)	P(2)–Cu(1)–I(1)#1	123.31(4)
P(1)–Cu(1)–Cl(1)	114.77(8)	P(1)–Cu(1)–Br (1)	122.66(7)	P(1)–Cu(1)–I(1)	111.53(4)
P(2)–Cu(1)–Cl(1)	110.87(8)	P(2)–Cu(1)–Br (1)	116.31(7)	P(2)–Cu(1)–I(1)	115.93(4)
Cl(1)#1–Cu(1)–Cl(1)	97.15(7)	Br(1)#1–Cu(1)–Br(1)	99.26(5)	I(1)#1–Cu(1)–I(1)	102.85(2)
Cu(1)#1–Cl(1)–Cu(1)	82.85(7)	Cu(1)#1–Br(1)–Cu(1)	80.74(5)	Cu(1)#1–I(1)–Cu(1)	77.15(2)
C(3)–P(1)–Cu(1)	122.7(3)	C(3)–P(1)–Cu(1)	124.6(3)	C(3)–P(1)–Cu(1)	117.43(18)
C(9)–P(1)–Cu(1)	112.8(2)	C(9)–P(1)–Cu(1)	113.4(3)	C(9)–P(1)–Cu(1)	119.98(19)
C(1)–P(1)–Cu(1)	102.6(2)	C(1)–P(1)–Cu(1)	102.3(2)	C(1)–P(1)–Cu(1)	102.78(15)
C(2)–P(2)–Cu(1)	102.4(2)	C(2)–P(2)–Cu(1)	102.4(2)	C(2)–P(2)–Cu(1)	102.97(15)
C(21)–P(2)–Cu(1)	117.8(3)	C(21)–P(2)–Cu(1)	117.2(3)	C(21)–P(2)–Cu(1)	125.57(18)
C(15)–P(2)–Cu(1)	117.6(3)	C(15)–P(2)–Cu(1)	119.1(3)	C(15)–P(2)–Cu(1)	112.59(17)
C(2)–C(1)–P(1)	115.3(4)	C(2)–C(1)–P(1)	115.7(4)	C(2)–C(1)–P(1)	114.6(3)
C(1)–C(2)–P(2)	113.6(4)	C(1)–C(2)–P(2)	113.4(4)	C(1)–C(2)–P(2)	114.5(3)

Symmetry transformations used to generate equivalent atoms: complex **1**, #1 $-x+1, -y+2, -z$; complex **2**, #1 $-x, -y+2, -z$; complex **3**, #1 $-x+1/2, -y+3/2, -z+1$.



Scheme 1.

$Cu_2(\mu\text{-}I)_2[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]_2$ (0.0280 mmol) and KO^tBu (4.70 mmol). The mixture was then heated to 115 °C, and stirred for 3.5 h at this temperature. After cooling to room temperature, the reaction mixture was filtered to remove the undissolved base. Initial and final samples were analyzed by GC using a capillary column. In the presence of complex **3**, the conversion of amine is 58%, while without the CuI complex the conversion of amine is very poor. These results indicate that $Cu_2(\mu\text{-}I)_2[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}]_2$ is active for the amination of iodobenzene with aniline. The catalytic ability of cluster **3** (with the conversion of amine 58%) is similar to CuI in the presence of 2,2′-dithiobis(5-nitropyridine) 53%, while the conversion is 100% with CuI and 2,2′-bipyridine.[46]

Considering the characteristics of the above reaction, it can be viewed as a type of Ullmann condensation (loosely defined here as copper-catalyzed nucleophilic aromatic substitutions on unactivated aryl halides). So it is reasonable to postulate a mechanism similar to other Ullmann-type reactions.[47] The insertion of a Cu(I) species to the carbon–halogen bond (in this case the halogen is iodine) should initially take place, followed by the halogen–nitrite exchange reaction and reductive elimination of the Cu species. The data above show that the catalytic ability of the complex **3** is lower than that of CuI with 2,2′-bipyridine. Its relative lower catalytic ability may be attributed to the large volume, electron withdrawing power and extensive electronic delocalization ability of the

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carborane skeleton, which can confer a rather unusual stability to the molecule and is disadvantageous for inserting the Cu(I) into the carbon–halogen bond.

Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC, no. 283030 for **1,** no. 280280 for **2**, and no. 276314 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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