Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Contents:

1. Materials

Toluene, *n*-hexane, methanol, ethanol, acetonitrile and sodium hydroxide were purchased from Nacalai Tesque, Inc. Phenylacetylene, iodomethane, copper iodide and 50% aqueous solution of phosphinic acid were purchased from Wako Pure Chemical Industry, Ltd. *p*-Bromophenylacetylene was purchased from Tokyo Chemical Industry Co., Ltd. Arsenic trioxide was purchased from Kanto Chemical Co., Inc. All commercially available chemicals were used without further purification. Pentamethylcyclopentaarsine (**1**) was prepared by following the literature.[1]

2. Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometers, and samples were analyzed in $CDCl_3$ using Me_4Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. The CD and UV-vis spectra were recorded on a JASCO J-820 spectropolarimeter with $CHCl_3$ as a solvent at room temperature.

3. X-ray crystallographic data for single crystalline products

The single crystal was mounted on glass fibers with epoxy resin. Intensity data were collected at room temperature on a Rigaku RAXIS RAPID II imaging plate area detector with graphite monochromated Mo Kα radiation. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were collected at room temperature to a maximum 2θ value of 55.0°. Data were processed by the PROCESS-AUTO [2] program package. An empirical or numerical absorption correction [3] was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction [4] was applied. The structure was solved by heavy atom Patterson methods [5] and expanded using Fourier techniques. [6] Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. In the case of the crystalline product recrystallized from acetone, the final cycle of full-matrix least-squares refinement on F was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure[7,8] crystallographic software package except for refinement, which was performed using SHELXL97[9]. Only the crystal data of $[Cu_2I_2(\mathbf{2b})_3]$ has been treated by the PLATON SQUEEZE for the analysis of solvent-containing voids. Crystal data and

more information on X-ray data collection are summarized in Table S1-S7.

4. Syntheses

*cis-1,4-Dimethyl-2,5-diphenyl-1,4-dihydro-1,4-diarsinine (**2a**) and 1,4-dimethyl-2,6-diphenyl-1,4-dihydro-1,4-diarsinine (**3a**)*

To a refluxed toluene solution (120 mL) of phenylacetylene (5.13 g, 50.3 mmol) was added **1** (4.50 g, 10.0 mmol) a toluene solution (30 mL) of AIBN (76.0 mg, 0.463 mmol) under N_2 atmosphere. After stirring for 15 h under reflux condition, the reaction mixture was cooled to room temperature and condensed in vacuo. The condensed solution was poured into *n*-hexane (600 mL), and the precipitate was removed by filtration. After removal of the solvent in vacuo, the residue was subjected to recrystallization from dichloromethane and methanol to give pale yellow cubic and needle-like crystals (total: 1.54 g, 4.00 mmol, 16%). The cubic crystals were picked up and recrystallized from dichloromethane and methanol again to give **2a** (0.48 g, 1.25 mmol, 5%). The needle like crystals were picked up and recrystallized from dichloromethane and methanol again to give **3a** (48 mg, 0.125 mmol, 0.05%). **2a**; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.24 (m, 10H), 6.77 (s, 2H), 1.08 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.5, 142.7, 134.0, 128.3, 126.4, 8.2 ppm. HRMS (FAB) calcd. for $C_{18}H_{18}As_2$ $[M+H]^+$: 384.9920, found: 384.9923. Anal. calcd for $C_{18}H_{18}As_2$: C 56.27; H 4.72, found: C 56.03; H 4.70. **3a**; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.21 (m, 10H), 6.67 (s, 2H), 1.39 (s, 3H), 0.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ150.0, 143.7, 132.3, 128.3, 126.9, 126.8, 8.7, 7.6 ppm. HRMS (FAB) calcd. for $C_{18}H_{18}As_2$ $[M]^+$: 383.9840, found: 383.9833. Anal. calcd for $C_{18}H_{18}As_2$: C 56.27; H 4.72, found: C, 56.09; H, 4.97.

*2,5-Bis(p-bromophenyl)-cis-1,4-Dimethyl-1,4-dihydro-1,4-diarsinine (**2b**)*

To a refluxed toluene solution (175 mL) of *p*-bromophenylacetylene (8.13 g, 44.9 mmol) was added **1** (4.30 g, 9.56 mmol) a toluene solution (25 mL) of AIBN (76.7 mg, 0.467 mmol) under N_2 atmosphere. After stirring for 16 h under reflux condition, the reaction mixture was cooled to room temperature and condensed in vacuo. The condensed solution was poured into *n*-hexane (600 mL), and the precipitate was removed by decantation. After removal of the solvent in vacuo, the residue was subjected to recrystallization from dichloromethane and methanol three times to give pale yellow crystals (0.97 g, 1.80 mmol, 8%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, J = 8.4 Hz, 4H), 7.13 (d, J = 8.4 Hz, 4H), 6.76 (s, 2H), 1.07 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 141.4, 134.6, 131.5, 128.5, 121.0, 8.1 ppm. HRMS (FAB)

calcd. for $C_{18}H_{16}As_2Br_2$ $[M+H]^+$: 540.8131, found: 540.8119. Anal. calcd for $C_{18}H_{16}As_2Br_2$: C 39.89; H 2.98, found: C 39.79; H 2.95.

*Copper iodide complex with rac-**2a** ($[Cu_2I_2(\mathbf{2a})_3]$)*

An acetonitrile solution (40 mL) of *rac*-**2a** (0.193 g, 0.502 mmol) and CuI (94.8 mg, 0.498 mmol) was stirred at room temperature for 3 h. White precipitates generated and were isolated by filtration to give $[Cu_2I_2(\mathbf{2b})_3]$ (0.244 g, 0.159 mmol, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.31 (m, 30H), 5.95 (s, 6H), 1.54 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 137.7, 129.8, 128.7, 128.5, 126.7, 11.0. Anal. calcd for $C_{54}H_{54}As_6I_2Cu_2$: C 42.30; H 3.55, found: C 42.01; H 3.59.

*Copper iodide complex with rac-**2b** ($[Cu_2I_2(\mathbf{2b})_3]$)*

Crystals of *rac*-**2b** (0.136 g, 0.252 mmol) was dispersed in an acetonitrile solution (20 mL) of CuI (0.0479 g, 0.252 mmol). The crystals of *rac*-**2b** gradually disappeared, and white precipitates generated. After stirring for 19 hours, the precipitates were collected with filtration to obtain $[Cu_2I_2(\mathbf{2b})_3]$ (0.161 g, 0.081 mmol, 96%).^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, J = 8.8 Hz, 12H), 7.36 (d, J = 8.8 Hz, 12H), 6.02 (s, 6H), 1.51 (s, 18H). ^{13}C NMR was not able to be measured because of the low solubility in any organic solvents.

5. NMR spectra

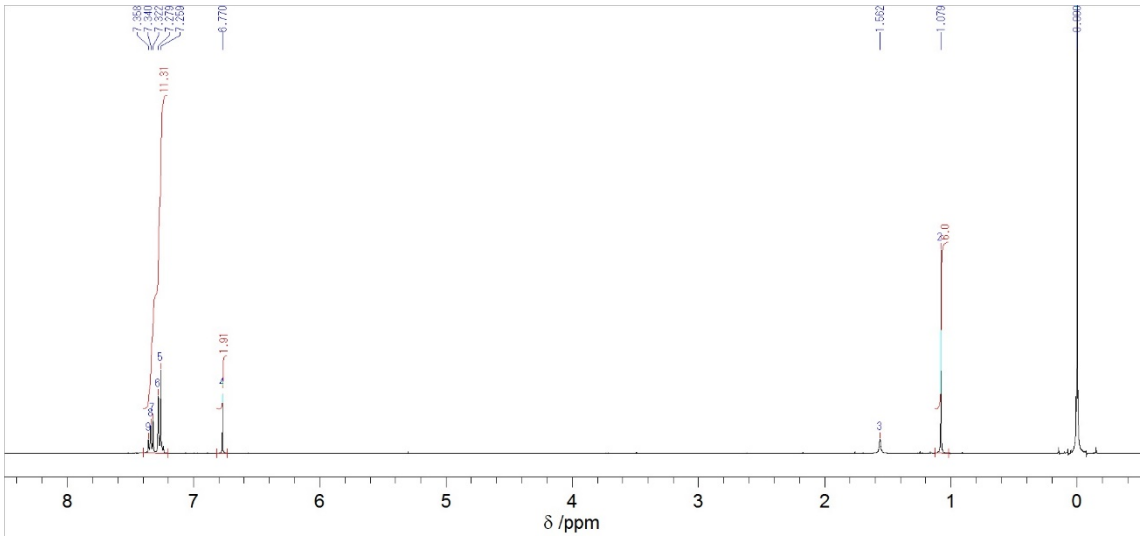


Fig. S1 ^{1}H NMR spectrum (400 MHz) of **2a** in $CDCl_3$.

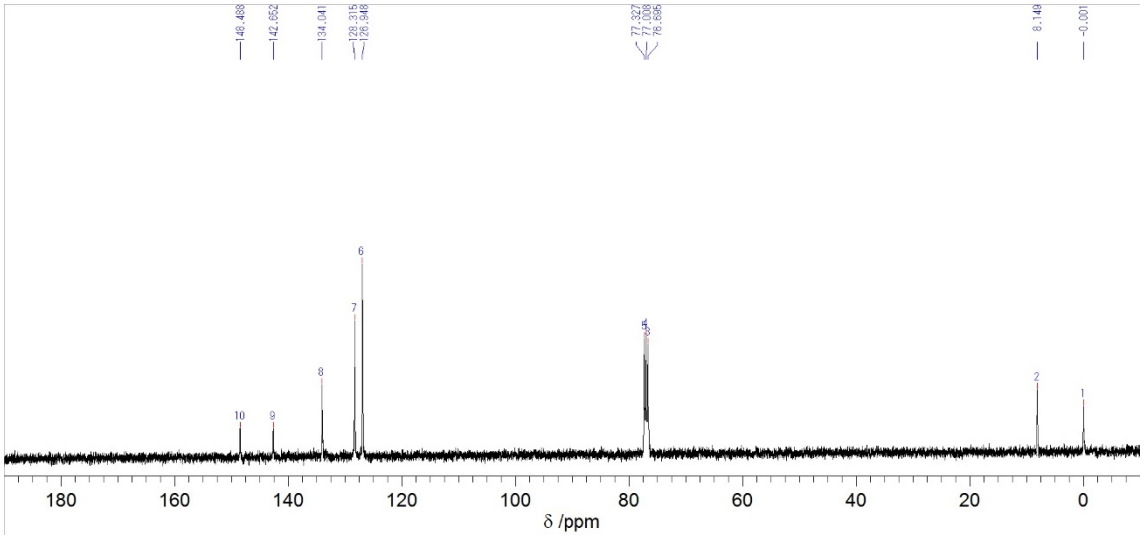


Fig. S2 ^{13}C NMR spectrum (100 MHz) of **2a** in $CDCl_3$.

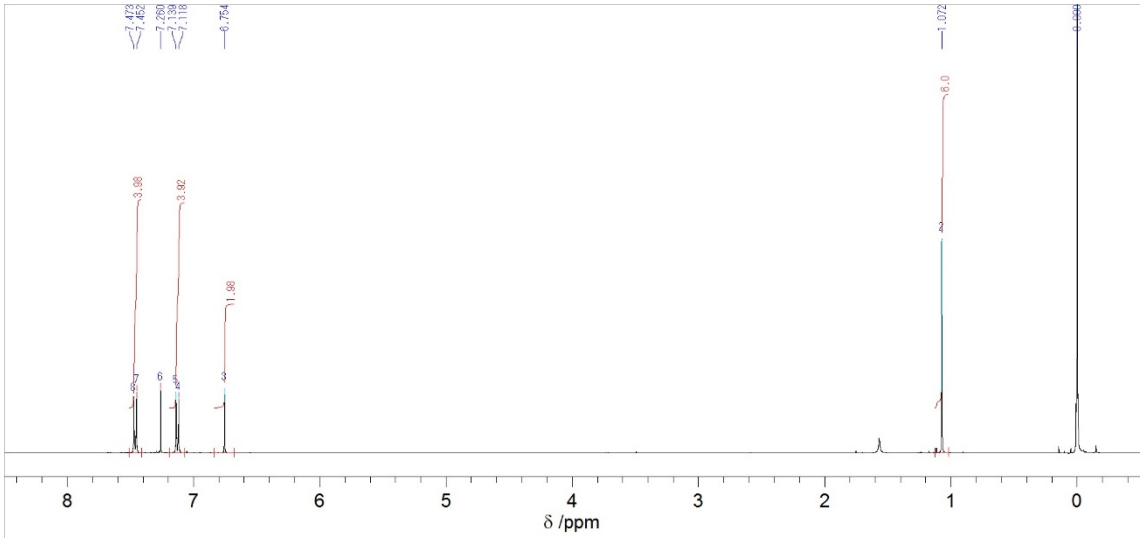


Fig. S3 ^{1}H NMR spectrum (400 MHz) of **2b** in $CDCl_3$.

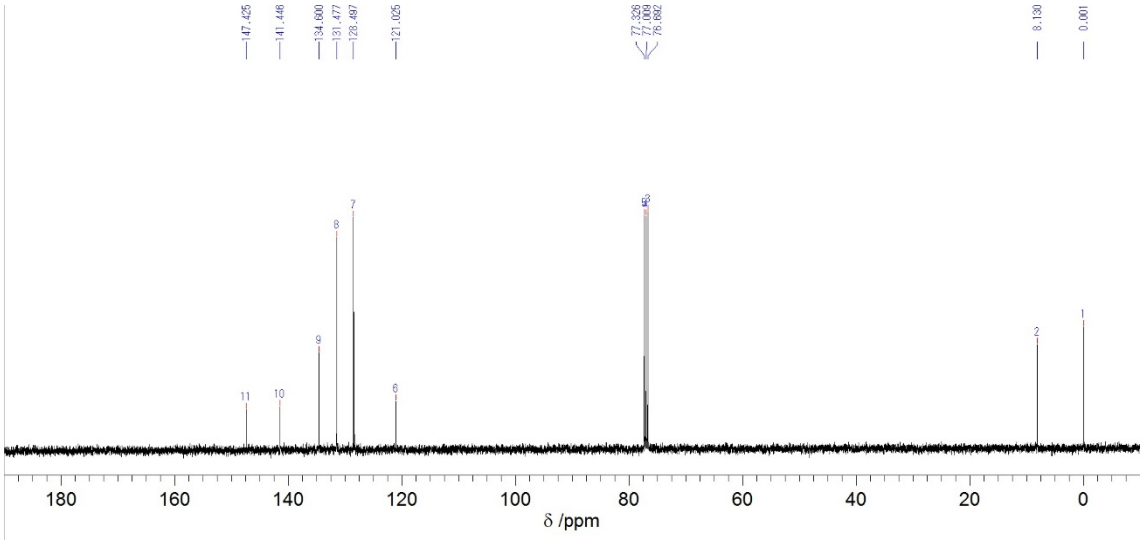


Fig. S4 ^{13}C NMR spectrum (100 MHz) of **2b** in $CDCl_3$.

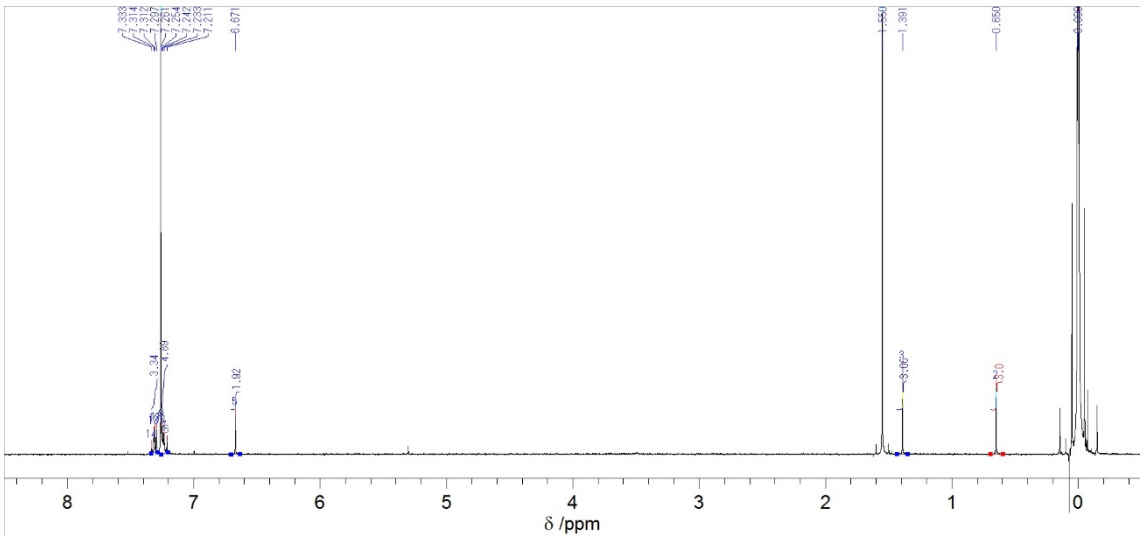


Fig. S5 ^{1}H NMR spectrum (400 MHz) of **3a** in $CDCl_3$.

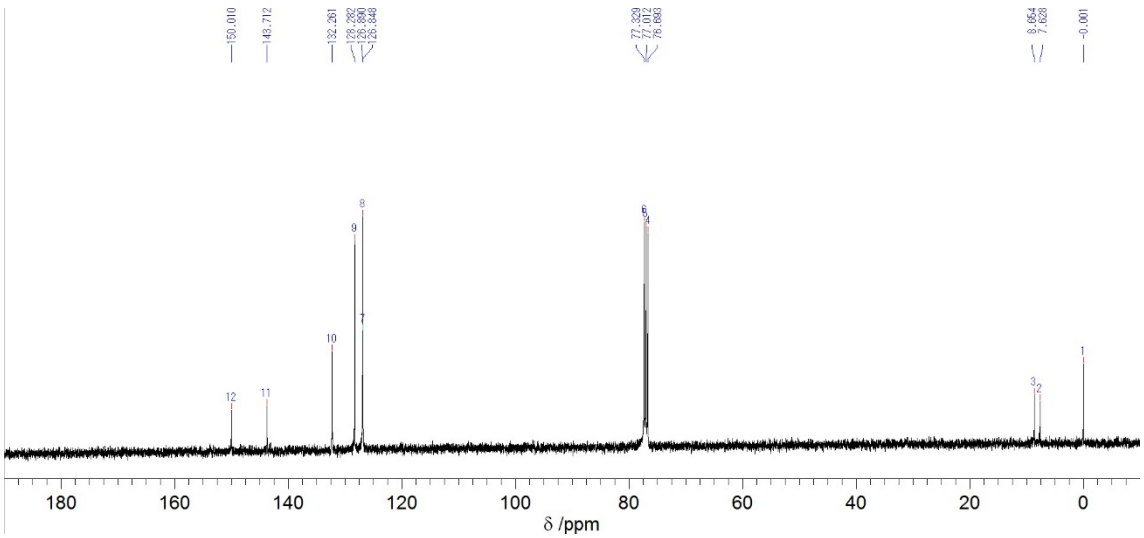


Fig. S6 ^{13}C NMR spectrum (100 MHz) of **3a** in $CDCl_3$.

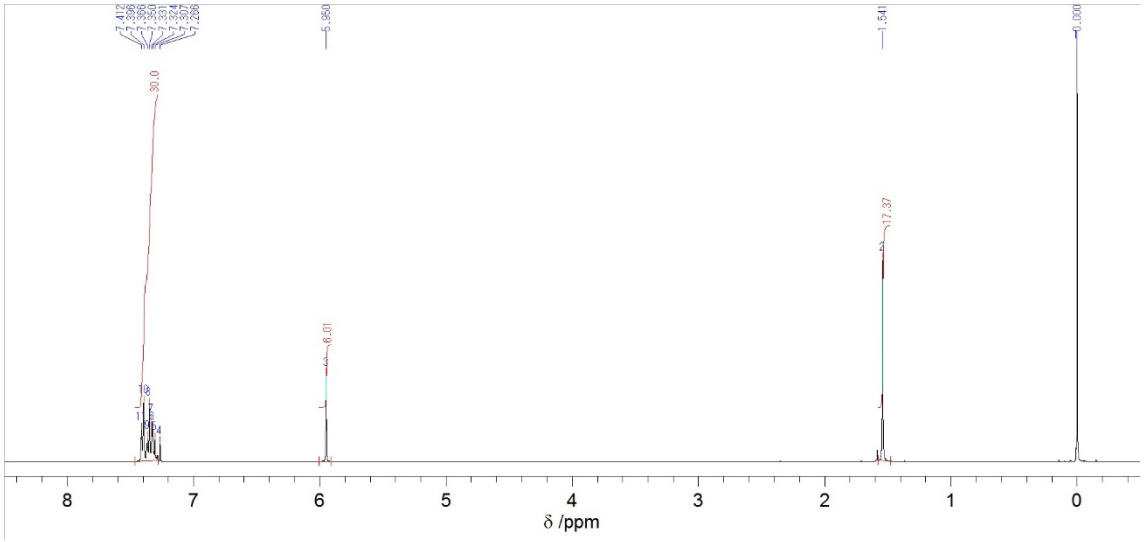


Fig. S7 ^{1}H NMR spectrum (400 MHz) of $[Cu_2I_2(\mathbf{2a})_3]$ in $CDCl_3$.

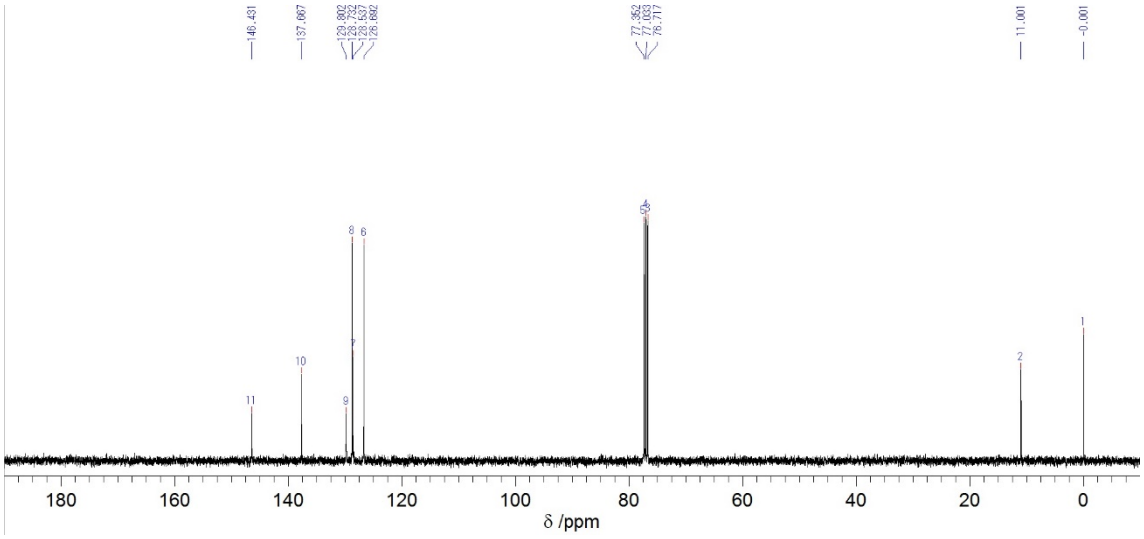


Fig. S8 ^{13}C NMR spectrum (100 MHz) of $[Cu_2I_2(\mathbf{2a})_3]$ in $CDCl_3$.

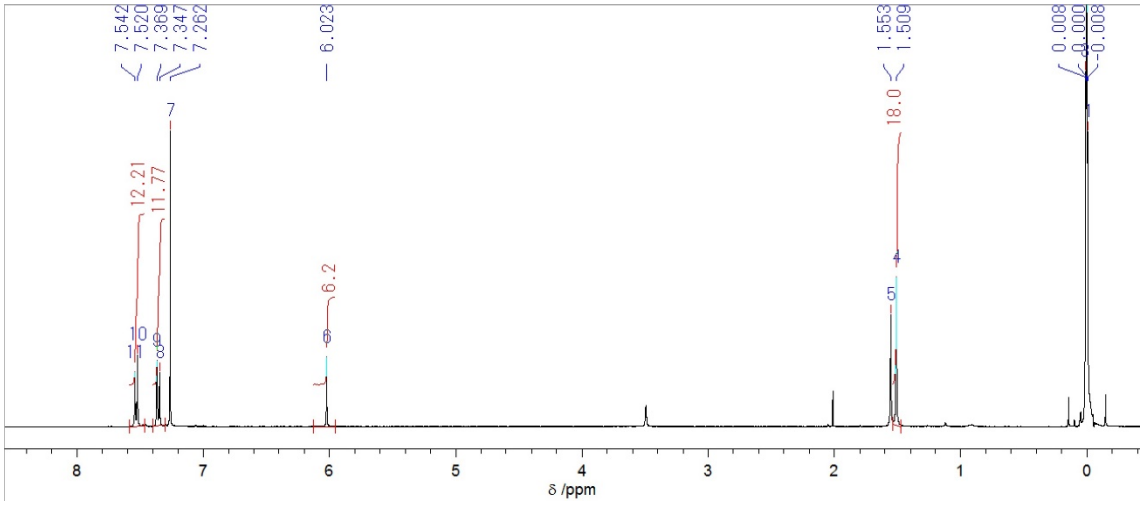


Fig. S9 ^{1}H NMR spectrum of (400 MHz) of $[Cu_2I_2(\mathbf{2b})_3]$ in $CDCl_3$.

6. Crystallographic data

Table S1. Crystallographic Data for **2a**, (*S*,*S*)-**2b** and (*R*,*R*)-**2b**.

	2a	(*S*,*S*)-**2b**	(*R*,*R*)-**2b**
A. Crystal data			
Empirical Formula	C18 H18 As2	C18 H16 As2 Br2	C18 H16 As2 Br2
Formula Weight	384.18	541.98	541.98
Crystal Dimension, mm^3	0.15 × 0.10 × 0.10	0.180 × 0.180 × 0.080	0.250 × 0.200 × 0.130
Crystal System	triclinic	orthorhombic	orthorhombic
Space Group	P -1	$P2_12_12$	$P2_12_12$
a, Å	9.3345(12)	9.9977(4)	9.9940(3)
b, Å	10.5322(15)	18.5103(8)	18.5146(6)
c, Å	10.7027(14)	4.96616(17)	4.97201(18)
α, deg	65.877(4)	90.000	90.000
β, deg	63.959(3)	90.000	90.000
γ, deg	65.470(3)	90.000	90.000
Volume, $Å^3$	826.40(19)	919.04(6)	919.99(5)
D_{calcd}, g cm^{-3}	1.544	1.958	1.956
Z	2	2	2
F(000)	384.00	520.00	520.00
Data Collection			
Temperature, deg	23(1)	23.0	23.0
2θmax, deg	55.0	54.9	54.9
Tmin/Tmax	0.247 / 0.668	0.157 / 0.528	0.147 / 0.354
Refinement			
No. of Observed Data	2119	2103	2108
No. of Parameters	199	100	100
R1[a], wR2[b]	0.0522, 0.0819	0.0262, 0.0740	0.0384, 0.0913
Goodness of Fit Indictor	1.017	1.225	1.157
Flack Parameter	-	-0.01(4)	0.01(5)

[a]$R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$ [b]$wR2 = [\ \Sigma\ w\ ((Fo^2-Fc^2)^2 / \Sigma\ w\ (Fo^2)^2\ ]^{1/2}$ $w = [\ \sigma^2(Fo^2)\ ]^{-1}$

CCDC #1058095 (**2a**), #1058094 ((*S*,*S*)-**2b**) and #1058093 ((*R*,*R*)-**2b**)

Table S2. Crystallographic Data for $[Cu_2I_2(\mathbf{2a})_3]$ and $[Cu_2I_2(\mathbf{2b})_3]$.

	$[Cu_2I_2(\mathbf{2a})_3]$	$[Cu_2I_2(\mathbf{2b})_3]^c$
A. Crystal data		
Empirical Formula	C54 H54 As6 Cu2 I2	C54 H48 As6 Br6 Cu2 I2
Formula Weight	1533.45	2006.83
Crystal Dimension, mm^3	0.200 × 0.200 × 0.160	0.150 × 0.150 × 0.150
Crystal System	monoclinic	trigonal
Space Group	$P2_1/c$	R-3
a, Å	22.9707(4)	18.0767(3)
b, Å	12.1624(2)	18.0767(3)
c, Å	22.9851(5)	38.3573(8)
α, deg	90.0000	90.0000
β, deg	117.7162(7)	90.0000
γ, deg	90.0000	120.0000
Volume, $Å^3$	5684.73(19)	10854.6(4)
D_{calcd}, g cm^{-3}	1.792	1.842
Z	4	6
F(000)	2960.00	5664.00
Data Collection		
Temperature, deg	23.0	23.0
2θmax, deg	55.0	54.9
Tmin/Tmax	0.210 / 0.426	0.216 / 0.324
Refinement		
No. of Observed Data	13001	5509
No. of Parameters	577	232
R1[a], wR2[b]	0.0306, 0.0689	0.0353, 0.0963
Goodness of Fit Indictor	1.07	1.071

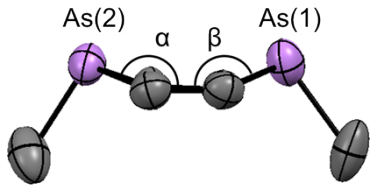
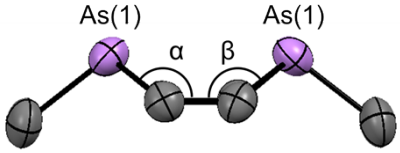
CCDC #1058096 ($[Cu_2I_2(\mathbf{2a})_3]$) and 1058097 ($[Cu_2I_2(\mathbf{2b})_3]$)

[a] $R1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$

[b] $wR2 = [\, \Sigma \, w \, ((Fo^2-Fc^2)^2 \, / \, \Sigma \, w \, (Fo^2)^2 \,]^{1/2} \qquad w = [\, \sigma^2(Fo^2) \,]^{-1}$

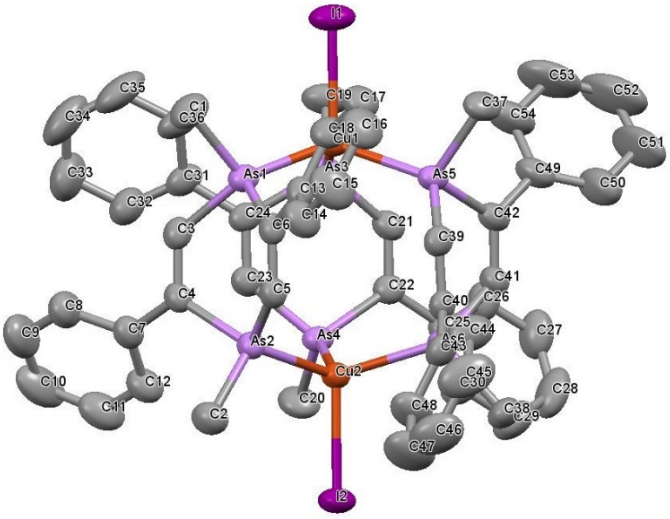
[c] The structure was analyzed omitting solvent molecules in the crystal.

Table S3. Selected angles (deg) and distance (Å) of the frame of **2a** and **2b**[a].

	α	C(2)As(2)C(3)-C(1)C(2)C(3)C(4)	160.03
	β	As(1)C(1)C(4)-C(1)C(2)C(3)C(4)	155.31
	C-As-C[b]	C(2)-As(2)-C(3)	100.1(3)
		C(1)-As(1)-C(4)	99.5(3)
	As-C=C	As(2)-C(2)-C(1)	123.8(6)
		As(2)-C(3)-C(4)	130.1(6)
		As(1)-C(1)-C(2)	129.3(6)
		As(1)-C(4)-C(3)	122.7(6)
2a	As-As	As(1)-As(2)	3.636(1)
	A	C(1)As(1)C(2)-C(1)C(2)C(1)C(2)	141.45
	B	C(1)As(1)C(2)-C(1)C(2)C(1)C(2)	141.45
	C-As-C[b]	C(1)-As(1)-C(2)	95.8(3)
	As-C=C	As(1)-C(2)-C(1)	117.6(5)
		As(1)-C(1)-C(2)	125.7(5)
2b	As-As	As(1)-As(1)	3.370(1)

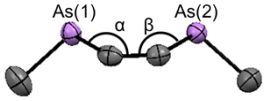
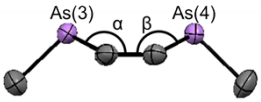
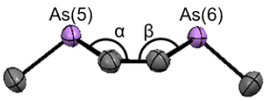
[a](*S*,*S*)-**2b** was employed as a representative example. [b]Interior angles of the six membered ring.

Table S4. Selected angles (deg) and distance (Å) around the copper centers of the frame of $[Cu_2I_2(\mathbf{2a})_3]$.



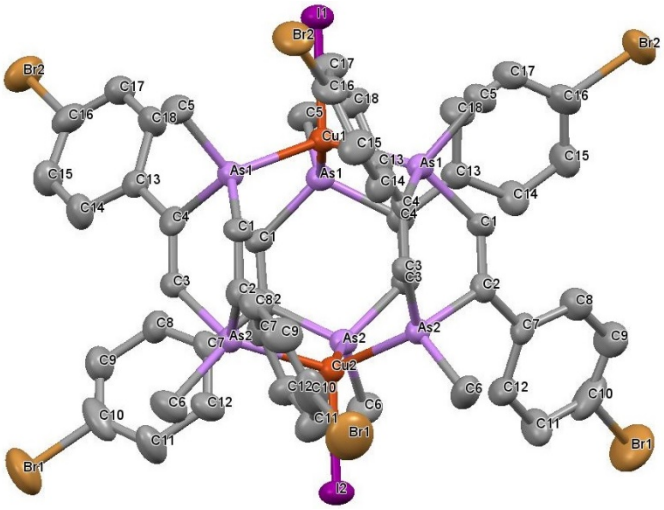
Cu-I	I(1)-Cu(1)	2.5914(6)
	I(2)-Cu(2)	2.5878(6)
Cu-As	Cu(1)-As(1)	2.3961(5)
	Cu(1)-As(3)	2.3874(6)
	Cu(1)-As(5)	2.3971(7)
	Cu(2)-As(2)	2.4056(5)
	Cu(2)-As(4)	2.3917(7)
	Cu(2)-As(6)	2.4118(6)
As-Cu-As	As(1)-Cu(1)-As(3)	114.04(2)
	As(1)-Cu(1)-As(5)	110.07(2)
	As(3)-Cu(1)-As(5)	113.02(2)
	As(2)-Cu(2)-As(4)	113.34(2)
	As(2)-Cu(2)-As(6)	112.74(2)
	As(4)-Cu(2)-As(6)	110.86(2)
Cu-As-As-Cu	Cu(1)-As(1)-As(2)-Cu(2)	5.56(3)
	Cu(1)-As(3)-As(4)-Cu(2)	6.43(3)
	Cu(1)-As(5)-As(6)-Cu(2)	11.41(3)

Table S5. Selected angles (deg) and distance (Å) of the frame of **2a** in $[Cu_2I_2(\mathbf{2a})_3]$.

	α	C(3)As(1)C(6)-C(3)C(4)C(5)C(6)	149.83
		C(21)As(3)C(24)-C(21)C(22)C(23)C(24)	152.83
		C(39)As(5)C(42)-C(39)C(40)C(41)C(42)	147.37
	β	C(4)As(2)C(5)-C(3)C(4)C(5)C(6)	150.47
		C(22)As(4)C(23)-C(21)C(22)C(23)C(24)	151.64
		C(40)As(6)C(41)-C(39)C(40)C(41)C(42)	147.79
	C-As-C[a]	C(3)-As(1)-C(6)	100.9(2)
		C(4)-As(2)-C(5)	100.9(2)
		C(21)-As(3)-C(24)	101.8(2)
		C(22)-As(4)-C(23)	101.3(2)
		C(39)-As(5)-C(42)	99.1(2)
		C(40)-As(6)-C(41)	99.5(2)
	As-C=C	As(1)-C(3)-C(4)	127.9(3)
		As(1)-C(6)-C(5)	119.1(3)
		As(2)-C(4)-C(3)	119.3(3)
		As(2)-C(5)-C(6)	127.8(3)
		As(3)-C(21)-C(22)	128.6(3)
		As(3)-C(24)-C(23)	118.9(3)
		As(4)-C(22)-C(21)	119.5(3)
		As(4)-C(23)-C(24)	129.1(3)
		As(5)-C(39)-C(40)	126.9(3)
		As(5)-C(42)-C(41)	119.6(3)
		As(6)-C(40)-C(39)	119.1(3)
		As(6)-C(41)-C(42)	126.9(3)
	As-As	As(1)-As(2)	3.4661(6)
		As(3)-As(4)	3.4846(6)
2a of Cu complex		As(5)-As(6)	3.4514(6)

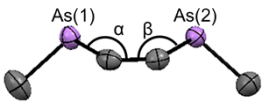
[a]Interior angles of the six membered ring.

Table S6. Selected angles (deg) and distance (Å) around the copper centers of the frame of $[Cu_2I_2(\mathbf{2b})_3]$.



Cu-I	I(1)-Cu(1)	2.577(1)
	I(2)-Cu(2)	2.586(1)
Cu-As	Cu(1)-As(1)	2.4069(6)
	Cu(2)-As(2)	2.3917(5)
As-Cu-As	As(1)-Cu(1)-As(1)	112.11(4)
	As(2)-Cu(2)-As(2)	112.37(4)
Cu-As-As-Cu	Cu(1)-As(5)-As(6)-Cu(2)	11.93(4)

Table S7. Selected angles (deg) and distance (Å) of the frame of **2b** in $[Cu_2I_2(\mathbf{2b})_3]$.



	α	C(1)As(1)C(4)-C(1)C(2)C(3)C(4)	152.08
	β	C(2)As(2)C(3)-C(1)C(2)C(3)C(4)	151.60
	C-As-C[a]	C(1)-As(1)-C(4)	101.4(2)
		C(2)-As(2)-C(3)	101.7(2)
	As-C=C	As(1)-C(1)-C(2)	129.1(3)
		As(1)-C(4)-C(3)	119.4(3)
		As(2)-C(2)-C(1)	118.5(3)
		As(2)-C(3)-C(4)	128.3(3)
	As-As	As(1)-As(2)	3.484(1)

[a]Interior angles of the six membered ring.

7. Photographs

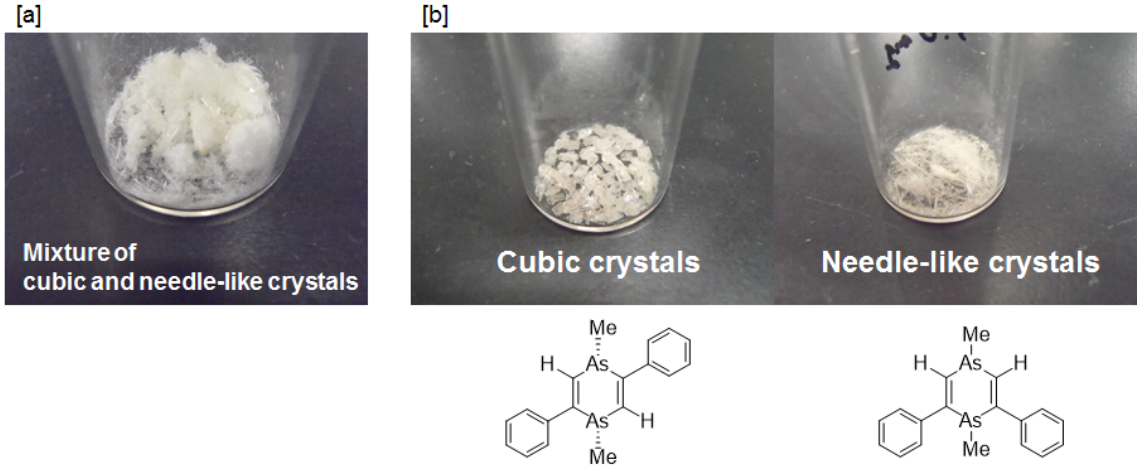


Fig. S10 Photographs of the crystals of **2a** and **3a**; [a] before sorting the crystals, and [b] the sorted cubic crystals (left, **2a**) and needle-like crystals (right, **3a**)

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