

<https://helda.helsinki.fi>

The Unusual Structural Behavior of Heteroleptic Aryl Copper(I) Thiolato Molecules : Cis vs Trans Structures and London Dispersion Effects

Zou, Wenxing

2022

Zou , W , Fettinger , J C , Vasko , P & Power , P P 2022 , ' The Unusual Structural Behavior of Heteroleptic Aryl Copper(I) Thiolato Molecules : Cis vs Trans Structures and London Dispersion Effects ' , Organometallics , vol. 41 , no. 6 , pp. 794 801 .

<http://hdl.handle.net/10138/355803>

<https://doi.org/10.1021/acs.organomet.2c00018>

unspecified

acceptedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

**The Unusual Structural Behavior of Heteroleptic Aryl
Copper(I) Thiolato Molecules. Cis vs. Trans Structures and
London Dispersion Effects**

Journal:	<i>Organometallics</i>
Manuscript ID	om-2022-00018h.R1
Manuscript Type:	Article
Date Submitted by the Author:	16-Feb-2022
Complete List of Authors:	zou, wenxing; University of California Davis, Chemistry Fettinger, James; University of California Davis, Department of Chemistry Vasko, Petra; University of Helsinki, Department of Chemistry Power, Philip; University of California Davis, Department of Chemistry; University of California, Department of Chemistry,

SCHOLARONE™
Manuscripts

The Unusual Structural Behavior of Heteroleptic Aryl Copper(I) Thiolato Molecules.

Cis vs. Trans Structures and London Dispersion Effects

Wenxing Zou,^a James C. Fettingner,^a Petra Vasko,^{b,*} Philip P. Power^{a,*}

^a Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, United States

^b Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014, Finland

ABSTRACT

A series of heteroleptic aryl copper(I) thiolato complexes of formula $\{\text{Cu}_2(\text{SAr})\text{Mes}\}_2$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_2\text{-}2,4,6\text{-Me}_3)_2$ ($\text{Ar}^{\text{Me}6}$), **1**; $\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-iPr}_2)_2$ ($\text{Ar}^{\text{iPr}4}$), **2**; $\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_2\text{-}2,4,6\text{-iPr}_3)_2$ ($\text{Ar}^{\text{iPr}6}$), **3**) and $\{\text{Cu}_4(\text{SAr})\text{Mes}_3\}$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_2\text{-}2,4,6\text{-iPr}_3)_2\text{-}3,5\text{-iPr}_2$ ($\text{Ar}^{\text{iPr}8}$), **4**) were synthesized by the reactions of the corresponding bulky terphenyl thiols with mesitylcopper(I) with elimination of mesitylene. All complexes were characterized by single crystal X-ray diffraction analysis and spectroscopy (NMR, infra-red and UV-vis). The data for **1-3** revealed tetrametallic Cu_4 core structures in which two thiolato or two mesityl ligands bridge the metals. Although **1** and **2** feature the expected conventional alternating thiolato and mesityl bridging patterns, **3** has a previously unknown structural arrangement in which the two thiolato ligands are

1
2
3 adjacent to each other. Since complex **3** has a more crowding aryl group on the thiolato ligands,
4
5
6 the cis arrangement of the ligands in **3** is sterically counterintuitive and is likely due to London
7
8 dispersion (LD) energy effects. Complex **4**, also has an unusual structural pattern in which only a
9
10 single thiolato ligand is incorporated in the structure probably for steric reasons. It has a planar
11
12 trapezoidal Cu₄ core in which three Cu--Cu edges are bridged by the mesityl groups while the
13
14 remaining Cu--Cu edge is thiolato ligand bridged. Dispersion connected DFT calculations show
15
16 that **3** has the highest LD effect stabilization arising from the increased numbers of C-H...H-C
17
18 interactions of the isopropyl ligand substituents.
19
20
21
22
23
24
25
26
27
28
29
30
31
32

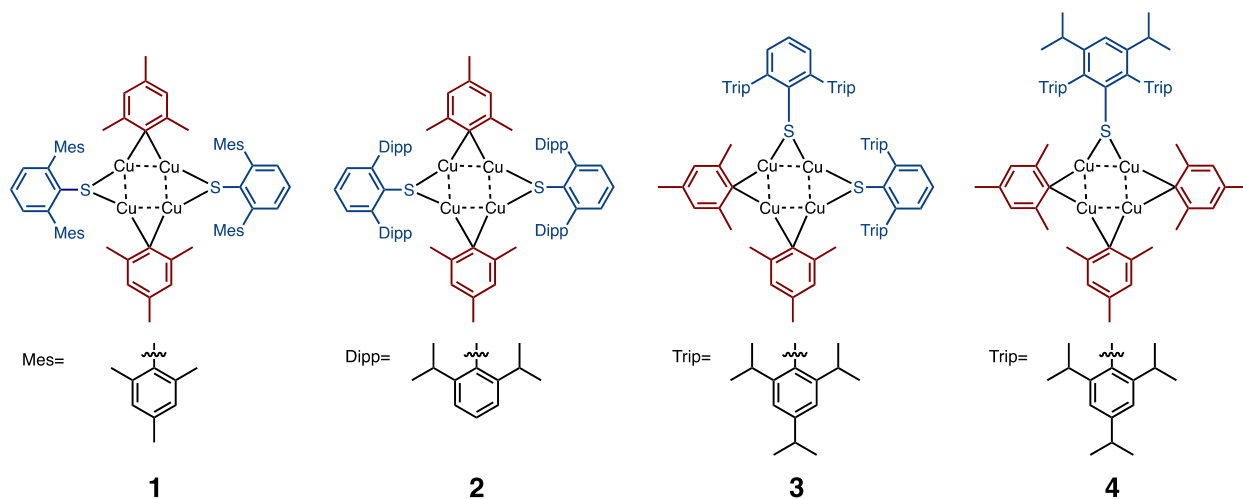
33 INTRODUCTION

34
35 Sterically crowding ligands are widely used in inorganic/organometallic chemistry to stabilize
36
37 compounds with unusual coordination numbers, bonding and/or oxidation states.¹⁻⁵ Their use is
38
39 predicated on the notion that such ligands repel each other due to their overlapping electron clouds.
40
41
42
43

44 In effect, there is intrusion of electronic wave functions on each other's space contrary to the Pauli
45
46 exclusion principle, i.e., Pauli repulsion. However, in addition to this repulsion, there is growing
47
48 evidence that attractive London dispersion (LD) interactions between the C-H moieties of the
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 hydrocarbyl substituents of the ligands⁵⁻⁷ can generate unexpected effects and enable the formation
4
5
6
7 of species with unusual structures. Such effects are manifested for example, in the stable
8
9
10 hexaphenylethane derivative $\{C(C_6H_3-3,5-tBu_2)_3\}_2$ of Grimme and Schreiner,⁸ the divalent group
11
12
13
14 chalcogenetates,⁹ high oxidation state mid to late transition metal alkyls,^{10,11} or in the low
15
16
17 coordinate copper (II) amides.¹² In pursuit of further examples of low coordinate copper (II)
18
19
20 species, we investigated the use of large terphenyl substituted thiolato ligands where dispersion
21
22
23 effects had been noted earlier by Ziegler.⁵ The use of the terphenyl thiolato ligands has recently
24
25
26 afforded the first dimeric copper(I) thiolato derivatives¹³ $\{CuSAr^{iPr4}\}_2$ and $\{CuSAr^{iPr6}\}_2$ from the
27
28
29 reaction of the thiol with a mesitylcopper(I)¹⁴ precursor. Upon further investigation we found that
30
31
32
33 adjustment of the ratio of the thiolate ligand to copper yielded unknown types of heteroleptic
34
35
36 organo/thiolato copper molecules $\{Cu_2(SAr)Mes\}_2$ (Mes = $-C_6H_2-2,4,6-Me_3$; Ar = $-C_6H_3-2,6-$
37
38 $(C_6H_2-2,4,6-Me_3)_2$ (Ar^{Me6}), **1**; $-C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$ (Ar^{iPr4}), **2**; $-C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)_2$
39
40
41 $(C_6H_2-2,4,6-Me_3)_2$ (Ar^{Me6}), **1**; $-C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$ (Ar^{iPr4}), **2**; $-C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)_2$
42
43 (Ar^{iPr6}) , **3**) and $\{Cu_4(SAr)Mes_3\}$ (Ar = $C_6H-2,6-(C_6H_2-2,4,6-Me_3)_2-3,5-iPr_2$ (Ar^{iPr8}), **4**. Whereas **1**
44
45
46
47 and **2** feature the expected alternating thiolato and mesityl ligands in which the pairs of mesityl
48
49
50 and thiolato groups appear trans to each other, the more crowded Ar^{iPr6} substituted **3** has a structure
51
52
53
54 in which the mesityl and thiolato groups have mutually cis positions apparently as a result of
55
56
57
58
59
60

1
2
3
4 enhanced ligand dispersion effects. This cis structural arrangement of ligands was unknown in
5
6
7 organocopper chemistry featuring Cu_4 core arrays. X-ray crystallographic studies revealed that
8
9
10 complexes **1-4** display Cu_4 cores but their thiolato ligands were found to have different
11
12
13 arrangements relative to the Cu_4 core, Thus, whereas **1** and **2** have symmetrical structures and
14
15
16 alternating aryl and thiolate ligands (Figure 1), **3** has a unique cis disposition of these ligands. The
17
18
19
20 very large size of the aryl substituents in **4** prevents the incorporation of further thiolato groups.
21
22
23



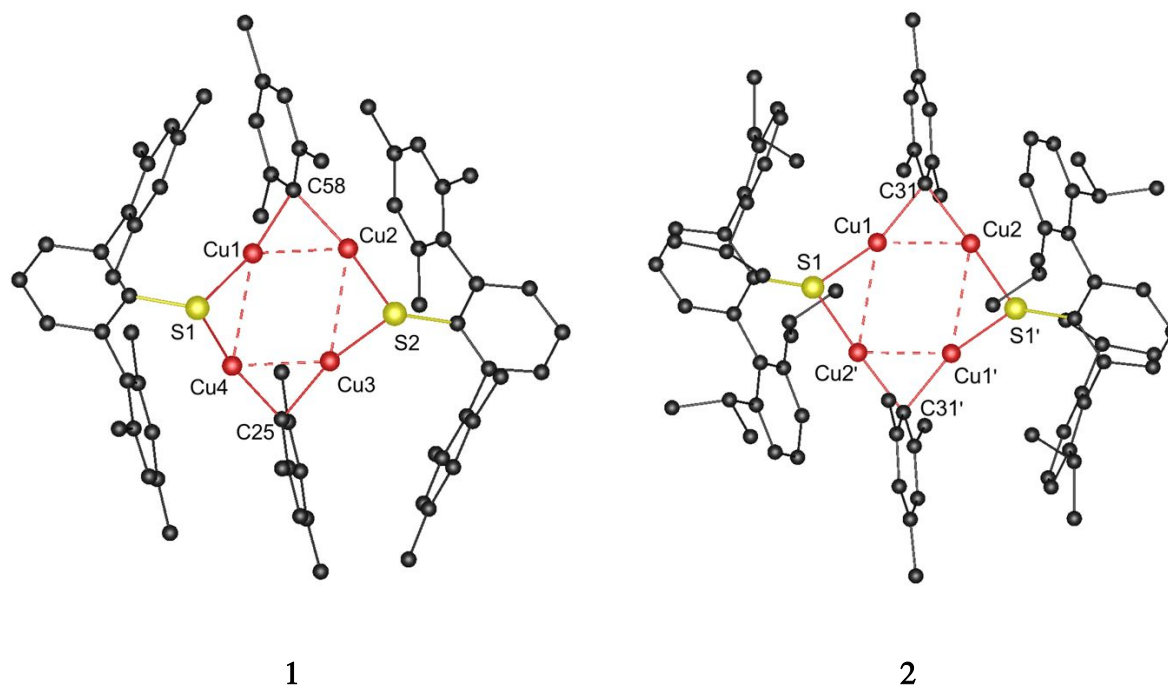
41 Figure 1. complexes **1-4** with different ligand arrangements.
42
43
44
45
46

47 RESULTS AND DISCUSSION

48 Structures 49 50 51 52 53 54 55 56 57 58 59 60

1
2
3
4 The reactions of the terphenyl thiols ($\text{HSAr}^{\text{Me}6}$ for **1**, $\text{HSAr}^{\text{iPr}4}$ for **2**, $\text{HSAr}^{\text{iPr}6}$ for **3** and $\text{HSAr}^{\text{iPr}8}$
5
6
7 for **4**) and half equiv of $\{\text{CuMe}\}_4$ in THF at 80°C for two days (in toluene at 110°C, four days for
8
9
10 **4**) afforded the aryl copper terphenyl thiolates **1-4**. The structures of the heteroleptic aryl/thiolato
11
12
13 copper derivatives **1** and **2** have little precedent but they are related to previously reported
14
15
16 heteroleptic tetracopper species $\{\text{Cu}_2\text{RindBr}\}_2$ (Rind= rigid fused-ring s-hydrindacenyl skeleton)¹⁵
17
18
19 and $\{\text{LAl(R)OCu}\cdot\text{MesCu}\}_2$ (L= $\text{HC}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$, R=Me or Et).¹⁶ The compound **1** (Figure 2,
20
21
22 left) displays a Cu_4 core array arranged in a non-planar parallelogram in which the metals are
23
24
25 bridged by the C_{ipso} atoms of the mesityls or thiolato ligand sulfur atoms in an alternating manner.
26
27
28
29
30 The two sulfur atoms are located on the same side of the Cu_4 core. The S atoms have pyramidalized
31
32
33 coordination in which the sum of the angles at S = $302.22(14)^\circ$. The Cu--Cu distances bridged by
34
35
36 the thiolato groups are 2.82(7) and 2.86(7) Å whereas those bridged by the mesityl ligands are ca.
37
38
39 0.4 Å shorter at 2.43(5) and 2.43(5) Å. The latter pair of distances are greater than the sum of the
40
41
42 covalent radii (2.24 Å)¹⁷ of two Cu atoms but lie within the sum of the van der Waals radii (2.8
43
44
45 Å),¹⁸ suggesting either no covalent Cu--Cu bonding or weak van der Waals interactions. The
46
47
48
49 lengths of Cu-S bonds range from 2.16(11) to 2.18(9) Å, which are similar to those in other copper
50
51
52 thiolates.¹⁹ Likewise, the structure of complex **2** (Figure 2, right) is similar to that of **1**, but it has
53
54
55
56
57
58
59
60

1
2
3
4 a center of symmetry in which the planar, rectangular Cu₄ core is also coplanar with C_{ipso} atoms
5
6
7 C31 and C31' of the mesityl groups. The two pyramidally coordinated S atoms of the thiolato
8
9
10 ligands are located on the opposite side of the Cu₄ plane with a distance between of 0.76(8) Å the
11
12
13 S atom and extended Cu₄ core that generates an interplanar angle of 24.91(18)°. As before, the
14
15
16 separation of the Cu atoms bridged by the thiolates (2.92(6) Å) is much greater than the separation
17
18
19
20 between copper atoms bridged by the mesityl groups (2.45(5) Å).



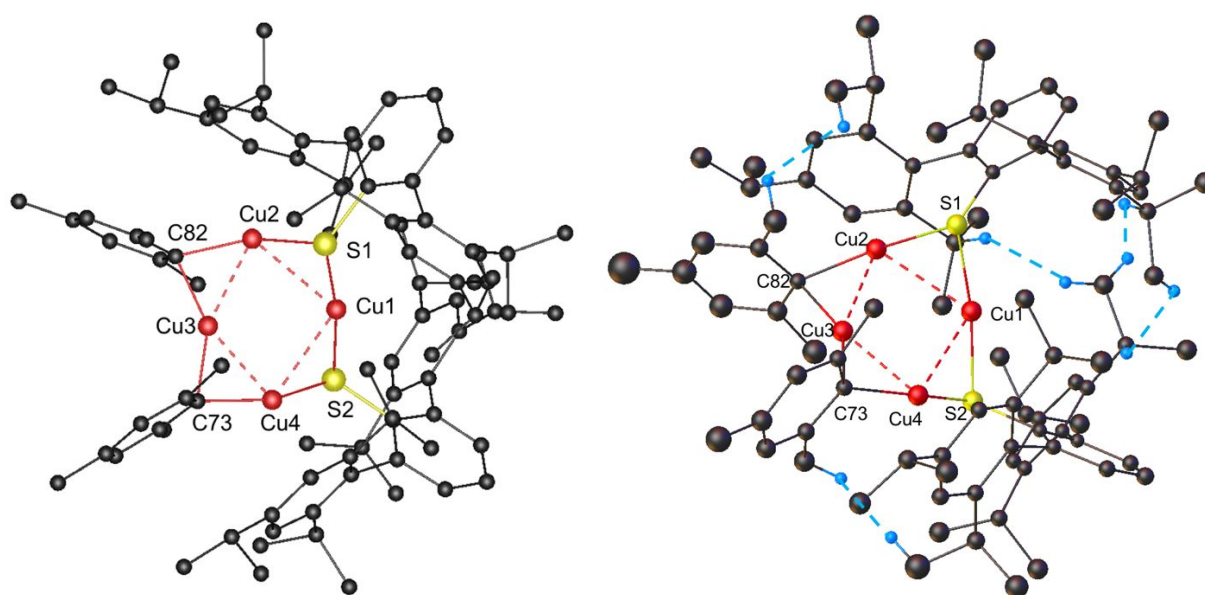
47 Figure 2. Molecular structures of 1 and 2 with thermal ellipsoids shown at 30% probability.

48
49
50 Hydrogen atoms are not shown. Selected lengths (Å) and angles (deg) of 1: Cu1--Cu2 2.43(5),
51
52
53 Cu2--Cu3 2.86(7), Cu3--Cu4 2.43(5), Cu4--Cu1 2.82(7), S1-Cu1 2.16(8), S1-Cu4 2.18(8), C58-

1
2
3 Cu1 2.00(2), C58-Cu2 1.99(2), Cu1-Cu2-Cu3 77.97(17), Cu2-Cu3-Cu4 101.86(2), Cu1-C58-Cu2
4
5
6
7 75.20(8), Cu2-S2-Cu3 80.96(3), and for **2**: Cu1--Cu2 2.45(5), Cu1--Cu2' 2.92(6), S1-Cu1 2.17(6),
8
9
10 S1-Cu2' 2.16(6), C31-Cu1 2.00(2), C31-Cu2 1.97(18), Cu1-Cu2-Cu1' 80.58(17), Cu2-Cu1'-Cu2'
11
12
13 99.42(17), Cu1-C31-Cu2 75.86(7), Cu1-S1-Cu2' 84.73(2).
14
15
16
17
18
19

20 The combination of the thiol HSAr^{iPr6} and {CuMes}₄ in THF with stirring at 80°C for two days
21
22
23 gave a pale yellow solution which, upon removal of the solvent under reduced pressure and
24
25
26 recrystallization from toluene, yielded complex **3** in 16% yield. Complex **3** incorporates two
27
28
29 bulkier thiolato ligands, but its structure displays a cis arrangement of the ligands in which the S
30
31
32 atoms of thiolato groups bridge the two adjacent Cu--Cu edges. In the solid state, **3** was observed
33
34
35
36 to have a previously unknown and sterically counterintuitive cis arrangement of the ligands (shown
37
38
39 in Figure 3, left). The Cu1--Cu2 and the adjacent Cu1--Cu3 edges are bridged by the S atoms of
40
41
42
43 thiolato groups while the Cu2--Cu4 and the adjacent Cu3--Cu4 edges are bridged by the C_{ipso} atoms
44
45
46
47 of mesityl groups. The Cu--Cu distances spanned by the thiolato ligands are more than ca. 0.3 Å
48
49
50 longer than the Cu--Cu distances bridged by the mesityl groups (2.42(5) Å), which is consistent
51
52
53
54 with the distances in **1** and **2** above. Complex **3** also has several close interligand H-H contacts
55
56
57
58
59
60

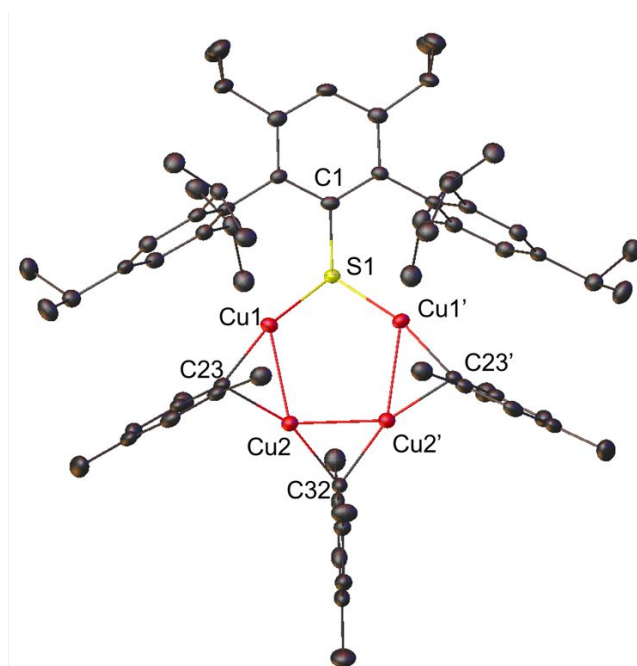
1
2
3
4 across the Cu₄ core within the sum of their van der Waals radii (ca. 2.4 Å) arising from the
5
6
7 isopropyl groups of the thiolato and mesityl substituents (indicated with dashed blue lines in Figure
8
9
10
11 3, right), suggesting the LD interaction between thiolato and mesityl CH₃ groups. In contrast, no
12
13
14 close interligand H-H contacts were observed in the molecular structures of either 1 or 2,
15
16
17 suggesting the sterically counterintuitive structure of 3 is a consequence of enhanced LD effects
18
19
20 caused by increased number of isopropyl substituents.
21
22



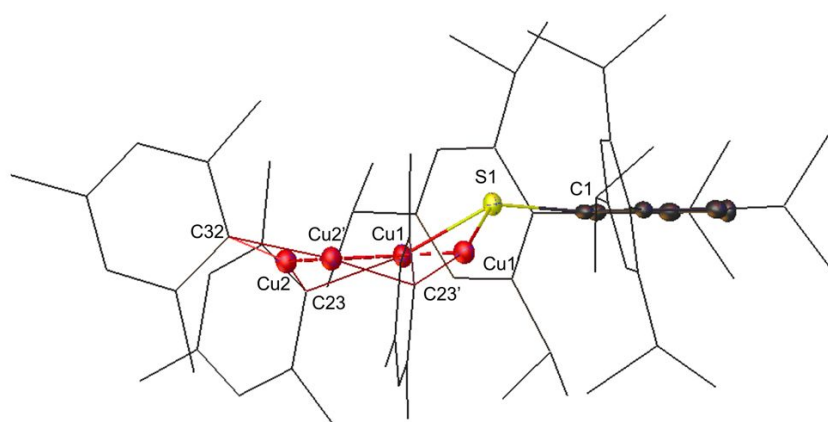
44 Figure 3. Molecular structure of 3 with thermal ellipsoids shown at 30% probability (left). Selected
45
46
47 interatomic distances (Å) and angles (deg): Cu1--Cu2 2.73(5), Cu1--Cu4 2.76(5), Cu2--Cu3
48
49 2.42(5), Cu3--Cu4 2.42(5), S2-Cu1 2.17(6), S2-Cu4 2.20(6), C82-Cu2 2.01(2) C82-Cu3 2.00(2),
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 94.10(16), Cu1-S2-Cu4 78.02(2), Cu3-C73-Cu4 74.60(8). Some interligand H-H contacts across
5
6
7 the Cu₄ core within the sum of their van der Waals radii (ca. 2.4 Å) are indicated with dashed blue
8
9
10 lines (right). All other hydrogens are not shown.

11
12
13
14
15
16
17 We also investigated the reaction of the extremely bulky Ar^{iPr8} substituted thiol HSAr^{iPr8} and
18
19
20 {CuMes}₄ under similar conditions to those used for **3**, expecting to isolate a further example of a
21
22
23 cis-substituted aryl thiolato copper isomer, i.e. {Cu₂(SAr^{iPr8})Mes}₂, with a structure analogous to
24
25
26
27 that of **3**. The reaction of HSAr^{iPr8} and {CuMes}₄ in toluene at 110°C for four days gave a yellow
28
29
30 solution, from which some colorless crystals were isolated after 4-5 days' storage in a ca. 5 °C
31
32
33 refrigerator. However, crystallographic and spectroscopic results showed that the complex
34
35
36
37 incorporated only a single thiolato ligand, which resulted in an unusual, trapezoidal Cu₄ core array
38
39
40 in which three Cu--Cu edges are bridged by the mesityls while one Cu--Cu edge is bridged by the
41
42
43 thiolato ligand (Figure 4).



top view



side view (ligands are shown as wire frames)

Figure 4. Top view and side view of the molecular structures of **4** with thermal ellipsoids shown at 30% probability (top view). Hydrogen atoms are not shown. Selected distances (Å) and angles (deg): Cu1--Cu2 2.45(5), Cu2--Cu2' 2.37(8), Cu1--Cu1' 3.21(8) S1-Cu1 2.17(6), C1-S1 1.78(3),

1
2
3
4 Cu1-C23 1.98(2), Cu2-C32 1.99(2), Cu1-Cu2-Cu2' 99.91(13), Cu1-S1-Cu1' 95.43(4), Cu1-C23-
5
6
7 Cu2 76.31(7), Cu2-C32-Cu2' 73.14(10).
8
9
10
11
12

13 As depicted in Figure 4, complex **4** has an unusual trapezoid-shaped Cu₄ core with bridging by
14
15
16
17 three mesityl groups and a single thiolato ligand. The essentially planar Cu₄ core lies parallel to
18
19
20 the central ring of the thiolato ligand with a vertical distance of 2.11(17) Å (see side view in Figure
21
22
23
24 4), the mesityl group that bridges Cu2 and Cu2' is essentially perpendicular to the Cu₄ core plane.
25

26
27 The sulfur atom S1 is located on the opposite side of the central ring of the thiolato ligand relative
28
29
30 to the Cu₄ core (a distance of 0.058(12) Å between the sulfur and the extended central ring). C32
31
32
33 atom is located on the same side of the Cu₄ plane relative to the sulfur atom with a distance between
34
35
36
37 S1 and extended Cu₄ plane of 0.97(9) Å, C23 and C23' atoms lie on the other side (a distance
38
39
40 between C23 and extended Cu₄ plane of 0.74(3) Å). The molecule is symmetric with respect to a
41
42
43
44 mirror plane that is perpendicular to the Cu₄ plane and contains the C1-S1 single bond. The Cu1-
45
46
47 -Cu2 and Cu2--Cu2' distances are slightly different (by ca. 0.08(5) Å). The Cu1--Cu2 distance is
48
49
50 2.45(5) Å, which is in the normal range for aryl copper species.^{14,20} However, the Cu2--Cu2'
51
52
53
54 distance was determined to be 2.37(8) Å, which is at the shortest end of the range for Cu(I)
55
56
57
58
59
60

1
2
3
4 thiolates,^{13,21} aryl copper complexes^{14,20} or even copper amides.²²⁻²⁴ The Cu1--Cu1' distance is
5
6
7 3.21(8) Å, which is considerably greater than the sum of the van der Waals radii (2.8 Å),¹⁷
8
9
10 suggesting no significant interaction between these two copper centers.
11
12
13
14

15 Spectroscopy

16
17
18 The ¹H NMR spectrum of complex **1** is relatively simple and well resolved, showing two singlet
19
20
21 signals at 1.98 (12H) and 1.85 (24H) ppm in C₆D₆ attributable to the protons of the methyl groups
22
23
24 of the thiolato ligands. There are also two singlet signals centered at 2.28 (12H) and 2.21 (6H)
25
26
27 ppm which can be assigned to the methyl hydrogens of the copper mesityl substituents. The ¹H
28
29
30
31 NMR spectrum of complex **2** displays two singlets at 1.20 and 1.00 ppm in the aliphatic region for
32
33
34 the methyl groups of the isopropyls of the thiolato ligands, each integrating to 24 hydrogens, and
35
36
37 the hydrogens of the mesityl groups are observed as 2.33 and 2.29 ppm. In contrast, complex **3**
38
39
40
41 displays a rather complicated ¹H NMR spectrum, which is expected due to the magnetic
42
43
44 inequivalence caused by the lower symmetry of this molecule. Each isopropyl group has a unique
45
46
47 chemical environment, which yields unique chemical shift values making it close to impossible to
48
49
50
51 distinguish them by 1D ¹H NMR alone. The ¹H NMR spectrum of **4** has two sets of singlets
52
53
54 centered at 2.63/2.51 and 1.99/1.76 ppm, respectively, corresponding to para and ortho methyls of
55
56
57
58
59
60

1
2
3 the mesityl groups. The spectrum also shows three broadened signals (2.97, 2.54 and 2.41 ppm)
4
5
6 expected for the methine hydrogens of isopropyls of the terphenyl thiol. The signals for methyl
7
8
9
10 groups of the isopropyls resonate at 1.77, 1.23 and 1.08 ppm, which are comparable to those of
11
12
13 complexes **2** and **3**. The UV–Vis spectra of complexes **1-4** show broad absorption bands in the
14
15
16 range of 273 to 303 nm with the molar extinction coefficient in the range of 1700 M⁻¹ cm⁻¹ to 3000
17
18
19 M⁻¹ cm⁻¹, featuring a charge transfer process which is also seen in some related species.^{13,25}
20
21
22
23
24
25
26

27 Computational Studies

28
29
30 To investigate the bonding in the copper species, the structures of compounds **2** and **3** were
31
32 optimized using density functional theory (DFT) at the PBE1PBE/Def2-TZVP level of theory with
33
34 and without empirical dispersion correction (GD3BJ) (see SI, Table S2). Inspection of the
35
36 optimized bond parameters (Table S2 in SI) reveals that the calculated structures are generally in
37
38 good agreement with those experimentally observed. The dispersion corrected structures show
39
40 slightly shorter Cu-Cu distances than those measured in the solid state, but this could be accounted
41
42 for by the solid-state packing effects. In contrast, the optimizations conducted without a dispersion
43
44 correction returned gas phase structures with slightly underestimated bond interactions.
45
46

47
48 Then, the hypothetical structures of cis-**2** and trans-**3** molecules were optimized and the energies
49
50 of the two isomers were compared (Table 1). The results show that for both compounds **2** and **3**
51
52 the cis isomer is more stable than the trans isomer. In the case of **2**, however, the Gibbs free energy
53
54 difference is only 0.2 kJ·mol⁻¹ in favor of the cis-isomer, for **3** the energy difference is more
55
56
57
58
59
60

substantial, amounting to 15.8 kJ·mol⁻¹. The experimentally obtained isomer **2** is most likely stabilized by solid state effects, which cannot be reproduced by these gas phase calculations.

Table 1. Calculated energies (in a.u.) and the energy difference (in kJ·mol⁻¹) of the **2** and **3** cis- and trans-isomers.

	2 _{cis}	2 _{trans}	3 _{cis}	3 _{trans}
	PBE1PBE-D3	PBE1PBE-D3	PBE1PBE-D3	PBE1PBE-D3
<i>E</i> (a.u.)	-10383.77692	-10383.774290	-10854.820530	-10854.81715
<i>H</i> (a.u.)	-10383.77598	-10383.773346	-10854.819586	-10854.81621
<i>G</i> (a.u.)	-10384.00867	-10383.008598	-10855.092833	-10855.0868
$\Delta E_{\text{cis-trans}}$ (kJ·mol ⁻¹)	-6.9		-8.9	
$\Delta H_{\text{cis-trans}}$ (kJ·mol ⁻¹)	-6.9		-8.9	
$\Delta G_{\text{cis-trans}}$ (kJ·mol ⁻¹)	-0.2		-15.8	

The thermodynamic data for the dissociation reaction of **2/3** → 2 MesCu and 2 TerphSCu fragments were investigated. The data are summarized in Table 2. Without the dispersion effects, the Gibbs free binding energies are 336 and 320 kJ·mol⁻¹ for **2** and **3**, respectively.

Table 2. Energies for the dissociation reaction $2/3 \rightarrow 2 \text{ TerphSCu} + 2 \text{ MesCu}$ ($\text{kJ}\cdot\text{mol}^{-1}$) with/without LD effects.

	2 PBE1PBE-D3	2 PBE1PBE	3 PBE1PBE-D3	3 PBE1PBE
ΔE	740	508	759	502
ΔH	747	515	767	510
ΔG	549	336	562	320

However, when the dispersion correction is applied, the ΔG value is increased to 549 (for **2**) and 562 (for **3**) $\text{kJ}\cdot\text{mol}^{-1}$. These data clearly suggest that dispersion effects play a significant role in the energy of the association of **2** and **3**. This is further corroborated by an energy decomposition analysis (EDA) which confirms that ca. 25 % (**2**) and 28 % (**3**) of the overall bonding energy can be attributed to dispersion (Figure 5).

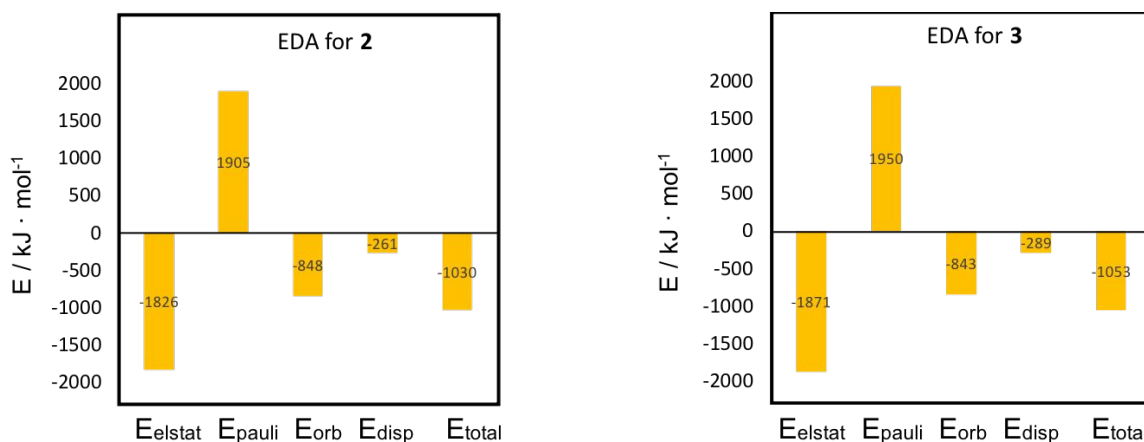


Figure 5. Summary of Energy Decomposition Analysis (EDA) results for **2** and **3** ($\text{kJ}\cdot\text{mol}^{-1}$).

Conclusion

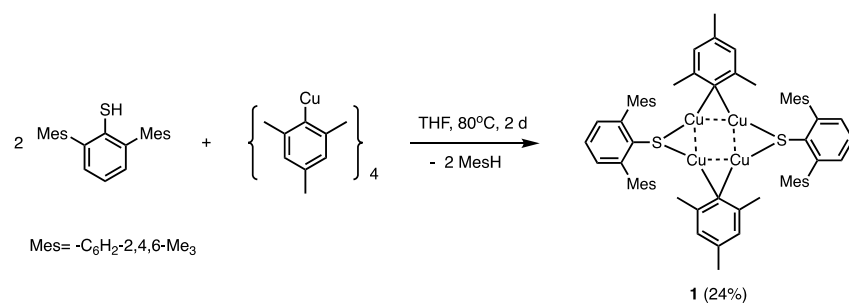
1
2
3
4 Four new mixed-ligand copper(I) thiolato compounds were synthesized by the treatment of large
5
6
7 terphenyl thiols with mesitylcopper(I). These species have rare Cu₄ core arrays that are bridged
8
9
10 by thiolato and organic groups and display a counterinitative structural arrangement in the case of
11
12
13
14 3. Dispersion forces are shown to be a significant factor in the molecular structures of the
15
16
17 compounds, which is evidenced by structural and theoretical studies.
18
19
20
21
22

23 **EXPERIMENTAL SECTION**

24 **General considerations.**

25
26
27
28
29
30 All manipulations were carried out under anaerobic and anhydrous conditions by using Schlenk
31
32
33 techniques or in a Vacuum Atmospheres OMNI-Lab drybox under an atmosphere of dry argon or
34
35
36 nitrogen. Solvents were dried by the method of Grubbs²⁶ and co-workers, stored over potassium
37
38
39 or sodium, and then degassed by the freeze-pump-thaw method. All physical measurements were
40
41
42 made under strictly anaerobic and anhydrous conditions. The NMR spectra were recorded on a
43
44
45 Varian Inova 600 MHz spectrometer, and the ¹H NMR spectra were referenced to the residual
46
47
48 solvent signals in deuterated benzene, while the ¹³C NMR spectra were referenced to the residual
49
50
51 solvent signals in deuterated THF. IR spectra were recorded as Nujol mulls between CsI plates on
52
53
54
55
56
57
58
59
60

1
2
3 a PerkinElmer 1430 spectrometer. UV-vis spectra were recorded as dilute hexane solutions in 3.5
4
5
6
7 mL quartz cuvettes using an Olis 17 modernized Cary 14 UV-vis-near-IR spectrophotometer or
8
9
10 an HP 8452 diode-array spectrophotometer. The terphenyl thiols HSAr^{Me6} , $\text{HSAr}^{\text{iPr4}}$, $\text{HSAr}^{\text{iPr6}}$ ²⁷
11
12
13 and mesitylcopper(I)¹⁴ were prepared via literature methods. Unless otherwise stated, all materials
14
15
16
17 were obtained from commercial sources and used as received.



38 Figure 6. Synthesis of the complex 1

39
40
41 $\{\text{Cu}_2(\text{SAr}^{\text{Me6}}\text{Mes})_2\}$ (1) Solid terphenyl thiol HSAr^{Me6} (0.346 g, 1 mmol) was combined with
42
43
44 $\{\text{CuMes}\}_4$ (0.364 g, 0.5 mmol), and ca. 60 mL of THF was added. The solution was heated at 80°C
45
46
47 for 2 days, yielding a pale yellow color. The solvent was then evaporated under reduced pressure
48
49
50 to dryness, and the pale yellow residue was extracted with ca. 50 mL of hexane. The solution was
51
52
53
54
55 filtered through Celite and concentrated to ca. 15 mL under reduced pressure until the formation
56
57

of small colorless crystals was observed. The solution was stored in a ca. -18 °C freezer for 4 days to yield 0.287 g (24%) of **1** as colorless crystals which were suitable for X-ray crystallography.

Mp: 198-201°C. ¹H NMR (600 MHz, benzene-*d*₆): δ= 7.11 (s, 1H), 6.82 (t, J = 7.2 Hz, 2H), 6.65

(d, J = 1.0 Hz, 2H), 6.64 (d, J = 1.0 Hz, 2H), 6.61 (s, 4H), 6.58 (s, 7H), 2.28 (s, 12H), 2.21 (s, 6H),

1.98 (s, 12H), 1.85 (s, 24H). ¹³C NMR (150 MHz, benzene-*d*₆): δ= 155.96, 143.29, 139.72, 139.25,

137.12, 136.20, 134.71, 129.30, 128.84, 128.16, 125.49, 125.33, 29.02, 21.21, 21.03, 20.08.

UV/vis: λ/nm (ε/M⁻¹ cm⁻¹): 303 (1700). IR (Nujol; $\tilde{\nu}$ /cm⁻¹): 1659w, 1590w, 1562w, 1455s, 1370s,

1258w, 1048w, 841m, 792m, 769w, 737m, 719w, 705w, 571w.

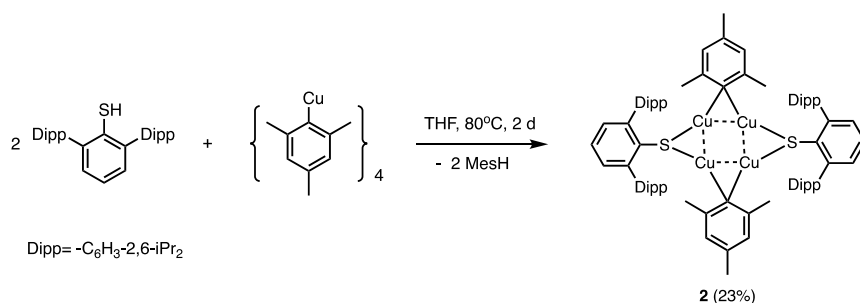


Figure 7. Synthesis of the complex **2**

{Cu₂(SAr^{iPr4})Mes}₂ (**2**). The synthesis of **2** was accomplished in a similar manner to that of **1** with the use of the terphenyl thiol HSAr^{iPr4} (0.43 g, 1 mmol) and {CuMes}₄ (0.364 g, 0.5 mmol) in ca. 60 mL of THF, yielding 0.31 g (23%) of colorless crystals which were suitable for X-ray

crystallographic studies. Mp: decomposed at 190°C. ^1H NMR (600 MHz, benzene- d_6): δ 6.97-6.92 (m, 4H), 6.90 (d, $J = 6.7$ Hz, 8H), 6.88- 6.83 (m, 6H), 6.71 (s, 4H), 2.73 (m, $J = 7.0$ Hz, 8H), 2.33 (s, 6H), 2.29 (s, 12H), 1.20 (d, $J = 6.9$ Hz, 24H), 1.00 (d, $J = 6.8$ Hz, 24H). ^{13}C NMR (150 MHz, benzene- d_6) δ 156.17, 145.03, 142.55, 140.68, 139.96, 137.24, 132.73, 129.62, 129.60, 126.36, 126.34, 123.04, 30.74, 30.66, 30.11, 24.32, 23.76, 23.73. UV/vis: λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 279 (3000). IR (Nujol; $\tilde{\nu}/\text{cm}^{-1}$): 1930w, 1584w, 1569w, 1458s, 1371s, 1350m, 1319w, 1275w, 1255w, 1097w, 1050w, 1035m, 929w, 838s, 810m, 791s, 782s, 751s, 742s, 693w, 595w, 566w, 543w, 525w, 462w, 350w.

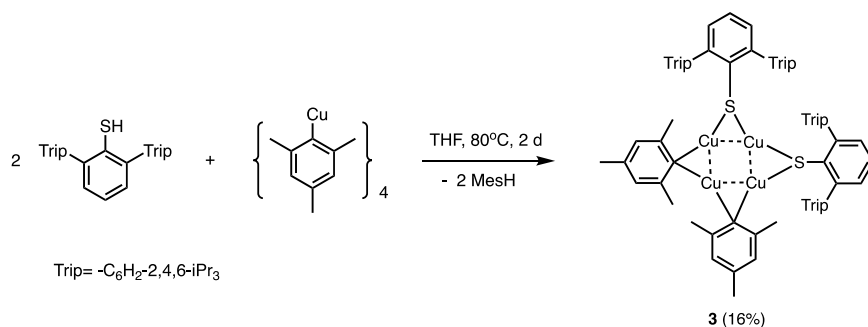


Figure 8. Synthesis of the complex **3**

{Cu₂(SAr^{iPr6})Mes}₂ (3). The terphenyl thiol HSAr^{iPr6} (0.514 g, 1 mmol), {CuMes}₄ (0.364 g, 0.5 mmol) and ca. 60 mL of THF were combined in a Schlenk tube, and the solution was allowed to stir at 80°C for 2 days. The solvent was removed under reduced pressure, and the residue was extracted with ca. 50 mL of toluene, the resulting solution was filtered through Celite and the

1
2
3
4 filtrate was concentrated to ca. 10 mL under reduced pressure and stored at room temperature for
5
6
7 4 days, yielded 0.24 g (16%) colorless crystals which were suitable for X-ray crystallography. Mp:
8
9
10 227-231°C. ^1H NMR (600 MHz, benzene- d_6): δ 7.26 (d, $J = 13.0$ Hz, 3H), 7.11 – 7.03 (m, 3H),
11
12
13 6.96 (dd, $J = 14.8, 7.5$ Hz, 3H), 6.76 – 6.64 (m, 4H), 6.54 (s, 2H), 6.36 (d, $J = 18.9$ Hz, 3H), 3.14
14
15
16 (q, $J = 7.0$ Hz, 2H), 2.95 (m, $J = 19.8, 6.8$ Hz, 5H), 2.89 – 2.64 (m, 3H), 2.61 – 2.53 (m, 2H), 2.52
17
18
19 – 2.32 (m, 8H), 2.26 (s, 5H), 2.08 (d, $J = 13.4$ Hz, 1H), 2.05 (s, 2H), 1.83 (s, 5H), 1.61 (d, $J = 6.8$
20
21
22 Hz, 5H), 1.47 – 1.24 (m, 24H), 1.23 (d, $J = 6.9$ Hz, 2H), 1.18 – 1.09 (m, 15H), 1.05 (d, $J = 7.0$ Hz,
23
24
25 6H), 1.01 (d, $J = 6.9$ Hz, 6H), 0.97 (d, $J = 6.9$ Hz, 6H), 0.72 (d, $J = 6.8$ Hz, 5H). ^{13}C NMR (150
26
27
28 MHz, benzene- d_6): δ 153.69, 153.02, 147.52, 147.42, 147.37, 145.57, 144.88, 142.78, 139.25,
29
30
31 138.04, 137.97, 137.65, 134.96, 130.66, 130.43, 128.92, 127.93, 124.09, 123.71, 121.52, 121.41,
32
33
34 120.98, 34.63, 32.56, 31.68, 31.01, 30.67, 30.64, 30.32, 28.82, 26.15, 25.74, 25.14, 24.98, 24.81,
35
36
37 24.79, 24.44, 24.08, 23.66, 23.25, 23.03, 22.19, 20.92. UV/vis: λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 273 (2900). IR
38
39
40
41 (Nujol; $\tilde{\nu}/\text{cm}^{-1}$): 1600m, 1589w, 1560w, 1455s, 1375s, 1355m, 1310w, 1255w, 1164w, 1096w,
42
43
44
45
46
47 936w, 872m, 843m, 796m, 761w, 741m, 723m, 688w, 645w, 518w, 459w.
48
49
50
51
52
53
54
55
56
57
58
59
60

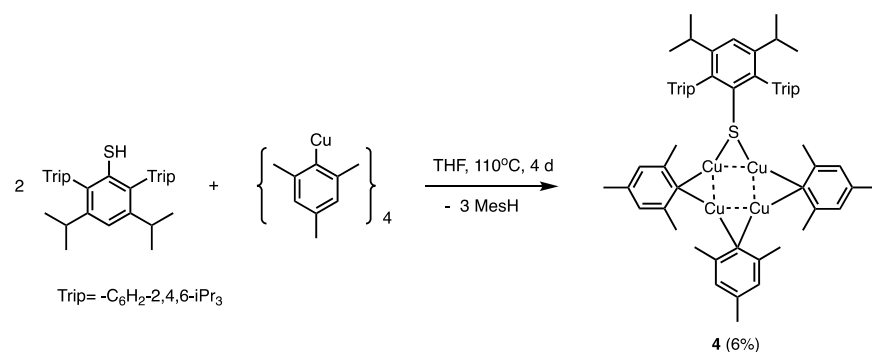


Figure 9. Synthesis of the complex 4

{Cu₄(SAr^{iPr8})Mes₃} (4). Complex 4 was prepared in a manner analogous to that used for complex

3. HSAr^{iPr8} (0.4 g, 0.67 mmol) and {CuMes}₄ (0.243 g, 0.33 mmol) were combined as solids and

ca. 50 mL of toluene was added, mixture was stirred at 110°C for 4 days. The solvent was then

removed under reduced pressure to afford an off-white residue. The residue was dissolved in ca.

50 mL of toluene, and the solvent was concentrated under reduced pressure to ca. 4 mL. The

solution was then stored at a 5°C refrigerator for 5 days to afford 0.11 g (6%) of product 4 as

colorless blocks. Mp: 185-188°C. ¹H NMR (600 MHz, benzene-*d*₆): δ 7.29 (d, J = 1.8 Hz, 1H),

7.08 (d, J = 1.9 Hz, 4H), 6.59 (s, 4H), 6.40 (s, 2H), 2.99 (td, J = 6.8, 2.0 Hz, 4H), 2.63 (d, J = 1.9

Hz, 12H), 2.55 (s, 2H), 2.51 (s, 6H), 2.44 – 2.39 (m, 2H), 1.99 (d, J = 1.7 Hz, 6H), 1.83 – 1.76 (m,

12H), 1.76 (s, J = 1.7 Hz, 3H), 1.22 (dd, J = 7.0, 1.9 Hz, 12H), 1.07 (ddd, J = 13.4, 6.8, 1.9 Hz,

24H). ¹³C NMR (150 MHz, benzene-*d*₆): δ 154.19, 153.28, 146.90, 145.68, 140.18, 136.69, 136.54,

1
2
3 135.58, 126.07, 125.91, 122.10, 32.32, 30.82, 30.32, 29.54, 28.53, 26.76, 24.67, 24.36, 23.03,
4
5
6
7 21.05, 20.92. UV/vis: λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 294 (2300). IR (Nujol; $\tilde{\nu}/\text{cm}^{-1}$): 1589w, 1518w, 1456s,
8
9
10 1372s, 1308w, 871w, 842w, 798w, 765w, 720w.
11
12
13
14
15
16

17 **X-ray Crystallographic Studies.**

18
19
20 Crystals of complexes **1** and **2** suitable for X-ray crystallographic study were obtained from
21
22 concentrated hexane solution at -18°C after 4 to 5 days, **3** and **4** were recrystallized from
23
24 concentrated toluene. Single crystals were removed from Schlenk tubes and immediately covered
25
26 concentrated toluene. Single crystals were removed from Schlenk tubes and immediately covered
27
28 with a layer of hydrocarbon oil. Suitable crystals were selected, mounted on a nylon cryo loop,
29
30
31 and then placed in the cold nitrogen stream of the diffractometer. Data for **1-4** were collected at
32
33
34 90(2) K with Cu $K\alpha_1$ radiation ($\lambda = 1.5418 \text{ \AA}$) using a Bruker DUO diffractometer in conjunction
35
36
37 with a CCD detector. The collected reflections were corrected for Lorentz and polarization effects
38
39
40 and for absorption by using Blessing's method as incorporated into the program SADABS.^{28,29}
41
42
43
44 The structures were solved by direct methods and refined with the SHELXTL (2012, version 6.1)
45
46
47 or SHELXTL (2013) software packages.³⁰ Refinement was by full-matrix least-squares procedures,
48
49
50
51 with all carbon-bound hydrogen atoms included in calculated positions and treated as riding atoms.
52
53
54
55
56
57
58
59
60

1
2
3
4 The thermal ellipsoid plots were drawn using OLEX2 software.³¹ A summary of the
5
6
7 crystallographic and data collection parameters is given in Table S1 in SI.
8
9
10
11
12

13 **Computational details**

14
15
16
17 The geometry optimizations of both isomers **2** and **3** were performed with the Gaussian16
18
19
20 (Revision C.01) program³² using the PBE1PBE hybrid exchange functional³³ and Def2-TZVP
21
22
23 basis sets.³⁴ In addition, Grimme's empirical dispersion correction with Becke-Johnson damping
24
25
26 (GD3BJ)³⁵ was used as well as an ultrafine integration grid. Full analytical frequency calculations
27
28
29 were performed for the optimized structures to ensure the nature of the stationary points found
30
31
32 (minima, no imaginary frequencies). The energy decomposition analyses (EDA)³⁶ were performed
33
34
35 using ADF2021.102 program package.³⁷ These calculations utilized the PBE1PBE functional and
36
37
38 TZ2P basis sets³⁸ for all atoms with empirical dispersion correction (GD3BJ) and good numerical
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60 quality.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge. ^1H and ^{13}C $\{^1\text{H}\}$ spectra, crystallographic data, and details of computational studies (PDF)

Accession Codes

CCDC 2129403-2129404, 2129407-2129408 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION**Corresponding Author**

Philip P. Power – Department of Chemistry, University of California, Davis, Davis, California 95616, United States; orcid.org/0000-0002-6262-3209; Email: pppower@ucdavis.edu

Petra Vasko – Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014, Finland, orcid.org/0000-0003-4202-6869; Email: petra.vasko@helsinki.fi

Authors

Wenxing Zou – Department of Chemistry, University of California, Davis, Davis, California 95616, United States; orcid.org/0000-0002-5462-8982

1
2
3 James C. Fettinger – Department of Chemistry, University of California, Davis, Davis, California
4
5 95616, United States; orcid.org/0000-0002-6428-4909
6
7

8 **Notes**

9

10 The authors declare no competing financial interest.
11
12

13 **ACKNOWLEDGMENTS**

14

15 We thank the U.S. National Science Foundation for funding (Grant No. CHE-1565501) and for
16 purchase of a dual source X-ray diffractometer (Grant No. CHE-0840444). PV would like to thank
17 the Academy of Finland for funding (project numbers 314794, 338271 and 338271) and the CSC
18 – IT Center for Science, Finland, for computational resources.
19
20
21
22
23
24
25

26 **References**

27
28

- 29
30
31 [1] Bradley, D. C. Steric Control of Metal Coordination. *Chem. Br.* **1975**, *11*, 393-397.
32
33
34 [2] Power, P. P. Some Highlights from the Development and Use of Bulky Monodentate Ligands,
35
36
37
38 *J. Organomet. Chem.*, **2004**, *689*, 3904-3919.
39
40
41 [3] Lappert, M. F. Use of the Bulky Alkyl Ligand $(\text{Me}_3\text{Si})_2\text{CH}^-$ to Stabilize Unusual Low Valent
42
43
44
45 Transition Metal Alkyls and Dialkylstannylene Derivatives, *Adv. Chem.*, **1976**, *150*, 256-265.
46
47
48 [4] Coles, M. P. the Role of the Bis-trimethylsilylamido Ligand, $[\text{N}\{\text{SiMe}_3\}_2]^-$, in Main Group
49
50
51
52 Chemistry. Part 1: Structural Chemistry of the s-block Elements, *Coord. Chem. Rev.*, **2015**, *297-*
53
54
55 *298*, 2-23.
56
57
58
59
60

- 1
2
3
4 [5] Seidu, I.; Seth, M. and Ziegler, T. Role Played by Isopropyl Substituents in Stabilizing the
5
6
7 Putative Triple Bond in $\text{Ar}'\text{EEAr}'[\text{E}=\text{Si, Ge, Sn; Ar}'=\text{C}_6\text{H}_3\text{-}2,6(\text{C}_6\text{H}_3\text{-}2,6\text{-Pri}_2)_2]$ and $\text{Ar}^*\text{PbPbAr}^*$
8
9
10 $[\text{Ar}^*=\text{C}_6\text{H}_3\text{-}2,6(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Pri}_3)_2]$. *Inorg. Chem.*, **2013**, *52*, 8378-8388.
11
12
13
14 [6] Wagner, J. P. and Schreiner, P. R. London Dispersion in Molecular Chemistry-Reconsidering
15
16
17 Steric Effects, *Angew. Chem. Int. Ed.*, **2015**, *54*, 12274-12296.
18
19
20 [7] Pollard, V. A.; Kennedy, A. R.; McLellan, R.; Ross, D.; Tuttle, T. and Mulvey, R. E.
21
22
23 Structurally Defined Ring-Opening and Insertion of Pinacolborane into Aluminium-Nitrogen
24
25
26 Bonds of Sterically Demanding Dialkylaluminium Amides, *Eur. J. Inorg. Chem.*, **2021**, 2021, 50-
27
28
29 53.
30
31
32
33 [8] Grimme, S. and Schreiner, P. R. Steric Crowding Can Stabilize a Labile Molecule: Solving the
34
35
36 Hexaphenylethane Riddle, *Angew. Chem. Int. Ed.*, **2011**, *50*, 12639-12642.
37
38
39
40 [9] Rekker, B. D.; Brown, T. M.; Fettinger, J. C.; Lips, F.; Tuononen, H. M.; Herber, R. H. and
41
42
43 Power, P. P. Dispersion Forces and Counterintuitive Steric Effects in Main Group Molecules:
44
45
46 Heavier Group 14 (Si-Pb) Dichalcogenolate Carbene Analogues with Sub-90° Interligand Bond
47
48
49 Angles, *J. Am. Chem. Soc.*, **2013**, *135*, 10134-10148.
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 [10] Liptrot, D. J.; Guo, J.; Nagase, S.; Power, P. P. Dispersion Forces, Disproportionation, and
5
6
7 Stable High-Valent Late Transition Metal Alkyls, *Angew. Chem. Int. Ed.*, **2016**, *55*, 14766-14769.

8
9
10 [11] Li, H.; Hu, Y.; Wan, D.; Zhang, Z.; Fan, Q.; King, R. B.; Schaefer, H. F. Dispersion Effects
11
12
13 in Stabilizing Organometallic Compounds: Tetra-1-norbornyl Derivatives of the First-Row
14
15
16
17 Transition Metals as Exceptional Examples, *J. Phys. Chem. A*, **2019**, *123*, 9514-9519.

18
19
20 [12] Wagner, C. L.; Tao, L.; Thompson, E. J.; Stich, T. A.; Guo, J.; Fettinger, J. C.; Berben, L. A.;
21
22
23
24 Britt, R. D.; Nagase, S.; Power, P. P. Dispersion-Force-Assisted Disproportionation: A Stable
25
26
27 Two-Coordinate Copper(II) Complex, *Angew. Chem. Int. Ed.*, **2016**, *55*, 10444-10447.

28
29
30 [13] Zou, W.; Zhu, Q.; Fettinger, J. C. and Power, P. P. Dimeric Copper and Lithium Thiolates:
31
32
33 Comparison of Copper Thiolates with Their Lithium Congeners, *Inorg. Chem.*, **2021**, *60*, 17641-
34
35 17648.

36 [14] Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T. and Saegusa, T. Preparation of Thermally
37
38
39
40 Stable and Soluble Mesitylcopper(I) and its Application in Organic Synthesis, *J. Org. Chem.*, **1981**,
41
42
43 *46*, 192-194.

44
45
46 [15] Ito, M.; Hashizume, D.; Fukunaga, T.; Matsuo, T. and Tamao, K. Isolated Monomeric and
47
48
49
50 Dimeric Mixed Diorganocuprates Based on the Size-Controllable Bulky "Rind" Ligands. *J. Am.*
51
52
53 *Chem. Soc.*, **2009**, *131*, 18024-18025.

- 1
2
3
4 [16] Li, B.; Zhang, C.; Yang, Y.; Zhu, H. and Roesky, H. W. Synthesis and Characterization of
5
6
7 Heterobimetallic Al-O-Cu Complexes toward Models for Heterogeneous Catalysts on Metal
8
9
10 Oxide Surfaces, *Inorg. Chem.*, **2015**, *54*, 6641-6646.
- 11
12
13 [17] Pyykkö, P. and Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1-118, *Chem.*
14
15
16 *Eur. J.*, **2009**, *15*, 186-197.
- 17
18 [18] Tatewaki, H.; Hatano, Y.; Naka, T.; Noro, T. and Yamamoto, S. Atomic Radii for Depicting
19
20
21 Atoms in a Molecule II: the Effective Atomic Radius and van der Waals Radius from ^1H to ^{54}Xe ,
22
23
24 *Bull. Chem. Soc. Jpn.*, **2010**, *83*, 1203-1210.
- 25
26 [19] Dance, I. G.; Bowmaker, G. A.; Clark, G. R. and Seadon, J. K. the Formation and Crystal
27
28 and Molecular Structures of Hexa(μ -organothiolato) Tetracuprate(I) Cage Dianions:
29
30 Bis(tetramethylammonium) Hexa(μ -methanethiolato)-Tetracuprate(I) and Two Polymorphs of
31
32 Bis(tetramethylammonium) hexa(μ -benzenethiolato)-Tetracuprate(I), *Polyhedron*, **1983**, *2*, 1031-
33
34 1043.
- 35 [20] Stollenz, M. and Meyer, F. Mesitylcopper-A Powerful Tool in Synthetic Chemistry,
36
37 *Organometallics*, **2012**, *31*, 7708-7727.
- 38 [21] Rungthanaphatsophon, P.; Barnes, C. L. and Walensky, J. R. Copper(I) Clusters with Bulky
39
40 Dithiocarboxylate, Thiolate, and Selenolate Ligands, *Dalton Trans.*, **2016**, *45*, 14265–14276.
- 41 [22] Satyachand Harisomayajula, N. V.; Wu, B.-H.; Lu, D.-Y.; Kuo, T.-S.; Chen, I.-C. and Tsai,
42
43 Y.-C. Ligand-Unsupported Cuprophilicity in the Preparation of Dodecacopper(I) Complexes and
44
45 Raman Studies, *Angew. Chem. Int. Ed.*, **2018**, *57*, 9925-9929.
- 46 [23] Satyachand Harisomayajula, N. V.; Makovetskyi, S.; Tsai, Y.-C. Cuprophilic Interactions in
47
48 and between Molecular Entities, *Chem. Eur. J.*, **2019**, *25*, 8936-8954.
- 49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 [24] Chiarella, G. M.; Melgarejo, D. Y.; Rozanski, A.; Hempfle, P.; Perez, L. M.; Reberb, C. and
4
5 Fackler, J. P. Jr. A Short, Unsupported Cu(I)--Cu(I) interaction, 2.65 Å, in A Dinuclear Guanidine
6
7 Chloride Complex, *Chem. Commun.*, **2010**, *46*, 136-138.

8
9
10 [25] Pratt, J.; Bryan, A. M.; Faust, M.; Boynton, J. N.; Vasko, P.; Recken, B. D.; Mansikkamaki,
11
12 A.; Fettinger, J. C.; Tuononen, H. M. and Power, P. P. Effects of Remote Ligand Substituents on
13
14 the Structures, Spectroscopic, and Magnetic Properties of Two-Coordinate Transition-Metal
15
16 Thiolate Complexes, *Inorg. Chem.*, **2018**, *57*, 6491–6502.

17
18
19 [26] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and
20
21 Convenient Procedure for Solvent Purification, *Organometallics*, **1996**, *15*, 1518-1520.

22
23
24 [27] Barnett, B. R.; Mokhtarzadeh, C. C.; Lummis, P.; Wang, S.; Queen, J. D.; Gavenonis, J.;
25
26 Schüwer, N.; Tilley, T. D.; Boynton, J. N.; Power, P. P.; Ditri, T. B.; Weidemann, N.; Agnew, D.
27
28 W.; Figueroa, J. S.; Smith, P. W.; Carpenter, A. E.; Pratt, J. K.; Mendelson, N. D.; Figueroa, J. S.
29
30 Terphenyl Ligands and Complexes, *Inorganic Synthesis*, **2018**, *37*, 85-122.

31
32
33 [28] Sheldrick, G. M. SADABS, Siemens Area Detector Absorption Correction; Göttingen
34
35 Universität: Göttingen, Germany, **2008**, p33.

36
37
38 [29] Blessing, R. H. An Empirical Correction for Absorption Anisotropy. *Acta Cryst. Sect. A:*
39
40 *Found. Cryst.*, **1995**, *51*, 33–38.

41
42
43 [30] Sheldrick, G. M. SHELXTL, version 6.1; Bruker AXS: Madison, WI, **2002**.

1
2
3
4 [31] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2:
5
6
7 A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, **2009**, *42*,
8
9
10 339–341.

11
12
13 [32] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.;
14
15
16 Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.;
17
18
19 Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian,
20
21
22 H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini,
23
24
25 F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V.
26
27
28 G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.;
29
30
31 Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell,
32
33
34 K.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.;
35
36
37 Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.;
38
39
40 Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.;
41
42
43 Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J.
44
45
46 B. and Fox, D. J. Gaussian, Inc., Wallingford CT, 2019.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 [33] a) Perdew, J. P.; Burke, K. and Ernzerhof, M. Generalized Gradient Approximation Made
5
6 Simple, *Phys. Rev. Lett.*, **1996**, *77*, 3865-3868. b) Perdew, J. P.; Burke, K. and Ernzerhof, M.
7
8 Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, **1997**, *78*, 1396-1396. c)
9
10 Adamo C. and Barone, V. Toward Reliable Density Functional Methods without Adjustable
11
12 Parameters: the PBE0 Model. *J. Chem. Phys.*, **1999**, *110*, 6158-6169.
13
14
15
16
17
18
19
20 [34] a) Weigend, F. and Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence
21
22 and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys.*
23
24 *Chem. Chem. Phys.*, **2005**, *7*, 3297-3305. b) Weigend, F. Accurate Coulomb-Fitting Basis Sets
25
26 for H to Rn. *Phys. Chem. Chem. Phys.*, **2006**, *8*, 1057-1065.
27
28
29
30
31
32
33
34 [35] Grimme, S.; Ehrlich S. and Goerigk, L. Effect of the Damping Function in Dispersion
35
36 Corrected Density Functional Theory. *J. Comp. Chem.* **2011**, *32*, 1456-1465.
37
38
39
40
41 [36] a) Rodríguez, J. I.; Bader, R. F. W.; Ayers, P.W.; Michel, C.; Götz, A.W. and Bo, C. A High
42
43 Performance Grid-Based Algorithm for Computing QTAIM Properties. *Chem. Phys. Lett.*, **2009**,
44
45 *472*, 149-152, b) Rodríguez, J. I. An Efficient Method for Computing the QTAIM Topology of A
46
47 Scalar Field: the Electron Density Case. *J. Comp. Chem.*, **2013**, *34*, 681-686.
48
49
50
51
52
53
54
55
56
57
58
59
60

[37] a) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S.

J. A.; Snijders, J. G. and Ziegler, T. Chemistry with ADF. *J. Comp. Chem.*, **2001**, *22*, 931-967, b)

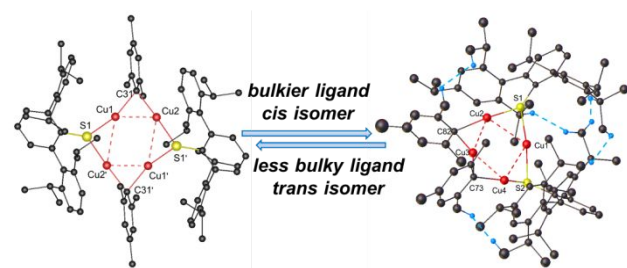
ADF 2021.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands,

<http://www.scm.com>.

[38] van Lenthe, E. and Baerends, E. J. Optimized Slater-type Basis Sets for the Elements 1-118.

J. Comp. Chem., **2003**, *24*, 1142-1156.

Table of contents



Synopsis

Four new aryl copper(I) thiolato complexes were prepared and characterized crystallographically and spectroscopically and by DFT calculations. These complexes exhibit a Cu₄ core array that is bridged by bulky terphenyl ligands or mesityl groups, one complex has a distinctive bridging pattern caused by different degree of dispersion energy and steric effects, which has been demonstrated by computational studies.