Supporting Information

Interaction of Germanium Analogue of Organic Isonitrile with Cu(I) imide in Side-on Mode

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Content

Experimenal Section

General procedures

All manipulations were carried out in a standard Schlenk technology in a dry argon atmosphere or in the glovebox (Mikrona Super 1220/750/900) with oxygen content less than 0.1 ppm. Solvents needed for synthesis in the laboratory were pre-dried with the molecular sieve 4Å for 3 days, then added with appropriate Na/K alloy and benzophenone, heated, and refluxed to make the solvents dark blue or purple. After distillation, the solvents were stored in anhydrous and oxygen-free solvent bottles in the argon atmosphere for reserve. Reagents involved in this article were purchased from Aladdin without special instructions.

The melting point of obtained compounds was measured on a digital display micro melting point meter (X-4B$^+$). Infrared spectra were recorded by using KBr pellets with a NEXUS670 (Thermo Fisher Scientific) FT-IR spectrometer. The ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Bruker Advance II 400 MHz NMR instrument at ambient temperature. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Thermo Quest Italia SPA EA1110 instrument.

NHC→Ge[N(H)Ar]$_2$ (**1**)

In a glove box LiN(H)Ar (2.041 g, 8 mmol, Ar = 2,6-*i*Pr$_2$(C$_6$H$_3$)),[1] GeCl$_2$·dioxane (0.926 g, 4.0 mmol), and N-heterocyclic carbene (NHC, 0.721 g, 4 mmol)[2] were weighed into a 100 mL Schlenk flask. 25 mL of anhydrous ethyl ether was introduced on a vacuum line using a double needle. After 12 h of continuous stirring at room temperature, a white precipitate was produced and the filtrate was concentrated to 5 mL after filtration. The solution was left to stand for 1 day, and yellow crystals of **1** were formed (1.937 g, 3.2 mmol, 80%).

M.p.: 135.2-135.6°C. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 298 K, ppm): δ 7.21 (d, J = 7.6 Hz, 4H, Ar*H*), 6.96 (t, J = 7.6 Hz, 2H, Ar*H*), 5.98 (br, 2H, N*H*), 4.34 (m, 2H, C*H*Me$_2$), 3.51 (sept, J = 6.7 Hz, 4H, C*H*Me$_2$), 1.54 (s, 6H, C*Me*), 1.34 (d, J = 6.8 Hz, 24H, CH*Me*$_2$), 1.12 (d, J = 5.6 Hz, 12H, CH*Me*$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C$_6$D$_6$, 298 K, ppm) δ 148.0, 136.6, 123.5, 117.7 (*Ar*), 28.9 (*C*HMe$_2$), 28.2 (*C*HMe$_2$), 24.5 (CH*Me*$_2$), 22.6 (CH*Me*$_2$), 9.8 (C*Me*). **FT-IR** (cm^{-1}): ν 3348.6 (m), 2955.13 (vs), 1468.12 (s), 1468.23 (w), 1346.25 (m), 1325.49 (s), 1236.35 (w), 1115.35 (w), 845.18 (vw), 817.47 (s), 737.21 (w), 676.38 (vw), 615.08 (w). **EA**: calcd. for C$_{35}$H$_{56}$GeN$_4$ (605.49): C, 69.43; H, 9.32; N, 9.25%; found C, 69.29; H, 9.14; N, 9.41%.

[NHC→LiN(H)Ar]$_2$ (**2**): To a solution of H_2NAr (0.2 mL, 1 mmol, Ar = 2,6-*i*Pr$_2$(C_6H_3)) and NHC (0.181 g, 1 mmol, NHC = C[N(*i*Pr)CMe]$_2$) in 25 mL of anhydrous ethyl ether solvent at 0 °C was added dropwise *n*BuLi (0.4 mL, 2.5 M, 1 mmol) to form a colorless solution. The mixture was warmed to room temperature and kept stirring for 6 h. Hexane (25 mL) was layered on the solution to obtain the product **2** (0.530 g, 0.73 mmol) in 73% yield as colorless crystals after filtration.

M.p.:124.7-125.9°C. **^{1}H NMR** (400 MHz, C_6D_6, 298 K, ppm): δ 7.22 (d, *J* = 7.4 Hz, 4H, Ar*H*), 6.72 (t, *J* = 7.4 Hz, 2H, Ar*H*), 4.47 (m, 4H, C*H*Me$_2$), 3.51 (m, 4H, C*H*Me$_2$), 1.60 (s, 12H, C*Me*), 1.51 (d, *J* = 6.8 Hz, 24H, CH*Me*$_2$), 1.15 (d, *J* = 6.8 Hz, 24H, CH*Me*$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K, ppm): δ 158.2, 132.3, 131.3, 123.1, 122.8, 110.4 (*Ar*), 28.9 (*C*HMe$_2$), 28.1 (*C*HMe$_2$), 24.1 (*C*HMe$_2$), 22.6 (*C*HMe$_2$), 9.6 (C*Me*). **FT-IR** (cm^{-1}): *v* 2961.59 (m), 2931.29 (m), 2867.94 (w), 1457.69 (m), 1438.41 (m), 1410.86 (m), 1342.00 (s), 1308.95 (s), 1256.62 (s), 1129.92 (w), 1099.62 (m), 733.28 (s), 645.14 (m), 587.30 (m), 523.95 (s). **EA**: calcd. for $C_{46}H_{74}Li_2N_6$ (726.64): C, 76.20; H, 10.26; N, 11.59%; found C, 76.13; H, 9.96; N, 11.32%.

[NHC→GeN(Ar)Cu$_2$NAr]$_2$ (**3**): The precursor germylene NHC→Ge[N(H)Ar]$_2$ (**1**) (2 mmol) was lithiated *in situ* using *n*BuLi (4.3 mmol, 1.7 mL, 2.5 M) in 50 mL of anhydrous ethyl ether solvent and then mixed with CuCl(PPh$_3$)$_3$ (3.536 g, 4 mmol).The reaction was carried out at room temperature for 12 h. After workup, the white precipitate was filtered off and the filtrate was concentrated to 10 mL and chilled under 4°C in the refrigerator for 1 day before producing dark yellow crystals of **3** (1.161 g, 0.80 mmol, 40%).

M.p. 150.3-150.6°C. **^{1}H NMR** (400 MHz, C_6D_6, 298 K, ppm): δ 7.05 (d, J = 7.6 Hz, 8H, Ar*H*), 6.90 (t, J = 7.6 Hz, 4H, Ar*H*), 3.83 – 3.76 (m, 4H, C*H*Me$_2$), 2.64 (m, J = 6.8 Hz, 8H, C*H*Me$_2$), 1.28 (d, 12H, CH*Me*$_2$), 1.27 (d, J = 2.6 Hz, 24H, CH*Me*$_2$), 1.15 (d, J = 6.8 Hz, 48H, CH*Me*$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K, ppm): δ 137.9, 129.3, 128.5, 123.1, 118.9 (*Ar*), 28.1 (*C*HMe$_2$), 24.2 (*C*HMe$_2$), 22.6 (*C*HMe$_2$), 21.4 (*C*HMe$_2$), 8.5 (C*Me*). **FT-IR** (cm^{-1}): *v* 2957.23 (vs), 1468.12 (s), 1468.23 (w), 1346.25 (m), 1325.49 (s), 1236.35 (w), 1115.35 (w), 845.18 (vw), 817.47 (s), 737.21 (w), 676.38 (vw), 615.08 (w). **EA**: calcd. for $C_{70}H_{110}Cu_4Ge_2N_8$ (1463.15): C, 57.46; H, 7.58; N, 7.66%; found C, 57.34; H, 7.35; N, 7.52%.

ArNNAr (**4**): In an extended reaction study of lithiated **1** with other metal halides (i.e. $PbCl_2$), a side product ArNNAr (**4**) was unexpectedly isolated as from the complicated reaction mixture under mild conditions. In a typical synthesis, the precursor germylene NHC→Ge[N(H)Ar]$_2$ (**1**)

(2 mmol) was lithiated *in situ* using *n*BuLi (1.7 mL, 2.5 M, 4.3 mmol) in 50 mL of anhydrous ethyl ether solvent and then mixed with $PbCl_2$ (0.556 g, 2 mmol).The reaction was carried out at room temperature for 12 h. After workup, the white precipitate was filtered off. The colorless crystals of **4** were obtained under 4 °C from the concentrated filtrate (about 3 mL) of the reaction mixture, after 4 days standing. The solid structure of diazo compound **4** in *trans* arrangement was confirmed by single crystal X-ray diffraction (Fig. S17), which have been previously reported with different arrangement[8] or different space group.[9]

The reactivity of **1** as well as the formation of **4** deserve further in-depth investigation.

X-ray crystallographic analysis

The crystallographic data were measured on a Bruker SMART APEX II CCD single crystal diffractometer with MoKα radiation. The data were refined by SHELXL[3] and OLEX2,[10] and all non-proton coordinate values and anisotropic temperature factors were refined by the full-matrix least-squares method. All proton positions in the structure were determined by theoretical calculation.

*As for compound **3**, the crystallographer pointed out that the ADP (atomic dispacement parameters) of Ge(1) is visibly 'larger' than that of Cu(2) and the residual density suggested over-assignment of Ge. When refined freely, the occupancy of Ge will refine to 93%. Refining the occupancy of both Ge and Cu atoms freely will reduce the R_1 to 4.9%, with occupancies as follows:*

Atom	*Type*	*X*	*Y*	*Z*	*Ueq*	*Um*	*Uvol*	*ChemOccu*	*R-bond*	*R-VdW*
Ge(1)	*Ge*	*0.418*	*0.157*	*0.382*	*0.057*	*0.057*	*0.056*	*0.885*	*1.22*	*2*
Cu(2)	*Cu*	*0.468*	*0.021*	*0.369*	*0.044*	*0.043*	*0.038*	*0.917*	*1.28*	*1.4*
Cu(1)	*Cu*	*0.378*	*0.049*	*0.511*	*0.046*	*0.045*	*0.040*	*0.948*	*1.28*	*1.4*

This could be due to the crystal that was too large (0.8×0.71×0.59 mm^3), with an absorption coefficient μ of 2. The results of this crystal analysis are recommended to be treated with caution.

Crystal data and structural refinement are summarized in Table S3. CCDC 2201109~2201112 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details

All quantum chemical calculations were carried out using the Gaussian 16 program suite.[4] The NBO calculations were performed with the Version 6.0 of the NBO program[5] which was implemented in the Gaussian16 C.01 and and analyzed using Multiwfn software package.[6] The molecular structure optimizations were performed using the PBE1PBE/genecp functional[7] along with the def2-tzvp basis set for the elements Ge and Cu and def2SVP basis set for the elements C, N, and H. Constraints of heavy-atom positions were employed in the geometry optimization of **3′**, since otherwise the full optimization resulted in a severe prolongation of the Ge-C bond and a large deviation from the N-Ge-C linearity. Every stationary point was identified by a subsequent frequency calculation as minimum (Number of imaginary frequencies (NIMAG): 0).

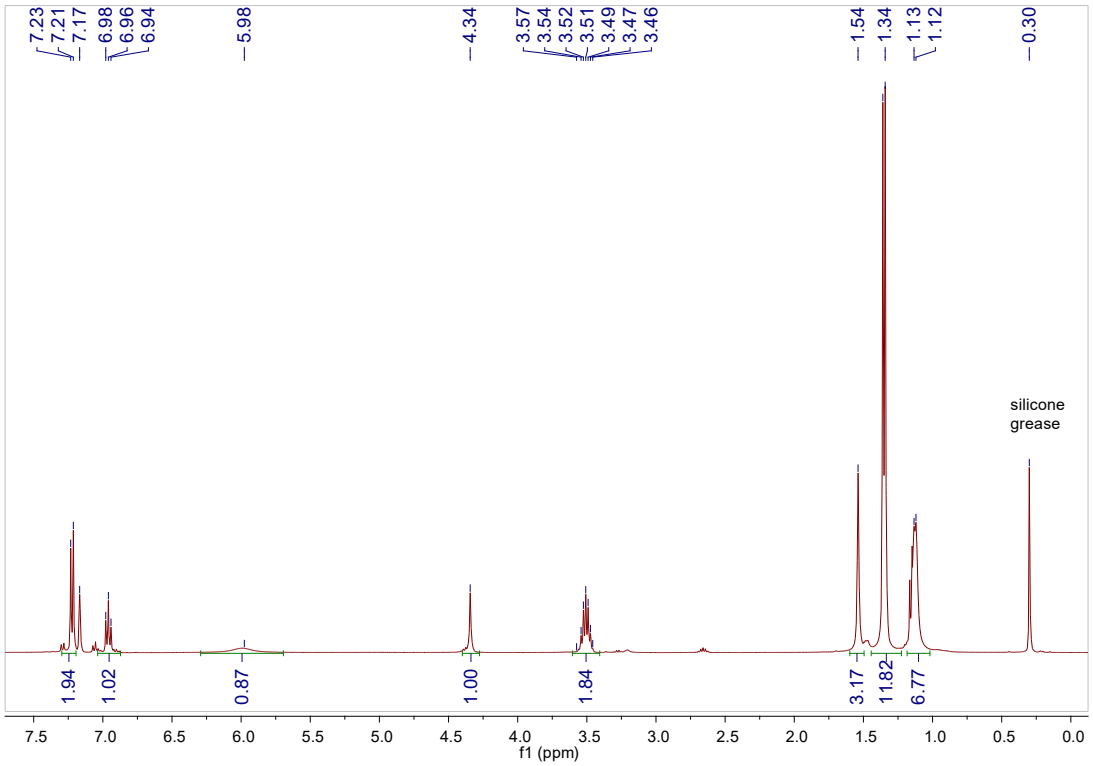

Fig. S 1 ^{1}H NMR spectrum of 1.

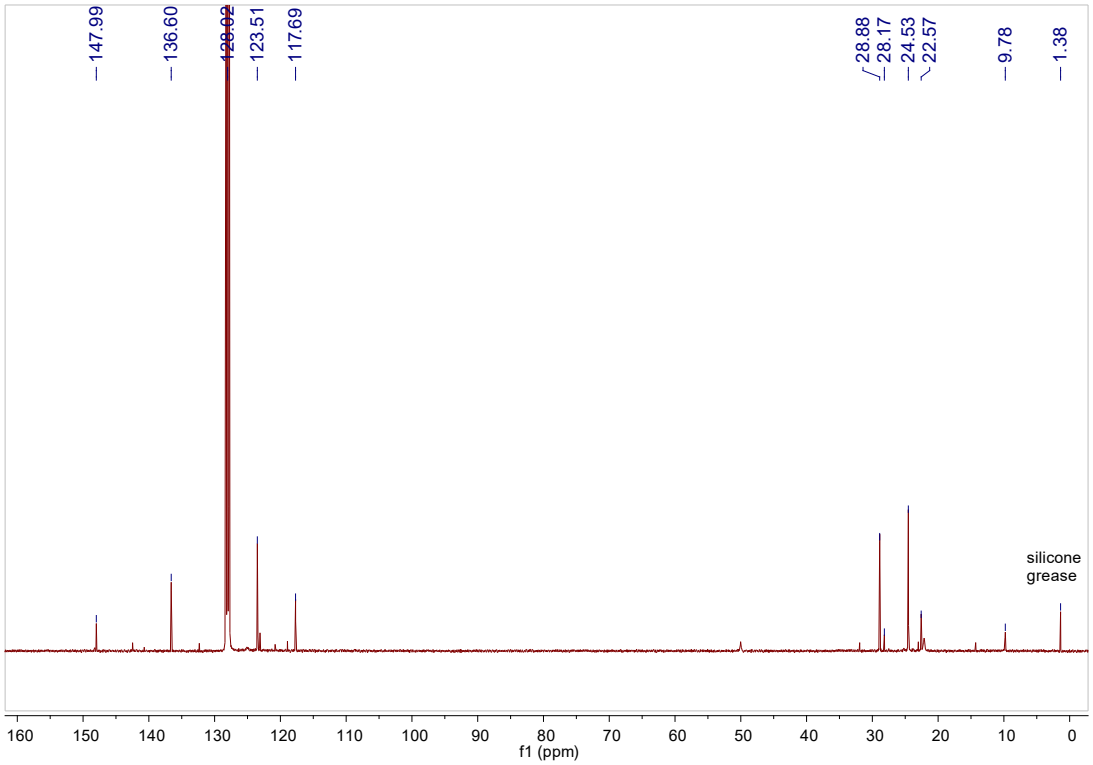

Fig. S 2 ^{13}C{^{1}H} NMR spectrum of 1.

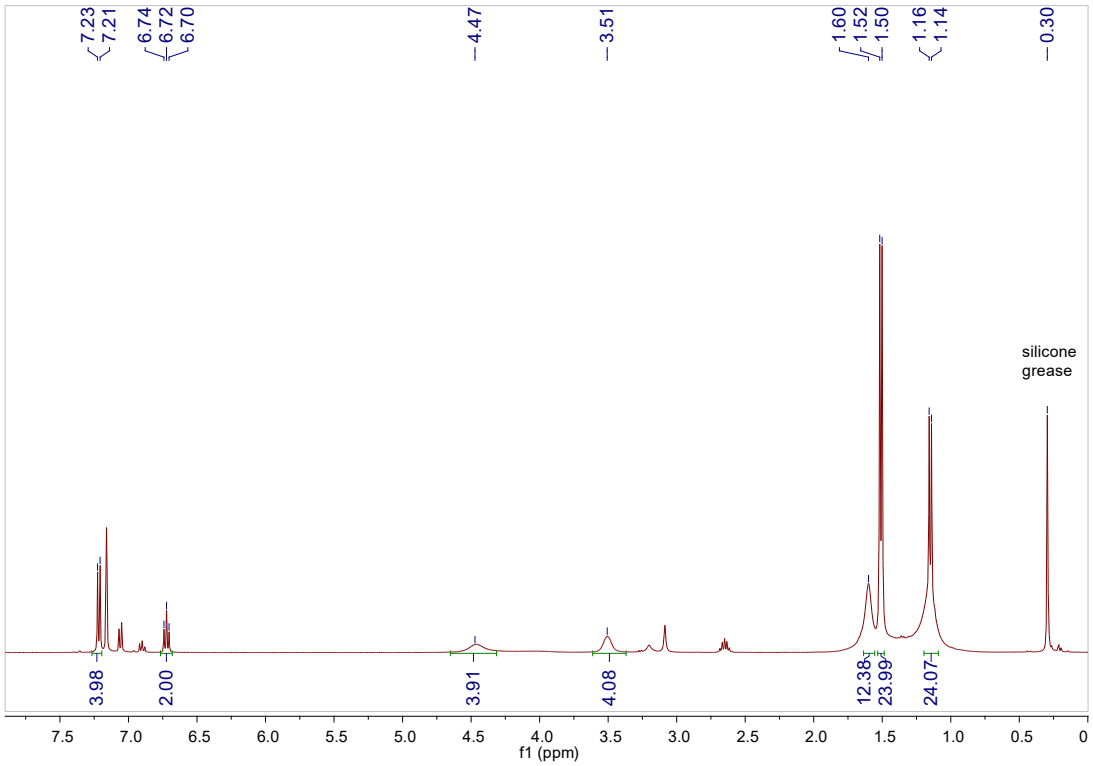

Fig. S 3 ^{1}H NMR spectrum of 2.

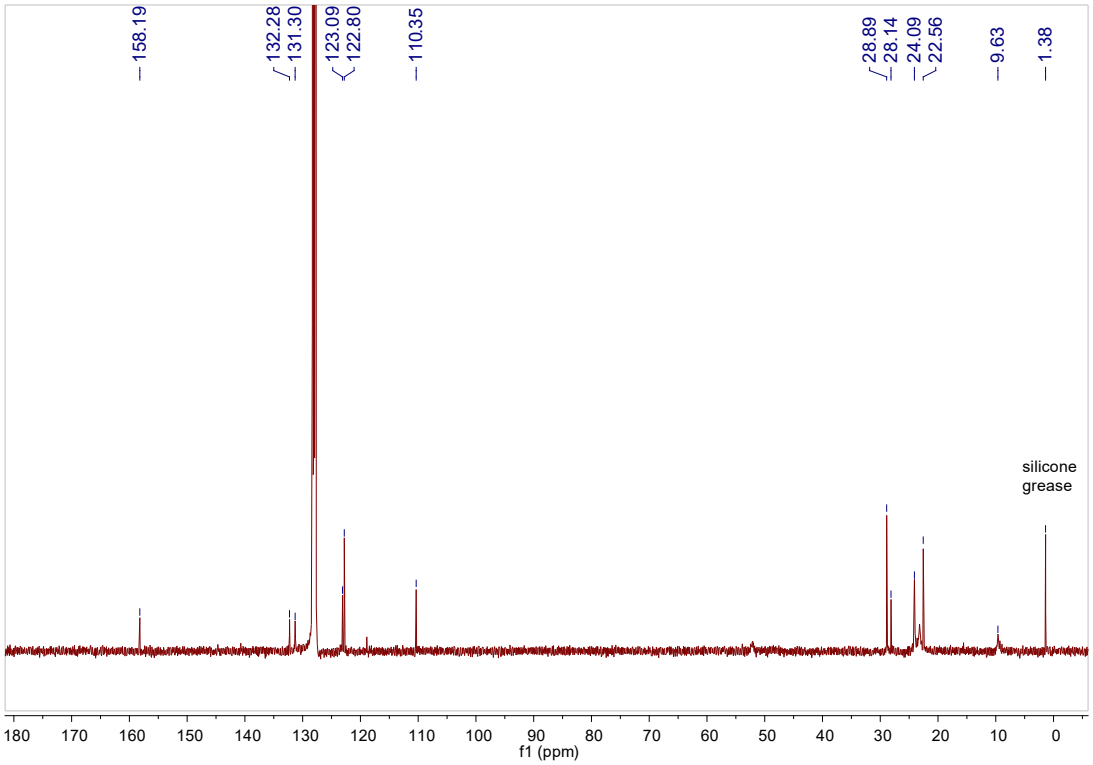

Fig. S 4 ^{13}C{^{1}H} NMR spectrum of 2.

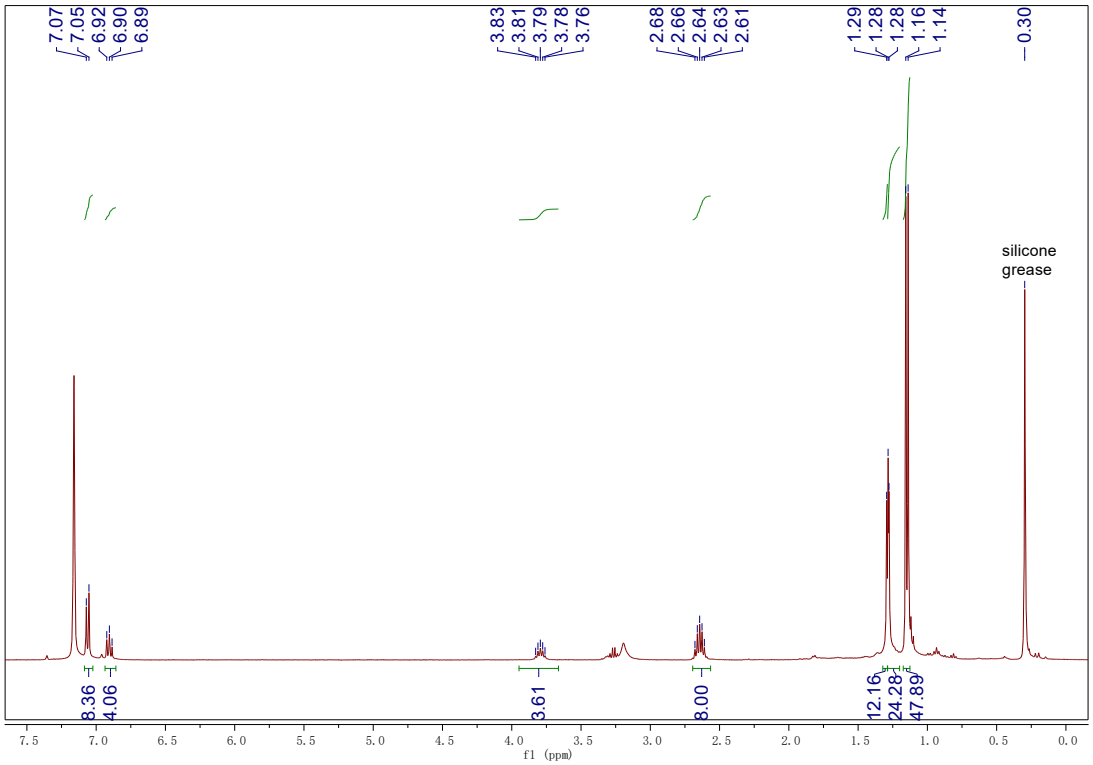

Fig. S 5 ^{1}H NMR spectrum of 3.

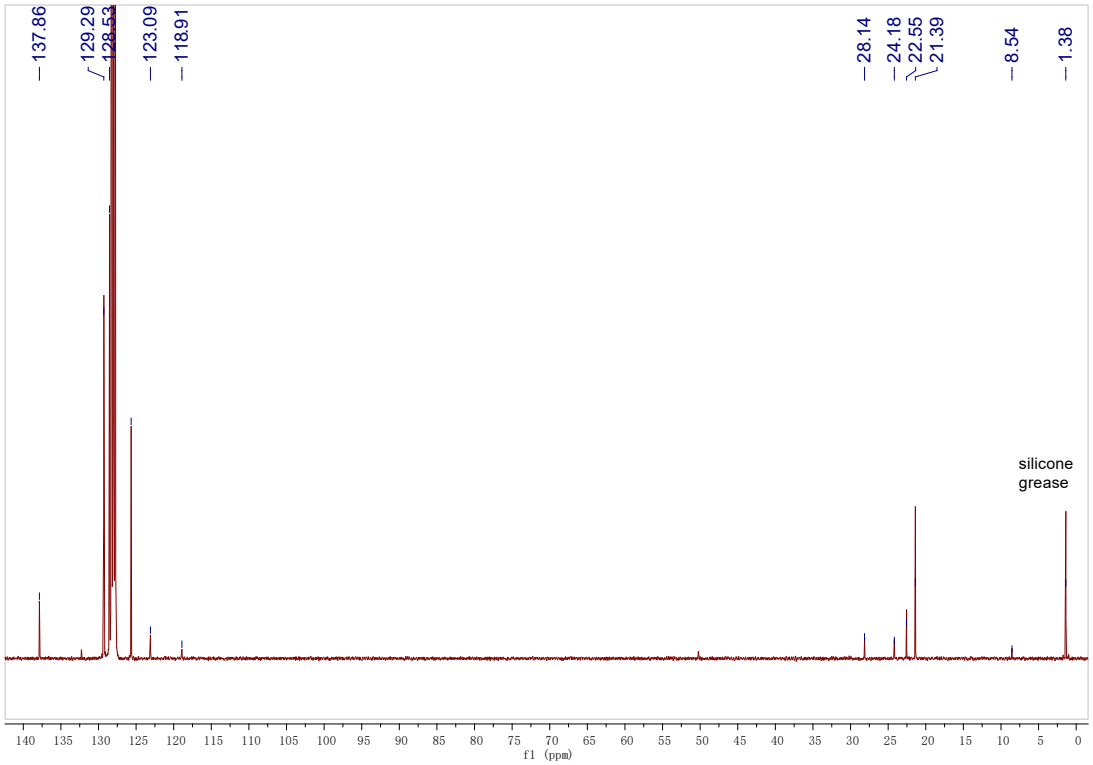

Fig. S 6 ^{13}C{^{1}H} NMR spectrum of 3.

Natural atomic orbital (NAO) analysis (Fig. S7) suggested the contribution of atoms to HOMO (left) and LUMO (right).

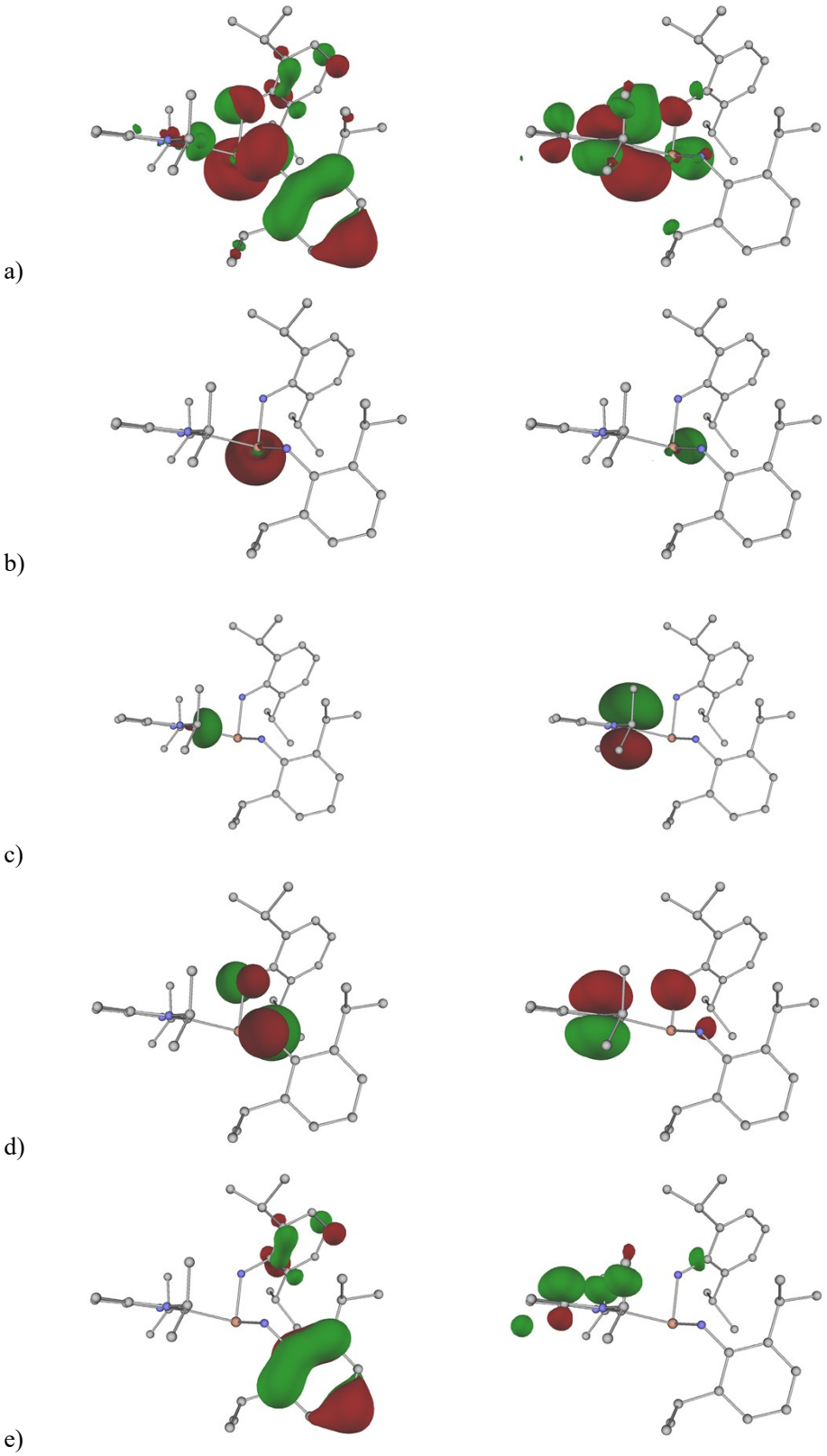

Fig. S 7 Contribution of atoms to HOMO (left) and LUMO (right) of 1' by NAO analysis. Ge (b), carbene C (c), N (d) and other C (e)

Note:

For HOMO

NAO#	Center	Label	Type	Composition
4	**1(Ge)**	**s**	**Val(4s)**	**9.419 %**
19	**1(Ge)**	**pz**	**Val(4p)**	**9.530 %**
52	2(N)	px	Val(2p)	1.713 %
54	2(N)	py	Val(2p)	3.154 %
56	2(N)	pz	Val(2p)	3.663 %
71	4(N)	px	Val(2p)	3.244 %
73	4(N)	py	Val(2p)	7.113 %
75	**4(N)**	**pz**	**Val(2p)**	**15.163 %**
120	8(C)	py	Val(2p)	0.612 %
134	9(C)	py	Val(2p)	1.469 %
167	12(C)	py	Val(2p)	2.094 %
205	16(C)	py	Val(2p)	1.618 %
373	37(C)	py	Val(2p)	1.454 %
375	37(C)	pz	Val(2p)	5.406 %
387	38(C)	py	Val(2p)	1.080 %
389	38(C)	pz	Val(2p)	2.893 %
401	39(C)	py	Val(2p)	1.339 %
403	39(C)	pz	Val(2p)	5.885 %
417	40(C)	pz	Val(2p)	0.604 %
432	42(C)	px	Val(2p)	0.516 %
434	42(C)	py	Val(2p)	2.344 %
436	42(C)	pz	Val(2p)	7.215 %
862	96(C)	s	Val(2s)	0.867 %
864	96(C)	px	Val(2p)	1.721 %

Core composition: 0.075 %
Valence composition: 98.911 %
Rydberg composition: 1.007 %

For LUMO

NAO#	Center	Label	Type	Composition
4	1(Ge)	s	Val(4s)	0.966 %
9	**1(Ge)**	**px**	**Val(4p)**	**6.482 %**
14	**1(Ge)**	**py**	**Val(4p)**	**2.739 %**
50	2(N)	s	Val(2s)	2.120 %
63	3(H)	s	Val(1s)	0.717 %
90	6(N)	px	Val(2p)	0.721 %
92	**6(N)**	**py**	**Val(2p)**	**8.003 %**
94	6(N)	pz	Val(2p)	4.215 %
104	7(N)	px	Val(2p)	0.624 %
106	**7(N)**	**py**	**Val(2p)**	**9.000 %**
108	7(N)	pz	Val(2p)	3.126 %
655	70(C)	py	Val(2p)	1.259 %
657	70(C)	pz	Val(2p)	0.645 %
669	71(C)	py	Val(2p)	1.613 %
671	71(C)	pz	Val(2p)	0.707 %
864	96(C)	px	Val(2p)	4.141 %
866	**96(C)**	**py**	**Val(2p)**	**25.654 %**
868	**96(C)**	**pz**	**Val(2p)**	**11.930 %**

Core composition: 0.022 %
Valence composition: 95.236 %
Rydberg composition: 4.735 %

The Wiberg bond order of the Ge(II)-C bond is 0.62 (Fig. S8). This bond is also described as an almost completely filled (1.96e) natural bond orbital (Fig. S8), which is strongly polarized towards the carbon atom (80.5%, Fig. S9), while the Ge(II) centre uses a hybrid orbital of high p character ($sp^{7.81}$) for bonding to C ($sp^{1.35}$). A lone pair (LP) of electrons (1.92e filled) on Ge(II) is found in a natural bond orbital of high s character ($sp^{0.32}$), which can be visualized in the electron localization function (ELF) graph (Fig. S10).

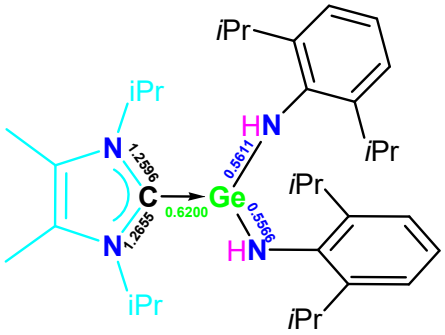

Fig. S 8 Selected Wiberg bond orders of 1'.

Note:

96,1

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.1544	862	96(C)	Val(2s) s	---	9	1(Ge)	Val(4p) px
0.0680	862	96(C)	Val(2s) s	---	19	1(Ge)	Val(4p) pz
0.1578	864	96(C)	Val(2p) px	---	9	1(Ge)	Val(4p) px
0.0960	864	96(C)	Val(2p) px	---	19	1(Ge)	Val(4p) pz

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.2248	2	96(C)	2s	---	9	1(Ge)	4p
0.0637	4	96(C)	2p	---	4	1(Ge)	4s
0.3007	4	96(C)	2p	---	9	1(Ge)	4p

Total Wiberg bond order: 0.6200

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2,1

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.1337	50	2(N)	Val(2s) s	---	14	1(Ge)	Val(4p) py
0.0733	54	2(N)	Val(2p) py	---	14	1(Ge)	Val(4p) py
0.0737	54	2(N)	Val(2p) py	---	19	1(Ge)	Val(4p) pz
0.0836	56	2(N)	Val(2p) pz	---	14	1(Ge)	Val(4p) py

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.1706	2	2(N)	2s	---	9	1(Ge)	4p
0.0557	4	2(N)	2p	---	4	1(Ge)	4s
0.3064	4	2(N)	2p	---	9	1(Ge)	4p

Total Wiberg bond order: 0.5611

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4,1

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.0983	69	4(N)	Val(2s) s	---	19	1(Ge)	Val(4p) pz
0.0561	71	4(N)	Val(2p) px	---	19	1(Ge)	Val(4p) pz
0.0504	73	4(N)	Val(2p) py	---	19	1(Ge)	Val(4p) pz
0.0522	75	4(N)	Val(2p) pz	---	9	1(Ge)	Val(4p) px

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.1541	2	4(N)	2s	---	9	1(Ge)	4p
0.0536	4	4(N)	2p	---	4	1(Ge)	4s
0.3205	4	4(N)	2p	---	9	1(Ge)	4p

Total Wiberg bond order: 0.5566

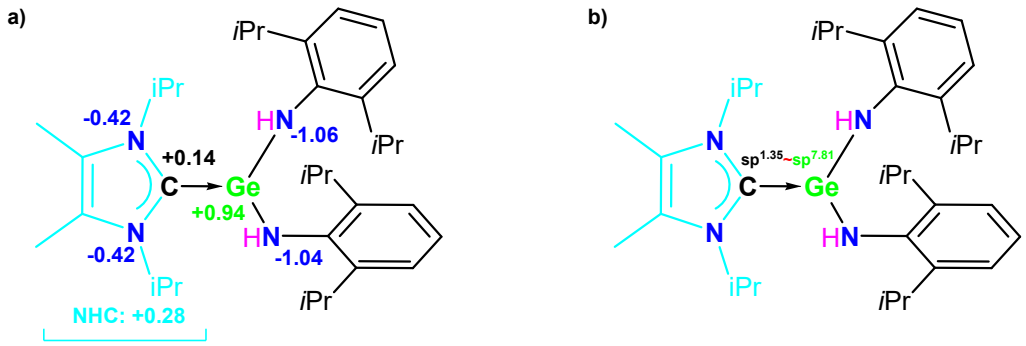

Fig. S 9 Selected natural charges (a) and hybrids (b) of 1'.

Note1:

Summary of Natural Population Analysis (selected):

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Ge	1	**0.94394**	27.99437	3.03112	0.03057	31.05606
N	2	**-1.04146**	1.99938	6.02833	0.01375	8.04146
H	3	0.38911	0.00000	0.60512	0.00577	0.61089
N	4	**-1.06213**	1.99942	6.04984	0.01287	8.06213
H	5	0.39872	0.00000	0.59479	0.00649	0.60128
N	6	**-0.42333**	1.99895	5.41215	0.01223	7.42333
N	7	**-0.42192**	1.99895	5.41024	0.01272	7.42192
				...		
C	96	**0.13554**	1.99916	3.81585	0.04946	5.86446
* Total *		-0.00000	105.95710	219.23698	0.80592	326.00000

Natural Population	
Core	105.95710 (99.9595% of 106)
Valence	219.23698 (99.6532% of 220)
Natural Minimal Basis	325.19408 (99.7528% of 326)
Natural Rydberg Basis	0.80592 (0.2472% of 326)

Note2:

(Occupancy) Bond orbital/ Coefficients/ Hybrids (selected)

1. (1.95689) BD (1)Ge 1 - C 96
(19.47%) 0.4412*Ge 1 s(11.30%)p 7.81(88.25%)d 0.04(0.43%)
f 0.00(0.02%)

(80.53%) 0.8974* C 96 s(42.63%)p 1.35(57.37%)d 0.00(0.00%)

...

158. (1.91546) LP (1)Ge 1 s(75.89%)p 0.32(24.05%)d 0.00(0.06%)
f 0.00(0.00%)

To investigate the electron transfer between the NHC and $[ArN(H)]_2Ge$ fragments, a difference map of electron density was drawn by subtracting electron density of them in their isolated states from the whole system of NHC→$Ge[N(H)Ar]_2$. As shown in Fig. S11, it is noticeable that the electron density in the direction of the lone pair on Ge(II) centre was largely increased so as to strengthen the donor ability of the Ge(II) site.

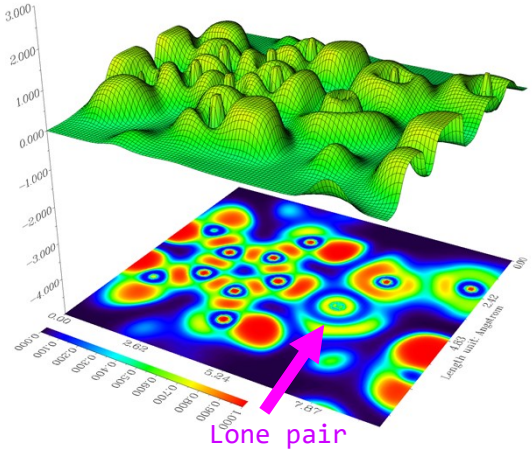

Fig. S 10 Electron localization function (ELF) graph of 1'.

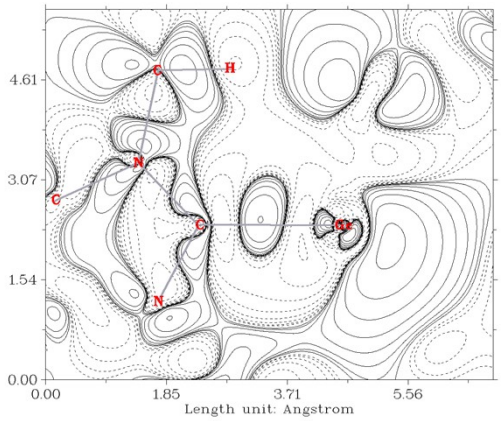

Fig. S 11 The contour map of electron density difference of 1'.

Note1: In the plane defined by atoms N, C, and Ge atoms. The solid and dashed contour lines exhibit where electron density is increased and decreased, respectively.

Note2 (frag1 = NHC, frag2 = $Ge[N(H)Ar]_2$):

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     ========== Extended Charge decomposition analysis (ECDA) ==========
  Contribution to all occupied complex orbital:
 Occupied, virtual orbitals of fragment  1:    4968.8840%       12.0533%
 Occupied, virtual orbitals of fragment  2:   11282.8036%       36.2591%
  Contribution to all virtual complex orbital:
 Occupied, virtual orbitals of fragment  1:      31.1160%     23187.9467%
 Occupied, virtual orbitals of fragment  2:      17.1965%     47863.7409%
 PL( 1) + CT( 1-> 2) =    0.6223      PL( 1) + CT( 2-> 1) =    0.2411
 PL( 2) + CT( 1-> 2) =    0.7252      PL( 2) + CT( 2-> 1) =    0.3439
 The net electrons obtained by frag. 2 = CT( 1-> 2) - CT( 2-> 1) =    0.3813
```

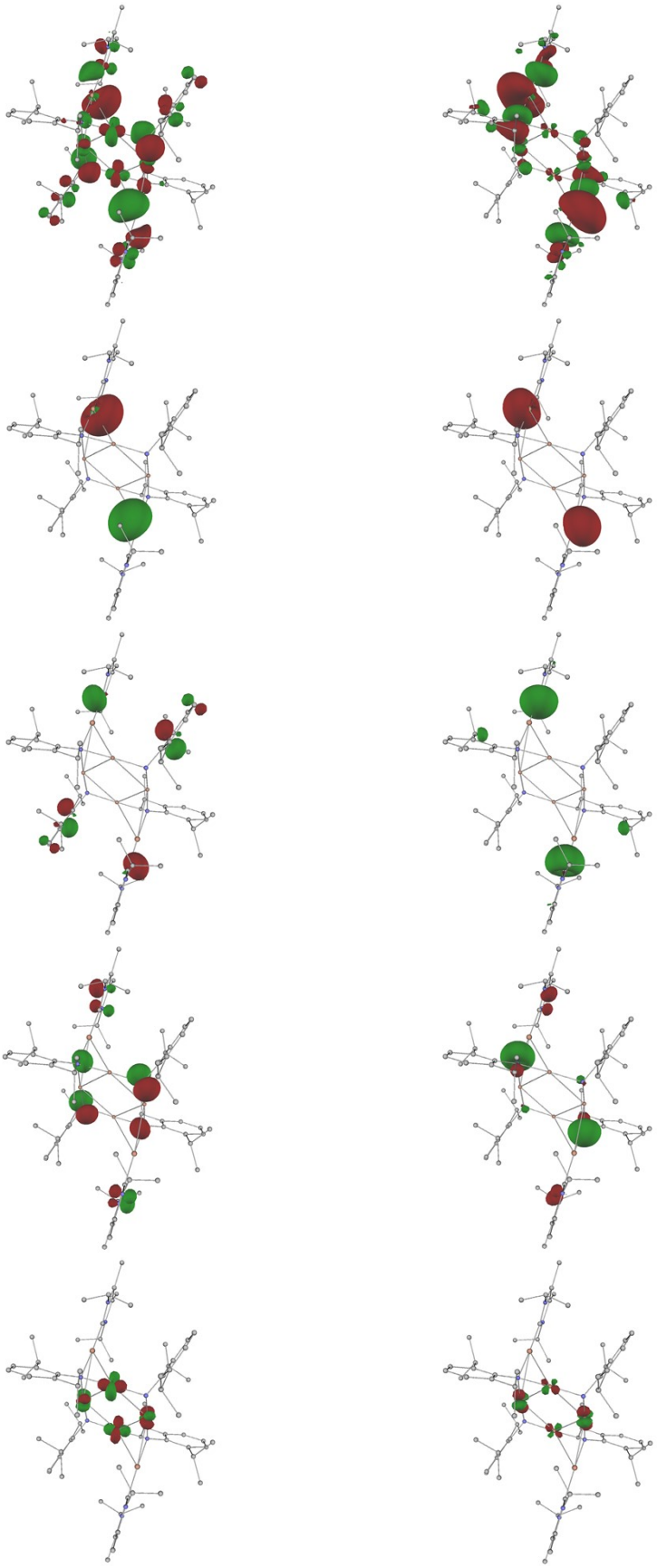


Fig. S 12 Contribution of atoms to HOMO (left) and LUMO (right) of 3' by NAO analysis.

Ge (b), C (c), N (d) and Cu (e)

Note: All Rydberg NAOs/shells or contributions <= 0.50 % will not be printed

For HOMO

NAO#	Center	Label	Type	Composition
4	**1(Ge)**	**s**	**Val(4s)**	**3.893 %**
9	**1(Ge)**	**px**	**Val(4p)**	**4.268 %**
14	1(Ge)	py	Val(4p)	0.992 %
19	**1(Ge)**	**pz**	**Val(4p)**	**4.744 %**
50	2(N)	s	Val(2s)	0.696 %
52	2(N)	px	Val(2p)	0.506 %
64	3(C)	s	Val(2s)	0.666 %
66	3(C)	px	Val(2p)	2.399 %
94	5(N)	px	Val(2p)	1.042 %
108	6(N)	px	Val(2p)	1.295 %
632	65(Cu)	dz2	Val(3d)	0.824 %
646	66(N)	px	Val(2p)	0.667 %
648	**66(N)**	**py**	**Val(2p)**	**12.020 %**
660	67(Cu)	s	Val(4s)	0.630 %
675	67(Cu)	dxy	Val(3d)	1.275 %
687	67(Cu)	dx2y2	Val(3d)	1.963 %
705	68(Cu)	s	Val(4s)	0.630 %
720	68(Cu)	dxy	Val(3d)	1.275 %
732	68(Cu)	dx2y2	Val(3d)	1.963 %
764	70(N)	px	Val(2p)	0.667 %
766	**70(N)**	**py**	**Val(2p)**	**12.020 %**
809	71(Cu)	dz2	Val(3d)	0.824 %
823	72(C)	px	Val(2p)	1.297 %
837	73(C)	px	Val(2p)	0.832 %
921	79(C)	px	Val(2p)	1.297 %
935	80(C)	px	Val(2p)	0.832 %
954	82(C)	px	Val(2p)	0.908 %
956	82(C)	py	Val(2p)	0.760 %
1165	108(C)	px	Val(2p)	0.908 %
1167	108(C)	py	Val(2p)	0.760 %
1315	129(Ge)	s	Val(4s)	3.893 %
1320	129(Ge)	px	Val(4p)	4.268 %
1325	129(Ge)	py	Val(4p)	0.992 %
1330	129(Ge)	pz	Val(4p)	4.744 %
1361	130(N)	s	Val(2s)	0.696 %
1363	130(N)	px	Val(2p)	0.506 %
1389	132(C)	s	Val(2s)	0.666 %
1391	132(C)	px	Val(2p)	2.399 %
1433	135(N)	px	Val(2p)	1.042 %
1447	136(N)	px	Val(2p)	1.295 %

Core composition: 0.113 %

Valence composition: 98.250 %

Rydberg composition: 1.641 %

Orbital delocalization index: 8.41

For LUMO

NAO#	Center	Label	Type	Composition
4	**1(Ge)**	**s**	**Val(4s)**	**15.288 %**
9	**1(Ge)**	**px**	**Val(4p)**	**3.968 %**
19	1(Ge)	pz	Val(4p)	0.654 %
50	2(N)	s	Val(2s)	1.659 %
54	**2(N)**	**py**	**Val(2p)**	**7.442 %**
64	**3(C)**	**s**	**Val(2s)**	**3.176 %**
68	**3(C)**	**py**	**Val(2p)**	**3.857 %**
624	65(Cu)	dyz	Val(3d)	1.284 %
648	66(N)	py	Val(2p)	0.771 %
650	66(N)	pz	Val(2p)	0.533 %
766	70(N)	py	Val(2p)	0.771 %
768	70(N)	pz	Val(2p)	0.533 %
801	71(Cu)	dyz	Val(3d)	1.284 %
1315	129(Ge)	s	Val(4s)	15.288 %
1320	129(Ge)	px	Val(4p)	3.968 %
1330	129(Ge)	pz	Val(4p)	0.654 %
1361	130(N)	s	Val(2s)	1.659 %
1365	130(N)	py	Val(2p)	7.442 %
1389	132(C)	s	Val(2s)	3.176 %
1393	132(C)	py	Val(2p)	3.857 %

Core composition: 0.288 %
Valence composition: 96.751 %
Rydberg composition: 2.967 %

Orbital delocalization index: 12.01

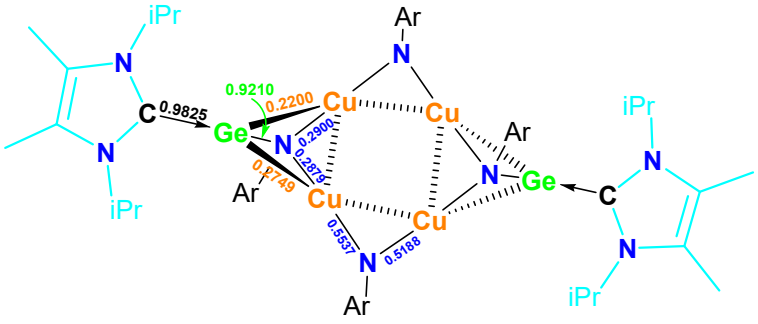


Fig. S 13 Selected Wiberg bond orders of 3'.

Note:

1,2

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.2844	4	1(Ge)	Val(4s) s	---	54	2(N)	Val(2p) py
0.0656	9	1(Ge)	Val(4p) px	---	50	2(N)	Val(2s) s
0.1508	9	1(Ge)	Val(4p) px	---	54	2(N)	Val(2p) py
0.0601	14	1(Ge)	Val(4p) py	---	50	2(N)	Val(2s) s
0.0541	14	1(Ge)	Val(4p) py	---	52	2(N)	Val(2p) px
0.1680	19	1(Ge)	Val(4p) pz	---	56	2(N)	Val(2p) pz

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.3127	4	1(Ge)	4s	---	4	2(N)	2p
0.1282	9	1(Ge)	4p	---	2	2(N)	2s
0.4554	9	1(Ge)	4p	---	4	2(N)	2p

Total Wiberg bond order: 0.9210

####################

3,1

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.0700	64	3(C)	Val(2s) s	---	4	1(Ge)	Val(4s) s
0.1515	64	3(C)	Val(2s) s	---	14	1(Ge)	Val(4p) py
0.1498	66	3(C)	Val(2p) px	---	9	1(Ge)	Val(4p) px
0.1605	66	3(C)	Val(2p) px	---	14	1(Ge)	Val(4p) py
0.2030	68	3(C)	Val(2p) py	---	4	1(Ge)	Val(4s) s
0.0706	68	3(C)	Val(2p) py	---	9	1(Ge)	Val(4p) px
0.0620	68	3(C)	Val(2p) py	---	14	1(Ge)	Val(4p) py

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.0700	2	3(C)	2s	---	4	1(Ge)	4s
0.1629	2	3(C)	2s	---	9	1(Ge)	4p
0.2185	4	3(C)	2p	---	4	1(Ge)	4s
0.5014	4	3(C)	2p	---	9	1(Ge)	4p

Total Wiberg bond order: 0.9825

####################

1,65

Contribution from NAO pairs that larger than printing threshold:

Contri.	NAO	Center	NAO type		NAO	Center	NAO type
0.0523	19	1(Ge)	Val(4p) pz	---	632	65(Cu)	Val(3d) dz2

Contribution from NAO shell pairs that larger than printing threshold:

Contri.	Shell	Center	Type		Shell	Center	Type
0.0978	9	1(Ge)	4p	---	11	65(Cu)	3d

```
 Total Wiberg bond order:  0.2200
###################
1,67
 Contribution from NAO pairs that larger than printing threshold:
  Contri.  NAO   Center   NAO type            NAO   Center   NAO type

 Contribution from NAO shell pairs that larger than printing threshold:
  Contri. Shell  Center   Type       Shell  Center   Type
  0.0514     9    1(Ge)     4p   ---     4   67(Cu)     4s
  0.0651     9    1(Ge)     4p   ---     9   67(Cu)     4p
  0.0869     9    1(Ge)     4p   ---    11   67(Cu)     3d

 Total Wiberg bond order:  0.2749

###################
2,65
 Contribution from NAO pairs that larger than printing threshold:
  Contri.  NAO   Center   NAO type            NAO   Center   NAO type
  0.0600    56    2(N )  Val( 2p) pz     ---   601   65(Cu)  Val( 4s) s

 Contribution from NAO shell pairs that larger than printing threshold:
  Contri. Shell  Center   Type       Shell  Center   Type
  0.0714     4    2(N )     2p   ---     4   65(Cu)     4s
  0.0643     4    2(N )     2p   ---     9   65(Cu)     4p
  0.0533     4    2(N )     2p   ---    11   65(Cu)     3d

 Total Wiberg bond order:  0.2900

###################
2,67
 Contribution from NAO pairs that larger than printing threshold:
  Contri.  NAO   Center   NAO type            NAO   Center   NAO type

 Contribution from NAO shell pairs that larger than printing threshold:
  Contri. Shell  Center   Type       Shell  Center   Type
  0.0566     2    2(N )     2s   ---     9   67(Cu)     4p
  0.0653     4    2(N )     2p   ---     4   67(Cu)     4s
  0.0716     4    2(N )     2p   ---     9   67(Cu)     4p

 Total Wiberg bond order:  0.2879

###################
66,65
 Contribution from NAO pairs that larger than printing threshold:
  Contri.  NAO   Center   NAO type            NAO   Center   NAO type
  0.0754   644   66(N )  Val( 2s) s      ---   601   65(Cu)  Val( 4s) s
  0.0584   644   66(N )  Val( 2s) s      ---   614   65(Cu)  Val( 4p) pz
  0.0665   648   66(N )  Val( 2p) py     ---   610   65(Cu)  Val( 4p) py
  0.1810   650   66(N )  Val( 2p) pz     ---   601   65(Cu)  Val( 4s) s

 Contribution from NAO shell pairs that larger than printing threshold:
  Contri. Shell  Center   Type       Shell  Center   Type
  0.0754     2   66(N )     2s   ---     4   65(Cu)     4s
  0.0608     2   66(N )     2s   ---     9   65(Cu)     4p
  0.1886     4   66(N )     2p   ---     4   65(Cu)     4s
  0.1555     4   66(N )     2p   ---     9   65(Cu)     4p
```

```
 Total Wiberg bond order:  0.5537

###################
66,68
 Contribution from NAO pairs that larger than printing threshold:
  Contri.  NAO   Center   NAO type            NAO   Center   NAO type
  0.0650   644   66(N )  Val( 2s) s      ---   705   68(Cu)  Val( 4s) s
  0.1434   646   66(N )  Val( 2p) px     ---   705   68(Cu)  Val( 4s) s

 Contribution from NAO shell pairs that larger than printing threshold:
  Contri. Shell  Center   Type        Shell  Center   Type
  0.0650     2   66(N )     2s   ---     4   68(Cu)     4s
  0.0589     2   66(N )     2s   ---     9   68(Cu)     4p
  0.1782     4   66(N )     2p   ---     4   68(Cu)     4s
  0.1482     4   66(N )     2p   ---     9   68(Cu)     4p

 Total Wiberg bond order:  0.5188
```

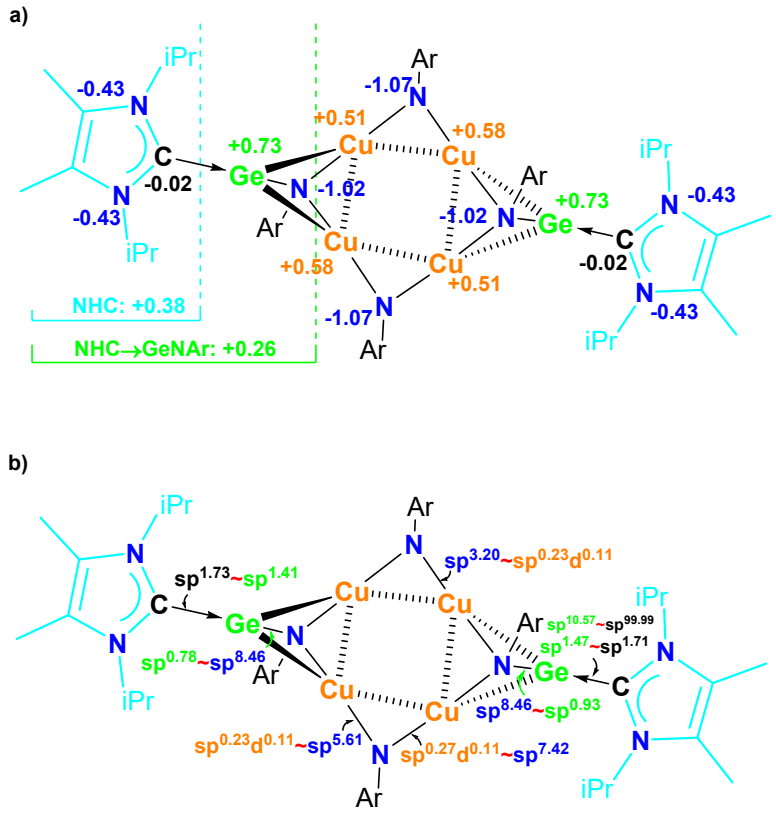


Fig. S 14 Selected natural charges (a) and hybrids (b) of 3'.

Note1:

Summary of Natural Population Analysis (selected):

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Ge	1	0.73341	27.98924	3.23764	0.03972	31.26659
N	2	-1.02068	1.99941	6.00526	0.01600	8.02068
C	3	-0.02001	1.99852	3.97241	0.04908	6.02001
N	5	-0.42925	1.99891	5.41505	0.01529	7.42925
N	6	-0.43128	1.99890	5.41767	0.01471	7.43128
Cu	65	0.57658	17.99279	10.41343	0.01719	28.42342
N	66	-1.07389	1.99948	6.05931	0.01510	8.07389
Cu	67	0.50540	17.99229	10.48479	0.01751	28.49460
Cu	68	0.50540	17.99229	10.48479	0.01751	28.49460
N	70	-1.07389	1.99948	6.05931	0.01510	8.07389
Cu	71	0.57658	17.99279	10.41343	0.01719	28.42342
Ge	129	0.73341	27.98924	3.23764	0.03972	31.26659
N	130	-1.02068	1.99941	6.00526	0.01600	8.02068
C	132	-0.02001	1.99852	3.97241	0.04908	6.02001
N	135	-0.42925	1.99891	5.41505	0.01529	7.42925
N	136	-0.43128	1.99890	5.41767	0.01471	7.43128
* Total *		-0.00000	283.86916	478.34303	1.78781	764.00000

Natural Population

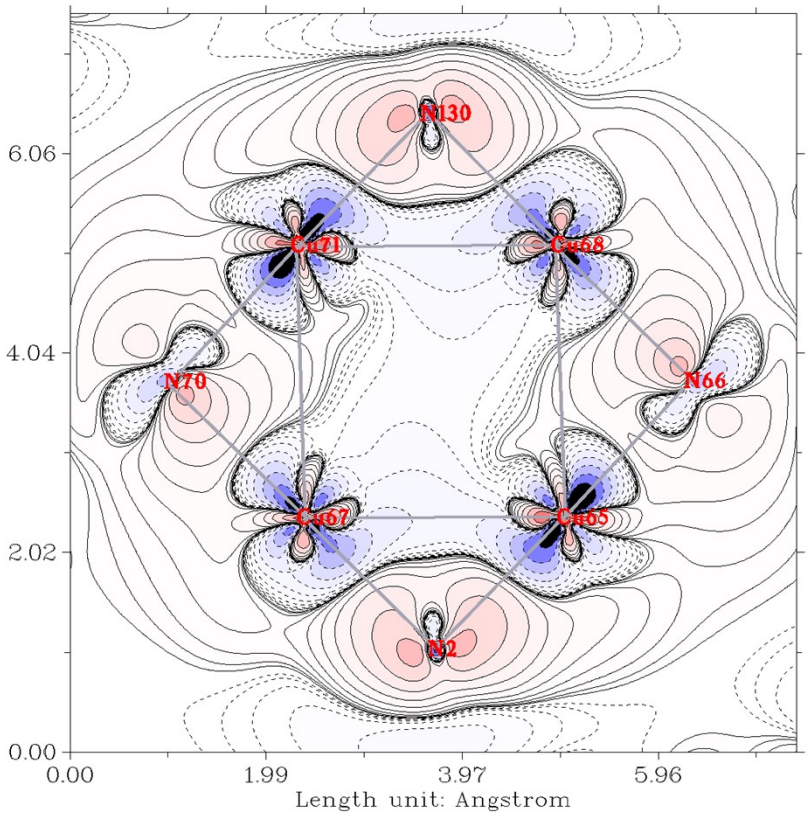
Core	283.86916 (99.9539% of 284)
Valence	478.34303 (99.6548% of 480)
Natural Minimal Basis	762.21219 (99.7660% of 764)
Natural Rydberg Basis	1.78781 (0.2340% of 764)

Note2:

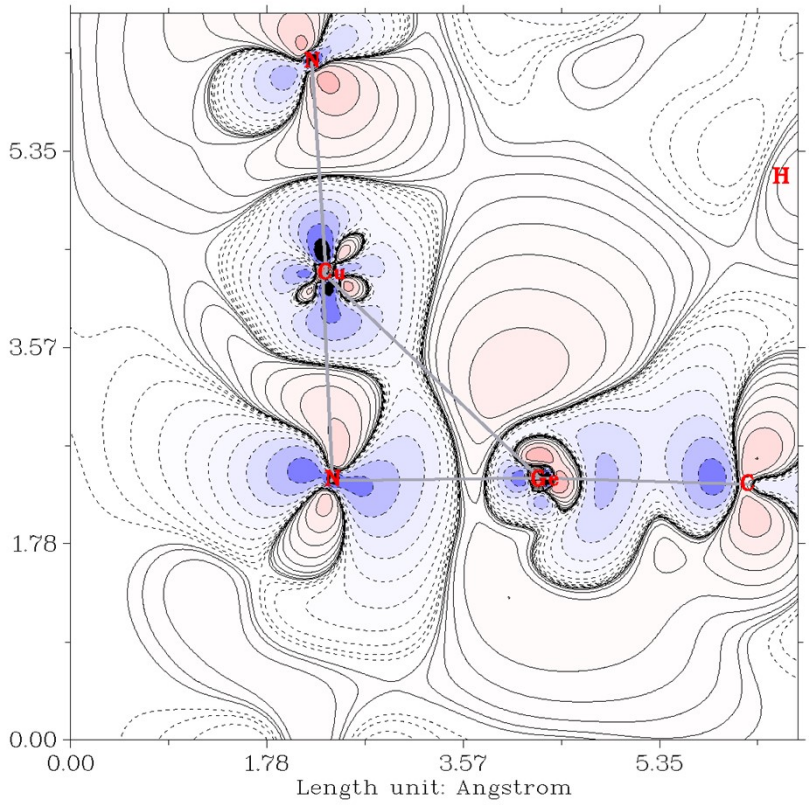
(Occupancy) Bond orbital/ Coefficients/ Hybrids (selected)

```
  1. (1.88578) BD ( 1)Ge   1 - N   2
           ( 30.20%)   0.5496*Ge   1 s( 55.98%)p 0.78( 43.68%)d 0.00(  0.19%)
                                      f 0.00(  0.15%)
           ( 69.80%)   0.8354* N   2 s( 10.57%)p 8.46( 89.41%)d 0.00(  0.02%)

  2. (1.92629) BD ( 1)Ge   1 - C   3
           ( 28.13%)   0.5304*Ge   1 s( 41.41%)p 1.41( 58.29%)d 0.00(  0.17%)
                                      f 0.00(  0.13%)
           ( 71.87%)   0.8478* C   3 s( 36.61%)p 1.73( 63.39%)d 0.00(  0.00%)
 71. (1.84425) BD ( 1)Cu  65 - N  66
           ( 14.30%)   0.3781*Cu  65 s( 74.56%)p 0.23( 16.97%)d 0.11(  8.46%)
                                      f 0.00(  0.00%)
           ( 85.70%)   0.9258* N  66 s( 15.12%)p 5.61( 84.87%)d 0.00(  0.01%)
 72. (1.76083) BD ( 1) N  66 -Cu  68
           ( 85.39%)   0.9241* N  66 s( 11.87%)p 7.42( 88.11%)d 0.00(  0.02%)
           ( 14.61%)   0.3822*Cu  68 s( 72.36%)p 0.27( 19.59%)d 0.11(  8.05%)
                                      f 0.00(  0.00%)
 76. (1.81386) BD ( 1) N  70 -Cu  71
           ( 85.72%)   0.9258* N  70 s( 23.83%)p 3.20( 76.17%)d 0.00(  0.01%)
           ( 14.28%)   0.3779*Cu  71 s( 74.56%)p 0.23( 16.97%)d 0.11(  8.46%)
                                      f 0.00(  0.00%)
139. (1.88816) BD ( 1)Ge 129 - N 130
           ( 29.32%)   0.5415*Ge 129 s( 51.69%)p 0.93( 47.95%)d 0.00(  0.20%)
                                      f 0.00(  0.16%)
           ( 70.68%)   0.8407* N 130 s( 10.57%)p 8.46( 89.41%)d 0.00(  0.02%)
140. (1.91900) BD ( 1)Ge 129 - C 132
           ( 28.32%)   0.5321*Ge 129 s( 40.32%)p 1.47( 59.38%)d 0.00(  0.17%)
                                      f 0.00(  0.13%)
           ( 71.68%)   0.8467* C 132 s( 36.86%)p 1.71( 63.13%)d 0.00(  0.00%)
141. (1.83894) BD ( 2)Ge 129 - C 132
           ( 62.69%)   0.7917*Ge 129 s(  8.60%)p10.57( 90.96%)d 0.04(  0.34%)
                                      f 0.01(  0.09%)
           ( 37.31%)   0.6109* C 132 s(  0.13%)p99.99( 99.83%)d 0.26(  0.04%)
351. (1.33233) LP ( 1)Ge   1          s(  3.22%)p29.91( 96.41%)d 0.09(  0.29%)
                                      f 0.03(  0.09%)
```



a) Cu_4 planeaaa



b) GeNCu plane

Fig. S 15 The contour map of electron density difference of 3'.

Note1: In the plane defined by atoms N, C, and Ge atoms. The solid and dashed contour lines exhibit where electron density is increased and decreased, respectively.

Note2 (frag1 = NHC, frag2 = GeN(Ar)[Cu_2NAr]$_2$GeN(Ar)←NHC):

========== Extended Charge decomposition analysis (ECDA) ==========

Contribution to all occupied complex orbital:

Occupied, virtual orbitals of fragment 1: 4939.4927% 25.9809%

Occupied, virtual orbitals of fragment 2: 33138.9190% 95.6075%

Contribution to all virtual complex orbital:

Occupied, virtual orbitals of fragment 1: 60.5073% 23174.0192%

Occupied, virtual orbitals of fragment 2: 61.0810% 129304.3926%

PL(1) + CT(1-> 2) = 1.2101 PL(1) + CT(2-> 1) = 0.5196

PL(2) + CT(1-> 2) = 1.9121 PL(2) + CT(2-> 1) = 1.2216

The net electrons obtained by frag. 2 = CT(1-> 2) - CT(2-> 1) = 0.6905

Note3 (frag1 = NHC→GeNAr, frag2 = [Cu_2NAr]$_2$GeN(Ar)←NHC):

========== Extended Charge decomposition analysis (ECDA) ==========

Contribution to all occupied complex orbital:

Occupied, virtual orbitals of fragment 1: 11350.6334% 31.8016%

Occupied, virtual orbitals of fragment 2: 26753.9771% 63.5879%

Contribution to all virtual complex orbital:

Occupied, virtual orbitals of fragment 1: 49.3666% 48268.1983%

Occupied, virtual orbitals of fragment 2: 46.0229% 104236.4121%

PL(1) + CT(1-> 2) = 0.9873 PL(1) + CT(2-> 1) = 0.6360

PL(2) + CT(1-> 2) = 1.2718 PL(2) + CT(2-> 1) = 0.9205

The net electrons obtained by frag. 2 = CT(1-> 2) - CT(2-> 1) = 0.3513

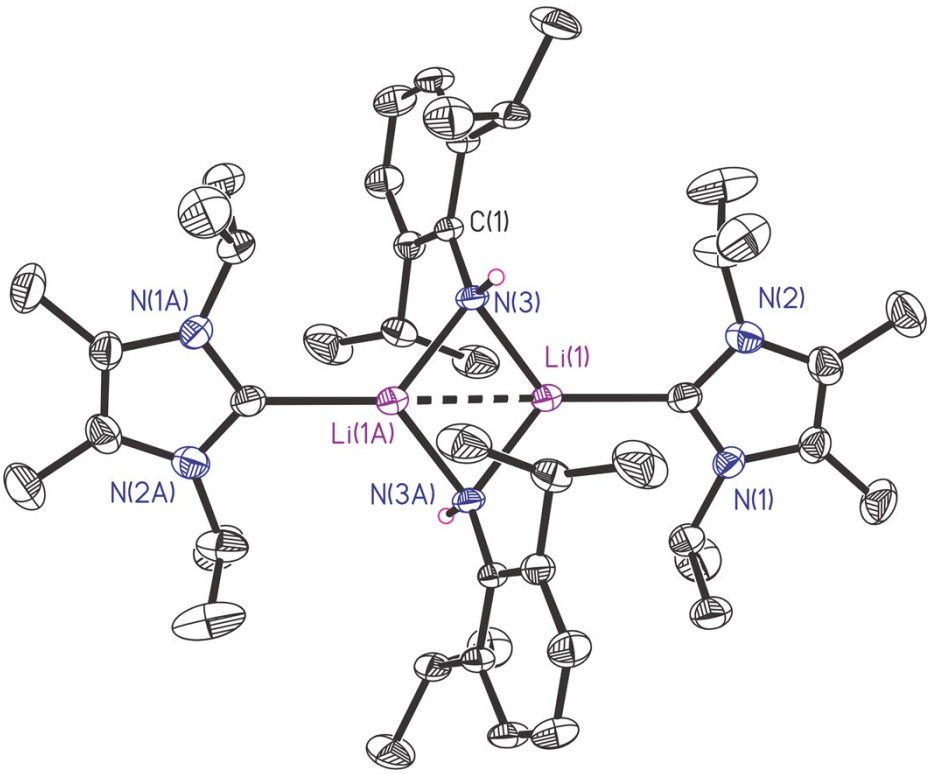


Fig. S 16 Molecular structure of [NHC→LiN(H)Ar]$_2$ (2).

Ellipsoids are drawn at 30% probability. H atoms except for NH groups have been omitted for clarity.

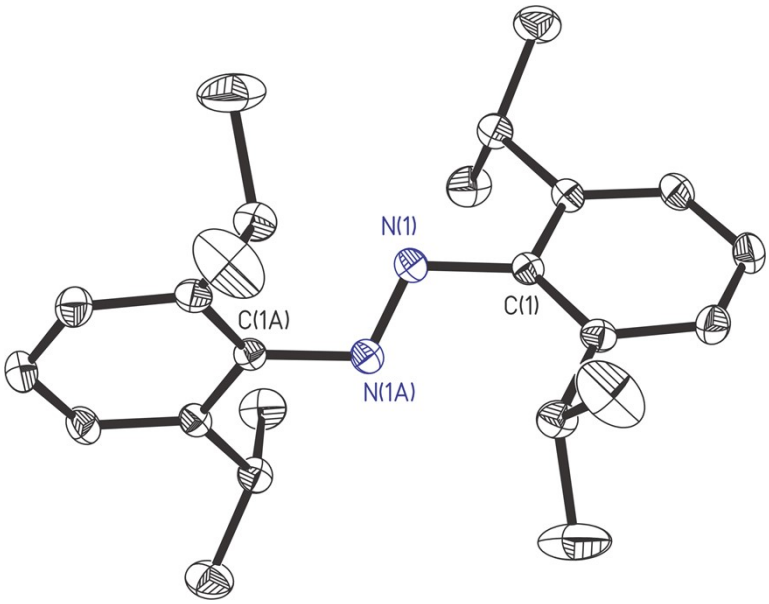


Fig. S 17 Molecular structure of ArNNAr (4).

Ellipsoids are drawn at 30% probability.

Table S 1 Optimized geometry of 1'

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	0.315021	0.113640	-0.896819
2	7	0	-0.200752	-1.602202	-0.117910
3	1	0	0.286571	-1.748409	0.756356
4	7	0	-0.533347	1.251357	0.434763
5	1	0	-1.030808	0.656304	1.089649
6	7	0	3.162078	-0.899863	-0.655280
7	7	0	2.876591	0.356598	1.074474
8	6	0	-1.489683	-2.127066	-0.050422
9	6	0	-2.013212	-2.583626	1.199361
10	6	0	-3.311883	-3.090875	1.259374
11	1	0	-3.708254	-3.434490	2.217082
12	6	0	-4.121250	-3.161060	0.129557
13	1	0	-5.140392	-3.548038	0.198703
14	6	0	-3.601379	-2.742917	-1.088886
15	1	0	-4.221215	-2.817657	-1.987136
16	6	0	-2.301633	-2.244736	-1.210640
17	6	0	-1.789161	-1.890166	-2.596317
18	1	0	-0.727797	-1.615716	-2.496971
19	6	0	-1.845733	-3.090413	-3.544446
20	1	0	-1.300455	-3.952242	-3.129688
21	1	0	-1.398094	-2.836720	-4.519265
22	1	0	-2.881537	-3.414407	-3.734515
23	6	0	-2.514994	-0.680786	-3.186816
24	1	0	-3.589004	-0.887511	-3.323796
25	1	0	-2.096311	-0.411895	-4.170073
26	1	0	-2.425117	0.201301	-2.533959
27	6	0	-1.143448	-2.555696	2.446049
28	1	0	-0.563485	-1.612951	2.417687
29	6	0	-1.917292	-2.532420	3.760897
30	1	0	-2.659808	-1.720949	3.781944
31	1	0	-1.226683	-2.384291	4.605892
32	1	0	-2.446552	-3.481160	3.941756
33	6	0	-0.142978	-3.719466	2.446030
34	1	0	0.553149	-3.652167	3.298534
35	1	0	0.450722	-3.756150	1.519614
36	1	0	-0.681139	-4.677452	2.522486
37	6	0	-2.722097	2.358180	0.359209
38	6	0	-1.331129	2.331868	0.042569
39	6	0	-0.769170	3.420863	-0.674151
40	6	0	-1.594083	4.479736	-1.066020
41	1	0	-1.155385	5.313304	-1.622490
42	6	0	-2.947348	4.508801	-0.758266
43	1	0	-3.572716	5.347328	-1.073431
44	6	0	-3.494231	3.448929	-0.040201
45	1	0	-4.558742	3.465433	0.202969
46	6	0	-3.350242	1.222333	1.150017
47	1	0	-2.862453	0.283738	0.830600

48	6	0	-3.097066	1.398615	2.652471
49	1	0	-2.024443	1.499489	2.882792
50	1	0	-3.490675	0.543519	3.225631
51	1	0	-3.593995	2.311308	3.018834
52	6	0	-4.839402	1.020505	0.883849
53	1	0	-5.449203	1.846501	1.284208
54	1	0	-5.183980	0.093885	1.367801
55	1	0	-5.046279	0.933324	-0.193175
56	6	0	0.714979	3.509710	-0.992232
57	1	0	1.202038	2.623965	-0.553664
58	6	0	0.992475	3.486817	-2.496143
59	1	0	0.585578	2.574488	-2.956527
60	1	0	2.076462	3.518959	-2.696592
61	1	0	0.536180	4.354612	-2.999283
62	6	0	1.351947	4.739358	-0.338299
63	1	0	0.942341	5.673185	-0.754934
64	1	0	2.441609	4.756698	-0.507547
65	1	0	1.169927	4.756856	0.746881
66	6	0	5.210987	0.337361	2.121207
67	1	0	4.828968	0.236566	3.146363
68	1	0	5.548757	1.377446	1.991967
69	1	0	6.095979	-0.306607	2.035646
70	6	0	4.202798	-0.056153	1.099651
71	6	0	4.382619	-0.856477	0.002295
72	6	0	5.626452	-1.545039	-0.438161
73	1	0	5.440764	-2.585723	-0.737365
74	1	0	6.108244	-1.034236	-1.286573
75	1	0	6.351493	-1.564806	0.385958
76	6	0	2.833207	-1.658917	-1.874159
77	1	0	1.838394	-1.273216	-2.154363
78	6	0	2.679093	-3.144788	-1.586730
79	1	0	3.617922	-3.612175	-1.252139
80	1	0	2.355566	-3.662725	-2.501848
81	1	0	1.903196	-3.299265	-0.823697
82	6	0	3.762534	-1.339296	-3.036753
83	1	0	3.879014	-0.252493	-3.160677
84	1	0	3.318125	-1.734058	-3.962086
85	1	0	4.757938	-1.793218	-2.935189
86	6	0	2.180332	1.170034	2.087125
87	1	0	1.201166	1.373956	1.620435
88	6	0	1.930741	0.376693	3.363475
89	1	0	1.414478	-0.570160	3.146356
90	1	0	1.286114	0.962524	4.035785
91	1	0	2.855957	0.143894	3.912888
92	6	0	2.856775	2.510491	2.338069
93	1	0	3.770190	2.431453	2.944553
94	1	0	2.157992	3.160798	2.884451
95	1	0	3.102607	3.014864	1.392746
96	6	0	2.236545	-0.165818	0.005156

Table S 2 Optimized geometry of 3'

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-0.759979	2.992280	-1.667432
2	7	0	-1.663012	1.346048	-1.666165
3	6	0	0.105647	4.688224	-1.801373
4	6	0	-2.884144	1.286776	-2.373193
5	7	0	0.396829	5.546712	-0.815477
6	7	0	0.528682	5.271384	-2.919661
7	6	0	-3.075415	0.361368	-3.439369
8	6	0	-3.975692	2.133792	-2.040805
9	6	0	1.021617	6.676704	-1.335185
10	6	0	0.035834	5.397576	0.601397
11	6	0	1.109842	6.489328	-2.654878
12	6	0	0.471117	4.665280	-4.268931
13	6	0	-4.322926	0.292536	-4.057667
14	6	0	-1.989021	-0.581248	-3.890065
15	6	0	-5.163656	1.990392	-2.719665
16	6	0	-3.878478	3.219808	-0.994347
17	6	0	1.487915	7.833464	-0.494356
18	1	0	0.669077	6.172260	1.068065
19	6	0	0.512459	4.139480	1.209836
20	6	0	-1.329278	5.787624	0.891532
21	6	0	1.707476	7.363112	-3.694294
22	1	0	0.723033	5.499017	-4.942023
23	6	0	1.487746	3.611768	-4.433716
24	6	0	-0.916603	4.252288	-4.618220
25	1	0	-4.456747	-0.432401	-4.865333
26	6	0	-5.345375	1.097488	-3.708378
27	1	0	-1.031555	-0.227564	-3.462854
28	6	0	-2.245532	-1.929208	-3.350639
29	6	0	-1.820466	-0.663464	-5.292854
30	1	0	-5.992805	2.648642	-2.440702
31	1	0	-2.880935	3.154269	-0.517773
32	6	0	-4.012911	4.594536	-1.599969
33	6	0	-4.864556	3.070672	0.129575
34	1	0	2.260360	7.530228	0.230444
35	1	0	0.660869	8.296803	0.066305
36	1	0	1.923895	8.605215	-1.140797
37	1	0	0.442761	4.230098	2.303258
38	1	0	1.557706	3.938884	0.943991
39	1	0	-0.072130	3.244849	0.936073
40	1	0	-2.066612	5.075615	0.484965
41	1	0	-1.575032	6.781083	0.485900
42	1	0	-1.496672	5.814651	1.978569
43	1	0	2.109509	8.273675	-3.233005
44	1	0	0.967470	7.676682	-4.448606
45	1	0	2.537345	6.870211	-4.226097
46	1	0	2.505732	3.988766	-4.263036
47	1	0	1.458050	3.193765	-5.450693

48	1	0	1.343903	2.766405	-3.737852
49	1	0	-0.961178	3.951117	-5.675115
50	1	0	-1.644319	5.059459	-4.453439
51	1	0	-1.270989	3.370071	-4.046404
52	1	0	-6.310326	1.021481	-4.216338
53	1	0	-3.190115	-2.341805	-3.744892
54	1	0	-2.318850	-1.937022	-2.252107
55	1	0	-1.439083	-2.625575	-3.629111
56	1	0	-0.962670	-1.301977	-5.556421
57	1	0	-1.638170	0.314676	-5.770872
58	1	0	-2.690469	-1.102034	-5.813413
59	1	0	-5.009935	4.733692	-2.048430
60	1	0	-3.267670	4.776143	-2.391053
61	1	0	-3.889924	5.379175	-0.837138
62	1	0	-4.736530	3.877645	0.868157
63	1	0	-4.744984	2.118028	0.666032
64	1	0	-5.904235	3.120421	-0.232951
65	29	0	-1.672541	0.943954	0.157321
66	7	0	-1.566740	0.636696	2.022496
67	29	0	-0.050654	0.394254	-1.843203
68	29	0	0.050654	-0.394254	1.843203
69	6	0	-2.552081	0.097512	2.908394
70	7	0	1.566740	-0.636696	-2.022496
71	29	0	1.672541	-0.943954	-0.157321
72	6	0	-3.374504	-0.986592	2.529528
73	6	0	-2.678670	0.642432	4.205552
74	6	0	2.552081	-0.097512	-2.908394
75	6	0	-4.222557	-1.516216	3.473172
76	6	0	-3.356901	-1.569752	1.135189
77	6	0	-3.541507	0.059272	5.097084
78	6	0	-1.938825	1.927296	4.587235
79	6	0	3.374504	0.986592	-2.529528
80	6	0	2.678670	-0.642432	-4.205552
81	1	0	-4.864552	-2.360974	3.204128
82	6	0	-4.301081	-1.021008	4.739344
83	1	0	-2.379310	-1.327552	0.684887
84	6	0	-4.460101	-0.982768	0.312670
85	6	0	-3.509923	-3.099352	1.121105
86	1	0	-3.641948	0.466754	6.105979
87	1	0	-0.936820	1.837416	4.132454
88	6	0	-2.594484	3.137592	3.960486
89	6	0	-1.782848	2.116584	6.091431
90	6	0	4.222557	1.516216	-3.473172
91	6	0	3.356901	1.569752	-1.135189
92	6	0	3.541507	-0.059272	-5.097084
93	6	0	1.938825	-1.927296	-4.587235
94	1	0	-4.985961	-1.473206	5.463237
95	1	0	-5.444974	-1.213333	0.751434
96	1	0	-4.455408	-1.363431	-0.722693
97	1	0	-4.383833	0.113710	0.249577
98	1	0	-4.485298	-3.421760	1.518385
99	1	0	-2.717497	-3.593846	1.701642
100	1	0	-3.454761	-3.472478	0.085456

101	1	0	-3.620350	3.275992	4.341496
102	1	0	-2.643381	3.014660	2.867919
103	1	0	-2.028238	4.059780	4.181596
104	1	0	-1.127999	2.977806	6.303810
105	1	0	-1.343721	1.231114	6.576704
106	1	0	-2.746876	2.323570	6.584463
107	1	0	4.864552	2.360974	-3.204128
108	6	0	4.301081	1.021008	-4.739344
109	1	0	2.379310	1.327552	-0.684887
110	6	0	4.460101	0.982768	-0.312670
111	6	0	3.509923	3.099352	-1.121105
112	1	0	3.641948	-0.466754	-6.105979
113	1	0	0.936820	-1.837416	-4.132454
114	6	0	2.594484	-3.137592	-3.960486
115	6	0	1.782848	-2.116584	-6.091431
116	1	0	4.985961	1.473206	-5.463237
117	1	0	5.444974	1.213333	-0.751434
118	1	0	4.455408	1.363431	0.722693
119	1	0	4.383833	-0.113710	-0.249577
120	1	0	4.485298	3.421760	-1.518385
121	1	0	2.717497	3.593846	-1.701642
122	1	0	3.454761	3.472478	-0.085456
123	1	0	3.620350	-3.275992	-4.341496
124	1	0	2.643381	-3.014660	-2.867919
125	1	0	2.028238	-4.059780	-4.181596
126	1	0	1.127999	-2.977806	-6.303810
127	1	0	1.343721	-1.231114	-6.576704
128	1	0	2.746876	-2.323570	-6.584463
129	32	0	0.759979	-2.992280	1.667432
130	7	0	1.663012	-1.346048	1.666165
131	6	0	2.884144	-1.286776	2.373193
132	6	0	-0.105647	-4.688224	1.801373
133	6	0	3.075415	-0.361368	3.439369
134	6	0	3.975692	-2.133792	2.040805
135	7	0	-0.396829	-5.546712	0.815477
136	7	0	-0.528682	-5.271384	2.919661
137	6	0	4.322926	-0.292536	4.057667
138	6	0	1.989021	0.581248	3.890065
139	6	0	5.163656	-1.990392	2.719665
140	6	0	3.878478	-3.219808	0.994347
141	6	0	-1.021617	-6.676704	1.335185
142	6	0	-0.035834	-5.397576	-0.601397
143	6	0	-1.109842	-6.489328	2.654878
144	6	0	-0.471117	-4.665280	4.268931
145	1	0	4.456747	0.432401	4.865333
146	6	0	5.345375	-1.097488	3.708378
147	1	0	1.031555	0.227564	3.462854
148	6	0	2.245532	1.929208	3.350639
149	6	0	1.820466	0.663464	5.292854
150	1	0	5.992805	-2.648642	2.440702
151	1	0	2.880935	-3.154269	0.517773
152	6	0	4.012911	-4.594536	1.599969
153	6	0	4.864556	-3.070672	-0.129575

154	6	0	-1.487915	-7.833464	0.494356
155	1	0	-0.669077	-6.172260	-1.068065
156	6	0	-0.512459	-4.139480	-1.209836
157	6	0	1.329278	-5.787624	-0.891532
158	6	0	-1.707476	-7.363112	3.694294
159	1	0	-0.723033	-5.499017	4.942023
160	6	0	-1.487746	-3.611768	4.433716
161	6	0	0.916603	-4.252288	4.618220
162	1	0	6.310326	-1.021481	4.216338
163	1	0	3.190115	2.341805	3.744892
164	1	0	2.318850	1.937022	2.252107
165	1	0	1.439083	2.625575	3.629111
166	1	0	0.962670	1.301977	5.556421
167	1	0	1.638170	-0.314676	5.770872
168	1	0	2.690469	1.102034	5.813413
169	1	0	5.009935	-4.733692	2.048430
170	1	0	3.267670	-4.776143	2.391053
171	1	0	3.889924	-5.379175	0.837138
172	1	0	4.736530	-3.877645	-0.868157
173	1	0	4.744984	-2.118028	-0.666032
174	1	0	5.904235	-3.120421	0.232951
175	1	0	-2.260360	-7.530228	-0.230444
176	1	0	-0.660869	-8.296803	-0.066305
177	1	0	-1.923895	-8.605215	1.140797
178	1	0	-0.442761	-4.230098	-2.303258
179	1	0	-1.557706	-3.938884	-0.943991
180	1	0	0.072130	-3.244849	-0.936073
181	1	0	2.066612	-5.075615	-0.484965
182	1	0	1.575032	-6.781083	-0.485900
183	1	0	1.496672	-5.814651	-1.978569
184	1	0	-2.109509	-8.273675	3.233005
185	1	0	-0.967470	-7.676682	4.448606
186	1	0	-2.537345	-6.870211	4.226097
187	1	0	-2.505732	-3.988766	4.263036
188	1	0	-1.458050	-3.193765	5.450693
189	1	0	-1.343903	-2.766405	3.737852
190	1	0	0.961178	-3.951117	5.675115
191	1	0	1.644319	-5.059459	4.453439
192	1	0	1.270989	-3.370071	4.046404

Table S 3 Crystal data and structural refinement (1-4)

Identification code	**[ArN(H)]$_2$Ge←NHC** **(1)**	**[ArN(H)Li←NHC]$_2$** **(2)**	**[NHC→GeN(Ar)Cu$_2$N)Ar]$_2$** **(3)**	**ArNNAr** **(4)**
CCDC	2201109	2201110	2201111	2201112
Empirical formula	$C_{35}H_{56}GeN_4$	$C_{46}H_{74}Li_2N_6$	$C_{70}H_{108}Cu_4Ge_2N_8$	$C_{24}H_{34}N_2$
Formula weight	605.42	724.99	1460.98	350.53
Temperature/K	296(2)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*P*-1	*P*-1	$P2_1/n$	*Aea*2
a/Å	11.128(3)	10.2780(4)	13.4421(2)	16.1758(9)
b/Å	11.721(3)	10.8626(4)	19.1200(3)	14.0586(6)
c/Å	15.731(4)	11.2179(5)	14.3811(3)	9.7277(5)
α/°	108.667(13)	104.378(2)	90	90
β/°	90.773(13)	98.823(2)	101.6620(10)	90
γ/°	115.078(13)	99.932(2)	90	90
Volume/Å^3	1733.8(8)	1169.48(8)	3619.83(11)	2212.17(19)
Z	2	1	2	4
ρ_{calc}g/cm^3	1.160	1.029	1.340	1.052
μ/mm^{-1}	0.911	0.060	2.017	0.061
F(000)	652.0	398.0	1528.0	768.0
Crystal size/mm^3	0.173×0.124×0.086	0.70×0.545×0.222	0.80×0.71×0.59	0.43×0.30×0.12
Radiation (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.05 to 54.79	3.83 to 55.004	3.784 to 55.032	5.036 to 54.764
Index ranges	-14 ≤ h ≤ 13 -15 ≤ k ≤ 15 -19 ≤ l ≤ 20	-13 ≤ h ≤ 13 -14 ≤ k ≤ 14 -14 ≤ l ≤ 14	-17 ≤ h ≤ 15 -24 ≤ k ≤ 24 -18 ≤ l ≤ 17	-20 ≤ h ≤ 20 -17 ≤ k ≤ 18 -12 ≤ l ≤ 12
Reflections collected	27349	18908	33050	17366
Independent reflections	R_{int} = 0.0612 R_{sigma} = 0.0654	R_{int} = 0.0285 R_{sigma} = 0.0258	R_{int} = 0.0674 R_{sigma} = 0.0839	R_{int} = 0.0189 R_{sigma} = 0.0130
Data/restraints/parameters	7718/0/382	5248/0/257	8306/2/398	2465/1/123
Goodness-of-fit on F^2	1.002	1.047	0.975	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0416 wR_2 = 0.0991	R_1 = 0.0642 wR_2 = 0.1935	R_1 = 0.0557 wR_2 = 0.1309	R_1 = 0.0438 wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0636 wR_2 = 0.1073	R_1 = 0.0908 wR_2 = 0.2169	R_1 = 0.1337 wR_2 = 0.1644	R_1 = 0.0549 wR_2 = 0.1312
Largest diff. peak/hole / e Å^{-3}	0.51/-0.39	0.36/-0.29	0.57/-0.64	0.22/-0.12

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