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A novel α,ω silyl dianionic salt. The synthesis and characterization of remotely connected benzannulated silole monoanions

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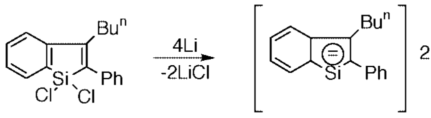
The novel dilithium salt of 1,2-bis((BPSI)$_2$)ethane (BPSI = 3-butyl-2-phenyl-1-silaindenyl) **4** was prepared from the reaction of **2** with 1,2-bis(chloro-BPSI)ethane **3** and characterized by NMR spectroscopy and by X-ray crystallography. It is demonstrated that dianions of silicon not only can perform stepwise reactions but also that, when a quenching reagent possesses two remote electrophilic centers, they can be attacked separately and maintain single charges on the silicon centers. The two lithium ions in **4** are η^1 -coordinated to two remote silyl anions. NMR and X-ray data are consistent with a low degree of π-electron delocalization in the C$_4$Si ring.

Introduction

Recently we demonstrated that the lithium and sodium salts of the silaindenyl dianion exhibited aromaticity as evidenced by the downfield ^{29}Si NMR shift and the near equivalence of the carbon–carbon bonds in the C$_4$Si ring [eqn. (1)].[1] This example of aromaticity in a silole system was striking because it could not occur without cost of aromaticity to the benzene ring in the precursor. Indeed, the structure of the dianion showed bond alternation in the six membered ring.



1 **2** (1)

During the course of our studies to expand the chemistry of these novel dianions we found that they are efficient nucleophiles and that the degree of substitution can be controlled stoichiometrically. In the example we report here, it is demonstrated that not only can stepwise electrophilic quenching of **2** be executed but that, when a quenching agent possesses two remote electrophilic centers, they can be attacked separately and single charges on the nucleophilic silicon centers can be maintained.

Results and discussion

The reaction of Li$_2$[η^5,η^1-BPSI] **2** with 1,2-bis(chloro-BPSI)ethane **3** (2 : 1 mol ratio) at room temperature produces an orange solution of **4** [eqn. (2)]. Crystals of **4** suitable for X-ray diffraction can be grown from a concentrated dioxane–THF solution.

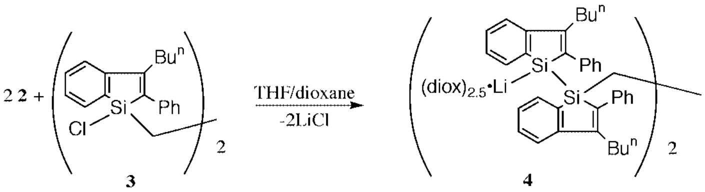
The dianion **4** crystallized in the triclinic space group $P\bar{1}$ with a center of inversion at the middle of the central ethane unit (Table 1). The lithium ion is η^1-coordinated to the silicon atom Si(2) and also coordinated to three dioxane molecules. One of the three chair-shaped dioxanes is linked to another η^1-coordinated lithium ion to give a polymeric crystal (Fig. 1).

Table 1 Crystal data and structure refinement for **3** and **4**

Compound	3	4
Empirical formula	C$_{19}$H$_{20}$ClSi	C$_{47}$H$_{58}$LiO$_5$Si$_2$
M	311.89	766.05
T/K	298(2)	298(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.9575(10)	13.2710(9)
b/Å	9.4809(11)	13.9844(9)
c/Å	11.2364(13)	14.0125(9)
α/°	98.377(2)	64.6360(10)
β/°	112.958(2)	77.4500(10)
γ/°	96.817(2)	74.0300(10)
V/Å^3	853.00(17), 2	2244.3(3), 2
μ/mm^{-1}	0.286	0.121
Reflections collected	3754	10702
Independent reflections (R_{int})	2724 (0.1995)	7319 (0.0801)
Goodness-of-fit (on F^2)[a]	1.052	1.086
Final R indices [$I > 2\sigma(I)$][b]	$R1 = 0.0696$ $wR2 = 0.1520$	$R1 = 0.0838$ $wR2 = 0.1967$

[a] Goodness of fit $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$; n = no. of parameters, p = no. of variables. [b] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Fig. 2 shows a view of half the molecular structure of **4**. Selected bond lengths and angles are given in Table 2. The C$_4$Si(2) ring is comprised of a tetrahedral silicon atom Si(2) and a slightly distorted diene fragment with C(19)–C(24), C(24)–C(25) and C(25)–C(26) bond lengths of 1.422, 1.486 and 1.352 Å, respectively. The Si–C$_\alpha$ distances (d(Si(2)–C(19)) = 1.896 Å, d(Si(2)–C(26)) = 1.899 Å) are slightly longer than typical single silicon (sp^3)– carbon (sp^2) bond lengths (1.853 Å).[2] The carbon–



3 **4** (2)

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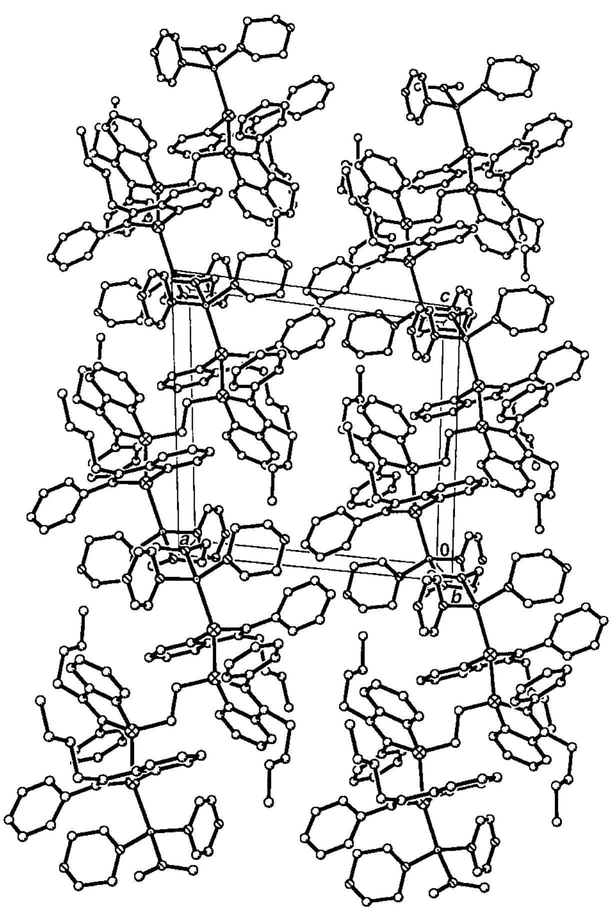


Fig. 1 View of crystal structure of **4** in the solid state. All hydrogens are omitted for clarity. Symmetry transformations used to generate atoms: #1 $-x$, $-y + 2$, $-z$; #2 $-x$, $-y + 1$, $-z + 1$.

carbon bonds and carbon–silicon bond lengths in the C$_4$Si(2) ring are very similar to those in the C$_4$Si(1) ring.

The ^{13}C NMR spectrum contains the expected methylene carbon peak (9.27 ppm) for the central ethane unit and two sets of peaks for the two silaindene unit. The ^{29}Si NMR spectrum of **4** shows two resonances (−23.06 and 7.38 ppm) for each silaindene unit. Interestingly, the ^{29}Si NMR resonance for the Si(2) atom of the C$_4$Si(2) ring (−23.06 ppm) is in the range of aryl-substituted silyllithium compounds and also shifted upfield ($\Delta\delta = -53.54$ ppm) relative to the corresponding resonance for the parent dianionic silaindene **2** (30.48 ppm). The ^{7}Li NMR spectrum of **4** in THF-d$_8$ shows a signal at −0.23 ppm (external ref.: 0.1 mol of LiBr in THF-d$_8$) which is downfield of η^5-lithium of the dianionic silaindene (**2**: −3.81 ppm)[3] and of the lithium ion in phosphoindole[4] (−4.6 ppm). The spectral and structural data indicate that the monoanionic silaindene unit in **4** is not aromatic and is closely related to the silyl-substituted silole monoanion {[K(18-crown-6)][C$_4$Me$_4$Si-SiMe$_3$]}[5] and silafluorene monoanion (LiMeSiC$_{12}$H$_8$).[6]

Bis(chloro-BPSI)ethane **3** was prepared by the addition of 1,2-bis(trichlorosilyl)ethane to a hexane suspension of (*E*)-1,8-dilithio-1,2-diphenylhex-1-ene·2TMEDA at −78 °C to give **3** in good yield (75%) [eqn. (3)].[7]

The structure of **3** was obtained by single-crystal X-ray analysis of a crystal grown from a concentrated chloroform solution at room temperature. The compound crystallized in the triclinic space group $P\bar{1}$. It is centrosymmetric through the middle of the ethane units to give a staggered geometry (Table 1). The molecular structure is shown in Fig. 3 with selected bond lengths and angles given in Table 3.

Compounds **3** and **4** have two and four chiral centers respectively, but we have not investigated their stereochemistries. We observe only one stereoisomer for each com-

Table 2 Selected bond lengths (Å) and angles (°) for **4**[a]

Si(1)–C(1)	1.871(4)	Si(1)–C(8)	1.888(4)
Si(1)–C(47)	1.889(4)	Si(1)–Si(2)	2.3501(14)
Si(2)–C(19)	1.896(4)	Si(2)–C(26)	1.899(4)
Si(2)–Li(1)	2.645(8)	Li(1)–O(3)	1.917(10)
Li(1)–O(5)	1.939(8)	Li(1)–O(1)	1.944(10)
C(1)–C(2)	1.395(5)	C(1)–C(6)	1.410(5)
C(2)–C(3)	1.381(6)	C(3)–C(4)	1.372(7)
C(4)–C(5)	1.375(7)	C(5)–C(6)	1.397(6)
C(6)–C(7)	1.494(6)	C(7)–C(8)	1.349(6)
C(7)–C(15)	1.513(6)	C(19)–C(20)	1.400(5)
C(19)–C(24)	1.422(6)	C(20)–C(21)	1.383(6)
C(21)–C(22)	1.386(7)	C(22)–C(23)	1.375(7)
C(23)–C(24)	1.391(6)	C(24)–C(25)	1.486(6)
C(25)–C(26)	1.352(5)	C(25)–C(33)	1.515(6)
C(47)–C(47)#2	1.541(7)	C(45)–C(46)#1	1.468(8)
C(46)–C(45)#1	1.468(8)		
C(1)–Si(1)–C(8)	90.62(18)	C(1)–Si(1)–C(47)	112.98(16)
C(8)–Si(1)–C(47)	110.53(17)	C(1)–Si(1)–Si(2)	113.20(12)
C(8)–Si(1)–Si(2)	119.91(12)	C(47)–Si(1)–Si(2)	108.74(12)
C(19)–Si(2)–C(26)	87.84(17)	C(19)–Si(2)–Si(1)	93.46(12)
C(26)–Si(2)–Si(1)	105.26(12)	C(19)–Si(2)–Li(1)	116.7(2)
C(26)–Si(2)–Li(1)	118.8(2)	Si(1)–Si(2)–Li(1)	125.90(18)
C(6)–C(1)–Si(1)	108.4(3)	C(3)–C(2)–C(1)	120.4(4)
C(4)–C(3)–C(2)	120.2(5)	C(3)–C(4)–C(5)	120.8(5)
C(4)–C(5)–C(6)	120.3(5)	C(5)–C(6)–C(1)	119.0(4)
C(5)–C(6)–C(7)	126.0(4)	C(1)–C(6)–C(7)	115.0(4)
C(8)–C(7)–C(6)	115.5(3)	C(8)–C(7)–C(15)	126.4(4)
C(6)–C(7)–C(15)	118.0(4)	C(7)–C(8)–C(9)	124.9(4)
C(7)–C(8)–Si(1)	110.1(3)	C(9)–C(8)–Si(1)	125.0(3)
C(14)–C(9)–C(10)	116.3(4)	C(20)–C(19)–C(24)	117.9(4)
C(20)–C(19)–Si(2)	131.5(3)	C(24)–C(19)–Si(2)	110.5(3)
C(21)–C(20)–C(19)	121.0(4)	C(20)–C(21)–C(22)	120.4(5)
C(23)–C(22)–C(21)	120.0(5)	C(22)–C(23)–C(24)	120.6(5)
C(23)–C(24)–C(19)	120.0(4)	C(23)–C(24)–C(25)	125.9(4)
C(19)–C(24)–C(25)	114.1(3)	C(26)–C(25)–C(24)	114.7(4)
C(26)–C(25)–C(33)	126.8(4)	C(24)–C(25)–C(33)	118.2(4)
C(25)–C(26)–C(27)	123.7(4)	C(25)–C(26)–Si(2)	112.8(3)
C(47)#2–C(47)–Si(1)	115.3(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 2$, $-z$; #2 $-x$, $-y + 1$, $-z + 1$.

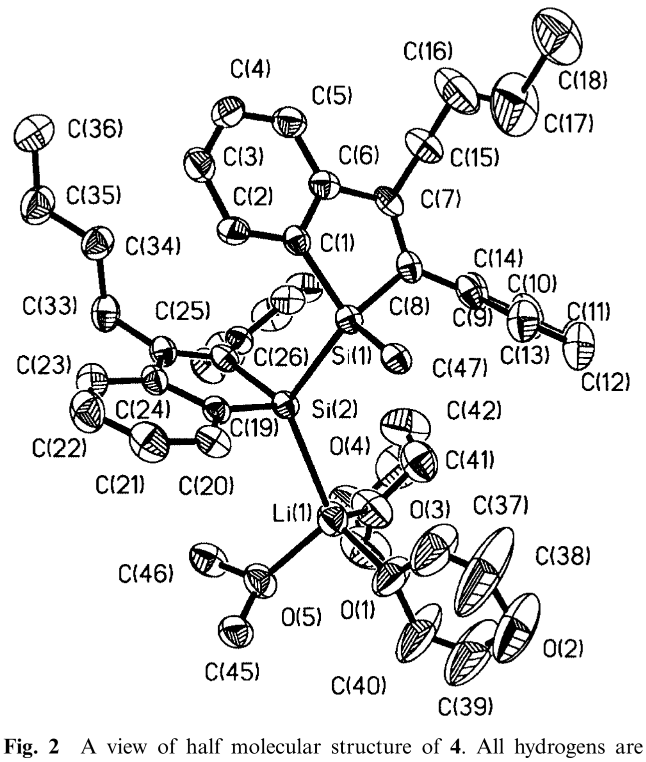
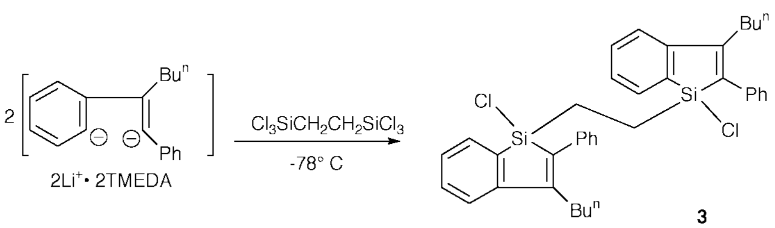


Fig. 2 A view of half molecular structure of **4**. All hydrogens are omitted for clarity. Symmetry transformations used to generate equivalent atoms through the atoms C(47), C(45) and C(46): #1 $-x$, $-y + 2$, $-z$; #2 $-x$, $-y + 1$, $-z + 1$.



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(3)

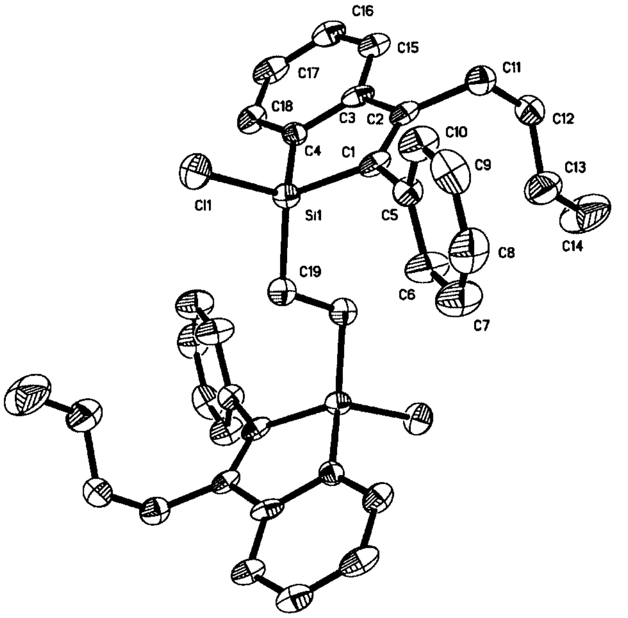

Fig. 3 Structure of **3** in the solid state. All hydrogens are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$.

Table 3 Selected bond lengths (Å) and angles (°) for **3**[a]

Si(1)–C(1)	1.850(5)	Si(1)–C(4)	1.853(4)
Si(1)–C(19)	1.865(5)	Si(1)–Cl(1)	2.0684(19)
C(1)–C(2)	1.355(6)	C(1)–C(5)	1.487(6)
C(2)–C(3)	1.510(6)	C(2)–C(11)	1.511(7)
C(3)–C(4)	1.402(7)	C(3)–C(15)	1.384(7)
C(4)–C(18)	1.391(6)	C(15)–C(16)	1.400(7)
C(16)–C(17)	1.365(8)	C(17)–C(18)	1.386(7)
C(19)–C(19)#1	1.542(9)		
C(1)–Si(1)–C(4)	93.5(2)	C(1)–Si(1)–C(19)	115.6(2)
C(4)–Si(1)–C(19)	116.4(2)	C(1)–Si(1)–Cl(1)	110.94(15)
C(4)–Si(1)–Cl(1)	112.43(15)	C(19)–Si(1)–Cl(1)	107.53(17)
C(2)–C(1)–C(5)	126.2(5)	C(2)–C(1)–Si(1)	108.5(3)
C(5)–C(1)–Si(1)	125.3(4)	C(1)–C(2)–C(3)	115.7(4)
C(1)–C(2)–C(11)	125.3(4)	C(3)–C(2)–C(11)	119.0(4)
C(4)–C(3)–C(15)	120.3(4)	C(4)–C(3)–C(2)	115.3(4)
C(15)–C(3)–C(2)	124.4(5)	C(3)–C(4)–C(18)	119.5(4)
C(3)–C(4)–Si(1)	106.9(3)	C(18)–C(4)–Si(1)	133.5(4)
C(3)–C(15)–C(16)	118.7(5)	C(17)–C(16)–C(15)	121.5(5)
C(16)–C(17)–C(18)	119.8(5)	C(17)–C(18)–C(4)	120.2(5)
C(19)#1–C(19)–Si(1)	111.5(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$.

pound in solution and in the solid state but cannot offer an explanation for this.

Experimental

All reactions were performed under an inert argon atmosphere using standard Schlenk techniques. Air sensitive reagents were transferred in an argon-filled glove box. THF was freshly distilled under nitrogen from sodium/benzophenone ketyl immediately prior to use. Hexane was stirred over sulfuric acid, distilled from calcium hydride, and stored over 4 Å molecular sieves. MS data were obtained on a Hewlett-Packard 5988A GC-MS system equipped with a HP-1 crosslinked methyl silicone capillary column. NMR spectra were recorded on a JEOL GSX400 or JEOL GSX270 spectrometer at 400 MHz (^{1}H), 155 MHz (^{7}Li), 100 MHz (^{13}C) and 54 MHz (^{29}Si). The structures were solved by the direct method and refined anisotropically on F^2 by full matrix least-squares techniques using the Siemens SHELXTL program.[8]

CCDC reference number 186/1831.

See http://www.rsc.org/suppdata/dt/a9/a906915a/ for crystallographic files in .cif format.

Preparations

1,2-Bis(1-chloro-BPSI)ethane 3. 1,8-Dilithio-1,2-diphenylhex-1-ene•2TMEDA was prepared by a modification of the Rausch's[9] procedure. To a suspension of 20 mmol of 1,8-dilithio-1,2-diphenylhex-1-ene•2TMEDA in hexane (150 mL) was added 1,2-bis(trichlorosilyl)ethane (1.78 g, 10 mmol) at −78 °C. After the mixture became a white suspension, it was stirred at room temperature for 8 h. The volatiles were removed under vacuum and toluene (50 mL) was added to the residue. The resulting suspension was filtered to give a clear yellow solution. 1,2-Bis(1-chloro-BPSI)ethane (4.0 g, 65%) was obtained as a white crystalline solid from dichloromethane. mp 157–159 °C. ^{1}H NMR ($CDCl_3$, ref: $CDCl_3 = 7.24$ ppm): 0.82 (t, 3H, $J = 7.25$ Hz), 1.03–1.21 (md, 2H), 1.34 (m, 2H), 1.54 (m, 2H), 2.51 (t, 2H, $J = 7.89$ Hz) and 7.14–7.54 ppm (m, 9H). ^{13}C NMR ($CDCl_3$, ref: $CDCl_3 = 77.09$ ppm): 7.09 (CH_2), 13.91 (CH_3), 22.98 (CH_2), 27.80 (CH_2), 31.40 (CH_2), 156.79, 148.70, 138.85, 136.09, 132.10, 132.08, 131.58, 128.56, 127.89, 127.70, 126.36 and 122.66 ppm. ^{29}Si NMR ($CDCl_3$, external ref: TMS = 0.00 ppm): 14.90 ppm. EI-MS (M^+, relative abundance): 627 ($M^+ + 5$, 2), 626 ($M^+ + 4$, 10), 625 ($M^+ + 3$, 16), 624 ($M^+ + 2$, 32), 623 ($M^+ + 1$, 24), 622 (M^+, 44) and 219 ($M^+ - 403$, 100%). Anal. Calc. for $C_{38}H_{40}Cl_2Si_2$: C, 73.17; H, 6.46. Found: C, 72.75; H, 6.73%.

[Li(diox)$_{2.5}$]$_2$[1,2-((BPSI)$_2$)$_2$C$_2$H$_4$] 4. Stirring of **3** (0.5 g, 0.80 mmol) and [Li(0.5 diox)$_2$][Li(diox)$_3$][η^5,η^1-BPSI][(0.5 diox)$_2$] **2** (diox = 1,4-dioxane) (1.0 g, 1.6 mmol) in THF (20 mL) at room temperature for a week gave an orange solution. Yield: >50% (based on ^{1}H NMR spectroscopy). Crystals (350 mg) of **4** suitable for X-ray diffraction were obtained from concentrated dioxane–THF solutions. Lithium chloride free NMR samples were prepared by dissolving the X-ray quality crystals of **4** in THF-d$_8$. ^{1}H NMR (THF-d$_8$, ref: THF-d$_8 = 1.72$ ppm): 0.62–1.68 (m, 32H), 2.37–2.45 (m, 8H), 3.63 (br s, 40H), and 6.57–7.67 ppm (m, 36H). ^{13}C NMR (THF-d$_8$, ref: THF-d$_8 = 24.45$ ppm): 163.03, 161.26, 151.66, 150.41, 149.70, 148.72, 148.56, 145.68, 143.60, 141.75, 133.06, 133.02, 129.72, 129.33, 128.06, 127.28, 127.23, 124.88, 124.41, 123.58, 123.09, 122.05, 121.34, 120.98, 33.86 (CH_2), 33.26 (CH_2), 29.12 (CH_2), 28.58 (CH_2), 24.11 (CH_2), 24.00 (CH_2), 14.69 (CH_3), 14.65 (CH_3) and 9.27 ppm (CH_2). ^{29}Si NMR (THF-d$_8$, external ref: TMS = 0.00): 7.38 and −23.06 ppm. ^{7}Li NMR (THF-d$_8$, external ref: LiBr–D_2O (0.1 M) = 0.00): −0.23 ppm.

Acknowledgements

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