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(*E*)-1-[1-(3-Phenylcyclopenta-2,4-dien-1-ylidene)-ethyl]pyrrolidine

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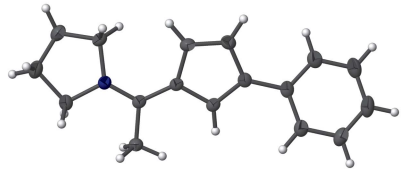
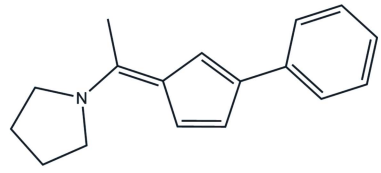
The title compound, $C_{17}H_{19}N$, is a disubstituted pentafulvene obtained from the hydroamination of 1-phenyl-3-trimethylsilylethynylcyclopentadiene and has monoclinic $P2_1/n$ symmetry at 100 K. C—H$\cdots\pi$ ring interactions between neighboring molecules consolidate the packing. To the authors' knowledge, this reaction is the first reported example of a non-transition metal catalyzed hydroamination with concomitant desilylation.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Within the fulvene system, the expected alternating short and long bond distances as well as intra-ring bond angles were observed. The 2-phenyl substituent is rotated 24.24 (6)° from the fulvene plane. The geometry around N1 is trigonal planar and the N1/C14/C17 plane is rotated by only 15.42 (9)° from the fulvene plane, presumably to allow partial conjugation of the nitrogen lone pair into the fulvene π system. Only two broad peaks are observed for the pyrrolidine methylene protons in the ^{1}H NMR spectrum, indicating N—C bond rotation and nitrogen inversion on the NMR timescale. C—H$\cdots\pi$ ring interactions (Table 1, Fig. 2) between neighboring molecules consolidate the packing.

Synthesis and crystallization

Synthesis of 1-phenyl-3-trimethylsilylethynylcyclopentadiene. To a vigorously stirred solution of ethynyltrimethylsilane (7.0 ml, 50.6 mmol) in anhydrous Et_2O (25 ml) at −94°C under N_2, *n*-BuLi (2.5 *M*, 19.2 ml, 48.0 mmol) was added dropwise over 20 min. and allowed to stir for 1 h. A solution of 3-phenylcyclopent-2-en-1-one (3.99 g, 25.2 mmol) in anhydrous Et_2O (250 ml) was added dropwise over 20 min. The resulting

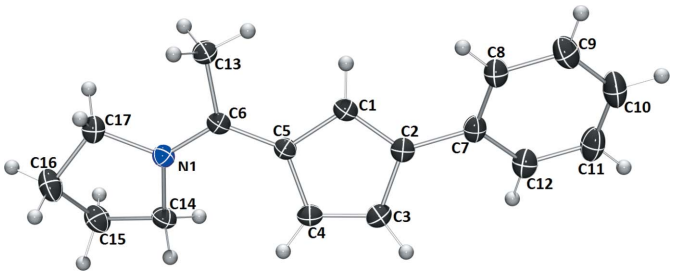


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level.

solution was allowed to come to room temperature and stirred under N_2 for 24 h, then exposed to air. The solvent was removed by rotary evaporation and the residue dissolved in CH_2Cl_2 (100 ml). 1 *M* H_2SO_4 (100 ml, 100 mmol) was added and allowed to stir for 1 h. The CH_2Cl_2 layer was separated and washed sequentially with $NaHCO_3$ (3 × 50 ml), water (2 × 50 ml), and saturated brine (1 × 50 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum to afford a red–yellow solid, which was recrystallized from ethanol (100 ml) to yield a pale-yellow solid (2.42 g, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.20 (*m*, 6H), 6.56 (*m*, 1H), 3.35 (*m*, 2H), 0.23 (*s*, 9H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 146.0, 139.0, 134.9, 128.7, 128.5, 128.2, 127.7, 127.6, 126.0, 125.3, 102.1, 98.1, 46.1, 0.13.

Synthesis of (*E*)-1-(1-(3-phenylcyclopenta-2,4-dien-1-yl-idene)ethyl)pyrrolidine. To a vigorously stirred solution of 1-phenyl-3-trimethylsilylethynylcyclopentadiene (0.336 g, 1.42 mmol) in absolute EtOH (8 ml), pyrrolidine (0.14 ml, 1.70 mmol) was added (Fig. 3). An immediate color change from pale yellow to golden brown was observed. The reaction mixture was allowed to stir at room temperature for 5 h, then to stand for 48 h. During this time, yellow, needle-like crystals of the product fulvene formed, and were isolated by vacuum filtration (0.21 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (*dd*, 2H, J_1 = 8 Hz, J_2 = 1.5 Hz), 7.32 (*t*, 2H, J = 7.5 Hz), 7.15–

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 and *Cg*3 are the centroids of the C1–C5 and C7–C12 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···*Cg*3^{i}	0.95	2.75	3.4505 (7)	131
C13—H13*C*···*Cg*2^{ii}	0.98	2.70	3.5435 (7)	145
C17—H17*A*···*Cg*2^{iii}	0.99	2.67	3.6104 (7)	159

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+2, -z$; (iii) $-x, -y+1, -z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{19}N$
M_r	237.33
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	6.7724 (13), 7.1774 (14), 26.793 (5)
β (°)	93.184 (3)
V (Å^3)	1300.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.44 × 0.33 × 0.26
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2017)
T_{min}, T_{max}	0.82, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14212, 3185, 2252
R_{int}	0.054
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.132, 1.03
No. of reflections	3185
No. of parameters	164
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.23

Computer programs: *APEX3* (Bruker, 2017), *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008), *publCIF* (Westrip, 2010).

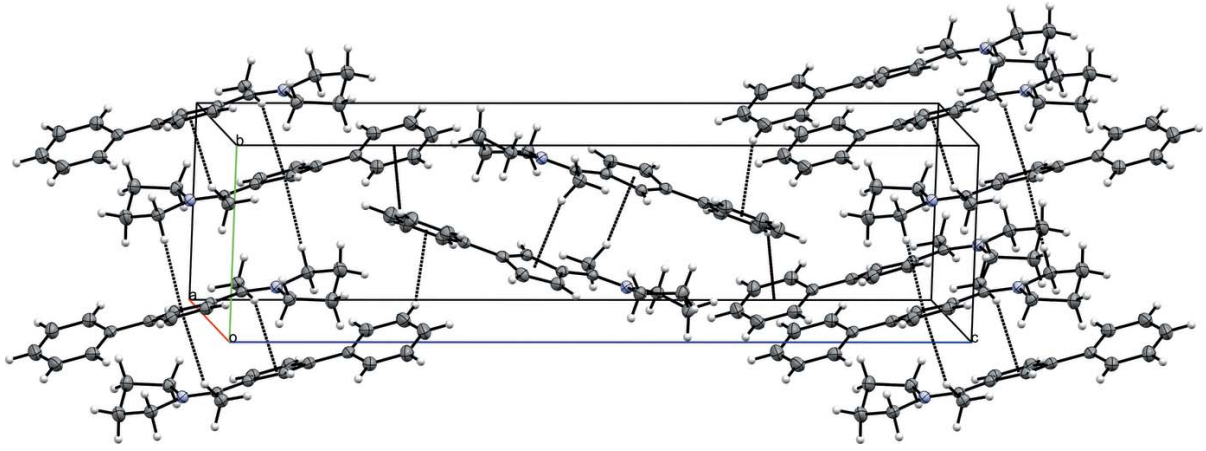


Figure 2
The crystal packing of the title compound, viewed along the *a* axis. Displacement ellipsoids are shown at the 50% probability level. C—H···π ring interactions are shown as dashed lines.

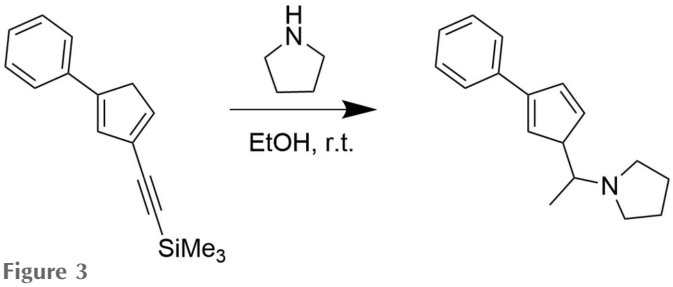


Figure 3
Reaction scheme.

7.11 (*m*, 1H), 3.77 (*s*, 4H), 2.56 (*d*, 3H, J = 15 Hz), 2.04 (*s*, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 156.3, 138.9, 136.2, 133.3, 128.4, 125.3, 121.3, 118.8,115.6, 112.2, 51.9, 25.5, 21.2.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2018). **3**, x180764 [https://doi.org/10.1107/S2414314618007642]

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(*E*)-1-[1-(3-Phenylcyclopenta-2,4-dien-1-ylidene)ethyl]pyrrolidine

Crystal data

$C_{17}H_{19}N$
$M_r = 237.33$
Monoclinic, $P2_1/n$
$a = 6.7724$ (13) Å
$b = 7.1774$ (14) Å
$c = 26.793$ (5) Å
$\beta = 93.184$ (3)°
$V = 1300.3$ (4) Å^3
$Z = 4$
$F(000) = 512$
$D_x = 1.212$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2164 reflections
$\theta = 2.9$–$29.9°$
$\mu = 0.07$ mm^{-1}
$T = 100$ K
Needle, translucent yellow
0.44 × 0.33 × 0.26 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2017)
$T_{min} = 0.82$, $T_{max} = 0.98$
14212 measured reflections
3185 independent reflections
2252 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 28.3°$, $\theta_{min} = 3.1°$
$h = -9\rightarrow8$
$k = -9\rightarrow9$
$l = -35\rightarrow35$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.132$
$S = 1.03$
3185 reflections
164 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.5603P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.61400 (18)	0.80353 (18)	0.44578 (5)	0.0216 (3)
C1	0.5199 (2)	0.6602 (2)	0.57666 (6)	0.0216 (3)
H1	0.382106	0.636262	0.577195	0.026*
C2	0.6539 (2)	0.6400 (2)	0.61681 (6)	0.0227 (3)
C3	0.8437 (2)	0.6917 (2)	0.60003 (6)	0.0259 (4)
H3	0.963888	0.691376	0.620061	0.031*
C4	0.8249 (2)	0.7413 (2)	0.55085 (6)	0.0240 (3)
H4	0.929248	0.781084	0.531106	0.029*
C5	0.6195 (2)	0.7230 (2)	0.53385 (6)	0.0204 (3)
C6	0.5240 (2)	0.7603 (2)	0.48717 (6)	0.0202 (3)
C7	0.6129 (2)	0.5764 (2)	0.66719 (6)	0.0245 (4)
C8	0.4256 (3)	0.5944 (2)	0.68581 (6)	0.0286 (4)
H8	0.322051	0.649477	0.665473	0.034*
C9	0.3875 (3)	0.5334 (3)	0.73339 (7)	0.0348 (4)
H9	0.258614	0.546292	0.745281	0.042*
C10	0.5364 (3)	0.4538 (3)	0.76354 (7)	0.0392 (5)
H10	0.510707	0.411977	0.796189	0.047*
C11	0.7229 (3)	0.4356 (3)	0.74589 (7)	0.0361 (4)
H11	0.826046	0.381445	0.76657	0.043*
C12	0.7609 (3)	0.4953 (2)	0.69846 (6)	0.0303 (4)
H12	0.889963	0.480998	0.686822	0.036*
C13	0.3032 (2)	0.7549 (2)	0.48095 (6)	0.0243 (3)
H13A	0.253437	0.878064	0.470704	0.036*
H13B	0.248508	0.720008	0.512746	0.036*
H13C	0.262881	0.662932	0.455323	0.036*
C14	0.8271 (2)	0.7903 (2)	0.43937 (6)	0.0251 (4)
H14A	0.882633	0.675685	0.455208	0.03*
H14B	0.897478	0.899698	0.454144	0.03*
C15	0.8436 (3)	0.7848 (3)	0.38320 (6)	0.0322 (4)
H15A	0.831669	0.655811	0.370312	0.039*
H15B	0.970807	0.838305	0.373602	0.039*
C16	0.6702 (3)	0.9039 (3)	0.36401 (7)	0.0349 (4)
H16A	0.703317	1.038045	0.366376	0.042*
H16B	0.63124	0.873165	0.328811	0.042*
C17	0.5070 (2)	0.8549 (2)	0.39806 (6)	0.0258 (4)
H17A	0.418844	0.962931	0.402617	0.031*
H17B	0.427141	0.749132	0.384447	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0229 (6)	0.0207 (7)	0.0214 (7)	0.0000 (5)	0.0025 (5)	−0.0006 (5)
C1	0.0233 (7)	0.0181 (8)	0.0238 (8)	−0.0006 (6)	0.0041 (6)	−0.0021 (6)
C2	0.0271 (8)	0.0178 (8)	0.0232 (8)	0.0017 (6)	0.0016 (6)	−0.0025 (6)
C3	0.0240 (8)	0.0272 (9)	0.0261 (9)	0.0014 (6)	−0.0015 (6)	−0.0027 (7)

C4	0.0207 (7)	0.0230 (8)	0.0285 (9)	−0.0001 (6)	0.0036 (6)	−0.0013 (7)
C5	0.0209 (7)	0.0170 (8)	0.0233 (8)	0.0005 (6)	0.0029 (6)	−0.0007 (6)
C6	0.0224 (7)	0.0152 (7)	0.0233 (8)	0.0004 (6)	0.0040 (6)	−0.0026 (6)
C7	0.0341 (9)	0.0182 (8)	0.0210 (8)	−0.0008 (6)	0.0005 (6)	−0.0034 (6)
C8	0.0349 (9)	0.0259 (9)	0.0250 (9)	0.0006 (7)	0.0026 (7)	0.0000 (7)
C9	0.0427 (10)	0.0352 (10)	0.0276 (9)	−0.0018 (8)	0.0107 (8)	0.0009 (8)
C10	0.0590 (12)	0.0339 (10)	0.0250 (10)	0.0008 (9)	0.0060 (8)	0.0052 (8)
C11	0.0516 (11)	0.0285 (9)	0.0276 (10)	0.0046 (8)	−0.0037 (8)	0.0039 (7)
C12	0.0381 (9)	0.0240 (9)	0.0288 (9)	0.0032 (7)	0.0003 (7)	−0.0003 (7)
C13	0.0217 (7)	0.0257 (8)	0.0256 (8)	0.0009 (6)	0.0016 (6)	0.0003 (7)
C14	0.0230 (8)	0.0266 (9)	0.0262 (9)	−0.0017 (6)	0.0058 (6)	−0.0009 (7)
C15	0.0341 (9)	0.0346 (10)	0.0288 (9)	0.0006 (7)	0.0106 (7)	0.0016 (7)
C16	0.0421 (10)	0.0351 (10)	0.0283 (10)	0.0065 (8)	0.0104 (8)	0.0070 (8)
C17	0.0315 (8)	0.0228 (8)	0.0232 (9)	0.0022 (7)	0.0014 (6)	−0.0004 (6)

Geometric parameters (Å, º)

N1—C6	1.331 (2)	C10—C11	1.379 (3)
N1—C14	1.4658 (19)	C10—H10	0.95
N1—C17	1.481 (2)	C11—C12	1.379 (2)
C1—C2	1.376 (2)	C11—H11	0.95
C1—C5	1.435 (2)	C12—H12	0.95
C1—H1	0.95	C13—H13A	0.98
C2—C3	1.434 (2)	C13—H13B	0.98
C2—C7	1.466 (2)	C13—H13C	0.98
C3—C4	1.364 (2)	C14—C15	1.516 (2)
C3—H3	0.95	C14—H14A	0.99
C4—C5	1.446 (2)	C14—H14B	0.99
C4—H4	0.95	C15—C16	1.519 (2)
C5—C6	1.402 (2)	C15—H15A	0.99
C6—C13	1.496 (2)	C15—H15B	0.99
C7—C8	1.395 (2)	C16—C17	1.513 (2)
C7—C12	1.397 (2)	C16—H16A	0.99
C8—C9	1.386 (2)	C16—H16B	0.99
C8—H8	0.95	C17—H17A	0.99
C9—C10	1.381 (3)	C17—H17B	0.99
C9—H9	0.95		
C6—N1—C14	125.57 (13)	C10—C11—H11	119.8
C6—N1—C17	123.53 (13)	C11—C12—C7	121.21 (16)
C14—N1—C17	110.66 (12)	C11—C12—H12	119.4
C2—C1—C5	109.85 (14)	C7—C12—H12	119.4
C2—C1—H1	125.1	C6—C13—H13A	109.5
C5—C1—H1	125.1	C6—C13—H13B	109.5
C1—C2—C3	106.92 (14)	H13A—C13—H13B	109.5
C1—C2—C7	127.05 (14)	C6—C13—H13C	109.5
C3—C2—C7	126.02 (14)	H13A—C13—H13C	109.5
C4—C3—C2	109.48 (14)	H13B—C13—H13C	109.5

C4—C3—H3	125.3	N1—C14—C15	104.22 (13)
C2—C3—H3	125.3	N1—C14—H14A	110.9
C3—C4—C5	108.49 (14)	C15—C14—H14A	110.9
C3—C4—H4	125.8	N1—C14—H14B	110.9
C5—C4—H4	125.8	C15—C14—H14B	110.9
C6—C5—C1	124.02 (14)	H14A—C14—H14B	108.9
C6—C5—C4	130.70 (14)	C14—C15—C16	102.90 (14)
C1—C5—C4	105.26 (13)	C14—C15—H15A	111.2
N1—C6—C5	125.31 (14)	C16—C15—H15A	111.2
N1—C6—C13	114.48 (13)	C14—C15—H15B	111.2
C5—C6—C13	120.20 (14)	C16—C15—H15B	111.2
C8—C7—C12	117.41 (15)	H15A—C15—H15B	109.1
C8—C7—C2	121.55 (14)	C17—C16—C15	104.02 (13)
C12—C7—C2	121.04 (15)	C17—C16—H16A	111.0
C9—C8—C7	121.30 (16)	C15—C16—H16A	111.0
C9—C8—H8	119.3	C17—C16—H16B	111.0
C7—C8—H8	119.3	C15—C16—H16B	111.0
C10—C9—C8	120.11 (17)	H16A—C16—H16B	109.0
C10—C9—H9	119.9	N1—C17—C16	103.85 (13)
C8—C9—H9	119.9	N1—C17—H17A	111.0
C11—C10—C9	119.47 (17)	C16—C17—H17A	111.0
C11—C10—H10	120.3	N1—C17—H17B	111.0
C9—C10—H10	120.3	C16—C17—H17B	111.0
C12—C11—C10	120.50 (17)	H17A—C17—H17B	109.0
C12—C11—H11	119.8		

Hydrogen-bond geometry (Å, º)

Cg2 and Cg3 are the centroids of the C1–C5 and C7–C12 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···*Cg*3^{i}	0.95	2.75	3.4505 (7)	131
C13—H13*C*···*Cg*2^{ii}	0.98	2.70	3.5435 (7)	145
C17—H17*A*···*Cg*2^{iii}	0.99	2.67	3.6104 (7)	159

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) −*x*, −*y*+2, −*z*; (iii) −*x*, −*y*+1, −*z*.