Supporting Information

Electrocatalytic Hydrogen Generation by a μ^3-thiolato dimanganese hexacarbonyl anion with Turnover Frequency exceeding 40,000 s^{-1}

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1 General Procedures. Manganese carbonyl (Sigma-Aldrich, 98%), diphenyl disulfide (Sigma-Aldrich, 99%), 2,2'-bipyridine (Sigma-Aldrich, 99%), trifluoroacetic (Sigma-Aldrich, 99%), HBF_4 in diethyl ether(Sigma-Aldrich, 51-57%). Hexane (AR grade) was purchased from Lab-Scan Analytical Science. CD_3CN was purchased from Cambridge Isotope. All reactions were carried out under vacuum using standard vacuum line and Schlenk techniques unless otherwise stated. Photochemical reactions were performed using Legrand broadband ultraviolet lamp (200W, 200-800 nm). ^1H NMR spectra were recorded using either Bruker ACF300 NMR spectrometer at room temperature. Single crystal X-ray structural studies were performed on Bruker-AXS Smart Apex CCD Single-Crystal Diffactometers. Data were collected at 100(2)K using graphite monochromated Mo Kα radiation (λ =0.71073Å). Data collection was evaluated using SMART CCD system.

2 Electrochemical Experiments. (a) Cyclic voltammetry experiments were conducted with a computer-controlled potentiostat using a three electrode system. Working electrodes were 1 mm diameter planar glassy carbon disks, used in conjunction with a platinum auxiliary/counter electrodeand a silver wire miniature reference electrode connected to the test solution via a salt bridge (containing 0.5 mol dm^{-3} Bu_4NPF_6 in CH_3CN). Prior to each scan, the solutions used for voltammetric analysis were de-oxygenated by purging with high purity nitrogen gas, and the working electrodes were prepared by polishing with alumina oxide (grain size 0.3 micrometer) slurry on a Buehler Ultra-pad polishing cloth, rinsing with ultrapure

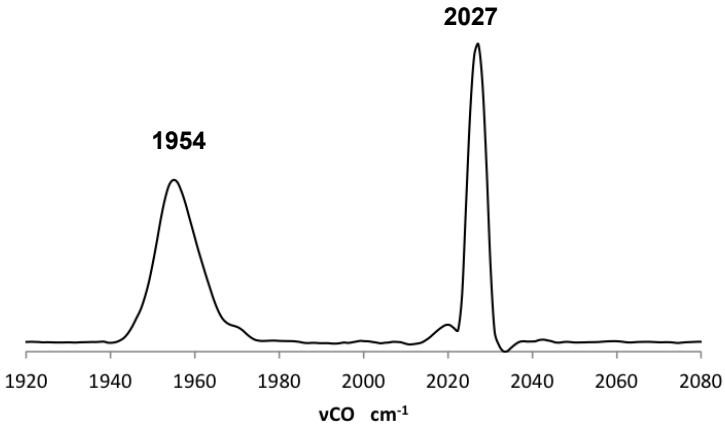
water, acetone, and then dried. Accurate potentials were obtained by using ferrocene (Fc) as an internal standard, which was added to the test solution at the end of the measurements. The test solutions were comprised of 1 mM of analyte and 0.1 M of the supporting electrolyte, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), in CH_3CN.

(b) Controlled Potential Electrolysis. A solution of 1mM **1** with 50 mM TFA in 0.1M Bu_4NPF_6 in CH_3CN was electrolyzed at -1.50 V vs Fc^+/Fc in a gas-tight electrochemical cell. The gaseous content of the reaction vessel was analyzed using a mass spectrometer, which revealed an intense signal at m/z = 2, corresponding to the production of H_2 with a Faraday yield of 95%.

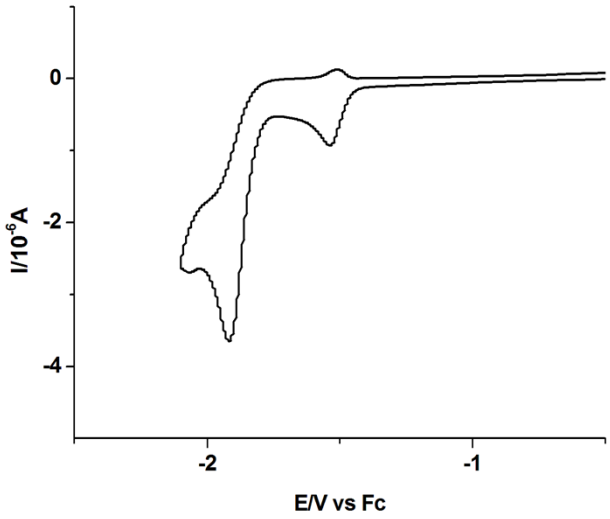
3 Synthesis of $[Mn(bpy)_3]^+[(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]^-$. (a) $Mn_2(CO)_{10}$ (100 mg, 0.26 mmol), diphenyl disulfide (113 mg, 0.52 mmol) and 2,2'-bipyridine(162 mg, 1.04 mmol) were added to a 50 mL of hexane and subjected to photolysis for 2 h and the product was obtained as yellow precipitate. Yield: 108mg, 57% (based on $Mn_2(CO)_{10}$). (b) $[Mn(CO)_4(\mu\text{-}SPh)]_2$ was prepared according to the previous report. $[Mn(CO)_4(\mu\text{-}SPh)]_2$ (55 mg, 0.1mmol) and 2,2'-bipyridine (54 mg, 0.35 mmol) were added to 30mL hexane and stirred under visible light for 8h. Yield: 25 mg, 33%. Suitable crystal of **1** was grown by dissolving them in acetone and stored at low temperature. Anal. Calc. for $C_{54}H_{39}Mn_3N_6O_6S_3$: C, 57.45; H, 3.48; N, 7.44; S, 8.52; Mn, 14.60. Found: C, 58.19; H, 3.59; N, 6.91; S, 9.02; Mn, 13.92. ESI-MS (m/z): 604.7 $[Mn_2(\mu\text{-}SPh)_3(CO)_6]^-$, 520.7 $[Mn_2(\mu\text{-}SPh)_3(CO)_3]^-$, 464.7 $[Mn_2(\mu\text{-}SPh)_3(CO)]^-$,

437.0 $[Mn_2(\mu\text{-}SPh)_3]^-$. IR ν_{CO} (CH_3CN): 1910(s), 1992(s). ^1H NMR $\delta(CD_3CN)$: 6.94-8.72 (m, 15H, from Ph, 24H, from 2,2′-bipyridine).

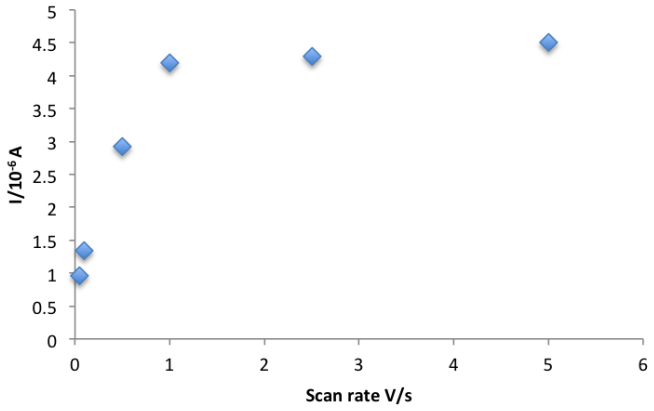
4 νCO IR of $[Mn(\mu_3\text{-}SPh)(CO)_3]_4$ in hexane



5 Cyclic voltammograms of 1 (1.0 mM) in 0.1 M Bu_4NPF_6 in CH_3CN at a scan rate of 0.1 V/ sec.



6 Scan rate (V/s) vs i_p (10^{-6}A) for 1 mM 1 in 0.1 M Bu_4NPF_6 in CH_3CN.



7 Cyclic information of complex 1 and the corresponding k_{obs}.

Complex 1 (mM)	TFA(mM)	i_c (10^{-6}A)	i_p (10^{-6} A)	k_{obs} (s^{-1})
1.0	10	4.20	43.9	211
1.0	20	4.20	102	1138
1.0	50	4.20	256	7167
1.0	100	4.20	402	17672
1.0	300	4.20	638	44567

8 Crystal structure information

(1) Data collection and structure refinement

Theta range for data collection	2.17 to 27.00°
Index ranges	-37<=h<=37, -24<=k<=24, -24<=l<=24
Reflections collected	92570
Independent reflections	9816 [R(int) = 0.1186]
Coverage of independent reflections	99.5%
Absorption correction	multi-scan

Max. and min. transmission	0.7457 and 0.6630	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9816 / 69 / 553	
Goodness-of-fit on F^2	1.056	
Δ/σ_{max}	0.001	
Final R indices	6171 data; $I>2\sigma(I)$	R1 = 0.0684, wR2 = 0.1679
	all data	R1 = 0.1270, wR2 = 0.1908
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0898P)^2+35.1184P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.239 and -0.717 eÅ^{-3}	
R.M.S. deviation from mean	0.111 eÅ^{-3}	

(2) Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2)

	x/a	y/b	z/c	U(eq)
C6X	0.0062(15)	0.0933(12)	0.7779(16)	0.188(5)
C5X	0.0529(10)	0.0504(15)	0.8461(15)	0.188(5)
C4X	0.0181(10)	0.9994(13)	0.8577(11)	0.188(5)
C3X	0.0567(7)	0.9956(16)	0.9522(12)	0.188(5)
C2X	0.0103(8)	0.9853(18)	0.9655(13)	0.188(5)
C1X	0.0409(10)	0.0121(17)	0.0527(14)	0.188(5)
O3W	0.9680(18)	0.034(2)	0.853(3)	0.196(16)
O2W	0.0442(12)	0.0875(15)	0.743(2)	0.250(12)
O1W	0.9770(10)	0.7992(13)	0.738(2)	0.244(12)
C1S	0.9893(8)	0.7971(8)	0.8850(10)	0.18
Cl3	0.9865(6)	0.8903(7)	0.8728(9)	0.215(7)
Cl2	0.9472(5)	0.7988(8)	0.7800(10)	0.206(6)

Cl1	0.0406(4)	0.8083(6)	0.8670(9)	0.263(7)
Mn1	0.22227(3)	0.92429(4)	0.25961(4)	0.02617(19)
Mn2	0.34116(3)	0.92457(4)	0.30018(4)	0.0293(2)
Mn3	0	0.61578(5)	0.25	0.0282(3)
S1	0.26275(4)	0.97757(6)	0.19048(7)	0.0279(3)
S2	0.28016(5)	0.82990(6)	0.27191(7)	0.0283(3)
S3	0.30257(5)	0.96389(6)	0.37877(7)	0.0276(3)
O1	0.16021(14)	0.0539(2)	0.2359(2)	0.0392(9)
O2	0.17733(15)	0.86035(19)	0.3523(2)	0.0426(9)
O3	0.13610(14)	0.8675(2)	0.1023(2)	0.0455(10)
O4	0.40471(14)	0.0545(2)	0.3342(2)	0.0488(10)
O5	0.42958(15)	0.8545(2)	0.4451(2)	0.0443(9)
O6	0.38343(16)	0.8706(3)	0.1994(3)	0.0730(15)
N1	0.01286(15)	0.6964(2)	0.1758(2)	0.0306(9)
N2	0.08897(14)	0.6314(2)	0.3117(2)	0.0277(9)
N3	0.98894(14)	0.5207(2)	0.1725(2)	0.0309(9)
C1	0.23734(18)	0.9416(2)	0.0895(3)	0.0287(11)
C2	0.20887(19)	0.9874(3)	0.0240(3)	0.0347(11)
C3	0.1874(2)	0.9653(3)	0.9437(3)	0.0402(13)
C4	0.1936(2)	0.8967(3)	0.9267(3)	0.0385(12)
C5	0.2219(2)	0.8504(3)	0.9915(3)	0.0407(13)
C6	0.2440(2)	0.8723(3)	0.0730(3)	0.0364(12)
C7	0.30373(18)	0.7712(2)	0.3583(3)	0.0272(10)
C8	0.30459(19)	0.7873(3)	0.4303(3)	0.0307(11)
C9	0.32393(19)	0.7382(3)	0.4938(3)	0.0314(11)
C10	0.34335(17)	0.6738(3)	0.4876(3)	0.0294(10)
C11	0.34251(18)	0.6576(3)	0.4158(3)	0.0334(11)
C12	0.32256(18)	0.7059(3)	0.3514(3)	0.0318(11)
C13	0.30901(17)	0.0569(2)	0.3977(3)	0.0263(10)
C14	0.3329(2)	0.0796(3)	0.4778(3)	0.0339(11)
C15	0.3411(2)	0.1506(3)	0.4974(3)	0.0400(13)
C16	0.32524(19)	0.2011(3)	0.4367(3)	0.0325(11)

C17	0.3007(2)	0.1794(3)	0.3568(3)	0.0392(12)
C18	0.2919(2)	0.1082(3)	0.3360(3)	0.0396(13)
C19	0.18504(19)	0.0039(3)	0.2460(3)	0.0307(11)
C20	0.1964(2)	0.8847(2)	0.3177(3)	0.0309(11)
C21	0.1697(2)	0.8890(3)	0.1643(3)	0.0311(11)
C22	0.37888(19)	0.0040(3)	0.3193(3)	0.0377(13)
C23	0.3945(2)	0.8821(3)	0.3890(3)	0.0339(11)
C24	0.3652(2)	0.8908(3)	0.2370(3)	0.0442(14)
C25	0.97381(19)	0.7302(3)	0.1111(3)	0.0425(13)
C26	0.9815(16)	0.787(2)	0.0780(19)	0.045(5)
C27	0.0334(8)	0.8076(11)	0.1071(10)	0.055(4)
C28	0.0738(10)	0.7712(13)	0.1721(14)	0.047(4)
C26X	0.9820(16)	0.773(2)	0.054(2)	0.045(5)
C27X	0.0333(8)	0.7851(11)	0.0735(11)	0.055(4)
C28X	0.0757(10)	0.7522(13)	0.1458(13)	0.047(4)
C29	0.06335(18)	0.7123(3)	0.1997(3)	0.0385(12)
C30	0.10527(17)	0.6748(2)	0.2731(3)	0.0273(10)
C31	0.15937(18)	0.6821(3)	0.3000(3)	0.0294(11)
C32	0.19627(18)	0.6425(3)	0.3658(3)	0.0316(11)
C33	0.17947(18)	0.5982(3)	0.4061(3)	0.0318(11)
C34	0.12567(18)	0.5947(3)	0.3771(3)	0.0316(11)
C35	0.97609(19)	0.5235(3)	0.0936(3)	0.0406(13)
C36	0.9666(2)	0.4645(4)	0.0464(4)	0.0559(18)
C37	0.9708(3)	0.3995(4)	0.0800(5)	0.067(2)
C38	0.9850(3)	0.3951(3)	0.1616(5)	0.0574(17)
C39	0.9929(2)	0.4566(3)	0.2062(3)	0.0373(12)

(3) Bond lengths (Å)

C6X-C5X	1.540(10)	C5X-C4X	1.503(10)
C4X-C3X	1.548(10)	C3X-C2X	1.524(10)
C2X-C1X	1.502(10)	O1W-O1W	1.19(5)
C1S-Cl2	1.715(10)	C1S-Cl1	1.724(10)

C1S-Cl3	1.774(10)	Cl3-Cl1	2.267(9)
Cl3-Cl2	2.306(10)	Cl2-Cl1	2.366(9)
Mn1-C21	1.790(5)	Mn1-C20	1.794(5)
Mn1-C19	1.799(5)	Mn1-S3	2.3892(14)
Mn1-S2	2.3930(14)	Mn1-S1	2.4017(12)
Mn1-Mn2	3.1646(10)	Mn2-C23	1.789(6)
Mn2-C22	1.790(6)	Mn2-C24	1.796(6)
Mn2-S1	2.3817(14)	Mn2-S2	2.3899(14)
Mn2-S3	2.4111(13)	Mn3-N1	2.236(4)
Mn3-N1	2.236(4)	Mn3-N3	2.238(4)
Mn3-N3	2.238(4)	Mn3-N2	2.263(4)
Mn3-N2	2.263(4)	S1-C1	1.790(5)
S2-C7	1.794(5)	S3-C13	1.786(5)
O1-C19	1.148(6)	O2-C20	1.158(5)
O3-C21	1.148(6)	O4-C22	1.160(6)
O5-C23	1.153(6)	O6-C24	1.155(6)
N1-C25	1.331(6)	N1-C29	1.342(6)
N2-C34	1.341(6)	N2-C30	1.341(6)
N3-C35	1.341(6)	N3-C39	1.347(6)
C1-C2	1.384(7)	C1-C6	1.385(7)
C2-C3	1.375(7)	C3-C4	1.371(7)
C4-C5	1.381(7)	C5-C6	1.394(7)
C7-C8	1.386(6)	C7-C12	1.388(7)
C8-C9	1.387(7)	C9-C10	1.377(7)
C10-C11	1.384(7)	C11-C12	1.389(7)
C13-C14	1.370(7)	C13-C18	1.398(7)
C14-C15	1.382(7)	C15-C16	1.378(7)
C16-C17	1.361(7)	C17-C18	1.389(7)
C25-C26	1.32(4)	C25-C26X	1.46(4)
C26-C27	1.38(5)	C27-C28	1.37(3)
C28-C29	1.33(3)	C26X-C27X	1.37(4)

C27X-C28X	1.43(3)	C28X-C29	1.46(2)
C29-C30	1.478(7)	C30-C31	1.403(6)
C31-C32	1.376(7)	C32-C33	1.385(7)
C33-C34	1.380(6)	C35-C36	1.366(8)
C36-C37	1.360(10)	C37-C38	1.381(10)
C38-C39	1.385(8)	C39-C39	1.488(10)

(4) Bond angles (°)

C4X-C5X-C6X	94.8(8)	C5X-C4X-C3X	93.0(8)
C2X-C3X-C4X	90.9(7)	C1X-C2X-C3X	93.6(8)
Cl2-C1S-Cl1	86.9(6)	Cl2-C1S-Cl3	82.7(6)
Cl1-C1S-Cl3	80.8(6)	C1S-Cl3-Cl1	48.7(4)
C1S-Cl3-Cl2	47.5(4)	Cl1-Cl3-Cl2	62.3(3)
C1S-Cl2-Cl3	49.7(4)	C1S-Cl2-Cl1	46.7(4)
Cl3-Cl2-Cl1	58.0(3)	C1S-Cl1-Cl3	50.6(4)
C1S-Cl1-Cl2	46.4(4)	Cl3-Cl1-Cl2	59.7(3)
C21-Mn1-C20	92.6(2)	C21-Mn1-C19	91.4(2)
C20-Mn1-C19	91.0(2)	C21-Mn1-S3	169.83(15)
C20-Mn1-S3	94.34(16)	C19-Mn1-S3	95.87(16)
C21-Mn1-S2	91.06(16)	C20-Mn1-S2	97.77(16)
C19-Mn1-S2	170.79(14)	S3-Mn1-S2	80.67(5)
C21-Mn1-S1	91.00(15)	C20-Mn1-S1	176.08(17)
C19-Mn1-S1	90.42(14)	S3-Mn1-S1	81.88(4)
S2-Mn1-S1	80.66(4)	C21-Mn1-Mn2	120.82(15)
C20-Mn1-Mn2	128.13(16)	C19-Mn1-Mn2	123.11(15)
S3-Mn1-Mn2	49.06(3)	S2-Mn1-Mn2	48.53(3)
S1-Mn1-Mn2	48.31(3)	C23-Mn2-C22	92.1(2)
C23-Mn2-C24	90.7(2)	C22-Mn2-C24	91.0(3)
C23-Mn2-S1	171.88(16)	C22-Mn2-S1	92.33(16)
C24-Mn2-S1	95.97(17)	C23-Mn2-S2	93.70(16)
C22-Mn2-S2	171.34(17)	C24-Mn2-S2	95.35(19)
S1-Mn2-S2	81.14(5)	C23-Mn2-S3	91.16(16)

C22-Mn2-S3	93.22(18)	C24-Mn2-S3	175.36(19)
S1-Mn2-S3	81.83(4)	S2-Mn2-S3	80.29(4)
C23-Mn2-Mn1	123.14(15)	C22-Mn2-Mn1	122.72(16)
C24-Mn2-Mn1	127.20(18)	S1-Mn2-Mn1	48.85(3)
S2-Mn2-Mn1	48.62(3)	S3-Mn2-Mn1	48.46(3)
N1-Mn3-N1	94.0(2)	N1-Mn3-N3	161.31(13)
N1-Mn3-N3	98.59(14)	N1-Mn3-N3	98.59(14)
N1-Mn3-N3	161.31(13)	N3-Mn3-N3	73.0(2)
N1-Mn3-N2	73.10(14)	N1-Mn3-N2	96.49(14)
N3-Mn3-N2	91.71(13)	N3-Mn3-N2	100.34(13)
N1-Mn3-N2	96.49(14)	N1-Mn3-N2	73.10(14)
N3-Mn3-N2	100.34(13)	N3-Mn3-N2	91.71(13)
N2-Mn3-N2	165.03(19)	C1-S1-Mn2	116.91(16)
C1-S1-Mn1	112.00(15)	Mn2-S1-Mn1	82.84(4)
C7-S2-Mn2	111.65(15)	C7-S2-Mn1	117.96(16)
Mn2-S2-Mn1	82.85(5)	C13-S3-Mn1	116.67(16)
C13-S3-Mn2	113.15(14)	Mn1-S3-Mn2	82.48(4)
C25-N1-C29	118.5(4)	C25-N1-Mn3	124.2(3)
C29-N1-Mn3	117.3(3)	C34-N2-C30	118.5(4)
C34-N2-Mn3	124.8(3)	C30-N2-Mn3	116.2(3)
C35-N3-C39	118.1(5)	C35-N3-Mn3	124.1(4)
C39-N3-Mn3	117.7(3)	C2-C1-C6	118.7(5)
C2-C1-S1	116.5(4)	C6-C1-S1	124.9(4)
C3-C2-C1	121.4(5)	C4-C3-C2	120.4(5)
C3-C4-C5	118.9(5)	C4-C5-C6	121.2(5)
C1-C6-C5	119.5(5)	C8-C7-C12	118.9(4)
C8-C7-S2	124.4(4)	C12-C7-S2	116.6(3)
C7-C8-C9	119.9(5)	C10-C9-C8	121.3(4)
C9-C10-C11	118.9(4)	C10-C11-C12	120.2(5)
C7-C12-C11	120.7(4)	C14-C13-C18	117.7(4)
C14-C13-S3	118.1(4)	C18-C13-S3	124.2(4)
C13-C14-C15	121.4(5)	C16-C15-C14	120.8(5)

C17-C16-C15	118.4(5)	C16-C17-C18	121.4(5)
C17-C18-C13	120.2(5)	O1-C19-Mn1	178.4(5)
O2-C20-Mn1	176.8(5)	O3-C21-Mn1	178.7(4)
O4-C22-Mn2	177.7(5)	O5-C23-Mn2	178.2(4)
O6-C24-Mn2	176.2(5)	C26-C25-N1	123.4(18)
N1-C25-C26X	123.5(17)	C25-C26-C27	118.(3)
C28-C27-C26	118.(2)	C29-C28-C27	120.(2)
C27X-C26X-C25	118.(3)	C26X-C27X-C28X	118.(2)
C27X-C28X-C29	119.0(19)	C28-C29-N1	119.6(12)
N1-C29-C28X	120.9(11)	C28-C29-C30	121.6(12)
N1-C29-C30	116.5(4)	C28X-C29-C30	121.3(11)
N2-C30-C31	121.4(4)	N2-C30-C29	116.7(4)
C31-C30-C29	121.9(4)	C32-C31-C30	119.2(4)
C31-C32-C33	119.4(4)	C34-C33-C32	118.2(5)
N2-C34-C33	123.3(5)	N3-C35-C36	122.8(6)
C37-C36-C35	119.6(6)	C36-C37-C38	118.8(6)
C37-C38-C39	119.4(6)	N3-C39-C38	121.4(5)
N3-C39-C39	115.8(3)	C38-C39-C39	122.8(4)