Supporting Information

Silacyclobutadiene Cobalt Complex

Yoshihiro Kon, Kenkichi Sakamoto, Chizuko Kabuto, and Mitsuo Kira*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Contents

1. X-ray Crystallographic Analysis of Silacyclobutadiene Cobalt Complex 1

A. Crystal Data

Empirical Formula	$C_{28}H_{53}CoSi_3$
Formula Weight	532.92
Crystal Color, Habit	red, plate
Crystal Dimensions	0.35 X 0.20 X 0.08 mm
Crystal System	monoclinic
Lattice Type	Primitive
Detector Position	39.95 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 12.238(4) Å b = 15.096(4) Å c = 17.226(5) Å β = 95.811(5) ° V = 3166.0(16) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.118 g/cm^3
F_{000}	1160.00
μ(MoKα)	6.69 cm^{-1}

B. Intensity Measurements

Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	900 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-77.0 - 103.0°
Exposure Rate	75.0 sec./°
Detector Swing Angle	13.12°
ω oscillation Range (χ=45.0, ϕ=90.0)	-77.0 - 103.0°
Exposure Rate	75.0 sec./°
Detector Swing Angle	13.12°
Detector Position	39.95 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 30133 Unique: 7052 (R_{int} = 0.055)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8938 - 1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$1/[0.0058Fo^2+1.0000\sigma(Fo^2)]/(4Fo^2)$
$2\theta_{max}$ cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6399
No. Variables	342
Reflection/Parameter Ratio	18.71
Residuals: R (All reflections)	0.139
Residuals: R1 (I>2.00σ(I))	0.084
Residuals: wR2 (All reflections)	0.257
Goodness of Fit Indicator	1.003
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.99 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.72 e$^-$/Å^3

Table S1. Atomic coordinates, B_{iso}/B_{eq} and occupancy of silacyclobutadiene complex **1**.

atom	x	y	z	B_{eq}
Co(9)	0.45748(6)	0.42910(4)	0.24645(4)	3.21(2)
Si(1)	0.61970(11)	0.36302(11)	0.27772(8)	3.53(3)
Si(5)	0.7776(1)	0.43911(11)	0.32196(11)	4.41(4)
Si(6)	0.45468(12)	0.29395(12)	0.41211(9)	4.17(4)
C(2)	0.5024(3)	0.3137(2)	0.3101(2)	1.20(6)
C(3)	0.4536(4)	0.2999(3)	0.2235(3)	3.09(10)
C(4)	0.5413(4)	0.3432(4)	0.1851(3)	3.43(11)
C(7)	0.3577(5)	0.2383(4)	0.1946(4)	4.42(13)
C(8)	0.5682(7)	0.3490(5)	0.1008(4)	5.4(2)
C(10)	0.4481(8)	0.5538(5)	0.1998(5)	6.7(2)
C(11)	0.4677(6)	0.5594(4)	0.2834(5)	5.9(2)
C(12)	0.3809(6)	0.5180(4)	0.3142(4)	5.0(2)
C(13)	0.3060(6)	0.4879(5)	0.2523(5)	5.8(2)
C(14)	0.3460(8)	0.5107(5)	0.1839(5)	7.1(2)
C(15)	0.7984(7)	0.5364(5)	0.2587(6)	8.4(2)
C(16)	0.7707(9)	0.4891(8)	0.4199(6)	9.8(3)
C(17)	0.8976(5)	0.3609(5)	0.3273(4)	5.3(2)
C(18)	0.8728(8)	0.2802(6)	0.3753(6)	8.6(3)
C(19)	0.9195(8)	0.3245(9)	0.2495(6)	10.7(4)
C(20)	0.9985(8)	0.4062(9)	0.3705(9)	13.0(4)
C(21)	0.3104(6)	0.3188(7)	0.4307(5)	7.9(3)
C(22)	0.5460(7)	0.3735(5)	0.4725(4)	6.6(2)
C(23)	0.4900(5)	0.1759(5)	0.4503(3)	5.0(2)
C(24)	0.4113(9)	0.1064(6)	0.4168(5)	9.8(3)
C(25)	0.4882(7)	0.1785(8)	0.5399(4)	8.3(3)
C(26)	0.6057(7)	0.1519(5)	0.4358(4)	6.6(2)
C(27)	0.2723(5)	0.2349(5)	0.2506(5)	5.5(2)
C(28)	0.3003(6)	0.2605(7)	0.1166(4)	7.9(2)
C(29)	0.4058(6)	0.1419(5)	0.1921(6)	7.5(2)
C(30)	0.6685(7)	0.4124(7)	0.1031(4)	8.0(3)
C(31)	0.5947(11)	0.2573(7)	0.0720(5)	10.5(4)
C(32)	0.4797(8)	0.3889(7)	0.0422(4)	7.9(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S1. Atomic coordinates, B_{iso}/B_{eq} and occupancy of silacyclobutadiene complex **1**.

atom	x	y	z	B_{eq}
H(1)	0.8663	0.5637	0.2776	9.897
H(2)	0.8026	0.5162	0.2071	9.900
H(3)	0.7402	0.5761	0.2610	9.898
H(4)	0.8365	0.5177	0.4346	11.736
H(5)	0.7106	0.5303	0.4172	11.727
H(6)	0.7570	0.4435	0.4559	11.728
H(7)	0.8598	0.3005	0.4251	10.456
H(8)	0.8144	0.2510	0.3498	10.456
H(9)	0.9383	0.2449	0.3791	10.456
H(10)	0.8568	0.2919	0.2288	13.044
H(11)	0.9331	0.3721	0.2184	13.045
H(12)	0.9808	0.2862	0.2580	13.042
H(13)	1.0580	0.3654	0.3738	15.041
H(14)	1.0144	0.4562	0.3420	15.043
H(15)	0.9849	0.4228	0.4224	15.041
H(16)	0.2944	0.3767	0.4158	9.694
H(17)	0.2630	0.2780	0.4014	9.697
H(18)	0.3034	0.3103	0.4849	9.696
H(19)	0.6191	0.3583	0.4697	7.791
H(20)	0.5296	0.4307	0.4537	7.795
H(21)	0.5286	0.3693	0.5258	7.788
H(22)	0.3452	0.1199	0.4301	11.354
H(23)	0.4165	0.1017	0.3623	11.341
H(24)	0.4376	0.0492	0.4397	11.348
H(25)	0.5354	0.2233	0.5593	9.997
H(26)	0.4129	0.1950	0.5491	10.000
H(27)	0.5044	0.1236	0.5594	9.994
H(28)	0.6206	0.0961	0.4588	8.091
H(29)	0.6065	0.1490	0.3812	8.097
H(30)	0.6518	0.1957	0.4580	8.088
H(31)	0.2390	0.2907	0.2524	6.444
H(32)	0.2198	0.1910	0.2336	6.457
H(33)	0.3065	0.2192	0.3010	6.451
H(34)	0.2642	0.3161	0.1215	9.358
H(35)	0.3503	0.2625	0.0807	9.367
H(36)	0.2445	0.2165	0.1030	9.358
H(37)	0.3470	0.1026	0.1741	8.969
H(38)	0.4588	0.1416	0.1559	8.980
H(39)	0.4352	0.1271	0.2418	8.986
H(40)	0.7251	0.3896	0.1393	9.665
H(41)	0.6925	0.4137	0.0525	9.660
H(42)	0.6469	0.4688	0.1181	9.660
H(43)	0.5317	0.2242	0.0683	13.117
H(44)	0.6235	0.2638	0.0230	13.116
H(45)	0.6506	0.2321	0.1084	13.113
H(46)	0.4651	0.4472	0.0582	9.368
H(47)	0.5106	0.3919	-0.0073	9.383
H(48)	0.4190	0.3532	0.0387	9.376
H(49)	0.5280	0.5864	0.3120	6.832
H(50)	0.3720	0.5116	0.3671	6.058
H(51)	0.4911	0.5784	0.1636	8.144
H(52)	0.2404	0.4580	0.2581	6.820
H(53)	0.3089	0.4981	0.1358	8.200

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2. Anisotropic displacement parameters of silacyclobutadiene complex **1**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(9)	0.0456(4)	0.0313(4)	0.0436(4)	0.0114(3)	-0.0034(3)	-0.0014(3)
Si(1)	0.0369(7)	0.0501(9)	0.0472(8)	-0.0016(6)	0.0036(6)	0.0009(7)
Si(5)	0.0569(10)	0.0429(9)	0.0672(11)	-0.0050(7)	0.0031(8)	0.0054(7)
Si(6)	0.0405(8)	0.0681(11)	0.0509(9)	-0.0014(7)	0.0095(6)	-0.0164(8)
C(2)	0.029(2)	0.010(2)	0.008(2)	-0.001(1)	0.0022(13)	0.0000(12)
C(3)	0.036(3)	0.034(3)	0.044(3)	0.004(2)	-0.012(2)	-0.008(2)
C(4)	0.055(3)	0.041(3)	0.034(2)	0.017(2)	0.004(2)	0.005(2)
C(7)	0.044(3)	0.051(3)	0.068(4)	0.003(3)	-0.015(3)	-0.022(3)
C(8)	0.100(5)	0.058(4)	0.053(4)	0.009(4)	0.037(3)	0.008(3)
C(10)	0.119(7)	0.044(4)	0.095(6)	0.030(4)	0.023(5)	0.022(4)
C(11)	0.079(5)	0.035(3)	0.102(6)	0.017(3)	-0.023(4)	-0.020(3)
C(12)	0.076(4)	0.046(4)	0.070(4)	0.023(3)	0.012(3)	-0.011(3)
C(13)	0.057(4)	0.055(4)	0.105(6)	0.021(3)	-0.005(4)	-0.007(4)
C(14)	0.105(6)	0.055(4)	0.100(6)	0.051(5)	-0.036(5)	-0.006(4)
C(15)	0.079(5)	0.064(5)	0.170(9)	-0.027(4)	-0.021(6)	0.055(6)
C(16)	0.103(7)	0.131(9)	0.137(8)	-0.019(6)	0.003(6)	-0.062(7)
C(17)	0.047(3)	0.080(5)	0.073(4)	-0.006(3)	0.002(3)	0.023(4)
C(18)	0.109(7)	0.090(6)	0.132(8)	0.038(6)	0.028(6)	0.037(6)
C(19)	0.103(7)	0.199(13)	0.111(7)	0.091(8)	0.045(6)	0.034(7)
C(20)	0.075(6)	0.135(10)	0.27(2)	-0.015(6)	-0.065(9)	0.028(10)
C(21)	0.067(4)	0.160(9)	0.080(5)	0.015(5)	0.042(4)	-0.004(5)
C(22)	0.092(5)	0.078(5)	0.076(5)	-0.002(4)	-0.007(4)	-0.018(4)
C(23)	0.063(4)	0.082(5)	0.044(3)	-0.020(3)	0.006(3)	0.014(3)
C(24)	0.171(10)	0.081(6)	0.107(7)	-0.058(7)	-0.042(7)	0.046(5)
C(25)	0.087(6)	0.174(10)	0.055(4)	-0.001(6)	0.008(4)	0.030(5)
C(26)	0.108(6)	0.063(5)	0.085(5)	0.016(4)	0.030(5)	0.017(4)
C(27)	0.047(4)	0.054(4)	0.104(5)	-0.007(3)	-0.011(3)	-0.007(4)
C(28)	0.064(5)	0.162(9)	0.071(5)	-0.012(5)	-0.012(4)	-0.036(5)
C(29)	0.071(5)	0.056(4)	0.157(8)	-0.007(4)	0.011(5)	-0.045(5)
C(30)	0.092(6)	0.159(9)	0.055(4)	0.030(6)	0.026(4)	0.035(5)
C(31)	0.206(12)	0.109(8)	0.100(7)	0.042(8)	0.096(8)	0.004(5)
C(32)	0.141(8)	0.120(7)	0.036(3)	-0.029(6)	-0.006(4)	0.020(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S3. Bond lengths(Å) of silacyclobutadiene complex **1**.

atom	atom	distance	atom	atom	distance
Co(9)	Si(1)	2.238(2)	Co(9)	C(2)	2.102(3)
Co(9)	C(3)	1.989(5)	Co(9)	C(4)	2.016(5)
Co(9)	C(10)	2.046(7)	Co(9)	C(11)	2.067(6)
Co(9)	C(12)	2.065(7)	Co(9)	C(13)	2.067(7)
Co(9)	C(14)	2.060(8)	Si(1)	Si(5)	2.310(2)
Si(1)	C(2)	1.757(4)	Si(1)	C(4)	1.801(5)
Si(5)	C(15)	1.861(9)	Si(5)	C(16)	1.86(1)
Si(5)	C(17)	1.879(7)	Si(6)	C(2)	1.930(4)
Si(6)	C(21)	1.864(8)	Si(6)	C(22)	1.881(8)
Si(6)	C(23)	1.933(7)	C(2)	C(3)	1.564(6)
C(3)	C(4)	1.469(7)	C(3)	C(7)	1.541(7)
C(4)	C(8)	1.524(8)	C(7)	C(27)	1.492(9)
C(7)	C(28)	1.490(9)	C(7)	C(29)	1.572(9)
C(8)	C(30)	1.55(1)	C(8)	C(31)	1.52(1)
C(8)	C(32)	1.53(1)	C(10)	C(11)	1.44(1)
C(10)	C(14)	1.41(1)	C(11)	C(12)	1.38(1)
C(12)	C(13)	1.41(1)	C(13)	C(14)	1.37(1)
C(17)	C(18)	1.52(1)	C(17)	C(19)	1.50(1)
C(17)	C(20)	1.54(1)	C(23)	C(24)	1.50(1)
C(23)	C(25)	1.545(9)	C(23)	C(26)	1.51(1)

Table S4. Bond angles (deg) of silacyclobutadiene complex **1**.

atom	atom	atom	angle	atom	atom	atom	angle
Co(9)	Si(1)	C(2)	62.1(1)	C(2)	Co(9)	Si(1)	47.6(1)
C(3)	Co(9)	Si(1)	67.3(1)	Co(9)	Si(1)	C(4)	58.7(2)
C(4)	Co(9)	Si(1)	49.8(1)	C(10)	Co(9)	Si(1)	121.2(3)
C(11)	Co(9)	Si(1)	109.0(2)	C(12)	Co(9)	Si(1)	126.6(2)
C(13)	Co(9)	Si(1)	163.3(2)	C(14)	Co(9)	Si(1)	156.5(3)
Co(9)	Si(1)	Si(5)	123.35(9)	Co(9)	C(2)	Si(1)	70.3(1)
Co(9)	C(2)	C(3)	63.8(2)	C(3)	Co(9)	C(2)	44.9(2)
C(4)	Co(9)	C(2)	67.7(2)	C(10)	Co(9)	C(2)	165.7(3)
C(11)	Co(9)	C(2)	128.6(2)	C(12)	Co(9)	C(2)	110.7(2)
C(13)	Co(9)	C(2)	121.3(2)	C(14)	Co(9)	C(2)	153.3(3)
Co(9)	C(2)	Si(6)	121.0(2)	Co(9)	C(3)	C(2)	71.4(2)
Co(9)	C(3)	C(4)	69.5(3)	C(4)	Co(9)	C(3)	43.0(2)
C(10)	Co(9)	C(3)	145.6(3)	C(11)	Co(9)	C(3)	173.4(3)
C(12)	Co(9)	C(3)	138.3(2)	C(13)	Co(9)	C(3)	115.3(2)
C(14)	Co(9)	C(3)	118.7(3)	Co(9)	C(3)	C(7)	131.2(4)
Co(9)	C(4)	Si(1)	71.5(2)	Co(9)	C(4)	C(3)	67.5(3)
C(10)	Co(9)	C(4)	113.4(3)	C(11)	Co(9)	C(4)	139.0(3)
C(12)	Co(9)	C(4)	176.2(2)	C(13)	Co(9)	C(4)	143.8(3)
C(14)	Co(9)	C(4)	117.1(3)	Co(9)	C(4)	C(8)	129.3(4)
Co(9)	C(10)	C(11)	70.4(4)	C(11)	Co(9)	C(10)	40.9(3)
C(12)	Co(9)	C(10)	67.2(3)	C(13)	Co(9)	C(10)	67.0(4)
Co(9)	C(10)	C(14)	70.5(4)	C(14)	Co(9)	C(10)	40.2(4)
Co(9)	C(11)	C(10)	68.7(4)	Co(9)	C(11)	C(12)	70.3(4)
C(12)	Co(9)	C(11)	39.1(3)	C(13)	Co(9)	C(11)	66.6(3)
C(14)	Co(9)	C(11)	66.9(3)	Co(9)	C(12)	C(11)	70.5(4)
Co(9)	C(12)	C(13)	70.1(4)	C(13)	Co(9)	C(12)	39.9(3)
C(14)	Co(9)	C(12)	66.0(3)	Co(9)	C(13)	C(12)	70.0(4)
Co(9)	C(13)	C(14)	70.4(5)	C(14)	Co(9)	C(13)	38.6(4)
Co(9)	C(14)	C(10)	69.4(5)	Co(9)	C(14)	C(13)	70.9(5)
C(2)	Si(1)	Si(5)	142.1(1)	C(4)	Si(1)	Si(5)	136.7(2)
Si(1)	Si(5)	C(15)	111.0(3)	Si(1)	Si(5)	C(16)	112.8(3)
Si(1)	Si(5)	C(17)	109.1(2)	Si(1)	C(2)	C(3)	89.9(2)
C(4)	Si(1)	C(2)	80.3(2)	Si(1)	C(2)	Si(6)	133.4(2)
Si(1)	C(4)	C(3)	91.3(3)	Si(1)	C(4)	C(8)	133.4(4)
C(16)	Si(5)	C(15)	103.4(5)	C(17)	Si(5)	C(15)	111.9(4)
C(17)	Si(5)	C(16)	108.5(4)	Si(5)	C(17)	C(18)	109.5(5)
Si(5)	C(17)	C(19)	113.3(6)	Si(5)	C(17)	C(20)	109.2(6)
Si(6)	C(2)	C(3)	136.6(3)	C(21)	Si(6)	C(2)	120.3(3)
C(22)	Si(6)	C(2)	100.8(3)	C(23)	Si(6)	C(2)	112.0(2)
C(22)	Si(6)	C(21)	107.2(4)	C(23)	Si(6)	C(21)	108.1(4)
C(23)	Si(6)	C(22)	107.5(3)	Si(6)	C(23)	C(24)	113.7(5)
Si(6)	C(23)	C(25)	106.9(6)	Si(6)	C(23)	C(26)	110.3(5)
C(2)	C(3)	C(4)	98.3(3)	C(2)	C(3)	C(7)	126.4(4)
C(7)	C(3)	C(4)	133.7(4)	C(3)	C(4)	C(8)	133.8(5)
C(3)	C(7)	C(27)	111.9(5)	C(3)	C(7)	C(28)	115.4(6)
C(3)	C(7)	C(29)	107.0(5)	C(4)	C(8)	C(30)	104.9(5)
C(4)	C(8)	C(31)	109.5(6)	C(4)	C(8)	C(32)	116.4(6)
C(28)	C(7)	C(27)	107.1(5)	C(29)	C(7)	C(27)	105.9(6)
C(29)	C(7)	C(28)	109.1(6)	C(31)	C(8)	C(30)	112.1(8)
C(32)	C(8)	C(30)	106.2(6)	C(32)	C(8)	C(31)	107.8(6)
C(10)	C(11)	C(12)	107.5(7)	C(14)	C(10)	C(11)	106.1(8)
C(10)	C(14)	C(13)	109.6(8)	C(11)	C(12)	C(13)	108.7(7)
C(12)	C(13)	C(14)	108.0(7)	C(19)	C(17)	C(18)	104.9(8)
C(20)	C(17)	C(18)	106.8(7)	C(20)	C(17)	C(19)	112.9(8)
C(25)	C(23)	C(24)	109.2(7)	C(26)	C(23)	C(24)	110.2(7)
C(26)	C(23)	C(25)	106.3(6)				

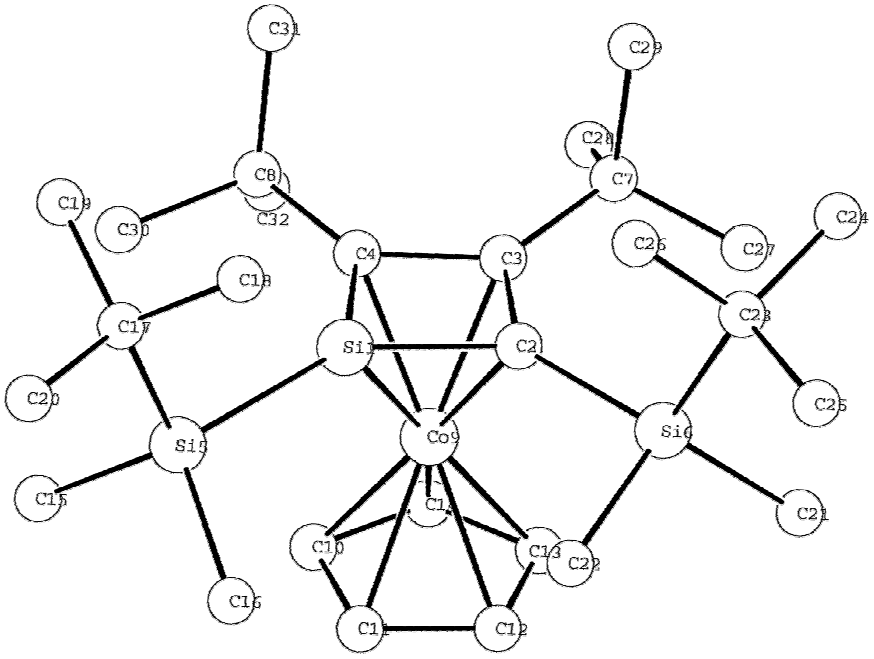


Figure S1. ORTEP drawings of silacyclobutadiene complex **1** with atom labeling scheme. Hydrogen atoms are omitted for clarity.

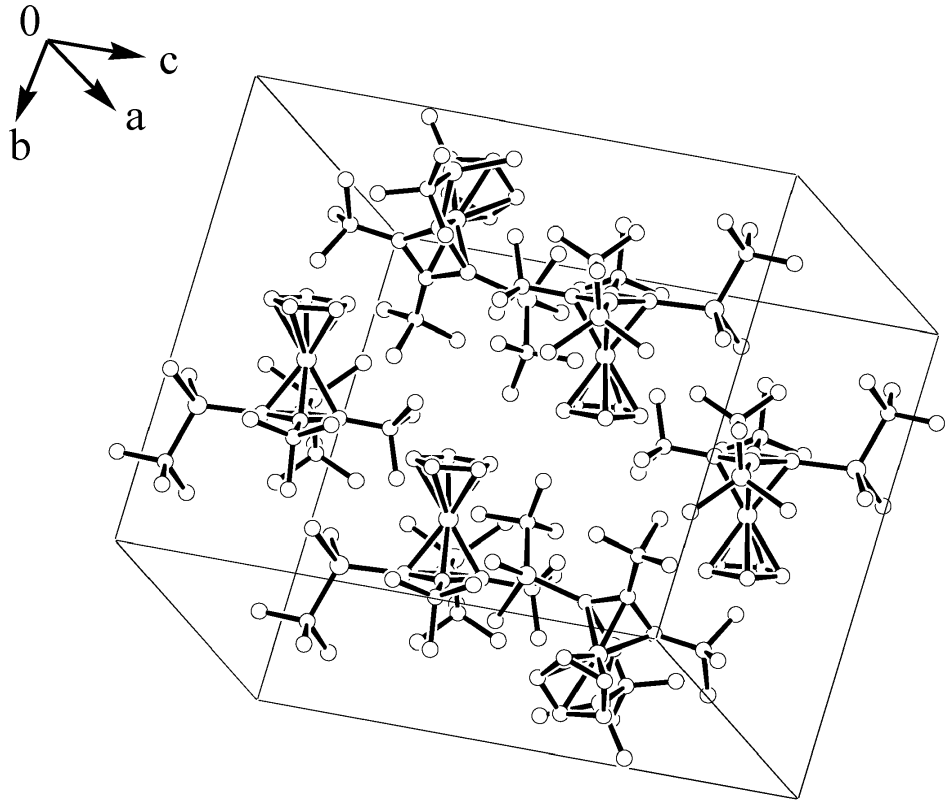
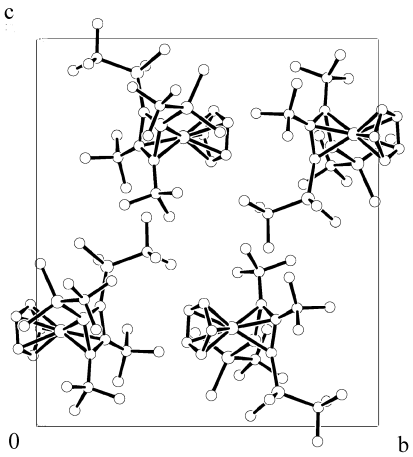
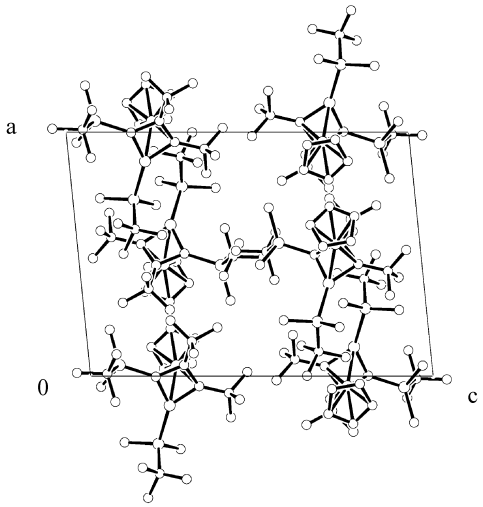


Figure S2. Views of crystal packing of silacyclobutadiene cobalt complex **1**.

(a)



(b)



(c)

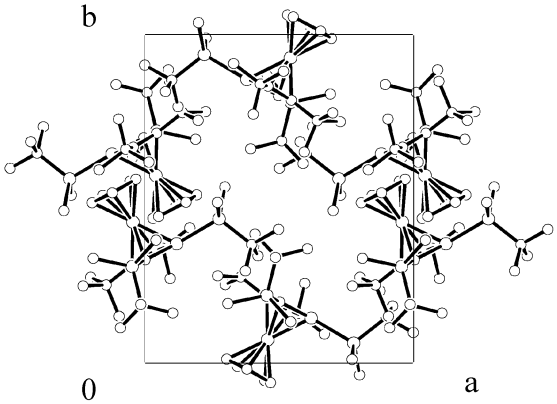
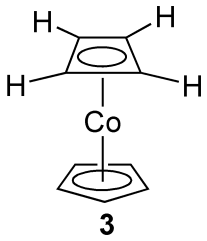


Figure S3. Views of crystal packing of silacyclobutadiene cobalt complex **1**. (a) along the a axis. (b) along the b axis. (c) along the c axis.

2. Optimized Structures at the B3PW91/ 6-311G(d) of Model Compounds 3 and 6

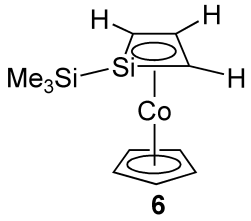
Table S5. Optimized positional parameter (xyz) of cyclobutadiene Complex **3**.



3

	X	Y	Z
C	-0.698562	0.671815	1.819693
C	0.750816	0.593682	1.824810
C	0.673011	-0.853666	1.749325
C	-0.776284	-0.775630	1.744203
H	-1.420208	1.470798	1.919271
H	1.553948	1.309960	1.929306
H	1.394004	-1.659033	1.772682
H	-1.579161	-1.499505	1.763857
Co	-0.000959	-0.005867	0.118137
C	-0.809000	0.968094	-1.505302
C	0.604013	1.132420	-1.474663
C	1.199343	-0.161156	-1.519147
C	0.150931	-1.125320	-1.576749
C	-1.089840	-0.425399	-1.567684
H	-1.541660	1.761990	-1.461987
H	1.132085	2.073335	-1.405459
H	2.258926	-0.374501	-1.492034
H	0.274623	-2.199139	-1.600735
H	-2.073246	-0.874536	-1.581520

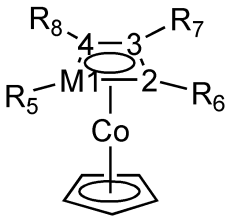
Table S6. Optimized positional parameter (xyz) of silacyclobutadiene complex **6**.



6

	X	Y	Z
Si	-0.747403	0.929209	-0.000006
C	0.524811	1.629638	-1.132881
C	1.246701	2.152459	0.000002
C	0.524805	1.629633	1.132880
Si	-2.773467	-0.257563	0.000000
H	0.756678	1.775963	-2.179892
H	2.124618	2.793981	0.000006
H	0.756667	1.775953	2.179892
C	-4.211424	0.963618	-0.000062
C	-2.845697	-1.322876	-1.554533
C	-2.845731	-1.322765	1.554607
H	-4.190556	1.610280	0.881795
H	-4.190528	1.610225	-0.881958
H	-5.170430	0.433471	-0.000061
Co	1.394027	0.206438	-0.000002
C	1.465459	-1.847555	0.000046
C	2.116597	-1.318046	-1.150876
C	3.183307	-0.481218	-0.711653
C	3.183350	-0.481187	0.711581
C	2.116665	-1.317994	1.150905
H	0.626494	-2.528817	0.000086
H	1.840707	-1.507304	-2.178940
H	3.856635	0.075001	-1.349286
H	3.856716	0.075060	1.349150
H	1.840832	-1.507203	2.178993
H	-2.774615	-0.716764	-2.462292
H	-2.035363	-2.055915	-1.582006
H	-3.793679	-1.870390	-1.599385
H	-2.035387	-2.055789	1.582158
H	-2.774688	-0.716586	2.462324
H	-3.793707	-1.870290	1.599468

3. Comparison of the Geometrical Parameters of 1 with Those of Model Compounds, 3 and 6

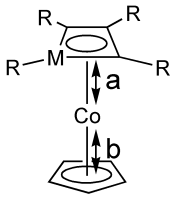


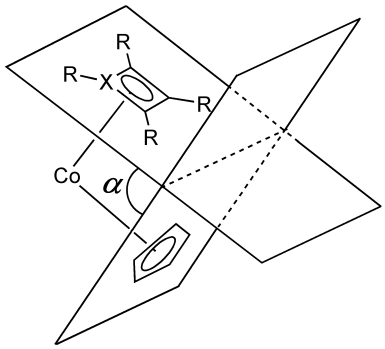
3 (calc.): M1 = C, R5 = H, R6 = H, R7 = H, R8 = H

6 (calc.): M1 = Si, R5 = $SiMe_3$, R6 = H, R7 = H, R8 = H

1(exp.): M1 = Si, R5 = Sit-$BuMe_2$, R6 = Sit-$BuMe_2$, R7 = t-Bu, R8 = t-Bu

Table S7. Distances between Cb and Co (a, Å), and Co and Cp (b, Å) and angles between the average planes of Cp and Cb (α, deg) of cyclobutadiene complexes **3**, **6**, and **1**.





Entry	a (Å)	b (Å)	α (deg)
3(Exp.)[4d]	**1.681(1)**	**1.660(1)**	**0.9**
3(Calc.)	**1.669**	**1.649**	**0.8**
6(Calc.)	**1.701**	**1.649**	**5.2**
1(Exp.)	**1.730(3)**	**1.681(4)**	**2.9**

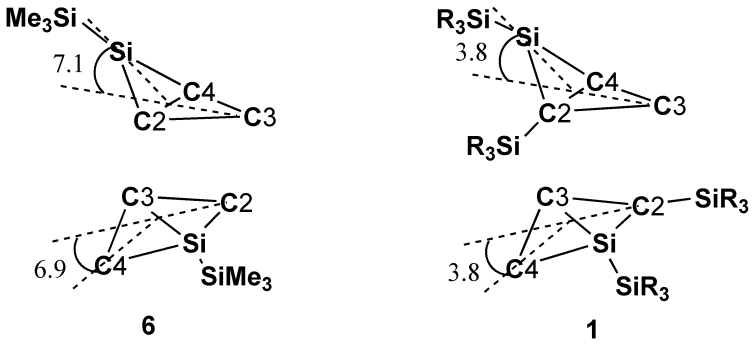


Figure S4. The angles (deg) between Si-C2-C4 and C2-C3-C4 planes, and Si1-C2-C3 and Si1-C3-C4 planes.

4. Theoretical ^{13}C NMR Resonances of 3 and 6 with Their Free Cyclobutadienes at the GIAO/B3PW91/6-311+G(d,p)//B3PW91/6-311G(d) Level.