Supporting Information for

Multinuclear rhodium complexes supported by tetra-*tert*-butoxy disiloxide ligand: Synthesis, structure, and reactivity

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General information

Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere using either Schlenk techniques or a glove box. All organic solvents were dried using a solvent purification system (MBraun SPS-5 or a Glass Contour Ultimate Solvent System). C_6D_6 and $(Me_3Si)_2O$ was dried using molecular sieves. All other reagents were purchased from commercial suppliers and were used without further purification. Solution-state ^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{29}Si, 119 MHz; ^{31}P, 243 MHz) were recorded using a Bruker AVANCE III HD 600 spectrometer. Chemical shifts are reported in δ (ppm) and referenced to the residual solvent signals for ^{1}H (7.16 ppm for C_6D_6) and ^{13}C (128.06 ppm for C_6D_6), 1,4-bis(trimethylsilyl)benzene for ^{29}Si, and H_3PO_4 for ^{31}P as external standard. Elemental analyses were performed using a PerkinElmer 2400II elemental analyzer. ATR/FT-IR spectroscopy was measured using a JASCO VIR-100 attached ATRS-100-VIR unit.

The single-crystal X-ray diffraction measurement was performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirror monochromated Mo Kα radiation (λ = 0.71075 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption (multiscan)[S1] using CrysAlis PRO.[S2] The structures were solved by direct methods (SHELXT)[S3] and refined by least-squares calculations on F^2 for all reflections (SHELXL-2014/7)[S4] by using Olex-2.[S5] Molecular graphics were generated in the program Mercury.[S6,S7] Further information has been deposited with the Cambridge Crystallographic Data Centre (CCDC reference numbers 2174530 for **4**, 2174531 for **7**, and 2174532 for **6**).

DFT calculations were performed with the Gaussian 09 program.[S8] The structures of intermediate **A**, **4**, **II**, and **III** were optimized using the M06 functional[S9] and the LANL2DZ (Rh)[S10,S11] and 6-31G* (other atoms) basis sets.[S12,S13] The Cartesian coordinates of the optimized structures of intermediate **A**, **4**, **II**, and **III** are listed in Tables S1–4, respectively.

Synthesis of {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (3)

To a THF suspension (30 mL) of KH (160 mg, 3.99 mmol), [(^{t}BuO)$_2$Si(OH)]$_2$O (**2**) (796 mg, 2.00 mmol) in THF (20 mL) was added at 0 °C. The solution was stirred for 2 h at 0 °C and further for 30 min at room temperature. Then, the solution was added to a THF suspension (20 mL) of [Rh(COD)Cl]$_2$ (986 mg, 2.00 mmol) at –80 °C. The reaction temperature was gradually increased to room temperature, and the volatiles were removed by evacuation. The residue was extracted with Et$_2$O and passed through a celite pad to remove inorganic salts. Following the removal of the solvent, recrystallization from *n*-hexane at –40 °C yielded {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) as yellow crystals (858 mg, 1.05 mmol, y. 52%).

^{1}H NMR (C$_6$D$_6$, 25 °C): δ 4.50–4.38 (m, 4H, C*H* (COD)), 4.38–4.26 (m, 4H, C*H* (COD)), 2.71–2.56 (m, 4H, CH_2 (COD)), 2.56–2.38 (m, 4H, CH_2 (COD)), 1.76–1.68 (m, 4H, CH_2 (COD)), 1.68–1.62 (m, 4H, CH_2 (COD)), 1.61 (s, 36H, CH_3 (^{t}Bu)).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 77.6 (d, $^1J_{C–Rh}$ = 14.6 Hz, *C*H (COD)), 75.3 (d, $^1J_{C–Rh}$ = 14.3 Hz, *C*H (COD)), 72.7 (*C*(CH$_3$)$_3$ (^{t}Bu)), 32.1 (C(*C*H$_3$)$_3$ (^{t}Bu)), 31.5 (*C*H$_2$ (COD)), 31.0 (*C*H$_2$ (COD)).

^{29}Si{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ –92.7.

Anal. calcd C$_{32}$H$_{60}$O$_7$Rh$_2$Si$_2$: C 46.94, H 7.39; found: C 47.09, H 7.46.

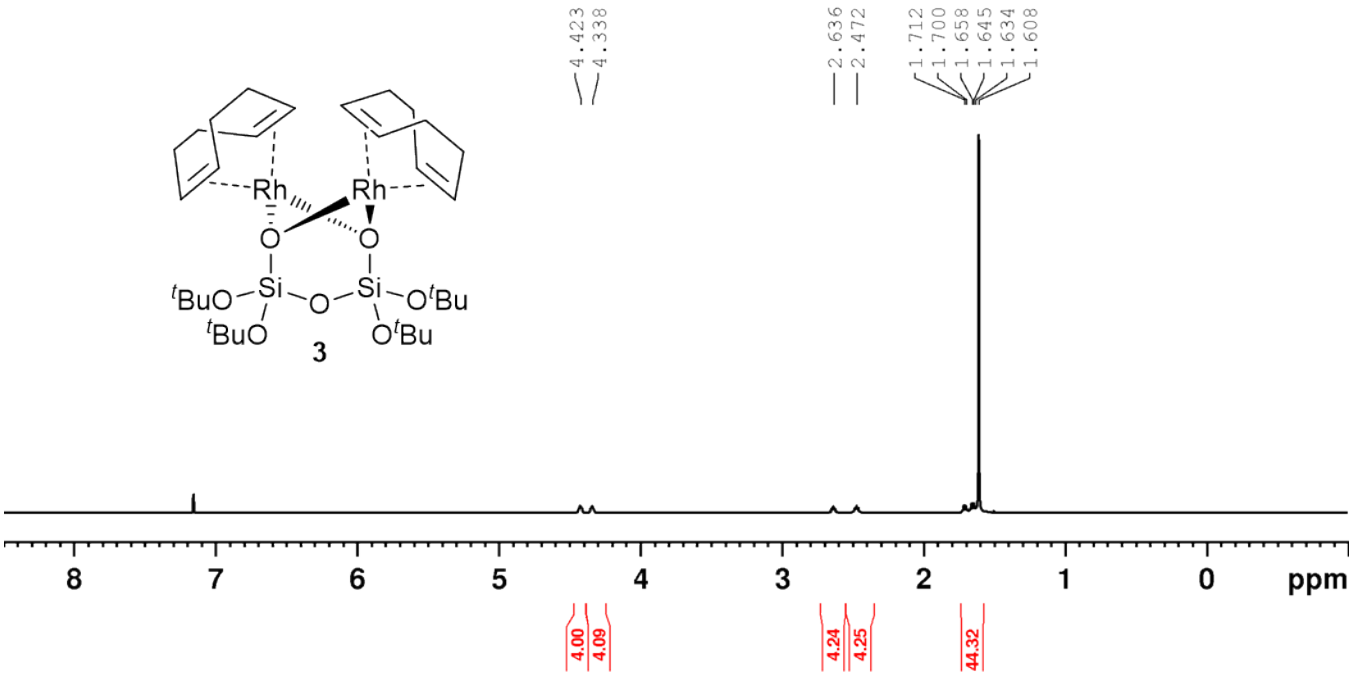


Fig. S1. ^{1}H NMR spectrum of **3**.

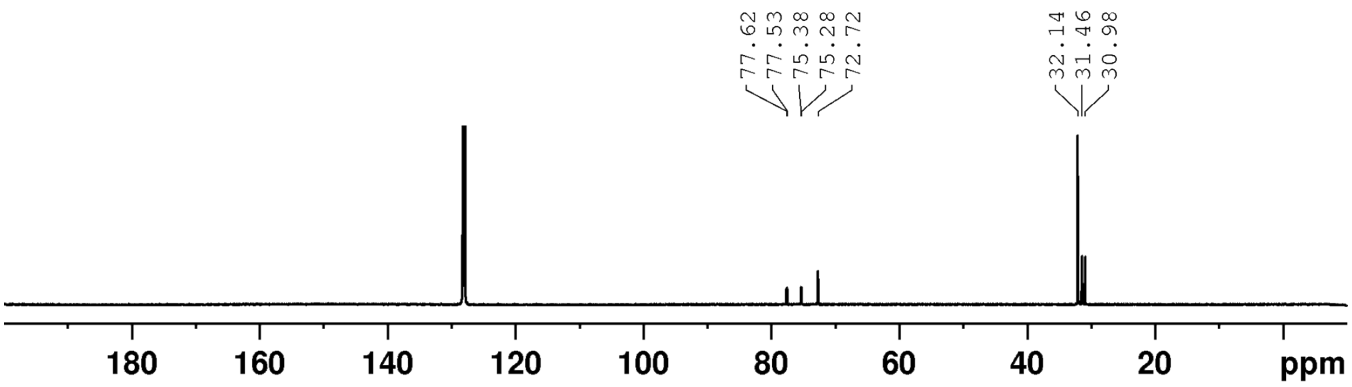


Fig. S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

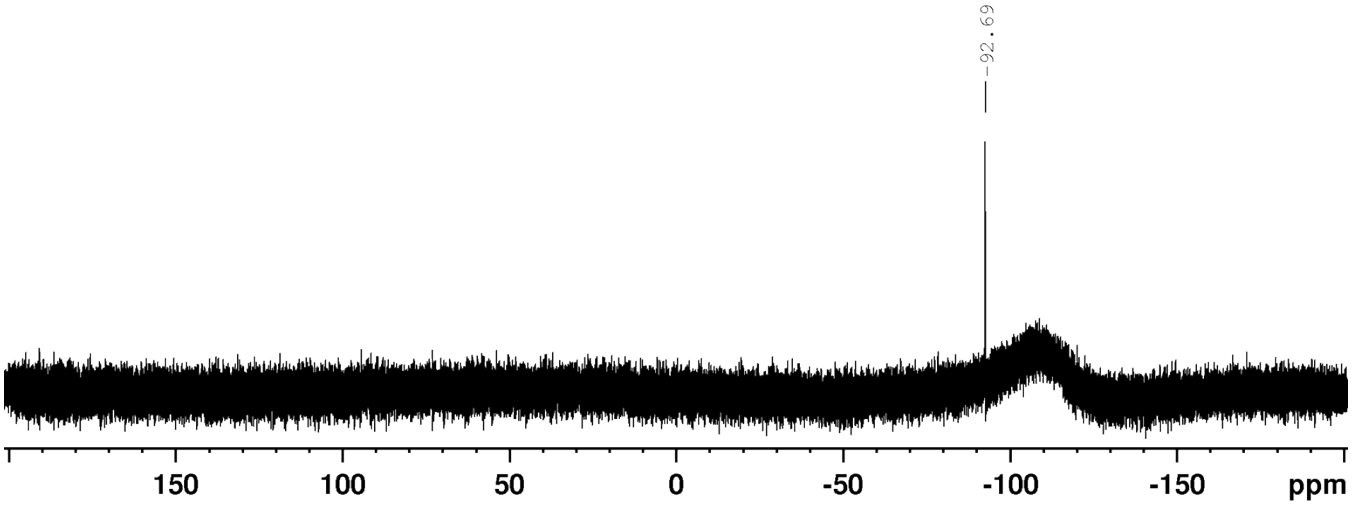


Fig. S3. $^{29}Si\{^{1}H\}$ NMR spectrum of **3**.

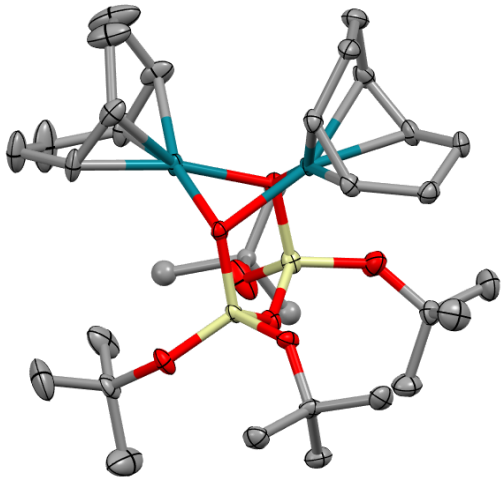


Fig. S4. Structure plot of {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**). Some different crystals were measured but only data of relatively low quality could be acquired. However, the data are sufficient to confirm the structure of the **3**.

NMR experiment for formation of A

To a J-Young NMR tube, {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) (18.2 mg, 22 μmol), C_6D_6 (400 μL), and $(Me_3Si)_2O$ (3 μL, 14 μmol) as internal standard were charged. After the solution was degassed by several freeze pump thaw cycles, carbon monoxide was introduced using rubber balloon. And then, the NMR spectra of this reaction mixture was measured immediately.

^{1}H NMR (C_6D_6, 25 °C): δ 1.48 (s, 36H, CH_3 (^{t}Bu)).

^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 182.7 (d, $^1J_{C–Rh}$ = 75.6 Hz, *C*O), 74.1 (*C*(CH$_3$)$_3$ (^{t}Bu)), 32.0 (C(*C*H$_3$)$_3$ (^{t}Bu)).

^{29}Si{^{1}H} NMR (C_6D_6, 25 °C): δ –92.7.

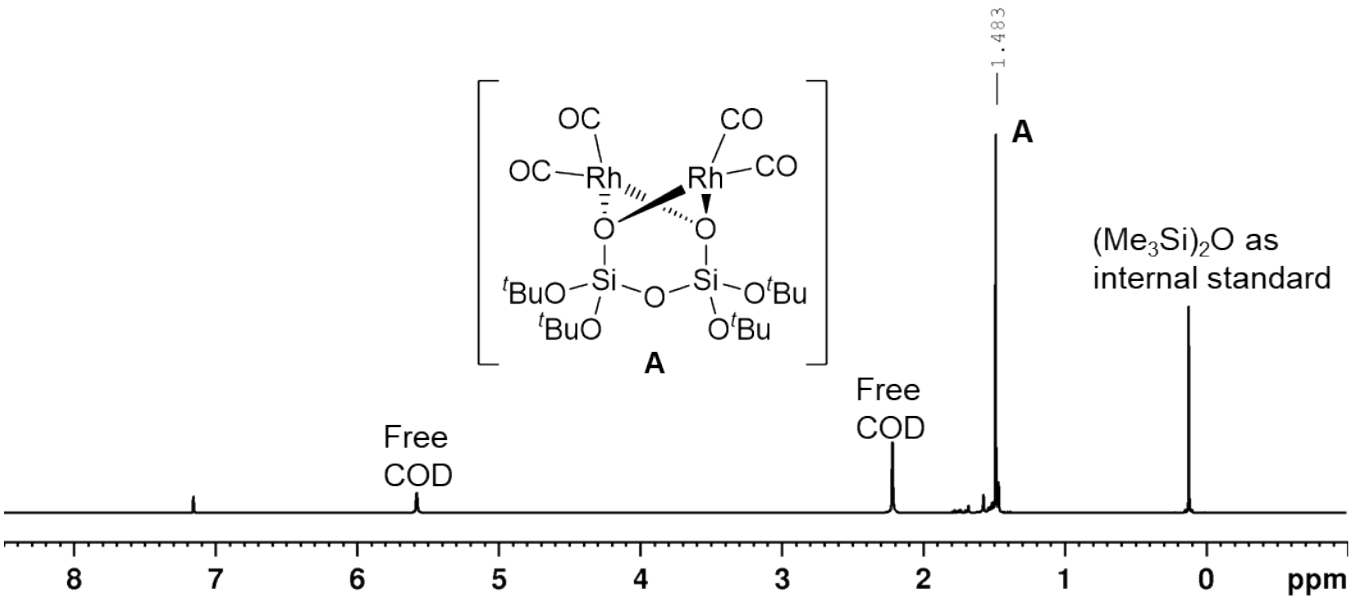


Fig. S5. ^{1}H NMR spectrum of reaction mixture after introducing carbon monoxide to solution of **3**.

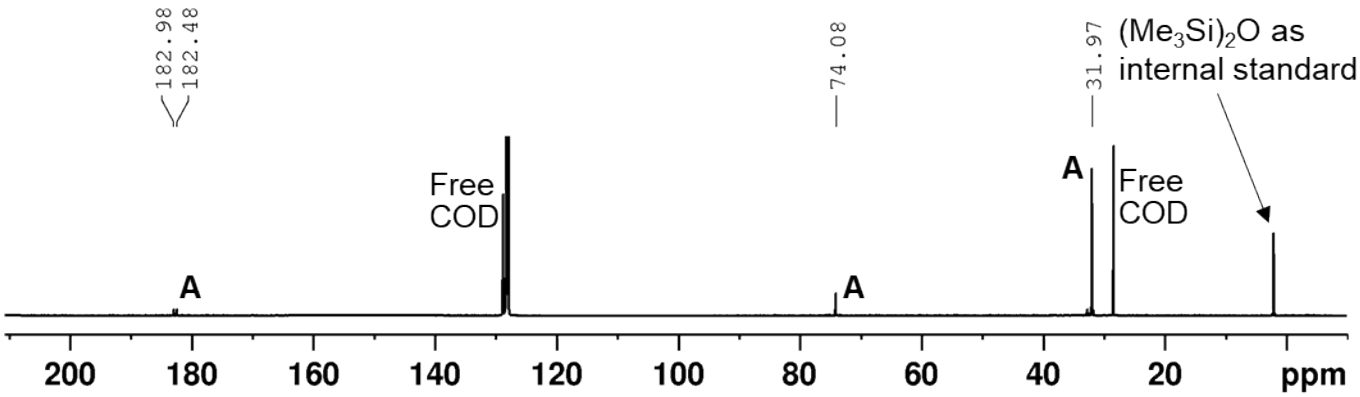


Fig. S6. ^{13}C{^{1}H} NMR spectrum of reaction mixture after introducing carbon monoxide to solution of **3**.

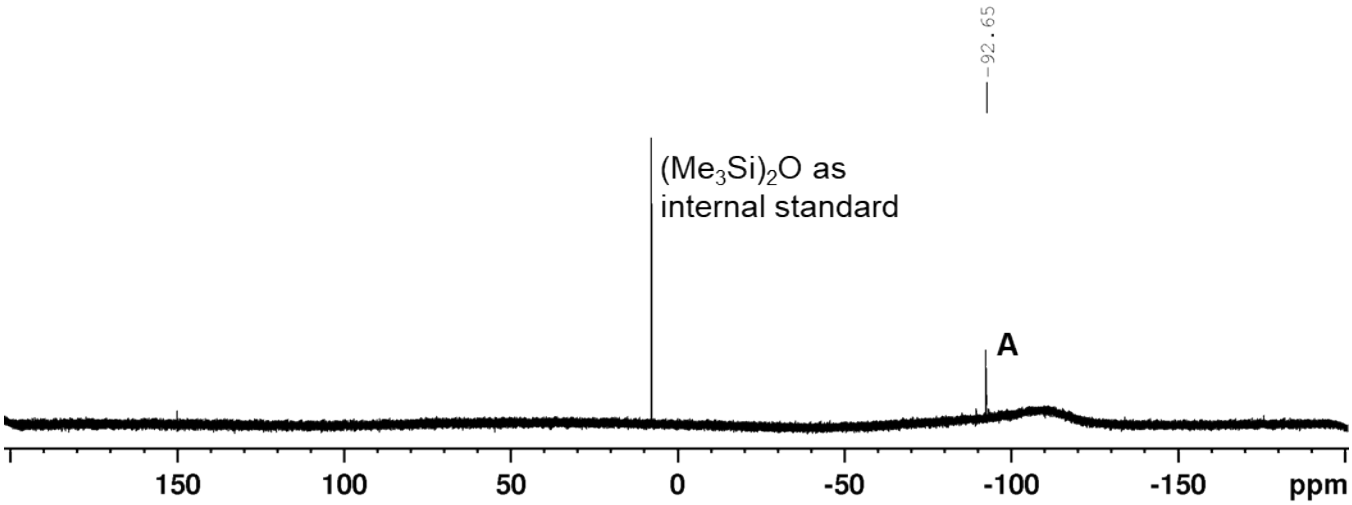


Fig. S7. $^{29}Si\{^{1}H\}$ NMR spectrum of reaction mixture after introducing carbon monoxide to solution of **3.**

Synthesis of [{Rh(CO)$_2$}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O}]$_2$ (4)

To a 10 mL reaction tube with PTFE cap, {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) (121 mg, 148 μmol) and toluene (7 mL), were charged. After the solution was degassed by several freeze pump thaw cycles, carbon monoxide was introduced using rubber balloon. After the reaction mixture was stand in static condition for 5 min, carbon monoxide was removed by several freeze pump thaw cycles. After the reaction mixture was stand in static condition at room temperature for 2 h, the precipitated light-yellow powder was collected as **4** by filtration and washing with pentane. After the solvent of filtrate was removed in vacuo, the residue was recrystallized from *n*-hexane at –40 ºC. Combined with thus-obtained crystals and the precipitate, complex **4** was obtained as light-yellow powder (41 mg, 29 μmol, y. 39%).

^{1}H NMR (C_6D_6, 25 °C): δ 1.68 (s, 36H, C*H*$_3$ (^{t}Bu)), 1.51 (s, 36H, C*H*$_3$ (^{t}Bu)).

^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 181.7 (d, $^1J_{C–Rh}$ = 74.7 Hz, *C*O), 181.3 (d, $^1J_{C–Rh}$ = 74.4 Hz, *C*O), 75.0 (*C*(CH$_3$)$_3$ (^{t}Bu)), 73.4 (*C*(CH$_3$)$_3$ (^{t}Bu)), 32.8 (C(*C*H$_3$)$_3$ (^{t}Bu)), 31.7 (C(*C*H$_3$)$_3$ (^{t}Bu)).

^{29}Si{^{1}H} NMR (C_6D_6, 25 °C): δ –93.5.

Anal. calcd $C_{40}H_{72}O_{22}Rh_4Si_4$: C 33.62, H 5.08; found: C 34.21, H 4.79

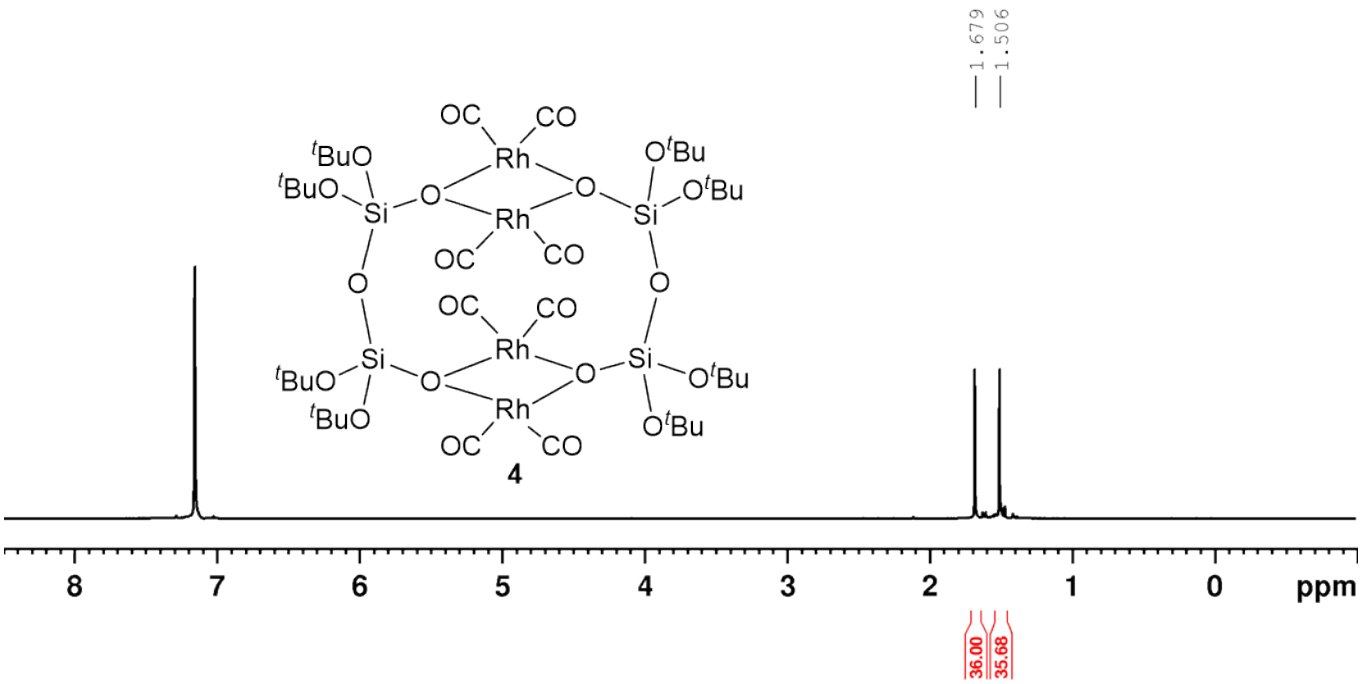


Fig. S8. ^{1}H NMR spectrum of **4**.

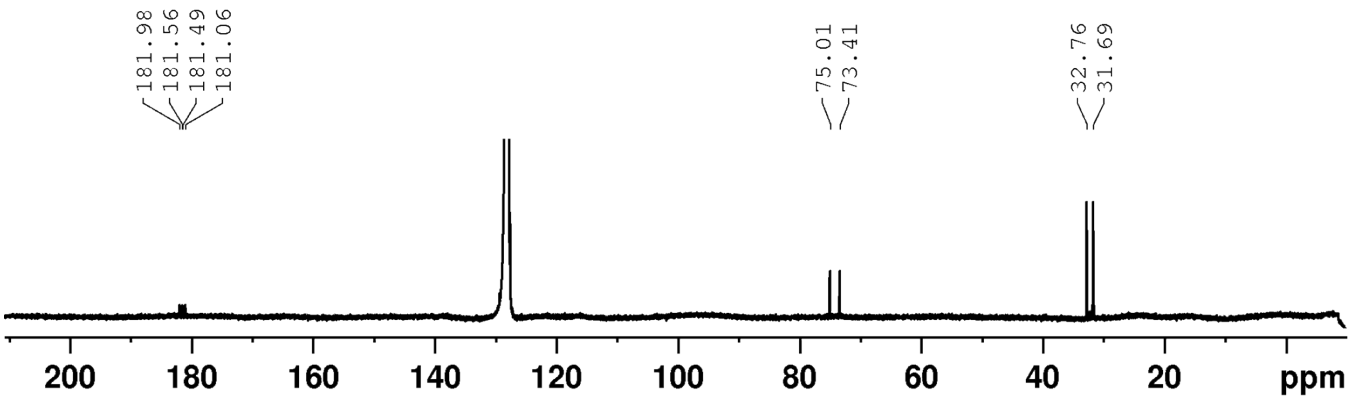


Fig. S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

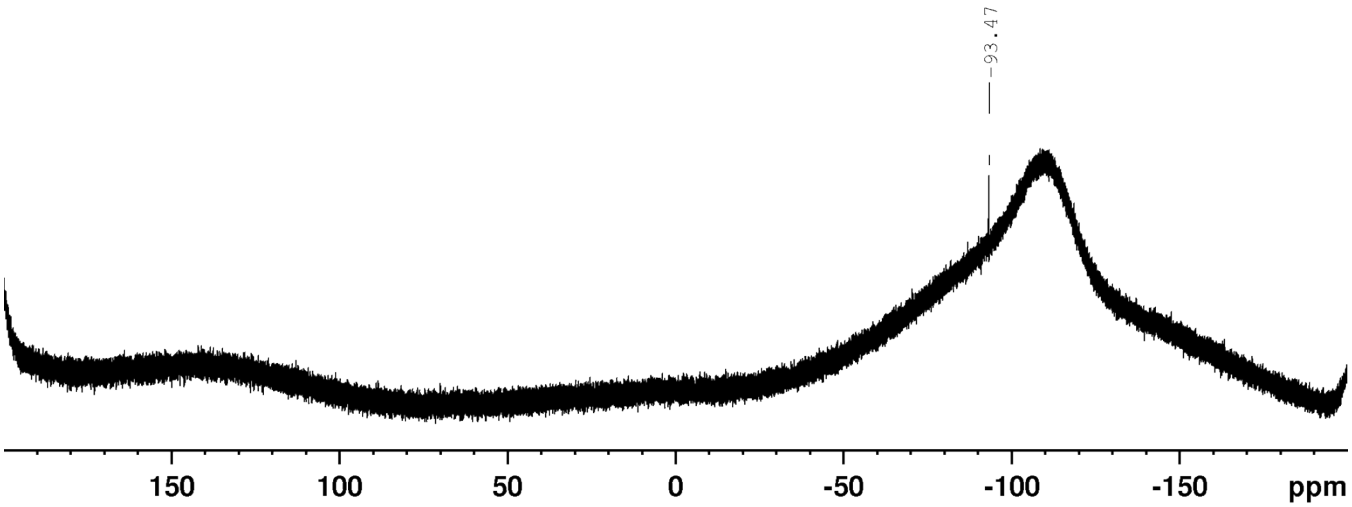


Fig. S10. $^{29}Si\{^{1}H\}$ NMR spectrum of **4**.

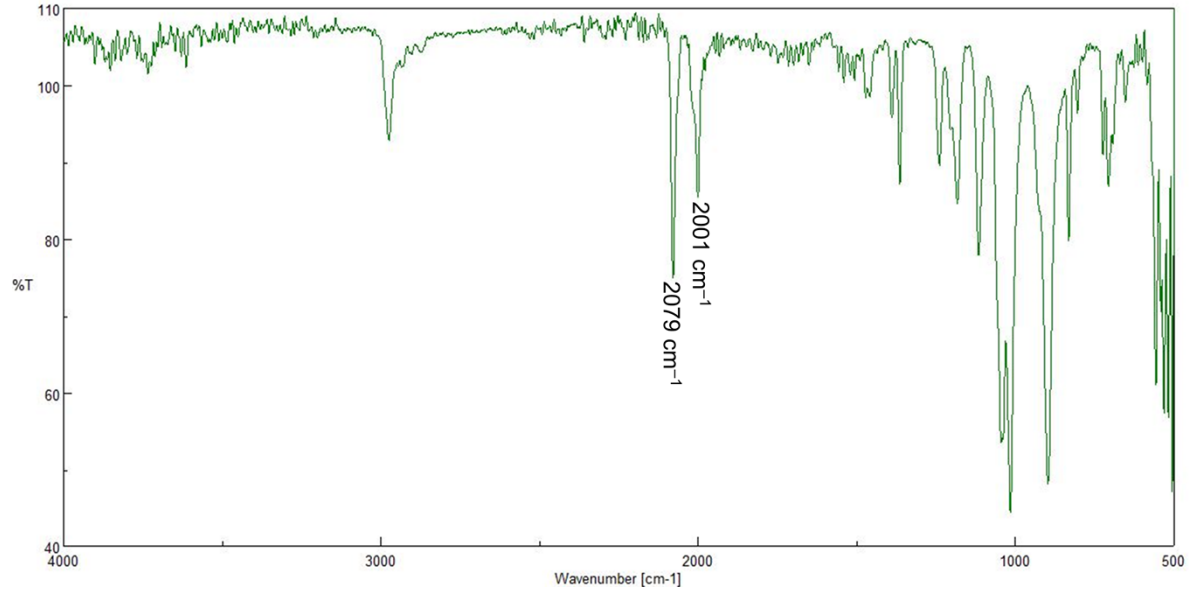
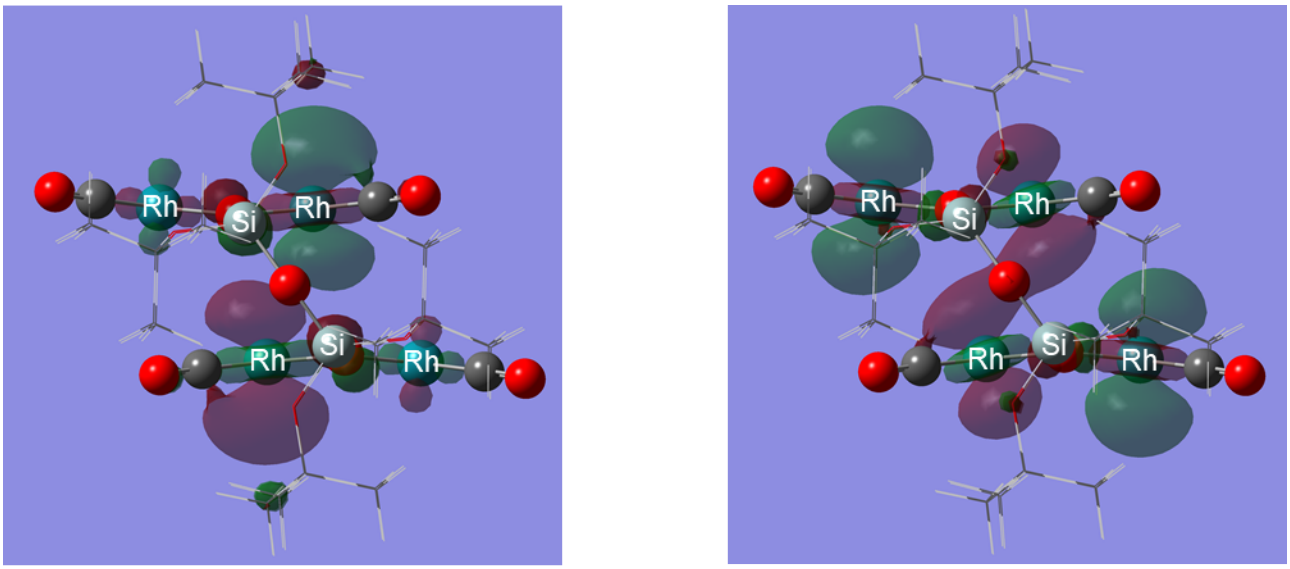
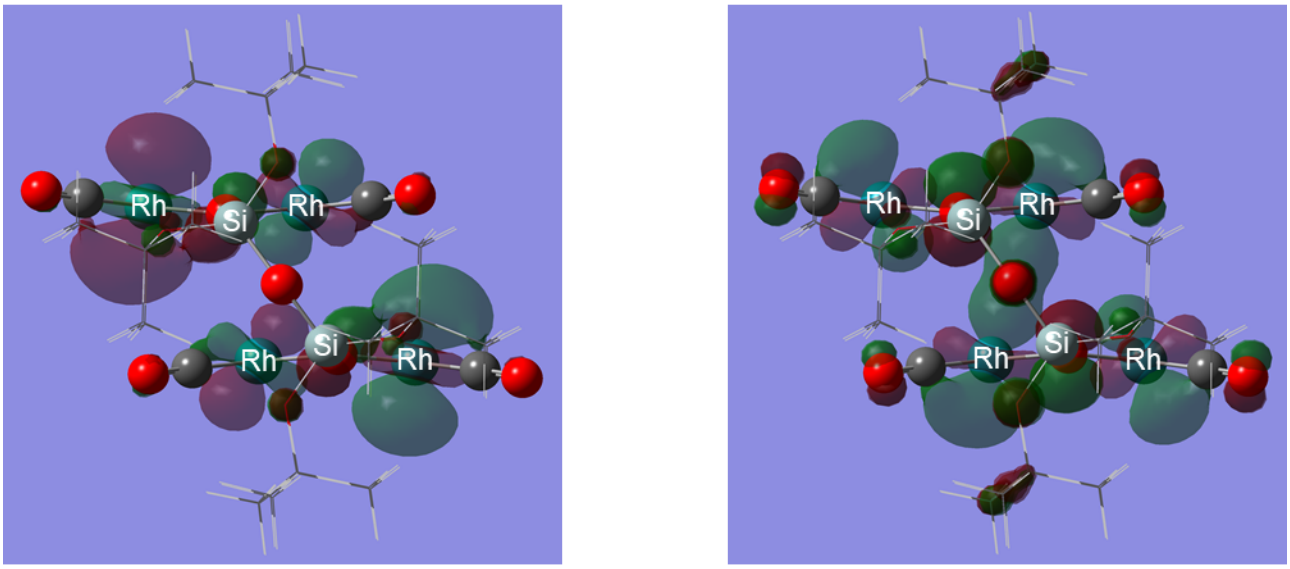


Fig. S11. ATR/FT-IR spectrum of **4**.



HOMO HOMO–1



HOMO–2 HOMO–4

Fig. S12. Molecular orbitals of optimized structure **4** involving d_{z2} orbitals of Rh center, where the isovalue is 0.02 a.u. Eight ^{t}BuO groups were represented as wireframe to clarity.

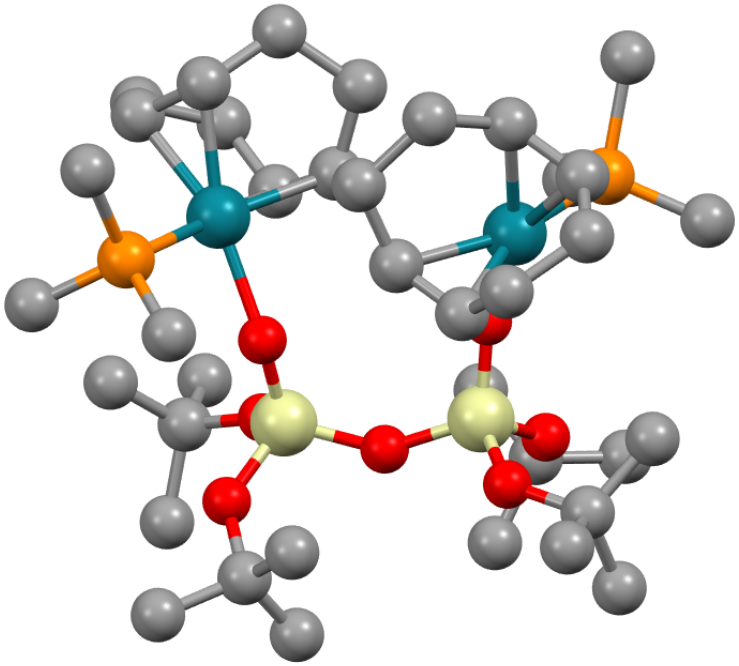


Fig. S13. Structure plot of **5**. Hydrogen atoms are omitted for clarity. Some different crystals were measured but only data of relatively low quality could be acquired due to disorder derived from rotation of O–Rh bond. However, molecular structure of **5** was barely confirmed.

Synthesis of {(COD)Rh(PMe$_3$)}$_2${(OSi(O^{t}Bu)$_2$}$_2$O} (5)

To a 13.5 mL vial, {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) (89 mg, 109 μmol) and toluene (2 mL), were charged. After the solution was cooled at –80 °C, stock toluene solution (220 μL) of PMe$_3$ (22 μL, 216 μmol) was added. After the reaction mixture was stirred at –80 °C for 30 min, reaction temperature was gradually warmed up to RT for 3 h. Following the volatiles were removed by evacuation, crystallization of the residue from *n*-hexane at –40 °C yielded {(COD)Rh(PMe$_3$)}$_2${(OSi(O^{t}Bu)$_2$}$_2$O} (**5**) as yellow crystals (13 mg, 13 μmol, y. 12%). In addition, since **5** was converted to {(PMe$_3$)$_2$Rh}{Rh(COD)}{μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**6**) at room temperature in the solution state, minor signals derived from **6** were observed in NMR spectra of **5**.

^{1}H NMR (C$_6$D$_6$, 25 °C): δ 6.09–5.97 (m, 4H, C*H* (COD)), 2.94–2.84 (m, 4H, C*H* (COD)), 2.53–2.32 (m, 8H, C*H*$_2$ (COD)), 2.01–1.88 (m, 8H, C*H*$_2$ (COD)), 1.71 (s, 36H, C*H*$_3$ (^{t}Bu)), 1.05 (d, $^2J_{H–P}$ = 9.3 Hz, 18H, C*H*$_3$ (PMe$_3$)).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 105.5 (dd, $^1J_{C–Rh}$ = 13.3 Hz, $^2J_{C–P}$ = 6.7 Hz, *C*H (COD)), 70.7 (*C*(CH$_3$)$_3$ (^{t}Bu)), 60.8 (d, $^1J_{C–Rh}$ = 14.0 Hz, *C*H (COD)), 34.1 (*C*H$_2$ (COD)), 32.7 (C(*C*H$_3$)$_3$ (^{t}Bu)), 28.8 (*C*H$_2$ (COD)), 13.2 (d, $^1J_{C–P}$ = 24.9 Hz, *C*H$_3$ (PMe$_3$)).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ –8.9 (d, $^1J_{P–Rh}$ =159.1 Hz).

^{29}Si{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ –95.3 (d, $^2J_{Si–Rh}$ = 5.2 Hz).

Anal. calcd C$_{38}$H$_{78}$O$_7$P$_2$Rh$_2$Si$_2$: C 47.01, H 8.10; found: C 47.33, H 7.91.

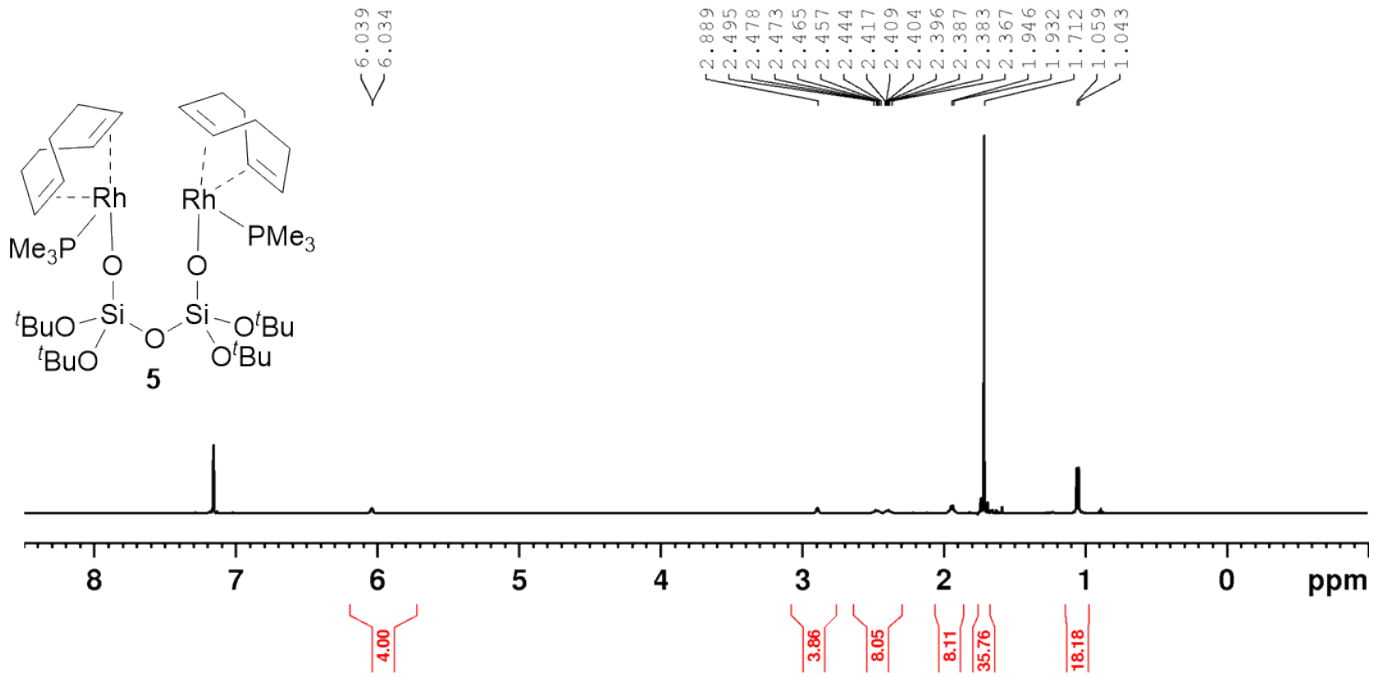


Fig. S14. ^{1}H NMR spectrum of **5**.

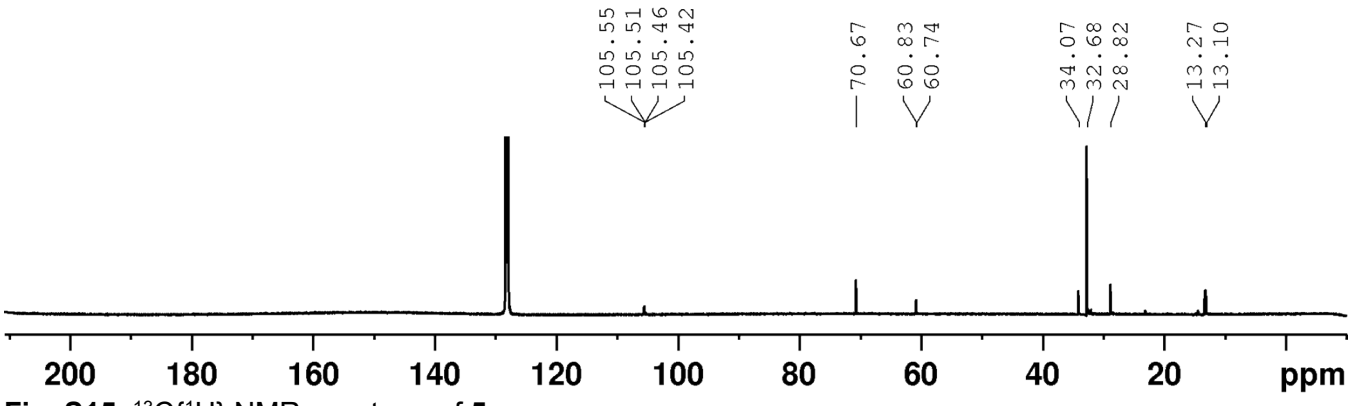


Fig. S15. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

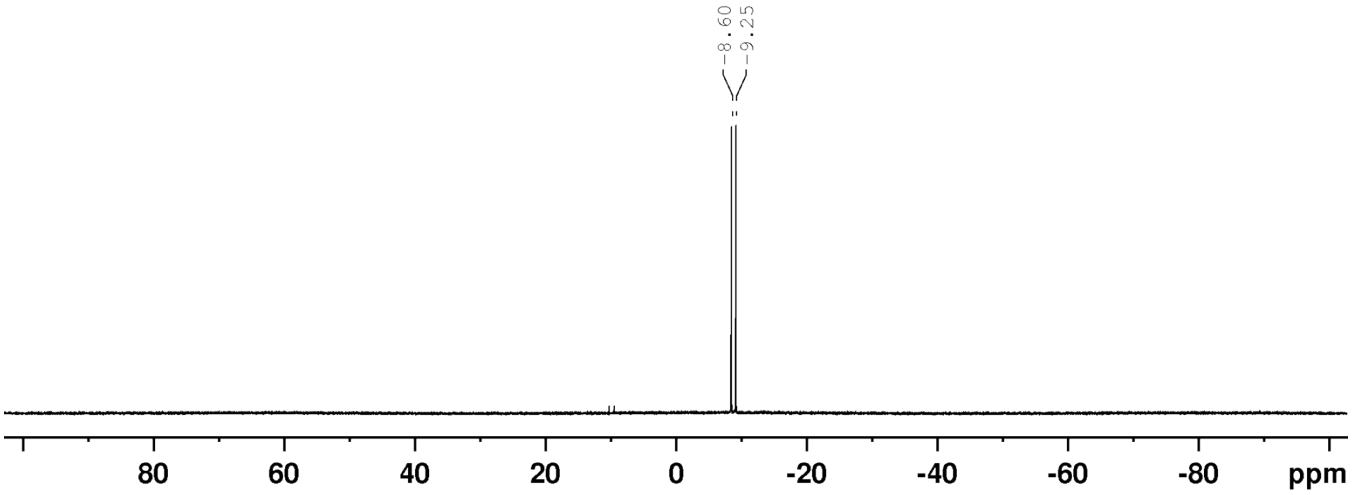


Fig. S16. $^{31}P\{^{1}H\}$ NMR spectrum of **5**.

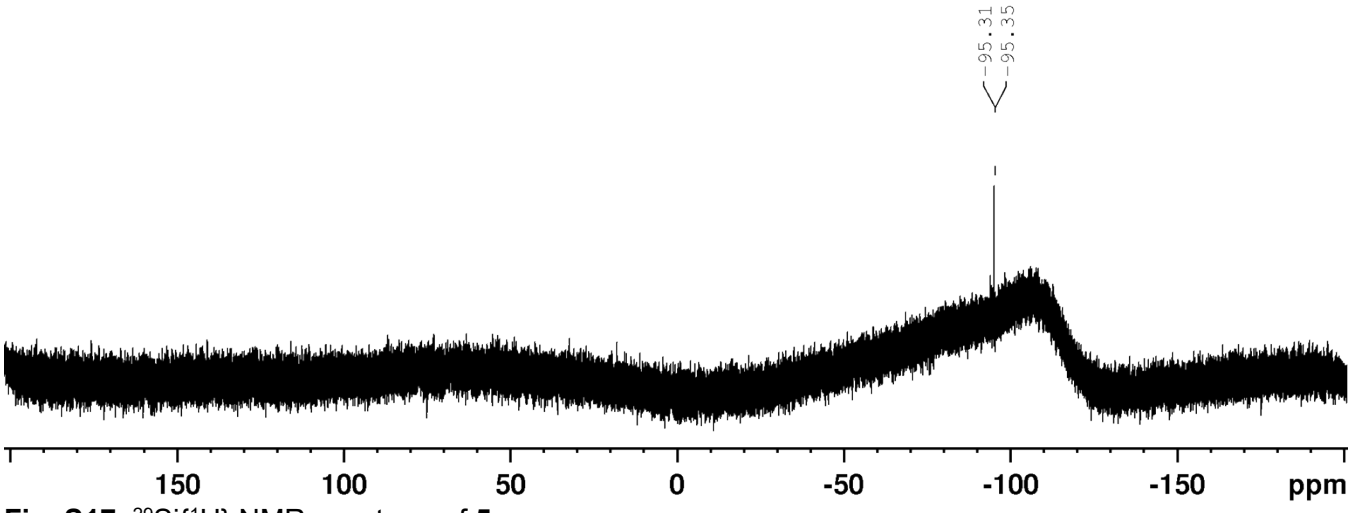


Fig. S17. $^{29}Si\{^{1}H\}$ NMR spectrum of **5**.

Synthesis of {(PMe$_3$)$_2$Rh}{Rh(COD)}{μ-(OSi(O^{t}Bu)$_2$)$_2$O} (6)

To a 10 mL reaction tube with PTFE cap, {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) (102 mg, 125 μmol) and toluene (4 mL), were charged. And then, stock toluene solution (250 μL) of PMe$_3$ (25 μL, 246 μmol) was added. The reaction mixture was stirred at 80 °C for 16 h, and the volatiles were removed in vacuo. Recrystallization of the residue from *n*-hexane at –40 °C yielded {(PMe$_3$)$_2$Rh}{Rh(COD)}{μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**6**) as yellow crystals (63 mg, 73 μmol, y. 59%).

^{1}H NMR (C$_6$D$_6$, 25 °C): δ 4.39–4.24 (m, 2H, C*H* (COD)), 4.02–3.80 (m, 2H, C*H* (COD)), 2.68–2.40 (m, 4H, C*H*$_2$ (COD)), 1.80–1.56 (m, 40H, C*H*$_2$ (COD) and C*H*$_3$ (^{t}Bu)), 1.25–1.19 (m, 18H, C*H*$_3$ (PMe$_3$)).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 74.9 (d, $^1J_{C–Rh}$ = 14.0 Hz, *C*H (COD)), 72.6 (*C*(CH$_3$)$_3$ (^{t}Bu)), 72.3 (*C*(CH$_3$)$_3$ (^{t}Bu)), 72.2 (d, $^1J_{C–Rh}$ = 14.7 Hz, *C*H (COD)), 32.5 (C(*C*H$_3$)$_3$ (^{t}Bu)), 32.3 (C(*C*H$_3$)$_3$ (^{t}Bu)), 31.5 (*C*H$_2$ (COD)), 31.4 (*C*H$_2$ (COD)), 19.4 (dvt, $^2J_{C–Rh}$ = 1.8 Hz, $^1J_{C–P}$ = 14.6 Hz,*C*H$_3$ (PMe$_3$)).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 9.8 (d, $^1J_{P–Rh}$ =194.1 Hz).

^{29}Si{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ –91.3.

Anal. calcd C$_{30}$H$_{66}$O$_7$P$_2$Rh$_2$Si$_2$: C 41.76, H 7.71; found: C 41.31, H 7.50.

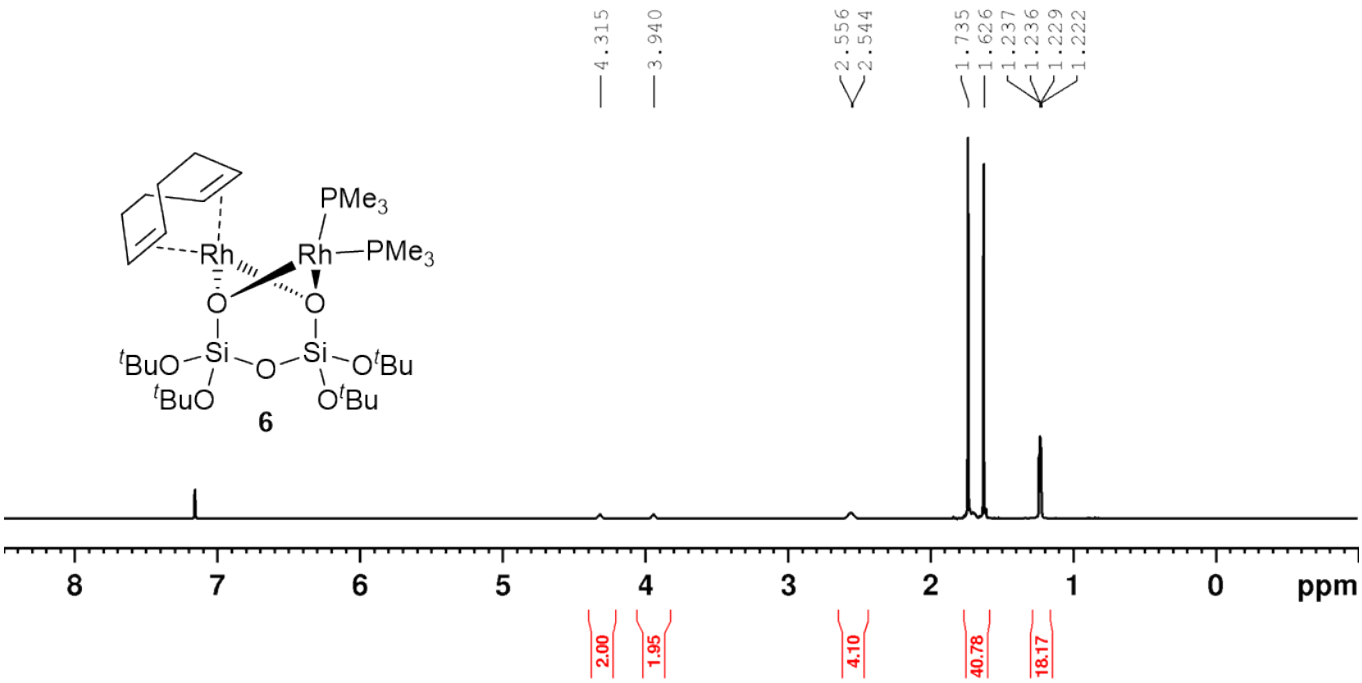


Fig. S18. ^{1}H NMR spectrum of **6**.

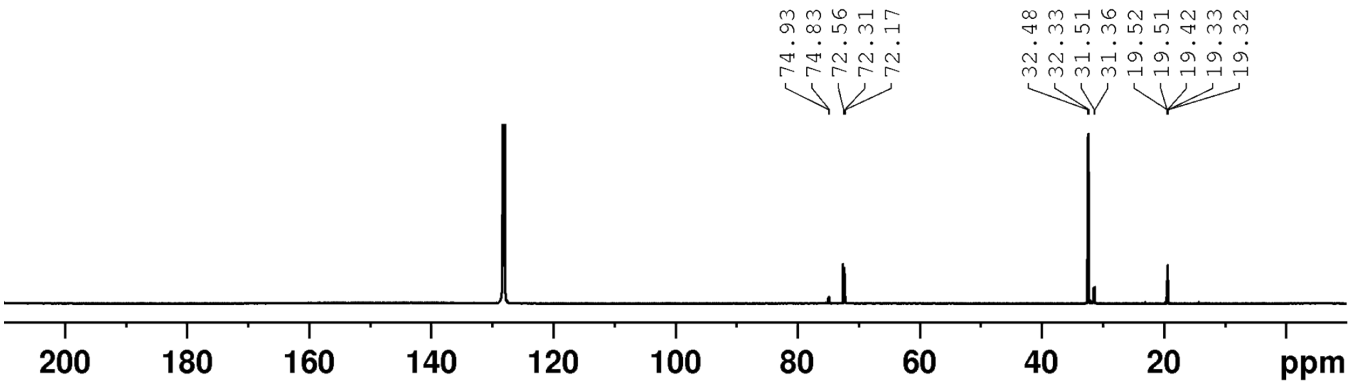


Fig. S19. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

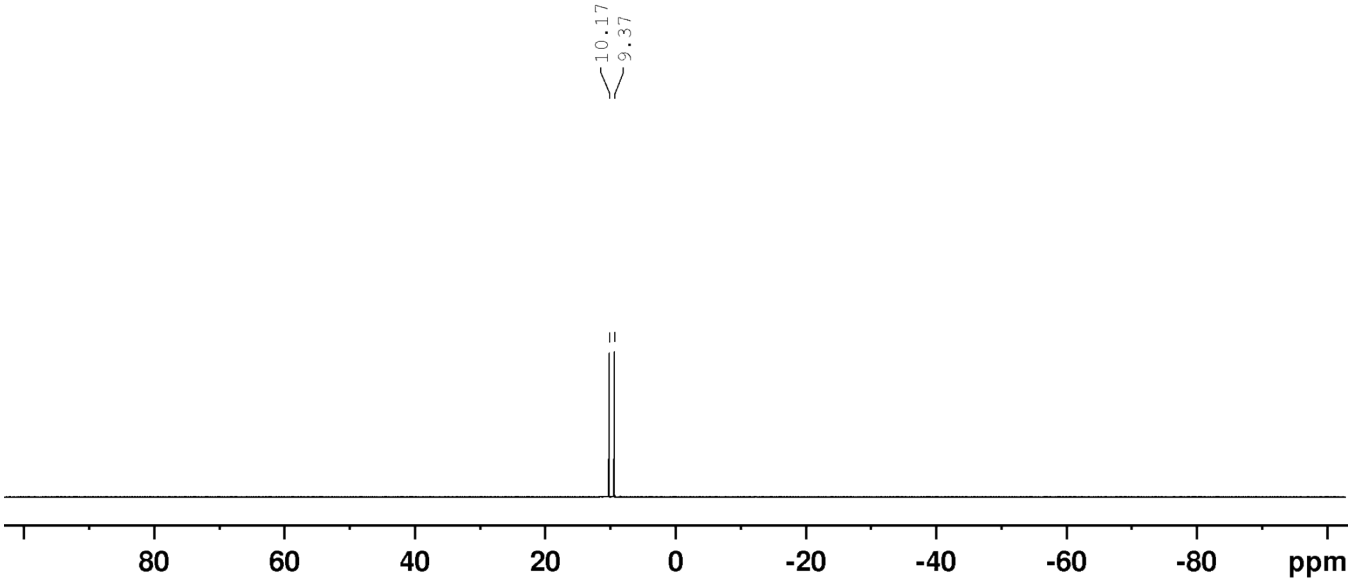


Fig. S20. $^{31}P\{^{1}H\}$ NMR spectrum of **6**.

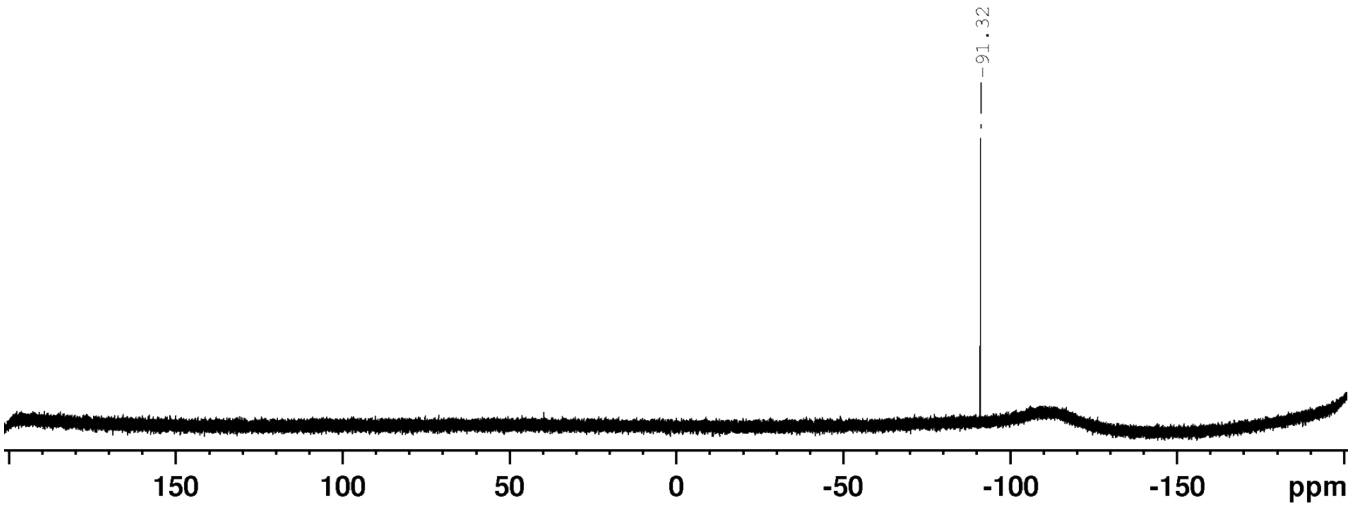


Fig. S21. $^{29}Si\{^{1}H\}$ NMR spectrum of **6**.

Synthesis of {(PMe$_3$)$_2$Rh}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (7)

To a 10 mL reaction tube with PTFE cap, {Rh(COD)}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**3**) (500 mg, 611 μmol) and C_6H_6 (15 mL), were charged. And then, neat of PMe_3 (295 μL, 2.85 mmol) was added. The reaction mixture was stirred at RT for 2 h, and the volatiles were removed by evacuation. Recrystallization of the residue from *n*-hexane at –40 °C yielded {Rh(PMe$_3$)$_2$}$_2${μ-(OSi(O^{t}Bu)$_2$)$_2$O} (**7**) as yellow crystals (393 mg, 433 μmol, y. 71%).

^{1}H NMR (C_6D_6, 25 °C): δ 1.75 (s, 36H, C*H*$_3$ (^{t}Bu)) 1.32–1.26 (m, 36H, C*H*$_3$ (PMe$_3$)).

^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 72.3 (*C*(CH$_3$)$_3$ (^{t}Bu)), 32.8 (C(*C*H$_3$)$_3$ (^{t}Bu)), 19.5 (dvt, $^2J_{C–Rh}$ = 1.9 Hz, $^1J_{C–P}$ = 14.1 Hz, *C*H$_3$ (PMe$_3$)).

^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 8.9 (d, $^1J_{P–Rh}$ =193.2 Hz).

^{29}Si{^{1}H} NMR (C_6D_6, 25 °C): δ –91.1.

Elemental analysis was precluded because **7** was smoothly oxidized under atmosphere.

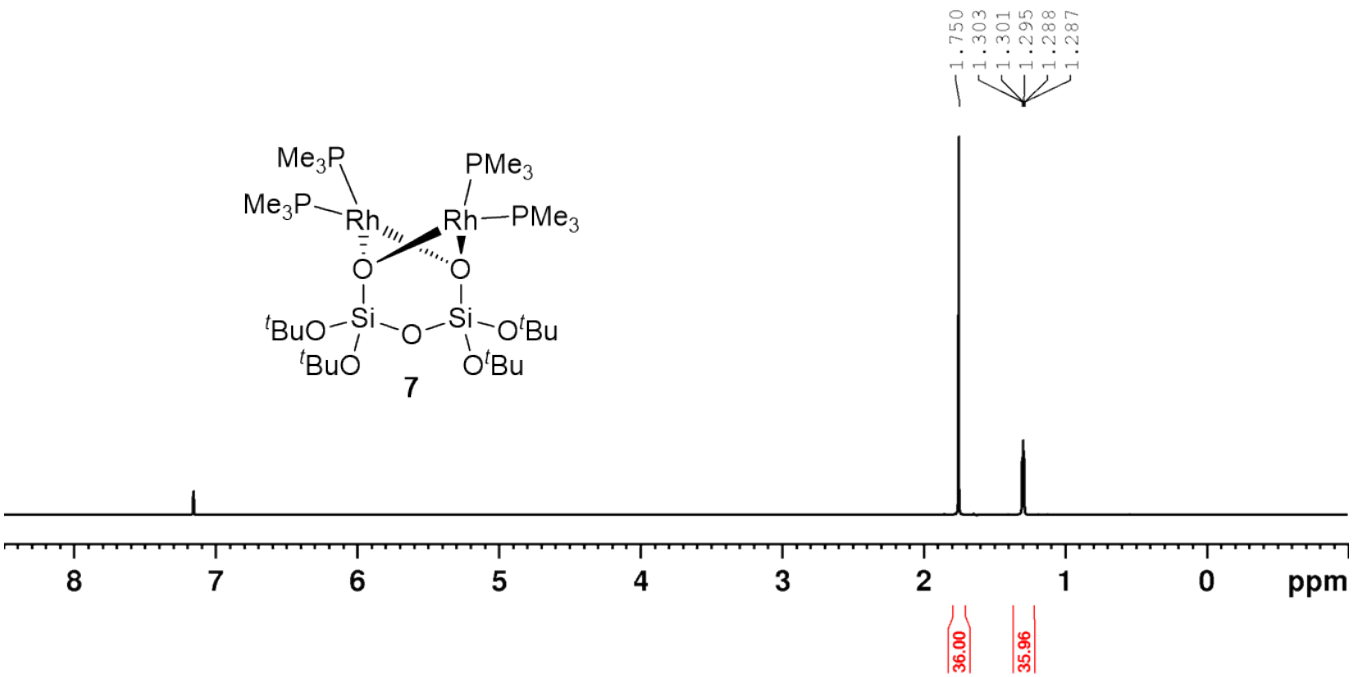


Fig. S22. ^{1}H NMR spectrum of **7**.

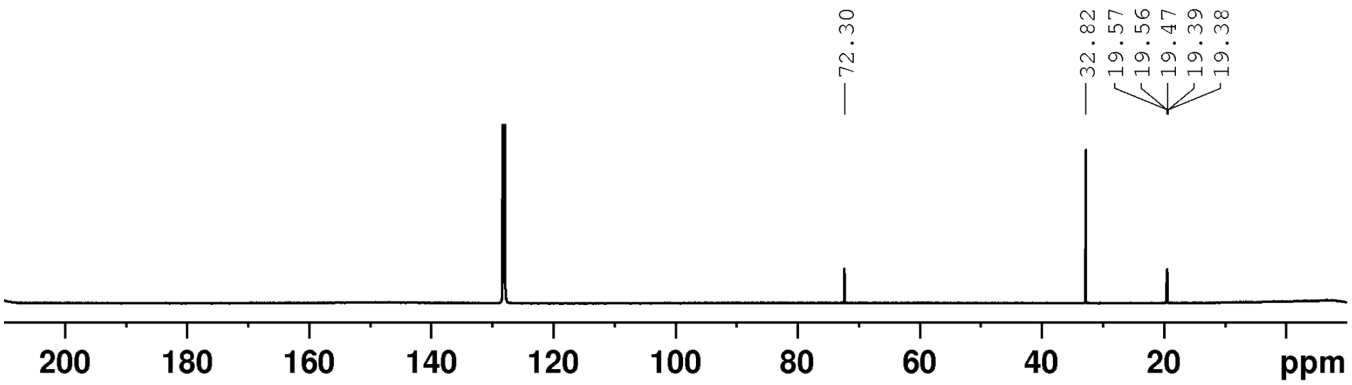


Fig. S23. $^{13}C\{^{1}H\}$ NMR spectrum of **7**.

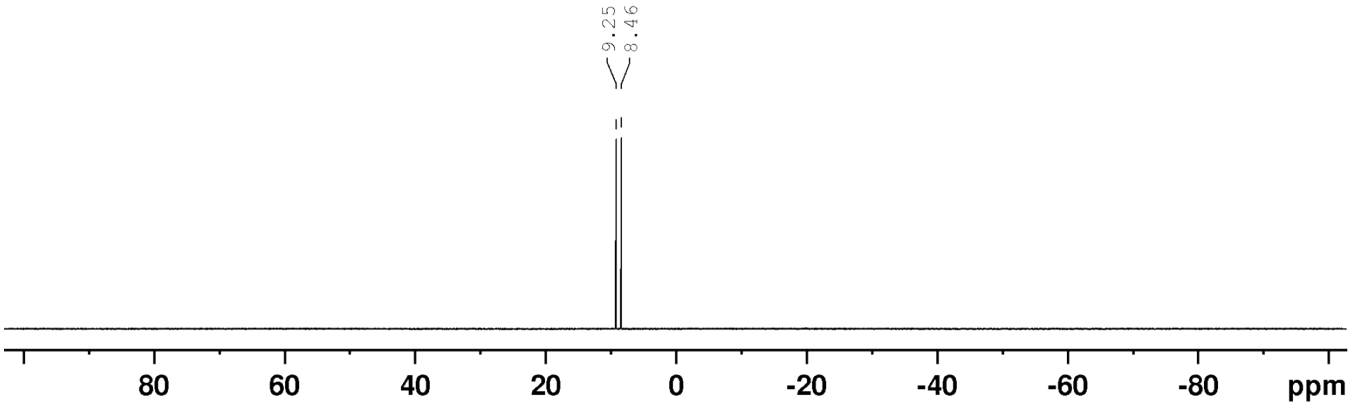


Fig. S24. $^{31}P\{^{1}H\}$ NMR spectrum of **7**.

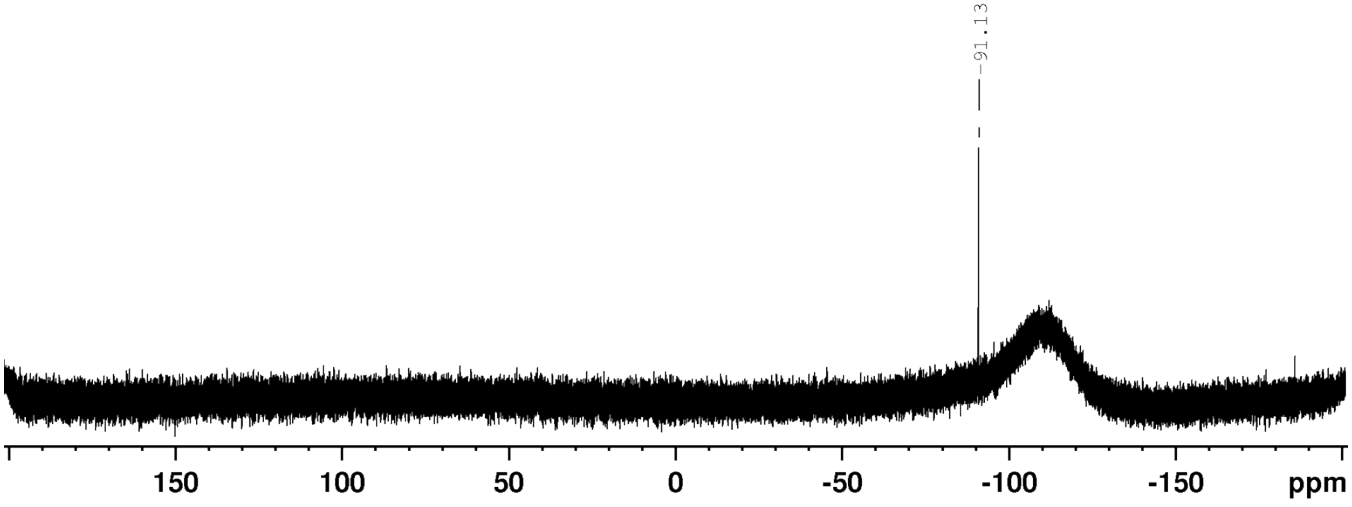


Fig. S25. $^{29}Si\{^{1}H\}$ NMR spectrum of **7**.

Synthesis of $[(^{t}BuO)_2Si(OH)]_2O$ (2)

To a *n*-hexane solution (16 mL) of $(^{t}BuO)_2Si(OAc)_2$ (**1**) (600 μL, 2.1 mmol), NaOH powder (170 mg, 4.2 mmol) was added at 0 °C. The solution was vigorously stirred for 16 h at 0 °C. Then, the suspension was filtrated with celite pad to remove inorganic salt. Following the concentration of the solvent, crystallization from $(Me_3Si)_2O$ at –40 °C yielded $[(^{t}BuO)_2Si(OH)]_2O$ (**2**) as colorless crystals (162 mg, 0.41 mmol, 39%).

^{1}H NMR (C_6D_6, 25 °C): δ 2.89 (s, 2H, Si–O*H*), 1.42 (s, 36H, C*H*$_3$ (^{t}Bu)).

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ 73.3 (*C*$(CH_3)_3$ (^{t}Bu)), 31.6 (C(*C*$H_3)_3$ (^{t}Bu)).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ –92.6.

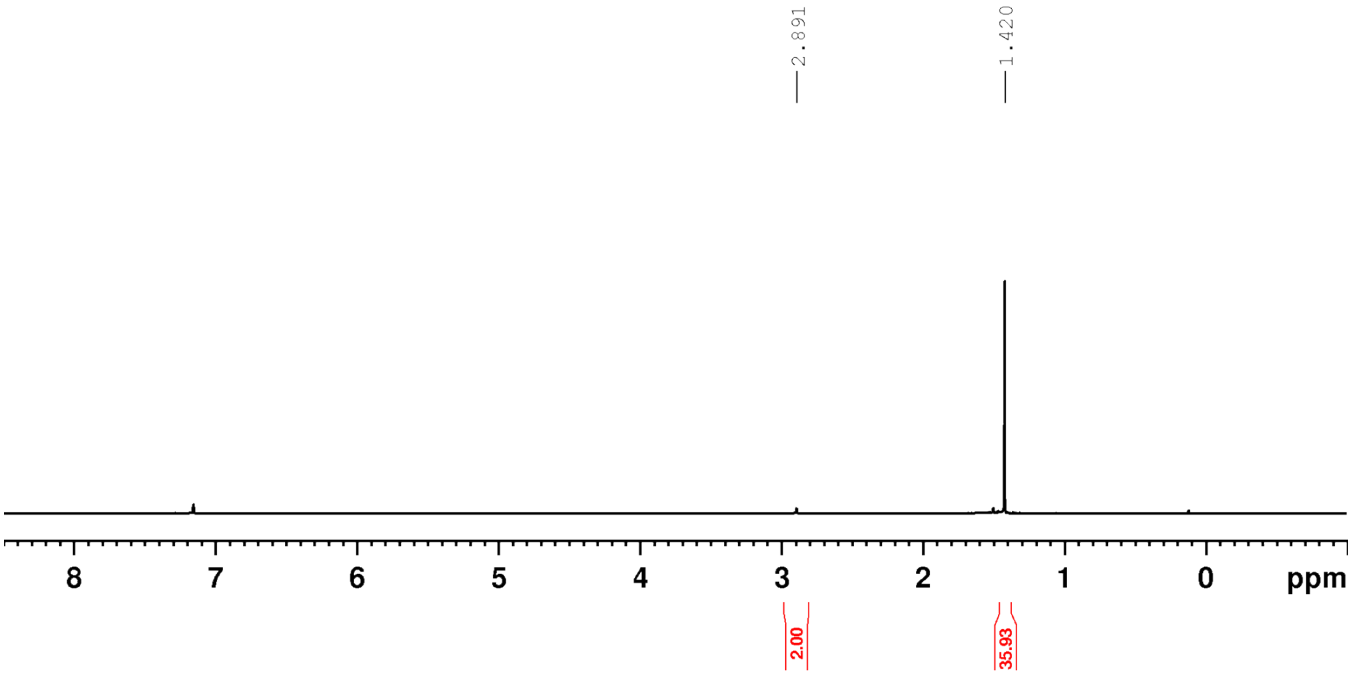


Fig. S26. ^{1}H NMR spectrum of **2**.

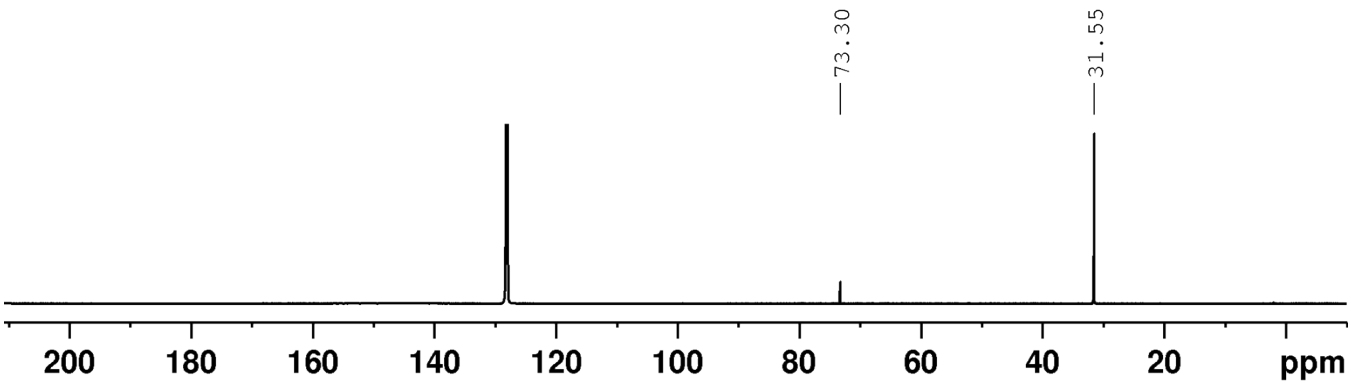


Fig. S27. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

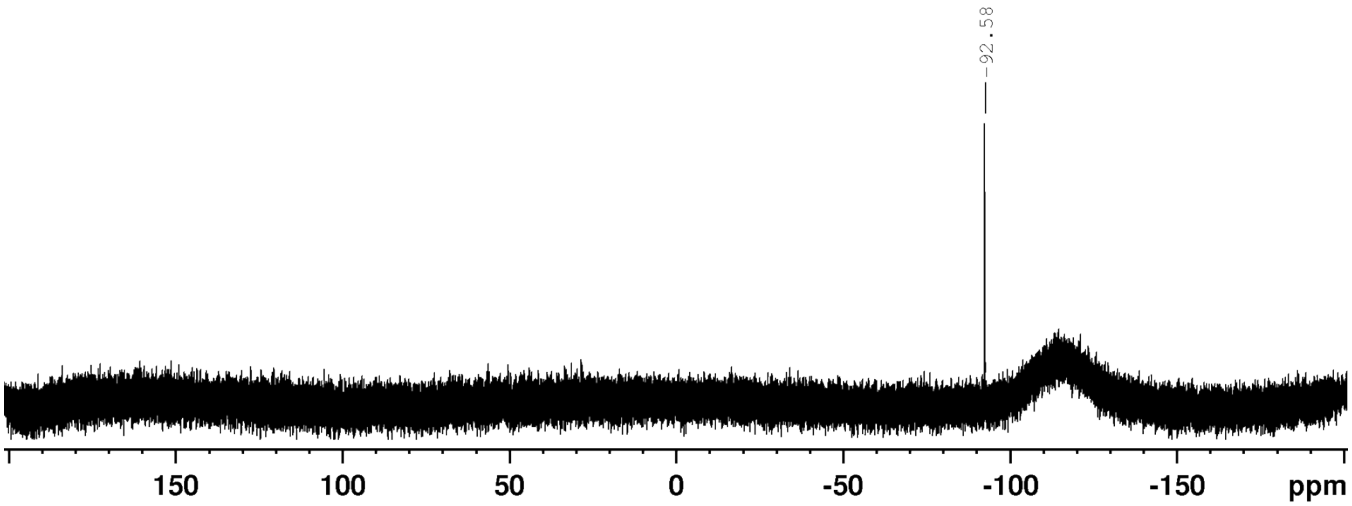


Fig. S28. $^{29}Si\{^{1}H\}$ NMR spectrum of **2**.

Table S1. Cartesian coordinates of the optimized structure of A.

Tag	Symbol	X	Y	Z
1	Si	-1.4186490	-0.4592240	0.6583150
2	Si	1.4184850	0.4588390	0.6586550
3	O	-1.2758350	-0.3781810	-0.9849360
4	O	1.2760120	0.3783340	-0.9847040
5	O	0.0000640	-0.0008580	1.3534790
6	O	-2.5153860	0.6240640	1.1921110
7	O	1.8025500	2.0030670	1.0244180
8	O	-1.8035510	-2.0033900	1.0237110
9	O	2.5155900	-0.6242650	1.1921670
10	C	-2.0243600	2.2144270	-2.2083120
11	C	-0.5789620	-2.9475830	-2.1303000
12	C	0.5798270	2.9477340	-2.1297220
13	C	-3.9464940	0.6039810	1.1177830
14	C	1.3206860	2.8543490	2.0784020
15	C	2.0253020	-2.2138780	-2.2074920
16	C	-1.3220870	-2.8552360	2.0774400
17	C	-4.3708760	2.0603000	1.2099070
18	H	-3.9487870	2.6305030	0.3714300
19	H	-4.0028690	2.5028760	2.1445280
20	H	-5.4642340	2.1548740	1.1822630
21	C	-4.4167930	-0.0086190	-0.1934170
22	H	-5.5135340	0.0090350	-0.2450880
23	H	-4.0906280	-1.0536520	-0.2853540
24	H	-4.0269150	0.5526260	-1.0521140
25	C	1.4001970	2.1379770	3.4200690
26	H	1.0558740	2.8030790	4.2233740
27	H	2.4335030	1.8418510	3.6449240
28	H	0.7674720	1.2406600	3.4292420
29	C	-4.4784330	-0.1925460	2.2991100
30	H	-4.0920870	0.2209640	3.2401760
31	H	-4.1648680	-1.2427330	2.2245150

32	H	-5.5757790	-0.1601720	2.3284610
33	C	-0.1113100	3.2743080	1.7749230
34	H	-0.7930040	2.4140320	1.7778790
35	H	-0.1633030	3.7579400	0.7887670
36	H	-0.4641470	3.9945740	2.5257800
37	C	0.1096980	-3.2759220	1.7738810
38	H	0.4620150	-3.9967530	2.5244530
39	H	0.7918780	-2.4160430	1.7773200
40	H	0.1615750	-3.7591820	0.7875200
41	C	2.2406520	4.0631860	2.0658500
42	H	1.9404720	4.7869080	2.8348100
43	H	2.2032000	4.5577500	1.0865310
44	H	3.2785860	3.7611300	2.2581010
45	C	-2.2427140	-4.0635470	2.0644400
46	H	-2.2056300	-4.5576380	1.0848980
47	H	-3.2804350	-3.7609220	2.2569430
48	H	-1.9428930	-4.7878120	2.8330300
49	C	4.3719960	-2.0593040	1.2108420
50	H	3.9508030	-2.6299940	0.3722430
51	H	4.0038040	-2.5019680	2.1453450
52	H	5.4654330	-2.1531330	1.1838090
53	C	3.9467170	-0.6032680	1.1183660
54	C	-1.4013070	-2.1393500	3.4194040
55	H	-1.0579900	-2.8051010	4.2225980
56	H	-2.4343880	-1.8421810	3.6439330
57	H	-0.7676510	-1.2427030	3.4291400
58	C	4.4169970	0.0094840	-0.1927680
59	H	4.0275520	-0.5519970	-1.0515010
60	H	5.5137520	-0.0075750	-0.2442180
61	H	4.0902740	1.0543410	-0.2848220
62	C	4.4778510	0.1937130	2.2997640
63	H	5.5752070	0.1619050	2.3294980
64	H	4.0913990	-0.2198150	3.2407780
65	H	4.1638490	1.2437390	2.2248560

66	O	3.0325390	-2.6709580	-2.5160930
67	O	-1.2292440	-3.8636380	-2.3602370
68	O	1.2302550	3.8637940	-2.3592110
69	O	-3.0313490	2.6716160	-2.5175830
70	Rh	-0.4156580	1.4328510	-1.6567460
71	Rh	0.4161490	-1.4326710	-1.6567130

Table S2. Cartesian coordinates of the optimized structure of 4.

Tag	Symbol	X	Y	Z
1	Rh	-0.0083320	-3.1300170	-0.8036810
2	Rh	-0.0032470	0.7904150	-1.4611100
3	Si	-2.9389990	-1.5799430	0.2118620
4	Si	-2.9367510	1.5885700	-0.1961430
5	O	-1.3340640	-1.8657490	0.2130390
6	O	-3.5893820	-1.9317320	1.6758350
7	O	-1.3316350	1.8752430	-0.2200840
8	O	-3.5784470	-2.4438600	-1.0200880
9	O	-3.2465810	0.0056440	0.0181840
10	O	-3.5610070	2.4644170	1.0358850
11	O	-3.6073730	1.9221930	-1.6548550
12	O	1.9917000	-0.6708820	-3.1839490
13	O	-1.9637000	-0.6666680	-3.2236970
14	O	-2.0780800	-4.8920720	-2.1054160
15	O	2.0511650	-4.8909000	-2.1243720
16	C	-1.3152330	-4.1923840	-1.6104210
17	C	-3.4655420	-4.3746520	1.5251850
18	H	-4.3108010	-4.4122250	0.8262870
19	H	-3.4811970	-5.2879040	2.1346760
20	H	-2.5338710	-4.3793430	0.9406210
21	C	-2.3213560	-3.1122900	3.3422450
22	H	-1.3927180	-3.0892420	2.7531150
23	H	-2.2971000	-3.9996720	3.9894290
24	H	-2.3530160	-2.2203230	3.9820120
25	C	-3.5387000	-3.1501090	2.4286090
26	C	-5.1479330	-3.7485810	-2.2084930
27	H	-4.4040430	-3.9392630	-2.9917560
28	H	-6.1485100	-3.7935350	-2.6583480
29	H	-5.0644860	-4.5492920	-1.4611140
30	C	1.2919610	-4.1923860	-1.6224730
31	C	1.2662910	-0.0941750	-2.5058670

32	C	-4.9093310	-2.3888180	-1.5718560
33	C	-4.8153340	-3.1690390	3.2546390
34	H	-4.8702700	-2.2663550	3.8771270
35	H	-4.8460130	-4.0496970	3.9096320
36	H	-5.6987750	-3.1873110	2.6028620
37	C	-1.2627650	-0.0885010	-2.5214020
38	C	-4.8857140	2.4110080	1.6031480
39	C	-4.9685610	-1.2961870	-2.6302880
40	H	-4.7363930	-0.3095780	-2.2068130
41	H	-5.9740580	-1.2562150	-3.0718660
42	H	-4.2486420	-1.5001580	-3.4316030
43	C	-3.4497990	4.3637660	-1.5507450
44	H	-4.2692100	4.4237860	-0.8234420
45	H	-3.4743870	5.2680620	-2.1731360
46	H	-2.4979540	4.3628950	-0.9996710
47	C	-3.5711460	3.1261640	-2.4301820
48	C	-5.9491420	-2.1277670	-0.4897180
49	H	-5.9460180	-2.9183210	0.2717800
50	H	-6.9490960	-2.0983490	-0.9423180
51	H	-5.7803770	-1.1645910	0.0112580
52	C	-5.1112400	3.7665700	2.2534620
53	H	-4.3563090	3.9482020	3.0282410
54	H	-6.1054560	3.8103590	2.7173560
55	H	-5.0362000	4.5741160	1.5127590
56	C	-5.9372050	2.1632880	0.5294350
57	H	-5.9376420	2.9616930	-0.2238450
58	H	-6.9330810	2.1322810	0.9907880
59	H	-5.7748070	1.2053740	0.0162340
60	C	-2.3881510	3.0552650	-3.3856280
61	H	-1.4407930	3.0178140	-2.8279830
62	H	-2.3678070	3.9361780	-4.0416270
63	H	-2.4591420	2.1584000	-4.0153990
64	C	-4.9400920	1.3120720	2.6554280
65	H	-4.7185590	0.3260280	2.2255220

66	H	-5.9413190	1.2758210	3.1068600
67	H	-4.2114750	1.5078730	3.4508290
68	C	-4.8763110	3.1471780	-3.2106620
69	H	-4.9703460	2.2280280	-3.8038290
70	H	-4.9134550	4.0093090	-3.8895450
71	H	-5.7360790	3.2020660	-2.5298120
72	Rh	0.0084870	3.1396290	0.7829870
73	Rh	0.0027460	-0.7864240	1.4489120
74	Si	2.9392670	1.5760930	-0.2321540
75	Si	2.9338670	-1.5849960	0.2128350
76	O	1.3341980	1.8634630	-0.2200840
77	O	3.5673190	1.9011290	-1.7115640
78	O	1.3273280	-1.8617460	0.2004840
79	O	3.5928090	2.4558990	0.9804560
80	O	3.2544800	-0.0064410	-0.0206200
81	O	3.5803000	-2.4828430	-0.9906510
82	O	3.5656410	-1.8972450	1.6939250
83	O	-1.9334620	0.6739710	3.2351020
84	O	1.9840820	0.6793650	3.1817700
85	O	2.0875040	4.8937810	2.0816410
86	O	-2.0417890	4.9145730	2.0992070
87	C	1.3201950	4.1981450	1.5879650
88	C	3.4619290	4.3461470	-1.5928330
89	H	4.3008400	4.3878050	-0.8866840
90	H	3.4879040	5.2518400	-2.2130970
91	H	2.5248950	4.3625020	-1.0169970
92	C	2.3261320	3.0679910	-3.4036440
93	H	1.3931520	3.0454710	-2.8215800
94	H	2.3060450	3.9530450	-4.0541040
95	H	2.3635130	2.1739740	-4.0400610
96	C	3.5351760	3.1097850	-2.4796020
97	C	5.1743920	3.7630920	2.1480430
98	H	4.4345960	3.9660960	2.9320960
99	H	6.1770150	3.8078380	2.5932820

100	H	5.0917100	4.5561000	1.3923750
101	C	-1.2873890	4.2105520	1.5975510
102	C	-1.2455680	0.0942300	2.5214010
103	C	4.9254320	2.3976510	1.5275340
104	C	4.8188330	3.1073750	-3.2951190
105	H	4.8717120	2.1944960	-3.9029040
106	H	4.8607910	3.9773980	-3.9636510
107	H	5.6979370	3.1294720	-2.6375290
108	C	1.2714290	0.0983130	2.4940190
109	C	4.9190640	-2.4529420	-1.5244410
110	C	4.9830250	1.3169540	2.5982640
111	H	4.7431790	0.3269830	2.1872960
112	H	5.9903020	1.2768320	3.0358200
113	H	4.2676040	1.5335890	3.4003680
114	C	3.2292370	-4.3254400	1.6677470
115	H	3.9801920	-4.4557700	0.8774730
116	H	3.2465470	-5.2160950	2.3097240
117	H	2.2364100	-4.2722260	1.1972250
118	C	3.5008490	-3.0795310	2.5017930
119	C	5.9585280	2.1183280	0.4433750
120	H	5.9490740	2.8967580	-0.3304860
121	H	6.9615270	2.0984170	0.8897950
122	H	5.7892860	1.1462170	-0.0401080
123	C	5.0898410	-3.7642790	-2.2745000
124	H	4.3289760	-3.8606330	-3.0590130
125	H	6.0823680	-3.8138460	-2.7414730
126	H	4.9836480	-4.6183200	-1.5920230
127	C	5.9502490	-2.3602510	-0.4078960
128	H	5.8632090	-3.2127090	0.2783170
129	H	6.9612220	-2.3716800	-0.8363290
130	H	5.8443840	-1.4369110	0.1785480
131	C	2.3981210	-2.8961550	3.5356490
132	H	1.4175540	-2.7787240	3.0492400
133	H	2.3491670	-3.7655280	4.2052650

134	H	2.5937980	-2.0033120	4.1447010
135	C	5.0627500	-1.2780200	-2.4807390
136	H	4.8760610	-0.3183560	-1.9813630
137	H	6.0772710	-1.2608600	-2.9022180
138	H	4.3485140	-1.3728060	-3.3066550
139	C	4.8506690	-3.1793520	3.1963790
140	H	5.0579440	-2.2491690	3.7416960
141	H	4.8639030	-4.0148970	3.9086070
142	H	5.6557510	-3.3325640	2.4663630

Table S3. Cartesian coordinates of the optimized structure of II.

Tag	Symbol	X	Y	Z
1	Si	-0.0411560	1.4954330	-0.7506560
2	Si	0.0411880	-1.4951780	-0.7508130
3	O	0.0303610	1.3345280	0.9045150
4	O	-0.0304970	-1.3345060	0.9043810
5	O	0.0000590	0.0001640	-1.4661150
6	C	-2.6459970	1.4336420	2.0544370
7	C	2.7046470	1.2747240	2.1532000
8	C	-2.7044670	-1.2749540	2.1533860
9	C	2.6457720	-1.4338590	2.0541960
10	O	3.3247610	-2.3259930	2.2938630
11	O	3.4236170	2.0990590	2.5007780
12	O	-3.4231570	-2.0994850	2.5010860
13	O	-3.3251500	2.3256340	2.2941690
14	Rh	-1.4923190	0.0323420	1.5776330
15	Rh	1.4922320	-0.0323880	1.5775690
16	C	1.4548470	2.4601960	-1.2947020
17	C	2.0310290	2.2413610	-2.5526580
18	C	2.0404120	3.4143900	-0.4521860
19	C	3.1582770	2.9495730	-2.9552150
20	H	1.5943710	1.4971100	-3.2206810
21	C	3.1696760	4.1231400	-0.8488100
22	H	1.6097370	3.5936750	0.5350470
23	C	3.7286910	3.8898170	-2.1018460
24	H	3.5963490	2.7670790	-3.9353870
25	H	3.6165640	4.8553280	-0.1779260
26	H	4.6136890	4.4425070	-2.4136290
27	C	-1.6700770	2.3028930	-1.1570480
28	C	-2.7808960	1.5451180	-1.5517980
29	C	-1.8420370	3.6775690	-0.9505630
30	C	-4.0262500	2.1403330	-1.7222420
31	H	-2.6692390	0.4719910	-1.7191920

32	C	-3.0852730	4.2773260	-1.1192710
33	H	-0.9883280	4.2905740	-0.6531830
34	C	-4.1791930	3.5063040	-1.5011320
35	H	-4.8804020	1.5379190	-2.0280120
36	H	-3.2030480	5.3468030	-0.9521150
37	H	-5.1546750	3.9726800	-1.6314640
38	C	1.6700690	-2.3027260	-1.1571570
39	C	2.7810770	-1.5451710	-1.5517770
40	C	1.8417250	-3.6774490	-0.9507140
41	C	4.0263110	-2.1406490	-1.7222000
42	H	2.6696570	-0.4720000	-1.7190540
43	C	3.0848360	-4.2774700	-1.1194010
44	H	0.9878740	-4.2902940	-0.6534070
45	C	4.1789370	-3.5066720	-1.5011940
46	H	4.8806160	-1.5384010	-2.0278670
47	H	3.2023670	-5.3469830	-0.9523100
48	H	5.1543250	-3.9732450	-1.6315170
49	C	-1.4547240	-2.4599240	-1.2951860
50	C	-2.0405650	-3.4140150	-0.4527460
51	C	-2.0305270	-2.2412140	-2.5533390
52	C	-3.1697260	-4.1227850	-0.8496240
53	H	-1.6101890	-3.5931940	0.5346390
54	C	-3.1576810	-2.9494320	-2.9561450
55	H	-1.5936920	-1.4970060	-3.2212940
56	C	-3.7283680	-3.8895760	-2.1028460
57	H	-3.6168220	-4.8548990	-0.1787980
58	H	-3.5954770	-2.7670210	-3.9364560
59	H	-4.6132930	-4.4422700	-2.4148320

Table S4. Cartesian coordinates of the optimized structure of III.

Tag	Symbol	X	Y	Z
1	Rh	0.3051220	2.8029720	-0.0718270
2	Rh	-0.1846710	-0.0614950	1.8905410
3	Si	-2.7238260	1.4682300	-1.0882030
4	Si	-3.1531200	-1.0545960	0.8363800
5	O	-1.0820490	1.5366380	-1.0507310
6	O	-1.5749240	-1.4507250	1.0878240
7	O	-3.3181920	0.2406400	-0.1667720
8	O	1.8807620	1.7662650	3.1218700
9	O	-2.0724720	1.9861440	3.0537750
10	O	-1.4201380	4.7366910	1.4629540
11	O	2.1968350	4.8635820	1.0386930
12	C	-0.8605190	3.9634960	0.8250100
13	C	1.5769940	4.0025500	0.5997180
14	C	1.1320200	1.0427900	2.6345320
15	C	-1.4028180	1.1652550	2.6081010
16	Rh	-0.3051910	-2.8029300	0.0719040
17	Rh	0.1847800	0.0614610	-1.8904700
18	Si	2.7239320	-1.4683660	1.0880960
19	Si	3.1531100	1.0545820	-0.8363830
20	O	1.0821330	-1.5367770	1.0509240
21	O	1.5748840	1.4507230	-1.0876360
22	O	3.3182220	-0.2410080	0.1663080
23	O	-1.8805710	-1.7665330	-3.1216180
24	O	2.0726520	-1.9861300	-3.0536160
25	O	1.4197490	-4.7367490	-1.4630710
26	O	-2.1969240	-4.8637650	-1.0381460
27	C	0.8603630	-3.9634940	-0.8249940
28	C	-1.5771210	-4.0026050	-0.5993660
29	C	-1.1318610	-1.0430310	-2.6342720
30	C	1.4030040	-1.1651860	-2.6080230
31	C	3.2387590	-1.1703560	2.8607620

32	C	2.4141990	-1.5370970	3.9332020
33	C	4.4794890	-0.5900760	3.1531880
34	C	2.7981820	-1.2970870	5.2491630
35	H	1.4448620	-1.9989430	3.7322620
36	C	4.8665100	-0.3409040	4.4652240
37	H	5.1492860	-0.3161900	2.3359090
38	C	4.0206400	-0.6879060	5.5151610
39	H	2.1408480	-1.5815970	6.0695940
40	H	5.8293820	0.1249980	4.6702920
41	H	4.3179920	-0.4887490	6.5436200
42	C	3.4730900	-3.0653380	0.4867140
43	C	3.3159170	-4.2200400	1.2697640
44	C	4.2205590	-3.1630300	-0.6923650
45	C	3.8606600	-5.4351750	0.8740120
46	H	2.7522390	-4.1665110	2.2044390
47	C	4.7705090	-4.3765300	-1.0919440
48	H	4.3650040	-2.2806210	-1.3159080
49	C	4.5856560	-5.5137620	-0.3123690
50	H	3.7241530	-6.3221410	1.4906850
51	H	5.3412680	-4.4348660	-2.0174540
52	H	5.0118980	-6.4650140	-0.6274880
53	C	4.1272290	2.4638660	-0.1019800
54	C	4.5257730	3.5166250	-0.9397670
55	C	4.5164640	2.5039650	1.2428240
56	C	5.2616670	4.5866700	-0.4458840
57	H	4.2560570	3.4961240	-1.9980030
58	C	5.2589100	3.5693120	1.7405110
59	H	4.2228610	1.6962110	1.9130510
60	C	5.6264270	4.6135520	0.8976950
61	H	5.5576710	5.3987400	-1.1081800
62	H	5.5480650	3.5859980	2.7903040
63	H	6.2050090	5.4499730	1.2870000
64	C	3.8868800	0.6421520	-2.5072610
65	C	3.2950750	1.0992460	-3.6924330

66	C	5.0785830	-0.0876480	-2.6066310
67	C	3.8507140	0.8045230	-4.9339870
68	H	2.3744860	1.6836840	-3.6410980
69	C	5.6350790	-0.3923360	-3.8439200
70	H	5.5805260	-0.4267280	-1.6978660
71	C	5.0154190	0.0478620	-5.0105010
72	H	3.3730120	1.1641000	-5.8443600
73	H	6.5557560	-0.9713420	-3.9001670
74	H	5.4479210	-0.1911960	-5.9808680
75	C	-3.4731740	3.0650910	-0.4867310
76	C	-3.3163360	4.2197970	-1.2698540
77	C	-4.2205620	3.1626470	0.6924290
78	C	-3.8612570	5.4348260	-0.8740500
79	H	-2.7527260	4.1663500	-2.2045740
80	C	-4.7707060	4.3760550	1.0920350
81	H	-4.3649100	2.2801400	1.3158650
82	C	-4.5861380	5.5132930	0.3124130
83	H	-3.7250430	6.3218020	-1.4907760
84	H	-5.3413790	4.4343150	2.0176020
85	H	-5.0125330	6.4644680	0.6275580
86	C	-3.2383970	1.1703350	-2.8609590
87	C	-2.4137450	1.5371710	-3.9332910
88	C	-4.4790190	0.5899010	-3.1535490
89	C	-2.7975320	1.2971390	-5.2493040
90	H	-1.4444900	1.9991400	-3.7322170
91	C	-4.8658410	0.3406940	-4.4656400
92	H	-5.1488780	0.3158690	-2.3363690
93	C	-4.0198810	0.6878160	-5.5154690
94	H	-2.1401230	1.5817460	-6.0696420
95	H	-5.8286220	-0.1253430	-4.6708210
96	H	-4.3170590	0.4886210	-6.5439710
97	C	-3.8869400	-0.6417700	2.5071280
98	C	-5.0785350	0.0882400	2.6062690
99	C	-3.2953140	-1.0987610	3.6924260

100	C	-5.6350910	0.3932220	3.8434610
101	H	-5.5803200	0.4273080	1.6974040
102	C	-3.8510170	-0.8037470	4.9338810
103	H	-2.3748470	-1.6834020	3.6412750
104	C	-5.0156060	-0.0468890	5.0101700
105	H	-6.5556710	0.9723960	3.8995410
106	H	-3.3734520	-1.1632600	5.8443510
107	H	-5.4481480	0.1924080	5.9804600
108	C	-4.1273940	-2.4639270	0.1021880
109	C	-4.5163640	-2.5040740	-1.2427220
110	C	-4.5262470	-3.5165680	0.9399530
111	C	-5.2588530	-3.5693550	-1.7404780
112	H	-4.2225650	-1.6964400	-1.9130080
113	C	-5.2621870	-4.5865450	0.4459900
114	H	-4.2567240	-3.4960290	1.9982380
115	C	-5.6266840	-4.6134810	-0.8976530
116	H	-5.5478020	-3.5860930	-2.7903270
117	H	-5.5584350	-5.3985350	1.1082770
118	H	-6.2052830	-5.4498680	-1.2870070

Table S5. Crystal data and structure refinement for complex 3 and 5.

	Complex **3**	Complex **5**
Empirical formula	$C_{24}H_{48}O_7Si_2Rh_2$	$C_{38}H_{78}O_7Si_2P_2Rh_2$
Formula weight	710.62	970.94
Temperature/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
a/Å	11.6960(2)	23.6538(7)
b/Å	11.87930(10)	11.2340(2)
c/Å	13.9332(2)	18.5927(5)
α/°	80.5280(10)	90
β/°	76.8300(10)	109.801(3)
γ/°	87.7790(10)	90
Volume/Å^3	1859.27(5)	4648.5(2)
Z	4	4
ρ_{calc} g/cm^3	1.904	1.387
μ/mm^{-1}	1.474	0.872
F(000)	1098.0	2040.0
Crystal size/mm^3	1.81 × 1.10 × 1.08	1.20 × 0.86 × 0.62
Radiation	Mo K_α (λ = 0.71073)	Mo K_α (λ = 0.71073)
2Θ range for data collection/°	4.972 to 60.04	4.062 to 60.342
Index ranges	-16 ≤ *h* ≤ 15, -16 ≤ *k* ≤ 15, -18 ≤ *l* ≤ 18	-31 ≤ *h* ≤ 31, -15 ≤ *k* ≤ 15, -25 ≤ *l* ≤ 25
Reflections collected	54069	54160
Independent reflections	9545 R_{int} = 0.0257, R_{sigma} = 0.0165	12211 R_{int} = 0.0747, R_{sigma} = 0.0578
Data/restraints/parameters	9545/0/400	12211/0/461
Goodness-of-fit on F^2	1.323	3.125
Final R indexes [*I*>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.1441	R_1 = 0.1645, wR_2 = 0.4058
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.1471	R_1 = 0.1756, wR_2 = 0.4104
Largest diff. peak/hole / e Å^{-3}	2.85/-1.06	16.30/-3.05

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