Supporting Information

Reactions of a Tungsten–Germylyne Complex with Alcohols and Arylaldehydes

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Contents

1. General experimental procedures

All manipulations were performed using vacuum line techniques or in a drybox under an argon atmosphere. Hexane and toluene were dried using an Ultimate Solvent System (NIKKO HANSEN&CO., LTD) and degassed three times (freeze-pump-thaw), then stored over 4Å molecular sieves in a drybox before use. Benzene-*d*$_6$ and toluene-*d*$_8$ were distilled from CaH_2 and stored over 4Å molecular sieves in a drybox before use. Methanol and ethanol were dried over $Mg(OMe)_2$ and $Mg(OEt)_2$, respectively, and distilled before use. Anhydrous isopropyl alcohol was purchased and used without further purification. Benzaldehyde, 4-fluoro-benzaldehyde and 4-methoxy-benzaldehyde were dried over $CaCO_3$ and distilled before use. $Cp^*(CO)_2W{\equiv}GeC(SiMe_3)_3$ (**1**) was prepared by the literature procedure.[1] ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker AVANCE-300 or AVANCE-400 spectrometer. ^{1}H–^{1}H COSY and ROESY NMR spectra were recorded on a JEOL ECA-700 spectrometer at the Research and Analytical Centre for Giant Molecules, Graduate School of Science, Tohoku University. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual proton (C_6D_5H: 7.15 ppm, $C_6D_5CD_2H$: 2.09 ppm) and the carbon (C_6D_6: 128.0 ppm, $C_6D_5CD_3$: 20.4 ppm) of deuterated solvents. The ^{29}Si{^{1}H} NMR spectra were referenced to an external standard (TMS: 0.0 ppm). IR spectra were recorded on a HORIBA FT-720 spectrometer. Mass spectral data were obtained using a SHIMAZU GCMS-QP2010 SE. Elemental analyses were performed on a J-SCIENCE LAB JM-11 analyser at the Research and Analytical Centre for Giant Molecules, Graduate School of Science, Tohoku University.

2. Syntheses and characterization of complexes 3-8

Cp*$(CO)_2$(H)W=Ge(OMe){C$(SiMe_3)_3$} (**3**): An NMR tube equipped with a Teflon valve was charged with **1** (21 mg, 0.031 mmol), C_6D_6 (0.5 mL) and a small amount of $C_6H_3Me_3$ as an internal standard in a drybox. The NMR tube was brought out of a drybox, and MeOH (1.4 µL, *d* = 0.792 g/mL, 0.035 mmol) was added to the solution with a micro syringe under an argon flow. The colour of the solution immediately turned from orange to yellow. The ^{1}H NMR spectrum measured soon after the colour change showed formation of **3** in 97% NMR yield. All volatiles were removed under reduced pressure and the residue was washed with a small portion of cold hexane. After removal of the hexane under reduced pressure, **3** was obtained as a pale-yellow powder. Yield 83% (18 mg, 0.026 mmol). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ –5.26 (s, 1H, WH, $^1J_{WH}$ = 46.4 Hz), 0.44 (s, 27H, SiMe), 1.91 (s, 15H, Cp*), 3.91 (s, 3H, OMe); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 6.5 (SiMe), 11.8 (C_5*Me*$_5$), 44.1 (*C*$(SiMe_3)_3$), 52.4 (O*Me*), 100.9 (*C*$_5$Me$_5$), 224.6 (CO); ^{29}Si{^{1}H} NMR (79.5 MHz, C_6D_6, 300 K): δ –2.1; IR (KBr pellet, cm^{-1}): 1925 (s, ν_{CO}), 1853 (s, ν_{CO})); Mass (EI, 70 eV, *m*/*Z*): 73 ($SiMe_3$, 100), 201 ($C(SiMe_3)_3$-2Me, 22.4), 464 (M^+–MeOH–$C(SiMe_3)_3$+Me, 10.6), 605 (M^+–MeOH–5Me, 8.9), 620 (M^+–MeOH–4Me, 6.8), 635 (M^+–MeOH–3Me, 10.7), 665 (M^+–MeOH–Me, 16.4), 680 (M^+–MeOH, 31.2), 697 (M^+–Me, 1.0), 712 (M^+, 1.3); Elemental analysis: calcd. for $C_{23}H_{46}GeO_3Si_3W$; C: 38.84, H: 6.52; found C: 38.64, H: 6.49.

Cp*$(CO)_2$(H)W=Ge(OEt){C$(SiMe_3)_3$} (**4**): In a procedure similar to the synthesis of **3**, **1** (16 mg, 0.024 mmol) was treated with EtOH (1.5 µL, *d* = 0.789 g/mL, 0.026 mmol) in C_6D_6 (0.5 mL) to give **4** in 93% NMR yield. Volatiles were removed under vacuum. Recrystallisation of the residue from hexane at –30 °C afforded **4** as light yellow crystals in 67% yield (12 mg, 0.016 mmol). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ –5.23 (s, 1H, WH, $^1J_{WH}$ = 46.2 Hz), 0.45 (s, 27H, SiMe), 1.42 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2C*H*$_3$), 1.91 (s, 15H, Cp*), 4.25 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OC*H*$_2$CH$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 6.5 (SiMe), 11.8 (C_5*Me*$_5$), 19.0 (OCH_2*C*H$_3$), 43.4 (*C*$(SiMe_3)_3$), 61.0 (O*C*H$_2$CH$_3$), 100.9 (*C*$_5$Me$_5$), 224.8 (CO); ^{29}Si{^{1}H} NMR (79.5 MHz, C_6D_6, 300 K): δ –2.1; IR (KBr pellet, cm^{-1}): 1930 (s, ν_{CO}), 1863 (s, ν_{CO}); Mass (EI, 70 eV, *m*/*Z*): 73 ($SiMe_3$, 100), 201 ($C(SiMe_3)_3$–2Me, 23.6), 464 (M^+–EtOH–$C(SiMe_3)_3$+Me, 11.2), 545 (7.8), 605 (M^+–EtOH–5Me, 10.4), 635 (M^+–EtOH–3Me, 12.5), 665 (M^+–EtOH–Me, 20.2), 680 (M^+–EtOH, 38.2), 726 (M^+, 0.3); Elemental analysis: calcd. for $C_{24}H_{48}GeO_3Si_3W$; C: 39.74, H: 6.67; found C: 39.74, H: 6.57.

Cp*$(CO)_2$(H)W=Ge(O^{i}Pr){C$(SiMe_3)_3$} (**5**): In a procedure similar to the synthesis of **4**, **5** was obtained in 94% NMR yield by mixing **1** (30 mg, 0.044 mmol) and ^{i}PrOH (3.6 µL, *d* = 0.785 g/mL, 0.046 mmol) in C_6D_6 (0.5 mL), and was isolated as light yellow crystals in 53% yield (17 mg, 0.023 mmol). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ –5.26 (s, 1H, WH, $^1J_{WH}$ = 45.7 Hz), 0.46 (s, 27H, SiMe), 1.43 (d, $^3J_{HH}$ = 6.1 Hz, 6H, OCH*Me*$_2$), 1.93 (s, 15H, Cp*), 4.81 (sept, $^3J_{HH}$ = 6.1 Hz, 1H, OC*H*Me$_2$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 6.7 (SiMe), 11.9 (C_5*Me*$_5$), 26.7 (OCH*Me*$_2$), 42.9 (*C*$(SiMe_3)_3$), 67.8 (O*C*HMe$_2$), 101.0 (*C*$_5$Me$_5$), 225.4 (CO); ^{29}Si{^{1}H} NMR (79.5 MHz, C_6D_6, 300 K): δ –2.2; IR (KBr pellet, cm^{-1}): 1927 (s, ν_{CO}), 1867 (s, ν_{CO}); Mass (EI, 70 eV, *m*/*Z*): 73 ($SiMe_3$, 100), 201 ($C(SiMe_3)_3$–2Me, 25.6), 464 (M^+–PrOH–$C(SiMe_3)_3$+Me, 11.9), 545 (8.5), 605 (M^+–PrOH–5Me, 11.2), 620 (M^+–PrOH–4Me, 8.6), 635 (M^+–PrOH–3Me, 13.8), 650

(M^+–PrOH–2Me, 2.9), 665 (M^+–PrOH–Me, 22.4), 680 (M^+–PrOH, 46.5), 725 (M^+–Me, 0.4), 740 (M^+, 0.5); Elemental analysis: calcd. for $C_{25}H_{50}GeO_3Si_3W$; C: 40.61, H: 6.82; found C: 40.48, H: 6.61.

Cp*$(CO)_2$(PhC=O)W=Ge(OCH_2Ph){$C(SiMe_3)_3$} (**6**): In an NMR tube equipped with a Teflon valve, PhCHO (60 µL, *d* = 1.04 g/mL, 0.61 mmol) was added to a C_6D_6 (0.6 mL) solution of **1** (41 mg, 0.061 mmol) and a small amount of $C_6H_3Me_3$ as an internal standard in a drybox. The resulting solution was kept at room temperature for 4 days. During the time, the colour of the solution changed from orange to red and all signals for **1** disappeared in the ^{1}H NMR spectrum and complex **6** was formed quantitatively. After removal of volatiles, complex **6** was isolated as red crystals by recrystallisation from hexane at –30 °C. Yield: (43 mg, 0.048 mmol, 78%); The following data were collected from an equilibrium mixture of two diastereomers. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 0.49-0.61 (br, 27H, SiMe), 1.62 (s, 15H, Cp*), 4.4-5.5 (m, 2H, OCH_2Ph), 7-8 (m, 10H, Ph); ^{1}H NMR (300 MHz, toluene-d_8, 280 K, diastereomer ratio = 5 : 4): major diastereomer: δ 0.47 (s, 27H, SiMe), 1.65 (s, 15H, Cp*), 4.81 (d, $^2J_{HH}$ = 11.7 Hz, 1H, OCH_2Ph), 5.36 (d, $^2J_{HH}$ = 11.7 Hz, 1H, OCH_2Ph,), 7-8 (m, 10H, Ph), minor diastereomer : δ 0.61 (s, 27H, SiMe), 1.63 (s, 15H, Cp*), 4.46 (d, $^2J_{HH}$ = 15.0 Hz, 1H, OCH_2Ph), 4.89 (d, $^2J_{HH}$ = 15.0 Hz, 1H, OCH_2Ph), 7-8 (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, 280 K): δ 5.6, 5.9 (SiMe), 10.7 (C_5Me_5), 17.2, 19.2 ($C(SiMe_3)_3$), 63.7, 67.0 (OCH_2Ph), 103.4, 104.3 (C_5Me_5), 125.8, 126.3, 126.5, 126.9, 131.1, 132.7 (Ph, other signals for the phenyl carbons were not observed), 227.7, 231.6, 234.0, 235.5 (CO), 306.3, 311.3 (*C*(O)Ph); $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, 300 K): δ –1.6 (brs); IR (KBr pellet, cm^{-1}): 1936 (s, ν_{CO}), 1860 (s, ν_{CO}); Mass (EI, 70 eV, *m*/*Z*): 73 ($SiMe_3$, 71.6), 91 ($PhCH_2$, 100), 135 (Cp*, 14.3), 201 ($C(SiMe_3)_3$–2Me, 8.5), 319 (Cp*W, 11.2), 396 (Cp*WPh, 27.7), 424 (Cp*W{C(O)Ph}, 10.0), 452 (Cp*(CO)W{C(O)Ph}, 8.7), 480 (M^+–Ge(OCH_2Ph){$C(SiMe_3)_3$}, 15.8), 680 (M^+–C(O)Ph–OCH_2Ph, 4.2), 790 (M^+, 1.0); Elemental analysis: calcd. for $C_{36}H_{54}GeO_4Si_3W$; C: 48.50, H: 6.11; found C: 48.59, H: 6.11; Exact Mass: calcd. for [$C_{36}H_{54}{}^{74}GeO_4Si_3{}^{184}W$ + Na]; 915.1960; found C915.1955.

Cp*$(CO)_2$(*p*-FC_6H_4C=O)W=Ge($OCH_2C_6H_4F$-*p*){$C(SiMe_3)_3$} (**7**): In a procedure similar to the synthesis of **6**, a solution of **1** (36 mg, 0.053 mmol) and *p*-FC_6H_4CHO (56 µL, *d* = 1.16 g/mL, 0.53 mmol) in C_6D_6 (0.6 mL) was kept at room temperature for 45 hours to afford **7** almost quantitatively (by ^{1}H NMR). Complex **7** was isolated as dark-red crystals by recrystallisation from hexane at –30 °C. Yield: (35 mg, 0.038 mmol, 72%). The following data were collected from an equilibrium mixture of two diastereomers. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.45-0.59 (br, 27H, SiMe), 1.60 (s, 15H, Cp*), 4.3-5.3 (br, 2H, $OCH_2C_6H_4F$), 6.6-7.8 (m, 8H, C_6H_4F); ^{1}H NMR (400.1 MHz, toluene-d_8, 260 K, diastereomer ratio = 3 : 2) major diastereomer: δ 0.45 (s, 27H, SiMe), 1.60 (s, 15H, Cp*), 4.69 (d, $^2J_{HH}$ = 11.3 Hz, 1H, $OCH_2C_6H_4F$), 5.24 (d, $^2J_{HH}$ = 11.3 Hz, 1H, $OCH_2C_6H_4F$), 6.58 (dd, $^3J_{HH}$ = $^3J_{HF}$ = 8.8 Hz, 2H, C_6H_4F), 6.80 (dd, $^3J_{HH}$ = $^3J_{HF}$ = 8.8 Hz, 2H, C_6H_4F), 7.36 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.6 Hz, 2H, C_6H_4F), 7.49 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.6 Hz, 2H, C_6H_4F), minor diastereomer: δ 0.61 (s, 27H, SiMe), 1.58 (s, 15H, Cp*), 4.27 (d, $^2J_{HH}$ = 14.4 Hz, 1H, $OCH_2C_6H_4F$), 4.70 (d, $^2J_{HH}$ = 14.4 Hz, 1H, $OCH_2C_6H_4F$), 6.63 (dd, $^3J_{HH}$ = $^3J_{HF}$ = 8.8 Hz, 2H, C_6H_4F), 6.89 (dd, $^3J_{HH}$ = $^3J_{HF}$ = 8.8 Hz, 2H, C_6H_4F), 7.21 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.6 Hz, 2H, C_6H_4F), 7.75 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.6 Hz, 2H, C_6H_4F); $^{13}C\{^1H\}$ NMR (100.6 MHz, toluene-d_8, 265 K): major diastereomer: δ 5.4 (SiMe), 10.7 (C_5Me_5), 17.1

$(C(\mathrm{SiMe_3})_3)$, 66.1 $(\mathrm{O}C\mathrm{H_2C_6H_4F})$, 104.3 $(C_5\mathrm{Me_5})$, 114.7, 114.9 (d, $^2J_{\mathrm{CF}} = 22$ Hz, *m*-$C_6\mathrm{H_4F}$), 130.5 (d, $^3J_{\mathrm{CF}} = 8$ Hz, *o*-$C_6\mathrm{H_4F}$, the other signal for the *o*-$\mathrm{C_6H_4F}$ carbon was not observed), 137.9 (d, $^4J_{\mathrm{CF}} = 3$ Hz, *ipso*-$C_6\mathrm{H_4F}$), 149.7 (*ipso*-$C_6\mathrm{H_4F}$), 162.3 (d, $^1J_{\mathrm{CF}} = 243$ Hz, *p*-$C_6\mathrm{H_4F}$), 164.6 (d, $^1J_{\mathrm{CF}} = 253$ Hz, *p*-$C_6\mathrm{H_4F}$), 227.7, 231.8 (CO), 308.6 $(C(\mathrm{O})\mathrm{C_6H_4F})$, minor diastereomer: δ 5.9 (SiMe), 10.6 $(\mathrm{C_5}\mathit{Me}_5)$, 19.0 $(C(\mathrm{SiMe_3})_3)$, 62.8 $(\mathrm{O}C\mathrm{H_2C_6H_4F})$, 103.3 $(C_5\mathrm{Me_5})$, 115.1, 115.2 (d, $^2J_{\mathrm{CF}} = 22$ Hz, *m*-$C_6\mathrm{H_4F}$), 127.2 (d, $^3J_{\mathrm{CF}} = 8$ Hz, *o*-$C_6\mathrm{H_4F}$), 130.8 (d, $^3J_{\mathrm{CF}} = 9$ Hz, *o*-$C_6\mathrm{H_4F}$), 138.0 (d, $^4J_{\mathrm{CF}} = 3$ Hz, *ipso*-$C_6\mathrm{H_4F}$), 146.6 (*ipso*-$C_6\mathrm{H_4F}$), 161.8 (d, $^1J_{\mathrm{CF}} = 243$ Hz, *p*-$C_6\mathrm{H_4F}$), 165.7 (d, $^1J_{\mathrm{CF}} = 253$ Hz, *p*-$C_6\mathrm{H_4F}$), 234.1, 235.2 (CO), 302.5 $(C(\mathrm{O})\mathrm{C_6H_4F})$; ^{19}F NMR (376.5 MHz, $\mathrm{C_6D_6}$, 300 K): major diastereomer, δ −108.0, −116.3; minor diastereomer, δ −105.7, −116.5; $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, toluene-d_8, 265 K): major diastereomer, $\delta = -1.0$ (SiMe); minor diastereomer, δ −1.2 (SiMe); IR (KBr pellet, cm^{-1}): 1940 (s, ν_{CO}), 1867 (s, ν_{CO}); Mass (EI, 70 eV, *m*/*Z*): 73 ($\mathrm{SiMe_3}$, 57.8), 109 ($\mathrm{CH_2C_6H_4F}$, 100), 123 ($\mathrm{C(O)C_6H_4F}$, 30.6), 201 ($\mathrm{C(SiMe_3)_3{-}2Me}$, 10.9), 319 (Cp*W, 7.6), 414 (Cp*W$\mathrm{C_6H_4F}$, 6.5), 442 (Cp*W$\{\mathrm{C(O)C_6H_4F}\}$, 11.5), 470 (Cp*(CO)W$\{\mathrm{C(O)C_6H_4F}\}$, 6.9), 498 ($\mathrm{M^+{-}Ge(OCH_2C_6H_4F)\{C(SiMe_3)_3\}}$, 14.8), 680 ($\mathrm{M^+{-}2FC_6H_4CHO}$, 2.3); Elemental analysis: calcd. for $\mathrm{C_{36}H_{52}F_2GeO_4Si_3W}$; C: 46.62, H: 5.65; found C: 46.69, H: 5.65.

Cp*$\mathrm{(CO)_2}$(*p*-$\mathrm{MeOC_6H_4C{=}O}$)W=Ge($\mathrm{OCH_2C_6H_4OMe}$-*p*)$\{\mathrm{C(SiMe_3)_3}\}$ (**8**): In a procedure similar to the synthesis of **6**, a solution of **1** (51 mg, 0.075 mmol) and *p*-$\mathrm{MeC_6H_4CHO}$ (91 µL, *d* = 1.12 g/mL, 0.75 mmol) in $\mathrm{C_6D_6}$ (0.6 mL) was kept at room temperature for 86 hours to afford **8** in 94% NMR yield. After removal of volatiles under reduced pressure at 70 °C, **8** was isolated as red needles by recrystallisation from toluene at −30 °C. Yield: (44 mg, 0.046 mmol, 62%). The following data were collected from an equilibrium mixture of two diastereomers. ^{1}H NMR (400.1 MHz, $\mathrm{C_6D_6}$, 300 K, diastereomer ratio = 3 : 2) major diastereomer: δ 0.66 (s, 27H, SiMe), 1.72 (s, 15H, Cp*), 3.21 (s, 3H, OMe), 3.33 (s, 3H, OMe), 4.46 (d, $^2J_{\mathrm{HH}} = 14.1$ Hz, 1H, $\mathrm{O}C\mathit{H}_2\mathrm{C_6H_4OMe}$) , 4.84 (d, $^2J_{\mathrm{HH}} = 14.1$ Hz, 1H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4OMe}$), 6.64 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 6.89 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 7.40 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 7.92 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), minor diastereomer: δ 0.52 (s, 27H, SiMe), 1.72 (s, 15H, Cp*), 3.20 (s, 3H, OMe), 3.26 (s, 3H, OMe), 4.86 (d, $^2J_{\mathrm{HH}} = 11.3$ Hz, 1H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4OMe}$), 5.38 (d, $^2J_{\mathrm{HH}} = 11.3$ Hz, 1H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4OMe}$,), 6.64 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 6.80 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 7.54 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$), 7.70 (d, $^3J_{\mathrm{HH}} = 8.8$ Hz, 2H, $\mathrm{C_6}\mathit{H}_4\mathrm{OMe}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{C_6D_6}$, 300 K, diastereomer ratio = 3 : 2), major diastereomer : δ 6.1 (SiMe), 10.9 $(\mathrm{C_5}\mathit{Me}_5)$, 19.2 $(C(\mathrm{SiMe_3})_3)$, 54.7, 55.0 $(\mathrm{O}\mathit{Me})$, 63.5 $(\mathrm{O}C\mathrm{H_2C_6H_4OMe})$, 103.4 $(C_5\mathrm{Me_5})$, 113.4, 114.0, 127.1, 131.2, 134.7, 144.0, 158.9, 164.0 $(C_6\mathrm{H_4OMe})$, 235.4, 236.8 (CO), 300.3 $(C(\mathrm{O})\mathrm{Ph})$; minor diastereomer: $\delta = 5.7$ (SiMe), 11.0 $(\mathrm{C_5}\mathit{Me}_5)$, 21.3 $(C(\mathrm{SiMe_3})_3)$, 54.6, 55.0 $(\mathrm{O}\mathit{Me})$, 66.7 $(\mathrm{O}C\mathrm{H_2C_6H_4OMe})$, 104.3 $(C_5\mathrm{Me_5})$, 113.1, 113.8, 129.4, 130.4, 134.6, 146.7, 159.2, 162.8 $(C_6\mathrm{H_4OMe})$, 229.0, 232.4 (CO), 306.9$(C(\mathrm{O})\mathrm{Ph})$; $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.5 MHz, $\mathrm{C_6D_6}$, 300 K) major diastereomer: δ −1.3 (SiMe); minor diastereomer: δ −1.2 (SiMe); IR (KBr pellet, cm^{-1}): 1938 (s, ν_{CO}), 1857 (s, ν_{CO}); Mass (EI, 70 eV, *m*/*Z*): 73 ($\mathrm{SiMe_3}$, 100), 135 (Cp*, 46.2), 319 (Cp*W, 20.3), 426 (Cp*W+$\mathrm{C_6H_4OMe}$, 51.3), 454 (Cp*W+$\mathrm{C(O)C_6H_4OMe}$, 28.8), 482 (Cp*(CO)W+$\mathrm{C(O)C_6H_4OMe}$, 24.6), 510 (Cp*$\mathrm{(CO)_2}$W+$\mathrm{C(O)C_6H_4OMe}$, 29.4), 665 ($\mathrm{M^+{-}2MeOC_6H_4CHO{-}Me}$, 3.4), 680 ($\mathrm{M^+{-}2MeOC_6H_4CHO}$, 7.1); Elemental analysis: calcd. for $\mathrm{C_{38}H_{58}GeO_6Si_3W}$; C: 47.96, H: 6.14; found C: 48.10, H: 6.06.

3. Variable-temperature ^{1}H NMR spectra of 6

The variable-temperature ^{1}H NMR spectra of a mixture of *syn*/*anti*-diastereomers (syn:anti = 5:4) of $Cp^*(CO)_2(PhC{=}O)W{=}Ge(OCH_2Ph)\{C(SiMe_3)_3\}$ (**6**) are illustrated in Figure S1. At 260 K, two sets of singlet signals corresponding to two diastereomers are observed at 0.49 ppm (syn) and 0.64 ppm (anti) for the $SiMe_3$ groups and at 1.60 ppm (anti) and 1.64 ppm (syn) for the Cp* groups. Two doublet signals with an AB pattern observed at 4.45 and 4.91ppm ($^2J_{HH}$ = 15.0 Hz) are assigned to the diastereotopic benzyl protons of *anti*-diastereomer, while those at 4.82 and 5.42 ppm ($^2J_{HH}$ = 11.7 Hz) are assigned to those of s*yn*-diastereomer, judging from their intensities. Two benzyl protons on the same carbon atom are diastereotopic because the tungsten centre is chiral. There are also multiplet signals for the phenyl protons at 7.0 – 7.9 ppm. Both of two signals for Cp* and $SiMe_3$ groups are coalesced around 300 K and 310 K, respectively, and both gave sharp singlet signals at 340 K. The doublet signals at 4.45 (anti) and 5.42 (syn) ppm for the benzyl protons started to broaden around 300 K and coalesced around 340 K. The other benzyl signals at 4.82 (syn) and 4.91 (anti) ppm coalesced around 300 K and gave a doublet at 4.82 ppm splitted by a germinal coupling ($^2J_{HH}$ = 12.3 Hz) with the other coalescing very broad benzyl signal at 340 K. This germinal coupling is observed because the chirality of the tungsten centre is retained during the mutual exchange of two diastereomers even at 340 K.

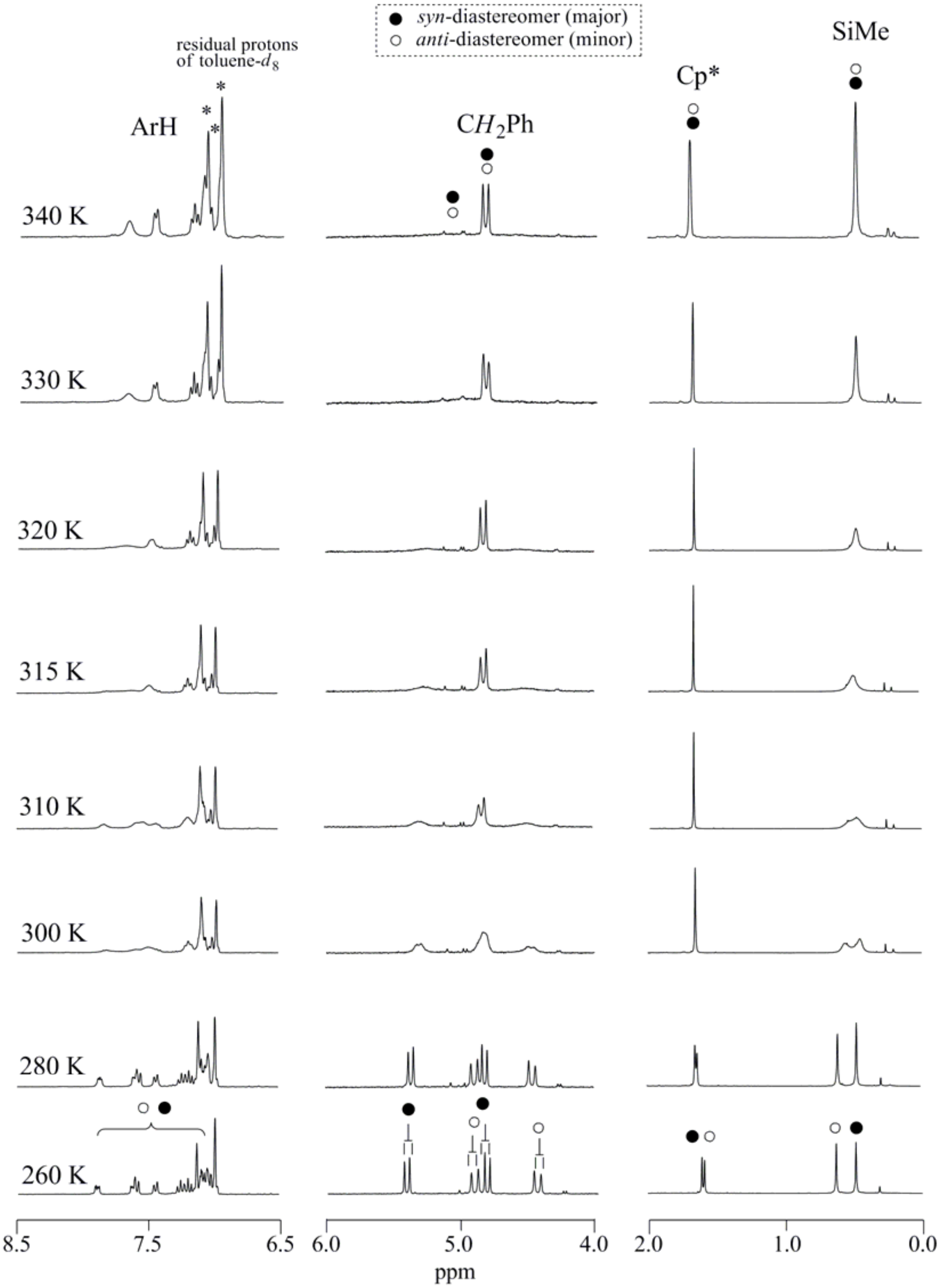

Figure S1. Variable-temperature ^{1}H NMR spectra (300 MHz, toluene-d_8) of Cp*(CO)$_2$(PhC=O)W=Ge(OCH$_2$Ph){C(SiMe$_3$)$_3$} (**6**) (SiMe$_3$, Cp*, CH$_2$Ph and aryl proton regions).

4. Assignments of two diastereomers of 6-8

(1) ROESY (Rotating-Flame Overhauser Effect Spectroscopy) experiment[2)]

The ROESY experiments have been applied to toluene-d_8 solutions of diastereomers of **6**, **7** and **8** to determine their stereochemistry using a 700 MHz NMR spectrometer. For example, in the case of $Cp^*(CO)_2(p\text{-}FC_6H_4C{=}O)W{=}Ge(OCH_2C_6H_4F\text{-}p)\{C(SiMe_3)_3\}$ (**7**), two sets of signals assigned to two diastereomers (dr 3:2) are observed in the ^1H NMR spectrum at 243 K (Chart S1). The signals at 0.44 ($SiMe_3$) and 1.58 ppm (Cp*) are assigned to the major species (left), while those at 0.60 ($SiMe_3$) and 1.56 ppm (Cp*) are assigned to the minor species (right), judging from their intensities. Irradiation was performed at these four chemical shifts for the Cp* and $SiMe_3$ groups. A strong NOE resonance was observed between the Cp* and $SiMe_3$ groups in the major species, while only very weak NOE resonance was observed in the case of the minor species. These results suggest that the major species of **7** is the *syn*-diastereomer with respect to the positions of Cp* and $SiMe_3$ groups, while the minor species is the *anti*-diastereomer.

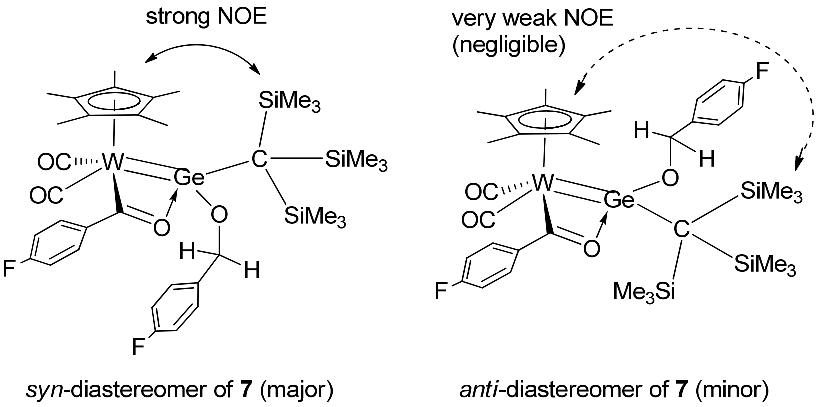

Chart S1. *Syn* and *anti*-diastereomers of **7**: *Syn* and *anti*-geometries are defined with respect to the the positions of Cp* and $SiMe_3$ groups.

Similarly, the stereochemistry of two diastereomers for **6** was also determined: the major species of **6** is the *syn*-diastereomer. In the case of **8**, determination of *syn* or *anti*-geometry by the ROESY experiment was not possible because the chemical shifts of the Cp* groups of two diastereomers are exactly the same. However, the major species of **8** was determined to be the *anti*-diastereomer because the chemical shifts of $SiMe_3$ and benzyl protons of the major isomer of **8** are very close to those of *anti*-diastereomers rather than those of *syn*-diastereomers for **6** and **7**.

By these ROESY experiments, some of the benzyl and aryl protons of complexes **6**–**8** were also assigned. The assignments for the protons of **7** are shown in Figure S2.

(2) ^1H-^1H COSY NMR

Assignments of the benzyl and aryl protons of two diastereomers **6-8** were supported by ^1H-^1H COSY NMR spectra. As an example, the ^1H-^1H COSY NMR spectrum of **7** is shown in Figure S2.

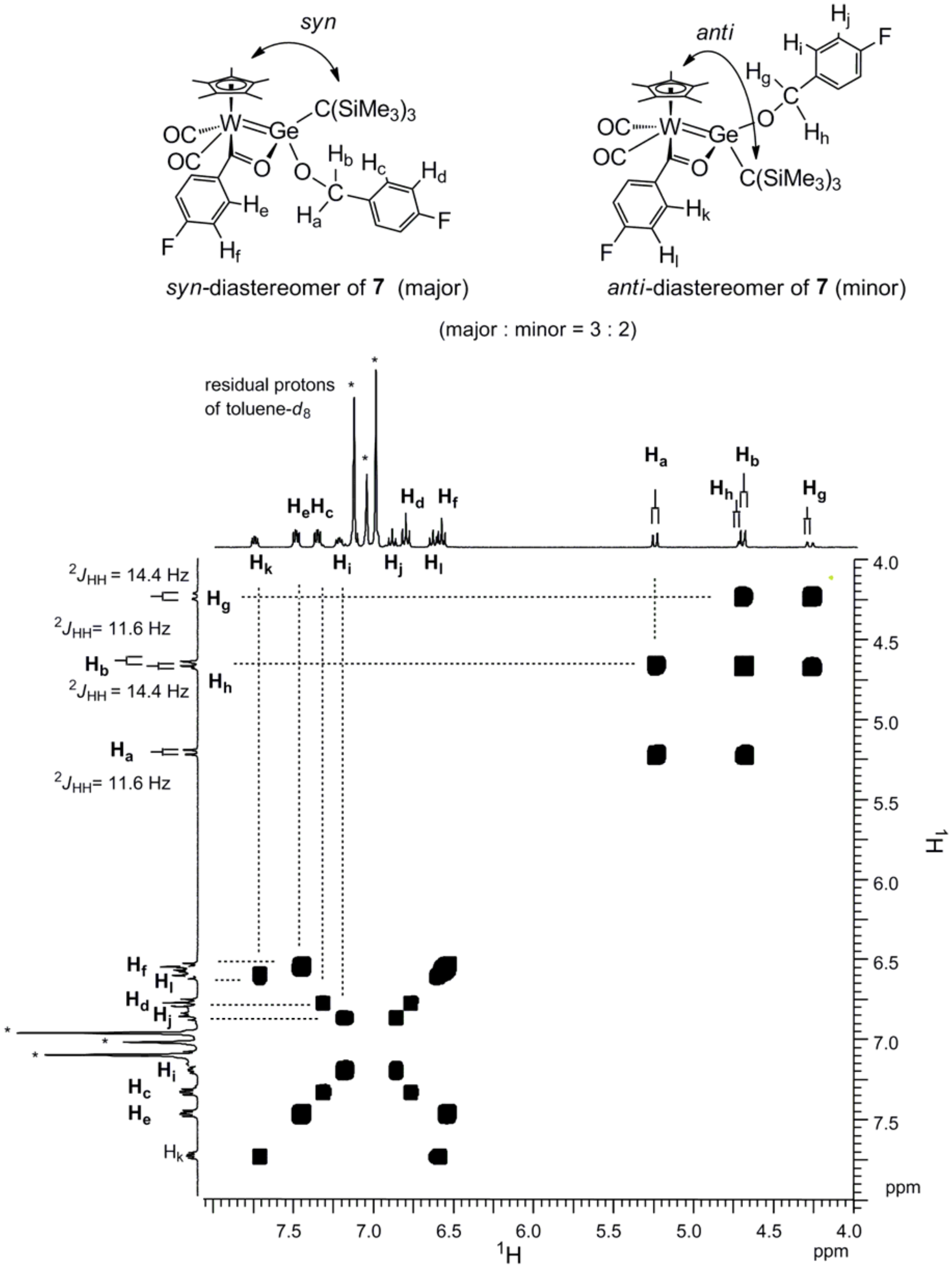

Figure S2. The ^{1}H-^{1}H COSY NMR spectrum (700 MHz, 243 K) of **7** in toluene-d_8 (benzyl and aryl proton regions).

5. X-ray crystallographic analysis and crystal data for 4 and 6

Single crystals suitable for X-ray diffraction of **4** and **6** were coated with paraffin oil and were mounted on a nylon loop, and held at a position under a cold stream of N_2 on the diffractometer. Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K_α radiation at 150(3) K. Empirical absorption collections were made using the program NUMABS.[3] The structures were solved by Patterson and Fourier transform methods and refined by full-matrix least-squares method on F^2 using SHELXS[4] and SHELXL.[5] For **4**, all non-hydrogen atoms except the carbon atoms of the Cp* group were refined anisotropically. All ten carbon atoms of the Cp* group were disordered in two sets of positions with occupancy factors 52% and 48%, which were refined isotropically. A hydrogen atom attached to the tungsten atom was not found by X-ray diffraction study, but the existence of the W-H bond was confirmed by ^{1}H NMR spectroscopy and other methods. For **6**, all non-hydrogen atoms were refined anisotropically. Crystallographic data of **4** and **6** are summarised in Tables S1 and Table S2. Crystallographic Information has been deposited with the Cambridge Crystallographic Data Centre: CCDC 901321 (**4**) and 901322 (**6**).

Table S1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{24}H_{48}GeO_3Si_3W$	
Formula weight	725.33	
Temperature	150(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 8.9459(8) Å	α = 99.178(4)°
	b = 9.7232(11) Å	β = 93.685(5)°
	c = 19.392(2) Å	γ = 108.562(5)°
Volume	1566.6(3) Å^3	
Z	2	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	4.764 mm^{-1}	
F(000)	728	
Crystal size	0.28 x 0.20 x 0.16 mm^3	
Crystal colour and habit	Light yellow plate	
Diffractometer	RIGAKU RAXIS-RAPID Imaging Plate	
Theta range for data collection	1.07 to 27.48°	
Index ranges	$-11 \leqq h \leqq 11$, $-12 \leqq k \leqq 12$, $-25 \leqq l \leqq 25$	
Reflections collected	20377	
Independent reflections	7052 [*R*(int) = 0.0896]	
Reflections with $I > 2\mathrm{sigma}(I)$	6407	
Completeness to theta = 27.48°	98.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5161 and 0.3489	
Solution method	SHELXS-97	
Refinement method	SHELXL-97	
Data / restraints / parameters	7052 / 0 / 300	
Goodness-of-fit on F^2	1.123	
Final *R* indices [I>2sigma(I)]	$R1$ = 0.0450, $wR2$ = 0.1158	
R indices (all data)	$R1$ = 0.0517, $wR2$ = 0.1193	
Largest diff. peak and hole	1.326 and -2.187 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **6**.

Empirical formula	$C_{36}H_{54}GeO_4Si_3W$	
Formula weight	891.50	
Temperature	150(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.9737(6) Å	
	b = 25.6747(16) Å	β = 100.4778(14)°
	c = 16.6602(10) Å	
Volume	3774.5(4) $Å^3$	
Z	4	
Density (calculated)	1.569 Mg/m^3	
Absorption coefficient	3.973 mm^{-1}	
F(000)	1800	
Crystal size	0.25 x 0.22 x 0.22 mm^3	
Crystal colour and habit	Red block	
Diffractometer	RIGAKU RAXIS-RAPID Imaging Plate	
Theta range for data collection	1.47 to 27.45°.	
Index ranges	$-11 \leqq h \leqq 11$, $-33 \leqq k \leqq 33$, $-21 \leqq l \leqq 20$	
Reflections collected	28563	
Independent reflections	8588 [R(int) = 0.0932]	
Completeness to theta = 27.45°	99.3 %	
Absorption correction	Numerical	
Max. and min. transmission	0.4752 and 0.4367	
Solution method	SHELXS-97	
Refinement method	SHELXL-97	
Data / restraints / parameters	8588 / 0 / 421	
Goodness-of-fit on F^2	1.146	
Final R indices [I>2sigma(I)]	$R1$ = 0.0492, $wR2$ = 0.1157	
R indices (all data)	$R1$ = 0.0637, $wR2$ = 0.1256	
Largest diff. peak and hole	1.991 and -1.500 e.$Å^{-3}$	

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