Dehydrogenative Double C—H Bond Activation in a Germylene-Rhodium Complex

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SUPPORTING INFORMATION

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1. Synthesis and characterization of new compounds

General considerations. All manipulations were carried out using standard Schlenk and glove-box techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. N-pentane (C₅H₁₂) were distilled under nitrogen over sodium. [D6]Benzene was distilled under argon over sodium/benzophenone. Compounds [(ArMes₂)₂Ge:] (ArMes = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂)¹, [RhCl(COD)]₂ (COD = 1,5-ciclooctadinene)² and NaBArF³ were prepared as described previously. Other chemicals were commercially available and used as received. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe₄ (δ: 0 ppm) using the residual proton solvent peaks as internal standards (¹H NMR experiments), or the characteristic resonances of the solvent nuclei (¹³C NMR experiments), while ³¹P was referenced to H₃PO₄. Spectral assignments were made by routine one- and two-dimensional NMR experiments (¹H, ¹³C{¹H}, ³¹P{¹H}, COSY, NOESY, HSQC and HMBC) where appropriate. Spectroscopic NMR resonances due to BArF anion: ¹H: δ 8.37 (s, 8H, o-Ar) and 7.67 (s, 4H, p-Ar) and ¹³C: 162.3 (q, ¹Jcb = 50 Hz, ipso-Ar), 135.1 (s, o-Ar) and 117.7 (s, p-Ar). For elemental analyses a LECO TruSpec CHN elementary analyzer, was utilized.
Compound 1. A solution of [(ArMes₂)₂Ge:] (300 mg, 0.43 mmol) and [RhCl(COD)]₂ (COD = 1,5-Cyclooctadiene) (106 mg, 0.21 mmol) in 5 mL of toluene was heated at 80 °C in a Schlenk flask equipped with a Teflon stopcock overnight, and a red-brown solution was formed. After this time, it was allowed to reach room temperature and the solvent was removed in vacuo. The resulting solid was washed with n-pentane and dried under vacuum to afford a dark orange solid. (310 mg, 86%).

**Anal. Caled** for C₄₈H₅₀ClGeRh: C, 68.8; H, 6.0. Found: C, 68.9; H, 6.2.

**¹H NMR** (400 MHz, C₆D₆, 298 K): δ 7.10 (t, 3JHH = 7.3 Hz, 2H, CH), 6.96 (s, 2H, CH), 6.85 (d, 3JHH = 7.3 Hz, 2H, CH), 6.79 (s, 2H, CH), 6.75 (d, 3JHH = 7.3 Hz, 2H, CH), 6.64 (s, 2H, CH), 5.16 (s, 2H, CH), 2.49 (s, 6H, CH₃ ArMes), 2.29 (s, 6H, CH₃ ArMes), 2.11 (s, 6H, CH₃ ArMes), 2.04 (s, 6H, CH₃ ArMes), 1.99 (s, 6H, CH₃ ArMes), 1.91 (s, 6H, CH₃ ArMes).

**¹³C{¹H} NMR** (100.63 MHz, C₆D₆, 298 K): δ 152.3 (d, 2JCRh = 7 Hz, i-C₆H₃), 147.1 (s, Cq), 146.1 (s, Cq), 140.7 (s, Cq), 137.0 (s, Cq), 135.4 (s, Cq), 135.0 (s, Cq), 131.3 (s, CH), 128.9 (s, p-C₆H₃), 128.3 (s, CH), 126.3 (s, Cq), 119.9 (d, JCRh = 9 Hz, CH), 100.0 (d, JCRh = 11 Hz, Cq), 97.0 (d, JCRh = 8 Hz, Cq), 23.5 (s, CH₃ ArMes), 22.0 (s, CH₃ ArMes), 21.8 (s, CH₃ ArMes), 21.1 (s, CH₃ ArMes), 21.0 (s, CH₃ ArMes), 20.9 (s, CH₃ ArMes).
Compound 2-NTf₂. In a NMR tube, to a solution of compound 1 (30 mg, 0.036 mmol) in C₆D₆ (0.5 mL) was added silver triflimide (14 mg, 0.036 mmol). The orange solution became yellow after 5 min. Compound 2-NTf₂ can be crystallized by slow evaporation of the C₆D₆ solution (27 mg, 67%).

Anal. Calcd for C₅₀H₄₉ClF₆GeNO₄RhS₂: C, 53.8; H, 4.4. Found: C, 54.0; H, 4.4.

¹H NMR (400 MHz, C₆D₆, 298 K): δ 7.12 (m, 1H, CH), 7.06 (t, J_HH = 7.5 Hz, 1H, CH), 6.89 (s, 1H, CH), 6.85 (s, 1H, CH), 6.83 (s, 1H, CH), 6.72 (s, 1H, CH), 6.63 (overlapping signals, 3H, CH), 6.49 (overlapping signals, 2H, CH), 6.18 (s, 1H, CH), 5.90 (d, J_HH = 7.5 Hz, 1H, CH), 5.06 (s, 1H, CH), 3.93 (br, 1H, Ar-CH₂Rh), 2.47 (s, 3H, CH₃ ArMes), 2.32 (s, 3H, CH₃ ArMes), 2.28 (s, 3H, CH₃ ArMes), 2.00 (s, 3H, CH₃ ArMes), 1.99 (s, 3H, CH₃ ArMes), 1.98 (s, 3H, CH₃ ArMes), 1.88 (s, 3H, CH₃ ArMes), 1.83 (s, 3H, CH₃ ArMes), 1.75 (s, 3H, CH₃ ArMes), 1.65 (s, 3H, CH₃ ArMes), 1.36 (br, 1H, Ar-CH₂Rh), 1.27 (s, 3H, CH₃ ArMes).

¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ 156.2 (s, Cq), 147.0 (s, Cq), 146.9 (s, Cq), 142.8 (s, Cq), 140.6 (d, J_CRh = 5 Hz, Cq), 139.1 (s, Cq), 137.3 (s, Cq), 137.2 (s, Cq), 137.1 (s, Cq), 136.8 (s, Cq), 136.7 (s, Cq), 136.1 (s, Cq), 135.7 (s, Cq), 135.6 (s, Cq), 133.5 (s, CH), 132.4 (s, CH), 131.2 (s, CH), 130.2 (s, CH), 130.1 (s, CH), 129.7 (s, CH), 128.9 (s, CH), 128.5 (s, CH), 126.7 (s, CH), 124.3 (s, CH), 123.0 (s, CH), 121.6 (s, Cq), 120.2 (s, Cq), 118.4 (s, Cq), 116.1 (d, J_CRh = 4 Hz, Cq), 104.4 (s, CH), 101.7 (d, J_CRh = 5 Hz, Cq), 94.4 (d, J_CRh = 13 Hz, Cq), 42.3 (d, J_CRh = 12 Hz, Ar-CH₂Rh), 22.2 (s, CH₃ ArMes), 21.8 (s, CH₃ ArMes), 21.7 (s, CH₃ ArMes), 21.4 (s, CH₃ ArMes), 21.0 (s, CH₃ ArMes), 20.8 (s, CH₃ ArMes), 20.7 (s, CH₃ ArMes), 20.6 (s, CH₃ ArMes), 19.0 (s, CH₃ ArMes), 18.2 (s, CH₃ ArMes), 17.1 (s, CH₃ ArMes).
**Compound 2.** In a NMR tube, to a solution of compound 1 (30 mg, 0.036 mmol) in C₆D₆ (0.5 mL) was added trityl tetrakis(pentafluorophenyl)borate (33 mg, 0.036 mmol). The orange solution became yellow after 5 min. A mixture of 2 and CHPh₃ was obtained.

Signals corresponding to 2 are the following:

**1H NMR** (400 MHz, C₆D₆, 298 K): δ 7.02 (m, 1H, CH), 6.91 (d, JHH = 7.6 Hz, 1H, CH), 6.82 (s, 1H, CH), 6.73 (s, 1H, CH), 6.64 (overlapping signals, 4H, CH), 6.56 (s, 1H, CH), 6.51 (t, JHH = 7.6 Hz, 2H, CH), 5.86 (d, JHH = 7.8 Hz, 1H, CH), 5.62 (s, 1H, CH), 4.23 (s, 1H, CH), 3.62 (br, 1H, Ar-CH₂Rh), 2.33 (s, 3H, CH₃ ArMes), 2.28 (s, 3H, CH₃ ArMes), 2.22 (s, 3H, CH₃ ArMes), 1.90 (s, 3H, CH₃ ArMes), 1.86 (s, 3H, CH₃ ArMes), 1.83 (s, 6H, CH₃ ArMes), 1.64 (s, 3H, CH₃ ArMes), 1.48 (s, 3H, CH₃ ArMes), 1.42 (s, 3H, CH₃ ArMes), 1.31 (br, 1H, Ar-CH₂Rh), 1.25 (s, 3H, CH₃ ArMes).

**13C[1H] NMR** (100.63 MHz, C₆D₆, 298 K): δ 155.8 (s, Cq), 147.1 (s, Cq), 142.5 (s, Cq), 142.0 (s, Cq), 140.2 (d, JCrh = 5 Hz, Cq), 138.6 (s, Cq), 137.4 (s, Cq), 137.0 (s, Cq), 136.6 (s, Cq), 136.4 (s, Cq), 135.7 (s, Cq), 135.4 (s, Cq), 134.1 (s, CH), 132.8 (s, CH), 131.3 (s, CH), 130.5 (s, CH), 130.2 (s, CH), 130.0 (s, CH), 128.6 (s, CH), 126.7 (s, Cq), 126.0 (s, Cq), 123.2 (s, CH), 121.5 (s, CH), 119.4 (s, Cq), 116.7 (d, JCrh = 5 Hz, Cq), 103.4 (s, CH), 102.0 (d, JCrh = 5 Hz, Cq), 94.8 (d, JCrh = 13 Hz, Cq), 42.7 (d, JCrh = 12 Hz, Ar-CH₂Rh), 22.1 (s, CH₃ ArMes), 21.7 (s, CH₃ ArMes), 21.6 (s, CH₃ ArMes), 21.1 (s, CH₃ ArMes), 21.0 (s, CH₃ ArMes), 20.8 (s, CH₃ ArMes), 20.6 (s, CH₃ ArMes), 20.4 (s, CH₃ ArMes), 18.9 (s, CH₃ ArMes), 17.4 (s, CH₃ ArMes), 16.5 (s, CH₃ ArMes).
**Compound 3-NTf₂.** In a NMR tube, to a solution of compound 1 (20 mg, 0.024 mmol) in C₆D₆ (0.5 mL) was added [PMe₂ArDipp₂]AuNTf₂ (45 mg, 0.048 mmol). The orange solution became yellow after 5 min. A mixture of 3-NTf₂ and [(PMe₂ArDipp₂)₂Au(μ-Cl)][NTf₂] was obtained. Compound 3-NTf₂ could be crystallized by slow evaporation of the C₆D₆ solution.

Signals corresponding to 3-NTf₂ are the following:

**¹H NMR** (400 MHz, C₆D₆, 298 K): δ 7.00 (d, ³J_HH = 7.6 Hz, 1H, CH), 6.93 (overlapping signals, 4H, CH), 6.76 (s, 1H, CH), 6.70 (s, 1H, CH), 6.64 (s, 1H, CH), 6.60 (overlapping signals, 2H, CH), 6.43 (d, ³J_HH = 7.6 Hz, 1H, CH), 6.34 (s, 1H, CH), 5.96 (s, 1H, Ge-H), 5.86 (t, ³J_HH = 4.5 Hz, 1H, CH), 5.08 (s, 1H, CH), 3.85 (br, 1H, Ar-CH₂Rh), 2.36 (s, 3H, CH₃ArMes), 2.26 (s, 3H, CH₃ArMes), 2.20 (s, 3H, CH₃ArMes), 2.00 (s, 3H, CH₃ArMes), 1.87 (s, 3H, CH₃ArMes), 1.83 (s, 3H, CH₃ArMes), 1.70 (s, 3H, CH₃ArMes), 1.66 (s, 3H, CH₃ArMes), 1.57 (s, 3H, CH₃ArMes), 1.45 (s, 3H, CH₃ArMes), 1.17 (br, 1H, Ar-CH₂Rh).

**¹³C{¹H} NMR** (100.63 MHz, C₆D₆, 298 K): δ 151.2 (s, Cq), 148.9 (s, Cq), 148.1 (s, Cq), 145.9 (s, Cq), 145.5 (d, J_CRh = 11 Hz, Cq), 145.4 (s, Cq), 141.9 (s, Cq), 139.1 (s, Cq), 137.2 (s, Cq), 136.0 (s, Cq), 135.9 (s, Cq), 135.6 (s, Cq), 134.8 (s, Cq), 134.2 (s, Cq), 132.2 (s, CH), 130.4 (s, CH), 129.5 (s, CH), 129.3 (s, CH), 129.1 (s, CH), 129.0 (s, CH), 128.6 (s, CH), 126.0 (s, Cq), 124.7 (s, CH), 122.4 (s, Cq), 121.0 (s, Cq), 119.2 (d, J_CRh = 19 Hz, Cq), 110.9 (d, J_CRh = 4 Hz, Cq), 101.9 (d, J_CRh = 5 Hz, Cq), 101.1 (s, CH), 94.6 (d, J_CRh = 13 Hz, Cq), 40.2 (d, J_CRh = 12 Hz, Ar-CH₂Rh), 22.3 (s, CH₃ArMes), 21.6 (s, CH₃ArMes), 21.3 (s, CH₃ArMes), 21.2 (s, CH₃ArMes), 21.1 (s, CH₃ArMes), 20.8 (s, CH₃ArMes), 20.4 (s, CH₃ArMes), 19.6 (s, CH₃ArMes), 18.3 (s, CH₃ArMes), 18.0 (s, CH₃ArMes), 15.8 (s, CH₃ArMes).
**Compound 3.** To a solution of compound 1 (50 mg, 0.06 mmol) in 3 mL of toluene was added sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (53 mg, 0.06 mmol) in a Schlenk flask equipped with a Teflon stopcock. The orange solution became yellow after 12 hours at room temperature. After this time, the resulting suspension was filtered through celite and the solvent was removed in vacuo. The resulting solid was washed with n-pentane and dried under vacuum to afford a yellow solid (76 mg, 76%).

**Anal. Calcd** for C₈₀H₆₂BF₂₄GeRh: C, 57.7; H, 3.8. Found: C, 57.8; H, 3.7.

**¹H NMR** (400 MHz, C₆D₆, 298 K): δ 8.49 (s, 8H, o-Ar), 7.80 (s, 4H, p-Ar), 7.08 (t, 3J_HH = 7.6 Hz, 1H, CH), 6.86 (s, 1H, CH), 6.83 (d, 3J_HH = 7.6 Hz, 1H, CH), 6.73 (overlapping signals, 6H, CH), 6.64 (s, 1H, CH), 6.57 (d, 3J_HH = 7.6 Hz, 1H, CH), 6.02 (s, 1H, Ge-H), 5.95 (d, 3J_HH = 7.6 Hz, 1H, CH), 5.45 (s, 1H, CH), 4.22 (s, 1H, CH), 3.44 (br, 1H, Ar-C₂H₃Rh), 2.43 (s, 3H, CH₃ArMes), 2.40 (s, 3H, CH₃ArMes), 2.15 (s, 3H, CH₃ArMes), 1.90 (s, 6H, CH₃ArMes), 1.79 (s, 3H, CH₃ArMes), 1.76 (s, 3H, CH₃ArMes), 1.66 (s, 3H, CH₃ArMes), 1.54 (s, 3H, CH₃ArMes), 1.51 (s, 3H, CH₃ArMes), 1.30 (s, 3H, CH₃ArMes), 1.17 (br, 1H, Ar-CH₂Rh).

**¹³C{¹H} NMR** (100.63 MHz, C₆D₆, 298 K): δ 162.3 (q, 1J_CB = 50 Hz, ipso-Ar), 150.7 (s, Cq), 148.9 (s, Cq), 146.6 (s, Cq), 145.4 (s, Cq), 144.3 (s, Cq), 141.6 (s, Cq), 138.3 (d, J_CRh = 11 Hz, Cq), 137.8 (s, Cq), 136.6 (s, Cq), 136.4 (s, Cq), 136.1 (s, Cq), 135.1 (s, o-Ar), 133.5 (s, Cq), 133.0 (s, CH), 130.9 (s, Cq), 130.0 (s, CH), 129.8 (s, CH), 129.4 (s, CH), 129.1 (s, Cq), 128.9 (s, CH), 126.2 (s, Cq), 125.8 (s, CH), 123.5 (s, CH), 123.2 (s, Cq), 121.9 (s, CH), 121.1 (s, Cq), 120.8 (s, Cq), 118.4 (s, Cq), 117.7 (s, p-Ar), 111.3 (s, Cq), 102.4 (s, Cq), 99.5 (s, CH), 95.6 (d, J_CRh = 12 Hz, CH), 40.4 (d, J_CRh = 13 Hz, Ar-CH₂Rh), 22.2 (s, CH₃ArMes), 21.5 (s, CH₃ArMes), 21.2 (s, CH₃ArMes), 20.7 (s, CH₃ArMes), 20.3 (s, CH₃ArMes), 19.4 (s, CH₃ArMes), 17.6 (s, CH₃ArMes), 17.2 (s, CH₃ArMes), 15.0 (s, CH₃ArMes).
Compound 4. In a NMR tube, a solution of 3 (30 mg, 0.018 mmol) in C₆D₆ (0.5 mL) was heated at 80 °C during 7 hours. After this time, it was allowed to reach room temperature and the solvent was removed in vacuo. The resulting solid was washed with n-pentane and dried under vacuum to afford an orange solid (16 mg, 53%).

Anal. Calcd for C₈₀H₆₂BF₂₄GeRh: C, 57.7; H, 3.8. Found: C, 57.9; H, 4.0.

¹H NMR (400 MHz, C₆D₆, 298 K): δ 8.37 (s, 8H, o-Ar), 7.67 (s, 4H, p-Ar), 7.03 (t, 3J_HH = 7.7 Hz, 1H, CH), 6.99 (d, 3J_HH = 7.7 Hz, 1H, CH), 6.61 (overlapping signals, 2H, CH), 6.51 (s, 1H, CH), 6.45 (s, 1H, CH), 6.27 (s, 1H, CH), 6.07 (s, 1H, CH), 5.83 (s, 1H, CH), 5.65 (d, 3J_HH = 7.7 Hz, 1H, CH), 3.44 (s, 1H, CH), 2.47 (d, 3J_HRh = 14.2 Hz, 1H, Ar-CH₂Ge), 2.15 (s, 3H, CH₃ArMes), 2.13 (s, 3H, CH₃ArMes), 2.10 (s, 3H, CH₃ArMes), 2.08 (overlapping signal, 1H, Ar-CH₂Ge), 1.96 (s, 3H, CH₃ArMes), 1.89 (s, 3H, CH₃ArMes), 1.79 (s, 3H, CH₃ArMes), 1.71 (s, 3H, CH₃ArMes), 1.66 (s, 3H, CH₃ArMes), 1.34 (s, 3H, CH₃ArMes), 1.25 (s, 3H, CH₃ArMes), 1.10 (s, 3H, CH₃ArMes), -18.12 (d, ¹J_HRh = 21.6 Hz 1H, Rh-H).

¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ 162.4 (q, ¹J_CB = 50 Hz, ipso-Ar), 151.2 (s, Cq), 148.7 (s, Cq), 145.6 (s, Cq), 144.9 (s, Cq), 141.8 (s, Cq), 138.1 (s, Cq), 136.2 (d, J_CRh = 10 Hz, Cq), 135.1 (s, o-Ar), 134.7 (d, J_CRh = 7 Hz, Cq), 134.0 (s, Cq), 133.5 (d, J_CRh = 10 Hz, CH), 133.2 (s, Cq), 132.3 (s, CH), 131.8 (s, CH), 130.4 (s, CH), 130.0 (s, CH), 129.9 (s, CH), 129.7 (s, CH), 129.5 (s, CH), 129.4 (s, CH), 128.9 (s, Cq), 126.2 (s, Cq), 125.9 (s, CH), 125.7 (s, Cq), 124.4 (s, Cq), 123.5 (s, Cq), 120.8 (s, Cq), 117.7 (s, p-Ar), 105.2 (s, CH), 102.7 (s, Cq), 96.0 (s, Cq), 29.9 (br, Ar-CH₂Ge), 27.0 (s, CH₃ArMes), 23.4 (s, CH₃ArMes), 22.9 (s, CH₃ArMes), 21.6 (s, CH₃ArMes), 21.0 (s, CH₃ArMes), 20.6 (s, CH₃ArMes), 20.5 (s, CH₃ArMes), 20.4 (s, CH₃ArMes), 18.7 (s, CH₃ArMes), 17.6 (s, CH₃ArMes), 16.0 (s, CH₃ArMes).
**Compound 5.** In a NMR tube, a solution of 3 (30 mg, 0.018 mmol) in C₆D₆ (0.5 mL) was heated at 80 °C during 48 hours. Compound 5 can be crystallized by slow evaporation of the C₆D₆ solution (23 mg, 77%).

**Anal. Calcd** for C₇₀H₆₀BF₂₄GeRh: C, 57.8; H, 3.6. Found: C, 58.0; H, 3.7.

**¹H NMR** (400 MHz, C₆D₆, 298 K): δ 8.37 (s, 8H, o-Ar), 7.67 (s, 4H, p-Ar), 7.06 (t, 3JHH = 7.6 Hz, 1H, CH), 6.98 (d, 3JHH = 7.6 Hz, 1H, CH), 6.87 (s, 2H, CH), 6.81 (d, 3JHH = 7.6 Hz, 1H, CH), 6.63 (overlapping signals, 3H, CH), 6.51 (s, 1H, CH), 6.36 (s, 1H, CH), 6.28 (s, 1H, CH), 5.78 (d, 3JHH = 7.6 Hz, 1H, CH), 5.36 (s, 1H, CH), 4.00 (s, 1H, CH), 3.37 (br, 1H, Ar-C₃H₃Rh), 2.50 (d, 3JHRh = 14.4 Hz, 1H, Ar-CH₂Ge), 2.21 (s, 3H, CH₃ArMes), 2.16 (s, 3H, CH₃ArMes), 2.10 (s, 3H, CH₃ArMes), 2.07 (s, 3H, CH₃ArMes), 2.06 (overlapping signal, 1H, Ar-CH₂Ge), 1.88 (s, 3H, CH₃ArMes), 1.78 (s, 3H, CH₃ArMes), 1.74 (s, 3H, CH₃ArMes), 1.58 (s, 3H, CH₃ArMes), 1.33 (s, 3H, CH₃ArMes), 1.24 (s, 3H, CH₃ArMes), 0.54 (br, 1H, Ar-CH₂Rh).

**¹³C {¹H} NMR** (100.63 MHz, C₆D₆, 298 K): δ 162.4 (q, 1JCB = 50 Hz, ipso-Ar), 152.2 (s, Cq), 148.3 (s, Cq), 146.5 (s, Cq), 142.0 (s, Cq), 141.6 (d, JCRh = 10 Hz, Cq), 141.3 (s, Cq), 141.2 (s, Cq), 138.5 (s, Cq), 138.1 (s, Cq), 137.5 (s, Cq), 136.2 (s, Cq), 136.1 (s, Cq), 136.0 (s, Cq), 135.1 (s, o-Ar), 134.3 (s, Cq), 133.8 (s, Cq), 133.2 (d, JCRh = 9 Hz, Cq), 132.1 (s, CH), 131.8 (s, CH), 130.4 (s, CH), 130.0 (s, CH), 129.7 (s, CH), 129.4 (s, CH), 129.1 (s, CH), 129.0 (s, CH), 126.2 (s, Cq), 123.5 (s, Cq), 123.0 (s, Cq), 122.1 (s, CH), 120.8 (s, Cq), 117.7 (s, p-Ar), 109.2 (s, Cq), 103.0 (d, JCRh = 6 Hz, Cq), 100.0 (s, CH), 40.6 (d, JCRh = 13 Hz, Ar-CH₂Rh), 25.0 (br, Ar-CH₂Ge), 23.7 (s, CH₃ArMes), 21.6 (s, CH₃ArMes), 21.1 (s, CH₃ArMes), 20.6 (s, CH₃ArMes), 20.5 (s, CH₃ArMes), 20.1 (s, CH₃ArMes), 18.5 (s, CH₃ArMes), 17.2 (s, CH₃ArMes), 15.8 (s, CH₃ArMes).
2. Solution NMR analysis of compounds of type 2 and 3

As highlighted in the main text, we observed some slight but distinctive NMR spectroscopic differences in compounds 2 and 3 as a result of varying the counteranion. Thus, $^1$H NMR signals associated to the activated mesityl ring in compounds 2 and 3 containing the triflimidate anion are similar, while differing from the corresponding resonances due to same species when a non-coordinating anion (BAr$^F$ or [B(C$_6$F$_5$)$_4$]) was used (Figure S1). This would be consistent with triflimidate binding to rhodium accompanied by coordination rearrangement from $\eta^3$-pseudoallylic to $\eta^1$-methylenic forms. Nonetheless, these differences do not seem to be present in the solid-state, where in all cases $\eta^3$-coordination of the flanking aryl ring in a pseudoallylic fashion was elucidated. Also, our prior investigations on a somewhat related cationic gold germylene compound revealed similar effects upon counteranion coordination.

\[\text{Figure S1. Stacked } ^1\text{H NMR spectra of compounds of type 2 and 3}\]
3. X-Ray structural characterization of new compounds

Crystallographic details. Low-temperature diffraction data were collected on a Bruker APEX-II CCD diffractometer (1) or on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IμS 3.0 microfocus X-ray source (2, 3 and 5) at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-II or APEX-III software, respectively. The structures were solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Despite many attempts, we could not obtain good quality crystals for compound 3 when pairing with the non-coordinating anion BArF ((B(C₆H₂-3,5-(CF₃)₂)₄)^⁻). However, we could grow crystals of enough quality for X-ray diffraction studies from the reaction between 1 and two equivalents of (PMe₂Ar₂Dipp²)Au(NTf₂). Thus the structure of 3 contains triflimidate as the counteranion. Similarly, good quality crystals of 2 were obtained after anion exchange by triflate (OTf⁻).

The full numbering scheme of all the reported structures can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information.
Figure S2. ORTEP diagram of compound 2. Counteranion, solvent molecules and hydrogen atoms are excluded for clarity. Thermal ellipsoids are set at 50% probability.
|                | 1                                      | 2                                      | 3                                      | 5                                      |
|----------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| Formula        | C₇₈H₵₂ClGeRh                          | C₅₈H₵₂Cl₃GeO₃Rhs                      | C₅₈H₵₂F₆GeNO₃Rhs₂                    | C₅₈H₵₀BF₅GeRh                        |
| Fw             | 839.84                                 | 1103.05                                | 1160.63                                | 1663.59                                |
| cryst.size, mm | 0.21 × 0.17 × 0.13                     | 0.18 × 0.13 × 0.04                     | 0.10 × 0.09 × 0.03                     | 0.06 × 0.05 × 0.03                     |
| crystal system | Monoclinic                             | Monoclinic                             | Triclinic                              | Monoclinic                             |
| space group    | P₂₁/c                                  | P₂₁/c                                  | P-I                                    | P₂₁/n                                  |
| a, Å           | 11.3820 (4)                            | 18.0808 (10)                           | 11.9789 (7)                            | 21.1124 (11)                           |
| b, Å           | 15.5958 (6)                            | 18.003 (1)                             | 11.9989 (7)                            | 15.8188 (9)                            |
| c, Å           | 22.3021 (9)                            | 17.1196 (8)                            | 18.8617 (11)                           | 23.3236 (12)                           |
| α, deg         | 90                                     | 90                                     | 75.067 (2)                             | 90                                     |
| β, deg         | 95.959 (1)                             | 111.751 (2)                            | 87.227 (2)                             | 112.895 (2)                            |
| γ, deg         | 90                                     | 90                                     | 89.740 (2)                             | 90                                     |
| V, Å³          | 3937.5 (3)                             | 5175.8 (5)                             | 2616.3 (3)                             | 7175.8 (7)                             |
| T, K           | 193                                    | 193                                    | 193                                    | 193                                    |
| Z              | 4                                      | 4                                      | 2                                      | 4                                      |
| ρcalc, g cm⁻³  | 1.417                                  | 1.417                                  | 1.473                                  | 1.541                                  |
| μ, mm⁻¹ (MoKα) | 1.28                                   | 1.05                                   | 1.04                                   | 0.76                                   |
| F(000)         | 1736                                   | 2272                                   | 1188                                   | 3356                                   |
| absorption corrections | multi-scan, 0.60-0.75 | multi-scan, 0.63-0.75 | multi-scan, 0.60-0.75 | multi-scan, 0.67-0.75 |
| θ range, deg  | 1.6 – 25.3                             | 2.3 – 27.2                             | 2.4 – 28.2                             | 2.1 – 25.3                             |
| no. of rflns measd | 38659                                 | 101254                                 | 80384                                  | 101525                                 |
| Rint          | 0.029                                  | 0.084                                  | 0.051                                  | 0.251                                  |
| no. of rflns unique | 7135                                 | 11471                                  | 9488                                   | 12975                                  |
| no. of params / restraints | 472 / 0                               | 609 / 7                                | 641 / 178                              | 974 / 7                                |
| R₁ (I > 2σ(I)) | 0.025                                  | 0.069                                  | 0.086                                  | 0.085                                  |
| R₁ (all data) | 0.030                                  | 0.119                                  | 0.105                                  | 0.175                                  |
| wR₂ (I > 2σ(I)) | 0.069                                 | 0.135                                  | 0.238                                  | 0.206                                  |
| wR₂ (all data) | 0.072                                  | 0.174                                  | 0.269                                  | 0.263                                  |
| Diff.Fourier.peaks min/max, eÅ⁻³ | -0.87 / 0.41                         | -2.00 / 2.10                           | -1.79 / 3.04                           | -0.98 / 1.61                           |
| CCDC number    | 2083762                                | 2083760                                | 2083759                                | 2083761                                |
4. Computational details

Optimized geometries of Ge—Rh complexes and transition states have been obtained from DFT calculations with Gaussian 09.6 Optimizations were carried out without symmetry restrictions in bulk solvent (benzene) using DFT methods: the oB97xD functional7 was chosen, which includes empirical dispersion corrections8 and was used in conjunction with the 6-31g(d,p) basis set9 for non-metal atoms, including Ge, and the SDD basis and associated electron core potential (ECP)10 for Rh. Bulk solvent effects (benzene) were included during optimization with the SMD continuum model.11 Topological analysis of the electron density within the Atoms In Molecules (AIM) formalism),12 and NBO analysis were performed with the Multifwn code13 and the NBO6.014 software respectively. The extended wavefunction [.wfx] and NBO [.47] files required for such analyses were calculated on the geometries previously optimized with the triple-ζ basis set Def2TZVP15 for all atoms, which includes an ECP for Rh.16 The CYLview visualization software has been used to create some of the figures.17

- DFT-calculated free energy profile in benzene for the formation of species 3, 4, and 5 from the cationic germylene-rhodium A is shown below (Figure S3). At variance with the profile discussed in the main text, herein intermediates A’, B’, and 3’ en route to 3 are also shown. These intermediates are conformers of A, B and 3, which result from analysis of the minima connected by TS A→B and TS B→3 and their geometries can be found in the xyz coordinates file provided.

![Figure S3](image)

**Figure S3.** Calculated free energy profile in bulk benzene for the formation of 3, 4, and 5.

Direct formation of 3 via C—H activation across the germanium-rhodium bond of A was explored and, although a transition state was not located, relaxed
potential energy scans suggest a barrier in excess of 30 kcal·mol\(^{-1}\) for this transformation. Similarly, the calculations indicate that direct formation of 4 from A and B requires overcome barriers of 33.6 and 34.3 kcal·mol\(^{-1}\) respectively, which is at odds with the experiments since the formation of 5 from 4 should have a higher energy barrier than the steps leading to 4 from 3.

- **AIM analysis** of the electron density of species 1, A, B‘, and 3 shows bond critical points (bcp) and the corresponding bond paths connecting their germanium and rhodium atoms. Figures S4-S7 illustrate these bcps and bond paths overlaid on the Laplacian of the electron density of the corresponding species.

![AIM analysis of the electron density](image)

**Figure S4.** Bond critical points and bond paths of the calculated electron density of 1 on the C4-Ge-Rh plane, overlaid on the Laplacian of the electron density, \(\nabla^2 \rho\) (solid and dashed lines correspond to positive and negative values respectively). The orange arrow points to the germanium-rhodium bcp.
Figure S5. Bond critical points and bond paths of the calculated electron density of A on the C3-Ge-Rh plane, overlaid on the Laplacian of the electron density, $\nabla^2 \rho$ (solid and dashed lines correspond to positive and negative values respectively). The orange arrow points to the germanium-rhodium bcp.

Figure S6. Bond critical points and bond paths of the calculated electron density of B’ on the C12-Ge-Rh plane, overlaid on the Laplacian of the electron density, $\nabla^2 \rho$ (solid and dashed lines correspond to positive and negative values respectively). The orange arrow points to the germanium-rhodium bcp.
Figure S7. Bond critical points and bond paths of the calculated electron density of 3 on the C3-Ge-Rh plane, overlaid on the Laplacian of the electron density, $\nabla^2 \rho$ (solid and dashed lines correspond to positive and negative values respectively). The orange arrow points to the germanium-rhodium bcp.

- Analysis of the electron density at the germanium-rhodium bcps of germyl-rhodium species 1 and 3 and germynes A and B' (Table S2) reveal electron density values of approximately 0.1 e·bohr$^{-3}$ and values of the Laplacian of their electron densities ($\nabla^2 \rho_b$) at the same bcps close to 0. This, in addition to negative values for the total energy density ($H_b$) and values for the absolute electronic potential energy and kinetic energy densities ratio ($|V_b|/G_b$) close to 2 indicate a strong covalent character for the Ge—Rh interaction in these species. Interestingly, the ellipticity of the Ge—Rh bond increases from 0.09 to ca. 0.2 from the parent germyl 1 to the germylene A, which is consistent with an increase in the double bond character (for cylindrical bonds, the ellipticity is expected to be 0). As we shall discuss later, this reflects back-donation from rhodium to germanium that may offset the effect of the loss of the chloride ligand.
Table S2. QTAIM indicators at Ge—Rh BCPs. All data are in atomic units. \( \rho_b \) electron density (e·bohr\(^{-3} \)); \( H_b \) total energy density (hartree·bohr\(^{-3} \)); \( \nabla^2 \rho_b \) Laplacian of the electron density (e·bohr\(^{-5} \)); \( |V_b|/G_b \) ratio between the absolute electronic potential energy and kinetic energy densities; \( \varepsilon_b \) ellipticity (ratio between the largest and smallest negative eigenvalues of the Hessian – 1).

| Ge—Rh bond | \( \rho_b \) | \( \nabla^2 \rho_b \) | \( G_b \) | \( V_b \) | \( H_b \) | \( \rho |V_b|/G_b \) | \( \varepsilon_b \) |
|------------|---------|----------------|--------|--------|--------|-----------------|--------|
| 1          | 0.099   | -0.005         | 0.048  | -0.0967| -0.049 | 2.03            | 0.091  |
| A          | 0.112   | 0.038          | -0.068 | -0.127 | -0.059 | 1.86            | 0.191  |
| B'         | 0.110   | 0.025          | 0.064  | -0.122 | -0.058 | 1.90            | 0.077  |
| 3          | 0.083   | -0.018         | 0.034  | -0.072 | -0.038 | 2.13            | 0.033  |

- NBO analysis was used to complete the insight into the germanium-rhodium interaction of the species studied by AIM. Table S3 summarizes relevant donor-acceptor interactions and Wiberg Bond Order (WBO) of the germanium-rhodium bonds. Typical NBO terminology has been used to name the different types of NBOs: LP for Lone Pair and LV for Lone Vacancy, which refers to an empty valence orbital localized on one atom. Also, the main Atomic Orbital contribution to the LVs has been included in parenthesis. The NLMO column indicates the percentage of non-Lewis orbitals from the acceptor atom that are mixed with the parent donor NBO.

Table S3. Relevant NBO results including major donor-acceptor interactions.

| Complex | WBO | Donor NBO | Acceptor NBO | \( \Delta E_g \) kcal·mol\(^{-1} \) | NLMO |
|---------|-----|-----------|--------------|------------------------------|------|
| 1       | 0.7020 | LP(d) Rh | LV(p) Ge | 12.32 | 1.49% |
| A       | 0.9043 | LP(d) Rh | LV(p) Ge | 13.77 | 2.35% Ge |
| B'      | 0.7824 | LP(d) Rh | LV(p) Ge | 15.53 | 3.60% Ge |
| 3       | 0.542 | LP(d) Rh | LV(p) Ge | 109.57 | 24.59% Ge |
|         |       | BD Rh-H  | LV(p) Ge | 19.29 | 4.86% Ge |
|         |       | BD Rh-C\(_{aryl}\) | LV(p) Ge | 13.44 | 0.75% Ge |
Natural Bonding Orbital (NBO) analysis of the species 1, 3, and intermediate A, locates 4 Lone Pairs (LPs), almost pure d orbitals, on their rhodium atoms, which agrees with a Rh(I)/Ge(II) formulation. Consistent with C—H activation at rhodium, only 3 LPs were located in the case of species B'.

Second order perturbation theory analysis of the Fock matrix, reveals electron donation from 4d orbitals of the rhodium atoms to 4p orbitals of the germanium, both in the germyl and germylene species studied, as shown in Table S3. This is supported by the Ge contribution to the corresponding NLMOs. Notice that the contribution of Ge orbitals to the NLMO corresponding to the donation of electron density from Rh in complex 3 is by far the highest, but it must be recognized that in this case the germanium-rhodium bond is described in terms of electron delocalization (24.59%; \( \Delta E_{ij} = 109.57 \text{ kcal⋅mol}^{-1} \)) between fragments (Figure S8, right).

In complex B', the Ge atom also accepts electron density from the Rh-H bonding orbital, i.e. the bond is delocalized on the germanium (NLMO contribution 4.8%). In complex 1 the donation from 4d orbitals of Rh to the 4p orbital of Ge is the weakest (1.49%), which is consistent with the germyl character of this species. In addition, the chloride ligand is a σ and π donor, which affects the back-donation from rhodium to germanium.

**Figure S8.** NLMOs involved in the Rh→pGe back donation and in A (left) and the germanium-rhodium interaction in 3 (right).
5. NMR spectra of new compounds

Compound 1
$^{1}H$ NMR
C$_6$D$_6$, 25°C

Compound 1
$^{13}$C NMR
C$_6$D$_6$, 25°C
Compound 2·NTf$_2$
$^1$H NMR
C$_6$D$_6$, 25°C

Compound 2·NTf$_2$
$^{13}$C NMR
C$_6$D$_6$, 25°C
Compound 2 + CHPb₃

$^1$H NMR
C₆D₆, 25°C
Compound 3
$^1$H NMR
C$_6$D$_6$, 25°C

Compound 3
$^{13}$C NMR
C$_6$D$_6$, 25°C
Compound 3-NTf$_2$ + [(PMe$_2$ArDipp)$_2$Au(n-Cl)]

$^1$H NMR
C$_6$D$_6$, 25°C
Compound 4

$^1$H NMR
CDCl$_3$, 25°C

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$^13$C NMR
CDCl$_3$, 25°C
Compound 5
$^1$H NMR
C$_6$D$_6$, 23°C

Compound 5
$^{13}$C NMR
C$_6$D$_6$, 23°C
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