

ELECTRONIC SUPPLEMENTARY INFORMATION

Influence of the volume of the NR groups of amidinate germylenes in their reactivity with ruthenium carbonyl: Isolation of a coordinatively unsaturated diruthenium(0) derivative

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General procedures. All manipulations were performed under argon using standard glove-box and Schlenk-vacuum line techniques. Solvents were dried over sodium diphenyl ketyl and distilled under nitrogen before use. The reactions were routinely monitored by solution IR spectroscopy (carbonyl stretching region). The reagents PhLi (1.8 M solution in dibutyl ether), 1,3-bis(*tert*-butyl)carbodiimide, 1-*tert*-butyl-3-ethylcarbodiimide, Li(HMDS) (1.0 M solution in hexanes) and [Ru₃(CO)₁₂] were purchased from Sigma-Aldrich; GeCl₂·dioxane was purchased from Gelest. Ge(^tBu₂zam)(HMDS) (**4**)¹ was prepared following a previously reported procedure.¹ All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run in C₆D₆ on a Bruker DPX-300 instrument; the residual protic solvent resonance [δ (C₆HD₅) 7.16 ppm] was used as reference for ¹H, while the solvent resonance [δ (C₆D₆) 128.1 ppm] was used as reference for ¹³C. Microanalyses were obtained from the University of Oviedo Microanalytical Service. Positive FAB mass spectra were obtained from the University of A Coruña Mass Spectrometric Service (30 kV Cs⁺ gun, 3-nitrobenzyl alcohol as matrix); the given MS data refer to the most abundant molecular ion isotopomer.

Ge(Etbzam^tBu)Cl: LiPh (5.4 mL of a 1.8 M solution in dibutyl ether, 9.7 mmol) was added to a cold solution (−78 °C) of 1-*tert*-butyl-3-ethylcarbodiimide (1.5 mL, 9.7 mmol) in diethyl ether (100 mL). The solution was allowed to warm up to room temperature and was then stirred for 4 h. The resulting pale orange solution was cooled down again to −78° C and then transferred dropwise with a cannula to a stirred suspension of GeCl₂·dioxane (2.23 g, 9.7 mmol) in diethyl ether (20 mL) kept at −78° C. The reaction mixture was allowed to warm up to room temperature and was then stirred for 18 h. The solvents were removed under reduced pressure and the residue was extracted with hexane (2 x 30 mL). The filtrate was evaporated to dryness under vacuum to yield

Ge(Etbzam^tBu)Cl as a pale yellow oil (2.83 g, 94 %). Anal. Calcd. for C₁₃H₁₉ClGeN₂ (MW = 311.37 amu): C, 50.15; H, 6.15; N, 9.00. Found: C, 50.25; H, 6.28; N, 8.87. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ = 7.08–6.87(m, 5 H; 5 CH of Ph), 2.76–2.68 (m, 2 H; CH₂ of Et), 1.04 (s, 9 H; Me₃ of ^tBu), 0.91 (t, *J* = 7.2 Hz, 3 H; Me of Et) ppm. ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ = 174.1 (NCN), 132.5 (C_{ipso} of Ph), 129.9 (2 CH of Ph), 128.6 (2 CH of Ph), 127.5 (CH of Ph), 53.7 (C of ^tBu), 39.6 (CH₂ of Et), 31.8 (Me₃ of ^tBu), 16.4 (Me of Et) ppm.

Ge(Etbzam^tBu)(HMDS) (5): Li(HMDS) (8.2 mL of a 1.0 M solution in hexanes, 8.2 mmol) was added to a cold (−78 °C) solution of Ge(Etbzam^tBu)Cl (2.56 g, 8.2 mmol) in diethyl ether (30 mL). The resulting suspension was allowed to warm up to room temperature and was then stirred for 12 h. The solvents were removed under reduced pressure and the residue was extracted into hexane (2 x 30 mL). The filtered extract was evaporated to dryness under vacuum to give **5** as a yellowish oily solid (3.24 g, 91 %). Anal. Calcd. for C₁₉H₃₇GeN₃Si₂ (MW = 436.30 amu): C, 52.30; H, 8.55; N, 9.63. Found: C, 52.52; H, 8.70; N, 9.59. ¹H NMR (C₆D₆, 300.1 MHz, 293 K): δ = 7.12–6.84(m, 5 H; 5 CH of Ph), 3.05–2.81 (m, 2 H; CH₂ of Et), 1.15 (s, 9 H; Me₃ of ^tBu), 1.05 ppm (t, *J* = 7.2 Hz, 3 H; Me of Et), 0.49 (s, 18 H; Me₆ of HMDS) ppm. ¹³C{¹H} NMR (C₆D₆, 75.5 MHz, 293 K): δ = 165.3 (NCN), 134.2 (C_{ipso} of Ph), 129.1 (2 CH of Ph), 128.5 (CH of Ph), 128.4 (CH of Ph), 127.4 (CH of Ph), 53.7 (C of ^tBu), 40.3 (CH₂ of Et), 32.4 (Me₃ of ^tBu), 17.3 (Me of Et), 5.8 (Me₆ of HMDS) ppm.

Reaction of Ge(^tBu₂zham)(HMDS) (4) with [Ru₃(CO)₁₂]: Germylene **4** (0.25 mL of a 0.32 M solution in toluene, 0.080 mmol) was added to a suspension of [Ru₃(CO)₁₂] (50 mg, 0.080 mmol) in toluene (10 mL) and the mixture was stirred at room temperature for 60 min. As no reaction occurred (IR analysis), the temperature was progressively raised to 90 °C. After 60 min, a complex mixture was formed (¹H NMR analysis) that could not be separated. The use of different Ru₃/Ge ratios led in all cases to complex mixtures of products that could not be identified.

[Ru₂{μ-κ²Ge,N-Ge(Etbzam^tBu)(HMDS)}(CO)₆] (6): Germylene **5** (3.2 mL of a 0.38 M solution in toluene, 1.20 mmol) was added to a suspension of [Ru₃(CO)₁₂] (0.5 g, 0.8 mmol) in toluene (20 mL) and the mixture was heated at 90 °C for 2 h. The initial orange color changed to dark red. Purification by flash chromatography (2 x 5 cm silica gel column packed in hexane) with hexane as eluant furnished compound **6** as a dark orange solid (620 mg, 64 %). Leaving to stand a concentrated solution of **6** in hexane at −20 °C afforded suitable crystals for X-ray crystallographic analysis. Anal. Calcd. for C₂₅H₃₇GeN₃O₆Ru₂Si₂ (MW = 806.50 amu): C, 37.23; H, 4.62; N, 5.21. Found: C, 37.53; H, 4.50; N, 4.89. (+)-FAB MS: *m/z* = 751 [*M* − 2CO]⁺. IR (toluene): ν_{CO} = 2073 (m), 2000 (vs), 1985 (s), 1977 (m), 1992 (m), 1924 (m) cm^{−1}. ¹H NMR (C₆D₆, 300.1 MHz, 293 K):

$\delta = 7.14\text{--}6.78$ (m, 5 H; 5 CH of Ph), 3.39 (m, 1 H; CH of Et), 2.42 (m, 1 H; CH of Et), 0.86 (s, 9 H; Me_3 of t Bu), 0.84 (t, $J = 7.2$ Hz, 3 H; Me of Et), 0.45 (s, 9 H; Me_3 of HMDS) 0.43 (s, 9 H; Me_3 of HMDS) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 293 K): $\delta = 203.6$ (COs), 203.0 (CO), 197.7 (CO), 164.4 (NCN), 135.8 (C_{ipso} of Ph), 128.9 (2 CH of Ph), 128.7 (CH of Ph), 128.1 (CH of Ph), 127.5 (CH of Ph), 63.6 (C of t Bu), 40.0 (CH_2 of Et), 27.1 (Me_3 of t Bu), 17.9 (Me of Et), 6.4 (Me_3 of HMDS), 4.8 (Me_3 of HMDS) ppm.

$\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge}, N\text{-Ge}(\text{Et}bzam^t\text{Bu})(\text{HMDS})\}(\text{CO})_7$ (7): Carbon monoxide was gently bubbled for 15 min through a solution of complex **6** (56 mg, 0.069 mmol) in toluene (8 mL) at room temperature. The initial dark red-orange color changed to red. An IR spectrum of this solution confirmed the quantitative formation of complex **7**. This product was only characterized in solution because it loses CO rapidly, regenerating complex **6** upon removal of the CO atmosphere. IR (toluene): $\nu_{\text{CO}} = 2085$ (m), 2033 (s), 2014 (m), 2004 (s), 1994 (m), 1977 (w), 1956 (w) cm^{-1} . ^1H NMR (C_6D_6 , 300.1 MHz, 293 K, CO atmosphere): $\delta = 7.13\text{--}6.84$ (m, 5 H; 5 CH of Ph), 3.47 (m, 1 H, CH of Et), 2.43 (m, 1 H, CH of Et), 1.11 (s, 9 H, Me_3 of t Bu), 0.81 (t, $J = 7.1$ Hz, 3 H; Me of Et), 0.47 (s, 9 H; Me_3 of HMDS) 0.42 (s, 9 H, Me_3 of HMDS) ppm.

$[\text{Ru}_2\{\mu\text{-}\kappa^2\text{Ge}, N\text{-Ge}(\text{Et}bzam^t\text{Bu})(\text{HMDS})\}(\mu\text{-H})(\text{SnPh}_3)(\text{CO})_5]$ (8): Solid HSnPh_3 (33 mg, 0.094 mmol) was added to a solution of complex **6** (30 mg, 0.037 mmol) in toluene (10 mL) and the resulting solution was stirred at room temperature for 1 h. The initial orange color changed to dark orange. The solvent was removed under reduced pressure and the crude reaction mixture was separated by column chromatography on silica-gel (2 x 5 cm). Compound **8** was eluted with hexane/ CH_2Cl_2 (1:1) and was isolated as an orange solid (38 mg, 91 %). Anal. Calcd. for $\text{C}_{42}\text{H}_{53}\text{GeN}_3\text{O}_5\text{Ru}_2\text{Si}_2\text{Sn}$ (MW = 1129.52 amu): C, 44.66; H, 4.73; N, 3.72; found: C, 4.69; H, 4.84; N, 3.66. (+)-FAB MS: $m/z = 1129$ [M] $^+$. IR (toluene): $\nu_{\text{CO}} = 2071$ (w), 2013 (vs), 1995 (m), 1944 (m) cm^{-1} . ^1H NMR (C_6D_6 , 300.1 MHz, 293 K): $\delta = 8.05\text{--}7.92$ (m sat, 6 H; CH_{ortho} of Ph), 7.30 (t, $J = 7.1$ Hz, 6 H; CH_{meta} of Ph), 7.11–6.90 (m, 8 H; CH of Ph), 3.46 (m, 1 H; CH of Et), 2.40 (m, 1 H, CH of Et), 0.97 (t, $J = 7.0$ Hz, 3 H; Me of Et), 0.68 (s, 9 H; Me_3 of t Bu), 0.47 (s, 9 H; Me_3 of HMDS) 0.40 (s, 9 H; Me_3 of HMDS), -10.50 (s sat, 1 H; Ru–H–Ru) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz, 293 K): $\delta = 202.7$ (CO), 200.5 (CO), 198.2 (CO), 197.3 (CO), 195.7 (CO), 164.7 (NCN), 144.7 (C_{ipso} of Ph), 137.9–125.7 (Ph groups of germylene and SnPh_3 ligands), 63.6 (C of t Bu), 41.1 (CH_2 of Et), 27.9 (Me_3 of t Bu), 17.7 (Me of Et), 6.0 (Me_3 of HMDS), 5.4 (Me_3 of HMDS) ppm.

X-Ray diffraction analyses of **6 and **8**· C_7H_8 :** Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer. Empirical absorption corrections

were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.² The structure was solved using SIR-97.³ Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.⁴ All non-H atoms were refined anisotropically. The crystal of **6** was found to contain two symmetry-independent but analogous molecules in the asymmetric unit. The toluene molecule of **8**·C₇H₈ was found disordered over two positions with a 63:37 occupancy ratio. The H atoms of the methyl groups that are close to Ru1 (C3 for **6** and **8**·C₇H₈) and Ru3 (C21 for **6**) and the hydride ligand of **8**·C₇H₈ were located in Fourier difference maps and were freely refined. All remaining H atoms were set in calculated positions and refined riding on their parent atoms. The WINGX program system⁵ was used throughout the structure determination. The molecular plots were made with MERCURY.⁶ A selection of crystal, measurement and refinement data is given in Table SI-1. CCDC deposition numbers: 999866 (**6**) and 1001195 (**8**·C₇H₈).

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- 1 P. P. Samuel, A. P. Singh, S. P. Sarish, J. Matussek, I. Objartel, H. W. Roesky and D. Stalke, *Inorg. Chem.*, 2013, **52**, 1544.
 - 2 *CrysAlisPro RED*, version 1.171.34.36, Oxford Diffraction Ltd., Oxford, UK, 2010.
 - 3 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. C. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
 - 4 *SHELXL*: G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
 - 5 *WINGX*, version 1.80.05 (2009): L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
 - 6 *MERCURY*, CSD 3.1 (build RC5), Cambridge Crystallographic Data Centre, 2013.

Table SI-1 X-ray crystal, measurement and refinement data for compounds **6** and **8·C₇H₈**.

	6	8·C₇H₈
formula	C ₂₅ H ₃₇ GeN ₃ O ₆ Ru ₂ Si ₂	C ₄₂ H ₅₃ GeN ₃ O ₅ Ru ₂ Si ₂ Sn·C ₇ H ₈
fw	806.46	1221.61
cryst syst	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	12.0005(3),	13.0728(5),
<i>b</i> , Å	17.7747(3)	13.3171(4)
<i>c</i> , Å	17.9712(4)	17.1692(5)
α , deg	102.810(2)	73.514(3)
β , deg	102.108(2)	72.315(3)
γ , deg	94.844(2)	72.066(3)
<i>V</i> , Å ³	3396.0(1)	2649.1(2)
<i>Z</i>	4	2
<i>F</i> (000)	1616	1228
<i>D</i> _{calcd} , g cm ⁻³	1.577	1.532
μ (Cu K α), mm ⁻¹	9.157	9.680
cryst size, mm	0.20 x 0.06 x 0.05	0.24 x 0.09 x 0.08
<i>T</i> , K	153(4)	154(4)
θ range, deg	2.98 to 68.00	3.57 to 67.98
min./max. <i>h</i> , <i>k</i> , <i>l</i>	-14/14, -21/21, -21/21	-15/14, -15/11, -20/15
no. collected reflns	30345	19749
no. unique reflns	12298	9561
no. reflns with <i>I</i> > 2 σ (<i>I</i>)	11667	8416
no. params/restraints	731/0	659/0
GOF (on <i>F</i> ²)	1.030	1.034
<i>R</i> ₁ (on <i>F</i> , <i>I</i> > 2 σ (<i>I</i>))	0.022	0.025
<i>wR</i> ₂ (on <i>F</i> ² , all data)	0.060	0.062
min./max. $\Delta\rho$, e Å ⁻³	-0.633/1.144	-0.573/0.627

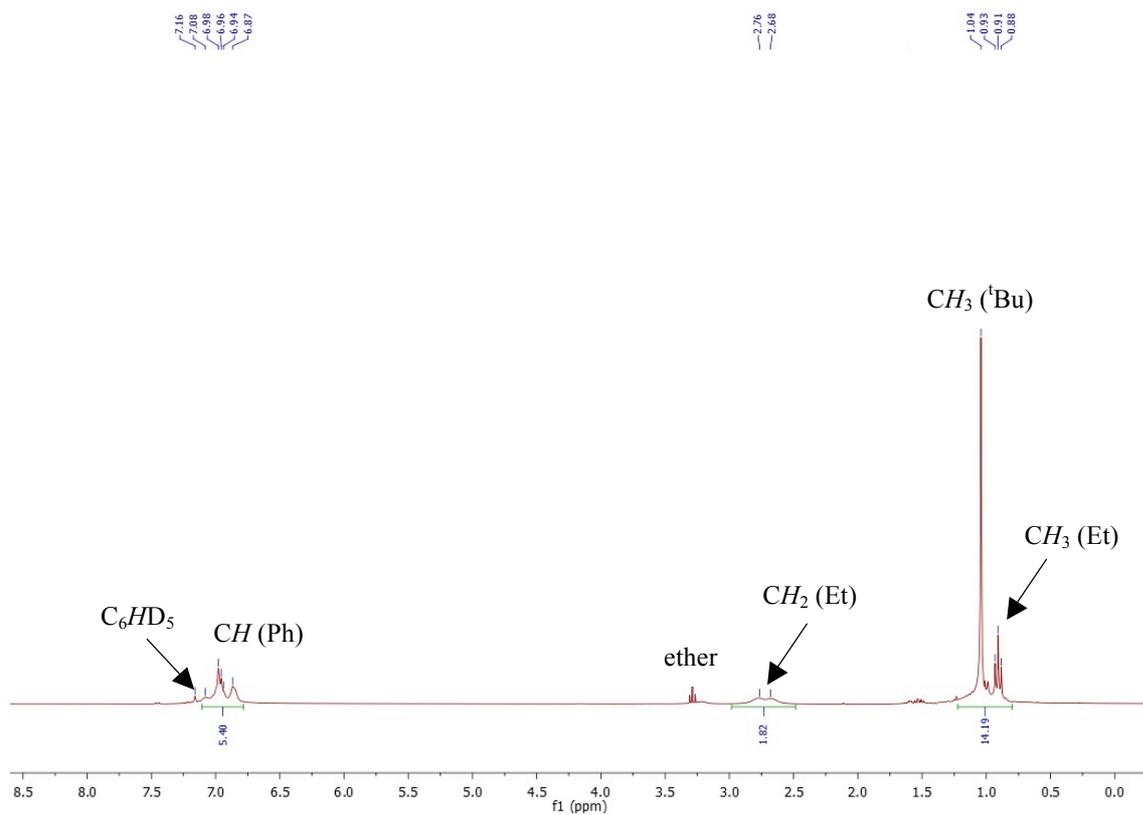


Fig SI-1 ^1H NMR spectrum of $\text{Ge}(\text{Etbzam}'\text{Bu})\text{Cl}$ (C_6D_6 , 25 $^\circ\text{C}$, 300.1 MHz).

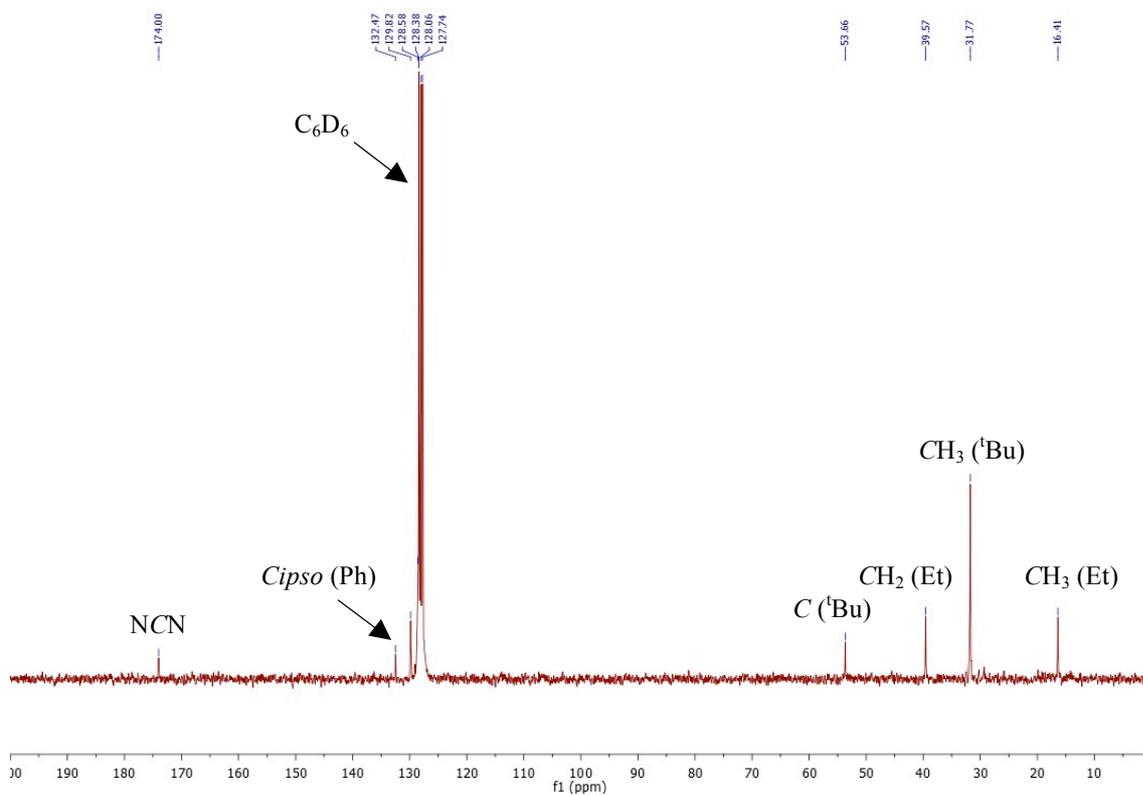


Fig SI-2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ge}(\text{Etbzam}'\text{Bu})\text{Cl}$ (C_6D_6 , 25 $^\circ\text{C}$, 75.5 MHz).

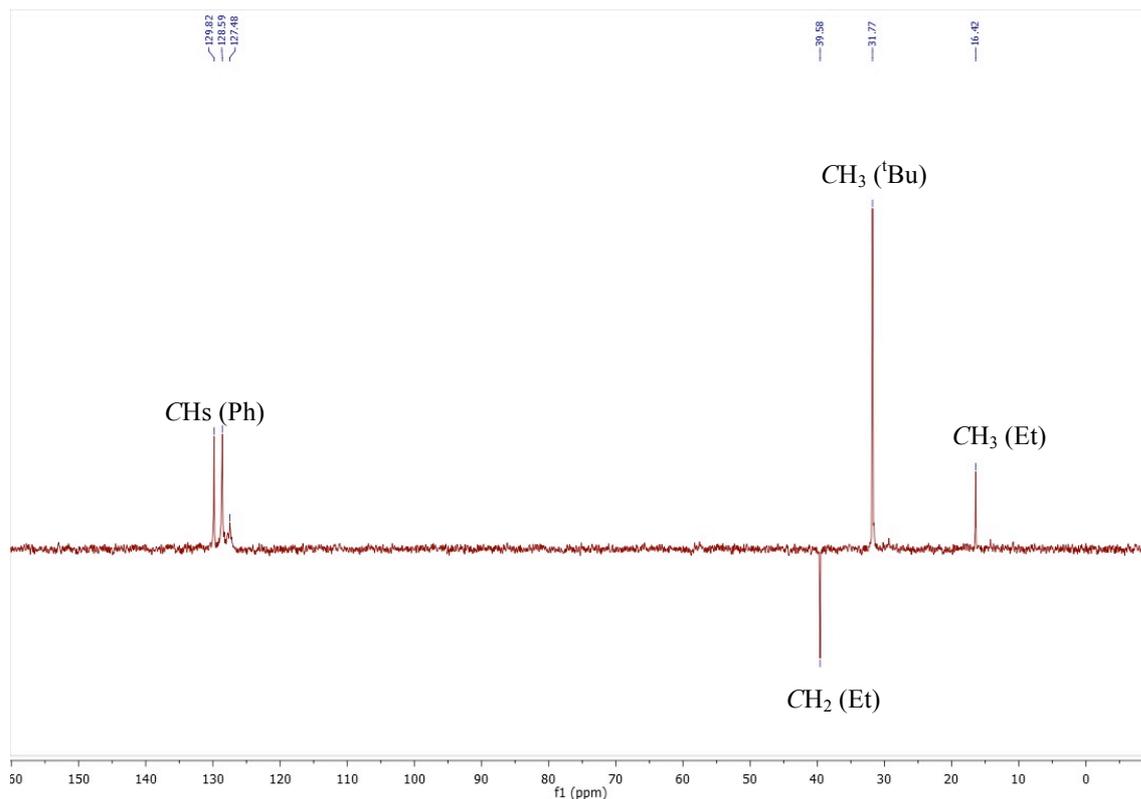


Fig SI-3 ¹³C DEPT-135 NMR spectrum of Ge(Etbzam^tBu)Cl (C₆D₆, 25 °C, 75.5 MHz).

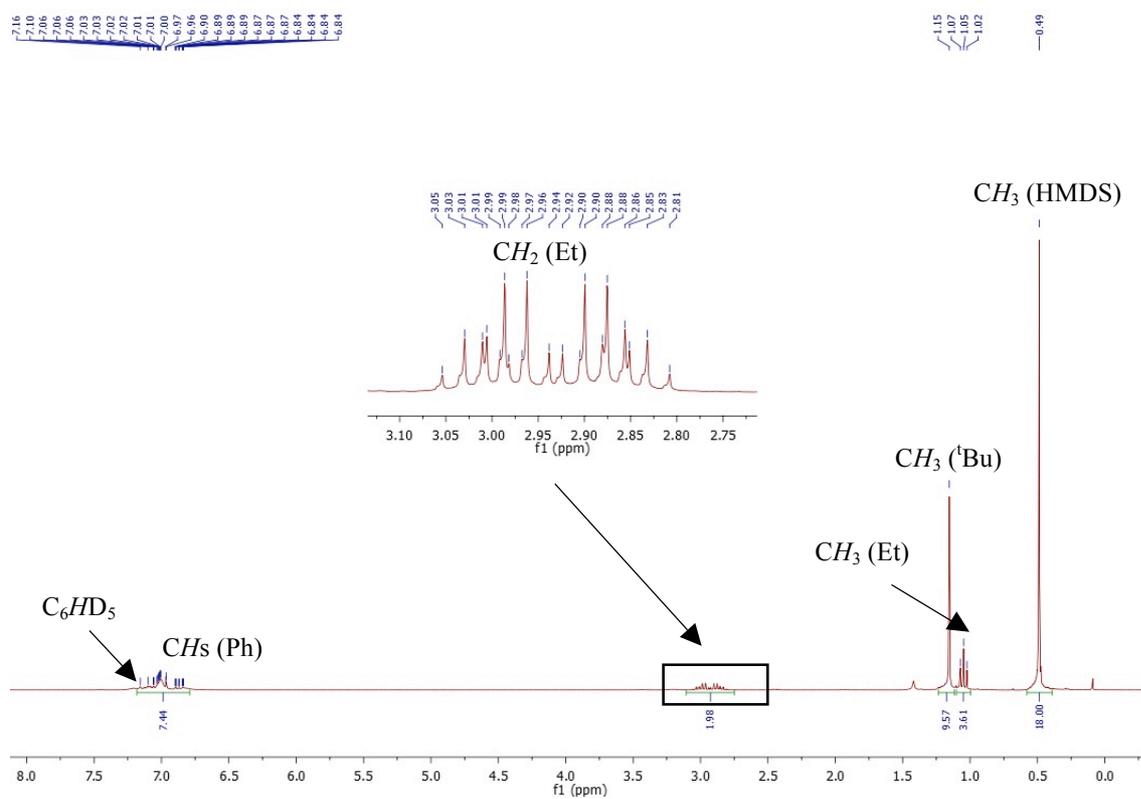


Fig SI-4 ¹H NMR spectrum of germylene **5** (C₆D₆, 25 °C, 300.1 MHz).

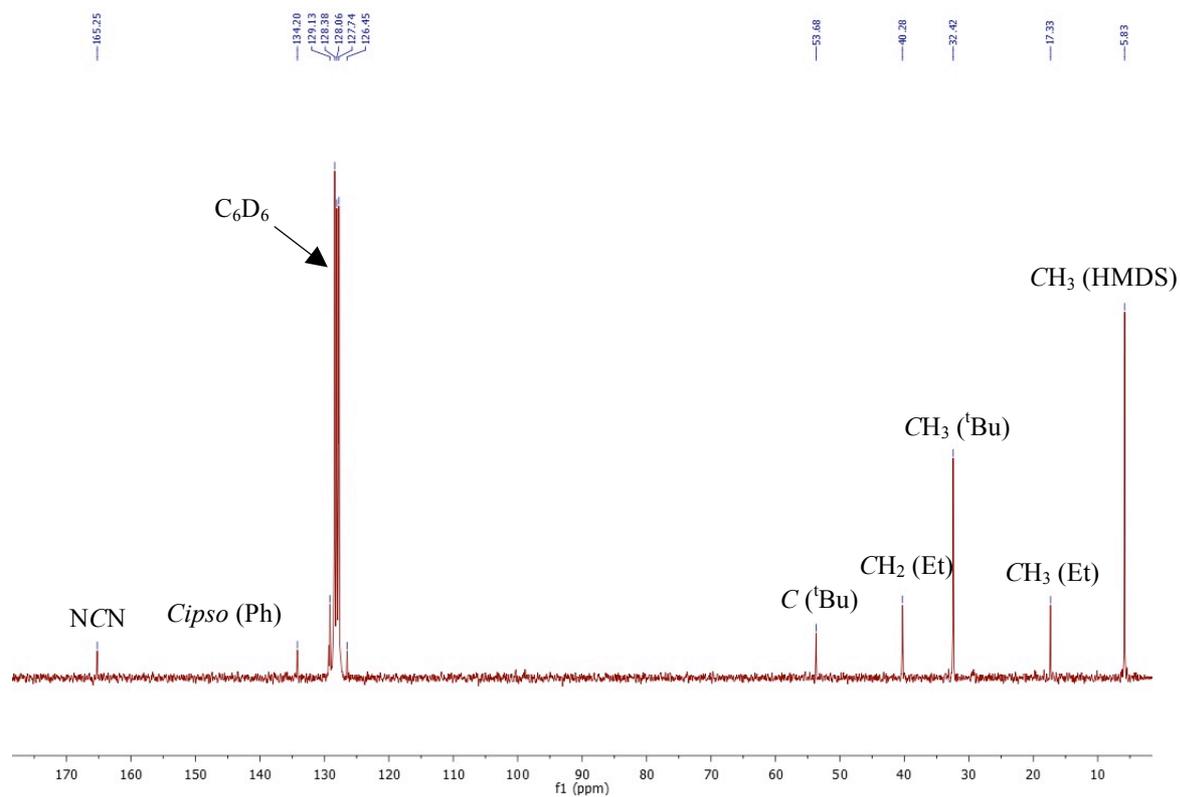


Fig SI-5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of germylene **5** (C_6D_6 , 25 °C, 75.5 MHz).

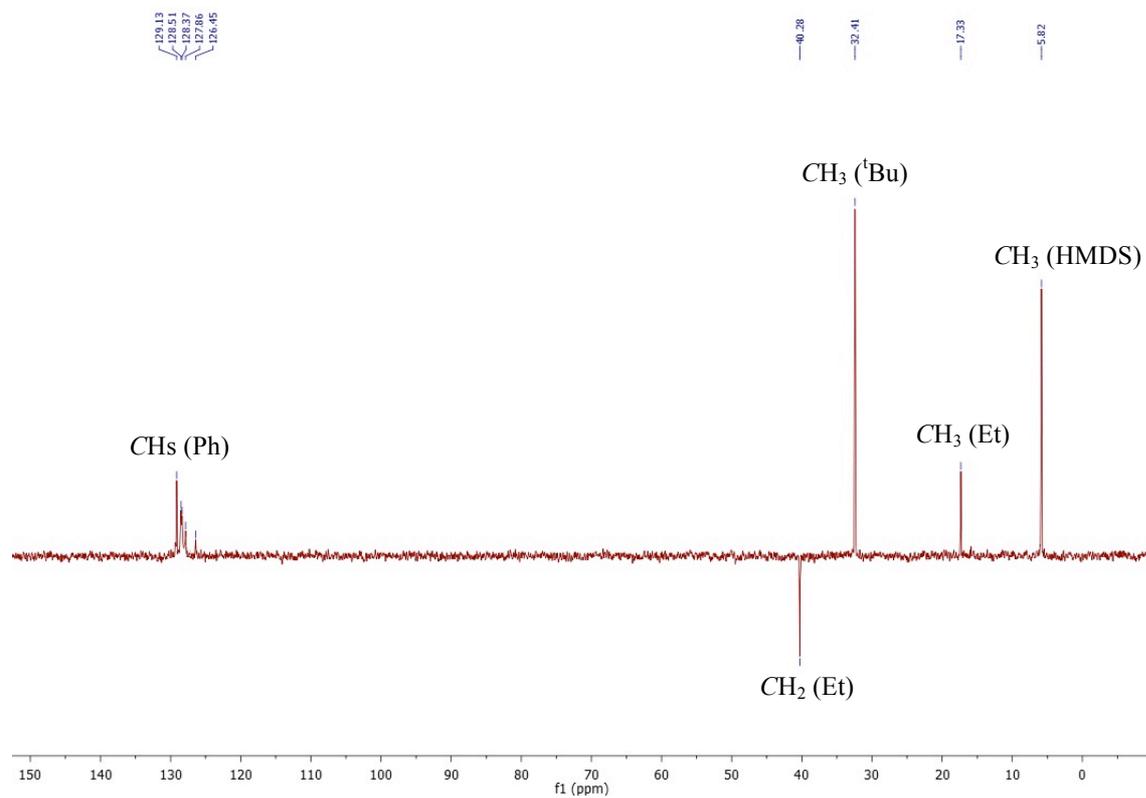


Fig SI-6 ^{13}C DEPT-135 NMR spectrum germylene **5** (C_6D_6 , 25 °C, 75.5 MHz).

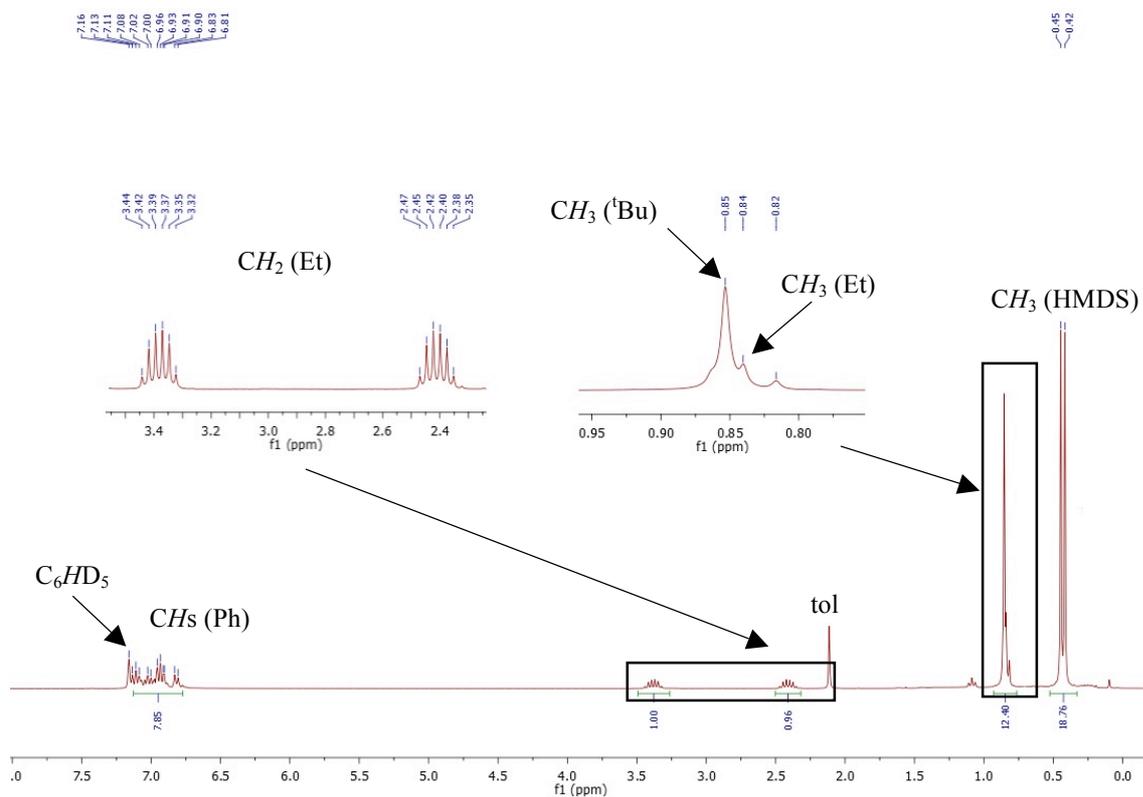


Fig SI-7 ^1H NMR spectrum of complex **6** (C_6D_6 , 25 $^\circ\text{C}$, 300.1 MHz).

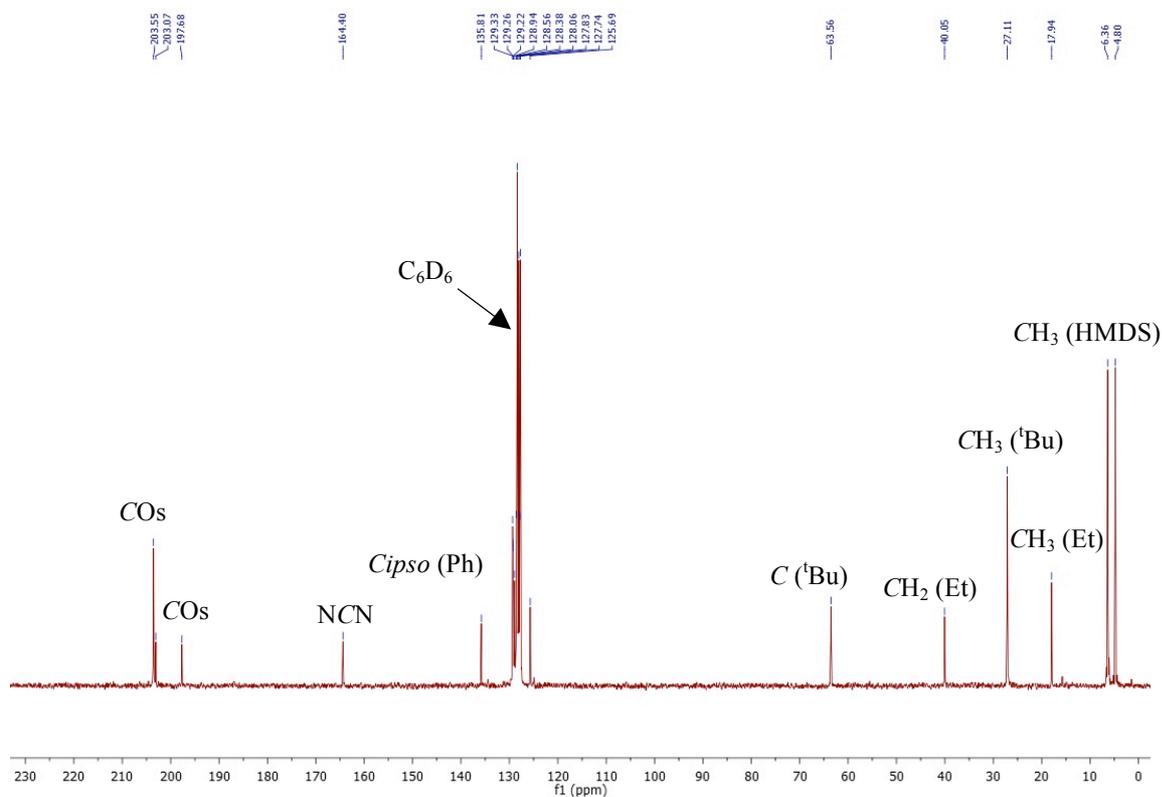


Fig SI-8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6** (C_6D_6 , 25 $^\circ\text{C}$, 75.5 MHz).

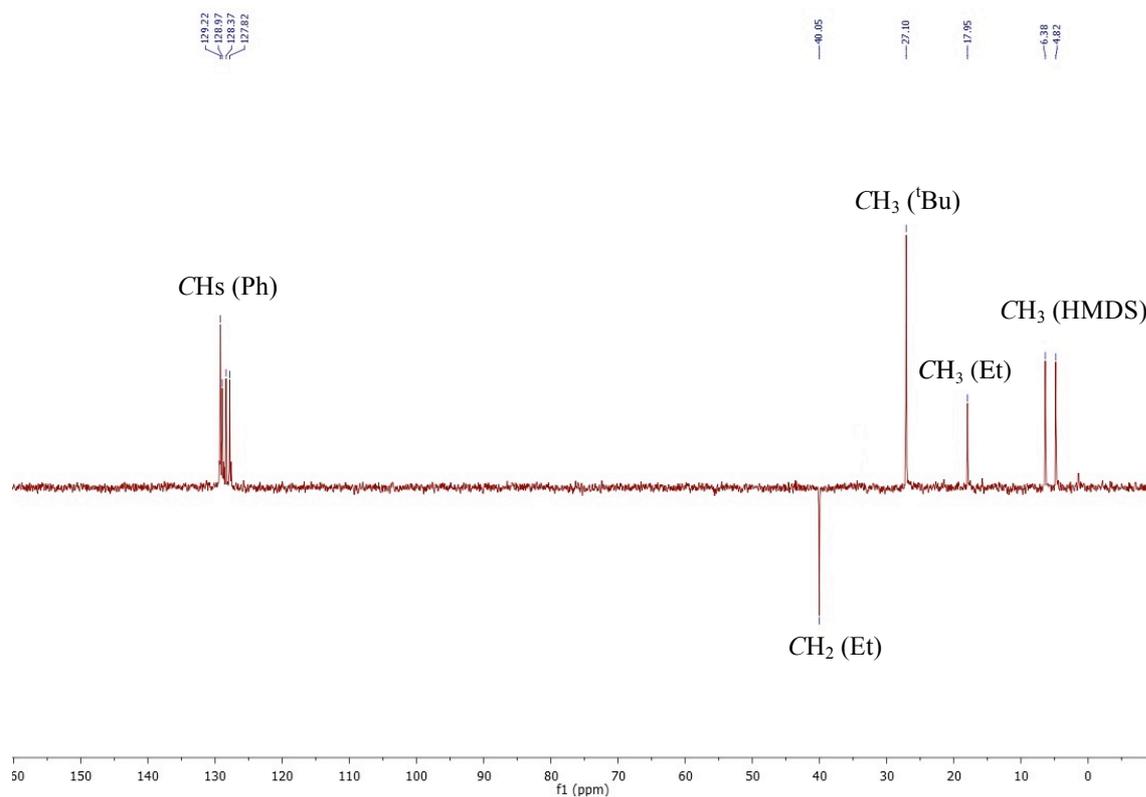


Fig SI-9 ¹³C DEPT-135 NMR spectrum complex **6** (C₆D₆, 25 °C, 75.5 MHz).

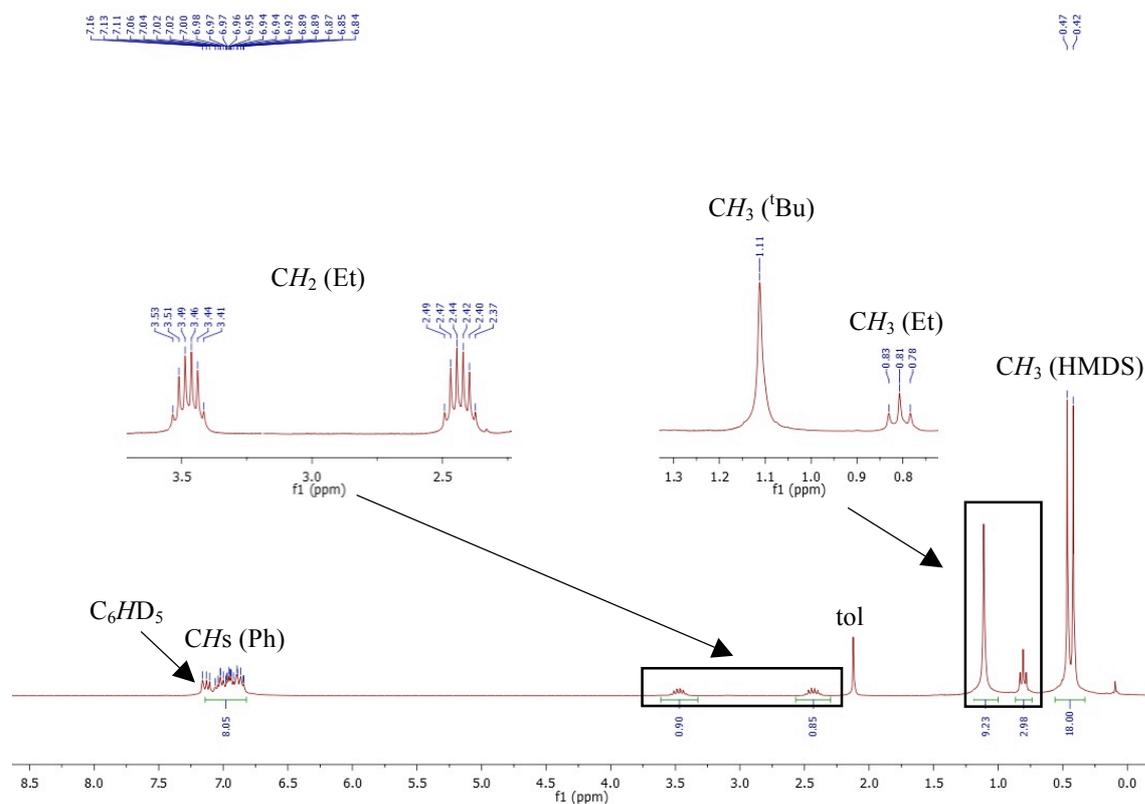


Fig SI-10 ¹H NMR spectrum of complex **7** (C₆D₆, 25 °C, 300.1 MHz, CO atmosphere).

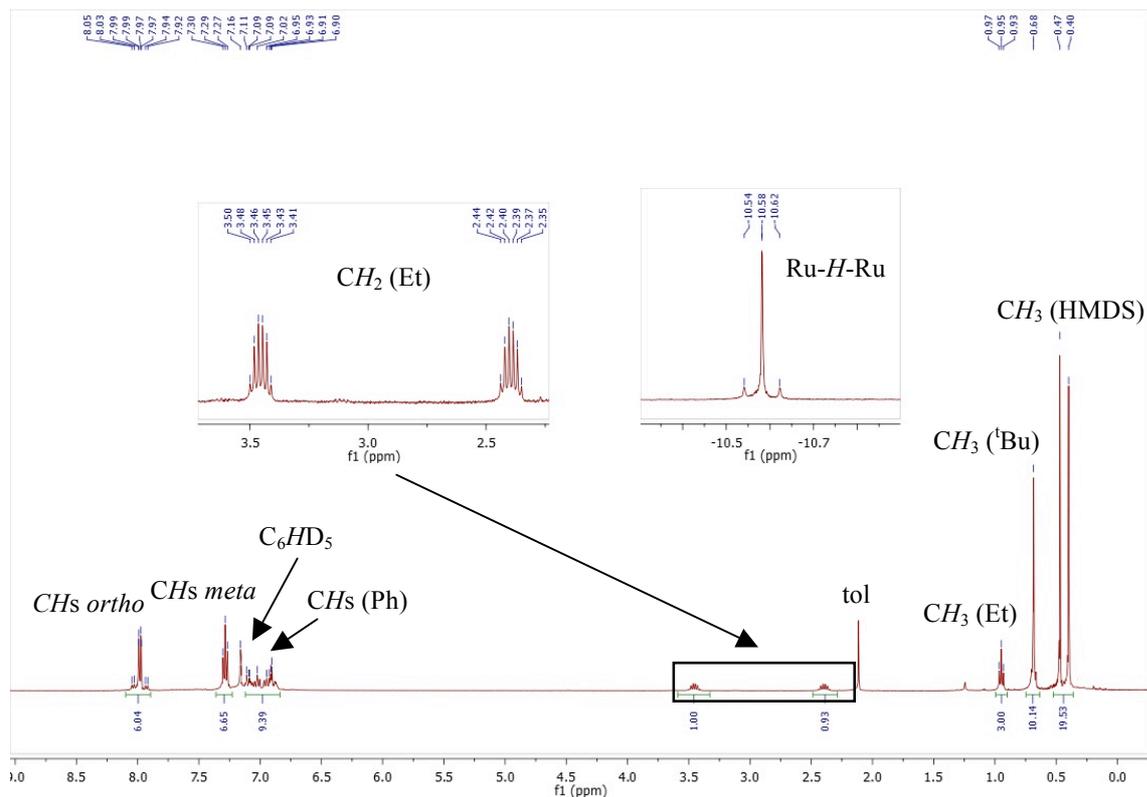


Fig SI-11 ¹H NMR spectrum of complex **8** (C₆D₆, 25 °C, 300.1 MHz).

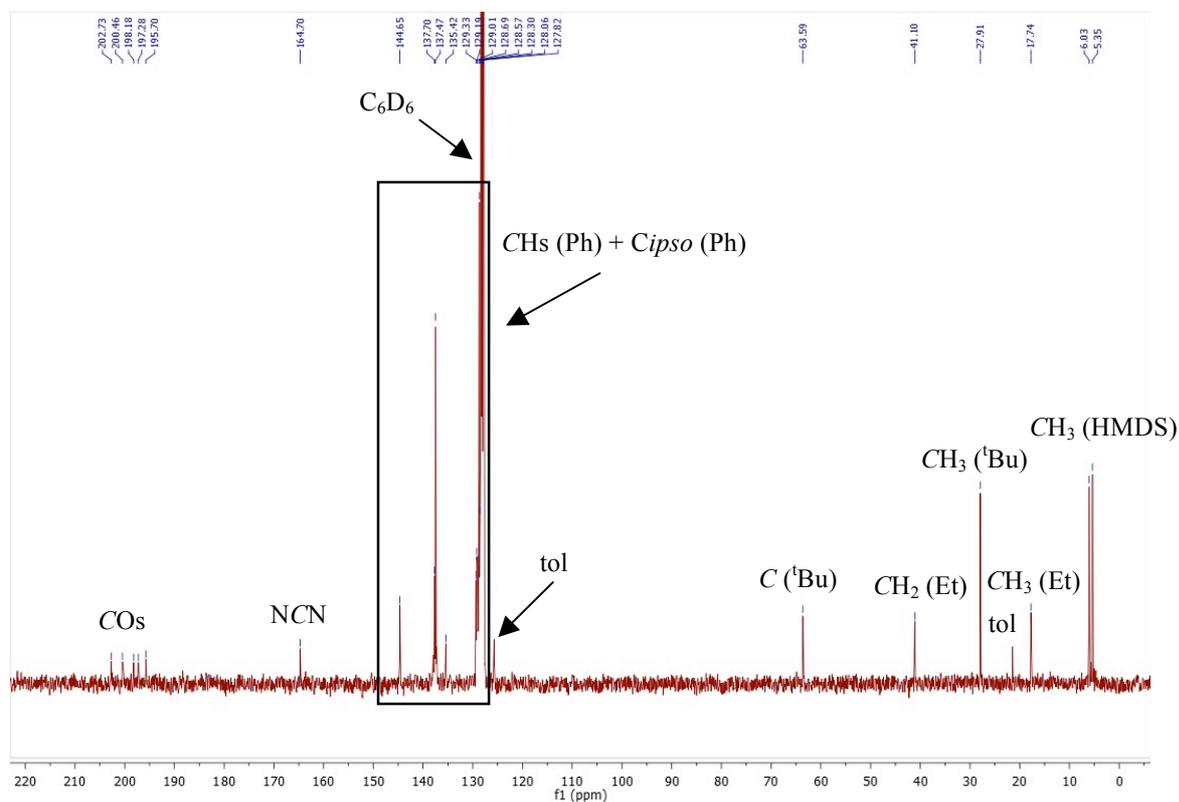


Fig SI-12 ¹³C{¹H} NMR spectrum of complex **8** (C₆D₆, 25 °C, 75.5 MHz).

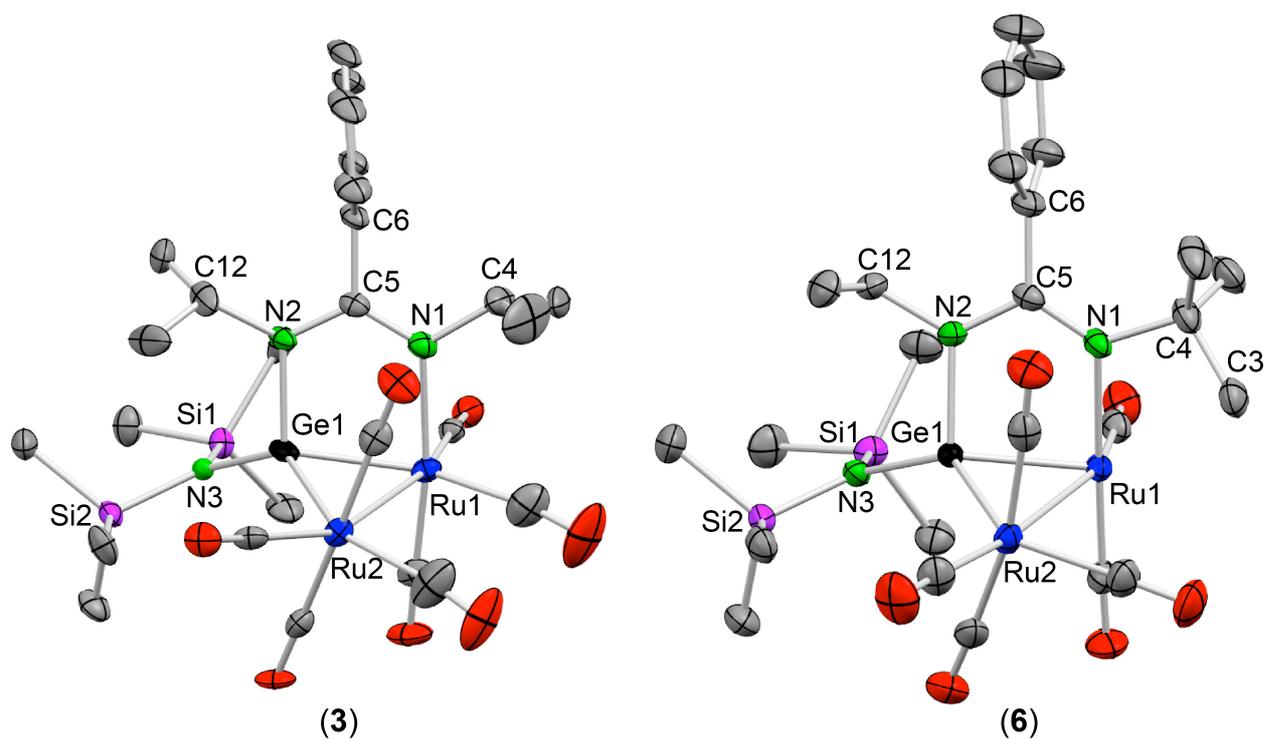


Fig SI-13 Comparative ORTEP views of the molecular structures of complexes **3** and **6**.

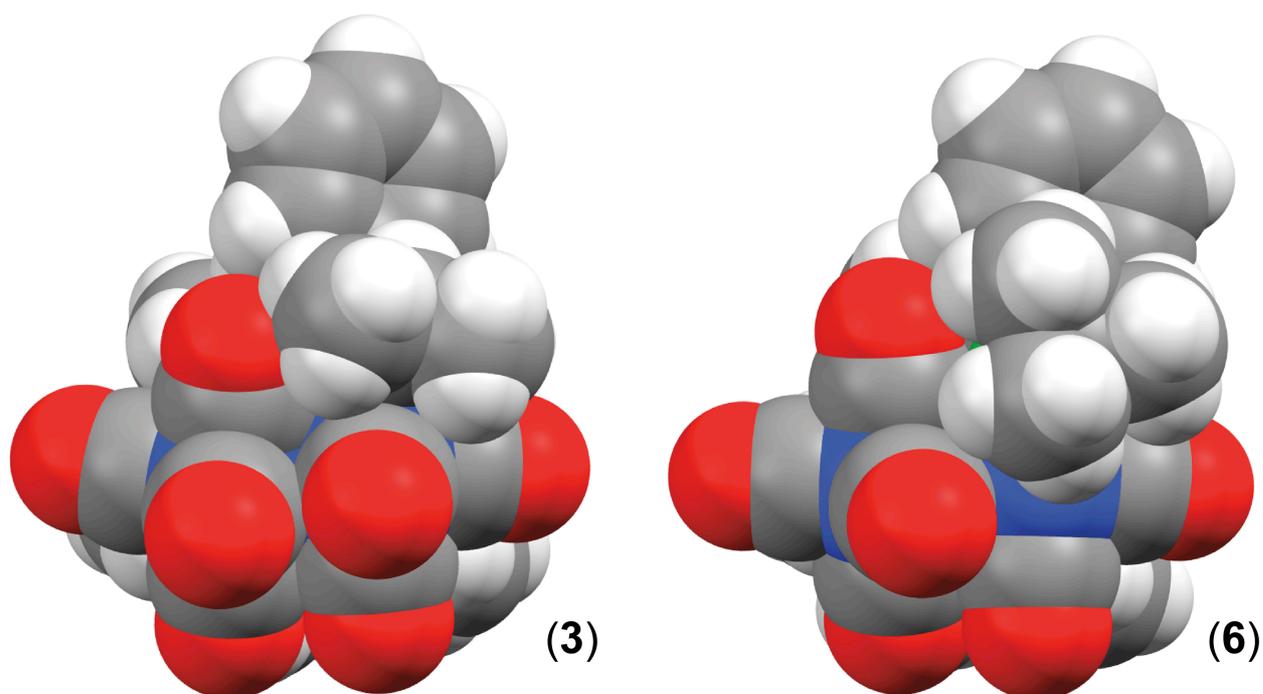


Fig SI-14 Comparative space-filling views of the molecular structures of complexes **3** and **6**, showing that atom Ru1 of **6** is only partially protected by a *tert*-butyl methyl group.

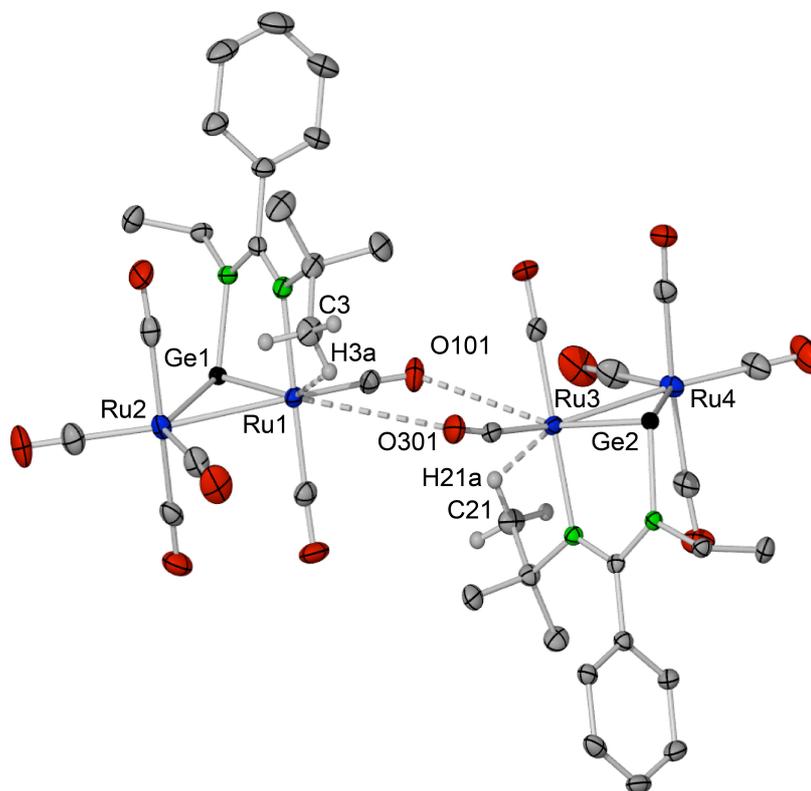


Fig SI-15 The molecular pair found in the crystals of complex **6**. All H atoms (except those attached to C3 and C21) have been omitted for clarity. The Ru1–O301 and Ru3–O101 distances are 4.252(2) Å and 3.599(2) Å, respectively. The Ru1–H3a and Ru3–H21a distances are 2.21(4) Å and 2.27(4) Å, respectively.

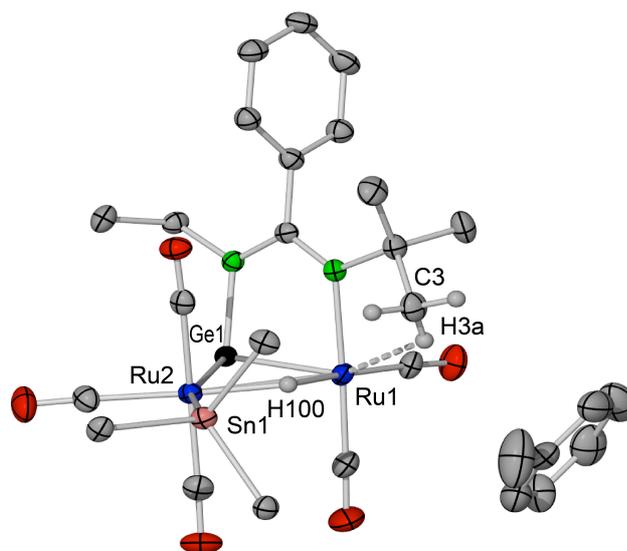


Fig SI-16 Structure **8**·C₇H₈. The HMDS fragment, the SnPh₃ phenyl groups (except the C_{ipso} atoms) and all H atoms (except the hydride and those attached to C3) have been omitted for clarity. Only one of the two positions in which the toluene molecule was found to be disordered is depicted. The Ru1–H3a distance is 2.26(4) Å.