ELECTRONIC SUPPLEMENTARY INFORMATION

for

Expanding the coordination chemistry of donor-stabilized group-14 Metalenes

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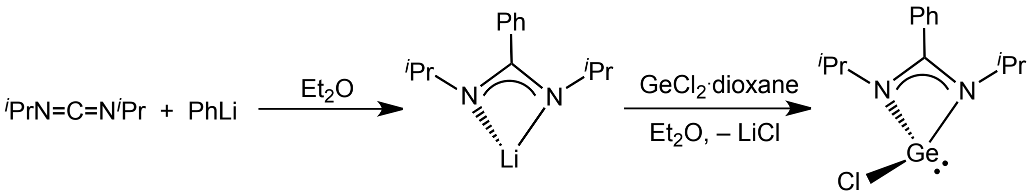
General methods

All manipulations were performed under nitrogen gas using standard glove-box and Schlenk-vacuum line techniques. Solvents were dried over sodium diphenyl ketyl (hexane, diethyl ether, toluene) and distilled under nitrogen before use. PhLi (1.8 M solution in dibutyl ether), Li(HMDS) (1.0 M solution in hexanes), *N,N'*-bis(*iso*-propyl)carbodiimide, $GeCl_2$·dioxane and $[Co_2(CO)_8]$ were purchased from Aldrich Chemicals. $[Ru_3(CO)_{12}]$ was prepared following a published method.[1] The reactions were routinely monitored by solution IR spectroscopy (carbonyl stretching region; Perkin-Elmer Paragon 1000) and spot TLC (silica gel). All reaction products were vacuum-dried for several hours prior to being weighed and analysed. NMR spectra were run on 300 MHz Bruker DPX-300 and Bruker AV-300, using as standards a protic residual solvent resonance for ^1H [$\delta(C_6\mathit{H}D_5) = 7.16$] and a solvent resonance for ^{13}C [$\delta(\mathit{C}_6D_6) = 128.1$]. Microanalyses were obtained from the University of Oviedo Microanalytical Service (Perkin-Elmer 2400 instrument). FAB mass spectra of pure samples of **2** and **3** were obtained from the University of A Coruña Mass Spectrometric Service (VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; positive ions were produced with a standard Cs^+ gun at *ca.* 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix). In all cases, the given MS data refer to the most abundant molecular ion isotopomer.

Synthesis and characterization of GeCl{PhC(N^{i}Pr)$_2$}

PhLi (10.8 mL, 19.4 mmol, 1.8 M in dibutyl ether) was added to a solution of *N,N'*-bis(*iso*-propyl)carbodiimide (3.0 mL, 19.4 mmol) in diethyl ether (100 mL) at −78° C. The solution was allowed to warm up to room temperature and then stirred for 4 h. The resulting pale yellow solution was cooled down again to −78° C and then added dropwise to a stirred suspension of $GeCl_2$·dioxane (4.49 g, 19.4 mmol) in diethyl ether (20 mL) at −78° C. The reaction mixture was allowed to warm up to room temperature and then stirred for 3 days. The precipitated LiCl was filtered off, the solvent was removed, and the resulting residue was extracted into hexane (2 x 30 mL). Solvent removal allowed the isolation of GeCl{PhC(N^{i}Pr)$_2$} as a white powder (5.35 g, 89 %).



Anal. Calcd. for $C_{13}H_{19}ClGeN_2$ (311.37): C, 50.15; H, 6.15; N, 9.00. Found: C, 50.21; H, 6.26; N, 8.87. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ = 7.00–6.87 (m, 5 H, 5 C*H* of Ph), 3.32 (sept, *J* = 6.3 Hz, 2 H, 2 C*H* of ^{i}Pr), 1.11 (d, *J* = 6.3 Hz, 6 H, 2 CH_3 of ^{i}Pr), 0.90 (d, *J* = 6.3 Hz, 6 H, 2 CH_3 of ^{i}Pr). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ = 172.7 (N*C*N), 140.3 (C_{ipso} of Ph), 130.2 (*C*H of Ph), 129.0 (2 *C*H of Ph), 127.2 (2 *C*H of Ph), 47.2 (2 *C*H of ^{i}Pr), 25.4 (2 *C*H_3 of ^{i}Pr), 24.2 (2 *C*H_3 of ^{i}Pr).

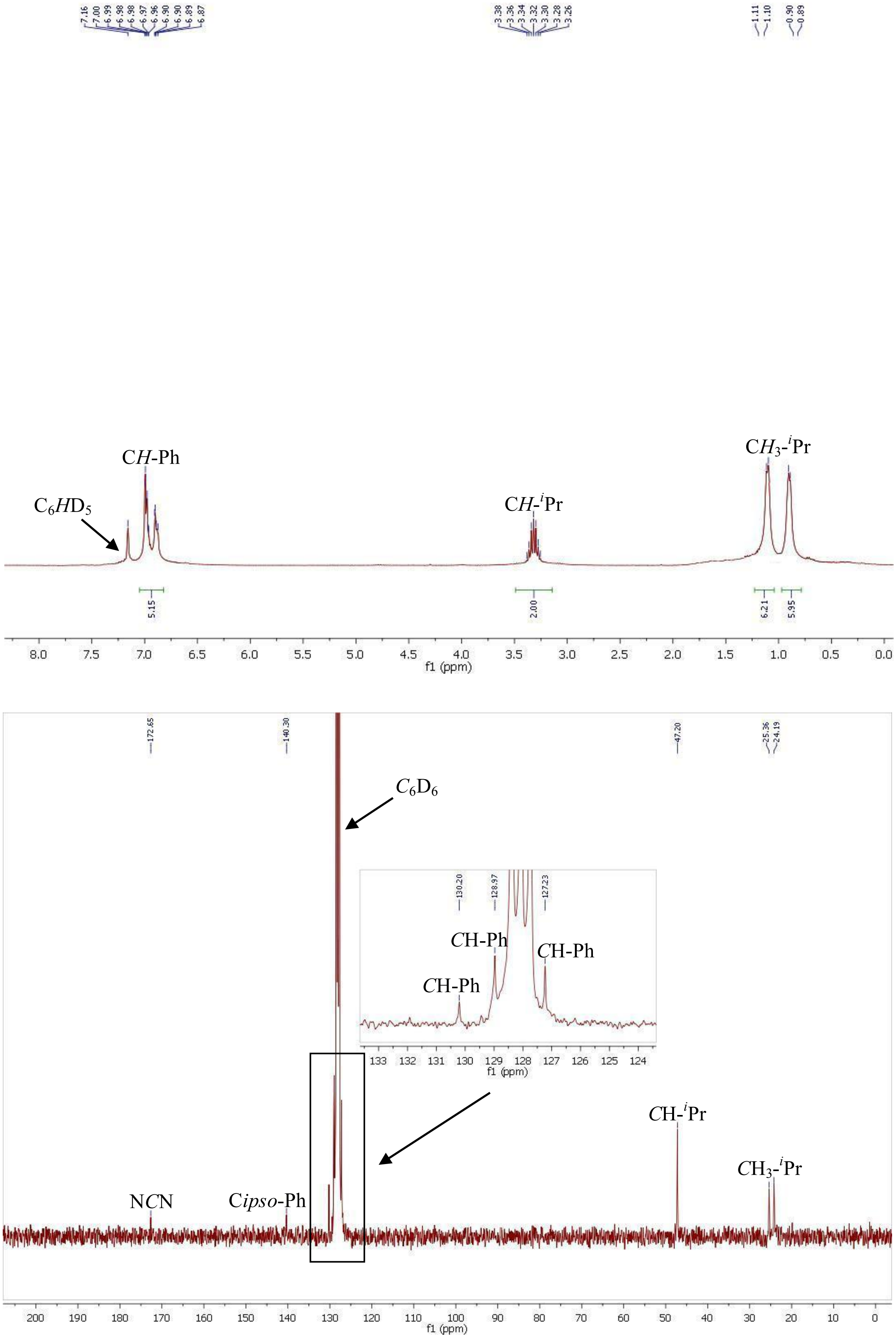
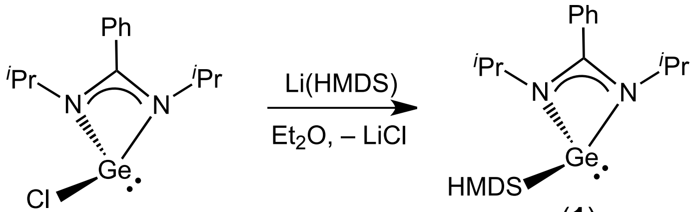


Figure S1. ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of GeCl{PhC(N^{i}Pr)$_2$} in C_6D_6 (20 °C).

Synthesis and characterization of Ge(HMDS){PhC(N^{i}Pr)$_2$} (1)

Li(HMDS) (12.8 mL, 1.0 M in hexanes, 12.80 mmol) was added to a solution of GeCl{PhC(N^{i}Pr)$_2$} (4.00 g, 12.80 mmol) in diethyl ether (30 mL) at −78 ºC. The resulting suspension was allowed to warm up to room temperature and then stirred for 12 h. The solvents were removed under reduced pressure and the residue was extracted into hexane (2 x 30 mL). The solvent of the filtrate was removed to give **1** as a yellowish oily material (4.75 g, 85 %).



(**1**)

Anal. Calcd. for $C_{19}H_{37}GeN_3Si_2$ (436.30): C, 52.30; H, 8.55; N, 9.63. Found: C, 52.52; H, 8.70; N,9.59. ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ = 7.05 (s, br, 5 H, 5 C*H* of Ph), 3.41 (sept, *J* = 6.4 Hz, 2 H, 2 C*H* of ^{i}Pr), 1.12 (d, *J* = 6.4 Hz, 6 H, 2 CH_3 of ^{i}Pr), 1.11 (d, *J* = 6.4 Hz, 6 H, 2 CH_3 of ^{i}Pr), 0.51 (s, 18 H, 6 CH_3 of HMDS). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ = 164.6 (N*C*N), 134.9 (C_{ipso} of Ph), 129.5 (*C*H of Ph), 129.0 (2 *C*H of Ph), 127.2 (2 *C*H of Ph), 47.5 (2 *C*H of ^{i}Pr), 27.2 (2 CH_3 of ^{i}Pr), 24.5 (2 CH_3 of ^{i}Pr), 5.9 (6 CH_3 of HMDS).

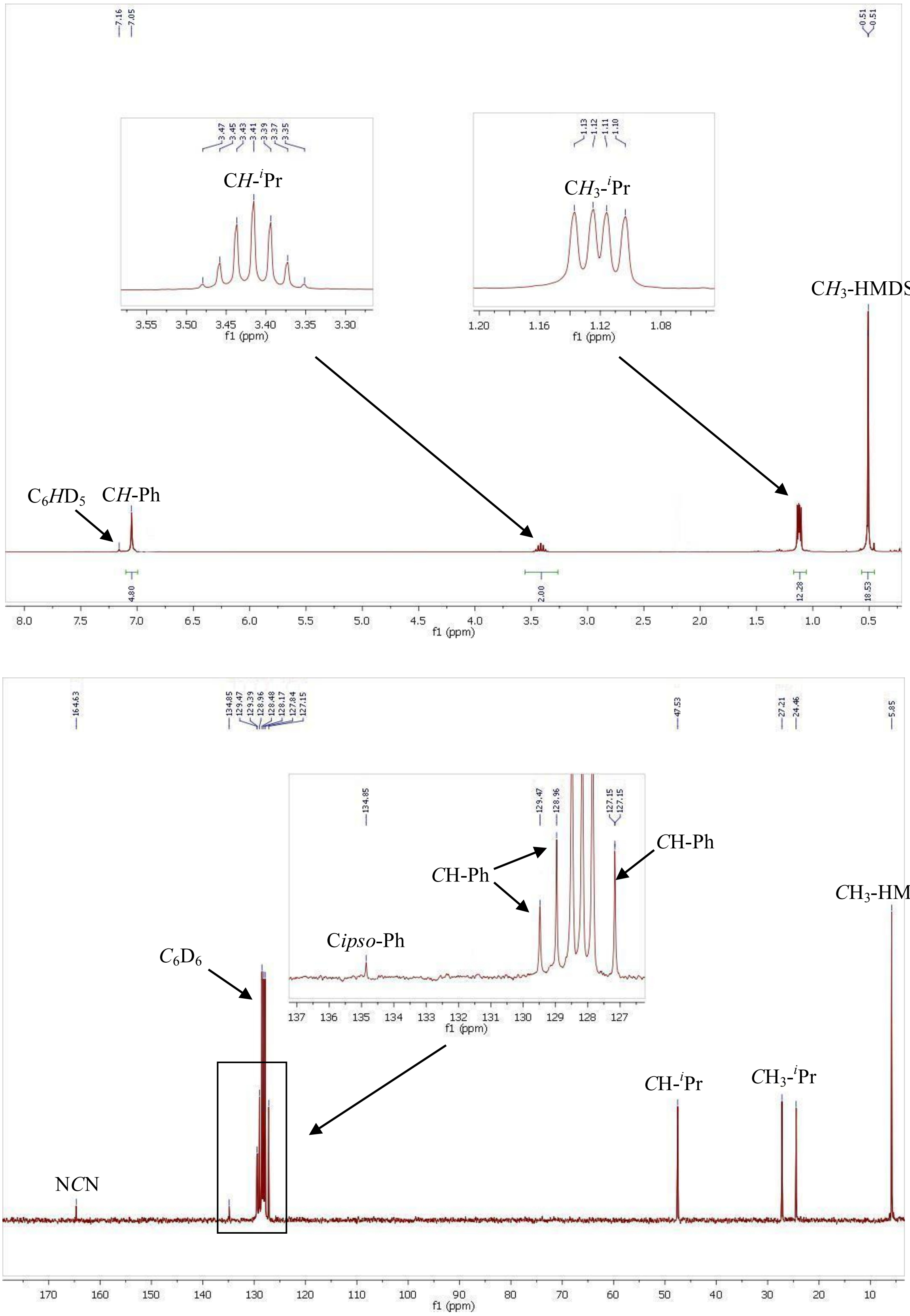
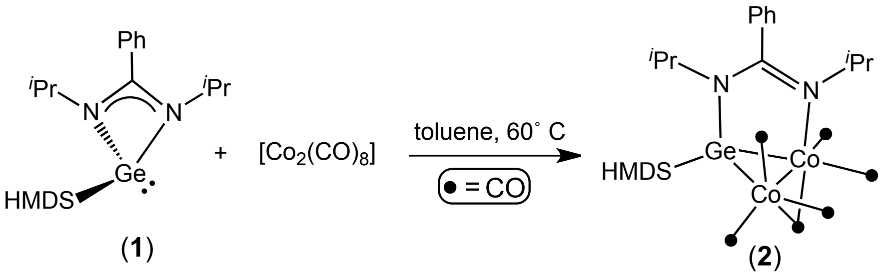


Figure S2. ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of **1** in C_6D_6 (20 °C).

Synthesis and characterization of $[Co_2\{\mu\text{-}\kappa^2 Ge,N\text{-}Ge(HMDS)(PhC(N^iPr)_2)\}(\mu\text{-}CO)(CO)_5]$ (2)

1 (0.8 mL of a 0.27 M solution in toluene, 0.216 mmol) was added to a solution of $[Co_2(CO)_8]$ (73 mg, 0.214 mmol) in 20 mL of toluene and the mixture was stirred at 60 ºC for 1 h. The initial dark red color changed to dark orange. Purification by flash chromatography eluting with hexane (2 x 5 cm silica gel column packed in hexane) furnished **2** as a light orange solid (110 mg, 71 %). Slow evaporation of a concentrated solution of **2** in hexane deposited crystals suitable for X-ray crystallographic analysis.



Anal. Calcd. for $C_{25}H_{37}Co_2GeN_3O_6Si_2$ (722.23): C, 41.58; H, 5.16; N, 5.82. Found: C, 41.69; H, 5.19; N, 5.70. (+)-FAB MS: $m/z = 722$ $[M]^+$. IR (toluene, cm^{-1}): ν_{CO} = 2058 (m), 2017 (vs), 1996 (m), 1974 (m, br), 1814 (w, br). ^1H NMR (C_6D_6, 300.1 MHz, 293 K): δ = 7.03–6.97 (m, 5 H, 5 C*H* of Ph), 4.23 (m, 1 H, C*H* of ^{i}Pr), 3.45 (m, 1 H, C*H* of ^{i}Pr), 1.41 (d, J = 6.4 Hz, 3 H, CH_3 of ^{i}Pr), 1.15 (d, J = 6.5 Hz, 3 H, CH_3 of ^{i}Pr), 0.92 (d, J = 6.5 Hz, 3 H, CH_3 of ^{i}Pr), 0.86 (d, J = 6.6 Hz, 3 H, CH_3 of ^{i}Pr), 0.45 (s, 9 H, 3 CH_3 of HMDS), 0.36 (s, 9 H, 3 CH_3 of HMDS). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 293 K): δ = 205.4 (*C*Os), 205.1 (*C*Os), 167.3 (N*C*N), 135.9 (C_{ipso} of Ph), 129.0 (2 *C*H of Ph), 128.4 (*C*H of Ph), 128.2 (*C*H of Ph), 127.7 (*C*H of Ph), 54.7 (*C*H of ^{i}Pr), 48.0 (*C*H of ^{i}Pr), 24.8 (CH_3 of ^{i}Pr), 23.9 (CH_3 of ^{i}Pr), 23.7 (CH_3 of ^{i}Pr), 23.5 (CH_3 of ^{i}Pr), 5.5 (3 CH_3 of HMDS), 4.9 (3 CH_3 of HMDS).

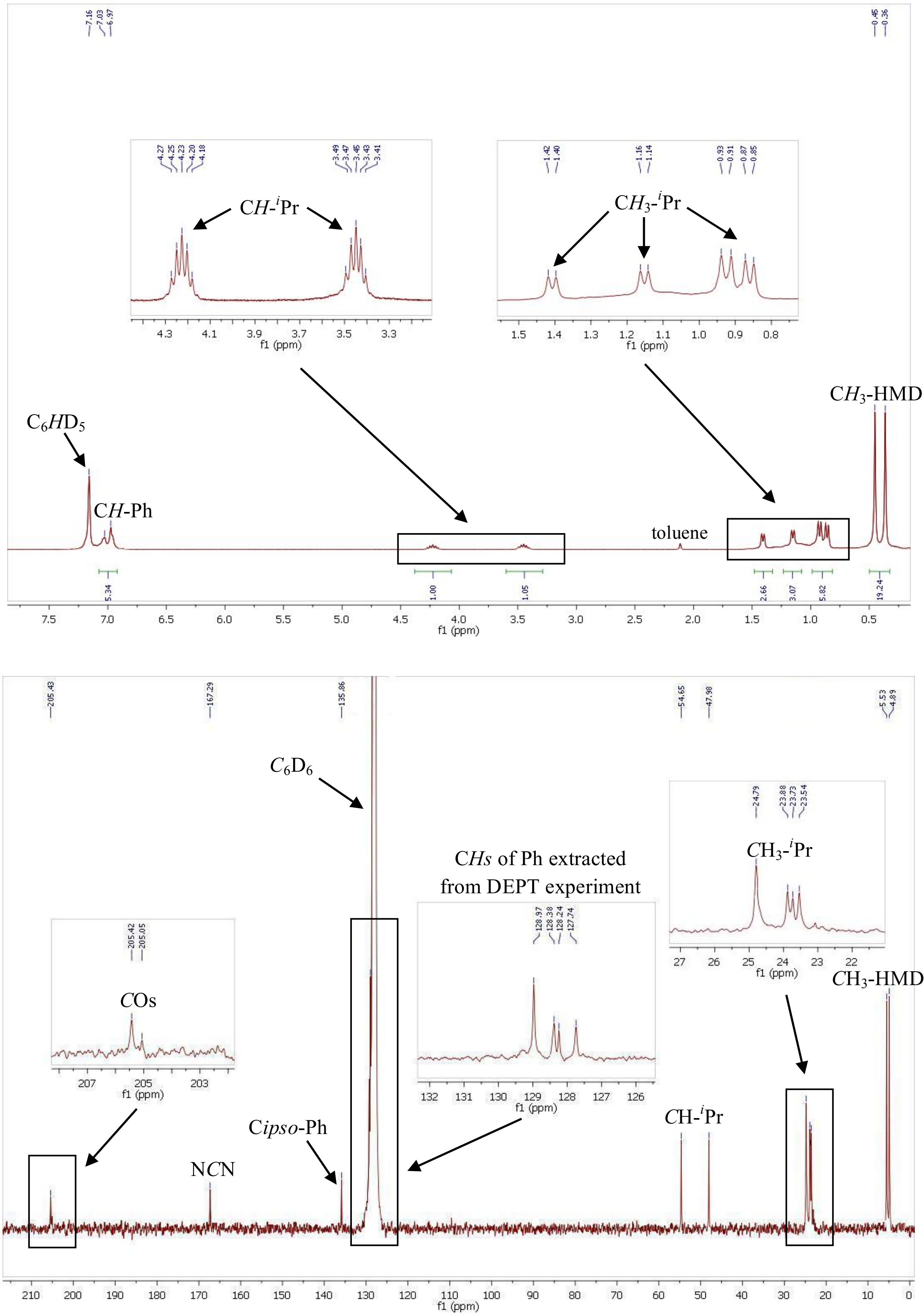
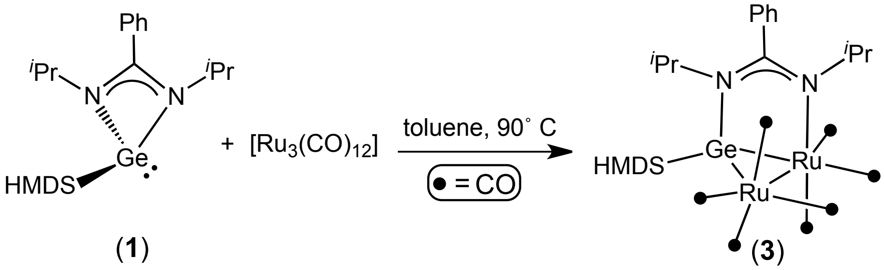


Figure S3. ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of **2** in C_6D_6 (20 °C).

Synthesis and characterization of $[Ru_2\{\mu\text{-}\kappa^2$*Ge,N*-Ge(HMDS)(PhC(N^{i}Pr)$_2$)$\}(CO)_7]$ (3)

1 (3.0 mL of a 0.35 M solution in toluene, 1.05 mmol) was added to a suspension of $[Ru_3(CO)_{12}]$ (0.5 g, 0.8 mmol) in 20 mL of toluene and the mixture was stirred at 90 ºC for 3 h. The initial orange color changed to dark red. Purification by flash chromatography eluting with hexane (2 x 5 cm silica gel column packed in hexane) furnished **3** as a light orange solid (620 mg, 62 %). Keeping a concentrated hexane solution of **3** at –20 °C afforded crystals suitable for X-ray crystallographic analysis.



Anal. Calcd. for $C_{26}H_{37}GeN_3O_7Ru_2Si_2$ (834.51): C, 37.42; H, 4.47; N, 5.04. Found: C, 37.53; H, 4.50; N, 4.89. (+)-FAB MS: *m/z* = 751 $[M - 3\ CO]^+$. IR (toluene, cm^{-1}): ν_{CO} = 2085 (m), 2034 (vs), 2013 (m), 2002 (s), 1992 (m), 1973 (w), 1959 (w). ^{1}H NMR (C_6D_6, 300.1 MHz, 293 K): δ = 6.97–6.83 (m, 5 H, 5 C*H* of Ph), 3.88 (m, 1 H, C*H* of ^{i}Pr), 3.41 (m, 1 H, C*H* of ^{i}Pr), 1.15 (d, *J* = 6.6 Hz, 3 H, CH_3 of ^{i}Pr), 1.06–1.03 (m, 6 H, 2 CH_3 of ^{i}Pr), 0.80 (d, *J* = 6.5 Hz, 3 H, CH_3 of ^{i}Pr), 0.52 (s, 18 H, 6 CH_3 of HMDS). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 293 K): δ = 201.7 (*C*Os), 201.5 (*C*Os), 200.2 (*C*Os), 166.8 (N*C*N), 137.3 (C_{ipso} of Ph), 128.9 (*C*H of Ph), 128.5 (*C*H of Ph), 128.4 (*C*H of Ph), 127.7 (*C*H of Ph), 126.6 (*C*H of Ph), 55.7 (*C*H of ^{i}Pr), 50.4 (*C*H of ^{i}Pr), 26.5 (CH_3 of ^{i}Pr), 24.6 (CH_3 of ^{i}Pr), 24.4 (CH_3 of ^{i}Pr), 22.8 (CH_3 of ^{i}Pr), 6.5 (3 CH_3 of HMDS), 5.6 (3 CH_3 of HMDS).

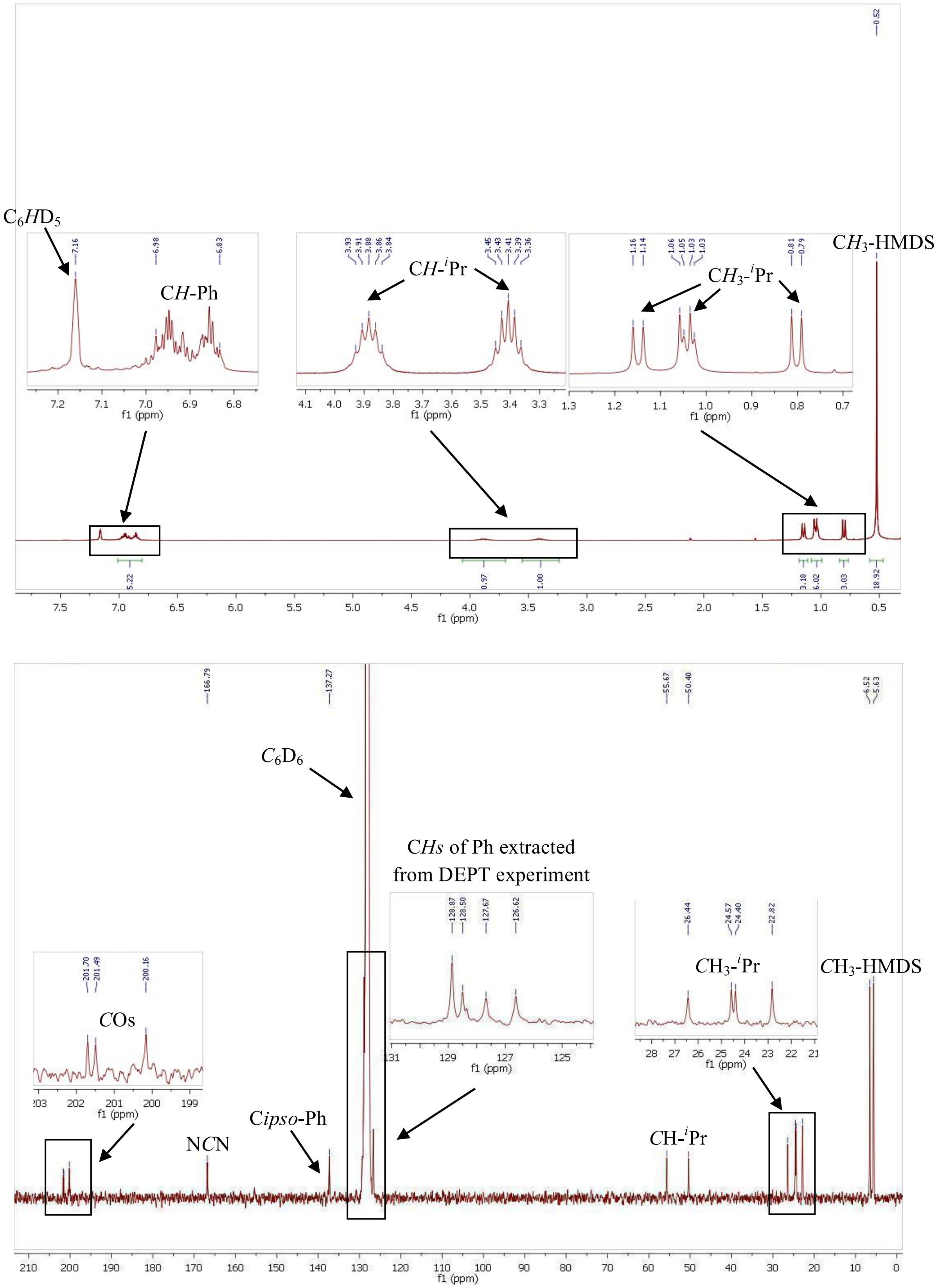


Figure S4. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **3** in C_6D_6 (20 °C).

X-Ray diffraction data

Crystals of **2** and **3** were analyzed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table S1. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.[2] The structures were solved using the program SIR-97.[3] Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL-97.[4] All non-H atoms were refined anisotropically, except some atoms on the carbonyl ligands of **3**, which were kept isotropic due to their tendency to give nonpositive definite ellipsoids. The hydrogen atoms were set in calculated positions and refined riding on their parent atoms. In the crystal of **3**, the $Ru(CO)_4$ and HMDS fragments were disordered over two positions (in a 58:42 and 61:39 ratios, respectively) and the methyl groups of the *iso*-propyl moieties were disordered over two positions (in a 67:33 (N1-*i*Pr) and 60:40 (N2-*i*Pr) ratios). The molecular plots (Figures 2 and 3 of the manuscript) were made with the X-SEED program package.[5] The WINGX program system[6] was used throughout the structure determinations. Crystallographic data (excluding structure factors) for the compounds reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC deposition numbers: 901726 (**2**) and 901725 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table S1. Crystal, Measurement and Refinement Data for **2** and **3**

	2	**3**
formula	$C_{25}H_{37}Co_2GeN_3O_6Si_2$	$C_{26}H_{37}GeN_3O_7Ru_2Si_2$
fw	722.21	834.50
cryst sys	monoclinic	triclinic
space group	$P2_1/n$	$P-1$
a, Å	12.1099(1),	9.7198(4),
b, Å	15.1369(2)	12.3160(6)
c, Å	17.7003(2)	15.8797(7)
α, deg	90	73.393(4)
β, deg	98.614(1)	75.016(4)
γ, deg	90	71.092(4)
V, Å^3	3207.98(6)	1694.2(1)
Z	4	2
F(000)	1480	836
D_{calcd}, g cm^{-3}	1.495	1.636
μ, mm^{-1} (Cu Kα)	10.168	9.224
cryst size, mm	0.22 x 0.18 x 0.14	0.44 x 0.09 x 0.09
T, K	134(2)	123(2)
θ range, deg	3.86 to 68.00	3.89 to 69.96
min./max. h, k, l	–14/12, –15/18, –20/21	–8/11, –11/14, –18/19
no. collected reflns	12914	11248
no. unique reflns	5801	6297
no. reflns with $I > 2\sigma(I)$	5261	5468
no. params/restraints	362/0	548/0
GOF on F^2	1.032	1.047
R_1 (on F, $I > 2\sigma(I)$)	0.028	0.045
wR_2 (on F^2, all data)	0.069	0.113
min./max. $\Delta\rho$, e Å^{-3}	–0.318/0.313	–1.769/1.094

References

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