

Supporting Information

Simple but Effective: Thermally Stable Cu-ESiMe₃ via NHC Ligation†

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Detailed Experimental

General considerations

All synthetic and handling procedures were carried out under an inert atmosphere of high purity dried nitrogen using Schlenk line techniques and inert atmosphere glove boxes. Non-chlorinated solvents were dried using an MBraun MB-SP Series Solvent Purification system with tandem activated alumina (THF) or activated alumina-activated copper redox catalyst (pentane). Chloroform-d and dichloromethane were dried and distilled over P₂O₅. Dichloromethane-d was purchased from CIL. Mercuric(II) acetate was used as received from commercial source (Aldrich). The corresponding carbene copper(I) acetate IPrCu(OAc),¹ S(SiMe₃)₂,² Se(SiMe₃)₂³ and Te(SiMe₃)₂³ were prepared according to literature procedures.

NMR spectra were recorded on Varian Mercury 400, Inova 400 and Inova 600 NMR spectrometers. ¹H and ¹³C chemical shifts are referenced to SiMe₄, using residual solvent as a secondary peak (¹H chemical shifts of compound **1** reference to trace amount of thf because of overlapping and low intensity of the CDCl₃ solvent peak). ⁷⁷Se chemical shift is referenced to Me₂Se and ¹²⁵Te chemical shift is referenced to Me₂Te. The peak from CO₂ in the ¹³C NMR spectra arises from dry ice, used for making NMR samples at low temperature. Elemental analysis was performed by Laboratoire d'Analyse Élémentaire de l'Université de Montréal, Canada.

Single-crystal X-ray diffraction measurements were completed on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. Single crystals of the complexes were carefully selected, immersed in paraffin oil and mounted on

MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL. All non-hydrogen atoms, with the exception of disordered carbon atoms of the solvent, were refined with anisotropic thermal parameters. Hydrogen atoms were included as riding on their respective carbon atoms. In compound **4**, one of the iso-propyl groups of the carbene was modelled as being disordered over two positions, with refined complementary site occupancy factors. Files CCDC 1045224-1045227 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

Synthesis of IPrCuSSiMe₃ (1). 46 μ L of S(SiMe₃)₂ (0.218 mmol) was added to a cold (-70 °C) solution of one equivalent of IPrCu(OAc) (111 mg, 0.217 mmol) in 10 mL tetrahydrofuran, followed by storing the solution at -25 °C overnight. The reaction was layered with 30 mL of pentane at low temperature. Five to six days later colourless plate-like single crystals were obtained and identified by X-ray crystallography to be IPrCuSSiMe₃. The crystals were washed with 3 \times 10 mL cold pentane (-70°C) and dried under dynamic vacuum at 0°C.

1 can be precipitated in higher yields by adding 40 mL of cold pentane to reaction solutions; storing at -25°C overnight forms an off-white suspension. Washing and drying the precipitated solid with 5 \times 10 mL cold pentane, followed by drying under vacuum at 0 °C, gives **1** as an analytically pure product as small crystals (61.5% yield); m.p. 171-172 °C. ¹H NMR (CDCl₃, 399.76 MHz, -10 °C): δ 7.46 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.28 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 7.13 (s, 2H, NCH), 2.57 (sept., *J* = 7.0 Hz, 4H, CH(CH₃)₂), 1.31 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 1.22 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), -0.17 (s, 9H, -Si(CH₃)₃) ppm; ¹³C{¹H} NMR

(CDCl₃, 100.53 MHz, -10 °C): 181.1 (NCCu), 145.4 (*ortho*-C), 134.4 (*ipso*-C), 130.2 (*para*-C), 124.0 (*meta*-C), 122.6 (NCH), 28.6 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 6.7 (-Si(CH₃)₃) ppm. Anal. Calcd for C₃₀H₄₅CuN₂SSi: C, 64.64; H, 8.14; N, 5.03; S, 5.75. Found: C, 64.24; H, 8.28; N, 4.97; S, 5.49.

Synthesis of IPrCuSSiMe₃ (2). 53 μL of Se(SiMe₃)₂ (0.211 mmol) was reacted with one equivalent of IPrCu(OAc) (108 mg, 0.211 mmol) in 10 mL tetrahydrofuran as described for the preparation of **1**. Colourless single crystals suitable for X-ray diffraction were obtained after five to six days by layering the mother liquor with 30 mL of pentane at -25°C.

The product can be isolated as an off-white powder by adding 40-50 mL of cold pentane to reaction solutions at -25°C, as described for **1**. Washing and drying the precipitated solid with 5×10 mL cold pentane, followed by drying under vacuum at 0 °C, gives **2** as small crystals (55.4% yield); m.p. 166-168 °C. ¹H NMR (CDCl₃, 399.76 MHz, -10 °C): δ 7.46 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.28 (d, *J* = 7.8 Hz, 4H, *meta*-CH), 7.12 (s, 2H, NCH), 2.58 (sept., *J* = 7.0 Hz, 4H, CH(CH₃)₂), 1.31 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 1.21 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), -0.04 (s, 9H, -Si(CH₃)₃) ppm; ¹³C{¹H} NMR (CDCl₃, 100.53 MHz, -10 °C): 181.6 (NCCu), 145.4 (*ortho*-C), 134.4 (*ipso*-C), 130.2 (*para*-C), 124.0 (*meta*-C), 122.6 (NCH), 28.6 (CH(CH₃)₂), 25.0 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 7.3 (-Si(CH₃)₃) ppm; ⁷⁷Se NMR (CDCl₃, 76.20 MHz, -10°C): -481 ppm. Anal. Calcd for C₃₀H₄₅CuN₂SeSi: C, 59.63; H, 7.51; N, 4.64. Found: C, 58.43; H, 7.89; N, 4.47.

Synthesis of IPrCuTeSiMe₃ (3). 67 μL of Te(SiMe₃)₂ (0.237 mmol) was reacted with one equivalent of IPrCu(OAc) (121 mg, 0.237 mmol) in 10 mL tetrahydrofuran as described for the preparation of **1**. Colourless single crystals suitable for X-ray diffraction were obtained after five to six days by layering the mother liquor with 35 mL of pentane at -25°C.

Compound **3** was isolated as an off-white powder according to the procedure for **1** and **2**; (50.3% yield); m.p. 178-180 °C. ¹H NMR (CDCl₃, 399.76 MHz, -15 °C): δ 7.47 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.8 Hz, 4 H, *meta*-CH), 7.12 (s, 2H, NCH), 2.58 (sept., *J* = 7.0 Hz, 4 H, CH(CH₃)₂), 1.33 (d, *J* = 7.0 Hz, 12 H, CH(CH₃)₂), 1.22 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 0.15 (s, 9H, -Si(CH₃)₃) ppm; ¹³C{¹H} NMR (CDCl₃, 100.53 MHz, -15 °C): 145.5 (*ortho*-C), 134.4 (*ipso*-C), 130.3 (*para*-C), 124.0 (*meta*-C), 122.6 (NCH), 28.7 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 8.3 (-Si(CH₃)₃) ppm; ¹²⁵Te NMR (CDCl₃, 126.12 MHz, -15 °C): -1179 ppm. Although thermally stable, the air sensitive nature of **3** prevented combustion analytical data from being obtained.

Synthesis of (IPrCuS)₂Hg (4). 41 μL of S(SiMe₃)₂ (0.194 mmol) was added to a cold (-7 °C) solution of one equivalent of IPrCu(OAc) (99 mg, 0.194 mmol) in 10 mL tetrahydrofuran, followed by storage at -25 °C overnight. The reaction solution was cooled to -70 °C to mix with 0.097 mmol Hg(OAc)₂ (31 mg in 5 mL of thf) at this temperature. After warming to -25 °C and keeping the solution at this temperature for 2 hrs, the solvent was removed under vacuum at 0 °C. The off-white solid was redissolved in a minimum amount of cold dichloromethane and the solution layered with 30 mL cold pentane (-70 °C). Colourless blocks as single crystals suitable for X-ray diffraction were obtained after six to seven days (~20 % yield); m.p. 139-141 °C. ¹H NMR (CD₂Cl₂, 599.38 MHz, 25 °C): δ 7.48 (t, *J* = 7.6 Hz, 4H, *para*-CH), 7.28 (d, *J* = 7.6 Hz, 8H, *meta*-CH), 7.08 (s, 4H, NCH), 2.54 (sept., *J* = 7.0 Hz, 8H, CH(CH₃)₂), 1.27 (d, *J* = 7.0 Hz, 24H, CH(CH₃)₂), 1.18 (d, *J* = 7.0 Hz, 24H, CH(CH₃)₂) ppm; ¹³C{¹H} NMR (CD₂Cl₂, 150.73 MHz, 25 °C): δ 146.2 (*ortho*-C), 135.3 (*ipso*-C), 130.9 (*para*-C), 124.7 (*meta*-C), 123.3 (NCH), 29.2 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.2 (CH(CH₃)₂) ppm. Anal. Calcd for C₅₄H₇₂Cu₂HgN₄S₂: C, 55.48; H, 6.21; N, 4.79; S, 5.49. Found: C, 56.74; H, 6.38; N, 4.78; S, 5.40.

Table S1. Crystallographic data

	1·THF	2·THF	3	4·4CH ₂ Cl ₂
formula	C ₃₀ H ₄₅ CuN ₂ SSi·THF	C ₃₀ H ₄₅ CuN ₂ SeSi·THF	C ₃₀ H ₄₅ CuN ₂ SiTe	C ₅₄ H ₇₂ Cu ₂ HgN ₄ S ₂ ·4CH ₂ Cl ₂
formula weight	629.47	676.37	652.91	1508.64
crystal system	monoclinic	monoclinic	Monoclinic	monoclinic
space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> [Å]	28.986(15)	29.597(6)	9.789(3)	13.026(3)
<i>b</i> [Å]	12.887(7)	12.842(3)	21.443(11)	16.803(3)
<i>c</i> [Å]	19.067(9)	19.184(4)	15.580(6)	16.264(4)
α [°]	90.00	90.00	90.00	90.00
β [°]	92.619(12)	93.196(5)	100.673(19)	106.93(3)
γ [°]	90.00	90.00	90.00	90.00
<i>V</i> [Å ³]	7115(6)	7280(3)	3214(2)	3405.6(14)
<i>Z</i>	8	8	4	2
ρ_{cal} [g cm ⁻³]	1.175	1.234	1.349	1.471
μ (MoK α) [mm ⁻¹]	0.733	1.659	1.626	3.279
<i>F</i> (000)	2704	2848	1336	1524
temperature [K]	110	110	110	110
$\theta_{\text{min}}, \theta_{\text{max}}$ [°]	2.51, 27.46	2.47, 36.21	2.83, 36.00	2.66, 29.58
total reflns	60384	150833	109050	18008
unique reflns	8905	17704	11631	5492
<i>R</i> (int)	0.0771	0.0306	0.0305	0.0380
<i>R</i> 1	0.0573	0.0365	0.0249	0.0518
w <i>R</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.1633	0.1025	0.0836	0.1454
<i>R</i> 1 (all data)	0.1080	0.0625	0.0328	0.0658
w <i>R</i> 2 (all data)	0.2016	0.1284	0.0984	0.1676
GOF	1.195	1.081	1.313	1.216

Additional Figures

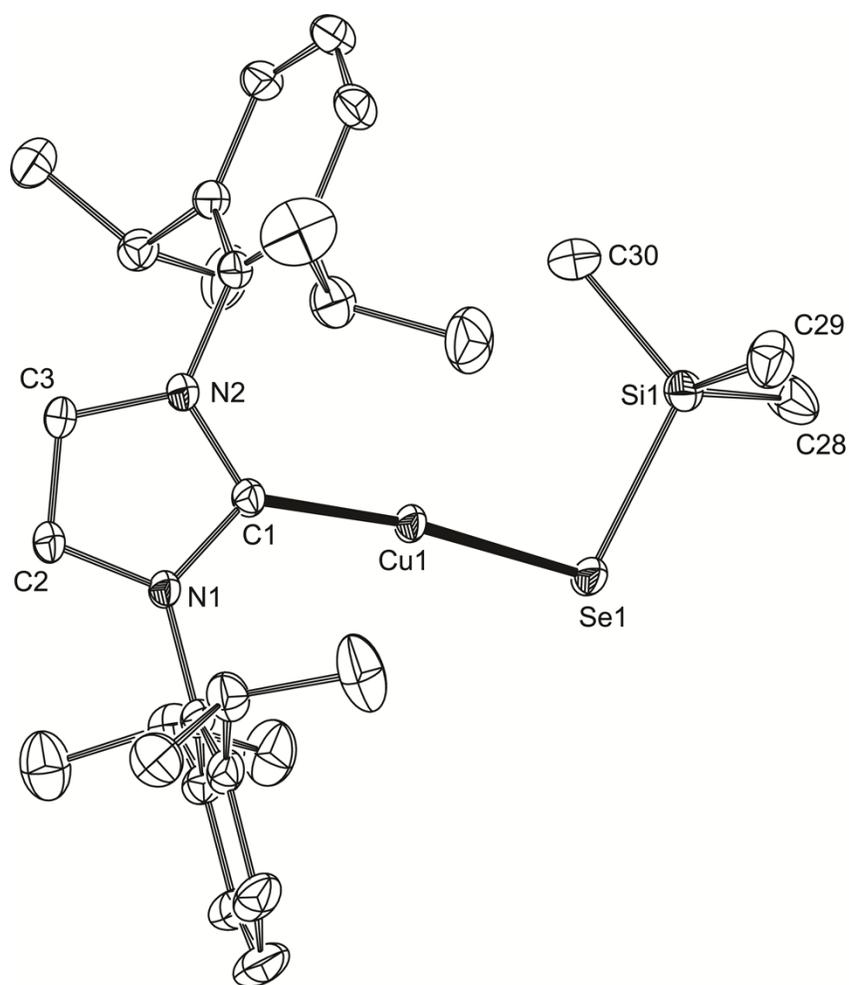


Fig. S1. The molecular structure of complex **2**. The thermal ellipsoids have been drawn at 40% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-Cu1 1.884(1), Cu1-Se1 2.2431(7), Se1-Si1 2.2502(7), C1-Cu1-Se1 170.68(5), Cu1-Se1-Si1 100.42(2).

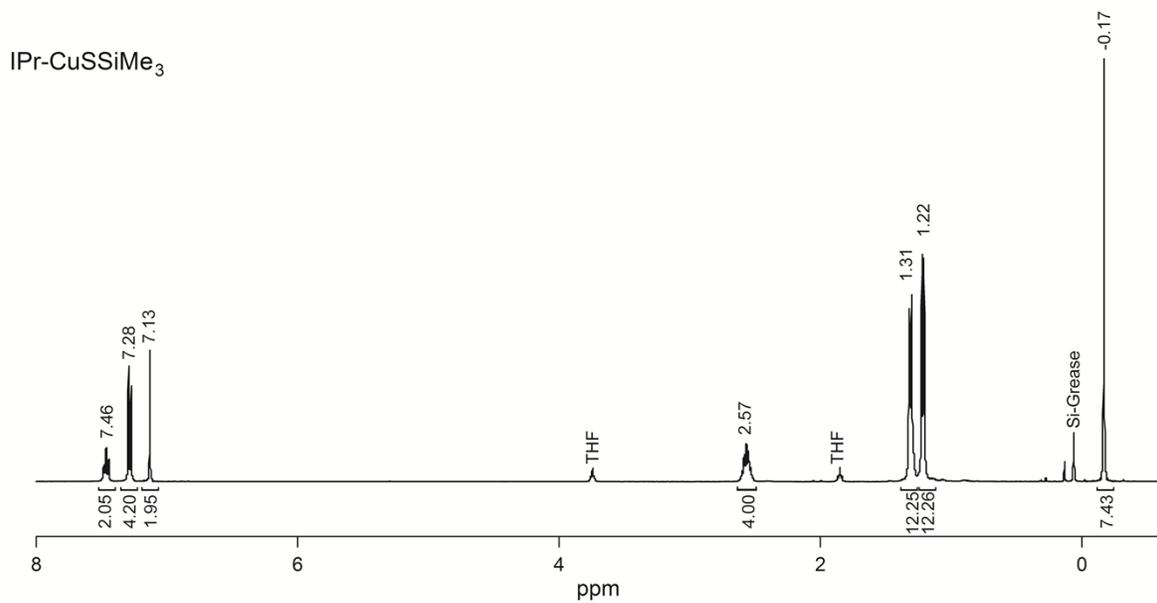


Fig. S2. ¹H NMR spectrum of **1** (CDCl₃, -10 °C, 399.76 MHz).

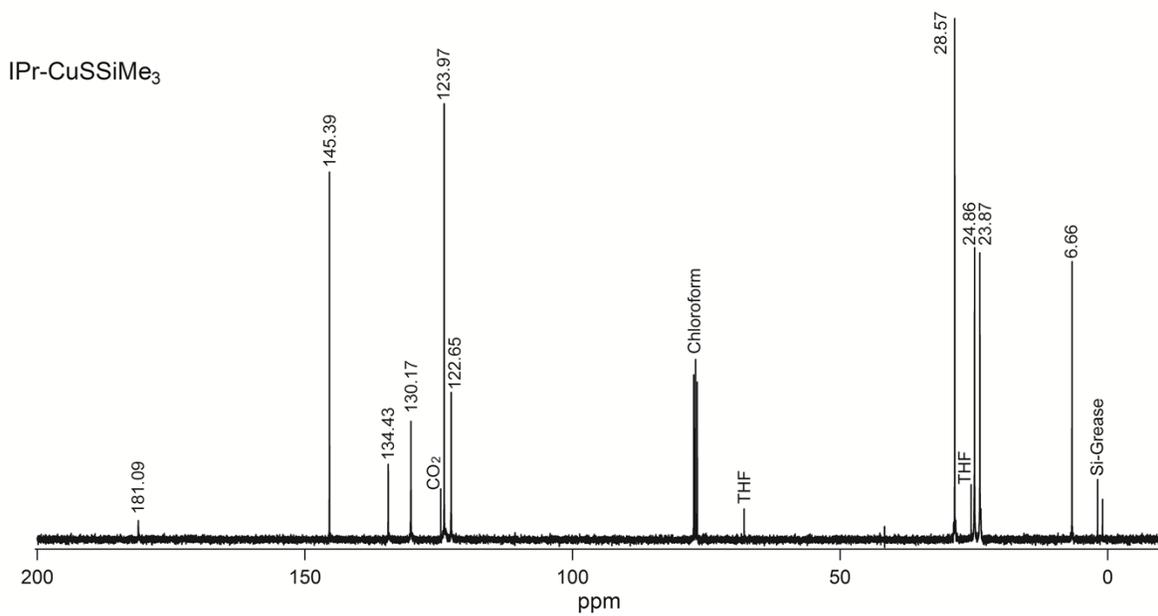


Fig. S3. ¹³C{¹H} NMR spectrum of **1** (CDCl₃, -10 °C, 100.53 MHz).

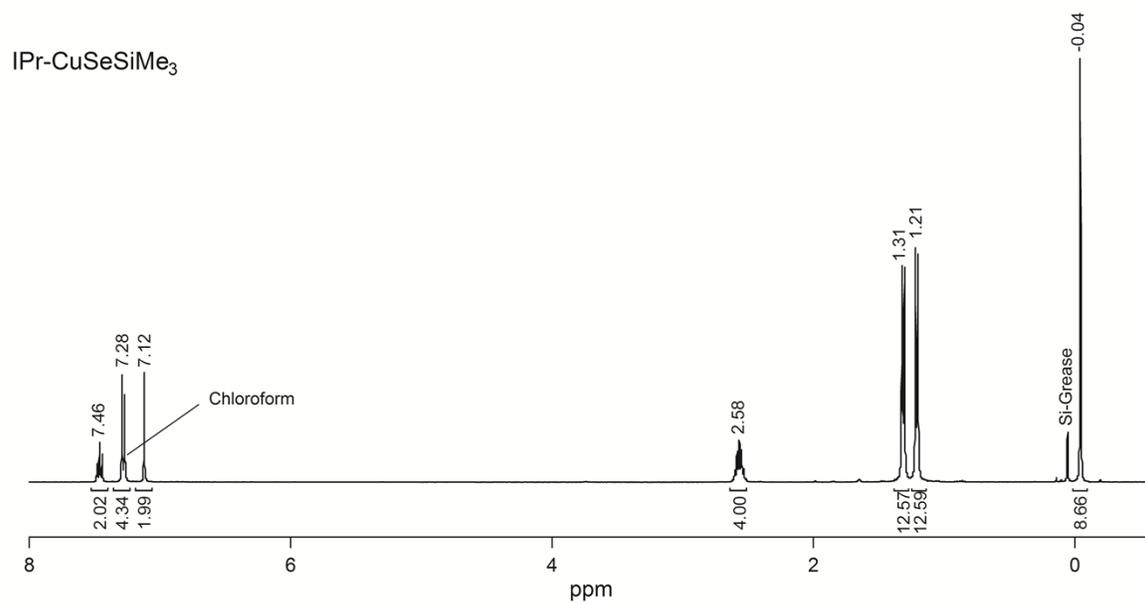


Fig. S4. ¹H NMR spectrum of **2** (CDCl₃, -10 °C, 399.76 MHz).

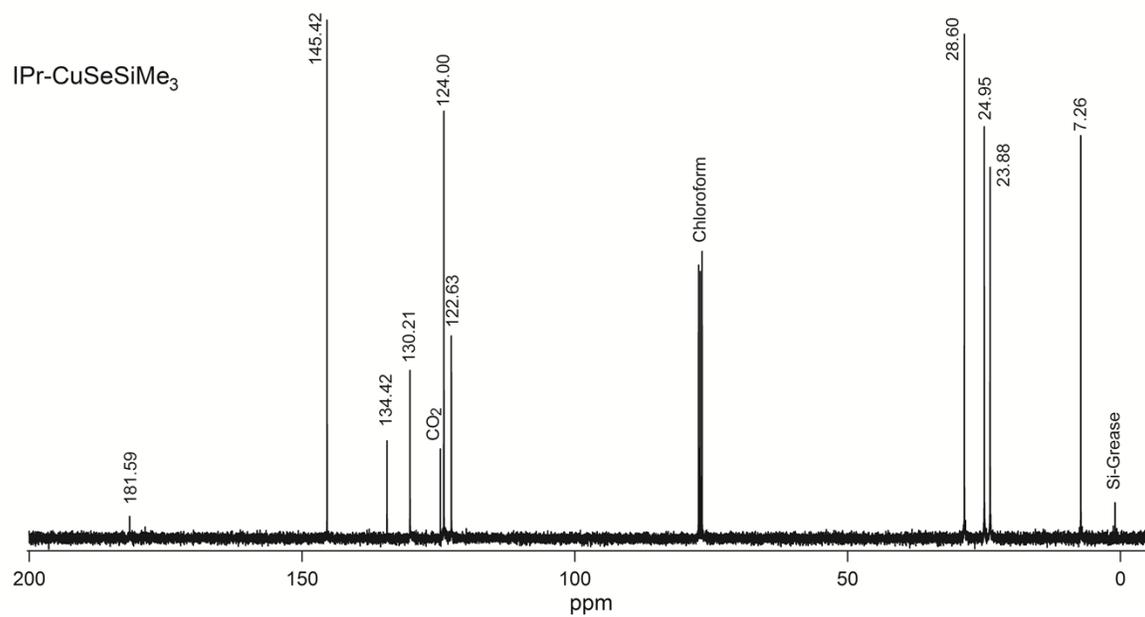


Fig. S5. ¹³C{¹H} NMR spectrum of **2** (CDCl₃, -10 °C, 100.53 MHz).

IPr-CuTeSiMe₃

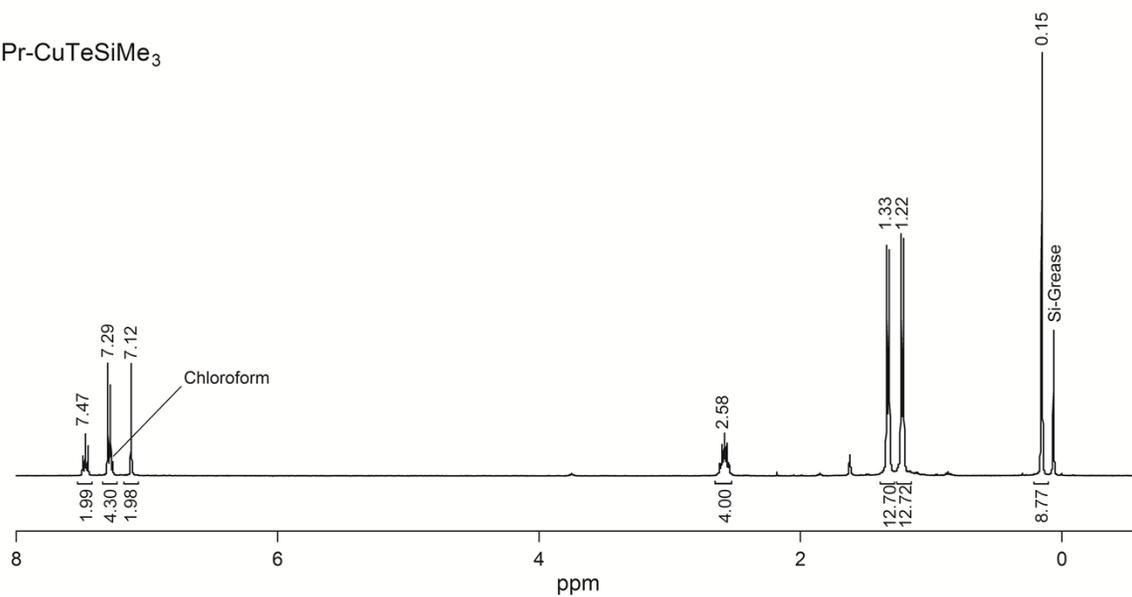


Fig. S6. ¹H NMR spectrum of **3** (CDCl₃, -15 °C, 399.76 MHz).

IPr-CuTeSiMe₃

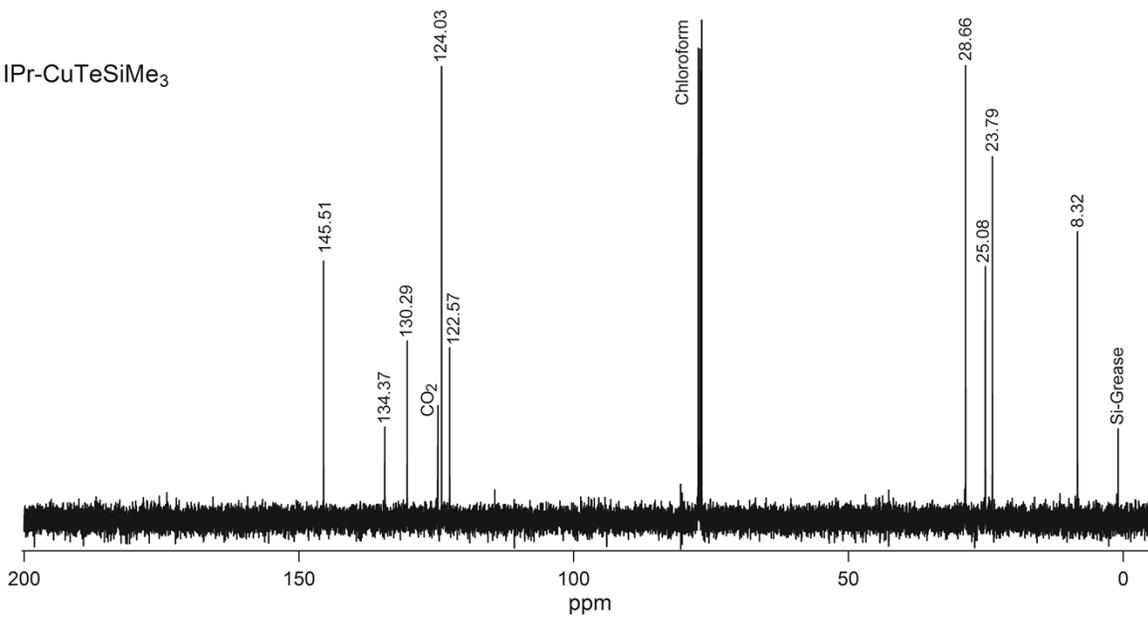


Fig. S7. ¹³C{¹H} NMR spectrum of **3** (CDCl₃, -15 °C, 100.53 MHz).

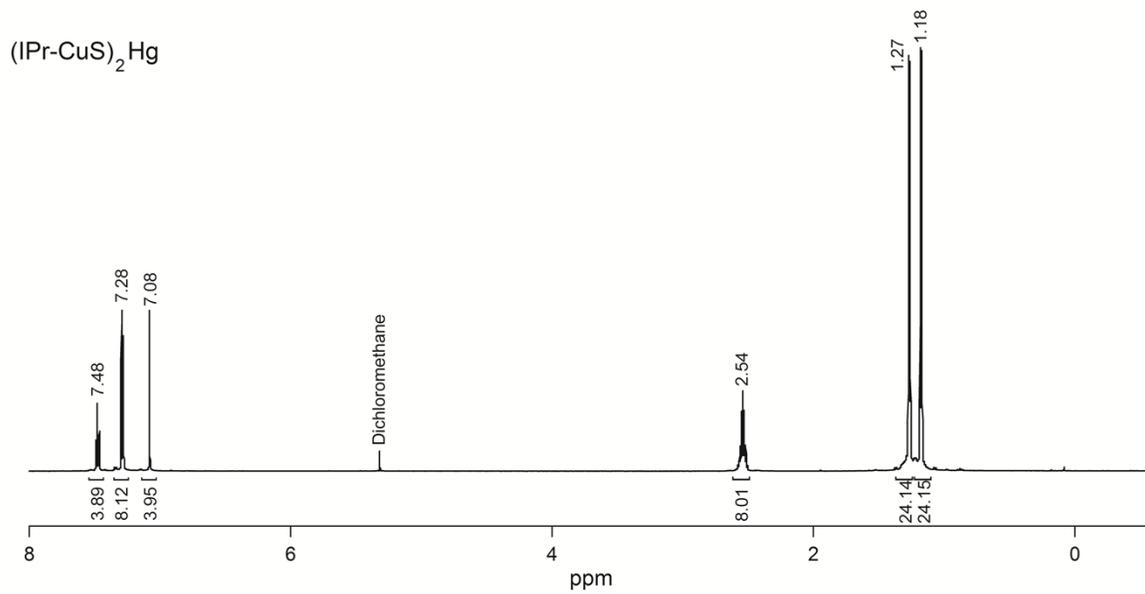


Fig. S8. ¹H NMR spectrum of **4** (CD₂Cl₂, 25 °C, 599.38 MHz).

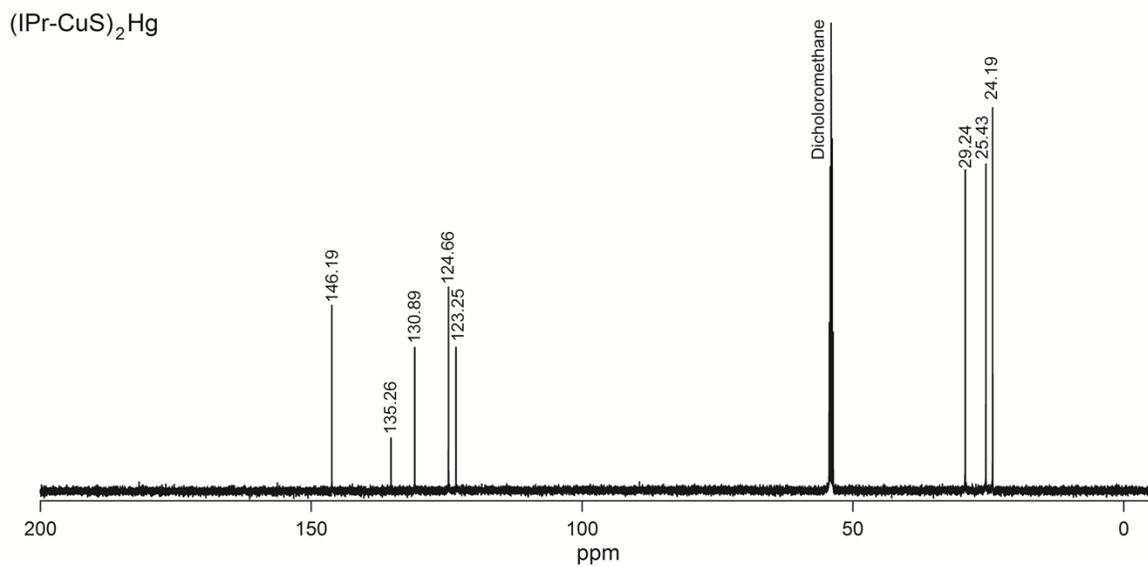


Fig. S9. ¹³C{¹H} NMR spectrum of **4** (CD₂Cl₂, 25 °C, 150.73 MHz).

1. Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P., *Organometallics* 2004, **23**, 1191-1193.
2. So, J. H.; Boudjouk, P., *Synthesis* 1989, 306-307.
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