

Supplementary information for

$\{\text{Ge}_9\text{R}_3\text{Cr}(\text{CO})_5\}^-$ and $\{\text{Ge}_9\text{R}_3\text{Cr}(\text{CO})_3\}^-$: A metalloid cluster
compound (Ge_9R_3^-) as a flexible ligand in coordination chemistry



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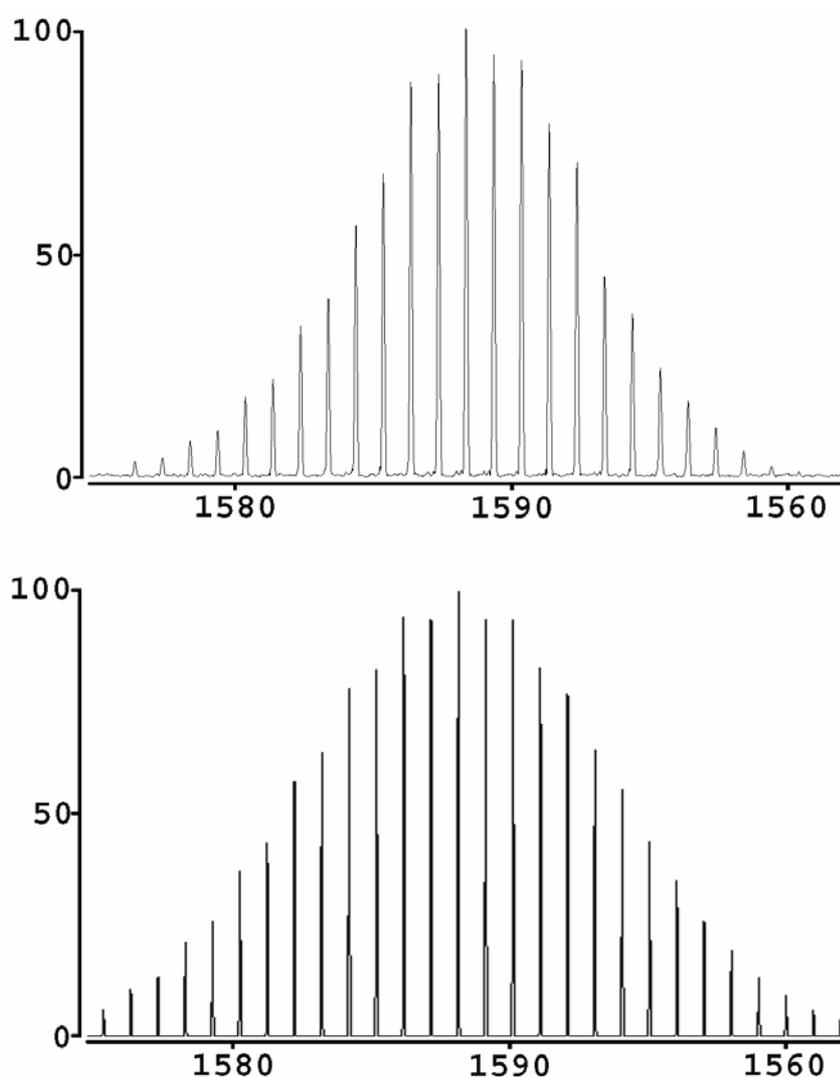


Figure S1: Calculated (bottom) and measured (top) molecular peak of $\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_5\}^- \cdot 2$

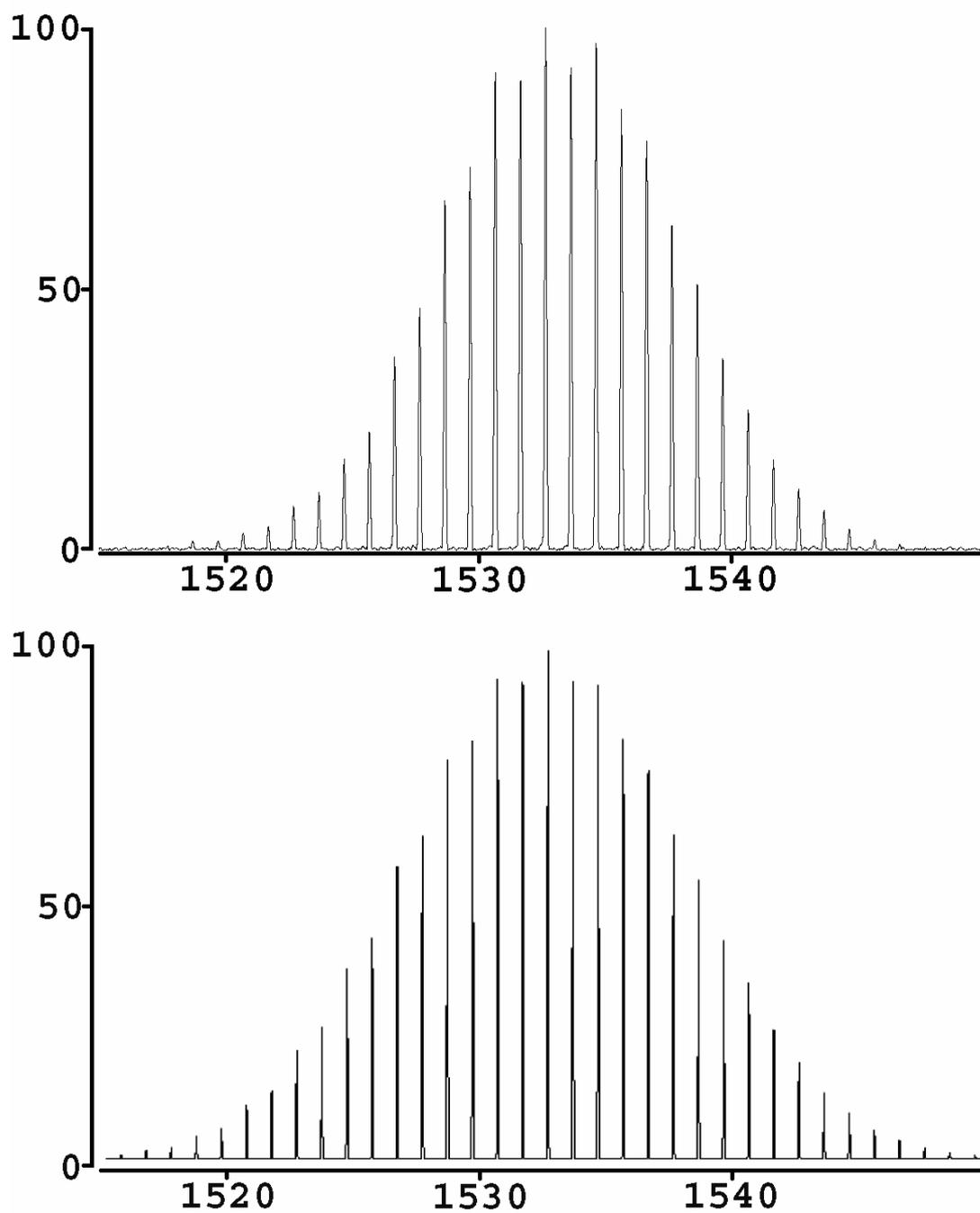


Figure S2: Calculated (bottom) and measured (top) molecular peak of $\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_3\}^- 3$

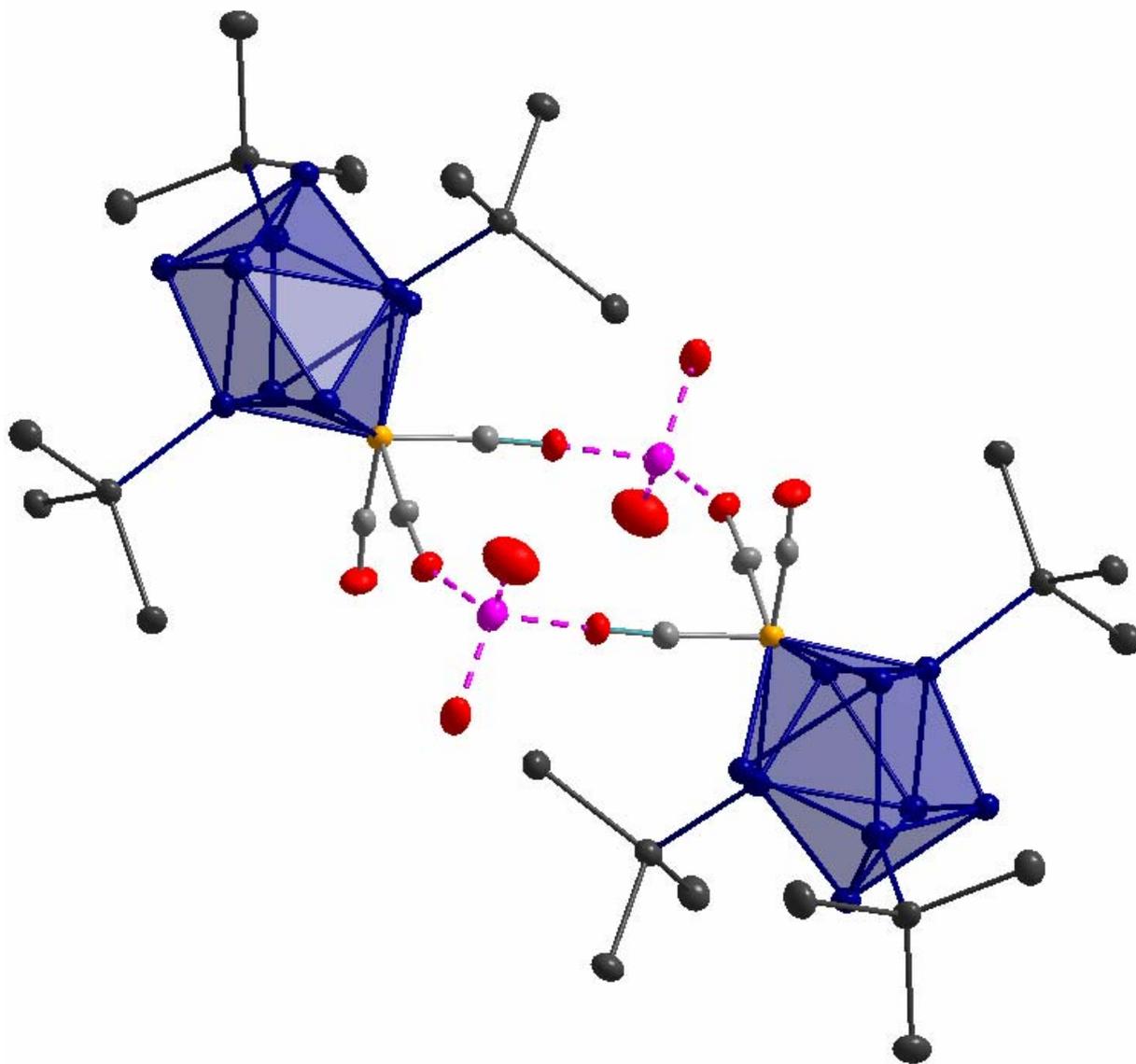


Figure S3: Molecular structure of the dimer $[\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3\text{Cr}(\text{CO})_3\}\text{Li}(\text{thf})_2\}]_2$. Methyl groups are omitted for clarity and from the thf molecules only the directly coordinated oxygen atoms are shown. The two Ge_9Cr polyhedra are emphasized by a polyhedral presentation (vibrational ellipsoids with 25% probability).

Experimental details:

Preparation of $\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_5\}\text{Li}(\text{thf})_4$

At -40°C $[\text{Ge}_9\text{R}_3][\text{Li}(\text{thf})_4]$ (177 mg, 0.108 mmol) is dissolved in thf (ca. 100 ml) and treated with a -40°C cold solution of $[\text{Cr}(\text{CO})_5\text{COE}]$ (65 mg, 0.216 mmol) dissolved in 10 ml thf. During warming to room temperature the reaction mixture changed colour from orange to deep red. After 24h the solvent was removed in vacuum and the dark red residue was extracted with pentane leading to a dark red pentane extract, which was stored at -28°C giving red crystals of $[\text{Ge}_9\text{R}_3\text{Cr}(\text{CO})_5][\text{Li}(\text{thf})_4]$ in nearly quantitative yield (190 mg, 0.103 mmol, 96 %).

NMR: C_6D_6 : ^1H NMR(250 MHz): $\delta = 0.33$ (s, SiMe₃); ^{13}C NMR (100 MHz): $\delta = 2.29$ (CH₃); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz): $\delta = -9.34$ (SiMe₃), -106.2 (Si). IR (Crystal): $\nu = 2031$; 1913; 1882; 1810.

CCDC-718082 contains the supplementary crystallographic data for this structure.

Preparation of $\{[\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_3]\text{Li}(\text{thf})_2\}_2$

At -45°C $[\text{Ge}_9\text{R}_3][\text{Li}(\text{thf})_4]$ (156 mg, 0.095 mmol) is dissolved in thf (ca. 100 ml) and treated with a -45°C cold solution of $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ (25 mg, 0.095 mmol / 10 ml thf). During warming to room temperature the reaction mixture changed colour from orange to black. After 24h the solvent was removed in vacuum and the black residue was extracted with pentane leading to a dark red pentane extract. This extract was stored -15°C , while red crystals of $[\text{Ge}_9\text{R}_3\text{Cr}(\text{CO})_3\text{Li}(\text{thf})_2]_2$ in low yield (15 mg, 0.0045 mol, 9.4 %) were obtained.

NMR THF- d_8 : ^1H NMR(250 MHz): $\delta = 0.89$ (s, SiMe₃), 1.31 (s, SiMe₃); ^{13}C NMR (100 MHz): $\delta = 2.27$ (CH₃), 2.66 (CH₃) ; $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz): $\delta = -9.54$ (SiMe₃), -10.07 (SiMe₃), -68.30 (Si), -106.07 (Si). IR (crystal): $\nu = 1899$; 1871; 1791; 1714.

CCDC- 718081 contains the supplementary crystallographic data for this structure.

Table S1 Crystal data and detail of structural determinations of **2** and **3**.



Formula	$\text{CrGe}_9\text{Si}_{12}\text{O}_9\text{C}_{48}\text{LiH}_{113}$	$\text{Cr}_2\text{Ge}_{18}\text{Si}_{24}\text{O}_{10}\text{C}_{81}\text{Li}_2\text{H}_{206}$
Formula weight	1883.71	3439.06
T/K	150	150
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/n
a/Å	14.419(3)	17.492(4)
b/Å	41.714(8)	20.471(4)
c/Å	14.636(3)	23.186(5)
a/°	90	90
b/°	99.39(3)	98.39(3)
c /°	90	90
V/Å ³	8690(10)	8213(3)
Z	4	2
μ/mm ⁻¹	3.391	3.577
δ/g cm ⁻³	1.441	1.420
Reflections measured	31969	54773
Reflections independent	18525	15500
Reflections observed (I > 2σI)	15222	8388
R(int)	0.0256	0.0925
Goof	1.072	0.827
R1 (I < 2r)	0.0519	0.0483
wR2 (all data)	0.1603	0.1083

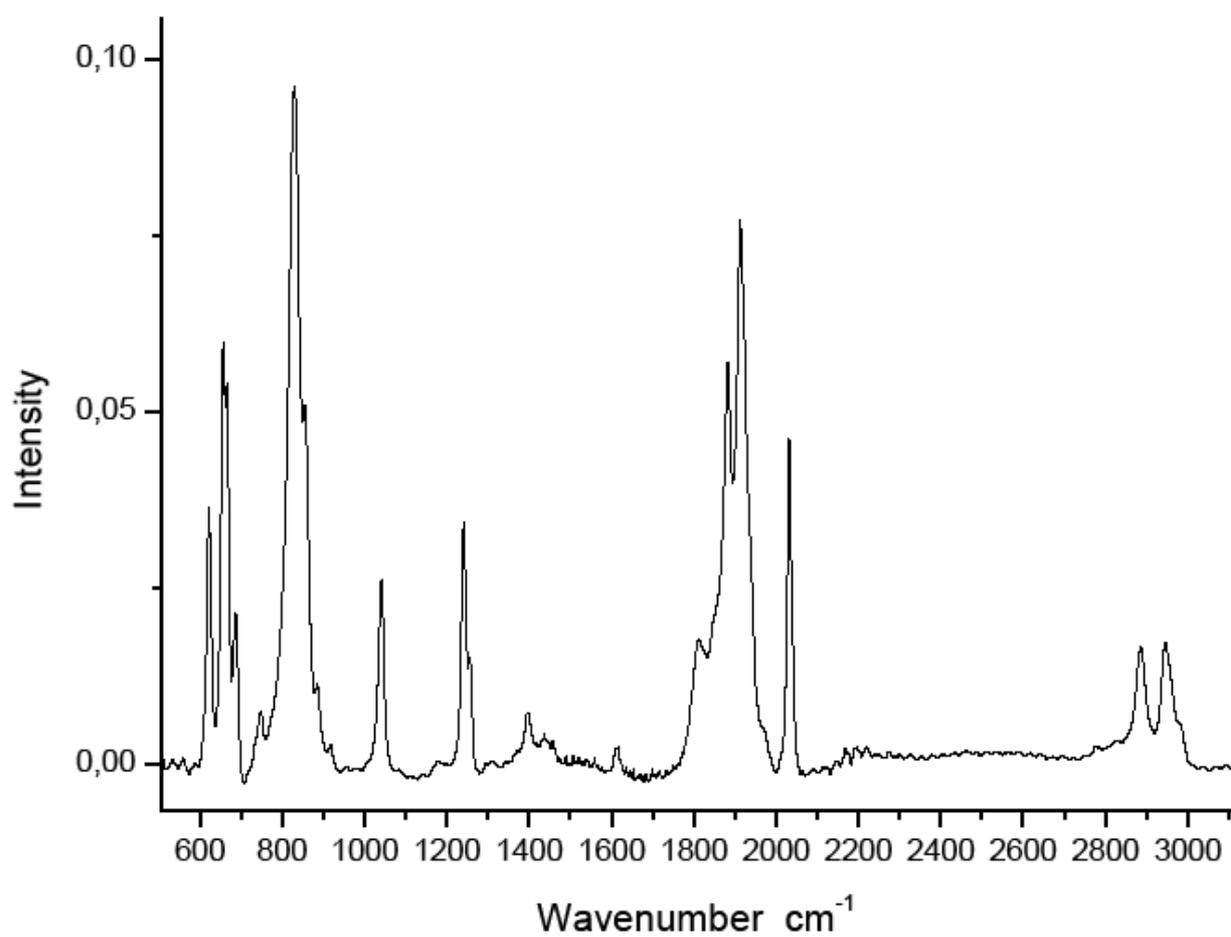


Figure S4: IR spectra of crystals of $\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_5\}\text{Li}(\text{thf})_4$.

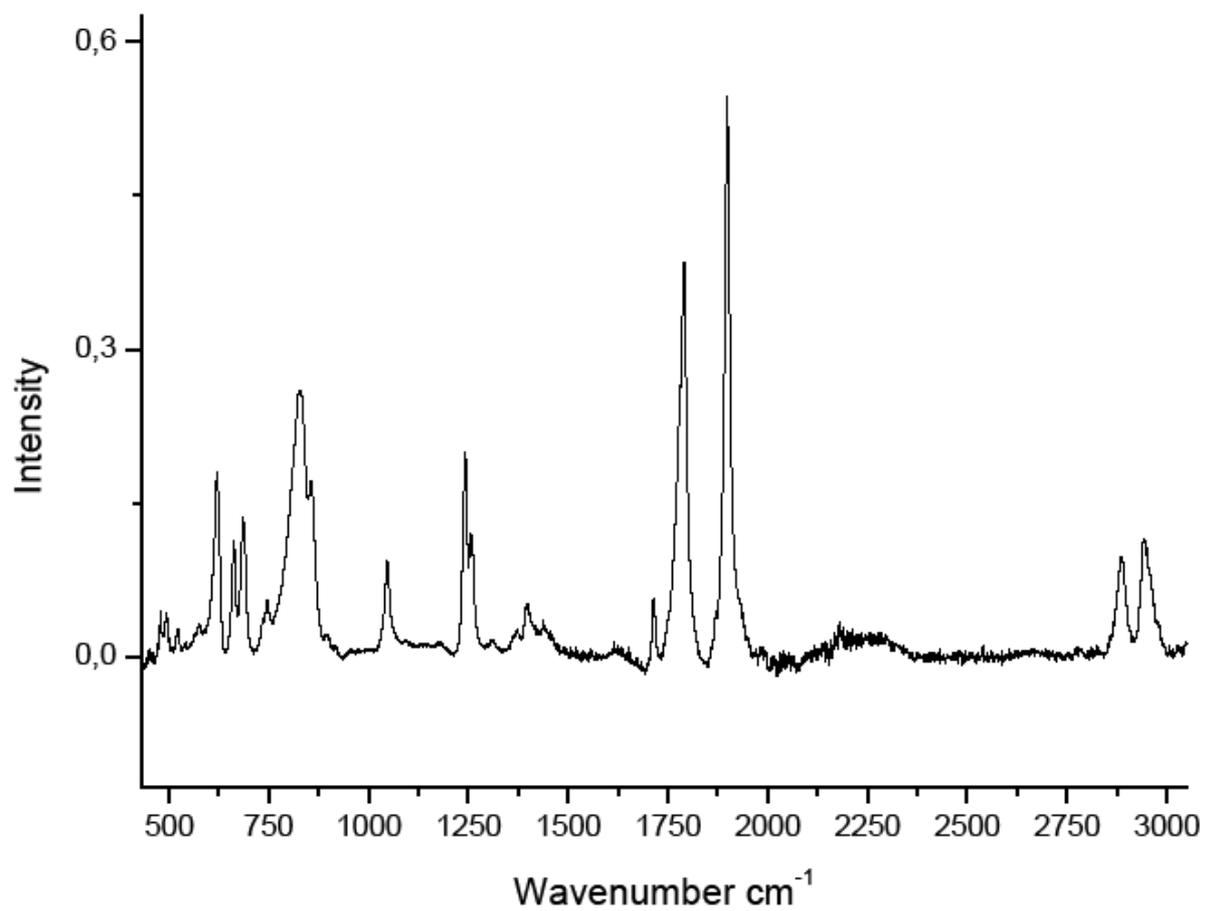


Figure S5: IR spectra of crystals of $[\{\text{Ge}_9[\text{Si}(\text{SiMe}_3)_3]_3\text{Cr}(\text{CO})_3\}\text{Li}(\text{thf})_2]_2$