Trans-metal-trapping meets FLP chemistry: Ga(CH₂SiMe₃)₃ induced C-H functionalizations

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X-Ray Crystallography

Crystallographic data were measured at 123(2) K for compounds 21-24; at 153(2) K for compound 8 and at 162(2) K for compound 7 using an Oxford Diffraction Xcalibur S instrument with graphite monochromated Mo (λ =0.71073 Å) radiation. All structures were refined to convergence on F^2 using all unique reflections and programs from the SHELX family.¹ The final model for structure 8, 23 and 24 included constraints and restraints on bond lengths and displacement parameters that were required to model disorder for PMDETA ligand (8); one *tert*-butyl and two monosilyl groups (23) and for the phenyl ring of alkyl

¹ G. M. Sheldrick, Acta Crystallogr., **2008**, *A64*, 112.

ligand (24). Selected crystallographic data are presented in Tables S1 and S2 and full details in cif format can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* <u>www.ccdc.cam.uk/data_request/cif</u>.

compound	7	8	21
Empirical formula	C29H63GaLiN5Si3	C27H62GaLiN4Si3	C ₂₉ H ₅₉ GaN ₂ OSi ₃
Formula weight	642.77	603.73	605.77
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2 ₁ /c	P n a 2 ₁	P 2 ₁
χ(Å)	0.71073	0.71073	0.71073
<i>a</i> (Å)	12.830(2)	25.9691(15)	9.5862(3)
b (Å)	10.9373(19)	10.6662(5)	16.5434(5)
<i>c</i> (Å)	27.630(5)	13.3616(7)	11.7072(4)
β (°)	90.296(16)	90	101.757(3)
$V(Å^3)$	3877.0(12)	3701.1(3)	1817.67(10)
Ζ	4	4	2
$\mu (\text{mm}^{-1})$	0.826	0.860	0.877
2θmax (°)	54.00	60.44	55.99
Measured reflections	34096	36351	9232
Unique reflections	8439	9868	6976
Observed reflections	5228	7155	4410
R _{int}	0.1070	0.0650	0.0636
R [on F, obs refln only]	0.0620	0.0511	0.0549
wR [on F ² , all data]	0.1107	0.0947	0.0807
GoF	1.008	1.040	0.837
Largest diff peak/hole (e Å ⁻³)	0.472/-0.380	0.513/-0.451	0.986/-0.857
Flack parameter		-0.016(6)	-0.002(13)

Table S1: Selected crystallographic and refinement parameters for compounds 7,8 and 21.

compound	22	23	24
Empirical formula	C ₃₅ H ₆₄ GaN ₃ Si ₃	$C_{31}H_{59}GaN_2Si_3$	$C_{43}H_{63}GaN_2Si_2$
Formula weight	680.88	613.79	733.85
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /c	P 2 ₁ /c
χ(Å)	0.71073	0.71073	0.71073
<i>a</i> (Å)	10.4334(6)	10.0970(7)	10.7085(8)
<i>b</i> (Å)	19.2196(11)	19.0428(10)	22.2871(12)
<i>c</i> (Å)	20.0396(12)	19.8443(12)	18.6492(12)
β (°)	99.822(6)	100.657(6)	103.075(7)
$V(\text{\AA}^3)$	3959.6(4)	3749.8(4)	4335.5(5)
Ζ	4	4	4
$\mu (\mathrm{mm}^{-1})$	0.811	0.849	0.719
2θmax (°)	58.00	60.70	54.00
Measured reflections	39044	37838	20903
Unique reflections	10363	10241	9459
Observed reflections	7200	6898	5703
R _{int}	0.0637	0.0603	0.0742
R [on F, obs refln only]	0.0464	0.0577	0.0700
wR [on F^2 , all data]	0.1002	0.1298	0.1065
GoF	1.009	1.046	1.057
Largest diff peak/hole (e Å ⁻³)	0.709/-0.349	0.919/-0.594	1.301/-0.911

 Table S2: Selected crystallographic and refinement parameters for compounds 22-24.

 Table S3: Selected bond lengths (Å) and bond angles (°) for compounds 21-23.

compound	21 (X = O)	22 (X = N)	23 (X = C)
Ga-C _{alkyl}	2.000(6)	2.022(2)	2.011(3)
Ga-C _{alkyl}	2.029(6)	2.031(2)	2.038(4)
Ga-C _{alkyl}	2.020(5)	2.015(2)	2.018(4)
Average Ga-C _{alkyl}	2.016	2.023	2.022
Ga-X	1.981(4)	2.0150(17)	2.031(3)
Average angle around Ga	108.87	109.33	109.36



Figure S1: ¹H NMR spectrum of **7** in d₈-THF.



Figure S2: ¹³C NMR spectrum of **7** in d₈-THF.



Figure S4: ¹H NMR spectrum of **8** in C_6D_6 .



Figure S5: 13 C NMR spectrum of 8 in C₆D₆.



Figure S6: ⁷Li NMR spectrum of **8** in C_6D_6 .



Figure S8: ¹³C NMR spectrum of 8 in d₈-THF.



Figure S10: ¹H DOSY NMR spectrum of 8 in d₈-THF.

From the NMR shifts it can clearly be seen that the PMDETA that is capping the lithium atom coordinated to the N-donor atom of the substrate in compounds 7 and 8 is free in the THF solution based on the sharpness and chemical shifts of the resonances. This was confirmed by performing a ¹H NMR DOSY of compound 8 (Figure S10). Whether Li atom is still coordinated to the donor atom of deprotonated substrate or if it exists as a solvent separated ion pair is difficult to determine based on the data we collected. However, comparing the NMR spectra of said compound 8 in C₆D₆ and d₈-THF (especially ⁷Li NMR spectra) it is highly likely that the Li-ion is fluctuating (coming on and off the substrate) and that both solvent separated and contacted ion-pair species are present in the solution (comparison of S9 and S6).



Figure S11: ¹H NMR spectrum of **21** in d₈-THF.



Figure S12: ¹³C NMR spectrum of **21** in d₈-THF.



Figure S13: ¹H NMR spectrum of 22 in d_8 -THF (* denotes unreacted Ph₂NH).



Figure S14: Aromatic region of ¹H NMR spectrum of 22 in d_8 -THF (* denotes unreacted Ph₂NH).



Figure S15: ¹³C NMR spectrum of 22 in d₈-THF.



Figure S16: Low field region of 13 C NMR spectrum of 22 in d₈-THF (* denotes unreacted Ph₂NH).



Figure S17: ¹HNMR spectrum of 23 in d₈-THF.



Figure S19: ¹H NMR spectrum of 24 in C₆D₆.



Figure S20: ¹³C NMR spectrum of 24 in C_6D_6 .

Reactivity of 24 towards excess phenylacetylene

Pure, crystalline compound **24** (100 mg) and ferrocene (14 mg) were dissolved in C_6D_6 followed by the addition of two equivalents of phenylacetylene (0.03 mL). The mixture was sealed in Young's tap NMR tube and ¹H NMR spectrum was immediately recorded revealing no reaction at room temperature (**Figure S21** and **S22**). The sealed tube was heated at 100 °C for a specific time (i.e. 14 h (**Figure S23**) and 46 h (**Figure S24**)) followed by recording of ¹H NMR spectra (at room temperature) on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz. Yields were calculated *versus* ferrocene which was used as an internal standard. Overview of the experiment is presented in **Figure S25**.



Figure S21: ¹H NMR spectrum of **24** with $FeCp_2$ (14 mg) and 2 equivalents of PhCCH in C_6D_6 at room temperature.



Figure S22: ¹³C NMR spectrum of 24 with FeCp₂ (14 mg) and 2 equivalents of PhCCH in C_6D_6 at room temperature.



Figure S23: ¹H NMR spectrum of mixture of **24** and [IPr·GaR(CCPh)₂] (56 %) with FeCp₂ (14 mg) unreacted PhCCH and RH (RH = Me₄Si) in C₆D₆ after 14h at 100 °C.



Figure S24: ¹H NMR spectrum of mixture of $[IPr \cdot GaR(CCPh)_2]$ (80 %) with FeCp₂ (14 mg) unreacted PhCCH and RH (RH = Me₄Si) in C₆D₆ after 46h at 100 °C.



Figure S25: Comparison of ¹H NMR spectra (2.0 - 5.0 ppm region) of 24 with FeCp₂ and 2 equivalents of PhCCH in C₆D₆.