Supplementary Information

Activation of Olefins with Low-valent Gallium Compounds under Ambient Conditions

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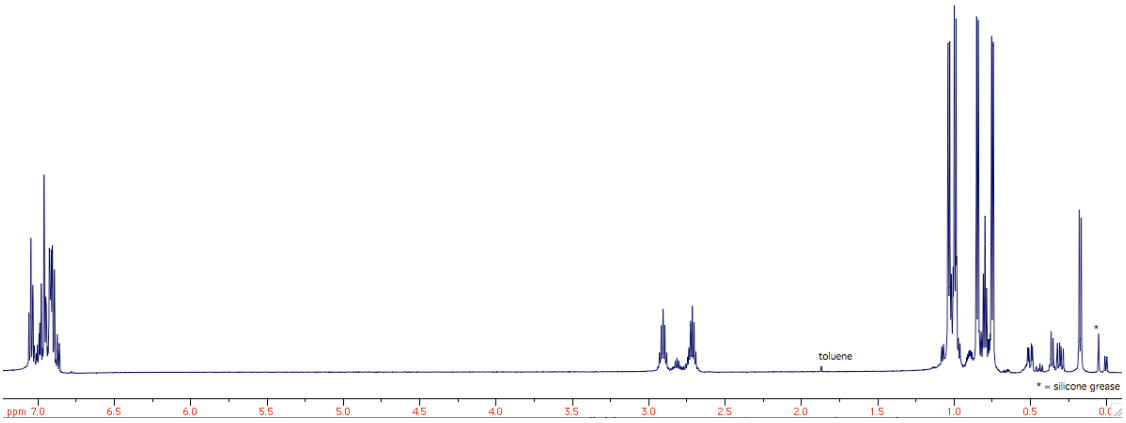
General Procedures. All manipulations were carried out under anaerobic and anhydrous conditions. All reagents were trap-to-trap vacuum distilled and dried over 4 Å molecular sieves prior to use. Ar′GaGaAr′ was prepared according to literature procedures.[1] ^{1}H, ^{13}C NMR were recorded on a Varian spectrometers and referenced to known standards. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN) with a ThermoFinnigan Flash EA™ 1112 analyzer.

Ar´Ga(CH$_2$CH$_2$)$_2$GaAr´ (1) Ethylene gas was bubbled at ca. 25 °C through a solution of Ar´GaGaAr´ (0.30 g, 0.32 mol) in dry toluene (30 mL) . A rapid colour change from dark green to colourless was observed (within 1 min). The solution was concentrated under reduced pressure to ca. 10 mL then stored at a -18 °C to afford X-ray quality crystals of **1**. Yield: 0.12 g, 38 %; m.p. 281 °C. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 0.28 (s, Ga(CH_2CH_2)$_2$Ga, 8H), 1.05 (d, *o*-CH(CH_3)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 24H), 1.18 (d, *o*-CH(CH_3)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 24H), 2.98 (sept, CH(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 8H), 7.16 (d, *m*-Dipp (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$), $^{3}J_{HH}$ = 8.4 Hz, 8H), 7.21-7.27 (m, *m*-C$_6$H$_3$, *p*-C$_6$H$_3$, 6H), 7.33 (t, *p*-Dipp, $^{3}J_{HH}$ = 7.8 Hz, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 150.8 MHz, 298 K): δ 22.6, 25.8, 26.3, 30.6, 123.2, 127.3, 128.6, 141.8, 145.145.7, 147.1, 156.7. Anal. calcd for $C_{64}H_{82}Ga_2$: C, 77.58; H, 8.34 %. Found: C, 77.67; H, 8.36 %.



Ar´Ga{(CH$_2$CH(CH$_3$)}$_2$GaAr´ (**2**) A solution of Ar´GaGaAr´ (0.19 g, 0.20 mol) in dry degassed toluene (10 mL) was exposed to propene gas (~50 mL) at ca. 25 °C. An immediate colour change from dark green to bright yellow was observed. The solution was stirred for 1 h and concentrated under reduced pressure to ca. 2 mL then stored at -18 °C to afford colourless crystals of **2**. Yield: 0.11 g, 55%; m.p. 239 – 241 °C. ^{1}H NMR (600 MHz, C_6D_6, 298 K) Major conformer: 0.41 (d, CH$_2$CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 5.4 Hz, 6H), 0.54 (dd, CH*H´*CH(CH$_3$), $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 9.0, 2H), 0.74 (dd, C*H*H´CH(CH$_3$), $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 4.2 Hz, 2H), 0.98 (d, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 3H), 1.08 (d, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 3H), 1.13 (m, CH$_2$C*H*(CH$_3$), 2H), 1.22 (d, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 3H), 1.27 (d, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 3H), 2.95 (sept, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 4H), 3.14 (sept, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz, 4H), 7.10 (d, *p*-C$_6$H$_3$, $^3J_{HH}$ = 7.8 Hz, 2H), 7.12 – 7.22 (m, *m*-^{i}Pr$_2$-C$_6$H$_3$, *m*-^{i}Pr$_2$-C$_6$H$_3$, 12H), 7.82 (t, *p*-^{i}Pr$_2$-C$_6$H$_3$, $^3J_{HH}$ = 7.8 Hz, 4H). The minor conformer is present in a much smaller proportion and several peaks were obscured due to overlap with the major conformer and could not be explicitly assigned, a scan of the ^{1}H NMR spectrum is given for reference purposes. ^{13}C{^{1}H} NMR (C_6D_6, 150.8 MHz, 298 K): **2**$_{ax}$: 22.0, 22.3, 23.1, 25.9, 26.3, 26.4, 27.8, 30.5, 30.6, 123.0, 123.6, 128.9, 141.9, 145.5, 146.7, 147.6, 156.0. **2**$_{eq}$: 22.3, 22.7, 22.9, 25.4, 26.1, 26.3, 26.5, 30.5 (this peak is a shoulder under the corresponding signal for **2**$_{ax}$), 30.6, 123.2, 123.3, 126.6, 142.0, 145.8, 147.0, 147.3, 155.7. Anal. calcd for $C_{66}H_{86}Ga_2$: C, 77.81; H, 8.51 %. Found: C, 78.01; H, 8.49 %.

Ar´Ga{CH$_2$CH(C$_4$H$_9$)}$_2$GaAr´ (**3**) To a solution of Ar´GaGaAr´ (0.22 g, 0.24 mol) in dry degassed toluene (10 mL) was added freshly distilled 1-hexene (150 µL, 1.20 mmol, 5 eq,). A gradual colour change from dark green to pale yellow was observed over 12 h

while stirring at ca. 25 °C. The solution was concentrated under reduced pressure. The residue was washed with pentane and the pale yellow powder was dried *in vacuo* to afford pure **3**. Yield: 0.038 g, 20 %; m.p. 184 – 187 ºC; Due to the mixture of isomers and numerous overlapping multiplets a tentative assignment is given based on the similarity to the spectrum of **2**: ^{1}H NMR (400 MHz, C_7D_8, 298 K) 0.34 (dd, {CH*H*′CH(C_4H_9)}$_2$, $^{2}J_{HH}$ = 14.8 Hz, $^{3}J_{HH}$ = 4.4 Hz, 2H), 0.62 – 0.70 (m, {CHH′C*H*(C_4H_9)}$_2$, 2H), 0.71 (dd, {C*H*H′CH(C_4H_9)}$_2$, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 4.4 Hz, 4H), 0.96 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 12H), 0.98 – 1.02 (m, {CHH′CH(C_4H_9)}$_2$, 18H), 1.06 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 12H), 1.22 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 12H), 2.92 (sept, C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 4H), 3.11 (sept, C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.8 Hz, 4H), 6.77 – 6.87 (m, Ar, 2H), 6.89 – 7.00 (m, Ar, 12H), 7.05 – 7.09 (m, Ar, 4H). Anal. calcd for $C_{72}H_{98}Ga_2$: C, 78.40; H, 8.96 %. Found: C, 78.70; H, 8.99 %.

Ar′Ga{CH$_2$CH(Ph)}$_2$GaAr′ (4) To a solution of Ar′GaGaAr′ (0.22 g, 0.24 mol) in dry degassed hexane (10 mL) was added freshly distilled styrene (68 µL, 0.59 mol) at ca. 25 °C for 18 h. A colourless precipitate was obtained. The solution was decanted and the solid dried *in vacuo*. The solid was redissolved in toluene then stored at -18 °C to afford colourless crystals of **4**. Yield: 0.06 g, 22 %; m.p. 217 – 220 °C. ^{1}H NMR (600 MHz, C_6D_6, 298 K) 0.43 (dd, Ga(CHPhC*H*H')$_2$, $^{2}J_{HH}$ = 15.6, $^{3}J_{HH}$ = 4.8 Hz, 2H), 0.81 (d, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz, 12H), 0.93 (dd, Ga(CHPhCH*H'*)$_2$, $^{2}J_{HH}$ = 15.6, $^{3}J_{HH}$ = 9.0 Hz, 2H), 0.93 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz, 12H), 0.98 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz ,12H), 1.0 (d, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz ,12H), 2.07 (dd, (GaC*H*PhCHH')$_2$, $^{3}J_{HH}$ = 4.8, 9.0 Hz), 2.94 (sept, C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz, 4H), 3.00 (sept, C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.6 Hz, 4H), 6.48 (d, *o*-C$_6$H$_5$, $^{3}J_{HH}$ = 7.8 Hz, 4H), 6.88 (t, *p*-C$_6$H$_3$, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.95 (t, *m*-C$_6$H$_3$ $^{3}J_{HH}$ = 7.8 Hz, 4H), 7.05 – 7.12 (m, *m*-^{i}Pr$_2$-C$_6$H$_3$, *p*-C$_6$H$_5$, 10H), 7.13 – 7.18 (m, *m*-C$_6$H$_5$, 4H), 7.25 (t, *p*-^{i}Pr$_2$-C$_6$H$_3$, $^{3}J_{HH}$ = 7.8 Hz, 4H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.8 MHz, 298 K): 23.4, 24.2, 25.6, 26.8, 26.9, 31.4, 37.8, 124.1, 124.2, 128.0, 128.8, 128.9, 129.0, 129.7, 142.2, 147.0, 148.2, 148.9, 154.8; λ_{max} (ε) 340 nm (821 Lmol^{-1}cm^{-1}). Anal. calcd for $C_{76}H_{90}Ga_2$: C, 79.86; H, 7.94 %. Found: C, 79.91 ; H, 8.01 %.

Table 1 Summary of X-ray data collection and refinement for structures **1**, **2** and **4**.

Compound	**1**	**$2_{ax}/2_{eq}$**	**4**
Formula	$C_{64}H_{82}Ga_2$	$C_{66}H_{86}Ga_2$	$C_{76}H_{90}Ga_2$
FW	990.74	1018.79	1142.92
Colour, habit	colourless, needle	colourless, block	colourless, block
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.9322(10)	10.8470(13)	11.216(7)
b (Å)	10.4139(8)	19.606(2)	11.335(7)
c (Å)	39.129(3)	13.780(2)	24.561(15)
α (°)	90	90	90
β (°)	98.865(1)	97.028(1)	94.241(11)
γ (°)	90	90	90
V (Å^3)	5609.4(7)	2908.5(7)	3114(3)
Z	4	2	2
d_{calc} (g cm^{-3})	1.173	1.163	1.219
μ (mm^{-1})	0.997	0.964	1.366
no. obsd. reflns.	7578	5900	4756
R_1 [I >2σI]	0.0618	0.0564	0.0430
wR_2, all	0.1650	0.1419	0.1140

1. N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 2667-2679.