Addition of alkynes to digermynes: experimental insight into the reaction pathway

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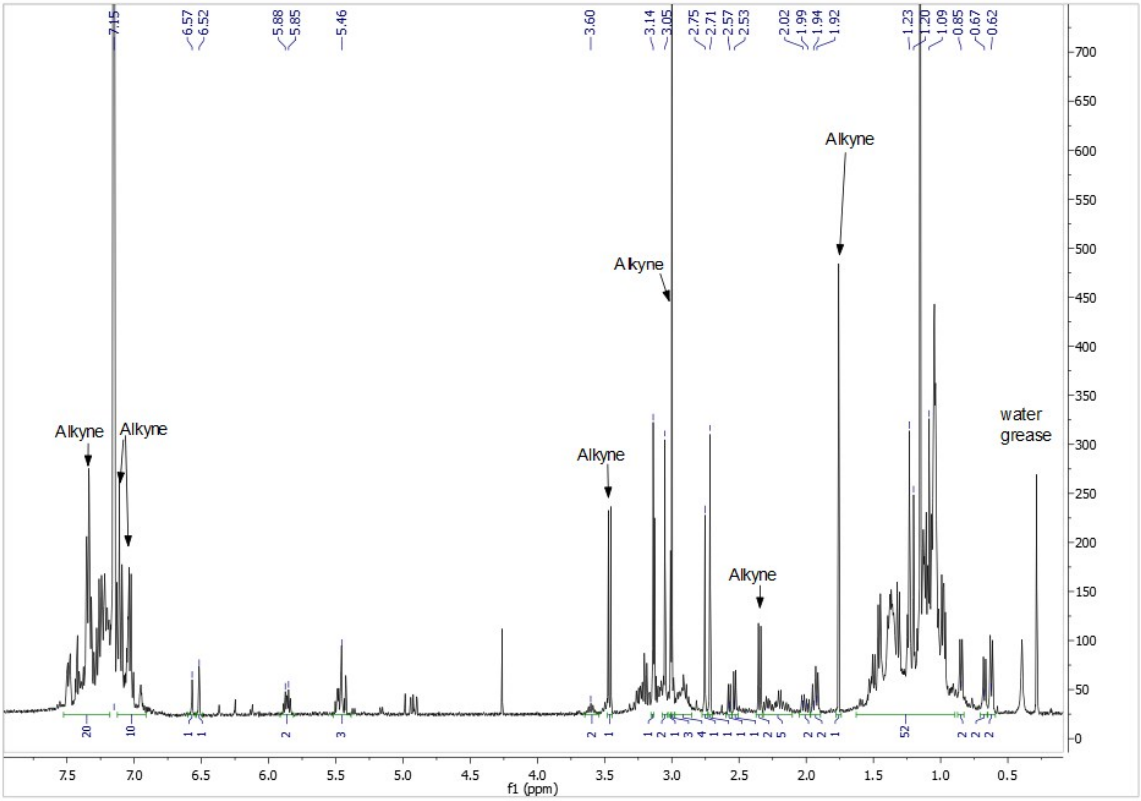

Figure S1 ^{1}H NMR (400 MHz) spectrum of **5c** in C_6D_6, X indicates excess alkyne **9**

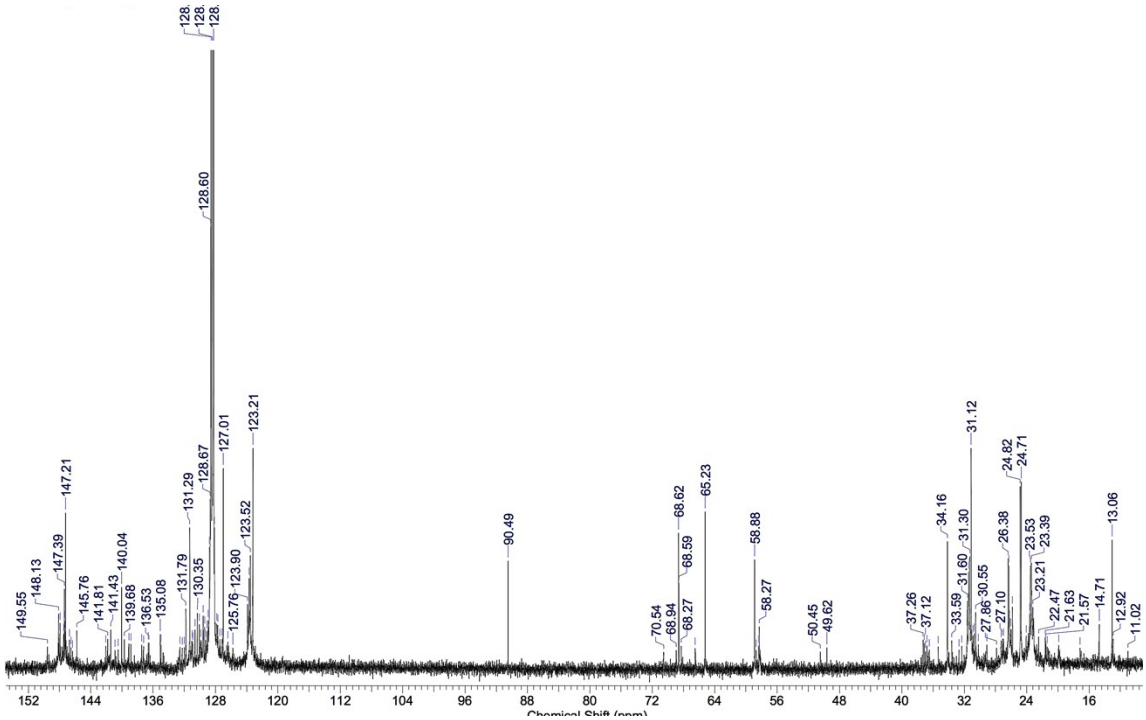

Figure S2 ^{13}C NMR (150 MHz) spectrum of **5c** in C_6D_6

General Experimental Details

All air sensitive reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk techniques or a glove box. Hexanes were obtained from a solvent purification system (SPS-400-5, Innovative Technology Inc). NMR spectra were recorded on a Varian INOVA spectrometer operating at 400 or 600 MHz for ^{1}H. Electrospray ionization mass spectra were recorded on a Bruker microTOF II mass spectrometer. X-ray data were obtained using a Bruker Apex II Diffractometer.

Single crystal X-ray diffraction experimental details

Data Collection and Processing. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 150 K. The unit cell dimensions were determined from a symmetry constrained fit of 9904 reflections with $5.3° < 2\theta < 55.2°$. The data collection strategy was a number of ω and φ scans which collected data up to 54.21° (2θ). The frame integration was performed using SAINT.[1] The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[2]

Structure Solution and Refinement. The structure was solved by direct methods using the XS program.[3] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the

parent atom. The asymmetric unit contained three regions of included solvent molecules. The first region contained a hexane molecule which lay across a crystallographic center of symmetry. The second region contained a hexane at a general position in the lattice. The C-C distances and anisotropic displacement parameters (ADP's) of the hexane molecules were restrained to keep the refinement stable and physically reasonable. The third region probably contained disordered or fractionally occupied CH_2Cl_2 molecule(s) as well as possibly some (disordered) hexane(s). No chemically sensible model could be found for this third region of solvation. To improve the fit of the known part of the structure, the SQUEEZE procedure[4] as implemented in PLATON[5] was used to subtract out the unaccounted for solvents' contribution to the diffraction pattern. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.[6] Graphic plots were produced using the XP program suite.[7] Additional information and other relevant literature references can be found in the reference section of this website (http://xray.chem.uwo.ca).

Table S1: Crystallographic data of **5c**

CCDC #	1434234
Formula	$C_{95}H_{123}Ge_2O_2$
Formula Weight (*g/mol*)	1442.11
Crystal Dimensions (*mm*)	0.328 × 0.123 × 0.042
Crystal Color and Habit	colourless plate
Crystal System	triclinic
Space Group	P -1
Temperature, K	150
a, Å	12.871(7)
b, Å	16.645(10)
c, Å	23.354(13)
α,°	71.593(14)
β,°	87.449(7)
γ,°	67.404(8)
V, Å^3	4366(4)
Number of reflections to determine final unit cell	9904
Min and Max 2θ for cell determination, °	5.3, 55.2
Z	2
F(000)	1546

ρ (*g/cm*)	1.097
λ, Å, (MoKα)	0.71073
μ, (cm^{-1})	0.733
Diffractometer Type	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans
Max 2θ for data collection, °	54.21
Measured fraction of data	1.000
Number of reflections measured	114140
Unique reflections measured	19249
R_{merge}	0.0951
Number of reflections included in refinement	19249
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[sigma^2(Fo^2)+(0.0710P)^2+3.5180 P]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	893
R_1	0.0532
wR_2	0.1288
R_1 (all data)	0.0915
wR_2 (all data)	0.1487
GOF	1.011
Maximum shift/error	0.001
Min & Max peak heights on final ΔF Map (e^-/Å)	-0.631, 1.696

References:

1 Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS, Madison, WI 53711, USA.
2 Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA.
3 Bruker-AXS, XS version 2013.12, **2013**, Bruker-AXS, Madison, WI 53711, USA.
4 P. v.d. Sluis and A. L. Spek, *Acta Cryst.*, **1990**, *A46*, 194-201 (in this manuscript, SQUEEZE is referred to as the BYPASS procedure).
5 A. L. Spek, , *J. Appl. Cryst.*, **2003**, *36*, 7-13.
6 G. M. Sheldrick, *Acta Cryst.*, **2015**, *C71*, 3-8.
7 Bruker-AXS, XP version 2013.1, **2013**, Bruker-AXS, Madison, WI 53711, USA.