BES: 020

Heavy Cycloadditions: Reactions of digallene with cyclic polyolefins

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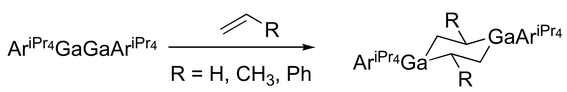
Introduction

We were interested in testing the cycloaddition reactivity of terphenyl-stabilized digallene with cyclic polyolefins and to compare it to the reactivity of alkenes and to the reactivity of the heavier Group 14 alkyne analogues (Ge and Sn).

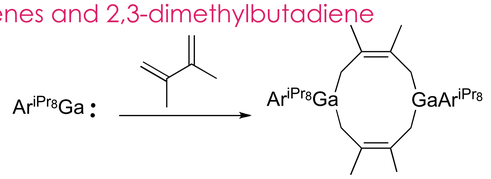
Key Questions:

Are there differences in reactivity seen? Are they due to sterics, electronics or both? Does monomeric gallium diyl play a role or does digallene react as a dimer?

Previous results: [2+2+2] Reaction of digallene with simple alkenes and 2,3-dimethylbutadiene

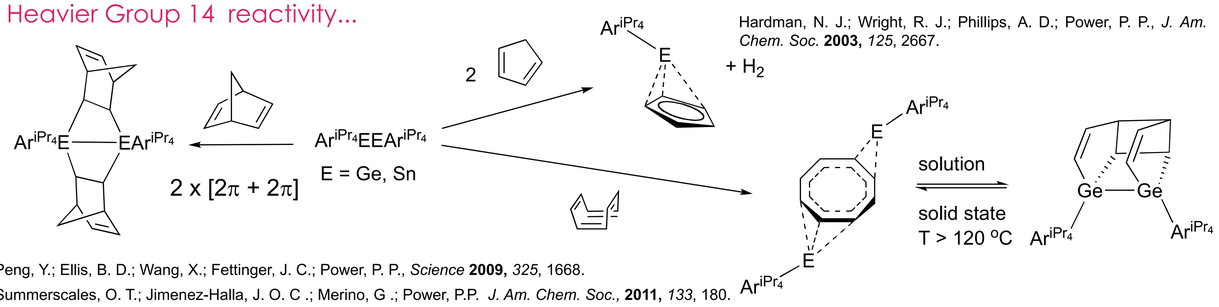


Caputo, C.A..; Zhu, Z.; Brown, Z.D.; Fettinger, J. C.; Power, P. P., *Chem. Commun.* **2011,** *47*, 7506.



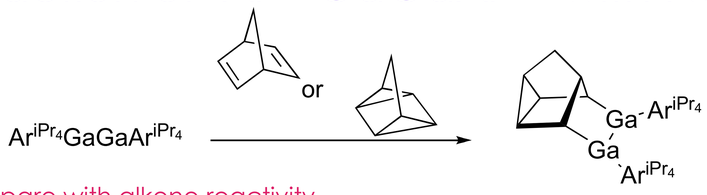
Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P., *J. Am. Chem. Soc.* **2003,** *125*, 2667.

Heavier Group 14 reactivity...

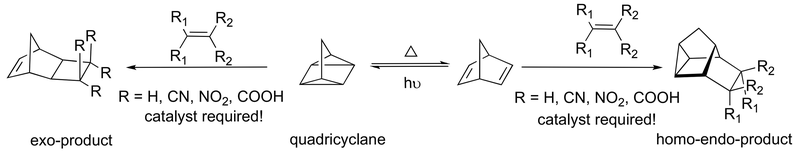


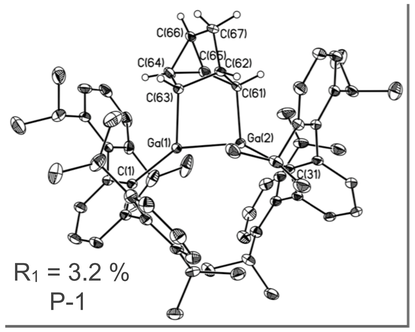
Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P., *Science* **2009,** *325*, 1668.
Summerscales, O. T.; Jimenez-Halla, J. O. C .; Merino, G .; Power, P.P. *J. Am. Chem. Soc.,* **2011,** *133*, 180.
Summerscales O. T.; Fettinger, J.C.; Power, P. P. *J. Am. Chem. Soc.,* **2011**,*133*, 11960.

Reaction of $Ar^{iPr4}GaGaAr^{iPr4}$ with Norbornadiene



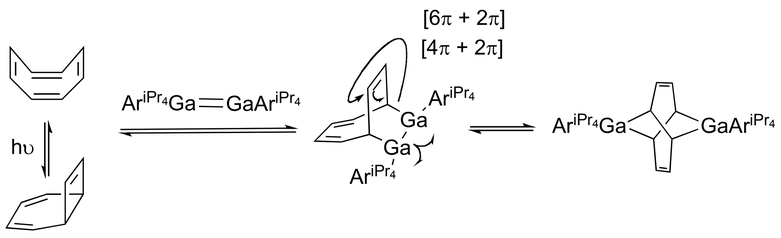
Compare with alkene reactivity...



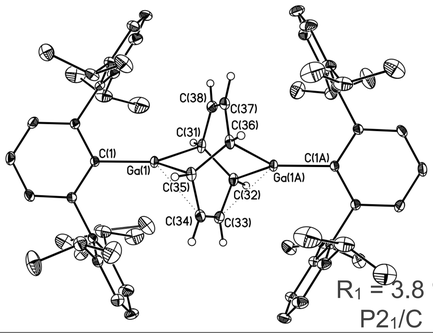


R1 = 3.2 %
P-1

Reaction of $Ar^{iPr4}GaGaAr^{iPr4}$ with Cyclooctatetraene

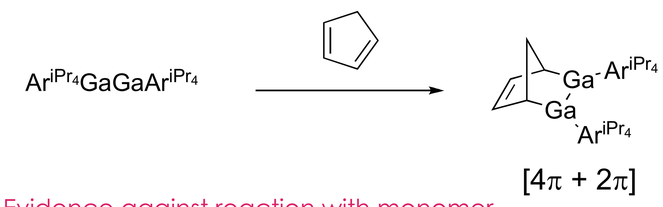


VT ^{1}H NMR spectroscopy showed free COT and a small amount of the intermediate indicating that the cycloaddition reactions are reversible

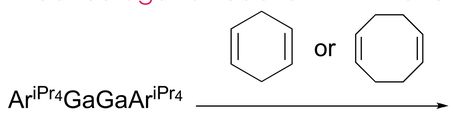


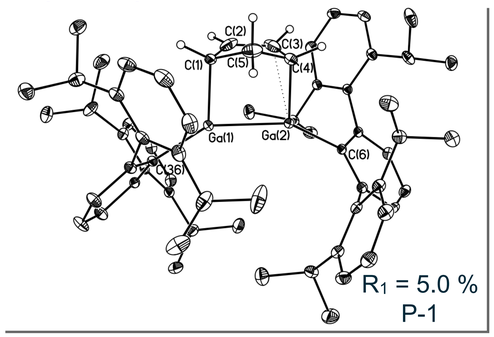
R1 = 3.8 %
P2$_1$/C

Reaction of $Ar^{iPr4}GaGaAr^{iPr4}$ with Cyclopentadiene



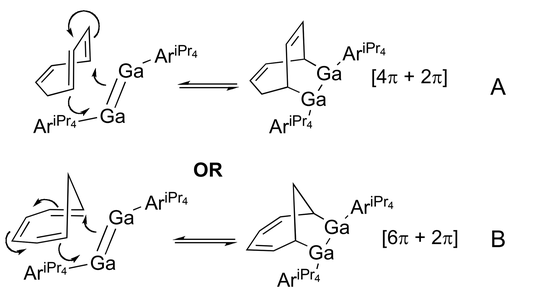
Evidence against reaction with monomer..

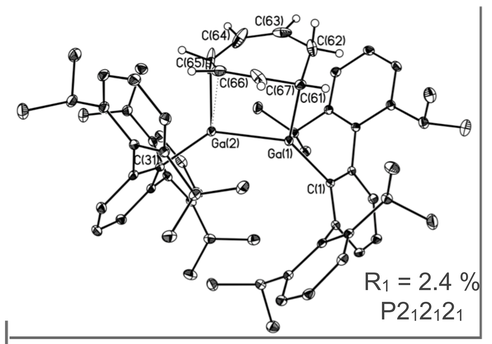




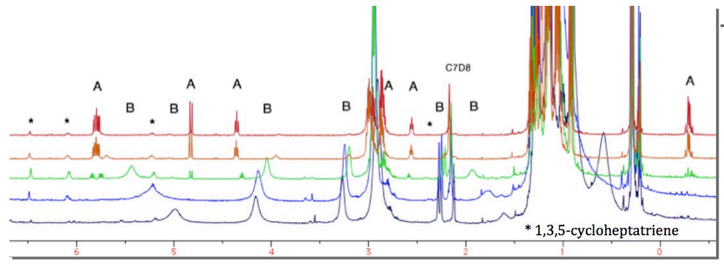
R1 = 5.0 %
P-1

Reaction of $Ar^{iPr4}GaGaAr^{iPr4}$ with 1,3,5-Cycloheptatriene





R1 = 2.4 %
P2$_1$2$_1$2$_1$

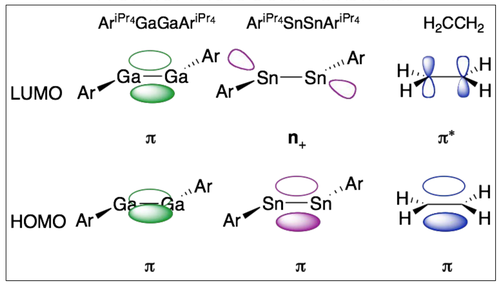


VT ^{1}H NMR spectroscopy from 313 K to 373 K (bottom to top) shows isomerization from kinetic [6+2] product B to thermodynamic [4 + 2] product A

Conclusions

- Digallene Frontier Molecular Orbital symmetry is π-π rather than π-n$_+$ for Sn/Ge metallynes and π-π* for alkenes. This is likely the reason for the differences in reactivity.
- Reactions seem to be operating via a cycloaddition mechanism with digallene rather than with the monomeric diyl. No examples isolated had just a single '$Ar^{iPr4}Ga$' incorporated.

Frontier Molecular Orbitals



References

Caputo, C.A., Guo, J.-D., Nagase, S., Fettinger, J.C., Power, P.P. *J. Am. Chem. Soc.* **2012**, **DOI:** 10.1021/ja301247h.

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