Supporting Information for:

# Are sp lithiated carbons more nucleophilic than $sp^2$ or $sp^3$ ones? A comparative DFT study of the condensation of propynyllithium aggregates on formaldehyde.

*Catherine Fressigné[†,‡] and Jacques Maddaluno[‡,*]*

[†] Laboratoire de Chimie Théorique, CNRS UMR 7616, Université P. & M. Curie, Case Courrier 137, 4, place Jussieu, 75252 Paris Cedex 05 (France)

[‡] Institut de Recherche en Chimie Organique Fine, CNRS UMR 6014 & FR 3038, Université de Rouen, 76821 - Mont St Aignan Cedex (France)

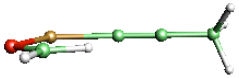
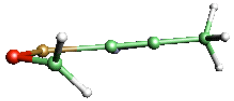
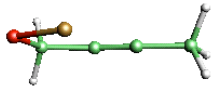
**Table of content**

**Propynyllithium + $H_2CO$ (-238.81961481456 a. u.)**

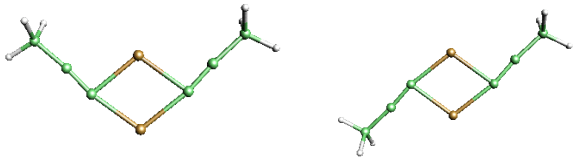
Jaguar 4.1 B3P86 6-31G** uncorrected (X = fictious atom)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| H1 | | | | | | | | |
| C2 | H1 | 1.0970650255 | | | | | | |
| C3 | C2 | 1.4583796085 | H1 | 111.8955461678 | | | | |
| X4 | C3 | 1.0000000000 | C2 | 90.0000000000 | H1 | 179.9999985212 | | |
| X5 | X4 | 1.1815620000 | C3 | 91.9256060000 | C2 | 176.7657620000 | | |
| C6 | X5 | 1.0257097955 | X4 | 90.7850600488 | C3 | 5.0931438840 | | |
| Li7 | C6 | 1.9362998360 | X5 | 96.1161020006 | X4 | -179.2254659973 | | |
| O10 | Li7 | 1.9477218751 | C6 | 113.1933783480 | X5 | 124.4123775745 | | |
| C11 | O10 | 1.2219043328 | Li7 | 109.5010978098 | C6 | -.1341470324 | | |
| H30 | C11 | 1.1038560088 | O10 | 119.6678626776 | Li7 | 179.7167784617 | | |
| H29 | C11 | 1.1060674931 | O10 | 119.9474497593 | H30 | -179.9565455008 | | |
| H32 | C2 | 1.0970624052 | H1 | 107.2009694582 | C3 | -122.9704961807 | | |
| H33 | C2 | 1.0967483536 | H1 | 107.0717870255 | C3 | 122.3884645948 | | |

**Table S1.** Values of energy for the propynyllithium-formaldehyde system at various levels of calculation (the basis set is 6-31G**).

| | | | | |
|---|---|---|---|---|
| | Uncorrected structures |  |  |  |
| 1 | Internal energy | -238.819615 a.u. | TS: -238.815844 a.u.<br>(+2.3 kcal.mol$^{-1}$) | Cond.: -238.856968 a.u.<br>(-25.8 kcal.mol$^{-1}$) |
| 2 | ZPE correction | ZPE = 52.292 kcal.mol$^{-1}$<br>$E_{corr.}$ = -238.736282 a.u. | ZPE = 52.338 kcal.mol$^{-1}$<br>$E_{corr.}$ = -238.732438 a.u.<br>(+2.4 kcal.mol$^{-1}$) | ZPE = 56.560 kcal.mol$^{-1}$<br>$E_{corr.}$ = -238.766834 a.u.<br>(-21.6 kcal.mol$^{-1}$) |
| 3 | Thermal corrections | T= 298.15 K<br>$S_T$ = 81.9228 cal.mol$^{-1}$K$^{-1}$<br>$H_T$ = 4.8614 kcal.mol$^{-1}$<br>$G_T$ = -19.5639 kcal.mol$^{-1}$<br>G = -238.767459 a.u. | T= 298.15 K<br>$S_T$ = 81.2066 cal.mol$^{-1}$K$^{-1}$<br>$H_T$ = 4.8318 kcal.mol$^{-1}$<br>$G_T$ = -19.3800 kcal.mol$^{-1}$<br>G = -238.763322 a.u.<br>(+2.6 kcal.mol$^{-1}$) | T= 298.15 K<br>$S_T$ = 74.2662 cal.mol$^{-1}$K$^{-1}$<br>$H_T$ = 3.9560 kcal.mol$^{-1}$<br>$G_T$ = -18.1865 kcal.mol$^{-1}$<br>G = -238.795816 a.u.<br>(-20.4 kcal.mol$^{-1}$) |
| 4 | MP2 | MP2<br>EUMP2= -237.364278 a.u. | MP2<br>EUMP2= -237.357562 a.u.<br>(+4.2 kcal.mol$^{-1}$) | MP2<br>EUMP2= -237.394604 a.u.<br>(-23.2 kcal.mol$^{-1}$) |
| 5 | CCSD(T)[a] | Single point MP2<br>$E_{CCSD(T)}$= -237.428938 a.u.<br>E(corr)= -237.400316 a.u. | Single point MP2<br>$E_{CCSD(T)}$= -237.421910 a.u.<br>(+4.4 kcal.mol$^{-1}$)<br>E(corr)= -237.392981 a.u.<br>(+4.6 kcal.mol$^{-1}$) | Single point MP2<br>$E_{CCSD(T)}$= -237.455573 a.u.<br>(-21.1 kcal.mol$^{-1}$)<br>E(corr)= -237.427310 a.u.<br>(-21.5 kcal.mol$^{-1}$) |

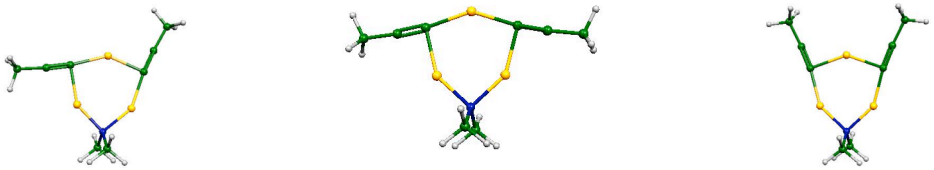
[a] The CCSD energy is labeled $E_{(corr)}$, and the energy including the non–iterative triples contribution is labeled $E_{CCSD(T)}$



-248.096239 a.u. -248.096613 a.u.

$C_{2v}$ $C_2$

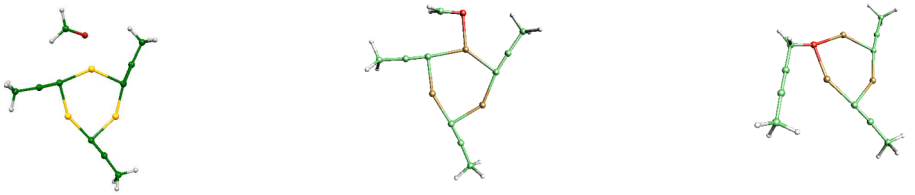
**Figure S1.** Absolute energy of the $C_{2v}$ and $C_2$ propynyllithium dimer.



-390.763679 a.u. -390.763706 a.u. -390.763155 a.u.

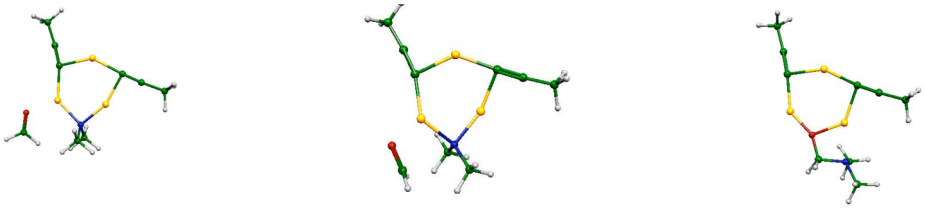
**Figure S2.** Absolute energies of the heterogeneous trimers involving propynyllithium.

**Complex** **TS** **Product**



-486.979398 a.u. -486.974906 a.u. -487.036923 a.u.

$E^{\dagger}$=2.8 kcal.mol$^{-1}$ $E_{cond}$= -38.9 kcal.mol$^{-1}$



-505.562290 a.u. -505.557368 a.u. -505.633067 a.u.

$E^{\dagger}$= 3.1 kcal.mol$^{-1}$ $E_{cond}$= -47.5 kcal.mol$^{-1}$

**Figure S3.** Condensation pathways of homogeneous and heterogeneous propynyllithium trimer on formaldehyde.

**Table S2.** Main geometrical parameters used to describe the monomeric and dimeric complexes between methyllithium or vinyllithium and HCHO at the steady and the transition states. The angles α, β and γ as well as the distance d are displayed on Figure 2. These values have been measured on optimized complexes published before (see footnotes). In the mixed aggregates, the atom written bold and italic is the nucleophilic one.

| Entry | Nucleophile | Complex | | | | TS | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | α | β | γ | d | α | β | γ | d |
| 1 | MeLi[a] | 108.1 | 0.0 | 0.0 | 1.97 | 99.8 | 40.9 | 2.3 | 1.23 |
| 2 | $LiCH=CH_2$[b] | 110.6 | 0.9 | 7.1 | 1.22 | 107.7 | 43.6 | 18.9 | 1.23 |
| 3 | $(MeLi)_2$[a] | 121.1 | 0.2 | 0.9 | 1.22 | 127.5 | 97.3 | 0.2 | 1.84 |
| 4 | $(LiCH=CH_2)_2$[b] | 118.5 | 0.9 | 15.3 | 1.99 | 104.4 | 60.2 | 18.3 | 1.99 |
| ***5*** | ***Me***Li-$LiNMe_2$[a] | 121.9 | 0.3 | 0.7 | 2.00 | 103.4 | 59.3 | 20.3 | 1.99 |
| 6 | $CH_2$=***C***HLi-$LiNMe_2$[b] | 117.6 | 1.3 | 16.6 | 2.00 | 103.4 | 58.8 | 14.8 | 2.00 |
| 7 | MeLi-Li***N***$Me_2$[a] | 111.6 | 0.0 | 0.0 | 2.00 | 122.7 | 22.5 | 26.4 | 1.97 |
| 8 | $CH_2$=CHLi-Li***N***$Me_2$[b] | 112.2 | 0.3 | 4.2 | 2.00 | 101.5 | 51.0 | 5.6 | 1.98 |

[a] measured on complexes described in *J. Org. Chem.* **2000**, *65*, 8899-8907 (Ref. 8)
[b] measured on complexes described in *J. Org. Chem.* **2005**, *70*, 7816-7828 (Ref. 9)

**Table S3.** Docking of HCHO on $T_d$ (top) and $S_4$ (bottom) homogeneous tetramers of propynyllithium. The absolute energy values are given in a.u. while the docking, transition barrier and condensation energies are given in kcal.mol$^{-1}$.

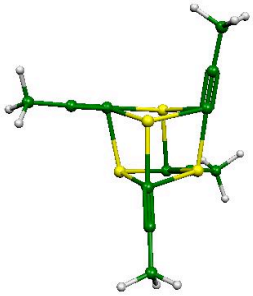
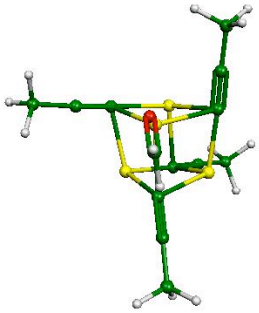
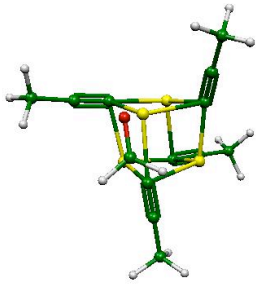
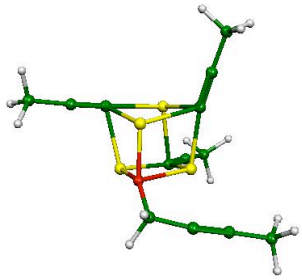
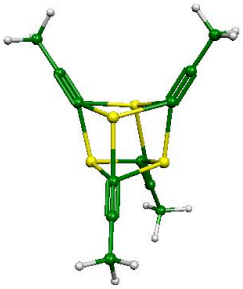
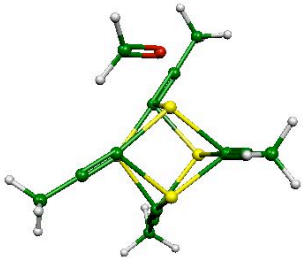
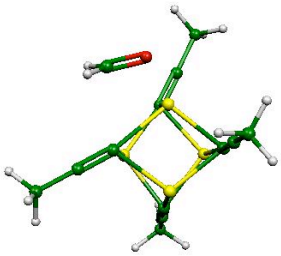
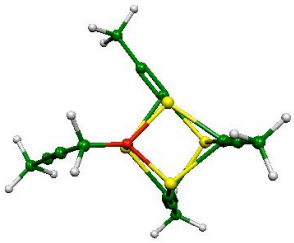
| Entry | Homogeneous tetramer | Docking complex (docking energy) | TS (activation barrier) | Product (condensation energy) |
|---|---|---|---|---|
| 1 |  -496.269160 |  -611.072569 (-13.5) |  -611.068043 (+2.8) |  -611.130241 (-39.0) |
| 2 |  -496.268572 |  -611.072525 (-13.8) |  -611.068140 (+2.8) |  -611.130430 (-39.1) |

**Table S4.** Various cubic conformers of the heterogeneous tetramer [(MeCH≡CLi)$_3$(Me$_2$NLi)]. The energy values are given in a.u.

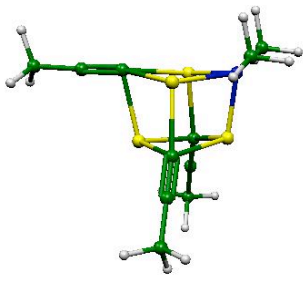
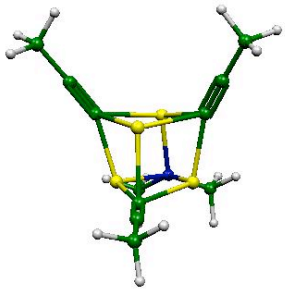
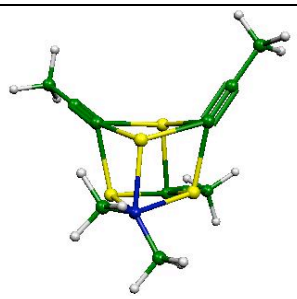
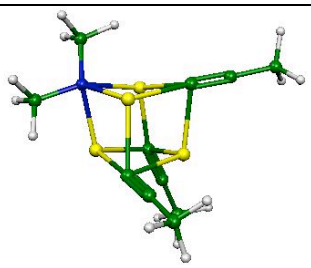
| | | | |
|---|---|---|---|
|  -514.849724 |  -514.849574 |  -514.849569 |  -514.849419 |

**Table S5.** Docking of HCHO on the various lithium cations of the more stable cubic conformer of the heterogeneous tetramer [(MeCH≡CLi)$_3$(Me$_2$NLi)]. The absolute energy values are given in a.u. while the docking, transition barrier and condensation energies (between parentheses) are given in kcal.mol$^{-1}$.

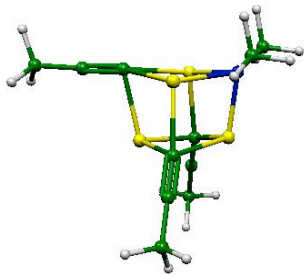
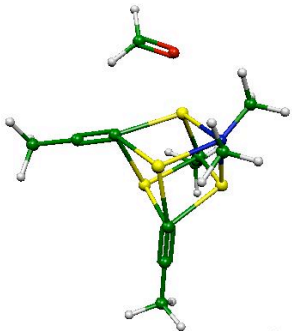
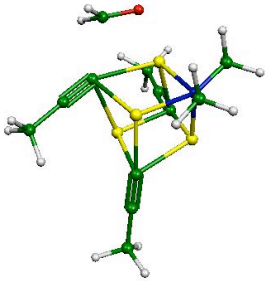
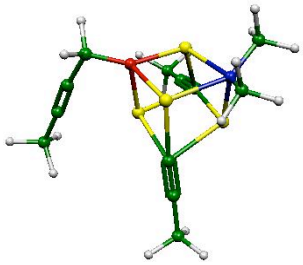
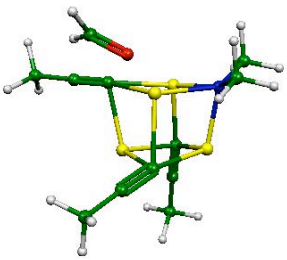
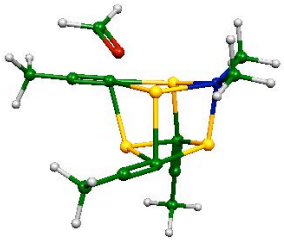
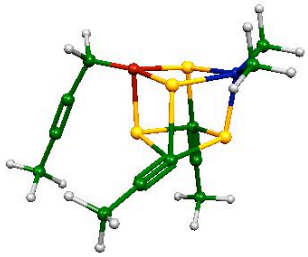
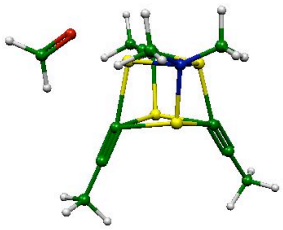
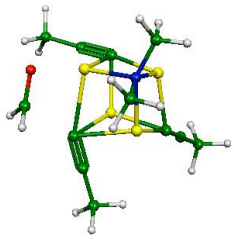
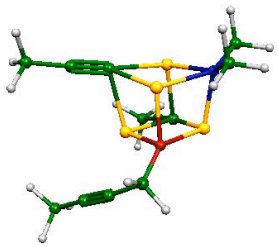
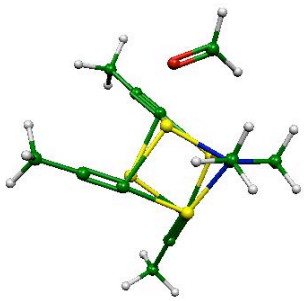
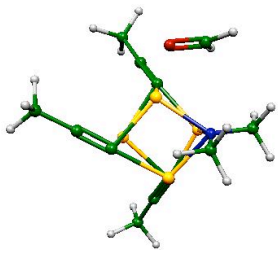
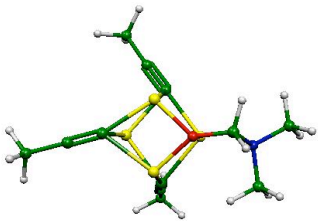
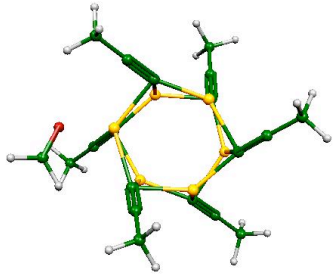
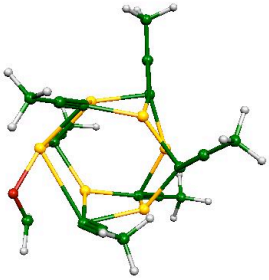
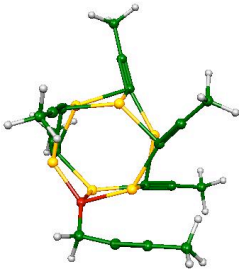
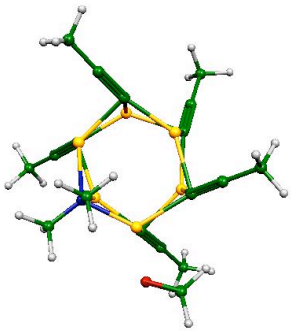
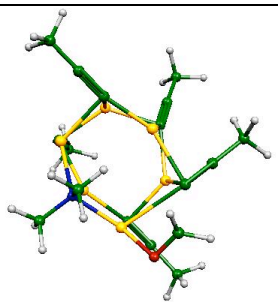
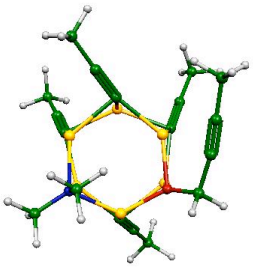
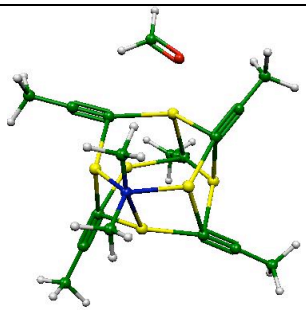
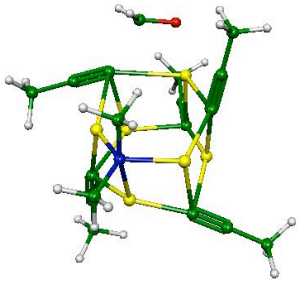
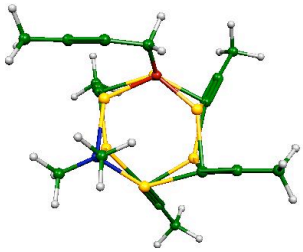
| Heterogeneous tetramer | Docking complex (docking energy) | TS (activation barrier) | Product (condensation energy) |
|---|---|---|---|
|  -514.849724 |  -629.651705 (-12.6) |  -629.646476 (+3.3) |  -629.711114 (-40.6) |
| |  -629.651764 (-12.6) |  -629.647777 (+2.5) |  -629.711327 (-39.9) |
| |  -629.651531 (-12.5) |  -629.646797 (+3.0) |  -629.710486 (-40.0) |
| |  -629.650161 (-11.6) |  -629.646048 (+2.6) |  -629.727349 (-51.02) |

**Table S6.** Docking of HCHO on various lithium cations of the hexagonal conformer of the homogeneous and heterogeneous hexamers $(MeCH{\equiv}CLi)_6$ and $[(MeCH{\equiv}CLi)_5(Me_2NLi)]$. The absolute energy values are given in a.u. while the docking, transition barrier and condensation energies (between parentheses) are given in kcal.mol$^{-1}$.

| Docking complex (docking energy) | TS (activation barrier) | Product (condensation energy) |
|---|---|---|
|  -859.231751 (-11.0) |  -859.221530 (+6.4) |  -859.292924 (-44.8) |
|  -877.814819 (-16.5) |  -877.805198 (+6.0) |  -877.876083 (-44.5) |
|  -877.813819 (-15.8) |  -877.806229 (+4.8) |  -877.875589 (-43.5) |