Supplementary Material

Title: Structure and reactivity of species analogous to the 'intermediates' in the phosphine catalysed transformations of electron deficient alkenes and alkynes

Authors: N. N. Bhuvan Kumar, Manab Chakravarty and K. C. Kumara Swamy*

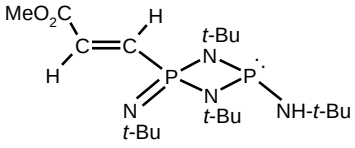
Theoretical Calculations

We have optimized the structures for the isomers **3** and **3a-3d** presented in the following table at B3LYP/6-31G** level[1] using Gaussian 03 program package.[2]

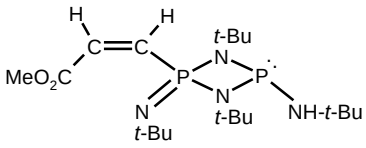
Table S1: Energies (au) of the optimized structures for **3** and **3a-d**

Input structure[a]	Total Optimized Energy	Destabilization w.r.t. **3** (kcal/mole)
3	-1839.67228	0.00
3a	-1839.66037	+7.40
3b	-1839.62337	+30.68
3c	-1839.66440	+4.94
3d	-1839.61429	+36.38

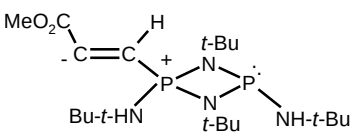
[a] The coordinates from X-ray structure of **3** were used. Modifications of the substituents (change of linkages) were then performed for **3a–d** and the structures were optimized for minimum energy. Energy in atomic units: 1 a.u. = 627.51 kcal/mol



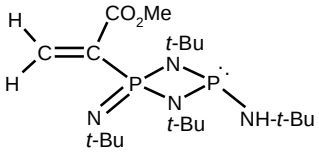
3



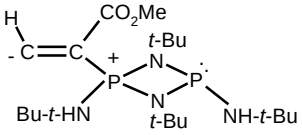
3a



3b



3c



3d

References:

1 a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; b) A. D. Becke *Phys. Rev. A*, 1988, **38**, 2398; c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

2. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson,W. Chen,M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.